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1. Learning Outcomes

In this module,

- You shall learn about the information regarding the interaction of microwave radiation with diatomic molecule.

- You shall learn about rotational spectra of diatomic molecule having permanent dipole moment.

- You shall learn about rotational energy level diagram, possible rotational transitions.

2. Introduction:

Pure rotational spectra are caused by rotational energy transitions of molecules due to interactions with rotation. According to the wave theory, we can consider the radiation as a fluctuating electric field. A rotating dipole also generates a fluctuating electric field and hence interacts with the radiation.

Suppose a molecule has a permanent dipole moment, so it has one end positively charged and the other end negatively charged. When this molecule rotates, the positive and negative ends change place periodically, as a result of this, the component dipole moment in a given direction, such as the vertical component fluctuates regularly.

This is exactly similar in form to the fluctuating electric field of rotation and therefore interaction occurs, leading to the energy transitions which we observe in the form of rotational spectra.

A molecule which does not possess dipole moment does not give pure rotational spectra, e.g. H_2, N_2, O_2, Cl_2, CO_2, CS_2, etc. Molecules such as CO, HCl, NO, etc. have permanent dipole moments and they show pure rotational spectra in the region of far infra-red or microwave.
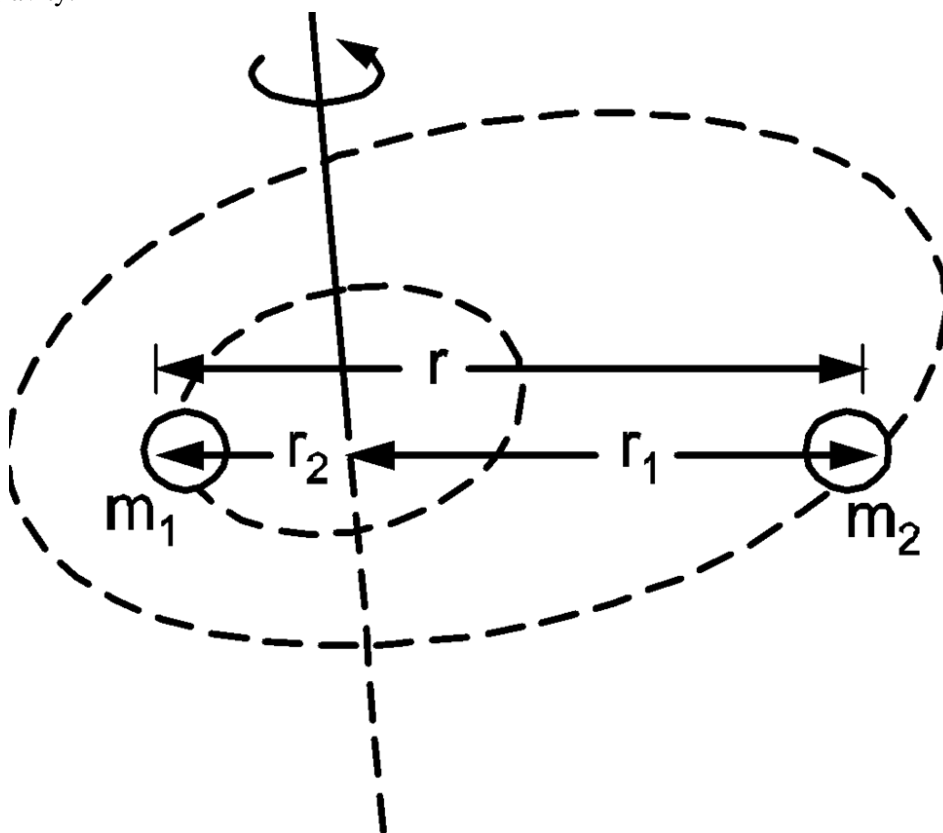
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3. ROTATIONAL SPECTRA

- As a suitable model for diatomic molecule, we shall consider a dumb bell which consists of two balls of masses m_1 and m_2 representing the atoms, connected by a rigid rod of length r that represents a chemical bond between two atoms.

