Doctoral Thesis

Four-wave mixing spectroscopy of small carbon clusters

Author[s]:
Sych, Yaroslav

Publication Date:
2014

Permanent Link:
https://doi.org/10.3929/ethz-a-010153020

Rights / License:
In Copyright - Non-Commercial Use Permitted
Four-Wave Mixing Spectroscopy of Small Carbon Clusters

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by
Yaroslav Sych

M. sc., Bauman Moscow State
Technical University

born on 07.05.1983

citizen of Russian Federation

accepted on the recommendation of
Prof. Dr. Alexander Wokaun, examiner
Prof. Dr. Frédéric Merkt, co-examiner
Dr. Peter P. Radi, co-examiner

2014
Declaration of Authorship

I, Yaroslav Sych, declare that this thesis titled, 'Four-Wave Mixing Spectroscopy of Small Carbon Clusters' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree in the Paul Scherrer Institute.

- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.

- Where I have consulted the published work of others, this is always clearly attributed.

- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.

- I have acknowledged all main sources of help.

- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed: ________________________________

Date: ________________________________
Abstract

Molecular states can play the role of "gate-ways" through which the population flows towards thermodynamic equilibrium. After a chemical transformation takes place, the excess energy is released into the environment via molecular motion. Partition functions built on rotational, vibrational and electronic states allow accurate estimation of the standard enthalpy of formation for combustion modeling. Since errors in the heat of formation are translated into errors in the activation energy of equilibrium constants, poorly known thermochemical data can be a serious problem. In contrast to stable molecules where the standard enthalpy of formation is generally accessible from direct calorimetrical measurements, values for radicals stem mainly from spectroscopic experiments (vide infra). Where such experiments are not available, ab initio calculations or estimations based on group additivity or hydrogen bond increments are applied. However, such estimated values must by treated cautiously, substantial uncertainty limits need to be assigned.

In this work we apply nonlinear four-wave mixing spectroscopy for the selective detection of radical species which are relevant for combustion chemistry. For example C₂ and C₃ may play a significant role in the formation of soot and polyaromatic hydrocarbons [1, 2], the formation of carbon nanostructures [3] (e.g. carbon nano-tubes [4], fullerenes [5]) and astro-chemistry [6–8]. In our studies several four-wave mixing energy level schemes are employed to study electronic states of different spin multiplicity relative to the ground state of the respective C₂ and C₃ molecular species. Note that in the dipole approximation it is not possible to couple two states of different spin multiplicities by a single molecule dipole operator $\mu_{xyz}$ due to the $\Delta S = 0$ selection rule. Levels that are inaccessible by optical transitions are called dark states in contrast to the dipole allowed transitions to bright states. Bright states can be detected in linear absorption spectroscopy by observation of the attenuation of the transmitted light or in emission by measuring the fluorescence from excited molecular states. Dark states may appear as weak resonances near strong transitions to bright states but are mostly not observed. However, it is important to mention that dark states can be dynamically active and play an important role in energy transfer processes governing intra- and intermolecular energy redistribution. The aim of this work is to explore advantages of the two-color resonant four-wave mixing spectroscopy (TC-RFWM) for the detection of dark states. Application of TC-RFWM spectroscopy simplifies the evaluation of perturbed spectra due to the $\Delta J = \pm 1, 0$ selection rule, where $J$ denotes the total angular momentum, in the spectral region where the density of molecular states is high. In addition, the TC-RFWM signal is essentially background free because it appears in emission and is scattered in the well-defined "phase matched" direction.
Perturbation effects provide ways to observe dark states via interaction with optically accessible bright states. We perform double resonance two-color four-wave mixing measurements in the spectral range of the "Swan system" ($d^3\Pi_g - a^3\Pi_u$) of the $C_2$ radical. The $d^3\Pi_g - a^3\Pi_u$ transition is observed in the emission of most hydrocarbon flames. In recent work we demonstrate that the vibrational level $d^3\Pi_g, v = 6$ is perturbed by the quintet $1^5\Pi_g$ state [9]. The quintet state is observed through an intensity borrowing mechanism which renders the otherwise inaccessible dark state visible by acquiring partial character of the bright state. In particular, the $1^5\Pi_g$ state gains some triplet character through spin-orbit interaction with the closely spaced $d^3\Pi_g$ state. The narrow band ($\Delta \nu = 0.02$ cm$^{-1}$) PUMP lasers of the same frequency selectively excite levels of a defined angular momentum $J$. The signal photons are generated via the nonlinear polarization induced by the interaction of one PROBE and two PUMP lasers. By intermediate level labeling of a specific $J$-level, it is possible to record a simplified spectrum due to the stringent $\Delta J = \pm 1, 0$ selection rules. On the example of $C_2$ we demonstrate that the combination of the double resonance selection rules and the coherence of the four-wave mixing technique results in a favorable detection of dark states. In spite of the fact that in linear spectroscopy weak resonances can also be detected it is usually hard to assign the spectral lines to a particular dark state due to the congested nature of the recorded spectrum containing intense transitions to the bright states. A rotational analysis of measured TC-RFWM spectra revealed the five spin-levels of the dark $1^5\Pi_g$ state crossing the three spin-levels of the bright $d^3\Pi_g$ state. The presence of the dark $1^5\Pi_g$ state rationalizes the anomalous non-thermal emission observed by Fowler in 1910 [10].

The perturbation facilitated TC-RFWM (PF TC-RFWM) technique is applicable to detect the triplet manifold of the $C_3$ molecule exhibiting a $\tilde{X}^1\Sigma_g^+$ ground state. Excited triplet rovibronic levels are accessed by taking advantage of the strong spin-orbit interaction in the intermediate levels. The addressed $J$-levels occur in the vicinity of the "Comet band" ($\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$) where the bright $\tilde{A}^1\Pi_u$ and the dark $3\Sigma_u^-$ vibronic levels interact. Selective tuning of the PUMP lasers to the intermediate levels with substantial triplet or singlet character facilitates the observation of the respective spin multiplicity levels in the final state. A new triplet vibronic $3\Pi_g$ state (of $3\Delta_u$ electronic symmetry) has been detected [11]. Ab initio calculations for the $C_3$ singlet and triplet states have been performed to confirm the experimental assignments.
Zusammenfassung


Arbeit war es, die Vorteile der resonanten Zwei-Farben Vier-Wellen Mischmethode (TC-RFWM) zur Detektion dunkler Zustände zu nutzen. Die Anwendung der TC-RFWM Spektroskopie vereinfacht die Spektren gemischter Zustände und deren Auswertung in Regionen hoher spektraler Liniendichte aufgrund der $\Delta J = \pm 1,0$ Auswahlregel. TC-RFWM ist im Wesentlichen eine hintergrundfreie Messmethode, da die Signale aufgrund des kohärenten phasenangepassten Anregungsprozesses in eine spezifische Richtung propagieren und deshalb von störenden Lichtquellen örtlich getrennt werden können.

Die Störung "heller" Zustände durch die Kopplung an dunkle Zustände ermöglicht den Nachweis der Letzteren. In dieser Arbeit wurde der spektrale Bereich des $C_2$ "Swan" Bandensystems ($d^3\Pi_g - a^3\Pi_u$) mittels TC-RFWM untersucht. In diesem Zusammenhang konnte die Störung des vibronischen $d^3\Pi_g$, $v = 6$ durch den $1^5\Pi_g$ Quintett Zustand nachgewiesen werden [9]. In diesem Fall erhält der $1^5\Pi_g$ Zustand teilweise Triplet Charakter aufgrund der Spin-Bahn Kopplung zum benachbarten $d^3\Pi_g$ Zustand. Am Beispiel von $C_2$ konnte gezeigt werden, dass die inhärente Kombination von doppel-Resonanz Spektroskopie und kohärenter Signalerzeugung in TC-RFWM einen grossen Vorteil bei der Detektion dunkler Zustände bietet. Obwohl auch mit linearen spektroskopischen Methoden schwache Übergänge zu dunklen Zuständen beobachtet werden können, ist es oftmals schwierig, aufgrund der hohen Liniendichte, die Übergänge den entsprechenden Linien zuzuordnen. Eine detaillierte Rotationsanalyse der gemessenen TC-RFWM Spektren zeigt deutliche Signaturen der fünf Spin Zustände des $1^5\Pi_g$ im Bereich des $C_2$ "Swan" Bandensystems. Der Einfluss des $1^5\Pi_g$ Zustands erklärt die von Fowler [10] und später auch anderen [12–14] beobachteten Anomalitäten im Emissionsspektrum von $C_2$.

Im weiteren Verlauf dieser Arbeit wurden die Triplet Zustände des $C_3$ Radikals mit Hilfe der "perturbation facilitated" TC-RFWM Methode untersucht. Hierbei konnten die $C_3$ Triplet Zustände vom $\tilde{X}^1\Sigma_{g}^+$ Grundzustand via diverser Zwischenzustände, aufgrund der vorliegenden Spin-Bahn Wechselwirkung, angeregt werden. Die für die Übergänge relevanten Zwischenzustände im "Comet Band" ($A^1\Pi_u - X^1\Sigma_{g}^+$) sind Linearkombinationen der hellen ($A^1\Pi_u$) und dunklen ($3\Sigma_{u}^-$) Zustände. Die gezielte Anregung von Zwischenzuständen mit unterschiedlich gewichteter Spin-Multiplizität (Verhältnis Singlett-Triplett Charakter) ermöglicht die Selektion der Endzustände. Mit dieser Methode konnte ein neuer vibronischer Triplet Zustand $3\Pi_g$ nachgewiesen werden [11]. Zusätzlich durchgeführte ab initio Berechnungen bestätigten die experimentellen Ergebnisse.
Acknowledgements

I would like to thank my family and Rita for the constant support during the last years.

I would like to thank the Molecular Dynamics group where I had a pleasure to work for four years:

My supervisor Dr. Peter Radi who was ready to help me in the lab, was patient to explain me the details of the experiment and had introduced me to the field of molecular spectroscopy.

Dr. Gregor Knopp for many work related and unrelated discussions, creative approach to work and granting many ideas for free.

Dr. Peter Bornhauser for the help and profound analysis of the molecular spectra.

Dr. Thomas Gerber for managing our group and keeping the team spirit.

Postdocs Dr. Pavlo Maksyutenko and Dr. Yuzhu Liu for the good times in the dark lab and even better times outside in the sunny day light.

Visiting scientist Dr. Dimitrii Kozlov for suggesting me the group and a moral mentoring during many years.

Prof. Alexander Kouzov for explaining me TC-RFWM theory particularly related to the detection of molecular orientation and alignment.

Prof. Roberto Marquardt for introducing me to the *ab initio* calculations and giving the possibility to perform computations on the "Quantadyn" cluster of the Strasbourg University.

Prof. Alexander Wokaun for accepting me to the PhD position in the General Energy Department.

Prof. Dr. Frédéric Merkt for reviewing my thesis and providing useful corrections.

I would like to acknowledge the Swiss National Science Foundation project # 200020-146387 and 200020-124542/1 for the financial support.
## Contents

<table>
<thead>
<tr>
<th>Acknowledgements</th>
<th>vi</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>x</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xvi</td>
</tr>
<tr>
<td>Symbols</td>
<td>xviii</td>
</tr>
</tbody>
</table>

### 1 Introduction
- 1.1 Structure of the thesis .............................................. 1
- 1.2 Introduction .......................................................... 3
  - 1.2.1 The role of carbon radicals in combustion, space and plasma chemistry ........................................ 3
  - 1.2.2 State-resolved energy transfer between electronic states ........................................ 5
  - 1.2.3 Low-frequency bending motion of $C_3$: isomerization pathway ............................. 6

### 2 Spectroscopy of di- and tri-atomic carbon molecules
- 2.1 Molecular quantum states .............................................. 7
  - 2.1.1 Born-Oppenheimer Approximation .................................... 7
  - 2.1.2 Rotational structure ................................................ 9
  - 2.1.3 Vibrational structure .............................................. 10
  - 2.1.4 Orbitals and electronic states ................................... 11
  - 2.1.5 Electronic transitions ............................................ 13
  - 2.1.6 Vibrational angular momentum ..................................... 15
  - 2.1.7 Vibronically allowed transitions .................................. 16
- 2.2 Perturbations of molecular states .................................... 17
  - 2.2.1 Selection rules for the spin-orbit interaction .................... 17
  - 2.2.2 Intensity borrowing ................................................ 18
  - 2.2.3 Perturbation in $C_3$ Comet band $A^1\Pi_u - \tilde{X}^1\Sigma^+_g$ ..................... 19
  - 2.2.4 Renner-Teller Interaction ........................................ 21

### 3 Light-Matter Interaction: Four-Wave Mixing Spectroscopy
- 3.1 Wave equation .......................................................... 24
  - 3.1.1 Coherent laser pulses ............................................. 24
  - 3.1.2 Spatial transformation of the electric field by optical elements ....................... 26
  - 3.1.3 Polarization expansion in a wave equation ........................................ 27
  - 3.1.4 Density matrix formalism ........................................... 28
3.1.5 Perturbation theory ............................................. 29
3.1.6 Diagrammatic technique ........................................ 32
3.2 Four-wave mixing spectroscopy .................................. 33
  3.2.1 Third order nonlinear polarization ............................ 34
  3.2.2 Rotating wave approximation ................................ 36
  3.2.3 Phase matching .............................................. 37
  3.2.4 Degenerate four-wave mixing spectroscopy ................... 39
  3.2.5 Two-color four-wave mixing spectroscopy ................... 42

4 Experimental setup ................................................. 47
  4.1 Radical source ................................................. 47
    4.1.1 Molecular jet ............................................. 49
    4.1.2 Pulsed discharge nozzle .................................... 51
    4.1.3 Femtosecond ionization of the pulsed discharge products .. 54
  4.2 Spectroscopy in the molecular jet ................................ 55
    4.2.1 Apparatus for nonlinear optical spectroscopy ............. 55
    4.2.2 Two-photon laser induced fluorescence spectroscopy ...... 57

5 Results I: Application of Four-Wave Mixing Spectroscopy to study dark states 60
  5.1 Measurement of a dark quintet state of C2 by applying the UP-TC-RFWM scheme ......................... 60
    5.1.1 Spin-orbit coupling of the 1\(^5\)Π\(_g\), a\(^3\)Π\(_u\), d\(^3\)Π\(_g\) and b\(^3\)Σ\(_g^-\) \text{states} ........ 62
    5.1.2 UP TC-RFWM measurement of the lowest quintet 1\(^5\)Π\(_g\) state ......................... 65
  5.2 Perturbation-facilitated two-color resonant four-wave-mixing spectroscopy of C\(_3\) .......................... 77
    5.2.1 TC-RFWM measurements via perturbed intermediate \(\psi_1\) and \(\psi_2\) states ............................. 79
    5.2.2 Dependence of the RFWM signal intensity on the intermediate state mixing coefficient \(c_J\) .......... 80
    5.2.3 Rotational analysis of the observed 3\(^3\)Π\(_g\) state ........................................ 83
    5.2.4 Saturation behavior of the intermediate states \(\psi_1\) and \(\psi_2\) ................................. 84
    5.2.5 The Spin Filter TC-RFWM measurement ...................... 85
    5.2.6 Comparison between the “Spin Filter” TC-RFWM measurement and Laser Induced Fluorescence ....................... 86

6 Results II: Perturbation-Facilitated Two-Photon LIF 88
  6.1 Perturbation-Facilitated Two-Photon Laser Induced Fluorescence ........................................ 88
    6.1.1 Dispersed LIF from the 3\(^3\)Π\(_g\) vibronic level ........................................ 89
    6.1.2 Vibrational structure of the triplet manifold: signature of the \(\tilde{a}\)\(^3\)Π\(_u\) and \(\tilde{b}\)\(^3\)Π\(_g\) electronic states ......................... 90
  6.2 Comparison between coherent and non-coherent techniques: spatial aspects .................................. 94

7 Results III: Pumped TC-RFWM as a probe of molecular alignment 100
  7.1 Pumped TC-RFWM as a probe of molecular alignment .................................................. 100
    7.1.1 Rotation of field polarization vectors .................................. 101
    7.1.2 Angular momentum anisotropy ................................ 102
    7.1.3 Four-photon expectation value and vector recoupling ........................................... 104
## Contents

7.1.4 Experiment: pumped TC-RFWM response from the P,Q and R resonances ........................................ 108
7.1.5 Calculation: UP TC-RFWM response from the P,Q and R resonances in the presence of anisotropy ............... 110
7.1.6 Comparison of the experimentally measured and computed P, Q and R transitions .................................. 112
7.1.7 P, Q and R line intensities at the high-J limit ................................................................. 114
7.1.8 Laser polarizations for specific detection of molecular alignment .......................................................... 117
7.2 TC-RFWM signal intensity: summary .................................................................................. 119

8 Ab initio quantum chemical calculations .................................................................................. 121

8.1 Potential energy surfaces of the C\textsubscript{2} radical .............................................................. 121
8.1.1 Active Orbital Space of the C\textsubscript{2} radical for the Self-Consistent Field (CASSCF) theory ......................... 121
8.1.2 Excited state energies of the C\textsubscript{2} singlet, triplet and quintet spin-multiplicities ............................. 123
8.1.3 Potential energy surfaces of C\textsubscript{2} quintet manifold .................................................... 123
8.2 Potential energy surfaces of the C\textsubscript{3} radical .................................................................. 125
8.2.1 Active Orbital Space of the C\textsubscript{3} radical for the Self-Consistent Field (CASSCF) theory ................. 125
8.2.2 Excited state energies of the C\textsubscript{3} singlet manifold ............................................................. 126
8.2.3 Excited state energies of the C\textsubscript{3} triplet manifold ........................................................... 126
8.2.4 Symmetric-stretching potential energy surfaces of the C\textsubscript{3} triplet manifold ................................... 127
8.2.5 Bending potential energy surfaces of the C\textsubscript{3} triplet manifold ..................................................... 129
8.2.6 Vibrational frequencies of a C\textsubscript{3} triplet manifold ............................................................... 131
8.2.7 Comparison of ab initio calculations and the PF-RFWM observations ........................................... 131

9 Summary .......................................................................................................................... 134

9.1 Summary ....................................................................................................................... 134

Bibliography ......................................................................................................................... 137
List of Figures

2.1 Formation of the $\tilde{X}^1\Sigma_g^+$ $C_2$ ground state from atomic $2p$ orbitals of the carbon atoms. ........................................ 12

2.2 Walsh’s diagram for the $C_3$ molecule. The abscissa refers to the bending angle between peripheral carbon atoms. The ordinate is the energy of a molecular orbital. ........................................ 12

2.3 a: Classical picture of vibrational angular momentum. b: Vibrational energy-level pattern for the bending mode of a linear molecule. .......................... 16

2.4 The nearly-degenerate four-wave mixing spectrum shows strong P,Q and R resonances from $J'' = 6$ to the bright $\tilde{A}^1\Pi_u$ state. Weak transitions $^5P_1$ and $^9R_1$ to the dark $3\Sigma_u^-$ state are also present due to the spin-orbit interaction between $\tilde{A}^1\Pi_u$ and $3\Sigma_u^-$. Lines caused by the intensity borrowing mechanism are designated with the * and a blue font. The upper (red) trace is a measured spectrum and the lower (green) is a spectrum simulated with inclusion of the spin-orbit interaction between $\tilde{A}^1\Pi_u$, $3\Sigma_u^-$ and an unknown $P = 1$ states [15]. ............................... 20

2.5 The spectrum shows the Renner-Teller splitting in the $\tilde{A}^1\Pi_u$ state of $C_3$ between (01$^0_0$) $\Sigma$ and (01$^2_0$) $\Delta$ components. The upper (red) trace is the measured spectrum and the lower (black) is the simulated spectrum for a 150 K rotational temperature. The degenerate four-wave mixing laser is sampling the population of the vibrationally excited (01$^1_0$) $X^1\Sigma_g^+$ level of the ground state. ............................... 22

3.1 Double-sided Feynman diagrams for absorption (a) and (d) and emission (b) and (c) of a photon. ........................................ 32

3.2 Double-sided Feynman diagrams for the derivation of $\rho^{(3)}$. Note that the last interaction originates from $P = Tr(\mu\rho^{(3)})$ and is not included in the $\rho^{(3)}$. ........................................ 34

3.3 Double-sided Feynman diagrams for the interaction at the ket side with the $\exp(-i\omega_1t)$ and $\exp(i\omega_1t)$ fields. ........................................ 37

3.4 Double-sided Feynman diagrams relevant for the DFWM signal. Note that prime labels of $|g'\rangle$ and $<g'|$ (and the excited level $|i'\rangle$ and $<i'|$) points out one of few possible $m_g$-levels on the ket or bra side respectively. 40

3.5 Energy level diagrams for TC-RFWM spectroscopy: a for the SEP, b for the UNFOLDED and c for the UP energy level schemes. The emitted SIGNAL is drawn with the dashed arrow line. ............................... 43

3.6 Double sided Feynman diagrams for TC-RFWM spectroscopy: a for the SEP, b for the UNFOLDED energy level schemes. ............................... 43

3.7 Double sided Feynman diagrams for the UP TC-RFWM energy scheme. 45
4.1 Scheme of the pulsed discharge nozzle containing the valve, mounted slit-flow body and the discharge assembly (anode (A), isolation plates (I drawn in white color in the figure) and the cathode (C)). The temporal distribution of \( C_2 \) obtained by applying DFWM is given along the axis \( t \). Two traces are shown: the red trace is observed at a longitudinal position of \( z \approx 5 \) mm from the discharge source. The black trace is recorded at a distance of \( z \approx 7 \) mm. In addition, the laser fields in the BOXCAR geometry \( E_1, E_2, E_3 \) and the resulting \( E_4 \) are shown.

4.2 Time-of-flight mass spectrum acquired by fs-ionization in the molecular beam. The discharge is consecutively set ON and OFF yielding two traces whose difference is presented on the figure. Because of a change of the electric field when the discharge is ON the ion optics and the repeller are biased. This leads to a small shift and distortion of the mass-peaks after time-of-flight to mass renormalization.

4.3 Experimental arrangement: \( M \) Mask used for laser beam alignment along the main diagonals of the parallelepiped drawn in dotted lines; \( L_1, L_2 \) 1000 mm focal length focusing and collimating objectives, respectively; \( RS \) Radical source for the generation of \( C_2 \) and \( C_3 \); \( MJ \) Molecular jet, plane of the \( MJ \) is given by the dashed rectangle intersecting the dotted parallelepiped; \( SSF \) Set of spatial filters; \( SF \) Spectral filter; \( PMT \) Photomultiplier tube with the integrated amplifier.

4.4 Experimental setup for simultaneous linear and non-linear spectroscopic measurements. A mask is used for laser beam alignment; \( L_1, L_2 \) 1000 mm focal length focusing and collimating lenses respectively; \( RS \) Radical source for the generation of \( C_2 \) and \( C_3 \); \( MJ \) Molecular jet; \( SSF \) Set of spatial filters; \( SF \) Spectral filter; \( PMT \) Photomultiplier tube with an integrated amplifier. Dispersed fluorescence \( E_{LIF} \) upon perturbation facilitated excitation of the \( 3\Pi_g \) state, i.e. \( 3\Pi_g \leftarrow \Sigma_u^- \leftarrow \tilde{X}^1\Sigma_u^+ \) is imaged by the high numerical aperture \( M_{i1} \) mirror located below the molecular jet and the \( M_{i2} \) mirror located in front of the monochromator \( Mn \). The lens \( L_3 \) focuses the collimated LIF signal onto the monochromator slit \( Mn \). The experimental layout is arranged such that \( MJ \), excitation lasers \( E_1, E_2, E_3 \) and collimated LIF signal \( E_{LIF} \) propagate orthogonally to each other. The corresponding arrangement eliminates first order Doppler broadening and provides supreme efficiency in collecting LIF photons.

5.1 \( 1^5\Pi_g \) - character of perturbed \( d^3\Pi_g, v = 6 \) rotational energy terms. Strongly mixed eigenfunctions are “gateway” states through which population flows from one electronic state to the other.

5.2 DFWM spectrum in the wavelength region of the \( \Delta v = 1 \) sequence bands of the \( d^3\Pi_g - a^3\Pi_u \) electronic system. The bottom trace shows a simulation of the spectral region neglecting perturbations. A comparison with the experimental DFWM shows significant discrepancies. The top trace is a simulation including perturbation effects which has been obtained by the detailed deperturbation analysis in this work. The deperturbed assignments for the three R-subbands, \( R_i(J) \), are shown on the top for two vibronic bands \( (v', v'') \).
5.3 TC-RFWM in the wavelength region of the $\Delta v = 1$ sequence bands of the Swan system. Intermediate level labeling is performed by tuning the PUMP laser to the $R_1(5)$ (upper trace) and $R_2(2)$ (lower trace, inverted) transitions in the $(4,5)$ band, respectively, and scanning the PROBE laser near 21400 cm$^{-1}$. Apart from the intense UP and SEP lines accessed in the $d_3^3\Pi_g - a_3^3\Pi_u$ system, several transitions from the $a_3^3\Pi_u$ state to spin sublevels ($F_i, i = 1...5$) of the quintet state are observed and emphasized in the figure by the shaded area. These dark states gain intensity by the electronic interaction of $d_3^3\Pi_g - 5^3\Pi_u$. Transitions labeled with asterisks denote weak lines in the Swan band with $\Delta \Omega \pm 1$. See text for details.

5.4 Observed term energies of the $d_3^3\Pi_g, v = 6, 1^5\Pi_g$ and $b_3^3\Sigma_g^−, v = 19$ states vs rotational quantum number $J$ (a). The solid lines are computed term values by taking into account the deperturbed molecular constants listed in Table 5.4. Parities are denoted by $⊕$ and $⊖$ signs for e and f levels, respectively, (b) shows an expanded view of the $d_3^3\Pi_g, v = 6 \sim 1^5\Pi_g$ interaction. See text for details.

5.5 Shifts of the perturbed rotational term energies in the $d_3^3\Pi_g, v = 6$ state plotted against the upper state rotational quantum number $J'$ for the three $F$ components. Filled and open circles denote e and f parity, respectively. Note, strong shifts are observed for $J = 4, 5$ and 12 in the $F_1$ sublevel and for $J = 10$ and 11 in $F_2$. For these perturbations both, e and f parity terms are affected simultaneously which is expected for a $5^3\Pi_g$ perturber state. See text for details.

5.6 Energy level diagrams for the (a) UP, (b) SEP, (c) UNFOLDED TC-RFWM scheme and (d) for direct absorption. Schemes (b) and (c) describe SEP and UNFOLDED experiments performed on $C_3$. Gateway mediated intersystem-crossing from the $X^1\Sigma_g^+$ singlet ground state ($|g>^g$) to a triplet final state $|f>^f$ is achieved by the UNFOLDED scheme and selecting the mixed singlet - triplet rovibronic intermediate level $|i>^i$ with $\approx 80\%$ triplet character ($|\psi_2>^\psi$). The spacing of the perturbed level pair is shown exaggerated in the figure. Scheme (d) is the direct absorption experiment.

5.7 Term energies of the $A^1\Pi_u, ^3\Sigma_g^−$ and $P = 1$ states vs rotational quantum number $J$. Parities are denoted by $⊕$ and $⊖$ signs for e and f levels, respectively. Note that the unknown electronic $P = 1$ state perturbs $A^1\Pi_u$ only in the $1 \leq J \leq 3$ range [15]. See text for details.

5.8 SEP transitions by applying TC-RFWM from the ground state (000) $X^1\Sigma_g^+ via |\psi_1>^\psi$ and $|\psi_2>^\psi$ exhibiting $\approx 20$ and $80\%$ triplet character, respectively. P(6) and R(4) are SEP transitions to the vibrationally excited (022) level of the ground state $X^1\Sigma_g^+$. Resonances discussed in the text are emphasized by the shaded area. The lower trace is shifted by 1.72 cm$^{-1}$ unambiguously indicating SEP type transitions.

5.9 UNFOLDED transitions by applying TC-RFWM from the ground state (000) $X^1\Sigma_g^+ via |\psi_1>^\psi$ and $|\psi_2>^\psi$ exhibiting $\approx 20$ and $80\%$ triplet character, respectively. The lower trace is shifted by -1.72 cm$^{-1}$ unambiguously indicating UNFOLDED transitions. Final state transitions are accentuated by the shaded area. The inset shows three relevant Feynman diagrams.
5.10 PFOODR spectrum by tuning the PROBE laser to several overlapping Q lines in the $^3\Pi_g - ^3\Sigma_u^-$ ($= \psi_2$) vibronic system and scanning the PUMP lasers. Exclusively transitions from the ground state $\tilde{X}^1\Sigma_g^+$ to the perturbing $^3\Sigma_u^-$ state are observed showing further evidence that the final state exhibits substantial triplet character. For comparison, a simulation of the Comet band absorption spectrum is shown at the bottom where the significant features are governed by the $\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma_g^+$ transition.

5.11 Comparison between PF-TC-RFWM spectrum and LIF spectrum measured by Zhang et al. [15]. Black (top) trace indicates the excitation LIF experiment. The triangles specify the lines belonging to the perturbing triplet state, while hexagons specify perturbing state $P = 1$. Rather intense lines with no assignment belong to the allowed $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ band transition. The green (inverted bottom) trace demonstrates the spectrum recorded by the PF TC-RFWM experiment, where transitions from the ground state $\tilde{X}^1\Sigma_g^+$ to the perturbing $^3\Sigma_u^-$ state are exclusively observed further simplifying the spectrum.

6.1 Dispersed fluorescence upon perturbation facilitated excitation of the $c_1$ $^3\Pi_g$ state, i.e. $^3\Pi_g \xrightarrow{h\nu_{2}} ^3\Sigma_u^- \xleftarrow{h\nu_{2}} \tilde{X}^1\Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The corresponding Rayleigh peaks from one-photon fluorescence are indicated by arrows. The trace shows the difference signal obtained by switching the second photon ($\nu_2$) on and off. Weak feature marked with the asterisk originate from the third harmonic of the Nd:YAG laser.

6.2 Dispersed fluorescence upon perturbation facilitated excitation of the $c_2$ $^3\Pi_g$ state, i.e. $^3\Pi_g \xrightarrow{h\nu_{2}} ^3\Sigma_u^- \xleftarrow{h\nu_{2}} \tilde{X}^1\Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The corresponding Rayleigh peaks from one-photon fluorescence are indicated by arrows. The trace shows the difference signal obtained by switching the second photon ($\nu_2$) on and off. The $C_2$ feature is the fluorescence from the high-$J$ of the Swan band $d^3\Pi_g - a^3\Pi_u$ excited due to the overlap with the $\nu_2$.

6.3 Dispersed fluorescence upon perturbation facilitated excitation of the $d^3\Pi_g$ state, i.e. $^3\Pi_g \xrightarrow{h\nu_{2}} ^3\Sigma_u^- \xleftarrow{h\nu_{2}} \tilde{X}^1\Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The blue trace labeled as (#)10 $\mu$s is recorded by the two-photon excitation i.e. $2h\nu_{1}$ energy. The emitted photons are detected by the PMT and averaged with the BOXCAR integrator over 10 $\mu$s. Note that all traces are shifted relative to the $c_2$ $^3\Pi_g$ vibronic level.

6.4 Energy level and Feynman diagrams for PF TC-RFWM spectroscopy shown in the figure a and two-photon LIF shown in the figure b.

6.5 Energy level diagrams 1 and 2 for the two competing $Im\{\chi_{1}^{(3)}\}$ and $Im\{\chi_{2}^{(3)}\}$ processes respectively.

6.6 Comparison of the PF TC-RFWM measurement and the depletion of the two-photon LIF excitation. The red trace is measured by integrating on the oscilloscope the 7 ns photo-current pulse generated by the FWM signal. The black (inverted) trace corresponds to the depletion LIF signal that is measured by detecting LIF emission at 27979 cm$^{-1}$ (357 nm) from the doubly $2h\nu_1$ excited (#) level and scanning the $\nu_2$ over the $c_2$ $^3\Pi_g$-$^3\Sigma_u^-$ transition. Furthermore, the signal is averaged by the BOXCAR integrator over 10 $\mu$s.
7.1 The trace a shows a pumped UP TC-RFWM spectra from the vibronic $3\Sigma_u^-$ state. The PUMP TC-RFWM laser is tuned to the $c_1 P(5)\, 3\Pi_g^0 - 3\Sigma_u^-$ transition (as depicted by the blue arrows on the energy level diagram). Subsequently, the PROBE laser is scanned in the 21140-21150 cm$^{-1}$ range (denoted by the red arrows in the inset) and characterized by the $c_2 P(5)\, 3\Pi_g^0 - 3\Sigma_u^-$ transition. The trace b shows a pumped UP TC-RFWM from the $3\Sigma_u^-$ where the PUMP laser is resonantly tuned to the $c_1 Q(5)\, 3\Pi_g^0 - 3\Sigma_u^-$ transition and the PROBE is scanned in the vicinity of the $c_2 P(5)\, 3\Pi_g^0 - 3\Sigma_u^-$ transition. The trace c is recorded by applying an UNFOLDED TC-RFWM measurement and contains $P$, $Q$ and $R$ transitions measured by scanning the PROBE laser frequency.

7.2 The trace a shows pumped UP TC-RFWM from the (02$^1$0)$\tilde{A}\, ^1\Pi_u$ with the PROBE laser resonantly tuned to the (14$^3$0$^+$)$^1\Delta_g$ state by the $P(5)$ transition (given with blue arrows on the energy level diagram). The PUMP laser is scanned in the 19400-19450 cm$^{-1}$ range providing the red trace a and b (given with red arrows on the energy level diagram). The trace b shows pumped UP TC-RFWM from the (02$^1$0)$\tilde{A}\, ^1\Pi_u$ with the PROBE laser resonantly tuned to the (14$^2$0)$^1\Delta_g$ state by the $Q(5)$ transition. The trace c is recorded by applying UNFOLDED TC-RFWM measurement and contains all resonances which correspond to the Renner-Teller components of the (12$^6$0) vibronic levels of the electronic $^1\Delta_g$: $\Sigma^+_g\, (4), \Sigma^+_g\, (6)$ rovibronic levels belong to the (12$^0$+0) vibronic level, $\Delta_g\, (4), \Delta_g\, (5), \Delta_g\, (6)$ belong to the (12$^2$0) and $\Sigma_g\, (5)$ belongs to the (12$^0$−0) vibronic level.

7.3 UP TC-RFWM nonlinear optical response $< O_{4321} >$ (evaluated according to Eq. 7.25) dependence on the total angular momentum quantum number $J$ for different branch selections. The first letter in each inset corresponds to the PUMP laser which is tuned to the $P, Q$ and $R$ transition for inset a, b and c, respectively. The second letter corresponds to the PROBE transition. A solid line represents the response $< O_{4321} >^{(0)}$ from the molecular population. Dashed line represents the response $< O_{4321} >^{(2)}$ from molecular alignment. The evaluated response for the PROBE laser are depicted for $P, Q$ and $R$ transitions in blue (squares), green (circles) and red (triangles) respectively.

7.4 UP TC-RFWM $| < O_{4321} > |^2$ evaluated for arbitrary polarization angles from $-90^\circ$ to $90^\circ$ of the PROBE laser. Each inset contains the polarization vectors written as $X - XY$ $40^\circ$ $V$ $80^\circ$, where the first $X$ is $0^\circ$ polarization of the excitation laser. The following notation $XY, 40^\circ, V, 80^\circ$ maps directly onto the order of the polarization unit vectors $\varepsilon_1^X, \varepsilon_3, \varepsilon_2^X, \varepsilon_1$ entering the polarization tensor $F_Q^{K(\varepsilon)}(\varepsilon_1^X, \varepsilon_3, \varepsilon_2^X, \varepsilon_1; k_1, k_2)$ given in Eq. 7.18 for the TC-RFWM. $XY$ are both $0^\circ$ and $90^\circ$ polarizations of the TC-RFWM signal field $\varepsilon_1^X$, $40^\circ$ and $80^\circ$ are polarizations of the PUMP fields $\varepsilon_3$ and $\varepsilon_1$ respectively. The PROBE beam polarization $\varepsilon_2^X$ is varied and assigned as $V$. Insets a and b correspond to the QQ branch selection and inset c and d to the PP branch selection. Solid red curve represents the $| < O_{4321} > |^2$, dashed blue is $| < O_{4321} >^{(0)} |^2$ and dotted green curve is $| < O_{4321} >^{(2)} |^2$.

8.1 Potential energy curves as a function of the symmetric stretching coordinate for linear $C_3$ in a triplet manifold. Potential energy curves are calculated by the ab initio MRCI method in $D_{2h}$ point group.
8.2 Potential energy curves as a function of the bending coordinate for C\textsubscript{3} triplet excited states. Potential energy surfaces are calculated by the \textit{ab initio} MRCI method in C\textsubscript{2v} point group with the bond length fixed to 1.3\Angstr. Two states 4\textsuperscript{3}A\textsubscript{2} and 4\textsuperscript{3}B\textsubscript{1} are given in bold lines (in the notation where the C\textsubscript{2} axis is perpendicular to the molecular axis at linearity, see text for details). ................................................................. 130
## List of Tables

2.1 Comparison of energy and time for different molecular motions in carbon trimer ............................................. 8  
2.2 Character table of the $D_{2h}$ group .................................................. 14  
2.3 Product table for the $D_{2h}$ point group ........................................... 15  
5.1 TC-RFWM transitions to $d^3\Pi_g, v = 6 \text{ (cm}^{-1})$ .................................................. 69  
5.2 TC-RFWM transitions to $1^5\Pi_g \text{ (cm}^{-1})$ .................................................. 70  
5.2 cont’d, TC-RFWM transitions to $1^5\Pi_g \text{ (cm}^{-1})$ .................................................. 71  
5.3 TC-RFWM transitions to $b^3\Sigma_g^-, v = 19 \text{ (cm}^{-1})$ .................................................. 71  
5.4 Optimized molecular constants for the $1^5\Pi_g, d^3\Pi_g, v = 6$ and the $b^3\Sigma_g^-, v = 19$ states. All values are in cm$^{-1}$. The origin, $T$ is relative to the $a^3\Pi_u, v = 0$ level. Numbers in parenthesis are one standard deviation. $^a$Ref. [16], $^b$ listed values are for $v = 0$ Ref [17], $^c$ extrapolated from the results in Ref. [18] .................................................. 72  
5.5 Molecular constants for the $3\Pi_g$ vibronic level. All values are in cm$^{-1}$. The origin, $T$, is relative to the $(0,0,0)$ $X^1\Sigma_g^+$ state. For comparison, constants for the two known triplet states $\tilde{a}$ and $\tilde{b}$ are reproduced from Ref. [19] .................................................. 84  
5.6 Oscillator strength, transition dipole moment and saturation intensities .................................................. 85  
6.1 The energy levels of the triplet manifold observed via two-photon LIF given in cm$^{-1}$ relative to the $\tilde{X}^1\Sigma_g^+$. .................................................. 99  
7.1 The estimated nonlinear optical response of the population at $K = 0$, alignment $^a K = 2, |< O_{4321} >|^2$ for the UP TC-RFWM and nonlinear optical response from the isotropic contribution in the UNFOLDED TC-RFWM experiment. .................................................. 112  
7.2 Comparison of the modulus squared nonlinear optical response Eq. 7.25 for the UP, UNFOLDED TC-RFWM and line strengths $S^b$. The TC-RFWM PUMP is tuned to the $P(5)$ transition for both UP and UNFOLDED energy schemes. .................................................. 114  
8.1 Symmetry product table for carbon atomic orbitals .................................................. 122  
8.2 MRCI energies at the $r_e$ Å bond length in $D_{2h}$ point group for the $C_2$ molecule. A comparison with the experimentally observed origin $T_o^0$ is provided .................................................. 123  
8.3 $C_{2v}$ symmetry product table of the $C_2 1\Sigma_g^+ (A_1)$ ground state and a first excited $3\Pi_u$ state with the $C_3^3P_0$ states ($A_2, B_1, B_2$) .................................................. 125  
8.4 Electronic term values of $C_3$ calculated at the MRCI level of theory, at a fixed bond length of $r = 1.2950$ Å and linear geometry .................................................. 127
List of Tables

8.5 Comparison of CASPT2 calculated $T_e$ and MRCI energies at $r = 1.2950$ Å bond length in $D_{2h}$ point group for the $C_3$ triplet manifold and observed $T_f$ .................................................. 128

8.6 Vibrational frequencies calculated for excited triplet states in $C_s$ point group ............................................................... 132
Symbols

$x$ scalar
$v$ vector or tensor
$T^{(n)}$ tensor of rank $n$

$B_e$ rotational constant in a fixed electronic configuration
$c$ speed of light
$D(\omega;\omega_1,-\omega_2,\omega_3)$ resonant denominator for the four-wave mixing process
$d_i$ degeneracy of $i$-th mode
$E(t)$ total electric field
$E(\omega)$ Fourier transform of $E(t)$
$F_{Q}^{(K)}$ four-wave mixing polarization tensor
$h$ Planck constant
$h = h/(2 \cdot \pi)$ Dirac constant
$\hat{H}$ Hamiltonian operator
$\hat{H}_0$ unperturbed Hamiltonian operator
$I$ field intensity
$I_{sat}$ saturation intensity
$I_{a,b,c}$ moment of inertia along the three principal axes (a,b,c) in the molecular frame
$k_B$ Boltzmann constant
$k$ wave vector of the electromagnetic wave
$L(\omega)$ velocity averaging integral
$\hat{L}$ electronic orbital angular momentum operator
$l$ vibrational angular momentum quantum number
$M$ Mach number
$m_e$ electron mass
$m_g$ magnetic quantum number for sublevels $g$
$N$ number density
$N_{\alpha_gJ_g}$ total population of the selected rovibronic level
Symbols

\(< O^{(K)} >\)  
nonlinear optical response of rank \(K\)

\(P(t)\)  
total polarization

\(P^{(n)}(t)\)  
n-th order component of total polarization

\(R\)  
gas constant

\(\dot{R}\)  
rotational angular momentum operator

\(R_{Q}^{(K)}\)  
response tensor

\(r_{e}\)  
equilibrium bond length

\(r_{ij}\)  
electron coordinates

\(r_{\alpha\beta}\)  
nuclear coordinates

\(\hat{S}\)  
spin angular momentum operator

\(\hat{T}_{N}(R, \theta, \varphi)\)  
the nuclear kinetic energy operator

\(\hat{T}_{e}(r_{ij})\)  
the electron kinetic energy operator

\(< T_{Q}^{(K)} >\)  
state multipole expansion of the density matrix with \(2K + 1\) mulipole components for each rank \(K\) and integer index \(Q\) restricted to \(-K\ldots + K\)

\(T\)  
temperature

\(\hat{V}(r, R)\)  
electrostatic potential energy operator for the nuclei and electrons

\(W\)  
molar average molecular weight

\(Z\)  
collisional frequency

\(\gamma\)  
heat capacity ratio

\(\Delta k\)  
phase mismatch

\(\delta_{gg'}\)  
canonical Kronecker delta symbol

\(\varepsilon\)  
polarization unit vector of the electric field

\(\chi^{(n)}\)  
n-th order susceptibility

\(\varepsilon_{0}\)  
vacuum permittivity

\(\Gamma_{ee}\)  
coherence decay rate of \(e\) level

\(\Gamma_{eg}\)  
population decay rate between levels \(e\) and \(g\)

\(\rho\)  
density matrix

\(\omega\)  
angular frequency

\(\hbar \cdot \omega\)  
the energy of a photon with angular frequency \(\omega\)

\(\omega_{i}\)  
wavenumber of \(i\)-th vibration

\(\sigma\)  
collisional cross section

\(\mu_{\alpha}\)  
component of the electric transition dipole moment \(\alpha = (x, y, z)\)

\(\mu\)  
reduced mass

\(\phi_{el}, \phi_{vib}, \phi_{rot}\)  
electronic, vibrational and rotational eigenfunctions, respectively

\(\bar{\psi}_{1}, \bar{\psi}_{2}\)  
unperturbed wavefunctions

\(\psi_{1}, \psi_{2}\)  
perturbed wavefunctions
Chapter 1

Introduction

1.1 Structure of the thesis

In the introductory chapter 1 the role of carbon radicals in combustion, space and plasma chemistry is reviewed. The state-to-state energy transfer is discussed with the focus on the perturbation assisted energy-transfer between different electronic states. This example highlights potential application of TC-RFWM for the detection of ”gateway” levels. Such levels are mixed e.g. by spin-orbit interaction and allow population to flow between two electronic states of different spin multiplicities.

The spectroscopy of C$_2$ and C$_3$ molecules is discussed in chapter 2. The electronic state symmetries for the ground and few excited states of di- and tri-carbon radicals are introduced. The Born-Oppenheimer approximation and perturbation theory (non-Born-Oppenheimer interactions) are considered for the discussion of perturbed spectra. Selection rules are given in the section 2.1.5 for electric dipole moment transitions between two electronic states. Vibronically allowed transitions are examined based on the example of the linear triatomic C$_3$ molecule in the section 2.1.7.

Chapter 3 introduces a diagrammatic technique followed by the discussion on degenerate resonant four-wave-mixing and two-color resonant four-wave mixing spectroscopy. The nonlinear polarization created by the resonant interaction of three laser beams in the molecular ensemble is described as spatial population and coherence gratings (laser induced gratings - LIGs). Feynman diagrams are used to obtain the DFWM and TC-RFWM signal dependence on the PUMP and PROBE laser intensity, the polarization and the detuning of the electromagnetic radiation frequency from the molecular resonance.
Chapter 4 describes the experimental setup. The molecular beam apparatus and the pulsed slit discharge nozzle for the production of small carbon C$_2$ and C$_3$ radicals are introduced. The chemical mechanisms to produce reactive carbon C$_2$, C$_3$ and C$_2$H species are considered. The optical layout for the FWM measurements in the molecular beam is explained. The iterative adjustment procedure for tracing the signal beam to the detector is presented and based on the visible by eye four-wave mixing signal generation in a dye cell. The experimental setup for a multiplexed detection of the TC-RFWM signal and two-photon perturbation facilitated laser induced fluorescence (PF-LIF) is described.

Chapter 5 is dedicated to measurement results. Section 5.1.2 illustrates the experiment and spectroscopic analysis of the lowest quintet state of the C$_2$ molecule by the UP TC-RFWM scheme. In section 5.2 the perturbation-facilitated TC-RFWM is applied to access the triplet (dark) manifold from the C$_3$ $\tilde{X}^1\Sigma^+_g$ ground state. The observation of a newly found $3\Pi_g$ vibronic levels (assigned to the electronic $3\Delta_u$ state) employs a two-step excitation via singlet-triplet mixed “gateway” levels. The TC-RFWM signal dependence on the intermediate state mixing coefficients is emphasized. Molecular constants are determined from the rotationally resolved spectra.

In chapter 6 the application of the Perturbation-Facilitated Two-Photon Laser Induced Fluorescence (PF - Two-Photon LIF) to study vibrational dynamics of the C$_3$ molecule in the triplet manifold is discussed. A comparison between coherent i.e. TC-RFWM and non-coherent i.e. LIF techniques is presented.

In chapter 7 the application of pumped UP TC-RFWM to measure molecular anisotropy is discussed. A laser with linear polarization resonantly excites the population from the ground $\tilde{X}^1\Sigma^+_g$ to the $\tilde{A}^1\Pi_u$ and $3\Sigma^-_u$ states of the C$_3$. Due to the difference in dipole moment transition for magnetic sublevels, the excited state contains a disparity in the population between eigenstates which differ by $|m_g|$ (alignment). The alignment of magnetic sublevels is measured by the UP TC-RFWM energy level scheme and compared to the UNFOLDED TC-RFWM applied from the $\tilde{X}^1\Sigma^+_g$ ground state with an isotropic distribution in the molecular ensemble.

In chapter 8 ab initio quantum chemical calculations are explained. These calculations complement the analysis of the experimentally measured $1^5\Pi_g$ quintet electronic state in C$_2$ and $3\Delta_u$ triplet electronic state in C$_3$. Computations in the D$_{2h}$ point group facilitate the assignment of the electronic symmetry. The potential energy surface corresponding to the symmetric stretching coordinate is determined by iteratively extending the internuclear bond length. Computations in the C$_{2v}$ point group of the bent C$_3$ molecule provide estimates of the bending vibrational frequency. The angle-dependent energy difference between irreducible representations which constitute the same electronic state in
linear geometry and gradually increases upon bending can be regarded as a zero-order measure of the Renner-Teller interaction. For the asymmetric stretching coordinate computations are performed in the C$_S$ point group.

Chapter 9 contains a brief summary of the results.

1.2 Introduction

The application of the two-color resonant four-wave mixing (TC-RFWM) technique is demonstrated on the small carbon radicals C$_2$ and C$_3$. The data obtained from the TC-RFWM experiment on the C$_2$ molecule indicate a state-selective energy transfer via a curve crossing between the $d^6\Pi_g$, $v = 6$ and the $1^5\Pi_g$ state. The newly found curve crossing explains the underlying mechanism of the high pressure bands [20]. The “gateway” model initially developed by Gelbart and Freed [21] suggests that intramolecular interactions such as spin-orbit perturbation between electronic states may have an important effect on the luminescence behavior of small molecules. High-resolution TC-RFWM spectra measured in the spectral region of the perturbation reveal essential details of the interaction between the electronic states.

Furthermore, the development of PF TC-RFWM is demonstrated on C$_3$. The nonlinear dependence of the four-wave mixing signal on the singlet-triplet mixing coefficient of the intermediate state (“gateway”) is utilized to determine a new excited $3\Pi_g$ state. The observation of the dark triplet manifold of C$_3$ is facilitated by a spin-orbit perturbation in the “Comet band” ($\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$). The importance of the excited triplet states for the isomerization of the linear carbon trimer to an equilateral triangular structure has been pointed out by Fueno and Taniguchi [22] and others [23, 24]. The multi-photon TC-RFWM spectroscopy and perturbation-facilitated two-photon laser induced fluorescence have the potential to observe the lowest equilateral triplet state which is expected at 1.0-1.88 eV above the linear ground state [22–24]. It is shown in the following, that in addition to switching the spin- multiplicity of the final rovibronic level (probed relative to the ground level), multiphoton techniques are able to provide information on PES that are inaccessible by one-photon experiments. Spectroscopic information extracted from such experiments yields knowledge on the unimolecular isomerization reactions.

1.2.1 The role of carbon radicals in combustion, space and plasma chemistry

Emission from small carbon radicals has been observed in different environments ranging from hot ($T_{rot} \approx 1500$ K) hydrocarbon flames to low temperature ($T_{rot} \approx 10-20$ K)
interstellar medium. The spectral signature of the C$_2$ “Swan band” ($d^3\Pi_g - a^3\Pi_u$) is detected in most flames containing carbon. Spontaneous emission from C$_2$ ($d^3\Pi_g$) and C$_3$ ($\tilde{A}^1\Pi_u$) was also detected by irradiating soot particles at 532 nm [25]. At low fluences (< 0.22 J cm$^{-2}$) the spectra are featureless and are dominated by incandescence from the soot. Above 0.25 J cm$^{-2}$, features on top of the broadband incandescence signal become apparent. The evaporation of carbon species via multiphoton excitation with 532 nm laser radiation raises the question, whether carbon radicals are directly ejected from the surface of a soot particle in the excited electronic state or whether there are more contributing mechanisms (such as multi-photon laser-induced fluorescence of thermalized C$_2$ ($\tilde{X}^1\Sigma^+_g$) and C$_3$ ($\tilde{X}^1\Sigma^+_g$) or chemiluminescence).

