# Vibrations of Carbon Dioxide and Carbon Disulfide

Purpose
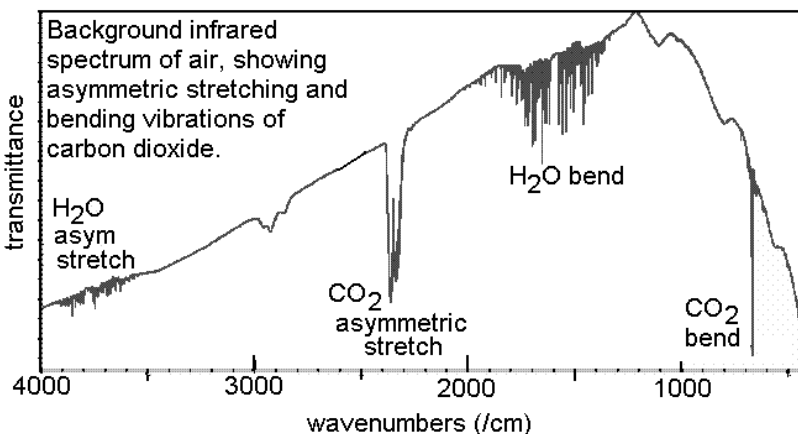
Vibration frequencies of CO_2 and CS_2 will be measured by Raman and Infrared spectroscopy. The spectra show effects of normal mode symmetries on gross selection rules. A Fermi resonance in the Raman spectrum will be interpreted in terms of interacting normal modes. Vibration frequencies will be calculated 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 stretching mode is totally symmetric so it is inactive in infrared spectra and active in Raman spectra. The
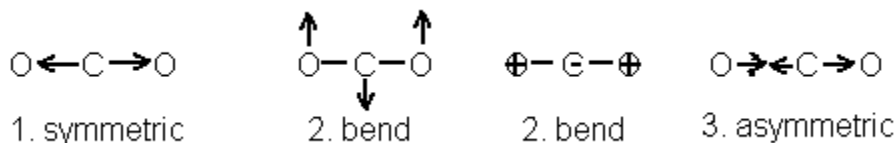
asymmetric stretching vibration and the degenerate bending vibrations are infrared active and Raman inactive. Infrared activities follow from the gross selection rule that "displacements of a normal mode must cause a change in dipole moment in order to be spectroscopically active in the infrared."[1] 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 both CO_2 and CS_2, using three methods: Hartree Fock, Hartree Fock plus second-order Moller-Plesset correction, and density functional theory. Hartree-Fock calculations are the simplest and most robust of the three methods and are good for initial geometry optimization. Vibration frequencies calculated from simple Hartree Fock theory are usually too large by about 10%. Second-order Moller-Plesset

perturbation theory (MP2) corrects Hartree-Fock results for electron correlation, usually greatly improving calculated vibration frequencies. Density functional theory (DFT) includes electron correlation and gives vibration frequencies similar to those from HF/MP2 calculations.

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 (ψ_{100}) of the symmetric stretching mode of CO_2 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 $v_1=v_3=0$ and $v_2=2$. Both states have the same symmetry so they mix to form two new symmetric states, which splits the totally symmetric CO_2 Raman band into two peaks. Such mixing is called "Fermi resonance." [2,4]

The Fermi resonance can be analyzed in terms of the vibrational Hamiltonian, two zero-order vibrational states, and two mixed states.
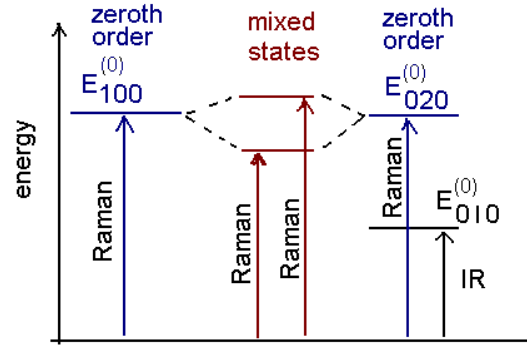
$$H = H_o + H' \tag{1}$$

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

$$H_o\psi_{100} = E_{100}^{(0)}\psi_{100} \quad and \quad H_o\psi_{020} = E_{020}^{(0)}\psi_{020} \tag{2}$$

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_-.

$$(H_o + H')\psi_+ = E_+\psi_+ \quad and \quad (H_o + H')\psi_- = E_-\psi_- \tag{3}$$

