Raman Spectroscopy

Part I: Introduction of Raman spectroscopy

B.Sc. (H) Chemistry

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Introduction

- The Raman effect was named after one of its discoverers, the Indian scientist C. V. Raman, who observed the effect in organic liquids in 1928 together with K. S. Krishnan, and independently by Grigory Landsberg and Leonid Mandelstam in inorganic crystals.

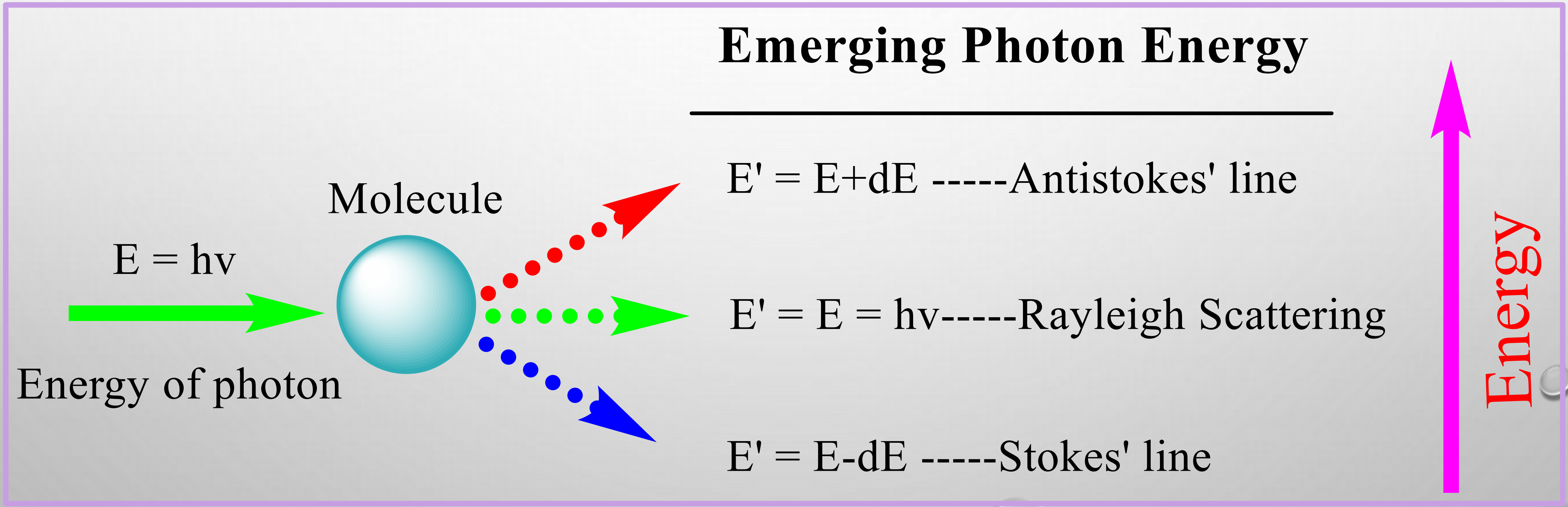
- Raman won the **Nobel Prize** in Physics in **1930** for this discovery.

- The first observation of Raman spectra in gases was in 1929 by Franco Rasetti.

Sir Chandrasekhara Venkata Raman

Quantum Theory of Raman Effect

- Raman Scattering could be understood in terms of the quantum theory of radiation.
- Photons can be imagined to undergo collisions with molecules.



