Stark Spectroscopy, Lifetimes and Coherence Effects in Diatomic Molecular Systems

Annie Hansson
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The impossible takes just a little longer
Abstract

In this dissertation is exemplified how different laser based methods are applied in high-resolution spectroscopic studies of internal properties of diatomic molecules.

A molecular beam apparatus assembly is described, where a laser ablation source is combined with a time-of-flight mass spectrometer. Compounds investigated with this equipment are hafnium sulfide and hafnium oxide. The molecules are excited and ionized applying the resonant two-photon ionization (R2PI) scheme, which is a sensitive absorption and detection technique for probing the population of an excited state.

By means of the DC Stark effect, permanent electric dipole moments of HfS in the $D^1\Pi$ state and HfO in the $b^3\Pi_1$ state are determined while the molecules are exposed to a static electric field. Under field-free conditions low temperature rotationally resolved spectra are recorded, generating line positions from which molecular parameters are derived.

The R2PI method, modified with an adjustable delay time, is also used in lifetime measurements of individual rotational levels of the HfS $D^1\Pi$ and HfO $b^3\Pi_1$ states. Oscillator strengths for transitions from the ground state are calculated, and in this connection basic concepts like Einstein coefficients, line strengths and Hönl-London factors, are surveyed. Theoretical calculation of lifetimes is discussed in view of the fact that a commonly available computer program (LEVEL 7.5 by Le Roy) gives erroneous output.

Some coherence and quantum interference related phenomena, such as electromagnetically induced transparency (EIT) and Autler-Townes (AT) splitting, are presented in the latter part of this thesis. Fundamental concepts and relations are introduced and explained. The driven three-level cascade system is elucidated, including some of its experimental applications to alkali metal dimers, Na$_2$ and Li$_2$.

A triple resonance spectroscopy experiment is described in terms of a three-laser, four-level inverted-Y excitation scheme, implemented in Na$_2$. The accompanying density matrix formalism, providing the basis for theoretical simulations, is accounted for. From analysis of the results an absolute value of the electric dipole moment matrix element (transition moment) is extracted, using the AC Stark effect.

Some recently reported unexpected experimental results and unforeseen features, occurring in Doppler broadened samples and related to the open character of molecular systems, are briefly commented.
List of papers

This thesis is based on the following works:

Paper 1
On the dipole moments of some excited electronic states of HfS and HfO
A. Hansson, A. Pettersson, P. Royen, and U. Sassenberg

Paper 2
Lifetime Measurements of the $D^1\Pi$ State of HfS and the $b^3\Pi_1$ State of HfO
M. Aldener, A. Hansson, A. Pettersson, and U. Sassenberg

Paper 3
A comment on Hönl-London factors
A. Hansson and J. Watson

Paper 4
Measurement of the $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ of Na$_2$ Transition Dipole Moment by Autler Townes Splitting: Comparison of Three and Four Level System Excitation Schemes
In manuscript (June-05 version).

Paper 5
Electromagnetically Induced Transparency in Open Molecular Systems

Paper 6
The Role of Doppler Broadening in Electromagnetically Induced Transparency and Autler-Townes Splitting in Open Molecular systems
Contribution from the author

In the works on dipole moments and lifetimes of HfS and HfO, reported in Papers 1 and 2, I was involved in all activities concerning the experimental achievement, the analysis and calculations as well as the writing - albeit as a novice at that time.

My finding that the computer program LEVEL 7.5, claiming to calculate Einstein coefficients, was based on relative and not absolute Hönl-London expressions, resulting in erroneous outcome, was an incitement to write Paper 3. Literally my contribution to this paper is section 4: Application to emission bands.

The triple resonance experiment on Na$_2$, reported in Paper 4, was performed at Temple University, Philadelphia. Together with another Ph.D. student I set up and performed the experiment. I was responsible for the simulations, the analysis of data and part of the writing.

Besides participating to some extent in the measurements of the Na$_2$ cascade co-propagating system, my main contribution to the last two Papers 5 and 6 are lifetime calculations and theoretical simulations.
Acknowledgements

Still surprised – but very happy – that I got the unexpected opportunity to enter physics research, I realize that a fantastic period of my life has come to an end. A backward glance at the past years brings to my memory many episodes and persons, reminding me of all the goodwill and support, making it possible for me to complete this venture.

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Contents

1 Introduction 1

Stark Spectroscopy and Lifetime Measurements

2 Experimental 3
  2.1 The cluster machine 3
  2.2 Resonant two-photon ionization technique (R2PI) 7

3 Stark measurements and Dipole moments 9
  3.1 Permanent electric dipole moment 10
  3.2 The Stark effect 12
  3.3 Dipole moments of HfS and HfO 16
  3.4 Molecular parameters for HfS and HfO 18

4 Lifetimes - in Theory and Experiment 21
  4.1 Einstein coefficients and lifetimes 22
  4.2 Oscillator strength 24
  4.3 Lifetimes of HfS and HfO 27
  4.4 Hönl-London factors and lifetime calculations 29
  4.5 Just a moment, please 32

Coherence Phenomena in Molecular Systems

5 Fundamental concepts 35
  5.1 The driven three-level system 36
  5.2 Experimental set-up 40
  5.3 Observed spectra 42
  5.4 Theoretical modeling and simulations 45
  5.5 Quantum interference and level splitting 48
  5.6 AC Stark effect and Autler-Townes splitting 50
  5.7 Collected basic relations 52

6 Multiple Resonance Spectroscopy in molecular sodium 55
  6.1 The inverted-Y system 56
  6.2 Experimental conditions 58
  6.3 Analysis and results 60
  6.4 Density matrix formalism 63

7 EIT and AT effect in open molecular systems 69
  7.1 EIT in co-propagating cascade systems 69
  7.2 Conditions affecting EIT and AT splitting 73

References 75

Appended papers 1 - 6
1 Introduction

Much of our knowledge about the structure of matter is based on spectroscopy. Studies of spectra have made valuable contributions to the present state of atomic and molecular physics, as well as other fields like chemistry and molecular biology [1].

Spectroscopy has been a field of research ever since 1860, when Kirchoff and Bunsen introduced the spectral analysis [2]. During the years many new techniques and instruments have been developed and proved to be fruitful. A really stimulating impetus to the whole field of spectroscopy was the introduction of lasers in the 1960's. These new light sources, nowadays involved in most spectroscopic experiments, have increased spectral and time resolution by several orders of magnitude, thus greatly expanding the amount of information, which can be extracted from a spectrum. Also, the intense and coherent light available by lasers initiated a new domain of nonlinear phenomena, including a wide range of important applications and devices [3].

Molecular spectroscopy may be defined as the study of interaction between photons and molecules. The absorption or emission spectra emanating from this interaction provide powerful tools to explore molecular properties in many different aspects [1,4].

Spectroscopic investigations in the frequency domain generate spectral line positions, from which molecular constants and the discrete energy levels of the molecular system can be derived. This, in turn, implies detailed information about the internal molecular structure, for example the distribution of electrons, the vibration and rotation of the nuclei in the molecule [4]. The splitting of spectral lines, caused by external magnetic or electric fields, is an important means of measuring magnetic or electric moments of a molecule, and demonstrates the coupling of the different angular momenta.

With time-resolved spectroscopy, lifetimes of excited states in molecules can be determined. Lifetimes are closely associated with transition probabilities and line intensities, and provide a possibility to calculate oscillator strengths (f-values). Such results are important for example in astrophysics, where knowing the f-values of different electronic transitions is essential in order to estimate the relative abundance and concentration of the elements in the environment of stars. For stellar atmosphere modeling, accurately determined oscillator strengths of the involved transitions or the radiative lifetimes of excited states are facts of considerable interest [5]. Time resolved spectroscopy also gives important information in the study of chemical reactions, e.g., in the interpretation of collisional investigations [6]. Still another field of application is, that
radiative lifetimes and transition moments can be used to determine orbital mixing coefficients in a perturbed system, as reported, e.g., by Zare et al. [7].

The development of monochromatic or narrow-band, continuously tunable, and intense laser sources combined with the technique of exposing matter to several laser fields simultaneously has produced new branches of science. The novel spheres of interest offer a rich variety of exciting, sometimes counter-intuitive, phenomena, such as electromagnetically induced transparency [8], lasing without inversion [9], and population trapping [10], just to name a few. Whereas coherence phenomena in atoms interacting with lasers have been the subject of intense research for decades, the study of coherence in the interplay between laser and molecules is still in its infancy. However, thoroughly investigated atomic systems [e.g., 11-13] have established the base for further research on signs of coherence in more complex and realistic systems. In atoms every excited state is coupled to a limited number of energy levels, constituting a closed system. Molecules, in contrast, exhibit open systems where each electronic state contains a multitude of rovibrational levels, which are radiatively coupled to a large number of other rovibronic levels. A consequence of this and an unavoidable difficulty is the much smaller oscillator strengths for molecular transitions. Only with very accurate knowledge of the molecular structure and properties, it is possible to explore coherence effects in molecular systems.

Quantum optics, the discipline that unites quantum field theory and physical optics, is undergoing a time of revolutionary change [14]. The appealing prospects of controlling and changing optical properties of materials, such as absorbance and refractive index, through quantum interference have attracted much attention in recent years [15,16]. Multiple resonance spectroscopy is manifested as an effective tool for selective control and transfer of population in molecular quantum states, attaining alignment of non-polar molecules, an important goal in modern reaction dynamics [17]. Our ability to manipulate atoms and molecules with photons has considerably increased during the last few years and has opened the way to many new applications. Further progress is expected and future development looks promising [18].
Stark Spectroscopy and Lifetime Measurements

The first part of my thesis is based on two experimental works performed at Fysikum, Stockholm University. Stark spectroscopy and Lifetime measurements of the transition metal containing diatomic molecules hafnium sulfide and hafnium oxide are reported in Papers 1 and 2. Convinced that the experiment is the fundament of all physical insight, I start by describing in Chapter 2 the experimental equipment and techniques used in the present works on HfS and HfO. Chapter 3 focuses on how the Stark effect is used for determining the permanent electric dipole moments of the said molecules. In Chapter 4 the central theme is lifetimes of excited states and in this connection closely related topics, with reference also to Paper 3.

2 Experimental

"Experiments are the only means of knowledge at our disposal. The rest is poetry, imagination."

Max Planck (1858 -1947)

2.1 The cluster machine

The heart of our experimental set-up, illustrated in Fig. 2.1 a), is the cluster apparatus shown in Fig. 2.1 b). The method of laser vaporization for production of atomic clusters, combined with the pulsed supersonic nozzle technology, was developed by Smalley et al. [19] about 20 years ago. The machine, used in the current experiments, is the second-generation molecular beam apparatus of Smalley-type, designed and constructed by a team at Fysikum and recurrently subject to development and modification. The detailed properties of the apparatus, its peripheral equipment and its general way of operating are issues, thoroughly treated in previous reports [20,21]. Here I will give a more summary description with the emphasis on application to the present works.

The molecules of interest are produced by focusing the fundamental (1064 nm) of a pulsed Nd:YAG laser on to a rotating metal rod, close to a supersonic nozzle. The laser pulses are synchronized with the opening of a fast valve, allowing a carrier gas to flush into the zone, where metal atoms are ablated from the rod. In our experiments the metal is hafnium, and the species we want to study are the diatomic compounds hafnium mono sulfide and oxide. The carrier gas used is argon at high pressure (usually around 9 atm), appearing in pulses of around 250 μs duration. Small amounts of gaseous carbon disulfide
or oxygen, mixed into the argon gas, incite the formation of HfS or HfO, respectively, when the metal vapor is cooled and swept by the gas flow through a narrow channel.

Mixtures of newly formed molecules (and also unwanted clusters) now expand freely into the first vacuum chamber (pressure about $10^{-4}$ torr) under substantial cooling. Through a 3 mm skimmer, see Fig. 2.1 b), the central part of the diverging molecules is selected, and a well-collimated beam is transferred into the second vacuum chamber (pressure $10^{-6} - 10^{-7}$ torr), where the time-of-flight (TOF) mass spectrometer is attached.

In the experimental reaction region between the first couple of three parallel accelerator plates, the molecular beam is exposed to two perpendicularly oriented and counter-propagating laser beams, spatially overlapping each other and the molecules in the beam. The purpose of the first laser, in more detail described in section 2.2, is to excite the molecules, when it is tuned into resonance with discrete transitions. The second laser, an ArF (193 nm) or KrF (248 nm) excimer laser, ionizes the molecules, and the ions are accelerated into the time-of-flight tube towards the reflectron assembly. The reasonably homogenous, extracting electric field, can be either static or switched. When doing Stark spectroscopy, a static field is used, causing line splitting, which allows determination of the electric dipole moment (Paper 1). In lifetime measurements (Paper 2) the desire is to avoid Stark splitting, so in this case we use a pulsed field, controlled by a fast high-power switch.

When the ionized molecules reach the reflectron, including two electric fields, they will decelerate, turn and accelerate towards the detector, mounted at the opposite end of the flight tube. The reflectron not only reduces the total tube length, but also serves the important purpose of compensating for the velocity spread among identical ions due to ion creation at somewhat different positions between the accelerator plates. Ions with slightly more kinetic energy will go deeper into the reflectron before turning, thus spending more time there. The result is a focusing, so that equally charged ions, with the same mass, reach the detector simultaneously, whereas ions with unequal masses will differ in flight time and thus be detected at separate times. Fig. 2.2 shows a mass spectrum, recorded when the apparatus works entirely as a TOF spectrometer (i.e., no resonant excitation laser is present). The mass resolution is $m/\Delta m \approx 1000$, high enough to separate the different isotopomers.

When the fast ions hit the dual micro-channel plate (MCP) detector, electrons are knocked out, resulting in a charge pulse. The output signal from the detector is monitored
Fig. 2.1  

a) The experimental set-up used in Stark spectroscopy and in lifetime measurements.  

b) The total cluster machine assembly, combining a laser ablation source with a time-of-flight mass spectrometer.

Our molecules are created when metal atoms from a Hf rod are vaporized by the pulsed YAG laser and react with oxygen or sulfur, mixed into the carrier gas.  
The products expand rapidly into a vacuum chamber. Here is the experimental region, where the molecules are excited by dye laser light, which is pulse-amplified in an excimer-pumped Bethune cell. Then they are ionized by another excimer laser pulse.  
By an electric field the ions are accelerated into the time-of-flight tube. At the reflectron, the ions decelerate, turn and accelerate backwards to the detector.

The system is evacuated by five pumps, ensuring a vacuum of ~10^-6 torr.
by a fast PC data acquisition card, or recorded with a digital oscilloscope (LeCroy) and transferred to the computer. A pulse generator is used for triggering, synchronizing and timing of all the events. The operating frequency is 10 Hz.

The present method of production provides very cold molecules. The translational beam temperature is estimated to be less than 1 K (depending on the kind of carrier gas and the Mach number (the ratio $v_{\text{beam}}/v_{\text{sound}}$), given by the geometrical dimensions of the apparatus) [21]. The rotational temperature, determined from the intensity distribution of a rotation spectrum, is in the region of 5-10 K [20]. Generally the relations between different temperatures are $T_{\text{trans}} < T_{\text{rot}} < T_{\text{vibr}} < T_{\text{elec}}$. Nevertheless, normally only the lowest vibrational and electronic states of the molecules are populated under the existing experimental conditions.

The speed of the molecular beam varies with the carrier gas. When argon is used, the beam velocity in the forward direction, $v_z$, is around 570 m/s. The molecules also have a small transversal velocity, $v_{xy}$, parallel with the excitation laser beam and thus involving a possible Doppler-shift, $\pm v_0 \cdot v_{xy}/c$, where $v_0$ is the laser frequency. Values of $v_{xy}$ in the order of 5-10 m/s are obtained from measurements of the beam divergence, since this quantity reflects the ratio $v_{xy}/v_z$. With $v_0 \approx 5 \cdot 10^{14}$ Hz, the corresponding Doppler line width of the transitions is estimated to 10-15 MHz, consistent with the value obtained from calculation of the Doppler broadening from the approximate translational beam temperature.
2.2  Resonant two-photon ionization technique (R2PI)

The laser absorption method used in our experiments is the resonant two-photon ionization technique, R2PI, Fig. 2.3. A molecule is first excited by a resonant laser photon and then, after some delay, ionized by a second photon from another laser. A crucial quantity is the energy of the second, non-resonant photon. It must be large enough to ionize the molecule from the excited state, otherwise no resonant signal will be seen, when the wavelength of the first laser is tuned. On the other hand, the energy must be smaller than the total ionization potential (I.P.), making it impossible for one photon to ionize a molecule directly from the ground state. Thus we need to know approximately the I.P. of the investigated molecules. Under the right conditions, R2PI is a sensitive method, where the ion production is recorded as a function of the exciting photon energy.

In spectroscopic studies we usually want the two lasers to be coincidental, i.e., the delay time \( t \) is very small, just sufficient to ensure, that the ionization does not take place before the excitation. In lifetime measurements, on the other hand, the ionizing photon is deliberately delayed with adjustable values of the time \( t \). By stepping the delay time, it is possible to obtain a decay curve of the excited state.

The ionizing photons are simply delivered from an excimer laser, as mentioned earlier, but the excitation laser system is somewhat more complex. See Fig. 2.1 a). For excitation we use a tunable, single-mode, continuous wave (cw), ring dye laser, pumped by an argon ion laser. The narrow bandwidth cw laser light (~1 MHz FWHM) is pulse-amplified in a special device, called a Bethune cell [22], filled with a circulating dye. An excimer laser, XeCl (308 nm), is used for pumping the Bethune dye cell. With this setup, it is possible to amplify the ring dye laser light 500-1000 times in one step, giving ~1 \( \mu \)J output energy in a pulse of about 10 ns duration. The observed line width is 150 MHz or less (a combination of power broadening and the natural line width of the pump laser). At the transition energies present in the investigated Hf systems, mostly Rhodamine 6G is a suitable dye, used in the ring laser as well as the Bethune cell.

