STUDIES ON SOME ASPECTS OF MOLECULAR COMPLEXES

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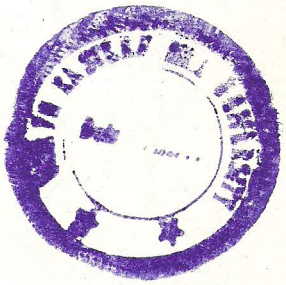

A THESIS
SUBMITTED IN FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG - 793001
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DECEMBER, 1983

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I certify that the thesis entitled, "Studies on Some Aspects of Molecular Complexes", submitted by Mr. Vinay P. Shedbalkar for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph. D. Degree. This work has not been submitted for any Degree of any other University.

Place: Shillong

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ACKNOWLEDGEMENT

I write this opening page only after completing and finalizing the other pages in this thesis. This gives me the opportunity to think back about myself. In the complex phenomena of "knowledge-transfer" I find myself a "small molecule" for whose present "property" many "higher molecules" have contributed continuously. I have drawn heavily on them and they have been my most formative "DONORS" with me as the "ACCEPTOR".

I aspire to spiral-up the pyramid of knowledge, but I cannot forget the many molecules at the base and at the progressively higher strata. I recall my gratitude to my teachers during my formative period at the primary school at Belgaum, specially Sri Deshpande, who tought me to think in terms of numbers and their manipulation, my teachers at college at Belgaum, and specially Sri Kausalgi who created in me the lasting interest in science.

Nearer at home, now in the land of eternal clouds, I cannot but remember Dr. S.N. Bhat who cleared the clouds of knowledge that had been shrouding me when I entered this

University. He untiringly trained me to see through the properties of charge-transfer, and made me worth contributing some iota to the vast knowledge of the phenomena, so intimate to him in his own untiring academic pursuit. It is my duty to be worthy to continue contribute to his organized research. Without his help and supervision it would have been difficult to complete the present work.

I shall be highly indebted to:

Professor T.S.B. Narasaraju, Professor H. Junjappa, Dr. Raj Kumar Poddar, Dr. J. Subramanian, Dr. K. Ismail, Dr. M.K. Chowdhuri Dr. M.P. Mahajan, Dr. O.K. Medhi and Dr. K.K. Dwivedi for their encouragement.

Dr. S. Mahiuddin, Mr. M.N. Bhattacharjee, Mr. Aseem Sinha, Mr. B.L. Marwein for their help and to Mr. Vijayan for excellent typing of the thesis.

Miss Bharati Bhattacharjee, Mr. Kaushik Bhattacharjee, Mr. Aka Moa Lemtur, Mr. Basab Chakravorti, Mr. K.P. Sharma, Miss Mitra Bhattacharjee and all other research colleagues whose co-operation has played an important role in completing this work.

The Administrative Staff, Library Staff and Mr. E.J. Philip for their best co-operation.

Late Dr. J.R. Bardoloi, Dr. Dev Sharma, Mr. Tufan Bardoloi and Lily aunty for providing me excellent accommodation during my stay in Shillong.

My family members, Mr. Ajeet Kolhapure and Capt. S. Srinath for their patience and encouragement at times when it was necessary.

Mrs. Bhat, Mrs. P.V. Bhide, Mrs. Usha Paranjape, Mrs. Poddar, Mrs. Subramanian, Mr and Mrs. Narayan Chakravorti, Mr and Mrs. Bahra, Mr. R. Sadhu, Tona, Kiran, Madhu, Nagesh, Deisy, Rosy, Primly, Dolly, Kong Nancy and little Kalpa due to whom I could get a family atmosphere in Shillong which made working here, a pleasure.

The University Grants Commission and the Council of Scientific and Industrial Research, New Delhi for financial support;

and

the people of this beautiful City - SHILLONG

Vinay P. Shedbalkar

C O N T E N T S

CHAPTER I

INTRODUCTION

In this chapter the general aspects of molecular complexes and some of the nonspectral methods which are of relevance to the studies reported in this thesis have been briefly reviewed.

I.1 MOLECULAR COMPLEXES

It has been well known for many years that when molecules, like aromatic hydrocarbons, amines, phenols, etc. are mixed with a large class of molecules like nitrocompounds, quinones, halogens, etc. in suitable solvents, the colour of the solutions change. When the solutions of the two such reagents are mixed, the profound change in colour clearly indicates the formation of a complex. The principal feature of the type of complex formation is the appearance of a new and intense absorption band in ultraviolet or visible region of the spectrum. Pfeiffer[1] who first classified these complexes suggested that the utilization of secondary valencies was involved in their formation.

When the molecules interact strongly, the molecules come very close to each other and the distance between the molecules will

be very small; this leads to the formation of new chemical entities and the 'chemical' (valence) forces are operative in such cases. The energies of such interaction are of the order of 200-400 KJ/Mole. The interaction occurring at large separation (i.e. weak interactions) are due to 'physical' (Van der Waal) forces and the energies of such interactions are of the order of a few KJ/Mole. This comprises of electrostatic (or coulombic), induction and dispersion energies. In between these two extremes of 'chemical' and 'physical' forces, there are forces which arise due to the interactions occurring at 'intermediate' separations. These are called 'charge-transfer' forces[2-5]. They are cohesive in nature and are an 'admixture' of the chemical and physical forces, whose contributions depend on the molecules taking part in the interaction. They are relatively stronger than physical forces but much weaker than chemical forces. Thus, they lead to the possibility of "graded" interaction between the molecules and the formation of "molecular complexes".

It is difficult to define precisely the term "molecular complex". However, according to Mulliken and Person[5,3], " A molecular complex between two unlike molecules is an 'association', somewhat stronger than ordinary Van der Waal interactions, of definite stoichiometry. The partners are often already closed-shell (saturated valence) electronic structures. In weak complexes, the identities of the original molecules are preserved to a large extent".

I.2 GENERAL FEATURES OF MOLECULAR COMPLEXES

Any theory of molecular complexes should explain satisfactorily the following general features of absorption spectra and energy changes associated with such complex formation[4].

(1) Generally, a new absorption band (due to the complex) is observed in ultraviolet or visible region of the spectrum. However, the absence of such band in the ultraviolet or visible region, does not necessarily mean that the complex does not exist.

(2) The broad absorption band suggests the loose nature of binding in the ground state of the complex. The λ max corresponds to the energy required to excite the electron from the most probable ground state to the excited state of the complex.

(3) The enthalpies of formation of molecular complexes are of the order of 5-75 KJ/Mole. This indicates the weak nature of binding in the ground state of the complex.

(4) The charge-transfer band is generally highly intense. The molar extinction coefficient of the complex can be as large as 10^4 dm^3 mol^{-1} m^{-1}.

(5) The intermolecular separation of the complex is much larger than normal ionic or co-valent bond lengths, but slightly smaller than the Van der Waal radii.

(6) The complex formation affects the charge-distribution, in the donors and acceptors to some extent. Thus, generally, the colour of iodine changes from violet to red or to brown as

the ability of donor to donate electron increases. At the same time, the position of iodine absorption maximum shifts to shorter wavelength (blue-shift). When an iodine molecule in the complex is excited, the promoted electrons of donor passes from a bonding (or non-bonding) orbital to an antibonding orbital of iodine. The result is an increase in the size of the molecule. Therefore, due to the exchange repulsion in the complex and iodine molecule, more energy is required to promote the electron. So, iodine absorption shifts to lower wavelength. The molar absorptivity coefficient of complexed iodine may increase or decrease.

