LASER SPECTROSCOPIC STUDIES
OF
MOLECULAR OVERTONES

Maria Nela

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Academic Dissertation

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Laser spectroscopic studies of molecular overtones

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Abstract

Two laser spectroscopic methods have been used to measure high resolution overtone spectra of monochloroacetylene, acetylene, and water.

Photoacoustic intracavity spectroscopy has been employed to record overtone spectra of monochloroacetylene (HCCCl) in the region 9400 -14400 cm$^{-1}$. The laser and additional FTIR spectra have been rotationally and vibrationally analysed. A vibrational model based on the conventional rectilinear normal coordinate theory including anharmonic Fermi, Darling-Dennison, and vibrational $l$-resonances has been used to attach quantum labels to the studied vibrational states. The vibrational calculation covers a range from the $\nu_1 + \nu_5$ band up to the $4\nu_1$ band system, where $\nu_1$ is the CH stretching and $\nu_5$ is the CCl stretching fundamental. The model reproduces very well both the observed vibrational term values and rotational constants.

The laser-induced fluorescence method has been used to investigate overtone states of acetylene (HCCH) and water (H$_2$O) in the ground electronic states. Many transitions are observed due to changes in excited state populations, which makes it possible to study collision-induced processes such as a local mode state change in acetylene. New spectroscopic information has been obtained from symmetric states, which are not reachable by one-photon absorption from the ground vibrational state.
Contents

1 Introduction 5

2 Absorption measurements 9
  2.1 Experiments .............................. 9
  2.1.1 Sample preparation ................... 9
  2.1.2 Fourier transform infrared spectroscopy 9
  2.1.3 Photoacoustic laser spectroscopy ....... 10
  2.2 Theory and analysis .................... 12
    2.2.1 Vibration-rotation properties of monochloro-acetylene 12
    2.2.2 Rotational analysis .................. 13
    2.2.3 Vibrational analysis ................ 16
  2.3 Results and discussion ................ 19

3 Fluorescence measurements 21
  3.1 Experiments .............................. 21
    3.1.1 Laser-induced fluorescence .......... 21
  3.2 Theory .................................. 24
    3.2.1 Vibration-rotation properties of acetylene 24
    3.2.2 Vibration-rotation properties of water 25
    3.2.3 Collisions .......................... 26
  3.3 Results and discussion ................. 27

4 Conclusions 32

Acknowledgements
References
1 Introduction

Breaking and making bonds is one of the key issues in chemistry. Laser selective chemistry is a field where a bond (or a group) of a molecule is excited with the aim to break the bond directly or to select a favourable reaction pathway, i.e. to control chemical reaction by laser light [1].

It is possible to place chemically significant amount of energy to a desired bond with lasers, but it is more difficult to keep the energy there for a chemically relevant time period. For example, if we want to produce a bimolecular reaction, the inserted energy should stay localized in the desired bond at least for the average time between collisions of the reactive species. In reality, after a bond excitation, energy flows rapidly to the other vibrational modes in the molecule. This phenomenon is called intramolecular vibrational energy redistribution (IVR).

The mechanism of IVR can be considered in the context of Fig. 1. A rovibrational transition from the ground state to a zeroth-ordered state is assumed to carry all the intensity. Only one line is seen in the spectrum if there are no other states nearby. However, the density of the states in a polyatomic molecule is such that there are often other states close by. If these do not carry directly any transition probability, they are called dark states.

![Diagram](image)

Figure 1. A bright state is coupled with two dark states (coupling terms $W_{12}$ and $W_{13}$) and a high resolution spectrum with three lines is obtained.

The bright and the dark states may be coupled through higher order Hamiltonian terms. All the properties of the wavefunctions of the states involved are shared if the coupling is significant enough. This can be observed in the spectrum, where, in addition to one line corresponding to a transition to the bright state, extra struc-
ture appears. The transitions to the dark states borrow intensity from the transition to the bright state and become visible.

The mixing of the states does not occur only between bright and dark states, but also between the bright states. In any case, there is intensity sharing between transitions involving interacting states. Anomalous intensities in the spectrum are an indication of couplings between the states. These are called resonances.

The IVR processes may be investigated both in the time and in the frequency domains. In the time domain experiments, a short laser pulse is used to prepare the initial state and then energy redistribution is observed as a function of the time. However, the measurements in the frequency domain, high resolution spectroscopic techniques, provide often more detailed information about vibrational dynamics. From the fully rotationally resolved spectrum, it is possible to determine the role of rovibrational resonances in the energy redistribution process.

The experimental IVR rates show that the bond breaking in unimolecular reactions by laser selective excitation is not easy to achieve because of fast energy redistribution [2]. On the other hand, there are some other examples of the IVR lifetimes (CH stretch excitation in R-\(\text{C} \equiv \text{C-H}\) terminal acetylenes) which give more hope for laser selective chemistry [3]. Some of these lifetimes are long enough, several hundreds of picoseconds, so that they are comparable to typical gas kinetic collision times at 1 atm [4]. This might be significant in the context of chemical reactions.

Although IVR hinders the idea of laser controlled chemistry, it does not totally destroy the hopes to achieve it. There are some possibilities to increase IVR lifetimes in the molecule. For example, in the case of R-\(\text{C} \equiv \text{C-H}\) terminal acetylenes, one can change the IVR rate of the CH stretch by changing the molecular structure by adding some "block" groups. If the \((\text{CH}_3)_3\text{C-}\) group is attached to the place of R, the IVR lifetime for the CH stretch is about 200 ps, but if the \((\text{CH}_3)_3\text{Si-}\) group is attached, the lifetime is already as long as 2000 ps [2, 5, 6].

In order to be able to influence the IVR lifetimes, a deep understanding of the nature of IVR in molecules is needed. Work related to this field has been performed in the four papers of this doctoral thesis. Investigation of vibrational behavior at the highly excited overtone regions gives information related to IVR
processes.

It is demanding to study overtone states experimentally due to the small transition moments involved. The development of the laser technology offers a powerful tool for such experiments and, indeed, many sensitive measurement methods have been developed. As an example, there is plenty of high resolution work published on stimulated emission pumping (SEP) [7], laser induced fluorescence (LIF) method with a supersonic slit jet [8], photoacoustic method (PA) [9], intracavity laser absorption spectroscopy (ICLAS) [10], stimulated Raman spectroscopy [11], and high resolution laser Stark spectroscopy [12] to mention some of the work done.

