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Topic — Vibrational Spectra

Vibrational spectra

The vibrational spectra are obtained by those molecules which show a change in the dipole moment during the course of vibration. The homonuclear diatomic molecules like Cl_2, N_2, O_2 etc. not show vibrational spectra. In general $E_{vib-rot} = E_{vib} + E_{rot}$.
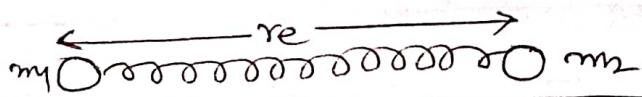
Two models can be applied to the diatomic molecules.

Harmonic Oscillator model —

Here diatomic molecule is supposed as a system of two atoms connected by a spring capable of showing vibrations similar to a linear harmonic oscillator about their mean positions.
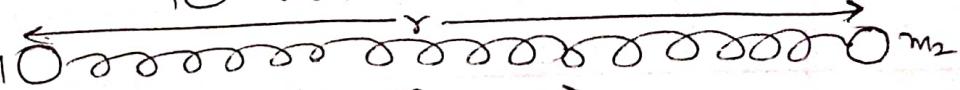
(a) Harmonic Oscillator but not rotator (only vibrational spectra) —

In case of diatomic molecule; the masses m_1 and m_2 vibrate back and forth relative to their centre of mass in opposite directions as shown in figure.
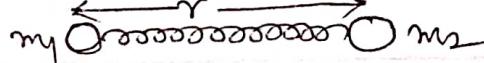
Normal position

Stretching position

compressed position

Here the bond between two atoms is distorted from its equilibrium length r_e to a new length r. From the Hook's law the restoring force is proportional to displacement of vibratory atom from the original position. So the restoring force on each atom is given by,

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r-r_e) \qquad \text{and} \qquad m_2 \frac{d^2 r_2}{dt^2} = -k(r-r_e)$$

$$\text{---(1)} \qquad\qquad\qquad\qquad \text{---(2)}$$

where k is the force const. regarded as the stiffness of the bond, r_1 and r_2 are the positions of atom 1 and 2 relative to centre of gravity of the molecule. we know that,

$$r_1 = \frac{m_2}{m_1+m_2}\cdot r \quad \text{and} \quad r_2 = \frac{m_1}{m_1+m_2}\cdot r$$
—(3) —(4)

using equation (3) in equation (1), $\left(\frac{m_1 m_2}{m_1+m_2}\right)\frac{d^2 r}{dt^2} = -k(r-r_e)$
—(5)

Since r_e is constt. hence $\frac{d^2 r}{dt^2} = \frac{d^2(r-r_e)}{dt^2}$

Therefore, $\left(\frac{m_1 m_2}{m_1+m_2}\right)\cdot\frac{d^2(r-r_e)}{dt^2} = -k(r-r_e)$ —(6)

Put $r-r_e = x$ and $\frac{m_1 m_2}{m_1+m_2} = \mu$ we can write equation (6) as,

$$\mu\frac{d^2 x}{dt^2} + kx = 0$$

or $\frac{d^2 x}{dt^2} + \left(\frac{k}{\mu}\right)x = 0$ or $\frac{d^2 x}{dt^2} + \omega^2 x = 0$ — (7)

where $\omega^2 = \frac{k}{\mu}$ or $\omega = \sqrt{k/\mu}$. Equation (7) is the expression of a simple harmonic motion. The frequency of vibration ν_0 is equal to $\omega/2\pi$. So $\nu_0 = \frac{1}{2\pi}\sqrt{k/\mu}$ — (8)

The potential energy of simple harmonic oscillator (SHO) is given by parabolic Hook's law i.e,

$$U(x) = \frac{1}{2}k(r-r_e)^2 = \frac{1}{2}kx^2$$ —(9)

The vibrational energy may now be determined from Schrodinger wave equation (only one direction of oscillation being considered) as $\nabla^2 \psi + \frac{8\pi^2\mu}{h^2}\left(E_{vib} - \frac{1}{2}kx^2\right)\psi = 0$

