

Rigid and Non-Rigid Rotor Models for Microwave Rotational Spectroscopy of Diatomic Molecules

Rohit Singh

Department of Physics, Patna Women's College (Autonomous), Patna University,
Patna – 800001, Bihar, India

RESEARCH ARTICLE

ABSTRACT: In microwave rotational spectroscopy, absorption spectra arise from molecular rotation and correspond to transitions between the rotational energy levels associated with a given vibrational state of a particular electronic state. The rotational transitions, which fall in the microwave region, are induced through the interaction of the molecular electric dipole with the electric vector of the radiation. The microwave region extends roughly from $10^2 \mu\text{m}$ to $10^4 \mu\text{m}$. The article explains the pure rotational absorption spectra of diatomic molecules such as HCl, HBr, HI, CO, ... etc. In order to explain the absorption spectra, diatomic molecules are treated as rigid rotor and non-rigid rotor.

KEYWORDS: Rotational spectra, Heteronuclear diatomic molecules, rigid-rotor, non-rigid rotor, absorption rotational spectra, intensity of rotational spectral lines.

<https://doi.org/10.29294/IJASE.7.4.2021.1936-1942> © 2021 Mahendrapublications.com, All rights reserved

1. INTRODUCTION

Rotational Spectroscopy is a field of research concerned with study of high-resolution molecular rotation spectra in the gas phase [1]. The applications of the technique range from determination of the most precise molecular geometries to searches for manifestations of prebiotic chemistry through studying the molecular composition of circumstellar molecular clouds. The technique has very often been colloquially called Microwave Spectroscopy [2, 3] as it received a considerable impetus after the Second World War from the development of radar and subsequent general availability of microwave devices [4]. Rotational Spectroscopy has been characterised by a rather tightly-knit and well organised scientific community. The unavoidable changes enforced by the passage of time mean that many of the laboratories and people that were crucial to the evolution of the field are no longer active. Much information on the heroic age of rotational spectroscopy is still available so it seems a good moment to collect it and to make more widely available [3].

In molecular spectroscopy, rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gaseous phase [1] and is observed in the far infra-red ($\approx 10^2 \mu\text{m} - 10^3 \mu\text{m}$) or microwave ($\approx 10^3 \mu\text{m} - 10^4 \mu\text{m}$) region of the electromagnetic spectrum.

The rotational spectra of polar molecules can be measured in absorption or emission processes by microwave spectroscopy because the permanent

electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The rotational spectra of non-polar molecules cannot be observed by these methods, but can be observed and measured by Raman spectroscopy [3]. For polar heteronuclear diatomic molecules such as HF, HCl, HBr, CO, etc., the rotational spectra consist of a series of absorption maxima which are very closely equidistant on a wave number scale [2]. Non-polar homonuclear diatomic molecules such as H_2 , O_2 , N_2 ; symmetric linear molecules such as CO_2 ($O = C = O$) and SO_2 ($O = S = O$); and spherical-top polyatomic molecules such as CCl_4 , CH_4 and SF_6 do not exhibit rotational spectra. In practice, rotational spectra are observed in absorption [1].

To develop a description of the rotational states, we will consider the diatomic molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. A theoretical analysis of the quantized rotational energy levels and the rotational transitions exhibited by the polar heteronuclear molecules is presented. The absorption spectrum of rigid rotor is expected to consist of a series of equidistant lines with constant separation $2B$ while from the actual experimental data, it is obvious that the separation between successive absorption lines decreases progressively with increasing rotational quantum number J . The discrepancies of theoretical and experimental data have been resolved by

*Corresponding Author: rohit.phy@patnawomenscollege.in

Received: 11.04.2021

Accepted: 12.05.2021

Published on: 31.05.2021

Rohit Singh

considering the diatomic molecule as a non-rigid rotor.

**2. THE MOLECULE AS A RIGID ROTOR:
EXPLANATION OF ROTATIONAL SPECTRA**

The simplest model of a rotating diatomic molecule is that of a rigid rotor, that is, the bond length or internuclear separation between two atoms is assumed to be fixed at the equilibrium value [1].

