

## **Scientific Writing Assignment**

### **Rotation Of Molecules**

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## **Concepts**

### **Molecules**

A combination of different kinds of atoms is known as a molecule. We have two different types of molecules classified in terms of dipole moment, which are Homonuclear and Heteronuclear molecules. Homonuclear molecules do not possess a dipole moment, whereas Heteronuclear molecules possess a permanent dipole moment. Diatomic molecules contain two atoms, and the distance between them is known as the internuclear distance, as it connects the nucleus of the two atoms.

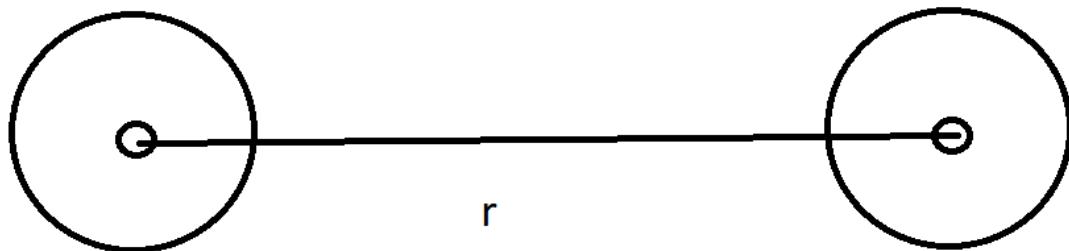


Figure 1: Two atoms forming a molecule

As shown in figure 1, the two atoms that form a molecule have their own nucleus and are separated by a distance  $r$  which is the internuclear distance between them. Molecules are also classified based on their arrangement. The most common types are linear, spherically top, symmetrically top, and asymmetrically top molecules, which are discussed below in detail. These can be further classified based on

diatomic and polyatomic molecules. Diatomic molecules are molecules made up of two atoms, whereas polyatomic molecules are molecules that contain more than two atoms. In this report, we will be looking at diatomic linear molecules for the most part.

## Vibrational and Rotational Energy

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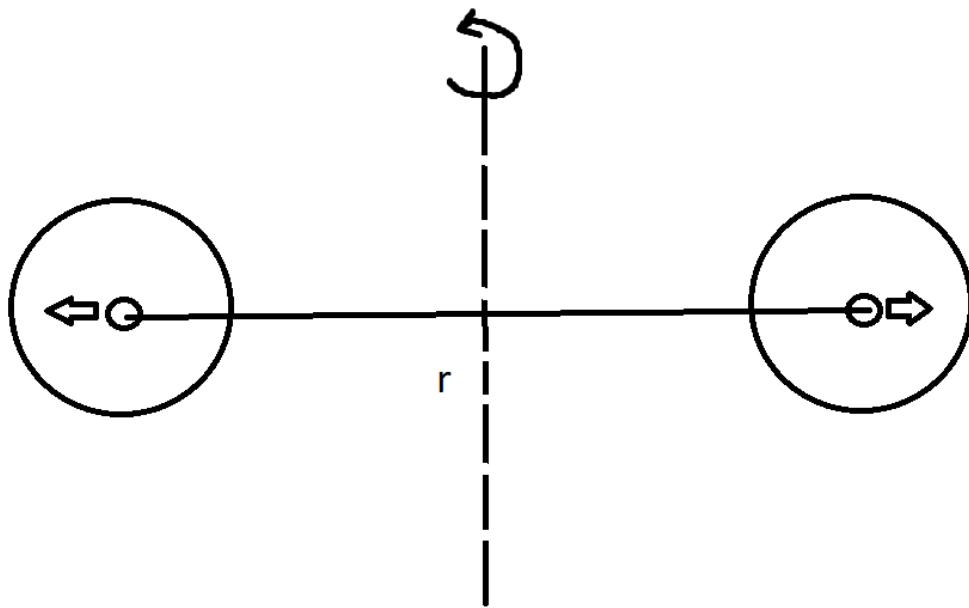


Figure 2: Different energies possessed by the molecule

There are a total of three types of energies the molecule can possess. The first kind of energy of a molecule is gained when an electron in an atom jumps from a higher excited state to a lower excited state and releases photons as energy in the process. The second kind of energy comes in the form of vibrational energy. As the nucleus of these two atoms can vibrate in the direction of the arrows, as shown in figure 2, they will possess some vibrational energy. Similarly, the entire system can rotate about a given axis around its center of mass, and thus it will also possess some rotational energy. Both these vibrational and rotational energies are quantized, which is where the effects of quantum mechanics come into the picture. The levels of energy in these molecules are greater than in an atom because they radiate light

in lower frequencies as compared to atoms, and thus the energy states are called bands.

## Molecular Spectroscopy

The analysis of all wavelengths of light emitted and absorbed by the given molecule arising from the different energies of the molecule is known as Molecular Spectroscopy, and the different wavelengths together are called the molecule's spectra.

### Types of Molecular Spectra

The types of molecular spectra can be classified as follows

#### 1. Pure rotational spectra

- Rotational spectra arise due to the transition between rotational levels shown in the figures below.

