

(Classical Raman theory)

(1) e

~~The~~ Pure rotational Raman Spectrum

The rotational energy levels of linear molecules are $E_J = BJ(J+1) - DJ^2(J+1)^2$ cm^{-1} ($J=0, 1, 2, \dots$)

But the ^{poor} precision of Raman spectroscopy does not allow the precise measurement

of the centrifugal distortion constant D .

\therefore In Raman spectroscopy,

$$E_J = BJ(J+1) \text{ cm}^{-1} \quad (J=0, 1, 2, 3, \dots)$$

The selection rule is $\Delta J = 0$ (or) $\Delta J = \pm 2$ only.

(In microwave $\Delta J = \pm 1$)

During end-over-end rotation, the polarizability α ellipsoid gives the same appearance twice during one complete rotation.

rotation

~~the~~ In pure rotational mode $\Delta J = -2$ ~~cannot be~~ ignored, since

the upper state J no, should be larger than the lower state J no & hence

$\Delta J = -2$ is not possible.

$\Delta J = 0 \rightarrow$ represents no change in energy & represents only Rayleigh

scattering not Raman

Hence $\Delta J = +2$

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$$\begin{aligned}\therefore \Delta E &= E_{J'=J+2} - E_{J''=J} \\ &= B(J+2)(J+3) - B J(J+1) \\ &= B [J^2 + 3J + 2] + 6 - J^2 - J\end{aligned}$$

$$\Delta E = B(4J+6) \text{ cm}^{-1}$$

Since $\Delta J = +2$, these lines are S branch lines.

$$\Delta E_S = B(4J+6) \text{ cm}^{-1}$$

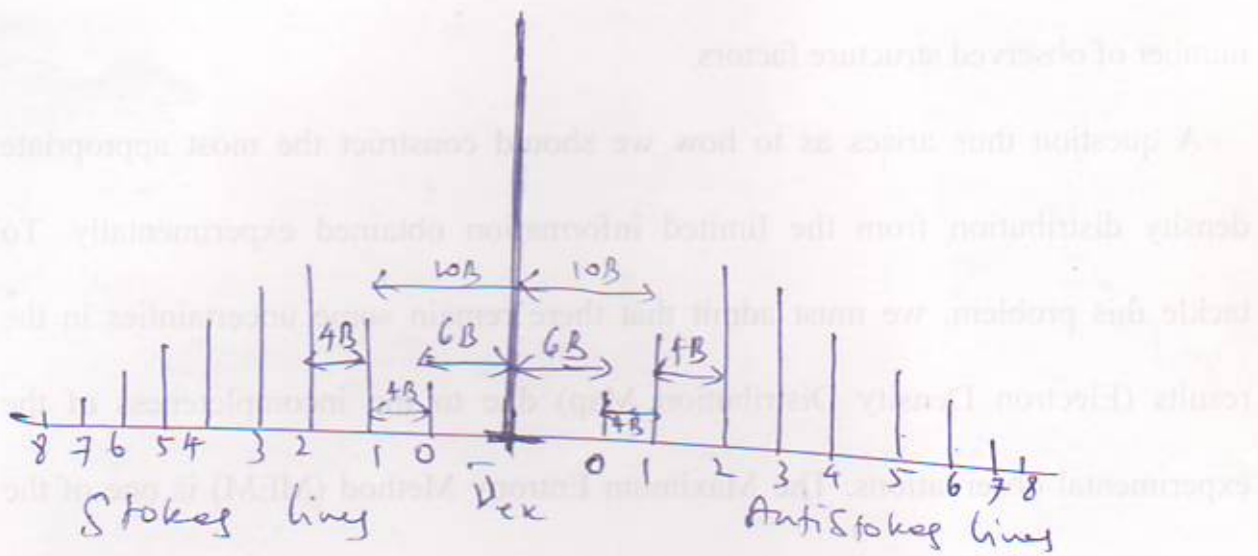
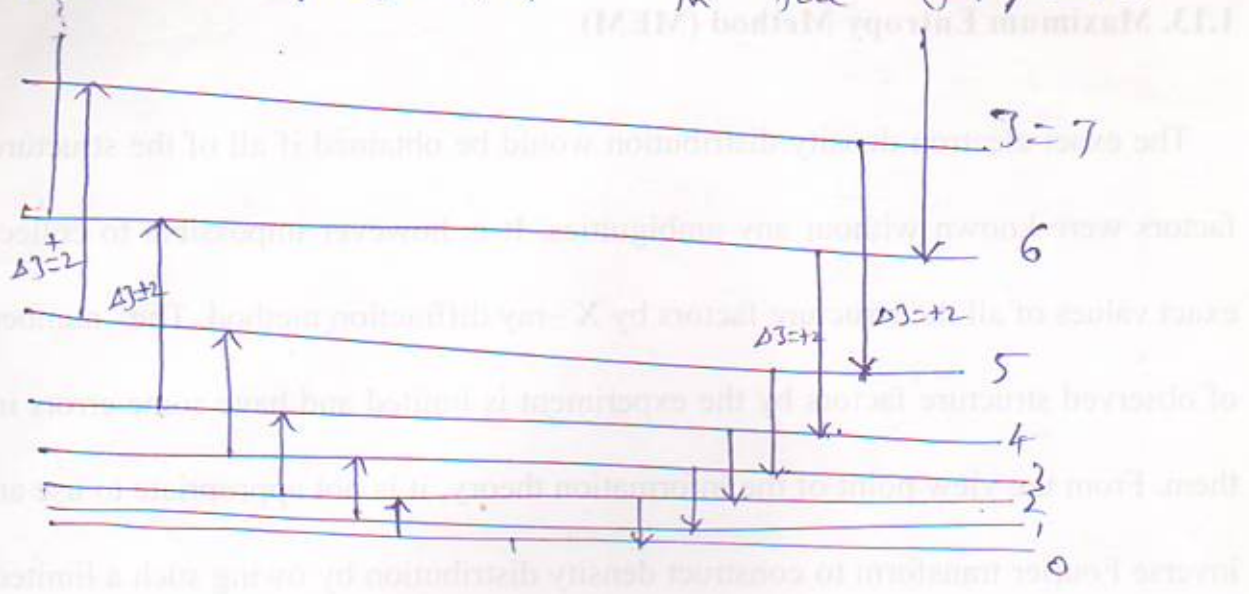
If the molecule gains rotational energy from the incident photon, we get S branch lines ^(Stokes lines) to the lower wave no. side of the incident line.

