

**Degenerate Four-Wave Mixing
as an Analytical Tool**

Diploma project

by

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Degenerate Four-Wave Mixing as an Analytical Tool

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A. Introduction

Degenerate Four-Wave Mixing, DFWM, is a non-linear spectroscopic method for measuring concentrations and temperatures. The signal is obtained as a phase conjugated beam with regard to the probe beam. The media we are investigating act as a phase-conjugating mirror, and the reflectivity gives information about concentration and temperature.

In this work we have tried to compare DFWM with other laser probing methods and have investigated methods of increasing the sensitivity of DFWM.

B. Theory

B1. Laser Probing

We will study laser probing. To start with, we will discuss some of the advantages and the disadvantages connected with laser probing. Laser optical techniques are remote and almost always non-perturbing. This makes them well suited for applications in locations which are difficult to reach. There is no upper temperature limit, due to the non-intrusive nature of the laser techniques. The laser techniques require optical access, therefore windows are often necessary in the enclosure. This can be avoided if fibre optics can be used. Laser techniques are capable of measuring several species and temperature at the same time. Laser techniques also require a certain level of operator skill.

There are several different techniques available and we will try to present some of them: Degenerate Four-Wave Mixing, Coherent Anti-Stokes Raman Scattering, Laser-Induced Fluorescence and Raman Scattering.

B2. DFWM - Degenerate Four-Wave Mixing

The beams in degenerate four-wave mixing spectroscopy have the same frequency; two of the beams are intense pump-beams and two are weak (Fig. 1).

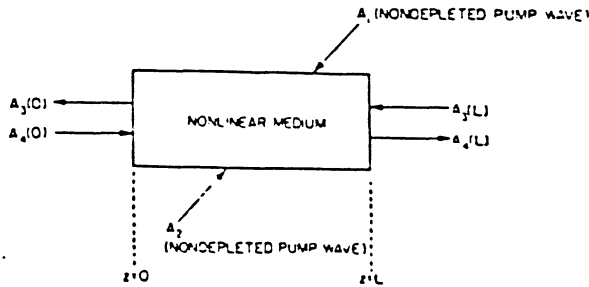


Fig. 1. Four-wave mixing geometry. From [8].

The forward pump beam and the probe beam form a grating from which the backward pump beam is scattered and vice versa (Fig. 2).

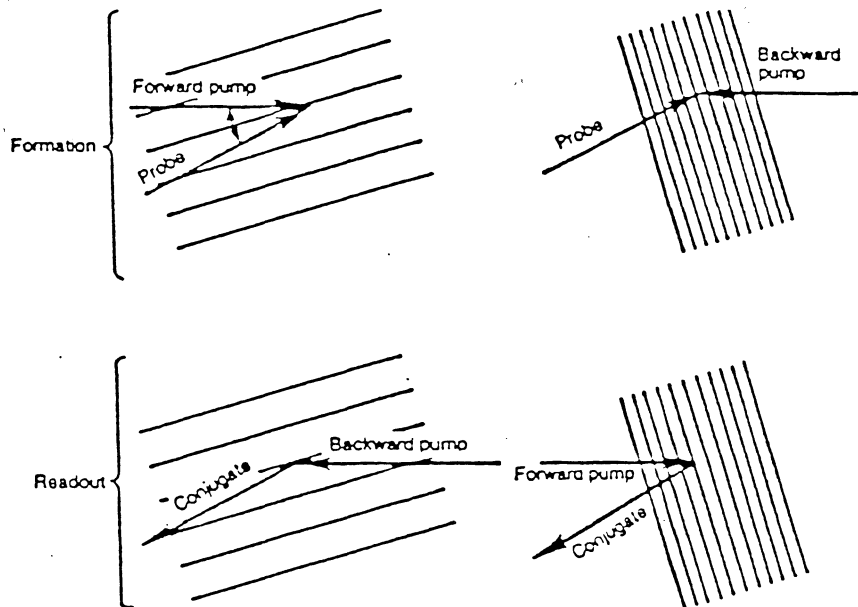


Fig. 2. Each pump beam forms a grating with the probe beam, from which the other pump beam is scattered. From [12].

We will now study the phenomenon in more detail.

We assume that the fields are plane waves, and we can write

$$E_i(r,t) = A_i(r) (e^{i(\omega t - k_i r)} + e^{-i(\omega t - k_i r)}) / 2.$$

The non-linear medium creates a polarization

$$P^{NL}(\omega_4) = \chi^{(3)} A_1 A_2 A_3^* (e^{i(\omega_4 t - (k_1 + k_2 - k_3)r)} + e^{-i(\omega_4 t - (k_1 + k_2 - k_3)r)}) / 2$$

$$P^{NL}(\omega_3) = \chi^{(3)} A_1 A_2 A_4^* (e^{i(\omega_3 t - (k_1 + k_2 - k_4)r)} + e^{-i(\omega_3 t - (k_1 + k_2 - k_4)r)}) / 2$$

Since all frequencies are the same we can write

$$P^{NL} = \chi^{(3)} A_1 A_2 A_4^* (e^{i(\omega_3 t - kz)} + e^{-i(\omega_3 t - kz)}) / 2$$

Inserting in the wave equation yields

$$\Delta E + \frac{\epsilon \delta^2 E}{c^2 \delta t^2} = \frac{4 \delta^2 P^{NL}}{c^2 \delta^2 t} \Rightarrow \frac{dA_3}{dz} = \frac{i 2\pi\omega}{cn} \chi^{(3)} A_1 A_2 A_4^* = i\kappa A_4^*$$

$$\frac{dA_4^*}{dz} = i\kappa A_3$$

$$A_3(z) = \left(\frac{\cos|\kappa|z}{\cos|\kappa|L} \right) A_3(L) + i\kappa \left(\frac{\sin|\kappa|(z-L)}{|\kappa| \cos|\kappa|L} \right) A_4^*(0)$$

=>

$$A_4(z) = -i \left(\frac{|\kappa| \sin|\kappa|z}{\kappa \cos|\kappa|L} \right) A_3^*(L) + \left(\frac{\cos|\kappa|(z-L)}{\cos|\kappa|L} \right) A_4(0)$$

If only one beam $A_4(0)$ reaches the medium at $z=0$ we have

$$A_3(0) = 0 - i \left(\frac{\kappa \sin|\kappa|L}{|\kappa| \cos|\kappa|L} \right) A_4^*(0) = - \left(\frac{\kappa}{|\kappa|} \right) \tan(|\kappa|L) A_4^*(0)$$

At $z=L$

$$A_4(L) = 0 + \frac{1}{\cos|\kappa|L} A_4(0)$$

If $|\kappa|L = \pi/2$ we obtain $\frac{A_3(0)}{A_4(0)} = \infty$ and $\frac{A_4(L)}{A_4(0)} = \infty$ which means

self-oscillation (Figs 3,4.).

