Molecular Spectra

Molecular Energy

We can picture a molecule as an assembly of small almost point masses-the nuclei of its component atoms , linked together by almost mass less springs-the bonding electrons the total energy of a molecule , $E_{\text{molecules}}$ can be viewed as the sum of its electronic energy , $E_{\text{electronic}}$ its vibrational energy , $E_{\text{vibration}}$ and its rotational energy , E_{rotation} :

$E_{\text{molecule}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$

The vibrational and rotational energies are both related to the motion of the nuclei of the molecules constituent atoms .

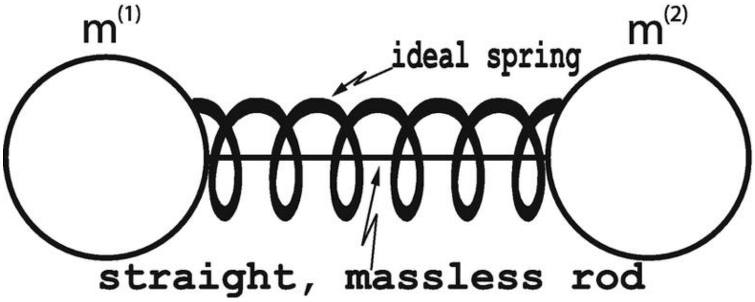


Fig. 4 A diatomic molecule pictured as two spherical massless spring

Also quantized , i.e. , they can only take certain discrete values . Thus , every molecule has a characteristic set of vibrational energy levels and rotational energy levels . Typical values for the differences ΔE_{elec} , ΔE_{vib} and ΔE_{rot} , between adjacent , electronic , vibrational and rotational energy levels are , respectively

$$\Delta E_{elec} = 1\text{- }10 \text{ eV}$$

$$\Delta E_{vib} \approx 10^{-1} \text{ eV}$$

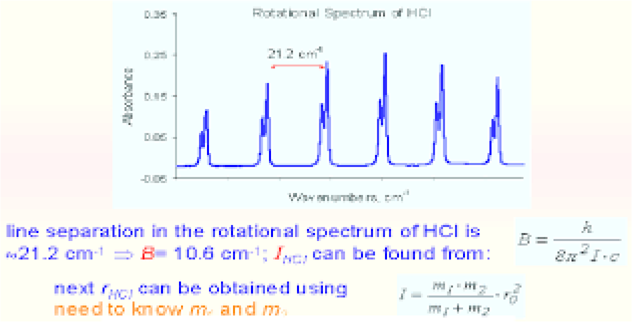
$$\Delta E_{rot} \approx 10^{-4} \text{ eV}$$

Rotational Spectra

Fig. 6 , shows a typical rotational absorption spectrum , that of gaseous hydrogen chloride ,$HCL_{(g)}$. The spectrum exhibits two principle characteristics:

1. It comprises many lines, all of comparable intensity.

2. The absorption lines are equally spaced along the frequency axis.



line separation in the rotational spectrum of HCl is ≈21.2 cm^{-1} ⇒ B= 10.6 cm^{-1}; I_{HCl} can be found from:

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

next r_{HCl} can be obtained using

need to know m_1 and m_2

$$I = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot r_0^2$$

Fig. 5 Rotational absorption spectrum of HCL

By analogy with the expression K= $\frac{p2}{2m}$, that relates an object 's Kinetic energy , K , to its linear momentum ,P, and the rotational energy , E_{rot} , of a diatomic molecule , such as that pictured schematically in fig. 4 , revolving around an axis through its center of mass is given by:

$$E_{rot} = L^2/2I \qquad \text{..........(1)}$$

Where L is the molecule s angular momentum and I is its moment of inertia about this axis,

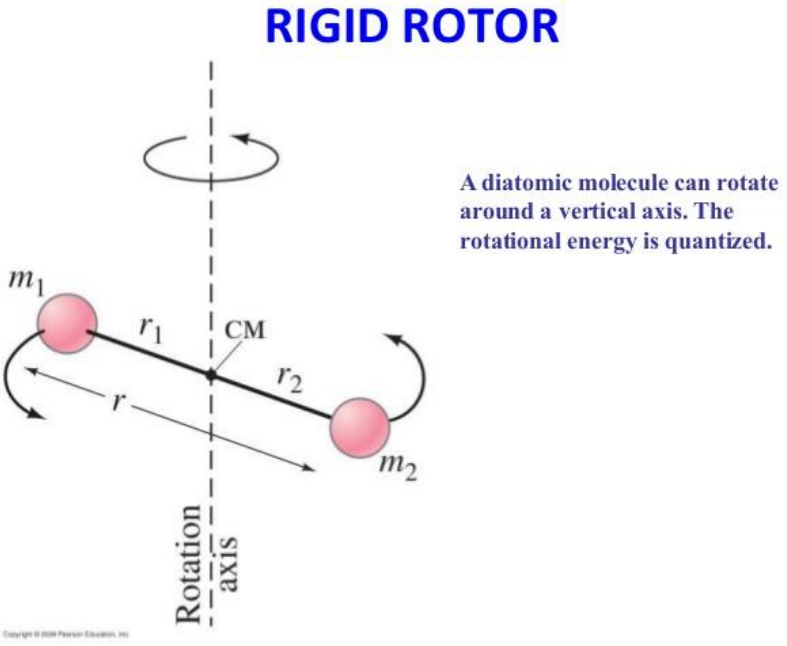


Fig. 6 A schematic representation of diatomic molecule such as HCL around an axis through its center of mass

The rotational energy eigenvalues of the molecule emerge from the quantization of its angular momentum. The square, L^2, of the magnitude of the molecule s angular momentum obeys the quantization condition:

$$L^2 = J(J+1)\hbar^2 \qquad \text{..........(2)}$$

Where the rotational quantum number J can take the values J= 0,1,2,3,…. Substituting the allowed values of L^2 in equation (2) gives for the rotational energy eigenvalues (the rotational energy levels):

$E_{rot =}\ J(J+1)ŋ^{2} / 2I = J(J+1)Bh$ ……..(3)

Where the constant B is defined by

$B = h \Big/ 8\pi^2 I$ …………..(4)

The difference, ΔE_{rot}, between two adjacent rotational energy levels, the J level and the J+1 level, is:

$\Delta E_{rot} = [(J+1)(J+2)-J(J+1)]\ Bh$ ……….(5)

$=2Bh(J+1)$

It follows, that the difference, ΔE_{rot}, increases by an amount 2Bh with each unit increase in the quantum number J, i.e, the differences between adjacent rotational energy levels increase linearly with the quantum number J.

The selection rule for radiative rotational transitions is $\Delta J = \pm 1$. Hence, the frequencies, V of the photons associated with such transitions will be:

$V = \Delta E_{rot} \Big/ h = 2B(J+1)$ ……….(6)

And the difference, ΔV, between the frequencies of successive spectral lines a constant :

$\Delta V = 2B$ ………(7)