High Resolution Spectra I: Using the Asymmetric Stretch Band of Atmospheric CO_2 to Obtain the C=O Bond Length

Introduction

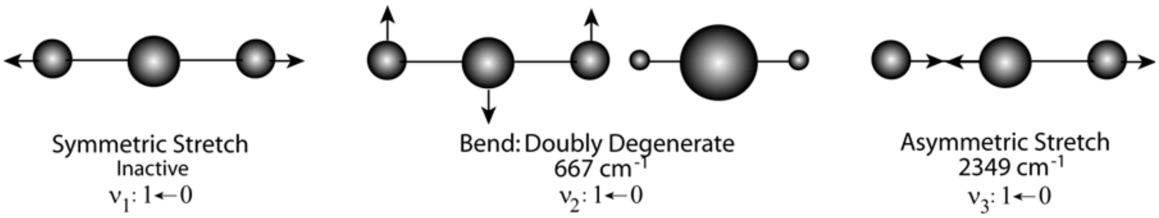
This is the first experiment in which a high resolution vibronic spectrum will be obtained utilizing the Bruker Vector 22 FTIR spectrometer. The spectral frequencies will be analyzed using the LINEST function Microsoft Excel to determine several coefficients and the equilibrium bond length.

Carbon dioxide is one of the most abundant gases in our atmosphere. This fact coupled with the fact that it is a greenhouse gas makes it a viable topic to study. It has a spectrum which is more complex than other linear molecules (e.g. CO and HCl). For example, there is The "greenhouse property" of this gas is largely accounted for by the presence of a Q-branch in the doubly degenerate bend vibration at 677 cm^{-1}. In this experiment, we will be primarily concerned with asymmetric stretch band centered at 2350 cm^{-1}.

The complete description of the vibronic energy stretching modes of a linear molecule (in wavenumbers) is

$$E\left(v_1, v_2, \ldots, j\right) = \underbrace{\sum_i \omega_i \left(v_i + \frac{d_i}{2}\right)}_{\textit{HO vibrations}} + \underbrace{\sum_i \sum_{j \geq i} x_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right)}_{\textit{anharmonic term}} + \sum_i g_i l^2 + \underbrace{B_{[v]} J\left(J+1\right)}_{\textit{RR term}} - \underbrace{D_{[v]} J^2 \left(J+1\right)^2}_{\textit{centrifugal distortion}}$$

where $\omega_i =$ HO normal mode frequencies, v_i, d_i = quantum numbers and degeneracies of ω_i frequencies, and $x_{ij} =$ the first-order anharmonic corrections. For CO_2, there are three fundamental transition frequencies for Δv_i :



The l_i terms are zero for stretching modes (see ν_1). The asymmetric stretch of interest is given by $\nu_3 = \omega_3 + 2x_{33} + \frac{1}{2}x_{13} + x_{23}$. The rotational constant, $B_{[v]}$, for a certain vibronic state includes vibration-rotation terms, α_i, from all vibrational modes. The relationship between the rigid model which described by the equilibrium rotational constant, Be, and $B_{[v]}$ is

$$B_{[v]} \equiv B_{v_1 v_2 v_3 \ldots} = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2}\right)$$

For lowest vibrational state (i.e. $\nu_1 = \nu_2 = \nu_3 = 0$), the rotational constant is given by $B_{[0]} \equiv B_{[000]}$. We will be calculating this constant which we can then utilize to determine the equilibrium bond length

$$B_{[0]} = \frac{h}{8\pi^2 I_{[0]} c} \text{ where } I_{[0]} = 2m_{oxygen} r^2$$

As previously mentioned, we are concerned with the asymmetric mode. Therefore, our rotational constant will be $B_{[001]}$ since only the asymmetric mode will be excited while the other two remain in the ground state. The centrifugal distortion, $D_{[0]}$, is quite small for polyatomic linear systems and will therefore be approximated by D_e. The asymmetric may be mathematically expressed as

$$B_{[001]} = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2} \right) - \alpha_3 = B_{[0]} - \alpha_3$$

The transitions that occur within this band may be labeled by the P and R branch terminology using $\Delta J = \pm 1$.

$$R-branch: \Delta J = +1\, or\ J \to J+1 \quad v = v_3 + 2B_{[0]}\left(J+1\right) + \alpha_3\left(J+1\right)\left(J+2\right) - 4D_e\left(J+1\right)^3$$

$$P-branch: \Delta J = -1\, or\ J \to J-1 \quad v = v_3 + 2B_{[0]}\left(-J\right) + \alpha_3\left(J-1\right)J - 4D_e\left(-J\right)^3$$

The equation will be utilizing to fit our data in this experiment is

$$\boxed{v(m) = v_3 + B_{[0]}(2m) + \alpha_3\left(-m - m^2\right) + D_e\left(-4m^3\right)}$$

where D_e is the equilibrium bond dissociation energy and m is an index parameter not to be confused with mass. This parameter is defined as m = J + 1 for the R-branch and m = -J for the P-branch. We will come back to this in a moment.

