Measurement of Hydrogen Peroxide Concentration in Liquid Phase Using Raman Spectroscopy

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Master of Science Thesis
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Abstract

At Tetra Pak, hydrogen peroxide (H$_2$O$_2$) is used to sterilize food packages. The main focus of this work was to investigate the potential of Raman spectroscopy as a method to make concentration measurements of H$_2$O$_2$/H$_2$O solutions. In these experiments a continuous wave frequency doubled Nd:YAG laser was used to illuminate the sample. As a first experiment the sample was placed in a quartz glass cuvette. In a second experiment a levitator was used to enable measurements on much smaller sample volumes in the form of levitated droplets. Raman spectra of H$_2$O$_2$/H$_2$O solutions with different concentrations of H$_2$O$_2$ were recorded. The calibration curves of both experiments showed good agreement with a linear function.

Raman scattering is a weak process compared to other scattering and radiation processes, for example fluorescence. Time-resolved measurements were made using 30 ps pulses from a mode-locked frequency-doubled Nd:YAG laser to investigate the possibility to distinguish the Raman signal in the presence of fluorescence. The results indicate a good potential for the concept.

With ultrashort pulses from a mode-locked laser it is possible to get the high peak intensity needed for the stimulated Raman effect to appear. Scattering from a stimulated Raman process is much stronger than scattering from a spontaneous Raman process. In contrast to spontaneous Raman scattering, the stimulated Raman scattering forms a coherent laser-like beam, which results in a very efficient signal collection. Due to the fact that the enhancement of the scattering from the two species could not be predicted, the stimulated Raman scattering spectra could not be used to determine H$_2$O$_2$ concentration.
1 Introduction

Tetra Pak uses hydrogen peroxide ($\text{H}_2\text{O}_2$) to sterilize food packages. In this process it is crucial that the dose of $\text{H}_2\text{O}_2$ is high enough to kill all microorganisms. It is also important to be able to control the residue of $\text{H}_2\text{O}_2$ left in the package for consumer safety reasons. The present-day technique used to analyze $\text{H}_2\text{O}_2$ concentration is by microbiological testing. This is both time consuming and expensive. A laser-based technique, such as Raman spectroscopy, has the advantage of being non-intrusive and having high spatial and temporal resolution. All of these properties could be beneficial in the aim for making monitoring of $\text{H}_2\text{O}_2$ concentration as effective as possible. In this diploma work, Raman spectroscopy is investigated as an alternative technique to determine hydrogen peroxide concentration in $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solutions.

The Raman effect is an inelastic process, i.e. the light illuminating the sample will, after being scattered by the molecules in the sample, be shifted in frequency from the frequency of the illuminating light. The shift in frequency corresponds to the energy of the vibrational motion of the molecules in the sample. The vibrational motions and corresponding frequency shifts are unique for each molecular species. Each molecular species therefore has its own unique fingerprint. Raman spectroscopy can therefore be used for multi-species concentration measurements.
2 Background Theory

2.1 Classical Description of Raman Scattering

An electric dipole consisting of two charges $q$ of equal magnitude and opposite sign, separated by a distance $d$, has a dipole moment $P$.

$$P = qd$$

(1)

If the dipole is oscillating, the dipole will send out electromagnetic radiation of the same frequency as the frequency of the oscillation.

A molecule that is put into an electric field $E$ will be distorted. The negatively charged electrons of the molecule are drawn towards the positive pole of the E-field and the positively charged nucleus of the molecule is drawn towards the negative pole of the E-field. The E-field induces an electric dipole moment in the molecule. The molecule is said to be polarized. The size of the induced dipole moment is determined by the magnitude of the applied electric field and the polarizability $\alpha$ of the molecule:

$$\mu = \alpha E$$

(2)

The polarizability of a molecule is a measure of how easy it is to distort its charge distribution. A molecule that is equally easy to polarize regardless of the direction of the applied E-field, has an isotropic polarizability. This is not always the case. The diatomic $H_2$ molecule is an example of a molecule with isotropic polarizability. When the E-field is applied along the axis of the molecule, the electrons are more easily displaced than when the E-field is applied across the axis of the molecule, as seen in Fig. 1a and Fig. 1b. The polarizability of the molecule in various directions is described by a polarizability ellipsoid, as seen in Fig. 1c and Fig. 1d. The molecule is easiest to polarize if the E-field is applied in the direction of the shortest line through the ellipsoid that also passes the middle point of the ellipsoid.

![Figure 1](image-url)

*Figure 1. In (a) and (b) the electric field is applied respectively across and along the axis of a $H_2$ molecule. The polarizability ellipsoids corresponding to the situation in (a) and (b) are shown in (c) and (d) respectively. [1]*
If the polarizability of the molecule is anisotropic, the polarizability is represented by a tensor.

\[
\alpha = \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\]

If a molecule is subjected to radiation from a laser of frequency \(v_{exc}\), \(E\) will be a time varying electric field described by:

\[
E = E_0 \sin 2\pi v_{exc}t
\]  

(3)

where \(E_0\) is the amplitude of the electric field. This results in the molecule taking the form of an oscillating dipole radiating at the same frequency as the frequency of the applied electric field, i.e. Rayleigh scattering.

If the molecule at the same time undergoes a vibration, the polarizability of the molecule may change with the vibration. The polarizability is then best described as a time varying term that depends on the vibrational frequency of the molecule.

\[
\alpha = \alpha_0 + \left(\frac{\delta \alpha}{\delta Q}\right)_0 Q
\]  

(4)

where \(\alpha_0\) is the polarizability of the molecule at its equilibrium position and \((\delta \alpha/\delta Q)_0\) is the rate of change of the polarizability with the vibration at the equilibrium position of the molecule. \(Q\) describes the vibration of the molecule:

\[
Q = Q_0 \sin 2\pi v_{vib}t
\]  

(5)

where \(Q_0\) is the amplitude of the vibration and \(v_{vib}\) is the frequency of the molecular vibration.

