# Raman Spectroscopy

Introduction

You are already aware that photons interact with molecules to induce transitions between energy states. In the discussion of Raman spectroscopy, we use language from particle theory and we say that a photon is scattered by the molecular system. Most photons are elastically scattered, a process which is called Rayleigh scattering. In Rayleigh scattering, the emitted photon has the same wavelength as the absorbing photon. Raman Spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules. The Raman effect comprises a very small fraction, about 1 in $10^{7,}$ of the incident photons. In Raman scattering, the energies of the absorbed and emitted photons are different. A simplified energy diagram that illustrates these concepts is given below.
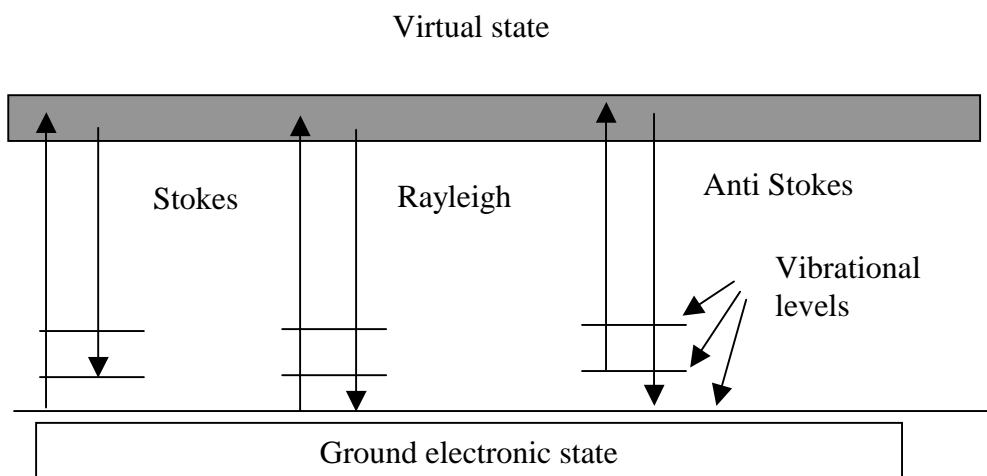

Note that energy is lost in the Stokes line and energy is produced in the anti-Stokes line. The energy gained or lost is related to the vibrational energy spacing in the molecule and therefore the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule. A schematic Raman spectrum may appear as:
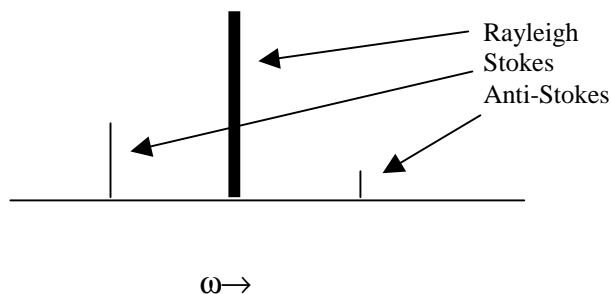

In the example spectrum, notice that the Stokes and anti-Stokes lines are equally displaced from the Rayleigh line. This occurs because in either case one vibrational quantum of energy is gained or lost. Also, note that the anti-Stokes line is much less intense than the Stokes line. In Raman

spectroscopy, usually the more intense Stokes line is measured. Raman spectroscopy requires a high power source because of the minute Raman intensities. Raman became a common experimental technique after the development of high power lasers. In a typical setup, the laser beam irradiates the sample and the Raman scattering is observed at a 90° angle. This viewing angle minimizes interference from the laser.

Infrared (IR) and Raman spectroscopy both measure the vibrational energies of molecules but these method rely only different selection rules. Recall that for a vibrational motion to be IR active, the dipole moment of the molecule must change. Therefore, the symmetric stretch in carbon dioxide is not IR active because there is not change in the dipole moment. The asymmetric stretch is IR active due to a change in dipole moment.

