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Hybrid rotational
femtosecond/picosecond coherent
anti-Stokes Raman Spectroscopy of
Nitrogen at high Pressures and
Temperatures



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*For auld lang syne, my dear,
for auld lang syne,
w**E**'ll tak' a c**U**p o' kindness yet,
for auld lang syne!*

Abstract

In this thesis, the use of two-beam hybrid rotational femtosecond/picosecond coherent anti-Stokes Raman spectroscopy (HR-CARS) for temperature measurements in nitrogen gas at high pressures (1-70 atm) and temperatures (300-1000 K) is demonstrated.

An experimental setup for 1 kHz measurements of well-resolved frequency-domain HR-CARS spectra across all investigated pressures and temperatures was built. To achieve the required spectral pump/Stokes excitation bandwidth, a pulse shaper was used to create an almost transform limited 42 fs pump/Stokes pulse at the interaction volume, after having passed through a 28 mm fused silica window of a high pressure cell. To obtain nonresonant background free spectra at the required spectral resolution, a narrow-bandwidth, frequency-upconverted 5.5 ps probe pulse was created in a beta barium borate (BBO) crystal (Type 1) via sum frequency generation (SFG) using second harmonic bandwidth compression (SHBC).

A computational code has been developed to model S-branch HR-CARS spectra and fit to experimental results to obtain best-fit temperatures. The model spectra are based on transition frequencies calculated from a non-rigid rotor approximation, taking rotational-vibrational interaction into account. Linewidths are taken from published measurements and interpolated to the required temperature. The model assumes impulsive pump/Stokes excitation and the probe pulse is modelled with chirp, as this was observed experimentally. The fitting is done through a nonlinear least-squares algorithm.

Good qualitative fits, including good accuracy and precision between thermocouple measured and best-fit temperatures over all the explored pressure and temperature regimes are shown. Across all experimental spectra, the average percentage temperature difference between best-fit and thermocouple measured temperatures (as a percentage of the thermocouple measurement), is -0.3% with a standard deviation of 7.1%.

Overall, accurate nitrogen thermometry is demonstrated, showing the suitability of HR-CARS for characterising high pressure and temperature environments.

Lay Summary

Being able to characterise and understand gas-phase reactions is not only of interest to the scientific community but is of significant importance for the wider society. Gas-phase reactions include, for example, combustion. Even though we try to reduce the use of combustion in most of its forms, it will remain an integral part of modern life for many decades to come. It is therefore vital to understand combustion processes as much as possible, so that more efficient engines and fuels can be developed, reducing emissions of greenhouse gases, pollutants and toxic particles.

One technique to study gases and gas-phase reactions is coherent anti-Stokes Raman spectroscopy (CARS). This technique uses three laser beams that are focused to the same spot in the studied gas. The interaction between the beams and the gas produces a fourth laser beam that contains spectral information about the gas. This spectral information can be used to calculate the temperature of the gas. Chemical reactions, including combustion, are exponentially temperature dependent, so accurate temperature measurements are critical.

The research presented in this thesis makes use of a special type of CARS, called hybrid rotational femtosecond/picosecond CARS (HR-CARS). The aim is to extend the use of HR-CARS to previously unexplored pressures and temperatures and to prove the suitability of this technique for temperature measurements under these extreme conditions. More precisely, nitrogen gas at pressures between 1-70 atm and temperatures between 300-1000 K was probed. An experimental setup was built that overcomes the challenges associated with high pressure HR-CARS measurements and that allows for the detection of well resolved spectra under all probed pressures and temperatures. Further, a computational code was developed that can model theoretical HR-CARS spectra and fit them to the experimentally measured ones, to obtain the temperature of the probed nitrogen gas.

It was found that the temperatures calculated from fitting the modelled spectra to the experimental ones have very good accuracy and precision when compared to the temperatures of the probed gas that were measured with a thermocouple. Overall, it is shown that HR-CARS is suitable for accurately measuring the temperature of nitrogen gas at high pressures and temperatures. In the future, this could be used to study and optimise combustion related processes.

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Declaration

I declare that this thesis was composed solely by myself and I certify that the work contained within is my own, except where indicated by referencing. Parts of this thesis have already been published, as noted in the text, but no part has been submitted in support of another degree or qualification from this, or any other university or institute of learning.

The data presented in this thesis was obtained in an experiment carried out at the Sandia National Laboratories in Livermore, CA. I played a major role in the preparation and execution of the experiment, and the data analysis and interpretation are entirely my own work. Any contributions from colleagues are explicitly referenced in the text.

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Nomenclature

Acronyms

BBO	beta barium borate
CARS	coherent anti-Stokes Raman spectroscopy
FROG	frequency-resolved optical gating
FWHM	full width at half maximum
GDD	group delay dispersion
GVD	group velocity dispersion
HR-CARS	hybrid rotational coherent anti-Stokes Raman spectroscopy
LIF	laser induced fluorescence
LIGS	laser-induced grating spectroscopy
MEG	modified exponential gap
MIIPS	multiphoton intrapulse interference phase scan
NR	nonresonant
RCARS	rotational coherent anti-Stokes Raman spectroscopy
RWA	rotating wave approximation
SFG	sum frequency generation
SHBC	second harmonic bandwidth compression
SLM	spatial light modulator
TDLAS	tunable diode laser absorption spectroscopy
TL	transform limit
VCARS	vibrational coherent anti-Stokes Raman spectroscopy

Symbols

$ \Psi(t)\rangle$	generic time-dependent wavefunction
$\mathcal{U}(t, t_0)$	time evolution operator
$\rho(t)$	density operator/matrix
$H(t)$	time-dependent Hamiltonian
$E(t)$	electric field
$P^{(3)}(t)$	3 rd order polarisation
$R_{CARS}(t)$	3 rd order nonlinear molecular response function
ΔE	Raman transition frequency
Γ	Raman transition linewidth
v	vibrational quantum number
J	rotational quantum number
ω_e	fundamental vibrational constant
$\omega_e x_e$	second order vibrational constant
B_e	equilibrium rotational constant
D_e	equilibrium centrifugal constant
α_e	first rotational-vibrational interaction constant
β_e	second rotational-vibrational interaction constant
γ_e	third rotational-vibrational interaction constant
$\Delta\rho$	normalised Boltzmann population difference
γ'_v	polarisation anisotropy
$b_{J,J+2}$	S-branch Placzek-Teller coefficient
$F_{rot}(J)$	Herman-Wallis factor
g_J	rotational nuclear degeneracy
α	probe beam chirp factor

Chapter 1

Introduction

This opening chapter will introduce the concept of coherent anti-Stokes Raman spectroscopy (CARS). After a brief introduction to laser-based thermometry, the basic theoretical principles and history of CARS spectroscopy are explained. Then, the different main types of CARS are presented, along with their advantages and disadvantages. A special focus is given to hybrid femtosecond/picosecond (fs/ps) CARS, the technique explored in this PhD project. At the end of the chapter, an overview of the research presented in this thesis will be given, along with the aims and motivations for the project.

There exist several laser-based techniques for temperature measurements in the gas-phase [1, 2] and CARS is only one of them. Another prominent example is laser induced fluorescence (LIF), whereby absorption of a photon excites a molecule to a higher energy level, before returning to a lower level through spontaneous emission of a different photon [3]. Tuning the incident laser light to a certain frequency allows controlled excitation and fluorescence of a specific species. A more complex variant of this is two-line planar LIF [4]. Here, a two-dimensional plane of molecules is excited by two different frequencies, probing different ro-vibrational transitions of the target molecule. The ratio of the two signals can then be used to determine the temperature. Other techniques for gas-phase thermometry include spontaneous Rayleigh and Raman scattering. Rayleigh scattering is an elastic process and the resulting signal is proportional to the number density of the probed molecules [3]. The temperature can be calculated from the Rayleigh signal by using the ideal gas law and performing a calibration measurement at a known temperature. Spontaneous Raman scattering is an inelastic process and temperature information can be extracted as different spectral features are temperature dependent.

In order to obtain 2D and 3D temperature profiles, tomography can be used [5]. For example, tunable diode laser absorption spectroscopy (TDLAS) based tomography works by using several sensors at different locations around the domain of interest to take simultaneous laser absorption measurements [6]. The laser frequency is tuned to

that of an absorption line of the species of interest and the corresponding reduction in signal intensity can be detected by photodiodes. Reconstruction algorithms can then compute a full picture from the individual measurements. However, tomographic reconstruction algorithms, in general, come with a loss of spatial resolution.

Laser-induced grating spectroscopy (LIGS) is also an established method for gas-phase temperature measurements [7, 8]. Here, two laser beams are crossed at an angle, creating an interference pattern and ultimately a thermal grating, which can be probed with a third beam to extract temperature information. While offering high precision, the temperature evaluation requires modelling using parameters that are generally unknown, such as the exact composition of the probed gas. Further, calibration measurements are necessary.

Of course, the technique for gas-phase thermometry that is of interest for this thesis is CARS spectroscopy. The field of CARS spectroscopy is very large and continues to grow, a complete summary is far beyond the scope of this introductory chapter. Instead, an overview of the most relevant aspects will be given here. However, a lot of very detailed literature on CARS exists, for example the book *Laser Diagnostics for Combustion Temperature and Species* by Alan C. Eckbreth [9], which provides a thorough theoretical and practical background on many laser diagnostic techniques, including CARS. Further, Roy *et al.* [10] give an excellent overview of the various different types of CARS spectroscopies and their developments over time.

Many CARS experiments are performed in the condensed phase, for example on lipids in biological and medicinal research [11], as the high density of condensed phase samples results in strong CARS signals. However, the focus of the following overview will be solely on the application of CARS to gas-phase measurements, which are of particular importance to combustion related processes and applications, such as flames, engines, gas turbines, etc. in which harsh conditions like high pressures, temperatures and turbulent mixing prevail.

1.1 The CARS Process

CARS is a nonlinear four-wave mixing technique, in which three laser beams interact to produce a coherent laser-like output signal containing the desired spectral information. The so-called pump and Stokes beams set up a molecular (e.g. rotational or ro-vibrational) Raman coherence between two molecular states, and this coherence is then probed with a probe beam, thereby creating the signal beam. A schematic energy level diagram of this process is shown in Figure 1.1.

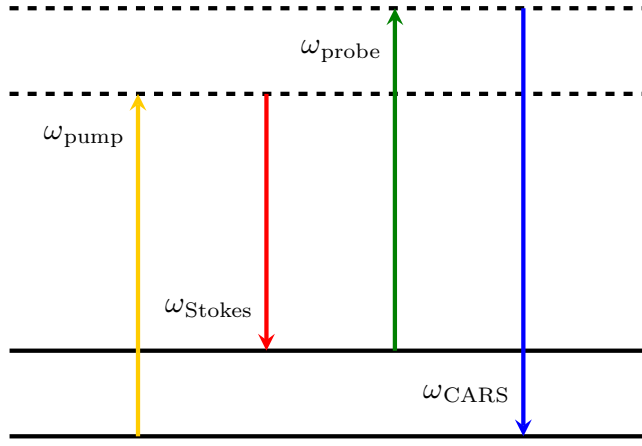


Figure 1.1: Schematic energy level diagram of the four-wave mixing CARS process. It can be seen how the pump and Stokes photons interact to set up a Raman coherence between two molecular states (energy levels), which is then probed with the probe beam to produce a CARS signal photon. Solid lines represent real molecular energy levels and dashed lines represent virtual levels.

The spectrum encoded in the CARS signal beam can easily be detected and used for both, temperature and relative species concentration measurements [10]. The temperature can be inferred through the temperature-dependent Boltzmann equilibrium population distribution of molecular states. Relative species concentration measurements are possible as the CARS signal intensity is proportional to the square of the number density of the probed species.

From the point of view of the Raman coherences being probed, there are two types of CARS, vibrational CARS (VCARS) and rotational CARS (RCARS). For VCARS, the pump and Stokes beams set up Raman coherences between different vibrational states, while for RCARS, pure rotational transitions are being probed. Vibrational CARS is most accurate at temperatures above 1200 K [12], therefore it is often performed in flames. This is because it is only above 1200 K that a vibrational hot band appears and grows with temperature. Rotational CARS, on the other hand, is mostly used at temperatures below 1500 K, as several rotational levels of an ensemble of molecules are usually populated even at room temperature, making this technique more sensitive at lower temperatures. However, RCARS has been successfully employed at higher temperatures (>1500 K) as well, [13, 14]. In addition, RCARS is very useful for high pressure studies, as the energy separations of rotational transitions of a linear diatomic molecule, such as N_2 or O_2 , are relatively widely spaced compared to the vibrational ones. This means that the line broadening due to pressure results in significantly less overlap of lines for RCARS compared to VCARS [15].

Another important aspect of CARS is the phase-matching condition. If the pump, Stokes, probe and CARS signal beams have wavevectors $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$ and $\vec{k}_4$ respectively, then the phase matching condition says that the CARS signal beam must satisfy the

following, for momentum to be conserved [10]:

$$\vec{k}_4 = \vec{k}_1 - \vec{k}_2 + \vec{k}_3 \quad (1.1)$$

This can be achieved in a number of ways, but BOXCARS or collinear geometries are most common. Both of these configurations are shown in Figure 1.2, along with respective vector diagrams of the phase-matching condition. In the BOXCARS geometry, the pump, Stokes and probe beams are crossed at different angles, overlapping only at the probe volume. The CARS signal is then generated along the direction that satisfies the phase-matching condition. In the collinear geometry, the pump, Stokes and probe pulses propagate along the same line, automatically satisfying the phase-matching condition in the forward direction along this line.

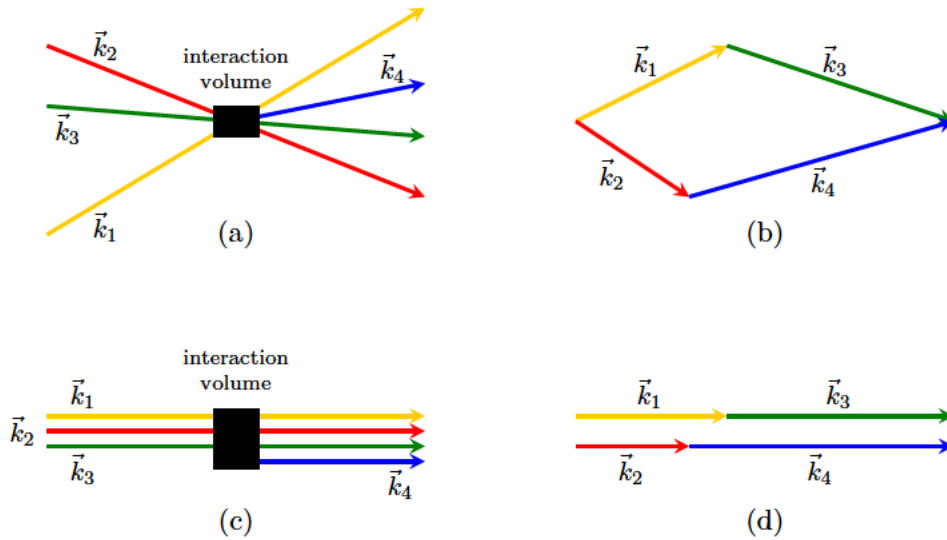


Figure 1.2: (a) BOXCARS geometry: the pump, Stokes and probe beams are crossed at different angles, overlapping only at the probe volume, the CARS signal is generated in the direction that satisfies the phase-matching condition. (b) Vector diagram of the phase-matching condition for BOXCARS. (c) Collinear geometry: the pump, Stokes and probe beams propagate along the same line, the CARS signal is generated along this line in the forward direction. (d) Vector diagram of the phase-matching condition for collinear CARS.

1.2 History of CARS

The first *light amplification by stimulated emission of radiation* (laser) device was built in 1960 [16], however, the concept of stimulated emission of photons dates back to 1917 [17]. Since their invention 60 years ago, lasers have become an integral part not only of commercial and industrial technology, but also of science. Many spectroscopic techniques have benefited greatly from the availability of high power, monochromatic, coherent light sources, and among others, the field of laser diagnostics was born.

The term *CARS* was only coined in 1974 by Begley *et al.* [18], but it was already in 1965, just five years after the invention of the laser itself, that coherent anti-Stokes Raman emission was first observed by Maker and Terhune [19]. The first gas-phase CARS measurements were reported by Régnier and Taran [20] who measured the concentration of H_2 in a flame. Two years later, in 1975, gas-phase CARS thermometry was first shown by Moya *et al.* [21]. Since then, CARS spectroscopy has become a widely used technique for non-invasive measurements of species concentration and temperature in gas-phase environments. Together with the advances of laser technology, the field of CARS spectroscopy has evolved over the years. Some of the milestones in the development of this technique include nonresonant (NR) background suppression using picosecond CARS in 1980 [22] and femtosecond CARS thermometry in 1999 [23]. Even more recently, in 2006, Prince *et al.* [24] invented hybrid fs/ps CARS, which has since been extended to 1D [25] and 2D measurements [26].

1.3 Nanosecond CARS

Most of the early work in the field of gas-phase CARS spectroscopy was performed using pulsed nanosecond (ns) lasers, which have a pulse width on the order of 5-10 nanoseconds, as those were the shortest laser pulses available at the time. Nanosecond CARS has a few significant advantages over other techniques, especially with regard to temperature and species concentration measurements in unsteady combustion related environments. One of the main advantages is the strong signal that is created with this coherent technique. Even in low concentrations, sufficient signal can be created. This is in stark contrast to other techniques, such as spontaneous Raman scattering. The CARS signal can be several orders of magnitude stronger than the signal from spontaneous emission [27]. Another reason for the strength of the CARS signal is the detuning of the pump, Stokes and probe beams from any direct single-photon vibrational or electronic transition, so that absorption by the sample is minimal [10]. A further clear advantage of ns-CARS is the laser-like signal, which is coherent and highly directional. It can be sent long distances to a detector that is far away from the experiment, which usually is necessary when performing experiments inside of difficult to access engines and turbines. In addition, the directionality of the CARS signal helps to spatially filter other background interferences, like thermal emission from soot. Finally, high spatial resolution can be achieved using ns-CARS, as the signal is produced only in the small region of overlap of the three input beams. When using BOXCARS geometry, a resolution of 0.001 mm^3 is possible [28].

When the technique was first developed, narrowband pump and Stokes pulses were used and only a single ro-vibrational transition could be probed. This early

variant of ns-CARS is called scanning-CARS [9]. A full spectrum could only be resolved by scanning the frequency of either the pump or the Stokes pulse to slowly build the complete spectrum. This rather cumbersome way of acquiring a CARS spectrum was overcome by Roh *et al.* [29], who were the first to introduce broadband multiplex CARS. For this technique, a broadband Stokes pulse is used, which allows the simultaneous excitation of the full ro-vibrational transitions of an ensemble of molecules. A narrowband probe pulse can then be used to probe these Raman coherences, enabling the acquisition of single-shot spectra, a major advancement on the way to studying turbulent conditions.

The broadband approach has been extended to dual-broadband CARS, for which both the pump and the Stokes pulses are broadband. This can be used to simultaneously generate a rotational and vibrational CARS spectrum [30], or to excite the rotational transitions of different species [31]. Dual-pump [32] and even triple-pump [33] approaches have been developed for the simultaneous CARS measurement of one and two pairs of molecules respectively. Many different species have been probed with the numerous variants of ns-CARS. Of particular interest to combustion science are molecules that are present in combustion processes, such as N_2 , O_2 , H_2 , CH_4 , etc.

However, despite the usefulness of ns laser pulses for CARS spectroscopy, they have a few limitations. The main disadvantage of ns-CARS is the interference caused by the nonresonant background signal, which arises from off-resonance transitions and limits the accuracy of this technique. Polarisation methods for NR background suppression have been proposed [34, 35], but they also reduce the resonant signal significantly. In addition, windows used for high pressure studies cause polarisation rotation as a result of pressure-induced birefringence, rendering any polarisation technique ineffective [36]. The nanosecond timescale is another disadvantage of ns-CARS. On this timescale, there is a dependence on collisional dephasing, as molecular collisions happen on a much shorter timescale [10]. A further drawback is the low acquisition rates of high power ns lasers, which are only on the order of 10's of Hz; too slow to resolve the time history of temperature and species concentration in turbulent flows [37].

1.4 Picosecond CARS

The use of picosecond lasers overcomes the problem of nonresonant background interference. On the picosecond timescale, the probe beam can be delayed in time from the pump/Stokes excitation, allowing for CARS measurements at points in time at which the nonresonant signal has already decayed significantly, while the resonant CARS signal is still relatively strong. This can be done as the NR signal decays much

faster than the resonant CARS signal. After an initial proof of concept by Kamga and Sceats [22], the technique was refined to allow a reduction of the NR background of three orders of magnitude, while reducing the CARS signal only by a factor of three [38]. Quantitative thermometry [39] and species concentration measurements [40] have been performed using ps-CARS. In addition to allowing NR background-free measurements, delaying the probe pulse in time relative to the pump/Stokes excitation makes it possible to acquire CARS spectra in the time domain. This has enabled the study of Raman linewidths of individual molecular transitions using ps-CARS [41]. Accurate knowledge of these linewidths is important for understanding the time domain CARS signal, as the CARS intensities corresponding to different Raman transitions decay at different rates in time, based on the linewidths.

Despite the advantage of being able to measure CARS spectra without NR background contributions, the other limitations that apply to ns-CARS also apply to ps-CARS. Collisional energy transfer is still a problem, especially at low temperatures and long probe time delays [42]. Also the repetition rates of ps lasers with powers high enough for single-shot CARS measurements are usually only on the order of 10's of Hz [37], similar to ns lasers and too slow to time resolve rapid changes in temperature and species concentration. However, ps-CARS at a rate of 100 kHz using a burst-mode laser has recently been demonstrated [43].

1.5 Femtosecond CARS

Femtosecond CARS overcomes most of the limitations of ns and ps-CARS. High power femtosecond lasers with high repetition rates are readily available, allowing for single-shot measurements at 1 kHz or more [10]. Further, the short time scales mean that collision-free measurements are possible, at least up to a certain pressure [44]. However, while ns and ps-CARS can achieve very high spectral resolution, fs-CARS measures the signal in the time domain. This is because the laser pulses used are on the order of 100 fs in the time domain and accordingly broad in the spectral domain, resulting in a poor spectral resolution. Instead, a high resolution time domain spectrum is resolved by delaying the probe in time relative to the pump/Stokes excitation. The slope of the measured decay of the broadband CARS signal with time can then be used to extract the temperature [45].

Apart from temperature and species concentration measurements, fs-CARS has been used to accurately determine Raman linewidths [46] and other molecular parameters such as rotational constants and molecular anharmonicity [47]. Efforts have been made to achieve single-shot measurements in the time domain, using a chirped probe pulse.

This was first demonstrated by Lang and Motzkus [48], who used it for temperature measurements of H_2 . In this approach, the probe beam is chirped significantly by passing it through a long glass rod. This results in the red part of the beam interacting with the Raman coherence before the blue part. The detected frequency domain signal then represents the Fourier transform of the time domain fs-CARS signal. However, this technique is not ideal, as it is highly dependent on the probe pulse shape, hence the CARS signal is challenging to model unless the probe has been characterised to great accuracy [37]. This is further complicated in the presence of windows and pressure gradients in an experimental setup, that can distort the initial probe pulse.

1.6 Hybrid fs/ps CARS

To overcome the challenges associated with ps and fs-CARS and to combine their advantages, a technique was created that allows good temporal resolution for nonresonant background suppression while retaining enough spectral resolution for frequency domain single-shot measurements at high repetition rates. This technique is called hybrid fs/ps CARS, first developed in 2006 by Prince *et al.* [24]. It is a combination of frequency-resolved ps-CARS and time-resolved fs-CARS. Broadband fs pump and Stokes beams are used to set up the molecular coherences, which are then probed in the frequency domain using a narrowband ps probe beam that is delayed in time relative to the pump and Stokes beams. This way, the nonresonant background can be suppressed, while at the same time avoiding collisional dephasing, even at higher pressures, as long as the probe pulse time delay is short. Additionally, kHz repetition rates are possible, and because of the ps probe pulse, enough spectral resolution is maintained for accurate single-shot temperature and species concentration measurements in the frequency domain [37]. A schematic energy level diagram of this process is shown in Figure 1.3.

This hybrid fs/ps CARS approach has been successfully employed under atmospheric pressure conditions for vibrational and pure rotational thermometry and species concentration measurements at a range of temperatures [37, 49–52]. Mostly N_2 and O_2 thermometry and species ratios have been studied. The reported accuracies for thermometry using hybrid fs/ps CARS vary slightly, but most are between 1% for pure N_2 RCARS [37] and 3% for N_2/O_2 mixtures [50] of the respective thermocouple measured temperatures. Shot-to-shot precisions of single shot measurements are reported as about 2.5% [49]. The traditional point measurements have recently been extended by Bohlin *et al.* to 1D [25] line measurements and even 2D [26] measurements, though only a proof of concept has been reported for this so far. The 1D technique, however, made possible the development of two-beam hybrid fs/ps

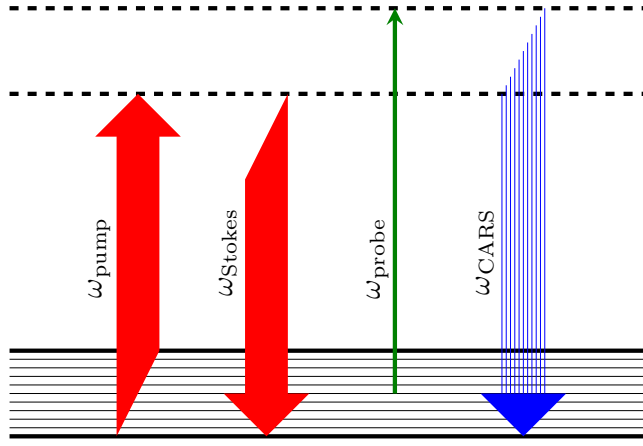


Figure 1.3: Schematic energy level diagram of the hybrid fs/ps CARS process, showing the interaction between the broadband fs pump and Stokes beams to set up many molecular Raman coherences and the narrowband ps probe beam that generates the CARS signal of all these coherences. Solid lines represent real molecular (pure rotational or ro-vibrational) energy levels and dashed lines represent virtual levels.

CARS, whereby just one fs laser pulse is used to provide the photons for both the pump and Stokes beams. Ultra short fs beams (on the order of 10's of femtoseconds) are broad enough to excite all the required rotational transitions. This not only has the advantage that the pump and Stokes photons automatically arrive at the same time, resulting in an optimal pump/Stokes excitation of the molecular coherences, it also simplifies the experimental setup, as only two beams are required.

1.7 Research Project

As discussed before, CARS is used extensively in combustion related environments. It is therefore vital to be able to measure and analyse CARS spectra under conditions present in real world applications, such as engines and turbines. Because of this, one very important aspect that needs to be addressed is high pressure. Even though the hybrid fs/ps CARS technique has shown a lot of potential at or near atmospheric pressure conditions, its usefulness at high pressures needs to be explored.

Therefore, the two main questions that need to be answered if hybrid fs/ps CARS is to be used for the studies of real combustion environments are:

- (i) Can an experimental setup be developed that allows measurements of well-resolved hybrid fs/ps CARS spectra at a range of different temperatures and pressures?
- (ii) Can a computational model and fitting routine be built to fit such experimental spectra for accurate gas-phase thermometry?

Previous research on short pulse CARS (fs-CARS and hybrid fs/ps CARS) is limited to narrow ranges of pressures and temperatures. Published studies include room temperature measurements at pressures up to 49.3 atm [53, 54] and elevated temperature measurements at low pressures (up to 885 K at up to 8.4 atm) [55]. These temperature and pressure regimes are not enough to cover the conditions present in real combustion applications and more work is needed.

The research presented in this thesis answers the above questions using two-beam hybrid rotational fs/ps CARS (HR-CARS) to measure pure rotational S-branch CARS spectra of N_2 at high pressures (up to 70 atm) and temperatures (up to 1000 K). Figure 1.4 shows the temperature and pressure regimes explored in this thesis compared with previously published studies. It can be seen that this thesis greatly extends the previous research.

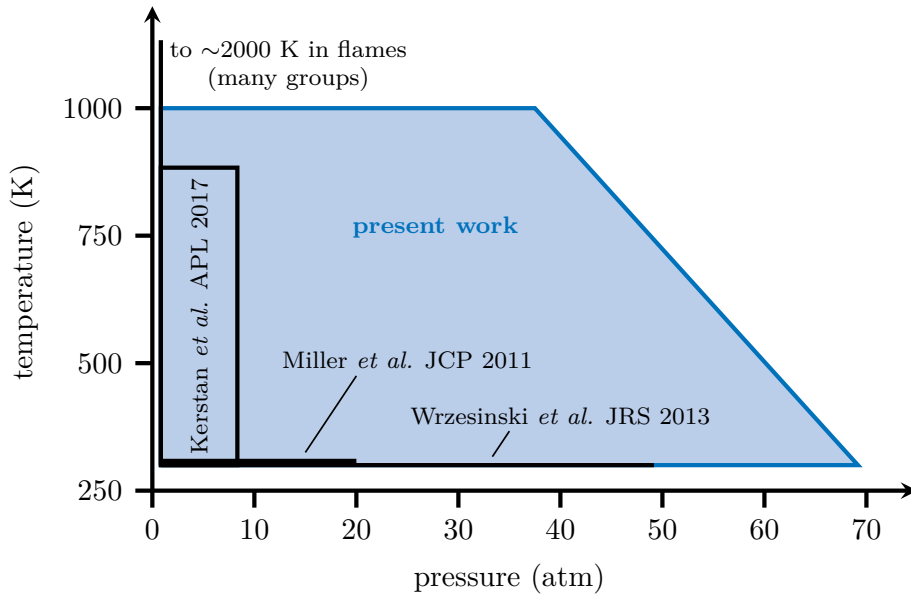


Figure 1.4: Diagram showing the temperatures and pressures that were explored for this research project using HR-CARS (blue trapezoid). Shown also are the temperature and pressure regimes of previous publications that use short pulse CARS techniques (fs-CARS and hybrid fs/ps CARS).

This project is a collaboration between Prof. Mark Linne's group at the University of Edinburgh and Dr. Christopher Kliwer's group at the Sandia National Laboratories in Livermore, CA. The experiments were conducted at the Sandia National Laboratories.

The following papers have been published as part of this research:

- T. L. Courtney, N. T. Mecker, B. D. Patterson, M. Linne & C. J. Kliwer, "Generation of narrowband pulses from chirped broadband pulse frequency mixing", *Opt. Lett.* **44**, 835-838 (2019).

- T. L. Courtney, N. T. Mecker, B. D. Patterson, M. Linne & C. J. Kliewer, "Hybrid femtosecond/picosecond pure rotational anti-Stokes Raman spectroscopy of nitrogen at high pressures (1-70 atm) and temperatures (300-1000 K)", *Appl. Phys. Lett.* **114**, 101107 (2019).
- N. T. Mecker, T. L. Courtney, B. D. Patterson, D. Escofet-Martín, B. Peterson, C. J. Kliewer & M. Linne, "Optimizing hybrid rotational femtosecond/picosecond coherent anti-Stokes Raman spectroscopy in nitrogen at high pressures and temperatures", *J. Opt. Soc. Am. B.* **37**, 1035-1046 (2020).

Chapter 2

Theoretical Background

In this chapter, the theoretical background for hybrid rotational fs/ps CARS spectroscopy will be explained in detail. The relevant mathematics and physics will be presented and discussed, to give a thorough picture of how this technique works in theory. The chapter starts with a presentation of the semi-classical, quantum mechanical basis of CARS and includes a derivation of the theoretical frequency domain CARS signal. This is followed by a discussion of the third order molecular response function. Then, the Raman transition frequencies are explained, including derivations of the required rotational and vibrational energy levels. The chapter continues with a discussion of the Raman transition linewidths, before concluding with an explanation of the Raman transition strengths. While the discussion on the quantum mechanics of CARS is very general and applies to different types of CARS transitions, the rest of the chapter is mostly specific to pure rotational S-branch transitions, which is the type of CARS transitions explored in this thesis.

Full derivations of every theoretical aspect of CARS spectroscopy would fill an entire book, so only the most important steps and equations are covered here, but numerous references to background literature containing more thorough explanations are included. The theory presented in this chapter forms the basis of the computational model, which is discussed in the next chapter.

2.1 Quantum Mechanics of CARS

Quantum mechanics forms the theoretical basis of CARS spectroscopy. In a semi-classical treatment, using the density matrix and the Schrödinger equation, together with a classical electromagnetic optical wave, the 3rd order time domain polarisation, which generates the CARS signal, can be derived. Here, only the most relevant theory is included, but a more thorough derivation of the 3rd order time domain polarisation is given in Appendix B. Additionally, Appendix A contains the basics of Dirac bra-ket notation as well as some highly useful quantum mechanical

relations and identities, that act as a supplement to the quantum mechanical discussion of CARS. The presented theory follows the book *Principles of Nonlinear Optical Spectroscopy* by Shaul Mukamel [56]. A condensed version of this is *Principles of Nonlinear Optical Spectroscopy: A Practical Approach* by Peter Hamm, also referred to as *Mukamel for Dummies* [57]. Both provide even more background theory on the quantum mechanics of CARS and related nonlinear optical spectroscopies.

A generic time-dependent wavefunction, $|\Psi(t)\rangle$ can be represented as:

$$|\Psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2.1)$$

where $|n\rangle$ forms a time-independent, orthonormal basis set and $c_n(t)$ is a time-dependent complex number. This wavefunction propagates in time as described by the time evolution operator, $\mathcal{U}(t, t_0)$:

$$|\Psi(t)\rangle = \mathcal{U}(t, t_0) |\Psi(t_0)\rangle \quad (2.2)$$

Further, the time evolution of the wavefunction is also described by the famous time-dependent Schrödinger equation:

$$\frac{d}{dt} |\Psi(t)\rangle = -\frac{i}{\hbar} H |\Psi(t)\rangle \quad (2.3)$$

where H is the Hamiltonian of the system, assumed to be time-independent. To start the quantum mechanical treatment of CARS spectroscopy, the *Density Operator* or *Density Matrix* needs to be introduced. It is defined as the outer product of a generic wavefunction (Equation 2.1):

$$\rho \equiv |\Psi\rangle\langle\Psi| = \sum_{n,m} c_n c_m^* |n\rangle\langle m| \equiv \sum_{n,m} \rho_{nm} |n\rangle\langle m|$$

$$\text{where } \rho_{nm} \equiv c_n c_m^* \quad (2.4)$$

The time dependence of the wavefunction (and therefore the density matrix) is still assumed, but not written explicitly. The fundamental advantage of the density matrix is, that for a given quantum mechanical system, the expectation value of any generic operator, A , is equal to the trace of the matrix product of this operator with the density matrix:

$$\langle A \rangle = \text{Tr}[A\rho] \quad (2.5)$$

So if the density matrix is known, then the expectation value of any other operator can be easily calculated.

Using the Schrödinger equation, the time evolution of the density operator can be found. It is given by the Liouville-Von Neumann equation, which holds true for pure as well as mixed states:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H, \rho] \quad (2.6)$$

where $[H, \rho] = H\rho - \rho H$ is a commutator. The Liouville-Von Neumann equation also holds true in the interaction picture, in which the total Hamiltonian governing a quantum system is the sum of a time-independent part, H_0 , and a very weak and time-dependent part, $H'(t)$:

$$H(t) = H_0 + H'(t) \quad (2.7)$$

In this interaction picture, the density operator is defined as:

$$\rho(t) = \mathcal{U}_0(t, t_0) \cdot \rho_I(t) \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (2.8)$$

where $\rho_I(t)$ is the interaction density operator. It describes the time evolution of the quantum system with respect to the time-dependent part of the Hamiltonian, $H'(t)$, while $\mathcal{U}_0(t, t_0)$ is the time evolution operator describing the time evolution of the system with respect to the time-independent part of the Hamiltonian, H_0 . It can be shown that the Liouville-Von Neumann equation holds true for the interaction density operator:

$$\frac{d}{dt}\rho_I(t) = -\frac{i}{\hbar}[H'_I(t), \rho_I(t)] \quad (2.9)$$

where the weak perturbation, $H'_I(t)$, in the interaction picture is defined as:

$$H'_I(t) = \mathcal{U}_0^\dagger(t, t_0)H'(t)\mathcal{U}_0(t, t_0) \quad (2.10)$$

Differential Equation 2.9 can be solved by integrating with respect to time and recursively substituting the result into itself $n - 1$ times:

$$\begin{aligned} \rho_I(t) = \rho_I(t_0) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\ [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho_I(t_0)] \cdots]] \end{aligned} \quad (2.11)$$

The result is an expression for the interaction density operator in terms of the weak interaction perturbation.

A corresponding expression for the overall density operator that is governed by the total Hamiltonian, $H(t)$, can be found by multiplying both sides by the time evolution operator, $\mathcal{U}_0(t, t_0)$ from the left and $\mathcal{U}_0^\dagger(t, t_0)$ from the right:

$$\rho(t) = \rho^{(0)}(t_0) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1$$

$$\mathcal{U}_0(t, t_0) \cdot [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho(t_0)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (2.12)$$

The physical interpretation of this is that the system with density matrix $\rho(t_0)$ propagates freely under the time-independent Hamiltonian, H_0 , until time τ_1 , as described by the time evolution operator, $\mathcal{U}_0(\tau_1, t_0)$. At time τ_1 , the system interacts with a perturbation described by $H'(\tau_1)$, after which it propagates freely again until time τ_2 and so on. These interactions can be from the left or the right, as the density matrix is the outer product of two wavefunctions (i.e. containing a ket and a bra).

$\rho^{(0)}(t_0)$ can be assumed to be an equilibrium density operator, not evolving in time under the time-independent Hamiltonian, H_0 . In this case, the starting time, t_0 can be set to minus infinity, $t_0 \rightarrow -\infty$. The density operator can then be compactly written as:

$$\rho(t) = \rho^{(0)}(-\infty) + \sum_{n=1}^{\infty} \rho^{(n)}(t) \quad (2.13)$$

with the n^{th} order density operator being:

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1$$

$$\mathcal{U}_0(t, t_0) \cdot [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho(-\infty)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (2.14)$$

Making the specification that the time-dependent part of the Hamiltonian (the perturbation) is due to an electric field, $E(t)$, for example from a laser beam in the case of CARS spectroscopy, it can be expressed as:

$$H'(t) = E(t) \cdot \mu \quad (2.15)$$

where μ is the transition dipole operator.

The n^{th} order density matrix can then be written as:

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) \\ \mathcal{U}_0(t, t_0) \cdot [\mu_I(\tau_n), [\mu_I(\tau_{n-1}), \cdots [\mu_I(\tau_1), \rho(-\infty)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (2.16)$$

where $\mu_I(t) = \mathcal{U}_0^\dagger(t, t_0) \mu \mathcal{U}_0(t, t_0)$ is the dipole operator in the interaction picture.

Of interest for CARS spectroscopy is the polarisation of a molecule, with the overall polarisation being given by the expectation value of the dipole operator. The n^{th} order polarisation of a molecule, $P^{(n)}(t)$, can be found from the expectation value (Equation 2.5) of the dipole operator, using the n^{th} order density matrix:

$$P^{(n)}(t) = \text{Tr}[\mu \rho^{(n)}(t)] \equiv \langle \mu \rho^{(n)}(t) \rangle \quad (2.17)$$

Substituting Equation 2.16 into this expression, the n^{th} order polarisation can be found to be:

$$P^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) \\ \langle \mu(t) \cdot [\mu(\tau_n), [\mu(\tau_{n-1}), \cdots [\mu(\tau_1), \rho(-\infty)] \cdots]] \rangle \quad (2.18)$$

where the fact that the trace, $\langle \cdots \rangle$, is invariant to cyclic permutations was used. Additionally, the subscript I has been dropped for simplicity, but the equation is still in the interaction picture, $\mu(t) = \mathcal{U}_0^\dagger(t, t_0) \mu \mathcal{U}_0(t, t_0)$.

At this point it is useful to define a new set of time variables according to:

$$\begin{aligned} \tau_1 &= 0 \\ t_1 &= \tau_2 - \tau_1 \\ t_2 &= \tau_3 - \tau_2 \\ &\vdots \\ t_{n-1} &= \tau_n - \tau_{n-1} \\ t_n &= t - \tau_n \end{aligned} \quad (2.19)$$

The old time variables τ_n represent fixed points in time, while the new time variables t_n represent the time intervals between these fixed points and can be thought of as continuous integration variables across time blocks from τ_n to τ_{n+1} . The relation

between the old and new time variables is illustrated in Figure 2.1. Because the choice of the time zero point is arbitrary, it was set to $\tau_1 = 0$.

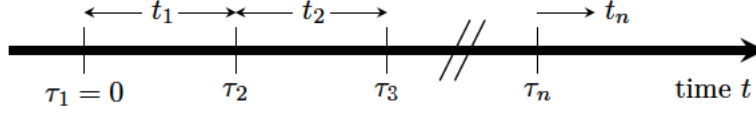


Figure 2.1: Illustration of the relation between the time variables τ_n , representing fixed points in time, and the time variables t_n , representing the time intervals between these fixed points.

Using this change of time variables, the n^{th} order polarisation (Equation 2.18), can be rewritten as:

$$\begin{aligned}
 P^{(n)}(t) &= \int_0^\infty dt_n \int_0^\infty dt_{n-1} \cdots \int_0^\infty dt_1 \\
 &\quad E(t - t_n) E(t - t_n - t_{n-1}) \cdots E(t - t_n - t_{n-1} - \cdots - t_1) \\
 &\quad S^{(n)}(t_n, t_{n-1}, \cdots, t_1)
 \end{aligned} \tag{2.20}$$

where the n^{th} order nonlinear response function is defined as:

$$\begin{aligned}
 S^{(n)}(t_n, t_{n-1}, \cdots, t_1) &= \\
 &\quad \left(-\frac{i}{\hbar} \right)^n \langle \mu(t_n + \cdots + t_1) [\mu(t_{n-1} + \cdots + t_1), \cdots [\mu(0), \rho(-\infty)] \cdots] \rangle
 \end{aligned} \tag{2.21}$$

The polarisation of a molecule depends linearly on the incident electric field. However, for very high electric fields, like the laser beams in CARS spectroscopy, higher order terms start to contribute:

$$\begin{aligned}
 P &= \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots \right) \\
 &= P^{(1)} + P^{(2)} + P^{(3)} + \cdots = \sum_{n=1}^{\infty} P^{(n)}
 \end{aligned} \tag{2.22}$$

where $\chi^{(n)}$ is the n^{th} order susceptibility of the n^{th} order polarisation, $P^{(n)}$. E is the incident electric field and ϵ_0 the permittivity of free space. For gases, however, this is not true, as they are isotropic (uniform in all directions), so they possess an inversion symmetry, which causes all the even order susceptibilities to vanish. Therefore, their lowest nonlinear order of polarisation is the 3rd order. For this reason, the 3rd order polarisation is the one that contributes most strongly to the CARS signal of gases.

From Equation 2.20 it can be seen that the 3rd order polarisation is given by:

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \quad (2.23)$$

$$E(t - t_3)E(t - t_3 - t_2)E(t - t_3 - t_2 - t_1) \cdot S(t_3, t_2, t_1)$$

with the 3rd order nonlinear response function being:

$$S(t_3, t_2, t_1) = \left(-\frac{i}{\hbar}\right)^3 \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), [\mu(t_1), [\mu(0), \rho(-\infty)]]] \rangle \quad (2.24)$$

This expression consists of eight terms, if the individual commutators are written out explicitly. It can, however, be simplified, by applying the rotating wave approximation (RWA) to the individual commutators. This approximation says that terms of the Hamiltonian that oscillate rapidly in time can be neglected, as they average out to zero, while those terms that vary slowly in time are kept. It is a valid approximation when the frequency of light interacting with a quantum system is close to a transition frequency of that system. For CARS, with a transition frequency of ω_T and a laser frequency of ω_L , with respective time dependences of $e^{-i\omega_T t}$ and $e^{-i\omega_L t} + e^{i\omega_L t}$, the assumption is that $\omega_T \approx \omega_L$. This means that terms including $\omega_T - \omega_L$ oscillate rapidly in time and can be ignored, while terms including $\omega_T + \omega_L$ vary slowly in time and are kept. When the RWA is applied to Equation 2.24, only one commutator survives, so that the 3rd order polarisation is given by:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \quad (2.25)$$

$$E(t - t_3)E(t - t_3 - t_2)E(t - t_3 - t_2 - t_1) \cdot R_4(t_3, t_2, t_1)$$

where the 3rd order nonlinear response function, $R_4(t_3, t_2, t_1)$ (the only commutator of $S(t_3, t_2, t_1)$ that survives the rotating wave approximation), is:

$$R_4(t_3, t_2, t_1) = \langle \mu(t_3 + t_2 + t_1)\mu(t_2 + t_1)\mu(t_1)\mu(0)\rho(-\infty) \rangle \quad (2.26)$$

In hybrid fs/ps CARS spectroscopy, the electric fields are due to the pump, Stokes and probe laser pulses, labelled as E_1 , E_2 and E_3 respectively. Their corresponding frequencies and wave vectors are denoted as ω_1 , ω_2 , ω_3 and k_1 , k_2 , k_3 . Using this, the

electric fields in Equation 2.25 can be expressed explicitly as:

$$E(t - t_3 - \tau) = E_3(t - t_3 - \tau)e^{i[k_3 r - \omega_3(t - t_3 - \tau)]} + c.c.$$

$$E(t - t_3 - t_2) = E_2(t - t_3 - t_2)e^{i[k_2 r - \omega_2(t - t_3 - t_2)]} + c.c.$$

$$E(t - t_3 - t_2 - t_1) = E_1(t - t_3 - t_2 - t_1)e^{i[k_1 r - \omega_1(t - t_3 - t_2 - t_1)]} + c.c. \quad (2.27)$$

where *c.c.* denotes the complex conjugate. τ in the probe electric field, E_3 , is a time delay relative to the pump and Stokes electric fields, E_1 and E_2 . It has been introduced to account for the fact that in hybrid fs/ps CARS, the probe is delayed in time from the pump/Stokes interaction, to avoid interference with the NR background signal.

It can be seen that the product of the three electric fields, $E(t - t_3)E(t - t_3 - t_2)E(t - t_3 - t_2 - t_1)$, has eight components with an overall wavevector:

$$k = \pm k_1 \pm k_2 \pm k_3 \quad (2.28)$$

However, due to the phase-matching condition (Equation 1.1), the CARS signal propagates with a wavevector:

$$k = k_1 - k_2 + k_3 \quad (2.29)$$

Hence, the only term of the product of the three electric fields that survives is:

$$\begin{aligned} & E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1) \\ & e^{i[-\omega_3(t - t_3 - \tau) + \omega_2(t - t_3 - t_2) - \omega_1(t - t_3 - t_2 - t_1)]} \end{aligned} \quad (2.30)$$

The 3rd order polarisation can then be written as:

$$\begin{aligned} P^{(3)}(t) &= \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \cdot R_4(t_3, t_2, t_1) \\ & E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1) \\ & e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_3(\omega_1 - \omega_2 + \omega_3) + t_2(\omega_1 - \omega_2) + t_1(\omega_1) + \tau(\omega_3)]} \end{aligned} \quad (2.31)$$

This expression can be simplified further by applying two assumptions. The first assumption is that the molecular response is fast compared to the pump and probe pulse coherence time scales, t_1 and t_3 . This assumption is valid as the pump and probe

pulses are detuned from any direct one-photon vibrational or electronic transition, so that molecular dephasing over the t_1 and t_3 timescales is almost instantaneous. Under this assumption, the molecular 3rd order response function can be replaced by the following:

$$R_4(t_3, t_2, t_1) \rightarrow \delta(t_3)R_4(0, t_2, 0)\delta(t_1) \quad (2.32)$$

Using this and solving the integrals over t_1 and t_3 , simplifies the 3rd order polarisation to:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_2 \cdot R_4(t_2)$$

$$E_3(t - \tau)E_2^*(t - t_2)E_1(t - t_2)$$

$$e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_2(\omega_1 - \omega_2) + \tau(\omega_3)]} \quad (2.33)$$

where $R_4(0, t_2, 0)$ is simply denoted as $R_4(t_2)$. The second assumption is that the pump and Stokes pulses are impulsive and short compared to the probe pulse, so that they can be replaced by delta functions:

$$E_1(t - t_2) \rightarrow \delta(t - t_2)$$

$$E_2^*(t - t_2) \rightarrow \delta(t - t_2) \quad (2.34)$$

This is a valid assumption for hybrid fs/ps CARS, as the pump and Stokes pulses are on the order of femtoseconds, while the probe pulse is on the order of picoseconds. Applying this assumption and carrying out the integral over t_2 , results in the following 3rd order polarisation:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 E_3(t - \tau)R_4(t)e^{-i\omega_3(t - \tau)} \quad (2.35)$$

To get from this time domain 3rd order polarisation to the corresponding frequency domain 3rd order polarisation, a simple Fourier transform needs to be performed:

$$P^{(3)}(\omega) = \mathcal{F} \left[P^{(3)}(t) \right] \quad (2.36)$$

The frequency domain CARS signal is proportional to the square of the absolute value of the frequency domain 3rd order polarisation (assuming that the probe is delayed

from the pump/Stokes excitation long enough so that no NR contribution is present):

$$I_{CARS}(\omega) \propto \left| P^{(3)}(\omega) \right|^2 \quad (2.37)$$

This frequency domain CARS signal contains the CARS spectrum of the probed molecule and this information is what is detected with a spectrometer in a hybrid fs/ps CARS experiment.

2.2 The 3rd Order Response Function

The 3rd order nonlinear response function, $R_4(t)$, from now on denoted as $R_{CARS}(t)$, is also called the *molecular response*. It describes the time-domain response of an ensemble of molecules to a pump/Stokes excitation and can be calculated from the following phenomenological expression [36]:

$$R_{CARS}(t) = \sum_{m,n} I_{m,n} \times \exp \left[\frac{t}{\hbar} \left(i\Delta E_{m,n} - \frac{\Gamma_{m,n}}{2} \right) \right] \quad (2.38)$$

where the sum is over Raman active transitions from initial state m to final state n and $\hbar = \frac{h}{2\pi}$ is the reduced Planck constant. $I_{m,n}$, $\Delta E_{m,n}$ and $\Gamma_{m,n}$ are the Raman transition strength, transition frequency and transition linewidth, respectively. For pure rotational S-branch transitions, the vibrational state of a molecule does not change, while the rotational state increases by two, so that the selection rules are $\Delta v = 0$ and $\Delta J = +2$ (where v and J are the vibrational and rotational quantum numbers respectively). The S-branch specific molecular response function therefore is:

$$R_{CARS}(t) = \sum_v \sum_J I_{v,J;v,J+2} \times \exp \left[\frac{t}{\hbar} \left(i\Delta E_{v,J;v,J+2} - \frac{\Gamma_{v,J;v,J+2}^S}{2} \right) \right] \quad (2.39)$$

where the sum is performed over rotational states J at each vibrational level v . $\Delta E_{v,J;v,J+2}$ and $\Gamma_{v,J;v,J+2}^S$ are the frequency and linewidth of a transition between rotational states J and $J + 2$ in vibrational level v respectively. $I_{v,J;v,J+2}$ is the corresponding Raman transition strength.

The quantum mechanical treatment of CARS and the 3rd order molecular response function presented above are in the time domain. However, hybrid fs/ps CARS spectra are measured in the frequency domain and the two are related by a Fourier transform (Equation 2.36). To understand the time and frequency domain molecular response functions and their Fourier transform relationship, it is useful to consider just one molecular Raman transition.

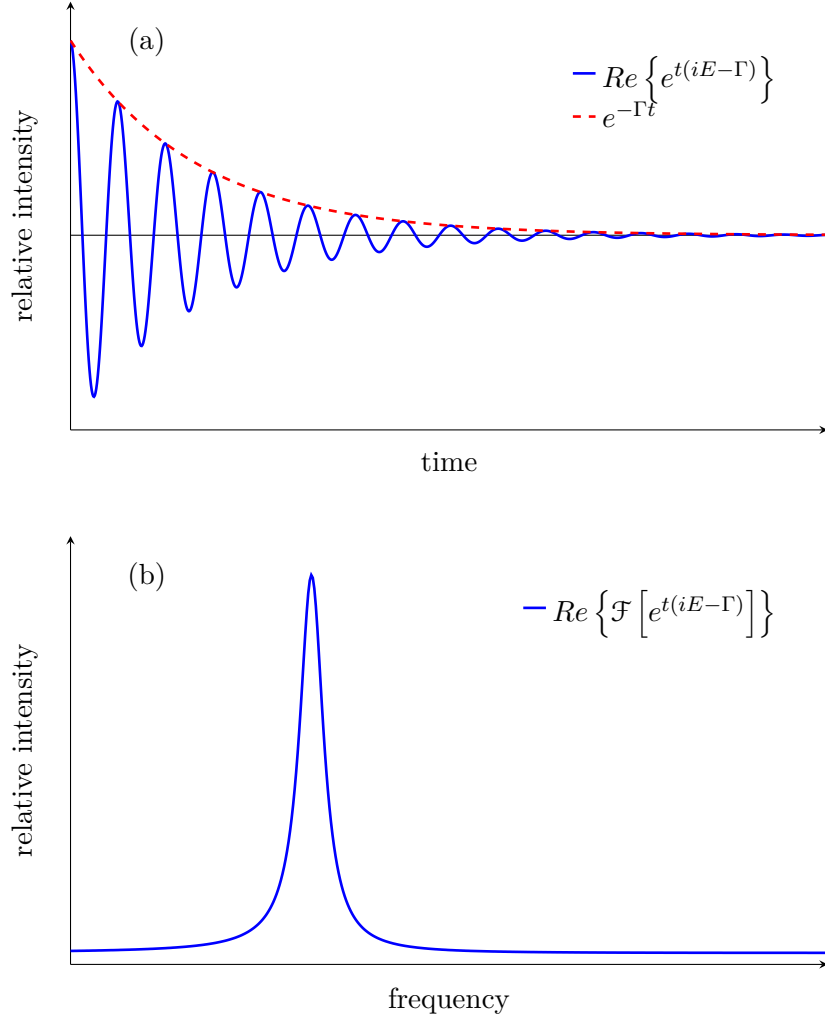


Figure 2.2: Illustration of the 3rd order molecular response function in the time and frequency domains. (a) shows the real part of the molecular response of a single transition in the time domain (blue line), which is an exponentially decaying sinusoidal oscillation. The exponential decay due to the linewidth is also shown separately (dashed red line). (b) shows the real part of the corresponding molecular response in the frequency domain, which is a Fourier transform of the time domain response and has a Lorentzian shape.