Using the trigonometric formula \(\sin A \sin B = \frac{1}{2} \{\cos(A - B) - \cos(A + B)\}\),

Eq. (2) can now with the help of Eq. (3), Eq. (4) and Eq. (5) be written as:

\[
\mu = \left(\alpha_0 + \left(\frac{\delta \alpha}{\delta Q}\right)_0 Q_0 \sin 2\pi v_{vib}t\right)\left(E_0 \sin 2\pi v_{exc}t\right)
\]

\[
\mu = \frac{\alpha_0 E_0}{\text{Rayleigh}} \sin 2\pi v_{exc}t + \frac{1}{2} \left(\frac{\delta \alpha}{\delta Q}\right)_0 Q_0 E_0 \left\{\cos 2\pi \left(v_{exc} - v_{vib}\right)t - \cos 2\pi \left(v_{exc} + v_{vib}\right)t\right\}
\]  

(6)
This expression has three terms; the first term corresponds to the elastic Rayleigh scattering, while the other two terms correspond to the inelastic Raman scattering. The Raman component at the lower frequency \( (v_{exc} - v_{vib}) \) is called the Stokes component whereas the higher frequency term \( (v_{exc} + v_{vib}) \) is called the anti-Stokes component.

By this classical picture the Stokes and anti-Stokes components are predicted to be of equal intensity. To get a correct picture of the intensities quantum mechanical theory of Raman scattering has to be addressed.

### 2.2 Quantum Mechanical Theory of Raman Scattering

Rayleigh scattering is an elastic process meaning that the scattered light is of the same frequency as the frequency of the photons impinging on the molecules. The scattered light is thus unshifted in frequency. Some of the light will however be shifted in frequency after interacting with the molecule. This frequency shift corresponds to the frequency of the vibration of the molecule. The shift can be either to a lower frequency (Stokes shift) or to a higher frequency (anti-Stokes shift), as was shown in the classical description of Raman scattering (see Fig. 2).

![Figure 2](image_url) Elastic Rayleigh scattering and the two components of the inelastic Raman scattering process.
The population of molecules at the different vibrational energy levels is given by the Boltzmann distribution. The population ratio of two energy levels is given by:

\[
\frac{N_u}{N_l} = e^{-(E_u - E_l)/k_BT} \tag{7}
\]

where \(N_u\) and \(N_l\) are the populations of the upper and lower state, \(k_B\) is the Boltzmann constant, \(T\) is the temperature and \(E_u\) and \(E_l\) are the energies of the upper and lower state. In the Rayleigh process and Stokes process, the molecules usually originate from the ground state because of the abundance of molecules in this state at normal temperatures. Molecules situated at higher states can contribute both to the Rayleigh- and Stokes signals. The contribution is however small at room temperature due to the much lower populations at higher vibrational states.

In the anti-Stokes process, where the scattered light is shifted towards higher frequencies, molecules in the ground state can not contribute to the signal. In this case only the much lower populated higher states can contribute to the signal. This is the reason why the anti-Stokes component is weaker than the Stokes component at normal temperatures as schematically shown in Fig. 3. The distribution of the molecules over the energy states will change with the temperature according to the Boltzmann distribution. As the temperature rises more molecules will populate higher energy states. By comparing the intensities of the anti-Stokes and Stokes components, the temperature can be determined.

Not all vibrations will result in Raman scattering. To determine if a vibration is Raman active, it is a good idea to first study the different ways a molecule can vibrate, which will be discussed in the following section.

Figure 3. Intensity of Rayleigh scattering, anti-Stokes Raman scattering and Stokes Raman scattering. Note that the relative intensities of the Rayleigh, Stokes and anti-Stokes components depicted here are not in scale. Rayleigh scattering is typically 1000 times stronger than Raman scattering. The anti-Stokes component is also at normal temperatures much weaker than the Stokes component.
2.3 Vibrational Modes

Vibrational motions of molecules where each atom is oscillating with the same frequency and pass its equilibrium position at the same time as all of the other atoms, are called fundamental modes of vibration. The number of fundamental vibrational modes of a molecule depends on the number of atoms in the molecule and whether it is linear or non-linear. Linear molecules consisting of N atoms have 3N-5 fundamental vibrational modes while non-linear molecules have 3N-6 fundamental modes. The linear CO$_2$-molecule and the non-linear H$_2$O-molecule will here serve as examples. As can be seen in Fig.4 the linear CO$_2$-molecule has four fundamental vibrational modes, and the non-linear H$_2$O-molecule has three fundamental vibrational modes as seen in Fig. 5.

![Figure 4. The CO$_2$ molecule and its four fundamental vibrational modes. There are two bending motions. One is moving in the plane of the paper (c) and the other one perpendicular to this, in and out of the paper(d). The energy of the two motions is the same i.e. the two bending modes are in this case degenerate.](image)

![Figure 5. The H$_2$O molecule and its three fundamental vibrational modes.](image)

2.4 Raman Active Vibrational Modes

For a vibrational mode to be Raman active, the vibration has to cause some change of the polarizability of the molecule. The polarizability ellipsoid of the molecule has to change either in magnitude, shape or direction during the vibration. In Fig. 6 the vibrational modes of water is shown. For each vibration the polarizability ellipsoids of the molecule is shown at the equilibrium position of the molecule and at the turning-points of the vibration. When the bond is stretched out, causing the hydrogen atoms to be situated further away from the oxygen atom, the molecule will be polarized more easily, whereas when the hydrogen atoms at the other extreme is situated closer to the oxygen atom, the molecule will be less easy to polarize. In all of the three vibrational modes depicted in Fig. 6, the vibrational motion causes a change of the polarizability ellipsoid. In (a) the size changes, in (b) the shape changes and in (c) the direction of the ellipsoid changes. Thus, all three fundamental vibrational modes of the water molecule are Raman active.
Figure 6. The three vibrational modes of $\text{H}_2\text{O}$ and the change in shape, size and direction of the polarizability ellipsoid of the water molecule. The column in the middle shows the equilibrium position of the molecule, while to the left and right the exaggerated extremes of the vibrations are shown. All three modes are Raman active.

