

Vibrational Raman Spectra : For every vibrational mode, we can write an expression of the form

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

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

$\bar{\omega}_e \rightarrow$  equilibrium vibrational frequency

$x_e \rightarrow$  anharmonicity constant.

Perfectly general expression  $\rightarrow$  whatever the shape of molecule or the nature of vibrations.

The selection rule

$$\Delta v = 0, \pm 1, \pm 2, \dots \quad (2)$$

which is the same for Raman as for infra-red spectroscopy.  $\Delta v = \pm 2, \pm 3$  probability decreases rapidly.

For Raman active modes, we apply selection rules (2) to the energy level expression (1) and obtain the transition energies:

$$v=0 \rightarrow v=1: \Delta \epsilon_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v=0 \rightarrow v=2: \Delta \epsilon_{\text{overtone}} = 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

$$v=1 \rightarrow v=2 \quad \Delta \epsilon_{\text{hot}} = \bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

Raman scattering light  $\rightarrow$  is any case of light intensity  $\rightarrow$  we can ignore all the weaker effects such as 'overtones' and 'hot' bands. and resort to fundamentals (3)

We expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibrational. In other words, we can write:

$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \Delta \epsilon_{\text{fundamental}} \text{ cm}^{-1} \quad \text{--- (4)}$$

minus sign → Stokes lines  
molecules have gained energy at the expense of radiating

plus sign → anti-Stokes lines  
↳ often too weak to be observed, very few of the molecules exist in the  $\nu=1$  state at normal temperature.

Vibrational Raman Spectrum of a molecule

→ A series of reasonably intense 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.



Rotational fine structure → Rotational fine structure of Raman spectra is rarely resolved, except in case of

diatomic molecule. We can write the vibrational-rotation energy levels as; (12)

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

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

where we write  $\bar{\nu}_0$  for  $\bar{\omega}_e (1 - 2x_e)$  and use the subscripts O, Q and S to refer to the O branch line ( $\Delta J = -2$ ) Q branch line ( $\Delta J = 0$ ) and S branch lines' ( $\Delta J = +2$ ) respectively.

$$\Delta J = 0, \quad \Delta \epsilon_Q = \bar{\nu}_0 \text{ cm}^{-1} \quad (\text{for all } J) \quad (6)$$

$$\Delta J = +2, \quad \Delta \epsilon_S = \bar{\nu}_0 + B(4J+6) \quad (J=0,1,2, \dots)$$

$$\Delta J = -2, \quad \Delta \epsilon_O = \bar{\nu}_0 - B(4J+6) \quad (J=2,3,4, \dots)$$

Stoke's lines (i.e. lines to low frequency of the exciting radiation) will occur at wavenumbers given by;

$$\bar{\nu}_Q = \bar{\nu}_{ex} - \bar{\nu}_0 \text{ cm}^{-1} \quad (\text{for all } J)$$

$$\bar{\nu}_O = \bar{\nu}_{ex} - \Delta \epsilon_O = \bar{\nu}_{ex} - \bar{\nu}_0 + B(4J+6) \text{ cm}^{-1} \quad (J=2,3,4, \dots)$$

$$\bar{\nu}_S = \bar{\nu}_{ex} - \Delta \epsilon_S = \bar{\nu}_{ex} - \bar{\nu}_0 - B(4J+6) \text{ cm}^{-1} \quad (J=0,1,2, \dots)$$

for larger molecules, we can ignore the rotational fine structure since it is not resolved. Even the O and S band contours are seldom observed, very weak compared to Q branch.

# Polarization of light and The Roman Effect (14)

## The Nature of Polarized Light

A beam of light passed through a Nicol prism or a piece of crystal filter  $\rightarrow$  The only light passing has its electric (or magnetic) vector confined to a particular plane  $\rightarrow$  It is plane polarized light.

Previously polarized light  $\rightarrow$  fall on a second polarizing device (now called the 'analyser') it will be passed with undiminished intensity only if the polarizing axes of the two prisms are parallel to each other.

At any other orientations  $\rightarrow$  The intensity passed will decrease until, the axes are perpendicular  $\rightarrow$  no light at all passes through the analyser.

Analyser  $\rightarrow$  serves both to detect polarized light and to determine its plane of polarization.

Light incident upon the analyser  $\rightarrow$  partially polarized  $\rightarrow$  the light will not be completely extinguished at any orientation of the analyser; its intensity will merely go through a minimum when the analyser is perpendicular to ~~the plane of polarization~~ the plane of maximum polarization.

~~the~~ Degree of depolarization

$$P = \frac{I_{\perp}}{I_{\parallel}} \quad \text{--- (3)}$$

$I_{\parallel} \rightarrow$  maximum and  $I_{\perp} \rightarrow$  minimum intensity passed by the analyser.

For completely plane-polarised light  $I_{\perp} = 0$  and hence the degree of depolarisation is zero also; for completely unpolarised (i.e. ordinary) light  $I_{\perp} = I_{\parallel}$  and  $\rho = 1$ . For intermediate degrees of polarisation  $\rho$  is between 0 and 1.

The relevance of this to Raman spectroscopy is that ~~the~~ lines in some Raman spectra are found to be plane-polarised to different extents even though the exciting radiation is completely depolarised. To understand the reason, we consider the vibrations of spherical top molecules.

Vibrations of Spherical Top Molecules

Tetrahedral molecule  $CH_4 \rightarrow$  good example of a spherical top molecule  $\rightarrow$  its polarizability ellipsoid is spherical.