Crossed molecular beam experiments have been performed by Kaiser et al. [1] on C$_2$ / C$_3$ and unsaturated hydrocarbons such as acetylene, methyl-acetylene, or ethylene. Reaction paths leading to the formation of hydrogen deficient hydrocarbon radicals have been inferred. The combination of experimental data and ab initio calculations suggests an addition of C$_2$ / C$_3$ to the unsaturated hydrocarbons, hence forming unsaturated cyclic structures. The authors conclude that the addition reaction i.e. C$_2$(\tilde{X}^1\Sigma^+_g) + C$_2$H$_4$ has no entrance barrier and is strongly exothermic. This is in contrast to the C$_3$ ($\tilde{X}^1\Sigma^+_g$) + C$_2$H$_4$ reaction, which proceeds over a 26.4 kJ mol$^{-1}$ barrier. Hence, the latter reaction is kinetically favorable only in a high temperature environment (T$_{rot} \geq$ 2200 K) [2]. A precise knowledge of the ground state PES for carbon radicals is essential for an accurate estimate of the rate constants of the above mentioned reactions. The application of a stimulated emission pumping (SEP) TC-RFWM scheme is demonstrated below and yields information on the $\tilde{X}^1\Sigma^+_g$ ground state of C$_3$. Molecular constants of vibrationally excited states can be determined with a high accuracy thereby providing the information on the thermodynamically relevant ground-state PES.

The first observation of the emission spectrum of C$_3$ at 405 nm in space was made by Huggins in 1882 [26]. Emission in the same spectral range was found in carbon stars and in the interstellar medium [7, 27]. In 1951 Douglas and co-workers synthesized C$_3$ in the laboratory [28] and an initial spectroscopic analysis of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$ band has been performed by Gausset et al. [29]. The linear C$_3$ is a remarkably stable molecule with an unusually large amplitude bending motion in its ground state (the bending vibrational wavenumber is 63 cm$^{-1}$). This large-amplitude motion creates a high density of vibrational states which has important consequences for the formation of carbon clusters. For example, since a large amplitude motion probably does not occur for the cyclic isomers, the formation of linear carbon chains is entropically favored for most conditions even when cyclic structures are thermodynamically more stable [30]. Clusters with $\pi_u$ symmetry orbitals exhibit constructive overlap of valence orbitals when the molecule is bent about the center of symmetry increasing the bending vibrational
amplitude. The bending motion of clusters with highest occupied molecular orbitals of $\pi_g$ symmetry on the contrary results in a destructive overlap destabilizing the bent configuration [30].

1.2.2 State-resolved energy transfer between electronic states

One of the first models which accounted for collision induced energy transfer between different electronic states that incorporates state mixing by perturbations was put forth by Gelbart and Freed in 1973 [21]. It is possible to quantify electronic state and $J$-dependent cross-sections with the help of a “gateway” model which accounts for the level dependent mixing between interacting states. The cross-sections for collision-induced transitions between levels of total angular momentum $J$ and $J'$ in two different electronic states $E$ and $E'$ are given in Eq. 1.1. This model introduces the intramolecular energy redistribution in a context of the perturbation-assisted “gateway mechanism” [31] between electronic states denoted by $E$ and $E'$.

\[
\sigma_{EJ,E'J'} \approx \sigma_{EJ,EJ'} c_{EE'}(J')^2 + \sigma_{E'J,EJ'} c_{EE}(J)^2
\]  

(1.1)

$\sigma_{EJ,EJ'}$ and $\sigma_{E'J,EJ'}$ are cross-sections for collision-induced pure rotational transitions in the respective electronic states. $c_{EE'}(J')$ and $c_{EE}(J)$ are the mixing coefficients between corresponding $E \sim E'$ electronic states. In this work we will focus on a particular class of non-Born-Oppenheimer interactions [32] between $E$ and $E'$ states which allows a mixing of the spin-quantum number $S$. From the Eq. 1.1 we see that the magnitude of the cross-section for collision induced electronic transitions depends on a pure rotational transition cross-section multiplied by the electronic state mixing coefficient of either the final $c_{EE'}(J')$ or initial $c_{EE}(J)$ rotational level. The model can be illustrated by a Gedankenexperiment where the population is prepared in the excited electronic state (e.g. by means of a chemical or photo-chemical reaction) and the radiative decay to the ground state is prohibited by the spin selection rule $\Delta S = 0$. In other words the excited state is a metastable state with a long life time. There will be no emission from such a metastable state unless some levels are mixed, for example by spin-orbit interaction with a nearby state which has optically allowed transition to the ground state. Mixed levels will serve as “gateways” through which population flows between the electronic states.

In this work we examine advantages of the TC-RFWM technique for the detection of dark states which become dipole allowed due to the intensity borrowing mechanism. These levels appear as weak spectral features that originate from the dark states gaining transition strength through the interaction with a bright state. This mechanism is called
intensity borrowing and has been recently reviewed by Lefebvre-Brion and Field [32].

The application of TC-RFWM to the numerous perturbations in the “Swan bands” \((d^3\Pi_g - a^3\Pi_u)\) of the \(C_2\) radical unveiled the presence of the energetically lowest high-spin state in the vicinity of the \(d^3\Pi_g, v = 6\) vibrational level [9]. It can be shown that this level is responsible for a non-thermal emission of \(C_2\). The so-called “high-pressure bands” were detected more than hundred years ago [10] and appear in numerous plasma reactions (e.g. \(C_3^* + N \rightarrow CN + C_2\), \(C_2O + C \rightarrow C_2(d^3\Pi_g, v = 6) + CO\), or in a reacton of \(CM + C \rightarrow C_2(d^3\Pi_g, v = 6) + M\), where \(M\) is alkali metal molecule [33, 34]). The non-thermal emission from \(C_2(d^3\Pi_g, v = 6)\) has been observed in a low-pressure discharge of CO (≈ 0.4 kPa) [35]. It has been argued that the collision of two carbon atoms may lead to the \(C_2(1^5\Pi_g)\) final product [13].

1.2.3 Low-frequency bending motion of \(C_3\): isomerization pathway

The specific ground-state dynamics of \(C_3\) have been subject to intense studies [30, 36–40]. A rovibrational analysis confirmed the linear ground-state structure [29] with a low bending vibrational energy. The ground-state PES has been found to be anharmonic [37, 41]. Rohlfing and co-workers [37] applied stimulated emission pumping spectroscopy with the PUMP frequency tuned to the \(\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+\) band system and observed the depletion signal of the DUMP laser scanning through the bending vibrational progressions with two and four quanta in the asymmetric stretching mode [37]. The studies revealed that the bending potential of \(\tilde{X}^1\Sigma_g^+\) exhibits a barrier to linearity if the asymmetric stretching vibration is excited. On the contrary the symmetric stretching vibration in \(\tilde{X}^1\Sigma_g^+\) can be well described by a harmonic potential [41].

The interesting possibility of the \(C_3\) isomerization via the bending vibration was examined by applying \textit{ab initio} calculations [22–24]. The lowest triplet state of the equilateral triangular structure is predicted at 1.0-1.88 eV above the linear ground state, hence this state would be the lowest excited electronic state of \(C_3\). Recent \textit{ab initio} calculations [42] analyse reactions of several radicals such as \(C(3P) + C_2H(X^2\Sigma^+)\) and \(CH(X^2\Pi\Omega) + C_2(X^1\Sigma_g^+)\) to the formation of linear l-\(C_3\) and cyclic c-\(C_3\) molecules. Authors [42, 43] report a barrierless additions of the respective radicals to generate c-\(C_3H(X^2B_1)\) and l-\(C_3H(X^2\Pi\Omega)\) intermediates with high exothermicities. Both the cyclic and the linear \(C_3H\) dissociate into the l-\(C_3\) as a major reaction product and the c-\(C_3(X^3A_2')\) as a minor reaction product and the H(\(^2S_{1/2}\)) atom.
Chapter 2

Spectroscopy of di- and tri-atomic carbon molecules

2.1 Molecular quantum states

This chapter follows closely the book “Spectra of atoms and molecules” written by P. F. Bernath [44]. Selection rules for one-photon spectroscopy are discussed for electronic and vibronic transitions. Perturbations arising due to the spin-orbit interaction between electronic states of different spin-multiplicity ($\Delta S = \pm 1$) are discussed based on the chapters 3-5 of the book “The Spectra and Dynamics of Diatomic Molecules” written by H. Lefebvre-Brion and R.W. Field [32]. For linear triatomic molecules the Renner-Teller effect is discussed by pursuing the book “The Jahn-Teller Effect” written by I. Bersuker [45]. Both spin-orbit interaction and the Renner-Teller effect are essential for the analysis of the observed spectra of $C_3$.

2.1.1 Born-Oppenheimer Approximation

The time independent Schrödinger equation is given by the non-relativistic Hamiltonian $\hat{H}$ which can be approximated by the sum of three operators

$$\hat{H} \psi = E \psi$$

$$\hat{H} = \hat{T}_N(R, \theta, \varphi) + \hat{T}_e(r_{ij}) + \hat{V}(r_{ij}, R)$$

$\hat{T}_N(R, \theta, \varphi)$ is the nuclear kinetic energy operator, $\hat{T}_e(r_{ij})$ is the electron kinetic energy operator, $\hat{V}(r, R)$ is the electrostatic potential energy operator for the nuclei and
electrons. \( R \) is the internuclear distance in case of diatomic molecules (for polyatomic molecules \( R \) should be substituted by the difference \( r_{\alpha \beta} \) between corresponding nuclear coordinates \( \alpha \) and \( \beta \)), \( \theta \) and \( \varphi \) determine the orientation of the internuclear axis relative to the laboratory coordinate system and \( r_{ij} \) specifies electron coordinates in the molecule fixed system. It is apparent that the Hamiltonian becomes complex with the increase of the number of atoms and electrons. However in many cases it is possible to separate the complete Hamiltonian into a sum of operators which describe independent parts of the molecular system \( \text{i.e.} \) an electronic \( \hat{H}_{\text{el}} \), a vibrational \( \hat{H}_{\text{vib}} \), a rotational \( \hat{H}_{\text{rot}} \) and a nuclear spin \( \hat{H}_{\text{ns}} \). The eigenstates of the molecular system are defined by a solution of the Schrödinger equation. Additional couplings \( \text{e.g.} \) spin-orbit interaction arising due to a non-relativistic term of the Hamiltonian (not shown) are regarded as perturbations. Similarly coupling of nuclear motion to the electronic motion such as the Renner-Teller effect in linear molecules is solved with additional operators and is treated in general as a perturbation.

Table 2.1: Comparison of energy and time for different molecular motions in carbon trimer.

<table>
<thead>
<tr>
<th>Molecular motion</th>
<th>Energy</th>
<th>Time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons</td>
<td>25000 cm(^{-1})</td>
<td>( \leq 1.3 ) fs</td>
</tr>
<tr>
<td>Vibrations</td>
<td>100-1500 cm(^{-1})</td>
<td>300-10 fs</td>
</tr>
<tr>
<td>Rotations</td>
<td>1-10 cm(^{-1})</td>
<td>30-3 ps</td>
</tr>
</tbody>
</table>

The Coulombic forces acting on the nuclei and on the electrons are similar in magnitude, but the electrons have much lighter mass, therefore, move much faster. The time-scales listed in the Table 2.1 show that the nuclear motion differs by few orders of magnitude compared to the fast orbital motion of the electrons. Hence it is possible to treat the nuclei as being static and solve the time independent Schrödinger equation for the operators involving only electronic degrees of freedom.

In order to calculate molecular vibrations the nuclear coordinates are changed and the equation for the electronic motion is solved. This results in different numerical values of the total electronic energy and different wavefunctions. As the nuclei move the electrons move so quickly that the total electronic energy serves as a potential energy for the nuclear motion. Similarly because molecules rotate much slower compared to a vibrational motion, it is possible to describe the molecular rotation according to the rotation of a rigid body with an average internuclear distance.

\(^{12}\)C is the most abundant isotope and accounts for 98.89% of carbon in nature. As a consequence \( \text{C}_2 \) and \( \text{C}_3 \) molecular species have a nuclear spin \( \hat{H}_{\text{ns}} = 0 \) because both molecules are composed mainly of \(^{12}\)C carbon atoms with an even number of protons \( Z = 6 \) and neutrons \( N = 6 \). Hence, the total nuclear spin is zero \( I = 0 \).
\[ \hat{H} = \hat{H}_{el} + \hat{H}_{vib} + \hat{H}_{rot} \]  
\[ \psi = \phi_{el}\phi_{vib}\phi_{rot} \]  
\[ E = E_{el} + E_{vib} + E_{rot} \]  

The time-independent Schrödinger equation is solved separately for each energy operator. In the next subchapters a separate treatment of the energy terms in Eq. 2.3 is presented. The electronic structure of the \( \text{C}_2 \) molecule is introduced. The vibrational energy \( E_{vib} \) is discussed with the example of \( \text{C}_3 \). A consideration of the rotational energy \( E_{rot} \) in section 2.1.2 is not specific to either the \( \text{C}_2 \) or the linear \( \text{C}_3 \) molecule.

### 2.1.2 Rotational structure

For a rigid linear molecule with no net orbital and spin angular momentum the classical expression for the rotational kinetic energy is given as

\[ E_{rot} = \frac{1}{2} I_c \omega_c^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_a \omega_a^2 \]

\[ = \frac{1}{2} I_c \omega_c^2 + \frac{1}{2} I_b \omega_b^2 = J_c^2 \frac{2}{2I} + J_b^2 \frac{2}{2I} = J^2 \]

Each molecule has three principal axes \((a, b, c)\) in the molecular frame.\(^1\) The moments of inertia of a rigid linear molecule for corresponding axes are given as \( I_a = 0 \) and \( I_b = I_c = I \). \( J \) represents the total angular momentum (exclusive of nuclear spin). The expression for \( I \) of a body composed of point masses \( m_i \) for each axis \( i \) is defined as :

\[ I = \sum_i m_i r_i^2 \]

where \( r_i \) is the distance between the mass \( m_i \) and the molecular center of mass. For a rigid rotor in the isotropic (field-free) space the rotational Hamiltonian operator for a linear molecule can be written as

\[ \hat{H}_{rot} = \frac{J^2}{2I} \]

\(^1\)Note that for a dipole transitions the \((x, y, z)\) notation is used for axes in the laboratory frame. \( m_{a} \) denotes the projection of the total angular momentum \( J_a \) on the quantization axis. The space-fixed quantization axis is chosen along the polarization direction of the incoming field \( \varepsilon \) in the laboratory frame.
Chapter 2. Spectroscopy of di- and tri-atomic molecules

The Schrödinger equation is solved by using one of the spherical harmonics \( \phi_{\text{rot}} = Y_{JM} \) as eigenfunctions, where \( M \) is a projection of \( J \) on to the quantization axis. So that

\[
\frac{J^2 \phi_{\text{rot}}}{2I} = J(J+1)\hbar^2 \phi_{\text{rot}} = B_e J(J+1) \phi_{\text{rot}}
\]  

The energy eigenvalue \( B_e J(J+1) \) is proportional to the rotational constant \( B_e = \hbar^2 / 2I \). \( B_e \) is directly related to the moment of inertia around the principal axes (\( b \) and \( c \)) in a fixed electronic configuration (for the subscript \( e \)). Hence, if measured, \( B_e \) allows to deduce the internuclear bond distance. Note the effective rotational constant is specific for each electronic state \( e \) and vibrational level \( v \). That is why for every measured vibrational level the effective rotational constant should be independently identified. It is also possible to include a \( D_e \) correction term for the centrifugal distortion which is dependent on \( J^2(J+1)^2 \). It accounts for the increased moment of inertia for higher rotational states due to the centrifugal force which changes the mean positions of the nuclei.

2.1.3 Vibrational structure

A molecule containing \( N \) atoms has \( 3N \) degrees of freedom which describe its motion. There are 3 translational and 3 rotational degrees of freedom for every nonlinear molecule. However, in the case of a linear molecule, there are only 2 rotational degrees of freedom because the rotation about the internuclear axis is not distinguishable. Hence, a linear molecule has \( 3N - 5 \) vibrational modes compared to the \( 3N - 6 \) vibrational modes of the non-linear molecule. \( C_2 \) has a symmetric stretching vibration (of \( \Sigma_g \) symmetry) along the internuclear coordinate. \( C_3 \) is linear in the \( X^1\Sigma_g^+ \) ground state and has 3 vibrational modes: the symmetric stretching vibration (of \( \Sigma_g \) symmetry), the bending vibration (of \( \Pi_u \) symmetry) and the antisymmetric stretching vibration (of \( \Sigma_u \) symmetry).

The energy \( E \) depends on the molecular geometry, e.g. the value of the internuclear bond distance. As a result, the solution of the Schrödinger equation is a parametric function of \( r \). The vibrational energy can be determined if the wavefunction \( \phi_{\text{vib}} \) is substituted to

\[
-\frac{\hbar^2}{2\mu} \nabla^2 \phi_{\text{vib}} + V(r) \phi_{\text{vib}} = E \phi_{\text{vib}}
\]

One of the general forms of potential \( V(r) \) is a Taylor series expansion about the equilibrium position \( r_e \).

\[
V(r) = V(r_e) + \frac{dV}{dr} \big|_{r_e} (r - r_e) + \frac{1}{2!} \frac{d^2V}{dr^2} \big|_{r_e} (r - r_e)^2 + ...
\]
$V(r_e) = 0$ because the bottom of the well is arbitrary chosen as the point of zero energy. In the expansion about the minimum at $r_e$, the first derivative is zero $\left(\frac{dV}{dr}\right)|_{r_e} = 0$. If the distortion $r - r_e$ is small it is possible to take the leading term $V(r) = 1/2k(r - r_e)^2$ where $k = (d^2V/dr^2)|_{r_e}$ in the potential energy expansion and to obtain the harmonic oscillator solution [44]. The solution $\phi_{vib}$ is only valid around the equilibrium and for a non-rotating molecule

$$\phi_{vib} = N_v H_v(\sqrt{\alpha}(r - r_e))e^{-\alpha(r-r_e)^2}$$

where $\alpha = (\mu \omega)/\hbar$, $N_v = (1/(2^v v!)) \times (\alpha/\pi)^{1/2}$, $v$ is the vibrational quantum number and $\mu$ is the reduced mass. The $H_v(\sqrt{\alpha}x)$ functions are the Hermite polynomials. The eigenvalues are $E_{vib} = \hbar \omega(v + \frac{1}{2})$, $v = 0, 1, 2...$ and $\omega = (k/\mu)^{1/2}$. The vibrational eigen-modes are orthogonal only in the case of a harmonic potential. However, anharmonicity arises when the atoms are pulled away from each other towards the dissociation limit. This corresponds to a flattening of the potential energy surface. Anharmonicity of the nuclear motion can be accounted for by a Morse potential [44].

The eigenvalues for the Morse potential (including the centrifugal term and anharmonic corrections) can be written as:

$$E(e, v) = \omega_e(v + \frac{d}{2}) - \omega_e x_e(v + \frac{d}{2})^2 + B_e J(J+1) - D_e(J(J+1))^2 - \alpha_e(v + \frac{d}{2}) J(J+1)$$

(2.11)

where $\omega_e$ is the harmonic wave-number of the vibration. $d$ is the mode degeneracy. $v$ is the integer number which indicates the amount of vibrational excitation. $x_e$ is the first anharmonic correction term. $D_e$ is the correction term for the centrifugal distortion. $\alpha_e$ is the vibration-rotation coupling constant.

### 2.1.4 Orbitals and electronic states

In molecular orbital (MO) theory molecular orbitals are represented by linear combinations of atomic orbitals (LCAO). These orbitals are divided into bonding orbitals (e.g. $\sigma_g$ and $\pi_u$), anti-bonding orbitals (e.g. $\sigma_u^*$ and $\pi_g^*$), and non-bonding orbitals. In order to find the ground state electronic configuration molecular orbitals are occupied by the electrons in order of increasing energy. The resulting diagram for C$_2$ is shown in the Fig. 2.1. Note, that the core electrons are omitted. The electrons are filled into molecular orbitals to give the ... $2\sigma_g^2 1\pi_u^4$ configuration. The $1\pi_u$ subshell can be identified as the highest occupied molecular orbital (HOMO) with four electrons. The $\tilde{X}^1\Sigma_g^+$ ground state results from the fully occupied $1\pi_u^4$ subshell.
The ground state configuration of the $C_3$ is $\ldots 4\sigma_g^2 3\sigma_u^2 1\pi_u^4$. The $1\pi_u^4$ shell is occupied by four electrons resulting in the singlet $\tilde{X}^1\Sigma_g^+$ ground state in a linear geometry, see Fig. 2.2.

The notation for the electronic states of diatomic molecules is given by capital Greek letters $2\Sigma^+ \Lambda \Omega$. $\hat{S}$ is the spin angular momentum operator where $\Sigma$ is the projection onto the internuclear axis. $\hat{L}$ is the orbital angular momentum operator and $\Lambda$ is the projection of the orbital angular momentum onto the internuclear axis. $\Omega = (\Lambda + \Sigma)$ is used to specify a spin-component of the particular rovibronic level, but is often omitted. Instead for molecules with an inversion symmetry the label $g$ for gerade and $u$ for ungerade levels is given. The total angular momentum operator is $\hat{J} = \hat{L} + \hat{S} + \hat{R}$, where $\hat{R}$ is the nuclear rotation angular momentum operator.
2.1.5 Electronic transitions

“As for diatomic molecules we distinguish allowed and forbidden electronic transitions. Allowed electronic transitions give rise to the most intense absorption spectra of polyatomic molecules. But forbidden electronic transitions do occur weakly and are, in fact, much more important for polyatomic than for diatomic molecules.”

— G.Hertzberg, [46]

Electronic transitions take place when bound electrons usually from the highest occupied molecular orbital (HOMO) in a molecule are excited to a higher energy level. If the transition dipole moment is allowed the matrix element \( <\phi_{el}|\mu_\alpha|\phi'_{el}> \) containing electronic eigenfunctions of the upper \( \phi_{el} \) and lower \( \phi'_{el} \) states is non zero. \( \mu_\alpha \) is an electric dipole moment operator with \( \alpha = (x,y,z) \). In other words, an electronic transition between nondegenerate states is allowed if the product between electronic eigenfunctions and the dipole moment operator is totally symmetric for at least one orientation of \( \mu_\alpha \) [46] where \( \alpha \) indicate the projection onto the laboratory frame \((x,y,z)\).

Furthermore, if one or both electronic states are degenerate the product in Eq. 2.12 will not be totally symmetric even for an allowed transition. However, if the transition is allowed, linear combinations of the degenerate eigenfunctions and the dipole components that are transformed into one another can be found which make the product totally symmetrical [46]. Use of the symmetry considerations helps to define selection rules for optical transitions among various eigenstates. It can be shown by group theory that an electronically allowed transition obeys the condition:

\[
\Gamma_{el}^{(f)} \otimes \Gamma_{\mu_\alpha} \otimes \Gamma_{el}^{(g)} \supseteq \Gamma(T_\alpha) \tag{2.12}
\]

\( \Gamma(T_\alpha) \) transforms as totally symmetric representation. The symmetry product between irreducible representations of the final and initial electronic states \( \Gamma_{el}^{(f)} \) and \( \Gamma_{el}^{(g)} \), respectively, should belong to the same species as one of the components of \( \Gamma_{\mu_\alpha} \). In this case the direct product will contain at least one totally symmetric component \( \Gamma(T_\alpha) \).
For symmetrical linear molecules such as C$_2$ and C$_3$ (point group D$_{2h}$) the $g$ (gerade) and $u$ (ungerade) rule should be added, i.e., $g \leftrightarrow u$ are allowed and transitions between states of the same $g$ or $u$ symmetry are forbidden. Transitions between $\Sigma^+ \leftrightarrow \Sigma^+,$ $\Sigma^- \leftrightarrow \Sigma^-,$ $\Pi \leftrightarrow \Pi,$ $\Delta \leftrightarrow \Delta$ are possible with $\mu_z$ while $\Sigma^\pm \leftrightarrow \Pi,$ $\Pi \leftrightarrow \Delta,$ ... are possible with $\mu_x$ or $\mu_y$.

Possible electronic transitions between the energy levels are generalized by the selection rules:

1. $\Delta \Lambda = 0, \pm 1$. The transitions $\Sigma^\pm \leftrightarrow \Sigma^\pm,$ $\Sigma^\pm \leftrightarrow \Pi,$ $\Pi \leftrightarrow \Pi,$ $\Delta \leftrightarrow \Delta$ are possible with $\mu_z$ while $\Sigma^\pm \leftrightarrow \Pi,$ $\Pi \leftrightarrow \Delta,$ ... are possible with $\mu_x$ or $\mu_y$.

2. $\Delta S = 0$. Transitions that change multiplicity are very weak for molecules formed from light atoms, however, as spin-orbit coupling increases in heavy atoms, transitions with $\Delta S \neq 0$ become more probable.

3. $\Delta \Sigma = 0$ (for Hund’s case (a)).

4. $\Delta \Omega = 0, \pm 1$.

5. $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-.$

Table 2.2: Character table of the D$_{2h}$ group.

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>C$_2$ (z)</th>
<th>C$_2$ (y)</th>
<th>C$_2$ (x)</th>
<th>i</th>
<th>$\sigma$ (xy)</th>
<th>$\sigma$ (xz)</th>
<th>$\sigma$ (yz)</th>
<th>$x^2,$ $y^2,$ $z^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, g</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x^2,$ $y^2,$ $z^2$</td>
</tr>
<tr>
<td>B, 3u</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x$</td>
</tr>
<tr>
<td>B, 2u</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$y$</td>
</tr>
<tr>
<td>B, 1g</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$I_z,$ $xy$</td>
</tr>
<tr>
<td>B, 1u</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
</tr>
<tr>
<td>B, 2g</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$I_y,$ $xz$</td>
</tr>
<tr>
<td>B, 3g</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$I_x,$ $yz$</td>
</tr>
<tr>
<td>A, u</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The character Table 2.2 describes the transformation of the irreducible representation under the symmetry operations. The 1 means that the orbital transforms in itself, whereas $-1$ points at a change of $\pi$ in the orbital phase. The Table 2.2 provides the information on the symmetry of a given irreducible representation relative to the internuclear axis usually specified along the $z$ axis ($z \to z$). The spectroscopic notation for electronic states in the $D_{\infty h}$ point group can be correlated to irreducible representations in the $D_{2h}$ point group with the help of tables given in Appendix I - IV [46].

---

Note that the Molpro package for ab initio calculations uses finite Abelian groups (geometry is given in Cartesian ($x,y,z$) coordinates), therefore the reduced symmetry group $D_{2h}$ is used instead of the $D_{\infty h}$. 
Selection rules for the transition dipole moment along various molecular axes can be calculated from the direct product given in Eq. 2.12. For the $D_{2h}$ point group, the electric dipole moment can be represented as a sum of $B_{1u} + B_{2u} + B_{3u}$ for the $(z, y, x)$ axis respectively. As an example, let us take the $\tilde{g}$ correlates to $A_g$ and $\tilde{a}$ correlates to the $B_{2u} + B_{3u}$ sum of irreducible representations. Hence, it can be written as $(B_{2u} + B_{3u}) \otimes (B_{1u} + B_{2u} + B_{3u}) \otimes A_g$. Evaluation of the product with the help of the Table 2.3 leads to $A_g + B_{1g} + B_{3g}$ and $A_g + B_{1g} + B_{2g}$ both containing the totally symmetric irreducible representation $A_g$. The dipole transition between these electronic states is allowed along the $x$ and $y$ axis.

Table 2.3: Product table for the $D_{2h}$ point group.

<table>
<thead>
<tr>
<th>$\otimes$</th>
<th>$A_g$</th>
<th>$B_{3u}$</th>
<th>$B_{2u}$</th>
<th>$B_{1g}$</th>
<th>$B_{1u}$</th>
<th>$B_{2g}$</th>
<th>$B_{3g}$</th>
<th>$A_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$A_g$</td>
<td>$B_{3u}$</td>
<td>$B_{2u}$</td>
<td>$B_{1g}$</td>
<td>$B_{1u}$</td>
<td>$B_{2g}$</td>
<td>$B_{3g}$</td>
<td>$A_u$</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>$B_{3u}$</td>
<td>$A_g$</td>
<td>$B_{2u}$</td>
<td>$B_{2g}$</td>
<td>$B_{1u}$</td>
<td>$A_u$</td>
<td>$B_{3g}$</td>
<td>$B_{3u}$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$B_{2u}$</td>
<td>$B_{1g}$</td>
<td>$A_g$</td>
<td>$B_{3u}$</td>
<td>$B_{3g}$</td>
<td>$A_u$</td>
<td>$B_{1u}$</td>
<td>$B_{2g}$</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$B_{1g}$</td>
<td>$B_{2u}$</td>
<td>$B_{3u}$</td>
<td>$A_g$</td>
<td>$A_u$</td>
<td>$B_{3g}$</td>
<td>$B_{2g}$</td>
<td>$B_{1u}$</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>$B_{1u}$</td>
<td>$B_{2g}$</td>
<td>$B_{3g}$</td>
<td>$A_u$</td>
<td>$A_g$</td>
<td>$B_{3u}$</td>
<td>$B_{2u}$</td>
<td>$B_{1g}$</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$B_{2g}$</td>
<td>$B_{1u}$</td>
<td>$A_u$</td>
<td>$B_{3g}$</td>
<td>$B_{2u}$</td>
<td>$A_g$</td>
<td>$B_{1g}$</td>
<td>$B_{2u}$</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>$B_{3g}$</td>
<td>$A_u$</td>
<td>$B_{1u}$</td>
<td>$B_{2g}$</td>
<td>$B_{2u}$</td>
<td>$B_{1g}$</td>
<td>$A_g$</td>
<td>$B_{3u}$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>$A_u$</td>
<td>$B_{3g}$</td>
<td>$B_{2g}$</td>
<td>$B_{1u}$</td>
<td>$B_{1g}$</td>
<td>$B_{2g}$</td>
<td>$B_{3g}$</td>
<td>$A_g$</td>
</tr>
</tbody>
</table>

2.1.6 Vibrational angular momentum

The total angular momentum operator in a linear molecule is given $\hat{J} = \hat{R} + \hat{L} + \hat{S} + \hat{\ell}$, where $\hat{R}, \hat{L}, \hat{S}$ and $\hat{\ell}$ are the rotational, electronic orbital, spin and vibrational angular momentum operators, respectively.

Vibrationally-excited polyatomic molecules may display the effect of vibrational angular momentum. For the linear $C_3$ the vibrational angular momentum $\hat{\ell}$ originates from the bending vibration. The bending vibration is doubly degenerate since the molecule can bend in and out of plane. In general the solution for the two-dimensional harmonic oscillator is $E_v = \hbar \omega (v + \frac{d}{2})$ where $v = 0, 1, 2, ...$ and $d = 2$ is the degeneracy of vibration. The two-dimensional harmonic oscillator Hamiltonian operator can be converted to plane polar coordinates [44]. In the new coordinate system the problem results in a wavefunction $\phi_{vl}$ where $l$ is a new quantum number associated with the vibrational angular momentum of $\pm |l| \hbar$. Classically the two oscillators in $x$ and $y$ directions can be phased such that the nuclei execute a circular motion of small amplitude about the $z$-axis. In quantum mechanics this motion is quantized, hence, only $\pm l \hbar$ units of angular momentum are possible [44]. $K = \Lambda \pm l$ is often used as a superscript for bending vibrational quantum number $v_{\ell}^K$. Note that the $\pm |l|$ values are possible. The double
degeneracy for each value of \( l \) is associated with clockwise or counterclockwise motion of the nuclei in a linear molecule (see Fig. 2.3 a).

![Figure 2.3: a: Classical picture of vibrational angular momentum. b: Vibrational energy-level pattern for the bending mode of a linear molecule.](image)

Selection rules for vibrational transitions in the vibrational energy-level pattern of a linear molecule can be summarized [44] as \( \Delta l = 0, \pm 1 \), \( g \leftrightarrow u \) and \( \Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^- \). The various transitions are possible:

1. Parallel transitions for \( \Delta l = 0 \) and \( l = 0 \) with strong P and R branches (\( \Delta J = \pm 1 \));
2. Perpendicular transitions for \( \Delta l = \pm 1 \) with a strong Q branch and weak P and R branches;
3. Transitions with \( \Delta l = 0 \) where \( l \neq 0 \) exhibiting P and R branches and a weak Q branch.

Note, the vibrational energy-level pattern of the bending vibrational mode for the linear molecule has an alteration between \( g \) and \( u \) levels. For example, in the electronic \( 1\Sigma_g^+ \) state the vibrationally excited \( v_2 = 1 \) level will have \( 1\Pi_u \) symmetry due to the \( \Gamma_{\Sigma_g^+} \otimes \Gamma_{\Pi_u} \) product (see Fig. 2.3 b). However, vibrationally excited \( v_2 = 2^0 \) and \( v_2 = 2^2 \) levels have \( g \) symmetry \( 1\Sigma_g^+ \) and \( 1\Delta_g \) respectively. The alteration between \( g \) and \( u \) levels characteristic to a linear molecule results in the \( \Delta l = \pm 1 \) selection rule for the infrared dipole moment transitions between vibrational levels in the ground state. On the other hand, by applying two-photon resonant or Raman spectroscopy, levels which differ by \( \Delta l = 0, 2 \) can be observed.

### 2.1.7 Vibronically allowed transitions

For a linear polyatomic molecule the symmetry for excited vibronic levels is obtained by taking the direct product of the symmetry species for each vibration multiplied by the electronic symmetry (Eq. 2.13). \( \Gamma_{ev} \) is the total symmetry of the vibronic wavefunction. A vibronically allowed transition satisfies the condition:

\[
\Gamma_{ev}^{(f)} \otimes \Gamma_{\mu_\alpha} \otimes \Gamma_{ev}^{(g)} \supseteq \Gamma(T_\alpha) \quad \text{where} \quad \Gamma_{ev} = \Gamma_{vib} \otimes \Gamma_{el} \quad (2.13)
\]
As discussed in the section 2.1.6 the vibrational angular momentum quantum number $l$ originating from the bending vibration plays an important role in the spectroscopy of linear C$_3$. In the electronic $\tilde{A}^1\Pi_u$ state the odd number of $l$ in the bending vibration (of $\Pi_u$ symmetry) generates the $\Sigma_g^+$, $\Delta_g$ and higher angular momentum $g$ levels from the product with the electronic $\tilde{A}^1\Pi_u$ state. The even number $l$ generates $\Sigma_u$, $\Delta_u$ and higher angular momentum $u$ levels. Additionally, due to the anharmonicity of the potential energy surfaces in $\tilde{X}^1\Sigma_g^+$, $\tilde{A}^1\Pi_u$ and $\tilde{3}\Delta_u$ electronic states, different values of $|l|$ are split by few cm$^{-1}$ [40].

The vibronic transition strength is defined by:

$$| < \phi_{el}\phi_{vib}|\mu_\alpha|\phi'_{el}\phi'_{vib}>|^2 = | < \phi_{el}|\mu_\alpha|\phi'_{el}>|^2 | < \phi_{vib}|\phi'_{vib}>|^2$$  \hspace{1cm} (2.14) 

$| < \phi_{vib}|\phi'_{vib}>|^2$ is the Franck-Condon factor which indicates the square of the overlap integral between vibrational wave-functions and is the important parameter for dipole-allowed optical transitions.

**2.2 Perturbations of molecular states**

**2.2.1 Selection rules for the spin-orbit interaction**

A detailed theory of the spin-orbit interaction derived from the application of the non-relativistic Hamiltonian is discussed in the book of Lefebvre-Brion and Field [32]. In this section we summarize selection rules for the spin-orbit coupling since application of these rules primarily assists the analysis of the measured spectra.

The selection rules for the spin-orbit $\hat{H}_{SO}$ interaction Hamiltonian can be summarized as follows [32]:

1. $\Delta J = 0$, $\Delta \Omega = 0$, $\Sigma^+ \leftrightarrow \Sigma^-$, $\Delta S = \pm 1$ and $\Delta \Lambda = 0$, $\Delta \Sigma = \pm 1$

2. $\Delta J = 0$, $\Delta \Omega = 0$, $\Sigma^+ \leftrightarrow \Sigma^-$, $\Delta S = \pm 1$ and $\Delta \Lambda = -\Delta \Sigma = \pm 1$

There are two cases covered by the presented selection rules. First is the interaction between states of the same configuration $\Delta \Lambda = 0$ and $\Delta \Sigma = 1$. This accounts for the intersystem crossing in C$_2$ [9] between ($\Lambda = 1$, $\Sigma = 2$) $1^3\Pi_g$ and ($\Lambda = 1$, $\Sigma = 1$) $d^3\Pi_g$. Second is the interaction between states which differ by one spin-orbital $\Delta \Lambda = -\Delta \Sigma = \pm 1$ such as the case of the perturbation in the C$_3$ between a ($\Lambda = 1$, $\Sigma = 0$) $\tilde{A}^1\Pi_u$ state and a ($\Lambda = 0$, $\Sigma = 1$) $3\Sigma_u^-$ [15].
2.2.2 Intensity borrowing

The material presented in this section closely follows the book of Lefebvre-Brion and Field [32]. Polyatomic molecules often have perturbations in the electronic states, for example via spin-orbit interaction also referred as intersystem crossing. In the present work we describe the intersystem crossings between $\tilde{\tilde{\Delta}}^1\Pi_u - ^3\Sigma_u^\prime$ electronic states of C$_3$ and the $d^3\Pi_g - ^1\Sigma_g^\prime$ electronic states of C$_2$. Because of perturbations extra resonances appear in the measured spectra. States of different spin multiplicity relative to the ground state are usually called dark states, however these states can “borrow” intensity from a nearby lying bright state. The strongest appearing spectral lines while performing the experiment usually originate from the bright state and the weak extra-lines originate from transitions to dark states exhibiting partial bright character.

Vibronic wavefunctions of the excited levels belong to the interacting pair of the electronic states. The corresponding matrix elements give eigenenergies of these states: $E^0_1 = <\tilde{\psi}_1|\hat{H}_0|\tilde{\psi}_1>$, $E^0_2 = <\tilde{\psi}_2|\hat{H}_0|\tilde{\psi}_2>$ and spin-orbit Hamiltonian describes the mixing of these states $H^{12} = <\tilde{\psi}_1|\hat{H}_{SO}|\tilde{\psi}_2>$. The basis function $\tilde{\psi}_2$ is chosen such that it has a negligible transition probability between $\tilde{\psi}_1$ and the ground state. Hence, it is possible to assume that the $\tilde{\psi}_2$ level has infinitely long lifetime. The result of the interaction via $\hat{H}_{SO}$ leads to a shift in eigenenergies of the $\tilde{\psi}_{1,2}$ states by

$E_+ = \tilde{E}_0 + ((\Delta E^0/2)^2 + H^2_{12})^{1/2}$ \hspace{1cm} (2.15)
$E_- = \tilde{E}_0 - ((\Delta E^0/2)^2 + H^2_{12})^{1/2}$ \hspace{1cm} (2.16)

where $\tilde{E}_0 = (E^0_1 + E^0_2)/2$ and $\Delta E^0 = E^0_1 - E^0_2$, $E^0_{1,2}$ energies are calculated with respect to the unperturbed Hamiltonian $\hat{H}_0$.

New eigenfunctions can be constructed from the unperturbed eigenfunctions by adding and subtracting initial wavefunctions with weighting coefficients $c_{ij}$, where indices $i, j$ correspond to the two interacting states.

$|\psi_1> = c_{11}|\tilde{\psi}_1> + c_{21}|\tilde{\psi}_2>$ \hspace{1cm} (2.17)
$|\psi_2> = c_{12}|\tilde{\psi}_1> + c_{22}|\tilde{\psi}_2>$ \hspace{1cm} (2.18)

with $c_{11} = c_{22}$ and $c_{12} = -c_{21} = (1 - c^2_{11})^{1/2}$. By the orthogonality requirement the second equation (Eq. 2.18) follows from the first one (Eq. 2.17). Since each new state is represented by the linear combination of unperturbed wavefunctions the transition probability from the ground state to both $\psi_1$ and $\psi_2$ is non-zero. If the ground state is
designated by the wavefunction $|g>$, the one photon-transition probability is

$$I_{g,\psi_{1,2}} \propto <\psi_{1,2}|\mu_\alpha|g>$$

$$I_{g,\psi_1} = c_{11}^2 <\psi_1|\mu_\alpha|g>$$

$$I_{g,\psi_2} = (1 - c_{11}^2) <\psi_1|\mu_\alpha|g>$$ (2.19)

In the absence of an interaction between level $\psi_1$ and $\psi_2$ only resonances which belong to a $<\psi_1|\mu_\alpha|g>$ transition from the ground state appear, namely $\Delta J = -1, 0, 1$ for a $\Sigma \leftrightarrow \Pi$ transition and $\Delta J = -1, 1$ for a $\Sigma \leftrightarrow \Sigma$ transition. These resonances represent transitions to the bright state ($|\psi_1>$). The intensity of a one photon transition to a dark state is determined by the interaction strength between the bright and the dark state and, therefore, depends on the mixing coefficients $c_{i,j}$. Note that the mixing coefficients in Eq. 2.19 may refer to any type of interaction between levels and not only spin-orbit perturbation as discussed here.

In a high-resolution experiment when the laser bandwidth $\Delta \nu$ is smaller that the separation of two lines each transition can be resolved separately. The radiative decay $\tau_{10}/c_{11}^2$ of the bright-state $\psi_1$ will be smaller compared to a radiative decay $\tau_{10}/(1 - c_{11}^2)$ of a dark-state $\psi_2$, where $\tau_{10}$ is the life-time of the unperturbed bright state.

It is important to mention that we have described a two-level perturbation model, though in more complex molecular systems (with many motional degrees of freedom or/and many electronic states located energetically close to each other) the perturbation model should be extended to

$$|i; J_p> = \sum_j c_{ji}|j^{(0)}; J_p>$$ (2.20)

where $n$ is the number of effectively interacting states. Here, zero order states are product states characterizing an (adiabatic) electronic state of well defined spin multiplicity and a well defined vibrational state. $p$ is the parity. As the total angular momentum and parity are conserved, they are equal on the right and left hand side of Eq. 2.20.

### 2.2.3 Perturbation in $C_3$ Comet band $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$

The intermediate levels $|i; J_p>$ addressed in this work are related to the rotational $J = 5$ level of parity $p$ of the (000) $\tilde{A}^1\Pi_u$ state which is perturbed by a nearby lying triplet state of $3\Sigma^+_u$ symmetry by spin-orbit coupling. The perturbation gives rise to mixed states exhibiting both singlet and triplet character [15]. These mixed states are expressed as a superposition of unperturbed, zero order rovibronic states $|j^{(0)}; J_p>$ with
respective mixing coefficients $c_{ji}$.

\[ |\psi_1 \rangle = c_{11} |\tilde{A}^1\Pi_u \rangle + c_{21} |3\Sigma^-_u \rangle \]  \hspace{1cm} (2.21)

\[ |\psi_2 \rangle = c_{22} |3\Sigma^-_u \rangle + c_{12} |\tilde{A}^1\Pi_u \rangle \]  \hspace{1cm} (2.22)

with $c_{11} = c_{22} = 2/\sqrt{5}$ and $c_{12} = -c_{21} = \sqrt{1 - c_{11}^2} = 1/\sqrt{5}$, where we take into account the molecular constants for the perturbing $3\Sigma^-_u$ from the deperturbation analysis of Zhang et al. [15] to deduce a mixing coefficient of $|c_{12}| \approx 0.2$ for the two $J = 5$ levels. For brevity, the quantum numbers for the vibrational and rotational levels, as well as the parity quantum numbers are omitted in Eq. 2.21 and Eq. 2.22. The corresponding interaction between the $|3\Sigma^-_u \rangle$ and $|\tilde{A}^1\Pi_u \rangle$ states scales with the square of the overlap integral between vibrational wavefunctions (Franck-Condon factor). Note that the $|\psi_1 \rangle$ level, which is more singlet like, is expected to have degenerate even and odd symmetry states, whereas the $|\psi_2 \rangle$ level, which is more triplet like, will be composed of two nearly degenerate levels, one of them containing even and one odd states, and a third level containing only even states [15].

\[ \begin{align*}
&|3\Sigma^-_u \rangle = c_{11} |\tilde{A}^1\Pi_u \rangle + c_{21} |3\Sigma^-_u \rangle \\
&|\tilde{A}^1\Pi_u \rangle = c_{12} |\tilde{A}^1\Pi_u \rangle + c_{22} |3\Sigma^-_u \rangle 
\end{align*} \]

Figure 2.4: The nearly-degenerate four-wave mixing spectrum shows strong P,Q and R resonances from $J'' = 6$ to the bright $\tilde{A}^1\Pi_u$ state. Weak transitions $^oP_1$ and $^qR_1$ to the dark $3\Sigma^-_u$ state are also present due to the spin-orbit interaction between $\tilde{A}^1\Pi_u$ and $3\Sigma^-_u$. Lines caused by the intensity borrowing mechanism are designated with the * symbol and a blue font. The upper (red) trace is a measured spectrum and the lower (green) is a spectrum simulated with inclusion of the spin-orbit interaction between $\tilde{A}^1\Pi_u$, $3\Sigma^-_u$ and an unknown $P = 1$ states [15].
Chapter 2. Spectroscopy of di- and tri-atomic molecules

The measurement of the perturbed Comet band $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ is performed by two-color four-wave mixing spectroscopy. The nearly-degenerate four-wave mixing spectrum is shown in the upper trace of Fig. 2.4. The measurement is obtained by fixing the PROBE to the R(6) transition and scanning the frequency of the PUMP. Hence, intermediate level labeling is realized and only transitions with $\Delta J = \pm 1, 0$ are possible. Lines to the $^3\Sigma_u^-$ state observed due to the intensity borrowing mechanism are denoted with the * and a blue font in Fig. 2.4.

2.2.4 Renner-Teller Interaction

The Renner-Teller effect describes the coupling between the electronic structure and vibrational motion of the nuclei in a linear molecule. The effect was first described for triatomic molecules and later extended to tetra-atomic and higher order interactions. The Hamiltonian $\hat{H}_{eN}$ for the vibronic interaction is represented \[45\] by

$$\hat{H}_{eN} = \sum_{\Gamma, \gamma} \left( \frac{\partial V}{\partial Q_{\Gamma, \gamma}} \right)_0 Q_{\Gamma, \gamma} + \frac{1}{2} \sum_{\Gamma_1, \Gamma_2} \sum_{\gamma_1, \gamma_2} \left\{ \frac{\partial^2 V}{\partial Q_{\Gamma_1, \gamma_1} \partial Q_{\Gamma_2, \gamma_2}} \right\}_{\Gamma, \gamma} \{Q_{\Gamma_1} \otimes Q_{\Gamma_2}\}_{\Gamma, \gamma}$$

where $Q_{\Gamma, \gamma}$ is a symmetrized displacement of the nuclei in a particular symmetry group. $V$ is the potential introduced by the electronic configuration. The tensor convolution $\left\{ \frac{\partial^2 V}{\partial Q_{\Gamma_1, \gamma_1} \partial Q_{\Gamma_2, \gamma_2}} \right\}_{\Gamma, \gamma}$ forms a linear combination of second derivatives with respect to $Q_{\Gamma_1}$ and $Q_{\Gamma_2}$ symmetrized nuclear coordinates. The second coefficient in the Eq. 2.23 \[45\] transforms according to line $\gamma$ of the representation $\Gamma_1 \otimes \Gamma_2 \supseteq \bar{\Gamma}_\gamma$. For a degenerate state this operator can be both totally-symmetric and non-totally-symmetric. The totally symmetric part contains the $\bar{\Gamma}_\gamma = A_1$ irreducible representation.

The matrix elements of the electronic wave-function of degenerate states calculated with the derivative over $Q_{\Gamma_1, \gamma}$ denote the vibronic coupling strength (vibronic constants). For a degenerate state $\Gamma$ the diagonal matrix element $F_{\Gamma}^{\Gamma'}$ given in Eq. 2.24 is non-zero if the product $[\Gamma \otimes \Gamma']$ contains the totally symmetric part $A_1$. Let us consider a doubly degenerate $\Pi$ state where the projection of the orbital quantum number $\Lambda = 1$. In the space of a doubly degenerate bending vibration of $e$ symmetry the electronic degeneracy of the $\Pi$ state will be lifted \[45\]. The quadratic terms of the $e$ bending in the vibronic interaction (Eq. 2.23) transform as $[E \otimes E] = A_1 \oplus E$. Hence the matrix element of the vibronic coupling is non-zero, resulting in the non-zero interaction energy and splitting between otherwise (without bending-vibration) degenerate levels.

$$F_{\Gamma}^{\Gamma'} = \langle \Gamma | \left\{ \left( \frac{\partial^2 V}{\partial Q_{\Gamma_1, \gamma} \partial Q_{\Gamma_2, \gamma}} \right)_0 \right\}_{\bar{\Gamma}_\gamma} | \Gamma' \rangle$$

(2.24)
An example of the Renner-Teller splitting in the $\tilde{A}^1\Pi_u$ state is shown in the Fig. 2.5. The degenerate state $\tilde{A}^1\Pi_u$ is split due to the interaction between the vibrational angular momentum and the electronic angular momentum giving rise to $K = \Lambda - l \ (01^00) \Sigma$ and $K = \Lambda + l \ (01^20) \Delta$ states. Both Renner-Teller components of $\Sigma$ and $\Delta$ symmetry are accessed from the vibronic $^1\Pi_u$ level, which is a $(01^10)$ vibrational level of the $\tilde{X}^1\Sigma_g^+$ ground state. The vibrational excitation is expressed as $(v_1 \ v_2^k \ v_3)$, where $v_1$ is the symmetric stretching vibrational quantum number, $v_2^k$ is the bending vibrational quantum number, $v_3$ is the antisymmetric stretching vibrational quantum number.

$$\tilde{A}^1\Pi_u \leftarrow (01^10) \tilde{X}^1\Sigma_g$$

![Figure 2.5: The spectrum shows the Renner-Teller splitting in the $\tilde{A}^1\Pi_u$ state of $C_3$ between $(01^00) \Sigma$ and $(01^20) \Delta$ components. The upper (red) trace is the measured spectrum and the lower (black) is the simulated spectrum for a 150 K rotational temperature. The degenerate four-wave mixing laser is sampling the population of the vibrationally excited $(01^10) \tilde{X}^1\Sigma_g^+$ level of the ground state.](image)

The Renner-Teller effect can be estimated by an ab initio calculation. If a triatomic molecule has its potential energy minimum at a bent configuration it can not be described anymore by the $D_{\infty h}$ but rather by the $C_{2v}$ point group. For example, the lowest triplet $^3\Pi_u$ state in $C_3$ in a linear geometry correlates to the $B_1 + B_2$ sum of irreducible representations (see section 8.2.1). Potential energy surfaces computed at different bending angles for the two representations will not be degenerate. The energy splitting with increasing bending angle is given by the Renner-Teller parameter. When
the splitting is large, two potential energy surfaces originating from the same electronic state with different $K$ can be treated as independent electronic states. For example, the linear $^3\Pi_u$ splits into nondegenerate components with $B_1$ and $B_2$ symmetries.

Note that the Renner-Teller effect is not the only effect which can distort a linear molecular geometry. A bending force may arise upon mixing two closely spaced electronic states (e.g. $\Sigma$ and $\Pi$) under the bending distortion. This effect is called Pseudo-Jahn-Teller effect. For example, for a displacement of $\Pi$ vibrational symmetry the vibronic product between electronic $\Gamma_{\Sigma}$ and vibrational $\Gamma_{\Pi}$ symmetry will produce $\Gamma_{\Sigma} \otimes \Gamma_{\Pi} = \Gamma_{\Pi}$. If the coupling is strong the vibronic $\Pi$ state can interact with a nearby lying electronic $\Pi$ state which may lead to a double-potential well or an avoided crossing between adjacent states.
Chapter 3

Light-Matter Interaction:
Four-Wave Mixing Spectroscopy

3.1 Wave equation

In the following section the theory of the resonant FWM spectroscopy technique is introduced. The semiclassical nonlinear optical perturbation theory describes successive light-matter interaction \emph{via} expansion of polarization terms in the wave-equation. The perturbation theory and diagrammatic technique are formulated closely to the book of Y. R. Shen ”Principles of Nonlinear Optics” [47]. The diagrammatic technique helps to theoretically formulate degenerate and two-color four-wave mixing methods which were experimentally applied in the current work. In the semiclassical perturbation theory the molecular states are treated quantum-mechanically (see Chapter 2) while the electromagnetic radiation is described classically. Furthermore, molecular relaxation processes influencing the lifetime of the excited intermediate and final states (\emph{e.g.} collisional dephasing, excited state population quenching) are represented with lifetime constants.

