

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 *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

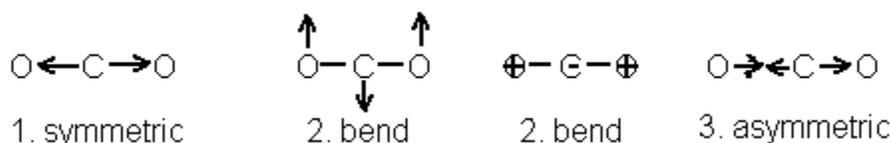


Figure 1: normal vibrational modes of carbon dioxide

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.

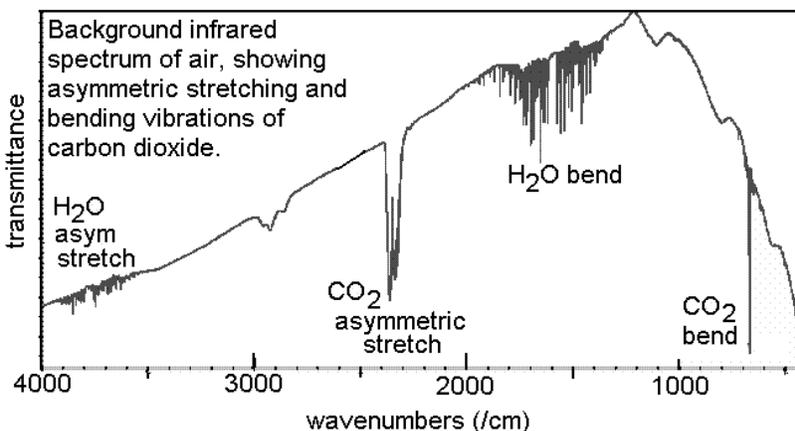


Figure 2: background infrared spectrum

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 CO₂, routinely observed in the background scan on an FTIR instrument.³

Vibration frequencies will be calculated quantum-mechanically for CO₂ and CS₂ using density functional theory. The hybrid functional B3LYP will be used to account for electron exchange and 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 CO₂ shows asymmetric stretching and bending vibrations. However, the Raman spectrum of CO₂ 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 (ψ_{100}) of the symmetric stretching mode of CO₂ is nearly the same as the energy of the second excited state (ψ_{020}) of the bending vibration. The notation ψ_{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, ψ_{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 CO₂ Raman band into two peaks. Such mixing is called “Fermi resonance.”^{2,4}

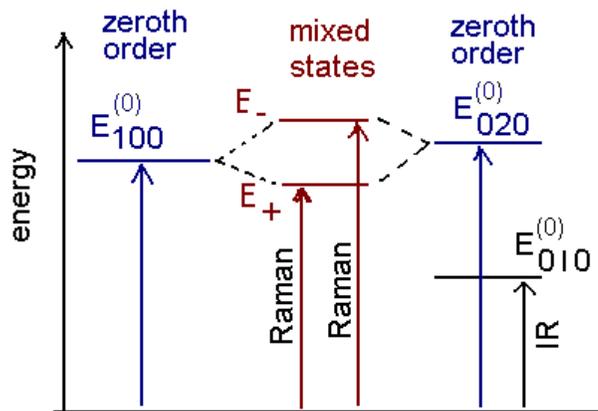


Figure 3: mixing of vibrational energy levels

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

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (1)$$

where H_0 is the zeroth-order harmonic-oscillator Hamiltonian.

$$\hat{H}_0 \psi_{100} = E_{100}^{(0)} \psi_{100} \quad \text{and} \quad \hat{H}_0 \psi_{020} = E_{020}^{(0)} \psi_{020} \quad (2)$$

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 $\tilde{\nu}_1 = E_{100}^{(0)}$ and $2\tilde{\nu}_2 = E_{020}^{(0)}$. Define mixed states $\psi_{\pm} = c_1 \psi_{100} + c_2 \psi_{020}$ where c_1 and c_2 are constants that reflect the mixing and keep ψ_+ and ψ_- normalized and orthogonal. Energies of ψ_+ and ψ_- are E_+ and E_- .

$$(\hat{H}_0 + \hat{H}') \psi_+ = E_+ \psi_+ \quad \text{and} \quad (\hat{H}_0 + \hat{H}') \psi_- = E_- \psi_- \quad (3)$$

The two-state secular equation is

$$\begin{pmatrix} E_{100}^{(0)} - E & F \\ F & E_{020}^{(0)} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (4)$$

where the interaction energy $F \equiv \int \psi_{100}^* \hat{H}' \psi_{020} d\tau = \int \psi_{020}^* \hat{H}' \psi_{100} d\tau$.

Expanded, the two-by-two secular determinant is

$$(E_{100}^{(0)} - E)(E_{020}^{(0)} - E) - F^2 = 0 \quad (5)$$

Solutions of the secular determinant, E_+ and E_- , satisfy the following two equations:

$$\begin{aligned} E_- + E_+ &= E_{100}^{(0)} + E_{020}^{(0)} \\ (E_- - E_+)^2 &= (E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2 \end{aligned} \quad (6)$$

(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 ψ_+ and ψ_- can be calculated from the secular equation plus the normalization condition. Those two conditions lead to equations 7.

$$\left(E_{100}^{(0)} - E\right)c_1 + F c_2 = 0 \quad \text{and} \quad c_1^2 + c_2^2 = 1 \quad (7)$$

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 CS₂ and CO₂ 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 CO₂/H₂O. Otherwise the instrument attempts to subtract CO₂ absorption from the spectrum.
- On the Sample tab, type a name for the background.
- Click “Start,” and then “Scan.”

