

Raman Spectroscopy

Part II: Rotational Raman spectroscopy

B.Sc. (H) Chemistry

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Correction in last PPT, Raman Spectroscopy, Part-I, Slide No. 11, Molecular Polarizability
The corrected version is following,

We know the trigonometric expression,

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

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

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

$$\mu = \alpha_0 E_0 \sin 2\pi\nu t + \frac{1}{2} \beta E_0 \{ \cos 2\pi(\nu - \nu_{vib}) - \cos 2\pi(\nu + \nu_{vib}) t \}$$

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

Rayleigh Scattering

Stokes line

Antistokes line

Rotational Raman Spectra

Rotational energy level of linear molecules is

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

Neglecting the centrifugal distribution constant, D , the expression will be:

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

Selection Rule

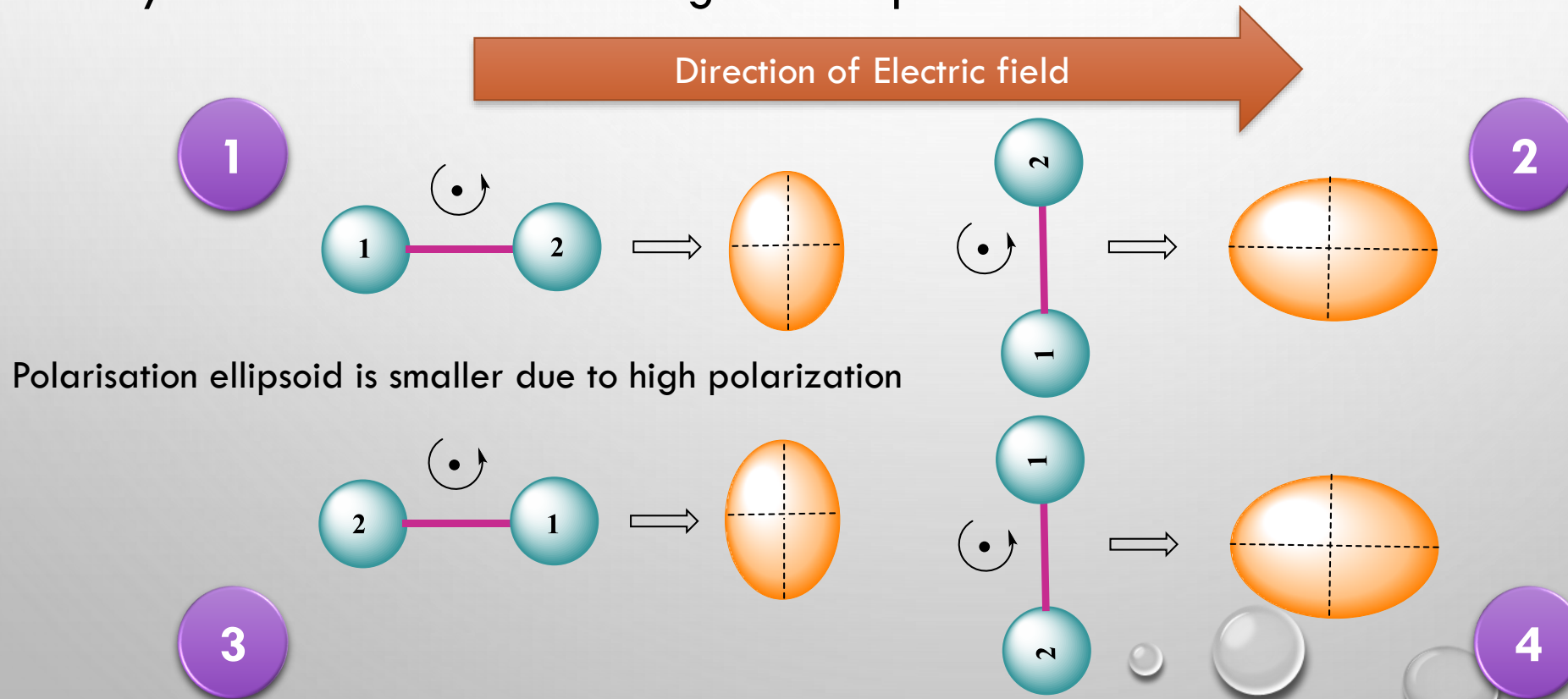
In Microwave Spectroscopy: $\Delta J = \pm 1$ (Already learnt in unit 2)

In Raman Spectroscopy: $\Delta J = 0, \pm 2$

In Raman spectroscopy the rotational quantum number changes by two units rather than one is connected with the symmetry of the polarizability ellipsoid.