3.1.1 Coherent laser pulses

Laser pulses are characterized by the central frequency $\nu_L$ or wavelength $\lambda_L$, duration $\tau_L$, bandwidth $\Delta \nu_L$, intensity $I$ and polarization unit vector $\varepsilon$. These parameters should be carefully adjusted before starting the experiment since the signal intensity has a nonlinear dependence on most of these parameters. Note that the bandwidth of the laser pulse is given in Hz and is closely related to the pulse duration $\Delta \nu_L \Delta \tau_L \approx 1$ if the laser pulse is “Fourier transform-limited”. The trade-off between frequency and time resolution is an important issue for the time or frequency domain pump-probe
experiments. For example, in case of frequency-resolved measurements high spectral resolution is needed in order to address specific molecular quantum states. However, rotational state specific measurements are rarely achievable in time-domain femtosecond pump-probe experiments.

According to the specification of the NarrowScan (Radiant Dyes (c⃝)) lasers the spectral resolution is $\Delta \nu_L \approx 600 \text{ MHz}$ (in high resolution spectroscopic experiments the bandwidth is sometimes defined in wavenumbers $\approx 0.02 \text{ cm}^{-1}$). The duration of the laser pulse is $\tau_L \approx 7 \text{ ns}$. The relation between intensity $I$ and a slowly varying envelope function of an electric field $E(r, t)$ at a defined space $r$ and time $t$ coordinates is expressed as

$$ I(r, t) = \frac{1}{2} \epsilon_0 c n |E(r, t)|^2 $$

(3.1)

$\epsilon_0$ is the permittivity of the free space, $c$ is the speed of light and $n$ is the refractive index coefficient. A plane wave can be expressed in the form of a complex-valued amplitude with an electric field component oscillating at the carrier frequency $\omega_0$ and a spatial $\exp(ik \cdot r)$ term. It is important to mention that the electric field has a complex conjugate part denoted as c.c.

$$ E(r, t) = \frac{1}{2} \epsilon_0 c n |E(r, t)|^2 + \text{c.c.} $$

(3.2)

According to the separation of time and space variables in Eq. 3.2, the complex envelope function can be divided into polarization unit vector $\varepsilon$, spatial $E_r(r)$ and temporal $E_t(t)$ parts. $E_r(r)$ specifies the spatial distribution of the electric field. Usually $E_r(r)$ is expressed as a Gaussian beam in the transverse plane (plane orthogonal to the propagation direction $k$ of the electromagnetic wave) and a hyperbolic function along the propagation direction $z$ of $k$.

The coherence of the plane wave or the Gaussian beam can be understood as a spatial and/or temporal correlation of phases of superimposed waves from the same or different radiation sources. Temporal coherence implies the correlation between the wave and itself delayed by time $\tau$ at any moment of time. This tells us how monochromatic the laser source is. Spatial coherence refers to the ability of the electromagnetic wave to interfere in space (e.g. for two points in space orthogonal to the propagation direction $k$). Both types of coherences are important for four-wave mixing experiments, where a careful spatial and temporal adjustment is needed.
3.1.2 Spatial transformation of the electric field by optical elements

Transformation of a Gaussian laser mode is illustrated with the help of an \( ABCD \) matrix formalism [48]. In spite of the fact that laser beams from dye lasers used in our experiments have a slightly elliptical mode we discuss the theory based on paraxial Gaussian beam propagation. It is rather convenient to consider a Gaussian mode in situations where the beam divergence is relatively small, hence a paraxial approximation can be applied. This approximation states that wave-vectors \( \mathbf{k}_i \) which constitute a laser mode \( \sum_i a_i \cdot \mathbf{k}_i \) (with a weighting coefficient \( a_i \)) build small angles relative to the optical axis \( z \).

Within this approximation, a Gaussian beam propagating in free space remains Gaussian but its parameters such as the wavefront phase curvature and the cross section diameter change. For a monochromatic beam, propagating in \( z \) direction with the wavelength \( \lambda \), the complex electric field amplitude is expressed in

\[
E(r) = E_0 \frac{\varpi_0}{\varpi(z)} \exp \left( -\frac{(x^2 + y^2)}{\varpi(z)^2} \right) \exp \left( -i \left[ kz - \arctan \frac{z}{z_0} + \frac{k}{2} \frac{x^2 + y^2}{R(z)} \right] \right) \quad (3.3)
\]

The \( r = (x, y, z) \) is the space vector, \( \mathbf{k} = (0, 0, \frac{2\pi}{\lambda}) \) is the wave-vector, \( \lambda \) is the wavelength of the laser radiation. The Rayleigh length at the focal point is defined as a longitudinal length at which the beam waist radius \( \varpi_0 \) changes to \( \sqrt{2} \varpi_0 \) see Eq. 3.4.

This parameter can be a measure of the intersection of several laser beams at the focal point of the lens and therefore tentatively defines the interaction length

\[
z_0 = \frac{\pi \varpi_0^2}{\lambda} \quad (3.4)
\]

The beam radius changes along the optical axis \( z \) according to

\[
\varpi(z) = \varpi_0 \sqrt{1 + \left( \frac{z}{z_0} \right)^2} \quad (3.5)
\]

For a Gaussian beam it is possible to estimate the beam divergence \( \theta \) if the exact knowledge of the beam-waist and the laser wavelength is available: \( \theta = \lambda / (\pi \varpi_0) \). The wavefront radius \( R(z) \) is \( R(z) = z \left( 1 + (\frac{z}{z_0})^2 \right) \).

The \( ABCD \) matrix formalism can be used to calculate the effect of optical elements on the Gaussian beam propagation [48]. The complex parameter \( q \) is introduced in Eq. 3.6 to account for the information about the beam radius \( \varpi(z) \) and the curvature of the wavefront \( R(z) \).

\[
\frac{1}{q} = -i \frac{\lambda}{\pi \varpi^2} + \frac{1}{R} \quad (3.6)
\]

The subsequent transformation of the \( q \)- parameter by the optical element is represented via a product with the matrix parameters \( ABCD \). The parametric form \( M_0 \), a free space
transformation $M_1$ along the distance $d$ and a transformation by a lens with focal length $f$ expressed in $M_2$ are shown in Eq. 3.8.

$$q' = Aq + B$$

$$Cq + D$$

(3.7)

$$M_0 = \begin{pmatrix} A & B \\ C & D \end{pmatrix}$$

$$M_1 = \begin{pmatrix} 1 & d \\ 0 & 1 \end{pmatrix}$$

$$M_2 = \begin{pmatrix} 1 & 0 \\ -1/f & 1 \end{pmatrix}$$

(3.8)

In order to obtain new parameters e.g. of the wavefront curvature $R$, one should take the real part from $R = \text{Re} \left[ \frac{1}{q'} \right]$. A Gaussian beam diameter $\varpi$ is derived from the imaginary part of $\varpi^2 = \text{Im} \left[ \frac{1}{q'} \right]$.

### 3.1.3 Polarization expansion in a wave equation

The propagation of electromagnetic waves is described by the Maxwell equations. Assuming the charge density in free space equals zero ($\rho = 0$) the wave equation can be written [47]

$$\nabla \times \nabla \times \mathbf{E}(r,t) - \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E}(r,t) = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}(r,t)$$

(3.9)

The polarization term $\mathbf{P}(r,t)$ on the right hand side of the equation plays the role of the source for the generated field $\mathbf{E}(r,t)$ and both are vector quantities. $n$ is the refractive index coefficient. $c$ is a speed of light. The polarization which is induced by the oscillating field is time-dependent, although a stationary (time-independent) polarization may also exist (see e.g. optical rectification effect), we confine our discussion to the time-dependent term. Therefore, it is convenient to separate $\mathbf{P}(r,t)$ into linear and nonlinear parts

$$\mathbf{P}(r,t) = \mathbf{P}_L(r,t) + \mathbf{P}_{NL}(r,t)$$

(3.10)

The linear polarization $\mathbf{P}_L(r,t) = \int_{-\infty}^{+\infty} \chi^{(1)}(r-r',t-t') \cdot \mathbf{E}(r',t')dr'dt'$ is a function of the linear susceptibility $\chi^{(1)}$ and a field $\mathbf{E}$ acting in space $r'$ and time $t'$. A second and a third-order nonlinear polarization arises from the multiple-wave-mixing. Every n-th polarization term is a tensor and can be regarded as a result of a perturbation by the n-th electric field $\mathbf{E}$.

$$\mathbf{P}_{NL}(r,t) = \int_{-\infty}^{+\infty} \chi^{(2)}(r-r_1,t-t_1; r-r_2,t-t_2):$$

$$: \mathbf{E}(r_1,t_1) \cdot \mathbf{E}(r_2,t_2) \, dr_1 \, dt_1 \, dr_2 \, dt_2 +$$

$$+ \int_{-\infty}^{+\infty} \chi^{(3)}(r-r_1,t-t_1; r-r_2,t-t_2; r-r_3,t-t_3):$$

$$: \mathbf{E}(r_1,t_1) \cdot \mathbf{E}(r_2,t_2) \cdot \mathbf{E}(r_3,t_3) \, dr_1 \, dt_1 \, dr_2 \, dt_2 \, dr_3 \, dt_3 + ...$$

(3.11)
\( \chi^{(n)} \) is the \( n \)-th order nonlinear susceptibility. \( : \) is the double dot product. If the field is represented as a sum of monochromatic plane waves \( E(r, t) = \sum_j E_j(k, \omega) \exp(2\pi i k r) \) then the Fourier transform of the nonlinear polarization Eq. 3.11 gives Eq. 3.12:

\[
P_{NL}(k, \omega) = P^{(2)}(k, \omega) + P^{(3)}(k, \omega) + ... \tag{3.12}
\]

\[
P^{(2)}(k, \omega) = \chi^{(2)}(k = k_1 + k_2, \omega = \omega_1 + \omega_2) : E(k_1, \omega_1) \cdot E(k_2, \omega_2)
\]

\[
P^{(3)}(k, \omega) = \chi^{(3)}(k = k_1 + k_2 + k_3, \omega = \omega_1 + \omega_2 + \omega_3) : E(k_1, \omega_1) \cdot E(k_2, \omega_2) \cdot E(k_3, \omega_3)
\]

In analogy to \( \chi \), the induced dipole moment \( \mu \) can be expanded in series around \( E = 0 \). A quantity \( \mu^{(3)} \) is caused by the resonant interaction of three fields and essentially is a tensor of rank three. Physical meaning of each tensor rank will be discussed below.

### 3.1.4 Density matrix formalism

It should be pointed that both \( \chi \) and \( \mu \) are defined through the volume integral (space where light fields interact). Hence, \( \chi \) and \( \mu \) are ensemble averaged quantities but each is expressed as a sum of one-molecule polarizabilities of \( N \) number of molecules. Every molecular state is described quantum mechanically but the ensemble represents a thermodynamically mixed system, where we do not know \textit{a priori} the state of the chosen molecule. Therefore we describe molecular ensembles as a system in a mixed state. The density matrix formalism helps to operate on microscopic systems and specifically when relaxations should be taken into account.

The density operator is defined \textit{via} wavefunction \( \psi \) as given in Eq. 3.13. The density matrix is an ensemble averaged product of the ket and bra state vectors.

\[
\rho = \langle \psi | \psi \rangle \tag{3.13}
\]

Note that the ensemble average (expectation value) of the physical quantity \( P \) is given as 3.14:

\[
\langle P \rangle = \langle \psi | P | \psi \rangle = Tr(\rho P) \tag{3.14}
\]

\( P \) corresponds to the electric polarization induced by laser fields. \( \rho \) is defined in Eq. 3.13. The Liouville-von Neumann equation for the evolution of \( \rho \) is obtained from the Schrödinger equation which describes the evolution of the wave-function \( \psi \):

\[
i\hbar \frac{\partial \rho}{\partial t} = [\hat{H}, \rho] \tag{3.15}
\]
Where $\hat{H}$ is the Hamiltonian of the system with eigenstates $|n>$.
If $\psi$ is expanded into a basis set $|n>$, the density operator represents a matrix $\rho_{nm}$ as shown in Eq. 3.18. The normalization of the density matrix is $Tr(\rho) = 1$.

$$\psi = \sum_n c_n(t)|n>$$ (3.16)

$$\rho = \sum_{n,m} c_n(t)c_m^*(t)|n><m|$$ (3.17)

$$\rho_{nm}(t) = c_n(t)c_m^*(t)$$ (3.18)

The diagonal matrix element $\rho_{nn} = <n|\rho|n> = |c_n(t)|^2$ represents the population of the system in state $|n>$ while the off-diagonal matrix element $\rho_{nm} = <m|\rho|n> = c_n(t)c_m^*(t)$ indicates the coherence between states $|n>$ and $|m>$. If the relative phase between $c_n$ and $c_m$ is random then $\rho_{nm} = 0$ through the ensemble average. Therefore, thermal equilibrium is given only by the population distribution $\rho_{nn}^{(0)}$. Note that for time-independent measurements when the field causing polarization in the system $P$ is present simultaneously with a generated signal photons $c_n(t) = c_n$ and $c_m(t) = c_m$.

### 3.1.5 Perturbation theory

The Hamiltonian $\hat{H}$ in the Liouville-von Neumann Eq. 3.15 can be represented by a sum of three contributions $\hat{H}_0 + \hat{H}_{el} + \hat{H}_{relax}$. In a semi-classical approach, $\hat{H}_0$ is a molecular unperturbed Hamiltonian and has the highest contribution to the energy eigenstates of the system. The term $\hat{H}_{el}$ indicates the interaction of light with resonant molecular states (Eq. 3.19). The electronic contribution is considered in $\hat{H}_{el}$ as a perturbation to $\hat{H}_0$.

$$\hat{H}_{el} = -\mu_\alpha \cdot E$$ (3.19)

$\hat{H}_{relax}$ is responsible for the relaxations of molecular excitations back to thermal equilibrium. It is possible to introduce a phenomenological model [47] for thermally induced transitions due to the interaction with a “thermal reservoir” (quasi-continuum of states which can be coupled to the molecular quantum state via collisions). Therefore, population relaxation can be written as

$$\left( \frac{\partial \rho_{nm}}{\partial t} \right)_{relax} = \sum_m \left[ W_{m\rightarrow n}\rho_{mm} - W_{n\rightarrow m}\rho_{nm} \right]$$ (3.20)
Where $W_{m\rightarrow n}$ and $W_{n\rightarrow m}$ are phenomenological rate coefficients of transitions from levels $m \rightarrow n$ and $n \rightarrow m$ respectively. At thermal equilibrium equation takes the form

$$\frac{\partial \rho_{nn}^{(0)}}{\partial t} = \sum_{m} \left[ W_{m\rightarrow n} \rho_{nm}^{(0)} - W_{n\rightarrow m} \rho_{nn}^{(0)} \right] = 0$$

(3.21)

By taking into account 3.21 we can rewrite 3.20 as 3.22 with $T_1$ being the population relaxation time. The phase coherence decay $T_2$ is introduced similarly to $T_1$ but indicates a loss of phase between states $n$ and $m$. For example,

$$\frac{\partial}{\partial t} \left( \rho_{nn}^{(0)} - \rho_{nn} \right)_{relax} = -T_1^{-1} (\rho_{nn} - \rho_{nn}^{(0)})$$

(3.22)

If we expand density matrix elements and polarization into series [47], we can find the expectation value of the polarization at any order of perturbation $< P^{(n)} > = \operatorname{Tr} \rho^{(n)} P$. Assuming no permanent polarization $< P^{(0)} >$ in the medium at thermal equilibrium $\rho^{(0)}$. $\hat{H}_{el}$ is regarded as a first-order perturbation:

$$\frac{\partial \rho^{(1)}}{\partial t} = \frac{1}{i\hbar} \left[ (\hat{H}_0, \rho^{(1)}) + (\hat{H}_{el}, \rho^{(0)}) \right] + \left( \frac{\partial \rho^{(1)}}{\partial t} \right)_{relax}$$

(3.23)

$$\frac{\partial \rho^{(2)}}{\partial t} = \frac{1}{i\hbar} \left[ (\hat{H}_0, \rho^{(2)}) + (\hat{H}_{el}, \rho^{(1)}) \right] + \left( \frac{\partial \rho^{(2)}}{\partial t} \right)_{relax}$$

(3.24)

Because the field can be decomposed into Fourier components (Eq. 3.2) the $\hat{H}_{el}$ and the operator $\rho^{(n)}$ can be expanded into a Fourier series [47]:

$$\rho^{(n)} = \sum_{j} \rho^{(n)}(\omega_j)$$

and

$$\frac{\partial \rho^{(n)}(\omega_j)}{\partial t} = -i\omega_j \rho^{(n)}(\omega_j)$$

(3.25)

Taking into account the Hamiltonian $\hat{H}_0$ in the basis of its eigenstates $|n><m|$ equals $\hat{H}_0 = \sum_{m} \hbar \omega_{nm} |n><m|$ where the frequency corresponds to the energy difference $\omega_{nm} = (E_n - E_m)/\hbar$ between levels $n$ and $m$.

The interaction Hamiltonian is solved according to $(-i)/(\hbar) \times \sum_{i}(\hat{H}_{el} |n\rangle \rho_{i} |m\rangle - \rho_{nm} |\hat{H}_{el}|n\rangle |m\rangle)$. Therefore the Eq. 3.24 can be represented in successive orders of $\rho^{(1)}, \rho^{(2)}, ... \rho^{(n)}$ [47].
\[ \rho_{nm}^{(1)} = \frac{[\hat{H}_{el}]_{nm}}{\hbar(\omega_j - \omega_{nm} + i\Gamma_{nm})}(\rho_{mm}^{(0)} - \rho_{nm}^{(0)}) \]  

\[ \rho_{nm}^{(2)} = \frac{[\hat{H}_{el}(\omega_j), \rho_{nm}^{(1)}(\omega_k)]_{nm} + [\hat{H}_{el}(\omega_k), \rho_{nm}^{(1)}(\omega_j)]_{nm}}{\hbar(\omega_j + \omega_k - \omega_{nm} + i\Gamma_{nm})} = \frac{1}{\hbar(\omega_j + \omega_k - \omega_{nm} + i\Gamma_{nm})} \times \sum_l ([\hat{H}_{el}(\omega_j)]_{nl}\rho_{m}^{(1)}_{lm}(\omega_k) - \rho_{nl}^{(1)}(\omega_j)[\hat{H}_{el}(\omega_j)]_{lm} + [\hat{H}_{el}(\omega_k)]_{nl}\rho_{m}^{(1)}_{lm}(\omega_j) - \rho_{nl}^{(1)}(\omega_j)[\hat{H}_{el}(\omega_j)]_{lm}) \]  

Eq. 3.27 contains three states \( l, m, n \) connected by two-photons with frequencies \( \omega_j \) and \( \omega_k \). Note that the denominator 3.27 of a two-photon interaction is very different from the one-photon case 3.26. The one-photon interaction contains only detuning of a field frequency \( \omega_j \) from the molecular resonance between \( nm \) levels \( \omega_j - \omega_{nm} \) and a phenomenological relaxation rate \( \Gamma_{nm} \). Whereas the density matrix perturbed by a two-photon excitation contains the product of denominators with the beat frequencies of laser fields, difference from the molecular resonance and decay rates corresponding to each of \( l, m, n \) levels (especially while treating a three-level system).

Note that off-diagonal elements of the density matrix contain population difference term \( \rho_{nm}^{(0)} - \rho_{mn}^{(0)} \) between corresponding dipole coupled levels \( n \) and \( m \).

The full microscopic expressions for the polarization \( P^{(1)}, P^{(2)} \) and nonlinear susceptibilities \( \chi_{ij}^{(1)}, \chi_{ij}^{(2)} \) follow from the expressions 3.26 and 3.27 with \( \hat{H}_{el} = e r \cdot E \) and \( P_0 = N e r \).

\[ \chi_{ij}^{(1)} = \frac{P_{ij}^{(1)}(\omega)}{E_{j(\omega)}} \]  

\[ \chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2) = \frac{P_{ijk}^{(2)}(\omega)}{E_{j(\omega_1)}E_{k(\omega_2)}} \]  

It is also possible to obtain high-orders of the \( \rho_{nm}^{(n)} \) expansion. Particularly we are interested in the third-order perturbation of the density matrix \( \rho_{nm}^{(3)} \) which is important to describe four-wave mixing phenomena. Although in a present discussion we confine ourselves up to the second order due to the complexity of equations 3.26 and 3.27. The diagrammatic technique is introduced in the next chapter to provide a simple physical picture of the high-order interactions.
3.1.6 Diagrammatic technique

The scheme for calculating $\rho^{(n)}$ involves double-sided Feynman diagrams with two vertical lines of propagation (see Fig 3.1) the left line designates the ket-side of the density matrix $|\psi>$ and the right line designates the bra-side $<\psi|$ of the density matrix. A system in thermal equilibrium starts with $|g><g|$ with a population $\rho_{gg}^{(0)}$. The ket state propagates from e.g. $|a>$ to $|b>$ through interaction with a resonant field denoted with the vertex (see Fig. 3.1). The bra state propagates from $<a|$ to $<b|$ through the interaction with the complex conjugate field.

Figure 3.1: Double-sided Feynman diagrams for absorption (a) and (d) and emission (b) and (c) of a photon.

The sequence of general rules to obtain the microscopic expression for a diagram is described in [49–51] and outlined here:

1. The system starts with $|g><g| = \rho_{gg}^{(0)}$.
2. The propagation of the ket state appears as a multiplication factor on the left and the bra state on the right side of the diagram. Note that the time is advanced along both vertical lines upwards.
3. A vertex bringing $|a>$ to $|b>$ through absorption of $\omega_i$ on the ket (left) side of the diagram is described by the matrix element $\frac{1}{\hbar} <b|\hat{H}_{el}(\omega_i)|a>$ with $\hat{H}_{el}(\omega_i) \propto \exp(-i\omega t + ik \cdot r)$ denoted by 3.1a. If it is emission the vertex is described by a $\frac{1}{\hbar} <a|\hat{H}^\dagger_{el}(\omega_i)|b>$ with $\hat{H}^\dagger_{el}(\omega_i) \propto \exp(i\omega t - ik \cdot r)$, the corresponding diagram is shown on the figure 3.1b. The rule of changing the sign of the exponent expresses the convention for the operator of photon annihilation (absorption) and of photon creation (emission). Note that the field is expressed as a complex numbered amplitude and has both positive and negative frequencies. An absorption process on the ket side appears as emission on the bra side and vice versa, since the bra and ket are adjoint. Therefore, on the bra (right) side of the diagram, the vertices for emission 3.1c and absorption 3.1d are described by $-\frac{1}{\hbar} <a|\hat{H}_{el}(\omega_i)|b>$ and $-\frac{1}{\hbar} <a|\hat{H}^\dagger_{el}(\omega_i)|b>$ respectively.
4. Propagation from the $j$-th vertex to the next $j+1$th vertex along e.g. the $|l><k|$ double lines is described by the propagator $U_j = [\omega_{lk} - i\Gamma_{lk} - (\sum_{i=1}^{j} \pm \omega_i)]^{-1}$. $U_j$ is given by the inverse of the energy difference of the states on both sides of the diagram including the damping, minus all photon frequencies $\omega_i$ [51]. The frequency $\omega_i$ is chosen positive if absorption of $\omega_i$ at the $i$-th vertex occurs on the left or emission of $\omega_i$ on the right. The frequency $\omega_i$ is taken negative if emission occurs on the left and absorption on the right. Furthermore, if the interaction takes place on the bra side $U_j$ is multiplied by $(-1)$.

5. The last interaction originates from the trace $Tr(\mu \rho^{(m)})$ and is often drawn with a dashed arrow (not shown on the diagram). The final state of the system is described by the product of the ket and bra states after the last vertex.

6. The product of all factors describes the propagation from $|g><g|$ to $|f><f|$ through a set of states shown in a diagram. Summation of these products over all possible sets of states yields the final result.

With the help of the diagrammatic technique, more complicated diagrams accounting for the three-photons-matter interaction ($\rho^{(3)}_{nm}$) can be derived. If photons with identical frequencies participate in the multi-photon process then similar diagrams are obtained by the permutation of corresponding vertices. These diagrams should be taken into account with a degeneracy factor attached to the particular term in $\rho^{(3)}_{nm}$ as each “permuted” diagram equally contributes to the polarization generated by the multi-photon interaction. For the time-independent measurement, when all three-photons are simultaneously present, another set of diagrams should be generated by the permutation of vertices in time.

For the derivation of $\rho^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3)$ and $\chi^{(3)}_{ijkl}(\omega = \omega_1 + \omega_2 + \omega_3)$ Eq. 3.29 we need to take into account 48 diagrams (8 basic diagrams with a permutation of three vertices).

In the next few chapters we introduce the third-order nonlinear optical response, phase matching condition as a consequence of the diagrammatic derivation of $\chi^{(3)}_{ijkl}$ and the proportionality of $\chi^{(3)}_{ijkl}$ to the four-wave mixing signal.

$$\chi^{(3)}_{ijkl}(\omega = \omega_1 + \omega_2 + \omega_3) = \frac{Tr(\rho^{(3)} P)}{E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)}$$ (3.29)

3.2 Four-wave mixing spectroscopy

The generation of a four-wave mixing signal is discussed. The diagrammatic derivation of the non-linear optical susceptibility $\chi^{(3)}_{ijkl}$ is introduced. The diagrams relevant for
the resonant four-wave mixing process are selected. Analytical expressions for signal intensity in case of two-color resonant four-wave mixing spectroscopy are presented and follow the work of Zare et al. [52]. Interested reader may find the theory of the four-wave mixing signal reduction to relative populations in the weak-field limit in Ref. [53].

3.2.1 Third order nonlinear polarization

Double-sided Feynman diagrams were introduced by Yee and Gustafson [49], Druet et al. [50] and Prior [51] to derive a complete expression for the third-order non-linear susceptibility $\chi^{(3)}_{ijkl}$.

A set of diagrams for the derivation of $\rho^{(3)}$ and therefore third order nonlinear susceptibility $\chi^{(3)}_{ijkl}$ (Eq. 3.29) is shown on the Fig. 3.2. Each vertex designates a photon absorption or emission event. $1, 2, 3$ are intermediate levels which are resonantly coupled by photons with frequencies $\omega_1, \omega_2, \omega_3$. Permutation of photons in time allows to generate more diagrams from those which are already present on the Fig. 3.2. For example, in the diagrams 3.2a and 3.2b photons are acting always on either ket or bra side of the density matrix. These interactions are called parametric processes. By the emission of a photon the density matrix $|g>\rho^{(0)}_{gg}|<g$ returns back to the initial level. Parametric frequency up-conversion is usually described as a sequential excitation of energy levels $1, 2, 3$ with the fourth-photon emission of the frequency $\omega = \omega_1 + \omega_2 + \omega_3$.
Chapter 3. Light-Matter Interaction: RFWM Spectroscopy

Diagrams 3.2c - 3.2h involve absorption of all three-photons, e.g. scheme 3.29c describes one of few possible three-photon interactions for the unfolded scheme of four-wave mixing spectroscopy. The name unfolded suggests a sequential excitation which happens twice on the ket-side with photons $\omega_1$ and $\omega_2$ and once on the bra-side with a photon $\omega_3$. The emission of the signal photon takes place from the level $|2\rangle >$ ket-side and connects levels $|2\rangle$ and $<3|$, hence frequency of the emitted photon $\omega = \omega_1 + \omega_2 - \omega_3$.

Let us follow the procedure described in section 3.1.6 to derive the third-order nonlinear polarization $P^{(3)}(r, t)$ given in Eq. 3.31. Where $\varepsilon_4$ is a polarization unit vector. The signal field is oscillating at the sum or difference frequency $\omega_4$ of fields which constitute to $\rho^{(3)}$ with a propagation direction $k_4$.

\[
P^{(3)}_{RFWM} \approx Tr(-N\mu\rho^{(3)}) \quad (3.30)
\]

\[
P^{(3)}(r, t) = P^{(3)}_{RFWM}\varepsilon_4 \exp(-i(\omega_4 t - k_4 \cdot r)) \quad (3.31)
\]

Absorption of a first photon on the diagram 3.2c leads a system to:

\[
|1\rangle < 1|\varepsilon_1 \cdot \mu_1|g \rangle \rho^{(0)}_{gg} < g| \quad \frac{1}{\omega_{1g} - \omega_1 - i\Gamma_{1g}}
\]

The second excitation couples levels $|1\rangle >$ and $|2\rangle$.

\[
|2\rangle < 2|\varepsilon_2 \cdot \mu_2|1\rangle < 1|\varepsilon_1 \cdot \mu_1|g \rangle \rho^{(0)}_{gg} < g| \quad \frac{1}{\omega_{1g} - \omega_1 - i\Gamma_{1g}} \quad \frac{1}{\omega_{2g} - (\omega_1 + \omega_2) - i\Gamma_{2g}}
\]

The third photon generates a coherence between level $|2\rangle$ and level $<3|$. If the frequency $\omega_1 = \omega_3$ then $|2\rangle >$ and $<1| = <3|$ are coherently coupled by the three-photon interaction.

\[
|2\rangle < 2|\varepsilon_2 \cdot \mu_2|1\rangle < 1|\varepsilon_1 \cdot \mu_1|g \rangle \rho^{(0)}_{gg} < g|\varepsilon_3^* \cdot \mu_3|3\rangle < 3| \quad \frac{1}{\omega_{1g} - \omega_1 - i\Gamma_{1g}} \quad \frac{1}{\omega_{2g} - (\omega_1 + \omega_2) - i\Gamma_{2g}} \quad (-1) \quad \frac{1}{\omega_{23} - (\omega_1 + \omega_2 - \omega_3) - i\Gamma_{23}}
\]
The coherent emission of the signal due to \( \text{Tr}(\rho^{(3)}P) \) at frequency \( \omega_1 + \omega_2 - \omega_3 \) closes the four-photon product of corresponding one-photon interactions.

\[
\text{Tr}(\rho^{(3)}P) \propto <2|\epsilon_2 \cdot \mu_2|1><1|\epsilon_1 \mu_1|g> \rho_{gg}^{(0)} <g|\epsilon_3^* \cdot \mu_3|3><3|\epsilon_4^* \cdot \mu_4|2>
\]

Similarly to the discussion in the “Perturbation theory” (section 3.1.5), we obtain a complex denominator which contains field detuning from the molecular resonance, sum- or difference-frequencies of photons participating in \( \rho^{(3)} \) and decay rates of different levels connected by the multi-photon process. The denominator obtained in Eq. 3.32 looks like a product of several Lorentzian functions. Therefore, we can conclude that the system behaves as a damped harmonic oscillator in a frequency domain. By performing the Fourier-transform of the integral over frequencies \( \omega \) it is possible to evaluate the response of \( P^{(3)} \) in the time domain.

### 3.2.2 Rotating wave approximation

In this section we introduce a way to discard some of the Feynman diagrams. The rotating wave approximation (RWA) states that only terms containing either \( \exp(-i\omega t) \) or \( \exp(i\omega t) \) of the electromagnetic field contribute to the polarization. In the time-domain the first order polarization is defined as.

\[
P^{(1)}(t) = -\frac{i}{\hbar} \int_{-\infty}^{\infty} d\tau_1 \Theta(\tau_1) E_1(t - \tau_1) S^{(1)}(\tau_1)
\]

After absorption of a photon at the time instance \( 0 \) the off-diagonal density matrix element evolves in time \( \tau_1 \) according to 3.34 with a life-time constant \( \Gamma_{1g} \).

\[
\rho_{1g}(t) \propto \mu_{1g} \exp(-i\omega_{1g}\tau_1) \exp(-\Gamma_{1g}\tau_1)
\]

If the emission from the excited state takes place, the \( P(t) = \text{Tr}(\mu_{1g} P^{(1)}) \). Hence, the optical response \( S^{(1)}(\tau_1) \) is given as a product of the time evolution of \( \rho^{(1)} \) and the transition dipole moment to the ground state \( \mu_{1g}^* \)

\[
S^{(1)}(\tau_1) \propto \mu_{1g}^2 \exp(-i\omega_{1g}\tau_1) \exp(-\Gamma_{1g}\tau_1)
\]

The product of the electric field \( E_1(t - \tau_1) \) at the frequency close to the resonance \( \omega_1 = \omega_{1g} \) with the optical response function \( S^{(1)}(\tau_1) \) gives two terms oscillating at \( \exp(-i\omega_1 t) \) and \( \exp(-i2\omega_1 t) \) in 3.36. The integral in the first term is a slowly varying function with time \( \tau_1 \), because the field is slowly varying as a function of \( \tau_1 \). On the
other hand, the integral of the second term is oscillating at the double frequency and, therefore, can be neglected. Disregard of the “fast oscillating term” is called rotating wave approximation.

\[
P^{(1)}(t) = -\frac{i}{\hbar}\mu_2^2\exp(-i\omega_1 \tau_1) \int_{-\infty}^{\infty} d\tau_1 \Theta(\tau_1) E_1(t - \tau_1) \exp(-\Gamma_1 g \tau_1) -
\]

\[
-\frac{i}{\hbar}\mu_2^2\exp(+i\omega_1 \tau_1) \int_{-\infty}^{\infty} d\tau_1 \Theta(\tau_1) E_1(t - \tau_1) \exp(-\Gamma_1 g \tau_1) \exp(-i2\omega_1 \tau_1) \quad (3.36)
\]

**Figure 3.3:** Double-sided Feynman diagrams for the interaction at the ket side with the \(\exp(-i\omega_1 t)\) and \(\exp(i\omega_1 t)\) fields.

Considering the RWA the diagram 3.3b is not physical. Diagram 3.3a gives a straightforward physical meaning: the ground state density matrix is transformed by the absorption of the photon at \(\omega_1\) with the later emission at \(\omega\) which brings the system back to the ground state. While the 3.3b corresponds to the de-excitation of the ground state, which is impossible. Thus, the RWA preselects a set of physically sound diagrams [54].

### 3.2.3 Phase matching

So far we were concerned whether three interacting fields \(E_i\) are in resonance \(\omega_i = \omega_{jg}\) with the molecular medium where \(j\) is the designation for an arbitrary intermediate level. However, Feynmann diagrams do not take into account neither polarizations of the interacting fields with respect to transition dipole moments nor the propagation direction (wave-vectors) \(k_i\) of the interacting fields. If we substitute the full expression for the electric field given in Eq. 3.2 into the field-product Eq. 3.32 given for the specific diagram 3.2c then we can calculate the phase factor which describes the propagation of the signal field \(k_4\) which is generated by the nonlinear polarization \(P_{RFWM}^{(3)}\). In the space of wave-vectors we are only concerned with the phase-terms which are multiplied by \(k_i\), where \(i\) is the arbitrary field with polarization vector \(\varepsilon_i\). Similarly to the phase-matching in a spatial-domain we should consider the \(\omega\)-terms of laser fields in the frequency
Based on the collected phase-factors we can conclude that the signal generated by the diagram 3.2c propagates along the direction \( k_4 = k_1 + k_2 - k_3 \) and has a frequency \( \omega_4 = \omega_1 + \omega_2 - \omega_3 \). Note that the complex conjugate field \( E_3^* \) represents the absorption on the bra-side.

Phase-terms derived from \( \rho^{(3)} \) are sums and differences of wave-vectors and frequencies of interacting in a medium fields. Generally these relations can be written as vectorial sums of wave-vectors (Eq. 3.38) and sum- or difference-frequencies of laser fields (Eq. 3.39). Note that the fields are assumed to be monochromatic.

\[
\begin{align*}
  k_4 & = \pm k_1 \pm k_2 \pm k_3 \\
  \omega_4 & = \pm \omega_1 \pm \omega_2 \pm \omega_3
\end{align*}
\]  (3.38)  (3.39)

To produce four-wave mixing signals in a medium both of these equations should be fulfilled. Eq. 3.38 is regarded to be analogous to momentum conservation and the Eq. 3.39 to energy conservation (angular frequencies). The four-wave mixing signal intensity in a medium of length \( L \) in the weak field limit (such that assumption of the perturbation theory holds) is affected by a possible phase-mismatch \( \Delta k = \pm k_1 \pm k_2 \pm k_3 - k_4 \). In the plane-wave limit the solution of the wave-equation gives the signal intensity dependence on a wave-vector mismatch [47, 54]

\[
I_4 \propto \left( \frac{\sin(\Delta k L/2)}{\Delta k L/2} \right)^2
\]  (3.40)

The phase-matching (PM) condition is of great importance for experimentalists, because it defines the propagation direction of the signal field which should be detected. A proper alignment of the input laser beams with \( k_1, k_2 \) and \( k_3 \) enables to design experiments for a particular set of Feynman diagrams, because the signal is generated by the interaction of three laser beams in \( P^{(3)} \). The signal field obtains spatial and temporal properties from the interacting laser beams. Hence, the generated field is coherent and can propagate through free-space as a “laser-like” spatial beam without substantial divergence. This property facilitates a sensitive detection of the signal in the experiments where background emission and a stray-light are limiting factors. The advantages of the coherent FWM spectroscopy were summarized by Zare et al. for measurements in
plasmas [55] and flames [56] where chemiluminescence hinders a sensitive detection of trace species.

3.2.4 Degenerate four-wave mixing spectroscopy

We start the discussion on four-wave mixing techniques with degenerate four-wave mixing spectroscopy (DFWM). For DFWM all laser frequencies are equal and laser beams are arranged in the phase-matching geometry. From the derivation of the nonlinear polarization (Eq. 3.32) it is possible to conclude that if the frequency is set close to the one-photon molecular resonance there is an enhancement of the signal amplitude $\varepsilon_4 \exp(-i(\omega_4 t - k_4 r))$ due to the enhancement in $P_{\text{RFWM}}^{(3)}$ (Eq. 3.30). Note that the nonlinear polarization is taken as a sum over all possible $m_g$ states, where $m_g$ is the projection of total angular momentum quantum number onto the quantization axis defined by the polarization of the laser field. The molecular resonance can include all possible resonances (e.g. rotational, vibrational and electronic) which fulfill the one-photon transition selection rules (Eq. 2.13). Hence, the degenerate four-wave mixing signal carries similar information compared to the information obtained in one-photon absorption or laser-induced fluorescence experiments. The DFWM signal is essentially background-free because the optical axis for detection is defined by the phase-matching condition. This is in contrast to an absorption spectrum which is usually measured on a fluctuating background of the laser intensity. Compared to laser induced fluorescence, DFWM is less limited by the life-time of the excited state, facilitating the observation of predissociative states [57].

The stationary absorber model was introduced by Abrams and Lind [58] to interpret four-wave mixing phenomena in a non-degenerate two-level system. The model accounts only for the population contribution and neglects contributions from orientation and alignment. A diagrammatic perturbation theory is applied to derive these contributions to the DFWM signal expression [53]. Owing to the modulation of the polarization of the molecular medium by three interacting fields, it is important to account for the different time ordering of photon-matter interactions and for permutation of quantum states involved in DFWM. In a two-level resonant system the DFWM signal is generated by 16 terms. The first 8 diagrams are shown in Fig. 3.4. While the other 8 diagrams can be generated by permutation of photons with frequencies $\omega_1$ and $\omega_3$. Note that Fig. 3.4 contains insets A, B, C and D. For example, Fig. 3.4A includes two diagrams one starting from the population at the ground state $|g > \rho_{gg}^{(0)} < g|$ and another from the excited state $|i > \rho_{ii}^{(0)} < i|$. If we assume that all molecules are at thermal equilibrium and, therefore, at the ground state, we can exclude every right term at each A, B, C and D inset.
Chapter 3. Light-Matter Interaction: RFWM Spectroscopy

Figure 3.4: Double-sided Feynman diagrams relevant for the DFWM signal. Note that prime labels of $|g'\rangle$ and $<g'|$ (and the excited level $|i'\rangle$ and $<i'|$) points out one of few possible $m_g$-levels on the ket or bra side respectively.

The resonant DFWM signal intensity is proportional to the absolute value squared of the scalar amplitude of Eq. 3.30.

$$I_{DFWM} = I_4 \propto \langle \mathbf{P}(3) \rangle^2 = \frac{1}{2} |\mathbf{P}_{RFWM}^{(3)}|^2$$  (3.41)

Therefore our aim is to calculate the $\mathbf{P}_{RFWM}^{(3)}$, where the magnitude of the nonlinear optical response is written via the third-order susceptibility $\chi_{DFWM}^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3)$

$$\mathbf{P}_{RFWM}^{(3)} = \mathbf{P}(3)(\mathbf{r}, \omega) \mathbf{e}_4^* = \frac{3}{4} \epsilon_0 \chi_{DFWM}^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3) \mathbf{E}_1 \mathbf{E}_2^* \mathbf{E}_3$$  (3.42)

The contributions to $\chi_{DFWM}^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3)$ derived from the diagrammatic approach are summarized in the Fig. 3.4 and equations below (Eq. 3.44- 3.48). Note that each contribution to the signal may enter either with “+” or with “−” sign and is later coherently averaged by the modulus squared as given in Eq. 3.41. A physical interpretation of $\chi_{DFWM}^{(3)}$ is discussed below in terms of the spatial modulation of the molecular resonant medium.

$$\chi_{DFWM}^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3) = \frac{1}{6\epsilon_0 \hbar} [\mathbf{E}(-\omega_4, \omega_1, -\omega_2, \omega_3) + \mathbf{E}(-\omega_4, \omega_3, -\omega_2, \omega_1)]$$  (3.43)
where \( E(-\omega_4, \omega_3, -\omega_2, \omega_1) \) is produced from \( E(-\omega_4, \omega_1, -\omega_2, \omega_3) \) by the permutation of indices 1 and 3.

\[
E(-\omega_4, \omega_1, -\omega_2, \omega_3) = N \sum_{m_g} <g|\varepsilon_4^* \cdot \mu|i' > <i'|\varepsilon_3 \cdot \mu|g' > <g'|\varepsilon_2^* \cdot \mu|i > \times <i|\varepsilon_1 \cdot \mu|g > (A-B) + \sum_{m_g} <i'|\varepsilon_3 \cdot \mu|g' > <g'|\varepsilon_2^* \cdot \mu|i > \times <i|\varepsilon_1 \cdot \mu|g > <g|\varepsilon_4^* \cdot \mu|i' > (C-D) \]
\]

(3.44)

and resonant denominators \( A, B, C \) and \( D \), each of them is calculated as propagator for a particular diagram in Fig. 3.4. Please keep in mind, that for DFWM \( \omega_1 = \omega_2 = \omega_3 = \omega_4 = \omega \).

\[
A = (\rho_{gg}^{(0)} - \rho_{ii}^{(0)})([\omega_{ig} - \omega + k_1 \cdot v - i\Gamma_{ig}] \times \]
\[
[(k_1 - k_2) \cdot v - i\Gamma_{g'g}] \times [\omega_{i'g} - \omega + k_4 \cdot v - i\Gamma_{i'g}]^{-1} \]
\]

(3.45)

\[
B = (\rho_{g'g'}^{(0)} - \rho_{ii}^{(0)})([\omega_{ig} - \omega + k_2 \cdot v + i\Gamma_{ig}] \times \]
\[
[(k_1 - k_2) \cdot v - i\Gamma_{g'g}] \times [\omega_{i'g} - \omega + k_4 \cdot v - i\Gamma_{i'g}]^{-1} \]
\]

(3.46)

\[
C = (\rho_{g'g'}^{(0)} - \rho_{ii}^{(0)})([\omega_{ig} - \omega + k_3 \cdot v - i\Gamma_{ig}] \times \]
\[
[(k_3 - k_2) \cdot v - i\Gamma_{i'g}] \times [\omega_{i'g} - \omega + k_4 \cdot v - i\Gamma_{i'g}]^{-1} \]
\]

(3.47)

and

\[
D = (\rho_{g'g'}^{(0)} - \rho_{ii}^{(0)})([\omega_{ig} - \omega + k_2 \cdot v + i\Gamma_{ig}] \times \]
\[
[(k_3 - k_2) \cdot v - i\Gamma_{i'g}] \times [\omega_{i'g} - \omega + k_4 \cdot v - i\Gamma_{i'g}]^{-1} \]
\]

(3.48)

Eq. 3.44 contains the total number of absorbers \( N \), \( |n> \) is a molecular wavefunction characterized by the total angular momentum \( J \). \( \mu \) is the electric dipole moment operator. \( A, B, C \) and \( D \) are energy resonant denominators containing the first order Doppler effect. \( k_i \) is the wave-vector of \( i \)-th laser field and \( v \) is the velocity vector of the absorbing molecule. \( \Gamma_{nm} \) is the total dephasing rate of the coherence between magnetic sublevels \( m_n \) and \( m_m \). The initial density matrix element for the magnetic sublevel \( m_g \) is designated as \( \rho_{gg}^{(0)} \). Throughout the derivation we assume that the population among ground-state sublevels \( m_g \) is homogeneous, hence no orientation or alignment is present before the photon absorption.

It is instructive to look closer at any of the resonant denominators. For example, Eq. 3.45 and Eq. 3.46 contain the contribution from wave-vectors \( k_1 - k_2 \). The difference between wave-vectors of two laser fields at the resonance frequency generates a bright and dark fringe pattern with a spatial period defined by \( \Delta k_{12} = k_1 - k_2 \). At the places where \( k_1 \) and \( k_2 \) interfere constructively the population is pumped to the excited state. Hence, “burning” a hole in the ground state population \( |g> \rho_{gg}^{(0)} <g| \). Because the ground state
is periodically depopulated it is convenient to describe this phenomenon as emergence of a ground-state population grating with a coherence decay time $\Gamma_{g'g}$. A third laser beam with the wave-vector $k_3$ diffracts on the grating build by $k_1$ and $k_2$. A DFWM signal is efficiently scattered towards a phase-matched direction $k_4$ (Eq. 3.2.3). Note that terms A 3.45 and B 3.46 contribute differently to the third-order susceptibility $\chi^{(3)}_{DFWM}$. The grating described by the diagram A 3.45 has a “+” sign while the grating depicted by the diagram B 3.46 has a “−” sign.

Similar phenomena occur in the excited state. The difference between wave-vectors at the resonance frequency generates a population grating in the excited state $|i > p_i^{(0)} < i|$. This grating has a spatial modulation defined by $\Delta k_{32} = k_3 - k_2$ and decays with $\Gamma_{i'j}$. A third laser beam with the wave-vector $k_1$ diffracts on the grating. The DFWM signal is scattered towards the phase-matched direction $k_4$. Terms C (Eq. 3.47) and D (Eq. 3.48) contribute with a “+” and a “−” sign respectively, rendering the overall signal intensity.

Note that the permutation of indices 1 and 3 would indeed produce more gratings. For example, the ground-state with $\Delta k_{32} = k_3 - k_2$ and excited state $\Delta k_{12} = k_1 - k_2$. If we discard all high-order multipole components which can be derived from the four-photon matrix product (Eq. 3.44) [59, 60], then the DFWM signal is described by a doubly-degenerate population grating at the ground state and a doubly-degenerate population grating at the excited state. Therefore, the signal is a coherent sum of 4 gratings. Gratings can be distinguished by spacing ($\Delta k_{32}$ or $\Delta k_{12}$), by the level in which the grating is formed (ground or excited state) and by the multipole nature of the grating (population, orientation or alignment). In the present discussion the multipole components of the grating are omitted. Interested reader should refer to works of Williams et al. [59] and Wasserman et al. [60].

3.2.5 Two-color four-wave mixing spectroscopy

The Two-Color Resonant Four-Wave-Mixing (TC-RFWM) spectroscopy is a nonlinear four-wave mixing process where two distinct laser frequencies are in resonance with two molecular transitions. Hence, the technique is similar to other double-resonance methods [61, 62] where two transitions share a common level. However, the FWM signal is generated by a coherent scattering from the nonlinear polarization and is, therefore, background-free. There are several ways to arrange resonantly interacting photons e.g. if PUMP ($E_1$ and $E_2$) and PROBE ($E_3$) fields share the excited level, the energy scheme is defined as SEP (stimulated emission pumping) TC-RFWM. If PUMP and PROBE are connected via the intermediate level, the energy scheme is defined as UNFOLDED
TC-RFWM. If PUMP and PROBE share the ground level the energy scheme is defined as UP TC-RFWM, (see Fig. 3.5 a, b and c respectively).

Figure 3.5: Energy level diagrams for TC-RFWM spectroscopy: a for the SEP, b for the UNFOLDED and c for the UP energy level schemes. The emitted SIGNAL is drawn with the dashed arrow line.

Figure 3.6: Double sided Feynman diagrams for TC-RFWM spectroscopy: a for the SEP, b for the UNFOLDED energy level schemes.