- As a first approximation, we consider a rotating diatomic molecule to be a *rigid rotor*. This is known as *rigid rotor model.* We consider the rotation of this rigid rotor about an axis perpendicular to its own axis and passing through the centre of gravity.

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The moment of inertia (I) for the system consisting of many particles is defined as

$$I = \sum m_i r_i^2 \qquad \qquad \dots (1)$$

where m_i is the mass of ith particle at a distance r_i from the axis of rotation.

For a diatomic molecule, let r_1 and r_2 be the distances of two atoms from the centre of gravity (C.G.) of the system, then the moment of inertia (I) is given by,

$$I = m_1 r_1^2 + m_1 r_1^2 \qquad \qquad \dots (2)$$

It is more convenient to express the moment of inertia in terms of a single distance 'r'.
Let $r = r_1 + r_2$. Then,

$$I = (m_1 m_2/m_1 + m_2)\, r^2 \qquad \qquad \dots (3)$$

The factor $(m_1 m_2/m_1 + m_2)$ replaces the mass factor of a simple particle in the moment of inertia relationship $I = mr^2$ and is called the reduced mass μ of the rotating molecule.

$$\therefore \qquad \qquad I = \mu r^2 \qquad \qquad \dots (4)$$

If v_1 and v_2 are the linear velocities of balls of masses m_1 and m_2, then the kinetic energy of the rotating system can be written as,

$$K.E. = \tfrac{1}{2}\, (m_1 v_1^2 + m_2 v_2^2) \qquad \qquad \dots (5)$$

The velocities v_1 and v_2 are related to the angular velocity ω (omega) by the relations,

$$v_1 = r_1 \omega$$

and

$$v_2 = r_2 \omega$$

$$K.E. = \tfrac{1}{2}\, (m_1 r_1^2\, \omega^2 + m_2 r_2^2\, \omega^2)$$

$$\therefore \qquad K.E. = \tfrac{1}{2}\, \omega^2\, (m_1 r_1^2 + m_2 r_2^2)$$

∴From equation (2),

$$I = m_1r_1^2 + m_2r_2^2$$

The K.E. of rotation is E_{rot}.

$$E_{rot} = \tfrac{1}{2} I \omega 2 \qquad \qquad \text{… (6)}$$

The angular momentum P_{rot} is defined as the product of angular velocity (ω) and the moment inertia (I).

$$P_{rot} = I \omega \qquad \qquad \text{… (7)}$$
$$E_{rot} = P^2_{rot}/2I \qquad \qquad \text{… (8)}$$

This is the classical expression for the rotational kinetic energy of the rigid model.

The rotations of individual molecules are restricted by the quantization conditions requiring its angular momentum P_{rot} to have the values of multiples of $h/2\pi$ where h is the Planck's constant.

From the wave mechanical treatment of the rigid rotor model for diatomic molecules,

$$P_{rot} = I\omega = \sqrt{J(J+1)} . h/2\pi \qquad \qquad \text{… (9)}$$

(According to the quantization rule for angular momentum)

Again, $E_{rot} = \tfrac{1}{2} I \omega^2 = \tfrac{1}{2} I^2\omega^2/I = J(J+1)h^2/2I. 4\pi^2$

$$E_{rot} = h^2/8\pi^2I . J(J+1) \qquad \qquad \text{… (10)}$$

Using equation (10), the rotational energies of a rotating diatomic (linear) molecule are given by the quantization equation

$$E = h^2/8\pi^2I . J(J+1) \text{ Joules} \qquad \qquad \text{… (11)}$$

where E is the rotational energy in joules.

J is the rotational quantum number having only integral values 0, 1, 2, ...

The restriction to integral values of J arises directly from Schrodinger's equation.

I is the moment of inertia of the molecule and it is the characteristic property of the molecule.

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Equation (11) gives the rotational energies of rotating linear diatomic molecule. Again the value of E obtained in equation (11) is in joules. However, in spectroscopy, spectra are usually expressed in wave number ($\bar{\upsilon}$). For simplicity, let us express the unit of rotational energy in the same unit in which is expressed i.e. in cm^{-1}.

