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Physical Chemistry - IV (Theo)

Topic : Rotational Spectroscopy

2.2 ROTATIONAL SPECTRA

We have seen that rotational energy, along with all other forms of molecular energy, is quantized: this means that a molecule cannot have any arbitrary amount of rotational energy (i.e., any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values—the so-called rotational energy levels—may in principle be calculated for any molecule by solving the Schrödinger equation for the system represented by that molecule. For simple molecules the mathematics involved is straightforward but tedious, while for complicated systems it is probably impossible without gross approximations. We shall not concern ourselves unduly with this, however, being content merely to accept the results of existing solutions and to point out where reasonable approximations may lead.

We shall consider each class of rotating molecule in turn, discussing the linear molecule in most detail, because much of its treatment can be directly extended to symmetrical and unsymmetrical molecules.

I_A = Moment of inertia due to rotation about the bond axis
 I_B = due to end-over-end rotation in the plane of the paper
 I_C = ... \perp to ...

2.3 DIATOMIC MOLECULES *for linear molecules*

$I_B = I_C, I_A = 0.$ ✓

2.3.1 The Rigid Diatomic Molecule

We start with this, the simplest of all linear molecules, shown in Fig. 2.1. Masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is

$r_0 = r_1 + r_2$ (2.5)

The molecule rotates end-over-end about a point C , the centre of gravity; this is defined by the moment, or balancing, equation:

$m_1 r_1 = m_2 r_2$ (2.6) *rotation about the bond axis is supposed to be zero ($= I_A = 0$)*

The moment of inertia about C is defined by:

$I = m_1 r_1^2 + m_2 r_2^2$
 $= m_2 r_2 r_1 + m_1 r_1 r_2$ (from (2.6))
 $= r_1 r_2 (m_1 + m_2)$ (2.7)

But, from (2.5) and (2.6):

$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$

therefore,

$r_1 = \frac{m_2 r_0}{m_1 + m_2}$ and $r_2 = \frac{m_1 r_0}{m_1 + m_2}$ (2.8) *$r_1 \neq r_2$ is the distance of particle from the centre of gravity*

Replacing (2.8) into (2.7):

$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$ (2.9)

where we have written $\mu = m_1 m_2 / (m_1 + m_2)$, and μ is called the *reduced mass* of the system. Equation (2.9) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

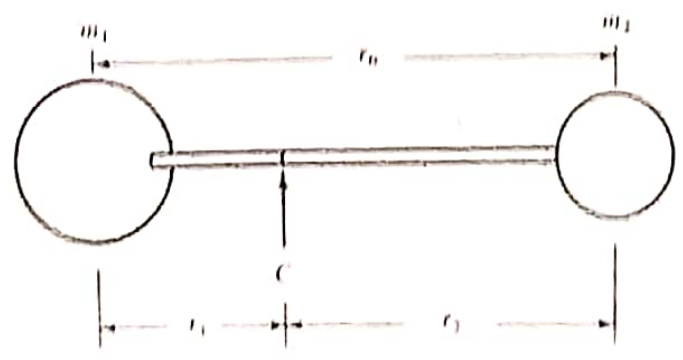


Figure 2.1 A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$.

In general, to raise the molecule from the state J to state $J + 1$, we would have:

$$\begin{aligned}\bar{\nu}_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)]\end{aligned}$$

or

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J+1) \text{ cm}^{-1} \quad (2.16)$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots, \text{cm}^{-1}$, while a similar lowering would result in an identical emission spectrum. This is shown at the foot of Fig. 2.3.

In deriving this pattern we have made the assumption that a transition can occur from a particular level only to its immediate neighbour, either above or below—we have not, for instance, considered the sequence of transitions $J = 0 \rightarrow J = 2 \rightarrow J = 4 \dots$. In fact, a rather sophisticated application of the Schrödinger wave equation shows that, for this molecule, we need only consider transitions in which J changes by one unit—all other transitions being spectroscopically *forbidden*. Such a result is called a *selection rule*, and we may formulate it for the rigid diatomic rotator as:

$$\text{Selection rule } \Delta J = \pm 1 \quad (2.17)$$

Thus Eq. (2.16) gives the *whole* spectrum to be expected from such a molecule.