The allowed solutions of this equation are given by,

$$E_{vib} = \frac{h}{2\pi}\sqrt{k/\mu}\left(V+\frac{1}{2}\right)$$ —(10)

From equation (8) and (10) we have,
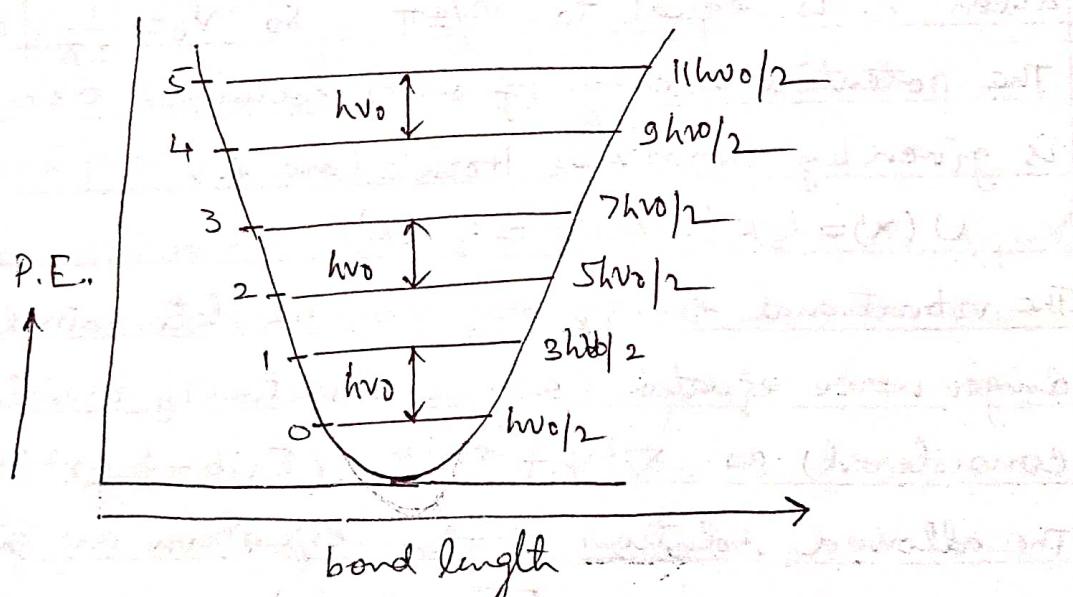
$$E_{vib} = \left(V+\frac{1}{2}\right).h\nu_0$$ —(11)

Here V is the vibrational q. no. and has values $0, 1, 2, 3 \cdots$

v_0 is the fundamental vibrational frequency. The equation (11) gives value of energy in different vibrational energy levels.

From equation (11), $E_0 = \frac{1}{2}hv_0$. This is called **Zero point energy** and it is present even at absolute zero ie (-273 K). So when translational & rotational motions stop, vibrational motion still persists. The selection rule for a vibrational transition in SHO is $\Delta V = \pm 1$. The operative part for absorption spectrum is, $\Delta V = +1$. Taking account of this equation (11) gives,

$$\Delta E_{vib} = (V+1+\frac{1}{2})hv_0 - (v+\frac{1}{2})hv_0 = hv_0 \quad \text{---(12)}$$

Equation(12) shows that frequency of absorbed (or emitted) radiation during vibrational transition is the same as the fundamental frequency of vibration (v_0) of the molecule. Putting $V=0, 1, 2, 3--$ in equation (11) we can prove that energy levels of SHO are equally spaced by the spacing equal to hv_0 as shown in figure.