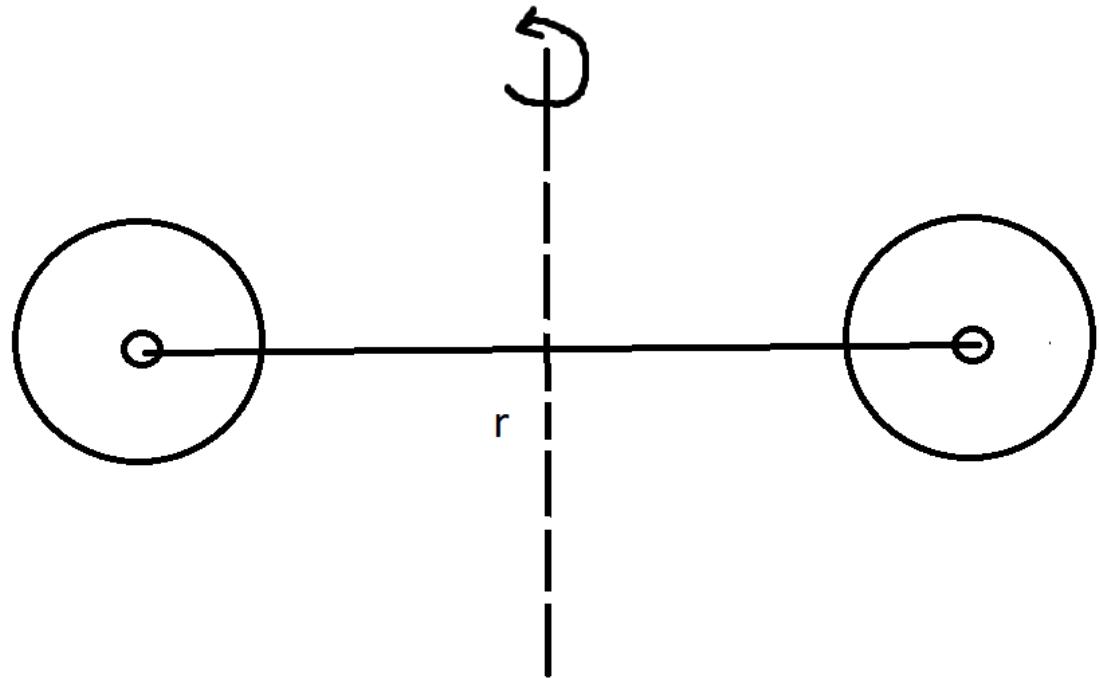


Figure 3: Rotation about the center of mass of the molecule

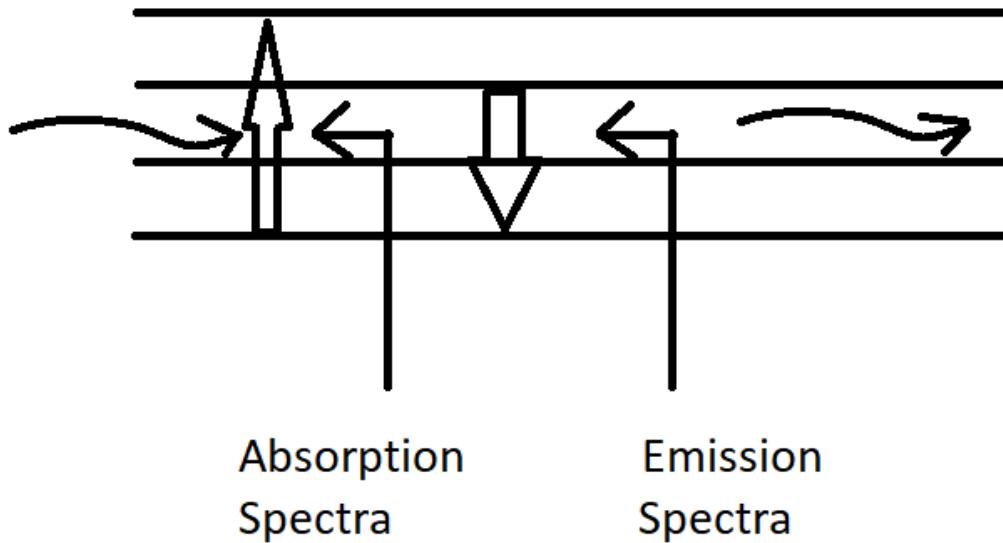


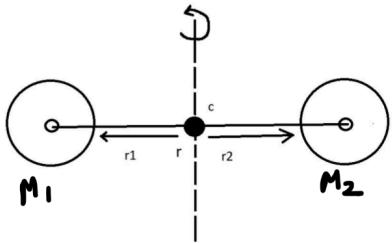
Figure 4: Absorption and Emission spectra

- Rotational spectra are observed in the Infrared ( $10^{-3}$  to  $10^{-2}$ ) and Microwave ( $10^{-2}$  to  $10^{-1}$ ) spectra of the electromagnetic spectrum.
- The rotational energy of the molecule is given as  $E = I\omega^2$
- The rotational spectra only arise for heteronuclear molecules.
- It is used to find the internuclear distance between atoms and also the moment of inertia of the atoms.

### Molecule as a Rigid Rotator

The derivation for Molecule as a Rigid Rotator is as follows

## Molecule as Rigid Rotator



Here by the definition of center of mass we know  
 $M_1 r_1 = M_2 r_2$  and also  $r = r_1 + r_2$

Therefore from the two equations we have

$$r_2 = \frac{M_1}{M_1 + M_2} r \text{ and } r_1 = \frac{M_2 r}{M_1 + M_2}$$

Now we know that Moment of Inertia about the axis of rotation is given as

$$\begin{aligned} I &= \sum_i m_i r_i^2 = M_1 r_1^2 + M_2 r_2^2 \\ &= M_1 \left( \frac{M_2 r}{M_1 + M_2} \right)^2 + M_2 \left( \frac{M_1 r}{M_1 + M_2} \right)^2 \\ &= \frac{M_1 M_2^2 r^2}{(M_1 + M_2)^2} + \frac{M_2 M_1^2 r^2}{(M_1 + M_2)^2} = \frac{M_1 M_2}{M_1 + M_2} r^2 \end{aligned}$$

We know that

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \text{ where } \mu = \text{reduced mass}$$

Therefore the Moment of Inertia of the diatomic molecule is given as

$$I = \mu r^2$$

Now, we will determine the possible energy states of the rigid rotator using Schrodinger's equation

The Schrödinger's equation of a rigid rotator is given as

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} E \psi = 0$$

In spherical polar coordinates, the equation is given as

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} E \psi = 0$$

Now we know  $I = \mu r^2$ , therefore we can replace  $\mu$  by  $\frac{I}{r^2}$

Therefore we have

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I E}{h^2} \psi = 0$$

Now we separate out the variables  $\theta$  and  $\phi$  by  
making the substitution  
 $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) \Phi + \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} \Theta + \frac{8\pi^2 I E}{h^2} \Theta \Phi = 0$$

Multiplying the equation by a factor of  $\frac{\sin^2\theta}{\Theta\Phi}$

$$\frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{8\pi^2 I E \sin^2\theta}{h^2} = -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2}$$

Here the L.H.S is only a function  $\theta$  whereas the  
R.H.S is only a function  $\Phi$  only. Assuming a constant  
 $K^2$

We have two equations

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -K^2 \Phi \text{ and } \frac{\sin \theta}{H} \frac{d}{d\theta} \left( \sin \theta \frac{d\Phi}{d\theta} \right) + \frac{8\pi^2 I E \sin^2 \theta}{h^2} = K^2 \quad -②$$

On multiplying by  $\frac{H}{\sin^2 \theta}$ , the second equation becomes

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Phi}{d\theta} \right) + \left( \frac{8\pi^2 I E}{h^2} - \frac{K^2}{\sin^2 \theta} \right) \Phi = 0$$

The solution of eqn ① is given as

$\Phi_M(\phi) = A e^{iK\phi}$ ,  $\Phi_M(\phi)$  is single valued for all values of  $\phi$ , provided  $K$  is an integer (i.e  $K=0, \pm 1, \pm 2, \dots$ )

Now we calculate the normalization constant

$$\int_0^{2\pi} \Phi_M^*(\phi) \Phi_M(\phi) d\phi = A^2 \int_0^{2\pi} e^{iK\phi} e^{-iK\phi} d\phi = A^2 \int_0^{2\pi} d\phi$$

$$= A^2 (2\pi) = 1 \quad \therefore A = \frac{1}{\sqrt{2\pi}}. \text{ Therefore the sol'n of eq'n ①}$$

$$\Phi_M(\phi) = \frac{1}{\sqrt{2\pi}} e^{iK\phi} \quad K=0, \pm 1, \pm 2$$

Now we find the solution for eq<sup>n</sup> ② by again separating the variables such that

$$x = \cos\theta, P(x) = H(\theta)$$

$$\text{Therefore } \sin^2\theta = (1-x^2), \frac{dH}{d\theta} = \frac{dP}{dx}, \frac{d\theta}{d\theta} = -\frac{dP}{dx} \sin\theta$$

$$\text{Furthermore } \frac{d}{d\theta} = -\sin\theta \frac{d}{dx}$$

Thus eq<sup>n</sup> ② becomes

$$\frac{1}{\sin\theta} \left[ -\sin\theta \frac{d}{dx} \left\{ \sin\theta \left( -\frac{dP(x)}{dx} \sin\theta \right) \right\} \right] + \left( \frac{8\pi^2 IE}{h^2} - \frac{k^2}{\sin^2\theta} \right) P(x) = 0$$

$$\therefore \frac{d}{dx} \left\{ (1-x^2) \frac{dP(x)}{dx} \right\} + \left( \frac{8\pi^2 IE}{h^2} - \frac{k^2}{1-x^2} \right) P(x) = 0$$

$$\therefore (1-x^2) \frac{d^2P(x)}{dx^2} - 2x \frac{dP(x)}{dx} + \left( \frac{8\pi^2 IE}{h^2} - \frac{k^2}{1-x^2} \right) P(x) = 0$$

Comparing it to the associated Legendre's differential equation, we have

$$\frac{8\pi^2 I E}{h^2} = J(J+1) \therefore E = \frac{h^2}{8\pi^2 I} J(J+1), J=+z$$

Now the function  $P(x)$  is identified with the associated Legendre Polynomial  $P_J^{(K)}(x)$  of degree  $J$  and order  $K$ . Then the accepted solution are

$$\Theta_{J,K}(\theta) = N P_J^{(K)}(x) = N P_J^{(K)} \cos \theta, J=0, 1, 2, 3$$

These functions are found to vanish except when  $|K| < J$  therefore  $K$  can only take the values

$$K = J, J-1, J-2, \dots, -J$$

Now we normalize the equation

$$\int_0^\pi \Theta_{J,K}^*(\theta) \Theta_{J,K}(\theta) \sin \theta d\theta = 1$$

$$N^2 \int_{-1}^1 P_J^{(K)*}(x) P_J^{(K)}(x) dx = 1$$

Using orthogonal property of associated Legendre polynomials, we have

$$N^2 \frac{2}{2J+1} \left| \frac{(J+|K|)!}{(J-|K|)!} \right|^2 = 1, \text{ and therefore we have}$$

$$N = \sqrt{\frac{2J+1}{2} \frac{(J-|K|)!}{(J+|K|)!}}$$

Therefore the accepted solutions of the

(H) equation are

$$\Theta_{J,K}(0) = \sqrt{\frac{2J+1}{2} \frac{(J-|K|)!}{(J+|K|)!}} P_J^{|K|} \cos\theta$$

Therefore the total eigenfunctions for the rigid rotator are

$$\Psi(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi}} \frac{(J-|K|)!}{(J+|K|)!} P_J^{|K|} \cos\theta e^{iK\phi}$$

$$\hat{L}^2 = -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

$$\text{and } \hat{L}_z = -\frac{i\hbar}{2\pi} \frac{\partial}{\partial\phi}$$

Therefore we have acceptable solutions for Schrodinger equation when  $\frac{8\pi^2 IE}{h^2}$  gets replaced by  $J(J+1)$  and

$J$  is a positive integer, therefore we have

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \psi = -J(J+1) \psi$$

$$-\frac{h^2}{4\pi^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \psi = J(J+1) \frac{h^2}{4\pi^2} \psi$$

$$\hat{L}^2 \psi = J(J+1) \hbar^2 \psi$$

where  $J(J+1)\hbar^2$  are the eigenvalues given  $J=0, 1, 2, \dots$   
Now considering normalized eqn for  $\Phi$  and differentiating it, we get

$$\frac{d\Phi_K(\phi)}{d\phi} = \frac{1}{\sqrt{2\pi}} e^{ik\phi} (ik) = ik \Phi_K(\phi)$$

$$\therefore -\frac{ih}{2\pi} \frac{d\Phi_K(\phi)}{d\phi} = \frac{K\hbar}{2\pi} \Phi_K(\phi)$$

From classical mechanics, we know

$$E = \frac{I\omega^2}{2} \quad L = I\omega \quad L = \sqrt{2EI}$$

Therefore the angular momentum  $L$  of the system in quantum state  $J$  is given by

$$L = \hbar \sqrt{J(J+1)}$$

which is the same as the general angular momentum in quantum mechanics.

Substituting in the operator, we get

$$\hat{L}_z \Phi_K(\phi) = K \hbar \Phi_M(\phi)$$

$$\hat{L}_z \psi = K \hbar \psi, \text{ where } K = 0, \pm 1, \pm 2, \dots, \pm J$$

Therefore the values of energy for rigid rotator are

$$E = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$J = 0, 1, 2, 3, \dots$   
 $J = \text{rotational quantum number}$

Since only discrete values of energy and angular momentum of rigid rotator are possible, the rotational frequencies are also discrete and are given as

$$\omega = \frac{L}{\lambda} = \frac{\hbar}{\lambda} \sqrt{J(J+1)}$$

$$v_{\text{rot}} = \frac{\omega}{2\pi} = \frac{\hbar}{2\pi\lambda} \sqrt{J(J+1)}$$

where  $v_{\text{rot}}$  = wave number

We get

$$F(J) = 0, 2B, 6B, 12B, 20B, 30B, \dots$$

Now we will talk about rotation spectra for a rigid rotator. Therefore the energy equation in terms of wave-number can be written as

$$F(J) = \frac{E}{hC} = \frac{\hbar}{8\pi^2 I C} J(J+1)$$

Let  $\frac{\hbar}{8\pi^2 I C} = B$  = rotational constant

$$\boxed{F(J) = BJ(J+1)} \quad J = 0, 1, 2, \dots$$

When a transition happens between an upper layer  $J'$  and a lower layer  $J''$ , then  $v = 2B(J'+1)$ . There each of the lines is equispaced with a distance of  $2B$ .

## **Non-rigid Rotator**

For the non-rigid rotator, the rotational lines are not equidistant as the molecule is not rigid. Therefore the modified rotational term becomes

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

Here, D is the centrifugal distortion constant and is much smaller than B, and thus the spacing between successive rotation levels decreases. The wavenumber is now given by  $\nu = 2B(J+1) - 2D(J+1)^3$ . This shows that the separation between lines decreases slightly as J increases.

## **2. Vibrational Rotational Spectra**

- Vibrational Rotational Spectra arise from transitions between vibrational energy states associated with the same electronic states.
- The energy due to transition is again observed in the near-infrared region of the electromagnetic spectrum.
- These spectra are only defined for molecules with permanent dipole moment as they oscillate with the fluctuating electromagnetic field. Thus they are shown by Heteronuclear molecules.
- These spectra are obtained in absorption.
- These spectra are divided into two bands which are the fundamental(intense) band which has the highest frequency, and overtones(weak), which have less frequency as compared to the fundamental band.

## **Potential energy curve $V(r)$ vs. $r$**

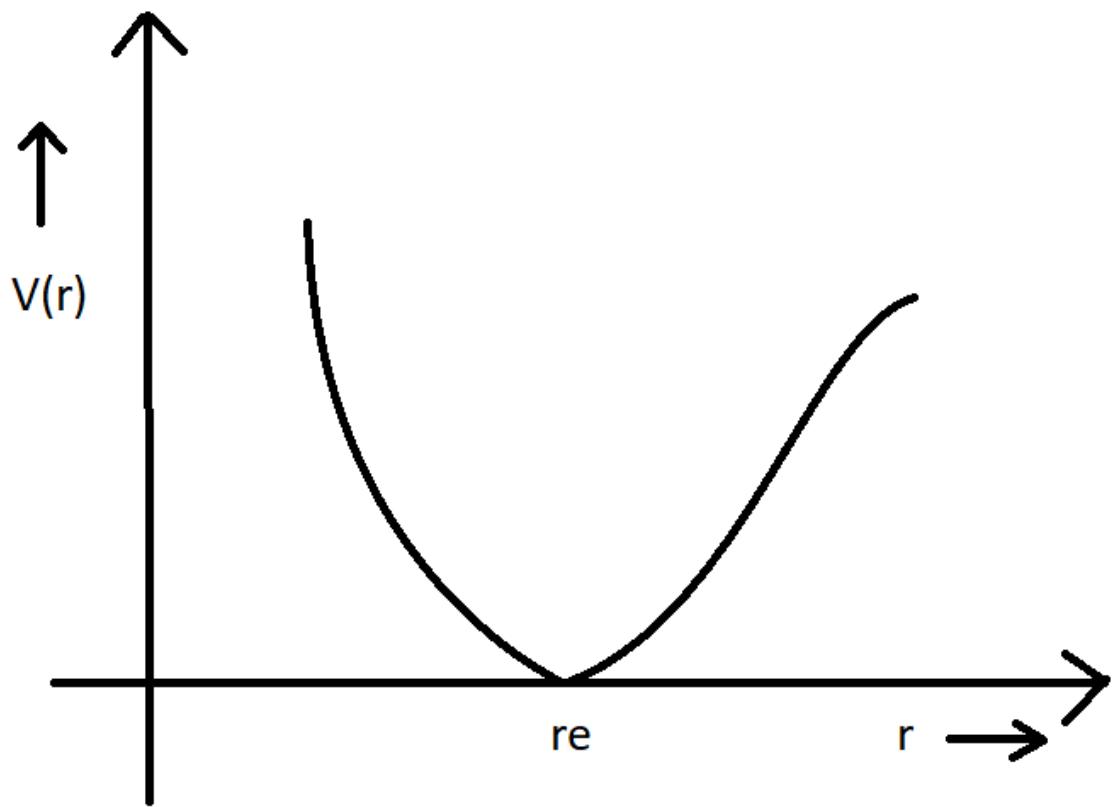


Figure 6: Potential energy curve

We find the expression for this curve using the Taylor series expansion of  $V(r)$  in  $(r-r_e)$ . Which is given as

$$V(r) = V(r_e) + (r-r_e)(\partial(V(r)/\partial r)_{r=r_e} + (r-r_e)^2/2!(\partial^2(V(r)/\partial r^2)_{r=r_e} + \dots + (r-r_e)^3/3!(\partial^3(V(r)/\partial r^3)_{r=r_e}$$

As the first term has only  $r_e$  we can set it equal to zero as we are interested in finding the potential difference and not the potential. The second term is minimum at  $r = r_e$  and thus won't contribute much and can be neglected.

If we retain only the first term after that, we get  $V(r) = k(r-r_e)^2/2$ , which we can use to define the molecule and then solve Schrodinger's Equation for the molecule. Solving the equation, we get a form of Hermite differential

equation, and solving it gives us the solution in terms of the Hermite Polynomial, which we restrict to positive integers and get the form of Energy as

$$E = h\nu_{\text{osc}}(v + 1/2)$$

where  $v$  is the vibrational quantum number. Here at  $v = 0$ , we get the zero point energy as  $E = h\nu_{\text{osc}}/2$ .

## Spectrum

Now, we will look at the spectrum analysis of this oscillator. The vibration terms for this oscillator are

$$G(v) = \nu_{\text{osc}}/c(v + 1/2)$$

Where  $\nu_{\text{osc}}/c$  is the classical frequency and is known as the vibrational constant and is denoted by  $\omega$ . Thus we get

$$G(v) = \omega(v + 1/2)$$

Where  $v = 0, 1, 2, 3, \dots$  which gives us  $G(v) = 1/2\omega, 3/2\omega, 5/2\omega, 7/2\omega, 9/2\omega$ . If we calculate the wavenumber for successive rotational frequencies where  $\Delta v = \pm 1$ , we observe that the only band obtained is at  $\omega$ . However, there are still weak bands present which cannot be explained by the above formulation. Thus we consider the molecule as an anharmonic oscillator.

## Molecule as an anharmonic oscillator

Now we will get the weak bands for the anharmonic oscillator by not taking  $\Delta v = \pm 1$  strictly and allowing other transitions to happen by which we first change the approximation in the  $V(r)$  term by taking the first two terms instead of just the first and then putting it in the Schrodinger equation giving us the energy levels as

$$E(v) = hc\omega_e(v + 1/2) - hc\omega_e\chi_e(v + 1/2)^2$$

and the corresponding term values as

$$G(v) = \omega_e(v + 1/2) - \omega_e\chi_e(v + 1/2)^2$$

The zero point energy is again obtained by putting  $v = 0$  and thus we get

$$G(0) = \omega_0(v) - \omega_0\chi_0(v)^2$$

On equating the coefficients of power of  $v$  we get

$$\begin{aligned}\omega &= \omega_e - \omega_e\chi_e + \dots \\ \omega_0\chi_0 &= \omega_e\chi_e - \dots\end{aligned}$$

The wavenumber separation between two absorption bands is given as

$$\Delta G(v + 1/2) = \omega_0 - \omega_0\chi_0 - 2\omega_0\chi_0(v)^2$$

The second difference is given by

$$\Delta^2 G(v + 1/2) = -2\omega_0\chi_0(v)^2$$

Which determines the anharmonicity constant  $\omega_0\chi_0$ , and thus we also get weak bands along the main band at  $\omega$ .

## **Vibrational Frequency and Force Constant for Anharmonic Oscillator**

We know that the classical vibration is given as

$$\nu_{\text{osc}} = 1/2\pi\sqrt{k/\mu}$$

where  $k$  is the force constant and  $\mu$  is the reduced mass. Now we get

$$\nu_{\text{osc}}(v) = c(\omega_e - \omega_e\chi_e - 2\omega_e\chi_e(v))$$

Thus, we can say as  $v$  increases, the classical vibrational frequency  $\nu_{\text{osc}}(v)$  decreases.

### **Isotope effect on vibrational levels**

From the above equations for isotopes, the harmonic frequencies can be given as

$$\nu_{\text{osc}}(v) = 1/2\pi\sqrt{k/\mu}$$

$$\nu_{\text{osc}}(v') = 1/2\pi\sqrt{k/\mu'}$$

Therefore from the above equations we can get

$$\nu_{\text{osc}}(v')/\nu_{\text{osc}}(v) = \sqrt{\mu'/\mu} = \rho$$

Therefore the vibrational terms of these two isotopes are given by

$$\begin{aligned} G(v) &= \omega(v + 1/2) \\ G(v') &= \rho \omega(v + 1/2) \end{aligned}$$

Therefore the isotropic shift in the vibrational level is given as

$$G(v') - G(v) = (\rho - 1) \omega(v + 1/2)$$

since  $\rho < 1$  the vibrational level of the heavier isotope are lower than the corresponding levels of the lighter isotope.

If anharmonicity is taken into account, we get

$$G(v) = \omega_e(v + 1/2) - \omega_e\chi_e(v + 1/2)^2$$

$$G(v') = \omega_e(v + 1/2) - \rho^2 \omega_e\chi_e(v + 1/2)^2$$

Therefore, the isotropic shift in vibration now is given as

$$G(v') - G(v) = (\rho - 1)(v + 1/2) - (\rho^2 - 1) (\omega_e - 2 \omega_e\chi_e(v + 1/2))$$

since  $\rho < 1$  the vibrational level of the heavier isotope are lower than the corresponding levels of the lighter isotope and the shift between corresponding levels increases with increasing  $v$ .

The band shift  $\Delta v$  is given as

$$\Delta v = (\rho - 1)\omega(v' - v'')$$

Thus for the fundamental band we have  $v' = 1$  and  $v'' = 0$  therefore

$$\Delta v = (\rho - 1)\omega$$

Therefore the shift increases as the value of  $v'$  increases.

### **Molecule as vibrating rotator**

The near-infrared spectra of molecules consist of bands composed of closed lines arranged in a particular manner. In the series of lines that are not equidistant, a line is missing at the center of the band. The missing line is known as the null line or zero line. Furthermore, the lines show a rather poor tendency of convergence toward the high-wave number side, and the band is said to be degraded towards the low-wave number side, which is towards red. This observed structure suggests that in a vibrational transition, the molecule also changes its rotational energy state, and thus it should be treated as a vibrating rotator.

By ignoring any interaction between vibration and rotation of molecule, the eigenstates of the vibrating rotator would be the sum of eigenvalues of the anharmonic oscillator and the rigid rotator, both of which we have derived above and are given as

$$G(v) + F(J) = \omega_e(v + 1/2) - \omega_e\chi_e(v + 1/2)^2 + BJ(J+1)$$

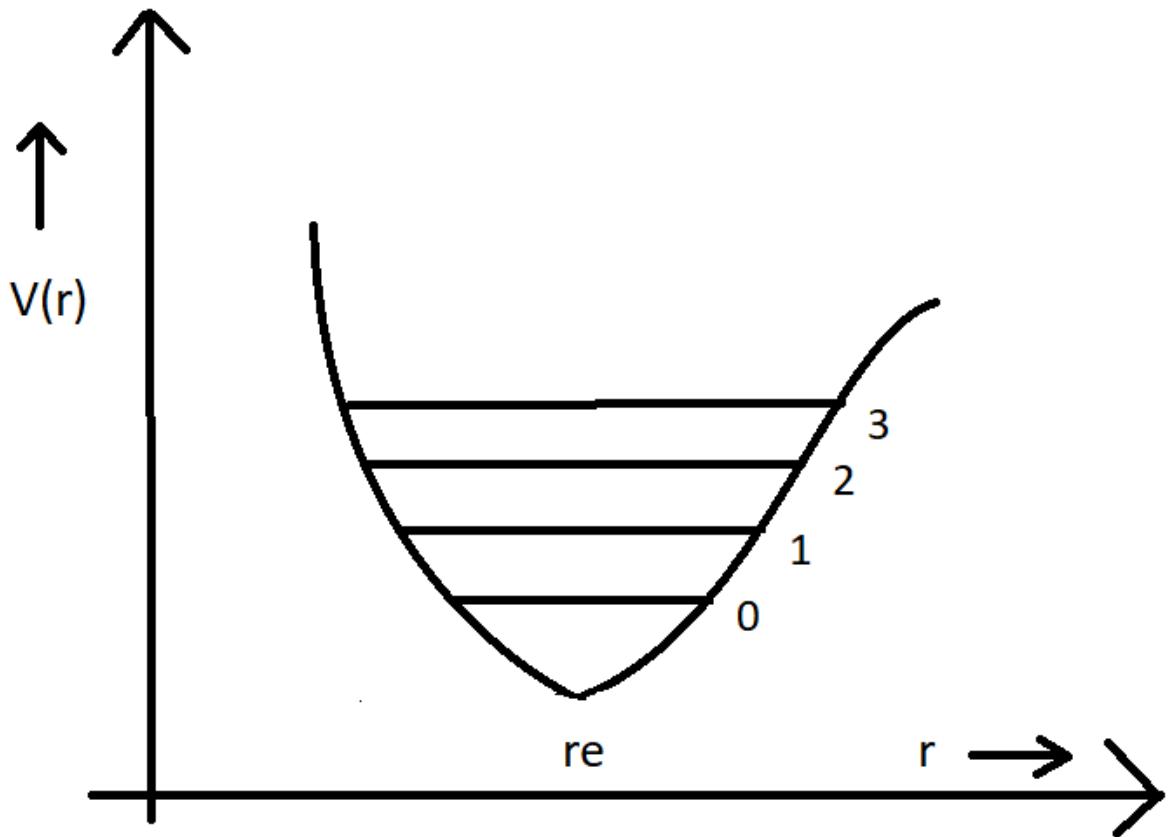


Figure 7: Eigenstates of the vibrating rotator

Here B is different for different vibrational states thus the equation of the rotational constant associated with a vibrational state  $v$  is given as  $B_v = h/8\pi^2\mu c(1/r^2)_v$ , where  $(1/r^2)_v$  is the mean value of  $(1/r^2)$  in the vibration state  $v$  during the vibration. Where  $B_v$  can also be written as

$$B_v = B_e - \alpha_e(v + 1/2) + \dots$$

Where  $\alpha_e$  is a constant that depends on the shape of the potential curve ( $\alpha_e \ll B_e$ ) and  $B_e$  is the rotational constant corresponding to the separation  $r_e$  at the minimum of the potential curve and is given as

$$B_e = h/8\pi^2 \mu c r_e^2$$

Now the term values for the vibrating rotator are given as

$$G(v) + F(J) = \omega_e(v + 1/2) - \omega_e \chi_e(v + 1/2)^2 + B_v J(J+1)$$

and  $B'_v < B''_v$  which means that the factor decreases slightly with increasing  $v$ . Since the eigenfunctions for the vibrating rotator are the products of the eigenfunctions of the oscillator and the rotator, the selection rules are the same as for these systems individually, that is  $\Delta v = \pm 1, \pm 2, \pm 3, \dots$  and  $\Delta J = \pm 1$

For  $J$ , both the transitions  $\Delta J = \pm 1$  are now valid in absorption as the two  $J$  levels involved now belong to different vibrational levels. For a given vibrational transition, the rotational transition  $\Delta J = + 1$  gives one set of lines known as the ‘R-branch’ while the rotational transition  $\Delta J = - 1$  gives another set of lines known as the ‘P-branch’. All the lines of both branches form a vibration-rotation band. The wave numbers of branch lines of a particular band  $v'$ ,  $v''$  are given by

$$v = v_0 + B'_v J'(J'+1) + B''_v J''(J''+1)$$

where  $v_0 = G(v') - G(v'')$  is the wave number for pure vibrational transition(for  $J' = J'' = 0$ ) which is not allowed as  $\Delta J$  cannot be zero and thus corresponds to the missing line in the band.  $v_0$  is also known as the wave number of band origin.

