Raman Spectroscopy of Symmetric Oxyanions

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Rationale

Raman spectroscopy has been the subject of several recent articles in this Journal (1–7). Most undergraduate physical chemistry texts discuss Raman scattering, and laboratory experiments with pure substances such as CCl₄ as samples are well established (8), but relatively few undergraduate students currently get lab experience with this important technique (9). As an increasing number of commercial Raman instruments are being developed for industrial, medical, and educational applications, many students are likely to encounter Raman spectroscopy in their careers. Raman techniques are usually described as alternatives to infrared (IR) spectroscopy, providing complementary information about molecular vibrations. In fact, Raman spectroscopy is the only tool for studies of highly symmetric vibrational motions, since these are totally IR-inactive.

In this report, we describe a laboratory experiment that features Raman spectroscopy to illustrate periodic trends in molecular bonding. Using a relatively inexpensive instrument constructed in our laboratory, we record Raman spectra of aqueous salt solutions and measure the symmetric stretching vibrational frequencies for a variety of oxyanions. Ions in aqueous solution are good samples for these experiments because their spectra are free from splittings caused by the reduced symmetry of the ions in a crystalline lattice and because the solvent (water) exhibits very weak Raman scattering. In addition, symmetric molecular motions are especially simple to treat using either classical or quantum mechanical models.

Experimental Details

Modular, custom-made Raman instruments for teaching laboratories have been reported previously (2, 4). These authors describe the relative merits of different laser light sources, monochromators, and photodetectors. Instruments based on low-power HeNe lasers and photomultiplier tubes (PMTs) are generally considered least expensive but also least sensitive. A significant fraction of the cost in traditional Raman instruments is a double monochromator to reject intense elastic light scattering. Our instrument, though based on a HeNe laser and a PMT, employs two optical improvements that enable enough sensitivity to observe anions in solution with multi-passing is a key design feature that proves to be a very cost-effective alternative to using a more powerful laser.

Light scattered from the sample at a 90° angle from the laser beam path is imaged at 1:1 magnification onto the entrance slit of the monochromator (Spex model 270M) by a pair of 50-mm diameter, 100-mm focal length glass lenses. To rotate the image of the horizontal laser path onto the vertical monochromator slit, the scattered light is reflected 90° vertically and then 90° horizontally by a pair of plane mirrors. The collimated light is also passed through a 50-mm-diameter linear polarizer (Edmund) to analyze for depolarization of the Raman scattering.

The second essential component in our instrument is a 633-nm holographic notch filter (Kaiser Optical, Ann Arbor, MI, model HSNF-633-1.5) located between the imaging lenses. This filter attenuates elastic scattering by more than 10⁴-fold while completely transmitting Raman signals shifted by as little as 4 nm (100 cm⁻¹) from 633 nm and thus eliminates the need for a double monochromator to reject elastic scattering. To be effective, scattered light must not pass through the outer edge of the filter or through it at different angles, so a 25-mm aperture is set to limit the speed of collection optics to f/4, which well matches that of the monochromator. The notch filter suppresses elastic scattering so dramatically that Raman spectra may be scanned continuously from Stokes to anti-Stokes shifts without overloading the PMT. Although the notch filter–single monochromator combination is limited to one excitation wavelength, the relatively low cost of this approach makes it well justified. The scattered light finally passes through the monochromator (1200 grooves/mm, 3.1 nm/mm dispersion) and is focused onto a red-sensitive PMT (Hamamatsu model R928 or R5600U-01). The PMT current is amplified by a simple op-amp circuit and then digitized under control of LabVIEW (National Instruments board model NI-MIO-16L-9) on a Macintosh computer. The same software performs the step scan and slit controls of the monochromator. The total cost of our Raman spectrometer, excluding the computer, is less than $14,000.

We have also worked with a cooled charge-coupled device (CCD) detector (Hamamatsu model C5809-1006) mounted at an alternate, flat-field image plane of the monochromator. A digital oscilloscope (LeCroy model 9310) interfaced to the computer records and averages the CCD response. The C5809 is less expensive than most CCD systems, but its dark current is

10-mm glass fluorometer cell.
variety of powdered solids can also be studied by mounting a small (<10 mm$^3$) pressed sample in place of the multi-pass liquid cell. In this case, redirecting the laser beam into a back-scattering geometry (angle ~150°) increases the light collection efficiency.

