Single- and double-resonance spectroscopy of formaldehyde by four-wave mixing and multiphoton ionization

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SINGLE- AND DOUBLE-RESONANCE SPECTROSCOPY OF FORMALDEHYDE BY FOUR-WAVE MIXING AND MULTIPHOTON IONIZATION

A dissertation submitted to ETH ZURICH for the degree of Doctor of Sciences

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Abstract

This thesis examines the application of several linear and nonlinear single- and double-resonance techniques to study the spectroscopy and photodissociation dynamics of gaseous formaldehyde. Because formaldehyde is an intermediate in the oxidation cycle of hydrocarbons, the understanding of its energy level structure is important in the field of combustion research as well as in atmospheric chemistry. Being composed of only four atoms, formaldehyde is the smallest molecule of the aldehyde family and has therefore been the subject of many experimental and theoretical studies. However, many questions have remained open. For instance, the molecular channel of the dissociative decomposition, which leads to the products CO and H₂, has been studied extensively and is mostly understood, but only recently the attention has been drawn to the radical dissociation channel. Moreover, the presence of formaldehyde in interstellar space encourages further analysis of higher-lying states, where rotationally resolved data is scarce.

For these investigations sensitive high-resolution laser-spectroscopic techniques are required, which ideally yield quantitative information about quantum state populations. Furthermore, a state-selective technique which enables the acquisition of spectra exhibiting only a small number of peaks would be favorable. In this work, the use of appropriate spectroscopic techniques meeting the above-mentioned demands was required. Chemically relevant results were found for formaldehyde and additional experiments were performed on C₃ molecules.

The pump-probe technique photofragment excitation (PHOFEX) was applied for the analysis of the radical dissociation channel of formaldehyde, H₂CO → HCO+H. The dependence of the formation of HCO in a specific quantum state on excited states from which formaldehyde dissociates was investigated by determining the quantum yields for these processes. Therefore, one requires the combination of a quantitative absorption-like technique to monitor the excitation of the parent molecule and another which allows the detection of the formed product molecules in a specific quantum state. For this purpose, degenerate four-wave mixing (DFMW) and laser-induced fluorescence (LIF) were used to determine the quantum yields of the photodissociation of H₂CO to HCO. The dissociation from two vibronic levels of H₂CO was investigated in this work. The ˜A₁A₂ 2¹4⁵ level is situated slightly above the threshold for the radical dissociation channel, therefore the reaction competes with the molecular channel which is already accessible at lower energies. The ˜A₁A₂ 2¹4¹ level lies at the threshold for the dissociation via intersystem crossing to the triplet state. Here, the magnitude of the quantum yield was found to depend crucially on the rotational level in the excited vibronic state of formaldehyde. The results obtained for the vibronic state at the triplet threshold display a strong preference of the formation of all probed product states from two specific rotational levels of H₂CO, thus indicating
that dissociation from these states occurs via the triplet state.

In addition, experiments which justify the use of DFWM as an absorption-like spectroscopic technique that enables the determination of quantum state populations were carried out. This condition is essential for the evaluation of the quantum yields in PHOFEX experiments. Therefore, the dependence of degenerate four-wave mixing on the strengths and the polarizations of the interacting electric fields was investigated and compared with two theoretical models by Abrams and Lind (R. L. Abrams and R. C. Lind, Optics Letters, 2:94-96, 1978), and Williams, Rahn and Zare (S. Williams and R. N. Zare and L. A. Rahn, Journal of Chemical Physics, 101:1072-1092, 1994). Furthermore, DFWM spectra were recorded simultaneously with cavity ring-down and laser-induced fluorescence spectra allowing the direct comparison of signal intensities. The saturation behavior of selected rovibronic transitions of the carbon trimer C$_3$ and H$_2$CO was examined by recording the DFWM signal intensity at the line center as a function of the intensity of the incident fields. The application of three different configurations of the electric field polarizations for the acquisition of DFWM spectra was demonstrated to have an effect on the relative intensities of transitions with small angular momenta. From these results it can be concluded that both, the intensities of the incident fields as well as their polarizations have to be controlled when quantitative conclusions shall be drawn from the intensities in degenerate four-wave mixing spectra.

Two-color resonant four-wave mixing (TC-RFWM) was applied for the rotational characterization of the higher-lying predissociative $\tilde{A}^1A_2 2^2\tilde{5}^1$ vibrational level. The double-resonance nature of the method allows the simplification of spectra by intermediate-state labeling where one electric field is in resonance with a rovibronic transition in the same or another vibronic band of the molecule. In this experiment, rovibronic transitions in the strong $2^2_04^1_0$ band were chosen for this purpose, while the wavenumber of the second field is scanned in the region of the $2^2_05^1_0$ band of the $\tilde{A}^1A_2-\tilde{X}^1A_1$ transition. The band origin ($T_0 = 33508.88(2)$ cm$^{-1}$) and the rigid rotor rotational constants ($A = 8.2677(53)$ cm$^{-1}$, $B = 1.1029(18)$ cm$^{-1}$ and $C = 0.9955(20)$ cm$^{-1}$) were derived. The assignment was tested by intermediate-state labeling by rovibronic transitions in the $2^2_05^1_0$ band and recording TC-RFWM spectra of the $2^2_04^1_0$ vibrational band. The rotational constants and the band origin were also determined and found to be consistent with the literature.

The rotational structure of the three lowest vibrational levels of the $^1A_2(3p_x)$ Rydberg state was analyzed with double-resonance multiphoton ionization (MPI). Similar to two-color resonant four-wave mixing, by intermediate-state-labeling in the $\tilde{A}^1A_2 2^14^3$ and $\tilde{A}^1A_2 2^34^1$ levels, double-resonance spectra displaying only few rovibronic transitions were obtained. The wavenumbers of the band origin and the rotational constants of the $0^0$ level were found to be $T_0 = 67728.939(82)$ cm$^{-1}$, $A = 9.006(19)$ cm$^{-1}$, $B = 1.331(20)$ cm$^{-1}$ and $C = 1.135(22)$ cm$^{-1}$. A strong Coriolis interaction between the $6^4$ and the $4^1$ levels along the $a$-axis was found to enable the observation of the vibronically forbidden transitions to the $^1A_2(3p_x) 6^4$ level. The Coriolis coupling constant ($\xi_{46}^a = 8.86(89)$ cm$^{-1}$) and the deperturbed vibrational wavenumbers of the out-of-plane bending mode ($\tilde{v}_4 = 984.92(26)$ cm$^{-1}$)
and the in-plane-rocking mode ($\nu_6 = 808.88(25) \text{ cm}^{-1}$) were also determined. In addition, the relative intensities in a double-resonance MPI spectra were found to depend on the selected transition to the intermediate state. In some cases, expected transitions in the double-resonance MPI spectra were not observed. By applying different excitation schemes or choosing appropriate electric field polarizations, all transitions required to rationalize the observed Coriolis interaction were measured.
Zusammenfassung

Die vorliegende Arbeit befasst sich mit der Anwendung verschiedener linearer und nichtlinerer einfach- und doppelresonanter Methoden zur Untersuchung vibronisch angeregter Quantenzustände und des radikalen Dissoziationskanals von Formaldehyd.


In dieser Arbeit wurden verschiedene spektroskopische Techniken angewendet, die die obengenannten Forderungen im jeweiligen Experiment erfüllen:

Mit Hilfe der Photofragmentanregungsmethode (Photofragment Excitation oder PHO-FEX) wurde der radikale Dissoziationskanal, \(H_2CO \rightarrow HCO + H\) studiert. Das Auftreten des Dissoziationsproduktmoleküls HCO in einem bestimmten Quantenzustand wurde in Abhängigkeit von der Anregung des Muttermoleküls H_2CO in verschiedene Rotationszustände oberhalb der Dissoziationsgrenze analysiert. Dafür wurden hier zwei vibronische Zustände untersucht, \(A^1A_2 \ 2^1A^3\) an der Schwelle zum radikalen Dissoziationskanal und \(A^1A_2 \ 2^1A^1\) an der Schwelle zur radikalen Dissoziation von Formaldehyd über den niedrigsten Tripletzustand \(a^3\)A_2. Um die Quantenausbeute für einen solchen Prozess zu bestimmen, benötigt man eine absorptionsartige Methode, mit der der Anregungsprozess in Formaldehyd aufgezeichnet werden kann. Zu diesem Zweck wurde das entartete Vierwellenmischen (degenerate four-wave mixing, DFWM) verwendet, wobei das Auftreten der Dissoziationsprodukte in einem bestimmten Quantenzustand mit laser-induzierter Fluoreszenz (LIF) gemessen wurde. Die Quantenausbeute hängt sehr stark davon ab, in
welches Rotationsniveau im angeregten vibronischen Zustand Formaldehyd angeregt wurde. Im Speziellen ergibt sich für die Photodissoziation aus dem $\tilde{A}^1 A_2$ $2^4 A^4$ Niveau, dass alle überprüften Produktquantenzustände vornehmlich aus der Dissoziation von zwei spezifischen Rotationsniveaus resultieren, was darauf hindeutet, dass es sich hierbei um Dissoziation aus dem Tripletzustand handelt.


Die Rotationsstruktur des prädissoziativen vibrationsangeregten $2^2S^1$ Zustandes im $\tilde{A}^1 A_2$ Niveau wurde mit zweifarben resonantem Vierwellenmischen (two-color resonant four-wave mixing, TC-RFWM) bestimmt. Ein Zweifarbenspektrum erhält man, indem man die Wellenzahl des ersten Feldes in Resonanz mit einem starken Übergang zum $2^2S^1$ Zustand im $\tilde{A}^1 A_2$ Niveau einstellt, während der $2^2S^1$ Zustand durch Durchstimmen der Wellenzahl des zweiten Feldes abgefragt wird. Der erste Schritt ermöglicht die Vorauswahl eines Rotationsniveaus im elektronischen Grundzustand, sodass nur noch wenige Übergänge in den $2^2S^1$ Zustand möglich sind, sodass das Spektrum stark vereinfacht wird und eine rasche Zuordnung möglich ist. Die Rotationskonstanten für einen starren Rotor und der Bandenursprung des $2^2S^1$ Niveaus wurden bestimmt: $T_0 = 33508.88(2) \text{ cm}^{-1}$, $A = 8.2667(53) \text{ cm}^{-1}$, $B = 1.1029(18) \text{ cm}^{-1}$ und $C = 0.9955(20) \text{ cm}^{-1}$. Die Überprüfung der Zuordnung der Übergänge gelang durch die Vorauswahl von Zuständen durch Übergänge in der $2^2S^1$ Bande und der Aufnahme von Spektren zum $2^2S^1$ Niveau. Die Rotationskonstanten für den $2^2S^1$ Zustand konnten so berechnet werden und stimmen mit den Literaturwerten überein.

Die Doppelresonanz-Multiphotonionisations-Methode diente zur rotatorischen Charakterisierung der drei niedrigsten Vibrationsniveaus im $^1 A_2(3p_{\pi})$ Rydbergzustand. Dafür wurde ein Anregungsschema gewählt, in dem im ersten Anregungsschritt ein Übergang vom elektronischen Grundzustand zum $\tilde{A}^1 A_2 2^4 1^4 3^1$ oder $\tilde{A}^1 A_2 2^2 4^1$ Niveau ausgewählt wurde. Die aus wenigen Übergängen bestehenden Doppelresonanzspektren entsprechen den
Übergängen vom vorausgewählten Rotationszustand im \( \tilde{\mathrm{A}}^1\mathrm{A}_2\ 2^14^3 \) oder \( \tilde{\mathrm{A}}^1\mathrm{A}_2\ 2^24^1 \) Niveau zum \( ^1\mathrm{A}_2(3p_x) \) Zustand. Der Bandenursprung und die Rotationskonstanten des \( ^1\mathrm{A}_2(3p_x) \) 0\( ^0 \) Niveaus konnten so bestimmt werden: \( T_0 = 67728.939(82) \text{ cm}^{-1} \), \( A = 9.006(19) \text{ cm}^{-1} \), \( B = 1.331(20) \text{ cm}^{-1} \) und \( C = 1.135(22) \text{ cm}^{-1} \). Die zwei niedrigsten angeregten Vibrationsniveaus, \( ^1\mathrm{A}_2(3p_x)\ 6^1 \) und \( ^1\mathrm{A}_2(3p_x)\ 4^1 \), sind durch eine starke Corioliswechselwirkung gekoppelt, die die Beobachtung der vibronisch-verbotenen Übergänge zum 6\( ^1 \) Zustand ermöglicht. Die Wellenzahlen der beiden Normalschwingungen \( \tilde{\nu}_6 = 808.88(25) \text{ cm}^{-1} \) und \( \tilde{\nu}_4 = 984.92(26) \text{ cm}^{-1} \) als auch die Coriolis-Kopplungskonstante \( \xi_{\alpha,\delta} = \text{ cm}^{-1} \) konnten bestimmt werden und sind vergleichbar mit den entsprechenden Größen für andere elektronische Zustände.
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Part I

Introduction
For the development and optimization of advanced, efficient and clean combustion engines, simulations at multiple scales are carried out which should replace the empirical hardware-intensive fuel and engine tests one day. In order to obtain accurate results with large scale simulations, a detailed knowledge about the energy dependence of the chemical reactions governing the combustion process is required. High-resolution and sensitive spectroscopic techniques are essential for the characterization of molecules and their thermodynamical and kinetic quantities. Thus, molecular constants can be provided which allow the comparison of the simulations with results from in-situ measurements. The spectroscopic measurements from which molecular constants are derived, can be carried out in flames to a limited extent only. Due to the high pressures and temperatures and the large number of species present in flames many interactions occur hampering a detailed analysis of the molecular species. Therefore, spectroscopic experiments are rather carried out under controlled conditions, for example, a molecular beam in a vacuum chamber which enables the production of cold molecules with defined energies in the absence of collisions.

Optical absorption spectroscopy is a widely used tool to study the geometrical and electronic structure of molecules due to its overall applicability and conceptual simplicity. But quite often its practical application is restricted by the need to extract weak signals from large and fluctuating levels of background light. Cavity ring-down is an advanced absorption technique benefitting from an increased absorption path length. It has several advantages over conventional absorption spectroscopy. According to the Lambert-Beer law of absorption, the increased absorption path length, which can be in the range of several hundred meters or kilometers, brings about the high sensitivity of the technique. The disadvantage of the technique is the price of the mirrors that form the cavity, which are applicable only in a restricted range of wavenumbers. In addition, the only user selectable degree of freedom is the excitation wavenumber, therefore all absorbing species contribute to the signal intensity.

Alternatively, other spectroscopic methods which comprise the absorption of light as part of the process such as e.g. fluorescence in laser induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI) can be used to produce analogous results. LIF is a highly sensitive and in theory background-free technique that is based on the detection of fluorescence from an excited state. The technique is, however, not applicable for fast predissociative states, because no fluorescence to lower-lying states can be detected. Resonance-enhanced multiphoton ionization is also a highly sensitive technique relying on the detection of ions as opposed to incoherent radiation. Therefore, it is also species-selective technique, if mass-spectrometry is applied simultaneously. Unfortunately, these techniques rely upon secondary interactions, such as fluorescence and ionization and therefore, are subjected to some constraints. Furthermore, REMPI is limited to neutral molecules. Moreover, in the case of complex, overlapping spectral features, linear single-resonance techniques fail to unambiguously assign rotational lines.
A technique which is not restrained by these difficulties would be an advantageous spectroscopic tool. Nonlinear resonant four-wave mixing methods provide a suitable tools for sensitive spectroscopy. The degenerate version, DFWM, has been used as an absorption-like technique exhibiting excellent signal-to-noise ratios. The reason for this is the generation of a coherent signal which can be easily discriminated against scattered radiation. The signal beam may be detected remotely, making DFWM a useful probe of hostile environments such as flames and plasmas (see e.g. [1, 2, 3, 4]). DFWM has an advantage over laser-induced fluorescence and resonance-enhanced multiphoton ionization as it can be used to detect rapidly predissociating species without a resultant loss of signal. In comparison to cavity ring-down spectroscopy, a better temporal resolution can be obtained. This means that whereas the four-wave interaction occurs within nanoseconds, the cavity ring-down process comprises all processes occurring during the passage of the laser beam in the cavity. However, necessitating more accurate experimental adjustments, the four-wave mixing techniques are more difficult to implement.

Double-resonance techniques, such as two-color resonant four-wave mixing and the two-color version of resonance-enhanced multiphoton ionization provide an increased spectral selectivity compared to their single-resonance counterparts. Congested spectra obtained with single-resonance techniques are reduced to a small number of transitions in a double-resonance experiment allowing unambiguous assignments. Moreover, it offers means to characterize perturbations which might be difficult to identify otherwise.

In this work, the above mentioned techniques are applied for the characterization of excited states of formaldehyde and its radical photodissociation channel. Being an intermediate in hydrocarbon oxidation cycles, formaldehyde is a combustion relevant molecule. The dissociation mechanism, which is investigated with optical methods in this work, can be induced also thermally [5].

In particular, photofragment excitation spectroscopy, a method that combines DFWM and laser-induced fluorescence, is used to investigate the radical dissociation channel in the wavenumber regime at the threshold. The dependence of the occurrence of a product molecule in a specific quantum state on the excitation of the parent molecule is investigated. DFWM is used to record absorption-like spectra of the excitation process of formaldehyde. Therefore, a justification of the comparability of DFWM with an absorption technique is sought by studying the technique in relation to models as well as in direct comparison with cavity ring-down spectroscopy.

In further experiments, two-color resonant four-wave mixing is applied to characterize a higher-lying predissociative vibronic state of formaldehyde, whereas double-resonance multiphoton ionization is utilized for the determination of rotational constants of the $3p_z$ Rydberg state of formaldehyde.

This thesis is divided into three parts, an introduction and two parts devoted to degenerate four-wave mixing experiments and double-resonance experiments. The introduction consists of two chapters explaining the applied single- and double-resonance spectroscopic methods which is followed by a description of the experimental setup used for all the ex-
periments. The second part covers the investigation of the radical dissociation channel of formaldehyde with photofragment excitation and the justification of DFWM as an absorption-like technique. In the third part, the double-resonance techniques are applied for the characterization of higher-excited states of formaldehyde.
Chapter 1

Single-resonance spectroscopic techniques

In this chapter the single-resonance techniques used in this work will be introduced. Laser-induced fluorescence (LIF), which is a rather common technique, will be explained only briefly, while cavity ring-down (CRD) and degenerate four-wave mixing (DFWM) will be described in more detail because these techniques are more intricate. A part of chapter 5 compares these three techniques and points out their advantages and disadvantages.

1.1 Laser-induced fluorescence

Laser-induced fluorescence (LIF) spectroscopy is a sensitive and robust technique. The process consists of two steps: a molecule $M$ is excited from the ground state $g$ by a photon of wavenumber $\tilde{\nu}$ to an excited state $e$. Subsequently, the molecule relaxes by spontaneous emission of a photon with wavenumber $\tilde{\nu}_{fl}$ to a final state $f$, which may be the same as the initial state. Schematically, the process can be written as:

$$M_g + \tilde{\nu} \rightarrow M_e \rightarrow M_f + \tilde{\nu}_{fl}. \quad (1.1)$$

LIF spectra are obtained by collecting and imaging the fluorescence signal onto the entrance of a monochromator, which acts as a bandpass filter at $\tilde{\nu}_{fl}$, while $\tilde{\nu}$ is scanned. To achieve high signal-to-noise ratios it is useful to select intense transitions for detection by the monochromator. This can be done by recording dispersed fluorescence spectra, which are obtained by scanning the detection wavenumber $\tilde{\nu}_{fl}$ at a fixed $\tilde{\nu}$.

1.2 Cavity ring-down

Cavity ring-down (CRD) spectroscopy is a powerful direct absorption technique, which was developed by O'Keefe and Deacon [6] in 1988 to record electronic spectra of jet-cooled molecules and clusters with very high sensitivity and high spectral resolution. This optical technique is based on measuring the absorption of light by a sample located within a closed optical cavity formed by a pair of highly reflective ($R > 99.9\%$) concave mirrors. In order to maintain the high finesse of the cavity, a set of mirrors can be applied for a limited wavelength range only, typically a few tens of nanometers depending on the nature of the coating. For most CRD experiments, pulsed laser light is used, but also
applications with cw-lasers have been developed [7].

The small amount of light that is trapped inside the cavity is reflected back and forth between the two mirrors. With each pass, a small fraction \( \approx 1 - R \) is transmitted through each mirror. The resultant transmission through one mirror is monitored as a function of time and enables the determination of the decay time of the pulse intensity in the cavity. The intensity envelope of the discrete transmitted pulses exhibits a simple exponential decay:

\[
I(t) = I_0 e^{-t/\tau}.
\] (1.2)

\( \tau \) is the time required for the output intensity to decay to \( 1/e \) of the initial output pulse intensity \( I_0 \) and is called the ring-down time. The setup constitutes a sensitive absorption spectrometer if an absorbing medium is placed between the two mirrors and the frequency-dependent ring-down time of the cavity is recorded, which is determined by

\[
\tau(\tilde{\nu}) = \frac{L}{c(1 - R + \alpha(\tilde{\nu}) l)},
\] (1.3)

where \( L \) is the length of the cavity, \( c \) the speed of light, \( R \) the average reflectivity of the two mirrors and \( \alpha(\tilde{\nu}) l \) the absorbance for a sample present in the cavity with absorption coefficient \( \alpha(\tilde{\nu}) \) and a sample length \( l \). The term \( R \) represents an effective reflectivity which contains losses such as transmission through the mirror as well as diffraction and scattering in the empty cavity, i.e. without the investigated species. The ring-down time reflects the rate of absorption rather than the magnitude of the absorption. As such it has an important advantage in comparison to conventional absorption techniques: the method is independent of pulse-to-pulse fluctuations in the laser power. Moreover, the technique is ideal to study species in low concentrations because of the long absorption path lengths that are obtained because of the confinement of the light pulse is inside the cavity for several microseconds.

The minimum absorbance measured with this technique is limited by the mirror reflectivity \( R \) and the minimum time interval \( \Delta t \) that can be detected. For a mirror reflectivity as high as \( R = 99.99\% \) and for typical accuracies \( \Delta \tau/\tau_{\text{min}} = 5 \cdot 10^{-3} \) to \( 2 \cdot 10^{-3} \) the minimum measured absorbance \( (\alpha l)_{\text{min}} \) is on the order of a few parts in \( 10^{-7} \) [8, 9].

There are two ways for extracting spectra from the exponential decays recorded at each laser wavelength:

1. Direct fitting (e.g. least-squares fitting) of the exponential decay or of its logarithm. The fit will give the decay time \( \tau \) but is time-consuming if it is implemented in the detection routine.

2. Setting two points on the exponential curve separated by \( \Delta \tau = t_2 - t_1 \). The signal is then measured as

\[
S = \ln \frac{S_{t_1}}{S_{t_2}} = -\frac{\Delta t}{\tau} - l\alpha(\tilde{\nu})
\] (1.4)

where \( S_{t_1} \) and \( S_{t_2} \) are the signals measured at the first and second point. The
resultant $S$ is directly proportional to the absorption coefficient.

In a cavity ring-down experiment, the ring-down time is determined only as a function of the excitation frequency, all other parameters are fixed. Therefore, it is crucial that the mirror reflectivity is constant over the duration of the measurement. Since all absorbing species in the cavity will contribute to the absorbance, the purity of the sample is more of an issue than for other techniques such as LIF where the frequency dependence of both the excitation and detection steps can be used to uniquely select a species.

1.3 Degenerate four-wave mixing

Degenerate four-wave mixing (DFWM) is a non-linear optical process: nonlinear optics often investigates phenomena which arise as a consequence of the modification of the optical properties of a material system in the presence of light. These processes typically occur only when the intensity of the present light is high. The appropriate source for such optical fields are lasers.

The interaction between material properties and an electrical field is described by the polarization $P(t)$, that is, the dipole moment per unit volume. Nonlinear phenomena are nonlinear in the sense that the response of the system to an applied field depends in a nonlinear manner on the strength of the electric field. In order to define the concept of optical nonlinearity more precisely, it is useful to consider the dependence of the polarization of the material upon the strength $E(t)$ of the applied field. This can be done by a power expansion:

$$ P(r, t) = \chi^{(1)}E(r, t) + \chi^{(2)}E(r, t)^2 + \chi^{(3)}E(r, t)^3 + \ldots $$ (1.5)

The expansion coefficients $\chi^{(i)}$ are known as susceptibilities and describe the polarizability of the nonlinear medium. The method assumes that the higher-order susceptibilities become progressively smaller so that the power series expansion converges to a finite polarization.

$\chi^{(i)}$ is a tensor of rank $i + 1$, thus, the products in Equation 1.5 are tensorial products. For centrosymmetric media such as gases, the even-order susceptibilities vanish because of symmetry reasons [10]. The lowest order nonlinear response of a gaseous system is thus characterized by the third-order susceptibility $\chi^{(3)}$ which describes four-wave mixing processes.

In general, for a four-wave mixing process, the applied electric field as a function of space and time is written as a sum of three distinct electric fields

$$ E(r, t) = E_1(r, t) + E_2(r, t) + E_3(r, t) $$ (1.6)

where each of the electric fields is represented by

$$ E_i(r, t) = A_i(r)e^{-i(k_i \cdot r - \omega_i t)} + c.c. $$ (1.7)

for $i = 1, 2, 3$, where $A_i(r) = A_{ki}^i(r)e_k$ are the amplitudes ($A_{ki}^i(r)$ is the $k$-th coordinate, and $e_k$ is the unit polarization vector), $k_i$ are the wave vectors, and $\omega_i$ the angular frequencies.
of the electric fields.

