Vibrations of Carbon Dioxide and Carbon Disulfide

Purpose

Vibration frequencies of CO\(_2\) and CS\(_2\) will be measured by Raman and Infrared spectroscopy. The spectra show effects of normal mode symmetries on gross selection rules. A Fermi resonance in the Raman spectrum will be interpreted in terms of interacting normal modes. Bond lengths and vibration frequencies of carbon dioxide and carbon disulfide will be calculated with \textit{ab initio} quantum-chemical methods and compared to experimental frequencies. CS\(_2\) has longer bonds and lower vibration frequencies than CO\(_2\).

Introduction

Linear triatomic molecules such as CO\(_2\) and CS\(_2\) have four vibrational normal modes but just three fundamental vibration frequencies because two modes are degenerate.\(^1\) The symmetric stretching mode is totally symmetric so it is inactive in infrared spectra and active in Raman spectra. The asymmetric stretching vibration and the degenerate bending vibrations are infrared active and Raman inactive. Infrared activities follow from the gross selection rule that “displacements of a normal mode must cause a change in dipole moment in order to be spectroscopically active in the infrared.”\(^1\) The CO\(_2\) and CS\(_2\) molecules have a center of symmetry located at the carbon atom. Such molecules obey the exclusion rule, “In a centrosymmetric molecule no Raman-active molecule is also infrared-active and no infrared-active vibration is also Raman active.”\(^2\) The symmetric stretching vibration is Raman active and infrared inactive. The bend and asymmetric stretch are infrared active and are, for CO\(_2\), routinely observed in the background scan on an FTIR instrument.\(^3\)

Vibration frequencies will be calculated quantum-mechanically for CO\(_2\) and CS\(_2\) using density functional theory. The hybrid functional B3LYP will be used to account for electron exchange and

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1. symmetric
2. bend
3. asymmetric

Figure 1: normal vibrational modes of carbon dioxide

Figure 2: background infrared spectrum of air, showing asymmetric stretching and bending vibrations of carbon dioxide.
correlation. With a medium-size basis set, we may expect calculated frequencies to be within a few percent of experimental, and bond lengths should differ from experimental bond lengths by less than one percent.

By taking both infrared and Raman spectra of carbon disulfide, all three vibration frequencies will be observed. Likewise, the infrared spectrum of CO$_2$ shows asymmetric stretching and bending vibrations. However, the Raman spectrum of CO$_2$ shows two peaks rather than the single symmetric-stretching peak that might be expected. Two peaks appear because the energy of the first excited state ($\psi_{100}$) of the symmetric stretching mode of CO$_2$ is nearly the same as the energy of the second excited state ($\psi_{020}$) of the bending vibration. The notation $\psi_{100}$ means the vibrational wave function for which $v_1=1$, $v_2=v_3=0$, where $v_i$ is the vibrational quantum number for mode $i$. Likewise, $\psi_{020}$ is the vibrational wave function with $v_1=0$, $v_2=2$ and $v_3=0$. Both states have the same symmetry so they mix to form two new symmetric states, splitting the totally symmetric CO$_2$ Raman band into two peaks. Such mixing is called “Fermi resonance.”

The Fermi resonance can be analyzed in terms of the vibrational Hamiltonian, two zero-order vibrational states, and two mixed states.

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

where $\hat{H}_0$ is the zeroth-order harmonic-oscillator Hamiltonian.

$$\hat{H}_0 \psi_{100} = E_{100}^{(0)} \psi_{100} \quad \text{and} \quad \hat{H}_0 \psi_{020} = E_{020}^{(0)} \psi_{020}$$

For convenience, let the zero-point energy $E_{000}^{(0)}=0$. Also for convenience, suppose that all energies are in units of wavenumber (cm$^{-1}$). Then $\nu_1 = E_{100}^{(0)}$ and $2 \nu_2 = E_{020}^{(0)}$. Define mixed states

$$\psi_\pm = c_1 \psi_{100} \mp c_2 \psi_{020}$$

where $c_1$ and $c_2$ are constants that reflect the mixing and keep $\psi_+$ and $\psi_-$ normalized and orthogonal. Energies of $\psi_+$ and $\psi_-$ are $E_+$ and $E_-$.