Rotational Raman Spectra

- For a linear molecule, it is evident that during end-over-end rotation the ellipsoid presents the same appearance to an observer *twice* in every complete rotation.
- Rotation about the bond axis produces no change in polarizability.
- Only end-over-end rotations give the spectra.



Rotational Raman Spectra

- For a pure rotational change, the transition, $\Delta J = -2$, can be ignored, so the upper state quantum number must necessarily be greater than that in the lower state.
- $\Delta J = 0$, represents no change in the molecular energy and hence we obtain **Rayleigh scattering** only.

For the transition, $\Delta J = +2$,

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

Putting the values of J in the equation,

$$= [B(J+2)(J+3)] - [BJ(J+1)]$$

$$= B(J^2+3J+2J+6) - BJ^2 - BJ$$

$$= BJ^2 + 5BJ + 6B - BJ^2 - BJ$$

$$= 4BJ + 6B$$

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

Rotational Raman Spectra

Since $\Delta J = +2$, we may label these lines **S branch lines** and write,

$$\Delta \varepsilon_S = B(4J+6) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

where, J is the rotational quantum number in the lower state.

If the molecule gains rotational energy from the photon during collision we have a series of **S** branch lines to the low wavenumber side of the exciting line (Stokes' lines), while if the molecule loses energy to the photon the **S** branch lines appear on the high wavenumber side (anti-Stokes' lines). The wavenumbers of the corresponding spectral lines are given by:

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

where the **plus** sign refers to anti-Stokes' lines, the **minus** to Stokes' lines, and $\bar{\nu}_{ex.}$ is the wavenumber of the exciting radiation.

