Vibrational Raman Spectroscopy

Background

The basic theory of Raman spectroscopy and a partial description of this experimental procedure are given in your lab text as experiment 35. Much of the following exercise was developed at ONU in a project sponsored by the National Science Foundation. The purposes of this lab are to introduce Raman spectroscopy, to operate laser-based instrumentation, to interpret Raman signals as molecular vibration frequencies, to study molecular symmetry, and to compare vibrational force constants. The data analysis involves computational chemistry software that performs quantum chemical ab initio calculations to predict the stretching frequencies. Refer to the R2001 and FluoroMax-4 manuals to learn the design and operation of those instruments. See also the theory of vibrational Raman spectra and molecular symmetry in Atkins and de Paula.

Many common five-atom molecules have tetrahedral symmetry. According to Garland, et al., these molecules have four distinct normal modes of vibration that are all Raman active. With pure substances such as CCl₄, it is usually possible to record Raman and IR spectra with sufficient sensitivity and resolution to observe and assign all four vibrational modes from either Stokes or anti-Stokes shifts.

In general, we may use group theory to determine which modes of a given molecule are Raman and/or IR active. Consider tetrachloroethylene (C₂Cl₂), which is a six-atom molecule. How many vibrational normal modes are there? What is its molecular point group? By analyzing the vibrational symmetry, it can be shown that the fundamentals are classified as follows: $v₁, v₂, v₃$ (all $A₁$), $v₄$ ($A₂$), $v₅, v₆$ (both $B₁g$), $v₇$ ($B₂g$), $v₈$ ($B₃g$), $v₉, v₁₀$ (both $B₂u$), $v₁₁, v₁₂$ (both $B₃u$). Given this, how many fundamentals are Raman active? How many are IR active? Which modes, if any, are degenerate? Answer these questions in your pre-lab report.

Raman spectra of tetrahedral oxoanions (XO₄⁻) may be observed by using solid salt samples or by using aqueous solutions. Since solid samples also contain cations that may perturb the symmetry and the vibrational frequencies of polyatomic anions, solution samples are preferred for this beginning study. Aqueous solutions are more difficult to measure, however, because solubility limits the ion concentration to only a few percent of that in a pure substance, and because the solvent may cause a broad Raman scattering background. Fortunately, water exhibits only weak Raman scattering, and the symmetric stretching vibration of an oxoanion, labeled as $v₁$ ($A₁$), is usually observable as the most intense and most polarized band in its Raman spectrum. Since the frequency of the $v₁$ mode does not depend on the mass of the center atom, $v₁$ alone determines the stretching force constant for the molecule, which is related to the strength of the X-O bond. It is much more difficult to determine these bond strengths using IR spectroscopy because $v₁$ is IR inactive and water absorbs strongly in the IR region.

Periodic trends in chemical bonding is a topic of most general chemistry and inorganic chemistry courses. Bond strength is usually assumed to be proportional to bond order. Consider the series of molecules PO₄³⁻, SO₄²⁻, and ClO₄⁻; the Lewis structures with lowest formal charges for these ions are:

\[
\begin{align*}
\text{PO}_4^{3-} & : \quad \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}} \\
\text{SO}_4^{2-} & : \quad \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}} \\
\text{ClO}_4^- & : \quad \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}} = & \overset{\text{O}}{\text{O}}
\end{align*}
\]

Therefore the average X-O bond order for these structures is 1.25, 1.5, and 1.75, respectively, which suggests that perchlorate ion should have the shortest bond length and the highest stretching frequencies. However, in all cases other structures may also contribute and the actual bond orders may not follow this simple prediction.

