PART I

INVESTIGATION ON THE SPECTROSCOPIC PROPERTIES OF SOME ORGANIC COMPOUNDS

CHAPTER 1

INTRODUCTION

1.1 General

During the last two and a half decades the spectra of organic molecules in different states have been extensively studied to have a more complete understanding of intermolecular as well as intramolecular properties. Particularly, spectroscopic studies of molecules of biological interest have been accelerated in recent years to understand them and their interaction forces which exist within and between molecules of a particular shape in a given situation favourable for a particular biological activity. High speed computers have multiplied the progress greatly. Their use has helped to test theories involving complex calculations of molecular orbitals of large biomolecules. An understanding of the electronic properties of molecules depends on the large accumulation of experimental data. The development of intense UV light sources for absorption and emission studies, UV and visible spectrophotometers has made available more complete sets of experimental data which serve more accurate interpretations of many phenomena associated with the biomolecules concerned.

The present investigation is concerned with the electronic properties of some conjugated molecules (polyenes). The goal of this research is to collect the spectral data experimentally and to interpret the data within the framework of the existing theories. In order to achieve the data the already well established experimental techniques of UV and visible spectroscopy have been adopted.

There are two aspects of the spectroscopic properties of polyenes of current interest. One regarding the existence of a low-lying π-electronic forbidden state[1-4] (^1A_g) below the strongly allowed ^1B_u state in the near UV or visible region of the spectrum and the other is the possibility of formation of charge-transfer complexes[5-10] of these compounds with suitable donor or acceptor molecules.

Adequate interpretation of the spectral data of molecules in different phases rests on modern theories. The free-electron MO theory, LCAO MO theory, resonance force theory, theory of vibrational-electronic interactions and the theory of intermolecular charge-transfer interaction — all aided to interpret the electronic properties of polyene molecules and for explaining some experimental results. The outlines of the relevant parts of these theories are discussed in the following sections of this chapter.

1.2 The Free-Electron MO Theory

The molecular orbital (MO) theory assumes the electrons to be located in the delocalized orbitals. The orbitals of lowest energy for the electrons satisfying the Pauli's exclusion principle are referred to as the ground state of the molecule. An electron when raised from one of these filled orbitals to the other one empty in the ground state corresponds to an excited state.

The free-electron MO theory[11-23] is generally used for determining the allowed energies and state wave functions of the π-electrons in conjugated organic molecules. This theory is based on the assumption that there is a region in space in which the potential energy of an electron is finite and constant and is infinitely high outside this region. From the molecular point of view the electrons move freely along the length (l) of the conjugated system. Hence the problem of an electron in the conjugated system becomes one-dimensional and the wave equation of an electron in a one-dimensional potential is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{1.1}$$

The electron is assumed to move freely along the length of the molecule and hence $V = 0$. The solutions of the wave equation (1.1) after normalization with the boundary condition $0 \leq x \leq l$ satisfied are

$$\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \tag{1.2}$$

$$E_n = \frac{n^2 h^2}{8ml^2} \tag{1.3}$$

where n is an interger, m is the electron mass and h is Planck's constant.

The one-dimensional solutions (1.2) and (1.3) will serve as an approximation to the orbitals of a long linear conjugated polyene for example. Thus the MO theory in free-electron approximation gives a simple description of the electronic states of linear conjugated polyenes. A conjugated hydrocarbon of k double bonds contain 2k π-electrons. Each of k orbitals of the molecule in the ground state is occupied with two electrons. The first electronically excited state of the conjugated molecule is obtained from the corresponding ground state by raising an electron from the highest occupied orbital (n = k) to the lowest empty orbital (n = k + 1). Therefore, the energy of excitation, ΔE, is given by

$$\Delta E = E_{k+1} - E_k$$

$$= \frac{(2k+1)h^2}{8ml^2} \qquad (1.4)$$

or $$\lambda = \left(\frac{8mc}{h}\right)\frac{l^2}{2k+1} \qquad (1.5)$$

where the variables are only l and k. It is seen that λ varies as l^2. From the variation of l with the number of double bonds in the system,

$$l \propto (k+1) \qquad (1.6)$$

and from (1.5), $$\lambda \propto \frac{(k+1)^2}{2k+1} \qquad (1.7)$$

At large k, k + 1 $\approx$ k and hence

$$\lambda \propto k \qquad (1.8)$$

which indicates that the increase in length of a conjugated system increases the wavelength of absorption. From (1.8) it is understood that the free-electron method provides a semiquantitative relation between the length of the conjugated system and the wavelength of absorption. The wavelengths of other bands in the higher energy side of the absorption spectrum of the molecule can also be readily predicted by the free-electron MO method.