For CO_2, the ground state is symmetric with respect to the two oxygen atoms – they are interchangeable. Therefore, both the ψ_{el} and ψ_{vib} are symmetric in their ground states or only the even J rotational states exist prior to IR photon absorption. As we know, the overall symmetry much be preserved. This is in fact the case since the product of the asymmetric upper vibrational state and the asymmetric odd J rotational state will generate a symmetric excited state. What does this really all mean? It means that half the rotational lines which would be observed for other linear molecules (e.g. HCl) will be dark for CO_2. The bright states or allowable transitions for each branch and the corresponding index parameter is given below.

$$R-branch: \Delta J = +1, m = J+1 \quad 0 \to 1\left(m=1\right), 2 \to 3\left(m=3\right), 4 \to 5\left(m=5\right), etc.$$

$$P-branch: \Delta J = -1, m = -J \quad 2 \to 1\left(m=-2\right), 4 \to 3\left(m=-4\right), 6 \to 5\left(m=-6\right), etc.$$

Experimental

You will record the high-resolution spectrum of CO_2 form 2300 cm^{-1} to 2380 cm^{-1}. In order to do this, we need to open the sample chamber of the Bruker FTIR and take spectrum of the atmosphere. Prior to running the instrument you should check the measurement parameters to ensure they are set appropriately.

- Open the Spectrum Program on the Desktop
- Hit OK to initialize the instrument
- Under the Instrument Menu - Choose Scan Sample
  - Select single beam
  - Rename the file and write a description
  - Set:
    - “Start” to 2380.0 cm^{-1} and “End” to 2300.0 cm^{-1}
    - “Number of scans” to 16
    - “Resolution” 1.0

- Choose the Setup button on the right
    - Apodization should be set to weak
    - Interferogram should be selected

After all parameters have been set you are ready to run the scan. It will take several minutes for all 16 scans to be completed and averaged. Save your file as ASCII and email copies to yourselves and me. You will need to include a plot of the spectrum in your report which may be generated in Excel.

Data Analysis

This is where the fun begins. First, you will import your ASCII file into Excel. Generate a scatterplot with line option and label all the spectral lines with the correct m value. Indicate on your plot the location of the P and R branches. You will be using the LINEST function to fit the boxed equation above such that you obtain the regression parameters ν_3, $B_{[0]}$, and α_3, and their uncertainties. You will make a column for each of the following in this order: in column A: "m", column B: "2m", column C: "-m-m^2", column D: "-4m^3" and column E: nu. To fit only the first three parameters, you will highlight a table on the side which is 3 x 2 and type "=LINEST(E2:E48,B2:C48,TRUE,TRUE)." DO NOT HIT RETURN, instead hold down "Ctrl" with "Shift" and then hit "Enter." Your 3 x 2 table is now filled with numbers which correspond to the following:

α_3	$B_{[0]}$	ν_3
Error in α_3	Error in $B_{[0]}$	Error in ν_3

You will use these computations to calculate the C=O bond length and its error. Repeat the process by including the centrifugal distortion term, D_e. Compare these values with the errors to the literature values ($\nu_3 = 2349.16$ cm^{-1}, $B_{[0]} = 0.3902$ cm^{-1}, $r_{C=O} = 116.21$ pm).

D_e	α_3	$B_{[0]}$	ν_3
Error in D_e	Error in α_3	Error in $B_{[0]}$	Error in ν_3

Notebook and Report

Make sure to record all of your data, etc. in your notebook which need to be dated and signed by me before you leave the lab. Your report should be written (as we discussed) in the form of a Communication/Letter publishable by *J. Phys. Chem.*

References

[1] D.A. McQuarrie, "*Quantum Chemistry*" 1983, University Science Books.
[2] M. Karplus and R. Porter, "*Atoms and Molecules: An Introduction for Students of Physical Chemistry*" 1970, W. A. Benjamin, Inc.
[3] P.J. Ogren, *J. Chem. Ed.* 2002, **79**, 117-119.
[4] G. Hertzberg, "*Molecular Spectra and Molecular Structure II*" 1991, Krieger: Malabar, Fl.
[5] J. M. Hollas, "*High Resolution Spectroscopy*" 1998, John-Wiley & Sons.
[6] M. Johal, New College of Florida – This lab was adapted from him.