Of course, only if the molecule is asymmetric (heteronuclear) will this spectrum be observed, since if it is homonuclear there will be no dipole component change during the rotation, and hence no interaction with radiation. Thus molecules such as HCl and CO will show a rotational spectrum, while N_2 and O_2 will not. Remember also, that rotation about the bond axis was rejected in Sec. 2.1; we can now see that there are two reasons for this. Firstly, the moment of inertia is very small about the bond so, applying Eqs. (2.10) or (2.11) we see that the energy levels would be extremely widely spaced; this means that a molecule requires a great deal of energy to be raised from the $J = 0$ to the $J = 1$ state, and such transitions do not occur under normal spectroscopic conditions. Thus diatomic (and all linear) molecules are in the $J = 0$ state for rotation about the bond axis, and they may be said to be not rotating. Secondly, even if such a transition should occur, there will be no dipole change and hence no spectrum.

To conclude this section we shall apply Eq. (2.16) to an observed spectrum in order to determine the moment of inertia and hence the bond length. Gilliam et al.† have measured the first line ($J = 0$) in the rotation

† Gilliam, Johnson, and Gordy, *Physical Review*, 7B, 140 (1950)

At higher quantum levels of rotation when the rotational energy is quite large, the rigid character of the rotator is affected and there is a tendency for the bond to stretch & x

$$\begin{aligned} \text{\AA} &= 10^{-8} \text{ cm} \\ &= 10^{-10} \text{ metre} \end{aligned}$$

$$\begin{aligned} 1 \text{ nm} &= 10^{-9} \text{ metre} \\ &= 10 \text{ \AA} \end{aligned}$$

spectrum of carbon monoxide as 3.84235 cm^{-1} . Hence from Eq. (2.16):

$$\bar{\nu}_{0-1} = 3.84235 = 2B \text{ cm}^{-1}$$

or,

$$B = 1.92118 \text{ cm}^{-1}$$

Rewriting Eq. (2.13) as: $I = h/8\pi^2 Bc$, we have

$$\begin{aligned} I_{\text{CO}} &= \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.99793 \times 10^{10} \times B} = \frac{27.9907 \times 10^{-47}}{B} \text{ kg m}^2 \\ &= 14.5695_4 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

Handwritten notes:
 h in joule
 $\frac{\text{Joule} \times \text{sec}}{\text{cm}^{-1} \times \text{cm}} = \text{Joule} \times \text{sec}^2$
 $\frac{\text{sec}}{\text{sec}} = \text{exp. sec.}^{-1} \times 10^{10}$
 $I = \text{kg} \cdot \text{m}^2$

where we express the velocity of light in cm s^{-1} , since B is in cm^{-1} . But the moment of inertia is μr^2 (cf. Eq. (2.9)) and, knowing the relative atomic weights ($H = 1.0080$) to be $C = 12.0000$, $O = 15.9994$, and the absolute mass of the hydrogen atom to be $1.67343 \times 10^{-27} \text{ kg}$, we can calculate the masses of carbon and oxygen, respectively, as 19.92168 and $26.56136 \times 10^{-27} \text{ kg}$. The reduced mass is then:

$$\mu = \frac{19.92168 \times 26.56136 \times 10^{-54}}{46.48303 \times 10^{-27}} = 11.38365 \times 10^{-27} \text{ kg}$$

Hence:

$$r^2 = \frac{I}{\mu} = 1.2799 \times 10^{-20} \text{ m}^2$$

and

$$r_{\text{CO}} = 0.1131 \text{ nm (or } 1.131 \text{ \AA)}$$

Handwritten calculations:
 $r = 1.131 \times 10^{-10} \text{ m}$
 $= 0.1131 \times 10^{-9} \text{ m}$
 $= 0.1131 \text{ nm}$