O ⟸ C ⟹ O   O ⟸ C ⟹ O

      no change in dipole   change in dipole
   Not IR active   IR active
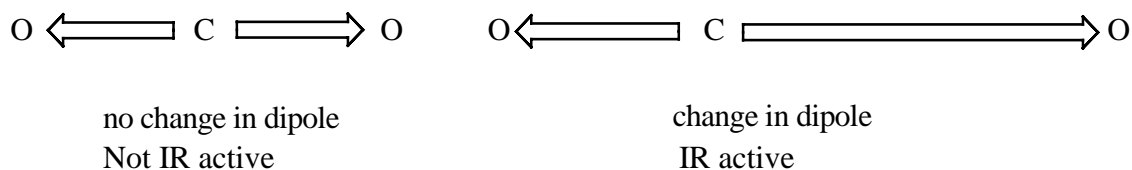
For a transition to be Raman active there must be a change in polarizability of the molecule. Polarizability is the change of the dipole moment with distance.

O ⟵ C ⟶ O   O ▬C▬ O   O ⟶ C ⟵ O

Molecular motion

polarizability
ellipsoid
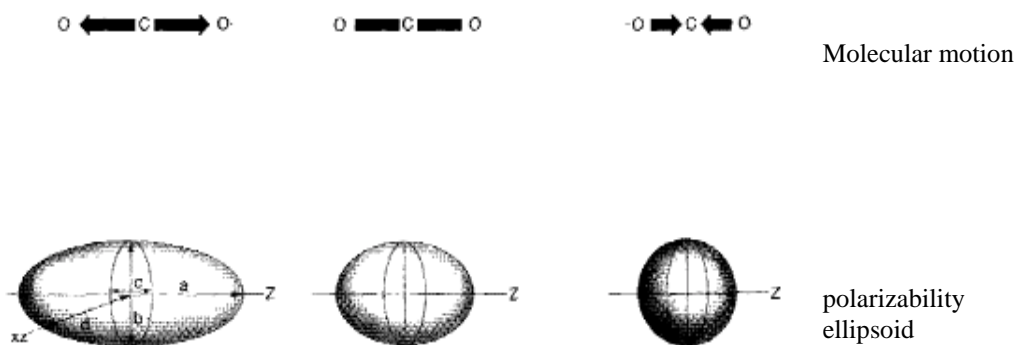
Notice that the symmetric stretch in carbon dioxide is Raman active because the polarizability of the molecule changes. You can see when you compare the ellipsoid at the equilibrium bond length to the ellipsoid for the extended and compressed symmetric motions. For a vibration to be Raman active, the polarizability of the molecule must change with the vibrational motion. Thus, Raman spectroscopy complements IR spectroscopy.

Experimentally, we only observe the Stokes shift in a Raman spectrum. Recall that the Stokes lines will be at smaller wavenumbers (or higher wavelengths) than the exciting light. Since the