**Results**

We typically set our Raman spectrometer for a bandpass of 70 cm$^{-1}$, scan steps of 5 cm$^{-1}$, and a detection time constant of 1 second. Fig. 1 shows Raman spectra of neat CCl$_4$, with the polarization analyzer oriented parallel (||) and perpendicular (⊥) to the laser polarization. The symmetric stretch ($\nu_1$) is easily identified by its disappearance in the perpendicular spectrum. The other mode assignments (10) are also labeled in Figure 1 for the Stokes bands. The strongly polarized peak at 0 cm$^{-1}$ is due mainly to residual Rayleigh scattering passing through the notch filter. The Raman spectrum of CCl$_4$ is a good warm-up exercise for students because it is thoroughly described in a lab text (8) and because it displays all four fundamental vibrations as both Stokes ($+cm^{-1}$) and anti-Stokes ($-cm^{-1}$) bands at 300 K. The relative intensities in Figure 1 are not quantitative because we do not use a polarization scrambler to offset monochromator bias (8), but the effect of thermal population on the anti-Stokes bands is nonetheless clearly evident.

After becoming familiar with the instrument (an advantage of modular design) and optimizing optical alignment, students should be ready to study salt solutions. Figure 2 shows Raman spectra of some tetrahedral oxyanions with center atoms from groups VA, VIA, VIIA, and VIB of the periodic table. The typical signal-to-noise ratio in these spectra is clearly inferior to that for CCl$_4$, but the strongest feature in each case, $\nu_1$, can definitely be assigned and measured. The $\nu_1$ band appears at between 800 and 1200 cm$^{-1}$ for all anions we have studied. At lower frequencies most spectra also contain unresolved bending modes superimposed on a broad background due to the solvent. The antisymmetric stretching vibration ($\nu_3$) is visible in some cases as a weak feature near $\nu_1$; any ambiguity in assignment is easily resolved by comparing || and ⊥ spectra. Observed spectral line widths are due to both the instrumental bandpass and the homogeneous (dephasing) line width in solution. We find similar spectra for trigonal planar ions in solution.

Table 1 summarizes results for some common symmetric oxyanions. Our observed Raman shifts generally agree well with previous observations (11, 12) and do not show systematic deviations. For these highly symmetric molecules the $\nu_1$ band frequency is directly related to the stretching force constant for a bond between the center atom and one oxygen atom. According to the simple classical valence-force model (13) often introduced in physical chemistry courses, the force constant, $k$, is related to the $\nu_1$ frequency and the mass of an oxygen atom (all in SI units) by

$$k = 4\pi^2 m_0 \nu_1^2$$  \(\text{(1)}\)

Using instead the wavenumber of the $\nu_1$ band in cm$^{-1}$ and the atomic mass of oxygen as $m_0 = 15.995$ amu, eq 1 becomes (8)

$$k = (5.892 \times 10^3) m_0 \nu_1^2$$  \(\text{(2)}\)

Note that $k$ does not depend on the mass of the center atom, since it is stationary during a symmetric stretching motion; nor does $k$ involve changes in bond angle. While $k$ might
also be determined from combinations of the antisymmetric stretching and bending frequencies, which are observable by IR absorption spectroscopy, such relationships are more complicated and less reliable when couplings between modes cause the valence-force approximation to break down. Table 1 lists force constants computed for oxyanions using eq 2 and our observed $\nu_1$ wavenumbers.

In introductory chemistry, students learn that heavier atoms in any given group of the periodic table should have decreasing orbital overlap with a light atom such as oxygen. It follows that bond strength, stretching force constant $k$, and thus $\nu_1$ frequency should also follow this trend. Our observed decrease in $\nu_1$ frequencies for heavier main-group center atoms does seem to validate this prediction. On the other hand, the group VIB oxyanions appear to contradict this simple prediction. Bond order based on Lewis structure is valuable when coupled to experiments. We have found the MacSpartan Plus program (v 1.1.7, Wavefunction, Inc., Irvine, CA) to be well suited for comparing stretching frequencies of oxyanions. This program has an intuitive graphical interface for creating and editing structures and for viewing animations of the calculated vibrational motions.

We first use an AM 1 or PM 3 semiempirical calculation to find a starting estimate for the geometry (i.e., bond length) of a given ion. We then perform ab initio calculations at the 3-21G* level to optimize the bond length and to determine the vibrational frequencies; together these calculations take 5 to 25 minutes on a Power Macintosh 8600/200 processor. It is very important to establish an optimum bond length before performing a frequency calculation. Output wavenumbers for all vibrational modes, labeled by symmetry type, are available while viewing the animation.

