Doctoral Thesis

High-resolution spectroscopic studies of non-Born-Oppenheimer effects

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High-resolution spectroscopic studies of non-Born-Oppenheimer effects

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Abstract

The Born-Oppenheimer approximation represents one of the most fundamental concepts in chemistry and forms the basis of the chemist's definition of molecular structure in terms of the relative positions of nuclei. However, it is often necessary to go beyond the Born-Oppenheimer approximation to fully account for the structural, dynamical and spectral properties of molecular systems. This dissertation consists of two parts which give an overview of studies, by high-resolution spectroscopy, of two classes of quantum systems that cannot be understood in the realm of the Born-Oppenheimer approximation.

The first part of the thesis is dedicated to studies of an important class of electronically excited states, called Rydberg states, and characterizes the influence of nuclear spins on the structure and dynamics of these states by high-resolution photoionization and pulsed-field ionization spectroscopy and Multichannel Quantum Defect Theory (MQDT). The second part presents the experimental characterization of the Jahn-Teller and Pseudo-Jahn-Teller effects in molecular cations by high-resolution photoelectron spectroscopy and the interpretation of these effects by ab initio quantum chemical methods and vibronic coupling theory. Each investigation relied on the development of original experimental techniques and required an extension of available theoretical formalisms.

Chapter 2 provides a description of the spectroscopic techniques, primarily photoionization and high-resolution photoelectron spectroscopy, and the laser systems and spectrometers used for the different investigations.

In chapter 3 the Multichannel Quantum Defect Theory formalism developed by Fano, Lee and Lu for the Rydberg states of the rare gas atoms is extended to include nuclear spins and is used to analyze high-resolution pulsed-field ionization spectra of $^{83}$Kr. The MQDT calculations reproduce the experimental spectrum quantitatively after adjustment of the (previously unknown) hyperfine structure of $^{83}$Kr$^+$. At principal quantum numbers below $n \approx 80$, the interactions between the nuclear and electron spins lead to a splitting of each fine-structure level into several hyperfine components. At higher values of the principal quantum number, the hyperfine structure of the ion begins to dominate the level structure and the Rydberg states can be assigned to series converging on distinct hyperfine levels of the cation. This decoupling leads to crossings between series that would not occur in the absence of a nuclear spin and thus gives access to additional dynamical parameters. We show that the hyperfine interactions lead to a crossing of s and d series around $n \approx 70$ that is avoided because of the sd interaction.
Chapter 4 describes the investigation of the hyperfine structure and dynamics of autoionizing Rydberg states of xenon. Hyperfine resolved photoionization spectra measured between \( n = 30 \) and 200 in the region between the ionization thresholds corresponding to the formation of the two spin-orbit components \( ^2P_{3/2} \) and \( ^2P_{1/2} \) of \( \text{Xe}^+ \) are presented. The MQDT formalism described in chapter 3 is extended to treat autoionization continua and to predict partial and total photoionization cross-sections. In the analysis, a quantitative agreement with the experimental data is demonstrated and the hyperfine structures of the upper spin-orbit component of \( ^{129}\text{Xe}^+ \) and \( ^{131}\text{Xe}^+ \) are determined for the first time. In addition, several dynamical processes related to the nuclear spin are described for the first time. The MQDT calculations show that cations can be prepared in selected hyperfine states by photoionization. A new type of autoionization, termed "hyperfine autoionization", is predicted to occur for high Rydberg states located between the thresholds corresponding to different hyperfine levels of the cation. In this process, the cation undergoes a transition to a lower hyperfine level and transfers the energy to the Rydberg electron that escapes the attractive potential of the ion core.

After the description of the fundamental aspects of hyperfine structure and dynamics in atomic systems, the role of nuclear spins in the structure and dynamics of molecular Rydberg states is investigated. In chapter 5 hyperfine-resolved pulsed-field-ionization spectra of bound gerade \((s \text{ and } d)\) Rydberg states belonging to series converging on the \( ^2\Sigma^+_g \) \((\nu^+ = 0, N^+ = 1)\) level of ortho \( \text{H}_2^+ \) are described. The hyperfine-resolved spectra reveal the evolution of the angular momentum coupling hierarchy involving nuclear spins. At principal quantum numbers below \( n \approx 40 \), the d states can be understood in terms of Hund's angular momentum coupling case (d), each level being split by the hyperfine interactions. At higher values of \( n \), a transition occurs toward a situation where the level structure is dominated by the hyperfine structure of \( \text{H}_2^+ \). The s states do not show hyperfine splittings in the investigated range because the exchange interaction between the two electrons is stronger than the hyperfine interaction in the \( \text{H}_2^+ \) ion core and only the singlet components can be excited. The same applies to low-\( n \) rotational and vibrational interlopers that are observed in the spectrum and lead to perturbations of the main series. The predissociation of the Rydberg states is significantly faster for the ndl₁ series than for the remaining series because of its interaction with a vibrationally excited interloper. The analysis of the spectra required the determination of quantum defect curves for the gerade states by \textit{ab initio} R-matrix methods which were subsequently adjusted to reproduce the highly accurate potential energy curves of Wolniewicz. The quantum defect curves obtained from this procedure accurately reproduce the complex photoionization spectra of \( \text{H}_2 \) in the region of its adiabatic ionization threshold and have led to the first definitive assignment of all observed low-\( n \) interlopers.

Chapter 6 is concerned with the hyperfine structure and dynamics of rotation-
ally autoionizing Rydberg levels of ortho-H₂. A triple-resonant three-photon excitation scheme has been developed to access the long-lived \( ^1\Sigma_g^+ (v = 0) \) state, which has led to an unprecedented resolution of 25 MHz in the photoionization spectra of the high ungerade (p) Rydberg states belonging to series converging on the \( ^2\Sigma_g^+ (v^+ = 0, N^+ = 3) \) level of ortho H₁². The spectra provide information on previously unknown dynamical processes related to nuclear spins in molecular systems and reveal the complete evolution of the angular momentum coupling hierarchy from the situation where the exchange interaction dominates the level structure to the situation where the ionic hyperfine structure dominates. Several intermediate angular momentum coupling cases are identified which are useful in rationalizing both the level structure and the autoionization dynamics. At principal quantum numbers below \( n \approx 70 \) the level structure corresponds to the singlet and triplet components of Hund’s case (d) Rydberg levels. Between \( n \approx 70 \) and \( n \approx 160 \), the hyperfine interaction in the core leads to a recoupling of the core electron spin to the nuclear spins and the total electron spin \( \mathbf{S} \) must be replaced by \( \mathbf{G} = \mathbf{I} + \mathbf{S} \) as a constant of motion. Up to \( n \approx 170 \) the Rydberg states can be described as a product of a Hund’s case (d) wave function and a total spin wavefunction. This property has several fundamental consequences, including the conservation of \( G \) in photoexcitation (\( \Delta G=0 \)) and a propensity rule \( \Delta N=\Delta F \). Above \( n = 150 \) the recoupling of the core electron spin to the rotational angular momentum of the core starts mixing the Hund’s case (d) wavefunctions, \( G \) is no longer conserved and only \( F \) remains a good quantum number.

In chapter 7, an investigation of the electronic and rovibronic structures of the cyclopentadienyl cation \( \text{C}_5\text{H}_5^+ \) and its fully deuterated isotopomer \( \text{C}_5\text{D}_5^+ \) by PFI-ZEKE photoelectron spectroscopy and *ab initio* calculations is described. Different single- and multiphoton excitation sequences have enabled the first experimental characterization of the vibronic structure of the two lowest electronic states. The cyclopentadienyl cation possesses a triplet ground electronic state of \( D_{2h} \) symmetry \( (\tilde{X}^+ 3\Sigma_g^+) \) and a first excited singlet state \( (\tilde{\alpha}^+ 1\Sigma_u^+) \). The analysis of the vibronic structure on the basis of a vibronic coupling model shows that the singlet state is subject to a strong Pseudo-Jahn-Teller distortion and allows the determination of the adiabatic singlet-triplet interval. A group-theoretical analysis of the vibronic coupling mechanisms in combination with *ab initio* calculations is presented which establishes unambiguously the topology of the singlet potential energy surfaces and proves that the lowest surface gives rise to free pseudorotation. The analysis of the rovibronic photoionization dynamics in rotationally resolved spectra and the dependence of the intensity distribution on the vibrational level of the \( (\tilde{A}^2\Sigma_u'^+) \) intermediate state selected in the two-photon experiments shows that a Herzberg-Teller mechanism is responsible for the observation of the forbidden \( \tilde{\alpha}^+ 1\Sigma_u^+ \rightarrow \tilde{A}^2\Sigma_u'^+ \) photoionizing transition.

Chapter 8 reports the measurement of the energy level structures of the lowest vibronic states of \(^{12}\text{CH}_4^+, \, ^{13}\text{CH}_4^+ \, \text{and} \, ^{12}\text{CD}_4^+ \) by PFI-ZEKE photoelectron spectroscopy.
The nuclear spin symmetries of the tunneling-rotational levels have been determined in double-resonance experiments via selected rotational levels of the $v_3 = 1$ and $v_3 = 2$ vibrational levels of the $\tilde{X}^1A_1$ ground state of CH$_4$. The energy level structures of $^{12}$CH$_4^+$, $^{13}$CH$_4^+$ and $^{12}$CD$_4^+$ have been analyzed with an effective tunneling-rotational Hamiltonian developed for this purpose. The analysis together with a group theoretical treatment of the $T\otimes(e+t_2)$ Jahn-Teller effect in the $T_d(M)$ group prove that the equilibrium geometry of $^{12}$CH$_4^+$, $^{13}$CH$_4^+$ and $^{12}$CD$_4^+$ is of $C_{2v}$ symmetry and characterize the pseudorotational dynamics in these fluxional cations. The tunneling behavior is discussed in terms of the relevant properties of the potential surface, some of which have been recalculated at the CCSD(T)/cc-pVTZ level of ab initio theory.

Chapter 9 describes high-resolution PFI-ZEKE photoelectron spectra of CH$_3$D and CD$_3$H that have been recorded at rotational resolution from the adiabatic ionization energy up to 600 cm$^{-1}$ of internal energy of the respective cations. The spectra are characterized by the effects of a large-amplitude pseudorotational motion exchanging the equivalent nuclei in each molecule. With increasing internal energy, a transition from the tunneling regime with splittings on the order of 1-10 cm$^{-1}$ to the free pseudorotation regime is observed. A theoretical model is presented that treats the simultaneous rotational and pseudorotational motions and incorporates the effects of the geometric phase. The model provides the appropriate rovibronic symmetries in the $C_{3v}(M)$ molecular symmetry group and reaches a near-quantitative agreement with the experimental data. The analysis of the spectra reveals the existence of two different isomers of both CH$_3$D$^+$ and CD$_3$H$^+$ which differ in the bond length between the carbon atom and the unique ligand atom. All isomers are subject to a fast pseudorotational motion between three equivalent minima with a period of 3-5 ps in CH$_3$D$^+$ and 18-28 ps in CD$_3$H$^+$. The analysis also provides the ordering of the tunneling sublevels for each isomer, which enables the location of the twofold conical intersections on the potential energy surface that could not be determined from experiments on CH$_4^+$ and CD$_4^+$. 
Zusammenfassung


Kapitel 2 beschreibt die spektroskopischen Methoden, hauptsächlich Photoionisations- und Photoelektronenspektroskopie und die Lasersysteme und Spektrometer, die in den nachfolgend beschriebenen Experimenten verwendet wurden.


Kapitel 4 beschreibt die Untersuchung der Hyperfeinstruktur und -dynamik auto-
Zusammenfassung


Nach der Beschreibung der fundamentalen Aspekte von Hyperfeinstruktur und -dynamik in atomaren Systemen, wendet sich die vorliegende Arbeit der Rolle des Kernspins in der Struktur und Dynamik molekularer Rydbergzustände zu. Kapitel 5 beschreibt hyperfeinaufgelöste gepulste Feldionisationsspektren von gebundenen s- und d-Rydbergzuständen von gerader elektronischer Symmetrie, die zu Serien gehören, die auf den \( X^2\Sigma^+_g (v^+ = 0, N^+ = 1) \) Grundzustand von ortho \( \text{H}_2 \) konvergieren. Die Spektren veranschaulichen die Evolution der Drehimpulskopplungshierarchie in Gegenwart eines Kernspins über einen ausgedehnten Spektralbereich. Im Bereich unterhalb von \( n \approx 40 \) folgt die Struktur der Energienniveaus im wesentlichen dem Hundischen Kopplungsfall (d), wobei jeder Zustand eine Hyperfeinaufspaltung erfährt. Zu höheren Hauptquantenzahlen hin findet ein Übergang zu einer von der ionischen Hyperfeinstruktur dominierten Niveaustruktur statt. Die s-Zustände weisen keine Hyperfeinstruktur auf, weil die Austauschwechselwirkung zwischen den beiden Elektronen grösser ist als die Hyperfeinwechselwirkung im Ion und nur die Singulettekomponenten anregbar sind. Dasselbe gilt auch für rotationsangeregte und vibrationsangeregte Rydbergzustände, die im Spektrum beobachtet werden und zu Störungen der Hauptserien führen. Die Analyse der Spektren erforderte die Bestimmung von Quantendefektkurven für die geraden Rydbergzustände mittels \textit{ab initio} R-Matrixrechnungen, die nachträglich geringfügig angepasst wurden, um die hochgenauen \textit{ab initio} Potentialkurven von Wolniewicz wiederzugeben. Die erhaltenen Quantendefektparameter ermöglichten die quantitative Voraussage der Photoionisationsspektren von \( \text{H}_2 \) in der Region des adiabatischen Ionisationspotentials und haben zur ersten eindeutigen Zuordnung aller beobachteten Störer geführt.

Kapitel 6 befasst sich mit der Hyperfeinstruktur und -dynamik rotationell autoion-
Zusammenfassung

Die Entwicklung eines resonanten Dreiphotonenanregungsschemas, das die lange Lebenszeit des $^1\Sigma_g^+ (v = 0)$ Zustandes ausnützt, ermöglichte eine bisher unerreichte Auflösung von 25 MHz in Photoionisationspektrten der ungeraden p-Rydbergzustände, die auf den $^2\Sigma_g^+ (v' = 0, N' = 3)$ Zustand von ortho $H_2^+$ konvergieren. Die Spektren enthalten Information über bisher unbekannte dynamische Prozesse der Kernspins in Molekülen und veranschaulichen die vollständige Entwicklung der Drehimpulskopplungshierarchie von der Situation einer dominierenden Austauschwechselwirkung zu einer Niveaustruktur, in der die ionische Hyperfeinstruktur dominiert. Mehrere intermediäre Kopplungsfälle konnten indentifiziert werden und erleichtern die Interpretation von Niveaustruktuern und der Autoionisationsdynamik. Bei Hauptquantenzahlen unterhalb von $n \approx 70$ können die p-Niveaux als Singulett- und Triplettkomponenten des Hundsfalls (d) verstanden werden. Zwischen $n \approx 70$ und $n \approx 160$ führen die Hyperfeinwechselwirkungen im Ion zu einer Kopplung des elektronischen Spins des Ions und die Kernspins, so dass der totale Spin $\vec{S} = \vec{I} + \vec{S}$ den elektronischen Spin $\vec{S}$ als Erhaltungsgröße ablöst. Bis zu $n \approx 160$ kann die Wellenfunktion der Rydbergzustände als ein Produkt einer Hundsfall (d) Wellenfunktion und einer totalen Spinwellenfunktion formuliert werden. Einige Konsequenzen davon sind die Erhaltung von $G$ in der Anregung ($\Delta G = 0$) und die Vorzugsregel $\Delta N = \Delta F$. Oberhalb von $n = 150$ führt die Spinrotationskopplung im Ion zu $G$-Mischung, und die Quantenzahl für den totalen Drehimpuls $F$ bleibt die einzige gute Quantenzahl.

Kapitel 7 beschreibt die Untersuchung der elektronischen und rovibronischen Struktur des Cyclopentadienykations $C_5H_5^+$ und seines vollständig deuterierten Isotopomers $C_5D_5^+$ mittels PFI-ZEKE Photoelektronenspektroskopie und ab initio quantenchemischen Rechnungen. Verschiedene Ein- und Mehrphotonenanregungssequenzen haben erstmals die Charakterisierung der vibronischen Struktur in den zwei tiefsten elektronischen Zuständen ermöglicht. Das Cyclopentadienykation besitzt einen Triplet-Groundzustand mit einer $D_{scb}$ Geometrie ($\tilde{X}^1\Sigma_g^+$) und einen ersten angeregten Singulettzustand ($\tilde{a}^1E_g$). Die Analyse der vibronischen Struktur im Singulettzustand mithilfe eines vibronischen Kopplungsmodells zeigt, dass dieser Zustand einer starken Pseudo-Jahn-Teller-Verzerrung unterliegt und ermöglicht die Bestimmung des adiabatischen Singulett-Triplet Intervalls. Die Kombination einer gruppentheoretischen Analyse der vibronischen Kopplungen mit ab initio Rechnungen zeigt, dass das Molekül auf der tiefsten Singulettfläch einer freien Pseudorotation unterliegt. Die Analyse der rovibronischen Photoionisationsdynamik in rotationsaufgelösten Spektren und die Abhängigkeit der Intensitätsverteilungen vom Schwingungsniveau des Zwischenzustandes der Zweiphotonenanregung ($\tilde{A}^2A'_2$) beweisen, dass ein Herzberg-Teller-Mechanismum für die Beobachtung des verbotenen $\tilde{a}^1E_2^+ - \tilde{A}^2A'_2^+$ Photoionisationsübergangs verantwortlich ist.

Kapitel 8 beschreibt die Bestimmung der Energieniveaustruktur der tiefsten vi-
Zusammenfassung

Die Kernspinsymmetrie der Tunnelrotationszustände wurde anhand von Doppelresonanzexperimenten über die \( v_3 = 1 \) und \( v_3 = 2 \) Schwingungsniveaux des \( \tilde{X}^1 \Sigma \) Grundzustandes von CH\(_4\) zugeordnet. Die Energieniveaustruktur von \(^{12}\)CH\(_4\), \(^{13}\)CH\(_4\) und \(^{12}\)CD\(_4\) wird anhand eines effektiven Tunnelrotations-Hamiltonoperators analysiert. Die Kombination der Analyse mit einer gruppentheoretischen Behandlung des \( T_\infty (e+t_2) \) Jahn-Teller-Effekts in der \( T_d (M) \) Symmetriegruppe beweist, dass die Minimumenergiestruktur von \(^{12}\)CH\(_4\), \(^{13}\)CH\(_4\) und \(^{12}\)CD\(_4\) C\(_2\)v Symmetrie besitzt und ermöglicht eine Charakterisierung der Pseudorotationsdynamik dieser flexiblen Moleküle. Die Tunnelbewegung wird anhand der relevanten Eigenschaften der Potentialfläche diskutiert, wovon einige auf CCSD(T)/cc-pVTZ-Niveau berechnet wurden.

Kapitel 9 beschreibt rotationsaufgelöste PFI-ZEKE Photoelektronenspektren von CH\(_3\)D und CD\(_3\)H von der adiabatischen Ionisationsschwelle bis zu 600 cm\(^{-1}\) interner Energie der Kationen. Die Spektren tragen die Merkmale von Bewegungen grosser Amplitude, die dem Austausch der äquivalenten Kerne entsprechen. Mit zunehmender interner Energie findet ein Übergang von einer Tunnelbewegung mit Aufspaltungen von 1-10 cm\(^{-1}\) zur freien Pseudorotation statt. Ein theoretisches Modell wird eingeführt und diskutiert, das Rotations- und Pseudorotationsbewegungen gleichzeitig behandelt und die Effekte der geometrischen Phase berücksichtigt. Das Modell liefert auch die rovibronischen Symmetrien in der C\(_{3v}\)(M)-Symmetriegruppe und ermöglicht eine nahezu quantitative Wiedergabe der experimentellen Übergänge. Die Analyse der Spektren beweist die Existenz von zwei Isomeren von CH\(_3\)D\(^+\) and CD\(_3\)H\(^+\), die sich in der Bindungslänge zwischen dem Kohlenstoffatom und dem einzelnen Ligandenatom unterscheiden. Alle Isomere unterliegen einer schnellen Pseudorotationsbewegung zwischen drei äquivalenten Minima mit einer Periode von 3-5 ps in CH\(_3\)D\(^+\) und 18-28 ps in CD\(_3\)H\(^+\). Die Analyse der Spektren ergibt auch die Reihenfolge der Tunnelniveaux in jedem Isomer, die eine Ortung der konischen Durchschneidungen auf der tiefsten Potentialfläche ermöglichen, die aus den Experimenten an CH\(_4\), CD\(_4\) nicht möglich war.
Résumé

L'approximation de Born et Oppenheimer est un des concepts fondamentaux de la chimie sur lequel repose la définition de la structure moléculaire en termes de la position relative des noyaux. Cette approximation est cependant insuffisante pour la description de nombreuses propriétés structurelles, dynamiques et spectrales de systèmes moléculaires. Cette thèse consiste en deux parties qui décrivent l'étude, par spectroscopie à haute résolution, de deux catégories de systèmes quantiques dont les propriétés ne peuvent pas être traitées dans le cadre de l'approximation de Born et Oppenheimer.

La première partie de cette thèse est dédiée à l'étude d'une importante catégorie d'états électroniques excités, dénommés états de Rydberg, et caractérise l'influence des spins nucléaires sur la structure et la dynamique de ces états par spectroscopie de photoionisation et d'ionisation par champ pulsé ainsi que par la théorie du défaut quantique à plusieurs voies (MQDT). Le seconde partie décrit l'étude expérimentale des effets Jahn-Teller et Pseudo-Jahn-Teller dans des cations moléculaires par spectroscopie photoélectronique et l'interprétation de ces effets par le calcul ab initio et la théorie du couplage vibronique. Ces études ont été rendues possibles grâce au développement de nouvelles techniques expérimentales et à l'extension de formalismes théoriques préexistants.

Le chapitre 2 décrit les techniques spectroscopiques et les systèmes laser employés au cours de ce travail.

Le chapitre 3 étend la théorie du défaut quantique à plusieurs voies développée par Fano, Lee et Lu pour les états de Rydberg des atomes de gaz rares afin d'inclure le spin nucléaire et applique la théorie à l'analyse de spectres d'ionisation pulsée de $^{83}\text{Kr}$. Le calcul reproduit les spectres expérimentaux de façon quantitative après ajustement de la structure hyperfine (inconnue au préalable) de $^{83}\text{Kr}^+$. Pour les nombres quantiques principaux $n$ inférieurs à 80, les interactions entre les spins nucléaires et électroniques mènent à un éclatement de chaque niveau en plusieurs composantes hyperfines. Pour des valeurs de $n$ plus élevées, la structure hyperfine de l'ion commence à dominer et les états de Rydberg peuvent être attribués à des séries convergeant vers des niveaux hyperfins distincts de $^{83}\text{Kr}^+$. Le découplage de l'électron de Rydberg qui intervient aux valeurs croissantes de $n$ induit des croisements entre des séries qui n'auraient pas lieu en l'absence d'un spin nucléaire et donne par conséquent accès à des paramètres dynamiques supplémentaires. En particulier, nous montrons que ces interactions sont à l'origine d'un croisement entre des séries s et d aux alentours de $n \approx 70$ qui est évité en raison de l'interaction sd.
Le chapitre 4 décrit l’étude de la structure et dynamique hyperfine des états de Rydberg autoionisants du xénon. Des spectres de photoionisation ont été mesurés entre les seuils d’ionisation correspondant à la formation des deux composantes spin-orbite (2P_{3/2} and 2P_{1/2}) du Xe^+. À une résolution suffisante pour déterminer la structure hyperfine, le formalisme MQDT décrit dans le chapitre 3 est étendu au traitement des continuas d’ionisation et à la prédiction de sections efficaces d’ionisation. Ce travail a permis l’analyse quantitative des spectres et a conduit à la première détermination des constantes de couplage hyperfin de l’état spin-orbite excité (2P_{1/2}) du ^{129}Xe^+ et du ^{131}Xe^+. Plusieurs processus dynamiques liés au spin nucléaire sont décrits pour la première fois. Un nouveau type d’autoionisation, dénommé "autoionisation hyperfine" est prédit pour les états de Rydberg situés entre les seuils d’ionisation correspondant à différents états hyperfins du cation. Au cours de ce processus, le cation subit une transition vers un état hyperfin d’énergie inférieure et transfert la différence d’énergie à l’électron de Rydberg qui échappe ainsi au potentiel attractif de l’ion.

La description des aspects fondamentaux de la structure et dynamique hyperfines dans les systèmes atomiques est suivie par l’étude du rôle des spins nucléaires dans les états de Rydberg moléculaires. Le chapitre 5 décrit des spectres d’ionisation par champ pulssé d’états de Rydberg liés gerade (s et d) appartenant à des séries convergeant vers l’état fondamental X 2Σ_g^+(v^+ = 0, N^+ = 1) de ortho H_2^+. Les spectres à résolution hyperfine révèlent l’évolution du couplage des moments cinétiques sous l’effet des interactions hyperfines. Pour un nombre quantique principal inférieur à n ≈ 40, les états d peuvent être décrits par le cas de couplage (d) de Hund, chaque niveau étant divisé en plusieurs composantes hyperfines. À des valeurs de n plus élevées, une transition a lieu vers un schéma de niveaux dominé par la structure hyperfine de H_2^+. Les états s ne révèlent pas de structure hyperfine dans l’intervalle étudié parce que l’interaction d’échange domine sur les interactions hyperfines de H_2^+. Les états d qui sont observés dans la même région spectrale (états intrus) et causent des perturbations des séries principales. La prédisociation est nettement plus rapide pour les séries nd1_3 que pour les autres, en raison d’une interaction avec un état intru (7d1_3, v^+ = 1). L’analyse des spectres a requis le prédiction de courbes de défauts quantiques pour les états de symétrie gerade par le calcul R-matrice ab initio qui ont ensuite été ajustées pour reproduire les courbes d’énergie potentielle hautement précises calculées par Wolniewicz. Les courbes de défauts quantiques ainsi obtenues reproduisent les spectres de photoionisation de H_2 dans la région du potentiel d’ionisation adiabatique et ont permis la première attribution de tous les états intrus observés.

Le chapitre 6 décrit la structure hyperfine et la dynamique d’autoionisation des états de Rydberg d’ortho H_2. Un schéma d’excitation triplement résonant a été dévelop-
résumé

pe pour accéder à l’état $H^1 \Sigma_u^+ (v = 0)$ possédant une longue durée de vie, et a permis d’atteindre une résolution de 25 MHz dans les spectres de photoionisation des états de Rydberg élevés (p) convergent vers l’état $X^2 \Sigma_u^+ (v^+ = 0, N^+ = 3)$ de ortho $H_2^+$. Les spectres permettent l’étude de processus moléculaires dynamiques inconnus au préalable qui sont liés aux spins nucléaires. Ils révèlent aussi pour la première fois l’évolution de la hiérarchie de couplage d’une situation où l’interaction d’échange détermine la structure des niveaux à une situation où la structure hyperfine de l’ion est déterminante. Pour un nombre quantique principal inférieur à $n \approx 70$, les niveaux peuvent être classifiés dans le cas de couplage (d) de Hund et en fonction de leur caractère singulet ($S = 0$) ou triplet ($S = 1$). Entre $n \approx 70$ et $n \approx 160$, les interactions hyperfines dans le cœur ionique mènent à un recouplage du spin électronique de $H_2^+$ au spin nucléaire total $I$. Le spin électronique total $\hat{S}$ est remplacé dans son rôle de constante du mouvement par le spin total $\hat{G} = \hat{I} + \hat{S}$. Jusqu’à $n \approx 170$, les états de Rydberg peuvent être décrits par un produit d’une fonction d’onde correspondant au cas (d) de Hund et d’une fonction d’onde de spin total $\hat{G}$. Cette propriété implique, entre autres, la conservation de $G$ lors de la photoexcitation ($\Delta G = 0$) et une règle de préférence $\Delta N = \Delta F$. Au delà de $n = 150$, le recouplage du spin électronique de $H_2^+$ avec le moment cinétique rotationnel commence à mélanger les fonctions d’onde du cas (d), $G$ n’est plus conservé et seul $F$ reste un bon nombre quantique.

Le chapitre 7 décrit l’étude de la structure électronique et rovibronique du cation cyclopentadiényle $C_5H_5^+$ et de son isotopomère entièrement deutéré $C_5D_5^+$ par la spectroscopie photoélectronique PFI-ZEKE et le calcul ab initio. Différentes séquences d’excitation à un ou plusieurs photons ont permis la première détermination expérimentale de la structure vibronique des deux premiers états électroniques fondamentaux. Le cation cyclopentadiényl possède un état fondamental triplet de symétrie $D_{5h}$ ($X^+ 3A_2')$ et un premier état excité singulet ($a^+ 1E'_2$). L’analyse de la structure vibronique de cet état sur la base d’un modèle de couplage vibronique montre que l’état singulet est sujet à un couplage Pseudo-Jahn-Teller très fort et permet la détermination de l’intervalle adiabatique singulet-triplet. Une analyse par la théorie des groupes combinée à des calculs ab initio établit la topologie des surfaces de potentiel singulet et prouve que la surface la plus basse donne lieu à une pseudorotation libre. L’analyse de la dynamique de photoionisation dans les spectres à résolution rotationnelle et la dépendance de la distribution d’intensité de l’état vibrationnel intermédiaire ($\tilde{A}^2 A''_g$) sélectionné dans l’excitation à deux photons montre que l’observation de la transition de photoionisation interdite $a^+ 1E'_2 \rightarrow \tilde{A}^2 A''_g$ résulte d’un mécanisme Herzberg-Teller.

Le chapitre 8 résume la détermination de la structure rotationnelle des états vibroniques les plus bas de $^{12}CH_4$, $^{13}CH_4$ et $^{12}CD_4$ par la spectroscopie photoélectronique PFI-ZEKE. La symétrie de spin nucléaire des états rotationnels a été déterminée par des expériences à double résonance utilisant des niveaux rotationnels sélectionnés de l’état fondamental $\tilde{X}^1 A_1$ de $CH_4$. La structure des niveaux de $^{12}CH_4$, $^{13}CH_4$ et
$^{12}$CD$_4^+$ a été analysée par un Hamiltonien effectif incluant simultanément l'effet tunnel et la rotation de la molécule. Cette analyse, en combinaison avec un traitement de l'effet Jahn-Teller $T\otimes(e+t_2)$ par la théorie des groupes, prouve que la géométrie d'équilibre de $^{12}$CH$_4^+$, $^{13}$CH$_4^+$ et $^{12}$CD$_4^+$ a la symétrie $C_{2v}$ et caractérise la dynamique de pseudorotation de ces cations. L'effet tunnel observé est discuté en relation aux propriétés des surfaces d'énergie potentielle dont certaines ont été recalculées par la méthode *ab initio* CCSD(T)/cc-pVTZ.

Le chapitre 9 décrit les spectres photoélectroniques PFI-ZEKE de CH$_3$D and CD$_3$H qui ont été mesurés à résolution rotationnelle depuis l'énergie d'ionisation adiabatique jusqu'à 600 cm$^{-1}$ d'énergie interne des cations respectifs. Les spectres sont caractérisés par les effets d'un mouvement pseudorotationnel de grande amplitude qui échange les noyaux équivalents dans chaque molécule. L'accroissement de l'énergie interne est accompagnée de la transition d'un régime tunnel avec des intervalles typiques de 1-10 cm$^{-1}$ à un régime de pseudorotation libre. Un modèle théorique décrivant la rotation et le mouvement tunnel simultanément et incorporant les effets de la phase géométrique est présenté. Le modèle fournit les symétries rovibrioniques appropriées dans le groupe $C_{3v}(M)$ et aboutit à un accord quasi-quantitatif avec les données expérimentales. L'analyse des spectres révèle l'existence de deux différents isomères de CH$_3D^+$ et CD$_3H^+$ qui diffèrent par la longueur de liaison entre l'atome central et l'atome unique lié. L'analyse permet également de déterminer l'ordre énergétique des niveaux tunnel de chaque isomère et de situer les intersections coniques doubles sur les surfaces de potentiel, une information qui n'est pas facilement déduite des spectres de CH$_4^+$ ou CD$_4^+$. 
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Chapter 1

Introduction

1.1 The role of non-Born-Oppenheimer effects

The Born-Oppenheimer (BO) approximation [1] constitutes the basis of the description of molecular structure and dynamics. Its validity relies on the substantial difference between the mass of an electron and that of a nucleus. This property leads to largely different motional timescales which translate to spacings between quantized states that are much larger for the electronic than for the internal nuclear motion. The motion of the electrons can be considered to be infinitely fast on the timescale of the nuclear motion and the separation (also termed "adiabatic" separation) of the electronic and nuclear motion constitutes an accurate approximation.

The BO approximation is discussed at length in most textbooks on quantum chemistry and spectroscopy [2–7] to which the reader is referred for a general introduction. The BO approximation is valid as long as the electronic intervals are sufficiently large that the nuclear motion can be described as taking place on a single potential energy surface. This assumption is, however, inappropriate to describe many processes of physical and chemical relevance, including photochemistry, charge transfer reactions and high-temperature superconductivity. This class of phenomena has stimulated substantial experimental and theoretical efforts over the past decades but the description of non-Born-Oppenheimer phenomena often poses problems and remains unsatisfactory. In view of the complexity of the problem, detailed experimental data are essential for testing and validating the theoretical methods. The present thesis illustrates how the latest progress in high-resolution spectroscopy, particularly in the vacuum-ultraviolet region of the electromagnetic spectrum and in photoelectron spectroscopy, can be exploited to collect highly detailed experimental information on non-Born-Oppenheimer dynamics in molecular systems.

Two kinds of systems are particularly amenable to an investigation of non-Born-Oppenheimer dynamics by high-resolution spectroscopy and are at the heart of the work summarized in this thesis: Rydberg states and open-shell polyatomic cations.
In these systems, the electronic states are closely spaced and the timescale of the electronic motion is similar to or even slower than that of nuclear motion.

## 1.2 Rydberg states

Rydberg states are excited electronic states in which the mean distance \( r \) of the excited electron from the ionic core is so large that the interaction potential is essentially Coulombic. The level positions are accordingly given by the Rydberg formula [8]:

\[
E(n, \ell, i) = IE(i) - \frac{Ry_M}{(n - \nu_\ell)^2}.
\]

In Eq. (1.1), \( n \) and \( \ell \) designate the principal and angular momentum quantum numbers, \( Ry_M = R_\infty \cdot \frac{M}{M+m_e} \) the mass corrected Rydberg constant and \( \nu_\ell \) is the quantum defect. Rydberg states with distinct values of \( n \) form a Rydberg series which converges to the ionization energy \( IE(i) \) of the \( i^{th} \) state of the cation for \( n \to \infty \). A Rydberg series and the associated ionization continuum located above the threshold form an "ionization channel". In first approximation, the energies of the Rydberg states of the hydrogen atom depend only on \( n \) because levels differing in \( \ell \) and \( m_\ell \) only are degenerate (\( \nu_\ell = 0 \)) and the ionization threshold is unique (see Fig. 1.1). In atoms possessing several electrons, the \( \ell \)-degeneracy is lifted (\( \nu_\ell \neq 0 \)) because the potential experienced by the Rydberg electron in the vicinity of the core is no longer Coulombic. The quantum defect \( \nu_\ell \) accounts for the interaction of the Rydberg electron with the core electrons and is proportional to the phase shift experienced by a free electron being scattered from the ionic core. The magnitude of the quantum defect depends on the penetration depth of the Rydberg electron into the core region and decreases with increasing \( \ell \). States with \( \ell > 3 \) usually possess very small quantum defects. Another property of polyelectronic atoms is the existence of additional Rydberg series converging to excited states of the cation. Most properties of Rydberg states scale with an integer power of the \( n \), including the classical orbit radius (\( \propto n^2 \)), the binding energy (\( \propto n^{-2} \)), the density of states (\( \propto n^3 \)), the radiative lifetime (\( \propto n^3 \)), the transition probability from the ground state (\( \propto n^{-3} \)) and the polarizability (\( \propto n^7 \)).

Molecules possess a wealth of Rydberg series converging to all electronically, vibrationally or rotationally excited levels (see right-hand side of Fig. 1.1). At increasing \( n \) values, the intervals between Rydberg states decrease and become smaller than the vibrational, the rotational and eventually even the hyperfine intervals of the cation. The corresponding complete breakdown of the BO approximation leads to a coupling between the Rydberg series which induces perturbations between the bound states below the first ionization threshold and causes autoionization above it. The description of Rydberg states is beyond standard non-adiabatic techniques because an infinity of states would need to be considered. Penetrating Rydberg states are par-
1.2. Rydberg states

Figure 1.1: Schematic representation of Rydberg series of atoms and molecules. The energy of the Rydberg states of the hydrogen atom depends on the principal quantum number $n$ only and states differing in the orbital angular momentum $\ell$ only are degenerate. This degeneracy is removed in atoms possessing several electrons. In molecules, Rydberg series arise that converge on each level of the cation.

particularly challenging because they combine a region of space where the BO approximation is valid (the so-called "close-coupling" region at short core-electron distances $r$) with a region where the motional timescales are inverted (the long-range or uncoupled region at large $r$). An elegant solution for the description of these systems is Multichannel Quantum Defect Theory (MQDT) [9-13]. The two essential ingredients of MQDT are an electronic quantum defect matrix representing the complex interactions in the close-coupling region and an analytical frame transformation to the uncoupled representation. In molecules, the transformation enables a smooth transition between Hund’s cases (a) or (b) at low $n$ values and Hund’s case (d) or (e) at high $n$ values [14,15]. In the rare gas atoms, the frame transformation connects the close-coupling region which is well approximated by $LS$ coupling to the asymptotic region which is adequately described by $jj$ coupling [16].

Mulliken has referred to Rydberg states as the "stepping stones toward ionization" [17-20] to emphasize the basic unity that exists between high Rydberg states and the adjacent ionization continua. The short-range interactions are common to both but the long-range boundary conditions are different in the bound and continuous regions. MQDT provides a unified description of discrete and continuous spectra in terms of the same parameters that describe the physics at short range. The theory
therefore accounts simultaneously for the structure of Rydberg states and their decay dynamics into the continua which includes autoionization (also called preionization) and, with suitable modification [21] predissociation.

A proper description of the structure and dynamics of Rydberg states is essential to understand the processes following the absorption of short-wavelength radiation by molecules, radiative decay, autoionization and predissociation. Rydberg states lying in the ionization continuum also correspond to resonances in the scattering of electrons from molecular cations and their properties provide valuable information on such collisions. A recent and impressive example is the explanation of the unusually large rate of dissociative recombination of $\text{H}_3^+$ with slow electrons which involves the Jahn-Teller effect in the Rydberg states of $\text{H}_3$ [22,23].

This thesis describes the first experimental and theoretical investigations of the role of nuclear spins in the dynamics of atomic and molecular Rydberg states and in photoionization. Up to present day, the role of nuclear spins was restricted to the conservation of nuclear spin symmetry in photoexcitation and photoionization, as a particular case of the general conservation rules formulated by Quack [24]. The interactions involving nuclear spins belong to the weakest among the electromagnetic interactions which justifies their neglect for many practical purposes. However, since the timescale of electronic motion can become arbitrarily slow in high Rydberg states, the hyperfine interactions will necessarily dominate the dynamics at sufficiently high $n$ values. The excitation of a closed-shell atom or molecule to a Rydberg state leads to an open-shell core and thus turns on fine and hyperfine interactions that were inexistent in the ground state. The resulting change in the angular momentum coupling hierarchy and its dynamical implications is investigated in chapters 3 to 6.

### 1.3 Molecular cations and the Jahn-Teller effect

Molecular cations are of fundamental importance in chemistry. They appear as reaction intermediates, are constituents of flames and plasmas and occur in the upper layers of the earth and other planetary atmospheres. Cations are essential in the chemistry of the interstellar medium because many ion-molecule reactions are barrierless and can thus occur in low-temperature and low-pressure environments. The spectroscopic investigation of cations has several motivations. First, a detailed knowledge of their energy level structure improves the understanding of their structure, internal dynamics and chemical reactivity. Second, many molecular cations are open-shell species which gives rise to physical phenomena that do not occur in closed-shell species, including (ro)vibronic coupling effects like the Jahn-Teller (JT), the Pseudo-Jahn-Teller (PJT) or the Renner-Teller (RT) effects which are often accompanied by large-amplitude motions. Molecular cations often represent prototypical systems for
1.3. Molecular cations and the Jahn-Teller effect

the investigation of these effects which are essential in the understanding of molecular structure and dynamics. Third, the knowledge of spectral positions and intensities can be exploited to detect molecular species and measure their concentrations, particularly in planetary atmospheres and in the interstellar medium.

The open-shell character of many molecular cations leads to electronic degeneracies or closely spaced electronic states which lead to a breakdown of the BO approximation [25]. The theory of vibronic coupling allows an elegant treatment of such situations [26]. In contrast to the adiabatic approximation, it assumes that the electronic wavefunctions strongly depend on the nuclear coordinates, i.e., that the electrons do no longer follow the nuclear motion adiabatically. The theory of vibronic coupling describes the mixing of the electronic states by the nuclear displacements and the back-influence on the nuclear motion. The resulting intimate coupling of electronic and nuclear dynamics influences many properties of polyatomic systems. The vibronic coupling operator is usually expanded in a Taylor series around the reference geometry. The order of the terms in the nuclear displacement coordinates is designated as the order of the vibronic coupling.

A special case of vibronic coupling is the Jahn-Teller effect [27]. It occurs in non-linear, polyatomic open-shell molecules and results from the interaction of the components of a degenerate electronic state mediated by nontotally-symmetric modes. The contribution of the linear term of the Taylor expansion mentioned above to the vibronic coupling is designated as linear JT effect. The contribution resulting from the quadratic term in the Taylor expansion is designated as quadratic JT effect. Group-theoretical methods can be used to predict which vibrational modes can contribute at which order ([28,29], see also chapter 7).

A simple and well-understood example is the E→e JT effect [30–33], resulting from the interaction of a doubly degenerate (E) electronic state with a doubly degenerate (e) vibrational mode. The necessary condition for the existence of a linear coupling is that the irreducible representation of the vibrational mode is contained in the symmetrized square of the electronic symmetry ([\Gamma_E]^2 \cong \Gamma_Q, where \Gamma_E represents the electronic and \Gamma_Q the vibrational symmetry). The JT effect profoundly affects the shape of the potential energy surface which is represented schematically in Fig. 1.2.

The splitting of the degenerate state along the JT active coordinate moves the minimum of the potential energy surface away from the symmetric configuration to a region corresponding to a distorted geometry thus lowering the potential energy minimum by an amount called JT stabilization energy. A linear JT effect leads to a continuous one-dimensional minimum-energy subspace, and the two-dimensional potential displays a circular trough (see Fig. 1.2). When the stabilization is large enough, the molecule performs a large-amplitude motion along this trough which is often referred to as "pseudorotation". Even small coupling effects lead to a highly irregular appearance of the vibrational level structure. When several vibrational modes
Figure 1.2: Schematic representation of the potential energy surfaces resulting from a linear E°e Jahn-Teller effect. The lower surface is stabilized by the energy $E_{JT}$ and forms a one-dimensional equipotential minimum energy trough in the space spanned by the two components $(Q_\epsilon, Q_\rho)$ of the degenerate vibrational mode (adapted from Ref. [34]).

contribute to the coupling, the level structure becomes entirely irregular and the assignment is only possible by a combination of experiment, ab initio quantum chemical and dynamical calculations [29].

Another consequence of the JT effect is that the configuration of highest symmetry does no longer correspond to a minimum on the potential energy surface but to an intersection of surfaces, more precisely, a 3N-6-2 (3N-6-5) dimensional seam of electronic degeneracy for a doubly (triply) degenerate electronic state. In the subspace of the linearly active vibrational modes, the intersection is conical, i.e., the first derivative of the potential energy with respect to the vibrational coordinate is nonzero. This type of intersections is not restricted to the JT effect but is ubiquitous in polyatomic systems. Conical intersections play a fundamental role in organic photochemistry where they mediate a rapid radiationless decay to a lower-lying electronic surface on which further reactions occur [35]. Many reaction mechanisms involve conical intersections including photochemical reactions in benzene, carbene formation from diazerine and diazomethane and the rearrangement of acylicyclopropenes to furans
and the photochemistry of amino acids and peptides [36]. At the position of the conical intersections and in their vicinity, a molecule can make a transition from one surface to another with great facility. Unfortunately, the energetic regions and the configurational space close to conical intersections are difficult to access and study by high-resolution spectroscopy. The JT conical intersection is a remarkable exception which can be probed in detail by high-resolution spectroscopy. The understanding of the spectroscopy of JT systems thus plays an essential role in studies of molecular quantum dynamics in the vicinity of conical intersections and has the potential to deepen our understanding of nonadiabatic processes.

The understanding of the JT and related vibronic coupling effects is also essential in the interpretation of ab initio quantum chemical calculations. In the presence of electronic degeneracy or pseudo-degeneracy, fixed-nuclei electronic structure calculations are partially meaningless and cannot predict observable properties. Although ab initio calculations can be used to calculate adiabatic potential energy surfaces, this information is insufficient to predict the dynamics occurring in the molecular systems unless a vibronic coupling model is invoked. A particularly striking example for such a situation is given in this thesis. In the methane cation, a tunneling treatment relying solely on the adiabatic potentials derived from ab initio calculations would predict a qualitatively incorrect tunneling structure in the ground state whereas a vibronic coupling model provides the correct answer (see chapter 8 and Ref. [37]).

This observation is closely related to the "topologic" or "geometric" phase problem that has been discussed extensively in the literature [38,39]. The first description of the geometric phase in the context of conical intersections was given by Herzberg and Longuet-Higgins [40]. Using valence-bond theory, they have shown that an adiabatic electronic wavefunction changes sign when transported once around a conical intersection, be it of JT origin or not. This sign change in the electronic wavefunction is accompanied by a sign change in the nuclear wavefunctions, so that the total vibronic wavefunction remains single-valued at every point in configuration space. The concept of the geometric phase thus results from the paradoxical attempt to interpret nuclear motion on a vibronically coupled surface in the realm of the BO approximation. As will be illustrated in chapter 7, the geometric phase is not needed in vibronic coupling calculations because they do not rely on an adiabatic separation of electronic and nuclear motions. In the case of the methane cation (see chapters 8 and 9), the very large JT stabilization implies that the nuclear motion is effectively confined to the lowest adiabatic potential energy surface but the adiabatic wavefunctions depend themselves on the nuclear geometry. We show how this effect can be integrated in a tunneling model without invoking a geometric phase.
Chapter 2

Experimental setups and methods

The experimental setups employed in the course of this thesis consist of three components: laser systems generating coherent tunable radiation in the near-infrared (NIR), visible (VIS) or ultraviolet (UV) ranges of the electromagnetic spectrum, nonlinear optical units used to generate sum- or difference-frequencies lying in the vacuum-ultraviolet (VUV) or in the mid-infrared (MIR) regions, and a high-vacuum chamber in which the spectroscopic experiment is carried out and which includes time-of-flight electron and ion mass spectrometers and detection systems.

2.1 Light sources

2.1.1 Generation of coherent tunable vacuum-ultraviolet radiation

The radiation that is needed to excite ground state atoms or molecules to Rydberg states typically lies in the VUV range of the electromagnetic spectrum. Because no nonlinear crystals exist that can be used to generate VUV radiation below ~189 nm,

Figure 2.1: Schematic diagram illustrating the process of VUV generation using two-photon resonance-enhanced four-wave mixing.
the nonlinear frequency upconversion is achieved in gases such as the rare gases [41] or mercury vapor [42]. The second-order susceptibility, which is used for sum- and difference-frequency mixing in nonlinear crystals, vanishes in isotropic media and the lowest-order nonlinear process in gases is four-wave mixing. The efficiency of a four-wave mixing process is proportional to the square of the third-order susceptibility and the square of the density of the nonlinear gas [43].

The generation of VUV radiation below 105 nm, a region also called extreme ultraviolet (XUV or EUV), is complicated by the fact that no solid-state material transmits radiation in this region of the electromagnetic spectrum. The nonlinear medium can therefore not be contained in a cell if radiation below 105 nm is generated and the nonlinear gas must be confined in a pulsed gas beam in the same extended vacuum system in which the spectroscopic experiments that use the XUV radiation are performed. By using small orifices between the different chambers of a differentially-pumped vacuum system, the background pressure in the photoexcitation region can be kept three orders of magnitude lower than the background pressure of typically $10^{-4}$ mbar in the part of the vacuum system where the XUV radiation is generated.

In the four-wave-mixing process, the interaction of intense laser beams, which overlap spatially and temporally, with the nonlinear gas gives rise to harmonic sum- and difference frequencies when they travel through the nonlinear medium. Because the third-order susceptibility is small compared to the first-order susceptibility but large compared to susceptibilities of higher orders, laser beams of moderate peak intensity ($10^9$-$10^{12}$ W/cm$^2$) can be used to generate VUV radiation of sufficient intensity for spectroscopic experiments to be performed.

The intensity of the generated VUV radiation can be enhanced if the combined energy of two input photons corresponds to a two-photon resonance (e.g., $2\nu_{\text{UV}}$) starting from the ground state of the nonlinear gas, see figure 2.1. The output frequencies are then equal to the third harmonic $\nu_{\text{UV}}' = 3\nu_{\text{UV}}$, the sum frequency $\nu_{\text{UV}}'' = 2\nu_{\text{UV}} + \nu_2$, and the difference frequency $\nu_{\text{UV}}''' = 2\nu_{\text{UV}} - \nu_2$. All other four-wave mixing frequencies, such as $\nu_{\text{UV}}''' = 3\nu_2$ for instance, are not resonantly enhanced at the two-photon level and therefore have a much lower intensity.

The experiments described in this thesis made use of tunable VUV radiation generated by resonance enhanced sum- and difference-frequency mixing using the two-photon resonances listed in Table 2.1. The VUV frequency was tuned by changing the frequency of the second laser, $\nu_2$.

The UV radiation required to reach the two-photon resonances in krypton and xenon are generated using frequency-doubling and mixing in $\beta$ Barium-Borate (BBO) crystals. The wave numbers $\tilde{\nu}_{\text{UV}} = 49427.535$ cm$^{-1}$ (47046.431 cm$^{-1}$) can be produced by doubling the frequency of a visible laser at 16475.845 cm$^{-1}$ (15682.143 cm$^{-1}$) and mixing the doubled output with the fundamental beam. The wave number $\tilde{\nu}_{\text{UV}} = 40059.487$ cm$^{-1}$, corresponding to the two-photon resonance in xenon, is
2.1. Light sources

Table 2.1: Two-photon resonances in rare gas atoms [44-46] used in the four-wave mixing process. The last column indicates which resonance was used in the experiments described in each of the following chapters.

<table>
<thead>
<tr>
<th>rare gas</th>
<th>transition</th>
<th>$2\tilde{\nu}_{\text{UV}}$ / cm$^{-1}$</th>
<th>chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>(4p)$^5$ ($^2P_{3/2}$) 5p [1/2] ($J = 0$) $\rightarrow$ (4p)$^6$ 1$S_0$</td>
<td>94092.862</td>
<td>4, 6, 7</td>
</tr>
<tr>
<td>Kr</td>
<td>(4p)$^5$ ($^2P_{1/2}$) 5p' [1/2] ($J = 0$) $\rightarrow$ (4p)$^6$ 1$S_0$</td>
<td>98855.071</td>
<td>3</td>
</tr>
<tr>
<td>Xe</td>
<td>(5p)$^5$ ($^2P_{3/2}$) 6p [1/2] ($J = 0$) $\rightarrow$ (5p)$^6$ 1$S_0$</td>
<td>80118.974</td>
<td>5, 8, 9</td>
</tr>
</tbody>
</table>

obtained by doubling the output of a dye laser at 20029.744 cm$^{-1}$ or doubling and sum-frequency mixing the radiation of a titanium-sapphire laser system at 13353.162 cm$^{-1}$.

2.1.2 Sources of laser radiation

Dye laser setup

In the experiments on methane described in chapters 8, and 9, VUV radiation was used to excite the molecules from their vibronic ground state to high Rydberg states. Tunable vacuum ultraviolet (VUV) radiation was generated using the laser system depicted schematically in Fig. 2.2 by resonance-enhanced sum-frequency mixing ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_{\text{UV}} + \tilde{\nu}_2$) in xenon using the two-photon resonance listed in Table 2.1. Before combining the two laser beams using a dichroic mirror and focusing them into a xenon gas jet, a telescope was used to prefocus the second laser so that the focal points of both beams coincided. The radiation of the input beams to the four-wave mixing process was generated by commercial dye lasers pumped by a pulsed Nd:YAG laser operating at a repetition rate of 10 Hz. The VUV radiation was separated from the fundamental beams in a vacuum monochromator using a toroidal dispersion grating which also recollimated the diverging VUV beam and redirected it toward a photoexcitation-photoionization chamber where it intersected the molecular beam at right angles. Calibration of the visible radiation was achieved by recording optogalvanic spectra of neon and comparing the observed wave numbers to the tables given in Ref. [47]. The VUV wave number was determined by building the sum of the two-photon resonance wave number and the wave number of the second laser which was also determined by recording optogalvanic spectra of neon.

In the experiments on the cyclopentadienyl radical described in chapter 7, VUV radiation was generated by resonance-enhanced difference-frequency mixing ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_{\text{UV}} - \tilde{\nu}_2$) in krypton using the two-photon resonance at 94092.862 cm$^{-1}$ listed in Table 2.1. The VUV radiation was generated inside a 30 cm long gold-coated cell filled with 15 mbar of krypton because higher VUV intensities could be generated than using a krypton beam in the wavenumber range 67000 - 75000 cm$^{-1}$. A MgF$_2$ prism with an apex angle of 45° was employed to separate the VUV difference-frequency
Chapter 2. Experimental setups and methods

Figure 2.2: Experimental setup used in the experiments on methane described in chapters 8 and 9 and in the experiments on H$_2$ described in chapter 6.

Figure 2.3: Gas cell used to generate VUV radiation for the experiments on the cyclopentadienyl cation described in chapter 7. The four-wave mixing cell replaced the gas jet used in the experiments carried out with VUV radiation (see Fig. 2.2).

beam from the fundamental laser beams of wave numbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$. The parts of the setup which differ from that displayed in Fig. 2.2 are shown in Fig. 2.3.

Narrow-bandwidth ring dye lasers

The laser system described in Ref. [48] and depicted in figure 2.4, was used to generate the visible, UV and VUV laser beams that were used in the experiments on krypton
2.1. Light sources

The single-mode outputs of two continuous-wave dye ring lasers were pulse amplified in three successive dye cells pumped by the doubled output of a pulsed Nd:YAG laser operating at a repetition rate of 25 Hz. In the experiments using VUV radiation, the wave number of the first ring laser was locked to a transition in molecular iodine such that $\bar{v}_1 = 2\bar{v}_{\text{UV}} = 94092.906 \text{ cm}^{-1}$. To generate $\bar{v}_{\text{UV}} = 3\bar{v}_1$, the pulse-amplified output was doubled in a BBO crystal and the doubled beam subsequently mixed with the fundamental beam in a second BBO crystal. The resulting VUV beam was then spatially and temporally overlapped with the doubled, pulse-amplified output of the second ring laser.

The four-wave mixing process took place in a pulsed, supersonic krypton beam and the sum- or difference-frequency radiation was separated from the other light beams using the first diffraction order of a grating monochromator. The number of photons per pulse of the resulting VUV radiation amounted to $10^8$ to $10^9$ after the monochromator. The bandwidth of the VUV laser is approximately 0.008 cm$^{-1}$ and the pulse length ~2 ns. The VUV radiation was therefore nearly Fourier-transform limited as expected for the amplification and frequency up conversion of a single-mode cw laser beam.

Figure 2.4: Experimental setup used in the experiments on krypton, xenon and the cyclopentadienyl radical described in chapters 3, 4 and 7.

and xenon described in chapters 3 and 4 and the rotationally resolved measurements of the PFI-ZEKE photoelectron spectra of the cyclopentadienyl radical presented in chapter 7.
Chapter 2. Experimental setups and methods

Figure 2.5: Experimental setup used in the experiments on bound and autoionizing Rydberg states of $\text{H}_2$ described in chapters 5 and 6.

Narrow-bandwidth titanium-sapphire ring lasers

The laser system described in Ref. [49] and depicted in figure 2.5 was used to generate the NIR and VUV laser beams that were used in the experiments on $\text{H}_2$ described in chapters 5 and 6. The primary source of NIR radiation is a commercial, tunable, cw ring Ti:Sa laser (Coherent 899-29) pumped by the output of a diode-pumped, frequency-doubled Nd:YVO$_4$ laser (Coherent, Verdi). The single-mode cw output of the laser with frequency $\nu_{\text{cw}}$ is passed through an acousto-optic modulator (AOM, Brimrose, GPF-1000-500-800) which is operated at a 1 GHz driving frequency. The first-order diffraction side-band of frequency $\nu_{\text{NIR}} = \nu_{\text{cw}} + 1 \text{ GHz}$ exits the AOM and is transferred to a nearby optical table where it is pulse amplified. The pulse duration and shape can be adjusted freely, the only limitation being the minimum rise time ($\approx 5-10 \text{ ns}$) required for the acoustic wave to spread over the region of the NIR laser focus.

The peak power and the pulse energies of the NIR pulses generated in the AOM are too low for frequency upconversion by nonlinear optical techniques. The pulses must be amplified by a factor of about $10^6$ for efficient extension of the tunable range into the VUV. To preserve the pulse shapes during the amplification process it is necessary to use an amplification medium with a sufficiently long relaxation time. The amplification of the NIR seed pulses is achieved in Ti:Sa crystals (0.15% doping) that are pumped by the frequency-doubled output of a Nd:YAG laser (Spectra Physics, Quanta-Ray Pro270) using a multipass configuration. Pump and seed beams are directed through the Ti:Sa crystals in a near-collinear arrangement with their polarization vectors in the plane of the $c$ axis of the crystal, which corresponds to the horizontal plane in the laboratory. Because the long population inversion time of
Ti:sapphire crystals translates into low amplification factors compared to dye amplification cells, a careful optimization of the amplification arrangement is essential. To obtain satisfactory amplification, the pump beam size was reduced to match the size of the NIR beam in the crystal and thus achieve optimal power densities and population inversion in the volume traversed by the seed beam. To minimize the number of Ti:Sa crystals, the NIR seed beam was passed through each crystal up to nine times, which represents the maximum number of passes compatible with the pumping configuration. Each pass contributes an amplification factor in the range 2-5 to the overall amplification.

2.1.3 Generation of tunable mid-infrared radiation

IR radiation around 3000 cm\(^{-1}\) (6000 cm\(^{-1}\)) was generated by difference-frequency mixing in a KTiOAsO\(_4\)/KTA (KTiOPO\(_4\)/KTP) crystal [50, 51]. A KTA crystal of dimensions 5 x 5 x 15 mm (5 x 5 x 10 mm) was used. The 532 nm (1064 nm) output of the Nd:YAG laser and the 630-640 nm (645-655 nm) output of a tunable dye laser were overlapped by means of a dichroic mirror and collimated to a beam of waist 1.5 mm before being sent into the crystal. Phase-matching was achieved by adjusting the angle between the laser beams and the crystal axis. The two input beams were aligned so that they crossed in the center of the crystal with a small angle between them. This alignment allowed a simple separation of the different beams after the crystal and avoided the use of filters. Pulse energies of up to 1 mJ were obtained around 3.3 \(\mu\)m using pulse energies of 10 mJ at 630 nm and 15 mJ at 532 nm. The IR beam was then sent into the photoexcitation chamber using gold-coated mirrors and counterpropagated against the VUV beam. The IR pulse was timed to precede the VUV pulse by \(\approx\) 10 ns. The IR frequency was calibrated by comparing the measured line positions of the \(v_3\) and \(2v_3\) bands of CH\(_4\) with literature values [52].

2.1.4 Frequency calibration

The calibration of the visible radiation was achieved by recording optogalvanic spectra of argon or neon in a hollow-cathode discharge lamp and comparing the observed spectra to literature values [47]. The accuracy of this procedure amounts to \(\sim\) 0.2 cm\(^{-1}\), but the atomic lines are relatively sparse.

The experiments on krypton, xenon and molecular hydrogen (see chapters 3, 4, 5 and 6) required a higher accuracy. In these cases, the wavenumber was calibrated by recording the laser-induced-fluorescence spectrum of molecular iodine at room temperature (chapter 3), its absorption spectrum in an oven heated to 570 °C (chapters 4 and 5) or a wavemeter (Burleigh EXFO WA-1500) with an absolute uncertainty of 60 MHz (chapter 6). The relative wave number was calibrated by monitoring the
transmission signal of two Vernier étalons integrated in the dye ring lasers or the transmission spectrum of a confocal étalon that was actively locked to the stabilized wavelength of a Helium-Neon cw laser [53].

2.2 Experimental chamber

2.2.1 Gas beam

Supersonic beams provide a collision free environment ideally suited for the high-resolution spectroscopic experiments described in this thesis. The supersonic gas beams were generated by expanding the gas sample into vacuum from a reservoir with a stagnation pressure of ~2 bar through a pulsed solenoid valve (General Valves, Series 9). The valve, with an orifice of 0.5 mm, was open for approximately 250 µs. The gas beams passed through a 0.5 mm diameter skimmer located at an adjustable (3 cm-15 cm) distance downstream of the nozzle orifice. In this manner internally and translationally cold gas samples were generated; the translational and rotational temperatures were of the order of 1 K and 10 K, respectively.

The skimmer (Beam dynamics, Inc) is shaped so as to minimize the interaction of the molecular beam with the skimmer. The 0.5 mm diameter orifice of the skimmer was small enough to maintain more than two orders of magnitude pressure difference between the nozzle chamber (background pressure 10⁻⁷ mbar, operating pressure 10⁻⁴ mbar) and the magnetically shielded photoexcitation region and flight tube (background pressure 5.10⁻⁸ mbar, operating pressure 3.10⁻⁷ mbar).

2.2.2 Photoexcitation region and ion and electron detection

The photoexcitation takes place in the middle of a 5.7 cm long stack of 5 resistively coupled cylindrical stainless-steel extraction plates designed to minimize stray electric fields and to optimize the homogeneity of the applied electric fields. This stack of extraction plates and the time-of-flight (TOF) region that separates it from the MCP detector are surrounded by two cylindrical mumetal shield tubes (resulting in a measured magnetic shielding factor of ≈ 5000 at the point of photoexcitation) to minimize stray magnetic fields.

Charged particles (ions or electrons, depending on the type of experiment carried out) are extracted in the direction of the pulsed gas expansion toward a multichannel plate detector in chevron configuration by applying a continuous or a pulsed voltage of appropriate polarity across the stack of extraction plates. The electron (or ion) time-of-flight spectra are accumulated and displayed on a 500 MHz digital oscilloscope and transferred to a PC via GPIB. By setting temporal gates at the corresponding
2.2.3 Source of internally cold radicals

Various sources of internally cold radicals have been described in the literature. These include flash pyrolysis in a supersonic expansion [54–56], corona discharges [57,58], linear plasma expansions [59] and laser photolysis in the high-pressure region of a supersonic expansion [60]. The generation of cyclopentadienyl radicals from dicyclopentadiene [61] or cyclopentadiene [62] has been described by several authors.

In this work, the cyclopentadienyl radicals were produced by photolysis of cyclopentadiene with the 248 nm output of a KrF excimer laser (Lambda Physik, Comp-Ex) in a quartz capillary mounted at the end of a pulsed nozzle (see Fig. 2.6). The cyclopentadienyl radicals were cooled in the pulsed supersonic expansion into vacuum to rotational temperatures around 8 K. The supersonic beam was skimmed and then intersected by the VUV beam at right angles in the photoionization region. Cyclopentadiene was produced from dicyclopentadiene (Fluka) through distillation and stored at -78 °C until used. It was introduced in a stream of neat helium into the nozzle reservoir at a stagnation pressure of 5 bar.

2.3 Photoionization spectroscopy

Photoionization spectroscopy consists of measuring mass selectively the photoionization yield of atomic or molecular species as a function of the excitation energy. Important contributions to the development of this method were made by Watan-
Chapter 2. Experimental setups and methods

Since every ionization threshold contributes intensity to the photoionization signal, an idealized photoionization spectrum would display a stepwise increase at each threshold which would in principle allow the reconstruction of the cationic level structure. In reality, the autoionization of Rydberg series converging on excited levels of the cation mask the direct ionization signal which renders the identification of ionization thresholds difficult or impossible. The lowest threshold (also termed adiabatic ionization threshold) is however usually observed and can be used to determine the adiabatic ionization energy. An illustration of these general principles is given in chapter 7, in which the photoionization spectra of the cyclopentadienyl radical are discussed.

2.4 PFI-ZEKE photoelectron spectroscopy

Photoelectron spectroscopy consists of measuring the electron kinetic energy distribution produced by photoionization. From the knowledge of the photon energy, this information can be used to determine ionization thresholds and thus the energetic positions of a cation with respect to those of a neutral molecule. In traditional photoelectron spectroscopy, fixed frequency radiation was used to photoionize the molecules. In more recent variants of the technique such as threshold photoelectron spectroscopy and pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy, the yield of threshold electrons is measured as a function of the frequency of a tunable light source.

In the early 1960s Vilesov, Kurbatov and Terenin [69] and Turner and Al-Joboury [70] developed the technique of photoelectron spectroscopy. Since these days, the spectral resolution could be improved from approximately 2000 cm\(^{-1}\) in the first studies by ultraviolet photoelectron spectroscopy UPS [71] to 0.06 cm\(^{-1}\) in studies by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy [72].

This progress in resolution was possible by using better light sources on the one hand, and by a better control of the experimental conditions on the other hand. Narrow bandwidth laser sources with a bandwidth of better than 0.01 cm\(^{-1}\) [48,49] have been developed so that the resolution is no longer limited by the light sources but by experimental or fundamental limitations such as electric stray fields, the Doppler effect and the intrinsic characteristics of high Rydberg states.

The development of zero-kinetic-energy (ZEKE) photoelectron spectroscopy by Müller-Dethlefs, Sander and Schlag [73] and of pulsed-field-ionization (PFI-)ZEKE photoelectron spectroscopy by Reiser et al. [74] were important steps in the evolution of photoelectron spectroscopy. In PFI-ZEKE photoelectron spectroscopy, electrons produced by the electric field ionization of the very high Rydberg states are measured as
a function of the wave number of a tunable light source [75-77]. The lines in a PFI-ZEKE photoelectron spectrum are located just below each ionization threshold and thus directly map out the relative positions of the ionic energy levels. To obtain the field-free ionization thresholds, a field correction has to be applied.