In this work, two experimental techniques have been applied to the overtone spectroscopy of acetylene, monochloroacetylene, and water. The absorption measurements have been recorded by the photoacoustic method and the emission measurements have been carried out with the dispersed laser-induced fluorescence (LIF) method. The LIF experiments have also been developed further.

The present study includes the following papers:

1. Maria Saarinen, Lauri Halonen, and Oliver Polanz,
   High-resolution photoacoustic overtone spectrum of monochloroacetylene using a titanium:sapphire ring laser spectrometer,

2. Maria Nela, Kirs Niskanen, Olavi Vaittinen, Lauri Halonen, Hans Bürger, and Oliver Polanz,
   High-resolution infrared and laser photoacoustic spectroscopy of monochloroacetylene,
   Mol. Phys., accepted for publication.

3. Maria Saarinen, Dmitri Permogorov, and Lauri Halonen,
   Collision-induced vibration-rotation fluorescence spectra and rovibrational symmetry changes in acetylene,

4. Maria Nela, Dmitri Permogorov, Andrea Miani, and Lauri Halonen,
   Vibration-rotation fluorescence spectra of water in the ground electronic state,
In the first article, the photoacoustic method has been used to record overtone spectra of monochloroacetylene (HCCCl) in the 9400-14400 cm$^{-1}$ wavenumber region. The high resolution spectra of the $3\nu_1 + \nu_2$ and $4\nu_1$ band systems ($\nu_1$ is the CH stretch and $\nu_2$ is the CC stretch) were rotationally analysed. Some rotational perturbations were observed in the spectra and two individual bands were analysed as a Fermi resonance pair.

In the second article, high resolution vibration-rotation spectra of HCCCl have been recorded in two different wavenumber regions. Fourier transform infrared interferometer measurements in the 4000 - 10000 cm$^{-1}$ range have been performed in the Universität-Gesamthochschule at Wuppertal, Germany. The photoacoustic measurements in the 12500 - 12600 cm$^{-1}$ and 12800 - 12860 cm$^{-1}$ regions have been carried out with a titanium:sapphire ring laser spectrometer in Helsinki. Altogether 55 vibrational bands have been rotationally assigned. A vibrational model based on the conventional rectilinear normal coordinate theory including anharmonic Fermi, Darling-Dennison, and vibrational $i$-resonances has been used to label the vibrational bands in the articles (1) and (2). Since the anharmonic resonances are responsible for fast energy flow within molecules, it is important to analyse their effects on the spectra in detail. Vibrational analysis, giving the vibrational labels for the studied vibrational states, is also important in understanding IVR. We need a system to label vibrational states in order to understand how the vibrational energy is distributed. At some point, when the states are mixed strongly, state labelling becomes ambiguous.

In the third article, the laser-induced fluorescence method has been employed to investigate collision-induced processes in the CH stretching overtone region of the ground electronic state of acetylene (HCCH). A particular vibration-rotation state has been excited with a high resolution titanium:sapphire ring laser. Experimental conditions were improved to enhance the emission signal. Rich collision-induced emission spectra were obtained. Spectroscopic information has been obtained of symmetric states, which are not reachable by direct one-photon absorption from the ground vibrational state. Collision-induced rovibraional symmetry changes have also been observed in the spectra.

In the fourth article, the laser-induced fluorescence method has been employed to investigate overtone states of water (H$_2$O) in the ground electronic state. The effects of collisions on the con-
ervation of the nuclear spin state has been examined. New experimental intensity information on the emission transitions has also been obtained.

2 Absorption measurements

2.1 Experiments

The overtone spectra of monochloroacetylene have been measured with two different methods. Below 10 000 cm\(^{-1}\), the measurements have been carried out by Fourier transform infrared (FTIR) spectroscopy and in the range over 10 000 cm\(^{-1}\), the intracavity photoacoustic laser spectroscopy has been employed.

2.1.1 Sample preparation

The sample of monochloroacetylene (monochloroethylene, H\(_2\)CCl) was prepared at the Universität Gesamthochschule in Wuppertal. It was synthesized by decomposition of Hg(CCl\(_4\))\(_2\) with KOH and KCN in H\(_2\)O and purified by fractional distillation under vacuum [13].

Because monochloroacetylene, like the other haloacetylenes, is an explosive and pyrophoric substance, when in contact with oxygen, attention was paid to the sample handling. The sample was stored frozen in liquid nitrogen in a special double valve glass ampoule between the measurements. Before using, volatile impurities above the frozen sample were pumped away.

2.1.2 Fourier transform infrared spectroscopy

Fourier transform infrared interferometer (FTIR) spectra in the 4000 - 10000 cm\(^{-1}\) range have been recorded with a Bruker IFS 120 HR spectrometer in Wuppertal with a resolution of 0.005 - 0.016 cm\(^{-1}\). Sample pressures between 2000-2200 Pa and path lengths from 1.2 m to 16.0 m were used in different measurements.
2.1.3 Photoacoustic laser spectroscopy

Photoacoustic spectroscopy (PAS) is an old technique [14, 15], originating from the experiments that A. G. Bell described already in 1880 [16]. It is based on a phenomenon where a substance warms up, when it absorbs light, i.e. part of the excess energy is transferred into thermal energy by molecular collisions. If the absorbing light is modulated, the temperature ($T$) is varied along the modulation and according to the perfect gas law ($pV = nRT$) pressure ($p$) waves are created if the sample cell is a closed one ($V$ is constant). Therefore, the absorption of the light can be detected as an acoustic signal with a microphone. Photoacoustic detection is a sensitive method, because heating of the substance occurs only, if light is absorbed. This means that a signal is not observed if no light is absorbed.

The high resolution photoacoustic ring laser spectrometer used in this work has been built at the University of Helsinki [17]. The experimental setup is shown in Fig. 2.

![Photoacoustic laser setup diagram]

**Figure 2.** The high resolution photoacoustic laser spectrometer. The abbreviation LPM in the figure means the laser power meter.
The main component of the spectrometer is a ring laser (Coherent 899-21), which is optically pumped by a continuous wave argon ion laser. The ring laser can operate as a dye laser or as a solid-state laser, but in this work it has been used only as a solid-state laser, titanium:sapphire (Al₂O₃·Ti³⁺) being the active medium. The wavenumber region, which can be covered continuously by the titanium:sapphire configuration, covers the region from 680 nm to 1025 nm (9800 - 14700 cm⁻¹).