The two-state secular equation is

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

where the interaction energy $F \equiv \int \psi_+^* \, H' \, \psi_- \, d\tau = \int \psi_-^* \, H' \, \psi_+ \, d\tau$. Expanded, the two-by-two secular determinant is

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

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

$$E_+ + E_- = E_{100}^{(0)} + E_{020}^{(0)}$$

$$\left(E_+ - E_- \right)^2 = \left(E_{100}^{(0)} - E_{020}^{(0)} \right)^2 + 4F^2 \tag{6}$$

Energies are in wavenumber units, so E_+ and E_- are peak locations directly from the Raman spectrum of CO_2. The bending energy $E_{020}^{(0)} = 2\tilde{v}_2$ and $\tilde{v}_2$ 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.

Coefficients c_1 and c_2 for the mixed states ψ_+ and ψ_- can be calculated from the secular equation plus the normalization condition. For ψ_+, let $a=c_1$ and $b=c_2$.

$$\psi_+ = a\psi_{100} + b\psi_{020} \tag{7}$$

The coefficients a and b are solutions of equation 4, with $E=E_+$.

$$\left(E_{100}^{(0)} - E \right)a + Fb = 0 \tag{8}$$

Normalizing ψ_+ gives an additional equation.

$$a^2 + b^2 = 1 \tag{9}$$

Equations 8 and 9 can be solved for a and b.

Because ψ_- is orthogonal to ψ_+, $\psi_- = -b\psi_{100} + a\psi_{020}$ where constants a and b are the same as for ψ_+. In state ψ_+, a^2 is the symmetric-stretch percentage. In state ψ_-, a^2 is the bending-overtone percentage.

Infrared and Raman spectra will directly measure $\tilde{v}_1$, $\tilde{v}_2$ and $\tilde{v}_3$ for CS_2 and $\tilde{v}_2$ and $\tilde{v}_3$ for CO_2. The Raman spectrum of CO_2 gives combinations E_+ and E_- from which $\tilde{v}_1$ can be calculated. All six frequencies $\tilde{v}_i$ plus C-S and C-O bond lengths, will be calculated quantum-chemically.

Procedure

FTIR and Raman spectra of CS_2 and CO_2 should be printed and turned in with your lab report.

1. FTIR spectra

Use a water aspirator or vacuum line (<u>with a trap</u>) to evacuate a gas cell, preferably the 10cm cell with KBr windows. The KBr windows absorb water so the cell is stored in a desiccator.

Record a background spectrum. Use a range of 370 cm^{-1} to 3000 cm^{-1}. Use 1 cm^{-1} resolution and average over multiple (e.g., 16) scans.

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.

Record the IR spectrum of gaseous CS_2. The asymmetric stretch will be a strong band near 1500 cm^{-1}. The bend will appear as a sharp weaker band near 400 cm^{-1}. 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 over 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. <u>Do not stare at the red light and, of course, do not look directly into the laser beam.</u>

If the *DeltaNU* software is not already running, start it. A red box will appear in the upper right corner of the graphing window until the instrument is ready. Then the box will turn blue. A range of 200-2000 cm^{-1} suffices for this experiment.

The instrument has two sample holders, one of which will be installed. The left-hand picture shows the normal sample holder. To use it, the sample (e.g., liquid CS_2) should be in a small glass vial. The vial should be pushed firmly down into the hole in the sample holder. The instrument's other sample holder is the "xyz" stage. It supports samples, typically irregular solids such as a chunk of dry ice, on a platform

normal sample holder   xyz stage

that can be moved in three directions. Sample vials can also 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 "Reference" to collect a reference spectrum. The reference is internal to the instrument and does not require a reference sample in the sample holder.

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

Practice collecting a spectrum of polymethylmethacrylate, PMMA. A clear colorless solid cylinder of PMMA was supplied by *DeltaNu*. It spectrum appears at on the cover of the Advantage200 spectrophotometer's manual, in the lab. Adjust the sample position (using the silver-knobbed screw or the knurled knobs on the xyz stage), the resolution, scan time, and number of scans until the PMMA spectrum resembles the reference spectrum. Your spectrum needn't be as sharp or well resolved as the reference spectrum shown. Adjustment may require time, patience and practice.

Record the Raman spectrum of liquid CS_2 that is in a small glass vial. The CS_2 sample is prepared and is near the Raman instrument. 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. Put a slice of cork or other insulating material on the xyz stage. Cut a block of CO_2 from the dry ice and place it on the cork. Handle the dry ice with glove, tongs, tweezers, etc., but <u>not with bare fingers</u>, to avoid skin burns. Locate two strong peaks near 1300 cm^{-1}.

