CHAPTER 2
This chapter describes briefly the theoretical aspects of photophysical processes, absorption spectra of porphyrins and their metal derivatives as well as theory of resonance Raman effect.

2.1 Basic Aspects of Photophysical Processes

2.1.1 Photochemical Energy

Generally speaking a certain amount of energy called activation energy, has to be supplied to molecules so as to bring about chemical reaction. In some reactions activation energy requirements have been so low that molecules undergo spontaneous transformations even at room temperature. But in most of the cases, additional energy has to be supplied to the molecules before they are able to undergo a chemical change. Very commonly, energy has been supplied by increasing the reaction temperature which yields an energy distribution in such a way that most molecules present in the system acquire the same amount of energy. This method involves molecules in their ground electronic state, and it is not possible to activate one specific component of a mixture by thermal methods.

Photochemical method provides an alternative way to add activation energy to the system. In photochemistry, energy is provided through absorption of electromagnetic radiation in the visible or ultraviolet region by the chromophore of molecules in the system. Unlike thermal activation, the absorption of light is able to excite an individual molecule to an excited electronic state without immediately
effecting the surrounding molecules. This selective excitation of individual molecules has been a unique feature of photochemical reactions. The importance of this alternative method is the capability of directing reactions in rather specific ways.

As radiation in the infrared region of the spectrum corresponds to 1-10 kcal/mole of energy, it is capable of producing vibrationally or rotationally excited molecules. However, light in the visible and ultraviolet region possesses sufficient energy to encompass the range of chemical bond energies and is often able to induce chemical changes by exciting molecules to higher electronic states. The energy associated with visible light vary from 38 kcal/mole (750 nm) to 71 kcal/mole (400 nm), whereas ultraviolet light provides energy up to 143 kcal/mole (200 nm).

2.1.2 Absorption of light

Beer and Lambert proposed laws of light absorption, which form the working principle of spectrophotometer. The laws state that the fraction of the incident light absorbed is proportional to the number of molecules in the path. Mathematically the law is expressed as follows:

\[ \text{Absorbance (A)} = \log_{10}(I_o/I) = \varepsilon \cdot b \cdot c \]  

where, \( I_o \) represents the intensity of incident light, \( I \) represents intensity of transmitted light, \( b \) is the optical path length, \( c \) represents concentration of the sample in moles/litre, and \( \varepsilon \) is the molar extinction coefficient. The significance of \( \varepsilon \) values lies in the fact that these are directly related to the probability of transitions taking place. Electronic transitions may be allowed (high probability) or forbidden (low probability) and the selection rules govern these probabilities.
2.1.3 Excitation of Electrons

Electrons in ground-state of organic molecules are assigned to orbitals labelled sigma (σ), pi (π), or non-bonding (n). When a photon is absorbed by a molecule one of the electrons in a bonding or non-bonding orbital is excited to an unoccupied orbital of higher energy, which is generally antibonding orbital. The excited state orbitals corresponding to σ and π bonds are referred to as the σ* and π*, respectively. There are five types of electronic transitions which are observed in the visible and ultraviolet region: σ→σ*; σ→π*; n→σ*; n→π*; and π→π*. The energies needed for σ→σ* and n→σ* transitions are usually very high, needing a wavelength of far less than 200 nm. Although photochemical excitation could be carried out using such light, only two of the possible transitions, n→π* and π→π*, are of interest in organic photochemistry. These transitions need lower energy and take place at longer excitation wavelengths.

2.1.4 Excitation Pathways

A molecule in which all the electrons are paired is said to be in singlet state (S). When two electrons are unpaired the molecule is said to be in a triplet state (T). A schematic representation of these electronic configurations for π→π* transition is given in Fig. 2.1. The first step in a photochemical reaction is excitation of a molecule through absorption of light to a higher electronic state, say from S₀ to S₁. The initially excited molecules may be in any of the allowed vibrational levels of the S₁ state but it rapidly decays to the lowest vibrational level of this electronic singlet
state via process called \textit{vibrational relaxation}. \( S_1 \) may further undergo one of the following energy-degradation processes.

(i) It may drop to \( S_0 \) by emitting the energy in the form of photon. This process generally takes place within \( 10^{-9} \) to \( 10^{-6} \)s. This process is known as \textit{fluorescence}.

(ii) It may return to \( S_0 \) state by non-radiative process in which the excited state looses its energy to vibrational modes.

(iii) It may involve chemical reaction.

(iv) It may decay to a triplet state (\( T_1 \)) through a process called \textit{intersystem crossing} which is radiationless process.

The singlet and triplet states have considerable excess energy and are thus quite labile. But the conversion of \( S_1 \) to \( T_1 \) has been energetically a slow process in accordance with the spectroscopic rule that change in multiplicity is a forbidden process. However, if the singlet state is sufficiently long-lived, the intersystem crossing can take place with a high degree of efficiency. For every singlet state there exists a corresponding triplet state, and the average lifetime of the latter is \( 10^{-5} \) to \( 10^{-3} \) s. The majority of photochemical reactions occur from the triplet state because of its long lifetime. The triplet state is also paramagnetic because of its two parallel unpaired electrons whereas the singlet state is diamagnetic. Photochemical reactions involving triplet states are thus susceptible to quenching by paramagnetic salts and by free radical scavengers like oxygen, iodine, nitric oxide, etc. If no chemical reaction takes place from the excited triplet state, the molecule can loose energy and return to the ground state by emitting photon, a process called phosphorescence, or by radiationless process.
2.1.5 **Photo-Induced Electron Transfer**

An electronically excited state is obtained when a molecule absorbs a photon of suitable energy [Eqn. 2.2],

\[ A + h\nu \rightarrow A^* \quad 2.2 \]

Each electronically excited state is virtually a new chemical species with its own chemical and physical properties. In dealing with electronically excited state the following features have to be taken into consideration: (i) the excited molecules are transient species whose lifetimes may range from \(10^{-12}\) to \(10^{-3}\) s. in fluid solution; (ii) an excited state has always a higher electronic affinity and a lower ionization potential compared to the ground-state molecule, and thus it is both a better oxidant and a better reductant than the ground state; (iii) the equilibrium nuclear geometry of the molecule in the excited state may be different from that of the ground state; and (iv) formation of an excited state usually involves population of high-energy, expanded molecular orbitals.