(7) The complex formation invariably occurs between molecules of low ionization potential and high electron affinity. It has been found that for a given acceptor λ_{max} varies directly with the ionization potential of donors having similar structures.

(8) Generally, the donor, acceptor and complex differ in polarity.

(9) The charge-transfer band position depends on the nature of the medium/solvent.

An evaluation of the thermodynamic parameters of molecular complexes, such as change in enthalpy, $-\Delta H^\circ$, entropy, $-\Delta S^\circ$ and standard free energy, $-\Delta G^\circ$ occurring on complex formation, provides useful evidences regarding the nature and strength of the binding of the complex. These thermodynamic parameters are determined from a knowledge of the equilibrium constants of complex formation

at different temperatures[6]. In addition, one can also obtain useful information regarding the oscillator strength and the transition dipole moment of the charge-transfer bands[5].

I.3 MULLIKEN'S THEORY OF MOLECULAR COMPLEXES

Electron transfer theory has been developed along two separate lines, namely Mulliken's[5,7] charge-transfer theory and Hush's[8] intervelance transfer theory. The former deals with electronic effects and is related to transitions in the UV and visible region (and is related to formation of molecular complexes) whereas the latter one deals with vibrational effects and is related to transitions in the infrared region. Mulliken's theory mainly concentrates on electronic effects (and it neglects molecular structural changes after complexation and vibrational structure in the transition is ignored), whereas Hush's theory in its use of two displaced harmonic oscillators neglects electronic effects (and neglects Franck-Condon overlap factor). So, recently Ying-Nan Chlu[9] has developed a unified molecular charge-transfer theory which relates the two theories and includes all ranges of molecular interactions. This unified theory of molecular charge-transfer reduces to Mulliken's theory of charge-transfer molecular complexes when only strong electronic effects are considered and becomes Hush's theory of intervelance of charge-transfer when the vibrational effects are more predominant. Person[3], in his recent article has examined the general theory of intermolecular forces. The resonance structure theory

of molecular complexes which has been developed by Mulliken[5,7], has been generally accepted (for electronic transitions). We will summarize the salient aspects of Mulliken's theory of molecular complexes.

The interaction between an electron donor, D, and an electron acceptor, A, leading to the formation of a complex, DA (in the absence of any media), can be represented by the following resonance structures,

$$D + A \longleftrightarrow (D,A) \longleftrightarrow (D^{+}-A^{-}) \longleftrightarrow (D^{-}-A^{+})$$

I II III IV

The structure I is for molecules, when they are far apart and there is no interaction between the molecules. In structure II, the donor and acceptor are at equilibrium separation of the complex, but only 'physical forces' are operative between them and it is called 'no-bond' structure. The structures III and IV are the dative structures; in III, an electron is transferred from donor to acceptor and in IV, from acceptor to donor. In view of the electron donating and accepting tendencies of D and A, the contribution of the structure IV, can be neglected.

The wavefunction for the ground state of complex, ψ_N, can be expressed as a linear combination of the wavefunctions of the 'no-bond' structure, ψ_o, and the dative structure, ψ_1, neglecting the contribution of the ionic structure, $(D^{-}-A^{+})$

$$\psi_N = a^{x}\psi_o\,(D\ldots A) + b\,\psi_1\,(D^{+}-A^{-}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{I.1}$$

A corresponding excited state of the complex can be represented by the wavefunction, ψ_E.

$$\psi_E = a^* \psi_1 (D^+-A^-) - b^* \psi_o (D,A) \quad \ldots\ldots\ldots \text{I.2}$$

The difference in energy between the two states is equal to the energy of quantum at the maximum of the absorption band. The ratio, b^2/a^2 in the normal state represents the proportion in which the dative and no-bond structures contribute and can vary from zero for no electron transfer to infinity for complete electron transfer. The coefficients, a^* and b^* are nearly equal to a and b. The energies of complexes, in its ground state (W_N) and excited state (W_E) can be obtained by solving Schrödinger wave equations, using exact Hamiltonian operator (H) and the above wavefunctions which are normalized. For weak interactions the ground state energy, W_N and the excited state energy, W_E, may be obtained approximately by second order perturbation theory.

$$W_N = W_o - \frac{(H_{o1} - W_o \cdot S_{o1})^2}{(W_1 - W_o)} \quad \ldots\ldots\ldots\ldots \text{I.3}$$

and

$$W_E = W_1 + \frac{(H_{o1} - W_1 S_{o1})^2}{(W_1 - W_o)} \quad \ldots\ldots\ldots\ldots \text{I.4}$$

where

$$W_o = \int \psi_o H \psi_o \, d\psi$$

$$W_1 = \int \psi_1 H \psi_1 \, d\psi$$

$$W_{o1} = \int \psi_o H \psi_1 \, d\psi$$

$$S_{o1} = \int \psi_o \psi_1 \, d\psi$$

The difference in energy between these two states, i.e. between W_E and W_N, is equal to the energy of the quantum at the maximum

of the absorption band.

The schematic energy diagrams for spectra of molecular complexes are shown in Fig. I.1 and Fig. I.2. It can be seen from the figure I.1 that,

$$h\nu_{CT} = I_D - (E_A + E_c + W_o) + X_E - X_N \quad \text{..... I.5}$$

$$= I_D - E_A - \Delta \quad \text{..... I.6}$$

where I_D is the ionization potential of donor, E_A is the electron affinity of the acceptor, E_c is Coulombic energy between $D^+ + A^-$ and $D^- - A^+$, W_o is the no-bond energy, X_E and X_N are resonance energies of the excited and ground states,

$$\Delta = E_c + W_o - X_E + X_N$$

$$W_N = \Delta H = W_o + X_N$$

The term, charge-transfer absorption, thus is applicable to all absorptions associated with the transitions from the normal (ground) state to the excited state of the complex.

As it can be seen from the above equation, (I.6), charge-transfer energy $h\nu_{CT}$, increases with the ionization potential of the donors (for a particular acceptor) having similar structure. The energy associated with the charge-transfer transition is related to the I_D of the donor (for a particular acceptor) is given by $h\nu_{CT} = I_D - E_A - \Delta + [\beta^2/(I_D - E_A - \Delta)]$. In the case