\( \chi^{(3)} \) is a fourth rank tensor with 81 elements. In an isotropic medium 21 of these are nonzero of which only 3 are independent. Each of these elements consists of a sum of 48 terms. \( \chi^{(3)} \) can be calculated with the density matrix formalism and consists of terms like:

\[
\chi^{(3)}(\omega_4, \omega_1, \omega_2, \omega_3) = \frac{N}{\hbar^3} \sum_{\nu,m,n,l} \mu^k_{\nu m} \mu^l_{nm} \mu^h_{ml} \rho^0_{ll} \\
\left( (\omega_{nl} - \omega_1 - \omega_2 - \omega_3) - i\gamma_{nl} \right) \left( (\omega_{nl} - \omega_2 - \omega_3) - i\gamma_{nl} \right) \left( (\omega_{nl} - \omega_3) - i\gamma_{nl} \right) + 47 \text{ other terms},
\]

the full expression can be found in Ref. \[11\]. \( \rho^0_{ll} \) is the initial population of the state \( l \) in the absence of any external field. \( \mu^k_{nm} \) designates the \( k \)-th component of the transition dipole moment from state \( m \) to \( n \):

\[
\mu^k_{nm} = e \langle n | r^k | m \rangle ,
\]

where \( \omega_{nm} \) is the transition frequency (in angular frequency units) from level \( n \) to \( m \) and \( \gamma_{nm} \) is the transition dipole dephasing rate. In the absence of collisions it is represented by

\[
\gamma_{nm} = \frac{1}{2} (\Gamma_n + \Gamma_m) ,
\]

where \( \Gamma_n \) and \( \Gamma_m \) denote the total decay rates of population out of level \( n \) and \( m \), respectively.

Each of the factors in the denominator in the expression for \( \chi^{(3)} \) shows that the nonlinear susceptibility increases at resonance. That is, if the sum of specific combinations of input frequencies equals the transition frequency \( \omega_{nl} \), the factors become small. Resonant four-wave mixing techniques such as degenerate or two-color resonant four-wave mixing exploit this property of the nonlinear susceptibility so that the signal strength is increased and high signal-to-noise ratios can be obtained.

The evaluation of all 48 terms in the expression for \( \chi^{(3)} \) is very tedious, however in a fully resonant four-wave mixing experiment the intensity at a particular resonance in the spectrum is dominated by only a few terms.

Whereas the general four-wave mixing process involves the interaction of waves with four different frequencies \( \omega_i, i = 1, 2, 3, 4 \), in the degenerate case waves with equal frequencies \( \omega \) but different wave vectors \( \mathbf{k} \), and electric field polarizations may interact. The expression of the third-order susceptibility \( \chi^{(3)}(-\omega, +\omega, -\omega, +\omega) \) must be determined, where the plus sign corresponds to an absorption of a photon and the minus sign to a stimulated emission. The \( i \)-th component of the polarization vector may be written as

\[
P^i(r, t) = 6\chi^{(3)}_{ijkl}(-\omega, \omega, -\omega, \omega) A_1^j(A_2^k)^* A_3^l \times e^{i(k_1-k_2-k_3) \cdot r - i\omega t} + \text{c.c.}
\]

where a summation over equal indices is carried out. The time varying polarization \( \mathbf{P}(r, t) \)
can be interpreted as a source of the fourth electric field according to the wave equation
\[
\nabla^2 E_4(r, t) - \frac{n^2}{c^2} \frac{\partial^2 E_4(r, t)}{\partial t^2} = \frac{1}{c^2} \frac{\partial^2 P(r, t)}{\partial t^2},
\]
where \( n \) is the refractive index of the medium. The direction of the signal field \( E_4 \) is thus determined by the spatial phase component of the nonlinear polarization in Equation 1.11:
\[
k_4 = k_1 - k_2 + k_3.
\]
This relation is known as the phase-matching condition. The wave vector of the emanating fourth electric field, of which the contribution to the polarization in Equation 1.11 is the source, is determined by the wave vectors of the three other interacting waves.

In order to obtain the resulting field \( E_4(r, t) \), the wave equation (Equation 1.12) must be solved. An analytical solution can be found only if specific assumptions are made (for example, rotating wave and slow-varying envelope approximations). In Chapter 5 the theory of Abrams and Lind [12] will be presented and an analytical expression for the intensity of the fourth electric field
\[
I_4 = \frac{c \varepsilon_0}{2} |E_4(r, t)|^2
\]
is found assuming two intense pump fields \( E_1(r, t) \) and \( E_2(r, t) \) and a weak probe field \( E_3(r, t) \).

A more qualitative and intuitive description of the degenerate four-wave mixing process than above is the following: two laser beams cross at a small angle to produce an optical fringe pattern, which, in an absorbing medium, will give rise to a spatial modulation of the refractive index of the medium. The third laser beam can then be diffracted from the grating obeying the Bragg condition to produce a signal beam. The degenerate four-wave mixing process is strongly enhanced at frequencies in resonance with transitions of the medium, as can be seen in the denominators of Equation 1.8. Spectral intensities obtained with degenerate four-wave mixing are proportional to the absolute square of the complex expression \( |\chi^{(3)}|^2 \). The index of refraction and the absorption coefficient, which correspond to resonances in \( \chi^{(3)} \), varies with the frequency of the input radiation.

As has been mentioned above, the geometrical setup of the four-wave mixing experiment is determined by the wave vectors \( k_1, k_2 \) and \( k_3 \). The most commonly used geometrical setups are phase-conjugate and forward box degenerate four-wave mixing. The first setup involves two counter-propagating beams and a third beam which is directed through the sample at a small angle resulting in a signal beam in the same direction as the probe beam but with phase-conjugated characteristics. The forward box geometry [13, 14] is used in the four-wave mixing experiments in this work. The three incident waves are directed through a molecular sample along the distinct diagonals of a rectangular parallelepiped,
i.e. a box. The nonlinear interactions with the medium produce a fourth wave, which emerges along the remaining diagonal and propagates with laser like properties which facilitates the detection. An advantage of this variant of DFWM is that the incoherent background light that is scattered into the full solid angle can be eliminated by remote probing and without having to insert collection optics into the path of the incident radiation as would be necessary for the phase-conjugate setup.

The experimental implementation of DFWM is not quite as simple as for other single-resonance techniques because the spatial and temporal overlap of three lasers beams is demanding. However, it is a rewarding technique because of the impressive signal-to-noise ratio and high spatial and frequency resolution which can be achieved. Moreover, the technique does not depend on secondary processes as has been mentioned for the methods which are based on the measurement of fluorescence or ions.
Chapter 2

Double-resonance spectroscopic techniques

The double-resonance techniques that are used in this work are photofragment excitation (PHOFEX), two-color resonant four-wave mixing (TC-RFWM) and double-resonant multiphoton ionization (MPI). The latter two methods can serve as a tool to simplify spectra in the sense that a specific rotational level is labeled by the first excitation step. Consequently, only a limited number of transitions can occur and their assignment is simplified. PHOFEX, on the other hand, is a pump-probe technique that permits the investigation of photodissociation processes. If PHOFEX is used in combination with a technique which provides the population of the excited state of the dissociating molecule the propensities for a product quantum state arising from a specific parent state can be determined.

2.1 Photofragment excitation

Photofragment excitation spectroscopy [15, 16] is a technique that allows the characterization of unimolecular reactions with both the initial state of the reactant and the final states of the products fully defined. The method is doubly resonant in the sense that one photon is needed to excite a parent molecule to a quantum state above the dissociation threshold for the reaction channel of interest. The yield of a specific product state \( p \) is monitored by tuning light from the second laser to a specific transition of the photofragment starting from \( p \). Photofragment excitation spectra are obtained by recording the fluorescence from the state to which the nascent molecule is excited while the first laser is scanned. A schematic illustration of the process is shown in Figure 2.1 using the example of the radical dissociation channel of formaldehyde, which is the topic of Chapter 4.

The combination of PHOFEX with an absorption-like spectroscopic technique to monitor the excitation of the parent molecule allows a more quantitative evaluation because the dissociation yield can be referenced to the population of the excited state of the parent molecule.

The PHOFEX signal \( S_{\text{PHOFEX}} \) is proportional to the number of product molecules in the probed state [16] and, for asymmetric rotors like H\(_2\)CO and HCO, it can be expressed as

\[
S_{\text{PHOFEX}} \propto N_g(J''_{K''_{a}K''_{c}})P(N_{k_{a}k_{c}}, J'_{K'_{a}K'_{c}}; E_{\text{exc}}),
\]

where \( N_g \) is the number of formaldehyde molecules in the initial state \( J''_{K''_{a}K''_{c}} \) and \( P(N_{k_{a}k_{c}}, J'_{K'_{a}K'_{c}}; E_{\text{exc}}) \)
Figure 2.1 The excitation scheme for photofragment excitation on formaldehyde. The parent molecule is excited to a rovibronic state above the dissociation threshold. A degenerate four-wave mixing spectrum is recorded to monitor this process. After dissociation has occurred, the rotational state of the product molecule is probed by recording the fluorescence from a higher electronic state which is excited by the radiation of the second beam.

is the probability that the state \( J'_a K'_a \) will be converted to the probed rotational state \( N_{ka,k_c} \) of HCO at the excitation energy, \( E_{exc} \). The population of the species in the molecular beam is assumed to be Boltzmann-distributed with a rotational temperature \( T \):

\[
N(J''_a K''_a, J''_c K''_c) \propto (2J'' + 1) e^{-E_{rot}/kT}.
\]

(2.2)

In the case of the dissociation of formaldehyde to HCO and H, the probability for dissociation \( P(N_{ka,k_c}, J'_{ka,k'_a}; E_{exc}) \) from \( J'_{ka,k'_a} \) to \( N_{ka,k_c} \), is the product of the absorption cross-section \( \sigma \) to an excited state \( J'_{ka,k'_a} \) and the quantum yield for dissociation from that state to the observed HCO state \( N_{ka,k_c} \):

\[
P(N_{ka,k_c}, J'_{ka,k'_a}; E_{exc}) \propto \sigma(J'_{ka,k'_a} \leftarrow J''_{ka,k''_a}) \cdot \Phi(N_{ka,k_c}, J'_{ka,k'_a}, E), \tag{2.3}
\]

where \( E = E_{exc} + E_{rot}(J''_{ka,k''_a}) \), which corresponds to the total energy of the \( J''_{ka,k''_a} \) above the rovibronic ground state. The absorption cross-section \( \sigma(J'_{ka,k'_a} \leftarrow J''_{ka,k''_a}) \) can be obtained from a spectral simulation as \( |\mu(J'_{ka,k'_a} \leftarrow J''_{ka,k''_a})|^2 \) or better, from a simultaneously recorded DFWM signal. The rotational temperature \( T \), which is needed for the simulation, has to be determined from an experiment anyhow as it is sensitively dependent on the optimization of the experimental setup which is in general carried out between the acquisition of two spectra. Under certain circumstances the square-root of the DFWM signal intensity is proportional to the number density of molecules in the ground state times the absolute square of the transition dipole moment \( |\mu(J'_{ka,k'_a} \leftarrow J''_{ka,k''_a})|^2 \).

This is explained in Chapter 5. The photofragment yield \( \Phi \) is then given by the ratio of the PHOFEX signal and the square root of the DFWM signal (see Equation 5.1):

\[
\Phi \propto \frac{S_{PHOFEX}}{N(J''_{ka,k''_a})|\mu(J'_{ka,k'_a} \leftarrow J''_{ka,k''_a})|^2} \propto \frac{S_{PHOFEX}}{\sqrt{4}}. \tag{2.4}
\]
In Chapter 4, the dissociation from two vibrational levels of the \( \tilde{\text{A}}^1\text{A}_2 \) state of \( \text{H}_2\text{CO} \) above the threshold for the radical channel are investigated with PHOFEX.

## 2.2 Two-color resonant four-wave mixing

The formalism for two-color resonant four-wave mixing (TC-RFWM) is essentially the same as for degenerate four-wave mixing, which has been explained in the previous chapter. The third-order susceptibility must be expressed for a different set of frequencies \( \omega_1, \omega_2 \) and \( \omega_3 = \omega_1 \), thus the frequencies of the incident light can be resonant with two distinct transitions in the medium. This allows three different excitation schemes, which are depicted in Figure 2.2.

**Figure 2.2** Excitation schemes for two-color resonant four-wave mixing (TC-RFWM). The first panel depicts the \( V \)-excitation scheme, which is suitable for the investigation of the vibrational and rotational structure of electronically excited states. The process depicted in the second panel, the \( \Lambda \)-scheme, is stimulated emission pumping (SEP) by TC-RFWM, which can be used as a tool to study highly excited vibrational levels of the electronic ground state. The third panel shows the \( \Xi \)- or unfolded excitation scheme which is appropriate to analyze higher lying electronic states, such as Rydberg states.

The process corresponding to the excitation scheme shown in Figure 2.2 (a) requires that the wavenumbers of the interacting waves are in resonance with two transitions \( e' \leftrightarrow g'' \) and \( e'_1 \leftrightarrow g'' \), which share a common rotational level in the electronic ground state \( g'' \). With this choice the level \( g'' \) can be labeled and only a small number of rotational levels \( e'_1 \) in the excited state can be accessed. Note that in principle the excited electronic state can also be an excited rovibrational level of the electronic ground state. However, in this work we consider only transitions between different electronic states. This excitation scheme is sometimes called \( V \)- or UP excitation scheme (see e.g. in Ref.[17]).

The second process (Figure 2.2(b)) is called folded TC-RFWM or \( \Lambda \)-excitation scheme. Here, the common state is a rotational level \( e' \) in the excited state. With this type of experiment stimulated emission pumping spectroscopy can be performed, which enables the characterization of highly excited vibrational levels of the electronic ground state \([18, 19, 4]\).

The use of the unfolded TC-RFWM or \( \Xi \)-excitation scheme (Figure 2.2(c)) allows the
accession of higher excited states such as Rydberg states. One transition is from $g''$ to an excited rotational level $e'$. From there, the highly excited rotational level $f$ can be accessed.

In general, one refers to the two electric fields with the same angular frequency as PUMP whereas the other is called PROBE. In section 1.3, where degenerate four-wave mixing was described qualitatively, we were speaking of a population grating which is formed in the medium because of the superposition of two fields which are in resonance with a transition of the medium. A third field which is diffracted from that grating produces the signal field. This qualitative description also holds for TC-RFWM but it would imply that the two PUMP fields must be in resonance with the first transition of the process, such that a grating can be formed. However, the qualitative description contains only a portion of resonant four-wave mixing processes. For example, when the PUMP fields are in resonance with the second transition and the PROBE field with the first transition a coherent process occurs which yields a contribution to the third-order susceptibility $\chi^{(3)}$ from Equation 1.8.

### 2.3 Double-resonance multiphoton ionization

Multiphoton ionization (MPI) involves, as its name already suggests, the ionization of a molecule by the absorption of more than one photon. The process can be written as:

$$M_g + n\tilde{\nu} \rightarrow M^+ + e^-,$$

where $M_g$ and $M^+$ are the molecule and the ion of interest, and $n$ is the number of photons of wavenumber $\tilde{\nu}$ necessary for the ionization of the molecule. Fields with high intensities are required for multiphoton absorption processes. The excitation cross-sections decrease strongly with increasing number of absorbed photons. The cross-section of the ionization process is considerably increased if there is a real excited state resonant at the energy of one or two absorbed photons. The resonance-enhanced multiphoton ionization (REMPI) technique typically involves the absorption of one or more photons to an electronically or vibrationally excited intermediate state followed by the absorption of one or more photons which ionize the molecule. By monitoring the photoionization yield while the laser is scanned, a spectrum corresponding to absorption to the resonant state is obtained.

There is a variety of multiphoton ionization excitation schemes for the investigation of resonant transitions to excited states in atoms and molecules, four of which are shown in Figure 2.3: (a) conventional one color MPI without resonance enhancement, (b) one-color MPI that is resonance enhanced at the energy of one photon, (c) one-color MPI resonance enhanced at the 2-photon energy, and (d) two-color double-resonance-enhanced (or just double-resonance) MPI.

The resonance-enhanced excitation schemes enable the spectroscopic characterization of
Chapter 2 Double-resonance spectroscopic techniques

The states at resonance. For instance, highly excited electronic states, for example Rydberg states, can be investigated. If the excitation scheme in Figure 2.3 (b), (1+1)-REMPI, is used, usually wavenumbers in the vacuum ultraviolet (VUV) are required. Moreover, one photon transitions to some states are symmetry forbidden thus preventing the excitation. This can be overcome by applying a two photon excitation scheme as in panel (c) of Figure 2.3, for which different selection rules from those for a one photon transition apply. The probability of a two photon excitation can be increased if an additional intermediate real state at resonance $i$ is accessed. Double-resonance MPI, as shown in panel (d) of Figure 2.3 is achieved by the adequate choice of the wavenumbers of the two photons needed for the excitation and both transitions from $g$ to $i$ and from $i$ to $e$, respectively, must be allowed. In order to characterize the excited state $e$, the wavenumber of the first photon is fixed at $\tilde{\nu}_1$ while $\tilde{\nu}_2$ is scanned.

Resonance-enhanced MPI is a very sensitive spectroscopic technique because measuring the ion yield allows the detection of single ions. Moreover, if REMPI is used in combination with time-of-flight (TOF) detection, it is a mass selective technique. A virtue of resonance enhanced MPI spectroscopy is that many different excitation schemes are applicable thus enabling to address excited quantum states which might be difficult to be accessed otherwise. The double-resonance variant exhibits an increased two-photon excitation probability and is, in addition, very selective. In a rotationally resolved experiment only few transitions arise due to the preselection of a rotational level by the first excitation, similar to labeling a state in TC-RFWM.

Figure 2.3 Four possible multiphoton ionization excitation schemes: (a) conventional MPI without intermediate resonances, (b) one-color MPI with resonance enhancement at the energy of one photon, (1+1)-REMPI, (c) one-color two photon resonance-enhanced MPI, (2+1)REMPI, (d) two-color double-resonance MPI, $(1 + 1') + 1''$ REMPI.
Chapter 3

Experimental

In this chapter the experimental tools used in this work are explained. First, the molecular beam apparatus and the sources of the investigated molecular species are described. The next sections focus on the experimental realization of the spectroscopic techniques described in Chapters 1 and 2, namely four-wave mixing, cavity ring-down, laser-induced fluorescence and resonance-enhanced multiphoton ionization.

3.1 The molecular beam apparatus

In this section, the molecular beam apparatus and the source of the investigated molecular species will be explained. For the experiments on formaldehyde, a heatable valve is needed. The production of C$_3$, on the other hand, requires the implementation of a DC-discharge. In addition to C$_3$ a variety of hydrocarbons is formed necessitating the characterization of the source by mass spectrometry.

In Figure 3.1 the molecular beam apparatus is depicted schematically. A molecular beam is generated by a supersonic expansion of a gas through a pulsed valve which is mounted on an $xyz$-translation stage. The source holder can be resistively heated by two separate heating loops (Thermocoax) for the generation of gases which at room temperature and atmospheric pressure are solid or liquid and exhibit low vapor pressures. For example, internally cold H$_2$CO can be produced by heating a sample of para-formaldehyde, a solid polymer, to $\approx 350$ K to liberate the monomer [20] which is subsequently co-expanded with a noble gas, e.g. helium, argon or krypton, at backing pressures behind the valve of 0.5 to 3 bar. The valve, which is also heatable [21], is operated at 10 Hz and creates a pulse of $\approx 500$ s duration.

Transient species, for example C$_3$, can be produced with the application of a DC-discharge. The pulsed discharge nozzle, which is constructed in a similar way as discharge sources in the literature [22, 23, 24], is described in detail in Ref. [25]. It consists of a pulsed valve (General Valve, Parker, 1 mm orifice) and a discharge fixture which is attached to the housing of the valve. The two electrodes located in front of the valve are insulated from each other and the valve with Macor. A typical experimental procedure for the production of C$_3$ starts with a trigger to the solenoid valve to expand $\approx 5\%$ of a precursor (acetylene or cyclopropane) diluted in argon. At a variable time after the initial trigger for the valve, a well-defined high-voltage pulse of $\approx 800$ V and adjustable duration is
applied to the discharge electrodes. A careful optimization of the voltage, trigger delay, trigger duration and polarity yields an intense and remarkably stable molecular beam. Rotational temperatures depend strongly on these adjustable parameters and are in the range of 10 to 100 K. Similar discharge sources have been applied to generate a significant abundance of transient and charged species [26, 22]. The molecular beam propagates into the vacuum chamber pumped by a 1400 l/s turbo pump (Pfeiffer TPH 1501P). During operation the pressure in the chamber is typically \( \approx 10^{-5} \) mbar. All spectroscopic techniques are performed by perpendicular crossing of the laser beams and the molecular beam. The interaction occurs at roughly 2 cm downstream from the nozzle/discharge exit.

An advantageous technique to characterize the discharge source is mass spectrometry by applying femtosecond ionization. The ultrashort pulse width combined with the high intensity (\( \approx 10^{15} \) W/cm\(^2\)) of the light source enables an excitation above the ionization threshold on a time scale comparable to that of the nuclear motion. The electric field generated by the laser pulse is \( E_0 = \sqrt{2I/e\epsilon_0} \) where \( E_0 \) is the electric field strength in V/m, and \( I \) is the intensity of the laser beam (in W/m\(^2\)). Thus, the laser intensity corresponds to an electric field strength of \( \approx 8.7 \) V/\( \AA \) which is sufficient to ionize most molecules [27]. The Ti:sapphire laser system makes use of the chirped pulse amplification (CPA) technique and produces bandwidth-limited output pulses of 100 fs and a bandwidth of 9 nm. Typical pulse energies are 250 J at a wavelength centered around 780 nm. The femtosecond pulses are focused into the ionization region of the source chamber to a diameter of \( \approx 20 \) m and intersect the supersonic molecular beam containing the neutral species produced by the radical source. The ions formed in the ionization process are accelerated in an electric field and directed through the first field-free region toward the reflector.
Ions are then reflected and travel through the second field-free region and are detected by a Daly detector. The resolution of the mass spectrometer, $m/\Delta m$, is typically 3000 at $m/z = 200$, where $m$ is the mass of the ion in atomic mass units (amu) and $z$ its charge number.

In comparison to electron impact, another mass spectrometric technique widely used, femtosecond ionization does not produce the unfavorable effect of fragmentation due to collisions with high energy electrons. In addition, excited molecules in intermediate states may dissociate prior to ionization (ladder ionization). However, it is important to mention that fragmentation can also take place by fs-ionization if the ion is unstable. The mass spectrum obtained by electron impact does not represent the mass distribution of the neutral molecules in the beam. Alternatively, single photo-ionization (SPI) by nanosecond laser pulses in the VUV ($\geq 10$ eV) can be applied to ionize a large number of species to yield molecular ions without fragmentation [28]. However, SPI with VUV photons is a technically demanding method and requires the knowledge of the ionization threshold. Multiphoton ionization in the visible or UV leads in general to a strong fragmentation. An excitation to an intermediate state will distribute energy into internal degrees of freedom and possibly dissociation occurs within nanoseconds and before the ionization step takes place. Mass spectra recorded with ultrashort laser pulses are generally less affected by unimolecular dissociation and therefore are better suited for the production of an intact molecular ion from a neutral parent [29, 27, 30].

Figure 3.2 shows a mass spectrum obtained by femtosecond ionization of $\approx 5$ % cyclopropane diluted in Ar at 1.5 bar backing pressure. The upper trace, which is obtained when no DC-voltage is present shows that fragmentation does not occur when this technique is applied. The loss of a single hydrogen is observed but negligible. The lower trace shows the fs-ionization mass spectrum of the cyclopropane precursor when the high-voltage pulse is applied to the discharge assembly. The graph clearly demonstrates the production of several carbon clusters, $C_n$, $n \leq 7$ and their corresponding hydrogenated complements in the discharge source. The ions are mainly formed from the neutral molecules emerging from the source even though a small contribution from the dissociation of small hydrocarbon ions following a field ionization mechanism cannot be excluded completely [29, 31].
Figure 3.2 Characterization of the discharge source by femtosecond ionization mass spectrometry. Mass spectra of cyclopropane obtained without (upper trace) and with (lower trace) an applied voltage of $\approx 800$ V. Fragmentation is mostly suppressed if femtosecond ionization is used, therefore only the peak corresponding to the mass of cyclopropane is present in the upper trace. The lower trace shows that several types of hydrocarbons with the general formula $C_nH_m$ are produced.

3.2 Setup for resonant four-wave mixing experiments

The DFWM setup which is depicted in Figure 3.3 is also described in Refs. [19, 32, 2]. The laser system consists of one or two dye lasers (narrow scan, Radiant Dyes) pumped by the second or third harmonic of one or two Q-switched Nd:YAG lasers (Quanta Ray PRO-270 and BMI) pulsed at 10 Hz. To obtain the desired wavelengths around 405 nm for the experiments on $C_3$ the dye laser is operated with methanol solutions of Exalite 405 laser dyes. For the experiments on the $^1A_2-^1A_1$ transition in formaldehyde, the used laser dye is DCM solved in DMSO. Wavelengths at 520 to 535 nm, which are necessary for the detection of the HCO fragments, are obtained using Coumarin 152 laser dye in methanol or ethanol. The output of the dye-lasers is then frequency-doubled by using $\beta$-barium borate (BBO) crystals. In the spectral region of 310 to 340 nm, average pulse energies of $\approx 1$ to 2 mJ are obtained. For the DFWM experiment, the output of the dye laser is directed through a variable attenuator (Newport, M-935-10), that allows an arbitrary adjustment of the pulse energies. A spatial filter, and several iris diaphragms are employed to ensure a very homogeneous intensity distribution over the entire laser beam diameter. The laser beam is then split into three beams which are then focused through a quartz window into the molecular beam apparatus by a lens ($f=1000$ mm) to
establish a forward boxcars DFWM configuration. Variable wave-plates (Berek compensator, New Focus) can be introduced in the path of two beams to rotate the field vectors. This allows arbitrary configurations of the unit polarization vectors $e_n$, $n = 1, 2, 3, 4$. The polarization geometry is conventionally specified as $e_4e_1e_3e_2$, (e.g. YYYY, YXXX) under the assumption that the wave-vectors form a nearly collinear phase-matching geometry. The emerging four-wave mixing signal beam passes through a polarization analyzer and is re-collimated by a second lens ($f = 1000$ mm). It is allowed to propagate roughly 3 m through several apertures, optical and spatial filters to remove interfering scattered light and unwanted fluorescence. Further reduction of stray light is achieved by the introduction of a spatial filter consisting of a lens with 30 mm focal length and a 50 m pinhole in front of the photomultiplier tube. In order to allow the measurement of small and large signals linearly, a photomultiplier tube (PMT) with a large dynamic range (Hamamatsu H3177) is required. Additionally, the intensity of one input laser beam is monitored by recording the energy per pulse with an energy meter (LaserProbe RJ-7610) after its pas-
For the two-color resonant four-wave mixing experiment, the setup is altered only to a minor extent. The frequency-doubled output of one dye-laser is split into two almost copropagating PUMP beams 1 and 2. The typical half-angle of crossing for the two identical frequency beams is \( \approx 0.7 \) degrees. The second laser beam is directed towards the interaction region to establish a forward boxcars setup and is referred to as PROBE beam 3. The generated beam wave-vector \( \mathbf{k}_4 \) is defined by the phase-matching condition \( \mathbf{k}_1 + \mathbf{k}_3 = \mathbf{k}_2 + \mathbf{k}_4 \) where \( \mathbf{k}_i \) denotes the wave vector of the corresponding beam. The line width of the PUMP and PROBE beams is specified to be 0.04 cm\(^{-1}\). A digital oscilloscope (LeCroy LC564A) and a PC are used to acquire and store the data for further processing. A typical signal is usually averaged 20 times for each scan step (\( \approx 0.03 \) cm\(^{-1}\) increment). Absolute wavelength calibration of the dye lasers is achieved either with a wavemeter (in the beginning Burleigh WA-5500, accuracy 0.1 cm\(^{-1}\), and after the purchase in 2007, High Finesse/Angstrom WS6 with an accuracy of \( \approx 0.03 \) cm\(^{-1}\)) or an \( \text{I}_2 \) absorption spectrum is simultaneously recorded, if the wavelengths employed match the absorption regime of \( \text{I}_2 \) \cite{33}.

