



Lectures of Molecular Spectroscopy
Second Semester, Scholar year 2024-2025
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Lecture No. 4: 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.
- 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.
- Requires little to no sample preparation and is insensitive to aqueous absorption bands.
- Is highly selective, which allows it to identify different molecules and chemical species.

2-Theory of Raman Scattering:

They found two interpretations for theoretical explanation, they are
First: - Classical wave interpretation

- Light is considered as electromagnetic radiation, which contains an oscillating electric field that interacts with a molecule through its polarizability.

- Polarizability is determined by the electron cloud's ability to interact with an electric field.

For example, soft molecules such as benzene tend to be strong Raman scatterers while harder molecules like water tend to be weak Raman scatterers.

Second: - Quantum particle interpretation

- Light is a photon that strikes the molecule and then inelastically 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 scatterer. Figure 2 shows a visual comparison of the two methods.

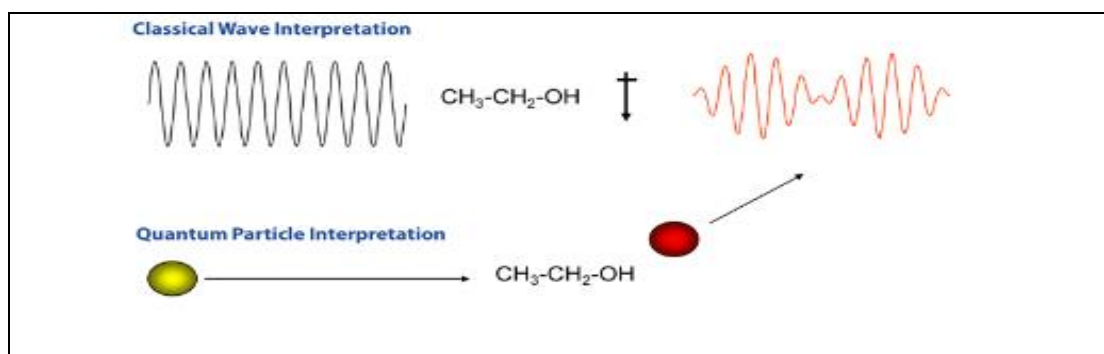


Figure 1. Comparison of Raman Scattering Interpretations

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 2, where m is represent the atomic mass, x is represent the displacement, and K is represent the bond strength.

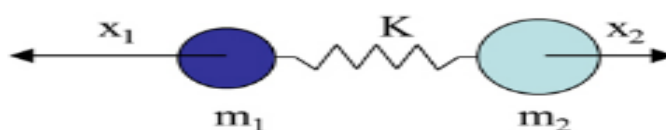


Figure 2. Diatomic Molecule as a Mass on a spring.

When using this approximation, the displacement of the molecule can be 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 determined 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,

$$P = \alpha E_0 \cos(2\pi\nu_0 t),$$

Where E_0 is the intensity and ν_0 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. Measure the vibrational motions of a molecule based on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.

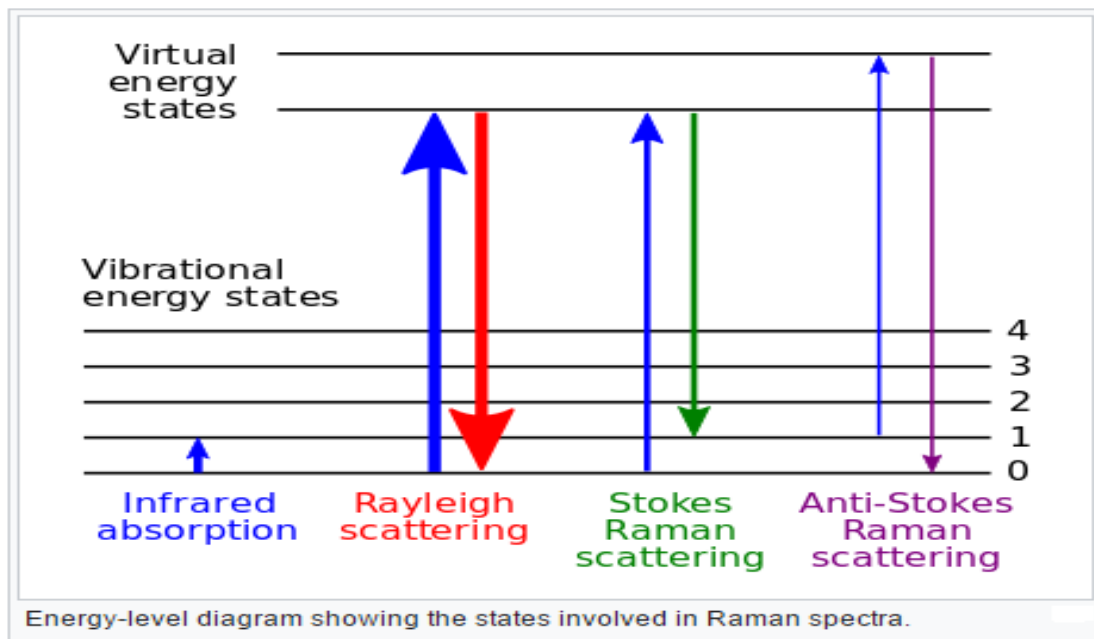
2. Uses in chemistry to provide a fingerprint by which molecules for identified.
3. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shift up or down.
4. Elastic scattered radiation at the wavelength corresponding to the laser line (Rayleigh scattering) is filtered out, while the rest of the collected light is dispersed onto a detector.
5. 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) .
- Raman effect, which is a form of inelastic light scattering, a photon 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 excited 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.
- 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 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.



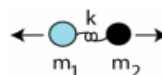
Raman Spectroscopy: Classical Treatment

- 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
<p>Raman: 1335 cm⁻¹</p>	<p>Raman + IR: 3657 cm⁻¹</p>
<p>IR: 2349 cm⁻¹</p>	<p>Raman + IR: 3756 cm⁻¹</p>
<p>IR: 667 cm⁻¹</p>	<p>Raman + IR: 1594 cm⁻¹</p>