In the experiment, a 200 mm long gas cell with the volume of about 40 cm³ is placed inside the laser cavity. The cell has been designed in a way that acoustic longitudinal resonances are formed. This is achieved by placing a 180 mm long copper waveguide into the cell. The advantage of the resonance effect is that the signal and background levels rise above the random noise level [15]. The noise has different sources. It is due to, for example, laboratory noise and electronic noise [18, 15]. The resonance effect does not improve much the signal-to-background ratio, because background arises mainly from heating of the windows of the cell, i.e. the background signal is also a photoacoustic signal and thus is amplified with the signal of the sample [15].

The sound wave is created by chopping the ring laser beam mechanically at the frequency of 890 Hz. The optimal chopping frequency has been determined experimentally. In practice, it is close to the acoustic resonance frequency \( f = \frac{vn}{2l} \), where \( v \) is the speed of sound inside the gas sample, \( n=1,2,3,... \), and \( l \) is the length of the waveguide [15]. The microphone (Knowles BT1759) signal is amplified with the phase sensitive detection method, which greatly increases the sensitivity.

Several optical components inside the laser cavity are needed in order to tune the ring laser wavenumber and to achieve single-mode operation with a narrow linewidth. The ring laser is made to lase unidirectionally by using an optical diode. The operation of this kind of a diode is based on the concepts of optical activity and the Faraday effect. The laser linewidth is reduced down to 20 MHz with a birefringent filter (anisotropic plates glued together) and two different etalons (thin quartz plates).
High resolution spectra, in practise with the Doppler-limited resolution, are measured in segments of 1 cm\(^{-1}\) (30 GHz). The wavenumber tuning inside these segments is performed by tilting a Brewster plate (a quartz plate) inside the ring laser cavity. This changes the optical length of the laser cavity.

In order to linearise the spectrum, a Fabry-Perot transmission signal with a 1 GHz free spectral range is recorded simultaneously with the photoacoustic spectrum. It is assumed that the distance between two adjacent Fabry-Perot fringe maxima are constant on the wavenumber scale. An iodine transmission spectrum is also recorded, in order to determine an absolute wavenumber scale. The absolute wavenumber accuracy of the measurement is better than 0.01 cm\(^{-1}\). The quality of the iodine spectrum is the limiting factor in the calibration procedure.

Spectra with a resolution of about 1 cm\(^{-1}\) can also be measured. This broadband operation is achieved by removing the etalons and the Brewster plate from the laser cavity. The bandwidth is then about 2 GHz (\(\sim 0.07\) cm\(^{-1}\)). The photoacoustic signal is collected once per cm\(^{-1}\), and the frequency is tuned by rotating the birefringent filter around its optical axis. The wavenumbers for the low resolution measurement are obtained directly from a wavemeter with the accuracy of about \(\pm 0.02\) cm\(^{-1}\).

2.2 Theory and analysis

2.2.1 Vibration-rotation properties of monochloroacetylene

Monochloroacetylene (H–C≡C–Cl) is a linear four-atomic molecule, which does not possess a center of symmetry and thus belongs to the C\(_{\infty v}\) point group. It contains seven normal modes, three non-degenerate stretching modes of the \(\Sigma^+\) symmetry and two doubly degenerate bending modes of the \(\Pi\) symmetry. All the fundamental transitions are infrared active. The fundamentals are shown in Fig. 3 [19].

There exist two isotopic species, HCC\(^{35}\)Cl and HCC\(^{37}\)Cl. The species appear in a 3:1 intensity ratio in the spectra owing to the natural abundancies of the two chlorine isotopes.
Figure 3. The fundamental vibrations of monochloroacetylene. Two wavenumbers are given in the case of $\nu_8$. The values 758 and 750 cm$^{-1}$ refer to HCC$^{35}$Cl and HCC$^{37}$Cl, respectively.

When analysing a vibration-rotation spectrum, as a starting point, the nuclear and electronic motions can be separated according to the Born-Oppenheimer approximation. As a further approximation, the nuclear wavefunction is expressed as a product of vibrational and rotational wavefunctions. This approach neglects interactions between the three types of motions and allows the vibrational and rotational analysis to be made separately. Thus, as the first approximation, the total vibrational-rotational energy is expressed as a sum of vibrational and rotational term values $G_v$ and $F_v$, respectively.

### 2.2.2 Rotational analysis

There is a stack of rotational energy levels associated with vibrational energy levels. The rotational fine structure is often analysed first and the vibrational modelling is performed afterwards. Therefore, besides infrared selection rules, rotational energy level structure and selection rules also have to be taken into account.
The rovibrational energy level expression for a linear molecule is [20]

\[ E_v / \hbar c = G_v + F_v(J, k) = G_v + B_v[J(J+1) - k^2] - D_v[J(J+1) - k^2]^2 + \ldots, \quad (1) \]

where \( B_v \) is the rotational constant and \( D_v \) is the quartic centrifugal distortion constant of the vibrational state \( v \). The quantity \( J \) is the total angular momentum quantum number and \( k = \sum \xi_l \) is the total vibrational angular momentum quantum number, which defines the component of \( J \) about the molecular axis. The vibrational angular momentum is zero for the non-degenerated stretching motions in HCCCI. These states are called \( \Sigma \) states. When \( |k|=1 \), the states are called \( \Pi \) states and when \( |k|=2 \) the states are \( \Delta \) states, for example.

The transition moment lies along the molecular axis for a parallel band. On the other hand, a transition moment is perpendicular to the molecular axis for a perpendicular band. The distinction of the different transition types can be made by considering the change of the total vibrational angular momentum. For a parallel band, \( \Delta k=0 \) and, for a perpendicular band, \( \Delta k=1 \). Thus, \( \Sigma-\Sigma \) and \( \Pi-\Pi \) transitions are parallel, and \( \Sigma-\Pi \) and \( \Pi-\Sigma \) transitions perpendicular. In the case of a \( \Sigma-\Sigma \) transition, \( P \) and \( R \) branches are observed, which means that the change of the total angular momentum \( J \) in a transition is \( \pm 1 \). In the case of \( \Sigma-\Pi \) and \( \Pi-\Sigma \) transitions, \( P, R, \) and strong \( Q \) branches are observed in a spectrum. This means that the change of the total angular momentum \( J \) in a transition is 0 or \( \pm 1 \).

