Doctoral Thesis

Investigation of organic cations by high-resolution photoelectron spectroscopy

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Investigation of organic cations by high-resolution photoelectron spectroscopy

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To Tony
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Abstract

This thesis is concerned with the use of high-resolution photoionisation and pulsed-field ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy to study the energy level structure of small to medium-sized molecular cations and the photoionisation dynamics of the corresponding parent neutral molecules.

The four molecules selected for these studies, allyl, methyl, formaldehyde and allene are all prototypical systems in physical-organic chemistry: allyl as the smallest radical with a conjugated $\pi$-electron system, methyl as one of the simplest organic radicals, formaldehyde as the simplest aldehyde and allene as the first member of the cumulene family. Despite their fundamental importance, little is known on the photoionisation dynamics and singly-ionised forms of these molecules: the spectroscopic data available in the literature are often incomplete because of insufficient spectral resolution, ambiguous or even internally inconsistent.

The combination of narrow-bandwidth, tunable laser sources with high-resolution photoionisation and PFI-ZEKE photoelectron spectroscopy enabled the clarification of several open questions in the literature concerning both qualitative and quantitative aspects of the photoionisation dynamics of these molecules. In particular the ability to resolve the rotational fine structure of the photoelectron spectra provided important information not available in previous studies of these systems.

Rovibronic photoionisation selection rules and predictions of rovibrational intensity distributions in the realm of a simple orbital ionisation model (S. Willitsch and F. Merkt, *Int. J. Mass Spectrom.* 245(1-3), 14 (2005)) turned out to be particularly helpful in the analysis of the photoionisation and photoelectron spectra: firstly, they permitted the interpretation of the rotational branch structure of the photoelectron spectra in terms of the angular momentum composition of the molecular orbital out of which the photoelectron is ejected. Secondly, they enabled the detection of perturbations caused by interactions between different photoionisation channels. Finally, they led to the derivation of improved sets of molecular constants, including ionisation energies, by comparison of experimental with calculated spectra.

The investigation of the threshold ionisation of allyl following single-photon excitation enabled the resolution of a controversy concerning the first adiabatic ionisation energy which was determined to be $65580.1(20)\ \text{cm}^{-1}$ by modelling the intensity distribution of the PFI-ZEKE photoelectron spectrum using the orbital ionisation model. The analysis of the rovibrational photoionisation selection rules pointed at several inconsistencies and deficiencies of the previous analysis of Xing et al. (*J. Chem. Phys.* 126(17), 171101 (2007)). Predictions of the intensity distribution of photoelectron spectra of allyl recorded via selected intermediate electronic states ($B^2A_1, C^2B_2, D^2A_1, E^2B_1$) revealed a strong dependence on the selected intermediate levels which should assist in the assignment of the very complex electronic spectrum of allyl.
High-resolution photoionisation and PFI-ZEKE photoelectron spectra of CH\textsubscript{3}, CH\textsubscript{2}D, CHD\textsubscript{2} and CD\textsubscript{3} have been recorded in the vicinity of the first adiabatic ionisation threshold following single-photon excitation from the ground neutral state using narrow-bandwidth vacuum-ultraviolet radiation. The radicals were produced from the precursor molecules methyl bromide, methyl iodide, dimethyl sulphide, acetone and nitromethane by 193 nm excimer photolysis in a quartz capillary and were subsequently cooled to a rotational temperature \(T_{\text{rot}} \approx 30\) K in a supersonic expansion. Nitromethane was identified as a particularly suitable photolytic precursor of methyl for studies by photoionisation and threshold photoelectron spectroscopy. Thanks to the cold rotational temperature reached in the supersonic expansion, the rotational structure of the threshold ionisation spectra could be resolved, and the photoionisation dynamics investigated. Rydberg series converging on excited rotational levels of CH\textsuperscript{+}\textsubscript{3} could be observed in the range of principal quantum number \(n = 30\) to 50, and both rotational autoionisation and predissociation were identified as decay processes in the threshold region. The observed photoionisation transitions could be understood in the realm of the orbital ionisation model but the intensity distributions could only be fully accounted for by considering the rotational channel interactions mediated by the quadrupole of the cation. Improved values of the adiabatic ionisation thresholds were derived for all isotopomers (CH\textsubscript{3}: 79356.2(15) cm\textsuperscript{-1}, CH\textsubscript{2}D: 79338.8(15) cm\textsuperscript{-1}, CHD\textsubscript{2}: 79319.1(15) cm\textsuperscript{-1}, CD\textsubscript{3}: 79296.4(15) cm\textsuperscript{-1}).

Rotationally-resolved PFI-ZEKE photoelectron spectra of the 0\(^0\), 6\(^1\) and 4\(^1\) vibrational levels of the \(X^+\text{B}_2\) ground electronic state of the formaldehyde cation were recorded using a resonant three-colour three-photon excitation scheme. The first adiabatic ionisation energy of CH\textsubscript{2}O (87793.33(1.30) cm\textsuperscript{-1}) and the rigid-rotor rotational constants (\(A^+ = 8.874(8)\) cm\textsuperscript{-1}, \(B^+ = 1.342(15)\) cm\textsuperscript{-1}, \(C^+ = 1.148(18)\) cm\textsuperscript{-1}) of the vibronic ground state of CH\textsubscript{2}O\textsuperscript{+} were derived. A strong \(a\)-type Coriolis interaction between the 6\(^1\) and 4\(^1\) vibrational levels was observed. The Coriolis coupling parameter \(\xi_{6,4}\) and the deperturbed fundamental vibrational wave number of the in-plane rocking mode \(v_6\) and the out-of-plane bending mode \(v_4\) were determined to be 8.70(10) cm\textsuperscript{-1}, 823.67(30) cm\textsuperscript{-1} and 1036.50(30) cm\textsuperscript{-1}, respectively. The intensity distribution of the photoelectron spectra were also analysed in the realm of the orbital ionisation model.

The VUV photoionisation and PFI-ZEKE photoelectron spectra of allene were recorded from the first adiabatic ionisation energy (78142.92(50) cm\textsuperscript{-1}) up to 2300 cm\textsuperscript{-1} of internal energy of the allene cation. The spectra of C\textsubscript{3}H\textsubscript{4} and C\textsubscript{3}D\textsubscript{4} consist of vibrational progressions associated with the torsional mode (\(v_4\)) of the cations. The overall appearance of the vibrational structure is consistent with previous measurements of the vibrational structure of the spectrum at low resolution (Z. Z. Yang et al., Chem. Phys. Lett. 171, 9 (1990), P. Baltzer et al., Chem. Phys. 196, 551 (1995)) and their analysis (C. Woywod and W. Domcke, Chem. Phys. 162, 349 (1992)) and clearly indicates a distortion of the allene cation along the torsional mode resulting from a strong E\(\otimes(b_1 \oplus b_2)\) Jahn-Teller effect. Both positions and intensities of the bands associated with the torsional progression could be satisfactorily reproduced using the Jahn-Teller Hamiltonian reported by Woywod and Domcke. These calculations indicate that the equilibrium
structure of the allene cation is of $D_2$ symmetry with a dihedral angle of $\approx 50^\circ$ between the two planes of the CH$_2$ units. Measurement of the PFI-ZEKE photoelectron spectrum of C$_3$H$_4$ at high resolution revealed the full rotational structure and several so far unidentified weak vibrational bands.

The analysis of the rotational structure of the lowest two ($0^0$ and $4^1$) torsional bands led to the derivation of a set of molecular constants for the allene cation. The observed rotational structure is consistent with that of a near-symmetric prolate top and does not reveal significant perturbations except a slight broadening of the lines of the $4^1$ band. The rotational structure of the high torsional bands $4^2$ and $4^3$ was found to be strongly perturbed by (ro-)vibronic interactions with neighbouring states, vibronic interactions related to the Jahn-Teller effect and reveals splittings indicative of a tunnelling motion through the $D_{2h}$ potential energy barrier. These perturbations cannot be explained by current theoretical models of the E$\otimes$(b$_1 \oplus$ b$_2$) Jahn-Teller effect in allene which disregard the possibility of tunnelling through the $D_{2h}$ potential energy barrier. In an attempt to account for the experimental observations a theoretical model to treat the Jahn-Teller effect in allene jointly with the large amplitude torsional motion was developed. This model was successful in predicting both the qualitative structure of the torsional progression and level splittings resulting from the tunnelling through the $D_{2h}$ potential energy barrier and thus appears promising for the treatment of the Jahn-Teller effect in allene and other members of the cumulene family.
Zusammenfassung


Durch die Kombination schmalbandiger, abstimmbarer Laserlichtquellen mit hochauflösender Photoionisationsspektroskopie und PFI-ZEKE-Photoelektronenspektroskopie konnten mehrere offene Fragen in der Literatur bezüglich qualitativer und quantitativer Aspekte der Photoionisationsdynamik dieser Moleküle aufgeklärt werden. Die Fähigkeit, die Rotationsfeinstruktur von Photoelektronenspektren aufzulösen, erlaubte es, wichtige Informationen über diese Molekülsysteme zu erhalten, die in früheren Untersuchungen nicht gewonnen werden konnten.


Die Untersuchung der Photoionisation des Allylradikals in der Nähe der ersten adiabatischen Ionisationsschwelle führte zu einer Klärung einer Kontroverse über den Wert der adiabatischen Ionisationsenergie, welche durch die Modellierung der Intensitätsverteilung der PFI-ZEKE-Photoelektronenspektren anhand des Orbitalionisationsmodells auf 65580.1(20) cm⁻¹ bestimmt wurde. Die Analyse der rovibronischen Photoionisationsauswahlregeln zeigten mehrere Unzulänglichkeiten in der bisherigen Auswertung durch Xing et al. (J. Chem. Phys.
Die Vorrausrechnung der Intensitätsverteilung im Photoelektronenspektrum von Allyl, welches über ausgewählte elektronische Zwischenzustände (B $^2$A$_1$, C $^2$B$_2$, D $^2$A$_1$, E $^2$B$_1$) aufgenommen wurde, wies eine starke Abhängigkeit von den elektronischen Zwischenzuständen auf. Diese Simulationen durften bei der Zuordnung des sehr komplexen elektronischen Spektrums von Allyl hilfreich sein.

Grundzustandes des Formaldehydkations wurden mittels eines Dreifarben-Dreiphotonenanregungsschemas gemessen. Die ersten adiabatischen Ionisationsenergien für alle Isotopomere (CH$_3$: 79356.2(15) cm$^{-1}$, CH$_2$D: 79338.8(15) cm$^{-1}$, CHD$_2$: 79319.1(15) cm$^{-1}$, CD$_3$: 79296.4(15) cm$^{-1}$) bestimmt.

Die VUV Photoionisations- und PFI-ZEKE-Photoelektronenspektren von Allen wurden von der ersten adiabatischen Ionisationsenergie bis 2300 cm$^{-1}$ innerer Energie des Kations gemessen. Die Spektren von C$_3$H$_4$ und C$_3$D$_4$ zeigten Vibrationsprogressionen, welche der Tor-

Die Analyse der Rotationsstruktur der zwei energetisch tiefsten Torsionsbanden ($0^0$ und $4^1$) erlaubte die Bestimmung der Rotationskonstanten, der fundamentalen Vibrationswellenzahl $\nu_4^+$ und der adiabatischen Ionisationsenergie. Die beobachtete Rotationsstruktur deute auf einen fast symmetrischen spindelförmigen (prolate) Rotor, welche, abgesehen von einer leichten Verbreiterung der Linien in der $4^1$ Bande, keine signifikante Störungen aufzeigte. Die stark gestörte Rotationsstruktur der energetisch höheren Torsionsbanden ($4^2$ und $4^3$) weist auf (ro)vibronische Wechselwirkungen mit naheliegenden Zuständen und vibronischen Wechselwirkungen, welche auf den Jahn-Teller Effekt zurückzuführen sind, hin. Zudem deuten Aufspaltungen einzelner Linien auf eine Tunnelbewegung durch die Barriere in der Potentialenergiefläche bei einer $D_{2h}$ Geometrie hin. Diese Störungen konnten im Rahmen der gängigen theoretischen Behandlung des $E \otimes (b_1 \oplus b_2)$ Jahn-Teller Effektes in Allen nicht erklärt werden, da diese Modelle ein Tunneln durch die Barriere in der Potentialenergiefläche bei einer $D_{2h}$ Geometrie vernachlässigten. Um die experimentellen Beobachtungen theoretisch zu erklären, wurde ein theoretisches Modell entwickelt, welches sowohl den Jahn-Teller Effekt in Allen als auch die Torsionsbewegung grosser Amplitude behandelt. Dieses Modell konnte die qualitative Struktur der Torsionsprogression und die durch eine Tunnelbewegung durch die $D_{2h}$ Barriere verursachte Aufspaltung der Niveaus erfolgreich vorhersagen und erscheint für die Behandlung des Jahn-Teller Effektes in Allen und anderen Mitgliedern der Kumulenfamilie vielversprechend.
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Chapter 1

Introduction

This chapter provides background information and introductory material on the experimental and analysis methods used in the investigations described in this thesis. Sections 1.1 and 1.4 summarise the principles of photoelectron spectroscopy and its high-resolution version of PFI-ZEKE photoelectron spectroscopy, respectively. Because PFI-ZEKE photoelectron spectroscopy relies on the pulsed-field ionisation of high Rydberg states, the latter section is preceded by a brief overview of the properties of atomic and molecular Rydberg states in Section 1.3. Sections 1.5 and 1.7 are devoted to photoionisation spectroscopy and provide information on photoionisation selection rules and the modelling of rotational line intensities in photoelectron spectra. Because two of the molecular systems investigated in this thesis are radical species (C$_3$H$_5$ and CH$_3$), Section 1.2 reviews the methods used to generate radicals in the context of photoionisation and photoelectron spectroscopic studies.

1.1 Spectroscopic investigation of molecular cations

Molecular cations play an important role in combustion chemistry, plasmas, reaction dynamics and interstellar and atmospheric chemistry. Radicals and molecular radical cations formed from closed-shell neutrals have a ground state configuration with an unpaired electron. This open-shell configuration may give rise to interesting dynamics involving the nuclear and electronic degrees of freedom, such as (ro)vibronic coupling phenomena like the Jahn-Teller effect, the Renner-Teller effect, spin-orbit or spin-rotation interactions. However, since cations and radicals are highly reactive species and therefore difficult to generate and store, they have not been studied spectroscopically as extensively as neutral closed-shell molecules.

High densities of cations in the gas phase are difficult to obtain, because the positively charged particles repel each other. The number densities are limited to at most $\sim 10^{10}$ ions/cm$^{-3}$ by space-charge effects. An elegant way to circumvent space-charge problems in the spectroscopic investigation of molecular cations is to use photoelectron spectroscopy which enables one to obtain spectra of cations starting from the neutral parent molecule [1, 2]. This advantage, when combined with the very efficient and background-free detection of photoelectrons,
results in a very high sensitivity. The traditional drawback of photoelectron spectroscopy to study molecular cations is its lower spectral resolution compared to conventional methods of spectroscopy in regions of the electromagnetic spectrum ranging from the microwave to the ultraviolet: The resolution in HeI photoelectron spectroscopy is orders of magnitudes lower and at best 10 cm$^{-1}$ [3] and is usually insufficient to observe the rotational structure. Recent progress in threshold photoelectron and photoionisation spectroscopy has partially compensated this drawback [4, 5, 6, 7]. Today, Pulsed-Field Ionisation ZEro-Kinetic-Energy (PFI-ZEKE) photoelectron spectroscopy enables a resolution of up to 0.06 cm$^{-1}$ [7] to be achieved, which suffices to resolve the rotational structure of small to medium-sized molecules. Photoelectron spectroscopy also allows for the direct investigations of the photoionisation dynamics and gives access to a wide range of rovibronic states of molecular cations.

1.2 Production of radicals

Molecules with unpaired electrons and therefore an open-shell ground state electronic configuration are called radicals. Many radicals are highly reactive, short-lived species that need to be produced from suitable precursor molecules during a spectroscopic experiment. High densities of radicals in the gas phase are difficult to obtain and the demands on a radical source for spectroscopy, especially photoelectron spectroscopy, are manifold:

1. High conversion efficiency of the precursor molecule to the desired radical to avoid contamination of the spectra by resonances of the precursor molecule and to achieve high sensitivity. For photoelectron spectroscopy, it is important that the precursor molecule has an ionisation energy higher than that of the desired radical, not only to prevent high densities of charged particles in the ionisation region and the formation of a plasmas [8] but also to avoid the occurrence of spectral features of the precursor in the photoelectron spectrum of the radical.

2. Selective and specific production of the desired radical. In particular in mass-unselective methods of spectroscopy, such as absorption, laser-induced fluorescence or photoelectron spectroscopy, a clean production of only or mostly the desired species is required, because other dissociation products, recombination products or other species in the measurement volume contaminate the spectra.

3. Control of the internal energy distribution of the radical product. The ability of cooling the radicals to low temperatures is particularly desirable. This reduces spectral congestion, eliminates the possibility of further dissociation or rearrangement of the desired radical product and facilitates the interpretation of the spectra.

4. Isolation of the highly reactive species in order to avoid reactive collisions after the desired radical has been formed.
1.2. Production of radicals

The last two of these requirements can be met by generating the radicals in a pulsed supersonic molecular beam which offers the possibility to cool the species present in the beam efficiently and provides a collision-free environment for spectroscopic investigation. Supersonic beams further lead to negligible Doppler broadening in the dimensions perpendicular to the propagation axis and enable efficient differential pumping by use of a skimmer between the radical source region and the detection region, a necessary condition for the detection of charged particles. Here only those methods compatible with a pulsed supersonic beam will be discussed. The reader is referred to Ref. [9] for a more complete overview of radical sources for spectroscopic experiments.

1. Discharge methods

In discharge methods a voltage is applied across a mixture of inert gas and radical precursor resulting in electron impact dissociation of the precursor molecule R-X and the formation of the radical R⁺:

\[ R + X \rightarrow e^- \rightarrow R^+ + X^- \quad \text{and} \quad R + X + e^- \rightarrow R^+ + X^- \].

(1.1)

In the early 1980s, discharge methods have been adapted for the use with supersonic jets [10, 11]. Recently, methods have been developed, which use transverse or longitudinal electrodes attached directly after the gas nozzle, so that the radicals are produced in a region of high pressure and efficiently cooled to rotational temperatures below 30 K in the initial stage of the supersonic expansion [12, 13]. The conversion efficiency and the main radical product are sensitive to the voltages applied, the geometry of the discharge and the gas mixtures and the pressure employed. Competing processes such as ionisation or excitation can occur, which may result in the formation of molecular plasmas undesirable for the use of PFI-ZEKE photoelectron spectroscopy. A recent use of a discharge to produce a supersonic beam of metastable He₂⁺ molecules is reported in Ref. [14].

2. Flash Pyrolysis

Flash pyrolysis is a variant of pyrolysis adapted for experiments in a supersonic jet expansion first developed by Kohn et al. in 1991 [15]. In flash pyrolysis a mixture of a suitable precursor molecule R-R⁰ is entrained in a stream of an inert carrier gas. The gas mixture is heated for 10-100 μs to temperatures of up to 2000 K just before the exit orifice of the pulsed nozzle where it dissociates thermally according to:

\[ R + R' \rightarrow T \rightarrow R^+ + R'^- \].

(1.2)

The radical production can be optimised, and recombination and secondary dissociation processes can be minimised [9] by varying the nozzle temperature, the stagnation pressure and the time the sample is heated. Number densities on the order of \(10^{14} \text{ cm}^{-3}\) after the nozzle [16] can be obtained.

The usually very high temperatures in the nozzle initially produce radicals with a wide
internal energy distribution. Subsequent cooling in the supersonic expansion leads to rotational temperatures in the range of 40 K to 250 K [16, 17, 18], but other degrees of freedom may not be cooled as efficiently. The main advantages of this method are its high chemical selectivity and the high number densities of the radicals that can be produced.

3. Hydrogen abstraction

Many radicals can be produced chemically. Halogen or oxygen atoms or OH radicals (all represented as X in Eq. (1.3)) can easily be produced both photolytically and in a discharge. These radicals then efficiently react with another precursor molecule abstracting a hydrogen atom

\[ R - H + X^- \rightarrow R \cdot + H - X. \]  

(1.3)

The reaction is highly specific to hydrogen abstraction [19]. However, the hydrogen abstraction is not selective: if many non-equivalent hydrogen atoms are present in the precursor, hydrogen abstraction usually yields a wide range of structurally different radical products. Hydrogen abstraction has been particularly useful for the production of small radicals such as HCO [20], N\(_3\) [21], NH\(_2\) [22, 23] and C\(_3\)F\(_5\)OH\(_2\) [24] and has been extensively used by Berkowitz and co-workers [19] and Dyke and co-workers to study the photoionisation and photoelectron spectra of radicals [25].

4. Photolysis

Radicals produced photolytically are formed by the homolytic cleavage of a covalent bond by irradiation of the sample with strong monochromatic light, usually in the UV:

\[ R - X + h\nu \rightarrow R \cdot + X^- \]  

(1.4)

In the group of Smalley a photolysis radical source was developed, where the precursor was photolysed just after the exit orifice of the nozzle [26] or through a small hole in the nozzle [27] with subsequent expansion into the vacuum and cooling of the radicals. Willitsch et al. [28, 29] devised a method, in which the photolysis laser is focused on a quartz capillary mounted at the orifice of the nozzle. The precursor molecules are dissociated under high-pressure conditions before the radicals are cooled in the supersonic expansion into vacuum taking place at the end of the capillary. Number densities of the desired radical in the excitation volume of 10\(^{12}\) cm\(^{-3}\) can be obtained [29]. Photolysis in the capillary, rather than at the exit orifice of a pulsed gas nozzle allows for more efficient cooling and typically rotational temperatures of 10-40 K are achieved. The choice of photon energy of the photolysis laser radiation and the precursor molecule allows for highly selective production of the desired radical.

All methods of radical production outlined above suffer from the very high reactivity and sometimes the lack of internal stability of the desired radicals. Recombination and fragmentation are processes that limit the conversion of the precursor into the desired radical and the number
dynamics of the radical in the molecular beam.

In the present spectroscopic experiments on radicals, the photolysis radical source developed by Willitsch et al. [28] was used for the reasons of ease and control in producing the desired species. The efficiency and selectivity of the dissociation (Eq. (1.4)) at a certain photon energy $h\nu$ depends strongly on the absorption cross section of the precursor R-X, the yield of a given product radical following dissociation of a specific bond of the molecule [30], secondary fragmentation, multiphoton ionisation and recombination reactions following radical production.

The internal temperature of a molecular radical can be controlled by varying the stagnation pressure of the gas mixture, by seeding the precursor molecules in different rare gases and by optimising the geometry of the supersonic expansion. Rotational temperatures of typically 20 K can be achieved for small to medium-sized radicals in the photolytic source used in the present work. Recombination can be circumvented by producing the radical in low concentration and/or carrying out the photolysis close to the capillary exit, however, reducing number densities and/or cooling (see Section 2.4). Varying the position of the photolysis laser focus along the axis of the capillary enables one to find the best compromise between optimal radical production, which requires as few reactive collisions as possible [28], and optimal cooling, which requires as many collisions as possible. The choice of photolysis wavelength, laser intensity and focus position on the capillary requires considerable care. The choice of the precursor molecule also plays an important part in the efficient production of a selected radical and requires chemical intuition.

### 1.3 Molecular Rydberg states

Molecular Rydberg states are electronically highly excited states of an atom or a molecule in which the excited electron is located, on average, at a large mean distance $r$ from the atomic or molecular ion core. The Rydberg electron can be approximately described as moving in the Coulombic potential of the positively charged ion core. A formula describing the spectral positions of atomic Rydberg states was first derived for atomic hydrogen by J. J. Balmer [31] in 1885. His empirical formula was later generalised to the Rydberg formula by J. R. Rydberg [32]:

$$E(n, l, j) = E_i(j) - \frac{R_M}{(n-\delta_l)^2}.$$  \hspace{1cm} (1.5)

In Eq. (1.5) $E(n, l, j)$ is the energy of the Rydberg state with principal quantum number $n$ and orbital angular momentum quantum number $l$. $R_M = R_\infty \cdot \frac{M}{M+m_e}$ is the mass-corrected Rydberg constant of an atom or molecule of mass $M$. The quantum defect $\delta_l$ in non-hydrogenic systems ($\delta_l=0$ for H) accounts for the specific structure of many-electron atoms and molecules and results from the interaction of the Rydberg electron with core electrons at short distances $r$. It reflects the collisional phase shift of the Rydberg electron wavefunction induced by the
ion core and is usually only significantly different from zero for low-$l$ ($l \leq 3$) states. States of distinct $l$- and increasing $n$-values form a Rydberg series which converge on a specific ionisation threshold $E_i(j)$, where $j$ represents the quantum numbers of the ionic state to which the Rydberg series converge at $n \to \infty$. These series and the adjacent ionisation continua are called ionisation channels. As can be seen in Fig. 1.1, the Rydberg states are $n^2$-fold degenerate in the hydrogen atom. In non-hydrogenic atoms, the $l$ degeneracy is lifted because of the non-zero values of the quantum defect of penetrating series. Molecules have a particularly rich Rydberg structure: many different series converge on each rovibronic energy level of a molecular cation, overlap spectrally and interact [33].

The large average distance of the Rydberg electron from the positively charged ion core results in exaggerated properties of the Rydberg atoms and molecules [34, 35], of which the ones most important to this work are collected in Table 1.1. The table indicates how these properties scale with $n$ and lists numerical values for $n = 1$, 100 and 200 for H, $n = 200$ being typical of the Rydberg states probed by PFI-ZEKE photoelectron spectroscopy [36, 35, 37]. From the Rydberg formula in Eq. (1.5), one can immediately see that the binding energy of the electron scales with $n^{-2}$ and that the energy separation of two adjacent Rydberg states scales with $n^{-3}$. The resulting high density of states at high $n$ leads to a pseudocontinuum of Rydberg states just below each ionisation threshold where the energy level separation is so small relative to the bandwidth of the radiation sources used to excite them or to the Doppler broadening that individual Rydberg states cannot be resolved anymore in a spectroscopic experiment.
1.3. Molecular Rydberg states

Table 1.1: Summary of some of the relevant properties of Rydberg atoms in dependence of the principal quantum number \( n \). The exemplary numerical values for \( n = 1 \), 100 and 200 correspond to those of the hydrogen atom.

<table>
<thead>
<tr>
<th>Property</th>
<th>scaling</th>
<th>( n = 1 )</th>
<th>( n = 100 )</th>
<th>( n = 200 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean radius ( r )</td>
<td>( n^2 )</td>
<td>0.5Å</td>
<td>0.5µm</td>
<td>2µm</td>
</tr>
<tr>
<td>binding energy ( E_{n+1} - E_n )</td>
<td>( n^{-2} )</td>
<td>109678 cm(^{-1} )</td>
<td>( \sim 11 ) cm(^{-1} )</td>
<td>( \sim 2.7 ) cm(^{-1} )</td>
</tr>
<tr>
<td>radiative life time</td>
<td>( n^3 )</td>
<td>( \sim 82259 ) cm(^{-1} )</td>
<td>( \sim 0.2 ) cm(^{-1} )</td>
<td>( \sim 0.02 ) cm(^{-1} )</td>
</tr>
<tr>
<td>ionising field</td>
<td>( n^{-4} )</td>
<td>2 \cdot 10^9 V/cm</td>
<td>3 V/cm</td>
<td>100 mV/cm</td>
</tr>
</tbody>
</table>

Figure 1.2: The Coulomb potential experienced by an electron in hydrogen in the absence of an external electric field (dashed line), an external electric field along the \( z \)-direction of magnitude \( F \) (dot-dashed line) and the potential resulting from the application of that field(solid line). A saddle point is obtained at \( z = -\frac{1}{\sqrt{F}}, 2\sqrt{F} \) below the unperturbed ionisation threshold.

PFI-ZEKE photoelectron spectroscopy makes use of selective pulsed-field ionisation of high-\( n \) Rydberg states, and the process of field ionising is now briefly described. A homogeneous electric field causes the potential felt by the Rydberg electron, which is spherically symmetric under field-free conditions, to adopt cylindrical symmetry. In atomic units, the potential \( V(r) \) experienced by the electron in a hydrogenic atom in an external homogeneous electric field of magnitude \( F \) applied along the \( z \)-direction is given by

\[
V(r) = -\frac{1}{|r|} + Fz. \tag{1.6}
\]

In a homogeneous electric field, \( V(r) \) exhibits a saddle point along the \( z \)-axis as shown in Fig. 1.2. The ionisation threshold is lowered by \( 2\sqrt{F} \) in atomic units (6.12 \( \sqrt{F/(V\text{cm}^{-1})} \) in units of cm\(^{-1} \)). Moreover, the Rydberg states are shifted by the electric field and the near-degenerate Rydberg states of a given \( n \) split into a Stark manifold [34]. States shifted to higher (lower) energies are called blue- (red-) shifted. The red- and blue-shifted Stark states ionise at different rates, which results in different effective field ionisation thresholds. For red-shifted
Stark states, the lowering of the ionisation threshold $\Delta E$ can be approximated by

$$\frac{\Delta E}{hc \text{ cm}^{-1}} = 4.35 \sqrt{F/(\text{V cm}^{-1})}$$  \hspace{1cm} (1.7)

if the experimental time scale is such that Rydberg states with ionisation rates $> 10^8 \text{ s}^{-1}$ [38, 35] are detected as is typical in PFI-ZEKE photoelectron spectroscopic experiments. For blue shifted states with $n \approx 100$ the field-induced shift of the ionisation potential can be approximated with

$$\frac{\Delta E}{hc \text{ cm}^{-1}} = 2.35 \sqrt{F/(\text{V cm}^{-1})}.$$  \hspace{1cm} (1.8)

The differences between the effective ionisation thresholds of the red- and blue-shifted Stark states can be explained qualitatively by the fact that the Rydberg electron wavefunction is located in the vicinity of the saddle point in the case of red-shifted Stark states and on the opposite side in the case of blue-shifted Stark states. A more sophisticated model of determining the field induced shift has been developed by Hollenstein et al. [7, 39].

The lifetimes of high-$n$ Rydberg states are generally long. Apart from spontaneous radiative decay to the ground state or lower lying electronic states, a molecule in a Rydberg state in a collision free environment can also decay by autoionisation, predissociation or transitions between Rydberg states induced by blackbody radiation. The rate of spontaneous emission (the inverse of the radiative lifetime) of a Rydberg state is governed by the Einstein $A_{GS-n,l}$ coefficient [40] for a transition from a Rydberg state $(n, l)$ to the ground state (GS). Because $A_{GS-n,l}$ is proportional to the square of the transition dipole moment between the Rydberg state and the ground state, which itself is proportional to the electron density close to the ion core, the radiative lifetime scales with $n^3$ [34]. Ionisation induced by the coupling of a bound Rydberg state with an ionisation continuum of a different ionisation channel is termed autoionisation. For energetic reasons this can only occur for Rydberg states that lie above the first ionisation threshold. In electronic, vibrational, rotational or hyperfine autoionisation the ion core transfers electronic, vibrational, rotational or hyperfine energy to the Rydberg electron, respectively. Autoionisation processes are subject to restrictive selection rules (see Chapter 4 or Refs. [41, 42]). Predissociation can only occur in molecular systems. In this case the kinetic energy of the Rydberg electron is transferred to the ion core resulting in the breaking of a bond [43]. Both predissociation and autoionisation occur when the electron is in close enough proximity to the ion core in order for an exchange of energy between the electron and the ion core to take place, and their rates therefore also decrease as $n^{-3}$.

The spectrum of blackbody radiation emitted by a body at 300 K peaks at $\approx 1000 \text{ cm}^{-1}$ and stimulated transitions between close-lying Rydberg states may occur. Stimulated emission or absorption are especially efficient to neighbouring Rydberg states and is therefore particularly efficient around $n = 20 – 30$ at room temperature. The effects of blackbody radiation are negligible in the experiments conducted as part of the present work because they probed the high ($n > 200$) Rydberg states by PFI-ZEKE photoelectron spectroscopy, because the spacing
1.4. PFI-ZEKE photoelectron spectroscopy

between adjacent Rydberg states (< 1 cm\(^{-1}\)) is much smaller than the wave number at the maximum of the blackbody radiation intensity distribution at room temperature.

1.4 PFI-ZEKE photoelectron spectroscopy

High-resolution photoelectron spectra contain information on a molecular system in the form of line positions and line intensities. The former corresponds to energy differences between the quantum states of a molecular cation and its neutral parent molecule and can be exploited to determine thermochemical quantities such as ionisation energies and information on the structural and dynamical properties of both neutral and ionic molecules. The latter contains information on the photoionisation dynamics and selection rules which are very sensitive to the changes in molecular structure and symmetry occurring upon ionisation.

In conventional photoelectron spectroscopy developed by D. W. Turner and M. I. Al Jobory [1] and F. I. Vilesov, B. L. Kurbatov and A. N. Terenin [44], a gaseous sample is exposed to ionising radiation of fixed wavelength, typically the HeI and HeII lines at 58.4 nm and 53.7 nm, respectively, from helium lamps, and the kinetic energy of the photoelectrons is measured. According to the photoelectric effect [45], the kinetic energy \( E_{\text{kin}} \) of a photoelectron emitted from a molecule with an ionisation energy \( E_i(j) \) corresponding to the \( j \)’th quantum state of the resulting cation upon irradiation with light of frequency \( \nu \) is given by

\[
E_{\text{kin}} = h \nu - E_i(j).
\] (1.9)

The photoelectron spectrum therefore contains, in principle, information about all accessible rovibronic ionisation channels and thresholds of the species under investigation that lie less than \( h \nu \) in energy above the neutral ground state. Since electrons are very light charged particles, which are highly sensitive to stray fields, the measurement of their kinetic is difficult and the energy resolution is typically limited to about 5-8 meV (40-65 cm\(^{-1}\)). This is usually sufficient for resolving the vibrational but not the rotational energy level structure of molecular cations.

