

MOLECULAR SPECTROSCOPY

PURE - ROTATIONAL SPECTROSCOPY :

The transitions among rotational energy levels of ground vibrational state, which corresponds to ground electronic state are studied under pure-rotational or microwave spectroscopy.

Rotational energy of a particle :

In classical mechanics, the energy of an particle which rotates around an axis is given by

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

$\omega \rightarrow$ angular velocity in radian per second.

$I \rightarrow$ moment of inertia.

$$E = \frac{1}{2} \frac{(I\omega)^2}{I} = \frac{p^2}{2I} \quad (p \rightarrow \text{angular momentum})$$

Quantum mechanics energy :

$$E = \frac{\hat{p}^2}{2I}$$

$\therefore \hat{p} = \sqrt{J(J+1)}\hbar$ only few rotation are allowed.

$$= \frac{(\sqrt{J(J+1)}\hbar)^2}{2I}$$

$J \rightarrow$ rotational quantum number

$$= J(J+1) \frac{\hbar^2}{2I}$$

$J = 0, 1, 2, 3, \dots$

$$= J(J+1) \frac{h^2}{8\pi^2 I} = J(J+1)B \quad B \rightarrow \text{rotational constant ; } B = \frac{h^2}{8\pi^2 I} \text{ Joule}$$

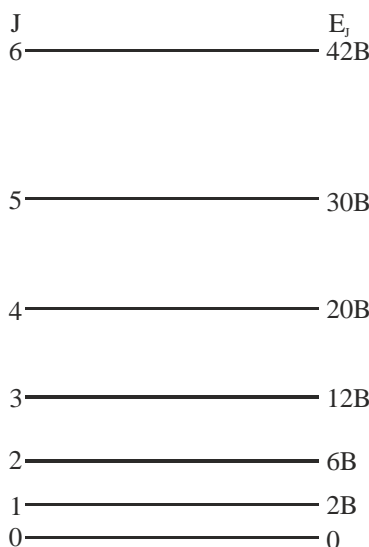


Fig. The allowed rotational energies of a rigid diatomic molecule

For absorption, $\Delta J = +1$ (important to study)

For emission, $\Delta J = -1$

Difference between energy levels under, $\Delta J = +1$ or position of peaks in microwave spectrum.

$$\Delta E = E_{J_2} - E_{J_1} = J_2(J_2 + 1)B - J_1(J_1 + 1)B = 2B(J_1 + 1) \quad (\because J_2 - J_1 = +1)$$

$$\Delta E_{0 \rightarrow 1} = 2B$$

$$\Delta E_{1 \rightarrow 2} = 4B$$

$$\Delta E_{2 \rightarrow 3} = 6B$$

\vdots

$$\Delta E_{11 \rightarrow 12} = 24B$$

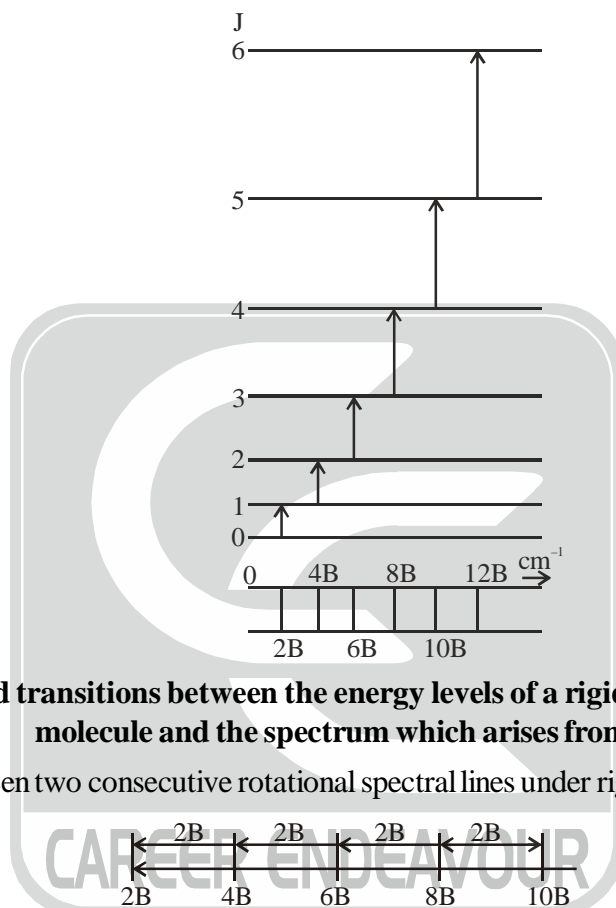


Fig. Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

The difference between two consecutive rotational spectral lines under rigid rotor approximation is $2B$.

