Chapter 10: Vibrational Spectroscopy

After describing rotation, as we move up the energy scale, the next hierarchy of energy levels of the molecule is associated with the vibrational motion of the molecule.

Vibrational motion is a periodic, concerted displacement of the nuclei (more accurately, the atoms) in a molecule, which leaves the center of mass unaltered in laboratory space. The motion of the molecular center of mass is described as translation.

The energy associated with vibrational motion contains two distinct distributions: the kinetic energy which arises from the motion of the nuclei and the potential energy which comes from the compression or expansion of the bond (internuclear distance) from its equilibrium value:

\[ E_{\text{Total}} = E_{\text{Kinetic}} + E_{\text{Potential}} \]  \hspace{1cm} (54)

As the nuclei move back and forth, the energy (which is constant for an isolated molecule) is transferred between the kinetic and potential forms.
The simplest possible assumption about the form of the vibrations in a diatomic molecule is that each atom moves toward or away from the other in simple harmonic motion, i.e., the displacement from the equilibrium position is a sine function of the time. Such a motion of the two atoms can easily be reduced to the harmonic vibration of a single mass point about an equilibrium position—the model of the harmonic oscillator.

\[
\begin{align*}
\text{In classical mechanics, a harmonic oscillator can be defined as a mass point of mass } m \text{ which is acted upon by a force } F \\
\text{proportional to the distance } x \text{ from the equilibrium position and directed toward the equilibrium position.}
\end{align*}
\]

\[F = -kx = m \frac{d^2x}{dt^2} \quad (55)\]

Here, \( k \) is called the force constant.

The solution to Eq. (55) is

\[x = x_0 \sin (\omega_{\text{vib}} t + \phi) \quad (56)\]

Where \( \omega_{\text{vib}} \) is the vibrational frequency given by

\[\omega_{\text{vib}} = \sqrt{\frac{k}{m}} \quad (57)\]

\( x_0 \) is the amplitude of the vibration and \( \phi \) is a phase constant depending on the initial conditions.
Since the force is the negative derivation of the potential energy \( V \), i.e., \( F = -\frac{\partial V}{\partial x} = -kx \), for the harmonic oscillator, the potential energy is

\[
V = \frac{1}{2} k x^2 = \frac{1}{2} m \omega_{\text{vib}}^2 x^2. \quad (58)
\]

We can therefore define a harmonic oscillator as a system whose potential energy is proportional to the square of the distance from its equilibrium position, i.e., the potential energy curve is a parabola.

The restoring force exerted by the two atoms of a molecule on each other when they are displaced from their equilibrium position is, at least approximately, proportional to the change of internuclear distance. If we assume that this relation holds exactly, it follows immediately that the atoms in the molecules will execute harmonic vibrations when they are left to themselves after being displaced from their equilibrium positions.

For the first atom with mass \( m_1 \),

\[
m_1 \frac{d^2 r_1}{dt^2} = -k (r - r_e) \quad (59)
\]
and for the 2nd atom with mass $m_2$,

$$ m_2 \frac{d^2 r_2}{dt^2} = -k (r - R_e) \quad (60) $$

where $r_1$ and $r_2$ are distances of the two atoms from the center of gravity, $r$ is the internuclear distance of the two atoms from each other, and $R_e$ is the equilibrium internuclear distance. From Eq. (59) and (60), we obtain

$$ \frac{m_1 m_2}{m_1 + m_2} \frac{d^2 r}{dt^2} = -k (r - R_e) \quad (61) $$

Introduce reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$, we have

$$ \mu \frac{d^2 (r - R_e)}{dt^2} = -k (r - R_e) \quad (62) $$

This is identical to Eq. (55), except $x$ is replaced by $(r - R_e)$. Thus, we have reduced the vibrations of the two atoms of a molecule to the vibration of a single mass point of mass $\mu$, whose amplitude equals the amplitude of the change of internuclear distance in the molecule.