Then, $\varepsilon_{rot} = E_{rot} /hc$ in cm^{-1}

Substituting the value of E from equation (11),

$$\varepsilon_{rot} = h^2/8\pi^2 I\ hc \cdot J(J+1)$$

$$\bar{\upsilon} = \varepsilon_{rot} = h/8\pi^2 I\ c \cdot J(J+1) \text{ in } cm^{-1} \qquad \dots (12)$$

But, $h/8\pi^2 I\ c =$ B

where B is rotational constant expressed in cm^{-1} or m^{-1}.

$$\bar{\upsilon} = \varepsilon_{rot} = BJ\ (J+1) \text{ in } cm^{-1} \qquad \dots (13)$$

where J = 0, 1, 2, ……

4. SELECTION RULE

Equation (13) gives the energy of rotational level, but there is restriction on energy transitions. All transitions between the energy levels are not permissible. There is selection rule on the basis of wave mechanical treatment.

It is given as, "A molecule can increase or decrease its rotational energy only to the next higher or lower level when it absorbs or emits a quantum of electromagnetic radiation."

i.e. $\Delta J = \pm 1$ only

The positive sign applies when radiation is absorbed and negative sign when the radiation is emitted.

Consider now absorption spectrum.

For J = 0, $\varepsilon_{rot} = 0$

Hence the molecule is not rotating at all and is in rest, when E = 0 i.e. at ground level.

We can now apply the selection rule to identify the absorption lines in the pure rotational spectrum. Each absorption line in the spectrum gives transition from one rotational level to the next higher level. The energy change associated with this transition gives the energy or wave number of absorbed radiation. For transition of molecule from J = 0 to J = 1 from equation (13),

$$\varepsilon_{rot\ (J=1)} - \varepsilon_{rot\ (J=0)} = 2B - 0 = 2B\ cm^{-1}$$

i.e. $\bar{\upsilon}_{J=0 \rightarrow J=1} = 2B\ cm^{-1}$ … (14)

Similarly the molecule with J = 1 raises to J = 2 by absorption of quantum of radiation as per selection rule. For each transition,

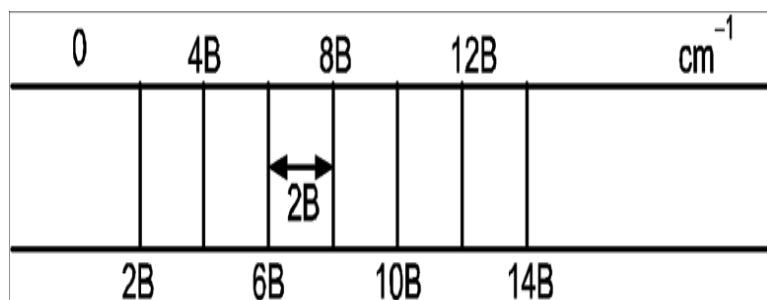$\varepsilon_{rot\ (J=2)} - \varepsilon_{rot\ (J=1)} = 6B - 2B = 4B\ \text{cm}^{-1}$

$$\text{i.e. } \bar{\upsilon}_{J=1 \rightarrow J=2} = 4B\ \text{cm}^{-1} \qquad \qquad \text{… (15)}$$