The ring dye laser is equipped with an auto scan system and an internal wavelength meter. When performing a scan, it is possible to choose scan parameters. Depending on the purpose, different settings are appropriate. A usual combination is scan distance 30 GHz (1 cm\(^{-1}\)), scan steps 10 MHz and 10-20 recorded points at each wavelength. In order to calibrate the spectra, an absorption signal from iodine I\(_2\) is simultaneously recorded.
Stark Spectroscopy and Lifetime Measurements

The resonant two-photon ionization (R2PI) scheme.
The R2PI laser absorption and detection technique is a sensitive method for probing the population of an excited state.
In frequency domain investigations, the delay time $t$ is small.
The excitation laser is scanned ⇒ the ion production is recorded as a function of the exciting photon energy ⇒ information about resonant transitions (line positions).
In lifetime measurements, the excitation laser is held fixed at resonance.
The delay time $t$ is adjustable ⇒ the ion signal shows the number of molecules still remaining in the excited state after a certain time ⇒ decay curve of the excited state.

Fig. 2.2 Mass spectrum of Hf, HfO and HfS. The numbers refer to the masses of naturally occurring Hf isotopes. The different isotopomers are well resolved. In the measurements we select the peaks associated with the isotope $^{180}\text{Hf}$.

Fig. 2.3 The resonant two-photon ionization (R2PI) scheme.
3 Stark measurements and Dipole moments

In Paper 1, appended to this thesis, we report on measurements of the permanent electric dipole moments of HfS in the $D^1\Pi$ state and of HfO in the $b^3\Pi_1$ state. Energy level diagrams of HfS and HfO are shown in Fig. 4.2. The experiments are based on the conditions attained, when an external electric DC field is applied to the molecules, while their rotational spectra are observed. The field causes a splitting of rotational spectral lines, known as Stark effect.

The large interest in the electric dipole moment $\mu$, especially when a metal atom is a part of the molecule, has recently led to an overview paper: "Permanent electric dipole moments of metal containing molecules" by T.C. Steimle [23]. The spectra of diatomic transition metal compounds have been widely studied for a long time, in particular the oxides, due to their presence in spectra of late-type stars. A large amount of spectroscopic data has been collected for mono oxides and sulfides of group IVb transition metals (Ti, Zr, Hf). These molecules are of great interest, because they are simple systems, which give information on the role of the metal $d$ electrons in the bonding.

In the following sections, I will first present some basic ideas about the electric dipole moment (section 3.1) and next a description of the Stark effect and its influence on rotational spectra (3.2). In section 3.3 I give some comments on our experimental procedure in measuring the dipole moments of HfS and HfO, and finally the calculation of molecular parameters is described (3.4).

Who was Stark?

Johannes Stark was a German experimental physicist, living 1874-1957. His main field of interest was electrical conduction in gases. He studied an optical phenomenon known as the Doppler effect in canal rays, and he examined Bremsstrahlung. After Zeeman’s discovery (1896) of the spectral lines splitting under the influence of a magnetic field, Stark searched for a similar effect of electric fields. In 1913 he "was naturally very excited" when he "observed several lines at the position of the blue hydrogen line". This "Entdeckung des Stark-Effekts" ensured Stark the Nobel Prize in 1919.

In sharp contrast to Stark’s scientific talent appears his heavy anti-Semitic engagement. Together with Lenard he was the driving force in "Deutsche Physik", a movement glorifying the pure Aryan physics opposed to the suspect and depraved Jewish physics. These trends of opinion brought dreary consequences; for instance Einstein was persecuted and derided. Internationally recognized Jewish scientists as Lise Meitner and others were forced to leave the country, and their sympathizers like Planck and Heisenberg were victimized.

At the end of his life, Stark appeared increasingly pathologically quarrelsome. When he retired, he had made almost all his former colleagues his enemies. Nevertheless, his contribution during several decades to the development of physics is undoubtedly substantial. [2,24]
3.1 Permanent electric dipole moment

The electric dipole moment $\mu$ is the most fundamental electrostatic property of a neutral molecule. It is essential for probing the ionic character of a chemical bond, and of great usefulness in the construction of molecular orbital-based models. It can even be useful in understanding macroscopic properties, because there is a connection between the dipole moment of an isolated molecule and macroscopic quantities, such as dielectric constants and permittivity \([23]\). The dipole moment, permanent or temporary, also enters into the general description of light-matter interaction. In microwave spectroscopy, the permanent electric dipole moment is a necessary condition for allowed, pure rotational transitions.

The simplest picture of an electric dipole is two equal and opposite point charges, $+q$ and $-q$, separated a small distance $d$. The dipole moment is then defined as a vector with magnitude $qd$ and direction from the negative to the positive charge. The definition of the unit debye (D), frequently used to give the value of a dipole moment, is based on this picture: 1 D is the dipole moment of two opposite charges of magnitude $10^{-10}$ esu, $1 \text{ esu} = 3.3356 \times 10^{-10} \text{ C}$) separated by the distance 1 Å. In terms of SI units this means that $1 \text{ D} = 3.3356 \times 10^{-30} \text{ Cm}$. Sometimes atomic units (a.u.) are used to express dipole moments: 1 a.u. = $1 \cdot a_o = 8.4784 \times 10^{-30} \text{ Cm} = 2.5417 \text{ D}$ ($a_o$ = Bohr radius).

A molecule can be regarded as a collection of discrete particles of charge $e_j$, located in space by the position vectors $r_j$. In this case, the dipole moment is obtained by summing over all products $e_j r_j$. Some molecules, named polar, possess a permanent electric dipole moment, whereas non-polar molecules do not, but may be polarized in an electric field or by changing charge distribution in a vibrational motion.

Diatomic transition metal oxides and sulfides are permanent dipoles. Their observed electric dipole moment can generally be expressed as a sum of several components \([25]\):

$$\mu_{obs} = \mu_p + \mu_b + \mu_h + \mu_{ind} \cdot$$

(3-1)

Even though the four contributions are not independent, a short description of each individual component is given separately below.

$\mu_p$ is the primary moment, originating from the ionic character of the bond and closely related to the difference in electro-negativity between the atoms involved. The primary moment is a result of a transfer of electric charge between the bonded atoms and can be expressed \([25]\) as $\mu_p = e \cdot d \cdot i_c$, where $e$ is the elementary charge, $d$ is the internuclear distance of the molecule, and $i_c$ is the ionicity parameter. A pure covalent bond is
attributed the value $i_c = 0$, whereas $i_c = 1$ indicates complete ionicity.

$\mu_b$, the bond overlap moment, results from distortions caused by the overlap between the bonding orbitals. It is proportional to the covalent component of the bond and is most important when $i_c$ is small and the atomic covalent radii are very different, but vanishes for $i_c = 1$ or equal covalent radii. The direction of $\mu_b$ can be the same or opposite to the direction of $\mu_p$.

$\mu_h$ is a dipole moment contribution caused by electrons in a hybridized atomic orbital if the center of the hybridized orbital does not coincide with the center of the nuclear charge. Hybridization moments can be very large [25]. Either direction of $\mu_h$ is possible.

$\mu_{ind}$ is an induced moment, resulting from self-polarization of the molecular electron cloud due to the electric field produced by the three first dipole moment components. In this way also non-bonding orbitals may affect the observed moment. $\mu_{ind}$ is always of opposite polarity to the resultant $\mu_{obs}$.
3.2 The Stark effect

Stark effect is a generic term for the changes, which may be observed in spectra from atoms as well as molecules, when the system is subject to an external electric field. In molecular spectra, an applied static electric field causes a shift of the rotational energy levels and a consequential splitting of the rotational lines. The electric dipole moment plays a crucial role in these phenomena, and Stark spectroscopy is the most commonly used method for the extraction of the $\mu$-value from experimental data [23].

Let us look at a rotating diatomic molecule with a permanent electric dipole moment $\mu$ (along the internuclear axis). Without external influence, the pure rotational energy $W_0$ depends only on $J$, the total angular momentum quantum number. The degeneracy of a level, due to $(2J+1)$ possible values of $M$ for a given value of $J$, can be lifted, if an external electric field is applied. The quantum number $M$ represents the projection of $J$ on a laboratory-fixed axis, in this case the direction of the electric field $E$. Substates with different values of $M$ correspond to different orientations of the rotating molecule relative to the field. The energies $W$ of these possible states are given by $W = W_0 - \mu_E \cdot E$, where $E$ is the electric field strength and $\mu_E$ is the mean component of the electric dipole moment in the field direction. Consequently the energy shift caused by the field is $\Delta W = W - W_0 = -\mu_E \cdot E$. One way to derive the details behind $\mu_E$ is perturbation theory [4]. It turns out that the explicit $\Delta W$ formula varies according to the electronic state of the molecule and depends on the quantum number $\Omega$, specifying the projection of $J$ on the internuclear axis. Distinguishing two cases, we find for the energy change $\Delta W$, due to the field, the following expressions [26], often referred to as the first order and the second order Stark effect:

First order Stark effect  \[ \Delta W_{(i)} = \pm \frac{\mu E |M| \Omega}{J(J+1)}; \]  \hspace{1cm} (3-2)

Second order Stark effect  \[ \Delta W_{(ii)} \propto \frac{(\mu E)^2}{\hbar BJ(J+1)}. \]  \hspace{1cm} (3-3)

Generally, the second order energy level shift is much smaller than the one of first order. Usually $\Delta W_{(ii)}$ is unimportant unless $\Omega = 0$, when the first order energy is zero [26].

The molecules HfS and HfO, examined in our experiment, have $^1\Sigma$ ground states, i.e., $\Omega = 0$, and there is no first order Stark shift. However, in their excited states ($^1\Pi$ and $^3\Pi_1$, respectively), the condition $\Omega = 1$ implies first order energy shift, resulting in
substantial effects on the rotational spectra owing to the electric field. (The second order shift, certainly present in both kinds of states, is negligible compared to the first order effect, which completely dominates the splitting of the transition energies).

So let us focus on our diatomic molecules in their excited $\Pi$-states. We have to consider also the $\Lambda$-doubling, present in all states with $\Lambda>0$, involving a degeneracy associated with the two possible values of $\pm|\Lambda|$. In a rotating molecule these two components, labeled with parity $e$ and $f$, are separated. In the presence of an electric field, both sublevels experience the first order Stark shift, Eq. (3-2). This can be described [27] as an interaction, where the $e$ and $f$ levels are coupled through the Stark operator $\hat{\mu} \cdot \hat{E}$:

$$\langle J,M,e|\hat{\mu} \cdot \hat{E}|J,M,f\rangle = V_E = \frac{\mu E|M|}{J(J+1)} \quad (\Omega = 1). \quad (3-4)$$

Let the pure rotational energy be $W_0 = BJ(J + 1)$, where $B$ is the rotational constant, and the $\Lambda$-splitting $\Delta_{ef} = qJ(J + 1)$, where $q$ is the $\Lambda$-doubling constant. The two separated $\Lambda$-components with energies $W_0 \pm \frac{1}{2}\Delta_{ef}$ interact through the Stark energy, $V_E$. We find the resulting energy eigenvalues $W$ by solving the secular determinant equation:

$$\begin{vmatrix}
W_0 - \frac{\Delta_{ef}}{2} - W & V_E \\
V_E & W_0 + \frac{\Delta_{ef}}{2} - W \\
\end{vmatrix} = 0 \quad \Rightarrow \quad W_{1,2} = W_0 \pm \sqrt{\frac{\Delta_{ef}^2}{4} + V_E^2}. \quad (3-5)$$

The solutions account (after Taylor expansion) even for the extremes:

- weak electric field, $V_E < \Delta_{ef} \Rightarrow W_1 \approx W_0 - \frac{\Delta_{ef}}{2} - \frac{V_E^2}{\Delta_{ef}}, \quad W_2 \approx W_0 + \frac{\Delta_{ef}}{2} + \frac{V_E^2}{\Delta_{ef}}; \quad (3-6)$

- $\Lambda$-doubling small, $\Delta_{ef} < V_E \Rightarrow W_1 \approx W_0 - \frac{\Delta_{ef}^2}{8V_E} - V_E, \quad W_2 \approx W_0 + \frac{\Delta_{ef}^2}{8V_E} + V_E. \quad (3-7)$

If $\Delta_{ef}^2$ is negligible, Eq. (3-7) gives $W_2 - W_1 \approx 2 \cdot V_E$, i.e., the first order Stark effect, Eq. (3-2), whereas Eq. (3-6) is in agreement with first-order perturbation theory ($V_E$ small).

The energy situation, as a function of the electric field strength, is illustrated in Fig. 3.1.

Another consequence of the coupling in Eq. (3-4) is a mixing of the $e/f$ wave functions. From perturbation theory we get the wave functions, corrected to first order, as

$$\psi_1^{(1)} = \psi_f^{(0)} - \frac{V_E}{\Delta_{ef}} \cdot \psi_e^{(0)} \quad \text{and} \quad \psi_2^{(1)} = \psi_e^{(0)} + \frac{V_E}{\Delta_{ef}} \cdot \psi_f^{(0)}, \quad \text{respectively.} \quad (3-8)$$
This Stark mixing between \( \Lambda \)-doublet \( e \) and \( f \) sublevels may result in the appearance of "forbidden" lines. In a \( ^1\Pi \leftrightarrow ^1\Sigma^+ \) transition, for example, an allowed \( Q \) line means \( f \leftrightarrow e \), according to ordinary parity selection rules. However, when a primary \( f \)-parity state through the Stark interaction attains also some \( e \)-character, also a forbidden \( Q \) line \( e \leftrightarrow e \) is possible. The \( R \) and \( P \) lines exhibit corresponding behavior, giving forbidden \( f \leftrightarrow e \) transitions besides the allowed \( e \leftrightarrow e \). In the lower, enlarged part of Fig. 3.2 there are two peaks marked, referring to an allowed and a forbidden \( Q(9) \) transition. In this case \((J = 9)\), the individual \(|M|\)-components are not resolved. However, for low \( J \) values, the \((2J+1)\) Stark components are possible to resolve, as illustrated by the \( P(2) \) line \((J = 1)\). The central peak \((M' = 0)\) and the right side peak \(|M'| = 1\) originate from allowed \( e \leftrightarrow e \) transitions, whereas the left side peak \(|M'| = 1\) is the result of a forbidden \( f \leftrightarrow e \) transition.
Stark Spectroscopy and Lifetime Measurements

**Fig. 3.1** Stark pattern of the energy levels of a \(^1\Pi, J = 5\) molecular level as a function of the electric field. Coupling occurs between each pair \(|J,M,e⟩\) and \(|J,M,f⟩\), \(M \neq 0\). Note that \(|M|\) and \(-|M|\) substates are identically shifted. (From reference [27]).

The mixing of \(e/f\)-parity wave functions, as a consequence of the coupling, gives rise to "forbidden" lines in the spectrum. For example Q lines may be excited from a lower \(^1\Sigma^+\)-state, \(J = 5\) \(e\), to \(f\) as well as \(e\)-parity levels in the depicted \(^1\Pi\)-state.

**Fig. 3.2** The upper part shows the \((0,0)\) band of the \(D^1\Pi - X^1\Sigma\) transition of HfS under field-free conditions. The Stark splitting is avoided by using a switched field in the cluster machine.

The lower part shows an enlarged section of the Stark spectrum. In this case the electric field is held fixed at \(~1000\) V/cm. The \(P(2)\) line is resolved, displaying three peaks originating from one "forbidden" (left) and two allowed transitions. Each of the two \(Q(9)\) lines conceals 10 unresolved sub-peaks. The left (right) line corresponds to allowed ("forbidden") transitions.
3.3 Dipole moments of HfS and HfO

In the dipole measurements, we used the cluster apparatus and the experimental setup demonstrated in Chapter 2. Molecules in gas phase were prepared with the ablation method explained in section 2.1. The R2PI technique was used (Fig. 2.3), and the laser systems as well as the detection method were those described in section 2.2.

The first step, after producing the desired kind of molecules, was to record an overview absorption spectrum, rotationally resolved and referring to a selected vibrational band of the electronic transition. In this procedure, the ring-dye laser was slowly scanned over the wavelength interval of interest. At the experimental reaction area in the machine, the molecules were exposed to a switched electric field, implying that the accelerating field was applied about 1 μs after the ionization pulse. In this way, the excitation process took place in a field-free region, where no Stark effects existed. A pure spectrum was obtained without line splittings and "forbidden" transitions, which facilitated the identification of the rotational branches and lines. A typical spectrum is shown in the upper part of Fig. 3.2. At the low temperatures present, only the first few lines (up to J ~ 20) of each branch were intense enough to be seen. Three bands in the $D^1\Pi - X^1\Sigma$ transition of HfS were recorded: (0,0), (1,0) and (2,0), but only the (0,0) band in the $b^3\Pi_1 - X^1\Sigma$ transition of HfO. From the observed line positions, sets of molecular parameters were extracted as described in next section 3.4.

Utilizing survey spectra, recorded when a static electric field was applied to the molecules during the whole R2PI process, we chose suitable candidates for Stark measurements. Usually the lines $R(0)$, $R(1)$, $R(2)$, $Q(1)$, $Q(2)$, $Q(3)$, $P(2)$ and $P(3)$ of each band were sufficiently resolved and therefore selected for Stark splitting analysis. The field strengths were accurately registered in each measurement and held at 800 - 1000 V/cm. Due to the first order Stark shift, Eq. (3-2), affecting the excited states, their sublevel structure could be determined from the resulting line splittings. Paper 1, Table 1 contains all the investigated line structures in terms of the energy splitting $\Delta W_{|\mu|}$ between pair of peaks corresponding to the same $|M|$-value. The dipole moment values reported in Paper 1, Table 3, are compensated for the Λ-doubling according to Eqs. (3-4) and (3-5) with $W_2 - W_1 = \Delta W_{|\mu|}$:

$$\mu = \frac{J(J+1)}{E \cdot |M|} \sqrt{\left(\frac{\Delta W_{|\mu|}}{2}\right)^2 - \left(\frac{\Delta_{\text{eff}}}{2}\right)^2} \quad (3-9)$$
As can be seen (Table 3, Paper 1), our measurements gave $\mu \approx 3.4$-3.5 D in the HfS $D^1\Pi$ state and $\mu \approx 2.7$ D in the HfO $b^3\Pi_1$ state. A more relevant comparison is made by regarding the reduced moments, $\mu_{\text{red}} = \mu / r_0$, where $r_0$ is the internuclear distance. Nevertheless we still have $\mu_{\text{red}}(\text{HfS}) > \mu_{\text{red}}(\text{HfO})$, although the primary ionic contribution $\mu_p$ in Eq. (3-1) most likely is smaller in sulfides than in oxides, since oxygen is more electronegative than sulfur. One explanation to the result obtained might be that the induced (and always opposite) moment $\mu_{\text{ind}}$ is smaller in HfS than in HfO, because the non-bonding Hf 6s$\sigma$ orbital is probably less polarized in the sulfide due to larger bond length compared to the oxide.

