Investigation of high resolution vibrational CARS thermometry

Master’s Thesis

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Abstract

This master’s thesis investigates high resolution vibrational CARS (coherent anti-Stokes Raman spectroscopy) thermometry in terms of precision and accuracy of the technique. The study focuses on the performance of evaluating temperatures below 1000 K, where the resolution of measurements becomes evident for quantitative results. The experimental approach of broadband vibrational CARS, with a single mode Nd:YAG laser and the detection system of a back-illuminated charged coupled device (CCD) camera where used to perform measurements in a set of calibrated oven temperatures. The temperature was extracted by fitting, in a least-square sense, the experimental single-shot spectra to theoretically calculated spectra at the prevailing conditions with the computational code CARSFT. The resulting standard deviation (relative or precision) was calculated to be 9 K (3.2 %), 16 K (2.7 %), 22 K (2.52 %) and the accuracy (relative) was found to be 9 K (3.0 %), 8 K (1.3 %), 50 K (5.6 %) at the temperatures 300 K, 600 K, and 900 K respectively.
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Chapter 1

Introduction

Vibrational coherent anti-Stokes Raman spectroscopy (CARS) is a laser based measuring technique by which it is possible to extract thermodynamic quantities such as temperature, pressure and concentrations from small volumes. This makes the technique very suitable to perform diagnostics on combustion processes, as the temperature is an important indicator of the process related chemical reactions. Accurate measurement of the temperature is important for validation and development of theoretical models. These not only improve our knowledge but also constitute a base of designing combustion devices, but as the technique has been proven strong the applications are only limited by imagination.

As the CARS technique is referred to as either rotational or vibrational, they are distinguished by which Raman resonance of the probed molecule that is driven. Since the energy of this type of shift differs depending on whether it is rotational or vibrational the operating laser light of respective technique is different. One of the characteristics of the techniques is the ability of making accurate predictions how the signals induced by the light from the lasers, are related to temperature. It has been argued that the working areas or range of temperature has been different of respectively technique, especially since vibrational CARS has been unsuitable for temperatures below 1000 K at atmospheric pressure.

The aim of this study is to investigate how vibrational CARS perform below 1000 K using such high spectral resolution that large part of the line structure can be resolved. With the experimental approach of broadband vibrational CARS, equipped with a single mode Nd:YAG laser (reducing the mode noise) and the detection system of a back-illuminated charged coupled device (CCD) camera a higher resolution of the lower temperature spectra will be received. A highly resolved spectrum has more spectral information and should be able to lead to more precise temperature data.
Chapter 2

Background physics

To understand what the CARS process is probing and how physical quantities can be extracted from quantum systems as molecules a physical explanation of these needs to be given.

This chapter will serve as an overview of the fundamentals of molecular physics in terms of the structure of a diatomic molecule, the internal energy of the system and the probabilistic population distribution between different states of energy. It will also contain a minor explanation in how light is scattered by matter.

2.1 The diatomic vibrating rotator

In order to explain the vibrating and rotating molecule two simplified pictures that can serve as intuitive descriptions of the phenomenon are presented in Fig.1;

![Fig. 1. The rigid rotator (to the left) and the harmonic oscillator (to the right)](image)

In both cases the atoms in the molecules are modeled as point masses while the bonds are represented by a massless spring and a massless stiff rod in the vibrational and rotational case respectively. To regard the atoms as point masses is a valid approximation as the weight of the atom is dominated by the nucleus and the extension of the same is on the femto \((10^{15})\) meter scale.

This intuitive description of the diatomic structure makes it possible to derive the internal energy of the system by the use of concepts from classical mechanics. Energy quantities later have to be quantized in order to fit the more accurately description of quantum mechanics. All these steps are not going to be showed in detail but can be found in the reference literature [1].
Chapter 2 – Background physics

The total internal energy of the diatomic molecule is divided into kinetic and potential energy contributions. Kinetic energy components are due to translational, vibrational and rotational motion of the molecule. As the system contains only two atoms it is possible to define a symmetry axis which will further determine the degrees of freedom of these different motions.

Every molecule regardless of species in the probed volume will hold translational energy. This energy which is manifested by the speed of the molecule is affected by the surrounding temperature. High translational energy will cause frequent collisions between the molecules which have an impact on the broadening of the spectral lines. Despite this the translational energy component are not going to be further discussed as the main kinetic energy components of interest for the CARS process are the rotational and vibrational motion.

The molecule is making 1000 vibrations during the course of a single rotation and these motions can according to the Born-Oppenheimer approximation be considered to proceed independently of each other. The total energy can therefore be expressed as a sum of both these motional energy contributions (excluding the electronic energies);

\[ E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}} \quad \text{[Joule]} \]

\[ \varepsilon_{\text{total}} = \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}} \quad \text{[cm}^{-1}] \]

2.1.1 Vibrational motion

The vibrational motion of the molecule is modeled as a simple harmonic motion, i.e. a sinusoidal oscillation centered about a point of equilibrium internuclear distance. This model is widely used in physics and is called the harmonic oscillator. The basic idea of this theory is that when the two masses are separated from their equilibrium distance they experience a force that is proportional to the distance of separation. The mathematical description derives the force \((F)\) as the gradient of the potential \((V)\);

\[ V = \frac{1}{2} k r^2, \quad F = -\text{grad}(V) = -\frac{d}{dr} \left( \frac{1}{2} k r^2 \right) = -k r, \quad r = r_{eq} - r' \quad (1) \]

The strength of this force is determined by the spring constant \((k)\) or the bonds between the atoms. This force is electromagnetic and the physical explanation is made by the attraction (repulsion) of the opposite (same) charge. When the two atoms get compressed the positively charged nuclei will act repulsive on each other. On the other hand when the atoms will be distanced from each other the positive charged nucleus and the negatively charged electron cloud from the opposite atom will act attractively on each other. This behavior is to be studied in Fig.2 where the dotted curve shows the harmonic oscillator potential.
Chapter 2 – Background physics

Fig. 2. The realistic anharmonic oscillator potential together with the harmonic oscillator potential (dotted curve). The vertical axis is scaled with the dissociation energy constant and the horizontal axis with the equilibrium distance between the atoms of the molecule. The rotational bands of each vibrational level is indicated.

The energy solutions ($E_v$) of this potential are the calculated eigenvalues to a given set of eigenfunctions to the Hamilton operator ($H$);

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2} k r^2, \quad r = r_{eq} - r', \quad \frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

(2)

$$E_v = \hbar \omega_{vib} \left( v + \frac{1}{2} \right) \text{[Joule],} \quad (v = 0, 1, 2, \ldots), \quad \omega_{vib} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{[Hz]}$$

(3)

where $\mu$ is the reduced mass of the system, $\omega_{vib}$ is the vibrational frequency and $v$ is the vibrational quantum number. However, the modeled harmonic oscillator is only valid in the bottom of the potential in the vicinity of the equilibrium internuclear distance. At larger distances the attractive force between the atoms is no longer that strong to hold the atoms together and the bond between the atoms will brake. A better potential that simulates this behavior is the empirical Morse potential [1];
\[ V = D_{eq} \left[1 - \exp(ar)\right]^2, \ r = r_{eq} - r' \]  

(4)

where \( a \) is a constant that is specific for each species and \( D_{eq} \) is the dissociation energy. In contrast to the harmonic oscillator potential there exists no analytical solutions to this potential and the only so called self consistent solutions have to be retained by numerical iterative methods.

The energy solutions of this anharmonic potential contain higher order terms which is found to be;

\[ E_v = \hbar \omega_{vib} \left(v + \frac{1}{2}\right) - \hbar \omega_{vib} x_e \left(v + \frac{1}{2}\right)^2 + \ldots \text{ [Joule], } (v = 0,1,2...) \]  

(5)

where \( x_e \) is the anharmonicity constant. The reason of showing these equations explicitly is to underline that the energies of a vibrational band are not equidistant as for the analytical solutions of the harmonic oscillator. The way of broadening the potential is different which will affect the positions of the higher energies (see Fig.2).

At these energies the molecule vibrates more strongly and what can be studied in Fig.2 is that the average distance between the atoms will increase. This fact will have an impact on the rotational motion of the molecule; something that is going to be discussed further after the concepts of rotational motion has been introduced.

### 2.1.2 Rotational motion

The rotational motion shown in Fig.1 is modeled as a rigid rotator. The two point masses (atoms) with a fixed distance from each other are rotating around a central symmetry axis. For a linear rotor the Hamilton operator together with corresponding eigenenergies are as follows [1];

\[ H = \frac{\vec{J}^2}{2I}, \ E_J = \frac{\hbar^2}{2I} J(J+1) \text{ [Joule], } (J = 0,1,2,...) \]  

(6)

where \( J \) is the rotational quantum number. This energy expression is often rearranged as;

\[ \varepsilon_J = \frac{E_J}{\hbar c} = BJ(J + 1) \text{ [cm}^{-1}], \ B = \frac{\hbar}{8\pi^2 I c}, \ (J = 0,1,2,...) \]  

(7)

where \( c \), the velocity of light is expressed in \( \text{cm s}^{-1} \) making the resulting energies to be expressed in wavenumbers (\( \lambda^{-1}, \text{ [cm}^{-1}] \)) which is of common use in spectroscopy. The constant \( B \) is called the rotational constant which is inversely proportional to the moment of inertia (I).
To improve the simplified description of the molecule as a rigid rotator a correction term is introduced:

\[ e_J = B J(J+1) - D J^2(J+1)^2 \, [\text{cm}^{-1}], \quad D = \frac{4B^3}{\omega_{\text{vib}}}, \quad (J = 0, 1, 2, \ldots) \quad (8) \]

where \( D \) is called the centrifugal constant and is about hundred thousand times smaller than the rotational constant \( B \). This correction takes into account that the real molecule is non-rigid and will experience distortion of shape when rotating fast.

A comment here can be made from another perspective, which is to consider the molecule as a container of energy. This correction decreases the molecules ability to bind the energy as a rotation. The higher moment of inertia of a non-rigid body in comparison to a rigid body makes it rotate less. In fact this has a very practical application, as it is almost the only nonintrusive way in how to determine whether a stored egg in the refrigerator is boiled or not.

The energy expression (8) is correct if considering the potential as harmonic. To correct for the anharmonicity in the force field more correction terms are required and the complete expression to calculate the rotational energy is to be found in reference literature [1].

What is extremely important though in explaining the positions of the spectral lines of vibrational CARS is to introduce correction terms to the constants \( B \) and \( D \) caused by the anharmonic potential. This is called the breakdown of the Born- Oppenheimer approximation and these correction terms is aiming what was mentioned earlier, namely that strong vibrations will have an indirect impact on the rotational motion of the molecule. Without this link between the vibrational and rotational motion caused by the anharmonicity potential all spectral lines would be placed on top of each other.

