

We consider hypothetical energy state obtained by putting $v = -\frac{1}{2}$ (at which $\epsilon = 0$ according to eqⁿ (3)) the molecule would be at the equilibrium point with zero vibrational energy.

It's oscillator frequency (in cm^{-1}) would be:

$$\bar{\omega}_{osc} = \bar{\omega}_e$$

$\bar{\omega}_e \rightarrow$ equilibrium oscillator frequency of the anharmonic system (hypothetical)

For any real state \rightarrow positive integral $v \rightarrow$ the oscillator frequency will be given by eqⁿ (14).

In ground state ($v=0$)

$$\bar{\omega}_0 = \bar{\omega}_e (1 - \frac{1}{2} x_e) \text{ cm}^{-1}$$

$$\text{and } \epsilon_0 = \frac{1}{2} \bar{\omega}_e (1 - \frac{1}{2} x_e) \text{ cm}^{-1}$$

This zero point energy differs from that of the harmonic oscillator.

The selection rules for anharmonic oscillator are found to be

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

Same as harmonic oscillator, additional possibility of larger jumps. Observed in practice to be rapidly diminishing probability and normally the lines of $\Delta v = \pm 1, \pm 2, \pm 3$ have observable intensity.

The spacing between the vibrational level is, of order 10^3 cm^{-1} and at room temp, we may

Show by Boltzmann distribution that

(35)

$$\frac{N_{v=1}}{N_{v=0}} \approx \exp(-4.8) \approx 0.008$$

\Rightarrow Population of the $v=1$ state is nearly 0.01 or some one% of the ground state population. Thus, we may ignore all transitions originating at $v=1$ or more, and restrict to three transitions;

1. $v=0 \rightarrow v=1$, $\Delta v = +1$ large intensity

$$\Delta E = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1} \quad \text{--- 15(a)}$$

2. $v=0 \rightarrow v=2$, $\Delta v = +2$, small intensity

$$\Delta E = 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1} \quad \text{--- 15(b)}$$

3. $v=0 \rightarrow v=3$, $\Delta v = +3$, negligible intensity

$$\Delta E = 3\bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1} \quad \text{--- 15(c)}$$

To a good approximation, since $x_e \approx 0.01$, the three spectral lines lie very close to $\bar{\omega}_e$, $2\bar{\omega}_e$ and $3\bar{\omega}_e$.

line for $v=0$ to 1 \rightarrow fundamental absorption near $\bar{\omega}_e$.

near $2\bar{\omega}_e$ for $v=0$ to 2 \rightarrow first overtone (second harmonic)

near $3\bar{\omega}_e$ for $v=0$ to 3 \rightarrow second overtone (third harmonic)

Spectrum of HCl, shows a very intense absorption^{ch.} at 2886 cm^{-1} , a weaker one at 5668 cm^{-1} and very weak one at 8347 cm^{-1} . To find the equilibrium frequency of the molecule

from these values, we solve any two of three eqⁿs

$$\bar{\omega}_e (1 - 2x_e) = 2886$$

$$2\bar{\omega}_e (1 - 3x_e) = 5668$$

$$3\bar{\omega}_e (1 - 4x_e) = 8347 \text{ cm}^{-1}$$

and find $\bar{\omega}_e = 2990 \text{ cm}^{-1}$, $x_e = 0.0174$

We see that for anharmonic molecule the observed fundamental absorption frequency and the equilibrium frequency may differ considerably \rightarrow different from harmonic oscillator spectral absorption.

The force constant of the bond in HCl may be calculated directly

$$k = 4\pi^2 \bar{\omega}_e^2 c^2 \mu \text{ N m}^{-1}$$
$$= 516 \text{ N m}^{-1}$$

The Interactions of Rotations and Vibrations :- The

Diatomic Vibrating-Rotator

Typical diatomic molecule has rotational energy separations of 1-10 cm^{-1} , vibrational energy separations of HCl were nearly 3000 cm^{-1} .

Two motions have very different energies, as a first approximation \rightarrow consider that a diatomic molecule can execute rotations and vibrations quite independently.

Born-Oppenheimer approximation \rightarrow combined rotational - vibrational energy is simply the sum of the separate energies:

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \quad (\text{Joules}) \quad (37)$$

$$\Sigma_{\text{total}} = \Sigma_{\text{rot}} + \Sigma_{\text{vib}} \quad (\text{cm}^{-1}) \quad \text{--- (16)}$$

Taking separate expressions for Σ_{rot} and Σ_{vib} , we have:

$$\Sigma_{J,v} = \Sigma_J + \Sigma_v$$

$$= B J(J+1) - D J^2(J+1)^2 + H J^3(J+1)^3 + \dots + (v + \frac{1}{2}) \bar{\omega}_e - \chi_e (v + \frac{1}{2})^2 \bar{\omega}_e \quad \text{--- (17)}$$

Ignoring small centrifugal distortion constants D, H, \dots

$$\Sigma_{\text{total}} \approx \Sigma_{J,v} = B(J+1)J + (v + \frac{1}{2}) \bar{\omega}_e - \chi_e (v + \frac{1}{2})^2 \bar{\omega}_e \quad \text{--- (18)}$$

However, it is not logical to ignore $D \rightarrow$ that implies molecule to be rigid \rightarrow vibrable?