$$\left(\hat{H}_0 + \hat{H}' \right) \psi_+ = E_+ \psi_+ \quad \text{and} \quad \left(\hat{H}_0 + \hat{H}' \right) \psi_- = E_- \psi_-$$

The two-state secular equation is

$$\begin{pmatrix} E_{100}^{(0)} - E & F \\ F & E_{020}^{(0)} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

Figure 3: mixing of vibrational energy levels
where the interaction energy \( F = \int \psi_{100}^{*} \hat{H}' \psi_{020} \, d\tau = \int \psi_{020}^{*} \hat{H}' \psi_{100} \, d\tau \). Expanded, the two-by-two secular determinant is
\[
\begin{vmatrix}
E_{100}^{(0)} - E & F \\
F & E_{020}^{(0)} - E
\end{vmatrix} - F^2 = 0
\tag{5}
\]

Solutions of the secular determinant, \( E_+ \) and \( E_- \), satisfy the following two equations:
\[
\begin{align*}
E_- + E_+ &= E_{100}^{(0)} + E_{020}^{(0)} \\
(E_- - E_+)^2 &= (E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2
\end{align*}
\tag{6}
\]
(See the Appendix for a derivation.) Energies are in wavenumber units, so \( E_+ \) and \( E_- \) are peak locations directly from the Raman spectrum of CO\(_2\). The higher Raman frequency is \( E_- \); the lower is \( E_+ \). The overtone bending energy \( E_{020}^{(0)} = 2 \tilde{\nu}_2 \); \( \tilde{\nu}_2 \) is observed in the infrared spectrum of CO\(_2\). The symmetric stretching fundamental \( E_{100}^{(0)} \) and the interaction energy \( F \) will be calculated from equations 6. Because equations 6 constrain only \( F^2 \), the sign of \( F \) is arbitrary. Let \( F \) be negative, corresponding to an energy-lowering interaction.

Coefficients \( c_1 \) and \( c_2 \) for the mixed states \( \psi_+ \) and \( \psi_- \) can be calculated from the secular equation plus the normalization condition. Those two conditions lead to equations 7.
\[
\begin{align*}
E_{100}^{(0)} - E &| c_1 + F c_2 = 0 \quad \text{and} \quad c_1^2 + c_2^2 = 1
\end{align*}
\tag{7}
\]
Solve equations 7 for two sets of \( (c_1, c_2) \) constants, one set for \( E=E_+ \) and one set for \( E=E_- \). In each solution set, \( c_1^2 \) is the symmetric-stretch fraction and \( c_2^2 \) is the bending contribution.

Infrared and Raman spectra will directly measure \( \tilde{\nu}_1 \), \( \tilde{\nu}_2 \) and \( \tilde{\nu}_3 \) for CS\(_2\) and \( \tilde{\nu}_2 \) and \( \tilde{\nu}_3 \) for CO\(_2\). The Raman spectrum of CO\(_2\) gives combinations \( E_+ \) and \( E_- \) from which \( \tilde{\nu}_1 = E_{100}^{(0)} \) can be calculated. With our cell and FTIR instrument, the low-frequency \( \tilde{\nu}_2 \) for CS\(_2\) is obscured by noise, so we will take \( \tilde{\nu}_2 \) for CS\(_2\) from the literature.
Procedure

FTIR and Raman spectra of CS$_2$ and CO$_2$ should be saved as or converted to images and incorporated in your lab report.

1. FTIR spectra

Use a vacuum pump to evacuate a gas cell, preferably the 10cm cell with KBr windows. Because the KBr windows absorb water the cell is stored in a desiccator.

There have been some problems working with the “Spectrum” software that operates the FTIR instrument. Here are detailed instructions that produced good spectra.

Start the Spectrum-6 software. (Do not start the “Spectrum” software. Even though it is newer it does not seem able to collect spectra.)

- The Perkin-Elmer login is “Analyst.”
- Choose the instrument “Spectrum 100.”
- If asked about activating the “IR Assistant,” select No.

Place the empty evacuated cell in the FTIR sample compartment.

In the software, choose Scan on the Instrument menu.