If the molecule loses energy to the photon, the S branch lines appear on the higher ~~wave no.~~ wave no. side of the incident line called anti Stokes lines.

The wave no. of the corresponding spectral lines are,

$$\bar{\nu}_S = \bar{\nu}_{ex} + \Delta E_S = \bar{\nu}_{ex} \pm B(4J+6) \text{ cm}^{-1}$$

The allowed Raman transitions (3) are represented in the figure.



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

~~for J~~ If $J=0, \rightarrow 6B$

If $J=1, \rightarrow 10B$

$J=2, \rightarrow 14B$

$J=3, \rightarrow 18B$

Vibrational Raman Spectra.

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The vibrational mode can be represented using,

$$E = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2 \text{ cm}^{-1}$$

$(v = 0, 1, 2, 3, \dots)$

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

For $v=0 \rightarrow v=1$: $\Delta E_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$
 $v=0 \rightarrow v=2$: $\Delta E_{\text{overtone}} = 2\bar{\omega}_e (1 - 3x_e)$
 $v=1 \rightarrow v=2$: $\Delta E_{\text{hot bands}} = \bar{\omega}_e (1 - 4x_e)$

$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \Delta E_{\text{fundamental}} \text{ cm}^{-1}$

$\bar{\nu}_{\text{ex}}$
 $\leftarrow \Delta E \rightarrow$
 ΔE

() weak

The vibrational Raman Spectrum will show a series of lines to the low frequency side of the exciting line with a much weaker mirror-image series on the high frequency side.

The separation of each line from the centre of the exciting line gives the Raman active fundamental vibrational frequencies of the molecule.

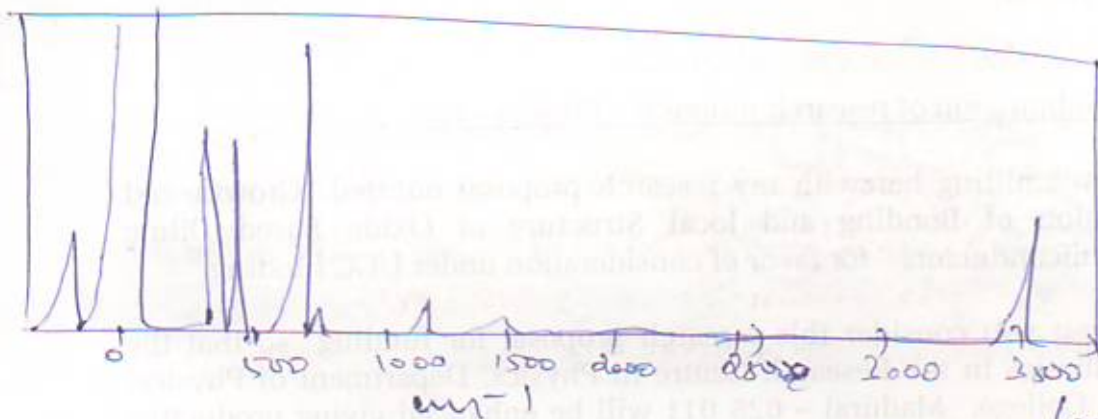
eg. Chloroform. CHCl_3 .

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↓
Symmetric top molecule

The exciting line is 488 nm argon ion laser at 100 mW.

Raman lines appear at 262, 366, 668, 761, 1216, 3019 cm^{-1} on the low frequency side



Similar lines at similar positions are observed in IR too, but with differences in intensities.