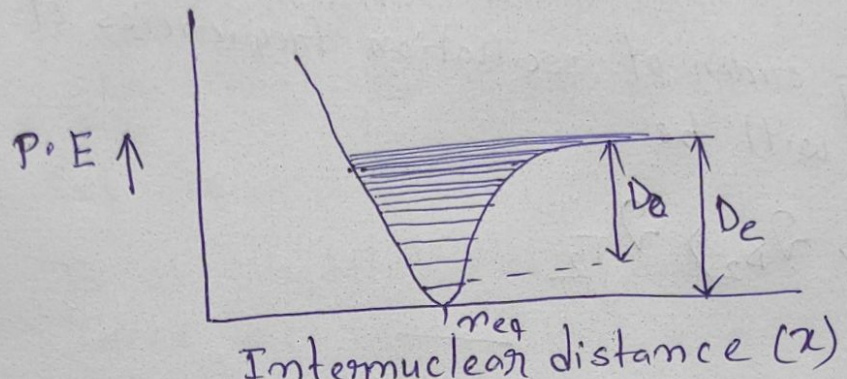
Effect of Isotope Substitution :-



In the potential energy diagram,

D_0 ⇒ Dissociation energy of the molecule

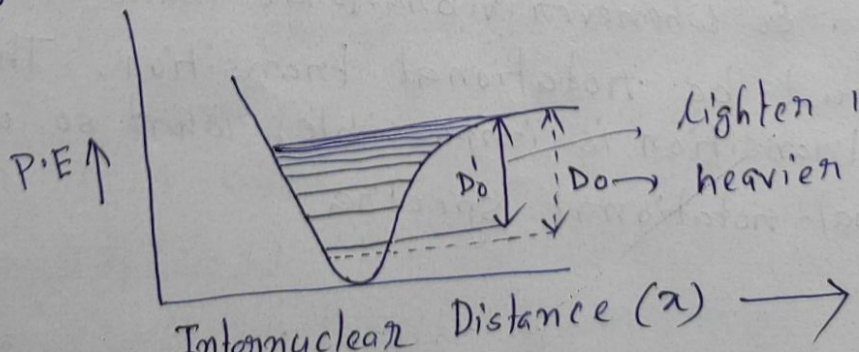
D_e = Equilibrium dissociation or binding energy

The oscilation frequency $\bar{\nu}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ k = force const. μ = Reduced mass

Now if we use heavier isotope, then reduced mass μ will increase. Hence oscillation frequency $\bar{\nu}_{osc}$ will decrease

As $\bar{\nu}_{osc}$ changes, zero point energy will be lower in case of heavier isotope.

The dissociation energy (D_0) of the heavier isotope become greater than that of higher isotope.



$$\bar{\nu}_{osc} \propto \frac{1}{\sqrt{\mu}}$$

The higher is the reduced mass, lower will be oscilation frequency.

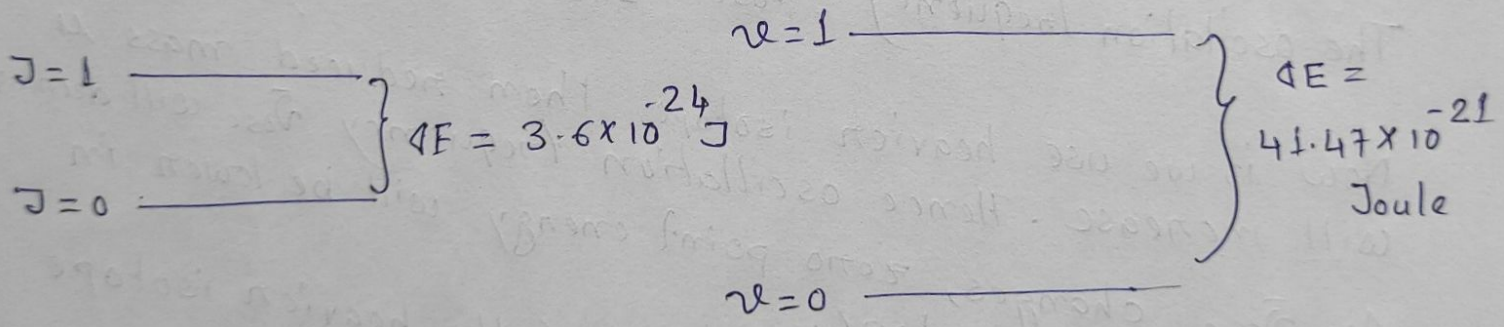
The decreasing order of oscillation frequencies of these isotope of H' will be