PFI-ZEKE photoelectron spectroscopy [46, 47] is a high-resolution variant of photoelectron spectroscopy and was developed in the group of Schlag and Müller-Dethlefs [4, 5]. This experimental technique made an improvement of the resolution of photoelectron spectroscopy by three orders of magnitude (0.06 cm\(^{-1}\) in Ref. [7]) possible. An energy level diagram illustrating the principle of PFI-ZEKE photoelectron spectroscopy is presented in Fig. 1.3 b). The neutral molecule in a well defined quantum state, often the rovibronic ground state, is excited by tunable monochromatic VUV radiation the region of the ionisation thresholds. A small pulsed electric field is applied to field ionise the long-lived high-\( n \)-Rydberg states and extract the electrons. An electron signal is detected whenever the wave number corresponds to a transition to the pseudo-continuum of high Rydberg states. The resulting spectrum therefore maps out the relative rovibronic energy level structure of the cation. The positions of the ionic energy levels
relative to those of the neutral molecule can be derived by introducing a small correction to account for the small displacement of the pseudo-continuum of high-$n$ Rydberg states from the field-free ionisation thresholds (see Section 1.3).

Hollenstein et al. have investigated the dynamics of pulsed-field ionisation in high-$n$ Rydberg states in detail \cite{7, 39} and devised electric field-pulse sequences that optimise the resolution and selectivity of the pulsed-field-ionisation process: a first electric field pulse, usually shorter than 1µs in duration, is applied a few µs after photoexcitation to sweep electrons formed by direct ionisation away from the excitation region which may otherwise contribute to an undesirable background signal. This first pulse is sometimes referred to as the ‘discrimination pulse’. The discrimination pulse also field-ionises the highest $n$-members of the pseudocontinuum. Subsequent electric field pulses (called ‘detection pulses’) with opposite polarity to that of the discrimination pulse are applied and the electrons produced by these pulses are accelerated onto the detector. Typically the full width at half maximum (FWHM) of the lines in the photoelectron spectra amounts to 0.2 cm$^{-1}$ for a simple two-pulse sequence. A better resolution can be achieved by a multi-pulse sequence of detection pulses. The best resolution can be achieved for a field pulse sequence in which the detection pulses are of smaller magnitude (but opposite polarity) than the discrimination pulse \cite{39}. The gain in resolution by using multi-pulse sequences is typically accompanied by a loss of sensitivity, because each field pulse diminishes the population of the pseudo-continuum. The best compromise between resolution and sensitivity is usually found when the energetic breadth of the pseudo-continuum ionised by a certain electric

Figure 1.3: Schematic diagram of a) the ionisation channels of a molecule, b) an idealised PFI-ZEKE photoelectron and c) an idealised photoionisation spectrum mapping out different ionisation thresholds.
field pulse sequence corresponds to the bandwidth of the radiation source. A two-pulse sequence is therefore usually chosen when overview spectra are recorded at moderate resolution with the broadly tunable laser system (Subsection 2.2.1), whereas multi-pulse sequences are employed in experiments with the high-resolution laser system (Subsection 2.2.2). The field-induced shifts of the rovibronic ionisation thresholds in the PFI-ZEKE photoelectron spectra recorded as part of this work were calculated using the model of Hollenstein et al. [7]. It was assumed that all rovibronic ionisation thresholds are shifted by the same amount by the field ionisation and that the different lines in the PFI-ZEKE photoelectron spectra can be directly used to determine the relative positions of the cationic states.

The sensitivity of high-\(n\) Rydberg states to electric fields requires the application of highly homogeneous pulsed fields and the minimisation of stray fields. Unavoidable stray and inhomogeneous electric fields usually arise from charged particles produced in the excitation region [48].

PFI-ZEKE photoelectron spectroscopy is now a well-established spectroscopic method to study the energy level structure of molecular cations and the photoionisation dynamics of neutral molecules. Several review articles provide further details and summarise applications of this technique [36, 42, 35, 49, 37].

### 1.5 Photoionisation spectroscopy

Photoionisation spectroscopy probes the ionisation continuum rather than the pseudo-continuum of high Rydberg states as in PFI-ZEKE photoelectron spectroscopy. However, because of the continuity of oscillator strengths across ionisation thresholds [50] both techniques are closely related. In photoionisation spectroscopy, the ion yield is monitored as a function of the wave number of the ionising radiation. The ion signal can be recorded mass selectively as in the set-ups described in Section 2.3. Mass-selective photoionisation spectroscopy is complementary to mass-unselective photoelectron spectroscopy and is very important in assigning bands recorded with photoelectron spectroscopy if more than one molecular species is present in the photoionisation region (see Chapter 6).

Each time an ionisation threshold is crossed, an ionisation continuum is made accessible to the molecule and the ion yield increases. In an idealised photoionisation spectrum a step is therefore expected in the ionisation yield at each threshold as depicted in Fig. 1.3 c). In the ideal case in which interactions between different ionisation channels are negligible, this photoionisation spectrum would correspond to the integrated signal of the PFI-ZEKE photoelectron spectrum, and would therefore allow for the reconstruction of the ionic energy level structure. However, interactions between the ionisation continuum and high-lying Rydberg states lead to more complicated ionisation dynamics as will be discussed in Chapter 4. In general the photoionisation spectra of molecules are dominated by sharp autoionising resonances which obscure the idealised step-like structure depicted in Fig. 1.3 c) [51, 50, 52, 53].
1.6 Rovibronic symmetry selection rules

Rovibronic selection rules and qualitative models to describe the rovibronic intensity distribution of PFI-ZEKE photoelectron spectra are essential for the interpretation of PFI-ZEKE photoelectron spectra. To this end Müller-Dethlefs and co-workers [36, 54] have formulated the so-called compound-state model to model the intensity distribution in the PFI-ZEKE photoelectron spectra of NH$_3$, C$_6$H$_6$ and even larger polyatomic molecules. General rovibronic photoelectron symmetry selection rules have been derived in Ref. [55] and a simple orbital ionisation model, originally formulated for diatomic molecules [56, 57], has been extended to model the intensity distribution in the photoelectron spectra of polyatomic molecules [29, 58, 59]. This section provides a brief derivation of the rovibronic photoionisation selection rules employed in the analysis of the photoelectron spectra presented in this thesis and follows closely the derivation in Ref. [60, 59], and Section 1.7 describes the orbital ionisation model which was used to model the intensity distribution of the photoelectron spectra.

The line strength $S(f \leftarrow i)$ of a single-photon transition from any initial state $\psi_i$ to any final state $\psi_f$ in the electric dipole approximation is given by

$$S(f \leftarrow i) \propto |\langle \psi_f | \hat{\mu} | \psi_i \rangle|^2,$$  \hspace{1cm} (1.10)

where $\hat{\mu} = \sum_i q_i \hat{r}_i$ represents the electric dipole moment operator, with $q_i$ the charge and $\hat{r}_i$ the position vector operator of the particle $i$. For the integral in Eq. (1.10) to be non-zero the following symmetry requirements must be met:

$$\Gamma_f \otimes \Gamma_{\hat{\mu}} \otimes \Gamma_i \supseteq \Gamma_{\text{tot. sym.}},$$ \hspace{1cm} (1.11)

where $\Gamma_f$, $\Gamma_i$, $\Gamma_{\hat{\mu}}$ and $\Gamma_{\text{tot. sym.}}$ are the irreducible representation of the final and initial states, of the electric dipole moment and the totally symmetric representation in the molecular symmetry group [61] of the system under investigation.

The electric dipole moment of the molecule is not affected by any permutation of identical nuclei, but only by operations of the molecular symmetry group including the inversion $E^*$ of all space-fixed coordinates of all particles in the system. Consequently

$$\Gamma_{\hat{\mu}} = (\Gamma^*)^p,$$ \hspace{1cm} (1.12)

where $\Gamma^*$ is called the antisymmetric representation, which has character -1 under all inversion-permutation operations of the molecular symmetry group and character +1 for all other operations. $p$ represents the number of photons involved in the transition. Eq. (1.11) translates into

$$\Gamma_{\text{int}}' \otimes \Gamma_{\text{int}}'' \supseteq (\Gamma^*)^p$$ \hspace{1cm} (1.13)

for a $p$-photon transition from some initial bound state (indicated by $''$) to some final bound state (indicated by $'$). The irreducible representation of the internal wave function $\Gamma_{\text{int}}$ is the direct
product of the irreducible representation of the nuclear spin \((\Gamma_{ns})\) and rovibronic wavefunctions \((\Gamma_{rve})\). Eq. (1.13) can be rewritten as

\[ \Gamma'_{ns} \otimes \Gamma'_{rve} \otimes \Gamma''_{ns} \otimes \Gamma''_{rve} \supseteq (\Gamma^*)^p . \] (1.14)

Since the nuclear spin symmetry remains unaltered in a transition described in the electric dipole approximation, Eq. (1.14) reduces further to

\[ \Gamma'_{rve} \otimes \Gamma''_{rve} \supseteq (\Gamma^*)^p . \] (1.15)

In PFI-ZEKE photoelectron spectroscopy the electron is promoted from a valence orbital to a pseudo-continuum of high-\(n\) Rydberg states. The neutral ground state of a molecule can usually be described using Hund’s angular momentum coupling case (a) or (b) (or their generalisation to nonlinear molecules), whereas high-lying Rydberg states are best labelled using Hund’s case (d) nomenclature, because the photoelectron can in good approximation be regarded as completely decoupled from the ion core in the asymptotic long-range part of the electron-core potential [56, 62, 63, 64]. In the asymptotic region, the final wavefunction in a PFI-ZEKE photoelectron transition can therefore be described as the product of the internal wavefunction of the cation \(\psi_{\text{int, ion}}\) and the wavefunction of the photoelectron \(\psi_{e^-}\).

\[ \psi_f = \psi_{\text{int, ion}} \psi_{e^-} . \] (1.16)

The wavefunction of the photoelectron is conveniently described in a single-centre partial wave expansion [56] in the centre of mass of the molecular system

\[ \psi_{e^-} = \sum_{\ell=-m_{\ell}}^{\ell_m} c_\ell Y_{\ell,m_{\ell}}(\theta,\phi) R_{n,\ell}(r) , \] (1.17)

where \(c_\ell\) represents the expansion coefficient which weights the electron partial wave component of orbital angular momentum quantum number \(\ell\). \(Y_{\ell,m_{\ell}}(\theta,\phi)\) represents the spherical harmonics of orbital angular momentum quantum number \(\ell\) and space-fixed projection quantum number \(m_{\ell}\), and \(R_{n,\ell}(r)\) the radial part of the wavefunction.

Like the electric dipole moment of the molecule, the outgoing photoelectron is not affected by any permutation of identical nuclei, but only by operations of the molecular symmetry group including the inversion \(E^*\) of all space-fixed coordinates of all particles in the system. The symmetry of the ejected photoelectron wavefunction thus depends of the even/odd nature of \(\ell\) according to:

\[ \Gamma_{e^-} = (\Gamma^*)^\ell . \] (1.18)
Because the irreducible representation of the electric dipole moment is also \( \Gamma^+ \) (see above), the photoionisation symmetry selection rules can be derived from Eqs. (1.11) and (1.15) as

\[
\Gamma_{\text{rve}}^+ \otimes \Gamma_{\text{rve}}^0 \geq (\Gamma^*)^{(\ell+p)},
\]

where the + superscript labels the irreducible representation of the cationic state. The symmetry selection rules of Eq. (1.19) are general and result from the assumed conservation of nuclear spin symmetry and parity during photoionisation. They enable one to attribute certain rotational branches of a photoelectron spectrum to even- or odd-\( \ell \) photoelectron partial waves (see Ref. [55] for additional details).

The conservation of total angular momentum leads to the additional selection rule for single-photon ionisation

\[
\Delta J = J^+ - J'' = \ell + \frac{3}{2}, \ell + \frac{1}{2}, \ldots, -\ell - \frac{1}{2}, -\ell - \frac{3}{2},
\]

(1.20)

where \( J'' (J^+) \) is the total angular momentum excluding nuclear spin of the neutral (cationic) state [65]. One unit of angular momentum originates from the dipole moment operator in the electric dipole approximation and \( \frac{1}{2} \) unit of angular momentum from the electron spin of the outgoing electron. However, since spin-rotation interactions are usually weak and not observed in the PFI-ZEKE photoelectron spectra of polyatomic molecules, it often suffices to use \( N \), the total angular momentum quantum number excluding spin, rather than \( J \), under which the condition in Eq. (1.20) reduces to:

\[
\Delta N = N^+ - N'' = \ell + 1, \ell, \ldots, -\ell, -\ell - 1.
\]

(1.21)

The change in the quantum number of the projection of the total angular momentum excluding spin onto the principal axis, \( \Delta K \) for symmetric tops or \( \Delta K_a \) and \( \Delta K_c \) for asymmetric tops, can be deduced from Eq. (1.19) and also depend on the parity of the outgoing photoelectron partial waves.

### 1.7 The orbital ionisation model

The orbital ionisation model is a physically appealing but approximate and qualitative model to describe relative rovibrational line intensities in photoelectron spectra. The model (see Ref. [59] for more details) represents an adaptation to non-linear polyatomic molecules of the model developed originally by Buckingham, Orr and Sichel [56] to describe rovibronic intensities in the photoelectron spectra of diatomic molecules. Other models have been devised and used to calculate rovibronic line intensities in photoelectron spectra [36, 66].

In the orbital ionisation model, the angular momentum of the photon is assumed to be fully absorbed by the outgoing photoelectron, creating a hole of the same angular-momentum composition as the molecular orbital out of which ionisation occurs. This molecular orbital is described in a single-centre expansion of atomic-like orbitals of angular momentum quantum number \( \ell'' \).
and projection quantum number $\lambda''$ onto the molecular symmetry axis [67]:

$$
\Psi_{\text{MO}, \alpha''} = N_C \sum_{\ell''} \sum_{|\lambda''| \leq \ell''} C^{(\alpha')}_{\ell'' \lambda''} Y_{\ell'' \lambda''}(\theta, \phi) R_{\alpha'', \ell''}(r),
$$

(1.22)

where $N_C$ is a normalisation constant, $C^{(\alpha')}_{\ell'' \lambda''}$ the expansion coefficient of the $\ell''$ and $\lambda''$ angular momentum component, $Y_{\ell'' \lambda''}(\theta, \phi)$ and $R_{\alpha'', \ell''}(r)$ the spherical harmonics and radial wavefunction, respectively. In symmetric-top molecules the quantisation axis is chosen to coincide with the $C_n$ or $S_n$ symmetry axis of highest order $n$. In asymmetric-top molecules, the quantisation axis corresponds to that of the reference symmetric-top with the rotational wavefunctions $|N, K, M \rangle$ which are used to express the asymmetric-top wavefunctions. $\alpha''$ stands for all quantum numbers other than the angular momentum quantum numbers $\ell''$ and $\lambda''$. $\ell''_{\text{max}}$ is the maximal angular momentum component contributing significantly to the single-centre expansion, and can be determined either experimentally or numerically. The value of $\lambda''$ is given by the symmetry and number of nodal planes of the molecular orbital containing the quantisation axis. For a molecular orbital that has no, one, two, etc. nodal planes containing the principal axis, $\lambda''$ takes the values $0, \pm 1, \pm 2$, etc., respectively. Whereas $\ell'' = 0, 1, 2, \ldots$ angular momentum components of the single-centre expansion are labelled as atomic orbitals by $s, p, d$, the values of $\lambda'' = 0, \pm 1, \pm 2, \ldots$ are labelled by the subscripts $\sigma, \pi, \delta, \ldots$. Any molecular orbital can be constructed as a (in principle infinite, but in practice rapidly converging) sum of different $\ell''$ components, but often only one value of $|\lambda''|$ is allowed to contribute by symmetry. The change in total angular momentum excluding spin reduces to

$$
\Delta N = N^+ - N^- = \ell''_{\text{max}}, \ldots, -\ell''_{\text{max}}.
$$

(1.23)

The total ionization cross section $\sigma_{\text{tot}}$ can then be modelled on the basis of Eqs. (1.24) and (1.25):

$$
\sigma_{\text{tot}} \propto \rho'' \sum_{|\lambda''| \leq \ell''} \frac{1}{2\ell'' + 1} Q(\ell'') \left[ C^{(\alpha')}_{\ell'' \lambda''} \right]^2 \left[ \ell'' \left( F_{E, \ell''} - 1 \right)^2 + (\ell'' + 1) \left| F_{E, \ell'' + 1} \right|^2 \right] B^{(\alpha)}_{\ell'' \lambda''}
$$

(1.24)

with $Q(\ell'') = (2N^+ + 1) \sum_{K^+, K''} (-1)^{N^+K^+K''} c_{K^+}^{N^+K''} c_{K''}^{N''K^+} \left( \begin{array}{ccc} N^+ & \ell'' & N'' \\ -K^+ & \lambda'' & K'' \end{array} \right) ^2$, (1.25)

as explained in Refs. [58, 59]. In Eq. (1.24),

$$
\rho'' = \chi''(2N'' + 1) \exp \left[ -(E''(N'', K_a'', K_c'') - E_{n{s,0}})/k_B T \right]
$$

(1.26)
represents the Boltzmann weighting factor of the initial rovibronic level of the neutral state with spin-statistical weight $\chi^0$, and $E^0(N^0, K^0_a, K^0_c)$ stands for the energy of the state labelled by the quantum number $N^0$ and the usual asymmetric-top quantum numbers $K^0_a$ and $K^0_c$. $E_{ns,0}$ represents the energy of the lowest level of the same nuclear spin symmetry as the state with energy $E^0(N^0, K^0_a, K^0_c)$. $k_B$ and $T$ stand for the Boltzmann constant and the rotational temperature, respectively. $c^K_{NK_aK_c}$ are the expansion coefficients of the asymmetric-top rotational wavefunction in the basis of the symmetric-top rotational wavefunction $|N, K, M\rangle$. The sum over $K^+$ and $K''$ thus applies only to the treatment of asymmetric-top molecules and must be omitted for symmetric tops. $F_{E,\ell}^{E^0,\ell}$ represents a radial transition integral of the form

$$F_{E,\ell}^{E^0,\ell} = \int_0^\infty R_\ell(E, r)R_{\ell^0,\ell}^{E^0,\ell}(r)r^2 dr,$$

where $R_\ell(E, r)$ denotes the radial part of the photoelectron partial wave of orbital angular momentum quantum number $\ell$ and energy $E$ \cite{59} and $R_{\ell^0,\ell}^{E^0,\ell}$ represents the radial wavefunction introduced in Eq. (1.22). In modelling the rotational intensity distribution, the product of the factors in square brackets and $j\alpha_00^\ell$ in Eq. (1.24) can be treated as an adjustable parameter $b_{E^0,\ell}^{E^0,\ell}$. The 3$j$-symbol in Eq. (1.25) ensures the conservation of angular momentum (cf. Eq. (1.23)). The selection rule $\Delta K = \pm\lambda''$ implied by the 3$j$-symbol is more restrictive than those implied by the symmetry selection rules (Eq. (1.20)) but turns out to be adequate to describe the branch structure of the photoelectron spectra.

The orbital ionisation model relies on a single-determinantal description of the electronic wavefunctions and does not incorporate possible changes of the molecular orbital resulting from photoionisation. It therefore only represents a crude approximation. Its main merits are

1. to give an accurate description of the relative intensities within a given rotational branch of the photoelectron spectrum,
2. to naturally lead to the correct symmetry and angular momentum labels for the ionic levels,
3. to enable reliable predictions of the rotational branch structure of the photoelectron spectra,
4. to facilitate the identification of intensity perturbations or anomalies caused by interactions between the different channels or by configurational mixing either in the neutral or cationic state, and
5. to make assignments of intermediate states by comparison between experimental and predicted rotational intensity distributions.

Chapters 3-6 will provide examples of the comparison of experimental spectra with spectra calculated on the basis of this model, and illustrate the limitations and advantages of the model and show how it can be used to detect intensity perturbations.
Chapter 2

Experimental

This chapter describes the main components of the spectrometers used to obtain the results presented in this thesis. Most experiments relied on the use of broadly tunable vacuum-ultraviolet (VUV) radiation and Section 2.1 summarises the principles of its generation by four-wave mixing. The primary radiation sources used to generate the VUV generation are described in Section 2.2 and the experimentation chambers and the photoelectron spectrometers in Section 2.3. The chapter ends in Section 2.4 with a brief account of the way the methyl and allyl radicals were produced and entrained in a cold supersonic expansion. While most components of the experimental set-up used in the realm of this dissertation were available from the outset, several components had to be modified to meet specific requirements of each experiment described in Chapters 3-6. The combination of the high-resolution laser described in Subsection 2.2.2 with the four-wave-mixing cell to generate intense narrow-bandwidth VUV radiation was realised for the first time to record the high-resolution photoelectron spectra of allene presented in Chapter 6. This combination turned out to be almost ideal for photoelectron spectroscopic experiments in the wavelength range above 105 nm and is expected to find many future spectroscopic applications.

2.1 Generation of narrow-bandwidth, tunable VUV radiation

Dye lasers that are tunable from the near infrared (\(\lambda \approx 900\) nm) to the near ultraviolet (UV) are commercially available. Well-established techniques of nonlinear optics such as three- and four-wave mixing can be used to generate UV radiation down to 60 nm by frequency up-conversion of dye-laser radiation [68, 69, 70, 71, 72, 73, 74, 75]. The nonlinearity of the frequency up-conversion processes requires relatively high intensities, on the order of \(10^{12}\) W/m\(^2\) or more, of the fundamental dye laser radiation. Such intensities can routinely be obtained by focussing the output of pulsed nanosecond lasers.

Different frequency up-conversion schemes are employed, depending on the wavelength range of the radiation to be generated: Three-wave mixing in birefringent crystals such as potas-
sium dihydrogen phosphate (KDP) or β-barium borate (BBO) crystals is most efficient in the wavelength range down to $\lambda \approx 200$ nm but cannot be used below 180 nm because the crystals absorb the generated radiation and the phase-matching condition cannot be fulfilled [70]. VUV radiation below 190 nm is therefore generated in gases, commonly rare gases or mercury vapour, by four-wave mixing because three-photon processes are forbidden in isotropic media [68, 76]. Four-wave mixing is a nonlinear process of higher order than three-wave mixing and the density of a nonlinear gas is smaller than that of a crystal. Consequently, the generation of VUV radiation below 180 nm is much less efficient than above 180 nm. This loss of efficiency can be partially compensated if the VUV radiation is produced by resonance-enhanced four-wave mixing as schematically shown in Figures 2.1 a) and b) for difference- and sum-frequency mixing, respectively. The resonant nature of the four-wave mixing process necessitates the use of two lasers. The wave number of the first laser $\tilde{\nu}_1$ is set at half the wave number of a suitable two-photon transition of the nonlinear medium, typically krypton or xenon. A second laser generated the wave number $\tilde{\nu}_2$ which is set or scanned so that the desired VUV wave number $\tilde{\nu}_{\text{VUV}}$ is given by

$$\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2$$  \hspace{1cm} (2.1)

for difference-frequency generation (DFG) as shown in Fig. 2.1 a) and by

$$\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 + \tilde{\nu}_2$$  \hspace{1cm} (2.2)

for sum-frequency generation (SFG) as shown in Fig. 2.1 b). The advantage of this two-colour four-wave mixing scheme is that tunable radiation can be produced by scanning $\tilde{\nu}_2$ only while leaving $\tilde{\nu}_1$ fixed at the position of the two-photon resonance. Resonance-enhancement of the VUV radiation can thus be achieved at all frequencies.

Figure 2.1: Schematic diagram of a) the difference-frequency mixing and b) the sum-frequency mixing processes.
In the wavelength region above the LiF cutoff wavelength $\lambda = 105$ nm, the nonlinear gas is usually confined in a four-wave mixing cell equipped with a LiF or an MgF$_2$ exit window. The conversion efficiency is optimised by varying the partial pressure in a gas mixture so as to fulfill the phase-matching condition [77].

The generation of VUV radiation in the region below $\lambda = 105$ nm is more complicated because no known material transmits VUV radiation in this region: The nonlinear gas must be confined in the same (evacuated) experimental volume in which the experiments using the VUV radiation are performed. The most elegant solution consists of using pulsed gas beams as the nonlinear medium, grating monochromators to separate the VUV radiation from the fundamental laser beams and making extensive use of differential pumping between the relatively high pressure region (typically $10^{-3}$ mbar) where the VUV radiation is generated and the high-vacuum region ($< 10^{-6}$ mbar) where the spectroscopic experiments are performed [72, 75].

The spectroscopic experiments described in this thesis were all conducted in the wavelength region above $\lambda = 105$ nm and the VUV radiation was generated in a cell of krypton gas by resonance-enhanced difference-frequency mixing (Fig. 2.1 a) and Eq. (2.1)). The two-photon resonance $(4p)^5(5p^1)J = 2\rightarrow (4p)^6S_0$ in krypton at $2\nu_1 = 94092.862$ cm$^{-1}$ [78, 73] was used to enhance the conversion efficiency.

The laser beam of wave number $\nu_1$ was focused with a quartz lens of focal length $f = 30$ cm into the 30 cm long gold-coated cell (inner diameter 5 cm). The focal point was chosen so as to coincide with the focal point of the MgF$_2$ or LiF exit lens ($f = 10$ cm at 212 nm) which separates the cell from the high-vacuum system. In this manner the VUV beam did not diverge when it propagated out of the four-wave mixing cell. The laser beam of tunable wave number $\tilde{\nu}_2$ was pre-focused with a telescope and overlapped with the laser beam of the fixed wave number $\tilde{\nu}_1$ using a dichroic mirror so that both beams traversed the quartz lens co-linearly and had their focus at the same point in the cell. Because the transmission of the MgF$_2$ and LiF drops sharply at 115 nm [79] and 105 nm [80, 81], respectively, the sum-frequency beam was not transmitted for the wave numbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$ used in the experiments presented here. The difference-frequency beam was separated from the fundamental beams by a MgF$_2$ or LiF prism and deflected by an angle of $38^\circ$ into the photoexcitation chamber as shown in Fig. 2.2 a). This angle corresponds to the deflection angle of a grazing incidence vacuum grating [82] and was chosen so as to permit a facile replacement of the prism with a grating for experiments below $\lambda = 105$ nm. Fig. 2.2 b) shows an enlarged view of the prism used to separate the VUV radiation from the fundamental beams of wave numbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$. The path of the VUV beam is indicated by a solid line, its hypothetical unrefracted paths by dashed-dotted lines and the lines normal to the prism surfaces by dashed lines. The figure also defines the apex angle $\gamma$, the incidence angle $\alpha_{in}$ and the refraction angle $\alpha_{out}$ that are required to characterise the operational principle of the monochromator. The angle of refraction of the outgoing beam $\alpha_{out}$ can be calculated by applying Snell’s law at both relevant surfaces of the prism (see Fig. 2.2 b)):

$$\alpha_{out} = \sin^{-1} \left[ n_{\text{MgF}_2}(\lambda) \sin \left( \gamma - \sin^{-1} \left[ n_{\text{MgF}_2}(\lambda) \sin (\alpha_{in}) \right] \right) \right].$$  (2.3)
The condition on $\alpha_{\text{out}}$ that has to be met in order for the outgoing VUV beam to be deflected by an angle of 38° is

$$\alpha_{\text{out}} = 38^\circ - \alpha_{\text{in}} + \gamma.$$  \hspace{1cm} (2.4)

Fig. 2.3 shows as stars and circles the incident angle $\alpha_{\text{in}}$ required for a prism with apex angle $\gamma = 55^\circ$ and $\gamma = 45^\circ$, respectively, in dependence of the refractive index $n_{\text{MgF}_2}(\lambda)$ of MgF$_2$ (on the bottom scale) and the corresponding wavelength $\lambda$ (on the top scale) for an angle of refraction of the outgoing relative to the incoming beam of 38° as required by the geometry of the set-up. The angles are defined in Fig. 2.2 b). The prism of 55° apex angle is suited to the deflection of VUV beams of wavelength down to about 127 nm, whereas the prism of 45° apex angle must be used below 127 nm.

A pinhole between the prism and the photoexcitation chamber blocked the laser beams of fundamental wave numbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$ and allowed only the VUV beam to enter the excitation region. The VUV intensity was recorded with a home-built VUV detector mounted on an exit port of the photoexcitation chamber. The VUV radiation produced photoelectrons from the Al$_2$O$_3$ surface of the detector, which were subsequently accelerated onto a mesh held at a constant voltage of +250 V and measured as a photocurrent.

A gentle constant flow of the nonlinear gas through the cell was maintained to avoid a gradual decrease of the VUV intensity caused by the depletion of the nonlinear gas by photoionisation [29]. The pressure of the nonlinear gas in the cell was monitored with a Pirani gauge and was typically in the range of 10-40 mbar.
2.2. The laser systems

Two different laser systems with complementary properties have been used to obtain the results presented in this thesis. These two systems, described in Sections 2.2.1 and 2.2.2, are based on the same principle for the generation of VUV radiation but differ in their resolution and intensity.

The first laser system produces intensive VUV radiation with a bandwidth of about 0.3 cm$^{-1}$ and is easily tunable over the energy range between 5 eV and 20 eV [83, 75]. The second laser system produces less intensive VUV radiation with a much narrower bandwidth of 0.008 cm$^{-1}$ [74]. This laser system is more difficult to operate and cannot easily be tuned over the complete energy range. The easy tunability of the former laser system is ideally suited to search for and identify the spectral features of the species of interest. Its high intensity enables the investigation of compounds, such as radicals, that can only be produced in low densities or the observation of weak transitions. Once the interesting spectral regions have been identified, the latter system permits the recording of high-resolution spectra which is particularly useful in the study of the rotational structure of polyatomic molecules as will be shown in Chapter 6.

Figure 2.3: Incidence angle $\alpha_{in}$ required in order to ensure that the VUV beam exits the prism at an angle of 38° with respect to the direction of propagation of the incoming VUV beam. The incident angle is plotted as a function of the wavelength of the VUV radiation (upper horizontal scale) and the corresponding index of refraction of MgF$_2$ (lower horizontal scale, values taken from [79]). The full and open circles correspond to MgF$_2$ prisms with apex angles of $\gamma = 55^\circ$ and $\gamma = 45^\circ$, respectively.
2.2.1 The broadly tunable laser system

Figure 2.4 shows a schematic representation of the low-resolution laser system [84, 60]. An injection seeded Q-switched Nd:YAG laser (Continuum Powerlite 9010, Quantel YG 981E or Spectra-Physics Quanta-Ray Pro) is operated at a repetition rate of 10 Hz, 16$^{2/3}$ Hz or 25 Hz and generates pulses of about 8 ns duration. Two dye lasers (Lambda Physik Scanmate) are pumped by the second (532 nm) or third harmonic (355 nm) of the Nd:YAG laser to produce radiation between 360-900 nm with a bandwidth of 0.1 cm$^{-1}$, or 0.03 cm$^{-1}$ if an intracavity étalon is employed. The second and third harmonic of the fundamental frequency of the first dye laser is generated in nonlinear crystals ($\beta$-bariumborate crystals cut at different angles depending on the wavelength) so that the up-converted wave number $\tilde{\nu}_1$ corresponds to half the frequency of the two-photon resonance in krypton or xenon employed for four-wave mixing [85]. Pulse energies of up to 5 mJ in the second harmonic and 0.5 mJ in the third harmonic at a pulse duration of about 5 ns were used. The crystals were rotated as the laser frequency was scanned so that optimal phase-matching conditions were ensured for all frequencies. Using resonance-enhanced four-wave mixing, a bandwidth in the VUV of $\sim$0.1 cm$^{-1}$ and a resolution of up to 0.2 cm$^{-1}$ in the PFI-ZEKE photoelectron spectra could be achieved [85] with this system.

The spectra were calibrated by recording the optogalvanic spectra of Ne/Fe or Ar/Ag simultaneously to scanning $\tilde{\nu}_2$ and comparing the transition wave numbers of neon, iron, argon and silver with tabulated reference data [86]. The wave number $2\tilde{\nu}_2$ of the two-photon resonance [78, 73] used in the four-wave mixing process was taken from the literature to determine the VUV wave number $\tilde{\nu}_{\text{VUV}}$ with Eq. (2.1).
2.3. The experimentation chamber

Two experimentation chambers were used in this work and are shown in Figures 2.4 (set-up 1) and 2.6 (set-up 2). Both chambers are very similar and are described jointly in this section. The probe gas, usually seeded in an inert gas at stagnation pressures of 1 – 4 bar, expands...
into the skimmer chamber through a pulsed solenoid valve (General Valve Series 9) and cools to rotational temperatures of 5-30 K in a supersonic expansion. The nozzle opening time is synchronized to the laser pulses using delay generators (Stanford Research Systems, Inc. DG 535). The central part of the gas beam was guided through a skimmer (Beam Dynamics Modell 2) placed 2-3 cm away from the nozzle orifice and enters the photoexcitation chamber, where it intersects the VUV radiation at right angles. The skimmer aperture of 1 mm represents the only opening between the probe gas chamber and the photoexcitation chamber. Efficient differential pumping is thus possible enabling much lower pressures to be maintained in the photoexcitation chamber than the probe gas chamber. The system was held at a background pressure of about $6 \times 10^{-8}$ mbar with two turbomolecular pumps (Pfeiffer Vacuum TC600 and TMH261). During operation of the pulsed valve the pressure rises to $5 \times 10^{-4}$ mbar and $1 \times 10^{-6}$ mbar in the probe gas and photoexcitation chambers, respectively.