From Eq. (62), the classical vibrational frequency of the molecule is

$$ \nu_{\text{vib}} = \sqrt{\frac{k}{\mu}} \quad (\text{angular freq.}) $$

and

$$ \nu_{\text{vib}} = \frac{\nu_{\text{vib}}}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (63) $$

Whereas, even on the classical theory, only one vibrational frequency is possible. However, classically the amplitude, and therefore the energy, of this vibration can assume any desired value.
In Quantum Mechanics, the energy level is determined by the energy eigenvalue equation (i.e., time-independent Schrödinger Eq.):

$$\hat{H} \psi = E \psi$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + V = -\frac{\hbar^2}{8\pi^2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2$$  \hspace{2cm} (64)$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{\hbar^2} (E - \frac{1}{2} k x^2) \psi = 0$$ \hspace{2cm} (65)

The solutions to Eq. (65) in QM are quantized with allowable values

$$E(v) = \hbar \sqrt{\frac{\hbar}{\mu}} (v + \frac{1}{2}) = \hbar \nu_{\text{vib}} (v + \frac{1}{2})$$ \hspace{2cm} (66)

where the vibrational quantum number \( v = 0, 1, 2, \ldots \)

Thus, the energy level diagram of the harmonic oscillator consists of a series of equally spaced levels.

The state of lowest energy, \( v = 0 \), has

$$E(0) = \frac{1}{2} \hbar \nu_{\text{vib}} = \frac{1}{2} \hbar \omega_{\text{vib}}$$ \hspace{2cm} (67)

Thus, even in the lowest vibrational state, vibrational energy is present, which is called zero-point energy.

**Spectrum**: If the molecule in its equilibrium position has a dipole moment (as is always for heteronuclear diatomic molecule), this dipole moment will in general change if the internuclear distance changes. To a first approximation it may be assumed that the change of dipole moment with internuclear distance is linear.
Therefore, the dipole moment changes with a frequency equal to the frequency of the mechanical vibration. On the basis of classical EM theory, this would lead to the emission of light of frequency. Conversely, the oscillator could be set in vibration by absorption of light.

From QM, emission and absorption of radiation takes place as a result of a transition of the oscillator from one state to another. The wave number of the emitted/absorbed light is given by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{E(v') - E(v)}{hc}$$  \(68\)

where \(v'\) and \(v\) are the vibrational quantum numbers of the upper and lower states.

In order to determine which particular transitions can occur, we have to evaluate the matrix elements of the electric dipole moment. These matrix elements are zero except when the permanent dipole moment is different from zero, and when \(v'\) and \(v\) differ by unity, i.e., the selection rule for the vibrational quantum number of the harmonic oscillator is

$$\Delta v = v' - v = \pm 1$$  \(69\)

As mentioned above, such transitions only occur for molecules with nonzero permanent electric dipole moment, such as the heteronuclear diatomic molecules. Homonuclear diatomic
molecules like N₂, O₂, H₂ etc do not have such infrared transition spectrum.

Using selection rule, Eq. (69), from Eq. (68), we obtain

\[ \vec{S} = \frac{1}{\lambda} = \frac{h\nu_{\text{vib}}}{hc} = \frac{\nu_{\text{vib}}}{c} \quad (70) \]

\[ \therefore \text{the transition frequency of vibrational transition is} \]

\[ \nu = c \cdot \vec{S} = \nu_{\text{vib}} \quad (71) \]

i.e., the transition frequency of the radiation is equal to the vibrational frequency of the oscillator. This is true no matter what the \( S \) value of the initial state may be.

Therefore, the vibrational spectrum of the harmonic oscillator will contain single transition frequency, as all transitions \((\Delta J = \pm 1)\) give rise to the same frequency.

It must be pointed out here that for a system that is not exactly a harmonic oscillator, transition can also appear with \( \Delta J > 1 \), even though very weakly, whereas for the rotator the selection rule \((\Delta J = \pm 1)\) holds strictly, even if the system deviates from the model of the rigid rotator (this is because of the conservation of angular moment — photons have angular momentum of \( \hbar \), so \( \Delta J \) has to be \( \pm 1 \)).
Non-classical behaviour of quantum harmonic oscillator.

The eigenfunction of the harmonic oscillator can be derived by solving Eq. (65). The results are shown in the figure below.

Fig. 5.7 The form of the eigenfunctions for the first few levels of a harmonic oscillator. The point where the wavefunction crosses through zero is known as a node.

Fig. 5.8 The probability distribution function for a harmonic oscillator (a) for the \( v = 0 \) level where the maximum probability is at \( q = 0 \) and (b) the classical probability distribution, approached by the quantum system at large \( v \).

Three major nonclassical behavior of the QM Harmonic Oscillator

1. **Quantum mechanical tunneling**: the molecule has finite probability, although small, to occur outside the classical accessible region. The extent of tunneling depends on the steepness of the potential wall; most pronounced at low \( V \), less evident at high \( V \).

2. **Distribution probability of particle be found at \( x = 0 \)** is maximum — contradictory to classical picture.

3. **Zero-point energy**: determined by Heisenberg uncertainty principle. There is no way in which the oscillator can lose this zero-point energy \( \frac{1}{2} \hbar \omega \).
§10.2. The anharmonic oscillator

The harmonic oscillator is characterized by a parabolic potential curve (dashed-line in the above Figure). The potential energy, and the restoring force, increase indefinitely with increasing distance from the equilibrium position. However, in real molecules, this can not be true — when the atoms are at a great distance from one another, the attractive force is zero, and correspondingly, the potential energy has a constant value. Thus, the potential curve of the molecule has the form of the solid curve in fig. The minimum of the curve corresponds to the equilibrium position. In its neighborhood, the curve can be represented approximately by a parabola (dashed-line curve). This is why the harmonic oscillator model captures the main characteristics of the vibration spectrum.
We introduce an anharmonic oscillator model to describe the real molecule. As a first approximation to the actual potential energy function, we add a cubic term to the parabolic function of the harmonic oscillator:

\[ V = f (r-re)^2 - g (r-re)^3 \]  

(72)

where \( g \) is much smaller than \( f \). This function Eq. (72) (dotted curve in fig) does not represent the whole of the potential energy curve, but at any rate gives a much better approximation for not too great values of \( r-re \).

From classical mechanics, the motion of the anharmonic oscillator may be represented as a superposition of fundamental and overtone vibrations (harmonic of fundamental frequency):

\[ x = x_0 \sin 2\pi \nu_{ib} t + x_0 \nu \left(1 + \cos 2\pi \cdot 2 \nu_{ib} t\right) + x_0 \nu_{3} \sin 2\pi \cdot 3 \nu_{ib} t + \cdots \]  

(73)

where \( \begin{cases} x_0 \gg x_0 \nu \gg x_0 \nu_{3} \cdots \\ 2\nu_{ib} = \frac{\hbar}{k} \sqrt{\frac{k}{\mu}} \text{ when } x_0 \text{ is small.} \end{cases} \)

In QM, to derive energy levels under anharmonic oscillator, we solve the energy eigenvalue equation again, with \( V \) represented by Eq. (72). It is found that for small anharmonicity of the oscillator \( (g \ll f) \), the energy eigenvalues are given by

\[
E(n) = \hbar \omega_{ib} (n + \frac{1}{2}) - \hbar^2 \nu_{ib} \chi \varepsilon (n + \frac{1}{2})^2 + \hbar^2 \nu_{ib} \chi \varepsilon (n + \frac{1}{2})^3 + \cdots
\]

\[
= \hbar \omega_{ib} (n + \frac{1}{2}) - \hbar \omega_{ib} \chi \varepsilon (n + \frac{1}{2})^2 + \hbar \omega_{ib} \chi \varepsilon (n + \frac{1}{2})^3 + \cdots
\]

(76)
Here, $Xe$ and $Ye$ are small numbers (compared to 1) to represent the deviation of the energy levels from harmonic oscillator.

**Spectrum:** Just as for the harmonic oscillator, an infrared spectrum of the anharmonic oscillator arises only when a dipole moment is associated with the motion. Therefore, only heteronuclear molecules have infrared spectrum, while homonuclear molecules do not have infrared spectrum.

**Selection rules:** With anharmonic oscillator,

$$\Delta \nu = \pm 1, \pm 2, \pm 3, \pm 4, \ldots \quad (75)$$

The wave number of real transition between different vibrational states is

$$\nu = \frac{1}{\lambda} = \frac{E(\nu') - E(\nu)}{hc}$$

$$= \frac{\nu_{\text{Vib}}}{c} (\nu' - \nu) - \frac{\nu_{\text{Vib}}}{c} Xe \left[ (\nu' + \frac{1}{2})^2 - (\nu + \frac{1}{2})^2 \right] + \ldots$$

$$= \frac{\nu_{\text{Vib}}}{c} \Delta \nu - \frac{\nu_{\text{Vib}}}{c} Xe \left[ (\nu')^2 - \nu^2 + \Delta \nu \right] + \ldots \quad (76)$$
Let us denote \( \frac{\hbar \nu_{\text{vib}}}{c} = \tilde{\nu}_e \) (wave number).

\[ E(\nu) = \hbar c \tilde{\nu}_e (\nu + \frac{1}{2}) - \hbar c \tilde{\nu}_e Xe (\nu + \frac{1}{2})^2 + \hbar c \tilde{\nu}_e Xe (\nu + \frac{1}{2})^3 + \cdots \tag{77} \]

\( \tau = \frac{1}{\lambda} = \frac{E(\nu') - E(\nu)}{\hbar c} \)

\[ \tilde{\nu} = \tilde{\nu}_e (\nu' - \nu) - \tilde{\nu}_e Xe \left[ (\nu' + \frac{1}{2})^2 - (\nu + \frac{1}{2})^2 \right] + \cdots \tag{78} \]

For \( \Delta \nu = \nu' - \nu = 1 \), \( \tilde{\nu} = \tilde{\nu}_e - \tilde{\nu}_e Xe \cdot 2 (\nu + 1) + \cdots \tag{79} \)

For \( \Delta \nu = \nu' - \nu = 2 \), \( \tilde{\nu} = 2 \tilde{\nu}_e - \tilde{\nu}_e Xe \cdot 2 (2\nu + 3) + \cdots \tag{80} \)

The wave number of the first band \((1-0)\), i.e., from \( \nu = 1 \to \nu = 0 \),

\( \tilde{\nu}(1-0) = \tilde{\nu}_e - 2 \tilde{\nu}_e Xe \tag{81} \)

Thus, we can determine the vibrational constants \( \tilde{\nu}_e \) and \( \tilde{\nu}_e Xe \) from the observed positions of the infrared absorption bands of a diatomic molecule.

For example, \( \tilde{\nu}_{\text{obs}}(1-0) = 2885.9 \text{ cm}^{-1} \)

\( \tilde{\nu}_{\text{obs}}(2-1) = 2782.1 \text{ cm}^{-1} \)

\[ \tilde{\nu}(2-1) = \tilde{\nu}_e - \tilde{\nu}_e Xe \cdot 4 = \tilde{\nu}_e - 4 \tilde{\nu}_e Xe \tag{82} \]

\[ \Delta \tilde{\nu} = \tilde{\nu}(2-1) - \tilde{\nu}(1-0) = -2 \tilde{\nu}_e Xe \tag{83} \text{ cm}^{-1} \]

\[ \Delta \tilde{\nu}_{\text{obs}} = \tilde{\nu}_{\text{obs}}(2-1) - \tilde{\nu}_{\text{obs}}(1-0) = 2782.1 - 2885.9 = -103.8 \]

\[ \tilde{\nu}_e Xe = -\frac{\Delta \tilde{\nu}_{\text{obs}}}{2} = -\frac{-103.8}{-2} = 51.9 \text{ cm}^{-1} \]
\[ \tilde{v}_e = \tilde{v}_{obs} (1-\alpha) + 2 \tilde{v}_e \text{Xe} \]
\[ = 2885.9 + 2 \times 51.9 \]
\[ = 2989.7 \text{ cm}^{-1} \]

\[ \text{Xe} = \frac{\tilde{v}_e \text{Xe}}{\tilde{v}_e} = \frac{51.9}{2989.7} = 0.01735 = 1.7 \times 10^{-2} \]

The zero-point energy of the anharmonic oscillator is

\[ E(0) = \frac{1}{2} \hbar c \tilde{v}_e - \frac{1}{4} \hbar c \tilde{v}_e \text{Xe} + \frac{1}{8} \hbar c \tilde{v}_e \text{Y} + \ldots \quad (84) \]

Continuous Spectrum and Dissociation:

When an anharmonic oscillator with a potential curve of the type given in the following figure, receives more energy than corresponds to the horizontal asymptote, the mass point will be completely removed from its equilibrium position and will not return to it. If the energy of the system just corresponds to the asymptote, the atoms at a great distance from each other will have zero velocity. With increasing energy above that of the asymptote, the atoms at a great distance apart have increasingly relative kinetic energy. This kinetic energy is not quantized. Therefore, above the asymptote, a continuous term spectrum, corresponding to dissociation, joins onto the discrete vibrational term series. This is quite similar to the continuum that adjoins the atomic term series and corresponds to ionization of atoms. However, there is a distinguished
difference between these cases: in the molecule dissociation case, there is only a finite number of vibration levels present; which is in contrast to the case of ionization where there is an infinite number of discrete levels lying below the limit.

Let us calculate the dissociation energy and how many vibrational levels exist below the dissociation energy \( D_e \). (Unfortunately, the \( D_e \) here has the same symbol as the rotational constant \( D_e \). But indeed, they are very very different. So we should point out each time what \( D_e \) stands for in our computation.)

\( D_0 \): the height of the asymptote (i.e., the beginning of the continuum) above the lowest vibrational level is equal to the work that must be done in order to dissociate the molecule — the so-called heat of dissociation or dissociation energy.
It is obvious that the dissociation energy $D_0$ (in cm$^{-1}$) is equal to the sum of all the vibrational quanta:

$$D_0 = \sum_{\nu} \frac{E(\nu+1) - E(\nu)}{hc} \quad (85)$$

The energy difference, $D_e$, between the minimum of potential energy and the asymptote is a little greater than $D_0$, by an amount equal to the zero-point energy:

$$D_e = D_0 + E(0) = D_0 + \frac{\hbar}{2} \nu_e - \frac{1}{4} \frac{\nu_e}{\nu_e^2} + \ldots$$

(86)

From Eq. (79), we know the wave number for neighboring transition is:

$$\Delta \nu (\nu+1 \rightarrow \nu) = \nu_e - 2 \nu_e \nu_e \nu_e - 2 \nu_e \nu_e \nu_e \nu_e + \ldots$$

(87)

To derive $D_0$ and $D_e$, we set $\Delta \nu (\nu+1 \rightarrow \nu) = 0$, i.e., the spectrum become continuous.

$$\nu_e - 2 \nu_e \nu_e - 2 \nu_e \nu_e \nu_e \nu_e D_e = 0 \quad (89)$$

$$\nu_e = \frac{\nu_e - 2 \nu_e \nu_e}{2 \nu_e \nu_e} = \frac{\nu_e}{2 \nu_e \nu_e} - 1 \quad (90)$$

Where $\nu_e$ is the vibrational quantum number that the next smaller integral value of $\nu$ corresponds to the last discrete vibrational level before dissociation, i.e., $(\nu_e + 1)$ corresponds to the last discrete vibrational level before dissociation:

$$\nu_e + 1 = \frac{\nu_e}{2 \nu_e \nu_e} = \frac{1}{2 \nu_e \nu_e}$$

(91)
For HCl molecule, $Xe = 1.735 \times 10^{-2}$,

\[
\therefore \quad \nu_D + 1 = \frac{1}{2 Xe} = \frac{1}{2 \times 1.735 \times 10^{-2}} \approx 28
\]

So HCl has max 28 vibrational levels before dissociation.

The energy difference between the asymptote and the potential minimum is equal to the maximum value of vibrational energy level in cm$^{-1}$:

\[
\Delta E = E_{\text{max}} (\nu) = \frac{E (\nu_D + 1)}{\hbar c}
\]  

(92)

