

Raman Spectroscopy: A beam of light passed through a transparent substance \rightarrow a small amount of radiative energy is scattered.

Scattering persists even if all dust particles or extraneous matter are excluded.

If monochromatic radiation or radiation of very narrow frequency band \rightarrow the scattered energy will consist almost \rightarrow the radiation of incident frequency, so called "Rayleigh Scattering". In addition, certain discrete frequencies above and below that of the incident radiation will be scattered

\hookrightarrow Raman Scattering

Quantum Theory of Raman Effect: Radiation of frequency ν \rightarrow consists of a stream of particles (photons) having energy $h\nu$.

Photons undergo collisions with molecules \rightarrow If collision is perfectly elastic \rightarrow they will be deflected unchanged \rightarrow radiation of frequency ν after the collision.

If collisions are inelastic

↳ energy exchange between photon and molecule. The molecule can gain or lose amounts of energy according to quantum laws.

ΔE → represent a change in the vibrational and/or rotational energy of the molecule.

If molecule gains energy ΔE , the photon will be scattered with energy $h\nu - \Delta E$ or frequency $\nu - \frac{\Delta E}{h}$.

If the molecule loses energy ΔE , the scattered frequency will be $\nu + \frac{\Delta E}{h}$.

Radiation scattered with a frequency lower than that of the incident beam → "Stokes radiation" while at higher frequency → "anti-Stokes"

'Stokes' radiation is generally more intense than 'anti-stokes'

However, the total radiation scattered at any point is extremely small, and sensitive apparatus is needed for its study.

Pure Rotational Raman Spectra

Linear Molecules

The rotational energy levels for a linear molecule are stated as

$$E_J = B J(J+1) - D J^2(J+1)^2 \text{ cm}^{-1} \quad (3)$$

The centrifugal constant D ($J = 0, 1, 2, \dots$) may not be measured with high precision in Raman spectroscopy, so

$$E_J = B J(J+1) \text{ cm}^{-1} \quad \text{--- (1)}$$

$(J = 0, 1, 2, \dots)$

represent the energy levels.

Transitions between these levels follow the formal selection rule:

$$\Delta J = 0, \text{ or } \pm 2 \text{ only} \quad \text{--- (2)}$$

which is in contrast with the corresponding selection rule for microwave spectroscopy $\Delta J = \pm 1$

In Raman with the rotational quantum number changes by two units rather than one \rightarrow

connected with the symmetry of polarizability ellipsoid. For a linear molecule, during end-on-end rotation the ellipsoid presents the same appearance to an observer twice in each complete rotation. Rotation about bond axis produces no change in polarizability.

following usual practice $\Delta J = J_{\text{upper state}} - J_{\text{lower state}}$

then we can ignore selection rule $\Delta J = -2$

Since, for a pure rotational change the upper state quantum ~~state~~ ^{number} must be greater than lower state quantum number

transition $\Delta J = 0$ is normal (4)

no change in molecular energy

↳ Rayleigh scattering

So combining $\Delta J = +2$ with the energy levels of eqⁿ(1), we have

$$\Delta \epsilon = \epsilon_{J' = J+2} - \epsilon_{J'' = J}$$

$$= B(4J+6) \text{ cm}^{-1} \quad (2)$$

Since $\Delta J = +2$, we may label these lines S branch lines and

$$\Delta \epsilon_s = B(4J+6) \text{ cm}^{-1} \quad (3)$$

$$(J=0, 1, 2, \dots)$$

$J \rightarrow$ rotational quantum number in the lower state.

If the molecule gains rotational energy from the photon during collision \rightarrow we have a series of S branch lines to the low wavenumber side of the existing line (Stoke's lines). If the molecule loses energy to the photon the S branch lines appear on the high wavenumber side (anti-Stoke's lines). The wave numbers of the corresponding spectral lines are

