Molecules as anharmonic oscillator-

The observed near infra red spectrum with that expected from a diatomic molecule treated as harmonic oscillator shows an important. In spectrum of harmonic oscillator would give a single band at wave number ω which is classical frequency of molecule. The actual infrared spectrum is however found to consist of an intense band called fundamental band at ω plus a number of weak bands called as overtones at wave numbers slightly lesser and lesser than $2\omega, 3\omega, 4\omega$ ---

The selection rules $\Delta v = \pm 1$ is not strictly obeyed for overtones and transitions $\Delta v > 1$ also take place. This is attributed to the fact that the dipole moment of molecule is not strictly linear with respect to linear displacement

$$x = r - r_e$$

This is expressed as electrical anharmonicity.

The observation that overtone does not appear exactly at $2\omega, 3\omega, 4\omega$ implies that the vibrational energy levels are not equally spaced but converge slowly due to the fact that the potential energy of molecule is not parabolic in nature. It means potential energy $V(r)$ is not harmonic and need to include terms higher than quadratic in Taylor's series expansion of $V(r)$.

The potential energy near equilibrium position is

$$V(x) = V(0) + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 + \cdots$$

$$\simeq \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 \quad \text{---(1)}$$

Here $V(0)$ is constant corresponding to energy $x = 0$.

The first derivative of V is zero because slope is zero at minimum.

According to first approximation

$$\frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 = \frac{1}{2}Kx^2 \quad -(2)$$

The second derivative $K = \left(\frac{d^2V}{dx^2}\right)_0$ is force constant.

Now considering third and fourth term also.

$$V(r) = \frac{1}{L2}\left(\frac{\partial^2 V}{\partial r^2}\right)_{r=r_0}(r-r_0)^2 + \frac{1}{L3}\left(\frac{\partial^3 V}{\partial r^3}\right)_{r=r_0}(r-r_0)^3$$

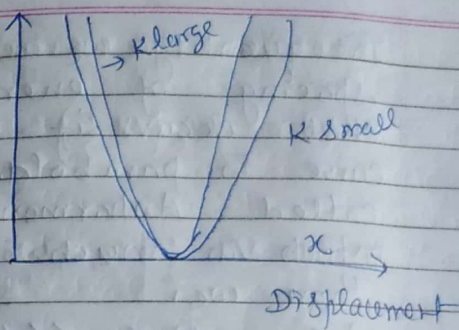
$$= f(r-r_0)^2 + g(r-r_0)^3 \quad -(3)$$

we put $r - r_0 = x$

$$\boxed{V(r) = fx^2 - gx^3}$$

Here $g \ll f$.

Now using this value of V(r) in Schrondinger equation and solving by Perturbation Method.



If K is large, V(x) is sharply curved

If K is small, V(x) is wide and shallow

The energy eigen value of anharmonic oscillator is given by

$$E(V) = hc\omega_e\left(V+\frac{1}{2}\right) - hc\omega_e x_e\left(V+\frac{1}{2}\right)^2 \quad -(4)$$