For each individual transition, the molecular response in the time domain (Equation 2.38 for the general case and Equation 2.39 for S-branch transitions), is essentially an exponentially decaying sinusoidal curve, where the frequency of the sinusoidal oscillation is based on the Raman transition frequency, $\Delta E_{m,n}$ or $\Delta E_{v,J;v,J+2}$, and the rate of exponential decay is based on the Raman transition linewidth, $\Gamma_{m,n}$ or $\Gamma_{v,J;v,J+2}^S$. The amplitude is given by the Raman transition strength, $I_{m,n}$ or $I_{v,J;v,J+2}$. This exponentially decaying sinusoidal curve is shown schematically in Figure 2.2 (a). The Fourier transform of such an exponentially decaying sinusoidal oscillation is a Lorentzian, whose position is based on the frequency of the time domain oscillation (i.e. the transition frequency) and whose width is based on the rate of the exponential time domain decay (i.e. the transition linewidth). This is shown in Figure 2.2 (b).

The relationship between the molecular response in the time and frequency domains is as follows: the larger the transition frequency, the faster the sinusoidal oscillations in the time domain and the more shifted towards higher frequency the peak of the Lorentzian in the frequency domain; the larger the linewidth, the faster the exponential decay in the time domain and the wider the Lorentzian peak in the frequency domain.

When not just one individual transition is considered, but all transitions from an ensemble of molecules, then the time domain molecular response is the sum of many exponentially decaying sinusoidal oscillations, one for each molecule. As different transitions have different transition frequencies, the oscillations corresponding to different transitions have different periods. When summed, these individual sinusoidal oscillations are mostly out of phase and there is no overall molecular response. But in regular intervals, the oscillations are in phase, so that there is a strong molecular response. For rotational S-branch transitions, this rephasing has a revival period of:

$$\tau_{full} = \frac{1}{2B_e c} \quad (2.40)$$

where B_e is the equilibrium rotational constant and c is the speed of light. For N_2 , the first full revival occurs at 8.4 ps after the initial pump/Stokes excitation. Partial rephasing of the molecular response also occurs at $1/4 \tau_{full}$, $1/2 \tau_{full}$ and $3/4 \tau_{full}$. Figure 2.3 shows the real part of the molecular response of N_2 for S-branch transitions at 293 K and 1 atm, illustrating this rephasing behaviour.

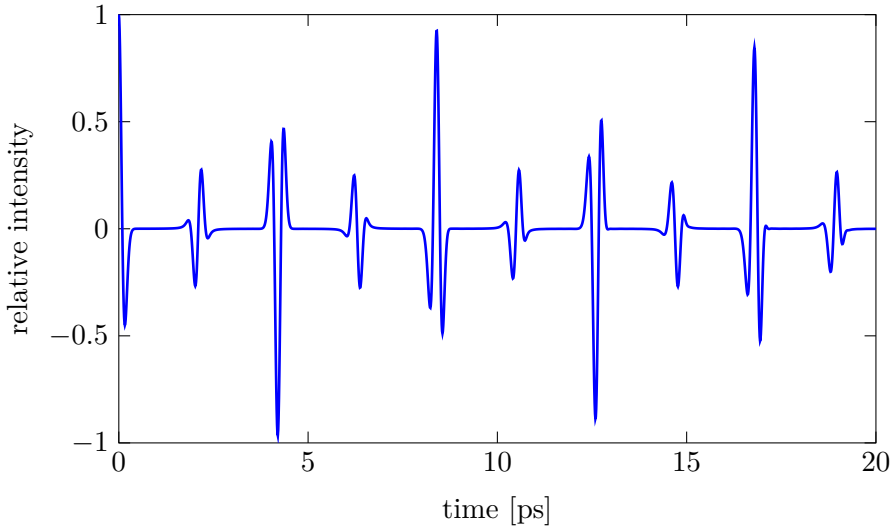


Figure 2.3: Real part of the molecular response function of N_2 in the time domain for pure rotational S-branch transitions at 293 K and 1 atm. The first full revival is at 8.4 ps (and the second at 16.7 ps). Partial rephasing occurs at $1/4 \tau_{full}$, $1/2 \tau_{full}$ and $3/4 \tau_{full}$.

Following this qualitative discussion of the molecular response, the next subchapters will explain the Raman transition frequencies, linewidths and strengths in detail.

2.3 Raman Transition Frequencies

The Raman transition frequencies (or transition energies) are the differences in energy between the final and initial states (energy levels) of the CARS transitions. As molecules are of the size of Angstroms (10^{-10} m), they are governed by quantum mechanics. This means the energies they can have are quantised and only take certain values, leading to discrete energy levels. In general, the total energy of a molecule is the sum of its electronic energy level, T_e , vibrational energy level, $G(v)$, and rotational energy level, $F(J)$:

$$T(v, J) = T_e + G(v) + F(J) \quad (2.41)$$

For hybrid fs/ps CARS, only the rotational and vibrational energy levels are of interest, and it is assumed that the molecules always remain in their ground electronic energy level. The discussion of rotational and vibrational energy levels given in this subchapter holds true for linear diatomic molecules, such as N_2 , O_2 and H_2 . Similar to the derivation of the CARS signal, only the most relevant theory will be presented here, but a more thorough derivation of rotational and vibrational energy levels can be found in Appendix C.

While most of the theory presented here follows the book *Molecular Spectra and Molecular Structure Volume I - Spectra of Diatomic Molecules* by Gerhard Herzberg [58], some derivations can be found in the books *Atoms, Molecules and Photons: An Introduction to Atomic-, Molecular- and Quantum Physics* by Wolfgang Demtröder [59] and *Rotational Spectroscopy of Diatomic Molecules* by John M Brown and Alan Carrington [60]. All three books provide very detailed discussions on molecular energy levels.

2.3.1 Rotational Energy Levels

The rotational energy levels of a diatomic molecule can be calculated by assuming a rigid rotor model, in which the two atoms of such a molecule are modelled as point masses connected by a rigid stick. This approach is justified because almost all of the mass of an atom is concentrated in its nucleus, which has a size on the order of a femtometer (10^{-15} m), about five orders of magnitude smaller than the molecule itself. A general rigid rotor model is shown in Figure 2.4. It can be seen that there are two point masses, M_1 and M_2 , separated by a fixed distance, r_e , rotating around their centre of mass. In the case of a homonuclear diatomic molecule, the two masses are equal and so their centre of mass is exactly in the middle between them.

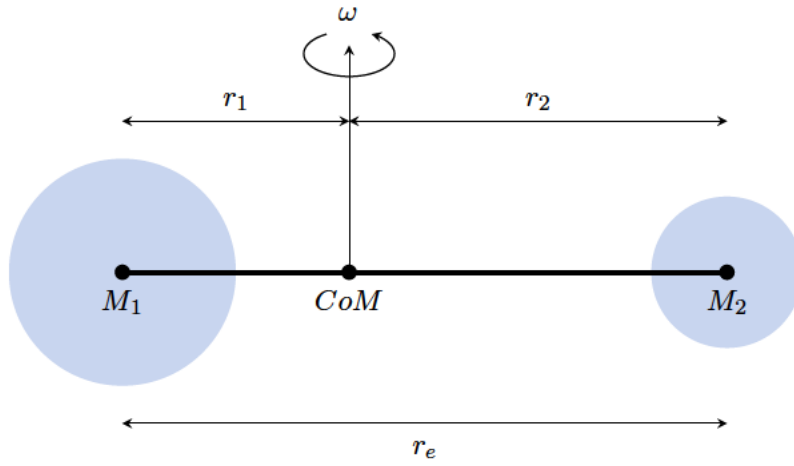


Figure 2.4: A diatomic molecule modelled as a rigid rotor. Two point masses, M_1 and M_2 , are connected by a rigid stick of length r_e and rotate around their centre of mass (CoM) at angular speed ω .

This two-body problem can be reduced to a one-body problem by using the concept of reduced mass, treating the two masses as one. The problem then becomes that of a single point mass rotating around a centre point at a fixed radius, r_e , i.e. following the surface of a sphere, as shown in Figure 2.5.

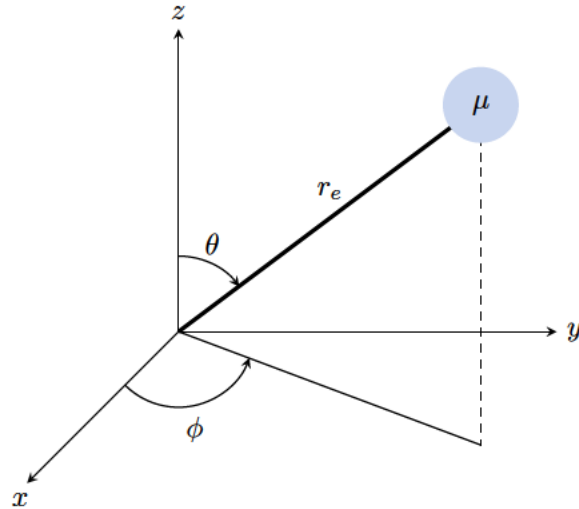


Figure 2.5: A diatomic molecule modelled as a point mass, μ , undergoing free motion around a centre point at a fixed distance, r_e .

where the reduced mass is defined as follows:

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (2.42)$$

This one-body problem can be solved using quantum mechanics. The time-independent Schrödinger equation for a single non-relativistic particle of mass μ is:

$$\hat{H}\Psi(r) = [\hat{T} + \hat{V}(r)]\Psi(r) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\Psi(r) = E\Psi(r) \quad (2.43)$$

where $\Psi(r)$ is the wavefunction of the particle and E its energy. $\hat{H}$ is the Hamiltonian consisting of a kinetic term, $\hat{T}$, and a potential term, $\hat{V}(r)$. As the radius is fixed at $r = r_e$, the potential energy of the particle is zero at this radius and infinity everywhere else. The solution of this eigenvalue equation is:

$$E(J) = \frac{\hbar^2}{2\mu r_e^2} J(J+1) \quad J = 0, 1, 2, 3, \dots \quad (2.44)$$

It can be seen that these rotational energy levels are quantised by the rotational quantum number, J . For historic reasons, the standard unit in spectroscopy is the wavenumber (cm^{-1}), so it is convenient to express the energy levels in this unit:

$$F(J) = \frac{E(J)}{hc} = \frac{\hbar}{4\pi c \mu r_e^2} J(J+1) = B_e J(J+1) \quad (2.45)$$

where the equilibrium rotational constant, B_e , in units of wavenumbers, is:

$$B_e = \frac{\hbar}{4\pi c \mu r_e^2} \quad (2.46)$$

As can be seen from Equation 2.45, the separation of adjacent rotational energy levels increases with increasing J . This is illustrated in Figure 2.6 for the first six rotational energy levels.

The rigid rotor model is a good first approximation, but to get more realistic rotational energy levels, centrifugal distortion has to be taken into account. As the molecule rotates faster, the bond between the atoms stretches and so the equilibrium separation between them, r_e , increases, altering the energy levels. When this effect is taken into account, the rotational energy levels, up to order J^3 , are given by:

$$F(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \quad (2.47)$$

with the rotational constants defined as:

$$B_e = \frac{\hbar}{4\pi c \mu r_e^2} \quad D_e = \frac{\hbar^3}{2\pi c k \mu^2 r_e^6} \quad H_e = \frac{3\hbar^5}{4\pi c k^2 \mu^3 r_e^{10}} \quad (2.48)$$

where k is the force constant of the restoring force that tries to keep the atoms of the molecule at their equilibrium separation.

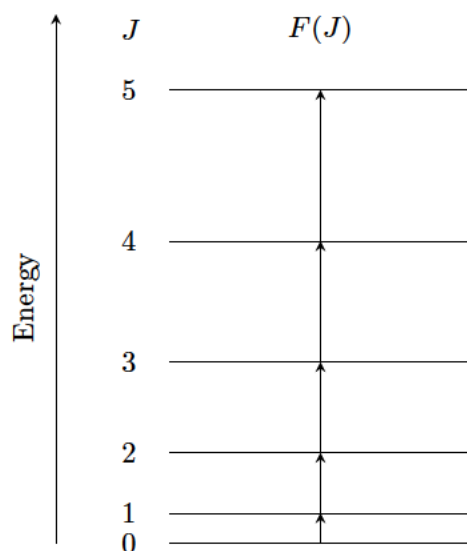


Figure 2.6: Illustration of the first six rotational energy levels of a diatomic molecule, showing the increasing energy separation between adjacent levels with increasing rotational quantum number, J .

2.3.2 Vibrational Energy Levels

Analogous to the rigid rotor model, a diatomic molecule can be represented in a simple way to calculate its vibrational energy levels. In the case of vibrations, the molecule is modelled as two point masses connected by a spring undergoing simple harmonic motion about their equilibrium separation, r_e , as shown in Figure 2.7.

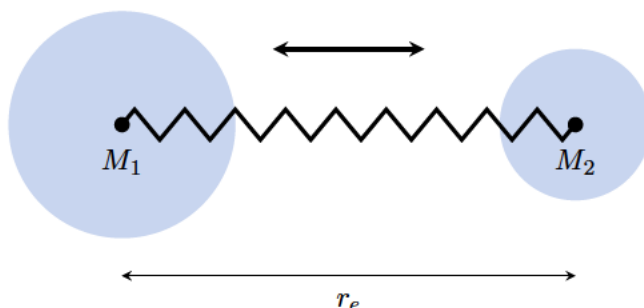


Figure 2.7: A diatomic molecule modelled as a simple harmonic spring oscillator. Two point masses, M_1 and M_2 , are connected by a spring and undergo simple harmonic motion about their equilibrium separation, r_e .

Like the rigid rotor model, this spring model can be simplified to a one-body problem using the concept of reduced mass. The molecule is then represented by a point mass attached to a spring, with the other end of the spring fixed to a wall. The point mass undergoes simple harmonic motion about its equilibrium distance from the wall. This is illustrated in Figure 2.8.

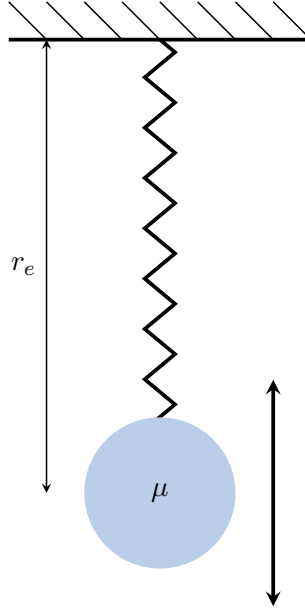


Figure 2.8: A diatomic molecule modelled as a point mass, μ , attached to a spring with the other end of the spring attached to a fixed wall, undergoing simple harmonic motion about its equilibrium distance from the wall, r_e .

As with the rotational levels, the Schrödinger equation (Equation 2.43) can be used to solve this one-body problem, to find the energy levels. However, for the vibrational case, the potential is different. Assuming a linear restoring force, $\vec{F}$, on the point mass, the potential is parabolic and only depends on the distance from the equilibrium position, r :

$$\vec{F} = -kr\hat{r} \quad V(r) = \frac{1}{2}kr^2 = \frac{1}{2}\mu\omega^2r^2$$

$$\text{where} \quad \omega = \sqrt{\frac{k}{\mu}} \quad (2.49)$$

where k is the "spring constant" (the force constant of the restoring force that tries to keep the point mass at its equilibrium position) and ω the frequency of oscillation. Using this potential, the Schrödinger equation becomes:

$$\hat{H}\Psi(r) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}\mu\omega^2r^2 \right] \Psi(r) = E\Psi(r) \quad (2.50)$$

Solving this leads to the vibrational energy levels, quantised by the vibrational quantum number, v :

$$E(v) = \left(v + \frac{1}{2} \right) \hbar\omega \quad v = 0, 1, 2, 3, \dots \quad (2.51)$$

Expressed in units of wavenumber, the energy levels are given by:

$$G(v) = \frac{E(v)}{hc} = \omega_e \left(v + \frac{1}{2} \right) \quad \omega_e = \frac{\omega}{2\pi c} \quad v = 0, 1, 2, 3, \dots \quad (2.52)$$

where ω_e is the fundamental vibrational constant. It can be seen from Equation 2.51 that unlike the rotational energy levels, the vibrational energy levels are spaced equally, with an energy difference of $\hbar\omega$ between adjacent levels. This is shown in Figure 2.9.

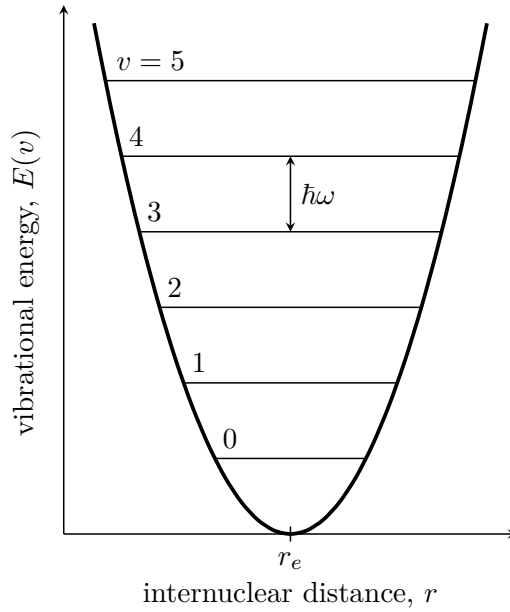


Figure 2.9: Illustration of the first six vibrational energy levels of a diatomic molecule, assuming a parabolic potential. Adjacent energy levels have a constant energy separation of $\hbar\omega$.

For low vibrational levels, the approximation of a harmonic potential is accurate, but the true potential of a diatomic molecule exhibits anharmonicity, which needs to be taken into account for higher vibrational levels. This can be done by adding cubic and higher order terms to the quadratic potential used in the Schrödinger equation (Equation 2.50). Solving this new Schrödinger equation with the anharmonic potential results in the following vibrational energy levels:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \mathcal{O}(v^4) \quad (2.53)$$

where $\omega_e x_e$ and $\omega_e y_e$ are the vibrational constants of second and third order in v , respectively. A particularly useful anharmonic potential is the so-called *Morse potential*, defined as:

$$V_{Morse}(r) = D_e \left[1 - e^{-a(r-r_e)} \right]^2 \quad (2.54)$$

If this is used as the potential in the Schrödinger equation, the solution is:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \quad (2.55)$$

This is the same as the solution to a generic anharmonic potential, truncated at the term that is quadratic in v . The second order vibrational constant, $\omega_e x_e$, is defined as:

$$\omega_e x_e = \frac{\hbar \omega^2}{8\pi c D_e} = \omega_e^2 \frac{hc}{4D_e} \quad (2.56)$$

with D_e being the binding energy of the molecule. In this anharmonic approximation, the separation of the vibrational energy levels is not constant anymore, but decreases with increasing v , as is shown schematically in Figure 2.10.

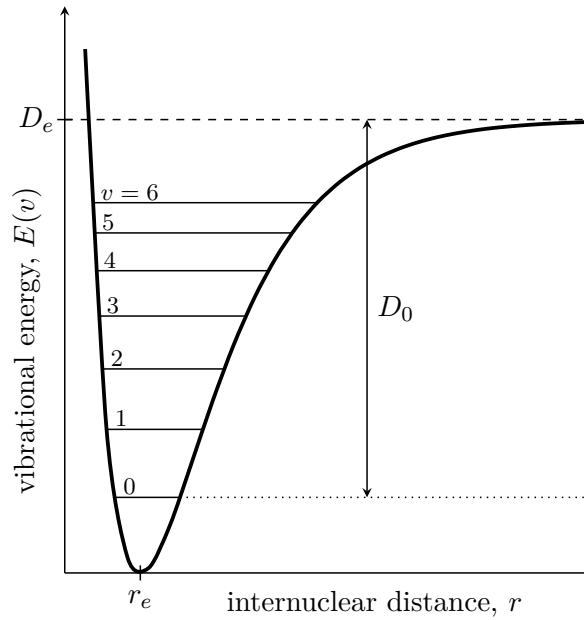


Figure 2.10: Illustration of the first seven vibrational energy levels of a diatomic molecule, assuming an anharmonic Morse potential. Adjacent energy levels have a decreasing energy separation with increasing v . D_0 and D_e are the dissociation and binding energies of the molecule, respectively.

2.3.3 Rotational-Vibrational Energy Levels

The above treatment of a diatomic molecule has completely neglected the fact that rotations and vibrations occur at the same time, i.e. as the molecule rotates it vibrates as well, and thus there is an interaction between the two. Typically, a molecule undergoes several vibrations (about 5-100) during a single rotation [59]. This is also the reason why the above treatment of rotations and vibrations independent of each other is valid up to a certain degree of accuracy. It is called the Born-Oppenheimer

approximation, which allows the total energy of a molecule's vibration and rotation to be expressed as the simple sum of the energies of these two different types of motion. But in order to obtain more realistic energy levels, the interaction between rotations and vibrations needs to be accounted for.

The stronger the vibration (i.e. the higher the vibrational level), the more the equilibrium distance between the atoms varies. It can be shown that this affects the rotational constants so that they are not constant anymore, but instead depend on the vibrational level. Assuming a generic anharmonic potential, the rotational constants become:

$$\begin{aligned} B_v &= B_e - \alpha_e \left(v + \frac{1}{2}\right) + \gamma_e \left(v + \frac{1}{2}\right)^2 + \mathcal{O}(v^3) \\ D_v &= D_e + \beta_e \left(v + \frac{1}{2}\right) + \delta_e \left(v + \frac{1}{2}\right)^2 + \mathcal{O}(v^3) \end{aligned} \quad (2.57)$$

where α_e , β_e , γ_e and δ_e are the rotational-vibrational interaction constants. If a Morse potential is assumed instead, the result is the same, truncated at order v :

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) \quad D_v = D_e + \beta_e \left(v + \frac{1}{2}\right) \quad (2.58)$$

By combining all of the above results, an equation for the energy levels of a diatomic molecule can be found, that includes centrifugal distortion, anharmonicity and vibrational-rotational interaction:

$$\begin{aligned} T(v, J) &= T_e + G(v) + F(J) \\ &= T_e + \left[\omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \mathcal{O}(v^4) \right] \\ &\quad + \left[B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 - \mathcal{O}(J^4) \right] \end{aligned} \quad (2.59)$$

Assuming a Morse potential and truncating the centrifugal distortion correction at order J^2 , this is reduced to:

$$T(v, J) = T_e + \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 \quad (2.60)$$

The definitions of the various rotational and vibrational constants are summarised below:

$$\begin{aligned}
\omega_e &= \frac{\omega}{2\pi c} & \omega_e x_e &= \frac{\hbar \omega^2}{8\pi c D_e} \\
B_v &= B_e - \alpha_e \left(v + \frac{1}{2} \right) & D_v &= D_e + \beta_e \left(v + \frac{1}{2} \right) \\
B_e &= \frac{\hbar}{4\pi c \mu r_e^2} & D_e &= \frac{\hbar^3}{2\pi c k \mu^2 r_e^6} \tag{2.61}
\end{aligned}$$

Equations 2.60 and 2.61 can be used to calculate the ro-vibrational energy levels of a diatomic molecule with high accuracy. For S-branch transitions, with selection rules $\Delta v = 0$ and $\Delta J = +2$, the Raman transition frequencies, $\Delta E_{v,J;v,J+2}$, i.e. the energy differences between rotational levels $J + 2$ and J in vibrational level v , are calculated according to:

$$\begin{aligned}
\Delta E_{v,J;v,J+2} &= T(v, J + 2) - T(v, J) \\
&= 2B_v(2J + 3) - 4D_v(2J + 3)(J^2 + 3J + 3) \tag{2.62}
\end{aligned}$$

2.4 Raman Transition Linewidths

The Raman transition linewidths, $\Gamma_{m,n}$ in Equation 2.38 and $\Gamma_{v,J;v,J+2}^S$ (for S-branch transitions) in Equation 2.39, are primarily a result of collision broadening. This arises because of inelastic collisions between molecules, causing an energy transfer between them. This energy transfer is mostly rotational, as adjacent vibrational and electronic energy levels have large spacings in comparison. Collision broadened linewidths of a specific molecule depend on several factors, such as its collision partner, temperature and pressure. It should be noted, that Doppler broadening also exists, due to positive and negative Doppler shifts of molecules moving towards and away from a detector respectively. However, for most molecules under atmospheric pressure or higher, including N₂, the contribution of Doppler broadening to the total linewidths is many orders of magnitude smaller than that of collision broadening and can therefore be ignored [36].

The Raman linewidths can be found experimentally, for example by using ps-CARS. For this approach, CARS spectra are recorded at different probe pulse time delays and the decay of the signal of each individual line (corresponding to a particular Raman

transition) with time can be used to infer the linewidth of that transition. Kliewer *et al.* [61] have used this method to measure N₂-N₂ S-branch linewidths. Part of their published results is given in Figure 2.11, which shows the linewidths of several Raman transitions at different temperatures.

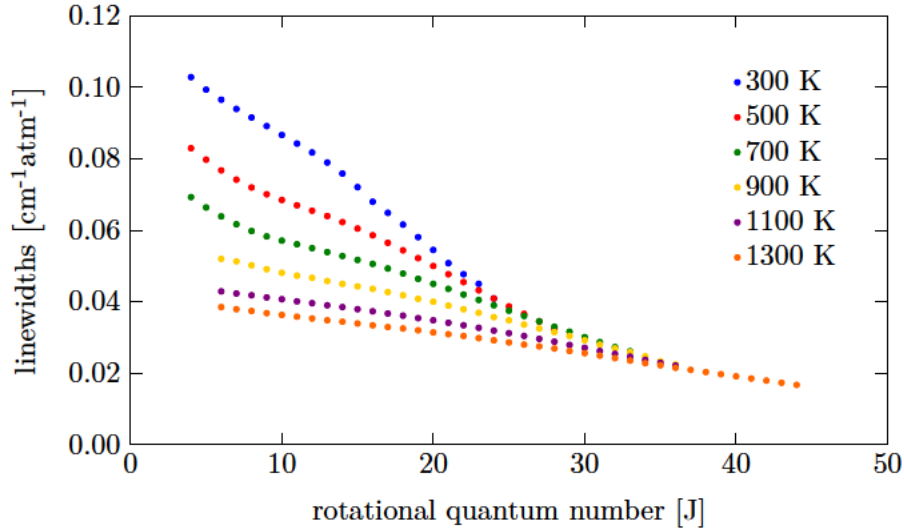


Figure 2.11: S-branch linewidths of N₂-N₂ collisions at different temperatures, as measured by Kliewer *et al.* [61] using ps-CARS. The rotational quantum number on the x-axis is the final state of the transition $J \rightarrow J + 2$.

It can be seen that the linewidths decrease with increasing rotational level and also with increasing temperature. The linewidths are linearly proportional to pressure, so to obtain linewidths at a certain pressure, the data presented in Figure 2.11 simply needs to be multiplied by that pressure (in atm).

Instead of experimental measurements, theoretical models can also be used to obtain the required Raman linewidths. Several of these models, also called scaling laws, have been proposed to calculate the linewidths of different molecules at different conditions [62, 63]. The scaling laws that have been developed can be divided into two main categories: statistical and angular momentum scaling laws [46]. Statistical scaling laws are based on the amount of energy transferred during an inelastic collision, while angular momentum scaling laws are based on angular momentum transfer during the inelastic scattering process.

A commonly used statistical linewidth model is the so-called Modified Exponential Gap (MEG) model. Using this model, the energy transition rate of an upward transition from an initial rotational state i to a final rotational state f (such that $i < f$), with

respective rotational quantum numbers J_i and J_f , is given by:

$$\Gamma_{f,i} = P\alpha f(T) \left(\frac{T}{T_0}\right)^{-n} \left[\frac{1 + \frac{AE_i}{k_B T \delta}}{1 + \frac{AE_i}{k_B T}} \right]^2 \exp\left(-\beta \frac{(E_f - E_i)}{k_B T}\right) \quad f \neq i$$

$$f(T) = \frac{1 - e^{-m}}{1 - e^{-m \frac{T}{T_0}}} \quad \text{for } N_2 - N_2 \text{ collisions}$$

$$f(T) = 1 \quad \text{for } O_2 - O_2 \text{ and } O_2 - N_2 \text{ collisions} \quad (2.63)$$

where P is the pressure in atm, α is an adjustable parameter in $\text{cm}^{-1}\text{atm}^{-1}$, T is the temperature in K, $T_0 = 295$ K, n is a unitless and species-dependent constant, to account for the temperature dependence of the rotational energy transfer, m , δ and β are adjustable and unitless scaling parameters, k_B is the Boltzmann constant, A is another species-dependent constant and E_f and E_i are the energies of the final and initial energy level of the transition, respectively. The adjustable parameters, α , β , δ and m can be optimised by fitting experimentally measured linewidths to this model. Note that α in the context of the MEG model is different from the probe beam chirp parameter α , which will be introduced in Chapter 3.

Downward transition rates, from state f to state i , are found using the detailed balance principle [49]:

$$\Gamma_{i,f} = \Gamma_{f,i} \frac{2J_i + 1}{2J_f + 1} \exp\left(\frac{(E_f - E_i)}{k_B T}\right) \quad f \neq i \quad (2.64)$$

Equations 2.63 and 2.64, can be used to compute a complete transition rate matrix, also called Γ -matrix, containing the transition rates of all possible rotational transitions between initial states i and final states f . The diagonal elements of this Γ -matrix are found by summing each column of upward and downward transitions:

$$\Gamma_f = \sum_{i \neq f} \Gamma_{i,f} \quad (2.65)$$

At pressures where line mixing is negligible, these diagonal elements are the Q-branch Raman transition linewidths. The corresponding S-branch linewidths ($i = J$ and $f = J + 2$) can be calculated from these Q-branch linewidths, under the assumption that they are not significantly different from each other [63]:

$$\Gamma_{v,J;v,J+2}^S = \frac{1}{2} (\Gamma_{J,J} + \Gamma_{J+2,J+2}) \quad (2.66)$$

These S-branch linewidths can then be used in the molecular response function (Equation 2.39). At very high pressures, collisions between molecules happen on

increasingly shorter time scales, leading to line-mixing, which affects the transition linewidths. This can be accounted for theoretically using the G-matrix formalism [64]. However, it was found that for pure rotational fs/ps CARS, line-mixing is not significant even at 70 atm (the highest pressure that was achieved experimentally), therefore it is not included in the computational CARS model (see Chapter 3).

2.5 Raman Transition Strengths

The Raman transition strengths, $I_{m,n}$ in Equation 2.38 and $I_{v,J;v,J+2}$ (for S-branch transitions) in Equation 2.39, are proportional to the Raman cross-section and the normalised population difference between the initial and final state of the respective molecular transition [36]. For S-branch transitions, the transition strengths are proportional to:

$$I_{v,J;v,J+2} \propto \left(\frac{\partial \sigma}{\partial \Omega} \right) \Delta \rho_{v,J;v,J+2} \quad (2.67)$$

where $\left(\frac{\partial \sigma}{\partial \Omega} \right)$ is the Raman cross-section and $\Delta \rho_{v,J;v,J+2}$ is the normalised population difference. The Raman cross-section itself is the product of several factors. For rotational S-branch transitions it is given by [37]:

$$\left(\frac{\partial \sigma}{\partial \Omega} \right) \propto \frac{4}{45} (\gamma'_v)^2 b_{J,J+2} F_{rot}(J) \quad (2.68)$$

where γ'_v is the polarisation anisotropy, $b_{J,J+2}$ is the Placzek-Teller coefficient and $F_{rot}(J)$ is the Herman-Wallis factor. The following subsections will explain each of these three factors, and also the population difference.

2.5.1 Population Difference

The population of a specific ro-vibrational state is a function of temperature, described by the famous Boltzmann distribution [65]. The percentage of molecules in a certain ro-vibrational state, v, J , at a temperature, T , is given by:

$$\rho_{v,J} = \frac{N_{v,J}}{N_{tot}} = \frac{(2J+1) \exp\left(-\frac{E_{v,J}}{k_B T}\right)}{Z_{v,J}} \quad (2.69)$$

where the partition function, $Z_{v,J}$, is the sum over all states:

$$Z_{v,J} = \sum_v \sum_J (2J+1) \exp\left(-\frac{E_{v,J}}{k_B T}\right) \quad (2.70)$$

$N_{v,J}$ is the number of molecules in state v, J and N_{tot} is the total number of molecules. $E_{v,J}$ is the energy of the ro-vibrational state v, J , given by Equations 2.60 and 2.61. The factor $2J + 1$ accounts for the degeneracy of each rotational state. Figure 2.12 shows the Boltzmann population distribution of the rotational states of N_2 in the first three vibrational energy levels, at room temperature (293 K) and 1000 K. These temperatures correspond to the lowest and highest temperatures that were explored experimentally using HR-CARS for the research presented in this thesis.

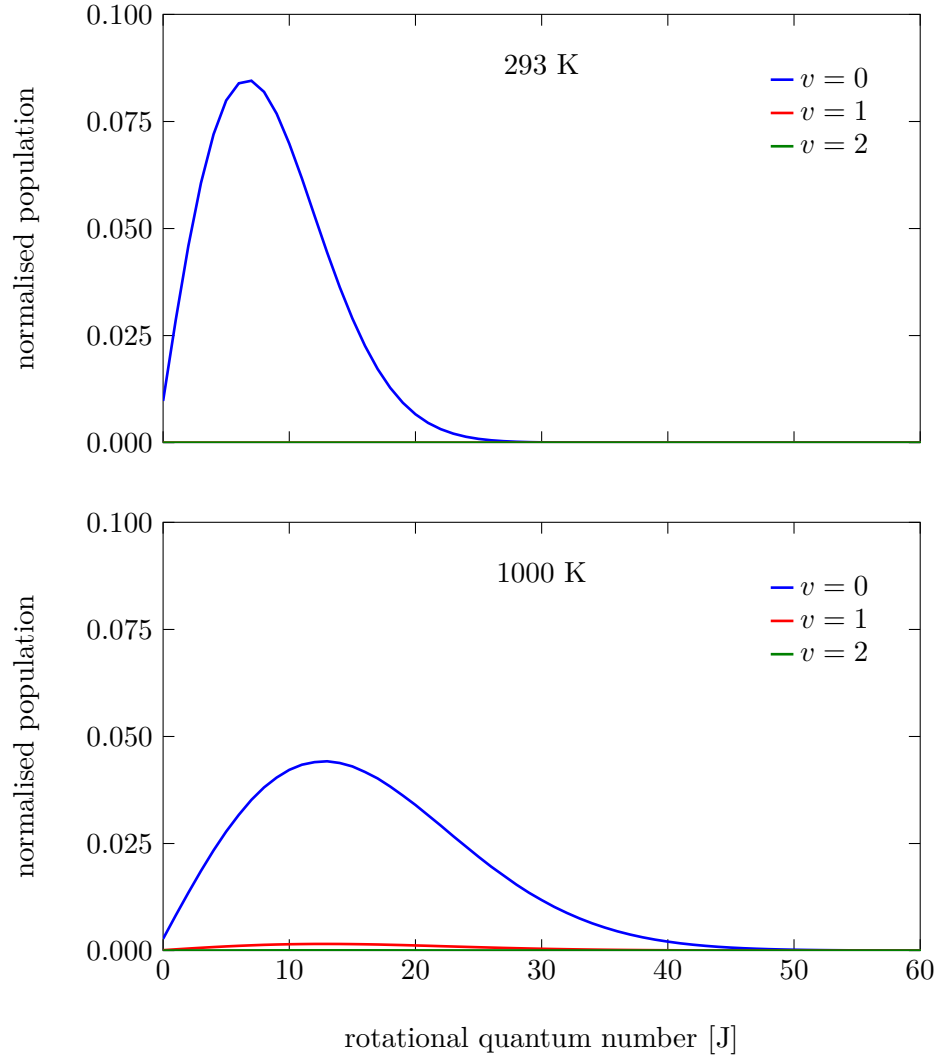


Figure 2.12: Boltzmann population distribution of the rotational states of N_2 in the first three vibrational energy levels, at room temperature (293 K) and 1000 K.

It can be seen that at room temperature, only the first 30 rotational levels of the ground vibrational level ($v = 0$) have a significant population. The combined percentage of molecules in the first ($v = 1$) and second ($v = 2$) vibrational levels is just 0.001%. At 1000 K the rotational population of the ground vibrational level is shifted towards higher rotational levels, and the first 50 are significantly populated. With

96.5%, most of the molecules remain in the ground vibrational state, but at this higher temperature, 3.4% of the molecules are in the first excited vibrational state and 0.1% in the second. This explains why pure rotational CARS is sensitive at low and medium temperatures, when there are large shifts in the rotational but not the vibrational population, while vibrational CARS only becomes sensitive at higher temperatures, when a significant number of molecules are in first and subsequent vibrational levels.

The normalised population difference, $\Delta\rho_{v,J;v,J+2}$, is the difference between the normalised population of initial and final ro-vibrational states, v, J and $v, J + 2$ respectively. Explicitly including the rotational nuclear degeneracy, g_J , it is given by:

$$\begin{aligned}\Delta\rho_{v,J;v,J+2} &= \frac{\rho_{v,J}}{Z_{v,J}} - \frac{2J+1}{2J+5} \frac{\rho_{v,J+2}}{Z_{v,J}} \\ &= \frac{g_J(2J+1)}{Z_{v,J}} \left[\exp\left(-\frac{E_{v,J}}{k_B T}\right) - \exp\left(-\frac{E_{v,J+2}}{k_B T}\right) \right]\end{aligned}\quad (2.71)$$

where the rotational nuclear degeneracy is also included in the calculation of the partition function. This rotational nuclear degeneracy is different for different molecules, depending on their nuclear spin and if their total wavefunction is even or odd. For N_2 , $g_J = 6$ for even J and $g_J = 3$ for odd J , so that the intensity ratio of even to odd Raman transition strengths is 2:1. For O_2 , $g_J = 0$ for even J and $g_J = 1$ for odd J , so that only transitions from odd rotational levels are present.

2.5.2 Polarisation Anisotropy

The anisotropic component of the polarisability of an ensemble of molecules accounts for the space averaging of the polarisability ellipsoid of this ensemble. It is dependent on the vibrational level according to [66]:

$$\gamma'_v = \epsilon_e + \epsilon'_e r_e \left[\frac{3B_e}{\omega_e} + \frac{\alpha_e}{2B_e} \right] \left(v + \frac{1}{2} \right) \quad (2.72)$$

where ϵ_e is the equilibrium polarisation anisotropy and ϵ'_e is the first derivative of the polarisation anisotropy with respect to the internuclear separation. r_e is the equilibrium internuclear distance, α_e is the first rotational-vibrational interaction constant, B_e is the equilibrium rotational constant and ω_e is the fundamental vibrational constant, as defined before.

2.5.3 Placzek-Teller Coefficient

As discussed in the section on the rotational energy levels above, when a molecule rotates faster (i.e. when its rotational quantum number increases), there is centrifugal distortion, which results in an increasing internuclear separation and affects the energy of the rotational levels. However, this centrifugal distortion does not only affect the energy, but it also changes the polarisability of the molecule, which in turn changes the Raman transition strengths. This dependence of the Raman transition strengths on the rotational level is expressed through the Placzek-Teller coefficient, first described by Placzek and Teller in 1933 [67]. The Placzek-Teller coefficient, which is different for different types of transitions, is given by [36]:

$$\begin{aligned}
 b_{J,J+2} &= \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} & (S - branch) \\
 b_{J,J-2} &= \frac{3J(J-1)}{2(2J+1)(2J-1)} & (O - branch) \\
 b_{J,J} &= \frac{J(J+1)}{(2J-1)(2J+3)} & (Q - branch)
 \end{aligned} \tag{2.73}$$

2.5.4 Herman-Wallis Factor

Similar to the change in polarisability (and hence the Raman transition strengths) due to the rotation of a molecule, there is also a change in polarisability due to the interaction between rotations and vibrations. This interaction, which arises from there being many vibrations during a single rotation, has already been discussed with respect to the effect it has on the ro-vibrational energy levels of a diatomic molecule. Its effect on the polarisability of a molecule was first studied by Herman and Wallis [68], who introduced the Herman-Wallis factor to account for the change in the Raman transition strengths due to the change in polarisability as a result of this ro-vibrational interaction.

Different forms of the Herman-Wallis factor have been suggested in the literature, [69, 70], depending on the exact assumptions made. The factor proposed by Tipping and Ogilvie [71] was found to be closest to experimental results of rotational CARS

experiments [72]. This particular version of the Herman-Wallis factor is:

$$F_{rot}(J) = \left[1 + \kappa^2 \left(\frac{p_1}{p_0} \right) (J^2 + 3J + 3) \right]^2$$

$$where \quad \kappa = \frac{2B_e}{\omega_e} \quad (2.74)$$

$\frac{p_1}{p_0}$ is the ratio between the first two coefficients of the anisotropic polarisability expansion.

Chapter 3

Computational Model

This chapter explains the details of the computational CARS code that has been developed to model theoretical CARS spectra at different pressures and temperatures and fit them to experimental ones. The chapter starts with an overview of the entire model, introducing all the different subcodes and explaining the interactions between them. Then, each of these subcodes is discussed in detail, including the exact equations and constants used. At the end of the chapter, model spectra of pure N₂, pure O₂ and N₂/O₂ mixtures at different pressure and temperature conditions are shown, to illustrate the capability of the model.

The physics and theory behind this CARS model are the same as presented in the previous chapter and will not be discussed again. The code was built for modelling hybrid rotational fs/ps CARS spectra of S-branch transitions of pure N₂, pure O₂ and mixtures of N₂ and O₂. It was programmed using MATLAB, and all relevant MATLAB codes for this model and the accompanying fitting routine can be found in Appendix D.

3.1 Overall Structure

The CARS model for simulating theoretical HR-CARS spectra and at the same time fitting them to experimental spectra is distributed over several subcodes, that each perform part of the overall calculations. Input and output parameters are passed between these subcodes. The complete structure of the computational model is shown in Figure 3.1, including all subcodes and their interactions.

As can be seen, the code is accessed and operated through the *Edinburgh CARS Code* subcode. All relevant input parameters are passed to the code here, including the experimental data (e.g. the CARS spectrum to be fit and its corresponding NR argon spectrum). Further, the fixed parameters (those that do not change during a fit) are set, such as the type of molecule(s) to be modelled and fit (N₂, O₂ or N₂/O₂). The last set of parameters that is input to the *Edinburgh CARS Code* are the fitting parameters

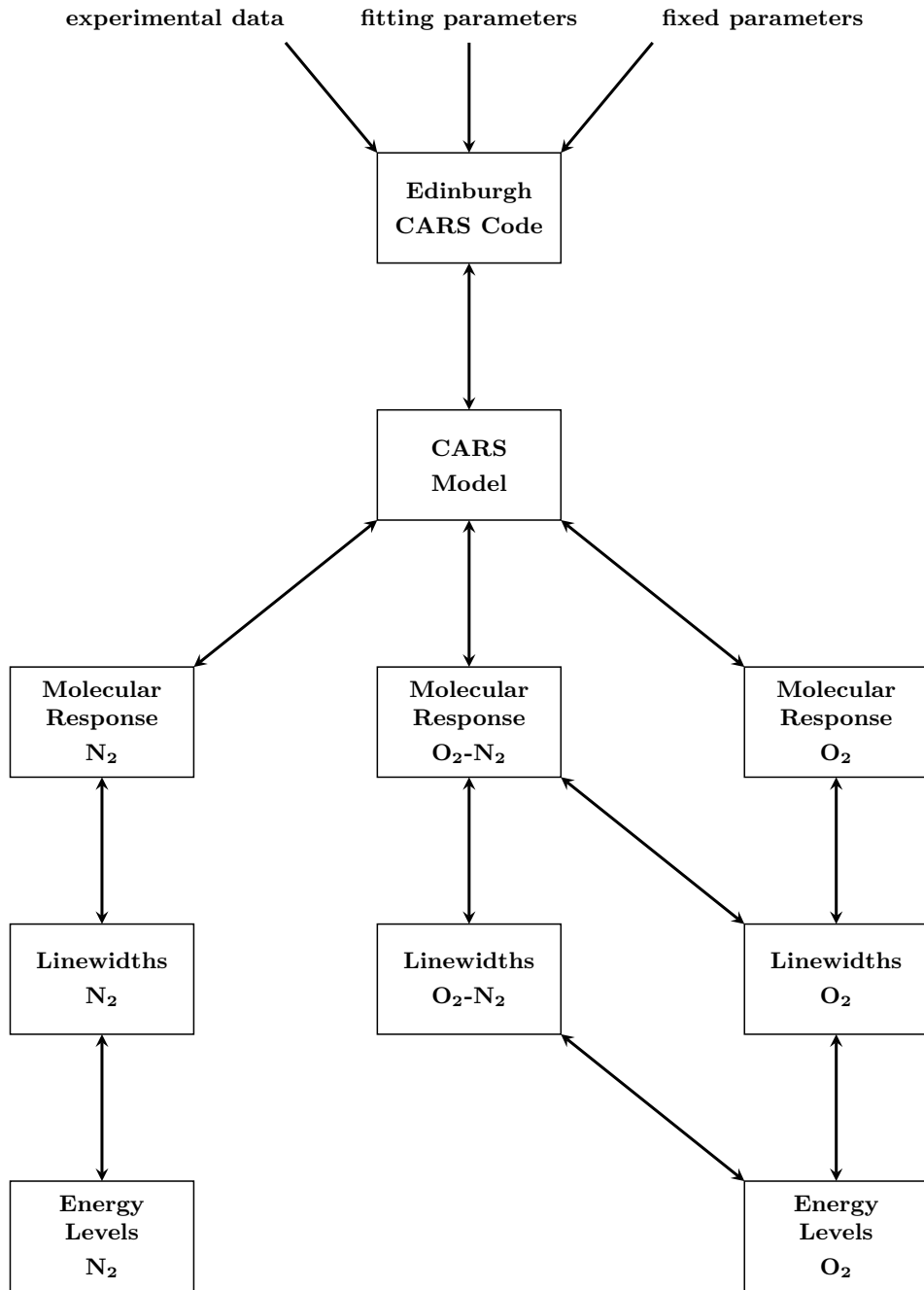


Figure 3.1: Schematic diagram of the computational CARS code for modelling and fitting HR-CARS spectra of rotational S-branch transitions of pure N₂, pure O₂ and N₂/O₂ mixtures. Shown are all subcodes and the flow of information between them, depicted by arrows. Arrows pointing down represent input information (parameters needed by a subcode to perform its calculations), arrows pointing up represent output information, that is passed to the next subcode for further processing.

(those that change during a fit). These include, for example, the temperature and probe pulse time delay. After all parameters have been input and the code is executed, a nonlinear least-squares fitting routine function, called *lsqcurvefit*, is started.

Upon execution of the fitting routine, the fixed and fitting parameters are passed to a subcode called *CARS Model*, which, based on those parameters, generates a theoretical CARS spectrum. This model spectrum is passed back to the *Edinburgh CARS Code*, where the nonlinear fitting routine compares it to the experimental spectrum that is to be fit. The fitting parameters are then automatically adjusted, and the new fitting parameters are passed back to the *CARS Model*. There, a new model spectrum is generated and passed back to the *Edinburgh CARS Code* for comparison with the experimental spectrum. This loop continues, until the difference between the modelled and experimental CARS spectra is small enough, at which point the fitting loop stops. The best fit parameters, including the desired best fit temperature, are then displayed.

The *CARS Model* itself makes use of further subcodes to generate the model spectrum, as shown in Figure 3.1. In the case of modelling a pure N₂ spectrum, the relevant model parameters are passed down to a *Molecular Response N₂* code. From there, they are passed down further to a *Linewidths N₂* code, and from there to an *Energy Levels N₂* code, which is in the last layer of subcodes. This *Energy Levels N₂* code generates the transition frequencies and passes them back up to the *Linewidths N₂* code, which generates the transition linewidths. Once calculated, the transition frequencies and linewidths are passed back to the *Molecular Response N₂* code, which generates the corresponding molecular response (based on Equation 2.39). This is then passed back to the *CARS Model*, and used for the calculation of the model spectrum.

In the case of modelling a pure O₂ spectrum, the computational algorithm is the same as for pure N₂, using the corresponding *Molecular Response O₂*, *Linewidths O₂* and *Energy Levels O₂* subcodes.

If a spectrum of a mixture of N₂ and O₂ is to be modelled, the overall molecular response is calculated as a combination of the molecular responses of pure N₂ and of O₂ in the presence of N₂. This is done by combining the molecular response outputs from the *Molecular Response N₂* and the *Molecular response O₂-N₂* subcodes in the corresponding ratio. The linewidths are calculated similarly, as a combination of the linewidths of pure O₂ and of O₂ in the presence of N₂, through the *Linewidths O₂* and *Linewidths O₂-N₂* subcodes, respectively.

Before discussing the individual subcodes in detail, Table 3.1 contains all relevant molecular constants of N₂ [66, 72, 73] and O₂ [36, 66, 74, 75], that are used throughout the CARS model code. In addition, the code uses the following physical constants (expressed in wavenumber compatible units): the Boltzmann constant, $k_B = 0.6950345432 \text{ cm}^{-1}\text{K}^{-1}$ and the Planck constant, $h = 3.33564084 \times 10^{-11} \text{ cm}^{-1}\text{s}$.

Term	N ₂	O ₂
ω_e (cm ⁻¹)	2358.518	1580.19
$\omega_e x_e$ (cm ⁻¹)	14.2935	11.98
B_e (cm ⁻¹)	1.99826	1.44563
D_e (cm ⁻¹)	5.774×10^{-6}	4.839×10^{-6}
α_e (cm ⁻¹)	1.73035×10^{-2}	1.59×10^{-2}
β_e (cm ⁻¹)	1.55×10^{-8}	0.0
γ_e (cm ⁻¹)	$-3.1536099 \times 10^{-5}$	-8.25×10^{-5}
r_e (cm)	1.098×10^{-8}	1.207×10^{-8}
ϵ_e (cm ³)	6.91×10^{-25}	1.080×10^{-24}
ϵ'_e (cm ²)	1.4×10^{-16}	3.89×10^{-16}
p_1/p_0	3.168	4.348
g_J (even)	6	0
g_J (odd)	3	1

Table 3.1: Molecular constants of N₂ [66, 72, 73] and O₂ [36, 66, 74, 75] used in the computational CARS model. Shown are values for the fundamental vibrational constant (ω_e), the second order vibrational constant ($\omega_e x_e$), the equilibrium rotational constant (B_e), the equilibrium centrifugal constant (D_e), the ro-vibrational interaction constants (α_e , β_e , γ_e), the equilibrium internuclear separation (r_e), the equilibrium polarisation anisotropy (ϵ_e), the first derivative of the polarisation anisotropy with respect to internuclear separation (ϵ'_e), the ratio between the first two coefficients of the anisotropic polarisability expansion (p_1/p_0) and the rotational nuclear degeneracy of even and odd rotational levels (g_J).

3.2 Energy Levels Code

In the *Energy Levels N₂* and *Energy Levels O₂* subcodes, the energies of the ro-vibrational levels and the corresponding S-branch transition frequencies of N₂ and O₂ are calculated, respectively. The energy calculations are based on the rigid rotor approximation along with centrifugal distortion and taking into account the interaction between rotations and vibrations.

The vibrational and rotational quantum numbers are defined as:

$$\begin{aligned} v &= 0, 1 \\ J &= 0, 1, 2, \dots, 89 \end{aligned}$$

The ground and first excited vibrational states ($v = 0$ and $v = 1$) are included, because even at the highest temperature that was probed experimentally (1000 K), 99.9% of the molecules are in either of these states. At this highest temperature, 3.4% of the molecules are in the first excited vibrational level, as discussed before, but this is still enough to make a difference to the theoretical CARS spectrum and needs to be included for a more accurate model. For the rotations, the first 90 rotational levels are included ($J = 0$ to $J = 89$), because this covers even more rotational states than are populated significantly at up to 1000 K, as can be seen in Figure 2.12. The computational code is built to allow for both, the number of vibrational and rotational levels, to be easily changed and set as desired.

