



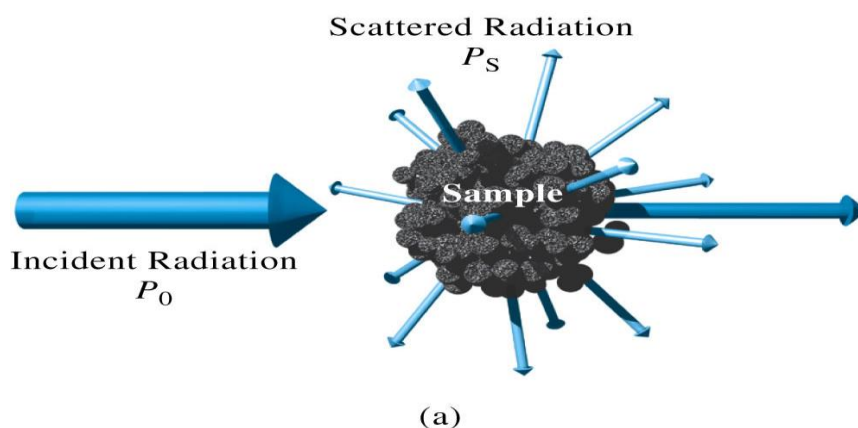
Lectures of Molecular Spectroscopy
Second Semester, Scholar year 2020-2021
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Lecture No. Four: Raman Spectroscopy

1-Introduction

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.

- Raman spectroscopy is observed as inelastic scattered light and allows for the identification of vibrational (phonons) states of molecules.
- Raman spectroscopy provides an invaluable analytical tool for molecular fingerprinting as well as monitoring changes in molecular bond structure.
- Raman Effect manifests itself in the light scattered off a sample as opposed to the light absorbed by a sample.



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- Raman spectroscopy requires little to no sample preparation and is insensitive to aqueous absorption bands. This property of Raman facilitates the measurement of solids, liquids, and gases not only directly, but also through transparent containers such as glass, quartz, and plastic.
- Similar to FT-IR, Raman spectroscopy is highly selective, which allows it to identify and differentiate molecules and chemical species that are very similar. Figure 1. Shows an example of five similar molecules – Acetone, Ethanol, Dimethyl Sulfoxide, Ethyl Acetate, and Toluene. Although each chemical has a similar molecular structure, their Raman spectra are clearly differentiable, even to the untrained eye. Using Raman spectral libraries it is easy to see how easily Raman spectra can be used for material identification and verification.

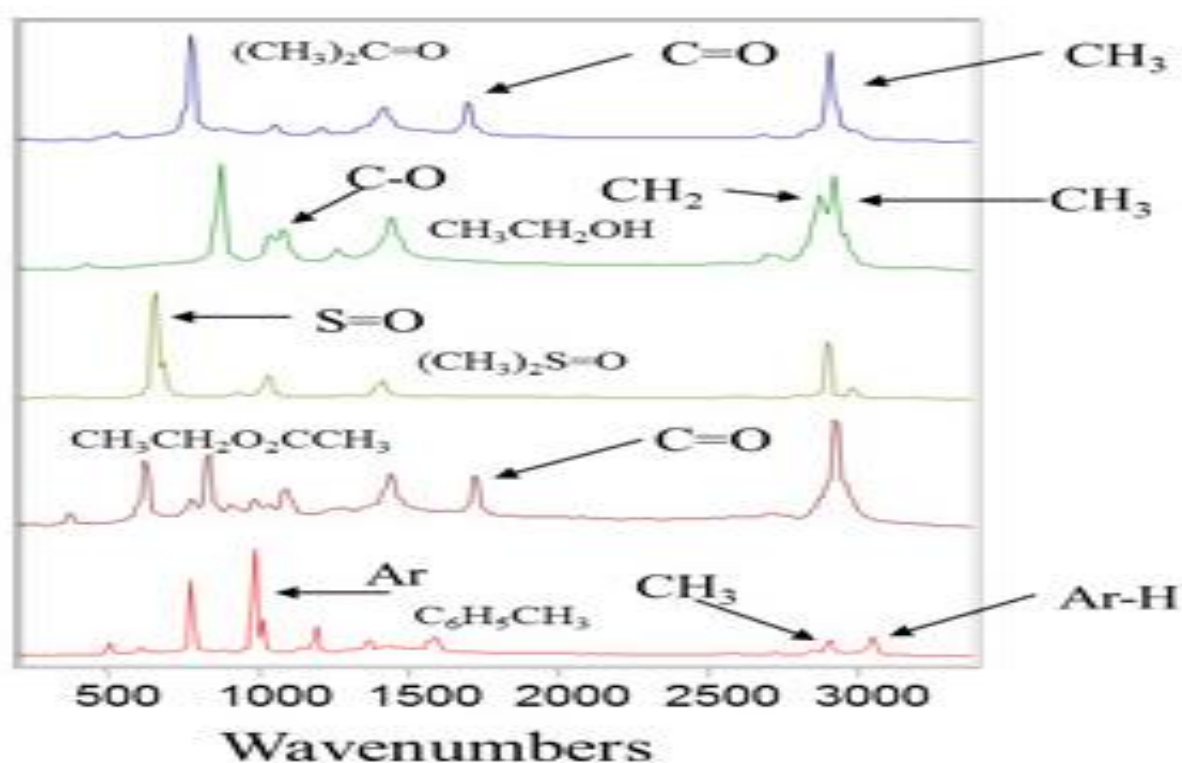


Figure 1. Raman spectra of various molecules.