The theoretical description of the TC-RFWM is considered similarly to the DFWM spectroscopy where three input fields interact with an isotropic molecular ensemble to produce the fourth field. Here and below we assume that levels coupled by the TC-RFWM process can be defined by the angular momentum $J$. The level labels $g, i$ and $f$ correspond to the individual magnetic sublevels of the rovibronic state and are connected by the resonant transition. For the derivation of the FWM signal intensity given in Eq. 3.41 the nonlinear polarization given in Eq. 3.42 and, consequently the third-order nonlinear susceptibility $\chi^{(3)}$ provided in Ref. [51, 52] is required. The energy diagrams a and b in the Fig. 3.5 illustrate the situation when the energy level $i$ is common for both transitions. In case of the SEP TC-RFWM scheme the three resonant terms given in the Eq. 3.49 and shown in the Fig 3.6 a contribute to the third-order susceptibility. The first two diagrams correspond to the intermediate state population grating which is
introduced by the PUMP lasers with frequencies $\omega_1 = \omega_2$. Note the permutation of the two pump beams leads to the net two terms in $\chi_a^{(3)}$ 1 and 2 respectively. The PROBE laser of the frequency $\omega_3$ (conventionally for SEP scheme can be called DUMP laser) stimulates emission from the level $i$ to the level $f$ in a phase-matched direction and generates the SIGNAL beam at the frequency $\omega_4$. The third diagram 3 in $\chi_a^{(3)}$ describes the coherence induced between levels $g$ and $f$ by a sequential absorption of the PUMP ($\omega_1$) and the DUMP ($\omega_3$) photons. The SIGNAL photon emerges when the PUMP ($\omega_2$) is absorbed.

$$\chi_a^{(3)}(-\omega_1, \omega_1, \omega_3, -\omega_2) = \frac{N}{6\epsilon_0 \hbar^3} \left\{ \sum_{m_g} \rho_{gg}^{(0)} < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > < i'|\varepsilon_3 \cdot \mu|f > < f|\varepsilon_4^* \cdot \mu|i > \right. \cdot (|\omega g - \omega_1 + k_1 \cdot v - i\Gamma_1|)[(k_1 - k_2) \cdot v - i\Gamma_{if}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if})$$

$$- \sum_{m_g} \rho_{gg}^{(0)} < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > < i'|\varepsilon_3 \cdot \mu|f > < f|\varepsilon_4 \cdot \mu|i > \cdot (|\omega f - \omega_2 + k_2 \cdot v + i\Gamma_3|)[(k_1 - k_2) \cdot v - i\Gamma_{if}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if})$$

$$+ \sum_{m_g} \rho_{gg}^{(0)} < f|\varepsilon_4^* \cdot \mu|i > < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > < i'|\varepsilon_3 \cdot \mu|f > \cdot (|\omega f - \omega_2 + k_2 \cdot v + i\Gamma_3|)[-\omega g - \omega_3 + \omega_2 + (k_3 - k_2) \cdot v - i\Gamma_{fg}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if}) \right\} \quad (3.49)$$

For the UNFOLDED energy scheme diagrams 1 and 2 in Fig 3.6 describe the scattering process from the intermediate level population gratings created by the PUMP beams. The PROBE coherently scatters off the $P_{RFWM}^{(3)}$ and, hence, generates the SIGNAL beam at the frequency $\omega_4$. The third diagram 3 in Fig 3.6 that enter the expression for the $\chi_b^{(3)}$ in the Eq. 3.50 corresponds to a coherence induced between levels $g$ and $f$ by a sequential absorption of the PUMP ($\omega_1$) and the PROBE ($\omega_3$) photons. The SIGNAL photon emerges when the PUMP ($\omega_2$) is absorbed.

$$\chi_b^{(3)}(-\omega_4, \omega_1, \omega_3, -\omega_2) = \frac{N}{6\epsilon_0 \hbar^3} \left\{ \sum_{m_g} \rho_{gg}^{(0)} < i|\varepsilon_1 \cdot \mu|g > < f|\varepsilon_3 \cdot \mu|i > < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > \right. \cdot (|\omega g - \omega_1 + k_1 \cdot v - i\Gamma_1|)[(k_1 - k_2) \cdot v - i\Gamma_{if}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if})$$

$$- \sum_{m_g} \rho_{gg}^{(0)} < i'|\varepsilon_3 \cdot \mu|f > < f|\varepsilon_3 \cdot \mu|i > < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > \cdot (|\omega f - \omega_1 + k_1 \cdot v - i\Gamma_1|)[(k_1 - k_2) \cdot v - i\Gamma_{if}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if})$$

$$- \sum_{m_g} \rho_{gg}^{(0)} < f|\varepsilon_3 \cdot \mu|i > < i|\varepsilon_1 \cdot \mu|g > < g|\varepsilon_2^* \cdot \mu|i' > < i'|\varepsilon_3 \cdot \mu|f > \cdot (|\omega f - \omega_1 + k_1 \cdot v - i\Gamma_1|)[\omega f - \omega_4 + (k_3 - k_2) \cdot v - i\Gamma_{fg}] \times (\omega f - \omega_4 + k_4 \cdot v - i\Gamma_{if}) \right\} \quad (3.50)$$

The UP energy scheme has a $\chi_c^{(3)}$ expression given in Eq. 3.50 that contains four terms.
Thus four Feynman diagrams contribute to the resonant generation of the SIGNAL (see Fig. 3.7). The first two diagrams i.e. 1 and 2 correspond to the ground state “hole-burning” experiment. The population is removed from the ground level \( g \) when both PUMP lasers are in resonance with the \( i \leftarrow g \) transition. Note that crossing PUMP beams in a BOXCAR geometry creates a spatial interference pattern. Regions in the medium where PUMP beams interfere constructively (bright fringes) contain target molecules in the excited level \( i \) and regions where PUMP beams interfere destructively mainly contain molecules in the ground level \( g \). The PROBE beam (\( \omega_3 \)) is coherently scattered on the ground state population grating and produce a SIGNAL beam in the direction of the phase-matching. The diagrams 3 and 4 in Fig. 3.7 can be described as the coherence induced by the PUMP (\( \omega_2 \)) and the PROBE (\( \omega_3 \)) between excited levels \( i \) and \( f \). After the stimulated emission of a photon from \( i \rightarrow g' \) initiated by the PUMP (\( \omega_1 \)) the SIGNAL photon is emitted.

\[
X_c^{(3)}(-\omega_4, \omega_1, \omega_3, -\omega_2) = \frac{N}{6\epsilon_0 \hbar^3} \left\{ \ldots \right. \\
\sum_{m_g} \rho_{gg}^{(0)} \left| g' \langle \epsilon_4^* \cdot \mu | f \rangle < f \langle \epsilon_3 \cdot \mu | g \rangle < g \langle \epsilon_2^* \cdot \mu | i \rangle < i \langle \epsilon_1 \cdot \mu | g' \rangle > \right| \omega_{ig'} - \omega_1 + k_1 \cdot v - i\Gamma_{ig} \right| \left( \omega_{f} - \omega_4 + k_4 \cdot v - i\Gamma_{fg} \right) \\
- \sum_{m_g} \rho_{gg}^{(0)} \left| g' \langle \epsilon_4^* \cdot \mu | f \rangle < f \langle \epsilon_3 \cdot \mu | g \rangle < g \langle \epsilon_2^* \cdot \mu | i \rangle < i \langle \epsilon_1 \cdot \mu | g' \rangle > \right| \omega_{ig} - \omega_1 + k_1 \cdot v + i\Gamma_{ig} \right| \left( \omega_{f} - \omega_4 + k_4 \cdot v - i\Gamma_{fg} \right) \\
- \sum_{m_g} \rho_{gg}^{(0)} \left| f \langle \epsilon_3 \cdot \mu | g \rangle < g \langle \epsilon_2^* \cdot \mu | i \rangle < i \langle \epsilon_1 \cdot \mu | g' \rangle > \right| \omega_{ig} - \omega_1 + k_1 \cdot v + i\Gamma_{ig} \right| \omega_{fi} - \omega_3 + \omega_2 + (k_3 - k_2) \cdot v - i\Gamma_{fi} \\
\times \left[ \omega_{fg'} - \omega_4 + k_4 \cdot v - i\Gamma_{fg} \right] \\
+ \sum_{m_g} \rho_{gg}^{(0)} \left| f \langle \epsilon_3 \cdot \mu | g \rangle < g \langle \epsilon_2^* \cdot \mu | i \rangle < i \langle \epsilon_1 \cdot \mu | g' \rangle > \right| \omega_{fg} - \omega_3 + k_3 \cdot v - i\Gamma_{fg} \right| \omega_{fi} - \omega_3 + \omega_2 + (k_3 - k_2) \cdot v - i\Gamma_{fi} \\
\times \left[ \omega_{fg'} - \omega_4 + k_4 \cdot v - i\Gamma_{fg} \right] \right\} \tag{3.51}
\]
The equations for $\chi^{(3)}$ have a dependence on the number of absorbers $N$. $\rho^{(0)}_{gg}$ is the initial density matrix element for the magnetic sublevel $m_g$. The density matrix specifies the probability of the system being in that sublevel. $\mu$ is the electric dipole moment operator. $h\omega_{ji}$ is the energy difference ($E_j - E_i$) between levels $j$ and $i$. $v$ is the velocity vector of the absorbing molecule. $\epsilon_0$ is the permittivity of free space. $\hbar = h/(2 \cdot \pi)$ is the Dirac constant. The relaxation and dephasing rates $\Gamma_{ji}$ are defined as

$$\Gamma_{ji} = \frac{\Gamma_j + \Gamma_i}{2} + \Gamma_{ji}^d$$

(3.52)

The $\Gamma_j = 1/\tau_j$ where $\tau_j$ is the lifetime of the level $j$. The $\Gamma_{ji}^d$ is the collisional dephasing rate of the coherence between the levels $j$ and $i$.

It is interesting to mention that coherence terms in $\chi^{(3)}$ exist only when both PUMP and PROBE pulses overlap in time. Furthermore, the UP TC-RFWM experiment differs from the SEP and UNFOLDED because PUMP and PROBE transition sample the initially populated level $g$. Therefore any of the input fields may interact first. This is in contrast to the SEP or UNFOLDED schemes where only PUMP beams can interact first.
Chapter 4

Experimental setup

The experiments are performed in a molecular beam apparatus designed for simultaneous linear and non-linear spectroscopic measurements of stable and transient molecules [63]. The molecular beam apparatus coupled to the pulsed discharge slit nozzle for the production of small carbon C$_2$ and C$_3$ radicals is presented. The chemical mechanisms to produce reactive carbon C$_2$, C$_3$ and C$_2$H species are considered. The optical setup for perturbation facilitated TC-RFWM (section 4.2.1) and two-photon perturbation facilitated laser induced fluorescence (PF-LIF) (section 4.2.2) is described.

4.1 Radical source

The complexity of chemical reactions in acetylene plasmas has been reviewed in Ref. [64, 65]. The pulsed discharge nozzle (section 4.2.1) applied to generate C$_2$ and C$_3$ carbon clusters has an electron energy ranging from 3.16 to 75 eV according to the numerical investigation provided in [66]. The non-equilibrium character of the low pressure plasma is the result of the high mobility of electrons compared to heavy molecules and atoms. Electrons are heated by the electromagnetic field. In addition, due to the small energy transfer to heavy particles in elastic collisions the electron energy is much higher compared to the energy of the ion or the neutral particle. Collisions with the energetic electrons cause electronic excitation, dissociation and ionization of the atomic and molecular gas species. Cooperatively with purely molecular collisions these mechanisms lead to the generation of the reactive products. The generated reactive species are rotationally and translationally cooled during the expansion in the molecular jet. Note, the translational temperature perpendicular to the propagation direction of the molecular jet is usually as low as 25 K. However, the effective vibrational excitation of the molecules in collisions with electrons yields a substantial population in higher vibrational levels.
that are not cooled via collisions with the buffer gas during the expansion. For example, we were able to produce C\textsubscript{2} radicals in the $a^3\Pi_u$ state with substantial population in the vibrational $v = 5$ level, $\approx 7900$ cm$^{-1}$ above the ground state $\tilde{X}^1\Sigma_g^+$.

Reaction mechanisms in low pressure plasmas are discussed in [64] and classified as follows. Reactions involving electrons include electron impact ionization, where upon the collision of a free incoming electron with a valence electron of a target molecule a sufficient energy (larger than ionization energy) is transferred to the valence electron. Electron impact dissociation where the collision of a free electron with a valence electron leads to the electronic excitation of the target molecule or, in case of dissociative excitation the electron impact leads to the dissociation of the target molecule. Vibrational excitation by electron impact and dissociative electron attachment is an important mechanism in plasma chemistry responsible for the vibrational excitation of polyatomic species in collisions with electrons. During the excitation process the incoming electron is captured into a low-lying unoccupied molecular orbital having typically anti-bonding character. The geometry of the newly formed complex starts to rearrange due to the new electronic configuration. When the electron leaves the molecule by autodetachment after a typical time from $10^{-15}$ to $10^{-11}$ s, the atomic nuclei are at much larger distances compared to the equilibrium geometry in the ground state, therefore the neutral molecule is in a vibrationally excited state. If the lifetime of the resonance (electron being captured in the low-lying unoccupied molecular orbital) is long enough for the nuclei to reach large distances, dissociative attachment resulting in the formation of a stable negative ion fragment of the original particle can occur [64]. Reactions involving ions include ion-neutral reactions, ion-ion recombinations in binary collisions and charge transfer reactions. Reactions with neutral species can proceed via vibrationally excited electronic states or the ground state, hence enabling endothermic reactions. These numerous reaction mechanisms lead to the low selectivity in the plasma and a complex chemical and physical behavior. For the discharge nozzle applied in these experiments the most important reaction mechanisms according to Ref. [67] are direct electron impact dissociation e.g. \textit{C}_2\textit{H}_2 + e^- \rightarrow \textit{C}_2\textit{H} + \textit{H} + e^- and Penning dissociation e.g. \textit{C}_2\textit{H}_2 + \textit{Ar}^* \rightarrow \textit{C}_2\textit{H} + \textit{H} + \textit{Ar}. Recursive application of these reaction mechanisms leads to the production of \textit{C}_2, \textit{CH} and \textit{C}. On the other hand \textit{C}_3 can be produced in the collision of \textit{C}_2(X^1\Sigma_g^+) + \textit{C}(^3P_j) + K \rightarrow \textit{C}_3(X^1\Sigma_g^+) + K or \textit{C}_2\textit{H}(X^2\Sigma^+) + \textit{C}(^3P_j) + K \rightarrow \textit{C}_3\textit{H}(X^2\Pi_{\Omega}) + K and \textit{C}_2(X^1\Sigma_g^+) + \textit{CH}(X^2\Pi_{\Omega}) + K \rightarrow \textit{C}_3\textit{H}(X^2\Pi_{\Omega}) + K with a later dissociation of the \textit{C}_3\textit{H}(X^2\Pi_{\Omega}) \rightarrow \textit{C}_3(X^1\Sigma_g^+) + \textit{H}(^2S_{1/2}) [42] where \textit{K} is a collisional partner carrying out the excess kinetic energy. For the optimal generation of reactive species the discharge expansion is analyzed by relevant state variables such as temperature, pressure, axial speed and particle number density.
4.1.1 Molecular jet

The structure of the molecular jet is usually described by separating the expansion region into three zones. The first zone is located at the valve orifice where the gas starts to accelerate by the imposed pressure difference \( P_0 - P_c \). \( P_0 \) is the stagnation pressure and \( P_c \) is the ambient pressure in the molecular jet chamber. The radical source consists of a slit-flow body and discharge electrodes matching the slit geometry. The flow may reach a sonic speed with a Mach number \( M \) reaching the value of 1 if the pressure ratio \( P_0 / P_c \) exceeds the critical value \( G = \left[ \frac{(\gamma + 1)}{2} \right]^{\gamma/(\gamma - 1)} \) \( [68] \) (e.g. \( G_{\text{Ar}} = 2.05 \)). \( \gamma \) is defined as a heat capacity ratio \( C_P / C_V \) and is usually close to \( 5/3 \) for a monoatomic gas at the room temperature. In present experiments we use the Ar as a buffer gas. The back pressure behind the pulsed valve \( P_0 = 2 - 10 \cdot 10^5 \) Pa = 1.5 - 75 \( 10^2 \) Torr is usually expressed as a multiple of the orifice diameter.

For the orifice diameter of \( d = 0.2 \) cm and a stagnation pressure of \( 6 \cdot 10^3 \) Torr, \( P_0 \cdot d = 1200 \) Torr-cm and can be conveniently recalculated to the source density as \( n_0 \cdot d = 3.22 \cdot 10^{16} P_0 \cdot d = 3.864 \cdot 10^{19} \) cm\(^{-2} \) \( [68] \). Note, it is convenient to express the source density as a parameter of the distance from the pulsed valve. Hence, it has a dimension of cm\(^{-2} \). Simulations of the flow pattern in the slit-flow body and the discharge region \( [66] \), however, suggest that the flow velocity steadily increases but remains subsonic. The expansion becomes supersonic \( (M > 1) \) at the beginning of the second zone in the discharge region \( I \) between cathode(\( C \)) and anode(\( A \)) (see Fig. 4.1 for details). The growth of the Mach number in the first \( \sim 200 \) µm is followed by a drop in the next \( \sim 200 \) µm \( [66] \). A drop in the molecular velocity is caused by compression waves from the expansion which reaches the electrode walls in the interelectrode region. The third zone is the post discharge zone (after the cathode) where the Mach number gradually increases \( (M \gg 1) \) and can be characterized by a planar expansion with a temperature being inversely proportional to the distance from the orifice exit. The region where \( M \gg 1 \) is called the “zone of silence”. Very few collisions are taking place in this low-temperature region. Hence, one can expect that reactive \( \text{C}_2 \) and \( \text{C}_3 \) molecules are “frozen” in the quantum state produced in the second zone.

After leaving the discharge source, the Mach number for a freely expanding molecular jet can be calculated according to Eq 4.1 (see Ref. \( [68] \) for details). An estimate for a centerline Mach number \( (M) \) in a longitudinal direction \( z \) is evaluated with the help of established correlations for the planar expansions if \( z/d > 0.5 \), see Ref. \( [68] \) for details. The correlation coefficients \( C_1 = 3.038, C_2 = -1.629, C_3 = 0.9587 \) and \( C_4 = -0.2229 \)
are given for a planar (2D $j = 2$) gas expansion where $\gamma = 5/3$.

$$M = \frac{z^{\gamma - 1}}{d} \left( C_1 + \frac{C_2}{(\frac{\gamma}{d})} + \frac{C_3}{(\frac{\gamma}{d})^2} + \frac{C_4}{(\frac{\gamma}{d})^3} \right)$$

(4.1)

The Mach number $z = 5$ mm downstream a valve orifice of $d = 2$ mm is $M = 3.42$. Note that the flow body contains a planar distribution of apertures, i.e. close to the center of the slit $d = 1$ mm and at the edges $d = 2$ mm. Therefore the $M = 3.42$ rather represents a Mach number lower bound after 5 mm of the molecular jet propagation.

Assuming an isentropic flow, ideal gas behavior, constant $C_P$ or $\gamma$ and a continuum flow, all relevant thermodynamic state variables (temperature $T$, pressure $P$, gas density $\rho$ and gas velocity $v$) can be calculated by involving only two parameters, i.e. $\gamma$ a property of the gas (fluid), and $M$- a property of the flow field. For an ideal gas the speed of sound is $a = \sqrt{\frac{\gamma R T}{W}}$. By definition the Mach number is $M \equiv \frac{v}{a}$.

$R = 8.31$ J/(mol·K) is the gas constant and $W$ is the standard atomic weight. In the expansion of $\simeq 2\%$ of $C_2H_2$ diluted in 98 % of Ar, $W \simeq 39.9$ is assumed to be close to a standard atomic weight of Ar.

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\frac{1}{\gamma - 1}}$$

(4.2)

$$v = M \sqrt{\frac{\gamma R T_0}{W} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\frac{1}{2}}}$$

(4.3)

$$\frac{P}{P_0} = \frac{T}{T_0} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\frac{\gamma}{\gamma - 1}}$$

(4.4)

$$\frac{\rho}{\rho_0} = \frac{n}{n_0} = \frac{T}{T_0} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\frac{1}{\gamma - 1}}$$

(4.5)

From Eqs. 4.2 - 4.5 [68] all thermodynamic variables can be computed. For the experimentally relevant parameters such as an initial temperature $T_0 = 300$ K and a stagnation pressure of $6 \cdot 10^3$ Torr. The temperature and pressure for the distance $z = 5$ mm downstream the discharge nozzle are obtained as $T = 61$ K and the $P = 113$ Torr. A substantial decrease in translational temperature and pressure is observed at the longitudinal distance $z \leq L$ where $L \simeq 30$ mm is the slit length. The root mean square average thermal velocity in the molecular jet $v_{\|,\perp} = \sqrt{3RT_{\|,\perp}/W}$ decreases with the temperature. The temperature is defined as a spread in the velocities for a Gaussian distribution for the parallel $f(v_{\|})$ and the perpendicular $f(v_{\perp})$ direction relative to the propagation direction of the molecular jet. Upon the increase of an overall jet velocity $v \equiv Ma$ the $v_{\|,\perp}$ are further reduced.

The total number of binary collisions experienced by a molecule during the free jet planar expansion is in the order of $10^4 - 10^5$. Any kinetic process which requires a higher
amount of collisions will not be able to approach equilibrium. Therefore, the following succession of temperatures is established $T_{\parallel} \leq T_{\text{rot}} \ll T_{\text{vib}}$ in the pulsed discharge nozzle. It is possible to compare the calculated $T_{\parallel}$ temperature with a supreme value set by the measured rotational temperature of the $\text{C}_2$ and $\text{C}_3$ molecules. The translational temperature parallel to the propagation direction of the jet is approximately $T_{\parallel} = 61$ K for a 5 mm distance downstream the nozzle. Experimentally the rotational temperature $T_{\text{rot}} \approx 150$ K has been estimated from the DFWM spectra of the $\text{C}_2$ (Fig. 5.2) and $\text{C}_3$ (Fig. 2.5) in the molecular jet for $z \simeq 5$ mm. The vibrational temperature $T_{\text{vib}} \approx 6000$ K. The cooling inherent to the intramolecular degrees of freedom (for rotations and vibrations) requires collisional partners to have energy levels that fit the energy $k_B(T_i - T_f)$, where $T_i$ is the initial temperature and $T_f$ is the final (desired) temperature of the target molecule produced in the discharge. Ar is a relatively heavy atom and can slow down molecules with the molar weight less than 40. However, it can not effectively cool vibrationally excited species. Therefore, the difference between translational, rotational and vibrational temperatures is established as a result of cooling by the Ar buffer gas.

According to the Eq. 4.5 the number density $n$ drops rapidly from the $n_0 \cdot d = 3.9 \cdot 10^{19}$ cm$^{-2}$ to $n \cdot d = 3.5 \cdot 10^{18}$ cm$^{-2}$ at $z = 5$. The hard-sphere two-body collisional frequency $Z$ is given by,

$$Z = n\sigma\sqrt{\frac{3RT_{\parallel,\perp}}{\mu_{AB}}}$$  \hspace{1cm} (4.6)

$\sigma_{\text{Ar}} = 3.3 \cdot 10^{-17}$ m$^2$ is the collisional cross section given in [69]. $\mu_{AB} = \mu_{\text{Ar}-\text{Ar}}$ is the reduced mass of two colliding particles, e.g. for Ar atoms $\mu_{\text{Ar}-\text{Ar}} = 20$ g/mol. The inverse value of the mean free path of the Ar atoms is given by $n\sigma = 4.2 \cdot 10^7$ m$^{-1}$. The collisional frequency $Z = n\sigma v_{th} = 20 \cdot 10^9$ s$^{-1}$ for $z = 5$ mm. A collisional rate of 20 collisions/ns is obtained for the longitudinal position of 5 mm away from the discharge orifice.

### 4.1.2 Pulsed discharge nozzle

Small carbon radicals $\text{C}_2$ and $\text{C}_3$ in the ground $\tilde{X}^1\Sigma_g^+$ state are prepared in the molecular beam environment by expansion of $\approx 2\%$ acetylene diluted in Ar buffer gas through a solenoid valve (General Valve, Parker) [70]. Typical backing pressures are between 2 and $10 \times 10^5$ Pa. The molecular pulse has a duration of about 750 $\mu$sec. Prior to the expansion, the pulse passes through a multichannel flow-body producing a planar flow appropriate to the slit geometry of the discharge source [71]. The slit-expansion geometry increases the interaction volume between the crossing area of four-wave mixing laser beams and the molecular jet (given in dark blue in the Fig. 4.1). Compared to
a more common pinhole expansion, the application of the pulsed discharge nozzle with a planar geometry can potentially enhance the signal intensity by nearly two orders of magnitude due to the quadratic dependence of the four-wave mixing signal on interaction length [72].

Figure 4.1: Scheme of the pulsed discharge nozzle containing the valve, mounted slit-flow body and the discharge assembly (anode (A), isolation plates (I drawn in white color in the figure) and the cathode (C)). The temporal distribution of $C_2$ obtained by applying DFWM is given along the axis t. Two traces are shown: the red trace is observed at a longitudinal position of $z \simeq 5$ mm from the discharge source. The black trace is recorded at a distance of $z \simeq 7$ mm. In addition, the laser fields in the BOXCAR geometry $E_1, E_2, E_3$ and the resulting $E_4$ are shown.

A pulsed tension of -800 to -900 V and $\simeq 4 \mu$s duration is applied to the anode (A) prior to the expansion zone. Electrons ($e^-$) are ejected from the anode and move upstream the molecular jet following the direction of the electric field. Along the way of approximately the thickness of the 2 mm insulator plate (I), the electrons collide with Ar and $C_2H_2$ producing radical molecules predominantly via direct electron impact and Penning dissociation [67]. After the electrons reach the cathode (C) the tension drop on the ballast resistor ($R_b=1.5 \Omega$) is measured on the oscilloscope ($U_{osc}$). From the $U_{osc}$ waveform it is possible to estimate the “instantaneous” electron density $n_e$ integrated over $dt$ within the duration of the discharge. Taking the current flowing through $R_b$ (see Fig. 4.1) as $I = U_{osc}/R_b = 0.2$ A and dividing by $q(e^-) = 1.6 \times 10^{-19}$ C results in $n_e = 12.5 \times 10^{17}$ m$^{-3}$. This value can be compared to the electron densities estimated in the simulation reported in Ref. [66] yielding for the cathode $n_e \leq 1 \times 10^{17}$ m$^{-3}$, the anode regions $n_e \leq 1 \times 10^{17}$ m$^{-3}$ and the central plasma bulk $n_e \approx 3 \times 10^{18}$ m$^{-3}$ for a -500 V tension applied to the anode. Note that direct detection of the electron density in the plasma bulk is hindered by the mismatched impedance and the sheath thickness
near the anode (should be in the order of a few Debye length as given by Ref. [73]). Thus, the order of magnitude of the experimental $n_e$ value agrees with the simulated electron densities for a discharge source of similar design. This gives the possibility to simulate and optimize the source for the efficient production of radicals. The duration of the discharge is mainly determined by the thickness of the isolation plate ($I$). However many parameters may influence it as well, i.e. the local pressure, stagnation pressure (pressure behind the solenoid valve), the number density of the precursor $C_2H_2$ molecules, the type of the carrier gas (Ar), the discharge tension, the direction of the electrons (counter propagating relative to the direction of the expansion) etc. By optimizing the source on the DFWM or LIF signal $z \approx 5$ mm downstream of the expansion region from $C_2$ or $C_3$ species, we noticed a gain in the signal if the discharge trigger is set at the onset of the gas pulse. Usually the delay between the valve trigger and the discharge trigger is approximately 789 - 800 $\mu$s. In this operational mode the actual plasma region is limited to $\approx 4$ $\mu$s (as observed on the ballast resistor).

A DFWM measurement of the $C_2$ temporal distribution in the molecular jet is shown in Fig. 4.1. The duration of the gas pulse (the valve opening time $\approx 750$ $\mu$s) is much larger than the duration of the discharge ($\approx 4$ $\mu$s). The temporal distribution of the $C_2$ radical in the molecular jet is evaluated by scanning the trigger time of the valve and of the high-voltage pulse simultaneously relative to the trigger time of the DFWM laser. The red trace exhibiting a more intense signal corresponds to a longitudinal position of $z \approx 5$ mm between the pulsed discharge nozzle and the intersection region of the DFWM laser beams. The black trace is measured by setting the source $z \approx 7$ mm away from the laser overlap region. This $C_2$ pulse propagated 2 mm further and, according to the change of the pulse shape, it experienced substantial dispersion of the molecular velocities. In fact, the product of the molecular jet velocity (0.6 mm/$\mu$s) and the discharge duration measured either from the ballast resistor (4 $\mu$s) or by the DFWM of the $C_2$ temporal distribution (3 - 4 $\mu$s) shown in Fig. 4.1 reflects exactly the 1.8 - 2.4 mm length of the isolating plate ($I$). The temporal distribution of the $C_3$ radical in the molecular jet is much wider, i.e. the DFWM signal drops by $\approx 15\%$ after a 12 mm and by 50% after a 21 mm of propagation. This behavior might be related to the fact that $C_3$ is produced in the reaction of $C + C_2 \rightarrow C_3$ which takes place in the expansion region of the molecular jet. The evaluated translational velocity of $C_3$ is similar to the one of $C_2$ and is 0.68 mm/$\mu$s after the 21 mm propagation in the molecular jet to the intersection region of the DFWM laser beams.

It is interesting to note that another discharge regime is possible if the stagnation pressure behind the solenoid valve is reduced to (0.5 - 1 $\times 10^5$ Pa) and the discharge voltage is set to the range between -200 and -400 V. In this case, electrons are generated in the plasma jet and are present for the duration of the gas-pulse ($\approx 300 - 750$ $\mu$s). As
mentioned above, these observations are made by monitoring the voltage drop on the ballast resistor.

4.1.3 Femtosecond ionization of the pulsed discharge products

For a time-of-flight mass spectrum measurement the molecular jet is collimated by a skimmer. The molecular beam is subsequently ionized by the 120 fs duration laser pulse (of 800 nm wavelength) along the propagation direction. An efficient multiphoton ionization process takes place when the peak laser intensity is high (see energy scheme for multiphoton ionization in the inset of Fig. 4.2). The laser chirp is optimized relative to the signal (the ion counts on the detector from the C$_2$H$_2$ molecule) by a double-pass diffraction grating and the mirror of the fs-laser system. Ions are generated in the focus of the lens (FL= 20 mm) and repelled by a field of +580 V. A set of ion optics guides and prefocusses the ion beam along the way to the Daly detector (voltage at the detector -2 kV). Two deflectors X and Y control the transversal position of the ion beam and are set to 1.054 V and 0.268 V respectively. The ion lens is set to -840 V.

Figure 4.2: Time-of-flight mass spectrum acquired by fs-ionization in the molecular beam. The discharge is consecutively set ON and OFF yielding two traces whose difference is presented on the figure. Because of a change of the electric field when the discharge is ON the ion optics and the repeller are biased. This leads to a small shift and distortion of the mass-peaks after time-of-flight to mass renormalization.
Numerous hydrocarbon radicals are generated in the pulsed discharge environment which can be rationalized by one or several reaction mechanisms mentioned above and in Ref. [64]. The peak at mass 36 is related to the C\textsubscript{3} molecule and is emphasized on the Fig. 4.2 by the blue rectangle. Many hydrocarbon molecules have ionization energies close to 11 eV, however it is not certain if the abundance of particular species in the molecular beam can be directly related to the peak intensity at the selected molecular mass. For example, peaks marked by asterisks * are present if the discharge voltage is not applied. The occurrence of C\textsubscript{2} and C\textsubscript{2}H peaks can be rationalized by the dissociation of the C\textsubscript{2}H\textsuperscript{+} cation after excitation by the fs laser. The presence of the C\textsubscript{2}H\textsubscript{3} is somewhat more challenging to explain. This mass may stem from the dissociation of a cation cluster carrying a water molecule.

4.2 Spectroscopy in the molecular jet

4.2.1 Apparatus for nonlinear optical spectroscopy

Two separately pumped dye lasers (narrowscan, Radiant Dyes) are used for the PUMP and the PROBE laser beams for the TC-RFWM experiment. The specified bandwidth of both laser systems is $\approx 0.02 \text{ cm}^{-1}$. To obtain optimized spatial intensity profiles both beams pass through spatial filters. Absolute wavelength calibration is performed for each scan step by a wavemeter (High Finess/Ångstrom, WS6). A forward BOXCARS configuration is set up by a combination of optical components as detailed in Ref. [74] and outlined in the following. The PUMP laser beam is split into two beams of the same intensity by a beamsplitter. Usually a Pellicle beamsplitter (BP145B1 /Thorlabs) with an optimized chromatic dispersion in the range of 400 – 700 nm is used. Further, the two PUMP and the PROBE beams are adjusted to propagate along the main three axes of a parallelepiped (shown with dotted lines in the Fig. 4.3 between objective $L_1$ and $L_2$) by the combination of aluminum coated mirrors and reflective prisms. For example, after passing a spatial filter the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. Subsequently, the beam is focused by an achromatic objective ($L_1$). The adjustment procedure is as following. First, by tilting the prism the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. The adjustment procedure is as following. First, by tilting the prism the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. Subsequently, the beam is focused by an achromatic objective ($L_1$). The adjustment procedure is as following. First, by tilting the prism the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. Subsequently, the beam is focused by an achromatic objective ($L_1$). The adjustment procedure is as following. First, by tilting the prism the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. Subsequently, the beam is focused by an achromatic objective ($L_1$). The adjustment procedure is as following. First, by tilting the prism the PROBE beam is reflected twice (not shown in the Fig. 4.3), first by a prism and second by an aluminum mirror mounted on a motorized stage such that the tilt-X and -Y axes in the laboratory frame can be adjusted. Subsequently, the beam is focused by an achromatic objective ($L_1$).
of molecular jet are precisely adjusted. The same adjustment algorithm is applied to both PUMP beams. Note that the Pellicle beamsplitter for the reflected PUMP beam plays the role of the prism as described for the PROBE.

A 1000 mm focal length achromatic objective ($L_1$) focuses three parallel propagating laser beams to pass along the three main diagonals of a parallelepiped and cross with a small angle of $\approx 0.7^\circ$ (see Fig. 4.3). These beams are arranged orthogonally to the propagation direction of the molecular beam, hence eliminating the Doppler broadening. The wave vectors, $k_i$, of the interacting beams fulfill the phase-matching condition $k_1 + k_2 = k_3 + k_4$ discussed in the section 3.2.3 and generate the signal beam $k_4$ along the forth (dark) diagonal of the parallelepiped. The two laser beams of equal frequencies are usually referred to as PUMP beams $k_1$, $k_2$ and the third beam, $k_3$, as the PROBE beam. The signal beam is collimated by the achromatic objective ($L_2$) (FL=1000 mm). A number of spatial (SSF) and spectral (SF) filters remove scattered light and unwanted fluorescence along the $\approx 5$ m propagation of the signal in the free-space. Further reduction of the stray light is achieved by a 30 mm focal lens and a 50 $\mu$m pinhole in front of a photomultiplier tube (PMT, head-on H10492-011 series or side-on R11568 tube from Hamamatsu). Typically 20-30 pulses are averaged per scan step ($5 \times 10^{-4}$ nm/step) of the dye-laser on the oscilloscope and transferred to the PC for further analysis.
Note, that for the precise tracing of the signal beam $E_4$ to the photodetector ($PMT$), the knowledge on the propagation direction defined by the wave-vector $k_4$ is required. After the iterative procedure of alignment relative to the mask ($M$) and the pinhole which is preliminary positioned at the plane of molecular jet, the pinhole is substituted by a thin cell (1 mm thick) filled with a dye. The dye should effectively absorb radiation mainly at the wavelength of the PUMP field and to a lesser extend at the wavelength of the PROBE field. For example, if a TC-RFWM experiment is planned on $C_3$ to measure the $^3\Pi_g$ vibronic level from the $\tilde{X}^1\Sigma^+_g$ ground state, the PUMP laser couples the selected mixed $J$-level of predominantly $^3\Sigma_u^-$ character with the ground state via the $P$-transitions in the range of 24665-24685 cm$^{-1}$. This corresponds to a wavelength around 405 nm. Exalite 404 dye (Radiant Dyes) is selected for the PUMP laser. The PROBE laser is set to the range of 21130-21160 cm$^{-1}$ which corresponds to the wavelength range close to 472 nm. Thus, Coumarin 102 dye (Radiant Dyes) is selected for the PROBE laser. The maximum quantum efficiency at 472 nm is close to 14 %. PUMP and PROBE are focused and crossed in the plane of the dye cell for the further adjustment. Considering PUMP and PROBE wavelengths the dye for the adjustment cell could be e.g. Coumarin 307 (or higher wavelength in the list such as Coumarin 153, Rhodamin 6G etc.). As soon as the optimal absorption coefficient and dye concentration is found a TC-RFWM signal visible by eye is generated in the dye cell. This beam is traced through several meters of a free space and coupled to the $PMT$. After this step the optical alignment is established, the discharge source is set up and the molecular chamber for the pulsed discharge nozzle is evacuated.

### 4.2.2 Two-photon laser induced fluorescence spectroscopy

The experimental setup for two-photon laser induced fluorescence spectroscopy (LIF) is shown in the Fig. 4.4. The arrangement of the detection optics (i.e. LIF signal collimating mirrors $M_{i1}$ and $M_{i2}$) allows simultaneous detection of the TC-RFWM signal and the two-photon LIF signal. The PUMP and PROBE fields can be either focused by the objective $L_1$ or propagate along the main diagonals of the parallelepiped without focusing. If $L_1$ and $L_2$ are not used in the optical setup, the interaction volume is larger compared to the experiment with focused laser beams. The focusing parameters such as laser beam waist diameter and Rayleigh length can be estimated with the help of the equations presented in the section 3.1.2. Note that optimal experimental conditions depend on the transition dipole moments which contribute to the TC-RFWM and two-photon LIF signal. In case of weak dipole moment transitions high intensities of the interacting PUMP $E_1, E_2$ and PROBE $E_3$ fields are required. Hence, the laser beams
are focused by $L_1$ and later the TC-RFWM signal $E_4$ is collimated by $L_2$. The two-photon LIF emission (drawn as a wide beam in green color in Fig. 4.4) is collected from the overlap region of the PUMP/PROBE laser beams and the molecular jet (drawn in blue color). The LIF emission is collimated by a high numerical aperture mirror $M_{t1}$ with 50 mm diameter and 25 mm focal length. The $\approx 500$ mm focal length lens $L_3$ images the collimated emission onto the monochromator slit ($M_n$). The spectrally resolved detection of the LIF signal from the newly found excited triplet state $^3\Pi_g$ is established by scanning the monochromator grating. The photon flux is converted into current by a photomultiplier tube (R11568 PMT). The signal current has a few hundred MHz carrier frequency which corresponds to a $\approx 3$ μs exponential LIF decay time from the two-photon excited $^3\Pi_g$ state. It is amplified by a broad-band current amplifier (made in house PSI MAR-AMP) and optionally gated in a time-window of $\approx 10$ μs by a BOXCAR integrator. A detailed comparison between the coherent TC-RFWM technique and the incoherent detection of the LIF emission is given in the section 6.2.

A two-photon perturbation facilitated LIF experiment is developed to access the low-lying electronic states via radiative decay from the excited triplet $^3\Pi_g$ level measured by perturbation facilitated TC-RFWM and analyzed in the section 5.2.3. The vibrational progressions of the low-lying electronic triplet states are measured by scanning the monochromator grating ($M_n$) and simultaneously recording the change of the photocurrent on the PMT. The resolution of $\approx 30$ cm$^{-1}$ is achieved by a slightly closed monochromator slit. Natural trade-off between signal to noise ratio and the resolution arises. For the two-photon LIF experiment the population brought to the excited state can be 1/4 of the ground state population at most. The low C$_3$ population in the doubly excited state demands that the measurement of radiative decay at a fixed laser frequency is performed with a relatively low resolution (open slit of the $M_n$).
Figure 4.4: Experimental setup for simultaneous linear and non-linear spectroscopic measurements. A mask is used for laser beam alignment; \( L1, L2 \) 1000 nm focal length focusing and collimating lenses respectively; \( RS \) Radical source for the generation of \( \text{C}_2 \) and \( \text{C}_3 \); \( MJ \) Molecular jet; \( SSF \) Set of spatial filters; \( SF \) Spectral filter; \( PMT \) Photomultiplier tube with an integrated amplifier. Dispersed fluorescence \( E_{LIF} \) upon perturbation facilitated excitation of the \( ^3\Pi_g \) state, i.e. \( ^3\Pi_g \xleftarrow{\hbar \nu_{2}} ^3\Sigma_u^- \xleftarrow{\hbar \nu_{1}} ^1\Sigma_g^+ \). is imaged by the high numerical aperture \( M_{i1} \) mirror located below the molecular jet and the \( M_{i2} \) mirror located in front of the monochromator \( Mn \). The lens \( L_3 \) focuses the collimated LIF signal onto the monochromator slit \( Mn \). The experimental layout is arranged such that \( MJ, \) excitation lasers \( E_1, E_2, E_3 \) and collimated LIF signal \( E_{LIF} \) propagate orthogonally to each other. The corresponding arrangement eliminates first order Doppler broadening and provides supreme efficiency in collecting LIF photons.
Chapter 5

Results I: Application of Four-Wave Mixing Spectroscopy to study dark states

5.1 Measurement of a dark quintet state of C$_2$ by applying the UP-TC-RFWM scheme

This chapter is organized in accordance with our recent paper [9]. Double-resonant four-wave mixing experiments have been applied for a deperturbation study of the $d^3\Pi_g, v = 6$ state of C$_2$. Rotational levels with $N \leq 11$ are perturbed by a high-spin state which is experimentally identified for the first time. The vibronic origin, rotational, spin-orbit, spin-spin constants and the $\Lambda$-doubling parameter of the $1^5\Pi_g$ are accurately determined. In addition, the curve crossing at $N = 19$ and 21 with the $b^3\Sigma_g^-, v = 19$ state is quantitatively evaluated and yield origin, rotational and spin-spin constants of the perturber state. Results are obtained by performing intermediate level labeling for unambiguous assignment of perturbed and perturbing transitions. The sensitivity of the method allows the observation of 122 transitions including 76 low-intensity excitations to 'dark states' that are made visible by electronic state-mixing. The quintet character of the $d^3\Pi_g, v = 6$ electronic state has been already presented in the introductory chapter (see Fig. 5.1) in order to support the “gateway” model [31]. The observed spectra are rationalized in the following sections 5.1.1-5.1.2.

The crossing of the $1^5\Pi_g$ with $d^3\Pi_g, v = 6$ is examined in the discussion below. The observation of a dark electronic $1^5\Pi_g$ state via spin-orbit interaction with the bright $d^3\Pi_g, v = 6$ state is verified. The coupling between these states leads to the enhanced
emission in the high-pressure (HP) bands, as suggested by Little and Brown [20]. The perturbation is characterized in detail and exactly calculable. The occurrence of the large and level-specific interaction elucidates the nonthermal population distribution in the \( v=6 \) level that is observed in numerous environments at different pressures and temperatures. The mechanism involved has been put forth by Gelbart and Freed [21] who realized that intrinsic intramolecular interactions such as perturbations between electronic states can have an important effect on the pressure dependent details of the luminescence behavior of small molecules. In this “gateway” model the cross sections for collision-induced transitions between two different electronic states, \( E \) and \( E' \), are

\[
\sigma_{E,J,E',J'} \simeq \sigma_{E,J,E,J'} c_{E,E'}(J')^2 + \sigma_{E',J,E',J'} c_{E,E'}(J)^2
\]

where \( \sigma_{E,J,E',J'} \) and \( \sigma_{E',J,E',J'} \) are the \( J \rightarrow J' \) purely rotation-changing cross-sections within the \( E \) and \( E' \) electronic states, respectively, and \( c_{E,E'} \) is the isolated-molecule mixing coefficient. If only few vibronic levels are significantly mixed they should act as a “gateway” through which the population flows from one electronic state to the other. In the following we show qualitative evidence that gateway states are essential to rationalize the observed emission anomalies of the HP bands. In this respect, the curve crossing of the \( F_1 \) component of the \( d^3\Pi_g, v = 6 \) with \( F_4 \) of the \( 1^5\Pi_g \) state is of particular interest (Fig. 5.4 below). The energy separation of the unperturbed levels at \( J = 12 \) is only 0.28 cm\(^{-1}\). Spin-orbit interaction between the electronic states shifts the two levels 1.93 cm\(^{-1}\) apart. Note however, the unperturbed \( F_1(12) \) is not a pure \( \Omega \) state but due to the spin-orbit interaction (\( \hat{A}\hat{L} \cdot \hat{S} \)) (Equation 5.1) an admixture of the nominal \( d^3\Pi_g(49\%), d^3\Pi_{1g}(41\%) \) and \( d^3\Pi_{0g}(10\%) \) levels. Upon perturbation by the \( 1^5\Pi_g \) the resulting \( F_1(12) \) state reduces its \( d^3\Pi_{1g} \)-character to 53\%, \( i.e. \) \( d^3\Pi_{2g}(28\%), d^3\Pi_{1g}(21\%) \) and \( d^3\Pi_{0g}(4\%) \) and gains 47\% \( 1^5\Pi_g \)-character, \( i.e. \) \( 1^5\Pi_{1g}(7\%), 1^5\Pi_{0g}(16\%), 1^5\Pi_{1g}(1\%) \) \( 1^5\Pi_{2g}(7\%) \) and \( 1^5\Pi_{3g}(16\%) \). Fig. 5.1 depicts the fractional \( 1^5\Pi_g \)-character gain of perturbed \( d^3\Pi_g, v = 6 \) rotational terms for the three \( F \) components. Clearly, \( F_1(12) \) and to a lesser extend \( F_1(4), F_1(5), F_2(1) \) and \( F_2(2) \) have to be considered as “gateway” states.

Therefore, if a chemical reaction \( e.g. \) \( C + C_2O \rightarrow C_2 + CO \) as suggested by several authors [33–35] populate the metastable \( 1^5\Pi_g \) state, perturbation-facilitated transfer to the \( d^3\Pi_g, v = 6 \) can occur and promote enhanced emission in the Swan system. It is interesting to mention that the HP bands are characterized by a double-headed spectral feature \([10, 12–14]\). The “gateway” states discussed below readily rationalize the observation. The band head of \( v = 6 \) is formed by closely-spaced rotational levels of the \( P \)-branches. Enhanced emission is observed by the nonthermal population of the low \( J \) “gateway” states. In addition, a second “head” is formed that originates mainly from the strongly mixed \( F_1(12) \) increasing the emission in the \( R \)-branch \( via \) \( R_1(11) \).
Chapter 5. *Results I: Application of RFWM Spectroscopy to study dark states*

5.1.1 Spin-orbit coupling of the $1^5\Pi_g$, $a^3\Pi_u$, $d^3\Pi_g$ and $b^3\Sigma_g^-$ states

The $1^5\Pi_g$, $a^3\Pi_u$, $d^3\Pi_g$ and $b^3\Sigma_g^-$ states are modeled by using a conventional Hamiltonian for a linear molecule [75] implemented in the computer program pgopher [76] with
terms omitted as appropriate

\[
\hat{H} = T + B\hat{N}^2 - D\hat{N}^4 + A\hat{L} \cdot \hat{S} + \frac{A_D}{2} [\hat{N}^2, \hat{L} \cdot \hat{S}]_+ + \frac{2}{3} \lambda (3\hat{S}_z^2 - \hat{S}^2) \\
+ \frac{1}{2} \beta (\hat{S}_+^2 e^{-2i\phi} + \hat{S}_-^2 e^{2i\phi}) - \frac{1}{2} \gamma (\hat{N}_+ \hat{S}_+ e^{-2i\phi} + \hat{N}_- \hat{S}_- e^{2i\phi}) \\
+ \frac{1}{2} q (\hat{N}_+^2 e^{-2i\phi} + \hat{N}_-^2 e^{2i\phi}) (5.1)
\]

where \([\hat{O}, \hat{Q}]_+ = \hat{O} \hat{Q} + \hat{Q} \hat{O}\)

The first term is the vibronic origin followed by the rotational kinetic energy and spin-orbit coupling terms including their corresponding centrifugal distortion terms. The term containing the spin-spin coupling constant \(\lambda\) is followed by the three terms determining the \(\Lambda\)-doubling parameters \(o, p\) and \(q\).

The Hamiltonian energy matrix elements for the Swan \(d^3\Pi_g\) and \(a^3\Pi_u\) states are given by

\[
< 3^3\Pi_0 | H | 3^3\Pi_0 > = T - A + (B - A_D)(x + 2) - D(x^2 + 6x + 4) + \frac{2}{3} \lambda \mp (o + p + q) \\
< 3^3\Pi_1 | H | 3^3\Pi_1 > = T + B(x + 2) - D(x^2 + 8x) - \frac{4}{3} \lambda \mp \frac{1}{2} qx \\
< 3^3\Pi_2 | H | 3^3\Pi_2 > = T + A + (B + A_D)(x - 2) - D(x^2 - 2x) + \frac{2}{3} \lambda \\
< 3^3\Pi_0 | H | 3^3\Pi_1 > = -\sqrt{2}x[B - \frac{1}{2} A_D - 2D(x + 2) \mp \frac{1}{2}(p + 2q)] \\
< 3^3\Pi_0 | H | 3^3\Pi_2 > = -\sqrt{x(x - 2)}(2D \pm \frac{1}{2} q) \\
< 3^3\Pi_1 | H | 3^3\Pi_2 > = -\sqrt{2}(x - 2)(B + \frac{1}{2} A_D - 2Dx)
\]

where \(x = J(J + 1)\). The upper and lower signs before \(o, p\) and \(q\) refer to \(e\) and \(f\) sublevels for \(d^3\Pi_g\) and to \(f\) and \(e\) sublevels for the \(a^3\Pi_u\) state, respectively.
For the $1^5\Pi_g$ state, the energy matrix elements are applied as follows:

\[
\begin{align*}
< 5\Pi_{-1}|H|5\Pi_{-1} > &= T + B(x + 2) - 2A + 4\lambda \\
< 5\Pi_{0}|H|5\Pi_{0} > &= T + B(x + 6) - A - 2\lambda \pm 3\sigma \\
< 5\Pi_{1}|H|5\Pi_{1} > &= T + B(x + 6) - 4\lambda \\
< 5\Pi_{2}|H|5\Pi_{2} > &= T + B(x + 2) + A - 2\lambda \\
< 5\Pi_{3}|H|5\Pi_{3} > &= T + B(x - 6) + 2A + 4\lambda \\
< 5\Pi_{-1}|H|5\Pi_{0} > &= -2B\sqrt{x} \\
< 5\Pi_{-1}|H|5\Pi_{1} > &= \pm \sqrt{6}\sigma \\
< 5\Pi_{0}|H|5\Pi_{1} > &= -B\sqrt{6x} \\
< 5\Pi_{1}|H|5\Pi_{2} > &= -B\sqrt{6(x - 2)} \\
< 5\Pi_{2}|H|5\Pi_{3} > &= -2B\sqrt{x - 6}
\end{align*}
\]

The ± signs before $\sigma$ refer to the $e$ and $f$ sublevels, respectively.

The Hamiltonian energy matrix elements for the $b^3\Sigma_g^-$ state are given by

\[
\begin{align*}
< 3\Sigma_0|H|3\Sigma_0 > &= \frac{1}{2}(1 \pm 1)[T + B(x + 2) - D(x^2 + 8x + 4) - \frac{4}{3}\lambda] \\
< 3\Sigma_1|H|3\Sigma_1 > &= T + Bx - D(x^2 + (1 \pm 1)2x) + \frac{2}{3}\lambda \\
< 3\Sigma_0|H|3\Sigma_1 > &= -(1 \pm 1)\sqrt{x}[B - 2D(x + 1)]
\end{align*}
\]

Upper signs refer to $e$ levels and lower signs to $f$ levels.

The spin-orbit interaction parameters between the triplet $d^3\Pi_g, v = 6$ and quintet $1^5\Pi_g$ states are given by

\[
< 3\Pi_1|H_{so}|5\Pi_1 >
\]

and the dependent terms

\[
< 3\Pi_0|H_{so}|5\Pi_0 > = < 3\Pi_2|H_{so}|5\Pi_2 > = \frac{\sqrt{3}}{2} < 3\Pi_1|H_{so}|5\Pi_1 >
\]

and for the spin-orbit and $L$-uncoupling parameters between the two triplet states $d^3\Pi_g, v = 6$ and $b^3\Sigma_g^-, v = 19$

\[
< 3\Pi_1|H_{so}|3\Sigma_1 > \\
< 3\Pi_0|H_{so}|3\Sigma_0 > = \sqrt{2} < 3\Pi_1|H_{so}|3\Sigma_1 >
\]
and

\[
\langle \tilde{3}\Pi_0 | \mathbf{B} \mathbf{L}_+ | \tilde{3}\Sigma^- \rangle \\
\langle \tilde{3}\Pi_1 | \mathbf{B} \mathbf{L}_+ | \tilde{3}\Sigma^0 \rangle \Rightarrow \sqrt{2} \langle \tilde{3}\Pi_0 | \mathbf{B} \mathbf{L}_+ | \tilde{3}\Sigma^- \rangle \\
\langle \tilde{3}\Pi_2 | \mathbf{B} \mathbf{L}_+ | \tilde{3}\Sigma^- \rangle \Rightarrow \sqrt{x-2} \langle \tilde{3}\Pi_0 | \mathbf{B} \mathbf{L}_+ | \tilde{3}\Sigma^- \rangle
\]

respectively.

For the Swan-band transition excluding perturbation effects, molecular constants from Tanabashi et al. [16] are applied. The term energies are defined such that \( T = 0 \) for \( v'' = 0 \) of the \( a \tilde{3}\Pi_u \) state yielding the lowest energy level of -9.8258 cm\(^{-1}\) for \( v'' = 0, J'' = 2 \) and \( N'' = 1 \). Absolute energies above the \( X \tilde{1}\Sigma^+ \) ground state of \( \text{C}_2 \) can be obtained by taking into account the difference of 1536.0731 cm\(^{-1}\) reported by Amiot et al. [18] and considering the different formulation of the effective Hamiltonian by the authors. To obtain the molecular parameters for the \( 1 \tilde{5}\Pi_g, b \tilde{3}\Sigma^- \) states and their interaction with \( d \tilde{3}\Pi_g, v = 6 \), the constants for the unperturbed \( d \tilde{3}\Pi_g - a \tilde{3}\Pi_u \) system are adopted with the exception of the augmented values listed in Table 5.4 (vide infra).

