

Raman Spectroscopy

In 1928, C. V. Raman noted that the visible wavelength of a small fraction of light scattered by certain molecules differed from that of the incident beam and, furthermore, that the difference in wavelength depended on chemical structure. It has since been shown that this phenomenon results from the same quantized vibrational changes associated with infrared absorption (i.e., that the difference in wavelength between incident and scattered light corresponds to mid-infrared light). There are, however, enough differences in the groups that are infrared and Raman active that the two techniques are *complimentary* rather than competitive. Two advantages of Raman spectroscopy are: 1) water does not cause interference (it can be done with *aqueous* solutions) and 2) glass or quartz cells can be used.

Samples are irradiated with a high-powered laser source at visible or near-infrared wavelengths and the spectrum of the scattered light is measured with a suitable spectrometer at some angle (usually 90°). At best, Raman line intensities are 0.001% of the incident beam.

[Fig. 18-2 p. 482]

Mechanism of Rayleigh and Raman Scattering

[Fig. 18-3 p. 483]

Wave Model of Rayleigh and Raman Scattering

Radiation with a frequency ν_{ex} has an electric field E of

$$E = E_0 \cos(2\pi\nu_{\text{ex}}t)$$

where E_0 is the amplitude of the wave. When the radiation interacts with the electron cloud of a bond of a sample molecule, it induces a dipole moment m given by

$$m = \alpha E = \alpha E_0 \cos(2\pi\nu_{\text{ex}}t)$$

where α is a proportionality constant called the *polarizability* of the bond. This constant depends on the deformability of the bond. To be Raman active, the polarizability must vary as a function of the distance between the nuclei of the two atoms that are connected by the bond according to the equation

$$\alpha = \alpha_0(r - r_{\text{eq}})(\partial\alpha/\partial r)$$

where α_0 is the polarizability of the bond *at the equilibrium internuclear distance* r_{eq} and r the internuclear separation at any instant. This change in internuclear separation varies with the frequency of the vibration *of the bond* ν_v by the relationship

$$r - r_{\text{eq}} = r_m \cos(2\pi\nu_v t)$$

where r_m is the *maximum* internuclear separation relative to the equilibrium position. Substitution of this equation into the previous one gives

$$\alpha = \alpha_0 + (\partial\alpha/\partial r)r_m \cos(2\pi\nu_v t)$$

Wave Model of Rayleigh and Raman Scattering (cont'd)

Combining this last expression with the above expression for dipole moment, we get

$$m = \alpha_0 E_0 \cos(2\pi v_{\text{ex}} t) + E_0 r_m (\partial\alpha/\partial r) \cos(2\pi v_v t) \cos(2\pi v_{\text{ex}} t)$$

And recalling from trigonometry that $\cos x \cos y$ is equivalent to $[\cos(x + y) + \cos(x - y)]/2$, we get the relationship

$$m = \alpha_0 E_0 \cos(2\pi v_{\text{ex}} t) + (E_0/2) r_m (\partial\alpha/\partial r) \cos[2\pi(v_{\text{ex}} - v_v)t] + (E_0/2) r_m (\partial\alpha/\partial r) \cos[2\pi(v_{\text{ex}} + v_v)t]$$

The first term of the relationship represents *Rayleigh* scattering, while the second and third terms represent the *Stokes* and the *anti-Stokes* frequencies of the Raman scattering, respectively. Also note that Raman scattering *requires* that the polarizability of the bond varies as a function of internuclear distance (i.e., $\delta\alpha/\delta r > 0$).

The Relationship between Raman and Infrared Spectra

Energy *shifts* seen in Raman experiments should be identical to the energies of infrared *absorption* for a given bond, if the vibrational mode involved is active to both infrared absorption and Raman scattering, as in the two spectra below, when the $\Delta\nu$ value of a peak in the Raman spectrum (lower) corresponds to the ν value of a peak in the infrared spectrum. There are, however, important differences in the spectra due to the fact that the two spectra, though based on the same vibrational *modes*, stem from different *mechanisms*. Infrared absorption requires that a vibrational mode of the molecule have an associated change in *dipole moment*, while Raman scattering involves a momentary *distortion* of the bond's electron distribution (it is *temporarily* polarized) followed by reemission of the radiation as the bond returns to its normal state. Thus Raman activity can differ markedly from infrared activity for a mode. This too can be seen from the spectra below, where some infrared absorption peaks have no matching Raman peaks, and *vice versa*.

[Fig. 18-4 p. 485]

Raman Depolarization Ratios

One additional variable obtained from Raman measurements that may provide useful information for elucidation of molecular structure is the *depolarization ratio*. [We must be careful in this discussion to distinguish between the terms *polarizability* and *polarization*. *Polarizability* is a molecular property involving the deformability of a bond, and *polarization* is a property of radiation describing the plane in which it vibrates.]

When Raman scattering is induced by a laser source (plane polarized), the resultant radiation itself is found to be polarized to varying degrees, according to the active mode of vibration. This is illustrated below where the source radiation is polarized in the yz plane, and the intensity of the scattered light polarized in the xz plane (parallel to the source) and the xy plane (perpendicular to the source) is measured. The depolarization ratio, p , is defined as

$$p = I_{\perp}/I_{\parallel}$$

[Fig. 18-5 p. 487]

[Block diagram of a Raman spectrometer: Fig. 18-6 p. 487]

**[Common laser sources for Raman instruments:
Table 18-1 p. 488]**