All three vibrational modes of the $\text{CO}_2$ molecule, seen in Fig. 7, cause a change in the polarizability ellipsoid. One might think that all three therefore are Raman active, but this is not the case. Even though both the bending motion and the asymmetric stretch cause the polarizability ellipsoid to change in size, these modes are not Raman active. For the bending motion, $\xi$ describes the angle with which the molecule is distorted from its equilibrium position. It is clear that the polarizability will increase equally much independent of whether the angle is positive or negative. Therefore the derivative of the polarizability near the equilibrium position of the molecule is zero. For the asymmetric stretch, $\xi$ is a parameter of how stretched out or compressed the bond is. It is evident that a compression on one side or the other will cause an equal decrease in the polarizability of the molecule as a whole. The derivative of the polarizability will also in this case be zero for small displacements from the equilibrium position.
2 Theory

![Vibrational modes of CO2](image)

**Figure 7.** Vibrational modes of CO2. The symmetric stretching mode is Raman active, while the asymmetric stretching mode and the bending mode are not.

### 2.5 Overtones and Combination Bands

For Raman scattering the most common transition is when the molecule makes its way from one vibrational level to an adjacent vibrational level, also called fundamental transitions or first order harmonic:

\[
\Delta v = \pm 1
\]

It is also possible for the molecule to make transitions:

\[
\Delta v = \pm 2, \pm 3...
\]

These transitions are called overtones or higher order harmonics. The probabilities of these transitions decrease rapidly with increasing order of the harmonic. The same rules apply to higher orders harmonics as first order when determining whether the transition is Raman active or not.
2 Theory

\[ \frac{d^n}{d_n T} \neq 0, \text{ for the } n^{th} \text{ order} \tag{8} \]

This means, for example that the second order harmonic might be Raman active even if the first order harmonic is not. There is also a possibility of combinations of two harmonics being active even if the harmonics separately are not.

2.6 Fermi Resonance

Generally, fundamental frequencies are the only vibrations that need to be considered in Raman spectroscopy since most overtones and combination bands are too weak to be observed. However, there is a resonance phenomenon called Fermi resonance that can occur if an overtone of a vibration is close in frequency to a fundamental vibration of the same molecule. The closeness of the frequencies of the two vibrations enables an exchange of energy from the stronger fundamental vibration to the weaker overtone vibration, i.e., the overtone vibration “steals” energy from the fundamental vibration.

When a fundamental vibrational mode resonates with an overtone of another vibrational mode, the energy levels of the two vibrations usually make a slight shift in frequency. The frequency of the upper level makes a small shift towards higher energy while the lower level makes a small downward shift from its original energy.

For a molecule with several Raman active fundamental vibrational modes, overtones and combination bands, the chance of two of these having about the same frequency and thereby give rise to Fermi resonance between them would be reasonably high. However merely the fact that two vibrational levels are set close together does not necessarily mean that they will resonate. The symmetry of the molecule and the nature of the vibrational modes involved are determining factors in whether or not the near degeneracy of the energy levels will result in Fermi resonance.

2.7 Non-linear Effects

2.7.1 Hyper Raman Scattering

Earlier in Eq. 2 the induced dipole moment was described to be linear to the electric field. This approximation works well as long as the electric field intensity is not too high. For high electric field strengths the non-linear contributions can no longer be neglected and the expression for the induced dipole is:

\[ \mu = \frac{\alpha E}{\rho^{(1)}} + \frac{1}{2} \frac{\beta E^2}{\rho^{(2)}} + \frac{1}{6} \frac{\gamma E^3}{\rho^{(3)}} \ldots \quad \alpha \gg \beta \gg \gamma \tag{9} \]

Where \( \alpha, \beta \) and \( \gamma \) are the polarizability, hyperpolarizability and the second hyperpolarizability of the molecule.
The electric field of the radiation from the laser is given by:

\[ E = E_0 \cos 2\pi \nu_{\text{exc}} t \]  \hspace{1cm} (10)

where \( \nu_{\text{exc}} \) is the frequency of the laser.

A simple harmonic oscillation approximates the vibration of the molecule:

\[ Q = Q_0 \cos 2\pi \nu_{\text{vib}} t \]  \hspace{1cm} (11)

and the hyperpolarizability is given by:

\[ \beta = \beta_0 + \left( \frac{\delta \beta}{\delta Q} \right)_0 Q \]  \hspace{1cm} (12)

With (10), (11) and (12) put into the expression for the second-order induced dipole moment \( P^{(2)} \) and using the trigonometric identity,

\[ 2 \cos A \cos B = \cos(A + B) + \cos(A - B) \]

the expression for the second-order induced dipole moment can now be written:

\[
P^{(2)} = \frac{1}{4} \beta_0 E_0^2 + \frac{1}{4} \beta_0 E_0^2 \cos 2\pi \nu_{\text{exc}} t + \frac{1}{8} \left( \frac{\delta \beta}{\delta Q} \right)_0 Q_0 E_0^2 \left[ \cos(2\nu_{\text{exc}} + \nu_{\text{vib}})2\pi t + \cos(2\nu_{\text{exc}} - \nu_{\text{vib}})2\pi t \right] + \frac{1}{4} \left( \frac{\delta \beta}{\delta Q} \right)_0 Q_0 E_0^2 \cos 2\pi \nu_{\text{vib}} t \]  \hspace{1cm} (13)

For hyper Rayleigh scattering to occur the hyperpolarizability tensor can not be equal to zero at the equilibrium position of the molecule. Hyper Raman scattering only occur if the derivative of the hyperpolarizability tensor is non-zero at equilibrium. The hyper Raman scattering processes are extremely weak and have not been observed in the present work.

