Raman Spectroscopy

Raman spectroscopy deals with the scattering of light & not with its absorption. When a photon of freq. ν falls on a molecule, it undergo collision with the molecule. The collision could be elastic or inelastic. If the collision is perfectly elastic, then the scattered photon will have same energy as the incident photon. A detector placed to collect energy at right angles to an incident beam will thus recieve photons of energy $h\nu$, ie radiation of freq. ν This type of scattering is called Rayleigh scattering. However, the energy may be exchanged b/w photons & the molecules during the collision. Such collisions are called inelastic. ie, the scattered photon will have either a higher or a lower energy than the incident photon. The molecule can gain or lose amounts of energy only in accordance with the quantum-mechanical laws. ie, the change in energy ΔE must be the difference in energy b/w two of its allowed state. If the molecule gains energy ΔE, the photon will be scattered with energy $h\nu - \Delta E$ & the resulting radiation will have a freq. $\nu - \frac{\Delta E}{h}$. On the other hand, if the molecule loses energy ΔE, the scattered freq. will be $\nu + \Delta E/h$ This type of scattering is called Raman scattering or Raman effect.

~~Rayleigh scattering~~

If ν is the freq. of incident photon & ν' is the freq of scattered photon, then consider the following cases,

case 1: $\nu = \nu'$ → Rayleigh scattering

case 2: $\nu < \nu'$

case 3: $\nu > \nu'$ → Raman scattering.

Thus, in the Rayleigh scattering, the scattered photon has the same freq. (or energy) as the incident photon while in the Raman scattering, when the photon collides with the molecule, the energy is either transfered to or taken away from the molecule.

Rayleigh scattering is seen when the molecule excited to a higher vibrational or rotational level returns to the same level, so that $\Delta E = E' - E = 0$

(Where E' → energy of scattered ~~light~~ photon

E → energy of incident photon.

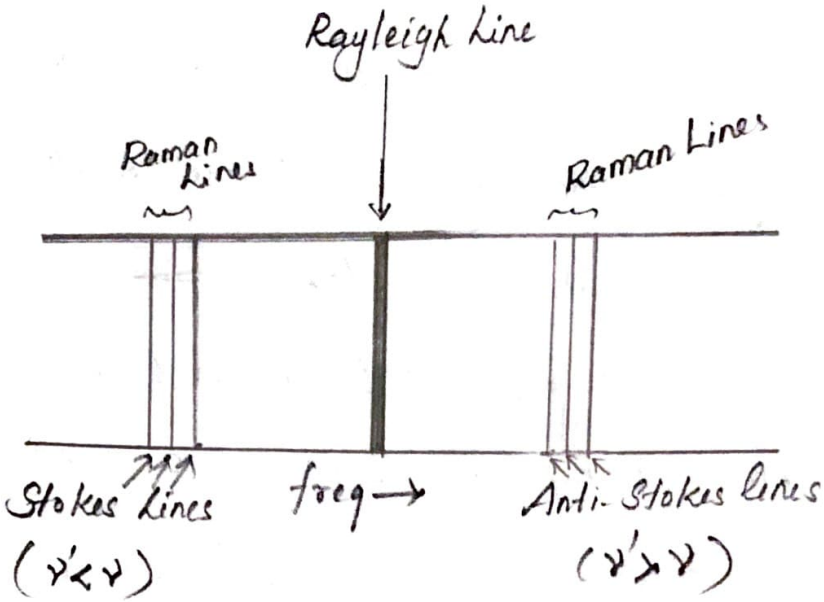
Raman scattering is seen when the molecule excited to a higher vibrational or rotational level returns to a diff. level ~~so that $\Delta E = (E' - E')$~~

so that $\Delta E = E' - E$ will be ~~sig~~ either positive or negative

When a photon collides with a molecule & gives up some of its energy to the molecule, the scattered radiation is less energetic & is known as Stokes ~~lines~~ radiation. Here the excited molecule returns to a level higher than the original level, thereby giving out less energy than what has been gained during excitation. ie, $\nu' < \nu$ so that spectral line results at a lower freq. than ν and this is called Stokes line. Since the molecule gains energy $E' > E$ so that ΔE is positive.

If, on the other hand when the irradiating photon takes up energy from an excited molecule in collision, the scattered rad^n is more energetic & is known as anti-Stokes radiation. Here, the excited molecule returns to a level lower than the original level, thereby giving out more energy than what has been gained during excitation. ie, $\nu' > \nu$, so that spectral line results at a higher freq. than ν # and this is called anti-Stokes line. Since the molecule loses energy, $E' < E$ so that ΔE is negative.

Thus the Raman spectrum of a molecule consists of Stokes lines & ant-stokes lines, situated symmetrically about the Rayleigh line.



Schematic Representation of Raman Spectrum.

The Rayleigh line is far more intense than the Stokes-lines which in turn have greater intensity than the anti-Stokes lines. This is because the anti-stokes lines corresponds to the return of a molecule from the unstable excited vibrl state to the ground state and initially there are very few molecules in the excited vibrl level

We've $E' - E = h|\nu - \nu'| = h\Delta\bar{\nu} = hc\Delta\nu$

ie, The diffce in frequencies of the Rayleigh and Raman line ($\Delta\nu = |\nu - \nu'|$) is called Raman Shift (or Raman frequency)

∴ $\Delta\nu$ is +ve for Stokes lines

$\Delta\nu$ is −ve for anti-stokes lines

Raman Shift ($\Delta\nu$) is a characteristic of that subce and is independant of the incident radiation.