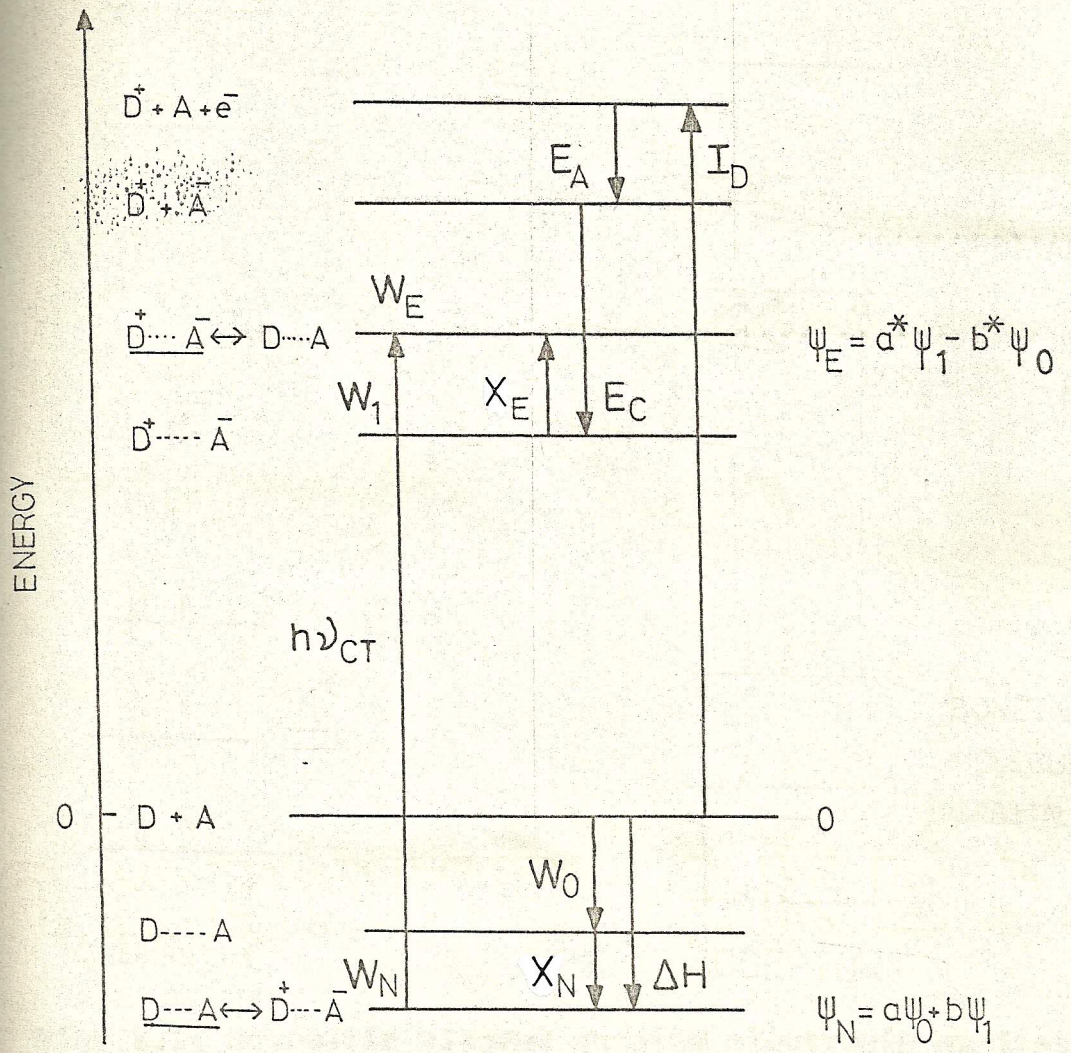

Fig. I.1 : Schematic energy level diagram showing various contributions.

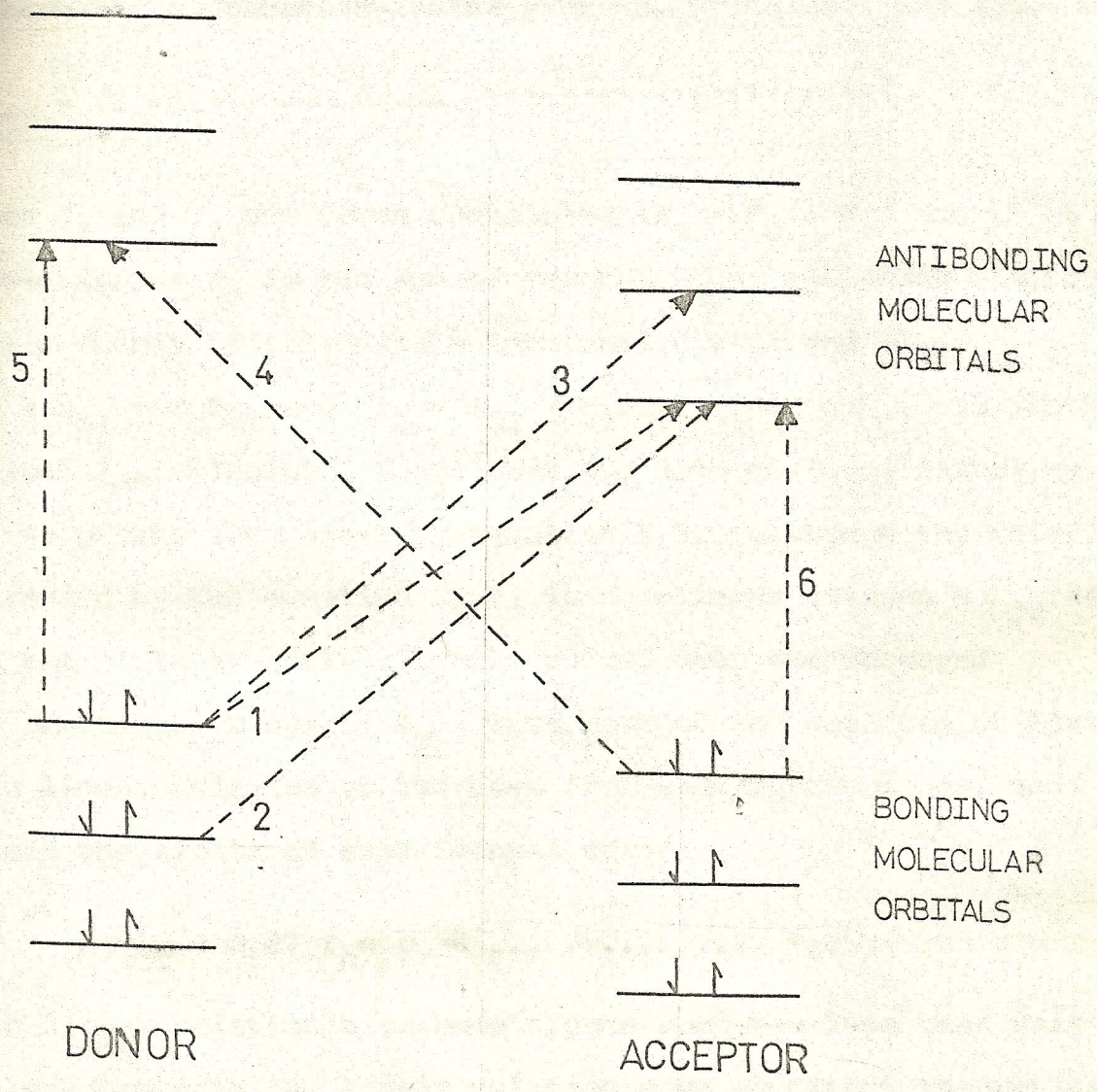

Fig. I.2: Schematic Diagram showing electronic excitations; (1) lowest energy CT band; (2) excitation from penultimate donor level; (3) excitation to higher empty acceptor level; (4) higher energy acceptor to donor CT band; (5) intramolecular donor excitation and; (6) intramolecular acceptor excitation.

of aromatic hydrocarbon-iodine systems, Briegleb[10] has shown that

$$h\nu_{CT} = (I_D - C_1) + \frac{C_2}{(I_D - C_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{I.7}$$

where C_1 and C_2 are terms containing $(E_A - E_c + W_o)$ and $(\beta_o^2 + \beta_1^2)$ respectively; W_o is the sum of several terms including electrostatic energy (dipole-dipole interaction, etc.) and $\beta_o = H_{o1} - W_o S_{o1}$ and $\beta_1 = H_{01} - W_1 S_{01}$. When $h\nu_{CT}$ was plotted against I_D, Briegleb[10] found that the data could be fitted by curves of the form given by equation I.7. Although, the relation expressed by the equation (I.7) is non-linear between $h\nu_{CT}$ and I_D, the plots are only slightly curved over the observed (or practical) range of I_D. Thus, most of the data can be fitted by a linear relation of the form (for weak I_2 complexes, and within the limits of experimental error)

$$h\nu_{CT} = 0.87\ I_D - 0.36 \quad \ldots\ldots\ldots\ldots\ldots \text{I.8}$$

Such linear relationships have slopes somewhat less than unity. The constants in the linear relation have no direct theoretical significance.