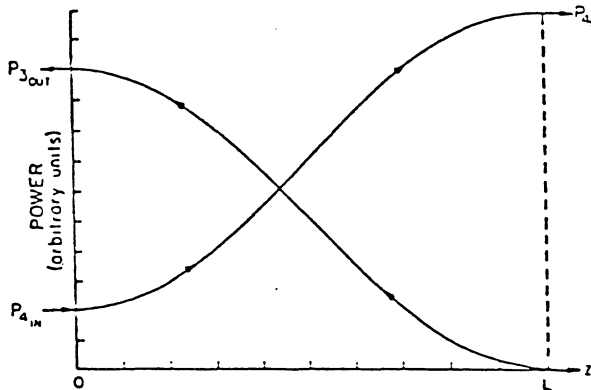


Fig. 3. Amplification by four-wave mixing. From [11].

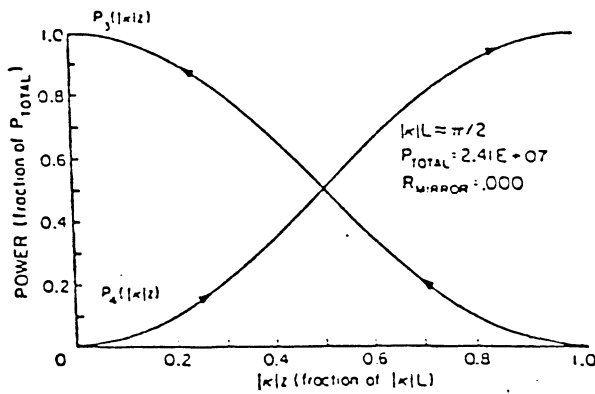


Fig. 4. When $|\kappa|L = \pi/2$ we obtain self-oscillation. From [11].

DFWM is a sensitive method of detecting relatively small concentrations of atoms and molecules.

B3. Related Methods

B3.1. CARS - Coherent Anti-Stokes Raman Scattering

CARS is a case of four-wave mixing. Two photons of frequency ω_p and one photon of frequency ω_s are mixed through the third order susceptibility $\chi^{(3)}$ and generate an anti-Stokes photon of frequency ω_{AS} (Fig. 5).

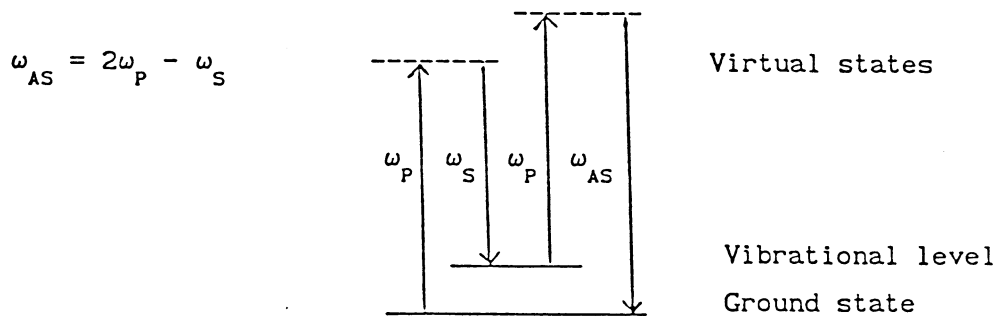


Fig 5. Energy levels in CARS.

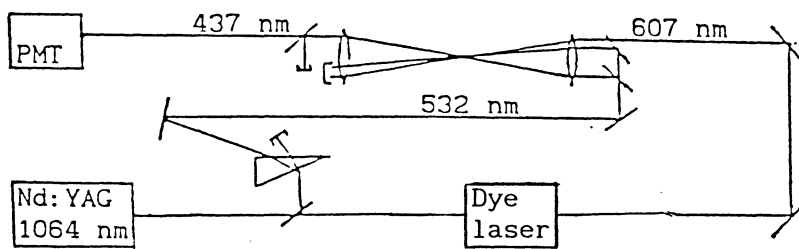
The anti-Stokes component depends on the variation of polarizability α . When the molecule vibrates, we have

$$\alpha = \alpha_0 + \alpha_1 \sin \omega_{\text{vibr}} t \quad \text{where } \alpha_1 \ll \alpha_0.$$

The polarization becomes

$$\mathcal{P} = \alpha \mathcal{E} = (\alpha_0 + \alpha_1 \sin \omega_{\text{vibr}} t) \mathcal{E}_0 \sin \omega t = \alpha_0 \mathcal{E}_0 \sin \omega t + \alpha_1 \mathcal{E}_0 [\cos(\omega - \omega_{\text{vibr}}) t - \cos(\omega + \omega_{\text{vibr}}) t] / 2$$

The first term in the expression is Rayleigh-scattered light, the second is the Stokes component and the third is the anti-Stokes component. CARS is useful in the examination of combustion processes with large emissions of light, i.e. flames with many particles.



$$\omega_{AS} = 2\omega_P - \omega_S \Leftrightarrow 1/473 = 2/532 - 1/607$$

Fig. 6. An experimental set-up for CARS.

CARS gives information on concentrations, distributions and temperatures.

B3.2. LIF - Laser-Induced Fluorescence

The principle of LIF is that the atom or molecule which is being examined is exposed to laser light and is excited from the ground state to an excited state. The atom or molecule re-emits radiation after a short time, which can then be analysed to give information on temperature and concentrations. LIF is a very powerful diagnostic tool.

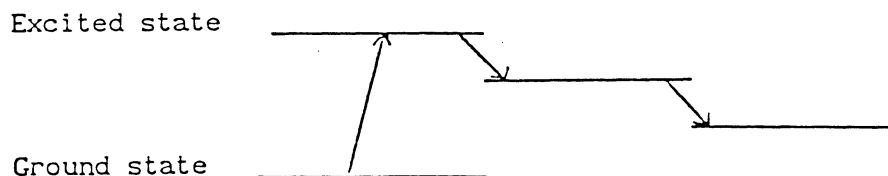


Fig. 7. LIF scheme.

The disadvantage with LIF is that the re-emitted radiation is radiated in all directions and only a small part of the light is captured by the detector.

B3.3. RS - Raman Scattering

In Raman scattering gas is exposed to laser light and the scattered light is analysed using a spectrometer. When using this method it is important that the sample which is to be examined is free from fluorescent gases or particles, otherwise the fluorescence tends to cover the weak Raman lines. It is also necessary to suppress Rayleigh- and Mie-scattered light.

B4. Applications of Laser Probing in Combustion Research

It is becoming more and more evident that the environment is not able to receive and decompose all pollution that is produced in, for instance, combustion processes. It is thus important to be able to prevent harmful species from being spread in the environment. To be able to understand more about combustion processes, it is necessary to study the combustion process on a molecular level. Using laser techniques, non-intrusive measurements on aggressive media, such as flames and exploding gases, can be performed.

Lidar, LIght Detecting And Ranging, is a technique which has similarities to the radar technique. In lidar, pulses of light are scattered in the atmosphere. The backscattered signal can give us information on the nature and distribution of the scatterer.

DIAL, Differential Absorption Lidar, uses two wavelengths, one absorbed by the molecule under study and one that is less affected. The ratio of the returning signals from the two wavelengths is formed, which removes the influence of scattering and attenuation by clouds.

In DOAS, Differential Optical Absorption Spectroscopy, light from a lamp, normally a xenon high-pressure lamp, is directed towards a telescope at 1-10 km distance. The light is focused at the input of a spectrometer. The output slit is replaced by a rotating slotted disc, which scans the spectrum in front of a photomultiplier.

