

# Rotational Spectroscopy

## Rotational Spectra

Like all other forms of energy, rotational 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 Schrodinger equation for the system represented by that molecule.

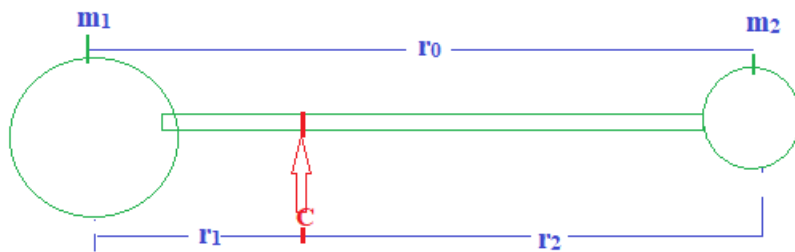
## The Rigid Diatomic Molecule

The simplest of all linear molecules shown in the Figure 3. Masses  $m_1$  and  $m_2$  are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2 \quad \dots\dots\dots(1)$$

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

$$m_1 r_1 = m_2 r_2 \quad \dots\dots\dots(2)$$



**Figure3:** A rigid diatomic molecule treated as two masses,  $m_1$ , and  $m_2$ , joined by a rigid bar of length  $r_0 = r_1 + r_2$ .

The moment of inertia about C is defined by:

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_2 r_1 \quad \text{(From Eq.2)} \\ &= r_2 r_1 (m_1 + m_2) \end{aligned}$$

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However from Eq.1 and Eq.2:

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

Therefore,

$$r_1 = \frac{m_2}{m_1 + m_2} r_0$$

$$r_2 = \frac{m_1}{m_1 + m_2} r_0$$

Replacing r values in Eq.2

$$\begin{aligned}
 I &= m_1 \left( \frac{m_2}{m_1 + m_2} r_0 \right)^2 + m_2 \left( \frac{m_1}{m_1 + m_2} r_0 \right)^2 \\
 &= \left( \frac{m_1 m_2}{m_1 + m_2} \right) r_0^2 \\
 &= \mu r_0^2 \dots\dots\dots(3)
 \end{aligned}$$

Where

$$\mu = \left( \frac{m_1 m_2}{m_1 + m_2} \right)$$

and  $\mu$  is called *reduced mass* of the system.

Equation (3) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

The Schrodinger equation for the rigid rotator is given by

$$-\frac{\hbar^2}{8\pi^2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = E \psi \dots\dots\dots(4)$$

By the use of the Schrodinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \text{ Joules} \dots\dots\dots(5)$$

Where  $J=0,1,2,\dots\dots\dots$



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In this expression  $h$  is Planck's constant, and  $I$  is the moment of inertia, either  $I_B$  or  $I_C$ , since both are equal. The quantity  $J$ , which can take integral values from zero upwards, is called the **rotational quantum number**: its restriction to integral values arises directly out of the solution to the Schrodinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy level to the molecule.

Eq. (5) expressed the allowed energies in joule; but differences of energy is more interested in the present discussion or, more particularly, in the corresponding frequency,  $\nu = \Delta E/h$  Hz, or wave number,  $\bar{\nu} = \Delta E/hc$   $\text{cm}^{-1}$ , of the radiation emitted or absorbed as a consequence of changes between energy levels. In the rotational region spectra are usually discussed in terms of the wavenumber, so it is useful to consider energies expressed in these units.

$$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \quad (J=0,1,2,\dots) \dots\dots\dots(6)$$

Where velocity of light, is here expressed in  $\text{cm s}^{-1}$ , since the unit of wavenumber is reciprocal centimeters.