The rotational (B_v) and centrifugal (D_v) constants are calculated as:

$$\begin{aligned} B_v &= B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 \\ D_v &= D_e + \beta_e \left(v + \frac{1}{2} \right) \end{aligned} \quad (3.1)$$

From this, the ro-vibrational energy levels, $E(v, J)$, are calculated:

$$E(v, J) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 \quad (3.2)$$

Finally, this is used to compute the S-branch transition frequencies according to the selection rules $\Delta v = 0$ and $\Delta J = 2$:

$$\Delta E_{v,J;v,J+2} = E(v, J+2) - E(v, J) \quad (3.3)$$

The ro-vibrational energies ($E(v, J)$) and transition frequencies ($\Delta E_{v,J;v,J+2}$) calculated this way, are passed to the corresponding *Linewidths* subcodes.

3.3 Linewidths Code

The linewidths subcodes for N₂, O₂ and O₂-N₂ compute the corresponding Raman transition linewidths, based on the Modified Exponential Gap model and using the ro-vibrational energies that are passed from the respective *Energy Levels* subcodes.

Alternatively, for pure N₂ only, experimentally measured linewidth values can be used instead of the MEG model, if desired.

The MEG model parameters for computing the linewidths of N₂-N₂ collisions [76–78], O₂-O₂ collisions [77, 78] and O₂-N₂ collisions [77, 78], are given in Table 3.2.

Term	N ₂ -N ₂	O ₂ -O ₂	O ₂ -N ₂
α (cm ⁻¹ atm ⁻¹)	0.023	0.016	0.017
β	1.67	1.45	1.41
δ	1.21	1.32	1.30
m	0.1487	—	—
n	0.5	1.32	1.31
A	1.5	1.5	1.5
T_0 (K)	295	295	295

Table 3.2: MEG model parameters for calculating the linewidths of N₂-N₂ collisions [76–78], O₂-O₂ collisions [77, 78] and O₂-N₂ collisions [77, 78], that are used in the computational model.

Using the MEG model, the Q-branch transition rate matrix for upward transitions from initial rotational state i to a final rotational state f ($i < f$), with respective rotational quantum numbers J_i and J_f , is given by:

$$\Gamma_{f,i} = P\alpha f(T) \left(\frac{T}{T_0}\right)^{-n} \left[\frac{1 + \frac{AE_i}{k_B T \delta}}{1 + \frac{AE_i}{k_B T}} \right]^2 \exp\left(-\beta \frac{(E_f - E_i)}{k_B T}\right) \quad f \neq i$$

$$f(T) = \frac{1 - e^{-m}}{1 - e^{-m \frac{T}{T_0}}} \quad \text{for } N_2 - N_2 \text{ collisions}$$

$$f(T) = 1 \quad \text{for } O_2 - O_2 \text{ and } O_2 - N_2 \text{ collisions} \quad (3.4)$$

where P is the pressure in atm, T is the temperature in K and E_f and E_i are the energies of the final and initial energy level of the transition, respectively. All other parameters are as shown in Table 3.2. The corresponding downward transitions, from

state f to state i , are calculated from the detailed balance principle:

$$\Gamma_{i,f} = \Gamma_{f,i} \frac{2J_i + 1}{2J_f + 1} \exp\left(\frac{(E_f - E_i)}{k_B T}\right) \quad f \neq i \quad (3.5)$$

The diagonal elements of this transition rate matrix, which represent the Q-branch transition linewidths, are found by summing each of its columns:

$$\Gamma_f = \sum_{i \neq f} \Gamma_{i,f} \quad (3.6)$$

The corresponding S-branch linewidths ($i = J$ and $f = J + 2$) are then calculated from these Q-branch linewidths according to [63]:

$$\Gamma_{v,J;v,J+2}^S = \frac{1}{2} (\Gamma_{J,J} + \Gamma_{J+2,J+2}) \quad (3.7)$$

As stated before, when modelling CARS spectra of pure N₂, experimentally measured S-branch linewidths of N₂-N₂ collisions can be used instead of the MEG model. These experimental linewidths, reported by Kliwer *et al.* [61] (see Figure 2.11), are for S-branch transitions from $J = 2 \rightarrow J = 4$ to $J = 40 \rightarrow J = 42$, at temperatures ranging from 300 K to 1400 K in steps of 100 K. If the experimental linewidths are chosen over the MEG model, they are loaded to the *Linewidths N₂* subcode and interpolated linearly to the temperature of the spectrum to be modelled. For the cases that the temperature of the spectrum to be modelled is lower than 300 K or higher than 1400 K, the following temperature correction is used [79]:

$$\begin{aligned} \text{if } T < 300K : \quad \Gamma_{v,J;v,J+2}^S(T) &= \Gamma_{v,J;v,J+2}^S(300K) \times \left(\frac{300}{T}\right)^{0.704} \\ \text{if } T > 1400K : \quad \Gamma_{v,J;v,J+2}^S(T) &= \Gamma_{v,J;v,J+2}^S(1400K) \times \left(\frac{1400}{T}\right)^{0.704} \end{aligned} \quad (3.8)$$

where $\Gamma_{v,J;v,J+2}^S(T)$ are the linewidths at temperature T and $\Gamma_{v,J;v,J+2}^S(300K)$ and $\Gamma_{v,J;v,J+2}^S(1400K)$ are the experimentally measured linewidths at 300 K and 1400 K respectively.

After the linewidths ($\Gamma_{v,J;v,J+2}^S$) have been calculated (either from the MEG model or, in the case of pure N₂, from interpolation of the experimental linewidths), they are passed to the corresponding *Molecular Response* subcode, together with the ro-vibrational energies ($E(v, J)$) and transition frequencies ($\Delta E_{v,J;v,J+2}$), that have been computed before in the respective *Energy Levels* subcodes.

3.4 Molecular Response Code

The molecular response subcodes for N₂, O₂ and O₂-N₂ compute the corresponding molecular responses, as described by Equation 2.39. Input parameters include the temperature at which the model spectrum is to be generated, passed down from the *CARS Model* subcode. Further input parameters are the ro-vibrational energies, transition frequencies and transition linewidths, passed up from the corresponding *Linewidths* subcode.

For pure N₂ and pure O₂, the linewidths calculated in the corresponding *Linewidths* subcode are used directly for the calculation of the molecular response. For N₂/O₂ mixtures, the linewidths of O₂-O₂ collisions (from the *Linewidths O₂* subcode) is combined with the linewidths of O₂-N₂ collisions (from the *Linewidths O₂-N₂* subcode). This combination is performed as the sum of the scaled mole fractions of N₂ and O₂ in the mixture (which is an input parameter that can be set to match the composition of any N₂/O₂ mixture):

$$\Gamma_{v,J;v,J+2}^S = x_{O_2} \times \Gamma_{v,J;v,J+2,O_2-O_2}^S + x_{N_2} \times \Gamma_{v,J;v,J+2,O_2-N_2}^S \quad (3.9)$$

where x_{O_2} and x_{N_2} are the mole fractions of O₂ and N₂ in the mixture, respectively, such that $x_{O_2} + x_{N_2} = 1$. For reference, in air at atmospheric composition, the weighted and scaled mole fractions are: $x_{O_2} = 0.21151$ and $x_{N_2} = 0.78849$.

The factors of the Raman transition strength, $I_{v,J;v,J+2}$, are computed as follows (with constants as defined before):

The polarisation anisotropy, which depends on the vibrational level, is calculated according to [66]:

$$\gamma'_v = \epsilon_e + \epsilon'_e r_e \left[\frac{3B_e}{\omega_e} + \frac{\alpha_e}{2B_e} \right] \left(v + \frac{1}{2} \right) \quad (3.10)$$

The Placzek-Teller coefficient of linear diatomic molecules is computed for S-branch transitions at each rotational level [36]:

$$b_{J,J+2} = \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \quad (3.11)$$

The S-branch Herman-Wallis Factor is calculated at each rotational level, based on the model by Tipping and Ogilvie [71]:

$$F_{rot}(J) = \left[1 + \kappa^2 \left(\frac{p_1}{p_0} \right) (J^2 + 3J + 3) \right]^2$$

$$\text{where} \quad \kappa = \frac{2B_e}{\omega_e} \quad (3.12)$$

The normalised Boltzmann population difference of each transition is calculated using the energies of the ro-vibrational levels, $E(v, J)$, and the temperature, T , at which the model spectrum is to be generated. The nuclear spin degeneracy, g_J , takes different values, depending on the type of molecule modelled and whether the transition is from an even or an odd rotational level (see Table 3.1):

$$\Delta\rho_{v,J;v,J+2} = \frac{g_J(2J+1)}{Z_{v,J}} \left[\exp\left(-\frac{E_{v,J}}{k_B T}\right) - \exp\left(-\frac{E_{v,J+2}}{k_B T}\right) \right] \quad (3.13)$$

where $Z_{v,J}$ is the partition function:

$$Z_{v,J} = \sum_v \sum_J g_J(2J+1) \exp\left(-\frac{E_{v,J}}{k_B T}\right) \quad (3.14)$$

Then, the polarisation anisotropy, the Placzek-Teller coefficient, the Herman-Wallis factor and the Boltzmann population difference factor are combined, to form the Raman transition strengths of each individual rotational S-branch transition in each vibrational level:

$$I_{v,J;v,J+2} = \frac{4}{45} (\gamma'_v)^2 b_{J,J+2} F_{rot}(J) \Delta\rho_{v,J;v,J+2} \quad (3.15)$$

Together with the transition frequencies and the transition linewidths, this is used to generate the molecular response of each individual rotational S-branch transition in each vibrational level, at times, t :

$$R_{CARS}(t, v, J) = I_{v,J;v,J+2} \times \exp\left[\frac{t}{\hbar} \left(i\Delta E_{v,J;v,J+2} - \frac{\Gamma_{v,J;v,J+2}^S}{2} \right)\right] \quad (3.16)$$

The times at which this molecular response is calculated is an input parameter that can be set as desired. For the modelling and fitting of spectra presented in this thesis, the time grid was chosen to run from 0 ps (the moment of the pump/Stokes excitation) to 100 ps in steps of 5 fs, as 100 ps more than covers the time range in which the CARS signal is generated and the 5 fs steps are small enough to resolve it.

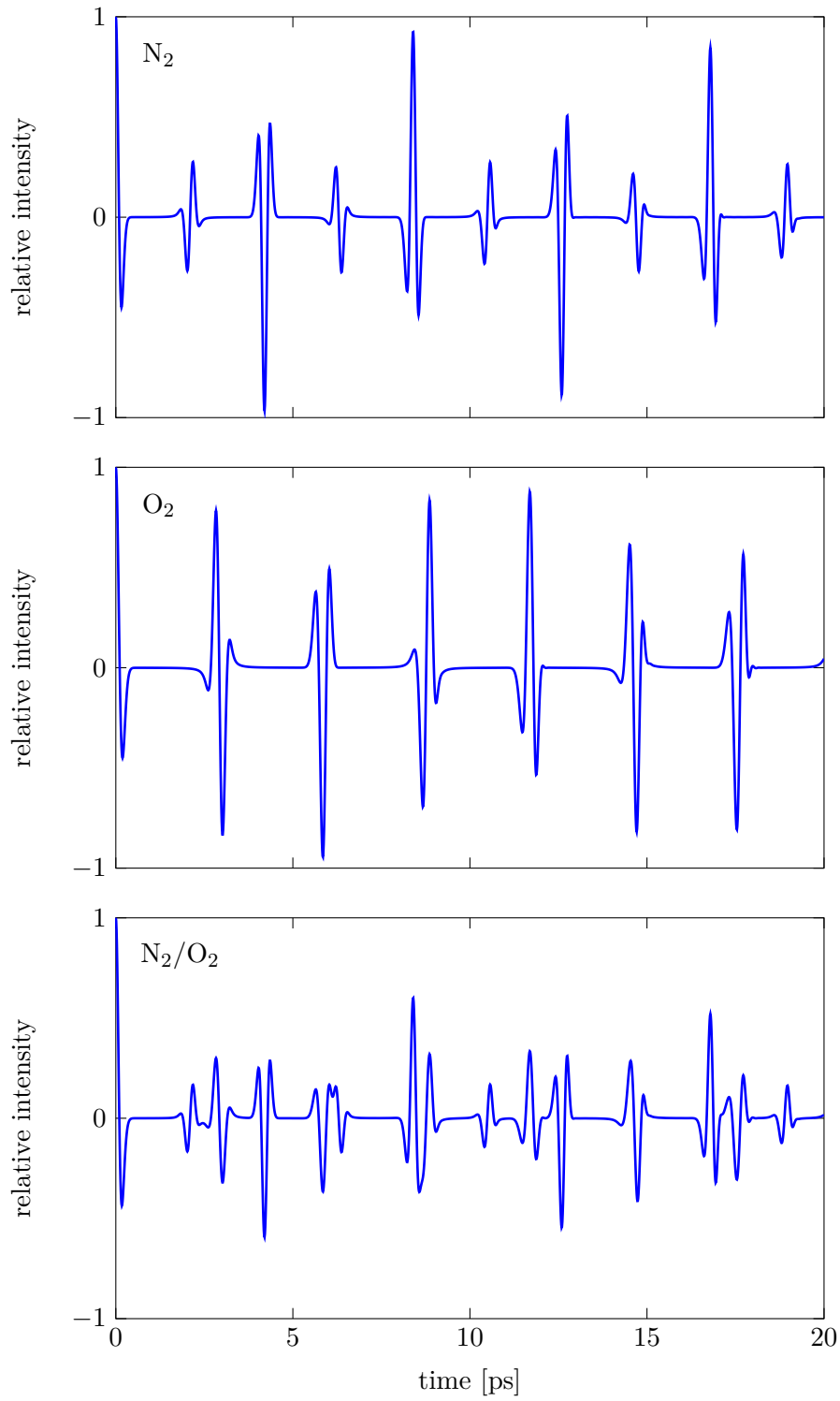


Figure 3.2: Real part of the molecular response function (modelled according to Equation 3.17) of pure N₂, pure O₂ and a mixture of N₂/O₂ (air at atmospheric composition) in the time domain for pure rotational S-branch transitions at 293 K and 1 atm. The N₂/O₂ response function is a combination of the pure N₂ and O₂ in the presence of N₂ response functions, according to Equation 3.18. The molecular response of N₂ is the same as shown in Figure 2.3.

In the last step, the molecular response function calculated according to Equation 3.16 is summed over all rotational S-branch transitions in all vibrational levels that are included in the model, to get the overall molecular response function at each time step, t , of the time grid:

$$R_{CARS}(t) = \sum_v \sum_J R_{CARS}(t, v, J) \quad (3.17)$$

This time-domain molecular response at each time step, $R_{CARS}(t)$, is then passed to the *CARS Model* subcode for the computation of the model CARS spectrum. The appearance of the time domain molecular responses of N₂, O₂ and N₂/O₂ mixtures at atmospheric conditions are shown in Figure 3.2.

3.5 CARS Model Code

This subcode is where the theoretical CARS spectra are computed. The fixed and fitting parameters, such as the temperature and pressure of the spectrum to be modelled, are passed to this subcode from the *Edinburgh CARS Code*. Further, the time domain molecular response, passed on from the corresponding *Molecular Response* subcode, is used.

For models of pure N₂ and pure O₂, the molecular response function is called from the corresponding *Molecular Response* subcode and used directly in the computation of the model spectrum. In the case of N₂/O₂ mixtures, a combination of the molecular responses of pure N₂ (from the *Molecular Response N₂* subcode) and O₂ in the presence of N₂ (from the *Molecular Response O₂-N₂* subcode) is used. This combination is performed as the sum of the scaled mole fractions of N₂ and O₂ in the mixture, similarly to the combination of the linewidths for N₂/O₂ mixtures:

$$R_{CARS,N_2/O_2}(t) = x_{N_2} \times R_{CARS,N_2}(t) + x_{O_2} \times R_{CARS,O_2-N_2}(t) \quad (3.18)$$

In addition to the molecular response, the electric field of the probe beam is needed to generate a model CARS spectrum. Often, the electric field of a laser pulse is modelled with a symmetric function, such as a Gaussian. However, measured cross correlations of the probe beam that was used for the HR-CARS experiments show that it is not a perfect Gaussian, but has significant asymmetry. Careful modelling of the probe pulse shape is required for accurate CARS spectral fits, therefore the probe beam electric field is constructed using the sum of two Gaussians, to better match the real probe

beam shape. Additionally, linear chirp is included in the probe beam [80]:

$$\begin{aligned}
E_{pr}(t - \tau) &= E_{probe}(t - \tau) \times E_{chirp}(t - \tau) \\
E_{probe}(t - \tau) &= \exp \left[-\frac{2\ln(2)(t - \tau)^2}{\Delta\tau^2} \right] + A \exp \left[-\frac{2\ln(2)(t - \tau + \tau_{gauss})^2}{(f\Delta\tau)^2} \right] \\
E_{chirp}(t - \tau) &= A_{chirp} \exp \left[-i \frac{2\ln(2)\alpha(t - \tau + \tau_{chirp})^2}{\Delta\tau_{chirp}^2} \right]
\end{aligned} \tag{3.19}$$

where τ and $\Delta\tau$ are the time delay and width of the first Gaussian. The second Gaussian is calculated relative to the first Gaussian, with the amplitude adjusted by a factor, A , the time delay adjusted by, τ_{gauss} and the width adjusted by a factor f . The linear chirp, included through a third Gaussian, has an amplitude of A_{chirp} , a time delay adjusted by τ_{chirp} relative to the first Gaussian and a width of $\Delta\tau_{chirp}$. α is the chirp factor. All of these parameters are input parameters that can be set in the code to match a certain probe pulse shape and chirp. Time t is the same time grid as is used for the molecular response.

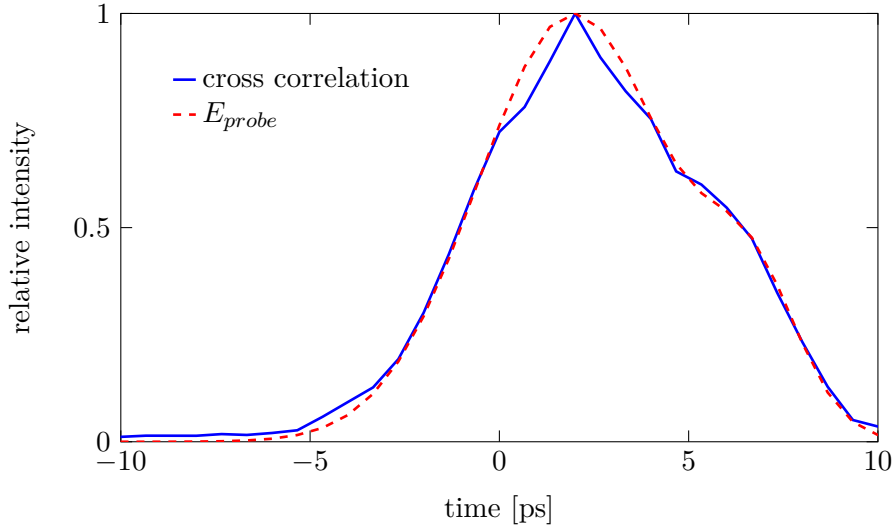


Figure 3.3: Probe pulse in the time domain (shown as the square root of the measured probe intensity) as measured by a cross correlation in argon (blue line), together with the corresponding two-Gaussian fit (dashed red line), as modelled by Equation 3.19. The time axis is defined such that the early part of the pulse is at a larger time, hence the inversion of the pulse in Figure 3.4.

The chirp is included in the model, because the measured bandwidth of the probe beam is $\nu = 3.0 \text{ cm}^{-1}$. This bandwidth has a transform limit (TL) of 4.9 ps, but measured cross correlations in argon gave a pulse duration, $\Delta\tau_{chirp}$, of about 5.5 ps, 12% longer than the TL. Including the chirp stretches the probe beam from its transform limit

to the required length. Without this chirp factor, the model has narrower lines and shifted frequencies when compared with experimental spectra. Further, including the chirp allows better modelling of spectrally overlapping transitions that are observed in the experimental data. Figure 3.3 shows a measured cross correlation of the probe beam, along with a corresponding two-Gaussian fit, as modelled by Equation 3.19.

The molecular response and probe beam electric field can then be combined (see Equation 2.35) to get the corresponding third order polarisation (the time domain CARS signal):

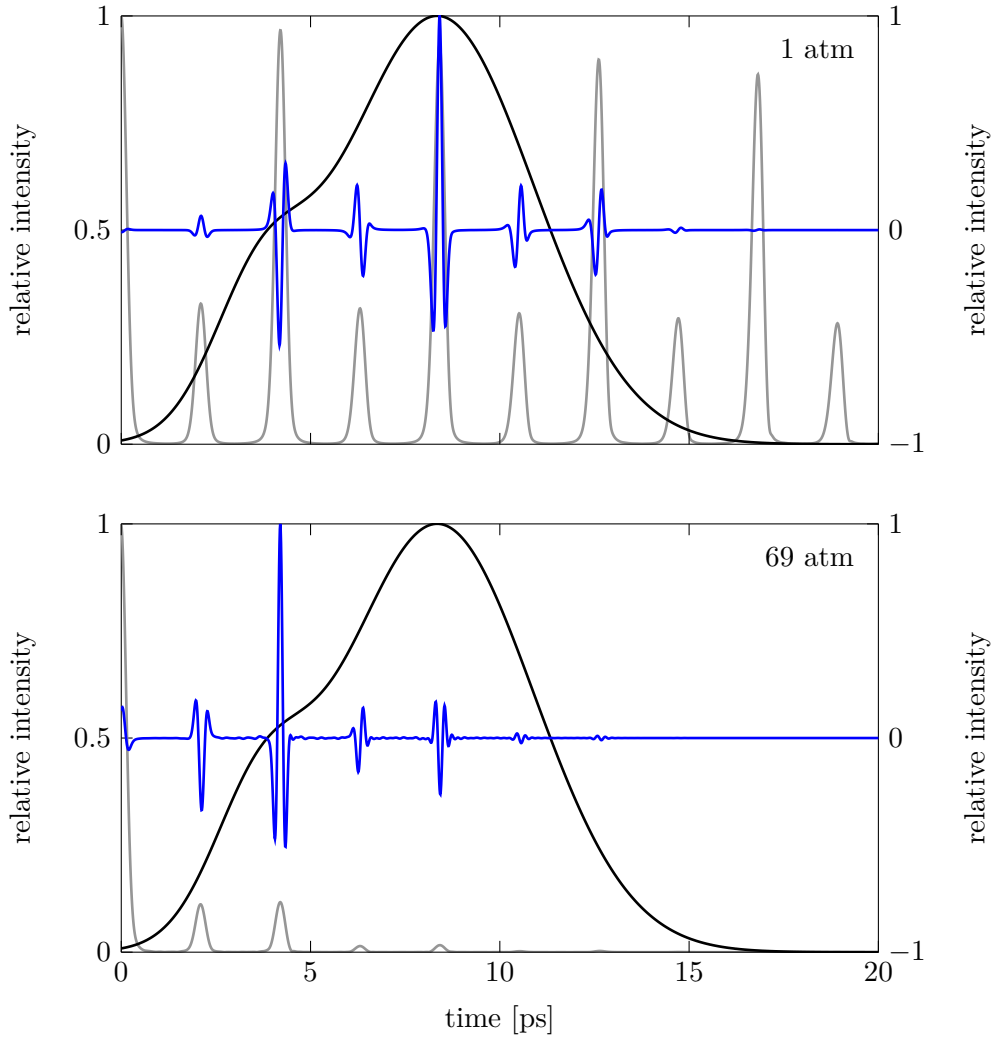
$$P_{CARS}^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \times E_{pr}(t - \tau) \times R_{CARS}(t) \times e^{-2i\pi(t-\tau)} \quad (3.20)$$

The only difference between this and Equation 2.35 is the exponential term, which does not contain the frequency of the probe beam. This is because this frequency simply causes the final frequency domain model spectrum to shift by the frequency of the probe beam, which is unnecessary, as the frequency of the final spectrum is defined relative to the frequency of the probe beam. However, a factor of 2π is included in the exponential, as this is needed to ensure that the frequency domain spectrum has a matching frequency axis after the Fourier transform (see below).

Figure 3.4 shows this time domain CARS signal, together with the corresponding molecular response and probe beam for N_2 at the lowest (1 atm) and highest (69 atm) pressures that were probed experimentally. The Figure illustrates the advantage of using a short ps probe for high pressure CARS measurements. At low pressure, the molecular response (grey line) decays slowly with time, but at high pressure, it drops by more than an order of magnitude within the first 10 ps, because the decay is exponential with pressure. However, even at this high pressure, there remains a significant CARS signal (blue line), as the short picosecond probe (black line) overlaps with most of the molecular response. At the same time, the probe is not present at time zero, so none or very little NR signal is generated experimentally, which means it is not necessary to include it in the model. For a longer ps probe to avoid nonresonant signal generation, it would have to be delayed more in time, but then it would not overlap with the molecular response anymore at high pressure, and there would not be a sufficient CARS signal.

To get from the time domain model of the CARS signal to the corresponding frequency (wavenumber) domain model, a simple Fourier transform is performed on the time domain CARS signal:

$$P_{CARS}^{(3)}(\omega) = \mathcal{F} \left[P_{CARS}^{(3)}(t) \right] \quad (3.21)$$



$$- \text{Re}[R_{CARS}(t)] \quad - E_{\text{probe}}(t - \tau) \quad - \text{Re}[P_{CARS}^{(3)}(t)]$$

Figure 3.4: Time domain model of the absolute value of the real part of the molecular response (grey line, same as Figure 3.2 N_2 , but as an absolute value), the two-Gaussian probe pulse shape (black line) and the real part of the time domain CARS signal (blue line). These functions, which are all normalised, are shown at pressures of 1 atm and 69 atm. In both cases, the model is for pure N_2 at 293 K and the peak of the probe pulse is centred at a time delay of 8.4 ps, the first full revival of the molecular response of N_2 . The probe pulse shape shown here is an example, based on one of the measured cross correlations (the same as shown in Figure 3.3).

The final frequency domain CARS intensity is the square of the absolute value of this frequency domain CARS signal:

$$I_{CARS}(\omega) = \left| P_{CARS}^{(3)}(\omega) \right|^2 \quad (3.22)$$

Next, the *CARS Model Code* transforms the time grid, t to a corresponding wavenumber grid, ω , so that the frequency domain CARS intensity has a matching wavenumber axis that it can be plotted on. In a final step, the CARS intensity is convolved with a slit

function, which accounts for the spectrometers small, but finite, entrance slit width. This slit function, $F_{slit}(\omega)$, is defined as a Gaussian on the wavenumber grid, according to:

$$F_{slit}(\omega) = \exp \left[- \left(\frac{2\sqrt{\log(2)}\omega}{\Delta\omega_{slit}} \right)^2 \right] \quad (3.23)$$

where $\Delta\omega_{slit}$ is the FWHM of the slit in wavenumbers. For this model, the slit width is fixed at 1.5 cm^{-1} , based on measurements of the spectral linewidths of mercury emission lines near the probe frequency. This value, however, can be changed to match any spectrometer's slit width.

The slit function-convolved, frequency domain CARS intensity is the model spectrum. This final model spectrum is what is passed to the *Edinburgh CARS Code* where the fitting algorithm compares it iteratively to an experimental spectrum in order to obtain a best fit model, with best fit parameters, as explained before. An example model spectrum of N_2 at 293 K and 1 atm is shown in Figure 3.5. It corresponds to the time domain CARS signal (blue line) at 1 atm shown in Figure 3.4, that was Fourier transformed and squared according to Equations 3.21 and 3.22 respectively, to get the frequency domain CARS intensity. It was then convolved with a 1.5 cm^{-1} Gaussian spectrometer slit function. For this model spectrum, the chirp factor of the probe beam was set to $\alpha = 0$ for simplicity.

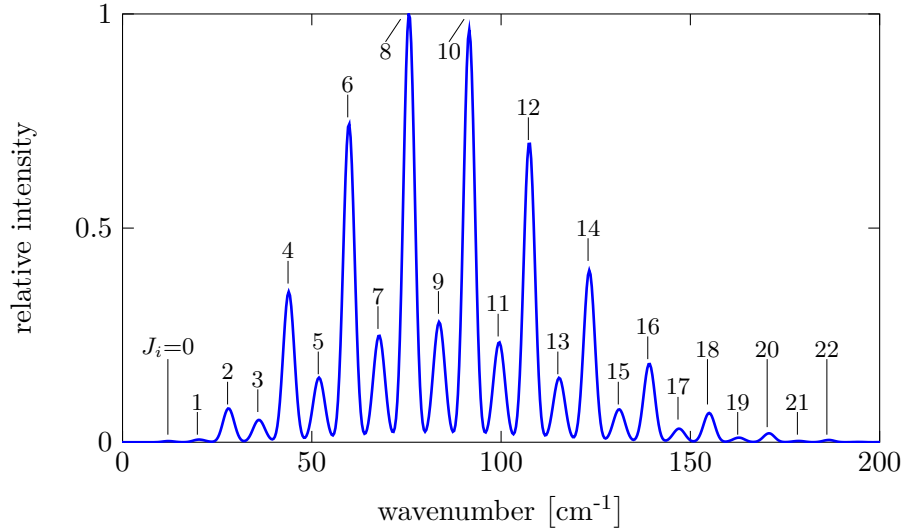


Figure 3.5: Model CARS spectrum of N_2 at 293 K and 1 atm, corresponding to the time domain CARS signal (blue line) at 1 atm shown in Figure 3.4, that was Fourier transformed (Equation 3.21), squared (Equation 3.22) and convolved with a 1.5 cm^{-1} Gaussian spectrometer slit function. The chirp factor of the probe beam was set to $\alpha = 0$ for simplicity. The S-branch transitions ($J_i \rightarrow J_i + 2$) corresponding to each line are labelled.

It can be seen that the N_2 model spectrum consists of large (even- J) and small (odd- J) lines, corresponding to the rotational nuclear degeneracy of even and odd rotational levels. Each line corresponds to one S-branch transition, $J_i \rightarrow J_i + 2$ (labelled in the figure). They follow a temperature-dependent Boltzmann-like intensity distribution.

3.6 Edinburgh CARS Code

This is the front surface of the overall code, where all fitting and fixed input parameters are set and where the experimental data are loaded to the code. Further, the fitting routine allows for lower and upper bounds to be placed on the fitting parameters, which can not be exceeded during the fit. These are defined in this part of the code as well. After everything is set, the fitting routine is executed and all relevant parameters are passed to the *CARS Model* and subsequent subcodes where the model spectrum is generated, according to the above-described procedure. When the fitting routine finishes, the best fit parameters are displayed and the best fit model data are saved automatically. More detail on the fitting parameters and fitting procedure is given in chapter 5.

The *Edinburgh CARS Code* is designed to allow for maximum flexibility. Most parameters (e.g. the time grid, N_2/O_2 mole ratio, pressure, temperature, chirp factor, etc.) can be changed easily, to suit many different experimental conditions. This makes the *Edinburgh CARS Code* universal and applicable to many different types of hybrid fs/ps CARS experiments.

3.7 Model Examples

To illustrate the capabilities of the computational CARS code, model spectra of pure N_2 (Figure 3.6), pure O_2 (Figure 3.7) and an N_2/O_2 mixture at atmospheric composition (Figure 3.8) are presented. For each of these figures, four spectra at very different temperatures and pressures are shown: low temperature and low pressure (293 K and 1 atm), low temperature and high pressure (293 K and 69 atm), high temperature and low pressure (1000 K and 1 atm) and high temperature and high pressure (1000 K and 38 atm). These conditions correspond to the temperature and pressure extremes that were achieved experimentally (see Figure 4.8). All of the model spectra shown were modelled using very similar conditions, without any chirp (for simplicity) and using the probe pulse shown in Figure 3.3.

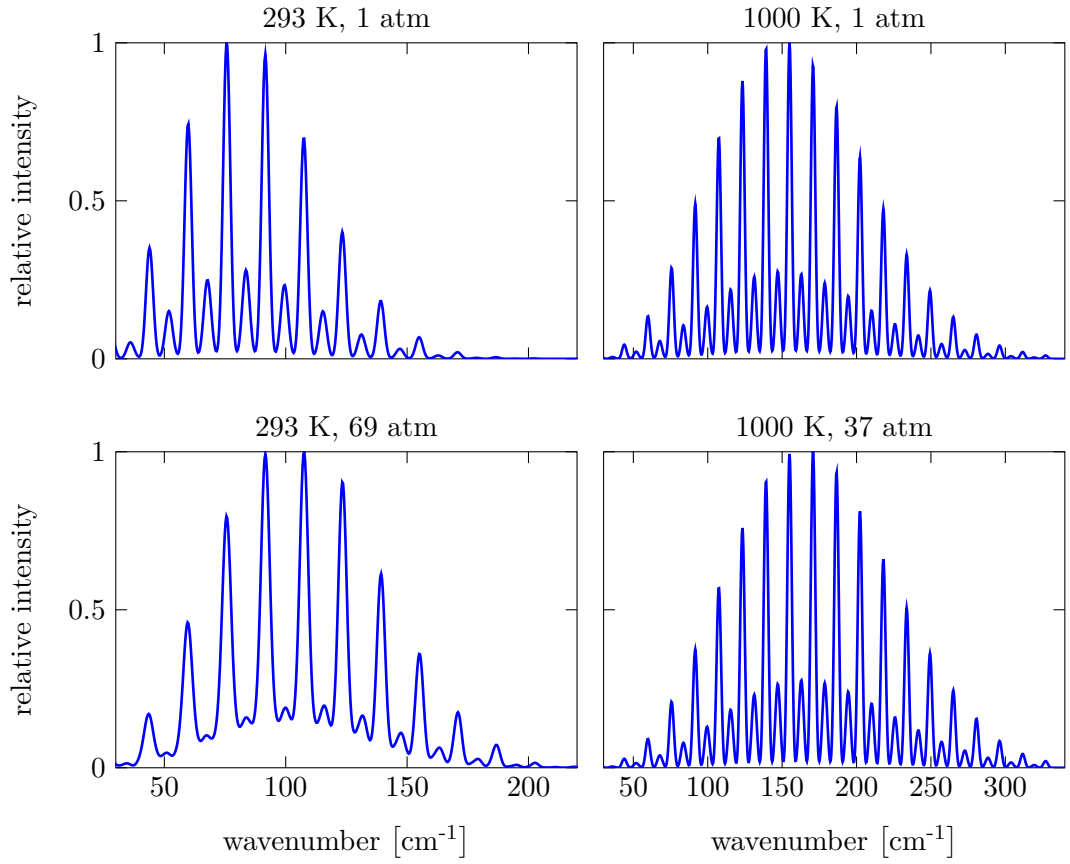


Figure 3.6: HR-CARS spectra of N_2 under different temperature and pressure conditions, as modelled by the above described computational code. All spectra were modelled without chirp and using the probe pulse shown in Figure 3.3 at a time delay of 8.4 ps (the first full revival of the molecular response of N_2).

For N_2 , more rotational states are populated at higher temperatures and the Boltzmann intensity distribution is shifted towards higher wavenumbers accordingly. At the highest pressure (69 atm), the lines get wider (as the linewidths increase) and the odd- J lines start to grow into the even- J lines, though overall the spectrum is still well-resolved. The widening of lines only appears to occur at the highest pressure, as at lower pressures it is the width of the probe beam that dictates the widths of the lines.

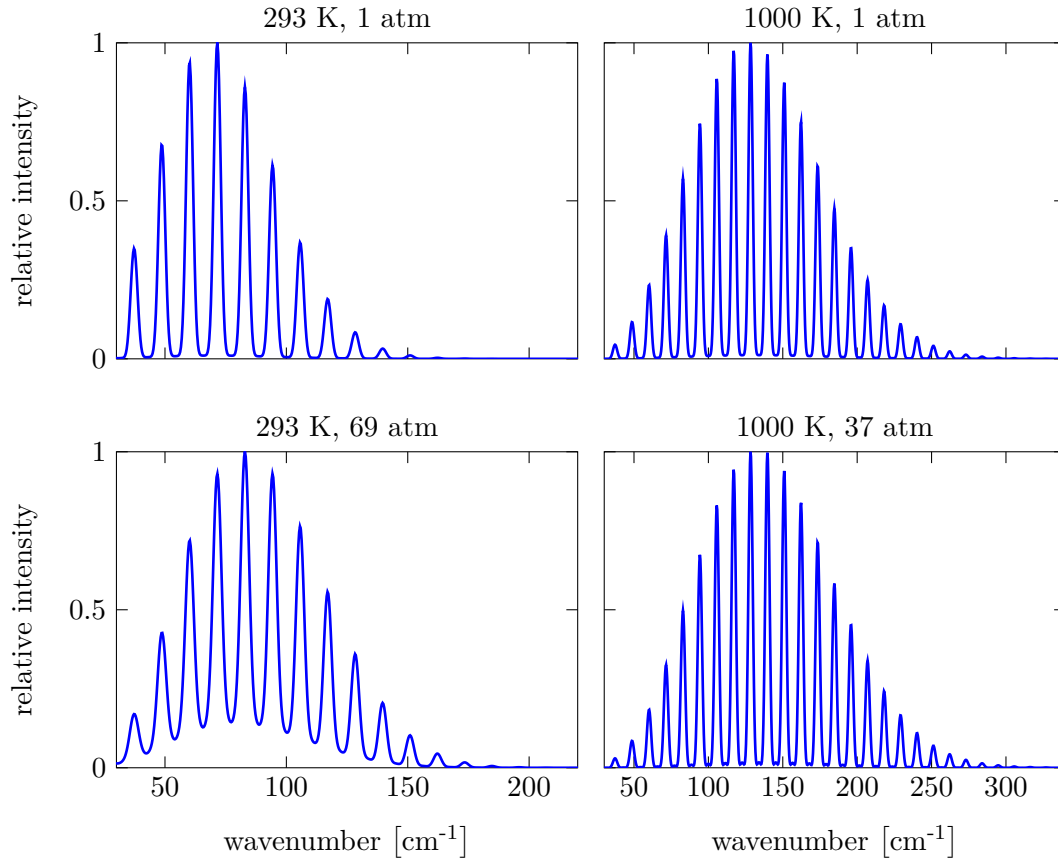


Figure 3.7: HR-CARS spectra of O_2 under different temperature and pressure conditions, as modelled by the above described computational code. All spectra were modelled without chirp and using the probe pulse shown in Figure 3.3 at a time delay of 11.5 ps (the first full revival of the molecular response of O_2).

For O_2 , the trends with temperature and pressure are the same as for N_2 : with increasing temperature more rotational levels are populated, shifting the Boltzmann intensity distribution towards higher wavenumbers and at the highest pressure (69 atm), the lines get wider, but the spectrum stays well-resolved. However, for O_2 , the rotational nuclear degeneracy of even rotational levels is zero, so no lines corresponding to transitions from these levels are present.

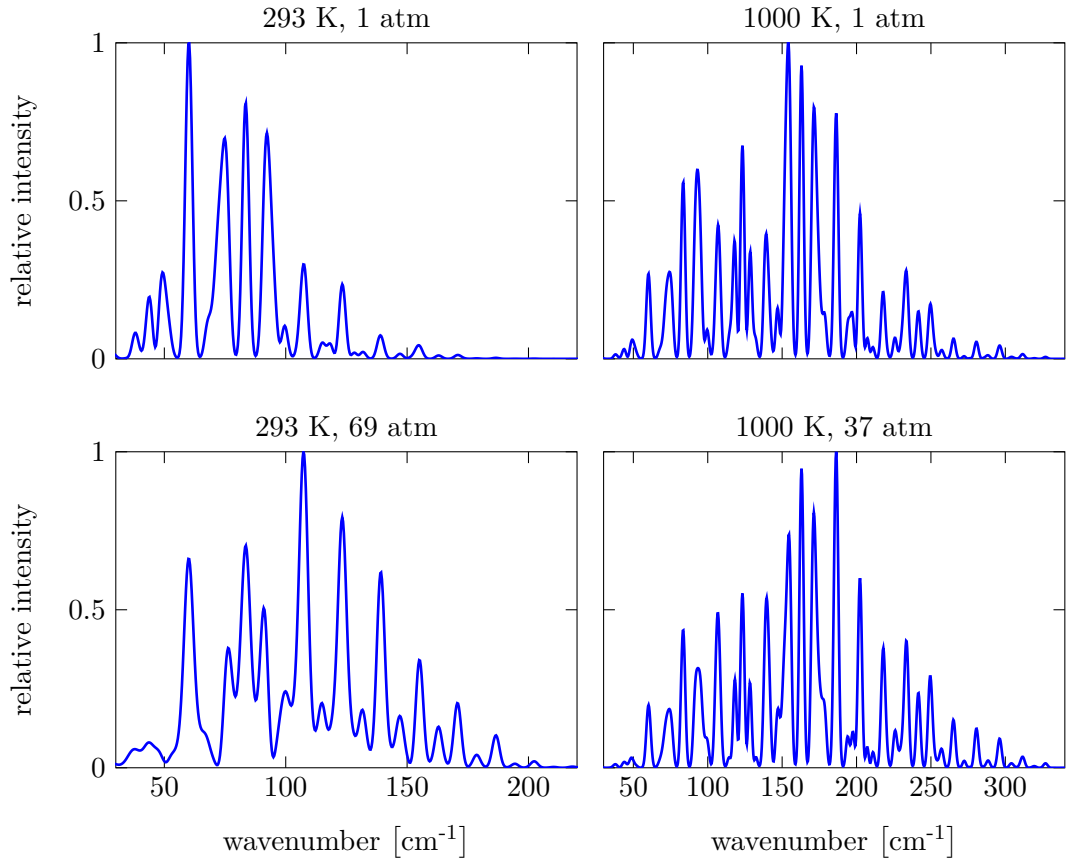


Figure 3.8: HR-CARS spectra of an N_2/O_2 mixture at atmospheric composition under different temperature and pressure conditions, as modelled by the above described computational code. All spectra were modelled without chirp and using the probe pulse shown in Figure 3.3 at a time delay of 10.0 ps (approximately halfway in between the first full revivals of the molecular responses of N_2 and O_2).

Like pure N_2 and O_2 , the N_2/O_2 spectra shift towards higher wavenumbers with increasing temperature. However, they appear to be very random, no smooth Boltzmann intensity distribution can be seen. This is because each N_2/O_2 spectrum comes from a molecular response that is a sum of the molecular responses of pure N_2 and of O_2 in the presence of N_2 (Equation 3.18). This means that no clear trends can be observed, as subtle changes of the N_2 and O_2/N_2 molecular responses at different conditions can lead to a large difference in their interaction. However, at very high pressures the time domain molecular responses of higher rotational transitions of oxygen decay relatively faster than those of nitrogen as they have larger linewidths. This results in some isolated nitrogen lines at high pressures and large wavenumbers, as can be seen for the 69 atm spectrum in Figure 3.8.

Chapter 4

Experimental Setup

The experimental setup that was built for measuring well-resolved HR-CARS spectra over a large range of temperatures and pressures will be discussed in detail in this chapter. After a presentation of the overall setup, its different parts will be explained in-depth, including some background theory. A special focus is given to the pulse shaper, that is used to create a nearly transform limited pump/Stokes beam, and the second harmonic bandwidth compression (SHBC), that is used to generate the picosecond probe pulse. Next, a presentation of the high pressure cell in which the experiments are conducted will be given, before the chapter ends with a discussion of the experimental procedure. The setup presented here is the same as reported in a paper published as part of this research project (Courtney *et al.* [81]), but much more detail and background theory are given in this chapter.

4.1 Overall Setup

To achieve the beam characteristics required for generating well-resolved HR-CARS spectra, both, the pump/Stokes and the probe beam, need to undergo several important pulse shaping steps before the actual CARS experiment, making the experimental setup relatively complex. Figure 4.1 shows a schematic diagram of the entire HR-CARS experimental setup, including all relevant optics.

It can be seen that both the pump/Stokes and the probe beams originate from the same laser system, a Coherent Legend Elite Ti:Sapphire regenerative amplifier (795 nm, 1 kHz), that is seeded by a Coherent Vitara oscillator (100 MHz). The output from this is split into two beams of equal power using a beam splitter, and each of them is amplified to about 9 mJ/pulse in a single pass amplifier. The resulting 795 nm broadband beams have a spectral width of $\Delta\nu = 360 \text{ cm}^{-1}$ and are strongly positively chirped ($>100 \text{ ps}$). One of these amplifier output beams is used to create the femtosecond pump/Stokes beam and the other is used to generate the picosecond probe beam.

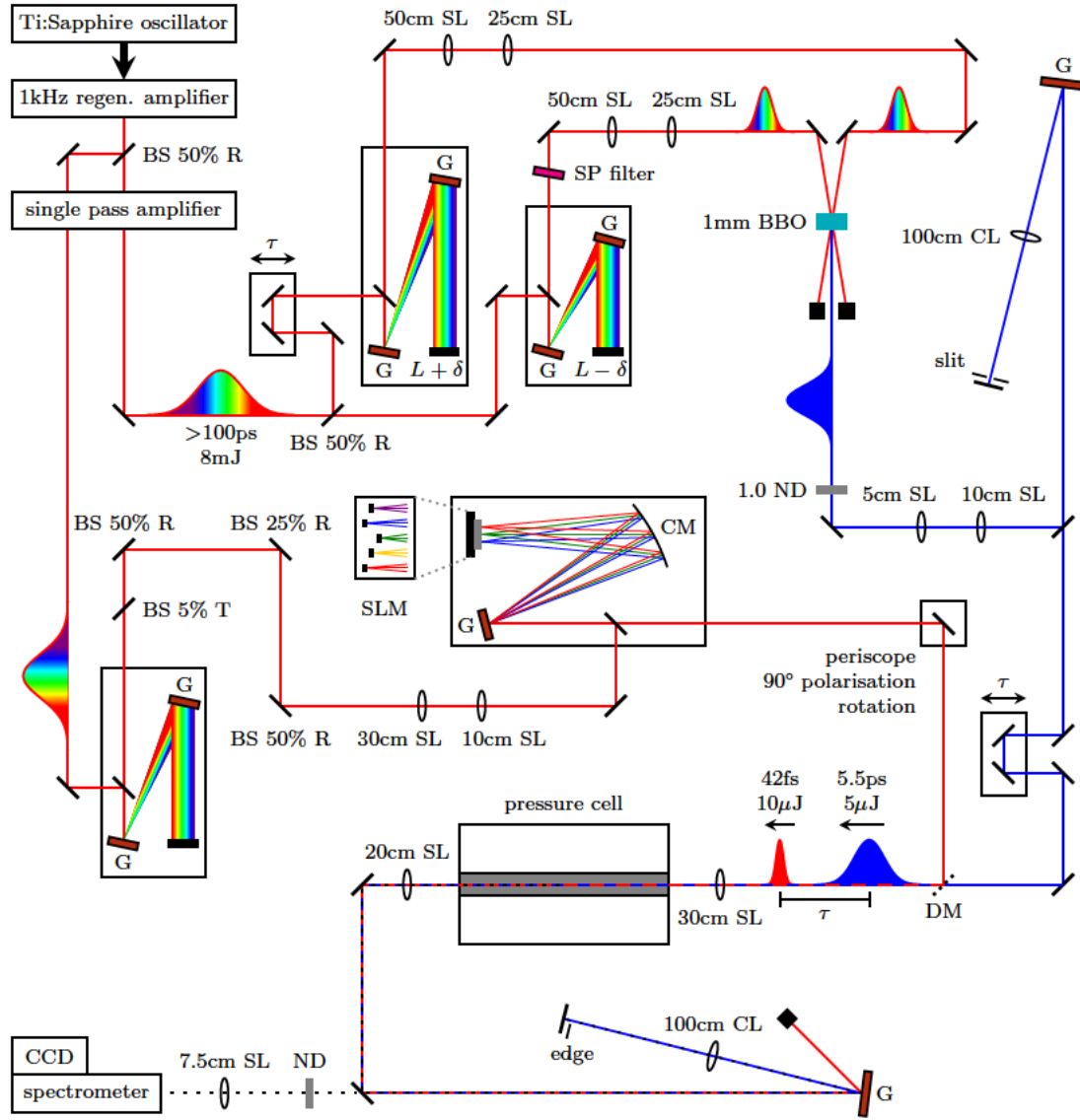


Figure 4.1: Schematic diagram of the complete two-beam HR-CARS experimental setup. The beam from a 1 kHz Ti:Sapphire laser system is split into two equal power beams that are each single pass amplified. The pump/Stokes pulse is generated by grating-compressing one of these beams, followed by dispersion compensation in a pulse shaper that uses a spatial light modulator (SLM). The probe pulse is generated using second harmonic bandwidth compression (SHBC), by splitting the other amplifier output in two, chirping the two beams in grating compressors equally and opposite and combining them in a beta barium borate (BBO) crystal. Spectral wings and satellite peaks are filtered out in a folded $4f$ grating filter. The pump/Stokes and probe beams are combined collinearly and focussed into a pressure cell. The resulting CARS signal is filtered in a folded $4f$ grating filter, focussed into a spectrometer and dispersed onto a CCD chip. R: reflection, T: transmission, SL: spherical lens, CL: cylindrical lens, G: grating, CM: curved mirror, DM: dichroic mirror, BS: beam splitter, SP: short pulse, ND: neutral density.

The amplifier output beam that is used as the pump/Stokes beam, is first compressed to its near-transform limit in a grating compressor, followed by energy reduction using partially reflective mirrors and down collimation. It is then dispersion compensated in

a pulse shaper, that pre-compensates the beam using a spatial light modulator (SLM), to account for the chirp induced in the pressure cell entrance window. After the pulse shaper, the beam's polarisation is rotated in a periscope to match that of the probe beam.

The probe beam is created via sum frequency generation (SFG), using second harmonic bandwidth compression (SHBC). This is achieved by splitting the other amplifier output beam in two, chirping the two beams in grating compressors equally and opposite, down collimating them and then combining them in a beta barium borate (BBO) crystal. In this crystal, the beams' frequencies add up to produce a spectrally narrow picosecond probe beam, which is collimated before a folded $4f$ grating filter is used to reduce spectral wings and satellite peaks that are present in the beam.

The pump/Stokes and probe beam are then combined collinearly in a dichroic mirror and focussed into a high pressure cell. A translation stage in the probe beam is used to control the time delay between the two beams. The CARS signal emerging from the pressure cell is collimated and the spatially overlapping probe beam is filtered out in a folded $4f$ grating filter. In a final step, the CARS signal is focussed into a spectrometer and dispersed onto a CCD chip, where the CARS spectrum is recorded.

Following this brief introduction and overview of the experimental setup, the next subsections provide more detail and explanation on each of the individual parts of this setup.

4.2 Pump/Stokes Beam and Pulse Shaper

As discussed above, the pump/Stokes beam is created using one of the beams emerging from the single pass amplifier. First, this very chirped beam is compressed in a grating compressor to its near-transform limit of about 40 fs. Next, its power is reduced to 35 $\mu\text{J}/\text{pulse}$, using the transmission through a 5% transmissive mirror and the reflections off two 50% and one 25% reflective mirrors. Furthermore, the beam is down-collimated in a Keplerian telescope using 300 mm and 100 mm spherical lenses, from a $1/e^2$ beam diameter of 12 mm to 4 mm. The beam then enters a pulse shaper (Femtojock), which is used to pre-compensate the pump/Stokes pulse for the dispersion (chirp) induced in the pressure cell entrance window. The reduction in power prior to entering the pulse shaper is necessary to avoid damage to the spatial light modulator inside the pulse shaper, the reduction in size is necessary to fit the beam onto the SLM. A schematic diagram of the pulse shaper is shown in Figure 4.2.

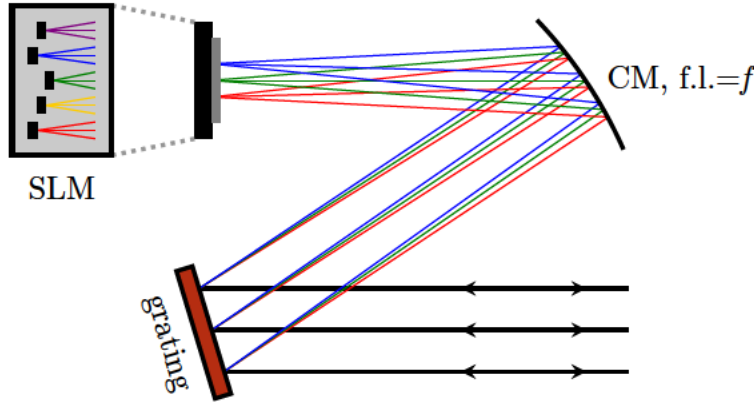


Figure 4.2: Schematic diagram of a $4f$ pulse shaper. Light is dispersed with a grating, and the different frequencies (colours) are focussed with a curved mirror (CM) of focal length f onto a spatial light modulator (SLM), that is located at the Fourier plane. The liquid crystal SLM array can delay the different frequencies by different amounts of time, which can be used to shape the pulse as required. The different frequencies are then recombined using the same curved mirror and grating.