### 3.3 Setup for cavity ring-down experiments

Cavity ring-down spectroscopy can be carried out simultaneously to degenerate four-wave mixing and does not interfere with it at the level of our accuracy. The cavity ring-down configuration is set up at 45 degrees with respect to the DFWM laser beams and perpendicular to the molecular beam. Two dielectric-coated mirrors (Los Gatos, 415 nm, \( R = 99.995\% \) at 405 nm and \( R > 99.9\% \) in the ultraviolet (UV)) form the 70 cm long optical cavity. A three-point micrometer mount for each mirror allows the alignment of the cavity. The laser beam employed for CRD originates from a reflection of the laser beam used for the RFWM techniques. In general, 5% of the output of the dye-laser used for DFWM are sufficient for CRD spectroscopy. A small fraction of this beam (0.1 to 0.005%, depending on \( R \)) is injected by transmission through the first mirror into the cavity where its amplitude decays as the pulses oscillate within the resonator. The path of the laser beam intersects the free-jet approximately 15 mm downstream from the nozzle tip. This position is equivalent to the interaction region for the DFWM experiments. The light which is transmitted through the end mirror is frequency filtered (Schott, DUG 11X) to reject stray light and detected by a fast PMT. The decay transient is typically averaged over 20-30 laser pulses on the digital oscilloscope and transferred to the PC where a single exponential fit to the waveform is performed. An accurate absorption spectrum is obtained by measuring the ring-down time vs wavelength, which reflects the losses experienced by the light-pulse inside the cavity due to mirror reflectivity and mirror absorption, optical scattering and, most importantly, the molecular absorption.
3.4 Setup for laser-induced fluorescence experiments

LIF originating from the resonant four-wave mixing fields or, alternatively, from a separately introduced excitation field is collected at right angles to both the molecular beam and electric field propagation by a spherical aluminium mirror (diameter 60 mm, $r = 50$ mm, $f/25$). Subsequently, the parallel LIF beam is focused onto the slit of a 1 m length monochromator and detected by a PMT.

3.5 Setup for double-resonance multiphoton ionization experiments

The double-resonance multiphoton ionization (MPI) experiments were part of a collaboration with Anna M. Schulenburg in the group of Prof. F. Merkt and carried out at the Laboratory of Physical Chemistry at ETH Zürich. The molecular beam source is the same as described in Section 3.1.

The experimental MPI setup has been employed and explained in detail in Ref. [34]. In this experiment two tunable laser radiation sources are needed to permit addressing single rovibronic transitions in both excitation steps. For that purpose, two dye lasers (Lambda Physik Scanmate and ScanMate Pro utilizing DCM and Coumarin 153 dyes) are pumped by the second and third harmonic of a pulsed Nd-YAG laser (Quan tel YG 981 E, $16.2\frac{2}{3}$ Hz). The output of the dye lasers at $\approx 660$ nm and $\approx 534$ nm is frequency-doubled with $\beta$-barium borate (BBO) crystals. The laser beams are guided collinearly into the vacuum chamber where they intersect the molecular beam at right angles. The produced ionized species is subsequently accelerated perpendicular to both the molecular beam and the laser beam by an electric field of 400 V/cm, which is provided by a set of six equally spaced cylindrical extraction plates housed in two concentric mu-metal cylinders. The ions are detected by a microchannel plate (MCP) detector at the end of a flight tube. The resistively coupled extraction plates provide a particularly homogeneous electric field in the extraction zone. The presence of the mu-metal cylinders prevents the interference of the ions with external magnetic fields, which are effectively shielded.

Also here, a digital oscilloscope and a PC are used to acquire and store the data for further processing. A typical signal is averaged 10-20 times for each scan step ($\approx 0.14$ cm$^{-1}$ increment). For absolute calibration, a wavelength meter (High Finesse/Angstrom WS6) with an accuracy of $\approx 0.03$ cm$^{-1}$ is employed. For support, a Ne/Fe spectra from an optogalvanic cell is recorded simultaneously to validate the absolute wavelength calibration of the wavelength meter.
Part II

Degenerate Four-Wave Mixing Experiments
Chapter 4

Photofragment excitation spectroscopy: Dissociation of $\text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}$

Whereas the molecular dissociation channel of formaldehyde, $\text{H}_2\text{CO} \rightarrow \text{CO} + \text{H}_2$ has received much attention over the years [35, 36], only recently interest has been drawn onto the radical channel $\text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}$ [37, 38, 39, 40]. The threshold for this reaction has been determined to be at $\tilde{\nu} = (30327.6 \pm 0.9)$ cm$^{-1}$ above the ground state [41] and is located about 2600 cm$^{-1}$ above the threshold for the molecular channel. Photofragment excitation spectroscopy is a favorable tool for rotational state-to-state analysis of the dissociation process. In this chapter, we want to examine the occurrence of a dissociation product in a specified quantum state, in this work HCO in a defined rotational level $N_{k_a,k_c}$, depending on the excitation of the parent molecule to a specified quantum state above the dissociation threshold, which here is H$_2$CO in a rotational state $J'_{K_a',K_c'}$ of a vibronic level $\tilde{A}^1A_2 2^14^3$ or $\tilde{A}^1A_2 2^34^1$. The excitation of the parent molecule is surveyed by recording DFWM spectra of the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ transition provided that a quantitative statement about the population of the excited state with DFWM spectroscopy can be made. The occurrence of the nascent HCO in a specific rotational level $N_{k_a,k_c}$ is detected by collecting the fluorescence from a higher-lying level to which HCO is excited from $N_{k_a,k_c}$ by the radiation of a second laser. The fluorescence from the excited level is then proportional to the population of $N_{k_a,k_c}$.

In the first section the emphasis is put on obtaining DFWM spectra of the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ transition and the comparison with simulated spectra. The ensuing part examines PHOFEX spectroscopy of the radical dissociation channel of formaldehyde via excitation of the vibronic levels $\tilde{A}^1A_2 2^14^3$ and $\tilde{A}^1A_2 2^34^1$. This work is part of Ref. [42]. There, the PHOFEX yields were compared with three statistical models for dissociation, in particular the Prior model, phase-space theory [43] and the statistical adiabatic channel model [44].

4.1 Introduction

The spectroscopy and photochemistry of formaldehyde have been investigated for a long time, primarily due to its importance in atmospheric chemistry [45]. Formaldehyde con-

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1To enable a better distinction from $\text{H}_2\text{CO}$, for HCO lower case letters are used to denote the asymmetric rotor labels $K_a$ and $K_c$. 

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stimates an intermediate product in the oxidation cycle of methane [46]

\[ \text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2 \] (4.1)

as well as of other hydrocarbon compounds, in both, high-temperature combustion processes and photochemical oxidation. Thus, combustion of biomass [47], forest fires, and incomplete fuel combustion in vehicles [48, 49] are a source of formaldehyde.

Consisting of only four nuclei, formaldehyde is tractable to a high level of theory and hence, it represents a meeting point for theory and experiment. For instance, already in 1934, Dieke and Kistiakowsky [50] succeeded in the analysis of the the rotational subband structure of several vibronic transitions in the \(^1\text{A}_2-\bar{\text{X}}^1\text{A}_1\) band system, which is recognized as the first interpretation of the electronic spectrum of a polyatomic molecule. Two detailed review papers on the spectroscopy of formaldehyde by Moule and Walsh [51], and Clouthier and Ramsay [52] are available. Here, we will only summarize the most important characteristics of the \(^1\text{A}_2-\bar{\text{X}}^1\text{A}_1\) transition, which are relevant in this chapter.

Formaldehyde is planar in the ground state and belongs to the \(C_{2v}\) point symmetry group. The inertial axes of the near prolate asymmetric rotor are shown in Figure 4.1. The first excited electronic singlet state has a nonplanar structure, but the \(C_{2v}\) point group can be used to label the electronic state because the lowest vibrational level lies above the barrier between the two minima in the potential energy curve along the \(\nu_4\) out-of-plane bending coordinate (see Ref. [53]). The electronic ground state \(\bar{\text{X}}\), which is also denoted as \(S_0\), is of \(A_1\) symmetry, the first excited singlet state \(\text{A}\), or \(S_1\), of \(A_2\) symmetry. The transition from \(\bar{\text{X}}^1\text{A}_1\) to \(\text{A}^1\text{A}_2\) is electric-dipole forbidden because the \(A_2\) irreducible representation is the only one not associated with one of the components of the transition dipole momentum vector. The excitation of vibrational modes in the \(\text{A}^1\text{A}_2\) state with symmetry \(B_1\) or \(B_2\), which comprises the \(\nu_4\), the \(\nu_5\) and the \(\nu_6\) modes, are allowed vibronically by Herzberg-Teller coupling, however. The weak appearance of the \(\text{A}^1\text{A}_2-\bar{\text{X}}^1\text{A}_1\) transition consists of progressions in the absorption spectrum involving the excitation of an uneven number of quanta of the out-of-plane bending (\(\nu_4\)) mode, which is excited in combination with any number of quanta of the CO-stretching (\(\nu_2\)) mode. The most intense vibronic transitions are of the form \(2^n\nu_4\) and \(2^n\nu_5\), and a little less intense, \(2^n\nu_6\), where transitions to levels \(2^n\nu_4\) with \(n\) up to 4 bear considerable intensity [54, 52, 55].

The photodissociation of formaldehyde is an interesting system to study from a molecular dynamics perspective because it involves at least three dissociation channels. After excitation to a rovibrational level of the \(\text{A}^1\text{A}_2\) state above the threshold the photodissociation processes occurs either by subsequent fast internal conversion to the electronic ground state or by intersystem crossing to the triplet state \(\bar{\text{a}}^3\text{A}_2\), which is also denoted as \(T_1\). The \(\text{A}^1\text{A}_2\) state is not dissociative at these energies, so the dissociation occurs from either \(\bar{\text{X}}^1\text{A}_1\) or \(\bar{\text{a}}^3\text{A}_2\). There are three major dissociation channels. The reaction with the lowest threshold at
\( \approx 27720 \ \text{cm}^{-1} \) is the molecular channel

\[ \text{H}_2\text{CO} \rightarrow \text{CO} + \text{H}_2 \]  \hspace{1cm} (4.2)

which competes with the radical-forming dissociation

\[ \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}. \]  \hspace{1cm} (4.3)

occurring at wavenumbers higher than \( \approx 30328 \ \text{cm}^{-1} \) [38, 37]. While the molecular channel occurs only via the \( S_0 \) surface, the radical channel can occur via both \( S_0 \) and \( T_1 \). Despite the importance of these reactions for the modeling of combustion processes some of their rate constants are not yet well established, in particular in the region where these two dissociation channels compete [5]. Below the threshold of the radical channel, dissociation via the molecular channel prevails, whereas dissociation via the radical channel is preferred when the triplet state opens up [35]. The branching ratio depends on the rotational level in the excited state of formaldehyde. Therefore, it is important to investigate the competition of these channels in rotationally resolved state-to-state experiments.

Recently, it has been shown that molecular products are also formed via a third channel of the intramolecular hydrogen-abstraction type, the so-called “roaming atom pathway” [57, 58].

\[ \text{H}_2\text{CO} \rightarrow \text{H} \cdots \text{HCO} \rightarrow \text{CO} + \text{H}_2. \]  \hspace{1cm} (4.4)

This channel is accessible only at and above the threshold energy of the molecular channel in Equation 4.3 and has dynamical properties which distinctly differ from the latter channel. In this chapter the radical channel will be investigated. The relevant potential energy curves are presented in Figure 4.2.
Chapter 4 Photofragment excitation spectroscopy: Dissociation of H$_2$CO → HCO+H

4.2 DFWM of the $2^{1}4^{3}_{0}$ vibrational band in the $\tilde{A}^{1}A_{2} - \tilde{X}^{1}A_{1}$ transition of H$_2$CO

The spectroscopic properties of the $2^{1}4^{3}_{0}$ band in the $\tilde{A}^{1}A_{2} - \tilde{X}^{1}A_{1}$ transition of formaldehyde are well known [52]. The rotational branch structure corresponds to $b$-type transitions with the transition moment lying in the H$_2$CO molecular plane but perpendicular to the CO axis ($a$-axis). The $b$-type selection rules for an asymmetric rotor are $\Delta J = 0, \pm 1$, $\Delta K_a = \pm 1$ and $\Delta K_c = \pm 1$. The nomenclature $J_{K_a,K_c}$ is used to label the rotational states, where $J$ is the total angular momentum and $K_a$ and $K_c$ are its projections on the $a$ and $c$ molecular axes, respectively. The rotational levels of HCO are denoted by $N_{K_aK_c}$, and $N$ is the rotational angular momentum. The total angular momentum $J$ includes also the spin, which is 1/2 for HCO. The asymmetric rotor nomenclature $\Delta K_a \Delta J_{K''_aK''_c}(J'')$ is used to label rotational transitions.

A typical DFWM spectrum in the range of $\approx 30320 - 30370$ cm$^{-1}$ recorded with a laser resolution of 0.04 cm$^{-1}$ is presented in Figure 4.3. The square root of the original DFWM signal of the $2^{1}4^{3}_{0}$ band in the $\tilde{A}^{1}A_{2} - \tilde{X}^{1}A_{1}$ transition of H$_2$CO is shown (dotted). The rotational absorption spectrum is simulated by taking into account line positions and Hön-London factors from the pgopher program package [59] with the relevant rotational constants for the ground and excited states taken from the literature [52]. The line positions and intensities are convoluted with a Lorentz-cubed line-shape [60] with a full width at half maximum (FWHM) of 0.2 cm$^{-1}$. The ground-state populations are obtained by assuming a Boltzmann distribution and performing a fit to the spectrum which yields the rotational temperature. In fact, the final temperature of the species in the molecular beam depends sensitively on the expansion conditions (i.e. backing pressure, H$_2$CO/He mixture and nozzle temperature) and can change from one experiment to the next. Moreover, a
Figure 4.3 A degenerate four-wave mixing spectrum of the $^2\Pi_{0}^{+}\Delta_{0}^{3}$ vibrational band of the $A^1A_2-X^1A_1$ electronic system of formaldehyde. The square-root of the DFWM signal is plotted (dotted trace). For comparison, a simulation is shown (solid trace). The line positions and intensities are computed with pgopher [59]. The simulation takes into account a Boltzmann population distribution at 8.6 K. The intensities of the transitions with $K''_{a}=0$ have been enhanced by a factor of 2.5 because para- ($K''_{a}=0$) and ortho- ($K''_{a}=1$) formaldehyde are not completely interconverted during the supersonic expansion.

A second fit parameter, which takes into account the nuclear spin conversion during expansion, must be implemented to yield a sufficient agreement with the experiment. Actually, ortho- ($K_{a}=0$) and para- ($K_{a}=1$) formaldehyde are not completely interconverted upon supersonic expansion and the final ratio of the nuclear spin in the beam must be determined for the specific conditions in the free jet. An enhancement of transitions with $K''_{a}=0$ (para states) by a factor of 2.5 in comparison to non-interconverted species is observed in the measured spectra [61].

4.3 PHOFEX studies of the radical dissociation channel of $H_2CO$

The experimental setup described in Chapter 3 is suitable for two types of experiments: (i) the measurement of product state distributions and (ii) photofragment excitation spectroscopy (PHOFEX). Product state distributions of nascent HCO molecules can be observed by tuning the DFWM laser to a specific rovibronic transition of $H_2CO$ above the dissociation threshold and scanning the LIF laser in the region of the $\tilde{B}^2A' - \tilde{X}^2A'(000)$ band. For this type of experiments, a single excitation laser is sufficient and a DFWM setup is not required. These types of experiments have been performed extensively on $H_2CO$ by the group of Kable in Refs. [41, 37, 62, 63, 64]).
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Figure 4.4 PHOFEX spectra of the dissociation of H$_2$CO to HCO+H after excitation to the $\tilde{A}^1A_2$ $2^14^3$ level. The bottom trace is an inverted DFWM spectrum of the $2_1^14_0^3$ band of the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ transition. PHOFEX spectra are recorded for several different probed states $N_{k_a k_c}$ of HCO, which are indicated on the left side. On the top, the rotational states $J'_{K_a' K_c'}$ of H$_2$CO in the $\tilde{A}^1A_2$ $2^14^3$ state are listed.

Alternatively, photofragment excitation spectra can be obtained by observing the LIF signal from an excited rotational level in HCO and tuning the DFWM laser frequency in the range of a selected vibrational band of the the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ electronic transition of formaldehyde. The result reflects the probability for dissociation into the probed HCO state. As will be shown below, the simultaneously recorded DFWM spectra are advantageous for referencing the PHOFEX data and providing sensitive information on the relative HCO quantum yield.

In this work, PHOFEX spectra are obtained for the radical dissociation channel of formaldehyde via excitation to the $2^14^3$ and the $2^34^1$ level in the $\tilde{A}^1A_2$ state. In Figure 4.4, a set of PHOFEX spectra is presented. The bottom trace shows a simultaneously acquired DFWM spectra of the $2_1^34_0^3$ band in the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ transition, which will be essential to quantify the PHOFEX data. In fact, a DFWM trace is recorded every time a PHOFEX experiment is carried out. For the sake of clarity in the graph, only one DFWM
trace is displayed as a representative. The upper traces show PHOFEX spectra of the probed rotational levels \( N_{ka_k c} \) in the electronic ground state of HCO which are listed on the left side of the image. The lowest PHOFEX trace is obtained by tuning the second laser to the \( ^{r}R_{00}(0) \) transition of HCO at 38697.8 cm\(^{-1}\), therefore \( N_{ka_k c} = 0_{00} \) is probed. In fact, one would have to distinguish between the doublet arising from the coupling of the spin of the unpaired electron \( S = 1/2 \) to the rotation, \( J = N \pm S \). However, the splitting of those two levels is not sufficiently large to be resolved, thus, both spin-rotation levels are probed simultaneously. In Ref. [41, 37] product distributions with the same \( N, k_a \) and \( k_c \) but different projection of \( S \) are found to be essentially equal.

In the same manner as described above, the levels 1\(_{01}\), 2\(_{02}\), 3\(_{03}\) and 4\(_{04}\) are probed by exciting the \( ^{r}R_{01}(1), ^{r}R_{02}(2), ^{r}R_{03}(3) \) and \( ^{r}R_{04}(4) \) transitions at 38699.5 cm\(^{-1}\), 38700.6 cm\(^{-1}\), 38685.0 cm\(^{-1}\), and 38680.4 cm\(^{-1}\), respectively. At the top of the figure, the rotational levels of \( H_2CO \) \( J'_{K_a'K_c'} \) that are accessed upon excitation are indicated.

![Figure 4.5](image)

*Figure 4.5* Energy level diagram of \( H_2CO \) \( \tilde{A}^1A_2 \) \( 2^14^3 \) and the electronic ground state of HCO. The \( H_2CO \) \( 0_{00} \) level is offset by 11.7 cm\(^{-1}\) with respect to the HCO \( 0_{00} \) level [37].

The energy level diagram in Figure 4.5 reveals which rotational levels \( N_{ka_k c} \) in HCO are accessible after excitation to a specific rotational state \( J'_{K_a'K_c'} \) of the \( \tilde{A}^1A_2 \) \( 2^14^3 \) state. The available energy is the difference of the term energy of the excited level and the dissociation threshold. Thus, the available energy ranges from 11.7 cm\(^{-1}\) to 49.8 cm\(^{-1}\).

Considering the conservation of energy, HCO can be produced in the rotational ground state \( 0_{00} \) from any rotational level in \( \tilde{A}^1A_2 \) \( 2^14^3 \). In that case we could expect that the intensities of the corresponding transitions are comparable in the PHOFEX and DFWM spectra. A survey of the lowest PHOFEX trace in Figure 4.4 reveals that this assumption is not valid; instead, the presence of dynamical constraints governs the \( 0_{00} \) product formation of the unimolecular dissociation of formaldehyde.

A qualitative investigation of the PHOFEX trace for \( N_{ka_k c} = 0_{00} \) in Figure 4.4 shows that the strongest peaks arise for \( J'_{K_a'K_c'} = 1_{01} \), whereas the overlapping transitions to \( J'_{K_a'K_c'} = 0_{00}, 3_{03} \), and \( 2_{21}, 2_{20} \), respectively, exhibit the largest intensities in the DFWM spectra. An interesting effect arises for excitation to levels with \( K_a' = 1 \): whereas no nascent HCO with \( N_{ka_k c} = 0_{00} \) is observed when levels with \( K_c' = J - K_a' \) are excited, a notable contri-
bution comes from the levels with $K'_c = J + 1 - K'_a$.

Only few peaks arise in the upper PHOFEX trace, where $N_{k_ak_c} = 4_{04}$ is probed. The products arise only from H$_2$CO which is excited to levels with $K'_a = 2$. A look at the energy level diagram in Figure 4.5 reveals that the excess energy after excitation to levels with lower $K'_a$ is not sufficient to populate HCO levels with $N_{k_ak_c} = 4_{04}$.

Figure 4.6 PHOFEX spectra of the dissociation of H$_2$CO to HCO+H after excitation to the $\tilde{A}^1A_2$ 2$^3$4$^1$ level. The inverted trace at the bottom depicts a simultaneously recorded DFWM spectra of the 2$^3_0$4$^1_0$ transition. A remarkable feature in all PHOFEX spectra is the large intensity of peaks for $J'_{K'_aK'_c} = 4_{04}$.

In Figure 4.6 PHOFEX spectra for dissociation via excitation of H$_2$CO to the higher-lying $\tilde{A}^1A_2$ 2$^3$4$^1$ are shown. Again, at the bottom one simultaneously obtained DFWM trace is shown. Due to the fact that the excess energy is now large enough to populate higher rotational states in HCO, more PHOFEX traces can be recorded. Levels with rotational
angular momentum quantum numbers up to 8 are probed. In all PHOFEX traces, large peaks are observed for dissociation from $J'_{K'_aK'_c} = 4_04$, the corresponding peaks are highlighted in gray. Considering only the PHOFEX traces, the probed product states seem to arise also from dissociation from other rotational levels of H$_2$CO but the presentation of only the DFWM and the PHOFEX spectra does not reveal all effects in a straightforward manner. A different presentation of the results will later reveal that this is a special case.

A useful method to quantify the results of the PHOFEX experiments is the display of the quantum yields of the dissociation process as explained in Chapter 2 at page 14. The quantum yield for a process H$_2$CO $J'_{K'_aK'_c} \rightarrow$ HCO $N_{k_a k_c}$ is obtained by dividing the integrated intensity of a peak in the PHOFEX spectra by the square-root of the integrated intensity of the corresponding DFWM peak. This procedure is justified provided that $I_{\text{DFWM}} \propto |\mu_{ge}|^{4} \cdot N_{0}^{2}$ (this will be shown in the next chapter). For these evaluations, the DFWM spectra which were obtained at the same time as the PHOFEX spectra are taken into account to determine the populations of the levels. Note that in general, a specific rotational level $J'_{K'_aK'_c}$ of the parent molecule is excited by more than one transition within one vibrational band. For example, the 3$_{03}$ level in the $\tilde{A}^1 \Delta_{2} 2^1 4^3$ state is accessible by three transitions, i.e. $^pP_{11}(4)$, $^pQ_{12}(3)$, and $^pR_{12}(2)$ at 30321.1 cm$^{-1}$, 30329.5 cm$^{-1}$ and 30337.5 cm$^{-1}$, respectively. Populations derived from isolated transitions are found to be similar and averaged in the procedure. Additionally, good estimations for populations for spectrally overlapped transitions can be often obtained. For example, the population of the 0$_{00}$ state, which is the upper level of the $^pP_{11}(1)$ transition and overlaps strongly with the $^pQ_{12}(3)$ transition to 3$_{03}$ at 30329.5 cm$^{-1}$, can be estimated as follows: the relative intensities of the $^pP_{11}(4)$ and $^pR_{12}(2)$ transitions which also lead to the 3$_{03}$ level can be determined directly because they do not overlap with other transitions. The fraction of the peak belonging to the overlapping transitions which corresponds to the excitation to 3$_{03}$ can be determined by comparison with the two other transitions, the remainder of the intensity is attributed to the transition leading to 0$_{00}$.

The results for the PHOFEX yields for dissociation via both vibronic levels, 2$^1 4^3$ and 2$^3 4^1$, are presented in part a) and b) of Figure 4.7, respectively. The probed rotational levels $N_{k_a k_c}$ are listed on the left side. For each probed state, two panels, one corresponding to $K'_a = 0$, the other to $K'_a = 1$ are shown. For $K'_a = 1$, the results for both components of the $K_a$-doublet, $K'_c = J' - 1'$ and $K'_c = J'$ are depicted within the same panel. Within one panel, the PHOFEX yields for all excited rotational levels with the same $K'_a$ can be compared.