Amines do not fall in line with the $h\nu_{CT}$ Vs I_D relation [Eq. I.7] obeyed by weak I_2 complexes. Yada, Tanaka and Nagakura[11] have derived the following equation for such strong complexes.

$$(h\nu_{CT})^2 = \left[\frac{W_1 - W_o}{1 - S_{01}}\right]^2 \left[1 + \frac{4\beta_o \beta_1}{(W_1 - W_o)^2}\right] \quad \ldots\ldots \text{I.9}$$

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It is now realized that linearity between $h\nu_{CT}$ and I_D is not a universal rule[11-13], since with the change of donor, the other factors such as the overlap integral vary as well[12]. A number of workers have correlated $h\nu_{CT}$ values with I_D for the interaction of a related series of donors with an acceptor and the results of such correlations are summarized by Rao, Bhat and Dwivedi[14].

In the spectra, the band width is due to the loose coupling between the donor and acceptor components in the ground state of the complex. This loose coupling permits a continuous range of relative orientations of the two and therefore, generally causes a continuous variation in the energy of the ground state. The absorption maximum corresponds to the transition from the most probable ground state alignment of the donor and acceptor species.

The charge-transfer absorption depends on the transition probability and transition moment. The oscillator strength, f, for an electronic transition is given by,

$$f = \frac{2.303\ mc^2}{e^2 N_0} \int \epsilon_\nu \, d\nu$$

$$= 4.318 \times 10^{-9} \int \epsilon_\nu \, d\nu$$

$$= 4.32 \times 10^{-9} \cdot \epsilon_{max} \cdot \Delta\bar{\nu}_{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots \text{I.10}$$

where $\Delta\bar{\nu}_{\frac{1}{2}}$ is the width in cm^{-1} of the band between the two frequencies at which $\epsilon = (\frac{1}{2})\ \epsilon_{max}$. Here it must be noted that the accuracy of the approximation depends on the band shape.

The intensity of a charge-transfer band is proportional to the square of the transition moment, μ^2_{VN}. The oscillator strenth, f, and electronic transition dipole, μ_{VN}, are related by

$$f_{VN} = \left(\frac{8\pi^2 mc}{3b} \right) \bar{\nu} \left(\frac{\mu^2_{VN}}{c^2} \right) \quad \ldots\ldots\ldots \text{I.11}$$

$$\text{or } \mu_{VN} = 0.0958 \left[\frac{\int \epsilon d\nu}{\bar{\nu}} \right]^{1/2} \approx 0.0958 \left[\frac{\epsilon_{max.} \bar{\Delta\nu}_{1/2}}{\bar{\nu}} \right]^{1/2} \ldots\ldots \text{I.12}$$

There has been considerable discussion in literature about the role of charge-transfer to the ground state stabilities of molecular complexes (particularly in the case of weak molecular complexes). Mulliken's[5] theory has been quite successful in explaining the spectral characteristics of strong as well as weak molecular complexes. However, recent quantum chemical studies have suggested that many such complexes, especially weak complexes, are formed primarily due to 'electrostatic' or 'polarization' interactions[15-17]. Umeyama et al[18] have shown that the interaction energy of a complex, comprises of five components, electrostatic, which arises from multiple interactions between the molecules D and A (which may be attractive or repulsive); polarization, which is due to induced multiple interactions and higher order coupling (and is always attractive), exchange repulsion, which is the short range repulsion due to electron distribution of A with that of D; charge-transfer, which is due to charge-transfer from donor to acceptor (it is always attractive); and coupling energy, which accounts for higher order interactions. In addition to this, there is a contribution from correlation energy, both intra-molecular and intermolecular. A part of intermolecular

correlation energy is dispersion energy, which results from instantaneous polarization of D and A. As mentioned in the beginning, Chlu[9] had developed unified molecular charge-transfer theory which includes all ranges of molecular interactions in the limit of strong electronic effect (uv and visible region), it reduces to Mulliken's theory. It must be mentioned here, as pointed out by Person[3] that Mulliken's theory still holds good for whole range of molecular complexes, in the case of weak complexes, the no-bond structure, which comprises of above interactions, except charge-transfer, is the major contribution to the overall wavefunction of the ground state of the complex (a >> b), and hence to the ground state stability. So, the term[11] "molecular complex" rather "charge-transfer" or "electrostatic complex" seems to be reasonable to represent these systems.

After Mulliken's[5] valence bond approach for the study of molecular complexes, attempts were made to describe the donor-acceptor interaction by molecular orbital method and the perturbation theory is used to describe weak interactions namely, π-π and π-σ complexes[19-23]. The stability of the complex is due to the decrease in the potential energy of the system. But this perturbation method could not be applied for strong interactions[17]. Fukui[24] used linear combination of atomic orbitals of the donor and acceptor for representing the molecular orbital of the complex. Gur'yanova et al[19] briefly summarised the

applicability of VB and MO method for the study of interaction between molecules, and are of the opinion that both these methods are approximate and semiempirical and for describing the weak complexes, the Mulliken's VB method which is simple, is better, while the more modern MO method may be more suitable for describing complexes with stronger intermolecular bonds.

Since the intermolecular interaction is fairly weak, the original bond energies are slightly changed, leaving the absorption bands of donor and acceptor almost unchanged. In otherwords, the interaction energies in the ground state are small compared with the transition energies to the excited states of the complex, in particular the intermolecular charge-transfer excited state. Each such transition may be considered as arising from the transfer of an electron from a filled orbital of the donor to an empty orbital of the acceptor. The energy of this transition is given by,

$$\Delta E_{ij} = h\nu = A_j - D_i \quad \ldots\ldots\ldots \text{I.13}$$

where A_j and D_i are the energies of the j^{th} (lowest unoccupied orbital) and i^{th} (highest occupied) orbital. In aromatic hydrocarbons the energy of the highest occupied M.O. in the ground state may be expressed in a simple Hückel treatment, $D_i = \alpha + \beta x_i$, where α is the coulomb integral, β is the resonance integral and x_i is the Hückel parameter for this orbital.

The energy of the first transition band of the complex of such hydrocarbon donors with the given acceptor is given by,

$$h\nu_{CT} = A_j - D_i + P$$
$$= A_j - \alpha - \beta x_i + P \quad \ldots\ldots\ldots \text{I.14}$$

where P is an energy term which corresponds to a perturbation of the appropriate energy levels in the donor and acceptor. The applicability of this model was tested with tetracyanoethylene as acceptor and different aromatic hydrocarbons as donors[6].

I.4 CLASSIFICATION OF DONORS AND ACCEPTORS

Mulliken[5] has classified donors and acceptors of various types leading to the formation of molecular complexes of varying strengths, i.e., the energy of formation of molecular complex in the ground state (Table I.1). At one extreme, we have the strong Lewis acid - Lewis base addition compounds, and at the other, the weak "contact pairs". The various types of donors and acceptors and the approximate energy ranges are shown in Table I.2. The π-donor-σ-acceptor complexes and the n-donor-σ-acceptor complexes may exist as $\infty:\infty$ or as 1:1 complexes: the $\infty : \infty$ complexes are generally found in solid state and the 1:1 complexes in solution and vapour phases.