Bond strength (and length) also depends on orbital overlap and thus on the relative size of the atoms involved. For example, in the series SO₄³⁻, SeO₄²⁻, TeO₄²⁻, we might predict the stretching frequency for tellurate ion to be smallest since the relatively large valence atomic orbitals on tellurium should overlap poorly with the small valence orbitals on oxygen.
Additions to and deviations from textbook procedure

**R2001 Spectrometer**

Have your instructor turn on the model R2001 Raman spectrometer. Select the C2CL4 calibration file, and use this for all samples. Be extremely careful when the nearly invisible 785-nm laser is on! Read, understand, and comply with all of the safety information below. Students must wear laser safety goggles whenever the laser is on.

A: Carbon tetrachloride and tetrachloroethylene at low resolution

Glass vials for liquid samples should be placed gently in contact with the probe lens. Record and print a survey spectrum of CCl4. Adjust the instrument settings to keep all bands on scale while optimizing the signal to noise ratio. Use the cursor to measure the position and FWHM of all four bands. Note the larger width of the ν3 band; this is caused by a Fermi resonance with the ν1 + ν4 combination band.

Next record and print a survey Raman spectrum of C2Cl4. Measure the position and FWHM of each band. Determine whether the number of observed bands agrees with the predicted number.

B: Oxyanions

Record a Raman spectrum of water in a glass vial. Adjust the exposure time and repeat if necessary to keep the signal on scale. Obtain a sample of CrO42- (aq) and record its Raman spectrum. Identify ν1 and use the cursor to measure its shift. Next record and measure the ν1 shifts for MoO42- (aq), WO42- (aq), SO42- (aq), ClO4- (aq), and IO4- (aq). Print one copy of each spectrum.

Save your data for later analysis if needed. Have your instructor turn off the instrument.

**Fluoromax 4 Spectrometer**

In a hood and using gloves, pipet CCl4 into a square fluorimeter cell and seal tightly with a stopper. Place this into the Fluoromax compartment that has been customized for 532.2 nm (18,790 cm⁻¹) laser excitation. Note the focusing lens, cell alignment, and beam dump for the laser. Note also the Raman edge filter and polarizer in the collection path for the scattered light. Although this laser beam is not polarized, in this set-up it effectively has vertical polarization because scattered light is detected at a 90° angle.

Set up an emission scan with the following parameters:

- excitation wavelength, slit width: 400 nm, 0.1 nm (lamp not being used; just to avoid stray light)
- start: 535.0 nm, end: ?? nm
- slit: 0.2 nm, step: 0.04 nm, integration time: 0.2 s

Use your R2001 spectrum of CCl4 to determine a suitable end wavelength beyond the Stokes shift of the highest wavenumber band. Set the polarizer to the parallel position and record a spectrum. Record the position of each band (in nm), and then compute the corresponding Stokes shifts (in cm⁻¹). Compare band positions with your spectrum from the R2001. Note that the Fermi resonance doublet is partly resolved.

Rotate the polarizer to the perpendicular position and record another spectrum. The totally symmetric mode (A1) should appear much weaker when extinguished by the crossed polarizer.

Repeat all of these experiments using C2Cl4 in place of CCl4. The end of the scan will need to be at a longer wavelength. Compute the depolarization ratio \( \rho = \frac{I_\perp}{I_\parallel} \) and identify all of the polarized A_g modes (\( \rho \leq 0.75 \)).
PART III: Calculations

(This part is usually done at a time other than during the regular lab period.) Quantum mechanical calculations based purely on theory are called ab initio (meaning “from first principles”). Standard computer routines are now widely available for performing such calculations on personal computers. Users control the sophistication of the calculation by selecting from among several available basis sets. Heavier atoms typically require basis sets having a larger number of orbitals to account for their greater polarizability. Calculations done with larger basis sets often agree better with experimental data, but at the cost of increased computation time.

Use WebMO to calculate the vibrational frequencies for CCl$_4$, C$_2$Cl$_4$, and the six oxyanions studied above. Make sure that the symmetries are all correct. View the motions of different modes to identify which is $v_1$, $v_2$, $v_3$, and $v_4$. Record the calculated frequencies and IR/Raman spectral intensities for each molecule (in cm$^{-1}$) for comparison to your lab measurements.