The lower left panel should be understood in the following manner: After excitation of H$_2$CO to specific rotational states in the vibronic level $\tilde{A}^1 \Delta_{2} 2^1 4^3$ and subsequent dissociation via the radical channel, HCO arises as a product in the rotational level $N_{k_a k_c} = 0_{00}$ preferentially from $J' = 1$, if only states with $K'_a = 0$ are considered. No products with $N_{k_a k_c} = 0_{00}$ arise for $J' = 0$, production from $J' = 2 - 5$ is also negligible.

The panel for $N_{k_a k_c} = 0_{00}$ and $K'_a = 1$ gives account of the effect that has been discussed
earlier: whereas the nascent HCO arises from states with \( K'_c = J' \), and among those, preferentially from \( 3_{13} \), no production of HCO with \( N_{k_a k_c} = 0_{00} \) is observed for levels with \( K'_c = J' - 1 \). This is an interesting effect, because for a near-prolate rotor like formaldehyde, those energy levels are almost degenerate in energy. The only difference between those rotational levels is \( K'_c \), which means that the rotational angular momentum vector \( J \) points in a different direction in the molecular frame.

For the \( 1_{01} \) product states, significant population is produced by excitation to \( J'_{K'_a K'_c} = 1_{01} \) and \( 3_{03} \). A preference of a component of the \( K'_a = 1 \) doublet is not observed. In fact, both the high \( (K'_a + K'_c = J') \) and low energy states \( (K'_a + K'_c = J' + 1) \) show distinct propensities for the formation of a product state \( 1_{01} \).

The \( 2_{02} \) state of HCO, which is probed in the experiment leading to the next panel above, lies \( \approx 3 \) cm\(^{-1} \) below the rotational ground state \( 0_{00} \) of the \( 2^{14} \) vibrational level in H\(_2\)CO. Therefore, this state is still energetically accessible from all rotational states in the \( 2^{14} \) level. Products in the \( 2_{02} \) level are formed to a larger extent from the \( 2_{02} \) level in the parent. This effect suggests that the total angular momentum of H\(_2\)CO is passed on to the HCO fragment.
b) show an unexpected effect. Unlike in the ground state $\tilde{X}$, due to the fact that only low levels $N_{k_a k_c} = 3_{03}$ and $4_{04}$ are not accessible from all parent states. $N_{k_a k_c} = 3_{03}$ lies 0.7 cm$^{-1}$ below $J'_{K_a K_c'} = 2_{02}$, and $N_{k_a k_c} = 4_{04}$ is situated above $J'_{K_a K_c'} = 2_{11}$. Thus, it is no surprise that the products also arise to a higher extent from levels with higher $J'$ and that the quantum yield for formation from rotational levels below is zero. In fact, for $K'_a = 0$, the maximum formation of $N_{k_a k_c} = 3_{03}$ states arises from $J' = 3$, 4 and 5. $N_{k_a k_c} = 4_{04}$ is produced preferentially from $J' = 5$ for the $K'_a = 0$ states. Similar effects are observed for the production from $K'_a = 1$ levels.

The available energy provided for the excitation of the parent molecule to the $2^14^3$ band is limited to a few tenths of wavenumbers above the dissociation threshold for radical formation. On the other hand, the origin of the $\tilde{A}^1A_2 \ 2^24^1$ level at 31803.2 cm$^{-1}$ is situated 1474.8 cm$^{-1}$ above the dissociation threshold. Although, from energetic considerations, all product states are accessible, the PHOFEX yields for dissociation after excitation of H$_2$CO to the $\tilde{A}^1A_2 \ 2^24^1$ level (see Figure 4.7 b) show an unexpected effect. Unlike in the previous case, here all product states in HCO seem to originate preferentially from the same rotational level. For $K'_a = 0$ levels, a remarkable peak at $J' = 4$ is observed. Similar, but less pronounced, for $K'_a = 1$ the HCO product states arise mainly from $J'_{K_a K_c'} = 3_{12}$. A possible explanation for this striking effect is the nature of the radical dissociation process of formaldehyde. As mentioned earlier, after excitation to $\tilde{A}^1A_2$, dissociation occurs either after internal conversion to a highly excited vibrational level in the electronic ground state or after intersystem crossing to the triplet state. The threshold for dissociation via the first excited triplet state $\tilde{a}^3A_2$ is proposed to be slightly above the $\tilde{A}^1A_2 \ 2^24^1$ level. For a dissociative reaction proceeding via internal conversion to the electronic ground state $\tilde{X}^1A_1$ no barrier exists. Thus, a statistical distribution of nascent HCO yielding states with high $N$ is expected and has been verified [41, 37, 65, 63, 38]. The pathway for a fragmentation following an intersystem crossing to the $\tilde{a}^3A_2$ potential energy surface passes through a transition state. In fact, recorded product state distributions revealed lower rotational temperatures [63, 38, 66]. These two pathways compete above the threshold for participation of the triplet state and the dependence of the product state on the excitation of the parent molecule becomes crucial.

The matrix elements for internal conversion from the $\tilde{A}^1A_2$ to the $\tilde{X}^1A_1$ state are two orders of magnitude lower than those for intersystem crossing to the triplet state. On the other hand, the density of states in the $\tilde{a}^3A_2$ state is only 0.3/cm$^{-1}$ in the investigated region, whereas in the $\tilde{A}^1A_2$ state it is about 100/cm$^{-1}$. Moreover, the line widths of the rotational levels of $\tilde{a}^3A_2$ are relatively small [67, 38]. Consequently, the pathway via the triplet state is preferred if the excited rotational level in $\tilde{A}^1A_2$ is energetically degenerate with a rotational level in $\tilde{a}^3A_2$. However, due to the small density of states on the triplet surface, these degeneracies are scarce for small energies. Taking into account that the pathway via $\tilde{X}^1A_1$ produces HCO fragments with higher rotational quantum numbers at the present excitation energies, agrees well with the presented PHOFEX yields in Figure 4.7 b). Due to the fact that only low $N$ (0-8) rotational levels were probed, a negligible
amount of nascent HCO molecules is observed for excited levels except for $J'_{K_a' K_c'} = 4_04$ at 31823.81 cm$^{-1}$ and $3_{13}$ at 31822.85 cm$^{-1}$. From this we propose that these two levels are in resonance with triplet states. In the literature, the threshold for dissociation via $\tilde{a}^3A_2$ has been benchmarked in the region between 31800 cm$^{-1}$ and 32350 cm$^{-1}$ [67, 68]. Assuming that the process does not occur via tunneling through the barrier, a new upper boundary of the threshold can be specified to the wavenumber of the $3_{13}$ state at 31822.85 cm$^{-1}$.

4.4 Conclusions

With the use of PHOFEX spectroscopy the radical dissociation channel of formaldehyde was investigated in two threshold regions: first, after excitation to the $\tilde{A}^1A_2 2^14^3$ state at $\approx 13$ cm$^{-1}$ above the threshold for HCO production and second, after excitation to the $\tilde{A}^1A_2 2^34^1$ state, which is situated in the region of the so far not accurately known threshold for fragmentation via the triplet state. Propensities that enable the conclusion from which parent state a specific product state arises preferentially were presented in the form of photofragment yields. These were calculated by dividing the signal intensities of the PHOFEX spectra by the square root of the DFWM spectra. Analysis of the PHOFEX yields revealed that dissociation via both vibronic levels exhibits a non-statistical behavior. When $2^14^3$ levels were excited in the parent, a preferential formation of HCO in the rovibronic ground state was found to occur if the parent is excited to the lower energy component of the $K'_a = 1$ doublet. This cannot be explained by energy or angular momentum conservation.

All the PHOFEX yields obtained for dissociation from rotational levels of $2^34^1$ with $K'_a = 0$ showed a characteristic peak at $J' = 4$. Knowing from literature that the dissociation pathway that includes an internal conversion to $\tilde{X}^1A_1$ yields a product state distribution with higher rotational temperatures, we can deduce that dissociation from $4_{04}$ occurs via the triplet pathway. Thus, we suggest that the barrier of the triplet potential energy surface must not lie higher than 31823 cm$^{-1}$. However, note that this procedure is valid only if the DFWM intensities can be related to an absorption technique such that the population of a quantum state can be derived from the signal intensity. This is the task of the next chapter.
Chapter 5

On the applicability of DFWM as an absorption-like spectroscopic technique

The previous chapter investigated the dependence of the formation of a dissociation product molecule in a specific quantum state on the excitation of the parent molecule. To monitor the excitation process, an absorption-like technique was desired such that the populations of the quantum states involved in the transition could be determined. Degenerate four-wave mixing (DFWM) was chosen as the spectroscopic technique with which the excitation of the parent molecule was recorded due to its favorable characteristics such as a high signal-to-noise ratio and the postulated dependence on the square of the ground state population. The assumption that the square-root of the DFWM signal intensity is comparable to that of an absorption spectra should, however, be treated with caution because it is valid only under certain circumstances such as a weak probe beam and strong pump fields.

In this chapter it will be shown that the use of DFWM as a technique with which populations can be determined is justified if parameters like the intensities and the polarizations of the three input fields are carefully controlled. For this purpose, the saturation behavior of the DFWM signal intensity is investigated. Moreover, degenerate four-wave mixing spectra are recorded for three different configurations of the electric field polarizations. Finally, DFWM spectra will be directly compared with other spectroscopic techniques, in particular an absorption technique. The simultaneous acquisition of cavity ring-down (CRD), laser-induced fluorescence (LIF) and DFWM spectra shows that the relative intensities of transitions in CRD spectra and their square-root in DFWM spectra which are obtained under equal experimental conditions do not exhibit substantial differences. The work which is described in this chapter is the content of Refs. [69, 61] and [25]. The experiments are mainly performed on the $0_0^0$ band of the $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma_g^+$ transition of $C_3$. Some qualitative results were also obtained on the $2_0^44_0^3$ band of the $\tilde{A}^1A_2-\tilde{X}^1A_1$ transition of formaldehyde.

5.1 Introduction

The quantitative analysis of degenerate four-wave mixing spectra such as for PHOFEX studies in the previous chapter or for the determination of temperature in plasmas and flames requires a theoretical model that represents the underlying process accurately.
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Such an expression is provided by one of the first models of degenerate four-wave mixing by Abrams and Lind [12]. This model for saturation of an absorbing medium is widely used and has proven to be remarkably successful in a range of situations. Several other models have been developed. For instance, Bloch et al. [70] have developed a theory for DFWM including two strong pump beams and the Doppler effect. Two types of results are found, one involving a numerical solution of the density matrix equations, the other providing an analytical expression. Similar results for the line shape and the intensity are found for both solutions. Ewart and co-workers focused on the effect of laser bandwidth in saturated media [71, 72, 73] obtaining an expression for the signal field strength. In this manner, nonvanishing interference terms arise in the simulation of close-lying transitions. A different approach has been used by Lucht et al. who integrated the time- and space-dependent density matrix equations numerically [74]. The model accounts for three strong fields as well as for the Doppler effect. Saturated line-profiles which were obtained in a jet of NO [74] and in a flame for OH [75] have validated the calculated lineshape in the saturation regime.

Attal-Tretout et al. [3] have obtained analytical solutions of the density matrix equations for a three-level system interacting with two strong fields in a crossed-polarization forward boxcars experiment. In contrast to the above-mentioned theories, which focus on the saturable absorption, Williams et al. [76, 77] have derived DFWM signal intensities for non-saturating incident intensities using diagrammatic perturbation theory in combination with a spherical tensor treatment. They found an expression for the DFWM signal intensity which includes geometric factors accounting for the polarizations of the electric fields.

For the task of interpreting spectra of molecular species, analytical expressions are mostly preferred over the most accurate but time-consuming numerical models. From that point of view, we analyze the degenerate four-wave mixing signal characteristics with the model by Abrams and Lind [12] to account for saturation effects and with the model by Williams, Zare and Rahn [76] to incorporate the dependence on the electric field polarizations. Additionally, we compare spectra obtained by DFWM with simultaneously recorded spectra obtained by a sensitive absorption technique, i.e. cavity ring-down spectroscopy, and laser induced fluorescence. This enables direct comparison of the relative intensities. In addition, we can discuss the advantages and disadvantages of the different single-resonance techniques.

As has been mentioned above, the experiments in this chapter are partly performed on the carbon trimer $C_3$. Along with other transient hydrocarbons, $C_3$ is produced with a DC-discharge (see Chapter 3). Within the last two decades two review papers on carbon molecules and clusters have been published, which give a good insight into the spectroscopy of $C_3$ [78, 79].

The history of the spectroscopy of $C_3$ has started with the discovery of the so-called comet band of $C_3$, the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^-$ emission spectrum at 4051.6 Å, which has been observed in the spectrum of the great comet in 1881 by the astronomer W. Tebbutt [80]. The band is the most prominent feature at this wavelength and it has been observed in other astrophysical objects since then [81, 82]. Only in 1951 $C_3$ was identified to be the carrier of
this band in the $^{13}$C isotope work by Douglas et al. [83]. Later, Gausset et al. [84, 85] showed that the band represents a $\tilde{A}^1\Pi_u(000)$-$\tilde{X}^1\Sigma_g^+(000)$ transition of a linear molecule.

Until recently, interest in C$_3$ has continued: the molecule has been detected in diffuse interstellar clouds [86] and can serve as a diagnostic for their temperature and density. C$_3$ was also investigated as a means to measure the soot concentration [87]. Soot is produced in high concentrations in inefficient hydrocarbon combustion processes. It consists to 90% of carbon in a graphite-like structure and C$_3$ has been measured to be a major constituent of graphite vapor [88, 79]. Moreover, carbon molecules such as C$_1$, C$_2$ and C$_3$ have been found to grow first into linear chains before closing to form monocyclic rings and eventually fullerenes [89].

McCall et al. [90] observed a couple of previously unobserved transitions in the $\tilde{A}^1\Pi_u(000)$-$\tilde{X}^1\Sigma_g^+(000)$ band and succeeded to reassign the position of the R(0) transition by cavity ring-down spectroscopy. The transition which was believed to be the R(0) transition before arises from a perturbation of another yet unassigned state. Only recently, this has been justified in two independent studies [91, 92]. Zhang et al. [92] applied laser induced fluorescence and recorded the fluorescence at two different delays. Whereas they could detect only the regular lines at short delays, the additional lines discovered by McCall et al. appeared when the fluorescence was recorded in a longer time slot and at a longer delay after the excitation. They tentatively assigned these lines to belong to at least two perturbing states, a state with $^3\Sigma_u^+$ symmetry which is likely to be the (050)$^-$ vibronic level of the $\tilde{b}^3\Pi_g$ electronic state, and the other with quantum number $P = \Lambda + \ell + \Sigma = 1$, where $\Lambda$, $\ell$ and $\Sigma$ are the projections of the electronic and vibrational angular momentum and the electron spin, respectively, onto the molecular axis.

5.2 Saturation effects in degenerate four-wave mixing spectroscopy

As has been discussed above, for a quantitative analysis of the degenerate four-wave mixing signals one requires theoretical models that reproduce the situations encountered in reality as good as possible. An exact or approximate solution of the density matrix equations can be obtained under certain assumptions. The model by Abrams and Lind, which provides an analytical expression of the signal intensity taking saturation effects into account, will be presented first.

5.2.1 The model of Abrams and Lind

Much theoretical work on DFWM is based on the nonlinear susceptibility formalism described in Chapter 1, which is derived for unsaturated weak fields, where optically induced Stark shifts and population transfers are neglected. Strong matter-field interactions accompanying the resonant excitation of molecular transitions can rapidly degrade
the convergence of the perturbation expansion employed for the calculation of the induced polarization in Equation 1.11. It would be more appropriate to use a non-perturbative scheme, which incorporates the dynamic coupling mechanisms responsible for optical saturation effects, but a complete theoretical description of the DFWM in the strong-field limit is difficult and, in general, does not lead to easily applicable analytical expressions. Abrams and Lind [12] have developed a relatively simple saturable absorber model for interpreting the near-resonance response of DFWM spectroscopy. An analytical expression for the DFWM signal intensity has been presented for a nondegenerate homogeneously broadened two-level saturable absorber. In fact, the derivation has been carried out for a phase-conjugate configuration in which the pump beams are counterpropagating. Yu et al. [93] have proven that the result applies also for a forward-boxcars configuration which is used in our experiments.

Yariv and Pepper [94] showed that the wave equation (Equation 1.12) has an analytical solution in the limit of weak probe and signal intensities. From these results, Abrams and Lind derived an analytical expression for the phase-conjugated DFWM reflectivity $R$, which is the factor of proportionality between the $I_{\text{DFWM}}$ and $I_{\text{probe}}$.

The main assumptions of the Abrams-Lind model are (i) a non-degenerate two-level system with a resonant transition between the ground state $g$ and the excited state $e$, (ii) stationary absorbers, (iii) monochromatic and steady-state laser radiation, (iv) arbitrary but equal pump intensities ($I_1 = I_2 = I$), and (v) a weak probe beam ($I_{\text{probe}} \ll I$).

From that, Farrow et al. [95] calculated the following expression for the DFWM signal intensity in the limit of small absorption

$$I_{\text{DFWM}} = (\alpha_0 L)^2 \frac{1}{1 + \delta^2} \left( \frac{4(I/I_{\text{sat}})^2}{(1 + 4I/I_{\text{sat}})^3} \right) I_{\text{probe}}$$

where

$$\alpha_0 = \frac{\omega_{ge} T_2}{2c \epsilon_0} \Delta N |\mu_{ge}|^2$$

is the unperturbed absorption coefficient at the line center. $L$ is the interaction length, $\delta$ is the normalized laser detuning from the molecular transition frequency $\omega_{ge}$,

$$\delta = (\omega - \omega_{ge}) T_2.$$ 

$\Delta N = N_g - N_e$ is the population difference between levels of the transition in the absence of laser fields, $|\mu_{ge}|^2$ the absolute square of the transition dipole moment, $T_2$ the coherence decay time. $c$ is the speed of light in vacuum, $h$ is Planck’s constant, and $\epsilon_0$ the electric constant. Then the saturation intensity at the line center $I_{\text{sat}}$ depends only on characteristic properties of the spectroscopic transition from $g$ to $e$ and is given by

$$I_{\text{sat}} = \frac{h^2 \epsilon_0}{2T_1 T_2 |\mu_{ge}|^2} (1 + \delta^2) =: I_{\text{sat}}^0 (1 + \delta^2),$$

where $T_1$ is the population decay time, which corresponds to the lifetime of the upper level.
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in a closed two-level system. \( I_{\text{sat}} \) provides a measure of the field strength for which the optically-induced oscillation of population between ground and excited states of the transition (i.e. the Rabi frequency) becomes comparable to the rates of relaxation/dephasing processes (see e.g. in Ref. [77]).

We see that the signal intensity \( I_{\text{DFWM}} \) is dependent on the square of the line-center absorption coefficient \( \alpha_0 \) and thus on the square of the unperturbed population difference. Note that in the environment of a molecular beam, where only rotational levels of the vibronic ground state are populated, \( \Delta N \approx N_g \). Moreover, in the limit of low pump intensity \( I_{\text{DFWM}} \propto I_{\text{sat}}^2/(1 + \delta^2) \propto (1 + \delta^2)^{-3} \), which corresponds to Lorentzian line profiles raised to the third power.

In the limiting cases of very large or very small input intensities the DFWM signal intensities at the line center, i.e. \( \delta = 0 \), are

\[
\begin{align*}
\text{for } I << I_{\text{sat}} & \quad I_{\text{DFWM}} \propto \alpha_0^2 L^2 (I/I_{\text{sat}})^2 I_{\text{probe}} \propto |\mu_{ge}|^8 T_1^2 T_2^4 I^3 \quad (5.5) \\
\text{for } I >> I_{\text{sat}} & \quad I_{\text{DFWM}} \propto \alpha_0^2 L^2 (I_{\text{sat}}/I) I_{\text{probe}} \propto |\mu_{ge}|^2 T_1^{-1} T_2 , \quad (5.6)
\end{align*}
\]

if all three incident fields originate from one source. In the limit of small input intensities, the DFWM signal intensity is proportional to the third power of the laser intensity. On the other hand, the signal intensity does not depend on the input intensities at all if the signal is strongly saturated. We must note that the dependence on the transition dipole moment is significantly different for the different regimes and that the proposed proportionality of the DFWM signal intensity \( I_{\text{sat}} \) to \( N_g^2 |\mu_{ge}|^4 \) holds only for \( I = I_{\text{sat}} \).

With these considerations we can now analyze the saturation behavior of selected rovibronic transitions in the \( 0^0_0 \) band of the \( \tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+ \) electronic transition of C₃ and the \( 2^14^0_0 \) band in the \( \tilde{A}^1\Delta_2 - \tilde{X}^1\Lambda_1 \) electronic transition of H₂CO.

5.2.2 Saturation behavior of selected transitions in C₃

Initially recorded DFWM spectra of the \( \tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+ \) transition of C₃ reveal that the R branch intensities are stronger than expected while the P transitions and the lines belonging to the perturbing \( P = 1 \) state appear weaker than in the work by Zhang et al. [92], in cavity ring-down spectra (which will be shown in Section 5.4) and in spectra simulated with the constants from Ref. [92]. In particular, the lines belonging to the perturbing \( 3\Sigma_u^- \) state do not appear at all. When higher intensities of the incident laser beams are used for recording a DFWM spectrum (see Figure 5.1) pedestals are observed for the peaks of the stronger transitions. In particular, the set of close-lying Q-transitions has a relatively large pedestal, which is not observed in the simulated spectrum or when the incident intensities are smaller.

To determine possible reasons for the incongruity with the simulation, the saturation behavior of selected transitions is investigated according to the model by Abrams and Lind. A saturation experiment of a specific transition is carried out by tuning the input lasers to the line center of a transition and recording the DFWM signal intensity as a function of the laser pulse energy. In this experiment, the radiation of all three input laser
beams originates from the same source. Thus, the total input intensity $I = I_1 + I_2 + I_3$ is modified while single shots of the DFWM signal are recorded together with the pulse energy of one pump beam $E_{L1}$. The total pulse energy $E_L$ is the sum of the pulse energies of the three input beams. With that, the spectral intensities are obtained from

$$I \left[ \text{GW}/(\text{cm}^2 \cdot \text{cm}^{-1}) \right] = \frac{E_L}{(\Delta \tau_L \cdot A) \Delta \tilde{\nu}_L},$$  \hspace{1cm} (5.7)$$

using $\Delta \tilde{\nu}_L = 0.02 \text{ cm}^{-1}$ for the laser bandwidth, a laser pulse length of $\Delta \tau_L = 7 \text{ ns}$ and a laser beam diameter of $d = 1 \text{ mm}$, and the area is $A = (d/2)^2 \pi$. Typical beam energies employed in the experiment are 0.01 to 0.1 J, which correspond to $I = 0.09$ to 0.91 MW/(cm$^2$·cm$^{-1}$). Approximately 2000 to 4000 data points are recorded in one measurement. For the evaluation, data points in a chosen energy interval are averaged and plotted with error bars. Then, least-squares fits to the Abrams-Lind expression in the form

$$I_{\text{DFWM}} \propto \frac{I^3/I_{\text{sat}}^2}{(1 + 4I/I_{\text{sat}})^3}$$  \hspace{1cm} (5.8)$$

are performed to obtain values for the saturation intensity $I_{\text{sat}}$. The strong Q(6), R(6), P(6) and the relatively weak R(0) transition were chosen for the
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Figure 5.2 Saturation dependence of the transitions Q(6), R(6), P(6), and R(0). Saturation for the Q(6) and R(6) transitions occurs at the same intensities ($I_{\text{sat}}=0.10 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$). However, the P(6)-transition is saturated only at seven times higher intensities ($I_{\text{sat}}=0.71 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$) (c). The R(0)-transition belonging to the $P=1$-state exhibits a higher saturation intensity ($I_{\text{sat}}=0.48 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$) than R-branch transitions with higher J (d).

saturation measurements. In particular, the R(0) transition is classified as the transition to the $J'=1$ rotational level arising from the perturbation as in Ref. [92]. The other transitions occur to rotational levels of the $\tilde{A}^3\Pi_u$ (000) state. The measured values and the saturation fit-curves are depicted in Figure 5.2. We found that the saturation intensities differ significantly for the different transitions. Whereas saturation occurs at relatively small input intensities for the strong R and Q transitions ($I_{\text{sat}}=0.10 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$), the weaker R(0) transition reaches the saturation regime only at almost five times higher intensities ($I_{\text{sat}}=0.48 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$). The transitions in the P-branch are saturated only at even higher intensities: input intensities seven times higher than for R(6) and Q(6) are needed to saturate the signal ($I_{\text{sat}}=0.71 \text{ MW}/(\text{cm}^2\text{cm}^{-1})$).

As has been explained above, the saturation intensity derived by the Abrams-Lind model depends on the inverse square of the transition dipole moment (see Equation 5.4), as well as on the inverse of the product of the population decay time $T_1$ and the coherence decay
time $T_2$. $T_1$ and $T_2$ are related to the collisional dephasing rate $\gamma_c$ \[10\] by

$$\frac{1}{T_2} = \frac{1}{2T_1} + \gamma_c. \quad (5.9)$$

Since $\gamma_c \approx 0$ for the collision-free environment of a molecular beam, $T_2 = 2T_1$. Assuming that the decay times are equal within one vibronic band, the product of the determined saturation intensity and the transition dipole moment $|\mu_{ge}|^2$ should yield the same value for all transitions. For the reason that we are interested only in transitions within one vibrational band, only the Hönl-London factors $S_{J''}$ are considered in the product $I_{\text{sat}} \cdot |\mu_{ge}|^2$.

The results of the fitted saturation intensities and the products $I_{\text{sat}} \cdot S_{J''}$ are presented in Table 5.1. The fifth column shows that those products differ greatly from each other. The value obtained for the P(6) transition is almost 3.5 times the value of the R(0) transition.