A project in progress is to supplement the work reported in Paper 1 by performing \textit{ab initio} calculations for the investigated molecules in the first place, but hopefully also for corresponding compounds of the other group IVb metals. The purpose is to achieve theoretical values of the permanent electric dipole moments and acquire knowledge of the electron density distributions in ground states as well as excited states. Our belief is that such results would give valuable guidance in understanding irregularities, as exemplified above, and provide excellent information concerning the different components of the observed dipole moments, as proposed in Eq. (3-1). A very interesting analysis would be to compare dipole moment values and corresponding orbital charge density plots

- within the group for the same kind of compound;
- between oxide and sulfide for each metal (Ti, Zr, Hf);
- between ground state and excited state of the same compound.
3.4 Molecular parameters for HfS and HfO

As already mentioned, the Stark measurements were accompanied by recordings of some low-temperature spectra under field-free conditions to completely avoid Stark splitting. By combining our recorded lines (Paper 1, Table 2) for low J-values with most previously reported spectra of HfS and HfO [28-31], in all more than 6000 lines for each molecule were used in ordinary spectroscopic investigations. We calculated sets of molecular parameters and determined potential energy curves for ground states as well as excited states.

Our calculation procedure is basically the term-value method [32] but slightly modified. Primarily the energy levels (term-values) of the two molecular electronic states, coupled by a large number of lines involving different rovibrational transitions, are determined. Each line defines an equation of the type

\[ \sigma = T'(v', J') - T''(v'', J'') \]  

where \( \sigma \) is the line wave number and \( T', T'' \) denote the upper and lower state term-values, respectively. Since the number of energy levels generally is far less than the number of lines, an over-determined system of linear equations is obtained for the unknown term values. The individual equations are generated with a specially designed numbering and assignment system [32], which creates coefficient matrices reflecting the simple selection rules \( \Delta J = 0, \pm 1 \).

In our approach, an explicit energy expression is assumed for the ground state, \( X^\Sigma^+ \), which is supposed to be unperturbed. The relation has the form

\[ T_{v, J} = T_v + B_v J(J + 1) - D_v (J(J + 1))^2 + H[J(J + 1)]^3 \]  

where

- the vibrational energy \( T_v = T_v + \omega_v (v + \frac{1}{2}) - \omega_v x_v (v + \frac{1}{2})^2 \),
- the rotational constant \( B_v = B_v - \alpha_v (v + \frac{1}{2}) + \gamma_v (v + \frac{1}{2})^2 \),
- the centrifugal distortion constant \( D_v = D_v + \beta_v (v + \frac{1}{2}) \)

and \( H \) is a higher order distortion parameter.

In this way the number of unknown parameters is considerably reduced to 7-8 molecular constants for the ground state besides \( \sim 3000 \) term values of the excited states.

The calculation method we use means solving this system of equations by least-squares techniques. From the resulting constants, the ground state energy levels are determined. Knowledge of the term values for both states, now allows the lines to be reconstructed and compared to the raw lines, thus providing the errors in the observed
lines, (Paper 1, Table 2). In next step, an appropriate energy model expression for the excited state, similar to Eq. (3-11), is least-squares fitted to the upper state term values, obtained in the first calculation.

To construct the potential curves we used the Rydberg-Klein-Rees (RKR) method, which is a procedure to determine a diatomic molecule potential energy function from knowledge of its rovibrational energies. In this application energies are represented by power series called Dunham expansions,

$$\sum_{k,l} Y_{kl} \left(v + \frac{1}{2}\right)^k \cdot (J(J + 1))^l.$$

(3-12)

The Dunham coefficients $Y_{kl}$, which are related to the conventional spectroscopic constants, are obtained from least-squares fitting to the calculated term values. In this context we utilized two programs designed by Le Roy [33,34]. First, RKR1, a code which generates the so called turning points, i.e., two internuclear distances associated with each vibrational energy and thus defining the potential curve. We also used LEVEL 7.4 to determine higher order rotational constants.

Combining and iterating the procedures outlined above results in the final and accurate molecular parameters for HfS and HfO, reported in Paper 1, Table 3. The potential energy curves are presented in Fig. 3, Paper 1.
4 Lifetimes – in Theory and Experiment

In Paper 2, appended to this thesis, we report on lifetime measurements of excited states of HfS and HfO. The high resolution, obtained by using a pulse-amplified, narrow-band cw laser for excitation, makes it possible to selectively measure lifetimes of individual rotational levels. The technique, developed in the current experiment, involves small statistic errors, enabling us to determine the lifetimes with a precision of 2-3%. A general discussion of possible systematic errors, usually associated with lifetime measurements, is carried out in the paper. From the lifetime value of each excited level, the absorption oscillator strength of the transition from the ground state is calculated.

Paper 3, appended to this thesis, demonstrates how tensor algebra is used to derive rotational line intensity formulas, usually called Hönl-London factors. Correct absolute expressions are of greatest importance when applied, for example, to lifetime calculations. Crucial parameters in theoretical simulations of the experiments reported in Papers 4 - 6 are the lifetimes of the excited states involved in the systems under investigation. Since data on experimentally known lifetimes of specific vibration-rotation levels are limited, radiative lifetimes are theoretically computed in several cases.

In the following sections, I will first briefly account for the fundamental interactions of electromagnetic fields with matter and the basic theories concerning spontaneous lifetime (4.1). In next section (4.2) the oscillator strength concept is introduced and the method for calculating f-values is derived. After that, I summarize our experimental procedure in measuring the lifetimes of HfS and HfO, and the results are presented (4.3). Section 4.4 treats the Hönl-London factors and their significance in calculating decay rates and lifetimes, using a commonly available computer program (LEVEL 7.5). Finally, in section 4.5 the reader is invited to spend a moment on analyzing dipole moment related transitions.

Note added in proof:
As a result of Paper 3 and after this thesis was written, a modified version of the LEVEL program was released. In the new code, LEVEL 7.7, the shortcomings in earlier versions, pointed out in section 4.4, are corrected.
4.1 Einstein coefficients and lifetimes

Einstein introduced (1917) three probability coefficients, describing the rates of possible transitions between two states \( |i\rangle \) and \( |k\rangle \) of a molecule. Let us assume that \( |i\rangle \) is the upper level, i.e., \( E_i > E_k \), where \( E \) denotes the energy. The Einstein coefficient of spontaneous emission, \( A_{ik} \), gives the probability that a molecule, initially in state \( |i\rangle \), will undergo spontaneous transition to the lower level \( |k\rangle \), emitting radiation with a frequency \( \nu \), corresponding to the energy difference \( E_i - E_k = h\nu \). In the presence of an external electromagnetic radiation field of frequency \( \nu \), molecules initially in state \( |k\rangle \) can absorb a photon from the field and be excited to the upper state. The rate of this transition is determined by the Einstein coefficient of induced absorption, \( B_{ik} \). The radiation field can also stimulate molecules in the excited state \( |i\rangle \) to make an induced transition to the lower level \( |k\rangle \), simultaneously emitting a photon of energy \( h\nu \). This process, which is the principle of light amplification in lasers, occurs with a probability \( B_{ik} \), the Einstein coefficient of induced or stimulated emission. Besides the \( B \)-coefficients, the photon density \( \rho(\nu) \) of the radiation field is a rate-determining factor of these induced processes, whereas the spontaneous emission is independent of the external field. Moreover, all transition intensities are proportional to the number of molecules in the initial level. Hence the expression for the total change with time of the population density \( N_i \) of the excited state \( |i\rangle \) is (if other depopulating processes, e.g., collision-induced radiation-less transitions are neglected):

\[
\frac{dN_i}{dt} = -A_{ik} \cdot N_i + B_{ik} \cdot \rho(\nu) \cdot N_k - B_{ik} \cdot \rho(\nu) \cdot N_i .
\]

(4-1)

It is possible to derive relations between the three Einstein coefficients [1], for example

\[
B_{ik} = \frac{g_i}{g_k} B_{ik} \quad \text{and} \quad A_{ik} = \frac{8\pi h \cdot \nu^3}{c^3} B_{ik} .
\]

(4-2), (4-3)

In Eq. (4-2) \( g_i \) and \( g_k \) are the statistical weights or the degeneracy factors of the states \( |i\rangle \) and \( |k\rangle \) respectively.

The lifetime \( \tau_i \) of an excited state \( |i\rangle \) is closely related to the Einstein coefficient of spontaneous emission, \( A_{ik} \). So let us focus on the case where no external field is present, i.e., in Eq. (4-1) the factors \( \rho(\nu) = 0 \). Integration of the remaining expression gives for the population of the excited state
\[ N_i(t) = N_i(0) \cdot e^{-A_{ik}t} . \] (4-4)

Apparently spontaneous emission behaves like the exponential decay of a radioactive element with the decay constant \( A_{ik} \). The radiative spontaneous decay curve is shown in Fig. 4.1 b). The mean spontaneous lifetime \( \tau_i \) of a state \( |i\rangle \) is defined as the time elapsed, until the population density \( N_i \) has decreased to the fraction \( 1/e \) of its initial value \( N_i(0) \).

**Fig. 4.1** Radiative decay of the level \( |i\rangle \):

a) The total rate of spontaneous emission is given by the sum of the individual rates of all possible transitions to lower states.

b) Population decay curve. After one lifetime \( \tau \) the initial population density has decreased by a factor of \( e \).

(From reference [1]).

If there is only one lower level accessible, to which the excited state can decay, the lifetime is the reciprocal of \( A_{ik} \): \( \tau_i = (A_{ik})^{-1} \). Very often, however, several transition paths from an energy level \( E_i \) are possible, as shown in Fig. 4.1 a). In this case, the total transition probability \( A_i \) is the sum over all the individual decay constants: \( A_i = \sum_k A_{ik} \).

Consequently the lifetime of the excited state \( |i\rangle \) is given by the relation

\[ \frac{1}{\tau_i} = \sum_k A_{ik} . \] (4-5)

The resulting lifetime \( \tau_i \) is the quantity measured experimentally, when contributions to the total transition probability others than spontaneous emission are negligible. The lifetime is a property of the state under investigation and has the same value, irrespective of which decay channel is observed.
4.2 Oscillator strength

From classical electrodynamics we know that an accelerated charge, e.g., an oscillating electron, radiates electromagnetic energy. This phenomenon can be regarded as the classical analogue of the quantum mechanical spontaneous emission process, where an atom or a molecule makes an electronic transition from an excited state to a lower energy level, emitting a photon. One way of defining the oscillator strength, or $f$-value, is by comparing the rate of a molecular transition with the radiation rate of a classical single-electron oscillator. Emission oscillator strength $f_{ik}$ is defined [35] by the relation

$$f_{ik} = -\frac{1}{3} \frac{A_{ik}}{\gamma_{cl}} \quad \gamma_{cl} = \frac{e^2 \omega^2}{6\pi\varepsilon_0 mc^3} \quad (s^{-1})$$

(4-6)

where $\gamma_{cl}$ is the classical radiative decay rate of an electron with mass $m$ oscillating at frequency $\omega$ [36]. For practical purposes, especially in astrophysics, when dealing with absorption from a continuous spectrum, absorption oscillator strength is more useful. An absorption $f$-value (with positive sign) is then defined as

$$f_{kl} = -\frac{g_i}{g_k} f_{ik}, \quad (4-7)$$

where $g_i$ and $g_k$ are the degeneracy factors as before.

Now the absorption oscillator strength can be related to the Einstein coefficient of spontaneous emission between two states with energy difference $E_i - E_k = \hbar \nu$:

$$f_{abs} = f_{ki} = \frac{\varepsilon_0 mc^3}{2\pi\varepsilon_0^2} \frac{g_i}{g_k} \frac{1}{\nu^2} A_{ik}.$$ 

(4-8)

From a quantum electro-dynamical treatment of spontaneous emission under certain assumptions (the electric dipole approximation for weak fields), it may be shown [35], that the Einstein $A$-coefficient of a transition from sublevel $M_i$ of an upper level $|i\rangle$ to all possible degenerate sublevels $M_k$ of a lower level $|k\rangle$, is described as

$$A_{ik} = \frac{16\pi^3 \cdot \nu^3}{3\varepsilon_0 \hbar c^3} \cdot e^2 \sum_{M_i} |k, M_k |r, i, M_i| \cdot \mu_{ik}^2.$$ 

(4-9)

In Eq. (4-9) the transition dipole moment $\mu_{ik}$ is defined, using the dipole operator $er$.

*) In older textbooks, e.g., Herzberg's, the quantity $\mu_{ik}$ is called just ‘transition moment’, whereas in recent literature the term ‘transition dipole moment’ is more frequently used.
Closely connected to the transition dipole moment is the line strength $S$, another quantity often used in this context. The line strength of a transition is symmetric with respect to the upper and lower levels, and is defined as a double sum [35]:

$$S_{ik} = S_{ki} = e^2 \sum_{M_k} \sum_{M_i} |\langle k, M_k | r | i, M_i \rangle|^2,$$

(4-10)

implicating that line strength $S_{ik} = g_i \cdot \mu_{ik}^2$ since the sum $\sum_{M_j}$ corresponds to $g_i$.

Hence we can relate the spontaneous emission rate and the line strength:

$$A_{ik} = \frac{16\pi^3 \cdot \nu^3 \cdot S_{ik}}{3\varepsilon_0 \hbar c^3 \cdot g_i}.$$

(4-11)

Eq. (4-11) is a useful relation, often referred to as the "$\nu^3$ factor", telling us, that if there are several possible decay channels with comparable line strengths, the transition with the shortest wavelength should dominate, due to the cubic frequency dependence.

In our experiments we study individual rotational lines, i.e., transitions between levels, characterized not only by their electronic states, but also labeled by specific vibrational and rotational quantum numbers. It can be shown [37], that in such cases the total transition moment (under assumptions like the Born-Oppenheimer approximation) may be split into three separate parts. Doing so, we can express the line strength of a rotational line as

$$S_{jj'} = e^2 a_0^2 \cdot q_{jj'} \cdot \mu_e^2(r) \cdot \varphi_{jj'} \quad (*).$$

(4-12)

where $q_{jj'} = |\langle \nu' | \nu' \rangle|^2$ is the vibrational part, the Franck-Condon factor;

$\mu_e^2(r)$ is the electronic part of the transition moment;

$\varphi_{jj'}$ is the rotational part, the Hönl-London factor.

Now the expression in Eq. (4-12) can be used in Eq. (4-11), which in turn is inserted into Eq. (4-8), thus relating $f_{abs}$ to the line strength components.

The last step is to find a relation between the oscillator strength and the lifetime. For that purpose, we use our knowledge from Eq. (4-5) and multiply the expression for $f_{abs}$ with unity, $1 = \frac{1}{\tau_i}$. After changing the frequency $\nu$ to wave number $\sigma = \nu / c$ (cm$^{-1}$)

*) It is worth noticing, that in Eq. (4-12) only $M'$-degeneracy is considered, i.e., a possible $\Lambda$-doubling is not included. Based on this definition of a rotational line, it follows that an unresolved $\Lambda$-doublet is composed of two rotational lines.
and replacing all constants by numerical values, we end up at the following expression (from now on the \( f \)-values refer to absorption irrespective of the order of the indices):

\[
\tau \phi_{\mu} \sigma_1 = (1499.12 \times \ldots) \sum_{\text{lower levels}} \sum_{\text{higher levels}} (J_{g'i} + J_{g'k}) \frac{q_{\nu'\nu} \cdot \mu_{\nu'}^2(r) \cdot \phi_{j'j'}}{\sigma_{\nu'\nu}} \cdot \frac{1}{\tau}.
\]

(4-13)

This is the formula, given in Paper 2 as the basis for calculation of oscillator strengths from the measured lifetimes of rotational levels in excited states. The degeneracy factors in this case are \( g_i = 2J' + 1 \) and \( g_k = 2J'' + 1 \). Assuming \( \mu_{\nu'}^2(r) \approx \) constant and replacing \( \sigma_{j'j'} \) by an average band wave number \( \sigma_{\nu'\nu'} \) we get, when the lower level is a \( ^1\Sigma \) state:

\[
f_{j'j''} = 1.499 \cdot \frac{2J' + 1}{2J'' + 1} \cdot \frac{1}{\tau} \cdot \sum_{\nu'} \frac{q_{\nu'\nu}}{\sigma_{\nu'\nu}} \cdot \frac{\phi_{j'j''}}{\phi_{j'j''}}.
\]

(4-14)

The sum \( \sum_{j''} \phi_{j'j''} \) of one multiplet is in this case \( 2 \cdot (2J' + 1) \), as elucidated in section 4.4.

However, the relevant sum corresponding to the lifetime \( \tau \) is \( (2J' + 1) \), because the transition from one specific upper level with definite \( e/f \)-parity is either of type \( f \leftrightarrow e \), i.e., a \( Q \) line, or \( e \leftrightarrow e \), i.e., a \( P \) or \( R \) line (Table 4.1).

In our calculations concerning HfS and HfO, the required Franck-Condon factors \( q_{\nu'\nu} \) included in Eq. (4-14), are computed with the program TRAPRB, using vibrational energies derived from previously known molecular constants.
4.3 Lifetimes of HfS and HfO

As the lifetime measurements of hafnium sulfide and hafnium oxide are thoroughly described in Paper 2, I limit myself to a shortened account here. Most of the technical details are left out, but can be found in the paper.

