USING THE OCEAN OPTICS
R-2000 RAMAN SPECTROMETER IN
THE UNDERGRADUATE LABORATORY

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ABSTRACT

The purpose of this work was to explore the productive use of a new Raman spectrometer in the undergraduate chemistry laboratory. The instrument is the Ocean Optics R-2000, (Ocean Optics, 2000). Infrared and Raman spectra were compared with each other and with normal mode calculations in Gaussian 98 and HyperChem, for the molecules CCl₄, CS₂, C₂Cl₄, C₆H₆, and C₅H₅N. Raman spectra were also observed for N₂ and O₂, for which there is no corresponding IR spectrum.

INTRODUCTION

Vibrational spectroscopy includes both infrared (IR) and Raman spectroscopy. Although Raman and IR spectra both explore the normal modes of vibration of a molecule, their intensity patterns may be quite different and distinctive. IR activity requires a changing dipole moment, while Raman activity requires a changing polarizability. For molecules of reasonably high symmetry, the irreducible representation for a particular normal mode may correspond to IR activity, Raman activity, both, or neither. For example if the molecule contains a center of inversion, the rule of mutual exclusion applies, and a normal mode cannot be active in both the Raman and the IR, although occasionally it might be inactive in both. (Herzberg, 1945, Cotton, 1990, Nakamoto, 1997). A discussion of Raman and IR spectra of four small molecules, together with quantum chemistry calculations on them, was published while the present work was in progress. (McClain, 2000).

METHODS

The Raman R-2000 was installed on a 486 PC under Windows 95. Beyond initial installation and testing, the R-2000 has been used in several chemistry courses during 1999-2000. The first two were an Honors section of Introduction to Chemistry, and Physical Chemistry. In the Honors general chem course the R-2000 was used by freshman honors students as part of their working on the identification of an organic unknown. They were informed that the unknown might possibly contain the elements C, H, O, Cl. With the help of instructor and lab assistants, each of the lab groups ran five types of spectra: Ra-
man, FTIR, GC/MS, NMR, and UV-visible. With these and other simple observations (such as water solubility), they proceeded to identify the unknown. Each lab group was successful in their identification. The Raman instrument is similarly being used in Organic Chemistry, as well as in Physical Chemistry, Quantum Chemistry, and Independent Study/Research.

RESULTS AND DISCUSSION

Raman and infrared spectra often have quite different patterns of intensities. This is particularly true with molecules of high symmetry. A classic example is CCl₄ (Shoemaker, 1996). This tetrahedral molecule, point group Td, has nine normal modes of vibration, of which \( \nu_1 (A_1) \) at 460 cm\(^{-1}\) is a Raman active symmetric stretch, \( \nu_2 (E) \) at 214 cm\(^{-1}\) is a Raman active CCl bend, \( \nu_3 (T_2) \) at 793 cm\(^{-1}\) is an asymmetric stretch active in both IR and Raman, and \( \nu_4 (T_2) \) at 314 cm\(^{-1}\) is a bend active in both both IR and Raman (Nakamoto, 1997). The Raman spectrum shown was taken with the Ocean Optics R-2000 instrument, with spectral range ca 200-2850 cm\(^{-1}\), and the FTIR spectrum was recorded with a Nicolet Avatar 360 FT-IR Spectrometer, with spectral range 400-4000 cm\(^{-1}\).

![Figure 1. CCl₄ Raman spectrum.](image)

![Figure 2. CCl₄ FTIR spectrum.](image)

All four vibrations are clearly shown in the Raman spectrum, while only \( \nu_3 \) appears in this FTIR spectrum. The \( \nu_1 \) and \( \nu_2 \) vibrations are symmetry forbidden in IR, and \( \nu_4 \) is outside the range of our FTIR instrument. Frequencies and intensities were calculated for the normal modes of CCl₄ with Gaussian 98 for Windows. At the Hartee-Fock 6-31G(d) level, the frequency scaling factor is 0.8929 (Foresman, 1996). The Raman activities calculated for frequencies 1-4 were 19.0 for 449 cm\(^{-1}\) (A₁), 3.4 for 218 cm\(^{-1}\) (E), 10.5 for 805 cm\(^{-1}\) (T₂), and for 5.1 for 311 cm\(^{-1}\) (T₂). The Gaussian calculations are in good agreement with the observed spectra. Note that the most intense Raman band is the breathing mode (symmetric stretch, which is forbidden in the IR spectrum.
Raman spectra were observed for liquid N2 and liquid O2, as shown in Figure 3 and Figure 4.