The corresponding term value

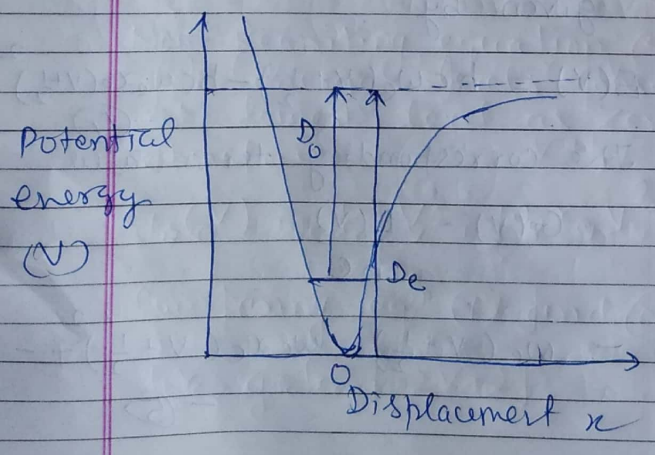
$$G(V) = \frac{E(V)}{hc}$$

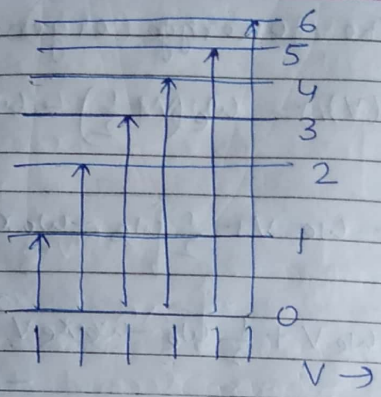
$$G(V) = \omega_e\left(V+\frac{1}{2}\right) - \omega_e x_e\left(V+\frac{1}{2}\right)^2 + - \quad -(5)$$

The quantity ω_e is wave number spacing of energy levels that occurs if potential curve is parabola. $\omega_e x_e$ is called Anharmonicity constant. which is much smaller than ω_e.

i.e. $\omega_e x_e << \omega_e$

The value of $\omega_e x_e$ is always positive. The equation (5) indicates that the energy levels of anharmonic oscillator are not equidistant but their separation decreases slowly with increasing V.





The molecule dissociates into atoms when it receives energy more than that corresponding to uppermost vibrational level. The excess energy appears as kinetic energy of these atoms and this energy is not quantised.

The zero point energy is obtained by putting $v = 0$ in equation (5)

$$G(V) = \omega_e\left(V+\tfrac{1}{2}\right) - \omega_e x_e\left(V+\tfrac{1}{2}\right)^2 + \cdots$$

$V = 0$

$$\boxed{G(V) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \cdots}$$

The energy eigen value

$$G(V) = \omega_e\left(V+\frac{1}{2}\right) - \omega_e x_e\left(V+\frac{1}{2}\right)^2$$

$$= \omega_e V + \frac{1}{2}\omega_e - \omega_e x_e\left(V^2+\frac{1}{4}+V\right)$$

$$= \omega_e V + \frac{1}{2}\omega_e - \omega_e x_e V^2 - \omega_e x_e V - \frac{\omega_e x_e}{4}$$

$$G_2(V) = (\omega_e - \omega_e x_e)V - \omega_e x_e V^2 + \left(\frac{1}{2}\omega_e - \frac{\omega_e x_e}{4}\right) + \quad -(7)$$

Now Rewriting equation (5) for energy levels considered at lowest level as zero. Therefore

$$G_0(V) = \omega_0 V - \omega_0 x_0 V^2 \quad -(8)$$

Comparing eqn (7) and (8) we get

$$\omega_0 = \omega_e - \omega_e x_e$$
$$\omega_0 x_0 = \omega_e x_e \quad \Big] -(9)$$

Eigen function: The eigen functions of anharmonic oscillator following the selection rules $\Delta V = \pm 1$. The selection rules $\Delta V = \pm 2, \pm 3$ also appear but with rapidly decreasing intensity. The transistions with $\Delta V = 2, 3, 4 \cdots$ have approximately two, three four --- times the wave number of the transistion $\Delta V = 1$ is in good agreement with observation.