If Eq. 1 is rearranged and the lower state energy is subtracted both from the upper and the lower state vibration-rotational energy, a so-called reduced transition wavenumber formula is obtained as

\[ \tilde{\nu}_{\text{red}} = \tilde{\nu} - B'\prime[J'(J'+1) - k'^2] + B''[J''(J'' + 1) - k''^2] + D''[J''(J'' + 1) - k''^2]^2 - \ldots = \Delta G_v + \Delta B[J'(J'+1) - k'^2] - \Delta D[J'(J'+1) - k'^2]^2 + \ldots, \quad (2) \]

where \( \tilde{\nu} \) is the observed transition wavenumber, \( \Delta G_v = G'_v - G''_v \), \( \Delta B = B' - B'' \), and \( \Delta D = D' - D'' \). The double and single primes refer to the lower and upper states, respectively. This is a useful equation, because it can be employed in a polynomial fit in \( [J'(J'+1) - k'^2] \) and the lower state parameters may be fixed to their accurate literature values. The upper state parameters are
obtained with higher accuracy than in the procedure where both the upper and the lower state parameters are optimised simultaneously.

Vibrational motion affects the rotational constants. This is because molecular vibrations change the positions of the nuclei. Therefore, the rotational constant $B$ possesses a slightly different value for each vibration state. The rotational constant for a specific vibrational state of HCCCl can be expressed as [20]

$$B_v = B_0 - \sum_{r=1}^{5} \alpha_r v_r,$$  \hspace{1cm} (3)

where the summation is over the normal modes (the degenerate modes are counted only once), $B_0$ is the rotational constant of the ground vibrational state, and $\alpha_r$ describes the strength of the vibrational dependence of the rotational constant. The $\alpha$ parameter consists of a harmonic part and contributions which arise from anharmonicity and Coriolis interaction [20]

$$\alpha_r = \alpha_r^{(har)} + \alpha_r^{(an)} + \alpha_r^{(Cor)}.$$  \hspace{1cm} (4)

Resonances change the simple picture given. Rotational perturbations are caused, for example, by Coriolis and rotational $l$-resonances [21]. A perturbation may appear in a spectrum either as a localised or as a global perturbation. In a localised perturbation, only some close lying $J$ states are perturbed and the other $J$ states remain almost unperturbed. It is possible to achieve rotational analysis of such a band by leaving out perturbed lines from the final fit. In a delocalised perturbation, resonance effects are spread over the whole band. For example, the Coriolis interaction is $J$ dependent, which often means that rotational state perturbations increase with $J$.

A vibrational perturbation, like anharmonic Fermi resonance, causes a shift of the interacting vibrational states from their unperturbed positions [21]. This perturbation also affects the rotational constant $B$ through the state mixing effect. The rotational parameters are changed in a way that the sum of the parameters remains unchanged. If the states $|a\rangle$ and $|b\rangle$ are in resonance, the perturbed rotational constants obey the equation [20]

$$B_a + B_b = B_a^{(0)} + B_b^{(0)},$$  \hspace{1cm} (5)
where $B_\alpha^{(0)}$ and $B_\beta^{(0)}$ are the rotational constants in the zeroth-order unperturbed case.

In the case of rovibrational resonances, the energies of two interacting states can be solved by diagonalising an effective Hamiltonian matrix for each value of $J$. The unperturbed energy levels obey Eq. 1 and are placed on diagonal and the coupling matrix element $W$ is on off-diagonal. Thus, the energies for each $J$ are obtained from the equation [20]

$$
\begin{pmatrix}
E_a - E & W \\
W & E_b - E
\end{pmatrix} = 0.
$$

2.2.3 Vibrational analysis

There are two commonly used approaches in modelling the vibrational states. Fundamentals and many low-lying vibrational states are often best represented by the normal mode picture where all or most of the nuclei are moving in phase during the vibration. The higher vibrational states, especially the high stretching vibrations, are sometimes better described by the local mode model. In this picture, the excitation can be thought to be localized in the excited bond. This behavior is observed in some symmetrical molecules such as H$_2$O where at high stretching energies the bond oscillators become decoupled [30].

The vibrational energies are still low enough in this work so that the normal mode theory describes the vibrational levels satisfactorily. Thus, the normal mode notation is used to label the vibrational states. A state is characterized by a vibrational quantum number $v_i$ for all the normal modes and the vibrational angular momentum quantum number $l_z$ for the bendings. The vibrational state is given in the form $|v_1 v_2 v_3 v_4 v_5^{(5)}\rangle$. The symmetry of the state is defined by the total vibrational angular momentum quantum number $k$.

The effective vibrational Hamiltonian is constructed in a way that the diagonal matrix elements come from the zeroth-order picture with isolated vibration-rotation states. In reality, the density of the vibrational states is so high that the zeroth-order picture fails and the close-lying vibrational states with the same symmetry interact via anharmonic resonance terms. Altogether three anharmonic resonances are included in the effective Hamiltonian matrix by introducing off-diagonal terms which couple the resonant
The diagonal Hamiltonian matrix elements are obtained as anharmonic expansions [20, 22]

\[
G_v - G_0 = \langle v | H_{vib} / \hbar c | v \rangle = \sum_{r} v_r \tilde{v}_r^* + \sum_{r} x_{r}^*(v_r^2 - v_r) + \sum_{r < r'} x_{r'}^* v_r v_{r'}
\]

\[
+ \sum_{t} g_{tt}^* (l_t^2 - v_t) + \sum_{t < t'} g_{tt'}^* l_t l_{t'},
\]

(7)

where the energy is measured from the ground vibrational state. The quantity \(v_r\) is the vibrational quantum number and \(\tilde{v}_r^*\) is the fundamental vibrational wavenumber of the \(r\)th normal mode. The indices \(r\) and \(r'\) span all the vibrational modes, whereas indices \(t\) and \(t'\) span only the doubly degenerate bending modes \((t = 4 \text{ or } 5 \text{ and } t' = 5)\), which are counted only once.

