Physics 6180: Graduate Physics Laboratory

Experiment AM3b: Raman scattering in transparent solids and liquids

Objectives: *To learn the essentials of inelastic light scattering, particularly Raman scattering in molecular liquids and transparent solids.*

Overview--In this experiment we shall use the SPEX grating spectrometer and a low power, air cooled argon laser to examine the Raman spectra of some simple transparent solids and liquids. You will be using the SPEX 1 meter grating spectrometer for the Raman analysis. Normally, for Raman scattering one uses a double or a triple spectrometer because the elastic light scattering is very much stronger than the inelastic Raman scattering and when the frequency shifts are small it is difficult to "see" the weak Raman lines in the vicinity of the very strong "Rayleigh" peak. Therefore you will have to use great care to avoid any unnecessary elastically scattered laser light entering the spectrometer. With a single grating instrument it is essentially impossible to obtain Raman scattering from absorbing liquids and solids. Furthermore, one must keep dirt out of the liquids and avoid imaging surfaces of the crystals and the walls of the cuvette into the spectrometer, since such sources yield very strong Rayleigh or Mie scattering (elastic scattering).

The amount of Raman scattered light may be only 10^{-14} times as strong as the incident laser beam and therefore it is necessary to be very careful to collect as much light as possible. Whereas in studying atomic emission lines, you can often just plop down a discharge lamp somewhere in front of the spectrometer, for Raman scattering you will have to use a high quality collecting lens to observe any kind of signal at all. Small misadjustments can kill you!! As described in Paragraph 2 under Set-up (below, *infra vida*), you will use the camera lens to collect the Raman light over as large a solid angle as possible and image the track of the laser beam carefully into the entrance slit of the spectrometer. Then you must also be certain that all of the light which enters the spectrometer also falls on the first (collimating) spherical mirror of the spectrometer. There are many ways to fail to see a signal, but if you exercise some care you should be able to collect state-of-the-art data with the equipment we have in this lab.

Background:

You may think of the Raman process as a temporary electric dipole absorption (to a virtual excited electronic state) followed by re-radiation back to the ground electronic state. This ground electronic state may, however, be associated with a different vibrational or rotational quantum number. (Actually in condensed matter there are no free rotational motions -- only “librations” or hindered rotations.) In the case of solids, the vibrational motions are actually propagating vibrational modes or phonons. There generally is no excited electronic state which is resonant in energy with the photon energy and thus this "absorption" is a virtual process -- or equivalently, absorption occurs to a "virtual" state. Actually, a better description is to say that the Raman process is facilitated through coupling to off-resonant electronic excited states.

Note that in second-order perturbation theory of quantum mechanics, such a two-photon scattering process would have an overall matrix element with the form

$$M_{i'i} = M_{i'k} M_{ki} / [(E_k - E_i) - h\nu + ih\Gamma_k].$$

The matrix elements $M_{i'k}$ and M_{ki} are just the usual electric dipole transitions from atomic spectroscopy. For transparent liquids and solids, the laser photon energy hν is 2 - 4 eV away from resonance with the lowest lying electronic excited state E_k. (This explains why the liquid or solid is transparent, of course.) This far-from-resonance condition is one reason the Raman scattering is so weak!

The intensity of any particular Raman line will depend, naturally, on the square of this matrix element.

Set-up:

WARNING!!! THE LASER BEAM USED IN THIS EXPERIMENT IS POWERFUL ENOUGH TO CAUSE IMMEDIATE RETINAL DAMAGE IF YOU LOOK DIRECTLY INTO THE BEAM. USE EXTREME CARE AT ALL TIMES!! ALWAYS KNOW WHERE THE BEAM IS GOING WHEN YOU MAKE ADJUSTMENTS. BE VERY CAREFUL NOT TO BRING SHINY METALLIC SURFACES OR MIRRORS NEAR THE BEAM.

1. Remember the discussion for Experiment A1 regarding the need to set up the beam to pass vertically through the sample an appropriate distance from the entrance slit of the spectrometer so that the collecting lens can image appropriately into the spectrometer and can achieve a good f/# match to the spectrometer. In the case of liquids and solids, you need to think a little about the index of refraction and recall that focal position (for example of the laser beam after the focusing lens) will move due to the index of refraction. Thus if water ($n=1.3$) occupies all the space after a lens with $f = 10$ mm, the focus will lie at 13 mm behind the lens. Similarly for the collecting lens which images into the spectrometer. *Think while you're setting up the optics!* Carefully position the lower mirror and the beam focusing lens to achieve a vertical beam with a beam waist slightly below the height of the slit of the spectrometer.