Inside the pulse shaper, which uses a $4f$ design, a grating is used to spatially separate the different frequencies (colours) of the pulse. A curved mirror of focal length f then focusses the different frequencies to different spots on the SLM, located at the Fourier plane, where the pulse shaping takes place. On the way out, the individual frequencies are recombined using the same curved mirror and grating. After exiting the pulse shaper, the beam's energy is $12 \mu\text{J}/\text{pulse}$, about a third of the input energy. The SLM itself is a liquid crystal array of 128 pixels, to each of which a different voltage can be applied. Depending on the voltage, the molecules of the liquid crystal change their orientation, resulting in a change of refractive index. As the speed of light depends on the refractive index, this can be used to shape the pulse, by adjusting the relative delay between the different frequencies of the input beam [82, 83]. When no voltage is applied to the SLM, the relative delays of the different frequencies are unaffected, so that the output beam is the same as the input beam.

To determine the voltage that needs to be applied to each pixel of the SLM to shape the beam, the so-called multiphoton intrapulse interference phase scan (MIIPS) algorithm [84, 85] is used. This generates a compensation phase mask to be applied to the SLM, to account for the dispersion of the pump/Stokes beam that is induced by the 28 mm pressure cell fused silica entrance window. Other optics in the setup, such as lenses, contribute to this dispersion as well, but to a lesser extent. Linear and nonlinear dispersion is accounted for using the pulse shaper, creating a nearly transform limited pump/Stokes beam at the interaction probe volume inside the pressure cell, after having passed through the entrance window.

4.2.1 Pump/Stokes Beam Characterisation

Frequency-resolved optical gating (FROG) [86, 87] was used to characterise the pump/Stokes beam. For this, the beam travelled through the pulse shaper and then a window that was the same as the pressure cell window, before being routed to the FROG apparatus. The time domain intensity and phase of the beam were recorded, with and without a dispersion compensating phase mask on the SLM of the pulse shaper. The result is shown in Figure 4.3.

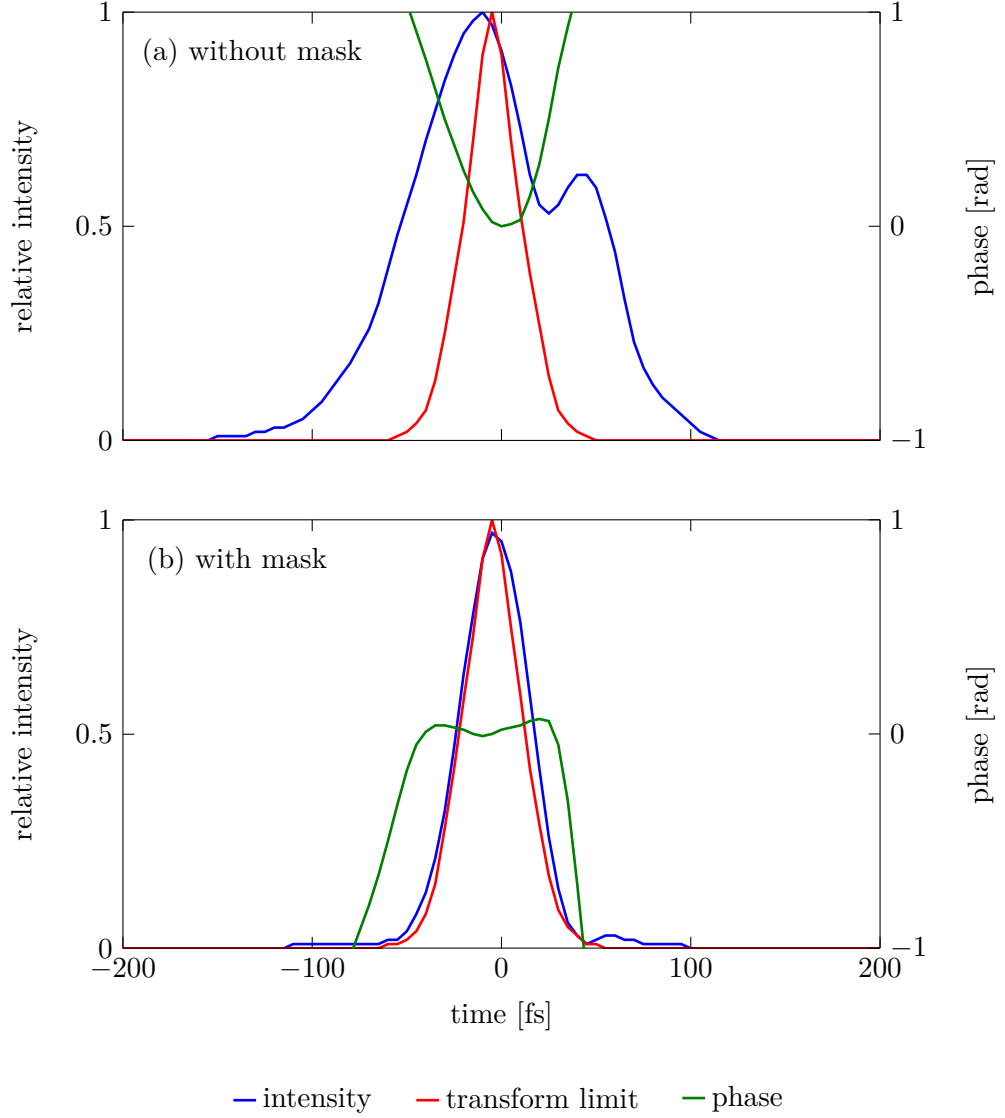


Figure 4.3: FROG measured intensity (blue), transform limit (red) and phase (green) of the pump/Stokes pulse after passing first through the pulse shaper and then a 28 mm quartz window. (a) with no compensation phase mask: the intensity is far from its TL and has a width (FWHM) of 112 fs; the phase changes significantly over the length of the pulse. (b) with a compensation phase mask: the intensity is almost at its TL and has a width of 42 fs; the phase is almost constant over the length of the pulse.

It can be seen that without the mask, the intensity is far from its transform limit and the shape of the pulse is asymmetric, with a width (FWHM) of 112 fs. Further, the phase varies significantly over the length of the pulse. However, when the appropriate phase mask is used, the beam is almost symmetric and has a width of only 42 fs, which is very close to its transform limit. In addition, the phase is nearly constant over the length of the pulse. This demonstrates the suitability of using a pulse shaper for effective dispersion correction of a femtosecond laser beam.

The efficient dispersion correction of the pump/Stokes beam using the pulse shaper can also be demonstrated directly, through CARS measurements of argon gas. Argon does not have any resonant CARS transitions and therefore a CARS spectrum of argon just contains a nonresonant contribution, arising from transitions between virtual states only and not involving any real rotational states. This nonresonant Ar signal is a representation of the pump/Stokes excitation efficiency (also denoted the experimental spectral response), which is a measure of the relative strength of the CARS signal at different frequencies. Figure 4.4 shows two nonresonant argon CARS spectra, one recorded with the appropriate phase mask on the SLM (blue line) and one without (red line).

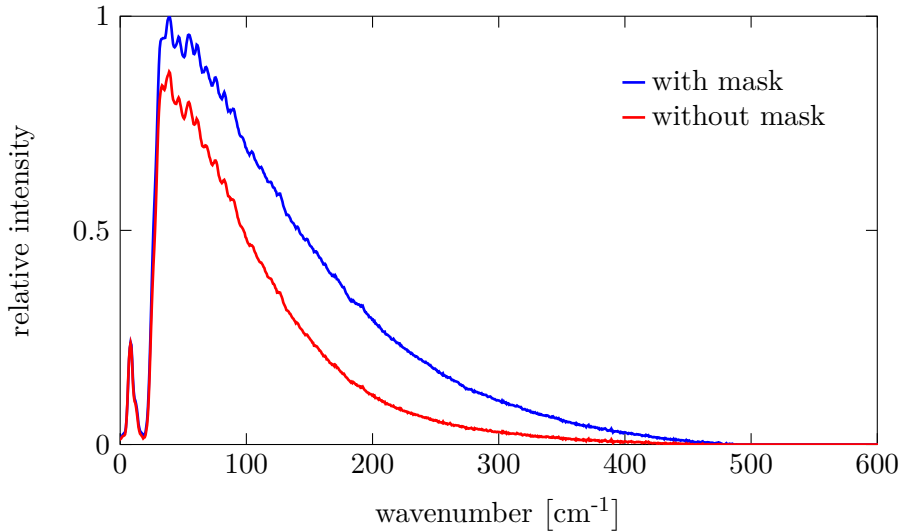


Figure 4.4: Nonresonant CARS spectra of argon. One is taken without the phase mask on the SLM (red line), corresponding to the pump/Stokes pulse of Figure 4.3 (a), and one is taken with the phase mask on the SLM (blue line), corresponding to the pump/Stokes pulse of Figure 4.3 (b).

It can be seen that using the mask significantly increases the excitation efficiency, as there is an increased NR signal across all wavenumbers, compared to not using a mask. Especially at higher wavenumbers ($>300 \text{ cm}^{-1}$), there remains a relatively large response when the mask is used. This is because pump/Stokes excitation at higher wavenumbers requires an increasingly larger frequency separation between

intrapulse pump and Stokes interactions, which quickly lose time coincidence with increasing pulse dispersion. Hence, the less dispersed, more transform limited a pulse is, the stronger and larger its excitation efficiency will be, confirming the FROG measurements.

4.3 Probe Beam and SHBC

The probe beam is generated from the other single pass amplifier output beam via chirped pulse sum frequency generation using second harmonic bandwidth compression. This SHBC setup, adapted from a technique by Raoult *et al.* [88], is described in detail in a paper published as part of this research project (Courtney *et al.* [89]). While most SHBC setups start with compressed beams [52, 80], the design presented here uses the uncompressed amplifier output directly, as can be seen in Figure 4.1. This reduces the number of gratings needed in the setup, making it simpler, while at the same time leading to a higher power throughput. The uncompressed, strongly chirped amplifier output beam is split into two equally powerful beams, that are each routed through a grating compressor (1500 grooves/mm) which have their gratings shifted in an equal but opposite way from the separation needed for complete pulse compression. Thus, the gratings are set at $L + \delta$ and $L - \delta$, where L is the grating separation that leads to complete (unchirped) pulse compression and δ is a small offset. This compresses the two beams but leaves a small chirp that is equal but opposite, with the $L - \delta$ grating separation resulting in a small positive chirp and the $L + \delta$ grating separation in a small negative chirp (for positive δ). A translation stage in the negatively chirped beam path is used to control the relative time delay between the oppositely chirped pulses, allowing for fine-tuning of the SFG pulse.

Further, two stacked angle-tuned short pass filters (FF01-842/SP-25 Semrock) in the positively chirped beam are used to cut out the leading edge of that pulse, resulting in an SFG pulse with a relatively clean and steep early time profile, albeit not as steep as anticipated. This is ideal for HR-CARS measurements at short time delays, as it ensures that the probe beam is not present at the pump/Stokes interaction, but does overlap with the molecular response, to result in a strong CARS signal without a significant nonresonant contribution.

After the chirping, the two beams are down collimated in a Galilean telescope with 500 mm and 250 mm spherical lenses, from a beam diameter of 10 mm to 5 mm. This increases the energy density and allows for a more efficient sum frequency generation, without damaging the SFG crystal, as would happen if the beams were focused onto it. The SFG crystal used is a 1 mm beta barium borate (BBO) crystal (Type 1), in which

the two beams are combined, such that their frequencies add via SFG to produce a narrowband picosecond pulse centred at 396.5 nm. The fundamental input beams are crossed at a very narrow angle ($\sim 1^\circ$), to minimise spatial chirp. The SFG process is depicted in Figure 4.5.

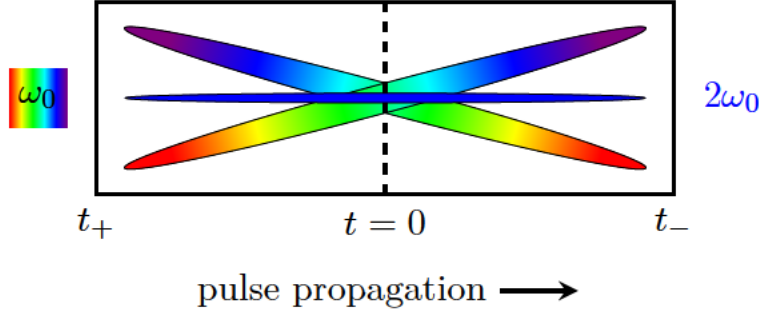


Figure 4.5: SFG process in the time domain of two oppositely chirped fundamental pulses with frequency ω_0 combining to create one frequency upconverted unchirped pulse with frequency $2\omega_0$. The chirp of the fundamental pulses is linear with respect to frequency.

This SFG process can be expressed as the sum of two time-dependent, linearly chirped frequencies, $\omega_1(t)$ and $\omega_2(t)$, which create a time-independent SFG frequency, ω_3 , as follows:

$$\omega_1(t) = \omega_0 + \alpha t$$

$$\omega_2(t) = \omega_0 - \alpha(t - \tau)$$

$$\omega_3 = \omega_1(t) + \omega_2(t) = 2\omega_0 + \alpha\tau \quad (4.1)$$

where ω_0 is the fundamental frequency of the input beams and $\alpha = d\omega/dt$ is the linear temporal chirp. τ is the relative time delay between the two input pulses and can be adjusted to tune ω_3 . When $\tau = 0$, the SFG frequency is exactly twice the fundamental frequency. However, the SFG process illustrated in Figure 4.5 is an ideal case. In reality, the chirp of the fundamental beams has nonlinear temporal contributions, induced by the optics in the beam path, such as the gratings. This results in a time-dependent SFG frequency, $\omega_3(t)$, that is slightly blue-shifted from its minimum of $2\omega_0$ at early and late t [89].

The SFG beam emerging from the BBO crystal is filtered with a neutral density filter (1.0 OD), to reduce its power to avoid damaging the grating of the grating filter (see below). Further, the beam is collimated with a 50 mm and a 100 mm spherical lens, to reduce spatial variations in the beam intensity. At this point, the beam has spectral wings arising from imperfect conjugate chirping (frequency distributions at each point

in time in the broadband fundamental pulses), together with blue-shifted satellite peaks, that are a result of interferences of the blue-shifted parts of the SFG beam (that in turn arise from the nonlinear chirp of the fundamental beams) [89]. These are filtered out in a folded $4f$ grating filter (f.l.=1 m, 1800 grooves/mm grating) with a slit at the Fourier plane. This filtering simplifies the probe pulse shape and therefore also the CARS signal lineshapes. The spectral wings, though a lot weaker than the peak of the probe, are similar in strength to the CARS signal. Their reduction diminishes the background noise coming from the probe, that otherwise is present in collinearly phase-matched CARS.

4.3.1 Probe Beam Characterisation

The picosecond SFG probe beam emerging from the BBO crystal, with spectral wings and satellite peaks filtered out in the folded $4f$ grating filter, has a frequency domain bandwidth (FWHM) of 3 cm^{-1} (deconvolved with the spectrometer's slit function, separately measured to be 1.5 cm^{-1}). Its time domain duration is about 5.5 ps, as confirmed with a pump-probe intensity cross correlation of the NR signal in pure argon. Figure 4.6 displays these beam characteristics.

The energy conversion efficiency of the SHBC setup is 20%, as the combined 6 mJ/pulse of the input beams result in a 1.2 mJ/pulse SFG beam (measured just after the BBO crystal). As different laser systems have different fundamental bandwidths, the bandwidth reduction from the fundamental beams to the SFG beam is quantified using the bandwidth reduction factor, $\Delta\nu_R$. This factor is defined as the quotient of the division of the fundamental bandwidth, $\Delta\nu_{fundamental}$, and the SFG bandwidth, $\Delta\nu_{SFG}$:

$$\Delta\nu_R = \frac{\Delta\nu_{fundamental}}{\Delta\nu_{SFG}} \quad (4.2)$$

In the literature, reported values of $\Delta\nu_R$ are in the range of 20-40 for ≥ 100 fs laser systems [52, 88] and about 60 for short pulse (35 fs) laser systems [90]. The SHBC system built for this project achieves a much higher bandwidth reduction of $\Delta\nu_R = 120$, as the fundamental bandwidth of the input beams is 360 cm^{-1} and the bandwidth of the SFG beam is 3 cm^{-1} .

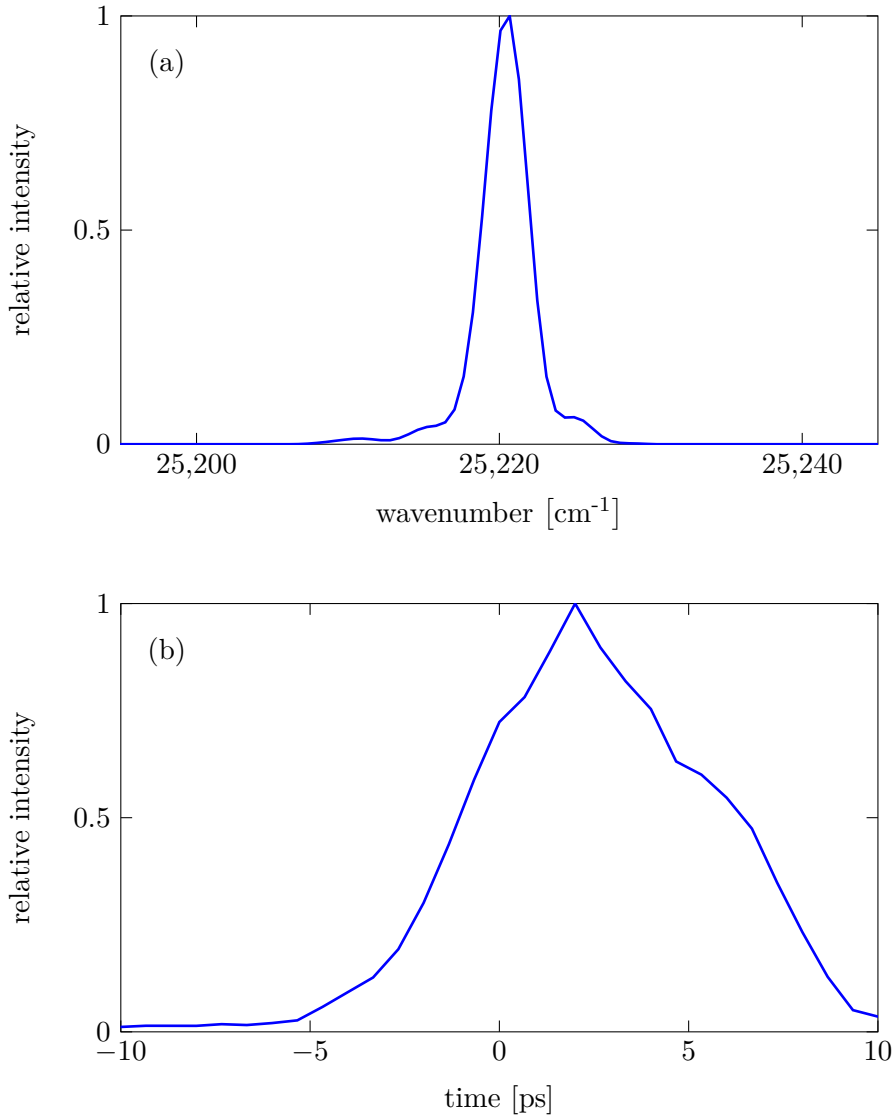


Figure 4.6: Characterisation of the probe beam created by the above described SHBC setup. (a) in the frequency domain, measured with a spectrometer. It has a FWHM bandwidth of 3.5 cm⁻¹ (3 cm⁻¹ after deconvolution with the spectrometer's 1.5 cm⁻¹ slit function). (b) in the time domain as the square root of the intensity ($E = \sqrt{I}$), measured with a cross correlation in nonresonant argon (the same as shown in Figure 3.3). It has a FWHM duration of about 5.5 ps.

4.4 Pressure Cell and Spectrometer

The pulse shaper adjusted fs pump/Stokes beam and the ps SFG probe beam are routed to a high pressure gas cell, in which they are combined collinearly through the use of a dichroic mirror that transmits the 396.5 nm probe beam and reflects the 795 nm pump/Stokes beam. Before combination in the dichroic mirror, the polarisation of the pump/Stokes beam is rotated by 90° in a periscope, so that the two beams have matched vertical polarisations. A time delay between the pulses is provided by

a computer-controlled translation stage (ThorLabs NRT100) in the probe beam. The beams are focussed into the cell with an uncoated spherical lens of focal length 300 mm. The power of the beams just before the cell was measured to be 10 $\mu\text{J}/\text{pulse}$ for the pump/Stokes beam and 5 $\mu\text{J}/\text{pulse}$ for the probe beam. The $1/e^2$ diameters at the beam waists are 100 μm and 70 μm respectively. The collinear geometry is chosen mainly to achieve an increased CARS signal from the rather low power input beams, by creating a longer CARS interaction region, which is still much shorter than the length of the cell (the Rayleigh range of the pump/Stokes and probe beam is 9.8 mm and 9.7 mm respectively). However, having all beams, including the signal beam, normal to the pressure cell windows, also avoids any spatial and temporal walk-off that could be caused by changes of the refractive index of the windows with increasing pressure. The custom-built pressure cell itself is an insulated stainless steel cylinder of length 30 cm and diameter 15 cm, with the gas to be probed being contained in a core of diameter 2.5 cm in the centre of the cylinder. A simplified schematic diagram of this pressure cell is shown in Figure 4.7. The cell contains four heating rods that are symmetrically arranged around its centre, which allow for the cell to be heated to up to 1000 K.

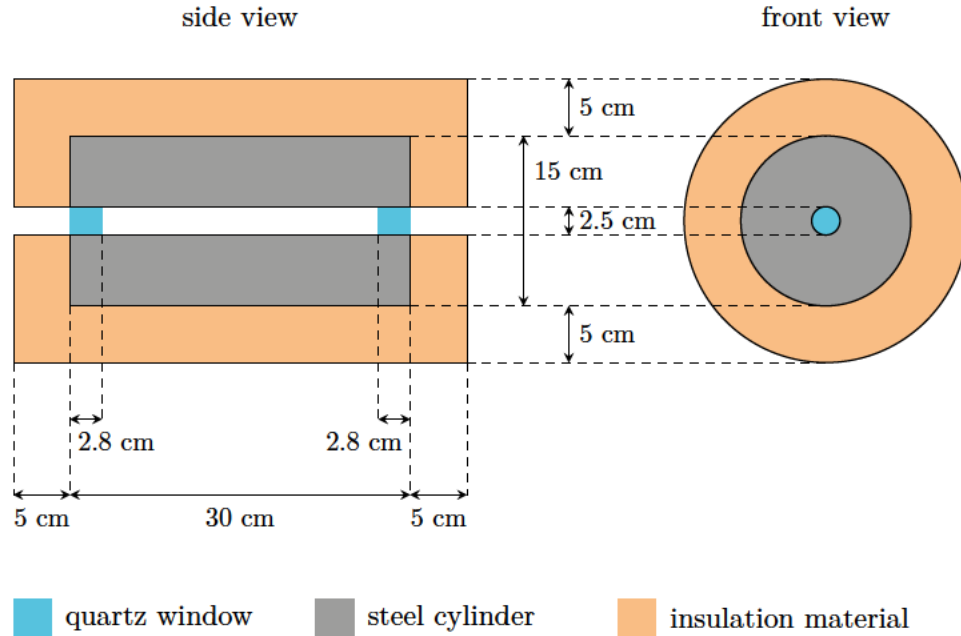


Figure 4.7: Simplified schematic diagram of the high pressure cell drawn to scale, with the most important dimensions marked. The gas to be probed is held in the centre of the cell, between the two quartz windows. It enters and leaves the cell through small tubes connecting the centre with the outside (not shown). The cell also contains heating rods that are symmetrically arranged around its centre, which allow for the cell to be heated to up to 1000 K (not shown).

After the cell, an uncoated 200 mm spherical lens is used to collimate the exiting pump/Stokes, probe and signal beams. Due to the collinear geometry, the signal is generated in the same direction as the probe beam, so the two spatially overlap. To remove the probe from the signal beam, a folded $4f$ grating filter with a sharp

edge at the Fourier plane is used. This ensures that the probe is almost completely removed from the signal, while retaining almost all CARS transitions, including even the $J = 2 \rightarrow J = 4$ lines, which are just 28 cm^{-1} from the centre of the probe. Optical short-pass filters are not able to provide a sufficiently sharp edge to retain enough of the low power CARS signal, which is why the grating filter is used. A 75 mm spherical lens then focusses the CARS signal onto the entrance of a 0.550 m Czerny-Turner spectrometer (Horiba iHR550, 2400 grooves/mm grating). The signal intensity entering the spectrometer is adjusted with neutral density filters just before the final focussing lens. Inside the spectrometer, the CARS signal is then dispersed onto a back-illuminated CCD (Andor DU971N-BV, 400×1600 pixel, $16 \mu\text{m}$ pixel size). 1 kHz single-shot data collection is achieved by vertically binning the CARS signal in an 11×1000 pixel region in $<1 \text{ ms}$ ($10 \mu\text{s}$ exposure).

4.5 Experimental Procedure

HR-CARS spectra of N_2 were measured over a large range of temperatures and pressures using the above described experimental setup. The pressure cell is rated for up to 70 atm at room temperature, with the maximum possible pressure decreasing linearly with increasing temperature, to 38 atm at 1000 K. This leads to a trapezoid of temperatures and pressures (T-P) that can be safely achieved with this cell, as shown by the red boundary in Figure 4.8, which also shows all the temperatures and pressures at which spectra were taken (blue dots).

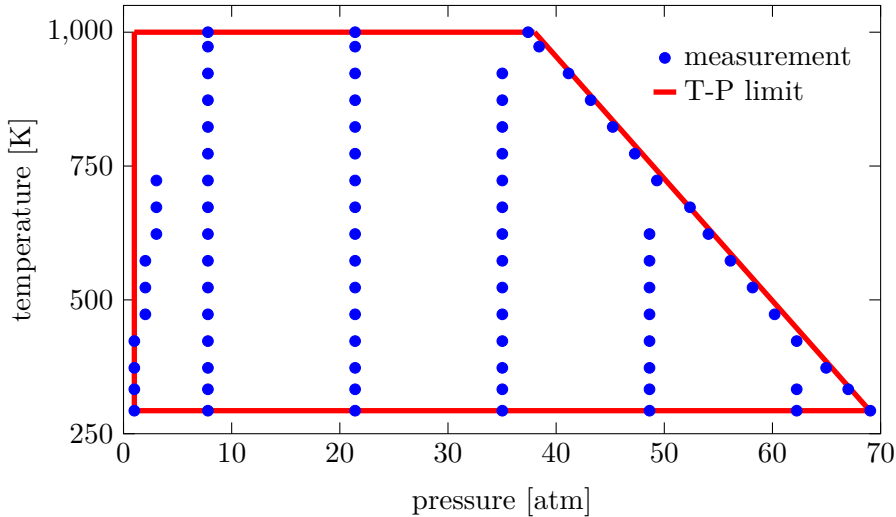


Figure 4.8: Graph showing the temperatures and pressures (T-P) for which the pressure cell is rated (bound by the red trapezoid) and the temperatures and pressures at which N_2 CARS spectra were recorded (blue dots).

At each of the T-P points, several (4-6) spectra were recorded at different probe time delays, all 1 ps apart and centred at about 8.4 ps, the time of the first full revival of the molecular response of N₂. Temperatures were measured with a thermocouple inserted into a separate hole in the steel cylinder, about 5 cm from the centre of the cell. The thermocouple measurements were validated by separately testing the cell with an additional thermocouple that was placed in the core of the cell, where the probed gas is held. It was found that the temperature readings for both thermocouples were in good agreement. To ensure that the gas had the same temperature as the cell, the cell was kept sealed for some minutes before measurement or kept at a minimum flow necessary for maintaining the desired pressure (as the cell did not seal completely at the highest pressures and leaking gas had to be replaced with fresh gas to hold the pressure constant). Nonresonant argon spectra were also recorded, as part of cross correlations to determine the probe pulse shape in time, and also to correct the N₂ spectra for the excitation efficiency of the pump/Stokes beam. In addition, background spectra were recorded with the pump/Stokes beam blocked, to correct for background light falling onto the CCD. At each temperature, pressure and probe time delay, 1000 single laser shots were collected.

Chapter 5

Results

In this chapter, all relevant experimental and modelling results are presented and explained in full detail. Part of the results shown have also been published in a paper as part of this research project (Mecker *et al.* [91]), but a much more thorough analysis is given here. The chapter starts with a discussion of the post-processing procedure, including an overview of a selection of experimental spectra to demonstrate trends between spectra recorded at different temperatures, pressures and probe time delays. Next, the computational method for fitting model spectra to experimental ones is discussed, including the associated difficulties and challenges. This is followed by a study of the sensitivity of the best fit temperature to different fitting parameters, to validate the reliability of the fitting procedure.

The chapter continues with a detailed analysis of the best fit results, starting with a qualitative presentation of best fit model spectra. Then the main aim of this research project, the accuracy of high pressure gas-phase thermometry using HR-CARS, is addressed, through a discussion of the best fit temperature results compared with measured thermocouple temperatures. After this, best fit temperature results of single shot, rather than averaged, spectra are shown, to prove that the experimental procedure presented in this thesis is capable of accurately measuring single shot spectra. Next, a comparison between best fit temperatures obtained using linewidths acquired experimentally and from the modified exponential gap model is included. Finally, room temperature spectra of air and the corresponding model fits are shown, as a validation of the computational model and fitting routine beyond pure nitrogen.

5.1 Post-Processing

After recording the raw experimental spectra as described at the end of Chapter 4, each of them was post-processed. The 1000 single shot spectra taken at each pressure, temperature and probe time delay were averaged, excluding any that were saturated. This averaging was performed not only on the N₂ spectra, but also on the nonresonant

argon and background spectra. From each averaged N₂ and Ar spectrum, the corresponding averaged background spectrum was subtracted, to correct the spectra for background light falling onto the CCD. Any resulting negative intensities, due to a background spectrum having a slightly higher intensity than the corresponding CARS spectrum at certain frequencies, were set to zero. The N₂ and Ar spectra were then normalised, ready to be fitted in the computational CARS code.

5.1.1 Wavenumber Axis Calibration

The post-processed experimental spectra display the relative CARS intensity recorded at each pixel of the CCD chip. To map the experimental spectra from this pixel axis onto a more useful wavenumber axis, a calibration is performed. This is done by making a linear fit of the position of the experimental CARS peaks in pixel space to their theoretical position in wavelength space. For this, a low pressure spectrum with a time delay close to the first revival of the N₂ molecular response is chosen (because of its simplicity and high resolution), and the pixel number of each CARS peak is recorded. Next, the theoretical wavenumber of each peak (i.e. each S-branch transition) is calculated according to Equation 2.62. To these, the wavenumber of the probe beam, 25221 cm⁻¹ (396.5 nm), is added and the result is converted to wavelength. The pixel number of each CARS peak is then fit linearly to its corresponding theoretical wavelength. This leads to a linear calibration equation of the form:

$$wavelength = m \times pixel + c \quad (5.1)$$

where m is a gradient in nm/pixel and c an intercept in nm. This calibration equation can be used to calculate the wavelength corresponding to each pixel of an experimental spectrum, i.e. a wavelength axis. The calibrated wavelength axis is then inverted to a wavenumber axis. From this, the wavenumber of the probe beam is subtracted, so that the final wavenumber axis is relative to the probe beam frequency. This calibration was performed on several well resolved spectra taken at different times, to account for possible changes in the calibration with time. An example calibration is shown in Figure 5.1.

The gradient and intercept values across all calibrated spectra are very similar, on average $m = -0.009560$ nm/pixel (with a standard deviation of 7×10^{-6} nm/pixel) and $c = 396.238$ nm (with a standard deviation of 0.015 nm), respectively. The small standard deviations indicate that the calibration is very repeatable and does not change significantly with time. Further, regression statistics give an average coefficient of determination of $R^2 = 0.999985$, showing that a linear wavelength calibration is satisfactory.

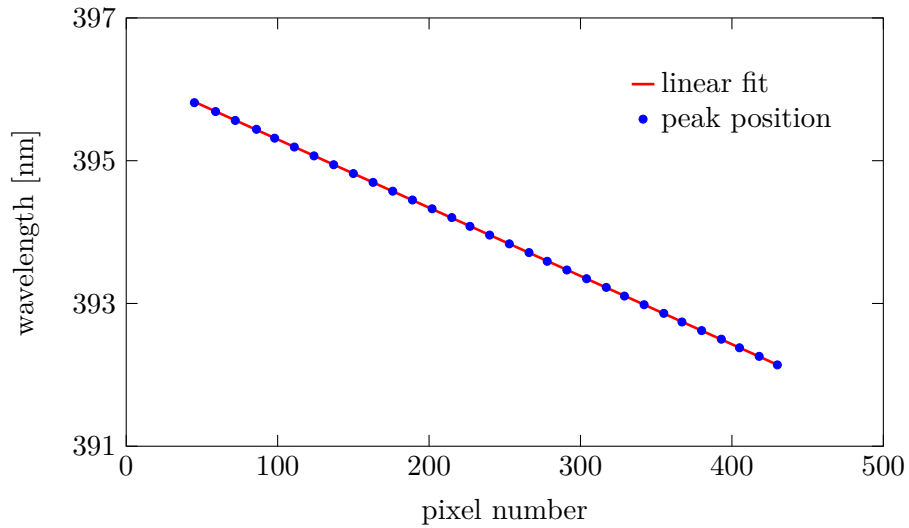


Figure 5.1: Wavelength calibration of an N_2 CARS spectrum at 823 K, 8 atm and a probe time delay of 8 ps. The peak position (blue dots) shows the pixel number of each CARS peak (on the x-axis) and the corresponding theoretical wavelength (on the y-axis). A linear fit (red line) to the peak position data is shown as well. The gradient and intercept of this fit are $m = -0.009567 \text{ nm/pixel}$ and $c = 396.255353 \text{ nm}$, respectively. The coefficient of determination is $R^2 = 0.999993$.

5.1.2 Experimental Spectra

To illustrate the similarities and differences between spectra recorded at different pressures, temperatures and probe time delays, a few selected experimental spectra are shown below, grouped in three sets. The first set shows spectra at the same pressure and probe time delay, but increasing temperatures. The second set shows spectra at the same temperature and probe time delay, but increasing pressures. The last set compares low and high pressure spectra at the same temperature but different probe time delays. The presented spectra are only a small fraction of the entire set of recorded experimental N_2 CARS spectra, but the trends shown represent general trends, that are seen across the complete set of spectra. Furthermore, they demonstrate how different the spectra can be at different conditions, making them a challenge to fit.

Figure 5.2 shows spectra at a fixed pressure of 8 atm and a fixed probe time delay of 9 ps, with temperatures ranging from 373 K to 973 K in steps of 200 K. Unsurprisingly, it can be seen that as temperature increases, the Boltzmann distribution of the S-branch transitions shifts towards higher wavenumbers, as more rotational states are populated.

Much more interesting is the change of the spectra with increasing pressure, at a fixed probe time delay and temperature. Figure 5.3 shows spectra at a probe time delay of 9 ps and a temperature of 373 K at pressures of 1 atm, 21 atm, 35 atm and 65

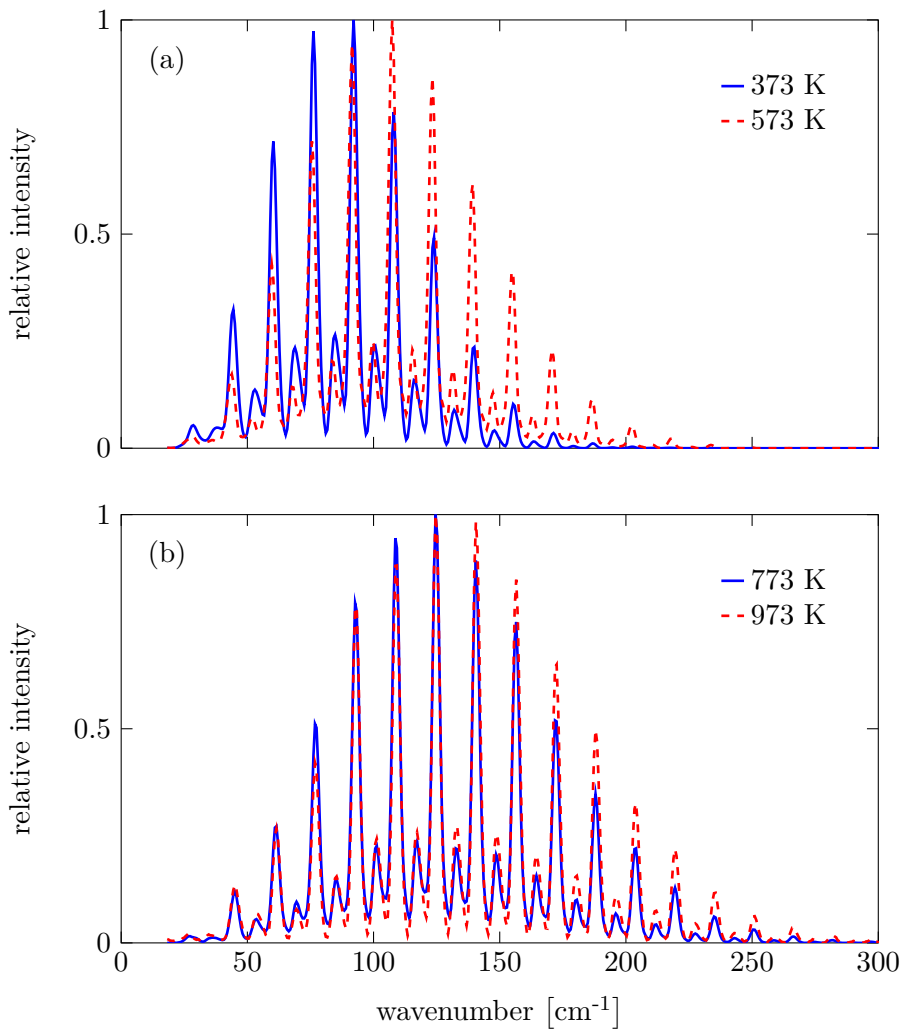


Figure 5.2: HR-CARS spectra of N₂ at a pressure of 8 atm and a probe time delay of 9 ps. (a) displays spectra at 373 K and 573 K. (b) displays spectra at 773 K and 973 K.

atm. Overall, the spectra remain well resolved at all pressures. At 65 atm, the lines can be seen to be marginally wider, due to the Fourier transform relationship between CARS signal decay in the time domain and line width in the frequency domain. This, however, only makes a difference at the highest pressures. For lower pressures, the width of the probe beam (3 cm⁻¹) is the limiting factor that dictates the line width. Much more significant is the change of the shape and relative intensity of the small lines (that result from transitions from odd rotational levels), which vary considerably across the different pressures. This is caused by the time domain molecular response decaying with increasing pressure, so that the parts of it that overlap with the probe pulse have different relative strengths at different pressures, resulting in different CARS signals. This effect is enhanced by the probe beam having an asymmetric shape and being chirped.

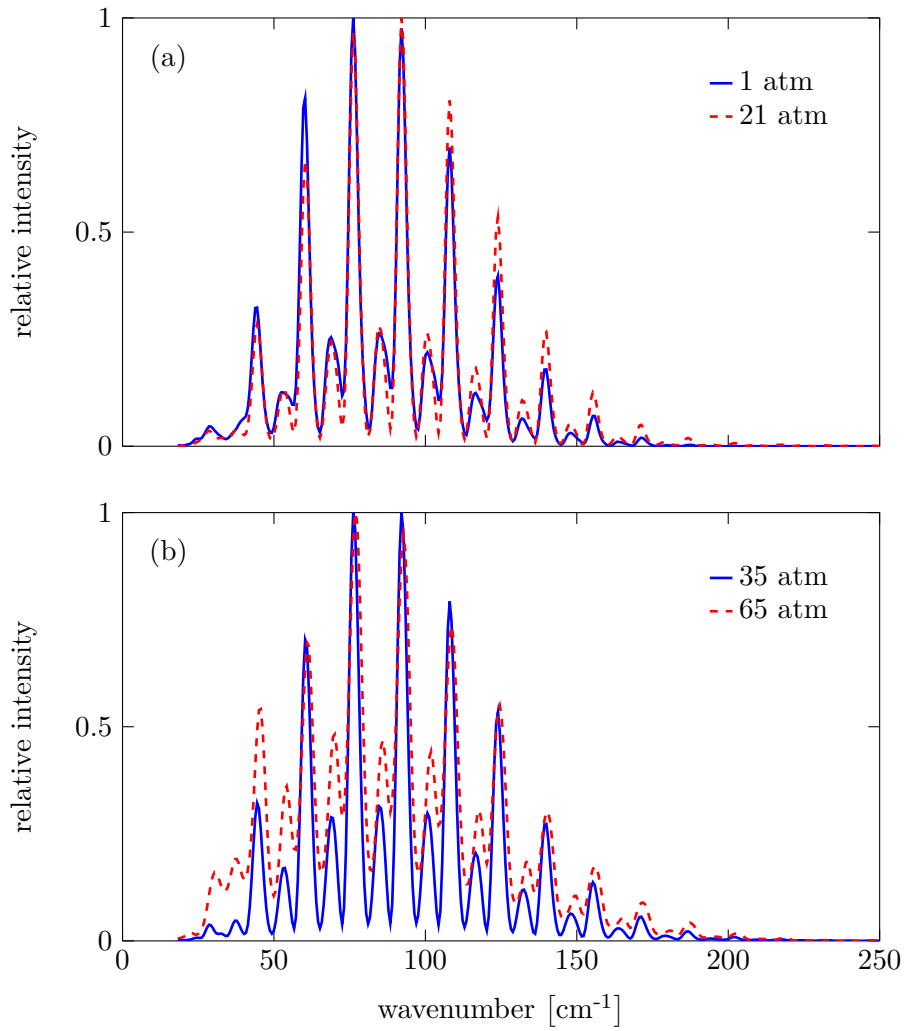


Figure 5.3: HR-CARS spectra of N_2 at a temperature of 373 K and a probe time delay of 9 ps. (a) displays spectra at 1 atm and 21 atm. (b) displays spectra at 35 atm and 65 atm.

Also interesting is the change of spectra with probe time delay, at a given temperature and pressure. Figure 5.4 (a) shows two spectra at 8 atm and 373 K, one at a probe time delay of 8 ps and one at a probe time delay of 9 ps. At this lower pressure, both spectra look very similar, especially the shapes of the small lines do not change significantly between the two probe time delays. This is a lot different in Figure 5.4 (b), which shows spectra at the same temperature and probe time delays as Figure 5.4 (a), but at a pressure of 65 atm. Here it can be seen that the small lines change significantly in shape and relative intensity when the probe time delay is altered by only 1 ps. The cause of this is the fast decay of the molecular time domain response at high pressure, which means that a probe pulse at a slightly different time delay overlaps with parts of the molecular response that have very different relative strengths, resulting in a different CARS signal. This is the converse effect of keeping the time delay fixed and increasing the pressure (as in Figure 5.3). Again, the asymmetric shape of the probe beam together with its chirp enhance the effect.

Additionally, high pressure spectra appear to get hotter at later probe time delays. This is a general trend, which unfortunately is barely noticeable in Figure 5.4 (b), as it requires a larger probe time delay difference than just 1 ps to become evident. This trend is a result of transitions with larger linewidths (lower J) decaying faster in time than those with smaller linewidths (larger J), with increasing pressure. Thus, at high pressure, a longer delay of a short probe pulse preferentially detects larger Raman shifts.

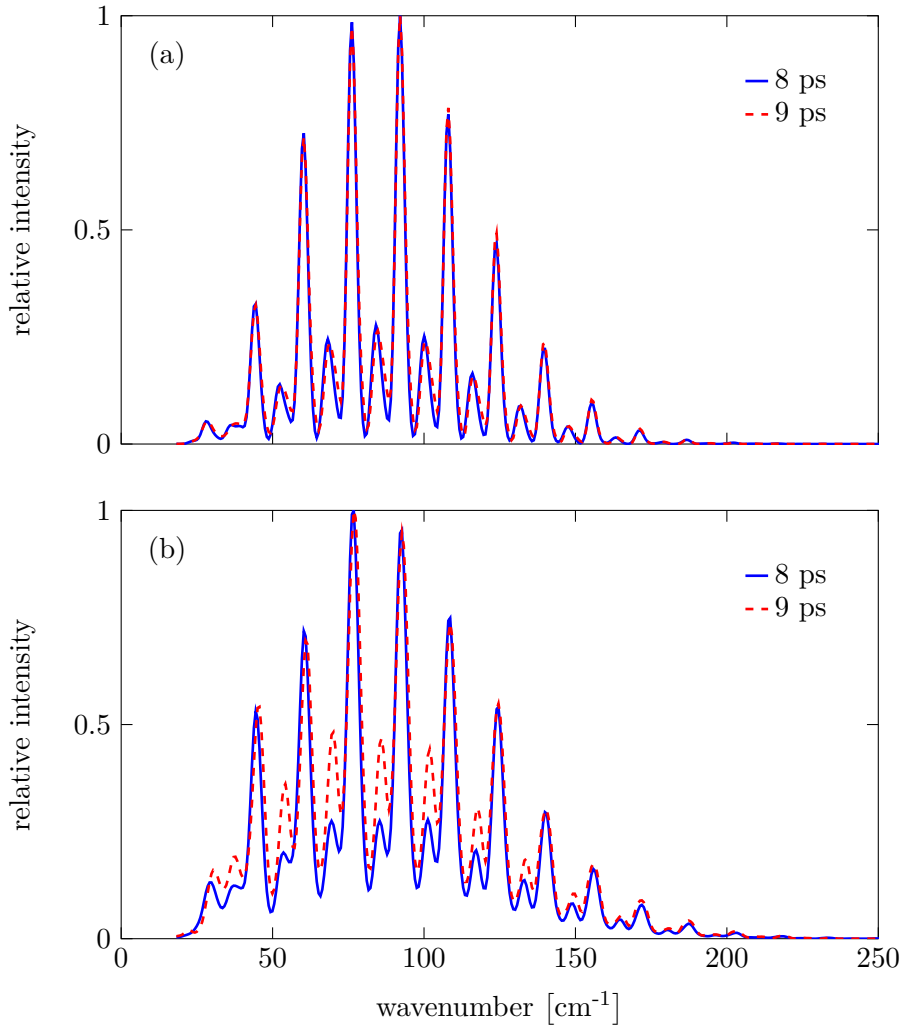


Figure 5.4: HR-CARS spectra of N₂ at a temperature of 373 K and probe time delays of 8 ps and 9 ps. (a) displays spectra at 8 atm and (b) displays spectra at 65 atm.

5.2 Fitting Procedure

A non-linear least squares fitting routine in MATLAB, called *lsqcurvefit*, is used to fit computational model spectra (modelled as described in Chapter 3) to the

post-processed experimental spectra. The *lsqcurvefit* algorithm allows one to define fitting parameters with initial values and to place lower and upper constraints on those parameters. The fitting algorithm then varies each of the fitting parameters in turn, within their respective lower and upper bounds, thereby computing different model spectra, until the difference to the experimental spectrum that is to be fitted is minimised in a least squares sense. The model spectrum that yields this minimised difference is the best fit model spectrum and the values of the fitting parameters required to generate this best fit model spectrum are the best fit values.

The fitting procedure that was used to fit the experimental CARS spectra operates with six fitting parameters: the temperature, the probe time delay, the probe pulse chirp factor, the wavelength axis calibration gradient and intercept and the relative height of the model to the experimental spectrum. The initial values and corresponding lower and upper bounds of these parameters are set follows:

- The initial value of the temperature is set to the thermocouple reading corresponding to the experimental spectrum to be fitted. The upper and lower bounds are set at $\pm 30\%$ from this value. This large variation range is chosen, as finding the best fit temperature is the primary aim of the fitting, and constraining the temperature range too much could lead to a falsely accurate best fit temperature.
- The probe time delay is initially set to the experimentally verified delay, as measured by the corresponding cross correlation. However, because of the non-Gaussian shape of the probe pulse, there is significant uncertainty in this delay. Therefore the probe time delay is allowed to vary within ± 2 ps of the initial value. This is done for the most resolved spectrum at a given temperature and pressure, to give a best fit probe time delay that is more accurate than the cross correlation measurement. The probe time delays for the fitting of the other spectra at the same temperature and pressure are then steps of 1 ps ± 0.2 ps from this best fit probe time delay.
- The probe beam chirp factor, α , is initially set to -0.7, which is the chirp required to stretch the probe beam from its transform limit of 4.9 ps to its measured length of about 5.5 ps. However, there is significant uncertainty in the exact chirp, due to the non-Gaussian probe pulse shape. For this reason, the constraints are chosen to be far apart, with upper and lower bounds of 0.0 and -2.0 respectively. Similar to the probe time delay, this is only done for the most resolved spectrum at a given temperature and pressure, to find a best fit chirp that is more accurate than the initial value. This best fit chirp is then used as the initial chirp for the fitting of all other spectra at the same temperature and pressure and is only allowed to vary by ± 0.2 .

- The wavelength axis calibration gradients (m) and intercepts (c) of all calibrated spectra were averaged and these averages are used as the initial values in the fitting procedure. Both, the gradient and intercept, are allowed to vary within $\pm$ three standard deviations from their respective averages. This allows a very subtle shift and stretch of the wavenumber axis and helps to optimise a fit.
- The initial value of the relative height of the normalised model to the normalised experimental spectrum is set to 1.0, so that the tallest peak of the model and experimental spectrum are at the same height. This factor is allowed to vary between 0.95 and 1.05 (corresponding to $\pm$ 5%). It accounts for a possible intensity offset of the tallest peak of the experimental spectrum.

5.2.1 Nonresonant Argon Spectra

Before the start of the fitting algorithm, the post-processed experimental N₂ spectrum to be fitted is divided by a corresponding nonresonant argon spectrum, to correct for the pump/Stokes excitation efficiency (which is discussed in Chapter 4). The argon spectrum used for the correction of a given N₂ spectrum is carefully selected to be one taken at the same pressure as, and close in time to, this N₂ spectrum. This is because of two important trends of the argon spectra that were observed. First, the Ar spectra (and therefore the pump/Stokes excitation efficiency) get narrower with increasing pressure. Second, the Ar spectra change over time, getting narrower or wider, from day to day, but also during the same day. Figure 5.5 (a) shows the narrowing of Ar spectra with increasing pressure and Figure 5.5 (b) shows the change of Ar spectra with time.

The narrowing of the NR argon CARS signal with pressure, implicating a reduced pump/Stokes excitation bandwidth, can be explained by increasing chirp induced in the beam as a result of the increasing number density of molecules inside the pressure cell that the pump/Stokes beam has to travel through before the probe volume. This chirp reduces the time coincidence of large frequency separations between intrapulse pump and Stokes interactions, the same reason as for the reduced excitation bandwidth observed when omitting the dispersion-correcting phase mask (see Figure 4.4), as in both cases the pump/Stokes beam is chirped at the probe volume. At atmospheric pressure, the group velocity dispersion (GVD) of argon at 800 nm and 15°C is 0.01887 fs²/mm [92]. Because the beam travels for about 15 cm inside the cell before the probe volume, this induces a small group delay dispersion (GDD) of 2.8 fs². Assuming a linear dependence of the GVD on pressure [93], the induced GDD at 62 atm is 175.5 fs². This is not negligible and equivalent to the dispersion induced in about 5 mm of fused silica glass (which has a GVD of 36.16 fs²/mm at 800 nm and 20°C [94]).

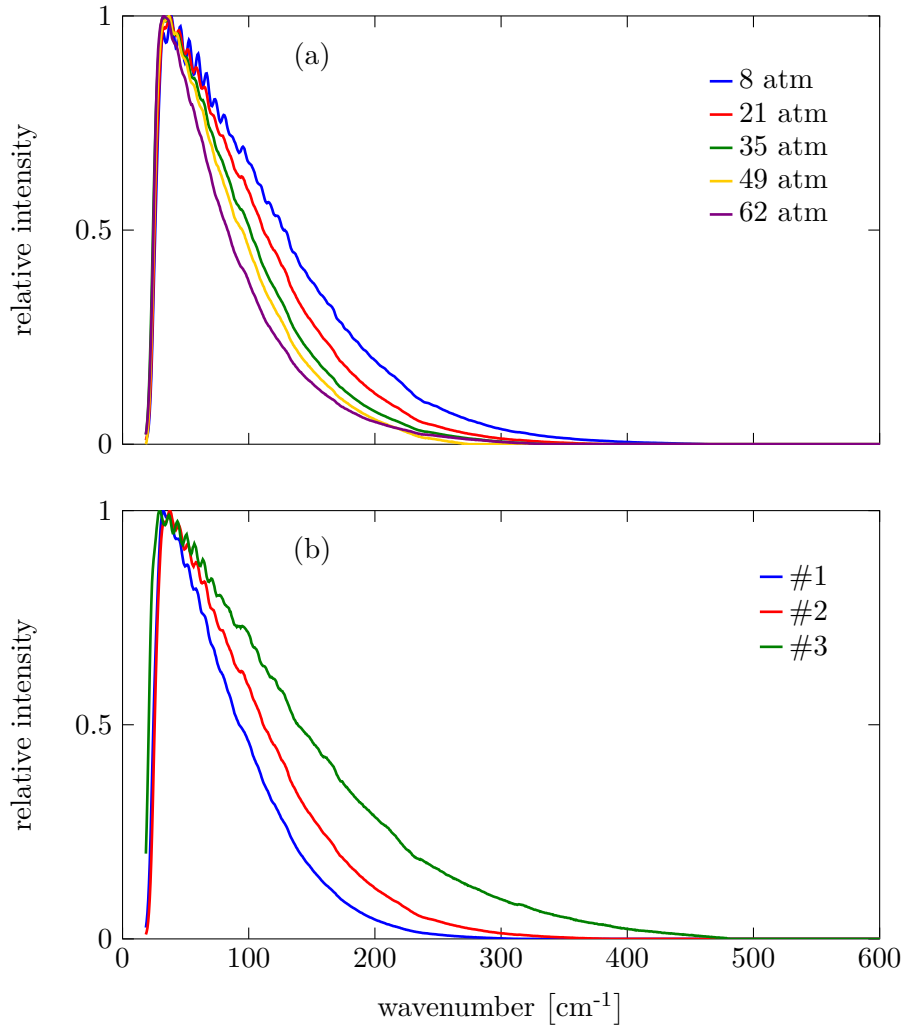


Figure 5.5: Nonresonant CARS spectra of argon. (a) displays spectra taken at the same time but different pressures. (b) displays spectra taken at the same pressure (21 atm) but at different times during the same day. The time elapsed between spectrum #1 and #2 is 2:18 h and between #2 and #3 is 1:41 h.