As the stronger vibrations will increase the average distance between the molecules, i.e. the bond length, the moment of inertia around the symmetry axis of the molecule will be increased. The rotational energies are then decreased due to the inversely dependence on the moment of inertia (see equation 7).

Since there is a rotational band for every vibrational energy level this affect can be modeled by changes in the constants \( B \) and \( D \) according to [1];

\[ B_v = B - \alpha v + \frac{1}{2} + \gamma (v + \frac{1}{2})^2 + \ldots, \quad D_v = D + \beta (v + \frac{1}{2}) + \ldots \quad (9) \]

where now \( B \) and \( D \) are the equilibrium values, and the constants \( \alpha, \gamma, \beta \) are called rotational-vibrational interaction constants.
2.2 Population distribution

One of the basic concepts within quantum mechanics is the wave-particle dualism. According to this discovery, wavefunctions were utilized in order to describe the state of a quantum mechanical particle. What’s instructive by this state representation is the use of general wave properties such as interference and superposition but what can be rather difficult is its interpretation. An incisive example of this is Schrödinger’s cat which does not only have “nine lives” like an ordinary cat but is dead and alive at the same time.

The formalism of quantum mechanics is constituted by tools of mathematics. In this language the probability distribution of a quantum mechanical particle is given by the squared modulus of its wavefunction. If the wavefunction is expressed as a linear combination (i.e. a superposition) of a linearly independent base ($\Phi_i$), the sum of the probability distribution would be the sum of the squared modulus of all the coefficients. If the wavefunction is normed this sum is equal to one which is called the enclosure relation. This formalism is written below;

$$\psi = a\phi_i + b\phi_j, \quad \sum |\psi|^2 = |a|^2 + |b|^2 = 1 \quad (10)$$

What can be read out of the above stated equations, is that the coefficients ($a, b$) is related to the statistical weight of the corresponding state. The statistical weight of each state holds the information about the relative population, why a sum of these is equal to one.

The meaning of this discussion was to show in a compact way how quantum mechanical formalism is expressing probabilities. The linearly independent base can be thought of as either vibrational or rotational states which are spread over a number of discrete energy levels. For each of these states there is a certain probability of being populated by the molecule if the system is in thermal equilibrium. This probability distribution was found by Boltzmann, and is one of the most powerful tools of statistical physics [2];

$$P(s) = \frac{1}{Z} \exp(-E(s)/kT), \quad Z = \sum \exp(-E(s)/kT) \quad (11)$$

where $s$ stands for state. Using this general description the exponential factor is called the Boltzmann factor and the sum ($Z$) of all Boltzmann factors is called the partition function. This function is expressing the probability distribution as normed, which means that the sum of all $P$’s is equal to one. To be more specific and to use energy values from above, the fractional population in a rotational state $J$ for an arbitrary vibrational state (and electronic state) is given by the following expressions;

$$P(J) = \frac{1}{Z} g_J m_J \exp(-E_J/kT), \quad Z = \sum g_J m_J \exp(-E_J/kT) \quad (12)$$
$E_J = \frac{\hbar^2}{2I} J(J + 1)$ [Joule], $(J = 0, 1, 2, \ldots)$, $m_J = (2J + 1)$

where $m_J$ is the degeneracy factor of each level, and $g_l$ is a statistical weight factor which depends on the coupling with the spin of the nucleus. This factor is species specific and for the particular case of nitrogen, $g_l$ is equal to 6 for even and 3 for odd rotational quantum numbers $J$. The strong temperature dependence of this distribution is presented in Fig.3.

![Figure 3](image-url)

*Fig. 3. The relative population distribution of the rotational levels in nitrogen at three different temperatures. To clarify the temperature dependence the odd rotational numbers have been omitted.*

Figure 3 illustrates, for three different temperatures, the relative population of the rotational levels belonging to the lowest vibrational level. It can be seen how the populations becomes more spread if the temperature increases.

The fractional population between vibrational levels is calculated in a similar way with the difference that among vibrational levels there is no degeneracy and statistical weight factor. This behavior is presented in Fig.4 showing how the fractional population of different vibrational levels is strongly dependent on temperature.
The fact is that it is the ability of making this accurate prediction, i.e. how the relative population distributions of the rotational and vibrational levels are dependent of temperature that makes CARS excellent as a thermometry technique [3].

2.3 Scattering of light

One of the ways that incident photons can interact with the molecule is called scattering. This process can be thought of classically like a collision between the two, which are illustrated in Fig. 5.

The combined system of a photon and a molecule can be considered as a virtual level of the molecule that will be relaxed to a real level by a spontaneously emitted photon. The molecule can either be left as changed or unchanged in energy and these processes are called inelastic (Raman) and elastic (Rayleigh) scattering respectively. In the case of inelastic scattering (Raman) there are two possibilities namely that the energy has been absorbed (Stokes scattering) - or have been lost (anti- Stokes scattering) - by the molecule. The energy difference is due to motional changes (vibrational or/and rotational) of the molecule and is called Raman shifts.
Fig. 5. Different possibilities of light being scattered by the molecule.

Even if Raman scattering is a linear principle and a spontaneous process only, the concepts of this is a good introduction to the next chapter. The photon coupling diagram of the CARS process very much resembles the ones from above but with an additional spice, namely the coherent excitation...
Chapter 3

Coherent anti-Stokes Raman Spectroscopy

3.1 Introduction

The CARS signal is generated through a non-linear optical process in a four wave mixing. The three incoming waves are converted into a fourth by the use of ro-vibrational energy levels in molecules. To relate the earlier discussions of these molecular energy levels and the different possibilities of photon coupling, the energy diagram of the CARS process is described in Fig. 6.

The molecule is coherently excited to levels that are resonant with the frequency difference of the two photons that are called pump and Stokes. The Stokes photon comes from a broadband dye laser with the effect of many transitions to be driven at the same time. A third signal, called the probe is coupled to the induced states which together with the anti-Stokes (CARS) signal complete the four wave mixing system. In case of any misunderstanding in the explanations of the coupling scheme it should be emphasized that all these couplings are generated at the same time.

Another instructive representation of the CARS process is to show how the intensity of the lasers is varying with wavelength which is illustrated in Fig. 7.
In this figure it is shown how the narrowband pump and probe signal act as a “mirror” when reflecting the generated CARS signal at the same energy distance from its center as to the position of the broadband Stokes signal. The energy distance is the Raman shift of the molecule. As this energy shift is species specific the information can serve as a fingerprint of which molecule is probed. This is the reason why the spectral output of the CARS signal is positioned on the corresponding shift from where it is coupled and not the signal itself.

3.2 Selection rules

Another fundamental dependence of the positions of the spectral lines is determined by the different transitions between the states of the molecule. When changing the motion induced by a field the molecule has to follow some selection rules. The selection rules are determined by the Raman scattering process, which for a diatomic molecule are defined as:

\[ \Delta \nu = 0, \pm 1, \quad \Delta J = 0, \pm 2 \]  \hspace{1cm} (13)

The different techniques of rotational and vibrational CARS have their own certain selection rules as can be expected by their different names. The main difference though is that the transitions induced by the vibrational CARS technique are changing the vibrational quantum number one step. The different changes in rotational quantum number are the ones mentioned above which are labeled O (\( \Delta J = -2 \)), Q (\( \Delta J = 0 \)) and S (\( \Delta J = 2 \)) transitions.

In the following table, the selection rules together with energies for a few different transitions are presented;
### Table 1. Different types and order of Raman shift for nitrogen with corresponding selection rules and energies calculated by CARSFIT.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta v = 1 )</th>
<th>( \Delta J = )</th>
<th>( \Delta E ) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>( J = 2 )</td>
<td>( J = 0 )</td>
<td>2317.97</td>
</tr>
<tr>
<td>O</td>
<td>( J = 3 )</td>
<td>( J = 1 )</td>
<td>2309.98</td>
</tr>
<tr>
<td>O</td>
<td>( J = 4 )</td>
<td>( J = 2 )</td>
<td>2301.95</td>
</tr>
<tr>
<td>Q</td>
<td>( J = 0 )</td>
<td>( J = 0 )</td>
<td>2329.91</td>
</tr>
<tr>
<td>Q</td>
<td>( J = 1 )</td>
<td>( J = 1 )</td>
<td>2329.87</td>
</tr>
<tr>
<td>Q</td>
<td>( J = 2 )</td>
<td>( J = 2 )</td>
<td>2329.80</td>
</tr>
<tr>
<td>S</td>
<td>( J = 0 )</td>
<td>( J = 2 )</td>
<td>2341.74</td>
</tr>
<tr>
<td>S</td>
<td>( J = 1 )</td>
<td>( J = 3 )</td>
<td>2349.60</td>
</tr>
<tr>
<td>S</td>
<td>( J = 2 )</td>
<td>( J = 4 )</td>
<td>2357.52</td>
</tr>
</tbody>
</table>

The notations \( J'' \) (\( J' \)) are the rotational quantum number of the ground (excited) state and the Raman shifts (\( \Delta E \)) are listed from bottom of the potential structure. It should be noticed that the Raman shifts are increasing for the S-branch with increasing \( J \) while the Raman shifts are decreasing for the O- and Q branch with increasing \( J \). This behavior is further studied in the following figures where theoretical Raman shifts are calculated.

---

**Fig. 8.** Raman shifts with corresponding rotational quantum number of the ground state of the molecule for O-, Q-, and S-branches. The change in vibrational quantum number is one.
In Figures 8 and 9 all transitions of each branch are indicated with the rotational quantum number of the ground state level ($J'$). In these figures it is evident that the transitions are affected by the difference in rotational constants for every vibrational level. Instead of a linear relation the different Raman shifts show a nearly parabolic shape on the corresponding order of rotational number. This is further showed by the following calculation of the Q-branch Raman shifts ($\Delta J = 0$), only considering the linear expansion and ignoring the centrifugal term;

\[
\Delta E_{\text{Raman}} = \Delta E_{\text{vib}} + \Delta E_{\text{rot}} = \hbar \omega_{\text{vib}} \left( 1 + \frac{1}{2} \right) - \left( 0 + \frac{1}{2} \right) + \left( B' - B'' \right) J (J + 1) =
\]

\[
\hbar \omega_{\text{vib}} + \left( B - \alpha \left( 1 + \frac{1}{2} \right) \right) - \left( B - \alpha \left( 0 + \frac{1}{2} \right) \right) J (J + 1) = \hbar \omega_{\text{vib}} - \alpha J (J + 1) \quad (14)
\]

As stated earlier without the modulation of the rotational constant, Eq. (9), the transitions would be placed on top of each other. It should also be mentioned that it is mainly the Q-branch that is resolved in the process depending on its relative strength towards the other O- and S-branches.
### 3.3 CARS signal strength

The incident electric fields from the lasers polarize a dielectric medium with a displacement of the electron cloud relative to the atomic nuclei. This relation is described by a power expansion as follows;

\[ \vec{P} = \varepsilon_0 \left( \chi \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \ldots \right) \]  \hspace{1cm} (15)

where \( P \) is the induced polarization, \( E \) is the applied electric field, \( \varepsilon_0 \) is the permittivity of free space and \( \chi^{(n)} \) is the \( n \)th order electrical susceptibility tensor. The higher order terms are much weaker than the linear term but as the field strength is considerable not only the linear term is significant. If the media of interest is a gas which has isotropic properties all even order terms are vanishing due to inversion symmetry reasons. When solving the wave equation the linear term can be added as a component to the field while the third order polarization will act as a source term. The derivation of the CARS signal intensity [4] is presented in appendix A with the following result;

\[ I_{\text{CARS}}(z) \propto \omega_{\text{CARS}}^2 I_{\text{pump}} I_{\text{Stokes}} I_{\text{probe}} |\chi_{\text{CARS}}|^2 z^2 \left( \frac{\sin(\Delta k z/2)}{\Delta k z/2} \right)^2 \]  \hspace{1cm} (16)

The different parameters are defined as follows;

- \( \omega_{\text{CARS}} \): The frequency of the CARS signal
- \( I_{\text{pump}}, I_{\text{Stokes}}, I_{\text{probe}} \): Intensity of the generating laser beams
- \( \chi_{\text{CARS}} \): The susceptibility of CARS
- \( z \): The distance of interaction in the probed volume
- \( \sin(\Delta k z/2) / \Delta k z/2 \): The phase matching condition

The most critical dependences of the CARS signal strength are the phase matching condition and the susceptibility, which is going to be further discussed below.