2. You should now be ready to mount the Raman scattering cuvette or crystal into position so that the beam waist passes through the middle of the cuvette or crystal. **Be careful to block the laser beam while you are adjusting the cell into position to avoid any reflections hitting your eyes!!** Although when you acquire Raman data you will want the beam to pass through the middle of the cuvette or crystal, for alignment purposes it is convenient to let the beam strike the front face of the crystal at grazing incidence and then image this line into the entrance slit of the spectrometer. (**When you do this be sure the spectrometer entrance shutter is closed and the spectrometer is NOT set at the wavelength of the laser line!!**) When the image disappears into the entrance slit, you can proceed with further optimization using the electronic signal -- but of course you must have the spectrometer reading a Raman

line first!

3. Before you turn on the PMT, be aware that the strong elastic scattering at the laser line can destroy the PMT photocathode. Therefore you must **never** scan the spectrometer through the laser wavelength without having at least 10^3 - 10^4 attenuation in front of the spectrometer.

4. You should now be ready to turn on the spectrometer, the PMT voltage, and the electronics. The recommended settings for the EMI 9658B are: PMT voltage 1200 V (absolute maximum for this tube is 2300 V), coarse gain 16 and fine gain ~0.8 and threshold 1. If the settings are correct, you should see a dark count of about 25 counts per second. Slit settings of about 300 μm are recommended to begin. Start by placing 10^2 or 10^3 attenuation in front of the Spex and scanning through the laser line so that you will know exactly its position. All frequency shifts are to be measured from this line. (You should plot your data as a function of frequency shift, in units of cm^{-1}, from the laser line. This is readily done in the spreadsheet.)

You may have to use a very slow scan to achieve good counting statistics since the Raman scattering is very weak. When the count rate becomes excessive (remember the system loses counts above about 100,000 cps, press P to pause the data acquisition cycle--put in the filter and press ESC to continue. Proceed in a similar fashion to remove the filter. Your final data should be analyzed in terms of frequency shift, not wavelength shift. (The traditional spectroscopy unit is $\nu = \nu/c(\text{cm/sec}) = 1/\lambda(\text{cm})$ and is called "wavenumbers" with the units of cm^{-1}.)

Experiments:

A. I suggest that you try two liquids--such as CCl_4 (carbon tetrachloride) or C_6H_6 (benzene) which are non-polar liquids, with weak inter-molecular forces, and water, a polar liquid with relatively strong inter-molecular forces.

B. Next try two transparent solids. Unfortunately, NaCl, and the other related fcc crystals have no Raman-active phonon modes. However, some possibilities are crystalline quartz (SiO_2), calcite ($CaCO_3$), cadmium sulfide (CdS), and zinc selenide (ZnSe).

Analysis:

A. Generate plots of your Raman spectra showing the intensity vs. frequency shift in cm^{-1}. You can easily use the spreadsheet to convert the data from absolute wavelength units with constant increments in Angstroms (10^{-10} m, or 10^{-8} cm) into units of wavenumber (frequency) shift where the zero of frequency shift is the laser line, λ=5145 Å or ν = 19,436 cm^{-1}.

B. 1. H_2O: This spectrum shows strong inter-molecular forces and consequently broad Raman bands. The lower frequency band arises from the bending mode in which the two H-atoms move in a kind of scissors-like movement with slight oscillations of the characteristic 105° angle at the oxygen atom. The higher frequency band near 3600 cm^{-1}

arises from the stretch mode of the two H atoms along the H-O bond. It shows evidence of being a double peak due to H-bonded and non-H-bonded locations.

2. CCl_4: This spectrum shows a liquid with strong intra-molecular forces and weak inter-molecular forces. Several normal modes of motion are Raman-active and you should be able to identify peaks near 218, 314, 455, 458, 461 cm^{-1}.
3. $CaCO_3$: The calcite crystal is a well-known birefringent, uniaxial crystal. There is a prominent peak near 1088, and smaller peaks near 156, 283, and 714 cm^{-1}.
4. SiO_2: crystalline quartz has strong Raman peaks at 466 and 207 cm^{-1}.

Notes on the write-up:

1. Please provide graphs showing the Raman intensity vs. frequency shift. (Remember to convert from the wavelength scale (Å) to the frequency shift in cm^{-1} measured from the laser line as observed from your data.) Do this for (a) water, (b) CCl_4, and (c) quartz. [Adjust this list if you measured another material in place of any of these.]
2. Identify on the figure for each material the center position of each peak. (Just write on the graph next to or above each peak the frequency shift. This is best obtained by looking at the table of numbers on the spreadsheet.)
3. Now compare your observed values with literature values of the vibrational modes. Where possible, from the literature, identify the motions involved in the normal modes--bond stretching, bond bending, breathing mode, etc.
4. Provide some estimate of errors in the observed frequency shifts and explain any discrepancies between the literature values and your observed values.