1.3 The LCAO MO Theory

The LCAO MO theory is based on the expectation that close to one atom of a molecule the influence of that atom will predominate and the molecular wave function will be similar to that of an atomic orbital. Consequently it seems natural to approximate the molecular orbitals as a linear combination of atomic orbitals. Each molecular orbital in the LCAO approximation[26,29-33] is regarded as the sum of various amounts of atomic orbitals. In this approximation the r th molecular orbital is written as

$$\Psi_r = \sum_j c_{rj}\, \phi_j \tag{1.9}$$

where ϕ_j is the j th atomic orbital and c_{rj} is a coefficient describing the amount of the j th atomic orbital to be found in the r th molecular orbital. These molecular orbitals are assumed to be eigenfunctions of an effective one-electron Hamiltonian for the equilibrium nuclear configuration of the molecule so that

$$H\Psi_r = E_r \Psi_r \tag{1.10}$$

The coefficients which correspond to stable molecular orbitals are to be considered. The orbital energies E_r and the coefficients c_{rj} can be evaluated by using the variation method if the matrix elements H_{ij} of the Hamiltonian and those, S_{ij} of overlap between the atomic orbitals are known. The secular equations are given by

$$\sum_j c_j (H_{ij} - E S_{ij}) = 0 \quad , \text{ for each } i \tag{1.11}$$

For n atomic orbitals in the expression (1.9) for the molecular orbitals there will be n secular equations of this type. The solutions of these secular equations will be non-trivial only if the n th order secular determinant vanishes :

$$| H_{ij} - E S_{ij} | = 0 \tag{1.12}$$

If this secular determinantal equation is expanded and solved, this will yield n solutions for the orbital energy E. If each of these solutions for E is substituted back into the secular equations, the coefficients c of the atomic orbital in the molecular orbital can be obtained.

Let us write for convenience

$$\alpha_i = H_{ii} \tag{1.13}$$

$$\beta_{ij} = H_{ij} = H_{ji} \quad (i \neq j) \tag{1.14}$$

Here α_i is the Coulomb integral of the atomic orbital ϕ_i. This integral represents the Coulomb energy of an electron in the atomic orbital ϕ_i. β_{ij} is the resonance integral between the atomic orbitals ϕ_i and ϕ_j and it amounts to the energy of interaction of the two atomic orbitals. Both these integrals α and β correspond to negative energy. If it is assumed that all the atomic orbitals are normalized, the secular equations (1.11) can be written in terms of α and β as

$$\sum_{j \neq i} c_j (\beta_{ij} - E S_{ij}) + c_i(\alpha_i - E) = 0 \quad \text{for each } i \qquad (1.15)$$

It is known that the absorption spectra of hydrocarbons are due to transitions of the π-electrons. The approximations to these secular equations for these π-orbitals, called the Hückel approximations[34-37] are the following :

(1) The Coulomb integrals α_i are taken to be the same for each atomic orbital and this is represented by α.

(2) All the overlap integrals S_{ij} are assumed to be zero for $i \neq j$.

(3) The resonance integrals β_{ij} are considered to be nonzero only between neighbouring atoms. So $\beta_{ij} \neq 0$ if atom i is bonded to j atom ($i \rightarrow j$).

(4) All the resonance integrals for neighbouring carbon atoms are assumed to be equal and are denoted by β.

With the above Hückel approximations the secular equation (1.15) becomes

$$\sum_{j \rightarrow i} c_j \beta + c_i(\alpha - E) = 0, \quad \text{for each } i \qquad (1.16)$$

On writing $v = \frac{\alpha - E}{\beta}$, the secular equations (1.16) reduce to

$$\sum_{j \to i} c_j + v c_i = 0 \qquad \text{for each } i \qquad (1.17)$$

Corresponding to the secular equations (1.17), the secular determinant becomes simple : the diagonal elements are v and the off-diagonal elements of row i, column j are 1 if atom i is bonded to atom j, otherwise the off-diagonal elements are zero. Thus the secular determinant for any conjugated π-system wholly of carbon π-centers can be built up. For the linear conjugated π-system, the energies of the Hückel molecular orbitals, v and the coefficients of the carbon $2p\pi$ atomic orbitals in the Hückel molecular orbitals, c, can be expressed in the analytic forms[33] as :

$$v_r = -2 \cos \frac{r\pi}{n+1} \quad , \quad r = 1, 2 \cdots n \qquad (1.18)$$

$$c_{ij} = \left(\frac{2}{n+1} \right)^{\frac{1}{2}} \sin \frac{jr\pi}{n+1} \qquad (1.19)$$

where r signifies the molecular orbitals. The carbon π-centers are numbered as 1,2 .... n from one end of the carbon chain and c_{rj} is the coefficient of j th carbon atom in the r th MO, Ψ_r . Substitution of (1.19) in (1.9) gives