In set-up 1 the gas beam travelled along the axis of a cylindrical stack of five extraction plates of a total length of 5.8 cm. These polished stainless steel plates were resistively coupled and were designed to generate very homogeneous fields with amplitudes ranging from 10 V/cm to 1000 V/cm with stray electric fields amounting to less than 1 mV/cm [91]. High electric field pulses of typically 400 V/cm were applied to extract ions using a fast switch (Behlke GHTS) with a rise time of 50 ns. To extract electrons in PFI-ZEKE photoelectron spectroscopic experiments an arbitrary-waveform generator (Agilent 33250 A) was employed to apply electric field pulse sequences of maximal amplitude of less than $\pm 100$ mV/cm, the rise time of individual pulses being on the order of 1 ns. The photoexcitation region, and the 20-cm-long flight length.
2.4 Photolytic source of cold radicals

Radicals are not readily available and generally have to be produced in or close enough to the measurement region to avoid depletion due to chemical processes. In the present work, the methyl and allyl radicals have been produced photolytically following the procedure described in Refs. [28, 29]. The experimental set-up is shown in Fig. 2.7. A quartz capillary of 1 mm inner diameter and approximately 5-6 cm length was mounted at the orifice of the pulsed gas nozzle. Quartz was chosen because of its transparency to UV radiation down to \( \sim 190 \) nm. The output of an excimer laser (Lambda Physik Compex 102e) was focused into the capillary and produced the radicals from suitable precursors by photolysis. Operating the excimer laser with different gas mixtures enabled the generation of UV beams of wavelengths 351 nm (XeF), 308 nm (XeCl), 248 nm (KrF) and 193 nm (ArF). A premix of normally 5-10% of the radical precursor in an inert gas, typically Ar, was fed into the high-pressure zone of the nozzle and passed through the quartz capillary each time the nozzle was triggered. The radicals were produced by excimer photolysis within the capillary and were supersonically cooled in the subsequent expansion into the vacuum system to rotational temperatures in the range of 10-40 K. The central cold part of the supersonic beam was selected by the skimmer and was intersected at right angles by the VUV laser beam in the photoexcitation region as described in Section 2.3.

To optimise production of the desired radical, the trigger of the excimer laser and of the gas nozzle have to be adjusted relative to the VUV pulse in order to select photodissociation of the part of the gas pulse with the highest density and optimally benefit from the efficient cooling in the first part of the gas pulse. By moving the position of the excimer beam along the capillary axis closer to the exit orifice of the capillary the radicals experience fewer collisions before and during the supersonic expansion, resulting in less efficient cooling but also in fewer reactive
collisions and therefore higher radical number densities. Consequently, a balance between the number density of radicals and the cooling efficiency has to be found. In practice, one tries to achieve the lowest possible temperature that is compatible with the desired signal-to-noise ratio by carrying out the photolysis as far as possible from the capillary exit.
Chapter 3

The PFI-ZEKE photoelectron spectra of allyl near its first ionisation threshold

This chapter is concerned with the PFI-ZEKE photoelectron spectrum of allyl near its adiabatic ionisation threshold and presents a study of the single-photon photoionisation dynamics of allyl and a measurement of the first adiabatic ionisation energy of this important radical. A controversy in the literature about the ionisation energy of the allyl radical could be resolved. The orbital ionisation model described in Section 1.7 and application of the rovibronic photoionisation selection rules outlined in Section 1.6 were instrumental in understanding the ionisation dynamics of the allyl radical. The allyl photoionisation selection rules derived in Ref. [18] were found to be incompatible with previous results and the modelling of the rotational envelope of the PFI-ZEKE photoelectron spectrum in Ref. [18] and had to be revised.

Predictions, based on the orbital ionisation model, of the intensity distribution of the 1+1 and 2+2 resonance-enhanced multiphoton ionisation photoelectron spectra revealed a strong dependence of the rotational envelope on the molecular orbital out of which ionisation occurs. These predictions contributed to a concerted effort with Michael Gasser, Jonas Hostettler, Dr. Andreas Bach and Prof. Dr. Peter Chen to understand the ionisation dynamics in their resonance-enhanced multiphoton ionisation photoelectron spectra and the energy level structure of electronically excited allyl.

3.1 Introduction

The allyl radical is the simplest organic molecule with a conjugated $\pi$-electron system. Allyl is represented schematically in Fig. 3.1 where its inertial axis system is also defined. The ground electronic state of allyl has been investigated by ESR spectroscopy [92, 93]. From these ESR studies and theoretical investigations [94], the spin density of the radical was determined to be mainly localised at the terminal carbon atoms. The qualitative structure of the highest occupied molecular orbital (HOMO), the singly occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) can be seen in the molecular orbital (MO) diagram dis-
played in Fig. 3.2. The next higher electronic states and the corresponding singly occupied Rydberg 3s, 3p_z, 3p_x and 3p_y orbitals as calculated on the MR-CISD level of theory, using an SA-7-MCSCF(3,7) calculation as the reference [95], are also displayed. The axis system used for the construction (and labelling) of this MO diagram is represented in Fig. 3.1. The symmetry labels are given below each electronic state in Fig. 3.2. The MO associated with the unpaired electron in the neutral ground state has indeed electron density at the terminal carbons and no density at the central carbon, in agreement with the results of the ESR studies mentioned above [92, 93]. The electronic spectrum of allyl has been studied extensively [16, 17, 96, 97, 98, 99] and the structural and dynamic properties of many vibronically excited states of allyl have been investigated.

The allyl radical plays an important role in combustion [100] and interstellar chemistry [101] and its adiabatic ionisation energy represents an important quantity in the evaluation of thermochemical reaction cycles. The first photoelectron spectrum of the allyl radical [102] enabled the determination of the adiabatic ionization energy as 8.13±0.02 eV. Slightly higher values, ranging up to 8.15 eV, were reported in later works [103, 104, 105, 106]. The most recent measurements of the adiabatic ionisation energy of allyl were carried out by PFI-ZEKE photoelectron spectroscopy, using multi-photon [104] and single-photon excitation schemes [18, 107]. Surprisingly, the resulting values of the adiabatic ionisation energy (8.153 eV [104] and 8.13146 eV [18]) differ by as much as 22 meV. Both measurements provided important information on the vibrational energy level structure of C_3H_5^+. Xing et al. [18] also obtained information on the photoionisation dynamics of C_3H_5 from the partially resolved rotational structure of the lowest three members (0^0, 7^1 and 7^2) of the vibrational progression associated with the C-C-C bending mode ν_7 of the cation. Several assumptions made in the derivation of
3.1. Introduction

![Molecular orbital diagram](image)

The configurations on the right-hand side are labelled in the C\textsubscript{2v}(M) group and, in each case, the configuration interaction coefficient of the dominant contribution to the electronic wavefunction is indicated as obtained in Ref. [95]. Each orbital is given a symmetry label reflecting its dominant \( \ell' \) single-centre expansion contribution, where \( \ell' \) and \( \lambda'' \) represent the quantum numbers associated with orbital angular momentum and its projection on to the \( z \)-axis of the molecule-fixed axis system. The 3s, 3p\( _x \), 3p\( _y \) and 3p\( _z \) orbitals are Rydberg orbitals, whereas the HOMO, SOMO and LUMO are valence orbitals.

The photoionisation selection rules in Ref. [18], however, appear inconsistent with the current knowledge of the electronic structure of allyl. The authors of Ref. [18] indeed state that the \( \bar{X}^+ \text{A}_1 \rightarrow \bar{X}^2 \text{A}_2 \) photoionising transition primarily results in the emission of photoelectron partial waves with gerade values of the total angular momentum quantum number \( \ell \), because, in their opinion, the molecular orbital out of which ionisation occurs is a 2p\( _\pi \) atomic-like orbital. Considerations of the SOMO however, leads to the conclusion that the electron should actually be ejected from a d\( _\delta \) orbital in the \( \bar{X}^+ \text{A}_1 \leftarrow \bar{X}^2 \text{A}_2 \) transition (see Fig. 3.2) and that therefore ungerade \( \ell \) photoelectron partial wave components with \( \ell = 1 \) and \( \ell = 3 \) should be at least as
important as those with $\ell = 0$ and $\ell = 2$. Furthermore, the propensity selection rules for $\Delta K_a$ and $\Delta K_c$ depend on the quantum number $\lambda''$ associated with the projection of the orbital angular momentum onto the quantisation axis of the molecular orbital out of which ionisation occurs as explained in the discussion of Eq. (1.25) in Section 1.7. Different $\Delta K_a$ and $\Delta K_c$ selection rules are obtained depending on whether ionisation occurs out of a $p_\pi$ or $d_\delta$ molecular orbital (the subscripts $\pi$ and $\delta$ correspond to $\lambda'' = \pm 1$ and $\lambda'' = \pm 2$, respectively).

To resolve these ambiguities in the interpretation of the photoelectron spectrum of allyl, a joint effort with the group of Professor Peter Chen (ETH Zürich) was undertaken. This chapter describes a new measurement of the PFI-ZEKE photoelectron spectrum of allyl by single-photon photoelectron spectroscopy for direct comparison with the results of Xing et al. [18]. In parallel to this measurement, Gasser, Bach and Chen [108] remeasured the PFI-ZEKE photoelectron spectrum of allyl obtained following resonant multi-photon excitation via selected vibrational levels of the $B$ and $C$ intermediate states. The present chapter also summarises the results of the analysis of the rotational contour obtained in both the single-photon photoionisation study performed in our laboratory and the multi-photon photoelectron spectra recorded via the $B$ and $C$ intermediate levels by Gasser, Bach and Chen [108]. The MR-CISD ab initio calculations performed by Hostettler [95] were used as a basis to derive the symmetry and angular momentum components of the molecular orbital out of which ionisation occurs.

Our method of production of the allyl radicals photolytically from 1-,5-hexadiene [28] leads to the generation of rotationally colder samples ($T_{\text{rot}} \approx 30$ K) than in Refs. [18] and [104], where the radicals were produced in a pyrolysis jet source and had rotational temperatures of $T_{\text{rot}} \approx 150$ K. A comparison of our single-photon photoelectron spectrum with that reported by Xing et al. [18] also offered the opportunity to directly compare these two methods of producing allyl radicals.

### 3.2 Experimental

The threshold photoionisation of $C_3H_5$ was studied from the ground neutral state by single-photon photoionisation and PFI-ZEKE photoelectron spectroscopy. The experimental setup has been described in Chapter 2 and only aspects specific to the measurements on allyl are summarised here. The allyl radicals were produced photolytically [109] from 1-,5-hexadiene (Aldrich, 97%). As a carrier gas argon was bubbled through a sample of the 1,5-hexadiene precursor at room temperature. Photolysis by the 193 nm output of an ArF excimer laser (LambdaPhysik, Compex) was achieved in a quartz capillary mounted at the end of a pulsed nozzle allowing for the cooling of the allyl radicals in a supersonic expansion from the capillary into vacuum. Rotational temperatures ranging from 20 K to 100 K were obtained in this way, depending on the experimental conditions (nozzle stagnation pressure, position of the focus of the 193 nm photolysis laser beam along the capillary axis), as determined from the rotational contours of the bands observed in the PFI-ZEKE photoelectron spectra. Tunable VUV radiation in the region of the adiabatic ionisation threshold was generated by resonance-enhanced difference-frequency
mixing ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2$) in a cell filled with krypton using the $(4p)^5 \left(^2P_{3/2}\right) 5p \left[1/2\right] (J = 0) \rightarrow (4p)^6 \left(^1S_0\right)$ two-photon resonance in krypton at $2\tilde{\nu}_1 = 94092.862 \text{ cm}^{-1}$ [78, 73] as described in Section 2.1.

Photoionisation spectra were measured by recording the $C_3H_5^+$ signal mass-selectively as a function of the VUV wave number $\tilde{\nu}_{\text{VUV}}$. The $C_3H_5^+$ ions were extracted by applying a 2 kV pulsed voltage to the extraction plates 2 $\mu$s after photoexcitation and detected on the microchannel-plate (MCP) detector. The experimental set-up is otherwise described in Section 2.3 (set-up 1).

PFI-ZEKE photoelectron spectra were recorded as a function of $\tilde{\nu}_2$ by monitoring the electrons produced by pulsed-field-ionisation of high-$n$ Rydberg states (see Section 1.4). A 'discrimination' pulse of 1 $\mu$s duration and $+88 \text{ mV/cm}$ amplitude was applied 2.5 $\mu$s after photoexcitation to field ionise the highest Rydberg states and sweep free electrons out of the photoexcitation region. This discrimination pulse was immediately followed either by a single 'detection' pulse of $-526 \text{ mV/cm}$ or three successive detection pulses of $-140 \text{ mV/cm}$, $-263 \text{ mV/cm}$ and $-877 \text{ mV/cm}$ each of 500 ns duration. These detection pulses field ionized the high-$n$ Rydberg states and accelerated the electrons toward the MCP detector.

The photoionisation and PFI-ZEKE photoelectron spectra were calibrated by recording, with each scan, an optogalvanic spectrum of Ne. To determine the position of the field-free adiabatic ionisation threshold, corrections of 1.3(2) cm$^{-1}$, 1.6(2) cm$^{-1}$, 2.3(4) cm$^{-1}$ and 1.8(2) cm$^{-1}$ for detection pulses of $-140 \text{ mV/cm}$, $-263 \text{ mV/cm}$, $-877 \text{ mV/cm}$ and $-526 \text{ mV/cm}$, respectively, were introduced to compensate for the shifts of the ionisation thresholds induced by the electric-field pulse sequence according to the procedure described in Ref. [7].

### 3.3 PFI-ZEKE photoelectron spectra

In Fig. 3.3 the photoionisation and PFI-ZEKE photoelectron spectra of allyl in the vicinity of the $^1A_1(0^0) \rightarrow ^2A_2(0^0)$ transition are displayed as top and middle traces, respectively. The photoionisation spectrum of allyl exhibits a sharp rise from zero at the position of the lowest band of the PFI-ZEKE photoelectron spectrum which indicates that (1) the PFI-ZEKE photoelectron signal indeed originates from the allyl radical, and (2) the contribution from hot bands is not significant. Because of the absence of sharp resonances in the photoionization spectrum which results, at least in part, from spectral congestion, the intensity distribution observed in the photoelectron spectrum is not expected to be strongly perturbed by the effects of channel interactions, which often complicate the interpretation of PFI-ZEKE photoelectron spectra [42, 111]. The PFI-ZEKE photoelectron spectrum is congested with little rotational structure resolved apart from a reproducible double-peak structure close to the band centre with a separation of 9 cm$^{-1}$. The full width at half maximum (FWHM) of the band amounts to $\approx 37 \text{ cm}^{-1}$. The bottom trace of Fig. 3.3 is a simulation of the PFI-ZEKE photoelectron spectrum based on the orbital ionisation model (see Sections 1.6-1.7) and a rotational temperature of 25 K. No attempt to fit the rotational constants of the neutral ($A''$, $B''$ and $C''$) or the cationic ($A^+_0$, $B^+_0$, and
Chapter 3. The PFI-ZEKE photoelectron spectra of allyl near its first ionisation threshold

Figure 3.3: Photoionisation (top trace) and PFI-ZEKE photoelectron (middle trace) spectra of allyl in the region of the first adiabatic ionisation threshold. A simulation of the spectrum based on the orbital ionisation model and assuming a rotational temperature of 25 K are displayed on the bottom trace and has been shifted along the vertical axis for clarity.

The C\(^+\)\(_0\) ground state of allyl was undertaken. The simulations were performed using the constants summarised in Table 3.1 [18, 17, 110]. The adiabatic ionisation energy \(E_i\) was determined to be 65580.1(20) cm\(^{-1}\) (8.13088(24) eV). This result thus confirms the value of the first adiabatic ionisation energy (65584.6(20) cm\(^{-1}\)) by Xing et al. [18]. The narrower rotational envelope of the origin band in our spectrum compared to the spectrum published in Ref. [18] which results from the colder rotational temperatures of our allyl sample, removes all ambiguity.

A second band was observed 434.5 cm\(^{-1}\) above the origin in the PFI-ZEKE photoelectron spectrum and is displayed as the upper trace in Fig. 3.4. This band is assigned to a transition to the first excited vibrational level of the totally symmetric C-C-C bending vibration \(\nu_7^+\) because its fundamental wave number agrees well with the \textit{ab initio} calculations of the harmonic wave number of the cation of \(\tilde{\nu}_7 = 427\) cm\(^{-1}\) [104]. This assignment corresponds to that made in Ref. [18]. The lower trace of Fig. 3.4 represents a simulation of this band performed with the orbital ionisation model using the rotational constants \((A_7^+, B_7^+ \text{ and } C_7^+)\) determined in Ref. [18] (see Table 3.1) and assuming a rotational temperature of 35 K. The \(\tilde{X}^+ 1A_1(7^1)\) state is of the same vibronic symmetry as the \(\tilde{X}^+ 1A_1(0^0)\) state, which explains the similarity of the band contours of both bands. Again, two peaks close to the band centre and separated by 8.5 cm\(^{-1}\) are observed. The FWHM of the \(7^1\) bands amounts to \(\approx 47\) cm\(^{-1}\) and is larger than that of the origin band (FWHM of \(\approx 37\) cm\(^{-1}\)). This observation is attributed to slightly different experimental conditions which led to a rotational temperature of about 35 K as estimated from
the simulations. The higher rotational temperature is a consequence of unavoidable day-to-day fluctuations that result from the need to regularly re-optimise the alignment of the laser beams and the efficiency of the radical source.

The photoionisation selection rules and the orbital ionisation model used in the simulations of the rotational intensity distribution are discussed in more detail in Section 1.7 and in Refs. [55, 59, 58]. When applied to allyl (molecular symmetry group $C_{2v}(M)$ [61]), the general rovibronic photoionisation selection rules are given by

$\Gamma'' \otimes \Gamma^+ \supseteq (A_2)^{\ell+1}$, \hspace{1cm} (3.1)

where $\ell$ represents the orbital angular momentum quantum number of the outgoing photoelectron partial wave and $\Gamma^+_{rve}$ and $\Gamma^0_{rve}$ the rovibronic symmetry of $C_3H_5^+$ and $C_3H_5$, respectively. For the $\tilde{X}^+ 1A_1 \leftarrow \tilde{X}^2A_2$ transition, the selection rules can be expressed in terms of changes in the usual asymmetric-top angular momentum projection quantum numbers $K_a$ and $K_c$ (see

Table 3.1: First adiabatic ionisation energy $E_i$, rigid-rotor asymmetric-top rotational constants and fundamental wave number of the C-C-C bending ($\nu_7^+$) mode used in the simulations of the experimental spectra. Selected values of the $\tilde{\nu}_7^+$ and $E_i$ from the literature are given for comparison.

<table>
<thead>
<tr>
<th>$\tilde{\nu}_7^+$ / cm$^{-1}$</th>
<th>$E_i/(hc$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>434.5(10)$^a$</td>
<td>65580.1(20)$^{a,b}$</td>
</tr>
<tr>
<td>436.3(20) [18]</td>
<td>65584.6(20) [18]</td>
</tr>
<tr>
<td>431 [104]</td>
<td>65762 [104]</td>
</tr>
<tr>
<td>423$^c$ [104]</td>
<td>65573(81) [107]</td>
</tr>
</tbody>
</table>

$^a$ This work

$^b$ corrected for the field-induced shift.

$^c$ ab initio value.
Chapter 3. The PFI-ZEKE photoelectron spectra of allyl near its first ionisation threshold

Figure 3.4: Upper trace: PFI-ZEKE photoelectron spectrum of the $\tilde{X}^+ 1A_2 (7^1) \leftarrow \tilde{X}^2A_2 (0^0)$ transition of allyl. Bottom trace: The simulation based on the orbital ionisation model and assuming a rotational temperature of 35 K. The simulated spectrum has been shifted along the vertical axis for clarity.

Table 3.2) as

$$\Delta K_a = K_a^+ - K_a'' = \text{odd/even} \quad \text{for} \quad \ell = \text{odd/even} \quad (3.2)$$

$$\Delta K_c = K_c^+ - K_c'' = \text{odd/even} \quad \text{for} \quad \ell = \text{odd/even}. \quad (3.3)$$

Conservation of the total angular momentum excluding spin can be expressed in the electric dipole approximation by the selection rule

$$\Delta N = N^+ - J'' = \ell + 1, \ell, \ldots, -\ell, -\ell - 1, \quad (3.4)$$

where $N^+$ is the total angular momentum excluding spin of the molecular cation. From the 3j-symbol in Eq. (1.25) the propensity rule $|\Delta K_a| + |\Delta K_c| = |\lambda''|$ for a I$^r$-type near-prolate top [112] is obtained.

The SOMO ($d_δ$) out of which ionisation occurs in the $\tilde{X}^+ 1A_1 \leftarrow \tilde{X}^2A_2$ transition of allyl is depicted in Fig. 3.2 and is of $A_2$ symmetry in the $C_{2v}(M)$ molecular symmetry group, where the labelling of the irreducible representations has been taken from Bunker and Jensen [61]. A molecular orbital of $A_2$ symmetry is antisymmetric with respect to the inversion operation $E^*$ and the inversion permutation of the terminal CH$_2$ entities, which are isomorphous to reflections in the $xy$- and $xz$-symmetry planes of the $C_{2v}$ point group. Both of these symmetry planes must correspond to nodal planes of a molecular orbital of $A_2$ symmetry of the $C_{2v}$ point group. The molecular orbital out of which ionisation occurs therefore has two nodal planes containing the
3.4. Comparison with other studies of the photoelectron spectrum of allyl

<table>
<thead>
<tr>
<th>$\Gamma_{ve}$</th>
<th>$\ell$</th>
<th>$\Delta K_a$</th>
<th>$\Delta K_c$</th>
<th>initial state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>even</td>
<td>odd</td>
<td>odd</td>
<td>odd</td>
</tr>
<tr>
<td></td>
<td>odd</td>
<td></td>
<td>even</td>
<td></td>
</tr>
<tr>
<td>$A_2$</td>
<td>even</td>
<td>odd</td>
<td>odd</td>
<td>even</td>
</tr>
<tr>
<td></td>
<td>odd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>even</td>
<td>odd</td>
<td>even</td>
<td>odd</td>
</tr>
<tr>
<td></td>
<td>odd</td>
<td></td>
<td>odd</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Table of the rovibronic symmetry selection rules for transitions from vibronic states of $\text{C}_3\text{H}_5$ of symmetry $\Gamma_{ve}$ to the cationic vibronic ground state $\tilde{X}^+ \, ^1A_1 \,(0^0)$ in dependence of the angular momentum of the ejected photoelectron $\ell$. The last column lists the states of neutral allyl of the corresponding electronic symmetry (i.e., $\Gamma_e = \Gamma_{ve}$).

symmetry or quantisation axis (i.e., the $z(b)$-axis along the central C-H bond in Fig. 3.1). Only molecular orbital components with $\lambda'' = \pm 2$ are of $A_2$ symmetry, and therefore only $d_5$ and $f_5$ are expected to contribute significantly to the single-centre expansion of the $A_2$ SOMO. In the simulations these contributions have been weighted in a ratio of 2:1, respectively.

The simulations shown on the bottom traces of Figs. 3.3 and 3.4 reproduce the countours of the experimental spectra well but underestimate the contrast of the central double peak structure. The analysis of the PFI-ZEKE photoelectron spectrum based on the qualitative structure of the SOMO shown in Fig. 3.2 thus supports the conclusion drawn from ESR spectra that the spin density is localised at the terminal carbon atoms [93, 92].

3.4 Comparison with other studies of the photoelectron spectrum of allyl

3.4.1 The single-photon PFI-ZEKE photoelectron spectrum of the allyl radical by Xing et al.

Xing et al. [18] have recorded a single-photon PFI-ZEKE photoelectron spectrum of the origin band, fundamental and first overtone bands of the $\nu_7^+$ normal mode. The allyl radical was produced by flash-pyrolysis of $\text{C}_3\text{H}_5\text{I}$ using a pyrolytic jet source of the type developed by Chen and co-workers [9] which resulted in a rotational temperature of 150 K of the radical. The bands have a FWHM of $\approx 80$ cm$^{-1}$ and the two lowest members of the progression display a double peak structure at the band head separated by about 15 cm$^{-1}$. From a fit of the rotational contours, they determined the first adiabatic ionisation energy as $65584.6 \pm 2$ cm$^{-1}$ (8.13146\pm0.00025 eV) and a vibrational fundamental wave number $\tilde{\nu}_7^+ = 436.3$ cm$^{-1}$.

As already mentioned in the introduction, the rovibronic selection rules they derived for the
Chapter 3. The PFI-ZEKE photoelectron spectra of allyl near its first ionisation threshold

\( \tilde{X}^+ \, ^1A_1(0^0, \, 7^1, \, 7^2) \leftarrow \tilde{X}^2A_2 \) transitions

\[
\Delta K_a = K'_a - K''_a = \text{odd/even} \quad \text{for} \quad \ell = \text{even/odd} \quad (3.5)
\]

\[
\Delta K_c = K'_c - K''_c = \text{odd/even} \quad \text{for} \quad \ell = \text{even/odd} \quad (3.6)
\]

are incompatible with Eqs. (3.2) and (3.3). Comparison of Eqs. (3.5) and (3.6) with Eqs. (3.2) and (3.3) suggests that Xing et al. assumed that the electronic ground state of \( C_3H_5 \) has \( A_1 \) symmetry, which clearly is incorrect. Moreover, Xing et al. argue that the electron is ionised out of a \( p_\pi \)-type molecular orbital of \( A_2 \) symmetry and that, as a result, the photoelectron partial wave must be emitted as a superposition of \( s \) and \( d \) partial waves.

Xing et al. have also compared their experimental results with simulations that are re-

![Figure 3.5: Comparison between the simulation of the origin band of the \( \tilde{X}^+ \, ^1A_1 \leftarrow \tilde{X}^2A_2 \) transition performed by Xing et al. (full line) and the attempt of the present work to reproduce them (dashed line). (a) the overall spectrum, (b) the \( \Delta N = 0 \) branch, (c) the \( \Delta N = \pm 1 \) branch and (d) the \( \Delta N = \pm 2, \pm 3 \) branches.](image)

produced in panels (a)-(d) of Fig. 3.5 (full line). Our attempt at reproducing these simulations turned out to be a challenge because the information provided in Ref. [18] on the way the simulations have been performed are contradictory and/or too scarce. The top dashed line shows the simulation of the experimental spectrum taking all \( \Delta N \) branches up to \( \Delta N = \pm 3 \) into account and including only transitions according to the selection rules for \( \ell = \text{even} \) derived by Xing et al. (Eqs. (3.5) and (3.6)). Fig. 3.5 (b), (c) and (d) show simulations of the contributions with \( \Delta N = 0, \, \Delta N = \pm 1, \, \text{and} \, \Delta N = \pm 2, \pm 3 \), respectively. The \( N; O; P; Q; R; S \) and \( T \)-type branches with \( \Delta N = -3; -2; -1; 0; +1; +2 \) and \( +3 \), respectively, were weighted by factors of 5:6:7:8:6:5:4, respectively, to obtain the dashed line in Fig. 3.5 (a). The weighting factors corre-
3.4. Comparison with other studies of the photoelectron spectrum of allyl

Correspond to those reported in Ref. [18]. In our attempt to reproduce the simulations of Xing et al., the values of $\Delta K_a$ and $\Delta K_c$ had to be restricted to $\pm 3, \pm 1$, except for the $Q$-branch in Fig. 3.5 (b), where only transitions with $\Delta K_a = \Delta K_c = \pm 1$ were taken into account. Giving different weights to the intensities of the different $\Delta K_a$- and $\Delta K_c$-branches could have potentially improved the agreement with the simulations of Xing et al. but was not attempted because there was no mention of the treatment of the intensities of the $\Delta K_a$- or $\Delta K_c$-branches in Ref. [18]. In order to reproduce the general shape and appearance of Fig. 3.5 (d), the weighting factor of the $\Delta N = \pm 2$ branch had to be reduced by a factor of 10 compared to what is listed in Ref. [18]. The rotational constants were varied by up to 1.5% in the work of Xing et al. Such adjustments were not attempted in our replication of their work and the rotational constants tabulated in Table 3.1 were used. A rotational temperature of 150 K and a FWHM=3 cm$^{-1}$ were assumed for our simulations displayed in Fig. 3.5.

The agreement between the simulations performed by Xing et al. and our attempt to reproduce them is qualitatively but not quantitatively satisfactory. The question on how to scale the $\Delta K_a$- and $\Delta K_c$-branches and the fact that the exact values of the rotational constants actually used in the simulations performed by Xing et al. were not reported rendered the quantitative replication of their work difficult.

3.4.2 Simulation of the multi-photon PFI-ZEKE photoelectron spectra of the allyl radical

Resonance-Enhanced Multi-Photon Ionisation (REMPI) spectra of allyl have been recorded by Gasser et al. [108]. Allyl was produced flash-pyrolytically from 1-,5-hexadiene and 1-iodoallyl and subsequently cooled in a supersonic expansion to rotational temperatures of about 150 K. The excitation schemes were

$$\tilde{X}^+ + 1 A_1(v_i^+) \rightarrow B^2 A_1(v_i') \leftarrow \tilde{X}^2 A_2(0^0)$$  \hspace{1cm} (3.7)

and

$$\tilde{X}^+ + 1 A_1(v_i^+) \rightarrow C^2 B_2(v_i') \leftarrow \tilde{X}^2 A_2(0^0),$$  \hspace{1cm} (3.8)

and different vibrational levels ($v_i'$) of the $\tilde{B}$ and $\tilde{C}$ electronic states were used as intermediate states. These states had been assigned previously [16, 17], but simulations of the intensity distributions in the PFI-ZEKE photoelectron spectra recorded via the different intermediate states had not been performed to date.

In the realm of the orbital ionisation model (Eqs. (1.24) and (1.25)), the angular momentum characteristics of the molecular orbital out of which the photoelectron is ejected are of decisive importance for the modelling of the rovibronic intensity distributions in photoelectron spectra. In a recent ab initio study [95] the geometries and orbitals of the five lowest lying electronic states have been computed at the MR-CISD level of theory, using a SA-7-MCSCF(3,7) reference. The basis set used was constructed from the DZP basis set and augmented with DZ++ functions for the C-atoms [113]. The $\tilde{B}$ and $\tilde{C}$ states were found to be separated by $\approx 0.5$ eV.
in energy and to be of 3s and 3p, Rydberg orbital character, respectively. Two further Rydberg states corresponding to 3p_z and 3p_x orbitals have been identified at higher energies [95]. The energetic ordering of the 3p states, however, could not be established unambiguously from these calculations. The 3p_z and 3p_y lie in the plane of the molecule and are almost degenerate. The molecular orbitals singly occupied in the main configurations contributing to the five lowest-lying electronic states from these ab initio calculations are displayed on the left hand side of Fig. 3.2. Except for the  \( \tilde{A^2}B_1 \), which is strongly mixed, most states can be represented by a dominant configuration, the square of the configuration interaction (CI) coefficients being at least 0.8. The  \( \tilde{E^2}B_1 \) has 80% 3p_x character and is mixed mainly with the LUMO of B_1 symmetry.

To facilitate the assignment of the congested spectra of the intermediate states, predictions of the rotational contours of these bands have been performed in the realm of the orbital ionisation model for different 3s and 3p molecular orbitals following the procedure described in Section 1.7. \( \ell' \) and \( \lambda' \) now represent the orbital angular momentum quantum number of the molecular orbital out of which ionisation occurs in the intermediate state and its projection on the symmetry axis, which is identified as the z-axis (see Fig. 3.1). Because of their Rydberg-character the 3s, 3p_z, 3p_x and 3p_y orbitals consist of only one dominant contribution in the single-centre expansion, i.e., s_\sigma (A_1), p_\sigma (A_1), p_\pi (B_1) and p_\pi (B_2), respectively. Depending on the vibronic symmetry of the intermediate state, different \( \Delta K_a \) and \( \Delta K_c \) selection rules are obtained which are summarised in Table 3.2. Moreover, for different values of the quantum number \( \lambda' \) of the projection of the orbital angular momentum onto the figure axis different propensity rules for \( \Delta K_a \) and \( \Delta K_c \) are obtained.

Figs. 3.6 (a)-(d) show the predictions of the rotational contours of transitions from selected intermediate levels to the cationic vibronic ground state (\( \tilde{X}^+A_1 \)). The different spectra were calculated assuming that the molecular orbitals are well represented by the dominant contributions listed above. In the simulations, a thermal distribution of the population of rotational states of the intermediate level at a rotational temperature of 150 K was assumed. Because the first step in the excitation scheme in Eqs. (3.7)-(3.8) led to the selective excitation of rotational levels with \( K_a \leq 5 \), only transitions from the intermediate state to the cationic ground state with \( K_a \leq 5 \) were taken into account. The spectra were convoluted with a Gaussian instrumental function of FWHM=3 cm\(^{-1}\), corresponding to the experimental resolution of Gasser et al. [108]. Whereas the spectra displayed in Figs. 3.6 (a) and (b) are very similar, because the molecular orbitals out of which ionisation occurs are of the same symmetry and have the same value of \( \lambda' \), the spectra shown in Figs. 3.6 (c) and (d) have distinctly different band shapes.