Combustion processes are in fact very complex and include many intermediate chemical reactions. OH is an important intermediate radical in flame chemistry. A fast increase in the emission of radicals will lead to an explosion.

Nitrogen oxides constitute the largest environmental problem in the combustion of natural gas. The production of nitrogen oxides could be reduced through a decrease in flame temperature and a reduction in oxygen concentration. This could, however, cause a decrease in efficiency, flame instability and an increase in the emission of soot and carbon monoxide, and the removal of these pollutants is complex and expensive.

Nitrogen oxides are formed both from atmospheric nitrogen and from nitrogen compounds in fuel. The atmospheric nitrogen is not only considered to be the most important source of nitrogen oxides, but is difficult to control and impossible to avoid. NO and NO₂ can, under the influence of sunlight, react with hydrocarbons in the atmosphere producing toxic compounds such as ozone. Nitrogen oxides break down the vegetation and are suspected of having a connection with the extensive forest damage observed at many places in Europe.

C. Experiments

C1. Introduction

The intention of the experiments was to study sodium atoms in low concentrations in a flame using DFWM, and finally to study OH in a flame. We started working with Na, due to the fact that Na lines are strong and the signal should be easy to find. By then lowering the concentration and later studying sodium in a cell, we would learn how to operate in experiments using DFWM.

C2. Experimental set-up

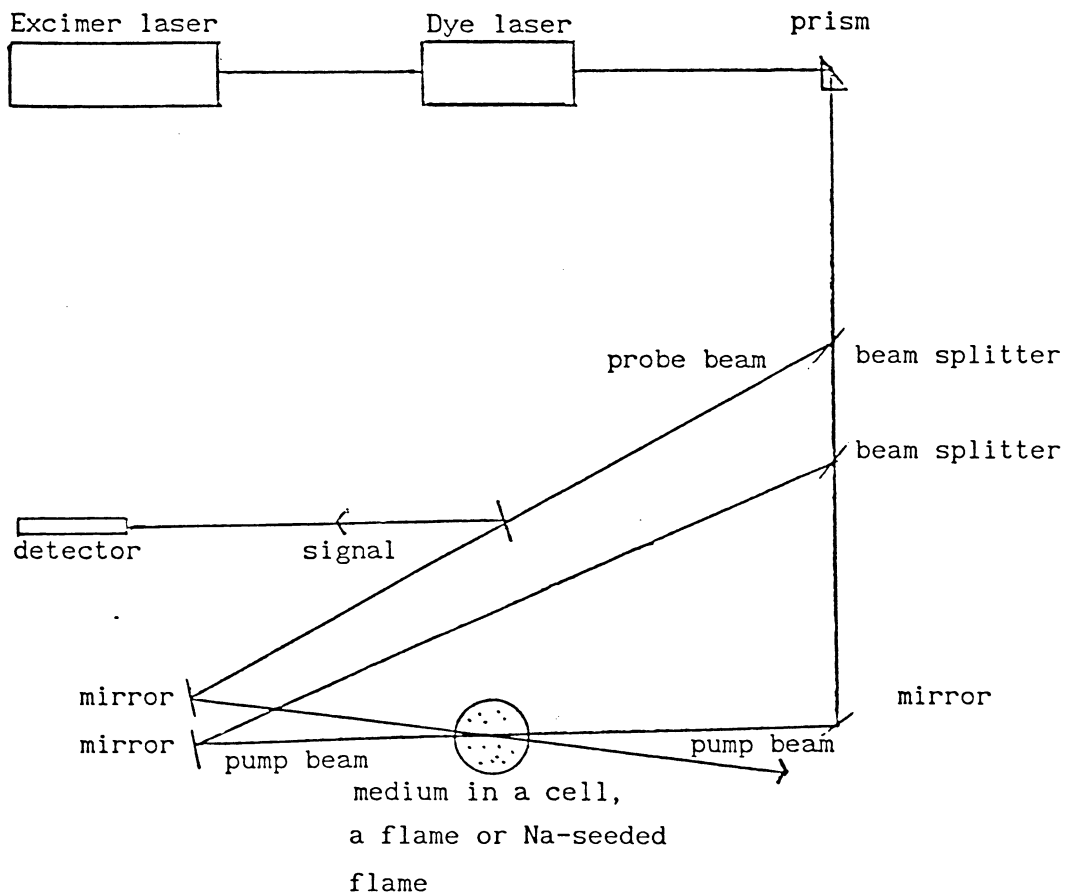


Fig. 8. Experimental set-up.

The Excimer laser was a Lambda Physik EMG 102 unit filled with 80 mbar He/HCl, 100 mbar Xe and 2420 mbar Ne.

The Dye laser was an FL 2002 with Rhodamine 6G in the initial experiments. Later we used Sulphorhodamine and Coumarin 153. The detector was a photomultiplier connected to a boxcar integrator and a strip-chart recorder.

The characteristic of excimer molecules is that they do not have a ground state. This means that they can only exist in excited states with short lifetimes. These molecules are created in an electrical discharge in a gas mixture of inert gases and F_2 or Cl_2 . The fact that the molecules do not have a ground state means that it is easy to obtain an inverted population and laser action. The radiance is improved in intensity and divergence by a resonator.

A dye laser uses a dye as the active medium. There are hundreds of dyes that can be used as laser media. The organic dyes have a complicated chemical structure. The two lowest singlet states are the states usually used by dye lasers. They are split up in a pseudo-continuum of vibrational and rotational levels. If the molecules are exposed to light, they can be excited from the ground state to the next singlet band (Fig. 9).

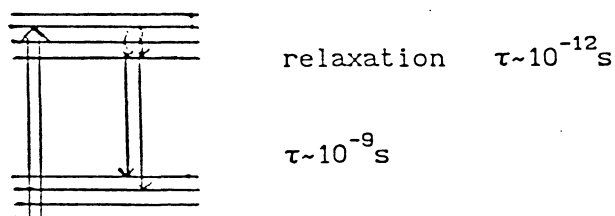


Fig. 9. Levels in a dye molecule.

Using a grating for the laser feedback it is possible to select the wavelength of interest (Fig. 10).

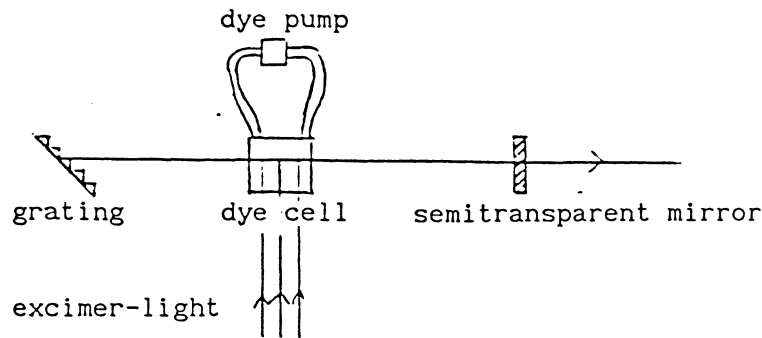


Fig. 10. The principles of a dye laser.