Quantum mechanical Selection Rule

The selection rule for the vibrational Raman spectrum of a diatomic molecule is $\Delta v = \pm 1$.

Where Δv is the net change in the vibl Q. no. during the Raman scattering. ie, the vibl Q. No. changes by one unit during the process. For anharmonic molecules, due to the appearance of overtones, the selection rule modifies to

$$\Delta v = \pm 1, \pm 2, \pm 3 \ldots$$

Polarizability concept of the Raman effect (Classical Concept)

When a molecule is subjected to a static electric field, ~~it suffers some~~ the centre of positive charges (nuclei) is slightly displaced towards the -ve pole of the field (due to attraction) and the centre of -ve charges ($\bar{e}$ cloud) is slightly displaced towards the +ve pole. This separation of charge centres, called polarization, causes an induced dipole moment (μ_{ind}) to be set up in the molecule which is directly proportional to the strength of the electric field (E)

ie, $\mu_{ind} = \alpha E$.

α is the proportionality const. called the polarizability of the molecule.

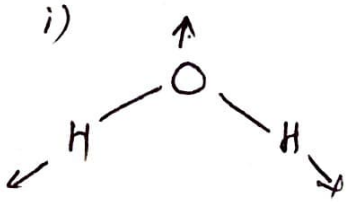
Therefore "inorder for a vibration or rotation to be Raman active, it must cause a change in the molecular polarizability."

Thus homonuclear diatomic molecules such as H_2, O_2 N_2, Cl_2 ~~etc~~ which do not show IR Spectra, do show Raman spectra since their vibration is accompanied by a change in the polarizability of the molecule.

Vibrational Modes and Raman activity

Let's consider the three vibrational modes of H_2O. In all the three vibrations, a change in the molecular polarizability occurs and therefore all are Raman active. Since each is accompanied by a change in the dipole moment of the molecule, the three vibrations are IR-active as well.

i)



Symmetric stretching

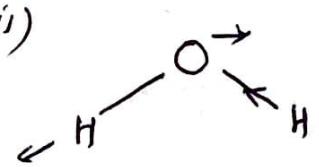
$\nu_s = 3652 cm^{-1}$

Raman active

&

IR active.

ii)



Assymmetric stretching

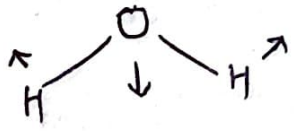
$\nu_{as} = 3756 cm^{-1}$

Raman active

&

IR active

iii)



Symmetric bending

$\nu_b = 1596 cm^{-1}$

Raman active

&

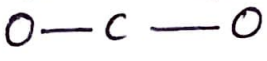
IR-active.

Rule of Mutual Exclusion

The rule of Mutual exclusion states that 'for a molecule with centre of symmetry, no vibrations can be both IR-active & Raman-active ie, vibrations which are IR-active will be Raman inactive and vice versa'

If there is no centre of symmetry, then some vibrations may be both Raman-active & IR-active

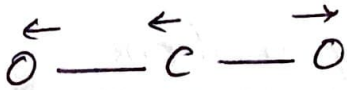
Consider the four vibrational modes of CO_2 which is a centrosymmetric molecule,

i) 

Symmetric Stretching

$\nu = 1347\ cm^{-1}$

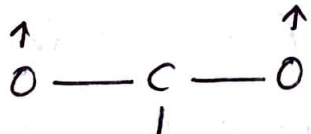
(Raman-active & IR inactive)

ii) 

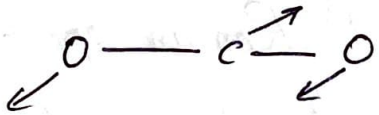
Assymmetric Stretching

$\nu = 2350 cm^{-1}$

(Raman-Inactive & IR-active)

iii) 

Bending (in plane)

iv) 

Bending (out of plane)

Degenerate pair ($\nu = 667 cm^{-1}$)

Raman inactive & IR-active)

A change in the molecular polarizability occurs only in the symmetric stretching vibration of CO_2, not in any of the other three.

Hence the only Raman-active vibl mode of CO_2 is symmetric stretch, the assymmetric stretching and the two degenerate bending vibrations are Raman-inactive. On the other hand, a change in dipole moment does not occur in symmetric stretch but does occur in the other three. Hence the only IR-inactive mode is symmetric stretch, the other three are IR-active. Thus the Raman spectra of CO_2 shows a single fundamental band. On the other hand, its IR spectrum shows two fundamentals - those of doubly generate bending modes.

Applications

Raman spectroscopy functions complementary to IR-spectroscopy and is helpful in almost all the applications of IR-spectroscopy.

1) Raman spectroscopy is particularly helpful in structural elucidation in organic & inorganic chemistry. Since functional grps show characteristic freq. of vibrn, Raman spectroscopy can be applied to know the presence or absence of specific grps in a molecule.

2) It can be used to study isomers, presence of H-bonding in compds, presence of impurities in dyes etc