Molecule

$E = h\nu$

Energy of photon

Emerging Photon Energy

$E' = E + dE$ -----Antistokes' line

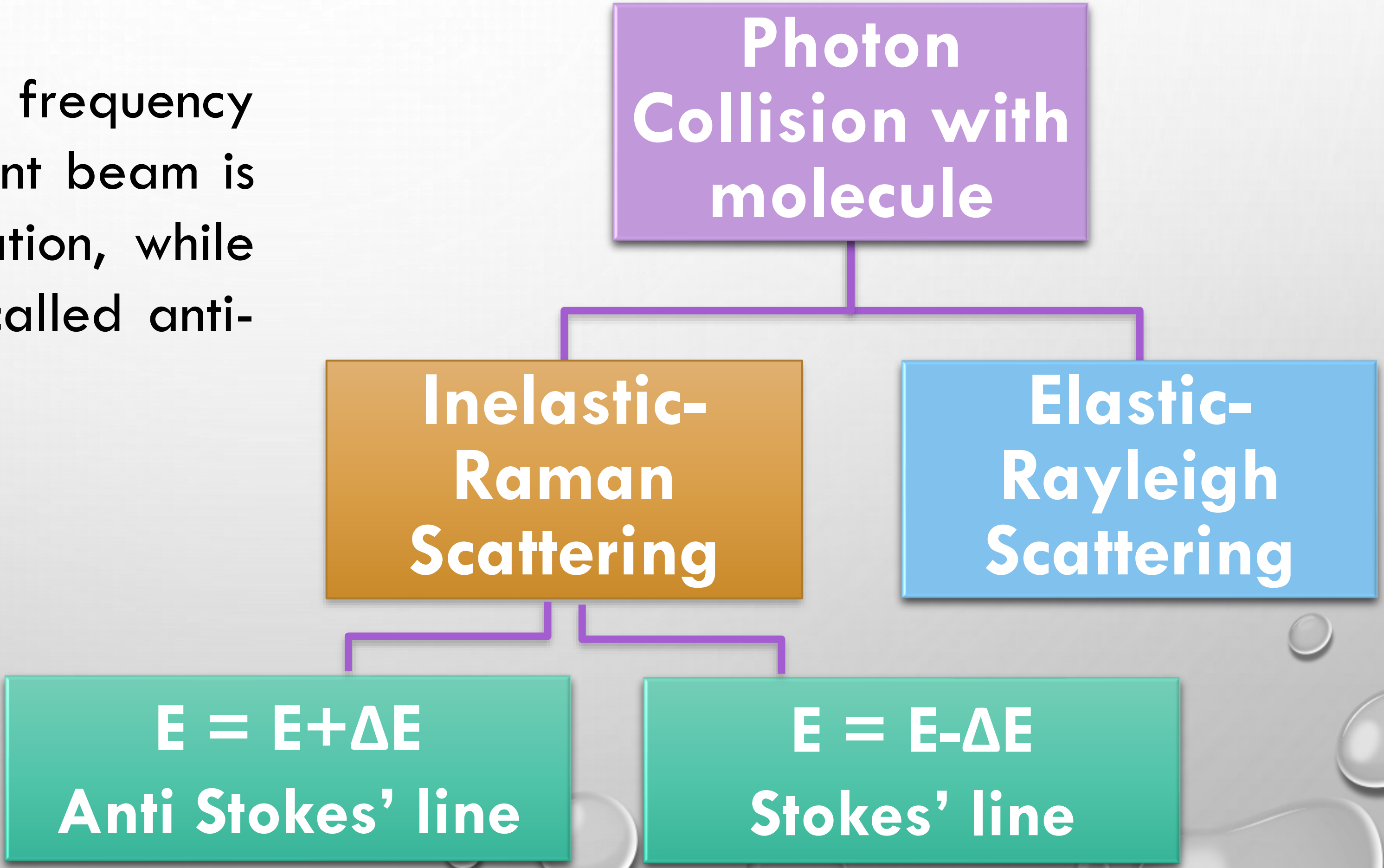
$E' = E = h\nu$-----Rayleigh Scattering

$E' = E - dE$ -----Stokes' line

Energy

Quantum Theory of Raman Effect

- Radiation scattered with a frequency lower than that of the incident beam is referred to as Stokes' radiation, while that at higher frequency is called anti-Stokes' radiation.