The Fermi resonance is a cubic anharmonic interaction that occurs between the vibrational states which possess the same symmetry and whose energies are close to each other. There is a strong Fermi resonance interaction between the \(|0010^0(0^0)\rangle\) (C–Cl stretching fundamental) and \(|0000^02^0\rangle\) (C=C–Cl bending overtone) states in monochloroacetylene. The appropriate off-diagonal matrix elements for the Fermi resonance are of the form

\[
\langle v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5} | H / \hbar c | v_1, v_2, v_3 - 1, v_4^{l_4}, (v_5 + 2)^{l_5} \rangle = k_{355} (v_5 + l_5 + 2)(v_5 - l_5 + 2)/8^{1/2},
\]

(8)

where the resonance coefficient \(k_{355}\) is a force constant which describes the strength of this interaction.

Another important resonance is the Darling-Dennison resonance. It is a quartic anharmonic resonance, which occurs, for example, between the \(|1000^0(0^0)\rangle\) and \(|0102^0(0^0)\rangle\) states in monochloroacetylene. The appropriate off-diagonal matrix elements for the Darling-Dennison resonance are of the form [19]

\[
\langle v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5} | H / \hbar c | v_1 - 1, v_2 + 1, v_3, (v_4 + 2)^{l_4}, v_5^{l_5} \rangle = \frac{1}{4} K_{1244} [v_1 (v_2 + 1)(v_4 + l_4 + 2)(v_4 - l_4 + 2)]^{1/2},
\]

(9)

where the coefficient \(K_{1244}\) is a spectroscopic parameter which describes the strength of the interaction.
The third important vibrational resonance included in this work is the vibrational $l$-type resonance. It couples states of identical main vibrational quantum number but different total vibrational angular momentum quantum label. This kind of resonance occurs, for example, in the case of the states $|0001^{1+1}\rangle$. By symmetry, there are three components involved: $\Pi \otimes \Pi = \Sigma^- + \Sigma^+ + \Delta$. The $\Sigma$ states, $|0001^{+1-1}\rangle$ and $|0001^{-1+1}\rangle$, form the $l$-resonance pair. The appropriate off-diagonal matrix elements for the $l$-type resonance are [23, 24]

$$
\left\langle v_{4}^{l4}, v_{5}^{l5}|H/\hbar c|v_{4}^{(l_{4}-2)}, v_{5}^{(l_{5}+2)}\right\rangle
$$

$$
= \frac{1}{4} r_{45} \left\{ ([v_{4} + 1]^{2} - (l_{4} - 1)^{2}) ([v_{5} + 1]^{2} - (l_{5} + 1)^{2}) \right\}^{1/2},
$$

where the coefficient $r_{45}$ describes the strength of the interaction. The effect of the resonance is shown in Fig. 4.

Figure 4. Vibrational $l$-type resonance between the $v_{4} + v_{5}$ ($\Sigma^+$) and $v_{4} + v_{5}$ ($\Sigma^-$) states.

The Hamiltonian matrix is in block diagonal form due to the resonance polyad model. The basis functions are arranged according to their energy and symmetry. Thus, for example, $\Sigma$, $\Pi$, and $\Delta$ states appear in separate vibrational blocks. The states possessing identical polyad quantum numbers belong to the same block. A polyad quantum number for HCCCI is defined by

$$
V = 10v_{1} + 6v_{2} + 2v_{3} + 2v_{4} + v_{5}.
$$

The factors 10, 6, 2, 2, and 1 arise from the relative energies of the fundamental states.
2.3 Results and discussion

There has been a lot of spectroscopic interest in monohalogenated acetylenes in recent years. Their spectra have been extensively studied [19, 23, 24, 25, 26, 27, 28, 29] and theoretical models have been constructed and tested [30, 31, 32].

In this study, high resolution vibration-rotation spectra of monochloroacetylene (HCCCl) have been investigated in several wavenumber regions. In the range 4000 - 10000 cm$^{-1}$, the spectra have been measured with the high resolution FTIR spectrometer using a resolution of 0.005 - 0.016 cm$^{-1}$. The spectroscopic measurements over 10000 cm$^{-1}$ have been carried out with the titanium:sapphire ring laser employing the intracavity photoacoustic method. Low resolution spectra have been recorded in the wavenumber region 9400-14400 cm$^{-1}$ and high resolution spectra with the Doppler-limited resolution around the $3\nu_1+\nu_2$, $3\nu_1+\nu_2+\nu_3$, $3\nu_1+\nu_2+\nu_4+\nu_5$, $4\nu_1$, and $3\nu_1+\nu_2+2\nu_3$ band system regions.

The rotational analysis has provided new spectroscopic parameters for 52 states in the case of HCC$^{35}$Cl isotopic species and for 21 states in HCC$^{37}$Cl.

The CH stretching vibration is a motion with the largest amplitude in HCCCl. This is due to the light H nucleus in comparison to the other nuclei. Thus, the CH stretch is the most anharmonic vibration of the molecule and gives rise to the most intense overtone transitions. This is observed in the structure of the overtone spectrum (see Fig. 1 in paper (1)), where the strongest bands are indeed the CH stretching overtones and weaker bands are other types of overtones and combinations.

Another interesting feature of the overtone spectra of HCCCl is the fact that the structure is simpler (there are less states) than one would expect when considering the calculated density of the states, 126 states per cm$^{-1}$ at 12500 cm$^{-1}$ [33]. However, we can observe that in each band system there are only a couple of upper states in the range of about 50 cm$^{-1}$. This kind of spectral structure indicates that the local mode picture might be appropriate in high overtones. According to the simple local mode model, for example, we should observe only one band in the range of the third overtone of the CH stretch, but this is not the real situation.
either. In reality, there are four different bands in the $4\nu_1$ band system instead of the expected one.

Anyhow, in the case of HCCCl, when dealing with the states only up to the third CH stretching overtone range, the vibrational model based on the conventional rectilinear normal coordinate theory including anharmonic Fermi, Darling-Dennison, and vibrational $i$-resonances gives a valid picture and good results. The vibrational term values and rotational constants are very well reproduced and the observed vibrational states can be assigned apart from few exceptions as is seen in paper (2).