Identification of other absorption lines can be done in a similar manner.
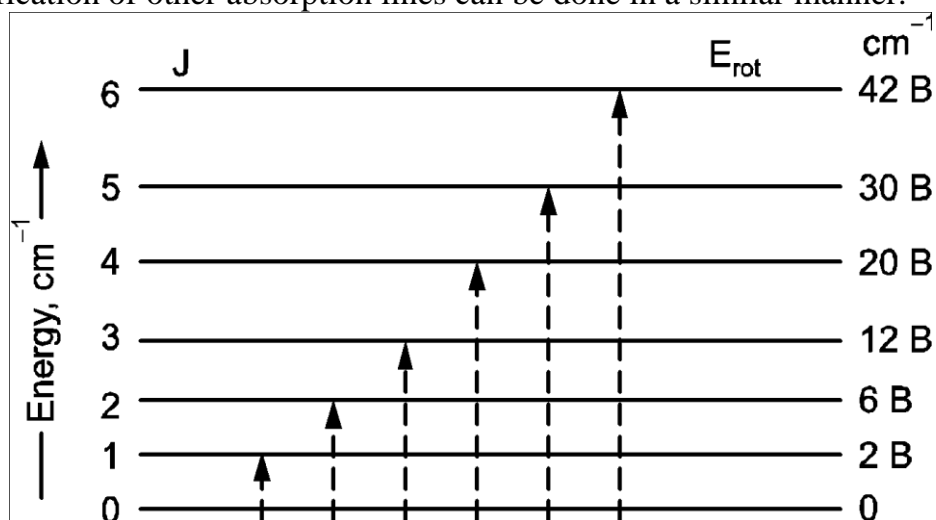
- Hence a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines 2B, 4B, 6B, … cm^{-1}.

For a diatomic molecule, the rotational spectrum consists of equally spaced lines i.e. difference between any two lines is that of 2B.

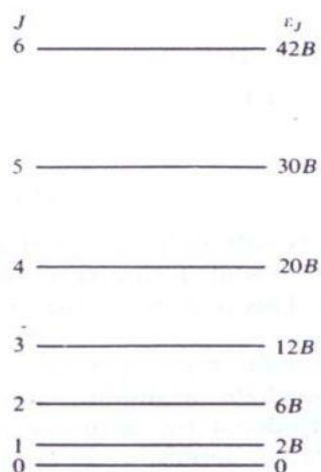| CHEMISTRY | PAPER No. : IX (PHYSICAL CHEMISTRY) |
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Rotational Spectra of Rigid Diatomic molecule
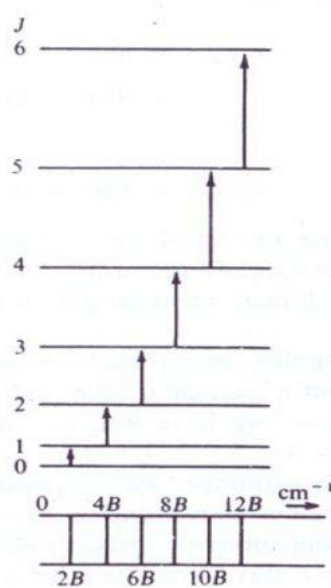
For rigid rotor, $J \rightarrow J + 1$,

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

Selection rule: $\Delta J = \pm 1$

The allowed rotational energy levels of a rigid diatomic molecule

Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum

5. SUMMARY

- The rotational energy is quantized.
- The rotational energy levels of any diatomic molecules can be calculated by solving the Schrodinger equation for the system represented by that molecule.
- For a diatomic molecule, the rotational spectrum consists of equally spaced lines i.e. difference between any two lines is that of 2B.
- The molecules having dipole moment only interacts with the microwave radiations.

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Video 1:
https://drive.google.com/file/d/1sRwtWoYRfWAxhhNjskqYV145gEcrw zHB/view?usp=sharing

Video 2:
https://drive.google.com/file/d/18jy2VWnSTpoBO2YJdEO5onYzb8a1e RF/view?usp=sharing

Video 3:
https://drive.google.com/file/d/1z7aPcW6C6OpXX9g5jSBhTgJCJzEosu 9/view?usp=sharing

Assignment:
https://forms.gle/aGbANwK7CTPuPd26A

Know more:
Suggested readings, web links
1. Fundamentals of molecular spectroscopy by C. N. Banwell and E. M. McCash
2. Modern aspects of microwave spectroscopy by G W Chantry
3. https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Ch emistry_Textbook_Maps/Supplemental_Modules_(Physical_and_The oretical_Chemistry)/Quantum_Mechanics/07._Angular_Momentum/7 5%3A_Rigid_Rotor
4. https://www.slideshare.net/FatimaSyed32/rigid-rotators-131378041

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