### 2.7.2 Stimulated Raman Scattering

For even higher laser irradiances, stimulated Raman scattering occurs. The irradiance of the laser is so high that Stokes shifted photons will give rise to further Stokes shifts, see Fig.8. The first anti-Stokes shifted photons can in the same way give rise to a second order anti-Stokes shift. The second order anti-Stokes shifted photons can result in a third order anti-Stokes shift and so on.
Figure 8. Stimulated Raman scattering. First, second and third order Stokes- and anti-Stokes-shifts.

The efficiency of the conversion of the pumping radiation to the first Stokes component can exceed 10%. The conversion to higher order components are much weaker and decrease rapidly with increasing order. Stimulated Raman will in most cases only increase the intensity of the strongest Raman line of a molecule. The appearance of a spectrum can therefore change when the threshold for the strongest Raman line is reached and stimulated Raman occurs for this line. Weaker vibrational modes can appear much weaker or even disappear in comparison to the mode that is enhanced by the stimulated Raman effect.
3 Methods

3.1 Hydrogen Peroxide Concentration Determination

The following section describes a method, based on Raman scattering, for measuring hydrogen peroxide (H$_2$O$_2$) concentration in solutions consisting of only H$_2$O$_2$ and water. Hydrogen peroxide molecules consist of two oxygen atoms and two hydrogen atoms. Fig. 9 shows how the atoms bond to form the molecule.

![Structure of a hydrogen peroxide molecule. θ (H-O-O angle): 95° ± 2°. Φ: 120° ± 3°.][2]

Figure 9. Structure of a hydrogen peroxide molecule. θ (H-O-O angle): 95° ± 2°. Φ: 120° ± 3°. [2]

![Structure of a water molecule.][3]

Figure 10. Structure of a water molecule.

In hydrogen peroxide molecules, the two most prominent vibrations giving rise to Raman scattering are the stretch between the two oxygen atoms (OO-stretch) and the symmetrical stretch between the oxygen and hydrogen atoms (OH-stretch). The water molecule consists of one oxygen atom and two hydrogen atoms as seen in Fig. 10. In water the symmetrical stretch between the oxygen and hydrogen atoms is the most prominent vibration (OH-stretch). The OO-stretch gives rise to a narrow peak at about 900 cm$^{-1}$. The OH-stretch in both the hydrogen peroxide molecule and in the water molecule gives rise to a broad peak at about 3400 cm$^{-1}$ as can be seen in Fig. 16. Since the OO-stretch only is present in the hydrogen peroxide molecule, the intensity of this peak could be used as a measure of the concentration of hydrogen peroxide. However this is not a reliable way of determining the concentration of hydrogen peroxide since the intensity of the peak besides the concentration of hydrogen peroxide molecules also will depend on the intensity of the laser, the size of the probe volume, the efficiency of the light collecting system of the signal, etc. To make measurements insensitive to fluctuations in these parameters, the Raman signal due to the OH-stretch may be used. The assumption that the OH-stretch in a hydrogen peroxide molecule and a water
molecule give equal contributions to the Raman scattering signal is made. The strength of the OH-peak is then proportional to the total number of hydrogen peroxide molecules and water molecules. The ratio of the OO-peak and the OH-peak intensities is proportional to the mole fraction of hydrogen peroxide:

\[
\frac{I_{\text{OO-stretch}}}{I_{\text{OH-stretch}}} = \frac{\text{number of } \text{H}_2\text{O}_2 \text{ molecules}}{\text{number of } \text{H}_2\text{O}_2 \text{ and } \text{H}_2\text{O} \text{ molecules}} = \text{mole fraction of } \text{H}_2\text{O}_2 \quad (14)
\]

An adjustment has to be made to Eq. 13 due to the fact that the Raman scattering cross sections are not the same for the OO-vibration and the OH-vibration. For the ratio to reflect the number of hydrogen peroxide molecules compared to the total number of molecules, the different scattering cross sections of the OO-stretch and the OH-stretch has to be taken into consideration. The intensities of the Raman scattered signals of the two vibrations are:

\[
\begin{align*}
I_{\text{OO-stretch}} &\propto \sigma_{\text{OO}} x_{\text{H}_2\text{O}_2} \\
I_{\text{OH-stretch}} &\propto \sigma_{\text{OH}} (x_{\text{H}_2\text{O}} + x_{\text{H}_2\text{O}_2})
\end{align*} \quad (15)
\]

Where \(\sigma_{\text{OO}}\) and \(\sigma_{\text{OH}}\) are the Raman scattering cross sections of the OO-stretch and the OH-stretch, \(x_{\text{H}_2\text{O}_2}\) is the number of \(\text{H}_2\text{O}_2\) molecules and \(x_{\text{H}_2\text{O}}\) is the number of \(\text{H}_2\text{O}\) molecules. The scattering cross section of the OH-stretch is assumed to be the same for hydrogen peroxide molecules as for water molecules. Tabulated values of the relative intensities of the OO-stretch and OH-stretch in hydrogen peroxide are used.