The ionization dynamics of high Rydberg states and recent progress in the resolution in PFI-ZEKE photoelectron spectroscopy is described in Ref. [72] in which the equations for ionization rates by Damburg and Kolosov [78-81] were utilized to obtain optimal electric field pulse sequences for high-resolution PFI-ZEKE spectroscopy and to determine the field correction. Using these methods one can determine accurate ionization thresholds in atomic and molecular systems (see for instance Refs. [37, 82-85] for recent examples).
Part I

Electron and nuclear spin effects on the structure and dynamics of Rydberg states
Photoionization is one of the fundamental processes that result from the interaction of short-wavelength radiation with matter. Photoionization spectra are a valuable source of information on the structure and dynamics of atoms and molecules and their cations. In the vicinity of the first adiabatic ionization energy, molecular photoionization spectra are characterized by a rich structure originating from the autoionization of Rydberg states belonging to series converging on excited vibrational and rotational levels of the cation \[65,86\]. The autoionization dynamics can be described in terms of interaction parameters between the different ionization channels \[7,87\] but a complete understanding of the rovibrational channel interactions has so far only been reached in prototypical molecular systems, primarily \(H_2\) \[88-91\].

Milestones in the history of Rydberg spectroscopy start with Balmer's formula describing the spectrum of the hydrogen atom \[92\] and Rydberg's discovery of the quantum defect modification of the latter to describe the s,p,d and f Rydberg states of sodium \[8\]. Molecular Rydberg systems were first described by W.C. Price and R.S. Mulliken as a distinct class of diffuse and highly polarizable systems violating the BO approximation. In 1935, Price assigned the regular progressions of sharp spectral structures in the 105-152 nm absorption spectrum of acetylene to Rydberg states \[93\], but the first full set of quantum defects for a molecule was determined for the s,p,d and f Rydberg series of NO by Miescher \[94\]. A series of articles on the Rydberg states of \(H_2\) and \(He_2\) by Mulliken \[17-20\] in the period 1964-1969 provided the conceptual basis for the understanding of molecular Rydberg dynamics. The first step in the development of quantitative models was the development of quantum defect theory by Seaton \[9\] to handle the multichannel Rydberg spectrum in atoms and in electron-ion scattering. High-resolution spectroscopic studies of \(H_2\) photoabsorption by Chupka and Berkowitz \[95\], Herzberg \[96\] and Herzberg and Jungen \[11\] have motivated the extension of Seaton's formulation of the quantum defect theory to molecular Rydberg spectra by Fano \[10\]. Two essential concepts were formulated in this article, namely, the physical significance of the eigenchannels in the close-coupling region and the necessity of a rotational frame-transformation between the eigenchannels at short electronic distances \(r\) and the fragmentation channels at large \(r\). A systematic development of these concepts led to the first quantitative analysis of the Rydberg spectrum of \(H_2\) by Herzberg and Jungen \[11\]. The subsequent extension to vibrational channel interactions by Jungen and Atabek \[12\] has permitted a nearly complete description of the experimental \(H_2\) photoabsorption spectrum \[86\] up to wavenumbers of 133000 cm\(^{-1}\) \[97\].

Current research in molecular photoionization, Rydberg spectroscopy and MQDT is oriented in two main directions: on the one hand, the formalism that has been so successfully developed and used to describe the rovibronic photoionization dynamics of \(H_2\) is increasingly applied to model the photoionization dynamics of larger molecules such as \(CaF\) \[98\] or \(N_2\) \[99\] and tri- and tetraatomic molecules \((H_2O\ [100-\)
103], HCO [104, 105], NH$_3$ [106], H$_3$ [107, 108]). On the other hand, the first spectra have been reported in which the hyperfine structure of bound and autoionizing Rydberg states could be resolved (Refs. [109-113] and chapters 3, 4, 5 and 6 in this thesis). The analysis of such spectra requires the inclusion of nuclear spins into the formalism of MQDT. The MQDT analysis also provides the hyperfine structure of the cations which is often unknown. The inclusion of nuclear spins in the description of Rydberg states necessitates the replacement of the total angular momentum quantum number, usually labeled $J$ with a total angular momentum quantum number including nuclear spins $F$. The additional hyperfine interactions lead to a significantly increased number of channels which gives rise to new structural and dynamical properties and provides entirely new information on previously unknown dynamical processes related to nuclear spins.

The first part of this thesis describes investigations of the role of electron and nuclear spins in the structure and dynamics of bound and autoionizing Rydberg states. These investigations required innovations in both the experimental and theoretical methods. On the experimental side, an unprecedented resolution of 25 MHz has been achieved in laser pulsed-field ionization and photoionization spectra of H$_2$ (chapter 6). This achievement was made possible by recent progress in laser technology in our laboratory [48, 49, 114] which has enabled us to resolve the hyperfine structure in the Rydberg spectra of $^{83}$Kr, $^{129}$Xe, $^{131}$Xe and ortho-H$_2$. On the theoretical side, an MQDT formalism has been developed that treats the nuclear spin angular momenta on the same footing as the other angular momenta and thus allows one to describe the hyperfine structure and dynamics of Rydberg states from the lowest levels to $n \to \infty$ [109-112]. This property distinguishes our formalism from earlier treatments of hyperfine structure of excited electronic states by perturbation theory [115].
Chapter 3

Hyperfine structure in bound Rydberg states of $^{83}$Kr

3.1 Introduction

The hyperfine structure of atomic and molecular Rydberg states and its treatment by MQDT have so far received little attention [116-118], primarily because of the lack of sufficiently resolved experimental data. Progress in experimental techniques in the past decade has been such that information on the hyperfine structure of high Rydberg states can now be derived by high-resolution laser spectroscopy [45, 113, 117-120] or by millimeter wave spectroscopy [121, 122]. A high-resolution (sub-MHz) measurement of the hyperfine structure of $ns$, $np$, $nd$ and $nf$ Rydberg states of ortho H$_2$ in the range $n = 50 - 65$ by millimeter wave spectroscopy [123, 124] has recently stimulated a detailed analysis by MQDT [110]. This analysis, which could account for the finest details of the energy level structure, also yielded, by extrapolation, the hyperfine structure of the ground rovibronic state of ortho H$_2^+$ and new information on the $p$ and $f$ Rydberg states of molecular hydrogen [110]. The success of this analysis and the desire to extend it to other systems represented the primary motivations of the present study of the hyperfine structure in high Rydberg states of $^{83}$Kr by high-resolution vacuum-ultraviolet laser spectroscopy and MQDT.

Important reasons for choosing $^{83}$Kr for a combined experimental and theoretical study of the hyperfine structure in atomic Rydberg states were, first, the availability of a large body of high quality spectroscopic data on the Rydberg states of krypton [125-139], second, the fact that a very detailed MQDT analysis of the Rydberg spectra of the $I = 0$ isotopes has been carried out [140], and, finally, experimental convenience: The Rydberg states of krypton are easily accessible from the ground neutral state using narrow-bandwidth vacuum-ultraviolet (VUV) lasers, and mass-analyzed spectra of $^{83}$Kr (natural abundance 11.5 %) can readily be obtained from natural probes of Kr following VUV laser excitation and pulsed field ionization in a time-of-flight mass...
Extensive tables of term values for the Rydberg states of krypton have been available for a long time [125, 126], the latest and most extensive compilation being that of Sugar and Musgrove [127]. The s and d Rydberg states of the \( I = 0 \) isotopes (\(^{78}\)Kr (natural abundance 0.35%), \(^{80}\)Kr (2.25%), \(^{82}\)Kr (11.6%), \(^{84}\)Kr (57.0%), \(^{86}\)Kr (17.3%)) converging to the lower \((^2\!P_{3/2})\) and upper \((^2\!P_{1/2})\) spin-orbit components of the ground \(^2\!P\) term of Kr\(^+\) have been extensively studied by VUV photoabsorption and photoionization spectroscopy [128–131], by nonresonant and resonant two-photon excitation from metastable levels [132–137] and by electron energy loss spectroscopy [138]. Laser spectroscopic measurements of the p and f Rydberg states have also been reported [139], and the behavior of the Rydberg Stark states of Kr has been exploited to demonstrate that the translational motion of Rydberg atoms and molecules can be controlled by inhomogeneous electric fields [141].

The Rydberg spectra of the rare gas atoms have played an important role in the development of MQDT and its early application to the analysis of photoabsorption and photoionization spectra [16, 142]. Detailed MQDT analyses of the \( ns \) and \( nd \) Rydberg series of krypton, particularly for \( J = 1 \) [138, 143], but also for \( J = 0, 2 \) and 3 [137, 140] have been reported. The most extensive MQDT study to date is that of Aymar et al. [140] who have reported complete sets of MQDT parameters for the \( \ell = 0 \) and \( \ell = 2 \) \((J = 0 - 3)\) channels, including eigenchannel quantum defects \( \mu_\alpha \), their energy dependence and the elements of the orthogonal transformation matrix \( U_{i\alpha} \) connecting the close-coupling eigenchannels \( \alpha \) to the fragmentation channels \( i \). MQDT has also been applied in studies of the Stark effect in the Rydberg states of the rare gas atoms of [144].

A recurring theme in the study of the Rydberg states of the rare gas atoms by MQDT is the deviation of the eigenchannels from purely \( LS \)-coupled channels which is, among others, at the origin of the interaction and the mixing between \( s \) and \( d \) series [137, 138, 140, 142, 143, 145–147]. The s-d interaction is particularly elusive in krypton because the separation between the \(^2\!P_{3/2}\) and \(^2\!P_{1/2}\) ionization thresholds is so large that the \( ns' \) and \( nd' \) levels are extremely sparse in the region below the \(^2\!P_{3/2}\) threshold where the \( ns \) and \( nd \) series are well developed (Rydberg series labeled by \( a' \) are commonly used to designate series converging on the upper spin-orbit component of the ion. The usual label for Rydberg states of the rare gas atoms is thus \( n\ell[k]_J \) or \( n\ell'[k]_J \), where \( k \) represents the quantum number of the angular momentum vector \( \vec{k} \) that results from the addition of \( \ell \) with the total angular momentum of the ion core \( \vec{J} \)). Consequently, it has proven difficult to distinguish the effects of the energy dependence of the eigenquantum defects on the energy level structure from the effects of the channel interactions induced by a departure from \( LS \) coupling.

Several high-resolution spectroscopic measurements have already been reported that provide information on the hyperfine structure of low-\( n \) Rydberg states of \(^{83}\)Kr,
3.1. Introduction

the earliest measurements leading to the determination of the nuclear spin quantum number \( I = 9/2 \) \([148, 149]\). Later studies \([150-154]\) primarily focused on the hyperfine structure of the microwave, infrared and visible spectra of metastable krypton Rydberg states and aimed at determining the term-dependent hyperfine constants. Trickl et al. \([45]\) reported ultrahigh-resolution \((1+1')\) resonance-enhanced two-photon ionization spectra of transitions from the \(^1S_0\) ground state to the \(5s[3/2]_i, 5s'[1/2]_i, 6s[3/2]_i, 6s'[1/2]_i, \) and \(7s[3/2]_i\) Rydberg states using a narrow bandwidth VUV laser system and analyzed the hyperfine coupling parameters both in terms of \(LS\) and \(jj\) coupling. Brandi et al. \([120]\) measured the hyperfine structure and determined the hyperfine coupling constants of the \(5p[5/2]_i\) Rydberg state. To our knowledge, no MQDT analysis of the hyperfine structure in any of the rare gas atoms has been reported yet.

In the close-coupling region of the electron-ion collision, both the kinetic energy of the electron and its interaction with the ion core are very large compared to the weak interactions responsible for the hyperfine structure. It thus appears surprising, at first sight, that a collision approach such as MQDT should at all be successful in providing a detailed description of the hyperfine structure of Rydberg states. A closer inspection, however, reveals that it is precisely the many orders of magnitude difference, in the close-coupling region, between the hyperfine interaction (at most a few GHz, but typically less) and other interactions such as the spin-orbit or the exchange interactions (typically \(10^4\) GHz, sometimes even more) which lie at the origin of the power of MQDT to treat the hyperfine structure in Rydberg states: The hyperfine interactions have an almost completely negligible effect on the close-coupling parameters (eigenquantum defects \(\mu_\alpha\), channel coupling parameters, etc.) used by MQDT.

In the long-range part of the electron-ion collision, where the electron is completely decoupled from the ion core, however, the hyperfine interaction strongly affects the energy level structure but corresponds primarily to that of the ionic core. Two conclusions can immediately be drawn from these remarks and form the basis of the MQDT model developed in the present work:

1. When the Rydberg level structure of an atom with an \( I = 0 \) nuclear spin is well described by a set of close-coupling MQDT parameters, this set of MQDT parameters can be employed without changes to treat the hyperfine structure of any \( I > 0 \) isotope of the same atom. The number of channels, however, must be enlarged, and identical close-coupling parameters must be assigned to all channels which only differ in the total angular momentum quantum number \( F \).

2. The origin of the hyperfine structure splittings in all Rydberg states, regardless of the value of \( n \), must be sought in the hyperfine structure of the ion. Consequently, the hyperfine structure in Rydberg states need only be parameterized
in terms of the ionic hyperfine structure rather than by separate hyperfine structure coupling constants for the successive members of the Rydberg series.

Although the nuclear spins have a negligible effect on the close-coupling parameters, they have a profound effect on the appearance of Rydberg state spectra, particularly at high \( n \) values. These effects are twofold: First, since \( J \) ceases to be a good quantum number when the effects of the nuclear spins are included, transitions that are strictly forbidden in \( I = 0 \) isotopes become weakly allowed. In the case of the rare gas atoms examined here, transitions from the \( ^1S_0 \) ground state to Rydberg states that would have been classified as \( J = 0 \) or \( J = 2 - 4 \) states in the absence of nuclear spin become observable whenever the Rydberg states gain \( J = 1 \) character by the hyperfine interactions. Second, at sufficiently high \( n \) values, the ionic hyperfine structure intervals inevitably become comparable to the \( 2R/n^3 \) intervals between adjacent Rydberg states and obscure the regular appearance of the Rydberg series.

As will be shown in the following sections, an MQDT analysis of the hyperfine structure of the rare gas atoms reduces the need to determine hyperfine coupling constants for each Rydberg level and leads to an adequate, although approximate, parameterization solely in terms of the hyperfine coupling constants of the ion. In addition, the hyperfine structure of the Rydberg states represents a very stringent test of the quality of MQDT parameters and may provide a way to extract precious information on the s-d interaction in the rare gases and on the ionic hyperfine structure.

This chapter is structured as follows. Section 3.2 provides a short description of our experimental procedure. The well known 16-channels QDT treatment of the \( s \) and \( d \) \((J = 0 - 4)\) channels of the \( I = 0 \) isotopes of the rare gas atoms and its extension to a 44 channels QDT treatment that includes the effects of the \( I = 9/2 \) nuclear spin of \(^{83}\text{Kr}\) are presented in Section 3.4. The experimental results on the hyperfine structure of \( ns \) and \( nd \) Rydberg states are compared with MQDT calculations in Section 3.5 in which we also explain how MQDT parameters and the hyperfine structure of \(^{83}\text{Kr}^+\) were extracted from the experimental data in a nonlinear least-squares-fit procedure. Section 3.6 provides a discussion of the applicability of the present model to study Rydberg states over a wide range of \( n \) values and of its use in determinations of the s-d interaction in the Rydberg spectrum of Kr and other rare gases (see also Ref. [155]).

## 3.2 Experiment

The spectra have been recorded using a narrow bandwidth (0.008 cm\(^{-1}\)) VUV laser system coupled to a photoion/photoelectron time-of-flight (TOF) mass spectrometer. This system has been described in Section 2.1.2.

The VUV radiation was generated by two-photon resonance-enhanced sum-fre-
3.3 Multichannel Quantum Defect Theory of the fine structure

Quency mixing ($\nu_{\text{VUV}} = 2\nu_1 + \nu_2$) in Kr using the $(4p)^5 5p'[1/2]_1 \rightarrow (4p)^6 1S_0$ two-photon resonance at $2\nu_1 = 98855.1$ cm$^{-1}$. The VUV wave number was calibrated to an absolute accuracy of 0.015 cm$^{-1}$ following the procedure described in Ref. [131] which involves the stabilization of the wave number of the first laser. Krypton gas (Pangas, spectroscopic grade purity) was used without further purification and is introduced into the spectrometer in a pulsed skimmed supersonic expansion. The krypton gas jet is crossed at a right angle by the VUV laser beam. The stray electric fields were measured and reduced to below 2 mV/cm following the procedure described in Ref. [156]. Under the experimental conditions used to record the spectra of the high Rydberg states of krypton, pressure shifts, dc and ac Stark shifts are negligible for the Rydberg states with principal quantum number between 30 and 150 used in the MQDT analysis. Most lines have a full width at half maximum of 0.01 cm$^{-1}$ which is slightly broader than the bandwidth of the VUV laser, presumably because of a residual Doppler broadening. Spectra of the Rydberg states located below the $^2P_{3/2}$ ionization threshold were recorded by monitoring the pulsed field ionization yield as a function of the VUV wave number. The pulsed electric field of up to 1000 V/cm was applied 1 $\mu$s after the VUV laser pulse, so that photoexcitation could take place under field-free conditions. The pulsed electric field also served the purpose of extracting the Kr$^+$ ions towards a microchannel plate detector at the end of the TOF tube. Spectra of the different isotopes were obtained by placing temporal gates at the corresponding positions in the TOF spectrum. The 1000 V/cm magnitude of the pulsed electric field implies that pulsed field ionization is observable down to about 200 cm$^{-1}$ below the $^2P_{3/2}$ field-free ionization threshold and that Rydberg states above $n \approx 25$ can be detected. To detect transitions to Rydberg states of lower $n$ values, the krypton atoms were ionized with the 532 nm radiation of a Nd:YAG laser.

3.3 Multichannel Quantum Defect Theory of the fine structure

The MQDT formalism of Refs. [16, 140, 142] provides an accurate description of the Rydberg spectra of the $I = 0$ isotopes of the rare gas atoms. It allows the calculation of line shapes, line positions and spectral intensities in terms of a set of close-coupling parameters consisting of 1) the eigenquantum defects $\mu_\alpha$, 2) the elements $U_{i\alpha}$ of the transformation matrix between the close-coupling eigenchannels $\alpha$ and the dissociation channels $i$, 3) the dipole amplitudes $D_\alpha$ for the transitions to the eigenchannels, and 4) the positions of the ionization thresholds. Whereas the dissociation channels are $jj$ coupled, the close-coupling eigenchannels are almost perfectly described by $LS$ coupling. Table 3.1 summarizes the notation generally used to designate both sets of channels. A total of 16 channels must be retained for the treatment of the s and
Table 3.1: Overview of the notation and the quantum numbers used to designate the close-coupling eigenchannels and the dissociation channels in the MQDT treatment of the s and d Rydberg series of Kr converging to the $^2P$ ground state of Kr$^+$. d Rydberg series associated with the $^2P$ ground state of the ion: two channels with $J = 0$, five with $J = 1$, five with $J = 2$, three with $J = 3$ and one with $J = 4$.

The elements $U_{i\alpha}$ of the transformation matrix are conveniently factorized as

$$U_{i\alpha} = \sum_{\alpha} U_{i\alpha} V_{\alpha\alpha}, \quad (3.1)$$

whereby the $U_{i\alpha}$ elements represent elements of the $jj$-LS transformation matrix and $V_{\alpha\alpha}$ accounts for the (typically very small) departure of the close-coupling eigenchannels from pure LS coupling and the resulting channel mixings, in particular the mixing between s and d channels. $V_{\alpha\alpha}$ can be represented in terms of generalized Euler angles [142]. Because $J$ is a good quantum number, the $U_{i\alpha}$ and $V_{\alpha\alpha}$ matrices have a block diagonal structure with a $(2 \times 2)$ $J = 0$, a $(5 \times 5)$ $J = 1$, a $(5 \times 5)$ $J = 2$, a $(3 \times 3)$ $J = 3$, and a $(1 \times 1)$ $J = 4$ block.
The MQDT parameters can be derived from experimental spectra of the bound Rydberg states semi-empirically. Each bound energy level is used to derive two effective principal quantum numbers \( \nu_{3/2} \) and \( \nu_{1/2} \) defined by the relations

\[
E = E(2P_{1/2}) - \frac{R_M}{\nu_{1/2}^2} = E(2P_{3/2}) - \frac{R_M}{\nu_{3/2}^2},
\]

where \( E(2P_{J^+}) \) with \( J^+ = 1/2, 3/2 \) represent the ionization energies corresponding to the formation of the two spin-orbit components of the \( \text{Kr}^+ \) ion, and \( R_M \) stands for the mass-dependent Rydberg constant.

In the discrete part of the spectrum, a second equation,

\[
\sum_{\alpha} U_{i\alpha} \sin \left( \pi (\mu_{\alpha} + \nu_{J^+}) \right) A_{\alpha} = 0,
\]

which requires the wavefunctions of the bound levels to vanish at infinity, is used jointly with Equation (3.2) to determine their positions for a given set of MQDT parameters. The coefficients \( A_{\alpha} \) enable the expansion of the dissociation channels in the basis of the close-coupling eigenchannels. The bound states of the electron-ion core system correspond to the energies \(-\frac{R_M}{\nu_{J^+}}\) for which Equation (3.3) has no trivial solution, i.e., the energies which satisfy the relation

\[
\det |U_{i\alpha} \sin \left( \pi (\mu_{\alpha} + \nu_{J^+}) \right)| = 0.
\]

The intensities of the transitions from the ground state to the bound Rydberg levels can be calculated from the dipole amplitudes \( D_{\alpha} \) and the expansion coefficients \( A_{\alpha} \) according to

\[
\text{Intensity} \propto \left( \sum_{\alpha} D_{\alpha} A_{\alpha} \right)^2,
\]

where \( D_{\alpha} \) can be expressed as a linear combination of dipole amplitudes to purely \( LS \)-coupled channels

\[
D_{\alpha} = \sum_{\alpha} V_{\alpha\alpha}^* D_{\tilde{\alpha}}.
\]

The MQDT parameters can either be evaluated \textit{ab initio} [143] or derived from experimental data in a least-squares-fit procedure [140]. Assuming that the energy dependence of the MQDT parameters \( \mu_{\alpha} \) and \( V_{\alpha\alpha} \) is only weak and can therefore adequately be described by the linear relations

\[
\mu_{\alpha} = \mu_{\alpha}^{(0)} + \epsilon \mu_{\alpha}^{(1)} \quad \text{with} \quad \epsilon = \frac{1}{\nu_{3/2}^2}
\]

and

\[
V_{\alpha\alpha} = V_{\alpha\alpha}^{(0)} + \epsilon V_{\alpha\alpha}^{(1)} \quad \text{with} \quad \epsilon = \frac{1}{\nu_{3/2}^2}
\]
leads to a number of MQDT parameters often too large to be determined from experimental data. A reduction of the number of parameters to be determined in a least-squares fit can be achieved either by making the approximation that the close-coupling eigenchannels are exactly LS coupled, in which case the elements $U_{i\alpha}$ of the transformation matrix become identical to the elements $U_{i\alpha}$ of the well-known $jj$-LS transformation matrix, by neglecting the energy dependence of certain parameters, or by fixing their values to values determined previously.

Several sets of $V_{\alpha\alpha}$ elements (or of the corresponding mixing angles) and of close-coupling eigenchannel quantum defects $\mu_{\alpha}$ have been determined in previous studies of the Rydberg spectrum of Kr [138,140,143]. Aymar et al. [140] have compared their transformation matrix $U_{i\alpha}$ for the $J = 1$ channels with previous results by Johnson et al. [143] and Geiger [138], and have also derived the complete transformation matrices for $J = 0 – 3$. From these data, the matrix elements $V_{\alpha\alpha}$ can be determined for each value of $J$ using Equation (3.9)

$$V_{\alpha\alpha} = \sum_{i} U_{\alpha i}^{*} U_{i\alpha}. \quad (3.9)$$

The different sets of $V_{\alpha\alpha}$ parameters that can be extracted from the literature on Kr differ markedly, both in sign and magnitude. Inspection of the available data on channel interactions in the rare gases [140,142,145,147] leads to the conclusions that a) the magnitude of the $V_{\alpha\alpha}$ elements (or of the mixing angles) increases in the sequence Ne, Ar, Xe although the mixing angles reported for Kr appear to be larger than those of Xe, and b) the discrepancies in the values reported for Kr by different authors are likely to originate either from the fact that they were derived from measurements in different energetic regions, or that the energy dependence of the MQDT parameters were taken into account differently. In the analysis presented in Section 3.5 we have used the energy dependences of the MQDT parameters reported by Aymar and coworkers [140] and did not attempt to refine them.

### 3.4 Multichannel Quantum Defect Theory of the hyperfine structure

The 16-channel MQDT analysis of the s and d series of the $I = 0$ isotopes of Kr outlined above can be extended to include the nuclear spin ($I = 9/2$) of the $^{83}$Kr nucleus if one assumes that the effect of the hyperfine interactions on the values of the close-coupling eigenquantum defects is negligible compared to that of the exchange and spin-orbit interactions. Consequently, $J$ remains a good quantum number in the close-coupling region, and the number of channels for $^{83}$Kr is readily obtained by considering the possible total angular momentum vectors that result from the addi-
3.4. Multichannel Quantum Defect Theory of the hyperfine structure

\begin{align*}
J^+ + F^+ = 0 \quad \ell = 0 \\
\ell = \frac{1}{2} \quad j = \frac{1}{2} \quad j = \frac{3}{2} \\
\frac{1}{2} \quad 4 \quad \frac{7}{2} \quad \frac{9}{2} \quad \frac{11}{2} \\
\frac{1}{2} \quad 5 \quad \frac{9}{2} \quad \frac{11}{2} \quad \frac{11}{2}
\end{align*}

\begin{align*}
J^+ + F^+ = 2 \quad \ell = 2 \\
\ell = \frac{1}{2} \quad j = \frac{1}{2} \quad j = \frac{3}{2} \\
\frac{1}{2} \quad 4 \quad \frac{7}{2} \quad \frac{9}{2} \quad \frac{11}{2} \\
\frac{1}{2} \quad 5 \quad \frac{9}{2} \quad \frac{11}{2} \quad \frac{11}{2}
\end{align*}

**Figure 3.1:** Schematic diagram (not to scale) of the hyperfine structure in the \(2P_{3/2}\) and \(2P_{1/2}\) spin-orbit components of \(\text{Kr}^+\). The total angular momentum quantum number \(F\) of the \(s\) and \(d\) dissociation channels associated with each hyperfine structure component is tabulated on the right-hand side of the figure. The numerical values given for the hyperfine structure intervals correspond to the results of the MQDT analysis.

The dissociation channels can be described by the following angular momentum coupling scheme

\[
\tilde{L}^+ + \tilde{S}^+ = \tilde{J}^+; \quad \tilde{F}^+ = \tilde{F}^+ + \tilde{F}^+ + \tilde{F}^+
\]

where \(\tilde{L}^+\) and \(\tilde{S}^+\) represent the orbital and spin angular momenta of the ionic core, \(\tilde{J}^+\) and \(\tilde{S}^+\) the corresponding angular momenta of the Rydberg electron, and \(\tilde{I}\) the nuclear spin. When treating the single-photon photoabsorption and photoionization spectra recorded following excitation from the \(1S_0\) (\(F = 9/2\)) ground state of \(\text{Kr}^+\), the \(\Delta F = 0, \pm 1\) (\(0 \leftrightarrow 0\)) electric dipole selection rule restricts the number of channels to three (degenerate) hyperfine components with \(F = 7/2, 9/2\) and \(11/2\) for each eigenchannel with \(J \geq 1\), and to a single component with \(F = 9/2\) for the \(J = 0\) eigenchannels. A total of \(44\) eigenchannels results, comprising \(10\) \(s\)-channels (\(\ell = 0\)) and \(34\) \(d\)-channels (\(\ell = 2\)).
where $J_+^\pi$ and $F_+^\pi$ represent the electronic and total angular momenta of the ionic core. The dominant interaction in the ionic core is the spin-orbit coupling which leads to an energy splitting of 5370.2 cm$^{-1}$ between the $2^3P_{3/2}$ and $2^1P_{1/2}$ levels, several orders of magnitude larger than the splittings induced by the hyperfine interactions. Under the assumption that the mixing of the $2^3P_{3/2}$ and $2^1P_{1/2}$ spin-orbit components of the ion by the hyperfine interactions is negligible (such a mixing is in principle possible for states with $F_+^\pi = 4, 5$ but is expected to be extremely weak because of the large energy separation between the two spin-orbit components), the hyperfine structure of the two spin-orbit components can be treated separately and expressed as a function of the magnetic dipole and electric quadrupole hyperfine constants $A_{J_+^\pi}$ and $B_{J_+^\pi}$ [157] ($B_{J_+^\pi=1/2} = 0$ for the $2^1P_{1/2}$ spin-orbit level):

$$v_{J_+^\pi,F_+^\pi} = v_{J_+^\pi} + A_{J_+^\pi} \frac{C}{2} + B_{J_+^\pi} \frac{3C(C+1) - I(I+1)J_+^\pi(J_+^\pi+1)}{2I(2I-1)J_+^\pi(2J_+^\pi-1)},$$  \hspace{1cm} (3.12)

where

$$C = F_+^\pi(F_+^\pi+1) - I(I+1) - J_+^\pi(J_+^\pi+1).$$ \hspace{1cm} (3.13)

In Equation (3.12), $v_{J_+^\pi}$ represents the energy of the center of gravity of the hyperfine structure of the two spin-orbit components ($J_+^\pi = 1/2, 3/2$). The dissociation channels are hence characterized by a pair of intermediate quantum numbers $J^\pi$ and $F^\pi$ designating each ionization threshold. The left-hand side of Fig. 3.1 displays schematically the energy level structure of the $^{83}$Kr$^+$ ion which consists of six hyperfine components forming a group of four levels at the $2^3P_{3/2}$ threshold and a group of two levels at the $2^1P_{1/2}$ threshold. The total number of dissociation channels to be retained in the treatment of the single-photon photoabsorption and photoionization spectra can be determined as above for the close-coupling eigenchannels by considering the restrictions imposed by the $\Delta F = 0, \pm 1$ ($0 \leftrightarrow 0$) electric dipole selection rule. All dissociation channels are listed on the right-hand side of Fig. 3.1. For the s states ($\ell = 0, j = 1/2$) two channels result for each ionic state with $F_+^\pi = 4$ and 5 whereas only one channel is associated with the $F_+^\pi = 3$ and 6 ionic states, resulting in a total of 10 s channels. Analogous considerations lead to the identification of 34 d channels ($\ell = 2, j = 3/2$ and 5/2).

The semi-empirical MQDT treatment outlined in the previous subsection can be adapted to treat the hyperfine structure of the Rydberg states of $^{83}$Kr, if

1. the close-coupling MQDT parameters are taken over without change from the treatment of the $I = 0$ isotopes, but the number of channels is enlarged from 16 to 44, identical close-coupling parameters being assigned to all channels which only differ in the total angular momentum quantum number $F$,

2. equation (3.2) is generalized to include a set of six effective principal quantum numbers $\nu_{J_+^\pi,F_+^\pi}$ defined relative to the position of each of the six ionization
3.4. Multichannel Quantum Defect Theory of the hyperfine structure

thresholds depicted in Fig. 3.1

\[ E = E(\ell P_{J+F^+}) - \frac{R_M}{V_{J+F^+}} \]  

(3.14)

3. the transformation matrix \( U_{i\alpha} \) is extended from a 16 channels to a 44 channels situation. This extension necessitates an additional label for the quantum number \( F \), and we denote the elements of the extended transformation matrix \( U_{i\alpha F} \).

Because the close-coupling MQDT parameters are not affected by the hyperfine interactions in our model, the elements of the transformation matrix can be factorized as in Equation (3.1) above

\[ U_{i\alpha F} = \sum_{\alpha F} U_{i\alpha \tilde{F}} V_{\tilde{F}F \alpha F}. \]  

(3.15)

To convert the matrix \( V_{\alpha F} \) into a \( 44 \times 44 \) \( V_{\tilde{F}F \alpha F} \) matrix, care has to be taken to only couple manifolds with equal \( F \) values. Standard angular momentum algebra [158] can be used to derive the angular momentum transformation \( U_{i\alpha \tilde{F}} \)

\[ U_{i\tilde{F}F} = \langle LSJF | J^+ F^+ jF \rangle \]  

(3.16)

between the \( LSJF \)-coupled eigenchannels and the \( J^+ F^+ jF \)-coupled dissociation channels

\[
\langle LSJF| J^+ F^+ jF \rangle = (2F + 1)\sqrt{(2J + 1)(2L + 1)(2S + 1)(2j + 1)(2F^+ + 1)(2J^+ + 1)} \\
\times \sum_{m_j, m_F, m_L, m_S, m_{F^+}, m_{J^+}, m_j} (-1)^{F^+-J^+ + 2l - J + L - S - 2s + 3m_F + m_L + 2m_j} \\
\times \begin{pmatrix} I & J & F \\ m_I & m_J & -m_F \end{pmatrix} \begin{pmatrix} L & S & J \\ m_L & m_S & -m_J \end{pmatrix} \begin{pmatrix} L^+ & \ell & L \\ m_{L^+} & m_\ell & -m_L \end{pmatrix} \begin{pmatrix} S^+ & s & S \\ m_{S^+} & m_s & -m_S \end{pmatrix} \\
\times \begin{pmatrix} F^+ & j & F \\ m_{F^+} & m_j & -m_F \end{pmatrix} \begin{pmatrix} \ell & s & j \\ m_\ell & m_s & -m_j \end{pmatrix} \begin{pmatrix} I & J^+ & F^+ \\ m_I & m_{J^+} & -m_{F^+} \end{pmatrix} \begin{pmatrix} L^+ & S^+ & J^+ \\ m_{L^+} & m_{S^+} & -m_{J^+} \end{pmatrix}.\]  

(3.17)

The \( U_{i\tilde{F}F} \) transformation has a block-diagonal structure. The \( s \) block consists of a \( (3 \times 3) F = 7/2 \), a \( (4 \times 4) F = 9/2 \) and a \( (3 \times 3) F = 11/2 \) subblock, whereas the \( d \) block is composed of an \( (11 \times 11) F = 7/2 \), a \( (12 \times 12) F = 9/2 \), and an \( (11 \times 11) F = 11/2 \) subblock. The elements of the \( U_{i\tilde{F}F} \) matrix can be calculated numerically and the positions of the Rydberg levels determined from the condition

\[ \sum_{\alpha F} U_{i\alpha F} \sin (\pi (\mu_{\alpha F} + \nu_{J^+ F^+})) A_{\alpha F} = 0, \]  

(3.18)
which has nontrivial solutions when

\[ \text{det} \left| U_{iF\alpha_f} \sin \left( \pi (\mu_{\alpha_F} + \nu_{J^2 F^+}) \right) \right| = 0. \] (3.19)

The general form of Equation (3.19) is also adapted to a treatment neglecting the departure of the close-coupling eigenchannels from pure LS coupling, in which case the transformation matrix \( U_{iF\alpha_F} \) must be replaced by the angular momentum transformation matrix \( U_{iF\vec{a}_F} \).

The intensity of a transition from the ground state \( ^1S_0, F = \frac{9}{2} \) to a Rydberg state is determined by the value of \( F \) and by the expansion coefficients \( A_{\alpha_F} \) of the total wave function of the target state in the basis of the close-coupled channels according to:

\[ \text{Intensity} \propto W_F \left( \sum_{\alpha_F} D_{\alpha_F} A_{\alpha_F} \right)^2. \] (3.20)

The dipole amplitudes \( D_{\alpha_F} \) are approximated by the \( D_\alpha \) dipole amplitudes used in the MQDT treatment of the \( I = 0 \) isotopes. The weighting factors \( W_F \) are calculated according to Ref. [159] and fulfill the condition \( W_{1/2} : W_{9/2} : W_{7/2} = 1.2 : 1.0 : 0.8 \) which is in accordance with the multiplicity sum rules for electric dipole transitions.

### 3.5 Results

A comparison of the pulsed-field ionization spectra of \(^{83}\text{Kr}\) and \(^{84}\text{Kr}\) in the region of effective principal quantum number \( \nu_{3/2} = 48 - 49 \) is presented in Figure 3.2. The spectra were recorded under identical experimental conditions, using a pulsed electric field of 100 V/cm applied 1 \( \mu s \) after photoexcitation. The intensity distribution of the \(^{84}\text{Kr}\) spectrum (Fig. 3.2a) is dominated by the \( ns[3/2] \) and \( nd[3/2] \) series. The \( nd[1/2] \) series, which only becomes visible on an enlarged scale, is particularly weak in this region of the spectrum because of its dominant \( ^3P_1 \) character. Although the overall appearance of the \(^{83}\text{Kr}\) spectrum (Fig. 3.2b) is similar, several differences are noticeable. First, the \( ns[3/2] \) line is split into a well-resolved triplet and the \( nd[3/2] \) line appears broadened. Second, features that are not present in the \(^{84}\text{Kr}\) spectrum can be observed on the low energy side of the \( ns[3/2] \) triplet and halfway between the positions of the transitions to the \( nd[3/2] \) and \( nd[1/2] \) states.

These differences have their origin in the hyperfine interactions with the \( I = 9/2 \) nuclear spin of \(^{83}\text{Kr}\) which leads to additional splittings in the energy level structure and induces sufficient \( J \) mixing that Rydberg states which would be classified as \( J = 2 \) states in the \( I = 0 \) isotopes become accessible in single-photon transitions from the \(^1S_0 \) ground state. Although available MQDT parameters, in particular those reported by Aymar et al. [140], have been an invaluable help to our initial progress in the
3.5. Results

Figure 3.2: Comparison of the pulsed-field ionization spectrum of a) $^{84}$Kr and b) $^{83}$Kr in the region of effective principal quantum number $\nu_{\frac{3}{2}}$ between 48 and 49 recorded following single-photon excitation from the $^1S_0$ ground state. The hyperfine interaction leads to the splitting of the $(n + 2)s[\frac{3}{2}]_1$ Rydberg states into three components, the broadening of the transition to the $nd[\frac{3}{2}]_1$ Rydberg state, the enhancement of the intensity of the transition to the $nd[\frac{1}{2}]_1$ state and to the observation of additional structures at the positions of the $J = 2$ components of the $(n + 2)s$ and $nd$ Rydberg states.

understanding of the $^{83}$Kr spectrum, they turned out not to be accurate enough for the quantitative modeling of the spectrum of the $^{83}$Kr isotope.

In order to be able to test the fundamental assumption of our MQDT model, namely that the same close-coupling MQDT parameters can be used to calculate the spectra of both isotopes, our analysis was carried out in two steps. First, the $^{84}$Kr spectrum was used to derive a set of MQDT parameters accurate enough to provide a quantitative description of the $J = 1$ series in the energetic region investigated, i.e. between 112800 and 112905 cm$^{-1}$. Then, this parameter set was kept fixed and used in the analysis of the $^{83}$Kr spectrum. The first step of the analysis is summarized in Subsection 3.5 A and the second in Subsection 3.5 B.

A. $^{84}$Kr

For the analysis of the $^{84}$Kr isotope, a set of 187 wave numbers corresponding to transitions to members of the $ns[\frac{3}{2}]_1$ series between $n = 33$ and $n = 115$, of the $nd[\frac{3}{2}]_1$ series between $n = 31$ and 113 and of the $nd[\frac{1}{2}]_1$ series between $n = 32$
Chapter 3. Hyperfine structure in bound Rydberg states of $^{83}\text{Kr}$

<table>
<thead>
<tr>
<th>eigenchannel</th>
<th>$\mu^{(0)}_\alpha$ from Ref. [140]</th>
<th>$\mu^{(1)}_\alpha$ from Ref. [140]</th>
<th>$\mu^{(0)}<em>\alpha$ fitted with $U</em>{\alpha\alpha}$</th>
<th>$\mu^{(0)}<em>\alpha$ fitted with $U</em>{\alpha\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(p^5d)^3P_1$</td>
<td>0.0941</td>
<td>0.075</td>
<td>0.09480(46)</td>
<td>0.09437(32)</td>
</tr>
<tr>
<td>$(p^5d)^3P_1$</td>
<td>0.4725</td>
<td>-0.516</td>
<td>0.4703(1)</td>
<td>0.4692(1)</td>
</tr>
<tr>
<td>$(p^5d)^3P_1$</td>
<td>0.2572</td>
<td>-0.818</td>
<td>0.2550(4)</td>
<td>0.2523(3)</td>
</tr>
<tr>
<td>$(p^5s)^1P_1$</td>
<td>0.0626</td>
<td>0.103</td>
<td>0.0580(20)</td>
<td>0.0575(20)</td>
</tr>
<tr>
<td>$(p^5s)^3P_1$</td>
<td>0.1126</td>
<td>0.238</td>
<td>0.1099(3)</td>
<td>0.1103(4)</td>
</tr>
</tbody>
</table>

IE ($^{84}\text{Kr}$) / cm$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>112914.434(15)$^b$</th>
<th>112914.4357(1)$^c$</th>
<th>112914.4356(1)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>rmsd / cm$^{-1}$</td>
<td>3.69-$10^{-3}$</td>
<td>3.64-$10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$The energy dependence $\mu^{(1)}_\alpha$ of Ref. [140] (third column) was held fixed in the present work. $^b$from Ref. [131] $^c$The uncertainty represents 1$\sigma$ in the fit and does not include the 0.015 cm$^{-1}$ uncertainty in the VUV calibration.

Table 3.2: Eigenquantum defects and ionization energy of $^{84}\text{Kr}$ determined from a nonlinear least-squares fit based on 187 experimental spectral positions of members of the $ns[3/2]_1$, $nd[3/2]_1$ and $nd[1/2]_1$ series with $n$ between 31 and 115. The values given in parentheses represent one standard deviation (1$\sigma$). In the MQDT calculations, the energy dependence of the MQDT parameters was kept fixed at the values of Reference [140]. 'rmsd' represents the root-mean-square deviation of the fit.

and 52 was used. The transition wave numbers were determined with an absolute accuracy of 0.015 cm$^{-1}$ and their relative positions with an accuracy of 0.008 cm$^{-1}$. These wave numbers, given in Table B.1, were then used in a nonlinear least-squares-fit procedure based on the MQDT model described in Subsection 3.4 A. Because our data set only covered a narrow energy range no attempt was made to refine the values of the energy dependence of the MQDT parameters. Originally, we intended to fit some of the elements of the $V_{\alpha\alpha}$ matrix. However, after it turned out that these elements cannot be determined from our data set, two types of fits were carried out to determine the eigenquantum defects $\mu^{(0)}_\alpha$ and the $^2P_{3/2}$ ionization threshold, one in which the $U_{\alpha\alpha}$ matrix reported by Aymar et al. [140] was used, the other in which the $V_{\alpha\alpha}$ matrix was set to unity.

Table 3.2 compares the MQDT parameters determined in both fits. Surprisingly, the fit based on the $U_{\alpha\alpha}$ transformation matrix did not lead to a significantly smaller root-mean-square deviation (rmsd) than the fit based on the approximate $U_{\alpha\alpha}$ transformation.

The following conclusions can be drawn from the MQDT analysis of the Rydberg spectrum of $^{84}\text{Kr}$:

- MQDT parameters available in the literature, while entirely adequate to describe earlier experimental data recorded at lower resolution, had to be slightly modified to account for the line positions determined in our high-resolution study. The only eigenquantum defect that was found to differ significantly from the results of Aymar et al. [140] is that of the $(p^5s)^1P_1$ channel (see Table 3.2). A satisfactory description of the relative intensities was reached by assum-
3.5. Results

...ing zero values for the dipole amplitudes to the triplet channels and a ratio $D_{\alpha=(p^5d) \, ^1P_1}/D_{\alpha=(p^5s) \, ^1P_1} = 1.5$ for the dipole amplitudes to the singlet channels.

- The simplified MQDT analysis based on the \emph{jj-LS} angular momentum frame transformation matrix $U_{i\alpha}$ gave an equally satisfactory description of our experimental data as that based on the $U_{i\alpha}$ transformation matrix reported by Aymar et al. [140]. The eigenquantum defects extracted from both analyses are very similar, and the positions of the $nd[3/2]_1$, $nd[1/2]_1$ and $ns[3/2]_1$ series at high $n$ values ($n \geq 30$) do not contain sufficient information to determine the $V_{\alpha\alpha}$ matrix elements.

- To determine the $V_{\alpha\alpha}$ matrix elements, the inclusion of the positions of low $n$ states in the MQDT analysis appears mandatory. However, when such states are included, one must also explicitly consider the energy dependence of the $V_{\alpha\alpha}$ matrix elements and of the eigenquantum defects by retaining a linear term in the former case and both a linear and a quadratic terms in the latter case. Available data on the s and d Rydberg states of $^{84}$Kr are insufficient to extract statistically meaningful values for all these parameters, and our attempts at obtaining a fully satisfactory set of MQDT parameters over the entire range from $n = 5$ to the $^2P_{3/2}$ threshold have remained unsuccessful.

Both parameter sets summarized in Table 3.2 will be shown in the next subsection to also be adequate to describe the hyperfine structure in the Rydberg spectrum of $^{83}$Kr. The spectrum of $^{83}$Kr, however, contains information that is helpful in determining MQDT parameters for the $J \neq 1$ channels and thus in obtaining a more global description of the s and d Rydberg states of krypton, as explained below.

\section*{B. $^{83}$Kr}

Fig. 3.3 shows an overview of the spectrum of the s and d Rydberg states of $^{83}$Kr in the ranges of effective principal quantum number $\nu_{3/2} = 30.5 - 31$, $\nu_{3/2} = 40.5 - 41$, $\nu_{3/2} = 50.5 - 51$ and $\nu_{3/2} = 60.5 - 61$. The use of an effective quantum number scale rather than a wave number scale facilitates the recognition of the evolution of the spectral structures as $n$ increases. Around $n = 30$, the main differences to the spectrum of $^{84}$Kr are the splitting of the $ns[3/2]_1$ line in a triplet with $F = 7/2, 9/2$ and $11/2$ and the broadening of the $nd[3/2]_1$ resonance. The $J$ mixing induced by the hyperfine interactions is hardly noticeable and leads to the additional groups of lines associated with transitions to the $34s[3/2]_2$, $32d[3/2]_2$, $32d[5/2]_2$, $32d[5/2]_3$ and $32d[7/2]_3$ Rydberg states that can only be discerned on an enlarged scale or at higher $n$ values.

At increasing $n$ values, the $J = 2$ and $J = 3$ components gradually gain in intensity, primarily because the spacings between the $J = 1$ and $J \neq 1$ components that are cou-
Figure 3.3: Comparison of the hyperfine structure in experimental spectra and MQDT simulations (inverted traces and stick spectra) of s and d Rydberg states of $^{83}$Kr corresponding to single-photon excitation from the $^1S_0$ ground state. For direct comparison of the hyperfine structure at different $n$ values, the spectra are displayed as a function of the effective principal quantum number $v_{3/2}$ defined with respect to the center of gravity of the hyperfine structure of the $^2P_{3/2}$ ground state of $^{83}$Kr$^+$. a) $v_{3/2} = 30.5 - 31$. b) $v_{3/2} = 40.5 - 41$. c) $v_{3/2} = 50.5 - 51$. d) $v_{3/2} = 60.5 - 61$. 

$$F = \frac{C_1}{C_2}$$
pled by the hyperfine interactions scale as \( n^{-3} \) whereas the dominant contributions to the hyperfine interactions, the interactions between \( \hat{f}^+ \) and \( \hat{I} \), are independent of \( n \). Particularly striking is the evolution of the \( (n + 2)s[3/2]_2 \) components which rapidly become as intense as the \( (n + 2)s[3/2]_1 \) components, and even stronger as they approach the \( nd[3/2]_1 \) components. This evolution can be attributed to the s-d interaction and will be discussed further in Section 3.6 C.

Only a subset of all observed features, namely those corresponding to \( ns \) Rydberg states, display a fully resolved hyperfine structure that could be used in a least-squares fit of the hyperfine structure of the \( ^{83}\text{Kr}^+ \, 2P_{3/2} \) ground state. The corresponding spectral positions are listed with their assignments in Table B.2.

Given that a similar agreement between theoretical predictions and experiment was reached using either the \( U_{\hat{f}\alpha\gamma} \) or the \( U_{\hat{f}\alpha\beta} \) transformations, only the results obtained with the \( U_{\hat{f}\alpha\beta} \) transformation are presented here. The MQDT analysis of the \( ^{83}\text{Kr} \) spectrum was carried out in three steps. First, the positions of the four hyperfine components of the \( ^{83}\text{Kr}^+ \, 2P_{3/2} \) state, i.e. the ionization energy and the hyperfine constants \( A_{J=-3/2} \) and \( B_{J=-3/2} \) (see Equation (3.12)) were determined in a nonlinear fit using the positions of the fully resolved hyperfine structure components of the \( ns[3/2]_1 \) states. The resulting constants are summarized in Table 3.3 and were used to draw the schematic diagram presented in Fig. 3.1. The hyperfine constants are compared to, and found to be in good agreement with, early and as yet untested \textit{ab initio} calculations of Fraga et al. [160]. Second, a forward simulation of the spectrum based on Equations (3.14), (3.18) and (3.19) was performed to assign the remaining features, in particular those associated with the \( J = 2 \) and \( J = 3 \) states. A good agreement between calculated and experimental line positions and intensities could be reached immediately, providing direct evidence for the reliability of our MQDT model and of the \( J = 1 \) parameter sets derived from the spectrum of \( ^{84}\text{Kr} \). The positions of the \( nd[3/2,5/2]_2 \) and \( nd[5/2,7/2]_3 \) components, however, appeared systematically shifted indicating the need for a slight adjustment of the eigenquantum defects of Ref. [140] in the region investigated here. In the last step, we attempted to fit the \( J = 2 \) and \( J = 3 \) eigenquantum defects to also reach a quantitative agreement between MQDT calculation and experiment for these levels. This last step turned out to be partially successful for the \( J = 2 \) levels (see Table 3.3), but our spectrum did not contain enough information to derive a statistically meaningful set of eigenquantum defects for the \( J = 3 \) levels.

Table 3.3 summarizes all parameters that could be derived from our least-squares fits of the hyperfine structure of \( ^{83}\text{Kr} \). Not only are the spectral positions very well reproduced by our MQDT calculations but also the intensities are faithfully accounted for, as illustrated in Fig. 3.3. Moreover, the hyperfine coupling constants of the \( 2P_{3/2} \) ground state of \( ^{83}\text{Kr}^+ \) could be determined.

The following conclusions can be drawn from the MQDT analysis of the Rydberg
3.6 Discussion

The results presented in Section 3.5 demonstrate that our MQDT model is well suited to describe the hyperfine structure in the Rydberg spectrum of $^{83}$Kr. The model could...
be used successfully to determine, by extrapolation, the hyperfine structure of the 
\( ^2\text{P}_{3/2} \) ground state of Kr\(^+\). Somewhat unexpectedly, the hyperfine structure of the Rydberg states in the range \( n = 34 \leq 69 \) was found to be equally well reproduced in calculations based on the assumption of purely \( LS \)-coupled eigenchannels as in calculations using the channel mixing parameters \( V_{\alpha\alpha} \) derived by Aymar et al. [140]. This observation does not imply that the channel mixings are unimportant, but, rather, that the \( V_{\alpha\alpha} \) matrix elements are not known accurately enough to reproduce the details of the hyperfine structure in the range of principal quantum number investigated here.

The results on both \(^{84}\text{Kr} \) and \(^{83}\text{Kr} \) suggest 1) that currently known MQDT parameters, while adapted to describe the Rydberg state structure over narrow energy ranges, do not provide a fully satisfactory description over the whole energy range where bound Rydberg states can be probed experimentally, and 2) that the number of MQDT parameters is too large to be determined from available experimental data.

While very encouraging as far as the modeling by MQDT of the hyperfine structure in Rydberg state spectra and the determination of ionic hyperfine structure are concerned, our study only led to the determination of a fraction of all MQDT parameters needed to fully describe the Rydberg spectrum of krypton. It is mainly the energy dependence of the MQDT parameters \( V_{\alpha\alpha} \) and \( \mu_\alpha \) that appears to be underdetermined.

The questions that are not answered by the results presented so far in this chapter are 1) whether, and how well, the parameter sets summarized in Table 3.3 can be used to predict the hyperfine structure outside the range \( n = 30 \leq 100 \) where it has been optimized, 2) whether the interactions between \( LS \)-coupled channels (in particular the \( s-d \) interaction) influences the hyperfine structure, and, if so, how such interactions are likely to manifest themselves in experimental spectra, and 3) whether a complete set of MQDT parameters can at all be extracted from experimental data. These questions are addressed in the next subsections.

### A. The hyperfine structure of \(^{83}\text{Kr} \) at \( n \geq 100 \)

Apart from the splitting of the \( ns[3/2]_1 \) resonances into three components with \( F = 7/2, 9/2 \) and \( 11/2 \), the spectrum of \(^{83}\text{Kr} \) in the range \( n \leq 35 \) is very similar to that of \(^{84}\text{Kr} \), and differences only become apparent in measurements at very high resolution. At high \( n \) values, the spectra of both isotopes differ radically. A comparison of the single-photon spectra of the \( s \) and \( d \) Rydberg series of \(^{83}\text{Kr} \) and \(^{84}\text{Kr} \) in the range \( n = 90 \leq 190 \) is presented in Fig. 3.4. Whereas the intensity distribution in the spectrum of the \(^{84}\text{Kr} \) isotope (Fig. 3.4b) follows the pattern typical for Rydberg series at high \( n \), i.e., a monotonic intensity decrease with \( n \) (the intensities scale as \( 1/n^3 \)) until the series can no longer be resolved and the spectrum becomes continuous, the spectrum of \(^{83}\text{Kr} \) (upper spectrum in Fig. 3.4a) reveals a rich structure with intensity
Figure 3.4: Comparison of experimental and calculated Rydberg spectra of a) $^{83}$Kr and b) $^{84}$Kr in the range of principal quantum number $n = 90 - 190$ below the $^2P_{3/2}$ ground state of Kr$^+$ recorded following single-photon excitation from the $^1S_0$ ground state. The inverted spectra represent MQDT simulations based on MQDT parameters and ionic hyperfine coupling constants determined in a least-squares-fit procedure based on the experimental line positions. A Gaussian line shape with a full width at half maximum of 0.011 cm$^{-1}$ was assumed in the simulations.
fluctuations reminiscent of a beat pattern. A similar behavior was observed in the high Rydberg state spectrum of Ba by Beigang et al. [119] and can be attributed to the overlap and to local interactions of Rydberg series converging to closely spaced limits. The maxima in the 'beat' pattern correspond to regions in which the positions of the members of the Rydberg series converging on different thresholds coincide.

Our MQDT calculations (lower inverted trace in Fig. 3.4a) reproduce the overall intensity patterns satisfactorily with the parameter sets presented in Tables 3.2 and 3.3. As explained in our investigation of NH$_3$ where a similar behavior was observed in series converging on neighboring spin-rotational states of the NH$_3^+$ ion [161], the beat pattern turns out to be very sensitive to the relative positions of the ionic states to which the series converge. The good agreement between our MQDT calculations and the experimental data at high $n$ values therefore demonstrates the reliability of the hyperfine structure constants determined for the $^2P_{3/2}$ ground state of $^{83}$Kr$^+$ (see Table 3.3).

The excellent agreement between our MQDT calculations and the experimental data at high $n$ values is not unexpected. The high $n$ Rydberg states lie energetically very close to those (with $n$ in the range 30 – 100 ) that have been used to derive the MQDT parameters listed in Tables 3.2 and 3.3. Consequently, the fact that the energy dependence of the MQDT parameters is not known precisely has no significant effect on the spectra.

**B. The hyperfine structure of $^{83}$Kr at low $n$**

Our set of MQDT parameters is less suitable to describe the low $n$ region of the spectrum because the energy dependence of the MQDT parameters and the departure of the eigenchannels from purely $LS$-coupled channels plays a much more important role in this region. The eigenquantum defects and ionic hyperfine structure constants listed in Tables 3.2 and 3.3 can nevertheless be used to predict the general appearance of the hyperfine structure at low $n$ values. Such predictions for the $ns$ series with $n = 5, 6, 7$ and 12 are presented in the bottom four spectra on the right-hand side of Fig. 3.5 and are compared with the experimental results (shown on the left-hand side of Fig. 3.5) on the 5s, 6s and 7s levels reported by Trickl et al. [45] and with a measurement of the 12s level carried out in our laboratory by $l_{VUV} + l_{VIS}$ resonance-enhanced two-photon ionization spectroscopy. Because of our inability to account for the energy dependence of the MQDT parameters, the absolute positions of the Rydberg levels are not predicted well by our calculations, with deviations between calculated and experimental positions being largest for the 5s levels (881 cm$^{-1}$) and gradually decreasing at higher $n$ values (33.6 cm$^{-1}$ for the 6s, 27.1 cm$^{-1}$ for the 7s, and 1.3 cm$^{-1}$ for the 12 s level). The relative positions and intensities of the hyperfine structure components, however, appears to be in almost quantitative agreement, with
the exception of the central \((F = 9/2)\) components in the spectra of the \(n = 6\) and 7 levels, the intensities of which are overestimated in the calculation. The overall good agreement of the hyperfine splittings, however, demonstrates convincingly that these splittings have their origin in the ionic hyperfine structure, even for the lowest values of the principal quantum number.

Trickl \textit{et al.} \cite{45} have also reported spectra of the hyperfine structure of the \(5s'\) and \(6s'\) Rydberg levels which have been redrawn at the top of Fig. 3.5 where they are compared with our MQDT predictions. Unfortunately, the experimental hyperfine structures in these spectra could only be accounted for qualitatively by our calculations which do not satisfactorily reproduce the decrease of the hyperfine structure intervals observed as \(n\) increases from 5 to 6. This deviation is likely to have its origin in a perturbation of either the \(5s'\) or the \(6s'\) levels (or both) by neighboring \(ns\) and \(nd\) levels and may provide a handle to extract information on the \(V_{\alpha\alpha}\) matrix elements and their energy dependences.

Despite this discrepancy, a rough estimate of the \(A_{J^+ = 1/2}\) hyperfine coupling constant of the \(^2P_{1/2}\) state of \(\text{Kr}^+\) can be derived using our MQDT model. Adopting the
3.6. Discussion

Assignment of Trickl et al. [45] and depending on whether the 5s' or the 6s' levels is assumed to be predominantly perturbed, one obtains values of \(-0.036\) cm\(^{-1}\) and \(-0.051\) cm\(^{-1}\) for \(A_{J' - 1/2}\), respectively. Inclusion of all hyperfine structure intervals observed in traces a) and b) of Fig. 3.5 in the fit yields \(A_{J' - 1/2} = -0.044\) cm\(^{-1}\). We suspect that the 5s' level is the more likely level to be perturbed and that the value of \(A_{J' - 1/2}\) lies closer to \(-0.036\) cm\(^{-1}\) than to \(-0.051\) cm\(^{-1}\). The magnetic dipole coupling constant of the \(^2\)P\(_{1/2}\) ionic level is thus about five times larger than that of the \(^2\)P\(_{3/2}\) level, a behavior that is similar to that observed in the \(^2\)P ground state of the isoelectronic halogen atoms [162, 163] (see, for instance, Fig. 4 of Ref. [162]). The MQDT model described in this chapter neglects the direct hyperfine interaction between the Rydberg electron and the nucleus. This interaction is likely to be relevant in the lowest members of each Rydberg series. It would translate into an \(F\) dependence of the eigenquantum defects which has been neglected here.

C. The hyperfine structure of \(^{83}\text{Kr}\) and the s-d interaction

Thanks to the energy level splittings that arise in \(^{83}\text{Kr}\) from the additional interactions with the nuclear spin, close encounters between s and d levels are more likely in \(^{83}\text{Kr}\) than in the \(I = 0\) isotopes, particularly at high \(n\) values, giving rise to the possibility of obtaining additional information on the s-d interaction. The MQDT formalism presented in Subsection 3.4 B can be used to investigate theoretically the effect of the s-d interaction on the appearance of the spectrum of \(^{83}\text{Kr}\), for example by setting selected \(V_{\alpha\alpha}\) matrix elements to zero in a reference calculation that is then compared with a calculation in which the same elements are held to a nonzero value. This procedure was used to obtain a qualitative picture of the role of the s-d interaction on the hyperfine structure of the Rydberg states of \(^{83}\text{Kr}\) and is discussed in this subsection.

The results of our MQDT calculations on the role of the s-d interaction turned out to be particularly easy to compare when represented in the form of the Lu-Fano plots [164] displayed in Fig. 3.6. To generate the Lu-Fano plots of Fig. 3.6, the position of each calculated energy level was used to first derive the fractional part of two effective quantum numbers \(v_{J' = F'}\) defined relative to distinct ionic hyperfine levels using Equation (3.14), and, second, to set a point in a two dimensional plot with coordinates corresponding to the fractional part of these effective quantum numbers. Rydberg series in Lu-Fano plots appear as sets of points forming trajectories, and the interactions between the series manifest themselves as avoided crossings between these trajectories, several of which are immediately recognized by inspecting Fig. 3.6.

The Lu-Fano plots displayed in Fig. 3.6 were obtained by deriving the effective quantum numbers of the \(F = 11/2\) levels with respect to the \(F^+ = 3\) and \(F^+ = 5\) hyperfine structure levels of the \(^2\)P\(_{3/2}\) ground state of \(^{83}\text{Kr}\). Similar plots, with the same
Figure 3.6: Theoretical investigation of the role of the s-d interaction on the hyperfine structure in Rydberg states of $^{83}$Kr. The two panels represent Lu-Fano plots based on calculated energies of the hyperfine structure components of the ns and nd Rydberg states with $F = 11/2$ located below the $^2P_{3/2}$ ground state of Kr$^+$. Panel a): The energies were calculated using the $V_{\alpha\alpha}$ matrix elements determined by Aymar et al. [140]. Panel b): The energies were calculated assuming that the eigenchannels are exactly LS coupled, i.e., neglecting channel mixings. The encircled area in panel a) indicates a region where the s-d interaction may be characterized experimentally. The two diagonal lines in panel a) indicate the range of $n$ values between 30 and 80 where resolved information on the hyperfine structure could be determined in the present experiments. The blank area below the diagonal of the plot originates from the fact that only states with $n \leq 130$ were used.
information content, can also be drawn by defining the effective quantum numbers with respect to the $F^+ = 4$ and 6 levels.

In the first model calculation, leading to the results presented in Fig. 3.6b, the $V_{\ell F \alpha \sigma}$ matrix was set to unity (i.e., the close-coupling eigenchannels were assumed to be exactly $LS$ coupled). The trajectories representing the various Rydberg series can thus be labeled by the values of $\ell$ (either s or d) and $J$. The trajectories have their origin along the diagonal of the plot which corresponds to the low $n$ limit. As expected, the trajectories corresponding to s and d series all cross exactly in Fig. 3.6b. The area between the two diagonal lines represents the range of $n$ values for which resolved data could be obtained in the present experiments. The blank area below the diagonal of the Lu-Fano plot stems from the fact that, for clarity, the states beyond $n = 130$ were not used.

In the second model calculation (Fig. 3.6a), the $V_{\ell F \alpha \sigma}$ matrix was taken from the work of Aymar et al. [140]. Although the overall appearance of the Lu-Fano plot resembles that shown in Fig. 3.6b, several avoided crossings are clearly observable, corresponding to interactions between channels differing either in the value of $J$ only or in the value of both $\ell$ and $J$ (see encircled region in Fig. 3.6a), the latter being a manifestation of the s-d interaction. It is important to realize that whereas in the $I = 0$ isotopes, the s-d interaction only manifests itself by level shifts and intensity perturbations affecting levels of the same $J$ value, in $^{83}$Kr the s-d interaction also causes perturbations between levels of different $J$ values and is therefore much easier to detect.

The Lu-Fano plots displayed in Fig. 3.6 provide a convenient way to analyze the channel interactions in krypton and to identify spectral regions where specific interactions ought to be observable in high-resolution spectra. A set of spectra of $^{83}$Kr in the region corresponding to the encircled area of Fig. 3.6a is displayed in Fig. 3.7. In this region, the s ($J = 2, F = 11/2$) channel interacts with the d ($J = 1, F = 11/2$) channel. The interaction, which manifests itself by the avoided crossing in Fig. 3.6a, is also clearly visible in the experimental spectra. To facilitate the comparison of spectra recorded at different values of $n$, the spectral intensities were plotted as a function of the effective principal quantum number defined with respect to the center of gravity of the hyperfine structure of the $^2P_{3/2}$ ground state of $^{83}$Kr. The experimental spectra are compared, in each panel of Fig. 3.7, with inverted calculated stick spectra and the corresponding intensity envelopes. Unfortunately, the values of the $V_{\alpha \sigma}$ matrix elements reported by Aymar et al. [140] were not accurate enough to reproduce the experimental positions and intensities satisfactorily, and it turned out to be more convenient, to recognize the effects of the s-d interaction, to compare the experimental spectra with calculations based on the assumption of a unit $V_{\alpha \sigma}$ matrix and on the parameter sets derived from our high resolution measurements (see Tables 3.2 and 3.3). The positions and intensities of the members of the two interacting $(n + 2)s$
$(J = 2, F = 11/2)$ and $nd$ $(J = 1, F = 11/2)$ series are represented by the bold vertical lines in Fig. 3.7. At $n$ values around 50, the spectra reveal the broad feature associated with the three (unresolved) components of the $nd[3/2]_1$, the three well resolved lines corresponding, in order of ascending effective principal quantum number, to the $(n + 2)s[3/2]_1, F = 11/2, 9/2$ and 7/2 hyperfine structure components, and the weaker $(n + 2)s(J = 2, F = 11/2)$ component already discussed in Subsection 3.5 B. As $n$ increases from 50 to 90, the position of the $(n + 2)s(J = 2, F = 11/2)$ moves across the $nd[3/2]_1$ manifold to reappear on the low energy side beyond $n = 80$. At this point, channel mixings induced by the hyperfine interactions lead to a large number of hyperfine structure components to become optically accessible.

