Molecular Constants of CO by Infrared Spectroscopy

Purpose

This experiment uses infrared spectroscopy to determine the bond length, vibration frequency, anharmonicity, and other properties of the carbon monoxide molecule. Also, molecular properties are calculated using \textit{ab initio} quantum mechanics.

Introduction

Diatomic molecules are valuable test cases for understanding molecular bonding and spectroscopy. Because a diatomic molecule is necessarily linear and has only one vibrational mode, its vibration-rotation spectrum is relatively simple. The equilibrium bond length, rotation constant, and harmonic vibration frequency are easily obtained from spectra. More subtle effects such as vibrational anharmonicity and vibration-rotation coupling can also be extracted from infrared spectra. Quantum-chemical methods are tested by comparing calculated properties to results from spectra.

Theory

The rotation-vibration energy of CO is \textbf{approximately} the sum of harmonic-oscillator energy and rigid-rotor energy:

\[ E \approx h \nu_e (v+\frac{1}{2}) + \frac{\hbar^2 J(J+1)}{(8\pi^2 \mu R_e^5)} ; \quad v=0,1,2,\ldots ; \quad J=0,1,2,\ldots \]  

(1)

\( \nu_e \) is the fundamental vibration frequency
\( J \) is the rotation quantum number
\( \nu_e \) is the fundamental vibration frequency in \textit{wavenumbers}, \text{cm}^{-1}.
\( \omega_e = \nu_e / c \), where \( c \) is the speed of light.
\( \mu \) is the CO reduced mass. \( \mu = m_C m_O / (m_C + m_O) \)
\( R_e \) is the equilibrium bond length

In wavenumber units,

\[ E \approx \omega_e (v+\frac{1}{2}) + h J(J+1)/(c 8\pi^2 \mu R_e^5) ; \quad v=0,1,2,\ldots ; \quad J=0,1,2,\ldots \]  

(2)

Units of wavenumbers are convenient because infrared spectra are usually recorded in wavenumbers. Notice that \( E = E/(hc) \) and \( \omega_e = 1/\lambda \). The equilibrium rotation constant \( B_e \) (also in wavenumbers) is defined as

\[ B_e \equiv h/(8\pi^2 c \mu R_e^5) \]  

(3)
The infrared absorptions observed in this experiment arise from transitions between \( v=0 \) and \( v=1 \), and various \( J'' \rightarrow J' \), with \( J''=J'\pm 1 \). Levels and J values are shown in Figure 1.\(^1\) The J for the initial, lower-energy, state is denoted \( J'' \). The absorption wavenumbers, \( \omega=[E(v=1,J')- E(v=0,J'')] \). Using equations 2 and 3, we see that absorptions are at the following wavenumbers:

\[
\omega \approx \omega_e + B_e \left[ J'(J'+1) - J''(J''+1) \right] \quad (4)
\]

Absorptions for which \( J''=J'+1 \) are said to belong to the "R" branch; those with \( J''=J'-1 \) are on the "P" branch. The spectrum should look qualitatively like Figure 2, which is an actual low-temperature CO spectrum.\(^1\) Note: spectrometers may plot \( \omega \) (also called \( \tilde{\nu} \)) increasing either to the left or to the right. It is higher wavenumber, not left-right orientation, that defines the R branch relative to the P branch.

Equation 4 is roughly correct in predicting rotation-vibration transition energies. Quantitative prediction of absorption frequencies requires consideration of three additional factors: centrifugal distortion, vibration-rotation coupling, and vibrational anharmonicity.

The effective moment of inertia increases as J increases. This can be understood as the result of centrifugal force increasing the bond length in states having greater angular momentum. The effect is that energy levels do not increase with J as rapidly as equation 1 implies. A correction term \(-J^2(J+1)^2D_e\) is added to the energy \( E(v,J) \), to account for centrifugal distortion. \( D_e \) is called the centrifugal distortion constant, here in units of \( \text{cm}^{-1} \). (The same symbol \( D_e \) is used for dissociation energy.)