Photon Collision with molecule

Inelastic- Raman Scattering

Elastic- Rayleigh Scattering

$E = E+\Delta E$

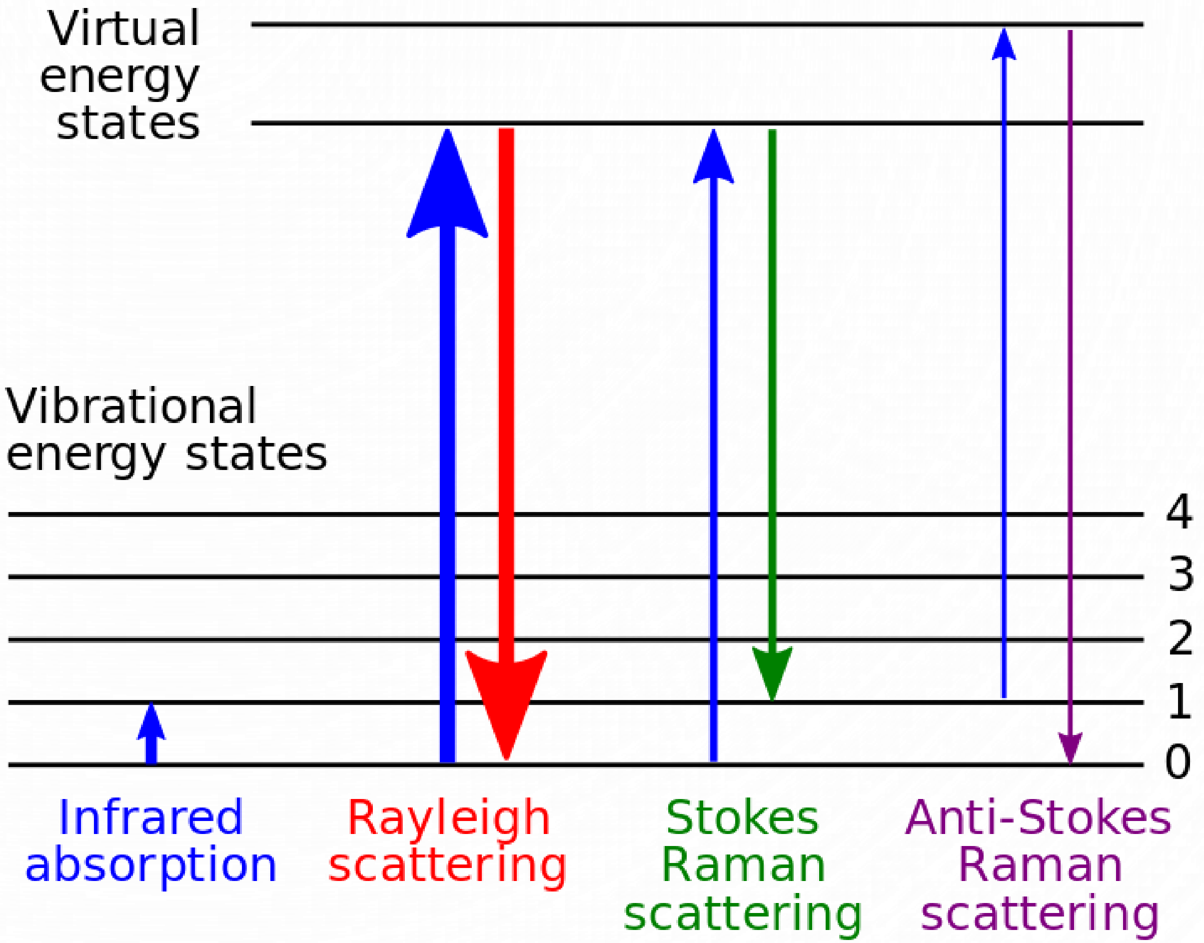
Anti Stokes' line

$E = E-\Delta E$

Stokes' line

Quantum Theory of Raman Effect

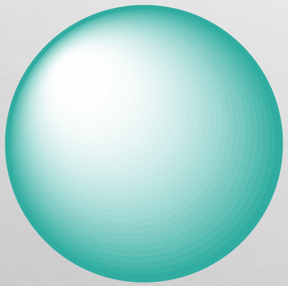
- The molecule can gain or lose amounts of energy only in accordance with the quantal laws; i.e. its energy change, *ΔE* joules, must be the difference in energy between two of its allowed states.