$$\Psi_r = \left(\frac{2}{n+1} \right)^{\frac{1}{2}} \sum_{j=1}^{n} \sin \frac{jr\pi}{n+1} \, \phi_j \qquad (1.20)$$

where the linear conjugated system contains n carbon atoms. The energy corresponding to ψ_r is

$$E_r = \alpha + 2\beta \cos \frac{r\pi}{n+1} \qquad (1.21)$$

The electronic transition from the highest bonding MO to the lowest antibonding MO gives rise to the first absorption band of the conjugated polyene molecule and the corresponding transition energy is given by

$$\Delta E = 4 \sin \frac{\pi}{2(n+1)} \qquad (1.22)$$

which is in units of $-\beta$. It can be said that for a constant value of $-\beta$ the transition energy decreases as the length of the conjugated polyene chain increases. Since for small angles $\sin\theta \sim \theta$, this simple LCAO MO theory predicts that for a long polyene molecule the wavelength λ_{max} of the first absorption band will be proportional to n, which is evident from (1.22), and will increase to infinity as the length of the conjugated chain increases to infinity. In the preceding section also the MO theory in free-electron approximation predicts for the energy of the transition to the lowest excited electronic state a similar relationship with the length of the conjugated polyene molecules.

1.4 The Resonance Force Theory

One of the basic problems in the application of quantum mechanics to spectroscopic problems is the selection of proper zero-order wave functions - that is, the choice of basic sets that allow one to obtain directly a reasonable picture of the electronic structure of the molecule in question. For many π-electron systems approaches based on delocalization of electrons such as the LCAO (Hückel) molecular orbital and the free-electron (FE) model have been successful. But these theories show some discrepancies with the experimental results of the polyene. For such molecules the molecular orbital theory both in FE and LCAO approximations discussed earlier predicts that the energy of the lowest excited electronic state approaches that of the ground state as the length of the chain increases. Experimentally this was not found to be so. The energy of the lowest allowed transition of long polyenes appears to have a non-zero limit. However, it has now been shown on theoretical grounds[33-41] that the assumption of equal bond lengths for longer polyenes is incorrect. An alternation of bond lengths, long and short, will always occur if the conjugated system (polyene) is long enough[42]. In the molecular orbital theory electrons are assigned to orbitals delocalized over the whole molecule. According to this theory the low-lying electronic excited states will have an electron raised from one of the bonding molecular orbitals to one of the antibonding set. This simple description of the excited states fails to take account of some important features for long molecules. Although it does predict a nonzero limit for long molecules, it does not necessarily give correct description of the lowest group of excited states. It has been suggested, however, that in situations where one can write only one plausible low energy ground state structure for a molecule, one should consider not delocalization of electrons, but rather delocalization of excitation, in approaching the low-lying excited states[43], a point of view, which has led to the "resonance force model" for such molecules. The resonance force model[44] of describing the excited states of polyenes treats the molecule as an assembly of ~~e~~ ethylene-type units, each with two π-electrons in which exchange forces between the double bonds are omitted, only the electrostatic interaction being considered. The Hamiltonian matrix between the states of the n double bonds is similar to the Hückel matrix for an n-atom chain; the Hückel α is replaced by the ethylene transition energy E_v and β is replaced by Γ, the interaction integral. The eigenvalues of this matrix can be taken from the Hückel problem (1.21)

$$E_r(n) = E_v + 2\,\Gamma \cos\frac{r\pi}{n+1} \qquad (1.23)$$

The resonance force approach has been applied with success in the interpretation of the spectra of polyenes[44].

1.5 The Theory of Vibrational-Electronic Interactions

The intensity of an optical (electric dipole) transition is proportional to the square of the transition moment between the initial and final states. The transition moment between two states i and j is

$$\vec{M}_{ij} = \int \Psi_i(x,X)\, \vec{M}(x,X)\, \Psi_j(x,X)\, dx\, dX \qquad (1.24)$$

where $\Psi_i(x,X)$ and $\Psi_j(x,X)$ are exact solutions of the

Schroedinger equation for the complete Hamiltonian. The collective coordinate symbols x and X form a complete set of internal coordinates and locate respectively all of the electrons and nuclei. $\vec{M}(x,X)$ is the dipole moment operator

$$\vec{M}(x,X) = e\sum_i \vec{r}_i - e\sum_\sigma Z_\sigma \vec{R}_\sigma \qquad (1.25)$$

where $\vec{r}_i$ and $\vec{R}_\sigma$ are the position vectors of the i th electron and σ th nucleus respectively.

