Fourier Transform Spectroscopy Laboratory

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We studied the molecular absorption and emission spectra implementing to different types of systems to recollect the data. For the emission spectra a grating spectrometer was used letting us observe four sets of the swan bands at wavenumbers $\sigma[cm^{-1}] = 516.52,\ 473.71,\ 438.22,\ 563.55$ with and error of $\Delta sigma = 0.4[cm^{-1}]$ from the theoretical value. The absorption spectrum was recollected using a Fourier transform spectrometer, with this measurement we were able to find the value for the rotational and centrifugal constants for a butane flame as $\sigma_{00} = 2142.94$, $B'_\sigma = 1.855$ $B''_\sigma = 1.879$ $D'_\sigma = 2.93x10^{-5}$ $D''_\sigma = 3.161x10^{-5}$ which show us that the transitions are primordially vibrational in motion.

Key words: Fourier spectroscopy, CO spectra, Swan Band , Vibrational transition.

I. INTRODUCTION

In this laboratory the main interest was to study molecular spectra in the state of emission and absorption. This spectra is going to be acquired using a Fourier transform spectrometer, giving us the advantage to capture a high resolution absorption spectrum in the infrared interval in this case. An application of Fourier transform spectroscopy is the analysis of gas emission form cars, so we will use it to study the spectrum of CO.

We also used a diffractive grating spectrometer with a CCD detector to acquire a low resolution spectrum from a gas flame in the visible wavelength interval. With this we obtain the characteristic band structure in a molecule such as the transition between vibrational levels in to different electronic states. This two sets of measurements where executed and will be analyzed in this document taking into account that the fine structure due to the molecular rotation will not be resolved.

II. THEORETICAL BACKGROUND

For any molecule one can describe its energy in three parts, the electronic energy E_{el}, rotational energy E_{rot} and the vibrational energy E_{vib}, where the total energy would be:

$$E = E_{el} + E_{vib} + E_{rot}.$$

The one the contributes the most is the electronic energy E_{el} which originates from the electron movement in the potential due to the nuclei, its magnitude is in the region of $1 - 10\ eV$, from this state the electron can vibrate adding vibrational energy E_{vib}, this being a first order fine structure correction with a magnitude of $0.1\ eV$. The final correction would be to consider the vibration of the molecule which gives a final contribution the the energy E_{vib} in the range of $0.001\ eV$ which would be the finest correction and would need a very high resolution experiment to be detected.

A graphical representation on how the different energy states are subdivided by each of this corrections is shown in Fig.1. Notice how we have the potential for the nuclei and then we have the discrete set of vibrational energy, then we amplify the image and one can see that each vibrational has different rotational levels.

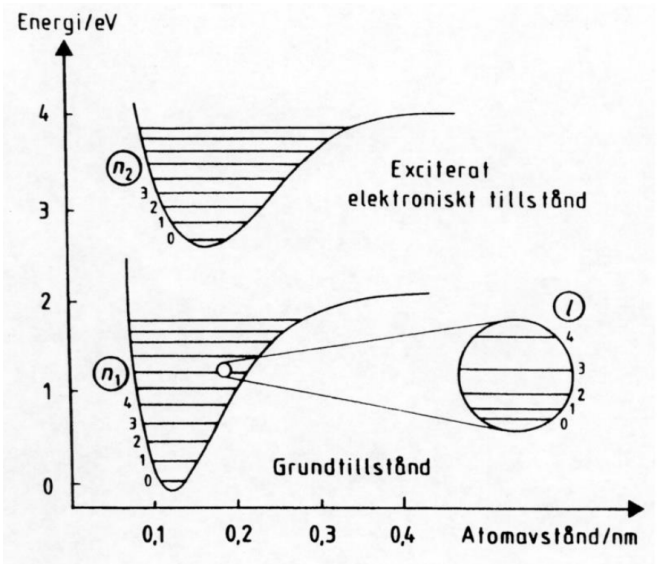


FIG. 1. Energy Structure for a diatomic molecule[2]

Now to calculate the total energy one can use the simplest approximation, where the vibration of the molecule is approximated to a harmonic oscillator and the rotation is described as a rigid rotator. Giving a quantum mechanical description of the total energy written as[2][1]:

$$E = E_{el} + \hbar w_0 \left(n + \frac{1}{2}\right) + \frac{\bar{\hbar}^2}{2\mu R_0^2}\left[l(l+1)\right]. \qquad (1)$$

Where the vibration is described with a resonance frequency w_0 and by the quantum number $n = 0, 1, 2, 3..$, the rotational motion is given by the quantum number=

