Optical Diagnostics Assignment 2

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August 4, 2024

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Question 1: Raman active and IR active vibrational modes of molecules

Molecules are IR active if they have a vibration which can result in a change in the dipole moment [3]. Similarly a molecule is Raman active if a vibration results in a change in the polarizability [3].

On a more simple level this means that molecules which have a dipole moment and have movement on the axis of that dipole are IR active.

Molecules which are Raman active can be recognized by the stretching of bonds which are polarizable, the longer they are the more polarizable. But one should keep in mind that for asymmetric stretching it could be the case that the higher polarisation of one longer bond gets compensated by the lower polarisation of a shorter bond [9].

A: N2

According to J.Nash N_2 only has one vibrational mode; **(symmetric)-stretching**, which is **not IR active** but is **Ramon active** [6].

This is logical because it is a simple two atom molecule which doesn't even have dipole moment [8].

The Raman activity can be expected because it is a single bond which can be polarized [7] which gets longer and shorter (and can't be compensated by another bond)

B: H2O

Again, according to J.Nash H_2O has three vibrational modes [5]:

- **Symmetric stretching** has a changing dipole moment due to molecule having a non-linear structure and thus is **IR active**. It also naturally is very polar [8]. It also is **Raman active** due to it being two bonds getting larger/smaller in phase.

- **Asymmetric stretching** also has a changing dipole moment and thus is **IR active**. This more is the most IR active due to not only the distances changing but also the symmetry changing [5]. One would not expect it to be Raman active (due to the stretching being opposite phase of same magnitude) but according to the source it is **Raman active** likely due to the changing relative positions [5].

- **Bending** again has a changing dipole moment due to the changing shape (and thus position of charges) it thus is **IR active**. Unexpectedly it also is **Raman active** [5] again due to the changing relative positions.

C: CO2

Lastly according to the same source, J.Nash, there are four vibrational modes in CO_2; symmetric stretching, asymmetric stretching and two types of bending. Of this the **asymmetric stretching** and the **bending** is **IR active** but **not Raman active** and the **symmetric stretching** is **Raman active** but **not IR active** [4].

CO_2 normally has no dipole moment [8] but this is because the negative charge in each Oxygen atom is offset by the charge is the other (symmetric) Oxygen atom. However this means that vibrations which are not (point) symmetric such as the asymmetric stretching or the bending result in a dipole and thus are IR active.

The Raman activity can only be seen in the symmetric stretching mode. Here there are two (polarizable) bonds [7] which, in phase, lengthen and shorten. The other modes also have bonds which can vary in length but those apparently cancel each other [9].

Question 2: E-FISH signal

According to the slides the signal is given by

$$\sqrt{\frac{I_{2\omega}}{(I_\omega)^2}} = C \left| \int_{-0.5L}^{0.5L} E_{ext} e^{-i\Delta k z} \mathrm{d}z \right| \tag{1}$$

[1] where $E_{ext} = 100$ V/m is the electric field with

$$C = \sqrt{4.5 \frac{\omega}{\epsilon_0 c^3 (n_\omega)^2 n_{2\omega}}} \left| \chi^{(3)} \right| \tag{2}$$

where ϵ_0 and c are natural constants, n_ω and $n_{2\omega}$ are refractive indexes and $\chi^{(3)} = 6419 \cdot 10^{-54}$ m^5/v^2 is the susceptibility for Nitrogen [1]. And where the phase difference is

$$\Delta k = 2 \frac{n_\omega \omega}{c} - \frac{(n_{2\omega})2\omega}{c} \tag{3}$$

[1]
The temperature dependence then comes from the change in refractive index which can be determined using a (modified) Sellmeier equation

$$n^2 = 1 + \frac{p}{p_0} \frac{T_0}{T} \left(\frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} \right) \tag{4}$$

where $p_0 = 1000$ mbar is a reference pressure, $T_0 = 273$ K is a reference temperature and $B_1 = 39209.95 \cdot 10^{-8}$, $B_2 = 18806.48 \cdot 10^{-8}$, $C_1 = 1146.24 \cdot 10^{-6}$ μm^2, $C_2 = 13.476 \cdot 10^{-6}$ μm^2 are coefficients at that reference pressure/temperature in this case for Nitrogen [2].

