Raman Spectroscopy
RAMAN'S SPECTROGRAPH

THE FIRST RAMAN SPECTRUM WAS

OBTAINED WITH THIS SPECTROGRAPH

IN 1928.
What happens when light falls on a material?

- Transmission
- Reflection
- Absorption
- Luminescence
- Elastic Scattering
- Inelastic Scattering
Raman scattering visible to the unaided eye, from a 488 nm laser beam passing through liquid cyclohexane. Left vial exhibits mostly Rayleigh scattering which obscures much weaker Raman scattering. Right vial is viewed through a 488 nm band rejection filter, which permits observation of longer wavelength Raman scattering.
Raman, Fluorescence and IR Absorption and emission
6.1 Scattering

In addition to being absorbed and emitted by atoms and molecules, photons may also be scattered (approx. 1 in $10^7$ in a transparent medium). This is not due to defects or dust but a molecular effect which provides another way to study energy levels.

This scattering may be:

- **Elastic** and leave the molecule in the same state (Rayleigh Scattering) or
- **Inelastic** and leave the molecule in a different quantum state (Raman Scattering)

6.2 Rayleigh Scattering

Lord Rayleigh calculated that a dipole scatterer $<< \lambda$ scatters with an intensity:

$$I = I_0 \frac{8\pi N \alpha^2}{\lambda^4 R^2} \left(1 + \cos^2 \theta \right)$$

**n.b.,** $I \propto \frac{1}{\lambda^4}$

5 times more effective for 400nm than 600nm

**Hence the sky is blue!**
Raman Scattering

Scattering is not an oscillating dipole phenomenon!

The presence of an electric field $E$ induces a polarization in an atom/ molecule given by $P = \alpha E$.

If the field is oscillating (e.g., photon) $P = \alpha E_0 \cos(2\pi\nu_0 t)$.

In atoms the polarizability is isotropic, and the atom acts like an antenna and re-radiates at the incident frequency – Rayleigh Scattering only.

In molecules the polarizability may be anisotropic, and depends on the rotational and vibrational coordinates. This can also give rise to Raman Scattering.

Gross Selection Rule:

**To be Raman active a molecule must have anisotropic polarizability**

[Less restrictive than the need for a dipole moment, symmetric molecules can be Raman active]
As discussed, when an atom or molecule is brought into an electric field \( E \), an electric dipole moment \( \mu \) is induced in the system. The magnitude of this induced dipole moment is proportional to the electric field, \( \mu = \alpha E \) where \( \alpha \) is known as the polarizability.

\[ \vec{\rho} = \alpha \vec{E} \]

\( \alpha \) - “polarizability” of a material

In an induced dipole, is the distance between the charges fixed? The distance is proportional to the strength of the applied field.
Except for the case of spherical symmetry, the magnitude of the induced dipole moment depends on the direction of the electric field. For example, in case of a diatomic molecule, the induce dipole moment will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.
Change in Polarizability

An electric field applied to a molecule results in its distortion, and the distorted molecule acquires a contribution to its dipole moment (even if it is nonpolar initially). The polarizability may be different when the field is applied (a) parallel or (b) perpendicular to the molecular axis (or, in general, in different directions relative to the molecule); if that is so, then the molecule has an anisotropic polarizability.
Anisotropic Nature of Polarizability

- The polarization of a molecule need not be identical in all directions.
Polarisability Change during Rotation

In case of a diatomic and linear molecule, the *induce dipole moment* will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.