We obtained about 4 mJ per pulse from the dye laser. The pulse length was about 10 ns, which gave us a power of the order of 100 kW in the pulse.

C3. Experiments and Results

We evacuated the excimer laser, introduced 200 mbar He/HCl and 800 mbar Ar and waited for 10 minutes, then evacuated again. This procedure is called passivation and was performed once more. We now exchanged Ar for Ne and introduced 80 mbar He/HCl, 100 mbar Xe and 2420 mbar Ne to a total pressure of 2600 mbar.

We mixed a dye, Rhodamine 6G, and installed it in the dye laser. We now had to adjust the optics in the dye laser to make it work well. The equipment was then arranged on the optical table, in principle as shown in Fig. 8. To obtain an optimal signal we calculated the reflectivity of the beam splitter which was placed in the probe beam. The intensity of the signal is proportional to the reflectivity, R , of the beam splitter and to $(1-R)$, since the probe beam first passes the beam splitter, and its intensity after the splitter is proportional to $(1-R)$, and is then reflected in the same splitter. The expression is then differentiated with respect to R and put equal to zero.

$$I_s = CR(1-R) \Rightarrow \frac{dI}{dR} = C(1-2R)=0 \Rightarrow R=0.5 \quad \frac{d^2I}{dR^2} = -2C < 0 \Rightarrow \text{maximum}$$

The result was that a beam splitter with a reflectivity of 50% was required.

We first tried to look at signals from sodium in a cell. The cell was heated to 160°C, but the fluorescence signal, as observed by the naked eye, was so weak that we had to use a detector, which was triggered by the laser signal, to detect the two strong Na lines. An interference filter was placed in front of the detector. It was a 600 nm filter tuned down to 590 nm by inclining it at an angle θ according to the equation

$$\lambda_{\theta} = \lambda_0 \left(1 - \left(\frac{\sin\theta}{n}\right)^2\right)^{1/2} \quad \text{and} \quad n = 1.45 \Rightarrow \theta = 15^\circ.$$

We found that we had to screen the detection side from the rest of the set-up. To obtain good spatial filtering we shot a small hole in an aluminium foil with a focused laser.

In order to place the pin-hole in the correct position between the two lenses in the spatial filter, we put a piece of paper with a hole in it in the probe beam path. We then reflected the probe beam back through the medium. The mirror used for this purpose was adjusted so that the reflected light overlapped the hole in the piece of paper. We now obtained a reflection from the beam splitter, which deflects the signal into the detector. The reflection was focused by a lens and we placed the pin-hole at the focus. The aluminium foil was mounted on a plate, which could be adjusted vertically and horizontally by micrometer screws. By holding a piece of paper behind the pin-hole it was possible to adjust the position of the foil until the beam passed through the pin-hole.

We exchanged the cell for a Na-seeded flame, and started with a NaCl solution of 10 000 ppm Na. A DFWM spectra was recorded (Fig. 12). The curves exhibit a dip since the signal beam is partly absorbed on its way out of the cell passing non-pumped regions.

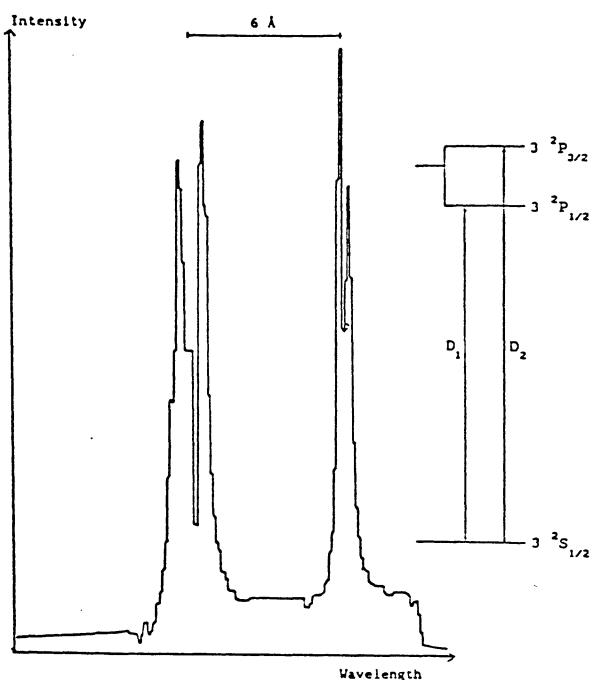


Fig. 12. DFWM in a sodium-seeded flame using a solution of NaCl. The concentration was 10 000 ppm.

We diluted the NaCl solution and recorded spectra for several different concentrations (Fig. 13 and Fig.14). We observed that the linewidth decreased with decreasing concentration. Only about 1% of the solution evaporated in the flame, the rest is poured out.