- Two warnings may come up: one that the desiccant needs changing and another that the instrument needs service. Dismiss the warnings. Staff have already been notified.
- Click on “Scan.”
- On the Scan tab, set the range (500 - 3000 cm$^{-1}$ will suffice). Set the scan type to “Background.” Ask to collect 4 spectra.
- On the Instrument tab, set resolution to 1 cm$^{-1}$. Click the “Advanced” button. Deselect CO$_2$/H$_2$O. Otherwise the instrument attempts to subtract CO$_2$ absorption from the spectrum.
- On the Sample tab, type a name for the background.
- Click “Start,” and then “Scan.”

Collect a sample of CS$_2$ gas from the head space over liquid CS$_2$. Do this by holding the evacuated IR cell over liquid CS$_2$ and briefly opening a stopcock.

Place the cell containing CS$_2$ in the sample beam.

Again choose Scan on the Instrument menu. Again type in a name, this time a name for the sample spectrum. Check on the Scan tab that a sample (not background) spectrum will be scanned. Click on Start and Scan.
To display the sample spectrum, remove the background spectrum from the screen. (Click on its name, hit the delete key.) Draw a box around the desired part of the spectrum. Autoscale the axes.

The asymmetric stretch will be a strong band near 1500 cm\(^{-1}\). The bend is a sharp weaker band near 400 cm\(^{-1}\), which is too low for our gas cell. (You might see a whiff of this peak; a sharp weak line.) If the spectrum is off scale (i.e., absorbance is too high) reduce the concentration of CS\(_2\) gas in the cell and try again.

Flush the IR cell with air, evacuate it, and collect a sample of carbon dioxide gas. The CO\(_2\) sample can be drawn from the vapor above dry ice. Look in the IR spectrum for the bending vibration near 700 cm\(^{-1}\) and the asymmetric stretch near 2400 cm\(^{-1}\).
2. Raman spectra

Raman spectra will be recorded using an “Advantage 200” instrument from DeltaNu, Inc. If the Raman instrument is not on, turn it on. The power switch is on the back at the upper right as you face the front of the instrument. The instrument uses a red helium-neon laser. Do not stare at the red light and, of course, do not look directly into the laser beam.

If the DeltaNU software is not already running, start it. Select Spectrometer Port com3.

The instrument has two sample holders. The “xyz” stage should be installed. It supports samples on a platform that can be moved in three directions. Irregular solids and sample vials can be used with the xyz stage simply by placing them on the platform. Especially when using the xyz stage, be careful to avoid looking into the laser beam.

Figure 5: xyz stage

Click "Acquire" to acquire a spectrum. To print a spectrum, you must first save it to a file (e.g., in ASCII “.prn” format), then import that file into Excel, make a graph, and print from Excel.

Practice collecting a spectrum of either cyclohexane or polymethylmethacrylate, PMMA. A clear colorless solid cylinder of PMMA was supplied by DeltaNu. Begin with low resolution and a scan time of just 1 or 2 seconds. Adjust the sample location until you get a spectrum. A distance of 7 mm between the instrument’s opening and the center of the sample may work well. Then choose high resolution and adjust the scan time and baseline. The cyclohexane spectrum at right resulted from the average of six 5-second scans. The PMMA spectrum averaged ten 10-second scans. Your spectrum needn’t be as sharp or well resolved as the reference spectra shown.

Record the Raman spectrum of liquid CS₂ that is in a glass vial, already prepared. Locate one strong peak between 600 and 700 cm⁻¹. Settings used successfully in the past are ten two-second scans at high resolution with baseline correction.
Record the Raman spectrum of solid carbon dioxide, dry ice, over the range 1200-1500 cm\(^{-1}\). Put a slice of cork or other insulating material on the xyz stage. Break a chunk of CO\(_2\) from the dry ice and place it on the stage. Handle the dry ice with glove, tongs, tweezers, etc., but not with bare fingers, to avoid skin burns. Locate two strong peaks near 1500 cm\(^{-1}\).

Save spectral data to ASCII files and import them into a spreadsheet or other graphing program. Then turn off the Raman instrument and close the DeltaNU software.

3. Analysis of the Fermi resonance in carbon dioxide

Calculate \(E_{020}^{(0)}\) by doubling \(\tilde{\nu}_2\).

Report \(E_+\) and \(E_-\) (in wavenumbers) as measured in your Raman spectrum.

Use equations 6 to calculate \(E_{100}^{(0)}\) and \(F\) (both in cm\(^{-1}\)).

The symmetric stretching fundamental, \(\tilde{\nu}_1\) equals \(E_{100}^{(0)}\).