The molecular states and transitions treated in the current work are specified in Fig. 4.2, showing schematic energy level diagrams of the electronic states of HfS and HfO. The experimental set-up and the cluster machine, used for the measurements, are described in Chapter 2. Molecules were prepared according to the process explained in section 2.1. After the supersonic expansion, the molecules reached the experimental reaction area, where the two laser pulses for excitation and ionization were applied. The ring dye laser, providing the excitation light after pulse-amplification, was kept at a fixed wavelength in resonance with an individual rotational line during the complete collection of data. Resonance was ensured by maximizing the signal at the time of coincidence with the ionizing pulse from an ArF excimer laser (6.4 eV photon energy). The line positions were known from previous experiments (reported in Paper 1).

The detection procedure was based on R2PI technique, described in section 2.2. When measuring lifetimes, the basic idea is to monitor the number of molecules still remaining in the excited state after a certain time. For that purpose, the ionization laser was fired after an adjustable delay time, which was changed in a randomized manner in order to avoid long term drifts. In this way, the ionizing photon was directly probing the population of the excited state as a function of time. In order to prevent the lines from splitting due to Stark effect and to obtain maximum intensity for a transition, the excitation and ionization took place in a field-free region. About 1 μs after the ionizing pulse, an extracting electric field was applied, accelerating the molecular ions into the flight tube and the detection system. A typical decay curve is shown in Fig. 4.3. From the parameters, obtained by fitting the data to an exponential function, the lifetime was available through the relation in Eq. (4-4).

The results of our measurements can be seen in Paper 2, Table 1, showing the obtained lifetimes as well as the final oscillator strength values. All lifetimes, belonging to the same molecule, are essentially the same, i.e., about 240 ns in the $D^1\Pi$ state of HfS and 650-700 ns in the HfO $b^3\Pi_1$ state. The corresponding f-values are almost constant, referred to $e$ and $f$ parity levels, respectively, within the same molecule and vibrational state. Thus we cannot establish any obvious perturbations exceeding the uncertainty of the model.
Stark Spectroscopy and Lifetime Measurements

Fig. 4.2  Schematic energy level diagrams of observed electronic states of HfS and HfO. The lifetimes determined in the current experiments refer to individual rotational levels of the $D^{1}\Pi$ state of HfS and the $b^{3}\Pi_1$ state of HfO.

Fig. 4.3  A typical decay curve of the first vibrational level of the $D^{1}\Pi$ state of HfS. Each dot in the graph represents the average of five laser-shots. Totally 1000 data-points are shown and the solid line is the result of a least squares fit to the data. The reported lifetime is the average obtained from ten similar recordings. The given error consists of two standard deviations of the average value. In this case excitation was obtained by the rotational line $R(3)$ in the (0, 0) transition from the ground state $X^{1}\Sigma$. Negative values of the randomly changed delay times correspond to the events when the ionization laser was fired before the excitation laser.
4.4 Hönl-London factors and lifetime calculations

The Hönl-London rotational line strength formulas are often presented in the literature, e.g., Herzberg [4], as relative intensity factors. Complete and accurate expressions of line strengths have been suggested by Whiting and Nicholls [38] and later the theory has been further reviewed by Tellinghuisen [39]. Nevertheless, expressions based on the relative relations but claiming to give absolute values are still occurring. One example is the commonly available computer program LEVEL 7.5, designed by Le Roy [34]. In order to calculate lifetimes associated with the experiments reported in Papers 4, 5, and 6, I used that code and discovered that the output gave erroneous results, e.g., for $\Pi \leftrightarrow \Sigma$ transitions. Therefore I would like to point out precautions essential when lifetimes are determined from calculations of decay rates.

The radiative lifetime $\tau_i$ of an excited electronic state $|i\rangle$ is calculated from the Einstein coefficients $A_{ik}$ of spontaneous emission and Eq. (4-5): $(\tau_i)^{-1} = \sum_k A_{ik}$, where the sum represents all possible transition paths to lower states $|k\rangle$. In the case of rotationally resolved spectra, a single Einstein A-coefficient describes the decay rate between two rovibronic levels $|i',v',J'\rangle$ and $|k,v'',J''\rangle$ and may be expressed as

$$A_{i',v',J';k,v'',J''} = C \cdot \frac{\varphi_{J',J''}}{g'(2J'+1)} \cdot v^3 \cdot \left|\mu_{vb}(r)\right|^2. \quad (4-15)$$

Here $v$ is the emission frequency and $\mu_{vb}(r)$ is the vibronic transition dipole moment function between the two levels; $\varphi_{J',J''}$ denotes the Hönl-London rotational intensity factor and $(2J'+1)$ represents the number of magnetic sublevels $M'$ of each rotational $J'$-level. The factor $g'$ accounts for the upper state electronic degeneracy and is given by $g' = (2 - \delta_{0,\Lambda}) \cdot (2S + 1)$, where $S$ is the spin [38,39]. Hence for singlet states ($S = 0$) we have $g' = 1$ for $\Lambda = 0$ and $g' = 2$ for $\Lambda \neq 0$ (the usual $\Lambda$-doubling). The numerical value of the constant factor $C$ depends on the units used. With frequency $v$ in cm$^{-1}$ and transition moment $\mu_{vb}(r)$ in D, $C = 3.13619 \cdot 10^{-7}$ (s$^{-1}$D$^{-2}$cm$^3$) ensures $A$ the unit s$^{-1}$.

Obviously the total radiative decay rate from the level $|i',v',J'\rangle$ to a specific lower state $|k\rangle$ is obtained as $A_{ik} = \sum_{v'} \sum_{J''} A_{i',v',J';k,v'',J''}$. When performing these summations, special attention must be paid to the explicit form of the $\varphi_{J',J''}$ Hönl-London factors. There is a

$$\mu_{vb}(r) = \mu_\lambda(r) \cdot \varphi_{J',J''} \quad \text{and} \quad \mu_{vb}^2 \cdot \varphi_{J',J''}/(2J'+1) = \mu_{ik}^2 \quad \text{defined in Eq. (4-9).}$$
convolution [38,39] that the sum of all intensity factors for a common value of \( J' \) or \( J'' \) is
\[
\sum \varphi_{J',J''}(J) = \left[ 2 - \delta_{\left( \Delta \Lambda + \Delta \gamma \right)} \right] (2S + 1) \cdot (2J + 1).
\]
(4-16)
The rule above implies for \( S = 0 \) that the line strengths are normalized to \( 2(J + 1) \) for \( \Sigma - \Sigma \) transitions and to \( 2(2J + 1) \) for all other singlet-singlet transitions.

The explicit expressions of individual Hönl-London factors, fulfilling the intensity factor sum rule Eq. (4-16), are given in Paper 3, Table 1. An inspection of the Hönl-London factors presented, e.g., by Bernath [40] shows expressions that agree for \( \Delta \Lambda = 0 \) but differ with a factor \( 2 \cdot (1 + \delta_{\left( \Delta \Lambda + \Delta \gamma \right)} \) for \( \Delta \Lambda = \pm 1 \). In order to fulfill the proper sum rule, the Bernath formulas should be four times bigger for \( \Pi \leftrightarrow \Sigma \) transitions and two times bigger for all other \( \Delta \Lambda = \pm 1 \) transitions. This also explains why the Le Roy program LEVEL 7.5 gives erroneous results in these cases.

Applying the rules outlined above we get the conditions for radiative decay from a common \( J' \)-level. For emission the Hönl-London factors expressed with the upper level quantum numbers are appropriate. Some basic and often occurring transitions are exemplified in Table 4.1, also illustrating the sum rule Eq. (4-16) and the summed ratio \( \varphi_{J',J''} / \left( g' (2J' + 1) \right) \), included in the Einstein coefficient \( A_{\nu',J',\nu,J} \) in Eq. (4-15).

Comments to Table 4.1:

- The \( ^1\Sigma \leftrightarrow ^1\Sigma \) case is straightforward. The LEVEL 7.5 gives correct output.
- For \( ^1\Sigma \leftrightarrow ^3\Pi \) there are single series of R, Q and P lines. Each upper level has only \( M' \)-degeneracy, \( g' = 1 \). The factor of 2 in the sum of \( \varphi_{J',J''} \) corresponds to the \( \Lambda \)-doubling components of the lower state. The A-coefficients from LEVEL 7.5 are one fourth of the correct values.
- In the \( ^1\Pi \leftrightarrow ^1\Sigma^+ \) transition there are again single series of R, Q and P lines. This case might need some extra attention since it can be treated in two different ways.
  a) The upper state is regarded as \( e- \) or \( f- \)parity, non-degenerate levels (apart from \( M' \)-degeneracy); \( g' = 1 \). Hence the A-coefficients for either Q lines solely or the sum of R and P lines are added separately, thus contributing to the total decay rate corresponding to the lifetime of the \( \Pi f \)-parity or \( \Pi e \)-parity levels, respectively. The individual A-coefficients in LEVEL 7.5 are one fourth of the correct values; consequently the sum of \( f - e \) Q lines or \( e - e \) R, P lines must be multiplied by 4.
  b) In practice, however, a frequent situation is that the \( \Lambda \)-doubling components are not resolved and an average lifetime of the upper level is calculated. Then the natural
procedure in the $\Pi \rightarrow \Sigma$ case is to sum the R, Q and P lines, just observing that with this approach the factor $g' = 2$, accounting for the electronic degeneracy. The individual A-coefficients in LEVEL 7.5 are still one fourth of the correct values, but the sum over relevant $\nu''$ must be multiplied by 2 in case b).

- Finally, for any transition between states with $\Lambda \neq 0$, e.g., $^1\Pi \rightarrow ^1\Pi$, $^1\Delta \leftrightarrow ^1\Pi$, each branch contains R, Q and P lines and is doubled. Summing over the lines with the upper level (e) gives $(2J'+1)$ and the same for the (f) upper component.

For $\Delta \Lambda = 0$, LEVEL 7.5 gives correct decay rates.

For $\Delta \Lambda = \pm 1$, the individual A-coefficients in LEVEL 7.5 are one half of the correct values, if upper level (e) and upper level (f) are treated separately. The output sum of R, Q and P lines over relevant $\nu''$, multiplied by 2, gives the lifetime of e-parity or f-parity upper level, (or an average lifetime of a doubly degenerate upper level).

| Table 4.1 |
| Hönig-London factors $\varphi_{J,J'}$ for some fundamental emission transitions between singlet states. |

| Transition | R line $\varphi_{J',J''}$ | Q line $\varphi_{J',J''}$ | P line $\varphi_{J',J''}$ | Summation over allowed $J''$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma \rightarrow ^1\Sigma$ $\Delta \Lambda = 0$</td>
<td>$J'$</td>
<td>$J'+1$</td>
<td>$2J'+1$</td>
<td>1</td>
</tr>
<tr>
<td>$^1\Sigma \rightarrow ^1\Pi$ $\Delta \Lambda = -1$</td>
<td>$J'-1$</td>
<td>$2J'+1$</td>
<td>$J'+2$</td>
<td>2</td>
</tr>
<tr>
<td>$^1\Pi \rightarrow ^1\Sigma$ $\Delta \Lambda = +1$</td>
<td>$J'+1$</td>
<td>$J'$</td>
<td>$e$</td>
<td>1</td>
</tr>
<tr>
<td>$^1\Pi \rightarrow ^1\Pi$ $\Delta \Lambda = 0$ (double branches)</td>
<td>$(J'+1)(J'-1)$</td>
<td>$(J'+2)(J'+1)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1\Pi \rightarrow ^1\Delta$ $\Delta \Lambda = -1$ (double branches)</td>
<td>$(J'-2)(J'-1)$</td>
<td>$2J'+1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1\Delta \rightarrow ^1\Pi$ $\Delta \Lambda = +1$ (double branches)</td>
<td>$(J'+2)(J'+1)$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.5 Just a moment, please

So far in this thesis we have met the concept of ‘moment’ in some variant situations. Chapter 3 has Dipole moments in its title and section 3.1 presents the permanent electric dipole moment $\mu$. In Chapter 4 the transition dipole moment occurs in different shapes, $\mu_{ik}$ or $\mu_{vib}$, and will be frequently reappearing in Chapters 5 and 6. It might be worthy to spend a moment considering the meaning of ‘moment’ in different contexts.

We know from 3.1 that molecules may have a permanent electric dipole moment. That moment is an inherent molecular property, arising from non-uniform distributions of positive and negative charges, mainly owing to differences in electro-negativity of the various atoms within the molecule. The different components accounted for in Eq. (3-1) are all contributions to a permanent electric dipole moment. As is evident from the name, this moment is present even in field-free surroundings, but polar molecules may have their existing dipole moment modified by an external applied electric field. In section 3.2 is explained how the Stark effect is used to measure the permanent dipole moment of molecules, for which a rotational spectrum can be observed.

All hetero-nuclear diatomic molecules are permanent electric dipoles, whereas homo-nuclear diatomics possess no permanent electric dipole moment, neither do atoms. Nevertheless, atoms as well as molecular dimers exhibit spectroscopic dipole transitions. The underlying idea is that for a molecule or atom to interact with an electromagnetic wave and absorb or create a photon, it must possess, at least transiently, an oscillating dipole. Classically an atom or a molecule can be regarded as an assembly of moving charges $[41]$, having at any instant an electric dipole moment (permanent or transient),

$$M = \sum_j e_j r_j,$$

(4-16)

where $e_j$ are the point charges at location $r_j$. For electric dipole transitions the instant moment $M$ is used as an operator to express quantum-mechanically the (total) dipole moment corresponding to a transition between two states $|i\rangle$ and $|k\rangle$, defined as the expectation value of $M$ between the wave functions $\psi_i$ and $\psi_k$:

$$\mu_{ik} = \int \psi_i^* M \psi_k d\tau = \langle i|M|k\rangle.$$

(4-17)

The quantity $\mu_{ik}$, previously defined in Eq. (4-9), is called the matrix element of the electric dipole moment or shorter the transition dipole moment or just transition moment. As we have seen (section 4.2), the intensity of a transition is proportional to the squared transition moment, $\mu_{ik}^2$, included in the line strength expression as well as in the Einstein A- and B-coefficients. Later on (in Chapters 5, 6) we will see how the absolute value of
the transition dipole moment is experimentally determined using the AC Stark effect.

The dipole moment matrix element $\langle i | M | k \rangle$ determines whether a transition can occur. If this factor is zero, as it is in most cases, the transition is said to be (dipole-) forbidden, and on the contrary, when $\mu_{ik}$ differs from zero, the transition is allowed. In general the absorption or emission of radiation can only occur between certain pairs of states $|i\rangle$ and $|k\rangle$ in a system. The restrictions, defining which energy levels can combine with each other in a dipole transition, provide the usual selection rules that govern the appearance of spectral lines.

Let us apply a simplified picture and limit the discussion to diatomic molecules. If we assume that the states $|i\rangle$ and $|k\rangle$ are characterized by the quantum numbers $\Lambda$, $v$ and $J$ (as usually denoting kind of electronic state, vibration and rotation, respectively), the dipole moment matrix element can be written as

$$\mu_{ik} = \langle \Lambda', v', J' | M | \Lambda'', v'', J'' \rangle. \quad (4-18)$$

We first consider a dipole transition between two separate electronic states. Since this process involves an electron changing orbital, there exists a dipole moment $M$ in all kinds of molecules. It can be shown [e.g., 4,41] that the matrix element $\mu_{ik}$ vanishes unless $\Delta \Lambda = 0, \pm 1$. Besides this well-known selection rule, there are additional restrictions concerning rotation, spin, magnetic sublevels and various parity rules. We can also state that the transition moment $\mu_{ik}$ is proportional to the product of the electronic transition dipole moment $\mu_e$ and the vibrational overlap integral $\langle v'|v'' \rangle$. In Eq. (4-15) this product is called the vibronic transition moment and denoted $\mu_{ vib}(r)$, also indicating that $\mu_e$ in a diatomic molecule is a function of the internuclear distance, $r$.

If $\Lambda'$ and $\Lambda''$ refer to the same electronic state, we may have a vibration-rotation transition, corresponding to the matrix element $\mu_{ik} = \langle v', J' | M | v'', J'' \rangle$. If $v'$ and $v''$ refer to the same vibrational level, the possibility of a pure rotational transition remains. Since none of these transitions includes any electron jump, the gross selection rule for $\mu_{ik}$ to have a non-zero value is that $M$ signifies a permanent dipole moment. The specific selection rules are $\Delta J = 0, \pm 1$ or in the case of pure rotational transitions $\Delta J = \pm 1$.

The conclusion is that hetero-nuclear diatomic molecules exhibit all three kinds of dipole transitions, obeying certain selection rules. Homo-nuclear diatomic molecules, on the other hand, are restricted to electronic dipole transitions and do not have electric dipole-allowed pure rotational or vibrational spectra.
Coherence Phenomena in Molecular Systems

The second part of my thesis is based on the research carried out at Temple University in Philadelphia, where the Lyyra group is involved in laser based fundamental photo-physics and photo-chemistry studies. Topics of vital interest include all-optical multiple resonance spectroscopy and alignment of molecules as well as development of new laser techniques in high-resolution spectroscopy. Experimental and theoretical investigations are done on molecular systems, mainly three- or four-level systems of alkali metal dimers in gas-phase. Frequency stabilized, single-mode, and narrow-band continuous-wave (cw) lasers are used for excitation, allowing a high degree of state selectivity and population transfer control. Coherence related phenomena such as electromagnetically induced transparency, dark fluorescence, and Autler-Townes splitting are experimentally observed.

Three works from this field of physics are reported in Papers 4, 5, and 6. The underlying elementary theoretical and experimental bases are presented in Chapter 5. Chapter 6 treats the three-laser experiment making the subject of Paper 4. Finally, in Chapter 7, I briefly touch on interesting, unexpected results presented in Papers 5 and 6.

5 Fundamental concepts

The principles of atomic coherence and quantum interference are instrumental in giving rise to a number of observations in this branch of science [42]. The phrases are frequently used and widely spread over the whole area of quantum optics, in textbooks as well as scientific journals. However, to find concise and easily comprehensible definitions of these concepts is not trivial. Said with Richard Feynman:

“Quantum interference is a phenomenon, which is impossible, absolutely impossible, to explain in any classical way, and which has in it the heart of quantum mechanics.”