$l = 0, 1, 2, 3..$, and he factors μ, R_0 are the reduced mas and the biding distance. When describing the rotational energy in a molecule its convenient to introduce two parameters, the rotational constant B and the centrifugal distortion constant D given by[2][1]:

$$B = \frac{\hbar^2}{2\mu R_0^2}, \; D = \frac{4B^3}{w_0^2} \tag{2}$$

this constants are introduced in the improved model elastic rotator and give rise to an improvement int the description of the rotational energy for high l or analogs faster rotations. From the definition of D one can tell that $D \ll B$ showing that model of rigid rotator gives an accurate description for small l, but to have the full picture of the rotational energy one can find it using the following expression[2][3]:

$$E_{rot} = B \cdot l(l+1) - D \cdot l^2(l+1)^2 \tag{3}$$

For this laboratory we are interested in obtaining the wave number for a transition between a set of vibrational states n' and n'' where $n' > n''$. The wave number σ can be obtained neglecting the centrifugal constant or taking it into account for a higher order approximation. In our case we studied both of the cases using the following two approximations[2][4];

$$\sigma_{00} = \hbar w_0(n' - n'') \tag{4}$$

$$\sigma = \sigma_{00} + (B'_\sigma + B''_\sigma)m + (B'_\sigma - B''_\sigma)m^2 \tag{5}$$

$$\begin{aligned}\sigma = \sigma_{00} + (B'_\sigma + B''_\sigma)m + (B'_\sigma - B''_\sigma - D'_\sigma + D''_\sigma)m^2 \\ -2(D'_\sigma + D''_\sigma)m^3 - (D'_\sigma - D''_\sigma)m^4\end{aligned} \tag{6}$$

With this general background we approach to acquire and analyze the data form this laboratory.

III. EXPERIMENTAL SETUP

For this experiment we used a Fourier transform spectrometer is a Michelson interferometer where one of the mirrors can move with a constant speed. All radiation incident on the interferometer is registered by a detector, and this system follows the same intensity fluctuations expected from a Michelson interferometer. To detect the absorption spectrum of a gas can be done by placing a sample between the beam splitter and the detector which in are case was a CO gas sample. This is one most common application of a Fourier transform spectrometer.

In this experiment a grating spectrometer was also used, the setup consist of a source of light in our case a flame then it is split using a 2400 $\frac{lines}{mm}$ and then this spectrum is recollected using a CCD[2].

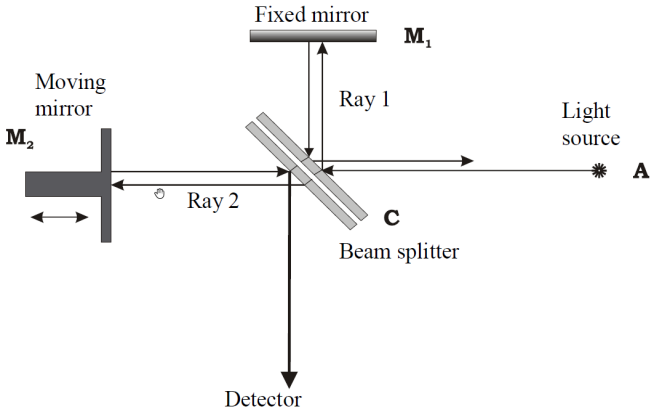


FIG. 2. Fourier transform Spectrometer. Consist of a movable mirror, a fixed mirror, a beam splitter, a light source and a detection system.[2]

IV. RESULT ANALYSIS

For the first part of this lab we used the grating spectrometer to recollect the emission spectrum of a butane flame as shown in Fig.3. From the data recollected we can identify the four most important swan bands or vibrational transitions in this emission spectrum as are shown in Fig.3 where a dot was plotted over the expected wavenumber where the transition would happen. An other measurement was executed using a grating with

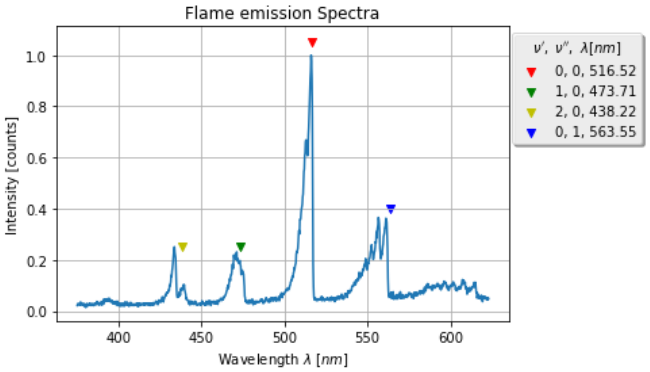


FIG. 3. Flame emission spectrum recollected using a grating spectrometer using 300 line/mm grating

2400 lines/mm giving us a closer look to the the principal swan band shown in Fig.4. With this close up we can tell that there is a small discrepancy with the expected value of the wavenumber this can be explained by two factors difference in the physical conditions of the flame it self due to the surrounding environment and a low capability of resolution of the CCD camera. Even thought there is a a difference in the wave number we can find that the difference is in a range of $\Delta 0.4$ nm which is still a good enough approximation to the expected value.