### 5.1.2 UP TC-RFWM measurement of the lowest quintet \( 1 \tilde{5}\Pi_g \) state

The middle trace of Fig. 5.2 shows a DFWM spectrum obtained in the wavelength range of the \( v' - v'' = \Delta v = 1 \) sequence bands of the \( d \tilde{3}\Pi_g - a \tilde{3}\Pi_u \) Swan system. For the applied intensities of a few \( \mu \)J/pulse, an absorption-like intensity distribution is obtained by degenerate resonant four-wave mixing spectroscopy (for the detailed description of the measurement technique see Section 3.2.4). The supersonic expansion from the slit-source produces radicals that are excited to high vibrational levels (\( T_{\text{vib}}=2000-6000 \) K) but in each vibrational level a relatively low \( J \) population is present (\( T_{\text{rot}}=50-100 \) K). The ensuing spectra exhibits, therefore, a reduced number of rotational transitions in each band and a significant simplification of the complex \( 3\Pi - 3\Pi \) transition is achieved. Nonetheless, the spectral features are difficult to assign because multiple sequence bands overlap, i.e. \((6,5),(5,4)\) and \((4,3)\). Furthermore, it has been recognized long ago [77] that all triplet components of the rotational levels with \( N = 19 \) and \( 21 \) and \( N \leq 11 \) in the \( d \tilde{3}\Pi_g, v = 6 \) state are considerably perturbed. The synthetic spectrum (lower trace) is obtained by taking into account line positions and intensities from the pgopher program package adopting molecular constants from Tanabashi et al. [16]. For the computation, a vibrational and rotational temperature of 3600 and 50 K, respectively, is assumed and the positions and intensities are convoluted with a Lorentzian line-shape assuming a bandwidth of 0.05 cm\(^{-1}\) (FWHM). As mentioned above, a global analysis of the rotational perturbations has not been achieved and is neglected in the simulations. As
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

a consequence, the experimental DFWM spectrum is poorly reproduced in the lower trace. Significant discrepancies are observed throughout the recorded spectral region. For example, strong transitions between 21420 and 21428 cm$^{-1}$ appear in the experiment that are not calculated in the simulation. To investigate the involved perturbation effects in detail, an unambiguous assignment of spectral features is required. This task is, however, often not feasible by analyzing one-color spectra such as DFWM, CRD or LIF.

Figure 5.2: DFWM spectrum in the wavelength region of the $\Delta v = 1$ sequence bands of the $d^3\Pi_g \rightarrow a^3\Pi_u$ electronic system. The bottom trace shows a simulation of the spectral region neglecting perturbations. A comparison with the experimental DFWM shows significant discrepancies. The top trace is a simulation including perturbation effects which has been obtained by the detailed deperturbation analysis in this work. The deperturbed assignments for the three R-subbands, $R_i(J)$, are shown on the top for two vibronic bands ($v',v''$).

The recent deperturbation study of the $d^3\Pi_g, v = 4$ state [78] performed in our laboratory disclose the potential of double-resonant four-wave mixing for deperturbation studies of the dicarbon molecule. In spite of the quadratic dependence of the four-wave mixing signal on number density [52], the technique is sufficiently sensitive for the detection and characterization of C$_2$ in a molecular beam that is emerging from a discharge slit-jet source [79]. As for all double-resonance techniques, the use of two distinct input frequencies for TC-RFWM is advantageous for the simplification of spectrally congested regions and the assignment of transitions in general and when perturbation effects are present in particular. A signal is obtained exclusively when both frequencies interact with distinct molecular transitions that share a common level. Straightforward assignments are often possible by tuning one frequency to a known transition and observing probe transitions from the labeled intermediate level. Two typical examples of TC-RFWM spectra are shown in Fig. 5.3. For the upper trace, intermediate level labeling
is achieved by tuning the PUMP lasers to coincide with the R₁(5) transition in the (4,5) band at 18319.46 cm⁻¹. Rotational transitions are denoted by \( \Delta N \Delta J F F′(J′′) \), where \( N \) is the total angular momentum, \( J \), exclusive spin. The spin sublevels, \( F \), for a \( 2S+1 \) \( \Lambda \)-state are classified by their energy ordering, i.e. \( F_1 : J = N + S \) for the lowest energy fine structure component and \( F_{2S+1} : J = N - S \) for the highest. For transitions with \( \Delta N = \Delta J = F = F′ \) the rotational notation is simplified to \( \Delta J F(J′′) \). Thus, by fixing the PUMP laser wavenumber position to 18319.46 cm⁻¹ and scanning the PROBE laser in the frequency range of the \( \Delta v = 1 \) sequence bands, several intense transitions within the Swan band system are observed. Three UP (or hole-burning) transitions are sharing the common lower state with the PUMP laser \( (v'' = 5, N'' = 4, J'' = 5, F'' = 1) \): (6,5) P₁(5), (6,5) Q₁(5) and (6,5) R₁(5). In addition, the SEP (stimulated emission pumping) type transition \((4,3) R₁(5)\) is observed sharing the common upper state with the PUMP laser \((v' = 4, N' = 5, J' = 6, F' = 1)\). For the scans shown in Fig. 5.3 the transitions within the Swan system are significantly broadened due to a strong saturation (\( I \approx 1000 I_{sat} \)). The intensity is applied above the saturation limit of the bright state in order to observe transitions to the perturbing states. These weak transitions appear because levels in the vicinity of a perturbation are actually mixed eigenstates containing state character of both levels. Dark states gain intensity from bright states and are accessible by TC-RFWM experiments. The double-resonance spectra unveil the presence of a \( 1^5 \Pi_g \) state in the vicinity of the \( d^3 \Pi_g, v = 6 \) level. Several UP transitions are observed from the common lower state to different spin sublevels of the \( 1^5 \Pi_g \) state. For example, the \( ^9 \) P₂₁(5), \( ^9 \) Q₂₁(5) and \( ^1 \) R₂₁(5) transitions excite the \( J′ = 4, 5 \) and 6 rotational states of the \( F_2 \) sublevel \((J′ = N′ + 1)\) of the \( 1^5 \Pi_g \) electronic state. Furthermore, several transitions to the \( F_1, F_3 \) and \( F_4 \) sublevels are observed: \( ^9 \) P₁(5) and \( ^9 \) R₁(5) to \( J′ = 4 \) and 6 of \( F_1 \). \( J′ = 4 \) of \( F_3 \) and \( F_4 \) are excited by \( ^9 \) P₃₁(5) and \( ^1 \) P₄₁(5), respectively.

The lower (inverted) trace, shown in Fig. 5.3, contains another set of dark states which are revealed by the \( 3 \Pi \) – \( 5 \Pi \) interaction. Here, the \((4,5) R₂(2)\) transition is used for intermediate level labeling by the PUMP lasers at 18308.34 cm⁻¹. Apart from two strong SEP and three UP transitions in the Swan system, i.e. \((4,3) Q₂(3), (4,3) R₂(2)\) and \((6,5) P₂(2), (6,5) Q₂(2), (6,5) R₂(2)\), respectively, several lines are observed owing to transitions to the \( 1^5 \Pi_g \) state. \( F₂(1) \) is clearly visible by the \( ^9 \) P₂(2) transition. \( F₃(1), F₃(2) \) and \( F₃(3) \) are observed by \( ^1 \) P₃₂(2), \( ^1 \) Q₃₂(2) and \( ^1 \) R₃₂(2), respectively. The \( F₄(3) \) and \( F₅(3) \) levels are measured by \( ^9 \) R₄₂(2) and \( ^1 \) R₅₂(2), respectively.

Table 5.1 lists the wavenumbers of 46 perturbed transitions (fourth column) in the \( 6,5 \) and \( 6,4 \) bands of the \( d^3 \Pi_g - a^3 \Pi_a \) electronic Swan system that have been observed by TC-RFWM and assigned unambiguously (second column) by intermediate level labeling in the \((4,5)\) and \((3,4)\) bands (third column). It is important to notice that several
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

Figure 5.3: TC-RFWM in the wavelength region of the $\Delta v = 1$ sequence bands of the Swan system. Intermediate level labeling is performed by tuning the PUMP laser to the $R_1(5)$ (upper trace) and $R_2(2)$ (lower trace, inverted) transitions in the (4,5) band, respectively, and scanning the PROBE laser near 21400 cm$^{-1}$. Apart from the intense UP and SEP lines accessed in the $d^3\Pi_g - a^3\Pi_u$ system, several transitions from the $a^3\Pi_u$ state to spin sublevels ($F_{i,i} = 1..5$) of the quintet state are observed and emphasized in the figure by the shaded area. These dark states gain intensity by the electronic interaction of $d^3\Pi_g - 5\Pi_g$. Transitions labeled with asterisks denote weak lines in the Swan band with $\Delta \Omega \pm 1$. See text for details.

Rotational levels of the $d^3\Pi_g$, $v' = 4$ state used for labeling are affected by perturbations owing to the $b^3\Sigma_u^-, v = 16$ state as well. Line shifts are taken into account by considering the results of our recent analysis [78]. Furthermore, most of the characterized energy levels in the upper electronic state $d^3\Pi_g$, $v' = 6$ are accessed from different rotational levels in the lower $a^3\Pi_u$, $v = 5$ or $v = 4$ states. For example, the $F_1(3)$ level is measured in all the three branches of the (6,5) band by $P_1(4)$, $Q_1(3)$ and $R_1(2)$, thus further impeding ambiguities due to perturbations that may occur in the lower level.

The last column in Table 5.1 lists the line shifts of the transitions relative to the simulation model omitting perturbation effects. It is noteworthy that the shifts obtained by performing measurements via different transitions to a specific upper term energy level are in excellent agreement. In the example above, the shifts measured independently in the three branches for $F_1(3)$ agree within 0.01 cm$^{-1}$. 
Table 5.1: TC-RFWM transitions to $^3\Pi_g, v = 6$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Upper Level</th>
<th>Assignment Intermediate</th>
<th>Observed Residuals</th>
<th>Perturbation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1(2)</td>
<td>(6,5)pP1(3) (4,5)R1(3)</td>
<td>21396.34</td>
<td>-0.01</td>
</tr>
<tr>
<td>F1(2)</td>
<td>(6,5)qQ1(2) (4,5)Q1(2)</td>
<td>21404.31</td>
<td>0.00</td>
</tr>
<tr>
<td>F1(3)</td>
<td>(6,5)pP1(4) (4,5)R1(4)</td>
<td>21393.23</td>
<td>0.01</td>
</tr>
<tr>
<td>F1(3)</td>
<td>(6,5)qQ1(3) (4,5)R1(3)</td>
<td>21403.97</td>
<td>0.01</td>
</tr>
<tr>
<td>F1(3)</td>
<td>(6,5)R1(2) (4,5)Q1(2)</td>
<td>21411.95</td>
<td>0.00</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)pP1(5) (4,5)R1(5)</td>
<td>21389.51</td>
<td>-0.03</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)qQ1(4) (4,5)R1(4)</td>
<td>21403.09</td>
<td>0.01</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)R1(3) (4,5)R1(3)</td>
<td>21413.84</td>
<td>0.02</td>
</tr>
<tr>
<td>F1(5)</td>
<td>(6,5)qQ1(5) (4,5)R1(5)</td>
<td>21407.43</td>
<td>-0.03</td>
</tr>
<tr>
<td>F1(5)</td>
<td>(6,5)R1(4) (4,5)R1(4)</td>
<td>21420.98</td>
<td>-0.02</td>
</tr>
<tr>
<td>F1(6)</td>
<td>(6,5)R1(5) (4,5)R1(5)</td>
<td>21423.59</td>
<td>0.03</td>
</tr>
<tr>
<td>F1(12)</td>
<td>(6,5)R1(11) (4,5)R1(11)</td>
<td>21444.59</td>
<td>0.00</td>
</tr>
<tr>
<td>F1(19)</td>
<td>(6,4)rR1(18) (3,4)R1(18)</td>
<td>22998.33</td>
<td>0.02</td>
</tr>
<tr>
<td>F1(20)</td>
<td>(6,4)rR1(19) (3,4)R1(19)</td>
<td>22999.79</td>
<td>0.05</td>
</tr>
<tr>
<td>F1(22)</td>
<td>(6,4)rR1(21) (3,4)R1(21)</td>
<td>23019.17</td>
<td>0.04</td>
</tr>
<tr>
<td>F1(23)</td>
<td>(6,4)rR1(22) (3,4)R1(22)</td>
<td>23016.96</td>
<td>0.01</td>
</tr>
<tr>
<td>F2(1)</td>
<td>(6,5)pP2(2) (4,5)R2(2)</td>
<td>21394.73</td>
<td>-0.04</td>
</tr>
<tr>
<td>F2(1)</td>
<td>(6,5)qQ2(1) (4,5)R2(1)</td>
<td>21400.68</td>
<td>-0.06</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)pP2(3) (4,5)R2(3)</td>
<td>21393.00</td>
<td>-0.04</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)qQ2(2) (4,5)R2(2)</td>
<td>21403.78</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)R2(1) (4,5)R2(1)</td>
<td>21407.71</td>
<td>-0.05</td>
</tr>
<tr>
<td>F2(3)</td>
<td>(6,5)pP2(4) (4,5)R2(4)</td>
<td>21390.96</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(3)</td>
<td>(6,5)qQ2(3) (4,5)R2(3)</td>
<td>21403.19</td>
<td>-0.01</td>
</tr>
<tr>
<td>F2(23)</td>
<td>(6,5)R2(2) (4,5)R2(2)</td>
<td>21411.95</td>
<td>-0.01</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)pP2(5) (4,5)R2(5)</td>
<td>21388.65</td>
<td>0.03</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)qQ2(4) (4,5)R2(4)</td>
<td>21403.41</td>
<td>-0.03</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)R2(3) (4,5)R2(3)</td>
<td>21415.65</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(5)</td>
<td>(6,5)R2(4) (4,5)R2(4)</td>
<td>21419.55</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(6)</td>
<td>(6,5)R2(5) (4,5)R2(5)</td>
<td>21423.27</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(10)</td>
<td>(6,5)rR2(9) (4,5)R2(9)</td>
<td>21438.97</td>
<td>0.02</td>
</tr>
<tr>
<td>F2(11)</td>
<td>(6,5)rR2(10) (4,5)R2(10)</td>
<td>21444.72</td>
<td>-0.08</td>
</tr>
<tr>
<td>F2(15)</td>
<td>(6,4)rR2(17) (3,4)R2(17)</td>
<td>22999.05</td>
<td>0.03</td>
</tr>
<tr>
<td>F2(19)</td>
<td>(6,4)rR2(18) (3,4)R2(18)</td>
<td>22999.64</td>
<td>-0.03</td>
</tr>
<tr>
<td>F2(21)</td>
<td>(6,4)rR2(20) (3,4)R2(20)</td>
<td>23016.64</td>
<td>-0.01</td>
</tr>
<tr>
<td>F2(22)</td>
<td>(6,4)rR2(21) (3,4)R2(21)</td>
<td>23016.46</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(0)</td>
<td>(6,5)pP3(1) (4,5)P3(1)</td>
<td>21397.61</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(1)</td>
<td>(6,5)pP3(2) (4,5)R3(2)</td>
<td>21394.29</td>
<td>0.00</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)pP3(3) (4,5)R3(3)</td>
<td>21391.79</td>
<td>0.03</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)rR3(1) (4,5)R3(1)</td>
<td>21410.00</td>
<td>0.03</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)rR3(2) (4,5)R3(2)</td>
<td>21413.89</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(4)</td>
<td>(6,5)rR3(3) (4,5)R3(3)</td>
<td>21418.48</td>
<td>0.06</td>
</tr>
<tr>
<td>F3(5)</td>
<td>(6,5)rR3(4) (4,5)R3(4)</td>
<td>21421.98</td>
<td>-0.02</td>
</tr>
<tr>
<td>F3(17)</td>
<td>(6,4)rR3(16) (3,4)R3(16)</td>
<td>22997.33</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(18)</td>
<td>(6,4)rR3(17) (3,4)R3(17)</td>
<td>22999.21</td>
<td>-0.02</td>
</tr>
<tr>
<td>F3(20)</td>
<td>(6,4)rR3(19) (3,4)R3(19)</td>
<td>23014.83</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(21)</td>
<td>(6,4)rR3(20) (3,4)R3(20)</td>
<td>23015.65</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

In addition to the measurement of precise line shifts of perturbed transitions, we take advantage of the sensitivity of the technique that allows the observation of the generally weak transitions to the perturbing state (Fig. 5.3). The inclusion of these extra lines were found to yield significantly modified $B$ and $\lambda$ parameters of the perturbing vibronic state in our recent deperturbation study of the $^3\Pi_g, v' = 4$ state.\[78\] Table 5.2 and Table 5.3 lists 68 transitions to the $^5\Pi_g$ and 8 transitions to the $^3\Sigma_g^-, v = 19$ state, respectively. As for the transitions within the Swan system, term energy levels of the $^5\Pi_g$ and $^3\Sigma_g^-, v = 19$ state are generally measured by multiple transitions. For example, the $F_3(2)$ level of the quintet state is observed by six independent TC-RFWM transitions.
applying unique intermediate level labeling schemes. For this measurement perturbation shifts agree within 0.03 cm$^{-1}$.

Table 5.2: TC-RFWM transitions to $1^5\Pi_g$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Upper Level</th>
<th>Assignment</th>
<th>Intermediate Level</th>
<th>Observed Residuals</th>
<th>Perturbation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1(2)</td>
<td>(6,5)P1(3)</td>
<td>(4,5)R1(3)</td>
<td>21392.47</td>
<td>-0.01</td>
</tr>
<tr>
<td>F1(2)</td>
<td>(6,5)P1(3)</td>
<td>(4,5)R1(3)</td>
<td>21370.01</td>
<td>0.00</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)P1(5)</td>
<td>(4,5)R1(5)</td>
<td>21379.12</td>
<td>0.00</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)P1(5)</td>
<td>(4,5)R1(5)</td>
<td>21403.42</td>
<td>0.03</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)P1(5)</td>
<td>(4,5)R1(5)</td>
<td>21380.92</td>
<td>-0.01</td>
</tr>
<tr>
<td>F1(4)</td>
<td>(6,5)P1(5)</td>
<td>(4,5)R1(5)</td>
<td>21397.50</td>
<td>0.02</td>
</tr>
<tr>
<td>F2(0)</td>
<td>(6,5)P23(1)</td>
<td>(4,5)P3(1)</td>
<td>21377.46</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(0)</td>
<td>(6,5)P23(1)</td>
<td>(4,5)P3(1)</td>
<td>21388.48</td>
<td>0.01</td>
</tr>
<tr>
<td>F2(1)</td>
<td>(6,5)P2(2)</td>
<td>(4,5)R2(2)</td>
<td>21405.44</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(1)</td>
<td>(6,5)P2(2)</td>
<td>(4,5)R2(2)</td>
<td>21413.41</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)P2(3)</td>
<td>(4,5)R1(3)</td>
<td>21382.95</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)P2(3)</td>
<td>(4,5)R1(3)</td>
<td>21382.17</td>
<td>0.01</td>
</tr>
<tr>
<td>F2(2)</td>
<td>(6,5)P2(4)</td>
<td>(4,5)R1(4)</td>
<td>21400.53</td>
<td>-0.01</td>
</tr>
<tr>
<td>F2(3)</td>
<td>(6,5)P2(4)</td>
<td>(4,5)R1(4)</td>
<td>21411.27</td>
<td>-0.01</td>
</tr>
<tr>
<td>F2(3)</td>
<td>(6,5)P2(4)</td>
<td>(4,5)R1(4)</td>
<td>21419.24</td>
<td>-0.02</td>
</tr>
<tr>
<td>F2(3)</td>
<td>(6,5)P2(4)</td>
<td>(4,5)R1(4)</td>
<td>21388.83</td>
<td>0.02</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21395.49</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21409.03</td>
<td>0.01</td>
</tr>
<tr>
<td>F2(4)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21419.77</td>
<td>0.00</td>
</tr>
<tr>
<td>F2(5)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21400.55</td>
<td>0.04</td>
</tr>
<tr>
<td>F2(5)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21414.09</td>
<td>0.03</td>
</tr>
<tr>
<td>F2(6)</td>
<td>(6,5)P2(5)</td>
<td>(4,5)R1(5)</td>
<td>21412.96</td>
<td>0.04</td>
</tr>
<tr>
<td>F3(1)</td>
<td>(6,5)P3(2)</td>
<td>(4,5)R2(2)</td>
<td>21403.03</td>
<td>0.02</td>
</tr>
<tr>
<td>F3(1)</td>
<td>(6,5)P3(2)</td>
<td>(4,5)R2(2)</td>
<td>21408.99</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(1)</td>
<td>(6,5)P3(2)</td>
<td>(4,5)R2(2)</td>
<td>21384.95</td>
<td>0.03</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21418.04</td>
<td>-0.02</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21426.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21395.58</td>
<td>0.00</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21404.34</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21410.29</td>
<td>-0.03</td>
</tr>
<tr>
<td>F3(2)</td>
<td>(6,5)P3(3)</td>
<td>(4,5)R1(3)</td>
<td>21394.78</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21411.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21421.76</td>
<td>-0.03</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21429.75</td>
<td>-0.02</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21399.34</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21408.09</td>
<td>0.00</td>
</tr>
<tr>
<td>F3(3)</td>
<td>(6,5)P3(4)</td>
<td>(4,5)R1(4)</td>
<td>21390.00</td>
<td>0.00</td>
</tr>
<tr>
<td>F3(4)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21404.90</td>
<td>-0.01</td>
</tr>
<tr>
<td>F3(4)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21429.14</td>
<td>-0.04</td>
</tr>
<tr>
<td>F3(4)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21406.72</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(4)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21387.69</td>
<td>0.00</td>
</tr>
<tr>
<td>F3(5)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21405.16</td>
<td>0.01</td>
</tr>
<tr>
<td>F3(5)</td>
<td>(6,5)P3(5)</td>
<td>(4,5)R1(5)</td>
<td>21403.53</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 5.4 lists the molecular constants including perturbation parameters that are obtained by performing a least-squares optimization procedure to the 122 listed transitions in tables 5.1, 5.2 and 5.3 using pgopher [76]. All parameters have been varied simultaneously until the best fit possible has been reached. An excellent agreement between the observed transitions and the simulation is obtained. The root mean square value for the reduction is 0.024 cm$^{-1}$ which is approximately half of the specified laser bandwidth of the dye lasers. Precise experimentally determined molecular constants for the $1^5\Pi_g$ are reported for the first time to the best of our knowledge. The centrifugal distortion
Table 5.2: cont’d, TC-RFWM transitions to $1^5\Pi_g$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Upper Level</th>
<th>Transition</th>
<th>Intermediate</th>
<th>Observed</th>
<th>Residuals</th>
<th>Perturbation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F4(2)</td>
<td>(6,5)Q41(2)</td>
<td>(4,5)Q1(2)</td>
<td>21335.04</td>
<td>-0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>F4(2)</td>
<td>(6,5)R42(3)</td>
<td>(4,5)R1(3)</td>
<td>21404.61</td>
<td>0.02</td>
<td>0.24</td>
</tr>
<tr>
<td>F4(2)</td>
<td>(6,5)P43(3)</td>
<td>(4,5)R3(3)</td>
<td>21285.60</td>
<td>0.02</td>
<td>0.27</td>
</tr>
<tr>
<td>F4(2)</td>
<td>(6,5)R43(1)</td>
<td>(4,5)R1(1)</td>
<td>21430.82</td>
<td>0.04</td>
<td>0.27</td>
</tr>
<tr>
<td>F4(3)</td>
<td>(6,5)P4(4)</td>
<td>(4,5)R2(4)</td>
<td>21394.87</td>
<td>-0.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>F4(3)</td>
<td>(6,5)R42(2)</td>
<td>(4,5)R2(2)</td>
<td>21415.89</td>
<td>0.01</td>
<td>-0.02</td>
</tr>
<tr>
<td>F4(3)</td>
<td>(6,5)R43(2)</td>
<td>(4,5)R3(2)</td>
<td>21397.78</td>
<td>0.00</td>
<td>-0.03</td>
</tr>
<tr>
<td>F4(4)</td>
<td>(6,5)P4(5)</td>
<td>(4,5)R1(5)</td>
<td>21415.83</td>
<td>-0.02</td>
<td>-0.24</td>
</tr>
<tr>
<td>F4(4)</td>
<td>(6,5)P41(5)</td>
<td>(4,5)R1(5)</td>
<td>21395.40</td>
<td>-0.02</td>
<td>-0.24</td>
</tr>
<tr>
<td>F4(4)</td>
<td>(6,5)R42(3)</td>
<td>(4,5)R1(3)</td>
<td>21417.64</td>
<td>-0.02</td>
<td>-0.24</td>
</tr>
<tr>
<td>F4(4)</td>
<td>(6,5)R43(3)</td>
<td>(4,5)R3(3)</td>
<td>21398.67</td>
<td>0.03</td>
<td>-0.19</td>
</tr>
<tr>
<td>F4(5)</td>
<td>(6,5)R42(4)</td>
<td>(4,5)R2(4)</td>
<td>21418.84</td>
<td>-0.01</td>
<td>-0.31</td>
</tr>
<tr>
<td>F4(6)</td>
<td>(6,5)R42(5)</td>
<td>(4,5)R2(5)</td>
<td>21419.61</td>
<td>0.01</td>
<td>-0.27</td>
</tr>
<tr>
<td>F4(12)</td>
<td>(6,5)R41(11)</td>
<td>(4,5)R1(11)</td>
<td>21446.77</td>
<td>-0.07</td>
<td>0.84</td>
</tr>
<tr>
<td>F5(3)</td>
<td>(6,5)P52(4)</td>
<td>(4,5)R2(4)</td>
<td>21404.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5(3)</td>
<td>(6,5)R52(2)</td>
<td>(4,5)R2(2)</td>
<td>21425.33</td>
<td>-0.01</td>
<td>-0.25</td>
</tr>
<tr>
<td>F5(3)</td>
<td>(6,5)R53(2)</td>
<td>(4,5)R3(2)</td>
<td>21407.26</td>
<td>0.01</td>
<td>-0.23</td>
</tr>
<tr>
<td>F5(4)</td>
<td>(6,5)R52(5)</td>
<td>(4,5)R2(5)</td>
<td>21403.02</td>
<td>-0.01</td>
<td>-0.62</td>
</tr>
<tr>
<td>F5(4)</td>
<td>(6,5)Q52(4)</td>
<td>(4,5)R2(4)</td>
<td>21417.86</td>
<td>0.01</td>
<td>-0.60</td>
</tr>
<tr>
<td>F5(4)</td>
<td>(6,5)R52(3)</td>
<td>(4,5)R1(3)</td>
<td>21430.08</td>
<td>0.00</td>
<td>-0.61</td>
</tr>
<tr>
<td>F5(4)</td>
<td>(6,5)R53(3)</td>
<td>(4,5)R3(3)</td>
<td>21411.09</td>
<td>0.03</td>
<td>-0.58</td>
</tr>
<tr>
<td>F5(5)</td>
<td>(6,5)R53(4)</td>
<td>(4,5)R3(4)</td>
<td>21412.05</td>
<td>0.01</td>
<td>-0.48</td>
</tr>
<tr>
<td>F5(6)</td>
<td>(6,5)R52(5)</td>
<td>(4,5)R2(5)</td>
<td>21437.52</td>
<td>0.02</td>
<td>-0.44</td>
</tr>
<tr>
<td>F5(10)</td>
<td>(6,5)R52(9)</td>
<td>(4,5)R2(9)</td>
<td>21442.86</td>
<td>-0.04</td>
<td>0.55</td>
</tr>
<tr>
<td>F5(11)</td>
<td>(6,5)R52(10)</td>
<td>(4,5)R2(10)</td>
<td>21440.05</td>
<td>0.04</td>
<td>-0.88</td>
</tr>
</tbody>
</table>

Table 5.3: TC-RFWM transitions to $b^3\Sigma_g^-, v = 19$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Upper Level</th>
<th>Assignment</th>
<th>Intermediate</th>
<th>Observed</th>
<th>Residuals</th>
<th>Perturbation</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1(18)</td>
<td>(6,4)R12(17)</td>
<td>(3,4)R2(17)</td>
<td>22994.70</td>
<td>0.02</td>
<td>-0.19</td>
</tr>
<tr>
<td>F1(20)</td>
<td>(6,4)R1(19)</td>
<td>(3,4)R1(19)</td>
<td>23031.07</td>
<td>-0.03</td>
<td>3.10</td>
</tr>
<tr>
<td>F1(22)</td>
<td>(6,4)R1(21)</td>
<td>(3,4)R1(21)</td>
<td>22996.06</td>
<td>-0.02</td>
<td>-0.80</td>
</tr>
<tr>
<td>F2(17)</td>
<td>(6,4)R23(16)</td>
<td>(3,4)R3(16)</td>
<td>22991.48</td>
<td>-0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>F2(19)</td>
<td>(6,4)R2(18)</td>
<td>(3,4)R2(18)</td>
<td>23027.49</td>
<td>0.01</td>
<td>2.56</td>
</tr>
<tr>
<td>F2(21)</td>
<td>(6,4)R2(20)</td>
<td>(3,4)R2(20)</td>
<td>22995.21</td>
<td>0.01</td>
<td>-4.91</td>
</tr>
<tr>
<td>F3(18)</td>
<td>(6,4)R3(17)</td>
<td>(3,4)R3(17)</td>
<td>23024.97</td>
<td>0.01</td>
<td>2.22</td>
</tr>
<tr>
<td>F3(20)</td>
<td>(6,4)R3(19)</td>
<td>(3,4)R3(19)</td>
<td>22994.31</td>
<td>0.00</td>
<td>-3.84</td>
</tr>
</tbody>
</table>

constant $D$ is not accessible owing to the low $J$ quantum numbers of the measured transitions. The same reason prevents the accurate evaluation of the $L$-uncoupling parameters $p$ and $q$. It is worth mentioning that for quintet states the higher order spin-spin term $\theta$ has to be considered. However, an improvement of the fit has not been achieved by the inclusion of this term in the Hamiltonian. This finding is anticipated by taking into account the small value for the first order spin-spin parameter $\lambda$.

The results from a configuration interaction study by Kirby and Liu [17] can be compared with our data. The authors predicted the $1^5\Pi_g$ valence state among others with a bond energy of 1.70 eV and calculated the origin, $T_o$, with an estimated accuracy of $\approx 2700$ cm$^{-1}$ which has been determined by comparison with experimentally measured valence states. The theoretically calculated rotational constant is about 10% smaller than the experimentally determined value. The good agreement with the computed ab initio
Table 5.4: Optimized molecular constants for the $^1\Sigma^+_g$, $^3\Pi_g$, $v = 6$ and the $^3\Sigma^-_g$, $v = 19$ states. All values are in cm$^{-1}$. The origin, T is relative to the $a^3\Pi_u$, $v = 0$ level. Numbers in parenthesis are one standard deviation. $^a$ Ref. [16], $^b$ listed values are for $v = 0$ Ref [17], $^c$ extrapolated from the results in Ref. [18]

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>T</td>
<td>29258.5922(48)</td>
<td>29941.99$^b$</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.14413(11)</td>
<td>1.012$^b$</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>8.9450(47)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>-0.0428(23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>-0.0744(39)</td>
<td></td>
</tr>
<tr>
<td>$^3\Sigma^-_g$, $v = 19$</td>
<td>T</td>
<td>29442.1348(843)</td>
<td>29434.25$^c$</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.179368(214)</td>
<td>1.178804$^c$</td>
</tr>
<tr>
<td></td>
<td>D $\times 10^6$</td>
<td>6.5066$^c$</td>
<td>6.5066$^c$</td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>0.142(22)</td>
<td>0.1548$^c$</td>
</tr>
<tr>
<td>$^3\Pi_g$, $v = 6$</td>
<td>T</td>
<td>29259.3736(32)</td>
<td>29259.704 (14)$^a$</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-12.8223(90)</td>
<td>-13.082 (35)$^a$</td>
</tr>
<tr>
<td></td>
<td>$p$</td>
<td>0.00467(91)</td>
<td>0.00104(65)$^a$</td>
</tr>
<tr>
<td></td>
<td>$q$</td>
<td>-0.000964(44)</td>
<td>-0.001514(17)$^a$</td>
</tr>
</tbody>
</table>

Coupling elements for the spin-orbit and $L$- uncoupling of relevant states are

$$< d^3\Pi_1, v = 6 | H_{so} | ^1\Sigma^+_1 >= 4.6220(88) \text{ cm}^{-1},$$

$$< d^3\Pi_1, v = 6 | H_{so} | ^3\Sigma^-_1, v = 19 >= 0.7855(110) \text{ cm}^{-1} \text{ and}$$

$$\frac{1}{\sqrt{2}} < d^3\Pi_0, v = 6 | BL_p | ^3\Sigma^-_1, v = 19 >= 0.31192(37) \text{ cm}^{-1}.$$
basis of the work by Amiot et al. [18] for the Ballik-Ramsay system \((b^3\Sigma_g^- - a^3\Pi_u)\) where 13 bands between (0,0) and (6,3) have been investigated. Owing to the low \(J\) quantum numbers measured in this study, the centrifugal distortion constant, \(D\) has been fixed at the extrapolated value. An overall good agreement of the experimental values for this state with the extrapolation is obtained, in particular, when considering that the Dunham expansion coefficients are determined for relatively low vibrational levels only \((v' \leq 6)\). A similar agreement with the extrapolated values has been obtained for \(v' = 16\) in the deperturbation study of \(d^3\Pi_g, v = 4\) [78], further indicating the consistency of the results obtained by applying the TC-RFWM technique.

The global fit to the measured transitions is significantly improved by floating the origin, \(T\), spin-orbit, \(A\), and the \(\Lambda\) doubling constants, \(p\) and \(q\), of the upper Swan level \(d^3\Pi_g, v = 6\). The average error of the fit is reduced from 0.189 to 0.024 cm\(^{-1}\). The obtained origin, \(T\) and spin-orbit, \(A\) are in good agreement with the computed values from the equilibrium constants reported by Tanabashi et al. [16]. In fact, the spectroscopic parameters obtained by Fourier transform spectroscopy for \(v = 6\) were not used to derive the equilibrium molecular constants for the \(d^3\Pi_g\) state owing to the extensive perturbation affecting the accuracy of the experimental precision. However, equilibrium constants were determined by performing a fit to the Dunham expansion using the relatively unperturbed vibrational levels \(v = 1, 2, 3, 5, 7\) and 8. By applying the reported coefficients, the origin and spin-orbit parameters for the unperturbed \(v = 6\) level are estimated as 29259.211 and -12.740 cm\(^{-1}\), respectively. The values obtained in this study for \(T\) and \(A\) are in significantly better agreement with this assessment than the previous constants (fourth row in Table 5.4), strongly supporting the appropriate deperturbation of this vibrational level.

The results are further sustained by adopting the new molecular constants in Table 5.4 and computing the residuals of 67 'unperturbed' line positions with \(2 \leq N \leq 27\) in the (6,5) and (6,8) bands reported by Tanabashi et al. [16]. The average error of these transitions is reduced by roughly a factor three to 0.040 cm\(^{-1}\). Similar accuracies are computed for their transitions in the relatively unperturbed vibrational bands. The deperturbation analysis clearly shows that perturbation affects a large number of these transitions. Computing residuals by taking into account the deperturbed constants for the \(d^3\Pi_g, v = 6\) state and neglecting the spin-orbit interaction with the \(1^5\Pi_g\) state and, in addition, the \(L\)-uncoupling and spin-orbit interactions with the \(b^3\Sigma_g^-, v = 19\) state yields a dramatically increased average error of 0.263 cm\(^{-1}\) thus indicating that significant perturbation-induced line shifts occur.

The term energies for the \(d^3\Pi_g, v = 6\), \(1^5\Pi_g\) and \(b^3\Sigma_g^-, v = 19\) states shown in Fig. 5.4
are evaluated from the observed transitions by subtracting the lower state rotational energies calculated by adopting the molecular constants of the $a^3\Pi_u$ state from Tanabashi et al. [16]. The value of 1.59984(J + 1) cm$^{-1}$ has been subtracted from the energies in order to display the the significant parts of the vibronic levels and their crossings. The solid lines are calculated by the model described above and adopting the molecular constants listed in Table 5.4. It is evident why the deperturbation of $d^3\Pi_g, v = 6$ is so difficult. Below $J \approx 15$, the three spin sublevels of the $d$ state are affected by the five $F$-levels of the quintet. At higher $J$ values, each sublevel is crossed by the three energy term curves of the $b^3\Sigma_g^-, v = 19$ state. Thus, many rotational levels in this range are affected by perturbations. The strongest interactions occur at rotational quantum numbers close to a term energy curve crossing. For example, the sublevel $F_4$ of the quintet state intersects $F_1$ of the $d^3\Pi_g, v = 6$ at $J = 12$. The unperturbed energies of the two rotational levels at the crossing point would be separated by $\approx 0.25$ cm$^{-1}$ only. However, spin-orbit interaction shifts each level in opposite direction by roughly 1 cm$^{-1}$. Even larger shifts occur by $L$-uncoupling and spin-orbit interactions for $b^3\Sigma_g^-, d^3\Pi_g$. For instance, the crossing of the $F_1$ term energy curves shifts each $F_1(22)$ level by $\approx 6.8$ cm$^{-1}$. 

Figure 5.4: Observed term energies of the $d^3\Pi_g, v = 6$, $1^5\Pi_g$ and $b^3\Sigma_g^-, v = 19$ states vs rotational quantum number $J$ (a). The solid lines are computed term values by taking into account the deperturbed molecular constants listed in Table 5.4. Parities are denoted by $\oplus$ and $\ominus$ signs for $e$ and $f$ levels, respectively, (b) shows an expanded view of the $d^3\Pi_g, v = 6 \sim 1^5\Pi_g$ interaction. See text for details.
Figure 5.5: Shifts of the perturbed rotational term energies in the $d^3\Pi_g, v = 6$ state plotted against the upper state rotational quantum number $J'$ for the three $F$ components. Filled and open circles denote $e$ and $f$ parity, respectively. Note, strong shifts are observed for $J = 4, 5$ and $12$ in the $F_1$ sublevel and for $J = 10$ and $11$ in $F_2$. For these perturbations both, $e$ and $f$ parity terms are affected simultaneously which is expected for a $^5\Pi_g$ perturber state. See text for details.
The term energy shifts are depicted in Fig. 5.5 by plotting the deviations of the rotational level energies of the $d^3\Pi_g, v = 6$ state determined in this study from the simulated values obtained from the molecular constants omitting perturbation effects [16]. Perturbations owing to two electronic states are clearly visible. On the one hand, strong shifts are observed for $J = 4, 5$ and 12 in the $F_1$ sublevel and for $J = 10$ and 11 in $F_2$. For these perturbations both, $e$ and $f$ parity terms are affected simultaneously which is expected for a $^5\Pi_g$ perturber state. On the other hand, substantial perturbations at $N = 19$ and 21 exhibit clear propensities for a specific parity level in each $F$ sublevel. The latter finding is in accordance with a perturbation by the $b^3\Sigma_g^-$ state because for this state only odd-$N$ rotational levels are allowed by nuclear spin-statistics. For example, for the $F_1$ component only $e$ parity levels are affected by the inhomogeneous $L$-uncoupling ($\Delta \Omega \pm 1$) and the homogeneous spin-orbit ($\Delta \Omega = 0$) interactions because for the $F_1$ sublevels ($J = N + 1$) of the $b^3\Sigma_g^-$ state solely $e$ parity levels exist.

In this work we presented a deperturbation study of the $d^3\Pi_g, v = 6$ state of C$_2$ by double-resonant four-wave mixing spectroscopy. Accurate line positions of perturbed transitions are unambiguously assigned by intermediate level labeling. In addition, extra lines are accessed by taking advantage of the sensitivity and high dynamic range of the UP TC-RFWM technique. These weak spectral features (e.g. emphasized by a shaded area in Fig. 5.3) originate from nearby-lying dark states that gain transition strength through the perturbation process. The deperturbation analysis of the complex spectral region in the (6,5) and (6,4) bands of the Swan system ($d^3\Pi_g - a^3\Pi_u$) unveils the presence of the energetically lowest high-spin state of C$_2$ in the vicinity of the $d^3\Pi_g, v = 6$ state. The term energy curves of the three spin components of the $d$ state cross the five terms of the $1^5\Pi_g$ state at rotational quantum numbers $N \leq 11$. The spectral complexity for transitions to the $v=6$ level of $d^3\Pi_g$ state is further enhanced by an additional perturbation at $N = 19$ and 21 owing to the $b^3\Sigma_g^-, v = 19$ state shown in Fig. 5.4). The spectroscopic characterization of interacting states is realized by the measurement of 122 “window” levels. A global fit of the positions to a conventional Hamiltonian for a linear diatomic molecule yields accurate molecular constants for the quintet and triplet perturber states for the first time. In addition, parameters for the spin-orbit and $L$-uncoupling interaction between the electronic levels are determined.

The detailed deperturbation study unravels major issues of the so-called high-pressure bands of C$_2$. The anomalous nonthermal emission initially observed by Fowler in 1910 [10] and later observed in numerous experimental environments are rationalized by taking into account “gateway” states, i.e. rotational levels of the $d^3\Pi_g, v = 6$ state that exhibit significant $^5\Pi_g$-character through which all population flows from one electronic state to the other.
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

5.2 Perturbation-facilitated two-color resonant four-wave-mixing spectroscopy of \( C_3 \)

This chapter describes perturbation-facilitated two-color resonant four-wave-mixing (PF-TC-RFWM) spectroscopy [11]. The method is developed to access the dark triplet manifold from the singlet ground state. Level diagrams for the (a) UP, (b) SEP, (c) UNFOLDED TC-RFWM scheme and (d) for direct absorption are shown in Fig. 5.6. The PF TC-RFWM technique shown in Fig. 5.6 scheme (b) for the SEP level diagram and (c) for the UNFOLDED level diagram utilize an intermediate state of a mixed character. By scanning the PROBE laser in PF TC-RFWM spectroscopy it is possible to access any final level via mixed intermediate \( |i\rangle \) levels.\(^1\) No direct one-photon absorption from the ground level \( |g\rangle \) to the final is level \( |f\rangle \) is possible due to the \( \Delta S \neq 0 \) selection rule.

![Energy level diagrams for the (a) UP, (b) SEP, (c) UNFOLDED TC-RFWM scheme and (d) for direct absorption. Schemes (b) and (c) describe SEP and UNFOLDED experiments performed on \( C_3 \). Gateway mediated intersystem-crossing from the \( \tilde{X}^1\Sigma_g^+ \) singlet ground state (\( |g\rangle \)) to a triplet final state \( |f\rangle \) is achieved by the UNFOLDED scheme and selecting the mixed singlet - triplet rovibronic intermediate level \( |i\rangle \) with \( \approx 80\% \) triplet character (\( |\psi_2\rangle \)). The spacing of the perturbed level pair is shown exaggerated in the figure. Scheme (d) is the direct absorption experiment.](image)

In the following experiment, PF-TC-RFWM is realized to access the (dark) triplet manifold of the \( C_3 \) molecule from the singlet \( \tilde{X}^1\Sigma_g^+ \) ground state. The inherent nonlinear signal dependence and coherence of the technique result in a favorable detection of the excited triplet states of interest. The observation of a newly found \( ^3\Delta_u \) electronic state is achieved by a two-step excitation \textit{via} “gate-way” levels (\( i.e. \) singlet - triplet mixed levels). Additionally, by fixing the probe laser on a transition exhibiting mainly triplet-triplet character and scanning the pump laser, we demonstrate an effective spin-filtering in a four-wave mixing measurement. The section 5.2.5 shows a spectrum where only transitions to the perturber \( ^3\Sigma_u^- \) state appear exclusively in the otherwise congested

\(^1\)Note, the deperturbation studies by applying the UP TC-RFWM energy scheme are performed on the \( C_2 \) molecule where the \( i \) levels have a mixed character (the dark \( ^1\Pi_g \) and the bright \( ^3\Pi_g \)). However, the UP TC-RFWM experiment allows the observation of dark levels only in the spectral range of the PROBE laser where the dark and the bright levels strongly interact, giving rise to the mixed states \( (|\psi_1\rangle \text{ and } |\psi_2\rangle) \).
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

Figure 5.7: Term energies of the $A^1Π_u$, $3Σ_u^−$ and $P = 1$ states vs rotational quantum number $J$. Parities are denoted by ⊗ and ⊖ signs for e and f levels, respectively. Note that the unknown electronic $P = 1$ state perturbs $A^1Π_u$ only in the $1 \leq J \leq 3$ range [15]. See text for details.

spectral range of the Comet band. *Ab initio* calculations of excited triplet states complement our analysis with an electronic assignment of the observed resonances and are presented in the section 8.2.3.

The perturbations of the Comet band occurring at $4 \leq J \leq 16$ are utilized as intermediate or “gate-way” levels to the triplet manifold for the PUMP-PROBE TC-RFWM experiments. Fig. 5.7 shows term energies for the three interacting electronic states vs $J$: $A^1Π_u$, $3Σ_u^−$ and $P = 1$ [15]. The PUMP laser is tuned to the resonance between the $X^1Σ_g^+$ ground state and the mixed intermediate levels $|ψ_1\rangle$ or $|ψ_2\rangle$. In order to identify the intermediate levels in question, we follow [15], but simplify the discussion by including only one perturber state ($3Σ_u^−$). We assume to have two intermediate levels as shown in the section 2.2.3 (Eq. 2.21 and Eq. 2.22):

$$
\left(\begin{array}{c}
|ψ_1\rangle \\
|ψ_2\rangle \\
\end{array}\right) = \left(\begin{array}{cc}
c_{11} & c_{12} \\
c_{21} & c_{22} \\
\end{array}\right) \left(\begin{array}{c}
|A^1Π_u\rangle \\
|3Σ_u^−\rangle \\
\end{array}\right)
$$

(5.2)

with $c_{11} = c_{22}$ and $c_{12} = -c_{21} = \sqrt{1-c_{11}^2}$, where we take into account the molecular constants for the perturbing $3Σ_u^−$ from the deperturbation analysis of Zhang et al. [15] to deduce a mixing coefficient of $|c_{12}| \approx 0.2$ for the two $J = 5$ levels. For brevity, the quantum numbers for the vibrational and rotational levels, as well as the parity quantum numbers are omitted in Eq. 2.21, Eq. 2.22 and, consequently, Eq. 5.2. The corresponding interaction between the $|3Σ_u^−\rangle$ and $|A^1Π_u\rangle$ states scales with the square of the overlap integral between vibrational wave-functions.

To characterize the PROBE transitions, two double-resonance schemes have been applied that are shown in Fig. 5.6. For the UNFOLDED (Fig. 5.6 (c)), the two PUMP beams of equal frequency link the ground state $|g\rangle$ and a level $|i\rangle \in \{ψ_1, ψ_2\}$ of the perturbed intermediate pair. Subsequently, the PROBE beam resonant with the $|f\rangle$
−|i⟩ transition excites the higher lying final state |f⟩ and generates a SIGNAL beam of the same frequency. Alternatively, the energy level scheme for the stimulated-emission pumping type experiment is used (Fig. 5.6 (b)). For both schemes the final |f⟩-state is connected to the ground |g⟩-state by optically allowed transitions, thus facilitating the direct assignment of the observed state by stringent two-color selection rules.

5.2.1 TC-RFWM measurements via perturbed intermediate ψ₁ and ψ₂ states

Results from TC-RFWM experiments are given in Figs. 5.8 and 5.9. The inverted spectrum in Fig. 5.8 is obtained by tuning the PUMP lasers of equal frequency to the perturbed P(6) transition of the Comet band (000-000) $\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma^+_g$ at 24669.697 cm$^{-1}$ and scanning the PROBE. The excited $|\psi_1\rangle$ intermediate level exhibits $\approx 80\%$ singlet character. Subsequently, the PROBE laser is scanned in the spectral region near 20560 cm$^{-1}$. Two relatively intense SEP type transitions, i.e. P(6) and R(4) are observed. These lines connect the upper $J = 5$ level of the (000) $\tilde{A}^1\Pi_u$ level and the $J = 4$ and $J = 6$ levels of the vibrationally excited (022) $\tilde{X}^1\Sigma^+_g$ ground state. Alternatively, excitation of the perturbing $3\Sigma^-_u$ state (|$\psi_2\rangle$) which is separated by 1.72 cm$^{-1}$ only, yields a weak signal at P(6) and R(4) transitions (upper trace in Fig. 5.8). Extra resonances denoted by an asterisk arise because of a spectral overlap of the PUMP laser with the Q-branch of the bright $|\psi_1\rangle$ state.

On the other hand, the upper trace in Fig. 5.9 is obtained by tuning the PUMP lasers to the perturbing P(6) $3\Sigma^-_u \rightarrow \tilde{X}^1\Sigma^+_g$ transition connecting the ground state with the $|\psi_2\rangle$ level exhibiting $\approx 80\%$ triplet character. Three major transitions with substantial intensities (please note the scaling factor of $10^{-2}$ in the ordinate) are observed around 21145 cm$^{-1}$. In contrast, the excitation via the $|\psi_1\rangle$, just 1.72 cm$^{-1}$ below $|\psi_2\rangle$, shows that the peaks are present exhibiting, however, an intensity close to the noise level. The frequency axis for the latter is shifted by $-1.72 \text{ cm}^{-1}$ indicating unambiguously an UNFOLDED transition to a high lying state. Note, that shifting the PROBE frequency axis by the $-\Delta$ or $+\Delta$, where $\Delta$ is the energy difference between the two intermediate states, provides the information on the observed double-resonance scheme, i.e. UNFOLDED or SEP, respectively.

The spectrum in Fig. 5.9 shows a three-line pattern measured from the $J = 5$ intermediate state. The singlet-triplet mixing is sufficiently strong to perform UNFOLDED double-resonance experiments involving intermediate states of the $3\Sigma^-_u (= |\psi_2\rangle)$ for $4 \leq J \leq 16$. From these spectra, a characteristic Q-branch is recognizable by the minor energy difference relative to the neighbouring $J$-lines. The appearance of the Q-branch
is a clear indication that the $|f>$ is a $\Pi_g$-state. Note that Saha et al. [40] performed double-resonance experiments for the Renner-Teller analysis of the excited $^1\Delta_g$ state and observed a similar rotational pattern for a vibronic $\Pi_g - \Sigma_u^+$ transition in the singlet manifold. Considering the triplet character of the intermediate levels $|\psi_1>$ and $|\psi_2>$ of $\approx 20\%$ and $80\%$, respectively, and assuming a P(5), Q(5) and R(5) rotational structure, the final state $|f>$ is likely a triplet state of $^3\Pi_g$ vibronic symmetry. Further evidence of the triplet character of the $|f>$ state is presented and discussed in the section 8.2.3.

Figure 5.8: SEP transitions by applying TC-RFWM from the ground state (000) $\tilde{X}^1\Sigma_g^+$ via $|\psi_1>$ and $|\psi_2>$ exhibiting $\approx 20$ and $80\%$ triplet character, respectively. P(6) and R(4) are SEP transitions to the vibrationally excited (022) level of the ground state $\tilde{X}^1\Sigma_g^+$. Resonances discussed in the text are emphasized by the shaded area. The lower trace is shifted by 1.72 cm$^{-1}$ unambiguously indicating SEP type transitions.

5.2.2 Dependence of the RFWM signal intensity on the intermediate state mixing coefficient $c_J$

The diagrammatic perturbation theory and spherical tensor formalism were used to derive FWM signal expressions [52, 81].

The induced polarization of a medium is defined as $P_{RFWM}^{(3)} = N \text{Tr}(\mu \rho^{(3)})$ a product of the total number of absorbing molecules $N$, a trace operation $\text{Tr}(...)$ over the scalar
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

Figure 5.9: UNFOLDED transitions by applying TC-RFWM from the ground state \((000) \tilde{X}^{1}\Sigma^+_g\) via \(|\psi_1\rangle\) and \(|\psi_2\rangle\) exhibiting \(\approx 20\) and \(80\) % triplet character, respectively. The lower trace is shifted by \(-1.72\) cm\(^{-1}\) unambiguously indicating UNFOLDED transitions. Final state transitions are accentuated by the shaded area. The inset shows three relevant Feynman diagrams.