#### 3.3.1 Phase matching condition

The phase matching condition is constituted by the difference in wave vectors between the incident laser beams and the generated CARS beam. This is stated by Eq. (17).

\[ \Delta k = (k_{\text{pump}} - k_{\text{Stokes}} + k_{\text{probe}}) - k_{\text{CARS}} \]  \hspace{1cm} (17)
The energy conversion is enhanced if this difference is minimized, which is said to be perfect phase matching which is illustrated by Fig.10.

\[ \text{sinc}^2\left(\frac{\Delta k_z}{2}\right) \]

**Fig. 10.** The phase matching condition of the CARS signal.

The length of the wave vector \([4]\):

\[ |k| = \frac{2\pi \cdot n}{\lambda} \] \hspace{1cm} (18)

is dependent on the wavelength \((\lambda)\) and the index of refraction \((n(\omega))\) which is frequency dependent but is approximately the same for all frequencies if the CARS signal is generated in a gas. While all quantities are known the phase matching condition is easily controlled by choosing suitable incoming angles of the generating laser beams in the experimental setup. There exist different approaches for the spatial geometry of this condition \([5]\) but what is used here is the so called planar BOXCARS scheme which is illustrated in Fig.11.
3.3.2 Susceptibility

Though the complete theoretical explanation of the third order susceptibility requires a lot of depth this chapter will only try to make an outline of the most important steps in how to interpret the tensor quantity.

The third order susceptibility is derived in reference literature [4], with the result that is presented in Appendix B. In the evaluation of the sum some of the indices and specifications need to be explained. The susceptibility tensor can be written with the identity matrix as:

$$\chi_{CARS} \cdot I$$

where

$$\chi_{CARS} = \chi_{lq}$$

and

$$l = g = i = h$$  \hspace{1cm} (19)

When summing all the ro-vibrational states, i.e. all the diagonal elements in the density matrix the following condition is valid;

$$\sum_{l} \rho_{ll}^{(l)} = 1$$  \hspace{1cm} (20)

In the sum there are terms that are resonant and non-resonant respectively and it can be subdivided into two parts as indicated below;

$$\chi_{CARS} = \chi_{R,CARS} + \chi_{NR,CARS}$$  \hspace{1cm} (21)

As stated earlier the CARS signal is generated when the pump together with the Stokes wave is resonant with the specific ro-vibrational transitions of the molecule which are the so called Raman shifts;

$$\omega_{Raman} = \omega_{pump} - \omega_{Stokes}$$  \hspace{1cm} (22)
If studying the second expression inside the brackets in the denominator of all the terms in the third order susceptibility (Appendix B) we see that the terms (1, 5 and 4, 8) become resonant with the following nomenclature:

\[ \omega_{nl} = \omega_{\text{Raman}} \quad \text{and} \quad \omega_{p} = \omega_{\text{pump}}, \quad \omega_{q} = -\omega_{\text{Stokes}} \quad (23) \]

Together with selection rules for the Q-branch transitions Table 2 is presented to give a better overview. As \( v \) is already used in the formula of Appendix B, the vibrational quantum number \( v \) will instead be read as \( l \) in this interpretation.

Table 2. Clarification of nomenclature in the description of the third order susceptibility in Appendix B.

<table>
<thead>
<tr>
<th>Terms</th>
<th>(1) and (5)</th>
<th>(4) and (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density element</td>
<td>( \rho_{l,j}^{(0)} \Rightarrow l, n = l + 1 )</td>
<td>( \rho_{l+1,j+1}^{(0)} \Rightarrow l = l + 1, n = l )</td>
</tr>
<tr>
<td>Raman shift</td>
<td>( \omega_{\text{Raman}} = \omega_{n+1,l} )</td>
<td>( \omega_{\text{Raman}} = \omega_{l+1,l} = -\omega_{l+1,l} )</td>
</tr>
</tbody>
</table>

In summing all \( (l) \) and \( (n) \) and to further specify the nomenclature Eqs. (24), the resonant part of the susceptibility can be written (25);

\[ \omega_{r} = \omega_{\text{probe}} \quad (24) \]

\[ X_{R,CARS} = \frac{N}{\hbar^3} P \sum_{p,v,m} \left\{ \begin{array}{l} 2 \rho_{l,j}^{(0)} \mu_{l,j}^x \mu_{l+1,j+1}^x \mu_{l+1,m}^x \mu_{m,l}^x \left[ (\omega_{r} - \omega_{\text{pump}} + \omega_{\text{Stokes}} - \omega_{\text{probe}}) - i \gamma_{v,l} \right] \left[ (\omega_{r+1,l} - \omega_{\text{pump}} + \omega_{\text{Stokes}}) - i \gamma_{v,l+1} \right] \left[ (\omega_{m,l} + \omega_{\text{pump}}) + i \gamma_{m,l} \right] \\
- \left[ (\omega_{m,l+1} - \omega_{\text{pump}} + \omega_{\text{Stokes}} - \omega_{\text{probe}}) - i \gamma_{m,l+1} \right] \left[ (\omega_{r+1,l} - \omega_{\text{pump}} + \omega_{\text{Stokes}}) - i \gamma_{l+1} \right] \left[ (\omega_{m,l} + \omega_{\text{pump}}) + i \gamma_{m,l} \right] \end{array} \right\} \]

\[ (25) \]

Here it has been assumed that the terms (1, 5) and (4, 8) respectively are of the same size. If furthermore the dipole matrix elements \( \mu^x \) is assumed to be relatively constant and the terms \( \gamma_{l+1} \) and \( \gamma_{l+1,l} \) (holding the information of lifetime and phase memory of the induced state) are the same the expression can be simplified to;

\[ X_{R,CARS} = A \cdot \sum_{p,v,m} \left\{ \begin{array}{l} 2 \rho_{l,j}^{(0)} \mu_{l,j}^x \mu_{l+1,j+1}^x \mu_{l+1,m}^x \mu_{m,l}^x \left[ (\omega_{r} - \omega_{\text{pump}} + \omega_{\text{Stokes}} - \omega_{\text{probe}}) - i \gamma_{v,l} \right] \left[ (\omega_{r+1,l} - \omega_{\text{pump}} + \omega_{\text{Stokes}}) - i \gamma_{v,l+1} \right] \left[ (\omega_{m,l} + \omega_{\text{pump}}) + i \gamma_{m,l} \right] \\
- \left[ (\omega_{m,l+1} - \omega_{\text{pump}} + \omega_{\text{Stokes}} - \omega_{\text{probe}}) - i \gamma_{m,l+1} \right] \left[ (\omega_{r+1,l} - \omega_{\text{pump}} + \omega_{\text{Stokes}}) - i \gamma_{l+1} \right] \left[ (\omega_{m,l} + \omega_{\text{pump}}) + i \gamma_{m,l} \right] \end{array} \right\} \]

\[ (26) \]
Chapter 3 – CARS

with

\[ A = \frac{N}{\hbar^3} P_i \cdot \mu^z_{\text{cons}} \]  \hspace{1cm} (27)

where \( N \) is the number density of the gas and \( P_i \) is a permutation operator. Together with the number density it is the frequency difference in the denominator that is assigned as the detuning and the fractional population difference between the states involved in the process that is the major components on which the resonant part of the third order susceptibility depends.

The non-resonant part of the third order susceptibility is associated with the fast response of the electrons of the medium to the incident fields [5]. As an example this can be manifested by one or two-photon sum absorptions but the relative strength of this coupling is weak in comparison to the resonant part which is shown by the following approximate calculation.

When the size of \( \omega \) and \( \gamma \) is \( 10^{15} \) and \( 10^9-10^{12} \) respectively, and Eq. (22) is valid, the resonant part, Eq. (26), can be written;

\[ \chi_{R,CARS} = A \cdot \sum_{v,m} \left( \rho^{(0)}_{li} - \rho^{(0)}_{i+1,j+1} \right) \left( \omega_{v,j} - \omega_{\text{pump}} + \omega_{\text{Stokes}} - \omega_{\text{probe}} \right) \left( -i \gamma_{i+1,j} (\omega_{m,j} + \omega_{\text{pump}}) \right) \]  \hspace{1cm} (28)

To do a comparison of the relative strength between the resonant and the non-resonant part of the susceptibility the size of the terms in the different parts are estimated;

\[ \chi^i_{R,CARS} \propto \frac{1}{10^{15} \cdot 10^{12} \cdot 10^{15}} \sim \frac{1}{10^{15} \cdot 10^9 \cdot 10^{15}} \]  \hspace{1cm} (29)

\[ \chi^i_{NR,CARS} \propto \frac{1}{10^{15} \cdot 10^{15} \cdot 10^{12}} \]

Thus the relative strength is approximated as;

\[ \frac{\chi_{R,CARS}}{\chi_{NR,CARS}} = 10^3 \sim 10^6 \]  \hspace{1cm} (30)

But despite the relative strength of the non-resonant part is weak in comparison to the resonant part it plays an important role on the influence of the line shape of each resonant line. The higher temperature and pressure the higher the influence of the non-resonant part which dependence can serve as one way of determining the concentration of the probed species. It is also of high importance to determine the non-resonant part experimentally as it can be used to compensate for the probability of generating the CARS signal, which is going to be further discussed below.
3.4 Spectral temperature dependence

As this diploma work is focusing the CARS technique capacity in determining temperature of certain probed species, it would be instructive to end this chapter with conclusions of the spectral temperature dependence.

