

The Non-Rigid Rotator: From the spectrum of hydrogen fluoride, it is evident that the separation between successive lines (and hence the B values) decreases steadily with increasing J .

Rotation Spectrum of HF

J	$\bar{\nu}_{obs}$ (cm^{-1})	$\bar{\nu}_{calc}$ (cm^{-1})	$\Delta\bar{\nu}_{obs}$ (cm^{-1})	B ($=\frac{1}{2}\Delta\bar{\nu}$)	r (nm)
0	41.08	41.11	41.11	20.56	0.929
1	82.19	82.18	40.96	20.48	0.0931
2	123.15	123.14	40.85	20.43	0.0932
4	204.62	204.55	40.31	20.16	0.0938
⋮	⋮	⋮	⋮	⋮	⋮
10	441.13	441.00	37.71	18.91	0.0969

The bond length increases with J and we see that our assumption of a rigid bond is only an approximation
 → all bonds are elastic to some extent, and the increase in length with J merely reflects ~~that~~ the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart.

Consequences of elasticity → (i) When the bond is elastic, a molecule may have ~~the~~ vibrational energy. — i.e.

The bond will stretch and compress periodically (12) with a certain fundamental frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond.

If the motion is simple harmonic, the force constant is given by

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \quad \text{--- (1)}$$

$\bar{\omega} \rightarrow$ vibrational frequency (in cm^{-1})

$c, \mu \rightarrow$ as usual

The variation of B with $J \rightarrow$ determined by the force constant

(ii) Second consequence \rightarrow r and B vary during a vibration. These quantities are measured by microwave techniques \rightarrow many hundreds of vibrations occur during a rotation, measured value is an average.

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

or $B \propto \frac{1}{r^2}$, other quantities are independent of vibration.

The average value of $\frac{1}{r^2}$ is not equal to $\frac{1}{r_e^2}$,

where $r_e \rightarrow$ equilibrium distance.

Real vibrations are not simple harmonic, since a real bond may be stretched more easily than it may be compressed, and this usually results in r_{av} being greater than r_{eq} .

Three different sets of values for B and r . (13)

At the equilibrium separation, r_e , between the nuclei, the rotational constant is B_e ; in the vibrational ground state the average internuclear separation is r_0 associated with a rotational constant B_0 ; while if the molecule has excess vibrational energy the quantities are r_v and B_v , where $v \rightarrow$ vibrational quantum number.

The Spectrum of a Non-Rigid Rotator

The Schrödinger wave eqⁿ may be set up for a non-rigid molecule and the rotational energy levels are found to be

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

$$\text{or } E_J = \frac{E_J}{hc} = B J(J+1) - D J^2(J+1)^2 \quad \text{--- (2)}$$

$B \rightarrow$ rotational constant as defined earlier

Centrifugal distortion constant D ;

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

eqⁿ (2) applies for a simple harmonic force field only, a positive quantity. If the force field is ~~anisotropic~~ anharmonic

$$E_J = B J(J+1) - D J^2(J+1)^2 + H J^3(J+1)^3 + K J^4(J+1)^4 \quad \text{--- (4)}$$

H, k, \dots small constants dependent upon the (14) geometry of the molecule. They are negligible compared with D

From the relation of B and D

$$D = \frac{16 B^3 \pi^2 \mu c^2}{k} = \frac{4 B^3}{\bar{\omega}^2} \quad \text{--- (5)}$$

$\bar{\omega} \rightarrow$ vibrational frequency of the bond.

The vibrational frequencies are usually of the order 10^3 cm^{-1} . $B \rightarrow$ of the order of 10 cm^{-1}

$D \rightarrow$ being of the order 10^{-3} cm^{-1} , is very small compared with B . For small J , the correction

term $DJ^2(J+1)^2 \rightarrow$ almost negligible, for J values of 10 or more it may become appreciable

There is lowering of rotational levels when passing from the rigid to non-rigid molecule. The selection rule is still $\Delta J = \pm 1$.

The analytical expressions for the transitions:

$$E_{J+1} - E_J = \bar{\nu}_J = B[(J+1)(J+2) - J(J+1)]$$

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

$$= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \quad \text{--- (6)}$$

$\bar{\nu}_J \rightarrow$ upward transition from J to $J+1$ or the downward from $J+1$ to J .

The spectrum of the elastic rotor is similar to that of the rigid molecule except that each line is displaced slightly to the low frequency, the displacement increases with $(J+1)^3$.

Knowledge of D gives rise to two useful items of information \rightarrow it allows to determine the J values of lines in an observed spectrum.

\rightarrow A knowledge of D enables us to determine the vibrational frequency (although ~~not~~ ^{not} accurate) of a diatomic molecule. For HF

The force constant
 $k = 4\pi^2 c^2 \omega^2 \mu$
 $= 960 \text{ Nm}^{-1}$
 H-F \rightarrow relatively strong bond

$$\omega^2 = \frac{4B^3}{D} = 16.33 \times 10^6 \text{ cm}^{-1}$$

i.e. $\omega \approx 4050 \text{ cm}^{-1}$, more precise determination leads to value 4138.3 cm^{-1}