Raman scattering is not very efficient, we need a high power excitation source such as a laser. We also need to have very sensitive amplification and detection equipment to monitor the weak Raman signal. In this experiment, a lock-in amplifier is used to detect the signal. A lock-in needs to have a pulsed source so the Helium-Cadmium laser beam ($\lambda = 442$ nm) is passed through an optical chopper to produce a pulsed beam. The scattered light is passed through a 0.5 meter CVI monochromator and detected by a PMT. Output from the tube is passed to the lock-in and then to either a computer or strip chart recorder.
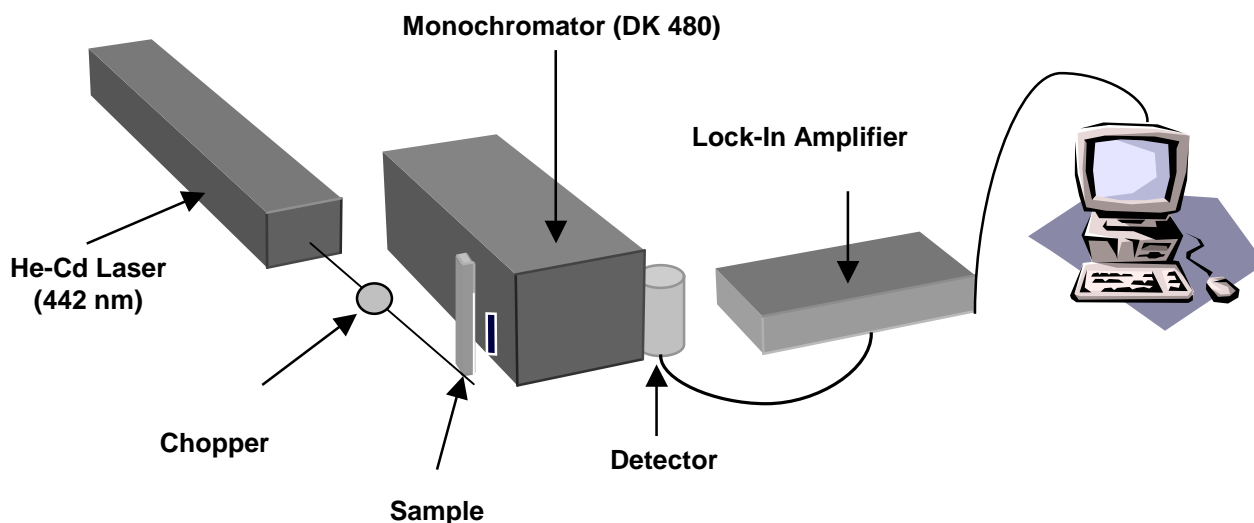
Default Instrument Parameters:

DK 480 Monochromator	SR 810 Lock-In Amplifier
Scan Range: typically 440 nm – 510 nm	Time Constant: 300 ms
Scan Speed: 20nm/min	Slope: 24 dB
Bandpass: 1.5 nm	Sensitivity: 2 mV/nA
Entrance Slit: 430 μm	Data Storage Rate: 64 Hz
Exit Slit: 430 μm	

External Raman Instrument Parameters:

PMT Voltage: 800 mV
Chopper: 400 Hz

Experimental

You will investigate the vibrational properties of three molecules: methylene chloride, chloroform, and carbon tetrachloride. You will use molecular orbital theory and group theory to classify the vibrational modes and determine which modes are IR active and which are Raman active.

Before you begin the experiment, complete these calculations:

1. Calculate the number of vibrational modes in each molecule.

2. Calculate the wavenumber for the laser line. Assuming that the highest observed vibration is at 3500 cm^{-1}, find the maximum wavenumber for the scan. Convert this wavenumber into wavelength.

The Raman spectrometer is home built and will be demonstrated to you. Samples are in 5 mm NMR tubes with flat bottoms and the laser beam is oriented to pass through the bottom of the NMR tube.

Good spectra depend on careful alignment of the laser beam and the optics.

You will obtain the IR and Raman spectra of each sample. For the Raman spectra, start the scan at 447.

Safety Note: These substances are potential carcinogens. Use gloves and minimize exposure.

Molecular Orbital Calculations

Each molecule will also be modeled on Spartan at the 3-21*G level. Optimize the geometry, and then calculate the vibrational frequencies using the 3-21*G basis.

Animate each vibration to determine which atoms contribute to the motion.

Calculations

1. Classify each molecule into its point group and then use the character table for that point group to determine, from your Spartan calculations, which modes are IR active and which are Raman active.

2. Predict the number of peaks for the IR and Raman spectra.

3. Convert the experimental peak positions from wavelength to wavenumbers. The Raman shift is the difference between the wavenumber of the laser line and the wavenumber of the observed peak (Since these are Stokes lines, the Raman shift is always >0).

4. It has been well documented that HF calculations always <u>overestimate</u> vibrational frequencies.[1] A correction or scaling factor is used to bring the calculated values in agreement with experimental data. The scaling factor is 0.9085 for the 3-21*G basis. After scaling your results, compare the calculated wavenumbers with the experimental values. What are the percent errors in the calculated results?

5. At what wavenumber would the Raman peak appear for $CDCl_3$?

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[1] L. Radom & A. Scott, *J. Phys. Chem.* **1996**, *100*, 16502.