$$\bar{\nu}_{H_2} > \bar{\nu}_{D_2} > \bar{\nu}_{T_2}$$

Vibrational - Rotational Spectra :-

In case of rotational motion of a rigid rotator,

$$\bar{\epsilon}_{rot} = BJ(J+1)\ cm^{-1}$$



The energy difference between any two rotational energy levels is lower than that in case of vibrational energy. So whenever vibrational transitions takes place, there must be rotational transition. Thus pure vibrational transition is impossible, ~~what~~ so we observe vibrational-rotational spectra.

Each vibrational level is equally composed of a bunch of rotational levels and, thus rotational promotion or demotion must be superimposed. The corresponding spectrum is called vibrational-rotational spectra.

Energy Expression :-

To obtain total energy some approximation are taken. These are below.

Approximation 1. :

Born Openheimer Aproximation :-

The total energy during the vibrational-rotational transition will be sum of the vibrational energy and rotational energy.

The energy level of diatomic molecule according to the approximation corresponding to harmonic oscillator and rigid rotator is

$$\bar{\varepsilon} = \bar{\varepsilon}_{vib} + \varepsilon_{rot}$$

$$\bar{\varepsilon}_{total} = (v + \tfrac{1}{2})\,\bar{\nu}_{osc} + BJ(J+1) \quad cm^{-1}$$

$v = 0, 1, 2, 3 \ldots$

$J = 0, 1, 2, 3 \ldots$

The fundamental transition with rotational promotion and demotion, the energy change in the wave number scale is

$$\Delta\bar{\varepsilon} = \Delta\bar{\varepsilon}_{v=0 \to v=1} + \Delta\bar{\varepsilon}_{rot}$$

$$= \bar{\nu}_{osc}(1-2xe) + BJ_f(J_f+1) - BJ_i(J_i+1)$$

$$= \bar{\omega}_0 + BJ_f(J_f+1) - BJ_i(J_i+1) \qquad [\bar{\omega}_0 = \bar{\nu}_{osc}(1-2xe)$$

$$\Delta\bar{\varepsilon}_{total} = \bar{\omega}_0 + BJ_f(J_f+1) - BJ_i(J_i+1) \text{ in } cm^{-1}$$

2nd Approximation :-

The total energy change ΔE_{total}, we concidered the value of rotational const (B) to be constant both in $v=0$ and $v=1$. vibrational level. But actually the value of B will be different in $v=0$ and $v=1$. vibrational level. $B = \frac{h}{8\pi^2 I c}$. Now $v=0$ level and in $v=1$ level the values of r_0 will be different. Hence the value of B in $v=0$ will be different from that $v=1$ level. So taking the constant value of B both in $v=0$ and $v=1$ level is an approximation.

3rd Approximation :-

The above energy expression $\Delta \bar{E}_{total}$, we concidered the rotational energy expression of a rigid rotator i.e., vibrational transition is not occuring with rotational transition simultaneously. So concidering the molecule as a rigid rotator is also another important approximation.

Selection rule :-

For vibrational-rotational spectroscopy selection rule is $\Delta v = \pm 1$ $\Delta J = \pm 1$.

In exceptional case, where diatomic molecule have an angular momentum about the internuclear axis (e.g. NO) the selection rule allows $\Delta J = 0$.

P- Branch :-

we have total energy expression as,

$\Delta \bar{E}_{total} = \bar{\omega}_0 + BJ_f(J_f+1) - BJ_i(J_i+1)$ in cm^{-1}