In fluid solution, an excited state which has a lifetime long enough to encounter other species can be deactivated ("quenched") in a bimolecular process. The intimate mechanism of the quenching process is often difficult to elucidate, but the final result [Fig. 2.1] is either (i) the electronic energy transfer from the excited state to the quencher, (ii) a chemical reaction between the excited state and the quencher or (iii) the deactivation of the excited state by some catalytic action of the quencher. The quenching of an excited state of a transition metal complex by chemical reaction can occur, in principle, by means of any of the intermolecular reactions which transition metal complexes are able to undergo. Intermolecular excited state reactions, however, can only occur if they are fast enough to compete
with the intramolecular deactivation modes of the excited state and with the other quenching process.

The most important classes of bimolecular reactions of transition metal complexes are ligand substitutions, reactions of the coordinated ligands and inner and outer sphere oxidation-reduction reactions.¹ Ligand substitution reactions are unlikely to be able to compete with the excited state decay unless the entering ligand is the solvent or a counter ion. Some intermolecular reactions involving the coordinated ligands may be fast enough to compete with the excited state decay.

Inner sphere oxidation-reduction reactions, which cannot be faster than ligand substitution reactions, are also unlikely to occur within the excited state lifetime. On the contrary, outer-sphere electron-transfer reactions, which only involve the transfer of one electron without any bond making or bond breaking processes, can be very fast (even diffusion controlled) and can certainly occur within the excited state lifetime of many transition metal complexes. In agreement with these expectations, no example of inner sphere excited state electron-transfer reaction has yet been reported, where as a great number of outer-sphere excited state electron-transfer reactions have been reported.

In dealing with neutral organic molecules in fluid solutions, it has been found that the formation of the electron transfer products in the excited state quenching process may be the result of a very complicated series of events. In particular, the encounter complex may give rise to an excited state complex (exciplex), i.e., a situation in which the excited state and the quencher are linked by some kind of interaction,²,³,⁵ as illustrated below.
Depending on its own properties and on the experimental conditions, the exciplex can deactivate by luminescence, radiationless transitions or chemical reaction. It is now generally accepted that the exciplex is an intermediate in many bimolecular photochemical transformations of organic molecules. In literature, there are many evidences of exciplex formation between excited state porphyrins and a number of electron acceptors and donors. Absorption spectra of exciplexes are slightly red shifted compared to the respective porphyrins as observed for Zn-etio- porphyrin and chloroindium(III) TPP. Since the lifetime of the exciplex is generally very short, these complexes can be detected only if a sufficient population is built up by irradiating with intense light source.

When the chemical reaction is electron transfer, a solvated ion pair is formed first, which then dissociates into solvent-separated ions. The encounter rate is determined by diffusion rate constant, which for the usual solvents is of the order of $10^{10} \text{ M}^{-1}\text{s}^{-1}$. Simple kinetic considerations show that even when high quencher concentrations are used, only those excited states that have lifetimes longer that $10^{-10}$-$10^{-9}$ s can be involved in encounters with the quencher. This usually precludes the participation in bimolecular processes to all the excited states except the lowest one of any multiplicity, i.e., $S_1$ or $T_1$. An important consequence of this kinetic constraint is that the excited states involved in electron-transfer processes in fluid
solution are thermally equilibrated species, so that their reactions can be dealt with using thermodynamic and kinetic arguments as in the case of any other chemical reactions.\textsuperscript{10}

### 2.2 Absorption Spectra

The porphyrin molecule is highly colored and possesses a number of absorption bands in the optical region, a qualitative description of which is given below.

The free base porphyrin shows a four-banded structure in the visible region numbered as I to IV and intense band between 380 and 420 nm called Soret or B or $\gamma$ band. In some cases another weak band is observed between the band I and II. The normal metalloporphyrin absorption spectra contain a Soret band and two visible bands called $\alpha$ or $Q(0,0)$ and $\beta$ or $Q(0,1)$ bands, where $\alpha$ band is considered to be related to the bands I and III and $\beta$ with bands II and IV respectively of free base porphyrins. In addition to this, some metalloporphyrins such as Mn-porphyrins show distinct additional features, which may arise due to charge transfer transitions, metal d$\rightarrow$d transitions or some other types of transitions. These bands arise for those metal-porphyrins for which there is a strong interaction between the metal electrons and those of the porphyrin ring. Fig. 2.2 gives the absorption spectra of free base octaethylporphyrin (H$_2$OEP) and Co(II) meso-tetraphenylporphyrin (Co$^{II}$TPP). The H$_2$OEP spectrum consists of four bands in the visible region of the spectrum along with strong Soret band. On going to Co$^{II}$TPP, the four-banded visible spectrum reduces to the normal metalloporphyrin absorption spectrum.
The electronic absorption spectra of porphyrins and metalloporphyrins vary with the nature of the chromophoric system and with the peripheral substituents which modify the basic structure. For example, electrophilic side chains such as vinyl and formyl groups, etc. cause a shift of the absorption bands to higher wavelengths due to increase in the $\pi$ electron density at the periphery of the porphyrin nucleus, i.e., with the decrease of the porphyrin basicity. The correlation between the nature of the side chains and optical absorption spectra were first described by Stern et al.,\cite{stern} and later by other workers.\cite{other1,other2,other3} The ratio of the intensities of the visible bands vary with the nature and distribution of the substituents and accordingly visible spectra can be classified as actio, phyllo, rhodo and oxorhodo type, as shown in Fig. 2.3.