2.3.2 The Intensities of Spectral Lines

We want now to consider briefly the relative intensities of the spectral lines of Eq. (2.16); for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy levels. Does, for instance, a molecule have more or less chance of making the transition $J = 0 \rightarrow J = 1$ than the transition $J = 1 \rightarrow J = 2$? We mentioned above calculations which show that a change of $\Delta J = \pm 2, \pm 3$, etc., was forbidden—in other words, the transition probability for all these changes is zero. Precisely similar calculations show that the probability of all changes with $\Delta J = \pm 1$ is almost the same—all, to a good approximation, are equally likely to occur.

* The energy of rotation (assuming non-rigid character) is then expressed as
 $E_J = \frac{E_J}{h\nu} = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}$
 $D = \text{centrifugal distortion constant of the order of } 10^{-4} B$. The spectral lines will not then be exactly equidistant especially at higher levels.

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

where J is the rotational quantum number that can have values 0, 1, 2, 3 etc., and I is the moment of inertia of the molecule about the axis of rotation, i.e.,

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r_0^2 = \mu r_0^2$$

where m_1 and m_2 are the atomic masses of the two atoms of the diatomic molecule and

$$\frac{m_1 m_2}{m_1 + m_2} = \mu$$

is called the *reduced mass*.

Derivation of the expression for rotational energy: Centre of gravity of a diatomic molecule is the point which satisfies the following conditions

$$m_1 r_1 = m_2 r_2 \quad \text{---(i)}$$

The moment of inertia of the diatomic molecule is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{---(ii)}$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad \text{---(iii)}$$

$$= r_1 r_2 (m_1 + m_2) \quad \text{---(iv)}$$

But

$$r_1 + r_2 = r_0 \quad \text{---(v)}$$

∴ From eqn. (i),

$$m_1 r_1 = m_2 (r_0 - r_1)$$

or

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{---(vi)}$$

Similarly,

$$r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad \text{---(vii)}$$

Substituting these values in eqn. (ii), we get

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

$$= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$= \mu r_0^2 \left(\text{where } \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ is reduced mass} \right) \quad \text{---(viii)}$$

Now, by definition, the angular momentum of a rotating molecule is given by

$$L = I\omega \quad \text{---(ix)}$$

where ω is the angular velocity (just as linear momentum is mass \times velocity).

But angular momentum is quantized whose values are given by

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \quad \text{---(x)}$$

where $J = 0, 1, 2, 3, \dots$, called the *rotational quantum numbers*.

Further the energy of a rotating molecule is given by

$$E = \frac{1}{2} I\omega^2$$

The quantized value of the rotational energy will be given by

$$E_r = \frac{1}{2} I \omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad \text{---(x)}$$

Substituting the value of L . From eqn. (ix), we get

$$E_r = J(J+1) \frac{h^2}{4\pi^2} \times \frac{1}{2I} \quad \text{or} \quad E_r = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{---(xi)}$$

Putting $J = 0, 1, 2, 3$ etc. in equation (xi), pattern of the rotational energy levels obtained will be shown in Fig. 18.19.

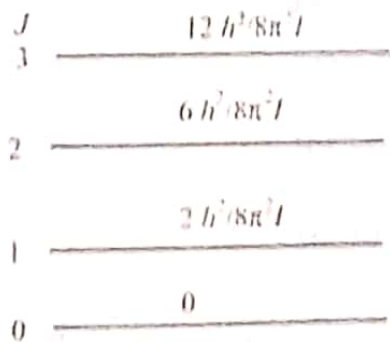


Fig. 18.19. Rotational energy levels of a diatomic molecule treating it as a rigid rotator

Evidently, the spacing between the energy levels increases as J increases, because of the $J(J+1)$ in eq. (xi).

Q.40. Derive an expression for the frequency and wave number of lines in the rotational spectrum.

Ans. Allowed rotational energies are given by the expression