Let us consider M_1 and M_2 are masses of two atoms which are chemically bonded to form a diatomic molecule [1]. The atoms may be treated as point masses because their masses are concentrated in their nuclei which have a size ($\approx 10^{-15} m$) much smaller than the internuclear separation ($\approx 10^{-10} m$). Let r be the distance between the atoms M_1 and M_2 , and r_1 and r_2 be the respective distances of the atoms from the centre of mass C of the molecule [5]. The system of two atoms is capable of rotation about an axis passing through its centre of mass C and perpendicular to the internuclear axis (see Fig. 1).

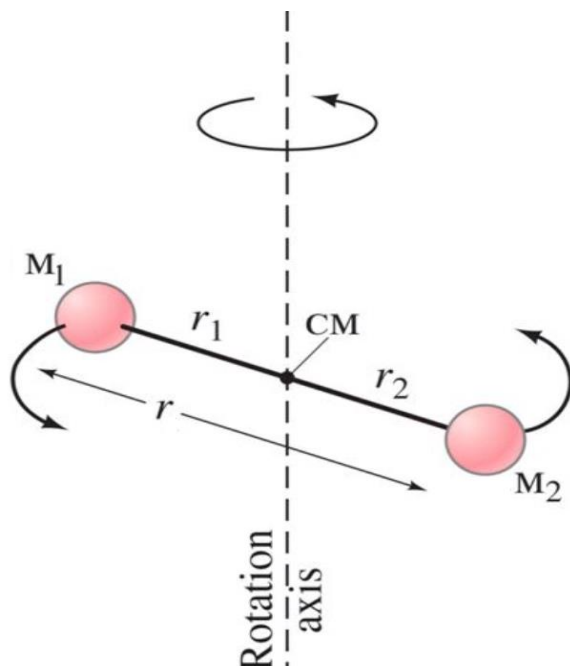


Fig. 1 Diatomic molecule as a rigid rotor

By the definition of centre of mass, we have

$$M_1 r_1 = M_2 r_2 \quad \dots (1)$$

$$\text{also } r_1 + r_2 = r \quad \dots (2)$$

From equations (1) and (2), we have

$$r_1 = \frac{M_2}{M_1 + M_2} r \quad \&r_2 = \frac{M_1}{M_1 + M_2} r \quad \dots (3)$$

Now, the moment of inertia of the molecule about the axis of rotation is given by

$$I = M_1 r_1^2 + M_2 r_2^2$$

$$I = M_1 \left(\frac{M_2}{M_1 + M_2} r \right)^2 + M_2 \left(\frac{M_1}{M_1 + M_2} r \right)^2$$

$$I = \left(\frac{M_1 M_2}{M_1 + M_2} \right) r^2$$

where $\frac{M_1 M_2}{M_1 + M_2}$ is the 'reduced mass μ ' of the diatomic molecule.

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

Thus, the diatomic molecule is equivalent to a single point-mass μ at a fixed distance r from the axis of rotation [6]. Such a system is called a 'rigid rotor' or 'rigid rotor'.

The energy of rotating diatomic molecule is given by

$$E = \frac{L^2}{2I} \quad \dots (5)$$

According to Quantum mechanics, the eigen-value of the angular momentum L is given by [7]

$$L \equiv \sqrt{J(J + 1)} \hbar \quad \dots (6)$$

where J is called the rotational quantum number which can take the integral values:

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

Substituting the value of L from equation (6) into equation (5), we get the energy of rotating molecule

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

Since only certain discrete values of energy and angular momentum of the rigid rotor are possible, it follows that only certain rotational frequencies are possible [7]. We have

$$\omega = \frac{L}{I} = \frac{h}{2\pi I} \sqrt{J(J + 1)} \quad \dots (8)$$

$$\text{and } \nu_{rot} = \frac{\omega}{2\pi} = \frac{h}{4\pi^2 I} \sqrt{J(J + 1)} \quad \dots (9)$$