In Fig.12 results are presented from theoretical calculations which show how the square root of the signal intensity is varying with temperature. For higher temperatures more high energy states of rotation and vibration are populated by the molecules according to Boltzmann statistics. Intuitively speaking the molecules rotate and vibrate faster with increased temperature. In Table 3, the number of rotational and vibrational states used by the CARSFT code at different temperatures is shown.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>300</th>
<th>600</th>
<th>900</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest vibrational quantum number retained</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Highest rotational quantum number retained</td>
<td>32</td>
<td>48</td>
<td>60</td>
<td>63</td>
</tr>
</tbody>
</table>

What can be studied in Fig.4 is that the second vibrational state \((v = 1)\) starts to get populated around 900 K which is indicated in Table 3. As the highest vibrational quantum number retained is 2 for temperature 900 K and 1200 K the molecule gets to be Stokes shifted from \(v = 1\) to \(v = 2\) which transitions can be viewed in respectively figures and in common speech are referred to as the hot band.

The strength of all square root intensities is all relative to the one of room temperature (300 K) which data is gathered below;

\[
T \text{ [K]} = 300: 600: 900: 1200 \quad \max I^{1/2} \text{ [a.u.]} = 1: 0.5: 0.3: 0.2 \quad (31)
\]

What can be studied in this set of data is the nearly linear relation between the different temperatures and the maximal values of the square root of the intensities. When doubling the temperature from 300 K to 600 K the square root of the intensity gets to be halved. This behavior is true in a first approximation for temperature values close to room temperature but starts to differ at higher temperatures where the population distribution gets more spread which will have an impact of the height of the signal. The behavior comes from the number density dependence in the third order susceptibility which is related to temperature by the perfect gas law. To be more explicit the following relations are shown;

\[
I \propto \left| \chi_{\text{CARS}} \right|^2 \propto N^2 \Rightarrow I^{1/2} \propto \left| \chi_{\text{CARS}} \right| \propto N \quad (32)
\]

\[
PV = NkT = \left( \frac{N}{2} \right)k(2T) \quad (33)
\]
Fig. 12. Theoretical nitrogen CARS spectra at four different temperatures calculated by CARSFIT.
Chapter 4

Experimental work

4.1 Introduction

In a historical context the development of experimental equipment have had an important role in the progress of the CARS technique. The experimental work of CARS is therefore involving a lot of equipment which are too complex to be explained in detail for this diploma work. The descriptions of the experimental work will instead be focusing what has been done in order to reproduce the measurements, pinpointing some of the procedures in recording data and explaining how to calibrate the measurements. In the second part of this chapter two issues that are essential for the temperature evaluation of the CARS spectrum is going to be discussed, namely how to calculate the dispersion and the instrument function needed to simulate how the resonant lines get broadened by the detector system. More details on the experimental equipment can be found in Ref.[6].

4.2 Experimental setup

A schematic view representing the experimental setup of vibrational CARS measurements is shown in Fig. 13.
Chapter 4 – Experimental work

Fig. 13. Experimental setup of the vibrational CARS measurements. The Nd:YAG laser generates the green pump and probe beam at the wavelength 532 nm and the dye laser a red broadband Stokes beam that is centered around 607 nm. BS = 50 % beam splitter; D1 = dichroic mirror transmitting green and reflecting red light; D2 = dichroic mirror transmitting green and reflecting blue light; L1: f = 50 cm lens; L2: f = 30 cm lens; L3: f = 15 cm lens; BD = beam dump; SP = short-pass filter.

The frequency doubled Nd:YAG laser (Quantel, Model YG 981E-SLM) is providing light at a wavelength of 532 nm which is used as both pump and probe beam (ω₁, ω₃) in the CARS process. A Q-switch technique makes the light being pulsed and an injection-seeding system gives the ability of running the laser in a single mode operation. The duration of the pulses is about 10 ns at a repetition rate of 10 Hz and the spectral bandwidth of the light is less than 0.005 cm⁻¹. As about 20 % of the light is used for the narrowband CARS beams (ω₁, ω₃) the remaining 80 % of the light is used as a pump source for the dye laser (Quantel, Model TDL 90). In pulse energy these fractions of the light was measured to be 56 mJ and 240 mJ respectively. The powder Rhodamine 640 was diluted in methanol and it was used in the dye laser that provides light centered at the wavelength 607 nm having an emission profile that is about 150 cm⁻¹ broad. At the output of the dye laser the pulse energy of the beam (ω₂) was measured to be 37 mJ. On the occasional time of measurements the pulse energy was measured at the spot right before the first lens (L1) with the results illustrated in Fig. 14.
Chapter 4 – Experimental work

Fig. 14. The energy per pulse (green 8.5mJ/pulse, green 7.5mJ/pulse + red 28mJ/pulse) measured at the spot right before the f = 50 cm lens (L1, see Fig. 15).

The green pump and probe beams (ω₁, ω₃) are separated by a 50 % beam splitter (BS) where one of the beams (ω₃) later is arranged to overlap with the red Stokes beam (ω₂) by a dichroic mirror (D1) which is transmitting green and reflecting red light. The separation distance of the parallel propagating beams is about 12 mm. In order to achieve the phase matching condition of the planar BOXCARS scheme (see Fig. 11) an f = 50 cm lens (L1) is focusing the beams together at the measuring point which is the probe volume. This volume has a geometrical shape of an ellipsoid with a size that is about 100 x 1000 μm and determined by the focal length of lens and incoming angles of the beams. After the overlap at the probed volume the beams are re-collimated by an f = 30 cm lens (L2) and while the two beams (ω₂, ω₃) being terminated by a beam dump (BD) the green beam (ω₁) is left to propagate superimposed with the CARS beam (ω₄). The intensity of the green beam (ω₁) is being lowered gradually by the dichroic mirrors (D2) which are transmitting green and reflecting blue light. As the CARS beam is barely visible to the naked eye (not as clearly seen as in narrowband dye laser operation) the green beam (ω₁) is used to align onto the entrance of the detector system. Later when all the set-up is being done a series of short-pass filters (SP) is inserted to spectrally filter the CARS beam (ω₄) from interfering light. The f = 15 cm lens (L3) is focusing the CARS beam (ω₄) on the entrance slit of the 1m spectrometer of Czerny-Turner type causing maximal spread on the grating of 600 grooves mm⁻¹ blazed for 473 nm in the fifth order (setting 9980.5). The signal is spectrally resolved on a back-illuminated unintensified Princeton Instruments CCD camera having 1100 x 330 pixels with the size of 24 x 24 μm [6]. Information is transferred from the CCD camera to a computer with properly software (WinSpec) to display the data. The experimental data is later analyzed in a least-square fit manner by a theoretical spectrum-modeling code (CARSFT) written in FORTRAN. To start this analysis the program CARSFT had to be fed by the experimental data in a certain format, which resulted from executing routines written in MATLAB. In order to investigate the properties of high resolution thermometry at different temperatures a hollow oven was placed in such a way that the lasers could be propagating through. The oven could provide temperatures in the temperature range under study and to get the temperature calibration a tube with three thermocouples was mounted to surround the
probe volume inside the oven. Oven measurements were performed at around 300, 600 and 900 K. To be able to measure the non-resonant spectra of argon (discussed in the next section) in between the given set of temperatures, the oven was arranged to be movable and a smaller pipe was inserted leading the gas to the measuring point.

4.3 Experimental procedure

In order to perform accurate quantitative measurements it is important to characterize the experimental setup and the operating conditions. The surrounding room temperature was estimated by a normal mercury thermometer to be 296 K. The measurements were probing the nitrogen of room air which ought to give sufficient signal intensity since the mole fraction is about 78%. The measured effects of the lasers, settings of the spectrometer and all equipment in the experimental setup were noted in the previous section. By running all equipment about 20 minutes before measurement, thermal stabilization of the lasers is reached and systematic errors for example due to drift of the dye laser spectrum with time were minimized. To all the resonant and non-resonant spectra, a background spectrum was recorded by blocking the green beam that propagates together with the red beam, and it was later subtracted from respective data.

In the schematic of the broadband CARS spectrum of nitrogen in Fig. 7 it can be seen how the intensity of the lasers are varying with wavelength. The intensity of the broadband dye laser providing the Stokes beam shows the characteristics of a Gaussian envelope. This variation will have an affect of the probability of generating a CARS photon at a certain Raman shift since the supply of photons is smaller at the edges of the envelope. While the CARS signal is coupled to the Raman shift by the narrow band probe beam the intensity will suffer from the same affect and needs to be compensated on the side band, where it is too low in comparison to the centre, relatively speaking. This compensation is made by dividing the CARS spectra with a non-resonant spectrum, recorded with the same operating conditions, which are reflecting this variation. As the non-resonant transitions are created by an intermediate photon coupling scheme the probabilistic events are dependent on the amount of photons. A spectrum from these is independent of the generating wavelengths and is reflecting the intensity of the broadband dye laser which variation needs to be compensated for. Experimentally this spectrum is recorded in a gas of argon which is single atomic and without any Raman resonances. An example from such non-resonant argon spectrum (where its background has been subtracted) is presented in Fig. 15. Here the similarity with a part of a Gaussian envelope can be seen.
The major importance of this non-resonant spectrum must be emphasized in the temperature evaluation of the CARS spectrum. By the shape and quality of this non-resonant spectrum it is also possible to check the validity of the measurements why the spectrum should preferably be recorded both prior to and after the experiment series [7]. The non-resonant spectrum example of Fig.15 has been averaged in the sense that the intensity has been divided by the number of accumulations (200) which make the intensity at each channel number to be considered on a single shot basis.

By the procedure of averaged referencing the structure will be smoothened and it has been claimed that instead by a simultaneous shot-to-shot referencing, systematic errors would be eliminated and the precision of the measurements would increase [8].

### 4.3.1 Dispersion

The dispersion is calculated by finding a polynomial that maps all channel numbers of the detector that are covered by the spectrally resolved CARS signal to the corresponding wave numbers of Raman shifts. A better polynomial at the right set of channel numbers will improve the fitting procedure in analyzing the temperatures of the computer code CARSFT.
To ensure that the dispersion calculation were covering the CARS signals of all temperatures that is of interest for this work (300 K, 600 K and 900K) a measurement in a flame of a Bunsen burner was made. With an approximate flame temperature of 2000 K the hot band is highly populated and observed in the experimental spectra. Even if the experimental condition is different for this measurement in comparison to the oven temperatures, making perhaps a shift in channel number for a specific Raman transition, the dispersion of the detection system is the same.

By identifying the peaks of the experimental spectrum with the ones from a calculated CARS spectrum a mapping polynomial can be found from its positions. Data of the peak positions from the measured (channel number) and the calculated (wavenumber) CARS signal are gathered in Table 4.