Gross selection rule :

The molecule with permanent dipole moment will be rotational or microwave active.

All Heteronuclear diatomic molecules are microwaves active.

e.g., HCl, CO, NO, HBr

All Homonuclear diatomic molecules are microwave inactive.

e.g., H_2, Cl_2, Br_2, N_2

Triatomic and Polyatomic molecules with permanent dipole moment will be microwave active

e.g. $H_2O, N_2O, OCS, NH_3, CHCl_3$

The Intensities of Spectral Lines:

We want now to consider briefly the relative intensities of the spectral lines, for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy level. 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 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.

This does not mean, however, that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule in the $J = 0$ state, say will move to $J = 1$ is the same as that of a single molecule moving from $J = 1$ to $J = 2$, in an assemblage of molecules, such as in a normal gas sample, there will be different number of molecules in each level to begin with, and therefore different total numbers of molecules will carry out transitions between the various levels. In fact, since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial number of molecules in each level.

The first factor governing the population of the levels is the Boltzmann distribution. Here we know that the rotational energy in the lowest level is zero, since $J = 0$, so, if we have no molecules in this state, the number in any higher state is given by:

$$N_J / N_0 = \exp(-E_J / kT) = \exp[-BhcJ(J+1) / kT] \quad \dots (i)$$

Where, we must remember, is the velocity of light in cm s^{-1} when B is in cm^{-1} . A very simple calculation shows how N_J varies with J ; for example, taking a typical value of $B = 2\text{cm}^{-1}$, and room temperature (say $T = 300\text{ K}$), the relative population in the $J = 1$ state is

$$\frac{N_1}{N_0} = \exp\left(-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right) = \exp(-0.019) \approx 0.98$$

and we see that there are almost as many molecules in the $J = 1$ state, at equilibrium, as in the $J = 0$.

A second factor is also required-the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more energy states which have exactly the same energy.

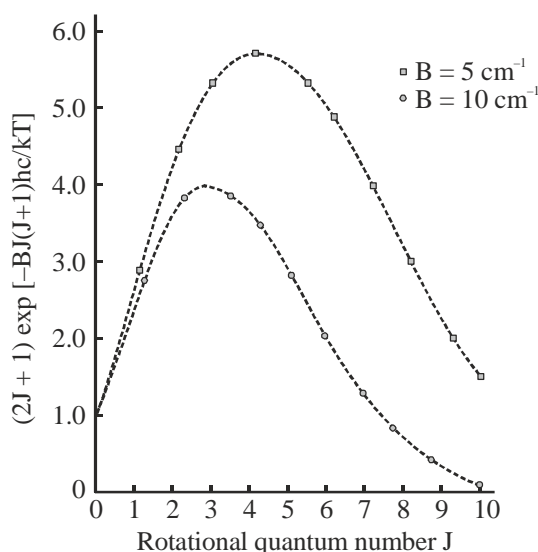
Thus we see that, although the molecular population in each level decreases exponentially, the number of degeneracy levels available increases rapidly with J . The total relative population at any energy E_J will plainly be

$$\text{Population} \propto (2J+1) \exp(-E_J / kT) \quad \dots (ii)$$

When this is plotted against J the points fall on a curve, indicating that the population rises to a maximum and then diminishes. Differentiation of equation (ii) shows that the population is a maximum at the nearest integral J value to