Energy is also reduced by interaction between vibration and rotation, generally decreasing as both \( v \) and J increase. This effect is incorporated with the vibration-rotation interaction constant, \( \alpha_e \). A
correction term \(-\alpha_e (v+\frac{1}{2})J(J+1)\) is added to the energy \(E(v,J)\). As \(v\) increases, so does the bond length, which decreases the rotation constant. This effect is incorporated in \(B_v\) through \(\alpha_e\):

\[
B_v = B_e - \alpha_e (v + \frac{1}{2})
\]

(5)

Specifically, \(B_0 = B_e - \frac{1}{2}\alpha_e\), \(B_1 = B_e - \frac{3}{2}\alpha_e\), and \(B_2 = B_e - \frac{5}{2}\alpha_e\).

Vibrational anharmonicity in CO causes energy to increase less rapidly with \(v\) than equation 1 predicts. This is because diatomic potential energy surfaces are generally less steep on the large-\(R\) side than perfect harmonic oscillator potential surfaces. A correction term \(- (v+\frac{1}{2})^2 \omega_e x_e\) is added to the energy to account for anharmonicity. This experiment will measure two vibration-rotation bands, the fundamental with \(v:0\rightarrow 1\) and the first overtone with \(v:0\rightarrow 2\). Combining data from the fundamental and overtone allows calculation of the anharmonicity, \(x_e\omega_e\).

When these three effects are included, the energy (in wavenumbers) of a \((v,J)\) state is

\[
E(v,J) = \omega_e(v+\frac{1}{2}) - \omega_e x_e (v+\frac{1}{2})^2 + B_e J(J+1) - \alpha_e (v+\frac{1}{2})J(J+1) - D_e J^2(J+1)^2
\]

(6)

Taking the difference of two \((v,J)\) states yields the following equations for the P- and R-branch absorption wavenumbers, as functions of the initial-state \(J''\):

\[
\omega_P(J'') = \omega_v - 2B_v J'' - \alpha_e J''(J''-2) + 4D_e (J'')^3 ; J''=1,2,3,...
\]

(7)

\[
\omega_R(J'') = \omega_v + 2B_v (J''+1) - \alpha_e (J''+1)(J'' + 3) - 4D_e (J''+1)^3 ; J''=0,1,2,...
\]

(8)

\[
\omega_v = v \omega_e - v(v+1) x_e \omega_e.
\]

(9)

Specifically,

- For the fundamental, \(v=1\) and \(\omega_v = \omega_1 = \omega_e - 2 x_e \omega_e\)
- For the overtone, \(v=2\) and \(\omega_v = \omega_2 = 2\omega_e - 6 x_e \omega_e\)

Equations 7 and 8 can be combined into a single equation in terms of the parameter \(m\).

\[
m \equiv -J''\text{ on the P branch} \quad \text{and} \quad m \equiv J''+1\text{ on the R branch}
\]

(10)

\[
\omega(v,m) = \omega_v + (B_v + B_0) m + (B_v - B_0) m^2 - 4 D_e m^3
\]

(11)

Equation 10 will be used to analyze the CO spectra recorded in this experiment. For the fundamental band \(v=1\) and for the overtone band \(v=2\), in equation 11.

Diatomic molecules have been used as test cases for quantum-chemical methods. Basis sets and electron-correlation methods have been tested on the first-row diatomics, including CO. The effects of various approximations on bond length, dipole moment, and vibration frequency have been studied. In this lab, restricted Hartree-Fock (RHF) theory and density functional theory (DFT, with the B3LYP functional) will be used to calculate \(\omega_e\) and \(B_v\), which can be compared with the experimental results obtained from analyzing infrared spectra. DFT, unlike RHF, includes electron
correlation. Electron correlation refers to the instantaneous repulsion between two electrons. Uncorrelated methods such as RHF include electron-electron repulsion only in a spatially-averaged way. Including electron correlation tends to lengthen bonds and lower vibration frequencies and rotation constants. Calculations done for this lab will test that generalization.

**Experimental Procedure**

This experiment uses three pieces of equipment.