Many different kinds of resonances have been observed in the HCCCl spectra. The effects of the interactions are seen, for example, as anomalous intensities. This is due to the redistribution of absorption intensity over the interacting states. Unfortunately, some of the small rotational perturbations cannot always be analysed, because there are not enough observed spectral lines connected with the unknown perturber. Anyhow, the understanding of these perturbations is important, because they provide a key in explaining the energy flow from one vibrational mode to another.

Finally, if there are two states in resonance, it means that the wavefunction oscillates between these states with a period $T=1/2\pi cW$, where $c$ is the speed of light and $W$ is the magnitude of the coupling matrix element [34]. Thus, intramolecular vibrational energy redistribution (IVR) occurs in the femtosecond range in the case of the Fermi resonance (for monochloroacetylene $k_{355}=40.3 \text{ cm}^{-1}$).
3 Fluorescence measurements

3.1 Experiments

The laser-induced fluorescence (LIF) method has been used to investigate overtone states of acetylene and water in the ground electronic states.

Several single vibration-rotation transitions from the $\nu_2 + 3\nu_3$ ($\Sigma^+_u$) and $\nu_1 + 3\nu_3$ ($\Sigma^+_u$) absorption bands of acetylene have been pumped and emission spectra around 2900-3100 cm$^{-1}$ have been recorded. The band centers for the absorption bands are at 12676 cm$^{-1}$ and 11600 cm$^{-1}$, respectively.

For water, several single vibration-rotation transitions from the $3\nu_3$ and $2\nu_1 + \nu_3$ absorption bands, whose band centers are located at 11032 cm$^{-1}$ and 10613 cm$^{-1}$, respectively, have been pumped and emission spectra around 3000-4000 cm$^{-1}$ have been recorded.

3.1.1 Laser-induced fluorescence

Laser-induced fluorescence is a standard method to study polyatomic molecules and it is commonly used to observe transitions from excited electronic states. In the case of rovibrational transitions within the ground electronic state, the fluorescence experiments are demanding due to small transition moments when compared to electronic transitions. However, there are some advantages in the LIF method over other spectroscopic techniques. For example, when comparing fluorescence with absorption, it is possible to obtain spectroscopic information of such states that are not accessible from the ground vibrational state by one-photon absorption. In addition, different kinds of collision-induced processes can also be observed in the spectra.
Figure 5. Spectroscopic information about the HCCH symmetric states, which are not accessible in direct one-photon absorption, can be obtained with the LIF method.

The setup for the laser-induced fluorescence (LIF) measurements has been constructed in our group [35] and is shown in Fig. 6.

Figure 6. Experimental setup of laser-induced fluorescence measurements.
The main component of the LIF setup is a single mode titanium:sapphire ring laser. The cell with a gaseous sample is placed inside the laser cavity. The sample is at room temperature and the total pressure has been chosen to be between 1 and 3 mbar. These values produce the maximum fluorescence signal. At lower pressures, the fluorescence signal is too weak for detection and at higher pressures non-radiative processes (collisions) more or less cancel the increase of the fluorescence signal.

The ring laser is optically pumped with 15 W all line light power from an argon ion laser. The ring laser intracavity power can be up to 30 W, depending on the wavenumber region. It is possible to tune the laser wavelength to a single vibration-rotation transition because the ring laser linewidth is only about 20 MHz (~ 0.00007 cm⁻¹). These transitions have either been measured beforehand by the photoacoustic method in our group or they are known from the literature.

The resulting fluorescent light is collected and collimated with a parabolic mirror and directed with plane and spherical mirrors into the entrance aperture of a high resolution interferometer (Bruker IFS 120 HR). Thus, the interferometer has been used as a monochromator where the fluorescence signal is dispersed. The signal is detected by a sensitive InSb detector (Infrared Laboratories, Tucson, Arizona), which has been estimated to be at least four times more sensitive than a standard InSb detector. It is equipped with a liquid nitrogen cooled band-pass filter to decrease the amount of thermal emission from the background. Several hundreds of interferograms, typically about 800, have been recorded with the instrumental resolution of about 0.1 cm⁻¹. Because the emission signal is weak, the interferograms have been recorded two-sided in order to avoid possible difficulties in correcting phase errors.

The ring laser wavelength is controlled by photoacoustic detection simultaneously with the fluorescence measurements. This setup has been illustrated graphically in Fig. 6 in the box 'laser frequency control'. Part of the ring laser beam is directed to a photoacoustic cell containing the species which is under study. The photoacoustic signal is detected using a lock-in amplifier and the laser frequency is kept fixed at the maximum absorption signal. The emission signal is too weak to be used for the laser frequency control, but the wavelength giving the maximum absorption signal is good enough to give a strong emission signal. It is impossible to
keep the laser stable without any laser frequency control system because the fluorescence measurements take a long time, typically several hours.

A new problem is encountered, when fluorescence spectra of water are measured. Atmospheric water makes the laser unstable. This happens particularly around 10600 cm\(^{-1}\). When there exists very strong water absorption, the laser power decreases significantly at frequencies close to water lines and in some cases the laser can even jump away from the absorption frequency to another laser mode. To be able to measure fluorescence spectra at such wavenumbers, the ring laser has been covered by a plexiglass box and a continuous flow of dry nitrogen vapour has been injected into the box.

We have tried to decrease the collisional quenching of the fluorescence signal by using neon as a buffer gas, but no desired effect was achieved. The experiments with some other vibrational states in acetylene indicate that there could be a drastic decrease in the collisional probability when neon is used [36], but in our case the strongest fluorescence signal was obtained when no buffer gas was used. In the case of C\(_2\)D\(_2\), there are some experimental results in the literature describing how a buffer gas even increases the probability of collisional relaxation [37].

3.2 Theory

3.2.1 Vibration-rotation properties of acetylene

Acetylene (H–C≡C–H) is a linear four-atomic molecule, which contains a center of symmetry and thus belongs to the D\(_{\infty v}\) point group. There are seven normal modes of vibration, but only the antisymmetric CH stretch \(\nu_1\) and the doubly degenerate cis bend \(\nu_2\) are infrared active, possessing the change of the dipole moment during the transition. The three stretching and the two doubly degenerate bending modes of acetylene are shown in Fig. 7. [38].
Figure 7. The fundamental vibrations of acetylene.

All the equations, which have been presented for the rovibrational analysis of monochloroacetylene, can also be used for the spectral analysis of acetylene.

