

Raman Spectroscopy

The Raman effect is the scattering of a photon by a molecule. In scattering, the photon transfers some (but not all) of its energy to the molecule. This is different than absorption spectroscopy in which the photon transfers all of its energy to the molecule. Raman spectroscopy complements absorption spectroscopy because the selection rules are different. In order to see this, we will assume that we have a diatomic molecule with characteristic vibrational frequency ω_{vib} . Also, we will assume that the electric field E (the photon) has frequency $\omega \Rightarrow E = E_0 \cos \omega t$. The electric field distorts the molecule slightly because the valence electrons ($-ve$) and the nuclei/core electrons (net $+ve$) get pulled in opposite directions. This induces a time-dependent dipole moment of magnitude $\mu_{\text{induced}}(t)$ in the molecule of the same frequency as the photon.

The selection rule for Raman comes from

$$(\alpha)_{12} = \int \psi_2^* \alpha \psi_1 \quad (1)$$

where α is the polarizability of the molecule.

In the linear response approximation, we have

$$\mu_{\text{induced}}(t) = \alpha E = \alpha E_0 \cos \omega t \quad (2)$$

where we have assumed that the induced dipole is linearly proportional to the strength of the applied field.

Since α depends on the bond length, we perform a Taylor expansion around the equilibrium position

$$\alpha(r) = \alpha(r_{\text{eq}}) + (r - r_{\text{eq}}) \left. \frac{d\alpha}{dr} \right|_{r_{\text{eq}}} + \dots \quad (3)$$

Due to the bond vibration,

$$r = r(t) = r_0 \cos \omega_{\text{vib}} t + r_{\text{eq}} \quad (4)$$

Combining everything and used trigonometric identities gives

$$\mu_{\text{induced}}(t) = \alpha E = \alpha(r_{\text{eq}}) E_0 \underbrace{\cos \omega t}_{\text{Rayleigh}} + \left. \frac{d\alpha}{dr} \right|_{r_{\text{eq}}} r_0 E_0 \left[\underbrace{\cos(\omega + \omega_{\text{vib}})t}_{\text{anti-Stokes}} + \underbrace{\cos(\omega - \omega_{\text{vib}})t}_{\text{Stokes}} \right] \quad (5)$$

Most of the incident photons undergo Rayleigh scattering. A few photons undergo Stokes scattering in which light causes a vibrational excitation, and a few photons (might) undergo anti-Stokes scattering in which light causes a vibrational de-excitation.

To observe the Stokes and anti-Stokes signals we need $\frac{d\alpha}{dr}|_{r_{eq}} \neq 0$. Thus for a vibrational mode in a molecule to be Raman active, the polarizability of the molecule must change during the vibrational motion. In particular, homonuclear diatomics are Raman active. Since homonuclear diatomics are IR inactive, absorption and Raman spectroscopy complement one another.

It is also possible to collect a rotational Raman spectrum but we will not consider this.

Advantages of Raman: we can use any ω as long as the photon energy is larger than the vibrational excitation energy of the molecule. This means that by selecting the wavelength of light appropriately, we can: 1. avoid absorption of light by H_2O , CO_2 , etc. 2. use optical microscopy to focus the light with a spatial resolution better than $10 \mu\text{m}$. With this technique we have what is known as a “Raman microscope”.