(b) <u>Harmonic oscillator and rotator (vibrational-rotational spectra)</u> –

Total energy in this case $E_{Total} = E_{vib} + E_{rot}$.

ie. $E_{V,J} = E_V + E_J$

or $\bar{E}_{V,J} = \bar{E}_V + \bar{E}_J$

or $\bar{E}_{V,J} = BJ(J+1) + \bar{V}_0 (V+\frac{1}{2})$ where centrifugal distortion
effects are neglected and $J = 0, 1, 2, 3 \cdots$
$$V = 0, 1, 2, 3 \cdots$$

The selection rule is $\Delta J = \pm 1$ and $\Delta V = \pm 1$

Now the energy change for the transition from J', V' to J'', V'' is
given by $\overline{\Delta E}_{J,V} = \bar{E}''_{J,V} - \bar{E}'_{J,V}$
$$= [B\{J''(J''+1) - J'(J'+1)\} + \bar{V}_0 (V''-V')]$$

At lower temperature, the molecules are generally in their
lowest vibrational level $(V=0)$. Hence the transitions from
$V=0$ to $V=1$ is of interest. Under such condition,

(i) $V''=1$ and $V'=0$, if $\Delta J = +1$ i.e. $J'' = J'+1$

So $\overline{\Delta E}_{J,V} = [2B(J'+1) + \bar{V}_0]$ cm^{-1} where $J' = 0, 1, 2, 3 \cdots$

(ii) $V''=1$, and $V'=0$, if $\Delta J = -1$ i.e. $J'' = J'-1$

So $\overline{\Delta E}_{J,V} = [\bar{V}_0 - 2B(J''+1)]$ cm^{-1} where $J'' = 0, 1, 2, 3 \cdots$

Both the expressions can be represented as,
$$\overline{\Delta E}_{J,V} = (\bar{V}_0 + 2Bm) \text{ cm}^{-1} \text{ where } m = \pm 1, \pm 2, \pm 3 \cdots$$

Discussion — $\bar{V}_0$ is called band origin or band centre. It
does not appear itself because $m \neq 0$. The vibrational—
rotational spectrum would consist of series of lines with
equal spacing of $2B$ cm^{-1}, on either side of the band origin
at $\bar{v}_0$. The spectral lines corresponding to $\Delta J = -1$ (i.e $m = -ve$)
i.e. at lower frequency side of $\bar{V}_0$ are called P-branch
lines. Similarly of $\Delta J = +1$ (i.e. $m = +ve$) i.e. at higher frequency
side of $\bar{V}_0$ are called R-branch lines. The vib.-rot. spectral
lines corresponding to $\Delta J = -2, -1, 0, +1, +2$ are called O, P, Q, R, S bran-

ch lines respectively. The intensity of spectral lines is given by,

P-branch $\quad \bar{V}_{max} = \bar{V}_0 - 2B\left(\sqrt{\dfrac{kT}{2Bhc}} + \dfrac{1}{2}\right)$ cm⁻¹

R-branch $\quad \bar{V}_{max} = \bar{V}_0 + 2B\left(\sqrt{\dfrac{kT}{2Bhc}} + \dfrac{1}{2}\right)$ cm⁻¹

Anharmonic Oscillator model

In practice, at higher vibrational levels, the vibrations become anharmonic. The spacing between vibrational energy levels is no longer constt. but goes on decreasing with increase in vibrational quantum number.

(a) Purely vibrational spectra – using schrodinger wave equation, the energy levels for anharmonic oscillator is given by,

$$\bar{E}_V = \left(V + \tfrac{1}{2}\right)\bar{V}_e - \left(V + \tfrac{1}{2}\right)^2 \bar{V}_e \, x \quad cm^{-1} \quad (V = 0, 1, 2, 3 \cdots)$$

where $\bar{V}_e$ = equilibrium oscillation frequency (wave number)

and x = Anharmonicity constt. It has small magnitude.

Because of anharmonicity the selection rule is no longer $\Delta V = \pm 1$. Instead $\Delta V = \pm 2, \pm 3$ etc are also observed in IR spectra. The lines appearing due to transitions from V=0 to V=1, V=0 to V=2 and V=0 to V=3 are called fundamental band, first overtone band (second anharmonic) and second overtone band (third anharmonic) etc respectively. The overtones are very weak as compared to highly intense fundamental vibrational frequency and their intensity keeps on falling with the increase in their degree.

Hotbands – At room temperature vibrational transitions originate from V=0. As temp. rises, molecules migrate from V=0 to V=1. Therefore at higher temperatures, vibrational transitions are originated from V=1

also. such transitions from V=1 to higher levels produce spectral lines called hot bands and their intensity increases with rise in temperature.

