The non rigid rotator

In rigid rotator concept predicts that the spectral lines are separated by $2B$.

i.e., $\bar{\nu}_{J \to J+1} = 2B(J+1)\ cm^{-1}$

But in some cases (eg. HF), the constant separation $2B$ is not observed. There is a decrease in the separation is observed in the case of HF. (The separation between successive spectral lines is not a constant.)

The internuclear distances (r) increases with J. This means that the bond-length increases with J. ∴ The assumption of a rigid bond is only an approximation.

When the bond is elastic, the bond will stretch and compress periodically with a fundamental frequency depending on the masses of the atoms and the elasticity of the bond. If the motion is simple harmonic, the force constant is given by

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu$$

The variation of B with J is determined by the force constant.

2c

Elasticity of the bond also effects the quantities γ and B during a vibration.

The measured B value is an average value over time.

$$B = \frac{h}{8\pi^2 c I} = \frac{h}{8\pi^2 c \mu r^2}$$

$$\therefore \; B \propto \frac{1}{r^2}$$

The average value (over time) of $\frac{1}{r^2}$ is not equal to $\frac{1}{r_e^2}$, where r_e is the equilibrium distance between the atoms.

Consider a bond with equilibrium separation r_e of 0.1 nm vibrating between the limits 0.09 and 0.11 nm.

$$\langle r \rangle_{av} = \frac{0.09 + 0.11}{2} = 0.1 = r_e$$

But

$$\left\langle \frac{1}{r^2} \right\rangle_{av} = \frac{\left(\frac{1}{0.09}\right)^2 + \left(1/_{0.11}\right)^2}{2} = 103.05 \text{ nm}^{-2}$$

and

$$\langle r \rangle_{av} = \sqrt{\frac{1}{103.05}} = 0.0985 \text{ nm.}$$

Hence usually 3 different B values are possible. At equilibrium separation r_e, $B = B_e$.

In the vibrational ground state the average internuclear separation r_0 is associated with $B = B_0$.

At any vibrational level the internuclear distance r_v has $B = B_v$

Spectrum of non rigid rotator (1) d

Using Schrodinger equation the rotational energy levels of a non-rigid rotator can be calculated using

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \quad \text{Joule.}$$

$$\varepsilon_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2(J+1)^2 \quad \text{cm}^{-1}$$

$B \rightarrow$ rotational constant

$D \rightarrow$ centrifugal distortion constant — harmonic approximation

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \quad \text{cm}^{-1}$$

For anharmonic oscillations

$$I = \mu r^2$$
$$\mu = \frac{I}{r^2}$$
$$\mu^3 = \frac{I^3}{r^6}$$
$$r^2 = \frac{I}{\mu}$$

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + kJ^4(J+1)^4 \ldots \quad \text{cm}^{-1}$$

