Determination of the C=O bond length in carbon dioxide

Objective: You will determine the C=O bond length of carbon dioxide as well as other molecular parameters from an analysis of the IR spectrum of air.

Background: Textbooks often present the Ro-Vib spectral analysis of diatomic molecules which leads to molecular constants and bond lengths. The analysis for the linear triatomic, carbon dioxide, is not much more complicated. The differences are discussed below. This is a summary derived from a paper published in the Journal of Chemical Education [1].

Total molecular energies are can be expressed as a sum of terms, each of which is quantized.

\[ E^{\text{tot}} = E^{\text{electronic}} + E^{\text{translational}} + E^{\text{rotational}} + E^{\text{vibrational}} \]

The optical spectrum of a molecule consists of absorption peaks that occur when the incident radiation is of a wavenumber such that it matches the energy difference between to two particular energy levels:

\[ \tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i \]

Carbon dioxide has four internal degrees of freedom. Because of its point group symmetry, these are represented by only three normal modes of vibration:

- \( x \): symmetric stretching mode
- \( y \): doubly degenerate bending mode
- \( z \): asymmetric stretching mode

Therefore, its vibrational energy is a sum of three parts. If we allow the symbols \((x,y,z)\) to represent the quantum numbers of each of the three modes [2] we use the harmonic oscillator approximation to express the total vibrational energy as:

\[ E^{\text{vibrational}}_{x,y,z} = \tilde{\nu}_x(x + 1/2) + \tilde{\nu}_y(y + 1) + \tilde{\nu}_z(z + 1/2) \]

The second term is slightly different because of the degeneracy of that mode. Here the set of constants, \((\tilde{\nu}_x, \tilde{\nu}_y, \tilde{\nu}_z)\), represent the fundamental vibrational frequencies of each of the three modes.

Carbon dioxide is a linear molecule whose rotational energy can be approximated as that of a rigid rotator:

\[ E^{\text{rotational}}_{J,x,y,z} = B_{x,y,z} J(J + 1) \]

Here the \( B \) constant is referred to as the rotational constant, and there would be a different one for each quantum level within each vibrational mode. Therefore, it has three subscripts, each representing the level within each mode. Just like in the analysis of a diatomic molecule, we will

[2] in discussions of diatomics, there is only one quantum number (n).
assume a simple relationship among the rotational constants using rotation-vibration interaction constants (alphas). Instead of one of these, we need three:

\[ \tilde{B}_{x,y,z} = \tilde{B}_e - \tilde{\alpha}_x (x + 1/2) - \tilde{\alpha}_y (y + 1) - \tilde{\alpha}_z (z + 1/2) \]

At this point there seems to be a lot of constants and a lot of levels, but please be patient. The measurements will involve transitions where many of these quantum states are not changing, so there will be much cancellation.

The final difference between carbon dioxide and a diatomic molecule such as HCl is that not all of the rotational states are eligible for absorption because of the symmetry of the wavefunction. This will have to be considered when assigning the peaks in the ro-vib spectrum to particular J transitions. The only transitions seen in the optical spectrum are absorptions that begin from an even numbered J state. Therefore, assign the peaks working out from the center as:

R branch: J=0 to J=1 ; J=2 to J=3 ; J=4 to J=5; etc …
P branch: J=2 to J=1 ; J=4 to J=3 ; J=6 to J=5; etc …

It is possible and will be convenient to use combination differences in the analysis. For this we define a new label “\(m\)” such that each peak has one and only one number associated with it and that number is unique:

R branch: \(m = J + 1\)  
(P rotational quantum number of the lower vibrational state!)
P branch: \(m = -J\)

In this experiment, you will examine the ro-vib spectrum from level 0 to level 1 of mode z (the asymmetric stretch). The electronic state is not changing. The other two vibrational states are not changing (they remain at level 0). The translational states are small perturbations and can be ignored. The rotational states are changing. Therefore, the transitions observed are given by:

\[
\tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i = \tilde{\nu}_z + \tilde{B}_{0,0,1,1} J'(J'+1) - \tilde{B}_{0,0,0,0} J(J+1) \\
\text{absorption from } J \rightarrow J'
\]

This formula can be specialized to each of the two branches (J is lower state):

R branch:

\[
\tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i = \tilde{\nu}_z + \tilde{B}_{0,0,1,1} (J+1)(J+2) - \tilde{B}_{0,0,0,0} J(J+1)
\]

P branch:

\[
\tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i = \tilde{\nu}_z + \tilde{B}_{0,0,1,1} (J-1)(J) - \tilde{B}_{0,0,0,0} J(J+1)
\]

Substitution of the index \(m\) finally gives us (for both branches):

R branch:

\[
\tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i = \tilde{\nu}_z + \tilde{B}_{0,0,1,1} (m)(m+1) - \tilde{B}_{0,0,0,0} (m-1)(m)
\]

P branch:

\[
\tilde{\nu} = \tilde{E}^{\text{tot}}_j - \tilde{E}^{\text{tot}}_i = \tilde{\nu}_z + \tilde{B}_{0,0,1,1} (-m-1)(-m) - \tilde{B}_{0,0,0,0} (-m)(-m+1)
\]
Can you see that these two equations are identical? You will use this one equation to determine the constants \( \tilde{B}_{0,0,0} \) and \( \tilde{B}_{0,0,1} \). Then from the 0,0,0 rotational constant you will be able to determine the moment of inertia (I) and from it, the C=O bond length:

\[
\tilde{B}_{0,0,0} = \frac{h}{8c\pi^2I}
\]

**Procedure:** Here is an outline of the steps you should follow.

1. First perform an Optimize+VibFreq Gaussian calculation of carbon dioxide to find out the frequencies of the three normal modes of vibration. Use the B3LYP 6-31G(d) model. Animate these and make a sketch of each in your notebook. Record the values of the frequencies as well as the rotational constants found in the output file. Also record the C=O bond length optimized at this method.

2. With the information from above, try to locate the 0-1 vibrational transition for the asymmetric stretching mode using the Varian 3100 FT-IR. No sample preparation is needed. There is plenty of carbon dioxide in the path of the light, just remove any samples that might already be sitting inside the instrument.

3. Now determine an appropriate wavenumber range to use in the final collection of the spectrum. Be sure to set the resolution of the instrument to the highest value. Collect the spectrum. To record the data, find the peak pick option under the operations tab. Set the sensitivity to the highest value (8). The peaks should now be identified and labeled by wavenumber value. You should have around 50 peaks identified. Export the data (both a screen capture and a file containing the absorptions) to a USB drive so that you can take it to a campus computer for analysis. Printout the screen capture of the spectrum.

4. Using your printout, assign values for the rotational transitions. Now assign the “m” value to each line. Enter the m values and their associated absorption values into a spreadsheet (or import from the file saved from the instrument).

5. Plot the absorptions (in wavenumbers) as a function of m value. Fit the data to a quadratic formula. Use the coefficients of this polynomial to determine the molecular constants for carbon dioxide. You will need to review the equations presented above to figure out how the two rotational constants are related to these coefficients.

6. Using the value of \( \tilde{B}_{0,0,0} \), calculate the moment of inertia and from it the ground state bond distance of C=O.

7. Compare your values for \( \tilde{B}_{0,0,0} \) and C=O bond distance to those calculated by Gaussian and to those you can find in the literature.

8. Using values for \( \tilde{B}_{0,0,1} \) and \( \tilde{B}_{0,0,0} \), determine the ro-vib interaction constant, \( \tilde{\alpha}_z \).