The spherical tensor solution of the four-photon matrix element product in \(\chi_{RFWM}^{(3)}\) (for a detailed discussion see chapter 7, Ref. [52] and references therein) factorizes the FWM signal expression into Einstein coefficients \(B_{1,3}\), geometrical factors \(G_{FI}^{T}(\varepsilon_4, \varepsilon_1, \varepsilon_3, \varepsilon_2; J_g, J_i, J_f)\) where \(\varepsilon_1, \varepsilon_2, \varepsilon_3\) and \(\varepsilon_4\) are polarization unit vectors for fields \(j = 1, 2, 3, 4\),

\[
I_{RFWM} \propto \frac{1}{2} |D_{RFWM}^{(3)}|^2 = \frac{1}{2} \left| \varepsilon_0 \frac{3}{2} \chi_{RFWM}^{(3)}(-\omega_4, \omega_1, \omega_3, -\omega_2) E_1 E_2^* E_3^* \right|^2 \tag{5.3}
\]
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

line-shape functions $L(\omega_1, \omega_3)$, laser intensities $I_1, I_2, I_3$ and the initial ground-state population $N_g$. Eq. 5.4 allows an independent evaluation of geometrical factors and Einstein coefficients. The geometrical factors are polarization dependent and yield spatial information for magnetic sublevels $m_J$ of the molecular ensemble in the laboratory frame [60]. $B_1$ and $B_3$ represent the interaction of target species with the resonant laser fields in the molecular frame.

\[ I_{\text{RFWM}} \propto N_g^2 B_1^2 B_3^2 I_1 I_2 I_3 L(\omega_1, \omega_3)^2 G_F^T(\varepsilon_4, \varepsilon_1, \varepsilon_3, \varepsilon_2; J_g, J_i, J_f)^2 \]  \tag{5.4}

Einstein coefficients are written via a square of the reduced matrix element $<|\mu^{(1)}||>^2$ for the involved transitions between $|g>, |i> \in \{|\psi_1>, |\psi_2>\}$ and $|f>$.  

\[ B_1 = B_{g,i} = \frac{2\pi^2}{3\epsilon_0 \hbar^2} \frac{|i<|\mu^{(1)}||g>|^2}{2J_g + 1} \]  \tag{5.5}

\[ B_3 = B_{i,f} = \frac{2\pi^2}{3\epsilon_0 \hbar^2} \frac{|f<|\mu^{(1)}||i>|^2}{2J_i + 1} \]  \tag{5.6}

The relevant diagrams contributing to $\chi_{\text{RFWM}}^{(3)}$ are shown in the inset of Fig. 5.9. The first two diagrams (from the left to the right) describe the PROBE beam scattering on the PUMP-induced population grating in the intermediate state $|\psi_1, 2>$. The third diagram may be interpreted as a coherence between $|g>$ and $|f>$ induced by a sequential absorption of a PUMP and a PROBE photon. In this case, the RFWM signal is emitted when the second PUMP photon is absorbed to the intermediate $|\psi_1, 2>$ state. For all three diagrams the signal emerges in the “phase-matched” direction (Eq. 3.38) and has the frequency $\omega_4 = \omega_1 + \omega_3 - \omega_2$ ($\omega_1 = \omega_2 \neq \omega_3$).

The optimal conditions to observe $|f>$ levels of triplet spin-multiplicity through the gateway $|\psi_1>$ or $|\psi_2>$ states are determined by inserting Eqs. 5.5, 5.6 and Eqs. 2.21, 2.22 into Eq. 5.4 resulting in a dependence of the signal intensity on the eighth power of the mixing coefficients. Considering the PUMP resonantly tuned to a $|\psi_2>$ state with $\approx 80\%$ triplet character and a PROBE resonant to a triplet $|f>$ final state, the FWM signal is scaled by a factor of $(|c_{12}|^4 = 0.2^4) \times (|c_{22}|^4 = 0.8^4)$, respectively. Similar reasoning holds for intermediate excitation via $\psi_1$ and transitions within the singlet manifold. From the Eqs. 5.5, 5.6 it is evident that one does not gain in signal strength directly while “switching” the manifold from the singlet $g$ ground state to the triplet $f$ final state, because the PUMP two-photon transition is weakened proportionally to $|c_{12}|^4$ and the PROBE is enhanced proportionally to $|c_{22}|^4$. However, saturation of transitions to the intermediate $|\psi_1>$ or $|\psi_2>$ levels by the PUMP laser, leads to a distinctive proportionality by $|c_J|^4$ for the PROBE laser exclusively 5.2.4.
It is important to mention that the RFWM signal depends on the eighth power of the mixing coefficient. However, in order to distinguish transitions to the triplet manifold by the signal intensity only, one should set experimentally the PUMP laser to the saturation intensity leading to $|c_J|^4$ dependence on the PROBE beam only. Linear methods such as absorption spectroscopy have a quadratic dependence on the mixing coefficient. Stimulated emission pumping and other double-resonance methods based on sequential absorption of two photons have quadratic dependence on $c_J$ for each consecutive step. The four-wave mixing eighth-power functional relationship between $c_J$ and the observable signal facilitates the spin-multiplicity assignment of the final state (e.g. by the observation of line-strength propensities for corresponding intermediate states). The eighth-power law appears to be of an exceptional advantage for the selectivity of the method which makes it rather insensitive to small perturbations. Although, in order to measure $J-$dependent spectra containing spin-forbidden transitions the potential energy surfaces of two intermediate states should strongly interact in a wide range of rotational levels. The challenge of weak spin-orbit interaction might be circumvented by selective Stark/Zeeman tuning of the magnetic sublevel $m_J$ of a dark state to interact with the $m_J$ of a bright state.

### 5.2.3 Rotational analysis of the observed $^3\Pi_g$ state

The singlet-triplet mixing is sufficiently strong to perform UNFOLDED double-resonance experiments involving intermediate levels of the $^3\Sigma_u^-(=|\psi_2>)$ state for $4 \leq J \leq 16$. For each accessed intermediate level $J$ a spectrum according to Fig. 5.9 is obtained displaying a P, Q and R line in accordance with the selection rules for a $\Pi \leftarrow \Sigma$ transition.

A preliminary fit [76] of the unambiguously assigned rotational structure by measuring 32 transitions in the $^3\Pi_g - ^3\Sigma_u^-$ system yields the molecular constants in Table 5.5 with an average error of 0.029 cm$^{-1}$. The rotational constant $B$ suggests a bond-length similar to that of the $^3\Pi_u$ state. From preliminary calculations of the potential energy surfaces (see ab initio calculations in section 8.2.4), we estimate that the equilibrium bond distance in the electronic $^3\Pi_g$ state should be at significantly larger values then that of the $^3\Pi_u$ state. The rotational constant in the $^3\Pi_g$ state therefore would not agree with the experimentally observed value and we might rule out this state as a possible candidate for being the final $|f>$ state. The spin-orbit constant $A$ determined from the rotational spectra is non-zero. This rules out the $^3\Sigma_u^-$ state. However, note that an accurate evaluation of $A$ requires measurements of several spin sub-states. Nevertheless, from the non-zero spin-orbit coupling constant we conclude that the observed resonances rather belong to the $^3\Delta_u$ electronic state. The $\Lambda$-type doubling parameters of $^3\Delta_u$ state are quite different compared to the known $^3\Pi$ states (Table 5.5).
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

Table 5.5: Molecular constants for the $^3\Pi_\text{g}$ vibronic level. All values are in cm$^{-1}$. The origin, $T$, is relative to the (0,0,0) $\tilde{X}^1\Sigma^+_\text{g}$ state. For comparison, constants for the two known triplet states $\tilde{a}$ and $\tilde{b}$ are reproduced from Ref. [19].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^3\Pi_{\text{g}}$ (vib.)</th>
<th>$^b^3\Pi_{\text{g}}$</th>
<th>$^a^3\Pi_{\text{u}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, origin</td>
<td>45846.348 (3711)</td>
<td>45846.348 (3711)</td>
<td>45846.348 (3711)</td>
</tr>
<tr>
<td>$A$</td>
<td>12.817 (1860)</td>
<td>13.919 (44)</td>
<td>13.556 (43)</td>
</tr>
<tr>
<td>$B$</td>
<td>0.41858 (176)</td>
<td>0.424524 (22)</td>
<td>0.416957 (19)</td>
</tr>
<tr>
<td>$o$</td>
<td>-0.1253 (94)</td>
<td>0.581 (54)</td>
<td>0.595 (54)</td>
</tr>
<tr>
<td>$p \cdot 10^3$</td>
<td>12.4 (32)</td>
<td>-2.2 (12)</td>
<td>-2.2 (12)</td>
</tr>
</tbody>
</table>

5.2.4 Saturation behavior of the intermediate states $\psi_1$ and $\psi_2$

For the applied pulse energies one should be cautious of the signal saturation behavior which consequently affects the intensity ratio between chosen $|\psi_1>$ and $|\psi_2>$ intermediate states. Considering a strong PUMP beam coupling the ground state with a dark $|\psi_2>$ or a bright $|\psi_1>$ state with the transition dipole moments evaluated in Table 5.6, the contribution of the PUMP beam to the four-wave mixing signal intensity is balanced by saturation for both $\psi_j - \tilde{X}^1\Sigma^+_\text{g}$ transitions ($j = 1, 2$). A weak PROBE explores the intermediate state population grating giving rise to a $|c_{22}|^4$ and a $|c_{12}|^4$ signal intensity dependence of the $^3\Pi_\text{g}$-$\psi_2$ and $^3\Pi_\text{g}$-$\psi_1$ transition, respectively. The RFWM signal intensity ratio for the observed P,Q and R branch resonances to the $^3\Pi_\text{g}$ state (Fig. 5.9) are on the order of 250 for the two intermediate states $|\psi_1>$ and $|\psi_2>$. This value is in a qualitative agreement with the ratio of the singlet-triplet mixing coefficients $|c_{22}|^4/|c_{12}|^4 = 256$.

An illustrative picture of the PROBE beam coherently scattering off the intermediate state population grating helps to rationalize the influence of the saturation phenomenon. As mentioned in [52], it is advisable to have the PUMP frequencies tuned to the weaker dipole moment transition of the double-resonance. Therefore, the 40 nJ PUMP beams are tuned to the $\psi_1/\psi_2 - \tilde{X}^1\Sigma^+_\text{g}$ transition. The spectral irradiance applied in the experiment is calculated as $I = E/\tau_L\Delta\nu_LA$. $\tau_L = 7$ ns is the laser pulse duration, $\Delta\nu_L = 0.02$ cm$^{-1}$ the laser bandwidth and $A \approx 1.510^{-3}$ cm$^2$ the beam overlap area which gives $I_{\text{sat}}^{\text{exp}} = 22$ kW/(cm$^2 \times$ cm$^{-1}$). Estimated from the life-time measurements, the saturation intensities $I_{\text{sat}}$ (see Table 5.6) are converted to the spectral irradiance yielding $\approx 0.3$ W/(cm$^2 \times$ cm$^{-1}$) for the Abrams-Lind (AL) model [58] and $\approx 37.5$ W/(cm$^2 \times$ cm$^{-1}$) for the bandwidth-corrected model. The latter defines the Rabi frequency as $\Omega_{\text{sat}} = \sqrt{\Delta\nu_L \Gamma_0}$ if $\Delta\nu_L \gg \Gamma_{ig}$, where the laser bandwidth $\Delta\nu_L$ is compared to the coherence dephasing rate $\Gamma_{ig}$. This approximation is similar to the results obtained by applying the model described in Ref. [83]. For details refer to Ref. [53]. Estimated
Table 5.6: Oscillator strength, transition dipole moment and saturation intensities

<table>
<thead>
<tr>
<th>Line</th>
<th>Life-time (^a) (ns)</th>
<th>Osc. strength (f_{gi}^b)</th>
<th>Dipole moment (\times 10^{-29}) (C·m)</th>
<th>Sat. intensity ((W/m^2)^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P(4) \tilde{A}^1\Pi_u)</td>
<td>202</td>
<td>0.0243</td>
<td>0.3416</td>
<td>62.01</td>
</tr>
<tr>
<td>(P(4) \tilde{3}\Sigma_u^-)</td>
<td>786</td>
<td>0.0063</td>
<td>0.1732</td>
<td>15.93</td>
</tr>
<tr>
<td>(R(2) \tilde{A}^1\Pi_u)</td>
<td>223</td>
<td>0.0221</td>
<td>0.3251</td>
<td>56.17</td>
</tr>
<tr>
<td>(R(2) \tilde{3}\Sigma_u^-)</td>
<td>2190</td>
<td>0.0022</td>
<td>0.1037</td>
<td>5.72</td>
</tr>
</tbody>
</table>

\(^a\) Based on the life-time measurements of the \(\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+\) band with an inclusion of the perturber \(3\Sigma_u^-\) state (Ref. [15]).

\(^b\) Electronic oscillator strength \(f_e = 0.033\) measured in Ref. [82] at 3200 K.

\(^c\) If saturation intensity is calculated for the Rabi frequency \(\Omega_{sat} = \sqrt{\Delta \nu L \Gamma_{ig}}\), when a laser bandwidth is large compared to a coherence life-time \(\Delta \nu L \gg \Gamma_{ig}\). Saturation intensity for the PUMP transition is \(\approx 7.5\) kW/m\(^2\). This value is about three orders of magnitude lower then experimentally applied PUMP intensities. See text and Ref. [53] for details.

saturation values for PUMP transition are at least three orders of magnitude inferior to the spectral irradiance \(I_{sat}^{exp}\) applied in current experiments. This significant saturation level is also reflected in the observed power-broadened linewidth of \(\approx 12\) GHz.

5.2.5 The Spin Filter TC-RFWM measurement

Further evidence for the triplet character of the final state \(|f>\) which is observed by applying UNFOLDED PF-RFWM via the \(|\psi_2>\) intermediate state, is shown in Fig. 5.10. Here, PF-RFWM spectroscopy is performed by tuning the PROBE laser to the narrowly spaced Q-branch region and scanning the PUMP lasers in the spectral region of the Comet band (000 – 000) \(\tilde{A}^1\Pi_u \leftarrow \tilde{X}^1\Sigma_g^+\). In the spectrum, exclusively P and R transitions are observed with significant intensities that involve the intermediate perturbing state \(3\Sigma_u^-\) with \(J=4\) to 16. For comparison, a typical absorption spectrum of the Comet band is simulated and shown inverted in the lower trace. The observation is rationalized in a straightforward manner by assuming an intermediate level labeling of several overlapping Q-lines in the \(3\Pi_g^- \tilde{3}\Sigma_u^-\) \((= |\psi_2>\) system which are addressed simultaneously by the PROBE laser. It is important to mention that the perturber transitions are generally weak and difficult to observe in common absorption spectroscopy. In fact, a detailed analysis has been achieved only recently by applying cavity ring-down and time-resolved LIF measurements [15, 84].
Chapter 5. Results I: Application of RFWM Spectroscopy to study dark states

Figure 5.10: PFOODR spectrum by tuning the PROBE laser to several overlapping Q lines in the $^{3}\Pi_{g} - ^{3}\Sigma_{u}^{-}$ vibronic system and scanning the PUMP lasers. Exclusively transitions from the ground state $\tilde{X}^{1}\Sigma_{g}^{+}$ to the perturbing $^{3}\Sigma_{u}^{-}$ state are observed showing further evidence that the final state exhibits substantial triplet character. For comparison, a simulation of the Comet band absorption spectrum is shown at the bottom where the significant features are governed by the $\tilde{A}^{1}\Pi_{u} \leftarrow \tilde{X}^{1}\Sigma_{g}^{+}$ transition.

It should be noted that the intensity distribution of observed rotational lines does not reflect the population distribution among rotational levels of the C$_{3}$ ground state. There are two reasons for the non-thermal $J$-dependence of the measured spectrum in Fig. 5.10. First, the rovibronic spectrum is truncated by the forth power of the mixing coefficient $c_{J}$ at the PUMP saturation limit which varies according to the interaction of $\tilde{A}^{1}\Pi_{u}$ and $^{3}\Sigma_{u}^{-}$ potential energy surfaces versus $J$. Second, there is a non-even overlap between the PROBE laser spectral-line and the narrowly spaced Q-branch of the $^{3}\Pi_{g} - ^{3}\Sigma_{u}^{-}$ transition.

5.2.6 Comparison between the “Spin Filter” TC-RFWM measurement and Laser Induced Fluorescence

It is instructive to compare the measurement method based on the four-wave mixing process with the conventional laser induced fluorescence (LIF) experiment. Zhang et al. [15] collected high-resolution excitation spectra from the $\tilde{A}^{1}\Pi_{u} - \tilde{X}^{1}\Sigma_{g}^{+}$ band. A time gating of the emitted signal at 20-150 ns and 800-2300 ns was introduced. The
authors observed that the 20-150 ns time delay measurement contains mainly transitions of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma'^+_g$ band. However, the excitation spectrum obtained with the 800-2300 ns delay exhibited additional lines. Some of these additional lines were assigned to the dark $3\Sigma^-_u$ state “borrowing intensity” from the nearby lying bright $\tilde{A}^1\Pi_u$ state. The experimental $C_3$ linewidths are about 0.025 cm\(^{-1}\) which is three times the laser bandwidth. Fig. 5.11 shows a comparison between the excitation LIF experiment and the “spin-filter” TC-RFWM measurement discussed in the previous chapter 5.2.5.

![Graph showing comparison between LIF and TC-RFWM spectra](image)

**Figure 5.11:** Comparison between PF-TC-RFWM spectrum and LIF spectrum measured by Zhang et. al.[15]. Black (top) trace indicates the excitation LIF experiment. The triangles specify the lines belonging to the perturbing triplet state, while hexagons specify perturbing state $P = 1$. Rather intense lines with no assignment belong to the allowed $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma'^+_g$ band transition. The green (inverted bottom) trace demonstrates the spectrum recorded by the PF TC-RFWM experiment, where transitions from the ground state $\tilde{X}^1\Sigma'^+_g$ to the perturbing $3\Sigma^-_u$ state are exclusively observed further simplifying the spectrum.

Note that the spectrum recorded by applying the PF TC-RFWM technique in the Fig. 5.11 is much more simple and exhibits only transitions to the triplet perturbing $3\Sigma^-_u$ state. Thus, on the $C_3$ Comet band we demonstrate the advantages of four-wave mixing nonlinear spectroscopy as compared to linear excitation techniques. The PF TC-RFWM can be applied to any molecular system with spin-orbit or other types of interactions opening “gate-way” levels. Furthermore, by utilizing the nonlinear signal dependence on the mixing coefficient $c_J$ of the intermediate state, it is either possible to apply “spin-filter” measurements for the intermediate state characterization or to observe transitions to final electronic states of a different spin multiplicity with respect to the initial state.
Chapter 6

Results II:
Perturbation-Facilitated
Two-Photon LIF

6.1 Perturbation-Facilitated Two-Photon Laser
Induced Fluorescence

In the following section we discuss the application of the Perturbation-Facilitated TwoPhoton Laser Induced Fluorescence (PF - Two-Photon LIF) to study vibrational dynamics of the C$_3$ cluster in the triplet manifold. The molecular population from the singlet $\tilde{X}^{1}\Sigma^+_g$ ground state is pumped to the triplet $^3\Pi_g$ vibronic level by a two-photon resonant excitation via “gate-way” levels (i.e. singlet - triplet mixed levels discussed in section 2.2.3 and utilized as intermediate levels for the PF TC-RFWM in section 5.2). Two types of LIF experiments are performed. Primarily, the PF-Two-Photon LIF experiment is performed by scanning the excitation laser in the vicinity of the $^3\Pi_g$ state. Hence, by detecting the fluorescence in the specific spectral range the rovibronic resonances allows unambiguous assignment of the final state. For the $\Pi \leftarrow \Sigma$ transition the $\Delta J = 0, \pm 1$ resonances are observed by depletion of the two-photon laser induced fluorescence. These measurements yield the same information on the rotational constants of the rovibronic final state as the PF-TC-RFWM experiment [11]. Secondarily, dispersed fluorescence measurements [85, 86] are performed from the selected spin component of the final rovibrational $c_1$ and $c_2$ $^3\Pi_g$ levels (see section 6.1.1). The radiative decays into the different vibrational levels of the triplet manifold are spectrally resolved by scanning the monochromator grating.
6.1.1 Dispersed LIF from the $^3\Pi_g$ vibronic level

By applying optical-optical double resonance excitation to the $^3\Pi_g$ state and observing the dispersed fluorescence new data on the triplet manifold of $C_3$ are obtained. For example the Fig. 6.2 is measured by exciting the vibronic perturber state $^3\Sigma_u^-$ in the Comet band via the P(6) transition of the $^3\Sigma_u^--\tilde{X}^1\Sigma_g^+$ electronic system at 24671.422 cm$^{-1}$. The second photon (21144.1 cm$^{-1}$) populates subsequently the $^3\Pi_g$ level analyzed in the section 5.2.3 at $\approx 45834$ cm$^{-1}$, i.e.

$$^3\Pi_g \overset{h\nu_2}{\longrightarrow} ^3\Sigma_u^- \overset{h\nu_1}{\longrightarrow} \tilde{X}^1\Sigma_g^+$$

Note that by applying the PF TC-RFWM spectroscopy we detect two vibrational bands of $^3\Pi_g$ symmetry in the range of 45000 cm$^{-1}$. The energetically lowest band designated here as $c_1$ $^3\Pi_g$ is observed if the second laser $\nu_2$ is tuned to 20718 cm$^{-1}$. The $c_2$ $^3\Pi_g$ band is observed if the $\nu_2$ is tuned to 21144 cm$^{-1}$ (i.e. 426 cm$^{-1}$ above $c_1$). Some weak transitions to the levels of predominantly triplet character were observed at 20802 and 20804 cm$^{-1}$. However, because of the weak intensity no analysis of the rotational structure is performed.

The two-photon dispersed LIF technique enables the observation of non-coherent radiative decays into the $C_3$ triplet manifold. Note, the information provided by two-photon dispersed LIF yields the vibrational frequencies of the lowest triplet states. Therefore, the technique is complementary to the PF-TC-RFWM spectroscopy which enables to study the rovibronic structure of the final state. The experimental setup is discussed in section 4.2.2 and briefly outlined in the following. The high-numerical aperture mirror is collecting the two-photon LIF emission from the overlap region of two laser beams in the molecular jet. The objective of $\approx 0.5$ m focal length in front of the monochromator is imaging the LIF emission from the “point source” in the laser overlap region onto the monochromator slit. A spectrally resolved detection of the LIF emission from the vibronic $^3\Pi_g$ levels is established by scanning the monochromator grating. The photon flux is converted into the current with the photomultiplier tube (PMT detector). The signal current is integrated on the oscilloscope over $\approx 3$ $\mu$s. Every LIF trace is $\approx 20$ times averaged on the oscilloscope. For the detection of weak two-photon LIF signals a broadband current amplifier is introduced in front of the oscilloscope BNC port. Optionally the signal can be detected by a BOXCAR integrator in a time window of $\approx 10$ $\mu$s.

The black trace shown in the Fig. 6.1 and Fig. 6.2 is the on and off measurement implemented by subtracting the LIF signal with only $\nu_1$ present in the experiment from the trace when both photons $\nu_1$ and $\nu_2$ are present. The one-photon LIF from the $^3\Sigma_u^--(0n0)\tilde{X}^1\Sigma_g^+$ band in the range of 24700 cm$^{-1}$ and from the $^3\Sigma_u^--(0n2)\tilde{X}^1\Sigma_g^+$ in
the range of 21140 cm\(^{-1}\) combination band with two quanta of asymmetric stretching vibration and \(n\) quanta of bending vibration appear inverted in the LIF trace because of the depletion of the one photon fluorescence \(hc\nu_1\) from the intermediate \(3^\Sigma_u^+\) state. That is, the measurement with \(\nu_2\) resonantly tuned to \(c_1\) or \(c_2\) \(3^\Pi_g\) removes the population from the intermediate state.

On the other hand new vibrational progressions appear when the radiative decays are observed from the excited triplet \(c_1\) and \(c_2\) \(3^\Pi_g\) vibronic levels, see Fig. 6.1 and 6.2, respectively. Major transitions from the \(3^\Pi_g\) state within the triplet manifold are labeled by their transition wavenumbers and are highlighted by the \(\times 5\) trace. Persistent on the range of 4000 cm\(^{-1}\) vibrational progressions indicate a low-frequency bending-vibration combined with the symmetric and asymmetric stretching vibrations. The following bands are measured under a resolution of \(\approx 30\) cm\(^{-1}\). Note that if the molecule is linear (\(i.e.\) \(D_\infty h\)), selection rules prohibit transitions between \(u \leftrightarrow u\) (ungerade) and \(g \leftrightarrow g\) (gerade) levels. Therefore, the energetically lowest recurrence in the vibrational progression should correspond to \(2hc\omega_2\) where \(\omega_2\) is the bending vibrational wavenumber. However, the interpretation is more ambiguous due to the fact that the vibrational band is additionally split by the Renner-Teller interaction [87, 88]. Decays to the respective Renner-Teller components are governed by the one-photon selection rules. Furthermore, the possibility of the bent \(C_3\) structure should be examined (\(i.e.\) \(C_{2v}\) or \(C_s\) point group). The reduced symmetry of the molecule affects selection rules, hence, the ungerade and gerade description is not valid and vibronic transitions may take place between levels that differ by one vibrational quanta. Attributed to all arguments mentioned above, the interpretation of the energy map in the triplet manifold is preliminary and far from being conclusive.

6.1.2 Vibrational structure of the triplet manifold: signature of the \(\tilde{a}\) \(3^\Pi_u\) and \(\tilde{b}\) \(3^\Pi_g\) electronic states

The zoom (\(\times 5\)) in Fig. 6.1 and Fig. 6.2 emphasizes the two-photon excitation LIF decays into numerous vibrational levels of the \(\tilde{a}\) \(3^\Pi_u\) and the \(\tilde{b}\) \(3^\Pi_g\) electronic states. Sasada et al. [19] assigned the \(\tilde{b}\) \(3^\Pi_g\) - \(\tilde{a}\) \(3^\Pi_u\) transition by analyzing the emission of \(C_3\) in the range of \(\approx 6500\) cm\(^{-1}\). From these studies the spectroscopic constants of the upper and the lower states were determined. However, the origin energies of the \(\tilde{a}\) and \(\tilde{b}\) states in the gas phase are not known. The origins of the \(\tilde{a}\) and \(\tilde{b}\) and \(\tilde{A}\) states have been determined in argon matrices [89, 90] and are located at 16930, 23408 and 24374 cm\(^{-1}\), respectively. The \(\tilde{b} - \tilde{a}\) transition has been measured in the gas phase and lies at 6482 cm\(^{-1}\) [19]. If the gas to matrix shift of the \(\tilde{A}\) \(1^\Pi_u\) state is applied to the \(\tilde{a}\) state (which originates from
Chapter 6. Results II: Vibrational structure of the C$_3$ triplet manifold

Figure 6.1: Dispersed fluorescence upon perturbation facilitated excitation of the c$_1$ $^3\Pi_u$ state, i.e. $^3\Pi_u \xleftarrow{h\nu_1} ^3\Sigma_u^- \xrightarrow{h\nu_2} \tilde{X}^1\Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The corresponding Rayleigh peaks from one-photon fluorescence are indicated by arrows. The trace shows the difference signal obtained by switching the second photon ($\nu_2$) on and off. Weak feature marked with the asterisk* originate from the third harmonic of the Nd:YAG laser.

the same electron configuration) then the origin is predicted to lie at 17232 cm$^{-1}$. As a consequence, the $b$ state is located at 23714 cm$^{-1}$.

According to the estimated origins of both electronic states relative to the $\tilde{X}^1\Sigma_g^+$ we model the LIF spectrum by numerous vibronic levels of the triplet manifold shown in the inverted black trace Fig. 6.3. The LIF signal to the $\tilde{a}^3\Pi_u$ electronic state appears in the range of 24810 - 28600 cm$^{-1}$ and to the $\tilde{b}^3\Pi_g$ state in the range 19800 - 23200 cm$^{-1}$. The fluorescence emitted to a vibrational level at 28363 cm$^{-1}$ is located 17471 cm$^{-1}$ above the ground state level (000) $\tilde{X}^1\Sigma_g^+$. The energy of the (010) $\tilde{a}^3\Pi_u$ level can be computed by taking into account the molecular constants determined by Tokaryk et al. [87, 88] to lie 225 cm$^{-1}$ above the (000) $\tilde{a}^3\Pi_u$ origin which places the state at 17457 cm$^{-1}$ above the $\tilde{X}^1\Sigma_g^+$ ground state. This value is in excellent agreement with the level observed by fluorescence at 17471 cm$^{-1}$. However, selection rules for the linear molecule can not be applied since a g $\leftrightarrow$ g transition is established by the product of $\Gamma_{\Pi_u} \otimes \Gamma_{\Pi_u} = \Gamma_{\Sigma_g^\pm} \oplus \Gamma_{\Delta_g}$ in the $\tilde{a}^3\Pi_u$ final electronic state.

Furthermore, the fluorescence signal at 25977 cm$^{-1}$ (19857 cm$^{-1}$ above the singlet ground state) lies 2625 cm$^{-1}$ above the origin of the $\tilde{a}^3\Pi_u$ state. The (101) combination band has been measured in a neon matrix to occur at 2610 cm$^{-1}$ [89]. By taking into account uncertainties due to the matrix to gas phase shift a preliminary assignment
Chapter 6. Results II: Vibrational structure of the $C_3$ triplet manifold

Figure 6.2: Dispersed fluorescence upon perturbation facilitated excitation of the $c_2$ $3\Pi_g$ state, i.e. $3\Pi_g \leftrightarrow \nu_2$ $3\Sigma_u^+ \leftrightarrow \tilde{X} \Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The corresponding Rayleigh peaks from one-photon fluorescence are indicated by arrows. The trace shows the difference signal obtained by switching the second photon ($\nu_2$) on and off. The $C_2$ feature is the fluorescence from the high-$J$ of the Swan band $d^3\Pi_g - a^3\Pi_u$ excited due to the overlap with the $\nu_2$.

to this level seems reasonable. The next level at 20912 cm$^{-1}$ is separated roughly by three quanta of the symmetric stretch mode ($\omega_1 \approx 1154$ cm$^{-1}$ [89]) from the (010) level. The intense fluorescence emission at 22124 cm$^{-1}$ populates a level at 23710 cm$^{-1}$. Considering the matrix to gas phase corrected value of 23714 cm$^{-1}$ an assignment to the origin of the $\tilde{b}^3\Pi_g$ is probable.

The Fig. 6.3 shows a comparison of three measurements and a simulation superimposed on each other. Note that all two-photon LIF decays are shifted relative to the $c_2$ $3\Pi_g$ level (green trace). That is, the emission wavenumber from the $c_1$ $3\Pi_g$ level (red trace) can be calculated by subtracting 426 cm$^{-1}$ (i.e. the difference between the $c_1$ and $c_2$) from the abscissa. The blue trace (designated as (#)10 $\mu$s) in Fig. 6.3 is the LIF emission from the $2h\nu_1$ excitation of an unknown rovibronic level. The emitted photons are detected by a PMT and time-gated over 10 $\mu$s by the BOXCAR integrator. The emission from the (#) level is also shifted relative to $c_2$ level. Therefore, the relatively intense band plotted at 24452 cm$^{-1}$ in Fig. 6.3 is detected at the wavenumber $24452+(\nu_1-\nu_2)=27979$ cm$^{-1}$ (357 nm). On the other hand the position relative to the ground state is given as the sum over excitation wavenumbers $\nu_1+\nu_2$ minus the abscissa value of $\nu$ (i.e. the $\nu_1+\nu_2=45834$ cm$^{-1}$ because all traces are shifted relative to $c_2$). Regarding the (#) trace it is interesting to
mention that there are several electronic triplet states present in the energy range $2h\nu\tau_1$ (see \textit{ab initio} calculations in section 8.2.3). The density of states is high which makes a two-photon transition $2h\nu\tau_1$ within the laser bandwidth rather feasible. A further argument that these bands originate from the $2h\nu\tau_1$ transition is the depletion of the LIF emission at the 27979 cm$^{-1}$ (357 nm) if the second photon is tuned to one of the rotational transitions $\Delta J = 0, \pm 1$ to the $c_2 \tilde{3}\Pi_g$ state (see Fig. 6.6 and energy level diagram for the depletion of the two-photon LIF given in the Fig. 6.4 b). From the (#) level we observe emission which terminates at a low lying vibronic levels above ground state \textit{i.e.} 13342, 14352, 14762, 15372, 15812, 16372 cm$^{-1}$. Note that the lowest $\tilde{a}\tilde{3}\Pi_u$ electronic state in a C$_3$ linear geometry should have the origin at approximately 17232 cm$^{-1}$, therefore only radiative decays to the bend or cyclic-C$_3$ structure are possible. According to the \textit{ab initio} calculations [22–24] the lowest excited triplet state appears in cyclic-C$_3$ geometry and is $\approx 1$ eV above the linear C$_3$ ground state. The isomerization reaction can occur \textit{via} the low-frequency bending motion which could represent a feasible deformation path to generate the equilateral triangular structure of C$_3$. To date neither bend- not cyclic-C$_3$ isomers were observed experimentally. However, the authors in the Ref. [91] discuss the possibility of photo-induced $^{13/12}$C isotopic scrambling. The rearrangement of the C$_3$ (13$- 12- 12$) $\rightarrow$ (12$- 13- 12$) and (13$- 12- 13$) $\rightarrow$ (12$- 13- 13$) isotopomers by irradiation of 405 nm light is observed. The authors could distinguish isotopomers by the application of matrix isolation infrared spectroscopy and analyzing the shift of zero-point energy differences for each isotopomer. The proposed mechanism of isotopic scrambling should involve the formation of the cyclic C$_3$ intermediates.

![Figure 6.3](image_url)

**Figure 6.3:** Dispersed fluorescence upon perturbation facilitated excitation of the $3\Pi_g$ state, \textit{i.e.} $3\Pi_g \leftarrow 3\Sigma_u^-$ $\leftrightarrow \tilde{X}^1\Sigma_g^+$. The exciting wavenumbers are labeled by their transitions. The blue trace labeled as (#)10 µs is recorded by the two-photon excitation \textit{i.e.} $2h\nu\tau_1$ energy. The emitted photons are detected by the PMT and averaged with the BOXCAR integrator over 10 µs. Note that all traces are shifted relative to the $c_2 \tilde{3}\Pi_g$ vibronic level.
Chapter 6. Results II: Vibrational structure of the $C_3$ triplet manifold

Table 6.1 contains a collection of observed transitions from the $c_1, c_2 \, ^3\Pi_g$ final levels as well as from the unidentified (#) level via two-photon ($2h\nu_1$) excitation, where $\nu_1 = 24671$ cm$^{-1}$. Note that all values are given in cm$^{-1}$ relative to the $\tilde{X}^1\Sigma^+_g$ ground state. Levels denoted by an asterisk (*) have a high relative intensity.

However, we would like to emphasize that this initial assignment of the recently obtained data on the triplet structure of $C_3$ is preliminary. A complete analysis of these states, including spin-orbit and Renner-Teller effects has to be performed and is under way in our laboratory. Careful considerations of the g/u symmetry and $\Delta K$ selection rules must be included and further experiments might be required for an unambiguous assignment.

6.2 Comparison between coherent and non-coherent techniques: spatial aspects

The application of double resonance methods in gas phase spectroscopy yields information on the rovibronic molecular structure. In section 5.2 the rotational pattern with $\Delta J = 0, \pm 1$ resonances characteristic for the $\Pi \leftrightarrow \Sigma$ or $\Sigma \leftrightarrow \Pi$ transitions is observed by PF-TC-RFWM (UNFOLDED energy scheme) with high signal to noise ratio. Hence, the analysis of the rotational structure presented in section 5.2.3 can be performed in the range of $4 \leq J \leq 16$. Note that the same rotational resonances were observed by the LIF depletion experiments and can be compared to the PF TC-RFWM (see Fig. 6.6) and diagrams shown in the Fig. 6.4 (for the PF TC-RFWM experiment measured resonances are specified as $f$ levels and for the LIF depletion experiment as $e$ levels). It is easy to notice that the signal to noise ratio is much lower for the LIF depletion double resonance experiment. The coherence of the PF TC-RFWM spectroscopy is the major difference between both experiments. The LIF depletion experiment relies purely on two-photon absorption and, hence, is non-coherent.

The excited state absorption or emission experiments are described by a $\chi^{(3)}$ process [92]. The nonlinear polarization $P^{(3)}$ is obtained by the interaction of two excitation fields $E_1$ and $E'_1$. $E_1$ and its complex conjugate pump population to the intermediate level $i$, therefore the density matrix is expressed as $|i > \rho^{(0)}_{ii} < i|$. The excitation field $E_2$ couples $i$ and the excited level $e$. By applying the diagrammatic technique discussed in section 3.1.6 the relevant double-sided Feynman diagrams are obtained. The dipole moment matrix element $<i|\vec{\varepsilon}_1 \cdot \vec{\mu}|g>$ is drawn with a solid line in the diagram of Fig. 6.4 a while the $<g|\vec{\varepsilon}^*_i \cdot \vec{\mu}|i>$ is depicted with a dashed line.

The field $E_2$ acts on the ket-side and is drawn with the solid line connecting levels $e$ and $i$. The absorption coefficient from the doubly excited state is proportional to the
imaginary part of the third-order susceptibility $\chi^{(3)}(\omega)$. The non-coherent radiative decay is observed from the doubly excited level $e$ and is integrated over the life-time $\Gamma_{ei}$. Hence, the LIF signal depends on the population in the level $e$ and can be evaluated as $\text{Im}\{\chi^{(3)}(\omega)\}$.

$$I_{\text{LIF}}(\omega) \propto E_2^* \text{Im}\{\chi^{(3)}\} E_2 E_1^* E_1$$

$$\chi^{(3)} = (-2) < e|\varepsilon_2 \cdot \mu_{ei}|i > < i|\varepsilon_1 \cdot \mu_{ig}|g > \rho_{gg}^{(0)} < g|\varepsilon_1^* \cdot \mu_{ig}|i > < i|\varepsilon_2^* \cdot \mu_{ei}|e > ... \times \frac{1}{(\omega_{ei} - (\omega_1 + \omega_2 - \omega_1) + k_2 \cdot v - i\Gamma_{ei})} \frac{1}{(\omega_{ig} - \omega_1 + k_1 \cdot v - i\Gamma_{ig})} \frac{1}{((k_1 - k_1) \cdot v - i\Gamma_{ii})}$$

The imaginary part of $\chi^{(3)}$ equals $(\chi^{(3)} - \chi^{(3)*})/2i$. The two-photon absorption coefficient depends on the resonance frequencies of the laser fields, line strengths for the transitions $i \leftarrow g$ and $e \leftarrow i$ respectively and the life-times of excited levels $\Gamma_{ei}$ and $\Gamma_{ig}$.

Depletion of the $I_{\text{LIF}}$ signal can be described by a fast depopulation of the intermediate level $i$ from the competing $\chi^{(3)}$ process where resonant excitations connect different excited levels. Note that the same type of Feynman diagrams (see Fig. 6.4 a) are used to describe these two-photon resonant absorption processes. Therefore, the depletion signal should be described as a difference between two third order nonlinear susceptibilities $\text{Im}\{\chi_1^{(3)}\} - \text{Im}\{\chi_2^{(3)}\}$. Where $\chi_1^{(3)}$ connects $f \leftarrow e \leftarrow i \leftarrow g$ (the last transition $f \leftarrow e$ appears in emission) and $\chi_2^{(3)}$ connects $j \leftarrow h \leftarrow i \leftarrow g$ (the last transition $j \leftarrow h$ either appears in emission or can even be any fast intramolecular relaxation process leading to the depopulation of the $h$ level). For details see Fig. 6.5.

**Figure 6.4**: Energy level and Feynman diagrams for PF TC-RFWM spectroscopy shown in the figure a and two-photon LIF shown in the figure b.
Chapter 6. Results II: Vibrational structure of the $C_3$ triplet manifold

**Figure 6.5:** Energy level diagrams 1 and 2 for the two competing $\text{Im}\{\chi_1^{(3)}\}$ and $\text{Im}\{\chi_2^{(3)}\}$ processes respectively.

**Figure 6.6:** Comparison of the PF TC-RFWM measurement and the depletion of the two-photon LIF excitation. The red trace is measured by integrating on the oscilloscope the 7 ns photo-current pulse generated by the FWM signal. The black (inverted) trace corresponds to the depletion LIF signal that is measured by detecting LIF emission at 27979 cm$^{-1}$ (357 nm) from the doubly 2hc$\nu_1$ excited (#) level and scanning the $\nu_2$ over the $c_2^2 \Pi_g \leftrightarrow 3 \Sigma_u^-$ transition. Furthermore, the signal is averaged by the BOXCAR integrator over 10 $\mu$s.

In the current experiment $\nu_2$ is set to the $c_2^2 \Pi_g \leftrightarrow 3 \Sigma_u^-$ transition at 21144 cm$^{-1}$. The dispersed fluorescence from the $2hc\nu_1$ is observed at 27990 cm$^{-1}$ while the $\nu_2$ laser is scanned across the $\Delta J = 0, \pm 1$ resonances to the $c_2^2 \Pi_g$ vibronic level. The resonances from two-photon LIF appear as a depletion of the two-photon LIF while in case of PF TC-RFWM experiment the transitions to final states appear in emission with essentially no background (see Fig. 6.6). As a consequence the signal to noise ratio is much higher when the rovibronic structure of the $c_2^2 \Pi_g$ level is observed by applying the four-wave mixing technique.

Let us consider the four-wave mixing process where the signal wave $E_4^*$ is generated via interaction with the nonlinear polarization $P_{RFWM}^{(3)}$. The relevant Feynman diagrams are shown in the Fig. 6.4 b (see chapter 3.2.5 for details). The resonant FWM signal
intensity can be expressed as a polarization $|\varepsilon_4^* \cdot P^{(3)}(\omega)|^2$ in Eq. 7.26 (see section 7.2 for the details)

$$I_{\text{FWM}}(\omega) \propto |\varepsilon_4^* \cdot P^{(3)}(\omega)|^2 = \left| \frac{N_{\text{coh}}}{8\hbar^3} E(\omega_1) E(\omega_2^*) E(\omega_3) \exp(i k_\sigma \cdot r) \delta_\omega < O_{\text{FWM}} > D(\omega_\sigma) \right|^2$$

Where the Dirac Delta function specifies the energy conservation criteria $\delta_\omega = \delta(\omega_1 - \omega_2 + \omega_3 = \omega_\sigma)$ and $\omega_\sigma = \omega_4$. The complex exponential factor $\exp(i k_\sigma \cdot r)$ refers to the linear momentum conservation $k_1 - k_2 + k_3 = k_\sigma$ where $k_\sigma = k_4$. The notation is similar to Ref. [93]. The resonant denominator $D(\omega_\sigma) = D(\omega; \omega_1, -\omega_2, \omega_3)$ contains the life-times of excited levels and detunings of laser frequencies from the molecular resonances. Note that for the FWM the $D(\omega; \omega_1, -\omega_2, \omega_3)$ is more complex compared to the two-photon LIF expression. The $D(\omega; \omega_1, -\omega_2, \omega_3)$ is obtained in Eq. 3.45, 3.46, 3.47 and 3.48 for the Degenerate RFWM spectroscopy. The four-photon expectation value is given in Eq. 7.24.

By assuming the slowly-varying envelope approximation (SVEA) (see Ref. [54]) the wave-equation Eq. 3.9 for the four-wave mixing signal reads as

$$\frac{\partial E_4(\omega)}{\partial r} = \frac{i \omega}{2c\varepsilon_0} \varepsilon_4^* \cdot P^{(3)}(\omega) \exp(i k_4 \cdot r) = \frac{i \omega}{2c\varepsilon_0} \varepsilon_4^* \cdot \tilde{P}^{(3)}(\omega) \exp(i \Delta k \cdot r)$$

The third order polarization $\varepsilon_4^* \cdot P^{(3)}(\omega) \exp(i k_4 \cdot r) = \varepsilon_4^* \cdot \tilde{P}^{(3)}(\omega) \exp(i \Delta k \cdot r)$ by definition depends on the phase matching geometry and phase mismatch, this leads to a spatial dependence on the wave-vectors $\exp(-i (k_4 - k_\sigma) \cdot r) = \exp(-i \Delta k \cdot r)$. Further, by assuming the small signal limit when laser beams propagate through the sample of length $l$ with minimal absorption, the integration of the wave equation yields [54]

$$E_4(\omega) \propto \varepsilon_4^* \cdot \tilde{P}^{(3)}(\omega) \exp(-ikl/2) l \cdot \text{sinc}(\Delta kl/2) \quad (6.1)$$

The signal intensity is given as

$$I_{\text{FWM}}(\omega) \propto |E_4(\omega)|^2 \propto |\varepsilon_4^* \cdot \tilde{P}^{(3)}(\omega)|^2 l^2 \text{sinc}^2(\Delta kl/2) \quad (6.2)$$

The momentum conservation is reflected in the behavior of the $\text{sinc}^2$ function given in Eq. 6.2. The function has an extremum for the finite length $l$ when the detuning from the phase matching condition is $\Delta k = 0$ and $k_4 = k_\sigma$. The important aspect of the FWM technique is a quadratic dependence on the interaction length $l$. In the BOXCAR FWM geometry the crossing angle is small $\approx 0.7^\circ$. The third-order polarization is induced in the overlap region of three laser beams. The longitudinal dimension of the overlap
can be approximated by the Rayleigh length (Eq. 3.4) as \( l \approx z_0 = \pi \omega_0^2 / \lambda \approx 6 \text{mm} \). Hence, the coherent propagation of \( E_4(\omega) \) along \( l \) leads to an in-phase accumulation of the stimulated emission in the volume defined by the nonlinear polarization \( \tilde{P}^{(3)}(\omega) \). Furthermore, if the interaction length is long the signal wave \( E_4(\omega) \) will quadratically increase its amplitude. This property is in strong contrast to the non-coherent two-photon LIF emission or depletion experiments where the signal has a linear dependence on the interaction length \( l \). Note that it is experimentally challenging to collect the laser induced fluorescence from the volume. In the first place only cylindrical optics can potentially collect the signal from the longitudinal trace \( l \). In this hypothetical experiment \( l \) will be limited by the aperture of a mirror or a lens employed to collect emission. In the second place, the spontaneous radiative decays have equivalent probability to emit photons in the \( 4\pi \) volume angle. Therefore, employed optics will collect only a fraction of photons which were emitted in the direction of the solid angle defined by the numerical aperture. This is again in strong contrast to the coherent FWM experiment where the generated signal is laser-like and propagates in free-space with a well-defined direction given by the phase-matching condition. This allows to efficiently separate the stray-light and unwanted fluorescence (e.g. one photon-fluorescence from other species present in the molecular beam) from the signal beam.
### Table 6.1: The energy levels of the triplet manifold observed via two-photon LIF given in cm$^{-1}$ relative to the $\tilde{X}^1\Sigma_g^+$.

<table>
<thead>
<tr>
<th>LIF from $c_1,^{3}\Pi_g$ (cm$^{-1}$)</th>
<th>LIF from $c_2,^{3}\Pi_g$ (cm$^{-1}$)</th>
<th>Emission exp.$^a$ (cm$^{-1}$)</th>
<th>Emission exp.$^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{a},^{3}\Pi_u$, electronic configuration: $\ldots$ $1\pi^1_u\ldots$ $4\sigma^2_u\ldots$ $3\sigma^1_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\tilde{a},^{3}\Pi_u$, electronic configuration: $\ldots$ $1\pi^1_u\ldots$ $4\sigma^2_u\ldots$ $3\sigma^1_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\ldots$ $1\pi^1_u\ldots$ $4\sigma^2_u\ldots$ $3\sigma^1_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\ldots$ $1\pi^1_u\ldots$ $4\sigma^2_u\ldots$ $3\sigma^1_u\ldots$ $1\pi^1_u\ldots$</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>13342</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>14352</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>14762</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>15372</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>15812</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>16372</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16753</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16917</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17002</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17024</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17024</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17076</td>
</tr>
<tr>
<td>-</td>
<td>17471$^*$</td>
<td>17492$^c$</td>
<td>-</td>
</tr>
<tr>
<td>17933</td>
<td>17925</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18283</td>
<td>18295</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18668$^*$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19122</td>
<td>19080</td>
<td>18952</td>
<td>-</td>
</tr>
<tr>
<td>19500</td>
<td>19490</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19723$^*$</td>
<td>19857$^*$</td>
<td>19882</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>20317</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>20912</td>
<td>20852</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>21242</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>21872</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>22532</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>22812</td>
<td>-</td>
</tr>
<tr>
<td>$\tilde{b},^{3}\Pi_g$, electronic configuration: $\ldots$ $1\pi^1_u\ldots$ $4\sigma^1_u\ldots$ $3\sigma^2_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\tilde{b},^{3}\Pi_g$, electronic configuration: $\ldots$ $1\pi^1_u\ldots$ $4\sigma^1_u\ldots$ $3\sigma^2_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\ldots$ $1\pi^1_u\ldots$ $4\sigma^1_u\ldots$ $3\sigma^2_u\ldots$ $1\pi^1_u\ldots$</td>
<td>$\ldots$ $1\pi^1_u\ldots$ $4\sigma^1_u\ldots$ $3\sigma^2_u\ldots$ $1\pi^1_u\ldots$</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>23322</td>
<td>23331$^c$</td>
</tr>
<tr>
<td>23761</td>
<td>23701</td>
<td>23712$^*$</td>
<td>-</td>
</tr>
<tr>
<td>24000$^*$</td>
<td>24000$^c$</td>
<td>23882</td>
<td>24044</td>
</tr>
<tr>
<td>24218$^*$</td>
<td>24213</td>
<td>-</td>
<td>24271</td>
</tr>
<tr>
<td>-</td>
<td>24323</td>
<td>-</td>
<td>24390</td>
</tr>
<tr>
<td>24683$^*$</td>
<td>-</td>
<td>-</td>
<td>24557</td>
</tr>
<tr>
<td>25775</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25900$^*$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The LIF measurement with the BOXCAR averaging over $\approx$ 10$\mu$s upon one-color two-photon excitation $2h\nu_1$ ($\nu_1 = 24671$ cm$^{-1}$) of an unidentified level 49343 cm$^{-1}$ above the ground state.

$^b$ Weltner et al. have observed phosphorescence after excitation at 27397 cm$^{-1}$ (mercury light) [90]. The emission in the range of 16950 cm$^{-1}$ was attributed to the phosphorescence from the $\tilde{a}\,^{3}\Pi_u$ to the $\tilde{X}^1\Sigma_g^+$. Authors imply that fast intravibrational relaxation occurs first and is later followed by phosphorescence. Therefore, the values presented for the current column are converted directly into cm$^{-1}$ without subtraction of the emission from the excitation energy.

$^c$ Transitions to these levels coincide in multiple experiments.
Chapter 7

Results III: Pumped TC-RFWM as a probe of molecular alignment

7.1 Pumped TC-RFWM as a probe of molecular alignment

The incorporation of the angular momentum anisotropy into the analysis of resonant four-wave mixing spectroscopy has been accomplished by Vaccaro et al. [94]. The state multipole expansion [95] represents the density matrix and enables the four-wave mixing signal analysis in terms of contributions from population, orientation and alignment gratings [60, 94]. Wasserman et al. [60] implemented degenerate RFWM with the judicious selection of PUMP and PROBE beam polarizations to separate contributions from population, orientation and alignment.