2-Theory of Raman Scattering:

They found two interpretation for theoretical explanation, they are

First: - Classical wave interpretation

- In the classical wave interpretation, light considered as electromagnetic radiation, which contains an oscillating electric field that interacts with a molecule through its polarizability.
- Polarizability is determine by the electron cloud's ability to interact with an electric field. For example, soft molecules such as benzene tend to be strong Raman scatters while harder molecules like water tend to be weak Raman scatters.

Second: - Quantum particle interpretation

- Light is a photon that strikes the molecule and then inelasticity scatters.
- The number of scattered photons is proportional to the size of the bond. For example, molecules with large Pi bonds such as benzene tend to scatter many photons, while water with small single bonds tends to be a very weak Raman scattered. Figure 2 shows a visual comparison of the two methods.

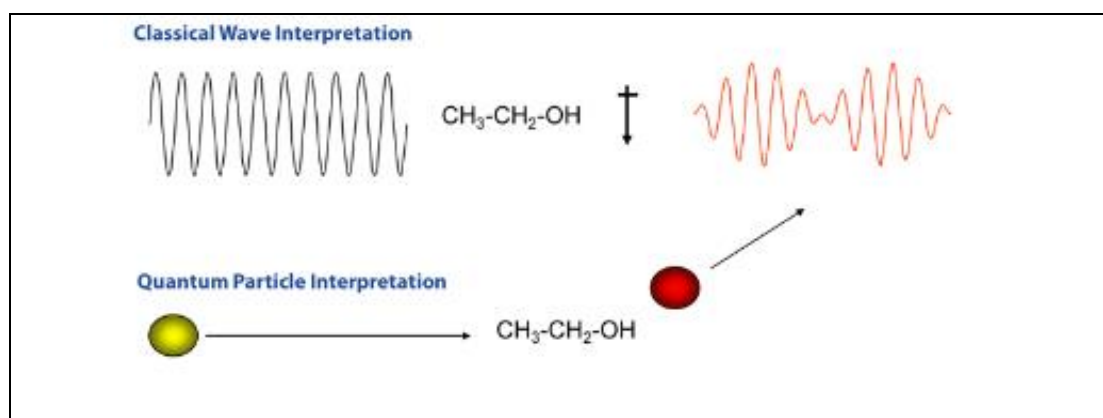


Figure 2. Comparison of Raman Scattering Interpretations

When deriving the Raman Effect, it is generally easiest to start with the classical interpretation by considering a simple diatomic molecule as a mass on a spring as shown in figure 3, where m is represent the atomic mass, x is represent the displacement, and K is represent the bond strength.

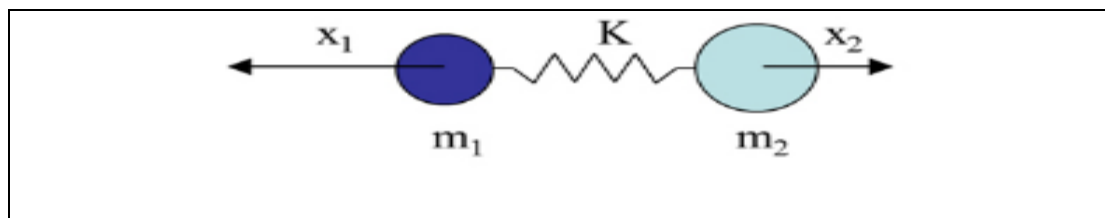


Figure 3. Diatomic Molecule as a Mass on a Spring.

When using this approximation, the displacement of the molecule can expressed by using Hooke's law as,

$$\frac{m_1 m_2}{m_1 + m_2} \left(\frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2} \right) = -K(x_1 + x_2).$$

By replacing the reduced mass ($m_1 m_2 / [m_1 + m_2]$) with μ and the total displacement ($x_1 + x_2$) with q , the equation can be simplified to,

$$\mu \frac{d^2 q}{dt^2} = -Kq,$$

By solving this equation for q we get,

$$q = q_0 \cos(2\pi\nu_m t),$$

Where ν_m is the molecular vibration and is defined as,

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}.$$

From this equation, each molecule will have its own unique vibrational signatures, which are determine not only by the atoms in the molecule, but also the characteristics of the individual bonds. Through **the Raman Effect, these vibrational frequencies can be measured because the polarizability of a molecule, α , is a function of displacement, q .** When incident light interacts with a molecule, it induces a dipole moment, P ,

equal to that of the product of the polarizability of the molecule and the electric field of the incident light source. This can be expressed as,

$$P = \alpha E_o \cos(2\pi\nu_o t),$$

Where E_o is the intensity and ν_o is the frequency of the electric field. Using the small amplitude approximation, the polarizability can represent a linear function of displacement.