Table 4. Data of the peak positions from the measured and the calculated CARS signal. The wave numbers are expressed in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>channel number</th>
<th>wave number</th>
<th>channel number</th>
<th>wave number</th>
</tr>
</thead>
<tbody>
<tr>
<td>417</td>
<td>2282.8</td>
<td>708</td>
<td>2312.7</td>
</tr>
<tr>
<td>439</td>
<td>2285.0</td>
<td>718</td>
<td>2313.7</td>
</tr>
<tr>
<td>459</td>
<td>2287.1</td>
<td>729</td>
<td>2314.8</td>
</tr>
<tr>
<td>479</td>
<td>2289.0</td>
<td>738</td>
<td>2315.8</td>
</tr>
<tr>
<td>496</td>
<td>2290.8</td>
<td>748</td>
<td>2316.8</td>
</tr>
<tr>
<td>512</td>
<td>2292.4</td>
<td>756</td>
<td>2317.7</td>
</tr>
<tr>
<td>526</td>
<td>2293.9</td>
<td>766</td>
<td>2318.6</td>
</tr>
<tr>
<td>540</td>
<td>2295.3</td>
<td>774</td>
<td>2319.5</td>
</tr>
<tr>
<td>552</td>
<td>2296.5</td>
<td>782</td>
<td>2320.3</td>
</tr>
<tr>
<td>562</td>
<td>2297.6</td>
<td>789</td>
<td>2321.1</td>
</tr>
<tr>
<td>571</td>
<td>2298.5</td>
<td>797</td>
<td>2321.9</td>
</tr>
<tr>
<td>585</td>
<td>2300.0</td>
<td>803</td>
<td>2322.6</td>
</tr>
<tr>
<td>599</td>
<td>2301.4</td>
<td>811</td>
<td>2323.3</td>
</tr>
<tr>
<td>626</td>
<td>2304.1</td>
<td>817</td>
<td>2324.0</td>
</tr>
<tr>
<td>651</td>
<td>2306.7</td>
<td>828</td>
<td>2325.2</td>
</tr>
<tr>
<td>663</td>
<td>2308.0</td>
<td>838</td>
<td>2326.3</td>
</tr>
<tr>
<td>675</td>
<td>2309.2</td>
<td>848</td>
<td>2327.2</td>
</tr>
<tr>
<td>686</td>
<td>2310.4</td>
<td>855</td>
<td>2328.0</td>
</tr>
<tr>
<td>698</td>
<td>2311.5</td>
<td>861</td>
<td>2328.7</td>
</tr>
</tbody>
</table>

The routine “POLYFIT” of MATLAB finds the coefficients of a polynomial \(P(x)\) of degree \(N\) that fits the data \(y\) best in a least-squares sense. The explicit formula is written;

\[
P = a \cdot x^N + b \cdot x^{N-1} + \ldots \Rightarrow [N = 2] \Rightarrow a \cdot x^2 + b \cdot x + c \quad (34)
\]

\[
a = 4.2488 \cdot 10^{-6}, \; b = 0.0978, \; c = 2.2413 \cdot 10^{-5}
\]
where $x$ is the channel numbers. The conversion between channel numbers and wavenumbers of the Raman shifts are approximately linear but the use of a second order translational polynomial gives a better result. The polynomial distribution together with data set of Table 4 is illustrated in Fig. 16.

**Fig. 16** The translational polynomial distribution between channel numbers and wavenumbers of the Raman shifts. The dots are marked as the identified peaks of measured and calculated CARS signal.

Only small deviations from the approximate linear distribution can be seen which marks that the dispersion calculation is successful. This behavior of small deviations can be explained according to Fig. 17 where the maximum values of five corresponding peaks are indicated. The maximum value of a corresponding peak can be picked right next to the left or the right side of its center position. The deviations could of course be minimized by extrapolating the peaks.
Fig. 17. The maximum values of five peaks are indicated. What is shown is the difficulty in determining the exact position of the peaks which give rise to the small deviations from the translational polynomial distribution shown in Fig. 16.

Another way of showing the results from the dispersion calculation is to display the measured CARS signal together with the calculated when the channel numbers have been translated to wave numbers. This is done in Fig. 18 where it can be verified that the correct identification of peaks has been made. The complete coverage of the distinct hot band in this figure also guarantees that temperature measurements of 300 K, 600 K and 900 K have a correct dispersion.
Fig. 18. The figure verifies that the right identification of peaks has been made.

4.3.2 Instrument function

The temperature of the measured nitrogen CARS spectrum is evaluated by fitting theoretical spectra to the experimental spectrum. In the generation of theoretical spectra a parameter to consider is how the spectral lines are broadened. Molecular collisions are broadening the lines due to its effect on the lifetimes of molecular states but the spectral lines are also broadened by the detector. The theoretical calculations of the CARS susceptibility therefore has to be convolved with a detector instrument function [9]. This function (also called the slit function) simulates how the line shape of the spectral CARS signal is changed by the detector system. The mathematical description is made by the convolution of a Gaussian (\( G \)) and a Lorentzian (\( L \)) function which is called a Voigt (\( V \)) profile instrument function and is written according to Eq. (35).

\[
V(x;\sigma,\gamma) = \int G(x';\sigma)L(x-x';\gamma)dx \\
G(x;\sigma) = \frac{\exp(-x^2/(2\sigma^2))}{\sigma\sqrt{2\pi}}, \quad L(x;\gamma) = \frac{\gamma}{\pi(x^2+\gamma^2)}
\]
As the computational code CARSFT needs to be fed by this line shape profile and it requires the information about the full width at half maximum value (FWHM) an approximate calculation of this is made according to Eq. (36).

\[
f_G = 2\sigma \sqrt{2\ln(2)}, \quad f_L = 2\gamma, \quad f_V \approx f_G \left(1 - c_0 c_1 + \sqrt{\left(\frac{f_L}{f_G}\right)^2 + 2c_1 \left(\frac{f_L}{f_G}\right) + c_0^2 c_1^2}\right)
\]

(36)

In the equation, where \(c_0 = 2.0056\) and \(c_1 = 1.0593\) the nomenclature \(f\) (FWHM) that is used with indices \(G, L\) and \(V\) stands for Gaussian, Lorentzian and Voigt respectively. Since the solutions of the above stated equations are many the instrument function for each detector system must be determined by trial and error. The solution is found by minimizing the error between theoretical nitrogen CARS spectra calculated by a specific instrument function and experimental nitrogen spectra of room air [9].

The result from such calculation is presented in Fig. 19 and Fig. 20.

![Fig. 19. The mesh of finding the proper instrument function, determined by the minimization of the difference between calculated nitrogen CARS spectra and experimental spectra of room air.](image-url)
Fig. 20. The error between calculated and experimental spectrum is minimized by choosing the Voigt profile 0.1519 cm\(^{-1}\) (FWHM) with contributions of Gauss 0.09 cm\(^{-1}\) (FWHM) and Lorentz 0.095 cm\(^{-1}\) (FWHM) respectively.

In Fig.19 the mesh is presented that indicates which trials of instrument functions that have been made. The corresponding errors of these calculations are presented in Fig.20 where the Voigt profiles of the parabola to the left (right) varies the Lorentzian (Gauss) function FWHM with a fixed Gaussian (Lorentzian) FWHM of 0.095 (0.09) cm\(^{-1}\). The best fit between calculated and experimental spectrum is made by the use of a Voigt profile 0.1519 cm\(^{-1}\) (FWHM) with contributions of Gauss 0.09 cm\(^{-1}\) (FWHM) and Lorentz 0.095 cm\(^{-1}\) (FWHM) respectively. This Voigt profile together with contributions is presented in Fig.21.

The only criterium of the computational code CARSFT is that the instrument function has to be generated within the defined area (wavelengths) of the calculations. While the code is renormalizing the instrument function in a sense that the area under the graph is equal to one, the code has to be fed by the FWHM value to be held by the unique solution. In generating the instrument function file though, one has to pay attention to the grid of calculation since the wings of the Voigt function is more extended than the ones of a Gaussian function (see Fig.21). It is the shape of the instrument function that is of most interest but to minimize possible sensitiveness one has to let the wings of the Voigt function decline to a certain distinct.
Fig. 21. The Voigt profile 0.1519 cm\(^{-1}\) (FWHM) instrument function together with contributions of Gauss 0.09 cm\(^{-1}\) (FWHM) and Lorentz 0.095 cm\(^{-1}\) (FWHM).
Chapter 5

Computational code

To extract quantities such as temperature of an experimental spectrum this has to be compared with a “library” of theoretically calculated spectra at the prevailing conditions. For the generation of theoretical spectra the computational code CARSFT [10] is used, which also fits these to the experimental spectrum by a non-linear least square algorithm. The theoretical spectrum is compared with the experimental data on a point-by-point basis and the code is utilizing a chi-square technique to evaluate at which degree the fitting procedure has been accomplished. The chi-square value, based on the sum of the squares of the residuals between the computed and measured spectrum, is wished to be minimized and it is referred to as a goodness-of-fit parameter. The major source of error is assumed to be shot noise, and the variance for each point is taken to be proportional to the data. Thus the square of the residual is divided by the data at each point [10]. By this procedure all fitting points of the entire spectrum are being weighted the same, i.e. given the same importance. Even though the chi-square technique is of standard procedure in statistics the nomenclature is a bit unfortunate for this work and needs to be commented on, since it risks being confused with the susceptibility.