The molecular complexes formed between n-donors and σ-acceptors are very strong and there is a considerable contribution of the dative structure (D^+-A^-) to the stability of the

Table I.1

Classification of Donors and Acceptors

Number of Electrons	Function type	Donor Type Structure	Donor Type Examples	Acceptor Types Structure	Acceptor Types Examples
Odd	Free Radical	R	NO, C_2H_5, H	Q	X, H, OH
Even	(a) Increvalent	n	R_3N, R_2S, R_2O, R_2CO	V	BF_3, AIX_3, $SnCl_4$
	(b) Sacrificial	σ	Aliphatic hydrocarbons	σ	X_2, CCl_4 (x=halogens)
		π	Aromatic and unsaturated hydrocarbons and those substituted with electron donating groups; intramolecular donor island groups.	π	Aromatic and unsaturated hydrocarbons with electron withdrawing groups; intramolecular acceptor island groups.

Table I. 2

Donor-Acceptor Systems and Their Energy Ranges

Type	Examples	Energy ranges, KJ/Mole
1. Contact pairs	Cyclohexane + I_2, Benzene + CCl_4	< 5
2. $\pi - \sigma$	Benzene + I_2; Phenanthrene + I_2	5 - 15
3. $\pi - \pi$	Naphthalene + sym-trinitrobenzene	5 - 15
4. n- σ	Amines + I_2; Carbonyl Compounds + I_2	15-75
5. n-V	Ether + BF_3; Amines + BF_3	Very Strong addition compounds

ground state. Several attempts have been made to establish a pattern of the relationship between $h\nu_{CT}$ and μ_{DA}, the dipole moment of the charge-transfer complex in the ground state, and the heat of formation, $-\Delta H$, of the complex[19]

$$-\frac{\Delta H}{\mu_{DA}} = \frac{h\nu_{CT}}{er} \quad \frac{1}{a^2(1+\frac{a}{b}S_{01})\left[1+\frac{b^2}{a^2}+\frac{(b^*)^2}{(a^*)^2}\right]}$$

$$= \frac{h\nu_{CT}}{erA} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{I.15}$$

where $A = a^2(1+\frac{a}{b}S_{01})\left[1+\frac{b^2}{a^2}+\frac{(b^*)^2}{(a^*)^2}\right]$ I.16

From the experimental values of $-\Delta H$, μ_{DA}, and $h\nu_{CT}$ equation I.10 can be used to estimate the overlap integral S_{01}. The contact molecular complexes arise out of collisions between donor and acceptor species. The enthalpies of formation of such complexes are very small. For weakly interacting systems, Ketelaar[20] assumed that $b^2 \ll a^2$ and $(b^*)^2 \ll (a^*)^2$ and derived the equation,

$$-\frac{\Delta H}{h\nu_{CT}} \approx \frac{b^2}{a^2} \quad \ldots\ldots\ldots\ldots\ldots \text{I.17}$$

The magnitude, b^2/a^2 is a measure of the polarity of the complex. After $-\Delta H$ and $h\nu_{CT}$ have been experimentally determined, one can use this equation to calculate b^2/a^2; this evaluation will be very approximate. In between these two extremes, the molecular complexes of varying strengths are formed depending on the particular donor and acceptor species forming the complexes. It

must be mentioned here that the terms donor and acceptor are only relative.

I.5 METHODS USED IN THE STUDY OF MOLECULAR COMPLEXES

The formation of molecular complexes may be proved and their compositions may be established from a study of the associated characteristic abrupt changes from ideal behaviour in certain physical properties. Any physical property will be suitable for such studies if it is reversible to the effects of dilution and temperature[25]. These properties include the absorption of ultraviolet or visible radiation, vapour pressure, dielectric constant, refractive index, conductivities etc[19,25-28]. Recently, valuable informations have been obtained from constant activity method[29], vibrational spectroscopy[30-31], nuclear magnetic resonance[32], resonance Raman spectroscopy[33], positron annihilation life time measurements[34], dielectric and dipole moment measurements[35], gas-liquid chromatography[36], NQR Spectroscopy[37], Mössbauer Spectroscopy[38], Mass Spectrometry[39], Overhaauser effects[40], optical dichroism of single crystals[41], magnetic circular dichroism[42], X-ray diffraction studies[43-45], electrical and optical properties of solid molecular complexes[43,46], and magnetic properties of molecular complexes[43,47-52]. In addition to this, Kinoshita and coworkers are working on delayed fluorescence of CT complexes,[52c] Nagakura and coworkers are working on exciplexes PES[53], Kuroda and others on ESCA[54] whereas Matsunaga et al[55] are

engaged in the studies of charge-transfer and proton-transfer processes. Recently, photoacaustic spectroscopy[56], Radiotracer techniques[57], Polarographic techniques[57a,b] are also being used in the study of molecular interactions. Such studies will undoubtedly be very useful in understanding the molecular interactions.

Generally, the molecular complexes cannot be isolated in pure state, but exist in solution in equilibrium with pure components. So, it is not surprising that molecular complexes have been studied most extensively in solutions, though many recent studies have been done in vapour phases as well[58]. Although, the interaction of an electron donor D, with an acceptor, A, may give rise to more than one species of complex in solution, most of the methods used for evaluating the association constant assumes that a single complex species with a definite stoichiometry is formed. Thus, for equilibrium

$$D + A \rightleftharpoons DA \quad \ldots\ldots\ldots\ldots\ldots \text{I.18}$$

a thermodynamic equilibrium constant, K, is obtained:

$$K = \frac{[DA]}{[D]\ [A]}$$

$$= \frac{[DA]}{([D]_0 - [DA])\ ([A]_0 - [DA])} \quad \ldots\ldots\ldots\ldots \text{I.19}$$

Here $[D]$, $[A]$ and $[DA]$ represent the equilibrium concentration

of donor, acceptor and complex and $[D]_o$ and $[A]_o$ are the initial concentrations of donor and acceptor, respectively. It is generally assumed that as the solutions are very dilute, the activity coefficients of the species DA, D and A are unity[59,60]. When the concentration of donor is very much in excess of that of acceptor (D >> A), then ($[D]_o - [AD]$) can be replaced by $[D]_o$ in the above equation. Expressing the concentration of the complex in terms of experimentally measurable absorbance ($[DA] = O.D./\epsilon.1$) the above equation (I.19) can be rewritten as,

$$\frac{[A]_o l}{O.D} = \frac{1}{K.\epsilon} \cdot \frac{1}{[D]_o} + \frac{1}{\epsilon} \quad \ldots\ldots\ldots\ldots \text{I.20}$$

This is the original Benesi-Hildebrand equation[59]. Eventhough, the Benesi-Hildebrand equation can be used to obtain the equilibrium constant, one has to use modified equations for obtaining the correct values. These modified and new equations are summarized by Rao et al[14] as well as by Foster[28] in recent reviews.

Recently, it has been felt that the data obtained by optical spectroscopy on molecular complexes should be supplemented by non-spectral methods[61,61a]. The arguments in favour of above ideas are:-

(1) In using spectral methods to study complex formation, it is necessary to infer two parameters from a set of measurements at various concentrations the equilibrium constant of complex formation, K, and the molar extinction coefficient, ϵ, of a spectral

band. Although, the product K.ϵ can be determined from spectral measurements restricted to the dilute solution region, the resolution of the product Kϵ into separate values of K and ϵ, requires spectral measurements extending into concentration ranges in which a sizable fraction of the least concentrated solute (usually the acceptor) is in the complexed form[62-64]. Thus, in studies of complexes for which K is considerably less than $1M^{-1}$, it is necessary to use solute concentration well in excess of 1M. At such concentration levels, the medium remains hardly equivalent to pure solvent, in fact it may be expected that both the spectral and the thermodynamic properties of the solute species are significantly different from those at infinite dilution[65]. Attempts have been made to account for the effects of sizable concentrations of dissolved solutes on specific and non-specific interactions of the solvent with donor, acceptor and complex molecules[66-67]. In addition, there may be higher order (n:m) complexes at higher donor/acceptor concentrations[68-69].