Polarisability Ellipsoid of Hydrogen in two different orientations.
Classical theory Raman scattering: Rotational Raman

\[ P_{in} = \alpha E \]
\[ \alpha = \alpha_0 + \Delta \alpha \cos (2\omega t) \]
\[ E = E_0 \cos (2\pi v_0 t) \]

\[ P_{in} = (\alpha_0 + \Delta \alpha \cos(2\omega t)) \times E_0 \cos (2\pi v_0 t) \]

\[ = \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} E \Delta \alpha \{ \cos (2\pi v_0 - 2\omega) t + \cos (2\pi v_0 + 2\omega) t \} \]

Rayleigh  Stokes  Anti-Stokes

\[ \Delta \alpha \neq 0 \]

Polarizability should be changed during rotation
Classical theory Raman scattering: Vibrational Raman

- An oscillating electric field (incident photon) causes the molecule to have an \textit{induced} dipole:

\[
P = \alpha E \quad \quad E = E_0 \cos(2\pi \nu_0 t)
\]

\[
P = \alpha E_0 \cos(2\pi \nu_0 t)
\]

\[
\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial r} \right)_{r_0} (r - r_0) + \ldots
\]

- \[
P = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \left( \frac{\partial \alpha}{\partial q_i} \right)_0 E_0 \cos(2\pi \nu_0 t) q_i^0 \cos(2\pi \nu_i t)
\]

\[
= \alpha_0 E_0 \cos(2\pi \nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q_i} \right)_0 E_0 q_i^0 \left[ \cos \left( 2\pi (\nu_0 - \nu_i) t \right) + \cos 2\pi (\nu_0 + \nu_i) t \right]
\]

\[
\left( \frac{\partial \alpha}{\partial r} \right)_{r_0} \neq 0
\]

\text{Rayleigh} \quad \text{Stokes} \quad \text{Anti-Stokes}
In order for a vibrational mode to be Raman active, the polarizability must change during the vibration, and for a rotation to be Raman active, the polarizability must change as the molecule rotates in an electric field.

\[ I_{\text{scatt}} \propto \left| \mathbf{P} \cdot \mathbf{E}_0 \right|^2 = \left| \left( \frac{\partial \alpha}{\partial q_i} \right)_0 \right|^2 I_0^2 \]

Thus, the polarizability must change linearly with vibrational motion for vibrational Raman scattering to occur. The greater the change, the more intense the Raman scattering. If \( \alpha \) is unchanged or at a minimum/maximum, there is no Raman scattering.
Quantum Picture of Raman scattering : Vibrational Raman

$$\mu_i = \left\langle v_f \left| \alpha(0) + \left( \frac{d\alpha}{dx} \right)_0 x + \cdots \right| v_i \right\rangle \mathcal{E}$$

$$= \langle v_f | v_i \rangle \alpha(0) \mathcal{E} + \left( \frac{d\alpha}{dx} \right)_0 \langle v_f | x | v_i \rangle \mathcal{E} + \cdots$$

$$\langle v_f | v_i \rangle = 0 \quad f \neq i$$

Raman active if \( (d\alpha/dx)_0 \neq 0 \) and \( \langle v_f | x | v_i \rangle \neq 0 \). Therefore, the polarizability of the molecule must change during the vibration; this is the gross selection rule of Raman spectroscopy. Also, we already know that \( \langle v_f | x | v_i \rangle \neq 0 \) if \( v_f - v_i = \pm 1 \); this is the specific selection rule of Raman spectroscopy.
Molecular Picture of Scattering Events

Real State

Virtual States

Ground Electronic State

Raman anti-Stokes ($\nu_A = \nu_0 + \Delta\nu$)

Rayleigh Scattering ($\nu_0 = \nu_R$)

Raman Stokes ($\nu_S = \nu_0 - \Delta\nu$)

$\nu_0 - \nu_t$  $\nu_0 + \nu_t$  $\nu \rightarrow$

$\nu = 1$  $\nu = 0$
Polarizability Ellipsoids of CO₂\textsuperscript{2}\textsubscript{c} rotational Modes and Raman Act

\( \alpha_0 \frac{\partial \alpha}{\partial Q} \neq 0 \)

\( \alpha_0 \frac{\partial \alpha}{\partial Q} = 0 \)

\( \alpha_0 \frac{\partial \alpha}{\partial Q} = 0 \)

\( v_1 \) Symmetric Stretch

\( v_2 \) Bending Mode

Assymetric stretching mode
Rotational Raman

Linear molecules \( \Delta J = 0, \pm 2 \)