The quantum nature of photons is essential in this context as well as the wave-particle duality of quantum micro-objects. Young’s double slit experiment is a fruitful model of reasoning. Quantum interference between different atomic states within the same atom is the origin to atomic coherence effects. Coherence is induced by an intense and coherent electromagnetic field, resonantly exciting a particular atomic transition. The system is forced into a phase coherent superposition of different states and exhibit constructive or destructive interference. An ensemble of phase coherent atoms may be viewed as a strong atomic local oscillator [43]. The new state of matter has been dubbed "phaseonium" [9].

Some of the most fundamental concepts, general ideas and common features on the quantum optics arena are introduced in sections 5.1 – 5.7.
5.1 The driven three-level system

The experiments in this branch of spectroscopy are based on a technique where two lasers, L1 and L2, are simultaneously interacting with a molecule via two transitions, sharing a common level. There are basically three possible level schemes: the $\Lambda$-type, the $V$-type, and the cascade- or ladder-type, as illustrated in Fig. 5.1. Usually the strong coupling laser L2 is held on resonance while the weak probe laser L1 is tuned across the resonance of the other transition.

Let us focus on the cascade three-level system, shown in Fig. 5.2. The three levels of interest have energies $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$. The probe field L1, with frequency $\omega_1$, connects levels $|1\rangle$ and $|2\rangle$, and the coupling field L2, with frequency $\omega_2$, couples levels $|2\rangle$ and $|3\rangle$.

We assume that each laser field interacts only with the corresponding two levels, and that the levels, coupled by the fields, have dipole allowed transitions. Another assumption is that all the molecules are initially in the lowest energy state $|1\rangle$, in most cases the ground state. From this follows the important conclusion that the coupling laser L2 has no effect on the dynamics of the system in the absence of L1 (assumed there is no other excitation mechanism). The resonance or Bohr transition frequency between two states is defined in the general way as $\Delta \varepsilon / \eta$, as noted in Fig. 5.2. For simplicity we usually take $\varepsilon_1 = 0$ and measure all the energies relative to level $|1\rangle$, then $\varepsilon_2 = \eta \omega_{21}$ and $\varepsilon_3 = \eta (\omega_{21} + \omega_{32})$. The detuning of each laser is defined as $\Delta_j = \omega_j - \omega_{ij}$ (or sometimes with the opposite sign).

An application of the model system described above is demonstrated with molecular lithium, $^7$Li$_2$ [44], where the energy term values for several states are well known. The experimental set-up is depicted in next section (5.2). The cascade three-level scheme, relevant for the investigation of the lithium dimer, is shown in Fig. 5.3 a), whereas Fig. 5.3 b) illustrates the same course of events by means of Li$_2$ potential energy curves. The process described here is a typical example of optical-optical double-resonance (OODR), a technique widely used in laser spectroscopy [1]. Molecules from a selected rovibrational level of the ground state $|1\rangle$, $X^1\Sigma_g^+ (v = 4, J = 15)$, are excited by the weak probe laser L1 to a specific vibration-rotation level of an intermediate state, $A^1\Sigma_u^+ (v = 13, J = 14)$. This level $|2\rangle$ is resonantly coupled by the coupling laser L2 to a selected higher excited electronic state level $|3\rangle$, $G^4\Pi_g (v = 11, J = 14)$.
Fig. 5.1 Possible configurations for a three-level system interacting simultaneously with two lasers. L2 is a strong coupling laser, usually on resonance. L1 is a weak, tunable probe laser.

Fig. 5.2 The cascade three-level system. A probe laser L1 with frequency $\omega_1$ excites molecules from the ground state $|1\rangle$ to the intermediate state $|2\rangle$. L2 is a strong coupling laser field with frequency $\omega_2$, coupling levels $|2\rangle$ and $|3\rangle$. The detunings are $\Delta_1 = \omega_1 - \omega_{21}$ and $\Delta_2 = \omega_2 - \omega_{32}$, respectively. Usually L2 is held fix at resonance while L1 is tuned across the first transition.
An important supposition is that laser induced fluorescence with high sensitivity reflects the population of the corresponding excited state [45]. Thus the populations of the excited levels in Li₂ are monitored by observing the fluorescence signals from levels |3⟩ and |2⟩ to some suitably chosen lower levels, for example the states \( A^1 \Sigma_u^+ (v = 12, J = 14) \) and \( X^3 \Sigma_u^+ (v = 4, J = 13) \), respectively. Single channel detection is obtained by using a mono-chromator as a narrow-band filter. By setting the mono-chromator window to the spontaneous emission wave length, a single fluorescence transition is selected.
The probe laser, L1 (~15643 cm\(^{-1}\)), is used to excite molecules from the ground state level \(X^1\Sigma_g^+(v=4, J=15)\) to an excited intermediate state level \(A^1\Sigma_u^+(v=13, J=14)\). The coupling laser, L2 (~17054 cm\(^{-1}\)), resonantly couples the intermediate level to a higher electronic state level \(G^1\Pi_g(v=11, J=14, f\)-parity). The populations of the excited states \(G^1\Pi_g\) and \(A^1\Sigma_u^+\) are monitored by detecting their fluorescence using a mono-chromator. A single fluorescence channel is selected in each case by setting the mono-chromator to the corresponding spontaneous emission wavelength.
5.2 Experimental set-up

Most of the experiments, designed for investigations of the related kind of coherence effects in molecular systems, have similar layout and equipment. The experimental set-up used for molecular lithium [44], schematically illustrated in Fig. 5.4 [46], serves as a representative example of the main principle features.

The heart of the experimental set-up is the heat pipe, a five-arm cross stainless steel oven, electrically heated to temperatures 300 – 1000 °C. The alkali metal of interest is vaporized in the centre of the heatpipe, which is filled with argon of variable pressure (100 – 1000 mTorr), acting as a buffer gas to prevent the hot metal condensing on the windows, located at the end of each arm.

Two single-mode, tuneable, and narrow-band ring dye cw lasers, each one pumped with an argon ion laser and equipped with auto-scan system, provide the probe and the coupling laser fields. In the Li₂ experiment the dyes used are DCM and Rhodamine 6G, suitable for the probe and coupling transition energies of ~15640 cm⁻¹ and ~17050 cm⁻¹, respectively. The two laser beams are counter-propagating, coaxially aligned, and linearly polarized in a common direction. A decisive condition is to find good spatial overlap of the two laser beams in the detection region at the centre of the heatpipe, and also the relative beam spot sizes are important parameters. Focusing of the coupling laser beam in order to increase its corresponding Rabi frequency must be balanced against reduced uniformity of the electric field. The probe laser beam waist should be smaller than that of the coupling laser to avoid non-uniform effects of the coupling field, but still not too small at the risk of getting transit out of interaction region too significant.

The typical experimental procedure is that the probe laser is scanned across the first transition of the excitation scheme in Fig. 5.3, while the coupling laser is held fixed on the second transition resonance frequency. During a scan, when usually the probe laser light is modulated by a chopper, the fluorescence light from the side window of the heat-pipe oven is guided into a grating spectrometer, used as a mono-chromator and equipped with a photo multiplier tube (PMT). A single fluorescence channel, as shown in the Fig. 5.3 detection scheme, is selected by setting the mono-chromator to the corresponding emission wavelength. The signal is registered by the PMT and sent to a lock-in amplifier, used for phase-sensitive detection and trigged by the chopper. The output signal is monitored on a computer, where simultaneously the frequency scan of the probe laser is recorded. A neutral density filter is often included to adjust the laser beam intensity entering the heatpipe. An iodine cell is used for calibration of the dye laser frequencies.
Fig. 5.4 Experimental set-up: Counter-propagating laser beams in gas phase molecular lithium.

M: mirror, B: beam splitter, L: lens, CP: chopper, ND: neutral density filter
PMT: photo multiplier tube;
Spex 1404: a grating spectrometer used as a mono-chromator, acting as a narrow-band filter to isolate the desired fluorescence channel from other emitted light.

Vaporized Li\textsubscript{2} Argon buffer gas
T \approx 1000 K
p = 100-300 mTorr
5.3 Observed spectra

Let us return to the excitation scheme in Fig. 5.3 and examine which experimental results we can observe in this three-level system of molecular lithium, Li₂, exposed to two counter-propagating laser beams.

We start with no coupling field present at all. The probe laser L1 is scanned across the first transition from the ground state to the intermediate A-state, while the selected fluorescence signal from the \( A^1 \Sigma_u^+ (13,14) \) level is monitored. The result is a Doppler broadened fluorescence spectrum, Fig. 5.5 a). The coupling laser L2 is now added, but with very low power, and set at the resonance frequency for the selected \( A - G \) transition. The probe laser is scanned again in the same way and simultaneously the fluorescence from the upper state level \( G^1 \Pi_g (11,14) \) (f-parity) to the chosen auxiliary level \( A^1 \Sigma_u^+ (12,14) \) is measured. This scan yields the characteristic OODR (optical-optical double-resonance) spectrum for the upper level, Fig. 5.5 b). Notice, that the horizontal axis represents the detuning \( \Delta_i \) of the probe laser, i.e., \( \Delta_i = 0 \) implies that both lasers are on resonance.

So far, there is nothing remarkable at all. The consequence of the Doppler effect in this particular situation is briefly illustrated and described in Fig. 5.6.

The coupling laser intensity is now significantly increased; the coupling frequency is set at resonance while the probe laser is scanned as before. In the Doppler broadened fluorescence spectrum from the intermediate state, now a dip appears at the centre, where the detuning \( \Delta_i = 0 \), Fig. 5.5 c). The dip becomes deeper and wider when the coupling laser is stronger. With the presumption that the fluorescence intensity is proportional to the population of the corresponding emitting level [45], the emerging dip indicates that the population of the \( A^1 \Sigma_u^+ \) state is greatly reduced, when the probe laser is close to resonance. A tempting guess might be, that with both lasers on resonance, the molecules are further excited to the upper level - but no! The narrow OODR fluorescence peak from the upper \( G^1 \Pi_g \) state undergoes a dramatic change during enhancement of the coupling laser power. The line shape first broadens and then splits into two symmetric components, separated by a deep dip, Fig. 5.5 d).

Obviously, under the simultaneous action of probe and coupling lasers, the majority of molecules are excited neither to the intermediate A-state nor to the upper G-state but are trapped in the ground state. The dips demonstrate dark fluorescence and indicate population trapping. Under influence of the strong coupling laser, the molecules are made
Coherence Phenomena in Molecular Systems

Experimentally observed fluorescence spectra [46]  
Theoretically calculated populations [46]

a) Intermediate state. No coupling field.  

b) Upper state. Weak coupling field.

Δ₁ is the detuning of the probe laser

Fluorescence / ρ₂₂ (Arbit. units)

Δ₁ (MHz)

Fluorescence / ρ₃₃ (Arbit. units)

Δ₁ (MHz)

Δ₁ is the detuning of the probe laser

c) Intermediate state. Strong coupling field.

d) Upper state. Strong coupling field.

Fig. 5.5 I. Experimentally observed fluorescence spectra (solid curves) in the Li₂ three-level cascade system.

a) No coupling laser field present. Scanning the probe laser and simultaneously monitoring the fluorescence from the intermediate A ¹Σ_u⁺ state results in this Doppler broadened spectrum.

b) The coupling laser is present with low intensity (~ 5 W/cm²) and on resonance. This OODR signal is obtained by monitoring a selected fluorescence channel from the G ¹Π₉ state while scanning the probe laser.

c) Fluorescence from the A ¹Σ_u⁺ state in the presence of a strong coupling laser field (~ 130 W/cm²). A large dip emerges in the Doppler profile. The dip is a signature of EIT (electromagnetically induced transparency) by showing dark fluorescence.

d) With increasing coupling laser intensity the OODR spectrum is broadened and a dip appears. The line profile splits into two symmetric peaks, designated Autler-Townes (AT) splitting and caused by AC Stark effect. The dip announces dark fluorescence also from the upper state.

II. Theoretically calculated populations (dotted curves) fitted to experimentally observed spectra.

Simulated populations c) ρ₂₂ of the intermediate level and d) ρ₃₃ of the upper level, in the presence of a strong, resonant coupling laser.

When all parameters are kept fixed while the coupling laser field strength is decreased, the simulated population ρ₂₂ transforms to the Doppler broadened profile a) and the population ρ₃₃ displays the single OODR peak b).
transparent to the resonant probe laser light, which is considerably less absorbed, and we observe electromagnetically induced transparency, EIT. The split signal from the upper excited level is designated Autler-Townes (AT) splitting and originates from the AC Stark effect. The origin and properties of these phenomena are topics further discussed in subsequent sections.

Fig. 5.6 The Doppler effect in a molecular system exposed to two counter-propagating laser beams: the probe laser, L1, and the coupling laser, L2.

A molecule with velocity component \( v \), parallel or anti-parallel with the laser beams, will “see” the probe laser and coupling laser frequencies \( \omega_1 \) and \( \omega_2 \), respectively, as

\[
\omega_1'(v) = \omega_1 - \frac{v}{c} \omega_1 \quad \text{and} \quad \omega_2'(v) = \omega_2 + \frac{v}{c} \omega_2
\]

A molecule is excited if \( \omega_1'(v) = \omega_{21} \) or \( \omega_2'(v) = \omega_{32} \)

where \( \omega_{21} \) and \( \omega_{32} \) are the resonance frequencies for transitions 1 and 2, respectively.

Usually the probe laser is scanned so the detuning \( \Delta_1 = \omega_1 - \omega_{21} \neq 0 \) (or = 0).

Thus the condition for excitation by the probe laser can be expressed as

\[
\omega_1 - \omega_{21} = \frac{v}{c} \omega_1 = \Delta_1 \neq 0 \text{ (or = 0)}
\]

⇒ different velocity groups of molecules are excited at different laser frequencies \( \omega_1 \)

⇒ a Doppler broadened excitation spectrum.

If the coupling laser is held at resonance, it means that \( \Delta_2 = \omega_2 - \omega_{32} = 0 \).

Thus the condition for excitation by the coupling laser can be expressed as

\[
\omega_2 - \omega_{32} = -\frac{v}{c} \omega_2 = \Delta_2 = 0
\]

⇒ only molecules with velocity \( v \approx 0 \) are excited

⇒ a narrow excitation peak.
5.4 Theoretical modeling and simulations

The density matrix formalism is a natural and widely used method to describe the atomic or molecular matter investigated by laser spectroscopy [45]. Since a detailed derivation of the complete density matrix is demonstrated in the Na$_2$ four-level system, reported in Chapter 6, only some broad and general features are given here.

The simplest example of a density matrix is a $2 \times 2$ matrix representing two atomic levels $|a\rangle$ and $|b\rangle$, excited from the same lower level $|I\rangle$. The complex density matrix $\rho$, is defined by the product of the two state vectors and is often expressed as

$$
\rho = \begin{pmatrix}
\rho_{aa} & \rho_{ab} \\
\rho_{ba} & \rho_{bb}
\end{pmatrix}
$$

(5-1)

The diagonal elements $\rho_{aa}$ and $\rho_{bb}$ represent the probabilities of finding the atoms in the levels $|a\rangle$ and $|b\rangle$, respectively. If the system is incoherently excited, i.e., no definite phase relations exist between the wave functions of different atoms, the nondiagonal elements are zero. On the other hand, if the levels are coherently excited, the matrix elements $\rho_{ab}$ and $\rho_{ba}$ describe the degree of coherence of the system and are therefore often called “coherences”. $\rho$ as well as its time derivative are expected to be Hermitian matrices.

The theoretical treatment based on the density matrix approach involves solution of the density matrix equations of motion. The homogeneous part of these equations can be expressed in a compact vector form as

$$
\frac{d\rho}{dt} = L \times \rho.
$$

(5-2)

In the present three-level cascade system, the relation above covers a system of nine differential equations, where $\rho$ in this application denotes a column vector containing the density matrix elements $\rho_{11}, \rho_{12}, \rho_{13}, \rho_{21}, \ldots, \rho_{33}$. As in the introductory example, the $\rho_{ii}$ elements represent the population density of level $|i\rangle$, whereas the coherences $\rho_{ij}, i \neq j$, are responsible for the physical interaction processes going on between levels $|i\rangle$ and $|j\rangle$. The $9 \times 9$ $L$-matrix contains all the relevant parameters characterizing the laser – molecule system, namely Rabi frequencies, wave vectors, detunings, dephasing rates and terms accounting for different relaxation processes.

In laser spectroscopy most experiments contain a time dependency, but often we are not concerned about the explicit time depending solution of Eq. (5-2). The observable properties measured in spectroscopy are considered to be ensemble-averaged properties of the system [45], which motivates the equations of motion (5-2) to be solved for steady
Coherence Phenomena in Molecular Systems

state conditions \((t \to \infty)\). In practice, the matrix element calculation method, based on matrix inversion and multiplication, is performed with the help of a computer, delivering exact numerical results of the populations \(\rho_{ii}\) and the coherences \(\rho_{ij}\). However, for many systems it is also possible to derive an approximate analytical solution using perturbation theory \([45]\), provided steady state and treating a weak probe field perturbatively and a strong coupling field exactly.

Both calculation methods, the matrix and the analytical, are used for theoretical modeling of the cascade three-level system by means of simulations, based on arbitrary values of the parameters. The simulations are carried out employing Fortran programs constructed by Kirova and Spano \([47]\). Besides feeding the program with factual conditions like wave numbers, spot sizes and lifetimes, other parameters are varied until the best fit to an experimental spectrum is obtained. When the theoretical calculations are in good agreement with the experimental results, it is an indication that a reliable model is found.