3.2.2 Vibration-rotation properties of water

Water (H₂O) is an asymmetric rotor belonging to the C₂ᵥ point group. It is a near-prolate rotor. Thus, there are two almost equal moments of inertia and the third one is smaller than the other two, i.e. \( I_a < I_b \approx I_c \).

Water contains three normal modes of vibration, symmetric and antisymmetric stretches and a bend. All the vibrations are infrared active. The fundamentals are shown in Fig. 8.

Figure 8. The fundamental vibrations of water. The \( a, b, \) and \( c \) inertial axes are shown.
Depending, whether the dipole moment is along the $a$-, $b$-, or $c$-axis, transitions are called $A$-, $B$- or $C$-type transitions, respectively. In our LIF experiments, only $A$-type transitions were observed. The selection rules for the $A$-type transitions are the following:

$$
\Delta J = 0, \pm 1
$$

$$
\Delta K_A = \pm 2n, n = 0, 1, 2, \ldots
$$

$$
\Delta K_C = \pm(2m + 1), m = 0, 1, 2, \ldots
$$

where $K$ is the quantum number of the component of the angular momentum about the inertial axis.

The rotational energy level expression of an asymmetric rotor cannot be expressed in closed form except for the lowest $J$ values. The energies are obtained by diagonalising the appropriate Hamiltonian matrices using symmetrized rigid rotor symmetric top wavefunctions [39].

There was no need for an extensive rotational analysis in the water spectra. It was possible to obtain the rotational labels combining the known literature values for the upper and lower state energies with the spectroscopic selection rules.

### 3.2.3 Collisions

The only collisional effects, which many spectroscopists usually consider, are spectral line broadenings and line shifts. The development of lasers has opened a wider selection of collision-induced processes to be investigated.

Lasers producing short pulses have made it feasible to investigate energy redistributions due to the collisions. First, a molecule is selectively excited and then with high time resolution the energy distribution is measured. In this method, the sampling frequency is higher than the average time between the collisions. From such measurements, it is possible to examine how the excited molecules undergo collisional relaxation and how the excited vibrational energy is redistributed.

Earlier in the text, when dealing with the mechanism of the intramolecular vibrational energy redistribution, the rovibrational
resonances were assumed to couple bright and dark states causing state mixing. In the same way, collisions may act as a source of perturbation, causing energy redistribution and transitions between bright and dark states.

When molecules collide, different types of energy transfer may occur. If a molecule \( M \) with an internal energy \( E_i = E_{\text{vib}} + E_{\text{rot}} \) collides in its electronic ground state with a molecule \( AB \), vibration-vibration \( (V \rightarrow V) \), vibration-rotation \( (V \rightarrow R) \), vibration-electronic \( (V \rightarrow E) \) or vibration-translation \( (V \rightarrow T) \) energy transfer to the molecule \( AB \) may occur [40]:

\[
M(E_i) + AB(E_m) \rightarrow M(E_i - \Delta E_1) + AB^*(E_m + \Delta E_2) + \Delta E_{\text{kin}}. \quad (13)
\]

For larger molecules, the internal energy of \( M \) may either be transferred to the molecule \( AB \) or an intramolecular energy redistribution may occur among the vibrational modes of \( M \).

The collision-induced energy transfer processes in the ground electronic state are important. This is because most of the thermally driven chemical reactions occur in the electronic ground state. It is also noteworthy to realise that the radiative processes are generally slow in the ground electronic state. This means that collisions play an important role in population redistribution within the ground electronic state.

### 3.3 Results and discussion

In this study, overtone states of acetylene and water in the ground electronic state have been investigated by the laser-induced dispersed fluorescence method.

Acetylene is a good test molecule both for new experimental laser methods and for theoretical models. Therefore, a lot of high resolution work exists concerning the rovibrational spectra of acetylene in the ground electronic state. Altogether 253 vibrational bands measured by several authors are listed in Ref. [41]. In spite of such intensive studies, the amount of experimental data is still limited because only antisymmetric vibrational states \( \Sigma_u^+ \) and \( \Pi_u \) can be accessed by one-photon absorption from the ground vibrational state. The spectroscopic parameters of the symmetric states have to be obtained in some other way. The LIF method
has been used to reach symmetric states in this work. Spectroscopic parameters for three symmetric states have been obtained by pumping two different antisymmetric vibrational states.

Fig. 9 shows a schematic picture of an acetylene experiment. The ring laser is used to pump a certain rotational state (upper state \( J=6 \)) in the \( \nu_1+3\nu_3 \) (\( \Sigma_u^+ \)) vibrational state, where \( \nu_1 \) and \( \nu_3 \) are the symmetric and antisymmetric CH stretching fundamentals. In the picture, the local mode notation \([4 \ 0 -]\) has been adopted. This notation indicates that one CH bond oscillator is excited by 4 quanta and the other is unexcited. The minus sign shows that the vibrational state is antisymmetric with respect to the permutation of the identical CH bonds [30].

According to the selection rules for acetylene, two emission transitions P(7) and R(5) should be observed when pumping the rovibrational state with \( J=6 \). This is shown in Fig. 9 a. These two lines are easily identified from the emission spectrum, see Fig. 10. In addition, many weaker transitions are also observed. The population distribution of the upper state (the initial state of the emission) is changed and additional transitions from other rovibrational states are observed due to the energy transfer processes caused by the molecular collisions.

![Diagram](image_url)

**Figure 9.** The expected fluorescence transitions in a LIF experiment for acetylene are shown in figure a), and in b) there is a schematic picture of rovibrational symmetry change, which is observed in the same experiment. The symmetry change is caused by the molecular collisions.
The analysis of these collision-induced transitions shows that there are two different bands in the spectrum: $[4 \ 0^-] \rightarrow [3 \ 0^+]$ and $[4 \ 0^+] \rightarrow [3 \ 0^-]$. In the first band, the rotational state has changed due to the collisions and part of the observed emission is from other rotational states than from the one originally pumped. In the second case, the vibrational state is also changed due to the molecular collisions and some of the observed emission is from the $[4 \ 0^+]$ vibrational state. This is understandable, because the vibrational states $[4 \ 0^-]$ and $[4 \ 0^+]$ are near each other, the separation between the states being only about 4 cm$^{-1}$, and there is a large transition moment between these states.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure10.png}
\caption{The laser-induced fluorescence spectra of acetylene, when pumping the $J=6$ rotational state of the $[4 \ 0^-]$ vibrational state. Many collision-induced transitions coming from both the $[4 \ 0^-]$ and $[4 \ 0^+]$ vibrational states are observed.}
\end{figure}

By pumping the $[4 \ 0^-]0$ and $[3 \ 0^-]1$ vibrational states, where the number outside of the square bracket describes the excitation of the CC stretch, the spectroscopic parameters have been determined in the case of three symmetric states of acetylene ([4 0+]0, [3 0+]0, and [2 0+]1). The rotational energy level structure of [4 0+]0 and [2 0+]1 states has been observed for the first time and the results for the [3 0+]0 state are more accurate than those in Ref. [35].
Water has also been studied by the LIF method in this work. All the water transitions from the ground vibrational state are infrared allowed. Thus, when compared with acetylene, there was not same kind of need to obtain spectroscopic information of the states which are not directly reachable by one-photon absorption.