3. SPECTRUM OF RIGID DIATOMIC MOLECULE

Let us now investigate the spectrum expected from a rigid rotor. In terms of wave-number, the energy equation can be written as

$$\epsilon_j = \frac{E}{hc} = \frac{h}{8\pi^2Ic} J(J + 1) \dots (10)$$

Let us put $\frac{h}{8\pi^2Ic} = B$, known as rotational constant. Then equation (10) gives

$$\epsilon_j = BJ(J + 1) \dots (11)$$

Substituting $J = 0, 1, 2, 3, \dots$, in equation (11), we get

- $\epsilon_0 = 0$ (ground state)
- $\epsilon_1 = 2B$ (first excited state)
- $\epsilon_2 = 6B$ (second excited state)
- $\epsilon_3 = 12B$ (third excited state)
- $\epsilon_4 = 20B$ (fourth excited state)
- $\epsilon_5 = 30B$ (fifth excited state)

Thus, we have a series of discrete rotational energy levels whose spacings increase with increasing rotational quantum number J . Fig. 2 shows the rotational energy level diagram of a rigid diatomic molecule for rotational quantum numbers $J = 0, 1, 2, 3, 4, \dots$ etc. For $J = 0, \epsilon_{j=0} = 0$ (ground state), hence the molecule is not rotating at all in ground state. For $J = 1$, the rotational energy level is $2B$ and rotating molecule has its lowest angular momentum. In this manner we may continue to calculate ϵ_j with increasing J values. With the increase in the value of J , value of ϵ_j increases. At normal temperatures, the centrifugal force of rapidly rotating molecule is always less than the strength of the bond. Hence the molecular bond is stable.

When a transition takes place between a lower level (J') and upper level (J''), the wave number of the emitted or absorbed radiation would be given by

$$\bar{\nu}_{J' \rightarrow J''} = \epsilon_{J''} - \epsilon_{J'}$$

$$i. e. \bar{\nu}_{J' \rightarrow J''} = BJ''(J'' + 1) - BJ'(J' + 1) \dots (12)$$

A study of the matrix element of the dipole moment shows that the rotational transitions can only occur such that rotational quantum number J changes by unity, so that the selection rule is

$$\Delta J = \pm 1 \dots (13)$$

Since we have chosen $J'' > J'$, we have

$$J'' = J' + 1$$

$$\text{Thus } \bar{\nu}_{J' \rightarrow J'+1} = B(J' + 1)(J' + 2) - BJ'(J' + 1)$$

$$i. e. \bar{\nu}_{J' \rightarrow J'+1} = 2B(J' + 1)$$

In this formula, the J values of only 'lower' state occur. Remembering this, we may write J at the place J' for simplicity. Thus

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J + 1) \dots (14)$$

Substituting $J = 0, 1, 2, 3, \dots$, we get

- $\bar{\nu}_{0 \rightarrow 1} = 2B$ (first absorption line)
- $\bar{\nu}_{1 \rightarrow 2} = 4B$ (second absorption line)
- $\bar{\nu}_{2 \rightarrow 3} = 6B$ (third absorption line)
- $\bar{\nu}_{3 \rightarrow 4} = 8B$ (fourth absorption line)

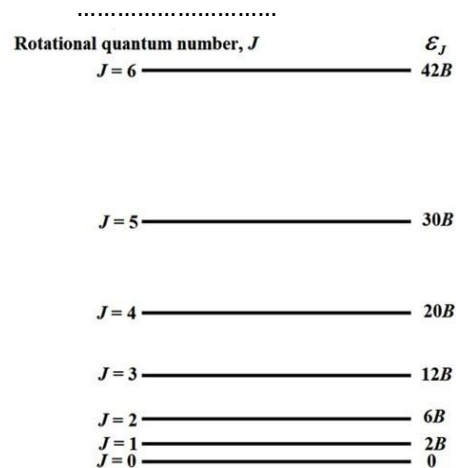


Fig. 2. Rotational energy level diagram of a rigid diatomic molecule

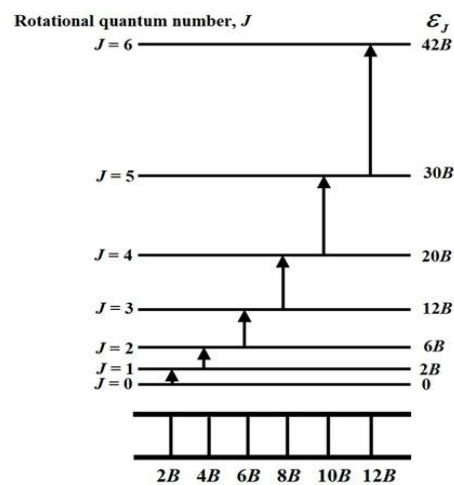


Fig. 3. Allowed transitions between the energy levels and the absorption spectrum of diatomic molecule