In the present chapter we discuss the applicability of the TC-RFWM technique to study molecular orientation and alignment. The detected rovibronic state-resolved TC-RFWM signals from different energy level schemes (i.e., UP and UNFOLDED) contain the evidence of a spatial correlation between the magnetic sublevels of the intermediate $\tilde{A}^1\Pi_u$ and $3\Sigma_u^-$ states of the $C_3$ molecule. It is shown that the signal intensity from the P,Q and R resonances may significantly change depending on the angular momentum anisotropy in the selected rovibronic level.
7.1.1 Rotation of field polarization vectors

The representation of polarization vectors $\varepsilon$ in terms of spherical components $T^{(1)}_{\pm 1}(\varepsilon)$ and $T^{(1)}_0(\varepsilon)$ simplify the calculation of the angular momentum anisotropy of molecular species. Spherical tensors can be constructed from the equations detailed in see Appendix B of Ref.[60]:

$$T^{(1)}_{\pm 1}(\varepsilon) = \frac{1}{\sqrt{2}} (\varepsilon_X \pm i \varepsilon_Y)$$

and its complex conjugate

$$T^{(1)}_{\pm 1}(\varepsilon^*) = \frac{1}{\sqrt{2}} (\varepsilon^*_X \pm i \varepsilon^*_Y)$$

The laboratory frame coordinates $x, y, z$ are connected to the $X,Y$-axes defining the polarization of the electromagnetic wave. Usually the polarization is expressed in terms of two phase factors $\varphi$ and $\delta$

$$\varepsilon_X = \cos(\varphi) \quad \varepsilon_Y = \exp(i\delta) \sin(\varphi)$$

For example, the X- and Y-axes of the linear polarization are defined by $(\varphi = 0, \delta = 0)$ and by $(\varphi = \pi/2, \delta = 0)$ respectively. The right-handed circular polarization is given by $(\varphi = 5\pi/4, \delta = -\pi/2)$ and the left-handed by $(\varphi = \pi/4, \delta = \pi/2)$. The transformation between the $X,Y$ (local) frame defining polarization axes and the $x,y,z$ (laboratory) frame is accomplished by a series of three rotations, specified by Euler angles $(\alpha,\beta,\gamma)$. These rotations transform the wave-vector $k$ and transverse polarization unit vector $\varepsilon$ to coincide with the propagation of electromagnetic waves in the laboratory frame. The rotation of Eq. 7.3 by Euler vectors specifies a rotation of $\alpha$ about the $x$ axis, then a rotation of $\beta$ about the intermediate $y'$ axis followed by a rotation of $\gamma$ about the resulting $z''$ axis. The transformation is given by three equations (Eq. 7.4) for the +1, 0 and −1 spherical components.

$$T^{(1)}_{+1}(\varepsilon) = \frac{\exp(i\alpha)}{\sqrt{2}} \left[ \cos(\beta) \left( \exp(i\delta) \sin(\gamma) \sin(\varphi) - \cos(\gamma) \cos(\varphi) \right) \right.$$

$$- \left. i (\sin(\gamma) \cos(\varphi) + \exp(i\delta) \cos(\gamma) \sin(\varphi)) \right]$$

$$T^{(1)}_0(\varepsilon) = \sin(\beta) \left( \exp(i\delta) \sin(\gamma) \sin(\varphi) - \cos(\gamma) \cos(\varphi) \right)$$

$$T^{(1)}_{-1}(\varepsilon) = \frac{\exp(-i\alpha)}{\sqrt{2}} \left[ \cos(\beta) \left( \cos(\gamma) \cos(\varphi) - \exp(i\delta) \sin(\gamma) \sin(\varphi) \right) \right.$$

$$- \left. i (\sin(\gamma) \cos(\varphi) + \exp(i\delta) \cos(\gamma) \sin(\varphi)) \right]$$

(7.4)
Analogous quantities apply for the transformation of the complex conjugate unit vectors

\[ T_{+1}^{(1)}(\varepsilon^*) = \exp(i\alpha) \sqrt{2} \left[ \cos(\beta) (\exp(-i\delta) \sin(\gamma) \sin(\varphi) - \cos(\gamma) \cos(\varphi)) \right. \]

\[ - i (\sin(\gamma) \cos(\varphi) + \exp(-i\delta) \cos(\gamma) \sin(\varphi)) \]

\[ T_{0}^{(1)}(\varepsilon^*) = \sin(\beta) (\exp(-i\delta) \sin(\gamma) \sin(\varphi) - \cos(\gamma) \cos(\varphi)) \]

\[ T_{-1}^{(1)}(\varepsilon^*) = \exp(-i\alpha) \sqrt{2} \left[ \cos(\beta) (\cos(\gamma) \cos(\varphi) - \exp(-i\delta) \sin(\gamma) \sin(\varphi)) \right. \]

\[ - i (\sin(\gamma) \cos(\varphi) + \exp(-i\delta) \cos(\gamma) \sin(\varphi)) \] (7.5)

Equations 7.4 and 7.5 provide means to transform the spherical components of \( \varepsilon \) and \( \varepsilon^* \) into an arbitrary phase-matching and polarization geometry. For example, they are applicable to describe the BOXCAR geometry where three laser beams propagate along three main diagonals of a parallelepiped. In this case, rotations around the \( x \) axis and the \( y' \) axis by approximately 0.7\(^\circ\) are required. For details on the laser beams layout see section 4.2.1.

### 7.1.2 Angular momentum anisotropy

The initial distribution and correlation probability among magnetic sublevels \( m_g \) of a rovibronic state can be specified by Eq. 7.6, where the zero-order density matrix is expressed as a sum over geometrical tensors [95]. The expansion coefficients \( < T^K_Q(\alpha_g J_g)^\dagger > \) are referred to as state multipole moments and defined as given in Eq. 7.7

\[
\rho^{(0)}(\alpha_g J_g) = \sum_{K=0}^{2J_g} \sum_{Q=-K}^{K} < T^K_Q(\alpha_g J_g)^\dagger > T^K_Q(\alpha_g J_g) \tag{7.6}
\]

\[
<T^K_Q(\alpha_g J_g)^\dagger = \text{Tr}[\rho^{(0)}(\alpha_g J_g)T^K_Q(\alpha_g J_g)^\dagger] = \sum_{m_g, m''_g} (-1)^{(J_g - m_g)} \sqrt{2K + 1} \begin{pmatrix} J_g & K & J_g \\ -m_g & Q & m''_g \end{pmatrix} \rho^{(0)}_{m_g, m''_g}(\alpha_g J_g) \tag{7.7}
\]

The parentheses denote a 3\(-J\) Wigner symbol. The representation of the state multipole expansion in terms of the zero-order density matrix allows evaluation of the molecular anisotropy embedded in the four-wave mixing signal expression. Conversely the density
matrix is represented by a state multipole expansion
\[
\rho_{m_g,m_g'}^{(0)}(\alpha_g J_g) = \sum_{K,Q} (-1)^{(J_g - m_g)} \sqrt{2K + 1} \begin{pmatrix} J_g & K & J_g \\ -m_g & Q & m_g' \end{pmatrix} < T^K_Q(\alpha_g J_g)^\dagger > (7.8)
\]

The density matrix \( \rho_{m_g,m_g'}^{(0)}(\alpha_g J_g) \) is described by the state multipole moments taken with respective coefficients \( < T^K_Q(\alpha_g J_g)^\dagger > \), shown in the Eq. 7.7 and Eq. 7.8. The vector recoupling in Eq. 7.7 emphasizes that state multipole moments and density matrix elements give equivalent descriptions of the molecular ensemble. Therefore, for the given rovibronic level, the set of complex numbers \( < T^K_Q(\alpha_g J_g)^\dagger > \) provide a measure of the angular momentum anisotropy in space (Ref. [60, 95]). The alignment between magnetic sublevels of the rovibronic level \( J_g \) suggests the disparity of the population between eigenstates which differ by modulus of the magnetic quantum number \( | m_g | \), where \( g \) is an index of the initial level. The orientation refers to the directional preference of the angular momentum distribution in the laboratory frame. Hence, orientation involves a different occupancy of magnetic \( +m_g \) and \( -m_g \) sublevels. There are \( 2K + 1 \) multipole components for each rank \( K \), with the integer index \( Q \) restricted to the range between \(-K\) and \(+K\). The range of \( K \) extends from zero to \( 2J_g \).

Alignment of the \( m_g \) sublevels in the present experiment is introduced by the resonant excitation of the \( J = 5 \) level of the \( \tilde{A}\Pi_u \) state via the \( P(6) \) transition from the thermally populated \( \tilde{X}\Sigma_g^+ \) ground state. The angular-momentum anisotropy among degenerate \( m_g \) sublevels of the \( 2J_g + 1 \) manifold is created, because the probability of the transition dipole moment depends on the magnetic sublevels of the involved initial \( | g > \) and final \( | i > \) states. In the perturbative approach the resulting density operator can be written via the state multipole expansion (Ref. [95]) as denoted in the Eq. 7.9

\[
<T^K_Q(\alpha_g J_g)^\dagger > = 3(-1)^{J_g+J_i} \sqrt{2K+1} \begin{pmatrix} 1 & 1 & K \\ J_g & J_g & J_i \end{pmatrix} \times \sum_{q,q'} \begin{pmatrix} 1 & 1 & K \\ q & q' & Q \end{pmatrix} T_q^{(1)}(\varepsilon) T_{q'}^{(1)}(\varepsilon^*) (7.9)
\]

\( \varepsilon \) is the polarization of the excitation beam. \( 3 - J \) and \( 6 - J \) Wigner symbols indicate the recoupling of the angular momentum \( J \). Both the \( \varepsilon \), \( 3 - J \) and \( 6 - J \) Wigner symbols determine the magnitude of the angular momentum \( J \). Both the \( \varepsilon \), \( 3 - J \) and \( 6 - J \) Wigner symbols determine the magnitude of the angular momentum expansion with \( K = 0, 1, 2 \). \( K = 0 \) denotes the population, \( K = 1 \) the orientation and \( K = 2 \) the alignment in the coefficient \( < T^K_Q > \).

A linear polarization of the excitation laser induces the disparity in the population \( N_{\alpha_g J_g} \) (or \( N_{\alpha_i J_i} \)) of the rovibronic level between the magnetic sublevels which differ in
magnitude of the total angular momentum projection \( |m_g| \). Therefore, the multipole expansion in Eq. 7.9 contains only contribution from the population and the alignment moments. The multipole expansion for the \( P(6) \) transition calculated according to Eq. 7.9 is shown in Matrix 7.10. The \( < T_Q^K(\alpha_gJ_g) > \) components are indexed over \( Q \) where \( Q \in [-4, +4] \) and represent the contribution from the population and the alignment, respectively (first and third line of the Matrix 7.10).

\[
< T_Q^K(\alpha_gJ_g) > = \begin{pmatrix}
0 & 0 & 0 & 0 & 0.2774 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -0.0958 & 0 & 0.0782 & 0 & -0.0958 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix} \quad (7.10)
\]

### 7.1.3 Four-photon expectation value and vector recoupling

The evaluated susceptibility terms (see Eq. 3.44 derived in section 3.2.4 for DFWM spectroscopy and Eq. 3.49 - 3.51 for TC-RFWM spectroscopy) contain the product of four dipole matrix elements. Its indices \( 1, 2, 3, 4 \) correspond to the field designation \( i, j, k, l \), the four-fold transition dipole moment is given in the same notation as in Wasserman et al. [60]

\[
O_{i,j,k,l} = (\varepsilon_i^\ast \cdot \mu_i)P_e(\varepsilon_j \cdot \mu_j)P_g(\varepsilon_k^\ast \cdot \mu_k)P_e(\varepsilon_l^\ast \cdot \mu_l) \quad (7.11)
\]

The subscripts can have any permutation of the \( i, j, k, l \) values. \( P_e \) and \( P_g \) are projection operators \( P_\alpha = \sum_\alpha |\alpha > < \alpha| \). The expectation value of \( O_{i,j,k,l} \) is defined via trace operator of the product with the zero-order density matrix operator \( \rho(0) \)

\[
< O_{ijkl} > = \text{Tr}[\rho(0)(\alpha_gJ_g)O_{i,j,k,l}] = \sum_{g,g''} < g|\rho(0)(\alpha_gJ_g)|g'' > < g''|O_{ijkl}|g > \quad (7.12)
\]

Therefore Eq. 3.44 can be reformulated in terms of expectation values of the \( < O_{ijkl} > \), where each \( i, j, k, l \) contribution is composed of a permutation of photons participating in the four-wave mixing process. The resonant denominators given in Eq. 3.44 are introduced into the product with the \( < O_{ijkl} > \) which finally leads to the susceptibility \( \chi(3) \). The state multipole expansion given in Eq. 7.8 substituted into Eq. 7.12 results in

\[
< O_{ijkl} > = \sum_{m_g,m_g''} \left( \sum_{K,Q} (-1)^{(J_g-M_g)} \sqrt{2K+1} \begin{pmatrix} J_g & K \\ -m_g & Q \end{pmatrix} < T_Q^K(\alpha_gJ_g) > \right) \times < \alpha_gJ_gm_g'|O_{ijkl}|\alpha_gJ_gm_g > \quad (7.13)
\]
Chapter 7. Results III: pumped TC-RFWM as a probe of molecular alignment

The expectation value of the four-photon matrix element \( \langle \alpha \gamma \gamma' \gamma'' \rangle_{ijkl} | \alpha \gamma \gamma' \gamma'' \rangle > \) is a tensor product between polarization field vectors and dipole moment operators.\(^1\)

The separation between the rank-one dipole moment and field polarization vectors (see Eq. 7.15 below) is achieved by the vector recoupling formalism developed by Greene and Zare [96, 97]. The recoupling algorithm employs the spherical tensor contraction shown in Eq. 7.14

\[
[T^{(k_1)} \otimes T^{(k_2)}]^{(K)}_Q = \sum_{q} (-1)^{k_1 - k_2 + Q} \sqrt{2K + 1} \begin{pmatrix} k_1 & k_2 \\ q & Q - q \end{pmatrix} T^{(k_1)}_q T^{(k_2)}_{Q - q} (7.14)
\]

\[
\varepsilon_i \cdot \mu_i = -\sqrt{3} [T^{(1)}(\varepsilon_i) \otimes T^{(1)}(\mu_i)]^{(0)}_{0} = \sum_{q} (-1)^{q} T^{(1)}_q (\varepsilon_i) T^{(1)}_{Q - q} (\mu_i) (7.15)
\]

The recoupling Eq. 7.14 isolates dipole and polarization tensor elements of Eq. 7.15 allowing for an independent evaluation of the dipole moment transitions in the molecular frame and field polarization tensors in the laboratory frame. The complete vector recoupling is given in Eq. 7.16. The interested reader will find a derivation in the article of Wasserman et al. [60].

\[
O_{i,j,k,l} = (2J_c + 1) \sqrt{(2J_g + 1)} \begin{bmatrix} 4 \\ \sum_{k=0}^{K} \sum_{Q=-K}^{Q} (-1)^{K-Q} 2 \sum_{k_1=0}^{2} T^{(K)}_Q (\varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l; k_1, k_2) T^{(K)}_{Q-k} (\tilde{\mu}; k_1, k_2) \end{bmatrix} (7.16)
\]

Here, the tensor operator \( T^{(K)}_Q (\varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l; k_1, k_2) \) describes the electromagnetic field polarization and \( T^{(K)}_{Q-k} (\tilde{\mu}; k_1, k_2) \) is the four-fold transition dipole moment. The field polarization tensor by definition is Eq. 7.17 and can be recast into individual spherical components of electromagnetic waves \( \text{via} \) repeated application of the vector recoupling Eq. 7.14. The resulting Eq. 7.18 corresponds to Eq.35 in [60].\(^2\)

\[
T^{(K)}_Q (\varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l; k_1, k_2) = [[T^{(1)}(\varepsilon_i^{*}) \otimes T^{(1)}(\varepsilon_j)]^{(k_1)}_{(k_1)} \otimes [T^{(1)}(\varepsilon_k^{*}) \otimes T^{(1)}(\varepsilon_l)]^{(k_2)}_{(k_2)}]^{(K)}_Q (7.17)
\]

\(^1\)Further in the text symbol \( \times \) refers to the scalar product and \( \otimes \) refers to the tensor product.

\(^2\)Note that every Feynman diagram shown in Fig. 3.4 for the DFWM scheme of the section 3.2.4 contains a different sequence of the applied laser fields. Because the fields can be permuted in time and have their origin from either the ket or bra side of the double-sided Feynman diagrams, the tensor product Eq. 7.17 and its recoupled version Eq. 7.18 should contain a rearrangement of laser fields \( \varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l \) into separate contributions from individual diagrams. For example, diagrams shown in Fig. 3.4 A and B give \( T^{(K)}_Q (\varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l; k_1, k_2) \) and diagrams shown in Fig. 3.4 C and D give \( T^{(K)}_Q (\varepsilon_j \varepsilon_k \varepsilon_l \varepsilon_i; k_1, k_2) \). Resonant denominators \( A, B, C \) and \( D \) given in Eqs. 3.45, 3.46, 3.47 and 3.48 are multiplied with the RFWM response \( R^{(K)}_Q (\varepsilon_i^{*} \varepsilon_j \varepsilon_k \varepsilon_l; J_g, J_c, J_f) \) (Eq. 7.22 below). Similarly SEP, UNFOLDED and UP RFWM energy schemes contain contributions from different Feynman diagrams. For example, diagrams for SEP and UNFOLDED schemes are shown in Fig. 3.6 and for the UP scheme in Fig. 3.7. Therefore, fields in \( F^{(K)}_Q \) for TC-RFWM are rearranged as given in the respective four-photon product in Eqs. 3.49 - 3.51.
\[ F_Q^{(K)} = T_Q^{(K)}(\varepsilon_i^* \varepsilon_j \varepsilon_k^* \varepsilon_l; k_1, k_2) = (-1)^{k_1-k_2} \sqrt{(2K+1)(2k_1+1)(2k_2+1)} \times \sum_{q,q',q''} \left( \begin{array}{ccc} k_1 & k_2 & K \\ q & Q-q & -Q \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & k_1 \\ q' & q-q' & -q \end{array} \right) \times \left( \begin{array}{ccc} 1 & 1 & k_2 \\ q'' & Q-q-q'' & q-Q \end{array} \right) \times T_q^{(1)}(\varepsilon_i^*)T_{q-q'}^{(1)}(\varepsilon_j)T_{q-q''}^{(1)}(\varepsilon_k^*)T_{Q-q-q''}^{(1)}(\varepsilon_l) \right) (7.18) \]

The summation over \(q, q'\) and \(q''\) in Eq. 7.18 is limited because polarization vectors have only \(T_{\pm1}(\varepsilon)\) and \(T_0^{(1)}(\varepsilon)\) components.

The expectation value of the four-photon transition dipole moment operator \(< O_{i,j,k,l} >\) in its final form can be written as

\[ < O_{i,j,k,l} > = \frac{1}{\alpha_g J_g} \left| < T^{(1)}(\mu) | \alpha_e J_e > \right|^4 \sum_{K,Q} T_Q^{(K)}(\alpha_g J_g)^\dagger \sum_{k_1, k_2} G(J_g, J_e; k_1, k_2, K) F_Q^{(K)}(\varepsilon_i^* \varepsilon_j \varepsilon_k^* \varepsilon_l; k_1, k_2) \right] (7.19) \]

The field polarization tensor \(F_Q^{(K)}(\varepsilon_i^* \varepsilon_j \varepsilon_k^* \varepsilon_l; k_1, k_2)\) is equal to the vector recoupled form of \(T_Q^{(K)}(\varepsilon_i^* \varepsilon_j \varepsilon_k^* \varepsilon_l; k_1, k_2)\) in Eq. 7.18. The geometrical factor \(G(J_g, J_e; k_1, k_2, K)\) derived by Wasserman et al. [60] for DFWM spectroscopy where only the ground \(g\) level is connected via four-photon interaction with the excited \(e\) level. The \(G(J_g, J_e; k_1, k_2, K)\) is given by a product of \(6-J\) symbols (Eq. 7.20) and corresponds to Eq. 37 in [60]:

\[ G(J_g, J_e; k_1, k_2, K) = (-1)^{2J_g+k_1+k_2} \sqrt{(2k_1+1)(2k_2+1)} \times \left\{ \begin{array}{ccc} k_1 & k_2 & K \\ J_g & J_g & J_g \end{array} \right\} \left\{ \begin{array}{ccc} 1 & 1 & k_1 \\ J_g & J_g & J_e \end{array} \right\} \left\{ \begin{array}{ccc} 1 & 1 & k_2 \\ J_g & J_g & J_e \end{array} \right\} (7.20) \]

The geometrical factor for the TC-RFWM (Eq. 7.21 below) has at most four connected \(J\)-levels via four-photon interaction. Hence, the photon-matter couplings may involve \(\pm2, \pm1, 0\) angular momentum changes which is depicted in following sequence \((J_g \rightarrow J_e \rightarrow J_h \rightarrow J_f \rightarrow J_g)\) of \(J\) levels. The sequence of rotational angular momentum changes from \(g\) back to \(g\) via intermediate \(e, h, f\) levels refers to the SEP energy scheme where the four-wave mixing signal links the excited \(f\) and ground \(g\) levels. Eq. 7.21 can be used for the UNFOLDED or SEP energy schemes where the final level does not connect to the initial \(g\). In this case the corresponding sequence of angular momentum changes follow the calculation of the geometrical factor \(G(J_g, J_e, J_h, J_f; k_1, k_2, K)\). The given Eq. 7.21 corresponds to Eq. 18 in [93] applicable to the rovibronic structure dissection.
by polarization resolved TC-RFWM spectroscopy.

\[ G(J_g, J_e, J_h, J_f; k_1, k_2, K) = (-1)^{k_1+k_2+J_e+J_f-J_g} \sqrt{(2k_1+1)(2k_2+1)} \times \begin{vmatrix} k_1 & k_2 & K \\ J_g & J_g & J_h \end{vmatrix} \begin{vmatrix} 1 & 1 & k_1 \\ J_g & J_h & J_f \end{vmatrix} \begin{vmatrix} 1 & 1 & k_2 \\ J_g & J_h & J_e \end{vmatrix} \]

(7.21)

The response tensor refers to the relative contributions from different multipole moments to the resonant four-wave mixing response \[ \text{[60]} \].\[ R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e) \] tensors for DFWM (Eq. 7.22) and TC-RFWM (Eq. 7.23) are defined as a summation of the polarization tensor and geometrical factors over indices \( k_1 \) and \( k_2 \). The DFWM geometrical factors can have PP, QQ and RR combinations of the rovibronic transitions, where the first letter indicates the PUMP and the second the PROBE transition. For TC-RFWM the application of the second laser allows for an independent selection of P, Q and R branches by tuning each of the lasers to a particular resonance. Therefore, in addition to PP, QQ and RR combinations (PQ, PR), (QP, QR) and (RP, RQ) can also be observed.

\[ R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e) = \sum_{k_1, k_2} G(J_g, J_e; k_1, k_2, K) \times F^{(K)}_Q(e_i^* e_j e_k^* e_l; k_1, k_2) \]  

(7.22)

\[ R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e, J_h, J_f) = \sum_{k_1, k_2} G(J_g, J_e, J_h, J_f; k_1, k_2, K) \times F^{(K)}_Q(e_i^* e_j e_k^* e_l; k_1, k_2) \]  

(7.23)

The compact expression of the four-photon expectation value is

\[ < O_{ij,k,l} > = | \langle \alpha_g J_g \| T^{(1)}(\mu) \| \alpha_e J_e \rangle |^4 \times \sum_{K,Q} < T^K_Q(\alpha_g J_g)^\dagger > \times R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e, J_h, J_f) \]  

(7.24)

The summation over index \( K \) extends from 0 to the minimum value of either 2\( J_g \) or 4. The response tensor refers to the relative contributions from different multipole moments to the resonant four-wave mixing response \[ \text{[60]} \]. \[ R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e) \] of DFWM or \[ R^{(K)}_Q(e_i^* e_j e_k^* e_l; J_g, J_e, J_h, J_f) \] of TC-RFWM contain all the information on the experimental phase-matching and polarization geometry, as well as angular momentum changes of selected rovibronic transitions accompanying the four-wave mixing process. Eq. 7.24 gives a general solution for the TC-RFWM optical response in the presence of angular momentum anisotropy as defined by non-zero multipole moments \( < T^K_Q(\alpha_g J_g)^\dagger > \) of rank \( K > 0 \) given in Eq. 7.9 and the matrix in Eq. 7.10 for the \( P(6) \) transition in the \( \tilde{A}^1 \Pi_u - \tilde{X}^1 \Sigma_g^+ \) band. In the forthcoming section 7.1.5 we perform calculations of the TC-RFWM response in the presence of molecular alignment defined by the \( K = 2 \) component of \( < T^K_Q(\alpha_g J_g)^\dagger > \).
7.1.4 Experiment: pumped TC-RFWM response from the P,Q and R resonances

In this section we compare pumped UP and UNFOLDED TC-RFWM signal intensities. The experiment employs a sequential light-matter interaction. Firstly, the excitation laser beam (pump beam of TC-RFWM) optically pumps population of the C₃ molecule by resonant excitation of the J = 5 level of the ˜_A¹Π_u ground state. Note that due to the spin-orbit interaction between ˜_A¹Π_u and ³Σ_u⁻ (see section 2.2.3 for details) the excitation laser can also be resonantly tuned to the J = 5 level of ³Σ_u⁺ state and, thereby, permit two-color RFWM experiments in the triplet manifold. Multiple magnetic sublevels of the J = 5 level with a (2J_g + 1) degeneracy are populated. The anisotropy is induced according to the Eq. 7.9. Secondly, the UP energy scheme of TC-RFWM spectroscopy is applied to connect the ³Π_g electronic state via the ³Σ_u⁻ intermediate state. A similar experiment is performed connecting the singlet ¹Δ_g state (vibronic (14⁰+⁰), (12⁰+⁰)/(12²⁰) and (14²⁰), (12²⁰)/(12⁰-⁰) ¹Δ_g levels) via the intermediate (02⁰) ˜_A¹Π_u.

The polarizations of the PUMP lasers are set to 80° and 40°. The polarization of the PROBE laser is set to 65°. Note, that polarizations of PUMP and PROBE beams are steered from the original orientation (90° in the laboratory frame) by optical elements in the setup.

The trace in Fig.7.1a shows a pumped UP TC-RFWM from the ³Σ_u⁻ state (exhibiting 80% triplet character 2.2.3). The PUMP laser is tuned to the P(5) c₁ ³Π_g⁻→³Σ_u⁻ transition. Subsequently the PROBE is scanned. The measurement shows Π_g(4) and Π_g(6) levels K = Λ ± l = 1 which correspond to P(5) c₂ ³Π_g⁻→³Σ_u⁻ and R(5) c₂ ³Π_g⁻→³Σ_u⁻ transitions respectively. In the trace in Fig.7.1b the PUMP laser is tuned to the Q(5) c₁ ³Π_g⁻→³Σ_u⁻ transition. The measured spectrum shows Π_g(5) level only, corresponding to the Q(5) c₂ ³Π_g⁻→³Σ_u⁻ transition. The trace in Fig.7.1c is obtained by applying the UNFOLDED TC-RFWM scheme with the PUMP laser tuned to P(6) ³Σ_u⁻→˜_X¹Σ_g⁻⁺ transition and the PROBE laser is scanned in the range of the P,Q and R c₂ ³Π_g⁻→³Σ_u⁻ transitions. In case of the 7.1c the measured transitions have approximately the same intensities and can be directly assigned according to the selection rules for the ³Π_g⁻→³Σ_u⁻ transition to the P(5), Q(5) and R(5) resonances.³

³Note that the vibronic final state of ³Π_g symmetry corresponds to the electronic ³Δ_u state as clarified by the ab initio calculations discussed in the Chapter 8.2.7.

Fig. 7.2 shows three experimental spectra in the singlet manifold. The trace in Fig 7.2a represents pumped UP TC-RFWM from the (02⁰) ˜_A¹Π_u with the PROBE laser resonantly tuned to the P(5) (14⁰+⁰) ¹Δ_g⁻→(02⁰) ˜_A¹Π_u transition. The spectrum is measured
Figure 7.1: The trace a shows a pumped UP TC-RFWM spectra from the vibronic $^3\Sigma_u^-$ state. The PUMP TC-RFWM laser is tuned to the $c_1\ P(5)\ ^3\Pi_g\rightarrow^3\Sigma_u^+$ transition (as depicted by the blue arrows on the energy level diagram). Subsequently, the PROBE laser is scanned in the 21140-21150 cm$^{-1}$ range (denoted by the red arrows in the inset) and characterized by the $c_2\ P(5)\ ^3\Pi_g\rightarrow^3\Sigma_u^+$ transition. The trace b shows a pumped UP TC-RFWM from the $^3\Sigma_u^-$ where the PUMP laser is resonantly tuned to the $c_1\ Q(5)\ ^3\Pi_g\rightarrow^3\Sigma_u^+$ transition and the PROBE is scanned in the vicinity of the $c_2\ P(5)\ ^3\Pi_g\rightarrow^3\Sigma_u^+$ transition. The trace c is recorded by applying an UNFOLDED TC-RFWM measurement and contains $P, Q$ and $R\ c_2\ ^3\Pi_g\rightarrow^3\Sigma_u^+$ transitions measured by scanning the PROBE laser frequency.

by scanning the PUMP laser. The trace in Fig. 7.2a has the most intense transitions to the $\Sigma_u^+(4)$ and $\Delta_g(4)$ levels, they correspond to $P(5)\ (12^0+0)^1\Delta_g - (02^1+0)^1\Pi_u$ and $P(5)\ (12^2+0)^1\Delta_g - (02^1+0)^1\Pi_u$ transitions respectively. In case of the trace in Fig. 7.2b the PROBE laser is tuned to the $Q(5)\ (14^2+0)^1\Delta_g - (02^1+0)^1\Pi_u$ transition. The measured spectrum has transitions to the $\Delta_g(5)$ and $\Sigma_g^-(5)$ levels, they correspond to $Q(5)\ (12^2+0)^1\Delta_g - (02^1+0)^1\Pi_u$ and $Q(5)\ (12^0-0)^1\Delta_g - (02^1+0)^1\Pi_u$ transitions respectively. The trace in Fig. 7.2c shows an UNFOLDED TC-RFWM measurement which contains all resonant levels present in the spectral region of the PROBE laser between 19400 cm$^{-1}$ and 19450 cm$^{-1}$. When the PUMP is tuned to the $P(6)\ (02^2+0)^1\Pi_u - \tilde{X}^1\Sigma_g^+$ transition, lines of approximately equal intensity are measured by applying UNFOLDED TC-RFWM (with the exception of the $\Delta_g(4)$). From low to high frequency the measured lines are assigned to the vibronic levels split by Renner-Teller interaction $\Sigma_g^+(4), \Sigma_g^+(6) \subset \Sigma_g^+$, $\Delta_g(4), \Delta_g(5), \Delta_g(6) \subset \Delta_g$ and $\Sigma_g^-(5) \subset \Sigma_g^-$ (the total angular momentum $J''$ is given in the ($J''$) for the assigned lines).
Chapter 7. Results III: pumped TC-RFWM as a probe of molecular alignment

7.1.5 Calculation: UP TC-RFWM response from the P,Q and R resonances in the presence of anisotropy

In this section we report theoretical predictions of the UP TC-RFWM response in the presence of anisotropy induced by the resonant laser excitation. Different combinations of rovibronic transitions are examined, where the isotropic and anisotropic contributions interfere constructively or destructively. As a consequence, they lead to an overall enhancement or decrease of the TC-RFWM signal intensity. Furthermore, the UNFOLDED TC-RFWM response is evaluated with the isotropic density matrix. Both predictions can be compared to the experiment discussed in the section 7.1.4.

Thus, intensities of the observed spectra in Fig. 7.1 and Fig. 7.2 are compared to the theoretically calculated UP and UNFOLDED TC-RFWM response. The generated nonlinear optical response for the total angular momentum change $J_g \rightarrow J_e \rightarrow J_h \rightarrow J_f$ and given polarizations of Excitation, PUMP and PROBE lasers is calculated by Eq. 7.24. Because the detection channel of the UP TC-RFWM signal contains no polarization...
analyzer, the response $R_Q^{(K)}(\varepsilon_4^* \varepsilon_3 \varepsilon_2 \varepsilon_1; J_g, J_e, J_h, J_f)$ is computed for $\varepsilon_4^* = 0^\circ$ and $\varepsilon_4^* = 90^\circ$. Both contributions are summed under the modulus square operation according to Eq. 7.25 below.

The data are summarized in the Table 7.1. Computed values do not include the reduced matrix elements $|\mu_{fg}|^2$, $|\mu_{fh}|^2$, $|\mu_{eh}|^2$, and $|\mu_{eg}|^2$, therefore line strengths $S_{eh}$ of the involved transitions estimated from the PGOPHER program [76] are shown in the Table 7.2.

$$<O_{4321}> = \sum_{K=0}^{4\leq 2J_g} \sum_{Q=-K}^{K} <T_Q^K(\alpha_g J_g) > \times R_Q^{(K)}(\varepsilon_4^* \varepsilon_3 \varepsilon_2 \varepsilon_1; J_g, J_e, J_h, J_f) (7.25)$$

Table 7.1 contains the nonlinear optical response for the selected rank $K = 0$ and $K = 2$ tensors $<O_{4321}>^{(0)}$ and $<O_{4321}>^{(2)}$ respectively. On the first place it should be mentioned that the choice of either the $P, Q$ or $R$ branch for the PUMP of UP TC-RFWM facilitates the nonlinear response from the PROBE if tuned to the same branch. That is, if the PUMP laser is set to the $P(5)$ transition, the generated signal will be an order of magnitude higher for the $P(5)$ and $R(5)$ transitions measured by the PROBE laser compared to the $Q(5)$-transition. If the PUMP laser is set to the $Q(5)$ transition, the generated signal is three times higher for the $Q(5)$-transition measured by the PROBE laser compared to the $P(5)$ and $R(5)$. The commensurate argumentation of the UP TC-RFWM signal dependence on the choice of rotational branch holds when PUMP and PROBE are interchanged, i.e. the PROBE beam is fixed and the PUMP is scanned. In that case, the signal is detected at the frequency of the PROBE laser along the dark diagonal of the parallelepiped (BOXCAR phase matching geometry).

Note that the optical response from population ($K = 0$) and alignment ($K = 2$) strictly depends on the particular choice of the PUMP and PROBE polarizations. For the present calculation we use the experimentally defined polarizations.

It is interesting to notice in the Table 7.1 that if the PUMP laser is tuned to the $P(5)$-transition the $<O_{4321}>^{(2)}$ component takes negative values and, therefore, interferes destructively with the $<O_{4321}>^{(0)}$ response. On the other hand, when the PUMP is set to $Q(5)$-transition the $<O_{4321}>^{(2)}$ takes positive values only and, therefore, interferes constructively with the $<O_{4321}>^{(0)}$ response. That is why modulus square of the expectation value ($|<O_{4321}>|^2$) for the $PQ$ measurement is 10 times inferior compared to the $PP$ and $PR$ (where the first $P$ label indicate the PUMP tuned to $P(5)$ transition and the label corresponds to the measured by the PROBE transitions). The value of

---

4A similar behavior of the rovibronic lines measured in Fig. 7.1 and Fig. 7.2 is observed experimentally.
TABLE 7.1: The estimated nonlinear optical response of the population at \( K = 0 \), alignment\(^a\) \( K = 2 \), \( \left| \left< O_{4321} \right> \right|^2 \) for the UP TC-RFWM and nonlinear optical response from the isotropic contribution in the UNFOLDED TC-RFWM experiment.

<table>
<thead>
<tr>
<th>PROBE transition(^b)</th>
<th>UP(^c) TC-RFWM</th>
<th>UP(^c) TC-RFWM</th>
<th>UP(^c) TC-RFWM</th>
<th>UNFOLDED(^d) TC-RFWM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( &lt; O_{4321} &gt;^{(0)} \times 10^{-3} )</td>
<td>( &lt; O_{4321} &gt;^{(2)} \times 10^{-4} )</td>
<td>( &lt; O_{4321} &gt;^{(2)} \times 10^{-6} )</td>
<td>( &lt; O_{4321} &gt;^{(2)} \times 10^{-5} )</td>
<td></td>
</tr>
<tr>
<td>P(5)</td>
<td>1.42</td>
<td>-0.23</td>
<td>1.97</td>
<td>0.85</td>
</tr>
<tr>
<td>Q(5)</td>
<td>0.77</td>
<td>-3.33</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>R(5)</td>
<td>1.28</td>
<td>-0.78</td>
<td>1.44</td>
<td>1.56</td>
</tr>
</tbody>
</table>

PUMP tuned to P(5) transition

<table>
<thead>
<tr>
<th>PUMP tuned to Q(5) transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(5)</td>
</tr>
<tr>
<td>Q(5)</td>
</tr>
<tr>
<td>R(5)</td>
</tr>
</tbody>
</table>

\(^a\) In order to compute the contribution from the alignment, only the tensor 2 component of the four-photon expectation value Eq. 7.25 is given.

\(^b\) The PROBE beam is tuned to the \( c_2 \ ^3\Pi_g - ^3\Sigma_u^- \) vibronic transition. The PUMP is tuned to the \( c_1 \ ^3\Pi_g - ^3\Sigma_u^- \) vibronic transition.

\(^c\) UP TC-RFWM scheme is implemented \( \text{via} \) \( P(6) \) excitation to the \( J' = 5 \) level of \( ^3\Sigma_u^- \) from the \( \tilde{X}_1 \ ^1\Sigma_g^+ \) ground state of the \( C_3 \) molecule (see inset for traces \( a \) and \( b \) of Fig. 7.2 and Fig. 7.1).

\(^d\) Only the isotropic contribution \( < T_0^0(\alpha_g J_g)^\dagger > \) (from the population) is considered in order to evaluate \( < O_{4321} >^{(2)} \) for the UNFOLDED TC-RFWM experiment. For the fully isotropic ensembles the total population of the rovibrational level \( N_{\alpha g J g} \) is uniform and partitioned evenly throughout the manifold of \( 2J_g + 1 \) eigenstates. Therefore, the value given for the isotropic contribution should be evaluated with respect to \( \rho^{(0)}(\alpha_g J_g) = \delta_{gg'}N_{\alpha g J g}/(2J_g+1) \) where \( \delta_{gg'} \) denotes the canonical Kronecker delta symbol (i.e., \( \delta_{gg'} = 1 \) if \( g = g' \) and zero otherwise).

\(^e\) The PROBE beam is tuned to the \( c_2 \ ^3\Pi_g - ^3\Sigma_u^- \) vibronic transition. The PUMP is tuned to the \( ^3\Sigma_u^- \tilde{X}_1 \ ^1\Sigma_g^+ \) vibronic transition.

\( \left| \left< O_{4321} \right> \right|^2 \) for QQ branch selection is three times larger compared to the QP and QR. QP and QR have approximately the same value.

7.1.6 Comparison of the experimentally measured and computed P, Q and R transitions

In Fig. 7.1 the experimentally determined \( P, Q \) and \( R \) transitions are presented. The transition intensity can be qualitatively compared with the computed \( \left| \left< O_{4321} \right> \right|^2 \) for the \( PP, PQ \) and \( PR \) branch selections for the UP and UNFOLDED TC-RFWM energy schemes respectively (see Table 7.2). The UP TC-RFWM scheme in the presence of
anisotropy allows the observation of \( PP \) and \( PR \) selected resonances. For example, the calculated \( S \times |< O_{4321}^{(0)} >|^2 \) values are 0.67, 0.25 and 1.48 (\( \times 10^{-6} \)) for the PROBE laser scanning over \( P, Q \) and \( R c_2 \Delta g - 3\Sigma_u^- \) transitions respectively, if the PUMP laser is set to the \( P(5) c_1 \Delta g - 3\Sigma_u^- \) transition. Provided line intensities are consistent with the experimental results shown in Fig. 7.1a where the \( \Pi_g (6) \) level appears more intense compared to the \( \Pi_g (4) \) level and both are much stronger (\( i.e. \times 6.1 \) and \( \times 2.8 \) stronger for \( PR \) and \( PP \) branch selection respectively) compared to the \( \Pi_g (5) \) level. On the other hand the \( S \times |< O_{4321}^{(0)} >|^2 \) values for the PROBE laser scanning over \( P, Q \) and \( R \) transitions are 0.39, 4.35 and 1.44 (\( \times 10^{-6} \)) respectively, if the PUMP laser is set to \( Q(5) c_1 \Delta g - 3\Sigma_u^- \) transition. This is also consistent with the experimental results shown in Fig. 7.1b where UP TC-RFWM scheme favors \( QR \) branch selection (\( PP \) and \( PR \) resonances are \( \times 11.1 \) and \( \times 3.0 \) weaker compared to \( QQ \)). The signal to noise ratio (SNR) can be estimated from the measured spectra in Fig. 7.1 and is \( \approx 3 \) for the trace a and \( \approx 12 \) for the trace b. Note that the SNR in Fig. 7.1b should allow a comparison of \( QQ \) and \( QR \) as being 3 : 1 in intensity ratio as calculated, however no \( QR \) line is observed. This contradiction can also be explained by the uncertainty in the line strengths \( S_{eh} \) given in Table 7.2 or the uncertainty in the experimentally determined polarization for the PUMP and PROBE lasers.

For the UNFOLDED TC-RFWM measurement line intensities \( S \times |< O_{4321}^{(0)} >|^2 \) are 0.29 , 0.40 and 1.61 (\( \times 10^{-5} \)) given in Table. 7.2 when the PUMP is tuned to the \( P(6) \) transition connecting the \( \tilde{X} 1\Sigma_u^+ \) ground state and the mixed vibronic \( 3\Sigma_u^- \) state and the PROBE laser is scanning over \( P, Q \) and \( R c_2 \Delta g - 3\Sigma_u^- \) transitions. Fig. 7.1c shows a measured spectrum with a \( P < Q < R \) intensity pattern. The measurement, therefore, corresponds favorably to the theoretically predicted intensity distribution of \( PP, PQ \) and \( PR \) resonances for the UNFOLDED TC-RFWM.

Similarly, the measured resonances in Fig. 7.2 belonging to the \( P, Q \) and \( R 1\Delta_g - \tilde{A} 1\Pi_u \) transition can be compared with the computed \( S \times |< O_{4321}^{(0)} >|^2 \) for the \( PP, PQ \) and \( PR \) branch selections for the UP and UNFOLDED TC-RFWM energy schemes respectively. The UP TC-RFWM scheme favors \( PP \) and \( PR \) resonances: line intensities \( S \times |< O_{4321}^{(0)} >|^2 \) for the \( \Sigma_u^+ (4) \), \( \Sigma_u^+ (6) \) are 2.68 and 1.63 (\( \times 10^{-6} \)) respectively, for the \( \Delta_g (4) \), \( \Delta_g (5) \), \( \Delta_g (6) \) line intensities are 0.53, 0.22 and 1.51 (\( \times 10^{-6} \)) respectively and for the \( \Sigma_u^- (5) \) is \( 0.47 \times 10^{-6} \). A disagreement for the \( \Delta_g (4) \) and \( \Delta_g (6) \) is observed compared to the measured intensities in Fig. 7.2 spectrum where \( PP \) resonances are \( \approx 3 \) times more intense compared to \( PR \) and \( QR \). Even if the SNR is as low as \( \approx 2.5 \) for the trace a and b in Fig. 7.2, the measured rovibronic lines can be compared with the theoretical predictions within the given by the SNR limits.
Table 7.2: Comparison of the modulus squared nonlinear optical response Eq. 7.25 for the UP, UNFOLDED TC-RFWM and line strengths $S^b$. The TC-RFWM PUMP is tuned to the $P(5)$ transition for both UP and UNFOLDED energy schemes.

<table>
<thead>
<tr>
<th>Vibronic final level</th>
<th>PROBE transition</th>
<th>UP TC-RFWM$^c$</th>
<th>UNFOLDED TC-RFWM$^d$</th>
<th>Line strength $S^b \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Pi_g$</td>
<td>$P(5)$</td>
<td>1.97</td>
<td>0.85</td>
<td>0.34</td>
</tr>
<tr>
<td>$^3\Sigma^+_g$</td>
<td>$Q(5)$</td>
<td>0.19</td>
<td>0.31</td>
<td>1.29</td>
</tr>
<tr>
<td>$^3\Pi_g$</td>
<td>$R(5)$</td>
<td>1.44</td>
<td>1.56</td>
<td>1.03</td>
</tr>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>$P(5)$</td>
<td>1.97</td>
<td>0.85</td>
<td>1.36</td>
</tr>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>$R(5)$</td>
<td>1.44</td>
<td>1.56</td>
<td>1.13</td>
</tr>
<tr>
<td>$^1\Delta_g$</td>
<td>$P(5)$</td>
<td>1.97</td>
<td>0.85</td>
<td>0.27</td>
</tr>
<tr>
<td>$^1\Delta_g$</td>
<td>$Q(5)$</td>
<td>0.19</td>
<td>0.31</td>
<td>1.16</td>
</tr>
<tr>
<td>$^1\Delta_g$</td>
<td>$R(5)$</td>
<td>1.44</td>
<td>1.56</td>
<td>1.05</td>
</tr>
<tr>
<td>$^1\Sigma^-_g$</td>
<td>$Q(5)$</td>
<td>0.19</td>
<td>0.31</td>
<td>2.49</td>
</tr>
</tbody>
</table>

$^a$ In order to compute the contribution from the alignment, only the tensor 2 component of the four-photon expectation value Eq. 7.25 is given.

$^b$ Line strengths are calculated by the PGOPHER program [76]. The molecular line strength $S_{eh} = |< \alpha_e J_e \parallel T(1)(\mu) \parallel \alpha_h J_h >|^2 = |< \alpha_h J_h \parallel T(1)(\mu) \parallel \alpha_e J_e >|^2$. Where $e$ and $h$ are levels connected by the PROBE photon.

$^c$ Pumped refers to the excitation via the $P(6)$ transition from the $\tilde{X}^1\Sigma^+$ ground state of $C_3$ (see inset for traces a and b of Fig. 7.1 and 7.2).

$^d$ The value of $|< O_{4321} >|^2$ given for the isotropic contribution should be evaluated with respect to $\rho^{(0)}(\alpha_g J_g) = \delta_{g''g''} N_{g''e''} J_g (2J_g+1)$ [60] where $\delta_{g''g''}$ denotes the canonical Kronecker delta symbol (i.e., $\delta_{g''g''} = 1$ if $g = g''$ and zero otherwise).

Line intensities for the UNFOLDED TC-RFWM measurement are for the $\Sigma^+_g(4)$, $\Sigma^+_g(6)$ levels are 1.16 and 1.76 ($\times 10^{-5}$), respectively, for the $\Delta_g(4)$, $\Delta_g(5)$, $\Delta_g(6)$ levels are 0.23, 0.36 and 1.64 ($\times 10^{-5}$), respectively, and for $\Sigma^-_g(5)$ is 0.77 ($\times 10^{-5}$). Fig. 7.2c shows the measured spectrum where the weakest $\Delta_g(4)$ resonance is predicted by the calculation. The measured $PQ$ branch combination have comparable intensities to the measured $PR$ combination. This behavior has not been captured by the present calculation where the $PQ$ branch selection appears to be $2 - 4$ times inferior to $PR$.

7.1.7 P, Q and R line intensities at the high-J limit

Fig. 7.3 shows the dependence of the optical response $< O_{4321} >$ on the total angular momentum quantum number $J$ as given in Eq. 7.25. It is assumed that the excitation laser is set to a transition in the $P$-branch. Calculations for the energy scheme shown on the inset for traces a and b of Fig. 7.1 and 7.2 are performed. Note that $J$ is given for the
excited state (in our experiments either \( ^3\Sigma_u^- \) or \( ^3\Pi_u \)) which is coupled by the excitation laser with the ground \( \tilde{X}^{1\Sigma_g^+} \) state. The same polarizations of the laser beams are used for the calculation as in section 7.1.4. The response of the signal field is calculated for 0° and 90° orientation of the \( \varepsilon_4 \) and summed in order to evaluate the \(<O_{4321}>\) response for a TC-RFWM signal detection without a polarization selection.

The calculations are consistent with the experimentally observed result i.e. the overall signal intensity rapidly decreases depending on the total angular momentum quantum number. In fact, the maximum intensity of the pumped TC-RFWM response occurs already at \( J = 1 \). Note that when the PUMP laser is tuned to the a \( P \)-transition (Fig. 7.3a) the alignment contribution has a minus sign, hence reducing the modulus square of the sum of \(<O_{4321}>^{(0)}\) and \(<O_{4321}>^{(2)}\). On the contrary if the PUMP laser is tuned to a \( Q \)-transition the alignment contribution has a plus sign, hence increasing the nonlinear optical response. An interesting behavior of the nonlinear optical response for \( J = 1 \) is found for the \( QP \) combination (see Fig. 7.3b) where the alignment contribution is \( 7.67 \times 10^{-3} \) and appears to be stronger than to the \( 4.92 \times 10^{-3} \) contribution from the population. However, the \(<O_{4321}>^{(2)}\) drops faster versus \( J \) and at \( J = 2 \) the contribution of the population prevails in the overall \(<O_{4321}>\).
Figure 7.3: UP TC-RFWM nonlinear optical response $<O_{4321}>$ (evaluated according to Eq. 7.25) dependence on the total angular momentum quantum number $J$ for different branch selections. The first letter in each inset corresponds to the PUMP laser which is tuned to the $P,Q$ and $R$ transition for inset a, b and c, respectively. The second letter corresponds to the PROBE transition. A solid line represents the response $<O_{4321}>^{(0)}$ from the molecular population. Dashed line represents the response $<O_{4321}>^{(2)}$ from molecular alignment. The evaluated response for the PROBE laser are depicted for $P,Q$ and $R$ transitions in blue (squares), green (circles) and red (triangles) respectively.
7.1.8 Laser polarizations for specific detection of molecular alignment

The dependence of the pumped TC-RFWM response $|< O_{4321} >|^{2}$ on the rotation of the PROBE laser polarization is shown in Fig. 7.4. The insets a and c contain a blue bar which is set to $65^\circ$ matching the experimental conditions at which the spectra in Fig. 7.1 and 7.2 were recorded. For the $QQ$ combination of resonances shown in Fig. 7.4a the modulus square of the overall optical response (solid red curve) is enhanced if the PROBE is set to $65^\circ$ linear polarization. For the $PP$ combination of resonances the overall optical response is slightly lower than the contribution from the population for a PROBE polarization of $65^\circ$. This opposite behavior is also reflected in the Table 7.1 where the anisotropic contribution is subtracted from the isotropic contribution. Fig. 7.4 refers to the modulus squared values for the expectation value from population and alignment, which corresponds to the “physical” detection of the signal in the laboratory (i.e. the photo-detector measures the intensity of the optical fields). Therefore, no negative values on the ordinate of Fig. 7.4 are possible. Note that taking the modulus squared of a separate rank of the tensor $< O_{4321} >$ can provide guidelines to choose a polarization scheme for a specific detection of either population $|< O^{(0)}_{4321} >|^{2}$ or alignment $|< O^{(2)}_{4321} >|^{2}$ by UP TC-RFWM.