<table>
<thead>
<tr>
<th>transition</th>
<th>$\nu/\text{cm}^{-1}$</th>
<th>$S_{J''}$</th>
<th>$I_{\text{sat}}$</th>
<th>$I_{\text{sat}} \cdot S_{J''}$</th>
<th>$GF$</th>
<th>$I_{\text{sat}} \cdot S_{J''} \cdot GF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(6)</td>
<td>24674.88</td>
<td>4.214</td>
<td>0.10</td>
<td>0.4214</td>
<td>0.199</td>
<td>0.083</td>
</tr>
<tr>
<td>R(6)</td>
<td>24680.51</td>
<td>2.232</td>
<td>0.10</td>
<td>0.2232</td>
<td>0.157</td>
<td>0.045</td>
</tr>
<tr>
<td>P(6)</td>
<td>24669.88</td>
<td>1.402</td>
<td>0.48</td>
<td>0.6730</td>
<td>0.146</td>
<td>0.098</td>
</tr>
<tr>
<td>R(0)</td>
<td>24675.85</td>
<td>0.291</td>
<td>0.71</td>
<td>0.2066^b</td>
<td>0.111</td>
<td>0.022^b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>a in MW/(cm^2·cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>b the long lifetime is not considered</td>
</tr>
</tbody>
</table>

Table 5.1 Experimentally obtained saturation intensities. The Hönl-London factors $S_{J''}$ of the transitions are obtained with the rotational constants from Ref. \[92\] with pgopher \[59\]. The values in the fifth column should be constant if $T_1$ and $T_2$ are assumed to be equal for all transitions. The expected dependence of the saturation intensity on the inverse square of the transition dipole moment is not very well reproduced. The last two columns incorporate the use of geometrical factors, which is explained in Section 5.3.

When the long lifetime component of the R(O) state is considered, a good agreement is obtained in the last column for the Q(6), the P(6) and the R(0) transitions.

A reason for this discrepancy could be that the assumption that the population and coherence decay rates are equal for all transitions within the vibrational band might be too general. For instance, the lifetimes of single rotational levels of the $\tilde{A}^1A_2$ $2^2A_1$ state of formaldehyde show a considerable variation \[96\] ranging from 6.1 to 9.9 ns. Lifetime measurements of single rotational levels of the $\tilde{A}^1\Pi_u$ (000) vibronic state of C$_3$ have been performed in Ref. \[92\] yielding values ranging from 192 to 227 ns. In addition, fluorescence lifetimes for rotational levels of the perturbed states have been measured. A bi-exponential decay has been observed yielding short- and long-lived components. The lifetimes of the long-lived component of rotational levels of the $P = 1$ perturbing state range from 470 to 786 ns, i.e. 2-3 times the lifetime for the other states. Considering this fact for the R(0) transition, 4-9 times the product $I_{\text{sat}} \cdot S_{J''}$ should be equal to the values of the other transitions. The other values in the last column of Table 5.1 do, however, still not match well, even when the value for R(0) is multiplied by 4.

There can be several reasons for these inconsistencies. A model where only the input intensities are considered might not be sufficient for the description of our experiment as
the results in Table 5.1 suggest. For instance, the polarizations of the fields involved in the four-wave mixing process are not taken into account. This is done in Section 5.3 (vide infra), the results are printed in the last column of Table 5.1, and yield a good agreement for three transitions, however, a discrepancy is still observed for the R(6) transition. Alternatively, the experimental conditions might have not been considered in a realistic manner. As mentioned above, a large number of data points were taken for a single experiment and one point in the plots in Figure 5.2 is obtained by averaging all data points in a specified intensity region. In fact, the DFWM signal intensity flickers with every single shot. As has been mentioned in Chapter 3, C_{3} is produced by applying a DC-discharge to a gas-mixture by which a plasma is formed. A possible reason for the flickering of the DFWM signal intensity, which is not observed in DFWM experiments on formaldehyde, is an uneven production of the species. We thought, however, that averaging over a large number of data points was sufficient to obtain good values for the intensities.

These results on C_{3} suggest that in the frame of the Abrams-Lind model it is very difficult to use a DFWM spectra of a vibrational band in order to obtain information from the intensities such as from an absorption spectrum. Carrying out saturation scans of each transition so that spectra of single transitions could be recorded at the respective saturation intensity is a tedious procedure and not very useful because we are interested in relative intensities of all the transitions within one band.

5.2.3 Saturation behavior of selected transitions in H_{2}CO

In addition to the experiments above, saturation curves are recorded in the same manner for some rovibronic transitions in the 2_{0}^{1}_{4}^{3} band of the A_{2}^{1}A_{2}^{-}X_{1}^{1}A_{1}^{1} electronic transition of formaldehyde. Figure 5.3 depicts two saturation curves for the relatively intense ^{r}R_{11}(1) transition which overlaps with the ^{r}R_{12}(1) transition at 30364.5 cm^{-1} (a) and the substantially weaker ^{r}Q_{12}/2(2) at 30360 cm^{-1} (b).

In these saturation experiments, a data point is obtained by averaging over 10-40 laser shots. Data points in energy intervals of 10 J are averaged. I/I_{sat} is evaluated from those averaged points by a fit to the equation for the saturation dependence, Equation 5.8. The solid lines represent the best fits.

For recording the DFWM spectra in Chapter 4, Figure 4.3, total laser energies up to 600 J/pulse were used, which results in an I/I_{sat} ratio of 1.5 to 3. At these energies, the dependence of the signal intensity on |μ_{ge}|^4 applies. This |μ_{ge}|^4 dependence of the DFWM signal for intensities I ≥ I_{sat} has been also confirmed experimentally by other authors [1, 10, 95, 97, 98].

The laser pulse energies at which I is equal to I_{sat} are 210 J and 430 J for the ^{r}R_{11}(1) and the ^{r}Q_{12}(2) transition, respectively. The HönL-London factors for these two transitions amount to 0.021 and 0.006. Thus, we obtain 4.41 and 2.58 for the products of S_{J'}. times the laser pulse energy at which saturation occurs. The disagreement with the Abrams and Lind model is substantial and might be due to the neglected polarization dependence of the DFWM signal which is the focus of the following section.
5.3 Polarization dependence of the DFWM signal intensity

In this section, the DFWM signal dependence on the polarization of the electric fields will be investigated. We will see that the use of certain polarization configurations affects the relative intensities of the transitions such that some transitions even disappear. The model by Abrams and Lind fails to describe these effects. A different model which allows for the polarizations of the fields although it does not account for saturation effects is applied. In this model, geometric factors are provided which are required for the simulation of spectra, especially if transitions from levels with low \( J \) occur. The effect of these factors is demonstrated on the example of the \( 0_1^0 \) band of the \( \tilde{A}^1A_2-\tilde{X}^1A_1 \) transition of formaldehyde.

5.3.1 The model of Williams, Zare and Rahn

The model mentioned above has been developed by Williams, Zare and Rahn [76]. It takes into account the dependence of the DFWM signal on the polarizations of the incident electric fields. The DFWM process is assumed to couple levels of definite angular momenta, as opposed to the model by Abrams and Lind where only the transition frequency is accounted for.

The expression for the signal intensity is derived under the assumption that the rates of collisional relaxation of the multipole moments, i.e. the population, the orientation and the alignment, are the same. Furthermore, if the distribution of the initial magnetic sublevels is assumed to be isotropic, then the DFWM signal intensity can be written as

\[
I_{\text{DFWM}} \propto I_1 I_2 I_3 \left[ N_g - \frac{2J_g + 1}{2J_e + 1} N_e \right]^2 \left| \frac{\mu_{ge}}{L(\omega)} \right|^2 |G_F(\epsilon_4, \epsilon_1, \epsilon_3, \epsilon_2; J_g, J_e)|^2,
\]
where $N_g$ and $N_e$ are the number densities, and $J_g$ and $J_e$ are the total angular momenta of the ground and excited level, respectively. $L(\omega)$ is the total line shape function, $\mu_{ge}$ is the transition dipole moment of the transition from $g$ to $e$, and $G_F(\epsilon_4, \epsilon_1, \epsilon_3, \epsilon_2; J_g, J_e)$ are geometric factors which depend only on the polarizations of the electric fields of the input beams. These factors are real numbers which account for the geometry of the interaction of the molecule with the electric fields in the laboratory frame only. They are calculated for different configurations in [76] and are listed in Table 5.2. The nomenclature is chosen in the same way as in Williams et al., i.e. the subscripts 1 and 3 refer to the pump beams, 2 to the probe and 4 to the signal beam (see Figure 5.4).

<table>
<thead>
<tr>
<th></th>
<th>$P (J_e = J - 1)$</th>
<th>$Q (J_e = J)$</th>
<th>$R (J_e = J + 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YYYY</td>
<td>$\frac{1}{\mu}$</td>
<td>$\frac{1}{\mu}$</td>
<td>$\frac{1}{\mu}$</td>
</tr>
<tr>
<td>YYXY</td>
<td>$\frac{2}{\mu}$</td>
<td>$\frac{2}{\mu}$</td>
<td>$\frac{2}{\mu}$</td>
</tr>
<tr>
<td>YYYY</td>
<td>$\frac{2}{\mu}$</td>
<td>$\frac{2}{\mu}$</td>
<td>$\frac{2}{\mu}$</td>
</tr>
</tbody>
</table>

**Figure 5.4** The three polarization configurations used in this experiment.

An investigation of the geometric factors in detail reveals that for certain transitions the factors vanish, e.g. in the configuration YYXY the $G_F$-factor is 0 for an R(0) transition. Additionally, depending on the polarization configuration, the P and R branches are enhanced with respect to the Q branch in the high-$J$ limit.

It is important to mention, however, that the derivation of the expression was conducted for molecular systems in collisionally dominated environments which does in principle not apply to the nearly collision-free environment of a molecular beam. In addition, in their derivation of the signal intensity Williams et al. [76] did not allow for the nuclear spin. A discussion about possible effects of the coupling of $J$ to the nuclear spin is included in the publication reasoning that because of the coupling to the nuclear spin, $J$ is depolarized in the laboratory frame.

Moreover, a selection of other nonlinear processes occurs in a DFWM experiment which
might contribute to the signal intensity. The contribution is minimal when DFWM is applied in a molecular beam, but can be substantial if the interaction region of the fields is very close to the opening of the pulsed valve, where collisions have an influence:

1. Thermal gratings: A thermal grating is formed, because laser energy is absorbed locally in the medium which is subsequently heated. This absorption leads to a spatial modulation of the density in gases, and the contribution to the signal can be of the order of the DFWM signal intensities under some conditions [99].

2. Electrostrictive gratings: At high laser intensities electrostrictive gratings are formed, which result from a modulation of the gas density induced by the electric field [100, 101].

Thermal and electrostrictive gratings can be formed only from the interference of two fields with parallel polarization. Orthogonally polarized fields do not produce these effects because there is no spatial modulation of the field intensity [102, 103], only its polarization is spatially modulated. If other gratings are present, the YXXY configuration is the best option to discriminate against their contribution [76]. In general, however, thermal gratings do not arise in the collision-free environment of the molecular beam. In addition, also electrostrictive gratings are assumed to be weak because of their dependence on the pressure in the gas.

Spectral simulations of the $\tilde{A}^1\Pi - \tilde{X}^1\Sigma^+$ band of $C_3$ are performed with pgopher [59] with the inclusion of the geometrical factors and are shown in Figure 5.5. The most prominent effect of the geometrical factors can be seen in YXXY configuration: the two R(0) transitions, the second of which arises from the perturbation, vanish. Additionally, P and R transitions with small $J$ appear much stronger in the crossed polarizations configurations YXXY and YYXX as opposed to the all-parallel case YYYY. DFWM spectra are subsequently recorded with the YYXX, YXXY and YYYY configuration. The square-root of the intensity is plotted in Figure 5.5. Least-squares fits of the simulated spectra to the experimental spectra yield rotational temperature of 64.7 K, 33.9 K and 45.0 K for the YYXX, YXXY and YYYY configurations, respectively. Also the measured traces display the above-mentioned absence of the two R(0) transitions in the YXXY configuration, which is a good evidence of the validity of the geometrical factors. The expected reduction of the intensities of the P and R transitions in the YYYY configuration is not observed, however. The Q-branch appears broadened in the YYXX and the YXXY configurations, but not in the all-parallel configuration. This effect is not caused by the geometry of the setup, but originates from the use of too high intensities of the incident fields such that the Q-branch is saturated. As can be deduced from the rotational temperatures obtained from the fits above, the spectra are not recorded at equal conditions. Changing to a different polarization configuration requires a new alignment of the laser beams to restore the phase-matching. The laser pulse power and the source of the molecular beam are adjusted each time to optimize the DFWM signal at a specific transition. Thus, the parameters which determine the expansion of the molecular beam as well as the position where the interaction of the fields with the species in the molecular beam...
beam occurs vary with the change to a different polarization configuration.

A more quantitative analysis can be carried out with the help of Boltzmann plots, which constitute a tool to determine rotational temperatures with linear fits (see for example in Ref. [104]).

Assuming that the quartic dependence on the absolute value of the transition dipole moment $|\mu_{ge}|$ holds for each rovibronic transition, then the DFWM signal intensity is proportional to the square of the product of the ground state population, the geometrical factors $G_F$ and the H"{o}nl-London factors $S_{j''}$,

$$I_{DFWM} = C^2 N_g^2 |G_F|^2 S_{j''}^2$$

where $C^2$ is a positive constant, which contains all other information like the vibronic transition dipole moment, the lineshape and the input intensities. Inserting

\[C^2 = 4\hspace{1cm}G_F = 1\hspace{1cm}S_{j''} = 1\hspace{1cm}N_g = 1\hspace{1cm}|\mu_{ge}| = 1\]

we get

$$I_{DFWM} = 1 \times 1 \times 1 \times 1 = 1$$

This calculation shows that the DFWM signal intensity is constant for each rovibronic transition, which is consistent with the experimental findings. The vanishing $R(0)$-transitions in the YYXX configuration and the enhancement of the $R$-branch transitions in the YYXY configuration are reproduced. In the all parallel YYYY case, the transitions of the $R$-branch are not as weak as the simulation suggests.
Figure 5.6 Boltzmann plots for DFWM with three different polarization configurations. The fits for each branch yield similar values for the temperatures of different branches within one configuration: $T_R = 50.2$ K, $T_P = 51.5$ K, $T_Q = 46.2$ K for YYXX, $T_R = 38.7$ K, $T_P = 43.4$ K, $T_Q = 43.1$ K for YXXY and $T_R = 38.8$ K, $T_P = 35.5$ K, $T_Q = 43.4$ K for YYYY. The ratios derived for the geometrical factors coincide quite well with the theoretical values for the YYXX configuration. For the other configurations the theoretical result could not be reproduced.
Table 5.3 Calculated (th) and experimentally determined (exp) ratios of the $G_P$-factors. The calculated values are determined from the tables of the geometrical factors given in Ref. [76].

$$N_g = N_0(2J'' + 1) \cdot e^{-\frac{E_{rot}}{kT}}$$ \hspace{1cm} (5.11)

for a Boltzmann population distribution in the electronic ground state yields

$$\ln \left( \frac{\sqrt{I_{DFWM}}}{S_{2J'+1}} \right) = -\frac{E_{rot}}{kT} + \ln(N_0 |C| |G_P|).$$ \hspace{1cm} (5.12)

$N_0$ is the number density in the interaction region, $k$ is the Boltzmann constant, and $T$ is the rotational temperature. The geometrical factors all have a limit for high $J$ (see in Ref. [76]), which is reached in a good approximation already for $J = 4$. In Figure 5.6, Boltzmann-plots for the single branches are displayed for each polarization configuration. The values for the Hönl-London factors have been taken from the simulations with pgopher [59] and the molecular constants from Ref. [92]. The factor $(2J + 1)$ denotes the degeneracy of the ground state. Linear fits to the experimental values for $E_{rot}$ and the values on the left-hand side of Equation 5.12, for which the integrated signal intensities are used, are performed for all three branches separately starting from $J = 4$. Thus, rotational temperatures can be obtained for each branch and are displayed in Figure 5.6. Assuming that the the value for $N_0|C|$ is constant within one measurement, fractions of the geometrical factors can be determined from the y-intercept values $d_y^P, d_y^Q, d_y^R$ obtained in the linear fit. For example,

$$\exp(d_y^P - d_y^Q) = \frac{|G_P|}{|G_Q|}.$$ \hspace{1cm} (5.13)

These can be compared to the values from [76] and are shown in Table 5.3. Transitions with $J \leq 4$ and transitions with higher rotational quantum numbers are omitted in the fit. The reason for not considering the transitions with higher $J$ is that the saturation regime $I = I_{sat}$ is most likely not reached in this experiment.

In addition to recording DFWM spectra, the saturation behavior of a single transition was investigated for the three different polarization configurations. Figure 5.7 shows the saturation scans of the Q(4) transition in the a) YXXY, b) YYXX and c) YYYY configuration, which are obtained in the same manner as in the previous section. The values for the saturation intensity are obtained from fits to the Abrams-Lind expression 5.1 and amount to 0.1 MW/(cm$^2$cm$^{-1}$) for the YXXY and the YYXX configuration and to 0.04 MW/(cm$^2$cm$^{-1}$) for the YYYY configuration. The geometrical factors for a Q(4) transition amount to 3/50 ≈ 1/16.7, 41/630 ≈ 1/15.4 and 59/300 ≈ 1/5.1 for the
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Figure 5.7 Saturation dependence of the transition Q(4) in (a) YXXY, (b) YYXX, and (c) YYYY polarization configuration.

YXXY, YYXX and the YYYY configuration, respectively. Multiplying the saturation intensity obtained from the fits with the geometrical factors yields $6.0 \times 10^{-3}$, $6.5 \times 10^{-3}$ and $7.8 \times 10^{-3}$, supporting the inclusion of the geometrical factors for determining the saturation intensity.

The geometrical factors can now be taken into account for the saturation intensities obtained for the saturation experiments on C$_3$ in the previous chapter in Figure 5.2 multiplying the values in the last column of Table 5.1 with the geometrical factors for a YYYY polarization configuration (see Table 5.1). The values for $I_{sat} \cdot S_{J''} \cdot G_F(Y, Y, Y, J', J'')$ amount to 0.083, 0.045, 0.098 and 0.022, for the Q(6), R(6), P(6), and R(0) transition, respectively. Accounting for the long-lived component of R(0) (see Section 5.2) by multiplying the 0.022 for R(0) by 4, the resultant value is 0.088, which is comparable to the values for Q(6) and P(6). However, the difference of the value obtained for R(6) by a factor 2 remains unclear and might be related to an experimental error.
The effect of different polarization configurations has been tested also on formaldehyde. As has been mentioned above, the derivation of the model by Williams et al. \cite{76} does not account for molecules with non-zero nuclear spin. DFWM spectra of the $\tilde{A}^1A_2-\tilde{X}^1A_1 \, 2^44^3$ transition with the application of the three configurations described above are shown in figure 5.8. Using the expressions in Table 5.2 one can calculate that the geometric factors are zero for $Q(1)$ and $P(1)$ transitions for the YXXY configuration. The relevant portion of the spectra obtained in the YXXY configuration is plotted in the upper trace of Figure 5.8. The $^PQ_1(1)$ and the $^PP_1(1)$ transitions do not disappear, but are significantly reduced in intensity in comparison to the peaks obtained with the YYXX and YYYY polarization configuration.

![Figure 5.8](image-url)  

**Figure 5.8** A part of the $\tilde{A}^1A_2-\tilde{X}^1A_1 \, 2^44^3$ vibronic band of formaldehyde is recorded with three different polarization configurations. The $Q(1)$ transition does not completely disappear for the YXXY configuration, is however significantly reduced in comparison with the other configurations.

### 5.4 Multiplexing

Multiplexing indicates the simultaneous recording of spectra with different spectroscopic techniques. This enables the comparison of the applied techniques at almost equal conditions. When a molecular beam is used, the rotational temperature depends very sensitively on many parameters, which are hardly controllable. With the molecular beam apparatus explained in Chapter 3, such multiplexing experiments can be carried out. In this section, cavity ring-down as an absorption technique is compared with degenerate four-wave mixing. In addition, laser-induced fluorescence spectra can be recorded simultaneously. Also, combinations of other spectroscopic techniques are feasible, as for instance, two-color res-
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onant four-wave mixing can be applied simultaneously with LIF (see Figure 6.1 and 6.3) which is shown in the next chapter.

5.4.1 Sensitive absorption spectroscopy: Cavity ring-down

First cavity ring-down experiments are performed on the $\tilde{A}^1A_2-\tilde{X}^1A_1 \, 2^1_04^3_0$ transition of formaldehyde but have been carried out before the molecular beam apparatus which is described in Chapter 3 was implemented. Then, the simultaneous use of CRD and DFWM was not possible. The experiments with the two techniques are conducted consecutively. The ring-down times of our CRD spectrometer are read directly from the decay curve (see Equation 1.3 in Chapter 1) on the oscilloscope and amount to $\approx 1.1$ s for off-resonant laser frequencies. By considering a transmission $T = 1 - R = 0.001$ and a cavity spacing of 0.7 m, the effective path length achieved in our instrument, $l/T$, is $\approx 700$ m and the losses $L \approx 0.001$. If the laser is tuned to an absorption frequency of formaldehyde, a significant decrease of the ring-down time is observed. For example, $\tau \approx 0.94$ s is measured for the $^rR_{11}(1)$ transition at 30364.5 cm$^{-1}$ and represents an additional cavity loss, or absorbance, $\alpha l$, of $\approx 550$ ppm/pass. It is important to mention that no systematic deviation from a single exponential has been observed in the ring-down transients.

The bandwidth of 0.04 cm$^{-1}$ of the injected pulse yields a short coherence length ($\approx 25$ cm) as compared to the 70 cm cavity length. Furthermore, the intensity variation of the input pulse is erratic resulting in a random distribution of the longitudinal mode structure. Therefore, mode competition is averaged out and the light trapped inside the cavity is essentially particle-like and undergoes first-order exponential decay in accordance with Equations 1.2 and 1.3 [105].

An estimation of the formaldehyde density in the molecular beam is obtained by taking into account recent high-resolution absorption cross section determinations for formaldehyde of the $2^3_34^3_0$ vibrational band of the $\tilde{A}^1A_2-\tilde{X}^1A_1$ electronic transition [106]. The authors deduce a value for the cross-section $\sigma$ of $1.0 \times 10^{-19}$ cm$^2$/molecule. Considering the low-resolution absorption spectrum of H$_2$CO [52], a reduction of the cross section of the $2^1_04^3_0$ vibrational band relative to $2^3_34^3_0$ by a factor of $\approx 0.6$ is estimated resulting in $6 \times 10^{-20}$ cm$^2$/molecule for the $^rR_{11}(1)$ transition. Assuming a diameter of $\approx 2$ cm for the molecular beam in the interaction region, the number density of the unresolved asymmetry levels $1_{11}$ and $1_{10}$ states in the molecular beam is estimated to be $\approx 2 \times 10^{15}$ molecules/cm$^3$.

Figure 5.9 shows a CRD spectrum of formaldehyde in the $2^1_04^3_0$ vibrational band (upper trace). Analogous to the simulations of the DFWM spectra a Boltzmann temperature fit to the experiment is performed that takes into account a partial interconversion of the nuclear spins during expansion by using an additional fit parameter describing the $\text{para/ortho}$ concentration ratio. A good agreement is achieved for a rotational temperature of $\approx 20$ K. As for the DFWM evaluation, we conclude that the spectral and intensity simulation approximated by an asymmetric rotor model and by using precise molecular constants available in the literature is in good agreement with the experimental data.
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Figure 5.9 The upper trace shows the $\tilde{A}^1A_2-\tilde{X}^1A_1$ band of formaldehyde recorded with the cavity ring-down spectroscopic technique. For comparison, a simulation obtained with the rotational constants found in Ref. [52] is shown in the lower trace.

5.4.2 Simultaneously recorded DFWM, CRD and LIF spectra

Figure 5.10 displays LIF, CRD and DFWM traces of the $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma^+$ transition of C$_3$. The spectra have been observed simultaneously and demonstrate clearly the applicability of the methods for multiplex spectroscopy in the low-density environment of a molecular beam. A simulation generated with the constants from Ref. [92] with pgopher [59] at 60 K is plotted for comparison. According to the results in Section 5.2, DFWM spectra are obtained in the spectral range of 24650-24690 cm$^{-1}$ at relatively low beam energies in the range of 0.01-0.4 J such that strong saturation for the Q-transitions is avoided.

The fluorescence originates from molecules which are excited by the radiation of the four-wave mixing laser beams. At the intensities which are used for recording the DFWM spectra, the LIF transitions are already strongly saturated, which can be seen in the pedestals observed for all transitions.

The cavity ring-down experiment is set up at 45 degrees with respect to the DFWM setup. The intensity of the laser pulse which is fed into the cavity can be controlled separately. Substantial sensitivities are observed for the linear and nonlinear spectroscopic techniques, although DFWM displays a reduced sensitivity due to the greater than linear dependence on the number density $N_g$. In fact, the square-root is plotted in Figure 5.10, assuming that the spectra is recorded at $I \approx I_{\text{sat}}$ for all transitions, which would mean that $\sqrt{I_{\text{DFWM}}} \propto N_g |\mu_{ge}|^2$ holds which is also true for a linear absorption technique. A compari-
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Figure 5.10 Multiplex spectroscopy of the $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma_g^+$ transition of $\text{C}_3$ by applying DFWM, CRD and LIF simultaneously. The square root of the DFWM signal is shown, which represents the functional dependence of the method on number density and transition dipole moment. The spectrum is simulated by an asymmetric rotor model for a rotational temperature of 60 K (lowest trace, inverted).

Comparison of the CRD and DFWM spectra in Figure 5.10 shows that a relatively good agreement is found for the intensities of the single rovibronic transitions. However, transitions belonging to the perturbing $^3\Sigma_g^-$ state are completely absent in the DFWM spectra, whereas they are observed with CRD. The transitions to the levels perturbed by the $P = 1$ state and P-transitions with large $J''$ are only minimally weaker than in the CRD.

