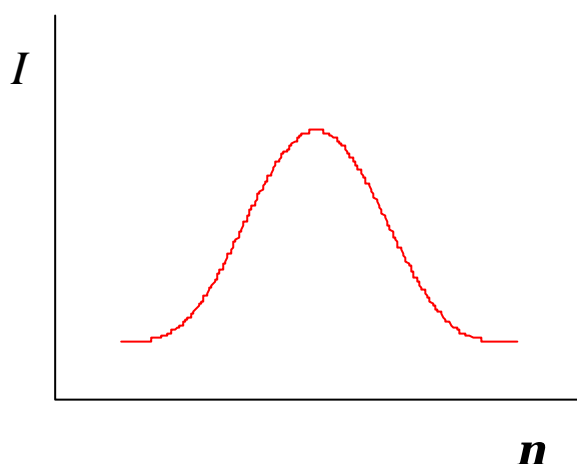


Introduction

We can define spectroscopy as branch of chemical or physical science that deals with the study of spectra. This is made up of two parts: experiment and theory. The experiment obtains the spectrum and measures it and theory extracts the information contained in the spectrum, such as the molecular structure of the molecule.

A spectrum is a graphical representation, fig. 1, of the distribution of the intensity of light absorbed or emitted from the sample as function of the wavelength or frequency of radiation.

Fig. 1



To obtain this, it is necessary to consider the interaction between the radiation and the sample. Spectra can be divided in emission spectra and absorption spectra. The first is obtained by exciting the sample, and then the sample emits radiation. For the second one, we illuminate the sample with continuous radiation and analyse the absorbed radiation as function of the wavelength. According to Bohr, electromagnetic radiation is not emitted while an electron moves in its orbit, but only when the electron goes from one quantum orbit of energy E_n to another of energy E_m . This process is called a quantum jump. The liberated energy $E_n - E_m$ is emitted as a light quantum (photon) of energy $E_n - E_m = h\nu$ (ν = wave number of the light) and this is the *Bohr's frequency condition*. Then the wave number of the emitted or absorbed light is

$$\nu = \frac{E_n - E_m}{hc} \quad (1)$$

where $\nu' = \frac{\nu}{c}$

If $E_n < E_m$, radiation of this wave number is emitted by the system. The frequencies of the emitted or absorbed spectral lines are determined by the energy values of the system. The probabilities of the transitions under the influence of radiation are determined by the eigenfunctions of the states involved. Thus the intensities of the emitted or absorbed spectral lines can be obtained. And knowing the eigenfunctions, we can calculate whether or not two states can combine with each other.

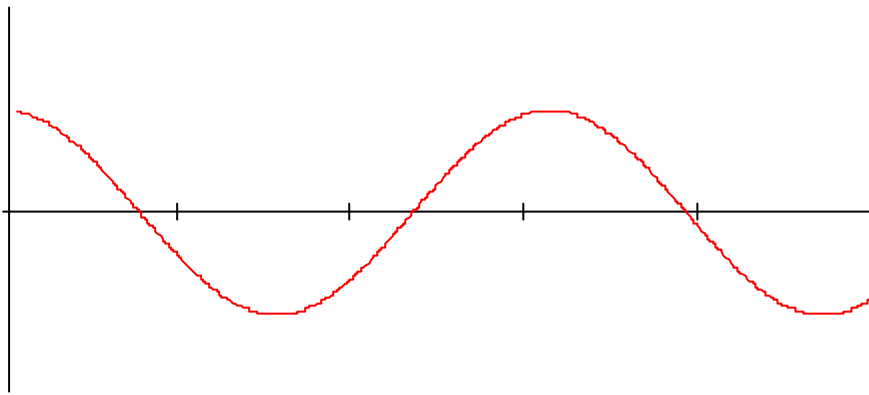
A description of rotational, vibrational and electronic motion is essential to understand the work.

Quantization-Particle on a ring

As an example of quantization we start with the solution for a particle on ring using

$E = \frac{p^2}{2m}$ then $E = \frac{L^2}{2I}$ because $L = pr$ and $I = mr^2$, L is the magnitude of the angular momentum, and if $p = \frac{h}{\lambda}$, then the angular momentum, l , is related to the wavelength of the particle's wavefunction. Suppose for the moment that λ can take an arbitrary value, then the wavefunction will vary around the ring as the angle ϕ increases, where ϕ is the angle that describes the ring, and its value is between 0 and 2π

It is necessary to find a solution where the wavelength is such that the wavefunction reproduces itself on successive circuits, fig 2:



Then, only some angular momentum values are acceptable, hence:

$$\lambda = \frac{2\pi r}{n} \text{ with } n = 0, 1, 2, \dots \quad (2)$$

hence

$$L = \frac{hr}{\lambda} = \frac{nh}{2\pi} \text{ and } L = n\hbar \quad (3)$$

therefore

$$E = \frac{n^2 \hbar^2}{2I} \text{ with } n = 0, 1, 2, \dots \quad (4)$$

Real molecules

The rotation of a body in 3-D can be broken down in three components, being their directions relative to the three normal axes, with the origin at the centre of gravity. Therefore, it has three principal inertia moments, one for each axis: I_a , I_b and I_c .