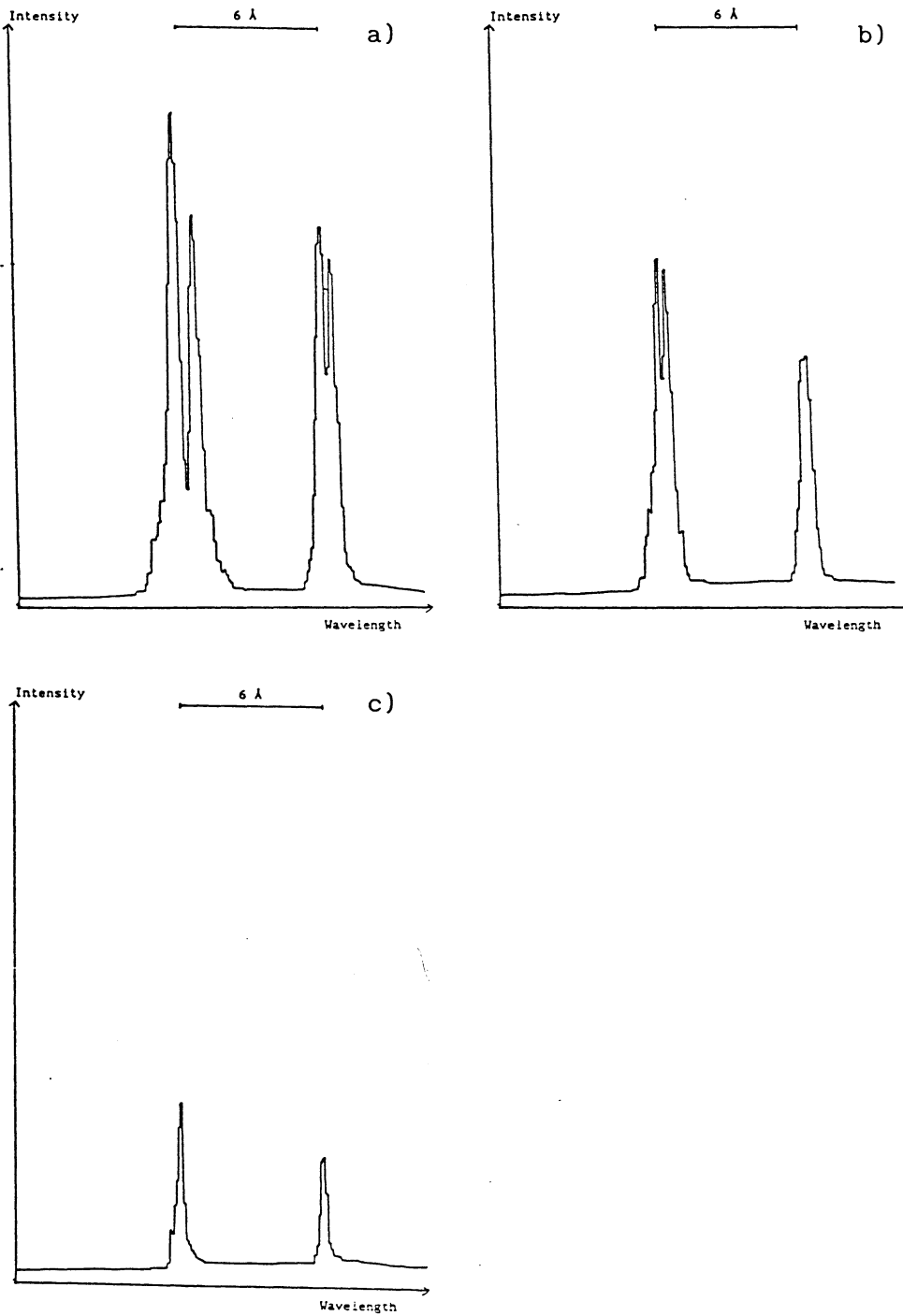


Fig. 13. DFWM in a sodium-seeded flame a) 2000 ppm Na, b) 500 ppm Na and c) 100 ppm Na. The same amplification has been used.

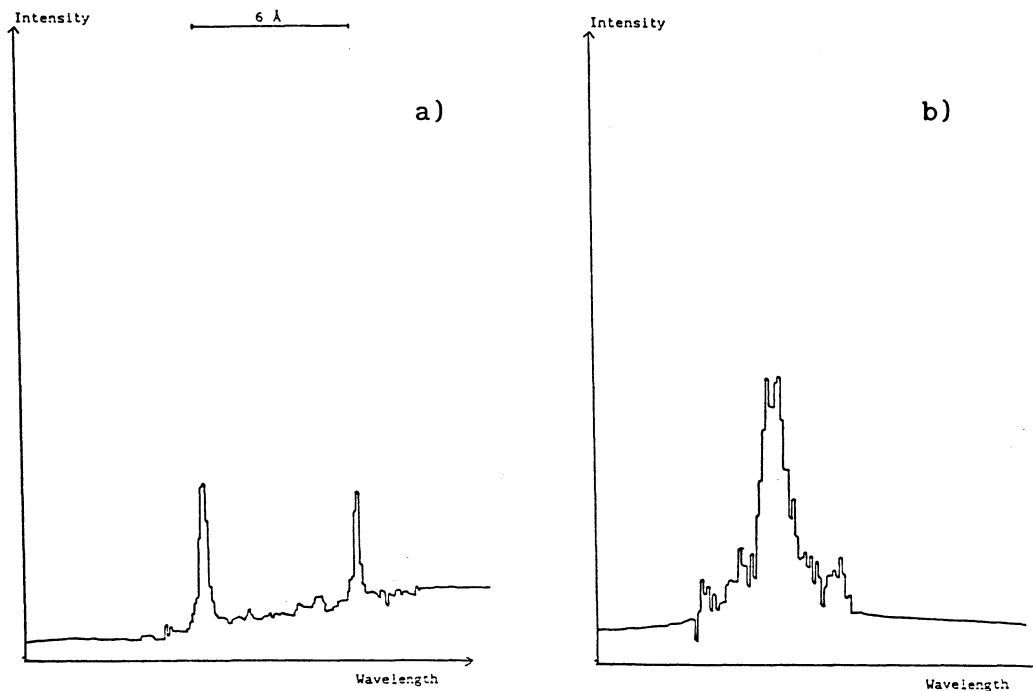


Fig. 14. DFWM in a sodium-seeded flame a) 20 ppm and b) 5 ppm. In b) it is only the D_2 line.

Fig. 15 shows the square root of the height multiplied by the half-value width as a function of concentration.

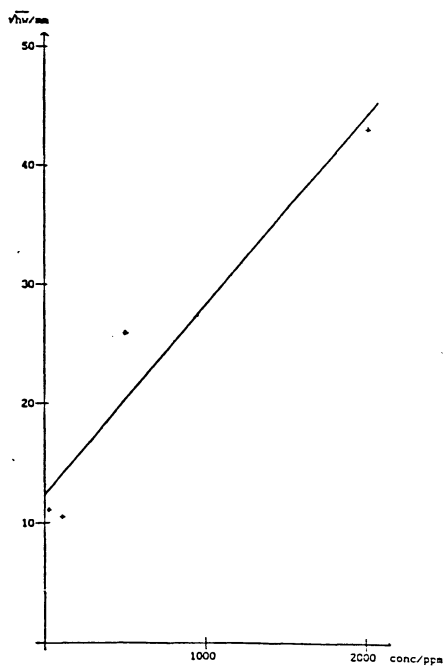


Fig. 15. Square root of the height (h) multiplied by the half-value width (w) as a function of the concentration of the seeded solution. The water that we diluted the solution with contained some sodium, that is why we obtained signal when the concentration was supposed to be zero.

Now we exchanged the burner for a cell containing sodium, placed it in an oven and heated it to 185°C. We found the DFWM signal for sodium and were able to record it down to 175°C. One problem using high temperatures is that sodium reacts with the walls of the cell, and the sodium is then consumed. Radio-frequency radiation was also a problem, especially when we were using the internal trigger from the excimer laser. Triggering with a photodiode on the laser light essentially solved that problem. With better screening of the detector we managed to record signals for the D₂ line in a sodium cell down to 130°C (Fig. 16).