To calculate n_ω of course is $\lambda = 0.8$ μm while for $n_{2\omega}$ we have $\lambda = 0.4$ μm. When computing all this with the relevant constant/parameters the plot from figure 1 is generated.
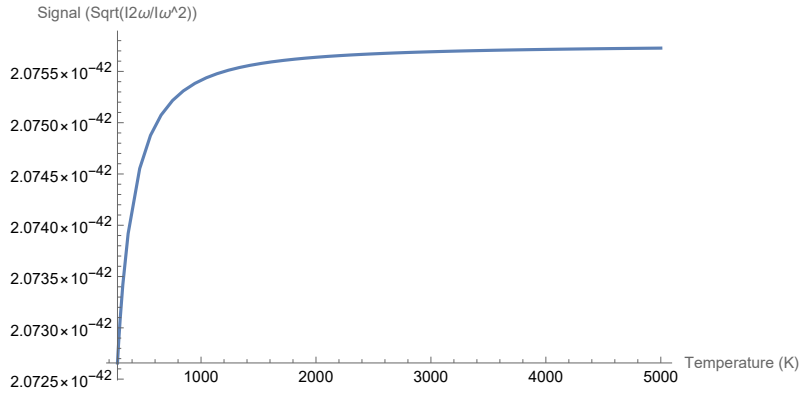

Figure 1: The calculated signal for a E-Fish experiment for different temperatures.

As can be seen in figure 1 there is a variation/dependence on the temperature of the signal. But not only is (for the current experiment parameters) the signal very low it also has very little relative change as the temperature changes (especially at higher temperatures). Thus it wouldn't really be suitable for use as a temperature sensor.

Question 3: Laser scattering on atmospheric pressure plasma jet experiment

A: Plot of signal and gas temperature
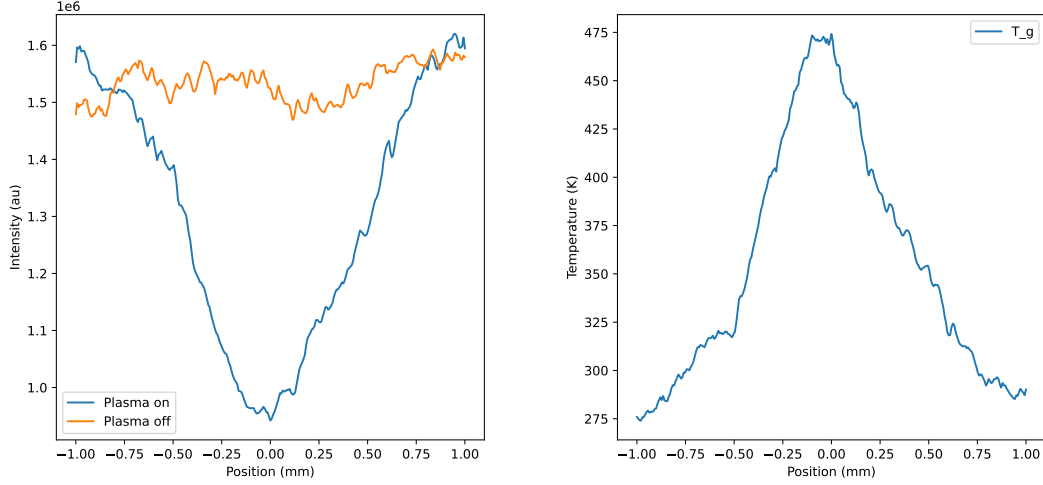
(a) Signal power versus position.