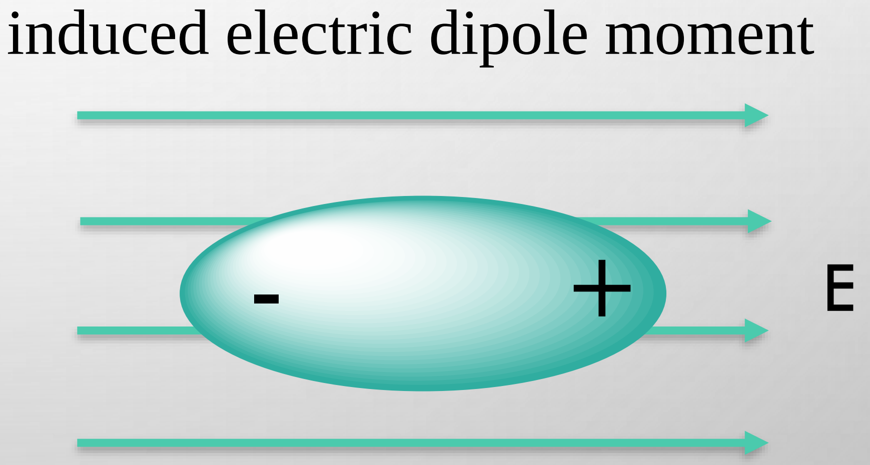
Picture credit: https://commons.wikimedia.org/w/index.php?curid=7845122

Classical Theory of the Raman Effect: Molecular Polarizability

- The basic concept of this spectroscopy depends on the polarizability of a molecule and the applied Electric field.
- When a molecule is put into a static electric field it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field, the electrons to the positive pole.



Molecule in zero electric field



Molecule in static electric field

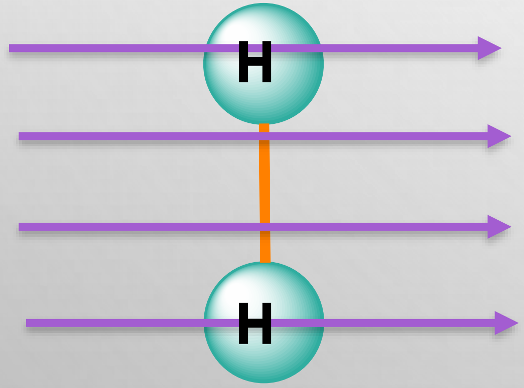
Molecular Polarizability

The size of the induced dipole ***μ,*** depends both on the magnitude of the applied field, **E**, and on the ease with which the molecule can be distorted.

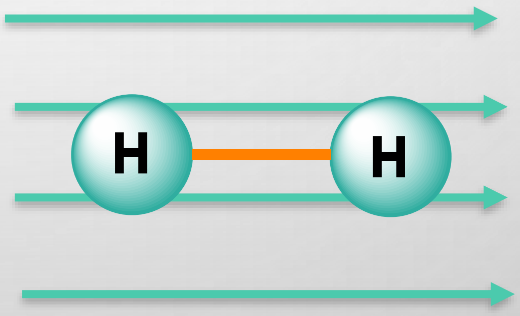
$$\boxed{\mu = \alpha E}$$

Polarizability is anisotropic

where α is the polarizability of the molecule.