Thus, the absorption spectrum of a rigid rotor is expected to consist of a series of equidistant lines with constant separation $2B$, provided transitions start from various energy levels $J = 0, 1, 2, 3, \dots$, as shown in Fig. 3. This, however, does take place because quite a good number of rotational energy levels are well-populated even at ordinary temperatures.

4. INTENSITY OF SPECTRAL LINE: THE POPULATION OF THE J^{th} ROTATIONAL ENERGY LEVEL RELATIVE TO THE LOWEST ENERGY LEVEL

The intensity of a spectral line is proportional to the number of molecules in the initial state. The number of molecules in the energy state E_J at temperature T is given by

$$N_J = N_0 e^{-\frac{BJ(J+1)hc}{k_B T}} \dots (15)$$

where N_0 is the number of molecules in the state $J = 0$. The degeneracy of the J^{th} state is $(2J + 1)$. Taking degeneracy of the J^{th} state into consideration, above formula for population of J^{th} state becomes

$$N_J = N_0(2J + 1)e^{-\frac{BJ(J+1)hc}{k_B T}} \dots (16)$$

A graph between N_J and J for a typical molecule at room temperature (300 K) is drawn in Fig. 4. It shows the relative population of various levels.

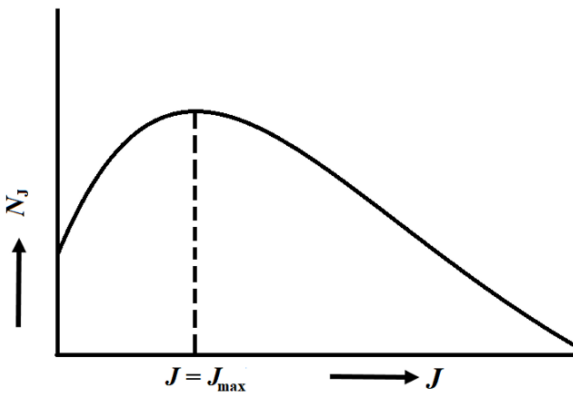


Fig. 4. The relative population of J^{th} rotational state with respect to ground state ($J = 0$) versus rotational quantum number (J)

Let $J = J_{max}$ is the rotational quantum number having maximum population (N_J),

$$\left. \frac{dN_J}{dJ} \right|_{J=J_{max}} = 0$$

$$i.e. \frac{d}{dJ} \left(N_0(2J + 1)e^{-\frac{BJ(J+1)hc}{k_B T}} \right) \Big|_{J=J_{max}} = 0$$

$$i.e. J_{max} = \frac{1}{2} \sqrt{\frac{2k_B T}{Bhc}} - \frac{1}{2}$$

$$i.e. J_{max} = \sqrt{\frac{k_B T}{2Bhc}} - \frac{1}{2} \dots (17)$$

Hence, the intensity of spectral line is maximum for this value of J . For lower and higher values of J , the intensity is less.

5. ISOTOPE EFFECT

In the rotational spectra of diatomic molecule, if we substitute the atom by its isotope, then there is a change in the spectral lines. As a matter of fact, there is no change in internuclear distance as well as the chemical properties of the molecule. However, there is change in the reduced mass and hence in the moment of inertia of the molecule and changing B value [1].