The observed frequencies are 2329 cm$^{-1}$ for liquid N$_2$ and 1538 cm$^{-1}$ for liquid O$_2$. From the gas phase data, and using $\omega_0 = \omega - 2\omega_2 x_2$, literature values of $\omega_0$ are 2330 cm$^{-1}$ for N$_2$ and 1556 cm$^{-1}$ for O$_2$, in satisfactory agreement with the liquid phase data observed here. (Huber and Herzberg, 1979, Shoemaker, 1996) After a few minutes, the liquid O$_2$ apparently absorbs a significant amount of N$_2$, as indicated by the growth of the Raman band of N$_2$.

The linear molecule CS$_2$ has 3N-5 = 4 normal modes of vibration. Like CO$_2$, CS$_2$ belongs to the D$_{\infty h}$ point group and has a symmetric stretch $\nu_1$ ($\Sigma_g^+$), a two-fold degenerate bend $\nu_2$ ($\Pi_u$), and an asymmetric stretch $\nu_3$ ($\Sigma_u^+$). The first is Raman active, and $\nu_2$ and $\nu_3$ are IR active. (Nakamoto, 1997, Herzberg, 1945) Figure 5 and Figure 6 show $\nu_1$ at 649 cm$^{-1}$ and $\nu_3$ at 1506 cm$^{-1}$, in reasonable agreement with CS$_2$ gas, for which $\nu_1 = 658$ cm$^{-1}$, $\nu_2 = 397$ cm$^{-1}$, and $\nu_3 = 1533$ cm$^{-1}$ (Nakamoto, 1997, p 166). Although $\nu_2$ falls just below the 400 cm$^{-1}$ limit of our FTIR, and is limited also by the cutoff of the NaCl windows, the Raman spectrum shows the classic Fermi resonance of $\nu_1$ with the overtone band 2$\nu_2$. This is the origin of the Raman band observed at 796 cm$^{-1}$. In terms of symmetry analysis, $\Pi_u \times \Pi_u = \Sigma_g^+ + \Sigma_g^- + \Delta_g$. Of these, $\Sigma_g^+$ becomes involved in Fermi resonance with the $\nu_1$ ($\Sigma_g^+$) fundamental, and thereby gains intensity. (Nakamoto, 1997, p 62, Herzberg, 1945, p 277).
Current practice in organic chemistry courses in the USA includes introduction and use of infrared spectroscopy, NMR spectroscopy, and mass spectroscopy on a routine basis. Raman spectroscopy is currently much less common. However, Raman spectra can often provide information on vibrational modes which may not be evident in the infrared spectrum. C=C vibrations serve as a case in point. Lambert provides a fine discussion of vibrational spectroscopy of organic compounds, including both IR and Raman spectra, and Nakamoto is an excellent resource on the inorganic side. (Lambert, 1998, Nakamoto, 1997) The Raman and IR spectra observed for C₂Cl₄ are shown in Figure 7 and Figure 8.

Since the point group of C₂Cl₄ is D₂h, which includes a center of inversion, the rule of mutual exclusion applies, and a given normal mode cannot be active in both the Raman and the IR. The observed spectra are in accord with this. Table 1 summarizes the spectral observations and normal mode calculations in Gaussian 98W, using 6-31G(d). The normal modes are numbered as in Herzberg (Herzberg, 1945, p 107, 329), but with rotation axes and irreducible representations consistent with international recommendations (Saltsburg, 1972, p 77). Note particularly the C=C stretch that is clearly present in the Raman spectrum but absent in the IR spectrum. Normal mode 1 is a symmetric stretch (breathing mode), A_g symmetry, observed at 1576 cm⁻¹. The Gaussian 98W results for the Raman bands are reasonably consistent with the observed spectrum, except that the 1576 cm⁻¹ C=C band appears somewhat less intense on our instrument than the Gaussian 98W prediction.

Benzene, C₆H₆, belongs to point group D₆h. Since there is a center of inversion, the rule of mutual exclusion applies. With N=12, 3N-6 = 30 normal modes. These are given by Herzberg. (Herzberg, 1945, p 118, 364) The Raman and IR spectra are shown in Figure 9 and Figure 10.