The intensities of the spectra obtained with CRD and DFWM match very well. A small difference in the rotational temperatures obtained by a non-linear least-squares fit to the simulated spectra - the temperatures for the CRD-spectra are generally 5-10 K higher than those for DFWM - can be explained by a closer investigation of the interaction regions for the two techniques. DFWM occurs in the volume determined by the overlap of the three input lasers together with the molecular beam, which is determined by the beam waists and the angle at which the three beams cross. The interaction region is
thus confined to a volume in the center of the molecular beam, whereas the CRD beam
encounters absorption on the entire transition through the molecular beam, i.e. also the
outer, higher temperature regions contribute to the absorption signal. Moreover, the laser
pulse in the cavity passes the molecular beam a large number of times, therefore, CRD
spectroscopy samples different spatial regions of the gas pulse exhibiting different tem-
peratures and pressures.

An excellent signal-noise-ratio is observed for the background-free DFWM technique. By
using neutral density filters in front of the photomultiplier tube, signal-to-noise ratios of
up to 50000 could be obtained. However, we must regard that weak transitions are not
observed at all at the chosen input intensities. In addition, it is important to indicate
that the beam alignment and the optimization of the signal for the nonlinear method are
considerably more complex than for LIF or absorption spectroscopy.

To conclude this chapter we emphasize that rotationally resolved multiplex spectroscopy
of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$ electronic transition of C$_3$ allows us to directly compare the relative
intensities of the transitions obtained for the different techniques.

5.5 Conclusions

The rotationally resolved spectrum of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$ transition of the C$_3$ molecule was
taken as a means to investigate the saturation behavior of degenerate four-wave mixing
as well as the dependence of the signal intensity on the configuration of the electric field
polarizations.

Saturation curves were recorded for four rovibronic transitions in the 0$_0^0$ band of the
$\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$ electronic transition and analyzed with the model for a saturable absorber
by Abrams and Lind $[12]$. Only with the incorporation of the geometrical factors derived
by Williams et al. $[76]$ a relatively good agreement was found for three of four investigated
transitions. The validity of the geometric factors has also been supported by recording
DFWM spectra of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$ transition with three different configurations of the
electric field polarizations. The effects of the geometric factors are dramatic for small
$J$. For some specific transitions, the geometric factors are zero, which could be observed
in the C$_3$ experiment for the R(0) transitions in the YXXY polarization configuration.
Although the derivation of the geometric factors does not incorporate nuclear spin, ex-
periments yielding the suppression of two transitions in a particular configuration of field
polarizations, an effect which can be attributed to the geometric factors, were carried out
on formaldehyde, for which the nuclear spin is non-zero.

The reduction of DFWM signal intensities to quantum state populations and transition
dipole moments as proposed by the model of Abrams and Lind is not easily accomplished
as has been shown here. The dependence on the square of $N_g|\mu_{ge}|^2$ such as for an ab-
sorption experiment is only valid when the input laser beam intensities correspond to the
saturation intensity of the transitions. However, the saturation intensities for all transi-
tions within one band might diverge significantly.
The direct, simultaneous acquisition of DFWM and CRD spectra, showed however, that the intensities of the transitions match well. Moreover, the multiplex spectroscopy delivered insight into the advantages and disadvantages of the techniques. LIF and CRD are both very sensitive techniques. When LIF is used together with DFWM, for which relatively intense fields are needed, the transitions are easily saturated. The comparison also shows the favorable signal-to-noise ratio of DFWM in comparison with CRD. However, weak transitions might not be observed in a DFWM spectra. Alternatively, if the intensity of the fields is increased so that the weak transitions can be observed, other transitions might be saturated.

An investigation of geometrical factors which depend on the configuration of the polarizations of the DFWM lasers was performed experimentally. The factors were shown to be valid if the experiment is conducted carefully. Additionally, saturation intensities were determined for transitions from different branches. The discovery that some transitions are saturated only at nearly six times higher intensities than others shows that the acquisition of spectra with quantitative significance in terms of signal intensities is feasible only in a small range of laser intensities. Alternatively, one could record a single spectrum in several steps, e.g. single branches, with appropriate intensities.
Part III

Double-Resonance Four-Wave Mixing and Multiphoton Ionization Experiments
Chapter 6

Two-color resonant four-wave mixing

In this chapter, the application of two-color resonant four-wave mixing (TC-RFWM) is presented for the detection of short-lived species. A part of the experiments has been performed on the $0^0$ band of the $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma_g^+$ transition of C$_3$, where the feasibility of the detection of a transient species produced with a DC-discharge is shown. Further experiments are carried out on high-lying vibrational levels of the $\tilde{A}^1\Lambda_2$ state of formaldehyde, which are situated above the threshold for both the molecular and the radical dissociation channel. Rotational constants of the predissociative vibrational level $2^2S^1$ are determined. The selectivity originating from the double-resonance nature of the technique simplifies the spectral assignment considerably. The results of this chapter are published in Ref. [25] and [107].

6.1 Introduction

We have seen in the previous two chapters that degenerate four-wave mixing is a sensitive spectroscopic technique. Spectra with high signal-to-noise ratios are obtained because of the coherent signal beam which enables a background-free detection. For TC-RFWM, electric fields with two different frequencies corresponding to two resonances in the investigated species are applied. In this manner, a state-selective resonant four-wave mixing technique is obtained. TC-RFWM has been shown to be applicable to the detection of highly predissociative electronic states exhibiting low fluorescence quantum yields, since the technique is based on molecular absorption and, therefore, the signal intensity is unaffected by the lifetime of the upper level [95]. The double-resonance technique permits the unambiguous assignment of rovibronic transitions with the help of intermediate level labeling. This feature of TC-RFWM has been shown to be advantageous for the determination of the rotational constants for vibrationally excited HCO $\tilde{X}^2A'$ radicals, which have been produced by photodissociation of formaldehyde in a low-pressure cell experiment (0.02 bar) [19] or very recently for HC$_4$S produced in a DC-discharge [108]. In the first part of this chapter, we show the applicability of TC-RFWM as a tool to simplify spectra by intermediate-state-labeling. In this part, both $V$ or UP and $A$ or SEP type (see on page 15 in Chapter 2) TC-RFWM processes are observed. In the second part, TC-RFWM is used in combination with DFWM for the rotational characterization of high-lying vibronic bands of formaldehyde exhibiting low fluorescence quantum yields. Rotational constants of the $2^2S^1$ band are determined by exploiting the
high sensitivity of the method, which allows measurements in a molecular beam. Additionally, we take advantage of the favorable selectivity offered by the double-resonance technique for the determination of transition wavenumbers, which are not resolved by one-color spectroscopy.

6.2 TC-RFWM on C₃: probing the same vibrational level

In Chapter 5, laser induced fluorescence (LIF), cavity ring-down (CRD) and degenerate four-wave mixing (DFWM) have been applied to record spectra of the A₁Πᵤ₋X₁Σ₊ᵢ transition of C₃. When the three techniques are used simultaneously, CRD and LIF prove to be very sensitive techniques. The LIF spectrum, however, is strongly saturated at the laser intensities needed for the DFWM experiment. We have seen that DFWM exhibits a larger signal-to-noise ratio as CRD. However, some transitions belonging to up-to-now unassigned perturbing states [92] are not observed when the intensity of the incident laser beams matches the saturation intensities of the major transitions in the band. In the CRD spectra, where these lines are present, the worse signal-to-noise ratio prevents a definite assignment, however.

TC-RFWM dramatically simplifies congested and complex spectra, which are often encountered for polyatomic molecules and radicals, and could be an ideal tool for the assignment of the transitions and possibly for the characterization of these perturbing states. As has been mentioned above, those transitions are not present in the DFWM spectra, when low input intensities are used. However, an observation and a subsequent deperturbation study is probably feasible if higher input intensities can be used. A successful example of a deperturbation study with TC-RFWM has been performed on the Swan band of C₂ in our laboratory [109].

Figure 6.1 depicts traces of the 0⁰ band of the A₁Πᵤ₋X₁Σ₊ᵢ transition of C₃ obtained with LIF and TC-RFWM. In addition, the spectral simulation of the absorption is shown for comparison (lower trace, inverted). For the TC-RFWM spectra, the PUMP laser is tuned to overlap with the (unperturbed) R(4) at 24679 cm⁻¹ exciting molecules with the total angular momentum J'' = 4 in the electronic ground state X₁Σ₊ᵢ to J' = 5 in the excited A₁Πᵤ state. Scanning the frequency of the PROBE laser in the range of the A₁Πᵤ₋X₁Σ₊ᵢ, 0⁰ band reveals four major transitions only, which are, in general, unambiguously assignable since they are required to share a common level with the PUMP transition. The two double-resonance processes involved correspond to (1) Λ-schemes or stimulated emission pumping (SEP) involving the same upper state (J' = 5) and (2) V- or UP-schemes due to depletion of the ground state population. Two transitions corresponding to the V-scheme are observed for P(4) and Q(4) at 24672 and 24675 cm⁻¹, respectively, and one Λ- transition for P(6) at 24669.7 cm⁻¹. All PROBE transitions are well-isolated and their spectral position is readily determinable. However, the transitions arising from the perturbations by the P=1 and the 3Σ₋ᵢ states are not present in the recorded TC-RFWM spectra. As mentioned above, the reason for that might be that the magnitude of the transition dipole moment is very small and that the used laser intensities are too low.
Chapter 6 Two-color resonant four-wave mixing

Figure 6.1 Simultaneously recorded LIF (top trace) and TC-RFWM (middle trace) spectra of the $A^1Π_u - X^1Σ_g^+$ (000-000) band of C$_3$. The PUMP laser is tuned to the R(4) transition at 24679 cm$^{-1}$ while the PROBE laser is scanned. A remarkable simplification in comparison to one-color spectra enables the straightforward assignment of the four remaining transitions. Two $V$-type transitions for P(4) and Q(4) at 24672 and 24675 cm$^{-1}$, one $Λ$-type transition for P(6) at 24669.7 cm$^{-1}$ and one transition which corresponds to DFWM are observed.

We showed the potential of TC-RFWM to simplify the assignments and to increase the accuracy of the determination of the transition wavenumbers, which is evident from the comparison of the TC-RFWM spectrum with the LIF trace in Figure 6.1 or with the DFWM trace in Figure 5.10. The LIF trace in Figure 6.1, which has been recorded simultaneously, shows the major features of the 0$^0_0$ band but is afflicted with substantial noise. In fact, significant fluorescence is produced by the PUMP lasers fixed on the P(4) transition, resulting in a constant background and reducing the S/N ratio to $≈2$. On the other hand, the fluorescence background remains constant, which indicates stable experimental conditions such as laser stability and a stable supersonic expansion.
6.3 Rotational characterization of the high-lying vibrational level $2^25^1$ in the $\tilde{A}^1 \text{A}_2$ state of H$_2$CO

The vibrational assignment for the $2^25^1$ band in the $\tilde{A}^1 \text{A}_2$-$\tilde{X}^1 \text{A}_1$ electronic transition is given by [55] from low-resolution ultraviolet absorption and fluorescence excitation spectra of H$_2$CO, but rotational constants are not available. The rotational branch structure of this band corresponds to the weak progression of $c$-type transitions next to the much stronger $b$-type transitions involving an odd quantum of the $\nu_4$ vibration in the excited state.

The $\nu_2$ and $\nu_5$ normal vibrations of H$_2$CO are of symmetry A$_1$ and B$_2$, respectively. Thus, the vibrational symmetries for the $2^25^1$ band are B$_2$ and A$_1$ for the excited and ground state, respectively. The transition moment consequently lies along the $c$-axis. The selection rules for a $c$-type transitions are $\Delta J = 0, \pm 1$, $\Delta K_a = \text{odd}$, $\Delta K_c = \text{even}$.

In this experiment, the rotational structure of the $2^25^1$ vibrational level of the $\tilde{A}^1 \text{A}_2$ state will be characterized by two-color resonant four-wave mixing. In the unsaturated regime, the dependence of the TC-RFWM signal intensity $I_4$ is given by [110]

$$I_4 \propto N_g^2 |\mu_{gi}|^4 |\mu_{if}|^4 I_1 I_2 I_3 \cdot G_F (\epsilon_4, \epsilon_1, \epsilon_2, \epsilon_3, J''),$$

where $N_g$ is the population of the ground state, $\mu_{gi}$ and $\mu_{if}$ are the transition dipole moments of the transitions from level $g$ to $i$ and $i$ to $f$, respectively. The geometrical factors $G_F (\epsilon_4, \epsilon_1, \epsilon_2, \epsilon_3, J'')$ account for the polarization $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ of the four interacting electric fields similar to those for the degenerate case (see Chapter 5) and are listed in Ref. [110]. $I_1$, $I_2$ and $I_3$ are the intensities of the incoming fields. We can see that the TC-RFWM signal intensity depends on the square of the ground state population $N_g$ just as its degenerate counterpart.

The dependence on the fourth power of the transition dipole moments of both involved transitions demonstrates the necessity of choosing a strong transition for the second resonant step to increase the signal intensity, in particular if the investigated transition is weak. Thus, for the characterization of the $2^25^1$ vibrational level of the $\tilde{A}^1 \text{A}_2$ state one of the most intense vibronic transitions, the $2^24^1$ band [111] is chosen as the second resonant transition.

In Figure 6.2, a DFWM spectrum of the $2^25^1$ vibronic band as well as two TC-RFWM traces are shown. The TC-RFWM spectra are obtained by tuning the PROBE laser in the $2^24^1_0$ band to the rotational transitions $^pR_{12}(2)$ and $^pR_{11}(1)/^rP_{04}(4)$, respectively. The neighboring $^rR_{11}(1)$ and $^rP_{04}(4)$ transitions occur at 30654.3 and 30654.2 cm$^{-1}$ and are excited concomitantly. Such overlapping transitions are often of advantage because they generate additional double resonances suitable for assignment. By keeping the PROBE laser fixed and scanning the PUMP laser in the spectral region of the $2^25^1_0$ band, well-isolated and easily assignable transitions are obtained. In fact, the PUMP laser scans over many absorption lines, but a signal appears only when the PUMP laser is tuned to a level in resonance with the PROBE laser. For $^pR_{12}(2)$, the common state of the PUMP and PROBE transitions is $2_{12}$ of the vibronic ground state $\tilde{X}^1 \text{A}_1 0_0$. Three PUMP transitions
Figure 6.2 TC-RFWM for the characterization of the $2^2S_0^1$ band. A DFWM spectra of the $2^2S_0^1$ transition is shown for comparison in the upper trace. Two TC-RFWM spectra are obtained by tuning the PROBE laser to the $^pR_{12}(2)$ (second trace) and $^pR_{11}(1)/r^P_{04}(4)$ (third trace) rotational transitions in the $2^2S_0^1$ band. The lowest trace depicts a simulation of a one photon transition to $2^2S_1^1$ from the labeled rotational levels $J''_{K''_{A}} = 1_{11}$ and $4_{04}$. These transitions occur well-separated and are perfectly suited for the determination of the wavenumbers of the transitions. Apart from the three expected TC-RFWM transitions, peaks of different origins are observed. Such transitions are due to a pump-dump scheme that very closely resembles stimulated emission pumping and may occur from the common upper level ($3_{03}$ in the $^1A_2$ $2^2S_1^1$ vibronic level) to a rovibrational level in the ground state $^1A_1$.

As mentioned above, the simultaneous excitation of the $^pR_{11}(1)/r^P_{04}(4)$ transitions by the fixed PUMP field does not cause any difficulty. On the contrary, the second TC-RFWM trace clearly shows three transitions from the common $4_{04}$ state ($^rP_{04}(4)$, $^rQ_{04}(4)$ and $^rR_{04}(4)$) and two occurring from the $1_{11}$ state ($^pQ_{11}(1)$ and $^rR_{11}(1)$). The $^rQ_{11}(1)$ transition is too weak to be observed. In addition, TC-RFWM transitions occur because of an energy transfer from the initial level to neighboring rotational levels [32]. For example, the rotational level addressed by the $^pQ_{12}(3)$ transition in the ground state, $3_{12}$, is separated from the close-lying $4_{04}$ rotational level by 1.01 cm$^{-1}$ only. While the field overlaps temporally and spatially with the molecular beam, the energy transfer from $3_{12}$ to $4_{04}$ takes place and gives rise to extra TC-RFWM resonances that are not connected by a common energy level (see for example Table 6.1, second row). From these experiments it is not clear whether the energy-transfer processes are initiated by collisions in the expansion region or by intramolecular relaxation processes. However, taking into account the residuals from the fitting procedure described below, these transitions are assigned unambiguously and are included for rotational analysis. Thus, the four PUMP
scans in the $2^2\Sigma^1_0^+$ band with the selected PROBE laser positions yield 16 well-separated TC-RFWM transitions, which can be assigned in a straightforward manner. Their line positions are included in Table 6.1 and utilized for the determination of the rotational constants (Table 6.3). It is worthwhile to mention that the complex $^pQ_1$ region around 33 497 cm$^{-1}$ of the DFWM spectrum is substantially simplified by using TC-RFWM and allows unambiguous spectral distinction of the $^pQ_{11}(1)$ and the $^pQ_{12}(2)$ transitions.

Table 6.1 Observed TC-RFWM and DFWM transitions and assignments for the $2^2\Sigma^1_0^+$ vibrational band of the $\tilde{A}^1\Sigma^1_2-\tilde{X}^1\Sigma^1_1$ electronic transition in cm$^{-1}$. The transitions are used to determine the rotational constants listed in Table 6.3. For TC-RFWM, the wavenumbers of the PROBE and excited transitions are shown in the last two columns.

<table>
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<th>PUMP $P_{K_1K_2}$</th>
<th>$J''_{K'_2K''_2}$</th>
<th>$\nu_{\text{obs}}$</th>
<th>$\nu_{\text{calc}}$</th>
<th>$\Delta\nu$</th>
<th>$\Delta \nu_{K} = \Delta J_{K_2K''<em>2}^{\nu''}(J')</em>{\nu''}$</th>
<th>$\nu_{\text{obs}}$</th>
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DFWM

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<th>$\Delta\nu$</th>
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[$^a$ $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$]

[$^b$ close-lying transitions (0.1-0.4 cm$^{-1}$) which are excited simultaneously]

[$^c$ energy transfer to close-lying rotational level in the ground state ([112, 32])]
Table 6.2 Observed TC-RFWM transitions (in cm$^{-1}$) and assignments for the 2$^2$3$^4$1 vibrational band of the $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ electronic transition. The rotational transitions in the 2$^2$3$^4$1 band, which are in resonance with the PUMP, are listed in the two columns on the right side.

<table>
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<tr>
<th>$J''_{K''}$, $K''$</th>
<th>PROBE</th>
<th>PUMP</th>
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</table>

$^a \Delta \nu = \nu_{calc} - \nu_{obs}$

$^b$ close-lying transitions (0.1-0.4 cm$^{-1}$) which are excited simultaneously

$^c$ energy transfer to close-lying rotational level in the ground state [32, 112]

Table 6.3 Rotational constants and origin for 2$^2$5$^4$1 and 2$^2$4$^4$1 determined from the wavenumbers of the transitions which are listed in Table 6.1 and by constraining the 0$^0$ rotational level of $\tilde{X}^1A_1$ to the values reported in Ref.[113]. Additionally, literature data for the 5$^5$, 2$^5$5$^5$1 and 2$^4$4$^4$1 vibrational levels are listed for comparison.

<table>
<thead>
<tr>
<th>2$^5$5$^4$1</th>
<th>5$^5$ (Ref. [114])</th>
<th>2$^5$5$^5$1 (Ref. [52])</th>
<th>2$^4$4$^4$1</th>
<th>2$^4$4$^4$1 (Ref. [52])</th>
</tr>
</thead>
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<td>$T_e$</td>
<td>33598.98(2)</td>
<td>31562.279(2)</td>
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<td>30658.46(2)</td>
</tr>
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<td>$A$</td>
<td>8.2677(53)</td>
<td>8.70441(91)</td>
<td>8.7419</td>
<td>8.6406(47)</td>
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<tr>
<td>$B$</td>
<td>1.1029(18)</td>
<td>1.126497(49)</td>
<td>1.1150</td>
<td>1.0948(26)</td>
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<tr>
<td>$C$</td>
<td>0.9955(20)</td>
<td>1.009298(38)</td>
<td>1.0001</td>
<td>0.9920(21)</td>
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</table>

shown in Table 6.1. Figure 6.3 displays such a TC-RFWM spectrum of the 2$^2$4$^4$1 band. The PUMP is fixed on the $^\nu R_{11}(1)$ transition of 2$^2$5$^5$1 band whereas the PROBE is scanned in the region of the 2$^2$4$^4$1 band. A simultaneously recorded LIF spectrum of the 2$^2$4$^4$1 band is presented in the lower trace for comparison. In the TC-RFWM spectrum, three transitions (to 000, 202, and 220) are observed from the 111 rotational level in the electronic ground state $\tilde{X}^1A_1$, which is labeled by the PUMP. Additional transitions labeled with an asterisk arise because the $^\nu R_{12}(2)$ transition which is near the $^\nu R_{11}(1)$ transition is also excited by the PUMP.

The restrictive selection rules for TC-RFWM remove ambiguities in most cases. Additionally, the observed line positions are suitable for computing rotational parameters for
Chapter 6 Two-color resonant four-wave mixing

Figure 6.3 Simultaneously recorded TC-RFWM (upper trace) and LIF (spectra) of the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ $2^24_0^0$ band of H$_2$CO which allow the verification of the assignment of the $2^25^1$ vibrational level. The PUMP is fixed on the $rR_{11}(1)$ transition of $2^25^1_0$ band.

the $2^24^1$ level in a similar fashion as described above for the $2^25^1$ level. By considering the rotational constants available in the literature [52] the accuracy of the method can then be estimated. Table 6.2 summarizes the observed and computed TC-RFWM transitions, residuals and assignments for three PUMP laser positions in the $2^25^1_0$ band. The least-squares fitted parameters are shown in the last two columns of Table 6.3 together with the values from the literature for comparison. Again, higher-order parameters are neglected and set to zero for fitting. The parameters determined in this work show a good agreement with the known rotational constants. The limited number of transitions, the omission of the centrifugal distortion parameters and the spectral resolution of the experiment most likely account for the deviations. A similar accuracy is expected for the evaluation of the rotational constants for the $2^25^1$ vibrational level.

For comparison of the results for the $2^25^1$ level, rotational constants for the $5^1$ and $2^15^1$ levels of $\tilde{A}^1A_2$ are also included in Table 6.3. Generally, the dependence of the effective rotational constant on vibrational quanta is linear to the first order, i.e.

$$A(\nu_1, \nu_2, \ldots, \nu_n) = A_{eq} - \sum_{s=1}^{n} \alpha^A_s \left( \nu_s + \frac{1}{2} \right),$$  \hspace{1cm} (6.2)

where $A_{eq}$ is the equilibrium value of the rotational constant $A$, $\nu_s$ is the quanta in the $s$-th normal mode and $\alpha^A_s$ is the first-order dependence of the rotational constant $A$ on quanta in the $s$-th normal mode. Analogous expressions exist for the $B$ and $C$ rotational constants. Obviously, it is not possible to determine the first-order dependence of the
rotational constants on $\nu_2$ for the limited set of the available data. Nevertheless, Equation 6.2 provides means to rationalize the results shown in Table 6.3 for the $2^25^1$ state. In fact, by comparing the $B$ and $C$ constants for $5^1$, $2^15^1$ and $2^25^1$, a relatively linear decrease of the values is observed for increasing quanta in the $\nu_2$ normal vibration. On the other hand, the dependence of the effective $A$ rotational constant is distinctly nonlinear. It is important to mention that the $5^1$ band is perturbed by $a$-type Coriolis interaction with the $1^14^1$ level, which is only 3.66 cm$^{-1}$ apart [114]. In this case, the $A$ rotational constant dependence is not accurately described by Equation 6.2, and a more complex analysis is required [115]. In addition, the determined $A$ constant of the $2^25^1$ level might also include contributions from Coriolis- or Fermi-type resonances. A comparison of the calculated and observed intensity distributions in the DFWM spectrum for $^7R_1$ region above 33530 cm$^{-1}$, which is shown in Ref. [107], provides a further indication for such perturbations. In fact, we were able to observe a weak band appearing approximately 50 cm$^{-1}$ above the $2^25^1$ level by DFWM and TC-RFWM. However, for determination of the band type and assignment of the newly observed transitions, more experiments are necessary.

It is important to note that the results listed in Table 6.1 could be improved by performing TC-RFWM experiments in the cell at low pressure and ambient temperatures [116]. For these conditions, high $J$ and $K$ levels are thermally populated and yield more accurate rotational constants including centrifugal and higher-order parameters. For the selection of suitable TC-RFWM transitions in the highly congested spectral region of the $2^20^1_0$ band, the rotational constants determined here are of significant value.

### 6.4 Conclusions

TC-RFWM has been shown to facilitate the assignment of molecular spectra by intermediate state labeling. It has been applied to detect transient species produced in a DC-discharge. However, a contribution to the assignment of the states that perturb the $\tilde{A}^1\Pi_u$ state of $C_3$ could not be made so far.

In a second project, TC-RFWM was applied in combination with DFWM for the rotational characterization of high-lying vibrational levels ($2^25^1$ and $2^24^1$) of the $\tilde{A}^1A_2$ state of formaldehyde. It has been demonstrated that TC-RFWM spectroscopy is applicable in the low-density environment of a molecular beam on transitions exhibiting low fluorescence quantum yields. Even though the molecules are cooled by the supersonic expansion to a rotational temperature of $\approx 15$ K causing a substantial reduction of the number of populated rotational levels of the $X^1A_1$ state, many observed transitions are congested in the DFWM spectrum. In fact, the high-lying vibrational bands are subject to predissociation on the picosecond timescale, exhibiting a bandwidth of roughly 0.6 cm$^{-1}$. By taking advantage of the high selectivity of a double-resonance method, TC-RFWM is applied to separate overlapping transitions by intermediate-level labeling. By performing several PUMP scans in the $2^25^1$ region by tuning the PROBE to selected rotational transitions in $2^20^1_0$, well-isolated peaks are observed and readily assigned by considering the restrictive double-resonance conditions. Line positions of TC-RFWM and isolated DFWM transitions are then utilized to compute the $A$, $B$ and $C$ rotational constants
and the band origin $T_e$ for the $2^25^1$ level. By performing TC-RFWM PROBE scans in $2^2_04^1_0$ by fixing the PUMP on a specific rovibronic transition in the $2^25^1_0$ band, the assignments for $2^25^1_0$ transitions are verified. Additionally, the line positions are suited for the determination of rotational constants for $2^24^1$, which can be compared to literature data yielding an estimation of the error bars for the constants of the $2^25^1$ level. While the $B$ and $C$ rotational constants exhibit an approximately linear dependence on the $\nu_2$ normal vibration as expected, the dependence of the $A$ constant is highly nonlinear. The cause of that might be Coriolis- or Fermi-type interactions. In fact, a close-lying vibrational state has been observed approximately 50 cm$^{-1}$ above the investigated $2^25^1$ level which might interact with the $2^25^1$ level. The disagreement of the computed and observed intensities in the $^7R_1$ band is also attributed to an interaction of closely spaced vibrational levels in this energy range.