Unfortunately, it is not possible to use a dispersion-correcting phase mask to correct for the high pressure induced chirp, as there is no way to get high pressure feedback signal to the pulse shaper algorithm. However, even though this results in a reduced excitation bandwidth at high pressures, using a nonresonant Ar spectrum taken at the same pressure as an N₂ spectrum to be fitted achieves an accurate bandwidth correction for that spectrum.

The changes of the NR argon CARS signal with time are believed to arise from the pulse shaper. Slight alignment drift over time (common to many laser systems) of the pump/Stokes beam onto the liquid crystal array of the SLM can have large effects on the efficiency of the phase mask to correct for the pump/Stokes pulse dispersion after passing through the pressure cell window. This, in turn, has a large effect

on the excitation bandwidth. It is therefore important to measure the nonresonant argon spectra close in time to the corresponding N₂ spectra, so that they have the same pump/Stokes excitation efficiency. Otherwise, if a wrong excitation efficiency correction is used, the fit of an N₂ spectrum, including the best fit temperature, will be less accurate.

5.2.2 Fitting Sensitivity

A study of the sensitivity of the best fit temperature on the different fitting parameters was performed. This was done to determine how much the different fitting parameters affect the best fit temperature and to validate the reliability of the fitting procedure. Four spectra covering very different temperature and pressure regimes were selected from the four corners of the T-P trapezoid (Figure 4.8): low temperature and low pressure (333 K and 8 atm), low temperature and high pressure (333 K and 67 atm), high temperature and low pressure (1000 K and 8 atm) and high temperature and high pressure (1000 K and 37 atm). Due to the small number of spectra included in this sensitivity study, the results are not statistically representative of all spectra. However, they should serve as a strong indication as to how much the various fitting parameters affect the best fit temperature at different pressure and temperature conditions.

For this study, each selected spectrum was fit according to the afore-described procedure, to obtain the best fit values of each of the fitting parameters (temperature, probe time delay, chirp, wavelength axis calibration gradient and intercept and relative height). The fitting was then repeated with only the temperature allowed to float, while all other parameters were fixed at their best fit values, apart from one, that was offset from its best fit value. This was done in turn for each fitting parameter, to determine how much offsetting each parameter from its best fit value affects the best fit temperature. In each case, the residual (quantified as the sum of the absolute difference between the best fit model and the experimental spectrum at each wavenumber) and the temperature of the fit were recorded.

For this sensitivity study, the probe time delay was offset by ± 0.2 ps and ± 1.0 ps from its best fit value, the chirp parameter, α , was offset by ± 0.2 and ± 0.5 , the wavelength axis calibration gradient and intercept were each offset by ± 3 and ± 6 standard deviations (determined from the gradients and intercepts of all calibrated spectra) and the relative height was offset by $\pm 5\%$ and $\pm 10\%$. Figure 5.6 shows the results for offsetting the probe time delay and chirp. The residual and temperature are quantified as a percentage difference to their best fit values (from the initial fit, when all parameters are allowed to float within their respective upper and lower bounds).

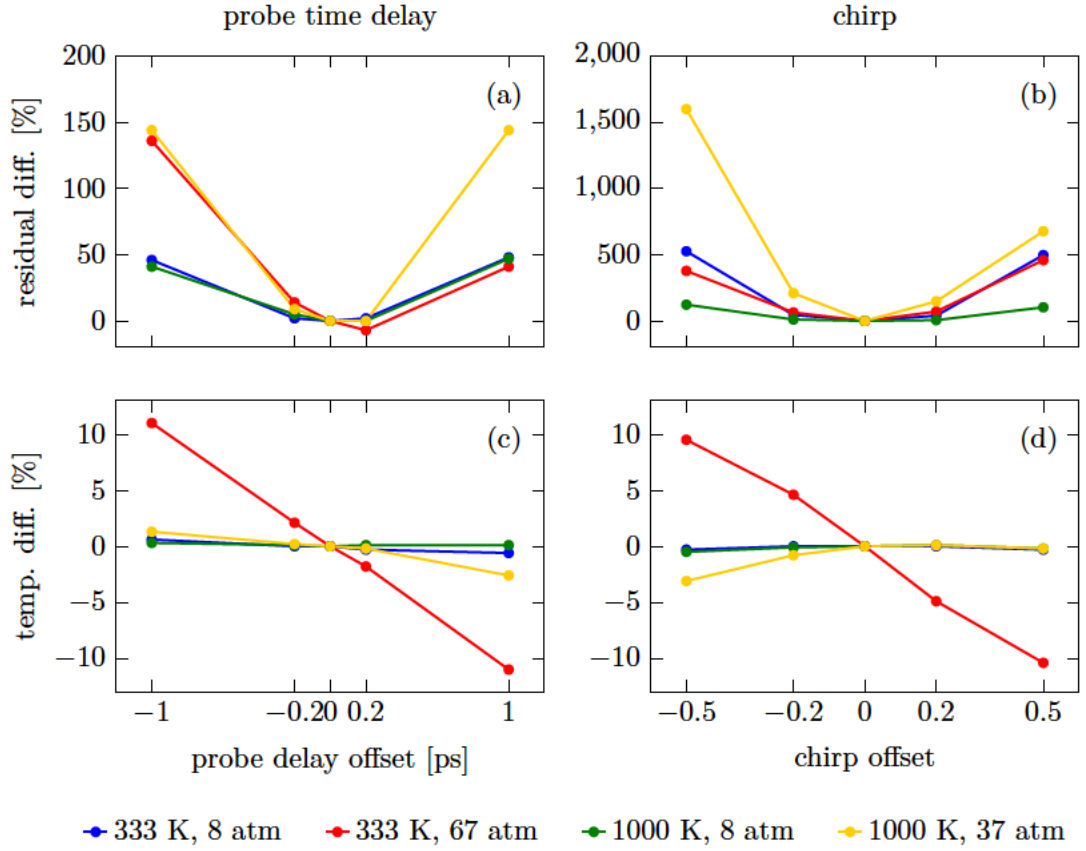


Figure 5.6: Sensitivity of the residual and temperature on probe time delay and chirp. (a) and (b) show the percentage differences in residual (as compared to the best fit residual) for probe time delay and chirp respectively. (c) and (d) show the percentage differences in temperature (as compared to the best fit temperature) for probe time delay and chirp respectively.

For an offset of the probe time delay by ± 0.2 ps, it can be seen that the residual does not change a lot from its best fit value, only by about 10%. However, when this offset is increased to ± 1.0 ps there is a significant increase in the residual of about 50% for the low pressure (8 atm) spectra and up to 150% for the high pressure (37 atm and 67 atm) spectra. When looking at the corresponding temperature differences, it is observed that they only change by about 2% from the best fit value, even at probe time delay offsets of ± 1.0 ps. The only exception is the highest pressure spectrum (67 atm), that has a temperature difference of about 10% at these large probe time delay offsets. For the chirp, the observations are similar. At a small chirp offset of ± 0.2 the residual increases, but not nearly as much as for the larger offset of ± 0.5 , in which case the residuals are between 100% and 1500% higher than the best fit residual. And for the temperature, it can be seen that it only changes by about 3% from its best fit value, even at the larger chirp offset. Again, the only exception is the highest pressure spectrum, which, at a chirp offset of ± 0.5 , has a temperature difference of about 10% to the best fit temperature.

Similar results were found for the wavelength axis calibration gradient and intercept and for the relative height. Offsetting these parameters from their best fit values by relatively large amounts increases the residual significantly, but does not affect the best fit temperature by more than a few percent, except for the highest pressure spectrum. The large increase in residual when the parameters are offset significantly from their best fit values shows that there exists a clear best fit spectrum at which the residual is minimised. Further, because the temperature does not change a lot from its best value at low and medium pressures, it can be concluded that it is not very sensitive to the other fitting parameters. It is only at high pressures that the other fitting parameters start to have a significant effect on the temperature. This shows the need for high pressure spectra to be modelled very carefully using accurate fitting parameters in order to get an accurate best fit temperature.

5.3 Fitting Results

All N₂ CARS spectra recorded at the different temperatures, pressures and probe time delays were post-processed and fitted according to the afore-described procedure and the best fit values of all fitting parameters were recorded. A detailed presentation and analysis of these best fit results is given below, focussing on the best fit temperature, as assessing the suitability of HR-CARS for high pressure gas-phase thermometry is the main aim of this research project.

5.3.1 Best Fit Spectra

Generally, the fits of spectra across all the different temperatures and pressures probed are very good, both qualitatively and quantitatively. This is confirmed by low residuals and accurate best fit temperatures. Due to the large number of spectra recorded and fitted, not all can be shown, but as an example, six fits of spectra taken at very different temperatures and pressures are presented in Figure 5.7. Three of them are low temperature spectra (333 K) at low (8 atm), medium (35 atm) and high (67 atm) pressures, one is a medium temperature, medium pressure spectrum (673 K, 35 atm) and two are high temperature (973 K) spectra at low (8 atm) and high (38 atm, the highest pressure at this temperature) pressures. The figure shows the best fit model spectra (dashed red line) overlaid with the experimental spectra (blue line) and the corresponding residual (green line). The spectra shown were all taken at a probe time delay of 8 ps, apart from the highest pressure one, (c), which was taken at a delay of 11 ps, as at this pressure the earlier probe time delay spectra have a nonresonant contribution due to the resonant CARS signal being relatively low at very high pressure.

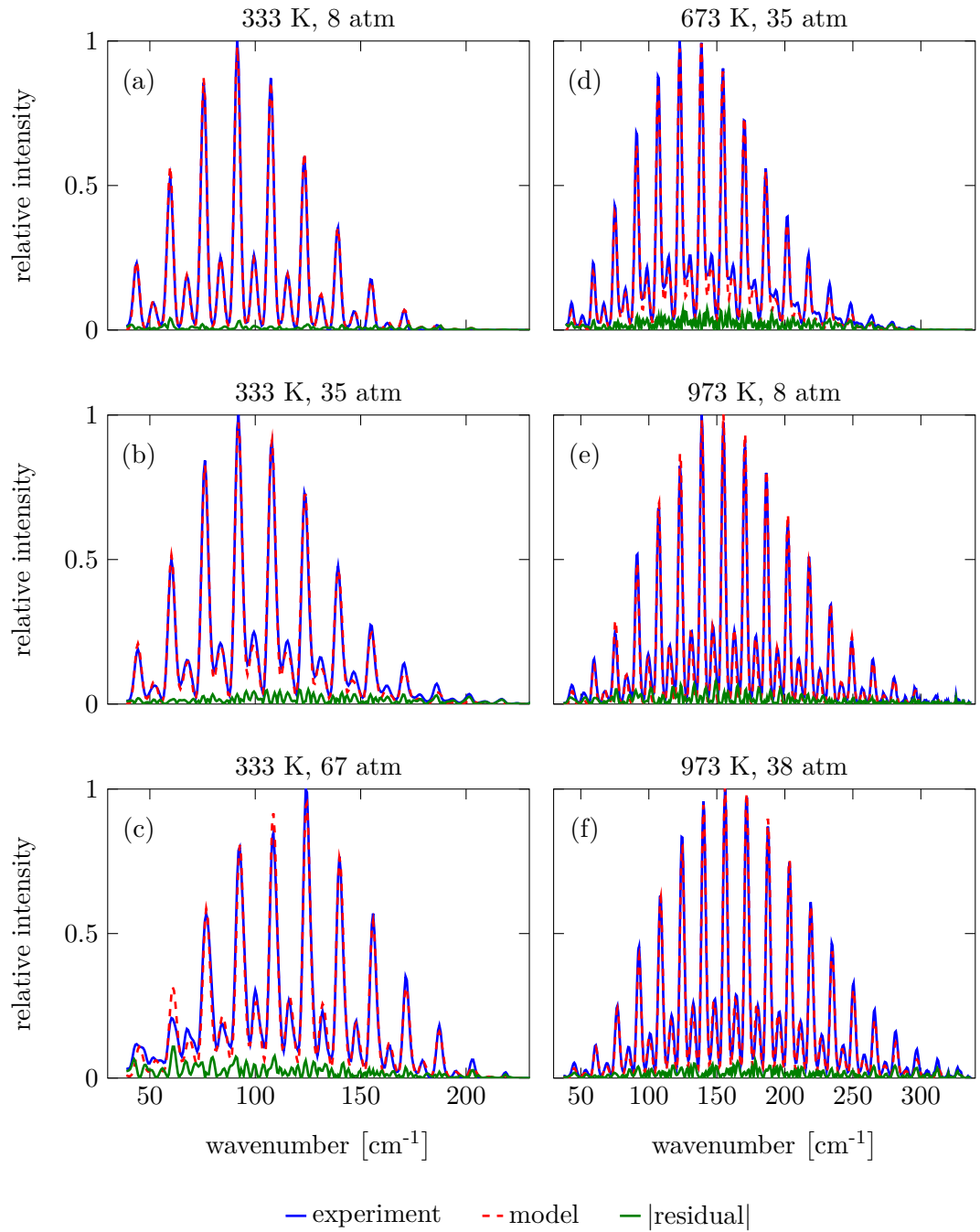


Figure 5.7: Experimental and corresponding best-fit model HR-CARS spectra of N₂ at different temperatures and pressures. Experimental (blue line) and best-fit model spectra (dashed red line) are shown together with their residual (absolute difference between the model and experimental spectra, green line). The spectra were all taken at a probe time delay of 8 ps, apart from (c), which was taken at a delay of 11 ps. The percentage differences between the best fit temperatures and corresponding thermocouple measurements (as a percentage of the thermocouple measurement) are: (a) 2.3%, (b) -3.2%, (c) -6.2%, (d) 0.4%, (e) 1.1%, (f) -1.8%.

It can be seen that the best fit model spectra agree very well with the experimental spectra, as the residuals are all very low. This shows that the model accurately reproduces the changes of the experimental spectra with changing temperature and

pressure conditions. The non-symmetric shapes of the odd-J lines in graphs (b) and (d), that are a result of the probe beam chirp, are also captured relatively well by the model. Even at the highest pressure, graph (c), the residual is not significantly larger than for the other fits, only some of the even-J lines of the experimental spectrum are not captured perfectly by the model. The good qualitative agreement of the fits is also reflected in the best fit temperature accuracy, as the best fit temperatures of all spectra, including the highest pressure one, are close to the corresponding thermocouple measurements. The percentage differences between best fit temperatures and thermocouple measurements (as a percentage of the thermocouple measurement) range from -6.2% to 2.3% (see Figure 5.7 caption for the best fit temperature of each spectrum). All of these best fit temperatures are within the range of acceptable accuracy, which, in the absence of any very high pressure HR-CARS thermometry studies in the literature, was defined as any best fit temperature between $\pm 10\%$ from the thermocouple temperature.

5.3.2 Best Fit Temperatures

Across all spectra recorded at the various pressures, temperatures and probe time delays, the average percentage temperature difference of the best fit temperature to the thermocouple temperature (as a percentage of the thermocouple reading) is -0.3%, with a standard deviation of 7.1%. This means that statistically, 84% of the fits fall within the acceptable accuracy range of $\pm 10\%$ from the measured thermocouple temperature (assuming a normal distribution of best fit temperatures). The average absolute percentage temperature difference (opposed to the average percentage temperature difference, which averages positive and negative percentage temperature differences) is 5.3%.

Focussing on a detailed breakdown of this overall result, Figure 5.8 shows the full set of best fit temperatures. Displayed are the percentage temperature difference of the best fit temperature to the corresponding thermocouple temperature against the thermocouple temperature. The graphs are grouped by pressure, and each line shows the percentage temperature difference at a different probe time delay. Note that the high pressure graph contains the data for the highest pressure spectra measured at each temperature, starting at 69 atm at 293 K and decreasing linearly to 37 atm at 1000 K, following the inclined edge of the T-P trapezoid (see Figure 4.8). Similarly, the low pressure graph data follows the left edge of the T-P trapezoid. Table 5.1 displays the average and standard deviation of the percentage temperature difference results over all temperatures and probe time delays at each pressure (corresponding to the average and standard deviation of the data of each graph in Figure 5.8).

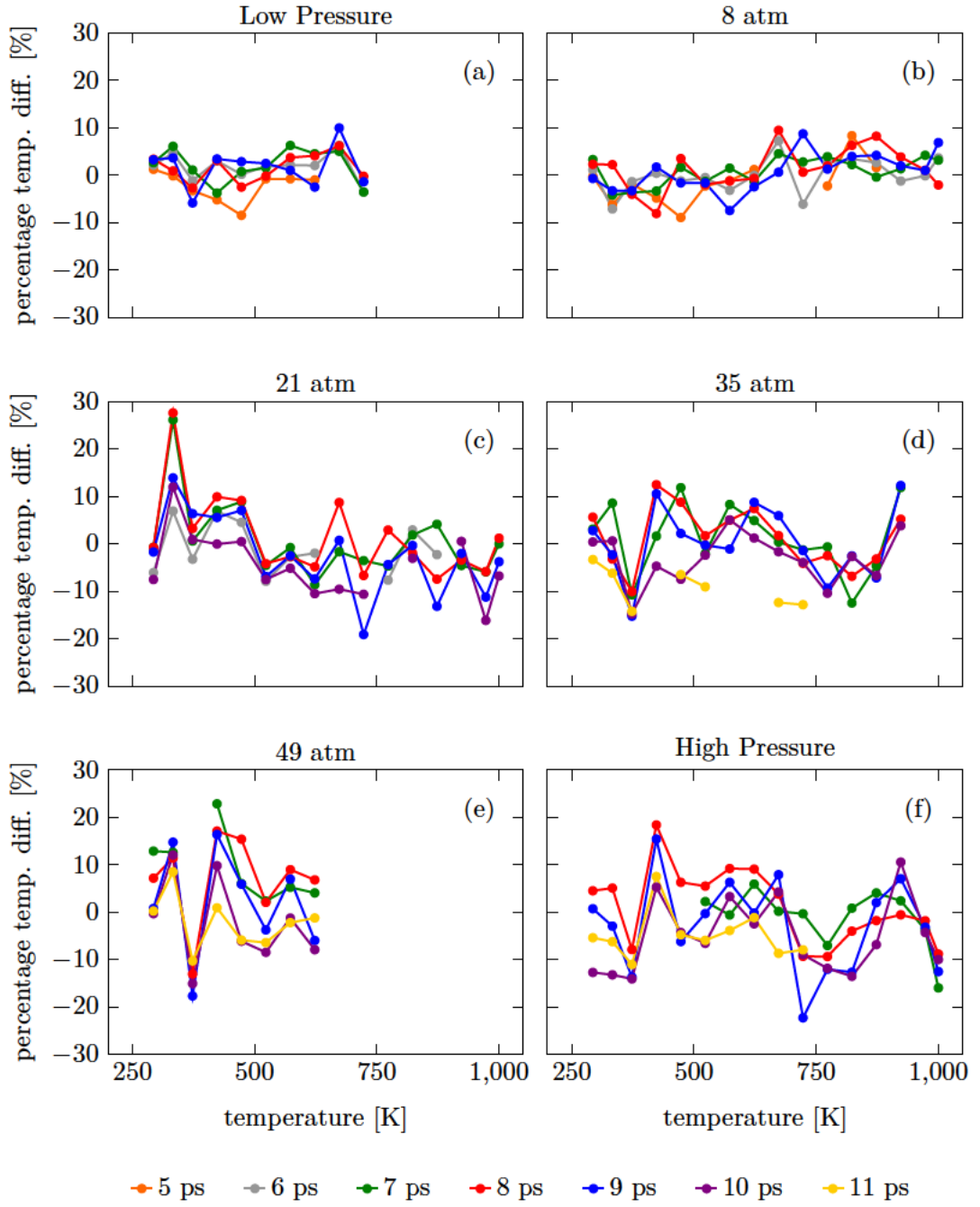


Figure 5.8: Percentage temperature difference of the best fit temperature to the corresponding thermocouple temperature (on the y-axis) against the thermocouple temperature (on the x-axis) at different pressures and probe time delays. Note that the high pressure graph contains the data for the highest pressure spectra measured at each temperature, starting at 69 atm at 293 K and decreasing linearly to 37 atm at 1000 K, following the inclined edge of the T-P trapezoid (see Figure 4.8). Similarly, the low pressure graph data follows the left edge of the T-P trapezoid.

From Figure 5.8 it can be seen that generally, the best fit temperatures at all pressures are accurate, as most of them are within the acceptable accuracy range of $\pm 10\%$ from the thermocouple temperature. However, at higher pressures, the variation of the

pressure	average (%)	std. dev. (%)
low P	1.1	3.8
8 atm	0.4	3.9
21 atm	-1.2	8.0
35 atm	-1.1	7.2
49 atm	2.7	9.6
high P	-2.2	8.4

Table 5.1: Average and standard deviation (std. dev.) of the percentage temperature differences between best fit and thermocouple measured temperatures over all temperatures and probe time delays at different pressures (corresponding to the average and standard deviation of the data of each graph in Figure 5.8).

best fit temperatures is larger than at lower pressures, indicating a reduced precision. Table 5.1 quantifies these accuracy and precision observations. The average difference between best fit and thermocouple-measured temperatures at the different pressures ranges from -2.2% to 2.7%, confirming the high accuracy. The precision (measured in terms of the standard deviation), however, is much better at lower pressures. It is 3.8% and 3.9% at low pressure and 8 atm respectively, compared with about 7-9% at all other pressures. At the lower pressures, statistically, 99% of the data lie between $\pm 10\%$ of the measured thermocouple temperature. For medium pressures (21 atm and 35 atm) this number drops to 78% and 83% respectively, but even at the highest pressures, 75% of the data lie within the $\pm 10\%$ range. This shows that while not perfect, the high pressure best fit temperatures are still relatively accurate.

It should be noted that while very accurate, the individual low pressure best fit temperatures (Figure 5.8 (a)) mostly lie within $\pm 5\%$ from the thermocouple temperature, not quite as accurate as previously reported accuracies, which are about 1% for rotational N_2 spectra at atmospheric pressure [37]. This is because the experimental setup is optimised for high pressure CARS experiments, and some of its components (e.g. the high pressure cell windows and the pulse shaper) add complexity to the setup making the experimental conditions less ideal than they could be for purely low pressure CARS studies. However, this complexity is necessary for the acquisition of well-resolved and relatively strong high pressure CARS spectra, thereby helping to improve the accuracy at higher pressures.

Further, Figure 5.8 shows that at all probe time delays the best fit temperatures at a given pressure vary by similar amounts and no delay is considerably more accurate than another one. This demonstrates that the probe time delay has no significant effect on the precision and accuracy, indicating that the model captures the time evolution

of the molecular response well. However, at certain pressures and temperatures, large deviations of the best fit temperature from the thermocouple measurement occur, at all probe time delays. These best fit temperature spikes happen, for example, at 21 atm and 333 K and also at 49 atm and 373 K. They can be explained by the NR argon spectrum that was used to correct for the pump/Stokes excitation correction having a different pump/Stokes excitation bandwidth than the N₂ spectrum it corrects, due to the afore-discussed changes of the NR argon spectra with time. While every effort was taken during the experimental process to collect many NR argon spectra, so that each N₂ spectrum has one taken at a similar time, the pump/Stokes excitation bandwidth did change between some of them, resulting in the best fit temperature spikes observed.

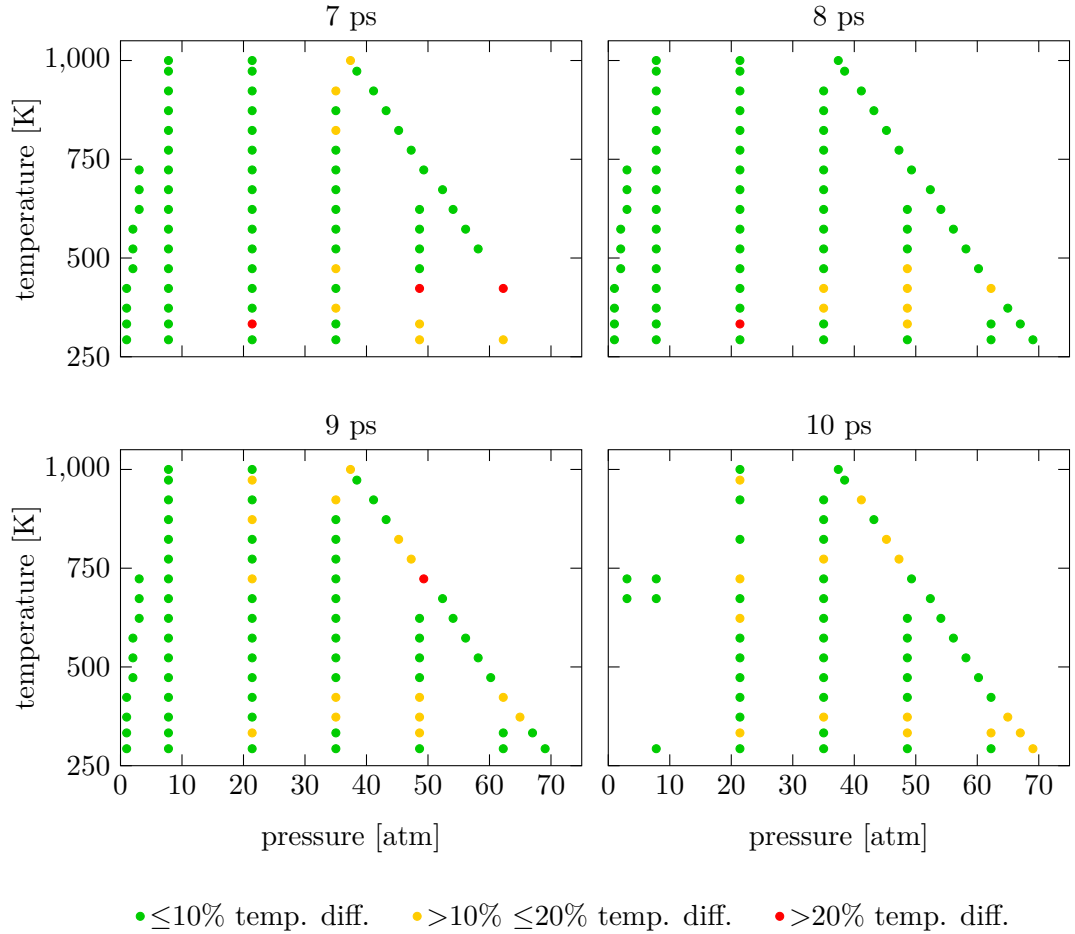


Figure 5.9: T-P graphs of the best fit temperature data (the same as in Figure 5.8) at probe time delays of 7 ps, 8 ps, 9 ps and 10 ps. Percentage temperature differences (temp. diff.) of the best fit to thermocouple-measured temperatures are grouped according to accuracy: fits within $\pm 10\%$ of the thermocouple reading (green dots), between 10% and 20% above or below the thermocouple reading (yellow dots) and more than 20% hotter or colder than the thermocouple reading (red dots).

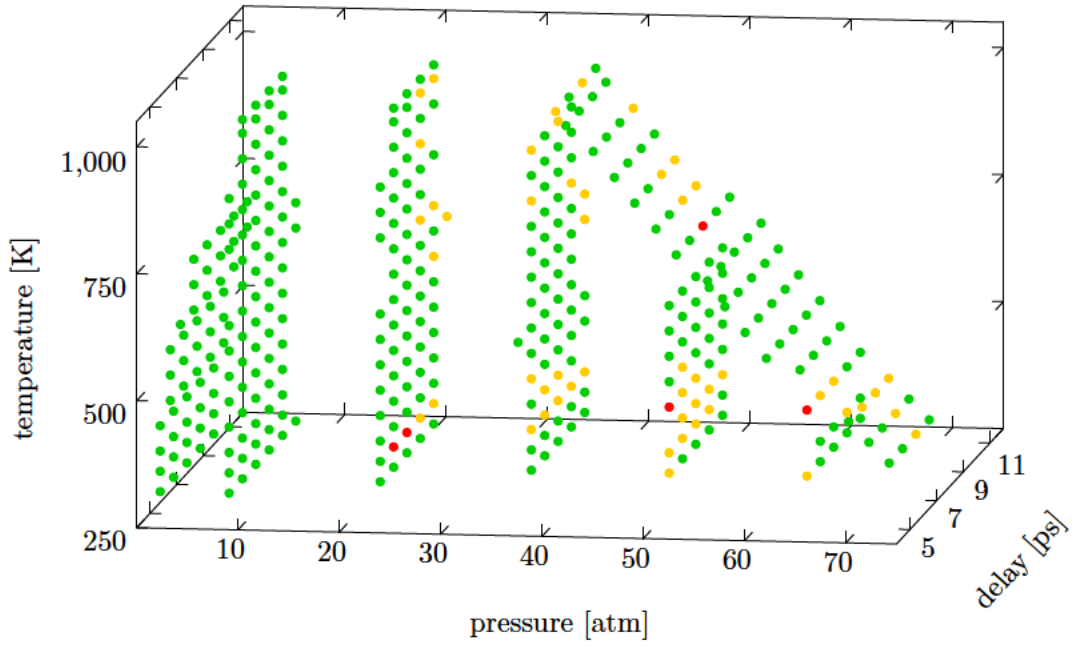
To get a better overall understanding of the best fit data presented in Figure 5.8, plots of the same data grouped by probe time delay instead of pressure are shown in Figure

5.9. The best fit data are shown on T-P trapezoids at probe time delays of 7 ps, 8 ps, 9 ps and 10 ps. The fits are grouped by colour, with all best fit temperatures within the desired $\pm 10\%$ accuracy range shown in green. Best fit temperatures between 10% and 20% above or below the thermocouple measurement are displayed in yellow and fits more than 20% hotter or colder are shown in red.

The same trends as discussed before can be seen. The majority of fits are within the desired accuracy range across all temperatures, pressures and probe time delays (indicated by most dots in Figure 5.9 being green). Especially at low pressures (< 10 atm), the fits are accurate. At medium pressures (10-40 atm), the accuracy is still very good, only a few best fit temperatures are outside the desired accuracy range (implied by the yellow and red dots). It is only at the higher pressures (> 40 atm) that a non-negligible number of fits are less accurate than desired, but even in this regime, most fits are still within the $\pm 10\%$ accuracy range. As discussed before, there is no significant difference in accuracy and precision at the different probe time delays, as the average temperature differences across all temperatures and pressures at probe time delays of 7 ps, 8 ps, 9 ps and 10 ps are 2.1%, 2.0%, -0.5% and -3.8% respectively, with corresponding standard deviations of 7.1%, 7.0%, 7.8% and 7.0%.

Figure 5.10 combines the best fit temperature data at all pressures, temperatures and probe time delays in one T-P graph, for further visualisation of the above-discussed trends. The accuracy colour code is the same as the one used in Figure 5.9. Again, it can be seen that the majority of best fit temperatures are within the desired accuracy, especially at lower pressures, but even at higher pressures, most fits are of acceptable accuracy.

Some of the larger deviations of the best fit to the thermocouple-measured temperatures can be explained by a change of the pump/Stokes excitation bandwidth between an N_2 spectrum and its corresponding NR argon correction spectrum. This change was briefly discussed above in regard to the best fit temperature deviation spikes seen in Figure 5.8. It is likely to be a result of drift of the pump/Stokes beam pointing and dispersion with time, affecting the capability of the pulse shaper to create an almost transform limited beam (see also the discussion on the NR argon spectra above). The usefulness of the pulse shaper to create an almost TL pulse after passing through the window of the pressure cell (see Figure 4.3), and therefore to generate a larger pump/Stokes excitation bandwidth (see Figure 4.4) has been explained before. However, this relies on perfect alignment onto the SLM of the pulse shaper. Any slight alignment deviations that occur in time, which are common for many laser systems, will result in a considerable change in the pump/Stokes excitation bandwidth (see Figure 5.5). If the excitation bandwidth changes between the measurement of an N_2 spectrum and its corresponding NR argon spectrum, then the division by the NR



• $\leq 10\%$ temp. diff. • $> 10\% \leq 20\%$ temp. diff. • $> 20\%$ temp. diff.

Figure 5.10: T-P graph of the best fit temperature data (the same as in Figure 5.8) at all temperatures, pressures and probe time delays. Percentage temperature differences (temp. diff.) of the best fit to thermocouple-measured temperatures are grouped according to accuracy: fits within $\pm 10\%$ of the thermocouple reading (green dots), between 10% and 20% above or below the thermocouple reading (yellow dots) and more than 20% hotter or colder than the thermocouple reading (red dots).

spectrum to correct for the pump/Stokes excitation bandwidth will result in a false correction, leading to inaccurate best fit temperatures. This, once more, highlights the need for taking many NR argon spectra throughout an experimental run when using a pulse shaper, to ensure that the pump/Stokes excitation bandwidth is the same for an N_2 spectrum and its corresponding NR argon spectrum.

Pump/Stokes beam alignment drift should affect low and high pressure spectra similarly, but from the best fit temperature data presented above, it can be seen that most of the less accurate best fit temperatures occur at higher pressures. One explanation for this is that while the pump/Stokes excitation differences due to alignment drift affect all spectra equally, the Ar spectra start to narrow with increasing pressure, as discussed before (see Figure 5.5). There could be a variation in the degree of narrowing depending on the initial pump/Stokes excitation bandwidth at atmospheric pressure. This could lead to a compounding of the two effects (a different pump/Stokes excitation bandwidth between an N_2 spectrum and its corresponding NR Ar spectrum and the narrowing of the excitation bandwidth with increasing pressure), leading to less accurate best fit temperatures at higher pressures. This also explains why the average accuracy at low and high pressures is similar, while the precision is

much lower at higher pressures (see Table 5.1), as the effect is random. This is further amplified by high pressure spectra, in general, having a lower signal-to-noise ratio, resulting in less precise fits. This decrease in signal strength at high pressures is due to the time domain CARS signal only increasing linearly with number density, but decreasing exponentially with pressure, leading to an overall decrease in the signal. As stated before, it is not possible to use a pulse shaper compensation mask to correct for the pressure-induced dispersion, as there is no way to get high pressure feedback signal to the pulse shaper algorithm.

Another factor that could contribute to the lower accuracy at higher pressures is uncertainty in the experimentally measured linewidths that are used in the model. Small errors in the linewidths have an increasingly larger effect on the model spectrum (and hence the best fit temperature), with increasing pressure, as is shown and explained in subsection *MEG vs. Measured Linewidths* below.

A potential solution for a chirp pre-compensation of the pump/Stokes pulse that is more stable with time could be the use of chirped mirrors. These mirrors induce a larger group delay dispersion to longer wavelengths than to shorter wavelengths. This pre-compensates a beam for the chirp induced while passing through an optical system, such as the fused silica pressure cell windows. However, chirped mirrors only correct for linear chirp, while the pulse shaper corrects for non-linear chirp as well. Using a pulse shaper therefore remains the better option.

5.3.3 Single Shot Fits

The above-presented results of best fit temperatures come from fits of model spectra to experimental spectra that are averages of 1000 single shots. Averaging single shots for gas-phase thermometry is sufficient for characterising static environments. However, as discussed before, one of the main advantages of hybrid fs/ps CARS is the ability to perform single shot measurements that do not require any averaging and can be used to resolve gas phase phenomena at very short time scales, for example as occur in combustion processes. In order to validate the ability of the experimental procedure and fitting routine to acquire and process single shot measurements, six N₂ spectra were selected, and for each of them, the individual single shots were fit. The chosen spectra cover a wide range of temperatures and pressures. Similar to the sensitivity study above, fitting single shots of just six spectra is not statistically representative of all spectra, but again, it should serve as a strong indication of how reliable single shot fits are. The single shots were fit using the same fitting procedure as for the averaged spectra, including the same initial fitting parameters and corresponding upper and

lower bounds and the same NR argon spectra were used for the pump/Stokes excitation bandwidth correction. Figure 5.11 shows the percentage temperature difference of the best fit to the thermocouple-measured temperature for every single shot of each of the six selected spectra. As the single shots were taken at a rate of 1 kHz, the time between two consecutive single shots is 1 ms, so that the total time covered by all 1000 single shots is 1 s. Table 5.2 displays the average and standard deviation of the best fit temperature results of each graph in Figure 5.11, to quantify the accuracy and precision of the single shot fits.

condition	average (%)	std. dev. (%)
333 K, 8 atm	2.1	0.8
333 K, 35 atm	-1.3	1.1
333 K, 67 atm	-7.1	1.8
673 K, 35 atm	5.8	1.6
973 K, 8 atm	4.3	1.8
973 K, 38 atm	-4.4	7.7*

Table 5.2: Average and standard deviation (std. dev.) of the percentage temperature differences between best fit and thermocouple-measured temperatures of all single shot fits of spectra at different temperature and pressure conditions (corresponding to the average and standard deviation of the data of each graph in Figure 5.11). *See text for an explanation of this seemingly large standard deviation.

It can be seen that the single shot fits at each temperature and pressure condition have very similar accuracies, mostly within $\pm 10\%$ from the measured thermocouple temperature. This is reflected in the average accuracy and precision (standard deviation), which are better than 8% and 2% respectively, for all but one condition, including the highest pressure condition. These values compare well with single shot accuracies and precisions of $<10\%$ and $<3.5\%$, respectively, for high temperature ambient pressure CARS measurements of flames reported in the literature [95], demonstrating that precise single shot thermometry is possible with the experimental setup and fitting procedure presented here.

The only exception to the high precision of the single shot best fits is the high pressure, high temperature condition (973 K, 38 atm), which has a standard deviation of 7.7% across all of its single shot best fit temperatures. However, this number is not an accurate quantification of the precision at this condition. As can be seen in Figure 5.11, the best fit temperatures of the high temperature, high pressure condition do not vary randomly, but follow well defined sharp rises and falls of temperature. Within these rises and falls, the precision is very high and comparable to the precisions at the

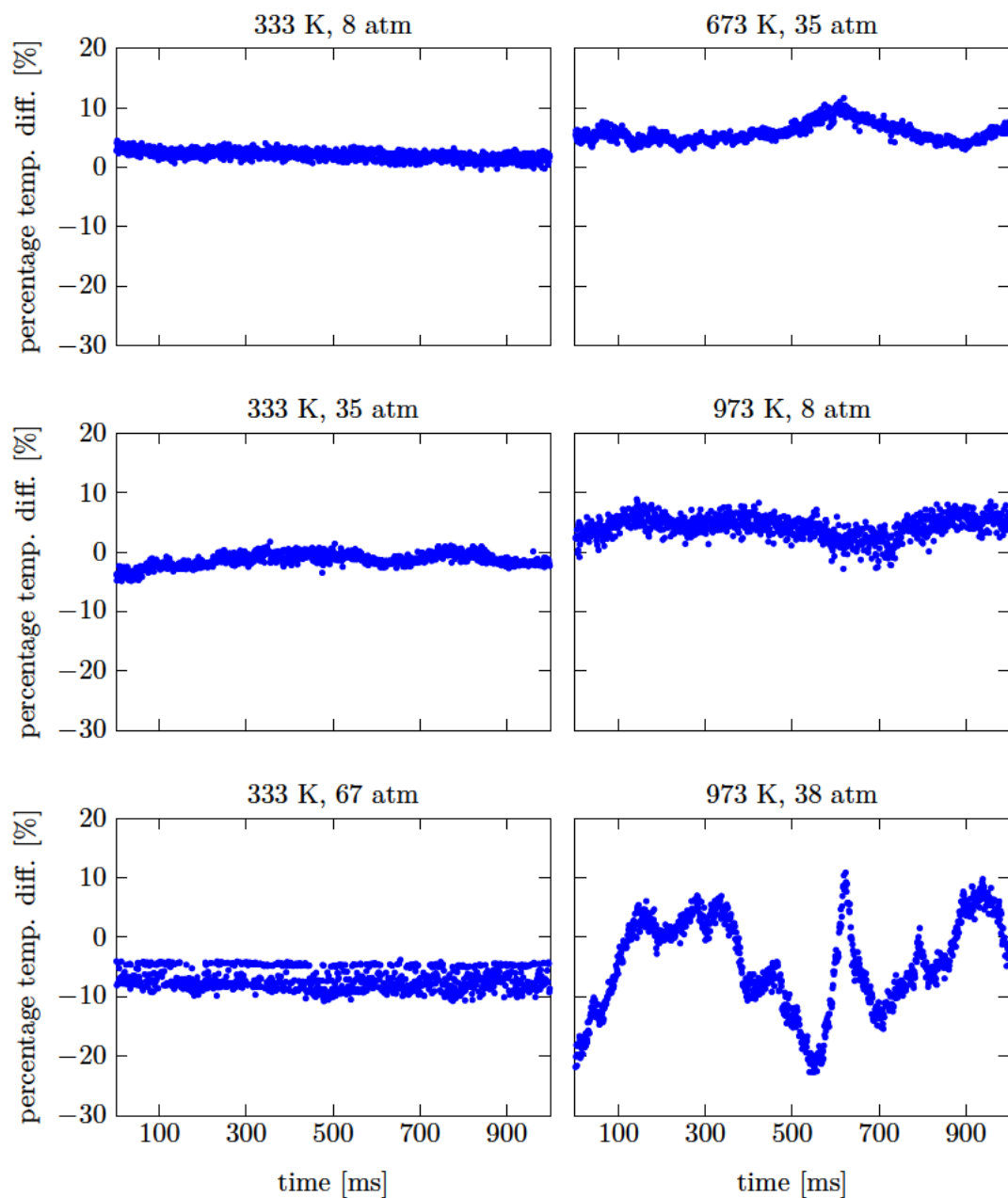


Figure 5.11: Percentage temperature difference of the best fit temperature to the corresponding thermocouple temperature for all single shots of six different N_2 CARS spectra at different temperatures and pressures. The time between two consecutive single shots is 1 ms.

other conditions. The rises and falls themselves can be explained by unstable thermal mixing. At high pressures, the pressure cell did not seal completely, but was gradually leaking some gas, resulting in a slow but steady pressure drop. To compensate this, the gas inlet valve was kept open just enough to hold the pressure inside the cell steady, by replacing leaking gas with fresh gas. The inflowing gas travels through a pre-heater to ensure that gas entering the cell is at the required temperature. However, at the highest experimental temperatures, the pre-heater is not able to fully heat the gas to the required temperature before it enters the cell. The resulting pockets

of cooler gas cause unstable thermal mixing, and when they hit the probe volume the result is a drop in best fit temperature. This is why all significant deviations from the thermocouple temperature at the high temperature, high pressure condition are towards colder rather than hotter temperatures. However, the most significant conclusion that can be drawn from this observation is the ability of single shot fits to capture fast changes in temperature very precisely, indicating that real gas-phase phenomena can potentially be resolved at a short timescale, even at higher pressures.

Important to note is also that the best fit temperatures of the averaged spectra (as shown in Figure 5.7) lie within two standard deviations of the average best fit temperatures of the respective single shots, for all conditions. This shows that averaging single shots prior to fitting a spectrum is a valid procedure that yields accurate best fit temperatures.

5.3.4 MEG vs. Measured Linewidths

The Modified Exponential Gap (MEG) model is often utilised for calculating the Raman transition linewidths used in CARS models, instead of taking experimentally measured linewidths (e.g. [36, 76]). The theoretical details of the MEG model have been discussed before in Chapter 2. Because it is a widely applied linewidth model, a comparison with the linewidths measured by Kliwer *et al.* [61] was performed. For this, all N₂ CARS spectra at the various pressures, temperatures and probe time delays were fitted with the same procedure as before, but using MEG model linewidths instead of measured ones. The best fit temperatures (as a percentage relative to the corresponding thermocouple measurement) obtained this way were averaged over all temperatures at each pressure and probe time delay. The same averaging was performed on the best fit temperature data acquired using the measured linewidths. The measured linewidths best fit temperature results were then subtracted from the MEG best fit temperature results. Figure 5.12 shows the resulting differences between the best fit temperatures at different pressures and probe time delays.

It can be seen that the MEG best fit temperatures get increasingly hotter with both pressure and probe time delay compared with the measured-linewidth results (hence the difference of MEG best fit temperatures and corresponding measured-linewidth best fit temperatures gets more positive). At low pressure and 8 atm, the difference is small, only up to about 2%, which is comparable to the best fit temperature precision. As the pressure increases, however, the difference gets bigger, reaching almost up to 17% at 49 atm. The fact that the best fit temperature difference of the high pressure data is slightly smaller than that of the 49 atm data can be explained by the high

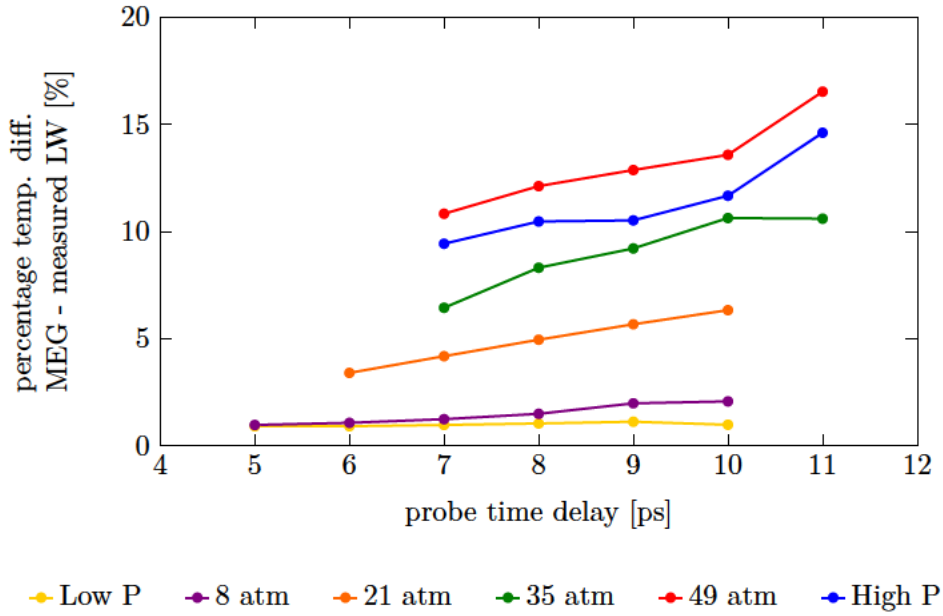


Figure 5.12: Comparison of best fit temperatures acquired from fitting experimental N₂ spectra using MEG model and measured linewidths. Shown are the percentage temperature differences (temp. diff.) of the best fit temperatures to the thermocouple measurement that were found using measured linewidths (LW), subtracted from the corresponding percentage temperature differences using the MEG model. The results are shown against probe time delay and each line corresponds to a different pressure. Each data point is an average over all experimental temperatures at each pressure and probe time delay. Note that the high pressure line contains the data for the highest pressure spectra measured at each temperature, starting at 69 atm at 293 K and decreasing linearly to 37 atm at 1000 K, following the inclined edge of the T-P trapezoid (see Figure 4.8). Similarly, the low pressure graph data follows the left edge of the T-P trapezoid.

pressure data containing pressures ranging from 69 atm (at room temperature) down to 37 atm (at 1000 K). The trend with probe time delay can be seen clearly as well. At 21 atm, the percentage temperature difference between MEG and measured-linewidth best fit temperatures increases from 3.4% to 6.3% between probe time delays of 5 ps and 10 ps respectively, a change of 2.9% over a 4 ps increase in probe time delay. At higher pressures, the trend with probe time delay is even more pronounced. At 49 atm, the difference increases by 5.7% over a 4 ps increase in probe time delay, from 10.8% at 7 ps, to 16.5% at 11 ps.

This increasing discrepancy between MEG and measured-linewidth best fit temperatures with increasing pressure and probe time delay can be explained by the effect they have on the linewidths. Looking at Equation 2.38 and explicitly including the pressure dependence of the linewidth (Γ), it can be seen that the time domain third order molecular response function depends on the linewidth according to:

$$R_{CARS}(t) \propto \exp \left[-\frac{t \times P \times \Gamma}{2\hbar} \right] \quad (5.2)$$

The molecular response is inversely exponentially dependent on the product of linewidth, pressure and probe time delay. This means that the larger the pressure or the longer the probe time delay, the faster the exponential decay of the molecular response in the time domain. Therefore, if a Raman transition is modelled with one linewidth and then again with a similar but slightly different linewidth, the decays of the resulting molecular responses are very similar, at low pressures and short probe time delays. But due to the exponential nature of the dependence of the molecular response on the product of linewidth, pressure and probe time delay, the decays will differ more and more when either pressure or probe time delay is increased. So if a model uses slightly different linewidths, but otherwise is the same, then this will not make a big difference at low pressures and short probe time delays, but will lead to increasingly different model spectra and ultimately result in different best fit temperatures at higher pressures and longer probe time delays.

As the experimentally measured and MEG linewidths are slightly different, this can be used to explain the increasing discrepancies of the best fit temperatures found using the MEG model and measured-linewidth with increasing pressure and probe time delay. More work needs to be done to investigate this and to confirm these results, but it is clear that slightly different linewidths will result in very different best fit temperatures at high pressures and large probe time delays, so for any high pressure CARS model to be accurate, it needs to use accurate linewidths.

5.3.5 Air Spectra

To test the experimental setup, computational model and fitting routine beyond pure nitrogen, room temperature CARS spectra of a mixture of N_2 and O_2 at atmospheric concentrations ("air") were taken at a range of pressures and probe time delays. The model was fit to these spectra using the same post-processing and fitting procedure as for the nitrogen spectra. CARS spectra of air, in general, are considerably more complicated than pure nitrogen spectra at the same condition, due to the simultaneous presence of N_2 and O_2 molecular responses and their interaction (see Figure 3.8). This is a big challenge for the modelling of air spectra, as such a model needs to capture this interaction accurately. Figure 5.13 shows some of the best fit model (dashed red line) and experimental (blue line) air spectra taken at the same probe time delay (7 ps) and increasing pressures (8 atm, 28 atm, 49 atm and 69 atm), together with the corresponding residuals (green line).

It can be seen that the peaks of the experimental spectra get considerably wider and start to grow into each other with increasing pressure, because both the N_2 and O_2

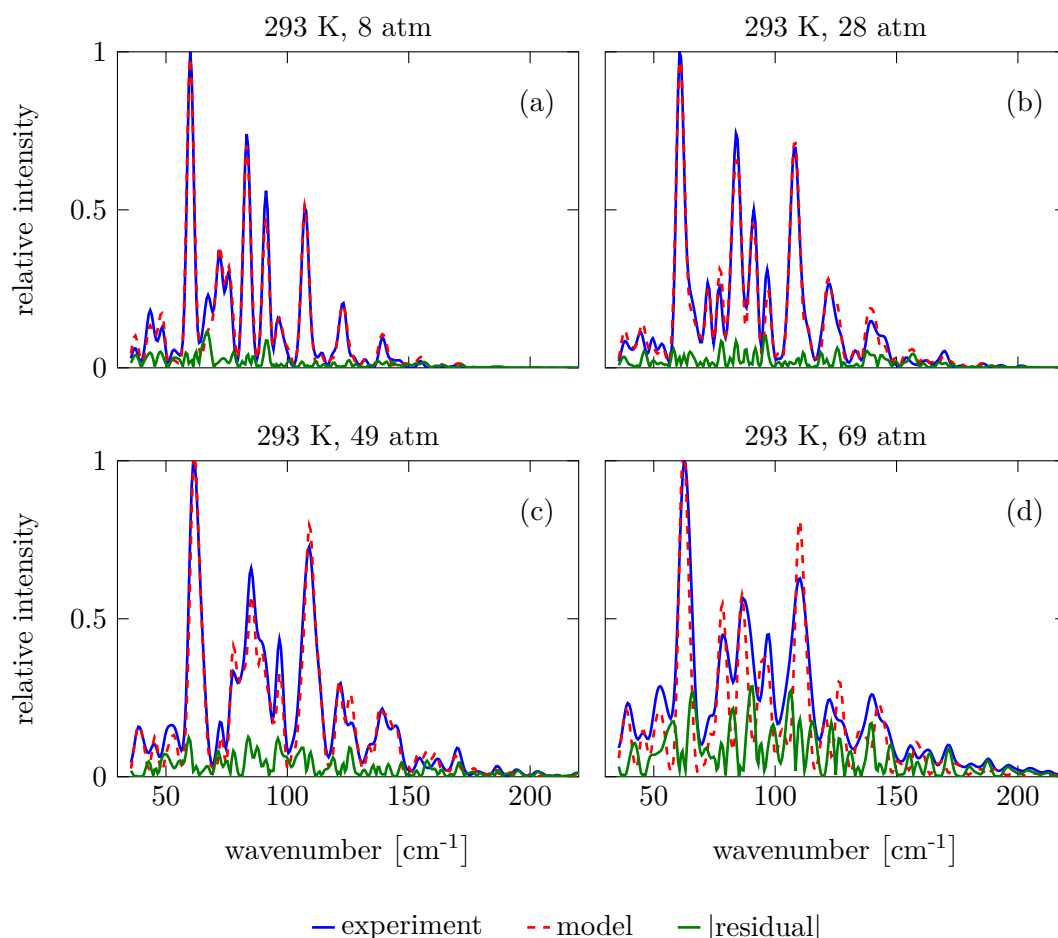


Figure 5.13: Experimental and corresponding best-fit model HR-CARS spectra of a mixture of N_2 and O_2 at atmospheric concentrations at a temperature of 293 K and a probe time delay of 7 ps at different pressures. Experimental (blue line) and best-fit model spectra (dashed red line) are shown together with their residual (absolute difference between the model and experimental spectra, green line). The percentage differences between the best fit temperatures and corresponding thermocouple measurements (as a percentage of the thermocouple measurement) are: (a) 3.4%, (b) 4.2%, (c) 0.5%, (d) -7.6%.

linewidths increase with pressure. The relatively well resolved spectra at low and medium pressures (8 atm and 28 atm) have very good qualitative fits, confirmed by low residuals. At these pressures, the model captures most of the lines well, including those that arise from N_2/O_2 interactions. Even at 49 atm, there is still a relatively good agreement between the model and experiment. These observations are supported quantitatively by good best fit temperature accuracies ($<5\%$) up to this pressure. It is only at the highest pressure (69 atm), that the model is not able to capture the experimental spectrum properly, resulting in high residuals. The poor fit at high pressure is likely to arise from inaccurate linewidths used in the model. As discussed in the previous subchapter, small differences in linewidths have a large effect on the model at high pressure. This effect is especially pronounced when the interaction of two species needs to be modelled. An accurate model for CARS spectra of air

therefore requires accurate linewidths of nitrogen and oxygen. The air model presented here uses measured linewidths for N₂, but due to the absence of similar experimental measurements for O₂, the MEG model is used instead, which is likely to be the reason for the poor fits of air spectra at very high pressure. A more accurate high pressure model for air could potentially be made by obtaining and using measured O₂ linewidths.