**Table 1. Relative Raman intensities for \(\text{H}_2\text{O}_2\). [3]**

<table>
<thead>
<tr>
<th>H(_2)O(_2)</th>
<th>Frequency (\text{cm}^{-1})</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O}_2)</td>
<td>(869)</td>
<td>10</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>(3593)</td>
<td>8</td>
</tr>
</tbody>
</table>

The ratio of the OO-peak and the OH-peak can now be written:

\[
\begin{align*}
\frac{I_{\text{OO-stretch}}}{I_{\text{OH-stretch}}} &= \frac{\sigma_{\text{OO}} x_{\text{H}_2\text{O}_2}}{\sigma_{\text{OH}} (x_{\text{H}_2\text{O}} + x_{\text{H}_2\text{O}_2})} = \frac{10 x_{\text{H}_2\text{O}_2}}{8 (x_{\text{H}_2\text{O}} + x_{\text{H}_2\text{O}_2})} \\
\Rightarrow \quad \frac{8}{10} \frac{I_{\text{OO-stretch}}}{I_{\text{OH-stretch}}} &= \text{mole fraction of } \text{H}_2\text{O}_2
\end{align*} \quad (16)
\]
3.2 Fluorescence Rejection by the Use of Time Resolved Measurements

Due to the weak signal of Raman scattering, experiments are sensitive to any impurities in the sample or materials that are causing fluorescence. The cross-section of fluorescence is several orders of magnitude larger than that of Raman scattering, making it difficult to distinguish the Raman signal in the presence of fluorescence. Unlike Rayleigh scattering that is emitting radiation of a single wavelength and usually can be filtered out, fluorescence is emitted at a broad range of wavelengths. This makes it hard to use spectral filters for discrimination against fluorescence. What can be taken advantage of, is the different time durations of fluorescence and Raman scattering. Raman scattering is essentially an instantaneous process (on the femto-second time scale) whereas fluorescence normally is more extended in time. If a pulsed laser is used, the Raman signal will be present only during the extent of the laser pulse. Using laser pulses whose durations are significantly shorter than the lifetime of the fluorescence radiation and only collect the very first part of the signal, all the Raman signal is collected but only a small part of the fluorescence is collected. With a streak camera it is possible to do such time-resolved measurements. A streak camera is described later on in the section on experimental equipment.
4 Experimental Equipment

4.1 Continuous Wave Laser

The continuous wave laser used in some of the experiments was a 40 mW frequency-doubled Nd:YAG laser radiating at 532 nm.

4.2 Spectrometer

A spectrometer resolves the light into its different wavelength components. Texas Instruments SpectraPro 150i is a reflection grating spectrometer with a Czerny-Turner arrangement seen in Fig. 11 that was used in the experiments. The spectrometer has two different gratings giving different resolutions and spectral ranges, one with 300 grooves/mm and the other with 1200 grooves/mm.

![Figure 11. Czerny-Turner spectrometer with entrance slit (B), mirrors (C and E), reflection grating (D) and exit slit (F).](image)

The resolving power of the reflection grating inside the spectrometer is given by:

\[
R = \frac{\lambda}{d\lambda} = kN
\]

(17)

where \(N\) is the number of grooves in the reflection grating being illuminated. Since the resolving power of the grating is proportional to the number of grooves illuminated, the best resolution is achieved if the whole width of the grating is illuminated. At the same time it is important that no part of the light is spread outside of the edges of the grating since this light then would be lost and result in weakening of the recorded signal.

The spectrometer is designed to have a lens of a specific f-number that focuses the light onto the entrance slit of the spectrometer. Choosing a lens that matches the optimal f-number for the spectrometer ensures that the light is spread across the entire grating, thereby resulting in the best possible resolving power as well as strength of the recorded signal.
The f-number of a lens or mirror is defined as:

\[ \frac{f}{\#} = \frac{f}{D} \]

where \( f \) is the focal length and \( D \) the diameter of the lens/mirror.

### 4.3 Notch Filter

To filter out Rayleigh scattered light, a holographic notch filter is used. Rayleigh scattering is a much stronger process than Raman scattering, typically three orders of magnitude stronger. Particularly Raman lines with a small shift may disappear in the “wings” of the much stronger Rayleigh scattered light. Even if the Raman lines of interest are spectrally well separated from the Rayleigh scattered light, there is another reason why a filter is useful. If a filter is not used, the much stronger Rayleigh scattered light will set the limit for the exposure time and gain of the CCD-camera before saturating the chip. A filter enables a longer exposure time which is advantageous in terms of a better signal-to-noise ratio. Without a filter the much stronger Rayleigh scattered light will set the limit for how long the exposure time and gain of the CCD-camera can be used before saturating the chip.

### 4.4 Pico-Second Pulsed Laser

In order to perform experiments with high temporal resolution, a laser generating very short laser pulses is needed. In addition, the laser must provide pulses of high intensity in order to generate stimulated Raman scattering. Such laser pulses can be generated using a technique called mode-locking, and this method will therefore be briefly explained in this section. In the cavity of a laser, standing waves, i.e. longitudinal modes, where multiples of half the wavelength of the light equals the length \( L \) of the laser cavity can emerge:

\[ L = \frac{\lambda_n}{2} \quad n = 1, 2, 3... \]

where \( \lambda_n \) is the wavelength of the mode \( n \).