The user has access to as much as 30 input variables which reflects the complexity of the computational code. The variables are being set before evaluation and many of these are held fixed during the fit as they are related to the known gas constituents, polarizations of the lasers beams or the choice of molecular collision model. Some of the variables though are allowed to be varied during a fit. These are the so called fitting variables [10], of which six of the most critical are:

1. \( W \) Wavenumber expansion
2. \( H \) Horizontal shift
3. \( V \) Vertical shift
4. \( I \) Intensity expansion
5. \( P \) Probe linewidth (FWHM)
6. \( T \) Temperature

The effect of these variables is understood by their name and they have a role of accurately adjusting the theoretical CARS spectrum to the experimental spectrum. The only variable of these which needs to be explained is the probe linewidth since it is not obvious why this should be allowed to vary. According to that the code was originally written for scanning CARS a broadband setup can be approximated by the use of a non Gaussian probe laser profile implemented by an instrument function file which was described in earlier chapter. The probe linewidth variable is the FWHM value of this instrument function discussed in the same chapter.
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As a matter of fact there is no standard procedure of using the computational code in the fitting process and this work requires some operator skill. In the user and programmer information [10], advices are given only to float a few variables at a time and what can be worth mentioning is that in order to get a convergence it is important to set all variables with limits (minimum and maximum) close to the real values. A more precise parametric room minimizes the possibility of the code to terminate in a local instead of global chi-squared minima. The later advice is especially important when evaluating several spectra repeatedly and the fitting processes are not followed in detail, which is the case when running the code in batch mode for analyzing single-shot spectra. Then the working procedure is to fit an average spectrum from all the single-shots to get an idea of the settings of all variables. When a rigorous investigation about the dispersion and the instrument function has been made only small variations of the related variables \((W, P)\) are expected and they can be held fixed during a fit. The parametric room of all fitting variables that are critical can then be thought of as expressed in Eq. (37).

\[
W \times \{H, V, I\} \times P \times T \quad (37)
\]

This equation is stated to illustrate the room of variables in where the minimization of the chi-square value takes place. The grid of all variables is determined by the step size of the calculation which is set by the code to be the nominal value divided by 200. As the minimization is in progress the step sizes are getting smaller and the calculation is terminated when all these steps are within a certain size, which in general is set by the code to be the starting step size divided by 20. To some variables there are exceptions namely the starting step size of the temperature variable \((T)\) is 10 K and the limiting value is 1 K.
Chapter 6

Results and Discussion

The results from this work are mainly going to be discussed in terms of accuracy and precision of the technique. Even if accuracy is sounding to be the most critical topic in the performance of a temperature measuring instrument, it can often be helped by the minimization of related systematic errors. In this case it is instead precision, which constitutes the main size of ability and in some sense expresses the sensitivity of the technique. If the precision is small, the technique can be used to detect small variations of the measured quantity on a single-shot basis, which is of great importance when operating in turbulent flows for example.

The CARSFT code are equipped with a batch mode routine, which enables the code to be run repeatedly in evaluating the temperature of several spectra from the same operating conditions. At each of the temperatures 300 K, 600 K and 900 K, 1000 single-shot CARS spectra were recorded. The term single-shot refers to a single spectrum collected after a single pulse of the Nd:YAG laser [3]. In between the temperature measurements (while waiting for the oven temperature to rise) non-resonant argon spectra were recorded with accumulations of 200 single-shots. This recording was made 5 times to ensure that a good quality spectrum had been obtained. One aspect of good quality is to avoid that the detector pixels of interest, for the spectrally resolved CARS signal, have been disturbed by cosmic radiation.

As this experimental setup demonstrates especially improvement of the resolution at room temperature, an averaged signal from this recording is presented in Fig.22.
Fig. 22. The spectrum, recorded in room air with temperature 296 K, is averaged from 1000 single-shots spectra. Different transitions of the nitrogen Q-branch are listed.

The first temperature measurement series, referred to as 300 K, was made in room air and the real temperature was estimated by a mercury thermometer to be 296 K. At the oven temperatures of 600 K and 900 K the real temperature at the probed volume were calculated as an average between the read temperature of the three thermocouples with the following results;

\[
\begin{align*}
[600 \text{ K}]: & \quad (597 + 604 + 604) / 3 = 601.67 \approx 602 \text{ [K]} \\
[900 \text{ K}]: & \quad (899 + 911 + 914) / 3 = 908 \text{ [K]} 
\end{align*}
\]

At 900 (600) K the difference between the highest and lowest temperature value, read from the thermocouple instrument, is 15 (7) K and the temperature distribution of the tube is considered to be homogeneous.

An averaged spectrum from all the single-shots at each temperature was made to find all settings of the fitting variables which are used in the fitting process of the batch mode calculations. These spectra along with the theoretical results from CARSFT are plotted together with the residuals (difference between theoretical and experimental spectra) in Fig.23.
Chapter 6 – Results and Discussion
Chapter 6 – Results and Discussion

For all temperatures the agreement of experimental and theoretical spectra is very good. The relative height of the square root of the intensity between the different temperatures is about 1: 0.5: 0.3 which was expected according to what was discussed earlier in the chapter of spectral temperature dependence. The evaluated temperatures from these averaged spectra were 287 K, 597 K and 859 K respectively.

The instrument function, a Voigt profile 0.1519 cm\(^{-1}\) (FWHM) with contributions of Gauss 0.09 cm\(^{-1}\) (FWHM) and Lorentz 0.095 cm\(^{-1}\) (FWHM), was found from the averaged spectrum of room air which process is described in earlier chapter. The same function was used in fitting all the single-shot spectra from all the temperatures.

By letting the CARSFT code float fitting variable \((W)\) or \((H)\) the linear term \(b\) (see Eq.(34)) of the calculated dispersion was corrected by a factor 1.003 which could be obtained by minimizing the errors according to the chi-square technique. The constant term \((c)\) was shifted 3.556 cm\(^{-1}\), 3.484 cm\(^{-1}\) and 3.461 cm\(^{-1}\) in the temperature cases of 300 K, 600 K and 900 K respectively. In Table 5 the information about the initial values of the fitting parameters are gathered. There also the information is given about the range of evaluated spectral region (in terms of wavenumbers) which is used for respective temperature.

Fig. 23. Comparison between the averaged experimental spectrum from 1000 single shots and the theoretical CARSFT spectrum from temperatures 300 K, 600 K and 900 K with order starting from above.
Table 5. The initial values of the fitting parameters and the range of evaluated spectral region (in terms of wavenumbers) for respectively temperature.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>300</th>
<th>600</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber expansion</td>
<td>1.003</td>
<td>1.003</td>
<td>1.003</td>
</tr>
<tr>
<td>Horizontal shift [cm⁻¹]</td>
<td>3.556</td>
<td>3.484</td>
<td>3.461</td>
</tr>
<tr>
<td>Vertical shift</td>
<td>17.855</td>
<td>6.556</td>
<td>4.152</td>
</tr>
<tr>
<td>Intensity expansion</td>
<td>1.021</td>
<td>0.943</td>
<td>0.884</td>
</tr>
<tr>
<td>Probe linewidth (FWHM)</td>
<td>0.1519</td>
<td>0.1519</td>
<td>0.1519</td>
</tr>
<tr>
<td>Beginning wavenumber [cm⁻¹]</td>
<td>2310</td>
<td>2300</td>
<td>2280</td>
</tr>
<tr>
<td>Ending wavenumber [cm⁻¹]</td>
<td>2340</td>
<td>2340</td>
<td>2340</td>
</tr>
</tbody>
</table>

In the ordinary cases (not investigating but instead using the technique) when the temperature is not known, the initial values of the temperatures have to be estimated for the batch mode calculations of all the single-shots. If an individual spectrum is of poor quality or if the specified initial values are too far from the true conditions, CARSFT may return the initial values, which is an indication that a fit could not be successfully performed [12]. Two methods have been used in this study in order not to include such cases in the statistical material and to discriminate other single-shot spectra which are badly fitted. Another reason of analyzing the data material with these methods is to eliminate the possibility of the results to be dependent on choice of initial temperature in the fitting procedure.

The first method is found in [12]. The spectra are fit starting from three different initial values of temperature. In this work these values were chosen as 90%, 100%, and 110% of the expected temperature, which for the three different cases of interest is {270 K, 300 K, 330 K}, {540 K, 600 K, 660 K} and {810 K, 900 K, 990 K} respectively. If two of the three fitting results (evaluated temperatures) are within a preset difference from each other, the spectrum with the lowest chi-squared (goodness-of-fit) value is retained with its evaluated temperature. However if all three fitting results are separated by more than the preset difference, the spectrum is discarded. The second method is to consider only the results which are limited by a certain chi-square value. This second criterion for a spectrum to be retained is made in addition to the first method. The method can be motivated if evaluated temperatures, far from the expected, are obviously related to a bad fit with high chi-square value.

The results depending on choice of tolerance (temperature “distance”, labeled tol) and maximum chi-square value of 0.5, 1.3 and 7.3 for the temperatures 300 K, 600 K, and 900 K respectively are presented in Table 6.
Table 6. Results from the different cases of calculations. In case I all spectra are considered. In cases II and III the approaches are indicated in the left column.

<table>
<thead>
<tr>
<th>Temperature 300 K</th>
<th>Case</th>
<th>Average T [K]</th>
<th>Precision %</th>
<th>Retained spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>288.4</td>
<td>3.06</td>
<td>1000</td>
</tr>
<tr>
<td>II ( tol \ 3 \text{ K} )</td>
<td></td>
<td>287.5</td>
<td>3.28</td>
<td>801</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 0.5 )</td>
<td></td>
<td>287.4</td>
<td>3.23</td>
<td>797</td>
</tr>
<tr>
<td>II ( tol \ 2 \text{ K} )</td>
<td></td>
<td>287.5</td>
<td>3.28</td>
<td>741</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 0.5 )</td>
<td></td>
<td>287.4</td>
<td>3.23</td>
<td>737</td>
</tr>
<tr>
<td>II ( tol \ 1 \text{ K} )</td>
<td></td>
<td>287.4</td>
<td>3.28</td>
<td>610</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 0.5 )</td>
<td></td>
<td>287.3</td>
<td>3.21</td>
<td>606</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature 600 K</th>
<th>Case</th>
<th>Average T [K]</th>
<th>Precision %</th>
<th>Retained spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>596.1</td>
<td>2.79</td>
<td>1000</td>
</tr>
<tr>
<td>II ( tol \ 3 \text{ K} )</td>
<td></td>
<td>596.8</td>
<td>2.77</td>
<td>899</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 1.3 )</td>
<td></td>
<td>596.7</td>
<td>2.75</td>
<td>894</td>
</tr>
<tr>
<td>II ( tol \ 2 \text{ K} )</td>
<td></td>
<td>595.5</td>
<td>2.73</td>
<td>827</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 1.3 )</td>
<td></td>
<td>595.4</td>
<td>2.71</td>
<td>822</td>
</tr>
<tr>
<td>II ( tol \ 1 \text{ K} )</td>
<td></td>
<td>594.3</td>
<td>2.72</td>
<td>643</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 1.3 )</td>
<td></td>
<td>594.2</td>
<td>2.70</td>
<td>640</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature 900 K</th>
<th>Case</th>
<th>Average T [K]</th>
<th>Precision %</th>
<th>Retained spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>857.1</td>
<td>2.99</td>
<td>977</td>
</tr>
<tr>
<td>II ( tol \ 3 \text{ K} )</td>
<td></td>
<td>858.6</td>
<td>2.83</td>
<td>845</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 7 )</td>
<td></td>
<td>859.0</td>
<td>2.61</td>
<td>841</td>
</tr>
<tr>
<td>II ( tol \ 2 \text{ K} )</td>
<td></td>
<td>858.5</td>
<td>2.79</td>
<td>793</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 7 )</td>
<td></td>
<td>858.9</td>
<td>2.56</td>
<td>789</td>
</tr>
<tr>
<td>II ( tol \ 1 \text{ K} )</td>
<td></td>
<td>858.0</td>
<td>2.78</td>
<td>666</td>
</tr>
<tr>
<td>III ( \chi^2 &lt; 7 )</td>
<td></td>
<td>858.4</td>
<td>2.52</td>
<td>664</td>
</tr>
</tbody>
</table>

In Table 6, different cases of data analyzing methods are presented. In case I all spectra are considered. In case II all the spectra that have been retained from the three different initial temperature values are considered. Case III considers the remaining spectra which have been selected by the additional chi-square value criterion. The averaged temperature is calculated from all the evaluated single-shot spectra and the precision, expressed as relative standard deviation, is the standard deviation divided by the averaged temperature. A comment is that the initial number of spectra is 977 instead of 1000, in the temperature case of 900 K. This is because the chi-square value did not converge in 23 of the 1000 batch mode fitting processes of the single-shot spectra.