Table 1 shows calculated equilibrium bond lengths and $\nu_1$ frequencies for tetrahedral “gas phase” oxyanions. These bond lengths appear to follow expected simple periodic trends in that they decrease across a period and increase down a group. We find calculated frequencies for tetrahedral ions to be systematically 3–10% larger than the observed (solution) values. According to the developers of MacSpartan Plus, this behavior is generally expected (14), and thus we conclude that the systematic difference is probably not simply an effect of the experimental samples being in solution. Interestingly, the (counterintuitive) increase in observed frequencies for heavier group VIB oxyanions is not supported by the calculations at this level. Nonetheless, computer modeling offers memorable visualizations, reasonably accurate results, and few restrictions on “sample” molecules.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Obsd Raman shift/ cm$^{-1}$</th>
<th>Exppt force constant N m$^{-1}$</th>
<th>Raman freq./ cm$^{-1}$</th>
<th>CIP freq./ cm$^{-1}$</th>
<th>Calcld force constant N m$^{-1}$</th>
<th>Calcld bond length/pm</th>
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<tr>
<td>CO$_2$ (aq)</td>
<td>1090 ± 30</td>
<td>1120</td>
<td>1087</td>
<td>1063</td>
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<tr>
<td>NO$_3$ (aq)</td>
<td>1080 ± 30</td>
<td>1099</td>
<td>1060</td>
<td>971</td>
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<tr>
<td>PO$_4$ (aq)</td>
<td>990 ± 50</td>
<td>924</td>
<td>938</td>
<td>964</td>
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<tr>
<td>AsO$_4$ (aq)</td>
<td>830 ± 30</td>
<td>649</td>
<td>837</td>
<td>852</td>
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<td>910</td>
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</table>

*Estimated uncertainties are based on wavelength calibration and observed linewidths.

There is an inherent danger in training students to use sophisticated quantum mechanical calculations without also providing sufficient background instruction on quantum theory. We expect that most physical chemistry lab courses that could benefit from Raman spectroscopy would also have a lecture component that introduces methods and concepts in quantum mechanics such as variational calculations, basis sets, and molecular orbitals. Students can fully appreciate and use proper caution in evaluating molecular modeling results only after learning these background principles.

**Discussion**

The laboratory exercise in Raman spectroscopy and molecular modeling as described above requires two 3-hour periods. Some class time can be saved by preparing solutions in advance, by reducing the number of ions studied, and by providing students with an example of a MacSpartan structure. Students at our institution do this exercise as part of the second quarter physical chemistry lab course. They are able to understand in detail the operation of the instrument and are stimulated by the computer modeling animations. On the other hand, they are not initially comfortable making predictive comparisons of molecular structure.

Raman spectroscopy can serve as a link between physical, analytical, and inorganic lab courses. For example, a modular Raman spectrometer is an excellent subject for in-depth study in an instrumental analysis course. Alternatively, the combination of Raman and IR spectroscopies clearly strengthens the characterization of symmetric inorganic or organometallic substances in synthesis courses. Assigning vibrational modes and comparing their IR and Raman activity encourages interpretation beyond simple fingerprinting. For instance, we have
recorded the Raman spectrum of ferrocene (Fig. 3) synthesized by students concurrently enrolled in an intermediate inorganic course. The peaks at 320 and 1100 cm$^{-1}$, which have been assigned to the symmetric Fe–C stretching motion and the symmetric C–C "ring breathing" motion (15), are dominant in the Raman spectrum, whereas these modes are absent in an IR spectrum. In fact, low-frequency motions involving metal atoms are generally more difficult to observe by IR than by Raman spectroscopy. The major investment in our modular Raman spectrometer is in the monochromator, detectors, and computer interface. Fortunately, these components are easily adapted for use in other forms of optical spectroscopy. For instance, we have used a pulsed Nd:YAG laser to excite molecular iodine vapor and substituted a boxcar integrator to process the resulting dispersed fluorescence spectrum. The instrument is also very suitable for studies of atomic emission.

Conclusions

Optimization of a modular HeNe laser-based Raman spectrometer has enabled a new study of periodic trends in molecular structure. The instrument, the technique, and the interpretation of results described here are suitable for most undergraduate physical chemistry courses. Molecular modeling using a personal computer in combination with experiments greatly enhances the experience. Raman spectroscopy is an important addition to an undergraduate curriculum.

Acknowledgment

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Note

Supplementary materials for this article, comprising a student handout, instructions for TAs, and a list of major parts, are available on JCE Online at http://jchemed.chem.wisc.edu/journal/issues/1999/Sep/abs1272.html.

Literature Cited