Collect a sample of CS₂ gas from the head space over liquid CS₂. Do this by holding the evacuated IR cell over liquid CS₂ and briefly opening a stopcock.

Place the cell containing CS₂ 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 CS₂ gas in the cell and try again.

Flush the IR cell with air, evacuate it, and collect a sample of carbon dioxide gas. The CO₂ 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.

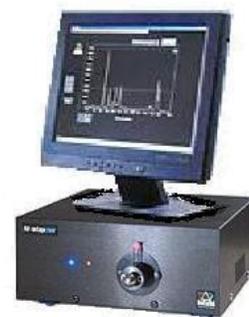


Figure 4:
Advantage 200
Raman

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



Figure 5: xyz stage

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.

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-

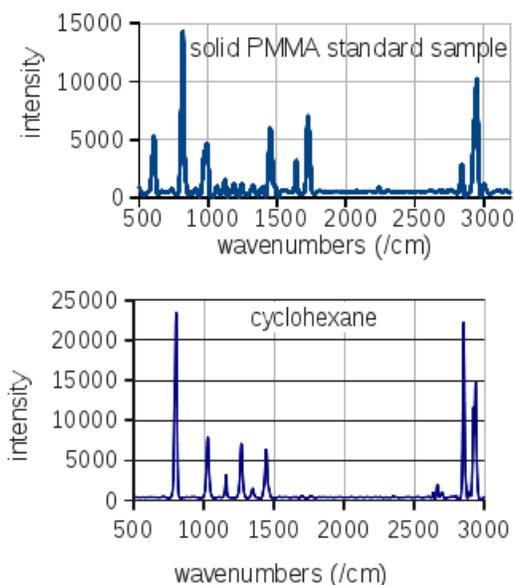


Figure 6: reference spectra

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 CO₂ 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 1300 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 ψ_+ . Calculate the fraction of ψ_+ that is symmetric stretching, c_1^2 .

4. Quantum-Chemical Calculations

Use Gamess to calculate the vibration frequencies and the bond length of CO₂. and of CS₂. Calculate using density functional theory (DFT). For DFT, use the B3LYP functional. Use the 6-311+G(2d) basis set. This basis set, which is larger than the more-commonly-used 6-31G(d,p) basis set, is used to get nearly the best result that the B3LYP functional can give.

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$BASIS GBASIS=N311 NGAUSS=6 NDFUNC=2 DIFFSP=.TRUE. $END
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For each molecule, optimize geometry and calculate frequencies. Geometry optimization proceeds more easily if the molecule lies on the z axis. The carbon atom could be placed at the origin, then one O or S above it and the other below. You may find that calculations take about ten minutes. Include bond lengths and vibration frequencies for both molecules.

Compare the calculated vibration frequencies with the experimental frequencies, either the frequencies you measured or literature values. Compare the calculated bond lengths with a literature values. The NIST Computational Chemistry Comparison and Benchmark DataBase⁵ is a convenient source of small-molecule experimental bond lengths and vibration frequencies. The CRC Handbook⁶ also lists bond lengths.

References

1. Engel, T. *Quantum Chemistry and Spectroscopy*, Person Prentice Hall: Upper Saddle River, NJ, Third Ed., 2013.
2. Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, Inc., New York: 1990, pages 338-340.
3. <http://www.colby.edu/chemistry/PChem/notes/NormalModesText.pdf>. Accessed 17 January 2016.
4. Bernath, Peter F. *Spectra of Atoms and Molecules*, Oxford University Press, New York: 1995, pages 270-272.
5. NIST Computational Chemistry Comparison and Benchmark DataBase, <http://cccbdb.nist.gov/>. Choose Section II "Experimental Data" and retrieve data for CO₂ and CS₂. This source gives $\tilde{\nu}_2 = 397\text{cm}^{-1}$ for CS₂. (downloaded 17 January 2016).
6. *CRC Handbook of Chemistry and Physics*, 82nd ed., David R. Lide, editor, CRC Press LLC, New York: 2001, page 9-19.

Appendix: Derivation of equations 6.

The secular determinant is $(E_{100}^{(0)} - E)(E_{020}^{(0)} - E) - F^2 = 0$, which can be rearranged into the standard quadratic form.

$$E^2 - (E_{100}^{(0)} + E_{020}^{(0)})E + E_{100}^{(0)}E_{020}^{(0)} - F^2 = 0 \quad (\text{A1})$$

The quadratic formula gives the following solutions.

$$E = \frac{1}{2} \left[E_{100}^{(0)} + E_{020}^{(0)} \pm \sqrt{(E_{100}^{(0)} + E_{020}^{(0)})^2 - 4E_{100}^{(0)}E_{020}^{(0)} + 4F^2} \right] \quad (\text{A2})$$

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

$$E = \frac{1}{2} \left[E_{100}^{(0)} + E_{020}^{(0)} \pm \sqrt{(E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2} \right] \quad (\text{A3})$$

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

$$E_+ = \frac{1}{2} \left[E_{100}^{(0)} + E_{020}^{(0)} + \sqrt{(E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2} \right] \quad (\text{A4})$$

$$E_- = \frac{1}{2} \left[E_{100}^{(0)} + E_{020}^{(0)} - \sqrt{(E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2} \right] \quad (\text{A5})$$

Taking the sum of the two roots cancels the discriminant.

$$E_+ + E_- = E_{100}^{(0)} + E_{020}^{(0)} \quad (\text{A6})$$

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

$$E_- - E_+ = \sqrt{(E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2} \quad (\text{A7})$$

Both sides of the equation may be squared.

$$(E_- - E_+)^2 = (E_{100}^{(0)} - E_{020}^{(0)})^2 + 4F^2 \quad (\text{A8})$$

Equations A6 and A8 are the desired results.