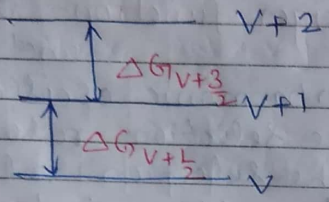
The wave number separation between two successive absorption bands is given by

$$\Delta G_{V+\frac{1}{2}} = G_1(V+1) - G(V)$$

$$= G_{10}(V+1) - G_0(V)$$

$G(V) = \omega_e(V+\frac{1}{2}) - \omega_e x_e (V+\frac{1}{2})^2$

$G_0(V) = \omega_0 V - \omega_0 x_0 V^2$



$\Delta G_{V+\frac{1}{2}} = G(V+1) - G(V)$

$= \omega_e(V+\frac{3}{2}) - \omega_e x_e (V+\frac{3}{2})^2$

$- \omega_e(V+\frac{1}{2}) + \omega_e x_e (V+\frac{1}{2})^2$

$= \omega_e (V+\frac{3}{2} - V - \frac{1}{2}) - \omega_e x_e \left[(V+\frac{3}{2})^2 - (V+\frac{1}{2})^2\right]$

$= \omega_e - \omega_e x_e \left[V^2 + \frac{9}{4} + 3V - V^2 - \frac{1}{4} - V\right]$

$= \omega_e - \omega_e x_e [2V+2]$

$\Delta G_{V+\frac{1}{2}} = \omega_e - 2\omega_e x_e (V+1)$ (1)

Similarly in terms of ω_0 and $\omega_0 x_0$ we get

$\Delta G_{V+\frac{1}{2}} = G_0(V+1) - G_0(V)$

$= \omega_0(V+1) - \omega_0 x_0 (V+1)^2$

$- \omega_0 V + \omega_0 x_0 (V^2)$

$= \omega_0(V+1-V) - \omega_0 x_0 (V^2+1+2V-V^2)$

$\Delta G_{V+\frac{1}{2}} = \omega_0 - (2V+1)\omega_0 x_0$ (2)

From (1) and (2) as V increases separation between successive Δ and decreases linearly that is in good agreement with observations.

The second differences are given by

$$\Delta^2 G_{V+1} = \Delta G_{V+\frac{3}{2}} - \Delta G_{V+\frac{1}{2}}$$

$$= [\omega_e - 2\omega_e x_e - 2\omega_e x_e (V+1)]$$

$$- [\omega_e - 2\omega_e x_e - 2\omega_e x_e V]$$

$$= -2\omega_e x_e = -2\omega_0 x_0$$

It means second difference directly determines the anharmonicity constant $\omega_e x_e$ or $\omega_0 x_0$.

The values of ω_e and ω_0 are obtained from observed wave number of fundamental band

For transition $V=0 \rightarrow 1$

$$\Delta G_{V+\frac{1}{2}} = G(1) - G(0)$$

$$= G_0(1) - G(0)$$

$$= \omega_e - 2\omega_e x_e$$

$$= \omega_0 - \omega_0 x_0$$

As $\omega_e x_e$ and $\omega_0 x_0$ have been determined already, ω_e and ω_0 can be evaluated.

Vibrational Frequency and force Constant for Anharmonic oscillator

We know that classical vibrational frequency for harmonic oscillator is

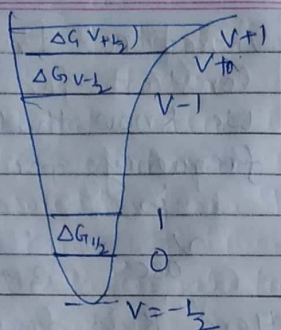
$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Here K is force constant and μ is reduced mass. The separation of successive vibrational levels is constant which is given by

$$\omega = \frac{\nu_{osc}}{c}$$

In the case of Anharmonic oscillator the classical frequency as given above holds for very small amplitudes only. It decreases slowly as the amplitude increases. The exact classical expression for vibrational frequency of anharmonic oscillator in the state V is given by

$$\nu_{osc}(V) = c\,\Delta G_V$$



$$\nu_{osc}(V) = c\,\frac{\Delta G_{V+\frac{1}{2}} + \Delta G_{V-\frac{1}{2}}}{2}$$

$$= \frac{1}{2}c\left[G(V+1) - G(V) + G(V) - G(V-1)\right]$$

$$= \frac{1}{2}c\left[G(V+1) - G(V-1)\right]$$

As we know

$$G(V) = \omega_e\left(V+\tfrac{1}{2}\right) - \omega_e x_e\left(V+\tfrac{1}{2}\right)^2$$

$$G(V+1) = \omega_e\left(V+\tfrac{3}{2}\right) - \omega_e x_e\left(V+\tfrac{3}{2}\right)^2$$

$$G(V-1) = \omega_e\left(V-\tfrac{1}{2}\right) - \omega_e x_e\left(V-\tfrac{1}{2}\right)^2$$

