CHAPTER 1
This chapter includes an introduction of the molecular spectroscopy in brief, selection rules for infrared, Raman spectra and electronic transitions. Electronic and vibrational spectra of benzene and phenol have been discussed. The effect of substituents, their position on vibrational and electronic spectra and the effect of polar and non polar solvents on electronic transitions have been discussed. The effect of pH variation on the electronic transition has also been discussed. The procedure followed for statistical computation of thermodynamic functions has also been given. A brief introduction of molecular polarizability has also been given.
GENERAL

Spectroscopy can be defined as the study of the interaction of electromagnetic radiation with matter. The nature of this interaction depends on the wavelength (or frequency) of the radiation, so that regions of the electromagnetic spectrum have become associated with various types of spectroscopy. A total change in the energy of a molecule occurs depends upon interaction with electromagnetic radiation. This change is reflected in the observed spectrum of the material. In order to describe this interaction and formulate a useful mathematical model, certain assumptions are usually made. The total energy of a molecule consists of contributions from rotational, vibrational, electronic and electromagnetic spin energies. The separation of the electronic and nuclear motions, known as Born-Oppenheimer approximation¹, depends on the large difference in mass between the electrons and nuclei. Since the former are much lighter, they have relatively greater velocities and their motion can be treated by assuming fixed positions of the nuclei. Conversely, the small (compared to interatomic distance) nuclear oscillations occur in an essentially averaged electron distribution. The change in energy of these nuclear vibrations depends upon interaction with radiation of suitable frequency is the origin of vibrational spectrum. The energy change is of course, quantized i.e. the molecule can exit only in distinct states which correspond to discrete energy contents. Thus absorption occurs only when radiation supplying exactly the right “packet” of energy impinges on the compounds under study. Each state is characterized by one or more quantum numbers and the energy difference between two such states, ΔE is related to a light frequency, ν by planck's constant, h, which can be expressed by the relations:
\[ \Delta E = h \nu = \frac{hc}{\lambda} \]

Where \( \lambda \), the wavelength of radiation and \( c \) is the speed of light.

Energy required by the molecule is different for different modes. Change in the electronic energy involves relatively large quanta, while the vibrational energy involves smaller quanta and the change in rotational energy involves even smaller than those of vibrational energy. If a molecule absorbs radiation in the microwave or far infrared region, only its rotational energy will change. If the energy of radiation is much greater, as in case of ultraviolet light, there will be a change in the electronic, vibrational and rotational energies of the molecule. Thus the infrared absorption spectra of the molecules result in transition between vibrational and rotational energy levels. In conclusion, molecular spectroscopy is the study of the absorption or emission of electromagnetic radiation by the molecules. The spectral regions i.e. infrared, Visible and ultraviolet are classified from 0.8 microes to 1000 microes, from 400 nm to 800 nm and from 1 nm to 4000 nm, respectively².

The interaction of electromagnetic interaction with matter (atoms or molecules) cause redirection of the radiation and / or transitions between the energy levels of the atoms or molecules. A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule is called absorption. If a molecule is placed in an electromagnetic field, the transfer of energy from the field to the molecule will occur only when the difference of energy, \( E \) between two quantized states as given below:

\[ \Delta E = h \nu = E_2 - E_1 \]
Where $h$ is the plank constant and $v$ is the frequency of radiation. These transitions ($E_1 \rightarrow E_2$ absorption or $E_2 \rightarrow E_1$ emission) involve different amount of energy. A transition from a higher level to a lower level is called emission if energy is transferred to the radiation field, or nonradiative decay-if no radiation is emitted. Redirection of light due to its interaction with matter is called scattering, and may or may not occur with transfer of energy i.e. the scattered radiation has a slightly different or the same wavelength.

Of the many tools that have been used so far for elucidating the structural features, vibrational spectroscopy has been applied most successfully in many ways to different problems yielding fundamental information of immense use\textsuperscript{3-7}. Vibrational spectroscopy provides useful information on the structure of molecules. Molecules absorb radiation of frequencies, which exactly match the frequencies of vibration within the molecule. The frequency at which a molecule vibrates depends upon

i. The force between atoms,

ii. The masses of the atoms,

iii. The geometry of the molecule.

Because of the distinct spectra that certain classes of materials give off due to their structural arrangement, vibrational spectroscopy can be used to determine the composition of unknown substances. As a spectroscopic tool it gives information about conformation of the biological material and a clear picture of the event going on in a living system. It can be used to make an image of the whole system which shows the component specific spatial distribution of the material at a resolution equal to that of a light microscope\textsuperscript{8}. The spectral studies of polyatomic molecules by techniques like infrared spectrophotometers and laser
vibrational state. Through direct absorption only vibrational modes can be excited that show a change of electric dipole moment during the vibrational motion. The intensity of the absorption is related to the magnitude of the change of the dipole moment upon a change of the vibrational quantum state. In addition, there is a possibility to excite vibrational overtones of combinations of vibrations. These transitions are generally weak.

![Graphs showing vibrational states](image)

**Fig 1.1 (a) Infrared absorption; (b) Raman scattering**

Raman spectra originate in the electronic polarization caused by ultraviolet or visible light. Standard Raman spectroscopy is a molecular light-scattering technique in which a change of frequency occurs. It does not involve absorption at all. Raman spectroscopy can simply be described as the inelastic interaction of light with a material. When light strikes a material, some of the light is transmitted, some is absorbed. But most of the light that is scattered is elastically scattered. This scattering is called Rayleigh scattering and the scattered light has the same energy and frequency as that of incident light. The smaller portion of the scattered light is inelastically scattered having a higher or lower frequency and therefore a different energy than the incident light. This inelastic scattered light makes up the
Raman spectrum. Raman scattering is achieved by sending light through a sample and measuring how the light is scattered. In fact molecules can also be irradiated using a monochromatic radiation source (usually from a laser) in the ultraviolet (UV), visible (VIS) or near-infrared (NIR) region of the spectrum, whose quanta have the energy $h\nu_0$. During the inelastic scattering process, vibrational energy $h\nu_R$ can be exchanged, whereby light quanta are scattered which have a scattered energy $h\nu_R = h\nu_0 + h\nu$, giving rise to the Raman lines. At the same time, exciting light quanta are elastically scattered, producing the Rayleigh line (of frequency $\nu_0$) with the same energy, as the exciting line. The intensity of the Rayleigh line is normally several orders of magnitude larger than the Raman lines. Fig 1.1 b.

The two experimental methods are complementary in character. The fundamental difference between absorption on the one hand and Raman scattering on the other is that in absorption we are concerned with the intrinsic electric dipole moment $\mu$ of the molecule whereas in the Raman effect this dipole moment is of no account at all, and we are concerned instead with the dipole moment $\mu$ which is induced in the molecule by the electric field of the incident light. When a molecule is irradiated by monochromatic light of frequency $n$, then, because of electric polarization induced in the molecule by this incident light, light of frequency $n$ (Rayleigh scattering) as well as $n \pm n_1$ (Raman scattering) is emitted (here, $n_1$ represents a vibrational frequency). Thus the vibrational frequencies are observed as Raman shifts from the incident frequency $n$ in the ultraviolet or visible region. Raman scattering is quite weaker than Rayleigh scattering, however, it is possible to observe the Raman scattering by using a strong exciting source.$^{9,10}$
The experimental data, provided by such studies are the frequencies or wavelengths of the radiation, the amount of radiation emitted or absorbed and exact measurement of the size, shape, flexibility and electronic arrangement of the molecules. If these data are properly analysed, valuable information can be obtained about the structure and characteristics of a molecule which is of considerable importance and interest in the field of chemistry as well as physics. Recently, increasing interest in the study of aromatic molecules is mainly due to their fundamental importance. Substituents like OH, CH₃, Cl, F, Br, NO₂ give rise to interesting results. Further, the molecules e.g. phenols, anilines and their derivatives are of great biological and pharmaceutical importance due to their vital role in the structure and properties of nucleic acid and wide application in biochemistry. The spectra of the solutions of these molecules change to a large extent with different polar and nonpolar solvents. Secondly, the various substituents modify the vibrational frequencies, although the aromatic character is retained in all substituted phenols. Thus such studies have stimulated a great research potential in the field of electronic and vibrational spectroscopy.

In view of the above, the present work comprises studies on:

(i) FTIR, laser Raman and near ultraviolet spectra of
   4-chloro-3,5-dimethyl phenol,
   4-bromo-2,6-dimethyl phenol,
   2,6-dibromo-4-methyl phenol,
   2,6-dichloro-4-fluoro phenol,
   5-fluoro-2-nitro phenol,
   4-bromo-2-fluoro phenol.

(ii) To study the electronic spectra in solutions and shift of n-π⁺, π-π⁺ transition by various substituents and their positions.
(iii) To study the effect of polar and nonpolar solvent on electronic transitions.

(iv) To study the effect of pH on electronic transitions.

(v) The calculation of thermodynamic parameters and polarizability.

THE THEORY OF MOLECULAR VIBRATIONS

The theory of molecular vibrations can be understood easily in terms of simple harmonic oscillator in the following way:

THE CLASSICAL THEORY OF THE VIBRATION OF TWO PARTICLES CONNECTED BY A SPRING

Consider the microscopic system of a spring and two particles, which provides the counterpart of the diatomic molecule. The particles will for simplicity, be allowed to move only along the line joining the particles.