In Figs. 3.6 (e) and (f) two PFI-ZEKE photoelectron spectra recorded via the \( \tilde{B}^2A_1 \) and the \( \tilde{C}^2B_2 \) intermediate states are displayed [17, 16], respectively. The \( \tilde{B}^2A_1 \rightarrow \tilde{X}^2A_2 \) transition is dipole forbidden in a one-photon transition and the spectrum displayed in Fig. 3.6 (e) was recorded with a 2+2 excitation scheme. The comparison of the contour of the bands displayed in Fig. 3.6 (e) with the contour displayed in Fig. 3.6 (a) leads to the conclusion that the transition originates a from totally symmetric intermediate state with a molecular orbital out of
3.4. Comparison with other studies of the photoelectron spectrum of allyl

Figure 3.6: Simulations and PFI-ZEKE photoelectron spectra of the origin band of allyl recorded through selected intermediate levels. The simulations were performed on the basis of the orbital ionization model assuming that ionization occurs out of a pure (a) 3s- (\( \tilde{\text{B}}^2\text{A}_1 \)), (b) 3p_\pi- (\( \tilde{\text{D}}^2\text{A}_1 \)), (c) 3p_\sigma- (\( \tilde{\text{E}}^2\text{B}_1 \)) and (d) 3p_\pi (\( \tilde{\text{C}}^2\text{B}_2 \)) Rydberg orbital. In each trace only transitions from rovibronic states with \( K_a \leq 5 \) were taken into account. PFI-ZEKE photoelectron spectra of the origin band (\( \tilde{\text{X}}^+ \text{^1A}_1(0^0) \)) of allyl recorded via (e) the \( \tilde{\text{B}}^2\text{A}_1(0^0) \) level in two-photon and (f) via the \( \tilde{\text{C}}^2\text{B}_2(0^0) \) in one-photon excitation are displayed. Each spectrum has been shifted such that the horizontal axis corresponds to the absolute energy above the neutral vibronic ground state. See text for more detail.

which ionisation occurs best described as \( s_\sigma (3s) \) or \( p_\sigma (3p_\pi) \). The rotational contour of Fig. 3.6 (c) is in good agreement with the simulations performed assuming that ionisation occurs out of a \( p_\pi \)-type molecular orbital. The \( \tilde{\text{C}}^2\text{B}_2 \) state is believed to be short lived [103] and the lines in the spectrum are therefore broadened and not very intense. This renders the detailed comparison of the experimentally observed rotational structure with that of the simulation displayed in Fig. 3.6 (d) difficult. Nevertheless, the agreement between the experimental and calculated
rotational envelopes suggests that the vibronic assignment of the intermediate state is correct in these two cases.

3.5 Conclusions

The photoionization dynamics of allyl have been investigated in the region of the adiabatic ionization thresholds by photoionisation and PFI-ZEKE photoelectron spectroscopy. The selection rules for the transitions $\tilde{X}^+ (0^0, 7^1) \; ^1A_1 \rightarrow \tilde{X} (0^0) \; ^2A_2$ were derived and compared to those derived in Ref. [18], which were found to be based on flawed assumptions about the molecular orbital out of which ionisation occurs. Simulations based on the orbital ionisation model were performed, describing the SOMO of allyl as a single-centre expansion with significant contributions from $d_\delta$ and $f_\delta$ angular momentum characteristics only in accordance with theoretical and ESR studies [94, 92, 93]. The present study allowed to resolve the controversy concerning the adiabatic ionisation energy of the allyl radical and to confirm the values derived in Ref. [18]. The value of 65580.1(20) cm$^{-1}$ determined here lies close to that of 65584.6(20) cm$^{-1}$ in Ref. [18]. The fundamental wave number of the C-C-C bending mode $\nu_+^+$ was determined to be 434.5(10) cm$^{-1}$, in good agreement with the value of 436.3(20) derived by Xing et al. [18].

The intensity distributions and rotational contours of the bands of the PFI-ZEKE photoelectron spectra of allyl recorded via different vibrational levels of the $e_B$ and $e_E$ states vary strongly. Predictions of these intensity distributions and band contours made in the realm of the orbital ionisation model suggest that the bands recorded through totally symmetric vibrational levels of the $\tilde{B} \; ^2A_1$ or $\tilde{D} \; ^2A_1$ intermediate states should be sharp and dominated by a strong $Q$-type branch, and that the bands recorded through the $\tilde{C} \; ^2B_2$ and $\tilde{E} \; ^2B_1$ levels should be significantly broader (see Fig. 3.6). These observations may turn out to be helpful in the assignment of the complex electronic spectrum of allyl in the region of the $\tilde{B}$, $\tilde{C}$ and $\tilde{D}$ states.
Chapter 4

Photoionisation dynamics in methyl and its deuterated isotopomers

This chapter summarises an investigation of the photoionisation dynamics and PFI-ZEKE photoelectron spectra of methyl. Particular emphasis was placed on the characterisation of interactions between the different rotational ionisation channels and on the investigation of the effects of deuteration on the photoionisation dynamics. Improved values for the adiabatic ionisation energy and molecular constants of methyl and its deuterated isotopomers were derived.

The main results presented in this chapter have been published in Ref. [111] and were obtained during an extended research visit of Dr. Ch. Alcaraz (CNRS, Université de Paris-Sud) at ETH Zürich.

4.1 Introduction

Several studies of the Rydberg spectrum [114], the photoionisation spectrum [115, 116], the photoelectron spectrum [117, 118, 119, 120] and the threshold ionisation spectrum of methyl (CH$_3$ [121, 122] and CD$_3$ [123]) have been conducted to date with the goals of understanding the electronic structure of this important radical, of studying its photoionisation dynamics, of determining its first adiabatic ionisation energy, and of obtaining spectroscopic information on the methyl cation. In the case of CD$_3$, the mass-analysed threshold ionisation spectrum [123] has provided information on the energy level structure that complements the information obtained on all the deuterated isotopomers of CH$_3$ and CH$_3^+$ by high-resolution spectroscopy (primarily in the IR) of the radical [124, 125] and the cation [126, 127, 128, 129, 130] and by \textit{ab initio} quantum chemistry [131, 132, 133, 134, 135, 136].

The adiabatic ionisation energy of methyl enables one, using suitable thermochemical cycles, to estimate other thermochemical quantities such as, for instance, the heat of formation of the methylene radical CH$_2$ [115, 137, 138, 139]. The first accurate values of the ionisation energy of methyl were derived by extrapolation of the spectral positions of low Rydberg states by Herzberg [114] and by careful measurements of the onset of the CH$_3^+$ signal in the
photoionisation of methyl by Chupka and Lifshitz [115]. Subsequent measurements by PFI-ZEKE photoelectron spectroscopy [121, 122] have permitted the reduction of the experimental uncertainty in the ionisation energy of CH$_3$ to a fraction of a meV (79349(3) cm$^{-1}$). Based on this value and on a new measurement of the photoionisation spectrum of hot CH$_3$ ($T_{rot} = 1000$ - 1500 K), Litorja and Ruscic have shown that the surprisingly low appearance energy of the CH$_3^+$ signal must originate from rotational autoionisation [116]. They were able to model the photoionisation spectrum quantitatively by assuming fully allowed quadrupole-induced and partially allowed dipole-induced rotational autoionisation, however, without resolving the autoionising Rydberg structure nor explaining in detail how dipole-induced rotational autoionisation can occur in the case of a planar cation of $D_{3h}$ point group symmetry. Their study pointed at the importance of channel interactions and at complex ionisation dynamics in the near-threshold ionisation of CH$_3$ and was an incentive for us to initiate a new investigation of the threshold ionisation dynamics of CH$_3$.

The study of the threshold ionisation dynamics of methyl presented in this chapter differs from previous studies of the photoionisation and photoelectron spectra of methyl in two respects: first, efficient cooling of the radicals to a rotational temperature of less than 40 K in a supersonic expansion enabled a great simplification of the rotational structure of the photoelectron spectra and, in the case of the photoionisation spectrum of CH$_3$, the observation of resolved Rydberg series up to high values of the principal quantum number. Second, the study of the rotationally resolved photoelectron spectra and of the photoionisation spectra of all isotopomers of methyl provided the opportunity to look at the effects of partial and complete deuteration on the photoionisation dynamics of methyl and to derive a more complete and accurate set of ionisation energies and spectroscopic data on the methyl cation than available so far.

### 4.2 Experimental

The measurements relied on the single-photon ionisation of jet-cooled radicals in the PFI-ZEKE photoelectron spectrometer (Section 2.3, set-up 1) using the tunable vacuum-ultraviolet (VUV) laser system described in Subsection 2.2.1. The VUV radiation was generated by resonance-enhanced difference-frequency mixing (\(\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2\)) using the (4p)$^5$ (2P$_{3/2}$) 5p [1/2] ($J = 0$) \(\rightarrow\) (4p)$^6$ 1S$_0$ two-photon resonance in krypton at 2\(\tilde{\nu}_1=94092.862\) cm$^{-1}$ [78, 73] in a four-wave mixing cell (see Section 2.1) filled with 15 mbar Kr. A MgF$_2$ prism with an apex angle of 45° was employed to separate the VUV difference-frequency beam from the fundamental laser beams of wave numbers \(\tilde{\nu}_1\) and \(\tilde{\nu}_2\). The difference-frequency beam was then directed through a small aperture into the excitation region.

The methyl radicals were produced by photolysis of the precursor molecules CH$_3$I, CH$_3$Br, (CH$_3$)$_2$CO, (CH$_3$)$_2$S and CH$_3$NO$_2$. The precursor molecules were diluted in a stream of Ar and were photolysed by the 193 nm output of an ArF excimer laser in a quartz capillary mounted at the end of a pulsed nozzle as described in Section 2.4 and Ref. [28]. The methyl radicals and other photolysis products were cooled in the pulsed supersonic expansion into vacuum to
rotational temperatures of between 20 K and 40 K.

To record PFI-ZEKE photoelectron spectra, a two-pulse electric field sequence was used [140, 6]. The first pulse with an amplitude between +0.034 V/cm and +0.129 V/cm served the purpose of discriminating against prompt electrons and field-ionise the highest Rydberg states and was immediately followed by an extraction pulse with amplitude between -0.134 V/cm and -0.517 V/cm used to field ionise Rydberg states with \( n \approx 200 \) and to extract the electrons. Optimal conditions were obtained using a delay time of \( \approx 1 \mu s \) between photoexcitation and the application of the electric-field pulse sequence. The photoionisation spectra were obtained using a delayed extraction field of 345 V/cm. Spectra of the different isotopomers were recorded by integrating the ion signal over the time windows corresponding to their times of flight to the MCP detector.

The VUV wave number was determined as the difference of the wave number \( 2\nu_1 \) of the two-photon resonance and that of the second laser \( \nu_2 \) which was calibrated by recording the optogalvanic spectra of argon or neon simultaneously to each photoionisation or photoelectron spectrum. The uncertainty in the VUV wave number is estimated to be less than 1 cm\(^{-1}\), and the accuracy of the VUV wave number calibration was checked by recording the laser-induced-fluorescence spectrum of the \((5p)^5 \left( ^2P_{3/2} \right) 5d \left[ J = 1 \right] \leftarrow (5p)^6 1S_0 \) transition of xenon and comparing its position with reference data [78, 141]. To determine the field-free ionisation energies, the field-induced shifts of the thresholds were taken into account using numerical simulations of the line shapes according to the procedure described in Ref. [7]. The relative positions of the ionic energy levels could be determined with an accuracy of 0.3 cm\(^{-1}\) and the uncertainty in the absolute positions of the ionisation energies is estimated to be 1.5 cm\(^{-1}\).

\( \text{CH}_3\text{I} \) (Fluka, purity \( \geq 99.5\% \)), \( \text{CH}_3\text{Br} \) (anhydrous, purity \( \geq 99.5\% \)), \( \text{(CH}_3\text{)}_2\text{S} \) (Fluka, purity 99%), \( \text{(CH}_3\text{)}_2\text{CO} \) (purity 98%) and \( \text{CH}_3\text{NO}_2 \) (Fluka, purity 99.0%) were tested as photolytic precursors. The 193 nm photolysis of \( \text{CH}_3\text{I}, \text{(CH}_3\text{)}_2\text{S}, \text{(CH}_3\text{)}_2\text{CO} \) and \( \text{CH}_3\text{NO}_2 \) yielded methyl radicals in sufficient quantities for subsequent investigations by PFI-ZEKE photoelectron spectroscopy (see Subsection 4.3.1). Nitromethane was identified as the best precursor because its ionisation potential, unlike those of \( \text{CH}_3\text{I}, \text{(CH}_3\text{)}_2\text{S} \) and \( \text{(CH}_3\text{)}_2\text{CO} \), lies above that of methyl. Consequently, no photoelectron/photoion signals from \( \text{CH}_3\text{NO}_2 \) interfered with the measurements of the PFI-ZEKE photoelectron and photoionisation spectra of \( \text{CH}_3\text{I} \) in the vicinity of the first ionisation threshold. \( \text{CD}_3\text{I} \) and \( \text{CD}_3\text{NO}_2 \) (both from Cambridge Isotope Laboratories, Inc., 99%) were used without further purification. The partially deuterated nitromethane precursors were synthesised either directly from \( \text{CH}_2\text{DI} \) and \( \text{CHD}_2\text{I} \) (both from Cambridge Isotope Laboratories, Inc., isotopic purity 98%), or from \( \text{CH}_2\text{DOH} \) and \( \text{CHD}_2\text{OH} \) (both from Cambridge Isotope Laboratories, Inc., isotope purity 98%), via the iodo-compounds. In this case, the methanol isotopomers were reacted with aqueous HI following the procedure described in Ref. [142]. After drying the raw products with \( \text{P}_2\text{O}_5 \), methyl iodide was isolated by condensation on a vacuum line with a yield of 83 - 91% [142] and a purity of 99.9% of the partially deuterated iodo-methanes, as determined by gas chromatography. The methyl-iodide isotopomers were then converted to the corresponding isotopomers of nitromethane by reaction with silver nitrite.
mixed with sand [143]. After the reaction, the by-product methyl nitrite was completely removed through the condenser held at $-40^\circ\text{C}$ by a slow stream of nitrogen. Finally, the reaction flask was cooled to room temperature and the nitromethane isotopomers were isolated with a yield in the range of 55 - 57%. The purity of the partially deuterated nitromethane samples was found to be 99.5-99.9% by gas chromatographic analysis.

4.3 Results

4.3.1 Choice of precursor

Potential precursors for the production of methyl radicals by 193 nm excimer photolysis were tested by mass spectrometry following VUV photoionisation just above the adiabatic ionisation threshold of CH$_3$ at a wave number of 79500 cm$^{-1}$. At this wave number, the dissociative ionisation of the precursors can be ruled out on energetic grounds. The time-of-flight (TOF) traces of the five CH$_3$ precursors tested in the course of the present study (CH$_3$I, CH$_3$Br, (CH$_3$)$_2$S, (CH$_3$)$_2$CO and CH$_3$NO$_2$) are displayed in the five panels of Fig. 4.1. In each panel, the upper and lower traces correspond to measurements with the excimer photolysis laser switched on and off, respectively.

An excimer-dependent CH$_3^+$ signal was observed for all precursors except CH$_3$Br which does not absorb significantly at 193 nm. CH$_3$Br is also the only precursor yielding a measurable CH$_3^+$ signal when the excimer laser is turned off (Fig. 4.1b). Given that, in this case, the CH$_3^+$ signal can only be observed by the absorption of two VUV photons, one for the dissociation of CH$_3$Br and one for the ionisation of CH$_3$, we conclude that the photolysis of CH$_3$Br to CH$_3$ and Br is particularly efficient at 79500 cm$^{-1}$. However, the methyl radicals produced by VUV photolysis in the ionisation region are internally hot and rapidly move out of the photoexcitation region. CH$_3$Br was therefore not used further.

The 193 nm photolysis of the remaining precursors yielded methyl radicals in sufficient quantities for measurements by PFI-ZEKE photoelectron spectroscopy. The TOF mass spectra of CH$_3$I, (CH$_3$)$_2$CO and (CH$_3$)$_2$S in Figs. 4.1(a), (c) and (d), respectively, are dominated by very strong signals at the masses of the undissociated precursors. The resulting large ion concentrations in the photoionisation region turned out to complicate the PFI-ZEKE photoelectron spectroscopic measurements, producing artefacts as described in Ref. [8]. The TOF mass spectrum of the CH$_3$I precursor (Fig. 4.1 (a) reveals an intense I$^+$ signal which is observed as a result of direct VUV photoionisation of the $^2P_{1/2}$ spin-orbit excited level of the I fragment (the $^2P_{3/2}$ ground state of I has an ionisation energy more than half an eV above the VUV photon energy [78]). In the case of the precursor acetone, the dimer ion is weakly observed in the TOF mass spectrum at $\sim5\ \mu$s (see Fig. 4.1c). Since CH$_3$S has an ionisation threshold of 74726 cm$^{-1}$ [144], the CH$_3$S$^+$ ion also contributes to the mass spectrum of the precursor (CH$_3$)$_2$S (see Fig. 4.1 (d)). The 193 nm photolysis of (CH$_3$)$_2$S in the capillary thus appears to
be a very promising method to generate a supersonically cooled sample of the methylsulfonyl radical.

The strongest CH$_3^+$ signal was obtained using CH$_3$NO$_2$ as a precursor. Compared to the other photolytic precursors tested in this study, CH$_3$NO$_2$ presents the additional advantage that its adiabatic ionisation energy lies above that of methyl. Consequently, the TOF mass spectrum (Fig. 4.1 (e)) does not show any signal when the photolysis laser is turned off and only shows NO$^+$ and CH$_3^+$ signals when it is turned on. We attribute the NO$^+$ signal to NO radicals produced from the NO$_2$ primary photolysis fragments either by predissociation of electronically excited NO$_2$ ($\tilde{A}$ 2B$_2$) or by photolysis of ground state NO$_2$ (X 2A$_1$) [145]. The other photolysis products, NO$_2$ and O, cannot be ionised at 79500 cm$^{-1}$. The remaining weak signals at higher masses observed in several TOF mass spectra correspond to acetone and dimethyl-sulfide molecules still adsorbed in the capillary and released by the photolysis laser. These signals diminished gradually over a period of several days.
4.3.2 The photoelectron spectra and their assignment

The PFI-ZEKE photoelectron spectra of CH$_3$, CD$_3$, CH$_2$D, CHD$_2$ are displayed in Figs. 4.2 (a), 4.2 (b), 4.3 (a) and 4.3 (b), respectively. The electric-field pulse sequences used to record these spectra are listed in the captions of the figures and were chosen so as to achieve, in each case, a satisfactory compromise between resolution and signal-to-noise ratio. The full widths at half maximum (FWHM) of the spectral lines all lie in the range 0.8 cm$^{-1}$ to 2.2 cm$^{-1}$, which suffices to resolve the main features of the rotational structure. Each panel of Figs. 4.2 and 4.3 also contains, for comparison, a calculated stick spectrum and its convolution with a Gaussian instrumental function with a FWHM of 0.9 cm$^{-1}$. These simulations, which are based on the orbital ionisation model described in Ref. [59] and Section 1.7, will be discussed in more detail in Subsection 4.3.3 below.

The lines in the spectra of the symmetric-top molecules CH$_3$ and CD$_3$ displayed in Fig. 4.2 are labelled by the value of $N''$ and grouped in P-type, Q-type and R-type branches, according to the values of $\Delta N = N^+ - N''$ of $-1$, 0 and $+1$, respectively (here and below, $N^+$ and $N''$ represent the quantum numbers of the total angular momentum excluding spins of the ion and the neutral, respectively, and $K^+$ and $K''$ represent the corresponding quantum numbers for the projection of the angular momentum on the principal axis.). The structure in these spectra is particularly simple because only transitions with $\Delta K = K^+ - K'' = 0$ are observed and the differences in the ionic and neutral rotational constants are too small for the $K$ substructure of the different lines to be resolved. Because of the low rotational temperature in the range from 30 K to 40 K in the supersonic expansion, only ground state levels with $N'' \leq 2$ and $N'' \leq 3$ are significantly populated in CH$_3$ and CD$_3$, respectively.

The photoelectron spectra of CH$_2$D and CHD$_2$ displayed in Figs. 4.3 (a) and (b) show a richer rotational structure, as expected for asymmetric-top molecules. The transitions are labelled using the notation $N^+_K K_0 \rightarrow N''_K K''$ ($K_a$ and $K_c$ represent the usual projection quantum numbers used to label the rotational levels of asymmetric-top molecules) and are grouped along the assignment bars according to the respective common neutral states.

The spectra displayed in Figs. 4.2 and 4.3 were used to derive the ionisation energies of all isotopomers of the methyl radical and the rotational constants of the methyl radicals and cations in a least-squares fitting procedure. For most isotopomers, accurate values of the rotational constants are known from high-resolution spectroscopic studies in the infrared [124, 130, 123, 125, 129]. These constants were not adjusted in the fits. Because of the low rotational temperature of the methyl samples, only low-lying rotational levels were observed and no attempt was made to fit centrifugal distortion constants, a rigid rotor Hamiltonian being sufficient to describe the line positions at the present resolution.

All molecular constants derived or used in the least-squares fits of the spectral positions are listed in Table 4.1. Compared to earlier studies, the present results provide more accurate values of the adiabatic ionisation energies of CH$_3$ and CD$_3$ and the first experimental values of the adiabatic ionisation energies of CH$_2$D and CD$_2$H. The photoelectron spectra also enabled the
4.3. Results

Figure 4.2: PFI-ZEKE photoelectron spectra of (a) CH$_3$ and (b) CD$_3$ recorded with the electric field pulse sequences (+0.121 V/cm, −0.224 V/cm) and (+0.129 V/cm, −0.345 V/cm), respectively. The rotational branches are grouped in P-type, Q-type and R-type branches according to $\Delta N = N^+ - N^0$ values of −1, 0, +1, respectively. The lines marked with an asterisk are impurity lines. The stick spectra and a convolution thereof (lower trace in each panel), using a Gaussian instrument function with a FWHM of 0.9 cm$^{-1}$, represent the intensity distribution calculated using the orbital ionisation model of Ref. [59] and Section 1.7. Rotational temperatures of 40 K and 30 K were assumed for CH$_3$ and CD$_3$, respectively.

derivation of rigid rotor rotational constants for the ground vibronic state of CD$_2$H and CD$_3^+$. In the latter case, the results are consistent with those derived by Dickinson et al. [123]. The values of the first adiabatic ionisation energy vary almost linearly with the number of deuterium atoms and spectral shifts of $-17.4$ cm$^{-1}$, $-19.7$ cm$^{-1}$ and $-22.7$ cm$^{-1}$ result at the successive
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Figure 4.3: PFI-ZEKE photoelectron spectra of (a) CH$_3$D and (b) CHD$_2$ recorded with an electric field pulse sequence of (+0.034 V/cm, -0.345 V/cm). The rotational lines are assigned as $N''_{K''',J'''} \rightarrow N''_{K'',J''}$. The stick spectra and a convolution thereof (lowest trace in each panel), using a Gaussian instrument function with a FWHM of 0.9 cm$^{-1}$, represent the intensity distribution calculated using the orbital ionisation model of Ref. [59]. A rotational temperature of 20 K was assumed for CH$_3$D and CHD$_2$. In a) the dashed line shows the PFI-ZEKE photoelectron spectrum of CH$_3$, which contributes to the spectrum as an impurity.

deuteration steps. Our new value (79356.4(15) cm$^{-1}$) of the adiabatic ionisation energy of CH$_3$ deviates by $\approx$1 meV from the previous value determined by PFI-ZEKE photoelectron spectroscopy (79349(3) cm$^{-1}$ [121]). We can rule out the possibility that the deviation stems from a systematic error arising in the calibration of the VUV wave number or in the determination of the field-induced shifts of the ionisation thresholds. To gain further confidence in our result, the
4.3. Results

<table>
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<th>$E_i$/cm$^{-1}$</th>
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<th>$B$/cm$^{-1}$</th>
<th>$C$/cm$^{-1}$</th>
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<td>79356.4(15) b</td>
<td>-</td>
<td>4.73831 c</td>
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<tr>
<td></td>
<td>79355.9(15) d</td>
<td>9.577926(91)</td>
<td>4.73831 c</td>
<td></td>
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<tr>
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<td>2.391 e</td>
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<td>-</td>
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<td>2.36(20) [123]</td>
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<td>4.91(5) f</td>
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<td>-</td>
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<td>4.69046(4)</td>
<td>2.815470(18)</td>
</tr>
</tbody>
</table>

*Numbers in parentheses represent one standard deviation.

- This work, from the analysis of the PFI-ZEKE photoelectron spectrum. Values include a correction for the field-induced shift of the ionisation thresholds.
- Estimated using a theoretical inertial defect.
- This work, from extrapolation of the Rydberg series converging on $N^+ = 3$.
- Calculated according to Sears et al. [125].
- This work.

Table 4.1: Molecular constants used in the simulations of the PFI-ZEKE photoelectron spectra.

VUV wave number was calibrated directly using the $(5p)^5 (^2P_{3/2}) 5d [1/2] (J = 1) \leftrightarrow (5p)^6 1S_0$ resonance in xenon. Moreover, an independent determination of the field-free ionisation threshold by extrapolation of the Rydberg series observed from $n = 30$ to $n = 55$ in the photoionisation spectrum yields a value of 79355.9(15) cm$^{-1}$ (see Subsection 4.3.4), indicating that our estimate of the field-induced shift of the ionisation thresholds is accurate.

4.3.3 Photoionisation selection rules and simulation of intensity distributions in the photoelectron spectra

The intensity distributions in PFI-ZEKE photoelectron spectra provide information on the photoionisation dynamics. They do not simply reflect the direct ionisation cross sections but are also influenced by rovibronic interactions between the different ionisation channels [42]. Photoionisation selection rules can be expressed in terms of changes of the rotational quantum numbers $\Delta N = N^+ - N^0$, $\Delta K = K^+ - K^0$ in the cases of the symmetric-top molecules CH$_3$ and CD$_3$, and in terms of $\Delta N$, $\Delta K_a = K^+_a - K^0_a$ and $\Delta K_c = K^+_c - K^0_c$ in the cases of the asymmetric-top molecules CH$_2$D and CD$_2$H.

In the $D_{3h}(M)$ molecular symmetry group (CH$_3$ and CD$_3$) the general rovibronic photoionisation selection rules (see Eqs. (1.19)) can be expressed as

$$A'_1 \leftrightarrow A''_1, A'_2 \leftrightarrow A''_2, E' \leftrightarrow E'' \text{ for } \ell \text{ even}$$

(4.1)
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Figure 4.4: Axis systems used to label the rotational levels of (a) CH$_3$ and CD$_3$, (b) CHD$_2$ and (c) CH$_2$D.

and

$$A_1'(2) \leftrightarrow A_1'(2), \quad A_1''(2) \leftrightarrow A_1''(2), \quad E' \leftrightarrow E', \quad E'' \leftrightarrow E'' \quad \text{for } \ell \text{ odd.} \quad (4.2)$$

Eqs. (4.1) and (4.2) can be further used to derive the allowed values of $\Delta K$.

The corresponding selections rules for the $C_{2v}(M)$ molecular symmetry group (CH$_2$D and CD$_2$H) are

$$A_1 \leftrightarrow A_2, \quad B_1 \leftrightarrow B_2 \quad \text{for } \ell \text{ even} \quad (4.3)$$

and

$$A_1(2) \leftrightarrow A_1(2), \quad B_1(2) \leftrightarrow B_1(2) \quad \text{for } \ell \text{ odd}, \quad (4.4)$$

which can also be expressed as $\Delta K_a = \text{odd (even)}$ and $\Delta K_c = \text{even (odd)}$ for even (odd) values of $\ell$ for CD$_2$H, and as $\Delta K_a = \text{odd (odd)}$ and $\Delta K_c = \text{even (odd)}$ for even (odd) values of $\ell$ for CH$_2$D. The differences in the odd/even nature of the allowed $\Delta K_a$ values between CH$_2$D and CD$_2$H result from the different principal axis systems displayed in Fig. 4.4.

The $\tilde{X}^+ 1A_1'$ electronic ground state of the methyl cation is obtained from the $\tilde{X}^2A''_2$ ground state of the neutral by removing an electron from the essentially atomic 2p$_z$ orbital centred on the carbon atom. Comparing the selection rules listed in Eqs. (4.1)-(4.4) with the experimental spectra shown in Figs. 4.2 and 4.3 and considering the angular momentum conservation $\Delta N = \ell + 1, \ldots, -\ell - 1$ (see Eq. (1.21)) leads to the conclusions that (1) the photoelectron departs as a superposition of even-$\ell$ partial waves, as expected for a $2p_z^{-1}$ single-photon ionisation, and (2) only a small subset of all transitions allowed by the general rovibronic photoionisation selection rules (see Eq. (1.20)) are observed experimentally. The number of ionisation channels is thus severely restricted.

The observed transitions are characterised by $\Delta N = 0, \pm 1$, and $\Delta K = 0$ for CH$_3$ and CD$_3$, and $\Delta N = 0, \pm 1$, and $\Delta K_c = 0, 2$ for CH$_2$D and CHD$_2$ (see Figs. 4.2 and 4.3). These propensity rules can be explained within the framework of the orbital ionisation model (see Section 1.7 and Refs. [56, 59]). From Eq. (1.25), the quantum states of the ions accessible from a given rovibronic level of the neutral can be derived from the angular momentum of the electron hole generated upon removal of an electron out of a given molecular orbital. In the case of the $\tilde{X}^+ \leftarrow \tilde{X} (2p_z)^{-1}$ photoionising transition of methyl, photoelectron partial waves of s and d character are expected to be dominant ($\ell = 0, 2$ in Eqs. (1.21) and (4.1)-(4.4)). The orbital ion-
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Ionisation model predicts transitions with $\Delta N = 0, \pm 1$ to be dominant (cf. Eq. (1.23)), whereas Eq. (1.21) leads to the less restrictive prediction $\Delta N = 0, \pm 1, \pm 2, \pm 3$. For CH$_3$ and CD$_3$, the additional propensity rule $\Delta K = 0$ results because the 2$p_z$ orbital lies parallel to the $C_3$ symmetry axis ($c = z$). For CH$_2$D and CD$_2$H, the $\Delta K_a$ and $\Delta K_c$ propensity rules result from the fact that the 2$p_z$ orbital lies parallel to the $c$ axis (see Fig. 4.4) which implies that the $p$ orbital out of which the electron is ejected lies along the $y = c$ axis and that $\Delta K_c$ must be even with dominant $\Delta K_c = 0$ contributions. The corresponding values of $\Delta K_a$ are unambiguously determined from the even nature of $\Delta K_c$ and the even nature of the photoelectron partial waves (see Eqs. (4.3) and (4.4)).

The $\Delta N = 0, \pm 1$ and $\Delta K = 0$ ($\Delta K_c = 0$) restrictions that follow from the orbital ionisation model are sufficient to explain the rotational structure of the photoelectron spectra of all four isotopomers of methyl studied. Only a few, usually weak lines with $\Delta K_c = \pm 2$ visible in the spectra of CH$_2$D and CD$_2$H do not follow $\Delta K_c = 0$ because $K_c$ is not a good quantum number in asymmetric-top molecules. The spin-statistical weights are (0, 0, 4, 4, 2, 2) and (10, 10, 1, 1, 8, 8) for states of rovibronic symmetries ($A_0^1$, $A_0^2$, $A_2^0$, $A'_0$, $E$, $E''$) in CH$_3$ and CD$_3$, respectively. In CH$_2$D and CHD$_2$, they are (3, 3, 9, 9) and (12, 12, 6, 6), respectively, for states of rovibronic symmetry ($A_1$, $A_2$, $B_1$, $B_2$).

Simulations of the photoelectron spectra of methyl are compared with the experimental spectra in Figs. 4.2 and 4.3. These simulations are based on Eq. (1.24)-(1.25), the rotational temperatures of 40 K (CH$_3$), 30 K (CD$_3$) and 20 K (CH$_2$D and CHD$_2$), and the assumption that the photoelectron is ejected out of a $p_z$-type orbital. Overall, the agreement between the simulations and the experimental spectra is good. Deviations in the cases of CH$_2$D and CD$_2$H lie within the experimental uncertainties. In the case of CH$_3$, the main deviation between the simulated and the experimental spectrum is the larger strength of the P-type ($N'' = 2$, $\Delta K = 0$) transition in the latter. As will be discussed in more detail in the next subsection, this large intensity can be attributed to a rotational channel interaction, specifically to an intensity enhancement originating from the coupling of the $n = 34$ Rydberg states belonging to the $nd$ series converging to the $N^+ = 3$, $K^+ = 0$ ($A'_2$) and $N^+ = 3$, $K^+ = 1$ ($E''$) rotational levels of the ion to the high Rydberg states below the $N^+ = 1$, $K^+ = 0$ ($A'_2$) and the $N^+ = 1$, $K^+ = 1$ ($E''$) ionic states, respectively (see also Figs. 4.6 and 4.7 below). Rotational channel interactions may also be responsible for the enhanced intensities of the P-type lines in the spectrum of CD$_3$.