The effect of the s-d interaction is most clearly recognized at the position, around $v_{3/2} \approx 69$ (see panel d) in Fig. 3.7, where the calculated positions of the $(n + 2)s(J = 2, F = 11/2)$ and $nd(J = 1, F = 11/2)$ series almost exactly coincide. In the experimental spectrum, however, an intensity minimum separating two strong lines is observed at this position and indicates the avoided crossing between the two interacting series.

Although the comparison of experimental and calculated spectra displayed in Fig. 3.7 enables the direct observation of the effect of the s-d interaction, the experimental data turned out not to be sufficient to extract unambiguous and statistically well-defined values for the relevant $V_{\chi \alpha}$ matrix elements. A very high resolution study of this spectral region by millimeter wave spectroscopy, following the same strategy as used to study the hyperfine structure in the Rydberg spectrum of $H_2$ [110, 123, 124], has recently confirmed the analysis presented above and led to the determination of the s-d interaction parameters and of even more precise hyperfine structure constants for the $^2P_{3/2}$ ground state of $^{83}\text{Kr}^+$ [155].

### 3.7 Conclusions

Multichannel quantum defect theory represents a powerful tool to analyze the hyperfine structure in atomic Rydberg states. Because the effects of the hyperfine interactions are negligible in the close-coupling region of the electron-core collision, the close-coupling MQDT parameters necessary to predict the hyperfine structure of Rydberg states are identical to those needed to calculate the Rydberg level structure in isotopes (or isotopomers, in the case of molecules) with zero nuclear spin.

The theory enables the parameterization of the hyperfine structure in terms of the hyperfine coupling constants of the ion core. If these constants are known, MQDT can be used to predict the hyperfine structure at any value of the principal quantum number $n$. If the hyperfine coupling constants are not known, they can be determined from the measured hyperfine structure of Rydberg states. Direct measurements of the hyperfine structure of molecular ions by high-resolution spectroscopy are notoriously
3.7. Conclusions

Figure 3.7: The hyperfine structure in the region of the (anti) crossing between the \((n + 2)s[3/2](J = 2, F = 11/2)\) and \(nd[3/2](J = 1, F = 11/2)\) levels corresponding to the encircled area in Fig. 3.6a. The inverted traces represent MQDT simulations which assume that the eigenchannels are purely LS coupled. For the comparison the spectra are displayed as a function of the effective principal quantum number \(V_{3/2}\) defined with respect to the center of gravity of the hyperfine structure of the \(^2P_{3/2}\) ground state of \(^{83}\text{Kr}^+\). The effect of the s-d interaction can be recognized from the fact that the experimental spectrum shows an intensity minimum in panel d) at the position where the calculated positions of the \((n + 2)s[3/2](J = 2, F = 11/2)\) and \(nd[3/2](J = 1, F = 11/2)\) levels become degenerate.
difficult, primarily because of problems associated with space-charge effects which limit the ion density in the experiment volume and can cause undesirable Doppler broadenings. Measurements of the hyperfine structure in Rydberg states of the neutral parent species is not subject to these limitations. When combined with MQDT, such measurements provide an attractive alternative to determine the ionic hyperfine structure. In the case of $^{83}$Kr$^+$ discussed in this chapter, high-resolution spectroscopy and MQDT of the Rydberg level structure has enabled the first determination of the hyperfine structure in the $^2P$ ground electronic state.

Thanks to the relaxation of the selection rules on $\Delta J$ and to the additional splittings in the energy level structure caused by the hyperfine interactions, high resolution spectroscopy of the hyperfine structure in Rydberg states facilitates the observation of channel interactions, such as the s-d interaction in krypton, that can be difficult to observe in isotopes (or isotopomers) with $I = 0$.

Whereas MQDT appears very well suited to describe the energy level structure of Rydberg states, little is known so far on the role of the hyperfine structure on the dynamics of atomic and molecular Rydberg states, although first results indicate that neighboring hyperfine structure components can be subject to different decay processes and have very different lifetimes [122]. The formalism used in this chapter represents a step toward a better understanding and a formal treatment of the role of nuclear spins in the decay dynamics of Rydberg states, and may turn out to be important for other lines of scientific investigations such as studies aiming at understanding the properties of cold Rydberg gases [165–167] and at controlling the translational motion of Rydberg atoms and molecules in inhomogeneous electric fields [168–170]. Further steps toward these goals are described in chapters 4-6.
Chapter 4

Hyperfine structure and autoionization dynamics of Rydberg states of xenon

4.1 Introduction

The role of nuclear spins in chemical reactions is well understood in terms of symmetry selection rules [24]. In molecular photoionization, these imply the conservation of nuclear spin symmetry [171,172]. Further dynamical effects of the nuclear spins in the photoionization of atoms and molecules have so far received little attention because the ionization channels associated with distinct hyperfine levels of the ions have not been resolved. The progress in high-resolution laser spectroscopy over the past years has been such that very high Rydberg states (up to \( n = 200 \) and beyond) can now be resolved even in the extreme ultraviolet [48], where a resolution of about 55 MHz has recently been achieved [114]. At this resolution, the hyperfine structure of Rydberg states can be observed and represents a valuable source of information on the hyperfine levels of the ion to which the Rydberg electron is attached and on the photoionization dynamics. In parallel to the experimental efforts, Multichannel Quantum Defect Theory (MQDT) [13,14,16,173] has been extended to treat the hyperfine structure of bound atomic and molecular Rydberg states [109,110,174] and has provided a theoretical framework to determine ionic hyperfine structures from extrapolation of Rydberg series. This method has been successfully applied to derive the hyperfine structure of the ground ionic state of \(^{83}\text{Kr}^+\) (see Refs. [109,155] and chapter 3 in this thesis) and ortho-\(\text{H}_2^+\) [110]. The desire to understand the role of nuclear spins in photoionization and to extend the experimental and theoretical investigation of the hyperfine structure of bound Rydberg states presented in the previous chapter to autoionizing states has motivated the present combined experimental and theoretical analysis of the Rydberg spectrum of \(\text{Xe}\).

In atomic and molecular physics the process of autoionization is classified as electronic, vibrational, spin-orbit or rotational according to the type of energy that is
transferred from the ionic core to the Rydberg electron (rather than according to the type of interaction responsible for the ionization) [7,175]. This nomenclature implies the name "hyperfine autoionization" for the autoionization process by which the hyperfine energy of the core is transferred to cause ionization. An important goal of the work presented in this chapter was to study this process of hyperfine autoionization on the basis of hyperfine resolved spectroscopic data. Figure 4.1 contrasts spin-orbit autoionization encountered in the $I = 0$ xenon isotopes and which leads to the well-known Beutler-Fano profiles [128,176] of the autoionization region of the xenon spectrum between the $2P_{3/2}$ and $2P_{1/2}$ ionization limits (Fig. 4.1a and b) with the qualitatively different situation that arises in the isotopes of xenon with $I \neq 0$ ($^{129}$Xe, $I = 1/2$, see Fig. 4.1c and d, and $^{131}$Xe, $I = 3/2$).

In the $I = 0$ isotopes, autoionization results in a change of spin-orbit state of the ionic core, whereas in the $I \neq 0$ isotopes, the autoionization may involve either a change of spin-orbit core state, hyperfine core state or both. The autoionization regions around $n = 68$ depicted in Fig. 4.1b and d, as obtained in the present study, reveals a completely different spectral structure for the $I \neq 0$ isotopes. Surprisingly, this autoionization structure of the $I \neq 0$ isotopes of xenon has not been observed or discussed in the literature so far, despite the fact that the spectral resolution required for its observation would have been available in several laboratories.

In particular we address here the following questions: (i) Is pure hyperfine autoionization, i.e., a process in which the ionization is solely accompanied by a change of the hyperfine state of the ion core, allowed? (ii) What are the propensity rules ($\Delta J$, $\Delta F$) describing the energy flow between core and Rydberg electron in the autoionization region of the $I \neq 0$ isotopes of Xe? (iii) Can such propensities, if they exist, be exploited to prepare ions in selected hyperfine states, with possible applications in ion-trap loading [177] and quantum computing [178]?

To answer these questions, we combine high-resolution spectroscopy and MQDT to describe the influence of the nuclear spin on the structure and dynamics of the states embedded in the autoionization continuum and to predict the branching ratios for ionization into the fine and hyperfine structure components accessible at a given photoionization energy. The MQDT model also enables a discussion and a characterization of the mechanism responsible for the process of hyperfine autoionization.

The autoionization resonances of xenon between its first ($2P_{3/2}$) and second ($2P_{1/2}$) ionization thresholds have been first observed by Beutler [128] and explained in a seminal contribution by Fano [176]. Since then, this region of the xenon spectrum has been thoroughly studied both experimentally [46,138,179,180] and theoretically [16,143]. The ab initio prediction of the line shapes of the lowest autoionizing resonances remains a challenge up to present day and continues to stimulate theoretical efforts [181,182]. The experimental methods include energy loss spectroscopy [138], single-photon [46,179,180] and three-photon spectroscopy [183] of the odd parity ($I = 1$
4.2 Experiments

The spectra were recorded using the VUV laser system described in chapter 2 and depicted in Fig. 2.4. VUV radiation was generated by two-photon resonance-enhanced sum-frequency mixing ($\nu_{\text{VUV}} = 2\nu_1 + \nu_2$) in Kr using the (4p)$^5$ 5p[1/2] 0 - (4p)$^6$ 1S$^0$ two-photon resonance at $2\nu_1 = 94092.9$ cm$^{-1}$. The VUV wave number is calibrated to an absolute accuracy of 0.016 cm$^{-1}$ following the procedure described in Ref. [131] which involves the stabilization of the wave number of the first laser. The wave
Figure 4.1: Schematic energy level diagram of the autoionizing Rydberg series of $^{132}\text{Xe}$ (a) and $^{129}\text{Xe}$ (c). The full arrows represent the process of spin-orbit autoionization that leads in both cases to an ion in the $^2P_{3/2}$ state. The dotted arrows in panel (c) represent hyperfine autoionization processes. Panels (b) and (d) show the observed photoionization spectra of $^{132}\text{Xe}$ (b) and $^{129}\text{Xe}$ (d) in the region around $n = 68$. Panel (b) shows the well-known Beutler-Fano profiles, whereas the spectrum in panel (d) is qualitatively different, because of additional interactions with the nuclear spin ($I = 1/2$ of $^{129}\text{Xe}$).

number of the second laser is calibrated by recording absorption spectra of molecular iodine in an oven heated to 600 °C and comparing them to spectra simulated with the program IodineSpec [192].
4.3. Multichannel Quantum Defect Theory of the hyperfine structure and autoionization

Xenon gas (Pangas, spectroscopic grade purity) is used without further purification and is introduced into the spectrometer in a pulsed skimmed supersonic expansion. The xenon gas jet is crossed at a right angle by the VUV laser beam in the middle of an array of resistively coupled cylindrical extraction plates. The photoexcitation region and the TOF mass spectrometer are surrounded by a double layer of Mumetal shielding. Under the experimental conditions used to record the photoionization spectra of the high Rydberg states of xenon, dc and ac Stark shifts are negligible for the Rydberg states with principal quantum number between 30 and 150 used in the MQDT analysis.

Spectra of the autoionizing Rydberg states located below the $^2P_{1/2}$ ionization threshold are recorded by monitoring the photoionization yield as a function of the VUV wave number. The ions were extracted towards a microchannel plate detector located at the end of the TOF tube by a pulsed electric field of 88 V/cm amplitude and 1 $\mu$s duration which was applied 1 $\mu$s after the VUV laser pulse so that photoexcitation could take place under field-free conditions. Spectra of the different isotopes were obtained by placing temporal gates at the corresponding positions in the TOF spectrum. Photoionization spectra with a satisfactory signal-to-noise ratio could be obtained for the isotopes $^{128-132,134,136}$Xe but not for $^{124}$Xe and $^{126}$Xe. The wave number range covered in these experiments extends from 108275 cm$^{-1}$ to 108371 cm$^{-1}$. A low efficiency in the resonance-enhanced sum-frequency mixing prevented the recording of spectra in the region between 108315 cm$^{-1}$ and 108340 cm$^{-1}$.

4.3 Multichannel Quantum Defect Theory of the hyperfine structure and autoionization

In a previous publication, an MQDT model was developed to analyze the hyperfine structure of bound Rydberg states of the rare gas atoms and used to quantitatively account for the Rydberg spectrum of $^{83}$Kr below the $^2P_{3/2}$ ionization limit and determine the hyperfine structure of $^{83}$Kr$^+$ in its $^2P_{3/2}$ ground state [109]. In the following, this formalism is briefly reviewed and extended to treat the hyperfine structure of autoionizing Rydberg states of the rare gas atoms.

MQDT relies on a partitioning of space into two regions. At short electron-core distances, the so-called close-coupling region, the interactions between the ion core and the Rydberg electron are dominated by electrostatic (including exchange) interactions. The following angular momentum coupling hierarchy provides an adequate description of the close-coupling eigenchannels [16]

$$L^+ + \ell = \tilde{L}; \quad S^+ + \tilde{s} = \tilde{S}$$

$$L + \tilde{S} = \tilde{J}, \quad \tilde{J} + \tilde{I} = \tilde{F},$$

(4.1)
where $\tilde{L}^+$ and $\tilde{S}^+$ represent the orbital and spin angular momenta of the ionic core, $\tilde{l}$ and $\tilde{s}$ the corresponding angular momenta of the Rydberg electron, and $\tilde{I}$ the nuclear spin. The parameter characterizing the interactions in the close-coupling region are the eigenquantum defects $\mu_{\alpha}$ which are assumed to be unaffected by the hyperfine interactions and can thus be taken from an analysis of the $I = 0$ isotopes [109]. The choice of this coupling scheme for the description of the close-coupling channels is equivalent to a neglect of the spin-orbit and hyperfine interactions in the core. This choice is further discussed in Section 4.5.

At large electron-core distances, the electron interacts only weakly with the core. In this region, the dissociation channels can be described by the following angular momentum coupling scheme

$$\tilde{L}^+ + \tilde{S}^+ = \tilde{J}^+, \tilde{F}^+ + \tilde{I} = \tilde{F}^+; \tilde{l} + \tilde{s} = \tilde{j}, \tilde{F}^+ + \tilde{j} = \tilde{F},$$

(4.2)

where $\tilde{J}^+$ and $\tilde{F}^+$ represent the electronic and total angular momenta of the ionic core, respectively. The dominant interaction in the ionic core is the spin-orbit coupling which leads to an energy splitting between the $^2P_{3/2}$ and $^2P_{1/2}$ levels, that is several orders of magnitude larger than the splittings induced by the hyperfine interactions. Under the assumption that the mixing of the $^2P_{3/2}$ and $^2P_{1/2}$ spin-orbit components of the ion by the hyperfine interactions is negligible, the hyperfine structure of the two spin-orbit components can be treated separately and expressed as a function of the magnetic dipole and electric quadrupole hyperfine coupling constants $A_{J^+}$ and $B_{J^+}$ [157] ($B_{J^+=1/2} = 0$ for the $^2P_{1/2}$ spin-orbit level):

$$\tilde{v}(J^+, F^+) = \tilde{v}_{J^+} + A_{J^+} \frac{C}{2} + B_{J^+} \frac{3C(C + 1) - I(I + 1)J^+(J^+ + 1)}{2I(2I - 1)J^+(2J^+ - 1)},$$

(4.3)

where

$$C = F^+(F^+ + 1) - I(I + 1) - J^+(J^+ + 1).$$

(4.4)

In Eq. (4.3), $\tilde{v}_{J^+}$ represents the wave number of the photoionization transition to the center of gravity of the hyperfine structure for each of the two spin-orbit $^2P_{J^+}$ components ($J^+ = 1/2, 3/2$). The dissociation channels are hence characterized by a pair of intermediate quantum numbers $J^+$ and $F^+$ designating each ionization threshold.

The parameter characterizing a closed dissociation channel $i$ built on an ionic core with intermediate quantum numbers $J^+$ and $F^+$ is the effective quantum number

$$\nu_i = \frac{R_M}{\sqrt{\tilde{v}_{J^+ F^+} - \tilde{v}}}.$$

(4.5)

The analytical frame transformation

$$U_{\alpha \alpha} = \langle L S J F | J^+ F^+ jF \rangle$$

(4.6)
between the bases of the $LSJF$-coupled eigenchannels and the $J^+F^+jF$-coupled dissociation channels was derived using angular momentum algebra (see Eq. 3.16).

If the total energy of the system lies below the lowest ionization energy, all channels are closed and the positions of bound Rydberg states are obtained by requiring the wave functions to vanish at an infinite ion-electron distance $r$. This condition translates into the equation

$$\sum_{\alpha} U_{i\alpha} \sin (\pi (\mu_\alpha + \nu_i)) A_\alpha = 0, \quad (4.7)$$

where the $A_\alpha$ are the expansion coefficients of the radial part of the Rydberg electron wave function in the basis of the close-coupling eigenchannels. This equation has nontrivial solutions when

$$\det |U_{i\alpha} \sin (\pi (\mu_\alpha + \nu_i))| = 0. \quad (4.8)$$

If the total energy lies between the lowest and the highest ionization energy included in the MQDT model, some dissociation channels are closed. The ensemble of closed channels is denoted $Q$ whereas the ensemble of open channels is labeled $P$. In this region of the spectrum, the boundary condition requires that the closed-channel wavefunctions remain finite for $r \to \infty$ and that the open-channel wavefunctions behave at large $r$ as collision eigenfunctions of the open channels, labeled $p$, with a phase-shift $\tau_p$. The following set of equations is obtained from these boundary conditions

$$\sum_{\alpha} U_{i\alpha} \sin (\pi (\mu_\alpha + \nu_i)) A_\alpha = 0 \quad \text{for } i \in Q, \quad (4.9)$$

$$\sum_{\alpha} U_{i\alpha} \sin (\pi (-\tau_p + \nu_i)) A_\alpha = 0 \quad \text{for } i \in P, \quad (4.10)$$

and the corresponding compatibility condition is solved in the form of a generalized eigenvalue problem [87].

For each value of the total energy in the autoionization region there are as many solutions $\tau_p$ and associated vectors of expansion coefficients $A^p$ as open channels. These coefficients are obtained in a single step by solving the equation

$$\Gamma A^p = \tan (\pi \tau_p) \Lambda A^p, \quad (4.11)$$

where

$$\Gamma_{i\alpha} = \begin{cases} U_{i\alpha} \sin (\pi (\nu_{j+F^+} + \mu_\alpha)) & \text{for } i \in Q \\ U_{i\alpha} \sin (\pi \mu_\alpha) & \text{for } i \in P \end{cases} \quad (4.12)$$
The single-photon excitation to a dissociation channel $i$ is described as the excitation into eigenchannels $\alpha$, followed by an expansion in a basis of collision eigenfunctions $\rho$, which are projected onto the dissociation channels $i$. The partial photoionization cross sections are obtained as a coherent sum over contributions from the collision eigenfunctions $\rho$ of all open channels. Each contribution is the product of an excitation amplitude, which depends on the close-coupling eigenchannel character $A_\alpha^\rho$ of $\rho$, a phase factor which contains the Coulomb phase and the phase shift of the collision function $\tau_\rho$, and the projection $\langle i | \rho \rangle$ of the collision eigenfunction $\rho$ onto the dissociation channel $i$. The partial photoionization cross section into a particular channel thus depends on (i) the importance of excitable close-coupling eigenchannel in the collision function, (ii) the strength of the channel coupling given by $\langle i | \rho \rangle$ and (iii) the collision phase shifts $\tau_\rho$. The partial photoionization cross section for the generation of an ion in the state labeled by the quantum numbers $J^+$ and $F^+$ is given by [193]

$$\sigma_{J^+F^+} \propto \omega \sum_F W_F \sum_{i \in P_{J^+F^+}} |D(i,F)|^2,$$

(4.14)

$\omega$ is the energy of the incident photon. In Eq. (4.14), the symbols have their usual meanings and $D(i,F)$ is the reduced dipole matrix element for the photoionization from the ground state. $W_F$ is a weighting factor that accounts for the multiplicity of the levels accessed by photoexcitation from the $1S_0$ ground state [159]

$$W_F = \frac{2F + 1}{2J + 1}.$$

(4.15)

The total photoionization cross section is given by

$$\sigma_{\text{tot}} = \sum_{J^+F^+} \sigma_{J^+F^+}.$$

(4.16)

The reduced dipole matrix element can be expressed as a function of the MQDT parameters [193]

$$D(i,F) = \sum_\rho e^{i(\sigma_i - \pi \ell_i/2)} \langle i | \rho \rangle e^{i \pi \tau_\rho} \sum_\alpha \frac{A_\alpha^\rho D_\alpha}{N_\rho},$$

(4.17)
where $\sigma_i$, $\langle i | \rho \rangle$ and $N_\rho$ are defined as

$$\sigma_i = \text{Arg} \left( \ell_i + 1 - i \sqrt{\frac{R_M}{\ell_i - 1}} \right)$$

(4.18)

$$\langle i | \rho \rangle = \sum_\alpha U_{i \alpha} \cos(\pi(-\tau_\rho + \mu_\alpha))A_\alpha^\rho$$

(4.19)

$$N_\rho^2 = \sum_{i \in P} \left( \sum_\alpha U_{i \alpha} \cos(\pi(-\tau_\rho + \mu_\alpha))A_\alpha^\rho \right)^2.$$  

(4.20)

The electric dipole transition amplitudes $D_\alpha$ were taken from Ref. [16] to be $D_{\alpha, (5d)^1P_1} / D_{\alpha, (5s)^1P_1} = 5$ and $D_\alpha = 0$ for all other channels, independently of their value of $F$.

### 4.4 Results

#### A. Photoionization spectra of the xenon isotopes with zero nuclear spin

The photoionization spectra of the xenon isotopes with zero nuclear spin are characterized by two series $ns'[1/2]_1$ and $nd'[3/2]_1$ converging to the $2P_j$ state of the ion. These spectra are usually analyzed with the effective two-channel formalism derived from MQDT [194], which represents the photoionization spectrum by the expression

$$\sigma = \sigma_{as} \frac{(\epsilon_s + q_s)^2}{(\epsilon_s^2 + 1)} + \sigma_{ad} \frac{(\epsilon_d + q_d)^2}{(\epsilon_d^2 + 1)} + \sigma_b$$

(4.21)

where

$$\epsilon_\ell = \frac{\tan(\pi(v_{j+} + \mu_\ell))}{W_\ell}.$$  

(4.22)

In Eq. (4.21), $\sigma_{as}$ and $\sigma_b$ are the resonant and nonresonant contribution to the photoionization cross section, $\mu_\ell$, $q_\ell$, and $W_\ell$ are the quantum defect, the quality factor and the linewidth parameter for the $n\ell'$ resonances, and $v_{j+}$ is the effective quantum number with respect to the $2P_j$ threshold.

The photoionization spectra of $^{128}$Xe, $^{130}$Xe, $^{132}$Xe, $^{134}$Xe and $^{136}$Xe were analyzed by numerically fitting Eq. (4.21) to the experimental photoionization spectra in the range $v_{1/2} \approx 33 - 42$ and $v_{1/2} \approx 60 - 92$ to extract accurate ionization energies $2P_{1/2}$ for the five xenon isotopes as well as line shape parameters for the $nd'[3/2]_1$ resonances. The experimental spectra were recorded with a step size of 100 MHz and all points were used in the fitting procedure. Unambiguous line shape parameters for the $ns'[1/2]_1$ resonances could not be obtained because the bandwidth of the laser and residual Doppler broadening (together about 0.01 cm$^{-1}$) contribute significantly
This work | Literature
---|---
IE(\(^2\text{P}_{1/2}\))/(hc cm\(^{-1}\)) | 108370.714±0.016 | 108370.8(2) [46]
\(W_d\) | 0.28(3) | 0.245-0.260 [179]
\(q_d\) | 1.38(10) | 1.40-1.53 [179]

Table 4.1: \(^2\text{P}_{1/2}\) ionization energy, quantum defects and line shape parameters for d' resonances obtained from numerical fits of Eq. (4.21) to the photoionization spectrum of \(^{132}\text{Xe}\) in the ranges \(\nu_{1/2} \approx 33 - 42\) and \(65 - 92\).

The value of the ionization energies were also derived independently by determining the central position of every s'- and d'-resonance in the range \(\nu_{1/2} \approx 33 - 42\) and \(\nu_{1/2} \approx 60 - 110\) and extrapolating the series to infinity using Rydberg's formula. The values obtained in both procedures agreed within the statistical uncertainties of the fits \((1\sigma = 0.002\text{ cm}^{-1})\). The ionization potential \(^2\text{P}_{1/2}\) and the line shape parameters of the d' resonances for \(^{132}\text{Xe}\) are listed in Table 4.1. Table 4.2 summarizes the isotopic shifts of the ionization energy for all other isotopes relative to that of \(^{132}\text{Xe}\) as obtained in the procedure described above.

The value of \((108370.714\pm0.016)\text{ cm}^{-1}\) for the \(^2\text{P}_{1/2}\) ionization energy derived in this study is in agreement with the value of \((108370.8 \pm 0.2)\text{ cm}^{-1}\) obtained by Yoshino [46] but not with the more recent value of \((108370.82 \pm 0.05)\text{ cm}^{-1}\) determined by Kortyna et al. [180]. The accuracy of the isotope shifts of the ionization energy is limited by the statistical uncertainty \((1\sigma = 0.002\text{ cm}^{-1})\) of the fitting procedure. These isotope shifts agree, within the uncertainties of the respective determinations, with the values determined for the \(^2\text{P}_{3/2}\) ionization energy by Brandi et al. [189]. The present results enable a determination of the spin-orbit splitting in \(\text{Xe}^+\) to \((10536.925 \pm 0.019)\text{ cm}^{-1}\), which is isotope independent within the precision of our measurements. This value is compatible with the previous result of Yoshino and Freeman [46] but is an order of magnitude more precise.

**B. Photoionization spectra of \(^{129}\text{Xe}\) and \(^{131}\text{Xe}\)**

This subsection describes the experimental spectra of the xenon isotopes with \(I \neq 0\) and their assignment. The assignments were made on the basis of MQDT simulations in an iterative procedure in which the MQDT parameters were refined and the assignments improved until a fully satisfactory agreement between MQDT predictions and experimental results was reached. The optimal MQDT simulations are already presented here together with the experimental results in the figures and, when necessary, also used to explain the experimental observations, although the fitting of the MQDT parameters is only discussed in the next subsection.
Figure 4.2: Schematic energy level diagram of the $^2P$ ground state of $^{129}$Xe$^+$ (a) and $^{131}$Xe$^+$ (b). The wave numbers given on the left of the diagram correspond to the $^2P_{1/2} \rightarrow ^1S_0$ ionization energies and the wave numbers on the right represent the spin-orbit and hyperfine splittings determined in the present study. The tables list the total angular momentum quantum number $F$ of all $s$ and $d$ dissociation channels associated with the $^2P_{J^+}, F^+$ ionic states.
Chapter 4. Hyperfine structure and autoionization dynamics of Rydberg states of xenon

Table 4.2: Isotope shifts of the $^2P_{1/2}$ ionization energy relative to the position of the most abundant isotope $^{132}$Xe. The ionization energies of the even mass number isotopes were derived in a least-squares fitting procedure of Eq. (4.21) to the photoionization spectra, and those for the odd mass number isotopes from the MQDT fit. These isotope shifts are compared to those determined at the $^2P_{3/2}$ threshold by Brandi et al. [189].

<table>
<thead>
<tr>
<th>A</th>
<th>$\Delta E(2^2P_{1/2}(^{132}Xe) - 2^2P_{3/2}(^{132}Xe))$ (hc cm$^{-1}$)</th>
<th>$\Delta E(2^2P_{3/2}(^{132}Xe) - 2^2P_{1/2}(^{132}Xe))$ (hc cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>-0.0110(20)</td>
<td>-0.0134(30)</td>
</tr>
<tr>
<td>129</td>
<td>-0.0094(30)</td>
<td>-0.0122(30)</td>
</tr>
<tr>
<td>130</td>
<td>-0.0057(20)</td>
<td>-0.0062(30)</td>
</tr>
<tr>
<td>131</td>
<td>-0.0030(30)</td>
<td>-0.0067(30)</td>
</tr>
<tr>
<td>132</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>134</td>
<td>+0.0055(20)</td>
<td>+0.0060(30)</td>
</tr>
<tr>
<td>136</td>
<td>+0.0121(20)</td>
<td>+0.0150(30)</td>
</tr>
</tbody>
</table>

\[ a \text{this work} \]
\[ b \text{see Ref. [189]} \]
\[ c \text{from MQDT analysis} \]

$^{129}$Xe has a nuclear spin $I = 1/2$. A total of 6 s- and 11 d channels with $F = 1/2$ or $F = 3/2$ are accessible following single-photon excitation from the $^1S_0$ ground state. Because of J-mixing induced by the hyperfine interaction, the eigenchannels with $J = 0, 1$ or 2 are required for the description of the spectrum of $^{129}$Xe. The fine and hyperfine structure of $^{129}$Xe$^+$ as it was determined from the analysis of the Rydberg spectrum (see below) is shown schematically on the left of Fig. 4.2a which also lists all possible values of the $J^+, F^+, \ell$ and $j$ quantum numbers of the optically accessible dissociation channels. There are 3 s series and 4 d series converging to the $^2P_{1/2}$, $F^+ = 0, 1$ ionic states instead of 1 s- and 1 d series in the case of the isotopes with zero nuclear spin.

The situation is more complex in $^{131}$Xe ($I = 3/2$), where a total of 10 s- and 29 d channels with $F = 1/2, 3/2$ or $5/2$ are needed to describe the photoionization spectra obtained following single-photon excitation from the $^1S_0$ ground state. Close-coupling eigenchannels with $J = 0, 1, 2, 3$ and 4 contribute to the spectrum, and 4 s- and 11 d series converge to the $^2P_{1/2}$, $F^+ = 1, 2$ ionic states. The ionic level structure is shown schematically in Fig. 4.2b together with the quantum numbers of all dissociation channels.

The low-lying Rydberg states $5 \leq \nu_{1/2} \leq 30$ are split by the hyperfine interactions but the observed resonances can still be classified in the extended $jK$-coupling scheme (Eq. (4.23)) in analogy to the situation encountered in the isotopes of zero nuclear spin

\[ \vec{L}^+ + \vec{S}^+ = \vec{f}^+, \vec{f}^+ + \vec{\ell} = \vec{K}; \vec{K} + \vec{s} = \vec{f}, \vec{f} + \vec{I} = \vec{F}. \]  

Accordingly, the low-lying Rydberg states can be labeled in $n\ell''[K]_j(F)$ notation. In the high Rydberg states with $\nu_{1/2} \geq 65$, the Rydberg electron angular momentum $\vec{\ell}$ is
decoupled from the core electronic angular momentum $J^+$. In this range, the Rydberg series are characterized by a well defined ionic hyperfine state. The coupling scheme appropriate for this situation is given in Eq. (4.2) and is the one that was chosen for the dissociation channels.

The photoionization spectra of $^{132}$Xe (a), $^{131}$Xe (b) and $^{129}$Xe (c) in the region of effective principal quantum number $\nu_{1/2} \approx 37$ are displayed in Fig. 4.3. The spectrum of $^{132}$Xe (a) consists of the characteristic and well-known broad 39d'[3/2], and sharp 41s'[1/2] resonances. The spectra of the fermionic isotopes reveal additional features that have their origin in hyperfine interactions. Two sharp resonances are observed in both spectra that can be assigned with the help of the MQDT simulation to distinct hyperfine components of $s'$-resonances (see below). In the spectrum of $^{131}$Xe, the lower sharp line consists of two overlapping $s'$-resonances with $F = 3/2$ and 1/2, that belong to series converging on the $^2P_{1/2}$, $F^+ = 1$ ionic level, whereas the higher sharp line corresponds to $s'$-resonances with $F = 3/2$ and 5/2 belonging to series converging on the $^2P_{1/2}$, $F^+ = 2$ ionic level. The situation is similar for $^{129}$Xe where the lower line is a superposition of two $s'$-resonances with $F = 3/2$ and 1/2 that belong to series converging on the $^2P_{1/2}$, $F^+ = 1$ level of $^{129}$Xe and the higher line is a single $s'$-resonance belonging to a series that converges on the $^2P_{1/2}$, $F^+ = 0$ ionic level.

The photoionization spectra of $^{131}$Xe and $^{129}$Xe also reveal a second d'-resonance on the low wave number side of the main d' line. This second line, assigned to the transition to the 39d'[3/2], level, originates from the relaxation of the selection rule on $\Delta J$ resulting from the fact that the total angular momentum $\vec{F}$ is the conserved quantity in the presence of nuclear spin.

At higher values of the principal quantum number, the spectra of $^{129}$Xe and $^{131}$Xe begin to differ markedly from the spectrum of $^{132}$Xe and from each other as illustrated in Fig. 4.4 where the spectra of $^{132}$Xe (a), $^{131}$Xe (b) and $^{129}$Xe (c) around $\nu_{1/2} \approx 65$ are compared. The reason for this behavior is that $J$-mixing is almost complete around $\nu_{1/2} \approx 65$, so that the $n\ell'[3/2]_2$ resonances become as intense as the $n\ell'[3/2]_1$ resonances. In Fig. 4.4, the resonances are labeled by the $\ell$ and $F$ values of the most significant contribution according to the MQDT simulations.

The nuclear spins have the following effects on the photoionization spectra of $^{129}$Xe and $^{131}$Xe as compared to the isotopes with zero nuclear spin: First, $\vec{F}$ and not $\vec{J}$ is the constant of motion in the presence of nuclear spin, and therefore additional nd' resonances are observed above $\nu_{1/2} \approx 30$ that can be assigned to $J = 2$ with a weak $J = 3$ contribution (see, e.g., Fig. 4.3b). Around $\nu_{1/2} \approx 65$, $J$-mixing is complete and nearly equally intense d'-resonances are observed for both $J = 1$ and $J = 2$ (Fig. 4.4). The integrated intensity of the $n\ell'[3/2]_2$ resonances, however, is weaker in the case of $^{131}$Xe than it is in $^{129}$Xe, reflecting the weaker hyperfine interaction in the ion (see Table 4.4 below). Second, the uncoupling of the Rydberg electron from the
Figure 4.3: Experimental relative photoionization cross section of xenon in the region of the $39d'[3/2]_1$ state (solid line) and its MQDT simulation (dotted line) for (a) $^{132}\text{Xe}$, (b) $^{131}\text{Xe}$ and (c) $^{129}\text{Xe}$. 
Figure 4.4: Experimental relative photoionization cross section of xenon in the region of the $66d'[3/2]_1$ state (solid line) and its MQDT simulation (dotted line) for (a) $^{132}$Xe, (b) $^{131}$Xe and (c) $^{129}$Xe.
core leads to the observation of series that converge on different hyperfine states of the ion. Strong perturbations of line positions and intensities arise when Rydberg states converging on different ionic states become nearly degenerate. The hyperfine interaction between quasi-bound states of the same total angular momentum $F$ but different principal quantum numbers then induces a strong mixing of these states that causes intensity alterations in the spectrum.

These effects are illustrated by the MQDT calculations presented in Fig. 4.5, which displays the predicted photoionization cross section associated with the $F = 3/2$ channels of $^{129}$Xe (Fig. 4.5a) and the fractional part of the effective quantum number $v_{J^+ = 1/2, F^+ = 1}$ (Fig. 4.5b) of the $s'$ and the three $d'$ quasi-bound levels plotted against $v_{1/2,1}$. The $s'$ series and two of the $d'$ series have a constant quantum defect and therefore correspond to channels that are built on a $^2\text{P}_{1/2}, F^+ = 1$ core. The remaining $d'$ series, converges to the higher $^2\text{P}_{1/2}, F^+ = 0$ state of the ion and therefore regularly traverses the other series, leading to a series of avoided crossings. In order to understand the intensity distribution in the spectrum, the series must be correlated with close-coupling channels at low values of the effective quantum number $5 \leq v_{J^+ = 1/2, F^+ = 1} \leq 30$. Figure 4.5 reveals that the $d'$ series converging to the higher $^2\text{P}_{1/2}, F^+ = 0$ state of the ion carries the intensity in the low energy part of the spectrum. Indeed this series correlates at low $n$ with the $\text{p}^5\text{d}, ^1\text{P}_1$ channel, which is
Figure 4.6: Experimental relative photoionization cross section (upper trace) and its MQDT simulation (inverted trace) of $^{129}$Xe (a) and $^{131}$Xe (b), in the region of effective quantum number $\nu_{1/2} = 100 - 150$. The photoionization profiles calculated by MQDT have been convoluted with a Gaussian of FWHM 0.011 cm$^{-1}$ in order to account for the finite bandwidth of the VUV laser.
the only d channel carrying intensity (see left-hand side of Fig. 4.5b). A very similar situation is also encountered for the $^{131}$Xe isotope (see discussion of Fig. 4.6 below).

As a consequence of the angular momentum uncoupling that takes place at higher \( n \)-values, the intensity spreads from the \( J = 1 \) d' series into the lower of the two d' series associated with a \( J = 2 \) close-coupling channel (see Fig. 4.5b). As observed experimentally (see Fig. 4.6), the intensity of the d' series converging on the $^2P_{1/2}$, \( F^+ = 1 \) level vanishes at the position of the avoided crossings because the hyperfine interaction between the series leads to a very small $p^5 d^1 P_1$ character.

In the photoionization spectrum of $^{129}$Xe (see Fig. 4.6a), two strong d' series ($nd'[3/2]$ and $nd'[3/2]$) are observed, the former converging to the \( F^+ = 0 \), the latter to the \( F^+ = 1 \) ionic hyperfine levels. The intensity of the second series vanishes at the positions where its members become degenerate with members of the first series. This is the case when the hyperfine splitting of two ionic levels $\Delta F^+,F^+,+1$ becomes equal to an integer multiple $k = 1, 2, ...$ of the spacing between neighboring Rydberg states [119], a condition that can be expressed as

$$\Delta E_{F^+,F^+,+1} = k \frac{2R_M}{n^3},$$

with $F^+ = 0$ for the $^2P_{1/2}$ ionization limit of $^{129}$Xe. Successive positions of near-degeneracy and the corresponding \( k \) values are indicated by vertical arrows in Fig. 4.6. In the spectra of $^{129}$Xe (Fig. 4.6a), these $n$-mixing perturbations induced by the hyperfine interactions are observed up to \( k = 5 \). They are more sparse in the spectrum of $^{131}$Xe because of the smaller splitting between the \( F^+ = 1 \) and \( 2 \) hyperfine levels of $^{131}$Xe$^+$ and occur only for \( k = 2 \) and \( 3 \) in the spectrum of Fig. 4.6b. Comparable intensity alterations have also been observed in the spectrum of the high bound Rydberg states of $^{83}$Kr \( (n \geq 100) \) [109]. The effects discussed above can be understood in a simple physical picture: At the position where the effective quantum numbers are related by $\nu_{F^+,+1} = \nu_{F^+} + k$ with \( k \) integer, the Rydberg electron orbital period is equal to \( k \) times the precession period of \( F^+ \) around \( \vec{J} \) which implies that the Rydberg electron "sees" a core with vanishing hyperfine structure. The analogous situation for a rotating molecular core was described by Labastie et al. [195] and was characterized as a "stroboscopic" effect.

C. Numerical fitting of the MQDT parameters

The adjustable parameters needed for the MQDT simulation of the photoionization spectra are the eigenquantum defects $\mu_\alpha$, which are assumed to be unaffected by the hyperfine interaction, the value of the (center of gravity) ionization energies corresponding to the formation of the $^2P_{3/2}$ and $^2P_{1/2}$ ionic states, the magnetic dipole hyperfine coupling constants of $^{129}$Xe$^+$ and $^{131}$Xe$^+$ and the electric quadrupole hyper-
close-coupling channels $\mu_{\alpha}^a$

<table>
<thead>
<tr>
<th>Channel</th>
<th>$\mu_{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s $^3P_0$</td>
<td>0.015</td>
</tr>
<tr>
<td>s $^1P_1$</td>
<td>-0.022</td>
</tr>
<tr>
<td>s $^3P_1$</td>
<td>0.0285</td>
</tr>
<tr>
<td>s $^3P_2$</td>
<td>0.030</td>
</tr>
<tr>
<td>d $^3P_0$</td>
<td>0.545$^b$</td>
</tr>
<tr>
<td>d $^1P_1$</td>
<td>0.140</td>
</tr>
<tr>
<td>d $^3P_1$</td>
<td>0.615</td>
</tr>
<tr>
<td>d $^3D_1$</td>
<td>0.375</td>
</tr>
<tr>
<td>d $^3P_2$</td>
<td>0.615</td>
</tr>
<tr>
<td>d $^1D_2$</td>
<td>0.544</td>
</tr>
<tr>
<td>d $^3D_2$</td>
<td>0.340</td>
</tr>
<tr>
<td>d $^3F_2$</td>
<td>0.475</td>
</tr>
<tr>
<td>d $^3D_3$</td>
<td>0.360</td>
</tr>
<tr>
<td>d $^1F_3$</td>
<td>0.455</td>
</tr>
<tr>
<td>d $^3F_3$</td>
<td>0.475</td>
</tr>
<tr>
<td>d $^3F_4$</td>
<td>0.475$^b$</td>
</tr>
</tbody>
</table>

$^a$ determined in this work
$^b$ unmodified from Ref. [185]

Table 4.3: Term symbols of all LS coupled eigenchannels included in the present MQDT model and eigenquantum defects determined by fitting the MQDT model parameters to the experimental spectra as explained in the text.

...fine coupling constant of $^{131}\text{Xe}^+$.

In the analysis of the spectra the quantum defects $\mu_{\alpha}$ available from the literature were adjusted iteratively. First, an MQDT simulation of the $^{132}\text{Xe}$ photoionization spectrum was undertaken using the different sets of quantum defects and corresponding $U_{i\alpha}$ matrices published in Refs. [16,138,143], but none of them reproduced the experimental line shapes in a fully satisfactory manner, probably because of the energy dependence of the eigenquantum defects. The only available channel parameters ($J = 1$) taking the departure of close-coupling channels from LS coupling into account did not reproduce the spectrum as well as achieved by a simple adjustment of the eigenquantum defects in LS representation. Realizing that too little information is contained in the photoionization spectra alone for a determination of the exact eigenchannels and eigenquantum defects, we therefore decided to neglect the departure of the close-coupling channels from LS coupling.

In a first step, the five quantum defects $\mu_{\alpha}(J = 1)$ were adjusted manually until a good agreement with the experimental spectra of $^{132}\text{Xe}$ was reached. In this adjustment the ionization energy derived in Section 4.4.A was used (see Table 4.1).

With these adjusted eigenquantum defects for the $J = 1$ channels and initial values for the $J = 0$ and $J = 2$ eigenquantum defects estimated from the quantum defect analysis of Ref. [185], an MQDT simulation of the $ns'$ photoionization resonances of
was performed. The s' resonances in the experimental spectra could be assigned on the basis of their relative intensities and the comparison with the MQDT predictions. \(^{129}\)Xe possesses two s' series converging to the \(^2P_{1/2}, F^+ = 1\) ionization limit with \(F = 1/2\) and \(F = 3/2\) and one s' series with \(F = 1/2\) converging to the \(^2P_{1/2}, F^+ = 0\) level (see Fig. 4.2a). The \(F = 3/2\) resonances are calculated to be stronger than those with \(F = 1/2\). By inspection of Fig. 4.3 one can thus conclude that the \(F = 3/2\) levels in \(^{129}\)Xe lie below the \(F = 1/2\) levels. In \(^{131}\)Xe, two s' series converge to each of the \(^2P_{1/2}, F^+ = 1\) and \(^2P_{1/2}, F^+ = 2\) states with total angular momentum quantum numbers \(F = 1/2, 3/2\) and \(F = 3/2, 5/2\) respectively. The observed intensities indicate that the levels with \(F = 1/2, 3/2\) lie below those with \(F = 3/2, 5/2\). These observations imply that the magnetic dipole coupling constants of the two isotopes have an opposite sign.

In a non-linear least-squares fitting procedure of the calculated positions of the \(F = 3/2\) and \(F = 1/2\) s' resonances to the experimental positions determined in a least-squares fit using Eq. (4.21), a preliminary value of the magnetic dipole hyperfine coupling constant \(^{129}A_{1/2}\) was derived. In the next step, the eigenquantum defects of the s channels with \(J = 0\) and \(J = 2\) and of the d channels with \(J = 2\) were adjusted manually in order to reproduce the line shapes and line positions in the spectrum of \(^{129}\)Xe. Finally, the least-squares fitting procedure of \(^{129}A_{1/2}\) and the ionization energy was repeated with the improved quantum defects, and a final value of \(^{129}A_{1/2}\) \((^{129}A_{1/2} = -0.4071(9)\text{cm}^{-1})\) was derived. At this stage, a satisfactory agreement between the experimental spectra and the MQDT simulation was reached, as can be seen from a comparison of calculated and experimental traces in Figs. 4.3, 4.4 and 4.6.

A similar procedure was followed to simulate the spectra of \(^{131}\)Xe where additional eigenquantum defects for the \(J = 0, 3, 4\) d channels were required. It turned out, however, that the \(J = 0\) and \(J = 4\) eigenquantum defects do not affect the line shapes and line positions. In fact, no quasi-bound d Rydberg states with \(J = 0\) or \(J = 4\) are found between the \(^2P_{3/2}\) and \(^2P_{1/2}\) ionic limits, so that the \(J = 0\) and \(J = 4\) channels consist almost exclusively of contributions from open channels in this region.

The eigenquantum defects obtained in the MQDT analysis and the values of the magnetic dipole hyperfine constants \(A_{1/2}\) are listed in Tables 4.3 and 4.4, respectively. The ratio \(^{129}A_{1/2}/^{131}A_{1/2}\) provides a consistency check of the hyperfine constants. The magnetic dipole constant \(A_{1/2}\) is proportional to the ratio of the nuclear magnetic moment \(\mu\) and the nuclear spin quantum number \(I\), \(^{129}A_{1/2}/^{131}A_{1/2} = (\mu^{129}I^{131})/(\mu^{131}I^{129})\). The ratio of the constants determined in this work \(^{129}A_{1/2}/^{131}A_{1/2} = -3.375(12)\) corresponds well to the value \(^{129}A_{1/2}/^{131}A_{1/2} = -3.37341\) obtained using the literature values \(\mu^{129} = -0.777977\mu_N\) and \(\mu^{131} = 0.691861\mu_N\) from Ref. [196].

An accurate determination of the hyperfine structure of the \(^2P_{3/2}\) state of \(^{129}\)Xe\(^+\) and \(^{131}\)Xe\(^+\) following the procedure of Ref. [109] requires the analysis of the hyperfine
Table 4.4: Magnetic dipole ($A_{1/2}$) and electric quadrupole ($B_{3/2}$) hyperfine coupling constants for the $^2P_{j+}$ states of $^{129}$Xe$^+$ and $^{131}$Xe$^+$. The constants for the $^2P_{3/2}$ states were derived from the MQDT analysis of the present experimental results, whereas the $^2P_{1/2}$ constants were derived from an MQDT fit using the hyperfine structure of low-lying bound Rydberg states as detailed in the text.

<table>
<thead>
<tr>
<th>isotope</th>
<th>$A_{1/2}$/cm$^{-1}$</th>
<th>$A_{3/2}$/cm$^{-1}$</th>
<th>$B_{3/2}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{129}$Xe</td>
<td>-0.4071(9)</td>
<td>$\approx$ -0.054(15)</td>
<td>$\approx$ 0.006(5)</td>
</tr>
<tr>
<td>$^{131}$Xe</td>
<td>0.1206(3)</td>
<td>$\approx$ 0.014(5)</td>
<td>$\approx$ 0.006(5)</td>
</tr>
</tbody>
</table>

structure in the bound Rydberg series of these isotopes. Unfortunately, the hyperfine structure has only been resolved for a few low-lying states with principal quantum numbers $n = 5 - 8$. The description of the absolute position of these states requires to take into account at least the energy dependence of the eigenquantum defects. To estimate the hyperfine structure of the $^2P_{3/2}$ state, we have chosen the highest Rydberg states for which the hyperfine structure has been resolved, i.e., $8d[3/2]_1$ and $8d[1/2]_1$ [189]. A fit of the MQDT model to the hyperfine structure of these states in $^{129}$Xe and $^{131}$Xe provides a rough estimate of the electric dipole and magnetic quadrupole hyperfine coupling constants $A_{3/2}$ and $B_{3/2}$. No fully satisfactory fit could be reached however, probably because of the unsatisfactory description of the energy dependence of the quantum defects and the deviation from LS coupling. The relative deviations between measured and calculated hyperfine intervals vary between 6% and 40%. The hyperfine constants are therefore characterized by large uncertainties (see Table 4.4).

The comparison of experimental and simulated spectra in Figs. 4.3, 4.4 and 4.6 demonstrates that the present MQDT model provides an adequate description of the line positions, line intensities and line shapes of both $I = 0$ and $I \neq 0$ isotopes in the autoionization regions of Xe. The main deviations between calculated and experimental spectra occur in the $s'$ resonances which appear more intense and narrower in the simulations than in the experimental spectra. These deviations can be fully explained by the limited resolution of the present experiments as already mentioned above. A weak shoulder on the high energy side of the $s'$ resonances in the spectra of all isotopes (see Fig. 4.3) can be accounted for by a (Doppler-broadened) contribution from the background gas (see Ref. [197]).

4.5 Discussion

A. Limitations of the present MQDT model

Multichannel Quantum Defect Theory describes the structure of Rydberg states with an accuracy comparable to the highest resolution of current spectroscopic methods.
This theory relies on the description of the interactions in the limiting coupling cases where the Rydberg electron is very close to the ionic core (close-coupling region) and very far from the core (dissociation region). The inclusion of the nuclear spin into the MQDT formalism for the rare gas atoms provides an opportunity to reconsider the description of both coupling cases and to discuss the major approximations.

In the close-coupling region, the electrostatic interactions (orbit-orbit and exchange) dominate the level structure. An adequate description is therefore provided by LS-coupling. The orbit-orbit and exchange interactions translate into differences in the values of the eigenquantum defects. This description neglects all other interactions in the core. As was pointed out by Lu [16], the spin-orbit and s-d interactions lead to a mixing of the pure LS-coupled channels and can\altered{be accounted for by modifying the transformation matrix and the quantum defects. For nuclei with }I \neq 0{, an additional mixing of the close-coupling channels can in principle be induced by the hyperfine interactions. However, these interactions are so much weaker, in the rare gas atoms, than the spin-orbit and exchange interactions, that they can be neglected in excellent approximation in the description of the short-range eigenchannels [109].

In the dissociation region, the dominant interactions are those in the ionic core, i.e., the spin-orbit and hyperfine interactions. Since the magnitude of these interactions differs by roughly four orders of magnitude in the \textsuperscript{2}P ground state of the singly-charged rare gas cations, the coupling case chosen in Eq. (4.2) is easily justifiable. Neglecting the hyperfine induced mixing of the ionic spin-orbit levels is thus expected to be an excellent approximation.

An exact description of \( N_s \) close-coupling s- and \( N_d \) d channels of the same total angular momentum requires the determination of \( (N_s + N_d)(N_s + N_d - 1)/2 \) independent matrix elements or generalized Euler angles [16] and their energy dependence. If the s-d interaction is neglected, this number reduces to \( N_s(N_s - 1)/2 + N_d(N_d - 1)/2 \). Given that the hyperfine induced mixing of the eigenchannels can be neglected (see above), this number is further reduced because only close-coupling channels with the same quantum number \( J \) are allowed to interact. It is however known [16] that the numerical fitting of the MQDT parameters to photoionization spectra does not provide sufficient information to derive a complete description of the eigenchannels. Indeed, when several series converge onto a common ionization threshold, the spectra of Rydberg states alone are insufficient for the derivation of unambiguous channel parameters, and additional information (not currently available) on the wavefunctions of the considered states is required.

To alleviate some of these difficulties we chose, in the present analysis, to approximate the close-coupling channels by pure LS coupled channels, and to adjust the corresponding quantum defects. This approximation implies that autoionization, as described by the present model, is only determined by the electrostatic close-coupling interactions. More specifically, the exchange interaction between the \textsuperscript{3}P\textsubscript{1} and \textsuperscript{1}P\textsubscript{1} cou-
figurations leads to the autoionization of the s'-states and the additional orbit-orbit interaction in the $^3D_1$ configuration induces the autoionization of the d'-states. The advantage of this procedure is that it enables to highlight the salient features of the hyperfine autoionization and to demonstrate that it is not caused by the hyperfine interaction. Moreover, despite the approximation, the model can quantitatively account for the spectra because the eigenquantum defects can be adjusted as effective constants to reproduce the experimental spectra, and also to adequately describe the positions and dynamics of the autoionizing Rydberg states. The drawback is that the constants determined in this work are only valid over a restricted energy range and do not provide a quantitatively correct representation of the complete xenon spectrum below, between and above the two $^2P$ ionization thresholds. A complete and fully satisfactory set of MQDT parameters for the xenon atom remains to be derived.

**B. Hyperfine and spin-orbit autoionization**

The results presented so far show that the phenomenon of spin-orbit autoionization in the presence of a nonzero nuclear spin can be well understood and interpreted with the help of an MQDT model. The same framework also provides a description of hyperfine autoionization and a characterization of the underlying mechanisms. In what follows we show some predictions of autoionizing spectra involving hyperfine autoionization. The observation of this phenomenon has been impossible so far, because the small magnitude of the hyperfine splittings of the ion (0.41 cm$^{-1}$ in the $^2P_{1/2}$ state of $^{129}$Xe$^+$, and typically much less in lighter atoms and molecules) sets a lower limit of $n \approx 520$ for the principal quantum number of the autoionizing Rydberg states to be observed, which represents an experimental challenge.

The MQDT model used here represents an adequate framework to discuss the mechanism and the propensity rules that govern autoionization. In the discussion, it is convenient to distinguish between three energetic regions. The first region is that between the lowest and the highest hyperfine component of the $^2P_{3/2}$ state. The second region is located between the highest hyperfine component of the $^2P_{3/2}$ state and the lowest component of the $^2P_{1/2}$ state, and the third corresponds to the region between the lowest and the highest hyperfine component of the $^2P_{1/2}$ state.

At first sight, spin-orbit and hyperfine autoionization would be expected to follow entirely different dynamics because the energy transferred between the ion core and the Rydberg electron in the two processes differs by several orders of magnitude. However, as discussed above, both processes have their origin in electrostatic (orbit-orbit and exchange) interactions, and are therefore governed by the same dynamics, determined by the values of the eigenquantum defects. The branching ratios for autoionization into various dissociation channels depend only on the values of the quantum numbers, or more specifically on the values of the transformation matrix.
Figure 4.7: MQDT prediction of the relative photoionization cross section of $^{129}$Xe in the region between the $^2P_{3/2}$, $F^+ = 2$ and 1 ionic hyperfine states. The displayed structures result from pure hyperfine autoionization. The contributions from the $F = 1/2, 3/2$ manifolds are shown in panels (a) and (b), respectively.
4.5. Discussion

1. Hyperfine autoionization within the $^2P_{3/2}$ sublevels

A simple situation of pure hyperfine autoionization occurs in the region between the $^2P_{3/2}$, $F^+ = 2$ and $F^+ = 1$ states of $^{129}$Xe$^+$ (see Fig. 4.2a) for which two sets of channels with $F = 1/2$ and $F = 3/2$, can be treated separately. In the $F = 1/2$ manifold, a single quasi-bound $d'$ series converging to the $F^+ = 1$ level exists, which interacts with two degenerate $F^+ = 2$ continua. To characterize the autoionization dynamics in this region, the photoionization cross section predicted by MQDT and shown in Fig. 4.7a, was analyzed with the parameterization of Eq. (4.21) resulting in parameters $W = 0.151$ or $I_r = 2.11 \cdot 10^4$ cm$^{-1}$ and $q = 0.403$. Figure 4.7b represents the contribution to the photoionization cross section from the $F = 3/2$ manifold. In this case, one $s$ and two $d$ quasi-bound series interact with one $s$ and two $d$ continua. Since the $s$ series does not interact with the $d$ series, it can be analyzed separately with the two-channel formula (Eq. (4.21)). A numerical fit of the isolated $s$ series led to the parameters $W = 8.25 \cdot 10^{-4}$ (or $I_r = 115$ cm$^{-1}$ ) and $q = 128$.

The reduced widths $I_{r\ell}$ are independent of $n$ and directly reflect the strength of the channel interactions. They can thus be used to compare the dynamics of pure hyperfine autoionization with that of spin-orbit autoionization of the $s'$ and $d'$ series of $^{132}$Xe. Analyzing the MQDT prediction of the photoionization cross section with Eq. (4.21) yields the following parameters for the $s'$ and $d'$ series of $^{132}$Xe: $W_d = 0.277$ (or $I_{r,d} = 3.87 \cdot 10^4$ cm$^{-1}$ ) and $q_d = 1.49$ and $W_s = 5.61 \cdot 10^{-3}$ (or $I_{r,s} = 783$ cm$^{-1}$ ) and $q_s = 9.40$. The values obtained for the $d'$ series slightly differ from those listed in Table 4.1 because they resulted from a fit to the MQDT calculation whereas the latter were determined in a fit to the experimental spectrum. The discrepancy lies within the statistical uncertainty. Although one might have naively expected a much slower dynamics for the hyperfine autoionization than for spin-orbit autoionization, the comparison of the reduced widths of the $s$ and $d$ resonances leads to the conclusion that the channel interactions causing spin-orbit and hyperfine autoionization have a comparable strength. Hyperfine autoionization is thus an allowed and even a very efficient process in the rare gas atoms.

2. $\Delta F^+$ propensity rules in spin-orbit autoionization

In the region above the $^2P_{3/2}$ ionization limit, the Rydberg states converging to the $^2P_{1/2}$ state decay by spin-orbit autoionization to a $^2P_{3/2}$ Xe$^+$ ion and a free electron. In the case of $^{129}$Xe and $^{131}$Xe, the ions can be produced in different hyperfine states. The question naturally arises whether the autoionization could be used as a means to produce ions in selected hyperfine levels. The experimental discrimination between different hyperfine product channels, for instance by high-resolution photoelectron
spectroscopy, is currently not possible, but the MQDT model developed in the present work allows quantitative predictions of the partial photoionization cross sections to selected ionic hyperfine structure levels to be made (see Eq. (4.14)).

The calculated partial cross sections show resonances similar to those of the total cross section (see Section 4.3). As a consequence of multiple interferences, spectral regions can be identified in which partial cross sections to a selected ionic hyperfine state dominate. Unfortunately, when many different ionic states are energetically accessible, the minima of the partial cross sections do not usually coincide, and therefore the entirely selective production of a single ionic hyperfine level is rarely possible. The maximal contrast between different hyperfine channels is therefore expected when only two ionic hyperfine states are available as in the case of the $^2P_{3/2}$ ground state of $^{129}$Xe$^+$. Such a case is illustrated in Fig. 4.8 where the experimental total cross section (Fig. 4.8a), the calculated cross section with the contributions from $F = 3/2$ and $F = 1/2$ (Fig. 4.8b) and the branching ratios between the two ionic hyperfine states of $^{129}$Xe$^+$ (Fig. 4.8c) are represented. An inspection of the partial cross sections enables one to identify regions where the branching ratio between the $^2P_{3/2}, F^+ = 2$ and $F^+ = 1$ states of $^{129}$Xe$^+$ is extremal. For instance, more than 85% of the ions are produced in
the $F^+ = 1$ state at a photon wave number of $(108278.77 \pm 0.02) \text{ cm}^{-1}$, whereas at $(108279.1 \pm 0.1) \text{ cm}^{-1}$ close to 80% of the ions are produced in the $F^+ = 2$ state.

These results show that it is possible to produce hyperfine selected ions through photoionization by exploiting the interference of the atomic channels. Indeed, the widths of the resonances in the partial cross sections are large enough that a selective production of hyperfine levels should be possible using broadly available lasers. This conclusion is expected to be valid for many other ions that possess a hyperfine doublet in the ground state. This is in particular the case for the odd mass number isotopes of earth-alkaline metals which are of interest in ion trap loading [177] and its applications to quantum computation [178].

3. Competition between hyperfine and spin-orbit autoionization in the $^2P_{1/2}$ levels

In the region between the two hyperfine components of the $^2P_{1/2}$ state of $^{129}Xe^+$ and $^{131}Xe^+$ the competition between pure hyperfine and spin-orbit autoionization can be studied. In what follows, a few cases with specified values of $\ell$ and $F$ are discussed and some general propensity rules are derived.

We first consider the $s'$ series of $^{129}Xe$ with $F = 1/2$ converging on the $F^+ = 0$ hyperfine level (see Fig. 4.2a). The associated Rydberg states can autoionize in either the $^2P_{1/2}$, $F^+ = 1$ $\epsilon s$ open channel (hyperfine autoionization) or the $^2P_{3/2}$, $F^+ = 1 \epsilon s$ open channel (spin-orbit autoionization). The partial cross sections corresponding to these two processes calculated by MQDT can again be analyzed with the parameterization of Eq. (4.21). The width parameter obtained in both cases is exactly the same ($W = 4.30 \times 10^{-3}$) because it is a property of the quasi-bound state. The resonant cross section $\sigma_a$ is 8.0 times larger for spin-orbit autoionization. The considered $s'$ states therefore preferentially decay via spin-orbit autoionization.

A similar situation is found in the $F = 3/2$ $s'$ series of $^{131}Xe$ converging on the $F^+ = 2$ ionic level (see Fig. 4.2b). The members of this series can decay into the $^2P_{1/2}$, $F^+ = 1$, the $^2P_{3/2}$, $F^+ = 2$ or the $^2P_{3/2}$, $F^+ = 1$ continua. The partial cross sections for these processes are characterized by the resonant cross sections $\sigma_a = 0.209, 0.502$ and $0.167$, respectively, and the width parameter amounts to $W = 2.12 \times 10^{-3}$. In this case, hyperfine autoionization efficiently competes with spin-orbit autoionization with a resonant cross section intermediate between that of the two spin-orbit contributions. In addition, it is noted that $\Delta F^+ = 0$ is preferred over $\Delta F^+ = -1$ for spin-orbit autoionization.

The situation for the $d'$ series in $^{131}Xe$ is even more interesting because more open channels are available (see Fig. 4.2b). Two cases are presented which are extremal concerning the values of resonant cross sections. The $F = 1/2$ manifold holds two almost degenerate quasi-bound $d'$ series converging to the $^2P_{1/2}$, $F^+ = 2$ level. These $d'$ levels can autoionize in any one of the five continua with $^2P_{1/2}$, $F^+ = 1$ and $^2P_{3/2}$
The situation of two closed channels having a common ionization threshold and five open channels can be approximated by the parameterization for two closed and one open channels [194]

\[
\sigma = \sigma_a \left(1 + \sum_{j \in Q} q_j \right)^2 + \sigma_b, \tag{4.25}
\]

where the symbols have the same meaning as in Eq. (4.21). In Eq.(4.25), a non-resonant cross section \(\sigma_b\) has been added to Eq.(25) of Ref. [194]. Although this parameterization is not exact, it turned out to provide an excellent fit of the calculated partial cross sections. The ratio of the resonant cross sections are found to be \(\sigma(1/2,1) : \sigma(3/2,3) : \sigma(3/2,2) : \sigma(3/2,1) = 0.155 : 3.40 : 0.555 : 0.104\). Considering the number of open channels built on each ionic state which is 1:1:2:1, the resonant partial cross sections are highly non-statistical and the autoionization dynamics is characterized by a strong preference for \(\Delta F^+ = +1\) over \(\Delta F^+ = 0\) over \(\Delta F^+ = -1\) in spin-orbit autoionization. Again, hyperfine autoionization has a significant contribution.

The \(F = 5/2\) manifold also holds two quasi-bound \(d'\) series converging to the \(^2\)P\(_{1/2}\), \(F^+ = 2\) level. These \(d'\) levels can autoionize in any one of the two \(^2\)P\(_{1/2}\), \(F^+ = 1\) and \(^2\)P\(_{3/2}\), \(F^+ = 3, 3, 2, 1, 1, 0\) continua. The same analysis as presented above for the \(F = 1/2\) case leads to the ratio of resonant cross sections \(\sigma(1/2,1) : \sigma(3/2,3) : \sigma(3/2,2) : \sigma(3/2,1) : \sigma(3/2,0) = 11.5 : 10.6 : 9.6 : 9.2 : 4.7\). This ratio corresponds closely to a statistical expectation since the ratio of the number of open channels is 2:2:2:1. Nevertheless a slight preference for \(\Delta F^+ = +1\) over \(\Delta F^+ = 0\) over \(\Delta F^+ = -1\) is found again and hyperfine autoionization even represents the most important contribution to the total cross section.

Two conclusions are drawn from the above results. First, the rate of autoionization for hyperfine and spin-orbit autoionization is comparable as already pointed out in Section 4.5.B.1 above. Second, the propensity rule for the spin-orbit autoionization favor processes in which \(\Delta F^+\) is largest, and is most pronounced for small values \((F = 1/2)\) of the total angular momentum, whereas at larger values \((F = 5/2)\) the partitioning is close to statistical. These observations can be interpreted by analyzing the properties of the angular momentum recoupling matrix elements (the values of the \(3j\) symbols become equal in the limit of high quantum number) and represent a geometric effect.
4.6 Conclusions

The photoionization spectra of $^{129}$Xe and $^{131}$Xe in the region between the $^2P_{3/2}$ and $^2P_{1/2}$ threshold markedly differ from those of the $I = 0$ isotopes of Xe, the differences being caused by the hyperfine interaction. The experimental and theoretical study of these differences have provided a way to quantify the role of the nuclear spin in the photoionization of the rare gas atoms and to characterize the process of hyperfine autoionization. It has also enabled us to derive the hyperfine structure of the Xe$^+$ ion.

In the modeling of the spectra by MQDT, excellent agreement between experimental spectra and spectra simulated by MQDT could be reached in a model in which the influence of the nuclear spin on the close-coupling eigenchannels was neglected. The process of pure hyperfine autoionization, i.e., the autoionization process in which the ionic core transfers hyperfine energy to the electron to cause ionization, is found to be very efficient in the rare gas atoms.