The Fig. 5.5 graphs illustrate the connection between experiment and theory for our \(\text{Li}_2\) three-level system. The populations \(\rho_{22}\) and \(\rho_{33}\) of the intermediate \(A^1\Sigma_u^+\) state and the upper \(G^1\Pi_g\) state levels, respectively, are calculated and fitted to the corresponding fluorescence spectra, by virtue of the presumption that the fluorescence from a level is proportional to the population of that level. In Fig. 5.5 c) and d) we see that the model is able to reproduce very well the experimental spectra recorded in the presence of a strong coupling laser field. The model is further controlled by keeping all parameters fixed but just decreasing the strength of the coupling laser in order to verify that the theoretical population curves are applicable also under weak coupling laser field conditions. As can be seen in Fig. 5.5 b) and a) the upper level population \(\rho_{33}\) transforms to the single OODR peak and the corresponding \(\rho_{22}\) recovers back to the Doppler broadened profile, observed in the experimental fluorescence spectra.

Since the derived model seems to be reliable, it can be used for computation of properties, which are not experimentally observable. For example, the population of the ground state, \(\rho_{11}\), is simulated in Fig. 5.7 a) \([46]\), clearly showing how the molecules are trapped in the ground state when a strong laser couples the upper transition and the probe laser is tuned to resonance. The imaginary part of the density matrix element \(\rho_{12}\) represents the absorption of the probe laser, Fig. 5.7 b) \([46]\), illustrating EIT, i.e., how the medium is made transparent when both lasers are on resonance. The resemblance with the population and fluorescence spectrum of the intermediate level, Fig. 5.5 c) is apparent.
Fig. 5.7  Theoretically calculated ground state population and absorption profiles versus probe laser detuning $\Delta_1$ while a strong coupling field resonantly couples the upper transition. 

a) The simulated population $\rho_{11}$ of the ground state level. The molecules populate the ground state when the probe laser frequency is far from resonance. When $|\Delta_1|$ approaches zero, the molecules are transferred to the excited state, but suddenly they get trapped in the ground state when $\Delta_1 = 0$, i.e., when both lasers are on resonance.

b) The simulated absorption $\text{Im} \rho_{12}$ of the probe laser under the same conditions. Both lasers on resonance induces a dramatic reduction of the absorption. The medium is made transparent due to EIT.
5.5 Quantum interference and level splitting

To really understand the interaction between light and matter is a central subject in this lively, rapidly evolving and challenging field of bridging quantum optics and molecular spectroscopy. In order to get some qualitative but fundamental insight into quantum interference, we can start by considering the simple example of atomic hydrogen.

Instead of using two lasers as in the previously related experiments, transparency is established in hydrogen atoms using a probe laser and an electric DC field [48]. Fig. 5.8 shows the lowest atomic states of hydrogen with and without the DC field. In the unaffected hydrogen atom the $|2s\rangle$ and $|2p\rangle$ states are degenerate and assigned the energy $\eta \omega_p$ relative to the ground state $|1s\rangle$. The effect of an applied electric DC field is to mix and split the two excited states, creating two new levels expressed as linear combinations of the original states and corresponding to different energies. Suppose now, that the hydrogen atoms are exposed to a probe laser with frequency $\omega_p$. At zero electric field the laser photons may be absorbed in a $|1s\rangle \rightarrow |2s\rangle$ transition. In the presence of a DC field, on the other hand, a probe beam sees zero absorption at the line centre, since the applied frequency is above one resonance and below the other. The electric field is said to create (destructive) quantum interference at the probe frequency, implying there is no electron motion and no time-varying transition dipole moment.

With this technique the effect of a medium on a propagating beam is eliminated; opaque resonant transitions are made transparent to laser radiation, often with most of the atoms remaining in the ground state. That is the essence of EIT.

Similar modifications of atomic properties as those due to an electric DC field, may be effected by a coherently oscillating electromagnetic field. Fig. 5.9 shows a typical situation, where two lasers are applied to a three-level system. The influence of the laser photons on the molecular energy levels includes a splitting of each of the two states, resonantly coupled by the strong laser. The notation used in the figure, where $n$ denotes the number of photons in the resonant coupling laser, is one way to express the matter-field interaction and illustrates the concept of dressed states. Investigation of the states $|2\rangle$ and $|3\rangle$ as a function of the probe laser detuning reveals that each state contributes a split line shape to the fluorescent emission spectra, as displayed in Fig. 5.5 c) and d).

Sufficiently strong coupling laser fields are able to resolve the magnetic sublevels within the highest excited state [17,49], thus separating levels $|J, M_J\rangle$ or $|J, M_J\rangle$ corresponding to linearly or circularly polarized coupling laser light, respectively.
Coherence Phenomena in Molecular Systems

Fig. 5.8 Quantum interference in atomic hydrogen, giving rise to transparency [48]. The energy level diagrams show the essential states of hydrogen atoms, without and with an electric DC field, corresponding to bare and mixed states, respectively, since the field causes mixing and splitting of the otherwise degenerate states $|2s\rangle$ and $|2p\rangle$. A probe laser beam with frequency $\omega_p$, resonant with the transition $|1s\rangle \rightarrow |2s\rangle$, is absorbed in the field-free case, but is unaffected at the line center in the presence of a DC field. If the probe laser is tunable, two absorption peaks appear at equal detunings from the original resonance frequency $\omega_p$.

Fig. 5.9 Energy level splitting caused by an oscillating electromagnetic field, in this case the light field itself of a strong laser, resonantly coupling two molecular states. The interaction between photons in the field and molecules, populating the original energy levels $|2\rangle$ and $|3\rangle$, each one including degenerate sublevels, results primarily in a doubling of each level. Higher resolution might expose the internal structure of magnetic sublevels.
5.6 AC Stark effect and Autler-Townes splitting

Analogous to the Stark effect caused by a static electric DC field, as described in section 3.2, there exists a similar phenomenon called dynamic or AC Stark effect, manifesting itself as Autler-Townes (AT) splitting. As proposed in the previous section, in this case an oscillating electromagnetic field causes a splitting of energy levels, accounted for as a coherence effect including quantum interference.

When exploring the population of the upper level $|3\rangle$ in Fig. 5.9 by monitoring the fluorescent emission, the spectrum in Fig. 5.10 may be recorded, showing the AT split line shape as an evidence of AC Stark shift. The separation $\Delta_{pp}$ of the obtained doublet is proportional to the Rabi frequency, $\Omega_{cp}$, of the resonant coupling field. The magnitude of $\Omega_{cp}$ is determined (Eq. 5-13) by the transition dipole moment $\mu_{ik}$ between the coupled levels and the electric field strength, $E_{cp}$, which in turn depends on the laser power and the beam spot size (Eqs. 5-7, 8, 9). In a similar way as in Eq. (4-12) the transition moment $\mu_{ik}$ can be separated into three parts, representing electronic, vibrational and rotational contributions. It is possible to derive a $J$- and $M$-dependent expression for the AT splitting and the Rabi frequency corresponding to each single magnetic sublevel component [17]:

$$\Delta_{pp}^M \propto \Omega_{cp}^M = \mu_e \cdot (q_{v'v} \cdot f(J,M) \cdot E_{cp}^M |\eta)$$

(5-3)

where $\mu_e$ is the electronic transition dipole moment, $q_{v'v}$ is the Franck-Condon factor and $f(J,M)$ is the orientation factor or the direction cosine matrix element [50].

The relation (5-3) involves a couple of interesting possibilities. One example is demonstrated in Fig. 5.11. From the dependence of the overall AT splitting $\Delta_{pp}$ on the laser field strength, the electronic transition dipole moment for the Li$_2$ $G^1\Pi_g - A^1\Sigma_u^+$ transition is extracted ($\mu_e \approx 2.4$ a.u.) [44], in very good agreement with ab initio calculations of this transition dipole moment matrix element (2.44 a.u.) [51].

Furthermore, according to the $M$-dependence in Eq. (5-3), it should be possible to resolve the individual magnetic sublevels, at least for small $J$-values, as shown in Fig. 5.12 [17]. This condition enables quantum state selectivity and provides an effective tool to attain and control molecular alignment, which is one of the most important goals in chemical reaction dynamics. Compared to DC Stark spectroscopy, which demand that the investigated molecules have a permanent electric dipole moment, the all-optical technique, outlined here, has the advantage of allowing alignment and orientation of the angular momentum also for non-polar molecules.
Fig. 5.10  Spectrum from molecular lithium, Li$_2$, showing the AC Stark effect due to a resonant coupling field [46]. The AT peak-to-peak splitting $\Delta_{pp}$ is proportional to the Rabi frequency $\Omega_{cp}$ of the coupling laser. $\Omega_{cp}$ in turn, is proportional to the electric field strength of the resonant coupling laser, $E_{cp}$, which depends on the laser power and the beam size.

Fig. 5.11  Dependence of the observed and calculated AT splitting $\Delta_{pp}$ in Li$_2$ on the coupling field strength [44].

The splitting of the upper level fluorescence spectrum is measured for various coupling field powers. The results are compared to theoretical calculations where the coupling Rabi frequency is varied until the simulated peak-to-peak separation matches experimental data. From the best agreement between experiment and theory, the electronic transition dipole moment $\mu_1$ is determined.

Fig. 5.12  Partly resolved AT spectrum of a Li$_2$ rovibronic state (recorded using single channel fluorescence detection) [77]. A level with $J=3$ is split, and the twin peaks are labeled according to the possible values of $|M|$. Tuning the probe laser to the $|M|$th magnetic sublevel component in the presence of a strong resonant coupling field, prepares aligned excited molecules, which are predominantly in the quantum states $\pm M$. The method can be used to align polar as well as non-polar molecules.
5.7 Collected basic relations

This section is a summary of fundamental definitions, formulas and equations providing the basis for laser – molecule interaction in the quantum optics approach.

The general expression for the electric field of a plane light wave with frequency $\omega$ and wave number $k$ travelling in vacuum in the z-direction is

$$ E = E_0 \cdot \cos(\omega t - kz) \tag{5-4} $$

Thus the magnitude of the field strength (at the beam axis) of a laser with frequency $\omega$ can be expressed as (setting $z = 0$ since $\lambda >>$ molecular dimensions)

$$ E(t) = E_0 \cos(\omega t) \tag{5-5} $$

For a laser beam with a Gaussian profile, the beam waist or radius $w$ is defined using the point at which the intensity drops to $1/e^2$ of its maximum value at the beam axis.

The electric field strength on distance $r$ from the beam axis of a Gaussian laser beam is

$$ E(r,t) = E_0 \cdot \exp(-r^2/w^2) \cdot \cos(\omega t) \tag{5-6} $$

For a laser with power $P$ and beam $1/e^2$-radius $w$, the intensity $I_0$ at the beam axis is

$$ I_0 = \frac{2P}{\pi w^2} \tag{5-7} $$

(If $w$ represents the $1/e$-radius, the maximum intensity is given by $I_0 = P/\pi w^2$).

The general relation between intensity $I_0$ and electric field strength $E_0$ is

$$ I_0 = \left(\frac{1}{2} \varepsilon_0 E_0^2\right) \cdot c \tag{5-8} $$

so that

$$ E_0 = \sqrt{\frac{2}{\varepsilon_0 c}} \cdot \sqrt{I_0} = 27.4492373 \cdot \sqrt{I_0} \quad \text{(SI units)} \tag{5-9} $$

For a specific rotational line, the Franck-Condon factor, $q_{v',v}$, and the vibronic transition dipole moment, $\mu_{vib}$, in units debye (D), is possible to obtain from the computer program LEVEL 7.5 by Le Roy [34].

Different units are occurring (such as a.u. = atomic unit = 1 e·aₐ₀):

$$ \mu_{vib} \text{ (a.u.)} = \frac{\mu_{vib} \text{ (D)}}{2.5417485 \text{ (D/a.u.)}} \tag{5-10} $$

$$ \mu_{vib} \text{ (SI units)} = \mu_{vib} \text{ (D)} \cdot 3.33564 \cdot 10^{-30} \text{ (Cm/D)} \tag{5-11} $$

The electronic transition dipole moment $\mu_e$ is given by

$$ \mu_e = \frac{\mu_{vib}}{\sqrt{q_{v',v}}} \quad \text{(D) or (a.u.) or (Cm)} \tag{5-12} $$
Each laser field is associated with a corresponding Rabi frequency $\Omega$, in units rad or Hz. The Rabi frequency at the beam axis ($r = 0$) and without the rotational dependence (see below) is defined through the relations

$$\Omega = \frac{\mu_e \cdot q_{\psi r} \cdot E_0}{\eta} \text{ (rad)} \quad \text{or} \quad \Omega = \frac{\mu_e \cdot q_{\psi r} \cdot E_0}{\hbar} \text{ (Hz)}$$

(5-13)

In a more detailed picture the Rabi frequency depends on both the molecule’s orientation as well as its distance from the beam axis [17]. When a laser is tuned near resonance with an $|j\rangle - |k\rangle$ transition, the $M$- and $r$-dependent Rabi frequency is defined as

$$\Omega^M(r) = \frac{\mu^M_{ik} \cdot E_0}{\eta} \cdot \exp(-r^2/w^2)$$

(5-14)

where $\mu^M_{ik}$ is the $M$-dependent transition dipole moment between levels $|i\rangle$ and $|k\rangle$ [44]::

$$\mu^M_{ik} = \mu_e \cdot q_{ijk} \cdot f(J, M)$$

(5-15)

The orientation factor $f(J, M)$ is the direction cosine matrix element, where $J$ and $M$ denote the lower level quantum numbers.

The orientation factors $f(J, M)$ for some singlet-singlet transitions are given below in the case of linearly polarized light, i.e., $M' = M$ [50]:

\[1\Sigma - 1\Sigma\] Singlet states: $\Omega' = \Omega = 0$

- **R line:** $\frac{\sqrt{(J + 1)^2 - M^2}}{\sqrt{(2J + 1)(2J + 3)}}$
- **Q line:** 0
- **P line:** $\frac{\sqrt{J^2 - M^2}}{\sqrt{(2J + 1)(2J - 1)}}$

(5-16)

\[1\Pi - 1\Sigma\] Singlet states: $\Omega' = 1$, $\Omega = 0$; $\Lambda$-doubling is included.

- **R line:** $-\frac{\sqrt{(J + 2)} \cdot \sqrt{(J + 1)^2 - M^2}}{\sqrt{(2J + 1)(2J + 3)}}$
- **Q line:** $\frac{M}{\sqrt{J(J + 1)}}$
- **P line:** $\frac{\sqrt{(J - 1)} \cdot \sqrt{J^2 - M^2}}{\sqrt{J(2J + 1)(2J - 1)}}$

(5-17)

\[1\Sigma - 1\Pi\] Singlet states: $\Omega' = 0$, $\Omega = 1$; $\Lambda$-doubling is included.

- **R line:** $\frac{\sqrt{J} \cdot \sqrt{(J + 1)^2 - M^2}}{\sqrt{(2J + 1)(2J + 3)}}$
- **Q line:** $\frac{M}{\sqrt{J(J + 1)}}$
- **P line:** $-\frac{\sqrt{(J + 1)} \cdot \sqrt{J^2 - M^2}}{\sqrt{J(2J + 1)(2J - 1)}}$

(5-18)

Similar expressions exist for circularly polarized light, i.e., $M' = M \pm 1$. 
6 Multiple Resonance Spectroscopy in molecular sodium

In Paper 4, appended to this thesis, we report on experiments based on double and triple resonance spectroscopy accomplished on sodium dimers. The main purpose in this work is to investigate the possibility and the technique of determining the transition dipole moment for the molecular resonance transition between the ground state and the first excited state in Na₂. Two different excitation schemes are examined and compared: the three-level two-laser cascade system and the four-level three-laser inverted-Y system.

In Chapter 5 the general features of the three-level cascade system are described and exemplified in configurations, where the strong coupling laser connects two excited states. As briefly outlined in section 5.6, a previous experiment [44] demonstrates measurements of the transition dipole moment between two electronically excited levels in molecular lithium. A vital difference in the present sodium experiments is, that the ground state constitutes the lower level of the coupling field transition, and the transition moment we look for is related to a resonance transition in an inhomogeneously line-broadening environment. The attendant consequences and general problems associated with Doppler broadening and saturation effects are elucidated in Paper 4. It turns out that the four-level triple resonance based excitation scheme is clearly favorable for the determination of the transition dipole moment in this case.

Hence in Chapter 6, I will focus on the inverted-Y system with main emphasis laid on the density matrix formalism applied to this scheme; section 6.4. Before that, though, the inverted-Y system is introduced (6.1) and the experimental conditions are touched upon (6.2). In section 6.3 the experimental data analysis and results are presented.
6.1 The inverted-Y system

In literature the arrangement used in our three-laser experiment is known as inverted-Y configuration. Fig. 6.1 shows the relevant energy levels of the investigated Na₂ four-level triple resonance excitation scheme. The pump laser L₁ excites a molecule from the ground state, $X^1Σ^+_g (v = 1, J = 19)$, to a selected intermediate level, $A^1Σ^+_u (v = 25, J = 20)$. This is the initial level of the probe laser, L₂, which further excites the molecule to the upper level $2^1Π_g (v = 25, J = 20 f$-parity). The third laser L₃ resonantly couples the intermediate $A^1Σ^+_u (25,20)$ level to a high vibrational level of the ground state, $X^1Σ^+_g (v = 38, J = 21)$, outside the range of thermally populated vibrational levels. Our main observation tool is the fluorescence from the upper level, recorded through detection of the selected single channel $2^1Π_g (25,20) → A^1Σ^+_u (20,20)$ transition. The fluorescent emission from the intermediate state, e.g., the $A^1Σ^+_u (25,20) → X^1Σ^+_g (4,21)$ channel, is only used in the build-up of the experiment and for control purposes. The wave numbers corresponding to the transitions of interest, are given in the figure caption.

Fig. 6.2 shows the potential energy curves for some Na₂ electronic states, occurring in our experiments. It could be noticed that the sodium atoms are very loosely bound in the dimer. The dissociation energy of the ground state amounts to puny ~ 0.75 eV, which can be compared to the previously studied hetero-nuclear diatomic molecules, possessing significantly higher dissociation energies, e.g., nearly 8 eV in HfO. Most shallow of the Na₂ potential curves displayed here, is the B-state, containing only ~30 vibrational levels below the dissociation limit.

