

What is a Photon?

A photon is a quantum of electromagnetic radiation.

It has:

zero mass

energy $h\nu$

linear momentum h/λ

spin ($j = 1, m_j = +1, -1$)

spin angular momentum

helicity ± 1

(left/right circularly polarized light)

When a photon is emitted or absorbed, angular momentum must be conserved, so the atom/molecule interacting with the light must change its angular momentum.

Symmetry and Selection Rules

The intensity of a stimulated electric dipole transition is proportional to the square of the transition dipole moment:

$$I \propto |\mu_{mn}|^2 = |\mu_{mn}^x|^2 + |\mu_{mn}^y|^2 + |\mu_{mn}^z|^2 \quad \text{where} \quad \mu_{mn}^x = \int \psi_m^* \mu^x \psi_n d\tau \quad \text{etc.}$$

Rotational transitions have no intensity if there is no dipole moment.

Vibrational transitions are allowed, even if the dipole moment is zero, provided that a dipole is created in the vibrational mode:

$$\begin{aligned} \mu_{mn}^x &= \mu_0^x \int \psi_m^* \psi_n d\tau + \int \psi_m^* \Delta\mu^x \psi_n d\tau \\ &= 0 + \frac{d\mu}{dx} \int \psi_m^* x \psi_n d\tau \end{aligned}$$

Specific Selection Rules are derived by considering

the conditions for which integrals such as $\int \psi_m^* x \psi_n d\tau$ are non-zero.

If only one of x , y or z gives a non-zero integral, the mode is active only for the corresponding plane polarized light.

In simple cases integrals can be shown to be zero by inspecting the even-odd symmetry of the wavefunctions. More generally, **Group Theory** is used to analyze symmetry.

Even and Odd Functions

Suppose $I = \int_{-\infty}^{+\infty} F(x) dx$

symmetrical limits

Then
$$I = \int_{-\infty}^0 F(x) dx + \int_0^{+\infty} F(x) dx$$

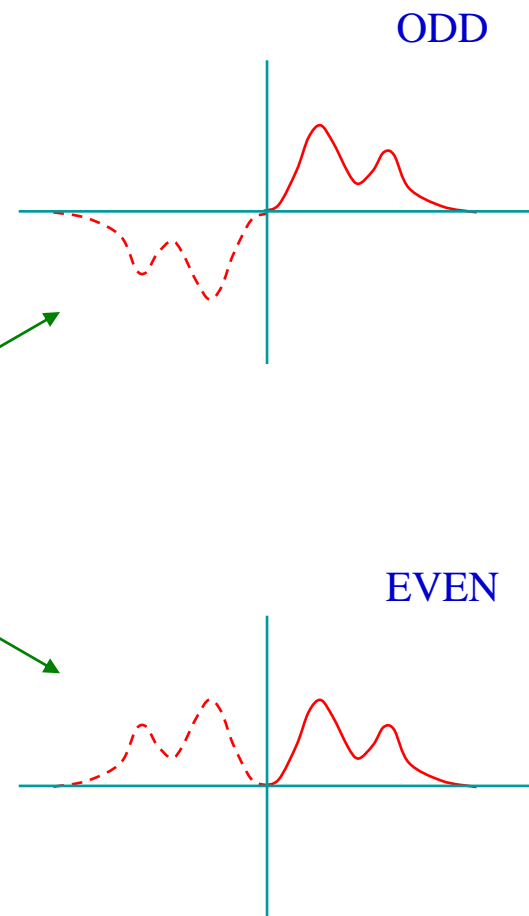
$$= \int_0^{+\infty} F(-x) dx + \int_0^{+\infty} F(x) dx$$

For $F(x)$ odd $F(-x) = -F(x) \Rightarrow I = 0$

For $F(x)$ even $F(-x) = F(x) \Rightarrow I \neq 0$

Since x is an odd function,

$$\mu_{mn}^x = \int \psi_m^* \mu^x \psi_n d\tau = 0 \text{ unless } \psi_m^* \psi_n \text{ is also odd.}$$



Group Theory and Selection Rules *Enrichment*

$\langle m | \hat{O} | n \rangle = 0$ unless the direct product of the irreducible representations spanned by $\langle m |$, \hat{O} and $| n \rangle$ contains the totally symmetric representation A_1 .

Translation: a spectroscopic transition is allowed between two states if the product of their wavefunctions has the same symmetry as the relevant operator.



same row of the molecule's character table

Infrared Spectroscopy

The electric dipole transition operator belongs to the same symmetry species as the functions x , y and z .

Raman Spectroscopy

The relevant functions are those of the polarizability tensor:

x^2 , y^2 , z^2 , xy , yz , zx (and combinations)

Exclusion Rule

Fundamental transitions in centrosymmetric molecules are either electric dipole (infrared) or Raman active, never both.