Substitute Eq. (77) and Eq. (90) into Eq. (92), we obtain:

\[
\Delta E = \tilde{\nu}_e \left( \nu_D + 1 + \frac{1}{2} \right) - \tilde{\nu}_e Xe \left( \nu_D + 1 + \frac{1}{2} \right)^2 + \ldots
\]

\[
= \tilde{\nu}_e \cdot \frac{\tilde{\nu}_e}{2 \tilde{\nu}_e Xe} + \frac{1}{2} \tilde{\nu}_e - \tilde{\nu}_e Xe \left( \frac{\tilde{\nu}_e}{2 \tilde{\nu}_e Xe} + \frac{1}{2} \right)^2 + \ldots
\]

\[
= \frac{\tilde{\nu}_e^2}{2 \tilde{\nu}_e Xe} + \frac{1}{2} \tilde{\nu}_e - \frac{\tilde{\nu}_e^2}{4 \tilde{\nu}_e Xe} - \frac{1}{2} \tilde{\nu}_e - \frac{1}{4} \tilde{\nu}_e Xe + \ldots
\]

\[
= \frac{\tilde{\nu}_e^2}{4 \tilde{\nu}_e Xe} - \frac{1}{4} \tilde{\nu}_e Xe + \ldots
\]  

(93)

\[
\therefore \quad Xe \ll 1 \quad \Rightarrow \quad \frac{1}{4} \tilde{\nu}_e Xe \ll \frac{\tilde{\nu}_e^2}{4 \tilde{\nu}_e Xe} = \frac{\tilde{\nu}_e}{4 Xe}
\]

\[
\therefore \quad \text{We can ignore the 2nd term in Eq. (93)}
\]

\[
\Delta E = \frac{\tilde{\nu}_e^2}{4 \tilde{\nu}_e Xe}
\]  

(94)

Dissociation Energy  

\[
D_0 = \Delta E - E(0) = \frac{\tilde{\nu}_e^2}{4 \tilde{\nu}_e Xe} - \frac{1}{2} \tilde{\nu}_e
\]  

(95)
For the HCl molecule, $\hat{\Delta e} = 2989.7 \text{ cm}^{-1}$, $\hat{\Delta e} \chi e = 51.9 \text{ cm}^{-1}$

\[
\Delta e = \frac{\hat{\Delta e}^2}{4 \hat{\Delta e} \chi e} = \frac{(2989.7)^2}{4 \times 51.9} = 43,055.4 \text{ cm}^{-1}
\]

\[
D_0 = \Delta e - \frac{1}{2} \hat{\Delta e} = 43,055.4 - \frac{1}{2} \times 2989.7 = 41,560 \text{ cm}^{-1}
\]

A better representation of the potential curve of molecule is given by Morse potential curve:

\[
U(r-re) = \Delta e \left[1 - e^{-\beta (r-re)} \right]^2 \tag{96}
\]

where $\Delta e$ is the dissociation energy, referred to the minimum, and $\beta$ is a constant:

\[
\beta = \sqrt{\frac{2 \pi^2 \hbar^2}{\Delta e m}} \hat{\Delta e} \tag{97}
\]

Where $\Delta e$ — in cm$^{-1}$,

$\hat{\Delta e}$ — in cm$^{-1}$,

$\mu$ — reduced mass (kg)

$c$ — light speed

$h$ — Planck constant.
§103. Vibrating Rotator or Rotating Oscillator.

It is necessary to combine the vibrational and rotational motion of a diatomic molecule. However, the time scale for rotational motion is much longer than that for vibrational motion. The period for rotational motion is of the order of $10^{-14}$ s whereas that for vibrational motion is about $10^{-11}$ s.

$$T_{\text{rot}} \sim 10^{-11} \text{s}, \quad T_{\text{vib}} \sim 10^{-14} \text{s}.$$ 

For each completed rotational cycle, the molecule vibrates back and forth about one thousand times. This difference in the time scales for the two motions is really the justification for the extension of the Born–Oppenheimer approximation to treat vibrational and rotational motion separately. We first solve the vibrational problem within the molecule-fixed axis system, so this solution is independent of the molecular orientation (rotation). Once this has been done, we can average the vibrationally dependent variable over the appropriate vibrational wavefunction and so solve the rotational problem.

The total energy of vibration–rotation molecule is given by the sum of the anharmonic oscillator energy and the vibrating rotator energy, i.e.,
\[ E_{\text{vib-rot}} = E_J + E_\nu (J) \]
\[ = h c v_e (v + \frac{1}{2}) - h c \sum_e x_e (v + \frac{1}{2})^2 + \ldots \]
\[ + h c B_\nu J (J+1) - h c D_\nu J^2 (J+1)^2 + \ldots \] 
\[ (98) \]