(2) The interpretation of the spectra of donor, acceptor and complex may be complicated by the presence of numerous orientation isomers, of the 1:1 complex or contact charge-transfer complexes and the calculated value of ϵ is the weighted average of extinction coefficients of various orientation isomers[70]. So, doubts have been raised on the validity of optically determined values of K and ϵ (from Kϵ), particularly in the case of weak molecular complexes.[71]

In developing and testing theories of molecular interactions, it is essential that we must have accurate values of K and ϵ for weak complexes too, for which the conventional spectral method alone cannot yield reliable results. It is believed that it will be fruitful to employ several nonspectral methods (such as solubility, vapour pressure, refractive index, dielectric constant, colligative property, conductivity, etc.). These methods are probably capable of giving reliable values of K for complexes even in solutions that are so dilute that only a small fraction of either of the donor or the acceptor molecules are in complexed form[72]. Thus, if spectral and nonspectral methods are employed conjunctively, accurate information can be obtained about both spectra and energetics of molecular complexes.

Although, it is mentioned in the literature that the stoichiometry of the complex can be determined by the continuous change method[73] or by the molar ratio method[74], these methods, using the measurements of physical properties like UV-Vis radiation absorption etc. are not much helpful when the complex dissociates to give ions in polar media[75]. Under such circumstances one can determine the stoichiometry of such ionizable complexes by measuring the electrical conductivities of the solutions in a suitable media. In addition to this, as the ions can carry current, one can determine the nature of charge-carriers as well.

This thesis embodies the results on studies on weak and strong molecular complexes obtained by constant activity method, determination of stoichiometry of the ionizable molecular complexes by conductometry, and the nature of charge carriers in solution. In addition to this, the optical and electrical properties of a few solid molecular complexes were also included.

I.6 CONSTANT ACTIVITY METHOD

Solubility measurements have been used to some extent not only to detect the formation of molecular complexes but also to determine their equilibrium constants. Kortüm[76] had shown that solubility of iodine in complexing solvents is higher than that in inert or non-complexing solvent. The increase in solubility of iodine in an inert solvent upon addition of a donor was attributed to the formation of the complex. Childs et al[61] and Singh and Bhat[77] have recently made use of constant activity method for determining spectral and thermodynamic parameters for molecular complexes of iodine. In this method the concentration of free iodine was kept constant (at particular temperature) by using solid mixture of tetramethylammonium pentaiodide ($TMAI_5$) and tetramethylammonium triiodide ($TMAI_3$). At a constant temperature following equilibrium exists;

$$TMAI_5\ (s) \overset{K_d}{\rightleftharpoons} TMAI_3\ (s) + I_2 \quad \ldots\ldots\ldots\ I.21$$

on the addition of a donor, the complex is formed and a second equilibrium is established,

$$D + I_2 \overset{K}{\rightleftharpoons} DI_2 \quad \ldots\ldots\ldots \text{I.22}$$

Thus, the addition of donor makes more $TMAI_5$ to dissociate so that more iodine is liberated in order to keep the equilibrium I.21. Thus, the constant activity method, which does not depend on any of the assumptions (like D >> A) which are made in spectroscopic methods, is used to determine equilibrium constant, K, and molar extinction coefficient, ϵ, independently, in solution as well as in vapour phases[58,61]. In addition to this, this technique is used to locate the blue shifted iodine band maximum precisely and directly even in weak molecular complexes.

I.7 CONDUCTOMETRIC TITRATION

If the interaction between the donor and acceptor is very strong, then a high dielectric media will facilitate the transformation of the 'outer complex' into the 'inner complex' by loosening the new bonds which are formed[78]. such donor and acceptor species are ionic. Gutmann and co-workers[79] had demonstrated that conductometry can be used to study the formation of such complexes. In addition to this, the stoichiometry of such ionizable complex can be determined conductometrically[80-86].

I.8 TRANSPORT NUMBER STUDIES

Reid and Mulliken[87] have explained the increased electrical conductance of iodine in pyridine, on the basis of an equilibrium

involving the outer and inner complexes.

$$C_5H_5N + I_2 \rightleftharpoons C_5H_5N.I_2 \quad \text{..... I.23}$$

$$C_5H_5N.I_2 \rightleftharpoons (C_5H_5N.I)^+ + I^- \quad \text{..... I.24}$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad \text{..... I.25}$$

The formation of cation as well as anion (and I_3^- species) in highly polar media is reported in the literature[88-96]. In such cases, it may be possible to determine the nature of majority charge-carriers in solutions, by determining the transport number of cation or anion.

I.9 SOLID MOLECULAR COMPLEXES

A number of crystalline molecular complexes have higher conductivities than are ordinarily observed for organic solids. Their specific conductivities, σ, vary with temperature[46],

$$\sigma = \sigma_0 \cdot e^{-E_g/2kT} \quad \text{..... I.26}$$

The term E_g, which is twice the thermal activation energy for conduction represents the valence band and conduction band, it corresponds to thermal excitation energy required to produce charge carriers by promoting electrons to the conduction band. The specific conductivities and energy gap depend on the nature of molecular complexes (organic semiconductors). Generally, a strong molecular complex has a higher value of σ and lower

value of Eg; lower σ and higher Eg is an indication of weak interaction between the donor and acceptor. In a number of cases the energy gaps for conduction of complexes of donors of closely related structure with a given acceptor vary in linear fashion with charge-transfer excitation energies of the solids[43,97].

$$Eg = h\nu_{CT}\ (solid) - \delta \qquad \text{..... I.27}$$

The single crystal polarized absorption spectra of molecular complexes give a reliable value of charge-transfer energy of the solid molecular complex[52].

The increase in bond lengths which result when donor acceptor interaction takes place are generally accompanied by corresponding decrease in vibration frequencies of the components[3,98]. These changes (and appearance of new bands as well) and other changes which are characteristic of symmetry losses leading to vibrations which are forbidden in free donors and acceptors, and generally apparent in the infrared spectra of the adducts[99].

The interaction of donor with acceptor results either in perturbation of the vibrational frequencies, (if the interaction is weak) or accompanied by pronounced changes in infrared spectra. So, the "shift" of the donor/acceptor band frequency is a measure of the strength of interaction. Yarwood and co-workers[3,100] have carried out systematic and exhaustive investigations on measurement and interpretation of vibrational spectra of molecular

complexes. Similarly, Haque[31] and coworkers[31] had carried out an exhaustive study on pyridine, picolines-halogen complexes to understand the nature of interactions.

The charge-transfer complexes are of interest and are being studied in all branches of chemistry. General areas of recent research (experimental) on charge-transfer complexes are;[101]

(1) Vapour phase charge-transfer complexes.
(2) Solvent effects on charge-transfer complexes.
(3) Pressure effects on charge-transfer complexes.
(4) Excited state properties of charge-transfer complexes.
(5) Structure of solid charge-transfer complexes.
(6) Electrical, optical and magnetic properties of charge-transfer complexes.
(7) PES/ESCA studies of molecular complexes.
(8) Polarized absorption or spectral studies of single crystals.
(9) Charge-transfer complexes of polymers.
(10) Optically active charge-transfer complexes.
(11) Charge-transfer complexes of biological interest involving carcinogenic compounds, drug receptors.
(12) Charge-transfer complexes in analysis, chromatographic separation, catalysis.
(13) Charge-transfer complexes involving donors with multiple sites, species which behave either as donors or acceptors.