Eq.(6) is usually abbreviated to

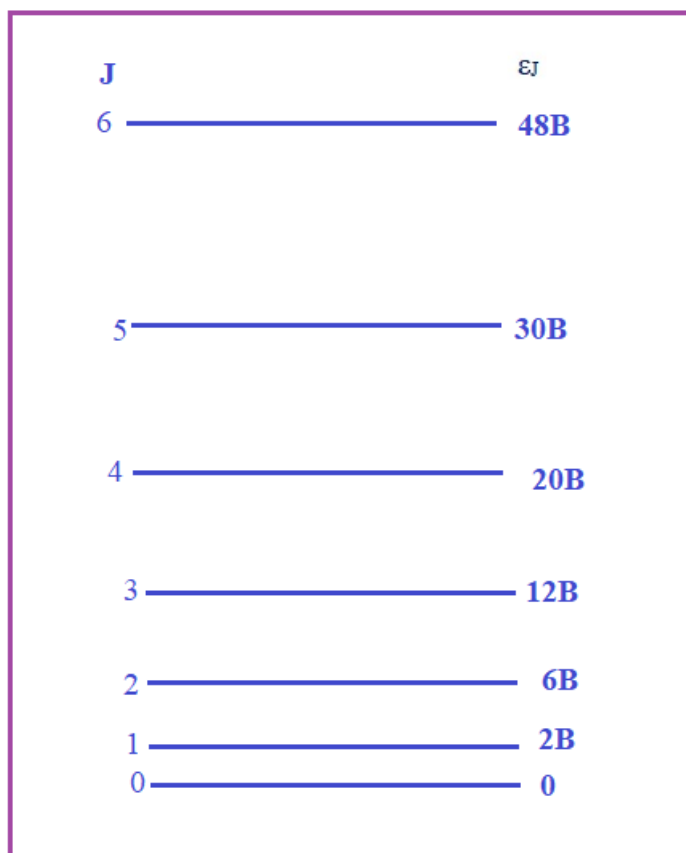
$$\epsilon_J = B J(J+1) \text{ cm}^{-1} \quad (J=0,1,2,\dots) \dots\dots\dots(7)$$

Where  $B$  is the **rotational constant**, is given by

$$B = \frac{h}{8\pi^2 I_B c} \text{ cm}^{-1} \dots\dots\dots(8)$$

in which  $I_B$  is explicitly used for moment of inertia.  $I_C$  may be used instead of  $I_B$  and a rotational constant as  $C$ , but the notation of Eq. (7) is conventional.

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**Figure 4: The allowed rotational energies of a rigid diatomic molecule**

From Eq.(7), the allowed energy level can be shown diagrammatically as Figure 4.

Plainly for  $J=0$ , as  $\epsilon_J=0$ , it can be understood that the molecule is not rotating at all. For  $J=1$ , the rotational energy is  $\epsilon_1 = 2B$  and a rotating molecule then has its lowest angular momentum. With the continuance of the process of calculation  $\epsilon_J$  with increasing  $J$  values, it can be seen that in principle, there is no limit to the rotational energy the molecule may have. *In practice, of course, there comes a point at which the centrifugal force of rapid rotating diatomic molecule is greater than the strength of the bond, and the molecule is disrupted, but this point is not reached at normal temperature.*

In order to discuss the spectrum, it need to consider the differences between the energy levels.

Let incident radiation be absorbed by the molecule in the  $J=0$  state ( the ground rotational state, in which no rotation occurs) to raise it to the  $J=1$  state.

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Plainly the energy absorbed will be :

$$\epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

and, therefore,

$$\bar{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1} \dots\dots\dots(9)$$

In general, to raise the molecule from the state J to state J+1:

$$\bar{\nu}_{J=1 \rightarrow J=2} = \epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1} \dots\dots\dots(10)$$

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

or, 
$$\bar{\nu}_{J \rightarrow J+1} = 2B (J+1) \text{ cm}^{-1} \dots\dots\dots(11)$$