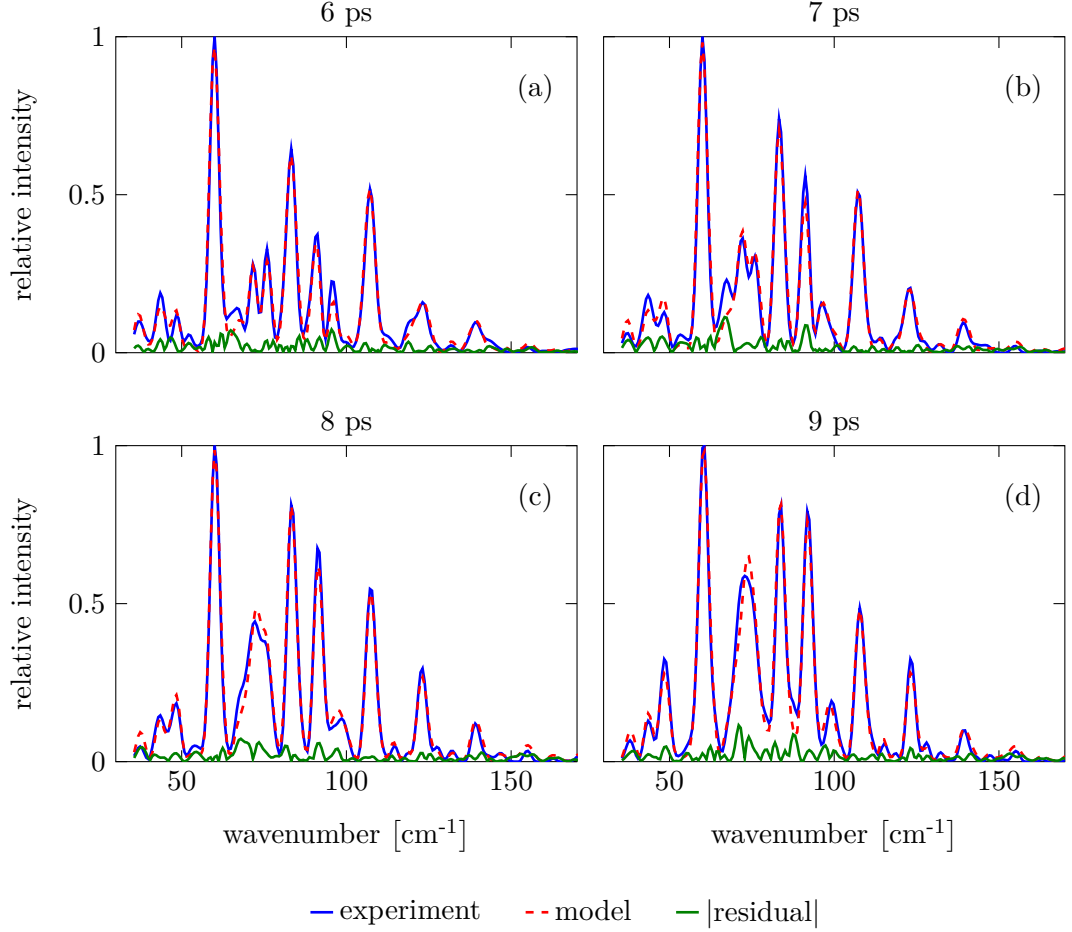


Figure 5.14: Experimental and corresponding best-fit model HR-CARS spectra of a mixture of N₂ and O₂ at atmospheric concentrations at a temperature of 293 K and a pressure of 8 atm at different probe time delays. Experimental (blue line) and best-fit model spectra (dashed red line) are shown together with their residual (absolute difference between the model and experimental spectra, green line). The percentage differences between the best fit temperatures and corresponding thermocouple measurements (as a percentage of the thermocouple measurement) are: (a) 3.0%, (b) 3.4%, (c) 7.4%, (d) 2.0%.

At lower pressures, however, where the exact linewidths are less important for accurate fits, the N₂/O₂ model is in very good agreement with the experiment. Moreover, the evolution of a spectrum with time and the corresponding N₂/O₂ interactions, can be captured accurately. These interactions manifest themselves in a beating structure of some of the closely spaced N₂ and O₂ peaks in time, due to the different dephasing and rephasing rates of the molecular responses of nitrogen and oxygen. This is shown

in Figure 5.14, which displays room temperature N₂/O₂ CARS spectra at a fixed pressure of 8 atm and an increasing probe time delay, from 6 ps to 9 ps in 1 ps steps.

The figure clearly shows some of the beating structures. The most prominent example of this is the region between about 65–80 cm⁻¹. At a probe time delay of 6ps, the experimental spectrum contains three individually resolved lines in this wavenumber range, the tallest of which being the right one, with a relative intensity of about 0.34. At 7ps, these three lines start to grow together, with the tallest one now being the middle line at a relative intensity of about 0.38. This trend continues at delays of 8 ps and 9 ps, at which point only one wide line with a relative intensity of about 0.6 is observed. It can be seen that the best fit model spectrum follows this beating behaviour and captures these significant changes well, resulting in low residuals at all probe time delays. Another example is the line at 90 cm⁻¹, which, from a 6 ps to a 9 ps probe time delay, more than doubles in relative intensity, from about 0.4 to more than 0.8. Again, the model captures this change almost perfectly.

To assess the quantitative accuracy of the fits to the N₂/O₂ spectra, Figure 5.15 shows the percentage temperature difference of the best fit temperature to the corresponding thermocouple measurement of all N₂/O₂ spectra at different pressures and probe time delays. Best fit temperatures for poor qualitative high pressure fits (i.e. fits with high residuals) have been omitted, as they are not very credible.

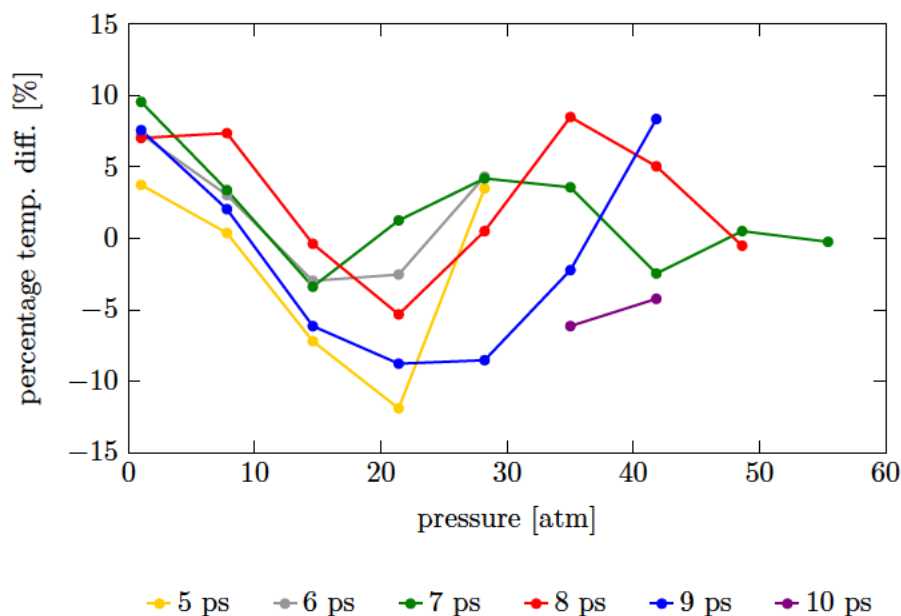


Figure 5.15: Percentage temperature difference of the best fit temperature to the corresponding thermocouple temperature (as a percentage of the thermocouple reading) against pressure for HR-CARS spectra of a mixture of N₂ and O₂ at atmospheric concentrations at room temperature (293 K). Each line shows the best fit data at a different probe time delay.

It can be seen that all but one best fit temperatures lie within the $\pm 10\%$ accuracy range. As for the pure nitrogen spectra, best fit temperatures at different probe time delays are of similar accuracy. The average percentage temperature difference of the data in Figure 5.15 is 0.5% with a standard deviation of 5.5%. This means that statistically, 93% of the best fits are within the desired accuracy range. The good qualitative and quantitative results prove the applicability of the model and fitting procedure to room temperature N_2/O_2 mixtures, at least at low and medium pressures.

Chapter 6

Conclusion

An experimental setup for two-beam hybrid rotational fs/ps coherent anti-Stokes Raman spectroscopy that enables measurements of well-resolved nitrogen spectra at high pressures and temperatures was built. Further, a computational code to model theoretical CARS spectra was developed, alongside a fitting procedure to fit the model to experimental spectra. The main aim of the research was to use this model and fitting routine to find the best fit temperatures of the experimental N₂ CARS spectra, to prove and assess the usefulness of HR-CARS as a technique for high pressure gas-phase thermometry. This conclusion summarises the main aspects of the experimental setup, computational model and fitting procedure. It then reviews the most important results and corresponding implications. The chapter concludes with an outlook on possible future work that could be done to extend the research presented in this thesis and to make it more applicable to real gas-phase environments.

6.1 Experiment and Model

Starting from the same laser system to create both the pump/Stokes and the probe beams, the experimental setup includes several features that make it ideally suited for high pressure CARS measurements. The initial laser output (795 nm, 1 kHz) is split in two beams of equal power and each of them is single pass amplified to about 9 mJ/pulse. At this point, the beams are strongly positively chirped (>100 ps) and have a bandwidth of $\Delta\nu = 360 \text{ cm}^{-1}$. One of these amplifier output beams is used as the pump/Stokes beam, by compressing it in a grating compressor to its near transform limit of 40 fs. A pulse shaper is then utilised to pre-compensate the pump/Stokes beam for the dispersion (chirp) induced in the optics of its beam path, especially the 28 mm fused silica entrance window of the pressure cell in which the CARS measurements are taken. The pulse shaper can correct for linear and nonlinear dispersion by using a spatial light modulator. It is able to create an almost transform limited pulse of 42 fs duration at the probe volume inside the pressure cell, as confirmed by FROG measurements. Nonresonant argon CARS spectra showed

that the pump/Stokes excitation bandwidth is significantly increased when using the pulse shaper, allowing for stronger CARS signals, especially at larger wavenumbers. The probe beam is generated via sum frequency generation using second harmonic bandwidth compression. For this, the other amplifier output beam is split in two equal power beams that are each routed through a grating compressor, that compress the beams but leave a slight residual chirp that is equal and opposite. The beams are then combined in a BBO crystal (Type 1), in which their frequencies add to produce a narrowband picosecond pulse. A $4f$ grating filter is used to remove satellite peaks and spectral wings, to give a clean probe beam. This probe beam has a frequency domain width (FWHM) of 3 cm^{-1} and a time domain duration (FWHM) of about 5.5 ps. The short picosecond duration makes the beam ideal for high pressure CARS, as it allows for measurements that are close in time to the pump/Stokes excitation, where the CARS signal has not decayed too much, while at the same time minimising any nonresonant contribution to the signal. The pump/Stokes and probe beams are combined collinearly and focussed into a high pressure cell. The probe beam is removed from the resulting CARS signal in a $4f$ grating filter and the signal is focussed into a spectrometer and recorded on the CCD chip of a camera.

The computational code can model HR-CARS spectra of S-branch transitions of pure N_2 , pure O_2 and mixtures of N_2 and O_2 . The underlying mathematics comes from a quantum mechanical treatment of the density matrix in combination with classical electromagnetic waves. The Raman transition frequencies are based on ro-vibrational energy levels of diatomic molecules, which are calculated using the non-rigid rotor approximation (i.e. taking centrifugal distortion into account), an anharmonic vibrational potential and including the rotational-vibrational interaction. The Raman transition linewidths are based on the modified exponential gap model, or, in the case of nitrogen, are interpolated values of experimental measurements. The modelled Raman transition strengths take into account polarisation anisotropy, the Placzek-Teller coefficient, the Herman-Wallis factor and a temperature-dependent normalised Boltzmann distribution of rotational states. S-branch transitions from the ground and first excited vibrational states are included in the model, as 99.9% of the molecules are in either of these vibrational levels at the highest temperature probed experimentally (1000 K). The probe beam is modelled as the sum of two Gaussians, as experimental cross correlations in argon confirmed this shape. Further, chirp is included in the probe beam model, as the experimental probe beam characterisation confirmed the presence of a slight chirp. The CARS signal is modelled in the time domain and then a Fourier transform is performed to obtain the corresponding frequency domain CARS spectrum. In a final step, this modelled frequency domain CARS spectrum is convolved with a Gaussian of width 1.5 cm^{-1} to account for the spectrometer's slit function.

The computational model spectra can be fitted to experimental spectra using a fitting routine that employs a nonlinear least squares algorithm. This algorithm allows one to define fitting parameters, such as the temperature and probe pulse time delay, and to set upper and lower constraints on these parameters. The fitting algorithm varies each fitting parameter in turn, within their pre-defined boundaries, until the difference between a model and experimental spectrum is minimised. This produces a best fit model spectrum for each experimental spectrum, with corresponding best fit values of each of the fitting parameters. The best fit temperatures of the numerous experimental spectra acquired this way were compared to thermocouple-measured temperatures of the probed gas, to assess the accuracy and precision of these best fit temperatures.

6.2 Results and Implications

CARS spectra of N_2 were taken at a large range of pressures (1-69 atm) and temperatures (293-1000 K). At all conditions, it was possible to obtain clean and well resolved spectra using the afore-described experimental setup. However, it was found that at high pressures, small changes in pressure or probe time delay have a significant effect on the appearance of the spectra, due to the fast decay of the molecular response. The slight chirp of the probe beam and its non-Gaussian shape enhance this effect.

The nonresonant argon spectra, used for the pump/Stokes excitation correction of the N_2 spectra, also show significant changes with increasing pressure, as they get narrower, implicating a reduced pump/Stokes excitation bandwidth due to the increasing number density that the pump/Stokes beam has to travel through in the pressure cell, before the probe volume. This induces increasing dispersion in the beam and results in the observed reduction of the excitation bandwidth. The NR argon spectra also change with time, an effect which is likely to arise from a slight alignment drift of the laser into the SLM of the pulse shaper. Changes in alignment will change the effectiveness of the applied phase mask to pre-compensate the beam dispersion and hence will result in a different excitation efficiency. It was concluded that many argon spectra need to be taken during an experimental run, to ensure that each N_2 spectrum has a corresponding nonresonant Ar spectrum with the same excitation bandwidth.

The robustness of the fitting procedure was tested, by assessing the sensitivity of the best fit temperature on the other fitting parameters. It was revealed that the best fit temperature is largely unaffected and just changes marginally when the fitting parameters are altered from their best fit values. The only exception to this general trend occurred at high pressure, where temperature changes of up to 10% from their best fit value were observed. This demonstrates that the temperature is not very

sensitive to the other fitting parameters, except at high pressures, where accurate fitting parameters are required to get an accurate best fit temperature.

The best fit model spectra themselves show very good agreement with the respective experimental spectra, across all temperatures and pressures, confirmed by low residuals. Non-symmetric odd-J lines, that are a result of the probe beam chirp, are captured relatively well by the model. Even at high pressures, the fits are of acceptable quality. This proves the capability of the computational model to accurately simulate CARS spectra across a wide range of pressures and temperatures.

As assessing the suitability of HR-CARS for high pressure gas-phase thermometry was the main aim of this research project, a special focus was given to the best fit temperatures. The average best fit temperature across all experimental pressures, temperatures and probe time delays, measured as a percentage temperature difference to the experimentally recorded thermocouple temperature (as a percentage of that thermocouple reading) is -0.3% with a standard deviation of 7.1%. This high accuracy and precision mean that statistically, 84% of all best fit temperatures lie within $\pm 10\%$ of the thermocouple measurement, which was defined as the threshold for acceptable accuracy. A breakdown of the overall best fit temperature result by pressure revealed that the average accuracy is similar across all pressures, but the precision is better at lower pressures than at higher ones. However, even at the highest pressures, statistically 78% of the data lie within the desired $\pm 10\%$ accuracy range. This trend can be explained by a combination of the laser alignment drift into the pulse shaper's SLM together with narrowing of the pump/Stokes excitation bandwidth with increasing pressure. This, again, shows the importance of a very careful determination of the exact pump/Stokes excitation bandwidth for obtaining accurate best fit temperatures, specifically as some best fit temperature outliers can be attributed to an especially large difference in excitation bandwidth between an N₂ spectrum and its corresponding nonresonant Ar correction spectrum. Uncertainty in the measured linewidths used in the model was identified as another possible contribution to the lower accuracy at high pressures. A breakdown of the best fit temperature results by probe time delay showed that the precision and accuracy are similar across all measured probe time delays, demonstrating that the computational code can accurately model the evolution of the time domain molecular response.

One of the main advantages of HR-CARS is the ability to perform single shot measurements, but the spectra that were fit to obtain the best fit temperatures were all averages of 1000 single shots. To test the capability of the experimental setup and fitting procedure to accurately acquire and process not only averaged spectra, but also single shot spectra directly, six different pressure and temperature conditions were chosen and all single shots from each condition were fitted. The single shot best fit

temperature precision (quantified in terms of the standard deviation of all single shot best fit temperatures at each condition) was found to be better than 2% for all but one condition, proving that single shot measurements are possible and can be fit with high precision. Only the highest temperature and pressure condition (973 K, 38 atm) had a large standard deviation of 7.7%. However, this is not an accurate representation of the precision at this condition, which shows sharp and well-defined rises and falls of the best fit temperature across the single shot fits, caused by unstable thermal mixing. Within these rises and falls, the precision is comparable to the precision at the other tested conditions. Moreover, this shows that rapid temperature changes can be resolved and potentially this can be used to study real gas-phase phenomena.

The scope of the project was extended from purely analysing best fit temperatures to investigating the differences between the use of linewidths generated from the MEG model compared with experimentally measured values. It was found that while at low pressures and probe time delays the results are very similar, the best fit temperatures acquired using the MEG model get hotter compared with the experimental linewidths with increasing pressure and probe time delay. This difference reaches up to more than 15% at high pressure and long probe time delay. It can be explained by the inverse exponential dependence of the time domain molecular response function on the product of linewidth, probe time delay and pressure. If two model spectra are computed using slightly different linewidths, then at low pressures and short probe time delays, the corresponding molecular response functions are very similar, but as pressure and probe time delay increase, the molecular response functions and hence the model spectra get increasingly different. This means that an accurate high pressure model requires accurate linewidths. However, the effect needs to be studied further before drawing any final conclusions about the MEG or other linewidths models.

Finally, the experimental setup, computational model and fitting procedure were validated beyond pure nitrogen, by taking and fitting HR-CARS spectra of a mixture of nitrogen and oxygen at atmospheric composition ("air"). Due to the interaction between the molecular responses of N_2 and O_2 , air spectra are a bigger challenge to model, as overlapping N_2 and O_2 peaks exhibit a beating structure in time, due to their different dephasing rates. It was shown that the model is able to accurately capture this beating behaviour at low pressures. Further, it was found that qualitative fits of experimental spectra are possible up to about 50 atm, as confirmed by low residuals. It is only at the very highest pressures that the model can not accurately capture the increasingly broad and overlapping N_2/O_2 peaks. The best fit temperatures of the air spectra (excluding the highest pressure spectra) show a similar overall accuracy and precision as the pure nitrogen spectra. The average percentage temperature difference to the thermocouple reading is 0.5% with a standard deviation of 5.5%, so that statistically 93% of fits are within the acceptable accuracy range.

6.3 Future Work and Outlook

Despite the comprehensive work accomplished, there remains more to be done. As with most scientific research projects, a lot of questions have been answered, but new ones have arisen. Below are some suggestions of work that could be carried out in the future, in an attempt to deepen our understanding of HR-CARS.

A direct extension of the project would involve a thorough investigation of the pump/Stokes excitation efficiency changes with time and the role the pulse shaper plays in this. Avoiding these changes would make the nonresonant correction spectra more reliable, and an experimental setup optimised for this could lead to an increased best fit temperature precision, especially at high pressures. Further, a detailed study of the fitting procedure, beyond the sensitivity study performed for this project, needs to be carried out to potentially improve the fitting routine.

A broader extension of the project includes a more in-depth study of the use of MEG model linewidths compared with measured linewidths in the computational code. The best fit temperature discrepancies that arise at high pressures and probe time delays when slightly different linewidths are used need to be quantified further and the use of other MEG model parameters or even other linewidths models (e.g. the energy corrected sudden model) could be explored. The capability of single shot spectra to resolve temperature changes on a short time scale needs to be confirmed as well, especially in real gas-phase phenomena. Also, the model could be improved to give more accurate high pressure fits of spectra of N_2/O_2 mixtures, for example by measuring and testing the use of experimental linewidths of O_2 in the model code.

In a much wider scope, the experimental setup could be extended to 1D measurements at high pressures. This would require much more powerful pump/Stokes and probe beams after the pulse shaper and the SHBC respectively, and poses an experimental challenge. Of course, the ultimate aim is to adopt this technique for use in real high pressure gas-phase environments, such as combustion processes in an optical engine. However, before this is achievable in an accurate, precise and reliable way a lot of research still needs to be done.

Overall, this PhD project achieved its aims of developing an experimental setup, computational model and fitting routine for acquiring well-resolved HR-CARS spectra across a wide range of temperatures and pressures and fitting them to the model. Accurate and precise gas-phase N_2 thermometry was demonstrated at all tested temperature and pressure regimes using this technique.

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Appendix A

Quantum Mechanics Background

This appendix covers some very basic but highly useful background on quantum mechanics. It aims to make understanding the quantum mechanical discussion of CARS spectroscopy easier (in Chapter 2 and more thoroughly in Appendix B). The quantum mechanical notation that is used throughout this thesis is introduced, and helpful identities are given. This background knowledge is presented in tables, with the left hand side stating quantum mechanical properties and the right hand side showing the corresponding mathematical representation. A much more thorough background on, and introduction to, quantum mechanics, together with lots of examples can be found in the book *Modern Quantum Mechanics* by Jun John Sakurai [96].

Table A.1 explains the basics of Dirac bra-ket notation to represent quantum states and the interaction between them. Table A.2 then introduces quantum mechanical operators, their actions on bras and kets and some highly useful identities. Quantum states and operators are very general concepts that are used in many areas of quantum mechanics. The quantum mechanical background given in Table A.3 is more specific to the discussion of CARS spectroscopy, as it presents the time evolution operator and the trace of an operator, both of which are very important in the derivation of the CARS signal. Throughout these tables, Greek letters are used to represent quantum states (bras and kets), capital letters represent operators and c represents a general complex number.

A.1 Dirac Bra Ket Notation

Property	Mathematical Representation
kets are column vectors	$ \alpha\rangle$
kets can be added to give another ket	$ \alpha\rangle + \beta\rangle = \gamma\rangle$
multiplication by a (complex) number, gives another ket	$c \alpha\rangle = \beta\rangle$
bras are row vectors	$\langle\alpha $
bras can be added to give another bra	$\langle\alpha + \langle\beta = \langle\gamma $
multiplication by a (complex) number, gives another bra	$c\langle\alpha = \langle\beta $
every ket has a corresponding bra (DC = dual correspondence)	$ \alpha\rangle \xleftrightarrow{\text{DC}} \langle\alpha $
generally (* denotes a complex conjugate , $i \rightarrow -i$):	$c \alpha\rangle \xleftrightarrow{\text{DC}} c^*\langle\alpha $
inner product of a bra and a ket is a (complex) number (1×1 matrix)	$\langle\alpha \beta\rangle = c$
useful property:	$\langle\alpha \beta\rangle = \langle\beta \alpha\rangle^*$
two kets are orthogonal if their inner product is zero	$\langle\alpha \beta\rangle = 0$
any ket that is not a null ket can be normalised	$ \tilde{\alpha}\rangle = \left(\frac{1}{\sqrt{\langle\alpha \alpha\rangle}}\right) \alpha\rangle \quad \langle\tilde{\alpha} \tilde{\alpha}\rangle = 1$
outer product of a ket and a bra is a square matrix, called an operator	$ \alpha\rangle\langle\beta = A$

Table A.1: Dirac bra-ket notation and related properties.

A.2 Operators

Property	Mathematical Representation
operators are square matrices	A
operators can act on a ket from the left, the result is another ket	$A \alpha\rangle = \beta\rangle$
operators can act on a bra from the right, the result is another bra	$\langle\alpha A = \langle\gamma $
$A \alpha\rangle$ and $\langle\alpha A$ are not dual to each other in general	$A \alpha\rangle \nleftrightarrow \langle\alpha A$
$A^\dagger$ is the Hermitian adjoint of A , such that:	$A \alpha\rangle \xleftrightarrow{\text{DC}} \langle\alpha A^\dagger$
operator A is Hermitian if:	$A = A^\dagger$
addition is commutative	$A + B = B + A$
addition is associative	$A + (B + C) = (A + B) + C$
multiplication is non-commutative	$AB \neq BA$
multiplication is associative	$A(BC) = (AB)C = ABC$
useful property:	$(AB)^\dagger = B^\dagger A^\dagger$
bra $\times$ operator $\times$ ket compact notation:	$\langle\alpha \times A \times \beta\rangle \rightarrow \langle\alpha A \beta\rangle$
useful property:	$\langle\alpha A \beta\rangle = \langle\beta A^\dagger \alpha\rangle^*$
expectation value of A for state $ \alpha\rangle$:	$\langle A \rangle \equiv \langle\alpha A \alpha\rangle$
commutator notation:	$[A, B] = AB - BA$
anti-commutator notation:	$\{A, B\} = AB + BA$

Table A.2: Quantum mechanical operators and useful identities.

A.3 Time Evolution Operator and Trace

Property	Mathematical Representation
kets (and bras) can evolve in time from starting time t_0 to time t	$ \alpha, t_0\rangle \xrightarrow{\text{time evolution}} \alpha, t\rangle$
time evolution is achieved by the time evolution operator	$\mathcal{U}(t, t_0) \alpha, t_0\rangle = \alpha, t\rangle$
the time evolution operator is unitary	$\mathcal{U}^\dagger(t, t_0)\mathcal{U}(t, t_0) = 1$
composition property of the time evolution operator ($t_2 > t_1 > t_0$):	$\mathcal{U}(t_2, t_0) = \mathcal{U}(t_2, t_1)\mathcal{U}(t_1, t_0)$
the trace (Tr) of an operator is the sum of its diagonal elements	$Tr(A) \equiv \sum_n A_{n,n}$
the trace of a product of operators is invariant to cyclic permutations	$Tr(ABC) = Tr(BCA) = Tr(CAB)$
the trace of a commutator vanishes	$Tr[A, B] = 0$
the trace is invariant to a unitary transformation (i.e. if $S^\dagger = S^{-1}$)	$Tr(S^\dagger AS) = Tr(A)$

Table A.3: Properties of the time evolution operator and the trace of an operator.

Appendix B

Quantum Mechanics of CARS

This appendix gives a very detailed analysis of the quantum mechanics that governs CARS spectroscopy, including a full semi-classical derivation of the CARS signal starting from the density matrix and using classical electromagnetic optical waves. It is an extension of the quantum mechanical discussion of CARS given in Chapter 2 and follows the same books: *Principles of Nonlinear Optical Spectroscopy* by Shaul Mukamel [56] and *Principles of Nonlinear Optical Spectroscopy: A Practical Approach* by Peter Hamm, also referred to as *Mukamel for Dummies* [57]. Both books provide even more theoretical background on the quantum mechanics of CARS and other related nonlinear optical spectroscopies.

B.1 Basics and the Density Matrix

A generic quantum mechanical wavefunction, can be represented as a simple column vector. In Dirac notation, this is referred to as a *ket* and represented as:

$$|\Psi\rangle \leftrightarrow \begin{bmatrix} c_1 \\ \vdots \\ c_n \end{bmatrix} \quad (\text{B.1})$$

where c_n is a complex number. This can be expanded as a linear combination of an orthonormal basis set, $|n\rangle$:

$$|\Psi\rangle = \sum_n c_n |n\rangle \quad \text{where} \quad |n\rangle \leftrightarrow \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix} \quad n^{th} \text{ component} \quad (\text{B.2})$$

The Hermitian conjugate of a ket is called a *bra*. It is a row vector, that in Dirac notation is represented as:

$$\langle \Psi | \leftrightarrow [c_1 \quad \cdots \quad c_n] \quad (\text{B.3})$$

Like a ket, this can also be expanded as a linear combination of an orthonormal basis set, $\langle m |$:

$$\langle \Psi | = \sum_m c_m^* \langle m | \quad \text{where} \quad \langle m | \leftrightarrow [0 \quad \cdots \quad 1 \quad \cdots \quad 0] \quad m^{th} \text{ component} \quad (\text{B.4})$$

where $*$ denotes a complex conjugate ($i \rightarrow -i$). A general wavefunction is a function of time, but as the wavefunctions of the orthonormal basis sets ($|n\rangle$ and $\langle m|$) are stationary in time, the coefficients c_n and c_m^* carry the time dependence:

$$|\Psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad \text{and} \quad \langle \Psi(t) | = \sum_m c_m^*(t) \langle m | \quad (\text{B.5})$$

In the following discussion, this dependence on time will not always be written explicitly, to allow for more concise notation, but it will always be assumed.

From simple matrix algebra, it can be seen that the wavefunctions of the orthonormal basis sets are such that:

$$\langle m | n \rangle \leftrightarrow [0 \quad \cdots \quad 1 \quad \cdots \quad 0] \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix} = \delta_{nm} \quad (\text{B.6})$$

This is called the *inner product* of a bra and a ket. In general, the inner product of two wavefunctions is a number. The corresponding *outer product* of these basis sets is:

$$|n\rangle \langle m| \leftrightarrow \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix} [0 \quad \cdots \quad 1 \quad \cdots \quad 0] = \begin{bmatrix} 0 & \vdots & 0 \\ \cdots & 1 & \cdots \\ 0 & \vdots & 0 \end{bmatrix} \begin{matrix} m^{th} \text{ column} \\ \downarrow \\ \leftarrow n^{th} \text{ row} \end{matrix} \quad (\text{B.7})$$

In general, an outer product of two wavefunctions returns a square matrix. In quantum mechanics, this is called an *operator*. The operator that is most important for the quantum mechanical theory of CARS spectroscopy is the so called *density operator* or

density matrix. It is defined as the outer product of a generic wavefunction:

$$\rho \equiv |\Psi\rangle\langle\Psi| = \sum_{n,m} c_n c_m^* |n\rangle\langle m| \equiv \sum_{n,m} \rho_{nm} |n\rangle\langle m|$$

$$\text{where } \rho_{nm} \equiv c_n c_m^* \quad (\text{B.8})$$

Represented as a square matrix, the density matrix is given by:

$$\rho = \begin{bmatrix} c_1 c_1^* & c_1 c_2^* & \cdots \\ c_2 c_1^* & c_2 c_2^* & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \quad (\text{B.9})$$

The density matrix represents the state of a quantum mechanical system, i.e. it contains all the information about that system through the complex coefficients, $c_n c_m^*$. To understand the advantage of the density operator it is useful to look at the expectation value of a general operator, A , which is defined as:

$$\langle A \rangle \equiv \langle \Psi | A | \Psi \rangle \quad (\text{B.10})$$

This is the probabilistic expected value of a measurement. For example, if the operator is the position operator, then the result is the expected position of the quantum system. When equation B.10 is expanded in the above defined wavefunction eigenbasis:

$$\langle A \rangle \equiv \sum_{n,m} c_n c_m^* \langle m | A | n \rangle = \sum_{n,m} \rho_{nm} A_{mn} = \text{Tr}[A\rho] \quad (\text{B.11})$$

where $\text{Tr}[A\rho]$ is the trace of the matrix product $A\rho$. A trace is the sum of the diagonal elements of a square matrix:

$$\text{Tr}[B] \equiv \sum_n B_{nn} \quad (\text{B.12})$$

So if the density operator is known, then the expectation value of any other operator can be easily calculated by taking the matrix product of the two and summing all of the diagonal elements of the resulting matrix.

B.2 Time Evolution

As stated above, a wavefunction, in general, is a function of time, i.e. $|\Psi\rangle \rightarrow |\Psi(t)\rangle$. Therefore, it is important to know how a quantum mechanical system evolves in time. This time evolution of a wavefunction is described by the famous time-dependent

Schrödinger equation, which for a ket and a bra is:

$$\begin{aligned}\frac{d}{dt}|\Psi\rangle &= -\frac{i}{\hbar}H|\Psi\rangle \\ \frac{d}{dt}\langle\Psi| &= +\frac{i}{\hbar}H\langle\Psi|\end{aligned}\tag{B.13}$$

where H is the Hamiltonian operator of the system, assumed to be time-independent. A similar expression can be found for the time evolution of the density matrix, using the product rule:

$$\frac{d}{dt}\rho = \frac{d}{dt}(|\Psi\rangle\langle\Psi|) = \left(\frac{d}{dt}|\Psi\rangle\right) \cdot \langle\Psi| + |\Psi\rangle \cdot \left(\frac{d}{dt}\langle\Psi|\right)\tag{B.14}$$

To simplify this expression further, the Schrödinger equation (B.13) can now be substituted:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}H|\Psi\rangle\langle\Psi| + \frac{i}{\hbar}|\Psi\rangle\langle\Psi|H = -\frac{i}{\hbar}H\rho + \frac{i}{\hbar}\rho H\tag{B.15}$$

Using commutator notation, this can be compactly written as:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H, \rho]\tag{B.16}$$

This is called the Liouville-Von Neumann equation, describing the time evolution of the density matrix. It can be seen that the Liouville-Von Neumann equation is identical to the Schrödinger equation.

B.3 Mixed States

One may ask why the density operator is introduced in the first place, since it is shown above that the Liouville-Von Neumann equation is identical to the Schrödinger equation. The answer is that the Liouville-Von Neumann equation is identical to the Schrödinger equation only if the system is in a *pure state*.

A system that can be characterised by one wavefunction is in a pure state. All information about this state is known, the system is in state $|\Psi\rangle$ with probability 1. In this case the density operator contains the same information as the wavefunction of the pure state. However, sometimes not all the information about the system is known. This is then called a *mixed state* and cannot be represented by one wavefunction, but by an ensemble of wavefunctions, $|\Psi_k\rangle$, such that the system is in state $|\Psi_k\rangle$ with probability P_k .

This is where the density matrix becomes useful, because even though a mixed state cannot be represented by a single wavefunction, it can be represented by a single density matrix. The density matrix of a mixed state is given by:

$$\rho \equiv \sum_k P_k |\Psi_k\rangle\langle\Psi_k|$$

$$\text{where } P_k \geq 0 \quad \text{and} \quad \sum_k P_k = 1 \quad (\text{B.17})$$

The individual matrix elements of the density operator of a mixed state are given by:

$$\rho_{nm} = \sum_k P_k \langle n|\Psi_k\rangle \langle\Psi_k|m\rangle \quad (\text{B.18})$$

In such a mixed state, the expectation value of a general operator is given by:

$$\begin{aligned} \langle A \rangle &\equiv \sum_k P_k \langle\Psi_k|A|\Psi_k\rangle = \sum_{n,m} \sum_k P_k \langle\Psi_k|m\rangle \langle m|A|n\rangle \langle n|\Psi_k\rangle \\ &= \sum_{n,m} \rho_{nm} A_{mn} = \text{Tr}[A\rho] \end{aligned} \quad (\text{B.19})$$

where the identity operator ($\sum_n |n\rangle\langle n|$ and $\sum_m |m\rangle\langle m|$) has been inserted twice. This is the same result as for a pure state, Equation B.11. Hence, the density operator can be used to calculate the expectation value of any operator regardless of whether or not a system is in a pure or mixed state. This is the key advantage of the density operator. Further, it can be shown that the Liouville-von Neumann equation (Equation B.16) also applies to mixed states in the same way it applies to pure states.

B.4 Time Evolution Operator

Now, the time evolution operator will be introduced. This operator evolves a wavefunction in time from a starting time t_0 to a later time t , according to:

$$|\Psi(t)\rangle = \mathcal{U}(t, t_0) |\Psi(t_0)\rangle \quad (\text{B.20})$$

This expression can be substituted into the Schrödinger equation:

$$\frac{d}{dt} |\Psi(t)\rangle = -\frac{i}{\hbar} H |\Psi(t)\rangle \quad \rightarrow \quad \frac{d}{dt} \mathcal{U}(t, t_0) |\Psi(t_0)\rangle = -\frac{i}{\hbar} H \mathcal{U}(t, t_0) |\Psi(t_0)\rangle \quad (\text{B.21})$$

But this must be true for any wavefunction $|\Psi(t_0)\rangle$, and therefore:

$$\frac{d}{dt}\mathcal{U}(t, t_0) = -\frac{i}{\hbar}H\mathcal{U}(t, t_0) \quad (\text{B.22})$$

If the Hamiltonian is still assumed to be independent of time, then the above equation can be solved by simply integrating both sides, to give an equation for the time evolution operator in terms of the Hamiltonian:

$$\mathcal{U}(t, t_0) = \exp\left[\frac{-iH(t - t_0)}{\hbar}\right] \quad (\text{B.23})$$

B.5 Schrödinger vs. Heisenberg Picture

There are two equivalent ways of looking at the time evolution of a quantum mechanical system. One is called the Schrödinger picture and the other is called the Heisenberg picture. Understanding the difference between them is important for the subsequent discussion of the derivation of the CARS signal.

In the Schrödinger picture, state kets evolve with time, while operators remain unchanged:

$$|\Psi\rangle \rightarrow \mathcal{U}|\Psi\rangle \quad \text{with } A \text{ unchanged} \quad (\text{B.24})$$

In the Heisenberg picture, state kets remain unchanged, while operators evolve with time:

$$A \rightarrow \mathcal{U}^\dagger A \mathcal{U} \quad \text{with } |\Psi\rangle \text{ unchanged} \quad (\text{B.25})$$

where $\mathcal{U}^\dagger$ denotes the Hermitian adjoint of $\mathcal{U}$. These two pictures are identical in terms of the physics they describe, they are just two different ways of thinking about the same thing. This can be seen when looking at the expectation value of an operator. In the Schrödinger picture, the expectation value of an operator A at a given time is:

$$\langle A \rangle = \langle \Psi | \mathcal{U}^\dagger \cdot A \cdot \mathcal{U} | \Psi \rangle = \langle \Psi | \mathcal{U}^\dagger A \mathcal{U} | \Psi \rangle \quad (\text{B.26})$$

And in the Heisenberg picture it is:

$$\langle A \rangle = \langle \Psi | \cdot \mathcal{U}^\dagger A \mathcal{U} \cdot | \Psi \rangle = \langle \Psi | \mathcal{U}^\dagger A \mathcal{U} | \Psi \rangle \quad (\text{B.27})$$

It can be seen that the two expressions are the same, even though the time evolution acts on the wavefunction in the Schrödinger picture and on the operator in the Heisenberg picture.

B.6 Wavefunction in the Interaction Picture

In the interaction picture, the Hamiltonian governing a quantum system is now treated as being time-dependent, however in a perturbative way, so that the total Hamiltonian is the sum of a time-independent part, H_0 , and a very weak and time-dependent part, $H'(t)$:

$$H(t) = H_0 + H'(t) \quad (\text{B.28})$$

This interaction picture is a mixture of the Schrödinger and Heisenberg pictures. The time-independent part of the Hamiltonian is described in the Heisenberg picture, while the time-dependent part is described in the Schrödinger picture. The total wavefunction in this interaction picture is defined as:

$$|\Psi(t)\rangle \equiv \mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle \quad (\text{B.29})$$

In this case, $|\Psi(t)\rangle$ is the wavefunction governed by the total Hamiltonian, $H(t)$. $\mathcal{U}_0(t, t_0)$ is the time evolution operator with respect to the time-independent part of the total Hamiltonian, H_0 , while $|\Psi_I(t)\rangle$ describes the time evolution of the wavefunction with respect to the time-dependent part of the Hamiltonian, $H'(t)$. At time $t = t_0$, the interaction wavefunction is the same as the overall wavefunction, $|\Psi_I(t_0)\rangle = |\Psi(t_0)\rangle$. In the following discussion, the subscript I is used to denote the interaction picture.

The time evolution operator with respect to the time-independent part of the Hamiltonian, $\mathcal{U}_0(t, t_0)$, is the same as found before (Equation B.23):

$$\mathcal{U}_0(t, t_0) = \exp \left[\frac{-iH_0(t - t_0)}{\hbar} \right] \quad (\text{B.30})$$

The wavefunction in the interaction picture (Equation B.29) can be substituted into the Schrödinger equation (B.13):

$$\begin{aligned} -\frac{i}{\hbar} H(t) \mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle &= \frac{d}{dt} [\mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle] \\ &= \left(\frac{d}{dt} \mathcal{U}_0(t, t_0) \right) \cdot |\Psi_I(t)\rangle + \mathcal{U}_0(t, t_0) \cdot \left(\frac{d}{dt} |\Psi_I(t)\rangle \right) \\ &= -\frac{i}{\hbar} H_0 \mathcal{U}_0(t, t_0) \cdot |\Psi_I(t)\rangle + \mathcal{U}_0(t, t_0) \cdot \left(\frac{d}{dt} |\Psi_I(t)\rangle \right) \quad (\text{B.31}) \end{aligned}$$

where the product rule was used in the first step and then equation B.22 was substituted in the second step. If now equation B.28 is substituted as well, the terms containing the

time-independent part of the Hamiltonian cancel, such that:

$$-\frac{i}{\hbar} H'(t) \mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle = \mathcal{U}_0(t, t_0) \left(\frac{d}{dt} |\Psi_I(t)\rangle \right) \quad (\text{B.32})$$

Multiplying both sides of this equation by $\mathcal{U}_0^\dagger(t, t_0)$ from the left and using the fact that the time evolution operator is unitary (i.e. $\mathcal{U}_0^\dagger(t, t_0) \mathcal{U}_0(t, t_0) = 1$) leads to:

$$-\frac{i}{\hbar} \mathcal{U}_0^\dagger(t, t_0) H'(t) \mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle = \frac{d}{dt} |\Psi_I(t)\rangle \quad (\text{B.33})$$

This can be written in a more concise way as:

$$\frac{d}{dt} |\Psi_I(t)\rangle = -\frac{i}{\hbar} H'_I(t) |\Psi_I(t)\rangle \quad (\text{B.34})$$

where $H'_I(t)$ is the weak perturbation in the interaction picture, defined as:

$$\begin{aligned} H'_I(t) &= \mathcal{U}_0^\dagger(t, t_0) H'(t) \mathcal{U}_0(t, t_0) \\ &= \exp \left[\frac{i H_0(t - t_0)}{\hbar} \right] H'(t) \exp \left[\frac{-i H_0(t - t_0)}{\hbar} \right] \end{aligned} \quad (\text{B.35})$$

Differential equation B.34 can now be solved by integrating both sides with respect to time:

$$|\Psi_I(t)\rangle = |\Psi_I(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau H'_I(\tau) |\Psi_I(\tau)\rangle \quad (\text{B.36})$$

This equation can then be solved by substituting it into itself:

$$\begin{aligned} |\Psi_I(t)\rangle &= |\Psi_I(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau H'_I(\tau) |\Psi_I(\tau)\rangle \\ &\quad + \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 H'_I(\tau_2) H'_I(\tau_1) |\Psi_I(\tau_1)\rangle \end{aligned} \quad (\text{B.37})$$

Continuing this process of solving the equation by substituting it into itself $n - 1$ times leads to the final result of:

$$\begin{aligned} |\Psi_I(t)\rangle &= |\Psi_I(t_0)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\ &\quad H'_I(\tau_n) H'_I(\tau_{n-1}) \cdots H'_I(\tau_1) |\Psi_I(t_0)\rangle \end{aligned} \quad (\text{B.38})$$

To get an expression for the overall wavefunction, that is governed by the total Hamiltonian, $H(t)$, both sides can be multiplied by $\mathcal{U}_0(t, t_0)$. Using the facts that $|\Psi(t)\rangle = \mathcal{U}_0(t, t_0) |\Psi_I(t)\rangle$ and $|\Psi_I(t_0)\rangle = |\Psi(t_0)\rangle$ results in:

$$|\Psi(t)\rangle = |\Psi^{(0)}(t)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \mathcal{U}_0(t, t_0) H'_I(\tau_n) H'_I(\tau_{n-1}) \cdots H'_I(\tau_1) |\Psi(t_0)\rangle \quad (\text{B.39})$$

where $|\Psi^{(0)}(t)\rangle \equiv \mathcal{U}_0(t, t_0) |\Psi(t_0)\rangle$ is the zero-order wavefunction, without subject to the time-dependent perturbation, $H'(t)$. Using the definition of $H'_I(t)$, Equation B.35, it can be shown that:

$$|\Psi(t)\rangle = |\Psi^{(0)}(t)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \mathcal{U}_0(t, \tau_n) H'(\tau_n) \mathcal{U}_0(\tau_n, \tau_{n-1}) H'(\tau_{n-1}) \cdots \mathcal{U}_0(\tau_2, \tau_1) H'(\tau_1) \mathcal{U}_0(\tau_1, t_0) |\Psi(t_0)\rangle \quad (\text{B.40})$$

where the following identity has been applied: $\mathcal{U}(\tau_n, \tau_{n-1}) = \mathcal{U}(\tau_n, t_0) \mathcal{U}(t_0, \tau_{n-1}) = \mathcal{U}(\tau_n, t_0) \mathcal{U}^\dagger(\tau_{n-1}, t_0)$. The physical interpretation of this expression is, that the system, represented by the wavefunction $|\Psi(t_0)\rangle$, propagates freely under the Hamiltonian H_0 , as described by the time evolution operator $\mathcal{U}_0(\tau_1, t_0)$. At time τ_1 , the system interacts with a small perturbation $H'(\tau_1)$. It then propagates freely again, as described by the time evolution operator $\mathcal{U}_0(\tau_2, \tau_1)$, until time τ_2 , where it interacts with the small perturbation $H'(\tau_2)$ and so on.

B.7 Density Matrix in the Interaction Picture

Similar to the above expansion of the wavefunction, an expression for the density matrix can be calculated. In the interaction picture, the density matrix is defined as:

$$\begin{aligned} \rho(t) &= |\Psi(t)\rangle \langle \Psi(t)| = \mathcal{U}_0(t, t_0) \cdot |\Psi_I(t)\rangle \langle \Psi_I(t)| \cdot \mathcal{U}_0^\dagger(t, t_0) \\ &= \mathcal{U}_0(t, t_0) \cdot \rho_I(t) \cdot \mathcal{U}_0^\dagger(t, t_0) \end{aligned} \quad (\text{B.41})$$

where $\rho_I(t)$ is the interaction density matrix. This is true for pure as well as mixed states. Similar to Equation B.34, where it is shown that the Schrödinger equation holds true for the interaction wavefunction, it can be shown that the Liouville-Von Neumann

equation holds true for the interaction density operator, such that:

$$\frac{d}{dt}\rho_I(t) = -\frac{i}{\hbar} [H'_I(t), \rho_I(t)] \quad (\text{B.42})$$

where the weak perturbation, $H'_I(t)$, in the interaction picture is still defined as in Equation B.35. Differential equation B.42 can then be solved by integrating both sides with respect to time and recursively substituting the result into itself $n - 1$ times, similar to the interaction wavefunction. The result is:

$$\begin{aligned} \rho_I(t) = \rho_I(t_0) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\ [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho_I(t_0)] \cdots]] \end{aligned} \quad (\text{B.43})$$

Multiplying both sides by $\mathcal{U}_0(t, t_0)$ from the left and $\mathcal{U}_0^\dagger(t, t_0)$ from the right to get the overall density operator governed by the total Hamiltonian, gives:

$$\begin{aligned} \rho(t) = \rho^{(0)}(t_0) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\ \mathcal{U}_0(t, t_0) \cdot [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho(t_0)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \end{aligned} \quad (\text{B.44})$$

The physical interpretation of this is similar to that of the interaction wavefunction. The system with density operator $\rho(t_0)$ propagates freely under the time-independent Hamiltonian, H_0 , until time τ_1 , as described by the time evolution operator, $\mathcal{U}_0(\tau_1, t_0)$. At time τ_1 , the system interacts with a small perturbation described by $H'(\tau_1)$, after which it propagates freely again until time τ_2 , where it interacts with the small perturbation $H'(\tau_2)$ and so on. However, unlike the interaction wavefunction, these interactions can be from the left or the right, as the density operator is the outer product of two wavefunctions (i.e. containing a ket and a bra).

$\rho^{(0)}(t_0)$ can be assumed to be an equilibrium density operator, not evolving in time under the time-independent Hamiltonian, H_0 . In this case, the starting time, t_0 can be set to minus infinity, i.e. $t_0 \rightarrow -\infty$. The density operator can then be compactly written as:

$$\rho(t) = \rho^{(0)}(-\infty) + \sum_{n=1}^{\infty} \rho^{(n)}(t) \quad (\text{B.45})$$

The n^{th} order density operator, $\rho^{(n)}(t)$, is given by:

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1$$

$$\mathcal{U}_0(t, t_0) \cdot [H'_I(\tau_n), [H'_I(\tau_{n-1}), \cdots [H'_I(\tau_1), \rho(-\infty)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (\text{B.46})$$

B.8 The n^{th} Order Polarisation

Now the specification is made that the time-dependent part of the Hamiltonian (the small perturbation) is due to an electric field, $E(t)$, for example a laser beam in the case of CARS spectroscopy, which can be expressed as:

$$H'(t) = E(t) \cdot \mu \quad (\text{B.47})$$

where μ is the transition dipole operator. The n^{th} order density matrix then is:

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1)$$

$$\mathcal{U}_0(t, t_0) \cdot [\mu_I(\tau_n), [\mu_I(\tau_{n-1}), \cdots [\mu_I(\tau_1), \rho(-\infty)] \cdots]] \cdot \mathcal{U}_0^\dagger(t, t_0) \quad (\text{B.48})$$

where $\mu_I(t) = \mathcal{U}_0^\dagger(t, t_0) \mu \mathcal{U}_0(t, t_0)$ is the dipole operator in the interaction picture.

Of interest for CARS spectroscopy is the polarisation of a molecule, with the overall polarisation being given by the expectation value of the dipole operator. The n^{th} order polarisation of a molecule, $P^{(n)}(t)$, can be found from the expectation value of the dipole operator, using the n^{th} order density matrix, as given by Equation B.11:

$$P^{(n)}(t) = \text{Tr}[\mu \rho^{(n)}(t)] \equiv \langle \mu \rho^{(n)}(t) \rangle \quad (\text{B.49})$$

Substituting Equation B.48 into this gives the n^{th} order polarisation as:

$$P^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1)$$

$$\langle \mu(t) \cdot [\mu(\tau_n), [\mu(\tau_{n-1}), \cdots [\mu(\tau_1), \rho(-\infty)] \cdots]] \rangle \quad (\text{B.50})$$

where the fact that the trace, $\langle \cdots \rangle$, is invariant to cyclic permutations was used.