Consider the carbon monoxide molecule as $^{12}C^{16}O$ and with the isotope as $^{13}C^{16}O$. Let the primed quantities are represented for isotopes [1].

$$B = \frac{h}{8\pi^2 I c} \& B'$$

$$= \frac{h}{8\pi^2 I' c} ; \text{ where prime refers to heavy molecule.}$$

The calculated values are $B = 1.92118 \text{ cm}^{-1}$ and $B' = 1.83669 \text{ cm}^{-1}$.

$$\text{Hence, } \frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is reduced mass and internuclear distance is considered unchanged by isotopic substitution. Taking mass of oxygen = 15.9994 and that of carbon 12 to be 12.00 we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994 m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 * 15.9994}$$

After solving, we get $m' = 13.0007$. This value is within 0.02 % of best value obtained by another method.

The change in the rotational energy levels of the molecule such as CO is shown in the Figure [see Fig. 5(a)].

The transitions in the heavier molecule are shown in Fig. 5(b) by dotted lines. Due to this shift in the spectral lines, we can determine the atomic weights with extreme precision. It can also help us to estimate the abundance of isotopes by comparison of absorption intensities.

6. DIATOMIC MOLECULE AS A NON-RIGID ROTOR

It is possible to calculate internuclear distances from microwave spectra. Consider the hydrogen fluoride, the internuclear distance for $J = 1$ is

0.931 Å; for $J = 4$, it is 0.938 Å; for $J = 6$, it is 0.946 Å and for $J = 10$, it is 0.969 Å. It means that the separation between successive lines (hence B) decreases steadily with increasing J . In the same way B is no longer constant, but it also decreases with increase in the J value. Hence bond length increases with increase in J value and the bond between the molecule is not a rigid but elastic. It is quite obvious that with increase in the frequency of rotation, the centrifugal force tends to increase, hence the atoms are more apart from each other [8].

As a matter of fact, all bonds are elastic in nature. When the molecules rotate with elastic bond between them, they may have vibrational energy also. As the bond stretches and compresses with change in the frequency of rotation, we can consider the motion of the molecule as a simple harmonic motion. The force constant k is given by

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \left(\because \bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \right) \dots (18)$$

where $\bar{\omega}$ is vibrational frequency, c is velocity of light and μ is the reduced mass of the system. Hence the variation in B with J is determined by the force constant [9].

Because of the elasticity, r and B changes during vibration [1]. If we measure these quantities by microwave techniques, we observe many vibrations during rotation. However, the rotational constant is given by

$$B = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c}$$

$$\therefore B \propto \frac{1}{r^2} \dots (19)$$

since all the quantities are independent of vibration.

In simple harmonic motion molecular bond is compressed and extended on equal distance from equilibrium hence the average distance remains constant but the average value of $1/r^2$ is not constant.

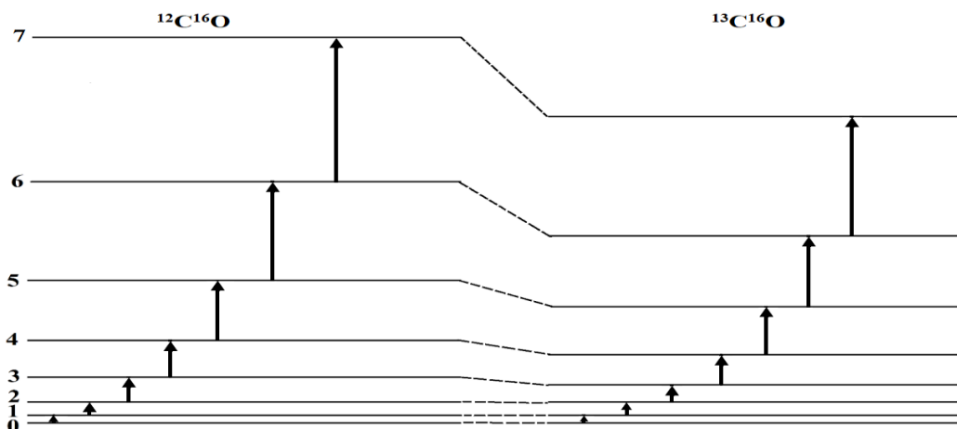


Fig. 5(a) Effect of isotopic substitution on the energy levels of diatomic molecule