For Linear Molecules

\[
\Delta \tilde{\nu}_R = \tilde{B} J'(J' + 1) - \tilde{B} J''(J'' + 1)
\]

\[
\Delta \tilde{\nu}_R = \nu_0 \pm \tilde{B} (4J + 6)
\]

Stokes (-) anti-stokes (+)

- a gap of 6\( B \) between \( \nu_0 \) and 1\textsuperscript{st} lines of each branch
- lines in each branch of equal spacing = 4\( B \)
Rotational Raman spectra of Diatomic Molecule

Rotational Raman Spectrum of $^{15}\text{N}_2$
Vibrational Raman Spectra

$\Delta \vartheta = \pm 1$

Real State

Virtual States

Ground Electronic State

- Raman anti-Stokes ($v_A = v_0 + \Delta v$)
- Rayleigh Scattering ($v_0 = v_R$)
- Raman Stokes ($v_S = v_0 - \Delta v$)
\( \vartheta = 0 \) to \( \vartheta = 1 \) transition

The 1–0 Stokes vibrational Raman spectrum of CO showing the \( O^- \), \( Q^- \), and \( S^- \) branch rotational structure.
Raman Spectra of CHCl$_3$
Polarizability Ellipsoids of H$_2$O

Vibrational Modes and Raman Activity

**Size**

\[ \frac{\partial \alpha}{\partial Q} \neq 0 \]

*\( \alpha_0 \)*

\( v_1 \), symmetric stretching mode

**Shape**

\[ \frac{\partial \alpha}{\partial Q} \neq 0 \]

\( \alpha_0 \)

\( v_2 \), bending mode

**Orientation**

\[ \frac{\partial \alpha}{\partial Q} \neq 0 \]

\( \alpha_0 \)

\( v_3 \), asymmetric stretching mode
Mutual Exclusion Principle

For molecules with a center of symmetry, no IR active transitions are Raman active and vice versa.
The *Vibrational Raman Spectra of Homonuclear diatomic molecules* are of Special interest because they yield force constants and rotational constants that are not available from microwave and Infrared Absorption spectroscopy.
Advantages of Raman over IR

• Water can be used as solvent.
• Very suitable for biological samples in native state (because water can be used as solvent).
• Although Raman spectra result from molecular vibrations at IR frequencies, spectrum is obtained using visible light or NIR radiation.
  =>Glass and quartz lenses, cells, and optical fibers can be used. Standard detectors can be used.
• Few intense overtones and combination bands => few spectral overlaps.
• Totally symmetric vibrations are observable.
• Raman intensities $\alpha$ to concentration and laser power.
Advantages of IR over Raman

• Simpler and cheaper instrumentation.

• Less instrument dependent than Raman spectra because IR spectra are based on measurement of intensity ratio.

• Lower detection limit than (normal) Raman.

• Background fluorescence can overwhelm Raman.

• More suitable for vibrations of bonds with very low polarizability (e.g. C–F).
Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

Additional Material Related to Polarisability Ellipsoid

Polarizability Tensor is Symmetric

\[ \alpha_{xy} = \alpha_{yx}, \ \alpha_{yz} = \alpha_{zy}, \ \text{and} \ \alpha_{xz} = \alpha_{zx}, \] which reduces the matrix components from 9 to 6.

\[ \begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \]

Symmetric tensors can be transformed to a new coordinate system of \( x', y' \) and \( z' \) such that only the diagonal elements \( \alpha_{xx'}, \alpha_{yy'}, \) and \( \alpha_{zz'} \) are nonzero. It is in this new coordinate system that we graphically represent the polarizability ellipsoid.
Conventional Mathematical Description of the Raman Polarizability Ellipsoid

\[
\frac{x'^2}{\sqrt{\alpha_{x'x'}}^2} + \frac{y'^2}{\sqrt{\alpha_{y'y'}}^2} + \frac{z'^2}{\sqrt{\alpha_{z'z'}}^2} = 1
\]

constitute the lengths of the polarizability ellipsoid's semi-axes
END