The hyperfine interaction is thus important in defining the hyperfine structure of the ion core and is propagated into the Rydberg spectrum by the angular momentum transformation. The autoionization dynamics (and the channel interactions) are entirely contained in the description of the eigenchannels, i.e., the eigenquantum defects which describe the electrostatic (orbit-orbit and exchange) interactions. Thus the dynamics of spin-orbit and hyperfine autoionization are both governed by the same interactions which, in our model, have nothing to do with the hyperfine interaction. The effect of the spin-orbit interaction on the dynamics are described by the spin-orbit structure of the ionic core on the one hand and by the different values of the eigenquantum defects of channels differing solely in their $J$-values on the other hand. An essential element in the description of the details of the dynamics is given by the frame transformation matrix elements. It is therefore not surprising that, at high $J/F$ values, the branching ratios for autoionization into different channels approach a statistical distribution closer than at low $J/F$ values.
Chapter 4. Hyperfine structure and autoionization dynamics of Rydberg states of xenon
Chapter 5

Spin-rovibronic interactions in the
gerade Rydberg states of ortho H₂:
High-resolution spectroscopy and
Multichannel Quantum Defect Theory

5.1 Introduction

Studies of the Rydberg spectrum of H₂ play a central role in acquiring fundamental
knowledge on the structural properties of electronically excited states of molecules
and establishing quantitative theoretical models to describe the dynamical processes
that result from the interaction of molecules with short-wavelength radiation [10-12,
86,88-91,95,97,110,112]. The potential energy curves of the low-lying electronic
states of H₂ and H₂⁺ can be calculated by ab initio quantum chemical methods to such
high accuracy that the energies of vibrational and rotational levels can be predicted
at least as accurately as they can be measured by high-resolution spectroscopy [198-
202]. Rydberg states above n = 5 pose problems for ab initio quantum chemistry and
these states are more conveniently treated by multichannel quantum defect theory
(MQDT) [13,14,87] which bridges the gap between the low n Rydberg states of H₂ and
the very high n Rydberg states that have potential curves identical to those of H₂⁺.

Whereas the ungerade np and nf Rydberg states of H₂ can be described by MQDT
to a level where quantitative agreement between experimental and theoretical de-
terminations of the hyperfine structure of high-n Rydberg states is at the sub-MHz
level [110], the treatment of the gerade (ns and nd) Rydberg states still poses prob-
lems because of the necessity to include repulsive doubly excited configurations,
primarily the (2pσ_u)² repulsive state which represents the lowest member of the
p Rydberg series converging on the ²Σ_u⁺ repulsive state of H₂⁺ and dissociates to
H(1s)+H(n = 2) fragments. At low n values, the interaction of the (2pσ_u)² state of ¹Σ_g⁺
symmetry with the \( ns \) and \( nd \) Rydberg levels leads to the characteristic double minimum shape of the \( EF \), \( GK \) and \( HH \) states \([199,203]\). At high \( n \) values the interaction leads to severe perturbations of the level structure and to rapid predissociation of the \( ns \) and \( nd \) Rydberg states with a vibrationally excited \( H_2^+ \) ion core \([110,204,205]\). In contrast to the levels of \( \Sigma_g^+ \) and \( \Pi_g^+ \) symmetry, the \( \Pi_g^- \) levels are immune to predissociation \([110,205,206]\). The dynamics of the gerade Rydberg states of \( H_2 \) is therefore particularly rich and interesting.

Although conceptually MQDT is capable of treating the complex channel situation of the gerade states of \( H_2 \), the assignments proposed for several prominent spectral structures in the Rydberg spectrum of \( H_2 \) in the vicinity of the ionization thresholds remain tentative or even contradictory. These spectral features correspond to predissociative and/or autoionizing low-\( n \) Rydberg states with an excited core and perturb the structure of the high Rydberg states converging on the lowest levels of \( H_2^+ \). These states are often referred to as "interlopers".

This chapter describes a combined experimental and theoretical investigation of the gerade Rydberg states of \( H_2 \) located in the vicinity of the \( X^2\Sigma_g^+ (v^+ = 0) \) ground state of \( H_2^+ \). Experimentally, the emphasis was placed on the characterization, by high-resolution laser spectroscopy, of the interlopers mentioned above and the study of the evolution of the hyperfine structure of Rydberg levels belonging to series converging to the \( X^2\Sigma_g^+ (v^+ = 0, N^+ = 1) \) level. Theoretically, the effort was invested first in the derivation, by \textit{ab initio} methods, a set of MQDT parameters of sufficient accuracy to assign the interloper levels, and then in the refinement of these parameters until the experimental hyperfine structure could be reproduced within the experimental uncertainty of 0.0075 cm\(^{-1}\). This work represents an important step toward a quantitative analysis of the hyperfine structure of millimeter wave spectra which have led to the experimental determination of the hyperfine structure of \( nd \) Rydberg levels between \( n = 51 \) and 55 at a resolution of 300 kHz \([110,123,124]\). Because the high-resolution laser spectra obtained in the present work cover a much broader range of \( n \) values (between \( n = 35 \) and \( n = 62 \)) than the millimeter wave spectra, these spectra have enabled us to explore the evolution of the angular momentum coupling hierarchy over a wider range.

### 5.2 Experiment

A resonant two-photon excitation scheme was used to selectively probe ortho-\( H_2 \) (\( I=1 \)) Rydberg states located below the \( X^2\Sigma_g^+ (v^+ = 0, N^+ = 1) \) ionization threshold from the \( X^1\Sigma_g^+(v''=0, J'') \) ground state via the \( B^1\Sigma_u^+(v'=0 \text{ or } 2, J'=J''+1, J'' \text{ or } J''-1) \) rotational levels.

The narrow-band vacuum-ultraviolet (VUV) radiation around 92500 cm\(^{-1}\) required
5.3. Theory

5.3.1 R-Matrix calculations

The variational R-matrix method has been described in Refs. [207, 208]. The calculations rely on a partitioning of space into a reaction volume and an asymptotic region. Spheroidal coordinates $\xi, \eta, \phi$ are used and the two-electron wavefunctions are constructed from symmetrized products of $H_2^+$ one-electron orbitals. The one-electron wavefunctions inside the $H_2^+$ core are denoted $n \ell \lambda$, where $\ell$ is the spheroidal analog of the orbital angular momentum quantum number in spherical coordinates and $\lambda$ is...
the quantum number associated with the projection of $\ell$ on the internuclear axis. The use of spheroidal coordinates has been found to result in a much faster convergence of the calculations compared to spherical calculations [207,208], so that $\ell_{\text{max}} = 3$ was sufficient.

Within the reaction volume $\xi \leq \xi_0$, a full configuration-interaction calculation is performed and the variational wavefunctions are determined by requiring that their logarithmic derivative is stationary with respect to $\xi$ at the volume boundary. The continuation of the wavefunctions beyond the R-matrix volume provides the reaction matrices $K$ and quantum defects $\mu$ invoking the equations of generalized quantum defect theory [13].

The spheroidal radius $\xi_0$ is chosen large enough that the amplitudes of the wavefunctions $1s\sigma$ and $2p\sigma$ are very small in the boundary region and essentially correspond to the $1\sigma_g$ and $1\sigma_u$ molecular orbitals, respectively. The two-electron channel functions included in the calculations are $1s\sigma e\bar{s}\sigma$ and $1s\sigma e\bar{d}\lambda$ with $\lambda = 0 - 2$ and those associated with the core-excited channels $2p\sigma e\bar{p}\sigma$ and $2p\sigma e\bar{d}\lambda$ with $\lambda = 0 - 2$. The explicit inclusion of these core-excited channels removes the resonances in the reaction matrices below the $2p\sigma$ ionization threshold. Inside the reaction volume, a basis set of approximately 200 antisymmetrized product basis functions of the type $n\ell\lambda n'\ell'\lambda'$ with $(n, n') = 1 - 6, (\ell, \ell') = 0 - 3$ and $\Lambda = \lambda + \lambda'$ is used. A variational procedure is applied to obtain the reaction matrix $K(E, R)$ as a function of the internuclear distance $R$ and the total energy $E$. The reaction matrix is then diagonalized to obtain the quantum defect functions $\mu_\alpha(E, R)$ according to

$$\mu_\alpha(E, R) = \frac{1}{\pi} \tan^{-1} \sum_{kk'} U^{-1}_{\alpha k} K_{kk'}(E, R) U_{k'\alpha},$$

where the columns of $U$ are the eigenvectors of $K(E, R)$.

The quantum defect functions obtained from this procedure can be used to calculate adiabatic potential energy curves of the bound electronic states of $H_2$ as well as scattering resonances of the $H_2^+$ - electron collision complex at arbitrary energies up to the region were higher-lying core-excited channels play a role [208]. In the present work, the quantum defect curves where used in subsequent dynamical calculations including all nuclear and spin degrees of freedom. Since the computational cost of a full dynamical calculation involving also the $2p\sigma$ channels was estimated to be too large, the problem was simplified by eliminating the latter channels. The elimination of these channels in the calculations leads to the appearance of resonances in the reaction matrices. These resonances manifest themselves as strongly avoided crossings in the low Rydberg states of $H_2$ (EF,GK,HH, see section 5.3.2) but their effects become less important with increasing principal quantum number.

The result of the R-matrix calculations are "effective" reaction matrices for the $s$ and $d$ channels associated with the $1s\sigma$ ionization threshold which take into account
their interactions with the doubly excited states. As a final step, the reaction matrices are transformed to a spherical angular momentum basis set and η quantum defects [209] instead of the more common μ quantum defects because the former avoid unphysical states with ℓ ≥ n. The quantum defects are represented on a grid of R values extending from R = 1 a.u. to 5 a.u. with a step size of 0.5 a.u. (0.1 a.u. for the 1Σ_g^+ symmetry). The energy dependence is represented by a Taylor expansion to second-order

\[ \eta(E, R) = \eta(E_0, R) + \frac{\partial \eta(E, R)}{\partial E} (E - E_0) + \frac{1}{2} \frac{\partial^2 \eta(E, R)}{\partial E^2} (E - E_0)^2 \]

(5.2)

5.3.2 Improvement of Accuracy

The adiabatic potential energy curves of the lowest Rydberg states of H_2 have been computed by traditional ab initio quantum chemical methods to spectroscopic accuracy by Wolniewicz and coworkers [199,200,210–213]. The R-matrix calculations described above are less accurate but they provide information on the close-coupling physics at energies near or above the ionization threshold, which cannot be obtained by the traditional quantum chemical calculations of Wolniewicz. However, the latter can be used to improve the accuracy of the R-matrix calculations by a slight adjustment of the η(E, R) functions. The analysis of the gerade states requires a quantum defect matrix with elements \( \eta_{\alpha\beta}(R) \) where \( \alpha\beta = ss^{1}\Sigma_g^+, ss^{3}\Sigma_g^+, dd^{1}\Sigma_g^+, dd^{3}\Sigma_g^+, dd^{3}\Pi_g, dd^{3}\Gamma_g, dd^{1}\Delta_g, dd^{3}\Delta_g \) represent the relevant s and d channels and \( \alpha\beta = sd^{1}\Sigma_g^+, sd^{3}\Sigma_g^+ \) stand for the sd interactions.

The channels corresponding to Π or Δ symmetry thus give rise to a simple single-channel problem, whereas both s and d channels and their interactions appear in Σ symmetry. The adiabatic potential energy curves of the lowest Rydberg states are obtained by solving the secular equation [13]

\[ \det \left| \frac{\tan (\pi v_k)}{A(E, \ell_k)} \delta_{kk'} + K_{kk'}(E) \right| = 0 \]

(5.3)

at each value of R. \( v_k \) is the effective principal quantum number \( v_k = (-\epsilon_k)^{-1/2} \) defined with respect to the 1sσ ionization threshold and \( A(E, \ell_k) \) is Ham’s scaling function defined in Eq. (2.31) of Ref. [13]. The quantum defect functions of Δ symmetry were adjusted to reproduce the adiabatic potential curves of the 3dδ^{1}\Delta_g (J), 4dδ^{1}\Delta_g (S), 3dδ^{3}\Delta_g (j) and 4dδ^{3}\Delta_g (s) states reported in Refs. [210,211] and those of Π symmetry to reproduce the 3dπ^{1}\Pi_g (l), 4dπ^{1}\Pi_g (R), 3dπ^{3}\Pi_g (i) and 4dπ^{3}\Pi_g (r) states [210]. The procedure involved the adjustment of the coefficients η(R) and η'(R) of the Taylor series (Eq. (5.2)) at several values of R. The coefficients η(R) were found to change by less than 0.015 in the range 1 a.u. < R < 3 a.u. Finally, cubic
polynomials (splines) were fitted to the optimized coefficients and used as input for the dynamical calculations.

The adjustment procedure of the quantum defect functions of $^1\Sigma_g^+$ symmetry was somewhat more delicate, because of the strong interactions of the 1sσ channels with the doubly excited channels. The situation in $^3\Sigma_g^+$ symmetry is still relatively simple because the lowest doubly excited configuration (2pσ)$^2$ is forbidden by the Pauli principle. In this symmetry, ab initio potential energy curves are available for the 2sσ $^3\Sigma_g^+$ (a), 3dσ $^3\Sigma_g^+$ (g) and 3sσ $^3\Sigma_g^+$ (h) states [213,214]. The g and h states have an avoided crossing around $R \approx 1.94$ a.u. which can in principle be used to extract accurate sd interaction elements, but the energy dependence complicates the determination of unambiguous parameters in the vicinity of the ionization threshold. In the fitting procedure of the 2×2 quantum defect matrices of $^3\Sigma_g^+$ electronic symmetry, the sd off-diagonal quantum defect was held fixed at the value determined from the width of the avoided crossings between the g and h states (using the E and R dependence provided by the R-matrix calculations) and only the diagonal quantum defects were adjusted. At $R = 2.0$ a.u., the coefficients $\eta_d$, $\eta_s$ and $\eta_d$ increased by 0.014, 0.011 and 0.03 quantum defect units, respectively. These surprisingly large changes were subsequently found to be in conflict with the observed (hyperfine) level positions, so that the unmodified quantum defect functions from the R-matrix calculations had to be used.

The most complicated situation arises in the $^1\Sigma_g^+$ electronic symmetry, where the diabatic curve corresponding to the doubly excited configuration (2pσ)$^2$ crosses all members of the series associated with the 1sσ ionization threshold and gives rise to the well-known double-minimum potential of the EF, GK and HH states. Fortunately, the potential energy curves of all five lowest members of this symmetry are available in the literature [199,200,212] which increases the physical meaning of the determined parameters. The five states are the 2sσ $^1\Sigma_g^+$ (EF), 3dσ $^1\Sigma_g^+$ (GK), 3sσ $^1\Sigma_g^+$ (HH), 4dσ $^1\Sigma_g^+$ (P) and 4sσ $^1\Sigma_g^+$ (O) states. All adiabatic potential energy curves could be reproduced quantitatively after a slight adjustment of the quantum defect parameters with the exception of the outer well of the EF state for $R > 3.2$ a.u. The difficulty is associated with the fact that this portion of the curve lies at an effective quantum number $\nu < 2$. This unusual situation, which cannot be handled by the methods and functions of MQDT, arises because this portion of the curve is associated with the (2pσ)$^2$ configuration. In particular, the Coulomb functions associated with the $\eta$ quantum defect have poles for $\nu \leq 2$. Since the lowest Rydberg states are irrelevant in the present study and the region of interest is located around the equilibrium internuclear distance of the cation ($R \approx 2$ a.u.) this deficiency does not have any consequences for the calculations. The changes in the coefficients $\eta(R)$ amounted to less than +0.012 for the s quantum defect and +0.008 for the d quantum defect in the region $1.4 < R < 2.6$ a.u. and the sd off-diagonal quantum defect function needed no
adjustment. The quantum defect functions obtained from the R-matrix calculations are compared to those resulting from the fitting procedure in Fig. 5.1. The large value of the off-diagonal quantum defect around $R = 3$ a.u. results from the interactions between potential curves associated with singly and doubly excited configurations. The strong interactions between $n\sigma/n\sigma (1\sigma\sigma)$ and $np\sigma(2p\sigma)$ channels are reflected in a large sd interaction because of the exclusion of the channels associated with the $2p\sigma$ core.

5.3.3 Multichannel Quantum Defect Theory

The quantum defect functions $\eta(E,R)$, the determination of which has been described in Sections 5.3.1 and 5.3.2 represent the purely electronic interactions for a fixed value of the internuclear distance. They are characterized by the quantum numbers appropriate to Hund’s case (b), i.e., $\Lambda$ defined above, $S$ the total spin angular momentum quantum number and $\Omega$ the quantum number associated with the projection of the total electronic angular momentum on the internuclear axis. These quantities are defined in the molecular frame and are usually referred to as "body-frame" quantum defects. In order to compute observable properties of the molecular wavefunctions, the nuclear degrees of freedom, and in the present case also the spin degrees of free-
dom, must be taken into account. This is achieved by transforming the body-frame quantum defect functions by means of the spin-rovibronic frame transformation

\[ C_{ii'} = \int X_{v+}'^{(N^+)}(R) \sum_{S\Lambda \Omega} \langle \langle i^{(sre)} | \alpha^{(sre)} \rangle \rangle 
\times \cos \left[ \pi \eta_{v',l',p'}^{(sre)}(E, R) \right] \langle \alpha^{(sre)} | i^{(sre)} \rangle 
\times X_{v+}'^{(N^+)}(R) dR, \]

and

\[ S_{ii'} = \int X_{v+}'^{(N^+)}(R) \sum_{S\Lambda \Omega} \langle \langle i^{(sre)} | \alpha^{(sre)} \rangle \rangle 
\times \sin \left[ \pi \eta_{v',l',p'}^{(sre)}(E, R) \right] \langle \alpha^{(sre)} | i^{(sre)} \rangle 
\times X_{v+}'^{(N^+)}(R) dR, \]

where the dependence of the ion core vibrational wavefunctions \( X_{v+}'^{(N^+)}(R) \) on \( G^+ \) and \( F^+ \) has been neglected (the corresponding hyperfine structure of the ion thresholds \( E_i^+ \) has of course been taken into account). The frame transformation elements \( \langle \alpha^{(sre)} | i^{(sre)} \rangle \) have been determined as described in Refs. [110,113]. The superscript \( (sre) \) stands for spin, rotation and electronic angular momenta. The body-frame quantum-defect functions \( \eta_{v',l',p'}^{(sre)}(E, R) \) were assumed to be unaffected by interactions with the nuclear spin, which is justified by the weakness of hyperfine interactions compared to electrostatic interactions. The quantization condition for bound Rydberg levels is obtained by requiring that the wavefunction vanishes for an infinite distance \( r \) between the ion core and the Rydberg electron. This condition is expressed by the equation

\[ \sum_{i'} \left[ \sin(\pi v_i) C_{ii'} + \sqrt{A(v_i)} \cos(\pi v_i) S_{ii'} \right] B_{i'} = 0, \]

where the index \( i \) designates a Rydberg channel attached to an ionic state of energy \( E_i^+ \) and

\[ v_i(E) = \left[ \frac{\text{Ry}_M}{E_i^+ - E} \right]^{1/2} \]

represents the effective principal quantum number as a function of the total energy \( E \). \( A(v_i) \) is Ham's scaling function and \( \text{Ry}_M = 109707.42 \text{ cm}^{-1} \) is the mass-corrected Rydberg constant for \( \text{H}_2 \).

The oscillator strength for photoionization to the final bound state with total an-
5.4. Results and Discussion

5.4.1 Overview spectra and assignment of interlopers

Fig. 5.2 displays the overview spectra of the gerade Rydberg states of ortho H\(_2\) in the vicinity of the \(X^+ v^+ = 0, N^+ = 1\) and \(N^+ = 3\) ionization thresholds.

The spectra were recorded following two-photon resonant excitation via the \(v = 0, J = 0\) level of the B \(1\Sigma^+_u^+\) state. The series accessible in photoexcitation from this level are the \(n s l_1, n d l_1\) and \(n d 3l_1\) series. The middle trace represent the \(H_2^+\) signal that results either from the direct ionization from the B(\(v = 0, J = 0\)) state, the autoionization of Rydberg levels located above the \(v^+ = 0, N^+ = 1\) ground state of ortho \(H_2^+\) or the delayed pulsed-field ionization induced by the 332 V/cm field. Only long-lived Rydberg states survive the delay of 200 ns between photoexcitation and field-ionization. Consequently, all structure observed below the \(v^+ = 0, N^+ = 1\) threshold indicated by a vertical arrow corresponds to non-predissociative Rydberg levels. The lower trace corresponds to the \(H^+\) signal that arises from ionization, during the laser pulses, of \(H(n = 2)\) fragments formed by predissociation into the continuum of the EF state. This predissociation results from the interaction of the gerade Rydberg states
Chapter 5. Spin-rovibronic interactions in the gerade Rydberg states of ortho H$_2$  

H$_2$^+ $2\Sigma_g^+$, N$^+=1$, v$^+=0$

N$^+=3$, v$^+=0$

Figure 5.2: Photoionization and pulsed-field-ionization spectrum recorded in the region of the X $^2\Sigma_g^+$ (v$^+=0$, N$^+=1$ and 3) levels of ortho H$_2^+$ following excitation via the B $^1\Sigma_u^+$ (v = 0, J = 0) state. The middle trace corresponds to the spectrum detected in the H$_2^+$ mass channel and the lower trace to the spectrum recorded in the H$^+$ channel. The top trace represents an MQDT prediction of the spectra using the quantum defect functions determined in Section 5.3.2. The main series converging on the v$^+=0$, N$^+=1$ and 3 thresholds are highlighted and the vibrationally excited interlopers are assigned on the basis of the MQDT calculation. The vertical dashed lines mark the positions of the N$^+=1$ and N$^+=3$ ionization thresholds.

with the repulsive $(2p\sigma_u)^2 \Sigma_g^+$ configuration which crosses the ionic and high Rydberg potential curves around $R = 2.8$ a.u. Whereas the $v^+=0$ channel is barely affected by this interaction, Rydberg levels associated with a vibrationally excited core level predissociate rapidly.

Rydberg series converging on the two lowest rotational levels N$^+=1$ and N$^+=3$ of ortho H$_2^+$ are easily recognized in Fig. 5.2. However, the intensity distribution in the spectrum is very irregular and is dominated by several intense spectral structures that do not belong to the main series. Below the N$^+=1$ threshold, the most striking observation is the absence of the members n < 36 in the H$_2^+$ channel and their appearance in the H$^+$ channel. The region in which this change takes place coincides with a perturbation of the Rydberg series which is observed in the H$^+$ channel. This
perturbation must result from a low-\(n\) \((v^+ > 0)\) interloper which causes the fast predissociation (within 10 ns) of the members of the \(n d\) \(1\) Rydberg series lying at lower energies. In the range \(n = 36\) to \(n = 47\) the transitions to the \(n d\) \(1\) levels are weak in the \(H_2^+\) channel, presumably also because of predissociation, but the process is not fast enough to produce \(H(n = 2)\) fragments within the duration of the laser pulse. Above the \(N^+ = 1\) ionization limit, the intensity distribution is entirely dominated by the vibrational interlopers. Four such interlopers are observed between the \(N^+ = 1\) and \(N^+ = 3\) threshold. In the vicinity of these interlopers, the gerade Rydberg series converging on the \(N^+ = 3\) ionic level, which is not observable otherwise, gains intensity. This effect is particularly pronounced around 124640 cm\(^{-1}\) where the \(n d\) \(3\) series appears with an asymmetric intensity distribution reminiscent of a Fano profile. Until now, no conclusive assignments of all resonances in this region has been reported.

The quantum defect function determined \textit{ab initio} were accurate enough to provide the first unambiguous assignment of all interlopers located in the vicinity of the \(v^+ = 0\) thresholds. The top trace of Fig. 5.2 represents the result of an MQDT calculation based on these functions and on transition moments reported by Jungen [215]. This calculation did not include spins and disregarded predissociation, and primarily aimed at predicting the discrete positions of the interlopers. This was accomplished by artificially closing the \(v^+ = 0, N^+ = 1\) channels above the \(N^+ = 1\) threshold.

The five interlopers observed experimentally at 124383 cm\(^{-1}\), 124430 cm\(^{-1}\), 124538 cm\(^{-1}\), 124640 cm\(^{-1}\) and 124750 cm\(^{-1}\) are assigned to the \(7d\) \(1\) \((v^+ = 1)\), \(7s\) \(1\) \((v^+ = 1)\), \(5d\) \(3\) \((v^+ = 2)\), \(7d\) \(3\) \((v^+ = 1)\) and \(3s\) \(1\Sigma^+_g (N = 1, v = 7)\) Rydberg levels, respectively. Whereas the lower four interlopers belong to series converging on well-defined ionic vibrational levels, the highest interloper is a high vibrational level of the HH state (see also Ref. [216]).

The sudden increase of predissociation below \(n = 40\) discussed above can thus be attributed to the interaction with the \(7d\) \(1\) \((v^+ = 1)\) interloper. The calculation reproduced the asymmetric enhancement of the \(n d\) \(1\) Rydberg levels on the lower wave number side of the resonance. The asymmetric intensity envelope of the \(n d\) \(3\) series around the \(7d\) \(3\) \((v^+ = 1)\) interloper noted above is qualitatively predicted by the MQDT calculations and represents the discrete analog of asymmetric autoionization lineshapes. It arises from a ratio of oscillator strengths for transitions into the interloper and series channels that departs from unity. The \(5d\) \(3\) \((v^+ = 2)\) state is also predissociative and causes the predissociation of the neighboring \(22d\) \(3\) level. Whereas the positions of the three lowest interlopers are predicted quantitatively, the calculated and experimental positions of the upper two resonances \(7d\) \(3\) \((v^+ = 1)\) and \(3s\) \(1\Sigma^+_g (v = 7, J = 1)\) differ slightly.

These results suggest that the \textit{ab initio} quantum defect functions, though sufficiently accurate to enable the assignment of the interlopers, still need slight adjust-
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Figure 5.3: Photoionization spectrum recorded in the region between the X $^2\Sigma_+^+$ ($v^+=0, N^+=1$ and 3) levels of ortho $\text{H}_2$ following excitation via the $B ^1\Sigma_+^+$ ($v=0, J=0$) state. The middle trace corresponds to the spectrum detected in the $\text{H}_2^+$ mass channel and the lower trace to the spectrum recorded in the $\text{H}^+$ channel (as in Fig. 5.2). The top trace represents an MQDT prediction of the autoionizing resonances using the quantum defect functions determined in Section 5.3.2 and $R$-independent transition moments.

Most of the predicted linewidths are in satisfactory agreement with the experimental data to be reached. The top trace of Fig. 5.3 shows the results of an MQDT calculation including the ionization continua after such an adjustment. The required modification of the quantum defect functions turned out to be minimal ($-0.004$ for $\eta_{dd}(^1\Sigma_g^+)$ and $+0.005$ for $\eta_{dd}(^1\Pi_g)$). The lower two traces of Fig. 5.3 are the same as those displayed in Fig. 5.2. The comparison between the calculated and experimental spectra provides interesting information on the decay of Rydberg states lying in the continuum.

Most of the predicted linewidths are in satisfactory agreement with the experiment, with the exception of the linewidths of the interlopers which are systematically underestimated. The calculations predict a symmetric autoionization width of less than $0.3 \text{ cm}^{-1}$ for this level whereas the observed resonance is asymmetric and has a width of $\sim 2 \text{ cm}^{-1}$. We attribute this discrepancy to predissociation that is not included in the calculations, a conclusion that is confirmed by the observation of a signal in the $\text{H}(n = 2)$ channel in the bottom trace of Fig. 5.3. The calculated autoionization widths of the other interlopers observed in Fig. 5.3 ($7s1_1 (v^+=1)$ and
7d31 (v^+ = 1)) are about ten times larger than for the 5d31 (v^+ = 2) resonance. This observation reflects the fact that autoionization processes with \( \Delta v^+ = -2 \) are less favorable than those with \( \Delta v^+ = -1 \) [97].

### 5.4.2 High-resolution spectra and hyperfine structure

**Overview**

Hyperfine-resolved pulsed-field-ionization spectra of the bound Rydberg states of ortho H\(_2\) lying just below the \( ^2\Sigma^+_g (v^+ = 0, N^+ = 1) \) ionization threshold have been recorded following two-photon resonant excitation via the B\((v = 2, J = 0 \text{ and } 2)\) states. An overview of the recorded spectra is given in Figs. 5.4 and 5.5. In each panel of these figures, the top trace represents the spectrum recorded via the B\((v = 2, J = 2)\) level and the lower trace was recorded via the B\((v = 2, J = 0)\) level.

The linewidths in the spectra amount to \( \sim 0.007 \text{ cm}^{-1} \) which is sufficiently narrow to resolve the fine and hyperfine structure. Excitation via the \( J = 0 \) level of the B state gives access to the hyperfine components of the ndl\(_1\), nd3\(_1\) and ns1\(_1\) levels, whereas excitation via the \( J = 2 \) level gives access to the hyperfine components of the ndl\(_1\), ndl\(_2\), ndl\(_3\), ns1\(_1\), nd3\(_1\), nd3\(_2\) and nd3\(_3\) levels. The hyperfine structure of the H\(_2^+\) ion in the X \( ^2\Sigma^+_g (v^+ = 0, N^+ = 1) \) level is dominated by the interval between its two \( G^+ (G^+ = I + S^+) \) levels which amounts to 0.042 cm\(^{-1}\) [110,217]. In the region \( n = 50 - 57 \) shown in Fig. 5.5, the spectra all have a similar appearance and consist of a doublet of almost equally intense lines that are spaced by \( \sim 0.04 \text{ cm}^{-1} \) which almost exactly corresponds to the main hyperfine structure interval of the ion. The transitions observed via the B\((v = 2, J = 0)\) level can thus be assigned to two hyperfine components of the ndl\(_1\) series and those observed via the B\((v = 2, J = 2)\) level in Fig. 5.5 correspond to the hyperfine components of the ndl\(_3\) levels. At lower values of the principal quantum number, most transitions still appear as doublets of lines separated by \( \sim 0.04 \text{ cm}^{-1} \) but additional isolated lines are also observed and, overall, the spectral structures are more irregular than above \( n = 50 \). The ns1\(_1\) series is observed between \( n = 43 \) and 45 in the spectra recorded through the \( J = 2 \) intermediate level. In this region the structure of the ndl\(_1\) series starts deviating from the doublet structure observed at higher \( n \) values. Both observations are related to the interactions with the 7dl\(_1\)(v\(^+\) = 1) interloper state as will be discussed in Section 5.4.2. In the region between \( n = 46 \) and 49, transitions to Rydberg levels associated with rotationally or vibrationally excited core levels are observed such as the 18s3\(_3\) and 18d3\(_2\) and the 7dl\(_2\) (v\(^+\) = 1) states. The presence of these states complicate the spectral assignments which can only be made unambiguously by comparison with MQDT calculations including spins. The transition wave numbers are listed in Table B.3.
Figure 5.4: Hyperfine-resolved pulsed-field-ionization spectra of the members $n = 42 - 49$ of the Rydberg series converging on the $X^2\Sigma_u^+ (v^+ = 0, N^+ = 1)$ level of ortho $H_2$. The spectra have been recorded following excitation via the $B^1\Sigma_u^+ (v = 2, J = 0$ and 2) states.
Figure 5.5: Hyperfine-resolved pulsed-field-ionization spectra of the members \( n = 50 - 57 \) of the Rydberg series converging on the \( X^2\Sigma_u^+ (v^+ = 0, N^+ = 1) \) level of ortho \( H_2^+ \). The spectra have been recorded following excitation via the \( B^1\Sigma_u^+ (v = 2, J = 0 \text{ and } 2) \) states.
MQDT calculations including all spins and angular momentum coupling cases

The analysis of the spectra shown in Figs. 5.4 and 5.5 requires MQDT calculations that include electronic and nuclear spins. Calculations of this kind were performed as described in Section 5.3.3 using the singlet and triplet quantum defect functions determined in Sections 5.3.1 and 5.3.2 and adjusted to reproduce the survey spectra as discussed in Section 5.3.2. These calculations enabled the assignment of all transitions observed in Figs. 5.4 and 5.5. However, in order to achieve a quantitative agreement with the high-resolution spectra, the quantum defect functions were subjected to further minor adjustments which finally resulted in a mean deviation between observed and calculated transitions of 0.0075 cm\(^{-1}\). The final set of quantum defect parameters is summarized in the last column of Table 5.1 and the remaining deviations between measured and calculated positions are listed in Table B.3.

\[
\begin{array}{ccc}
\hline
\text{R-matrix calc.} & \text{adj. to ab initio curves} & \text{adj. to experiment} \\
\hline
\eta_{\ell\ell'} & \eta_{ss} & \eta_{dd} & \eta_{sd} \\
(R = 2.0 \text{ a.u.}) & & & \\
^1\Sigma_g^+ & -0.1058 & -0.0962 & -0.0962 \\
^3\Sigma_g^+ & 0.0335 & 0.0447 & 0.0335 \\
^1\Pi_g & 0.0576 & 0.0524 & 0.0724 \\
^1\Delta_g & 0.0362 & 0.0296 & 0.0346 \\
^3\Sigma_g^+ & -0.0242 & -0.0149 & -0.0149 \\
^3\Pi_g & 0.0613 & 0.0923 & 0.0560 \\
^3\Delta_g & 0.0374 & 0.0426 & 0.0426 \\
^1\Sigma_g^+ & 0.0119 & 0.0141 & 0.0141 \\
^3\Sigma_g^+ & -0.0156 & -0.0011 & -0.0156 \\
\hline
\end{array}
\]

Table 5.1: Quantum defects determined from ab initio R-matrix calculations (first column), their values after adjustment to the potential energy curves of Wolniewicz (see text) and after adjustment to the experimental spectra.

The MQDT calculations were not only useful to reach unambiguous spectral assignments but also facilitated the analysis of the evolution of the hyperfine structure with increasing \(n\) values. The hyperfine structure of the gerade (s and d) Rydberg states of ortho-H\(_2\) and its evolution with increasing principal quantum numbers is best understood in terms of the correlation diagram displayed in Fig. 5.6. The figure shows the calculated positions of the \(F = 2\) hyperfine components of all s and d Rydberg levels converging on the \(^2\Sigma_g^+ (\nu^+ = 0, N^+ = 1)\) level of H\(_2^+\) at \(n = 30, 40, 50, 60\) and 70. The MQDT calculations have used the quantum defect functions obtained
5.4. Results and Discussion

Figure 5.6: Correlation diagram representing the level positions of the hyperfine components of the \( \text{n}d_{1,2,3} \) and \( \text{n}s_{1,1} \) (triplet component) at selected values of the principal quantum number \( n \). The vertical axis corresponds to the fractional part of the effective quantum number defined in Eq. (5.7) with respect to the center of gravity of the hyperfine structure of the \( ^2\Sigma_g^+ \) \((v^+ = 0, N^+ = 1)\) level. The \( G = 1 \) components of the \( \text{n}d_{1,2,3} \) levels are connected by dotted (\( N = 1 \)), dashed (\( N = 3 \)) and dotted-dashed (\( N = 2 \)) lines to guide the eye.

after adjustment to the experimental spectra and were performed under exclusion of the vibrationally excited interlopers, i.e., using a vibrational basis of the cation restricted to \( v^+ = 0 \). This choice eliminates accidental perturbations that originate from vibrational interactions and allows a direct understanding of the hyperfine structure and its evolution over the range of interest.

The vertical scale of Fig. 5.6 corresponds to the fractional part of the effective quantum number defined in Eq. (5.7) with respect to the center of gravity of the \( N^+ = 1 \) ionization threshold. The difference between the singlet and triplet quantum defects of the \( s \) series amounts to \( \approx 0.12 \), which implies that the singlet-triplet interval is larger than the ionic hyperfine structure below \( n \approx 86 \). Consequently, the hyperfine interactions are too weak to induce a significant mixing of singlet and triplet character of the \( s \) Rydberg levels observed experimentally. The triplet \( s \) Rydberg levels are thus not observable in the experiments and \( S \) represents a good quantum number for the \( s \) levels in the \( n \) range covered by Fig. 5.6.

In the \( d \) series, the exchange interaction is much smaller than in the \( s \) series, and already becomes similar to the ionic hyperfine splitting at \( n = 30 \). As shown in more detail in the next chapter (see also Ref. [112]), a quantum number \( G \) corresponding to the total spin angular momentum \( (G = I + S) \) can be defined in this case (and also for the \( s \) levels), which remains good until the relatively weak spin-rotation interaction
in the ion core becomes important [112]. The d levels are therefore labeled by their \( G \) value in Fig. 5.6. The good quantum numbers that are used to construct the correlation diagram are thus \( N^+, N \) and \( G \) for the \( nd \) levels and \( N^+, N, S \) and \( G \) for the \( ns \) levels. The conservation of \( G \) actually implies the conservation of \( N \) (see chapter 6).

The angular momentum coupling case appropriate for the \( s \) levels for which the exchange interaction dominates over the hyperfine interactions is denoted \( d_{\beta S} \) because the total nuclear spin \( I \) is not coupled to the internuclear axis (hence "\( \beta \)" in analogy to "\( b \)") but to the total electronic spin \( S \). The coupling case \( d_{\beta S} \) is defined by [112] (see also chapter 6)

\[
\begin{align*}
S &= S^+ + s \\
G &= I + S \\
F &= N^+ G.
\end{align*}
\]

In this coupling case, the level structure can be characterized by the total electron spin quantum number \( S = 0 \) or \( 1 \) with a \( G \) substructure \( G = 1 \) and \( G = 0, 1, 2 \) respectively. This situation clearly applies to the \( s_{11} \) levels over the complete \( n \)-range displayed in Fig. 5.6. The \( s_{11} \) levels found in the range represented in Fig. 5.6 belong to the triplet component and correspond to \( G = 1 \) and \( G = 2 \). A \( G = 0 \) level is also predicted, but it does not appear in Fig. 5.6 because it only has a \( F = 1 \) component. The \( G = 2 \) level is seen to be shifted to higher effective quantum numbers with increasing \( n \) and the \( G = 1 \) level to lower effective quantum numbers. The singlet component of \( s_{11} \) lies at an effective quantum number of \( \approx 0.1 \) and is also shifted to higher effective quantum numbers (not shown).

With increasing values of the principal quantum number in the \( nd_{1N} \) series, the hyperfine interactions in the core begin to compete with the exchange interaction which results in a gradual transition to the case \( d_{\beta S^+} \) which is defined by the angular momentum coupling scheme [112] (see also chapter 6)

\[
\begin{align*}
G^+ &= I + S^+ \\
F_s &= N^+ G^+ \\
F &= F_s + s.
\end{align*}
\]

The transition from case \( d_{\beta S} \) to case \( d_{\beta S^+} \) is characterized by a reordering of the \( G \) hyperfine components from a pattern of triplet levels with \( G = 0, 1 \) and \( 2 \) and of singlet levels with \( G = 1 \) to a pattern of \( G^+ = 1/2 \) levels with \( G = 0 \) and \( 1 \) and \( G^+ = 3/2 \) levels with \( G = 1, 2 \), the two groups of levels being separated by the main hyperfine interval in the cation, i.e., \( \approx 0.042 \text{ cm}^{-1} \).

At \( n = 30 \), the splittings between the \( G = 1 \) and \( G = 1, 2 \) groups of levels of the
5.4. Results and Discussion

Figure 5.7: Pulsed-field-ionization spectra recorded in the region of the $50d_{1/2}$ levels of ortho $H_2$ following excitation via the $B^1Σ_u^+$ ($v = 2, J = 0$ and 2) states (bottom and top trace, respectively) and positions and intensities predicted by MQDT calculations (stick spectra). The lower trace shows the two hyperfine components of the $50d_{1/2}$ level and the upper trace the two hyperfine components of the $50d_{1/3}$ level. The transitions to the components of the $50d_{1/2}$ levels appear as weak lines in the top trace and in the calculated spectrum.

High $n$ Rydberg states

The $n\ell_1\ell_2\ell_3$ series are largely unperturbed in the range $n = 50 - 57$ which also corresponds to the range investigated previously by millimeter wave spectroscopy [110, 123, 124]. Figures 5.7 and 5.8 compare the spectra recorded at $n = 50$ and 56, respectively, following excitation via $J = 2$ (top trace) and $J = 0$ (lower trace) with MQDT calculations.

Figure 5.8 displays the spectra recorded in the region of $n = 57$. All six hyperfine components of the $n\ell_1\ell_2\ell_3$ states are observed in the spectrum recorded via $J = 2$, but only the two hyperfine components of the $57d_{1/2}$ level appear in the spectrum.
Figure 5.8: Pulsed-field-ionization spectra recorded in the region of the $57d_{1N}$ levels of ortho $H_2$ following excitation via the $B^1Σ_u^+$ ($ν = 2, J = 0$ and 2) states (bottom and top trace, respectively) and positions and intensities predicted by MQDT calculations (stick spectra). The lower trace shows the two hyperfine components of the $57d_{11}$ level and the upper trace the two hyperfine components of each of the $57d_{13}$ and $57d_{12}$ levels.

recorded via $J = 0$. The simple structure which corresponds to excitation of the $nd_{11}$ and $nd_{13}$ doublets for the spectra recorded via $J = 0$ and 2, respectively, is preserved toward higher principal quantum numbers, but additional weak lines gradually appear in the spectra.

Figure 5.9 displays the spectra recorded via the $J = 0$ intermediate level in the region of $n = 58 – 61$. The dominant features in the spectra are the two hyperfine components of the $nd_{11}$ levels as observed at lower principal quantum numbers, but a weak pair of lines is observed to the high wave number side of the main transitions. The separation between the main lines and these additional transitions decreases and the intensity of the weak lines increases with increasing principal quantum number. By comparison with the MQDT calculations shown as stick spectra in Fig. 5.9, the weaker transitions can be assigned to the hyperfine components of the $nd_{12}$ levels. Although the effect is clearly recognizable in the calculations, these slightly overestimate the interval between the closest pair of lines and underestimate the intensity of the $nd_{12}$ levels.

The excitation of the $nd_{12}$ levels from the $J = 0$ intermediate state is forbidden
5.4. Results and Discussion

in the absence of spins. The level structure of the \( n d l_N \) states around \( n = 60 \) can be described in Hund’s case \( d^\text{+} \) defined in Eq. (5.10). In this range, the coupling of the Rydberg electron spin \( \mathbf{s} \) with the total core spin \( \mathbf{G}^+ \) is larger than the interaction of the latter with the rotational angular momentum \( \mathbf{N}^+ \), and therefore \( G \) is a good quantum number. Consequently, \( N \) is also a good quantum number and the optical selection rules on \( \Delta N \) are expected to apply with the additional condition \( \Delta G = 0 \) (see also chapter 6). In the situation where the interval between two series differing in \( N \) becomes comparable to the spin-rotation interaction in the ion, the latter leads to a mixing of the levels and neither \( G \) nor \( N \) remain good quantum numbers. This situation is observed in Fig. 5.9, where the \( ndl_2 \) series gradually gains intensity as it moves closer to the \( ndl_1 \) series, the lower hyperfine component being most strongly affected.

Effects of vibrational interactions on the hyperfine structure and predissociation

The level structure at lower principal quantum numbers is complicated by the perturbations induced by rotationally and/or vibrationally excited interlopers. On the basis of the MQDT calculations, the lines observed in the region corresponding to
Figure 5.10: Pulsed-field-ionization spectra recorded in the region of the $43d_l$ and $43s_1$ levels of ortho $H_2$ following excitation via the $B^1\Sigma_u^+$ ($\nu = 2, J = 0$ and 2) states (top and middle traces, respectively). The positions and intensities predicted by MQDT calculations are displayed as stick spectra. The lowest stick spectrum represents the results of an MQDT calculation excluding vibrationally excited levels of $H_2^+$ and assuming that the excitation takes place via the $B^1\Sigma_u^+$ ($\nu = 2, J = 0$) state.

$n = 46, 47$ and $49$ have been assigned to transitions to the rotationally excited levels $18d_N$ and $18s_3$ and to the vibrationally excited level $7d_2$ ($\nu^+ = 1$). The transition to the $18d_1$ level via the $J = 0$ level is weak which is in accordance with the observation made in Section 5.4.1 (see Fig. 5.2), that the corresponding series only gains intensity if it interacts with vibrationally excited interlopers.

Figure 5.10 shows the photoionization spectrum in the region corresponding to $n = 43$. The top trace was recorded via the $B(\nu = 2, J = 2)$ level and the lowest trace via the $B(\nu = 2, J = 0)$ level. The inverted trace corresponds to the $H^+$ mass channel and was recorded simultaneously with the top trace.

The experimental spectra are compared to MQDT calculations (stick spectra). The weak line at highest wave numbers corresponds to the transition to the $43s_1$ level and the group of lines at lower wave numbers to transitions to the hyperfine components of the $43d_N$ levels. In this group, the line pair at highest wave numbers corresponds to the $G^+ = 1/2$ and $G^+ = 3/2$ levels of the $nd_2$ state. At lower wave numbers, the MQDT calculations of the spectrum recorded via the $J = 2$ level predict a pair of intense transitions corresponding to the $nd_3$ levels but these transitions
are weak in the H$_2^+$ mass channel. The two lines however appear as predissociation signal in the H$^+$ channel. The three lowest lines are common to the spectra recorded via both intermediate levels and must therefore correspond to levels with $N = 1$. However, instead of the expected pair of $G^+$ components, three lines are observed. The MQDT calculation also predicts three lines with similar intensity ratios, but the predicted transition wave numbers differ slightly from the observed ones. An MQDT calculation excluding vibrationally excited channels (lowest stick spectrum) only predicts a pair of transitions spaced by $-0.042$ cm$^{-1}$ for the 43d$_{11}$ levels, just as for the other 43d$_{1N}$ states. The hyperfine structure of the 43d$_{11}$ level is thus perturbed by a vibrational interaction, most likely with the 7d$_{11}$ ($v^+ = 1$) state lying at 124380 cm$^{-1}$. In the calculations including vibrationally excited channels, the MQDT wavefunctions of all three components contain a significant amount of the $s^3\Sigma$ channel in the calculations including vibrationally excited channels. The interaction with the vibrational interloper thus appears to enhance the sd interaction leading to an admixture of s$^3\Sigma^+$ character to the hyperfine components of the 43d$_{11}$ levels and the observation of three lines instead of the expected $G^+$ doublet.

The situation just described at $n = 43$ applies to the whole range of Rydberg states between $n = 39$ and 45. Three lines are observed at the position of the transitions to the nd$_{11}$ levels from $n = 39$ to $n = 43$. The lowest of the three lines is weak at $n = 44$ and has almost disappeared at $n = 45$. This trend is reproduced by the MQDT calculations, although the intensity of the lowest line tends to be overestimated. These observations suggest that the perturbed hyperfine structure results from the interaction with a vibrational interloper lying below the observed range because the perturbation becomes less important toward higher wave numbers. A similar situation applies to the predissociation of the nd$_{13}$ levels. These levels are found to predissociate over the range $n = 39 - 45$, but the strength of the H$^+$ signal diminishes from $n = 39$ to $n = 44$ and becomes negligible at $n = 45$. This trend suggests that the predissociation results from the interaction with a vibrational interloper that lies below the investigated range. The most likely candidate is the 7d$_{13}$ ($v^+ = 1$) level that is predicted at 124388 cm$^{-1}$ by our calculations.

5.5 Conclusions

High-resolution laser spectroscopic experiments have enabled, for the first time, the resolution of the hyperfine structure of the gerade Rydberg states of H$_2$ located below the X$^2\Sigma_g^+$ ($v^+ = 0, N^+ = 1$) ground state of H$_2^+$ over a wide range of $n$ values. Variational R-matrix calculations have been used to predict quantum defect functions for the gerade electronic symmetry of H$_2$. In these calculations, the channels corresponding to doubly excited configurations have been closed, so that a set of
quantum defect functions for the s and d channels associated with the $^2\Sigma_g^+$ state of $H_2^+$ could be derived which effectively contains the interactions with the doubly excited states. The accuracy of the quantum defect functions has been improved by adjusting them to reproduce the adiabatic potential energy curves of the lowest Rydberg states of $H_2$ [199]. These body-frame quantum defects were used and further refined in MQDT calculations including vibrational and rotational degrees of freedom to predict the experimental spectra with near quantitative accuracy. These calculations permitted the first unambiguous assignment of all observed interloper states in the spectrum of the gerade states of molecular hydrogen near the lowest ionization thresholds. The comparison of experimental results with the results of MQDT calculations provided insights into nuclear and electron spin effects and into the angular momentum coupling hierarchy in molecular high Rydberg states.

The fine and hyperfine structure of the series converging on the $X^2\Sigma_g^+ (\nu^+ = 0, N^+ = 1)$ level of $H_2^+$ has been resolved. The MQDT calculations have been extended to include all spins and were used to assign the observed structures. In the investigated region ($n = 39 - 62$), the s series are still well described by Hund's case (d) and a total electronic spin quantum number $S$ because the exchange interaction dominates over the hyperfine interactions in the ionic core. The latter dominates in the d levels and leads to a transition from case d$_{\beta S}$ to case d$_{\beta S^+}$. Moreover, the level structure is reordered from a $G^+$ doublet structure for each of the three $ndl_1$ level to an $N$ triplet substructure of the two $G^+$ components. In the region where the $ndl_1$ and $ndl_2$ series cross, the spin-rotation interaction in the ion leads to a local mixing of $N$ and $G$ that leads to the observation of the $ndl_2$ levels in excitation from the $J = 0$ intermediate level.

Several consequences of vibrational interactions have been characterized. They perturb the hyperfine structure in the $ndl_1$ series over an extended range of principal quantum numbers and to cause the predissociation of both hyperfine components of the $ndl_3$ levels.

The present work demonstrates for the first time that the combination of ab initio R-matrix theory and spin-rovibronic MQDT calculations is capable for the first time of predicting the finest details of the photoionization spectrum of gerade symmetry of $H_2$. The quantum defect curves determined in this work will be essential for the analysis of the millimeter wave spectra of the s and d levels of ortho $H_2$ [110, 123].
Chapter 6

Hyperfine structure and autoionization dynamics in the p Rydberg states of molecular hydrogen and MQDT analysis

6.1 Introduction

The present chapter describes the results of an experimental and theoretical investigation of the role of nuclear spins in the autoionization of Rydberg series converging on the first rotationally excited level of ortho H$_2^+$ ($^2\Sigma_g^+, v^+ = 0, N^+ = 3$). Experimentally, these Rydberg states were accessed from the $v = 0, J = 3$ level of the H $^1\Sigma_g^+$ state of H$_2$ using a narrow-band (bandwidth < 10 MHz) solid-state near-infrared laser [49,114]. The H $^1\Sigma_g^+(v = 0, J = 3)$ level was chosen because its lifetime ($\tau = 102$ ns [218]) is much longer than that of singlet ungerade levels (0.5 ns [219] for B $^1\Sigma_u^+(v = 0, J = 0)$). The experimental resolution of down to 25 MHz enabled the observation of the fine and hyperfine structures of the autoionizing Rydberg states over a wide range of principal quantum number $n = 50 - 200$. The spectra provide completely new information on previously unknown dynamical processes related to nuclear spins and reveal the evolution of angular momentum coupling hierarchy from the situation where the exchange interaction dominates the level structure to the situation where the ionic hyperfine structure dominates. Several intermediate angular momentum coupling cases are identified which are useful in rationalizing both the level structure and the autoionization dynamics. An essential result is the observation that the total spin remains a conserved quantity in photoexcitation. Theoretically, the MQDT formalism developed to treat the hyperfine structure of bound Rydberg states of diatomic molecules [110,113] has been extended to also describe the hyperfine structure and dynamics of autoionizing Rydberg states. The calculations permit the exploration and quantification of phenomena not directly accessible in the present experiment such as spin-induced rotational autoionization.
This chapter is structured as follows: Section 6.2 provides a short description of the experimental procedure. The MQDT formalism describing the hyperfine structure of autoionizing Rydberg states of H\textsubscript{2} is presented in Section 6.3. Section 6.4 provides an analysis of the observed spectra and a comparison with the predictions from MQDT. We discuss in particular the evolution of the angular momentum coupling hierarchy and establish that the total spin quantum number G is conserved in photoexcitation over the whole range of observed spectra. In Section 6.4.2 the autoionization processes induced by the electron and nuclear spins are discussed and rationalized.

### 6.2 Experiment

The spectra have been recorded using sources of tunable vacuum-ultraviolet (VUV), visible (VIS) and near-infrared (NIR) laser radiation. The following three-photon excitation sequence was used to excite the high-n p Rydberg states of ortho H\textsubscript{2} below the X\textsuperscript{2}Σ\textsubscript{g} \textsuperscript{+} (v\textsuperscript{+} = 0, N\textsuperscript{+} = 3) ionization threshold

\[
\begin{align*}
X (v = 0, J = 1, F = 0 - 2) & \rightarrow \text{VUV} \rightarrow B (v = 5, J = 2, F = 1 - 3) \\
& \rightarrow \text{VIS} \rightarrow H (v = 0, J = 3, F = 2 - 4) \\
& \rightarrow \text{NIR} \rightarrow np (v\textsuperscript{+} = 0, N\textsuperscript{+} = 3, N = 2 - 4, F = 1 - 5).
\end{align*}
\] (6.1)

This excitation sequence is represented schematically in Fig. 6.1.

The H\textsubscript{2} sample was introduced into the spectrometer in a skimmed supersonic expansion. The excitation was detected by monitoring the ionization signal resulting from photoionization or pulsed field ionization of the long-lived Rydberg states. Ortho H\textsubscript{2} was selected by fixing the wave number of the VUV laser to the R(1) line of the B–X transition.

The VUV laser radiation around 96400 cm\textsuperscript{-1}, the visible and the narrow-band NIR laser radiation necessitated by this excitation sequence were necessitated by this excitation sequence were generated as described in chapter 2 using the experimental setups depicted in Figs. 2.2 and 2.5. The pulse energy of the visible laser had to be attenuated to below 1 μJ in order to prevent undesired two-photon ionization of the B state via the H state. In addition, the size of the laser beam was reduced to 0.2 mm in the direction perpendicular to the molecular beam by a cylindrical lens in order to reduce Doppler broadening. The NIR laser beam (pulse energies of 50 μJ energy with adjustable pulse lengths between 100 and 300 ns and a near Fourier-transform-limited bandwidth of better than 10 MHz) was directed into the experimental cham-
Figure 6.1: Schematic energy level diagram representing the resonant three-photon excitation sequence used to excite the Rydberg series converging on the $X^+ 2\Sigma^+_g, v^+ = 0, N^+ = 1$ rotationally excited level of $H_2$. The Rydberg series are designated with the Hund’s case (d) labels $n \ell N_\ell^N$ and the possible values of the total angular momentum quantum number including spins ($F$). The thick bent arrow represents rotational autoionization allowed in the absence of hyperfine and pf interactions and the dotted arrow represent autoionization that is permitted by hyperfine interactions. The latter affects the $F = 1 \rightarrow 4$ components of the $np3_3$ and $np3_4$ series.
ber, propagating perpendicular to the visible laser beam and to the supersonic molecular beam and counterpropagating relative to the VUV laser beam. The overlap of the three laser beams and the molecular beam was optimized by maximizing the ionization signal. The NIR radiation was calibrated by (1) recording absorption spectra of molecular iodine in an oven heated to 570°C, (2) recording the transmission spectrum of a home-built étalon (see below) and (3) by using a wave meter (Burleigh EXFO WA-1500) with an absolute accuracy of 60 MHz.

The error budget of the present measurements of transition frequencies from the $H(v = 0, J = 3)$ level to high Rydberg states located in the vicinity of the $N^+ = 3$ ionization threshold is summarized in Table 6.1. The uncertainty in the determination of the transition frequencies is dominated by the accuracy of the frequency calibration. The scans were linearized by using simultaneously recorded transmission spectra of a home-built confocal étalon with a free-spectra range of 150.08(3) MHz actively locked to a frequency-stabilized HeNe laser [53]. The linearization procedure resulted in a relative frequency uncertainty of at most 3 MHz over the total length of 15 GHz of each scan. For the laser intensities used in this work, AC Stark shifts and broadenings are negligible. The Doppler shift resulting from a possible deviation from 90° of the angle between the NIR and molecular beams was measured by recording the same transitions in expansions of pure H$_2$ (beam velocity 2900(50) m·s$^{-1}$), a 1:7 H$_2$:Ar mixture (beam velocity 550(10) m·s$^{-1}$) and a 1:7 H$_2$:Kr mixture (beam velocity 380(10) m·s$^{-1}$). The Doppler shift was determined with an accuracy of 2 MHz by extrapolating the observed Doppler shifts to zero velocity, the high accuracy resulting from the fact that the Doppler shifts in the three mixtures could be determined relative to the same transmission maximum of the stabilized étalon which remained locked throughout the procedure. At the density of the molecular beam of less than 10$^{14}$ cm$^{-3}$ in the measurement volume, the pressure shift is negligible (i.e. < 1 MHz) assuming that the pressure shift measured at $n = 10$ [11] can be extrapolated to the high $n$ region. On the basis of the measured residual stray electric fields of less than 2 mV/cm, DC Stark shifts can be neglected for Rydberg states with $n$ below 160 and an effective quantum defect of more than 0.06, for which the Stark effect is quadratic. A possible shift of the laser frequency resulting from a chirp occurring in the NIR pulse generation was measured to be less than 5 MHz [49].

Assuming a velocity of the H$_2$ beam of 2900 m·s$^{-1}$ and an opening angle of the supersonic beam of 0.3°, a Doppler broadening of 32 MHz is expected at a transition wavenumber of 11400 cm$^{-1}$. The <10 MHz bandwidth of the NIR laser thus makes a negligible contribution to the observed linewidth. The Doppler broadening could be decreased by seeding H$_2$ in Kr at a ratio of 1:7, which allowed us to measure a few transitions with a linewidth of 25 MHz or 0.0008 cm$^{-1}$. The narrowest lines observed experimentally still reveal a partially resolved substructure which eventually limits the observed linewidth. This observation is confirmed by the calculations presented
in Sec. 6.4 that predict each observed line to consist of at least three transitions corresponding to different values of the total angular momentum quantum number $F$.

### 6.3 Theory

The hyperfine structure of bound Rydberg states of ortho H$_2$ has been studied previously by MQDT as described in Refs. [110,113] which contain the essential equations. We discuss here how these equations are adapted to autoionizing Rydberg states and introduce the equations for the calculation of spectral intensities.

The quantization condition for bound Rydberg levels is obtained by requiring that the wavefunction vanishes for an infinite distance $r$ between the ion core and the Rydberg electron. This condition is expressed by the equation

$$
\sum_{i'} \left[ \frac{\sin(\pi \nu_i)}{\sqrt{A(v_i)}} C_{ii'} + \sqrt{A(v_i)} \cos(\pi \nu_i) S_{ii'} \right] B_{i'} = 0, \quad (6.2)
$$

where the index $i$ designates a Rydberg channel attached to an ionic state of energy $E_i^+$ and

$$
\nu_i(E) = \sqrt{\frac{\text{Ry}_M}{E_i^+ - E}}, \quad (6.3)
$$

represents the effective principal quantum number as a function of the total energy $E$. $A(v_i)$ is Ham's scaling function given in Eq. (2.31) of Ref. [13] and $\text{Ry}_M = 109707.42$ cm$^{-1}$ is the mass-corrected Rydberg constant for H$_2$. The spin-rovibronic quantum

<table>
<thead>
<tr>
<th>Error source</th>
<th>Estim. max. error / MHz</th>
</tr>
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<tbody>
<tr>
<td>Absolute errors</td>
<td></td>
</tr>
<tr>
<td>Frequency calibration</td>
<td>60 stat.</td>
</tr>
<tr>
<td>Doppler shift</td>
<td>2 syst.</td>
</tr>
<tr>
<td>AC Stark shift</td>
<td>negligible$^a$</td>
</tr>
<tr>
<td>DC Stark shift</td>
<td>negligible$^b$</td>
</tr>
<tr>
<td>Pressure shift</td>
<td>1 syst.</td>
</tr>
<tr>
<td>Chirp shift</td>
<td>5 syst.</td>
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<tr>
<td>Relative errors</td>
<td></td>
</tr>
<tr>
<td>Scan linearization</td>
<td>3 stat.</td>
</tr>
<tr>
<td>DC Stark shift</td>
<td>negligible$^b$</td>
</tr>
</tbody>
</table>

$^a$all pulse intensities < 10 W/mm$^2$

$^b$for $n < 160$ and $\eta > 0.06$

**Table 6.1:** Error budget of the experiment
defect matrices $C_{ii'}$ and $S_{ii'}$ are defined as

$$
C_{ii'} = \int \chi^{(N^+)}_{ii'}(R) \sum_{\Lambda \Omega} [ \langle i^{(sre)} | \alpha^{(sre)} \rangle 
\times \cos \left[ \pi \eta^{\Lambda \Omega}_{\ell,\ell'}(E,R) \right] \langle \alpha^{(sre)} | i'^{(sre)} \rangle ] \times \chi^{(N^+)}_{ii'}(R) dR,
$$

and

$$
S_{ii'} = \int \chi^{(N^+)}_{ii'}(R) \sum_{\Lambda \Omega} [ \langle i^{(sre)} | \alpha^{(sre)} \rangle 
\times \sin \left[ \pi \eta^{\Lambda \Omega}_{\ell,\ell'}(E,R) \right] \langle \alpha^{(sre)} | i'^{(sre)} \rangle ] \times \chi^{(N^+)}_{ii'}(R) dR,
$$

where $R$ is the internuclear distance. These matrices were evaluated using the procedure described in Ref. [90]. The frame transformation $\langle \alpha^{(sre)} | i'^{(sre)} \rangle$ between the close-coupling eigenchannels $\alpha^{(sre)}$ and the dissociation channels $i^{(sre)}$ has been defined in Ref. [110]. The superscript $(sre)$ stands for spin, rotation and electronic angular momenta. The body-frame quantum-defect functions $\eta^{\Lambda \Omega}_{\ell,\ell'}(E,R)$ were taken from Ref. [110] without modification and were assumed to be unaffected by interactions with the nuclear spin, which is justified by the weakness of hyperfine interactions compared to electrostatic interactions. Moreover, the very weak dependence of the ion core vibrational wavefunction $\chi^{(N^+)}_{ii'}$ on the total spin of the ion $G^+$ and the total angular momentum of the ion $F^+$ has been neglected. The quantum defect functions $\eta^{\Lambda \Omega}_{\ell,\ell'}(E,R)$ used in the present calculations include all possible $\eta_{D,p}$, $\eta_{L,t}$ and $\eta_{D,t}$ functions, because, although only p levels have been observed, the p and f channels interact with each other as a consequence of the nonspherical symmetry of the ion core.

To treat Rydberg states that lie above the lowest ionization limit, in the so-called autoionizing region of the spectrum, Eq. (6.2) needs to be adapted. A distinction is made between channels associated with ionic states that lie higher than the total energy of the system and those lying lower than the total energy. The first ensemble of channels is said to be closed and is designated with the letter $Q$, whereas the second ensemble is said to be open and is represented by the letter $P$. In this region of the spectrum, the boundary condition requires that the closed-channel wave functions remain finite for $r \to \infty$ and that the open-channel wave functions behave at large $r$ as collision eigenfunctions of the open channels, labeled $\rho$, with a phase shift $\tau_\rho$. The boundary condition for the closed channels is given by Eq. (6.2) and that for
the open channels by the equations:

\begin{align}
\sum_{i'} \left[ \sin(\pi \tau_{i'}) C_{ii'} - \cos(\pi \tau_{i'}) S_{ii'} \right] B^\rho_{i'} &= 0, \\
\sum_{i'} \left[ \cos(\pi \tau_{i'}) C_{ii'} + \sin(\pi \tau_{i'}) S_{ii'} \right] B^\rho_{i'} &= \langle i | \rho \rangle.
\end{align}

This set of equations is actually solved in the form of a generalized eigenvalue problem [87]. The elements \( \langle i | \rho \rangle \) are normalized according to the requirement

\[ \sum_i \langle \rho | i \rangle \langle i | \rho \rangle = 1. \tag{6.7} \]

The center positions of autoionizing resonances that are narrow compared to their spacings can be predicted by intentionally omitting the open channels. As a result, the same equations are solved as in the case of a bound-state calculation. The shift resulting from the interaction with the continua has been verified to be insignificant in the present case.

The partial oscillator strength for photoionization into the fragmentation channel \( \tilde{i} \) is calculated according to

\[ \frac{df}{dE} \bigg|_{\tilde{i}} = \frac{2 \hbar \nu}{3} \left[ 2F' + 1 \right] \left| \sum_{\rho} \langle \tilde{i} | \rho \rangle e^{i \pi \tau_{\rho}} \sum_i B^\rho_i \sum_\alpha \langle i | \alpha \rangle D_{H,F''}^{\alpha F'} \right|^2, \tag{6.8} \]

where \( \langle i | \alpha \rangle \) denotes the frame transformation \( \langle i^{(\text{sre})} | \alpha^{(\text{sre})} \rangle \) introduced above, and \( D_{H,F''}^{\alpha F'} \) is the molecule-fixed standing-wave dipole amplitude for the transition from the level \( F'' \) of the H state to the component \( F' \) of the excited channel \( \alpha \). The total oscillator strength is obtained by summing over all final state channels \( \tilde{i} \). \( D_{H,F''}^{\alpha F'} \) is related to the purely electronic radial transition moments \( d_{\nu}^{\alpha F'}(R) \) as spelled out in detail in Eqs. (27)-(29) of Ref. [15] which have been trivially extended to include nuclear in addition to electronic spins. The integration \( \int dR X_{\nu''}^{(N')} d_{\nu''}^{\nu} \alpha_{\nu'}(R) X_{\nu''}^{(N'')} \) over the vibrational motion is also implied to be included in \( D_{H,F''}^{\alpha F'} \). The \( d_{\nu'}^{\alpha} \alpha_{\nu'}(R) \) refer to specific transitions \( \ell' \rightarrow \ell \). Since no theoretical predictions of the transition moments from the H state were available to us, we have assumed the H state to be of s character and the transition moments \( d_{\nu}^{\alpha F'}(R) \) to be independent of \( R \) as well as of the excited state energy \( E \). The values of \( d^{p\Sigma}_{\nu\Sigma} \) and \( d^{p\Pi}_{\nu\Sigma} \) were then adjusted, keeping all other transition moments at zero.