In polyatomic molecules exact solutions are not known since the equations of motion of three or more interacting particles cannot be solved. The Born-Oppenheimer approximation[45] is used to obtain a simplification of the mathematical description of the system. This procedure separates the electronic and nuclear motions. The adiabatic wavefunctions are usually further simplified by fixing the nuclear coordinates which appear as parameters in the electronic wavefunctions. Thus the zeroth-order vibronic wavefunction for the μ th vibrational level of the i th electronic state can be written as the product function

$$\Psi_{i\mu}(x,X) = \Psi_i(x,X_0)\,\chi_{i\mu}(X) \qquad (1.26)$$

where $\Psi_i(x,X)$ is a solution of the electronic Schroedinger equation for the equilibrium nuclear configuration X_0 and $\chi_{i\mu}(X)$ is the vibrational wavefunction.

Since most information concerning the nuclear motions of polyatomic molecules relates to the ground state, it is convenient to express the nuclear coordinates X in terms of a complete set of normal coordinates Q for that state. The normal coordinates completely span the space of infinitesimal nuclear displacements. With appropriate choice of origin, the electronic wavefunctions belonging to the excited electronic states may be expressed in terms of the ground state Q . Thus the vibronic wavefunction for μ quanta of any normal mode in the k th excited electronic state is

$$\Psi_{k\mu}(x,Q) = \Psi_k(x,Q_0)\,\chi_{k\mu}(Q,\Delta) \qquad (1.27)$$

where the general displacement vector Δ accounts for the difference in the equilibrium geometry between the ground and excited electronic states.

The number of molecules in a state with energy ΔE greater than the lowest energy state is given by the Boltzmann distribution factor $\exp(-\Delta E/kT)$ so that, at very low temperatures, only the zeroth vibrational level of the ground state will be populated. The probability of the transition from the zeroth vibrational level of the ground state to the μ th vibrational level of the k th excited state is proportional to the square of the transition moment

$$\vec{M}_{00,k\mu} = \int \Psi_0(x,Q_0)\,\chi_{00}(Q)\left\{e\sum_i \vec{r}_i - e\sum_\sigma Z_\sigma \vec{R}_\sigma\right\}\Psi_k(x,Q_0)\,\chi_{k\mu}(Q,\Delta)\,dx\,dQ$$

$$= \vec{M}_{0k}(Q_0)\int \chi_{00}(Q)\,\chi_{k\mu}(Q,\Delta)\,dQ$$

where

$$\vec{M}_{0K}(Q_0) = \int \Psi_0(x, Q_0)\,\vec{M}(x)\,\Psi_K(x, Q_0)\,dx \qquad (1.28)$$

and $\int \chi_{00}(Q)\,\chi_{K\mu}(Q, A)\,dQ$

is the Franck-Condon overlap factor. The contribution from the operator $e\sum_{\sigma} Z_{\sigma}\vec{R}_{\sigma}$ vanishes in the integration over the electronic coordinates.

Equation (1.28) accounts for a number of features of a vibronic transition. The vector $\vec{M}_{0K}(Q_0)$ has a definite orientation in relation to the molecular skeleton and therefore predicts the polarization of the transition. Group theoretical[46] considerations classify the transition as symmetry allowed or forbidden. The electronic transition is said to be electric dipole allowed if the decomposition of the direct product of the irreducible representations of $\Psi_0(x, Q_0)$, $\vec{r}_i$, and $\Psi_K(x, Q_0)$ contains the totally symmetric representation of the point group. Otherwise $\vec{M}_{0K}(Q)$ vanishes and the transition is symmetry forbidden.

Experimental evidence shows that the transition moment as defined in equation (1.28) does not give an adequate account of vibronic spectra. The classic example is the weak benzene absorption system at 2600Å which is symmetry forbidden and shows a progression in totally symmetric vibrations built upon single quanta of non-totally symmetric vibrations which act as "false origins"[47]. A theoretical treatment to account for the appearance of these 'forbidden' components in the transitions of polyatomic molecules by vibronic mixing was formulated by Herzberg and Teller[48]. The theory has been refined and extended by Liehr[49], Murrell and Pople[50], Craig[51], Albrecht[52] and Yeranos[53].

The basis of the Herzberg-Teller theory is to express the dependence of the electronic Schroedinger equation on the motion of the nuclei as a perturbation. The electronic Hamiltonian is expanded as a power series in the normal coordinates Q_q about the equilibrium position of the ground state as

$$H(Q) = H_0 + \sum_q \left(\frac{\partial H}{\partial Q_q} \right)_0 Q_q + \cdots \qquad (1.29)$$

where H_0 is the Hamiltonian for the equilibrium nuclear configuration and the perturbation is $\sum_q \left(\frac{\partial H}{\partial Q_q} \right)_0 Q_q$. The perturbed electronic wavefunction $\Psi_{K\mu}(x, Q)$ is then expressed in the basis of the unperturbed wavefunctions $\Psi^0_{K,\mu}(x,Q) \equiv \Psi^0_{K\mu}$ as the linear combination