(14) Charge-transfer complexation for estimating electron affinity of acceptors.

(15) Reaction intermediates involving CT complexes.

(16) Organometallic charge-transfer complexes.

Care has been taken to give proper credit for the work of other authors in the literature. The author would like to apologize for any omission which might have occurred by oversight or error in judgement.

REFERENCES

1. P. Pfeiffer, "Organische Molekulverbindugen" second Ed. Fordinand Enke, Stuttgart, 1927.
2. J.O. Hirshfeider, Ed."Advances in Chemical Physics" Vol.12, "Intermolecular Forces" Interscience Publishers, New York, 1967.
3. "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973.
4. C.N.R. Rao, "Ultraviolet and Visible Spectroscopy, Chemical Applications", Second Ed. Butterworths, London, 1967.
5. R.S. Mulliken and W.B. Person, "Molecular Complexes, Lecture Note Reprints", John Wiley and Sons, New York, 1969 and the papers there in.
6. R. Foster, "Organic Charge-Transfer Complexes", Academic Press London, 1969.
7. a) R.S. Mulliken, J.Am. Chem. Soc., 74, 811 (1952).
   b) R.S. Mulliken, J. Phys. Chem. 56, 801 (1952).
8. N.S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
9. Ying-Nan Chlu., J. Phy. Chem., 80, 992 (1976).
10. G. Briegleb, "Elektronen-Donator-Acceptor Komplexe", Springer Verlag, Berlin, 1961.
11. H. Yada, S. Tanaka and S. Nagakura, Bull. Chem. Soc. Japan, 33, 1660 (1960).
12. S.H. Hastings, L.J. Franklin, J.S. Schiller and F.A. Matsen, J. Am. Chem. Soc., 75, 2900 (1953).

13. N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra" Marcel Dekker, INC, 1970, Chapter VI.

14. C.N.R. Rao, S.N. Bhat and P.C. Dwivedi, Appl. Spectros, Revs, 5, 1 (1972).

15. R.S. Mulliken and W.B. Person, Ann. Revs. Phys. Chem., 13, 107(1962).

16. M.W. Hanna and J.L.Lippert in "Molecular Complexes", Ed. R. Foster, Elek Science, London, 1973.

17. K. Morokuma, Accounts of Chemical Research, 10, 294 (1977).

18. H. Umeyama, K. Morokuma and S. Yamabe, J. Am. Chem. Soc. 99, 330 (1977).

19. E.N. Gur'yanova, I.P. Gol'dshtein and I.P. Romn, "Donor-Acceptor Bond", Translated by R. Kondor, John Wiley and sons, New York, 1975.

20. J.A.A. Ketelaar, J. Phys. Radium, Paris, 15, 197 (1954).

21. J.N. Murrel, J. Am. Chem. Soc., 81, 5037 (1957).

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

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

24. K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, Bull. Chem. Soc. Japan 34, 1076 (1961); 35, 33 (1962).

25. M.A. Slifkin, "Charge-transfer Interactions of Biomolecules", Academic Press, London, 1971.

26. L.J. Andrews, Chem. Revs., 54, 713 (1954).

27. J. Rose, "Molecular Complexes" Pergmon Press, Oxford, 1967.

28. "Molecular Complexes, Vol. II" Ed. by. R. Foster, Elek. Science, London, 1974, Chapter 3.

29. J.D. Childs, S.D. Christian, J. Grundnes and S.R. Roach, Acta. Chem. Scand., 25, 1679 (1971).

30. "Spectroscopy and structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973. Chapter II,III and IV.

31. a) S.G.W. Ginn, I. Haque and J.L. Wood, Spectrochim Acta, 24A, 1531 (1968).

b) I. Haque and J.L. Wood, 23A, 959, 2523 (1967).

c) M.J. Potasek, K.W. Beeson, The Review of Scientific Instrum. 52, 1301 (1981).

32. a) R. Foster and E.A. Fyfe in "Progress in NMR spectroscopy" Vol. 4, Ed. J.W. Emsley, J. Feeney and L.H. Sutcliffe, Pergmon Press, Oxford, 1969. Chapter I.

b) C.A. Fyfe and J. Ripmeester, Can.J. Chem., 48, 2283 (1970)

c) D.F.R. Gilson and C.A. Mc Dowell, Can. J. Chem., 44, 945 1966.

33. K.H. Michaelian, K.E. Rieckhoff and E.M. Voigt, J. Phy. Chem., 81, 1489 (1977).

34. Y.C. Jean and H.J. Ache, J. Phy. Chem., 80, 1693 (1976).

35. a) M. Kulvesky in "Molecular Associations" Vol. I Ed. by R. Foster, Academic Press, London, 1975.

b) S.N. Bhat and C.N.R. Rao, J. Am. Chem. Soc., 90, 6008 (1968).

35. c) A.H. Price in "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yorwood, Plenum Press, London, 1973 Chapter VII.

36. R.J. Laub and C.A. Wellington in "Molecular Associations", Vol. II Ed. by R. Foster, Academic Press, London, 1979.

37. a) R.A. Bennett and H.O. Hooper, J. Chem. Phys. 47, 4855 (1965).

b) Y.K. Maksyutin, T.A. Babushking, Y.N. Gur'yanova and G.K. Semin, Theor. Chim. Acta. 14, 48 (1969).

c) G.A. Bowmaker and S. Hacobian, Aust. J. Chem. 22, 2047 1969.

d) H.G. Fleming and M.W. Hanna, J. Am. Chem. Soc., 93, 5030 (1971).

38. a) S. Ichiba, M. Mishima, H. Sakai and H. Negita, Bull. Chem. Soc. Japan, 41, 49 (1968).

b) S. Ichiba, H. Sakai, H. Negita and Y. Maeda, J. Chem. Phys., 54, 1627 (1971), 72, 6192 (1980).

c) H. Sakai, T. Malsujama, H. Yamaoka and Y. Maeda, Bull. Chem. Soc., Japan, 56, 1016 (1983).

39. a) J.E. Collin and R. Cabay, Bull. Cl. Sci. Acad. Roy. Belg., 52, 606 (1966); C.A. 67, 58307e.

b) B.E. Job and W.R. Patterson in "Some Newer Phys. Methods, Struct. Chem., Proc. Symp. (R. Bonnett Ed.) United Trade Press, London (1966); C.A. 70, 52216g.

40. H. Goetz, H. Schulze and K. Werner, Phys. Status. Solidi, 24, K95 (1967); C.A. 68, 25308Y.

41. a) K. Yakushi, M. Iguchi and H. Kuroda, Bull. Chem. Soc., Japan, 52, 3180 (1979).

b) T. Sugano, K. Yakushi and H. Kuroda, Bull., Chem. Soc., Japan, 51, 1041 (1978).

42. a) E.L Kourashy, G. Adel and G. Roger, J. Chem. Soc., Faraday Trans. II, 72, 1860 (1976).

b) R. Solaro and E. Chiellini, J.C.S., Chem. Commun., 580, 583 (1980).

43. The scientific papers of Prof. H. Akamatu and his group, Tokyo University Press, 1971.

C.K. Prout and B. Kamener in "Molecular Complexes" Vol. I. Ed. by R. Foster, Elek Science, London, 1973.

44. a) H. Kobyashi, Bull. Chem. Soc., Japan, 46, 2595, 2675, 2945 (1973).

b) H. Kobayashi, Y. Ohashi, F. Marumo and Y. Saito, Acta. Cryst. B26, 459 (1970).