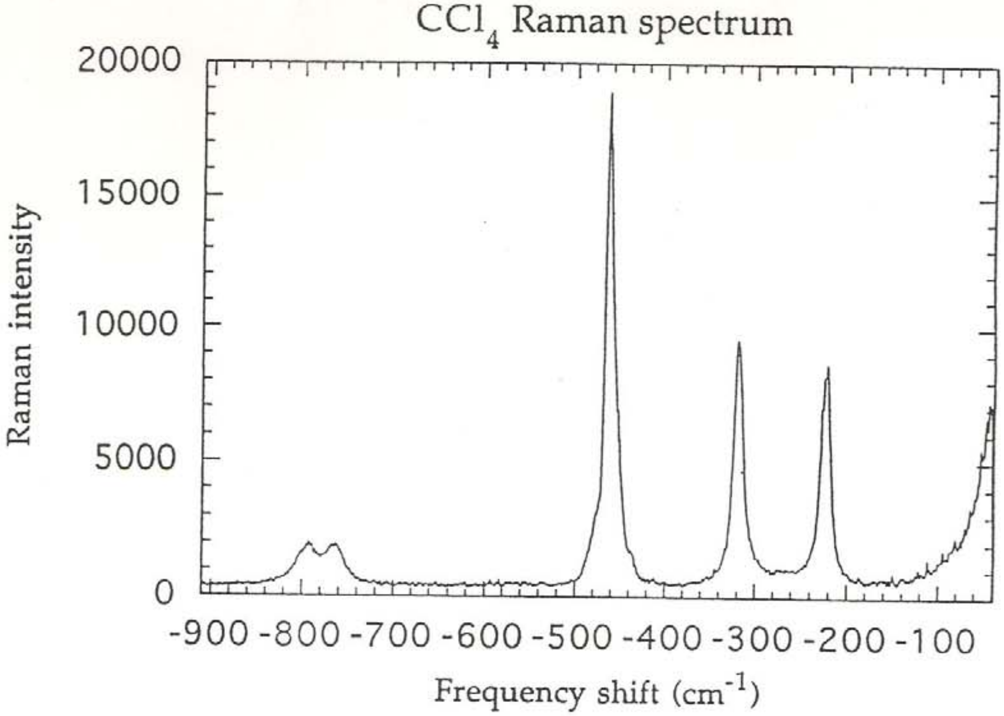


Table 6. CCl_4 vibrational modes

Observed frequency shift (cm^{-1})	Frequency shift from Hertzberg[3]	Frequency shift from Brame and Grasselli[4]	Mode label[5]	Description[6]
221.8±1.3	217.9	217	δ	doubly degenerate "skating on the sphere" mode
320.0±1.3	314.0	314	δ_a	triply degenerate "skating on the sphere" mode
464.1±1.3	461.5	459	ν_s	"breathing" mode
764.3±1.3 792.6±1.3	762.0 790.5	776	ν_a	translation of the central (C) atom against the Cl_4 shell

CCl_4 has the symmetrical tetrahedral structure. Molecules of tetrahedral structure have four fundamental frequencies. Hertzberg considers the two close frequencies above 700 cm^{-1} as a doublet. Figure 14 (reproduced from Brame and Grasselli) shows the normal modes of a tetrahedral XY_4 molecule.

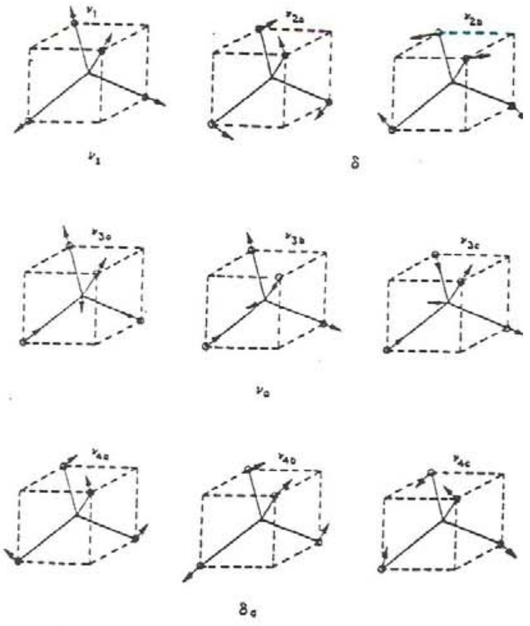


FIG. 14. Normal modes of a tetrahedral XY_4 molecule (schematic).

from R. Matulioniene / M. Mirkov (1995)