The overall agreement between simulated and experimental spectra for all four isotopomers indicates that the orbital ionisation model is able to reproduce the main aspects of the rotational intensity distribution. However, the model is not adequate to treat the effects of rovibronic channel interactions which are now discussed in more detail.
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4.3.4 Photoionisation spectra, rotational autoionisation and predissociation

The photoionisation spectra of CH$_3$, CH$_2$D, CD$_2$H and CD$_3$ in the region of the lowest ionisation thresholds are displayed in Fig. 4.5. These spectra were recorded by extracting the ions with a +345 V/cm pulsed field delayed by $\approx$ 20 ns with respect to the VUV laser pulse so that photoexcitation was carried out under almost field-free conditions. All photoionisation spectra reveal sharp structures in the near-threshold region that can be attributed to interactions between the different ionisation channels, primarily to rotational autoionisation of Rydberg states belonging to series converging on excited rotational levels of the ions. The most prominent effect of rotational autoionisation can be seen in the spectrum of CH$_3$ in which a well-resolved Rydberg series extends from 79290 cm$^{-1}$ to 79375 cm$^{-1}$ (i.e., from 60 cm$^{-1}$ below, to 20 cm$^{-1}$ above the adiabatic ionisation energy). Rydberg series cannot be observed with as much clarity in the other isotopomers. At our spectral resolution of 0.5 cm$^{-1}$, the structures become less pronounced in the sequence CH$_3$, CD$_3$, CH$_2$D, and CHD$_2$. Another difference between the spectra of the four isotopomers is the spectral separation between the onsets of the photoionisation signal and the adiabatic ionisation energies which are indicated by the thick vertical lines in Fig 4.5. This separation amounts to 60 cm$^{-1}$ in the case of CH$_3$, 35 cm$^{-1}$ in the case of CD$_3$ and less than 25 cm$^{-1}$ in the cases of CH$_2$D and CD$_2$H. These two main differences in the photoionisation spectra of methyl and its deuterated isotopomers can be accounted for as follows:
First, the energetic separation between the rotational levels of the cations becomes smaller in the sequence CH$_3$, CD$_3$, CH$_2$D and CHD$_2$, and consequently the principal quantum numbers of the autoionising Rydberg states are higher than in the case of CH$_3$. Because the spectral density of Rydberg levels within a series scales as $(2R/n^3)^{-1}$, the autoionising Rydberg series are more difficult to resolve. Second, the number of rotational levels populated in the ground neutral state is lowest in CH$_3$ and increases in the sequence CH$_3$, CD$_3$, CH$_2$D and CHD$_2$ leading to an increased spectral congestion in the photoionisation spectra. Third, the number of ionic levels accessible from a given rotational level of the neutral parent is higher in CH$_2$D and CHD$_2$ than in CH$_3$ and CD$_3$ because of the less restrictive photoionisation selection rules in these asymmetric-top molecules (see Subsection 4.3.3). These three reasons also explain why CD$_3$ takes on an intermediate position between CH$_3$ and the partially deuterated species despite its higher degree of deuteration.

Whereas the spectral congestion in the photoionisation spectra of CH$_2$D, CHD$_2$ and CD$_3$ prevents a detailed study of the rotational autoionisation dynamics, the spectrum of CH$_3$ is ideally suited to such a study and contains precious information on the decay dynamics of the Rydberg states of methyl. Fig. 4.6 compares, on an enlarged scale, the PFI-ZEKE photoelectron spectrum of CH$_3$ (dashed line) with two photoionisation spectra, one recorded by applying the 345 V/cm pulsed electric field $\approx 20$ ns after photoexcitation (lower full line), the other 100 ns later. 

**Figure 4.6**: Comparison of the photoionisation spectra (full lines) of CH$_3$ in the vicinity of the adiabatic ionisation threshold with the PFI-ZEKE photoelectron spectrum (dashed line) of CH$_3$. The upper (lower) photoionisation spectrum was recorded using an electric field pulse with an amplitude of 345 V/cm delayed by 100 ns ($\approx 20$ ns) with respect to photoexcitation. The assignment bar shows a Rydberg series with a quantum defect of 0 converging to the $N^+ = 3 \leftarrow N'' = 2$ ionisation thresholds. The dotted line drawn below the upper spectrum emphasises the step-like appearance of the photoionisation spectrum (see text for more details).
after photoexcitation (upper full line).

These two photoionisation spectra reveal a strong autoionising series which converges to the position of the \( N^+ = 3 \leftarrow N'' = 2 \) (\( \Delta K = 0 \)) thresholds as can be seen from the PFI-ZEKE photoelectron spectrum. A least-squares fit of the resolved spectral positions yields a series limit of \( \approx 79411.5 \text{ cm}^{-1} \) and a quantum defect close to zero. This series is assigned to a superposition of the almost degenerate \( nd \) (\( N^+ = 3, K^+ = 0, A_\perp^i \) \( \leftarrow \) \( N'' = 2, K'' = 0, A_\perp^n \)) and \( nd \) (\( N^+ = 3, K^+ = 1, E'' \) \( \leftarrow \) \( N'' = 2, K'' = 1, E' \)) series and represents the high-\( n \) part of the series observed by Herzberg [114].

The onset of the photoionisation spectrum recorded by extracting the ions after a delay of 100 ns coincides exactly with the position of the \( N^+ = 1 \leftarrow N'' = 2 \) (\( \Delta K = 0 \)) transitions in the PFI-ZEKE photoelectron spectrum. The unexpectedly large intensity of this transition in the PFI-ZEKE photoelectron spectrum already noted in the discussion of Fig. 4.2 in Subsection 4.3.3 can therefore be unambiguously attributed to an interaction between the \( N^+ = 3 \) (\( K^+ = 0, 1 \)) and the \( N^+ = 1 \) (\( K = 0, 1 \)) ionisation channels mediated by the quadrupole of the ion core.

In addition to the Rydberg series, the photoionisation spectrum also shows several sharp steps outlined by the dotted line in Fig. 4.6, the main step corresponding to the position of the \( Q \)-type transitions of the PFI-ZEKE photoelectron spectrum. The unexpectedly large intensity of this transition in the PFI-ZEKE photoelectron spectrum already noted in the discussion of Fig. 4.2 in Subsection 4.3.3 can therefore be unambiguously attributed to an interaction between the \( N^+ = 3 \) (\( K^+ = 0, 1 \)) and the \( N^+ = 1 \) (\( K = 0, 1 \)) ionisation channels mediated by the quadrupole of the ion core.

At first sight, it appears surprising that only one Rydberg series is observed in the near-threshold photoionisation spectrum of \( \text{CH}_3 \) at low temperature. As will be shown below, this observation reflects the restrictive propensity rules for direct photoionisation discussed in Subsection 4.3.3 and the equally restrictive selection rules for rotational channel interactions. To facilitate the discussion of these selection rules, a schematic diagram of the \( N'' \leq 3 \) and \( N^+ \leq 3 \) rotational levels of the \( \tilde{X} \) and \( \tilde{X}^+ \) ground electronic states of \( \text{CH}_3 \) and \( \text{CH}_3^+ \) is presented in Fig. 4.7. The single-headed arrows in this diagram represent the dominant direct ionisation transitions expected from the photoionisation selection and propensity rules discussed in Subsection 4.3.3: \( \Delta N = 0, \pm 1, \Delta K = 0, A_\perp^n \leftrightarrow A_\perp^i, E' \leftrightarrow E'' \). In the absence of any autoionisation selection rules other than those resulting from the conservation of nuclear spin symmetry and overall parity, thirteen channel interactions would be expected, namely (in the notation \( (N^+, K^+, \Gamma_{\text{ric}}^+) \leftarrow (N'^{+}, K'^{+}, \Gamma_{\text{ric}}^{+}) \)):

1) \( (3, 0, A_\perp^i) \leftrightarrow (3, 3, A_\perp^n), \) 2) \( (3, 0, A_\perp^i) \leftrightarrow (1, 0, A_\perp^i), \)
3) \( (3, 1, E'') \leftrightarrow (3, 2, E'), \) 4) \( (3, 1, E'') \leftrightarrow (2, 1, E''), \)
5) \( (3, 1, E'') \leftrightarrow (2, 2, E'), \) 6) \( (3, 1, E'') \leftrightarrow (1, 1, E''), \)
7) \( (3, 2, E') \leftrightarrow (2, 1, E''), \) 8) \( (3, 2, E') \leftrightarrow (2, 2, E'), \)
9) \( (3, 2, E') \leftrightarrow (1, 1, E''), \) 10) \( (3, 3, A_\perp^n) \leftrightarrow (1, 0, A_\perp^i), \)
11) \( (2, 1, E'') \leftrightarrow (2, 2, E'), \) 12) \( (2, 1, E'') \leftrightarrow (1, 1, E''), \)
13) \( (2, 2, E') \leftrightarrow (1, 1, E''). \)

The autoionisation processes 1), 3), 5), 7), 9), 10), 11) and 13) require a change of the parity of
the electron partial wave and therefore interactions mediated by an odd multipole of the ion core (e.g., octopole-induced rotational autoionisation) whereas the other processes require a conservation of the parity of the electron partial wave and are mediated by even multipoles (primarily the quadrupole) of the ion core.

Of the 13 possible processes listed above, only two (processes 2 and 6) suffice to account for the autoionisation structures observed experimentally (see Fig. 4.6), the eleven remaining ones being either forbidden or of negligible importance. The 345 V/cm pulsed ionisation field used to record the photoionisation spectra lowers the ionisation thresholds by about 100 cm\(^{-1}\) and would have been sufficient for the \( n d N^+ = 3, K^+ = 0, 1 \) Rydberg series to be observed at \( n \) values as low as 23. As we have not observed any ionisation signal below the \( n = 34 \) and \( n = 30 \) autoionising level in the spectra recorded with the field ionisation pulse delayed by 100 ns and 20 ns, respectively, we can conclude that the \( nd \) Rydberg states below \( n = 34 \) (\( n = 30 \)) have decayed to neutral channels on a timescale of less than 100 ns (20 ns). The radiative decay of Rydberg states with \( n \approx 30 \) takes place on a timescale of several microseconds [34] so that the \( nd \) Rydberg series of methyl converging to the ground vibronic state of \( \text{CH}_3^+ \) must be predissociative.

At delays as short as 20 ns between photoexcitation and the electric field pulse, it is impossible to avoid the overlap of the rising edge of the pulsed electric field with the laser pulse. Photoexcitation thus takes place in the presence of a stray field of several mV/cm which stabilises the Rydberg states located within \( \approx 25 \) cm\(^{-1}\) (i.e., with \( n \geq 65 \)) of the ionisation thresholds. The
stray field induces a pseudo-continuum of long-lived Stark states below the ionisation thresholds [42, 35]. This effect manifests itself as a less sharp photoionisation step in the photoionisation spectrum at the position of the Q-type lines of the PFI-ZEKE photoelectron spectrum than is observed when the pulsed electric field is applied 100 ns after photoexcitation (compare the two photoionisation spectra in Fig. 4.6). Below the \( N^+ = 1 \leftarrow N'' = 2 (\Delta K = 0) \) thresholds, the \( 30 \leq n \leq 34 \) s and d Rydberg states converging to the \( N^+ = 3 \leftarrow N'' = 2 (\Delta K = 0) \) thresholds, instead of predissociating, can now autoionise to the pseudo-continuum of long-lived Stark states below the \( N^+ = 1 \leftarrow N'' = 2 (\Delta K = 0) \) thresholds and be detected by pulsed-field ionisation. Quadrupole-induced rotational autoionisation therefore appears to dominate over predissociation as soon as the process becomes energetically allowed.

The step in the photoionisation spectrum at the position of the strong Q-type transitions implies that the allowed ns and nd Rydberg series converging on the \( \left| 2, 1, E'' \right> \), and the \( \left| 2, 2, E' \right> \) ionic rotational states do not autoionise to lower-lying continua of the same nuclear-spin symmetry, i.e., to ionisation continua above the \( \left| 1, 1, E'' \right> \) ionic state. Processes 12) and 13) therefore appear to be forbidden. Moreover, processes 1), 4), 7), 8), 9) and 10), which would have led to additional series above the Q-type line of the PFI-ZEKE photoelectron spectrum are not observed either.

The importance of interactions 3) and 11) cannot be assessed because the channels that are coupled have series limits that are too closely spaced for resolved Rydberg series to be observable at our spectral resolution. Summarizing these observations, one can state that rotational channel interactions with \( \Delta N = -2, \Delta K = 0 \) and \( \Delta \ell = \) even are observed in the photoionisation spectrum of \( \text{CH}_3 \) whereas interactions with \( \Delta N = -1 \), either in combination with \( \Delta K = 0 \) and \( \Delta \ell \) odd or with \( |\Delta K| = 1 \) and \( \Delta \ell \) even, are negligible. Because the \( \Delta N = -1, |\Delta K| = 1, \Delta \ell \) odd processes, which would be characteristic of dipole-induced rotational autoionisation are not observed, we conclude that the effects of dipole-induced rotational autoionisation are negligible in the near-threshold ionisation of methyl. This conclusion is consistent with the \( D_{3h} \) structure of the \( \text{CH}_3^+ \) cation but contradicts the earlier observation of partially allowed dipole-induced rotational autoionisation reported in Ref. [116].

### 4.4 Conclusions

The photoionisation dynamics of methyl and its isotopomers have been investigated in the region of the adiabatic ionisation thresholds by photoionisation and PFI-ZEKE photoelectron spectroscopy. Both direct ionisation and autoionisation are observed and are subject to very restrictive selection rules. The photoionisation selection rules can be described by a simple orbital ionisation model for direct ionisation. This model provides a consistent description of the photoionisation of all isotopomers despite the different rotor types and molecular symmetry groups involved. Sharp and extended autoionising Rydberg series have been observed up to \( n \approx 50 \) in the photoionisation spectrum of \( \text{CH}_3 \) for the first time. In the deuterated isotopomers, spectral congestion renders the observation and analysis of well-resolved progressions of Ryd-
bergs states difficult. Both predissociation and quadrupole-induced rotational autoionisation are identified as decay channels in the near-threshold ionisation of methyl; however, the decay by predissociation to neutral channels is found to be less efficient than the decay by autoionisation. Improved ionisation energies and molecular constants have been determined for CH$_3$ and all the deuterated isotopomers. Compared to earlier studies [121, 116], we find a slightly higher value (by $\approx 1$ meV) for the first adiabatic ionisation threshold of CH$_3$ and did not see any evidence for dipole-induced rotational autoionisation.
Chapter 5

The rovibrational energy level structure of the formaldehyde cation

This chapter describes an investigation of the photoionisation dynamics of formaldehyde and of the rovibrational energy level structure of the $\tilde{X}^+ \, ^2\text{B}_2$ ground state of the formaldehyde cation. A resonant three-photon excitation scheme via selected rovibrational levels of the $\tilde{A} \, ^1\text{A}_2$ state and the $3p_\pi$ Rydberg state enabled the recording of the PFI-ZEKE photoelectron spectra with nearly full rotational resolution. From the analysis of the spectra the first adiabatic ionisation energy of formaldehyde ($87793.33 \pm 1.30$ cm$^{-1}$) and rigid rotor constants ($A^+ = 8.874(8)$ cm$^{-1}$, $B^+ = 1.342(15)$ cm$^{-1}$, $C^+ = 1.148(18)$ cm$^{-1}$) for the formaldehyde cation were derived. The high-resolution of the photoelectron spectra enabled the detection and analysis of an $a$-type Coriolis interaction between the $6^1$ and $4^1$ vibrational levels of CH$_3$O$^+$.

The work presented in this chapter was carried out in collaboration with the group of Dr. P. P. Radi (Department of General Energy, Paul-Scherrer-Institute, 5232 Villigen, Switzerland) who provided a pulsed pyrolytic source of formaldehyde. The main results of this investigation have been published in Ref. [146]. A study of the $3p_\pi$ electronic state of formaldehyde preceded this investigation and will be reported elsewhere [147].

5.1 Introduction

Formaldehyde was one of the first asymmetric-top molecules the electronic spectrum of which could be studied spectroscopically with rotational resolution [148]. Since this pioneering study of the $\tilde{A} \, ^1\text{A}_2 \leftarrow \tilde{X} \, ^1\text{A}_1$ band system, extensive and comprehensive studies of the rotational structure and vibronic dynamics of the electronic ground [149, 150, 151] and electronic excited states [152, 153, 154, 155, 147] of neutral CH$_2$O have been performed. In particular, the rovibrational structure of the polyads in the 3.5 $\mu$m [156] and 5-10 $\mu$m (see Refs. [157, 158] and references therein) spectral regions have been investigated in great detail. These works are complemented by extensive theoretical investigations of the electronic structure and dynamics of CH$_2$O (see Refs. [159, 160, 161] and references therein).
The rovibronic energy level structure of the formaldehyde cation is not known in as much
detail and has been primarily studied by photoelectron spectroscopy [162, 163, 164, 165, 166,
122]. Niu et al. [164, 165] suggested that the cation is nonplanar on the basis of the observation
of a band at 777.1 cm$^{-1}$ above the adiabatic ionisation energy which they assigned to the
fundamental band of the out-of-plane bending mode (4$^1_1$). This band was later reassigned to
a transition to the 6$^1_1$ vibrational level of the cation, which corresponds to the CH$_2$-in-plane
rocking mode [167, 160]. A single-photon pulsed-field-ionisation zero-kinetic-energy (PFI-
ZEKE) photoelectron spectroscopic study has revealed the partially resolved rotational structure
of the vibronic ground state of the cation [122].

The aims of the work presented here were

1. to investigate the vibrational ground state and first two excited vibrational levels of the
cation at full rotational resolution,
2. to measure and analyse the rovibrational energy level structure of the cation from the
ground state up to $\sim$ 1000 cm$^{-1}$ of internal energy,
3. to clarify earlier conflicting assignments of the low vibrational levels of CH$_2$O$^+$ [165,
164, 166, 167, 160], and
4. to obtain reference information with which to compare the energy level structure of low-
lying Rydberg states, in particular the members of the 3p complex.

Because the rovibronic energy level structure of unperturbed Rydberg states closely resembles
that of the cation, the present analysis was also instructive for the assignment of the vibronic
structure of the 3$p_x$ Rydberg state of neutral formaldehyde [147]. The 3$p_x$ state is known to
be the only member of the 3p complex with a well-behaved energy level structure [152, 155].
The analysis of the intensity distribution in the rotationally-resolved photoelectron spectra also
provided insights into the photoionisation dynamics of formaldehyde.

5.2 Experimental

The threshold photoionisation of CH$_2$O was studied by photoionisation and PFI-ZEKE photo-
electron spectroscopy. The resonance-enhanced three-photon excitation sequence

$$
\tilde{X}^+ \quad ^2B^2_2(0^0, 4^1, 6^1)N^+_K^+ K^+= \tilde{v}_1 \quad 3p_x \quad ^1A_2(0^0, 4^1, 6^1)J_{K_aK_c}
$$

$$
\tilde{v}_2 \quad ^1A_2(2^14^3)J_{K'_{aK_c'}} \quad \tilde{v}_1 \quad \tilde{X}^+ \quad ^1A_1(0^0)J_{K''_{aK_c''}}^\nu \quad \nu_3
$$

was used to reach the region of the first adiabatic ionisation potential from the $\tilde{X}^+ \quad ^1A_1(0^0)$
ground state of CH$_2$O. In Eq. (5.1) $J$, $K_a$ and $K_c$ represent the asymmetric-top rotational quantum numbers and the labels in parentheses correspond to the usual notation for the vibrational levels of a polyatomic molecule [168]. For the ionic states the quantum number $N^+$ of the total
angular momentum excluding spin is used instead of $J$. To generate the UV wave numbers $\tilde{\nu}_1$ ($\approx 30300$ cm$^{-1}$) and $\tilde{\nu}_2$ ($\approx 37500$ cm$^{-1}$) required to drive selected rovibrational transitions in the $\tilde{A} \leftarrow \tilde{X}$ and $3p_x \leftarrow \tilde{A}$ bands, respectively, the outputs of the first two dye lasers were frequency doubled in BBO ($\beta$-bariumborate) crystals. Photoionisation was achieved using a third dye laser of fundamental wave number $\tilde{\nu}_3 \approx 20000$ cm$^{-1}$. The laser beams of wave numbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$ were combined using a dichroic mirror and directed collinearly into the photoionisation chamber through a quartz window and intersected the pulsed supersonic beam of formaldehyde at right angles. To simplify the optical layout, the third laser beam was introduced into the photoionisation chamber through the same quartz window but at a small angle ($\approx 1^\circ$) with respect to the other two laser beams and also intersected the supersonic beam at right angles.

Formaldehyde was produced by heating paraformaldehyde (Fluka, purum, $\geq 95\%$) to 350 K in a reservoir directly connected to, and held at the same temperature as, a pulsed solenoid valve designed and manufactured at the University of Berne [169]. MgSO$_4$ was mixed with the paraformaldehyde to remove water from the formaldehyde vapor [170]. The formaldehyde vapor was entrained in a stream of Kr at a stagnation pressure of 1 bar.

Photoionisation spectra from selected rovibrational levels of the $3p_x$ intermediate state were measured by recording the CH$_2$O$^+$ signal mass-selectively as a function of the fundamental wave number $\tilde{\nu}_3$ of the third dye laser. The CH$_2$O$^+$ ions were extracted by applying a an electric-field pulse of 400 V/cm to the extraction plates 2 $\mu$s after photoexcitation and detected on the ion detector of set-up 2 as described in Section 2.3.

PFI-ZEKE photoelectron spectra were recorded as a function of $\tilde{\nu}_3$ by monitoring the electrons produced by pulsed-field-ionisation of high-$n$ Rydberg states located immediately below the successive ionisation thresholds using a two-pulse sequence as explained in Section 1.4. A 'discrimination' pulse of 1 $\mu$s duration and $+50$ mV/cm was applied 3 $\mu$s after photoexcitation to field ionise the highest Rydberg states and sweep free electrons away from the photoexcitation region. This discrimination pulse was immediately followed by a second 'detection' pulse of $-100$ mV/cm which served the purpose of field ionising Rydberg states with $n \approx 200$ and extracting them towards the electron detector in set-up 2 (see Section 2.3).

### 5.3 Rovibronic photoionisation selection rules and rotational intensity distributions

In the $C_{2v}$(M) molecular symmetry group, the rovibronic photoionisation symmetry selection rules (Eq. (1.19) in Section 1.6) can be expressed in the notation $\Gamma_{\text{rve}}^+ \leftarrow \Gamma_{\text{rve}}$ as

$$A_1 \leftrightarrow A_1; \ A_2 \leftrightarrow A_2; \ B_1 \leftrightarrow B_1; \ B_2 \leftrightarrow B_2;$$

(5.2)

for $\ell$ odd and

$$A_1 \leftrightarrow A_2; \ B_1 \leftrightarrow B_2;$$

(5.3)
for \( \ell \) even. Eqs. (5.2) and (5.3) can in turn be expressed as

\[
\Delta K_a = K_a^+ - K_a = \text{odd/odd} \quad \text{for} \quad \ell = \text{odd/even} \tag{5.4}
\]
\[
\Delta K_c = K_c^+ - K_c = \text{odd/even} \quad \text{for} \quad \ell = \text{odd/even} \tag{5.5}
\]

for all three bands \( (\widetilde{X}^+ 2B_2 (0^0) \leftarrow 3p_x^1 A_2 (0^0) + \widetilde{X}^+ 2B_2 (4^1) [\Gamma_{ve}^+ = A_2] \leftarrow 3p_x^1 A_2 (4^1) [\Gamma_{ve} = B_2] \)

and \( \widetilde{X}^+ 2B_2 (6^1) [\Gamma_{ve}^+ = A_1] \leftarrow 3p_x^1 A_2 (6^1) [\Gamma_{ve} = B_1] \) observed in this study.

The \( 3p_x \) orbital of \( \text{CH}_2\text{O} \) out of which ionisation occurs in the present case is centred on the carbon atom and lies perpendicularly to the plane of the molecule. However, the centre of the molecular orbital does not coincide with the centre of mass. In a single-centre expansion around the centre of mass, this orbital has to be described as a linear combination of atomic-like orbitals of \( s-, p-, d-, f-, \ldots \) angular momentum character. The single nodal plane of the \( 3p_x \) orbital can only be represented by atomic-like orbitals with a projection of the angular momentum onto the \( C_2 \) axis in the \( C_{2v} \) point group of \( \lambda' = \pm 1 \), which we denote by a \( \pi \) subscript. Therefore the single-centre expansion describing the molecular orbital out of which ionisation occurs can be expressed as a linear combination of \( p_\pi, d_\pi, f_\pi, g_\pi, \ldots \) functions. The \( 3j \)-symbol in Eq. (1.25) implies the selection rule \( \Delta K = |\lambda'| \) and is therefore more restrictive than those implied by Eqs. (5.4)-(5.5) and results in dominant \( \Delta K_a = \pm 1 \) transitions for near-prolate symmetric tops.

5.4 Results and discussion

5.4.1 The vibrationless ground state of \( \text{CH}_2\text{O}^+ \)

The PFI-ZEKE photoelectron spectra of the cationic ground state of formaldehyde recorded via selected \( J_{K_a K_c} \) rotational levels of the \( 3p_x (0^0) \) intermediate state are presented in Fig. 5.1. For clarity, the intensity origins of the spectra have been shifted along the vertical axis and the rotational quantum numbers of the selected intermediate levels have been indicated above each trace on the left-hand side. The assignment bar indicates the absolute positions of the ionic rotational levels \( N^+_{K_a^+ K_c^+} \). In some cases, two rotational levels of the cation with the same \( N^+ \) and \( K_a^+ \) values but different \( K_c^+ \) values remain unresolved, in which case both sets of quantum numbers are indicated.

The full widths at half maximum (FWHM) of most lines are \( \approx 0.6 \text{ cm}^{-1} \) and are limited by the electric-field pulse sequence employed to field ionise the high-\( n \) Rydberg states (see Section 5.2) and the bandwidths of the dye lasers used, but not, as initially expected, by the predissociation lifetimes of the rovibronic levels of the \( 3p_x \) state used as the intermediate levels in the multiphoton excitation scheme (see Eq. (5.1)). Indeed, single lines of the \( 3p_x (0^0, 4^1, 6^1) \leftarrow \Lambda (2^1 4^3) \) bands display Lorentzian lineshapes with FWHM of \( 1.5 \text{ cm}^{-1} \), \( \approx 3 \text{ cm}^{-1} \) and \( \approx 11 \text{ cm}^{-1} \), respectively [147]. The multiphoton excitation through the \( 3p_x \) intermediate level thus takes place coherently and the widths of single lines of the PFI-ZEKE photoelectron spectra correspond to the convolution of the Gaussian bandwidths of the dye lasers used in
Figure 5.1: PFI-ZEKE photoelectron spectra of the $X^+ 2B_2 (0^0) \rightarrow 3p_x 1A_2 (0^0)$ transition of CH$_2$O recorded from selected rotational levels of the 3p$_x$ (0$^0$) intermediate state. The horizontal axis represents the total wave number above the $X 1A_1 (0^0) 0^00$ rovibronic ground state of CH$_2$O. The $J_{K_a,K_c}$ rotational states of the 3p$_x$ (1A$_2$) intermediate state are indicated above each trace on the left. The assignment bar labels the rotational states of the cation in $N^+_{K_a,K_c}$ notation.

The different spectra displayed in Fig. 5.1 have been positioned along the wave number axis so that the wave numbers of the lines correspond to their absolute positions above the $X (0^0) 0^00$ rovibronic ground state of CH$_2$O. The relative positions of the energy levels are summarised in the second column of Table 5.1 where the numbers in parentheses indicate the experimental standard deviation of all relative positions that were determined from three or more different spectra. These wave numbers were subsequently used to determine the asymmetric-top rigid-rotor constants $A^+$, $B^+$ and $C^+$ of the cation and the adiabatic ionisation energy $E_i$ in a non-linear least-squares fit. A rigid-rotor Hamiltonian turned out to be sufficient at the pre-
The maximal deviation amounting to \( \Delta \) as listed in Table 5.1. The constants determined from the least-squares fit are summarised in Table 5.2. The numbers in parentheses represent the experimental standard deviation of all relative positions that were determined from three or more different spectra. The uncertainty in the absolute wave numbers is ±1.5 cm\(^{-1}\).

In Fig. 5.2 the PFI-ZEKE photoelectron spectra recorded via the \( \nu_{30} \) rotational levels of the 3p\(_x\) (0\(^0\)) state are compared with simulations (bottom trace in each panel) based on the wave number calibration of the third dye laser \( \nu_3 \), of \( \sigma_2 = 0.2 \) cm\(^{-1}\) from the shift induced by the field ionisation pulse sequence (see Section 5.2). The numbers in parentheses in Table 5.1 represent the uncertainty in the value of the rotational constant \( \Delta \) of the adiabatic ionisation energy includes contributions of \( \sigma_1 = 0.5 \) cm\(^{-1}\) from the wave number calibration of the third dye laser \( \nu_3 \), of \( \sigma_2 = 0.2 \) cm\(^{-1}\) from the shift induced by the field ionisation pulse, of \( \sigma_3 = 0.6 \) cm\(^{-1}\) from the actual fit and of \( \sigma_4 = 1.0 \) cm\(^{-1}\) from the uncertainty in the wave number of the second laser \( \nu_2 \) (see above). The uncertainty in the value of the rotational constants of the cation leads to an inertial defect of \( \Delta_0 = 0.22(27) \) amuÅ\(^2\). The error on \( \Delta_0 \) of ±0.27 amuÅ\(^2\) is thus too large to draw a conclusion on the planarity or non-planarity of the formaldehyde cation [171].

Each spectrum in Fig. 5.1 exhibits a bimodal intensity distribution corresponding to two groups of lines associated with a change in the asymmetric-top projection quantum number \( \Delta K_a = K_a^+ - K_a \) of -1 at lower energies and of +1 at higher energies. No transitions with \( |\Delta K_a| \) even were detected, in agreement with the selection rules derived in Section 1.6 and only a few very weak \( |\Delta K_a| = 3 \) transitions were observed. The maximum observed change in total angular momentum excluding spin amounts to \( \Delta N_{\text{max}} = |N^+ - J| = 3 \). In the realm of the orbital ionisation model, this implies that the single-centre expansion of the 3p\(_x\) orbital converges rapidly and has only significant \( \pi, \sigma, f \) and \( d \) orbital contributions.

In Fig. 5.2 the PFI-ZEKE photoelectron spectra recorded via the \( \nu_{21}, \nu_{32} \) and \( \nu_{30} \) rotational levels of the 3p\(_x\) (0\(^0\)) state are compared with simulations (bottom trace in each panel) based on the wave number calibration of the third dye laser \( \nu_3 \), of \( \sigma_2 = 0.2 \) cm\(^{-1}\) from the shift induced by the field ionisation pulse sequence (see Section 5.2). The numbers in parentheses in Table 5.1 represent the uncertainty in the value of the rotational constant \( \Delta \) of the adiabatic ionisation energy includes contributions of \( \sigma_1 = 0.5 \) cm\(^{-1}\) from the wave number calibration of the third dye laser \( \nu_3 \), of \( \sigma_2 = 0.2 \) cm\(^{-1}\) from the shift induced by the field ionisation pulse, of \( \sigma_3 = 0.6 \) cm\(^{-1}\) from the actual fit and of \( \sigma_4 = 1.0 \) cm\(^{-1}\) from the uncertainty in the wave number of the second laser \( \nu_2 \) (see above). The uncertainty in the value of the rotational constants of the cation leads to an inertial defect of \( \Delta_0 = 0.22(27) \) amuÅ\(^2\). The error on \( \Delta_0 \) of ±0.27 amuÅ\(^2\) is thus too large to draw a conclusion on the planarity or non-planarity of the formaldehyde cation [171].

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5.4. Results and discussion

<table>
<thead>
<tr>
<th>$A^+$/cm$^{-1}$</th>
<th>8.874(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B^+$/cm$^{-1}$</td>
<td>1.342(15)</td>
</tr>
<tr>
<td>$C^+$/cm$^{-1}$</td>
<td>1.148(18)</td>
</tr>
<tr>
<td>$\xi_{4,6}^a$/cm$^{-1}$</td>
<td>8.70(10)</td>
</tr>
<tr>
<td>$\tilde{v}_4$/cm$^{-1}$</td>
<td>823.67(30)</td>
</tr>
<tr>
<td>$\tilde{v}_6$/cm$^{-1}$</td>
<td>1036.50(30)</td>
</tr>
<tr>
<td>$E_i^a$/($hc$/cm$^{-1}$)</td>
<td>87793.33±1.30</td>
</tr>
</tbody>
</table>

Table 5.2: First adiabatic ionisation energy $E_i$, rigid-rotor asymmetric-top rotational constants, Coriolis constant $\xi_{4,6}^a$ and fundamental wave numbers of the out-of-plane bending ($\nu_4$) and in-plane rocking ($\nu_6$) modes derived from the experimental spectra in a least-squares fit. The root-mean-square deviation amounted to 0.05 cm$^{-1}$ in the fit of the rotational constants and ionisation potential and 0.2 cm$^{-1}$ in the determination of the Coriolis parameter as well as the deperturbed vibrational wave numbers.

on Eqs. (1.24) and (1.25) and the constants summarised in Table 5.2. The simulations have been performed using the rotational constants and ionisation energy listed in Table 5.2. The $B_{\ell' K_c}^{(\alpha)}$ parameters in Eq. (1.24) used in the simulations are 2, 1 and 1 for $\ell' = 1, 2$ and 3, respectively. The top traces in panels (a) and (b) represent the corresponding photoionisation spectra. The agreement between simulated and experimental spectra is particularly good within a group of lines corresponding to transitions of the same $\Delta K_a$ value. However, the intensity ratio between $\Delta K_a = -1$ lines and $\Delta K_a = +1$ lines is systematically underestimated in the simulations. Moreover, $\Delta K_a = -3$ lines in panel (c) of Fig. 5.2 are stronger in the experimental spectrum than in the calculated one where they only gain intensity because $K_a$ is not a good quantum number in asymmetric-top molecules. A possible interpretation for these observations could be intensity perturbations induced by interactions between ionisation channels differing by 2 in $K_a$. Rotational states with $K_a = $even (odd) belong to para (ortho) formaldehyde and $\Delta K_a = 1$ channel interactions are forbidden because of the conservation of nuclear spin symmetry in photoionisation. Unfortunately, the photoionisation spectra are very congested in the corresponding spectra and isolated autoionisation resonances that would confirm this interpretation cannot be observed.