To explain the analyzing methods more explicit, illustrations are made in Figs 24 and 25. Figure 24 shows results from the evaluated temperature of the first 10 single-shots starting the fitting process with initial values of 90%, 100% and 110% (810 K, 900 K and 990 K) of the expected temperature. As the tolerance, i.e. preset difference of fitting
results is set to 1 K the only spectra to be retained for the statistical analysis is the first, the fourth, the sixth and the eighth spectra. The two figures in Fig. 25 show temperature as a function of chi-square value of all the evaluated single-shot spectra at 900 K after different restrictions. In the first figure, all fitting results with initial temperature 100 % (900 K) are shown. In the second only the spectra that have been retained from the different initial temperatures are shown. This means that some of the data points from the first to the second figure have disappeared and some may have changed place as the single-shot spectra that are retained from the different initial temperatures are the ones with the lowest chi-square value. In the second figure the single-shot spectra which are to be removed is indicated due to the additional condition of maximum chi-square value which is set to be 7.3 for the temperature 900 K.

![Fig. 24. Illustration of the first analyzing method. The figure show results from the batch mode fitting process with three different initial temperatures of the first ten single-shots. Two of three initial temperatures has to be within the preset difference of 1 K for the single-shot spectrum to be retained.](image-url)
Fig. 25. Illustrations of the second analyzing method of the data set. The figures show temperature as a function of chi-square value of all the evaluated single-shot spectra at 900 K after different restrictions.
Chapter 6 – Results and Discussion

The outcome of the results presented in Table 6 is approximately kept unchanged after the analyzing methods. The differences are at the most about 2 K in average temperature (temperature cases of 600 K) and about 0.5 % in precision (temperature cases of 900 K) in absolute numbers. Even if the tendencies are small, they are different for different temperatures. For temperature 900 K both accuracy and precision is getting slightly better, for temperature 600 K the precision is getting slightly better while the accuracy is getting slightly worse and for temperature 300 K both accuracy and precision is getting slightly worse.

While these methods are one way of analyzing the data, it needs to be commented that these tendencies could be different with other methods and therefore not needed to pay much attention to. Another comment is that why the results are kept almost unchanged is an effect of that the operating conditions of this work are ideal, in a sense that the recordings are made in room air. This analysis may serve as verification of the results and with harder operating conditions such a stability analysis may be essential.

As the relative precision (in percent) is calculated by dividing the standard deviation by the evaluated temperature, this quantity is further minimized if the accuracy of the obtained data set is decreased. This is a bit confusing why another discussion of the results instead is made by the obtained standard deviation expressed in Kelvin. Another presentation of the results is made by Figs 26, 27 and 28 where the evaluated temperature from all the retained single-shot spectra is plotted, as well as the temperature probability distribution.
Fig. 26. Temperature probability distribution functions calculated from 606 single-shot vibrational CARS spectra for temperature 300 K. $T_{th}$, thermocouple temperature; $T_{exp}$, CARS temperature; $\sigma$, standard deviation (Above). The temperature evaluated from all single-shots (Below).
Fig. 27. Temperature probability distribution functions calculated from 640 single-shot vibrational CARS spectra for temperature 600 K. $T_{th}$, thermocouple temperature; $T_{exp}$, CARS temperature; $\sigma$, standard deviation (Above). The temperature evaluated from all single-shots (Below).
Fig. 28. Temperature probability distribution functions calculated from 664 single-shot vibrational CARS spectra for temperature 900 K. $T_{th}$, thermocouple temperature; $T_{exp}$, CARS temperature; $\sigma$, standard deviation (Above). The temperature evaluated from all single-shots (Below).
What can be seen in Figs 25 and 26, of the temperature probability distribution functions, is the tendency of the temperature to be evaluated at the ten or so Kelvin closest to the expected temperature. This means that the counts of evaluated temperatures at 300 K (600 K) and 290 K (590 K) are more than at others and it seems like this appearance is related to the starting step size (10 K) of the fitting variable temperature ($T$). In fact when back tracking this tendency, the results from spectra fitted with initial temperature 100 % of the expected are the most affected why it is reasonable to suspect that the fitting procedure converge with making just one or without any further steps of this variable. As this appearance is more obvious in the temperature case of 300 K than at 600 K and has disappeared at 900 K, this problem seems to vanish for higher temperatures.

The results presented in Fig. 25, 26, 27 are also summarized in Table 7.

**Table 7.** The thermocouple and the evaluated temperature together with single-shot standard deviation from broadband vibrational CARS measurements of nitrogen in room air.

<table>
<thead>
<tr>
<th>Vibrational Cars this work</th>
<th>Thermocouple temperature [K]</th>
<th>296</th>
<th>602</th>
<th>908</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARS measurement [K]</td>
<td>287</td>
<td>594</td>
<td>858</td>
<td></td>
</tr>
<tr>
<td>Standard deviation [K]</td>
<td>9</td>
<td>16</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

To be able to compare these results with what has been found earlier; these are marked in Fig. 28 consisting of the results at the same operative conditions from reference literature [13].

![Fig. 29. The results from this work together with the ones from reference literature [13].](image-url)
The improvement of standard deviation for the technique of broadband vibrational CARS is very clear. The performance is comparable to rotational CARS at these operating conditions.

The accuracy of the results which is the difference between the thermocouple and evaluated mean temperature is calculated for respectively temperature according to;

\[
\begin{align*}
[300 \text{ K}]: & \quad 296 - 287 = 9 \text{ K (3.0 \%)} \\
[600 \text{ K}]: & \quad 602 - 594 = 8 \text{ K (1.3 \%)} \\
[900 \text{ K}]: & \quad 908 - 858 = 50 \text{ K (5.6 \%)}
\end{align*}
\]

For all temperatures the evaluated mean temperature of the CARS measurement is below the thermocouple (true) temperature. The relative accuracy is very small at temperature case of 600 K and about the same for temperature cases of 300 K and 900 K. The accuracy of the results at room temperature is improved in comparison to [13] where it is restricted to less than 25 K.

It is possible that the accuracy of these measurements could be improved with a better quality of the non-resonant spectrum, which also could lead to slightly better relative standard deviation. The source of uncertainty could also be something that is not yet discovered for this work.
Chapter 7

Conclusions

The aim of this master thesis work was to investigate how a broadband setup of the vibrational CARS technique is performing, in terms of accuracy and precision, when measuring temperatures below 1000 K. It has been of common knowledge according to the results of reference literature [13] that the technique is less suitable to use at these temperatures in comparison, for example, to rotational CARS.

With the experimental approach of using a single mode Nd:YAG laser and a back-illuminated charged coupled device (CCD) camera as detection system, a higher resolution of the lower temperature spectra has been received. The thought is that the temperature evaluation work, made by fitting theoretical spectra to the experimental spectrum with a non-linear least-square-algorithm, would be simplified with a better resolution of the experimental spectrum which thereby contains more information. It should be emphasized though that the measurements are made in room air and should probably be less resolved with increased pressure. Then the lines would be broadened by molecular collisions leading to lower resolution and in addition the total spectrum would undergo motional narrowing.

As the fitting algorithm requires wavenumbers along with the square root of the intensity of the single-shot spectra, the dispersion of the experimental data had to be calculated. This was made with a flame temperature spectrum of a Bunsen burner ensuring that all the detector pixels of interest for the spectrally resolved signal had been covered. To simulate how a spectral line is broadened by the detection system an instrument function has been calculated. This is made by trial and error, minimizing the chi-square value between a room temperature experimental spectrum averaged from all the single-shots and a theoretical spectrum calculated for the same operative conditions.

To be able to run the computational code CARSFT properly, maybe 60 % of all time for this work has been spent analyzing the required functions and the impact of all parameters involved in the fitting process. Afterwards, without exploring all its complexity the code seems easy to handle but I must say that it takes time to reach this level of understanding. This might be one of the critics of the technique, as a good evaluation of temperatures is very dependent on the knowledge of how to use the code.

Two methods have been used in this study in order to discriminate single-shot spectra of poor quality and the ones which are badly fitted. Another reason of analyzing the data material with these methods was to eliminate the possibility of the results to be dependent on choice of initial temperature in the fitting procedure.

The resulting standard deviation (relative or precision) was calculated to be 9 K (3.2 %), 16 K (2.7 %), 22 K (2.52 %) and the accuracy (relative) was found to be 9 K (3.0 %), 8 K (1.3 %), 50 K (5.6 %) at the temperatures 300 K, 600 K, and 900 K respectively. These
results show great improvement in precision of the technique. There are still uncertainties about the source of error for the inaccuracy, i.e. difference between the thermocouple and evaluated mean temperature, but if it is related to the quality of the non-resonant spectrum further experiments will find out.

It would have been interesting to extend this analysis in two ways. To further increase the temperature and see if the hot band has any effect of regaining precision and accuracy in the temperature evaluation. To see if the resolution becomes even higher, by the mounting of a relay lens system onto the charged coupled device (CCD) camera, and further increase the performance of the technique at room temperature.

At last, but not least I would like to express the great deal of knowledge I have been taught from this project. In the chain of constructing an experiment to interpret the results, it has been a lot of work including programming and the exercise in handling a larger amount of data.
Acknowledgements

References


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I would like to thank my supervisors Per-Erik Bengtsson and Fredrik Vestin for having been encouraging and very supportive throughout this work. Their knowledge about the subject and experimental skills have been essential for the results of this work. I would also like to thank David Sedarsky at the department for having introduced the CARSFT code and been helpful with some of the programming for this work.

I send thanks to Prof. Roger L. Farrow who answered questions about the CARSFT code and explained how to simulate a broadband setup by the implementation of an instrument function.

I would also like to send special thanks to Dr. Sukesh Roy who supplied us with an updated version of the computational code, containing the batch mode subroutine, which made it possible to evaluate several single-shots. I send thanks to Prof. Robert P. Lucht who answered questions about the choice of instrument function when using an unintensified CCD camera and helped us to get in contact with Dr. Sukesh Roy.