- A long-path (4.8 meter) gas cell.
- A Fourier-transform Infrared (FTIR) Spectrophotometer
- A gas manifold with a pump, pressure gauge and CO tank

The long-path gas cell is shown at right. It is shown with two rubber stoppers inserted in the base, to keep humid room air away from the potassium bromide windows that are in the base. The stoppers should be in place except when the instrument is in the sample compartment of the FTIR. The picture shows the cell’s stopcock closed, to prevent loss of CO to the lab.

The sample cell fits in the sample compartment of the FTIR.

The stopcock is closed.

The rubber stoppers have been removed from the base of the cell.
To evacuate the cell and then fill it with carbon monoxide gas, use the manifold and pump in the hood. Filling the cell involves slowly opening a closed glass system to a high-pressure gas, so

- Wear goggles
- Check that the hood is working (look at its gauge) before opening the CO tank.
- Keep the hood sash down as far as possible
- Open valves slowly and carefully.

The cell is attached to the manifold and evacuated by opening the stopcocks between the pump and the manifold and the cell and manifold. Rinse the cell with air several times in order to remove residual CO, CO₂, SO₂, CS₂ or other sample gases. To remove 99% of an earlier sample, fill the system with air and pump down at least four times.

Evacuate the cell to the extent the pump permits, about 200mbar. Close the stopcock to the cell. Remove the rubber stoppers from the cell base. Place the cell in the FTIR sample compartment. Record a background spectrum. Settings: 500 to 4500 cm⁻¹ range, 0.5 cm⁻¹ resolution, collect and average 4 or more scans.

After recording the background spectrum, reattach the cell to the manifold. Check that the needle valve on the CO tank is closed. Open the main valve on the CO tank. With the stopcock to the pump closed, CO gas is introduced from the tank by slowly opening the needle valve. Fill the manifold until the desired gas pressure is reached. A pressure of 30 mbar CO may work well. (If the evacuated pressure was 200 mbar, then the total pressure with CO would be about 230 mbar.)

Return the gas cell to the FTIR sample compartment. Record the infrared spectrum of the fundamental transition. Record the spectrum from 2050 to 2250 cm⁻¹. Mark peak locations. Print the spectrum or save it as an image.

Reattach the cell to the manifold. Bring the CO pressure in the cell to 200-300 mbar. The total pressure would be that plus the evacuated pressure. Return the gas cell to the FTIR sample compartment.
compartment. Record the overtone spectrum from 4150 to 4350 cm\(^{-1}\). Mark the locations of 30 to 40 peaks, in cm\(^{-1}\). (Peak absorbances are not needed.) Print the spectrum or save it as an image. Include both the fundamental spectrum and the overtone spectrum in your lab report.

After taking a spectrum, reconnect the cell to the manifold. Rinse with air and pump down a few times to remove nearly all carbon monoxide. Return the cell to the desiccator. The rubber stoppers should be in the base. Leave the cell’s stopcock closed in the desiccator.

**Hazard:**

**Carbon monoxide gas is poisonous.** It should be released only in the hood, not in the open lab. Keep the hood sash down so the hood draws air well.
Spectral-based calculations

Enter into a spreadsheet the wavenumbers of 30-40 lines each of the fundamental and the overtone spectrum. Assign each line to the P or R branch. Assign $J''$ and $m$ values to every line. (See equation 10 and the qualitative spectrum near equation 4.)

Plot wavenumbers versus $m$.

**Fit the fundamental lines** to equation 11. Letting $c_0$, $c_1$, $c_2$ and $c_3$ represent the constants in the cubic equation 11,

$$\omega(v,m) = c_0 + c_1 m + c_2 m^2 + c_3 m^3 \quad (12)$$

Do a linear regression calculation to obtain the values of the intercept $c_0$ and the three coefficients $c_1$, $c_2$ and $c_3$. From the coefficients, calculate $\omega_1$, $B_0$, and $B_1$. Units are wavenumbers (cm$^{-1}$) for each quantity.

$$\omega_1 = c_0, \text{ the intercept} \quad (13)$$

$$B_0 = \frac{1}{2}(c_1 - c_2) \quad (14)$$

$$B_1 = \frac{1}{2}(c_1 + c_2) \quad (15)$$

The uncertainty in $\omega_1$ is the same as that in $c_0$; take it directly from the regression statistics. The centrifugal distortion coefficient could be calculated from $c_3$ ($D_e = -c_3/4$) but we will calculate $D_e$ using a different method, below, because $c_3$ usually is excessively uncertain.