5.4.2 The $4^1$ and $6^1$ vibrational states of CH$_2$O$^+$

The PFI-ZEKE photoelectron spectra of the $\bar{X}^+$ ($6^1$) $\rightarrow$ $3p\chi$ ($6^1$) and $\bar{X}^+$ ($4^1$) $\rightarrow$ $3p\chi$ ($4^1$) transitions are displayed in Figs. 5.3 (a) and (b), respectively. The poorer signal-to-noise ratio of the two spectra displayed in panel (a) compared to those displayed in panel (b) reflects the weaker intensity of the corresponding $3p\chi \rightarrow A$ transitions. The spectra displayed in Figs. 5.3 (a) and (b) were recorded via the $2_{2K_c}$ and $3_{2K_c}$ rotational levels (indicated above each trace on the left) of the $3p\chi$ $6^1$ and $3p\chi$ $4^1$ intermediate states, respectively. The $K_c$ substructure of the intermediate $3p\chi$ state could not be resolved experimentally because of the rapid predissociation [147]. The spectra in Fig. 5.3 were positioned along the horizontal axis so that the line positions corre-
Figure 5.2: PFI-ZEKE photoelectron spectra recorded via (a) the $2_{21}$, (b) the $3_{22}$ and (c) the $3_{30}$ rotational levels of the $3\pi, (0^0)$ intermediate state and simulations based on the orbital ionisation model. The top traces in panels (a) and (b) represent the corresponding photoionisation spectrum.

The assignment bars indicate the positions of the rotational states of the cation in the notation $N^{+}_{K_d^+ K_i^+}$. The vibrational assignment of the $3\pi$ and $X^+$ vibrational levels, which contradicts an
5.4. Results and discussion

Figure 5.3: PFI-ZEKE photoelectron spectra of (a) the $\tilde{X}^+ (6^1) \leftarrow 3p_x (6^1)$ and (b) the $\tilde{X}^+ (4^1) \leftarrow 3p_x (4^1)$ transitions. The horizontal axis represents the total wave number above the $\tilde{X}^1 A_1 0_{00}$ rovibronic ground state. The rotational levels $J_{K_aK_c}$ of the $3p_x$ intermediate state are indicated above each trace on the left. The assignment bars give the rotational states of the cation in the notation $N_{K_aK_c}^+$. The earlier assignment of the He I photoelectron spectrum presented in Ref. [164], is justified by:

1. The fact that the intensity of the $3p_x (4^1) \leftarrow \tilde{A} (2^1 4^3)$ band is much stronger than that of the $3p_x (6^1) \leftarrow \tilde{A} (2^1 4^3)$. The vibronically forbidden $3p_x (6^1) [\Gamma_{ev} = B_1] \leftarrow \tilde{A} (2^1 4^3) [\Gamma_{ev}^* = B_2]$
Chapter 5. The rovibrational energy level structure of the formaldehyde cation

\[ N^+_K^a K^c \quad \nu_{\text{obs/cm}^{-1}} a \quad (\nu_{\text{calc}} - \nu_{\text{obs}}) / \text{cm}^{-1} \quad N^+_K^a K^c \quad \nu_{\text{obs/cm}^{-1}} a \quad (\nu_{\text{calc}} - \nu_{\text{obs}}) / \text{cm}^{-1} \]

<table>
<thead>
<tr>
<th>( N^+_K^a K^c )</th>
<th>( \nu_{\text{obs/cm}^{-1}} a )</th>
<th>( (\nu_{\text{calc}} - \nu_{\text{obs}}) / \text{cm}^{-1} )</th>
<th>( N^+_K^a K^c )</th>
<th>( \nu_{\text{obs/cm}^{-1}} a )</th>
<th>( (\nu_{\text{calc}} - \nu_{\text{obs}}) / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_{11}</td>
<td>88625.03</td>
<td>0.24</td>
<td>1_{11}</td>
<td>88838.94</td>
<td>-0.13</td>
</tr>
<tr>
<td>2_{12}</td>
<td>88630.48</td>
<td>-0.43</td>
<td>2_{12}</td>
<td>88843.95</td>
<td>-0.36</td>
</tr>
<tr>
<td>3_{13}</td>
<td>88637.16</td>
<td>0.07</td>
<td>3_{13}</td>
<td>88850.95</td>
<td>-0.18</td>
</tr>
<tr>
<td>3_{12}</td>
<td>88638.17</td>
<td>0.22</td>
<td>3_{12}</td>
<td>88851.77</td>
<td>0.16</td>
</tr>
<tr>
<td>3_{30}</td>
<td>88696.11</td>
<td>-0.06</td>
<td>3_{30}</td>
<td>88915.35</td>
<td>-0.16</td>
</tr>
<tr>
<td>4_{14}</td>
<td>88646.84</td>
<td>0.04</td>
<td>4_{14}</td>
<td>88860.51</td>
<td>-0.17</td>
</tr>
<tr>
<td>4_{13}</td>
<td>88648.53</td>
<td>0.20</td>
<td>4_{13}</td>
<td>88862.05</td>
<td>0.22</td>
</tr>
<tr>
<td>4_{31}</td>
<td>88706.05</td>
<td>-0.03</td>
<td>4_{31}</td>
<td>88925.23</td>
<td>-0.08</td>
</tr>
<tr>
<td>5_{32}</td>
<td>88718.64</td>
<td>-0.16</td>
<td>5_{32}</td>
<td>88937.57</td>
<td>0.05</td>
</tr>
</tbody>
</table>

\( a \) not corrected for the field-induced shift

Table 5.3: Table of the observed and calculated line positions of the \( e_X^+ 2\text{B}_2 (6^1) \) and \( e_X^+ 2\text{B}_2 (4^1) \) vibrational levels above the \( e_X^+ 2\text{A}_1 (0^0) 0_{00} \) rovibronic ground state using the rotational constants summarized in Table 5.2.

See text for details.

2. \textit{Ab initio} predictions of the \( 4^1 \) and \( 6^1 \) fundamental wave numbers of CH\(_2\)O\(^+\) [160] which clearly indicate the latter (841 cm\(^{-1}\)) to be less than the former (1088 cm\(^{-1}\)).

3. The expectation that the \( 4^1 - 4^1 \) and \( 6^1 - 6^1 \) transitions should be dominant. Indeed, because of its "Rydberg"-nature, the \( 3p_x \) electron only weakly interacts with the ion core. Consequently, the fundamental wave numbers and wavefunctions of the cation are expected to be similar to those of the \( 3p_x \) state.

The rovibronic photoionisation selection rules for the \( e_X^+ (6^1) \rightleftharpoons 3p_x (6^1) \) and \( e_X^+ (4^1) \rightleftharpoons 3p_x (4^1) \) transitions can be expressed in the same form as in the case of the \( e_X^+ (0^0) \rightleftharpoons 3p_x (0^0) \) transitions (see Eqs. (5.4) and (5.5)). Moreover, the orbital ionisation model predicts the same selection rules of \( \Delta N = 0, \pm 1, \pm 2, \pm 3 \) and \( \Delta K_a = \pm 1 \) and intensity distribution for all three bands because ionisation occurs out of the same molecular orbital in all three cases. This prediction is confirmed by the experimental results (compare Figs. 5.1-5.3) which do not only reveal the same rotational branch structures but also the same bimodal intensity distributions.

An asymmetric-top rigid-rotor analysis of the rotational structure of the \( 4^1 \) and \( 6^1 \) vibrational levels of CH\(_2\)O\(^+\) leads to very different values of the \( A^+ \) constant (8.55 cm\(^{-1}\) for the \( 6^1 \) level and 9.24 cm\(^{-1}\) for the \( 4^1 \) level) and to large deviations between calculated and measured rotational energies. This observation is indicative of an \( a \)-type Coriolis interaction between the \( 4^1 \) and \( 6^1 \) vibrational states as also observed in the neutral ground state [154, 157, 158] and the \( 3p_x \) Rydberg state [147] of CH\(_2\)O. The strength of the Coriolis coupling and the separation (> 200 cm\(^{-1}\)) between the interacting vibrational levels results in effective \( A^+ \) constants that
differ significantly from each other rather than in a local perturbation of the rotational states around a given $K_a^+$ value [168].

To account for this Coriolis interaction the rigid-rotor Hamiltonian has been extended by a fourth term $V_{\text{cor}}$:

$$
\hat{H}/\hbar = A^+\hat{j}_a^2 + B^+\hat{j}_b^2 + C^+\hat{j}_c^2 + A^+\zeta_{4,6}^a(\hat{Q}_4\hat{P}_6 - \hat{Q}_6\hat{P}_4)\hat{J}_a + \hat{\nu}_i,
$$

where $\zeta_{4,6}^a$ represents the Coriolis coupling constant as defined in Ref. [61] and $\hat{\nu}_i$ the unperturbed value of the fundamental wave number of modes $\nu_i$, which here is either $\nu_4$ or $\nu_6$. The Hamiltonian was expressed in matrix form in a symmetric top $|N,K,M\rangle$ basis with the off-diagonal elements of $V_{\text{cor}}$ taking the form:

$$
|\nu_4^+,1,N^+,K^+,M^+\rangle V_{\text{cor}} |\nu_6^+,1,N^+,K^+,M^+\rangle = \epsilon_{4,6}^a K^+,
$$

where $\epsilon_{4,6}^a$ is the Coriolis coupling parameter used in Ref. [156]. Diagonalisation of this matrix yielded the rovibrational eigenvalues of both coupled vibrational levels. $\epsilon_{4,6}^a$ and the unperturbed fundamental wave numbers $\tilde{\nu}_4$ and $\tilde{\nu}_6$ were determined in a least-squares fit, while keeping the rotational constants $A^+$, $B^+$ and $C^+$ fixed to the rigid-rotor value derived for the $\tilde{X}^+(0^0)$ vibronic ground state of $\text{CH}_2\text{O}^+$ (see Table 5.2). The fitted values are presented in the lower part of Table 5.2 and the third and sixth columns of Table 5.3 list the derivations between calculated and observed values. Overall the agreement between calculated and experimental spectrum is good (the largest deviation amounts to -0.43 cm$^{-1}$ for the $2_{12}$ level for the $6^1$ vibrational state). The Coriolis coupling constant of 8.70 cm$^{-1}$ is similar to those of the ground state (10.414368(140) cm$^{-1}$ [157]) and the $3p_x$ state (8.1 cm$^{-1}$ [147]). It thus appears that the strong Coriolis coupling between the out-of-plane bending ($\nu_4$) and the in-plane-rocking ($\nu_6$) modes is ubiquitous in the spectrum of formaldehyde including its ionised form.

5.5 Conclusions

This investigation of PFI-ZEKE photoelectron spectrum of $\text{CH}_2\text{O}$ has provided new information on the energy level structure and molecular constants of the lowest three vibrational levels of $\text{CH}_2\text{O}^+$. It has also led to the observation of a strong Coriolis interaction between the $4^1$ and $6^1$ vibrational levels and to the derivation of an improved value for the first adiabatic ionisation energy of $\text{CH}_2\text{O}$. The molecular constants of $\text{CH}_2\text{O}^+$ obtained here will be helpful in the analysis of the low Rydberg states of formaldehyde, in particular the $3p_x$ Rydberg state.


Chapter 6

The $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the allene cation

This chapter summarises a study of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect carried out on the allene cation using PFI-ZEKE photoelectron spectroscopy. The PFI-ZEKE photoelectron spectra turned out to be very complex, particularly in the regions corresponding to excitation of the cation beyond 1000 cm$^{-1}$.

To understand the origin of this complexity, a wide range of experiments, including experiments on fully deuterated allene, were performed. To guide the analysis of the photoelectron spectra, the usual Jahn-Teller Hamiltonian was reformulated in the basis of a hindered internal rotation in order to treat the large-amplitude torsional motion over the complete $2\pi$ range, i.e., including the $D_{2h}$ potential energy barrier which was neglected in previous treatments. Although the details of the rotational structure of the $4^2$ and $4^3$ torsional levels remains unassigned, the experimental and theoretical investigations provided a much better understanding of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in allene. The different aspects of this investigation such as the photoionisation dynamics from very high-resolution spectra of the origin and the $4^1$ bands, the calculation of the vibronic structure of $C_3H_4^+$ and $C_3D_4^+$ and the treatment of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the basis of a hindered internal rotor are presented here in a unified manner, but will be written up for publication separately.

6.1 Introduction

Allene has been the object of much investigation for its relevance to astrochemistry [172, 173, 174] and to studies of photodissociation dynamics [175, 176, 177, 178, 179, 180]. Allene is also the smallest member of the cumulene family and one of the simplest representatives of the $D_{2d}(M)$ molecular symmetry group. The $\tilde{X}^+ 2E$ electronic ground state of the cation exhibits the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller (JT) effect [181, 182] encountered only in molecules with one or more $4n$-fold axes of symmetry: A strong distortion along the torsional mode $v_4$ ($b_1$ symmetry) is revealed in the HeI photoelectron spectra by a long progression in that mode.
Chapter 6. The $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the allene cation

[183, 184, 185, 186, 187, 188]. Domcke and co-workers [189, 190] have successfully analysed the vibronic structure of the HeI photoelectron spectra with the aid of Jahn-Teller coupling parameters calculated \textit{ab initio} and a vibronic Jahn-Teller Hamiltonian which will be discussed in Section 6.3. They have determined the C=C=C asymmetric stretching mode $\nu_6$ of $b_2$ symmetry to be the other main JT-active mode.

The present work aimed at resolving the rotational structure in the photoelectron spectrum of allene and allene-$d_4$ and at obtaining previously unobserved details of its vibronic structure at low energies to characterise the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the allene cation in detail. The Jahn-Teller effect in a system of $4n$-fold symmetry, in particular its impact on the vibronic and the rovibronic structures, is the main focus of the present investigation.

6.2 Experimental

Both laser systems described in Subsections 2.2.1 and 2.2.2 have been employed in the study of the rovibronic structure of the photoelectron spectrum of allene. The complementary nature of these laser systems turned out to be essential in this study: The broadly tunable system was employed to obtain an overview of the vibronic structure over a range of nearly 2500 cm$^{-1}$ with partial rotational resolution. The high-resolution laser system allowed for the detailed study of the rotational structure of selected bands of the photoelectron spectrum. Resolving the full rotational structure in the photoelectron spectrum of a molecule of the size and complexity of allene is by no means a trivial task, but a prerequisite for the full understanding of the Jahn-Teller effect in this system.

Allene-$d_4$ was synthesised according to the method of Morse and Leitch [191] by the reaction of hexachloropropene with deuteriumoxide and zinc. The by-product propyne-$d_4$ was removed from the reaction product by Mayers reagent (mercury(II) chloride - potassium iodide solution). The yield of allene-$d_4$ was 50% with a deuterium content of at least 96% and a purity of 94% with 2% propene-$d_6$ and 4% propyne-$d_4$ as the main impurities.

Mixtures of 10% allene (allene-$h_4$: Aldrich, purity 97%) in Ar at a total stagnation pressure of about 2-3 bar were introduced into the chamber through a pulsed nozzle (General Valve) and cooled to a rotational temperature of $\approx 10$ K in a supersonic jet expansion into the high vacuum. The molecular beam was skimmed and subsequently intersected the VUV laser beam at right angles in the photoionisation region (see Section 2.3, Fig. 2.4).

The overview PFI-ZEKE photoelectron spectra were recorded with a simple two-pulse electric field sequence. A 'discrimination' pulse of +105 mV/cm and 1 $\mu$s duration was applied 3 $\mu$s after photoexcitation to remove electrons formed by direct ionisation and was immediately followed by an 'extraction' pulse of -140 mV/cm. To achieve nearly fully rotationally resolved photoelectron spectra the high-resolution laser system (see Section 2.2.2) was used in combination with a multipulse electric field sequence [7, 192] delayed by 1.7 $\mu$s relative to the time of photoexcitation was optimised to field-ionise narrow slices of the pseudo-continuum of high-$n$ Rydberg states below each ionisation threshold. A discrimination pulse of +172 mV/cm was
applied for 1 μs, followed immediately by stepwise increasing extraction pulses, of -86 mV/cm, -129 mV/cm, -172 mV/cm, -215 mV/cm, -259 mV/cm, -302 mV/cm and -345 mV/cm in amplitude, each step being 300 ns long. Electrons field-ionised by each of the extraction pulses were monitored according to their different extraction times and therefore different arrival times on a microchannel plate detector. The best compromise between high resolution and signal-to-noise ratio was achieved by monitoring the electrons extracted by the pulse of -172 mV/cm, resulting in a full width at half maximum (FWHM) of 0.15 cm⁻¹ for lines corresponding to a single transition. A correction of +1.8(2) cm⁻¹ was introduced to account for the shifts of all rovibronic ionisation thresholds induced by the -172 mV/cm step of the electric-field pulse sequence according to the procedure described in Ref. [7].

6.3 The Jahn-Teller Hamiltonian in linear coordinates

Jahn and Teller [181] investigated the dynamics of molecules in degenerate electronic states and found that ‘all non-linear nuclear configurations are (...) unstable for an orbitally degenerate state’ whenever this degeneracy arises because of symmetry. This statement implies that the nuclear framework of any molecule with an n-fold axis of symmetry $C_n$ or $S_n$ with $n \geq 3$ will distort in an orbitally degenerate state such that the point group symmetry is reduced, the degeneracy lifted and the energy lowered. The distortion arises because of a coupling of the nuclear motion to that of the electrons, i.e., a breakdown of the Born-Oppenheimer (BO) approximation [193]. The structural and dynamical consequences of this vibronic interaction are referred to as the Jahn-Teller (JT) effect. Here the JT effect, with special attention to the $E \otimes (b_1 \oplus b_2)$ JT effect in the $X^+ \, 2E$ ground state of the allene cation and its treatment starting from the BO approximation is outlined. A thorough review on the subject of the Jahn-Teller effect (with an emphasis on the $E \otimes e$ JT effect) is presented in Ref. [194]. The presented approach is based on the formalism of Köppel, Domcke and Cederbaum [195].

The Hamiltonian for a molecule neglecting spin, translation and rotation takes the form [63] (in units of cm⁻¹):

$$\hat{H} = \hat{T}_e (r) + \hat{T}_n (q) + \hat{V} (r, q),$$  \hspace{1cm} (6.1)

where $\hat{T}_e$, $\hat{T}_n$ and $\hat{V}$ are the kinetic energy operator for the electrons and nuclei and the potential energy operator, respectively. All electronic coordinates are collectively represented by $r$ and the $3N - 6$ dimensionless normal coordinates collectively by $q$. Assuming the electronic coordinates to be independent of the nuclear momenta and the vibrational coordinates, the eigenfunctions $\Psi(r,q)$ of the Hamiltonian $\hat{H}$ in Eq. (6.1), can be approximated by

$$\Psi(r,q) = \psi(r;q) \chi(q),$$  \hspace{1cm} (6.2)
where \( \chi(q) \) is a function of the normal coordinates only and \( \psi(r; q) \) is the electronic wavefunction at some geometry \( q \). An electronic wavefunction \( \psi(r; q) \) can be found that satisfies

\[
\hat{H}_e(q)\psi(r; q) = \left( \hat{T}_e(r) + \hat{V}(r, q) \right) \psi(r; q) = E(q)\psi(r; q),
\]

for any \( q \) and that varies smoothly with \( q \). At a reference configuration \( q^0 \) the wavefunctions \( \psi_k^0(r; q^0) \) are eigenfunctions of the electronic Hamiltonian \( \hat{H}_e(q) \) with the eigenvalue \( E_{0,k} \). If the reference geometry is at a highly symmetric geometry of the molecule, \( f \)-fold degenerate electronic eigenfunctions \( \psi_k^0(r; q^0) \) of \( \hat{H}_e(q) \) exist

\[
\hat{H}_e(q)\psi_k^0(r; q^0) = \left( \hat{T}_e(r) + \hat{V}(r, q^0) \right) \psi_k^0(r; q^0) = E_{0,k}\psi_k^0(r; q^0),
\]

such that \( E_{0,k} = E_0 \) for all \( f \) values of \( k \).

The potential energy operator can be expanded in a Taylor series around the reference geometry \( q^0 \):

\[
\hat{V}(r, q) = \hat{V}(r, q^0) + \sum_i \left( \frac{\partial V(r, q)}{\partial q_i} \right)_{q^0} q_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 V(r, q)}{\partial q_i \partial q_j} \right)_{q^0} q_i q_j + \ldots,
\]

where \( k_i \) is the linear JT coupling constant of the normal mode \( v_i \), \( g_{ii} = \tilde{v}_i \) the harmonic wave number, and \( g_{ij} (i \neq j) \) the bilinear JT coupling constants. All constants are given in units of \( \text{cm}^{-1} \) when \( V(r, q) \) is given in units of \( \text{cm}^{-1} \) because \( q_i \) is a dimensionless coordinate. With Eqs. (6.1)-(6.5) the Schrödinger equation for an orbitally degenerate electronic state can be expressed as:

\[
\hat{H}\Psi(r, q)/\hbar c = \left( \hat{T}_e(r) + \hat{T}_h(q) + \hat{V}(r, q) \right) \psi_k^0(r; q^0)\chi(q)
\]

\[
= \left( E_0 + \hat{T}_h(q) + \frac{1}{2} \sum_i \tilde{v}_i q_i^2 + \sum_i k_i q_i \right) \psi_k^0(r; q^0)\chi(q),
\]

where \( \hat{H}_h.o. \) represents the usual harmonic oscillator Hamiltonian [61] and \( \hat{H}_{JT} \) the JT Hamiltonian. All bilinear and higher terms in the Taylor expansion in Eq. (6.5) have been neglected following the usual approach [182, 196]. For a more thorough, yet more complicated approach the reader is referred to Ref. [194].

If the direct product of the representations of two electronic states \( \Gamma_k \) and \( \Gamma_l \) with the representation \( \Gamma_{q_i} \) of the normal mode \( v_i \) contains the totally symmetric representation \( \Gamma_{\text{tot. sym.}} \), i.e.,

\[
\Gamma_k \otimes \Gamma_{q_i} \otimes \Gamma_l \supseteq \Gamma_{\text{tot. sym.}},
\]

(6.7)
6.3. The Jahn-Teller Hamiltonian in linear coordinates

![Figure 6.1](image)

Figure 6.1: Schematic representation of (a) the torsion and (b) the asymmetric C=C=C stretch in allene. The motion of the atoms is indicated by the dashed arrows. Definition of the internal coordinates used are indicated.

the JT Hamiltonian $\tilde{H}_{JT}$ in Eq. (6.6) may have non-zero off-diagonal elements between the two wavefunctions $\psi_0^k(r; q^0)$ and $\psi_0^l(r; q^0)$. The normal modes that fulfill the symmetry condition in Eq. (6.7) are called JT active modes and cause a vibronic interaction that is referred to as the Jahn-Teller effect if $\psi_0^k(r; q^0)$ and $\psi_0^l(r; q^0)$ are degenerate by symmetry (the vibronic coupling is called a pseudo-JT effect if the electronic states are not degenerate, but lie close enough in energy).

The potential energy hypersurface of the allene cation

Ground state neutral allene has a $D_{2d}$ equilibrium geometry and the allene cation possesses a doubly degenerate $^2E$ ground state at the $D_{2d}$ equilibrium geometry of the neutral. The vibrational modes that can couple the two $E$ components of the electronic state in first order can be determined using Eq. (6.7) to be

$$E \otimes E = a_1 \oplus [a_2] \oplus b_1 \oplus b_2,$$

rendering all non-degenerate vibrational degrees of freedom of allene Jahn-Teller active. The totally symmetric modes cannot distort the molecule as to lower its symmetry. There are no vibrational modes of $a_2$ symmetry, so that the resulting JT effect is denoted $E \otimes (b_1 \oplus b_2)$, the capital $E$ representing the electronic symmetry label and the lower case letters $b_1$ and $b_2$ the symmetry labels of the JT active modes. The allene cation in its $D_{2d}$ structure has three modes of $b_2$ symmetry and one of $b_1$ symmetry. The torsional mode $v_4$ of $b_1$ symmetry and the $C=C=C$ asymmetric stretching mode $v_6$ of $b_2$ symmetry were identified as causing the greatest stabilisation of the molecular cation by *ab initio* calculations [190]. These two vibrational modes are depicted schematically in Figs. 6.1 (a) and (b), respectively, where the internal coordinates are also indicated. Quadratic and bilinear JT coupling parameters have not been determined to date, and we will limit the discussion here to the linear $E \otimes (b_1 \oplus b_2)$ JT effect in allene. Restricting the treatment to only the two strongly JT-active modes ($v_4$ and $v_6$), the Hamiltonian matrix $H$ for the electronic part of the $E \otimes (b_1 \oplus b_2)$ JT problem expressed in the
Chapter 6. The $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the allene cation

\[
\begin{array}{ccc}
\tilde{v}_{i,H} & k_{i,H} & V_{\text{min},i} \\
v_4 & 0.093 \text{ eV (750 cm}^{-1}) & 0.309 \text{ eV (2492 cm}^{-1}) & -0.513 \text{ eV (-1410 cm}^{-1}) \\
v_6 & 0.237 \text{ eV (1912 cm}^{-1}) & 0.280 \text{ eV (2258 cm}^{-1}) & -0.165 \text{ eV (-1334 cm}^{-1})
\end{array}
\]

Table 6.1: Table of the coupling constants, vibrational harmonic wave numbers and JT stabilisation energies from Ref. [190] for $C_3H_4^+$.

The diabatic basis of the two components of the electronic $^2E$ state from Eq. (6.6) is:

\[
H = E_0 I + \sum_{i=1}^{15} \begin{pmatrix}
\tilde{T}_i + \frac{1}{2} \tilde{v}_i q_i^2 & 0 \\
0 & \tilde{T}_i + \frac{1}{2} \tilde{v}_i q_i^2 \\
\end{pmatrix}
+ \begin{pmatrix}
k_{6q_6} & k_{4q_4} \\
k_{4q_4} & k_{6q_6} \\
\end{pmatrix}
\]

\[
H_{\text{JT}}
\]

where $I$ is the $2 \otimes 2$ unit matrix. Diagonalisation of Eq. (6.9) yields the adiabatic potential energy hypersurfaces $V_\pm$

\[
V_\pm = E_0 + \frac{1}{2} \sum_{i} \tilde{v}_i q_i^2 \pm \sqrt{k_{4q_4}^2 + k_{6q_6}^2},
\]

(6.10)

which are represented schematically in Fig. 6.2. In Fig. 6.2 only the cut through the potential energy hypersurface along the plane spanned by $q_4$ and $q_6$ is displayed. The potential energy hypersurface in all other 13 dimensions is assumed to be represented adequately by harmonic oscillators. At the point of $D_{2d}$ symmetry the two potential energy surfaces $V_+$ and $V_-$ touch and form a conical intersection. The minima $V_{\text{min},i}$ along $q_6$ ($q_{i \neq 6} = 0$) and $q_4$ ($q_{i \neq 4} = 0$) of the lower adiabatic potential energy sheet are easily determined from Eq. (6.10) to lie below the conical intersection at $E_0$. Using the coupling constants and harmonic wave numbers determined from values initially estimated by ab initio calculations and subsequently fitted to an experimental HeI spectrum [190] (tabulated in Table 6.1) two minima along $q_4$ located 4140 cm$^{-1}$ below the $D_{2d}$ conical intersection are obtained from Eq. (6.11). At the minimum geometry the torsional angle is reduced to $\tau = 46.6^\circ$, and both C=C bond lengths are equal. The two minima along $q_6$ have $C_{2v}$ symmetry and are located 1334 cm$^{-1}$ below the conical intersection. The four CH bonds $r_{\text{CH}}$ are of equal length and the two C-H-C angles $\alpha$ are equal (the internal coordinates of allene are defined in Fig. 6.1). This two-dimensional potential energy surface of the allene cation is depicted in Fig. 6.2. Unlike in the $E \otimes e$ Jahn-Teller effect, typical for molecules with an odd-fold symmetry axis, for which an isoenergetic circular path around the conical intersection results from linear JT coupling [196, 197, 182], the minimum energy path around the conical intersection in the $E \otimes (b_1 \oplus b_2)$ has two minima and two
6.3. The Jahn-Teller Hamiltonian in linear coordinates

The Jahn-Teller Hamiltonian in linear coordinates

\[ E_0 = \nu_i q_i^2 \pm k_i q_i, \quad i = 4, 6 \]  

and two shifted but uncoupled diabatic electronic potential energy surfaces are obtained. The eigenfunctions \( \psi_{1(2)} \) are simply

\[ \psi_{1(2)} = \psi_{k(i)}^0. \]

No vibronic perturbations can be induced by the JT effect associated with this potential energy surface and the only consequence of this one dimensional \( E \otimes b \) Jahn-Teller effect is that the observed harmonic wave number may be altered from that of the symmetric undistorted system.

Figure 6.2: Cut through the potential energy hypersurface of \( \text{C}_3\text{H}_4^+ \) along the torsion \( q_4 \) and the asymmetric \( \text{C} \equiv \text{C} \equiv \text{C} \) stretching mode \( q_6 \). The two minima correspond to a \( D_2 \) geometry in agreement with previous work, that found a torsional angle of 46.6° and 133.4° and \( r_{\text{CC}} = r_{\text{CC}}^0 \) \[190\]. At the saddle points located at a torsional angle of 90° and \( r_{\text{CC}} \neq r_{\text{CC}}^0 \), \( \text{C}_3\text{H}_4^+ \) is of \( C_{2v} \) symmetry. Below the cut through the potential energy hypersurface a contour diagram thereof is displayed.
The vibronic energy level structure

In order to obtain the vibronic energy level structure of the JT system, the matrix in Eq. (6.9) is constructed from the electronic wavefunctions $\psi_k^0(r,q^0)$ and all harmonic oscillator wavefunctions for each vibrational mode $i$ in a direct product basis. Eq. (6.2) is re-written as

$$\psi_k^0(r,q^0) \prod_i \chi_i(q_i) = |\Lambda\rangle |\nu_1, \ldots, \nu_i, \nu_j, \ldots, \nu_{3N-6}\rangle,$$

(6.14)

where $\Lambda$ is the quantum number of the projection of the orbital angular momentum onto the figure axis of the system. $\Lambda$ takes the values +1 and -1 for the two components $\psi_k^0$ and $\psi_l^0$ of a doubly degenerate electronic state. $|\nu_i\rangle$ is the harmonic oscillator vibrational wavefunction of the normal mode $\nu_i$ with vibrational quantum number $\nu_i$. Expressed in units of cm$^{-1}$, the harmonic oscillator Hamiltonian $\hat{H}_{h.o,i}$ yields the usual non-zero matrix elements [199, 61, 196]:

$$\langle \nu_i, \Lambda | \hat{H}_{h.o,i} | \nu_i', \Lambda' \rangle = \tilde{\nu}_i (\nu_i + \frac{1}{2}) \delta_{\nu_i, \nu_i'} \delta_{\Lambda, \Lambda'}.$$

(6.15)
The non-zero matrix elements of the JT-Hamiltonian $\hat{H}_{JT}$ from Eq. (6.9) are [196, 200]

$$\langle v_4, v_6, \Lambda = \pm 1 | \pm k_6 q_6 | v_4, v_6 - 1, \Lambda = \pm 1 \rangle = \pm k_6 \sqrt{v_6 + 1}$$ (6.16)

$$\langle v_6, v_4, \Lambda = \pm 1 | + k_4 q_4 | v_6, v_4 - 1, \Lambda = \mp 1 \rangle = + k_4 \sqrt{v_4 + 1}$$ (6.17)

$$\langle v_4, v_6, \Lambda = \pm 1 | \pm k_6 q_6 | v_4, v_6 + 1, \Lambda = \pm 1 \rangle = \pm k_6 \sqrt{v_6}$$ (6.18)

$$\langle v_6, v_4, \Lambda = \pm 1 | + k_4 q_4 | v_6, v_4 + 1, \Lambda = \mp 1 \rangle = + k_4 \sqrt{v_4},$$ (6.19)

Ideally, the matrix should be set up in the basis $| v_4, v_6, \Lambda \rangle$ up to $v_4 = v_6 = \infty$ and diagonalised to obtain the exact adiabatic eigenvalues and eigenvectors. However, in numerical calculations, the harmonic oscillator basis is truncated at a chosen maximal value of $v_4$ and $v_6$. The number $N_i$ ($i = 4, 6$) of harmonic oscillator functions needed in each mode depends on the coupling strength along that JT active mode, and is chosen such that the energy of the members of the vibronic states that are of interest have converged within the accuracy of the experiment [196].

In Fig. 6.3 a correlation diagram is displayed. The vibrational harmonic wave numbers $\tilde{\nu}_4$ and $\tilde{\nu}_6$ at $q^0$ were held at the *ab initio* values determined in Ref. [190] and summarised in Table 6.1 and the values for $k_4$ and $k_6 = k_4$ were increased from 0 to 5000 cm$^{-1}$. As $k_4$ and $k_6$ increase in magnitude, the vibronic structure changes from the harmonic limit at $k_4 = k_6 = 0$ through a very anharmonic structure to another harmonic limit with very different apparent harmonic wave numbers at large values for $k_4$ and $k_6$, which corresponds to deep (compared to the harmonic wave number) minima at the $D_2$ geometry. Each line in the correlation diagram in Fig. 6.3 corresponds to a doubly degenerate level $v_i$ with eigenvectors $\psi_{\pm}^i$

$$\psi_+^i = \sum_{v_4 + v_6 = \text{even}} c_{v_4, v_6}^i | v_4, v_6 \rangle | \Lambda = +1 \rangle + \sum_{v_4 + v_6 = \text{odd}} c_{v_4, v_6}^i | v_4, v_6 \rangle | \Lambda = -1 \rangle$$ (6.20)

$$\psi_-^i = \sum_{v_4 + v_6 = \text{odd}} c_{v_4, v_6}^i | v_4, v_6 \rangle | \Lambda = +1 \rangle + \sum_{v_4 + v_6 = \text{even}} c_{v_4, v_6}^i | v_4, v_6 \rangle | \Lambda = -1 \rangle,$$ (6.21)

where $c_{k,i}^j$ are expansion coefficients. These eigenvectors are perfectly degenerate and tunnelling between the two minima of $D_2$ symmetry is suppressed by symmetry. The vibronic symmetry (in $D_{2d}$) is

$$\Gamma_{ve} = \Gamma_v \otimes E = E$$ (6.22)

for every singly-degenerate normal mode in the $\tilde{X}^+ 2E$ electronic state. Every vibronic energy level of a singly-degenerate normal mode thus remains degenerate and cannot split into two tunnelling components. Vibrationally degenerate modes are not JT active and therefore have, neglecting pseudo-JT coupling to the $\tilde{B}^2B_2$ state, no double minimum potential energy surface and thus no tunnelling dynamics associated with them. The $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect thus leads to a pronounced anharmonic vibrational structure but does not lead to any tunnelling splitting. In this respect it differs from the $E \otimes e$ JT problems [197, 182, 196, 201].
Chapter 6. The \( E \otimes (b_1 \oplus b_2) \) Jahn-Teller effect in the allene cation

Table 6.2: Table of transition wave numbers observed in the PFI-ZEKE photoelectron spectra of \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{D}_6 \) displayed in Fig. 6.4 (e) and (f). The vibronic assignment has been taken from Ref. [202].