From the expressions for B and D

$$D = \frac{16 B^3 \pi^2 \mu c^2}{k}$$

$$B = \frac{h}{8\pi^2 I c}$$

$$B^3 = \frac{h^3}{8^3 \pi^6 I^3 c^3}$$

$$B^3 = \frac{h^3}{512\pi^6 I^3 c^3}$$

$$B^3 c^2 = \frac{h^3}{512\pi^6 I^3 c}$$

$$= \frac{h^3}{512\pi^6} \mu^3 r^6 c$$

$$B^3 c^2 = \frac{h^3}{512\pi^8} \mu^3$$

$$= \frac{4B^3}{\bar{\omega}^2}$$

D → of the order of 10^{-3} cm^{-1}

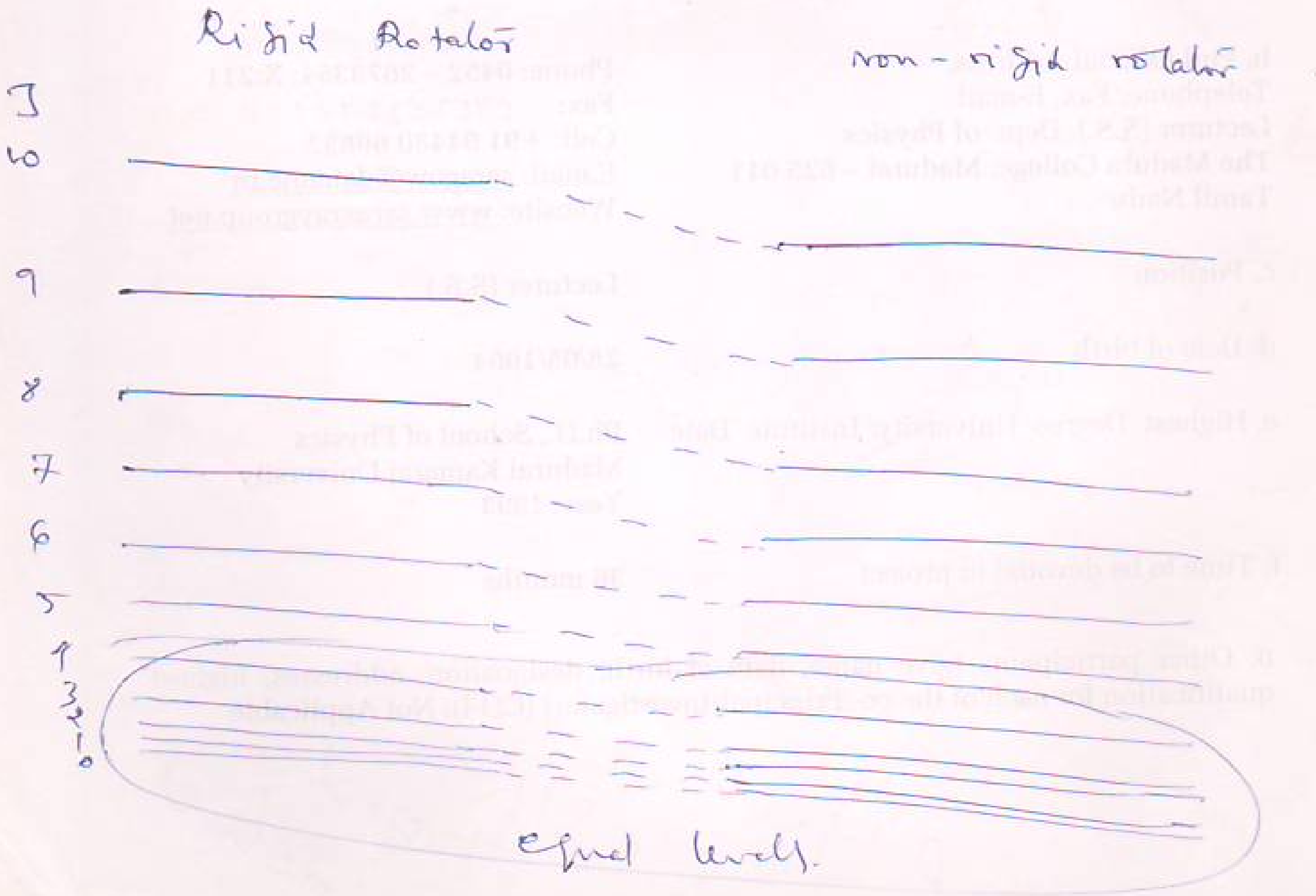
B → " " 10 cm^{-1}

∴ D is negligible compared to B

∴ $D(J+1)^2 J^2$ is also negligible, for small J.

For larger J values ~~the~~ the correction $D J^2 (J+1)^2$ becomes appreciable.

The lowering of energy levels when going from rigid to non-rigid rotator is shown in the figure.



As J increases, D becomes appreciable and energy is lowered in non-rigid rotator

E ($E_J = B J(J+1) - D J^2 (J+1)^2$ cm^{-1})

(3) d

$$\mathcal{E}_{J+1} - \mathcal{E}_J = \bar{\nu}_J$$

$$= B\left[(J+1)(J+2) - J(J+1)\right]$$

$$- D\left[(J+1)^2(J+2)^2 - J^2(J+1)^2\right]$$

$$\cancel{= B\left[J^2 + 2J + J + 2 - J^2 - J\right]}$$

$$\cancel{= D\left[\right.}$$

$$= B\left[(J+1)\left\{(\cancel{J}+2) - \cancel{J}\right\}\right]$$

$$- D\left[(J+1)^2 \left\{\underbrace{(J+2)^2 - J^2}_{(J^2+4+4J-J^2)}\right\}\right]$$

$$= 2B(J+1) - D\left[J^2 + 1 + 2J\,(4 + 4J)\right]$$

$$= 2B(J+1) - D\left[4J^2 + 4 + 8J + 4J^3 + 4J + 8J^2\right]$$

$$= \;,,\; \quad -4D\left[J^3 + 1 + 2J + J^3 + J + 2J^2\right]$$

$$= \;,,\; \quad -4D\left[J^3 + 3J^2 + 3J + 1\right]$$

$$\bar{\nu}_J = 2B(J+1) - 4D(J+1)^3 \quad cm^{-1}$$

From D, the $\bar{\omega}$ values can be determined.

$$\bar{\omega}^2 = \frac{4B^3}{D}$$

& hence the force constant

$K = 4\pi^2 c^2 \bar{\omega}^2 \mu$ can also be determined.