**Fit the overtone lines** to equation 11. Do a linear regression calculation to obtain the intercept and three coefficients. From the intercept and coefficients, calculate $\omega_2$, $B_0$, and $B_2$.

$$\omega_2 = c_0 \quad B_0 = \frac{1}{2}(c_1 - c_2) \quad B_2 = \frac{1}{2}(c_1 + c_2) \quad (16)$$

The uncertainty in $\omega_2$ is the same as that in $c_0$; take it directly from the regression statistics.

**Combine fundamental and overtone results** to calculate $\omega_e$, $x_e \omega_e$, $B_e$, $\alpha_e$ and $D_e$, all in wavenumbers (cm$^{-1}$).

$$\omega_e = 3 \omega_1 - \omega_2 \quad (17)$$

$$x_e \omega_e = (2 \omega_1 - \omega_2)/2 \quad (18)$$

$B_e$ depends linearly on $(v+1/2)$, as stated in equation 5.

$$B_e = B_e - \alpha_e(v+1/2) \quad (19)$$

The experiment should have provided four "y" values: $B_0$, $B_0$, $B_1$, and $B_2$. Graph these versus the "x" values 1/2, 1/2, 3/2 and 5/2. The intercept is $B_e$. The slope equals $-\alpha_e$. Include the graph and regression statistics (from which, take uncertainties for $B_e$ and $\alpha_e$) in your lab report. From $B_e$ calculate the bond length, $R_e$. (Equation 3 relates the two.)

Finally, calculate the centrifugal distortion constant from the "Kratzer" relationship$^{2,3}$ for diatomic molecules.

$$D_e = \frac{4 B_e^3}{\omega_e^2} \quad (20)$$

Compare $\omega_e$, $x_e \omega_e$, $B_e$, $\alpha_e$ and $D_e$ to literature values.$^{4-7}$
Quantum-chemical Calculations

Do two quantum-chemical calculations on the CO molecule. Each calculation should be a geometry optimization and vibration frequency calculation. Use two theories, Hartree-Fock (RHF) and density functional theory (DFT) with the B3LYP functional.

For each calculation, use the 6-311+G(d,p) basis set. That basis set is on WebMO’s menu of basis sets. When you preview the GAMESS input file you will see the basis set specified as

```
$BASIS GBASIS=N311 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.TRUE. $END.
```

The command "DIFFSP" corresponds to the "+" in the basis set name, NDFUNC=1 to the "d", and NPFUNC=1 to the "p".

When using density functional theory with the B3LYP functional it is necessary to add this line to the input file:

```
$FORCE METHOD=SEMINUM $END
```

That causes GAMESS to use a slower "semi-numerical" method of calculating the Hessian matrix, to calculate the vibration frequency. The default analytical method seems not to work with DFT B3LYP. If one forgets, an error message in the output file reminds.

For each calculation, report total energy, vibration frequency, bond length, and rotation constant $B_e$.

<table>
<thead>
<tr>
<th>Table 1. Quantum-Chemical Results</th>
<th>Hartree Fock (RHF)</th>
<th>DFT B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (Hartree)</td>
<td>6-311+G(d,p)</td>
<td>6-311+G(d,p)</td>
</tr>
<tr>
<td>$\omega_e$ (cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_e$ (Angstroms)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_e$ (cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Compare RHF and DFT-B3LYP results. Because correlation energy is negative (i.e., stabilizing), you should find the DFT energy to be lower than the RHF energy. Compare the better of the two theoretical calculation's results to your experimental results.
References


6. Mina-Camilde, Nairmen; Manzanares I; Caballero, Julio F. “Molecular constants of carbon monoxide at v=0, 1, 2 and 3.” *Journal of Chemical Education*, 1996, 73(8), 804-807.