Analysis

Assign the Stokes peaks for CCl$_4$ to the four vibrational modes using the facts that

1) the strongest observed band is the most polarized (smallest $\rho$ value), and
2) the only IR band below 600 cm$^{-1}$ is at 300 cm$^{-1}$. Compare with your results from WebMO.

For C$_2$Cl$_4$, assign the $A_g$ modes using the convention that the highest wavenumber fundamental is numbered first, and so on for that representation. Assign the other Raman-active modes by comparison with your WebMO results.

Reports

In your preliminary report, sketch the normal modes of a tetrahedral molecule and note the IR vs. Raman activity of each. Make a table for C$_2$Cl$_4$ showing the symmetries and Raman/IR activities for all of the modes. List each of the quantities that you will measure directly and state how these quantities will be related to your final result. Predict the relative bond strengths for the oxoanions within groups VIB and VIIA of the periodic table.

In your final written report, include copies of your spectra with assignments marked in pencil. For CCl$_4$ and C$_2$Cl$_4$, compare shift wavenumbers from R2001 data, Fluoromax4 data, computations, and literature values, including estimates of the uncertainty. Report the depolarization ratio for polarized bands. Discuss the valence force constants $k$ and $k_\delta/l^2$ for CCl$_4$ as calculated from your data using the model in the lab text. Compare with literature values.¹ ⁵

Tabulate the observed and calculated $v_1$ stretching frequencies for all of the ions you studied. Include uncertainty estimates. Compare results with literature values.⁶ Compare the observed and calculated force constants for different molecules and discuss them in view of their confidence limits and your predicted periodic trends in the bond strengths. Describe any systematic differences between the observed and calculated frequencies.

References

SAFETY ISSUES

- CCl₄ and C₂Cl₄ are suspected carcinogens. Handle with gloves and in a hood to avoid vapors.

- Several of the oxoanions (e.g. CrO₄²⁻, ClO₄⁻, etc.) are strong oxidizers. Avoid skin contact and flammable solvents.

- A class IIIb diode laser (500 mW) can cause permanent, catastrophic eye damage. **Do not work near the beam without proper laser safety glasses.** Remove reflective jewelry to avoid directing the beam up toward other people. Do not sit nearby with the beam at eye level. At the focal point 5 mm from the probe, the beam can rapidly burn skin or other materials that absorb 785 nm light. Be sure to keep fingers away from the beam when inserting samples.

- A class IIIb Nd:YAG laser (300 mW) can cause permanent, catastrophic eye damage. **Do not work near the unenclosed beam without proper laser safety glasses.** Remove reflective jewelry to avoid directing the beam up toward other people. Do not sit nearby with the unenclosed beam at eye level.
Chem 3421: "Vibrational Raman Spectroscopy"

TA's Instructions:

1) Put small vials (~ 10 mL), labeled in pencil, of CCl₄ and C₂Cl₄ in the center hood in MY 220.

2) Locate pre-made samples, or else dissolve each of the following salts in water to make 25 mL each of sample solutions:
   - 10.0 g Na₂SO₄
   - 10.0 g Na₂CrO₄
   - 10.0 g Na₂MoO₄
   - 15.0 g Na₂WO₄
   - 2.0 g NaClO₄
   - 4.0 g NaIO₄

   Put each sample in a small, clean, clear glass bottle with a tight lid. Place them near the R2001.

3) With help from the instructor, install the custom sample stage in the Fluoromax 4. Attach the laser with fiber-optic cable and lens adapter. Insert the beam dump and edge filter/polarizer stage. Remove and carefully store these special components immediately following each lab period.

4) After the last team does the experiment clear supplies away from the R2001 instrument area. Unused samples may be kept in well labeled containers for later use. Put salt solutions on the wooden shelves in the southeast corner of MY 220 and keep CCl₄ and C₂Cl₄ in the center hood.

Please check the equipment and supplies each week to make sure that they have been cleaned properly after use and that they haven’t been removed from the laboratory.