We can classify the molecules in three different groups according to the relative values of the three inertia moments. Each group has a characteristic rotation spectra.

Linear, diatomic and polyatomic molecules, asymmetric molecules and spherical top molecules.

Linear Molecules

All atoms are located in a straight line. Hence $I_b = I_c$; $I_a = 0$ (approximation for I_a).

Rigid Rotor Approximation (Rigid diatomic molecule)

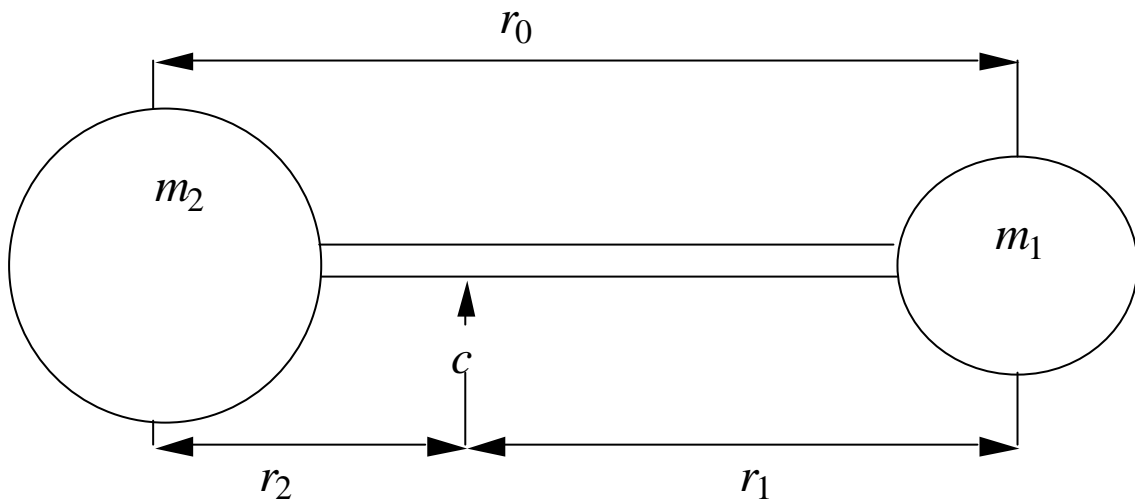


Fig 3. The molecule rotates around c , where c is the centre of gravity, and $r_0 = r_1 + r_2$. The centre of gravity and the moment of inertia, I , are defined by:

$$m_1 r_1 = m_2 r_2 \quad \text{and} \quad I = \sum m_i r_i^2 \quad (5)$$

then $I = \mu r_0^2$, where μ is called the reduced mass of the system, given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (6)$$

Using the Schrodinger equation, $\left(-\frac{\hbar^2}{2mr^2}\right)\Lambda^2\Psi = E\Psi$ we obtain:

$$E = \left(\frac{\hbar^2}{2I}\right)J(J+1) \quad (7)$$

Λ^2 is the Legendrian using spherical co-ordinates.

Then

$$E = \frac{\hbar^2}{8\pi^2 I} J(J+1) \text{ Joules, where } J=0,1,2,\dots \quad (8)$$

h = Planck constant and $I = I_C$ or I_B and J is the rotational quantum number.

Since $\nu = \frac{\Delta E}{h}$ Hz and $\tilde{\nu} = \frac{\Delta E}{h}$ cm^{-1} then

$$\bar{E}_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I_C} J(J+1) \quad J=0,1,2,\dots \quad (9)$$

c is the velocity of light.

Therefore

$$\bar{E}_J = \bar{B}J(J+1) \text{ cm}^{-1}, \quad J=0,1,2,\dots, \quad (10)$$

where \bar{B} is the rotational constant and has the value:

$$\bar{B} = \frac{h}{8\pi^2 I_C} \text{ cm}^{-1} \quad (11)$$

$I = I_B$ or I_C and c is in cm s^{-1}

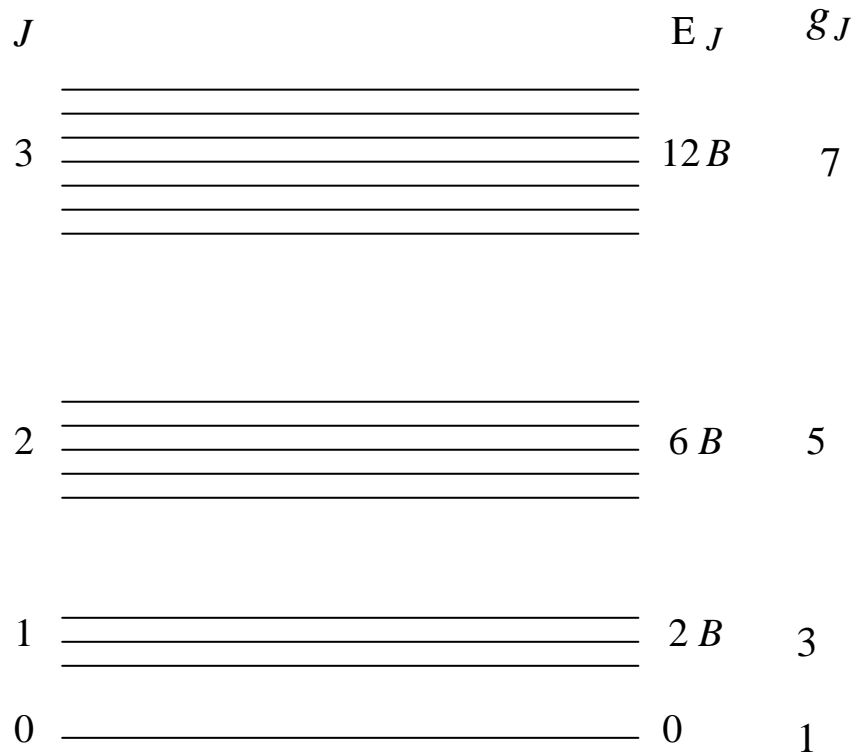
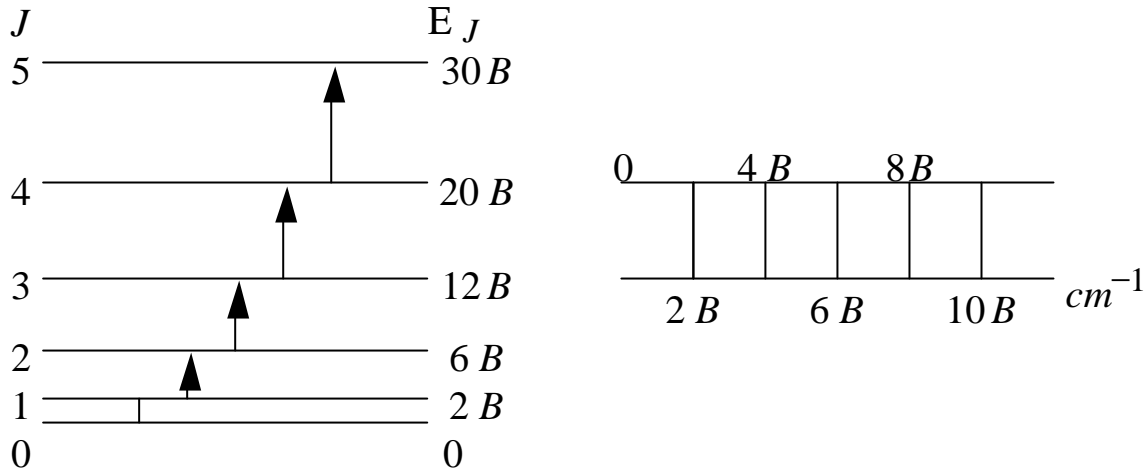


Fig 4. The allowed rotational energies of a rigid diatomic molecule, showing the $(2J+1)$ degeneracy.

The selection rule for transitions by a photon is $\Delta J = \pm 1$. For the promotion from state J to state $J+1$ we have

$$\omega_J = E_{J+1 \leftarrow J} = E_{J+1} - E_J = 2B(J+1) \text{ cm}^{-1} \quad (12)$$

Then, the transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them have the shape, fig 5:



The transition intensity is proportional to the square of the transition moment which is given by:

$$R_r = \int \Psi_r^{n*} \mu \Psi_r^m d\tau \quad (13)$$

The rotational selection rules the conditions for which the intensity, and therefore R_r , is non-zero.

This selection rules are:

- 1.- The molecule must be have a permanent dipole moment $\mu \neq 0$
- 2.- $\Delta J = \pm 1$
- 3.- $\Delta M_J = 0, \pm 1$, a rule which is important only if the molecule is in an electric or magnetic field.

1.- Only if the molecule is asymmetric (heteronuclear) will the spectrum be observed, since if it is homonuclear there will no dipole component change during the rotation, and hence no interaction with radiation.

2.- A more sophisticated application of Schrodinger equation shows that, for this molecule, we need only consider transitions in which J changes by one unit, all other transitions being spectroscopically forbidden.

