Quadrant II – Transcript and Related Materials

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Unit 7	: Raman Spectra
Module Name	: Pure rotational Raman spectra
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Notes

Classification of molecules based on Rotational behaviour

The rotational energy levels and hence the rotational spectrum of the molecule depends upon its symmetry. Based on the symmetries of their structure ,the molecules are divided into four different classes

- 1. Linear molecules
- 2. Symmetric tops
- 3. Spherical tops
- 4. Asymmetric tops
- 5. Linear molecules

The internuclear axis is the only axis of symmetry. Let the axis of symmetry be along x-axis

The moment of inertia I_{χ} about this axis is negligible and is taken equal to zero

For a linear molecule

$$I_x = 0$$
$$I_y = I_z = I$$

The separation of lines in rotational spectrum are related directly with the moment of inertia I.

Knowing atomic masses bond length can be calculated.

Example: Oxygen O_2 CO CO_2 etc.

Symmetric top molecule

They are like linear molecules. They have one axis of symmetry but $I_{\rm x}$ is not zero ,whereas $I_{\rm y}=I_{\rm z}=I$

 $I_x \neq I$

If $I > I_x$, the symmetric top is prolate

 $I < I_x$, the symmetric top is oblate

Example oblate benzene, ammonia

prolate : chloromethane. Propyne

Spherical top molecules

In this case $I_x = I_y = I_z$

They have same polarizability in all directions. i.e., polarizability ellipsoid is spherical.

Rotation of the polarizability ellipsoid produces no change in the polarizability. Therefore, pure rotation of spherical top molecules is completely Raman inactive

Example Carbon tetrachloride, sulphur hexafluoride, methane

Asymmetric -top molecules

All the three principal moments are different $I_x \neq I_y \neq I_z$.

All the rotations of asymmetric molecules are Raman active

Example: Water, nitrogen dioxide,

Pure rotation Raman spectra

The rotational energy for linear molecule neglecting the centrifugal distortion is given by

$$E_{J} = \frac{J(J+1)\hbar^{2}}{2\mu r_{o}^{2}}$$
$$E_{J} = \frac{J(J+1)h^{2}}{2\mu r_{o}^{2} \cdot 4\pi^{2}}$$
$$E_{J} = \frac{J(J+1)h^{2}}{8\pi^{2}I} \quad J = 0, 1, 2, 3, \dots$$

I is the moment of inertia for end over end rotation of the molecules. More the number of atoms in the molecules more will be I leading to closer energy levels.

In rotational region the spectra are discussed in terms of wavenumber .Energies are expressed in terms of wave number

$$\varepsilon_J = \frac{E_J}{hc}$$

$$\varepsilon_J = \frac{J(J+1)h^2}{8\pi^2 I hc}$$
$$\varepsilon_J = Bh J(J+1)$$

$$B = \frac{h}{8\pi^2 Ic}$$

selection rules for transition between rotational levels in Rottional Raman Spectra is given by

$$\Delta J = 0$$
 , ± 2

Pure rotation Raman spectra of linear molecule

The rotational energy level for linear molecule is given by

$$\varepsilon_I = BJ(J+1) - D J^2(J+1)^2 cm^{-1}$$
 J = 0,1,2,3,

In Raman spectroscopy only first term is taken to represent energy

$$\varepsilon_J = BJ(J+1)$$

The selection rule is

$$\Delta J = 0 \text{ or } \pm 2$$

In microwave spectroscopy $\Delta J = \pm 1$, whereas in Raman spectroscopy the rotation quantum number J changes by 2 units rather than one, it is because the polarizability ellipsoid symmetry.

During end over end rotation of a linear molecule, the ellipsoid appears unchanged twice in every complete rotation.

The selection rule $\Delta J = -2$ is ignored as for a pure rotational change the upper state quantum number should be greater than that of the lower state. and $\Delta J = 0$ is trivial as it represents no change in the molecular energy

(In this case there is no change in molecular energy. Molecules do not absorb energy from the exciting photon nor rejects energy to it

Collision between photon and the molecule is elastic. Ejected photon will have same frequency.

Hence Rayleigh scattering is observed)

For $\Delta J = +2$

$$\Delta \varepsilon = \varepsilon_{J+2} - \varepsilon_J$$

$$\Delta \varepsilon = B(J+2)(J+2+1) - BJ(J+1)$$

$$\Delta \varepsilon = B[(J+2)(J+3) - J(J+1)]$$

$$\Delta \varepsilon = B[J^2 + 3J + 2J + 6 - J^2 - J]$$

$$\Delta \varepsilon = B[4J+6] \text{ cm}^{-1}$$

As $\Delta J = +2$, the lines are labelled as S branch lines and are designated as

$$\Delta \varepsilon_s = B [4J + 6]$$
 J=0,1,2,3.....