When you are done, 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 $\tilde{\nu}_2$ measured in your infrared spectrum.

Report E$_+$ and E$_-$ (in wavenumbers) as measured in your Raman spectrum. E$_-$ refers the peak that is closer to $E_{020}^{(0)}$. E$_+$ refers to the other peak.

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 8 and 9 to calculate a and b for ψ_+. Calculate the fraction of ψ_+ that is symmetric stretching, a^2.

4. Quantum-Chemical Calculations

Use GAMESS under *WebMO* (at http://argon.d.umn.edu) to calculate the vibration frequencies and bond lengths of CO_2 and CS_2. At the *WebMO* login prompt, give your UMD username but use the password "guest". Alternatively, you can log in as user chem4644, also with password "guest".

For each molecule, proceed as follows. Draw the molecule. Make the bond lengths reasonable (you may want to look up experimental bond lengths before drawing) and keep the molecule linear. Use the RHF method (both molecules have singlet spin states) and a medium-sized basis set. For each method (RHF, RHF+MP2, DFT) optimize geometry *with that method* before

calculating frequencies. Turn in bond length and three vibration frequencies using all of the following methods:

- RHF with 6-311+g(d,p) basis set

- RHF with 6-311+g(d,p) basis set plus MP2 correction. To add MP2 corrections (which should improve both bond length and frequencies) add "MPLEVL=2" to the CONTRL line of the input file.

- DFT with 6-311+g(d,p) basis set and the B3LYP functional. If a calculation fails due to non-convergence of the electron density, adding the following line to the input file may help:

  `$SCF DAMP=.TRUE. $END`

  The line can be inserted anywhere before the $DATA line.

Compare each calculated vibration frequency with experimental frequencies, either those you measured or literature values. Compare each calculated bond length with a literature value. The NIST Computational Chemistry Comparison and Benchmark DataBase is a convenient source of small-molecule experimental bond lengths and vibration frequencies.

References

1. Engel, T. *Quantum Chemistry and Spectrsocopy*, Person Benjamin-Cummings: San Francisco, 2006. Carbon dioxide symmetry is discussed in section 17.2.
   Silbey, R.J.; Alberty, R.J.; Bawendi, M.G. *Physical Chemistry*, 4th ed., John Wiley & Sons, Inc., 2005. Carbon dioxide vibrations are discussed in section 13.8, pages 487-489.

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 8 December 2004.

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://srdata.nist.gov/cccbdb/ . Choose Section II "Experimental Data" and retrieve data for CO_2 and CS_2.

Sample GAMESS input files for RHF, RHF+MP2 and DFT calculations on CO_2.

RHF
```
 $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE ICHARG=0 MULT=1 COORD=CART $END
 $BASIS GBASIS=N311 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.TRUE. DIFFS=.TRUE.
$END
 $STATPT HSSEND=.TRUE. $END
 $DATA
CO2 6-311g(d,p) geom
C1 1
C 6 0.000000000 0.000000000 0.000000000
O 8 0.000000000 0.000000000 1.143261042
O 8 0.000000000 0.000000000 -1.14325603
 $END
```

RHF + MP2
```
 $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE ICHARG=0 MULT=1 COORD=CART MPLEVL=2 $END
 $BASIS GBASIS=N311 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.TRUE. DIFFS=.TRUE.
$END
 $STATPT HSSEND=.TRUE. $END
 $DATA
CO2 MP2 6311g(dp) geom
C1 1
C 6 0.000000000 0.000000000 0.000000000
O 8 0.000000000 0.000000000 1.135810746
O 8 0.000000000 0.000000000 -1.13581103
 $END
```

DFT with B3LYP
```
 $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE ICHARG=0 MULT=1 COORD=CART $END
 $BASIS GBASIS=N311 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.TRUE. DIFFS=.TRUE.
$END
 $STATPT HSSEND=.TRUE. $END
 $DFT DFTTYP=B3LYP $END
 $SCF DAMP=.TRUE. $END
 $DATA
CO2 DFT B3LYP 6311g(d,p)
C1 1
C 6 0.000000000 0.000000000 0.000000000
O 8 0.000000000 0.000000000 1.161109977
O 8 0.000000000 0.000000000 -1.16112772
 $END
```