Use equations 7 to calculate \(c_1\) and \(c_2\) for \(\psi_+\). Calculate the fraction of \(\psi_+\) that is symmetric stretching, \(c_1^2\).
4. Quantum-Chemical Calculations

Use Gamess under WebMO to calculate the asymmetric-stretching vibration frequency and the bond length of CO$_2$. and of CS$_2$. Calculate using density functional theory (DFT). For DFT, use the B3LYP functional. Use the medium-size 6-31G(d) basis set.

For each molecule, optimize geometry and calculate frequencies. WebMO uses "z-matrix" coordinates (bond lengths and angles) by default, instead of Cartesian (x,y,z) coordinates. For linear molecules such as these, Cartesian coordinates work better, so check that box on the "Advanced" menu.

Note: Calculating vibration frequencies with GAMESS and the B3LYP functional seems to require specifying a method of calculating the second derivative of energy with respect to atomic positions. That is done by adding a line to the input file:

\$FORCE METHOD=SEMINUM \$END

Record, for your report, the total energy, the bond length, and the asymmetric-stretch frequency for each molecule.

For one of the molecules, do one of the following extended calculations:

- Repeat the calculation using a larger basis set, the 6-311+G(d,p) basis set. The larger basis set is almost certain to lower the total energy, and may improve bond lengths and vibration frequencies.

- Repeat the calculation using the simpler density functional PBE, instead of B3LYP. PBE is a "pure" density functional, B3LYP is "hybrid" because it includes part of the Hartree-Fock exchange energy. The PBE functional is popular in solid-state calculations, but there it tends to give volumes and bond lengths a few percent too large.

Compare the calculated asymmetric-stretch frequencies with experimental (infrared) frequencies. Compare the calculated bond lengths with literature values. The NIST Computational Chemistry Comparison and Benchmark DataBase$^5$ is a convenient source of small-molecule experimental bond lengths and vibration frequencies. The CRC Handbook$^6$ also lists bond lengths.
References


5. NIST Computational Chemistry Comparison and Benchmark DataBase, [http://cccbdb.nist.gov/](http://cccbdb.nist.gov/). Choose Section II “Experimental Data” and retrieve data for CO$_2$ and CS$_2$. This source gives $\tilde{\nu}_2 = 397\text{cm}^{-1}$ for CS$_2$. (downloaded 17 January 2016).

Appendix: Derivation of equations 6.

The secular determinant is

\[ (E_{100} - E)(E_{020} - F^2) = 0, \]

which can be rearranged into the standard quadratic form.

\[ E^2 - (E_{100} + E_{020})E + E_{100}E_{020} - F^2 = 0 \]  \hspace{1cm} (A1)

The quadratic formula gives the following solutions.

\[ E = \frac{1}{2} \left[ E_{100} + E_{020} \pm \sqrt{(E_{100} + E_{020})^2 - 4(E_{100}E_{020} + 4F^2)} \right] \]  \hspace{1cm} (A2)

Simplifying the discriminant gives the following formula for the two solutions.

\[ E = \frac{1}{2} \left[ E_{100} + E_{020} \pm \sqrt{(E_{100} - E_{020})^2 + 4F^2} \right] \]  \hspace{1cm} (A3)

The solution corresponding to the upper (+) sign may be labeled “E_+”; “E_−” corresponds to the lower (-) sign.

\[ E_+ = \frac{1}{2} \left[ E_{100} + E_{020} + \sqrt{(E_{100} - E_{020})^2 + 4F^2} \right] \]  \hspace{1cm} (A4)

\[ E_- = \frac{1}{2} \left[ E_{100} + E_{020} - \sqrt{(E_{100} - E_{020})^2 + 4F^2} \right] \]  \hspace{1cm} (A5)

Taking the sum of the two roots cancels the discriminant.

\[ E_+ + E_- = E_{100} + E_{020} \]  \hspace{1cm} (A6)

Taking the difference of the two roots cancels all but the discriminant.

\[ E_- - E_+ = \sqrt{(E_{100} - E_{020})^2 + 4F^2} \]  \hspace{1cm} (A7)

Both sides of the equation may be squared.

\[ (E_- - E_+)^2 = (E_{100} - E_{020})^2 + 4F^2 \]  \hspace{1cm} (A8)

Equations A6 and A8 are the desired results.