J is the rotational quantum number in the lower state.

Thus, if the molecule gains rotational energy from the photon during collision, we get S branch lines to the low wavenumber side of the exciting line giving Stokes's line.

If the molecule loses energy to the photon the S branch lines appears on the high wavenumber side giving anti-stokes lines.

The wavenumber of the corresponding spectral lines is given by

$$\overline{v_s} = \overline{v_{ex}} \pm \Delta \varepsilon_s$$
$$\overline{v_s} = \overline{v_{ex}} \pm B[4J + 6] \text{ cm}^{-1}$$

The plus sign refers to antistokes lines, negative sign refers to stokes lines

The Stokes and Anti-stokes lines have comparable intensities because many rotational levels are populated and hence downward transitions are likely to occur as upward transitions.



For J = 0, for $\Delta \varepsilon_s = B [4J + 6]$ we get the separation of the first line from the exciting line equal to 6B cm⁻¹, while the separation between the successive lines is 4Bcm⁻¹.

Homonuclear diatomic molecules like O_2 , H_2 gives no infrared or microwave spectra as they possess no dipole moment, whereas they do give rotational Raman spectra.

Symmetric top molecules

$$I_Y = I_Z \neq I_X \qquad \qquad I_X \neq 0$$

There are two direction of rotation in which the molecule absorb or emit energy about the main symmetry of axis

We require two quantum numbers to describe the degree of rotation one

for I_{χ} and other for I_{Y} or I_{Z}

ie Total angular momentum J and K is the angular momentum about the top axis

Where
$$J = 0,1,2,3 \dots \dots$$
; $K = \pm J, \pm (J-1), \pm \dots$.

The allowed energy levels for rotation in case of spherical top is given by

$$\varepsilon_{J,K} = B J (J+1) + (A-B)K^2 \quad cm^{-1}$$

Where $B = \frac{h}{8\pi^2 I_Y C}$ and $A = \frac{h}{8\pi^2 I_X C}$

Above equation shows that except for K=0, all energy levels for any K are doubly degenerate.

When the radiation of frequency v_{ex} is incident on a system of symmetric top molecule, the exchange energy between photon and a molecule is based on the following selection rule $\Delta K = 0$

$$\Delta J = 0, \pm 1, \pm 2 \quad for K \neq 0$$

$$\Delta J = \pm 2 \qquad for K = 0$$

 $\Delta K = 0 \Rightarrow$ the change in the rotational quantum number for axial

rotation is zero

 \Rightarrow change in the angular momentum about the top axis will not

give rise to Raman spectra. They are Raman active

For $\Delta J = +1$ (R-branch lines)

$$\Delta \varepsilon_R = \varepsilon_{J+1} - \varepsilon_J$$

$$\Delta \varepsilon_R = 2B(J+1) \text{ cm}^{-1} \quad J=1,2,3.....(but \ J \neq o)$$

For $\Delta J = +2$ (S-branch lines)

$$\Delta \varepsilon_R = \varepsilon_{J+2} - \varepsilon_J$$

$$\Delta \varepsilon_R = B(4J+6) \text{ cm}^{-1} \quad J=0,1,2,3.....(but \ J \neq o)$$

Two series of lines in Raman spectrum

$$\overline{\nu_R} = \overline{\nu_{ex}} \pm \Delta \varepsilon_R = \overline{\nu_{ex}} \pm 2B(J+1) \text{ cm}^{-1} \text{ (J=1,2,3.....)}$$
$$\overline{\nu_S} = \overline{\nu_{ex}} \pm \Delta \varepsilon_S = \overline{\nu_{ex}} \pm B(4J+6) \text{ cm}^{-1} \text{ (J=0,1,2,3.....)}$$

In R branch lines appear at 4B, 6B, 8B..... from the exciting lines

In S branch lines appear at 6B, 10B, 14B.....from the exciting lines



Spherical Top Molecules

These are the molecules with tetrahedral symmetry. The polarizability ellipsoid for such molecules is spherical surface and the rotation of such molecule produces no change in polarizability. Hence the pure rotation of spherical molecules are completely inactive in Raman.

Asymmetric Top Molecules

The rotations of the asymmetric top molecules are Raman active. Their spectra is complicated.