<table>
<thead>
<tr>
<th>( \nu_i^v )</th>
<th>( (\nu_i^v + E_i) / \text{cm}^{-1} )</th>
<th>( \nu_i^v )</th>
<th>( (\nu_i^v + E_i) / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0^i</td>
<td>78601.5</td>
<td>0^i</td>
<td>78760.0</td>
</tr>
<tr>
<td>21^1</td>
<td>78701.0</td>
<td>21^1</td>
<td>78830.1</td>
</tr>
<tr>
<td>20^1/21^1</td>
<td>78816.8</td>
<td>20^1 + 21^1</td>
<td>78932.2</td>
</tr>
<tr>
<td>20^1 + 21^1</td>
<td>79015.6</td>
<td>14^1</td>
<td>79083.9</td>
</tr>
<tr>
<td>21^3</td>
<td>79312.2</td>
<td>21^3</td>
<td>79361.1</td>
</tr>
<tr>
<td>79475.2</td>
<td>79486.7</td>
<td>79451.0</td>
<td></td>
</tr>
<tr>
<td>79506.3</td>
<td>79732.2</td>
<td>79504.5</td>
<td></td>
</tr>
<tr>
<td>80031.7</td>
<td>80062.3</td>
<td>79671.4</td>
<td></td>
</tr>
<tr>
<td>80127.1</td>
<td></td>
<td>79701.0</td>
<td></td>
</tr>
</tbody>
</table>

6.4 The vibronic structure of \( \text{C}_3\text{H}_6^+ \) and \( \text{C}_3\text{D}_6^+ \)

The overview PFI-ZEKE photoelectron spectra of the \( \tilde{X}^+ \rightarrow \tilde{X} \rightarrow \tilde{A} \) photoionising transition of (a) allene and (c) allene-\( \text{d}_4 \) are displayed in Fig. 6.4. Both spectra exhibit a progression of regularly spaced bands of increasing intensity separated by \( \approx 745 \ \text{cm}^{-1} \) and \( \approx 533 \ \text{cm}^{-1} \), respectively. These progressions are interpreted as vibrational progressions in the torsional mode [187]. Each band of the progression is assigned to a torsional level of the cation in the usual notation \( 4^v \) [168]. Gray vertical bars mark transitions that originate from impurities of propene and propene-\( \text{d}_6 \) in the samples of allene and allene-\( \text{d}_4 \), respectively. These impurity lines were identified in separate measurements of the PFI-ZEKE photoelectron spectra of propene and propene-\( \text{d}_6 \) which are displayed in Figs. 6.4 (e) and (f), respectively. Although these impurity lines have been observed in previous HeI studies [187, 188], they have never been identified as such. The positions of the band centres extracted from the PFI-ZEKE photoelectron spectra of \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{D}_6 \) are summarised in Table 6.2 and their assignments correspond to those reported in Ref. [202].

The vibrational progression in the PFI-ZEKE photoelectron spectra is a clear indication of the cation being distorted along the torsional mode \( \nu_4 \) relative to the neutral ground state. Fig. 6.1 (a) depicts the torsional motion schematically and defines the inertial axis system of neutral allene as well as the torsional coordinate \( \tau \). Although Woywod and Domcke [190] determined the \( \text{C} = \text{C} = \text{C} \) asymmetric stretch \( \nu_6 \) of \( b_2 \) symmetry as a second strongly JT active mode, the spectrum does not reveal another vibrational progression that could be attributed to this mode. The absence of transitions to vibronic levels of the asymmetric \( \text{C} = \text{C} = \text{C} \) stretch result
6.4. The vibronic structure of $\text{C}_3\text{H}_4^+$ and $\text{C}_3\text{D}_4^+$

Figure 6.4: PFI-ZEKE photoelectron spectra of (a) $\text{C}_3\text{H}_4$, (c) $\text{C}_3\text{D}_4$, (e) $\text{C}_3\text{H}_6$ and (f) $\text{C}_3\text{D}_6$. The progressions observed in (a) and (c) are assigned to the torsional mode $\nu_4$ and labelled in the notation $4^i\nu_4$ [168]. Vibronic bands originating from $\text{C}_3\text{H}_6$ and $\text{C}_3\text{D}_6$ are highlighted by gray bars. Panels (b) and (d) show the calculations of the vibronic structure based on Eq. (6.9) and the linear JT coupling parameters and wave numbers reported in Ref. [190].

from the fact that only the $6^1$ band is expected to be observable in the energy region above the adiabatic ionisation threshold studied here ($\tilde{\nu}_6 \simeq 1911$ cm$^{-1}$ [190], see below). Moreover, because the distortion along $\nu_6$ is less than along $\nu_4$ [190], the intensity of the transition to the $6^1$ level of the cation is not expected to be as strong as the transition to the fundamental of the torsion. This qualitative argument is confirmed by a more rigorous treatment of the JT effect (see Section 6.3 and Refs. [189, 190]). As explained in Section 6.3, diagonalisation of the JT Hamiltonian in the complete basis of the JT active modes indeed yields two perfectly degenerate eigenfunctions for each vibronic level and a regular vibronic spacing at the values for $\tilde{\nu}_4$, $\tilde{\nu}_6$, $k_4$ and $k_6$ determined in Ref. [190].
The Franck-Condon factors can be estimated by considering the minimum energy structures of the neutral and cationic states and approximating the vibrational wavefunctions by harmonic oscillator wavefunctions in these local minima. By virtue of symmetry, there is no interaction nor tunnelling between the two minima of $D_2$ geometry through the point of the reference geometry at $D_{2h}$ symmetry ($\tau = 90^\circ$) and this remains valid even for vibrational levels located close to the conical intersection (cf. Subsection 6.3). In $D_2$ symmetry, the torsional mode transforms as the totally symmetric representation $a_1$. The representation of the torsion is therefore totally symmetric for both odd and even quanta of excitation and a smooth intensity distribution is expected.

In panels (b) and (d) of Fig. 6.4, the vibronic positions and intensity distributions calculated on the basis of the Jahn-Teller Hamiltonian of Eq. (6.9) are displayed as stick spectra and a Gaussian convolution with an instrumental function of FWHM=20 cm$^{-1}$. The linear JT coupling constants $k_i^H$ and vibrational frequencies $\tilde{\nu}_{i,H}$ of $C_3H_4^+$ were taken from Ref. [190] and are summarised in Table 6.1. The linear JT coupling parameter $k_i^D$ and the harmonic wave number $\nu_{i,H}$ for the torsion and asymmetric C=C=C stretch for $C_3D_4^+$ can be determined from those of $C_3H_4^+$ by appropriate mass scaling. Assuming the structure of the cation at the conical intersection to be that of the neutral, one obtains from the vibronic wave numbers $\tilde{\nu}_{i,H}^{\text{neutral}}$ for $C_3H_4^+$ ($C_3D_4$) and $\tilde{\nu}_{i,H(D)}^{\text{neutral}}$ for $C_3H_4^+$ ($C_3D_4^+$):

$$\frac{\tilde{\nu}_{i,D}}{\tilde{\nu}_{i,H}} = \frac{\tilde{\nu}_{i,D}^{\text{neutral}}}{\tilde{\nu}_{i,H}^{\text{neutral}}} \implies \tilde{\nu}_{i,D} = \tilde{\nu}_{i,D}^{\text{neutral}} \cdot \tilde{\nu}_{i,H}.$$

In first approximation, the stabilisation energy of the JT problem does not depend on the deuteration of the system as it is a purely electronic property of the system. Neglecting zero-point energy corrections, the following relationship between the linear JT coupling constants of the per- and undeuterated species can be obtained from Eq. (6.11):

$$-\frac{(k_i^D)^2}{2\tilde{\nu}_{i,D}} = -\frac{(k_i^H)^2}{2\tilde{\nu}_{i,H}} \implies k_i^D = k_i^H \cdot \sqrt{\frac{\tilde{\nu}_{i,D}}{\tilde{\nu}_{i,H}}}.$$ 

The linear JT coupling constants and the harmonic wave numbers for $C_3D_4^+$ are summarised in Table 6.3. In the calculations, Eq. (6.6) was expanded in the harmonic basis of $\nu_4$ and $\nu_6$, truncating the basis set at values of $\nu_4 \leq 34$ and $\nu_6 \leq 34$, so that the lowest eigenvalues obtained had converged as described in Section 6.3. No attempt to fit the JT parameters or harmonic wave numbers was attempted because of the small numbers of vibronic bands observed in the spectra.

The intensities $I_{vi}$ of the transitions to the final states $v_i$ from the $\tilde{X}^+ 1A_1 (0^0)$ initial vibronic state were estimated as the squares of the coefficients of the wavefunction $|v_6 = 0, v_4 = 0, \Lambda\rangle$, $c^i_{0,0}$ in Eqs. (6.20) and (6.21),

$$I_{vi} \propto |c^i_{0,0}|^2.$$
reflecting vibronic overlap integral between the neutral vibronic ground state wavefunction with the harmonic oscillator ground state wavefunction of the cation at the geometry of the neutral, i.e., $D_{2d}$. The excellent agreement of the vibronic structure of the low-resolution PFI-ZEKE photoelectron spectrum of allene (see Fig. 6.4) and the vibronic structure calculated using the JT coupling parameters reported in Ref. [190] suggests that these parameters are adequate to describe the JT effect in allene at low resolution. The comparison also indicates that the lowest vibrational levels of the allene cation can be described adequately by assuming that the cation has a $D_2$ equilibrium structure and is not subject to tunnelling between equivalent minima. The high-resolution PFI-ZEKE photoelectron spectra presented in the next sections, however, provide a more complete picture of the structure and dynamics of the allene cation.

**6.5 The rotational structure of the $0^0$ and $4^1$ bands**

The PFI-ZEKE photoelectron spectra of the lowest two members of the torsional progression ($\tilde{X}^+ +^1 E(0^0, 4^1) \leftarrow \tilde{X}^+ +^1 A_1^1$) were recorded at high resolution with the laser system described in Subsection 2.2.2. The spectra of the origin ($0^0$) and the torsional fundamental ($4^1$) bands are shown in Figs. 6.5 and 6.6, respectively. They show sharp rotational lines with full widths at half maximum (FWHM) of less than 0.15 cm$^{-1}$ for single transitions in the case of the $0^0$ band and 0.2 cm$^{-1}$ in the case of the $4^1$ band. The simulations of these spectra based on the photoionisation rules and orbital ionisation model discussed in Sections 1.6 and 1.7 are displayed for comparison below the experimental spectra.

Both bands exhibit a similar rotational structure with three strong peaks and weaker but sharp structures between them. As expected for prolate (near-prolate) symmetric-top molecules, the intensity distribution of the spectrum reveals a grouping of lines having the same $\Delta K$ ($\Delta K_a$) values leading to characteristic $K'' \rightarrow K^+$ ($K'_a \rightarrow K^+_a$) branches for all possible values of $\Delta N = N^+ - N''$. The three strong peaks correspond to $\Delta N = 0$, $Q$-type branches. The assignment bars are only given for the origin band in Fig. 6.5, because the rotational structure and assignment of the $4^1$ band are analogous. The assignment bars group transitions according to the same change in total angular momentum excluding spin $\Delta N = N^+ - N''$. The associated change in $K$ ($K_a$) is indicated above each assignment bar in the notation $K'' \rightarrow K^+ (K_a'' \rightarrow K_a^+)$. Individual
transitions are labelled according to the total angular momentum quantum number excluding spin $N''$ of the neutral ground state.

The selection rules derived from Eq. (1.19) in the $D_2(M)$ molecular symmetry group can be expressed in the notation $\Gamma_{rve}^+ \leftrightarrow \Gamma_{rve}''$ as:

$$A_1 \leftrightarrow A_1; \ B_1 \leftrightarrow B_1; \ B_2 \leftrightarrow B_2; \ B_3 \leftrightarrow B_3,$$

(6.26)

which translates into $\Delta K_a = K_a^+ - K_a'' =$odd, $\Delta K_c = K_c^+ - K_c'' =$odd for transitions from the vibronic ground state of allene to the $0^0 (\Gamma_{rve}^+ = B_2) \ (in \ D_2)$ and $4^1 (\Gamma_{rve}^+ = B_2) \ (in \ D_2)$ vibronic levels of the cation. The rovibronic symmetry selection rules do not depend on the parity of the outgoing electron because the $D_2(M)$ symmetry group does not contain any operations involving the inversion $E^*$, and the dipole moment representation is totally symmetric ($A_1$).

If the molecular cation is treated as being a prolate symmetric-top molecule of $D_{2d}$ sym-
6.5. The rotational structure of the $0^0$ and $4^1$ bands

Figure 6.6: Upper panel: PFI-ZEKE photoelectron spectrum of the $\tilde{X}^+ \, ^2E (4^1) \rightarrow \tilde{X} \, ^1A_1 (0^0)$ transition of allene. Lower panel: Simulation using a Gaussian instrument function with a FWHM of 0.2 cm$^{-1}$.

metry the rovibronic selection rules (Eq. (1.19)) can be expressed as

$$A_1 \leftrightarrow B_1; \quad A_2 \leftrightarrow B_2; \quad E \leftrightarrow E \quad (6.27)$$

for $\ell =$even, and

$$A_1 \leftrightarrow A_1; \quad A_2 \leftrightarrow A_2; \quad E \leftrightarrow E \quad (6.28)$$

for $\ell =$odd, which translates into $\Delta K = K^+ - K^0 =$odd for both even and odd photoelectron partial waves for the transitions $\tilde{X}^+ \, ^2E (0^0, \Gamma_{ve}^+ = E) \rightarrow \tilde{X} \, ^1A_1 (0^0)$ and $\tilde{X}^+ \, ^2E (4^1, \Gamma_{ve}^+ = E) \rightarrow \tilde{X} \, ^1A_1 (0^0)$. The selection rules in Eqs. (6.27)-(6.28) are of course compatible with those derived in Eq. (6.26) and differ only by the additional specification of the change in $K_c$. The fact that the selection rules derived in the $D_{2d}(M)$ molecular symmetry group are also insensitive to the parity of the partial wave of the outgoing electron results from the fact that the vibronic levels are doubly degenerate ($\Gamma_{ve} = \text{E}$).

In the $\tilde{X}^+ \rightarrow \tilde{X}$ photoionising transition of allene, the photoelectron is ejected from a molecular orbital of the qualitative shape shown in Fig. 6.7, which has only one nodal plane that contains the principal axis ($a$-axis) along the C=C=C bond and the centre of mass. Thus, the single-centre expansion describing such a molecular orbital can only have contributions of atomic-like
orbitals that conserve this nodal plane, i.e., atomic-like orbitals that have a quantum number \( \lambda'' = \pm 1 \) for the projection of the angular momentum of the molecular orbital onto the principal axis (\( z_m = a \)-axis, see Fig. 6.5), which is denoted with the subscript \( \pi \). For the simulations presented here, only contributions to the single-centre expansion of \( p_\pi \) and \( d_\pi \) angular momentum character have been taken into account with equal weights.

The adiabatic ionisation energy, the fundamental torsional wave number and rotational constants for both vibronic states of the cation were determined in a least-squares fitting procedure assuming an asymmetric-top rigid rotor Hamiltonian [168] because the analysis of the vibronic structure presented in the previous Section 6.4 clearly revealed the distortion of the cation along the torsional coordinate. Not surprisingly this analysis led to \( B^+ \) and \( C^+ \) rotational constants for the cationic states that are equal within the statistical uncertainties. Simulation of the spectra using a symmetric-top rigid rotor Hamiltonian yielded a similarly good agreement with experiment. The adiabatic ionization energy of \( \text{C}_3\text{H}_4 \), the fundamental torsional wave number and the rotational constants of \( \text{C}_3\text{H}_4^+ \) derived in a least-squares fitting procedure are summarized in Table 6.4 which also contains molecular constants for \( \text{C}_3\text{D}_4^+ \) determined from the low-resolution spectrum displayed in Fig. 6.4 (c). The experimental and calculated transition frequencies of the origin band of the PFI-ZEKE photoelectron spectrum of allene are compared in Table A.1. In this form, Table A.1 helps to assess the resolution that would be needed to resolve the \( K_c \) structure of specific lines. The assignments in Table A.1 can easily be converted into symmetric-top assignments by omitting the \( K_c^+ \) label because torsionally distorted allene is a near-prolate top and the \( K_d^+ \) quantum number is the good quantum number (\( K^+ \)) in the limit of a symmetric top. The agreement between observed and calculated line positions is excellent, all a deviations of less than 0.25 cm\(^{-1}\) (rms deviation of 0.07 cm\(^{-1}\)). Neutral allene is obviously a symmetric top of \( D_{2d} \) symmetry. However, when a transition between molecular states of different symmetries is considered, the selection rules in Eq. (1.19) are more conveniently derived in the largest symmetry subgroup common to both the initial and final state of the transition under investiga-

**Figure 6.7:** Schematic diagram of the highest occupied molecular orbital of neutral allene out of which ionisation occurs in the \( \bar{X}^+ \text{E} \leftrightarrow \bar{X} \text{A}_1 \) transition. The image was generated using the Molden package [207] with the input from a Hartree-Fock calculation using the MOLPRO package [208]. The different shadings of the lobes indicate opposite phases of the orbital.
6.6. The rotational structure of the $4^2$ and $4^3$ bands

The simulation captures the main features of the experimental spectrum and reproduces the relative intensities of the transitions almost quantitatively. A rotational temperature of 10 K was assumed in the simulations and only ground-state levels with $N'' \leq 8$, $K''_a \leq 2$ contribute significantly to the spectrum. At this low rotational temperatures, the centrifugal and higher-order rotational terms in the rotational Hamiltonian can be neglected at our experimental resolution.

A careful comparison of the spectra of the origin and the $4^1$ bands reveals that the lines of $(E_{\text{neutral}} - E_{\text{neutral}})/\text{cm}^{-1}$, $A/\text{cm}^{-1}$, $B/\text{cm}^{-1}$, $C/\text{cm}^{-1}$

<table>
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<tr>
<th>Compound</th>
<th>$(E - E_{\text{neutral}})/\text{cm}^{-1}$</th>
<th>$A/\text{cm}^{-1}$</th>
<th>$B/\text{cm}^{-1}$</th>
<th>$C/\text{cm}^{-1}$</th>
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<td>C$_3$H$_4$ neutral $^a$</td>
<td>0.0(0)</td>
<td>4.811655(11)</td>
<td>0.29627487(11)</td>
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<tr>
<td>C$_3$D$_4$ neutral $^b$</td>
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<td>2.4153(4)</td>
<td>0.23213(3)</td>
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<tr>
<td>C$_3$H$_4^+$ 0$^0$</td>
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<td>4.696(18)</td>
<td>0.298(5)</td>
<td>0.287(5)</td>
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<tr>
<td>C$_3$H$_4^+$ 4$^1$</td>
<td>78888.6(7)$^c$</td>
<td>4.65(2)</td>
<td>0.296(5)</td>
<td>0.296(5)</td>
</tr>
<tr>
<td>C$_3$D$_4^+$ 0$^0$</td>
<td>78248(2)$^c$</td>
<td>2.32(5)</td>
<td>0.23$^d$</td>
<td>0.23$^d$</td>
</tr>
</tbody>
</table>

$a$ Values taken from Ref. [209]

$b$ Values taken from Ref. [210]

$c$ Corrected for the field-induced shift.

d The $B^+$ and $C^+$ rotational constants of the cation were assumed to be equal to those of the neutral molecule when fitting the $A^+$ constant of C$_3$D$_4^+$.

Table 6.4: Ionization energies and rotational constants obtained from the PFI-ZEKE photoelectron spectrum of allene in a least-squares fit and used for the simulations of the rotational structure of the X$^+$ +E $(0^0, 4^1) \rightarrow X$ bands of C$_3$H$_4^+$. Values in parentheses represent one standard deviation.

The latter spectrum are slightly broader (FWHM=0.2 cm$^{-1}$) than those of the former (FWHM=0.17 cm$^{-1}$). The fact that the rotational lines appear broader in the $4^1$ band than in the $0^0$ band may be an indication of a small tunnelling splitting of the order of 0.1 cm$^{-1}$. This observation will be discussed in Sections 6.7 and 6.8.

6.6 The rotational structure of the $4^2$ and $4^3$ bands

Fig. 6.8 compares the PFI-ZEKE photoelectron spectra of the $0^0$, $4^1$, $4^2$ and $4^3$ bands of C$_3$H$_4$ recorded with both laser systems described in Subsections 2.2.1 and 2.2.2. As discussed in Section 6.5, the rotational structures of the $0^0$ and $4^1$ bands are qualitatively very similar and are dominated by the three strong $Q$-type branches. The rotational structures of the $4^2$ and $4^3$ bands, however, do not exhibit this clear rotational structure and appear strongly perturbed.

$Q$-type branches are approximately separated by $2A^+$ for a (near-)prolate top. The intervals between the strongest lines that could be interpreted as $Q$-type branches in the spectra of the $4^2$ and $4^3$ bands vary between 1 cm$^{-1}$ and 12 cm$^{-1}$, which may indicate heterogeneous rovibronic perturbations along the $a$-axis of the system, such as for example a perturbation resulting from an $a$-type Coriolis interaction.

In the rotational structure of the $4^2$ band, the central three '$Q$-type branch' features appear doubled with a separation of $\simeq 1$ cm$^{-1}$. By comparison to the assignment of the rotational
structure analysed for the $0^0$ and $4^1$ bands, the strong double peak at 79600 cm$^{-1}$ would then correspond to $Q$-type transitions of $K_a^+ = 0 \leftrightarrow K_a^+ = 1$ character. An $a$-type Coriolis interaction cannot shift levels of rotational quantum number $K_a = 0$, so that two distinct vibrational states separated by 1 cm$^{-1}$ may lie in this energy region. The outermost $Q$-type branch features at 79590 cm$^{-1}$ and 79630 cm$^{-1}$ are not doubled. Combined with the previous observation, this observation may indicate that two bands with a similar rotational structure overlap such that the lowest and highest energy $Q$-type transitions of each of these two bands are not overlapped by the rotational structure of the respective other band. These two bands would then have to be separated by $\approx 10 \pm 1$ cm$^{-1}$. Unfortunately, simulations performed with two overlapping non-interacting bands could not reproduce the spectra qualitatively, perhaps because of an additional $a$-type Coriolis interaction (see below). It can be concluded, though, that at least two
bands energetically not separated by more that 10 cm\(^{-1}\) but probably by \(\approx 1\) cm\(^{-1}\) contribute to the intensity distribution in this region of the spectrum.

In addition to the perturbation in the rotational structure of \(4^2\) and \(4^3\) bands of the PFI-ZEKE photoelectron spectra of \(C_3H_4\), seven less intense bands labelled I-VII are observed in their vicinity as illustrated in more detail in Figs. 6.9 (a) and (b). Surprisingly, no bands of low intensity near the strong bands belonging to the progression in the torsional mode are observed in the PFI-ZEKE photoelectron spectra of allene-\(d_4\). The stick spectrum obtained from the vibronic calculations performed on the basis of Eq. (6.9) (see Section 6.3) is also shown in Fig. 6.9 and only reveal two bands in each of the spectral regions. The linear JT effect as described in Eq. (6.9) can thus not be the reason for the large number of weak bands observed. Table 6.6 summarises the vibrational states that could contribute to the PFI-ZEKE photoelectron spectrum in the energy region 1100 cm\(^{-1}\) to 2000 cm\(^{-1}\) above the origin based on the harmonic wave numbers of neutral allene. Of the nine bands the \(11^4\) and \(3^1 + 4^1\), are unlikely, because neither the \(11^2\) nor the \(3^1\) bands are observed in the spectra, although they both are totally symmetric and allowed by symmetry. A weak transition to the fundamental of the JT
Table 6.5: Band centres of the seven bands observed in the vicinity of the $4^2$ and $4^3$ bands labelled as in Fig. 6.9.

<table>
<thead>
<tr>
<th>Band</th>
<th>$(E_{i,\text{obs}} - E_0)$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1358(5)</td>
</tr>
<tr>
<td>II</td>
<td>1391(7)</td>
</tr>
<tr>
<td>III</td>
<td>1420(15)</td>
</tr>
<tr>
<td>IV</td>
<td>1543(5)</td>
</tr>
<tr>
<td>V</td>
<td>2096(10)</td>
</tr>
<tr>
<td>VI</td>
<td>2122(10)</td>
</tr>
<tr>
<td>VII</td>
<td>2205(15)</td>
</tr>
</tbody>
</table>

Table 6.6: Summary of vibrational states $v_i$ possibly observed in the vicinity of the $4^2$ vibrational band. The wave numbers $\tilde{v}_{i,H}^{\text{neutral}}$ have been calculated using the harmonic wave numbers of neutral C$_3$H$_4$. The vibrational symmetry of each band is given in the third column.

<table>
<thead>
<tr>
<th>$\tilde{v}_{i,H}^{\text{neutral}}$/cm$^{-1}$</th>
<th>$v_i$</th>
<th>$\Gamma_{v_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1188.8$^a$</td>
<td>$11^1 + 10^1$</td>
<td>$a_1 + a_2 + b_1 + b_2$</td>
</tr>
<tr>
<td>1351.7$^a$</td>
<td>$11^1 + 9^1$</td>
<td>$a_1 + a_2 + b_1 + b_2$</td>
</tr>
<tr>
<td>1395.0$^c$</td>
<td>$7^1$</td>
<td>$b_2$</td>
</tr>
<tr>
<td>1393.4$^a$</td>
<td>$11^4$</td>
<td>$2(a_1 + a_2 + b_1 + b_2)$</td>
</tr>
<tr>
<td>1443.3$^a$</td>
<td>$2^1$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>1683.1$^a$</td>
<td>$10^2$</td>
<td>$a_1 + a_2 + b_1 + b_2$</td>
</tr>
<tr>
<td>1697.4$^a$</td>
<td>$4^2$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>1920.2$^b$</td>
<td>$6^1$</td>
<td>$b_2$</td>
</tr>
<tr>
<td>1920.8$^c$</td>
<td>$3^1 + 4^1$</td>
<td>$b_1$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [211] and references therein  $^b$ Ref. [205]  $^c$ Ref. [210] and references therein

active mode $v_6$ is expected from the vibronic calculations (see Section 6.3) in the vicinity of band IV, 1543 cm$^{-1}$ above the origin.

All bands in the vicinity of the $4^2$ band in Fig. 6.9 (a) reveal sharp rotational features, whereas sharp rotational structures are hardly present in the vicinity of the $4^3$ band (see Fig. 6.9 (b)). The sharp features in bands I, II, III and IV can be interpreted as clusters of $Q$-type transitions as observed in the rotational structure of the origin band ($0^0$) and first fundamental torsional band ($4^1$). Band I has a rotational structure with two strong lines spaced by $\approx 9.2$ cm$^{-1}$, reminiscent of the $\Delta K_a$ rotational structure of the $0^0$ and $4^1$ bands (see Figs. 6.5 and 6.6). However, the high-energy part of band I appears perturbed with a third $Q$-type branch weakly discernible or possibly split into several components. Bands II and III (see inset of Fig. 6.9 (a)) also show some rotational structure, with the two sharp peaks of band II being separated by $\approx 7.6$ cm$^{-1}$, and those of band III by $\approx 11.3$ cm$^{-1}$. A possible explanation of these spacings between the $Q$-type branches in the rotational structure of bands II and III could be an $a$-type Coriolis coupling which would reduce the spacing in the lower and increase it in the upper band [168].
6.6. The rotational structure of the \(4^2\) and \(4^3\) bands

An \(a\)-type Coriolis coupling is mediated by the operator \(\hat{J}_a\) of \(A_2\) symmetry (in \(D_{2d}\)), which implies the selection rules (in the notation \(\Gamma_i^+ \leftrightarrow \Gamma_j^+\))

\[
a_1 \leftrightarrow a_2 \quad \text{and} \quad b_1 \leftrightarrow b_2 \quad \text{and} \quad e \leftrightarrow e
\]

(6.29)

for two interacting levels \(i\) and \(j\). Fundamental modes of \(e\) symmetry do not carry any intensity and are unlikely to be observed. There are no fundamental vibrations of \(a_2\) symmetry and the only vibration of \(b_1\) symmetry is the torsion, which in this energy region appears only as the first overtone (\(4^2\)) and is thus of \(a_1\) symmetry. An \(a\)-type Coriolis interaction could therefore only involve an overtone of a doubly degenerate (\(e\)) mode, which contains all non-degenerate irreducible representations:

\[
e \otimes e = a_1 \oplus a_2 \oplus b_1 \oplus b_2.
\]

(6.30)

Consequently, at least one of the components of the overtones of a doubly degenerate mode with an even number of quanta possesses the right vibronic symmetry to interact with any non-degenerate vibrational level in an \(a\)-type Coriolis interaction. A component of the overtone may even interact with another component of the same overtone. At present the \(11^1 + 10^1\), \(11^1 + 9^1\) and \(10^2\) levels seem the most likely candidates to explain the weak features I-IV. (Ro)-vibrational interactions with the \(4^2\) torsional band provides the likely mechanism by which these features gain intensity. Unfortunately, the information contained in the PFI-ZEKE photoelectron spectra is not sufficient for a definitive interpretation to be proposed, but it is clear that a global treatment of the complete region must involve a polyad of many vibronic states.

The rotational structure of the \(4^3\) band is even more complex and perturbed than that of the \(4^2\) band and no regular spacing between \(Q\)-type branch features can be discerned. The density of states is already high \(2000 \text{ cm}^{-1}\) above the origin with more than 18 vibrational levels located in the vicinity (\(\pm 150 \text{ cm}^{-1}\)) of the strong \(4^3\) band. A polyad of many interacting bands is the likely origin of the complicated rotational structure and of the observation of the bands V-VII in Fig. 6.9 (b). No attempt to model the details of this highly complex spectral region has been attempted, nor is an assignment of the bands V-VII in Fig. 6.9 (b) possible because too little information is provided by the photoelectron spectra. Information from \textit{ab initio} quantum chemical calculations would be desirable to advance the current understanding of this spectral region.

Vibronic calculations which solely include the JT active modes \(v_4\) and \(v_6\), though adequate to describe the positions and intensities of the strong bands \(4^2\) and \(4^3\), clearly fail to account for the details of the (ro-)vibronic structure and do not provide an explanation for the perturbed rotational structure and the weak satellite bands. Most current theoretical treatments of the vibronic structure of molecules undergoing the JT effect concentrate on a very limited number of strongly JT active modes [197, 182]. The present results point out an urgent need to extend the theoretical treatment to include a more complete subset of interactions such as Fermi interactions, Coriolis interactions and interactions resulting from the bilinear coupling terms of the JT Hamiltonian which are often ignored. To determine bilinear JT coupling constants, for
instance, the *ab initio* calculations performed by Woywod and Domcke [190] would have to be extended to include all non-degenerate modes and the full 15-dimensional hypersurface would have to be calculated, which is no easy task and beyond the scope of the present work. The emphasis of this thesis on the rotational structure of photoelectron spectra, however, justifies an extension of the current models to treat rotational, torsional and electronic degrees of freedom in a unified manner. The next section describes initial steps in this direction, which may prove useful in understanding the details of the rotational structure of excited torsional levels of the allene cation.

6.7 The vibronic Jahn-Teller Hamiltonian in the basis of a hindered internal rotor

The potential energy surface

All Jahn-Teller systems, except the special case of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect, can be described as a coupling of the electronic angular momentum to the vibrational angular momenta [196, 194]. In allene, the two JT active vibrational modes are non-degenerate and therefore do not have an inherent vibrational angular momentum associated with them. The torsion, however, when regarded as an internal rotation, evidently possesses some angular momentum. When describing the torsional motion as a linear harmonic vibrational motion only small amplitude displacements along $q_4$ are considered, which, in the allene cation, is adequate for low excitations in $\nu_4$ for which the potential is deep and nearly harmonic, but fails at higher energies when large amplitude motion becomes important.