From the potential energy curves diagram (Fig. 6.2) we also get information about the decay channels of spontaneous emission, relevant to consider in lifetime calculations. As mentioned earlier, the excited state lifetime is a crucial parameter in the theoretical simulations. For example, the lifetime of the Na₂ $2^1Π_g$ state, occurring in the present work but also in Paper 6, is completely dominated by the decay rates to the $B^1Π_u$ and $A^1Σ^+_u$ states. Similarly the $4^1Σ^+_g$ state lifetime, of interest in Paper 5 and 6, is determined from spontaneous decay to the same two B and A states. More detailed accounts of the calculation procedure for the Na₂ $2^1Π_g$ and $4^1Σ^+_g$ states are given in Papers 4 and 5, respectively.
Fig. 6.1  Energy level diagram of Na₂ showing the inverted-Y excitation and fluorescence detection scheme, used in the triple resonance experiment.

The wave numbers associated with the transition resonance frequencies in this scheme are k₁ ~ 17188 cm⁻¹, k₂ ~ 15520 cm⁻¹, and k₃ ~ 12547 cm⁻¹, corresponding to the transitions |1⟩ ↔ |2⟩, |2⟩ ↔ |3⟩, and |2⟩ ↔ |4⟩, respectively.

Usually the pump laser L1 and the strong coupling laser L3 are held fixed on resonance, while the probe laser L2 is modulated and scanned.

The delicate observation and decisive for the result of this experiment is the upper level |3⟩ fluorescence. A selected single channel 2¹Π⁺ (25,20f) → A¹Σ⁺ (20,20) emission signal is monitored, and the recorded spectra for different coupling laser field strengths are analyzed.

Fig. 6.2  Selected potential energy curves for electronic states of Na₂.

The states involved in the triple resonance experiment (Paper 4) are, besides the X¹Σ⁺ ground state, the intermediate A¹Σ⁺ and the upper 2¹Π⁺ states.

The Na₂ co-propagating cascade experiment (Paper 5) includes the same ground and intermediate states, whereas the 4¹Σ⁺ state constitutes the upper level.

Paper 6 reports on experiments involving the 2¹Π⁺ as well as the 4¹Σ⁺ state apart from the X¹Σ⁺ and A¹Σ⁺ states.
6.2 Experimental conditions

The set-up of the triple resonance experiment is basically the same as the one described in section 5.2 but extended with an additional laser. A principal sketch is shown in Fig. 6.3.

All three lasers used for matter interaction are single-mode, tuneable and narrow-band cw lasers. Two argon ion pumped ring dye lasers, operating on Rhodamine 6G and DCM, respectively, are used as pump laser, L1, and probe laser, L2. The pump and probe lasers are in a co-propagating arrangement and counter-propagate with the coupling laser field, L3, provided by a titanium-sapphire laser. The laser beams are linearly polarized in the same direction and focused to the common interaction region in the centre of the heatpipe, where the sodium vapour is generated. The temperature in the present measurements was about 700 K and the pressure of the argon buffer gas 100-200 mTorr.

In a typical experiment the pump L1 and the strong coupling laser L3 are held fixed on the resonance frequency of respective transition (Fig. 6.1), while the probe laser L2 is modulated and scanned. The fluorescence light from the uppermost level is observed through a side window of the heatpipe. The mono-chromator is used to select a narrow wavelength window, and a single channel signal is registered by a PMT and monitored.

The recorded fluorescence spectra from the upper $2^{1}\Pi_g$ state, of which Fig. 6.4 gives an example, show split line shapes, which originate from the AT-splitting of the intermediate $A^{1}\Sigma_u^+$ state, caused by the coupling laser. A number of spectra for different coupling field powers are recorded and analysed in terms of the experimentally obtained AT peak-to-peak separation. In Fig. 6.5 the experimentally obtained splittings are plotted versus the square root of the corresponding coupling field powers. Since the electric field strength amplitude $E \propto \sqrt{P}$ [Eqs. (5-7), (5-8), (5-9)] and, in turn, the Rabi frequency $R \propto E$ [Eq. (5-13)], this graph confirms the expected linear dependence of the AT-splitting on the coupling field Rabi frequency [17,44].
Fig. 6.3 The experimental set-up used in the triple resonance measurements.

Fig. 6.4 Fluorescence spectrum from the Na$_2$ 2$^1\Pi_g$ (25,20) level recorded as a function of the probe laser detuning, while pump and coupling lasers are on resonance. In this case the coupling field laser power (before heatpipe) is 500 mW. Pump and probe laser powers are 80 mW and 5 mW, respectively, and the corresponding (effective) Rabi frequencies $\sim 40$ MHz and $\sim 60$ MHz are used in the theoretical simulation. In order to fit the peak splitting of the simulated graph as close as possible to the experimental spectrum, a proper value of the coupling field Rabi frequency $R_3$ is $(650 \pm 10)$ MHz.

$\mu = 5.33$ D.

R3 = 650 MHz and $P = 0.91 \times 500$ mW correspond to $\mu = 5.33$ D.
6.3 Analysis and results

Determination of the transition dipole moment $\mu$ ($\equiv \mu_{ab}$) from experimental data is based on the definition of Rabi frequency in terms of transition moment and electric field strength, Eq. (6-2). The procedure can be carried out in slightly different ways, utilizing theoretical simulations. A fundamental input parameter to the simulation program is the Rabi frequency, associated with each laser field and transition. The most common situation is that Eq. (6-2) is used to calculate the Rabi frequency, provided that the transition moment is known. Generally the Rabi frequency corresponding to a given laser field power and laser beam spot size is determined by applying the calculated transition moment value obtained with the program LEVEL 7.5 [34], using known potential RKR curves [references specified in Paper 4] and theoretical \textit{ab initio} transition dipole moment functions [51].

Let us return to the issue of determining a value of the transition dipole moment from the experimental data displayed in Fig. 6.5. One method is to simulate each individual experimental spectrum as exemplified in Fig. 6.4. As described above, the pump and probe laser Rabi frequency values are those corresponding to the estimated laser powers in the interaction region, considering that for the power range of interest typically 9% of the intensity measured before the heat pipe is lost in the heat pipe window. The coupling Rabi frequency, on the contrary, is varied until the simulated peak-to-peak separation matches the recorded experimental spectrum. Assuming that the effective power is 91% of the measured coupling field power value, 500 mW in this case, the Rabi frequency giving the best fit (650 MHz) corresponds to a transition moment value $\mu \approx 5.3$ D. The final result might be the mean value of all the simulated spectra.

Another method is to run a number of simulations for arbitrary, equidistant coupling field Rabi frequency values in the relevant range, keeping the pump and probe laser conditions the same as above. The AT peak-to-peak separation is determined in each simulated graph, giving a set of connected pairs of splitting versus Rabi frequency. The transition moment is now treated parametrically: an arbitrary but reasonable value of $\mu$ is fixed and combined with each coupling Rabi frequency used in the simulations. With this approach Eq. (6-2) now gives in each case the corresponding electric field strength and a consequential power value. In this way every simulated AT splitting is connected with a certain power value, and the sequence of splitting – power pairs is plotted in Fig. 6.5 for the chosen specific $\mu$-value. As an illustration two simulated series (extremes) are shown in the figure. The final result of the transition moment is the $\mu$-value used in the set of
points best matching the experimental measurements.

Mainly the latter procedure is applied in the work reported in Paper 4, but the former method is used for comparison and control purpose. The best fit to experimental data is obtained for $\mu \approx 5.2$ D (Paper 4, Fig. 5). The result can be compared with the theoretically calculated value $[51,34]$, $\mu = 5.9$ D for the $A' \Sigma_u^+ (25,20) \leftrightarrow X' \Sigma_g^+ (38,21)$ transition. Provided that the electronic part of the transition dipole moment, $\mu_e(r)$, does not vary too strongly with the internuclear distance $r$ of interest, Eq. (5-12) with known Franck-Condon factor (obtained from the LEVEL 7.5 program [34]), can be used to find the corresponding electronic part of the transition moment. That was the proceeding in the lithium experiment, outlined in section 5.6 and Fig. 5.12. In the present Na$_2$ case, the dependence of the theoretical electronic transition moment on the internuclear separation (Paper 4, Fig. 6) makes it questionable, if a value of $\mu_e$ is meaningful. Rather the total measured vibrationally averaged transition moment $\mu$ is the adequate quantity to report.

Besides the inverted-Y system described above, the conditions for determining an $X \leftrightarrow A$ transition moment using a three-level cascade system are investigated. Our observations are reported in Paper 4, section 3A and Figs. 1 and 2. When the strong coupling laser resonantly couples the intermediate $A$-state and a thermally populated vibrational level of the ground state, power saturation effects and Doppler broadening easily mask the expected level splitting. The strong coupling field excites a broad velocity group of molecules, accessible in the probe laser scan, leading to impaired resolution. Fluorescence spectra from the uppermost $2\Pi$-level exhibit very modest AT splittings, if any at all, compared to the inverted-Y scheme. With Rabi frequencies limited to those available from cw laser sources, the ordinary cascade system is not very useful for AT-effect based measurements of the $X \leftrightarrow A$ transition dipole moment.

Despite the fact that the inverted-Y configuration is a technically more complicated excitation scheme, its advantages in this context are apparent, as far as can be judged from our experimental results. The coupling field transition can be chosen to involve a high vibrational level of the ground state outside the thermal population range and still with a large Franck-Condon factor, making high Rabi frequencies possible. The purpose with the weak pump laser is to excite a much narrower velocity group from the low vibrational ground state level. As a consequence the probe laser scan creates an upper level population, manifesting itself in high resolution fluorescence spectra, showing significant AT splitting and well separated peaks.
**Fig. 6.5** Dependence of the observed and simulated AT-splitting on the coupling field laser power in the investigated Na2 four-level inverted-Y system.

The splitting of the intermediate state |2⟩ is monitored by recording the fluorescence signal from the uppermost level |3⟩ while scanning the probe laser.

The |2⟩ ↔ |4⟩ transition moment is determined by means of simulations based on different μ-values. Details in the simulation procedure are described in the text.

**Fig. 6.6** Excitation and decay scheme for the Na2 four-level three-laser system.

In our experiment the levels |1⟩, |2⟩, |3⟩, and |4⟩ signify the rovibronic levels $X'\Sigma_u^+\ (1,19)$, $A'\Sigma_u^+\ (25,20)$, $2\ ^1\Pi_g\ (25,20)$, and $X'\Sigma_u^+\ (38,21)$, correspondingly, as shown in Fig. 6.1.

The solid arrows indicate the lasers, each one designated with its photon frequency $\omega$ and the Rabi frequency $\Omega$, calculated according to Eqs. (6-2) and (5-7, 8, 9).

The dashed arrows indicate possible decay channels from the different energy levels. Two auxiliary levels |5⟩ and |6⟩ are incorporated as recipients for decays beyond the open system, formed by the four laser-interacting levels.

$W_{ik}$ denotes the total decay rate between levels |i⟩ and |k⟩. In the first place the $W_{ik}$ rates affect the populations of the two involved levels, but they are also included in the expression defining the phase-relaxation rates, i.e., the decay of the coherences.
6.4 Density matrix formalism

6.4.1 The Hamiltonian of the laser – molecule system

In this section is presented how density matrix formalism is applied to the current Na$_2$ inverted-Y system. For this scheme no analytical solution, as for the three-level systems, is derived so far, and consequently in the simulations only the matrix method is used.

The four-level molecular system interacting with three laser fields is illustrated in Fig. 6.6. The interacting levels are assigned energies $\varepsilon_j$, $j = 1, 2, 3, 4$, whereas the states $|5\rangle$ and $|6\rangle$ represent all other vibrational states in the A and X manifold, respectively.

The light fields are in this context most conveniently expressed in complex form as

$$E_j(t) = E_j \cos \omega_j t = E_j \cdot \frac{1}{2} (e^{i\omega_j t} + e^{-i\omega_j t}) \quad j = 1, 2, 3$$

(6-1)

where $E_j$ denotes the electric field amplitude and $\omega_j$ the frequency of the $j$th laser.

With $\mu_{ik}$ (= $\mu_{ki}$) denoting the (vibrational) transition dipole moment between states $|i\rangle$ and $|k\rangle$ we define the Rabi frequency for every laser field according to Eq. (5-13):

$$\Omega_{12} = \frac{\mu_{12} \cdot E_1}{\eta}; \quad \Omega_{23} = \frac{\mu_{23} \cdot E_2}{\eta}; \quad \Omega_{24} = \frac{\mu_{24} \cdot E_3}{\eta}.$$ (6-2)

We also define the detuning of each laser, assuming that the energy $\varepsilon_1 = 0$:

$$\Delta_1 = \frac{\varepsilon_2 - \omega_1}{\eta}; \quad \Delta_2 = \frac{\varepsilon_3 - \varepsilon_2 - \omega_2}{\eta}; \quad \Delta_3 = \omega_3 - \frac{\varepsilon_2 - \varepsilon_4}{\eta}.$$ (6-3)

In order to derive the density matrix elements we need to construct the Hamilton operator describing the laser - molecule system. The total Hamiltonian is the sum of two terms, one molecular part, $H_{mol}$, and another part accounting for the radiation – matter interaction:

$$H_{tot} = H_{mol} + H_{int}.$$ (6-4)

$H_{mol}$ is an “internal” Hamiltonian, diagonal in the basis set of the molecular states and its eigenvalues are the energy levels $\varepsilon_j$ of the four-level system ($\varepsilon_1 = 0$):

$$H_{mol} = \varepsilon_2 |2\rangle\langle 2| + \varepsilon_3 |3\rangle\langle 3| + \varepsilon_4 |4\rangle\langle 4|$$ (6-5)

It turns out that $H_{mol}$ with advantage is decomposed into two Hamiltonians, $H_0$ and $H_1$:

$$H_{mol} = H_0 + H_1 = \eta \omega_1 |2\rangle\langle 2| + \eta(\omega_1 + \omega_2) |3\rangle\langle 3| + \eta(\omega_1 - \omega_2) |4\rangle\langle 4| + \\
+ \eta \Delta_1 |2\rangle\langle 2| + \eta(\Delta_1 + \Delta_2) |3\rangle\langle 3| + \eta(\Delta_1 + \Delta_3) |4\rangle\langle 4|$$

where $H_0$ is based on the photon energies of the different laser fields, whereas $H_1$ is expressed using the detunings defined in Eq. (6-3).
The interaction Hamiltonian, originating from the energy of an oscillating dipole in an electric field, $\mu E \cos \omega t$, involves the nondiagonal elements and is given by

$$H_{\text{int}} = \eta \frac{\Omega^{12}}{2} (e^{i\omega t} + e^{-i\omega t})(1/2 \langle 2 | + 2 \langle 1 |) + \eta \frac{\Omega^{23}}{2} (e^{i\omega t} + e^{-i\omega t})(2 \langle 3 | + 3 \langle 2 |) + \eta \frac{\Omega^{24}}{2} (e^{i\omega t} + e^{-i\omega t})(2 \langle 4 | + 4 \langle 2 |)$$

The total Hamiltonian $H_{\text{tot}} + H_{\text{int}}$ is simplified through quantum mechanical subtleties, not depicted here. Briefly, in the interaction picture the time dependence is reduced to only the interaction energy, and thanks to the rotating wave approximation, high frequency terms can be neglected. As an ultimate result we get the total Hamiltonian:

$$H_{\text{tot}} = \eta \Delta_1 \langle 2 | 2 \rangle + \eta(\Delta_1 + \Delta_2) \langle 3 | 3 \rangle + \eta(\Delta_1 + \Delta_3) \langle 4 | 4 \rangle + \eta \frac{\Omega^{12}}{2} (2 \langle 1 | + 1 \langle 2 |) + \eta \frac{\Omega^{23}}{2} (3 \langle 2 | + 2 \langle 3 |) + \eta \frac{\Omega^{24}}{2} (4 \langle 2 | + 2 \langle 4 |)$$

Having derived a representative Hamiltonian, we now consider the time-dependent Schrödinger equation, which in the density matrix formalism is written as

$$\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho] + \text{relaxation terms}$$

where $\rho$ is the density operator and $H$ denotes the total Hamiltonian $H_{\text{tot}}$, Eq. (6-7).

The first part of the differential equation (6-8), the commutator of $H$ and $\rho$, representing the coherent terms, is obtained in component form as

$$\rho_{ij} = -\frac{i}{\hbar} \sum_k (H_{ik} \rho_{kj} - \rho_{ik} H_{kj})$$

where $H_{ik} = \langle i | H | k \rangle$, $i, j, k = 1 - 4$. (6-9)

In order to construct the relaxation terms, we have to introduce different kinds of decay rates concerning the density matrix diagonal elements, i.e., the populations, as well as the nondiagonal elements, the coherences.

### 6.4.2 Spontaneous relaxation rates

An excited molecular level can be depopulated by spontaneous emission as well as other radiation-less processes, such as collision-induced transitions. The total decay rate $W_i$ of an (electronically) excited level $|i\rangle$ is related to the effective lifetime $\tau_i$ of that level and is the sum of all possible decay channels from level $|i\rangle$ to lower energy levels $|k\rangle$, [1,15]

$$\frac{1}{\tau_i} = W_i = \sum_k W_{ik} \quad i = 2, 3, 5 \text{ (assuming } W_1 = 0 \text{).}$$

The decay rates $W_{ik}$, which are indicated in Fig. 6.6, imply a decrease of the initial level population and corresponding population increase of the terminate level.
The nondiagonal elements of the density matrix are affected by dephasing factors, \( \gamma_{ij} = \gamma_{ji} \), describing the decay rate of the coherence, i.e., of the definite phase relations between the atomic dipoles. The phase-relaxation terms are usually expressed as \[52\]

\[
\gamma_{ij} = \frac{1}{2} \sum_{k} (W_{ik} + W_{kj}) + \gamma_{ij}^e \quad i \neq j
\]  

(6-11)

where the additional term \( \gamma_{ij}^e \) is a pure dephasing contribution, induced by phase interrupting collisions, accounting for the condition that phase relaxation is faster than the population relaxation \[7\].

Molecules are moving in and out of the interaction region with a decay rate, \( w_i \), affecting all populations and coherences, and an equal rate of replenishment of the ground state population. This transit relaxation rate is calculated as suggested by Sagle et al. \[53\].