Putting these values

$$\nu_{osc}(V) = \frac{1}{2}c\left[G(V+1) - G(V-1)\right]$$

$$= \frac{1}{2}c\left[\omega_e\left(V+\tfrac{3}{2} - V + \tfrac{1}{2}\right) - \omega_e x_e\left(V^2 + \tfrac{9}{4} + 3V - V^2 - \tfrac{1}{4} + V\right)\right]$$

$$= \frac{1}{2}c\left[2\omega_e - \omega_e x_e(4V+2)\right]$$

$$\boxed{\nu_{osc} = c\left[\omega_e - \omega_e x_e(2V+1)\right]}$$

Thus as V increases classical oscillation frequency decreases

Consider a hypothetical state having $V = -\frac{1}{2}$ such that $2V+1=0$ then

$\nu_{osc} = c\omega_e$ which is classical frequency for harmonic oscillator.

It means that the anharmonic oscillator would have classically for an infinitesimal amplitude that is in imaginary

state at $V=-\frac{1}{2}$ at the very bottom of potential curve shown in the figure.
In order to get value of D_e, the spectroscopic dissociation energy measured from the Bottom of curve can be By using Morse Potential function

$$D_e = \frac{G(V)^2}{4 x_e \omega_e}$$

For the chloroform C-H Bond, D_e calculated by this equation is 39250 cm^{-1} which is in rough agreement with experiment.

The force constant K_e can be calculated for anharmonic oscillator for infinitesimal displacement

$$\nu_{osc} = c\omega_e = \frac{1}{2\pi}\sqrt{\frac{K_e}{\mu}}$$

$$\boxed{K_e = 4\pi^2 c^2 \mu \omega_e^2}$$

Example:
If we consider HCl molecule having fundamental band at 2989 cm^{-1}.

$$\mu = \frac{\mu_H \mu_{Cl}}{\mu_H + \mu_{Cl}} = 1.61 \times 10^{-27} \text{ kg}$$

$$\omega_e = 2989 \text{ cm}^{-1}$$
$$= 298900 \text{ m}^{-1}$$

then

$$K_e = 4\pi^2 c^2 \mu \omega_e^2$$
$$= 4 \times (3.14)^2 \times (3\times10^8)^2 \times (1.61\times10^{-27}) \times (298900)^2$$
$$= 510 \text{ N/m}$$

This is near the value of force constant $K = 480$ N/m for harmonic oscillator of HCl by using

$$K = 4\pi^2 \mu c^2 \omega^2$$

where $\omega = 2886$ cm^{-1}

Isotope effect of vibrational levels:

Different isotopic molecules have different vibrational levels and therefore vibrational frequencies are different.

The classical frequency of molecule assumed as harmonic oscillator is

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

The force constant K is determined by electronic motion only therefore value of K remains same for different isotopic molecules.

Hence $\nu_{osc} \propto \frac{1}{\sqrt{\mu}}$

The reduced mass is different for different isotopes. If ω^i is vibrational constant for heavier isotope having reducedmass μ^i then

$$\nu^i_{osc} \propto \frac{1}{\sqrt{\mu^i}} \propto \frac{1}{\sqrt{\mu^i}}$$

$$\frac{\omega^i}{\omega} = \frac{\nu^i_{osc}}{\nu_{osc}} = \sqrt{\frac{\mu}{\mu^i}} = \rho$$