If \( x_1 \) and \( x_2 \) represent displacement of two particles of mass \( m_1 \) and \( m_2 \) from initial positions in which the particles were separated by their equilibrium distance. If Hooke's law is assumed for the spring, the kinetic and potential energies can be written as

\[
T = \frac{1}{2} \left( m_1 x_1^2 + m_2 x_2^2 \right) \quad \ldots \ldots \quad (1.2)
\]

and

\[
U = \frac{1}{2} k (x_2 - x_1)^2 \quad \ldots \ldots \quad (1.3)
\]

The problem could have been solved by writing \( F = ma \) for each particle. Lagrange for each particle can be written as:

\[
\frac{d}{dt} \left( \frac{\partial T}{\partial \dot{x}_1} \right) + \frac{\partial U}{\partial x_1} = 0 \quad \ldots \ldots \quad (1.4)
\]
The motion that will occur clearly be one of the vibrations and will have the frequency:

\[ v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]  \[ \text{......... (1.5)} \]

Where \( \mu = \frac{m_1 m_2}{(m_1 + m_2)} \) = reduced mass.

If the masses of the two particles are not equal then the lighter one will move with greater amplitude than the heavier one.

THE QUANTUM-MECHANICAL THEORY OF THE VIBRATION OF TWO PARTICLES CONNECTED BY A SPRING

The solution of the two particle problem shows that the vibrational equation that arises for the vibration of the two particle system is identical in form to that for a single vibrating particle. It is only necessary to replace \( m \) by \( \mu \) and \( x \) by \( q = x_2 - x_1 \), where \( x \) the displacement of the single particle from its equilibrium position and \( q \) is the distortion of the distance between the two particles from the equilibrium bond length. The Schrodinger equation for a single atom of mass \( m \) subjected to a potential of \( U = \frac{1}{2} k x^2 \) is given as:

\[- \frac{\hbar^2}{8\pi^2 m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} (kx^2) \psi = \varepsilon \psi \]  \[ \text{......... (1.6)} \]

While that for the vibration of a diatomic molecule with reduced mass \( \mu \) is

\[- \frac{\hbar^2}{8\pi^2 \mu} \frac{d^2 \psi}{dq^2} + \frac{1}{2} (kq^2) \psi = \varepsilon \psi \]  \[ \text{......... (1.7)} \]

Where \( q = x_2 - x_1 \).

\( x_1 \) and \( x_2 \) are the displacements of the two particles of masses \( m_1 \) and \( m_2 \).
The value of $\psi$ is characterised by a quantum number. Thus, there are again certain allowed states, and each of these states has a specified energy. The integer that describes these states is usually represented by $V$ which can take values $0, 1, 2, \ldots$.

The energies of the allowed states are given by the expression:

$$E_V = \left( v + \frac{1}{2} \right) \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}}$$

\hspace{1cm} \ldots (1.8)

Where $V = 0, 1, 2, 3, \ldots$

**VIBRATIONS OF POLYATOMIC MOLECULES**

Molecules consist of atoms which have a certain mass and which are connected by elastic bonds. As a result, they can perform periodic motions. In the study of molecular vibrations we can start with a classical model of the molecule where the nuclei are represented by mathematical points with mass. The internuclear forces holding the molecule together are assumed to be similar to those exerted by massless springs which tend to restore bond lengths or bond angles to certain equilibrium values. Each mass require three coordinates to define its position, such as $x$, $y$ and $z$ in a cartesian system for example. As a result it has three independent degrees of freedom of motion, in the $x$, $y$ and $z$ direction. If there are $N$ atomic nuclei in the molecule, there will be a total of $3N$ degrees of freedom of motion for all the nuclear masses in the molecule.

The centre of gravity of the molecule requires three coordinates to define its position and therefore has three independent degrees of freedom of motion which are translations of the centre of gravity of the molecule. When a non-linear molecule is in its equilibrium configuration, it requires three rotational coordinates
to specify the molecular orientation about the centre of gravity. For example, there can be three angular coordinates specifying rotation about three mutually perpendicular axes, each going through the centre of gravity. A nonlinear molecule, therefore, has three independent rotational degrees of freedom. A linear molecule only has two independent rotational degrees of freedom about two mutually perpendicular axes, perpendicular to molecular axis. Rotation of a linear molecule about the molecular axis is not considered a degree of freedom of motion since no displacements of nuclei are involved. After subtracting the translational and rotational degrees of freedom from the total 3N degrees of freedom, we are left with (3N - 6) internal degrees of freedom for a nonlinear molecule and (3N - 5) internal degrees of freedom for a linear molecule. Translations of the centre of gravity and rotations about the centre of gravity can all take place independently without any change occurring in the shape of the molecule. The internal degrees of freedom change the shape of the molecule without moving the centre of gravity and without rotating the molecule.

NORMAL MODES OF VIBRATION

Mathematical analysis shows that each way in which vibrational energy can be stored is a normal mode of vibration of the molecule. A normal mode of vibration is a molecule motion in which all the atoms move in phase with the same frequency and all atoms pass through their equilibrium positions simultaneously. The relative vibrational amplitudes of the individual atoms may be different in magnitude and direction but the centre of gravity does not move and the molecule does not rotate. If the forces holding the molecule together are linear function of the displacement of the nuclei from their equilibrium configurations, then the molecular vibrations will be harmonic. In this case each cartesian coordinate of each atom plotted as a function of time will be a sine or cosine wave when the
molecule performs one normal mode of vibration. The actual vibration pattern of
the molecule can be expressed as the sum of vibrations in the normal modes. The
total vibrational energy of the molecule is the sum of the vibrational energies
stored in each mode being \( \sum (v_i + 1/2)h\omega_i \) where \( \omega_i \) is the vibration frequency of the
\( i^{th} \) mode and \( v_i \) is the relevant quantum number. It can be shown that the \((3N - 6)\)
internal degrees of freedom \((3N - 5\) in the case of linear molecules) of a nonlinear
molecule correspond to \((3N - 6)\) independent normal modes of vibration. These
\(3N - 6\) (or \(3N - 5\)) normal vibrations define the vibrational spectra of the molecules.
These spectra depend on the masses of atoms, their geometrical arrangement,
and the strength of their chemical bonds.

Normal modes can be classified as stretching or bending, according to whether it
is mainly bond length or bond angles that alter during the vibration. Normal modes
of symmetric molecule can be classified as symmetric or antisymmetric,
depending on whether the vibration would be in phase with, or \(180^0\) out of phase
with, a similar molecule turned through \(180^0\) about its axis of symmetry. It can be
seen that, as the number of normal modes of vibration of nonlinear \(N\) atomic
molecule is \((3N-6)\), the complexity of the description of the vibrations of the
molecule rises rapidly with \(N\). Fortunately a branch of mathematics, Group
Theory, which provides a technique for analyzing symmetry property, has proved
extremely useful in taking the problem of the normal modes of vibration of
polyatomic molecule. The fundamental frequencies of the normal vibrations are
dependent on the masses of the nuclei, their geometrical arrangement and the
strength of the chemical bonds\(^9,11\).
QUANTUM MECHANICAL TREATMENT OF THE VIBRATIONS OF POLYATOMIC MOLECULE

The Schrodinger equation of \( n \) particles, the position of each being described by three cartesian coordinates will be:

\[
- \frac{\hbar^2}{8\pi^2} \sum_{i=1}^{n} \frac{1}{m_i} \left( \frac{\delta^2 \psi}{\delta x_i^2} + \frac{\delta^2 \psi}{\delta y_i^2} + \frac{\delta^2 \psi}{\delta z_i^2} \right) + U(x,y_1,\ldots,z_i)\psi = \varepsilon \psi \tag{1.9}
\]

Where the function \( \psi \) will involve the \( 3N \) coordinates. For the treatment of the internal motion of molecule in terms of the \( 3N-6 \) normal coordinates, the Schrodinger equation can be deduced from the fact that the kinetic energy operator for a coordinate \( q_i \) is given by an expression of the type

\[
- \frac{\hbar^2}{8\pi^2} \frac{\partial^2}{\partial q_i^2}
\]

The denominator term of this kinetic energy operator is generally absorbed in the normal coordinate \( q_i \). In terms of the normal coordinates the kinetic energy is a function of squared terms, hence:

\[
- \frac{\hbar^2}{8\pi^2} \sum_{i=1}^{3N-6} \frac{\partial^2 \psi}{\partial q_i^2} + U(q_1, q_2, \ldots, q_{3N-6}) \psi = \varepsilon \psi \tag{1.10}
\]

Where the solution function \( \psi \) will be a function of \( 3N-6 \) normal coordinates.

The form of the potential energy function can be written as
\[ U(q_1, q_2, \ldots, q_{3N-6}) = \frac{1}{2} \lambda_1 q_1^2 + \frac{1}{2} \lambda_2 q_2^2 + \ldots \]
\[ + \frac{1}{2} \lambda_{3N-6} q_{3N-6}^2 = \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i q_i^2 \]  
\[
\tag{1.11}
\]

Where \( \lambda_i, q_i \) are the coefficients that depend on the force constants of the molecule. Now equation (1.10) can be written as:

\[ -\frac{\hbar^2}{8\pi^2} \sum_{i=1}^{3N-6} \frac{\delta^2 \psi}{\delta q_i^2} + \frac{1}{2} \left( \sum_{i=1}^{3N-6} \lambda_i q_i^2 \right) \psi = \epsilon \psi \]  
\[
\tag{1.12}
\]

This equation can be separated into 3N-6 equations each involving one of the normal coordinates:

\[ \psi = \psi_1(q_1) \psi_2(q_2) \ldots \psi_{3N-6}(q_{3N-6}) \]

or

\[ \psi = \psi_1 \psi_2 \ldots \psi_{3N-6} \]  
\[
\tag{1.13}
\]

Substituting equation (1.13) into (1.12), the 3N-6 expression is obtained of the type:

\[ -\frac{\hbar^2}{8\pi^2} \frac{\delta^2 \psi}{\delta q_i^2} + \left( \frac{1}{2} \lambda_i q_i^2 \right) \psi_i = \epsilon_i \psi \]  
\[
\tag{1.14}
\]

The solution functions for each of the 3N-6 equation like (1.14) are therefore the harmonic oscillator wave functions.

Since, the wave functions written in terms of normal coordinates, the selection rules for transitions between the vibrational states for each normal coordinates are:

\[ V = \pm 1 \]  
\[
\tag{1.15}
\]
Thus, an absorption of radiation corresponding to the transition from the \( V = 0 \) to \( V = 1 \) level of each energy-level pattern can be expected. For absorption experiment the pertinent rule is

\[ \Delta V = +1 \]

**THE POSSIBILITY OF OVERTONE AND COMBINATION BANDS**

Up to now, we have been discussing only harmonic vibrations. Mechanical anharmonicity results if the restoring force is not linearly proportional to the nuclear displacement coordinate. Electrical anharmonicity results if the change in dipole moment is not linearly proportional to the nuclear displacement coordinate. If a vibration is mechanically harmonic, the classical picture of a plot of nuclear displacement versus time is a sine or cosine wave. If mechanical anharmonicity is present this plot will be periodic but not a simple sine or cosine wave. One result of mechanical anharmonicity is that the vibrational frequency will no longer be completely independent of amplitude as it is in the harmonic case.

If a plot is made of dipole moment versus time for a classical vibration, a periodic but non-sinusoidal wave will result, if either mechanical or electrical anharmonicity is present. However, any such periodic function can be resolved to simple sine or cosine components, where the frequencies are integral multiples of the fundamental vibrational frequencies (Fourier analysis). This means that if the molecular vibration is anharmonic, the dipole moment will oscillate with the fundamental frequency and integral multiples thereof. There are called the fundamental first overtone, second overtone, etc., and these dipole moment oscillations can interact with electromagnetic radiation which has the fundamental frequency and integral multiples thereof. The intensity of overtone absorption is dependent on the amount of anharmonicity in the vibration. Overtones can be
detected in the infrared spectrum but they are usually quite weak which implies that although molecular vibrations are measurably anharmonic, the anhannonicity is not great and can be ignored in a reasonably good first approximation.

In polyatomic molecules, which can be looked on as 3N - 6 separate oscillators, anharmonicity causes not only the appearance of overtones but weak combination bands and difference bands. The former arise simply from the addition of two or more fundamental frequencies or overtones. Such combinations as \( v_1 + v_2 \), \( 2v_1 + v_2 \), \( v_1 + v_2 + v_3 \) etc., become allowed, although their intensities are normally very small. Similarly the difference bands, for example, \( v_1 - v_2 \), \( 2v_1 - v_2 \), \( v_1 + v_2 - v_3 \) have small Intensities but are often to be found in a complex spectrum\(^{10}\).

The intensities of overtone or combination bands may sometimes be considerably enhanced by a resonance phenomenon. It may happen that two vibrational modes in a particular molecule have frequencies very close to each other - they are described as accidentally degenerate. Normally the fundamental modes are quite different from each other and accidental degeneracy is found most often between a fundamental and some overtone or combination bands and are said to resonate. Similarly two close molecular vibrational frequencies resonate and exchange energy-the phenomenon being known as Fermi resonance, when a fundamental resonates with an overtone. In the spectrum of a complex molecule exhibiting many fundamentals and overtones, there is a good chance of accidental degeneracy, and Fermi resonance occurring. However, it should be mentioned that not all such degeneracy lead to resonance. It is necessary, also to consider the molecular symmetry and the type of degenerate vibrations\(^{12}\).
SYMmetry Properties of Polyatomic Molecules

Fundamental phenomena and laws of nature are related to symmetry and accordingly, symmetry is one of science's basic concepts. The word symmetry comes from the Greek syn-metron, to measure together. This means that we consider two or more things to observe symmetry. Plato, the Greek philosopher, felt that the world consists of earth, water, fire and air. He assumed that each of them possesses a definite geometric shape. According to him the earth is a cube, the fire a tetrahedron, the water an icosahedron and the air an octahedron. Symmetry is present in geometrical figures, crystalline solids and molecules. A French mathematician, Evariste Galois, formulated group theory in a letter to a friend the night before he was shot to death in a duel over a woman. Molecular symmetry, through the application of group theory, is in fact of general use in determining many molecular properties.

Each molecule possesses a definite symmetry and a particular point group. By symmetry of molecule, we mean that the symmetry of the configuration of its nuclei or, in other words, of the nuclear frame. If under certain coordinate transformation, the nuclear framework of the molecule remains indistinguishable from the original one, then the molecule is said to possess certain symmetry. A molecule is said to be more symmetrical if it possesses a larger number of symmetry elements and symmetry operation in it.

A symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation or reflection or inversion is done. A molecule, may have one or several symmetry elements, such as an axis of symmetry \((p - \text{fold}) \ (C_p)\), a plane of symmetry \((\sigma)\), \((p\)-fold\) rotation reflection axis (improper axis of symmetry) \((S_p)\), a centre of symmetry \((i)\) and an identity element \((E)\).
A symmetry operation is a movement of the molecule such that the resulting configuration of the molecule is indistinguishable from the original. To each symmetry element corresponds a symmetry operation, that is, a coordinate transformation (reflection or rotation) that will produce a configuration of the nuclei indistinguishable from the original one.

Fig 1.2: The two fold rotation axis of a molecule

Consider the example of water molecule shown in Fig 1.2 rotation of $180^\circ$ about the z axis interchanges the position of the two hydrogen atoms, $H_a$ and $H_b$, but since these atoms are equivalent, the new orientation is indistinguishable from the original and can be superimposed upon it. The symmetry operation in this example is the rotation about the z axis, while the symmetry element is the rotational axis itself.

To give a closer description of the reflection planes a letter h or v is used as index (horizontal or vertical), where h always means the reflection plane vertical to the rotational axis having the highest order, and v refers to those planes which contain the highest-fold symmetry axis. Using benzene as an example, it can be
seen from Fig 1.3 that the xy, xz and yz planes are all mirrors planes, designated \( \sigma (xy) \), \( \sigma (xz) \) and \( \sigma (yz) \), respectively. In molecules where the z axis is considered vertical, \( \sigma (xz) \) or \( \sigma (yz) \) (or both) is designated \( \sigma_v \). A mirror plane perpendicular to the principal rotation axis is designated \( \sigma_h \). A possible combination of symmetry operations, that leaves at least one point unchanged is called point group. The molecule is classified into some different points according to the number and type of symmetry elements. Any molecule must belong to one of the possible point groups which are designated as \( C_p \), \( S_p \), \( C_{pv} \), \( C_{ph} \), \( D_{ph} \), \( D_{pd} \), \( T_d \), \( T_h \) and \( O_h \). Here, we give a very brief account of \( C_s \) and \( C_{2v} \) point groups.

**POINT GROUP \( C_s \)**

This point group has only one element of symmetry i.e. "plane of symmetry (\( \sigma \)). Under this point group, the normal vibrations (and eigen functions) of the molecule may be symmetric (\( a' \)) or antisymmetric (\( a'' \)) with respect to this symmetry element (\( \sigma \)). The transformation properties of this point group are given in Table 1.1. In this Table the point group and symmetry operations are given in the first row. The symmetry species and behaviour of eigen functions for symmetry operation (\( \sigma \)) are given in first and third columns of second and third row. The non-genuine vibrations belonging to particular species are given in the last column.

<table>
<thead>
<tr>
<th>( C_s )</th>
<th>( E )</th>
<th>( \sigma (xy) )</th>
<th>Rot. And trans.</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a' )</td>
<td>+1</td>
<td>-1</td>
<td>( Tx, Ty, Rz )</td>
<td>( I, R \ (P) )</td>
</tr>
<tr>
<td>( a'' )</td>
<td>+1</td>
<td>-1</td>
<td>( Tz, Rx, Ry )</td>
<td>( I, R \ (dp) )</td>
</tr>
</tbody>
</table>

Table 1.1. Symmetry types and characters for the point group \( C_s \).
Fig 1.3: The symmetry elements of a molecule of benzene. The z-axis (a $C_6$ and $S_6$ symmetry axis) is perpendicular to the plane of the figure, which is the $\sigma_v$ symmetry plane.
**POINT GROUP C_{2v}**

This point group has one two-fold axis and two planes of symmetry going through that axis and at right angle to each other\textsuperscript{13,14}. These are designated by C_{2}(z), \sigma_{v}(xz) and \sigma_{v}(yz). Transformation properties of this point group are given in Table 1.2.

**Table 1.2. Symmetry types and characters for the point group C_{2v}**

<table>
<thead>
<tr>
<th>C_{2v}</th>
<th>E</th>
<th>C_{2}(z)</th>
<th>\sigma_{v}(xy)</th>
<th>\sigma_{v}(yz)</th>
<th>Rot. And trans.</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>a_{1}</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>T_{z}</td>
<td>I, R(P)</td>
</tr>
<tr>
<td>a_{2}</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>R_{z}</td>
<td>R (dp)</td>
</tr>
<tr>
<td>b_{1}</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>T_{x}, R_{y}</td>
<td>I, R (dp)</td>
</tr>
<tr>
<td>b_{2}</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>T_{y}, R_{x}</td>
<td>I, R (dp)</td>
</tr>
</tbody>
</table>

Tables 1.1 and 1.2 help in determining the number of fundamental frequencies as well as selection rules.

**SELECTION RULE**

The frequencies of the infrared absorption bands and the frequency shifts of the Raman bands are determined by the energy differences of the vibrational levels in which the transitions take place. In order to find out which transition occur and with what intensity, it is necessary to calculate the transition probabilities. For the infrared and Raman spectrum, the spectrum rule is:

\[ \Delta V \pm 1 \]

for each normal vibration v_{i}, since the oscillators in this approximation, are independent, no simultaneous jumps of two or more vibrations can occur. Transitions within the molecule which are possible according to the selection rules
are said to be allowed, while transitions which can not occur by interaction with
radiation are called forbidden transitions\(^\text{15}\).

**SELECTION RULES FOR INFRARED SPECTRA**

According to classical theory, absorption of electromagnetic radiation is possible
only when there is a change in the dipole moment of the molecule during the
normal vibration. The intensity of the resulting absorption band is proportional to
the square of the change in dipole moment (to the square of the transition moment
in quantum mechanical language). When there is no change in the dipole moment
of a molecule during a normal vibration, it will be infrared inactive. The dipole
moment \(\mathbf{M}\) of the molecule is represented in wave mechanics by the matrix
formed from the integrals:

\[
\int \bar{\psi}_n \bar{\psi}_m^* \mathbf{M} d\tau
\]

........... (1.17)

Where vector \(\mathbf{M}\) has the components

\[
M_x = \sum e_i x_i, M_y = e_i y_i, M_z = \sum e_i z_i
\]

........... (1.18)

Where \(e_i = \text{charge of particle, } i = \text{having coordinates } x_i, y_i, z_i\) and \(\bar{\psi}_n\) and \(\bar{\psi}_m\) are
the time dependent eigen functions of the systems in the two states \(n\) and \(m\). The
asterisk indicates the complex conjugate quantities.

It was pointed out that when a molecule possess symmetry it is possible to
determine many features of its spectrum without any additional information. The
spectral features may be predicted by the use of the group theory. The application
of the group theory for the classification of normal vibrations is based on the fact,
that the potential and kinetic energies of a molecule are invariant to symmetry
The transition probability is proportional to the square of the time independent factor of (equation 1.17) that is to square of

\[
    \left[ \mathbf{M} \right]^{nm} = \int \psi_n^* \psi_m \mathbf{M} \, d\tau 
\]

Consider the transition between two vibrational levels \( V' \) and \( V'' \) of the molecule produced by dipole radiation. Here \( V' \) and \( V'' \) stand for the sets of vibrational quantum numbers \( V_1', V_2', V_3' \ldots \) and \( V_1'', V_2'', V_3'' \ldots \) of the upper and lower states respectively. Thus the vibrational transition probability is proportional to the square of

\[
    \left[ \mathbf{M} \right]^{V'V''} = \int \psi_{V'}^* \psi_{V''} \mathbf{M} \, d\tau 
\]

Where \( \psi_{V'} \) and \( \psi_{V''} \) are the vibrational eigen functions of the upper and lower state respectively. \( \left[ \mathbf{M} \right]^{V'V''} \) is also called the transition moment of the transition \( V' - V'' \).

This is the general vibrational selection rule which is rigorous as long as the interaction with rotation and electronic motion is neglected. The above mentioned rule is strictly valid for gases and vapours. In liquids, the rule may break down due to the irregular external field from neighboring molecules. In the case of crystals, a new set of selection rule may be derived because of the regularity in the arrangement of the molecules.

**SELECTION RULES FOR RAMAN SPECTRA**

In the Raman effect, the light scattered by the molecule contains frequencies other than of the incident monochromatic light and the difference between these frequencies and the frequency of the incident light corresponds to the normal vibrational frequencies of the molecule. Raman scattering can occur only when
there is a change in the polarizability of the molecule, during a vibration. In an asymmetric molecule during all normal vibrations, a periodic change of the polarizability takes place and therefore, all normal frequencies appear in the Raman spectrum. However, in symmetric molecules for certain vibrations the polarizability may not change. The infrared and Raman spectra of a molecule compliment each other and information on the complete vibrational spectrum of a molecule often requires both infrared and Raman data\(^{17}\).

For incident radiation of frequency (\(\nu\)) and polarizability (\(\alpha\)) the magnitude of induced dipole moment \(P\) is given by

\[
|\mathbf{P}| = \alpha |\mathbf{E}|
\]  
\(.....\) (1.21)

Where \(|\mathbf{E}|\) is the electric vector of the incident radiation. If \(\alpha\) changes during the vibration \(i\), with frequency \(\nu_i\), \(\mathbf{P}\) will change with the frequencies \(\nu + \nu_i\) and \(\nu - \nu_i\) as well as with the frequency \(\nu\). In general \(\mathbf{P}\) and \(\mathbf{E}\) have different directions. Therefore, the \(X\) component \(P_x\) of \(\mathbf{P}\) depends in general not only on the \(X\) component of \(\mathbf{E}\) but also on the \(Y\) and \(Z\) components, therefore, we have:

\[
P_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \]  
\(.....\) (1.22)

\[
P_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \]  
\(.....\) (1.23)

\[
P_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \]  
\(.....\) (1.24)

Here \(x, y, z\) are the axes of a coordinate system fixed in the molecule and since we are assuming no rotation fixed in space. The \(\alpha_{xx}, \alpha_{xy}\) are constant independent of the direction of \(\mathbf{E}\) and \(\mathbf{P}\). They are called the components or the polarizability tensor \(\alpha\). It can be shown that
\[ \alpha_{xy} = \alpha_{yx} \]
\[ \alpha_{xz} = \alpha_{zx} \]
\[ \alpha_{yz} = \alpha_{zy} \]

The intensity of scattered light depends on the induced dipole moment \( \mathbf{P} \) which is represented by the matrix formed from the integrals.

\[ \int \bar{\psi}_n \, \bar{\mathbf{P}} \cdot \psi_m \, d\tau \]

\[ \therefore \quad (1.25) \]

Where \( \bar{\mathbf{P}} \) is a vector component, are given by equations. The time independent part of equation is

\[ \left[ \bar{\mathbf{P}}^\circ \right]_{nm}^{nm} = \int \bar{\psi}_n \, \bar{\mathbf{P}}^\circ \cdot \psi_m \, d\tau \]

\[ \therefore \quad (1.26) \]

Where \( \bar{\mathbf{P}}^\circ \) is the amplitude of \( \bar{\mathbf{P}} \). The intensity of a Raman transition \( nm \) is proportional to the square of \( \left[ \bar{\mathbf{P}}^\circ \right]_{nm}^{nm} \). Substituting \( \bar{\mathbf{P}} \) from equation (1.22 to 1.24), we obtain for the components of \( \left[ \bar{\mathbf{P}}^\circ \right]_{nm}^{nm} \).

\[ \left[ \bar{\mathbf{P}}_x \right]_{nm}^{nm} = E_x^* \int \alpha_{xx} \, \psi_n \, \psi_m^* \, d\tau + E_y^* \int \alpha_{xy} \, \psi_n \, \psi_m^* \, d\tau \]

\[ + E_z^* \int \alpha_{xz} \, \psi_n \, \psi_m^* \, d\tau \]

\[ \therefore \quad (1.27) \]

Similarly we can write components \( \left[ \bar{\mathbf{P}}_y \right]_{nm}^{nm} \) and \( \left[ \bar{\mathbf{P}}_z \right]_{nm}^{nm} \). Here, \( E_x^*, \ E_y^*, \ E_z^* \), are the components of the amplitude of the incident light wave and the integrals.

\[ \left[ \alpha_{xx} \right]_{nm}^{nm} = \int \alpha_{xx} \, \psi_n \, \psi_m^* \, d\tau \]

\[ \left[ \alpha_{yy} \right]_{nm}^{nm} = \int \alpha_{yy} \, \psi_n \, \psi_m^* \, d\tau \]

\[ \left[ \alpha_{zz} \right]_{nm}^{nm} = \int \alpha_{zz} \, \psi_n \, \psi_m^* \, d\tau \]

\[ \therefore \quad (1.28) \]
are the matrix elements of the six components of the polarizability tensor. A Raman transition nm is allowed if at least one of the six quantities $[\alpha_{\alpha\beta}]^m$, $[\alpha_{\gamma\delta}]^m$ is non zero. A Raman transition between the two vibrational levels $\nu'$ and $\nu''$ is allowed if at least one of the six products $\alpha_{\alpha\beta} \psi_{\nu'} \psi_{\nu''}, \alpha_{\gamma\delta} \psi_{\nu'} \psi_{\nu''}, \ldots$ is totally symmetrical, i.e., it remains unchanged for all symmetric operations permitted by the symmetry of the molecule.

**VIBRATIONAL SPECTRA OF BENZENE**

The Vibrational (infrared and Raman) spectrum of the benzene have been studied by a large number of investigators, but the first comprehensive study of vibrational spectra of benzene were carried out by Ingold et al.\textsuperscript{18-20}. The assignments and theoretical studies of normal modes of vibrations have been studied by several workers\textsuperscript{21-24}. The structure of benzene molecule has been established by various techniques as regular hexagon, the corners of which are carbon atoms, each attached to one hydrogen atom placed symmetrically. The benzene molecule belongs to the $D_{6h}$ point group. There are only twenty fundamentals, ten nondegenerate and ten doubly degenerate assignments of all the vibrational frequencies of benzene to different modes of vibrations with their symmetry species are given in Table 1.3.

As it is observed in Table 1.3 the infrared and Raman spectra give us directly only eleven of the twenty fundamentals of benzene while rest are the calculated ones. Wilson\textsuperscript{3} on the assumption of a valence force system, has derived formulae all the frequencies in terms of six force constants from the observed fundamentals. The assignment of $\nu_{20}(e_{2u})$ vibration has been confirmed by Lord et al.\textsuperscript{24,25}, as well as by the work on the electronic spectrum\textsuperscript{26}. 


<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Notation</th>
<th>Frequency (cm(^{-1}))</th>
<th>Mode of Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Herzberg</td>
<td>Wilson</td>
<td></td>
</tr>
<tr>
<td>e(_{1u})</td>
<td>12</td>
<td>20</td>
<td>3080</td>
</tr>
<tr>
<td>a(_{1g})</td>
<td>1</td>
<td>2</td>
<td>3073</td>
</tr>
<tr>
<td>b(_{1u})</td>
<td>5</td>
<td>13</td>
<td>3060(^*)</td>
</tr>
<tr>
<td>e(_{2g})</td>
<td>15</td>
<td>7</td>
<td>3046</td>
</tr>
<tr>
<td>a(_{2g})</td>
<td>3</td>
<td>3</td>
<td>1326(^*)</td>
</tr>
<tr>
<td>e(_{2g})</td>
<td>17</td>
<td>9</td>
<td>1178</td>
</tr>
<tr>
<td>b(_{2u})</td>
<td>10</td>
<td>15</td>
<td>1150(^*)</td>
</tr>
<tr>
<td>e(_{1u})</td>
<td>14</td>
<td>18</td>
<td>1033</td>
</tr>
<tr>
<td>e(_{2u})</td>
<td>7</td>
<td>5</td>
<td>985(^*)</td>
</tr>
<tr>
<td>e(_{2u})</td>
<td>19</td>
<td>17</td>
<td>970(^*)</td>
</tr>
<tr>
<td>e(_{1g})</td>
<td>11</td>
<td>10</td>
<td>850</td>
</tr>
<tr>
<td>a(_{2u})</td>
<td>4</td>
<td>11</td>
<td>671</td>
</tr>
<tr>
<td>e(_{2g})</td>
<td>16</td>
<td>8</td>
<td>1595</td>
</tr>
<tr>
<td>e(_{1u})</td>
<td>13</td>
<td>19</td>
<td>1485</td>
</tr>
<tr>
<td>b(_{2u})</td>
<td>9</td>
<td>14</td>
<td>1310(^*)</td>
</tr>
<tr>
<td>a(_{1g})</td>
<td>2</td>
<td>1</td>
<td>992</td>
</tr>
<tr>
<td>b(_{1u})</td>
<td>6</td>
<td>12</td>
<td>1010(^*)</td>
</tr>
<tr>
<td>e(_{2g})</td>
<td>18</td>
<td>6</td>
<td>608</td>
</tr>
<tr>
<td>b(_{2g})</td>
<td>8</td>
<td>4</td>
<td>703(^*)</td>
</tr>
<tr>
<td>e(_{2g})</td>
<td>20</td>
<td>16</td>
<td>404(^*)</td>
</tr>
</tbody>
</table>

Where \(^*\) = The calculated values, \(\nu\) = Stretching, \(\beta\) = In-plane bending, \(\gamma\) = Out-of-plane bending
Pitzer and Scott\textsuperscript{27} have tried to identify some of the weaker bands in the Raman and infrared spectra of liquid C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}D\textsubscript{6} with the inactive fundamentals. The symmetry of the molecule is reduced by the replacement of one or more hydrogen atoms in the ring by other atoms or groups of atoms. Randle and Whiffen\textsuperscript{28}, in their discussion of vibrational spectra of monosubstituted benzene have shown that even a group of atoms such as -CH\textsubscript{3}, -OCH\textsubscript{3}, -CH=CH\textsubscript{2}, -NH\textsubscript{2} etc. may be treated like a single mass point as the local symmetry of the benzene ring is not much affected by the substituent and thus the symmetry can be determined easily. The substituent (represented by X) behaves independently from other hydrogen atoms due to large difference between the mass of the substituent and hydrogen atom and due to different force constants for C-X and C-H bonds.

**ELECTRONIC TRANSITIONS AND SELECTION RULES**

Electronic levels in molecules are separated by much greater energy intervals than the vibrational levels, and the spectra originating in transitions from the ground to excited electronic levels occur mainly in the visible and ultraviolet region. The absorption of the light energy by organic compounds in the visible and ultraviolet region involves promotion of electron in $\sigma$, $\pi$ and $n$ orbitals from the ground to higher energy states. There higher energy states are described by molecular orbitals called anti bonding orbitals. The possible types of electronic transitions are:

\[
 n \rightarrow \sigma^*, n-\pi^*, \pi \rightarrow \pi^* \text{ and } \sigma \rightarrow \sigma^*
\]

Where

- $n$ is nonbonding molecular orbital
- $\sigma$, $\pi$ are bonding molecular orbitals
- $\sigma^*$, $\pi^*$ are antibonding molecular orbitals.
Transition to antibonding $\pi^*$ orbitals are associated only with unsaturated centres in the molecule. Energy required for the above transitions are in the following order\(^\text{29}\):

\[
\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n^* - \pi^*
\]

Higher Energy \hspace{1cm} Lower Energy

Fig 1.4 shows the general relative electronic excitation energies for these transitions. For polyatomic systems, detailed analysis of electronic spectrum may give information concerning the molecular orbital structure of the molecule. As we know, the selection rule will determine to a large extent whether a transition between two particular electronic states is observed or not in the absorption spectrum. The intensity of an electronic transition [This is the integrated absorption intensity \( \int_{\text{band}} \psi_{\text{initial}} \chi_{\text{transition}} \psi_{\text{final}} \, d\tau \)] is proportional to the square of the integral\(^\text{16}\).

\[
\int \psi_{a}^{*} \bar{\mu} \psi_{b} \, d\tau \hspace{1cm} \text{......... (1.29)}
\]

Where

\[
\psi_{is} = \text{wavefunction describing the electronic charge distribution in the initial state.}
\]

\[
\psi_{fs} = \text{wavefunction describing the electronic charge distribution in the final state.}
\]

\[
\bar{\mu} = \text{is the dipole moment operator and transforms as the same irreducible representation as the cartesian coordinates } x, y, \text{ and } z.
\]

Equation 1.29 represent, thus a transition dipole moment (between two electronic states) and it is this that may interact with the electric vector or the incident light beam and result in the absorption of energy via electric dipole process. However, electronic transition is possible only when the integral must be totally symmetric,
Fig 1.4: Schematic electronic excitation energies
i.e. it must belong to the highest symmetry irreducible representation of the molecular point group. Hence the allowed or forbidden nature of the electronic transition depends upon the symmetry properties of the two states. For polyatomic molecules, the situation is complicated by the existence of many vibrational modes, each with its own set of vibrational quantum numbers. The intensity of the vibrational bands for this can also be gauged from the Frank Condon Principle\(^{29}\). Which shows that the strongest vibrational transition in electronic spectra involves vibrational modes which are totally symmetrical, with the result, the symmetry of the excited state is destroyed and the forbidden transition becomes allowed. The selection rules for polyatomic molecular spectra are obtained completely from the behavior of the wave functions and the components of a general operator under symmetry operations which are applied to a given molecule\(^{30}\).

**ELECTRONIC SPECTRA OF BENZENE**

It has been discussed that benzene molecule belongs to the \(D_{6h}\) point group. In this point group there are twelve symmetry species of electronic and vibrational states of which eight are non degenerate \((A,B)\) and four are double degenerate \((E)\) as given in Table1.4 Ingold et al.\(^{31}\) have suggested that unionized benzene, because of even number of electrons, can not have electronic states which are antisymmetric with respect to the molecular plane. In this way the available symmetry classes for electronic states reduces to six and these are \(A_{1g}, A_{2g}, B_{1u}, B_{2u}, E_{2g}\) and \(E_{1u}\).

The electronic spectrum of benzene molecule was reported by several investigators\(^{29,31-36}\), while studying the planer structure of benzene. In terms of molecular orbitals, carbon atom is linked to its two neighboring carbon atoms and to one hydrogen atom by \(sp^2\) trigonal \(\sigma\) bonds. Each carbon has a 2p orbital for \(\pi\)
Fig 1.5: Structure and the $\pi$ valence orbitals of $\mathrm{C}_6\mathrm{H}_6$. 
Fig 1.6: Molecular orbitals of benzene
bonding and these six π valence orbitals (Fig 1.5) form six molecular orbitals (Fig 1.6) for benzene.

The molecular orbitals and their energies are:

\[ \psi_2 = x_A + x_B + x_C + x_D + x_E + x_F, \quad E_1 = \alpha + 2\beta, a_{1u} \]

\[ \psi_1 = x_B + x_C + x_E - x_F, \quad E_2 = \alpha + \beta, \theta_{1g} \]

\[ \psi^{'}_1 = 2x_A + x_B - x_C - 2x_D - x_E + x_F, \quad E_3 = \alpha + \beta, \theta_{1g} \]

\[ \psi^{-1} = x_B - x_C + x_E - x_F, \quad E_4 = \alpha - \beta, \theta_{2u} \]

\[ \psi^{\prime 1} = 2x_A - x_B - x_C + 2x_D - x_E - x_F, \quad E_5 = \alpha - \beta, \theta_{2u} \]

\[ \psi^{-2} = x_A - x_B + x_C - x_D - x_E - x_F, \quad E_6 = \alpha - 2\beta, b_{2g} \]

Table 1.4. TRANSFORMATION OF SYMMETRY SPECIES OF D_{6h} POINT GROUP TO THE REDUCED SYMMETRY C_{2v} AND C_{s}

<table>
<thead>
<tr>
<th>D_{6h}</th>
<th>C_{2v}</th>
<th>C_{s}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{1g}</td>
<td>A_{1}</td>
<td>A'</td>
</tr>
<tr>
<td>A_{1u}</td>
<td>A_{2}</td>
<td>A^{*}</td>
</tr>
<tr>
<td>A_{2g}</td>
<td>B_{2}</td>
<td>A'</td>
</tr>
<tr>
<td>A_{2u}</td>
<td>B_{1}</td>
<td>A^{*}</td>
</tr>
<tr>
<td>B_{1g}</td>
<td>A_{2}</td>
<td>A^{*}</td>
</tr>
<tr>
<td>B_{1u}</td>
<td>A_{1}</td>
<td>A'</td>
</tr>
<tr>
<td>B_{2g}</td>
<td>B_{1}</td>
<td>A^{*}</td>
</tr>
<tr>
<td>B_{2u}</td>
<td>B_{2}</td>
<td>A'</td>
</tr>
<tr>
<td>E_{1g}</td>
<td>A_{2}, B_{1}</td>
<td>A'^, A^{*}</td>
</tr>
<tr>
<td>E_{1u}</td>
<td>A_{1}, B_{2}</td>
<td>A', A^{*}</td>
</tr>
<tr>
<td>E_{2g}</td>
<td>A_{1}, B_{2}</td>
<td>A'^, A'</td>
</tr>
<tr>
<td>E_{2u}</td>
<td>A_{2}, B_{1}</td>
<td>A'^, A^{*}</td>
</tr>
</tbody>
</table>
(ψ₁ and ψ'₁) and (ψ⁻¹ and ψ') are degenerate pairs of molecular orbitals Fig 1.6. That is, each wave function of a degenerate pair is a distinct and independent wave function, but each has the same energy. In benzene, the degenerate molecular orbitals have the same number of nodal planes, but they differ in the orientation of their planes.

According to solar, out of the six available π electrons two move to occupy the ψ = 0 orbital and four to the ψ = 1 orbital. Thus the ground state configuration of benzene a²₁u, e⁴₁g has the symmetry A₁g and is singlet. The first excited configuration a²₁u, e³₁g, e₂u gives rise to states of symmetry B₁u, B₂u, and E₁u which can be either singlet or triplet. This state is a four fold degenerate and splits up due to inter electron interaction.

Clark has classified the absorption bands of benzene aromatic hydrocarbons into three types, mainly by their intensity and by their vibrational structure. The weak band near 256 nm (εₘₐₓ = 200), moderately intense band near 203.5 nm (εₘₐₓ = 7400) and the intense band near 184 nm (εₘₐₓ = 60000) are α, P and β bands respectively and are attributed to the transitions from the ground state ¹A₁g to the foregoing excited singlet states ¹B₁u, ¹B₂u... and ¹E₁u respectively. Fig 1.7 Benzene also exhibits a very weak band near 325 mμ which was first observed by Solar in an absorbing path of 20 cm of liquid benzene. A more detailed discussion of the identification of this transition has been given by Albrecht.

The benzene absorption at 2600 A° (E = 200) is associated with the ¹A₁g → ¹B₂u transition. It certainly arises from a symmetry forbidden transition since it is a weak band. A strong band at 1850A° (E = 5000) can only come from a symmetry allowed transition and must be ¹A₁g → ¹E₁u. This band has a shoulder
Fig. 1.7 Term level diagram of benzene

(a) Neglecting
(b) Including electron configuration
on it at 2000A (E= 7000) which must be due to another electronic transition. The nature of this transition may be due to \( \pi-\pi^* \) transition and is polarized\(^{41}\). Most molecular orbital calculation suggests that the 2000 A\(^o\) band is due to a \(^1\)B\(_{1u}\) exited state. This interpretation was first proposed by Goppert and Solar\(^{42}\). On the other hand, the valence bond calculations suggest that the 2000 A\(^o\) band is due to a \(^1\)E\(_{2g}\) state\(^{43}\).

Ingold et al.\(^{31}\) have carried out the experimental studies on benzene. In the electronic spectrum of benzene it shows three band systems mainly at 1800 A\(^o\), 2100 A\(^o\) and 2600 A\(^o\). In addition two more band systems around 1600 A\(^o\) and 3400 A\(^o\) appear.

Benzene has four pairs of E\(_{2g}\) vibrations, two of these are mainly C-C bending and stretching and the other two are C-H bending and stretching. The 606 cm\(^{-1}\) E\(_{2g}\) is mainly a bending frequency and the 1595 cm\(^{-1}\) is a mainly C-C stretching frequency. Murrell et al.\(^{34}\) found that it is mainly 606 cm\(^{-1}\) vibration which gives rise to the intensity of the 2600 A\(^o\) band, whereas it is the 1595 cm\(^{-1}\) which gives rise to most of the 2000 A\(^o\) band intensity. Garforth et al.\(^{44}\) found the 1595 cm\(^{-1}\) vibration to and Dunn and Ingold\(^{36}\) found no hot band of the 606 cm\(^{-1}\) in 2000 A\(^o\) band.

Below 1700 A\(^o\) there are serval strong Rydberg series first observed by Price et al.\(^{45}\), Wilkinson\(^{46}\) has reinvestigated the spectrum under high resolution and observed four such series.

Electronic spectra of most of the substituted benzenes are so close to the 2600 A\(^o\) band system that it seems reasonable to assume that their spectra correspond to the 2600 A\(^o\) band system of benzene.
SUBSTITUENT EFFECT

The change in the properties of organic molecules on the introduction of new substituents have always been a subject of great interest for chemists. The new substituents change the behavior of compound as regard to the chemical and biochemical processes, and it is therefore a subject of interest and investigation in modern physics. When benzene is substituted with a single functional group, the fine structure bands generally appear to be diminished in complexity. The intensity of this absorption is increased and there is generally a shift to longer wavelength. Several investigators \(^{41-59}\) have attempted to develop a theory to treat the change in the absorption wavelengths and intensity of a derivative with the help of perturbation theory.

If two or more chromophoric groups are present in a molecule and they are separated by two or more single bonds, the effect on the spectrum is usually additive. However, if two chromophoric groups are conjugated, the high intensity (\(\pi-\pi^*\) transitions) absorption band is generally shifted by 15-45 m\(\mu\) to longer wavelength with respect to the simple conjugated chromophore.

To describe the effect of a substituent group on the electron distribution in a molecule, the inductive and mesomeric properties of the group play important part \(^{60}\). In the analysis of electronic spectra, the \(\pi\) electrons of a molecule are mainly responsible for the low energy transition and thus mainly concerned with the effect of a substituent.

The inductive effect of a substituent is the effect of the potential field of the substituent on the \(\pi\) electrons of the unsubstituted molecule. The mesomeric effect of a substituent is defined as the ability of the substituent to extent the
space over which the $\pi$ electrons of the molecule are delocalized. The magnitude of the mesomeric effect depends on the energy and size of the orbitals of the substituent which have $\pi$ symmetry. All the substituents can be classified into two groups according to their influence as suggested by Platt.\(^\text{61}\)

(a) Ortho-Para Directing Groups
These are electron donor groups such as $-\text{CH}_3$, $-\text{Cl}$, $-\text{Br}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NHCOCH}_3$ and $-\text{N(CH}_3)\text{_2}$.

(b) Meta Directing Groups
These are electrons acceptor groups such as $-\text{SO}_2$, $-\text{COOCH}_3$, $-\text{COCN}$, $-\text{COOH}$, $-\text{COCH}_3$, $-\text{CHO}$, $-\text{NO}_2$.

The directing influence of a substituent arises from the following two effects.

(a) Conjugative effect (Mesomeric effect or migration effect or resonance effect)
Conjugative perturbation results due to inter-migration of nonbonding electron between the ring and the radical as a result of which excited level is pulled downwards, i.e. towards the ground level and spectrum shifts towards the longer wavelength side Fig.-1.8

(b) Inductive effect
The inductive perturbation is caused by the resultant charge on the substituent which in turn depends upon the polarity of the ring substituted bond. If the net positive charge on the substituent is higher than that of hydrogen atom, it will induce a negative charge on the atom at the other end of the connecting bond which due to excess positive charge than on its neighbour on the ring, induces
Fig 1.8: Energy levels in the $6\pi$ electron conjugated system in benzene
negative charge on them and chain reaction follows. On the other hand, if the net positive charge on the substituent is lower than that of hydrogen atom, the induction takes place with flow of charge in reverse direction.

Some workers\textsuperscript{32,56,62,63} classified the substituents into two groups according to their effects on the charge distribution of the ring, the substituent like $\text{-NH}_2$, $\text{-OH}$, $\text{-CH}_3$, $\text{-OCH}_3$ and halogens (viz F, Cl, Br and I) which bring additional electrons to the ring causes a decrease of electron density in the ortho and para position of the ring. These groups are known as "electron donors" or ortho-para directing groups i.e., the electrophilic substituent will prefer to attack at ortho or para position and will avoid the meta position.

The second category of the substituents is known as electron acceptors and are meta directing groups. These substituent bring only \(\pi\) electrons and draw the charge from the ring and prefer to go on meta position, these substituents are $\text{-SO}_2$, $\text{-NO}_2$, $\text{-CH}_3$, $\text{-CHO}$, $\text{-COOH}$, $\text{-COCH}_3$ and $\text{NH}_3^+$. In polysubstituted derivatives of benzene, the spectral shift in general is additive because of the resonance interaction but the intensity depends on the number and position of the substituents. It has been observed that the spectral shift in substituted benzene in the ultraviolet region $2600$\(\AA\) are usually the bathochromic shift (red shift). However, blue shift has been reported in the case of 1,3,5-trifluorobenzene\textsuperscript{64}.

In case of disubstituted benzene it has been observed that if both the substituents are of the same type, i.e. donor or acceptor, the order of the red shift is para, meta, ortho and if one substituents is donor and the other is acceptor, the order of the red shift is ortho, meta, para. If a substituent has both donor and acceptor
character, one can not separate these two effects from observation on the \( \pi - \pi^* \) spectra (although they may in principle by separated if an \( n - \pi^* \) band is also present, since donors and acceptors shift is in opposite direction).

If a group attached to an aromatic hydrocarbon, has orbitals which change sign on reflection in the plane of the molecule then these orbitals can extend the path of delocalization of the \( \pi \) electrons, and the group is said to exert a mesomeric effect. The mesomeric effect has a large influence on the spectrum\(^{48,53,65-69}\). The mesomeric effect lowers the ionization energy of the monosubstituted benzene by raising the energy of the highest occupied orbital. The \( ^1A_{1g} \rightarrow ^1B_{2u} \) transition is forbidden in benzene as a consequence of the hexagonal symmetry of the benzene molecule and in particular of the six \( \pi \) electrons. The migration of charge which accompanies the basic group substitution distorts the hexagonal symmetry and removes some of the forbiddenness from the \( ^1A_{1g} \rightarrow ^1B_{2u} \) transition, thereby intensifying the absorption. The greater the migration, the greater is the intensification\(^70\). Alkyl substitution intensifies and shifts the benzene spectrum towards the red\(^71\).

In benzene, the forbidden system becomes allowed on substitution due to reduction in symmetry. So that the \((0,0)\) band appears with considerable intensity and usually as the strongest band in the spectrum of substituted benzenes. Although, in view of Frank-Condon Principle intense band in the allowed transition should results from totally symmetric vibration only and odd transition of a non totally symmetric vibration appears with high intensity even in substituted benzene. It shows that electronic ring is not perturbed by the substituents\(^72\).
SOLVENT EFFECT

The effect of solvents on electronic transitions has been studied by Platt, Kasha and Ram et al. When the electronic spectrum in various solvents has been compared with that of the vapour phase, a shift is observed. When an absorption band is shifted towards longer wavelength the shift is called a bathochromic shift or a red shift, on the other hand, a shift of a particular band under discussion to shorter wavelength is called a hypsochromic shift or a blue shift. When the intensity of a particular band increases, the effect is called a hyperchromic shift and the effect resulting in the decrease in the intensity of a particular band is called a hypochromic shift.

Shift of absorption bands occurring upon a change from vapour to solution or from one solvent system to another are the result of differences in solvation energies of the solute in the ground and excited state. The shift $\Delta v = v_{\text{sol}} - v_{\text{vap}}$ equal to the difference in the solvation energies of the solute in the ground and excited states i.e. $S_0 - S_E$. Similarly, the shift of an absorption band of a chromophore in solution caused by change of solvent is given by difference between the respective shifts from vapour to each solvent system. It has been pointed out by McConnell, Pimental and Becker that the Frank-Condon Principle plays an important part to define the solvent effect in the form of orientation and packing strain.

Solvent polarity affects the electronic transition and depends on whether the solute becomes more or less polar after excitation. For a non polar solute in a non polar solvent, the intermolecular interaction between the solute and the solvent arises only from dispersion forces and generally is comparatively weak. In most cases, excited states of non polar molecules are also non polar. However,
any electronic excitation in a molecule is accompanied with a displacement of charge in the molecule and the spectra is shifted to longer wavelength side with the increasing dielectric constant of solvent, that is, with the increasing refractive index of the solvent.

In some cases, excited electronic states of non polar molecules are polar for example, the lowest energy singlet-singlet transition in phenanthrene.  Such a transition is expected to shift towards longer wavelength in dielectric solvents.

When the solvent is polar, the intermolecular interaction between the solute and solvent arises mainly from dipole-induced dipole forces, which are generally stronger than the dispersion forces. In most cases, the polarizability of an excited electronic state is larger than that of the ground state. Therefore, in this case, bathochromic shifts of bands by the solvent are expected. However, in some cases when the polarizability of the excited state is inferred to be smaller than that of the ground state, the transition shifts to shorter wavelength.

When the solute is polar and the solvent is non polar, the predominate intermolecular interaction is of the dipole-induced dipole type, corresponding absorption band will be shifted to longer wavelengths with increasing polarizability of the solvent. However, with the decrease in dipole moment of the solute, the corresponding absorption band will shift towards shorter wavelength with the increase in the polarizability of the solvent. When both the solute and solvent are polar, the predominant molecular interaction is of the dipole-dipole type. In most cases, the absorption bands due to electronic transitions which cause an increase in the dipole moment of the molecule can be expected to be shifted to longer wavelengths with increasing polarity of the solvent and vice-versa.
The effect of changing the solvent system on the position of the band in an absorption spectrum may often be used to classify the bands as \( \pi-\pi^* \), \( n-\pi^* \) or \( n-\sigma^* \). Polar solvents and those which can form hydrogen bonds tend to interact electrostatically with various chromophores. This changes the charge distribution and results in increased delocalization. For \( \pi-\pi^* \) transitions, both ground and excited states are stabilized and absorption moves towards longer wavelength, on the other hand for \( n-\pi^* \) transitions, the absorption moves towards shorter wavelength. The position of an absorption that involves nonbonding electrons (\( n-\pi^* \) and \( n-\sigma^* \)) is particularly sensitive to the polarity of the solvent. Purely aromatic solvents like benzene shift the spectra towards the red both ground and excited states\(^{80}\).

If the group is more polar in the ground state than in the excited state, the nonbonding electrons in the ground states are stabilized (relative to the excited state) by hydrogen bonding or electrostatic interaction with a polar solvent, thus the absorption is blue shifted with increasing solvent polarity. Conversely, if the group is more polar in the excited states the nonbonding electrons of the excited state are stabilized by interaction with a polar solvent and the absorption is shifted to longer wavelength (red shift)\(^{81}\). The blue shift is particularly noticeable on going from a hydrocarbon to a hydroxylic solvent; and it is fairly certain that this is due to the formation of hydrogen bonds\(^{82}-^{84}\). In the ground state, the nonbonding lone pairs of electrons are particularly suitable for forming a hydrogen bond, but this capacity is largely lost when one of these electrons is promoted to the \( \pi \) system\(^{85}\). The blue shift with increasing polarity, e.g. cyclohexane \( \rightarrow \) ethanol \( \rightarrow \) water is useful means of recognizing transition\(^{74,80}\).
**pH EFFECT**

The study of the dependence of spectral changes with pH allow to calculate the spectrum of clear ionic and tautomeric forms and their electronic structure. Moreover, protonation and deprotonation are the particular cases of electrophilic and nucleophilic reactions to find out the reactions ability of different nucleic acid components. The effect of variation in pH on electronic transitions has been studied by Mason et al.\textsuperscript{90}, Mishra\textsuperscript{91}, Fink et al.\textsuperscript{92} and several other workers\textsuperscript{93-95}. Mason et al.\textsuperscript{90} reported a red shift with increasing pH or decreasing acid concentration in 6-hydroxy-quinoline. However the apparent acid quenching and decrease in fractional concentration is accounted for by the blue shift and hypochromism. The electronic absorption spectrum of gallic acid as a function of pH has been observed by Fink et al.\textsuperscript{92}. Fully protonated gallic acid in acidic solution (pH 2.79) exhibits a single absorption band at $\lambda_{\text{max}}$ 268 nm. With increasing pH and dissociation of carboxyl proton the band is blue shifted to $\lambda_{\text{max}}$ 259 nm. In the pH range 7.26-10.44 further dissociation leads to red shift. Similar results were obtained by Goel et al.\textsuperscript{93} in phenol at a series of different pH values. Mishra\textsuperscript{91} have observed a blue shift while going from cationic to anionic form of the molecule 2-phenyl benzimidazole. Singh et al.\textsuperscript{96} and Seema et al.\textsuperscript{97} have also studied the effect of pH variation on some derivatives of uracils. Yadav et al.\textsuperscript{98} have also studied the effect of pH variation on some derivatives of anilines.

During the present investigation, we have discussed the effect of variation in pH on electronic transition in some derivatives of Phenol.

**SPECTRA OF PHENOL**

Phenol is six membered aromatic molecule. Phenol is derived from the old name for benzene (phene), to include the suffix that indicates it possesses a hydroxyl
group (ol). It is not a real alcohol because the hydroxyl group is fixed on unsaturated carbon. Despite, the absence of a carboxyl group (-COOH), phenol is slightly acidic; the phenol molecule has weak tendency to loss the H⁺ ion from the hydroxyl group due to the mesomeric effect. Phenol has antiseptic properties, and was used by Sir Joseph Lister in his pioneering technique of antiseptic surgery, through the skin irritation caused continual exposure to phenol eventually lead to the substitution of aseptic (germ-free) technique in surgery. It is used as a disinfectant and in production of drugs, weedkiller and synthetic resin. The spectra of phenol are similar to their corresponding hydrocarbon. Phenol has been the subject of numerous studies, since it is a good model for the investigation of hydrogen bonding and proton transfer in enzymes and other systems containing aryl alcohol⁹⁹. Phenol and its derivatives have been studied by many workers¹⁰⁰-¹⁰⁴. The ring vibrations are effected on substitution in the same manner as that of benzene. The electron distribution in phenol is best given by the molecular orbital distribution by which the phenol is regarded as a planar bond frame with six electrons lying in bonding molecular orbitals above and below the molecular plane¹⁰⁰. The resonance energy and conjugation energies of phenol are approximately equal to that of benzene. In early periods Evans¹⁰⁹ have studied the spectra of phenol. Recent spectroscopic studies of phenol derivatives have been motivated because of the vibrational spectra of these molecules is very useful for the understanding of specific biological processes and in the analysis of relatively complex systems. Along the macro molecular double helix chain, the vibrational modes of each base interact with those of other bases through hydrogen bonds or stacking effects these interactions affect the ring vibrations.

Phenol presents two band systems in near ultraviolet region¹¹⁰. The shorter wavelength system represents the n-π⁺ system analogous to the 2600 Å°
The analysis of the bands and the assignment of fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and help has been taken from assignments made by earlier works in the similar molecules.

**THERMODYNAMIC PARAMETERS**

In addition to the application of the study of vibrational spectra of polyatomic molecule to the determination of their structure, one of the most important application is the evaluation of their thermodynamic functions. Once the vibrational frequencies of a molecule are known from the vibrational spectra, it is possible to calculate the contribution of the vibrational energy to the total energy possessed by a molecule. In like manner the rotational energy contribution can be calculated if the moment of inertia of the molecule are known spectroscopically.
measured frequencies and the moment of inertia are important variables in
determining the thermodynamic functions of molecule\textsuperscript{116,117}. This possibility is of
great practical importance, particularly, since the direct experimental
measurement of these quantities is usually tedious and difficult.

The total internal energy ($E^0$) of one mol. of a perfect gas (including translations
as well as inner degree of freedom) is

$$E^0 = E + N_1 \varepsilon_1 + N_2 \varepsilon_2$$

.......... (1.30)

Where $E$ is the absolute zero (zero point energy) and $N_1, N_2$ .... are the number of
molecules having energies $E_1, E_2$ .... respectively above the lowest energy.

According to Maxwell-distribution law, the number of molecules $N$ having energy
is

$$N_i = \frac{N g_i}{Q} e^{-\varepsilon_i / kT}$$

.......... (1.31)

Where $N$ is Avogadro number, $K$ is Boltzmann's constant $T$ is the absolute
temperature, $g_i$ is the statistical weight and $Q$ is the partition function of the gas
given by

$$Q = \sum_i g_i e^{-\varepsilon_i / kT}$$

.......... (1.32)

All the thermodynamic functions can be expressed in terms of the partition
function.
EVALUATION OF THE PARTITION FUNCTION

As the total energy of a molecule is divided into translational, vibrational, rotational and electronic, the energy is:

\[ E = E_T + E_{rot} + E_{vib} + E_{elec} \]  \hspace{1cm} (1.33)

and since the partition function \( Q \) is related to the energy by an exponential function equation (1.32), the total partition function will be:

\[ Q = Q_T \cdot Q_{rot} \cdot Q_{vib} \cdot Q_{elec} \]  \hspace{1cm} (1.34)

\[ Q_n = \frac{1}{h^3} \left( \frac{2 \pi m k T}{N} \right)^{3/2} \frac{RT}{P} \]  \hspace{1cm} (1.35)

Where \( m \) is the molecular weight and \( P \) is the pressure and

\[ Q_{vib} = (1 - e^{-\nu_1 h c k T})^{-1} (1 - e^{-\nu_2 h c k T})^{-1} \]  \hspace{1cm} (1.36)

Where \( \nu_1, \nu_2 \) are vibrational frequencies in wave number.

The classical rotational partition function for a nonlinear symmetric top molecule is given by

\[ Q_{rot} = \left( \frac{\pi I_A I_B}{\sigma^2} \right)^{1/2} \left[ \frac{8\pi^2 k T}{h^2} \right]^{3/2} \]  \hspace{1cm} (1.37)

Where \( I_A \) is the principal moment of inertia about the symmetric axis, \( I_B \) is one of the two equal principal moment of inertia and \( \sigma_0 \) is the symmetry number of overall rotation of the molecule. This gives an approximate value of the partition function for a symmetric top molecule as:

\[ Q_{rot} = \left( \frac{\pi I_A I_B I_C}{\sigma^2} \right)^{1/2} \left[ \frac{8\pi^2 k T}{h^2} \right]^{3/2} \]  \hspace{1cm} (1.38)
Where $I_A$, $I_B$ and $I_C$ are the principal moments of inertia, $Q_{elec} = 0$, since the electronic energy is large compared to $KT$ at ordinary temperatures.

**THE PARTITION FUNCTION AND THE THERMODYNAMIC FUNCTIONS**

The thermodynamic functions derived from the above partition functions can be summarize as follows:

(a) The enthalpy $H^0$ is given by the relation:

$$H^0 = E^e + RT$$  \hspace{1cm} (1.39)

For one mol. of an ideal gas, the enthalpy function at one atmospheric pressure is given by

$$\frac{(H^0 - E_e)}{T} = \frac{(E^e - E_e)}{T} + R$$

$$= RT \frac{d}{dt} \ln Q + R$$

$$= 4R + R \sum_{n=0}^{\infty} \frac{v_n hc/KT}{(e^{v_n hc KT} - 1)}$$  \hspace{1cm} (1.40)

(b) The molar heat capacity at constant pressure $C_p^0$ is given by:

$$C_p^0 = \frac{dH^0}{dT} = 4R + R \sum_{n=0}^{\infty} \frac{\left[\frac{v_n hc}{KT}\right]^2 e^{v_n hc KT}}{(e^{v_n hc KT} - 1)^2}$$  \hspace{1cm} (1.41)

(c) The free energy function at $(F^0 - E_0^e) / T$ at one atmospheric pressure is expressed as:

$$\frac{F^0 - E^e}{T} = R \ln \frac{Q}{N}$$
\[
R \ln \left( \frac{\pi l_1 l_n l_r}{\sigma} \right) + \ln \left( \frac{8\pi^2 K T}{\hbar^2} \right)^{\frac{1}{2}} + \ln \left( \frac{2\pi m K T}{Nh^2} \right)^{\frac{1}{2}} \frac{RT}{P}
\]

\[- \left[ \ln N + \sum_{i=1}^{N-6} \ln \left( 1 - e^{-\gamma_e K T} \right)^{-1} \right]
\]

\[- R \left[ \frac{3}{2} \ln M + 4 \ln 1 + \frac{1}{2} \ln \left( l_\lambda l_\nu l_\gamma \right) - \ln \sigma_i + \sum_{i=1}^{N-6} \ln \left( 1 - e^{-\gamma_e K T} \right)^{-1} T \right]
\]

\( \text{(1.42)} \)

(d) The enthalpy \( S^0 \) is given as:

\[
S^0 = RT \frac{d}{dt} (\ln Q) + R + R \ln Q - R \ln N
\]

\[
= \frac{(H^0 - E_i)}{T} - \frac{(F^0 - E_i)}{T}
\]

\( \text{(1.43)} \)

This gives the entropy for an ideal gas in terms of the partition function \( Q \).

However, in case of those molecules which possess one or more internal torsional oscillations, it is necessary to apply certain modifications in their partition functions as discussed by various workers\(^{117-125}\).

In a good approximation, free internal rotation partition function of molecule with a single rotor is given as

\[
Q_i = \left( \frac{8\pi^2 l_m K T}{\hbar \sigma_i} \right)^{\frac{1}{2}}
\]

\( \text{(1.44)} \)

Where \( \sigma_i \) is the number of potential minima per revolution also the symmetry number of the rotation and \( l_m \) is reduced moment of inertia of the rotation top\(^{123}\), expressed as
\[ I_n = \Lambda_m - A_m = A_m - \sum_i \frac{(a_n^i \mu_n^i)^2}{M} + \frac{(B_m^i)^2}{l_i} \]

Here \( \Lambda_m = \sum m_i (x_i^2 + y_i^2) \) the top moment of inertia about the rotating bond where \( m_i \) is the mass of \( K \)th atom.

\[ U = \sum m_i x_i \] the off balance factor

\( n \) = mass of the molecule.

\( l_i \) = moment of inertia about \( i \)th principal arise and

\[ \beta_m^i = \alpha_m^x \Lambda_m - \alpha_m^y \beta_m^y - \alpha_m^z \beta_m^z + U_m \left[ \alpha_m^{ix}, \gamma_m^{ix}, -\alpha_m^{ix}, \gamma_m^{ix} \right] \]

\( u_m^x, \alpha_m^y, \alpha_m^z \) are the direction cosines between the axes of the top \((x,y,z)\) and the axes of the whole molecule \((1,2,3)\) and \( \gamma_m \) are the components of vector \( \gamma \) (from centre of gravity of the whole molecule to the origin of coordinates of the top) on principal axes and the terms \( B_m \) and \( C_m \) are the \( X_z \) and \( Y_z \) products of inertia respectively, i.e.

\[ \beta_m = \Sigma (m_i X_i Z_i) \quad \text{and} \quad C_m = \Sigma (m_i Y_i X_i) \]

In case of a hindered internal rotation, the potential function is given as

\[ V = \frac{1}{2} V, (1 - \cos \sigma, \phi) \] \hspace{1cm} (1.45)

Where \( \phi \) is the angle of rotation and \( V \), the maximum height of the barrier. The corresponding contributions to various thermodynamic functions may be obtained even for asymmetric top molecules with the help of table given by Pitzer and
for this purpose. Use of these tables needs the knowledge of barriers height $V$ which is related to the torsional frequency in harmonic oscillator approximation through the relation.

$$V = \sigma, \sqrt{V_{1}}, \quad \ldots \ldots \quad (1.46)$$

where,

$$F = \frac{\hbar}{8\pi^{2}C_{1}}$$

If $\sigma$, the symmetry number of the potentials function is known only approximately, then $R$ in $\sigma$ must be needed to the entropy and free energy function as in case of ortho and meta di-substituted benzene$^{122,124}$. The potential function represented by equation (1.45) in the simplest case of a more general form.

$$V = \sum_{i} \frac{1}{2} V_{i} (1 - \cos \sigma_{i} \phi) \quad \ldots \ldots \quad (1.47)$$

Pitzer and Gwinn$^{122}$ have further mentioned that even if the potential function in a molecule has a more complicated form, these equations give fairly good results for the thermodynamic functions.

**MOLECULAR POLARIZABILITY**

In recent years the conformational analysis of organic molecules have presented a wealth of reliable experimental data on equilibrium structure of molecules with the aid of improved techniques in electron diffraction studies and microwave spectroscopy. If these data are subjected to powerful theoretical tools, valuable information about the molecular properties can be achieved at molecular level. One of the fundamental electrical properties of a molecule is its molecular polarizability. It cannot be measured directly, but can be deduced from the measurement of some bulk macroscopic properties such as dielectric constant,
dipole moment and index of refraction by employing such well known relations as the Clausius-Mossotti equation, the Langevin-Debye equation or the Lorentz-Lorentz equation. When an atom or molecule is placed in an electric field, the electrons and nuclei are displaced in such a manner as to induce a dipole moment in the atom or molecule. The magnitude of the induced moment ($\mu_{\text{ind}}$) is proportional to the electric field strength ($E$) for weak field i.e.

$$\mu_{\text{ind}} \propto E$$

or,

$$\mu_{\text{ind}} = \alpha E$$

Where, $\alpha$ is called the polarizability of the molecule and is expected to be different for different molecules. The polarizability ($\alpha$) is a tensor. An average molecular polarizability may, however, be obtained by averaging the three directional diagonal components of the polarizability tensor i.e. if

$$\alpha_M = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

Where, $\alpha_M$ is the average or mean molecular polarizability.
REFERENCES