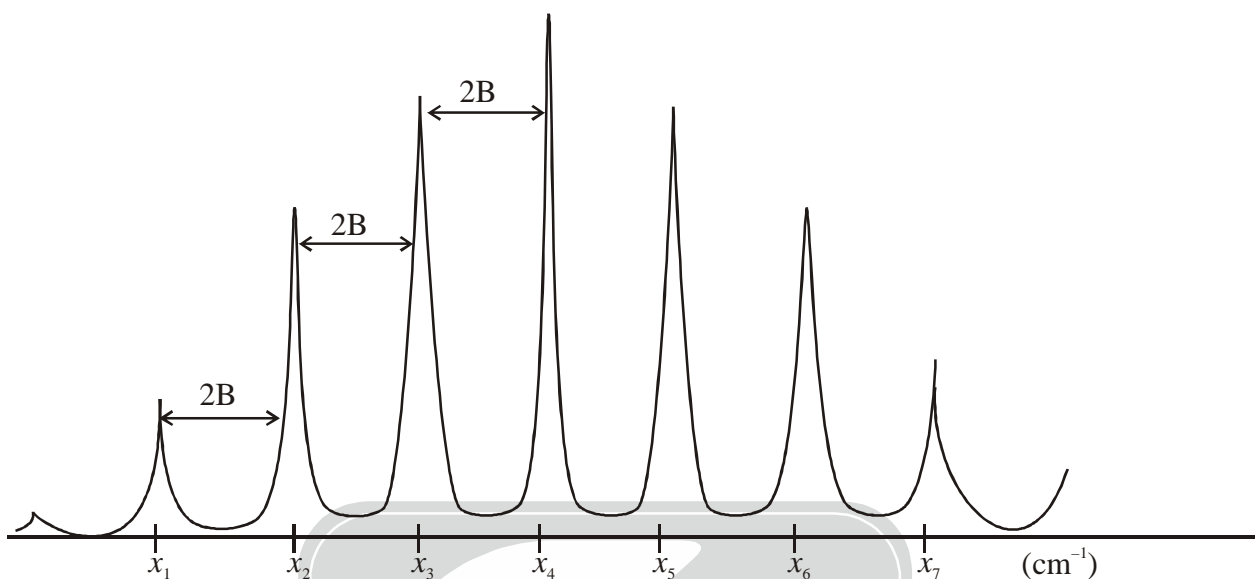
$$\text{Maximum population } J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad \dots (iii)$$

We have seen that line intensities are directly proportional to the populations of the rotational levels; hence it is plain that transitions between levels with very high J values will have small intensities while the intensity will be a maximum at or near J value by Eq. (iii).



Application of microwave spectroscopy :

- (i) To determine average bond length.



B can be calculated from the microwave spectra

$$2B = x_2 - x_1$$

$$B = \frac{h}{8\pi^2 Ic} \Rightarrow I = \frac{h}{8\pi^2 Bc}$$

$$\therefore I = \mu r^2 \Rightarrow r = \sqrt{\frac{I}{\mu}}$$

$r \rightarrow$ bond length

- (ii) To calculate mass of isotopically substituted nuclei.

$$\text{Rotational constant } (B) = \frac{h}{8\pi^2 Ic}$$

$$\therefore B \propto \frac{1}{I} \Rightarrow B \propto \frac{1}{\mu} \text{ (after isotopic substitution B will decrease)}$$

$$\therefore \frac{B}{B'} = \frac{\mu'}{\mu} \Rightarrow \mu' = \frac{B}{B'} \times \mu$$

$\mu' \rightarrow$ reduced mass after isotopic substitution

- (iii) To determine classical rotational frequency and periods.

$$\text{Kinetic energy} = \frac{1}{2} I \omega^2$$

$$BJ(J+1) = \frac{1}{2} I \omega^2 = \frac{1}{2} I (2\pi\nu)^2 \Rightarrow \nu^2 = \frac{h^2}{16\pi^4 I^2} J(J+1)$$

$$\nu = \frac{h}{4\pi^2 I} \sqrt{J(J+1)}$$

$$\nu = 2B\sqrt{J(J+1)}$$

$\nu \rightarrow$ classical rotational frequency

$$\therefore \text{Time period } (T) = \frac{1}{\nu} = \frac{1}{2B\sqrt{J(J+1)}}$$

SOLVED PROBLEMS

1. Among the following molecules which one shows pure rotation spectra? [BHU 2011]

(a) N_2 (b) H_2S (c) CO_2 (d) CH_4

Soln. A molecule having no permanent dipole moment does not generate the oscillating electrical field on rotation and hence cannot interact with the radiation. Such a molecule does not exhibit the rotational spectrum. Thus, the essential criterion for a molecule to exhibit rotational spectrum is that it must have a permanent dipole moment. The molecules with permanent dipole moment are known as microwave active molecules.

$$\mu_{H_2S} \neq 0$$

So, H_2S is active in rotation spectra

Correct option is (b)

2. Quantized rotational energy of molecule is given as [BHU 2012]

(a) $v(r) = D_e [1 - \exp(\beta(r - r_e))]^2$ (b) $\mu_s = -g \times e / 2m_e c \times \frac{h}{2\pi} \sqrt{S(S+1)}$
 (c) $E_J = J(J+1)h^2 / 8\pi^2 I$ (d) $\nu = \frac{\Delta E}{h} = \frac{\epsilon_{upper} - \epsilon_{lower}}{h}$