(b) The gas temperature versus position.

Figure 2: Signal and temperature plot.

In figure 2 the plots for the total signal power and gas temperature can be seen. The total power was obtained by integrating/summing over all the wavelengths. The gas temperature can be determined as follows

$$T_g = \frac{P_{ref}}{P_{plas}} T_{ref} \tag{5}$$

where T_g is the gas temperature, P_{ref} is a reference power (in this case for when the plasma is off), P_{plasma} is the power of the plasma and T_{ref} is a reference temperature (in this case room temperature) [10].

The lower signal from the center/plasma is counterintuitively caused by the higher temperature there. This is because the higher temperature causes a lower density of (heavy) particles to which the scattering signal is proportional [10].

B: Plot of spectral response

Initially a Voight profile was fitted to the spectrum but this resulted in a negative Lorentzian FWHM thus for this question only a Gaussian profile was fitted. The spectra was calculated by summing over the entire space.
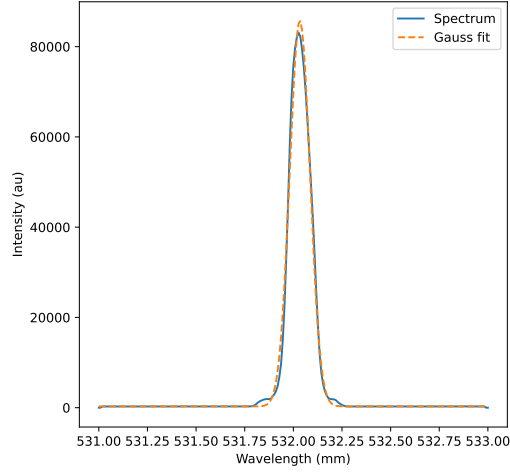
(a) The spectrum when the plasma was on.
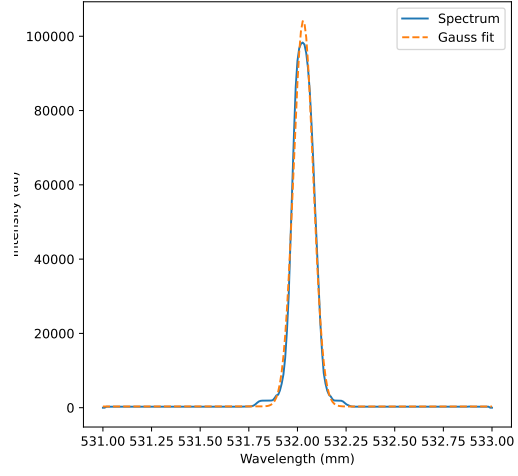
(b) The spectrum when the plasma was off.

Figure 3: Comparison and Gaussian fit of spectra measured with and without plasma.

The FWHM while the plasma was on is 0.1227 ± 0.0009 nm (see figure 3a) and while the plasma was off it is 0.1191 ± 0.0008 nm (see figure 3b). The limiting factor thus was the instrumental profile and only a small part was caused by the spectral broadening (as can be seen by the only slight increase between plasma off and on). The original paper also comes to the same conclusion [10].

Question 4: Three-level reduced energy scheme transitions

A: Rate equations

The first level has outgoing induced absorption (to level 2) and receives spontaneous and induced emissions (from level 2). Thus it's rate equation becomes:

$$\dot{N_1} = -B_{13}\rho N_1 + B_{31}N_3 + A_{31}N_3 \tag{6}$$

The third level had incoming (from level 1) induced absorption, outgoing induced emissions (to level 1) and outgoing spontaneous emissions (to both level 1 and 2).