Bra(c)ket Notation

Enrichment

Dirac proposed the bra-ket notation:

$$\langle \text{bra} | \text{c} | \text{ket} \rangle$$

$$|n\rangle = \text{ket} \equiv \psi_n$$

$$\langle m| = \text{bra} \equiv \psi_m^*$$

$$\langle m|n\rangle \equiv \int \psi_m^* \psi_n d\tau$$

$$\langle m|\hat{\Omega}|n\rangle \equiv \int \psi_m^* \hat{\Omega} \psi_n d\tau$$

Kets may be interpreted as vectors in Hilbert space.

Operators behave like matrices.

$\Omega_{mn} \equiv \langle m|\hat{\Omega}|n\rangle$ can be regarded as a matrix element.

Heisenberg developed a formulation of quantum mechanics using the language of matrix algebra.

Raman Spectroscopy

Raman effect \equiv inelastic scattering of light by molecules.

- ❖ Light may deposit energy during the scattering interaction by exciting internal modes of the molecule.
- ❖ Light may gain energy if the molecule is already excited.

A monochromatic beam is used for irradiation. Detection is in a \perp direction. Since the molecular energy is quantized, the scattered light includes components shifted in frequency from the excitation source by discrete amounts.

The **Rayleigh line** is due to light scattered at ν_{exc}
Stokes lines are at lower frequencies: $\nu \ll \nu_{\text{exc}}$
anti-Stokes lines are at higher frequencies: $\nu \gg \nu_{\text{exc}}$

The intensity of the Stokes lines is usually greater than the anti-Stokes, which depend on population of excited states. Both are weaker than Rayleigh scattering.

The Raman effect depends on the **polarizability** of molecules.

The polarizability is a measure of how easily a dipole moment is induced when the molecule is placed in an electric field.

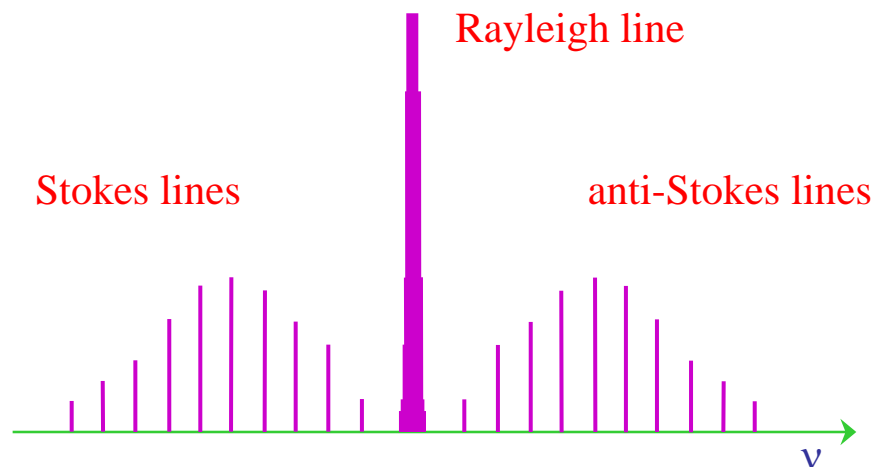
Rotational Raman Spectroscopy

For linear molecules, $E_J = BJ(J + 1)$

Selection rule: $\Delta J = \pm 2$ (and 0)

$$\Delta E = B(4J + 6)$$

$$\nu = \nu_{\text{exc}} \pm (B/h)(4J + 6)$$



Note: A linear molecule with a centre of symmetry has no dipole moment, and is therefore invisible to regular microwave spectroscopy. It *does* have a Raman spectrum, however, but the intensities depend on nuclear spin.

Vibrational Raman Spectroscopy

Pure vibration

$$\Delta v = 0, \pm 1, \pm 2, \dots$$

$$\nu = \nu_{\text{exc}} - \omega_0 / 2\pi, \quad \nu_{\text{exc}} + \omega_0 / 2\pi$$