### 2.2.1 Theoretical Aspects of Absorption Spectra

Considering the inner 16 membered ring with 18 $\pi$ electrons (each of the 16 atoms of the inner ring contributes one $\pi$ electron while the imine nitrogens contribute two electron each), as the delocalization pathway for the electrons, Simpson\cite{simpson} proposed the first theoretical treatment to explain the optical spectra of the porphyrins. Fig. 2.4 shows the $\pi$-electron system for free-base porphyrin. In his free electron model, Simpson predicted that the lower energy transitions would be forbidden whereas the higher energy transition would be allowed. In analogy with benzene, the electrons were placed in orbitals of increasing angular momentum, two in the lowest level ($l_z = 0$) and four each in the $l_z = 1, 2, 3, 4$ levels. The lowest excited states are formed by promoting one of the four electrons of the highest filled orbital with angular momentum $l_z = \pm 4$ to the empty orbital with angular momentum $l_z = \pm 5$. The change
in the orbital angular momentum \((\Delta l_r)\) will then be either \(\pm 1\) or \(\pm 9\) and the pairs of the transitions would be allowed or forbidden, respectively. Hund’s rules predict that the lower energy state will correspond to \(\Delta l_r = \pm 9\). This predicts, as observed, that the longer wavelength transitions are much weaker than the UV-transitions. Simpson also suggested that the two sets of visible bands observed in the metal free porphyrins were due to two forms of tautomers of the free base. However, the extra spectral features of the free base porphyrins are due to the large distortion from square-planar symmetry of the porphyrin skeleton as the free base porphyrin has protons on opposite nitrogen atoms. Replacement of the imine protons by a metal results in four-fold axial symmetry. Platt\(^{13}\) was the first to realize that the four visible bands of free base porphyrins collapse to two bands in the metal complexes.

In spite of early success, Simpson’s model was unable to explain many quantitative features, as the porphyrin was assumed to have cylindrical symmetry \(D_{ab}\), instead of the actual \(D_{4h}\) or \(D_{2h}\) symmetry for these molecules. In the subsequent theoretical work on the electron systems, the molecular orbitals were expressed as linear combination of atomic orbitals (LCAO) and the orbital coefficients were determined by a variational procedure. Later on, Longuet-Higgins et al\(^{16}\) made the first Huckel LCAO treatment and showed that the \(3a_{2u}(\pi)\) and \(1a_{1u}(\pi)\) were the top filled orbitals and lowest empty degenerate orbital was \(4e_g(\pi^*)\). The orbital coefficients for these orbitals are shown in Fig. 2.5. According to this model, the transition \(3a_{2u} \rightarrow 4e_g\) at lower energy was identified with the \(Q(0,0)\) band and the transition \(1a_{1u} \rightarrow 4e_g\) at higher energy as Soret band. This model predicts equal absorption intensities for both the transitions which is, however, not the case.
In order to account for the observed electronic absorption spectra, Gouterman\textsuperscript{17,18} developed the "four orbital model", which is a combination of the free electron model\textsuperscript{15} and the LCAO-MO\textsuperscript{16} description. In this model, Gouterman considered only the two lowest empty and the two highest filled orbitals of porphyrin in the ground state. Because of the four-fold symmetry, the two empty orbitals are degenerate and carry the $e_g$ label of the $D_{4h}$ symmetry. The two highest occupied molecular orbitals are designated as $a_{1u}$ and $a_{2u}$. Fig. 2.5 shows these four orbitals, depicting the electronic wave function amplitude on the molecular frame. The top filled orbitals are not symmetry degenerate but are assumed to be accidentally degenerate. The $a_{1u}$, $a_{2u}$ and $e_g$ orbitals are analogous to the free-electron orbitals with $l_z = \pm 4$ and $\pm 5$ respectively in the Simpson's model.\textsuperscript{19} The one-electron transitions arise due to excitation of electron from either $a_{1u}$ or $a_{2u}$ to the $e_g$ orbital. These excited states or configuration are denoted by $(a_{1u}, e_g)$ and $(a_{2u}, e_g)$. As they have the same symmetry, their overlap due to Coulomb repulsion energy is finite and the states mix together via configuration interaction. Thus the singly excited configurations are not adequate descriptions of the excited states. If $H_{\text{eff}}$ be the Hamiltonian of the pure configurations and if their interaction via Coulomb repulsion between electrons be represented by $H' = \frac{e^2}{r_y}$, then the total Hamiltonian of the system can be written as

$$H = H_{\text{eff}} + H'$$ \hspace{1cm} 2.3

The coefficients for the mixed states can be calculated by defining the parameters as follows:
\[ A'_{1g} = \frac{1}{2} \left[ E(a_{1u} e_{g_x}) + E(a_{2u} e_{g_y}) \right] \]  

\[ A'_{1g} = \frac{1}{2} \left[ E(a_{2u} e_{g_y}) - E(a_{1a} e_{g_x}) \right] \]  

\[ A'_{1g} = \int (a_{2u} e_{g_y}) H(a_{1u} e_{g_x}) \, dv \]  

\[ R_{1y} = \int (a_{1a} e_{g_x}) y \psi_y \, dv \]  

\[ R_{2y} = \int (a_{2u} e_{g_x}) y \psi_y \, dv \]  

Since \( R_1 \approx R_2 \), we have

\[ R = \frac{1}{\sqrt{2}} (R_1 \pm R_2) \]

where \( A'_{1g} \) is the center of gravity of the two configurations before their interaction, \( A_{1g} \) is the splitting between them, \( A'_{1g} \) is configurational interaction and R’s are the transition dipole moments. Because of X-Y degeneracy, the matrix describing only the Y-polarized mixed states is given in Table 2.1. The rows of the table represent approximate mixtures for the case in which the configurational interaction is much larger than the splitting between the pure states. This case predicts weak Q band and a minimum in the energy difference \( E(\text{Soret}) - E(\text{Q}) \) which is observed in the absorption spectra of metalloporphyrins. Moreover, it is expected that,

\[ E_B - E_Q \approx 2 A'_{1g} = \text{Constant} \]

and

\[ q_n^2 \approx R^2 = \text{Constant} \]

where the oscillator strength \( f_n \) of the Soret band is related to \( q_n \) by an expression
The major conclusion of this calculation is removal of the degeneracy of the Soret and Q states by configuration interaction.

The lower energy transition \( \alpha \), borrows back some intensity of the higher energy transition (Soret) (about 10\%) through vibronic coupling with the formation of a vibronic side band called \( \beta \) or Q(0,1) band on the higher energy side of the \( \alpha \)-band, such that

\[
f'_\beta \approx E_n q^\beta_n f_n
\]

2.12

where \( q^\beta_n \) is the frequency of vibrational modes in the excited electronic state which are responsible for the vibronic coupling.