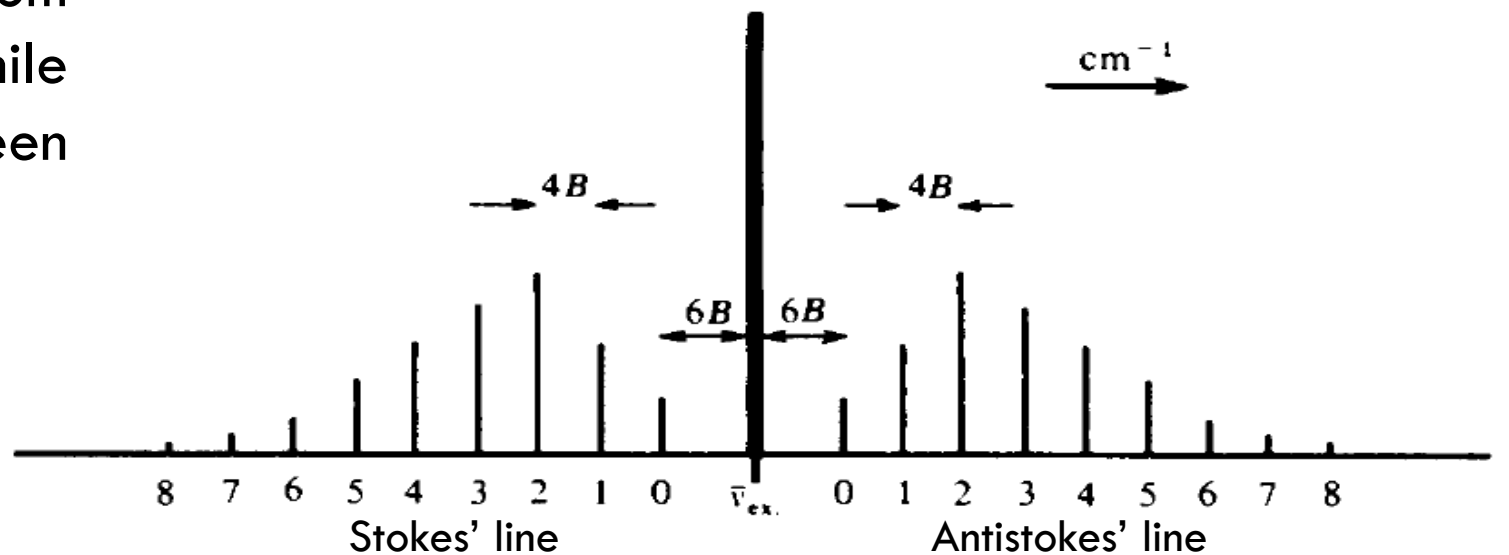
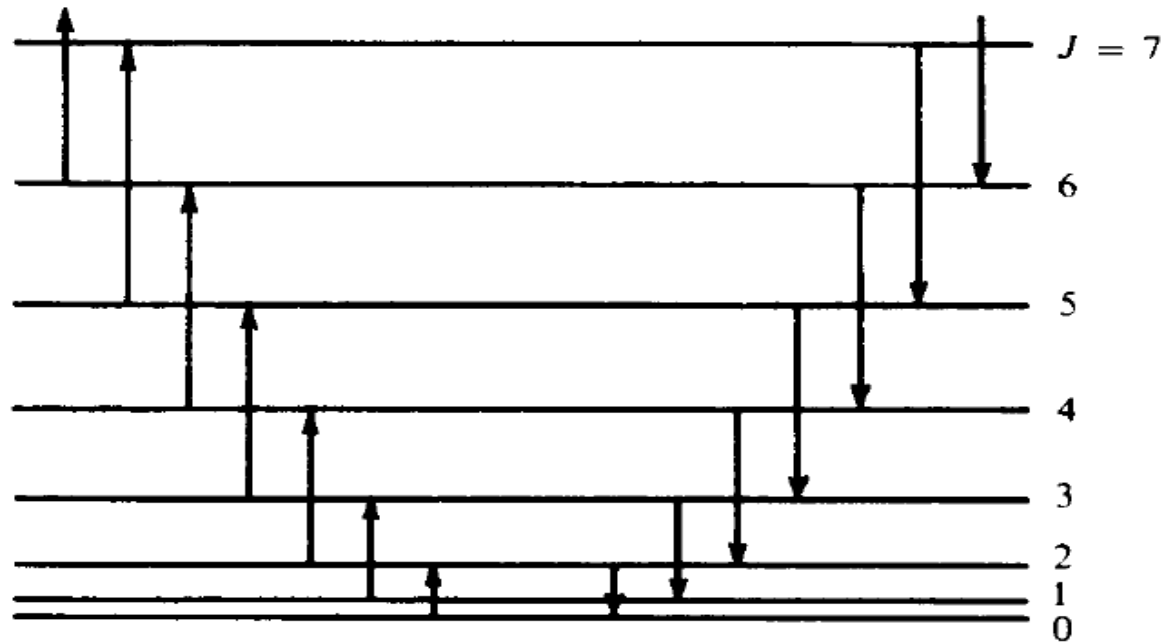
If, $\bar{\nu}_S = \bar{\nu}_{ex.}$ **Rayleigh line**

Rotational Raman Spectra

When the value $J = 0$, in the equation,

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

it is seen immediately that the separation of the first line from the exciting line is $6B \text{ cm}^{-1}$, while the separation between successive lines is $4B \text{ cm}^{-1}$.



Rotational Raman Spectra

Points to remember

- For diatomic and light triatomic molecules the rotational Raman spectrum will normally be resolved and we can immediately obtain a value of B , and hence the moment of inertia and bond lengths for such molecules.
- Homonuclear diatomic molecules (for example O_2 , H_2) give no infra-red or microwave spectra since they possess no dipole moment, whereas they **do** give a rotational Raman spectrum.
- If the molecule has a centre of symmetry (as, for example, H_2 , O_2 , CO_2), then the effects of nuclear spin will be observed in the Raman as in the infra-red.*
- Thus for O_2 and CO_2 (since the *spin of oxygen is zero*) every alternate rotational level is absent;
- For example, in the case of O_2 , every level with even J values is missing, and thus every transition labelled $J = 0, 2, 4, \dots$ is also completely missing from the spectrum.
- In the case of H_2 , and other molecules composed of nuclei with non-zero spin, the spectral lines show an *alternation of intensity*.

*(For detailed study about the influence of Nuclear spin on IR spectra, see page no. 79, : *Fundamentals of Molecular Spectroscopy, 4th Ed. By Colin N. Bahwell and Elaine M. McCash*)



Reference

Fundamentals of Molecular Spectroscopy, 4th Ed.

By Colin N. Banwell and Elaine M. McCash

Next: Vibrational Raman Spectra



The background features a light gray gradient with several realistic water droplets of various sizes scattered in the corners. A faint, circular watermark logo is visible in the upper center.

THANK YOU

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