The hyperfine structure in the rotational levels of the ground state of ortho \( \text{H}_2^+ \) is described by the following effective Hamiltonian [110,220]

\[ \hat{H}_{\text{HFS}} = b \hat{I} \cdot \hat{S}^+ + c I_z S_\Sigma^+ + d S_\Sigma^+ \cdot \hat{N}^+, \tag{6.9} \]

where \( \hat{I}, \hat{S}^+, \hat{N}^+ \) are the nuclear spin, core electron spin and core rotation angular mo-
mentum operators, and \( I_z \) and \( S_z^+ \) are the \( z \) components of \( \vec{I} \) and \( \vec{S}^+ \), respectively. The hyperfine-structure constants \( b, c \) and \( d \) have been determined experimentally for the \( X^2\Sigma_g^+, v^+ = 0, N^+ = 1 \) level by extrapolation of Rydberg series in Ref. [110], but there are, to our knowledge, neither experimental nor theoretical values of \( b, c \) and \( d \) for the \( N^+ = 3 \) level of ortho \( \text{H}_2 \). The constants \( b \) and \( c \) represent the hyperfine interactions between the core-electron and nuclear spins. These constants should therefore, to a first approximation, be independent of the level of rotational excitation, because they only depend on the electronic structure and the magnetic moments of the nuclei. The constant \( d \) represents the interaction between the core electron spin and rotation and can also be assumed to be independent of the quantum number \( N^+ \). We have therefore used the constants \( b, c \) and \( d \) determined previously for the \( N^+ = 1 \) level and calculated the hyperfine structure in \( N^+ = 3 \) for which we have obtained the following eigenvalues and eigenfunctions in the basis \( |G^+, F^+\rangle \) of the coupling case \( (b|S^+) \) defined in Ref. [110]

\[
\Psi^-(F^+ = 7/2) = -0.999907 |1/2, 7/2\rangle + 0.042493 0 |3/2, 7/2\rangle \quad (6.10)
\]
\[
\Psi^-(F^+ = 5/2) = +0.998059 |1/2, 5/2\rangle - 0.062275 1 |3/2, 5/2\rangle \quad (6.11)
\]
\[
\Psi^+(F^+ = 3/2) = |3/2, 3/2\rangle \quad (6.12)
\]
\[
\Psi^+(F^+ = 5/2) = -0.062275 |1/2, 5/2\rangle - 0.998059 |3/2, 5/2\rangle \quad (6.13)
\]
\[
\Psi^+(F^+ = 7/2) = +0.042493 0 |1/2, 7/2\rangle + 0.999907 |3/2, 7/2\rangle \quad (6.14)
\]
\[
\Psi^+(F^+ = 9/2) = |3/2, 9/2\rangle \quad (6.15)
\]

\[
E^-(F^+ = 7/2) = -0.031582 \text{ cm}^{-1} \quad (6.16)
\]
\[
E^-(F^+ = 5/2) = -0.030016 \text{ cm}^{-1} \quad (6.17)
\]
\[
E^+(F^+ = 3/2) = 0.011421 \text{ cm}^{-1} \quad (6.18)
\]
\[
E^+(F^+ = 5/2) = 0.014200 \text{ cm}^{-1} \quad (6.19)
\]
\[
E^+(F^+ = 7/2) = 0.016433 \text{ cm}^{-1} \quad (6.20)
\]
\[
E^+(F^+ = 9/2) = 0.017040 \text{ cm}^{-1} , \quad (6.21)
\]

where the wave numbers are given with respect to the center of gravity of the hyperfine structure of the \( N^+ = 3 \) level. These eigenvectors were used in the evaluation of the frame transformation \( \langle \alpha^{(\text{sre})} | i^{(\text{sre})} \rangle \) according to Eq. (A1) of Ref. [110].

The calculations performed in this study comprise three steps. The first step is an MQDT calculation of the three hyperfine components \( F = 2, 3, 4 \) of the \( \text{H} (v = 0, J = 3) \) level of \( \text{H}_2 \) using quantum defect functions for the channels of gerade electronic symmetry obtained from ab initio calculations [112]. The second is an MQDT calculation of the high \( p \) Rydberg states which is performed either as a continuum calculation, if line shapes are desired, or as a discrete calculation using the closed
channels only, if line positions are required. These calculations rely on the quantum
defect functions for the channels of ungerade symmetry determined in Ref. [110]. The
last step is the calculation of intensities according to Eq. (6.8) using \( R \)-independent
transition moments. The best agreement with the spectra was obtained by using
transition moments \( d_5 \) and \( d_{11} \) of equal magnitude and sign.

The quantum defect functions for the channels of ungerade symmetry have been
tested and improved to predict the positions of bound levels around \( n = 50 \) with
an accuracy of 600 kHz [110]. For Rydberg states of gerade symmetry, this level of
accuracy has not been reached yet because of additional difficulties caused by interac-
tions with doubly excited configurations of \( 1\Sigma_g^+ \) symmetry. The hyperfine structure of
rovibrational levels of the H state are experimentally unknown and therefore the ac-
curacy of the MQDT predictions of the hyperfine structure of the H state could not be
assessed directly. The calculations predict hyperfine splittings in the \( H(v = 0, J = 3) \)
level of less than 30 MHz, which is too small to be resolved in our experiment.

6.4 Results

6.4.1 Channel structure of \( H_2 \) p Rydberg states

Neglecting spin, the channel structure of p Rydberg states of \( H_2 \) is well understood
[11]. In Hund's case (b), which applies to the lowest members of the p Rydberg series,
each state can be assigned a value of \( \Lambda \) of either 0 or 1. For the high-\( n \) Rydberg
states investigated here, \( \ell \) uncoupling is complete and the Hund's case (b) quantum
number \( \Lambda \) is no longer a good quantum number but is replaced by the rotational
quantum number \( N^+ \) of the ion core. The total angular momentum without spins
is then given by \( \vec{N} = \vec{N}^+ + \vec{\ell} \), where \( \vec{\ell} \) represents the orbital angular momentum of
the Rydberg electron. The quantum defects in case (d) can be derived from those in
case (b) using the frame transformation \( \langle N^+ | \Lambda \rangle \) given in Ref. [11]. The results of this
transformation using the quantum defect functions derived in Ref. [110] are given in
Table 6.2. Neglecting relativistic effects and interactions with the nuclear spins, the
same procedure can be used to define quantum defects for the triplet channels which
are also summarized in Table 6.2.

In the present work we have studied autoionizing p Rydberg states of \( H_2 \) converg-
ning on the rotationally excited level \( N^+ = 3 \) of the ion. Neglecting all spins there
are three p series with different total angular momentum quantum number \( N \) that
are designated by \( npN_L^+ \), i.e., \( np3_{2,3,4} \). Since the total angular momentum is con-
served in photoionization, only the \( np3_2 \) series can autoionize at energies between
the ionization thresholds corresponding to \( N^+ = 1 \) and \( N^+ = 3 \) because the continua
associated with the \( N^+ = 1 \) threshold only comprise \( N = 0 \) to 2. If the pf interaction
is taken into account, the \( np3_{2,3,4} \) levels can autoionize into the \( efl_{2,3,4} \) continua. If
the spins are considered, the total angular momentum $\vec{F}$ is conserved and the open continua have $F = 0$ to 4 which relaxes the restriction mentioned above and opens an ionization channel for some hyperfine components of all three series $np3_{2,3,4}$. In order to assess the importance of these additional pathways for ionization it is necessary to understand the relative importance of the different interactions between angular momenta and their evolution with increasing level of excitation.

At sufficiently high $n$ values the interactions between the core electron spin and the $\text{H}_2^+$ nuclear spins, which are independent of $n$, become larger than the exchange interaction between the core and the Rydberg electrons which scales as $n^*^{-3}$, and therefore singlet and triplet levels are mixed. The mixing is almost complete when the singlet-triplet interval becomes equal or smaller than the largest ionic hyperfine interval. This situation is reached at effective principal quantum numbers of 104, 90 and 101 for the three series $np3_2$, $np3_3$ and $np3_4$, respectively.

To illustrate the gradual evolution of the coupling hierarchy with $n$, the next subsections describe the level patterns and spectral intensities at selected values of $n$ between 70 and 140.

**Energy level structure at $n = 70$**

At $n = 70$, the intervals between singlet and triplet levels of $N = 2, 3, 4$ are significantly larger than the ionic hyperfine splittings. Therefore one expects a level structure close to Hund's case (d). Because the H state is a nearly pure singlet state of s character and the total electronic spin is conserved in the absence of spin interactions, one expects to only observe the singlet components of p levels.

Figure 6.2 shows the photoionization spectrum of ortho $\text{H}_2$ recorded in the region corresponding to $n \approx 70$ from the $\text{H}(v = 0, J = 3)$ level and the results of MQDT calculations of all bound levels (including triplet levels) with $F = 1 - 5$ using Eq. (6.2), indicated by the symbols above the spectrum. The symbols encode the value of $N$ (crosses for $N = 2$, circles for $N = 3$ and squares for $N = 4$). Rectangular frames have been placed around the final states to which transitions are observed in the spectrum.

The spectrum reveals two sharp lines that can immediately be assigned to transitions to the Rydberg states $70p3_4$ and $70p3_3$ using the Hund's case (d) quantum defects given in Table 6.2. The lines consist of several unresolved transitions between the hyperfine components of the H level and the Rydberg states. In addition to the two sharp lines, a broad structure is observed which is assigned to the $70p3_2$ resonance which decays by rotational autoionization into the $\epsilon_{12}$ continuum. The width of this structure amounts to 0.075 cm$^{-1}$ corresponding to a reduced width $\Gamma_r = \Gamma \cdot n^*^3$ of $2.6 \times 10^4$ cm$^{-1}$.

Since the widths of the transitions to the $70p3_4$ and $70p3_3$ states are limited by experimental effects, these transitions are compared to calculations of all bound lev-
Figure 6.2: Photoionization spectrum of ortho H₂ in the region of \( n \approx 70 \) below the \( v^+ = 0, N^+ = 3 \) ionization limit (solid line) and MQDT calculations of the same spectral region. The results of three different MQDT calculations are shown in the spectrum. These include the result of continuum calculations of the broad \( N = 2 \) resonances using Eq. (6.6) for \( F = 1 \) (dotted line), \( F = 2 \) (dashed line) and \( F = 3 \) (dot-dashed lines) and their sum (thick dashed line), a calculation of positions and intensities of the \( F = 4 \) components using Eq. (6.2) (vertical lines) and a calculation of all level positions for \( F = 1 - 5 \) (symbols on top of the figure), including the positions of the \( N = 2 \) resonances. The \( np3_2 \) levels are marked with crosses, the \( np3_3 \) levels with circles and the \( np3_4 \) levels with squares. The final states that are actually observed in the spectrum are highlighted by rectangular frames and correspond to the singlet components of \( 70p3_2,3,4 \). The absolute positions above the \( X^1\Sigma^+_2 (v = 0, J = 0) \) ground state of H₂ can be derived by adding 113303.463 cm\(^{-1}\) to the wave numbers.

Table 6.2: Calculated case d singlet and triplet \( \eta \) quantum defects using the results of Ref. [110] for \( R = 2 \) a.u.
els (including triplet levels) with $F = 1 - 5$ using Eq. (6.2) which are also shown in Figure 6.2. The results of a full MQDT calculation of lines positions including all spins using Eq. (6.2) are shown as symbols (see above) in the spectra. For clarity, intensity calculations are presented for the $F = 4$ components only (stick spectra) because the singlet components of the autoionizing $np32$ resonances have no $F = 4$ components and the intensities only weakly depend on $F$. The natural linewidths of the transitions to the $F = 2 - 4$ components of the 70p33 level and the $F = 3 - 4$ components of the 70p34 levels were calculated from Eq. (6.6) (not shown) and found to lie in the range between 30 and 270 kHz, well below the experimental resolution. These results confirm the expectation that the hyperfine interactions are too small to lead to a significant singlet-triplet mixing in this region.

The analysis of the broad 70p32 resonance requires MQDT calculations using Eq. (6.6), the result of which is displayed in Fig. 6.2 for $F = 1$ (dotted line), $F = 2$ (dashed line) and $F = 3$ (dash-dotted line) and is in excellent agreement with the measured lineshapes and positions.

The intensities obtained from bound state calculations and those obtained from continuum calculations can be represented on a common scale by rescaling the calculated resonances so that their integrated intensity corresponds to that obtained from a bound calculation. In this process, which amounts to convoluting the calculated profiles with the experimental lineshape function, we have used the calculated natural linewidth for the components of the broad 70p32 resonance and the experimentally limited linewidth of 32 MHz or 0.001 cm$^{-1}$ for the sharp transitions. The results of this procedure are shown in Fig. 6.2 which illustrates the good agreement between calculated and observed linewidths for both bound and continuum calculations.

The finite autoionization linewidths of the $F = 2 - 4$ components of the 70p34 and 70p33 levels have two different contributions arising from hyperfine interactions and the pf interaction and are discussed in Subsection 6.4.2. The $F = 5$ components can only autoionize if both effects are combined.

The symbols outside the rectangular frames in Fig. 6.2 correspond to the triplet component of 70p33 that is expected to lie in this region and to produce sharp resonances. A subgroup of transitions to this component is very weakly observed close to the maximum of the 70p32 resonance. The observation of triplet components is a result of the hyperfine interactions in the core as is discussed further below.

**Energy level structure at $n = 80$**

Figure 6.3 compares the photoionization spectrum recorded in the region corresponding to $n = 80$ with the results of a MQDT calculation in the same spectral region. The results of discrete calculations of levels corresponding to $F = 1 - 5$ are shown as symbols (see above) in the spectrum and the transitions to $F = 4$ components are
Figure 6.3: Photoionization spectrum of ortho H₂ in the region of $n \approx 80$ below the $v^+ = 0, N^+ = 3$ ionization limit (solid line) and MQDT calculations in the same spectral region. A calculation of positions and intensities of the $F = 4$ components using Eq. (6.2) (dotted vertical lines) and a calculation of all level positions for $F = 1 - 5$ are shown. The $np3_2$ levels are marked with crosses, the $np3_3$ levels with circles and the $np3_4$ levels with squares. The final states that are actually observed in the spectrum are highlighted by rectangular frames. The absolute positions above the $X^1Σ^+_e (ν = 0, J = 0)$ ground state of H₂ can be derived by adding 113303.463 cm$^{-1}$ to the wave numbers.

shown as stick spectra. The resonances corresponding to $N = 2$ cannot be identified unambiguously in this measurement because of an insufficient signal-to-noise ratio.

In the region around $n = 80$, the interval between the singlet and triplet levels is comparable to the hyperfine splitting in the ion. Consequently, neither $S$ nor $G^+$ are good quantum numbers. The spin coupling hierarchy is modified and a new useful angular momentum can be defined, resulting from the coupling between total electronic and total nuclear spin

$$
\hat{S} = S^+ + \hat{s} \\
\hat{G} = \hat{I} + \hat{J} \\
\hat{F} = \hat{N} + \hat{G}
$$

The resulting angular momentum coupling case is case (d) to which one adds a total
spin angular momentum and is labeled as case \( (d_{\beta s}) \), indicating that the nuclear spin is coupled to the total electronic spin, according to the nomenclature introduced in Refs. [110,221]. The calculated level pattern can indeed be rationalized using this coupling case and the transitions are labeled by the values of \( S, G \) and \( N \) in Fig. 6.3. The group of levels corresponding to singlet states must have \( G = 1 \) and therefore \( F \) can take the values \( N - 1, N, N + 1 \). The triplet levels can be classified into three groups with \( G = 0 \), which only allows \( F = N \), \( G = 1 \) with \( F = N - 1, N, N + 1 \), and \( G = 2 \) with \( F = N - 2, N - 1, ... , N + 2 \). Of these three groups of levels, the \( G = 0 \) level always lies lowest in energy and the \( G = 2 \) levels highest because the eigenvalues of the effective Hamiltonian for the interaction of a total electron spin \( \vec{S} \) with a total nuclear spin \( \vec{I} \) (which is similar to Eq. (6.9) excluding the spin-rotation term and with \( \vec{s} \) replaced by \( \vec{S} \)) are given by [221]

\[
E_{G,S,I} = \frac{1}{6}(3b' + c')[G(G + 1) - S(S + 1) - I(I + 1)],
\]

where \( b' \) and \( c' \) are both positive and close to the values of \( b \) and \( c \) of the ion core. This result can also be interpreted physically: The opposite signs of the gyromagnetic ratios of proton and electron lead to a preferred antiparallel alignment of the respective spins.

Because of the singlet-triplet mixing induced by the hyperfine interaction the triplet levels gain intensity compared to the situation observed at \( n = 70 \). However, only a subset of these levels are observed, namely those of the \( G = 1 \) group. This observation reveals the role of \( G \) as a conserved quantity since the excitation takes place from a nearly pure singlet level of ortho \( \text{H}_2 \) with \( G = 1 \). This conservation rule actually applies to the whole range of Rydberg states observed in this work, up to \( n = 160 \), and represents an interesting case of total spin conservation in photoexcitation. The agreement between calculated and measured positions is excellent in this region and the agreement between measured and calculated intensities is satisfactory.

**Energy level structure at \( n = 110 \)**

At \( n \approx 110 \) the hyperfine splitting in the ion is larger than the singlet-triplet interval for \( N = 2, 3, 4 \). The level structure starts resembling the ionic structure and can be labeled according to the total spin quantum number of the ion \( G^+ \) as can be seen in Fig. 6.4. The transitions to singlet and triplet levels of \( N = 3 \) and \( 4 \) have nearly equal intensities which shows that singlet-triplet mixing is complete. The corresponding angular momentum coupling situation, while still intermediate, starts approaching
6.4. Results

The (d_βs+) limiting case defined by

\[ G^+ = I + S^+ \]
\[ \tilde{G} = G^+ + \tilde{s} \]
\[ F = \tilde{G} + \tilde{N}. \]

This coupling scheme differs from that encountered in high \( \ell \) (\( \ell \geq 3 \)) states of ortho \( \text{H}_2 \) [110,222,223] which can be represented by

\[ \tilde{G}^+ = I + S^+ \]
\[ F_s = \tilde{G}^+ + \tilde{N} \]
\[ \tilde{F} = \tilde{F}_s + \tilde{s}. \]

These two cases can both be described as \( d_{βs+} \) but they differ in that the exchange interaction dominates over the spin-rotation interaction in the core in the former case while the opposite is true in the latter.

A continuous transition actually occurs between the limiting cases \( (d_βs) \) and \( (d_{βs+}) \). The transition is described schematically in Fig. 6.5 which shows on the left-hand side...
Figure 6.5: Correlation diagram illustrating schematically the transition from case $d_{\beta S}$ to case $d_{\beta S^+}$ which occurs when the singlet-triplet interval decreases below the $G^+$ splitting in the ion. This angular momentum recoupling takes place for each a $np3j$ Rydberg series independently. When the spin-rotation interaction in the ion (the term $dS^+ \cdot N^+$ in Eq. 6.9) is neglected, $G$ remains a good quantum number throughout.

The level diagram appropriate for each $np3j$ level in case $d_{\beta S}$ (Eq. 6.22) and on the right-hand side the level diagram appropriate for the same levels in case $d_{\beta S^+}$ (Eq. 6.24). The good quantum number in this diagram is $G$ as can be seen from Eq. (6.9) in the case where the spin-rotation term is neglected. Indeed, the wavefunction of the molecule can then be written as the product of a $np3j$ Hund’s case (d) wavefunction without spins and a total spin wavefunction $|sS^+I; sIG\rangle$. Fig. 6.5 illustrates that the $G = 0$ and 2 components retain triplet character as long as the spin-rotation interaction in the core is negligible and are thus not observable in our experiment. It also shows that the $G = 1$ components which have pure singlet or triplet character at low $n$ values have a completely mixed character at high $n$. While only one $G = 1$ component corresponding to $S = 0$ is observed at low $n$ (Fig. 6.2) two are visible at high $n$ (Figs. 6.3 and 6.4).

When the last term of Eq. (6.9) becomes important, $G^+$ couples to $N^+$ and the resultant $F^+$ is a nearly good quantum number. In this situation, $G$ and $N$ have ceased to be good quantum numbers. The dynamical consequences are discussed below in Section 6.4.2.
The resulting level pattern can be represented schematically as follows:

\[ G^+ = \frac{3}{2} \quad [G = 1 \text{ of } S = 0] \quad F = N-1, N, N+1 \]
\[ [G = 2 \text{ of } S = 1] \quad F = N-2, N-1, N, N+1, N+2 \]

\[ G^+ = \frac{1}{2} \quad [G = 1 \text{ of } S = 1] \quad F = N-1, N, N+1 \]
\[ [G = 0 \text{ of } S = 1] \quad F = N \] (6.26)

The observed and calculated spectra shown in Fig. 6.4 are in good agreement and support the generalized spin conservation rule formulated in Section 6.4.1.

**Energy level structure at \( n = 140 \)**

At \( n = 140 \), the Hund’s case (d) fine-structure splittings are smaller than the ionic \( G^+ \) splitting, such that the spectrum displayed in Fig. 6.6 is dominated by the \( G^+ \) ionic structure. For \( N = 3 \) the level structure is characteristic of case \( d_{\beta S^+} \) outlined in Eq. (6.24). The calculations and the spectra show that within the \( G^+ = 1/2 \) manifold, the hyperfine components of the \( np3_{\beta} \) level with a given \( G \) value are shifted to lower energies with increasing \( F \) value, whereas the opposite is true for the \( G^+ = 3/2 \) manifold. This is interpreted as a signature of the hyperfine structure of the ion core for which an analogous ordering of the \( F^+ \) levels within a \( G^+ \) manifold is found (see Sec. 6.3). Transitions to the \( G = 1 \) groups of levels are still by far the most intense, confirming the \( G \) conservation rule already mentioned above.

**Correlation diagram**

To facilitate the visualization of the evolution of angular momentum coupling hierarchy, a correlation diagram, displayed in Fig. 6.7, was constructed on the scale of an effective principal quantum number defined with respect to the center of gravity of the hyperfine structure of the \( N^+ = 3 \) ionic state. At each \( n \) value, the same range of effective principal quantum number (from \( n - 0.15 \) to \( n + 0.85 \)) is shown. Fig. 6.7a shows photoionization spectra recorded from the \( H^1\Sigma_{\rho}^+(v = 0, J = 3) \) level. The results of MQDT calculations solving Eq.(2) for discrete states are displayed in Figs. 6.7b and 6.7c, respectively. In these figures the \( N = 4 \) (b) and \( N = 3 \) (c) levels have been connected by lines to guide the eye through the correlation diagram. For clarity, the levels corresponding to \( N = 2 \) have been suppressed because the corresponding resonances are very broad on the scale of the figure and do not reveal any observable hyperfine structure.

This correlation diagram highlights the continuous transition from case \( d_{\beta S} \) (top panel) to case \( d_{\beta S^-} \) (bottom panel). The singlet levels \((G = 1)\) correlate with the
Figure 6.6: Photoionization spectrum in the region of \( n = 140 \) (solid line) and MQDT calculations in the same spectral region. See caption of Fig. 6.3 for further details.

The transitions represented in Fig. 6.7 connect the \( F = 2, 3, 4 \) levels of H (\( v = 0, J = 3 \)) to \( np3N \) levels with \( F = N - G, ..., N + G \). However, only a subset of the transitions allowed by the \( \Delta F = 0, \pm 1 \) selection rule is predicted to carry intensity as is confirmed by the partially resolved structure observed in the experimental spectra. The calculations predict the transitions corresponding to \( \Delta F = \Delta N \) to be more intense than the other allowed transitions by more than 3 orders of magnitude. This propensity can be interpreted as follows: the total spin is conserved in the transition (i.e., \( \Delta G = 0 \), as discussed above) and is weakly coupled to the other angular
Figure 6.7: Comparison of photoionization spectra (a) and MQDT calculations (b) and (c) of the hyperfine structure in the np34 and np33 series. The MQDT calculations were performed using Eq. (6.2) and include intensities for all the transitions from the hyperfine components of the H(v = 0, J = 3) level to the hyperfine components of the np34 and np33 series. The spectra are represented on the scale of an effective quantum number v* defined with respect to the center of gravity of the hyperfine components of the N+ = 3 level of H2+. The horizontal scale only gives the fractional value of v*, the integer value being given on the left margin for each spectrum. The G = 0, 1 and 2 levels of N = 4 (b) and N = 3 (c) are connected by dotted, full and dashed lines, respectively.
momenta, so that the dipole transition only affects the orbit-rotational part of the wavefunction. The relative orientation of $\mathbf{N}$ and $\mathbf{G}$ is thus conserved which implies $\Delta F = \Delta N$. This result is expected to have a general validity in transitions between hyperfine components of Rydberg states in Hund's case (d).

The conservation of total spin over the whole range of principal quantum numbers presented here can be understood from the relative strengths of the interactions contained in the effective Hamiltonian given in Eq. 6.9. If the interactions in the ion core were limited to those between nuclear and core electron spins ($\mathbf{G}^+ = \mathbf{I} + \mathbf{S}^+$), $G$ would be a good quantum number up to $n \to \infty$. However, because the core electron spin is coupled to the core rotation, $G$ stops being a good quantum number as soon as this interaction becomes significant, i.e. when the intervals between groups of levels possessing the same value of $G$ become comparable to the splittings in the ionic levels that originate from the interaction term $d \mathbf{S}^+ \cdot \mathbf{N}^+$. The interaction between nuclear and core electron spins, characterized by the constants $b$ and $c$, results in a splitting of the ionic level into two $G^+$ components separated by 0.046 cm$^{-1}$. The interaction between the core electron spin and core rotation, characterized by the constant $d = 0.001399(6)$ cm$^{-1}$, is more than one order of magnitude smaller. Therefore, it is expected that $G$ will remain a good quantum number up to the region $n \approx 170$ where the singlet-triplet interval of the np3$^3$ levels becomes smaller than the largest splitting resulting from the core electron spin-rotation interaction, i.e., the $F^+ = 9/2$-$F^+ = 3/2$ interval of the $N^+ = 3, G^+ = 3/2$ manifold. This situation is reminiscent of what happens in series converging to rotationally excited levels of para $\text{H}_2^+$. Series converging on $N^+ = 0$ can be characterized by a total electron spin quantum number $S$ up to $n \to \infty$. However, the singlet and triplet components of series converging on rotationally excited levels of para $\text{H}_2^+$ will be mixed by the core electron spin-rotation interaction term, but this interaction remains insignificant below $n = 170$. In ortho $\text{H}_2$, $G$ plays the same role as $S$ in para $\text{H}_2$: both are conserved until the exchange interaction becomes less than the spin-rotation interaction, which occurs over a similar range of $n$ values in para and ortho $\text{H}_2$. For $n > 170$, $G$ and $N$ are no longer conserved and the admixture of $N = 2$ character impacts the autoionization of $N = 3$ and 4 levels as discussed below. A similar argument applies to the nd Rydberg levels discussed in chapter 5 and using the corresponding spin-rotation intervals of the $N^+ = 1$ level and the singlet-triplet splitting of Table 5.1 leads to the prediction that spin-rotation interactions ought to mix $G$ and $N$ above $n \approx 105$.

### 6.4.2 Autoionization dynamics

Only the np3$^2$ levels can autoionize in the absence of spins and the neglect of pf interaction. This restriction is however relaxed if the effects of electron and nuclear spin are considered, because in this case $N$ is no longer a good quantum number and
the autoionization of some hyperfine components of the $N = 3$ and 4 levels becomes allowed. In the presence of pf interaction, the $np3_3$ and $np3_4$ levels can autoionize into the continua $ef1_3$ and $ef1_4$, respectively. In the MQDT calculations, these two effects can be studied separately, the former by including all spins but restricting the calculations to $\ell = 1$ and the latter by excluding all spins but including $\ell = 1$ and pf interaction. Since the pf interaction results from short-range effects between the ionic core and the Rydberg electron but the dominant spin interactions are those of the ionic core, one expects that the latter dominate the autoionization dynamics at high $n$.

The autoionization linewidths presented in this section were determined in calculations which neglected predissociation. It is therefore possible that the actual linewidths of the resonances, which have contributions from predissociation and autoionization, are larger than determined here.

**Spin-induced rotational autoionization**

As can be seen in Fig. 6.1, open channels in the region investigated here have $F = 0 - 4$ and autoionization is possible for all hyperfine components of $np3_2$, all $G = 0$ and $G = 1$ components of $np3_3$, the $G = 0$ component of $np3_4$ and several $G = 1$ and $G = 2$ components of $np3_4$. Unfortunately, because of the limited experimental resolution, the spectra have not revealed any broadening of the transitions to $N = 3$ and 4 levels that could be attributed to autoionization, which sets an upper limit of approximately 30 MHz for the rate of spin-induced autoionization in these levels. Since the structure and intensity distribution observed experimentally are reproduced satisfactorily by the calculations, it is reasonable to assume that the MQD theory allows quantitative predictions of processes that cannot be seen in our experiment and can be used to explore the role of nuclear and electronic spins in rotational autoionization.

Two regions were investigated in detail. The first corresponds to the region around $n = 81$ where the level structure can be described in case (dgs) and the hyperfine-induced singlet-triplet mixing is weak. Calculated line shapes of the $F = 0 - 5$ resonances are summarized in columns 5 and 6 of Table 6.3. The line widths were extracted by fitting either a Lorentzian line to the density of states or the Fano line-shape formula [176] to the resonances predicted by MQDT.

The hyperfine components of the singlet components of $N = 2$ have a width of 0.06 cm$^{-1}$ corresponding to a reduced width of 32000 cm$^{-1}$. This large value reflects the fact that rotational autoionization is allowed for these series even in the absence of hyperfine interactions. The triplet components have a reduced width of approximately 80000 cm$^{-1}$. The autoionization in the triplet manifold is faster than in the singlet manifold of $N = 2$ as a result of the larger difference $|\eta^{2S+1I} - \eta^{2S+1\Sigma}|$ [11] in
Table 6.3: Linewidths and reduced linewidths of calculated line profiles at $n = 81$

<table>
<thead>
<tr>
<th>$N$</th>
<th>$S$</th>
<th>$G$</th>
<th>$F$</th>
<th>$\Gamma / \text{cm}^{-1}$</th>
<th>$\approx \Gamma_r / \text{cm}^{-1}$</th>
<th>$\Gamma / \text{cm}^{-1}$</th>
<th>$\approx \Gamma_r / \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.0612</td>
<td>32 500</td>
<td>0.0612</td>
<td>32 500</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0.0604</td>
<td>32 200</td>
<td>0.0604</td>
<td>32 200</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0.163</td>
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<td>0.163</td>
<td>87 000</td>
</tr>
<tr>
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<td>1</td>
<td>2</td>
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<td>6.4</td>
<td>$1.2 \cdot 10^{-5}$</td>
<td>6.4</td>
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<tr>
<td>3</td>
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<td>10^{-6}</td>
<td>2.6</td>
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<td>$4.9 \cdot 10^{-6}$</td>
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</tr>
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<td>0</td>
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<td>7.0</td>
<td>10^{-7}</td>
<td>0.37</td>
<td>7.0</td>
</tr>
</tbody>
</table>

$S = 1$ channels compared to $S = 0$ channels. In contrast, the reduced widths of the $F = 3, 4$ components of $N = 3, 4$ lie between 0 and 6 cm$^{-1}$, i.e. four orders of magnitude less than for $N = 2$ because their autoionization is only permitted by hyperfine interactions.

The second region that was investigated in detail lies around $n = 141$ and the results are summarized in columns 5 and 6 of Table 6.4. The reduced line width of the $G^i = 1/2, F = 3$ component of $N = 2$, with which the $G = 1, F = 3$ level correlates at high $n$, is still very large and has actually increased compared to the situation observed at $n = 81$. The singlet-triplet mixing induced by the hyperfine interaction thus manifests itself here as an increased rate of autoionization. The resonances corresponding to $N = 3$ and 4 are characterized by a very strong dependence on the quantum numbers $N$ and $F$. Overall the lifetimes are found to decrease with decreasing values of $N$ and $F$. This effect can qualitatively be explained by the increasing $N = 2$ character of states with low $N$ and $F$ values. The autoionization of the $np3_3$ and $np3_4$ series can thus be considered to result from $N$ mixing induced by the spin-rotation interaction. However, since the autoionization of the $N = 2$ levels is still about two orders of magnitude faster, the $N$ mixing must be weak at $n = 140$. This result is in accordance with the statement of Section 6.4.1 that the interactions between the spins conserve $G$ and therefore $N$. The autoionization rates of the series with $N = 2, 3, 4$ will thus only become comparable when $N$ mixing is complete, i.e. at $n > 170$ when the spin-rotation splitting in the ion core dominates the level structure. At $n = 140$ this mixing is weak. However, because in the absence of any mixing the autoionization lifetimes of the $np3_3$ and $np3_4$ series would be infinite, even a weak mixing leads to the large variation in lifetimes described in Table 6.4.
pf interaction and autoionization

The weak but nonvanishing pf interaction allows p levels to decay into an f continuum with the same value of the total angular momentum quantum number $N$. For this process, neglecting all spins, we have calculated a reduced natural linewidth of 0.32 cm$^{-1}$ and 0.05 cm$^{-1}$ for the np$^3\!\!3_4$ and np$^3\!\!3_3$ levels lying above the $N^+ = 1$ threshold, respectively. This contribution to the natural linewidth decreases with $n^*$ as expected, contributing 31 kHz and 5 kHz to the linewidth of the 70p$^3\!\!3_4$ and 70p$^3\!\!3_3$ levels, respectively. pf interactions are therefore expected to have a negligible effect at high $n$ values ($n > 100$).

The results of MQDT calculations including the hyperfine and the pf interactions are summarized in the last two columns of Tables 6.3 and 6.4, for $n = 81$ and 141, respectively. At $n = 81$, a competition between spin-induced and pf autoionization is found. The effect of pf interactions is directly noticeable in the $N = 4$ levels, where the autoionization of the $F = 5$ component becomes allowed. The autoionization of the $F = 3$ and 4 components is increased by up to one order of magnitude, mostly because the spin-induced autoionization is particularly slow. The reduced linewidths compare well with those expected in the absence of hyperfine interactions. The autoionization of the $F = 5$ component is only possible through a combination of spin

<table>
<thead>
<tr>
<th>$N$</th>
<th>$G^I$</th>
<th>$G$</th>
<th>$F$</th>
<th>without pf interaction</th>
<th>with pf interaction</th>
</tr>
</thead>
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<td>$\tilde{\Gamma}$/cm$^{-1}$</td>
<td>$\approx \Gamma_r$/ cm$^{-1}$</td>
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<td>0</td>
<td>$7.6 \cdot 10^{-8}$</td>
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</table>

Table 6.4: Linewidths and reduced linewidths of calculated line profiles at $n = 141$
and pf interactions. For the \( N = 3 \) levels, the spin-induced autoionization is already faster than a possible pf autoionization and the linewidths are independent of the pf interaction. The same applies to the \( N = 2 \) levels, where rotational autoionization dominates over all other processes. At \( n = 141 \), the effect of pf autoionization is completely negligible compared to spin-induced autoionization.

6.4.3 Determination of the binding energy of \( \text{H}(v = 0, J = 3) \)

The analysis of the observed spectra by MQDT enables us to determine, by extrapolation, a more accurate value for the binding energy of the \( \text{H}^1\Sigma_g^+(v = 0, J = 3) \) level of \( \text{H}_2 \) with respect to the center of gravity of the hyperfine structure of the \( \text{X}^2\Sigma_g^+(v^+ = 0, N^+ = 3) \) threshold. The value was obtained in a MQDT fit to the observed transitions and amounts to

\[
\frac{IE(\text{H}^1\Sigma_g^+(v = 0, J = 3))}{hc} = 11461.144 \pm 0.003 \text{ cm}^{-1}. \quad (6.27)
\]

The uncertainty in the determination of this value is dominated by the uncertainty in the frequency of the near-infrared radiation (see Table I) with a smaller contribution from the uncertainty in the extrapolation to the series limit. This value can be used to determine a more accurate value for the term value of the \( \text{H} \) state of \( 113303.463 \pm 0.003 \text{ cm}^{-1} \) using the theoretical value for the ionization energy of \( \text{H}_2 \) of \( 124417.512 \text{ cm}^{-1} \) [224]. As soon as a more accurate experimental value for this term value becomes available, the present result can be used to determine the ionization energy of \( \text{H}_2 \) to an accuracy of better than 90 MHz, which would represent a substantial progress over the present accuracy of 400 MHz [225].

Since the \( \text{H}^1\Sigma_g^+(v = 0, J = 3) \) level is very nearly a pure singlet level, the hyperfine splittings are expected to be very small and are indeed predicted to amount to \( \approx 10 \) MHz.

6.5 Conclusions

We have observed and quantitatively analyzed the evolution of the spin-rovibronic angular momentum coupling hierarchy and the autoionization dynamics in \( \text{p} \) Rydberg states belonging to series converging on the \( \text{X}^2\Sigma_g^+(v^+ = 0, N^+ = 3) \) level of ortho \( \text{H}_2^+ \). At principal quantum numbers below \( n = 70 \), the level structure is represented adequately by Hund’s case (d) and a total electron spin quantum number \( S \), which is conserved upon photoexcitation and leads to the observation of singlet levels only. The hyperfine interactions in the ion core lead to a gradual decoupling of the Rydberg electron spin from the core spins which takes place between \( n = 70 \) and \( n = 150 \) and
ultimately leads to a level structure that is dominated by the hyperfine splitting of the ion.

The hyperfine-induced singlet-triplet mixing has two main consequences. First, it causes the angular momentum coupling hierarchy to change with principal quantum number and to evolve from the simple case (d) channel structure at \( n = 70 \) to the fully decoupled situation through several intermediate coupling cases, characterized by distinct level patterns and intensities. Second, the mixing has an impact on the autoionization lifetimes of the hyperfine components of the \( np_3 \) and \( np_4 \) series that results from the admixture of the shorter-lived triplet states.

The spin interactions in the ion core lead to additional mechanisms for rotational autoionization and permit autoionization for some hyperfine components of the \( N = 3 \) and \( N = 4 \) levels. However, the interactions leading to autoionization follow a very strict hierarchy. The autoionization rate of levels that are directly coupled to the continuum by electrostatic interactions (\( np_3 \)) exceeds that of the other \( N \) levels even when the level structure is completely dominated by the hyperfine structure of the ion core; experimentally, only an upper limit of about 30 MHz could be established for the spin-induced rotational autoionization in the range \( n < 150 \). The MQDT calculations have shown that the largest expected linewidths indeed lie below 10 MHz at \( n = 150 \) and have revealed very pronounced propensities for hyperfine interactions. These propensities result in autoionization lifetimes differing by up to four orders of magnitude between the hyperfine components of a given \( np_3N \) level. An accurate prediction of the autoionization lifetime of the long-lived Rydberg states (\( np_3,4 \)) can only be reached if the pf interaction is included in the calculation. At low \( n \) \( (n < 70) \) the pf interaction determines the autoionization lifetime of the \( np_3,4 \) levels. At higher values of \( n \), spin-induced autoionization and pf autoionization are in competition but the former completely dominate above \( n \approx 100 \). The prediction of lifetimes would also need to include predissociation [226], but this is beyond the scope of the present work.

Over the entire range of principal quantum numbers characterized in the present work, up to \( n \approx 170 \), the observed level patterns and intensity distributions can be explained by the fact that the total spin angular momentum \( \hat{S} \) and the total angular momentum without spins \( \hat{N} \) are constants of motion as long as spin-rotation effects are negligible. This conservation rule strongly favors transitions with \( \Delta F = \Delta N \) and is responsible for the large differences in autoionization rates observed for \( N = 2 \) on the one hand and \( N = 3,4 \) on the other. Beyond \( n \approx 170 \), these propensity rules are expected to gradually break down as the spin-rotation interaction in \( H_2^+ \) induces \( N \) mixing.

The spin-induced rotational autoionization investigated in the present work represents a decay pathway that completely dominates over radiative decay. If other pathways of non-radiative decay, like predissociation, are neglected the spin inter-
actions shorten the lifetime of some components by up to five orders of magnitude compared to purely radiative decay. This number is obtained assuming a radiative lifetime of 1$\mu$s for $n = 10$, the $n^3$ scaling law and a spin-induced autoionization linewidth of 5 MHz.

In conclusion, we were able to characterize the role of nuclear and electron spins in the structure and autoionization dynamics of high Rydberg states of ortho H$_2$ and to rationalize the observed effects in terms of approximate conservation rules. A worthwhile extension of the present study would consist in an excitation scheme starting from a (metastable) triplet state of H$_2$ which would allow the observation of the $G = 0, 1$ and 2 levels and test the $\Delta G = 0$ conservation rule in the $G = 0$ and 2 manifolds.
Part II

Jahn-Teller effects in molecular cations
The discovery of the Jahn-Teller effect goes back to the early thirties of the twentieth century. L. D. Landau, in a discussion with E. Teller about his student's (R. Renner's) work, first formulated the statement that "a molecule in an orbitally degenerate electronic state is unstable with respect to spontaneous distortion of the nuclear configuration that removes the degeneracy" (see in [227]). This statement was later verified group-theoretically by E. Teller and H. Jahn and more rigorously formulated as what is now known as the Jahn-Teller (JT) theorem [27,228]. One of the simplest JT problems, the E\text{2}e problem, mentioned in the introduction (section 1.3), was first investigated by Van Vleck who showed that the adiabatic potential energy surface has a cylindrical symmetry in the subspace of the degenerate vibrational mode with an isoenergetic minimum-energy trough (see also Fig. 1.2) [30]. The first experimental observation was the temperature dependence of electron paramagnetic resonance (EPR) spectra of Cu(II) compounds [229] that was interpreted by A. Abragam and M. H. L. Pryce [230]. The theoretical understanding of the JT effect made essential progress between the late fifties and the early seventies of the last century. In 1957, Öpik and Pryce investigated the minima of the T\text{2}e(e+t_2) problem and considered for the first time the vibronic coupling between nondegenerate electronic states, also called the Pseudo-Jahn-Teller (PJT) effect [231]. Longuet-Higgins [31] calculated the vibronic levels of the linear E\text{2}e problem and the band shapes of optical absorption spectra thus demonstrating the first observable manifestations of the JT effect in optical spectroscopy. Liehr and Ballhausen [232] considered the quadratic coupling term in the E\text{2}e problem and found that it removes the cylindrical symmetry of the potential energy surface giving rise to maxima and minima along the trough. A molecule subject to a JT effect can distort in several equivalent directions giving rise to equivalent minima on the potential energy surface. Bersuker recognized that this situation leads (in some cases) to a splitting of the lowest vibronic levels by tunneling [233]. O'Brien first calculated the vibronic levels of the E\text{2}e problem including linear and quadratic coupling terms. In 1965, Ham showed that the expectation values corresponding to operators containing the electronic angular momentum are reduced by the JT effect [234]. Additional ramifications of the JT effect became apparent in the late 1980's and early 1990's with the discovery of high-temperature superconductivity that was apparently inspired by the JT effect [235]. In the same period, the relation of the JT effect to the so-called topological phase problem [38] was recognized and initially resulted in confusion and controversy [236-238], although the effect had already been discussed by Herzberg and Longuet-Higgins [40] (see Section 1.3).

The most detailed information on the JT effect has been obtained from rotationally resolved optical and photoelectron spectra. The following overview of previous work summarizes some of the most impressive achievements in this field and should by no means be regarded as an exhaustive list of important contributions. The best understood systems are the alkali metal trimers because they possess a single JT ac-
tive vibrational mode. High-resolution spectra of the $\tilde{A}^2E'' - \tilde{X}^2E'$ transition of Na$_3$ were reported by von Busch et al. and reproduced quantitatively by variational calculations [32]. Both the ground and first excited state of Na$_3$ are typical examples of an E\$e JT effect. Optical spectra of the so-called B system of Na$_3$ were reported by Delacrétaz et al. [236] who interpreted their results in terms of an E\$e effect but a subsequent analysis showed that the B system represents a pair of PJT coupled electronic states [237]. This conclusion was confirmed by rotationally resolved spectra [238], the analysis of Coriolis interactions confirming the integer quantization of the pseudorotational states. The JT effect in O$_3$ has been characterized using two-photon resonant continuous-wave ionization spectroscopy [239,240] and has shown that very small barriers arise along the trough of minimal energies in the ground state potential which gives rise to nearly-free pseudorotation.

A well understood multimode system subject to an E\$e effect is the benzene cation. The most detailed knowledge about C$_6$H$_{5}^+$ comes from the analysis of rotationally resolved PFI-ZEKE photoelectron spectra [241,242] that has proven that the linear JT effect dominates and the quadratic effect leads to very small barriers between the three equivalent minima. It could nevertheless be shown that the minima correspond to a D$_{2h}$ geometry with two acute C-C-C bond angles, and the rovibronic photoionization selection rules have proven that the cationic states can be described in D$_{6h}$(M) symmetry. Detailed studies have also been conducted on the cyclopentadienyl radical including rotationally resolved measurements of the $\tilde{A}^2A''_2 - \tilde{X}^2E''_1$ transitions in C$_5$H$_5$ [62] and C$_5$D$_5$ [243] and dispersed fluorescence studies of the vibronic energy level structure of the $\tilde{X}^2E''_1$ ground state which could be fully characterized in terms of a 3-mode JT effect [244,245]. The Jahn-Teller effect in the cyclobutadienyl cation has been characterized by classical photoelectron spectroscopy [246].

The development of the theoretical methodology for the interpretation of optical spectra of JT systems starts with the work of Longuet-Higgins who calculated the vibronic levels of a single-mode E\$e system by diagonalizing the vibronic coupling Hamiltonian in a basis set of two-dimensional harmonic oscillator functions [31]. O'Brien extended this treatment to include quadratic coupling terms [247]. A systematic exploitation of these concepts and their extension to the treatment of multimode systems and an arbitrary number of interacting electronic states by Köppel, Domcke and Cederbaum has permitted the interpretation of the photoelectron and optical spectra of many vibronically coupled systems [26]. Their method has been extended to treat spin-orbit coupling non-perturbatively by Barckholtz and Miller [29]. All of these methods rely on the ab initio determination of vibronic coupling constants and diabatic electronic intervals which are subsequently used to set up the vibronic coupling Hamiltonian which is diagonalized to obtain the vibronic eigenvalues and spectral intensities.

The present second part of this thesis describes the investigation of the JT and
PJT effects in the cyclopentadienyl cation and the methane cation. Both systems are of fundamental importance in chemistry and are prototypical systems in molecular physics but neither of them has been characterized in sufficient detail to obtain definitive structural and dynamical information. The reason for this situation lies in the difficulty of producing these charged species in sufficient quantities to allow for a spectroscopic investigation at high resolution. Indeed the repulsion forces between cations in a gas sample limit their concentration to below $10^{10}$ cm$^{-3}$, and cause undesired Doppler broadenings of the transitions. Moreover, the techniques used to generate the cations (electron impact ionization, discharges etc.) are neither chemically nor state selective and the extraction of relevant spectral features from experimental data represents a real challenge.

In photoelectron spectroscopy, the cation energy level structure is measured from the neutral ground state of the molecule. Efficient and chemically selective routes exist to produce neutral species and supersonic expansions can lead to the population of only the lowest quantum states. Moreover, the transitions are detected with almost 100% efficiency by measuring electrons. An immense gain in sensitivity results from these advantages which was systematically exploited in the investigations. A final advantage of photoelectron spectroscopy is that it is compatible with double-resonance excitation schemes that facilitate spectral assignments, an advantage that is also exploited in chapters 7 and 8.

The following chapters describe rotationally resolved PFI-ZEKE spectra of these two compounds which provide completely new insight into their structure and dynamics. The spectra of the cyclopentadienyl cation provide the first high-resolution data on this molecule and permit the characterization of its electronic and rovibronic structure. The spectra of the methane cation represent the first spectroscopic characterization of a molecule subject to the $T\otimes(e+t_2)$ JT effect at rotational resolution. The key to the analysis of the spectra was a double-resonance method to assign the nuclear spin symmetries of the cationic levels.

Molecules subject to a JT effect are characterized by a highly irregular level structure that results from the flatness of the potential energy surfaces, the strong vibronic interactions and the high density of states. \textit{Ab initio} calculations are therefore essential as a starting point in the interpretation of the spectra. The strategy followed in the present thesis consists of three steps. In a first step, \textit{ab initio} calculations were performed to characterize the stationary points of the potential surfaces and estimate the relevant energy intervals and barriers. A group-theoretical analysis of the vibronic coupling problem was then used to interpret the \textit{ab initio} results and develop the simplest qualitatively correct description of the topology of the potential energy surfaces. In the last step, numerical calculations were performed to predict the vibronic and rovibronic structure and were used to assign the experimental spectra.
Chapter 7

Diradicals, antiaromaticity and the Pseudo-Jahn-Teller effect: electronic and rovibronic structure of the cyclopentadienyl cation

7.1 Introduction

The cyclopentadienyl cation ($\text{C}_5\text{H}_5^+$) is one of the prototypical molecules in the theory of aromaticity. Because of its $4\pi$ electrons, it is usually considered to be antiaromatic but its diradical structure leads to several closely spaced electronic states, which can be expected to have different structural, dynamical and chemical properties [248-251]. The cyclopentadienyl cation is also a key molecule in the understanding of vibronic coupling effects including the Jahn-Teller (JT) and the Pseudo-Jahn-Teller (PJT) effects [33]. The nature of the distortion of $\text{C}_5\text{H}_5^+$ and its origin have been discussed controversially in the literature [248, 250] and a clarification of this situation is desirable.

Very little experimental information is available on the cyclopentadienyl cation. It has been observed by mass spectrometry [252, 253] but neither optical nor photoelectron spectra have been reported yet. The spectroscopic information on $\text{C}_5\text{H}_5^+$ is currently limited to an electron-paramagnetic-resonance (EPR) spectrum in a SbF$_5$ matrix which led to the conclusion that the ground electronic state is a triplet state with a small to negligible distortion from D$_{5h}$ symmetry [254] but that a singlet state lies very close in energy [255]. The ordering of the lowest electronic states of $\text{C}_5\text{H}_5^+$ has been established in a preliminary report of our investigations of $\text{C}_5\text{H}_5^+$ by Pulsed-Field-Ionization Zero-Kinetic-Energy (PFI-ZEKE) photoelectron spectroscopy [256], in which we have shown that the isolated cation possesses a triplet ground state of D$_{5h}$ symmetry and that the lowest singlet state lies higher than the triplet ground state.
by less than 1600 cm\(^{-1}\). The singlet state was found to possess a strongly distorted structure and low-frequency modes of nuclear motion. In the present chapter, we present a complete study of the PFI-ZEKE photoelectron spectra of the lowest singlet and triplet states of C\(_5\)H\(_5^+\) and C\(_5\)D\(_5^+\) recorded following single photon excitation from the ground state and two-photon excitation via excited electronic states of the neutral radical. The spectra are assigned on the basis of vibronic coupling calculations using \textit{ab initio} values of the coupling constants. The results show that the lowest singlet state of C\(_5\)H\(_5^+\) is subject to a large PJT distortion and give insight into the complex nuclear motion in the manifold of strongly interacting electronic states. The vibrationally resolved measurements have been complemented by a set of rotationally resolved spectra which have enabled us to assign vibronic symmetries and determine the mechanism through which the \(\tilde{\alpha}^+ 1E_2^+ - \tilde{\alpha}^2A_2''\) photoionizing transition, which is forbidden in the single-configuration approximation, draws its intensity.

The accurate prediction of the electronic structure of the cyclopentadienyl cation represents a challenge for \textit{ab initio} quantum chemistry and experimental information is essential. The electronic configuration \((\ldots)(\alpha_2')^2(\epsilon_1')^2\) leads to three electronic states of symmetries \(3A_2', 1E_2'\) and \(1A_1'\) in D\(_{5h}\) geometry. Most \textit{ab initio} calculations [248-250, 257, 258], but not all of them [259], agree on the triplet being the ground electronic state of C\(_5\)H\(_5^+\). Calculated values for the adiabatic singlet-triplet interval vary from nearly zero to more than 7000 cm\(^{-1}\) [257], recent values lying in the range 1200 - 2500 cm\(^{-1}\) [249, 250]. Investigations of the potential energy surfaces have shown that the \(1E_2'\) state is subject to a distortion leading to two structures of C\(_{2v}\) geometry and electronic symmetry \(1A_1'\) lying very close in energy [248-250, 258]. One of these structures is a minimum whereas the other is a first-order saddle point but this property can be reversed depending on the level of \textit{ab initio} theory and/or the basis set. Another stationary point with a C\(_{2v}\) geometry and a \(1B_2\) electronic symmetry has been identified by Lee and Wright [249] and shown to belong to the lowest singlet surface by Zilberg and Haas [250].

In order to understand the nuclear dynamics in the manifold of interacting electronic states, it is essential to establish the topology of the potential energy surfaces and to construct a transparent model in terms of vibronic coupling theory. This approach has been pioneered by Cederbaum and co-workers [260] and has been successfully applied to a range of molecular systems that are closely related to C\(_5\)H\(_5^+\) [244, 245, 261]. Unfortunately, the knowledge of the potential energy surface of C\(_5\)H\(_5^+\) remains incomplete and the relationship between the different stationary points has not been established unambiguously because the complete symmetry of the vibronic problem has not always been considered. The fundamental implications of such topological properties on the nuclear dynamics have been discussed in several molecular systems [32, 37] and are known in the more general context of the geometric phase [38]. The early work of Borden and Davidson [248] has been the most pre-
exercise in this respect, showing that the origin of the stabilization of the \( \tilde{\alpha} + ^1E'_2 \) state of C\(_5\)H\(_5^+\) is its vibronic coupling to the \(^1A'\) state of the same electronic configuration. The effect was called a "second-order JT" effect but we prefer the expression "Pseudo-Jahn-Teller" effect to distinguish it from the vibronic coupling effect within a degenerate state which is known as "quadratic" JT effect \[231\]. Borden and Davidson have also shown that the linear JT effect in the \( \tilde{\alpha} + ^1E'_2 \) state is very weak and would vanish in the absence of configuration interaction. Consequently, different kinds of electronic degeneracies are present on the lowest singlet potential surface of C\(_5\)H\(_5^+\) and must be considered in the prediction of the nuclear dynamics. The theoretical strategy followed in the present chapter consists of a group theoretical analysis of the vibronic coupling problem followed by \textit{ab initio} calculations at the CASSCF level to determine approximate relative energies and vibronic coupling constants. This information is then used in a calculation of the vibronic structure which is compared to the experimental data.

7.2 Theory

7.2.1 Electronic structure

The electronic structure of C\(_5\)H\(_5\) and C\(_5\)H\(_5^+\) at low energies can be understood qualitatively by considering the subset of molecular orbitals \( (a'_2, e'_1 \) and \( e'_2 \) in \( D_{3h} \) symmetry) associated with the \( \pi \) electron system. The \( \tilde{X}^2E'' \) ground state and the \( \tilde{A}^2A'' \) first excited electronic states of the neutral have configurations \( (a'_2)^2(e'_1)^3(e'_2)^0 \) and \( (a'_2)^1(e'_1)^4(e''_2)^0 \), respectively. Both states have been characterized by high-resolution spectroscopy \[62,244,245\]. The ground state is subject to a Jahn-Teller distortion along the \( e'_2 \) modes.

The low-energy electronic configurations of C\(_5\)H\(_5^+\) that derive from the \( \pi \) electron system and the corresponding states are:

\[
\begin{align*}
(i) & \quad (a''_2)^2(e''_1)^2(e''_2)^0 : ^1A'_1, ^3A'_2, ^1E'_2 \\
(ii) & \quad (a''_2)^1(e''_1)^3(e''_2)^0 : ^1E'_1, ^3E'_1 \\
(iii) & \quad (a''_2)^2(e''_1)^1(e''_2)^1 : ^1E'_1, ^3E'_1, ^1E'_2, ^3E'_2 \\
(iv) & \quad (a''_2)^0(e''_1)^4(e''_2)^0 : ^1A'_1.
\end{align*}
\]

The configurations, electronic states and potential curves that are relevant to our investigation of the photoelectron spectrum of C\(_5\)H\(_5\) below 10 eV are represented schematically in Fig. 7.1 which shows on the left, middle and right panels the ordering of the relevant electronic states, the corresponding configurations in the form of
Figure 7.1: One- and two-photon excitation schemes used to record photoionization and PFI-ZEKE photoelectron spectra of the cyclopentadienyl radical. The positions and symmetries of the low-lying electronic states of the cyclopentadienyl radical and cation are represented on the left-hand side of the figure by the horizontal lines and capital letters, respectively. The electronic configuration of the π molecular orbitals from which the electronic states derive are represented schematically in the central column. The right-hand side represents schematic cuts through the potential energy surface of the electronic states along nuclear displacements of e'_2 symmetry.

The three electronic states of the cation that result from the lowest electronic configuration (a'')^2(e'')^2 are represented schematically in Fig. 7.2.

The Hartree-Fock energies of these three states at the D_{sh} geometry are

\[
\begin{align*}
\tilde{3}A'_2 &\quad (2h + J_{23} - K_{23}), \\
\tilde{1}E'_2 &\quad (2h + J_{23} + K_{23}, 2h + J_{22} - K_{23}), \\
\tilde{1}A'_1 &\quad (2h + J_{22} + K_{23}),
\end{align*}
\]

(7.2)

where h, J_{ij} and K_{ij} represent the one-electron orbital energy, the Coulomb and the exchange integrals, respectively, and the indices designate the π molecular orbitals of
Consideration of the electronic configurations leads to the conclusion that single-photon ionization transitions to the ionic states associated with configurations (i) and (ii) are allowed from the X^2E' ground state of the radical, whereas transitions to ionic states associated with configuration (i) are forbidden from the A^2A'_2 state. However, transitions to electronic state of configuration (i) may nevertheless be observed from the A^2A'_2 state if the interactions between configurations (i) and (ii) are significant. In particular, if the PJT interaction between the 1E'_2 and 1A'_1 states of configuration (i) is strong, the e' modes that mediate this interaction also lead to a mixing of the 1E'_2 state of configuration (i) with the 1E'_1 state of configuration (ii). This mechanism would facilitate the observation of the 1E'_2 ionic state from the A^2A'_2 neutral state and is now discussed in more detail.

### 7.2.2 Vibronic coupling

**Potential energy surfaces**

Since the diradical structure leads to electronic degeneracy and closely spaced electronic states, vibronic coupling must be considered. The D_{5h} symmetry of the system restricts the possible interactions. The a^+ 1E'_2 state is subject to a Jahn-Teller
Table 7.1: Jahn-Teller and Pseudo-Jahn-Teller activity of the doubly degenerate modes of the cyclopentadienyl cation up to fifth order.

<table>
<thead>
<tr>
<th>JT activity in $E_2$</th>
<th>$\Gamma_{vib}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>order</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$e_1'$</td>
</tr>
<tr>
<td>2</td>
<td>$e_2', e_2''$</td>
</tr>
<tr>
<td>3</td>
<td>$e_1', e_2$</td>
</tr>
<tr>
<td>4</td>
<td>$e_1', e_2', e_2''$</td>
</tr>
<tr>
<td>5</td>
<td>$e_1', e_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PJT activity $E_2 \leftrightarrow A_1'$</th>
<th>$\Gamma_{vib}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>order</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$e_2'$</td>
</tr>
<tr>
<td>2</td>
<td>$e_1', e_1''$</td>
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<tr>
<td>3</td>
<td>$e_1', e_2$</td>
</tr>
<tr>
<td>4</td>
<td>$e_1', e_2', e_2''$</td>
</tr>
<tr>
<td>5</td>
<td>$e_1', e_2$</td>
</tr>
</tbody>
</table>

The symmetry of the inducing vibrational modes can be determined by group-theoretical methods [28,29] which we extend here beyond the second order.

For a vibrational mode to be Jahn-Teller (JT) active at the $n^{th}$ order in an electronic state of symmetry $\Gamma_{E}$, the symmetric $n^{th}$ power of its irreducible representation $[\Gamma_{JT}]^n$ must be contained in the symmetric square of the electronic symmetry

$$[\Gamma_{E} \otimes \Gamma_{E}] \supseteq [\Gamma_{JT}]^n.$$  \hspace{1cm} (7.3)

The condition for a nonvanishing $n^{th}$-order Pseudo-Jahn-Teller (PJT) coupling between two electronic states of symmetries $\Gamma_{E}$ and $\Gamma_{A}$ is

$$\Gamma_{E} \otimes \Gamma_{A} \supseteq [\Gamma_{PJT}]^n,$$ \hspace{1cm} (7.4)

where $\Gamma_{PJT}$ represents the irreducible representation of the PJT active vibrational mode. For the electronic states of relevance in the present study, the products of the electronic symmetries are $[E_2]^2 = A_1' \oplus E_1'$ and $E_2 \otimes A_1' = E_2'$. Table 7.1 lists the symmetries of all modes that are JT or PJT active up to fifth order in the present problem. Bilinear terms of the form $Q(e_1')Q(e_2')$ and $Q(e_1')Q(e_2'')$, which are allowed in the second order of both the JT and PJT effects, have been disregarded in the derivation of the table.

One finds that linear JT active modes can only have symmetry $e_1'$, linear PJT modes can only have symmetry $e_2'$, quadratic JT modes are of symmetry $e_2'$ or $e_2''$, and quadratic PJT modes of symmetry $e_1'$ or $e_1''$. This alternation of linear and quadratic activity and the mutual exclusion of JT and PJT activity are general features of the
groups possessing a \( C_n \) rotation axis with \( n \) odd and larger than 5 and leads to interesting topological properties of the potential energy surfaces.

Watson has shown that the linear JT effect in a degenerate state arising from an \((e)^2\) configuration vanishes in the single-configuration approximation [263] and therefore, the stabilization associated with the \( e'_1 \) modes is expected to be small. This property had already been noticed by Borden and Davidson who demonstrated that the weak linear JT effect in the \( \tilde{a}^+ 1E'_2 \) state of \( C_5H_5^+ \) has its origin in configuration interaction. They have also pointed out that the \( e'_2 \) modes mediate a strong PJT interaction between the \( \tilde{b}^+ 1A'_1 \) and the \( \tilde{a}^+ 1E'_2 \) states which leads to a large stabilization of the lower component (\( ^1A_1 \) in \( C_2\alpha \)) of the \( \tilde{a}^+ 1E'_2 \) state.

The Hamiltonian for nuclear motion in the coupled electronic manifold is most conveniently set up in a diabatic electronic basis, for which the matrix elements are smooth functions of the nuclear coordinates [260]. Using complex basis functions for the \( E \) state, the resulting Hamiltonian matrix \( H \) can be written as follows [261] (only linear terms are retained)

\[
H = H^{\text{PJT}} + H^{\text{JT}},
\]

where

\[
H^{\text{PJT}} = h_0^{\text{PJT}} \mathbf{1} + \left( \begin{array}{ccc}
E & 0 & \sum_j \lambda_j r_j e^{i\phi_j} \\
0 & E & \sum_j \lambda_j r_j e^{-i\phi_j} \\
H.c. & H.c. & E_A
\end{array} \right)
\]

and

\[
H^{\text{JT}} = h_0^{\text{JT}} \mathbf{1} + \left( \begin{array}{ccc}
0 & \sum_n \rho_n e^{-i\theta_n} \\
H.c. & 0 & 0 \\
0 & 0 & 0
\end{array} \right).
\]

The degenerate vibrational modes mediating the vibronic coupling are described by cylindrical mass-weighted dimensionless normal coordinates \( r_j, \phi_j, \) and \( \rho_n, \theta_n, \) respectively. The first and second terms in Eq. (7.5) represent the PJT and JT interactions, respectively (H.c. means "Hermitian conjugate"). The harmonic oscillator terms \( h_0^{\text{PJT}} \) and \( h_0^{\text{JT}} \) in Eqs. (7.6) and (7.7) take the form

\[
h_0^{\text{PJT}} = \sum_j \frac{\omega_j}{2} \left( -\frac{1}{r_j} \frac{\partial}{\partial r_j} r_j \frac{\partial}{\partial r_j} - \frac{1}{r_j^2} \frac{\partial^2}{\partial \phi_j^2} + r_j^2 \right)
\]

and

\[
h_0^{\text{JT}} = \sum_n \frac{\omega_n}{2} \left( -\frac{1}{\rho_n} \frac{\partial}{\partial \rho_n} \rho_n \frac{\partial}{\partial \rho_n} - \frac{1}{\rho_n^2} \frac{\partial^2}{\partial \theta_n^2} + \rho_n^2 \right),
\]

respectively. Although the adiabatic representation is of limited physical meaning in the case of strong vibronic coupling, it helps visualizing the topology and symmetry of the potential energy surfaces. The adiabatic potential surfaces are defined as the eigenvalues of the molecular Hamiltonian of Eq. (7.5), ignoring the nuclear kinetic
energy. The adiabatic potentials have a simple appearance when only either JT or PJT displacements are considered. In the case of a single JT active mode with cylindrical coordinates \((\rho, \theta)\) the characteristic "Mexican-hat" potential of the E state is obtained

\[
V_{E^\pm}(\rho, \theta) = V_{E^\pm}(\rho) = V_E(0) + \frac{\omega_{JT}}{2}\rho^2 \pm g\rho. 
\]

For a single PJT active mode with cylindrical coordinates \((r, \phi)\), two of the surfaces repel each other whereas the third remains unchanged. Assuming identical vibrational frequencies in the A and E states, the following potential surfaces are obtained

\[
\begin{align*}
V_A(r, \phi) &= V_A(r) \\
V_{E^+}(r, \phi) &= V_{E^+}(r) \\
V_{E^-}(r, \phi) &= V_{E^-}(r)
\end{align*}
\]

\[
\begin{align*}
&= \frac{V_A(0) + V_A(0)}{2} + \frac{\omega_{PJT}}{2}r^2 + \sqrt{\left[\frac{V_A(0) - V_E(0)}{2}\right]^2} + 2\lambda^2r^2 \\
&= \frac{V_A(0) + V_A(0)}{2} + \frac{\omega_{PJT}}{2}r^2 - \sqrt{\left[\frac{V_A(0) - V_E(0)}{2}\right]^2} + 2\lambda^2r^2.
\end{align*}
\]

JT and PJT interactions both lift the electronic degeneracy in the \(\tilde{a}^+ \, 1E_2\) state but the effects are qualitatively different. Both \(e'_1\) and \(e'_2\) modes have two components \(e'_i\) and \(e'_j\). A distortion along an \(e'_i\) component conserves \(C_{2v}\) symmetry, whereas a distortion along an \(e'_j\) component lowers the symmetry to \(C_5\). A distortion from \(D_{5h}\) to \(C_{2v}\) symmetry splits the \(\tilde{a}^+ \, 1E_2\) state into two components of symmetry \(1A_1\) and \(1B_2\). In the case of a linear JT effect, the potential energy surfaces have a nonzero slope at the point of \(D_{5h}\) symmetry and, consequently, their ordering is reversed when the sign of the distortion coordinate is changed. In the case of a quadratic JT or a PJT effect, the slope of the adiabatic electronic surfaces vanishes at the point of highest symmetry and the ordering of the two components is independent of the sign of the distortion coordinate. In the present case, the lower component is totally symmetric \((1A_1\) in \(C_{2v}\)) whereas the upper component has symmetry \(1B_2\) in \(C_{2v}\).