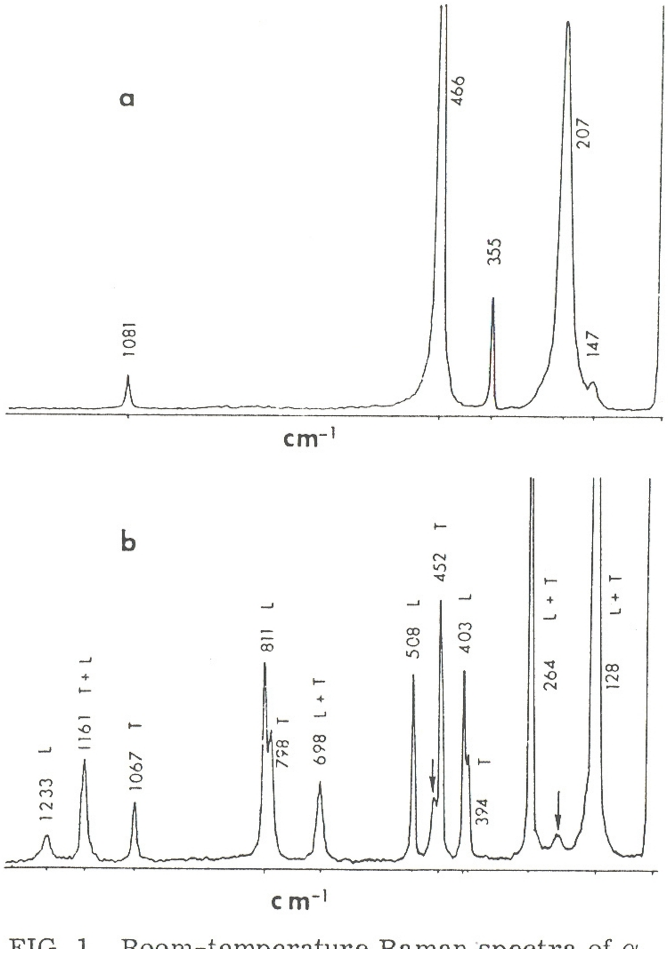


Fig. AM3b-2: Room temperature Raman spectra of amorphous (fused) silica (quartz). From Shapiro, et al, Phys. Rev. Lett. **19**, xxx (1967). A) the x[zz]y polarization showning the A_1 modes; and b) the x[yx+yz]y polarization showing the E modes. Arrows indicate some A_1 modes leaking through due to imperfect alignment and polarization.

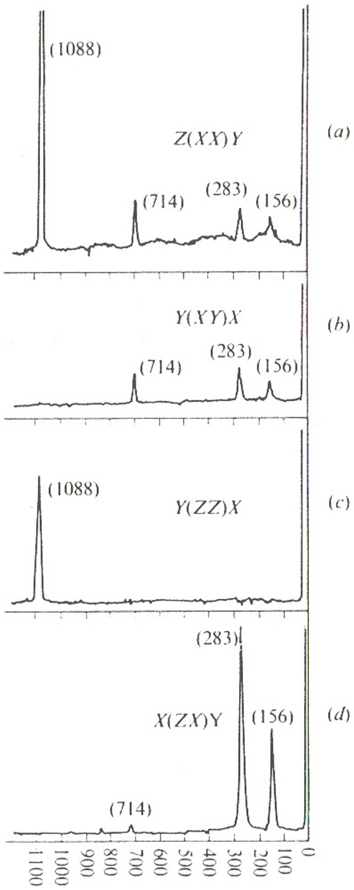


Fig. AM3b-3: Raman spectrum of calcite, from S.P.S. Porto, J.A. Giordmaine, and T.C. Damen, Phys. Rev. **147**, 608 (1966). [From J.C. Decius and R.M. Hexter, *Molecular Vibrations in Crystals*, McGraw-Hill.

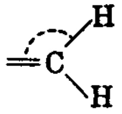
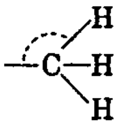
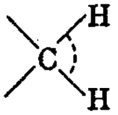
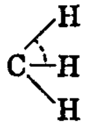
Group	Bond-stretching vibration	Group	Bond-stretching vibration	Group	Bond-bending vibration
≡C—H	3300	—C≡C—	2050		700
=C—H	3020	>C=C<	1650		1100
—C—H	2960	—C—C—	900		1000
—O—H	3680[67b]	—C—F	1100		1450
—S—H	2570	—C—Cl	650		1450
—N—H	3350	—C—Br	560		300
>C=O	1700	—C—I	500		
—C≡N	2100				
	cm^{-1}		cm^{-1}		cm^{-1}

Table AM3b-1: Characteristic frequencies of various bonding groups. From Herzberg, *Molecular Spectra*, vol. II p. 194.