Least polarizability

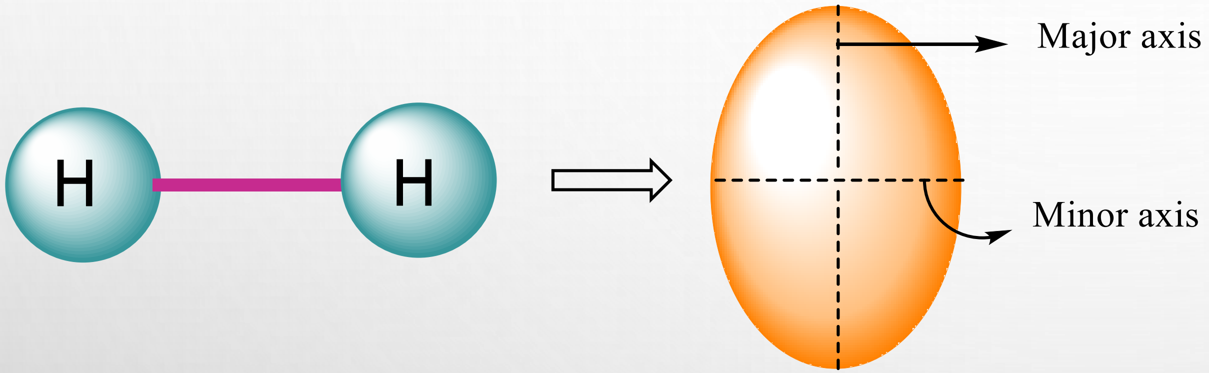


Greatest polarizability

- Electrons forming the bond are less easily displaced by the field across the bond axis
- Electrons forming the bond are more easily displaced by the field along the bond axis

Polarizability Ellipsoid

- The polarizability of a molecule in various directions is conventionally represented by drawing a polarizability ellipsoid.



Where the polarizability is least, the axis of the ellipsoid is greatest.

Where the polarizability is greatest, the axis of the ellipsoid is least.

In general a polarizability ellipsoid is defined as a three-dimensional surface whose distance from the electrical centre of the molecule (in H_2 this is also the centre of gravity) is proportional to $^1/_{\sqrt{\alpha}}$, where α is the polarizability along the line joining a point i on the ellipsoid with the electrical centre.

$$\boxed{\text{Ellipsoid axis} \propto {}^1/_{\sqrt{\alpha}}}$$

Polarizability Ellipsoid

Points to remember

- The student must not make the mistake of confusing a polarizability ellipsoid with electron orbitals or electron clouds.

- In a sense the polarizability ellipsoid is the inverse of an electron cloud-where the electron cloud is largest the electrons are further from the nucleus and so are most easily polarized.

- This, as we have seen, is represented by a small axis for the polarizability ellipsoid.

Molecular Polarizability

When a molecules is subjected to a beam of radiation of frequency ‘ν’ the electric field experienced by each molecule varies according to the equation

$$E = E_0 \, sin \, 2\pi \nu t$$

and thus the induced dipole also undergoes oscillations of frequency ν :

$$\mu = \alpha E$$

or, $\boldsymbol{\mu = \alpha E_0 \, sin \, 2\pi \nu t}$

This is the classical explanation of **Rayleigh scattering**. Here the oscillating dipole emits radiation of its own oscillation frequency ν.

Molecular Polarizability

If, in addition, the molecule undergoes some internal motion, such as vibration or rotation, which changes the polarizability periodically, then the oscillating dipole will have superimposed upon it the vibrational or rotational oscillation.

$$\alpha = \alpha_0 + \beta\ sin2\pi\nu_{vib}t$$

$$\mu = \alpha E$$

$$\mu = (\alpha_0 + \beta\ sin2\pi\nu_{vib}t)E_0\ sin\ 2\pi\nu t$$

We know the trigonometric expression,

sin A sin B = $\frac{1}{2}\{\cos(A-B) - \cos(A+B)$

$$\mu = (\alpha_0 + \beta\ sin2\pi\nu_{vib}t)E_0\ sin\ 2\pi\nu t$$

$$\mu = \alpha_0 E_0\ sin\ 2\pi\nu t + \beta\ sin2\pi\nu_{vib}t \cdot E_0\ sin\ 2\pi\nu t$$

$$\mu = \underbrace{\alpha_0 E_0\ sin\ 2\pi\nu t}_{\text{Rayleigh Scattering}} + \frac{1}{2}\beta E_0\{\underbrace{\cos 2\pi(\nu - \nu_{vib})}_{\text{Anti stokes line}} - \underbrace{\cos 2\pi(\nu + \nu_{vib})\ t}_{\text{stokes line}}\}$$

Molecular Polarizability

In order to be Raman active a molecular rotation or vibration must cause some change in a component of the molecular polarizability. **A** change in polarizability is, of course, reflected by a change in either the ***magnitude*** or the ***direction*** of the polarizability ellipsoid.

Reference

Fundamentals of Molecular Spectroscopy, 4th Ed.

By Colin N. Banwell and Elaine M. McCash

Next: Rotational & Vibrational Raman Spectra

THANK YOU