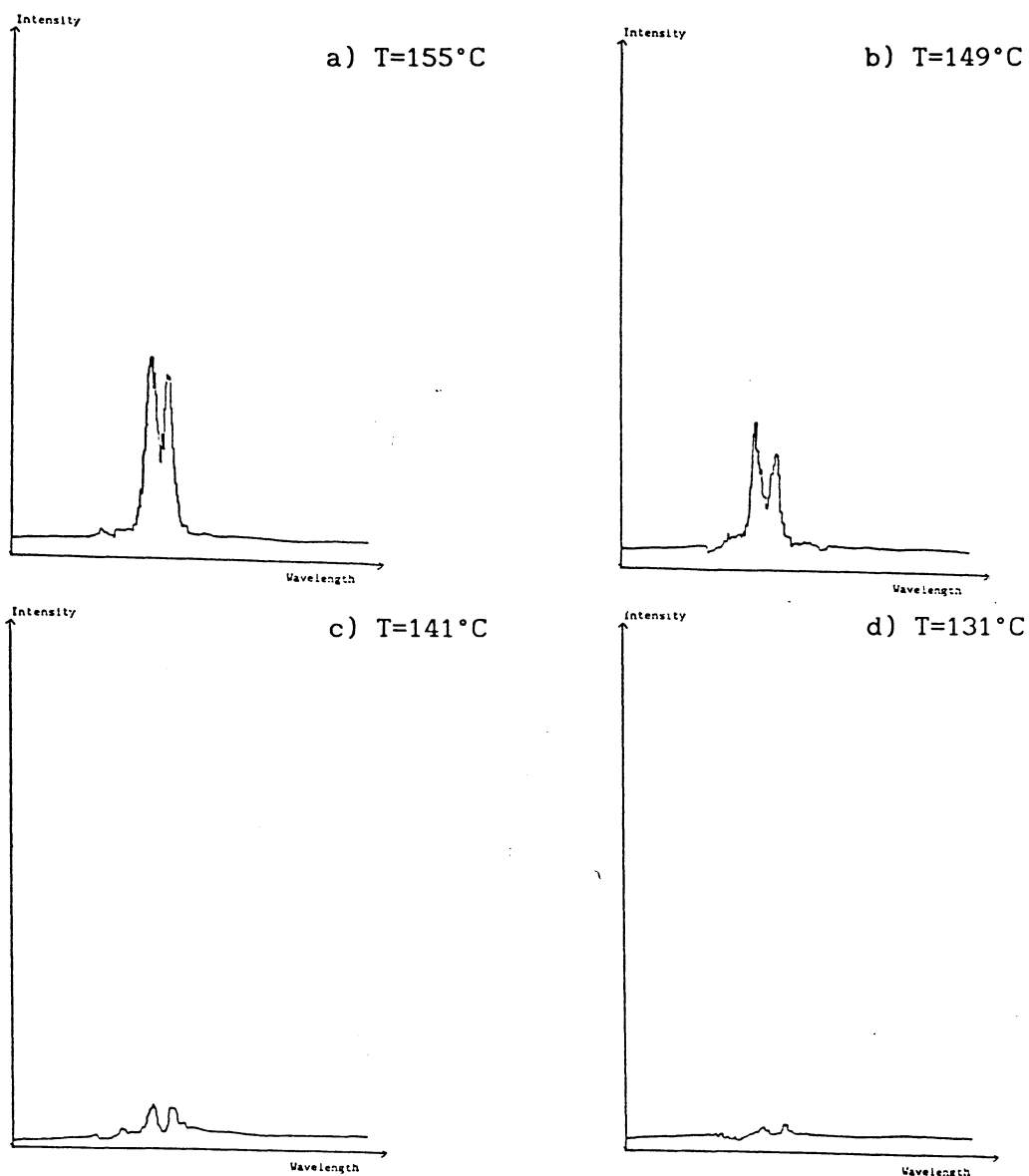


Fig. 16. DFWM of the D₂ line in a 75 mm long Na-cell at various temperatures.

The temperature can be translated to the pressure in the cell from which you can calculate number of atoms per volume unit. In Fig. 17 the square root of the height multiplied by the half-value width, the area of the peak approximately, as a function of number of atoms per m^3 is plotted. The area should be proportional to the intensity.

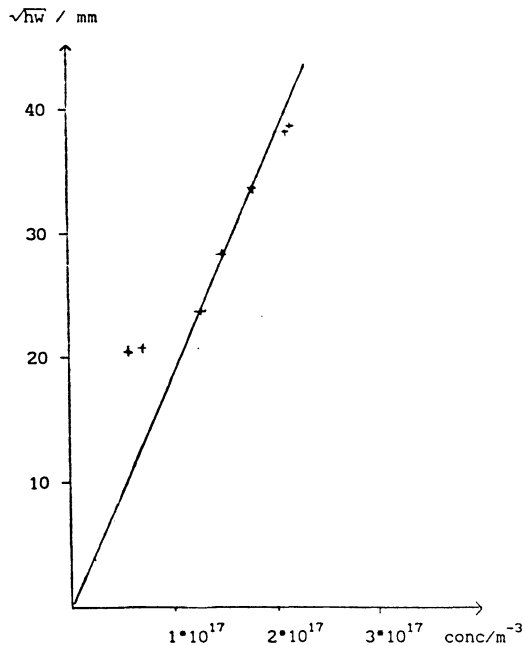


Fig. 17. \sqrt{hw} as a function of number of atoms per m^3 in the cell related to the temperature of the cell.

Sodium-vapor-density as a function of temperature data from [14].

We also placed neutral density filters in the beam paths at different places to see how the signal changed when the pump beams had different power. A concentration of 60 ppm sodium in a flame was used and the intensity as a function of the attenuation was recorded (Fig. 18). We found that the signal was greater in the case of backward saturation, that is when the forward pump is attenuated, than in the case of forward saturation. This illustrates the theory presented in Ref. [7]. In the case of backward saturation the signal is generated by two velocity groups only. For these velocity groups the Doppler effect tunes the incident frequency to obtain a resonant non-degenerate four-wave mixing emission on a Rabi side-band, in the atomic frame.

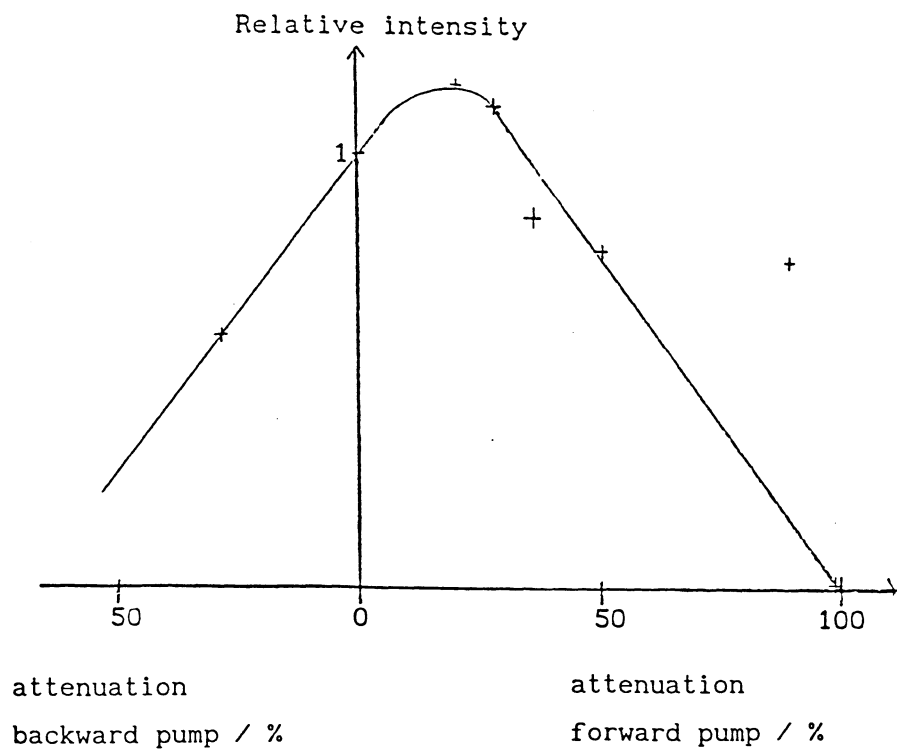


Fig. 18. The intensity of the DFWM signal as a function of the attenuation of the beams.

So far we have studied sodium and tried to find out how to measure weak signals. As an application of this technique, we wanted to study OH, and for that purpose we chose to use the $R_1(6)$ and $R_2(12)$ transitions at about 306 nm. The dye laser should then be tuned to 612 nm, since we had to frequency-double the light.