$$\Psi_{K\mu}(x,Q) = \Psi^0_{K\mu} + \sum_{l \neq K} \lambda_{Kl} \Psi^0_{l0} \qquad (1.30)$$

where $$(E^0_l - E^0_K) \lambda_{Kl} = \int \Psi^0_{K\mu} \left(\frac{\partial H}{\partial Q_q} \right)_0 Q_q \Psi^0_{l0} \, dx \, dQ_q \qquad (1.31)$$

$$= \int \Psi^0_K \left(\frac{\partial H}{\partial Q_q} \right)_0 \Psi^0_l \, dx \int \chi_{K\mu} Q_q \chi_{l0} \, dQ$$

The ground state is assumed not to mix with excited states since the value of $E^0_K - E^0_0$ is very large (usually greater than 20,000 cm^{-1}).

The transition moment corrected to first order in small displacements is then

$$\vec{M}_{00,\kappa\mu} = \vec{M}_{0\kappa}(Q_0)\int \chi_{00}(Q)\chi_{\kappa\mu}(Q,\Delta)\,dQ + \sum_{\lambda \neq \kappa} \vec{M}_{0\lambda}(Q_0)\int \chi_{00}(Q)\,\lambda_{\kappa\lambda}\chi_{\lambda 0}(Q,\Delta)\,dQ$$

where

$$\vec{M}_{0\lambda}(Q_0) = \int \Psi_0^0\, M(x)\, \Psi_\lambda^0\, dx \qquad (1.32)$$

The first term in the equation representing the 'allowed' part of the transition moment integral has already been discussed. The 'forbidden' term is polarized according to the sense of $\vec{M}_{0\lambda}(Q_0)$.

The condition for the non-vanishing of the nuclear dependent or forbidden term in the transition moment expression is that $\vec{M}_{0\lambda}$ and $\lambda_{\kappa\lambda}$ must be nonzero for at least one state λ. For finite $\vec{M}_{0\lambda}$, the direct product of the irreducible representations $\Gamma(\Psi_0^0)$, $\Gamma(\sum\vec{r}_i)$, $\Gamma(\Psi_\lambda^0)$ must contain the totally symmetric representation of the point group of the molecule. For finite $\lambda_{\kappa\lambda}$ the direct products of $\Gamma(\Psi_\kappa^0)$, $\Gamma(\frac{\partial H}{\partial Q_q})_0$, $\Gamma(\Psi_\lambda^0)$ and $\Gamma(\chi_{\kappa\mu})$, $\Gamma(Q_q)$, $\Gamma(\chi_{\lambda 0})$ must simultaneously contain the totally symmetric representation. These requirements imply that

$$\Gamma(\Psi_\kappa^0) \times \Gamma\left(\frac{\partial H}{\partial Q_q}\right)_0 = \Gamma(\Psi_\lambda^0) = \Gamma\left(\sum \vec{r}_i\right) \qquad (1.33)$$

Further, since the Hamiltonian is invariant to operations of the point group of the molecule, $(\frac{\partial H}{\partial Q_q})_0$ has the same symmetry properties in electron space that Q_μ has in nuclear space. In equation (1.33), $\Gamma(\psi_k^0)$ and $\Gamma(\psi_l^0)$ are specified, and $\Gamma\left(\frac{\partial H}{\partial a_q}\right)_0$ can be determined. This is equivalent to specifying the type of vibration that can mix the electronic state ψ_l^0 with ψ_k^0.

A quantitative treatment of the vibrational borrowing via the 606 and 1595 cm^{-1} e_{2g} vibrations between the allowed $^1E_{2u}$ (1800Å) electronic state and the forbidden $^1B_{2u}$ (2650Å) and $^1B_{1u}$ (2000Å) electronic states of benzene has been made[50]. The calculation involves an evaluation of λ_{kl}. The term in H which depends on both the electrons i and the nuclei σ is

$$\sum_i \sum_\sigma \frac{Z_\sigma e^2}{\vec{r}_{i\sigma}} \tag{1.34}$$

and therefore

$$\begin{aligned}\frac{\partial H}{\partial a_q} &= \sum_{i=1}^{N} \left\{ \sum_\sigma Z_\sigma e^2 \, \frac{\partial \vec{r}_\sigma}{\partial a_q} \cdot \frac{\vec{r}_{i\sigma}}{r_{i\sigma}^3} \right\} \\ &= \sum_{i=1}^{N} h_i \end{aligned} \tag{1.35}$$

where $\vec{r}_\sigma$ is the position vector of nucleus σ. The nuclear displacements in the normal modes are thus represented by the set of dipoles $ez_\sigma \frac{\partial \vec{r}_\sigma}{\partial a_q}$ interacting with electrons i. Since equation (1.35) is the sum of one electron operators h_i the calculation of the integral in (1.31) reduces to the integration of $\sum_{i=1}^{N} h_i$ with the transition density,

$$\rho_{kl} = \int \psi_k^0 \, \psi_l^0 \, dx' \tag{1.36}$$

The results of the calculation[31] show that the $^1E_{1u}$ state is mixed most effectively with the $^1B_{2u}$ state by the 606 cm^{-1} vibration and with the $^1B_{1u}$ state by the 1596 cm^{-1} vibration.