It is necessary to apply degenerate perturbation theory to linear combinations of the degenerate components as the electronic states of the metalloporphyrins are degenerate. Since only those vibrations contained in the cross product of the symmetries of the two excited states would be active and as both Q and B states originate from configurations of Eu symmetry, vibronic coupling between the two states can occur through vibrations having symmetry species given by:

\[
\Gamma_{\text{vib}} \subset \text{Eu} \times \text{Eu} = A_{1g} + A_{2g} + B_{1g} + B_{2g}
\]

2.14

It is argued that \( A_{1g} \) modes will not be vibronically active if the cyclic polyene model is strictly applicable to metalloporphyrins. Thus in D_{4h} point group, the only modes vibronically active are those belonging to \( B_{1g}, B_{2g} \) and \( A_{2g} \) symmetry species.

The vibrational structure that can be resolved in the Soret band region of the porphyrin can be assigned to the Franck-Condon activity of the symmetric vibrations while the vibrational transitions in the Q(0,1) or the \( \beta \)-band region have been
attributed to the vibronic borrowing from the Soret band. Experimental evidence of the correctness of this model came from Resonance Raman experiments, where it was shown that under Q band resonance excitation of porphyrin complexes, the A2g, B1g and B2g vibrational modes are strongly enhanced, identified by their depolarization ratios. The theoretical section on RR scattering in this chapter will cover further details on the vibronic coupling, Herzberg-Teller activity and the Raman activity of the non-totally symmetric vibrations based on group theoretical and other considerations.

In the case of free base porphyrins (H2Ps), the symmetry of the molecule is lowered from D4h to D2h. The molecular orbitals (MOs) a1u and a2u become a_u and b1u and degenerate pair of e_g MOs split into a b2g and a b3g MO in D2h symmetry as shown in Fig. 2.5. Under the changed situation, strong configuration interaction (CI) still exists between the electronic configurations of like symmetry, B2u and B3u, and again a strong Soret band and a weak Q-band arise. But because of the lowering of symmetry, the degeneracy of both the S1 (Δl = ±9) and S2 (Δl = ±1) states, which occurs in metal-porphyrin, is removed. The transition to lower state gives rise to the Qx band and the higher energy one produces Qy band.

2.3 Raman Scattering

The interaction of the electric field of electromagnetic radiation with the charge distribution of an atom or a molecule induces an oscillating dipole in the latter. The induced dipole becomes a source of secondary radiations, emitting at the frequency of incident primary radiation. The interference of these primary and secondary radiations is responsible for the phenomena of reflection, refraction and
scattering. Scattering refers to light deflected from the direction of incident-light propagation. The interaction of the electric vector of an electromagnetic wave with the electrons of a compound results in the scattering of the incident light. Such interaction induces periodic vibrations in the electrons of the compound, thereby producing oscillating electric moments. Such oscillating electrons become new sources for emitting radiation, that is, the scattered light. There are two basic types of scattering—elastic and inelastic scattering. Elastic scattering results in scattered radiation of the same frequency (wavelength) as the incident light. This phenomenon is called Rayleigh scattering. On the other hand, inelastic scattering produces radiations with frequencies lower and higher than that of incident light. The effect is called Raman scattering. If the scattered light has lower energy (lower frequency) than that of the incident light, the effect is called Stokes Raman scattering. On the other hand, if the scattered light has higher energy (higher frequency) than that of the incident light, the effect is called anti-Stokes Raman scattering.

In order for a molecule to exhibit the Raman effect, the incident light must induce a dipole-moment change or a change in molecular polarizability. The change in polarizability can be visualized as a change in the shape of the electron cloud of a molecule. The induced dipole moment couples with certain vibrational motion of the molecule through changes in the polarizability of the molecule and lead to scattered photons with altered frequency. The scattered light contains a small portion of light due to Raman scattering (different frequency than that of incident light), in addition to that due to normal Rayleigh scattering (same frequency as the incident light). The Raman scattering contains both Stokes and anti-Stokes lines; their frequencies correspond to the sum and difference of the frequency of the incident light and the
allowed molecular vibrational frequencies. When photons interact with a molecule, part of their energy can be converted into various modes of vibrations of the molecule. Stokes Raman effect is obtained when the scattered light loses energy equivalent to the energy given to molecular vibrations. If the energy is transferred to incident light from a molecule, the scattered light has more energy than the original incident light (anti-Stokes Raman effect). Observation of anti-Stokes Raman scattering requires that the scattering molecule must already be in an excited vibrational state of the electronic ground state.

The fraction of incident photons scattered during Raman process is always very small, and thereby Raman peaks are of extremely weak intensity – only about $10^{-8}$ fraction of the incident light appears as Raman scattered signal. Intense monochromatic laser, therefore, is used as excitation source to obtain good quality Raman spectra. In the case of normal Raman scattering, the excitation frequency of radiation is far away from the stationary energy states of the system. That is, the intermediate state is not associated with any particular molecular eigen state as such and is considered to be a statistical superposition/summation of a large number of excited electronic states of the system. When the incident light approaches an electronic absorption band, the intermediate state becomes more important and the summation term is dominated by this electronic state. Thus one obtains pre-resonance and resonance Raman scattering conditions by tuning the exciting frequency through the electronic absorption band (Fig. 2.6). In resonance Raman scattering, a few vibronic levels in the vicinity of the incident light energy dominate the intermediate state. Finally, the resonance fluorescence limit is reached when the incident light coincides with a single sharp level of the electronic state. Though both
resonance fluorescence and resonance Raman involve excitation and emission in the electronic absorption band, there is a very precise difference between these two processes. The resonant scattering processes depend not only on the energy difference between the molecule and the photon states, but also on the line shapes associated with them. In the case of resonance fluorescence, the molecular state is much sharper than the photon state and is thus completely in resonance with the incident beam. The scattering may then be described as a rapid population of the excited state followed by a slow decay characterized by the lifetime of this state. In the resonance Raman limit, the photon state is much sharper than the molecular state and thus is in resonance with only a small part of it. In this case two emission processes are involved; a fast one with the lifetime of the incident photon state and a slower one with the excited molecular state lifetime. The former part represents the resonant scattering, while the later represents the non-resonant part of the scattering. Thus the re-emission lifetime is characteristic of either the excited state or of the incident radiation, whichever has the narrower line-width. The resonance fluorescence is attributed to the later situation and resonance Raman scattering to the former. The physical process, however, remains the same in spite of this distinction between the two phenomenon.