Additionally, the subscript I has been dropped for simplicity, but the equation is still in the interaction picture, $\mu(t) = \mathcal{U}_0^\dagger(t, t_0)\mu\mathcal{U}_0(t, t_0)$. At this point it is useful to define a new set of time variables according to:

$$\begin{aligned}
\tau_1 &= 0 \\
t_1 &= \tau_2 - \tau_1 \\
t_2 &= \tau_3 - \tau_2 \\
&\vdots \\
t_{n-1} &= \tau_n - \tau_{n-1} \\
t_n &= t - \tau_n
\end{aligned} \tag{B.51}$$

The old time variables τ_n represent fixed points in time, while the new time variables t_n represent the time intervals between these fixed points and can be thought of as continuous integration variables across time blocks from τ_n to τ_{n+1} . The relation between the old and new time variables is illustrated in Figure B.1. Because the choice of the time zero point is arbitrary, it was set to $\tau_1 = 0$.

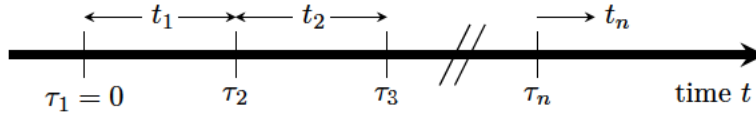


Figure B.1: Illustration of the relation between the time variables τ_n , representing fixed points in time, and the time variables t_n , representing the time intervals between these fixed points.

Using this change of time variables, the n^{th} order polarisation (Equation B.50), can be rewritten as:

$$\begin{aligned}
P^{(n)}(t) &= \int_0^\infty dt_n \int_0^\infty dt_{n-1} \cdots \int_0^\infty dt_1 \\
&\quad E(t - t_n)E(t - t_n - t_{n-1}) \cdots E(t - t_n - t_{n-1} - \cdots - t_1) \\
&\quad S^{(n)}(t_n, t_{n-1}, \cdots, t_1)
\end{aligned} \tag{B.52}$$

where the n^{th} order nonlinear response function is defined as:

$$\begin{aligned}
S^{(n)}(t_n, t_{n-1}, \cdots, t_1) &= \\
&\quad \left(-\frac{i}{\hbar}\right)^n \langle \mu(t_n + \cdots + t_1) [\mu(t_{n-1} + \cdots + t_1), \cdots [\mu(0), \rho(-\infty)] \cdots] \rangle
\end{aligned} \tag{B.53}$$

B.9 The 3rd Order Polarisation

Generally, the polarisation of a molecule depends on the incident electric field in a linear way:

$$P = \epsilon_0 \chi^{(1)} E \quad (\text{B.54})$$

where $\chi^{(1)}$ is the linear susceptibility, E is the incident electric field and ϵ_0 is the permittivity of free space. For very high electric fields however, for example in laser beams, higher order terms start to contribute to the polarisation, which can be expanded in powers of the electric field:

$$\begin{aligned} P &= \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \right) \\ &= P^{(1)} + P^{(2)} + P^{(3)} + \dots = \sum_{n=1}^{\infty} P^{(n)} \end{aligned} \quad (\text{B.55})$$

where $\chi^{(n)}$ is the n^{th} order susceptibility of the n^{th} order polarisation, $P^{(n)}$. However, for media that are isotropic (uniform in all directions), like gases, this is not true, as they possess an inversion symmetry, which causes all the even order susceptibilities to vanish. Therefore, their lowest nonlinear order of polarisation is the 3rd order. For this reason, the 3rd order polarisation is the one that contributes most strongly to the CARS signal of gases. From Equation B.52 it can be seen that the 3rd order polarisation is given by:

$$\begin{aligned} P^{(3)}(t) &= \int_0^{\infty} dt_3 \int_0^{\infty} dt_2 \int_0^{\infty} dt_1 \\ &\quad E(t - t_3) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1) \cdot S(t_3, t_2, t_1) \end{aligned} \quad (\text{B.56})$$

with the corresponding 3rd order nonlinear response function containing three nested commutators:

$$S(t_3, t_2, t_1) = \left(-\frac{i}{\hbar} \right)^3 \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), [\mu(t_1), [\mu(0), \rho(-\infty)]]] \rangle \quad (\text{B.57})$$

Writing out the individual commutators of this 3rd order nonlinear response function results in eight terms:

$$\begin{aligned}
& \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), [\mu(t_1), [\mu(0), \rho(-\infty)]]] \rangle = \\
& + \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(t_1) \mu(0) \rho(-\infty) \rangle \Rightarrow R_4 \\
& - \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(t_1) \rho(-\infty) \mu(0) \rangle \Rightarrow R_1^* \\
& - \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(0) \rho(-\infty) \mu(t_1) \rangle \Rightarrow R_2^* \\
& + \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \rho(-\infty) \mu(0) \mu(t_1) \rangle \Rightarrow R_3 \\
& - \langle \mu(t_3 + t_2 + t_1) \mu(t_1) \mu(0) \rho(-\infty) \mu(t_2 + t_1) \rangle \Rightarrow R_3^* \\
& + \langle \mu(t_3 + t_2 + t_1) \mu(t_1) \rho(-\infty) \mu(0) \mu(t_2 + t_1) \rangle \Rightarrow R_2 \\
& + \langle \mu(t_3 + t_2 + t_1) \mu(0) \rho(-\infty) \mu(t_1) \mu(t_2 + t_1) \rangle \Rightarrow R_1 \\
& - \langle \mu(t_3 + t_2 + t_1) \rho(-\infty) \mu(0) \mu(t_1) \mu(t_2 + t_1) \rangle \Rightarrow R_4^* \quad (B.58)
\end{aligned}$$

where R_1^* , R_2^* , R_3^* and R_4^* are the complex conjugates of R_1 , R_2 , R_3 and R_4 respectively. This expression can be simplified, by applying the rotating wave approximation (RWA) to the individual commutators. This approximation says that terms of the Hamiltonian that oscillate rapidly in time can be neglected, as they average out to zero, while those terms that vary slowly in time are kept. It is a valid approximation when the frequency of light interacting with a quantum system is close to a transition frequency of that system. For CARS, with a transition of frequency of ω_T and a laser frequency of ω_L , with respective time dependences of $e^{-i\omega_T t}$ and $e^{-i\omega_L t} + e^{i\omega_L t}$, the assumption is that $\omega_T \approx \omega_L$. This means that terms including $\omega_T - \omega_L$ oscillate rapidly in time and can be ignored, while terms including $\omega_T + \omega_L$ vary slowly in time and are kept. When the RWA is applied to Equation B.58, only one commutator, R_4 , survives. The resulting 3rd order polarisation therefore is:

$$\begin{aligned}
P^{(3)}(t) &= \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \\
& E(t - t_3) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1) \cdot R_4(t_3, t_2, t_1) \quad (B.59)
\end{aligned}$$

In hybrid fs/ps CARS spectroscopy, the electric fields in Equation (B.59) are due to the pump, Stokes and probe laser pulses, labelled as E_1 , E_2 and E_3 respectively. Their corresponding frequencies and wave vectors are denoted as ω_1 , ω_2 , ω_3 and k_1 , k_2 , k_3 .

Using this, the electric fields can be expressed explicitly as:

$$E(t - t_3 - \tau) = E_3(t - t_3 - \tau)e^{i[k_3 r - \omega_3(t - t_3 - \tau)]} + c.c.$$

$$E(t - t_3 - t_2) = E_2(t - t_3 - t_2)e^{i[k_2 r - \omega_2(t - t_3 - t_2)]} + c.c.$$

$$E(t - t_3 - t_2 - t_1) = E_1(t - t_3 - t_2 - t_1)e^{i[k_1 r - \omega_1(t - t_3 - t_2 - t_1)]} + c.c. \quad (\text{B.60})$$

where *c.c.* denotes the complex conjugate. τ in the probe electric field, E_3 , is a time delay relative to the pump and Stokes electric fields, E_1 and E_2 . It has been introduced to account for the fact that in hybrid fs/ps CARS, the probe is delayed in time from the pump/Stokes interaction, to avoid interference with the NR background signal. It can be seen that the product of the three electric fields, $E(t - t_3)E(t - t_3 - t_2)E(t - t_3 - t_2 - t_1)$ has eight components with an overall wavevector:

$$k = \pm k_1 \pm k_2 \pm k_3 \quad (\text{B.61})$$

However, due to the phase matching condition (Equation 1.1), the CARS signal propagates with a wavevector:

$$k = k_1 - k_2 + k_3 \quad (\text{B.62})$$

Hence, the only term of the product of the three electric fields that survives the phase matching condition is:

$$\begin{aligned} & E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1) \\ & e^{i[-\omega_3(t - t_3 - \tau) + \omega_2(t - t_3 - t_2) - \omega_1(t - t_3 - t_2 - t_1)]} \end{aligned} \quad (\text{B.63})$$

Thus, applying the phase matching condition to the 3rd order polarisation (Equation B.59), results in:

$$\begin{aligned} P^{(3)}(t) &= \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \cdot R_4(t_3, t_2, t_1) \\ & E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1) \\ & e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_3(\omega_1 - \omega_2 + \omega_3) + t_2(\omega_1 - \omega_2) + t_1(\omega_1) + \tau(\omega_3)]} \end{aligned} \quad (\text{B.64})$$

This expression can be simplified further by applying two assumptions. The first assumption is that the molecular response is fast compared to the pump and probe

pulse coherence time scales, t_1 and t_3 . This assumption is valid as the pump and probe pulses are detuned from any direct one-photon vibrational or electronic transition, so that molecular dephasing over the t_1 and t_3 timescales is almost instantaneous. Under this assumption, the molecular 3rd order response function can be replaced by the following:

$$R_4(t_3, t_2, t_1) \rightarrow \delta(t_3)R_4(0, t_2, 0)\delta(t_1) \quad (\text{B.65})$$

In this case, the 3rd order polarisation becomes:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \cdot \delta(t_3)R_4(0, t_2, 0)\delta(t_1) \\ E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1) \\ e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_3(\omega_1 - \omega_2 + \omega_3) + t_2(\omega_1 - \omega_2) + t_1(\omega_1) + \tau(\omega_3)]} \quad (\text{B.66})$$

Using the delta function of the first coherence time scale, $\delta(t_1)$, to solve the integral with respect to t_1 gives:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \cdot \delta(t_3)R_4(0, t_2, 0) \\ E_3(t - t_3 - \tau)E_2^*(t - t_3 - t_2)E_1(t - t_3 - t_2) \\ e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_3(\omega_1 - \omega_2 + \omega_3) + t_2(\omega_1 - \omega_2) + \tau(\omega_3)]} \quad (\text{B.67})$$

Solving the integral with respect to the third coherence time scale, t_3 , results in:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty dt_2 \cdot R_4(0, t_2, 0) \\ E_3(t - \tau)E_2^*(t - t_2)E_1(t - t_2) \\ e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_2(\omega_1 - \omega_2) + \tau(\omega_3)]} \quad (\text{B.68})$$

The second assumption is that the pump and Stokes pulses are impulsive and short compared to the probe pulse, so that they can be replaced by delta functions:

$$\begin{aligned} E_1(t - t_2) &\rightarrow \delta(t - t_2) \\ E_2^*(t - t_2) &\rightarrow \delta(t - t_2) \end{aligned} \quad (\text{B.69})$$

This is a valid assumption for hybrid fs/ps CARS, as the pump and Stokes pulses are on the order of femtoseconds, while the probe pulse is on the order of picoseconds. The resulting 3rd order polarisation (taking $E_3(t - \tau)$ outside the integral and denoting $R_4(0, t_2, 0)$ simply as $R_4(t_2)$) then is:

$$\begin{aligned} P^{(3)}(t) &= \left(-\frac{i}{\hbar}\right)^3 E_3(t - \tau) \int_0^\infty dt_2 \cdot R_4(t_2) \\ &\delta(t - t_2) \delta(t - t_2) e^{i[t(\omega_2 - \omega_1 - \omega_3) + t_2(\omega_1 - \omega_2) + \tau(\omega_3)]} \end{aligned} \quad (\text{B.70})$$

When the integral with respect to t_2 is calculated using the delta functions, $\delta(t - t_2)$, the final expression of the 3rd order polarisation can be found:

$$\begin{aligned} P^{(3)}(t) &= \left(-\frac{i}{\hbar}\right)^3 E_3(t - \tau) R_4(t) e^{i[t(\omega_2 - \omega_1 - \omega_3) + t(\omega_1 - \omega_2) + \tau(\omega_3)]} \\ &= \left(-\frac{i}{\hbar}\right)^3 E_3(t - \tau) R_4(t) e^{-i\omega_3(t - \tau)} \end{aligned} \quad (\text{B.71})$$

To get from this time domain 3rd order polarisation to the corresponding frequency domain 3rd order polarisation, a simple Fourier transform needs to be performed:

$$P^{(3)}(\omega) = \mathcal{F} \left[P^{(3)}(t) \right] \quad (\text{B.72})$$

The frequency domain CARS signal is proportional to the square of the absolute value of the frequency domain 3rd order polarisation (assuming that the probe is delayed from the pump/Stokes excitation long enough so that no NR contribution is present):

$$I_{\text{CARS}}(\omega) \propto \left| P^{(3)}(\omega) \right|^2 \quad (\text{B.73})$$

This frequency domain CARS signal contains the CARS spectrum of the probed molecule and this information is what is detected with a spectrometer in a hybrid fs/ps CARS experiment.

Appendix C

Diatomic Energy Levels

This appendix presents a derivation of the rotational and vibrational energy levels of diatomic molecules. The theory covered here is the same as in Chapter 2, but with significantly more detail. This more in-depth discussion of ro-vibrational energy levels is included, as it is not only relevant to CARS spectroscopy, but to a large area of science. Every spectroscopic method relies on some form of excitation and/or de-excitation of an atom or molecule by one or more photons, and therefore accurate knowledge of the energy levels is essential.

As molecules are of the size of Angstroms (10^{-10} m), they are governed by quantum mechanics. This means the energies they can have are quantised and only take certain values, leading to discrete energy levels. The total energy of a molecule is the sum of its electronic energy level, T_e , vibrational energy level, $G(v)$ and rotational energy level, $F(J)$:

$$T(v, J) = T_e + G(v) + F(J) \quad (\text{C.1})$$

where v and J are the vibrational and rotational quantum numbers respectively. For HR-CARS, only the rotational and vibrational energy levels are of interest and will be discussed here, while it is assumed that the molecules always remain in their ground electronic energy level.

Like Chapter 2, most of the theory presented here follows the book *Molecular Spectra and Molecular Structure Volume I - Spectra of Diatomic Molecules* by Gerhard Herzberg [58], but some of the derivations can be found in the books *Atoms, Molecules and Photons: An Introduction to Atomic-, Molecular- and Quantum Physics* by Wolfgang Demtröder [59] and *Rotational Spectroscopy of Diatomic Molecules* by John M Brown and Alan Carrington [60]. All three books provide much more detailed discussions on molecular energy levels.

C.1 Rotational Energy Levels

The rotational energy levels of a diatomic molecule can be calculated by assuming a rigid rotor model, in which the two atoms of such a molecule are modelled as point masses connected by a rigid stick. This approach is justified because almost all of the mass of an atom is concentrated in its nucleus, which has a size on the order of a femtometer (10^{-15} m), about five orders of magnitude smaller than the molecule itself. A general rigid rotor model is shown in Figure C.1.

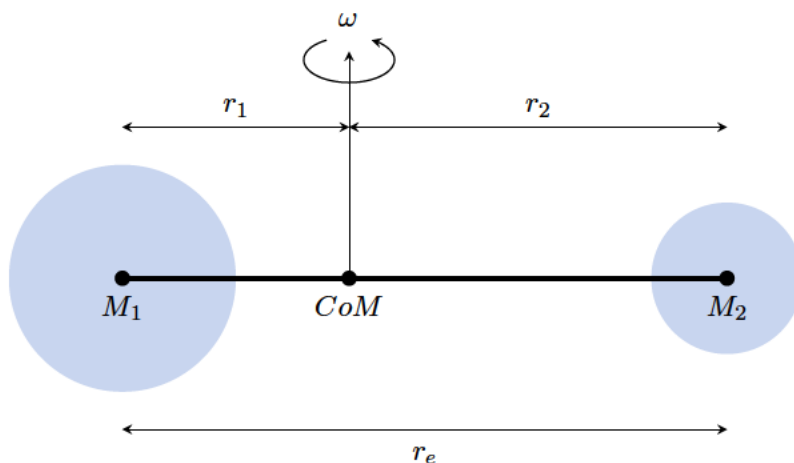


Figure C.1: A diatomic molecule modelled as a rigid rotor. Two point masses, M_1 and M_2 , are connected by a rigid stick of length r_e and rotate around their centre of mass (CoM) at angular speed ω .

It can be seen that in this rigid rotor approach, there are two masses, M_1 and M_2 , separated by a fixed distance, r_e , rotating around their centre of mass. In the case of a homonuclear diatomic molecule, the two masses are equal and so their centre of mass is exactly in the middle between them.

This two-body problem can be reduced to a one-body problem by using the concept of reduced mass, treating the two masses as one. The problem then becomes that of a single point mass rotating around a centre point at a fixed radius, r_e , i.e. following the surface of a sphere, as shown in Figure C.2.

The reduced mass is defined as follows:

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (C.2)$$

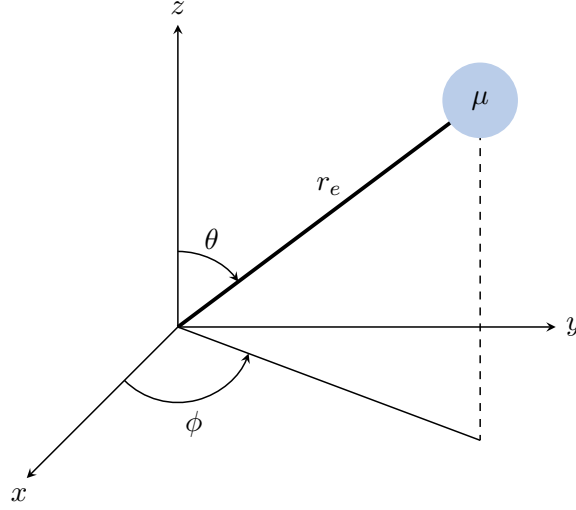


Figure C.2: A diatomic molecule modelled as a point mass, μ , undergoing free motion around a centre point at a fixed distance, r_e .

This one-body problem can be solved using quantum mechanics. The time-independent Schrödinger equation for a single non-relativistic particle of mass μ is:

$$\hat{H}\Psi(r) = [\hat{T} + \hat{V}(r)] \Psi(r) = \left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi(r) = E\Psi(r) \quad (\text{C.3})$$

where $\Psi(r)$ is the wavefunction of the particle. The Hamiltonian, $\hat{H}$, consists of a kinetic and a potential term, $\hat{T}$ and $\hat{V}$ respectively. This is nothing but an eigenvalue equation, with the eigenvalue, E , being the energy of the particle. Because of the spherical symmetry of this problem, it is convenient to work in spherical polar coordinates, so the Laplacian is expressed as:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \quad (\text{C.4})$$

As the distance of the point mass from the centre is constant, the potential energy is zero at $r = r_e$ and infinity everywhere else. This implies that $\Psi(r, \theta, \phi)$ becomes $\Psi(r_e, \theta, \phi)$ and its derivative with respect to r is zero. The resulting Schrödinger equation then is:

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right] \Psi(r_e, \theta, \phi) = E\Psi(r_e, \theta, \phi) \quad (\text{C.5})$$

where $I = \mu r_e^2$ is the moment of inertia of the point mass. To solve this equation, the following Ansatz can be made:

$$\Psi(r_e, \theta, \phi) = BY(\theta, \phi) = B\Theta(\theta)\Phi(\phi) \quad (\text{C.6})$$

If this is substituted into Equation C.5, the Schrödinger equation can be separated into a part that depends only on θ and one that depends only on ϕ . And because these

two are independent variables, each side of the equation must be equal to the same constant, m^2 :

$$\frac{\sin(\theta)}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \beta \sin^2(\theta) = -\frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = m^2$$

$$\text{where } \beta = \frac{2IE}{\hbar^2} \quad (\text{C.7})$$

The equation that depends only on ϕ is:

$$\frac{\partial^2}{\partial \phi^2} \Phi(\phi) = -m^2 \Phi(\phi) \quad (\text{C.8})$$

It has the following normalised solution:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad (\text{C.9})$$

where m is the magnetic quantum number, due to the periodic boundary condition:

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (\text{C.10})$$

The equation that depends only on θ is:

$$\frac{\sin(\theta)}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \beta \sin^2(\theta) = m^2 \quad (\text{C.11})$$

Upon change of variables and rearrangement, it can be shown that this leads to the Legendre equation:

$$(1 - x^2) \frac{d^2}{dx^2} P(x) - 2x \frac{d}{dx} P(x) + \left[\beta - \frac{m^2}{1 - x^2} \right] P(x) = 0$$

$$\text{variable change : } x = \cos(\theta) \quad \Theta(\theta) = P(x) \quad \frac{dx}{-\sin(\theta)} = d\theta \quad (\text{C.12})$$

This can be solved to find β , which is quantised because $\Theta(\theta)$ is continuous. The result, stated without derivation, is:

$$\beta = J(J + 1) \quad J = 0, 1, 2, 3, \dots \quad m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J_{max} \quad (\text{C.13})$$

where J is the rotational quantum number. Now the energy levels of the rigid rotor can be easily found using the previous definition of β (Equation C.7):

$$E(J) = \frac{\hbar^2}{2I} \beta = \frac{\hbar^2}{2I} J(J + 1) \quad J = 0, 1, 2, 3, \dots \quad (\text{C.14})$$

It can be seen that these rotational energy levels are quantised by the rotational quantum number, J . For historic reasons, the standard unit in spectroscopy is the wavenumber (cm^{-1}), so it is convenient to express the energy levels in this unit:

$$F(J) = \frac{E(J)}{hc} = \frac{\hbar}{4\pi cI} J(J+1) = B_e J(J+1) \quad (\text{C.15})$$

where the equilibrium rotational constant, B_e , in units of wavenumber is:

$$B_e = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c\mu r_e^2} \quad (\text{C.16})$$

As can be seen from Equation C.15, the separation of adjacent rotational energy levels increases with increasing J . This is illustrated in Figure C.3 for the first six rotational energy levels.

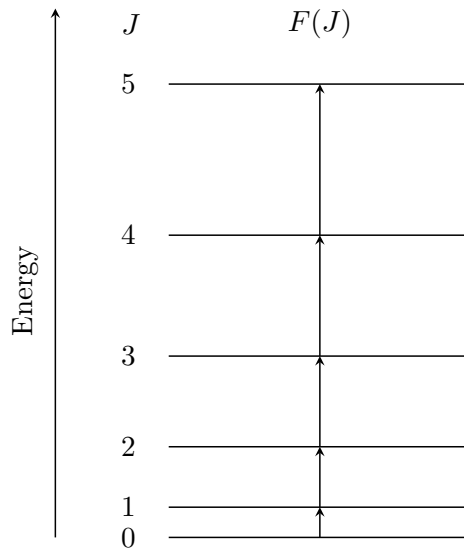


Figure C.3: Illustration of the first six rotational energy levels of a diatomic molecule, showing the increasing energy separation between adjacent levels with increasing rotational quantum number, J .

For every rotational quantum number, J , there is a set of corresponding magnetic quantum numbers, m (see Equation C.13). This means that there are energy levels that have the same energy (i.e. the same rotational quantum number), but different magnetic quantum numbers. These energy levels are degenerate. Table C.1 shows the first five rotational quantum numbers together with their corresponding magnetic quantum numbers.

It can be seen that for every J , there are $2J + 1$ possible values of m , so the rotational energy levels of a diatomic molecule are $2J + 1$ degenerate.

J	m
0	0
1	-1, 0, 1
2	-2, -1, 0, 1, 2
3	-3, -2, -1, 0, 1, 2, 3
4	-4, -3, -2, -1, 0, 1, 2, 3, 4

Table C.1: The first five rotational quantum numbers (J) and their corresponding magnetic quantum numbers (m).

C.2 Centrifugal Distortion

The above treatment of a diatomic molecule as a rigid rotor is a good first approximation, but to get more realistic rotational energy levels, centrifugal distortion has to be taken into account. As the molecule rotates faster, the bond between the atoms stretches and so the equilibrium separation between them increases, altering the moment of inertia and ultimately the energy levels.

Classically, there is a centrifugal force, $\vec{F}_C$, pushing the atoms away from their equilibrium separation, and a counteracting restoring force, $\vec{F}_R$, pulling the atoms towards their equilibrium separation:

$$\vec{F}_C = \mu\omega^2 r \hat{r} \quad \vec{F}_R = -\frac{dE_{pot}(r)}{dr} \hat{r} \quad (\text{C.17})$$

where ω is the angular velocity of the molecule and $E_{pot}(r)$ its potential. $\hat{r}$ is a unit vector pointing along the molecule's rotational axis. Making the approximation that r is close to the equilibrium separation, a parabolic potential can be assumed, so that the restoring force is linear in r :

$$\vec{F}_R = -k(r - r_e) \hat{r} \quad (\text{C.18})$$

where r_e is the equilibrium separation between the atoms when the molecule does not rotate and k is the restoring force constant. The centrifugal and restoring forces, which act along the same line, albeit in opposite directions, are balanced, so that the net force is zero:

$$\vec{F}_C + \vec{F}_R = \vec{0} \quad \rightarrow \quad \mu\omega^2 r = k(r - r_e) \quad (\text{C.19})$$

Relating the classical rotational energy to the quantum mechanical one found before (Equation C.14), the angular velocity can be expressed in terms of J :

$$E = \frac{1}{2}I\omega^2 = \frac{\hbar^2}{2I}J(J+1) \quad \rightarrow \quad \omega^2 = \frac{\hbar^2}{I^2}J(J+1) \quad (\text{C.20})$$

Substituting this into Equation C.19 and using the fact that $I = \mu r^2$ gives:

$$r(J) = r_e + \frac{\hbar^2}{k\mu r^3}J(J+1) \quad (\text{C.21})$$

Assuming again that r is close to the equilibrium separation, it can be approximated that $r \approx r_e$. Using this approximation, r can be replaced by r_e in the right hand side of Equation C.21, to give:

$$r(J) = r_e + \frac{\hbar^2}{k\mu r_e^3}J(J+1) = r_e \left[1 + \frac{\hbar^2}{k\mu r_e^4}J(J+1) \right] = r_e(1+x)$$

$$\text{where } x = \frac{\hbar^2}{k\mu r_e^4}J(J+1) \quad (\text{C.22})$$

It can be seen that as J increases (i.e. as the molecule is in a higher rotational level and therefore rotates faster), the internuclear separation increases as well. As this increase in internuclear separation is much smaller than the equilibrium internuclear separation itself, $x \ll 1$, Equation C.22 can be Taylor expanded around $x = 0$:

$$\begin{aligned} \frac{1}{r^2} &= \frac{1}{r_e^2(1+x)^2} \approx \frac{1}{r_e^2} \left[1 - 2x + 3x^2 - \mathcal{O}(x^3) \right] \\ &= \frac{1}{r_e^2} \left[1 - \frac{2\hbar^2}{k\mu r_e^4}J(J+1) + \frac{3\hbar^4}{k^2\mu^2 r_e^8}J^2(J+1)^2 - \mathcal{O}(J^3) \right] \end{aligned} \quad (\text{C.23})$$

Upon substitution of this into Equation C.14 and including terms of r up to the order of J^2 , the rotational energy becomes:

$$\begin{aligned} E(J) &= \frac{\hbar^2}{2\mu r^2}J(J+1) \\ &= \frac{\hbar^2}{2\mu r_e^2}J(J+1) - \frac{\hbar^4}{k\mu^2 r_e^6}J^2(J+1)^2 + \frac{3\hbar^6}{2k^2\mu^3 r_e^{10}}J^3(J+1)^3 \end{aligned} \quad (\text{C.24})$$

If this is expressed in wavenumbers, the rotational energy is given by:

$$F(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \quad (\text{C.25})$$

with the equilibrium rotational constants defined as:

$$B_e = \frac{\hbar}{4\pi c \mu r_e^2} \quad D_e = \frac{\hbar^3}{2\pi c k \mu^2 r_e^6} \quad H_e = \frac{3\hbar^5}{4\pi c k^2 \mu^3 r_e^{10}} \quad (\text{C.26})$$

C.3 Vibrational Energy Levels

Analogous to the rigid rotor model, a diatomic molecule can be represented in a simple way to calculate its vibrational energy levels. In the case of vibrations, the molecule is modelled as two point masses connected by a spring undergoing simple harmonic motion about their equilibrium separation, r_e , as shown in Figure C.4.

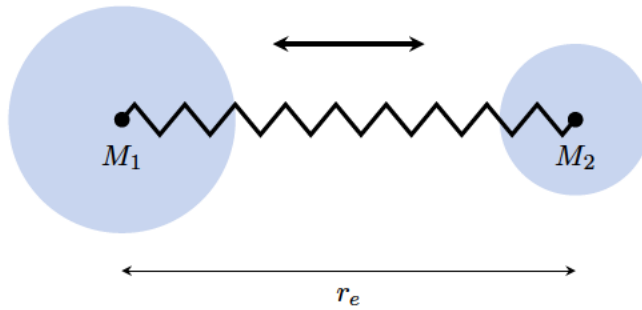


Figure C.4: A diatomic molecule modelled as a simple harmonic spring oscillator. Two point masses, M_1 and M_2 , are connected by a spring and undergo simple harmonic motion about their equilibrium separation, r_e .

Like the rigid rotor model, this spring model can be simplified to a one-body problem using the concept of reduced mass. The molecule is then represented by a point mass attached to a spring, with the other end of the spring fixed to a wall. The point mass undergoes simple harmonic motion about its equilibrium distance from the wall. This is illustrated in Figure C.5.

As with the rotational levels, the Schrödinger equation (Equation C.3) can be used to solve this one-body problem. However, for the vibrational case, the potential is different. Assuming a linear restoring force, $\vec{F}$, on the point mass, the potential is parabolic and only depends on the distance from the equilibrium position, r :

$$\vec{F} = -kr\hat{r} \quad V(r) = \frac{1}{2}kr^2 = \frac{1}{2}\mu\omega^2r^2$$

$$\text{where} \quad \omega = \sqrt{\frac{k}{\mu}} \quad (\text{C.27})$$

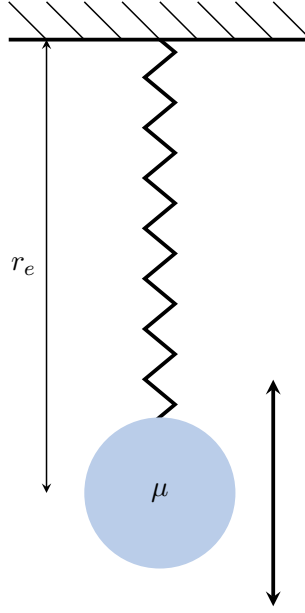


Figure C.5: A diatomic molecule modelled as a point mass, μ , attached to a spring with the other end of the spring attached to a fixed wall, undergoing simple harmonic motion about its equilibrium distance from the wall, r_e .

k is the "spring constant" (the force constant of the restoring force that tries to keep the point mass at its equilibrium position) and ω the frequency of oscillation. Using this potential, the Schrödinger equation becomes:

$$\hat{H}\Psi(r) = \left[-\frac{\hbar^2}{2\mu} \nabla^2 + \frac{1}{2} \mu \omega^2 r^2 \right] \Psi(r) = E \Psi(r) \quad (\text{C.28})$$

To solve this, the following change of variables is made:

$$\xi = r \sqrt{\frac{\mu\omega}{\hbar}} \quad C = \frac{2E}{\hbar\omega} \quad (\text{C.29})$$

The Schrödinger equation can then be written as:

$$\frac{d^2\Psi(\xi)}{d\xi^2} + (C - \xi^2) \Psi(\xi) = 0 \quad (\text{C.30})$$

For the special case that $C = 1$, the solution to this equation is:

$$\Psi_0(\xi) = A e^{-\frac{\xi^2}{2}} \quad E = \frac{1}{2} \hbar\omega \quad (\text{C.31})$$

where A is an amplitude. The result of this special case can be used to make the following Ansatz:

$$\Psi(\xi) = H(\xi) e^{-\frac{\xi^2}{2}} \quad (\text{C.32})$$

Upon substitution into Equation C.30, this results in a Hermitian differential equation:

$$\frac{d^2 H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (C - 1)H = 0 \quad (\text{C.33})$$

The solutions to this equation are the so-called Hermitian polynomials, $H_v(\xi)$, of order v :

$$H_v(\xi) = (-1)^v e^{\xi^2} \frac{d^v}{d\xi^v} (e^{-\xi^2}) \quad v = 0, 1, 2, 3, \dots \quad (\text{C.34})$$

These solutions of course need to be normalised, such that the inner products of the wavefunctions of the harmonic oscillator are equal to one:

$$\langle \Psi(\xi) | \Psi(\xi) \rangle = \langle \Psi(r) | \Psi(r) \rangle = 1 \quad (\text{C.35})$$

The Hermitian polynomials can be expressed as a power series, which must be finite as normalisation would not be possible if $\xi > 1$:

$$H(\xi) = \sum_{i=0}^v a_i \xi^i \quad (\text{C.36})$$

Substituting this into Equation C.33 and comparing the coefficients of equal powers of ξ yields:

$$(i + 2)(i + 1)a_{i+2} = (2i - C + 1)a_i \quad (\text{C.37})$$

But as ξ^v is the highest power of ξ^i , a_{v+2} must be zero and therefore:

$$(2v - C + 1) = 0 \quad \rightarrow \quad v = \frac{1}{2}(C - 1) \quad (\text{C.38})$$

Using the definition of C (Equation C.29), this result leads directly to the vibrational energy levels, quantised by the vibrational quantum number, v :

$$E(v) = \left(v + \frac{1}{2}\right) \hbar\omega \quad v = 0, 1, 2, 3, \dots \quad (\text{C.39})$$

Expressed in units of wavenumber, the energy levels are given by:

$$G(v) = \frac{E(v)}{hc} = \omega_e \left(v + \frac{1}{2}\right) \quad \omega_e = \frac{\omega}{2\pi c} \quad v = 0, 1, 2, 3, \dots \quad (\text{C.40})$$

where ω_e is the fundamental vibrational constant. It can be seen from Equation C.39 that unlike the rotational energy levels, the vibrational energy levels are spaced equally, with an energy difference of $\hbar\omega$ between adjacent levels. This is shown in Figure C.6.

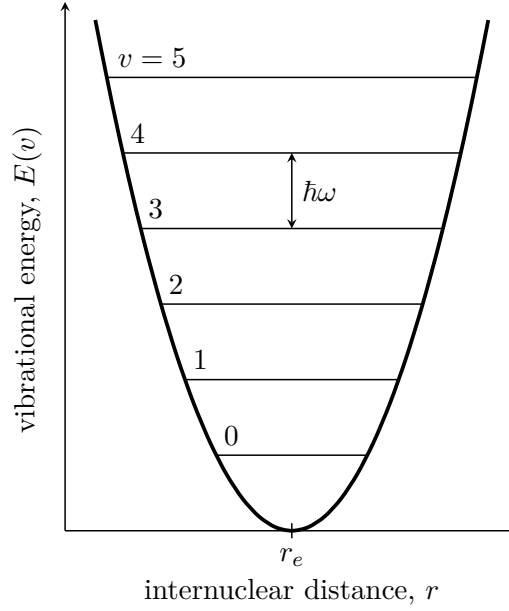


Figure C.6: Illustration of the first six vibrational energy levels of a diatomic molecule, assuming a parabolic potential. Adjacent energy levels have a constant energy separation of $\hbar\omega$.

C.4 Anharmonicity and the Morse Potential

The above treatment of a diatomic molecule as a harmonic oscillator is sufficient for low vibrational levels. But the true potential of a diatomic molecule exhibits anharmonicity, which needs to be taken into account to accurately model higher vibrational energy levels. This can be done by adding cubic and higher order terms to the quadratic potential of the one-body oscillator:

$$V(r) = \frac{1}{2}k(r - r_e)^2 - \frac{1}{2}g(r - r_e)^3 + \mathcal{O}(r^4) \quad (\text{C.41})$$

If this is used as the potential in the Schrödinger equation (Equation C.28), then the vibrational energy levels, in units of wavenumbers, are given by:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \mathcal{O}(v^4) \quad (\text{C.42})$$

where $\omega_e x_e$ and $\omega_e y_e$ are the respective vibrational constants of second and third order in v . A particularly useful anharmonic potential is the so-called *Morse potential*:

$$V_{\text{Morse}}(r) = D_e \left[1 - e^{-a(r-r_e)} \right]^2 \quad (\text{C.43})$$

If this is used as the potential in the Schrödinger equation, the solution is:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \quad (\text{C.44})$$

This is the same as the solution to a generic anharmonic potential (Equation C.41), truncated at the term that is quadratic in v . The second order vibrational constant, $\omega_e x_e$, is defined as:

$$\omega_e x_e = \frac{\hbar \omega^2}{8\pi c D_e} = \omega_e^2 \frac{hc}{4D_e} \quad (\text{C.45})$$

with D_e being the binding energy of the molecule. In this anharmonic approximation, the separation of the vibrational energy levels is not constant anymore, but decreases with increasing v , as is shown schematically in Figure C.7.

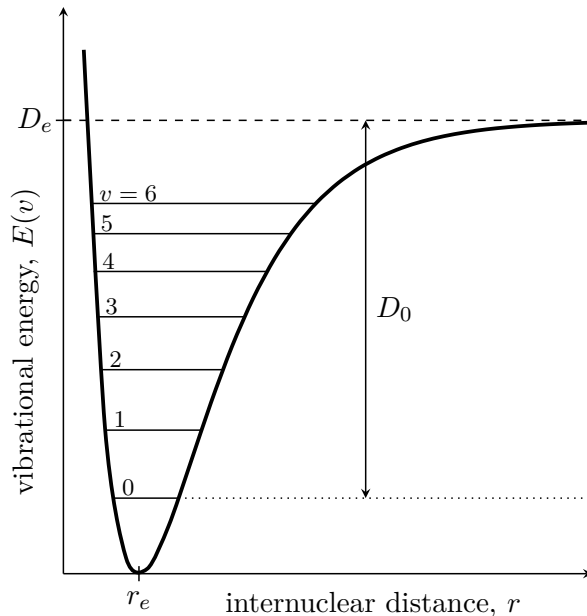


Figure C.7: Illustration of the first seven vibrational energy levels of a diatomic molecule, assuming an anharmonic Morse potential. Adjacent energy levels have a decreasing energy separation with increasing v . D_0 and D_e are the dissociation and binding energies of the molecule, respectively.

C.5 Interaction of Vibration and Rotation

The above treatment of a diatomic molecule has produced equations to calculate the energies of rotational and vibrational levels. However, it has completely neglected the fact that rotations and vibrations occur at the same time, i.e. as the molecule rotates it vibrates as well, and thus there is an interaction between the two. Typically, a molecule undergoes several vibrations (about 5-100) during a single rotation [59]. This is also the reason why the above treatment of rotations and vibrations independent of each other is valid up to a certain degree of accuracy. It is called the Born-Oppenheimer approximation, which allows the total energy of vibration and rotation to be expressed as the simple sum of the energies of these two different types of motion. But in order

to obtain more realistic energy levels, the interaction between rotations and vibrations needs to be accounted for.

As the molecule vibrates, its internuclear separation varies with a period equal to the period of vibration. The expectation (average) value of the internuclear separation, r , can be found using quantum mechanics:

$$\langle r \rangle = \langle \Psi_{vib} | r | \Psi_{vib} \rangle \quad (\text{C.46})$$

where Ψ_{vib} is the vibrational wavefunction. Similarly, the expectation value of $1/r^2$ is given by:

$$\left\langle \frac{1}{r^2} \right\rangle = \left\langle \Psi_{vib} \left| \frac{1}{r^2} \right| \Psi_{vib} \right\rangle \quad (\text{C.47})$$

This means that the equilibrium rotational constant is not constant, but instead depends on the vibrational level, such that B_e is modified as:

$$B_e = \frac{\hbar}{4\pi c \mu r_e^2} \quad \rightarrow \quad B_v = \frac{\hbar}{4\pi c \mu} \left\langle \Psi_{vib} \left| \frac{1}{r^2} \right| \Psi_{vib} \right\rangle \quad (\text{C.48})$$

Finding the expectation value of $1/r^2$ for a generic anharmonic potential results in the following expression for the rotational constant:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 + \mathcal{O}(v^3) \quad (\text{C.49})$$

Similarly, the equilibrium centrifugal constant, D_e , becomes:

$$D_e = \frac{\hbar^3}{2\pi c k \mu^2 r_e^6} \quad \rightarrow \quad D_v = \frac{\hbar^3}{2\pi c k \mu^2} \left\langle \Psi_{vib} \left| \frac{1}{r^6} \right| \Psi_{vib} \right\rangle$$

$$D_v = D_e + \beta_e \left(v + \frac{1}{2} \right) + \delta_e \left(v + \frac{1}{2} \right)^2 + \mathcal{O}(v^3) \quad (\text{C.50})$$

where α_e , β_e , γ_e and δ_e are the rotational-vibrational interaction constants. If a Morse potential is assumed, the result is the same, truncated at order v :

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) \quad D_v = D_e + \beta_e \left(v + \frac{1}{2} \right) \quad (\text{C.51})$$

C.6 Rotational-Vibrational Energy Levels

By combining all of the above results, an equation for the energy levels of a diatomic molecule can be found, that includes centrifugal distortion, anharmonicity

and vibrational-rotational interaction:

$$\begin{aligned}
T(v, J) &= T_e + G(v) + F(J) \\
&= T_e + \left[\omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \mathcal{O}(v^4) \right] \\
&\quad + \left[B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 - \mathcal{O}(J^4) \right] \quad (\text{C.52})
\end{aligned}$$

Assuming a Morse potential and truncating the centrifugal distortion correction at order J^2 , this is reduced to:

$$T(v, J) = T_e + \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 \quad (\text{C.53})$$

The definitions of the various rotational and vibrational constants are summarised below:

$$\begin{aligned}
\omega_e &= \frac{\omega}{2\pi c} & \omega_e x_e &= \frac{\hbar \omega^2}{8\pi c D_e} \\
B_v &= B_e - \alpha_e \left(v + \frac{1}{2} \right) & D_v &= D_e + \beta_e \left(v + \frac{1}{2} \right) \\
B_e &= \frac{\hbar}{4\pi c \mu r_e^2} & D_e &= \frac{\hbar^3}{2\pi c k \mu^2 r_e^6} \quad (\text{C.54})
\end{aligned}$$

Equations C.53 and C.54 can be used to calculate the ro-vibrational energy levels of a diatomic molecule with high accuracy.

Appendix D

MATLAB Code

This appendix contains the complete *Edinburgh CARS Code*, including all required subcodes. The code works as explained in Chapter 3. No further explanation of this computational model will be given here, but the code itself contains a lot of annotation that should make it easy to use and navigate.

The code is implemented in 64-bit MATLAB R2016a (9.0.0.370719) for Windows (win64). It requires the *optimization toolbox* to execute.

If measured linewidths are to be used (for N₂ only), a text file containing the measured linewidths of the first 42 rotational transitions of N₂ for temperatures ranging from 300 K to 1400 K in steps of 100 K needs to be loaded in the *Linewidths_N2* code. These linewidths are the ones reported by Kliwer *et al.* and can be found in Table 2 of the paper *Time-domain measurements of S-branch N₂-N₂ Raman linewidths using picosecond pure rotational coherent anti-Stokes Raman spectroscopy* [61].

For fitting experimental spectra, four text files need to be loaded into the *Edinburgh_CARS_Code*:

- A *CARS_spec* column matrix that holds the background subtracted and normalised experimental CARS spectrum to be fitted.
- An *exp_wn_axis* column matrix that holds the experimental wavenumber axis (wavenumber corresponding to each pixel of the CARS spectrum to be fitted, as found from the wavenumber axis calibration).
- An *NR_spec* column matrix that holds the background subtracted and normalised NR argon CARS spectrum corresponding to the experimental CARS spectrum to be fitted. This is used for the pump/Stokes excitation bandwidth correction.
- A *x_corr* column matrix that holds the parameters of the two-Gaussian probe beam to be used in the fit. These parameters are: $\Delta\tau$, τ_{gauss} , f , A , τ_{chirp} , $\Delta\tau_{chirp}$ and A_{chirp} , as defined by equation 3.19.

D.1 Edinburgh_CARS_Code

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Edinburgh_CARS_Code by Torge Mecker
%
% Version 1.1 (January 2020)
%
% Matlab code that can simulate hybrid rotational fs/ps S-branch CARS
% spectra of either N2, O2 or N2/O2 mixtures (air) and fit them to
% experimental CARS spectra using the lsqcurvefit algorithm.
%
% Acknowledgements:
% This code is partially based on a CARS code by Dr. Christopher J. Klierer
% from the Sandia National Laboratories in Livermore, CA. Parts of this
% code and its sub-routines were written by Dr. Trevor L. Courtney, also
% from the Sandia National Laboratories in Livermore, CA.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Clear the workspace and close all open figures
clear variables
close all

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Simulation and Fitting Parameters:
% Adjust as required for model/fit
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Molecule=1; % 1=N2, 2=O2, 3=air;
Linewidths=2; % 1=MEG model, 2=measured linewidths (for N2 only)
Gauss=2; % 1=single Gaussian probe shape, 2=double Gaussian probe shape

% Set variable model parameters in the format:
% [initial value, lower bound, upper bound, 0 or 1]
% where 0 means the parameter stays fixed at its initial value throughout
% the fit and 1 means it is allowed to float between its lower and upper
% bounds
T=[293.0, 200.0, 400.0, 1]; % temperature [K]
P=[ 1.0, 0.1, 2.0, 0]; % pressure [atm]
probe_delay=[ 8.4, 7.4, 9.4, 1]; % probe pulse delay [ps]
probe_width=[ 5.0, 4.0, 6.0, 0]; % probe pulse width [ps]
chirp=[ -0.7, -2.0, 0.0, 1]; % chirp (dimensionless)
ratio=[ 0.268247, 0.2, 0.3, 0]; % O2/N2 mole ratio
slit=[ 1.5, 1.0, 2.0, 0]; % slit function width [cm-1]
```

```

% Set variable experimental parameters in the format:
% [initial value, lower bound, upper bound, 0 or 1]
% where 0 means the parameter stays fixed at its initial value throughout
% the fit and 1 means it is allowed to float between its lower and upper
% bounds
% Gradient = experimental wavelength axis gradient [nm/pixel]
% Intercept = experimental wavelength axis intercept [nm]
% rel_height = height of modelled spectrum relative to experimental spectrum
gradient= [ -0.009560,    -0.009581,    -0.009539,    1];
intercept= [396.2761,      396.2308,      396.3214,      1];
rel_height=[ 1.0,          0.95,          1.05,          1];

time_beg=0; % start time of time axis [s]
time_end=100*1e-12; % end time of time axis [s]
dt=5*1e-15; % time steps of time axis [s]

probe_wl=396.5; % central wavelength of the probe pulse [nm]
v=2; % number of vibrational levels to be included in the model
J=90; % number of rotational levels to be included in the model

pixel=1000; % number of pixels of the experimental spectrum
min_px=35; % first pixel to be included in the fit
max_px=520; % last pixel to be included in the fit

% Set the title for the output figure
Title='<Insert Figure Title>';

% Decide if the model/best fit spectrum is to be saved in a text file
save=1; % 0=don't save, 1=save

% Path of file with model/best fit spectrum results
path='<Insert File Path>';

% Name of file with model/best fit spectrum results
filename='<Insert File Name>';

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Experimental Data for Fitting Routine:
% Adjust as required for model/fit
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Load the experimental CARS spectrum (this is a column array containing
% the experimental CARS spectrum intensity at each pixel)
CARS_spec=load('<Insert File Location>');

```

```

% Load the experimental wavenumber axis (this is a column array containing
% the wavenumber corresponding to each pixel of the experimental CARS
% spectrum
exp_wn_axis=load('<Insert File Location>');

% Load the corresponding nonresonant Argon spectrum (this is a column array
% containing the experimental nonresonant argon spectrum intensity at each
% pixel)
NR_spec=load('<Insert File Location>');

% Load the cross correlation parameters (for a double Gaussian probe pulse)
% (this is a column array containing the width of the first Gaussian, the
% delay, width and height of the second Gaussian relative to the first and
% the delay, width and height of the chirp term relative to the first
% Gaussian)
x_corr=load('<Insert File Location>');

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Model and fitting Routine:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create an array containing the initial model parameters
float_input=[T(1),P(1),probe_delay(1)*1e-12,probe_width(1)*1e-12,...
    chirp(1),ratio(1),slit(1),gradient(1),intercept(1),rel_height(1)];

% Create an array containing the initial lower bound values of the model
% parameters
initial_lb=[T(2),P(2),probe_delay(2)*1e-12,probe_width(2)*1e-12,...
    chirp(2),ratio(2),slit(2),gradient(2),intercept(2),rel_height(2)];

% Create an array containing the initial upper bound values of the model
% parameters
initial_ub=[T(3),P(3),probe_delay(3)*1e-12,probe_width(3)*1e-12,...
    chirp(3),ratio(3),slit(3),gradient(3),intercept(3),rel_height(3)];

% Create an array containing the Boolean parameters that decide if a
% variable is fixed or floating
boolean_input=[T(4),P(4),probe_delay(4),probe_width(4),chirp(4),...
    ratio(4),slit(4),gradient(4),intercept(4),rel_height(4)];

% Create an array containing the names of the initial model parameters
float_names='temperature','pressure','probe delay','probe width',...
    'chirp','N2/O2 ratio','slit width','gradient','intercept',...
    'relative height';

% Create an array containing the units of the initial model parameters
float_units='K','atm','ps','ps','','','cm-1','nm/pixel','nm','';

```

```

% Create an array containing the parameters that are always fixed
fix_input=[Molecule,Linewidths,Gauss,time_beg,time_end,dt,probe_wl,v,J,...
    pixel,min_px,max_px];

% Cut the experimental CARS spectrum, wavenumber axis and nonresonant argon
% spectrum between px_min and px_max
CARS_spec=CARS_spec(min_px:max_px);
exp_wn_axis=exp_wn_axis(min_px:max_px)';
NR_spec=NR_spec(min_px:max_px);

% Divide the experimental CARS spectrum by the nonresonant spectrum to
% account for the pump/Stokes excitation efficiency (add 1e^-5 to avoid
% division by 0)
CARS_spec=CARS_spec./(NR_spec+1e-5);

% Normalise the experimental CARS spectrum
CARS_exp_spectrum=CARS_spec/max(CARS_spec);

if sum(boolean_input)==0 % if all model parameters are fixed

    x=[]; % create an empty matrix

    % Get the model spectrum and wavenumber axis from the CARS_Model code
    [ , model_wn_axis, CARS_model_spectrum] = ...
        CARS_Model(fix_input, float_input, boolean_input, x, x_corr);

    % Find the index of the first and last value of the modelled CARS
    % spectrum that is greater than 10^-3 (0.1% of the maximum value)
    min_wn=find(CARS_model_spectrum>1e-3,1,'first');
    max_wn=find(CARS_model_spectrum>1e-3,1,'last');

    % Truncate modelled CARS spectrum and wavenumber axis between min_wn
    % and max_wn
    CARS_model_spectrum=CARS_model_spectrum(min_wn:max_wn);
    model_wn_axis=model_wn_axis(min_wn:max_wn)';

    % Plot the modelled CARS spectrum
    figure('DefaultAxesFontSize',14)

    plot(model_wn_axis,CARS_model_spectrum,'color',[1,0,0],'LineWidth',1)
    axis([model_wn_axis(1),model_wn_axis(end),0,max(CARS_model_spectrum)])

    title(Title)
    set(gca,'TickDir','in')
    set(gca,'TickLength',[0.02,0.02])
    set(gca,'XTick',0:50:model_wn_axis(end))
    set(gca,'YTick',[0,0.25,0.5,0.75,1.0])
    ylabel('normalised intensity')
    xlabel('wavenumber (cm^-1)')

```

```

% Save the modelled CARS spectrum and corresponding wavenumber axis
if save==1 % save only if save=1

    file=[path filesep filename '.txt']; % file path and name

    fid=fopen(file,'wt'); % open a text file to write the data to

    for i=1:size(model_wn_axis, 1) % for all data points

        % Print the data to the text file
        fprintf(fid,'%8.4f    %6.4f\n',model_wn_axis(i,:),...
            CARS_model_spectrum(i,:));
    end

    fclose(fid); % close the text file
end

else % if at least one parameter is floating (to be optimised in a fit)

    % Create zero arrays to hold the initial model parameters and
    % corresponding lower and upper bounds:
    x0=zeros(1,sum(boolean_input));
    lb=zeros(1,sum(boolean_input));
    ub=zeros(1,sum(boolean_input));

    % Create empty string arrays to hold the names and units of the
    % floating parameters
    names= repmat("",1,sum(boolean_input));
    units= repmat("",1,sum(boolean_input));

    for i=1:length(boolean_input) % for each variable model parameter

        if boolean_input(i)==1 % if the parameter is allowed to float

            % Input the initial parameter value into the x0 array
            x0(sum(boolean_input(1:i)))=float_input(i);

            % Input the lower bound into the lb array
            lb(sum(boolean_input(1:i)))=initial_lb(i);

            % Input the upper bound into the lb array
            ub(sum(boolean_input(1:i)))=initial_ub(i);