The four most prominent Raman bands within our spectral range are at 605, 990, 1178, and 1594 cm⁻¹. These are assigned by Herzberg as ν₁₈ (E₂g) at 605.6, ν₂ (A₁g) at 991.6, ν₁₇ (E₂g) at 1178.0, and ν₁₆ (E₂g) at 1584.8 cm⁻¹, with relative integrated intensities 2.1, 10.0, 2.2, and 1.9. Two additional bands in-
cluded by Herzberg are ν$_{11}$ (E$_{1g}$) at 848.9 cm$^{-1}$, intensity 0.9, and combination band 2+18 (E$_{2g}$) at 1606.4 cm$^{-1}$, intensity 1.6. (Herzberg, 1945, p 364) In Gaussian 98W, 6-31G(d) with frequency scaling factor 0.8929 (Foresman, 1996), the frequencies of the four prominent Raman bands are calculated as 594 cm$^{-1}$ (E$_{2g}$, activity 3.9), 968 cm$^{-1}$ (A$_{1g}$, activity 54.6), 1156 cm$^{-1}$ (E$_{2g}$, activity 7.2), and 1605 cm$^{-1}$ (E$_{2g}$, activity 12.8). The other Herzberg fundamental is calculated as 859 cm$^{-1}$ (E$_{1g}$, activity 3.3). An estimate of the Herzberg combination band ν$_{2}$+ν$_{18}$ (E$_{2g}$), from our observed Raman spectrum, is 605+990 = 1595 cm$^{-1}$, another instance of Fermi resonance. The four prominent normal modes are sketched in Figures 11-14, based on the Gaussian 98W calculations, with visualization through HyperChem. (HyperChem, 1999) The breathing mode (symmetric stretch) of the benzene ring, ν$_{2}$ (A$_{1u}$) at 990 cm$^{-1}$, is particularly noteworthy, and is the strongest band in the Raman spectrum.

Table 1. Spectral observations and normal mode calculations in Gaussian 98W.

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Raman obs/cm$^{-1}$</th>
<th>G98W/cm$^{-1}$, Raman activity</th>
<th>Irr Rep</th>
<th>Herzberg/cm$^{-1}$</th>
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<tr>
<td>1</td>
<td>1576</td>
<td>1629, 103.1</td>
<td>A$_{g}$</td>
<td>1571 s</td>
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<tr>
<td>2</td>
<td>452</td>
<td>435, 16.9</td>
<td>A$_{g}$</td>
<td>447 vs</td>
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<tr>
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<td>235, 5.0</td>
<td>A$_{g}$</td>
<td>237 s</td>
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<tr>
<td>4</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>not observed</td>
<td>997, 1.3</td>
<td>B$_{1g}$</td>
<td>1000 vw</td>
</tr>
<tr>
<td>6</td>
<td>354</td>
<td>338, 5.5</td>
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<td>347 m</td>
</tr>
<tr>
<td>7</td>
<td>&lt;400</td>
<td>574, 7.0</td>
<td>B$_{2u}$</td>
<td>512 m</td>
</tr>
<tr>
<td>8</td>
<td>515</td>
<td>909</td>
<td>B$_{2u}$</td>
<td>913 vs</td>
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<tr>
<td>9</td>
<td>?</td>
<td></td>
<td>B$_{2u}$</td>
<td>?</td>
</tr>
<tr>
<td>10</td>
<td>777</td>
<td></td>
<td>B$_{2u}$</td>
<td>782 vs</td>
</tr>
<tr>
<td>11</td>
<td>&lt;400</td>
<td></td>
<td>B$_{2u}$</td>
<td>387 ?</td>
</tr>
<tr>
<td>12</td>
<td></td>
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</tbody>
</table>

Figure 10. Benzene IR spectrum.

Figure 9. Benzene Raman spectrum.
Pyridine, C₅H₅N, is isoelectronic with benzene (C₆H₆), but one CH pair has become N in the ring. The point group is C₂ᵥ. Since there is no longer a center of inversion, the rule of mutual exclusion does not apply. Pyridine has 27 normal modes of vibration instead of the 30 of benzene. However, the vibrational spectra of pyridine are recognizably similar to those of benzene, as shown in Figure 15 and Figure 16.

The C₂ᵥ point group is a subgroup of D₆h. With conventional choices of axes (Salthouse, 1972), irreducible representation E₂g of D₆h becomes A₁ + B₂ in C₂ᵥ, and A₁g of D₆h becomes A₁ in C₂ᵥ. The most intense Raman bands of pyridine occur at 991 and 1027 cm⁻¹, in the vicinity of the 990 cm⁻¹ ν₂ (A₁g) breathing mode of benzene. In Gaussian 98W, 6-31G(d) with frequency scaling factor 0.8929 (Foresman, 1996), the frequencies of these two most prominent Raman bands are calculated as 976 cm⁻¹ (A₁, activity 23.6) and 1003 cm⁻¹ (A₁, activity 23.1), with visualization in HyperChem shown in Figure 17 and Figure 18.
CONCLUSION

Raman spectroscopy with the Ocean Optics R-2000 instrument is useful and practical in the undergraduate chemistry laboratory. (Ocean Optics, 2000). Observing both Raman and FTIR spectra provides significantly more thorough and complete vibrational information than the FTIR spectrum alone. Quantum chemistry calculations with Gaussian 98W and HyperChem software facilitate visualization of normal modes of vibration, and add support to spectral interpretation. Introduction of Raman spectra into the organic chemistry laboratory is currently in progress. Lambert and Nakamoto provide very good discussions of Raman and IR spectra for organic and inorganic compounds. (Lambert, 1998, Nakamoto, 1997).

LITERATURE CITED


ACKNOWLEDGMENTS

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