2.3.1 Theory of Resonance Raman Scattering

The charge distribution of a molecule is perturbed periodically by electric field of the exciting electromagnetic wave. The induced alternating dipole moment resulting from the interaction acts as a source of secondary radiation and forms a basis of light scattering phenomena. This treatment fairly demonstrates how
polarizability fluctuations give rise to frequency shifts in the scattered radiation. This simple classical treatment, however, offers no clues to the inherent nature of the interaction of radiation with matter, nor it explains important phenomena like resonance and stimulated Raman scattering. Therefore, a fully quantum mechanical electrodynamical approach in which both the radiation and matter are quantized was first applied by Jacob\textsuperscript{25} for understanding the RR scattering. However, the correct results for RR scattering may also be obtained by using semi-classical treatment of Kramers and Heisenberg\textsuperscript{26} that correlates the scattering tensors to the wave functions and the energy levels of the scatterer. The radiation is treated classically and is regarded as a source of perturbation to the energy levels of the scattering system while quantum mechanical techniques are used to investigate transitions between the quantized levels of the perturbed system. Many workers in the later studies have extended this approach.\textsuperscript{27-31}

Consider a non-rotating molecule at the origin of a space-fixed coordinate system interacting with an incident plane wave of light with electric vector represented as

\[ E^\sigma = E^\sigma_n \exp \left( i \vec{k} \cdot \vec{r} - \omega t \right) \]  \hspace{1cm} 2.15

Propagating along \( \vec{k} \) with angular frequency \( \omega \), the oscillating electric dipole moment induced in the molecule is given by

\[ (\vec{\mu}_n)_{mn} = (\vec{\alpha}_{\mu\alpha})_{mn} \vec{E}_n \]  \hspace{1cm} 2.16

where \((\vec{\mu}_n)_{mn} = <\psi_m|\vec{\alpha}_n|\psi_n>\) is the amplitude of the transition moment and \( \psi_m \) and \( \psi_n \) are the time dependent wavefunctions of the initial and final states respectively,
(\alpha_{\rho\sigma})_{mn}^{\rho\sigma\sigma} is the polarizability tensor for the transitions from m to n and \rho and \sigma are molecular cartesian axes of the scattering tensor (\alpha_{\rho\sigma})_{mn}^{\rho\sigma\sigma}.

Let us consider a molecule, initially in a vibronic state \ket{m}, which is perturbed by plane polarized incident light of frequency \nu_o and intensity I_o causing a transition to a vibronic state \ket{n} giving rise to the scattered light of frequency (\nu_o \pm \nu_{mn}). The scattered light intensity I_{mn} in terms of photons per molecule per second in the 4\pi solid angle, after averaging over all orientations of the molecule, is given by

\[ I_{mn} = \frac{128\pi^4}{9c^4} (\nu_o \pm \nu_{mn})^4 I_o \sum_{\rho,\sigma} |(\alpha_{\rho\sigma})_{mn}|^2 \]  

2.17

where c is the velocity of light and the sum goes over \rho, \sigma = x, y, z.

From equation 2.17, it is clear that the intensity of the scattered radiation depends upon the frequency of the incident radiation, and more critically it depends on \ket{(\alpha_{\rho\sigma})_{mn}}^2 when the exciting radiation approaches an electronic absorption band in the resonance Raman effect. Consequently, the main effort in the development of Raman theory is to provide a theoretical framework for calculating (\alpha_{\rho\sigma})_{mn} in terms of molecular parameters.

In order to determine the polarizability, the distortion of the wave functions due to periodic perturbations by the incident electromagnetic wave has to be known or calculated and then to evaluate the electric dipole transition moment with the new wave functions using time dependent perturbation theory. The molecular wave functions are obtained from time dependent Schrodinger equation
\[ i\hbar \frac{\partial}{\partial t} |\psi\rangle = (H_o + V)|\psi\rangle \quad 2.18 \]

where \( H_o \) is the unperturbed Hamiltonian and

\[ |\psi\rangle = \sum_i a_i(t) |\psi_i^o(t)\rangle \quad 2.19 \]

where

\[ |\psi_i^o(t)\rangle = |\psi_i^o\rangle \exp(-i\hbar/\omega) \quad 2.20 \]

is the solution for \( V=0 \)

\[ V = \frac{-1}{2} \left[ \bar{\mu}_\rho \left( \bar{E}_\rho^o \exp(-i\omega t) + \bar{E}_\rho^o \exp(i\omega t) \right) \right] \quad 2.21 \]

describes the major part of the interaction of the molecule with electromagnetic radiation.

The \((\rho\sigma)^{\text{th}}\) component of the matrix element of the polarizability tensor for the transition from vibronic state \(|m\rangle\) to a vibronic state \(|n\rangle\) is given by the second order perturbation theory as described by Kramers-Heisenberg-Dirac.\(^{26}\)

\[ (\alpha_{\rho\sigma})_{mn} = \frac{1}{\hbar} \sum_e \left[ \frac{\langle n|\mu_\sigma|e\rangle \langle e|\mu_\rho|m\rangle}{\nu_e - \nu_o + i\Gamma_e} + \frac{\langle n|\mu_\rho|e\rangle \langle e|\mu_\sigma|m\rangle}{\nu_e + \nu_o + i\Gamma_e} \right] \quad 2.22 \]

where \( \mu_\rho \) and \( \mu_\sigma \) are the dipole moment operators and the sum goes over the excited vibronic states \(|e\rangle\) of the molecule.

When \( \langle e|\mu|m\rangle \) is finite for a real state \(|e\rangle\), the transition from \(|m\rangle\) to \(|e\rangle\) is accompanied by light absorption with center frequency \( \nu_e \) and full-width at half maximum of \( 2\Gamma_e \), and the absorption intensity would be proportional to \( |\langle e|\mu|m\rangle|^2 \).

If the photon energy \( (h\nu_o) \) of Raman excitation were close to the energy of the
electronic transition, the first term of \( (\alpha_{\sigma\sigma})_m \) and thus \( I_{mn} \) would be remarkably large. This is called resonance Raman scattering. The vibrational modes which gain resonance enhancement in intensity are limited to the vibrations associated with the chromophore responsible for the absorption band.