In this section, an alternative approach to treat the $E \otimes (b_1 \oplus b_2)$ JT effect in allene is outlined: The torsion can also be understood as a hindered internal rotation of the two CH$_2$ entities. The potential energy operator along $\nu_4$ can, in this case, be expressed as a Fourier series [212]:

\[ \hat{V}(r, q_4 = \tau) = \hat{V}(r, q_4^0) + V_1 \cos(\tau) + V_2 \cos(2\tau) + \ldots + V_n \cos(n\tau) \]  

(6.31)

where $V_n$ represent expansion coefficients, $n$ an integer number, and $\tau$ the angle between the two CH$_2$ entities as defined in Fig. 6.1. For small values of $\tau$, Eq. (6.31) reduces to a harmonic oscillator:

\[ \hat{V}(r, q_4 = \tau) = \hat{V}(r, q_4^0 = 90^\circ) + V_1 (- (\tau - 90^\circ) + \ldots) + V_2 (-1 + 2(\tau - 90^\circ)^2 + \ldots) + \ldots \]  

(6.32)

In this case, the Hamiltonian matrix can then be set up in analogy to the Hamiltonian in the harmonic basis in Eq. (6.9), with the linear terms of the expansion in $\nu_4$ representing the off-
Saddle points at $E_0 - V_1 + 2V_2 (D_{2h})$

Conical intersections at $E_0 (D_{2d})$

Minima at $E_0 - V_2 (D_2)$

Figure 6.10: Potential energy surface along $q_4$ and $q_6$ obtained by diagonalising Eq. (6.33). The surface along $q_6$ is a displaced harmonic oscillator as in Fig. 6.2. Along $q_4$, the potential exhibits four minima at $D_2$ geometry with a conical intersection at a geometry of $D_{2d}$ symmetry at $\tau = 90^\circ$ and $270^\circ$. At $\tau = 0^\circ$ and $180^\circ$ the two CH$_2$ entities are coplanar and the cation is of $D_{2h}$ geometry at these saddle points.

In Eq. (6.33), $V_2$ has been added to $E_0$ so that the conical intersection is at $E_0$ rather than $E_0 - V_2$. The Hamiltonian in Eqs. (6.33) can easily be diagonalised, yielding the JT-coupled potential energy hypersurface, of which the cut along the plane spanned by $q_4 = \tau$ and $q_6$ is displayed in Fig. 6.10. The potential energy surface along $q_4$ and $q_6$ exhibits the same general features as that obtained by diagonalising $\hat{H}_{JT}$ in the harmonic oscillator basis which has two minima below the conical intersection at a $D_2$ geometry and a saddle point along the asymmetric stretch normal coordinate (see Fig. 6.2). However, there is now a second type of saddle point at $\tau = 180^\circ$ and $\tau = 0^\circ$, the $D_{2h}$ geometry, where the two CH$_2$ entities are coplanar as in ethene. In the ethene cation, this saddle point can be rationalised as a pseudo-JT effect, because of a coupling between a higher-lying electronic state and the $\tilde{X}^+$ state mediated by the torsion [58]. In constructing the potential energy surface displayed in Fig. 6.10, $V_1$ was set to twice the value.
Chapter 6. The $E \otimes (b_1 \pm b_2)$ Jahn-Teller effect in the allene cation

The rotation-torsion-vibronic energy level structure in the basis of a hindered internal rotor

Watson and co-workers have worked extensively on the $V - N$ transition in ethene [213, 214]. Ethene is planar (of $D_{2h}$ geometry) in the $N$ state and of $D_{2d}$ symmetry in the $V$ state. In order to describe this transition sufficiently well, the full $2\pi$ space spanned by the torsional angle had to be considered. The following approach has been adapted from that presented in Refs. [213, 214] to include the JT interaction of allene at the $D_{2d}$ geometry.

Fig. 6.11 depicts allene in a Newman-projection with the $z_m$- and $Z_s$-axes pointing out of the page. The H atoms are labelled 1, 2, 3 and 4 and the molecule-fixed ($x_m$, $y_m$, $z_m$) and the space-fixed ($X_s$, $Y_s$, $Z_s$) axis systems are also indicated. The Euler angle $\chi$ is defined as in Ref. [61] and is adequate to describe a rotational motion for which the $Z_s$- and $z_m$-axes remain co-linear; $\chi$ then represents the angle between the molecule-fixed $x_m$-axis and the space-fixed $X_s$-axis. The torsional angle $\tau$ is the dihedral angle between the H$_1$CH$_2$ and H$_3$CH$_4$ planes. A cut through the potential energy hypersurface along $q_4 = \tau$ is depicted in Fig. 6.12 (b) with the
6.7. The vibronic Jahn-Teller Hamiltonian in the basis of a hindered internal rotor

Newman projection shown at $\tau = 0^\circ, 90^\circ, 180^\circ, 270^\circ$ and $360^\circ$.

Alternatively, one can define the two CH$_2$ entities as rotating independently of each other about the $z_m$-axis, with two sets of rotational coordinates ($\phi$, $\theta$, $\chi_1$) and ($\phi$, $\theta$, $\chi_2$). ($\phi$, $\theta$) are the polar coordinates of the C=C=C bond direction. The rotation-torsion wavefunction $\psi_{rt}$ is thus

$$\psi_{rt} = \frac{1}{2\pi} S_{Jm}(\phi, \theta) \exp(ik_1\chi_1) \exp(ik_2\chi_2),$$  \hspace{1cm} (6.34)$$

where $S_{Jm}(\phi, \theta)$ describes the rotation of the $z_m$ axis in the space-fixed frame. Because the $2\pi$ periodicity of the rotational functions $k_1$ ($k_2$) are integer quantum numbers associated with the projection of the angular momentum of the internal rotation of the H$_3$CH$_2$ (H$_3$CH$_4$) entity onto the quantisation axis. It is convenient to use the coordinates $\chi$ and $\gamma$ to separate the internal rotation from the overall rotation:

$$\gamma = \frac{1}{2}(\chi_1 - \chi_2) \mod 2\pi$$  \hspace{1cm} (6.35)$$

and

$$\chi = \frac{1}{2}(\chi_1 + \chi_2) \mod 2\pi,$$  \hspace{1cm} (6.36)$$

so that $\psi_{rt}$ becomes

$$\psi_{rt} = \frac{1}{2\pi} S_{Jm}(\phi, \theta) \exp(ik_1\gamma) \exp(ik_2\chi),$$  \hspace{1cm} (6.37)$$

where $k_\gamma$ is the quantum number of the torsional motion and $k_a$ the projection of the rotational angular momentum onto the $z_m$-axis. By comparison of Eq. (6.34) with Eqs. (6.35)-(6.37), $k_\gamma$ and $k_a$ can be expressed as

$$k_a = k_1 + k_2, \ k_\gamma = k_1 - k_2.$$  \hspace{1cm} (6.38)$$

From Eq. (6.38) it is obvious that the restriction

$$|k_a - k_\gamma| = \text{even}$$  \hspace{1cm} (6.39)$$

applies. Because the inertial tensor of allene has off-diagonal elements in the treatment of the internal hindered rotation when the dihedral angle $\tau$ is used [212], the half-dihedral angle $\gamma = \frac{1}{2}\tau$ is used here, so that a diagonal inertial tensor is obtained. $\gamma$ is the angle between the plane of each CH$_2$ entity and the $x_mz_m$-plane, so that $(x_m, y_m, z_m)$ remains the principal inertial axes for all values of $\gamma$. As can be seen by comparing Figs. 6.12 (a) and (b) upon defining the torsional normal mode as $\gamma$, changing $\gamma$ to $\gamma + \pi$ corresponds to a rotation of the molecule about the $Z_s$ axis by $\pi$. This appears to result in a double-valuedness of the wavefunction. However, when considering both the rotational and the torsional motion, the restriction on the value of $k_\gamma$ in dependence of the value of $k_a$ in Eq. (6.39) removes the double-valuedness. Eq. (6.33) can be
The E⊗(b₁ ⊕ b₂) Jahn-Teller effect in the allene cation

**Figure 6.12:** Schematic representation of the cut through the potential energy hypersurface along the torsional mode defined as (a) the half-torsional angle \( \gamma \) and (b) the torsional angle \( \tau \).

re-written in terms of \( \gamma \) as

\[
\hat{H} = E_0 \mathbf{1} + \hat{T}_\gamma + V_2 (1 + \cos(4\gamma)) \mathbf{1} + \left( \frac{\hat{T}_n(q) + \frac{1}{2} \sum_i \vec{v}_i q_i^2}{\hat{H}_\text{tors}} \right) \mathbf{1} + \begin{pmatrix} k_6 q_6 & V_1 \cos(2\gamma) \\ V_1 \cos(2\gamma) & -k_6 q_6 \end{pmatrix} \left( \frac{\hat{J}_\gamma^2}{\hat{H}_\text{JT}} \right).
\]

In Eq. (6.40), which is similar in structure to Eq. (6.9), \( \hat{T}_\gamma \) is the kinetic energy operator (expressed in units of cm\(^{-1}\)) of the hindered internal rotation:

\[
\hat{T}_\gamma = -A \frac{\partial^2}{\partial \gamma^2} = \frac{\hat{J}_\gamma^2}{\hbar^2},
\]

where \( A \) (in units of cm\(^{-1}\)) is the rotational constant of the molecule about the \( a \)-axis.

The treatment can easily be extended to include the overall rotation of the molecule as was first demonstrated in Ref. [213] for ethene. The rotational Hamiltonian \( \hat{H}_\text{rot} \) is then

\[
\hat{H}_\text{rot} = \frac{1}{2} (B_x(\gamma) + B_y(\gamma)) (\hat{J}_x^2 + \hat{J}_y^2) + \frac{1}{2} (B_x(\gamma) - B_y(\gamma)) (\hat{J}_x^2 - \hat{J}_y^2) + A \hat{J}_z^2
\]

\[
= \frac{1}{2} (B_x(\gamma) + B_y(\gamma)) (\hat{J}_x^2 + \hat{J}_y^2) + \frac{1}{4} (B_x(\gamma) - B_y(\gamma)) (\hat{J}_+^2 + \hat{J}_-^2) + A \hat{J}_z^2,
\]

where the rotational constants \( B_x(\gamma) \) and \( B_y(\gamma) \) are functions of the torsion angle \( \gamma \). From the inertial tensor they are determined as [213]:

\[
\frac{1}{2} (B_x(\gamma) + B_y(\gamma)) = B \left( 1 - \frac{B^2}{4A^2} \cos^2(2\gamma) \right)^{-1}
\]

\[
\frac{1}{4} (B_x(\gamma) - B_y(\gamma)) = \frac{B^2}{4A} \cos(2\gamma) \left( 1 - \frac{B^2}{4A^2} \cos^2(2\gamma) \right)^{-1},
\]

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where $B$ is the rotational constant along $x_m$ and $y_m$ of the molecule in its $D_2d$ geometry. The rotation-torsion-vibronic energy level structure can be constructed in a product Ansatz as

$$
\Psi_{rtve} = \frac{1}{2\pi} S_{k_a m}(\theta, \phi) \exp(i k_a \chi) \exp(i k_\gamma \gamma) \Phi_{\text{rot}}(k_a, m; k_\gamma; v_6; \pm 1) \Phi_{\text{vib}}(q_1, q_2, \ldots, q_{3N-7}) \Phi_{\text{elec}}(\Lambda)
$$

$$
= |J, k_a, m; k_\gamma; v_i = 1, \ldots, 3N-7; \pm 1\rangle. \tag{6.44}
$$

The rotation-torsion-vibronic energy level structure

The rotation-torsion-vibronic Hamiltonian $H_{rtve} = \tilde{H} + \tilde{H}_{rot}$ can be set up in the infinite basis of harmonic oscillator wavefunctions for $v_6$, rotational wavefunctions and torsional wavefunctions. The non-zero matrix elements are listed below:

$$
\langle J, k_a, m; k_\gamma; v_6; \pm 1| \tilde{H}_{\text{h.o.}} |J, k_a, m; k_\gamma; v_6; \pm 1\rangle = \tilde{v}_6(v_6 + \frac{1}{2}) \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| \pm k_6 q_6 |J, k_a, m; k_\gamma; v_6 + 1; \pm 1\rangle = \pm k_6 \sqrt{v_6} \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| \pm k_6 q_6 |J, k_a, m; k_\gamma; v_6 - 1; \pm 1\rangle = \pm k_6 \sqrt{v_6 + 1} \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| V_2 \cos(4\gamma) |J, k_a, m; k_\gamma \pm 4; v_6; \pm 1\rangle = V_2/2 \tag{6.45} \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| V_1 \cos(2\gamma) |J, k_a, m; k_\gamma \pm 2; v_6; \pm 1\rangle = V_1/2 \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| -A \partial^2 / \partial \chi^2 |J, k_a, m; k_\gamma; v_6; \pm 1\rangle = Ak_a^2 \\
\langle J, k_a, m; k_\gamma; v_6; \pm 1| -A \partial^2 / \partial \gamma^2 |J, k_a, m; k_\gamma; v_6; \pm 1\rangle = Ak_\gamma^2
$$

The matrix elements associated with the perpendicular rotational constants in allene can be obtained from Eqs. (6.42) and (6.43) as

$$
B(J, k_a, m; k_\gamma; v_6; \pm 1| J, k_a, m; k_\gamma \pm n; v_6; \pm 1\rangle = \frac{1}{2\pi} B(J + 1 - k_a^2) \cdot \int_{-\pi}^{\pi} \exp(-i k_\gamma \gamma) \frac{1}{1 - \frac{B^2}{4A} \cos^2(2\gamma)} \exp(i(k_\gamma \pm n)\gamma) d\gamma
$$

$$
= \frac{1}{2\pi} B(J + 1) \cdot \int_{-\pi}^{\pi} \frac{\exp(\pm i n \gamma)}{1 - \frac{B^2}{4A} \cos^2(2\gamma)} d\gamma, \tag{6.46}
$$
Chapter 6. The $E \otimes (b_1 \pm b_2)$ Jahn-Teller effect in the allene cation

\[ C = \frac{B}{2\pi} \]

Table 6.7: Table of the integrals needed to evaluate the matrix elements of Eqs. (6.46) and (6.47).

<table>
<thead>
<tr>
<th>$n$</th>
<th>( \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\exp(\pm im\gamma)}{(1-C^2\cos^2(2\gamma))} d\gamma )</th>
<th>( \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\cos(2\gamma)\exp(\pm in\gamma)}{(1-C^2\cos^2(2\gamma))} d\gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \sqrt{(1-C^2)} )</td>
<td>0</td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>( 0 )</td>
<td>(-A(1 - \frac{1}{\sqrt{1-C^2}}))</td>
</tr>
<tr>
<td>$\pm 4$</td>
<td>( \frac{B-C}{C} \cdot \frac{(1-C^2)}{\sqrt{1-C^2}} \cdot \frac{(2-C^2-2\sqrt{1-C^2})}{\sqrt{1-C^2}} )</td>
<td>( -\frac{A}{C^2} \cdot \frac{(4 - \frac{4}{\sqrt{1-C^2}} - C^2 + \frac{3C^2}{\sqrt{1-C^2}})}{C^2} )</td>
</tr>
<tr>
<td>$\pm 6$</td>
<td>( 0 )</td>
<td>0</td>
</tr>
<tr>
<td>$\pm 8$</td>
<td>( \frac{B-C}{C} \cdot \frac{(8-C^4-8\sqrt{1-C^2}+4C^2(-2+\sqrt{1-C^2}))}{\sqrt{1-C^2}} )</td>
<td>0</td>
</tr>
<tr>
<td>$\pm 10$</td>
<td>( 0 )</td>
<td>(-\frac{A}{C^4} \left[ 16 - \frac{16}{\sqrt{1-C^2}} + C^4\left( 1 - \frac{5}{1-C^2} \right) + 4C^2\left( -3 + \frac{5}{1-C^2} \right) \right] )</td>
</tr>
</tbody>
</table>

and

\[
\frac{B^2}{4\lambda} \langle J,k_a \pm 2, m; k_\gamma; \nu_6; \pm 1 | \cos(2\gamma)(\hat{J}_+^2 + \hat{J}_-^2) | J,k_a, m; k_\gamma \pm n; \nu_6; \pm 1 \rangle = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\cos(2\gamma)}{1 - \frac{B^2}{4\lambda} \cos^2(2\gamma)} \exp(i(k_\gamma \pm n)\gamma) d\gamma \]

\[ (6.47) \]

The restriction placed on the values of $k_\gamma$ and $k_a$ in Eq. (6.39) dictates that $n$ has to be an even integer. The integrals in Eqs. (6.46) and (6.47) are non-zero for even $n$ but converge rapidly to zero with increasing values of $n$ and it is sufficient to only retain the first three non-zero matrix elements given in Table 6.7.

Setting $J = 0$, the vibronic structure can be calculated by diagonalising the Hamiltonian in Eq. (6.40). Fig. 6.13 shows a correlation diagram. On the left, the structure of a free internal rotor is obtained by setting $V_1 = V_2 = 0$, $k_b = 0$ and $\nu_6 = 1911$ cm$^{-1}$ corresponding to the value of the harmonic wave number reported in Ref. [190]. Upon increasing $V_2$ but keeping $V_1 = k_b = 0$ and $\nu_6 = 1911$ cm$^{-1}$ fixed, equivalent to increasing only the height of the $D_{2h}$ internal rotation barrier, the vibronic structure converges onto that of a torsional harmonic oscillator at the border between panels (a) and (b). Each torsion-vibronic energy level is doubly degenerate and of vibronic symmetry $\Gamma_{\nu_\text{e}} = \Gamma$. In Fig. 6.13 (b), $V_2$ is kept fixed at $V_2 = 4500$ cm$^{-1}$ and $V_1$ is increased. At large values of $V_1$, the degeneracy of the torsion-vibronic levels is lifted (see below). In Fig. 6.13 (c), the first-order JT coupling constant $k_b$ of the asymmetric C=C=C stretching mode is increased from 0 to 3000 cm$^{-1}$. To calculate the correlation diagram presented in Fig. 6.13, basis functions with $-40 \leq k_\gamma \leq 40$ and $\nu_6 \leq 20$ were used, which resulted
6.7. The vibronic Jahn-Teller Hamiltonian in the basis of a hindered internal rotor

![Figure 6.13](image)

**Figure 6.13:** Correlation diagram characterising key aspects of the global treatment of the JT effect in the basis of a hindered internal rotor. (a) Correlation from a free internal rotation of the CH₂ entities \((V_2 = 0)\) to that to a completely hindered internal rotation equivalent to a close-to-harmonic torsional vibration for high barriers \((V_2 = 4500 \text{ cm}^{-1})\). (b) Evolution of the energy level structure as a function of the parameter \(V_1\), which is analogous to a one-dimensional linear JT coupling in the torsional mode, from \(V_1 = 0\) to large values of \(V_1\) \((V_1 = 9000 \text{ cm}^{-1})\). The degeneracy is lifted at high values of \(V_1\). As the linear JT coupling constant \(V_1\) increases, the hindered internal rotation barrier is lowered (see Fig. 6.10). (c) Evolution of the energy level structure with increasing linear Jahn-Teller coupling constant \(k_6\). In (a), (b) and (c) \(\tilde{\nu}_6\) was held constant at 1911 \text{ cm}^{-1}.

In matrices of dimensions 1722 x 1722. For the particular values of \(V_1, V_2\) and \(k_6\) chosen here to construct the correlation diagram in Fig. 6.13, a tunnelling splitting of the states corresponding to \(4^2\) and \(4^3\) in the PFI-ZEKE photoelectron spectra (see labels at the right of Fig 6.13 (a)) is observed at the interface of Fig. 6.13 (b) and (c). The splitting of these states can be rationalised as arising from tunnelling through the \(D_{2h}\) barrier. The molecular symmetry group \(G_{16}\) \([61]\) there becomes the relevant symmetry group. In the \(G_{16}\) group, the vibronic label \(E\) splits into an \(E^+\) and an \(E^-\) component. This interpretation of the splitting as arising from the tunnelling through the \(D_{2h}\) barrier will be confirmed by the discrete-variable representation calculations presented in the next section.

As discussed in Section 6.6, the rotational fine structure of the \(4^2\) and \(4^3\) vibrational bands in the PFI-ZEKE photoelectron spectra reveals two vibronic bands split by \(\simeq 1-10 \text{ cm}^{-1}\) in the formed and more in the latter which could be attributed to a tunnelling splitting. Moreover, the broadening of the rotational lines of the \(4^1\) band compared to those of the \(0^0\) band also suggests a small tunnelling splitting. It is therefore encouraging that the JT formalism developed in this section enables the prediction of spectral features that the traditional JT formalism fails to predict. Clearly the magnitudes of the tunnelling splitting depend on the details of the potential
energy hypersurface (see Section 6.8).

The matrix elements in Eqs. (6.46) and (6.47) can be interpreted as $a$-type and $b/c$-type Coriolis interactions [212], and may be important in understanding the perturbed rotational structures observed in the high-resolution PFI-ZEKE photoelectron spectra of the first ($4^2$) and second ($4^3$) overtones of the torsional mode discussed in Section 6.6.

### 6.8 The ab initio and DVR calculations

$Ab\ initio$ calculations have been performed to get more information on the potential energy surface along the $v_4$ and $v_6$ normal modes. All calculations presented in this section have been performed using the Molpro $ab\ initio$ quantum chemistry programme package [208].

In Fig. 6.14 the results of $ab\ initio$ calculations are displayed as gray-shaded circles. The calculations have been performed at the MRCI/6-311G** level of approximation [113]. The geometry was optimised at the $D_{2d}$ point in a coupled-perturbed multi-configuration self-consistent field (CPMCSCF) state-averaged calculation of the two degenerate $E$ components of the HOMO using the 6-311G** basis. Each point shown in Fig. 6.14 was calculated by only decreasing $\tau$ in steps of 2.5° from 90° to 0°, whilst the remaining internal degrees of freedom were kept fixed at the values obtained from the optimisation at the point of the $D_{2d}$ geometry with
Table 6.8: Comparison of bond lengths, angles and energies with respect to the conical intersection obtained form the CPMCSCF/6-311G** state averaged optimisation of the geometry of the allene cation at the conical intersection and the MRCI/6-311G** calculations with values from Refs. [198, 190].

<table>
<thead>
<tr>
<th>Species</th>
<th>$r_{CC}$/Å</th>
<th>$r_{CH}$/Å</th>
<th>$\theta$/°</th>
<th>$\tau$/°</th>
<th>Energy/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.33</td>
<td>1.09</td>
<td>119.9</td>
<td>90.0</td>
<td>$E_0$</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.38</td>
<td>1.08</td>
<td>119.4</td>
<td>90.0</td>
<td>$E_0$</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.33</td>
<td>1.09</td>
<td>119.9</td>
<td>49.5</td>
<td>$E_0 - 4162$</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.32</td>
<td>1.08</td>
<td>118.7</td>
<td>50.4</td>
<td>-</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>46.6</td>
<td>$E_0 - 4140$</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.33</td>
<td>1.09</td>
<td>119.9</td>
<td>0.0</td>
<td>$E_0 - 110$</td>
</tr>
<tr>
<td>C$_3$H$_4^+$</td>
<td>1.32</td>
<td>1.08</td>
<td>118.3</td>
<td>90.0</td>
<td>0</td>
</tr>
</tbody>
</table>

This work

$r_{CC}$=1.33 Å, $r_{CH}$=1.09 Å and $\theta$=119.9°. The geometry and energies relative to the energy of the conical intersection at the most important stationary points are summarised in Table 6.8. Comparison to previous *ab initio* studies in Table 6.8 show good agreement between the structures determined here and those in the literature [198, 190]. At each point a CASSCF(4,4)/6-311G** calculation was carried out prior to a MRCI/6-311G** calculation. The active space was taken as the configuration space of the $\pi$-system of the allene cation, involving the HOMO, HOMO-1, LUMO and LUMO+1. The potential energy minimum was found to be located $\approx$4100 cm$^{-1}$ below the conical intersection, in good agreement with the JT stabilisation energies determined in Ref. [190]. Our calculations predict the $D_2$ minimum to lie $\approx$4000 cm$^{-1}$ below the $D_{2h}$ barrier. No value of the $D_{2h}$ barrier has been found in the literature. However, Bawagan *et al.* [198] and Chadhuri *et al.* [215] independently calculated the complete torsional minimum path over the full 360°, taking also interactions with higher-lying electronic states into account. In the IVO-CASCI calculations in Ref. [215], the $D_{2h}$ barrier appears twice as high as the $D_{2d}$ conical intersection relative to the potential energy minimum, whereas in the CASSCF calculations in Ref. [198] the point of $D_{2d}$ and $D_{2h}$ symmetry lie by about the same amount of energy above the potential energy minimum of $D_2$ symmetry. Unfortunately, neither of the authors state the relative or absolute energies of the important stationary points on the potential energy hypersurface explicitly. Here, no calculations including the excited states have been attempted for the full torsional path, because four electronic states and three conical intersections would have had to be taken into account along the torsional path. The *ab initio* potential energy cut calculated here allows for a more quantitative understanding of the main features of the cut through the potential energy hypersurface.

On the basis of the analytical one-dimensional function

$$V - E_0 = V_1 \cos(\tau) + V_2 \cos(2\tau) + V_4 \cos(4\tau),$$

where $E_0$ is the energy of the conical intersection, vibrational energy levels and wavefunctions can be computed using the discrete-variable representation (DVR) method [216] as was already
Chapter 6. The E⊗(b₁⊗b₂) Jahn-Teller effect in the allene cation

$$Jahn-Teller \text{ effect in the allene cation}$$

<table>
<thead>
<tr>
<th>νᵢ</th>
<th>experimental</th>
<th>(E′νᵢ − E₀) / cm⁻¹</th>
<th>DVR calc. fitting to experimentᵇ</th>
<th>DVR calc. fitting to ab initioᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0⁻</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>0⁺</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>4₁⁺</td>
<td>745.7</td>
<td>746.56</td>
<td>920.86</td>
<td></td>
</tr>
<tr>
<td>4₁⁻</td>
<td>-</td>
<td>746.57</td>
<td>920.89</td>
<td></td>
</tr>
<tr>
<td>4²⁻</td>
<td>1463.5ᵃ</td>
<td>1464.08</td>
<td>1783.57</td>
<td></td>
</tr>
<tr>
<td>4²⁺</td>
<td>1464.7ᵃ</td>
<td>1464.15</td>
<td>1784.42</td>
<td></td>
</tr>
<tr>
<td>4³⁻</td>
<td>2144.7ᵃ</td>
<td>2144.45</td>
<td>2572.96</td>
<td></td>
</tr>
<tr>
<td>4³⁺</td>
<td>2149.8ᵃ</td>
<td>2146.02</td>
<td>2585.60</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Estimates from strongly perturbed rotational structure
ᵇ $V_1 = 7369.6 \text{ cm}^{-1}$, $V_2 = 4647.1 \text{ cm}^{-1}$, $V_4 = 234.5 \text{ cm}^{-1}$
ᶜ $V_1 = 9444.9 \text{ cm}^{-1}$, $V_2 = 4554.6 \text{ cm}^{-1}$, $V_4 = 1021.3 \text{ cm}^{-1}$

Table 6.9: Summary of the vibrational energy levels from experiment (second column) and the DVR calculation (third column) using Eq. (6.48) to describe the potential function.

successfully done for ethene [58]. The parameters $V_1$, $V_2$ and $V_4$ can be determined either by a fit of Eq. (6.48) to the potential energy along the torsional mode calculated ab initio or by a least-squares fit of the energy level structure calculated in a DVR calculation to those observed experimentally.

The solid line in Fig. 6.14 displays the potential energy along $q_4$ obtained by fitting the potential parameters $V_1$, $V_2$, and $V_4$ in Eq. (6.48) to the experimental energy level structure summarised in Table 6.9 in a DVR calculation. The dashed line represents the potential energy along $q_4$ obtained by fitting the potential parameters $V_1$, $V_2$, and $V_4$ in Eq. (6.48) to the potential energy function calculated ab initio.

The vibrational energy level structure observed in the PFI-ZEKE photoelectron spectra are summarised in the first column of Table 6.9. The value derived for the fundamental wave number from the fit of the rotational structure (see Table 6.4) has been taken for the $4₁⁺$ levels. The values for the tunnelling doublets $4⁺²$, $4⁻₂$ and $4⁺₃$, $4⁻₃$ have been determined from the position of strongest $Q$-type branches in these bands. Because of the tentative nature of the spectral assignment and the perturbations of the rovibrational structure discussed in Section 6.6 these values remain uncertain. Table 6.9 also lists the vibrational energy levels relative to the vibrational ground state obtained from DVR calculations using the two different sets of potential parameters. By comparison of the energy level structures summarised in the first three columns of Table 6.9, one can deduce that the DVR calculation based on the potential energy cut obtained by fitting the parameters to the energy level structure observed in the experiment reproduces the fundamental frequencies well, but underestimated the tunnelling splitting observed in the the $4⁺²$ and $4⁻₃$ bands. These tunnelling splittings are better reproduced using the potential fitted to the ab initio data, but, in this case the harmonic vibrational wave number is overestimated. However, when comparing the DVR results with the experimental results one must consider that the DVR model is a one-dimensional model and does not take the JT coupling of the asym-
metric stretching mode into account. As was observed in the correlation diagram in Fig. 6.13, the linear JT coupling of $\nu_6$ can substantially lower the fundamental frequency observed.

## 6.9 Conclusions and discussion

The present investigation of the JT effect in the $\tilde{X}^+ 2E$ ground state of the allene cation has enabled the derivation of the first adiabatic ionisation energy of allene and the determination of a set of molecular constants: rotational constants describing the lowest two torsional levels and JT coupling constants describing the overall vibronic structure of the photoelectron spectra.

The high-resolution photoelectron spectra reveal complex spectral structures arising from perturbations not included in the standard treatment of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in Eq. (6.9) which neglects anharmonic and Coriolis interactions and bilinear JT couplings on the one hand and disregards the possibility of tunnelling through the $D_{2h}$ potential energy barrier. To account for the latter deficiency a JT model able to treat large amplitude torsional motion has been developed. The tunnelling splittings predicted by this new treatment were found to be compatible with tunnelling splittings calculated using a one-dimensional torsional potential.

In future it would be desirable to combine this new JT model with a complete treatment of the (ro-)vibronic interactions (Coriolis interactions, bilinear JT coupling and higher-order vibrational interactions) using *ab initio* quantum chemical calculations.
Chapter 6. The $E\otimes(b_1 \oplus b_2)$ Jahn-Teller effect in the allene cation
Chapter 7

Conclusions and outlook

The research described in this thesis was dedicated to the studies of ionisation dynamics of small to medium-sized organic molecules and radicals. Radicals could be produced in high number densities and at low rotational temperatures for investigation by photoionisation and PFI-ZEKE photoelectron spectroscopy using high-resolution VUV laser sources. The rotational structure observed in the PFI-ZEKE photoelectron spectra of the electronic ground states of C$_3$H$_5^+$, CH$_3^+$, CD$_3^+$, CH$_2$D$^+$, CHD$_2^+$, CH$_2$O$^+$, C$_3$H$_4^+$, and C$_3$D$_4^+$ could be fully resolved. The orbital ionisation model was important in understanding the intensity distributions and perturbations thereof and was successfully employed to simulate the photoelectron spectra of these molecular systems.

The single-photon PFI-ZEKE photoelectron spectrum of allyl helped to resolve the controversy in the literature concerning the adiabatic ionisation potential and clarified ambiguous and inconsistent previous analyses of the photoelectron spectra. The orbital ionisation model allowed for a prediction of different rotational envelopes observed in resonance-enhanced multiphoton spectra via different electronic states, which may be instrumental in the assignment of the complicated electronic spectra of the allyl radical.

The photoelectron spectrum of methyl represented a nice example of quadrupole-mediated rotational autoionisation. The fully rotationally resolved PFI-ZEKE photoelectron spectra of all deuterated isotopomers of methyl allowed for the comparison of the ionisation dynamics of symmetric- and asymmetric-top molecules with the same chemical properties and electronic structure. The list of molecular constants for all four isotopomers was completed.

Formaldehyde was studied in a three-photon three-colour excitation scheme, leading to ro-
tationally resolved spectra of the 3p, Rydberg state and the electronic ground state of the cation. The analysis of the PFI-ZEKE photoelectron spectra of the lowest three vibrational bands of the electronic ground state of CH$_2$O$^+$ helped to characterise the rovibrational dynamics in both the cationic ground and the Rydberg state. An $a$-type Coriolis interaction was identified between the $v_4$ out-of-plane bending and $v_6$ in-plane rocking normal modes of formaldehyde that appears ubiquitous in the spectra of formaldehyde and its cation.

Allene and allene-$d_4$ were studied in order to obtain detailed information on the so far little studied $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect. A possible interaction between the rotational and the vibronic degrees of freedom in such a system could be observed for the first time. Resolving the rotational structure of the first four members of the progression in the torsional mode $v_4$ revealed perturbations indicative of (ro-)vibronic interactions and tunnel dynamics previously not reported because of insufficient resolution. The current formalism of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect in the cumulenes could be modified so as to explicitly account for the large amplitude motion along the torsional normal mode.

The investigations summarised in this thesis illustrate the power of high-resolution photoelectron spectroscopy to study neutral polyatomic molecules and radicals and their cations. The resolution of 0.17 cm$^{-1}$ that could be achieved in the photoelectron spectrum of allene is sufficient to at least partially resolve the rotational structure of larger molecular systems.

In future it will be of particular interest to carry out studies by high-resolution photoelectron spectroscopy of molecular systems undergoing large amplitude motions, such as internal rotation, intramolecular proton transfers or pseudo-rotations. Such motions are very sensitive to the charge state. Consequently, large changes are expected to be introduced in these motions upon removal of an electron leading to interesting dynamics. Photoelectron spectroscopy is the ideal spectroscopic method to study these dynamics. The experimental tools and theoretical models developed in this thesis will hopefully facilitate such studies.
Appendix A

Spectral positions of the origin band of \( \text{C}_3\text{H}_4 \)
Table A.1: Observed and calculated line positions (in cm$^{-1}$) in the PFI-ZEKE photoelectron spectrum of the origin band of the $X^2 \Pi - \bar{X}^2 \Pi$ transition of allyl.
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Languages

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