The sensitivity and selectivity of the applied TC-RFWM method, which has been shown on the example of small polyatomic molecules here, indicate that the technique might be an excellent tool for further investigations on these systems in particular and on polyatomic molecules exhibiting congested spectra and low fluorescence quantum yields in general.
Chapter 7

Double-resonance MPI: the $^1A_2(3p_x)$ Rydberg state of $H_2CO$

In this chapter, the potential of the double-resonance multiphoton ionization (MPI) as a means to record and analyze spectra of transitions to higher excited electronic states is shown. The rotational structure of the vibrational ground state and the two lowest vibrationally excited states, $^61^1$ and $^41^1$ of the $3p_x$ Rydberg state could be characterized successfully. Similar to $^1A_1A_2$, the $^00^1$ state is not directly accessible by a one-photon transition from the electronic ground state. A vibrational assignment of the $3p_x$ Rydberg state has been carried out in a two-photon resonance-enhanced ionization experiment [117], but a rotational characterization is missing in the literature so far. This work aims at providing the rotational constants and the band origins of the lowest-lying vibronic levels. The experiment is based on a two-color resonance-enhanced multiphoton ionization (REMPI), i.e. double-resonance MPI scheme, which involves a resonant excitation to rotational levels of the $^1A_1A_22^14^3$ or $^1A_1A_22^24^4$ state of $H_2CO$. This preselection of the intermediate rotational state greatly simplifies the recorded spectra to the Rydberg state, because only few rotational levels of the excited state can be accessed. Moreover, an enhanced signal-to-noise ratio and full rotational resolution which has not been realized previously are achieved here.

These experiments were carried out in collaboration with the group of Prof. F. Merkt at the Laboratory of Physical Chemistry at ETH Zürich. Their laser equipment, vacuum chamber and spectrometer were used for the experiment, whereas our group provided the molecular beam source. The results presented in this chapter are the content of Ref. [118]. In the context of this collaboration, additional photoionization and PFI-ZEKE (pulsed-field ionization zero-kinetic-energy) photoelectron experiments led to the rovibrational characterization of the electronic ground state $X^+2^2B_2$ of the formaldehyde cation [119]. Parts of the REMPI experiments which answered remaining questions were performed at PSI with a similar experimental setup.

7.1 Introduction

Early VUV absorption studies [120, 121] revealed the presence of $n = 3$ Rydberg states in the energy range between 7.5 and 8 eV. A vibrational structure could be observed first by Lessard and Moule [122, 123, 124]. A more detailed work has been carried out more recently by Liu et al. [117] who could assign several vibrational states in the three $3p$
Rydon states in a (2+1) REMPI study. Theoretical works involving self-consistent field (SCF) and configuration interaction (CI) calculations by Peyerimhoff et al. [125] and Hachey et al. [126, 127, 128, 129] resulted in potential energy curves of several excited states along the C-O stretch mode (see Figure 7.1). In particular, in Ref. [127] the possibility of a third dissociation channel, \( \text{H}_2\text{CO} \rightarrow \text{CH}_2+\text{O} \) is discussed.

![Figure 7.1](image)

**Figure 7.1** The R(CO) stretching potential energy curves as determined by Hachey et al. [127]. The curves which are irrelevant to this study have been omitted for a better understanding. The 3p potential curves are crossed by the \((1)B_1\) and \((1)B_2\) valence states near 2.5 Bohr which corresponds to 1.32 Å.

Of the six normal modes of formaldehyde, the two of lowest wavenumbers are the out-of-plane-wagging mode \( \nu_4 \) and the in-plane-rocking mode \( \nu_6 \). The assignment of those two vibronic levels of \(^1A_2(3\text{p}_x)\), \(^1\) as well as in the cationic ground state, has been the subject of an ongoing debate [132, 122, 123, 117]. In the \(^1\tilde{X}A_1\) and \(^1\tilde{A}A_2\) electronic states, \(^4\) lies lower in energy than \(^6\), whereas the energetic ordering is reversed in the cation. This has been derived in CI calculations by Bruna et al. [128]. Also Liu et al. [117] assigned their photoelectron spectra likewise assuming that the ionization Franck-Condon factors are diagonal implying that upon ionization the vibrational mode accessed in the cation is the same as that in the initial state (i.e. in the Rydberg state). Thus, in Ref. [117] the vibrational levels in question were assigned to be \(^6\) at 68 542 cm\(^{-1}\) and \(^4\) at 68 709 cm\(^{-1}\). This assignment was justified by the assumption that the values of the vibrational wavenumbers (812 cm\(^{-1}\) and 979 cm\(^{-1}\), respectively) are very close to those of the parent cation, which were determined to be 812 cm\(^{-1}\) and 919 cm\(^{-1}\) in the same work. However, the reasoning includes the assumption that the \(^1A_2(3\text{p}_x)\) state is a well-behaved Rydberg state meaning that the vibrational structure in the Rydberg state resembles that of the

\(^1\)For referring to Rydberg and valence states the notation from the Ref. [128, 130, 131] is adopted.

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Chapter 7 Double-resonance MPI: the $^1A_2(3p_x)$ Rydberg state of H$_2$CO

A Rydberg state of H$_2$CO

Figure 7.2 The excitation scheme for the REMPI experiments. Formaldehyde is excited by a photon of wavenumber $\tilde{\nu}_1$ from a rotational level $J''_{K''_1K''_c}$ in the electronic ground state $\tilde{X}^1A_1$ to an intermediate level $\tilde{A}^1A_2 2^14^3$. A rotational level $J_{K_1K_c}$ in $^1A_2(3p_x)$ is accessed by a transition induced by a photon with wavenumber $\tilde{\nu}_2$, from where the molecule is ionized by a photon with wavenumber $\tilde{\nu}_1$ or $\tilde{\nu}_2$. The excitation scheme with $\tilde{A}^1A_2 2^24^1$ as intermediate vibronic level is similar, because it has the same symmetry as $\tilde{A}^1A_2 2^14^3$.

The double-resonance excitation scheme which is chosen here for the investigation of the $^1A_2(3p_x)$ Rydberg state is depicted schematically in Figure 7.2. The initial vibronic transition from $\tilde{X}^1A_1$ to $\tilde{A}^1A_2 2^14^3$ is of type $b$, and belongs to the $2^m4^n$ progression, which is allowed by vibronic coupling and exhibits significant intensity. The ensuing excitation from $\tilde{A}^1A_2 2^14^3$ to $^1A_2(3p_x)$ is vibronically allowed if the vibronic symmetry of the final state is $A_1$, $A_2$ or $B_2$. Hence, excitation to the $^1A_2(3p_x)$ $0^0$ state yields a $c$-type band. $a$-Type bands can be obtained by exciting an odd number of quanta in the $\nu_4$ mode (or any combination with a vibration belonging to the totally symmetric representation $A_1$, $\nu_1$, $\nu_2$ or $\nu_3$), but $b$-type bands will not be observed because vibrations with $A_2$ symmetry do not exist. Excitation of $\nu_5$ and $\nu_6$ in $^1A_2(3p_x)$, however, is not allowed by symmetry selection rules. Table 7.1 summarizes the selection rules for the experiments which are presented in this chapter.

In the following sections, the notable simplification of spectroscopic assignment with the help of the double-resonance technique will be shown. Previously undetermined rotational constants as well as improved values for the band origins of the three lowest vibronic levels of the $^1A_2(3p_x)$ Rydberg state are provided. In addition, we rationalize the observation of the $2^04^04^0$ band in the $^1A_2(3p_x)$-$\tilde{A}^1A_2$ transition, which is forbidden by electric dipole selection rules in the excitation scheme employed in this experiment.
A (1+2) REMPI experiment, with the first excitation step in resonance with the $^2P_{1/2}$ level, involves a maximum change of $\Delta K_a$ calculated by excitation from $\tilde{X} \approx 15$ K, rotational levels up to $K_a'' = 1$ are populated. In a two-photon transition, where a $b$- and a $c$-type transition are involved, a maximum change of $\Delta K_a = 2$ can occur. Thus, an excitation to rotational levels of $^1A_2(3p_x)$ with $K_a = 3$ is possible. The (1+2) REMPI spectrum is not reproduced here, but a DFWM spectrum of the same transition at similar experimental conditions is shown in Chapter 4 in Figure 4.3. For the reason that this process is resonant only in the first step and a two-photon absorption is necessary to ionize the molecules, the ionization cross-section is diminished. Thus, large laser powers are needed, which cause power broadening and a poor signal-to-noise ratio in the obtained spectra. The strongest transitions in that band are chosen as initial excitation steps for the double-resonance experiment.

For the main experiment a double-resonance MPI or $(1 + 1'(l))$ REMPI scheme is applied (see Figure 7.2): a selected rotational state $J''_{K_a''K_a''}$ in the $^1A_2(3p_x)$ state is populated by excitation from $\tilde{X}^1A_1$ $J''_{K_a''K_a''}$ by $\nu_1 \approx 30340$ cm$^{-1}$. Following this first step, UV light in the range of 37000 – 38500 cm$^{-1}$ ($\nu_2$) is used to excite the molecules to the $^1A_2(3p_x)$ Rydberg state. Subsequently, the molecules are ionized by further excitation to the continuum of the $X^+B_2$ electronic state of $H_2CO^+$ by a photon of wavenumber $\nu_1$ or $\nu_2$.

In a first series of measurements transitions from selected rovibronic states $^1A_2(3p_x)$ $J''_{K_a''K_a''}$ to the $^1A_2(3p_x)$ $0^0$ state are recorded. The spectrum for a single experiment with intermediate excitation of $J''_{K_a''K_a''} = 2_{20}$ and $2_{21}$ is shown in Figure 7.3. The first photon wavenumber coincides with the transition energy of the nearly overlapping transitions $\Delta K_a \Delta J_{K_a''K_a''} = K_a'' - K_a''$, where $K_a''$ is the asymmetric rotor label of the rotational level in the Rydberg state and $K_a''$ that of the $^1A_2(3p_x)$ level.

### Table 7.1 Selection rules for the vibronic transitions from the $^1A_2(2^14^3)$ state to the $^1A_2(3p_x)$ state.

<table>
<thead>
<tr>
<th>$\Gamma_{\nu''}$</th>
<th>$3p_x$</th>
<th>$\Gamma_{\nu''}$</th>
<th>transition type</th>
<th>$\Delta K_a$</th>
<th>$\Delta K_c$</th>
</tr>
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<tbody>
<tr>
<td>$B_2$</td>
<td>$0^0$</td>
<td>$A_2$</td>
<td>$c$-type</td>
<td>odd</td>
<td>even</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$4^1$</td>
<td>$B_2$</td>
<td>$c$-type</td>
<td>even</td>
<td>odd</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$6^1$</td>
<td>$B_1$</td>
<td>forbidden</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 7.2 The vibrational ground level of the $^1A_2(3p_x)$ state

A (1+2) REMPI experiment, with the first excitation step in resonance with the $2^14^3$ band of the $^1A_2-\tilde{X}^1A_1$ transition, is carried out to obtain information about the rotational population of the electronic ground state. At the prevailing experimental conditions in the molecular beam, i.e. rotational temperatures of $\approx 15$ K, rotational levels up to $K_a'' = 1$ are populated. In a two-photon transition, where a $b$- and a $c$-type transition are involved, a maximum change of $\Delta K_a = 2$ can occur. Thus, an excitation to rotational levels of $^1A_2(3p_x)$ with $K_a = 3$ is possible. The (1+2) REMPI spectrum is not reproduced here, but a DFWM spectrum of the same transition at similar experimental conditions is shown in Chapter 4 in Figure 4.3. For the reason that this process is resonant only in the first step and a two-photon absorption is necessary to ionize the molecules, the ionization cross-section is diminished. Thus, large laser powers are needed, which cause power broadening and a poor signal-to-noise ratio in the obtained spectra. The strongest transitions in that band are chosen as initial excitation steps for the double-resonance experiment.
Chapter 7 Double-resonance MPI: the $^1A_2(3p_x)$ Rydberg state of H$_2$CO

**Figure 7.3** Double-resonance multiphoton ionization of formaldehyde. Excitation to the vibrational ground state of $^1A_2(3p_x)$ is observed from the intermediate states $^3A^1A_2\,2^14^3\,2_{20}$ and $2_{21}$ which are simultaneously excited in the first excitation step $^3A^1A_2-X^1A_1\,2^14^3\,0_{00}$.

The values on the horizontal axis represent the total wavenumber above the ground state $X^1A_1\,(0^0)\,0_{00}$.

**Figure 7.4** Compilation of the double-resonance MPI spectra to the $^1A_2(3p_x)\,0^0$ state. On the $x$-axis the energy of the intermediate rovibrational state in $^3A^1A_2\,2^14^3$ relative to the $0_{00}$ rotational level of the electronic ground state $X$ has been added to the transition energy to reveal the term energies of the upper levels $J_{K_aK_c}$ of the transitions. The labels on the top represent the $J_{K_aK_c}$ levels. On the left side the intermediate rotational states $J'_{K_a'K_c'}$ in $^3A^1A_2\,2^14^3$ are indicated. The transitions marked with asterisks and pluses arise from excitation from the levels $^3A^1A_2\,2^14^3\,3_{12}$ and $1_{10}$, respectively, which are populated simultaneously with $J'_{K_a'K_c'} = 2_{11}$.
quantum number $K_c$ differing by 1 can be accessed from $J_{K_a'K_c'} = 2_{21}$. The $K_a=1$ doublets are not clearly resolved except for 3$_{12}$ and 3$_{13}$, and even less clearly still for 2$_{11}$ and 2$_{12}$ because the transitions overlap partly.

A collection of all recorded spectra is shown in Figure 7.4. The left side of the graph shows the upper rotational levels of the transitions in the $2^1_0 3^1_0$ band of the $\tilde{A}^1A_2-X^1A_1$ transition, which are selected as intermediate states for further excitation to the $^1A_2(3p_x)$ state.

Due to the simplicity of the double-resonance spectra, the rotational assignment of the transitions is carried out in a straightforward manner by intermediate level-labeling. In order to obtain best values for the transitions wavenumbers, Lorentzian-shaped lines are fitted to the experimental lines. These wavenumbers are listed in Table 7.2. Additionally, the wavenumbers of all accessed rotational levels of $^1A_2(3p_x)$ determined by adding the term energies of the intermediate rovibronic levels are listed in Table 7.3.

### Table 7.2

<table>
<thead>
<tr>
<th>$\Delta K_a \Delta J_{K_c'K_c'} (J')$</th>
<th>$\tilde{\nu}_{\text{obs}}$</th>
<th>$\tilde{\nu}_{\text{calc}}$</th>
<th>$\delta \tilde{\nu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^rR_{10}(1)^a$</td>
<td>37068.10</td>
<td>37067.97</td>
<td>0.13</td>
</tr>
<tr>
<td>$^pP_{10}(1)^a$</td>
<td>37069.49</td>
<td>37060.64</td>
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<td>$^pP_{12}(2)^a$</td>
<td>37071.20</td>
<td>37071.00</td>
<td>0.20</td>
</tr>
<tr>
<td>$^pP_{14}(2)^a$</td>
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<td>37058.79</td>
<td>0.04</td>
</tr>
<tr>
<td>$^pP_{14}(1)^a$</td>
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<td>37071.00</td>
<td>0.27</td>
</tr>
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<td>$^rP_{11}(2)^a$</td>
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<td>37094.84</td>
<td>0.52</td>
</tr>
<tr>
<td>$^rR_{10}(1)^a$</td>
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<td>37099.14</td>
<td>0.03</td>
</tr>
<tr>
<td>$^pP_{16}(1)^a$</td>
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<tr>
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<td>$^rQ_{01}(1)$</td>
<td>37396.71</td>
<td>37396.92</td>
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</tr>
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</tr>
<tr>
<td>$^rR_{11}(1)$</td>
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<td>37418.17</td>
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</tr>
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<td>37418.08</td>
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</tr>
<tr>
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<td>37386.91</td>
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<tr>
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<td>37421.10</td>
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</tr>
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<td>37375.74</td>
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</table>

$^a$: transitions from $^A^1A_2 2^2A_1$

The wavenumbers from Table 7.2 are used in a nonlinear least-squares fit to obtain values

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Chapter 7 Double-resonance MPI: the $^1A_2(3p_x)$ Rydberg state of $H_2CO$

Table 7.3 Observed and calculated absolute energies above the rovibronic ground state for rotational states in the $0^0$ level of the $^1A_2(3p_x)$ state in cm$^{-1}$. The observed values are obtained by adding the measured transition wavenumbers from Table 7.2 to term energies of the intermediate levels of the $\tilde{A}^1A_2^12^14^3$ state. If one state is accessed by more than one transitions the arithmetic average is listed.

<table>
<thead>
<tr>
<th>$J_{k_a k_c}$</th>
<th>$\tilde{\nu}_{obs}$</th>
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<th>$\delta\tilde{\nu}$</th>
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<tr>
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<td>67743.82</td>
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<td>211</td>
<td>67744.44(0.12)</td>
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<td>303</td>
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<td>67813.77</td>
<td>67813.70</td>
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</table>

* numbers in brackets are one standard deviation

for the rotational constants and the band origin. The results are displayed in Table 7.4. Only a small number of $J$ levels is accessed and the line widths of the observed transitions is relatively large, the full width at half maximum (FWHM) amounts to 1.2 cm$^{-1}$, therefore the precision in the determined wavenumbers of the rotational levels is reduced. Thus, a rigid-rotor Hamiltonian is found to be sufficient for the fit.

Table 7.4 Rigid-rotor asymmetric-top rotational constants, band origin $T_0$, Coriolis constant $\xi_{4,6}$ and fundamental wavenumbers 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.

<table>
<thead>
<tr>
<th></th>
<th>$A$ /cm$^{-1}$</th>
<th>$B$ /cm$^{-1}$</th>
<th>$C$ /cm$^{-1}$</th>
<th>$T_0$ /cm$^{-1}$</th>
<th>$\nu_4$ /cm$^{-1}$</th>
<th>$\nu_6$ /cm$^{-1}$</th>
<th>$\xi_{4,6}$ /cm$^{-1}$</th>
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<td>$\tilde{\nu}_{obs}$</td>
<td>9.006(19)</td>
<td>1.331(20)</td>
<td>1.135(22)</td>
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<td>808.88(25)</td>
<td>984.92(26)</td>
<td>8.86(89)</td>
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The band origin is found to be 67528.939(82) cm$^{-1}$, which is in good agreement with the 67530 ± 2 cm$^{-1}$ which was reported by Liu et al. [117]. The values for the rotational constants, $A = 9.006(19)$ cm$^{-1}$, $B = 1.331(20)$ cm$^{-1}$, and $C = 1.135(22)$ cm$^{-1}$ are comparable to those of other electronic states (see in Ref. [52]). For example, the constants for the electronic ground state $\tilde{X}$ are: $A = 9.4055$ cm$^{-1}$, $B = 1.2954$ cm$^{-1}$, $C = 1.1342$ cm$^{-1}$. The rotational constants of the formaldehyde cation in the electronic ground state, which have been determined in the other part of this collaboration [119, 133], are $A^+ = 8.874(8)$ cm$^{-1}$, $B^+ = 1.342(15)$ cm$^{-1}$, and $C^+ = 1.148(18)$ cm$^{-1}$. The values for $B^+$ and $C^+$ are very close to the rotational constants obtained here. The slightly smaller value of the rotational constant $A^+$ suggests that the HCH angle increases slightly upon ionization.
The calculated values for the rotational levels of the $^1A_2(3p_z)$ $0^0$ level are listed in the second column of Table 7.3. They are in good agreement with the measured positions. The average error of the fit, $\sum_i (\delta \nu_i)^2 / (n_{\text{obs}} - n_{\text{par}})$, where $n_{\text{obs}} = 30$ is the number of observed values, amounts to 0.22 cm$^{-1}$. The maximum deviation of 0.52 cm$^{-1}$ found for the transition $^rQ_{11}(2)$ originates most likely from fitting two overlapping transitions to two Lorentz lineshapes. The $^rQ_{11}(2)$ lies on the shoulder of the much stronger $^rR_{10}(1)$ transition, for which the error is only 0.03 cm$^{-1}$.

The resolution of the rotational substructure supports the conclusion of Liu et al. [117] that the observed band is not a doublet band resulting from an inversion manifold due to a non-planar geometry which has been suggested earlier by Mentall et al. [132]. In fact, three peaks in the origin band are reported in Ref. [132] and assigned to $K_a'' = 0$ and $\Delta K_a = 2$ originating from $K_a'' = 0$ and 1, respectively. Moreover, from the separation of the bands the authors derived an approximate value of the rotational constant $A$ of 9 cm$^{-1}$, which is in good agreement with the more accurate value obtained here.

In Figure 7.5 four selected spectra are compared with simulations; the values of the line strength correspond to the Hönl-London factors obtained with pgopher [59] assuming a transition from a level $J''_{K_a'K_a'}$ in $^1A_2$ 2$^1$4$^3$ to $J_{K_aK_c}$ in $^1A_2(3p_z)$.

Figure 7.5(a) is obtained via the intermediate rotational level $J''_{K_a'K_a'} = 1_{01}$, accessed by the $\Delta K_a \Delta J_{K_a'K_a'}(J''m) = r Q_{10}(1)$ transition. Both states in $^1A_2(3p_z)$ that are accessible according to the selection rules, $J_{K_aK_c} = 1_{11}$ and $2_{11}$, are observed with intensities that are in agreement with the simulation. Similarly, a good agreement is observed for the transitions via the simultaneously excited $J''_{K_a'K_a'} = 2_{20}$ and $2_{21}$ (Figure 7.5(b)) as discussed above (Figure 7.3), although the measured intensity of the transition to $J_{K_aK_c} = 3_{31}/0$ is somewhat smaller than expected. For excitation from $J''_{K_a'K_a'} = 1_{11}$ accessed via $^rQ_{02}(2)$, the transition to $J_{K_aK_c} = 1_{01}$ is missing while $2_{21}$ is present (Figure 7.5(c)). This will be discussed below. For $J''_{K_a'K_a'} = 1_{10}$ and $2_{11}$ accessed by the $^rQ_{01}(1)$ and $^rQ_{02}(2)$ transitions shown in Figure 7.5(d) a rather good agreement with the simulation is obtained with the exception of the missing lowest rotational state $J_{K_aK_c} = 0_{00}$.

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<td>$\frac{1}{2}J(J+1)$</td>
<td>$\frac{3}{2}J(J+1)$</td>
</tr>
</tbody>
</table>

Table 7.5 Geometrical factors for a two-photon absorption process with intermediate resonant excitation from Ref. [134]. The letters on the left side indicate the change of the angular momentum $J$ in the first excitation step, the letters on the top those in the second step. In the expressions in this table, $J$ is written instead of $J''$ for simplicity.

The simulation of the double-resonance spectra in Figure 7.5 has been performed by assuming a noncoherent excitation. In particular, it has been assumed that upon the initial
excitation to the $\tilde{A}^1A_2 2^14^3$ state the molecules are isotropically oriented in the molecular beam and that one-photon selection rules are applicable for the second transition $1^1A_2(3p_x)$-$\tilde{A}^1A_2$. However, such a treatment is inaccurate for a double-resonance multiphoton process.

In fact, geometric factors, which allow for the polarization similar to those for degenerate four-wave mixing (see Chapter 5) are required to calculate near-resonant two-photon absorption processes as shown by Chen and Young [134]. These factors are listed in Table 7.5 for two electric fields with parallel polarization. The factors are derived for all possible transition sequences in terms of the change of $J$ values in each step and depend only on $J''$ value of the initial state. An evaluation of these factors for the case of a transition sequence $(\Delta J(\text{first}),\Delta J(\text{second}))=(R,Q)$, i.e. a Q-type transition following an R-type transition, for $J''=0$ yields 0 and thus justifies the absence of the expected transition $^pQ_{11}(1)$ in Figure 7.5(c). The physical process that takes place is the following: before the absorption of the first photon the population is isotropic, i.e. all magnetic sublevels denoted by the quantum number $M$, are equally populated. Absorption of linearly-polarized

![Figure 7.5](image-url)
radiation yields a change of \( M \) by \( \pm 1 \) \cite{135}. In the case, where \( J'' = 0 \), the molecules are oriented by the absorption of the first photon. Consequently, it is not possible to obtain a molecule with \( J = 1 \) with the absorption of a second photon with the same polarization, just as it is impossible to add one vector of length 1 to an initial vector of length 1 and to obtain a vector with length 1 that is perpendicular to the first vector.

![Figure 7.6](image-url)

Figure 7.6 Spectra of the \( 2^1 \tilde{A}_0^0 \) vibrational band of the \( ^1A_2(3p_x) - \tilde{A}^1A_2 \) transition via the intermediate state \( J''_{K_a''K_c''} = 1_{11} \) recorded with two-color REMPI. \( \text{H}_2\text{CO} \) is excited to \( J''_{K_a''K_c''} \) from two different rotational levels of \( \tilde{X}^1A_1 \), \( J''_{K_a''K_c''} = 0_{00} \) (upper trace) and \( J''_{K_a''K_c''} = 2_{02} \) (bottom trace) by \( ^rR_{00}(0) \) and \( ^rP_{02}(2) \), respectively. Whereas the transition to \( J_{K_aK_c} = 1_{01} \) is absent in the lower trace (and in Figure 7.4), it is observed clearly in the upper trace. See text for details.