These results can be generalized to include an arbitrary number of JT or PJT modes. The surfaces exhibit an overall rotational symmetry, i.e., they are invariant under the simultaneous substitutions [261]

\[
\begin{align*}
\phi_j &\to \phi_j - \alpha, \\
\theta_n &\to \theta_n + 2\alpha.
\end{align*}
\]

This invariance reflects the existence of a vibronic angular momentum operator \(\tilde{L}\).
that commutes with the Hamiltonian of Eq. (7.5) and is defined by [261]

\[
\hat{\mathcal{L}} = \hat{\mathcal{L}}_{\text{vib}} \mathbf{1} + \hbar \begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 
\end{bmatrix},
\]

(7.14)

where

\[
\hat{\mathcal{L}}_{\text{vib}} = \frac{\hbar}{i} \sum_j \frac{\partial}{\partial \phi_j} - \frac{2\hbar}{i} \sum_n \frac{\partial}{\partial \phi_n}.
\]

(7.15)

The existence of this constant of motion reflects the continuous symmetry of the vibronic coupling Hamiltonian of Eq. (7.5) and the quantum number associated with \( \hat{\mathcal{L}} \) can take any integer value. The inclusion of quadratic and higher-order vibronic coupling terms reduces this continuous symmetry to the molecular symmetry of the molecule under consideration.

In the case of the cyclopentadienyl cation, the \( D_{5h} \) symmetry requires that the linearly and quadratically active JT modes are different and that the \( e'_2 \) PJT modes can only be quadratically JT active (see Table 7.1). If vibronic coupling terms beyond the quadratic ones are neglected, the lower potential surface of the cyclopentadienyl cation possesses a one-dimensional isoenergetic subspace along the pseudorotation coordinate. The structures along this isoenergetic minimum energy path are displayed in Fig. 7.3a which is adapted from Ref. [248]. The figure reveals that the allylic and dienylic structures that result from distortions along both directions of the \( e^{'}_{2x} \) coordinate are isoenergetic and that the conversion from an allylic to a dienylic form is an equipotential process on the lowest singlet potential sheet.

Upon distortion, the degenerate \( e''_1 \) orbitals are split in an \( a_2 \) and a \( b_1 \) orbital (in \( C_{2v} \) notation), the \( b_1 \) (\( a_2 \)) being energetically lowered (raised) when the distortion takes place along one direction of the \( e^{'}_{2x} \) coordinate and raised (lowered) when it takes place along the other direction (see Fig. 7.3b). Both distorted structure have \( C_{2v} \) symmetry and a \( ^1A_1 \) ground state. This qualitative discussion will be made quantitative in Section 7.4.1 where the results of \textit{ab initio} calculations are presented.

**Dynamical calculations**

The eigenstates of nuclear motion in the manifold of interacting electronic states is obtained by diagonalizing Hamiltonian (7.5) in a direct product basis of diabatic electronic functions and two-dimensional harmonic oscillator basis functions

\[
|\phi_k\rangle = |\Lambda\rangle \prod_i |\nu_i, \ell_i\rangle,
\]

(7.16)

where \( \Lambda = 0 \) and (-1,1) for the \( ^1A'_1 \) state and the two components of the \( ^1E'_2 \) state, respectively, and \( \nu_i \) and \( \ell_i \) are the vibrational quantum number and the vibrational
Figure 7.3: a) Schematic representation of the minimum energy pseudorotation path in the lowest singlet state. A distortion along the $e'_{2x}$ dimension preserves $C_{2v}$ symmetry and takes the molecule to either the allylic or dienylic structure. If vibronic coupling terms of third and higher orders are neglected, the displayed minimum energy path is isoenergetic. b) Electronic configurations of the $\tilde{a}^+\tilde{1}E'_2$ state at $D_{5h}$ symmetry (middle) and of the distorted dienylic and allylic structures (left and right, respectively). The ordering of the $a_2$ and $b_1$ molecular orbitals originating from the degenerate $e''_1$ orbital is opposite in the dienylic and allylic structures.
angular momentum quantum number of the harmonic oscillator basis state, respec-
tively. The index \( i \) runs over all degenerate vibrational modes that are included in
the basis. The vibronic angular momentum quantum number \( j \) associated with these
basis functions is

\[
j = \sum_i \ell_i + \Lambda, \tag{7.17}
\]

and the matrix representation of the Hamiltonian of Eq. (7.5) is block-diagonal in \( j \), a
property that can be exploited in the numerical calculations.

The eigenvalues possess a simple structure in the limit of very weak and very
strong coupling. Figure 7.4 shows the eigenvalues of Hamiltonian (7.5) for a single
PJT active vibrational mode with harmonic wave number \( \omega = 800 \text{ cm}^{-1} \) in the range
\( 0 < (\lambda/\omega) < 3.5 \) relative to the lowest level. The \( ^1A'_1 \) state has been assumed to lie
5600 cm\(^{-1} \) above the \( ^1E_2 \) state and a harmonic oscillator basis with vibrational
quantum number up to \( v = 100 \) was used. In the limit of a vanishing coupling, the
vibronic structure is that of a two-dimensional harmonic oscillator where each level
has the degeneracy \( 2(v + 1) \). The ground vibronic state is thus doubly degenerate.
As the coupling strength increases, the degeneracy of the vibronic levels is lifted and
the resulting substrates are singly (\( j = 0 \), \( \Lambda \) vibronic symmetry) or doubly (\( j \geq 1 \), \( \Lambda \) or \( \Lambda_1 \oplus \Lambda_2 \) vibronic symmetry) degenerate. For sufficiently strong coupling, the \( j = 0 \)
level becomes the ground state thus leading to a transition from a doubly degenerate
to a nondegenerate vibronic ground state. For values of \( \lambda/\omega \geq 2 \) the lowest vibronic
levels converge to the simple structure of a one-dimensional rotor and the pattern
repeats itself with the harmonic frequency of the PJT active vibration. This situation
is similar to the strong-coupling limit of the E\( \otimes e \) JT effect with the difference that
the vibronic angular momentum quantum number is integer instead of half-integer.
The emergence of the simple rotor structure is the result of the formation of a deep
trough with rotational symmetry in the two-dimensional space of the \( e \) mode which
results in a free pseudorotation around the trough and vibrations perpendicular to it.
This situation occurs in the B system of Na\(_3\) [238, 264, 265].

The eigenvectors of the Hamiltonian (7.5) are linear combinations of the basis
states of Eq. (7.16) with expansion coefficients \( a_k \). The relative intensities of the
vibronic bands in the photoelectron spectrum are calculated according to

\[
I \propto \left| \sum_k a_k \langle \phi_k | \hat{\mu}_\alpha \left( \prod_{i'} |v_{i'}, \ell_{i'} \rangle \right) |\Lambda' \rangle \right|^2 \tag{7.18}
\]

which separates to (see Eq. (7.16))

\[
I \propto \left| \sum_k a_k \left[ \prod_{i,i'} \langle v_i, \ell_i | v_{i'}, \ell_{i'} \rangle \right] \langle \Lambda | \hat{\mu}_\alpha | \Lambda' \rangle \right|^2. \tag{7.19}
\]
Figure 7.4: Eigenvalues of the PJT Hamiltonian displayed as a function of the coupling parameter \( \lambda/\omega \). The values are given with respect to the lowest level which is the doubly degenerate \( j = 1 \) level for \( \lambda/\omega < 1.6 \) and the nondegenerate \( j = 0 \) level for \( \lambda/\omega > 1.7 \).

In the calculations the overlap integral \( \prod_{i,i'} \langle v_i, \ell_i | v_{i'}, \ell_{i'} \rangle \) from the intermediate \( | \Lambda' \rangle \prod_{i'} | v_{i'} \ell_{i'} \rangle \) level is assumed to be diagonal (i.e., \( \langle v_i, \ell_i | v_{i'}, \ell_{i'} \rangle = \delta_{v_i,v_{i'}} \delta_{\ell_i,\ell_{i'}} \)). The simulation of the intensities thus depends on the transition moments to the diabatic components of \( ^1E_2 \) symmetry (\( \Lambda = -1,1 \)) and \( ^1A_1' \) symmetry (\( \Lambda = 0 \)) for which we have used \( \langle 1 | \mu_\alpha | \Lambda' \rangle = \langle -1 | \mu_\alpha | \Lambda' \rangle \) and \( \langle 0 | \mu_\alpha | \Lambda' \rangle = 0 \), as discussed below.

### 7.3 Experiment

Two excitation schemes to record PFI-ZEKE photoelectron spectra of the cyclopentadienyl radical which are illustrated in Fig. 7.1. The first consisted in single-photon vacuum ultraviolet (VUV) excitation from the ground state of the neutral radical to high Rydberg states located just below the rovibronic levels of the cation. The second scheme was a resonance-enhanced two-color two-photon excitation via selected vibrational levels of the \( \tilde{A}^2A''_g \) state.

Tunable VUV radiation was generated by resonance-enhanced difference-frequency mixing (\( \tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2 \)) in krypton using the \((4p)^5 (2P_{3/2}) 5p [1/2] (J = 0) \rightarrow (4p)^6 1S_0 \) two-photon resonance at \( 2\tilde{\nu}_1 = 94092.863 \text{ cm}^{-1} \) as described in chapter 2 (see Figs.
7.4 Results

7.4.1 Ab initio calculations

The geometry of the \( ^3\text{A}_2 \) state of \( \text{C}_5\text{H}_5^+ \) has been optimized at the CASSCF(4,5)/cc-pVTZ level of theory. The active space has been chosen to consist of the \( \pi \) molecular orbitals which are occupied by four electrons. The starting orbitals have been generated in a Hartree-Fock calculation of the cyclopentadienyl anion because \( \text{C}_5\text{H}_5^- \) is a closed-shell molecule. The geometry optimization led to a \( \text{D}_{5h} \) structure with a C-C bond length of 1.381 Å and a C-H bond length of 1.068 Å. The optimization was followed by a calculation of the vibrational normal modes and their frequencies which are listed in Table 7.2 for \( \text{C}_5\text{H}_5^+ \) and \( \text{C}_5\text{D}_5^+ \).
Table 7.2: Vibrational frequencies in the $\tilde{X}^+ 3A'_2$ state of $C_5H_5^+$ and $C_5D_5^+$ calculated ab initio at the CASSCF(4,5)/cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>vibration</th>
<th>symmetry</th>
<th>$C_5H_5^+$ $\omega$/cm$^{-1}$</th>
<th>$C_5D_5^+$ $\omega$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$a'_1$</td>
<td>3065</td>
<td>2285</td>
</tr>
<tr>
<td>$v_2$</td>
<td>$a'_2$</td>
<td>1063</td>
<td>1010</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$a'_2$</td>
<td>1286</td>
<td>1009</td>
</tr>
<tr>
<td>$v_4$</td>
<td>$a'_2$</td>
<td>670</td>
<td>491</td>
</tr>
<tr>
<td>$v_5$</td>
<td>$e'_1$</td>
<td>3054</td>
<td>2262</td>
</tr>
<tr>
<td>$v_6$</td>
<td>$e'_1$</td>
<td>1389</td>
<td>1240</td>
</tr>
<tr>
<td>$v_7$</td>
<td>$e'_1$</td>
<td>959</td>
<td>753</td>
</tr>
<tr>
<td>$v_8$</td>
<td>$e'_2$</td>
<td>916</td>
<td>647</td>
</tr>
<tr>
<td>$v_9$</td>
<td>$e'_2$</td>
<td>3054</td>
<td>2253</td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>$e'_2$</td>
<td>1420</td>
<td>1386</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>$e'_2$</td>
<td>1075</td>
<td>828</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>$e'_2$</td>
<td>803</td>
<td>722</td>
</tr>
<tr>
<td>$v_{13}$</td>
<td>$e'_2$</td>
<td>824</td>
<td>778</td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>$e'_2$</td>
<td>423</td>
<td>352</td>
</tr>
</tbody>
</table>

*a* scaled by multiplying the ab initio result with 0.90

Table 7.3: Intervals between the lowest electronic states of $C_5H_5^+$. The first interval is given at the optimized $D_{3h}$ geometry of the triplet state at the CASSCF(4,5)/cc-pVTZ/cc-pVTZ level of theory. The energies of the singlet states in the last two intervals are evaluated after optimizing their geometry at the CASSCF(4,5)/cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>interval</th>
<th>$\Delta E$(CASSCF(4,5))/(hc cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{min}}(\tilde{a}^+ 1E'<em>2)-E</em>{\text{min}}(\tilde{X}^+ 3A'_2)$</td>
<td>5580$^a$</td>
</tr>
<tr>
<td>$E_{\text{min}}(\tilde{a}^+ 1E'<em>2)-E</em>{\text{min}}(1B_2)$</td>
<td>230</td>
</tr>
<tr>
<td>$E_{\text{min}}(1A_1)-E_{\text{min}}(\tilde{X}^+ 3A'_2)$</td>
<td>1410</td>
</tr>
</tbody>
</table>

$^a$Average of the $1A_1$ and $1B_2$ components

The electronic energy of the $\tilde{a}^+ 1E'_2$ state was determined by optimizing the geometry of $C_5H_5^+$ at the $D_{3h}$ conical intersection using the coupled-perturbed multi-configurational self-consistent-field method implemented in MOLPRO [266]. The intervals between the electronic minima of the $\tilde{X}^+ 3A'_2$ and $\tilde{a}^+ 1E'_2$ states at $D_{3h}$ geometry was then calculated at the CASSCF(4,5)/cc-pVTZ level of theory. This quantity will subsequently be called the diabatic singlet-triplet interval and the calculated value is given in the top line of Table 7.3.

Table 7.3 also lists the energy intervals between the singlet states calculated after optimizing their $(C_{2v})$ geometry at the CASSCF(4,5)/cc-pVTZ level of theory and the
The optimization of the geometry of the singlet state in C$_{2v}$ symmetry led to two different stationary points with a totally symmetric ($^1A_1$) ground electronic state which are represented in Fig. 7.5a and correspond to the dienylic and the allylic structures discussed in Section 7.2.2. At the CASSCF(4,5)/cc-pVTZ the allylic structure is found to be more stable than the dienylic structure by 320 cm$^{-1}$ but the energetic ordering inverts at higher levels of theory and decreases below the accuracy of the calculations as shown in Refs. [249,258]. The geometry of C$_5$H$_5^+$ has also been optimized by requiring the electronic symmetry to be $^1B_2$. In this case, a different structure was obtained that is represented schematically in Fig. 7.5b.

These results are analyzed in panel c of Fig. 7.5 in terms of a linear JT effect along the $e'_1$ modes (right-hand-side) and a PJT effect along the $e'_2$ modes (left-hand side) following the symmetry considerations of Section 7.2. The figure depicts the calculated potential energies along effective $e'_2$ and $e'_1$ modes pointing from the D$_{5h}$ geometry to the relevant minimum energy structures. The degeneracy point in both figures lies at the same energy and the state labels are given in C$_{2v}$ symmetry. Since the stabilization of the $^1A_1$ component of the $^1E_2$ state ($\sim 3700-4000$ cm$^{-1}$) is much larger than that of the $^1B_2$ component ($\sim 200$ cm$^{-1}$), the linear JT effect is almost negligible in C$_5$H$_5^+$ and indeed only leads to a small geometrical distortion (compare Figs. 7.5a and b).

The choice of normal modes in vibronic coupling problems is a delicate matter because the potential energy surfaces are far from being harmonic. Different choices have been suggested in the past, including normal modes from a state-averaged calculation at the conical intersection [244] and normal modes of the neutral ground state in the investigation of vibronic coupling in molecular cations by photoelectron spectroscopy [261]. In the present case, we have chosen to use the normal vibrational modes of the $^3A'_2$ ground state of the cation because it is nondegenerate and well separated from excited triplet states. The calculations were performed starting from the optimized D$_{5h}$ geometry of the triplet ground state and distorting it stepwise along the $e'_{2x}$ components of the 4 normal modes of symmetry $e'_2$ in the $^3A'_2$ state. At each geometry, a Hartree-Fock calculation of the anion was performed first, followed by a CASSCF(4,5) calculation of the $^3B_2$, $^1A_1$ and $^1B_2$ states (in C$_{2v}$ symmetry).

The stabilization energies $E_{\text{stab}}$ along the 4 modes of symmetry $e'_2$ were determined for C$_5$H$_5^+$ and C$_5$D$_5^+$ and are summarized in Table 7.4. The coupling constants $\lambda_i$ were determined as follows. The total stabilization energy $E_{\text{stab}}^T$ in a multimode Pseudo-Jahn-Teller problem is given by [260]

\[
\begin{align*}
E_{\text{stab}}^T &= \frac{\left(e-\Delta E/2\right)^2}{2e} & \text{for } e \geq \Delta E/2, \\
E_{\text{stab}}^T &= 0 & \text{for } e \leq \Delta E/2,
\end{align*}
\]

(7.20)
Figure 7.5: a) Structures obtained from geometry optimization at the CASSCF(4,5)/cc-pVTZ level of theory. The dienylic structure (left) corresponds to a first-order saddle-point and the allylic structure to a minimum at this level of theory. These structures result from a PJT distortion along an e' mode. b) Minimum energy structure with a $^1B_2$ ground electronic state optimized at the same level of theory. This structure results from a JT distortion along an e^ mode. c) One dimensional cuts through the potential energy surfaces of the states deriving from the $X^+ 3A''_2, \tilde{\alpha}^+ 1E_2$ and $\tilde{\beta}^- 1A'_1$ states of $C_3H_5^+$ at $D_{3h}$ geometry. The cuts along effective modes of $e'_2$ (left) and $e'_1$ (right) connecting the $D_{3h}$ points to the relevant minimum energy structures are displayed. The distortion modes preserve $C_{2v}$ symmetry which is used to label the electronic symmetries.
Table 7.4: Harmonic frequencies $\omega$, stabilization energies $E_{\text{stab}}$ and reduced PJT coupling constants $\lambda/\omega$ for the four vibrational normal modes of symmetry $e'_2$ calculated at the CASSCF(4,5)/cc-pVTZ level of theory for $C_5H_5^+$ and $C_5D_5^+$ (see also text). The normal modes were obtained from a calculation of the $X^+ 3A'^2$ state at the CASSCF(4,5)/cc-pVTZ level. The last two columns show the values obtained after adjustment to the experimental spectra.

<table>
<thead>
<tr>
<th>mode</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$E_{\text{stab}}$(CASSCF(4,5))/(hc cm$^{-1}$)</th>
<th>$\lambda/\omega$</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$\lambda/\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$C_5H_5^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>3054</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>1420</td>
<td>1880</td>
<td>1.70</td>
<td>1460</td>
<td>1.61</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>1075</td>
<td>580</td>
<td>1.08</td>
<td>1140</td>
<td>1.00</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>803</td>
<td>600</td>
<td>1.28</td>
<td>820</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_5D_5^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>2253</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>1386</td>
<td>1960</td>
<td>1.82</td>
<td>1455</td>
<td>1.67</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>828</td>
<td>900</td>
<td>1.59</td>
<td>810</td>
<td>1.48</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>722</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$adjusted to the spectrum

where $\Delta E$ is the energetic interval between the $E$ and the $A$ state at the undistorted geometry. The total stabilization energy amounts to 4170 cm$^{-1}$ at the CASSCF(4,5)/cc-pVTZ level (see Table 7.3). The sum of the stabilization energies obtained by calculating cuts of the potential energy surfaces along the modes of symmetry $e'_2$ is smaller and amounts to 3060 cm$^{-1}$ in $C_5H_5^+$ and 2935 cm$^{-1}$ in $C_5D_5^+$ (see Table 7.4). The smaller values of the latter two quantities compared to the former one is attributed to anharmonicities in the potential energy surfaces which are not taken into account by the present potential model. The quantity $\frac{2\lambda_i}{\omega_i}$ corresponds to the contribution of each vibrational mode $i$ to the total stabilization energy. In order to obtain values of $\lambda_i$ that yield the correct total stabilization energy, Equation (7.20) was used to calculate the quantity $e$ corresponding to the ab initio value $E_{\text{stab}}^\text{ab} = 4170$ cm$^{-1}$, the calculated values of the harmonic frequencies $\omega_i$ of the $X^+ 3A'^2$ state and the calculated separation ($\Delta E = 5600$ cm$^{-1}$) between the $a^+ 1E'_2$ and $b^+ 1A'_1$ states at $D_{5h}$ geometry. $e$ was then partitioned among the active modes in proportionality of their calculated stabilization energy, yielding a contribution $e_i$ for mode $i$. This procedure provided the effective coupling constants $\lambda_i = (\omega_i e_i/2)^{1/2}$ summarized in Table 7.4.

7.4.2 Symmetry considerations and geometric phase

In combination with the symmetry analysis of Section 7.2.2 the results of the ab initio calculations show that the dominant mechanism for the stabilization of the $a^+ 1E'_2$ state is a PJT coupling to the $b^+ 1A'_1$ state mediated by the modes of symmetry $e'_2$. 
The distortion of C$_5$H$_5$ thus occurs in the 8-dimensional subspace of the $e'_2$ modes and in this subspace, the lifting of the electronic degeneracy is of second-order in the nuclear displacements and the electronic degeneracy corresponds to a "glancing intersection". The linear JT effect takes place in the 6-dimensional subspace of the $e'_1$ modes in which the lifting of the degeneracy is linear. These considerations are important in view of assessing a possible geometric phase resulting from a closed loop around a conical intersection [40]. Although an explicit consideration of the geometric phase is not required in a dynamical calculation, of the type performed in this work, because all relevant electronic states are included, the concept of a phase is useful in several respects. When the stabilization energy is large compared to vibrational frequencies, the nuclear motion can be viewed as taking place on the lowest potential energy surface only, but the geometric phase must be included and can have a profound impact on the dynamics as mentioned earlier [32,37]. In the present case, the stabilization resulting from the PJT effect dominates over that resulting from the linear JT effect. Consequently, the nuclear motion in the lowest vibronic levels is confined to the space of the $e'_2$ modes. This motion does not encircle any conical intersection and, therefore, no geometric phase is associated with it. The relevant nuclear configurations associated with the motion of C$_5$H$_5$ along the minimum energy path are represented schematically in Figs. 7.3 and 7.5.

7.4.3 Single-photon VUV photoionization and PFI-ZEKE PE spectra

PFI-ZEKE photoelectron spectra of C$_5$H$_5$ and C$_5$D$_5$ have been recorded following single-photon excitation from the X$^2E'$ neutral ground state. Figs. 7.6 a and b show the VUV photoionization (dashed lines) and PFI-ZEKE photoelectron spectra (full lines) of C$_5$H$_5$ and C$_5$D$_5$, respectively. The steps observed in both photoionization spectra at the position of the first band of each photoelectron spectrum mark the first adiabatic ionization thresholds.

<table>
<thead>
<tr>
<th></th>
<th>C$_5$H$_5$</th>
<th>C$_5$D$_5$</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE(X$^+$ $^3A'_2$)/(hc cm$^{-1}$)</td>
<td>67967±4</td>
<td>67949±4</td>
<td>67830±800$^a$ [252]</td>
</tr>
<tr>
<td>IE($\tilde{a}^+$ $^1E'_2$)/(hc cm$^{-1}$)</td>
<td>69501±4</td>
<td>69492±4</td>
<td>&lt; 69570 [256]</td>
</tr>
<tr>
<td>$\Delta$E(S$_0$-T$_0$)/(hc cm$^{-1}$)$^b$</td>
<td>1534±6</td>
<td>1543±6</td>
<td>&lt; 1600 [256]</td>
</tr>
</tbody>
</table>

$^a$value for C$_5$H$_5$

$^b$adiabatic singlet-triplet interval in the cation

From a comparison with the two-color photoelectron spectra (see below), the photoelectron band is assigned to the transition to the vibrationless $\tilde{X}^+$ $^3A'_2$ cationic
Figure 7.6: One-photon VUV photoionization (dotted lines) and PFI-ZEKE photoelectron spectra (full lines) in the region of the adiabatic ionization threshold of C₅H₅ (a) and C₅D₅ (b) and simulations using a rotational temperature of 8 K for C₅H₅ and 12 K for C₅D₅ (insets). The spectra are assigned to the origin of the $\tilde{X}^{+} \tilde{3}A'_2 - \tilde{X}^{2}E'_1$ transition.

ground state. Figure 7.6 also shows, in the insets, simulations of the rotational envelope of the first PFI-ZEKE photoelectron band of C₅H₅ and C₅D₅ using a rotational temperature of 8 K for C₅H₅ and 12 K for C₅D₅ and the orbital ionization model described in Refs. [267, 268] assuming ionization from an orbital of dₓ character. The simulation used the neutral ground state parameters from Refs. [62, 243], Boltzmann population factors including spin-statistical weights, and ionic rotational constants of the $\tilde{X}^{+} \tilde{3}A'_2$ state from the ab initio equilibrium geometry determined at the CASSCF(4,5)/cc-pVTZ level of theory. We attribute the different rotational temperatures in the two spectra to slightly different experimental conditions. No further vibronic structure was observed in the spectral region 67800 – 71500 cm⁻¹ indicating almost diagonal Franck-Condon factors. Our sensitivity to PFI-ZEKE signal originating from the cyclopentadienyl radical was however reduced by the presence of strong hot and sequence bands of the precursor covering the range above 68280 cm⁻¹. A careful subtraction of the spectra recorded with and without photolysis did, however, not reveal any vibrational structure that could be attributed to the cyclopentadienyl
cation. The satisfactory agreement between the calculated and measured rotational contours of the origin band of the $\tilde{X}^2E''_1 \rightarrow \tilde{X}^{2}E''_1$ transition suggests that the orbital ionization model captures the main features of the photoionization dynamics. It also permits the derivation of the accurate values of the adiabatic ionization energies of C$_5$H$_5$ and C$_5$D$_5$ given in Table 7.5.

### 7.4.4 Photoionization and PFI-ZEKE photoelectron spectra recorded via the $\tilde{A}^2A''_2$ state

Photoionization and PFI-ZEKE photoelectron spectra have also been recorded using a (1+1') two-photon excitation scheme via different vibrational levels of the $\tilde{A}^2A''_2$ intermediate state. The resonance-enhanced two-photon ionization spectrum of the $\tilde{A}^2A''_2 \rightarrow \tilde{X}^{2}E''_1$ transition of C$_5$H$_5$ is displayed in Fig. 7.7. The strong transitions observed in the spectrum are the same as those observed in the laser-induced fluorescence excitation spectrum reported in Ref. [245], but almost all weaker transitions observed in Ref. [245], several of which were assigned to hot and sequence bands, are absent from our spectrum. The vibrational temperature of the cyclopentadienyl radical thus appears to be lower in our experiment which suggests that vibrational degrees of freedom are more efficiently cooled in the expansion from the capillary into the high-vacuum region than in the experiment reported in Ref. [245] where the radicals were generated directly behind the nozzle. The assignments of the vibrational levels agree with those given in Ref. [245] which were derived from the analysis of dispersed fluorescence spectra.

The photoionization (dotted lines) and PFI-ZEKE photoelectron spectra (full lines) of C$_5$H$_5$ and C$_5$D$_5$ recorded following (1+1') two-photon resonant excitation via the ground vibrational level of the $\tilde{A}^2A''_2$ state are shown in Figs. 7.8a and 7.8b, respec-
The spectra have been recorded from the origin of the $\tilde{X}^1\tilde{A}'_2 \rightarrow \tilde{X}^2E''_1$ transition up to 4000 cm$^{-1}$ of excess energy in the ions. The photoionization signal is zero at the position of the first adiabatic ionization energy but increases slowly over the lowest 1500 cm$^{-1}$ and possesses several sharp resonances. A sharp increase of the photoionization signal is observed at the position of the strongest band in the PFI-ZEKE photoelectron spectrum of C$_5$H$_5$ (~ 69572 cm$^{-1}$). The corresponding feature in the photoionization spectrum of C$_5$D$_5$ at 69561 cm$^{-1}$ is less marked but still recognizable. In the photoionization spectrum of C$_5$D$_5$, 7 resonances form a progression and are assigned to the members $n = 13 - 19$ of and autoionizing Rydberg series (indicated in Fig. 7.8b by vertical lines on the assignment bar) with a small quantum defect and a series limit at 69263 cm$^{-1}$. The corresponding ionization threshold is also observed in the PFI-ZEKE photoelectron spectrum which possesses a band at 69261 cm$^{-1}$. In the photoionization spectrum of C$_5$H$_5$, the members $n = 12 - 17$ of a less pronounced Rydberg series (labeled in Fig. 7.8a) converging to 69634 cm$^{-1}$ are observed. This ionization threshold corresponds to the position of the band in the PFI-ZEKE photoelectron spectrum located immediately above the strongest band.

The PFI-ZEKE photoelectron spectrum of C$_5$H$_5$ is dominated by the strong transition at 69572 cm$^{-1}$ which is accompanied by three weaker bands lying 71 cm$^{-1}$ lower and 62 and 168 cm$^{-1}$ higher. The lowest of these four bands is narrower than the upper three which all have a similar appearance. At higher wave numbers the spectrum possesses a second group of closely spaced lines around 70380 cm$^{-1}$. The spacing and the relative intensities of the two strongest bands in this region is nearly identical to those of the two strongest bands around 69572 cm$^{-1}$. Beyond this second group of lines, the spectral density and the widths of the observed bands increase. The separation between the most intense bands amounts to 808 cm$^{-1}$ and the interval between the second groups of lines and the broad structure at 71120 cm$^{-1}$ amounts to ~ 740 cm$^{-1}$.

A few weaker bands are also observed at lower wave numbers. The band marked with an asterisk could be assigned to the origin transition of the photoelectron spectrum of the precursor C$_5$H$_6$. This band was also observed in the absence of photolysis and disappeared when the laser pulse inducing the ionization was delayed with respect to the laser pulse inducing the $\tilde{A}^2\tilde{A}''_2 \rightarrow \tilde{X}^2E''_1$ transition and is observed as a result of a nonresonant two-photon excitation process. The weak bands located between 68500 and 69700 cm$^{-1}$ have been tentatively assigned to transitions to a totally symmetric fundamental (2$^1$), totally symmetric overtones and combination bands of out-of-plane vibrations (14$^2$,13$^1$,14$^1$,13$^2$) and the 10$^1$ level of the $\tilde{X}^1\tilde{A}'_2$ ground state of the cation by comparison with the calculated vibrational frequencies (see Tables 7.2 and 7.6).

The PFI-ZEKE photoelectron spectrum of C$_5$D$_5$ possesses less vibronic structure than that of C$_5$H$_5$. The dominant features are four bands located at 69561, 70377,
Chapter 7. Electronic and rovibronic structure of the cyclopentadienyl cation

Figure 7.8: Two-photon resonant photoionization and PFI-ZEKE photoelectron spectra (dotted and full lines, respectively) recorded via the vibrationless level of the $\tilde{A}^2A''_2$ state of $\text{C}_5\text{H}_5$ (panel a) and $\text{C}_5\text{D}_5$ (panel b). Vertical arrows mark the positions of the adiabatic ionization thresholds corresponding to the formation of the $\tilde{X}^+ 3A'_2$ and lower component of the $\tilde{a}^+ 1E'_2$ states, respectively. The horizontal line with vertical assignment bars labels an autoionizing Rydberg series. The horizontal axis corresponds to the sum of the wave numbers of both lasers.

70568 and 71055 cm$^{-1}$. The overall intensity distribution and the intervals between the dominant features are similar to those observed in the spectrum of $\text{C}_5\text{H}_5$. A weak band is identified 70 cm$^{-1}$ below the strongest band which matches the corresponding interval in the spectrum of $\text{C}_5\text{H}_5$. The band marked with an asterisk was also observed in the absence of photolysis and is therefore not attributed to $\text{C}_5\text{D}_5^*$. The weak bands located between 68500 and 69700 cm$^{-1}$ have been tentatively assigned to transitions to a totally symmetric fundamental ($2^1$) and a totally symmetric overtone of an out-of-plane vibration ($8^2$) of the $\tilde{X}^+ 3A'_2$ ground state of the cation by comparison with the calculated vibrational frequencies (see Tables 7.2 and 7.7).

To obtain more information on the complex spectral patterns observed between 69500 cm$^{-1}$ and 71500 cm$^{-1}$, additional PFI-ZEKE photoelectron spectra of $\text{C}_5\text{H}_5$ have been recorded via the vibrational levels $2^1$, $11^1$ and $12^1$ of the $\tilde{A}^2A''_2$ state and are compared in Fig. 7.9. The spectrum recorded via the totally symmetric $2^1$ level has a poor signal-to-noise ratio but its overall intensity distribution is similar to that of the
Table 7.6: Positions and assignments of vibronic bands in the PFI-ZEKE photoelectron spectra of C₅H₅. The total wave number with respect to the neutral ground state of the radical is indicated. The table also lists the wave numbers relative to the origins of the $\tilde{X}^+ 3A'_2$ and $\tilde{a}^+ 1E'_2$ ($1A_1$ component) states and deviations between observed and calculated vibronic intervals.

<table>
<thead>
<tr>
<th>$\tilde{\nu}_{obs}$ cm⁻¹</th>
<th>$\tilde{\nu}<em>{obs}-IE(^{1}A'</em>{2})/(hc)$ cm⁻¹</th>
<th>($\tilde{\nu}<em>{obs}-IE(^{1}E'</em>{2})/(hc)$) cm⁻¹</th>
<th>($\tilde{\nu}<em>{obs}-\tilde{\nu}</em>{calc}$) cm⁻¹</th>
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- a measured transition without correction of the field-induced shift of the ionization thresholds
- b harmonic frequencies from ab initio calculations
- c assignment tentative and on the basis of ab initio calculations

The spectrum recorded via the 0⁰ level. The spectra recorded via the 11¹ and 12¹ levels have intensity distributions that differ strongly from those measured via 0⁰ and 2¹. In both spectra, the band at 69500 cm⁻¹, which coincides with a weak band in the spectra recorded via 0⁰ and 2¹, is dominant. The two following bands at 69572 cm⁻¹ and 69632 cm⁻¹ are also common to all four spectra but they are weak in the spectra recorded via the 11¹ and 12¹ intermediate levels. Two bands at 69760 and 69897 cm⁻¹ are observed in the spectra recorded via the 11¹ and 12¹ levels which are not observed via the 0⁰ or 2¹ levels. At higher wave numbers the spectra recorded via 11¹ and 12¹ begin to differ considerably from each other and from the spectra recorded
Table 7.7: Positions and assignments of vibronic bands in the PFI-ZEKE photoelectron spectra of C₅D₅. The total wave number with respect to the neutral ground state of the radical is indicated. The table also lists the wave numbers relative to the origins of the X⁺ 3A'₂ and a⁺ 1E'₂ (1A₁ component) states and deviations between observed and calculated vibronic intervals.

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<th>(Vobs-IE(1E'₂)/(hc))</th>
<th>(Vobs-Vcalc)</th>
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<td>-11</td>
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<td>å⁺ 1E'₂ u = 4, j = 1</td>
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*a* measured transition without correction of the field-induced shift of the ionization thresholds  
*b* harmonic frequencies from *ab initio* calculations  
*c* assignment tentative and on the basis of *ab initio* calculations

via 0₀ and 2₁ and both possess a high spectral density. The bottom spectrum in Fig. 7.9 represents the PFI-ZEKE photoelectron spectrum of the precursor C₅H₆ which contributes weak lines to all spectra because of the weak non-resonant two-photon excitation mentioned above.

The Å²A''₂ — X²E''₁ transition in C₅D₅ does unfortunately not give access to the 12¹ and 11¹ levels because of the weak JT activity of ν₁₂ and its interaction with ν₁₁ [245]. Therefore, PFI-ZEKE spectra could only be recorded via the vibrationally totally symmetric levels 8² and 2¹ and the corresponding spectra are shown in Fig. 7.10. The spectrum recorded via the 2¹ level also shows the band at 69561 cm⁻¹ which was dominant in the other two spectra and the two bands at 70377 and 70405 cm⁻¹ as observed via 0₀. The spectrum recorded via 8² shows in addition a weak band at 69490 cm⁻¹ and a satellite band to the higher wave number side of the main line. In all these cases, the intensity distributions are similar, as expected from the totally symmetric nature of the intermediate vibrational levels.

### 7.4.5 Rotationally resolved measurements

In order to assign the vibronic symmetry of the bands in the complex spectra of C₅H₅ reported in the preceding subsection, rotationally resolved PFI-ZEKE photoelectron
spectra have been recorded using the 1+1’ two-photon excitation scheme. For this purpose, the $\tilde{A}^2\tilde{A}_2 ^{''} \rightarrow \tilde{X}^2E_1 ^{''}$ transition was pumped by a narrow-bandwidth ultraviolet laser [48] which allowed the excitation of single rotational levels of the $\tilde{A}^2\tilde{A}_2 ^{''} 0^0$ state. The rotationally resolved two-photon resonant ionization spectrum of the $\tilde{A}^2\tilde{A}_2 ^{''} 0^0 \rightarrow \tilde{X}^2E_1 ^{''}$ transition of C$_5$H$_5$ is displayed in Fig. 7.11. The spectrum has been analyzed and assigned previously in Ref. [62]. The simulation of the spectrum based on the parameters and the Hamiltonian given in Ref. [62] and a temperature of 8K is in quantitative agreement with the experimental results, as illustrated by the inset which compares the experimental spectrum (upper trace) with the simulated spectrum (lower trace).

Rotationally resolved PFI-ZEKE photoelectron spectra of the region of the strongest band of the PFI-ZEKE photoelectron spectrum around 69572 cm$^{-1}$ recorded via the intermediate levels $(N'', K'') = (1,0), (3,0)$ and $(5,0)$ of the $\tilde{A}^2\tilde{A}_2 ^{''} 0^0$ state are shown in Fig. 7.12. For a direct comparison of the rotational structure the spectra have been shifted by the energy of the intermediate level. The vertical dotted lines mark the calculated positions of the $N^+ = 1 \sim 10$, $K^+$ levels using the rotational constant $B = \cdots$.
Figure 7.10: PFI-ZEKE photoelectron spectra of C$_5$D$_5$ recorded following two-photon resonant excitation via selected vibrational levels of the $\tilde{A}^2\Sigma^+_J$ state. The intermediate level is indicated on the right-hand side above the spectra. The horizontal axis corresponds to the sum of the wave numbers of both lasers.

0.286 cm$^{-1}$ for the $D_{5h}$ geometry of the $\tilde{a}^+ 1E'_2$ conical intersection. The comparison of the observed and predicted line positions shows that the ionic levels $N^+ = 1, 2, 3, 4$ are accessed from the (1,0) intermediate state, the levels $N^+ = 2 - 6$ from the (3,0) level and the levels $N^+ = 3 - 8$ from (5,0). The value of $K^+$ cannot be determined unambiguously because levels differing in $K^+$ lie too close to each other to be resolved at low values of $K^+$. Moreover, the spacings of rotational levels within a $K^+$ stack are equal in the symmetric top approximation. The analysis of these spectra thus requires the consideration of photoionization selection rules.

The intermediate levels used in this experiment are of $A''_i$ rovibronic symmetry. The rovibronic photoionization selection rules [172] in $D_{5h}$ symmetry are

\[
\Gamma' \rightarrow \Gamma'' \text{ for } \ell_p \text{ even}
\]

and

\[
\Gamma' \rightarrow \Gamma' \text{ or } \Gamma'' \rightarrow \Gamma'' \text{ for } \ell_p \text{ odd,}
\]

where $\Gamma$ represents one of the rovibronic symmetry labels ($A_1$, $A_2$, $E_1$ or $E_2$) without
Figure 7.11: Rotationally resolved resonance-enhanced two-photon ionization spectrum of the vibrationless $\tilde{A}^2A'' - \tilde{X}^2E''$ transition in C$_5$H$_5$. The inset shows a magnification of the central part of the spectrum, the rotational assignments in the form $(N',K') \rightarrow (N'',K'')$ and a simulation using the parameters reported in Ref. [62].

indication of parity and $\ell_p$ designates the angular momentum quantum number of the photoelectron partial wave component. In the photoelectron transition considered here, ionization occurs out of one of the $\pi$ molecular orbitals. The symmetry of the $\pi$ molecular orbitals are in order of increasing energy $a''_2$, $e''_1$ and $e''_2$. The terms that are allowed in a single-center expansion of these orbitals can be obtained by correlating the irreducible representations of the molecular point group ($D_{5h}$) to the $D_{\omega h}$ group (taking the $C_5$ and $C_\infty$ axes to coincide) which gives $\Sigma_u^+ \oplus I_g \oplus I_u$, $\Pi_g \oplus \Pi_u \oplus \Gamma_u$ and $\Delta_u \oplus \Phi_g$. The dominant terms in the single-center expansion of these orbitals are $p_{\sigma}$, $d_{\pi} + f_{\pi}$ and $f_{\sigma}$, respectively. Assuming a single-configuration approximation to be valid, ionization out of the orbitals $a''_2$, $e''_1$ and $e''_2$ would be associated with the selection rules $\Delta K = K^+ - K = (0,\pm 5)$, $(\pm 1, \pm 4)$ and $(\pm 2, \pm 3)$, respectively. The corresponding propensities for the change in the rotational angular momentum quantum number $\Delta N = N^+ - N$ are $(0,\pm 1)$, $(0,\pm 1,\pm 2,\pm 3)$ and $(0,\pm 1,\pm 2,\pm 3)$, if only the leading terms in the single center expansion of the $\pi$ orbitals are retained. The spectra shown in Fig. 7.12 show that the largest observed change in rotational angular momentum
amounts to 3 and that smaller changes are not significantly more probable, which rules out a contribution of the $a_2''$ molecular orbital. Moreover, the lowest ionic rotational quantum number amounts to $N^+ = 1$ which implies $\Delta K = \pm 1$. $\Delta K=0$ can be excluded because the rovibronic symmetry of the $K^+ = 0$ ionic levels would have to be $E$ for a vibronic $E$ symmetry and therefore cannot be accessed from the selected intermediate levels of $A'_2$ rovibronic symmetry, and every second rotational line would be missing for an $A$ vibronic band (the rovibronic levels of symmetries $A'_2$ and $A''_2$ have zero spin-statistical weights in $C_5H_5$).

This observation indicates that ionization takes place out of the $\pi$ molecular or-
bital of symmetry \( e''_i \), i.e., that the observed intensity in the photoelectron spectrum is borrowed from the transition to configuration (ii) in Eq. (7.1), the mechanism for intensity borrowing being of the Herzberg-Teller type in the cation (see discussion in Section 7.2.1). The conservation of nuclear spin symmetry dictates that ionic states must have rovibronic symmetry \( A'_1 \) or \( A''_1 \). All consecutive rotational levels in the ion are observed. The vibronic symmetry of the final state must therefore be doubly degenerate because every second rotational level would be missing otherwise (see above).

### 7.4.6 Vibronic calculations

The PFI-ZEKE spectra of \( \text{C}_5\text{H}_5^+ \) and \( \text{C}_5\text{D}_5^+ \) were simulated using the vibronic coupling model described in Section 7.2. The calculations consisted of a pure PJT model including the \( \tilde{a}^+ 1E'_2 \) and the \( \tilde{b}^+ 1A'_1 \) states, their spacing being fixed to the CASSCF(4,5)/cc-pVTZ value of 5600 cm\(^{-1}\). The calculations for \( \text{C}_5\text{H}_5^+ \) included the modes \( \nu_{10}, \nu_{11} \) and \( \nu_{12} \) with a harmonic oscillator basis with \( v_{\text{max}} = 13, 7 \) and 10, respectively, which sufficed to converge the vibronic eigenvalues up to 2000 cm\(^{-1}\) to better than 5 cm\(^{-1}\). The \textit{ab initio} values of the vibrational frequencies and coupling constants were slightly adjusted to improve the agreement with the spectrum and the resultant values are listed in Table 7.4. The simulations of the spectra of \( \text{C}_5\text{D}_5^+ \) only included the modes \( \nu_{10} \) and \( \nu_{11} \) because the contribution of \( \nu_{12} \) to the stabilization energy was found to be negligible. A similar observation has been made in the analysis of the \( \tilde{X}^2E'_1' \) state of \( \text{C}_5\text{D}_5 \) and was attributed to a rotation of the normal coordinates resulting from the change in mass \([245]\). The calculations of the spectra of \( \text{C}_5\text{D}_5^+ \) were carried out using a vibrational basis with \( v_{\text{max}} = 20 \) and 12 for the modes \( \nu_{10} \) and \( \nu_{11} \).

A very simple intensity model has been used to calculate the spectra. We have assumed that the normal modes of the intermediate \( \tilde{A}^2A''_2 \) and ionic \( \tilde{a}^+ 1E'_2 \) states are identical and that the Franck-Condon factors for the transition from the \( \tilde{A}^2A''_2 \) state to the harmonic oscillator basis states are diagonal. Further, we have assumed that the diabatic electronic transition moment for the transition \( \tilde{a}^+ 1E'_2 \rightarrow \tilde{A}^2A''_2 \) is unity and that for the transition to the excited singlet state \( 1A'_1 \) vanishes. This assumption is the translation of the Herzberg-Teller coupling between the "accessible" \( 1E'_1 \) state of configuration (ii) and the "forbidden" \( \tilde{a}^+ 1E'_2 \) state of configuration (i) already mentioned at the end of the previous section.

The results of the simulations are compared to the experimental spectra recorded via the \( \tilde{A}^2A''_2 \) \( 0^0, 12^1 \) and \( 11^1 \) intermediate levels for \( \text{C}_5\text{H}_5^+ \) (panel a)) and \( 0^0 \) for \( \text{C}_5\text{D}_5^+ \) (panel b)) in Fig. 7.13. The calculated transitions are labeled according to the vibronic angular momentum quantum number \( j \) and a second label \( u \) which serves to distinguish different states of the same \( j \). The most striking difference in the spectra of \( \text{C}_5\text{H}_5^+ \) and \( \text{C}_5\text{D}_5^+ \) is the much smaller spectral density in the spectra of the latter
species. This observation is reproduced by the calculations and can thus be attributed to the rotation of normal modes discussed above. The origin band, which is assigned to the band at 69501 cm\(^{-1}\) in C\(_5\)H\(_5\) and at 69491 cm\(^{-1}\) in C\(_5\)D\(_5\) is very weak in the spectra recorded via the 0\(^0\) intermediate level whereas the second band located 71 cm\(^{-1}\) above the origin is the dominant feature in both spectra. The intensity ratio of these two lines is inverted when the excitation occurs through the 11\(^1\) or 12\(^1\) levels of the \(\tilde{A}^2\!\!A^\prime\) state, in good agreement with the calculations. The third band in the spectra of C\(_5\)H\(_5\) (at 69577 cm\(^{-1}\)) is absent in the spectrum of C\(_5\)D\(_5\) and corresponds to the limit of a Rydberg series observed in the photoionization spectrum and is attributed to an excited vibrational level of the \(\bar{X}^+\!\!3A^\prime\) state, most likely the 13\(^2\) level (see Fig. 7.8). The transition to this level possesses a large Franck-Condon factor because the fundamental frequency \(v_{13}\) of the \(\bar{X}^+\!\!3A^\prime\) ionic state is almost twice that of the \(\tilde{A}^2\!\!A^\prime\prime\) state [245]. The next higher band is relatively weak in the excitation via 0\(^0\) but almost as intense as the origin band in the excitation via 12\(^1\) and 11\(^1\), in agreement with the calculations.

Overall, the calculations correctly predict the main features of the experimental spectra, particularly at low energies where calculated and observed positions are in quantitative agreement. The intensity calculations also reproduce several characteristic features of the observed intensity distributions, in particular the relative intensities of the lowest two transitions and their dependence on the intermediate vibrational level. The main difference between the calculated and measured intensities is that several weak lines in the experimental spectrum are predicted with zero intensity. This discrepancy is a consequence of the (crude) assumption of diagonal Franck-Condon factors in the evaluation of Eq. (7.19). At higher energies, the agreement between the calculated and experimental spectra deteriorates and the high spectral density prevents conclusive assignments.

The agreement between the calculated and observed spectra of C\(_5\)D\(_5\) is satisfactory. The band at 70567 cm\(^{-1}\) corresponds to a wave number of 1079 cm\(^{-1}\) and can be assigned to the 2\(^1\) C-C symmetric stretching mode. The positions of the vibrational bands in the PFI-ZEKE photoelectron spectra of C\(_5\)H\(_5\) and C\(_5\)D\(_5\) are listed with the corresponding assignments in Tables 7.6 and 7.7, respectively.

The comparison of the calculated and observed spectra indicates that the origins of the \(\bar{a}^+\!\!1E^\prime\) (\(1\!A^1\) component) states have actually been observed at the positions 69501 cm\(^{-1}\) in C\(_5\)H\(_5\) and 69491 cm\(^{-1}\) in C\(_5\)D\(_5\), respectively.

### 7.5 Discussion

All electronic states belonging to configuration (i) of Eq. (7.1) are accessible in the single-photon VUV experiment. By contrast, ionization from the \(\tilde{A}^2\!\!A^\prime\) state of con-
7.5. Discussion

Figure 7.13: PFI-ZEKE photoelectron spectra of C₅H₅ (panel a) and C₅D₅ (panel b) recorded following two-photon resonant excitation to the lower component of the a⁺1E₂ state via selected vibrational levels of the A₂A' state. The intermediate level is indicated on the right-hand side above the spectra. The spectra are compared to simulations (vertical stick spectra) of the vibronic structure including the modes ν₁₀, ν₁₁ and ν₁₂ in C₅H₅⁺ and ν₁₀ and ν₁₁ in C₅D₅⁺. The bands marked with an asterisk coincide with lines of the precursor C₅H₆ (see Fig. 7.9).
figuration \((a''_1)^1(e'_1)^4(e''_2)^0\) leads to the excited configurations (ii) and (iii) of Eq. (7.1) and the states of configuration (i) can only be observed through vibronic or configuration interactions. Since none of the accessible configurations possesses an electronic state of symmetry \(1E''_2\), the transition to the \(\tilde{a}^+ 1E''_2\) state must gain intensity and can only do so by three mechanisms.

1) The distortion along the \(e'_2\) modes mixes the \(\tilde{a}^+ 1E''_2\) state with the \(\tilde{b}^+ 1A'_1\) state and with the \(1E'_1\) state of configuration (ii). Since photoionization to the latter state is allowed, the transition to the \(\tilde{a}^+ 1E''_2\) state becomes allowed by a Herzberg-Teller mechanism. This mechanism cleanly selects the \(\tilde{a}^+ 1E''_2\) state and does not lend intensity to the transitions to the \(\tilde{X}^+ 3A'_2\) state because the \textit{ab initio} data show that the latter is not subject to significant vibronic coupling at low energies. According to this mechanism, the intensity in the spectrum should originate from the transition moment to the diabatic \(1E''_2\) component rather than from that to the \(1A'_1\) component.

2) The \(\tilde{b}^+ 1A'_1\) state could gain intensity from configuration interaction with the \(1A'_1\) state of configuration (iv). This mechanism would lead to a very different intensity distribution from that expected for the first mechanism because the intensity would be carried by the transition moment to the diabatic \(1A'_1\) component.

3) Forbidden transitions in photoelectron spectra can gain intensity from allowed ionization channels because of channel interactions in the close-coupling region of the ion-electron complex. Transitions to low members of Rydberg series converging on allowed ionization thresholds can lead to a local enhancement of the intensity of PFI-ZEKE photoelectron spectra and to the observation of forbidden transitions [269]. Such a mechanism is not expected to be highly selective in terms of electronic or vibronic symmetries of the ionic states because the vibronic structure of the collision complex is significantly perturbed by the Rydberg electron. In particular, this mechanism is not expected to be selective either in favor of the \(\tilde{a}^+ 1E''_2\) or the \(\tilde{X}^+ 3A'_2\) state.

The dominant mechanism responsible for the observation of the \(\tilde{X}^+ 3A'_2 \rightarrow \tilde{A}^2A''_2\) transition can be identified as the first mechanism listed above by considering the vibrational intensity distributions in the spectra and the results of the rotationally resolved measurements. The latter indeed directly indicate the mixing of configuration (ii) (see subsection 7.4.5). In the simulations of vibrational intensities, we have assumed that the only nonvanishing transition moment is that to the diabatic \(1E''_2\) component, which has explained the observed intensity distributions in the two lowest bands and their dependence on the intermediate level. In model calculations relying on a strong transition moment to the \(1A'_1\) component, the intensity pattern in these lowest bands was found to be inverted. The second mechanism can thus be ruled out.

The third mechanism also contributes to the observed intensity pattern. The absence of a sharp onset of the photoionization signal at the \(\tilde{X}^+ 3A'_2\) threshold indicates a negligible direct ionization to the \(3A'_2\) state. However, the structured photoion-
7.6. Conclusions

The results of our investigations of the cyclopentadienyl cation by high-resolution photoelectron spectroscopy and \textit{ab initio} quantum chemical calculations can be summarized as follows:
(i) The cyclopentadienyl cation possesses a ground electronic state of symmetry $^3A'_2$ with a $D_{5h}$ minimum energy structure.

(ii) The first excited electronic state of symmetry $^1E'_2$ is subject to a strong PJT interaction with the next higher singlet state of symmetry $^1A'_1$ which stabilizes the lower state by $\sim 4000$ cm$^{-1}$.

(iii) The adiabatic ionization energies corresponding to the formation of the $X^+ 3A'_2$ and $\ddagger^+ 1E'_2$ states are $67967 \pm 4$ cm$^{-1}$ and $69501 \pm 4$ cm$^{-1}$, respectively, so that the singlet-triplet interval amounts to $1534 \pm 6$ cm$^{-1}$. As discussed in Ref. [271] this interval is a key quantity in the characterization of diradicals and an important test for the quality of ab initio calculations.

(iv) The $\ddagger^+ 1E'_2 - \overline{A}^2A''_2$ photoionizing transition, which is forbidden in the single-configuration approximation, has been observed in our resonance-enhanced two-photon experiments because of a Herzberg-Teller interaction with the excited $^1E'_1$ state which is mediated by the JT active $e'_1$ and the PJT active $e'_2$ modes. Since the latter are responsible for a strong geometric distortion, their contribution is likely to be dominant.

(v) In the $D_{5h}(M)$ molecular symmetry group, the linear JT (PJT) and quadratic JT (PJT) interactions are restricted by symmetry to distinct sets of vibrational modes. Since the PJT stabilization dominates largely over the linear JT stabilization, the nuclear motion in the lowest vibronic levels of $C_5H_5^+$ does not encircle any conical intersection. This is in contrast to a recent analysis [250], in which the authors claimed that the distortion of $C_5H_5^+$ could be understood in terms of a linear JT effect and that the nuclear motion encircled six conical intersections. Although the latter statement may apply to highly excited vibronic levels lying close to the location of the electronic degeneracies, we find no evidence for the former.

(vi) The weakness of the linear JT effect in the $\ddagger^+ 1E'_2$ state confirms the general rule derived by Watson [263], that the linear JT effect vanishes in an electronic state containing an even number of electrons in $e$ orbitals. This result has an interesting consequence for antiaromatic molecules: Since they possess $4n$ electrons in $\pi$ molecular orbitals, the linear JT effect is expected to be negligible in all of their low-lying electronic states and vibronic coupling will thus be dominated by the PJT effect. In the special case of the molecules with $D_{4nh}(M)$ symmetry, the linear JT effect is inexistent anyway because the electronic states resulting from the most stable electronic configuration are nondegenerate (since $E \otimes E$ does not contain any degenerate representation in these groups).

(vii) The crossing of the singlet and triplet surfaces occurs close to the minimum of the lowest singlet surface. Vibrational perturbations are a probable consequence and a possible explanation for the complexity of the observed vibronic structure at higher energies. The cyclopentadienyl cation may thus represent an interesting test case for studying the joint effects of vibronic coupling and an intersystem crossing.
Chapter 8

The Jahn-Teller effect in tetrahedral symmetry: large-amplitude tunneling motion and rovibronic structure in CH$_4^+$ and CD$_4^+$

8.1 Introduction

The present chapter describes the results of experimental and theoretical investigations of the rovibronic structure of CH$_4^+$ and CD$_4^+$ which has provided the first complete assignment of the level structure of these cations at low energies. A brief account of the analysis of the CH$_4^+$ spectra has been given in Ref. [37]. Innovations in experimental and theoretical procedures were required to achieve this goal. Experimentally, we have implemented double-resonance excitation techniques combining sources of vacuum-ultraviolet (VUV) and infrared (IR) radiation to experimentally assign the nuclear spin symmetry of the observed ionic levels. Theoretically, a tunneling treatment adequate to describe the complex topological properties of the potential energy surface of CH$_4^+$ has been developed and extended to include end-over-end rotation of the molecule.

The methane radical cation CH$_4^+$ is of fundamental importance in chemistry. It plays a role in the chemistry of interstellar clouds and planetary atmospheres. In mass spectrometry it is commonly used as reagent in chemical ionization. The ion-molecule chemistry of CH$_4^+$ is very rich, leading to other fundamental molecular ions like CH$_3^+$ and C$_2$H$_4^+$. So far, CH$_4^+$ has not been detected spectroscopically because neither its structure nor its transition frequencies were precisely known.

The methane cation is the simplest organic cation possessing a threefold degenerate electronic ground state which makes it the prototypical system for studies of the Jahn-Teller (JT) effect in the cubic point groups. Despite many previous studies,
hardly any high-resolution experimental information is available on the JT effect in tetrahedral symmetry. The methane cation is subject to a particularly strong JT effect with a stabilization energy of 1.5 eV. The potential energy surface is pathologically flat near the minimum, and the cation is highly fluxional in its ground electronic state, the hydrogen atoms exchanging on a sub-ns timescale. The investigation of the rovibronic structure thus offers the opportunity to fully characterize the JT effect and to deepen the current understanding of the dynamics of fluxional molecules. With only nine electrons, the methane cation can serve as a test for ab initio quantum chemical calculations and full-dimensional calculations of its nuclear dynamics [272,273].

Studies by electron paramagnetic resonance [274,275] have proven that the protons in CH$_4^+$ exchange within the experimental timescale and that the hydrogen and deuterium atoms in CH$_2$D$_2^+$ occupy different positions. These observations were interpreted in terms of a C$_{2v}$ equilibrium structure of the methane cation. A group theoretical analysis of the anomalous temperature dependence of the ESR spectra of CH$_4^+$ [276] identified two molecular symmetry groups (A$_4$ or T$_4$) that are consistent with the observed spectra but no further restrictions could be made. The vibronic structure has been partially resolved by He I photoelectron spectroscopy [277,278] and the spectra have revealed that the Jahn-Teller stabilization of CH$_4^+$ amounts to more than 1 eV. However, the vibrational assignments provided in Refs. [277,278] are entirely different. A major progress was the recording of the rotationally resolved pulsed-field ionization zero-kinetic-energy photoelectron (PFI-ZEKE-PE) spectrum of CH$_4$ [279] which was followed by a study of partially and the fully deuterated isotopomers [280]. Although the vibrational structure of CH$_4^+$ and its isotopomers at low energies could be understood qualitatively with the help of a one-dimensional model for pseudorotation, the spectral structures could only be assigned in the lowest vibronic level of CH$_2$D$_2^+$ which could be analyzed with an asymmetric rigid rotor Hamiltonian [281]. This analysis established that the isolated CH$_2$D$_2^+$ cation possesses a C$_{2v}$ equilibrium structure. The model was however incapable of reflecting the full symmetry of the problem because of its reduced dimensionality and therefore, neither the vibronic nor the rovibronic symmetries could be predicted correctly. Moreover, the model did not incorporate the effects of the geometric phase and it has underestimated the size of the tunneling splittings.

Theoretically, a C$_{2v}$ equilibrium structure has first been predicted by Meyer [282] from ab initio configuration interaction calculations whereas earlier articles had reported a D$_{2d}$ or C$_{3v}$ minimum energy structure [283,284]. The distortion from the tetrahedral to the C$_{2v}$ geometry leads to twelve equivalent minima which can be separated in two enantiomeric sets. Detailed investigations of the potential energy surface [285,286] revealed that the barriers between the six minima within one set are low and that CH$_4^+$ undergoes a large-amplitude tunneling motion. The predicted barrier height lies in the range 350-1050 cm$^{-1}$ [285-287] but is strongly dependent on
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The large-amplitude motion can be understood as a cyclic exchange of three hydrogen atoms via a saddle-point of $C_s$ symmetry \[285\]. Apart from the attempts of Takeshita \[288\], Marinelli and Roche \[289\], Reeves and Davidson \[290\] and Signorell and Sommavilla \[291\], no calculations of the rovibronic structure of $\text{CH}_4$ have been reported.

The Jahn-Teller effect of an orbitally threefold degenerate state interacting with vibrations of symmetry $\epsilon$ and $f_2$, denoted $T\oplus(e\oplus t_2)$, has been studied theoretically. Öpik and Pryce \[231\] were the first to study the number and types of possible minima on the lowest potential energy surface and found that the minima are either trigonal or tetragonal, i.e., of $D_{2d}$ or $C_{3v}$ symmetry for a tetrahedral molecule. Bersuker and Polinger \[292\] have subsequently discovered that the inclusion of quadratic vibronic coupling terms allows points of $C_{2v}$ symmetry to become minima and have studied the tunneling splittings associated with this situation. Although the $T\oplus(e\oplus t_2)$ problem is very common in crystals, it could not be studied in detail so far, because high-resolution gas-phase spectroscopic data were not available or not assigned. This is in contrast to the $E\oplus e$ JT problem which is now well understood in several molecular systems \[33\].

Large-amplitude motions are of fundamental importance for the understanding of molecular structure and dynamics. The JT effect is often associated with a particularly interesting category of large-amplitude motions which are often referred to as "pseudorotations". This type of motion connects equivalent minima of the potential energy surfaces with each other and takes place when the barriers between them are low enough. This situation applies, for instance, to the ground states of $\text{Li}_3$ and $\text{Na}_3$ which possess three equivalent minima and has been characterized in detail by high-resolution spectroscopy \[32,240,265\]. Several theoretical methods have been developed to analyze the tunneling-rotation structure in such systems. The most accurate treatment is achieved by a full variational calculation including all degrees of freedom \[293\] which predicted the tunneling-rotation spectrum of $\text{Na}_3$ in excellent agreement with the experiment. Several effective Hamiltonian models have been developed for the alkali trimers. Ohashi et al. have derived an effective rotation-pseudorotation Hamiltonian \[294\] that includes all operators allowed by symmetry and have obtained a quantitative agreement with the experimental data. Mayer and Cederbaum \[295\] have developed a general formalism to calculate rotational structures of vibronically coupled systems. Its first step consists of solving the vibronic problem in a product basis of diabatic electronic and harmonic oscillator basis functions. In a second step, an effective rotational Hamiltonian is constructed for which all parameters can be calculated from the vibronic eigenvectors. To our knowledge, the combined treatment of rotation and pseudorotation in tetrahedral symmetry has not been considered so far.
The present chapter is organized as follows. The next section describes the experimental measurement and assignment procedures. Section 8.3 is devoted to the derivation of the tunneling matrix and the effective tunneling-rotation Hamiltonian. Section 8.4 presents the PFI-ZEKE spectra of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and $^{12}\text{CD}_4$, their assignment and the simulation of the spectra with the tunneling-rotation Hamiltonian. In Section 8.5 the results of the analysis are discussed and compared to \textit{ab initio} data and earlier results.

8.2 Experiment

The photoion/photoelectron spectrometer and the VUV light source used in the present experiments have been described in chapter 2 (see Fig. 2.2). Methane (Pangas, 99.995 \% purity), $^{13}\text{CH}_4$ (Cambridge isotope laboratories (CIL), 98 \% chemical purity, 98 \% isotopic enrichment) or $\text{CD}_4$ (CIL, 98 \% chemical purity, 98 \% isotopic enrichment) were introduced into the spectrometer by means of a pulsed, skimmed supersonic expansion. The valve was operated at a repetition rate of 10 Hz and a stagnation pressure of 2-3 bar. Expansions of either the pure gas or a mixture with Ar were used. VUV radiation was generated by two-photon resonance-enhanced sum-frequency mixing ($\nu_{\text{VUV}}=2\nu_1 + \nu_2$) of the output of two Nd:YAG-pumped dye lasers in Xe using the $(5p)^56p[1/2]_o^-(5p)^61S_0$ two-photon resonance at $2\nu_1=80118.964$ cm$^{-1}$ as described in chapter 2.

IR radiation around 3000 cm$^{-1}$ (6000 cm$^{-1}$) was generated by difference-frequency mixing in a KTiOAsO$_4$/KTA (KTiOP0$_4$/KTP) crystal [50,51] as described in Section 2.1.3. Pulse energies of up to 1 mJ were obtained around 3.3 $\mu$m (1.6 $\mu$m) using pulse energies of 10 mJ at 630 nm (650 nm) and 15 mJ at 532 nm (1064 nm). The IR beam was then sent into the photoexcitation chamber using gold-coated mirrors and counterpropagated against the VUV beam. The IR pulse was timed to precede the VUV pulse by $\approx$ 10 ns. The IR frequency was calibrated by comparing the measured line positions of the $\nu_3$ and $2\nu_3$ bands of $\text{CH}_4$ with literature values [52]. Calibration of the visible radiation was achieved by recording optogalvanic spectra of neon and comparing the observed wave numbers to the tables given in Ref. [47]. The VUV wave number was determined by building the sum of the two-photon resonance wave number and the wave number of the second laser which was also determined by recording optogalvanic spectra of neon.

PFI-ZEKE photoelectron spectra were recorded by monitoring the pulsed electric field ionization of high Rydberg states located immediately below the ionization thresholds as a function of the laser wave number. A positive pulsed electric field of less than 1 V/cm and of 1 $\mu$s duration was applied 1 $\mu$s after photoexcitation and was immediately followed by a negative pulsed electric field of comparable amplitude.
The first (discrimination) pulse served the purpose of removing prompt electrons and of ionizing the highest Rydberg states. The PFI-ZEKE spectra were obtained by recording the field-ionization yield of the second pulse.

The absolute positions of the ionic levels above the neutral ground state was determined from the measured wave numbers of the PFI-ZEKE lines after a correction was made to account for the shifts of the ionization thresholds induced by the electric fields according to the procedure described in Ref. [72].