Since $\mu^i > \mu$ therefore $\rho < 1$

The vibrational term of two isotopic molecules

Treating as Harmonic oscillator:-

For Harmonic oscillator

$$G(V) = \omega\left(V + \tfrac{1}{2}\right)$$

$$G^i(V) = \omega^i\left(V + \tfrac{1}{2}\right)$$

Isotopic shift

$$G^i(V) - G(V) = \left(V + \tfrac{1}{2}\right)(\omega^i - \omega)$$

$$= (\rho - 1)\left(V + \tfrac{1}{2}\right)$$

As $\rho < 1$ then

$$\boxed{G^i(V) \leq G(V)}$$

Vibrational levels of heavier isotope are lower than corresponding vibrational levels of

lighter isotope.

Treating as Anharmonic oscillator

For anharmonic oscillator

$$G(V) = \omega_e\left(V+\tfrac{1}{2}\right) - \omega_e x_e \left(V+\tfrac{1}{2}\right)^2$$

$$G'(V) = \omega_e'\left(V+\tfrac{1}{2}\right) - \omega_e' x_e' \left(V+\tfrac{1}{2}\right)^2$$

$$= \rho\omega_e\left(V+\tfrac{1}{2}\right) - \rho^2\omega_e x_e \left(V+\tfrac{1}{2}\right)^2$$

Because $\omega_e' = \rho\omega_e$

$\omega_e' x_e' = \rho^2 \omega_e x_e$

Isotopic shift

$$G'(V) - G(V) = (\rho-1)\omega_e\left(V+\tfrac{1}{2}\right) - (\rho^2-1)\omega_e x_e \left(V+\tfrac{1}{2}\right)^2$$

$$= (\rho-1)\left(V+\tfrac{1}{2}\right)\left[\omega_e - (\rho+1)\omega_e x_e \left(V+\tfrac{1}{2}\right)\right]$$

If ρ is slightly different from 1 then

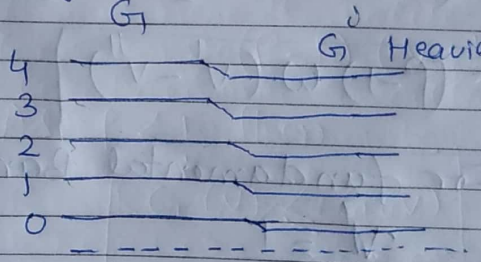
$\rho + 1 \simeq 2$

Then isotopic shift

$$G'(V) - G(V) = (\rho-1)\left(V+\tfrac{1}{2}\right)\left[\omega_e - 2\omega_e x_e \left(V+\tfrac{1}{2}\right)\right]$$

As $\rho < 1$ then $G'(V) < G(V)$

It means vibrational level of heavier isotope are lower than those of lighter and shift between corresponding levels increases with increasing V as shown in figure



If we ignore Anharmonicity then Band shift is

$$\Delta\nu = \nu' - \nu''$$

$$= (G_{i'} - G_{i''}) - (G' - G'')$$

use $G(v) = \omega(v+\frac{1}{2})$

$$\Delta\nu = [\rho\omega(v'+\tfrac{1}{2}) - \omega(v'+\tfrac{1}{2})]$$

$$- [\rho\omega(v''+\tfrac{1}{2}) - \omega(v''+\tfrac{1}{2})]$$

$$= [(\rho-1)\omega(v'+\tfrac{1}{2}) - (\rho-1)\omega(v''+\tfrac{1}{2})]$$

$$= (\rho-1)\omega(v'+\tfrac{1}{2} - v'' - \tfrac{1}{2})$$

$$\boxed{\Delta\nu = (\rho-1)\omega(v'-v'')}$$

For fundamental Band

$v' = 1$

$v'' = 0$

$$\boxed{\Delta\nu = (\rho-1)\omega}$$

The shift increases as the order of band increases.

Molecule as vibrating Rotator

OR

Fine structure of Infra Red Bands