The Eq. 2.22 can be made more meaningful by incorporating Born-Oppenheimer adiabatic approximation for all wave functions involved and then expanding the electronic wave functions in a Taylor’s series around the ground state equilibrium configuration of the nuclei. Thus a given vibronic state must now be identified according to electronic and vibrational levels, as \( |m\rangle = |g, i\rangle \), \( |n\rangle = |g, j\rangle \) and \( |e\rangle = |r, v\rangle \) which depends on both the nuclear and electronic wave functions for the ground and excited states, respectively; \( |i\rangle \), \( |j\rangle \) and \( |v\rangle \) are the vibrational wave functions with the quantum numbers \( i, j \) and \( v \), respectively. In this formulation it is also postulated that the vibrational wave functions in the electronic excited states are the same as those in the electronic ground state except for the origin of the coordinates, i.e., the equilibrium structure of the molecule, which differs between the two states. The change of the electronic wave function due to the origin shift is incorporated with Herzberg-Teller expansion. Then the main terms contributing to the polarizability tensor of Eq. 2.22 under resonance with a particular electronic state, \( |r\rangle \), are the following two terms

\[
(\alpha_{\sigma\sigma})_\gamma' = (A_{\sigma\sigma})_\gamma' + (B_{\sigma\sigma})_\gamma' \\
2.23
\]

where

\[
(A_{\sigma\sigma})_\gamma' = \frac{M_{\sigma\sigma}^r M_{\sigma\sigma}^r}{\hbar} \sum_v \frac{\langle j | v \rangle \langle v | i \rangle}{v_{\text{eq}} + (v - i)\Delta v_{\text{eq}} - v'_{\text{eq}} + iF_{\gamma}} \\
2.24
\]
and

$$(B_{\nu r})' = \frac{M_{\alpha}^x M_{\alpha}^y M_{\rho}^z}{\hbar^2 (v_r - v_s)} \sum \frac{\langle j|v\rangle\langle v|i \rangle}{v_{rg} + (v-i)\Delta v_a - v_s + i\Gamma_r} +$$

$$\frac{M_{\alpha}^x M_{\alpha}^y M_{\rho}^z}{\hbar^2 (v_r - v_s)} \sum \frac{\langle j|v\rangle\langle v|Q_a \rangle}{v_{rg} + (v-i)\Delta v_a - v_s + i\Gamma_r}$$

2.25

where $M_{\alpha}^x = \langle g^n | \mu_r | r^n \rangle$, $\hbar v_{rg}$ is the energy separation between the $|r\rangle$ and $|g\rangle$ states, $\Delta v_a$ is the frequency of the normal mode with coordinates $Q_a$ and $\hbar v_{rg} = \langle r | \frac{\partial}{\partial Q_a} | s \rangle$ is the vibronic coupling operator that mixes the two electronic states via a given normal mode $Q_a$.

The above results can be summarized as follows: when Raman spectra are obtained with excitation in the region of an electronic absorption band, the vibrational modes which are expected to show enhancement are the one which contribute intensity to the electronic spectrum, i.e., they are vibronically active modes, which are of two types: (i) modes which connect the ground state to the excited state involved in resonance through the Frank-Condon overlap (A-term); (ii) modes which mix the resonant electronic state to another one of higher energy state (B-term). The potential energy curve of the excited electronic state is shifted in the Frank-Condon effect so that the vibrational wave functions are non-orthogonal. Raman scattering from modes due to Frank-Condon effect can arise only when the orthogonality is removed between a ground state and an excited state vibrational wave function. Since A-term is the leading term, it is generally the dominant contribution to RR intensity. A-term enhancement varies directly with the strength of the electronic transition and inversely with its bandwidth and it also depends on the
magnitude of the product $\langle j|v\rangle\langle v|i\rangle$. This increases with increase in displacement of the excited state potential well along the normal coordinate, i.e., A-term modes gain intensity via origin shift. Hence, the extent of excited state distortion determines the degree of enhancement of a given mode. As for non-totally symmetric modes, there is no origin shift, the Frank-Condon product $\langle j|v\rangle\langle v|i\rangle$ is zero and thereby no enhancement of these modes via the Frank-Condon term.

However, non-totally symmetric modes can gain intensity via the B-term because of the Q-dependent vibrational integrals. The contributions of $\langle 1|Q|0\rangle\langle 0|0\rangle$ and $\langle 1|1\rangle\langle 1|Q|0\rangle$ terms are significant to the B-term for vibrational modes differing by one quantum. Therefore, the B-term becomes important in situations where a forbidden or weakly allowed transition gains intensity from vibronic mixing with a strongly allowed transition. The mixing modes are then prominent in the RR spectrum when excited at the weak transition. The enhancement depends on the magnitude of the mixing integral and on the proximity of the electronic states. A limiting case is the Jahn-Teller effect, in which the mixing states are degenerate. In this case, the mixing vibrations (Jahn-Teller active modes) are strongly enhanced.

### 2.4 Normal Modes of Vibration

In diatomic molecules, the vibration of the nuclei occurs only along the line connecting two nuclei. In polyatomic molecules, however, the situation is much more complicated because all the nuclei perform their own harmonic oscillations. It can be shown, however, that any of these extremely complicated vibrations of the
molecule may be represented as a superposition of a number of independent vibrations called *normal modes of vibration*. In each normal vibration, the individual nuclei carry out a simple harmonic motion, and all the nuclei have the same frequency of oscillation and are moving in the same phase. Although the motion of many atoms is involved in each of the normal modes, a simplification of the expressions for many properties of the molecule results. For example, the total vibrational energy of the molecule is then just the sum of the vibrational energy from each normal mode. For general N-atom molecule, the number of normal vibrations is 3N-6 (or, if linear, 3N-5 normal vibrations). Thus the general form of the molecular vibration is a superposition of the 3N-6 (or 3N-5) normal vibrations. For any given molecule, however, only vibrations that are permitted by the selection rule for the molecule appear in the infrared and Raman spectra. According to the selection rule for harmonic oscillator, any transitions corresponding to \( \Delta v = \pm 1 \) are allowed. Under ordinary conditions, however, only the normal modes that originate in the transition from \( v = 0 \) to \( v = 1 \) in the electronic ground state can be observed because of the Maxwell-Boltzmann distribution law. In addition to the selection rule for the harmonic oscillator, another restriction results from the symmetry of the molecule. Thus the number of allowed transitions in polyatomic molecules is greatly reduced. The overtones and combination bands of these normal vibrations are forbidden by the selection rule of the harmonic oscillator. However, they are weakly observed in the same spectrum because of anharmonicity of the vibration.