As I seldom have the opportunity to write acknowledgements I will take the chance to send thanks and love to my partner Charlotta and to our child Idun who meet us with a smile every morning.
Appendix A

Derivation of the CARS signal strength

To be derived from the equations of Maxwell the resulting wave equation is obtained [4];

\[ \nabla^2 E - \mu_0 \varepsilon_0 \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2} \]

The polarization can be divided into a linear and a non linear part respectively according to;

\[ P = P^{(1)} + P^{NL} \]

If the polarization is putted into the wave equation this will lead to;

\[ \nabla^2 E - \mu_0 \frac{\partial^2 (\varepsilon_0 E + P^{(1)})}{\partial t^2} = \mu_0 \frac{\partial^2 P^{NL}}{\partial t^2} \]

When the linear polarization is created in the material by the electric field following rewriting with the physical tensor \( \varepsilon \) can be made;

\[ \varepsilon_0 E + P^{(1)} \Rightarrow \varepsilon_0 \varepsilon \cdot E \]

The wave equation is now given by;

\[ \nabla^2 E - \mu_0 \varepsilon_0 \varepsilon \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P^{NL}}{\partial t^2} \]

The CARS signal can be written;

\[ \tilde{E}_{CARS} (z,t) = A_{CARS} \cdot \exp(ik_{CARS} z - i\omega_{CARS} t) + c.c \quad (I) \]

where \( \omega_{CARS} = \omega_{pump} - \omega_{Stokes} + \omega_{probe} \)

The polarization of the CARS signal is according to;

\[ P_{CARS} = 6 \cdot \varepsilon_0 \cdot \chi_{CARS} \cdot A_{pump}^2 A_{Stokes} A_{probe} \cdot \exp(i(k_{pump} - k_{Stokes} + k_{probe})z - i\omega_{CARS} t) \quad (II) \]

With I and II to be put into the wave equation the following equation is obtained;
Appendix A – Derivation of the CARS signal strength

\[
\left[ \frac{\partial^2 A_{\text{CARS}}(z)}{\partial z^2} + 2ik_{\text{CARS}} \frac{\partial A_{\text{CARS}}(z)}{\partial z} - (k_{\text{CARS}}^2 - \mu_0 \varepsilon_0 \varepsilon_0^2) \cdot A_{\text{CARS}}(z) \right] \cdot \exp(ik_{\text{CARS}}z - i\omega_{\text{CARS}}t)
\]

With the following rewriting to be made;

\[
\mu_0 \varepsilon_0 = \frac{1}{c^2} \quad , \quad \varepsilon = n^2 (\omega_{\text{CARS}}) \quad , \quad \mu_0 \varepsilon_0 \varepsilon_0^2 = \left( \frac{n(\omega_{\text{CARS}})}{c} \cdot \omega_{\text{CARS}} \right)^2 = k_{\text{CARS}}^2
\]

\[
\left[ \frac{\partial^2 A_{\text{CARS}}(z)}{\partial z^2} + 2ik_{\text{CARS}} \frac{\partial A_{\text{CARS}}(z)}{\partial z} \right] \cdot \exp(ik_{\text{CARS}}z - \omega_{\text{CARS}}t)
\]

and the use of “the slowly varying amplitude approximation” i.e.,

\[
\left| \frac{\partial^2 A_{\text{CARS}}(z)}{\partial z^2} \right| << k_{\text{CARS}} \left| \frac{\partial A_{\text{CARS}}(z)}{\partial z} \right|
\]

the following relations of equations is obtained;

\[
\left\{ \begin{array}{l}
2ik_{\text{CARS}} \frac{\partial A_{\text{CARS}}(z)}{\partial z} \cdot \exp(ik_{\text{CARS}}z - \omega_{\text{CARS}}t) = \mu_0 \frac{\partial^2 P_{\text{NL}}}{\partial t^2} \\
P_{\text{CARS}} = 6 \cdot \varepsilon_0 \cdot \chi_{\text{CARS}} \cdot A_{\text{pump}}^* A_{\text{Stokes}}^* A_{\text{probe}} \cdot \exp(i(k_{\text{pump}} - k_{\text{Stokes}} + k_{\text{probe}})z - i\omega_{\text{CARS}}t) 
\end{array} \right\} \Rightarrow
\]

\[
2ik_{\text{CARS}} \frac{\partial A_{\text{CARS}}(z)}{\partial z} = -\mu_0 \varepsilon_0 \cdot 6 \cdot \chi_{\text{CARS}} \cdot \omega_{\text{CARS}}^2 \cdot A_{\text{pump}}^* A_{\text{Stokes}}^* A_{\text{probe}} \cdot \exp(i\Delta k z)\quad \text{with} \quad \Delta k = (k_{\text{pump}} - k_{\text{Stokes}} + k_{\text{probe}}) - k_{\text{CARS}}
\]

\[
\frac{\partial A_{\text{CARS}}(z)}{\partial z} = i \cdot 3 \cdot \chi_{\text{CARS}} \cdot \frac{\omega_{\text{CARS}}}{c \cdot n(\omega_{\text{CARS}})} \cdot A_{\text{pump}}^* A_{\text{Stokes}}^* A_{\text{probe}} \cdot \exp(i\Delta k z)
\]

\[
\Rightarrow
\]

\[
\int_{A_{\text{CARS}}(0)}^{A_{\text{CARS}}(z)} dA_{\text{CARS}} = i \cdot \psi \cdot \int_{0}^{z} \exp(i\Delta k z')dz'.
\]

\[
\text{with} \quad \psi = 3 \cdot \chi_{\text{CARS}} \cdot \frac{\omega_{\text{CARS}}}{c \cdot n(\omega_{\text{CARS}})} \cdot A_{\text{pump}}^* A_{\text{Stokes}}^* A_{\text{probe}}
\]

\[
\Rightarrow
\]

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Appendix A – Derivation of the CARS signal strength

\[ A_{\text{CARS}}(z) - A_{\text{CARS}}(0) = 3 \cdot \chi_{\text{CARS}} \cdot \frac{\omega_{\text{CARS}}}{c \cdot n(\omega_{\text{CARS}})} \cdot A_{\text{pump}} A_{\text{Stokes}}^\ast A_{\text{probe}} \frac{1}{\Delta k} (\exp(i\Delta kz) - 1) \]

\[ A_{\text{CARS}}(0) = 0 \]

\[ A_{\text{CARS}}(z) = 3 \cdot \chi_{\text{CARS}} \cdot \frac{\omega_{\text{CARS}}}{c \cdot n(\omega_{\text{CARS}})} \cdot A_{\text{pump}} A_{\text{Stokes}}^\ast A_{\text{probe}} \frac{\exp(i\Delta kz / 2)}{\Delta k} (\exp(i\Delta kz / 2) - \exp(-i\Delta kz / 2)) \]

\[ \sin(\Delta kz / 2) = \frac{\exp(i\Delta kz / 2) - \exp(-i\Delta kz / 2)}{2 \cdot i} \]

\[ |A_{\text{CARS}}(z)| = \left| \frac{6 \cdot \chi_{\text{CARS}} \cdot \omega_{\text{CARS}}}{c \cdot n(\omega_{\text{CARS}}) \cdot \Delta k} A_{\text{pump}} A_{\text{Stokes}}^\ast A_{\text{probe}} \sin(\Delta kz / 2) \right| \]

As the intensity is proportional to the electric field strength the following condition is obtained;

\[ I \propto |A|^2 \]

and the signal strength of the CARS signal follows as;

\[ I_{\text{CARS}}(z) \propto \omega_{\text{CARS}}^2 I_{\text{pump}} I_{\text{Stokes}} I_{\text{probe}} |\chi_{\text{CARS}}|^2 z^2 \left( \frac{\sin(\Delta kz / 2)}{\Delta kz / 2} \right)^2 \]
Appendix B – Third order susceptibility

Appendix B

Third order susceptibility

The following expression has been derived in reference literature [4];

\[
\chi^{(3)}_{kijh}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) = \frac{N}{h^3} \sum_{vml} P_{ij}^{(0)} \times \left[ \begin{array}{l}
\mu_{vnm}^h \mu_{ml}^h \mu_{ml}^k \mu_{ml}^j \mu_{ml}^i \\
(\omega_{vl} - \omega_p - \omega_q - \omega_r) - i \gamma_{vl} \left( \omega_{ml} - \omega_p - \omega_q \right) - i \gamma_{ml} \left( \omega_{ml} - \omega_p \right) - i \gamma_{ml}
\end{array} \right] (1)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^h \mu_{ml}^h \mu_{ml}^j \mu_{ml}^k \mu_{ml}^i \\
(\omega_{vm} - \omega_p - \omega_q - \omega_r) - i \gamma_{vm} \left( \omega_{mv} - \omega_p - \omega_q \right) - i \gamma_{mv} \left( \omega_{ml} - \omega_p \right) + i \gamma_{vl}
\end{array} \right] (2)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^h \mu_{ml}^k \mu_{ml}^j \mu_{ml}^i \\
(\omega_{rn} - \omega_p - \omega_q - \omega_r) - i \gamma_{rn} \left( \omega_{ml} + \omega_p + \omega_q \right) + i \gamma_{rm} \left( \omega_{ml} - \omega_p \right) - i \gamma_{ml}
\end{array} \right] (3)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^k \mu_{ml}^h \mu_{ml}^j \mu_{ml}^i \\
(\omega_{vn} + \omega_p + \omega_q + \omega_r) + i \gamma_{vn} \left( \omega_{nv} - \omega_p - \omega_q \right) - i \gamma_{mv} \left( \omega_{ml} - \omega_p \right) - i \gamma_{vl}
\end{array} \right] (4)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^k \mu_{ml}^i \mu_{ml}^j \mu_{ml}^h \\
(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i \gamma_{nm} \left( \omega_{nm} + \omega_p - \omega_q \right) - i \gamma_{mv} \left( \omega_{ml} - \omega_p \right) + i \gamma_{vl}
\end{array} \right] (5)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^k \mu_{ml}^i \mu_{ml}^h \mu_{ml}^j \\
(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i \gamma_{nm} \left( \omega_{nm} + \omega_p + \omega_q \right) + i \gamma_{mv} \left( \omega_{ml} - \omega_p \right) - i \gamma_{ml}
\end{array} \right] (6)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^k \mu_{ml}^i \mu_{ml}^h \mu_{ml}^j \\
(\omega_{ml} + \omega_p + \omega_q + \omega_r) + i \gamma_{ml} \left( \omega_{ml} + \omega_p + \omega_q \right) + i \gamma_{vm} \left( \omega_{ml} + \omega_p \right) + i \gamma_{vl}
\end{array} \right] (7)
\]

\[
+ \left[ \begin{array}{l}
\mu_{vnm}^k \mu_{ml}^i \mu_{ml}^h \mu_{ml}^j \\
(\omega_{ml} + \omega_p + \omega_q + \omega_r) + i \gamma_{ml} \left( \omega_{ml} + \omega_p + \omega_q \right) + i \gamma_{vm} \left( \omega_{ml} - \omega_p \right) + i \gamma_{vl}
\end{array} \right] (8)
\]