For the specific detection of molecular alignment by applying UP TC-RFWM for the $QQ$ branch combination the PROBE should be set to $-33^\circ$ (polarizations of PUMP lasers are $80^\circ$ and $40^\circ$ for $\varepsilon_{1}$ and $\varepsilon_{3}$ respectively). In this case the $< O^{(0)}_{4321} > = -2.6 \times 10^{-6}$ and the $< O^{(2)}_{4321} > = -3.2 \times 10^{-4}$ (see Fig. 7.4a). Interestingly, by tuning the polarization of the excitation laser to orthogonal (from $0^\circ$ to $90^\circ$) it is possible to increase the alignment signal. That is $< O^{(0)}_{4321} > = -2.6 \times 10^{-6}$ and the $< O^{(2)}_{4321} > = -3.5 \times 10^{-4}$. Note that the anisotropic contribution denoted by the dotted green line is multiplied by $\times 10$ for the Fig. 7.4a, b and d and by $\times 100$ for the Fig. 7.4c.
Figure 7.4: UP TC-RFWM $|\langle O_{4321} \rangle|^2$ evaluated for arbitrary polarization angles from $-90^\circ$ to $90^\circ$ of the PROBE laser. Each inset contains the polarization vectors written as $X-XY$ $40^\circ$ $V$ $80^\circ$, where the first $X$ is $0^\circ$ polarization of the excitation laser. The following notation $XY$, $40^\circ$, $V$, $80^\circ$ maps directly onto the order of the polarization unit vectors $\varepsilon_4^*$, $\varepsilon_3$, $\varepsilon_2^*$, $\varepsilon_1$ entering the polarization tensor $F^{(K)}_{\varepsilon_4^*\varepsilon_3\varepsilon_2^*\varepsilon_1; k_1, k_2}$ given in Eq. 7.18 for the TC-RFWM. $XY$ are both $0^\circ$ and $90^\circ$ polarizations of the TC-RFWM signal field $\varepsilon_4^*$, $40^\circ$ and $80^\circ$ are polarizations of the PUMP fields $\varepsilon_3$ and $\varepsilon_1$ respectively. The PROBE beam polarization $\varepsilon_2^*$ is varied and assigned as $V$. Insets a and b correspond to the QQ branch selection and inset c and d to the PP branch selection. Solid red curve represents the $|\langle O_{4321} \rangle|^2$, dashed blue is $|\langle O_{4321} \rangle^{(0)}|^2$ and dotted green curve is $|\langle O_{4321} \rangle^{(2)}|^2$. 
7.2 TC-RFWM signal intensity: summary

Intensities of the observed spectra in Fig. 7.1 and Fig. 7.2 are compared to the theoretically calculated UP TC-RFWM response. The generated nonlinear optical response for the total angular momentum change \( J_g \rightarrow J_e \rightarrow J_h \rightarrow J_f \) and given polarizations of excitation, PUMP and PROBE lasers is calculated by Eq. 7.24. Because the detection channel of the UP TC-RFWM signal contains no analyzer, the response \( R_Q^{(K)}(\epsilon_4^* \epsilon_3 \epsilon_2 \epsilon_1; J_g, J_e, J_h, J_f) \) is computed for the \( \epsilon_4^* = 0^\circ \) and \( \epsilon_4^* = 90^\circ \). Both contributions are coherently summed under the modulus square operation according to Eq. 7.26 and 7.28. The computed values are presented in the Table 7.1 and 7.2. The intensities are given by

\[
| \epsilon_4^* \cdot P^{(3)}(\omega) |^2 = \left| \frac{N_{\alpha g} J_g}{8 \hbar^3} E(\omega_1) E(\omega_2)^* E(\omega_3) \exp(i k_\sigma \cdot r) < O_{4321} > D(\omega; \omega_1, -\omega_2, \omega_3) \right|^2
\]

(7.26)

where \( E(\omega_j) \) is a scalar amplitude of the electric field vector for the monochromatic plane wave \( \exp(-i(k_j \cdot r_j - \omega_j t)) \) i.e. \( E(\omega_j) = | E(\omega_j) | \) and \( \epsilon_j \) is a polarization unit vector of the optical field

\[
\epsilon_j = \frac{E(\omega_j)}{| E(\omega_j) |}
\]

(7.27)

such that \( E(\omega_j) = E(\omega_j) \epsilon_j \).

The term \( \exp(i k_\sigma \cdot r) \) refers to the experimental tuning to the phase-matching condition with \( k_\sigma = k_1 - k_2 + k_3 \). The resonant denominator \( D(\omega; \omega_1, -\omega_2, \omega_3) \) is given in Eq. 3.45, 3.46, 3.47 and 3.48 for the DFWM spectroscopy. Resonant denominators were discussed in the section 3.2.4. \( D(\omega; \omega_1, -\omega_2, \omega_3) \) contains the frequency response of the RFWM process. In the Eq. 7.26 they are decoupled from each other assuming that magnetic sublevels which differ in \( m_g \) are degenerate (\( \omega_{eg} = \omega_{e'g'} = -\omega_{ge} \)) and relaxation constants of the excited levels for the population and coherence are given as \( \Gamma_{ee} = \Gamma_{e'e'} \) and \( \Gamma_{eg} = \Gamma_{e'g'} = \Gamma_{ge} \) respectively [93]. The intensity of the TC-RFWM expressed as a polarization \( | \epsilon_4^* \cdot P^{(3)}(\omega) |^2 \) in Eq. 7.26 can be rewritten in terms of the vector-recoupled form for \( < O_{4321} > \) (see Eq. 7.24)

\[
I_4(\omega) \propto N_{\alpha g}^2 J_g | \mu_{fg} |^2 | \mu_{fh} |^2 | \mu_{eh} |^2 | \mu_{eg} |^2 I_1 I_2 I_3 L(\omega) \times \left| \sum_{4 \leq 2 \hbar} \sum_{K=0}^{K} \sum_{Q=-K}^{K} T_Q^K (\alpha_g J_g)^\dagger > \times R_Q^{(K)}(\epsilon_4^* \epsilon_j \epsilon_k \epsilon_l; J_g, J_e, J_h, J_f) \right|^2
\]

(7.28)
The complete theoretical treatment of the coherent TC-RFWM signal Eq. 7.28 includes a product of the nonlinear optical response given in Eq. 7.24, the reduced four-photon dipole moment transition \( \mu_{fg} = \langle \alpha_g J_g \parallel T^{(1)}(\mu) \parallel \alpha_f J_f > \) \( \mu_{fh} = \langle \alpha_h J_h \parallel T^{(1)}(\mu) \parallel \alpha_f J_f > \) \( \mu_{eh} = \langle \alpha_h J_h \parallel T^{(1)}(\mu) \parallel \alpha_e J_e > \) \( \mu_{eg} = \langle \alpha_e J_e \parallel T^{(1)}(\mu) \parallel \alpha_g J_g > \), the squared number of absorbing molecules \( N^2 \alpha_g J_g \) and the product of field intensities \( I_j = |E(\omega_j)|^2 \). Note that in a collisional environment the spectral response of TC-RFWM should include the velocity-averaged lineshape function \( L(\omega) \) given in Eq. 7.29.

For every Feynman diagram unique resonant denominators (e.g. \( A, B, C \) and \( D \) given for DFWM in Eq. 3.45, 3.46, 3.47 and 3.48) enter the integral Eq. 7.29 with the velocity component \( \mathbf{v} \) defined by the velocity distribution \( f(\mathbf{v}) \). Hence, for the electromagnetic waves participating in the FWM the molecular resonance is Doppler shifted according to \( \omega_j = \omega_j - k_j \cdot \mathbf{v} \).

\[
L(\omega) = \left| \int_\mathbf{v} D(\omega; \omega_1, -\omega_2, \omega_3) f(\mathbf{v}) d\mathbf{v} \right|^2 \quad (7.29)
\]

The FWM experiments are performed in the molecular beam environment where the propagation direction of electromagnetic waves is orthogonal to the velocity vector of the absorbing molecules \( \mathbf{k} \perp \mathbf{v} \). This allows us to eliminate the first-order Doppler shift. Therefore, the calculation of the \( I_4(\omega) \) does not include the velocity averaging integral \( L(\omega) \). We also assume that all relaxation rates \( \Gamma_{ee} = \Gamma_{e'e'} \) and \( \Gamma_{eg} = \Gamma_{eg'} = \Gamma_{ge} \) (where \( e \) can be any of \( e, e', f, f', h, h' \) are slow i.e. excited state intramolecular processes do not affect the FWM signal intensity on a scale of the laser pulse duration time of \( \approx 7 \) ns. Hence, all resonant denominators \( D(\omega; \omega_1, -\omega_2, \omega_3) \) and \( L(\omega) \) are excluded from the calculation of FWM intensity.
Chapter 8

Ab initio quantum chemical calculations

8.1 Potential energy surfaces of the C\textsubscript{2} radical

8.1.1 Active Orbital Space of the C\textsubscript{2} radical for the Self-Consistent Field (CASSCF) theory

For many-electron molecules the exact solutions for the energy separation between ground and excited states can be rather complicated due to the electron correlation. That is why for many-electron atoms and molecules Hartree-Fock Molecular Orbital theory has been extended to the Complete Active Space Self-Consistent Field (CASSCF) and subsequent Multi-Reference Configuration Interaction method.

In order to choose a minimal size of the complete active space for the carbon dimer molecule, in the first step, the description of the carbon atomic orbitals (AO) participating in the formation of C\textsubscript{2} is presented. The electronic configuration of C is [He] 2\textit{s}\textsuperscript{2} 2\textit{p}\textsuperscript{2}. Two valence electrons occupy the 2\textit{p} level coupling their spins to give a maximum spin $S = 1$ according to Hund’s first rule. Adding angular momentum of each electron of the \textit{p} shell leads to a possible vector sum of $L = 0, 1, 2$. The parity of a configuration is even or odd according to whether the sum of the orbital angular momenta $\sum_i l_i$ is even (symmetric) or odd (antisymmetric) states. Because the spin state is symmetric $S = 1$ the antisymmetric orbital state should be formed by the two valence electrons.
Chapter 8. *Ab initio* quantum chemical calculations

\[ m_{l_1} = 0 \text{ and } m_{l_2} = 1 \text{ resulting in } L = 1. \] The \( p \) shell is less then half filled that is why \( L \) and \( S \) couple to \( J \) as \( J = 1 - 1 = 0. \) The ground state has a term symbol \( ^3P_0. \)

In the second step, it is possible to construct molecular orbitals (MO) from the atomic orbitals (AO). Note the symmetry species describing MO in the point group are matched by the tensor product with the AO symmetry species constituting the MO. For example \( s \) transforms as totally symmetric representation, \( p \) transforms as \( x,y \) and \( z. \) In the \( D_{2h} \) point group (see Table 2.2) \( s \) correlates to \( A_g \) while \( p \) is described by \( B_{3u}, \) \( B_{2u} \) and \( B_{1u} \) for the \( x, \) \( y \) and \( z \) axis respectively when the internuclear axis is set along the \( z \) axis \( (z \to z). \)

In the third step, the active space for the \( C_2 \) molecule can be evaluated. The carbon atoms are brought close to each other. The respective AO interfere constructively to generate bonding molecular orbitals and destructively to generate anti-bonding molecular orbitals. Electrons are filled from the lowest to the highest MO according to the “Aufbau” principle. The symmetry product between the sum of irreducible representations \( A_g + B_{3u} + B_{2u} + B_{1u} \) for each carbon atom should produce an active space for a reliable calculation of the \( C_2 \) ground and few excited states. The products are given in Table 8.1.

<table>
<thead>
<tr>
<th>( \text{C} ) ( \text{,} / ) ( \text{C} )</th>
<th>( A_g )</th>
<th>( B_{1u} )</th>
<th>( B_{2u} )</th>
<th>( B_{3u} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>( A_g )</td>
<td>( B_{1u} )</td>
<td>( B_{2u} )</td>
<td>( B_{3u} )</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>( B_{1u} )</td>
<td>( A_g )</td>
<td>( B_{3g} )</td>
<td>( B_{2g} )</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>( B_{2u} )</td>
<td>( B_{3g} )</td>
<td>( A_g )</td>
<td>( B_{1g} )</td>
</tr>
<tr>
<td>( B_{3u} )</td>
<td>( B_{3u} )</td>
<td>( B_{2g} )</td>
<td>( B_{1g} )</td>
<td>( A_g )</td>
</tr>
</tbody>
</table>

Table 8.1 gives the reducible sum of \( 4A_g + 2B_{1u} + 2B_{2u} + 2B_{3u} + 2B_{1g} + 2B_{2g} + 2B_{3g} \) representations. According to the spectroscopic studies the \( C_2 \) radical has a \( ^1\Sigma^+_g \) (\( = A_g \)) ground state at the \( r_e \approx 1.252 (\text{Å}) \) and a low-lying \( \sigma^3\Pi_u \) (\( = B_{3u} + B_{2u} \)) electronic state at \( r_e \approx 1.325 (\text{Å}) \). Both states as well as excited states up to \( C^1\Pi_g \) with a \( T_e \) of 34261.3 \( \text{cm}^{-1} \) \cite{98} can be covered by these irreducible representations.

\(^1\)So far we consider only two unpaired electrons in the \( 2p \) shell. When chemical bonds are formed the energy is released, therefore, there is a possibility to undergo a chemical reaction \textit{via} the first excited state exhibiting an electronic configuration \([\text{He}] 2s^1 2p^3 \). The carbon chemistry is so rich because it has four available electrons in a first excited state to built chemical bonds. The formation of \( \text{CH}_4 \) can be explained by the \( sp^3 \)-hybridization of molecular orbitals when four hydrogen \( 1s \) electrons interact with the four electrons of \( C^\ast \).

\(^2\)Please note, that the irreducible representation for \( C^\ast \) also contains two \( p_{x,y} \) as given for a ground state carbon.
8.1.2 Excited state energies of the $C_2$ singlet, triplet and quintet spin-multiplicities

As mentioned above, for the full valence CASSCF calculation we use $4A_g$, $2B_{2u}$, $2B_{3u}$, $2B_{1u}$, $2B_{2g}$, $2B_{3g}$ roots for the active space. One $A_g$ orbital for a singlet state, $1B_{2u}$, $1B_{3u}$, $1B_{2g}$, $1B_{3g}$ orbitals for triplet states and $3A_g$, $2B_{1g}$, $2B_{2u}$, $1B_{3u}$, $1B_{2g}$, $1B_{3g}$ orbitals for quintet states are chosen for the full valence CAS space.

The analysis of the $C_2$ excited states by *ab initio* calculations has been performed at the multi-reference configuration interaction (MRCI) level with the MOLPRO package [99, 100]. The aug-cc-PVTZ basis was chosen first to CASSCF optimize orbitals followed by the MRCI computations. State energies and equilibrium bond lengths are summarized in Table 8.2. It should be mentioned that the computed quintet energies agree well with those calculated by Bruna and Grein [101] with the configuration interaction method. Their work outlines valence and Rydberg states in the 7-10 eV region. In contrary we focus only on states which appear energetically lower then the first electronic state with a Rydberg character [101].

**Table 8.2:** MRCI energies at the $r_e$ Å bond length in $D_{2h}$ point group for the $C_2$ molecule. A comparison with the experimentally observed origin $T_o^a$ is provided.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Dominant electronic configuration</th>
<th>Excitation</th>
<th>Calc. $r_e$ (Å)</th>
<th>Calc. MRCI energy (cm$^{-1}$)</th>
<th>Obs. $T_o^a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^1\Sigma^+_g$</td>
<td>$\sigma^2_u \pi^4_u$</td>
<td>-</td>
<td>1.252</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$a^3\Pi_u$</td>
<td>$\sigma^2_u \pi^3_u \pi^1_u$</td>
<td></td>
<td>1.320</td>
<td>479</td>
<td>716$^c$</td>
</tr>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>$\sigma^1_u \sigma^1_g \pi^2_u \pi^1_u$</td>
<td>$\pi_g \leftarrow \pi_u$</td>
<td>1.575</td>
<td>28833</td>
<td>29258$^d$</td>
</tr>
<tr>
<td>$^5\Sigma^+_g$</td>
<td>$\sigma^1_g \sigma^3_g \pi^2_u \pi^1_u$</td>
<td>$\pi_g \leftarrow \sigma_u$</td>
<td>1.420</td>
<td>39526</td>
<td>-</td>
</tr>
<tr>
<td>$^5\Delta_g$</td>
<td>$\sigma^1_g \sigma^3_g \pi^3_u \pi^1_u$</td>
<td>$\pi_g \leftarrow \sigma_u$</td>
<td>1.350</td>
<td>49612</td>
<td>-</td>
</tr>
<tr>
<td>$^5\Pi_u$</td>
<td>$\sigma^1_g \sigma^3_u \pi^2_u \pi^1_u$</td>
<td>$\sigma_u \pi_u$</td>
<td>1.55</td>
<td>51007</td>
<td>$\approx$ 50990$^e$</td>
</tr>
<tr>
<td>$^5\Sigma^-_g$</td>
<td>$\sigma^1_g \sigma^3_g \pi^3_u \pi^1_u$</td>
<td>$\pi_g \leftarrow \sigma_u$</td>
<td>1.35</td>
<td>56218</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Term energy including zero point vibration.

$^b$ Excitation is relative to the $a^3\Pi_u (\sigma^2_u \sigma^1_g \pi^3_u)$. $^c$Ref. [102]

$^d$Ref. [9]

$^e$ This work (not published). The $^5\Pi_u$ state is observed by PF TC-FWM which is accessed *via* the intermediate $^3\Pi_g$ state [9].

8.1.3 Potential energy surfaces of $C_2$ quintet manifold

The CAS space is the same as used for the excited states calculations. The interaction between two or more electronic states scales with the overlap of the vibrational wavefunction. Therefore, it is instructive to calculate potential energy surfaces for different
internuclear distances in order to identify the possibility of intersystem crossing (ISC). The first known ISC appears between the singlet \( \tilde{X}^1\Sigma_g^+ \) ground state and the triplet \( a^3\Pi_u \) excited state at \( r \approx 1.3 \) Å. The first excited state is only 716 cm\(^{-1}\) above the ground state which corresponds to a temperature of 1030 K. Therefore this state can easily be populated in a high-temperature combustion environment or in a plasma produced by the discharge source used to prepare a substantial population of \( \text{C}_2 \) in the vibrationally excited \( a^3\Pi_u \) state.\(^3\)

Another ISC which gained attention due to the nonthermal emission from the \( v = 6 \) of the \( d^3\Pi_g \) state in the Swan band (\( d^3\Pi_g - a^3\Pi_u \)) was first observed by Fowler in 1910 [10]. Indeed the existence of \( 1^5\Pi_g \) state which lies close to the \( v = 6 \) level of \( d^3\Pi_g \) state has been proposed by Kirby and Liu [17]. Hence, the ISC mechanism suggested by Little and Browne [20] could be verified and explain the existence of the high-pressure bands (HP bands) [103]. The occurrence of the large and level-specific interaction elucidates the nonthermal population distribution in the \( v = 6 \) level that was observed in numerous environments at different pressures and temperatures [103]. However, no spectroscopic observation of the electronically excited \( 1^5\Pi_g \) state was known up to date. Our recent double-resonant four-wave mixing experiments enabled the accurate observation (within \( \approx 0.02 \) cm\(^{-1}\)) of five term energy curves of the perturbing dark \( 1^5\Pi_g \) state crossing the three curves of the \( v = 6 \) \( d^3\Pi_g \) level [9]. According to the fit of the experimental data, the origin of the \( 1^5\Pi_g \) is \( T_o = 29258 \) cm\(^{-1}\) [9]. Indeed computed MRCI energies for triplet-quintet potential energy surfaces demonstrate a curve crossing at \( T_o = 29253 \) cm\(^{-1}\) for \( r = 1.525 \) Å (see reference [80]). These calculations show that the vibrational wavefunctions for \( v = 6 \) of the \( d^3\Pi_g \) state and for \( v = 0 \) of the \( 1^5\Pi_g \) state are almost resonant and can mix significantly if spin orbit coupling or non-adiabatic coupling is considered.

Our as well as the MRCI calculations provided in Refs. [80, 101] suggest the next possible optical \( 5\Pi_u - 5\Pi_g \) transition to be in the range of 21000 - 23000 cm\(^{-1}\). The \( 5\Pi_u \) appears at \( \approx 50652 \) cm\(^{-1}\) above the ground state and has a very shallow potential energy of 1200 cm\(^{-1}\) depth. Thereby only one stretching vibration of \( \approx 900 \) cm\(^{-1}\) is present in the \( 5\Pi_u \) electronic level [101]. The possibility to exploit the “gate-way” resonances (levels perturbed by spin-orbit interaction between \( 1^5\Pi_g \) and \( d^3\Pi_g \)) as intermediate levels for accessing the \( 5\Pi_u \) state is a subject of future investigations. Note that in our preliminary experiments we observe resonances that are possibly belonging to the \( 5\Pi_u - 5\Pi_g \) transition by applying PF TC-RFWM spectroscopy (see Table 8.2). The

\(^3\)Note, the supersonic expansion rotationally cools radicals in a molecular jet \( T_{rot} \approx 50 - 100 \) K while the vibrational temperature of the carbon dimer appears to be as high as \( T_{vib} \approx 6000 \) K. This fact is an obvious advantage for our spectroscopic experiments involving excited vibrational levels because the signal intensity is proportional to the square of the \( \text{C}_2 \) population.
relatively small binding energy of two carbon atoms on this PES may facilitate first experiments on the C₂ dissociation in the ⁵Πₜ state.

8.2 Potential energy surfaces of the C₃ radical

8.2.1 Active Orbital Space of the C₃ radical for the Self-Consistent Field (CASSCF) theory

The initial analysis of the C₃ ground state electronic configuration and the setup of the optimized wave functions for the Configuration Interaction (CI) methods is accomplished by the Hartree-Fock procedure. Subsequently, the Multi-Configuration Self-Consistent Field (MCSCF) method is applied where not only CI coefficients are iteratively optimized by the variational principle but also the molecular orbitals [104]. Each carbon atom contributes with all valence orbitals to the active space. Two core 1s₁ and 1s₂ orbitals are frozen and do not change during the energy minimization.

In order to discuss the roots to be included into the SCF calculation, one might consider the minimal set of roots that is necessary to correctly describe the dissociation pathway C₃ → C₂+C (refer to Table 8.3). Therefore we initially compose the C₃ space from irreducible representations of states which participate in the C₃ formation or dissociation. The C₂ molecule has a low lying triplet ³Πₜ state - only 716 cm⁻¹ above the ¹Σ⁺ₕ ground state. We should account for both states in the product Table 8.3. ¹Σ⁺ₕ correlates to A₁ and ³Πₜ to the B₁ + B₂ sum of irreducible representations in the C₂ᵥ point group.⁴ C₂ᵥ irreducible representations are present in the head of the column Table 8.3. As discussed in “Active Orbital Space of a C₂ radical for a Self-Consistent Field (CASSCF) theory” (section 8.1.1) the valence shell of the carbon atom has a ³P₀ term symbol and correlates to the sum of A₂ + B₁ + B₂ irreducible representations. The carbon atom sum of irreducible representations A₂ + B₁ + B₂ appears as a row entry in Table 8.3. The symmetry products of identified states between the C₂ molecule and the C carbon atom should lead to a sufficient set of roots for a correct description of the C₃ active space.

<table>
<thead>
<tr>
<th>C \ C₂</th>
<th>A₁</th>
<th>B₁</th>
<th>B₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₂</td>
<td>A₂</td>
<td>B₂</td>
<td>B₁</td>
</tr>
<tr>
<td>B₁</td>
<td>B₁</td>
<td>A₁</td>
<td>A₂</td>
</tr>
<tr>
<td>B₂</td>
<td>B₂</td>
<td>A₂</td>
<td>A₁</td>
</tr>
</tbody>
</table>

⁴The C₂ᵥ symmetry group is chosen to represent the symmetry of obtained roots, because the geometrically bent structure reduces the symmetry group from the D₂h to the C₂ᵥ.
Thus, summation over the roots $2A_1 + 2B_1 + 2B_2 + 3A_2$ should give a physically sound picture. The linear $C_3 \tilde{X}^1\Sigma_g^+$ ground state can be correlated to the $A_1$ irreducible representation in $C_{2v}$ point group. Low-lying triplet states $\tilde{a}^3\Pi_u$ and $\tilde{b}^3\Pi_g$ are also present in the product Table 8.3 each of them as a $B_1 + B_2$. Obtained state-averaged CASSCF energies for two lowest $\tilde{a}^3\Pi_u$ and $\tilde{b}^3\Pi_g$ triplet states are 17704 cm$^{-1}$ and 23517 cm$^{-1}$ respectively. These computations at the CASSCF level of theory are verified by existing experimental data. Weltner et al. [90] observed a long-lived emission at 17076 cm$^{-1}$ in a neon matrix which was rationalized as the $\tilde{a}^3\Pi_u - \tilde{X}^1\Sigma_g^+$ radiative decay channel. The $\tilde{b}^3\Pi_g - \tilde{a}^3\Pi_u$ transition has been detected [19] by a diode laser absorption spectroscopy and a Fourier transform spectrometer at around 6500 cm$^{-1}$ assigning the upper $\tilde{b}^3\Pi_g$ state to 23576 cm$^{-1}$ relative to the ground state. Note, however, that for the MRCI calculation discussed in the next section, a large number of roots should be included. For example, in the $C_{2v}$ calculation 1 root of $A_1$, 5 roots of $B_1$, 2 roots of $B_2$ and 6 roots of $A_2$ symmetry are requested. In the $C_s$ calculation 6 roots of $A'$ and 8 roots of $A''$ are requested.

8.2.2 Excited state energies of the $C_3$ singlet manifold

In the Table 8.4 the MRCI calculations based on the CASSCF optimized orbitals are compared to the experimental data and yield accurate results for the singlet excited states of $C_3$ within $\approx 300$ cm$^{-1}$. For example, the computed MRCI energy of the $^1\Delta_g$ state agrees with our experimentally obtained data as well as with the double-resonance experiments of Saha et al. [40]. Therefore, we have a clear evidence that the ab initio calculations give a good energy reference in order to support the further studies in the triplet manifold. Ab initio calculations may as well assist in assigning symmetry labels to the measured electronic states.

8.2.3 Excited state energies of the $C_3$ triplet manifold

A number of quantum chemical calculations have already been performed on the triplet manifold, in particular to examine cyclic $C_3$ structures [22–24]. According to quantum chemical calculations [22] the lowest $^3\Pi$ state undergoes isomerization into a cyclic (triangular) structure via a bent transition state. Therefore, the low-frequency bending motion is a possible deformation path to the formation of cyclic $C_3$ isomers. Linear and triangular isomers [42] with both singlet and triplet spin-multiplicities may play an important role in the reaction pathways to the formation of polyaromatic hydrocarbons [1].
Table 8.4: Electronic term values of C$_3$ calculated at the MRCI level of theory, at a fixed bond length of $r = 1.2950$ Å and linear geometry.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Dominant electronic configuration</th>
<th>Calc. $\Delta E^a/h\text{cm}^{-1}$</th>
<th>Obs. $T_e^b$/$\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_g^+$</td>
<td>$1\pi_u^4 4\sigma_g^2 3\sigma_u^2$</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$^1\Delta_u$</td>
<td>$1\pi_u^4 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$</td>
<td>24997</td>
<td>24675$^c$</td>
</tr>
<tr>
<td>$^1\Sigma_u^-$</td>
<td>$1\pi_u^3 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$</td>
<td>32123$^d$</td>
<td>-</td>
</tr>
<tr>
<td>$^1\Pi_u$</td>
<td>$1\pi_u^4 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$</td>
<td>32325$^d$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$1\pi_u^4 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$</td>
<td>32411</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$1\pi_u^4 4\sigma_g^2 3\sigma_u^2 1\pi_g^1$</td>
<td>42310</td>
<td>42059$^e$</td>
</tr>
</tbody>
</table>

$^a$ $\Delta E = E - E(\tilde{X}^1\Sigma_g^+) = -113.8420 E_h$ ($E_h \approx 4.3597 \times 10^{-18}$ J is the hartree); for the calculated values a (12,12) CAS and the aug-cc-pVTZ basis were used and they include the rotated frame Davidson correction.

$^b$ Vertical excitation energy.

$^c$ Ref. [29]

$^d$ Strongly perturbed levels.

$^e$ Ref. [40]

The analysis of the C$_3$ triplet manifold by ab initio calculations has been performed at the multi-reference configuration interaction (MRCI) level with the MOLPRO package [99, 100]. Active orbital spaces and reference states were obtained by applying complete active space self-consistent field theory [104]. Equilibrium bond lengths of few excited states were found by optimizing the geometry at the CASPT2 level [105] in the $D_{2h}$ point group. Energy differences $T_e$ from the singlet $\tilde{X}^1\Sigma_g^+$ ground state were determined.

MRCI calculations were conducted with equal bond lengths of (i) $r = 1.2950$ Å [40] and (ii) $r + 0.1 = 1.3950$ Å in order to account for an elongation of the bond. The cluster Davidson corrected MRCI energies were computed with the aug-cc-TZVPP basis set and are summarized in Table 8.5. We estimate the accuracy of the calculated values to be better than 200 $h\text{cm}^{-1}$, both with respect to the basis size used as well as with regard to the inclusion of additional electronic correlation.

### 8.2.4 Symmetric-stretching potential energy surfaces of the C$_3$ triplet manifold

Symmetric stretching potentials were calculated for the first nine triplet electronic states and are shown in Fig. 8.1. Fueno et al. [22] performed Configuration Interaction (CI) computation of bending potential curves for two lowest $^3\Pi$ state. Terentyev et al. [23]
Table 8.5: Comparison of CASPT2 calculated $T_e$ and MRCI energies at $r = 1.2950$ Å bond length in $D_{2h}$ point group for the $C_3$ triplet manifold and observed $T_f^f$.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Dominant electronic configuration</th>
<th>Calc. $r_e$ (Å)</th>
<th>Calc. $T_e$ CASPT2 (cm$^{-1}$)</th>
<th>Calc. MRCI energy$^d$ (cm$^{-1}$)</th>
<th>Obs. $T_f^f$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1^1\Sigma_g^+$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2$</td>
<td>1.3213</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$\tilde{a}^3\Pi_u$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^1 1\pi_g^1$</td>
<td>1.3276</td>
<td>15472</td>
<td>17205</td>
<td>17200$^a$</td>
</tr>
<tr>
<td>$\tilde{b}^3\Pi_g$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$</td>
<td>1.3120</td>
<td>22254</td>
<td>23696</td>
<td>23683$^b$</td>
</tr>
<tr>
<td>$^3\Sigma_u^+$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$</td>
<td>1.3809</td>
<td>24167</td>
<td>26120</td>
<td>-</td>
</tr>
<tr>
<td>$^3\Delta_u$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>29452</td>
<td>-</td>
</tr>
<tr>
<td>$^3\Sigma_u^-$</td>
<td>$4\sigma_g^2 1\pi_u^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>31164</td>
<td>-</td>
</tr>
<tr>
<td>$^3\Sigma_g^-$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>34695</td>
<td>-</td>
</tr>
<tr>
<td>$^3\Pi_u$</td>
<td>$1\pi_1^1 4\sigma_g^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>44859</td>
<td>45846$^g$</td>
</tr>
<tr>
<td>$^3\Sigma_u^-$</td>
<td>$4\sigma_g^2 1\pi_u^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>46070</td>
<td>-</td>
</tr>
<tr>
<td>$^3\Sigma_g^-$</td>
<td>$4\sigma_g^2 1\pi_u^1 3\sigma_u^2 1\pi_g^1$</td>
<td>-</td>
<td>-</td>
<td>47335</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Ref. [90]  
$^b$Ref. [19]  
$^c$Geometry optimization on a given state has been performed after multi-state multi-reference CASPT2 calculation.  
$^d$Davidson corrected MRCI energies computed with equal C-C bond lengths at $r = 1.2950$ Å.  
$^e$Strongly perturbed levels.  
$^f$Vertical excitation energy.  
$^g$This work. The observed state is likely (010) of $^3\Pi_g$ vibronic symmetry.

calculated bending potential energy surfaces for the excited triplet states up to 12 eV [23]. The Density Functional theory (DFT) yields highly approximate results. Particularly the DFT tends to overestimate the energies of excited singlet states and to underestimate excited states of triplet spin-multiplicity. The authors [23] suggested that in their work the spin-related errors reach 0.55 – 0.6 eV.

Presently we use state of the art Multi-Reference Configuration Interaction (MRCI) three-dimensional computations. We could determine numerous curve-crossings in the triplet manifold of $C_3$, many of them yield conical intersections.

There are some remarkable interactions of electronic states shown in the Fig. 8.1. For example, the three lowest ungerade states $^3\Sigma_u^+$, $^3\Delta_u$ and $^3\Sigma_u^-$ are nearly degenerate. Vibrational levels originating from these electronic states might strongly interact via non-adiabatic coupling leading to a substantial deviation from the unperturbed vibrational frequencies. Another interesting feature is the crossing of the potential energy surfaces between $^3\Pi_g$, $^3\Sigma_u^-$ and $^3\Delta_u$ shown in Fig. 8.1. The spectral range around 45000
cm$^{-1}$ has been measured in our laboratory by applying perturbation facilitated TC-RFWM. The $^3\Pi_g$ has the origin $T_e \approx 43300$ cm$^{-1}$ and the equilibrium bond length $r \approx 1.4$ Å. Two ungerade $^3\Sigma_-^u$ and $^3\Delta_u$ states are nearly degenerate with $T_e \approx 45000$ cm$^{-1}$ determined from the minimum value of the calculated energy at the equilibrium bond length $r \approx 1.3$ Å.

8.2.5 Bending potential energy surfaces of the C$_3$ triplet manifold

The active space for excited state energies in the C$_s$ point group is composed similarly to the discussion in the section “Active Orbital Space for the C$_3$ radical” (section 8.2.1). The results of a symmetry product table in linear geometry can be correlated to the bent structure accordingly to $A_1 \rightarrow A'$, $A_2 \rightarrow A''$, $B_1 \rightarrow A'$ and $B_2 \rightarrow A''$. It is found that a minimum of 6$A'$ and 8$A''$ roots are necessary for state-averaged CASSCF calculations in order to obtain converged results.

The CASSCF calculation was performed to obtain bending PES for two geometries. Firstly, a computation in the range 180° – 120° with slightly asymmetric bond lengths $r_1 = 1.3$ Å and $r_2 = 1.33$ has been performed in order to account for a possible asymmetric transition state from the linear-C$_3$ to the cyclic-C$_3$ isomerization pathway [22]. Secondly, the range 65° – 130° at a bond length $r_e = 1.4$ Å was examined. The second geometry describes a cyclic C$_3$ isomer which has a stable potential energy minimum at $\approx 60^\circ$ bending angle [24]. Unfortunately, CASSCF calculations could not give conclusive results because of the high density of states in the region of interest around 45000 cm$^{-1}$. 

Figure 8.1: Potential energy curves as a function of the symmetric stretching coordinate for linear C$_3$ in a triplet manifold. Potential energy curves are calculated by the \textit{ab initio} MRCI method in D$_{2h}$ point group.
Potential energy surfaces for the bending vibration are obtained with the MRCI method and presented in Fig. 8.2. Already in the range $180^\circ - 160^\circ$ the $\Pi$ states are split by the Renner-Teller interaction. For example, the degenerate at $180^\circ$ the lowest $^3\Pi_u$ state is split by $680 \text{ cm}^{-1}$ at $120^\circ$ into its $^1\Pi_1$ and $^3\Pi_2$ components (or $^3A'$ and $^3A''$ in $C_S$ point group).

The bending coordinate is the pathway to the formation of the cyclic $C_3$ isomer. At higher bending angles $160^\circ - 120^\circ$ the $^3\Pi_1$ and $^3\Pi_2$ states form a cyclic $C_3$ structure. The $^3\Pi_1$ component of the lowest $^3\Pi_g$ state undergoes isomerization at $120^\circ$ with a barrier of $6263 \text{ cm}^{-1}$. The most remarkable feature emerges at $120^\circ$ from the $^4\Pi_1$ component of the electronic $^3\Delta_u$ state in the vicinity of $45000 \text{ cm}^{-1}$: a double minima occurs at the potential energy surface probably due to multiple-state interactions. The first minima at $180^\circ$ has an energy of $44770 \text{ cm}^{-1}$ while the second at $\approx 120^\circ$ has an energy of $45600 \text{ cm}^{-1}$. The barrier of a linear-to-bend $C_3$ isomerization can be estimated to be in the order of $2500 \text{ cm}^{-1}$.

A previous analysis of the electronic configuration [24] suggests the lowest triplet $^3A'$ state to have a local minimum at an equilateral triangular geometry exhibiting a term energy of $0.78 \text{ eV}$ above the $\tilde{X}^1\Sigma_g^+$ linear ground state. The activation energy and excited state reaction pathways remain uncertain. The combination of the perturbation-facilitated optical spectroscopies and $ab\ initio$ calculations of the triplet manifold may

![Figure 8.2: Potential energy curves as a function of the bending coordinate for $C_3$ triplet excited states. Potential energy surfaces are calculated by the $ab\ initio$ MRCI method in $C_2v$ point group with the bond length fixed to $1.3\text{Å}$. Two states $^4\Pi_2$ and $^4\Pi_1$ are given in bold lines (in the notation where the $C_2$ axis is perpendicular to the molecular axis at linearity, see text for details).]
considerably extend our knowledge on the activation energies, local minima and a reaction pathways leading to the cyclic C\textsubscript{3} isomer.

Indeed, excited state energies at linear geometry agree with the results of the Configuration-Interaction (CI) method applied in [22] as well as with the Density Functional Theory (DFT) [23]. In the case of the cyclic C\textsubscript{3} structure the CI method gave a minimum of the energy at \(\approx 8100 \text{ cm}^{-1}\) for \(3\Delta_u\). The CASSCF calculation obtained the value of \(\approx 10100 \text{ cm}^{-1}\) [22] while DFT assigned for this state an even lower energy of \(\approx 7250 \text{ cm}^{-1}\) [23]. MRCI method applied in our work gives a qualitative agreement with previous studies on the behavior of the PES.

8.2.6 Vibrational frequencies of a C\textsubscript{3} triplet manifold

Vibrational frequencies of the triplet manifold are given in Table 8.6. One of the initial steps of the analysis is a comparison of the dominant electronic configuration and vibrational frequencies. The first excited triplet \(\tilde{a}^3\Pi_u\) state has one electron excited from the \(\sigma_u\) to the \(\pi_g\) orbital. The final symmetry of the electronic state is composed of the direct product between the orbital occupied by an electron and the orbital occupied by a hole. The same electronic configuration of the \(\tilde{a}^3\Pi_u\) leads to the well-know singlet \(\tilde{A}^1\Pi_u\) state. Vibrational wave numbers of the singlet state are \(\omega_1 = 1084 \text{ cm}^{-1}\), \(\omega_2 = 135 \text{ cm}^{-1}\) (the bending vibrational wavenumber of the energetically lowest Renner-Teller component \(A'\)) and \(\omega_3 = 540 \text{ cm}^{-1}\) for \(r_e = 1.305 \text{ Å}\) [40] and agree with the experimental results from the first excited triplet state (refer to Table 8.6).

\(3\Delta_u\) is another electronic state of interest. This state was measured by applying the UNFOLDED TC-RFWM technique. The knowledge of vibrational frequencies is particularly important for the assignment of observed vibronic transitions. In a preliminary analysis we find that the Hessian matrix defined through second derivatives along the bent-coordinate leads to an imaginary frequency. This usually indicates a transition state. The potential energy surface shown in the Fig 8.2 is indeed very shallow at linear (180°) geometry. The bent 105° configuration has a lower energy and a barrier to linearity of about 2000 cm\(^{-1}\). Furthermore, along the bending coordinate the fifth excited \(A'\) state (\(3\Delta_u\)) undergoes several curve-crossings.

8.2.7 Comparison of \textit{ab initio} calculations and the PF-RFWM observations

The newly measured excited state of \(3\Pi_g\) vibronic symmetry (\(i.e. \Gamma_{vib} \otimes \Gamma_{el}\)) can be assigned to a few possible final electronic states: \(3\Delta_u\), \(3\Sigma_u^-\) or \(3\Pi_g\) appearing in the
Table 8.6: Vibrational frequencies calculated for excited triplet states in $C_4$ point group.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Dominant electronic configuration</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$\omega_2$ (cm$^{-1}$)</th>
<th>$\omega_3$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^1\Sigma_g^+$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^4$</td>
<td>1224$^b$</td>
<td>63$^6$</td>
<td>2040$^6$</td>
</tr>
<tr>
<td>$\tilde{a}^3\Pi_u$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^1 1\pi_g^4$</td>
<td>1151</td>
<td>177</td>
<td>1436</td>
</tr>
<tr>
<td>$\tilde{b}^3\Pi_g$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^1 1\pi_g^4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$3\Sigma_u^+$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^2 1\pi_g^4$</td>
<td>1027</td>
<td>482</td>
<td>1469</td>
</tr>
<tr>
<td>$3\Delta_u$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^2 1\pi_g^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$3\Sigma_u^-$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^1 1\pi_g^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$3\Sigma_g^-$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^1 1\pi_g^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$3\Delta_g$</td>
<td>$1\pi_u^1 4\sigma_g^2 3\sigma_u^1 1\pi_g^2$</td>
<td>1294</td>
<td>2181</td>
<td>2032</td>
</tr>
</tbody>
</table>

$^a$ Note: CASSCF method does not include state interactions at curve crossing geometries.

$^b$ The known ground-state vibrational frequencies [37, 106].

vicinity of 45000 cm$^{-1}$ (see Fig. 8.1 and Table 8.5). Selection rules prohibit transitions between $u \leftrightarrow u$ (ungerade) states. As a consequence, no direct transitions to the (000) vibrational level of either the $3\Delta_u$ or $3\Sigma_g^-$ states are possible. However transitions might be vibronically allowed by considering the direct product with the vibrational state symmetry. When odd numbers of bent vibrations are excited (0$n$0), $n = 1, 3, ..$ both $\Delta_u$ and $\Sigma_g^-$ electronic states are dipole coupled to the intermediate state through the $\Gamma_{\Pi_u} \otimes \Gamma_{\Delta_u} = \Gamma_{\Pi_g} \oplus \Gamma_{\Sigma_g}$ and $\Gamma_{\Pi_u} \otimes \Gamma_{\Sigma_u^-} = \Gamma_{\Pi_g}$ symmetry product. Note that no $a$ priori knowledge on the electronic symmetry of the intermediate $3\Sigma_u^-$ state is known. Assuming the $\Gamma_{(050)} \otimes \Gamma_{\tilde{b}^3\Pi_g} = 3 \Sigma_u^-$ perturber state as suggested by Zhang et al. [15], the transition from $\tilde{b}^3\Pi_g$ to either $\Delta_u$ or $3\Sigma_g^-$ is electronically allowed.

An analysis of the rotational structure presented in the section 5.2.3 by measuring 32 transitions in the $3\Pi_g \rightarrow 3\Sigma_u^-$ ($= |\psi^->$) system for $4 \leq J \leq 16$ yields the molecular constants in Table 5.5 with an average error of 0.029 cm$^{-1}$. The rotational constant $B$ suggests a bond-length similar to the $\tilde{a}^3\Pi_u$ state. From calculations of the potential energy surfaces shown in Fig. 8.1, we estimate that the equilibrium bond distance in the electronic $3\Pi_g$ state should be at significantly larger values then that of the $\tilde{a}^3\Pi_u$ state. The rotational constant in the $3\Pi_g$ state therefore would not agree with the experimentally observed value and we might rule out this state as a possible candidate for being the final $|f>$ state of our observation. The determined spin-orbit constant $A$ is non-zero, however for the $3\Sigma_u^-$ state (another candidate for being the final state) the zero spin-orbit constant is expected. From the non-zero spin-orbit coupling constant we conclude that the observed resonances rather belong to the $3\Delta_u$ electronic state (see
Fig. 8.1). The Λ-type doubling parameters of $^3\Delta_u$ state are quite different compared to the known $^3\Pi$ states (Table 5.5). This might be attributed to a heterogeneous perturbation $B <^3\Pi|L_+|^3\Sigma >$ by a nearby lying $^3\Sigma_u^-$ state elucidated in the present calculation. Although, we should mention that the Λ doubling parameters may also exhibit variations because of the interaction between different Renner-Teller components of the electronic $^3\Delta_u$ state.
Chapter 9

Summary

9.1 Summary

In the current work we demonstrate the applicability of nonlinear four-wave mixing spectroscopy to study dark states. “Gate-way” (for example singlet-triplet mixed) levels are used as intermediate levels to access the dark manifolds by two-color resonant four-wave mixing (TC-RFWM) measurements. We perform TC-RFWM measurements in the spectral range of the “Swan system” ($d^3\Pi_g - a^3\Pi_u$) of the $C_2$ radical to unveil the perturbation by a $1^5\Pi_g$ state [9]. The quintet state is observed for the first time through an intensity borrowing mechanism which renders the otherwise inaccessible dark state visible by acquiring partial character of the bright state. In particular, the $1^5\Pi_g$ state gains some triplet character through spin-orbit interaction with the closely spaced $d^3\Pi_g$.

By intermediate level labeling of specific $J$-levels, it is possible to collect simplified spectra. The selection rules $\Delta J = \pm 1, 0$ facilitate the detection of weak resonances to the dark states near the dipole allowed resonances to the bright states. A rotational analysis of measured TC-RFWM spectra reveals the five spin-levels of the $1^5\Pi_g$ state crossing the three spin-levels of the bright $d^3\Pi_g$ state. The presence of the dark $1^5\Pi_g$ state rationalizes the anomalous non-thermal emission observed by Fowler in 1910 [10].

The UNFOLDED TC-RFWM energy scheme is applied to study excited triplet states of the carbon trimer molecule exhibiting a $\tilde{X}^1\Sigma^+_g$ ground state [11]. Intermediate $J$-levels in the vicinity of the “Comet band” ($\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$) are chosen due to the strong spin-orbit interaction between the bright $\tilde{A}^1\Pi_u$ and the dark $3\Sigma^-_u$ vibronic levels. Selective tuning of the PUMP lasers to the intermediate level with substantial triplet or singlet character facilitates the observation of the respective spin multiplicity in the final state. A new vibronic $3\Pi_g$ state (of $3\Delta_u$ electronic symmetry) is detected. Ab initio calculations for the $C_3$ singlet and triplet states are performed to confirm the experimental assignments.
We discuss the application of the Perturbation-Facilitated Two-Photon Laser-Induced Fluorescence (PF - Two-Photon LIF) to study vibrations of the C₃ cluster in the triplet manifold. The molecular population from the $\tilde{X}^1Σ^+_g$ ground state is pumped to the $3Π_g$ vibronic level by a two-photon resonant excitation via “gate-way” levels (i.e. singlet - triplet mixed levels). Two types of Two-Photon LIF experiments are performed. On the one hand, the excitation laser is scanned in the vicinity of the $3Π_g$ state. Therefore, by detecting the fluorescence in the specific spectral range the rovibronic resonances of the final state are assigned. For the $Π ← Σ$ transition the $ΔJ = 0, ±1$ resonances are observed by depletion of the two-photon laser induced fluorescence. On the other hand, dispersed fluorescence measurements are performed from the selected spin component of the final rovibrational $3Π_g$ levels. The radiative decays into the different vibrational levels of the triplet manifold are spectrally resolved by scanning the monochromator grating. The application of the perturbation facilitated Two-Photon LIF and TC-RFWM technique may reveal the lowest triplet state in cyclic C₃ geometry as predicted by Pople and co-workers [24] to be $≈ 1$ eV above the singlet $\tilde{X}^1Σ^+_g$ (linear) ground state. We would like to point out that obtained vibrational progressions are compared with the origin energies of the $\tilde{A}^3Π_u$ and $\tilde{B}^3Π_g$ [19, 89, 90] known from argon and neon matrix measurements. The obtained vibrational progressions are preliminarily compared with the ab initio calculations of the electronic states in the triplet manifold in the linear geometry. However, analysis does not include ab initio calculation of the potential energy surfaces of triplet states close to the cyclic C₃ geometry up to 60 degrees of the C₃ bending angle.

We apply the pumped UP TC-RFWM scheme to investigate the influence of anisotropy on the four-wave mixing signal intensity. The excitation laser beam (pump beam of TC-RFWM) optically pumps population of the C₃ molecule by resonant excitation of the $J = 5$ level of the $\tilde{A}^1Π_u$ state via the $P(6)$ transition from the thermally populated $\tilde{X}^1Σ^+_g$ ground state. Multiple magnetic sublevels defined by the quantum number $m_g$ in the $J = 5$ level with a $(2J + 1)$ degeneracy are populated in the $\tilde{A}^1Π_u$ state. Alignment of magnetic sublevels in the excited state is induced by the excitation beam with a linear polarization. Therefore, a disparity in the population between sublevels which differ by $|m_g|$ is induced in the laboratory frame and is pointing along the polarization axis of the resonant excitation. The UP TC-RFWM energy scheme is applied to study the influence of the non-uniform distribution among the magnetic sublevels in the $\tilde{A}^1Π_u$ state. The nonlinear optical response for selected rovibronic transitions (e.g. PP, PQ, PR or QP, QQ, QR) is examined. Interestingly, if the PUMP laser is tuned to a P-transition the isotropic and anisotropic contributions interfere destructively. On the contrary, if PUMP is tuned to a Q-transition the isotropic and anisotropic contributions
interfere constructively, leading to an overall enhancement of the TC-RFWM signal intensity. Furthermore, the UNFOLDED TC-RFWM response is evaluated by taking into account an isotropic density matrix and compared to the anisotropic UP TC-RFWM experiments. The dependence of the square of the nonlinear optical response $|<O_{4321}>|^2$ on the polarization rotation of the PROBE laser is determined by applying the theory presented in [60, 93, 94] where angular momentum anisotropy is incorporated into the four-wave mixing signal intensity. Note that by examining separate ranks of the tensor $<O_{4321}>$ it is possible to choose a polarization scheme for a specific detection of the population $|<O^{(0)}_{4321}>|^2$, the orientation $|<O^{(1)}_{4321}>|^2$ or the alignment $|<O^{(2)}_{4321}>|^2$. In the present work we examine the influence of alignment on the intensity distribution of measured resonances by UP TC-RFWM energy level scheme.
Bibliography


Yaroslav Sych

Education

2010–2013 PhD in Science, ETH, Zurich, Switzerland.
Department of Chemistry and Applied Biosciences

2010–2013 Research Assistant, Paul Scherrer Institute, Villigen, Switzerland.
General Energy Department, Molecular Dynamics Group

2007–2010 Research Assistant, Friedrich Alexander University, Erlangen, Germany.
Department of High-Frequency Electronics, Photonics Group

2005–2007 Master, Moscow State Technical Bauman University, Moscow, Russia,
Grade: with honors.
Department of Radio and Laser Physics, Laser Information Technologies

2001–2005 Bachelor, Moscow State Technical Bauman University, Moscow, Russia,
Grade: with honors.
Department of Radio and Laser Physics, Optoelectronics

PhD Thesis

- **title**: Four-Wave Mixing Spectroscopy of Small Carbon Clusters
- **supervisors**: Dr. P.P. Radi and Prof. Dr. A. Wokaun, ETH Zurich
- **description**: Application of Two-Color Four-Wave-Mixing spectroscopy to study singlet-triplet interaction.
  Application of Two-Photon Laser Induced Fluorescence: molecular dynamics via spin-forbidden transitions.
  Polarization schemes for the Two-Color Four-Wave-Mixing spectroscopy: a probe of molecular orientation and alignment.

Experience

Vocational

2008–2010 Research Assistant, Graduate School in Advanced Optical Technologies, Erlangen, Germany,
Fast absorption spectroscopy with a swept supercontinuum laser source,
Responsible: Prof. Dr.-Ing. B. Schmauss and Prof. Dr.-Ing. A. Leipertz.
Design and application of the sensor system based on the laser generated supercontinuum radiation.
Design of the experimental apparatus for the characterization of the fiber mode profiles and the inter-modal dispersion in a few-mode optical fiber

2005–2007 **Research Assistant**, *Laser Research Center Polus, Moscow, Russia*, Optical systems design for multimodal solid-state lasers, Supervisor: Dr. A. Shestakov.
Design and evaluation of the optical system for the laser waist displacement in the longitudinal direction for the 3D material processing.

**Internship**

Jun–Aug 2006 **Optical information storage**, Supervisor: Prof. Dr. Susanna Orlic, Berlin Technical University, Optical Institute, Berlin, Germany.
Optical information storage in a dot-hologram

Lateral crystals emerging by the laser impact

**Languages**

- **Russian** Native.

**Computer skills**

- Software Matlab, LabView, Quantum chemical calculations with Molpro
- Programming Languages C, C++

**Publications**


### Attended conferences and summer schools

1 European Conference on Nonlinear Optical Spectroscopy 2011, Enschede, Netherlands

2 European Conference on Nonlinear Optical Spectroscopy 2012, Aberdeen, United Kingdom

3 Modern Developments in Spectroscopy 2012, Noordwijk, Netherlands

4 International conference on Laser Spectroscopy 2013, UC Berkeley, United States

5 Leopoldina-Symposium 2013, ETH Zurich, Switzerland