If a molecule has a number of symmetry elements, the (3N-6 or 3N-5) normal vibrations are classified as various species according to the number and the kind of symmetry elements preserved during the vibration. The number of normal vibrations
in each species can be found using group theory. For the 38 atoms free base porphyrin (assuming side chain to be point masses), there are 108 normal modes of vibration, which classify as

\[ \Gamma_{\text{in-plane}} = 19 A_g + 18 B_{1g} + 18 B_{2u} + 18 B_{3u} \]

\[ \Gamma_{\text{out-of-plane}} = 8 A_u + 10 B_{1u} + 8 B_{2g} + 9 B_{1g} \]

vibrations for \( D_{2h} \) symmetry point group of free-base porphyrin. Similarly, assuming all the peripheral substituents as point mass in metalloporphyrin, the 37-atom \( D_{4h} \) model will have 105 normal modes of vibration which classify as

\[ \Gamma_{\text{in-plane}} = 9 A_{1g} + 8 A_{2g} + 9 B_{1g} + 9 B_{2g} + 18 E_u \]

\[ \Gamma_{\text{out-of-plane}} = 3 A_{1u} + 6 A_{2u} + 5 B_{1u} + 4 B_{2u} + 8 E_g \]

2.5 The Polarizability Tensor and Depolarization Ratios

As mentioned earlier, when electromagnetic radiation interacts with the charge distribution of a molecule, the polarization of the charge cloud induced by the electric field of the incident radiation results in an induced dipole moment. The dipole moment so induced is proportional to the electric field and the polarizability \( \alpha \) for small electric field strength is given by:

\[ \vec{\mu} = \alpha \vec{E} \]

For an isotropically polarizable molecule, the induced dipole moment vector \( \vec{\mu} \) is in the same direction as that of the electric field vector \( \vec{E} \). However, for an anisotropic molecule, the induced dipole moment in any direction is given by

\[ \mu_y = \sum \alpha_y \vec{E}_j \]
where \(i, j = x, y, z\). The polarizability tensor \(\alpha\) can be expressed as

\[
\alpha = \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\]  \hspace{1cm} \text{2.32}

Because of symmetry there are only six polarizability tensor components. The elements of \(\alpha\) generally depend on the frequency of the incident radiation, apart from the wave functions and electronic properties of the molecular systems. However, certain combinations of the polarizability tensor elements remain invariant with respect to change of coordinate system and are given by

\[
(\overline{\alpha})^2 = \frac{1}{9} \left[ \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right]^2
\]  \hspace{1cm} \text{2.33}

\[
\gamma_1 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right] + 3 \left[ (\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{yz} + \alpha_{zy})^2 + (\alpha_{zx} + \alpha_{xz})^2 \right]
\]  \hspace{1cm} \text{2.34}

\[
\gamma_{as} = \frac{3}{4} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right]
\]  \hspace{1cm} \text{2.35}

where \(\overline{\alpha}\), \(\gamma_1\), and \(\gamma_{as}\) represent the isotropic, symmetric isotropic and the antisymmetric anisotropic tensor invariants.

The scattering geometry for incident light propagating along the Y-axis is shown in Fig. 2.7. The scattered radiation is detected along the Z-axis. For this geometry, the depolarization ratio for randomly oriented molecules in fluid state in 90° scattering geometry is defined as follows:

\[
\rho_f(\theta = 90^\circ) = \frac{I_\perp}{I_\parallel}
\]  \hspace{1cm} \text{2.36}
The subscript on $\rho_i$ indicates that it is defined for linearly polarized radiation. In
terms of polarizability components,

$$\rho_i = \frac{3\gamma^2_s + 5\gamma^2_{as}}{45(\bar{\alpha})^2 + 4\gamma^2_s}$$  \hspace{1cm} (2.37)

For normal Raman effect, the tensor is symmetric and $\alpha_y = \alpha_\mu$. Hence

$\gamma^2_{as} = 0$ and $\rho_i$ has its well known form for non-resonant Raman scattering given by

$$\rho_i = \frac{3\gamma^2_s}{45(\bar{\alpha})^2 + 4\gamma^2_s}$$  \hspace{1cm} (2.38)

and reduces Eq. 2.34 to

$$\gamma_s^2 = \frac{1}{2} \left[ (\alpha_\alpha - \alpha_{yy})^2 + (\alpha_y - \alpha_{\mu\mu})^2 + (\alpha_\mu - \alpha_{\mu\mu})^2 \right]$$

$$+ \frac{3}{2} \left[ \alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 \right]$$  \hspace{1cm} (2.39)

For Raman scattering from non-totally symmetric modes, $(\bar{\alpha})^2 = 0$

and $\rho_i = \frac{3}{4} + \frac{5\gamma^2_{as}}{4\gamma^2_s}$.

If $\gamma^2_{as} = 0$, we have normal polarization with $\rho_i = \frac{3}{4}$.

Under resonance Raman scattering the tensor need not remain symmetric,
i.e., $\alpha_y \neq \alpha_\mu$.

If $\gamma^2_{as} \neq 0$, then $\rho_i > 3/4$ and we have anomalous polarization provided

$\gamma_s^2 \neq 0$; if $\gamma_s^2 = 0$, then $\rho_i = \infty$ (inverse polarization).

For totally symmetric modes, where $(\bar{\alpha})^2 \neq 0$ and $\gamma^2_{as} = 0$;

$$\rho_i = \frac{3}{45(\bar{\alpha})^2 + 4\gamma^2_s}$$  \hspace{1cm} (2.40)
and so $0 \leq \rho_i < 3/4$ according as $\infty \geq \frac{45(\alpha)^2}{\gamma_i^2} > 0$.

Group theoretical considerations can provide information about the invariants which are non-zero for particular vibrational modes in molecules of a given symmetry, and thus about the symmetry properties of the general polarizability tensor. McClain\textsuperscript{14} has given the symmetries of the scattering tensor for different molecular point groups. This helps in evaluating the contributions from any of the invariants for a Raman process transforming under any irreducible representations of a point group pertinent to the molecule. Dispersion of $\rho_i$ with exciting frequency often provides valuable structural information about the symmetry of the molecule.