(b) Vibrational rotational spectra — The total energy of anharmonic vibrating rotator is given by,

$$\bar{E}_{J,V} = \left[BJ(J+1) + \bar{v}_e\left(V+\tfrac{1}{2}\right)\left\{1 - x\left(V+\tfrac{1}{2}\right)\right\}\right] cm^{-1}$$

The selection rule is given by $\Delta J = \pm 1$, $\Delta V = \pm 1, \pm 2, \pm 3 \cdots$ etc. consider the transition from $V=0$ to $V=1$ involving a rotational change from level J' to J''. Now

$$\overline{\Delta E}_{J,V} = \left[\bar{v}_e(1-2x) + B(J''-J')(J''+J'+1)\right] cm^{-1}$$

where J'' is higher and J' is lower

Let $\Delta J = +1$ i.e. $J''-J' = 1$, then

$$\overline{\Delta E}_{J,V} = \bar{v}_e(1-2x) + 2B(J'+1) \; cm^{-1} \quad \text{where } J' = 0, 1, 2, 3 \cdots$$

when $\Delta J = -1$ i.e. $J''-J' = -1$, then

$$\overline{\Delta E}_{J,V} = \bar{v}_e(1-2x) - 2B(J''+1) \; cm^{-1} \quad \text{where } J'' = 0, 1, 2, 3 \cdots$$

combining these expressions,

$$\overline{\Delta E}_{J,V} = \bar{v}_e(1-2x) + 2Bm \; cm^{-1} \qquad —(1)$$

where $m = \pm 1, \pm 2, \pm 3 \cdots$ and not zero.

The equation (1) gives $\bar{v}_e(1-2x)$ as band centre and there will be a series of lines on either side of the band centre in rotational-vibrational spectrum of diatomic molecule. The frequency $\bar{v}_e(1-2x)$ is equal to fundamental frequency $\bar{v}_0$. Hence $\overline{\Delta E}_{J,V} = \left[\bar{v}_0 + 2Bm\right] cm^{-1} \qquad —(2)$

(i) For -ve value of m the spectral lines appear on the lower frequency side of the band centre $\bar{v}_0$ and they

are called P-branch.

(ii) For +ve value of m — the spectral lines appear on the higher frequency side of $\bar{\nu}_0$ and they are called R-branch.

The equation (2) is in good agreement with experimental results.

Q. The force constt. of CO is 1840 Nm^{-1}. what is vibrational frequency in cm^{-1} and spacing b/w vibrational energy levels.?

Ans.. Atomic masses are $C^{12} = 19.9 \times 10^{-27}$ kg, $O^{16} = 26.6 \times 10^{-27}$ kg

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = 11.4 \times 10^{-27} \text{ kg}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{K/\mu} = \frac{1}{2(3.14)(3\times10^8 \text{ ms}^{-1})(10^2 \text{ cm m}^{-1})}\left(\frac{1840 \text{ kg s}^{-2}}{11.4 \times 10^{-27} \text{ kg}}\right)^{1/2}$$

$$= 2140 \text{ cm}^{-1}$$

The spacing b/w energy levels $= \Delta E = E_{(v+1)} - E_v = h\nu$ Joules

In terms of wave number $\overline{\Delta E} = \frac{h\nu}{hc} = \bar{\nu} = 2140 \text{ cm}^{-1}$

Since $1 eV = 8066$ cm^{-1} So $\bar{\nu}$ (in eV) $= \frac{2140 \text{ cm}^{-1}}{8066 \text{ cm}^{-1}/eV} = 0.265$ eV

The thermal energy $= kT = \frac{(1.38 \times 10^{-23} \text{ JK}^{-1})(300 K)}{1.6 \times 10^{-19} \text{ J/eV}} = 0.026$ eV

So $kT < \Delta E$ i.e most of the molecules are in the ground vibrational level at room temp. But in rotational states $kT > \Delta E$ and consequently most of the molecules are in the excited rotational states at room temperature.

(In CGS system $1 \text{ Nm}^{-1} = 10^3 \text{ dyn cm}^{-1}$)