3-General features of Raman spectroscopy:

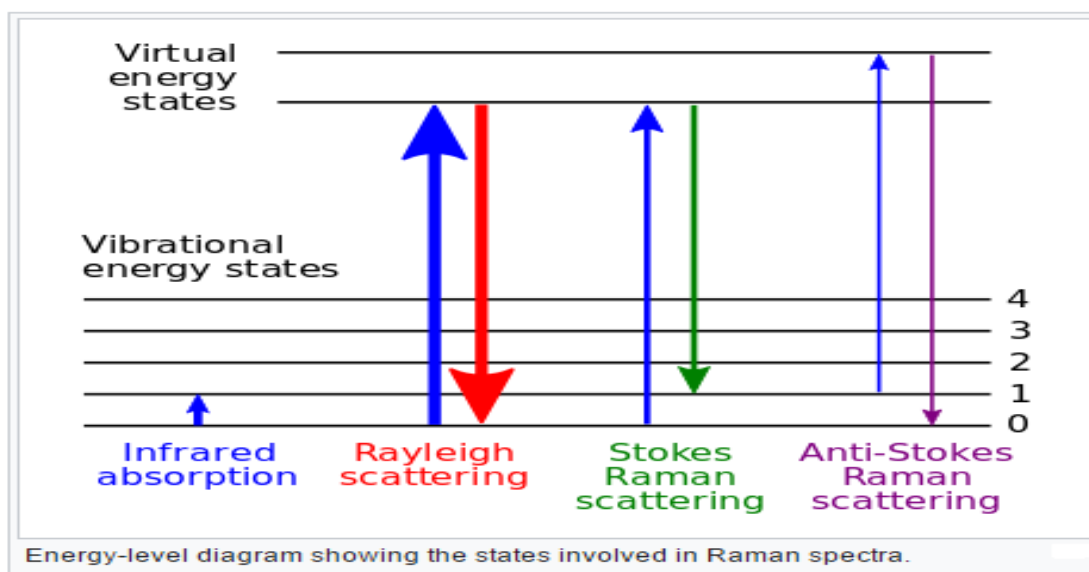
1. The Raman spectroscopy measures the vibrational motions of a molecule like the infrared spectroscopy.
2. The physical method of observing the vibrations is different from the infrared spectroscopy.
3. In Raman spectroscopy, one measures the light scattering while the infrared spectroscopy is based on absorption of photons.
4. Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.
5. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.
6. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.
7. Typically, a sample is illuminated with a laser beam (Electromagnetic radiation from the illuminated spot is collected with a lens and sent through a monochromator).
8. Elastic scattered radiation at the wavelength corresponding to the laser line (Rayleigh scattering) is filtered out, while the rest of the collected light is dispersed onto a detector.

9. Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light.

4-Mechanism of Raman Spectroscopy:

- The Raman Effect occurs when electromagnetic radiation impinges on a molecule and interacts with the polarizable electron density and the bonds of the molecule in the phase (solid, liquid or gaseous) and environment in which the molecule finds itself.
- For the spontaneous Raman effect, which is a form of inelastic light scattering, a photon (electromagnetic radiation of a specific wavelength) excites (interacts with) the molecule in either the ground rovibronic state (lowest rotational and vibrational energy level of the ground electronic state) or an excited rovibronic state.
- This results in the molecule being in a so-called virtual energy state for a short time period before an inelastically scattered photon results. The resulting inelastically scattered photon which is "emitted"/"scattered" can be of either lower (Stokes) or higher (anti-Stokes) energy than the incoming photon.
- In Raman scattering the resulting rovibronic state of the molecule is a different rotational or vibrational state than the one in which the molecule was originally, before interacting with the incoming photon (electromagnetic radiation).
- The difference in energy between the original rovibronic state and this resulting rovibronic state leads to a shift in the emitted photon's frequency away from the excitation wavelength, the so-called Rayleigh line.

- The Raman Effect is due to inelastic scattering and should not be confused with emission (fluorescence or phosphorescence) where a molecule in an excited electronic state emits a photon of energy and returns to the ground electronic state, in many cases to a vibrationally excited state on the ground electronic state potential energy surface.



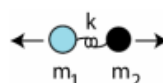
Raman Spectroscopy: Classical Treatment

- Number of peaks related to degrees of freedom

$$DoF = 3N - 6 \text{ (bent) or } 3N - 5 \text{ (linear) for } N \text{ atoms}$$

- Energy related to harmonic oscillator

$$\sigma \text{ or } \Delta\sigma = \frac{c}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$



- Selection rules related to symmetry

Rule of thumb: symmetric=Raman active, asymmetric=IR active

CO ₂	H ₂ O	
 Raman: 1335 cm ⁻¹	 Raman + IR: 3657 cm ⁻¹	
 IR: 2349 cm ⁻¹		Raman + IR: 3756 cm ⁻¹
 IR: 667 cm ⁻¹		Raman + IR: 1594 cm ⁻¹