Raman Spectroscopy

1. Introduction

When light is scattered from a molecule or crystal, most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. If the scattering is elastic, the process is called Rayleigh scattering. If it's not elastic, the process is called Raman scattering.

Raman scattering (or the Raman effect) was discovered in 1928 by V. C. Raman who won the Nobel prize for his work. If the substance being studied is illuminated by monochromatic light, for example from a laser, the spectrum of the scattered light consists of a strong line (the exciting line) of the same frequency as the incident illumination together with weaker lines on either side shifted from the strong line by frequencies ranging from a few to about 3500 cm⁻¹. The lines of frequency less than the exciting lines are called Stokes lines, the others anti-Stokes lines.

Raman spectroscopy is very important practical tool for quickly identifying molecules and minerals. A Raman spectrometer was deployed on the Viking landers in 1972 and in other missions. Raman spectroscopy also has important scientific applications in studying molecular structure. In this experiment we will study both kinds of applications.

2. More on Raman Scattering

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10^{-14} seconds or less. The virtual state description of the scattering is shown in Figure 1.

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 1. Numerically, the Raman shift in wave numbers (cm⁻¹), is calculated through Eq. 1,

$$\overline{\nu} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$
(1)

in which the λ 's are the wavelengths (in cm) of the incident and Raman scattered photons, respectively.



Figure 1. Energy level diagram for Raman scattering; (a) Stokes scattering, (b) anti-Stokes scattering

At room temperature the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state, and the scattered photon will have lower energy (longer wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. Figure 1(a) depicts Raman Stokes scattering.

A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, as shown in Figure 1(b). This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature it is strong enough to be useful for vibrational frequencies less than about 1500 cm⁻¹. The Stokes and anti-Stokes spectra contain the same frequency information. The anti-Stokes spectrum can be used when the Stokes spectrum is not directly observable, for example, because of poor detector response at lower frequencies.

3. A Bit of Molecular Theory

A complex molecule can absorb and emit energy by interacting with photons that can excite molecules to higher vibrational states. These vibrations are quantized and are called the normal modes of vibration of the molecule. A linear molecule with N atoms has 3N-5 normal modes, while a non-linear molecule has 3N-6 normal modes. The motion that characterizes each normal mode can be:

- Bending motion between three atoms connected by two bonds
- Stretching motion between two bonded atoms
- Out-of-plane deformation modes that change an otherwise planar structure into a non-planar one

Vibrational Modes

The vibrational spectrum of a molecule is composed of bands representing some active normal vibrations. The spectrum depends on the masses of the atoms in the molecule, the strength of their chemical bands and the atomic arrangement. Consequently, different

molecules have different vibrational spectra or different "finger prints." In a first approximation, groups of atoms have certain characteristic vibrations in the IR and Raman spectra. The vibrational spectra are useful in elucidating the molecular conformation/structure. For example, the stretching frequency of phosphorus-phosphorus bonds range from 460 to 610 to 775 cm⁻¹ for the single, double and triple bonded cases, respectively. Much effort has been devoted to estimation or measurement of force constants. For small molecules, and even for some extended structures such as peptides, reasonably accurate calculations of vibrational frequencies are possible with commercially available software.

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active. Their spectra are important in such fields as polymers and semiconductors. In the gas phase, rotational structure is resolvable on vibrational transitions. The resulting vibration/rotation spectra are widely used to study combustion and gas phase reactions generally. Vibrational Raman spectroscopy in this broad sense is an extraordinarily versatile probe into a wide range of phenomena ranging across disciplines from physical biochemistry to materials science.

Raman Selection Rules and Intensities

A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, P, induced in a molecule by an external electric field, E, is proportional to the field

$$P = \alpha E \tag{2}$$

The proportionality constant α is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave.

Raman scattering occurs because a molecular vibration can change the polarizability. The change is described by the polarizability derivative, $d\alpha/dQ$, where Q is the normal coordinate of the vibration. The selection rule for a Raman-active vibration, that there be a change in polarizability during the vibration, is

$$\frac{d\alpha}{dQ} \neq 0 \tag{3}$$

The Raman selection rule is analogous to the more familiar selection rule for an infrared-active vibration, which states that there must be a net change in permanent dipole moment during the vibration. From group theory it is straightforward to show that if a molecule has a center of symmetry, vibrations that are Raman active will be silent in the infrared, and *vice versa*. Scattering intensity is proportional to the square of the induced dipole moment, *i.e.*, to the square of the polarizability derivative.

If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak. An external electric field can not induce a large change in the dipole moment and stretching or bending the bond does not change this.