anti-Stokes often too weak to observe

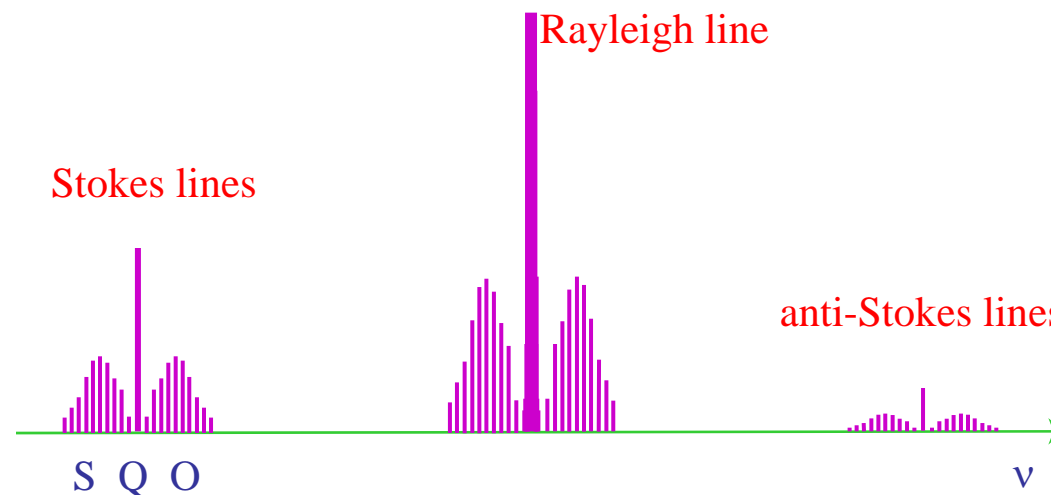
Rotational fine structure of diatomics

$$\Delta v = +1 \quad \Delta J = 0, \pm 2$$

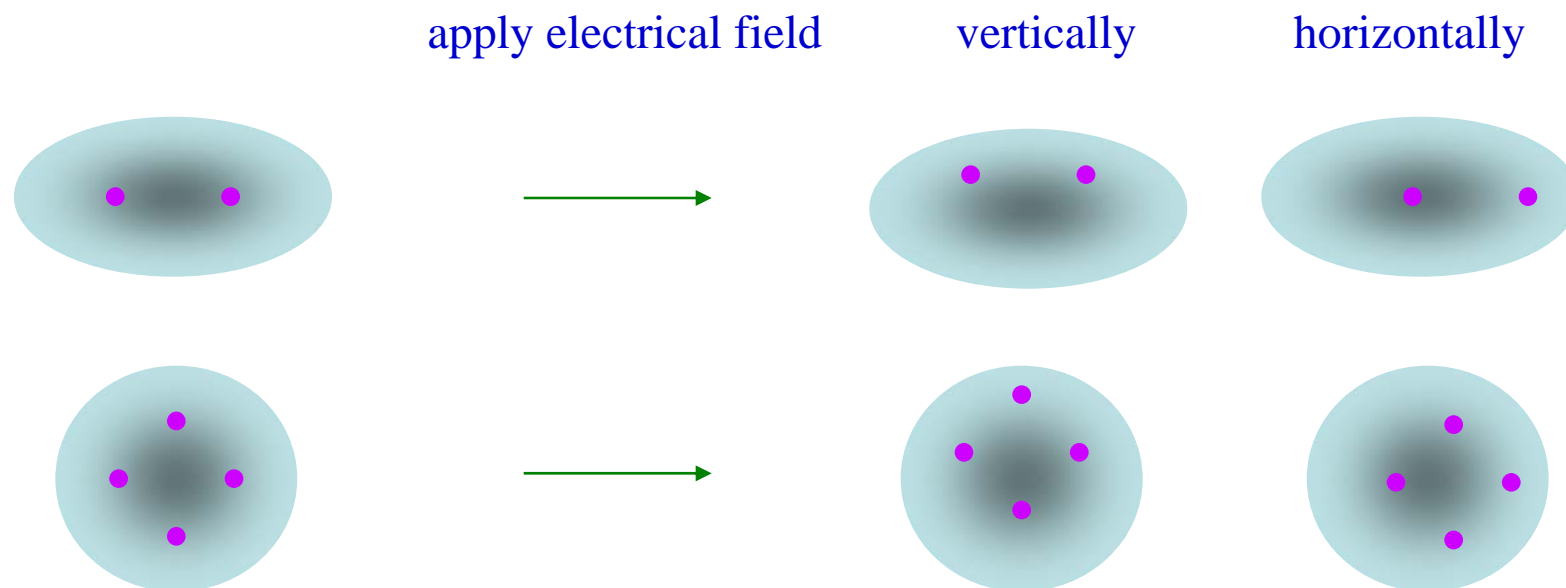
$$\Delta J = 0: \quad \Delta \nu_Q = \nu_{\text{vib}}$$

$$\Delta J = +2: \quad \Delta \nu_S = \nu_{\text{vib}} + B(4J + 6) \quad J = 0, 1, 2, \dots$$

$$\Delta J = -2: \quad \Delta \nu_O = \nu_{\text{vib}} - B(4J + 6) \quad J = 0, 1, 2, \dots$$



Polarizability and Raman Spectroscopy



Rotational Spectrum: Raman active if the polarizability of the molecule is anisotropic. Spherically symmetric molecules are Raman inactive.

Vibrational Spectrum : Raman active if the polarizability changes during the vibration. All homonuclear and heteronuclear molecules are Raman active.