The frequency between adjacent modes is:

\[ \Delta \omega = \frac{c}{2L} \]

The number of modes that can oscillate simultaneously is limited to the modes that fall within the gain profile of the laser (see Fig. 12). Since the difference in frequency between adjacent modes is small, many modes will fall within the gain profile. Unless the modes are phase-locked, the sum of all the modes will just add up to a noisy signal. In order to get short pulses of high peak intensity, mode-locking is required.
Mode-locking can either be active or passive. To achieve active mode-locking a device that sinusoidally modulates the amplitude of the light in the cavity, e.g. an acousto-optic modulator, is placed inside the cavity of the laser. If the frequency of the amplitude modulator is matched with the cavity mode spacing, each mode will have sidebands that couple to adjacent modes. Eventually all modes are coupled and phase-locked.

Passive mode-locking is achieved by e.g. placing a saturable absorber inside the laser cavity. Light of low intensity will be absorbed while high intensity spikes are transmitted. After many roundtrips in the cavity, mode-locking is achieved and only pulses of high intensity and short time-duration will exist in the cavity. At one side of the laser cavity there is an output coupler which transmits a small fraction of the laser light. This result in a train of pulses separated in time by the laser cavity roundtrip time i.e. \( 2L/c \).

**4.5 Streak Camera**

The use of a streak camera has the advantage of in addition to frequency resolution, which is accomplished using a spectrometer, adding time-resolution to the measurements. Due to the different durations of fluorescence and Raman scattered light, time-resolved measurements allows the Raman scattered light to be separated from most of the fluorescence.

The principle of a streak camera is schematically illustrated in Fig. 13. Inside the streak camera there is a photocathode. When photons hit the photocathode photoelectrons are emitted. The electrons are then accelerated in a tube where they pass in between two plates. To get a time-dependent deflection of the photoelectrons, a fast voltage sweep is applied across the two plates. Electrons arriving in the beginning of the sweep when the electric field is equal to zero will continue on moving in its original direction. Electrons
arriving later into the sweep will experience a stronger electric field and will therefore be more deflected. The later into the sweep the electrons arrive, the more altered the original direction of the electrons will be.

Figure 13. Principle of a streak camera. [4]

4.6 Levitator

A levitator (see Fig. 14) consists of an ultrasonic radiator and a reflector placed opposite to each other. The reflector has a micrometer screw attached to it so that the distance between the radiator and reflector can be adjusted. If the distance is a multiple of half wavelengths, a standing wave will be established. Droplets will levitate just below the nodes due to axial radiation pressure which acts opposite to the gravitational field. A radial Bernoulli stress is also present, that keeps the droplet in place vertical wise. The Bernoulli stress arises from a small divergence of the standing wave that is about 1/5 of the axial force. Without the effect of gravity, the droplet would have been positioned at the nodes. To compensate for the gravitational force on the droplets, an upward force is required which is reflected by the fact that the droplets have a small displacement from the nodes. The droplets are in a stable state a little bit underneath the nodes. The droplets have to be smaller than half of the wavelength in diameter in order to be able to levitate. The ultrasonic levitator that was used (Tec 5 AG) operates at 58 kHz, levitating droplets of diameters ranging from 15 μm to about 2.5 mm. The intensity of the soundwave can be adjusted to suit different sizes of droplets. If the intensity is to low the upward force will not be strong enough to make the droplet levitate. Too high intensity will result in deformation of the droplet. It will become compressed in the direction of the soundwave and expand in the horizontal direction.
**Figure 14.** Levitator and the acoustic pressure distribution in the resonator.
5 Experimental Work and Results

5.1 Sample in Cuvette

As a first experiment (see Fig. 15), a cuvette made of quartz glass was filled with a mixture of hydrogen peroxide and water in liquid form. A continuous wave frequency doubled Nd:YAG laser radiating at 532 nm with a power of about 40 mW was used to illuminate the sample. A plane convex lens (L1 in Fig. 15) put in between the laser and the sample focuses the laserbeam giving it a smaller beamwaist. This does not increase the intensity of the Raman scattered light but because it is generated from a smaller volume it is easier to collect a larger part of the scattered light. Also the volume of the sample contributing to the signal is smaller and therefore less sensitive to fluctuations in the sample itself. A lens of focal length 300 mm was used.

Two lenses were used to collect the signal (L2 and L3 in Fig. 15). To collect as much as possible of the isotropically scattered Raman signal, the lens nearest the sample needs to have a short focal length and a large diameter i.e. a low f-number. A lens with a diameter of 50 mm and a focal length of 50 mm was used. A second lens is needed to focus the signal onto the slit of the spectrograph. The focal length and diameter of this lens is chosen in such a way that it matches the f-number of the spectrograph used. A lens with a diameter of 50 mm and a focal length of 200 mm was used.

A notch filter is used to filter out the Rayleigh scattered light. The filter is designed for rays impinging normal to the filter and is therefore placed in between the two collecting lenses where the rays are parallel to one another and normal to the filter.

The spectrograph was placed so that the entrance slit is situated horizontally, collecting signal from most of the length of the laser passing through the sample. In the spectrograph there are two gratings giving different resolutions available. In order to fit the two Raman peaks of interest into the same spectral window, the low resolution grating with 300 grooves/mm is used.
Raman spectra of eleven different concentrations were recorded. Three measurements for each concentration were made and mean values of these measurements for each concentration was plotted, see Fig. 16.

![Experimental setup diagram](image)

**Figure 15.** Experimental setup.

The peak at about 876 cm\(^{-1}\) originates from the vibration between the two oxygen atoms in hydrogen peroxide molecules. The smaller peak at about 1409 cm\(^{-1}\) originates from a...
symmetrical bending motion in the hydrogen peroxide molecules[5]. The broad peak at about 3350 cm\(^{-1}\) corresponds to the symmetric vibration between the hydrogen and oxygen atom in both water molecules and hydrogen peroxide molecules.