A modification of the polarization configuration can be exploited for the deconvolution of overlapping lines or for the validation of assignments. The dramatic effect of the geometrical factors on the two-color spectrum is shown in Figure 7.6. Both traces originate from excitation of the intermediate rotational state \( J''_{K_a''K_c''} = 1_{11} \) that has been populated by \( ^rR_{00}(0) \) (lower) and \( ^rP_{02}(2) \) (upper) transitions, respectively. The intensities are substantially different for the two double-resonance transitions in the spectrum exhibiting transition sequences \((R,Q)\) and \((R,R)\) (lower), and \((P,Q)\) and \((P,R)\) (upper).

In panel (d) of Figure 7.5, the initial step also involves a simultaneous excitation to two intermediate states. The expected transitions resulting from both intermediate states are all present except the excitation to \( J_{K_aK_c} = 0_{00} \). Again, the absence of the transition is caused by the polarization dependence of the two-photon process. The factor from Ref. [134] is 0 for a P transition following a Q transition starting from a \( J'' = 1 \) level. In this case, the transition cannot be recorded in the same manner as in the previous case. An excitation from \( J''_{K_a''K_c''} = 2_{02} \) to \( J''_{K_a''K_c''} = 1_{01} \) is not possible in this experiment because \( K_a'' = 2 \) levels are not populated. To obtain the transition nevertheless a magic angle configuration is used, where the angle between the electric field vectors is altered to 54.7
Figure 7.7 Two double-resonance MPI spectra where the first excitation step is equal \((J'_{K'_aK'_c} = 1_{10} \leftarrow J''_{K''_aK''_c} = 1_{01})\), once recorded with parallel polarization (lower trace) and once with an angle of 54.7 degrees between the two electric field vectors (upper trace). The transition to \(J_{K_aK_c} = 0_{00}\) does not occur in the experiment with parallel polarizations. A simulation of a one-photon spectrum (dotted) is displayed for comparison. The peaks marked with asterisks are transitions originating from excitation from \(J'_{K'_aK'_c} = 2_{11}\).

degrees (see e.g. in [136]). This polarization configuration is often used in REMPI experiments to avoid the effect of intensity dependence on the polarization. The spectrum is presented in Figure 7.7. For comparison, a spectrum obtained with parallel polarization is shown.

These two spectra are recorded via the intermediate vibronic level \(\tilde{A}^1A_2 \, 2^24^1\) for reasons related to the experimental setup. The level has the same symmetry as the \(\tilde{A}^1A_2 \, 2^14^3\) state, thus, the same selection rules for both excitation steps apply. The transitions in the spectrum obtained with parallel polarizations exhibit different relative intensities to those shown in Figure 7.5 (d), but again, the transition to \(J_{K_aK_c} = 0_{00}\) is missing. With the use of the magic angle configuration, this transition appears as expected.

### 7.3 The two lowest-lying vibrationally excited levels of the \(^1A_2(3p_x)\) Rydberg state

The two lowest vibrational levels of the \(^1A_2(3p_x)\) Rydberg state assigned as the \(6^1\) and the \(4^1\) levels are situated approximately 800 cm\(^{-1}\) and 1000 cm\(^{-1}\) above the vibrational ground state of the \(^1A_2(3p_x)\) state. Double-resonance MPI spectra are recorded in the same manner as described in the previous section and are shown in Figure 7.8. Although transitions to the \(6^1\) vibronic level are not expected (\textit{vide supra}) transitions to both \(6^1\)
and $4^1$ are observed. Five spectra are recorded via selected intermediate rotational levels of $\tilde{A}^1A_2 \cdot 2^14^3$, $J'_{K_c'K_c} = 2_{02}, 2_{02}, 3_{21/2}, 1_{11},$ and $2_{11}$. Transitions to both vibrational levels of $^1A_2(3p_x)$ are observed via all intermediate levels except for $J'_{K_c'K_c} = 2_{02}$, where only transitions to $4^1$ are present. Another notable fact is the difference in the FWHMs. The transitions at lower energies are rotationally resolved and the FWHM ($\approx 1.8$ cm$^{-1}$) which corresponds to a lifetime of 1.47 ps) are comparable to those of the transitions to the vibrational ground state. The FWHMs of the higher energy component, however, amount to $\approx 6.3$ cm$^{-1}$ (corresponding to a lifetime of 0.42 ps) impeding a straightforward rotational assignment. Similar to the $^1A_2(3p_x)$ $0^0$ state, states with equal $J$ and $K_a$ but different $K_c$ cannot be resolved in either vibronic level.

From the spectra in Figure 7.8 it can be seen that the rovibronic transitions to both vibronic states are parallel, i.e. $\Delta K_a = 0$. Further evidence is obtained by superimposing the spectra to the $6^1$ and the $4^1$ levels via the same intermediate state $J'_{K_c'K_c}$ as shown in Figure 7.9. In addition, a deconvolution of the broad features to the $4^1$ state is feasible and yields approximate line positions for further analysis. As in the previous section, Lorentzian lineshape fits yield the wavenumbers of the transitions and the absolute term energies. The results are presented in Tables 7.6 and 7.7. It should be noted that in Figure 7.9(a) and (b) both asymmetry components are excited simultaneously, differing only by $K_c'$. The resulting REMPI spectra represent, therefore, a convolution of transitions originating from both components. Unfortunately, the substantial line widths of the transitions to both vibronic levels prevent the assignment to a specific asymmetry component. The gap between two such levels would increase as $J$ increases, but in this experiment we are limited to a small range of $J$ values.

Disregarding the fact that the transitions to the $6^1$ level are forbidden (vide infra), we obtain the rotational constants and the band origin for an asymmetric rigid rotor model with a fit analogous to that in the vibronic ground state. The resulting wavenumbers of the out-of-plane bending ($\nu_4$) and in-plane rocking ($\nu_6$) modes obtained from this fit are $\tilde{\nu}_6 = 809.5$ cm$^{-1}$, $\tilde{\nu}_4 = 985.6$ cm$^{-1}$. The fitted values of the rotational constants are $A = 8.62$ cm$^{-1}$, $B = 1.34$ cm$^{-1}$, and $C = 1.14$ cm$^{-1}$ and $\bar{A} = 9.52$ cm$^{-1}$, $\bar{B} = 1.36$ cm$^{-1}$, and $\bar{C} = 1.16$ cm$^{-1}$ for the $6^1$ and the $4^1$ vibrational levels, respectively. The wavenumbers obtained for $\tilde{\nu}_6$ and $\tilde{\nu}_4$ are in good agreement with those of Ref. [117], 812 cm$^{-1}$ and 981 cm$^{-1}$, and the rotational constants $B$ and $C$ are comparable to those for the vibronic ground state.

The inconsistency of the values of the $A$ constant for the $4^1$ and the $6^1$ state is striking and implies the presence of an irregularity. In fact, the reason for the observation of transitions to the $6^1$ vibronic level (i), the absence of transitions to $6^1$ rotational levels with $K_a = 0$ (ii), the difference in the rotational constants $A$ (iii) and the distinct line widths (iv) strongly suggest a considerable Coriolis interaction along the $a$-axis which couples the $4^1$ and the $6^1$ levels. Coriolis coupling between the $4^1$ and the $6^1$ vibrational states is a well-understood characteristic in the electronic ground state $\tilde{X}$ of formaldehyde. The same phenomenon occurs in the $\tilde{A}^1A_2$ state, between the $6^1$ and the $4^3$ vibrational states,
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Figure 7.8 The double-resonance MPI spectra of the two lowest vibrationally excited states. The various traces are transitions to the $3p_x$ Rydberg state via intermediate excitations to rotational states in $\tilde{A}^1A_2 2^14^3$ noted on the left side. The narrow lines at lower energies are vibronically forbidden transitions to the $^1A_2(3p_x)$ $6^1$ state which are observed due to Coriolis coupling with the $4^1$ state. The transitions at higher energies belong to the vibrational band exciting the $^1A_2(3p_x)$ $4^1$ state and exhibit an $a$-type structure. The transition marked with the asterisk arises from excitation from $J'_{K_a'K_c'}=1_{02}$ and those marked with a plus from $J'_{K_a'K_c'}=3_{03}$. These intermediate levels are simultaneously populated by close-lying transitions to the $\tilde{A}^1A_2 2^14^3$ state. The upper states of the transitions from $J'_{K_a'K_c'}=2_{02}$ lead to excitation of rotational levels with $K_a=0$ in the $4^1$ vibrational level. For the reason that the $a$ type Coriolis coupling matrix elements are zero for $K_a=0$ transitions to $3p_x$ $6^1$ do not appear in the trace with $J'_{K_a'K_c'}=2_{02}$.
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Figure 7.9 Coriolis-coupling between the $4^1$ and $6^1$ states. The positions of the transitions to the $6^1$ level (thin trace) are shifted by $\nu_4 - \nu_6 + E_{rot}^{4^1} - E_{rot}^{6^1}$ to illustrate that both vibronic transitions exhibit the same $a$-type rotational structure. $E_{rot}^{4^1}$ and $E_{rot}^{6^1}$ are the calculated rotational energies in the $6^1$ and $4^1$ vibrational levels, respectively. The larger line width of the transitions to $4^1$ results probably from vibronic coupling to a dissociative valence state of equal symmetry. The excitation was performed via the intermediate states (a) $J'_{K_a'K_c'} = 2_{20}$ and $2_{21}$, (b) $J'_{K_a'K_c'} = 3_{12}$ and $3_{13}$, (c) $J'_{K_a'K_c'} = 1_{11}$, and (d) $J'_{K_a'K_c'} = 1_{10}$ and $2_{11}$, respectively.

which are close-lying in energy in the $\tilde{A}^1A_2$ state due to its non-planar geometry [52]. Besides, we have found that in the electronic ground state of the formaldehyde cation the $4^1$ and $6^1$ vibrational levels interact by Coriolis coupling [119].

The Coriolis interaction implies that the molecular system is not sufficiently described by an asymmetric rigid rotor Hamiltonian. To account for the Coriolis coupling the Hamiltonian $H_{RR} = \hbar^{-2}(A\hat{J}_z^2 + B\hat{J}_x^2 + C\hat{J}_y^2)$ must be extended by the term

$$V_{Cor} = A\zeta_{4,6}^a(\hat{Q}_4\hat{P}_6 - \hat{Q}_6\hat{P}_4)\hat{J}_a,$$

where $Q_i$ is the $i$-th normal coordinate, $\hat{P}_i$ the $i$-th conjugate momentum and $\zeta_{4,6}^a$ the
Coriolis coupling constant as defined in Ref. [137]. In the basis of symmetric top wave functions $|JK, \nu_4\nu_6\rangle$ the Hamiltonian possesses off-diagonal matrix elements proportional to $\xi_{4,6}^a \cdot K$ for pairs of symmetric top wave functions in the $4^1$ and the $6^1$ states with equal $J$ and $K$, where

$$\xi_{4,6}^a = A \zeta_{4,6}^a \left( \sqrt{\frac{\nu_6}{\nu_4}} + \sqrt{\frac{\nu_4}{\nu_6}} \right)$$

as defined in Ref. [138]. Consequently, asymmetric rotor levels with equal $J$ and $K_a$ and $K_c$ differing by 1 are coupled, because only levels with equal rovibronic symmetry can interact. Thus, the reason that no transitions to $6^1$ for levels with $K_a = 0$ are observed, is that Coriolis coupling does not occur in this case. An intuitive explanation of the Coriolis coupling process is given in Ref. [139]. When the vibrational motion of the nuclei in a molecule that rotates about the $a$-axis is considered, the $\nu_4$ vibrational motion is converted into $\nu_6$ and vice-versa. The closer the two vibrational $4^1$ and $6^1$ levels are in wavenumbers, the stronger the perturbation of the rotational lines in either vibrational levels will be. The $K_a$ quantum number is the projection of the angular momentum vector $J$ on the molecular axis $a$. Therefore, for states with $K_a = 0$, rotation about the $a$-axis and consequently Coriolis coupling does not occur and the transitions to the $6^1$ level cannot steal intensity from the transition to the $4^1$ level. An $a$-type Coriolis interaction will cause a strong local perturbation of the rigid-rotor energy level structure if the $K$-manifolds overlap. However, if the vibrational states are well-separated energetically, a strong $a$-type Coriolis interaction will result in effective $A$ constants. The $A$ constant of the energetically lower-lying vibration is smaller than expected, that of the higher-lying level larger than expected, which is in good agreement with the values of the fitted rotational constants above.

A least-squares fit has been performed to determine the values for the band origins and the Coriolis coupling constant $\xi_{4,6}^a$. The rotational constants $A$, $B$ and $C$ are fixed at the rigid rotor value derived for the vibrational ground state because not enough transitions are observed in this experiment. Moreover, due to their large line widths the positions of the observed transitions to $4^1$ are afflicted with additional uncertainty even though they are determined with fits to Lorentzian lineshapes. The results of the fits are presented in Table 7.4. The deperturbed fundamental wavenumbers of the two vibrational modes amount to 808.88(25) cm$^{-1}$ and 984.92(26) cm$^{-1}$ for $\nu_6$ and $\nu_4$, respectively. The large Coriolis coupling constant of 8.86(89) cm$^{-1}$ is comparable to that of the electronic ground state (10.414368(140) cm$^{-1}$ [52]) and in the ionic ground state (8.70 cm$^{-1}$ [119]). The second and third, as well as the fifth and sixth columns of Table 7.6 list the calculated wavenumbers of transitions and the deviations between calculated and observed values. The overall agreement between calculated and experimental spectra is good, the average error of the fit, for which 14 observed transitions are taken into account, amounts to 0.44 cm$^{-1}$. The largest difference amounts to 0.42 cm$^{-1}$ for transitions to the $6^1$ level, and to 0.89 cm$^{-1}$ to the $4^1$ level. Note that not all assigned transitions are considered in the fit. When the wavenumbers of the transitions to $4^1$ are obtained by fits to a convolution of
two or three Lorentz lineshaped curves, the results are not very accurate because of the large FWHM. Thus, only those transitions for which the assignment is clear are considered.

Figure 7.10 Two spectra of the excited 6\(^1\) and 4\(^1\) vibrational states via \(\tilde{A}^1A_2\ 2^24^1\ 1_{11}\). The intermediate state was reached from two different states in \(\tilde{X}^1A_1\): 0\(_{00}\) (lower trace) and 2\(_{02}\) (upper trace). The transition to \(J_{K_aK_c}=1_{11}\) in the 6\(^1\) level is missing in the lower trace. See text for details.

With the fitted rotational constants it becomes evident that, such as in the previous section, two transitions are missing. In the spectrum recorded from the intermediate level \(J'_{K_aK_c}=1_{11}\) the transition to \(J_{K_aK_c}=1_{11}\) in 6\(^1\) and to 1\(_{10}\) in the 4\(^1\) level, respectively, are missing. The situation is shown in detail in the lower trace of Figure 7.10. Just as for the vibrational ground state the polarization configuration of the laser beams has to be taken into account. In fact, the lower trace in Figure 7.10 is obtained by excitation of the \(\tilde{A}^1A_2\ 2^24^1\) state \(J_{K_aK_c}=1_{11}\) level by the \(^rR_{00}(0)\) transition. The factors in Table 7.5 amount to zero for this excitation scheme for both cases, i.e. (R,Q) and \(J''=0\). Thus, the excitation scheme used in the lower trace impedes the transition to \(J_{K_aK_c}=1_{10}\) in the 4\(^1\) level, and consequently, because it interacts with this level by Coriolis coupling, the transition to 1\(_{11}\) in the 6\(^1\) level does not gain intensity. This effect related to the polarization of the electric fields can be resolved by exciting the 1\(_{11}\) state by the \(^pR_{02}(2)\) transition, i.e. \(J''=2\), which is shown in the upper trace.

The observed spectrum to the 4\(^1\) level is not markedly different from that in the lower trace of Figure 7.10, which stems from the large line width of the transition. However, a second peak corresponding to the excitation to the 6\(^1\) \(J_{K_aK_c}=1_{11}\) state is present. The observation of this transition implies the occurrence of the transition to the 4\(^1\) \(J_{K_aK_c}=1_{10}\) state because the two levels are coupled by the Coriolis interaction.

The intensity distribution among the two transitions leading to the Coriolis coupled vibrational levels can be estimated. The wave functions associated with the coupled rovibronic
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Table 7.6 Table of the observed and calculated transition energies (in cm$^{-1}$) for the $2^0_14^0_06^1_1$ (three columns on the left) and the $2^0_14^1_1$ (three columns on the right) band of the $^1A_2(3p_x)$-$\tilde{A}^1A_2$ transition. The energies have been obtained by fitting the experimentally recorded transitions to Lorentzian lineshapes. The accuracy is limited mainly by the large line widths of the transitions, which account to $\approx 1.8$ cm$^{-1}$ ($6^1_1$) and $\approx 6.3$ cm$^{-1}$ ($4^1_1$), respectively. Those transitions which cannot be clearly identified have been omitted in the fit. The average error amounts to 0.44cm$^{-1}$.

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</tbody>
</table>

Table 7.7 Table of the observed and calculated rotational levels of the $6^1_1$ and $4^1_1$ level in the $^1A_2(3p_x)$ state (in cm$^{-1}$). The values of $\tilde{\nu}_{obs}$ are obtained by adding the measured transition wavenumbers of Table 7.6 to the absolute energies to the rotational levels of the $\tilde{A}^1A_22^14^3_1$ state. The three left columns refer to the $6^1_1$ state, the three on the right side to the $4^1_1$ state. For the calculated levels with equal $J$ and $K_a$ but different $K_c$, which were excited simultaneously in the experiment, the arithmetic average is given.

<table>
<thead>
<tr>
<th>$J_{K_aK_c}$</th>
<th>$\nu_{obs}$</th>
<th>$\nu_{calc}$</th>
<th>$\delta \nu$</th>
<th>$\nu_{obs}$</th>
<th>$\nu_{calc}$</th>
<th>$\delta \nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^q R_{11}(1)$</td>
<td>38203.47</td>
<td>38203.55</td>
<td>0.08</td>
<td>38379.99</td>
<td>38379.89</td>
<td>0.10</td>
</tr>
<tr>
<td>$^q Q_{10}(1)$</td>
<td>38198.77</td>
<td>38198.34</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^q P_{10}(1)$</td>
<td>38203.19</td>
<td>38202.86</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^q Q_{11}(2)$</td>
<td>38198.75</td>
<td>38199.13</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^q R_{11}(2)$</td>
<td>38205.70</td>
<td>38205.61</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^q P_{02}(2)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>38379.99</td>
<td>38379.89</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^a$ the transitions are not taken into account in the fit

$^b$ $\delta \nu = \nu_{obs} - \nu_{calc}$
levels are linear combinations of the uncoupled wave functions \(|JKM_{v'0}\rangle\). The diagonalization of the Hamiltonian including the Coriolis coupling perturbation yields the expansion coefficients. The relevant coefficient amounts to \(\approx 0.01\), which would imply that a rovibronic transition to the 6\(^1\) level gain about 0.0001 of the intensity of the corresponding transition to the 4\(^1\) level. On the example of the transitions originating from \(J'_{K_a'K_c'} = 1_{11}\), where only one rotational state in each vibrational level is accessed, yields a ratio of 1 : 3.7.

Moreover, the difference of the line widths is conspicuous. The large line widths of the transitions to the 4\(^1\) level are probably caused by vibronic coupling to a close-lying dissociative valence state of equal symmetry. As shown in Figure 7.1, the potential energy curve of the (1)\(^1\)B\(_2\) valence state calculated by Hachey et al. [127] crosses the curve of the 3p states. The potential energy curve possesses a calculated minimum near \(r(\text{CO}) = 1.22\ \text{Å}\) and 8.25 eV (= 66542.27 cm\(^{-1}\)) and exhibits a repulsive shape beyond 1.53 Å. In Ref. [126] this valence state was suggested to interact with the \(^1\)B\(_2\)(3p\(_x\)) Rydberg state \((T_0 = 65483 \text{ cm}^{-1} \text{ according to Ref. [117]})\), but the assumption has been revoked already one year later by the same group [127]. The band origin of the 4\(^1\) level is situated at 68537.5 cm\(^{-1}\), thus, vibronic coupling between those two states is a possible effect that could account for the large line width of transitions to the 4\(^1\) level.

One more notable fact is the reduced FWHM of the transitions to 4\(^1\) levels with \(K_a = 0\) (see Figure 7.4). A presumed explanation is that this is an effect of intramolecular vibrational redistribution due to Coriolis coupling to the 6\(^1\) level. A similar effect is explained in Ref. [140] for C\(_6\)H\(_6\). The fact that the transitions to 4\(^1\) levels with \(K_a = 0\) (see Figure 7.4), for which Coriolis coupling to the 6\(^1\) states does not occur, definitely exhibit smaller line widths than the other transitions supports this theory.

### 7.4 Conclusions

The three lowest vibrational levels of the \(^1\)A\(_2\)(3p\(_x\)) Rydberg state were investigated with double-resonance multiphoton ionization spectroscopy. The double-resonance technique proved to be a capable tool to selectively excite only few rotational levels in each single experiment. Previously undetermined rotational constants and the values of the band origins were obtained. A strong \(a\)-type Coriolis interaction has been found to couple the 6\(^1\) and the 4\(^1\) vibrational levels of the \(^1\)A\(_2\)(3p\(_x\)) state. This enabled the observation of vibronically forbidden transitions to the 6\(^1\) level with the applied excitation scheme. Moreover, the dependence of the signal intensity on the polarization of the excitation fields was found as the reason why certain rovibronic transitions were not observed. A different choice of the initial excitation step or a change of the polarizations of the electric fields enabled the observation of those otherwise missing transitions.
Chapter 8
Conclusions and outlook

In this thesis, the advantages of several linear, nonlinear, single- and double-resonance spectroscopic techniques have been exploited to investigate the structure and the dissociation dynamics in formaldehyde. In addition, the applicability of degenerate four-wave mixing as an absorption-like technique has been justified by comparison with theory. These experiments have been carried out to some extent on C$_3$ which was produced in a DC-discharge.

Photofragment excitation (PHOFEX) spectroscopy was applied for the investigation of the radical dissociation channel of formaldehyde, H$_2$CO → HCO + H. Formaldehyde was excited to two vibrational levels of the $\tilde{\text{A}}^1\text{A}_2$ state, the $2^14^3$ level situated at the threshold for the radical channel, and $2^34^1$ level at the threshold to dissociation via the triplet state. With the PHOFEX technique, which involved the excitation of the parent formaldehyde to rotational levels of the state under investigation and the detection of nascent HCO in a specific rotational level with laser induced fluorescence (LIF), we could determine the dependence of the formation of a product state on the excited rotational level of the parent. In particular, the results for dissociation from the $2^34^1$ level indicated a preferential production of all formed product states from two rotational levels in formaldehyde, which led us to the conclusion that these processes are an example of dissociation via the triplet state.

To determine the relative populations of the excited rotational levels of formaldehyde in the PHOFEX experiment, a technique allowing a quantitative analysis of the recorded spectra was needed to monitor the excitation process. In our experiment DFWM was applied. Assuming that the DFWM signal intensity depends on the square of the population in the lower-lying state and on the fourth power of the transition dipole moment, the square-root of the intensity is plotted vs. the wavenumber and interpreted as an absorption spectrum. This procedure was justified by examining the DFWM process according to two theories, the saturable absorber model by Abrams and Lind, and a model by Williams, Zare and Rahn which incorporates the dependence of the DFWM signal intensity on the configuration of the four electric field polarizations. Our results imply that both the saturation degree and the polarization dependence have to be taken into account to make quantitative statements from DFWM spectra. In addition, DFWM was compared directly to the highly sensitive absorption technique cavity ring-down (CRD), as well as to LIF, by simultaneously recording spectra at equal experimental conditions,
yielding comparable intensities from the CRD and DFWM spectra.

The doubly resonant two-color resonant four-wave mixing (TC-RFWM) technique was used for the rotational characterization of a high-lying vibrational level of the \( \tilde{A}^1A_2 \) state of formaldehyde, \( 2^25^1 \). Rovibronic transitions in the stronger \( 2_0^24_0^1 \) vibronic band were chosen as the second resonance in the TC-RFWM scheme for intermediate state labeling. The assignment of the TC-RFWM spectra obtained in the wavenumber range of the \( 2_0^25_0^1 \) transition was straightforward and allowed the determination of the rotational constants and the band origin. The assignment was tested by recording TC-RFWM spectra of the \( 2_0^24_0^1 \) transition and calculating the rotational constants of the \( 2^24^1 \) level which are consistent with those from the literature. The \( B \) and \( C \) rotational constants of the \( 2^25^1 \) were found to be comparable to those for the \( 2^15^1 \) and the \( 5^1 \) level, the inconsistency of the \( A \) constant might be caused by Coriolis- or Fermi-type interactions.

The three lowest-lying vibrational levels \( 0^0, 6^1 \) and \( 4^1 \) of the \( 3p_x \) Rydberg state of formaldehyde were characterized in a double-resonance multiphoton ionization experiment. Similar to TC-RFWM, this technique enabled intermediate state labeling in the \( \tilde{A}^1A_2 \) state resulting in a simplified assignment of the obtained spectra. In addition to providing the rotational constants and the band origins, we could identify \( a \)-type Coriolis coupling between the \( 6^1 \) and the \( 4^1 \) levels as the reason for the observation of the vibronically forbidden \( 2_0^04_0^6_0^1 \) band. The rotational constants and the Coriolis-coupling constant obtained for the vibrational levels in the \( 3p_x \) state are comparable to those for the formaldehyde cation determined in an accompanying ZEKE-PFI experiment.

To gain further insight into the dissociation of formaldehyde, in particular the radical channel via intersystem crossing, detailed knowledge about the triplet state is needed. However, singlet-triplet transitions are weak and a sensitive spectroscopic technique is required to be able to observe these transitions. Laser-induced grating spectroscopy (LIGS) has been proven to be adequate for the detection of such weak transitions \cite{141}. The experimental realization of this technique is, however, challenging and we have so far succeeded to detect singlet-singlet transitions in formaldehyde.

An extension of the TC-RFWM and the double-resonant MPI experiments could be the detection of the \( 1A_2(3p_x) \) Rydberg state with a \( \Xi-TC-RFWM \) scheme. The application of this scheme to detect Rydberg states has so far only been accomplished for NO \cite{142}. The successful implementation of such an experiment might open up the investigation of short-lived higher-lying states.
Part IV

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