- 3.- Setting out from $E_J = \frac{h}{8\pi^2 I} J(J+1)$ Joules, the angular momentum is given by:

$$P_J = [J(J+1)]^{1/2} \hbar \quad (14)$$

In general, J is associated with the total angular momentum, i.e. rotational plus orbital plus electron spin, but when there is no orbital or electron spin angular momentum, it refers simply to rotation.

Just as with other angular moment there is space quantization of rotational angular momentum so that the Z component is given by

$$(P_J)_Z = M_J \hbar \quad M_J = J, J-1, \dots, -J \quad (15)$$

Therefore, in the absence of an electric or magnetic field, each rotational energy level is $(2J+1)$ -fold degenerate.

The intensities of spectral lines

A first factor governing the population of the levels is the Boltzmann distribution term in energy given by:

$$\exp(-E_J / kT) = \exp[-BJ(J+1) / kT] \quad (16)$$

A second factor is the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more energy states which have exactly the same energy. In the case of the diatomic rotator we may approach the problem in terms of its angular momentum.

$$E = \frac{1}{2} I \omega^2 \quad (17)$$

$$P = I \omega \quad (18)$$

where ω is the rotational frequency (rad s^{-1}).

Then

$$P = \sqrt{2EI} \quad \text{and} \quad 2EI = J(J+1) \frac{h^2}{4\pi^2} \quad (19)$$

and hence

$$P = [J(J+1)]^{1/2} \hbar \quad J = 0, 1, 2, \dots \quad (20)$$

Since each energy level is $(2J+1)$ -fold degenerate. Then the population N_n of the n th level relative to N_0 is obtained from Boltzmann's distribution law, and gives:

$$\frac{N_J}{N_0} = (2J+1) \exp\left(-\frac{E_J}{kT}\right) = (2J+1) \exp\left(-\frac{BJ(J+1)}{kT}\right) \quad (21)$$

Differentiation of this equation shows that the population is a maximum at the nearest integral J value to:

$$\text{Maximum population} = J_{\max} = \left(\frac{kT}{2hB} \right)^{1/2} - \frac{1}{2} \quad (22)$$

Centrifugal distortion

An important effect when the molecules rotate is centrifugal distortion. The atoms are subject to centrifugal forces that distort the molecular geometry and therefore change the moments of inertia. In the case of a diatomic molecule, the centrifugal distortion stretches the bond, and therefore increases the moment of inertia; as a result, the energy levels are less far apart than predicted by:

$$E_J = BJ(J+1) \quad (23)$$

The Schrodinger wave equation may be set up for a non-rigid molecule, and the rotational levels are found

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ Joules} \quad (24)$$

or

$$E_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \quad (25)$$

and D is defined as centrifugal distortion constant given by

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k} \text{ cm}^{-1} \quad (26)$$

which is a positive quantity, and k is the force constant for simple harmonic motion:

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \quad (27)$$

where $\bar{\omega}$ is the vibration frequency in cm^{-1} .

From

$$\bar{B} = \frac{h}{8\pi^2 c \mu r^2} \quad \text{and} \quad \bar{D} = \frac{h^3}{32\pi^4 I^2 r^2 k}$$

we obtain

$$\bar{D} = \frac{16B^3 \pi^2 \mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} \quad (28)$$

Then, the centrifugal distortion (for a diatomic molecule) constant is related to the vibrational wavenumber of the bond (which is a measure of its stiffness) and so the

observation of the convergence of the rotational levels as J increases can be interpreted in terms of the rigidity of the bond.

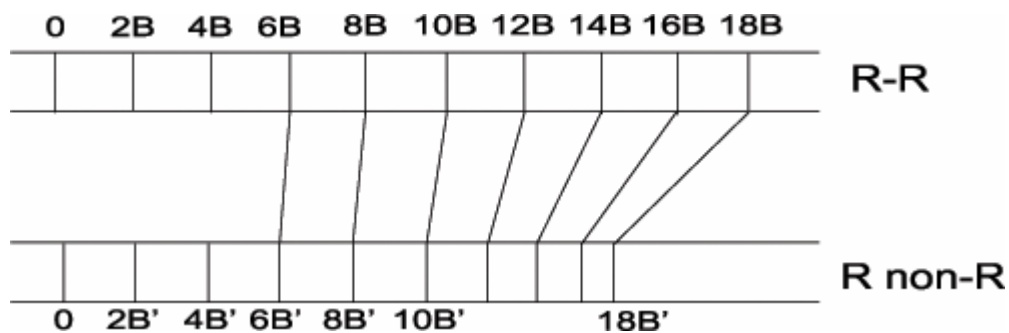


Fig 6. The change in the rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule.

This spectrum comes from, fig 7:

