RESEARCH ARTICLE

Harmonic and Anharmonic Oscillator Models for Pure Vibrational Infrared Spectroscopy of Diatomic Molecules

Rohit Singh

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

ABSTRACT: In molecular vibrational infrared spectroscopy, absorption spectra arise from molecular vibration and correspond to transitions between the vibrational energy levels associated with a given electronic state of the molecule. The vibrational transitions, which fall in the near infrared region, are induced through the interaction of the molecular electric dipole with the electric vector of the electromagnetic radiation. The near infrared region extends roughly from $1\mu m$ to $10^2\mu m$. The article explains the pure vibrational absorption spectra of diatomic molecules such as HCl, HBr, HI, CO, … etc. In order to explain the vibrational spectra, diatomic molecules are treated as harmonic oscillator and anharmonic oscillator. In the harmonic oscillator model, we get only one absorption band at the wavenumber value$\overline{\omega}_{osc}$ corresponding to frequency of oscillationν_{osc} while in the actual experimental data, there are many absorption bands corresponding to wave numbers slightly lesser than $\overline{\omega}_{osc}$, $2\overline{\omega}_{osc}$, $3\overline{\omega}_{osc}$, ……..The occurrence of these additional bandsis attributed to the selection rule $\Delta v = \pm 2, \pm 3, \pm 4$, ……The additional bands are having lesser intensity and are called overtone bands.

KEYWORDS: Pure vibrational spectra, Diatomic molecules, Harmonic oscillator, anharmonic oscillator, Population of excited states, Fundamental band, Overtone bands, Hot band.

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1.INTRODUCTION

Infrared (IR) spectroscopy, an analytical technique that takes advantage of the vibrational transitions of a molecule, has been of great significance to scientific researchers in many fields such as protein characterization, nanoscale semiconductor analysis and space exploration [1]. Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them [2]. Chemical compounds have different chemical properties due to the presence of different functional groups [3].

The atoms in a molecule do not remain in fixed relative position but vibrate about some mean position. The internuclear distance changes when the nuclei of these molecules vibrate relative to each other. Thus, these molecules possess an oscillating dipole, which according to classical electrodynamics, emits radiations of frequency that fall in near infrared region [4]. Heteronuclear diatomic molecules such as HCl, HI, CO, CN, …. etc. have intrinsic electric dipole moment and are capable of interacting with electromagnetic radiation. Hence, these molecules exhibit vibrational spectra. Homonuclear diatomic molecules do not have dipole moment and hence do not give vibrational spectra [5, 6].

To develop a description of the vibrational states, we will consider the diatomic molecule to be a Harmonic oscillator, i.e. atoms execute simple harmonic motion about their mean position and the restoring force applied on the atoms is directly proportional to displacement. A theoretical analysis of the quantized vibrational energy levels and the vibrational transitions exhibited by the polar heteronuclear molecules is presented. The harmonic oscillator model is a great approximation of a molecular vibration, but has key limitations:1. Due to equal spacing of energy, all transitions occur at the same frequency (i.e. single line spectrum). However, experimentally many other lines (called overtones) are often observed 2. The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced. The discrepancies of theoretical and experimental data have been resolved by considering the diatomic molecule as an anharmonic oscillator.

2. THEORY OF PURE VIBRATIONAL SPECTRA

Now, we will discuss the theory of vibrational spectra of diatomic molecules. There are two models to discuss the pure vibrational motion of heteronuclear diatomic molecule.

**Corresponding Author: rohit.phy@patnawomenscollege.in*

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i. Harmonic oscillator model
ii. Anharmonic oscillator model

2.1 DIATOMIC MOLECULE AS A HARMONIC OSCILLATOR

Consider a diatomic molecule consisting of two atoms $A$and B and separated by equilibrium distance $r_{eq.}$.Fig. 1 shows how the potential energy of diatomic molecule varies with the internuclear distance r. The minimum of this curve corresponds to the normal configuration of the molecule. The zero of the curves is found at the value $r = r_{eq.}$. Any energy in excess of this, for example, ε_1 arises because of extension or compression of the bond [1]. If one of the atoms (suppose A) is considered to be stationary on the $r = 0$ axis, the other will oscillate between B' and B''.If the energy is increased to ε_2, the oscillation will become more vigorous [1].

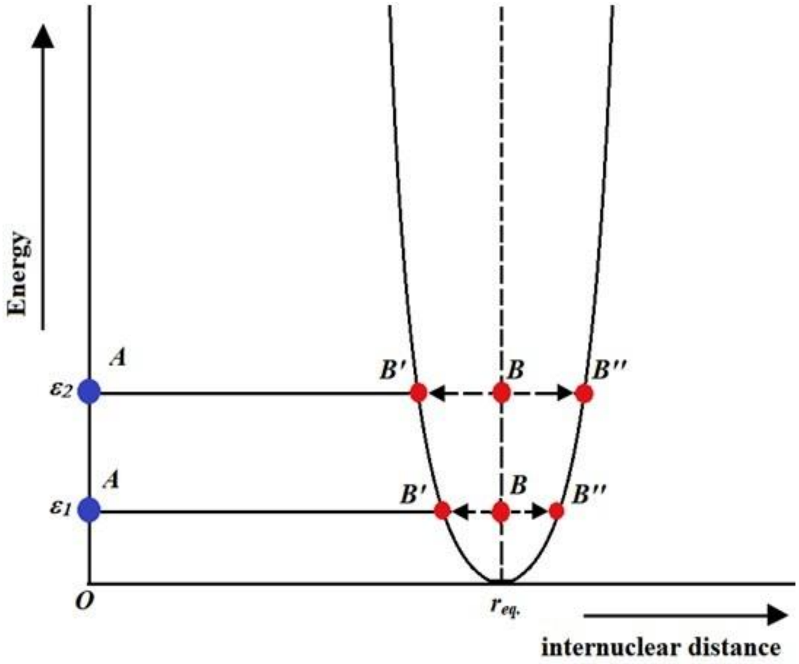

Fig 1. Parabolic curve of energy plotted against the expansion and compression of harmonic oscillator obeying Hooke's law

Suppose the bond is distorted from its equilibrium length r_e to new length r. The bond, like spring, obeys Hooke's law. Then

$$f = -k(r - r_{eq.}) \dots (1)$$

Here, f is the restoring force, k is the force constant, and r the interaction distance [3].

In this case, the potential energy curve is parabolic and has the form

$$V = \frac{1}{2}k(r - r_{eq.})^2 \dots (2)$$

This model of vibrating diatomic molecule is called "Simple Harmonic Oscillator" model [1, 2]. Fig. 1 shows the parabolic curve of energy plotted against the expansion and compression of harmonic oscillator.

Classically it is easy to show that the oscillation frequency is

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \dots (3)$$

where, μ is the reduced mass of the diatomic molecule.

The energy of Harmonic oscillator is given by [after solving Schrodinger equation]

$$E_v = h\nu_{osc}\left(v + \frac{1}{2}\right) \dots (4)$$

where, v is called the vibrational quantum number which can take values: $v = 0, 1, 2, 3, \dots\dots\dots$Equation (4) gives the allowed energies for the harmonic oscillator.

A special feature of the quantum mechanical oscillator is the existence of zero-point energy, $\frac{1}{2}h\nu_{osc}$.

Let us now investigate the expected spectrum of such an oscillator. The vibrational terms (energies in wavenumber units m^{-1} or cm^{-1}) are

$$G(v) = \frac{E_v}{hc} = \frac{\nu_{osc}}{c}\left(v + \frac{1}{2}\right) \dots (5)$$

where, $\frac{\nu_{osc}}{c}$ is the classical frequency in wave number unit and is called as vibrational constant denoted by $\bar{\omega}_{osc}$.

Thus,

$$G(v) = \bar{\omega}_{osc}\left(v + \frac{1}{2}\right) \dots (6)$$

Substituting $v = 0, 1, 2, 3$,………, we get

$$G(0) = \frac{1}{2}\bar{\omega}_{osc}$$
$$G(1) = \frac{3}{2}\bar{\omega}_{osc}$$
$$G(2) = \frac{5}{2}\bar{\omega}_{osc}$$
$$G(3) = \frac{7}{2}\bar{\omega}_{osc}$$

………………

Thus, we have a series of equidistant discrete vibrational levels, the common spacing being $\bar{\omega}_{osc}$[1].

When a transition takes place between a lower level v' and an upper level v'', the wave number of the absorbed electromagnetic radiation is

$$\bar{\nu}_{v' \to v''} = G(v'') - G(v')$$
$$\bar{\nu}_{v' \to v''} = \bar{\omega}_{osc}\left(v'' + \frac{1}{2}\right) - \bar{\omega}_{osc}\left(v' + \frac{1}{2}\right) \dots (7)$$

Now, for a harmonically oscillating molecule of dipole moment$M$, the matrix element is found to be non-vanishing only when

$$\frac{dM}{dx} \neq 0 \text{ and} \Delta v = \pm 1 \qquad \dots (8)$$

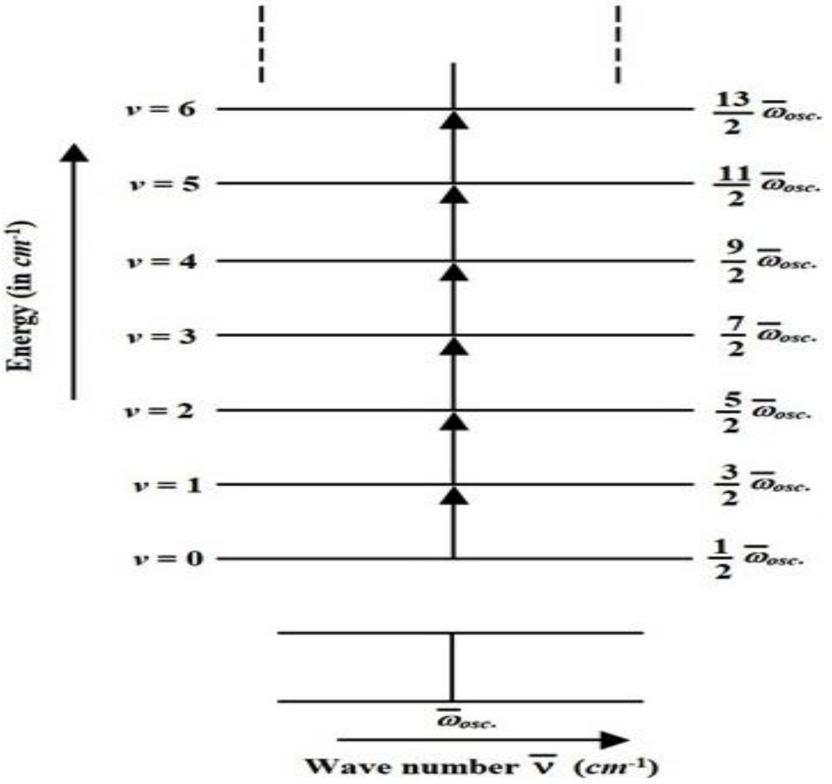

Fig 2. The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic oscillation

That is, vibrational transition can only occur when the molecule has a permanent dipole moment M which changes with distance x. Further, the selection rule $\Delta v = \pm 1$ gives [1]

$$v'' = v' + 1 \qquad (\because v'' > v') \dots (9)$$

The spacing between the vibrational energy levels is considerably larger than the spacing between the rotational energy levels of a molecule, in fact larger than $k_B T$ at room temperature. Hence, most of the molecules in a sample exists in the $v = 0$ state, with only their zero-point energies (except in case of very heavy molecules which have smaller vibrational spacings $\bar{\omega}_{osc}$).

Thus, the main vibrational transition in absorption is $v' = 0 \to v'' = 1$.

The absorbed wave number corresponding to the transition $\left(v^{'} = 0 \text{ to } v^{''} = 1\right)$ is

$$\bar{\nu}_{v^{'}\to v^{''}} = \bar{\omega}_{osc}\left(v^{''}+\frac{1}{2}\right) - \bar{\omega}_{osc}\left(v^{'}+\frac{1}{2}\right)$$

$$\bar{\nu}_{0\to 1} = \bar{\omega}_{osc}\left(1+\frac{1}{2}\right) - \bar{\omega}_{osc}\left(0+\frac{1}{2}\right)$$

$$\bar{\nu}_{0\to 1} = \frac{3}{2}\bar{\omega}_{osc} - \frac{1}{2}\bar{\omega}_{osc}$$

$$\bar{\nu}_{0\to 1} = \bar{\omega}_{osc} \ldots (10)$$

Thus, the vibrational spectrum is expected to consist of a single absorption band at $\bar{\omega}_{osc}$. Fig. 2 shows the energy level diagram with transitions in a diatomic molecule undergoing harmonic oscillations. The observation of a very intense band in the infrared spectrum thus leads to the conclusion that it is a vibrational spectrum, the nuclei carrying out harmonic vibrations along the internuclear axis [1].

However, the occurrence of weak overtone bands at wave numbers nearly two, three times the wave numbers of the main band is still to be explained, and is connected with the deviations from the oscillations being "harmonic" [1].

2.2 THE MOLECULE AS ANHARMONIC OSCILLATOR

A comparison of an observed near infrared spectrum with that expected from a diatomic molecule treated as harmonic oscillator shows an important disagreement. The harmonic oscillator would give a single band at wave number $\bar{\omega}_{osc}$, which is the classical frequency of vibration of the molecule. The actual infrared spectrum is, however, found to consist of an intense (fundamental) band at $\bar{\omega}_{osc}$, plus a number of weak bands (overtones) at wave numbers slightly lesser and lesser than $2\bar{\omega}_{osc}$, $3\bar{\omega}_{osc}$, ...The observation indicates that the selection rule $\Delta v = \pm 1$ is not strictly obeyed [2, 3], and transitions corresponding to $\Delta v > 1$ do take place. This, in turn, is attributed to the fact that the dipole moment of the molecule is not strictly linear with respect to the internuclear displacement $x\,(= r - r_{eq.})$. This is expressed as "electrical anharmonicity" of the molecule [7–9]. The observation that the overtones appear not exactly at $2\bar{\omega}_{osc}$, $3\bar{\omega}_{osc}$, ...but at lesser and lesser values indicates that the vibrational energy levels are not exactly equally spaced, but converge slowly. This is attributed to the fact that for an actual molecule the potential energy curve is not strictly parabolic (except near the minimum). That is, the potential energy function $V(r)$ is not harmonic and we must include terms higher than quadratic in the Taylor's series expansion of $V(r)$. This is expressed as "mechanical anharmonicity" of the molecule [2, 8].

A purely empirical expression which fits the potential energy curve (observed) to a good approximation was derived by P.M. Morse, and is called the Morse equation [1, 7]:

$$V(r) = D_e\left[1 - e^{\{-a(r-r_{eq.})\}}\right]^2 \ldots (11)$$

where, a is a constant for particular molecule and D_e is the depth of the potential energy curve.
To a first approximation, let us include the square and cubic terms in $V(r)$, so that

$$V(r) = f\left(r - r_{eq.}\right)^2 - g\left(r - r_{eq.}\right)^3 \ldots (12)$$

where $g \ll f$.

Substituting the value of $V(r)$from equation (13) in the Schrodinger equation and solving by perturbation method, we get the energy eigen values of the anharmonic oscillator as

$$E_v = hc\bar{\omega}_e\left(v+\frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v+\frac{1}{2}\right)^2 + \ldots\ldots\ldots. \quad \ldots (13)$$

The corresponding term values are given by

$$G(v) = \frac{E_v}{hc}$$

$$G(v) = \bar{\omega}_e\left(v+\frac{1}{2}\right) - \bar{\omega}_e x_e\left(v+\frac{1}{2}\right)^2 \ldots (14)$$

The quantity $\bar{\omega}_e$ is the wavenumber spacing of energy levels that would occur if potential energy curve were a parabola, $\bar{\omega}_e x_e$ is the "anharmonicity constant" which is much smaller than $\bar{\omega}_e$ and is always positive [4, 6].

The equation (14) shows that the energy levels of anharmonic oscillator are not equidistant, but their separation decreases slowly with increasing v. Fig. 3 shows the energy level diagram of a diatomic molecule undergoing anharmonic oscillations.

Substituting $v = 0, 1, 2, 3,$........., we get

$$G(0) = \frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e$$

$$G(1) = \frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e$$

$$G(2) = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e$$

$$G(3) = \frac{7}{2}\bar{\omega}_e - \frac{49}{4}\bar{\omega}_e x_e$$

....

When a transition takes place between a lower level $v^{'}$ and an upper level $v^{''}$ (due to absorption), the wave number of the emitted radiation is

$$\bar{\nu}_{v^{'}\to v^{''}} = G\left(v^{''}\right) - G\left(v^{'}\right)$$

$$\bar{\nu}_{v'\to v''} = \left[\bar{\omega}_e\left(v''+\frac{1}{2}\right) - \bar{\omega}_e x_e\left(v''+\frac{1}{2}\right)^2\right] - \left[\bar{\omega}_e\left(v'+\frac{1}{2}\right) - \bar{\omega}_e x_e\left(v'+\frac{1}{2}\right)^2\right]$$

$$\bar{\nu}_{v'\to v''} = \bar{\omega}_e\left(v''-v'\right) - \bar{\omega}_e x_e\left(v''-v'\right)\left(v''+v'+1\right) \quad \text{------ (15)}$$

Thus, as v increases, the separation between successive bands (or levels) decreases very nearly linearly, in agreement with observation [2, 5].

Let us now investigate the infrared spectrum for the anharmonic oscillator. Since the eigen function of anharmonic oscillator are very similar to those of the harmonic oscillator, the selection rule $\Delta v = \pm 1$ still holds giving the most intense transitions. In addition, for the anharmonic oscillator, transitions corresponding to $\Delta v = \pm 2$, ± 3, ……..also appear, even though with rapidly decreasing intensity. The possible transitions in absorption when all the molecules are initially in the $v = 0$ state are shown in Fig. 4. This explains the appearance of observed weak overtone bands together with intense fundamental band [1, 10].

It is also seen that transitions with $\Delta v = 2$, 3, 4,……. have approximately, but not exactly, two, three, four, ……. times the wave number of the transition $\Delta v = 1$, in agreement with observation.

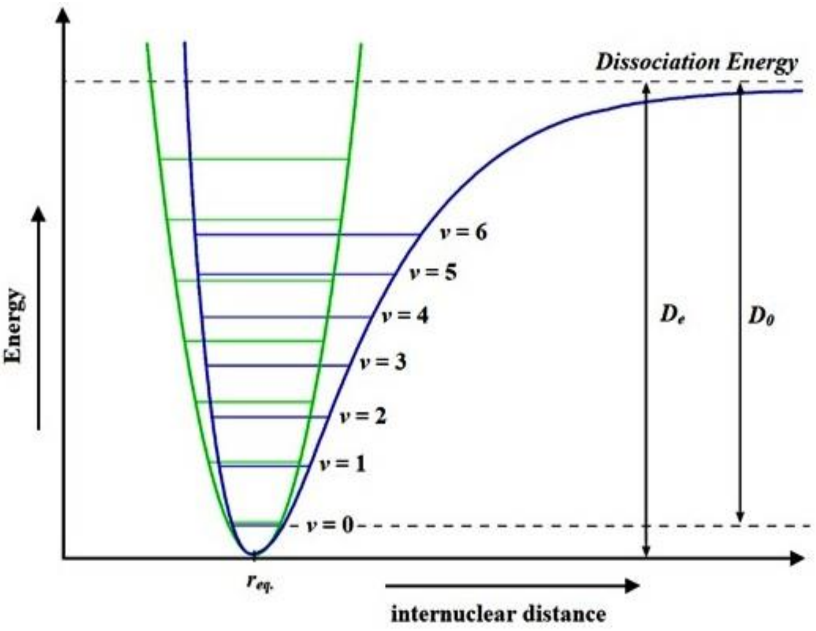

Fig 3. The Morse curve: the vibrational energy levels of diatomic molecule undergoing anharmonic expansions and compressions

1. Fundamental Band: The transition from $v' = 0$ to $v'' = 1$ gives most intense fundamental band with wavenumber [4, 5]

$$\bar{\nu}_{0\to 1} = \bar{\omega}_e(1-0) - \bar{\omega}_e x_e(1-0)(1+0+1)$$

$$\bar{\nu}_{0\to 1} = \bar{\omega}_e - 2\bar{\omega}_e x_e = \bar{\omega}_e(1-2x_e) \ldots (16)$$

2. First Overtone Band: The transition from $v' = 0$ to $v'' = 2$ gives weak band (with lesser intensity than fundamental band) with wavenumber [1, 5]

$$\bar{\nu}_{0\to 2} = \bar{\omega}_e(2-0) - \bar{\omega}_e x_e(2-0)(2+0+1)$$

$$\bar{\nu}_{0\to 2} = 2\bar{\omega}_e - 6\bar{\omega}_e x_e = 2\bar{\omega}_e(1-3x_e) \ldots (17)$$

3. Second Overtone Band: The transition from $v' = 0$ to $v'' = 3$ gives much weaker band with wavenumber

$$\bar{\nu}_{0\to 3} = \bar{\omega}_e(3-0) - \bar{\omega}_e x_e(3-0)(3+0+1)$$

$$\bar{\nu}_{0\to 3} = 3\bar{\omega}_e - 12\bar{\omega}_e x_e = 3\bar{\omega}_e(1-4x_e) \ldots (18)$$

4. Third Overtone Band:

The transition from $v' = 0$ to $v'' = 4$ gives muchweaker band (negligible intensity) with wavenumber

$$\bar{\nu}_{0\to 4} = \bar{\omega}_e(4-0) - \bar{\omega}_e x_e(4-0)(4+0+1)$$

$$\bar{\nu}_{0\to 4} = 4\bar{\omega}_e - 20\bar{\omega}_e x_e = 4\bar{\omega}_e(1-5x_e) \ldots (19)$$

Thus, the overtone bands are observed at wave numbers slightly lesser and lesser than $2\bar{\omega}_e$, $3\bar{\omega}_e$, $4\bar{\omega}_e$, ………(See Fig. 4).

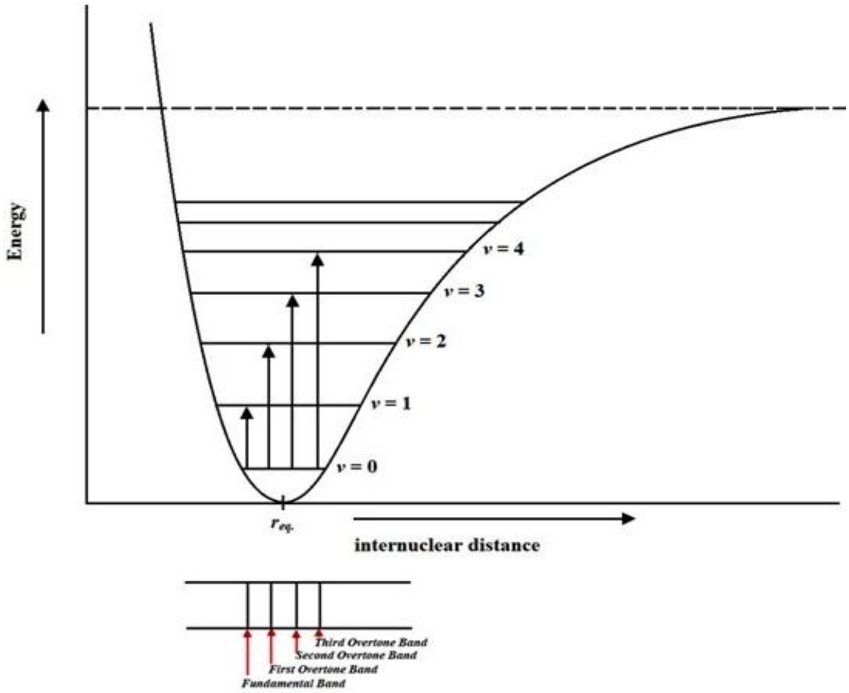

Fig 4. The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations

3. ISOTOPE EFFECT ON VIBRATIONAL ENERGY LEVELS

Different isotopic molecules have different vibrational levels, and hence different vibrational frequencies. From equation (3), the classical frequency of a molecule (assumed as harmonic oscillator) is given by [1]

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

The force constant k is determined by the electronic motion only and is therefore exactly the same for different isotopic molecules. The reduced mass is, however, different for different isotopes. If ω^i is vibrational constant for the heavier isotope, we have [1]

$$\frac{\bar{\omega}^i}{\bar{\omega}} = \frac{{\nu^i}_{osc}}{\nu_{osc}} = \sqrt{\frac{\mu}{\mu^i}} \ldots (20)$$

4. THERMAL DISTRIBUTION OF VIBRATIONAL ENERGY LEVELS (POPULATION RATIO)

According to Maxwell-Boltzmann distribution law [1], the number of molecules in the vth state, N_v, relative to that in the lowest state, N_0 is given by

$$N_v = N_0 e^{-(E_v - E_0)/k_B T}$$

where, $E_v = hc\bar{\omega}_e\left(v+\frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v+\frac{1}{2}\right)^2 \approx hc\bar{\omega}_e\left(v+\frac{1}{2}\right)$

(ignoring the second term with anharmonicity)

$$\frac{N_v}{N_0} = e^{-(E_v - E_0)/k_B T} \ldots (21)$$

Now, consider the spacing between the vibrational energy level as $1000\, cm^{-1}$, i.e.$\bar{\omega}_e \approx \bar{\omega}_{osc} = 1000\, cm^{-1}$. Let us consider the population of ground state is N_0.

Now, we will calculate and compare the population of first excited state, second excited state, third excited state relative to ground state.

(i) Ratio of populations of first excited state and ground state:

$$\frac{N_1}{N_0} = e^{-\frac{(E_1 - E_0)}{k_B T}} = e^{-\left(\frac{hc\bar{\omega}_{osc}}{k_B T}\right)}$$

$$\frac{N_1}{N_0} = \exp\left(-\frac{6.626\times10^{-34}\times3\times10^{10}\times1000}{1.38\times10^{-23}\times300}\right)$$
$$= \exp(-4.78) = 0.00822$$
$$\approx 0.01 \text{ or } 1\,\%$$

$N_1 \approx 1\,\%$ ofN_0

(ii) Ratio of populations of second excited state and ground state:

$$\frac{N_2}{N_0} = e^{-\frac{(E_2-E_0)}{k_BT}} = e^{-\left(\frac{2hc\bar{\omega}_{osc}}{k_BT}\right)}$$

$$\frac{N_2}{N_0} = \exp\left(-\frac{2\times 6.626\times 10^{-34}\times 3\times 10^{10}\times 1000}{1.38\times 10^{-23}\times 300}\right)$$

$= 0.0000675 \approx 0.00007$ or $0.007\ \%$

$N_2 \approx 0.007\ \%$ ofN_0

(iii) Ratio of populations of third excited state and ground state:

$$\frac{N_3}{N_0} = e^{-\frac{(E_3-E_0)}{k_BT}} = e^{-\left(\frac{3hc\bar{\omega}_{osc}}{k_BT}\right)}$$

$$\frac{N_3}{N_0} = exp\left(-\frac{3\times 6.626\times 10^{-34}\times 3\times 10^{10}\times 1000}{1.38\times 10^{-23}\times 300}\right)$$
$$= 0.000000555$$
$$\approx 0.0000006 \text{ or } 0.00006\ \%$$

$N_3 \approx 0.00006\ \%$ of N_0

From above calculations, it is clear that the population of the first excited state$(v = 1)$is approximately $1\ \%$ of the population of ground state$(v = 0)$, the population of the second excited state $(v = 2)$ is approximately $0.007\ \%$ of the population of ground state$(v = 0)$ and the population of third excited state $(v = 3)$ is $0.00006\ \%$ of the population of ground state$(v = 0)$. Thus, at low temperature we may ignore all transitions originating from vibrational quantum numbers $v \geq 1$ and restrict ourselves to the transitions originating at $v = 0$ only [1].

Effect of increasing temperature from $T = 300K$ to $600K$ (at $\bar{\omega}_{osc} = 1000cm^{-1}$)

Ratio of population of molecules in the first excited state to the ground state is

$$\frac{N_1}{N_0} = e^{-\frac{(E_1-E_0)}{k_BT}} = e^{-\left(\frac{hc\bar{\omega}_{osc}}{k_BT}\right)}$$

$$\frac{N_1}{N_0} = exp\left(-\frac{6.626\times 10^{-34}\times 3\times 10^{10}\times 1000}{1.38\times 10^{-23}\times 600}\right)$$
$$= exp(-2.40072464) = 0.0907$$

$N_1 \approx 9.07\ \%$ ofN_0

Here, the population of the first excited state$(v = 1)$ is approximately$9\ \%$of the population of ground state$(v = 0)$. Thus, at $T = 600\ K$, we may consider transitions originating from$v = 1$. The transitions starting from $v \geq 1$ are known as hot bands.

Effect of decreasing vibrational frequency from $1000cm^{-1}$ to $500cm^{-1}$ ($T = 300K$):

$$\frac{N_1}{N_0} = e^{-\frac{(E_1-E_0)}{k_BT}} = e^{-\left(\frac{hc\bar{\omega}_{osc}}{k_BT}\right)}$$

$$\frac{N_1}{N_0} = \exp\left(-\frac{6.6\times 10^{-34}\times 3\times 10^{10}\times 500}{1.38\times 10^{-23}\times 300}\right)$$
$$= \exp(-2.40072464) = 0.0907$$

$$N_1 \approx 9.07\ \% \text{ of } N_0$$

In other words, the population of the $v = 1$ state is nearly 9 percent of the ground state population. Thus, we can say that a similar increase in the excited state population would arise if the vibrational frequency is lowered from $1000\ cm^{-1}$ to $500\ cm^{-1}$. Thus, at $T = 300\ K$, we may consider transitions originating at $v = 1$ if the vibrational frequency is lowered.

Hot Bands: The transitions from first excited state $(v = 1)$ to the higher states $(v > 1)$ are not observed unless the temperature of the molecular sample is high or if the vibration has a particularly low frequency. This is due to the fact that the population in $v = 1$state is negligible at lower temperature and it becomes appreciable only at higher temperatures [1].

The transition $v' = 1 \longrightarrow v'' = 2$ appears at wave number

$$\bar{\nu}_{v'\to v''} = \bar{\omega}_e(v'' - v') - \bar{\omega}_e x_e(v'' - v')(v'' + v' + 1)$$

$$\bar{\nu}_{1\to 2} = \bar{\omega}_e(2 - 1) - \bar{\omega}_e x_e(2 - 1)(2 + 1 + 1)$$

$$\bar{\nu}_{1\to 2} = \bar{\omega}_e - 4\bar{\omega}_e x_e$$

$$\bar{\nu}_{1\to 2} = \bar{\omega}_e(1 - 4x_e) \ldots (22)$$

The transition $v' = 1 \longrightarrow v'' = 2$ is very weak and it will be observed closer to and at slightly lower wave numbers than the fundamental band [1]. These transitions are generallyknown as 'hot bands', since high temperature is the one condition for their existence. Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

5. DISSOCIATION ENERGY OF DIATOMIC MOLECULE

The energy of vibrational energy level may be written as:

$$E_v = hc\bar{\omega}_e\left(v + \frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v + \frac{1}{2}\right)^2 \ldots (23)$$

And therefore, separation between neighbouring levels, ΔE, is normally

$$\Delta E = E_{v+1} - E_v$$

$$\Delta E = \left[hc\bar{\omega}_e\left(v+1+\tfrac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v+1+\tfrac{1}{2}\right)^2\right] - \left[hc\bar{\omega}_e\left(v+\tfrac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v+\tfrac{1}{2}\right)^2\right]$$

$$\Delta E = hc\bar{\omega}_e - 2hc\bar{\omega}_e x_e(v+1)$$

$$\Delta E = hc\bar{\omega}_e[1 - 2x_e(v+1)]$$

This separation obviously decreases with increasing v and the dissociation limit is reached when $\Delta E \to 0$. Thus, the maximum value of v is given byv_{max}, where

$$\Delta E = hc\bar{\omega}_e[1 - 2x_e(v_{max}+1)] = 0$$

$$[1 - 2x_e(v_{max}+1)] = 0$$

$$v_{max} = \frac{1}{2x_e} - 1 \quad \dots(24)$$

If we recall that the anharmonicity constant,

$x_e \approx 10^{-3}$; hence $v_{max} = \frac{1}{0.001} - 1 = 500 - 1 = 499 \approx 500$.

Substituting value of v_{max} in equation (1), we get

$$E_{max} = D_e = hc\bar{\omega}_e\left(v_{max} + \frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(v_{max} + \frac{1}{2}\right)^2$$

$$E_{max} = hc\bar{\omega}_e\left(\frac{1}{2x_e} - 1 + \frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(\frac{1}{2x_e} - 1 + \frac{1}{2}\right)^2$$

$$E_{max} = hc\bar{\omega}_e\left(\frac{1}{2x_e} - \frac{1}{2}\right) - hc\bar{\omega}_e x_e\left(\frac{1}{2x_e} - \frac{1}{2}\right)^2$$

$$E_{max} = hc\bar{\omega}_e\left[\left(\frac{1}{2x_e} - \frac{1}{2}\right) - x_e\left(\frac{1}{2x_e} - \frac{1}{2}\right)^2\right]$$

$$E_{max} = hc\bar{\omega}_e\left[\frac{1}{4x_e} - \frac{x_e}{4}\right] \approx hc\left(\frac{\bar{\omega}_e}{4x_e}\right)$$

This will represent the dissociation energy of the molecule with respect to the bottom of the potential energy diagram. The true dissociation energy will be given by

$$D_0 = D_e - E_{v=0} = hc\bar{\omega}_e\left[\frac{1}{4x_e} - \frac{x_e}{4}\right] - hc\left[\frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e\right]$$

$$D_0 = hc\bar{\omega}_e\left[\frac{1}{4x_e} - \frac{x_e}{4} - \frac{1}{2} + \frac{x_e}{4}\right]$$

$$D_0 = hc\bar{\omega}_e\left[\frac{1}{4x_e} - \frac{1}{2}\right] \dots(25)$$

For HCl molecule, $\bar{\omega}_e = 2886\, cm^{-1}$ and dissociation energy (for $x_e = 0.001$)

$$D_0 = hc\bar{\omega}_e\left[\frac{1}{4x_e} - \frac{1}{2}\right] = (6.626 \times 10^{-34}) \times (3 \times 10^8) \times (2886 \times 100) \times \left(\frac{1}{4 \times 0.001} - \frac{1}{2}\right)$$

$$= 1431329304.6 \times 10^{-26} Joule$$

$$= 0.89458\, eV \approx 0.9\, eV$$

Thus, the dissociation energy of HCl molecule is approximately 0.9 eV.

TABLE 1: The population ratio of first, second, third, fourth and fifth excited state with the ground state at 300 K, 600 K and 900 K.

Energy Level /state	N_v/N_0 **(at** $T = 300K$**)**	N_v/N_0 **(at** $T = 600K$**)**	N_v/N_0 **(at** $T = 900K$**)**
First Excited State	0.00822	0.0907	0.202
Second Excited State	0.0000675	0.00822	0.0407
Third Excited State	0.000000555	0.000745	0.00822
Fourth Excited State	0.00000000456	0.0000675	0.00166
Fifth Excited State	0.000000000037	0.00000612	0.000335

6. CONCLUSIONS

This article explains the infrared spectra of heteronuclear diatomic molecules such as HCl, HBr, HI, CO, … etc. In order to explain the vibrational spectra, diatomic molecules are treated as harmonic oscillator and anharmonic oscillator. In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, $\Delta v = \pm 1$, are allowed while in the actual data, there wereadditional bandspresent corresponding to wave numberclose to $2\overline{\omega}_{osc}$, $3\overline{\omega}_{osc}$, $4\overline{\omega}_{osc}$, …… The additional bands are having lesser intensity and are called as overtone bands. The occurrence of these additional bands is attributed to the selection rule $\Delta v = \pm 2, \pm 3, \pm 4$, ……. In this article, we have also explained the effect of isotopic substitution on the infrared spectroscopy. The expression of dissociation energy of molecules is also discussed.

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