The area (i.e. the integrated signal) of the OO-peak and the OH-peak were calculated using MatLab. The ratios of the areas were then calculated. Since the Raman scattering cross sections of the OO-vibration and OH-vibration are not the same, the ratio of the two areas are multiplied by the ratio of the cross sections as described earlier. The ratio is then plotted against the mole fraction of hydrogen peroxide as seen in Fig.17.

\[
\frac{I_{OO-peak}}{I_{OH-peak}} \times \frac{\sigma_{OH}}{\sigma_{OO}}
\]

**Figure 17.** Ratio of the OO-peak and the OH-peak plotted against the mole fraction of H\(_2\)O\(_2\).

The plot shows good agreement with the linear proportionality between the ratio and the mole fraction of hydrogen peroxide that was expected.

### 5.2 Droplet in Levitator

In a second experiment, the setup was the same as in the first experiment except for the cuvette with the sample being replaced by a levitator holding a single droplet of the sample. This was carried out to investigate if a much smaller sample volume is enough to get a sufficient signal. Measurements were made on six different concentrations. Only one recording was made for each concentration. The Raman spectra of these measurements are shown in Fig. 18.
Figure 18. Raman spectra of levitated drop. Measurements were made for six different concentrations of hydrogen peroxide ranging from 0 wt% to 49.8 wt%.

Figure 19. Ratio of the OO-peak and the OH-peak plotted against the mole fraction of $H_2O_2$ when the sample volume was a drop in a levitator.
As seen in Fig. 18 the Rayleigh signal is limiting the exposure time and gain that can be used in order not to saturate the chip of the CCD-camera. The measurements could have been improved by choosing to scan the grating to a spectral range with insignificant Rayleigh signal as was done in the first experiment. The intensity of the peaks in the experiment with a droplet in a levitator is about one tenth of the strength of the intensity of the peaks in the experiment where a cuvette was filled with the sample. The smaller sample volume contributing to the signal as well as the laser not being focused enough to go through the droplet are the major reasons for the weaker signal. The weaker signal obviously results in a lower signal-to-noise ratio. Even under these relatively poor conditions the experiment shows that even a small volume of the sample gives a reasonable good agreement with a linear function. (see Fig. 19)

5.3 Evaporation

A test was also carried out aiming at investigating whether the concentration changes over time due to different evaporation rates of the two constituents when a drop is left hanging in a levitator for a longer time. A 49.8 %wt hydrogen peroxide droplet was placed in the levitator. In the short amount of time that was at hand to make measurements before the droplet was lost (130 minutes), a change in concentration was not observed (see Fig. 21). Thus, the evaporation rates of the two constituents do not differ to the extent that it poses a problem in the other experiments performed. The small variations of the ratio in Fig. 21 are ascribed to the relatively low signal-to-noise ratio of the spectra due to the relatively small sample volume.

Figure 20. Spectra from a hydrogen peroxide and water mixture droplet in levitator.
5.4 Time-Resolved Measurements

For the next experiment another setup was used. For less ideal conditions compared to the pure $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solutions discussed so far, fluorescence from other substances may be present. Fluorescence is much stronger than Raman scattering. Introducing a streak camera into the setup makes it possible to perform time resolved measurements. Because of the different durations in time of the Raman signal and the fluorescence, the Raman signal can then be detected even in the presence of fluorescence. The experimental setup is shown in Fig. 22. A small amount of the highly fluorescent substance Rhodamine was added to the hydrogen peroxide and water mixture. The exact amount of Rhodamine added was not measured since the purpose of the experiment only was to establish in a qualitative way if a potential problem with fluorescence could be dealt with by making time-resolved measurements.
30 ps pulses of wavelength 532 nm from a mode-locked Nd:YAG laser are sent through the sample that is placed in a cuvette. A system of two lenses is used to collect the signal and focus it onto the entrance slit of a streak-camera. A notch-filter is placed between the lenses to filter out Rayleigh scattered light.

A hydrogen peroxide and water solution was contaminated with a small amount of Rhodamine. The streak camera was set for a slow streak rate giving low temporal resolution. The time-resolved spectrum is shown in Fig.23. By integrating over a time window that includes all of the fluorescence result in the spectrum seen in Fig. 24a. By
integrating over a short time window at the beginning of the pulse result in the spectrum shown in Fig. 24b. The OO-peak is easily discerned in this spectrum. The OH-peak is not as easy to discern as the OO-peak mainly due to chromatic aberrations in the camera optics.

Figure 24a. Spectrum from time-resolved measurement, with a long time window.

Figure 24b. Spectrum from time-resolved measurement, with a short time window.
5.5 Surface Enhanced Raman Scattering

An attempt was made aiming at improving the signal by adding a silver colloidal solution to the sample. No improvement of the signal was observed probably due to a too low content of silver particles in the colloid that was used, only 10ppm or 100 μg/ml. The number of adsorbents (silver particles) added to a sample needs to be in the same range as the number of adsorbates in order to get a considerable enhancement effect [6]. Surface enhanced Raman scattering is usually employed to detect very small concentrations of a substance. The enhancement is also dependent on the size of the adsorbents compared to the size of the adsorbates. In the case where enhancement of scattering from two different substances is desired, the enhancement could be stronger for one substance than the other. Also the enhancement of two vibrational modes of the same molecule can differ. Unless the degree of enhancement of the different vibrational modes in hydrogen peroxide and water can be determined, a surface enhanced Raman technique is of no use in concentration measurements, at least not for the method that is chosen here to determine concentration.

5.6 Stimulated Raman Scattering

The intensity of the laser was increased. At irradiances high enough, the stimulated Raman effect appeared. A red light observable to the eye was scattered from the sample. The light was well collimated and observed in the direction of the laser. The experimental setup to study the scattering is shown in Fig. 25.

