1. Low Wave Number Cutoff

When obtaining infrared spectra, the instrument is usually configured with a source and beam splitter that limits the lowest wave number to about 450 cm\(^{-1}\). With a Fourier transform Raman instrument, sample emission is the source, and this emission occurs between ~9,400 (1.06 \(\mu\)m) to ~5,000 cm\(^{-1}\). These wave numbers are passed efficiently by every optical component of the interferometer. The low end of the vibrational frequencies is determined by the holographic filter used to reject the laser line. This limit is determined by preparing a sample of solid KBr, turning off the laser, and turning on the white light. What is the lower limit on wave number?

To demonstrate low wave number capabilities obtain the Raman spectrum of carbon tetrachloride (don't forget to turn off the white light). On the basis of wave number alone, how many of the CCl\(_4\) bands would have shown up in an infrared spectrum stopping at 450 cm\(^{-1}\)?

Although all major, molecular components of air are Raman active, they do not affect the transmission of ~9,400 to 5,000 cm\(^{-1}\) radiation through the spectrometer. Additionally, their number density is too low to contribute to Raman scattering in the sample cell. This is in stark contrast to infrared spectroscopy where strong absorption of CO\(_2\) and water require that the instrument be continually purged with dry nitrogen gas.

2. Signal-to-Noise Ratio

Set the laser power to 100 mW and obtain a spectrum of cyclohexane at a resolution of 4 cm\(^{-1}\). Measure the signal strength at the strongest band, ~2853 cm\(^{-1}\). Measure the rms noise using the spectral region, 2150-2050 cm\(^{-1}\). Repeat the measurement for laser powers of 200 mW, 400 mW and 800 mW. Is the rms noise independent of the signal strength?

Set the laser power to 100 mW and measure the signal strength and noise using a resolution of 1 cm\(^{-1}\). What has happened to the signal-to-noise ratio?

3. Wave Number Calibration

Use the 1 cm\(^{-1}\) resolution cyclohexane spectrum from part 2 and check the peak positions against those specified by the ASTM (E 1840-96, Standard Guide for Raman Shift Standards for Spectrometer Calibration).

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\begin{align*}
384.1 \pm 0.78 & \quad 426.3 \pm 0.41 & \quad 801.3 \pm 0.96 & \quad 1028.3 \pm 0.45 & \quad 1157.6 \pm 0.94 \\
1266.4 \pm 0.58 & \quad 1444.4 \pm 0.30 & \quad 2664.4 \pm 0.42 & \quad 2852.9 \pm 0.32 & \quad 2923.8 \pm 0.36 \\
2938.3 \pm 0.51 &
\end{align*}
\]

To check the low wave number calibration run the spectrum of sulfur at 1 cm\(^{-1}\).

\[
\begin{align*}
85.1 \pm 2.6 & \quad 153.8 \pm 0.50 & \quad 219.1 \pm 0.57 & \quad 473.2 \pm 0.49 \\
\end{align*}
\]

For the following parts use a resolution of 4 cm\(^{-1}\) unless specifically told otherwise.

4. Raman Versus Infrared

Measure the Raman spectrum of chloroform. Obtain the infrared spectrum from the spectral database and compare the two (you can get this spectrum "at home" by running OMNIC from ITaP's Software Remote). Since chloroform has C\(_{3v}\) symmetry all vibrational bands are both infrared and Raman active.
Measure the Raman spectrum of benzene. Again, compare against the infrared spectrum in the OMNIC database. Since benzene has a center of symmetry, the two spectra should have no vibrational bands in common.

5. Fluorescence

Fluorescence is the major spectral interference in Raman spectroscopy. One method of reducing fluorescence is to use an excitation wavelength in the near infrared, e.g. 1.06 μm. This is because very few compounds fluoresce in this spectral region. To demonstrate a fluorescence background obtain the spectrum of "3-in-1 Household Oil." See if a library search can identify any oil components.

Prior to FT Raman the most common excitation wavelength was an argon ion laser emitting at 488 nm. How much is the Raman cross section expected to decrease at 1.06 μm in comparison to 488 nm. This trade in scattering cross section is accepted because of the reduction in fluorescence.

6. Aqueous Solutions

One of the characteristics often touted for Raman is that unlike infrared spectroscopy it can easily obtain the spectrum of aqueous solutions. This is due to both the infrared absorption of water and the fact that water destroys most infrared transparent materials used to make cell windows.

Obtain the Raman spectrum of water. Why is the high wave number band so broad? To demonstrate the ability to examine aqueous solutions obtain the spectrum of a 1:1 mixture of water and acetonitrile.

7. Solid Mixtures

Raman spectroscopy is revolutionizing manufacturing quality control of pharmaceuticals. To demonstrate this grind up a tablet of Tylenol and obtain its spectrum. See if a library search will find acetaminophen (4-acetamidophenol or N-(4-hydroxyphenyl)acetamide).