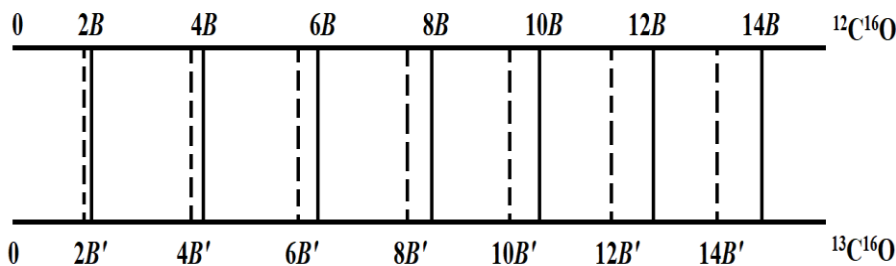


Fig. 5(b) Effect of isotopic substitution on the absorption spectrum of diatomic molecule

7. SPECTRUM OF NON-RIGID DIATOMIC MOLECULE

We can set up the Schrodinger's equation for rotational energy. Then we will get

$$E = \frac{h^2}{8\pi^2 I} J(J + 1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J + 1)^2 \dots (20)$$

Let us now investigate the spectrum expected from a non-rigid rotor. In terms of wave-number, the energy equation can be written as

$$\epsilon_J = \frac{E}{hc} = \frac{h}{8\pi^2 I c} J(J + 1) - \frac{h^3}{32\pi^4 I^2 r^2 k c} J^2(J + 1)^2$$

Rohit Singh

i. e. $\epsilon_J = BJ(J + 1) - DJ^2(J + 1)^2 \dots (21)$

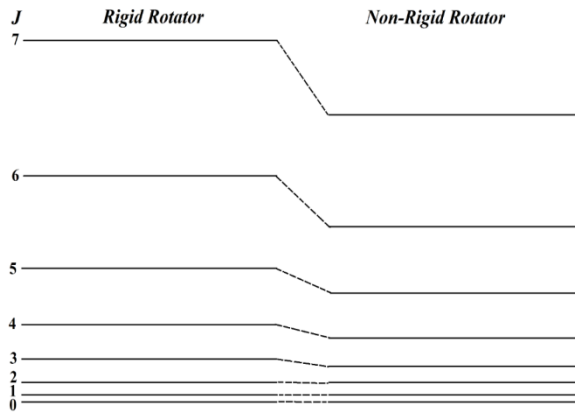


Fig. 6(a) The change in rotational energy levels when passing from a rigid to non-rigid diatomic molecule

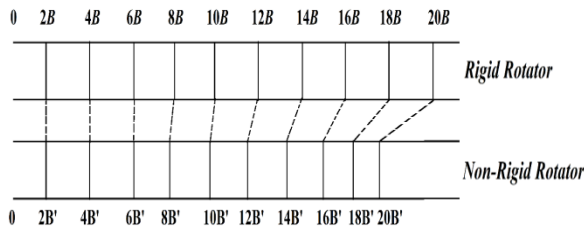


Fig. 6(b) Change in absorption spectrum when passing from a rigid to non-rigid diatomic molecule

From the values of B and D , we can prove that

$$D = \frac{16B^3\pi^2\mu c^2}{k}$$

i.e.

$$D = \frac{4B^3}{\bar{\omega}^2} \left(\because \bar{\omega}^2 = \frac{k}{4\pi^2 c^2 \mu} \right) \dots (22)$$

Substituting $J = 0, 1, 2, 3, \dots$ in equation (21), we get

$$\epsilon_0 = 0 \text{ (ground state)}$$

$$\epsilon_1 = 2B - 4D \text{ (first excited state)}$$

$$\epsilon_2 = 6B - 36D \text{ (second excited state)}$$

$$\epsilon_3 = 12B - 144D \text{ (third excited state)}$$

$$\epsilon_4 = 20B - 400D \text{ (fourth excited state)}$$

$$\epsilon_5 = 30B - 900D \text{ (fifth excited state)}$$

.....

where D is called as the ‘centrifugal distortion constant’ given by $D = \frac{h^3}{32\pi^4 I^2 r^2 k c}$ which is a positive quantity [1].