- Soln.** Quantized rotational energy of molecule is given as

$$E_J = J(J+1)h^2 / 8\pi^2 I$$

$J = 0, 1, 2, 3, \dots$ (only few rotational energy level is allowed)

Correct option is (c)

3. Centrifugal forces due to rotation of molecule about any given axis tend to [BHU 2012]

(a) increase the moment of inertia about the axis
 (b) decrease the effective rotational constant
 (c) both (a) and (b) (d) None of these

Soln. The molecule is rotating perpendicular to its principle axis experiences an outward force than this force is called the centrifugal force. Due to centrifugal force bond length of the molecule increases. So moment of

inertia of molecule increase ($\because I \propto r^2$) and rotational constant decrease ($\because B \propto \frac{1}{I}$).

Correct option is (c)

4. The third lowest microwave absorption frequency for $^{13}C^{16}O$ is 330567 MHz. The second lowest absorption frequency for $^{12}C^{16}O$ should be at [BHU 2014]

(a) 220378 MHz (b) 230542 MHz (c) 345813 MHz (d) 205032 MHz

Soln. The third lowest microwave absorption frequency appears at $= 6B$



Second lowest microwave absorption frequency appears at $= 4B$

$$\therefore 6B(^{13}\text{C}^{16}\text{O}) = 330567 \text{ MHz}$$

$$4B(^{12}\text{C}^{16}\text{O}) = ?$$

$$\therefore B \propto \frac{1}{\mu}$$

$$\frac{B(^{12}\text{C}^{16}\text{O})}{B(^{13}\text{C}^{16}\text{O})} = \frac{\mu(^{13}\text{C}^{16}\text{O})}{\mu(^{12}\text{C}^{16}\text{O})} \Rightarrow B(^{12}\text{C}^{16}\text{O}) = \frac{330567}{6} \times \frac{13 \times 16}{29} \times \frac{28}{12 \times 16} = 57,627.58 \text{ MHz}$$

$$\therefore 4B(^{12}\text{C}^{16}\text{O}) = 230510 \text{ MHz}$$

Correct option is (c)

5. HI and DI are made to undergo the same transition from $J = 0 \rightarrow J = 1$. The light frequency causing the transition for HI equals ν . Approximately which frequency would you expect to induce the same transition in DI? **[BHU 2015]**

- (a) 2ν (b) $\sqrt{2}\nu$ (c) $\nu/2$ (d) $\nu/\sqrt{2}$

Soln. Energy associated with $J = 0 \rightarrow J = 1$ transition

$$\Delta E_{0 \rightarrow 1} = 2B = \frac{2 \times h^2}{8\pi^2 I}; \Delta E_{0 \rightarrow 1} \propto \frac{1}{I}; \Delta E_{0 \rightarrow 1} \propto \frac{1}{\mu}$$

$$\therefore \frac{\Delta E_{DI}}{\Delta E_{HI}} = \frac{\mu_{HI}}{\mu_{DI}} = \frac{1}{2}$$

$$\Delta E_{DI} = \frac{\Delta E_{HI}}{2} = \frac{\nu}{2}$$

Correct option is (c)

6. Which of the following molecule will show pure rotational spectrum? **[BHU 2016]**

- (a) CH_4 (b) H_2O (c) C_6H_6 (d) Cl_2

Soln. A molecule having no permanent dipole moment does not generate the oscillating electrical field on rotation and hence cannot interact with the radiation. Such a molecule does not exhibit the rotational spectrum. Thus, the essential criterion for a molecule to exhibit rotational spectrum is that it must have a permanent dipole moment. The molecules with permanent dipole moment are known as microwave active molecules.

$\mu_{\text{H}_2\text{O}} \neq 0$ (So H_2O is microwave active molecule)

Correct option is (b)

6. Rotational spectra are observed in the **[BHU 2013]**

- (a) near infrared region (b) visible region
(c) far infrared region (d) UV region

Soln. The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately $1400\text{--}4000 \text{ cm}^{-1}$ ($0.7\text{--}2.5 \mu\text{m}$ wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000\text{--}400 \text{ cm}^{-1}$ ($2.5\text{--}25 \mu\text{m}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400\text{--}10 \text{ cm}^{-1}$ ($25\text{--}1000 \mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

Correct option is (c)