### R-branch

For  $\Delta J = J' - J'' = + 1$ , so that  $=J' - J'' = + 1$ , we get the lines of the R-branch with the wave number as

$$v_R = v_0 + 2B_v' + 3B_v' - B_v''J'' + B_v' - B_v''J''^2$$

where  $J''$ , the lower rotational quantum number can take the values of zero and positive integers. Thus the R-branch consists of a series of lines named as R(0), R(1), R(2),... on the high-wave side of the band origin  $v_0$ . Also  $B_v' < B_v''$  therefore the line spacing decreases very slowly as  $J''$  takes on increasing values.

### P-branch

For  $\Delta J = J' - J'' = -1$ , so that  $=J' - J'' = -1$ , we get the lines of the P-branch with the wave number as

$$v_P = v_0 - (B_v' + B_v''J'') + (B_v' - B_v'')J''^2$$

where  $J''$ , the lower rotational quantum number can take the values of negative integers. Thus the R-branch consists of a series of lines named as P(1), P(2),... on the low-wave side of the band origin  $v_0$ . Also  $B_v' < B_v''$  therefore the line spacing increases as  $J''$  takes on increasing values. If we neglect vibrational rotational interaction  $B_v' = B_v'' = B$  then the wave numbers of the R and P branches would have equispaced lines. The resulting equation for both branches is the equation of parabolas. Since they have common lower and upper states they should be inter-related and by fitting them into the same parabolic equation we get

$$v = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2$$

where  $m = J'' + 1 = 1, 2, 3, \dots$  for R(0), R(1), R(2),...

where  $m = -J'' = -1, -2, -3$  for lines P(1), P(2),...

and  $m = 0$  for zero gap  $v_0$

A plot for the above equation can be given as

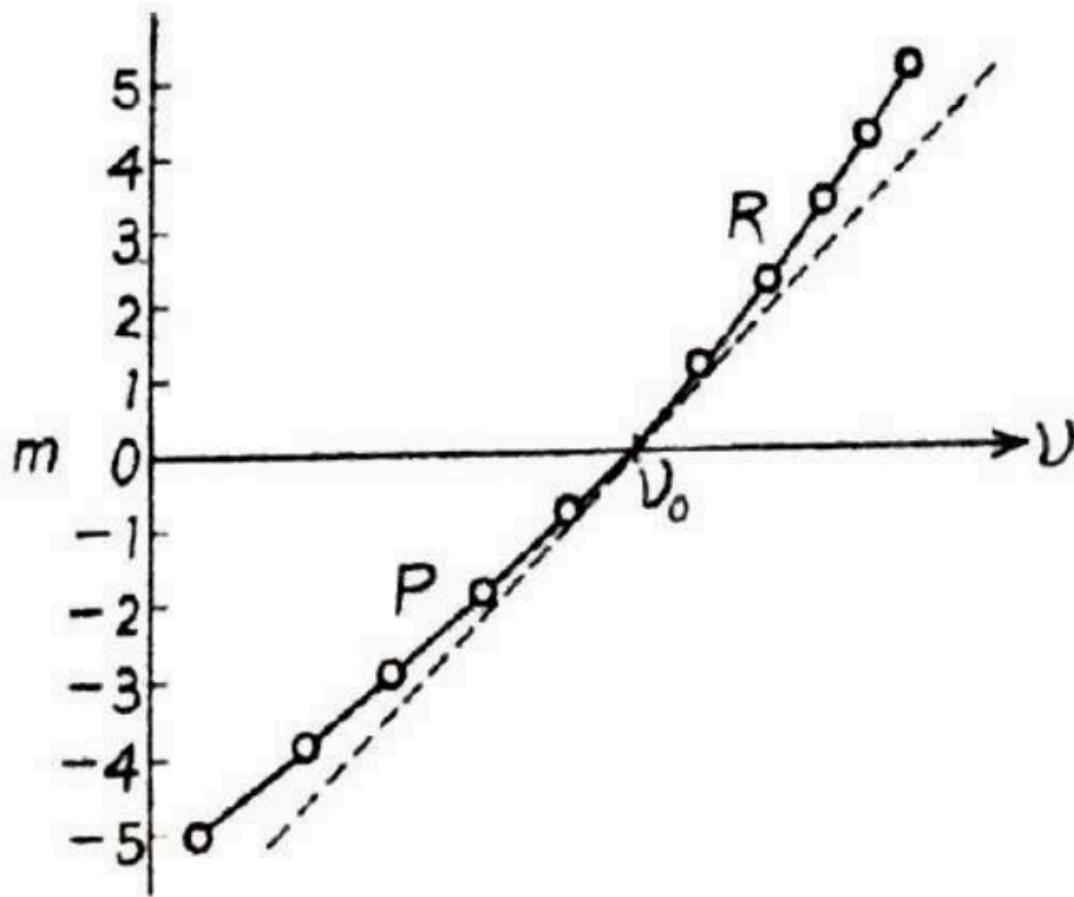


Figure 8: Plot for R and P branch for vibrating rotator

where the dashed line corresponds to  $B_v' = B_v''$ . Since  $\alpha_e$  is very small the difference between  $B_v' - B_v''$  is also very small. Hence the curve only slightly deviates from the straight line. This is the main reason why vibration-rotation bands show a very poor tendency for head formation. Where a band head is the abrupt edge of a spectroscopic band. Thus rotational-vibration bands are always degraded towards the lower wave number side towards red.

## References

Rajkumar(Atomic and molecular physics)