**6.4.3 Appropriate preliminaries**

In the Fig. 6.6 scheme, the four laser-interacting levels alone constitute an open system, whose population is not conserved. To formally create a closed, normalizeable system, the auxiliary levels \( |5\rangle \) and \( |6\rangle \) are incorporated to collect decays beyond the four-level system. We also need a source term for the ground state \( |6\rangle \), and therefore the element \( \rho_{66}^e \) is introduced, denoting the population at thermal equilibrium and used to regulate the population flow as demonstrated below. We now have a proper normalization condition:

\[
\rho_{11} + \rho_{22} + \rho_{33} + \rho_{44} + \rho_{55} + \rho_{66} = 1
\]

(6-12)

The populations \( \rho_{55} \) and \( \rho_{66} \) are eliminated from the final density matrix by regarding their time-derivatives, containing no laser-interaction associated terms:

\[
\dot{\rho}_{55} = W_{35} \rho_{33} - (W_5 + w_i) \rho_{55}
\]

(6-13 a)

\[
\dot{\rho}_{66} = W_{26} \rho_{22} + W_{36} \rho_{33} + W_{56} \rho_{55} - (W_6 + w_i) \rho_{66} + (W_6 + w_i) \rho_{66}^e
\]

(6-13 b)

Under steady state conditions, \( \dot{\rho}_{55} = \dot{\rho}_{66} = 0 \), the unwanted populations are substituted as

\[
\rho_{55} = A_{35} \cdot \rho_{33} \text{ and } \rho_{66} = A_{26} \cdot \rho_{22} + (A_{36} + A_{56} \cdot A_{35}) \cdot \rho_{33} + \rho_{66}^e
\]

(6-14 a)

where \( A_{35} = \frac{W_{35}}{W_5 + w_i} \); \( A_{26} = \frac{W_{26}}{W_6 + w_i} \); \( A_{36} = \frac{W_{36}}{W_6 + w_i} \); \( A_{56} = \frac{W_{56}}{W_6 + w_i} \).

(6-14 b)

Furthermore, with the purpose of reducing the number of equations to be solved, the population of state \( |1\rangle \) is substituted according to the Eqs. (6-12) and (6-14 a,b):

\[
\rho_{11} = 1 - (1 + A_{26}) \cdot \rho_{22} - (1 + A_{35} + A_{36} + A_{56}) \cdot \rho_{33} - \rho_{44} - \rho_{66}^e
\]

(6-15)
6.4.4 Equations of motion for the density matrix

At last we are ready to derive the density matrix equations of motion, where the substitution and abbreviations in Eqs. (6-15) and (6-14 b) are applied. Combining the results of the previous sub-sections we arrive at the following final form of the equations of motion of all the density matrix elements according to Eqs. (6-8),(6-9).

The abbreviations \( \Omega_i = \frac{\Omega_{12}}{2} ; \Omega_2 = \frac{\Omega_{23}}{2} ; \Omega_3 = \frac{\Omega_{24}}{2} \); are used in the equations.

\[
\begin{align*}
\rho_{12} &= i\Delta_1 \rho_{12} + i\Omega_2 \rho_{13} + i\Omega_3 \rho_{14} - i\Omega_1 (2 + A_{26}) \rho_{22} - i\Omega_1 (1 + A_{35} + A_{36} + A_{35} A_{36}) \rho_{33} \\
&\quad - i\Omega_1 \rho_{44} - (\gamma_{12} + w_i) \rho_{12} + i\Omega_1 (1 - \rho_{66}) \\
\rho_{13} &= i\Omega_2 \rho_{12} + i(\Delta_1 + \Delta_2) \rho_{13} - i\Omega_1 \rho_{23} - (\gamma_{13} + w_i) \rho_{13} \\
\rho_{14} &= i\Omega_3 \rho_{12} + i(\Delta_1 + \Delta_3) \rho_{14} - i\Omega_1 \rho_{24} - (\gamma_{14} + w_i) \rho_{14} \\
\rho_{21} &= -i\Delta_1 \rho_{21} + i\Omega_1 (2 + A_{26}) \rho_{22} - i\Omega_2 \rho_{31} + i\Omega_1 (1 + A_{35} + A_{36} + A_{35} A_{36}) \rho_{33} \\
&\quad - i\Omega_3 \rho_{41} + i\Omega_1 \rho_{44} - (\gamma_{12} + w_i) \rho_{21} - i\Omega_1 (1 - \rho_{66}) = \rho_{12}^* \\
\rho_{22} &= -i\Omega_1 \rho_{12} + i\Omega_1 \rho_{21} - (W_2 + w_i) \rho_{22} + i\Omega_2 \rho_{23} + i\Omega_3 \rho_{24} - i\Omega_2 \rho_{32} + W_{32} \rho_{33} - i\Omega_3 \rho_{42} \\
\rho_{23} &= -i\Omega_1 \rho_{13} + i\Omega_2 \rho_{22} + i\Delta_2 \rho_{23} - i\Omega_2 \rho_{33} - i\Omega_1 \rho_{43} - (\gamma_{23} + w_i) \rho_{23} \\
\rho_{24} &= -i\Omega_1 \rho_{14} + i\Omega_3 \rho_{22} + i\Delta_3 \rho_{24} - i\Omega_2 \rho_{34} - i\Omega_1 \rho_{44} - (\gamma_{24} + w_i) \rho_{24} \\
\rho_{31} &= -i\Omega_2 \rho_{21} - i(\Delta_1 + \Delta_2) \rho_{31} + i\Omega_1 \rho_{32} - (\gamma_{13} + w_i) \rho_{31} = \rho_{13}^* \\
\rho_{32} &= -i\Omega_2 \rho_{22} + i\Omega_1 \rho_{31} - i\Delta_2 \rho_{32} + i\Omega_2 \rho_{33} + i\Omega_3 \rho_{34} - (\gamma_{23} + w_i) \rho_{32} = \rho_{23}^* \\
\rho_{33} &= -i\Omega_2 \rho_{23} + i\Omega_2 \rho_{32} - (W_3 + w_i) \rho_{33} \\
\rho_{34} &= -i\Omega_2 \rho_{24} + i\Omega_3 \rho_{32} + i(\Delta_3 - \Delta_2) \rho_{34} - (\gamma_{34} + w_i) \rho_{34} \\
\rho_{41} &= -i\Omega_3 \rho_{21} - i(\Delta_1 + \Delta_3) \rho_{41} + i\Omega_1 \rho_{42} - (\gamma_{14} + w_i) \rho_{41} = \rho_{14}^* \\
\rho_{42} &= -i\Omega_3 \rho_{22} + i\Omega_1 \rho_{41} - i\Delta_3 \rho_{42} + i\Omega_2 \rho_{43} + i\Omega_3 \rho_{44} - (\gamma_{24} + w_i) \rho_{42} = \rho_{24}^* \\
\rho_{43} &= -i\Omega_3 \rho_{23} + i\Omega_2 \rho_{42} + i(\Delta_2 - \Delta_3) \rho_{43} - (\gamma_{34} + w_i) \rho_{43} = \rho_{34}^* \\
\rho_{44} &= W_{24} \rho_{22} - i\Omega_3 \rho_{24} + (W_{34} + A_{35} W_{34}) \rho_{33} + i\Omega_3 \rho_{42} - (W_4 + w_i) \rho_{44}
\end{align*}
\]

An asterisk denotes the complex conjugate, and we can state that \( \rho_{ij} = \rho_{ji}^* \), \( i \neq j \).
6.4.5 *The solution based on the L-matrix*

The equations of motion (6-16) are solved by the matrix method, where they are expressed in an equivalent vector - matrix form,

\[
\frac{d\mathbf{X}}{dt} = \dot{\mathbf{X}} = L\mathbf{X} + \mathbf{I}
\]  

(6-17)

\( \mathbf{X} \) is a 15 component column vector containing all the \( \rho_{ij} \) density matrix elements;

\( L \) is a 15 \( \times \) 15 matrix containing relevant parameters of the laser – molecule system;

\( I \) is a 15 component column vector containing the inhomogeneous terms in Eqs. (6-16).

The matrix equation (6-17) is illustrated in Table 6.1, in particular showing all elements of the \( L \)-matrix.

Eq. (6-17) is solved numerically under steady state conditions, \( \dot{\mathbf{X}} = 0 \), using matrix inversion and multiplication, ending in exact numerical results of the \( \mathbf{X} \) vector, i.e., the populations \( \rho_{ii} \) and the coherences \( \rho_{ij} \) of the system:

\[
\mathbf{X} = -(L^{-1})\mathbf{I}
\]  

(6-18)

The calculations are performed with a Fortran computer simulation program [47], to which the required input, among other figures, contains numerical values of the parameters included in the \( L \)-matrix.

Generally the simulations, carried out as described above, are powerful tools from several points of view. Comparing experiments and simulations offers a method to verify, modify or reject a theoretical model. From the best fit of a simulated to an experimental spectrum, values of parameters otherwise hard to determine, like dephasing rates, can be estimated. The possibility of arbitrarily varying the simulation parameters allows other appealing prospects, such as predictions for specified experimental conditions or systematic investigations of the influence of one specific variable.
Table 6.1 illustrating the vector-matrix equation $\dot{X} = LX + I$. Abbreviations: $\Omega_1 = \frac{\Omega_{12}}{2}$; $\Omega_2 = \frac{\Omega_{23}}{2}$; $\Omega_3 = \frac{\Omega_{24}}{2}$; $^*) A_{356} = (1 + A_{35} + A_{36} + A_{35'}A_{56})$

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7 EIT and AT effect in open molecular systems

Papers 5 and 6, appended to this thesis, treat the coherence and quantum interference related phenomena of electromagnetically induced transparency (EIT) and Autler-Townes (AT) peak splitting effect with emphasis on the open character of the investigated molecular systems and in the light of the role played by the Doppler effect. Using a co-propagating cascade scheme, it is demonstrated in Paper 5 experimental evidence of EIT, partly in opposition to previous belief, that high coupling field intensities are required to overcome the inhomogeneous Doppler broadening. The openness of a system is defined in Paper 5, Eq. (2), and its relevance illustrated in Fig. 3. The unexpected and drastic influence on the line profile of the AT splitting, depending on the frequency ratio of the two optical fields applied, is exemplified and discussed in Paper 6.

Since my personal contributions to Papers 5 and 6 are limited, I confine myself in this thesis to give summary accounts of these two works (sections 7.1 and 7.2).

7.1 EIT in co-propagating cascade systems

An obvious sequel to the studies of molecular lithium, using a counter-propagating cascade scheme as reported in section 5.3, was to modify the experiments to a co-propagating laser arrangement. Of vital importance for the degree of EIT effect is the proportion between the coupling field Rabi frequency and the residual two-photon Doppler line width, which for a cascade system is expressed as [54]

$$\Delta \nu_D = |k_1 + k_2| \cdot u ,$$

where the most probable velocity $u = \sqrt{2k_BT/M}$

(7-1)

($k_B$ is the Bolzmann constant, $T$ is the absolute temperature, $M$ is the molecular mass).

In the case of two counter-propagating laser beams, the wave vectors $k_1$ and $k_2$ have opposite signs, allowing the vector sum $|k_1 + k_2|$ and associated $\Delta \nu_D$ to be smaller than the experimentally accessible Rabi frequency. Traditionally this condition ensures well-pronounced EIT, which is confirmed in Fig. 5.5 and pointed out in Paper 6. On the contrary, if the lasers co-propagate, the two $k$ vectors have the same sign and the sum of their magnitudes easily makes the residual Doppler width exceed the laser field Rabi frequencies produced by available cw lasers. Experience from atomic, closed systems predicts absence of EIT effect in this case. Nevertheless, EIT is experimentally observed and theoretically verified in open molecular systems of Li$_2$ and Na$_2$, using co-propagating cascade schemes reported in Paper 5.
OODR excitation and fluorescence detection scheme for the co-propagating lithium experiment is given in Fig. 5.3. The sodium dimer potential curves are shown in Fig. 6.2 and the energy level diagram is depicted in Fig. 7.1. The experimental set-up is well illustrated by Fig. 5.4 with the exception that the two laser beams are arranged in a co-propagating geometry. The dye laser, used as coupling field in the Li$_2$ measurements, is in the Na$_2$ case exchanged to a titanium-sapphire laser. A ring dye laser operating on DCM provides the probe beam in both cases.

The observations are summarized by means of the graphs in Fig. 7.2. They show a coupling power study referring to sodium, but the trends in lithium are the same. Diversities from the counter-propagating configuration, as well as similarities, can be noticed by comparing these spectra to those in Fig. 5.5. For comparison it should also be mentioned that the residual Doppler line width of the Na$_2$ cascade system under the present experimental conditions is $\Delta \nu_D \approx 1.3$ GHz, which is more than the full Doppler width of the fluorescence observed from level $|2\rangle$ (FWHM $\approx 1.1$ GHz).

For coupling powers up to 1100 mW, corresponding to Rabi frequency $\sim$1000 MHz, the fluorescence spectrum recorded from the upper level $|3\rangle$ of the cascade system is power broadened and adopts a triangular line shape with increasing coupling power, displaying no AT splitting at all. This result is in full agreement with Paper 6, Fig.4, since the ratio $k_1/k_2 > 0$ for two co-propagating laser beams, and the absence of AT effect is also supported by theoretical simulations.

The fluorescence signal from the intermediate level $|2\rangle$, however, exhibits an unexpected behavior. Even for low coupling field powers a modest but obvious EIT dip emerges and then deepens slightly with stronger field just to later decrease and disappear. According to simulations, see Fig. 7.3, evidence of EIT is visible for coupling field Rabi frequencies in the range from $\sim$20 MHz to $\sim$800 MHz. The reason for this, though, is not intuitively obvious. A careful theoretical analysis might possibly clarify the surprising presence of EIT for Rabi frequencies smaller than the residual Doppler width.

For higher coupling field powers, not accessible in our experiment, theoretical simulations indicate not only reappearance of the EIT feature but also emergence of upper level AT splitting. Coupling field Rabi frequencies of magnitude 8 GHz, i.e., more than $6 \cdot \Delta \nu_D$, allows the characteristics of EIT as well as the AT effect to be well developed.
Fig. 7.1  Energy level diagram of Na$_2$, showing the excitation and fluorescence detection scheme used in the cascade co-propagating experiment.

The weak probe laser L1 (DCM, ~14829 cm$^{-1}$) is modulated and tuned across the transition $|1\rangle \rightarrow |2\rangle$, while the coupling field laser L2 (Ti-sapphire, ~13285 cm$^{-1}$) is held fixed on resonance of the $|2\rangle \rightarrow |3\rangle$ transition.

Single channel detection of the side fluorescence signal from the upper and intermediate levels is accomplished by using the monochromator as a narrow-band filter, selecting the spontaneous emission wavelengths of the indicated decay transitions.

**Upper State Fluorescence**

![Upper State Fluorescence Diagram](image)

**Intermediate State Fluorescence**

![Intermediate State Fluorescence Diagram](image)

Fig. 7.2  Recorded spectra for different coupling laser powers in the open Na$_2$ co-propagating cascade system. The diagrams show the measured single channel fluorescence signal from the upper and intermediate state levels, $4 \Sigma_g^+(0,17)$ and $A \Sigma_u^+(3,18)$, respectively, as a function of the probe laser detuning.

Comparing these spectra with corresponding graphs obtained in the counter-propagating scheme, Fig. 5.5, we see that they principally agree in the weak field limit but differ for strong coupling fields. In the co-propagating case, the EIT is present, but less pronounced, for a limited coupling power range and then disappears. No AT-splitting at all is observed, instead the upper level fluorescence signal broadens and adopts a triangular line shape.
Fig. 7.3 A sequence of simulated spectra, showing the population of the intermediate level $|2\rangle$ of the Na$_3$ cascade co-propagating system for some selected coupling field Rabi frequencies, R2. The graphs illustrate how the line shape changes with increasing coupling power: an EIT-dip emerges, gets deeper, disappears and reappears. The residual Doppler width is ~1.3 GHz.
7.2 Conditions affecting EIT and AT splitting

Another case is found where EIT, like in the previous section, unexpectedly appears in an open molecular system despite it does not occur in a closed atomic system under otherwise comparable conditions. This experiment, which will be described in a coming work, utilizes a V-type excitation scheme applied to a sodium dimer system.

Maybe a still more unforeseen behavior, however, originates from the relation between the probe and coupling laser frequencies as reported in Paper 6. Initially very surprising, the probe and coupling field wave number ratio is capable of dramatically changing the occurrence of AT splitting, whereas the simultaneously existing EIT is only marginally affected. This anomaly is thoroughly investigated in various Na₂ cascade systems, for example those in Fig. 1, Paper 6. Denoting the probe and coupling laser resonant transition wave vectors with $k_p$ and $k_c$, respectively, it is found that AT splitting of the fluorescence spectrum from the uppermost level of a cascade system is present when $-1 < k_p / k_c < 0$ but absent for other values of the wave vector ratio. The statement is nicely illustrated in Paper 6, Figs. 2 and 3, and we notice the agreement between experiment and simulations based on density matrix formalism. To make doubly sure, the result is theoretically supported through a careful analysis, where the integral, expressing the Doppler averaged signal from the uppermost level of the cascade system, is analytically solved. The summarized mathematical expressions are graphically displayed in Fig. 4, Paper 6 in terms of the threshold Rabi frequency of the coupling field as a function of the ratio $k_p / k_c$. Sophisticatedly the results provide a recipe for optimally resolved AT splitting in a cascade system, when moderate Rabi frequencies, produced by commercially available cw lasers, are accessible. The favourable condition for observing AT effect is to arrange the laser beams in a counter-propagating geometry and choose transitions so that the coupling laser wave number is larger than the one of the probe laser. Under these circumstances the Rabi frequency, required for well pronounced AT splitting, is independent of the residual Doppler line width $\Delta \nu_D$ of the system, as depicted in Paper 6, Fig. 5, based on the mathematical analysis of the Doppler integral.

The peculiar conclusion is that the mere presence of the Doppler broadening provides a gateway to overcome itself, allowing EIT as well as AT splitting to be observed under the right experimental conditions applied to an open molecular cascade system.
References

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