1.6 The Franck-Condon Principle

The intensity distribution of an electronic transition among its vibrational members is determined by the Franck-Condon principle, which states that the nuclear positions and velocities do not change during an electronic transition. That is, the starting configuration in the new electronic state represents a displacement from the new equilibrium nuclear configuration without change of symmetry. If the displacement of the equilibrium nuclear configuration is zero ($\Delta = 0$) and if the potential energy surfaces have the same shape in both electronic states, then all the intensity is concentrated in the (0-0) band. If the displacement is non-zero ($\Delta \neq 0$), transitions to higher vibronic states become more probable. The steepness of the potential energy curve in the excited state determines the number of excited state vibrational wavefunctions $\chi_{i\mu}(\alpha, \Delta)$ which will have appreciable overlap with the ground state vibrational wavefunctions $\chi_{00}(\alpha)$ and therefore the length of the progression in an electronic transition.

A number of quantitative applications of the Franck-Condon principle have been made. From a knowledge of the intensity distribution in the benzene band system at 2650Å and the vibrations active in forming the progression (ground state, 992 cm^{-1}, excited state, 923 cm^{-1}), the extension of the C-C bond length of benzene in the excited state was calculated to be 0.036Å [51]. The lowest benzene triplet state C-C bond length extension relative to the ground state was calculated to be 0.036Å [54] as well. The intensity distribution among the vibrational members of a transition has been calculated from the changes in geometry, the frequencies and the corresponding normal modes of the relevent vibrations in the progressions[55-58].

1.7 Intermolecular Charge-Transfer Complex

A loose reversible association of two or more distinct chemical components is called a complex. Charge-transfer complex (donor-acceptor complex) is formed between an electron donor and an electron acceptor. The acceptor and the donor may in general be molecules, molecule-ions, atoms or atom-ions, with the restriction that they are both in their totally symmetric ground states. The complex is characterized by a new absorption band called the charge-transfer (CT) band. This CT band is absent in the components of the complex. The complex exists in two states, a ground state and an excited state. In the ground state, the donor and the acceptor experience the normal physical forces one would expect from the two components in close proximity i.e., van der Waals forces etc. and in addition a small amount of charge is transferred from the donor to the acceptor which contributes some additional binding energy to the complex. The excited state is promoted when the ground state complex absorbs light of suitable energy. Mulliken[59-64] and other workers[65-67] have explained quantum mechanically the formation of charge-transfer complexes and their approach is of the valence bond type. Mulliken's valence-bond description provides a very adequate explanation of the characteristic electronic absorption in terms of an intermolecular charge-transfer transition.

According to Mulliken, the ground state of the complex has a wavefunction Ψ_N which is hybrid of two wavefunctions $\Psi_{(A,D)}$ and $\Psi_{(A^-D^+)}$. Here $\Psi_{(A,D)}$ is the no-bond function and is the wavefunction of the donor and the acceptor in close proximity with no charge transfer between them. However it can include contributions from classical electrostatic forces, van der Waals forces and various dispersion forces and dipole interactions. $\Psi_{(A^-D^+)}$ is called the dative function and is the wavefunction of the two components bound together by an electron being totally transferred from the donor D to the acceptor A.

The ground state of the complex is described by

$$\Psi_N = a\,\Psi_{(A,D)} + b\,\Psi_{(A^-D^+)} \quad \text{where } a \gg b \qquad (1.37)$$

The excited state of the complex is described by

$$\Psi_E = b^*\,\Psi_{(A^-D^+)} - a^*\,\Psi_{(A,D)} \quad \text{where } b^* \gg a^* \qquad (1.38)$$