Frequency Range (in cm ⁻¹)	Band Assignment	Remarks
2700-3100	C-H alkyl free vibrations	Medium intensity in Raman
2230	C≡N stretch	very strong band in Raman, found in most cyanide based compounds
2190-2300	$C \equiv C$ (triple bond stretch)	very strong in Raman
2100-2140	$C \equiv C$ (triple bond stretch)	very strong in Raman
1650-1750	C=O stretch	Ketones appear on the lower wavelength side, aldehydes appear on the higher side
1600-1675	C=C stretch	Very strong in Raman
1580-1620	C=C stretch	Very strong in Raman
990-1010	Aromatic ring breathing	Appears at 992 cm ⁻¹ for benzene, around 1004 cm ⁻¹ for toluene.
650-850	C-Cl stretch	Strong in Raman

In organic molecules, particularly, certain frequencies can be associated with typical types of molecular excitations such as $C \equiv C$ triple bond stretching. Some examples are given in Fig. 2.

Figure 2 – Typical features in Raman spectra and their origin.

4. Experimental Procedure

A Raman spectrometer manufactured by Raman Systems is used to obtain the Raman spectrum of various samples. This spectrometer utilizes a 785 nm laser to excite the molecular vibrations. It also comes with a probe to hold the sample to be examined. To use the software that controls the laser, log onto the computer with your own password. Turn on the power to the spectrometer. Then start up the R2001 Base program.

NOTE: DO NOT REMOVE THE FIBER OPTIC CABLE FROM THE SAMPLE HOLDER!!

THE LASER IS POWERFUL ENOUGH TO CAUSE SERIOUS EYE INJURY. SINCE THE LIGHT IS INVISIBLE, THIS CAN HAPPEN WITHOUT YOUR REALIZING IT. The laser light is not dangerous if the fiber cable is connected to the housing. You should also turn off the laser before you remove the cover from the sample holder.



Figure 3 – The Raman spectrometer, which is linked by a dual fiber optic cable to the sample holder (bottom right), and the sample bottles (left). [Thanks to Choon Kiat Sim (Fall, 2005) for this photo and parts of the write-up.]

The typical procedure for taking a spectrum is as follows:

- 1. The sample to be measured is placed in a glass bottle and a Raman spectrum of the glass+sample is taken.
- 2. A Raman spectrum of just the glass bottle is taken as a "dark" spectrum.
- 3. The effective Raman spectrum is the spectrum of sample in bottle minus the dark spectrum. (The subtraction can be done automatically with the software.)
- 4. If the spectra are "noisy" you can increase the integration time, but the program seems to go crazy if you choose integration times >200 sec. To get longer "runs", you can export the data from several runs and combine them using Excel or IGOR.
- 5. Save your spectra (on a memory key or floppy) for analysis via Excel or IGOR.

Take spectra for at least 6 different samples, including chloroform and carbon tetrachloride. One of these can be an unknown that you will be asked to identify. The unknown will be one of the sample spectra given in the <u>www.RamanSystems.com</u> web site. The others can be of your choosing; they need not be among those you find in the laboratory. You should also take a spectrum for the glass bottle.

The software has some idiosyncrasies that may make it confusing. Disregard the warning about

integration time as it starts up. It is a good idea to check an "easy" spectrum such as chloroform often. If the program starts giving very poor peaks, exit the program, cycle the power on the box, and restart the program. It's also a good idea to Clear Chart often to remove old spectra in memory.

Your lab report should include spectra for each sample. Label all prominent features and explain their origin.

5. Questions

- (1) Explain briefly how the Raman spectrometer works. (A diagram is appropriate.) What is the purpose of the notch filter?
- (2) Discuss the differences between the spectra for chloroform and carbon tetrachloride. What causes these differences?
- (3) What is the resolution of our spectrometer? Give examples from your spectra where nearby peaks are not resolved.
- (4) Make a table comparing relevant features in your spectra with the typical bands in Figure 2. Discuss the agreement (or lack thereof) between your observations and expectations.
- (5) Discuss the use and limitations of Raman spectroscopy for analyses. What advantages and disadvantages does it have over visible light spectroscopy, *e.g.*, the one used in the Atomic Spectroscopy experiment?

6. References

- [1] Harris, D.C., Bertolucci, M.D., *Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy*, Oxford University Press (1978)
- [2] Carey, P.R., *Biochemical Applications of Raman and Resonance Raman Spectroscopies*, Academic Press (1982)
- [3] Herzberg, G, Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules, Krieger Publishing (1991)
- [4] For sample spectra and information on the spectrometer, see www.ramansystems.com
- [5] For a comprehensive list of Raman frequencies, see Infrared and Raman Characteristic Group Frequencies by George Socrates (John Wiley & Sons, 2004).