$$\dot{N_3} = B_{13}\rho N_1 - B_{31}N_3 - (A_{31} + A_{32})N_3 \tag{7}$$

Finally the second level only has incoming spontaneous emissions (from level 3):

$$\dot{N_2} = A_{32}N_3 \tag{8}$$

B: Solved rate equations

If $N_2 \ll N_0$ that must mean that $A_{32} \ll A_{31}$ (or that $B_{13} \ll 1$ but that would result in $N_1 \approx N_0$ and $N_2 \approx N_3 \approx 0$ and that is a trivial non-interesting solution and thus is not considered) thus it essentially becomes a two-level system with $N_0 \approx N_1 + N_3$. Also if $g_1 = g_3 = 1$ then $B_{13} = B_{31}$

This allows us to rewrite the rate equation for the third level:

$$\dot{N_3} \approx B_{13}\rho(N_0 - N_3) - B13N_3 - A_{31}N_3 = B_{13}\rho N_0 - (2\rho B_{13} + A_{31})N_3 \tag{9}$$

which is an ODE which only depends on the population of itself and thus can more easily be solved.

First the final (asymptotic) value of the ODE can be found by setting $\dot{N_3} = 0$ resulting in

$$B_{13}\rho N_0 = (2\rho B_{13} + A_{31})N_{3,fin} \to N_{3,fin} = \frac{B_{13}\rho N_0}{(2\rho B_{13} + A_{31})} = B_{13}\rho\tau N_0 \tag{10}$$

This enables us to then ignore the constant part of the differential equation and focus on the dynamic part

$$\dot{N}_{3,dyn} = -(2\rho B_{13} + A_{31})N_{3,dyn} \to N_{3,dyn} = -\frac{B_{13}\rho N_0}{2\rho B_{13} + A_{31}}\exp(-(2\rho B_{13} + A_{31})t) \tag{11}$$

where the amplitude of the exponential function is $N_{3,fin}$ to comply with the initial condition. This than results in

$$N_3 \approx N_{3,fin} + N_{3,dyn} = \frac{B_{13}\rho N_0}{(2\rho B_{13} + A_{31})} - \frac{B_{13}\rho N_0}{2\rho B_{13} + A_{31}}\exp(-(2\rho B_{13} + A_{31})t) = \left(1 - \exp\left(-\frac{1}{\tau}\right)\right)B_{13}\rho\tau N_0 \tag{12}$$

Finally the equation for N_1 then easily follows from $N_0 \approx N_1 + N_3$

$$N_1 \approx N_0 - N_3 = N_0 - \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)B_{13}\rho\tau N_0 \tag{13}$$

C: Signal

The photon emission rate is the same rate as the (incoming) rate equation for N_2. Thus if we combine equation 8 and 12 we get

$$S = \dot{N_2} \approx A_{32}N_3 = A_{32}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right)B_{13}\rho\tau N_0 = (1 - \exp(-(2B_{13}\rho + A_{31})t))\frac{A_{32}B_{13}\rho N_0}{2B_{13}\rho + A_{31}} \tag{14}$$

assuming a large enough time $t \gg \frac{1}{2B_{13}\rho + A_{31}}$ one would asymptotically approach

$$S_{fin} = A_{32}N_{3,fin} = \frac{A_{32}B_{13}\rho N_0}{2\rho B_{13} + A_{31}} \tag{15}$$

D: Low excitation level vs high excitation level

At low laser power $B_{13}\rho \ll A_{31}$ then equation 14 becomes

$$S_{low} \approx (1 - \exp(-A_{31}t)) \frac{A_{32}B_{13}\rho N_0}{A_{31}} \tag{16}$$

which is linear in ρ.

While at high laser power $B_{13}\rho \gg A_{31}$ it becomes

$$S_{high} \approx (1 - \exp(-2B_{13}\rho t)) \frac{A_{32}B_{13}\rho N_0}{2B_{13}\rho} = (1 - \exp(-2B_{13}\rho t)) \frac{1}{2} A_{32} N_0 \tag{17}$$

which indeed is constant in ρ (assuming $t \gg \frac{1}{2B_{13}\rho}$).

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