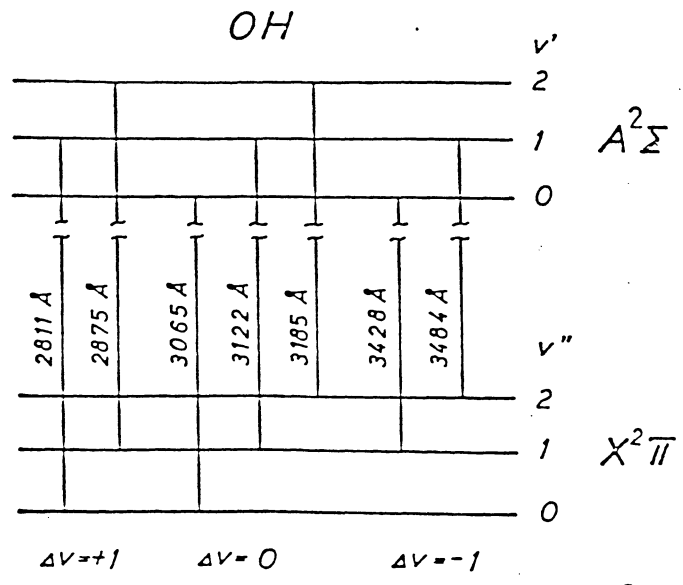


Fig. 19. Energy-level diagram for $A^2\Sigma - X^2\Pi$ transitions in OH. From [13].

We mixed a Sulphorhodamine solution. We were now using the fourth order of the grating in the dye laser. After optimization we obtained 4 mJ per pulse from the dye laser.

To frequency-double the light we used a KDP crystal and obtained a pulse energy of the order of 10 μ J/pulse out of the crystal. We used an interference filter for 310.5 nm and inclined it at an angle of 15°, tuning it to 306 nm.

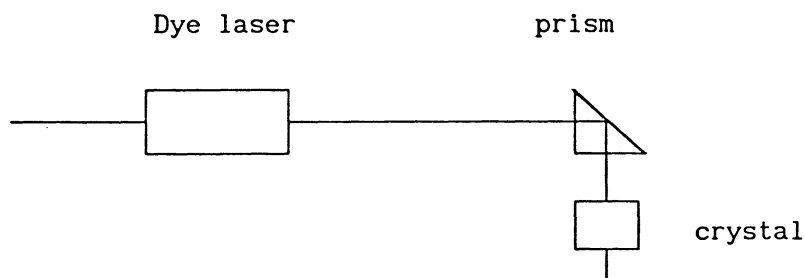


Fig. 20. We placed the crystal after the prism.

With this set-up we could detect absorption by OH at 306.36, 306.49 and 306.51 nm in a propane-oxygen flame. The phase-matching condition for frequency-doubling depends on the wavelength. On detuning from the wavelength at which we received the maximum doubled light signal, the intensity gradually decreased to zero. In order to sweep the laser further up or down in wavelength, it was necessary to turn the crystal a little. Fig. 21 shows an example of absorption at the 306.49 and 306.51 nm OH lines.

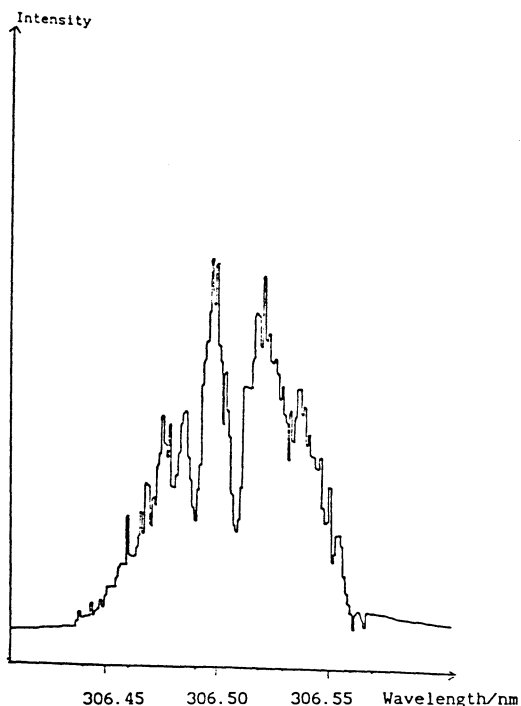


Fig. 21. Absorption at 306.49 nm and 306.51 nm for OH. We obtained maximum of frequency-doubled light at a certain angle to the optical axis due to the phase-matching conditions.

We measured the absorption for different heights above the burner, but could not see any DFWM signal. Fig. 22 shows the spectrum 5 mm above the burner, and the spectrum 20 mm above the burner. In the flame the central cone was about 10 mm high.

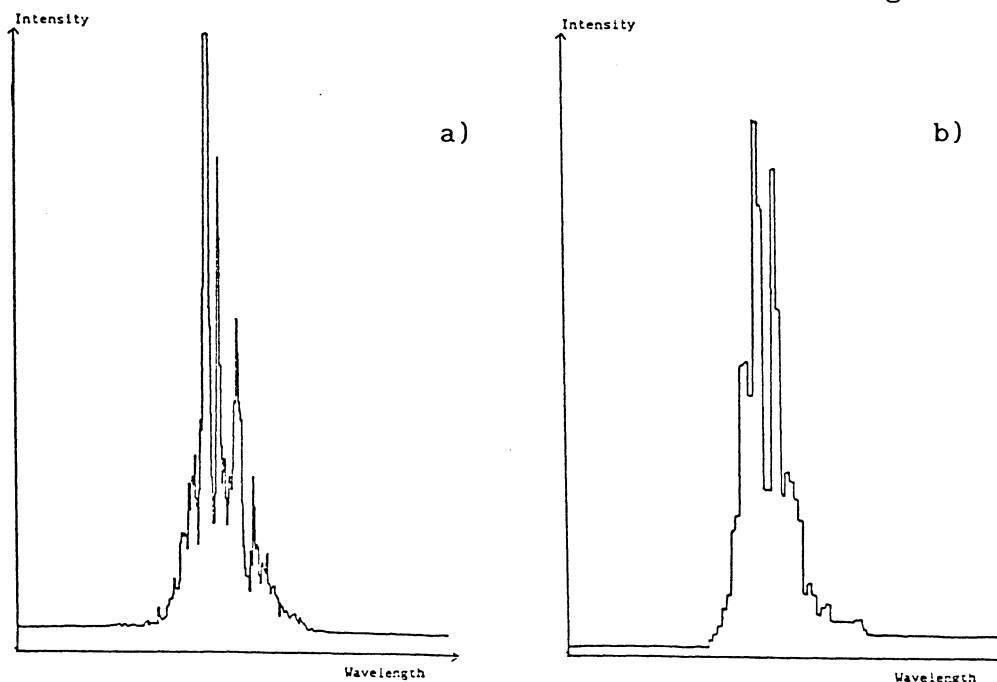


Fig. 22. The intensity at 5 mm above the burner in a) and at 20 mm in b) as a function of wavelength. The amplification is not the same in a) and b).