The energy levels of the complex can be found by solving the Schroedinger equation

$$H\,\Psi_N = W\,\Psi_N \qquad (1.39)$$

where H is the Hamiltonian operator and W is the energy. The difference between the two states (i.e., W_E and W_N) of the complex gives the energy (E_{CT}) of the charge-transfer transition and the solution of the equation (1.39) leads to an equation[68,69] for this energy :

$$E_{CT} = h\nu_{CT} = I_D^v - E_A^v + C_1 + \frac{C_2}{I_D^v - E_A^v + C_1} \qquad (1.40)$$

where ν_{CT} is the frequency corresponding to the intermolecular charge-transfer transition (lowest energy), I_D^v is the vertical ionization potential of the donor, E_A^v is the vertical electron affinity of the acceptor and C_1 and C_2 are constants. The last term is often small, so that its variation can be neglected, giving the equation

$$h\nu_{CT} = I_D^v - E_A^v + C_1 \qquad (1.41)$$

The above discussion from valence bond approach for the understanding of CT complex is useful in case of weak complexes. The formation of CT complex can also be explained in terms of simple molecular orbital (MO) treatment[70-79]. Here the complex is one to be formed by interaction between molecular orbitals of the donor and those of acceptor. This treatment leads to the conclusions similar to those given by the valence bond approach but the MO method seems better in that it gives satisfactory explanation of more than one intermolecular CT band in a complex often observed[80-87]. There should be bands corresponding to transitions between any of the occupied orbitals of the donor and the empty orbitals of the acceptor. In the MO method, the interaction between the highest occupied orbital of the donor and the lowest empty orbital of the acceptor is in general considered. Due to the interaction the donor orbital is depressed and the empty orbital of the acceptor is raised and the whole system becomes stabilized with a simultaneous transfer of electron from the donor to the acceptor.

References

1. B.S. Hudson and B.E. Kohler, Chem. Phys. Letters, **14**, 299 (1972).
2. K. Schulten and M. Karplus, Chem. Phys. Letters, **14**, 305 (1972).
3. K. Mandal and T.N. Misra, Chem. Phys. Letters, **27**, 57 (1974).
4. R.M. Gavin, Jr., C. Weisman, J.K. McVey and S.A. Rice, J. Chem. Phys., **68**, 522 (1978).
5. J.R. Platt, Science, **129**, 372 (1959).
6. M.A. Slifkin, Charge-Transfer Interactions of Biomolecules (Academic Press, London and New York, 1971) p 195.
7. B. Pullman and A. Pullman, Quantum Biochemistry (Interscience Publishers, New York, 1963) p 440.
8. F.U. Lichti and J.A. Lucy, Biochem. J., **112**, 221 (1969).
9. J.A. Lucy and U.F. Lichti, Biochem. J., **112**, 231 (1969).
10. J.A. Lucy, Am. J. Clin. Nut., **22**, 1033 (1969).
11. N.S. Bayliss, J. Chem. Phys., **16**, 287 (1948).
12. N.S. Bayliss, J. Chem. Phys., **17**, 1353 (1949).
13. N.S. Bayliss, Australian J. Sci., **12**, 12 (1949).
14. N.S. Bayliss, Quart. Rev. Chem. Soc., **6**, 319 (1952).
15. H. Kuhn, Helv. Chim. Acta., **31**, 1441 (1948).
16. H. Kuhn, Helv. Chim. Acta., **32**, 2247 (1949).
17. H. Kuhn, J. Chem. Phys., **16**, 840 (1948).
18. H. Kuhn, J. Chem. Phys., **17**, 1198 (1949).
19. H. Kuhn, Chimica, **4**, 203 (1950).
20. J.R. Platt, J. Chem. Phys., **17**, 484 (1949).
21. J.R. Platt, J. Chem. Phys., **21**, 1597 (1953).
22. W.T. Simpson, J. Chem. Phys., **16**, 1124 (1948).
23. W.T. Simpson, J. Chem. Phys., **17**, 1218 (1949).

24. K. Rudenberg and C.W. Scherr, J. Chem. Phys., 21, 1565 (1953).

25. C.W. Scherr, J. Chem. Phys., 21, 1582 (1953).

26. J.N. Murrell, The Theory of the Electronic Spectra of Organic Molecules (Chapman and Hall Ltd., London, 1971).

27. H.H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy (John Wiley and Sons, Inc., New York and London, 1962).

28. J.R. Platt, Radiation Biology, edited by A. Hollaender (McGraw-Hill, New York, 1956) p 71.

29. R.S. Mulliken, J. Chem. Phys., 7, 14 (1939).

30. R.S. Mulliken, J. Chem. Phys., 7, 364 (1939).

31. C.C.J. Roothaan, Revs. Mod. Phys., 23, 69 (1951).

32. H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules (Academic Press, New York and London, 1967).

33. A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists (John Wiley and Sons, Inc., New York and London, 1961).

34. E. Huckel, Z. Physik, 70, 204 (1931).

35. E. Huckel, Z. Physik, 72, 310 (1931).

36. E. Huckel, Z. Physik, 76, 628 (1932).

37. E. Huckel, Z. Physik, 83, 632 (1933).

38. C.A. Coulson, Proc. Roy. Soc. (London), A 169, 413 (1939).

39. H. Labhart, J. Chem. Phys., 27, 957 (1957).

40. Y. Ooshika, J. Phys. Soc. Japan, 12, 1238 (1957).

41. Y. Ooshika, J. Phys. Soc. Japan, 12, 1246 (1957).

42. H.C. Longuet-Higgins and L. Salem, Proc. Roy. Soc., A251, 172(1959).

43. W.T. Simpson, J. Am. Chem. Soc., 78, 3585 (1956).

44. W.T. Simpson, J. Am. Chem. Soc., **73**, 5363 (1951).

45. M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, London and New York, 1954).

46. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, New York, 1964).