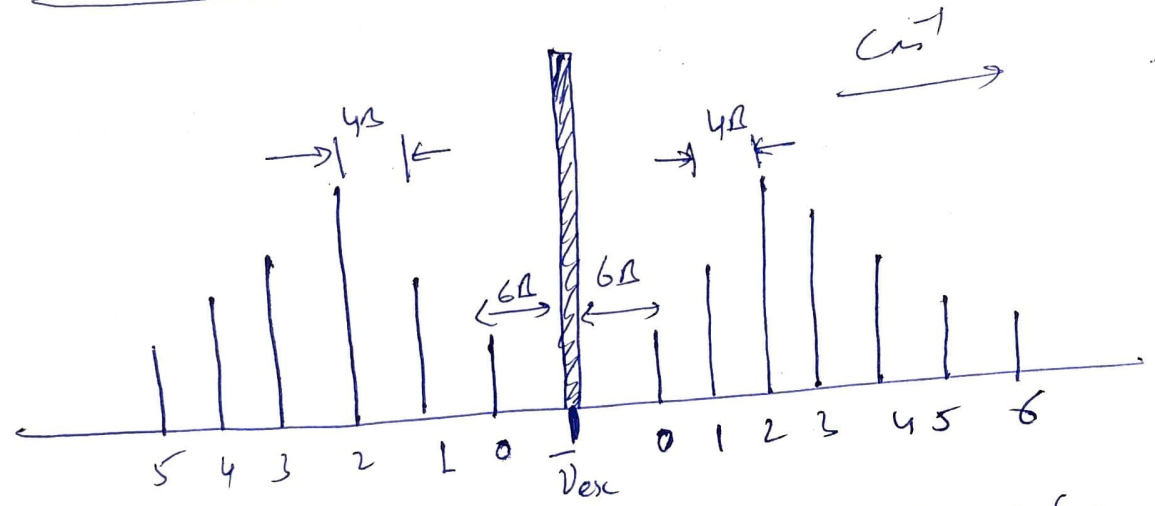
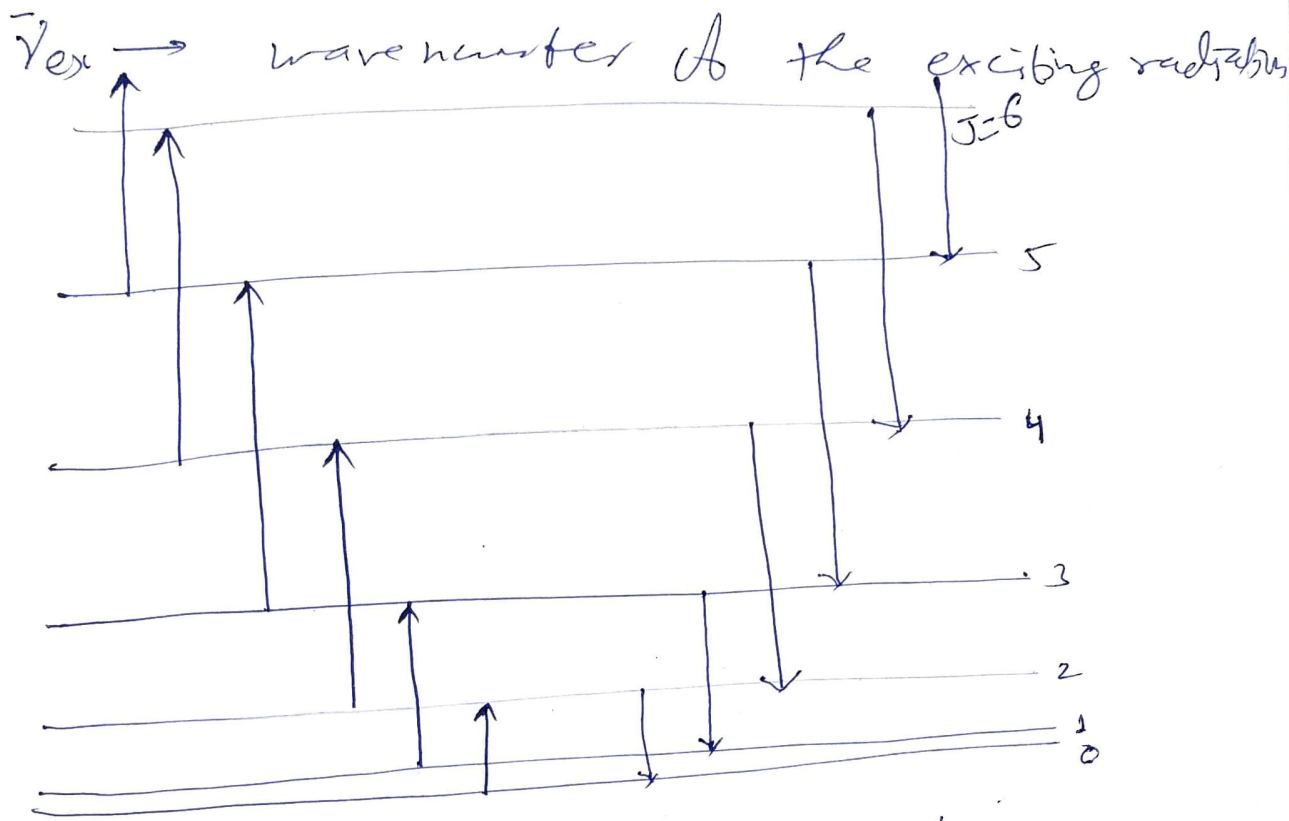
given by ~~equation~~ ~~equation~~ ~~equation~~

$$\bar{\nu}_s = \bar{\nu}_{ex} \pm \Delta \epsilon_s = \bar{\nu}_{ex} \pm B(4J+6) \text{ cm}^{-1} \quad (4)$$

(+) → 'anti-stokes' lines

(-) → stokes lines

(5)



Stokes' lines

Anti-stokes' lines

The rotational energy levels of a diatomic molecule and the rotational Raman spectrum arising from the transitions between them. Spectral lines are numbered according to their lower J values.