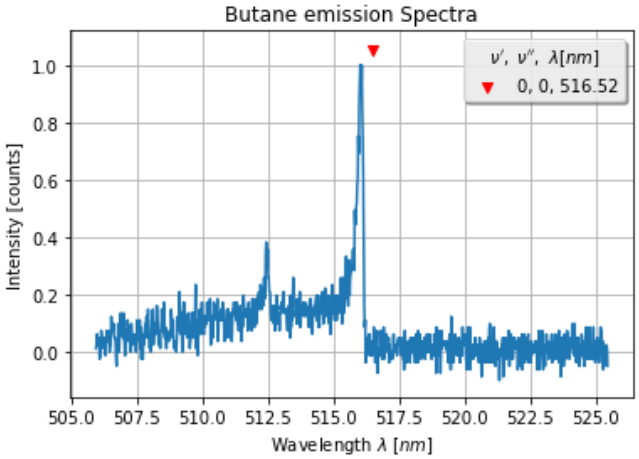


FIG. 4. Close up of swan band using a 2400 line/mm grating

It is also worthy to note that there exist a shading from red to violet, this can gives information on the rotational constant between the different rotational states giving us that the exited state has a smaller rotational constant than the starting state $B' > B''$.

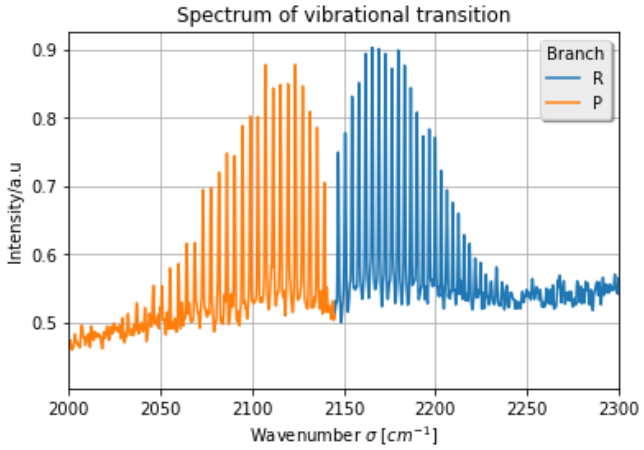


FIG. 5. Data recollected of the absorption spectrum of CO using the Fourier transform spectrometer

For the second part of the laboratory we used the Fourier transform spectrometer to recollect data fro the absorption spectrum of Carbon monoxide. The data recollected is shown in Fig.5 where we can see the two branches of the spectrum corresponding to P-branch for $m = -1, -2, -3...$ and R-branch that corresponds to $m = 1, 2, 3....$ With this we found the values for the wavenumbers where there was a peak and then assigned its corresponding magnetic quantum number m, thus allowing us to implement the models described in the previous section shown in Fig.6. With this we were able to find the values for the B coefficients considering the rigid rotator and the elastic rotator approximation.

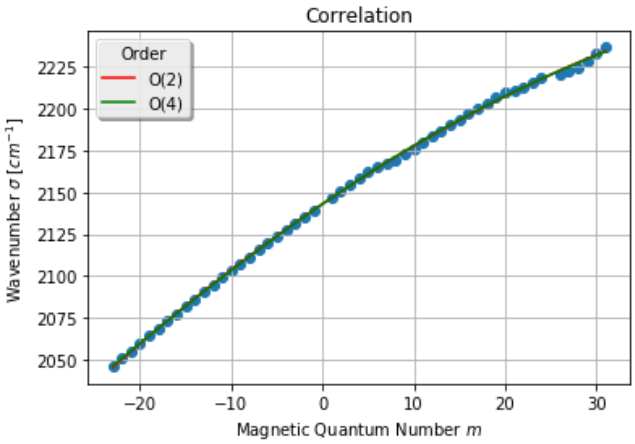


FIG. 6. Analysis using the information of the peaks obtained form the Fourier Transform Spectrometer

The values obtained for the rigid rotator for the B coefficients given in Eq.5 where:

$$\sigma_{00} = 2142.99[cm^{-1}] \ , \ B'_\sigma = 1.833 \ \ B''_\sigma = 1.857$$

And for elastic rotator the we calculated the value for the rotational and centrifugal constants B and D respectably giving a value of:

$$\sigma_{00} = 2142.94[cm^{-1}] \ , \ B'_\sigma = 1.855 \ \ B''_\sigma = 1.879$$
$$D'_\sigma = 2.93x10^{-5} \ \ D''_\sigma = 3.161x10^{-5}$$

concluding the analysis of the data recollected for this segment of the laboratory.

V. CONCLUSIONS

From the set of constants and the information given in the theoretical background one can build a better understanding of what type of transitions are taking place in the CO absorption spectrum, being mainly vibrational transitions. By looking at the magnitude of the constants it's clear why the centrifugal term doesn't play a role for slow rotating transitions since the value for both of the starting state and the arrival state have very small magnitudes, thus making the rigid rotator a good approximation for small l. For the grating spectrometer we obtained a very accurate measurement of the swan bands with a error of $0.4nm$ with respect to the expected value given in Ref.[2] which show the power of this technique only differing because of the differences in the pressure, the amount of light collected from the sample and the resolution of the measuring system.

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