Four different experiments were performed. First, single-photon VUV PFI-ZEKE photoelectron spectra were recorded by monitoring the pulsed-field ionization electron signal as a function of the VUV wave number for the species CH$_4$, $^{13}$CH$_4$ and CD$_4$. Second, IR spectra of the $v_3$ and $2v_3$ bands were recorded by setting the VUV wave number just below the adiabatic ionization energy and recording the ion signal as a function of the IR wave number. Third, IR+VUV resonance-enhanced two-photon spectra of CH$_4$ were recorded by holding the IR wave number fixed on a selected rovibrational transition of the asymmetric stretch fundamental ($v_3$) or its first overtone ($2v_3$) and tuning the VUV laser. Finally, "ZEKE dip" measurements were performed for CH$_4$ in which the VUV frequency was held at the position of a given line in the single-photon PFI-ZEKE spectrum and the depletion of the photoelectron signal was monitored at the three IR frequencies corresponding to the R(0), R(1) and R(2) lines of the $v_3$ band. In these measurements, pulse energies of $\approx 200$ $\mu$J (beam waist $\approx 2$ mm) were sufficient to entirely saturate the infrared transitions. Depletions of up to 50% were observed whenever the IR and VUV transitions had a common lower level.

The rotationally resolved IR spectra of CH$_4$ and $^{13}$CH$_4$ around 6000 cm$^{-1}$ are shown in Figs. 8.1a and b, respectively. The spectra correspond to the transition from the vibrationless ground state to the $v_3 = 2$ vibrational level. The observed transitions are easily assigned to P(2), P(1), an unresolved Q branch, R(0), R(1) and R(2) and the measured wave numbers correspond well with the literature values given in [52]. These spectra indicate that only the lowest state of each nuclear spin symmetry ($J = 0$ corresponding to nuclear spin symmetry $A_1$, $J = 1$ to $F_2$, $J = 2$ to $E$) is populated significantly in the supersonic beam, which corresponds to a rotational temperature of less than 7 K.

### 8.3 Theory

#### 8.3.1 The vibronic problem

A threefold degenerate electronic state of a polyatomic molecule in its tetrahedral reference geometry is subject to vibronic coupling with vibrational modes of e and $f_2$
Figure 8.1: IR+VUV two-photon resonance-enhanced ionization spectra of jet-cooled $^{13}\text{CH}_4$ (trace a) and $\text{CH}_4$ (trace b) in the region of the $2\nu_3$ overtone transition. The transitions are labeled according to the associated changes in rotational angular momentum $P$ ($\Delta J=-1$), $Q$ ($\Delta J=0$), $R$ ($\Delta J=+1$) and the rotational angular momentum quantum number of the initial level. The transitions of $^{13}\text{CH}_4$ are red-shifted by 17.7 cm$^{-1}$ compared to the transitions of $\text{CH}_4$.

symmetry and the corresponding Hamiltonian can be expressed as [292]

$$\hat{H}_{JT} = \sum_{\gamma \gamma'} \frac{\hbar^2}{2\mu_t} \frac{\partial^2}{\partial Q_{\gamma \gamma}^2} C_\alpha + U(Q)$$  \hspace{1cm} (8.1)

with

$$U(Q) = \sum_{\gamma \gamma'} \left( \frac{1}{2} G_{\gamma \gamma'} Q_{\gamma \gamma}^2 C_\alpha + V_{\gamma \gamma'} Q_{\gamma \gamma} C_{\gamma \gamma'} \right) + W [Q_\xi \left( -\frac{1}{2} Q_\eta + \frac{\sqrt{3}}{2} Q_z \right) C_\xi + Q_\eta \left( -\frac{1}{2} Q_\theta - \frac{\sqrt{3}}{2} Q_z \right) C_\eta + Q_\xi Q_\eta Q_\theta C_\zeta], \text{ with } \gamma \in \Gamma, \Gamma = e, f_2.$$  \hspace{1cm} (8.2)

$\gamma = \theta, \epsilon$, and $\xi, \eta, \zeta$ denote the components of the irreducible representations $e$ and $f_2$, respectively, with the transformation properties $\theta \sim 2z^2-x^2-y^2$, $\epsilon \sim \sqrt{3}(x^2-y^2)$, $\xi \sim y z$, $\eta \sim x z$, $\zeta \sim x y$, where $x, y, z$ are the Cartesian coordinates. $V_{\Gamma}$ stands for the linear vibronic coupling constants, $G_{\Gamma}$ for the sum of quadratic vibronic coupling constants and harmonic frequencies and $W$ for the bilinear vibronic coupling constants between modes of symmetry $e$ and $f_2$ and $\mu_t$ for the reduced mass corresponding to...
the $\Gamma = e$ and $f_2$ modes. The matrices $C_{\Gamma \nu}$ of Clebsch-Gordan coefficients defined in the space $|\xi\rangle, |\eta\rangle, |\zeta\rangle$ of functions of the electronic triplet in its reference geometry are given by

$$C_{\alpha} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_{\beta} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad C_{\gamma} = \begin{pmatrix} -\sqrt{3}/2 & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (8.3)$$

$$C_{\xi} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad C_{\eta} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad C_{\zeta} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (8.4)$$

In the Hamiltonian (8.1), only the most important terms have been included, i.e., those that can modify the composition of the electronic eigenfunctions of the potential term $U(Q)$, which will be used in setting up the tunneling matrices.

The adiabatic potential $E(Q)$ with the corresponding adiabatic electronic wavefunctions $|\alpha(Q)\rangle$ is defined by the eigenvalue equation

$$U(Q)|\alpha(Q)\rangle = E(Q)|\alpha(Q)\rangle \quad (8.5)$$

and its extremal points have been determined in Refs. [231,292]. In the absence of quadratic coupling, the distortion of a tetrahedral molecule leads to minima of either $C_{3v}$ or $D_{2d}$ symmetry whereas the points of $C_{2v}$ symmetry are always saddle-points on the lowest adiabatic potential surface [231]. If quadratic coupling is included, the points of $C_{2v}$ symmetry can become minima [292].

### 8.3.2 The potential energy surface of the methane cation

The most detailed study of the potential energy surfaces of CH$_4^+$ have been performed by Paddon-Row et al. [285] and Frey and Davidson [286] who agree on the essential properties of the potential energy surface, especially the $C_{2v}$ geometry of the minimum energy structure. More recently, the energies of several stationary points have been recalculated at a higher level of theory [287] and these results are in good agreement with those of Ref. [286]. The tetrahedral configuration of CH$_4^+$ corresponds to a triply degenerate conical intersection that lies approximately 12000 cm$^{-1}$ above the minima of $C_{2v}$ geometry. A distortion along the modes of symmetry $f_2$ ($\nu_3$ antisymmetric stretch and $\nu_4$ bending) leads to two different structures of $C_{3v}$ geometry that correspond to second-order saddle points on the lowest adiabatic surface. One of them has three equal C-H bonds that are shorter than the fourth C-H bond. This structure has a nondegenerate electronic ground state and a doubly degenerate excited state. The other $C_{3v}$ structure has three equal C-H bonds that are longer than the
fourth and a doubly-degenerate electronic ground state. A distortion along the mode of symmetry e ($v_2$, bending) leads to a $D_{2d}$ structure that is also a second-order saddle point on the lowest sheet of the potential energy surface. This structure has a non-degenerate ground state and a doubly-degenerate excited state. The minima of $C_{2v}$ geometry result from a distortion along $v_2$, $v_3$ and $v_4$. Two sets of first-order saddle points have also been located and possess a $C_s$ structure. The first lies approximately 1050 cm$^{-1}$ and the second about 5400 cm$^{-1}$ above the minima corresponding to the $C_{2v}$ structure [285]. The number of different possible arrangements of the four hydrogen atoms is equal to the ratio between the order of the complete permutation-inversion (CNPI) group of CH$_4^+$ (G$_{48}$ or $S_4^*$) and the order of the point group of the considered structure. Thus, the tetrahedral geometry allows for $O(G_{48})/O(T_d) = 2$ structures that are enantiomers of each other. In $C_{3v}$ geometry there are 8 equivalent structures, in $C_{2d}$ 6, in $C_{2v}$ 12, and in $C_s$ 24.

The twelve equivalent $C_{2v}$ minima of CH$_4^+$ can be subdivided into two enantiomeric sets of six structures that differ in the numbering of the identical H atoms, as depicted in Fig. 8.2. The two sets of twelve low-lying first-order saddle points of $C_s$ symmetry correspond to the transition states for the interconversions of minimum energy structures within each set and lie in the middle of the lines connecting the $C_{2v}$ minima, whereas the higher-lying saddle points correspond to the transition state of the inversion of a $C_{2v}$ structure into its enantiomeric structure. The former process corresponds to a cyclic exchange of three hydrogen atoms and repeated cyclic exchanges are referred to as pseudorotation. The latter process corresponds to the stereomutation of CH$_4^+$ ([296, 297]). At the resolution of up to 0.3 cm$^{-1}$ of the present experiments, one can expect to observe tunneling splittings resulting from the pseudorotational motion in the ground state. The barrier of about 5400 cm$^{-1}$ for stereomutation is too high for the inversion splittings to be observable. The order of the molecular symmetry group can therefore be reduced by removing all operations that interconvert enantiomers. G$_{48}$ and $S_4^*$ contain operations of the type $E(123)$, $(12)(34)$, $(12)$, $(1234)$, $E^*$, $(123)^*$, $(12)(34)^*$, $(12)^*$, $(1234)^*$. The operations $E^*$ and those of the type $(12)$, $(123)^*$, $(1234)$ and $(12)(34)^*$ interconvert enantiomers and are not feasible. The resulting group is known in the literature as $T_d(M)$ and is the adequate molecular symmetry group to describe the rovibronic levels of CH$_4^+$ and CD$_4^+$ as long as the inversion splittings are not resolved.

The correlation of the rovibronic symmetry labels in the $T_d(M)$ and $S_4^*$ groups including spin-statistical weights for CH$_4^+$ and CD$_4^+$ are given in Tables 8.1 and 8.2, respectively. At sufficient resolution, the stereomutation of CH$_4^+$ could be observed as a splitting of the levels of rovibronic symmetry E because both parity components of this symmetry have a nonzero spin-statistical weight. The observation of stereomutation is much easier in CH$_4^+$ than in CH$_4$ because the latter has a stereomutation barrier that is comparable to the C-H bond dissociation energy, i.e. about 36000 cm$^{-1}$ [296].
8.3. Theory

Figure 8.2: Topological representation of the connectivity of the twelve equivalent minimum energy structures of $C_{2v}$ symmetry of $\text{CH}_4$. The vertices correspond to the $C_{2v}$ minimum energy geometries and the edges to the equivalent pseudorotation-tunneling paths connecting the minima via the low-lying $C_s$ transition states. The dotted line represents the barrier for stereomutation separating each minimum structure from its enantiomer. Four faces of the octahedron correspond to a $C_{3v}$ geometry with a degenerate ground state (marked with a dot) and the other four to a $C_{3v}$ geometry with a nondegenerate ground state (adapted from Ref. [285]).

Because we have not observed tunneling splittings associated with the stereomutation $^a$, the following arguments will be restricted to one enantiomeric set of six $C_{2v}$ structures and will be developed using the $T_d(M)$ group. The derivation of the correlation presented in Table 8.1 is essential for the understanding of the spectra of $\text{CH}_4$, but does not correspond to the correlation given in Ref. [290], with the important consequence that the rotationless ground state of $\text{CH}_4$ has a nonzero spin-statistical weight.

8.3.3 The tunneling problem

In the light of the ab initio results summarized in Section 8.3.2, the lowest band of the PFI-ZEKE photoelectron spectrum of $\text{CH}_4$ is expected to reveal the effects of a tunneling motion. Tunneling is most simply treated in a matrix representation using basis states that are strongly localized in the vicinity of the minimum energy

$^a$An ab initio calculation of the reaction path for stereomutation at the UMP2/cc-pVDZ level gives a barrier of 5100 cm$^{-1}$ (4700 cm$^{-1}$ after zero-point correction). A WKB estimation of the splitting associated with stereomutation following Ref. [298] gives the value $1 \cdot 10^{-7}$ cm$^{-1}$. 
Table 8.1: Correlation table of the rovibronic symmetries from the $T_d(M)$ to the $S_4^*$ molecular symmetry group including nuclear spin statistical weights for CH$_4$.

<table>
<thead>
<tr>
<th>$T_d(M)$</th>
<th>$S_4^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1(5)$</td>
<td>$A_1^<em>(0) \oplus A_2^</em>(5)$</td>
</tr>
<tr>
<td>$A_2(5)$</td>
<td>$A_2^<em>(5) \oplus A_1^</em>(0)$</td>
</tr>
<tr>
<td>$E(2)$</td>
<td>$E^+(1) \oplus E^-(1)$</td>
</tr>
<tr>
<td>$F_1(3)$</td>
<td>$F_1^+(3) \oplus F_2(0)$</td>
</tr>
<tr>
<td>$F_2(3)$</td>
<td>$F_2^<em>(0) \oplus F_1^</em>(3)$</td>
</tr>
</tbody>
</table>

Table 8.2: Same as Table 8.1 but with nuclear spin statistical weights for CD$_4$.

<table>
<thead>
<tr>
<th>$T_d(M)$</th>
<th>$S_4^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1(15)$</td>
<td>$A_1^<em>(15) \oplus A_2^</em>(0)$</td>
</tr>
<tr>
<td>$A_2(15)$</td>
<td>$A_2^<em>(0) \oplus A_1^</em>(15)$</td>
</tr>
<tr>
<td>$E(12)$</td>
<td>$E^+(6) \oplus E^-(6)$</td>
</tr>
<tr>
<td>$F_1(18)$</td>
<td>$F_1^+(3) \oplus F_2(15)$</td>
</tr>
<tr>
<td>$F_2(18)$</td>
<td>$F_2^<em>(15) \oplus F_1^</em>(3)$</td>
</tr>
</tbody>
</table>

structures [299]. The basis states used in the present analysis are defined as follows

$$\phi_n = |n\rangle |\chi_n\rangle,$$  \hspace{1cm} (8.6)

where $|n\rangle = |a(Q_n)\rangle$ is the adiabatic electronic function in the $n^{th}$ potential well and $|\chi_n\rangle$ represents the ground state vibrational function (a product of 9 harmonic oscillator functions) of the molecule in the $n^{th}$ potential well.

The adiabatic electronic functions at the geometries of the six $C_2V$ minima $|n\rangle = \frac{1}{\sqrt{2}} (|\xi\rangle + |\eta\rangle), \frac{1}{\sqrt{2}} (|\xi\rangle + |\zeta\rangle), \frac{1}{\sqrt{2}} (-|\xi\rangle + |\eta\rangle), \frac{1}{\sqrt{2}} (-|\xi\rangle + |\zeta\rangle), \frac{1}{\sqrt{2}} (|\eta\rangle - |\zeta\rangle)$ and $\frac{1}{\sqrt{2}} (|\eta\rangle + |\zeta\rangle)$ are obtained by diagonalizing the potential term $U(Q)$ for CH$_4$ that was derived in Ref. [286].

These eigenfunctions have a general validity for $C_2V$ minima resulting from a $T_\infty(e\oplus t_2)$ Jahn-Teller effect and are indeed equivalent to those obtained by Bersuker and Polinger [292]. The construction of the tunneling matrix is significantly simplified by the permutational symmetry of CH$_4$ and CD$_4$ because all six $C_2V$ minima are equivalent and so are the twelve $C_5$ saddle-points connecting the minima. The elements of the matrix are defined by $H_{ij} = \langle i | H_{\text{vib}} | j \rangle$ and $S_{ij} = \langle i | j \rangle |\chi_i\rangle |\chi_j\rangle$ where $\hat{H}_{\text{vib}}$ is the vibrational Hamiltonian for the lowest potential energy surface. The resulting generalized eigenvalue problem takes the form of a determinantal equation (see also
Ref. [37])

\[
\begin{pmatrix}
H_{11} - E & H_{12} - S_{12}E & 0 & - (H_{12} - S_{12}E) & H_{12} - S_{12}E & H_{12} - S_{12}E \\
H_{12} - S_{12}E & H_{11} - E & - (H_{12} - S_{12}E) & 0 & - (H_{12} - S_{12}E) & H_{12} - S_{12}E \\
0 & - (H_{12} - S_{12}E) & H_{11} - E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E \\
- (H_{12} - S_{12}E) & 0 & H_{12} - S_{12}E & H_{11} - E & - (H_{12} - S_{12}E) & H_{12} - S_{12}E \\
H_{12} - S_{12}E & - (H_{12} - S_{12}E) & H_{12} - S_{12}E & - (H_{12} - S_{12}E) & H_{11} - E & 0 \\
H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & H_{12} - S_{12}E & 0 & H_{11} - E
\end{pmatrix} = 0, \quad (8.7)
\]

where \( H_{11} = \langle \chi_1 | \hat{H} | \chi_1 \rangle \), \( S_{11} = \langle \chi_1 | \chi_1 \rangle \), \( H_{12} = 1/2 \langle \chi_1 | \hat{H} | \chi_2 \rangle \), and \( S_{12} = 1/2 \langle \chi_1 | \chi_2 \rangle \).

The solutions of the determinantal equation (8.7) are two sets of triply degenerate levels (\( F_2 \) and \( F_1 \)):

\[
E_{F_2} = \frac{H_{11} + 2H_{12}}{1 + 2S_{12}} \quad \text{and} \quad E_{F_1} = \frac{H_{11} - 2H_{12}}{1 - 2S_{12}} \quad (8.8)
\]

with associated eigenvectors

\[
U = \frac{1}{2} \begin{pmatrix}
1 & 0 & -1 & -1 & 0 & 1 \\
0 & 1 & -1 & 0 & 1 & -1 \\
1 & 0 & 1 & -1 & 0 & -1 \\
0 & 1 & 1 & 0 & 1 & 1 \\
1 & -1 & 0 & 1 & 1 & 0 \\
1 & 1 & 0 & 1 & -1 & 0
\end{pmatrix}, \quad (8.9)
\]

where the first three columns are the eigenvectors of vibronic symmetry \( F_2 \) and the last three columns those of symmetry \( F_1 \). The tunneling integral \( H_{12} \) is negative which results in the \( F_2 \) level being the ground state. The value of the overlap integral \( S_{ij} \) has no influence on the nature of the eigenvectors but it affects the value of the tunneling splitting \( \delta = |E_{F_2} - E_{F_1}| \).

This tunneling model can also be used to predict the nature of the ground state in the case where the minimum energy structures have a different symmetry. If the minimum energy structure is of \( D_{2d} \) geometry and inversion is still neglected, only three minima must be considered. These structures correspond to a distortion along the \( e \) mode only and the corresponding Clebsch-Gordan matrices are diagonal. Consequently, the adiabatic wavefunctions corresponding to the lowest energy in the three minima are simply equal to the diabatic basis functions \( |\xi\rangle, |\eta\rangle, |\zeta\rangle \). Because these functions are orthogonal to each other, there is no tunneling and the lowest vibronic level has the vibronic symmetry \( F_2 \). This conclusion has also been reached in the analysis of the \( T \otimes e \) JT effect in Ref. [234]. If the minimum energy structure has \( C_{3v} \) geometry, which corresponds to the \( T \otimes t_2 \) JT effect, four minima arise with the following adiabatic electronic wavefunctions: \( 1/\sqrt{3}(|\xi\rangle + |\eta\rangle + |\zeta\rangle) \), \( 1/\sqrt{3}(|\xi\rangle - |\eta\rangle - |\zeta\rangle) \), \( 1/\sqrt{3}(-|\xi\rangle + |\eta\rangle - |\zeta\rangle) \) and \( 1/\sqrt{3}(-|\xi\rangle - |\eta\rangle + |\zeta\rangle) \). Assuming a negative tunneling matrix element, tunneling splits this fourfold degenerate ground state into a three-
fold degenerate state of symmetry $F_2$ lying below a singly degenerate state of $A_1$ symmetry. This result has also been obtained in Ref. [300], where the level ordering has been shown to derive from a geometric phase. A common feature of all three cases is that the lowest level has vibronic symmetry $F_2$, i.e., the same symmetry as the electronic state in the undistorted geometry. This situation is characteristic of most Jahn-Teller problems, although exceptions have been found for large values of the quadratic coupling constants [301, 302].

The symmetry of the tunneling states corresponding to a given minimum energy geometry can also be predicted from group-theoretical arguments. First, the electronic symmetry of the ground electronic state of the molecule is determined in the point group corresponding to the minimum energy structure. Then, the corresponding irreducible representation is correlated to the molecular symmetry group of the molecule. This procedure provides the symmetry labels for the tunneling states in the molecular symmetry group directly. A minimum energy structure of $C_{2v}$ symmetry in $\text{CH}_4^+$ has a ground state of electronic symmetry $B_2$ (according to the conventions in Ref. [280]). The correlation between $C_{2v}$ and $T_d(M)$, listed in Table 8.3, gives $F_1 \oplus F_2$ for the rovibronic symmetries of the tunneling states, which corresponds to the result of the tunneling calculation given above. Similarly, a $D_{2d}$ structure of $\text{CH}_4^+$ possesses a $B_2$ ground state which correlates with $F_2$ in $T_d(M)$, and a $C_{3v}$ structure has an $A_1$ ground state which correlates with $F_2 \oplus A_1$ in $T_d(M)$. The method can also be applied to distortions that do not result from a degeneracy on the ground state surface but occur, e.g., in molecules subject to a Pseudo-Jahn-Teller (PJT) effect [33]. For example, we consider a tetrahedral molecule with an electronic ground state of symmetry $A_1$ that is distorted by a PJT effect. The electronic symmetry in $C_{2v}$ geometry can only be $A_1$ as can be derived from Table 8.3. If a tunneling process analogous to the one discussed above were observable, the correlation to $T_d(M)$ would predict tunneling states of symmetries $A_1 \oplus E \oplus F_2$, a result that was also obtained from tunneling calculations excluding the geometric phase [37]. The absence of electronic degeneracy in the ground state of the tetrahedral geometry thus leads to a profoundly altered tunneling structure.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$T_d(M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1 \oplus E \oplus F_2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2 \oplus E \oplus F_1$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
</tbody>
</table>
8.3.4 The rovibronic problem

To treat the rotational structure in the lowest tunneling states, it is convenient to use a set of rotational basis functions defined in an axis system that is common to all distorted structures. This axis system is defined with respect to the undistorted molecule and is represented in Fig. 8.3. The derivation of the rotational Hamiltonian can be divided into two steps. First, the molecule is taken in its tetrahedral reference configuration and is distorted along one of the axes to a $C_2v$ minimum energy structure. The type of distortion is indicated in Table 8.4 by two numbers in square brackets designating the hydrogen atoms that are moved away from the carbon atom and by the axis along which the C atom is displaced. The distortion depicted by arrows in Fig. 8.4 is thus denoted [23]/z. Along each axis there are two possible distortions, so that a total of six distorted structures result. Second, the axis system is rotated such that it coincides with the principal axis system of the distorted structure as illustrated in Fig. 8.4 for the structure labeled 1 on the right-hand side of Fig. 8.2. In this axis system, the rotational Hamiltonian takes the simple form

$$\hat{H}^{(1)}_{\text{rot}}/\hbar c = B\hat{J}_x^2 + C\hat{J}_y^2 + A\hat{J}_z^2,$$

(8.10)

where the superscript in parentheses designates the minimum energy structure in Fig. 8.2. Inserting the expressions for the rotational operators $\hat{J}_x', \hat{J}_y', \hat{J}_z'$ in terms of the operators defined in the global axis system, one obtains the expressions given in Table 8.4 for the rotational Hamiltonian in each minimum.
Figure 8.4: Principal axis system used for the minimum energy structure labeled 1 on the right-hand-side of Fig. 8.2.

Table 8.4: Localized asymmetric top Hamiltonian for each minimum defined in the global axis system of Fig. 8.3. The second column indicates the type of distortion as discussed in the text.

<table>
<thead>
<tr>
<th>Min.</th>
<th>Type of distortion</th>
<th>Asymmetric top Hamiltonian</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[23]/-z-distortion</td>
<td>$\hat{H}^{rot}_{11}/\hbar c = \frac{1}{2}(C + B) (f_x^2 + f_y^2) + \frac{1}{2}(B - C) (f_x f_y + f_y f_x) + A f_z^2$</td>
</tr>
<tr>
<td>2</td>
<td>[13]/-y-distortion</td>
<td>$\hat{H}^{rot}_{22}/\hbar c = \frac{1}{2}(C + B) (f_x^2 + f_z^2) + \frac{1}{2}(B - C) (f_z f_x + f_x f_z) + A f_y^2$</td>
</tr>
<tr>
<td>3</td>
<td>[14]/z-distortion</td>
<td>$\hat{H}^{rot}_{33}/\hbar c = \frac{1}{2}(C + B) (f_x^2 + f_y^2) - \frac{1}{2}(B - C) (f_x f_y + f_y f_x) + A f_z^2$</td>
</tr>
<tr>
<td>4</td>
<td>[24]/y-distortion</td>
<td>$\hat{H}^{rot}_{44}/\hbar c = \frac{1}{2}(C + B) (f_z^2 + f_x^2) - \frac{1}{2}(B - C) (f_z f_x + f_x f_z) + A f_y^2$</td>
</tr>
<tr>
<td>5</td>
<td>[12]/-x-distortion</td>
<td>$\hat{H}^{rot}_{55}/\hbar c = \frac{1}{2}(C + B) (f_y^2 + f_x^2) + \frac{1}{2}(B - C) (f_y f_x + f_x f_y) + A f_z^2$</td>
</tr>
<tr>
<td>6</td>
<td>[34]/x-distortion</td>
<td>$\hat{H}^{rot}_{66}/\hbar c = \frac{1}{2}(C + B) (f_y^2 + f_z^2) - \frac{1}{2}(B - C) (f_y f_z + f_z f_y) + A f_x^2$</td>
</tr>
</tbody>
</table>

The basis used to solve the rovibronic problem consists of the direct product of the basis states of the pure tunneling problem and symmetric top eigenfunctions $|JK\rangle$, 

$$\phi_{nJK} = |n\rangle|\chi_n\rangle|JK\rangle,$$

where $J$ is the rotational angular momentum quantum number and $K$ the quantum number for its projection on the z axis.

The tunneling-rotation Hamiltonian is defined as 

$$\hat{H} = \hat{H}_{vib} + \hat{H}_{rot}.$$ (8.12)
Its matrix representation in the basis $\phi_{nJK}$ possesses the following elements:

\[
H_{ijJKJ'K'} = \langle i|j\rangle \left( \langle x_i|\hat{H}_{\text{vib}}|x_j\rangle \langle JK|J'K'\rangle + \langle x_i|x_j\rangle \langle JK|\hat{H}_{\text{rot}}|J'K'\rangle \right) \\
= \langle i|j\rangle \left( \langle x_i|\hat{H}_{\text{vib}}|x_j\rangle \delta_{JJ'}\delta_{KK'} + \delta_{ij}\langle JK|\hat{H}_{\text{rot}}|J'K'\rangle \right) \\
= \begin{cases} 
\langle JK|\hat{H}_{\text{rot}}^{ij}|J'K'\rangle & \text{for } i = j \\
\langle i|j\rangle 2\sigma \delta_{JJ'}\delta_{KK'} & \text{for } i \neq j
\end{cases}
\]

where we have defined $\sigma = 1/2 \langle x_i|\hat{H}|x_j\rangle$ and assumed that $\langle x_i|x_j\rangle = \delta_{ij}$.

The diagonalization of this matrix provides the tunneling-rotation eigenvalues and eigenvectors. For $J = 0$ we obtain two eigenvectors of rovibronic symmetry $F_2$ and $F_1$ with the eigenvalues $E_{F_2} = 2\sigma$ and $E_{F_1} = -2\sigma$, respectively. This result is indeed equivalent to Eq. (8.8) with $H_{11} = S_{12} = 0, H_{12} = \sigma < 0$ and, in the limit of zero overlap ($\langle x_i|x_j\rangle = 0$, for $i \neq j$), establishes the relation $\delta = 4|\sigma|$ between the tunneling matrix element $\sigma$ and the tunneling splitting $\delta$ of the $J = 0$ level.

### 8.3.5 A general effective tunneling-rotation Hamiltonian

The same effective tunneling-rotation Hamiltonian can also be obtained in the basis of the eigenstates of Eq. (8.7) as

\[
\hat{H}_{\text{tre}} = U^T \hat{H}_{\text{rot}} U + \hat{H}_{\text{ve}},
\]

where $\hat{H}_{\text{rot}}$ is a diagonal matrix of rotational operators of the form of Eq. (8.10) for the six local $C_{2v}$ structures and $U$ is the eigenvector matrix (Eq. (8.9)) of the determinantal equation (8.7). $\hat{H}_{\text{ve}}$ is diagonal with eigenvalues 0 for the lower tunneling component of $F_2$ symmetry and $\delta$ for the upper tunneling component of $F_1$ symmetry (see Eq. (8.8)). Equation (8.14) was used in Ref. [37] and has the same eigenvalues as the tunneling-rotation matrix defined by Eq. (8.13). Equation (8.14) can be used to derive the formal expression

\[
\hat{H}_{\text{tre}} = \frac{1}{4} \begin{pmatrix}
E^F - D^F & -(B - C)(J_x J_y + J_y J_x) & -(B - C)(J_x J_y + J_y J_x) \\
-(B - C)(J_x J_y + J_y J_x) & E^F - D^F & -(B - C)(J_x J_y + J_y J_x) \\
-(B - C)(J_x J_y + J_y J_x) & -(B - C)(J_x J_y + J_y J_x) & E^F - D^F + \delta
\end{pmatrix}
\]

for the tunneling-rotation Hamiltonian (H.c. means Hermitian conjugate), where the upper $3 \times 3$ block on the diagonal corresponds to the vibronic state of symmetry $F_2$, the lower block to the $F_1$ vibronic state, $E = 2A + B + C$ and $D = 2A - B - C$. In order to rationalize the rovibronic coupling terms contained in the Hamiltonian (8.15) we have classified the rotational operators in the $T_d(M)$ group and the result is given in Table 8.5. The diagonal elements in Eq. (8.15) correspond to the sum of a term of
symmetry $A_1$ and a term of symmetry $E$. The off-diagonal elements of the diagonal blocks have symmetry $F_2$. Turning to the off-diagonal blocks, one finds a term of symmetry $E$ on the diagonal and terms of symmetry $F_2$ on the off-diagonal positions. All angular momentum operators appearing in this Hamiltonian are multiplied by some linear combinations of the asymmetric top rotational constants $A, B, C$. Since the Hamiltonian (8.14) has been set up in the limit of a strong static distortion, it does not contain electronic and vibrational angular momentum operators and therefore the rotational angular momenta are equal to the total angular momenta.

An alternative way of deriving an effective rotational Hamiltonian for a pair of closely spaced vibronic levels of symmetries $F_2$ and $F_1$ is by introducing all components and products of components of the total angular momentum operators up to second order that are allowed by symmetry in a $6 \times 6$ matrix representing the vibronic basis. Such a Hamiltonian can be set up by assuming that the vibronic problem has been solved and that its eigenvalues and eigenfunctions are available as discussed in Ref. [295]. Angular momentum operators that are linear combinations of terms of the form $\tilde{J}_\alpha \tilde{J}_\beta (\alpha, \beta = x, y, z)$ will be designated collectively by $\tilde{J}_\alpha \tilde{J}_\beta$ and the terms linear in $\tilde{J}$ by $\tilde{J}_\alpha$. Total angular momentum operators of the form $\tilde{J}_\alpha$ and $\tilde{J}_\alpha \tilde{J}_\beta$ can couple two vibronic states if the total rovibronic operators are totally symmetric, i.e., if

$$\Gamma_{\psi_i} \times \Gamma_{\psi_j} \times \Gamma_{J_\alpha} \supset A_1 \text{ or } \Gamma_{\psi_i} \times \Gamma_{\psi_j} \times \Gamma_{J_\alpha} \times \Gamma_{J_\beta} \supset A_1,$$

respectively. In Eq. (8.16) $\Gamma_{\psi_i}$ and $\Gamma_{J_\alpha}$ designate the irreducible representations of the vibronic basis functions and the component of the total angular momentum operator, respectively. The positions of the angular momentum operators in the rovibronic Hamiltonian matrix is defined by the Clebsch-Gordan matrices for the products of irreducible representations of $T_d(M)$.

A comparison of such a general effective Hamiltonian with the one derived in Eq. (8.15) provides a physical interpretation of our effective Hamiltonian. The totally symmetric term on the diagonal represents the rotational energy of the undistorted molecule and takes the form of a spherical top Hamiltonian with rotational constant $(2A + B + C)/4$. The terms of symmetry $E$ and $F_2$ in the $3 \times 3$ blocks on the diagonal represent the effects of the molecular distortion on the rotation of the molecule. The off-diagonal block contains operators that represent rovibronic coupling between the two vibronic states. From this analysis, we conclude that the Hamiltonian (8.15) contains all allowed operators in the expected positions, with exception of terms of the form $\tilde{J}_\alpha$. These terms represent Coriolis interactions between the rotational and the electronic and vibrational angular momenta. These interactions are absent in Hamiltonians (8.14) and (8.15) because it does not contain any electronic or vibrational angular momenta. An electronic angular momentum is in principle present because
the ground state of CH$_4$ is triply degenerate in the tetrahedral configuration and vibrational angular momentum results from the pseudorotational motion. Although the effects of these angular momenta have not been quantified for CH$_4$, it has been shown that electronic and vibrational angular momenta are quenched by strong Jahn-Teller distortions [303]. Therefore, Coriolis interactions are not expected to dominate the level structure and the approximate relation $R = N^+ = \hat{J}$ can be used to label the ionic levels. Moreover, in a general effective Hamiltonian, the coefficients of the various terms are defined from the expectation values of the electronic and vibrational angular momentum operators over the vibronic functions, but the evaluation of such functions in the full-dimensional problem still represents a considerable challenge. In our effective Hamiltonian (8.14), these coefficients are simple linear combinations of the rotational constants. Therefore we use the Hamiltonian (8.14) in the following analysis although we realize that it only provides accurate results in situations where the wavefunction is strongly localized in the minima and the tunneling motion is slow on the timescale of molecular rotation.

### 8.4. Results

#### 8.4.1 Correlation diagram

The properties of the tunneling-rotation Hamiltonian derived in Eq. (8.14) are most easily understood in terms of the correlation diagram presented in Fig. 8.5. In this figure, the eigenvalues of $\hat{H}_{\text{rot}}$ for the total angular momentum quantum number excluding spins $N^+ = 0 \to 3$ calculated using the rotational constants $A, B, C$ derived in Ref. [37] are represented as a function of the tunneling integral $\sigma = \delta/4$. The case $\sigma = 0$ corresponds to a situation where tunneling is suppressed by infinite barriers.

---

**Table 8.5:** Rotational operators $\hat{H}_{\text{rot}}$ and their irreducible representation $\Gamma_y$ in the $T_d(M)$ molecular symmetry group.

<table>
<thead>
<tr>
<th>$\hat{H}_{\text{rot}}$</th>
<th>$\Gamma_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J^2$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$1/\sqrt{6}(J_x^2 + J_y^2 - 2J_z^2)$</td>
<td>$E_0$</td>
</tr>
<tr>
<td>$1/\sqrt{2}(J_x^2 - J_y^2)$</td>
<td>$E_c$</td>
</tr>
<tr>
<td>$1/\sqrt{2}(J_yJ_z + J_xJ_y)$</td>
<td>$F_{2x}$</td>
</tr>
<tr>
<td>$1/\sqrt{2}(J_xJ_z + J_xJ_y)$</td>
<td>$F_{2y}$</td>
</tr>
<tr>
<td>$1/\sqrt{2}(J_yJ_x + J_xJ_y)$</td>
<td>$F_{2z}$</td>
</tr>
<tr>
<td>$J_x$</td>
<td>$F_{1x}$</td>
</tr>
<tr>
<td>$J_y$</td>
<td>$F_{1y}$</td>
</tr>
<tr>
<td>$J_z$</td>
<td>$F_{1z}$</td>
</tr>
</tbody>
</table>
between the minima or, equivalently, the vibronic wavefunctions are completely localized in the minima of C_{2v} geometry. This situation results in the level structure of an asymmetric top molecule with rotational constants A, B and C, in which each level is sixfold degenerate. The value of J is indicated on the left-hand side of the figure. In the case of a nonzero tunneling splitting δ the sixfold degeneracy of each asymmetric top level is lifted, and the levels can be assigned a rovibronic symmetry \( \Gamma_{rve} \) in the \( T_d(M) \) molecular symmetry group (\( A_1, A_2, E, F_1 \) or \( F_2 \)). In the case of a vanishing barrier, which corresponds to nearly free pseudorotation, the eigenvalues of \( \tilde{H}_{rve} \) form two distinct stacks of rotational levels corresponding to two states of vibronic symmetries \( F_2 \) and \( F_1 \), respectively. The rotational structure in this limit does not correspond to a simple symmetric or asymmetric top, but the splittings between levels of the same \( J \) quantum number are smaller than in the asymmetric top limit which we attribute to the effects of pseudorotational averaging. Overall the grouping of levels is reminiscent of the rotational structure of a spherical top. One cannot, however, expect that the level structure in this limiting case is accurately predicted because the pseudorotational motion generates angular momentum that couples to the rotational angular momentum and these Coriolis interactions are not included in \( \tilde{H}_{rve} \). Moreover, the assumption of a strong localization of the vibronic functions in the minima is no longer adequate and the tunneling model for the pseudorotational motion is expected to break down.

The rovibronic symmetries indicated in Fig. 8.5 have been derived directly from the calculation, but they can also be obtained from group-theoretical arguments. In the case \( \delta = 0 \), all levels can be assigned to a rovibronic symmetry in the \( C_{2v} \) point group. The correlation to the \( T_d(M) \) molecular symmetry group provides the rovibronic symmetries of the levels into which the asymmetric top levels split as a result of tunneling. This procedure is illustrated for the \( J = 1 \) levels in Fig. 8.5. Their rovibronic symmetries are \( B_1 \) (\( J_K = K_e = 1_{01} \)), \( A_1 \) (\( 1_{11} \)) and \( A_2 \) (\( 1_{10} \)) which correlate with \( F_1 \oplus F_2 \), \( A_1 \oplus E \oplus F_2 \) and \( A_2 \oplus E \oplus F_1 \), respectively. As can be seen from Fig. 8.5, the rovibronic symmetries are correctly predicted from the diagonalization of \( \tilde{H}_{rve} \).

### 8.4.2 PFI-ZEKE photoelectron spectra

The rotationally resolved PFI-ZEKE photoelectron spectra of \( ^{13}\text{CH}_4 \), \( ^{12}\text{CH}_4 \) and \( ^{12}\text{CD}_4 \) recorded following one-photon VUV excitation are shown in Figs. 8.6, 8.8 and 8.9. The coincidence of the observed bands with a sharp onset of the photoionization signal (not shown) and the absence of PFI-ZEKE photoelectron signal at lower wave numbers provide strong evidence for the assignment of these bands to the origin of the photoelectron spectra (see also discussion in Ref. [280]). The spectra of \( \text{CH}_4 \) and \( ^{13}\text{CH}_4 \) have a linewidth of 0.5 and 0.8 cm\(^{-1} \) respectively, in good agreement with the linewidth expected from the electric field sequences used to record them.
8.4. Results

Figure 8.5: Correlation diagram of the eigenvalues of the tunneling-rotation Hamiltonian (8.14) as a function of the tunneling integral $\sigma$. In the limit $\sigma = 0$, all levels are sixfold degenerate and coincide with the pattern of an asymmetric top which is depicted on the left-hand side. Rovibronic symmetries in the $C_{2v}$ point group (left) and $T_d(M)$ molecular symmetry group (right) are assigned to the levels. The vibronic symmetry in the $T_d(M)$ group is indicated on the right-hand side.

Most lines in the spectra of $^{13}$CH$_4$ and CH$_4$ correspond to transitions between a single pair of rotational levels. The PFI-ZEKE photoelectron spectrum (Fig. 8.9) of CD$_4^+$ has a much lower signal-to-noise ratio than those of CH$_4^+$ and $^{13}$CH$_4^+$. Moreover, the linewidth in this spectrum amounts to 0.7-1.2 cm$^{-1}$, more than the value of 0.6 cm$^{-1}$ expected from the pulsed electric field sequence. Thus, most observed lines correspond to several transitions.

If a small isotopic shift indicated by diagonal lines in Fig. 8.6 is excepted, the PFI-ZEKE spectra of $^{12}$CH$_4$ and $^{13}$CH$_4$ are very similar. The main transitions are grouped according to the ground state level on the basis of the assignment procedure discussed in more detail in Subsection 8.4.2.

The analysis of the rotational structure in the spectrum of CH$_4^+$ with standard rigid rotor Hamiltonians has not been successful, a finding that has been attributed to the fluxional nature of the methane cation [279,280]. An additional difficulty in the analysis resulted from the fact that no combination differences could be identified in
the spectra which prevented the assignment of the initial level of the transitions. The reason for the absence of combination differences lies in the fact that the methane molecules are cooled to the lowest rotational level of each nuclear spin symmetry in the supersonic expansion, i.e. \( J = 0 \) for nuclear spin symmetry \( A_1 \), \( J = 1 \) for \( F_2 \) and \( J = 2 \) for \( E \), as already pointed out in Section 8.2 (see Fig. 8.1). For these reasons, an experimental assignment of nuclear spin symmetry in the spectrum of \( \text{CH}_4^+ \) was necessary.

\[ \text{CH}_4^+ \]

The assignment of the rovibronic symmetries of the ionic levels observed in the PFI-ZEKE photoelectron spectrum is a prerequisite to its analysis with the effective Hamiltonian \( \hat{H}_{\text{rve}} \). Two double-resonance techniques have been developed to assign the nuclear spin symmetries of the ionic levels, and the first results were reported in Ref. [37]. First, the depletion of the PFI-ZEKE photoelectron signal was monitored as a function of the IR radiation frequency that was chosen to be resonant with the \( R(0) \), \( P(1) \), \( R(1) \), \( P(2) \) or \( R(2) \) lines of the \( v_3 \) fundamental band. A depletion of up to \( \approx 50\% \) of the original signal indicated that the photoelectron and IR transitions had a common lower level. Second, PFI-ZEKE spectra were recorded from selected rotational levels of the \( v_3 = 1 \) vibrationally excited state of neutral methane following IR excitation. The results obtained from these two methods are displayed in Fig. 8.8. The top trace of Fig. 8.8 represents the single-photon PFI-ZEKE photoelectron spectrum of \( \text{CH}_4 \) that was recorded at an experimental resolution of 0.36 cm\(^{-1}\). The lower traces represent IR+VUV two-photon resonant PFI-ZEKE photoelectron spectra recorded via selected rotational levels of the intermediate \( v_3 = 1 \) vibrationally excited level of \( \text{CH}_4 \). The rovibronic symmetry label and the rotational angular momentum quantum number \( J \) of the intermediate level is indicated above each trace. The wave number scale corresponds to the sum of the IR and the VUV wave number. The linewidth in the IR+VUV two-photon spectra amounts to approximately 1 cm\(^{-1}\), limited by the amplitude of the pulsed ionization field which had to be chosen larger than in the one-photon experiments because of weaker signals. The coincidence of a PFI-ZEKE line in the single-photon and two-photon spectra (after field correction) was used to assign a nuclear spin symmetry to the ionic levels. Combining the results of the "ZEKE dip" and two-photon resonant PFI-ZEKE spectra, nuclear spin symmetries could be assigned to most lines in the PFI-ZEKE photoelectron spectrum and the map of the lowest rovibronic levels of the methane cation shown in Fig. 8.7a could be established.

A nonlinear least-squares fitting procedure of the eigenvalues of \( \hat{H}_{\text{rve}} \) to the experimental level positions provided the constants given in Table 8.6, and Fig. 8.7b shows the level structure calculated with the Hamiltonian \( \hat{H}_{\text{rve}} \). Table B.5 summarizes observed and calculated level positions and the spectral assignments. The value of
Figure 8.6: Single-photon PFI-ZEKE photoelectron spectrum of $^{12}$CH$_4$ (top trace, a) and $^{13}$CH$_4$ (bottom trace, b) in the region of the adiabatic ionization threshold. Spectrum a) was obtained with a sequence of pulsed electric fields of +26 mV cm$^{-1}$ and -88 mV cm$^{-1}$ and spectrum b) with +26 mV cm$^{-1}$ and -138 mV cm$^{-1}$.

the ionization energy differs slightly from the value reported in Ref. [37] because of a more accurate estimation of the field-induced shift of the ionization thresholds. The two values agree within their uncertainty.

Table 8.6: Adiabatic ionization energy, rotational constants (A, B, C) and tunneling splitting $\delta$ determined from a least-squares fitting procedure of the calculated to the observed line positions for CH$_4$, $^{13}$CH$_4$ and CD$_4$.

<table>
<thead>
<tr>
<th>constant / cm$^{-1}$</th>
<th>IE/(hc)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>101752.2(15)</td>
<td>6.40</td>
<td>5.55</td>
<td>4.03</td>
<td>16.4(40)</td>
</tr>
<tr>
<td>$^{13}$CH$_4$</td>
<td>101756.6(15)</td>
<td>6.30</td>
<td>5.70</td>
<td>4.05</td>
<td>16.2(40)</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>102196.9(15)</td>
<td>3.35</td>
<td>2.53</td>
<td>1.98</td>
<td>1.4(3)</td>
</tr>
</tbody>
</table>
**Figure 8.7:** Comparison of the experimentally determined level structure of CH₄⁺ (a) with the eigenvalues of the Hamiltonian (8.14) using the constants determined in a non-linear least-squares fitting procedure (see Table 8.6). The wave number scale is defined with respect to the ground state of CH₄.

The PFI-ZEKE photoelectron spectrum of ¹³CH₄ has been recorded under conditions similar to those used for ¹²CH₄ but using a slightly higher pulsed electric field as indicated in the figure caption. Except from a shift of +4.4 cm⁻¹ of the spectrum of ¹³CH₄ with respect to that of CH₄ the two spectra are very similar in appearance. No major differences are observed in the intensity distributions except for the region around 101800 cm⁻¹, where the relative intensities of several lines differ. Also, a few additional lines are observed in the spectrum of ¹³CH₄ at 101760.05 cm⁻¹, 101747.65, 101828.97 and 101831.72 cm⁻¹. The great similarity of the lowest band of the PFI-ZEKE photoelectron spectra of ¹²CH₄⁺ and ¹³CH₄⁺ is not surprising given that neither the rotational constants nor the pseudorotational tunneling dynamics are expected to be significantly affected by the substitution of the central atom. The observed and calculated positions of the lines in the spectrum of ¹³CH₄ are listed in Table B.6 which also contains the spectral assignments.
8.4. Results

Figure 8.8: Top trace: Single-photon PFI-ZEKE photoelectron spectrum of CH₄ in the region of the adiabatic ionization threshold obtained using electric field pulses of +86 mV cm⁻¹ and -138 mV cm⁻¹. Lower traces: two-photon IR+VUV PFI-ZEKE PE spectra recorded via selected rotational levels of the V₃ fundamental using electric field pulses of +17 mV cm⁻¹ and -860 mV cm⁻¹. The rotational angular momentum quantum number J of the intermediate levels and their rovibronic symmetries are indicated above the spectra. The letters A, E and F correspond to the experimentally assigned nuclear spin symmetries (A₁, E or F₂).

Figure 8.9a shows the PFI-ZEKE photoelectron spectrum of CD₄ and Fig. 8.9b a simulation using the effective tunneling-rotation Hamiltonian of Eq. (8.14). The signal-to-noise ratio of the experimental spectrum is significantly lower than in the case of the PFI-ZEKE spectra of CH₄, although the spectra were recorded under comparable conditions. Since the photoelectron transitions in the region of the adiabatic ionization threshold of CD₄ are considerably weaker than in CH₄ and only few individual transitions are resolved, an experimental assignment based on the double-resonance schemes described above was not undertaken for CD₄. In a previous analysis of the PFI-ZEKE spectrum of CD₄ [280], it was argued that the tunneling splitting was smaller than the spectral resolution and that the spectrum could be analyzed with an asymmetric top Hamiltonian. A reanalysis of the spectrum with the Hamiltonian ̂Hₑᵥₑ derived in the present work, however, leads to the conclusion that an adjust-
ment of the rotational constants $A, B, C$, the tunneling splitting $\delta$ and the ionization energy $IE$ leads to a better agreement between the experimental and theoretical spectra. In particular, the tunneling splitting was determined to be $1.4(3) \text{ cm}^{-1}$. The constants obtained in a nonlinear least-squares fitting procedure are given in Table 8.6. Table B.7 summarizes observed and calculated level positions and the spectral assignments. The positions of the transitions have been calculated using the rotational constant $B = 2.63273 \text{ cm}^{-1}$ [304] for the ground state of CD$_4$ and assuming that the nuclear spin symmetry is conserved in the photoelectron transition. The simulation of intensities was performed assuming a Boltzmann distribution of the neutral ground state levels at $7 \text{ K}$ for each nuclear spin symmetry. The simulations also include the spatial degeneracy $(2J + 1)$ of the lower level of the transition, the spin-statistical weight and the same weighting factor for different rotational branches $C_{\Delta N}$ ($C_0 = 1, C_1 = C_{-1} = 0.75, C_2 = C_{-2} = 0.50$) as already successfully used in the simulation of the spectrum of CH$_2$D$_2$ [281]. The transitions corresponding to the emission of a photoelectron with even or odd parity were weighted equally. Figure 8.9b shows a calculated stick spectrum and a convolution with a Gaussian envelope of FWHM 0.55 cm$^{-1}$.

The agreement between simulated and observed spectra in Fig. 8.9 is good as far as the line positions are concerned and satisfactory as far as the intensities are concerned. All strong features in the spectrum are reproduced well, especially in the low energy side of the spectrum. The effect of the tunneling splitting is most pronounced in the group of transitions originating from $J = 1$ at 102195.6 cm$^{-1}$ and 102197.8 cm$^{-1}$. If a rigid asymmetric top model is used, this pair of lines must be assigned to the transitions from $J = 1$ to $N^+_K_{Kc} = 101, 111, 110$, respectively, where $J$ designates the total angular momentum quantum number of the initial neutral level, $N^+$, $K_a$, $K_c$ the rotational angular momentum quantum number and its prolate and oblate top projections [280]. These final states are almost equally spaced and equally intense, in contrast to the observation. The introduction of a tunneling splitting of 1.4 cm$^{-1}$ moves the components of nuclear spin symmetry F$_2$ of the upper two levels to higher energies and leads to a splitting of the lower level in two components, which agrees very well with the observed structure. It also improves the agreement with the measured spectrum in the lowest wave number region, where the pair of transitions at 102186 and 102188 cm$^{-1}$ is now reproduced quantitatively.

8.5 Discussion

8.5.1 Comparison of experimental and simulated spectra

The agreement between calculated and observed level positions is satisfactory in CH$_4^+$ and good in CD$_4^+$. In CH$_4^+$ a one-to-one correspondence between the calculated and
8.5. Discussion

experimental level positions of nuclear spin symmetries $A_1$ and $E$ is found up to $J = 3$. More levels of nuclear spin symmetry $F_2$ have been calculated than observed which is most likely a result of the limited resolution and sensitivity of the experiment. However, the grouping of calculated levels closely reflects the experimental results. In CD$_4^+$, an experimental assignment of the nuclear spin symmetries was not required because the experimental spectrum could be assigned on the basis of the calculation. However, the lower signal-to-noise ratio of the CD$_4$ spectrum and the higher spectral congestion make a comparison more difficult than in the case of CH$_3^+$. The rotational constants obtained in the analysis of the spectra of CH$_3^+$ and CD$_3^+$ are both consistent with the experimental geometry derived from the PFI-ZEKE spectra of CH$_2$D$_2^+$ [281].

The tunneling splittings obtained from the present analysis are significantly larger than those obtained from one-dimensional calculations of the pseudorotational motion [280] but they are in agreement with the results of EPR spectra which have shown

Figure 8.9: Single-photon PFI-ZEKE photoelectron spectrum of CD$_4$ in the region of the adiabatic ionization threshold (a) obtained using a pulsed electric field of -53 mV cm$^{-1}$ and simulated spectrum using the Hamiltonian (8.14) and the constants indicated in Table 8.6 (b). Panel (b) shows a theoretical stick spectrum and its convolution with a Gaussian line profile of FWHM 0.55 cm$^{-1}$. The full, dashed and dotted sticks represent transitions to levels of rovibronic symmetries $A_1$ (or $A_2$), $E$ and $F_1$ (or $F_2$), respectively.
that the exchange of hydrogen atoms takes place on a sub-ns timescale [275]. In early *ab initio* calculations [285, 286] the barrier height depended strongly on the methods used and/or the representation of the potential surface. More recent calculations seem to converge to a purely electronic barrier height of approximately 1000 cm\(^{-1}\) [280, 287]. However, zero-point corrections must be added to this electronic value, which is not straightforward in highly anharmonic potential surfaces.

*Ab initio* calculations at the CCSD(T)/cc-pVTZ level of theory provide a harmonic zero-point energy of 8398 cm\(^{-1}\) and 6156 cm\(^{-1}\) at the C\(_2\)\(_v\) minimum for CH\(_3\)\(^+\) and CD\(_4\)\(^+\), respectively. At the C\(_s\) saddle-point corresponding to the pseudorotational motion, the zero-point energy amounts to 7782 cm\(^{-1}\) and 5673 cm\(^{-1}\), respectively. The purely electronic barrier amounts to 1014 cm\(^{-1}\) at this level of theory. The zero-point corrected barrier amounts to only 399 cm\(^{-1}\) for CH\(_3\)\(^+\) and 530 cm\(^{-1}\) for CD\(_4\)\(^+\). Zero-point effects thus strongly reduce the size of this barrier which explains the large value of the tunneling splitting of 16(4) cm\(^{-1}\) for CH\(_3\)\(^+\) which corresponds to a period of 2.1(5) ps for the exchange of hydrogen atoms.

A striking difference between the PFI-ZEKE spectra of CH\(_3\)\(^+\) and CD\(_4\)\(^+\) is the much lower signal-to-noise ratio in the CD\(_4\)\(^+\) spectra. The simplest explanation of this observation can be given in terms of a Franck-Condon argument [280]. The Franck-Condon factor depends on the amplitude of the ionic nuclear wavefunction in the vicinity of the tetrahedral geometry of the neutral molecule. As a consequence of deuteration, the zero-point energy of the lowest levels is reduced which results in a stronger localization of the wavefunction in the regions of the potential surface corresponding to the distorted structure. Consequently, the amplitude of the vibronic wavefunction in the Franck-Condon region of the photoelectron transition is decreased by deuteration which results in significantly weaker transitions in CD\(_4\)\(^+\) than in CH\(_3\)\(^+\).

### 8.5.2 Thermochemical implications

The present work has improved the accuracy in the ionization energy of methane by a factor of more than 20. This ionization energy is an important thermochemical quantity and several consequences are discussed. Since the appearance energy of CH\(_3\)\(^+\) from the photoionization of methane \(AE(\text{CH}_3^+, \text{CH}_4)\) is known accurately [305], the 0 K bond dissociation energy \(D_0(\text{H-CH}_3^+)\) can be determined to high accuracy

\[
D_0(\text{CH}_3^+ - \text{H}) = AE(\text{CH}_3^+, \text{CH}_4) - IE(\text{CH}_4) = 13769.7 \pm 8 \text{ cm}^{-1}. \tag{8.17}
\]

Upon ionization, the C-H bond of methane is thus dramatically weakened and the dissociation energy decreases by a factor of almost 3. A comparison of the appearance energy \(AE(\text{CH}_3^+, \text{CH}_4)\) of 115522.7 \pm 8 cm\(^{-1}\) [305] with the sum (115528.4 cm\(^{-1}\)) of the ionization energy of methyl radical 79356.4 \pm 1.5 cm\(^{-1}\) [85] and the bond dis-
8.6 Conclusions

The dissociation energy $D_0(H-CH_3) = 36172 \pm 10 \text{ cm}^{-1}$ shows that the dissociation of CH$_4^+$ into a methyl cation and a hydrogen atom is barrierless within the accuracy of these measurements.

The dissociation of methane cation into CH$_2^+$ and H$_2$ is another important process. Using the ionization energy $IE(CH_2)=83772 \pm 3 \text{ cm}^{-1}$ of CH$_2$ [306] and the 0 K dissociation energy $D_0(CH_2-H_2)$ of methane into CH$_2$ and H$_2$ improved in Ref. [306] one obtains the 0 K dissociation energy of CH$_4^+$ into CH$_2^+$ and H$_2$

$$D_0(CH_2^+ - H_2) = D_0(CH_2 - H_2) + IE(CH_2) - IE(CH_4) = 20251 \pm 50 \text{ cm}^{-1}. \quad (8.18)$$

In this evaluation, the sum of the dissociation energy of neutral methane (38232 ± 50 cm$^{-1}$) and the ionization energy of methylene (83772 ± 3 cm$^{-1}$) have been used because it is smaller than the appearance energy of CH$_2^+$ from the photoionization of CH$_4$ $AE(CH_2,CH_4)=122274 \text{ cm}^{-1}$ (Ref. [307]) by 270 cm$^{-1}$, which suggests the existence of a barrier for the dissociation of CH$_4^+$ into CH$_2^+$ and H$_2$.

8.6 Conclusions

The assignment of the origin band in the spectra of CH$_4^+$, $^{13}$CH$_4^+$, and CD$_4^+$ in terms of a tunneling doublet of vibronic symmetries F$_2$ and F$_1$ in T$_d$(M) confirms the C$_{2v}$ minimum energy geometry of CH$_4^+$ and CD$_4^+$ that results from the JT effect. C$_{3v}$ and $D_{2d}$ geometries would result in different tunneling structures as discussed in Section 8.3.3 and can be excluded. A model of the pseudorotation-tunneling dynamics has been developed that enables the interpretation of the irregular and complex spectral structures observed in the photoelectron spectra. The model can be used to explore the diversity of behaviors between the free pseudorotation and complete localization of the nuclear structure in the C$_{2v}$ minima by means of a correlation diagram. Deviations between measured and predicted level positions amount to about 1 cm$^{-1}$ for CH$_4^+$ and 0.3 cm$^{-1}$ for CD$_4^+$. We attribute the better prediction of the CD$_4^+$ spectrum to the stronger localization in the C$_{2v}$ potential wells. The present characterization of level positions and symmetries represent an important step toward the observation of the millimeter wave spectrum of CH$_4^+$. We indeed expect transitions between rotational levels of different tunneling components of the same nuclear spin symmetry to be observable.
Chapter 9

The Jahn-Teller effect in CH$_3$D$^+$ and CD$_3$H$^+$: conformational isomerism, tunneling-rotation structure and the location of conical intersections

9.1 Introduction

Isotopic substitution is one of the most elegant and useful methods in the investigation of the structure and dynamics of molecular systems. Partial isotopic substitution reduces the symmetry of the normal vibrations without affecting the electronic symmetry properties. It is therefore particularly valuable in the investigation of systems that are subject to vibronic coupling because the electronic and nuclear dynamics are strongly correlated in these systems. Isotopic substitution is also helpful in understanding the properties of molecules performing large-amplitude motions because it reduces the permutational symmetry and introduces asymmetries in the potential energy surface through vibrational zero-point effects.

Partial substitution of molecules subject to a Jahn-Teller (JT) effect [33, 36] has been considered theoretically for the E®e problem [308, 309] and its spectroscopic consequences were studied by electron paramagnetic resonance (EPR) in the cyclooctatetraene anion [310] and the benzene anion [311] and by optical spectroscopy in benzene [312] and the cyclopentadienyl radical [62]. All investigated systems possess a doubly degenerate ground electronic state that is subject to a dominantly linear interaction with some vibrational modes. In the case of benzene and cyclopentadienyl, the dominantly linear JT effect leads to a potential energy surface with a cylindrically symmetric trough [31, 40] which is occasionally referred to as "mexican hat". The weaker quadratic JT effect leads to minima along the trough connected by small to vanishing barriers. In these systems, partial deuteration leads to the appearance of
one minimum on the potential energy surface that corresponds to the most favorable structure. In the case of cyclopentadienyl, the barriers between the equivalent minima vanish by symmetry [245] and both C5H4D and C5D4H possess a single minimum on the lowest potential energy surface. An additional effect of partial deuteration is the splitting of the lowest vibronic level of symmetry E′ in D3h into two components of symmetries A2 and B1 in C2v. In the case of several excited electronic states of benzene and of the ground state of the benzene anion, quadratic coupling is weak and leads to very small barriers between the equivalent minima [311]. These minima are not deep enough to support localized nuclear wave functions and therefore single deuteration also leads to a single preferred geometry of the molecule that was identified in the EPR experiments. The effects of partial deuteration in the systems mentioned above can be summarized as a transition from a situation where pseudorotation takes place to a static JT distortion since vibrational zero-point effects result in a single preferred geometry of the molecule.

The situation is quite different in the methane cation which is the topic of this chapter. The methane cation is the prototypical system for the T®(e+t2) JT effect. In this system strong quadratic coupling leads to twelve equivalent minima of C2v symmetry that are separated by high barriers [285]. The effect of partial isotopic substitution on JT systems with deep minima has not been investigated before but the emergence of new isotopic effects has been anticipated by Miller and coworkers: "[...] there is the intriguing possibility of Jahn-Teller molecules being isolated sufficiently long in distorted geometries to exhibit strongly different chemical reactivity" [313]. A C2v minimum energy structure has been first predicted for CH4+ by Meyer [282] and has been confirmed by more recent ab initio quantum chemical calculations [285–287,314]. The C2v minimum energy structure has been verified experimentally from the determination of the symmetries of the tunneling sublevels of the ground state in a rotationally resolved photoelectron spectrum (see Ref. [37] and chapter 8). This study has also shown that the hydrogen atoms exchange with a period of 2.1(5) ps, i.e., on a timescale comparable to that of molecular rotation. CH3D+ and CD3H+ have been studied by EPR [275], which has revealed that the three protons of CH3D+ and the three deuterons of CD3H+ are equivalent on the timescale of the experiment. The same study has shown that the four protons in CH4+ are also equivalent on that timescale but that, in CH2D2+, the protons and deuterons must occupy different sites. The conclusion on CH2D2+ was subsequently confirmed by the analysis of a rotationally resolved photoelectron spectrum [281], which proved that CH2D2+ possesses two equal C-H bonds that are longer than the two equal C-D bonds.

A previous investigation of CH4+, CD4+, CH3D+ and CH2D2+ by pulsed-field ionization zero-kinetic energy (PFI-ZEKE) photoelectron spectroscopy [280] has provided a qualitative understanding of the dynamics of these molecules at low excitation energies using a one-dimensional model for the large-amplitude pseudorotational motion. The
model was, however, incapable of reflecting the full symmetry of the problem because of its reduced dimensionality, and neither the vibronic nor the rovibronic symmetries could be predicted correctly. Moreover, the model did not incorporate the effects of the geometric phase and has underestimated the size of the tunneling splittings. In chapter 8, the lowest bands in the PFI-ZEKE spectra of CH$_3$ and CD$_3$ have been reanalyzed using a tunneling treatment that reflects the full permutational symmetry and also includes the effect of the geometric phase. This analysis led to the assignment of the rotational structure of the spectrum (see also Refs. [37,314]). In the present chapter, the PFI-ZEKE photoelectron spectrum of CD$_3$H$^+$ is reported for the first time and a complete analysis of the tunneling-rotation structure of CH$_3$D$^+$ and CD$_3$H$^+$ at low energies is presented. The analysis required the extension of the model introduced in chapter 8 to treat the tunneling-rotation structure of partially deuterated species.

9.2 Experiment

The photoion/photoelectron spectrometer and the vacuum-ultraviolet (VUV) light source used in the present experiments have been described in chapter 2 (see Fig. 2.2). CH$_3$D and CD$_3$H (Cambridge isotope laboratories (CIL), 98% chemical purity, 98% isotopic enrichment) were introduced into the spectrometer in a pulsed supersonic expansion of a 1:1 mixture with argon (stagnation pressure 2-3 bar, 10 Hz repetition rate). VUV radiation was generated by two-photon resonance-enhanced sum-frequency mixing in Xe using the (5p)$^5$6p$^1$[1/2]$^6_0 \rightarrow (5p)^6$1$^1$S$_0$ two-photon resonance at $2\nu_1=80119.964$ cm$^{-1}$. The VUV radiation intersected the molecular beam at right angles.

PFI-ZEKE photoelectron spectra were recorded by monitoring the pulsed electric field ionization of high Rydberg states located immediately below the ionization thresholds as a function of the laser wave number. A positive pulsed electric field of less than 1 V/cm and of 1 $\mu$s duration was applied 1 $\mu$s after photoexcitation and was immediately followed by a negative pulsed electric field of comparable amplitude. Photoionization spectra were measured by recording the ion yield as a function of the laser wave number, which was calibrated as described in Section 2.1.4.

9.3 Theory

9.3.1 The potential energy surfaces

Partial isotopic substitution of methane lowers the symmetry of the normal vibrations but leaves the electronic symmetry properties unchanged. Therefore, the topological relations between the minima and saddle points on the potential energy surfaces of
CH$_4^+$ [285, 286] are conserved upon deuteration. The minimum energy structure of CH$_4^+$ has a C$_{2v}$ geometry [37, 112, 282, 285-287] two C-H bonds being elongated (1.186 Å) and two bonds shortened (1.098 Å) compared to the tetrahedral reference geometry. The long bonds form an angle of 55° that is substantially smaller than the tetrahedral angle and the short bonds enclose an increased angle (126°). These structural parameters were obtained by optimizing the geometry of the methane cation at the CCSD(T)/cc-pVTZ level of ab initio theory [112]. In CH$_4^+$, distortion from the tetrahedral geometry leads to six equivalent C$_{2v}$ structures which are connected by 12 equivalent first-order saddle points of C$_s$ symmetry. A cyclic exchange of three hydrogen atoms, which is often referred to as "pseudorotation" [285], transforms one minimum energy structure to an equivalent one and the corresponding minimum energy path leads through the C$_s$ saddle point. An additional set of six minima and twelve saddle-points is obtained by inverting the molecule. The topology of the potential energy surface is represented schematically in Fig. 9.1 which represents the distorted structures of CH$_3$D$^+$. The center of the triangular faces of the octahedron corresponds to structures of C$_{3v}$ symmetry in CH$_4^+$. Two types of triangular faces can be distinguished depending on whether a short or a long C-H bond (the C-D bond in the figure) is conserved in the motion encircling that face. In the former case, the center of the triangular face corresponds to a structure of C$_{3v}$ geometry with one short C-D and three long C-H bonds. This structure possesses a doubly degenerate lowest electronic state and a nondegenerate excited state [286] both arising from the threefold degenerate $^2F_2$ state of CH$_4^+$ at the tetrahedral reference geometry. The position of this structure in configuration space is indicated by a dot in Fig. 9.1. The other four triangular faces correspond to a structure of C$_{3v}$ geometry with a long C-D and three short C-H bonds possessing a nondegenerate ground electronic state and a doubly degenerate excited state [286].