Experimentally the evaluation of all the three tensor invariants requires three independent intensity measurements. The measurement of the total scattering at 90°, $(I_1 + I_{||})$, and the depolarization ratio $\rho_i$, may be supplemented by a measurement involving circularly polarized light. It is usual to measure the reversal coefficient $I_{\text{contra}}/I_{\text{co}}$, which is the ratio of the intensity of contra-rotating to that of co-rotating light for the back scattering of pure circularly polarized incident radiation. This is, however, not sufficient to determine the point group symmetry of the molecule having modes which show a dispersion of $\rho_i$. In addition to the measurement at a particular exciting frequency, one requires measurements at various values of $\nu_0$ and $i$ if $I_1$ and $I_{||}$ are measured at various exciting frequencies.
2.5.1 Antisymmetric Tensor Contributions

The first experimental evidence of inverse polarization in resonance Raman studies of porphyrins and heme proteins was provided by Verma and Bersntein and Spiro and Strekas, respectively. The modes, which are responsible for this effect, are of $A_{2g}$ symmetry. Since $A_{2g}$ modes are associated with antisymmetric scattering tensor i.e., $\alpha_y = -\alpha_x$, and they are inactive in normal Raman scattering. Warshell has explicitly demonstrated the antisymmetry of the scattering tensor in $D_{4h}$ symmetry, and has shown that such a situation can exist in the presence of a doubly degenerate electronic level and a rotational type vibrational mode, which leads to equal rotation of the two orthogonal transition moments. The $A_{2g}$ vibrations have rotational symmetry about the four-fold axis. Inverse polarization may be observed with proper exciting line, i.e., the plane of polarization of the incident light is rotated through $90^\circ$ on scattering and $\rho_i = \infty$. Some of the Raman bands in different systems have been observed with $\rho_i \neq \infty$ but $\rho_i > 3/4$, which are called anomalously polarized bands. There are two possible explanations for observation of anomalous polarization in resonance Raman spectra of porphyrins. The effective symmetry of the molecule may be less than $D_{4h}$ in which case the $A_{2g}$ mode may acquire symmetric as well as antisymmetric contributions from scattering tensors. Alternatively, there may be accidental degeneracies between $A_{2g}$ modes and the modes of other symmetries, which are polarized ($A_{1g}$) or depolarized ($B_{1g}$ or $B_{2g}$), giving an overall depolarization ratio less than $\infty$. From systematic RR studies and careful measurements of depolarization ratios of some selected Raman bands as a function of excitation wavelength on Cu-porphin and Cu-mesoporphyrin, Verma et
al, 37,38 had shown that the former has rigorous $D_{4h}$ symmetry while the symmetry of the latter is reduced to $C_s$ due to asymmetric placement of substituents.
References


Table 2.1 Hamiltonian for $y$ Polarized States

<table>
<thead>
<tr>
<th></th>
<th>Dipole Strength $(q^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(a_{2s}e_{g})$</td>
</tr>
<tr>
<td>$(a_{2s}e_{g})$</td>
<td>$A'<em>{1g} + A'</em>{1g}$</td>
</tr>
<tr>
<td>$(a_{1u}e_{g'})$</td>
<td>$A'_{1g}$</td>
</tr>
</tbody>
</table>

(a')

$B'^0_i = \frac{1}{\sqrt{2}} \left[ (a_{2s}e_{g}) + (a_{1u}e_{g'}) \right]$  
$Q'^0_i = \frac{1}{\sqrt{2}} \left[ (a_{2s}e_{g}) - (a_{1u}e_{g'}) \right]$  

(b) \[ \tan 2\nu = \frac{A_{1g}}{A'_{1g}} \]

$B_i = \cos \nu B'^0_i + \sin \nu Q'^0_i$  
$Q_i = -\sin \nu B'^0_i + \cos \nu Q'^0_i$  

(c) \[ 2\nu = \frac{A_{1g}}{A'_{1g}} \ll 1 \]

$B_i = B'^0_i + \nu Q'^0_i$  
$Q_i = Q'^0_i - \nu B'^0_i$  

\[
\begin{align*}
A'_{1g} + A'_{1g'}/\cos 2\nu & \quad 0 \quad \frac{1}{2}(1 + \cos 2\nu)R^2 + Rr\sin 2\nu \\
0 & \quad A'_{1g} - A'_{1g'}/\cos 2\nu \quad \frac{1}{2}(1 - \cos 2\nu)R^2 - Rr\sin 2\nu \\
A'_{1g} + A'_{1g'}(1 + 2\nu^2) & \quad 0 \quad R^2 - \nu^2R^2 + 2\nu Rr \\
0 & \quad A'_{1g} - A'_{1g'}(1 + 2\nu^2) \quad (\nu R - r)^2
\end{align*}
\]
Fig. 2.1 (A) Electronic configuration of singlet (S) and triplet (T) states (B) Bimolecular quenching process for an excited-state molecule.
Fig. 2.2 Electronic absorption spectra of: (A) free base octaethylporphyrin (H$_2$OEP); (B) cobalt(II) meso-tetraphenylporphyrin (Co$^{III}$TPP) in CH$_2$Cl$_2$. 
Fig. 2.3 Representative visible absorption spectra of typical porphyrins
(A) aetio-; (B) rhodo-; (C) oxorhodo-; (D) phyllo- type
Fig. 2.4  
(A) Resonance structure of free base porphyrin. The heavy bonds indicate the 18-membered cyclic polyene.  
(B) Resonance structure for metalloporphyrin.
Fig. 2.5  Atomic Orbital structure of porphyrin HOMO and LUMO orbitals in $D_{4h}$ and $D_{2h}$ symmetry point groups. The orbital coefficients are proportional to the size of the circles. Opened and filled circles indicate sign of the orbitals. Lines indicate the symmetry nodes.
Fig. 2.6 Illustration of various light scattering processes
Fig. 2.7 Raman scattering geometry. An electric vector $E$ lying in the $XZ$ plane characterizes light propagating along the $Y$ direction. Scattered radiation is detected along the $Z$ direction. Conventional scattering experiment has $\theta = 90^\circ$. 

\[ \rho_t = \frac{I_y}{I_x} \]