            % Input the parameter name into the names array
            namesum(boolean_input(1:i))=float_namesi;

```

```

        % Input the parameter unit into the units array
        unitssum(boolean_input(1:i))=float_unitsi;
    end
end

% Create a function for the lsqcurvefit algorithm
fun=@(x,xdata)CARS_Model(fix_input,float_input,boolean_input,x,x_corr);

% Run the lsqcurvefit fitting algorithm
x=lsqcurvefit(fun,x0,exp_wn_axis,CARS_exp_spectrum,lb,ub);

% Run the CARS_Model code with the best fit parameters
[CARS_interp, model_wn_axis, CARS_model_spectrum] = ...
    CARS_Model(fix_input, float_input, boolean_input, x, x_corr);

% Calculate the squared residuals at each pixel
sq_resid=(CARS_interp-CARS_exp_spectrum).^2;

% Sum of all squared residuals at each pixel
sum_sq_resid=sum(sq_resid);

% Print the best fit parameters to the terminal
fprintf('Best Fit Parameters: \n\n')

for i=1:1:sum(boolean_input) % for each floating parameter

    % If the name of the parameter is "probe delay" or "probe width"
    if strcmp(names(i),'probe delay') || strcmp(names(i),'probe width')

        x(i)=x(i)*1e12; % multiply by 10^12 to change s to ps
    end

    % Get the number of characters of the longest phrase in the names
    % array
    X=max(cellfun('length',names(1,:)));

    % Specify the format of printing the best fit parameters to the
    % terminal
    formatSpec='%*s    %9.4f %s \n';

    % Print best fit parameters to the terminal
    fprintf(formatSpec,X,namesi,x(i),unitsi)
end

% Print the sum of all squared residuals to the terminal
fprintf('\n %s    %3.4f \n', 'Sum of Squared Residuals:',sum_sq_resid)

```

```

% Find the index of the first and last value of the interpolated
% modelled CARS spectrum that is greater than 10^-3 (0.1% of the
% maximum value)
min_wn=find(CARS_interp>1e-3,1,'first');
max_wn=find(CARS_interp>1e-3,1,'last');

% Truncate the interpolated modelled CARS spectrum, the experimental
% CARS spectrum, the squared residuals and the experimental wavenumber
% axis between min_wn and max_wn
CARS_interp=CARS_interp(min_wn:max_wn);
CARS_exp_spectrum=CARS_exp_spectrum(min_wn:max_wn);
sq_resid=sq_resid(min_wn:max_wn);
exp_wn_axis=exp_wn_axis(min_wn:max_wn)';

% Plot best fit model CARS spectrum overlaid with the experimental CARS
% spectrum and separately the squared residuals
figure('DefaultAxesFontSize',14)

A(1)=subplot(2,1,1);
plot(exp_wn_axis,CARS_exp_spectrum,'color',[0,0,1],'LineWidth',1)
axis([exp_wn_axis(1),exp_wn_axis(end),0,max(CARS_interp)])
hold on
plot(exp_wn_axis,CARS_interp,'color',[1,0,0],'LineWidth',1)
legend('experiment','model')
legend('boxoff')
hold off

set(gca,'TickDir','in');
set(gca,'TickLength',[0.02,0.02])
set(gca,'XTick',0:50:exp_wn_axis(end))
set(gca,'YTick',[0,0.25,0.5,0.75,1.0])
set(gca,'XTickLabel','')
ylabel('normalised intensity')

A(2)=subplot(2,1,2);
plot(exp_wn_axis,sq_resid,'color',[0,0.8,0.2],'LineWidth',1)
axis([exp_wn_axis(1),exp_wn_axis(end),0,max(sq_resid)])

set(gca,'TickDir','in');
set(gca,'TickLength',[0.02,0.02])
set(gca,'XTick',0:50:exp_wn_axis(end))
set(gca,'YTick',0.0:0.5*round(max(sq_resid),1,'significant'):...
    max(sq_resid))
ax=gca;
ax.YRuler.Exponent=0;
xlabel('wavenumber (cm^-1)')
ylabel('residual^2')

```

```

set(subplot(2,1,2),'position',[0.15,0.2,0.75,0.15])
set(subplot(2,1,1),'position',[0.15,0.4,0.75,0.5])

axes('Visible','off')

text(0.5,1.07,sprintf('%s',Title),'HorizontalAlignment','center',...
    'VerticalAlignment','top','FontSize',14,'FontWeight','bold')

% Save the modelled best fit CARS spectrum, the experimental CARS
% spectrum and the corresponding wavenumber axis
if save==1 % save only if save=1

    file=[path filesep filename '.txt']; % file path and name

    fid=fopen(file,'wt'); % open a text file to write the data to

    for i=1:size(exp_wn_axis, 1) % for all data points

        % Print the data to the text file
        fprintf(fid,'%8.4f %6.4f %6.4f\n',exp_wn_axis(i,:),...
            CARS_exp_spectrum(i,:),CARS_interp(i,:));
    end

    fclose(fid); % close the text file
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.2 CARS_Model

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% CARS_Model Code by Torge Mecker
%
% Matlab code that simulates hybrid rotational fs/ps S-branch CARS spectra
% of either N2, O2 or N2/O2 mixtures (air).
%
% Input:
% fix_input:      array holding model parameters that are always fixed (e.g.
%                 the number of rotational levels to be included in the
%                 model)
% float_input:    array holding the model parameters that can be varied if
%                 real spectra are being fit (e.g. the temperature)
% boolean_input:  array holding ones and zeros, zeros meaning the
%                 corresponding parameter (in the float_input array) is
%                 fixed during a fitting routine and ones meaning that the
%                 corresponding parameter is allowed to float
% x:              array holding the model parameters that are varied during
%                 a fitting routine
% x_corr:         array holding the probe beam shape to be used based on a
%                 measured cross correlation (for the cases when a
%                 two-Gaussian probe shape is required)
%
% Output:
% CARS_interp:    array holding the modelled frequency domain CARS spectrum
%                 that has been interpolated onto the experimental
%                 wavenumber axis
% model_wn_axis:  array holding the wavenumber axis of the modelled
%                 frequency domain CARS spectrum
% CARS_model:     array holding the modelled frequency domain CARS spectrum
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called CARS_Model
function [CARS_interp, model_wn_axis, CARS_model_spectrum] = ...
    CARS_Model (fix_input, float_input, boolean_input, x, x_corr)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Model Parameters and Constants:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Define the fixed model parameters:
Molecule=fix_input(1); % 1=N2, 2=O2, 3=N2/O2 (air)
Linewidths=fix_input(2); % 1=MEG, 2=measured linewidths (for N2 only)
Gauss=fix_input(3); % 1=single Gaussian probe, 2=double Gaussian probe
time_beg=fix_input(4); % start time of the time axis [s]
```

```

time_end=fix_input(5); % end time of the time axis [s]
dt=fix_input(6); % time steps of the time axis [s]
probe_wl=fix_input(7); % central wavelength of the probe pulse [nm]
vib_levels=0:1:fix_input(8)-1; % vibrational levels
rot_levels=0:1:fix_input(9)-1; % rotational levels
pixel=fix_input(10); % number of pixels of the exp. spectrum to be fit
start_px=fix_input(11); % first pixel of the exp. spectrum to be included
end_px=fix_input(12); % last pixel of the exp. spectrum to be included

% Define a time axis from time_beg to time_end in steps of dt
time=time_beg:dt:time_end;

% Create a zero matrix to hold the floating parameters
float_parameters=zeros(1,length(boolean_input));

for i=1:1:length(boolean_input) % for each floating parameter

    % If the parameter is varied in the lsqcurvefit fitting routine
    if boolean_input(i)==1

        % Take the parameter from the x array and input it to the
        % float_parameters array
        float_para=@(x)x(sum(boolean_input(1:i-1))+1);
        float_parameters(i)=float_para(x);

    % If the parameter is kept constant throughout the fitting routine
    elseif boolean_input(i)==0

        % Take the parameter from the float_input array and input it to
        % the float_parameters array
        float_parameters(i)=float_input(i);
    end
end

% Define the floating model parameters:
T=float_parameters(1); % temperature [K]
P=float_parameters(2); % pressure [atm]
probe_delay=float_parameters(3); % probe pulse time delay [s]
probe_w=float_parameters(4); % probe pulse width (FWHM) [s]
chirp=float_parameters(5); % chirp parameter (dimensionless)
ratio=float_parameters(6); % ratio of O2/N2 mole fractions (dimensionless)
slit_width=float_parameters(7); % width of slit [cm-1]
gradient=float_parameters(8); % exp. wavenumber axis gradient [nm/pixel]
intercept=float_parameters(9); % exp. wavenumber axis intercept [nm]
rel_height=float_parameters(10); % relative height of spectrum

```

```

% Calculate the mole fractions of O2 and N2 (for reference: in air the
% mole fractions are 0.21151 and 0.78849 for O2 and N2 respectively,
% assuming atmospheric composition and scaled up to make 100%)
mol_frac_N2=1/(1+ratio);
mol_frac_O2=1-mol_frac_N2;

% Define constants
% NOTE: 1eV = 8065.543724cm-1 and hbar=h/2pi
c=29979245800; % speed of light [cm/s]
hbar=3.33564084e-11/(2*pi); % reduced Planck constant [cm-1*s]

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular Response Function:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Get the appropriate molecular response function (N2, O2 or air) from
% the corresponding Molecular_Response code
switch Molecule

    case 1 % N2

        % Get the N2 molecular response from the Molecular_Response_N2 code
        mol_response = ...
            Molecular_Response_N2(time, T, P, Linewidths, vib_levels,...
            rot_levels);

    case 2 % O2

        % Get the O2 molecular response from the Molecular_Response_O2 code
        mol_response = ...
            Molecular_Response_O2(time, T, P, vib_levels, rot_levels);

    case 3 % air

        % Get the N2 and O2 molecular responses from the
        % Molecular_Response_N2 and Molecular_Response_O2 codes
        % respectively and sum according to the mole fractions
        mol_response = ...
            mol_frac_N2*Molecular_Response_N2(time, T, P, Linewidths,...
            vib_levels, rot_levels) ...
            +mol_frac_O2*Molecular_Response_O2N2(time, T, P,...
            vib_levels, rot_levels, mol_frac_N2, mol_frac_O2);

end

```

```

%%%%%%%%%%%%
% Probe Beam:
%%%%%%%%%%%%

% Create the probe beam including a linear chirp contribution by either
% using a single or a double Gaussian probe pulse shape
switch Gauss

    case 1 % single Gaussian probe beam

        probe_width=probe_w; % width of probe beam (FWHM)

        % Calculate the probe pulse based on a single Gaussian
        probe_shape=exp(-2*log(2)*(((time-probe_delay)/probe_width).^2));

        % Calculate the linear chirp factor
        probe_chirp=exp(-1i*2*log(2)*chirp*...
            (((time-probe_delay)/probe_width).^2));

    case 2 % double Gaussian probe beam

        probe_width=x_corr(1,1); % width of 1st Gaussian (FWHM)
        Gauss_delay=x_corr(2,1); % delay of 2nd Gaussian relative to 1st
        Gauss_width=x_corr(3,1); % width of 2nd Gaussian relative to 1st
        Gauss_height=x_corr(4,1); % height of 2nd Gaussian relative to 1st
        chirp_delay=x_corr(5,1); % delay of chirp rel. to 1st Gaussian
        chirp_width=x_corr(6,1); % width of chirp
        chirp_height=x_corr(7,1); % height of chirp rel. to 1st Gaussian

        % Calculate the probe pulse based on a double Gaussian fit of
        % experimental cross correlation data
        probe_shape=exp(-2*log(2)*(((time-probe_delay)/probe_width).^2))...
            +Gauss_height*exp(-2*log(2)*(((time-probe_delay+Gauss_delay)...
            /(Gauss_width*probe_width)).^2));

        % Calculate the linear chirp factor
        probe_chirp=chirp_height*exp(-1i*2*(log(2))*chirp*...
            (((time-probe_delay+chirp_delay)/chirp_width).^2));
end

% Calculate the total electric field
probe_field=probe_shape'.*probe_chirp'; % transpose to a column matrix

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% 3rd Order Polarisation and CARS Signal:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the exponential term
exp_term=exp(-1i*2*pi*(time'-probe_delay));

% Calculate the time domain CARS signal
CARS_time_domain=((-1i/hbar)^3)*probe_field.*mol_response.*exp_term;

% Calculate the frequency domain CARS signal
CARS_freq_domain=(abs(fft(CARS_time_domain))).^2;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Wavenumber Axis
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

L=length(time); % number of time axis points

% Calculate the frequency axis in Hz
% NOTE: need to account for even/odd number of time axis points and use
% only half the frequency axis (see MATLAB fft function for details)
freq_axis=(0:((L+mod(L,2))/2)-1)/time_end; % time_end=L*dt if time_beg=0

% Change the frequency axis in Hz to frequency axis in cm-1
wn_axis=freq_axis/c;

% Take only first half of the frequency domain CARS signal
CARS_freq_domain=CARS_freq_domain(1:length(wn_axis));

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Slit Function
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Introduce an arbitrary wavenumber shift (arbitrarily chosen to be 10%
% of the largest wavenumber of the wavenumber axis)
shift=wn_axis(end)*0.1;

% Create a Gaussian slit function (FWHM=slit_width) centred at the shift
slit_function=exp(-(2*sqrt(log(2))*((wn_axis-shift)/slit_width)).^2);

% Convolve the slit function with the CARS spectrum
CARS_model_spectrum=conv(slit_function,CARS_freq_domain);

% Normalise the modelled CARS spectrum
CARS_model_spectrum=CARS_model_spectrum/max(CARS_model_spectrum);

```

```

% Find the wavenumber axis step size
step=mean(diff(wn_axis));

% Calculate the indices of the wavenumber axis, adjusted for the shift
index_wn=round((wn_axis-0.5*shift)/step);

% Calculate the new wavenumber axis, adjusted for the convolution
model_wn_axis=(2*index_wn(1):2*index_wn(end))*step;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Interpolation onto the Experimental Wavenumber Axis:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the probe beam wavenumber (convert from nm to cm-1)
probe_wn=1/(probe_wl*1e-7);

% Calculate the experimental pixel axis
pixel_axis=1:1:pixel;

% Calculate the experimental wavelength axis based on a linear fit of
% experimental CARS peaks on the pixel axis to their theoretical position
% in wavelength
wl_axis=gradient.*pixel_axis+intercept; % y=mx+c

% Calculate the experimental wavenumber axis and subtracting the probe beam
% wavenumber
exp_wn_axis=1./(wl_axis'*1e-7)-probe_wn;

% Interpolate the modelled CARS spectrum onto the experimental wavenumber
% axis
CARS_interp=spline(model_wn_axis,CARS_model_spectrum,exp_wn_axis);

% Truncate the interpolated CARS model spectrum between start_px and end_px
CARS_interp=CARS_interp(start_px:end_px);

% Normalise the interpolated CARS model spectrum
CARS_interp=CARS_interp/max(CARS_interp);

% Multiply the interpolated CARS model spectrum by a factor to account for
% a possible offset in the maximum peak height of the experimental spectrum
CARS_interp=CARS_interp*rel_height;

end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% END %%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

D.3 Molecular_Response_N2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular_Response_N2 Code by Torge Mecker
%
% Matlab code that computes the time domain third order molecular
% response function of N2, based on the Boltzmann population distribution
% and taking into account the polarisation anisotropy, the Herman-Wallis
% factor and the Placzek-Teller coefficient.
%
% Input:
% time:      array holding the time axis at which the molecular response
%            is to be calculated
% T:         temperature [K]
% P:         pressure [atm] (to be passed to the Linewidths_N2 code)
% linewidths: logic value that decides if to use experimentally measured
%            linewidths or the MEG model (to be passed to the
%            Linewidths_N2 code)
% vib_levels: number of vibrational levels to be included in the model (to
%            be passed to the Energy_Levels_N2 code)
% rot_levels: number of rotational levels to be included in the model (to
%            be passed to the Energy_Levels_N2 code)
%
% Output:
% mol_response_N2: array containing the time domain third order molecular
%                 response function of N2 at each time step (as defined by
%                 the time axis)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Molecular_Response_N2
function [mol_response_N2] = ...
    Molecular_Response_N2(time, T, P, linewidths, vib_levels, rot_levels)

% Get lw_N2, v, J, FJ and eJ from Linewidths_N2 code
[lw_N2, v, J, FJ, eJ] = ...
    Linewidths_N2(T, P, linewidths, vib_levels, rot_levels);

% Define constants for N2
% NOTE: 1eV = 8065.543724cm-1 and hbar=h/2pi
hbar=3.33564084e-11/(2*pi); % reduced Planck constant [cm-1*s]
kb=0.6950345432; % Boltzmann constant [cm-1/K]
```

```

% [R. E. Palmer, The carsft computer code calculating coherent anti-Stokes
% Raman spectra: User and programmer information, No. SAND-89-8206, Sandia
% National Laboratories, Livermore, CA (1989).]
we=2358.518; % first order vibrational constant [cm-1]
Be=1.99826; % equilibrium rotational constant [cm-1]
alpha=1.73035e-2; % rotational-vibrational interaction constant [cm-1]

% [C. Asawaroengchai et al. J. Chem. Phys. 72, 2664-2669 (1980).]
re=1.098e-8; % equilibrium internuclear distance [cm]
beta_e1=6.91e-25; % equilibrium polarisation anisotropy [cm^3]
beta_e2=1.4e-16; % first derivative of the polarisation anisotropy wrt to
% internuclear distance [cm^2]

% [A. Bohlin et al. J. Raman Spectrosc. 42, 1843-1847 (2011)]
p1p0=3.168; % ratio between the first two coefficients of the
% anisotropic polarisability expansion

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Polarisation Anisotropy, H.-W. Factor and P.-T. Coefficients:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the polarisation anisotropy
% [M. C. Drake. Opt. Lett. 7, 440-441 (1982)]
Gamma=beta_e1+beta_e2*re*(((3*Be)/we)+(alpha/(2*Be)))*(v+0.5);

% Calculate the Herman-Wallis factor based on Tipping and Ogilvie
% [R. H. Tipping et al. J. Raman Spectrosc. 15, 38-40 (1984).]
kappa=2*(Be/we);
HWF=(1+p1p0*kappa^2*(J.^2+3*J+3)).^2;

% Calculate the Placzek-Teller coefficient for S-branch transitions
PTC=(3*(J+1).*(J+2))./(2*(2*J+1).*(2*J+3));

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Boltzmann Population Distribution:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the Boltzmann population difference for each J->J+2 transition,
% including a (2J+1) spin degeneracy factor
Pdiff=(2*J(:,1:end-2)+1)...
.*(exp(-FJ(:,1:end-2)/(kb*T))-exp(-FJ(:,3:end)/(kb*T)));

ge=6; % rotational nuclear degeneracy for even J
go=3; % rotational nuclear degeneracy for odd J

```

```

if rem(J(end),2)==0 % if last J even
    Pdiff(:,1:2:end)=Pdiff(:,1:2:end)*ge; % multiply all even J by 6
    Pdiff(:,2:2:end-1)=Pdiff(:,2:2:end-1)*go; % multiply all odd J by 3

else % if last J odd
    Pdiff(:,1:2:end-1)=Pdiff(:,1:2:end-1)*ge; % multiply all even J by 6
    Pdiff(:,2:2:end)=Pdiff(:,2:2:end)*go; % multiply all odd J by 3
end

% Calculate the partition function (total sum of population in all
% ro-vibrational states
Psum=sum(sum(Pdiff));

% Calculate the relative Boltzmann population difference by dividing by
% the partition function
Pdiff=Pdiff/Psum;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular Response Function:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Select transition frequencies (eJ) of transitions for which linewidths
% have been calculated
EJ=eJ(:,1:size(lw_N2,2));

% Create a zero matrix to hold the exponential factor of the molecular
% response (at each time step, rotational and vibrational level)
exp_factors_N2=zeros(size(EJ,1)*size(time',1),size(EJ,2));

for k=1:size(EJ,1) % for each vibrational level

    % Calculate the exponential factor of the molecular response at each
    % time step, each vibrational level and each rotational level and input
    % this in every kth row of exp_factors_N2
    exp_factors_N2(k:size(EJ,1):end,:)=...
        exp(time'*(1i*EJ(k,:)-lw_N2(k,:)/2)/hbar);
end

for k=1:size(exp_factors_N2,1)/size(EJ,1) % for each time step

    % Calculate the molecular response function at each time step, each
    % vibrational level and each rotational level
    exp_factors_N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:)= ...
        (4/45)*Gamma(:,1:length(EJ)).^2.*HWF(:,1:length(EJ))...
        .*PTC(:,1:length(EJ)).*Pdiff(:,1:length(EJ))...
        .*exp_factors_N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:);
end

```

```

% Calculate the molecular response function at each time step and each
% vibrational level
mol_resp_N2=sum(exp_factors_N2,2); % sum of columns (rotational levels)

% Create a zero matrix to hold the overall molecular response function at
% each time step
mol_response_N2=zeros(size(mol_resp_N2,1)/size(EJ,1),1);

for k=1:size(mol_resp_N2,1)/size(EJ,1) % for each time step

    % Calculate the overall molecular response function at each time step
    % (sum molecular responses of each vibrational level at each time step)
    mol_response_N2(k,:)=...
        sum(mol_resp_N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:));
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.4 Molecular_Response_O2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular_Response_O2 Code by Torge Mecker
%
% Matlab code that computes the time domain third order molecular
% response function of O2, based on the Boltzmann population distribution
% and taking into account the polarisation anisotropy, the Herman-Wallis
% factor and the Placzek-Teller coefficient.
%
% Input:
% time:      array holding the time axis at which the molecular response
%            is to be calculated
% T:         temperature [K]
% P:         pressure [atm] (to be passed to the Linewidths_O2 code)
% vib_levels: number of vibrational levels to be included in the model (to
%            be passed to the Energy_Levels_O2 code)
% rot_levels: number of rotational levels to be included in the model (to
%            be passed to the Energy_Levels_O2 code)
%
% Output:
% mol_response_O2: array containing the time domain third order molecular
%                 response function of O2 at each time step (as defined by
%                 the time axis)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Molecular_Response_O2
function [mol_response_O2] = ...
    Molecular_Response_O2(time, T, P, vib_levels, rot_levels)

% Get lw_O2, v, J, FJ and eJ from Linewidths_O2 code
[lw_O2, v, J, FJ, eJ] = ...
    Linewidths_O2(T, P, vib_levels, rot_levels);

% Define constants for O2
% NOTE: 1eV = 8065.543724cm-1 and hbar=h/2pi
hbar=3.33564084e-11/(2*pi); % reduced Planck constant [cm-1*s]
kb=0.6950345432; % Boltzmann constant [cm-1/K]

% [G. Herzberg and K. P. Huber, Molecular spectra and molecular structure/
% Volume 4, Constants of diatomic molecules, Van Nostrand Reinhold, New
% York (1979).]
we=1580.19; % first order vibrational constant [cm-1]
Be=1.44563; % equilibrium rotational constant [cm-1]
alpha=1.59e-2; % rotational-vibrational interaction constant [cm-1]
```

```

% [C. Asawaroengchai et al. J. Chem. Phys. 72, 2664-2669 (1980).]
re=1.207e-8; % equilibrium internuclear distance [cm]
beta_e1=1.080e-24; % equilibrium polarisation anisotropy [cm^3]
beta_e2=3.89e-16; % first derivative of the polarisation anisotropy wrt to
% internuclear distance [cm^2]

% [J. D. Miller. Hybrid femtosecond/picosecond coherent anti-Stokes Raman
% scattering for gas-phase temperature measurements, Graduate Theses and
% Dissertations, Paper 12610, PhD thesis, Iowa State University (2012).]
plp0=4.348; % ratio between the first two coefficients of the
% anisotropic polarisability expansion

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Polarisation Anisotropy, H.-W. Factor and P.-T. Coefficients:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the polarisation anisotropy
% [M. C. Drake. Opt. Lett. 7, 440-441 (1982)]
Gamma=beta_e1+beta_e2*re*((3*Be)/we)+(alpha/(2*Be))*(v+0.5);

% Calculate the Herman-Wallis factor based on Tipping and Ogilvie
% [R. H. Tipping et al. J. Raman Spectrosc. 15, 38-40 (1984).]
kappa=2*(Be/we);
HWF=(1+plp0*kappa^2*(J.^2+3*J+3)).^2;

% Calculate the Placzek-Teller coefficient for S-branch transitions
PTC=(3*(J+1).*(J+2))./(2*(2*J+1).*(2*J+3));

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Boltzmann Population Distribution:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the Boltzmann population difference for each J->J+2 transition,
% including a (2J+1) spin degeneracy factor
Pdiff=(2*J(:,1:end-2)+1)...
.*(exp(-FJ(:,1:end-2)/(kb*T))-exp(-FJ(:,3:end)/(kb*T)));

% NOTE: if ge is set to exactly 0 then the code runs very slow!
ge=1e-100; % rotational nuclear degeneracy for even J
go=1; % rotational nuclear degeneracy for odd J

if rem(J(end),2)==0 % if last J even
    Pdiff(:,1:2:end)=Pdiff(:,1:2:end)*ge; % multiply all even J by 0
    Pdiff(:,2:2:end-1)=Pdiff(:,2:2:end-1)*go; % multiply all odd J by 1

```

```

else % if last J odd
    Pdiff(:,1:2:end-1)=Pdiff(:,1:2:end-1)*ge; % multiply all even J by 0
    Pdiff(:,2:2:end)=Pdiff(:,2:2:end)*go; % multiply all odd J by 1
end

% Calculate the partition function (total sum of population in all
% ro-vibrational states
Psum=sum(sum(Pdiff));

% Calculate the relative Boltzmann population difference by dividing by
% the partition function
Pdiff=Pdiff/Psum;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular Response Function:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Select transition frequencies (eJ) of transitions for which linewidths
% have been calculated
EJ=eJ(:,1:size(lw_O2,2));

% Create a zero matrix to hold the exponential factor of the molecular
% response (at each time step, rotational and vibrational level)
exp_factors_O2=zeros(size(EJ,1)*size(time',1),size(EJ,2));

for k=1:size(EJ,1) % for each vibrational level

    % Calculate the exponential factor of the molecular response at each
    % time step, each vibrational level and each rotational level and input
    % this in every kth row of exp_factors_O2
    exp_factors_O2(k:size(EJ,1):end,:)=...
        exp(time'*(1i*EJ(k,:)-lw_O2(k,:)/2)/hbar);
end

for k=1:size(exp_factors_O2,1)/size(EJ,1) % for each time step

    % Calculate the molecular response function at each time step, each
    % vibrational level and each rotational level
    exp_factors_O2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:)= ...
        (4/45)*Gamma(:,1:length(EJ)).^2.*HWF(:,1:length(EJ))...
        .*PTC(:,1:length(EJ)).*Pdiff(:,1:length(EJ))...
        .*exp_factors_O2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:);
end

% Calculate the molecular response function at each time step and each
% vibrational level
mol_resp_O2=sum(exp_factors_O2,2); % sum of columns (rotational levels)

```

```

% Create a zero matrix to hold the overall molecular response function at
% each time step
mol_response_O2=zeros(size(mol_resp_O2,1)/size(EJ,1),1);

for k=1:size(mol_resp_O2,1)/size(EJ,1) % for each time step

    % Calculate the overall molecular response function at each time step
    % (sum molecular responses of each vibrational level at each time step)
    mol_response_O2(k,:)=...
        sum(mol_resp_O2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:));
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.5 Molecular_Response_O2N2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular_Response_O2N2 Code by Torge Mecker
%
% Matlab code that computes the time domain third order molecular
% response function of O2 in the presence of N2, based on the Boltzmann
% population distribution and taking into account the polarisation
% anisotropy, the Herman-Wallis factor and the Placzek-Teller coefficient.
%
% Input:
% time:          array holding the time axis at which the molecular response
%                is to be calculated
% T:             temperature [K]
% P:             pressure [atm] (to be passed to the Linewidths_O2N2 code)
% vib_levels:    number of vibrational levels to be included in the model
%                (to be passed to the Energy_Levels_O2 code)
% rot_levels:    number of rotational levels to be included in the model (to
%                be passed to the Energy_Levels_O2 code)
% mol_frac_N2:   mole fraction of N2
% mol_frac_O2:   mole fraction of O2
%
% Output:
% mol_response_O2N2: array containing the time domain third order molecular
%                   response function of O2 in the presence of N2 at each
%                   time step (as defined by the time axis)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Molecular_Response_O2N2
function [mol_response_O2N2] = ...
    Molecular_Response_O2N2(time, T, P, vib_levels, rot_levels, ...
        mol_frac_N2, mol_frac_O2)

% Get lw_O2, v, J, FJ and eJ from Linewidths_O2 code
[lw_O2, v, J, FJ, eJ] = ...
    Linewidths_O2(T, P, vib_levels, rot_levels);

% Get lw_O2N2, v, J, FJ and eJ from Linewidths_O2N2 code
[lw_O2N2, , , , ] = ...
    Linewidths_O2N2(T, P, vib_levels, rot_levels);

% Perform a weighted sum of the linewidths according to the mole fractions
% of O2 and N2
lw_O2_O2N2=mol_frac_O2*lw_O2+mol_frac_N2*lw_O2N2;
```

```

% Define constants for O2
% NOTE: 1eV = 8065.543724cm-1 and hbar=h/2pi
hbar=3.33564084e-11/(2*pi); % reduced Planck constant [cm-1*s]
kb=0.6950345432; % Boltzmann constant [cm-1/K]

% [G. Herzberg and K. P. Huber, Molecular spectra and molecular structure/
% Volume 4, Constants of diatomic molecules, Van Nostrand Reinhold, New
% York (1979).]
we=1580.19; % first order vibrational constant [cm-1]
Be=1.44563; % equilibrium rotational constant [cm-1]
alpha=1.59e-2; % rotational-vibrational interaction constant [cm-1]

% [C. Asawaroengchai et al. J. Chem. Phys. 72, 2664-2669 (1980).]
re=1.207e-8; % equilibrium internuclear distance [cm]
beta_e1=1.080e-24; % equilibrium polarisation anisotropy [cm^3]
beta_e2=3.89e-16; % first derivative of the polarisation anisotropy wrt to
% internuclear distance [cm^2]

% [J. D. Miller. Hybrid femtosecond/picosecond coherent anti-Stokes Raman
% scattering for gas-phase temperature measurements, Graduate Theses and
% Dissertations, Paper 12610, PhD thesis, Iowa State University (2012).]
p1p0=4.348; % ratio between the first two coefficients of the
% anisotropic polarisability expansion

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Polarisation Anisotropy, H.-W. Factor and P.-T. Coefficients:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the polarisation anisotropy
% [M. C. Drake. Opt. Lett. 7, 440-441 (1982)]
Gamma=beta_e1+beta_e2*re*((3*Be)/we)+(alpha/(2*Be))*(v+0.5);

% Calculate the Herman-Wallis factor based on Tipping and Ogilvie
% [R. H. Tipping et al. J. Raman Spectrosc. 15, 38-40 (1984).]
kappa=2*(Be/we);
HWF=(1+p1p0*kappa^2*(J.^2+3*J+3)).^2;

% Calculate the Placzek-Teller coefficient for S-branch transitions
PTC=(3*(J+1).*(J+2))./(2*(2*J+1).*(2*J+3));

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Boltzmann Population Distribution:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Calculate the Boltzmann population difference for each J->J+2 transition,
% including a (2J+1) spin degeneracy factor
Pdiff=(2*J(:,1:end-2)+1)...
    .* (exp(-FJ(:,1:end-2)/(kb*T))-exp(-FJ(:,3:end)/(kb*T)));

% NOTE: if ge is set to exactly 0 then the code runs very slow!
ge=1e-100; % rotational nuclear degeneracy for even J
go=1; % rotational nuclear degeneracy for odd J

if rem(J(end),2)==0 % if last J even
    Pdiff(:,1:2:end)=Pdiff(:,1:2:end)*ge; % multiply all even J by 0
    Pdiff(:,2:2:end-1)=Pdiff(:,2:2:end-1)*go; % multiply all odd J by 1
else % if last J odd
    Pdiff(:,1:2:end-1)=Pdiff(:,1:2:end-1)*ge; % multiply all even J by 0
    Pdiff(:,2:2:end)=Pdiff(:,2:2:end)*go; % multiply all odd J by 1
end

% Calculate the partition function (total sum of population in all
% ro-vibrational states
Psum=sum(sum(Pdiff));

% Calculate the relative Boltzmann population difference by dividing by
% the partition function
Pdiff=Pdiff/Psum;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Molecular Response Function:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Select transition frequencies (eJ) of transitions for which linewidths
% have been calculated
EJ=eJ(:,1:size(lw_O2N2,2));

% Create a zero matrix to hold the exponential factor of the molecular
% response (at each time step, rotational and vibrational level)
exp_factors_O2N2=zeros(size(EJ,1)*size(time',1),size(EJ,2));

for k=1:size(EJ,1) % for each vibrational level

```

```

    % Calculate the exponential factor of the molecular response at each
    % time step, each vibrational level and each rotational level and input
    % this in every kth row of exp_factors_O2
    exp_factors_O2N2(k:size(EJ,1):end,:)=...
        exp(time'*(1i*EJ(k,:)-lw_O2_O2N2(k,:)/2)/hbar);
end

for k=1:size(exp_factors_O2N2,1)/size(EJ,1) % for each time step

    % Calculate the molecular response function at each time step, each
    % vibrational level and each rotational level
    exp_factors_O2N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:)= ...
        (4/45)*Gamma(:,1:length(EJ)).^2.*HWF(:,1:length(EJ))...
        .*PTC(:,1:length(EJ)).*Pdfff(:,1:length(EJ))...
        .*exp_factors_O2N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:);
end

% Calculate the molecular response function at each time step and each
% vibrational level
mol_resp_O2N2=sum(exp_factors_O2N2,2); % sum of columns (rotational levels)

% Create a zero matrix to hold the overall molecular response function at
% each time step
mol_response_O2N2=zeros(size(mol_resp_O2N2,1)/size(EJ,1),1);

for k=1:size(mol_resp_O2N2,1)/size(EJ,1) % for each time step

    % Calculate the overall molecular response function at each time step
    % (sum molecular responses of each vibrational level at each time step)
    mol_response_O2N2(k,:)=...
        sum(mol_resp_O2N2(size(EJ,1)*k-(size(EJ,1)-1):size(EJ,1)*k,:));
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.6 Linewidths_N2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Linewidths_N2 Code by Torge Mecker
%
% Matlab code that computes the linewidths of rotational S-branch
% transitions of N2. This can be done either by using experimentally
% measured linewidths or by using the Modified Exponential Gap Law (MEG).
%
% Input:
% T:          temperature [K]
% P:          pressure [atm]
% linewidths: logic value that decides if to use experimentally measured
%             linewidths or the MEG model
% vib_levels: number of vibrational levels to be included in the model (to
%             be passed to the Energy_Levels_N2 code)
% rot_levels: number of rotational levels to be included in the model (to
%             be passed to the Energy_Levels_N2 code)
%
% Output:
% lw_N2: matrix that contains the rotational S-branch transition linewidths
%       of N2 for each vibrational level
% v:     matrix that holds the quantum number v for each rotational level
%       (passed on from Energy_Levels_N2 code)
% J:     matrix that holds the quantum number J for each vibrational level
%       (passed on from Energy_Levels_N2 code)
% FJ:    matrix that holds the energy of each ro-vibrational level (passed
%       on from Energy_Levels_N2 code)
% eJ:    matrix that holds the S-branch transition frequencies for each
%       vibrational level (passed on from Energy_Levels_N2 code)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Linewidths_N2
function [lw_N2, v, J, FJ, eJ] = ...
    Linewidths_N2(T, P, linewidths, vib_levels, rot_levels)

% Get v, J, FJ and eJ from Energy_Levels_N2 code
[v, J, FJ, eJ] = Energy_Levels_N2(vib_levels, rot_levels);

% Either use MEG model to calculate the linewidths (linewidths=1) or use
% experimentally measured linewidths (linewidths=2)
switch linewidths
```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Modified Exponential Gap (MEG) Law:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

case 1

% Define constants for N2
% NOTE: 1eV = 8065.543724cm-1
kb=0.6950345432; % Boltzmann constant [cm-1/K]
T0=295; % standard temperature [K]

% [R. E. Palmer, The carsft computer code calculating coherent
% anti-Stokes Raman spectra: User and programmer information,
% No. SAND-89-8206, Sandia National Laboratories, Livermore, CA
% (1989).]
we=2358.518; % first order vibrational constant [cm-1]
wexe=14.2935; % second order vibrational constant [cm-1]

% Define adjustable MEG parameters
% [H. U. Stauffer et al. J. Chem. Phys. 140, 024316 (2014).]
alpha=0.023; % [cm-1atm-1]
beta=1.67; % dimensionless
delta=1.21; % dimensionless
n=0.5; % dimensionless
m=0.1487; % dimensionless

% Subtract vibrational contribution from the energy levels
FJ_MEG=FJ-(we.*(v+1/2)-wexe.*(v+1/2).^2);

% Define zero matrix to hold linewidths values
lw_N2=zeros(size(v,1),size(J,2)-2);

for k=1:size(v,1) % for each vibrational level

    % Define zero matrix to hold off-diagonal elements of the
    % transition rate matrix
    Gamma=zeros(size(J,2),size(J,2));

    % Calculate the temperature dependent MEG factor
    FT=(1-exp(-m))/(1-exp((-m*T)/T0));

    % Calculate the off-diagonal elements
    for i=0:1:size(J,2)-1 % initial rotational level J=i
        for f=0:1:size(J,2)-1 % final rotational level J=f

```

```

        if i<f % upward transitions
            Gamma(i+1,f+1)=alpha*P*FT*((T/T0)^-n)...
                *(((1+((1.5*FJ_MEG(k,i+1))/(kb*T*delta)))...
                /(1+((1.5*FJ_MEG(k,i+1))/(kb*T))))^2)...
                *exp((-beta*(FJ(k,f+1)-FJ(k,i+1)))/(kb*T));

        elseif i>f % downward transitions (detailed balance)
            Gamma(i+1,f+1)=Gamma(f+1,i+1)...
                *((2*f+1)/(2*i+1))...
                *exp((FJ_MEG(k,i+1)-FJ_MEG(k,f+1))/(kb*T));

        else % fill diagonal with zeros
            Gamma(i+1,f+1)=0;
        end
    end
end

% Sum over each row of Gamma (each up or downward transition
% from J=i to J=f to get the diagonal elements
diagonal=sum(Gamma.');
```

% Use the sum rule to calculate the S-branch linewidths
 for i=1:1:size(J,2)-2 % for each rotational transition
 lw_N2(k,i)=0.5*(diagonal(i)+diagonal(i+2));
 end
 end
end

%%%
 % Experimentally Measured Linewidths:
 %%%

case 2

% Import text file containing experimentally measured N2 linewidths
 % [cm-latm-1] at temperatures from 300 K to 1400 K in steps of
 % 100 K
 % [C. J. Kliewer et al. Appl. Phys. B 108, 419-426 (2012).]
 measured_lw=load('<Insert File Location>');

T_original=300:100:1400; % temperatures of measured linewidths
 T_interpolated=300:1:1400; % temperatures for interpolation

% Define zero matrix to hold interpolated linewidths values
 interpolated_lw=zeros(size(measured_lw,1),length(T_interpolated));

for i=1:1:size(measured_lw,1) % for each rotational level

```

        % Interpolate at each rotational level and combine the
        % interpolated linewidths into one matrix
        interpolated_lw(i,:)=interp1(T_original, measured_lw(i,:),...
            T_interpolated, 'linear');
    end

    Temp=round(T); % round temperature to nearest integer

    if 300<=Temp && Temp<=1400 % if 300<=T<=1400
        lw_N2=P*interpolated_lw(:,Temp-299);

        % If the temperature is outside the range at which interpolated
        % experimental linewidths measurements exist, multiply by a
        % temperature dependent factor
        % [H. Tran et al. J. Raman Spectrosc. 34, 994-998 (2003).]
    elseif Temp<300
        lw_N2=P*interpolated_lw(:,1)*(300/T)^0.704;

    elseif Temp>1400
        lw_N2=P*interpolated_lw(:,end)*(1400/T)^0.704;
    end

    % Use the same linewidths at each vibrational level
    lw_N2= repmat(lw_N2',size(v,1),1);
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.7 Linewidths_O2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Linewidths_O2 Code by Torge Mecker
%
% Matlab code that computes the linewidths of rotational S-branch
% transitions of O2, using the Modified Exponential Gap Law (MEG).
%
% Input:
% T:          temperature [K]
% P:          pressure [atm]
% vib_levels: number of vibrational levels to be included in the model (to
%              be passed to the Energy_Levels_O2 code)
% rot_levels: number of rotational levels to be included in the model (to
%              be passed to the Energy_Levels_O2 code)
%
% Output:
% lw_O2: matrix that contains the rotational S-branch transition linewidths
%        of O2 for each vibrational level
% v:     matrix that holds the quantum number v for each rotational level
%        (passed on from Energy_Levels_O2 code)
% J:     matrix that holds the quantum number J for each vibrational level
%        (passed on from Energy_Levels_O2 code)
% FJ:    matrix that holds the energy of each ro-vibrational level (passed
%        on from Energy_Levels_O2 code)
% eJ:    matrix that holds the S-branch transition frequencies for each
%        vibrational level (passed on from Energy_Levels_O2 code)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Linewidths_O2
function [lw_O2, v, J, FJ, eJ] = ...
    Linewidths_O2(T, P, vib_levels, rot_levels)

% Get v, J, FJ and eJ from Energy_Levels_O2 code
[v, J, FJ, eJ] = Energy_Levels_O2(vib_levels, rot_levels);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Modified Exponential Gap (MEG) Law:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Define constants for O2
% NOTE: 1eV = 8065.543724cm-1
kb=0.6950345432; % Boltzmann constant [cm-1/K]
T0=295; % standard temperature [K]
```

```

% [G. Herzberg and K. P. Huber, Molecular spectra and molecular structure/
% Volume 4, Constants of diatomic molecules, Van Nostrand Reinhold, New
% York (1979).]
we=1580.19; % first order vibrational constant [cm-1]
wexe=11.98; % second order vibrational constant [cm-1]

% Define adjustable MEG parameters
% [T. Seeger et al. J. Raman Spectrosc. 34, 932-939 (2003).]
alpha=0.016; % [cm-1atm-1]
beta=1.45; % dimensionless
delta=1.32; % dimensionless
n=1.32; % dimensionless

% Subtract vibrational contribution from the energy levels
FJ_MEG=FJ-(we.*(v+1/2)-wexe.*(v+1/2).^2);

% Define zero matrix to hold linewidths values
lw_O2=zeros(size(v,1),size(J,2)-2);

for k=1:size(v,1) % for each vibrational level

    % Define zero matrix to hold off-diagonal elements of the transition
    % rate matrix
    Gamma=zeros(size(J,2),size(J,2));

    % Calculate the off-diagonal elements
    for i=0:1:size(J,2)-1 % initial rotational level J=i
        for f=0:1:size(J,2)-1 % final rotational level J=f

            if i<f % upward transitions
                Gamma(i+1,f+1)=alpha*P*((T/T0)^-n)...
                    *(((1+((1.5*FJ_MEG(k,i+1))/(kb*T*delta)))...
                        /(1+((1.5*FJ_MEG(k,i+1))/(kb*T))))^2)...
                    *exp((-beta*(FJ(k,f+1)-FJ(k,i+1)))/(kb*T));

            elseif i>f % downward transitions (detailed balance)
                Gamma(i+1,f+1)=Gamma(f+1,i+1)...
                    *((2*f+1)/(2*i+1))...
                    *exp((FJ_MEG(k,i+1)-FJ_MEG(k,f+1))/(kb*T));

            else % fill diagonal with zeros
                Gamma(i+1,f+1)=0;
            end
        end
    end

    % Sum over each row of Gamma (each up or downward transition from J=i
    % to J=f to get the diagonal elements
    diagonal=sum(Gamma.');
```

```

    % Use the sum rule to calculate the S-branch linewidths
    for i=1:1:size(J,2)-2 % for each rotational transition
        lw_O2(k,i)=0.5*(diagonal(i)+diagonal(i+2));
    end
end

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.8 Linewidths_O2N2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Linewidths_O2N2 Code by Torge Mecker
%
% Matlab code that computes the linewidths of rotational S-branch
% transitions of O2 in the presence of N2, using the Modified Exponential
% Gap Law (MEG).
%
% Input:
% T:          temperature [K]
% P:          pressure [atm]
% vib_levels: number of vibrational levels to be included in the model (to
%              be passed to the Energy_Levels_O2 code)
% rot_levels: number of rotational levels to be included in the model (to
%              be passed to the Energy_Levels_O2 code)
%
% Output:
% lw_O2N2:    matrix that contains the rotational S-branch transition
%              linewidths of O2 in the presence of N2 for each vibrational
%              level
% v:          matrix that holds the quantum number v for each rotational level
%              (passed on from Energy_Levels_O2 code)
% J:          matrix that holds the quantum number J for each vibrational
%              level (passed on from Energy_Levels_O2 code)
% FJ:         matrix that holds the energy of each ro-vibrational level
%              (passed on from Energy_Levels_O2 code)
% eJ:         matrix that holds the S-branch transition frequencies for each
%              vibrational level (passed on from Energy_Levels_O2 code)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Linewidths_O2N2
function [lw_O2N2, v, J, FJ, eJ] = ...
    Linewidths_O2N2(T, P, vib_levels, rot_levels)

% Get v, J, FJ and eJ from Energy_Levels_O2 code
[v, J, FJ, eJ] = Energy_Levels_O2(vib_levels, rot_levels);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Modified Exponential Gap (MEG) Law:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Define constants for O2
% NOTE: 1eV = 8065.543724cm-1
kb=0.6950345432; % Boltzmann constant [cm-1/K]
T0=295; % standard temperature [K]
```

```

% [G. Herzberg and K. P. Huber, Molecular spectra and molecular structure/
% Volume 4, Constants of diatomic molecules, Van Nostrand Reinhold, New
% York (1979).]
we=1580.19; % first order vibrational constant [cm-1]
wexe=11.98; % second order vibrational constant [cm-1]

% Define adjustable MEG parameters
% [T. Seeger et al. J. Raman Spectrosc. 34, 932-939 (2003).]
alpha=0.017; % [cm-1atm-1]
beta=1.41; % dimensionless
delta=1.30; % dimensionless
n=1.31; % dimensionless

% Subtract vibrational contribution from the energy levels
FJ_MEG=FJ-(we.*(v+1/2)-wexe.*(v+1/2).^2);

% Define zero matrix to hold linewidths values
lw_O2N2=zeros(size(v,1),size(J,2)-2);

for k=1:size(v,1) % for each vibrational level

    % Define zero matrix to hold off-diagonal elements of the transition
    % rate matrix
    Gamma=zeros(size(J,2),size(J,2));

    % Calculate the off-diagonal elements
    for i=0:1:size(J,2)-1 % initial rotational level J=i
        for f=0:1:size(J,2)-1 % final rotational level J=f

            if i<f % upward transitions
                Gamma(i+1,f+1)=alpha*P*((T/T0)^-n)...
                    *((1+((1.5*FJ_MEG(k,i+1))/(kb*T*delta)))...
                    /(1+((1.5*FJ_MEG(k,i+1))/(kb*T))))^2)...
                    *exp((-beta*(FJ(k,f+1)-FJ(k,i+1)))/(kb*T));

            elseif i>f % downward transitions (detailed balance)
                Gamma(i+1,f+1)=Gamma(f+1,i+1)...
                    *((2*f+1)/(2*i+1))...
                    *exp((FJ_MEG(k,i+1)-FJ_MEG(k,f+1))/(kb*T));

            else % fill diagonal with zeros
                Gamma(i+1,f+1)=0;
            end
        end
    end

    % Sum over each row of Gamma (each up or downward transition from J=i
    % to J=f to get the diagonal elements
    diagonal=sum(Gamma.');
```

```

        % Use the sum rule to calculate the S-branch linewidths
    for i=1:1:size(J,2)-2 % for each rotational transition
        lw_O2N2(k,i)=0.5*(diagonal(i)+diagonal(i+2));
    end
end

end

%%%%%%%%%%
%%%  END  %%%
%%%%%%%%%%

```

D.9 Energy_Levels_N2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Energy_Levels_N2 Code by Torge Mecker
%
% Matlab code that computes ro-vibrational energy levels and S-branch
% transition frequencies of N2. The calculations are based on a non-rigid
% rotor approximation, assuming an anharmonic vibrational potential and
% taking rotational-vibrational interaction into account.
%
% Input:
% vib_levels: number of vibrational levels to be included in the model
% rot_levels: number of rotational levels to be included in the model
%
% Output:
% v: matrix that holds the quantum number v for each rotational level
% J: matrix that holds the quantum number J for each vibrational level
% FJ: matrix that holds the energy of each ro-vibrational level
% eJ: matrix that holds the S-branch transition frequencies for each
%     vibrational level
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Energy_Levels_N2
function [v, J, FJ, eJ] = Energy_Levels_N2(vib_levels, rot_levels)

% Define constants for N2
% [R. E. Palmer, The carsft computer code calculating coherent anti-Stokes
% Raman spectra: User and programmer information, No. SAND-89-8206, Sandia
% National Laboratories, Livermore, CA (1989).]
we=2358.518; % first order vibrational constant [cm-1]
wexe=14.2935; % second order vibrational constant [cm-1]
Be=1.99826; % equilibrium rotational constant [cm-1]
De=5.774e-6; % equilibrium centrifugal constant [cm-1]

% Rotational-vibrational interaction constants
alpha=1.73035e-2; % [cm-1]
beta=1.55e-8; % [cm-1]
gamma=-3.1536099e-5; % [cm-1]

% Create a matrix that holds the vibrational quantum number v for each
% rotational level
v=repmat(vib_levels',1,length(rot_levels));

% Create a matrix that holds the rotational quantum number J for each
% vibrational level
J=repmat(rot_levels,length(vib_levels),1);
```

```

% Calculate the rotational and centrifugal constants, taking into account
% rotational-vibrational interaction
B=Be-alpha.*(v+1/2)+gamma.*(v+1/2).^2; % rotational constant
D=De+beta.*(v+1/2); % centrifugal constant

% Calculate the ro-vibrational energy levels based on a non-rigid
% rotor approximation and assuming an anharmonic vibrational potential
FJ=we.*(v+1/2)-wexe.*(v+1/2).^2+B.*J.*(J+1)-D.*J.^2.*(J+1).^2;

% Calculate the transition frequencies for each vibrational level, based
% on the selection rule deltaJ=+2 for S-branch (anti-Stokes) transitions
eJ=abs(FJ(:,1:end-2)-FJ(:,3:end));

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```

D.10 Energy_Levels_O2

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Energy_Levels_O2 Code by Torge Mecker
%
% Matlab code that computes ro-vibrational energy levels and S-branch
% transition frequencies of O2. The calculations are based on a non-rigid
% rotor approximation, assuming an anharmonic vibrational potential and
% taking rotational-vibrational interaction into account.
%
% Input:
% vib_levels: number of vibrational levels to be included in the model
% rot_levels: number of rotational levels to be included in the model
%
% Output:
% v: matrix that holds the quantum number v for each rotational level
% J: matrix that holds the quantum number J for each vibrational level
% FJ: matrix that holds the energy of each ro-vibrational level
% eJ: matrix that holds the S-branch transition frequencies for each
%     vibrational level
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Create a function called Energy_Levels_O2
function [v, J, FJ, eJ] = Energy_Levels_O2(vib_levels, rot_levels)

% Define constants for O2
% [G. Herzberg and K. P. Huber, Molecular spectra and molecular structure/
% Volume 4, Constants of diatomic molecules, Van Nostrand Reinhold, New
% York (1979).]
we=1580.19; % first order vibrational constant [cm-1]
wexe=11.98; % second order vibrational constant [cm-1]
Be=1.44563; % equilibrium rotational constant [cm-1]
De=4.839e-6; % equilibrium centrifugal constant [cm-1]

% Rotational-vibrational interaction constants
alpha=1.59e-2; % [cm-1]
beta=0.0; % [cm-1]

% [R. R. Laher et al. J. Phys. Chem. Ref. Data 20, 685-712 (1991).]
gamma=-8.25e-5; % [cm-1]

% Create a matrix that holds the vibrational quantum number v for each
% rotational level
v=repmat(vib_levels',1,length(rot_levels));
```

```

% Create a matrix that holds the rotational quantum number J for each
% vibrational level
J= repmat(rot_levels,length(vib_levels),1);

% Calculate the rotational and centrifugal constants, taking into account
% rotational-vibrational interaction
B=Be-alpha.*(v+1/2)+gamma.*(v+1/2).^2; % rotational constant
D=De+beta.*(v+1/2); % centrifugal constant

% Calculate the ro-vibrational energy levels based on a non-rigid
% rotor approximation and assuming an anharmonic vibrational potential
FJ=we.*(v+1/2)-wexe.*(v+1/2).^2+B.*J.*(J+1)-D.*J.^2.*(J+1).^2;

% Calculate the transition frequencies for each vibrational level, based
% on the selection rule deltaJ=+2 for S-branch (anti-Stokes) transitions
eJ=abs(FJ(:,1:end-2)-FJ(:,3:end));

end

%%%%%%%%%%
%%% END %%%
%%%%%%%%%%

```