![Figure 25. Experimental setup. Stimulated Raman scattering experiment.](image)

30 ps pulses coming from a frequency-doubled mode-locked Nd:YAG laser are used to illuminate a quartz glass cuvette holding the sample. A dichroic mirror is used to separate the stimulated Raman scattering from the laser light at 532 nm. To further suppress residual light at 532 nm, a long-pass filter, blocking wavelengths shorter than 540 nm is placed in front of the detector. A fiber optic spectrometer from Ocean Optics with a built-in CCD-detector was used to analyze the scattered light.
Stimulated Raman scattering is a non-linear effect. Because of its non-linear nature, the signal increases rapidly with increasing pulse energy of the laser as well as increased concentration. Increasing the energy of the laser pulses, involves a risk of breaking the glass of the cuvette holding the sample. Spectra corresponding to different concentrations of hydrogen peroxide were recorded, as can be seen in Fig. 26. Four or five recordings were made for each concentration and mean values of these were calculated.

![Stimulated Raman scattering spectra. Notice the strong second order Stokes line at about 1710 cm⁻¹.](image)

For concentrations lower than 20 %, the intensity of the peak originating from the OO-vibration was too low to be measured. The spectrum in Fig. 26 shows the first Raman peak at 844 cm⁻¹. A distinct peak, not present in any of the spontaneous Raman spectra, is found at 1710 cm⁻¹. The Stokes shift of this peak is in agreement with the shift expected for the second-order Stokes line, see Table 2. A very weak peak is found at about 2585 cm⁻¹. This wavelength corresponds to the shift expected for the third-order Stokes line.

<table>
<thead>
<tr>
<th>Stokes line</th>
<th>λ(nm)</th>
<th>Stokes shift, σS (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>557.02</td>
<td>844.32 = σS₁</td>
</tr>
<tr>
<td>S2</td>
<td>585.24</td>
<td>1709.99 = 2.02 σS₁</td>
</tr>
<tr>
<td>S3</td>
<td>616.84</td>
<td>2585.33 = 3.06 σS₁</td>
</tr>
</tbody>
</table>
The ratios of the integrated areas of the OO-peak and the OH-peak were plotted against the mole fraction of hydrogen peroxide, seen in Fig. 27.

![Figure 27. Ratio of the OO-peak and the OH-peak as a function of time for stimulated Raman.](image)

The ratio of the integrated areas of the OO-peak and the OH-peak is no longer linear to the mole fraction of hydrogen peroxide. This result is not surprising since the thresholds for stimulated Raman scattering is probably not the same for the OO-vibration in hydrogen peroxide molecules and the OH-vibration in water and hydrogen peroxide molecules. The gain curves of the two vibrations might also not be the same. With this in mind, stimulated Raman scattering is ruled out as a method for determining concentration. Even though the scattering of both the OO-vibration and OH-vibration is much stronger compared to spontaneous Raman scattering, the relative enhancement of the two vibrations of interest is not easy to predict.
The method used for concentration measurements of H$_2$O$_2$ in H$_2$O$_2$/H$_2$O solutions showed good results. The ratio of the areas of the OO-peak and OH-peak was linearly proportional to the H$_2$O$_2$ concentration. The assumption that the cross-sections of the symmetrical OH-vibration are the same for H$_2$O$_2$ molecules and H$_2$O molecules seems to have been an adequate assumption.

Measurements on small sample volumes resulted in a decrease of signal-to-noise ratio in the recorded spectra. The uncertainty of the calibration curve was increased. In these experiments the Rayleigh signal was limiting the exposure time and gain that could be used in order not to saturate the chip of the CCD-camera. The measurements could have been improved by choosing to scan the grating to a spectral range with insignificant Rayleigh signal. Even under these relatively poor conditions the experiment showed that even a small volume of the sample gives a reasonable good agreement with a linear function.

Raman scattering is a weak process. Rayleigh scattering is typically three orders of magnitude stronger than Raman scattering. Suppression of Rayleigh scattered light is therefore important. Fluorescence is an even stronger process, and usually radiates light in a broad range of wavelengths. What can be taken advantage of, is the different time durations of fluorescence and Raman scattering. Raman scattering is essentially an instantaneous process (on the femto-second time scale) whereas fluorescence normally is more extended in time (on the nano-second time scale). If a pulsed laser is used, the Raman signal will be present only during the extent of the laser pulse. Using laser pulses whose durations are significantly shorter than the lifetime of the fluorescence radiation and only collect the very first part of the signal, all the Raman signal is collected but only a small part of the fluorescence is collected. A streak camera was used to do such time-resolved measurements. The measurements made demonstrate the principle of fluorescence rejection.

An attempt to enhance the Raman scattering signal was made by adding a silver colloid to the sample. No enhancement was observed. Unless the degree of enhancement of the different vibrational modes in hydrogen peroxide and water can be determined, a surface enhanced Raman technique is probably useless in concentration measurements, at least for the method that is chosen here to determine concentration. Surface enhancement techniques seem to be more suited for identification of species of low concentration rather than concentration measurements. Single molecule detection with the use of a surface enhancement technique has been reported in the literature [7][8].

With ultrashort pulses from a mode-locked laser it is possible to get the high peak intensity needed for the stimulated Raman scattering effect to appear. Scattering from a stimulated Raman process is much stronger than scattering from a spontaneous Raman process. In contrast to spontaneous Raman scattering, the stimulated Raman scattering forms a coherent laser-like beam, which results in a very efficient signal collection. Due to the fact that the enhancement of the scattering from the two species could not be
predicted, the stimulated Raman scattering spectra could not be used to determine H$_2$O$_2$ concentration.
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8 References