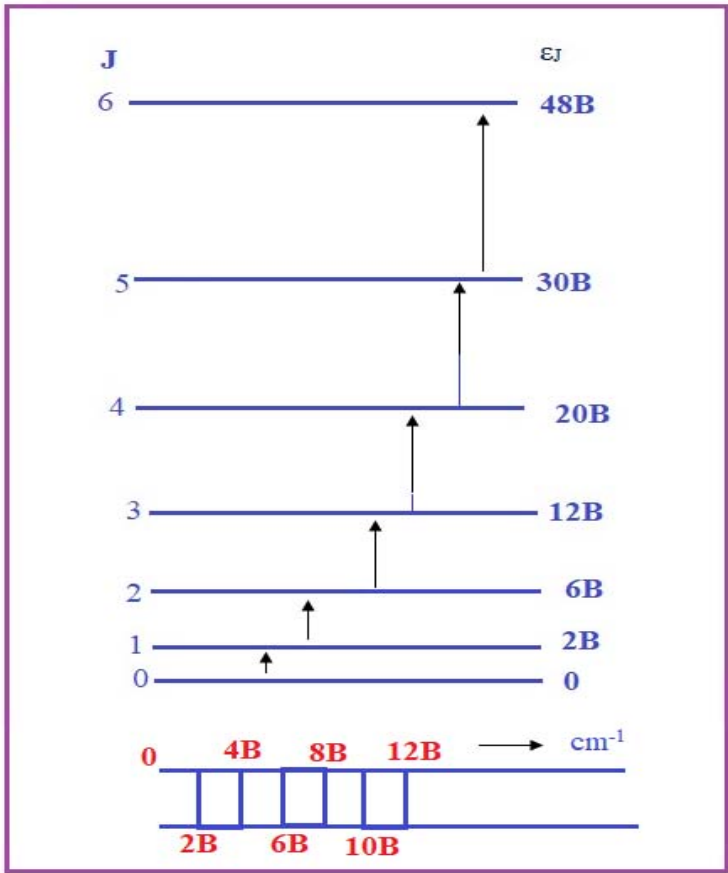


Figure 5: Allowed transition between the energy levels of a rigid diatomic molecule and the spectrum which arises from them



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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 in the foot of the Figure 5.

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

$$\text{Selection rule: } \Delta J = \pm 1 \quad \dots\dots\dots(12)$$

Thus Eq.(11) 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 for two reasons. **Firstly**, the moment of inertia is very small about the bond. So, applying Eq.(5) and Eq.(6) it can be seen that energy levels are extremely widely spaced: this mean that a molecule requires a great deal of energy to be raised from the  $J=0$  to the  $J=1$  state, and such transition 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.

**Application: Observed that the first line ( $J=0$ ) in the rotation spectrum of carbon monoxide as  $3.84235 \text{ cm}^{-1}$ . Now, we have to determine the moment of inertia and hence the bond length.**

Ans:  $\bar{\nu}_{0 \rightarrow 1} = 3.84235 \text{ cm}^{-1}$  (note: This is equal to  $2B$ )

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

Now from the equation,  $B = h/8\pi^2 Ic$  can be rewrite as

$$I = h/8\pi^2 Bc$$

$$I_{CO} = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.99793 \times 10^{10}} \times B = \frac{27.9907 \times 10^{-47}}{B}$$



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$$=14.5695 \times 10^{-47} \text{ kg m}^2$$

where the velocity of light in  $\text{cm}^{-1}$ , since B is in  $\text{cm}^{-1}$ . However, the moment of inertia is  $\mu r^2$  and, knowing the relative atomic weight (H=1.0080) to be C=12.000, O=15.9994, and the absolute mass of the hydrogen atom to be  $1.673 \times 10^{-27} \text{ kg}$ , 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;

$$\mu = \left( \frac{m_1 m_2}{m_1 + m_2} \right)$$

$$\mu = \frac{19.921 \times 26.561 \times 10^{-54}}{(19.921 + 26.561) \times 10^{-27}} = 11.38365 \times 10^{-27} \text{ kg}$$

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

and  $r = 0.1131 \text{ nm (or } 1.131 \text{ \AA)}$

**Note: How to get the value 19.92168 as the mass of carbon?**

Ans: C=12.000, then, mass of carbon =  $12 / (6.023 \times 10^{23}) \text{ g} = 1.992168 \times 10^{-23} \text{ g} = 19.92168 \times 10^{-27} \text{ kg}$