The potential energy surfaces of CH$_4^+$ can be interpreted in terms of a T$_2$$\otimes$($e+2t_2$) JT effect. The associated 8-dimensional hypersurfaces are complex but their topological relationship is easily understood from a decomposition into two consecutive distortions which is also very useful in understanding the JT effect in the partially deuterated isotopomers. We assume first that CH$_4^+$ is distorted along a linear combination of the two modes of symmetry $f_2$ to the C$_{3v}$ structure indicated by a dot in Fig. 9.1 with one short C-H bond and a doubly degenerate ground state. A second distortion along the e mode (in T$_d$), which has the same irreducible representation in C$_{3v}$, leads to one of the three C$_{2v}$ minima located at the corners of the corresponding face of the octahedron, e.g., structures 1, 2 and 3 in Fig. 9.1. This second distortion corresponds exactly to the well-known E$$\otimes$$e JT effect of a molecule of C$_{3v}$ (or D$_{3h}$) symmetry in a doubly degenerate ground state which leads to three equivalent minima connected by three equivalent saddle-points [31, 40, 315]. The motion connecting the three structures around a triangular face thus encircles a conical intersection.
Figure 9.1: Schematic representation of several stationary points on the potential energy surface of \( \text{CH}_3\text{D}^+ \) and their topological relationship. The empty circles correspond to the three equivalent minima of the more stable isomer \( \text{CH}_3\text{D}^+ \). The squares represent the three equivalent minima of the isomer \( \text{CH}_3\text{D}^+ \). The filled circles on four faces of the octahedron represent the \( \text{C}_3\text{V} \) structures possessing a doubly degenerate ground electronic state and the center of the remaining four faces correspond to the \( \text{C}_3\text{V} \) structures with a nondegenerate ground state. The structure of the \( \text{C}_2\text{V} \) and \( \text{C}_3\text{V} \) stationary points that are of importance in the present study are depicted.
Alternatively, CH$_4^+$ can be distorted to a C$_{3v}$ structure with one long C-H bond and a nondegenerate ground state. The second distortion along an e mode also leads to three C$_{2v}$ minima, e.g., structures 4, 5 and 6 in Fig. 9.1, but the local topology of the potential surfaces must be different from the case discussed previously. The lowest surface is nondegenerate, but the vibronic coupling to the degenerate excited state leads to a stabilization of the lower surface upon distortion that results from a (A$_1$ @ E) & e Pseudo-JT effect. Hence, the motion around a triangular face of this kind does not encircle a point of electronic degeneracy.

Although deuteration does not affect the properties of the electronic surfaces it has a profound impact on the dynamics of molecules through vibrational zero-point energy effects. Single or triple deuteration of CH$_4^+$ lifts the high permutational symmetry of the system and reduces the number of equivalent local minimum energy structures from six to two sets of three structures. After applying the zero-point correction to the potential energy surface, a structure of CH$_3$D$^+$ with the D atom on a long bond is no longer isoenergetic with a structure that has a short C-D bond. This effect is illustrated in Fig. 9.1 where the local minima 1, 2 and 3 corresponding to a structure with a short C-D bond are indicated by circles and those corresponding to a long C-D bond by squares (4, 5 and 6). A similar situation is encountered in CD$_3$H$^+$ which possesses two sets of three equivalent structures. Ab initio calculations of the vibrational frequencies show that the zero-point effects favor those structures where a maximum number of deuterium atoms are located on short bonds. This result is in agreement with the intuitive expectation that short bonds correspond to large force constants which cause the largest zero-point effects. Harmonic zero-point energy differences between the two possible structures amount to 114 cm$^{-1}$ in CH$_3$D$^+$ and 107 cm$^{-1}$ in CD$_3$H$^+$ at the CCSD(T)/cc-pVTZ level of theory. As will be demonstrated below, the two sets of structures (1,2,3) and (4,5,6) represent two isomeric forms of CH$_3$D$^+$ and CD$_3$H$^+$. These isomers are labeled CH$_3$D$_s^+$ (CD$_3$H$_s^+$) and CH$_3$D$_l^+$ (CD$_3$H$_l^+$) where the subscripts $s$ and $l$ indicate that the single ligand atom lies on a short or a long bond, respectively.

The molecular symmetry group C$_{3v}(M)$ contains permutation-inversion operations of the type E,(123) and (12)$^*$ which are all feasible if the splittings resulting from the pseudorotational motion are observable. We will therefore use the C$_{3v}(M)$ group to describe the symmetry of the rovibronic levels of CH$_3$D$^+$ and CD$_3$H$^+$.

### 9.3.2 The tunneling problem

The tunneling motion between the six equivalent minima of CH$_4^+$ and CD$_4^+$ in the rotationless ground state can be described by an effective Hamiltonian expressed in the basis

$$\phi_n = |n\rangle |\chi_n\rangle,$$

(9.1)
where |n⟩ is the adiabatic electronic function in the nth potential well and |χn⟩ represents the ground state vibrational wavefunction (a product of 9 harmonic oscillator functions) of the molecule in the nth potential well [37, 112]. |n⟩ is the eigenvector corresponding to the lowest eigenvalue of the 3x3 potential energy matrix for CH₄ that was derived in Ref. [286] and takes the form 

$$\frac{1}{\sqrt{2}} (|ξ⟩ + |η⟩), \frac{1}{\sqrt{2}} (|ξ⟩ - |η⟩), \frac{1}{\sqrt{2}} (|ξ⟩ + |ζ⟩), \frac{1}{\sqrt{2}} (|ξ⟩ - |ζ⟩), \frac{1}{\sqrt{2}} (|ξ⟩ + |ζ⟩), \frac{1}{\sqrt{2}} (|ξ⟩ - |ζ⟩)$$

for minima 1 through 6, where |ξ⟩, |η⟩, |ζ⟩ are the diabatic electronic wavefunctions of the electronic triplet in its tetrahedral reference geometry [37].

Neglecting the overlap between the vibrational basis functions and defining $\sigma = 1/2(⟨χ_1|̂H_{vib}|χ_2⟩$ and $⟨χ_1|̂H_{vib}|χ_1⟩ = 0$, where $̂H$ is the vibrational operator for the lowest potential energy surface, the tunneling eigenstates of CH₄⁺ are obtained from the diagonalization of the Hamiltonian matrix

$$H_{vib} = \begin{pmatrix}
0 & \sigma & \sigma & 0 & -\sigma & \sigma \\
\sigma & 0 & -\sigma & -\sigma & 0 & \sigma \\
-\sigma & 0 & \sigma & -\sigma & 0 & \sigma \\
0 & -\sigma & 0 & \sigma & \sigma & 0 \\
\sigma & -\sigma & 0 & \sigma & 0 & \sigma \\
-\sigma & -\sigma & 0 & \sigma & 0 & \sigma \\
\end{pmatrix}$$

which provides two sets of triply degenerate levels with eigenvalues $+2\sigma$ and $-2\sigma$, respectively, whereby $\sigma$ is negative. The high permutational symmetry of CH₄⁺ is responsible for the equality of all matrix elements $⟨χ_i|̂H_{vib}|χ_j⟩$ and all tunneling elements $⟨χ_i|̂H_{vib}|χ_j⟩$.

Deuteration of CH₄⁺ to CH₃D⁺ reduces the permutational symmetry and results in two distinct sets of three structures each that differ in zero-point energy. In addition, the 12 equivalent saddle points of Cs symmetry in CH₄⁺ are split into four distinct sets of three equivalent structures. The saddle-point structures for pseudorotation among the minima of CH₃D⁺ (CH₃D⁺) have a short (long) C-D bond. The saddle-point structures possessing one H and one D atom on the equal bonds are enantiomers of each other and therefore the corresponding pseudorotation paths are equivalent. Consequently, the following matrix elements can be defined:

$$⟨χ_i|̂H|χ_i⟩ = 0 \text{ for } i \in \{1, 2, 3\}$$

$$⟨χ_i|̂H|χ_i⟩ = \Delta \text{ for } i \in \{4, 5, 6\}$$

$$1/2⟨χ_i|̂H|χ_j⟩ = \sigma \text{ for } i \neq j, \{i, j\} \in \{1, 2, 3\}$$

$$1/2⟨χ_i|̂H|χ_j⟩ = \sigma' \text{ for } i \neq j, \{i, j\} \in \{4, 5, 6\}$$

$$1/2⟨χ_i|̂H|χ_j⟩ = \sigma'' \text{ for } i \neq j, i \in \{1, 2, 3\}, j \in \{4, 5, 6\} \text{ or vice versa,}$$

where $i$ and $j$ refer to the structures drawn in Fig. 9.1 and $\sigma$, $\sigma'$ and $\sigma''$ are negative.
The zero-point-corrected potential energy of the more stable structures (1,2,3 for CH$_3$D$^+$, see Fig. 9.1) has been chosen as origin of the energy scale. $\Delta$ represents the zero-point energy difference between the two sets of structures corresponding to minima 1-3 and 4-6 in the absence of tunneling. $\sigma$ is the tunneling matrix element for the interconversion of the structures 1, 2 and 3, $\sigma'$ that for structures 4, 5 and 6 and $\sigma''$ represents the interaction between vibrational basis functions localized in inequivalent minima. The tunneling matrix elements have negative values. The tunneling matrix for CH$_3$D$^+$ takes the form

$$H_{\text{tun}} = \begin{pmatrix}
0 & \sigma & \sigma & 0 & -\sigma'' & \sigma'' \\
\sigma & 0 & -\sigma & -\sigma'' & 0 & \sigma'' \\
\sigma & -\sigma & 0 & \sigma'' & -\sigma'' & 0 \\
0 & -\sigma'' & \sigma'' & \Delta & \sigma' & \sigma' \\
-\sigma'' & 0 & -\sigma'' & \sigma' & \Delta & \sigma' \\
\sigma'' & \sigma'' & 0 & \sigma' & \sigma' & \Delta 
\end{pmatrix}$$

(9.4)

and has the eigenvalues

$$E_E = \frac{1}{2}(\sigma - \sigma' + \Delta - S)$$

(9.5a)

$$E_{A_2} = -2\sigma$$

(9.5b)

$$E_{A_1} = 2\sigma' + \Delta$$

(9.5c)

$$E_E = \frac{1}{2}(\sigma - \sigma' + \Delta + S).$$

(9.5d)

In Eqs. (9.5a)-(9.5d) the subscripts correspond to the irreducible representations of the corresponding eigenvectors in C$_{3v}$(M) and

$$S = \sqrt{(\sigma + \sigma')^2 + 12\sigma'' - 2(\sigma + \sigma')\Delta + \Delta^2}. \quad (9.6)$$

In the limit $(|\sigma|, |\sigma'|, |\sigma''|) \ll \Delta$ one obtains

$$S \approx \Delta - (\sigma + \sigma') + \frac{(\sigma + \sigma')^2 + 12\sigma''}{2\Delta} \approx \Delta - (\sigma + \sigma'), \quad (9.7)$$

and the eigenvalues converge to

$$E_E = \sigma$$

(9.8a)

$$E_{A_2} = -2\sigma$$

(9.8b)

$$E_{A_1} = 2\sigma' + \Delta$$

(9.8c)

$$E_E = -\sigma' + \Delta,$$

(9.8d)

corresponding to two tunneling pairs with tunneling splittings $\delta = 3|\sigma|$ and $\delta' = 5|\sigma'|$. 

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The Jahn-Teller effect in CH$_3$D$^+$ and CD$_3$H$^+$
Figure 9.2: Tunneling levels of CH$_3$D$^+$ with zero total angular momentum and ground vibronic state of CH$_3$D (full lines). The quantities $\sigma$ and $\sigma'$ represent the tunneling integrals for the isomers CH$_3$D$^+$ and CH$_3$D$^+$, respectively, ZPED stands for the zero-point energy difference between these isomers and IE is the adiabatic ionization energy. $\Delta$ describes the zero-point energy difference in the absence of tunneling.

3|$\sigma'$, respectively. These tunneling states are represented schematically in Fig. 9.2 and 9.3 for CH$_3$D$^+$ and CD$_2$H$^+$, respectively. If the zero-point energy difference dominates over the value of the tunneling integrals, tunneling between inequivalent minima is suppressed by the asymmetry of the potential and one can consider the structures (1,2,3) and (4,5,6) as forming distinct isomers. The symmetry inherent to the system implies that the tunneling substates of symmetry $A_1$ and $A_2$ are entirely localized in the minima 4,5,6 on the one hand and 1,2,3 on the other, irrespective of the values of the parameters. These substates can thus always be identified with one of the isomers if their interaction with excited vibrational levels is neglected.

In an earlier work on the tunneling dynamics in CH$_4$ (see Ref. [37] and chapter 8), we have discussed the effect of the electronic degeneracies on the structure of the tunneling levels. The lowest potential energy surface of CH$_4$ contains 2 types of electronic degeneracies which are enforced by symmetry (additional "accidental" degeneracies also exist): one conical intersection corresponding to a threefold degeneracy at the tetrahedral geometry and four conical intersections corresponding to a twofold degeneracy at the four possible C$_3\nu$ structures with a single short C-H bond in-
Chapter 9. The Jahn-Teller effect in CH$_3$D$^+$ and CD$_3$H$^+$

When an adiabatic electronic wavefunction is transported in a closed loop around an odd number of conical intersections, its sign must change when the loop is completed [31, 38, 40]. One can indeed verify that the product of three consecutive overlaps of the adiabatic electronic wavefunctions in the sequence $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ is negative, whereas a positive number results from the sequence $4 \rightarrow 5 \rightarrow 6 \rightarrow 4$, where the numbers 1 to 6 refer to the structure labels introduced in Fig. 9.1. The sign change along the former loop is a direct manifestation of the presence of a conical intersection inside the former path and the sign conservation along the latter loop results from the absence of such a degeneracy point (or an even number of them) in the latter. The topological properties of the potential surfaces are thus properly encoded in the adiabatic electronic functions. The properties of the two tunneling paths discussed here are qualitatively unchanged by single deuteration. Therefore, the ordering of tunneling levels $E_E \leq E_A_2$ in the set (1,2,3) can be interpreted as a signature of the conical intersection encircled by the corresponding tunneling motion and the ordering $E_A_1 \leq E_E$ in the set (4,5,6) represents the "normal" splitting of tunneling between three equivalent minima. This conclusion is in agreement with the interpretation given above that minima (1,2,3) arise from an E$\oplus$e JT effect (for which the ordering $E_E \leq E_A$ has been established [316]) and minima (4,5,6) from a (A$\oplus$E)$\oplus$e Pseudo-JT effect. In conclusion, the ordering of the tunneling states in the partially deuterated isotopomers can directly be translated into topological information on the potential energy surface cannot be obtained directly from spectra of CH$_4^+$ or CD$_4^+$.

The tunneling structure of CD$_3$H$^+$ is in many respects similar to that of CH$_3$D$^+$, but the role of the two sets of minima is exchanged. Replacing all H (D) atoms by D (H) atoms in Fig. 9.1 renders the set of structures 4,5,6 more stable than the set 1,2,3. The tunneling substates in order of increasing energy are in this case

$$E_{A_1} = 2\sigma'$$
$$E_E = -\sigma'$$
$$E_A = \sigma + \Delta$$
$$E_{A_2} = -2\sigma + \Delta,$$

a situation that is schematically depicted in Fig. 9.3.

9.3.3 The rovibronic problem

A simple description of the rotational motion in the lowest tunneling states of CH$_3$D$^+$ and CD$_3$H$^+$ is obtained by expressing the rotational operators in an axis system that is common to all distorted structures. CH$_3$D$^+$ and CD$_3$H$^+$ both possess two sets of 3 equivalent minimum energy structures that differ in the value of the zero-point
energy. The transformation of the axes for the distorted structure of CH₃D⁺ in which the D atom is located on a short bond is represented schematically in Fig. 9.4. The C₃v equilibrium structure (a) of CH₃D is chosen as reference geometry and the axes x, y, z are chosen along the principal inertial axes. The y axis lies in the plane containing the H, D, and C atoms. The molecule is then distorted to the equilibrium structure (b) of CH₃D⁺ by 1) shortening the C-D and the C-H bonds lying in the yz plane, 2) increasing the corresponding (DCH) angle, 3) lengthening the two remaining C-H bonds and 4) decreasing their (HCH) angle. The origin of the axis system is moved to the new center of gravity of the molecule. Then, the axes are rotated by an angle θ about the x axis such that they coincide with the principal axis system (x', y', z') of the distorted structure indicated in (c). In this axis system, the rotational Hamiltonian takes the form

\[
\frac{\hat{H}_{\text{rot}}^{(1)}}{\hbar c} = C\hat{J}_{x'}^2 + B\hat{J}_{y'}^2 + A\hat{J}_{z'}^2,
\]  

where the superscript designates the minimum structure as defined in Fig. 9.1.

Inserting the expressions for the rotational operators \(\hat{J}_{x'}, \hat{J}_{y'}, \hat{J}_{z'}\) in terms of the
operators defined in the global axis system $\hat{J}_x', \hat{J}_y', \hat{J}_z$

$$
\begin{align*}
\hat{J}_x' &= \hat{J}_x \\
\hat{J}_y' &= \hat{J}_y \cos \theta - \hat{J}_z \sin \theta \\
\hat{J}_z' &= \hat{J}_z \cos \theta + \hat{J}_y \sin \theta,
\end{align*}
$$

one obtains the expression

$$
\frac{\tilde{H}_{\text{rot}}^{(1)}}{\hbar c} = (A \cos^2 \theta + B \sin^2 \theta)\hat{J}_z^2 + (A \sin^2 \theta + B \cos^2 \theta)\hat{J}_y^2 + C\hat{J}_x^2 + (A - B) \cos \theta \sin \theta (\hat{J}_z\hat{J}_y + \hat{J}_y\hat{J}_z)
$$

for the rotational Hamiltonian in the minimum labeled 1 in Fig. 9.1. The Hamiltonian for minima 2 (3) is obtained from two consecutive rotations of the axis system. First, the axes are rotated such that the hydrogen atom 2 (3) lies in the yz plane. The axis system is then rotated around the new x axis such that the axes coincide with the principal axes of rotation of the distorted structure. The rotational constants $A, B, C$ and the angle $\theta$ which are common to the minima 1,2,3 are calculated from the experimental structure of CH$_2$D$_2$ determined in Ref. [281] and confirmed in [314] and can be adjusted to reproduce the observed rovibronic structure. One can indeed expect a slight adjustment to be necessary because the experimental structures are slightly different for the different isotopomers (and even the two isomers of CH$_3$D$^+$ or CD$_3$H$^+$) because of vibrational averaging.
9.4 Results

9.4.1 Symmetry analysis and correlation diagrams

The analysis of the consequences of tunneling on the rovibronic levels is most transparent in a group-theoretical formalism. As shown previously for CH$_4$ and CD$_4$ [112], the rovibronic symmetries of the molecular levels in the presence of tunneling can be predicted using correlation tables. We first assume that the barrier separating the minima is so high that the tunneling splittings are not resolved. In this case, the rovibronic levels can be classified in the point group corresponding to the distorted structures. The minimum energy structures of CH$_3$D$^+$ and CD$_3$H$^+$ have C$_s$ symmetry. The singly occupied molecular orbital is symmetric with respect to the reflection in the plane containing the long C-H(D) bonds and antisymmetric with respect to the plane containing the short bonds. Therefore, the electronic symmetry in the ground state of CH$_3$D$_z$ and CH$_3$D$_t$ is A" and A', respectively. Similarly, CD$_3$H$_z$ has an electronic ground state of symmetry A' and CD$_3$H$_t$ has an A" ground state. The tunneling
between the three equivalent minima (1, 2, 3) or (4, 5, 6) in Fig. 9.1 for each of these isomers results in a splitting of the vibronic ground state into two sublevels. The symmetry of these sublevels is then predicted by correlating the vibronic symmetry from the C₃ point group to C₃ᵥ(M), which is the appropriate molecular symmetry group in the presence of tunneling. The corresponding correlation, which is given in Table 9.2, predicts that the tunneling leads to a doubly degenerate state (E) and a nondegenerate one (A₁ or A₂). The ordering of these tunneling levels, however, is not determined by group theory and can only be obtained from a quantitative model including the geometric phase. The method introduced in Section 9.3 predicts that in CH₃D⁺ the lower tunneling level has the vibronic symmetry E and the upper level is of A₂ symmetry, whereas CH₃D⁻ has an A₁ lower level and an upper level of symmetry E. CD₃H⁺ and CD₃H⁻ have the same sequence of tunneling levels as CH₃D⁻ and CH₃D⁺, respectively.

Figure 9.5a represents the eigenvalues of the tunneling-rotation Hamiltonian Hᵥₑ for the calculated rotational constants of CD₃H⁺ given in Table 9.1 as a function of the tunneling integral |σ| = δ/3 (see Eqs. (9.5a)-(9.5d)). In the limit σ = 0, the level pattern of an asymmetric top is obtained, each level being triply degenerate. This limit corresponds to the case of an infinite barrier that suppresses tunneling between the equivalent minima. In the case of a large tunneling splitting corresponding to a fast pseudorotational motion, two distinct stacks of rotational levels are obtained. The lower stack corresponds to a level of vibronic symmetry A₁ with a wavefunction that has equal amplitudes in all three minima; this level therefore possesses a simple rotational structure. In the particular case of CD₃H⁺ the rotational structure is very close to that of a spherical top because a specific relation between the rotational constants and the tilt angle θ is accidentally fulfilled and results in an isotropic inertial tensor in the limit of fast pseudorotation. The upper stack of rotational levels exhibits a complex rotational structure and corresponds to a vibronic level of symmetry E. This state has a more complicated structure because its two components have different amplitudes in the three minima. The correlation diagram for CD₃H⁺ is shown in Fig. 9.5b. Two main differences to Fig. 9.5a can be seen. First, the ordering of the tunneling levels is inverted, the degenerate vibronic level now lying below the nondegenerate one. Second, the rotational structure of the nondegenerate level has a normal oblate top rotational structure in the limit of fast pseudorotation. The correlation diagram for CH₃D⁻ and CH₃D⁺ are similar, with the difference that the rotational structure of the lower tunneling level of CH₃D⁻ does not show the accidental "spherical top" level structure seen in Fig. 9.5a.

The rovibronic symmetries of the rotationally excited levels under the effect of tunneling can also be predicted from group theory as found previously (Ref. [314] and chapter 8). In the limit σ = 0, the three J = 1 asymmetric top levels have the rovibronic symmetry A'' (Jₖₐₖₐ = 1₀₁), A'' (1₁₁) and A' (1₁₀) which correlate with A₂ ⊕ E,
Figure 9.5: Correlation diagram of the eigenvalues of the tunneling-rotation Hamiltonian (9.17) as a function of the tunneling integral $\sigma$ for CH$_3$D$^+$ (panel a) and CH$_3$D$^+$ (panel b). In the limit $\sigma = \sigma' = 0$, all levels are threefold degenerate and coincide with the pattern of an asymmetric top which is depicted on the left-hand side. Full lines correspond to levels of rovibronic symmetry $A_1$ or $A_2$ in the $C_3v(M)$ group, whereas dashed lines correspond to levels of symmetry $E$. The vibronic symmetries of the tunneling sublevels are indicated on the right-hand side of the figure by large capital letters.
Table 9.1: Constants calculated using the experimental structure of CH$_2$D$_2$ determined in Ref. [281] and adjusted to reproduce the experimental spectra. $A$, $B$, $C$ are the asymmetric top rotational constants, $\theta$ is the angle by which the $z$ axis has been tilted away from the symmetric top principal axis in the rotation of the axis system, $\delta = 3|\sigma|$ is the tunneling splitting, $IE$ the adiabatic ionization energy of the more stable isomer and ZPED is the zero-point energy difference between the two isomers.

Table 9.2: Reverse correlation table of irreducible representations of the Cs point group to the C$_{3v}(M)$ molecular symmetry group.

<table>
<thead>
<tr>
<th>isomer</th>
<th>$A$/cm$^{-1}$</th>
<th>$B$/cm$^{-1}$</th>
<th>$C$/cm$^{-1}$</th>
<th>$\theta$/°</th>
<th>$\delta$/cm$^{-1}$</th>
<th>IE/(hc cm$^{-1}$)</th>
<th>ZPED /cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$D$_5^+$</td>
<td>calc.</td>
<td>5.68</td>
<td>4.22</td>
<td>3.03</td>
<td>22.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>5.63(5)</td>
<td>4.08(10)</td>
<td>3.14(4)</td>
<td>22.2$^b$</td>
<td>9.5(6)</td>
<td>101802.8(15)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$D$^+$</td>
<td>calc.</td>
<td>6.13</td>
<td>3.76</td>
<td>3.13</td>
<td>17.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>6.08(6)</td>
<td>3.70(6)</td>
<td>3.11(2)</td>
<td>17.7$^b$</td>
<td>6.6(5)</td>
<td>120.9(10)</td>
<td></td>
</tr>
<tr>
<td>CD$_3$H$_7^+$</td>
<td>calc.</td>
<td>3.67</td>
<td>3.26</td>
<td>2.13</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>3.76(9)</td>
<td>3.17(12)</td>
<td>2.21(6)</td>
<td>50.0$^b$</td>
<td>1.2(6)</td>
<td>102021.4(20)</td>
<td></td>
</tr>
<tr>
<td>CD$_3$H$_5^+$</td>
<td>calc.</td>
<td>4.29</td>
<td>2.70</td>
<td>2.29</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>4.35(5)</td>
<td>2.74(6)</td>
<td>2.26(4)</td>
<td>11.4$^b$</td>
<td>1.8(4)</td>
<td>122.3(20)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ab initio value at the CCSD(T)/cc-pVTZ level of theory
$^b$Unchanged

9.4.2 CH$_3$D$^+$

An overview of the photoionization (dashed line) and PFI-ZEKE photoelectron (full line) spectra of CH$_3$D near the adiabatic ionization threshold is shown in Fig. 9.6. The coincidence of a sharp increase in the photoionization yield from a value of zero at $\sim$ 101800 cm$^{-1}$ with the first band (labeled A) in the PFI-ZEKE photoelectron spectrum indicates a transition to the vibrationless ground state of CH$_3$D$^+$. The following band (labeled B) in the PFI-ZEKE spectrum lies only 121 cm$^{-1}$ higher and possesses a rotational structure that is very different from the lowest band. Beyond 102100 cm$^{-1}$, the spectrum cannot be described by isolated bands any longer. This situation is reminiscent of CH$_4$ where only the lowest band can be identified as isolated
9.4. Results

Figure 9.6: PFI-ZEKE photoelectron spectrum (full line) and photoionization spectrum (dashed line) of CH$_3$D. The PFI-ZEKE photoelectron spectrum was recorded using a sequence of pulsed electric fields of +35 mV cm$^{-1}$ and -130 mV cm$^{-1}$. The position of the zero-point corrected $ab\ initio$ barrier for isomerization is indicated by an arrow.

spectral structure, an observation which reflects the flatness of the potential energy surface and the resultant large-amplitude motion and overlapping spectral structures at higher internal energies.

The results of the analysis of the two lowest bands of the PFI-ZEKE spectrum of CH$_3$D are shown in more detail in Figs. 9.7 and 9.8. In the analysis of these spectra, we have used the calculated rotational constants given in Table 9.1 and have adjusted the tunneling integral $\sigma$ (or $\sigma'$) until a good agreement was reached. The transitions were then assigned on the basis of the calculations, and the rotational constants, the tunneling integral and the band center were refined in a nonlinear least-squares fitting procedure. The constants obtained in the fit are also given in Table 9.1 below the calculated value. The band centers were transformed into an adiabatic ionization energy (IE) for the more stable isomer and a zero-point energy difference (ZPED) for the less stable isomer after correcting for the field-induced shift of the ionization thresholds. The transition wave numbers were calculated using the rotational constants $A_0 = 5.2508$ cm$^{-1}$ and $B_0 = 3.8802$ cm$^{-1}$ for the ground
electronic state of the neutral molecule from Ref. [317] and assuming that nuclear spin symmetry is conserved in the photoelectron transitions. For the calculation of the intensities, we have used a Boltzmann distribution with a rotational temperature of 7 K for both nuclear spin isomers and the same weighting factors for the different rotational branches as used in previous studies of isotopomers of the methane cation [112,281]. The spin-statistical weights were also included. The weights of transitions corresponding to the emission of even and odd photoelectron partial waves were chosen to be equal. Table B.8 lists the measured wavenumbers of the transitions in both bands, their assignment and the deviation between the measured and calculated positions.

In the spectra of the lowest band shown in Fig. 9.7, the agreement between observed and calculated level positions is good in the lower half of the spectrum (see also upper part of Table B.8). The strongest line (at 101811 cm\(^{-1}\)) corresponds to a cluster of primarily Q-type transitions, i.e., transitions with \(N^+ - J = 0\). The assignment bars label transitions from the \((J,K) = (0,0)\) and \((1,1)\) levels of the ground state. The three lines below and the four lines above the Q-branch are reproduced well by the calculation and suffice to define the tunneling splitting. If the tunneling splitting were negligible, an additional line would be observed to the higher wave number side of the pair of lines around 101801 cm\(^{-1}\). Transitions from \((J,K) = (0,0)\) to the upper tunneling component of \(N^+ = 0\) and to the two lower tunneling components of \(N^+ = 1\) nearly coincide and form the strong line cluster around 101811 cm\(^{-1}\). The pair of lines around 101801 cm\(^{-1}\) is assigned to the transition from \((J,K) = (1,1)\) to the lower tunneling component of \(N^+ = 1\) and the transition to the upper component is also located close to 101811 cm\(^{-1}\). The agreement between calculated and observed intensities is, however, less satisfactory. Although the lower part of the spectrum is well reproduced, the intensities are clearly overestimated by the calculation in the upper half. However, given the crude model used to calculate the intensities (see above) the agreement between the calculated and measured intensities can be regarded as satisfactory.

The second band of the PFI-ZEKE photoelectron spectrum of CH\(_3\)D and its simulation are shown in Fig. 9.8. The agreement between calculated and observed line positions is again good for the strongest transitions (see lower part of Table B.8). As in the spectrum of the lower band, the intensities are also overestimated on the high wave number side of the spectrum.

In the simulation of all spectra of CH\(_3\)D\(^+\) we were led to reduce the intensity of transitions originating from levels of rovibronic symmetry E by a factor of 2 compared to those originating from \(A_1\) or \(A_2\) levels. This observation might originate from a partial conversion of nuclear spin symmetries in the collisional cooling process.
The photoionization and PFI-ZEKE photoelectron spectra of CD$_3$H (dashed and full lines, respectively) over the range 101900 - 102600 cm$^{-1}$ are displayed in Fig. 9.9. The lowest band of the PFI-ZEKE photoelectron spectrum (labeled A) coincides with the onset of the photoionization signal and is therefore assigned to the adiabatic ionization threshold of CD$_3$H. In the PFI-ZEKE photoelectron spectrum of CD$_3$H$^+$, at least three isolated bands can be identified. The first and third bands (labeled A and C) have a similar rotational structure which differs from that of the second (labeled B). The band labeled C and the spectral lines around 102370 cm$^{-1}$ can be tentatively assigned to excited pseudorotational levels of the CD$_3$H$^+_f$ isomer. As expected the level of vibronic symmetry E (associated with band C) lies below the A$_2$ level. At higher energies, the simple band structure of the spectrum is lost which is another indication of the flatness of the potential energy surface at higher energies. The group
of lines beyond 102400 cm\(^{-1}\) could possibly be assigned to a strongly perturbed band.

The separation between the two lowest bands amounts to approximately 120 cm\(^{-1}\) as in the spectrum of CH\(_3\)D\(^+\). The analysis of the two lowest bands was performed in the same way as for the spectra of CH\(_3\)D\(^+\). For the calculation of the transition wave numbers we have used the rotational constants \(B_0 = 3.27916\) cm\(^{-1}\) and \(C_0 = 2.62896\) cm\(^{-1}\) for the ground vibronic level of CD\(_3\)H from Ref. [318] and assumed that nuclear spin symmetry is conserved in the photoelectron transitions. The intensities were simulated assuming a rotational temperature of 7 K and using the same weighting factors for different rotational branches and the same procedure as for CH\(_3\)D\(^+\) (see above). We have assumed that nuclear spin symmetry is conserved in the collisional cooling of the CD\(_3\)H molecules.

The spectrum of the lowest band and its simulation using the constants for CD\(_3\)H\(^+\) reported in Table 9.1 are compared in Fig. 9.10. The general structure of the band and most lines are reproduced by the simulation. The signal-to-noise ratio of the spec-
Figure 9.9: PFI-ZEKE photoelectron spectrum (full line) and photoionization spectrum (dashed line) of CD$_3$H. The PFI-ZEKE photoelectron spectrum was recorded using a sequence of pulsed electric fields of +26 mV cm$^{-1}$ and -138 mV cm$^{-1}$. The position of the zero-point corrected ab initio barrier for isomerization is indicated by an arrow.

The agreement between calculated and experimental spectra is better for the second band of the PFI-ZEKE spectrum which is shown in more detail in Fig. 9.11. The constants used for the calculation are listed in Table 9.1 for CD$_3$H$^+$. In this simulation, line positions and intensities are reproduced satisfactorily and the assignment of all strong transitions is unambiguous. The transitions to the rotational levels of
the lower tunneling component of vibronic symmetry E are located at 102137 cm\(^{-1}\) \((N^+ = 0)\), 102143 cm\(^{-1}\) \((N^+ = 1)\), 102153 cm\(^{-1}\) \((N^+ = 2)\) and those to the upper tunneling component of symmetry \(A_2\) are located at 102145 cm\(^{-1}\) \((N^+ = 0)\), 102153 cm\(^{-1}\) \((N^+ = 1)\), 102167 cm\(^{-1}\) \((N^+ = 2)\).

### 9.5 Discussion

The analysis of the rotational structure of the lowest two bands of the PFI-ZEKE spectra of CH\(_3\)D\(^+\) and CD\(_3\)H\(^+\) leads to several important conclusions. First, the ordering of the vibronic levels enable the identification of two distinct isomers of both CH\(_3\)D\(^+\) and CD\(_3\)H\(^+\). Second, the rotational constants allow an unambiguous identification of each band with one of the isomers of CH\(_3\)D\(^+\) and CD\(_3\)H\(^+\). This form of isomerism of a polyatomic molecule subject to a JT effect results from isotopic substitution and has not been observed previously. These assignments are supported by \textit{ab initio} quantum
chemical calculations which predict the isomer CH$_3$D$_x^+$ to be more stable than the isomer CH$_3$D$_y^+$ by 114 cm$^{-1}$ (see Table 9.1), and the isomer CD$_3$H$_x^+$ to be more stable than the isomer CD$_3$H$_y^+$ by 107 cm$^{-1}$ in good agreement with the experimental values. The good agreement with the predicted rotational constants (see Table 9.1) also supports the results of the present analysis.

In addition to the structural parameters, the present analysis also provides information on the topology of the potential energy surfaces and the tunneling dynamics. In the adjustment of the tunneling integrals, $\sigma$ and $\sigma'$ were found to be negative for both CH$_3$D$_x^+$ and CD$_3$H$_x^+$ thus confirming the ordering of tunneling levels predicted in Section 9.3. The analysis of the rovibronic structure of CH$_3$D$_x^+$ and CD$_3$H$_x^+$, in particular the determination of the ordering of the E and A$_1$ (or A$_2$) vibronic levels, thus constitutes an experimental determination of the location of the twofold conical intersections on the potential energy surface. The location of these conical intersections could previously only be predicted by theoretical methods.

The size of the tunneling splittings in CH$_3$D$_x^+$ and CD$_3$H$_x^+$ is consistent with the
values that we have determined previously for CH$_4^+$ and CD$_4^+$. In a first approxima-
tion, one could assume that single deuteration of CH$_4^+$ has a negligible effect on the 
value of the tunneling integral $\sigma$ for the isomer CH$_3$D$^+$. In CH$_4^+$, we have determined 
$\sigma = -4.1(10)\text{cm}^{-1}$ (the corresponding tunneling splitting is $\delta = 4|\sigma| = 16.4(40)\text{cm}^{-1}$ 
[37,112]). In CH$_3$D$^+$ we have obtained $\sigma = -3.2(2)\text{cm}^{-1}$ and a corresponding tunnel-
ing splitting $\delta = 3|\sigma|$ of $9.5(6)\text{cm}^{-1}$. The values of the tunneling integral in CH$_4^+$ and 
CH$_3$D$^+$ are thus similar, as expected, and the difference in the tunneling splittings 
results primarily from the ratio $\delta(\text{CH}_4^+)/\delta(\text{CH}_3\text{D}^+) \approx 4/3$ imposed by the topology. 
The smaller value of the tunneling integral in CH$_3$D$^+$ can be understood from the in-
creased reduced mass associated with the pseudorotational motion. The zero-point 
corrected barrier heights were calculated from the purely electronic barrier height of 
1014 cm$^{-1}$ (at the CCSD(T)/cc-pVTZ level [112]) by subtracting the harmonic zero-
point energy difference between the minimum energy structure of CH$_3$D$^+$ and the 
saddle-point structure. The zero-point energy of the saddle-point structure was cal-
culated by omitting the imaginary frequency from the zero-point energy sum. The 
values listed in Table 9.5 show that the zero-point corrected barrier height for the 
pseudorotational motion of CH$_3$D$^+$ is smaller than that in CH$_3$D$^+$, which explains the 
smaller value of the tunneling splitting ($\delta = 6.6(5)\text{cm}^{-1}$) found for this isomer.

The tunneling motion in CD$_3$H$^+$ involves three deuterium atoms instead of three 
hydrogen atoms and should therefore be characterized by tunneling integrals of 
similar magnitude as in CD$_4^+$. For CD$_4^+$, we have previously determined the value 
$\sigma=0.35(10)\text{cm}^{-1}$ [112]. The tunneling integral ($\sigma = -0.4(1)\text{cm}^{-1}$) for CD$_3$H$^+$ is equal 
to that of CD$_4^+$ within the experimental error, whereas that for CD$_3$H$^+$ ($\sigma = -0.6(1)\text{cm}^{-1}$) is slightly larger. The zero-point corrected barrier height for the pseudorota-
tional motion is similar for CD$_3$H$^+$ than for CD$_3$H$^+$ (see Table 9.5). One can therefore 
expect the tunneling integral of CD$_3$H$^+$ to be similar to that of CD$_3$H$^+$ which is indeed 
in agreement with the experimental results. The values of the tunneling integrals are 
thus compatible with ab initio quantum chemical calculations.

The number of isolated bands that can be identified by simple inspection of the 
PFI-ZEKE photoelectron spectra increases from one in CH$_4^+$ to two in CH$_3$D$^+$ and three 
in CD$_3$H$^+$. This observation can also be attributed to the zero-point effects and the 
usual effects associated with the substitution of a light by a heavier isotope. The 
largest number of localized bands is actually observed in CD$_4^+$ but their analysis was 
rendered difficult by the low signal-to-noise ratio of the PFI-ZEKE spectra [112]. Above 
the barrier hindering the pseudorotational motion, the configuration space accessible 
to the nuclear wave function increases strongly because the barriers separating the 
equivalent structures of one isomer are similar to those separating structures of the 
two isomers. At the internal energies where pseudorotation is no longer hindered, it 
is thus generally impossible to distinguish the two isomers from each other, because 
the nuclear wavefunctions start spreading over the configurational space associated
with both isomers and isomerization takes place. For simplicity, we consider levels of \( \text{CH}_3\text{D}^+ \) or \( \text{CD}_3\text{H}^+ \) corresponding to a zero total angular momentum. The lowest levels of \( \text{CH}_3\text{D}_d^+ \) and \( \text{CH}_3\text{D}_f^+ \) are of vibronic symmetries \( \text{E} \) and \( \text{A}_1 \) and \( \text{A}_2 \) and \( \text{E} \), respectively. In the simple tunneling model, the \( \text{A}_1 \) and \( \text{A}_2 \) levels are completely localized in the three minima corresponding to one of the isomers, whereas the wavefunctions of each \( \text{E} \) level have small amplitudes in the minima of the other isomer. The matrix element connecting basis states of the isomeric structures must become irrelevant because the zero-point levels of the two isomers are not resonant. This situation is comparable to the case of the hydrogen fluoride dimer, where the rotational levels of \( \text{(HF)}_2 \) and \( \text{(DF)}_2 \) are split by the effect of tunneling but no such splitting is observed in \( \text{HFDF} \) [319] (see also Ref. [320]). In the region below the barrier, the isomers will thus only interconvert in the case of an accidental vibrational degeneracy.

The present results on \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \) are compatible with the results of the EPR investigations of Knight et al. [275] who concluded that the three H (D) nuclei in \( \text{CH}_3\text{D}^+ \) (\( \text{CD}_3\text{H}^+ \)) are equivalent, that the D atom in \( \text{CH}_3\text{D}^+ \) lies in the plane perpendicular to the singly occupied (p-like) molecular orbital and the H atom of \( \text{CD}_3\text{H}^+ \) lies in the plane containing the orbital axis. From the absence of a spectral signature of a second isomer in the EPR spectrum, we conclude that thermalization in the 4K neon matrix has led to a complete conversion of the high energy to the low energy isomer.

<table>
<thead>
<tr>
<th>isomer</th>
<th>pseudorotation barrier / cm(^{-1})</th>
<th>isomerization barrier / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{D}_d^+ )</td>
<td>333</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3\text{D}_f^+ )</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>( \text{CD}_3\text{H}_d^+ )</td>
<td>485</td>
<td>360</td>
</tr>
<tr>
<td>( \text{CD}_3\text{H}_f^+ )</td>
<td>486</td>
<td>564</td>
</tr>
</tbody>
</table>

Table 9.3: Barrier heights at the CCSD(T)/cc-pVTZ level of \textit{ab initio} theory after harmonic zero-point corrections. The barrier heights for pseudorotations exchanging identical nuclei are given with respect to the minima of the corresponding isomers, whereas the isomerization barriers are given with respect to the minimum of the more stable isomer. The purely electronic barrier height amounts to 1014 cm\(^{-1}\) (see Ref. [314] and chapter 8).

9.6 Conclusions

The analysis of the spectra of \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \) has revealed a new kind of isotope-isomerism which is expected to occur whenever vibronic coupling leads to deep equivalent minima on the potential energy surface of a polyatomic molecule. The equivalent minima of \( \text{CH}_4^+ \) form two sets of three equivalent structures each in both \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \). These two sets are no longer isoenergetic because of different zero-point energies. Consequently, the interconversion of the isomers by tunneling
is suppressed and the molecules may be isolated in one of their isomeric forms long enough to exhibit different chemical properties. For example, deuterium abstraction from \( \text{CH}_3\text{D}^+ \) is likely to be much faster than from \( \text{CH}_3\text{D}^+ \) because the bond energies probably differ strongly. The two isomers of \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \) could be prepared selectively by PFI-ZEKE photoelectron spectroscopy or mass-analyzed threshold ionization spectroscopy [321] or by coincidence techniques [322] which would allow an investigation of their chemical reactivity.

The ground state of both isomers of \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \) can be described as a tunneling doublet resulting from the fast cyclic exchange of the three equivalent atoms. The period \( \tau = \frac{\hbar}{\delta} \) for this motion can directly be determined from the tunneling splittings \( \delta \) derived from the spectra and listed in Table 9.1 and amounts to 3.5(2) ps for \( \text{CH}_3\text{D}_3^+ \), 5.1(4) ps for \( \text{CH}_3\text{D}^+ \), 28(4) ps for \( \text{CD}_3\text{H}_3^+ \) and 18(5) ps for \( \text{CD}_3\text{H}_3^+ \). Moreover, each isomer possesses a threefold dynamical symmetry, i.e., the three H or D atoms are chemically equivalent.

The ordering of the tunneling sublevels in the two isomers of \( \text{CH}_3\text{D}^+ \) and \( \text{CD}_3\text{H}^+ \) has revealed the positions of twofold conical intersections on the potential energy surface, an information that cannot be obtained directly from the properties of \( \text{CH}_4^+ \) because of its high permutational symmetry.

In conclusion we have shown that partial isotopic substitution in polyatomic molecules is not only very helpful in understanding the dynamics and topological relationships of complex vibronic coupling problems but that it even leads to a previously unknown form of isomerism of chemical relevance.
Chapter 10

Conclusions and outlook

10.1 Electron and nuclear spin effects on the structure and dynamics of Rydberg states

Low \( l \) Rydberg states are prototypical systems in the investigation of non-Born-Oppenheimer effects because they combine a close-coupling region where the Born-Oppenheimer approximation is valid with an asymptotic region where the timescales for nuclear and electronic motions are inverted. The structure and dynamics resulting from this situation are highly peculiar and contain the complete information needed to characterize highly excited states and scattering events. Autoionization and predissociation are the most important pathways for the decay of molecular Rydberg states and have their origin in the breakdown of the Born-Oppenheimer approximation. In the realm of this thesis, the structure and dynamics of Rydberg states have been investigated at a resolution sufficient to resolve the effects of nuclear spins and has led to the characterization of the hyperfine structure of the Rydberg states of \(^{83}\text{Kr}\) (chapter 3) and of the influence of nuclear spin on the autoionization dynamics of \(^{129}\text{Xe}\) and \(^{131}\text{Xe}\) (chapter 4). In ortho \( \text{H}_2 \), the hyperfine structure of bound s and d Rydberg states has been observed and analyzed (chapter 5) and the effect of hyperfine interactions on the structure and dynamics of rotationally autoionizing states has been characterized (chapter 6). MQDT has been extended to include nuclear spins and been shown to quantitatively predict all of the observed spectral signatures of hyperfine interactions.

The combination of high-resolution spectroscopy and MQDT has provided fundamentally new insights into the nonseparable quantum dynamics involving spatial and spin degrees of freedom of highly excited atomic and molecular systems. In the rare gas atoms, the hyperfine interactions have been found to induce level crossings that allow the characterization of weak interactions, like the sd interaction. The interference of the hyperfine components of ionization channels has been shown to allow the preparation of cations in selected hyperfine states. In the regime where the electronic
motion becomes synchronous with the precession of nuclear spins around the total ionic angular momentum, a "stroboscopic" resonance situation arises that may lead to highly efficient energy transfer between the Rydberg electron and the hyperfine levels of the core. The analysis of the spectra has also led to the first determination of the hyperfine structure of the rare gas cations. Chapters 3 and 4 show that the interactions between the nuclear and electron spins endow the atomic ion core with structure and confer molecular complexity to the dynamics of atomic Rydberg states.

The investigations of ortho H₂ have focused on the characterization of the complete spin-rovibronic interactions occurring in this prototypical molecule. In the gerade electronic symmetry (s and d Rydberg states) the available quantum defect parameters were not of sufficient accuracy to permit an analysis of the hyperfine structure. Therefore, \textit{ab initio} R-matrix calculations were used to predict quantum defect functions. These parameters enabled the immediate assignment of the photoionization spectra including the hyperfine structure. An extended set of hyperfine resolved spectra of ortho H₂ Rydberg states \((n = 35 - 62)\) could be fitted to experimental accuracy, characterizing the finest details of the interactions between vibrational, rotational and spin degrees of freedom. The most accurate data have been obtained in measurements of the ungerade rotationally autoionizing Rydberg states of ortho H₂ in which a resolution of 25 MHz has been reached. The complete evolution of the angular momentum coupling hierarchy has been observed in the p Rydberg states, leading from a situation where the exchange interaction dominates over the hyperfine interactions to the inverted situation.

The rare gas atoms and molecular hydrogen have revealed two complementary aspects of hyperfine interactions in high Rydberg states that are expected to have general validity for heavy and light molecular systems, respectively. The large mass of the investigated atoms (Kr and Xe) leads to large spin-orbit interactions (the \(^{2}P_{3/2} - ^{2}P_{1/2}\) interval in Xe\(^{+}\) amounts to \(10536.925 \pm 0.019\) cm\(^{-1}\) as determined in chapter 4) and therefore, the core electron spin couples strongly to the orbital angular momentum of the ion \(L^+\). This coupling is so strong that even the lowest members of the Rydberg series converging on the two spin-orbit thresholds have a mixed singlet-triplet character. The hyperfine interactions in the ion split both ionic levels into several hyperfine components and lead to a recoupling of the Rydberg electron orbital angular momentum from the total electronic angular momentum of the ion \(J^+\) to its total angular momentum including nuclear spins \(F^+\). The situation is very different in ortho H₂ because spin-orbit interactions play no role in the ion and in high Rydberg states. In this system, the hyperfine interactions in the ion are the primary source of singlet-triplet mixing in the Rydberg states. As shown in chapter 5 and 6, this mixing becomes significant at \(n \approx 30\) and at \(n \approx 80\) in the d and p Rydberg states, respectively. The hyperfine interactions between the core electron and nuclear spins dominate over all other interactions in the core and are about one order of mag-
nitude larger than the electron spin-rotation and more than five orders of magnitude larger than the nuclear spin-rotation interaction. Consequently, as long as the latter two interactions remain unimportant, the molecular wave function is separable into a part depending only on the spatial variables, which can be labeled in Hund’s case (d) \((n\ell N^\ell G)\), and a spin wavefunction characterized by the total spin angular momentum \(\tilde{G}\). This property has been demonstrated in chapters 5 and 6.

The results of this thesis pave the way toward an investigation of new dynamical manifestations of hyperfine interactions in highly excited atomic and molecular states. A new phenomenon termed "hyperfine autoionization" has been predicted, in which the Rydberg electron gains energy from the ion core which is thereby transferred into a lower hyperfine state. The phenomenon could however not be observed because of experimental limitations. Two strategies can be pursued to observe hyperfine autoionization. The first consists in measuring the autoionization resonances located just above the threshold corresponding to the lowest hyperfine component of the ionic ground state. The smallness of hyperfine splittings (less than 0.4 cm\(^{-1}\)) sets a lower limit of \(n > 500\) on the principal quantum number of the states to be observed, which represents an experimental challenge. The second strategy is the measurement of the kinetic energy of the electrons released upon autoionization. This measurement can be done by exciting an atom or a molecule with a narrow-band laser to a region lying between the ionic hyperfine thresholds. A class of very slow electrons that are produced by hyperfine autoionization should then be detected. This strategy has the advantage that the Rydberg states don’t need to be resolved and that an excited ionic threshold can be used (e.g. the \(^2\!P_{1/2}\) level in \(^{129}\!Xe^+\)).

Another major goal is the observation of the effects of spin-rotation interaction on the autoionization dynamics in molecules. In chapter 6, we have shown that these interactions lead to \(G\) mixing, but that they remain insignificant below \(n = 150\). The first evidence for such effects has been obtained in chapter 5, where we have found a local \(G\) and \(N\) mixing between the \(ndl_1\) and \(ndl_2\) levels. Because of the smallness of the exchange interactions, the \(d\) series are more attractive candidates for the observation of the dynamical consequences of \(G\) mixing than the \(p\) series. A rough estimation shows that these effects become significant above \(n \approx 105\) for \(d\) series converging on the \(N^+ = 1\) ground level of ortho \(\text{H}_2^+\).

### 10.2 Jahn-Teller effects in molecular cations

The second part of this thesis has described the investigation of molecular cations that had escaped detailed experimental characterization before. The information on the cyclopentadienyl cation was limited to an EPR spectrum in a matrix which provided very limited information. Rotationally resolved spectra of the methane cation
were known [279,280], but the spectra could not be assigned. Both systems are of fundamental importance in the understanding of Jahn-Teller and related vibronic coupling effects and offer an opportunity to study quantum dynamics in the presence of conical intersections. The special charm of both systems is that they do not belong to the well-understood class of E®e Jahn-Teller systems but represent prototypical systems for two largely unknown effects: The cyclopentadienyl cation is subject to an (E+A)®e Pseudo-Jahn-Teller effect between its two lowest singlet states and the methane cation is characterized by the T®(e+t2) Jahn-Teller effect.

The characterization of the cyclopentadienyl cation in chapter 7 has provided the first detailed information on the electronic and rovibronic structure of an antiaromatic diradical cation. This investigation has shown that the ground state of the cation is a triplet state with five equal C-C bonds and a D$_{5h}$ geometry. The two first excited states are singlet states deriving from the same electronic configuration as the ground state and are subject to a strong Pseudo-Jahn-Teller interaction. The linear Jahn-Teller effect in the lower (degenerate) state has been found to be very weak. The complex vibronic structure of the lowest singlet state has been resolved and analyzed and an accurate adiabatic singlet-triplet interval has been determined. This interval is a key quantity for the properties of diradicals and represents a stringent test for ab initio quantum chemical methods. The agreement between vibronic level calculations and the experimental data can probably be improved by including more vibrational modes in the calculations and determining the relevant quadratic and bilinear coupling constants by ab initio calculations. The ab initio prediction of spin-orbit coupling elements and their inclusion in a complete vibronic calculation of the lowest singlet and triplet states of the cyclopentadienyl cation represents an attractive extension.

The study of the methane cations in chapters 8 and 9 has provided the first assignment of the rotational structure in the origin bands of CH$_4^+$, $^{13}$CH$_4^+$, CD$_4^+$, CH$_3D^+$ and CD$_3H^+$. This progress has allowed a detail characterization of the large-amplitude tunneling motions occurring in the ground state of these species. A general method for the treatment of tunneling dynamics on vibronically coupled surfaces has been developed and extended to include the molecular rotations. A new kind of isomerism has been discovered in CH$_3D^+$ and CD$_3H^+$ which results from zero-point-energy effects that inhibit tunneling. In the region below the isomerization barrier, the PFI-ZEKE spectra of these species could be assigned in terms of two distinct isomers and theoretical arguments have shown that the two isomers do not interconvert.

The investigation of the methane cation has set the stage for the analysis of the T®(e+t$_2$) Jahn-Teller effect in molecular systems. The systematic development of an effective Hamiltonian containing also Coriolis and centrifugal distortion terms should enable a fitting of the spectroscopic data to experimental accuracy. The next step in the analysis of the methane cation is the development of a reduced-dimensionality
model for the description of the combined rotational and large-amplitude tunneling motion to analyze the higher excited bands in the spectrum. A first step in this direction has been taken with the development of a two-dimensional model representing the stationary points of the lowest potential energy surface on a sphere, but more work is needed to achieve quantitative agreement with the spectra. The ideal solution would be a calculation including all degrees of freedom on a full-dimensional potential energy surface following the methods developed in Refs. [323,324], but the treatment of the methane cation would require to take into account all three electronic surfaces or find an appropriate parameterization of the topological effects (see chapter 8). Attractive extensions of the investigations of isomerism include the analysis of the spectra of CH₂D₃⁺ [325] that should possess three isomers. The most stable isomer is expected to possess two long C-H bonds and two short C-D bonds in agreement with the experimental geometry determined from the lowest band in the PFI-ZEKE photoelectron spectrum [281]. The second most stable isomer is expected to tunnel between four equivalent minima, but the minimum energy geometry only has C₁ symmetry and is therefore chiral. This system would be an interesting prototype for the investigation of the effect of parity violating interactions on multidimensional tunneling dynamics [297]. In chapter 9 we have argued that the interconversion of the two isomers of CH₃D⁺ and CD₃H⁺ is expected to be very slow. It would thus be tempting to investigate the chemical reactivity of these ions, e.g., by preparing them selectively by pulsed-field-ionization techniques [321] in an ion trap [326] and colliding them with reactive species. The long C-H(D) bond is expected to be weaker and thus more reactive than the short bond. Finally, the investigation of heavier analogues of methane, i.e. silane and germane would provide additional insights into the Tₜₒ(e⁺t₂) Jahn-Teller effect and reveal its change with increasing mass of the central atom. \textit{Ab initio} calculations predict a C₆ minimum energy geometry for SiH₄⁺ with two very long Si-H bonds which can be understood as a Van-der-Waals complex of SiH₂⁺ with H₂ [327]. The C₂ᵥ geometry of CH₄⁺ can also be viewed in this perspective, but the difference in bond lengths is much smaller. This observation suggests that the large-amplitude motion in SiH₄⁺ is actually limited to an internal rotation of the H₂ unit instead of an exchange of all light nuclei as observed in CH₄⁺ (see chapter 8).
Appendix A

Units and Constants

Constants

Table A.1: List of frequently used constants [328]

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light</td>
<td>$c$</td>
<td>299,792,458</td>
<td>m/s</td>
</tr>
<tr>
<td>Electric field constant</td>
<td>$\epsilon_0$</td>
<td>8.854,187,817 ...×10^{-12}</td>
<td>A s/(V m)</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h$</td>
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<td>J s</td>
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<tr>
<td></td>
<td>$\frac{h}{2\pi}$</td>
<td>1.054,571,68(18) ×10^{-34}</td>
<td>J s</td>
</tr>
<tr>
<td>Elementry charge</td>
<td>$e$</td>
<td>1.602,176,53(14) ×10^{-19}</td>
<td>C</td>
</tr>
<tr>
<td>Rydberg constant</td>
<td>$R_\infty = \frac{\alpha^2 m_e c}{2 \hbar^2}$</td>
<td>109,737,315,685 25(73)</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td>Bohr radius</td>
<td>$a_0 = \frac{4 \pi e^2}{m_e \hbar^2}$</td>
<td>0.529,177,210 8(18) ×10^{-10}</td>
<td>m</td>
</tr>
<tr>
<td>Mass of the electron</td>
<td>$m_e$</td>
<td>9.109,382 6(16) ×10^{-31}</td>
<td>kg</td>
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<tr>
<td>Constant of Avagadro</td>
<td>$N_A$</td>
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<td>mol(^{-1})</td>
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<td>Boltzmann constant</td>
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<td>1.380,650 5(24) ×10^{-23}</td>
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Atomic units

Table A.2: List of atomic units [328]

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Energy equivalents

Table A.3: List of energy equivalents [328]

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<td>$\frac{E}{h\nu} = 1$ cm$^{-1}$</td>
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<tr>
<td>$\frac{E}{h\nu} = 1$ GHz</td>
<td>0.033 356 409 ...</td>
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<tr>
<td>$E = 1$ eV</td>
<td>8 065.544 45(69)</td>
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<tr>
<td>$E = 1 E_h$</td>
<td>2.194 746 313 705(15)\times 10^5</td>
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</table>
Appendix B

Tables
Table B.1: Positions of the \((J = 1)\) \(ns\) and \(nd\) Rydberg states of \(^{84}\text{Kr}\) belonging to series converging to the \(^2P_{3/2}\) ground state of \(\text{Kr}^+\) determined following single-photon excitation from the \(^1S_0\) ground state. The states are labeled in the notation \(n\ell[k]_j\), where \(k\) represents the quantum number associated with the angular momentum vector \(\vec{k} = \vec{j} + \vec{\ell}\). The column \(\bar{\nu}_{\text{calc}} - \bar{\nu}_{\text{obs}}\) indicates the deviation between the experimental line positions and those calculated by multichannel quantum defect theory.

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<th>(nd[3/2]<em>1) (\bar{\nu}</em>{\text{obs}}) (\text{cm}^{-1})</th>
<th>(\bar{\nu}<em>{\text{calc}} - \bar{\nu}</em>{\text{obs}}) (\text{cm}^{-1})</th>
<th>((n + 2)s[3/2]<em>1) (\bar{\nu}</em>{\text{obs}}) (\text{cm}^{-1})</th>
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continuation on the following page
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Table B.2: Positions of the hyperfine structure components of the \( ns[3/2]_{1,2} \) Rydberg states of \(^{83}\text{Kr}\) determined following single-photon excitation from the \(^1S_0\) ground state. All states are characterized by \( k = J^+ = 3/2 \) and \( \ell = 0 \), and are only labeled by the quantum numbers \( n, J \) and \( F \). The column \( \tilde{\nu}_{\text{calc}} - \tilde{\nu}_{\text{obs}} \) indicates the deviation between the experimental line positions and those calculated by multichannel quantum defect theory.

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Table B.3: Positions of the hyperfine structure components of the $ndl_1$, $ndl_2$, $ndl_3$ and $nsl_1$ Rydberg states of ortho H$_2$ determined following resonant two-photon excitation via the B $^1\Sigma_u^+$ ($v = 2, J = 0$ or 2) intermediate levels. The column $\nu_{\text{obs}}$ lists the absolute wave numbers above the X $^1\Sigma_u^+$ ($v = 0, J = 0$) ground state of H$_2$ obtained by adding the term values 92743.960 cm$^{-1}$ and 92849.445 cm$^{-1}$ [329] of the B state ($v = 2, J = 0$ and 2, respectively) to the measured wave numbers. The column $\nu_{\text{calc}} - \nu_{\text{obs}}$ indicates the deviation between the experimental line positions and those calculated by multichannel quantum defect theory.

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Table B.4: Positions of the rotationally or vibrationally excited interlopers observed in the spectra of ortho H$_2$ following resonant two-photon excitation via the B $^1\Sigma_u^+$ ($v = 2, J = 0$ or 2) intermediate levels. The column $\tilde{\nu}_{\text{obs}}$ lists the absolute wave numbers above the X $^1\Sigma_g^+$ ($v = 0, J = 0$) ground state of H$_2$ obtained by adding the term values 92743.960 cm$^{-1}$ and 92849.445 cm$^{-1}$ [329] of the B state ($v = 2, J = 0$ and 2, respectively) to the measured wave numbers. The column $\tilde{\nu}_{\text{calc}} - \tilde{\nu}_{\text{obs}}$ indicates the deviation between the experimental line positions and those calculated by multichannel quantum defect theory.

<table>
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<th>State</th>
<th>$\tilde{\nu}_{\text{obs}}$ wrt B $^1\Sigma_u^+$ ($v' = 2, N' = 2$) (cm$^{-1}$)</th>
<th>$\tilde{\nu}<em>{\text{obs}} - \tilde{\nu}</em>{\text{calc}}$ (cm$^{-1}$)</th>
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<td>7d1$_2$ ($v^+ = 1$)</td>
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<td>124429.755</td>
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Table B.5: Measured line positions ($\tilde{v}_{\text{obs}}$) and deviations from the calculated line positions ($\tilde{v}_{\text{obs}} - \tilde{v}_{\text{calc}}$) of the vibrationless $\text{CH}_4 \ X^- \rightarrow \text{CH}_4 \ X$ photoelectronic transition. $\Gamma_{\text{ve}}$, $\Gamma_{\text{ve}}^+$, and $\Gamma_{\text{rve}}$ represent the vibronic and the rovibronic symmetries in the molecular symmetry group $T_d(M)$ for the neutral and the ionic state, respectively.

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<th>$N^+$</th>
<th>$\Gamma_{\text{rve}}^+$</th>
<th>$\tilde{v}_{\text{obs}}$ / cm$^{-1}$</th>
<th>$\tilde{v}<em>{\text{calc}} - \tilde{v}</em>{\text{obs}}$ / cm$^{-1}$</th>
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$^a$Measured transitions without field correction

$^b$Band origin
Table B.6: Measured line positions ($\tilde{\nu}_{\text{obs}}$) and deviations from the calculated line positions ($\tilde{\nu}_{\text{obs}} - \tilde{\nu}_{\text{calc}}$) of the vibrationless $^{13}\text{CH}_4^+ \tilde{X} \rightarrow ^{13}\text{CH}_4 \tilde{X}$ photoelectronic transition. $\Gamma_{\text{ve}}$, $\Gamma_{\text{ve}}^+$ and $\Gamma_{\text{ve}}^*$ represent the vibronic and the rovibronic symmetries in the molecular symmetry group $T_d(M)$ for the neutral and the ionic state, respectively.

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<th>$^{13}\text{CH}<em>4$ ($\Gamma</em>{\text{ve}} = A_1$)</th>
<th>$^{13}\text{CH}<em>4^+$ ($\Gamma</em>{\text{ve}}^+ = F_2, F_1$)</th>
<th>$\tilde{\nu}_{\text{obs}}$ / cm$^{-1}$</th>
<th>($\tilde{\nu}<em>{\text{calc}} - \tilde{\nu}</em>{\text{obs}}$) / cm$^{-1}$</th>
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a Measured transitions without field correction.
b Band origin
Table B.7: Measured line positions ($\tilde{v}_{\text{obs}}$) and deviations from the calculated line positions ($\tilde{v}_{\text{obs}} - \tilde{v}_{\text{calc}}$) of the vibrationless CD$_4$ $^1X \rightarrow$ CD$_4$ $^1X$ photoelectronic transition. $\Gamma_{\text{ve}}$, $\Gamma_{\text{ve}}^+$ and $\Gamma_{\text{ve}}^+$ represent the vibronic and the rovibronic symmetries in the molecular symmetry group T$_d$(M) for the neutral and the ionic state, respectively.

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$^a$Measured transitions without field correction.
Table B.8: Measured line positions ($\tilde{\nu}_{\text{obs}}$) and deviation from the calculated line positions ($\tilde{\nu}_{\text{calc}} - \tilde{\nu}_{\text{obs}}$) of the origin of the CH$_3$D$^+$ X $\rightarrow$ CH$_3$D X photoionizing transition of CH$_3$D. $\Gamma_{\text{ve}}$, $\Gamma_{\text{vre}}$ and $\Gamma_{\text{rve}}$ represent the vibronic and the rovibronic symmetries in the molecular symmetry group $C_{3v}(M)$ for the neutral and the ionic state, respectively.

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$^a$Measured transition wave numbers without correction for the field-induced shift of the ionization thresholds.

$^b$Assignment tentative.
Table B.9: Measured line positions ($\tilde{\nu}_{\text{obs}}$) and deviation from the calculated line positions ($\tilde{\nu}_{\text{calc}} - \tilde{\nu}_{\text{obs}}$) of the origin of the CD$_3$H$^+$ $X^1\Sigma^+ - CD_3H X$ photoionizing transition of CD$_3H$. $\Gamma_{ve}$, $\Gamma_{rve}$ and $\Gamma_{rve}^+$ represent the vibronic and the rovibronic symmetries in the molecular symmetry group $C_{3v}(M)$ for the neutral and the ionic state, respectively.

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$^a$Measured transitions without field correction.

$^b$Assignment tentative.
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