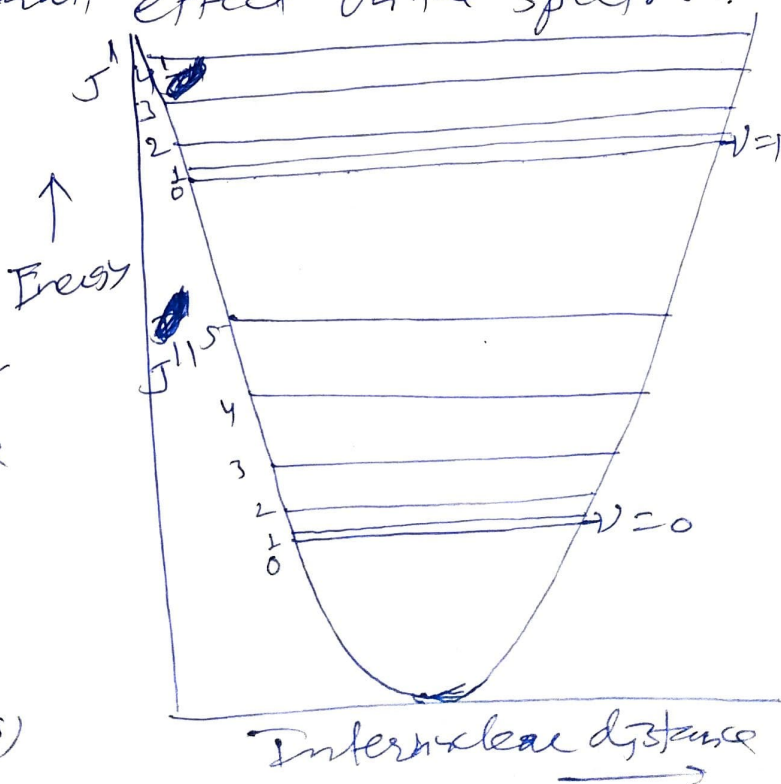
Retention of $D \rightarrow$ small effect on the spectrum.

Rotational levels \rightarrow for the two lowest vibrational levels $v=0$ and $v=1$

The selection rules for combined motions are the same as those for each separately;

$$\Delta v = \pm 1, \pm 2 \text{ etc.}$$

$$\Delta J = \pm 1 \quad \text{--- (15)}$$



We may also have $\Delta v = 0$ \rightarrow purely rotational (38)
transitions

However, a diatomic molecule, except under very special and rare circumstances, may not have $\Delta J = 0$; \rightarrow a vibrational change must be accompanied by a simultaneous rotational change.

Rotational levels J'' are filled to varying degrees in any molecular population \rightarrow transitions shown will occur with varying intensities.

Expression for spectrum \rightarrow obtained by applying the selection rules (eq 15) to the energy levels (eq 18), only the $v=0$ to $v=1$ transitions considered here

$$\begin{aligned} \Delta E_{J,v} &= E_{J', v=1} - E_{J'', v=0} \\ &= B J'(J'+1) + \frac{1}{2} \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e - \left\{ B J''(J''+1) + \frac{1}{2} \bar{\omega}_e - \frac{1}{4} x_e \bar{\omega}_e \right\} \\ &= \bar{\omega}_0 + B (J' - J'') (J' + J'' + 1) \text{ cm}^{-1} \end{aligned}$$

where $\bar{\omega}_0 \rightarrow \bar{\omega}_e (1 - 2x_e)$

$R \rightarrow$ identical in the upper and lower vibrational states
 \rightarrow direct consequence of the Born-Oppenheimer approximation \rightarrow rotation is unaffected by vibrational changes.

We can have:

1. $\Delta J = +1$, i.e. $J' = J'' + 1$ or $J' - J'' = +1$
 $\Delta E_{J,v} = \bar{\omega}_0 + 2B (J'' + 1) \text{ cm}^{-1}$ $J'' = 0, 1, 2, \dots$ 20 (a)
2. $\Delta J = -1$, i.e. $J'' = J' + 1$ or $J' - J'' = -1$; and
 $\Delta E_{J,v} = \bar{\omega}_0 - 2B (J' + 1) \text{ cm}^{-1}$ $J' = 0, 1, 2, \dots$ 20 (b)