The different rotational states in the $[2 \ 1 \ -]$ (in the normal mode notation $3\nu_3$) and $[3 \ 0 \ -]$ (in the normal mode notation $2\nu_1 + \nu_3$) vibrational states have been pumped. The local mode notation describes the degree of the excitation in each OH bond oscillators in the same manner as in the case of the CH bond oscillators of acetylene. The standard spectroscopic symbols $\nu_1$ and $\nu_3$ denote the symmetric and antisymmetric OH stretching fundamentals, respectively.

When pumping the $[3 \ 0 \ -]$ state, fluorescence signal is so weak that only two lines in each emission spectrum are seen. The weak signal is due to the small laser power in this wavenumber region. All the observed transitions belong to the $[3 \ 0 \ -] \rightarrow [2 \ 0 \ +]$ band.

Many collision-induced transitions are observed in the emission spectra when the $[2 \ 1 \ -]$ state is pumped. According to the simple local mode and bond dipole theory, if the $[2 \ 1 \ -]$ state is pumped, two emission bands with similar intensities should appear, corresponding to two different cases: 1) the quantum number of the first OH bond oscillator decreases by one resulting in $[1 \ 1 \ +]$ being the lower state 2) the quantum number of the second OH bond oscillator decreases by one resulting in $[2 \ 0 \ +]$ being the lower state. Many collision-induced transitions have been observed in the spectra, but all transitions belong to the $[2 \ 1 \ -] \rightarrow [1 \ 1 \ +]$ band. The experimental intensities disagree with the simple local mode and bond dipole moment models and therefore a discrete variable representation (DVR) calculation using an exact kinetic energy operator, an accurate potential energy surface, and an ab initio dipole surface has been performed to compute emission intensities, see paper (4). Calculations confirm the experimental intensities. This result is best understood if the vibrations in question are described by standard normal mode theory. The transition $[2 \ 1 \ -] \rightarrow [1 \ 1 \ +]$ corresponds to a transition from the $3\nu_3$ state to the $2\nu_3$ state and the transition $[2 \ 1 \ -] \rightarrow [2 \ 0 \ +]$ corresponds to a transition from the $3\nu_3$ state to the $2\nu_1$ state. As expected, the transition which keeps the excitation in the same vibrational mode is by far the strongest.
Nuclear spin conversion, relaxation between molecular ortho and para forms in HCCH and H$_2$O, has also been investigated with the LIF method in this work. In the water molecule, where the strongest spectrum was observed, the nuclear spin isomers probably convert very slowly if there is no catalyst involved. It has been suggested that intramolecular interactions might mix different nuclear spin states and collisions may have an effect on this process [42]. With our setup, it is possible to excite a certain spin state, which is either an ortho ($I=1$) or a para ($I=0$) state. When ortho rovibrational states have been optically pumped, only emission transitions between ortho states have been observed. Similar finding applies to the para states. No collision-induced spin state changes have yet been detected in our experiments.

Relative population distributions of the upper rotational states in the [2 1 –] vibrational state have also been studied. The results show that energy transfer can occur between states separated by up to 300-400 cm$^{-1}$. However, it is unknown how many energy transfer steps are needed to reach this distribution. We have assumed in this context that an equilibrium is reached between the states and we have made a Boltzmann plot to determine the sample temperature, see paper (4). These results indicate that the sample is at the room temperature.
4 Conclusions

Molecular overtones have been investigated by two different laser spectroscopic methods in this study. Photoacoustic intracavity laser spectroscopy is a sensitive method and is well suited for measuring weak overtone transitions. On the other hand, the laser-induced fluorescence method offers a way to obtain spectroscopic data of states which are not reachable by direct one-photon absorption from the ground vibrational state.

The overtone spectra of monochloroacetylene have been analysed both rotationally and vibrationally. Many rotational perturbations have been observed and one Fermi resonance pair has been characterised with the appropriate coupling constant. In the vibrational analysis, several anharmonic resonances have been taken into account and most of the vibrational levels have been assigned. The observed vibrational term values and rotational constants have been very well reproduced with our model, which is gratifying in the light of the simple approach adopted.

In the case of fluorescence measurements, the collision-induced effects have been investigated. The collisions have been seen to produce population redistribution in the molecules studied. The relative distributions of the upper rovibrational states have been investigated. Emission intensities have also been examined.

Because the fluorescence signal is very weak in our LIF experiments, I wanted to improve the sensitivity of the laser-induced fluorescence method. This aim has been achieved in comparison with the previous measurements published in our group [35]. For the first time, I have observed rich collision-induced spectra. In order to still improve the sensitivity of the LIF method, there are several things which can be considered. According to the preliminary experiments, the fluorescence light seems to come from a small mirror area which is close to the holes made for the ring laser beam. Thus, if the fluorescence light is directed along the laser beam, smaller holes in the parabolic mirror should increase the observed signal. Another thing, which would significantly improve the sensitivity, is to increase the laser power. This could be achieved, for example, by using active frequency stabilization methods to lock the ring laser to an external build-up cavity.
There have been two goals in this work: first to increase the sensitivity of the experimental methods used and second to investigate vibrational energy level patterns in polyatomic molecules. Results show that both aims have been achieved. The sensitivity of the laser-induced fluorescence method has been increased and a lot of new spectroscopic information of the molecular overtones of the studied molecules have been obtained by two different laser spectroscopic methods.
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