47. F.M. Garforth, C.K. Ingold and H.G. Poole, J. Chem. Soc., 406(1948).

48. G. Herzberg and E. Teller, Z. Physik Chim., **B21**, 410 (1933).

49. A.D. Liehr, Z. Naturforsch, **13a**, 311 (1958).

50. J.N. Murrell and J.A. Pople, Proc. Phys. Soc. (London), **A69**, 245 (1956).

51. D.P. Craig, J. Chem. Soc., 59 (1950).

52. A.C. Albrecht, J. Chem. Phys., **33**, 156 (1960).

53. W.A. Yeranos, Z. Naturforsch, **22a**, 183 (1967).

54. A. Grabowska, J. Mol. Spectrosc., **20**, 96 (1966).

55. E.F. McCoy and I.G. Ross, Aust. J. Chem., **15**, 573 (1962).

56. J.B. Coon, R.E. de Wames and C.M. Lloyd, J. Mol. Spectrosc., **8**, 285 (1962).

57. K. Miller and J.N. Murrell, Theoret. Chim. Acta (Berl.), **2**, 231(1965).

58. K. Miller and J.N. Murrell, Theoret. Chim. Acta (Berl.), **7**, 69 (1967).

59. R.S. Mulliken, J. Am. Chem. Soc., **72**, 600 (1950).

60. R.S. Mulliken, J. Am. Chem. Soc., **74**, 811 (1952).

61. R.S. Mulliken, J. Phys. Chem., **56**, 801 (1952).

62. R.S. Mulliken, J. Chem. Phys., **51**, 341 (1964).

63. R.S. Mulliken, J. Chem. Phys., **23**, 397 (1955).

64. R.S. Mulliken, J. Chem. Phys., **61**, 20 (1964).

65. S.P. McGlynn, Chem. Rev., **58**, 1113 (1958).

66. G. Briegleb, Elektronen-Donator-Acceptor-Komplexe (Springer-Verlag, Berlin, 1961).

67. W.B. Person and R.S. Mulliken, A. Rev. Phys. Chem., 13, 107 (1962).

68. M.A. Slifkin, Charge-Transfer Interactions of Biomolecules (Academic Press, London and New York, 1971) p 4.

69. E.C.M. Chen and W.E. Wentworth, J.Chem.Phys., 63, 3183 (1975).

70. M.J.S. Dewar and A.R. Lepley, J. Am. Chem. Soc., 83, 4560 (1961).

71. M.J.S. Dewar and H. Rogers, J. Am. Chem. Soc., 84, 395 (1962).

72. A.R. Lepley, J.Am. Chem. Soc., 84, 3577 (1962).

73. A.R. Lepley, J. Am. Chem. Soc., 86, 2545 (1964).

74. A.R. Lepley, Tetrahedron Letters, 2823 (1964).

75. A.R. Lepley and C.C. Thomson, Jr., J.Am.Chem. Soc., 89, 5523(1967).

76. J.N. Murrell, J. Am. Chem. Soc., 81, 5037 (1959).

77. K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, Bull. Chem. Soc. Japan, 34, 1076 (1961).

78. K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, Bull. Chem. Soc. Japan, 35, 33 (1962).

79. R.L. Flurry, Jr., J. Phys. Chem., 69, 1927 (1965).

80. S. Iwata, J. Tanaka and S. Nagakura, J. Am. Chem. Soc., 89, 2813 (1967).

81. H. Kuroda, I. Ikemoto and H. Akamatu, Bull. Chem. Soc. Japan, 39, 1842 (1966).

82. H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, J. Chem. Phys., 36, 457 (1962).

83. L.E. Orgel, J. Chem. Phys., 23, 1352 (1955).

84. A. Bier, Rec. Trav. Chim. Pay-Bas, 75, 866 (1956).

85. R.E. Merrifield and W.D. Phillips, J. Am. Chem. Soc., 80, 2778 (1958).

86. A. Kuboyama, J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi), 81, 558 (1960).

87. G. Briegleb, J. Czekalla and G. Reuss, Z. Physik. Chem. N.F., 30, 316 (1961).