Above result shows that if we go from rigid to non-rigid diatomic molecule, the energy of energy levels is lowered [9]. The selection rule for non-rigid diatomic molecular spectra is still $\Delta J = \pm 1$. When a transition takes place between a lower level (J) and upper level ($J + 1$), the wave number of the absorbed radiation would be given by

$$\bar{\nu}_{J \rightarrow J+1} = \epsilon(J + 1) - \epsilon(J)$$

$$\begin{aligned} \text{i. e. } \bar{\nu}_{J \rightarrow J+1} &= [B(J + 1)(J + 2) \\ &\quad - D(J + 1)^2(J + 2)^2] \\ &\quad - [BJ(J + 1) - DJ^2(J + 1)^2] \end{aligned}$$

$$\text{i. e. } \bar{\nu}_{J \rightarrow J+1} = 2B(J + 1) - 4D(J + 1)^3 \dots (23)$$

In this formula, the J values of only ‘lower’ state occur.

The above equation (23) represents transitions from J to $(J + 1)$. The energy level diagram for the rigid and non-rigid diatomic molecules is shown in Fig. 6(a). The spectrum of non-rigid diatomic molecule is similar to that of rigid diatomic molecule except that each line is displaced slightly to low frequency [see Fig. 6(b)], the displacement increases with $(J + 1)^3$. If we know the value of D , then we can determine the value of J of lines observed in a spectrum. Similarly, it can also be used to find the approximate value of vibrational frequency of diatomic molecule by using equation (22).

8. CONCLUSION

In this article, we have described various aspects of rotational spectroscopy of a diatomic molecule treated as a rigid rotor. We have discussed the theory of quantized rotational energy levels of the system and elucidated the rotational transitions exhibited by the system. A measurement of frequencies of these transitions in the rigid rotor model leads to a determination of moment of inertia and the internuclear distance (bond length) of the heteronuclear diatomic molecule. Further the article addressed the connection between the observed intensity envelope in the rotational spectrum and the population distribution of the molecules at the various rotational levels. In the rigid rotor model, the absorption spectrum of diatomic model is observed to consist of a series of equidistant lines with constant separation $2B$ while from the actual experimental data, it was clear that the separation between successive

absorption lines decreases progressively with increasing rotational quantum number]. The discrepancies of theoretical and experimental data were resolved by considering the diatomic molecule as a non-rigid rotor. The rotational transitions of the non-rigid molecule were also described.

REFERENCES

- [1] Banwell C N., McCash, E M, 2017. Fundamentals of Molecular Spectroscopy (McGraw Hill Education, 4th Edition).
- [2] Pavia, D L., Lampman, G M., Kriz, G A., Vyvyan, J R. 2015. Introduction to Spectroscopy (Cengage Learning India, 5th Edition).
- [3] Atkins, P., Paula J D., Keeler, J.2018. Physical Chemistry (Oxford University Press, 11th Edition).
- [4] Robert K Bohn, Microwave spectroscopy information letter, University of Connecticut, 2012, <http://www.ifpan.edu.pl/~kisiel/rothist/rothist.html>
- [5] McQuarrie, D A, 2008. Quantum Chemistry (University Science Books, 2nd Edition).
- [6] Brown JM. Carrington, A.2003. Rotational spectroscopy of diatomic molecule (Cambridge University Press, 1st Edition).
- [7] Li, L., Sun, M., Li, X H., Zhao, Z W., Ma, H M., Gan, H Y., Lin, Z H., Shi S C., Ziuryse L M, 2014, Recent Advances on Rotational Spectroscopy and Microwave Spectroscopic Techniques, Chinese Journal of Analytical Chemistry, 42 (9), 1369 – 1378.
- [8] Vavra, K., Lukova, K., Kania, P., Koucky J., Urban S, 2020, Rotational spectra in seven excited vibrational states of 1,2,3,4-tetrahydroquinoline, Journal of Molecular Structure 1215, 128181.
- [9] Sathyanarayana, DN,2020. Handbook of Molecular Spectroscopy: From radio waves to gamma rays (Dreamtech Press, 2nd Edition).