We now mixed a new dye solution of Coumarin 153. With this dye

we intended to study the peak at 283 nm. After installation of the dye and adjustment of the laser we obtained 4 mJ per pulse from the dye laser. The KDP crystal was now exchanged for a BBO crystal, and we used an interference filter for 289 nm tuned, by inclination, down to 284 nm. We could now record absorption at 282.94 nm and 282.95 nm and we tried to record a DFWM signal at the same time as we studied the absorption, but we were unable to record any DFWM signal (Fig. 23). There were too few photons reaching the detector. The method as we used it was not sensitive enough.

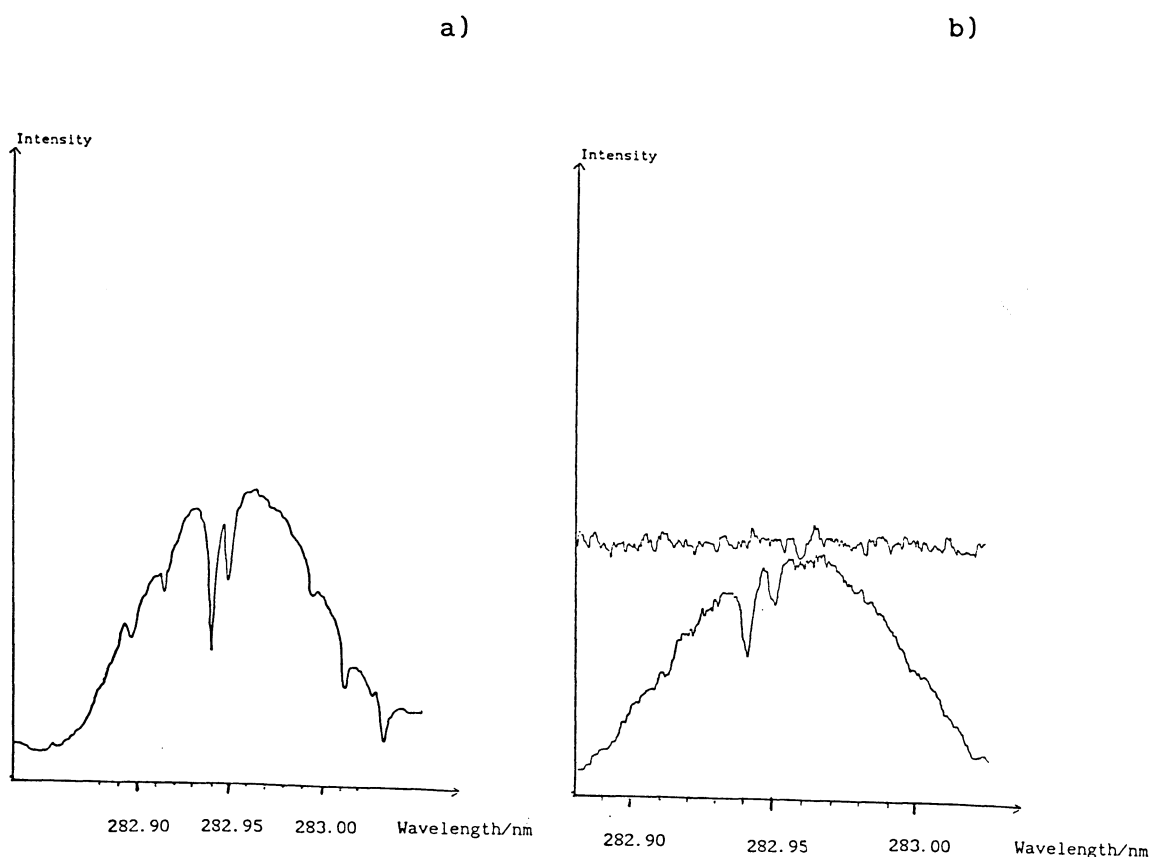


Fig. 23. Absorption at 282.94 nm and 282.95 nm for OH. In b) is an attempt to detect an OH DFWM signal while recording the absorption.

C4. Conclusions from the Experiments

It is clear that one has to be very careful in setting up the experiment. It is very important to obtain correct overlap of the pump beams and crossing the pump beams and the probe beam in the medium. Spatial filtering is necessary to be able to discriminate the signal from the reflections of the laser light. The problem is that all beams and reflections are of the same wavelength, so we could not get rid of the scattered light by using interference filters.

In the initial stages it is necessary to have a reasonably large signal to optimize spatial filtration and crossing of the beams. The signal from the Na cell was so weak that it was impossible to see it without using a photomultiplier and screening of as much as possible of the background light.

D. Increasing Sensitivity for Degenerate Four-Wave Mixing

The main purpose of this work was to find ways of increasing the sensitivity for DFWM measurements. In our experiment we used a pulsed laser, which means that in that fraction of time when the pulse is on, practically all light in the room reaching the detector is of the same wavelength. Reflections from walls must be prevented from reaching the detector. One way of achieving this is to screen off the detection region from the the rest of the set-up and only let light through, where the signal is expected to appear. If reflections are still reaching the detector, spatial filtering is necessary. A pin-hole in an aluminium foil provided a substantial improvement, although some of the reflections from the walls still gave a contribution. By putting black paper on the wall at the reflection spots we reduced this light considerably. Another method, which we did not try, is to move the detector several metres away from the set-up or even move it to another room. That is possible since the signal is a coherent beam.

Another possibility is to focus the probe beam. The phase-conjugated signal beam will be almost parallel, since it has passed the lens twice and is parallel when reaching the lens the first time. Light which is not phase-conjugated will be spread by the lens. Unfortunately, when we did this, it was not possible to spatially filter the beams since the lens makes it more difficult to set up the spatial filter.

There is also the possibility of polarizing the beams differently and minimizing the scattered light reaching the detector using analysers, if the scattered light is not linearly polarized in the same direction as the signal.

To suppress light that is not a DFWM signal, we can use an interference filter, but since most reflections are of the same wavelength as the signal, this is not enough. We had glare in the beam splitter deflecting the signal into the detector, but this light did not reach the detector at the same time as the signal. By moving the gate of the boxcar integrator later in time after the arrival of the glare photons, we can increase the sensitivity. Even light from the pump beams was picked up by the detector. To position the gate correctly in time and to determine how long a time it should be open, we studied the signal from the boxcar integrator on a fast oscilloscope. We also found that we had radio-frequency radiation affecting our measurements. This interference was reduced by using another electrical outlet for the high-voltage unit.

E. General Conclusions and Out-look

I believe DFWM spectroscopy can be a useful method of detecting weak signals due to its immunity to background radiation, but some effort has to be put into preventing the scattered light from being picked up by the detector. It is essential to know when the pulse arrives at the detector relative to the scattered light, so a fast oscilloscope is of great help. White walls in the room were found to reflect a lot of light, which is bad in this case. Using differently polarized beams an improvement would be obtained, especially if the backward pump beam and the signal have the same polarization.

F. Acknowledgements

I would like to thank Professor Sune Svanberg for his encouragement and help during my work. I would also like to thank Jonas Bengtsson and Jörgen Larsson and several other people at the Department for all the help and suggestions I have received.