45. a) O. Hassel and K.O. Strome, Acta. Chem. Scand., 12, 1178 (1958).

46. b) O. Hassel, C. Romming and T. Tufte, Acta. Chem. Scand., 15, 967 (1961).

c) T. Uchida, Bull. Chem. Soc., Japan, 40, 2244 (1967).

d) A.C. Bailey and C.K. Prout, J. Chem. Soc., 4867 (1965).

46. F. Gutmann and L.E. Lyons, "Organic Semiconductors", John Wiley, New York, 1967.

47. a) M. Kinoshita, Bull. Chem. Soc. Japan, 35, 1137, 1609 (1962).

47. b) M. Kinoshita, Y. Sato, M. Sano and A. Akamatu, Bull. Chem. Soc. Japan, 43, 2370 (1970).

48. M. Kinoshita, Bull. Chem. Soc. Japan, 37, 428 (1964).

49. Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, Bull. Chem. Soc., Japan, 40, 2539 (1967).

50. M. Ohmasa, M. Kinoshita, M. Sano and H. Akamatu, Bull. Chem. Soc., Japan, 41, 1998 (1968).

51. Y. Sato, M. Kinoshita, M. Sano and H. AKamatu, Bull. Chem. Soc., Japan, 43, 2370 (1970).

52. a) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, J. Chem. Phy., 36, 457 (1962).

b) M. Ohmasa, M. Kinoshita and H. Akamoto, Bull. Chem. Soc., Japan, 44, 391, 395 (1971).

c) N. Iwasaki and M. Kinoshita, Chem. Phys. Letter, 86, 81 (1982).

53. a) T. Kobayashi and S. Nagakura, Bull. Chem. Soc., Japan, 45, 987 (1972).

b) H. Hayashi and S. Nagakara, Mol. Phys. 19, 45 (1970).

c) M. Yagi and S. Nagakura, Chem. Phys. Lett., 21, 119 (1973).

d) S. Matsumoto and S. Nagakura, Mol. Phys., 26, 1465 (1973).

e) S. Matsumoto, S. Nagakura and Y. Shimozory, H. Hayashi and J. Nakamra, Bull. Chem. Soc., Japan, 47, 604 (1974).

f) Y. Achiba, K. Nomotu and K. Kimura, J. Phy. Chem., 86, 681 (1982).

54. a) I. Ichemoto, Y. Cao, M. Yamada, H. Kurada, I. Harada, H. Shirakawa and S. Ikeda, Bull. Chem. Soc., Japan, 55, 721 (1982).

b) I. Ichemoto, M. Yamada, T. Sugano, and H. Kuroda, Bull. Chem. Soc., Japan, 53, 1871 (1980).

55. a) Y. Matsunaga, Bull. Chem. Soc., Japan, 53, 3085 (1980).

b) Y. Matsunaga, Bull. Chem. Soc., Japan, 48, 37-8 (1975).

c) Y. Matsunaga, Bull. Chem. Soc., Japan, 47, 1020 and 1589 (1974).

56. H.E. Eaton, Jr. and J.D. Strun, Spectroscopy Letters, 15, 275 (1982).

57. S.P. Mishra and R.A. Singh, J. Chem. Soc., Faraday Trans. I, 78, 1967 (1982).

a) R. Nakata, S. Okazaki and T. Fujinaga, Electroanalytical Chem., 125, 413 (1981).

b) L. Ramaley and S. Gaul, Can. J. Chem. 56, 2381 (1978).

58. M. Tamres in "Molecular Complexes" Vol. I Ed. by R. Foster, Elek Science, London, 1973.

59. H.A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949).

60. J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, "Regular and Related Solutions", Von. Nostrand Reinhold Co., New York, 1970.

61. a) J.D. Childs, S.D. Christian and J. Grundnes, J. Am. Chem. Soc. 94, 5657 (1972).

61. b) M. Tamres and S.N. Bhat, J. Am. Chem. Soc., 95, 2516 (1973).

c) R. Foster, B. Dodson, A.A.S. Bright, M.I. Foreman and J. Gorton, J. Chem. Soc., B. 1283 (1971).

62. W.B. Person, J. Am. Chem. Soc., 87, 167 (1965).

63. R.A. Labudde and M. Tamres, J. Phy. Chem. 74, 4009 (1970).

64. D.A. Deranleau, J. Am. Chem. Soc. 91, 4044 (1969).

65. S.D. Christian and E.E. Tucker, J. Phy. Chem. 74, 214 (1970).

66. S. Carter, J. N. Marrel and E.J. Rosch., J. Chem. Soc., 2048 (1965).

67. R.S. Drago, T.F. Bolles and R.J. Niedzielski, J. Am. Chem. Soc., 88, 2717 (1966).

68. R.J. Bailey, J.A. Chudek and R. Foster, J. Chem. Soc., Perkin Trans. II, 1591 (1976).

69. B. Dodson, R. Foster, A.A.S. Bright, M.I. Foreman and J. Gorton, J. Chem. Soc., B, 1283 (1971).

70. L.E. Orgel and R.S. Mulliken, J. Am. Chem. Soc., 79, 4839 (1957).

71. M. Tamres and S.N. Bhat, J. Phy. Chem. 75, 1057 (1971).

72. S.D. Christian, A.A. Taha and B.W. Gash, Quart. Rev., Chem. Soc., 24, 20 (1970).

73. P. Job, Annals, Chim. 9, 113 (1928).

74. J.H. Joe and A.L. Jones, Ind. Engng. Chem. Analyt. Edn., 16, 111 (1944).

75. F. Gutmann and M. Keyzer, Electrochim. Acta, 11, 555, 1163 (1963).

76. G. Kortüm and W.M. Vogel, Z. Elektrochem., 59, 16 (1955).

77. R.A. Singh and S.N. Bhat, Can. J. Chem., 59, 1212 (1981).

78. S.N. Bhat and C.N.R. Rao, J. Am. Chem. Soc., 88, 3216 (1966).

79. F. Gutmann and M. Keyzer, Electrochimica Acta, 11, 555, 1163 (1963).

80. a) J.Kleinberg, E. Cotton, J. Sattizahn and C.A.Vanderwerf, J. Am. Chem. Soc., 75, 442 (1953).

b) L.F. Audrieth and E.J. Birr, J. Am. Chem. Soc., 55, 668 (1933).

c) A.E. Beezer, M. Orban and J.V. Tyrrell, Acta. Chim. Acad. Sci. Hung. 99, 415 (1974).

81. J.J. Tondear and A. Berghese, Electrochimica Acta., 22, 129 (1977).

82. C.A. Vanderwerf, J. Am. Chem. Soc., 75, 442 (1953).

83. R.D. Srivastava, V.M. Mishra and P.N. Tripathi, Electrochimica Acta, 27, 863 (1982).

84. A.K. Trofimchukao, E. Ya. Groenbein, Zh. Obsch. Khim., 41, 34 (1971), C.A. 74: 146998f.

85. H. Gasten and L. Klasini, J. Phys. Chem., 76, 2422 (1972).

86. M.V. Ramanmurthy and P.V.S.S. Prabhu, Electrochim. Acta., 27, 481 (1982).

87. C. Reid and R.S. Mulliken, J. Am. Chem. Soc., 76, 3869 (1954).

88. S.R. Palit, J. Ind. Chem. Soc., 53, 1238 (1976).

89. S.N. Bhat and C.N.R. Rao, J. Am. Chem. Soc., 88, 3216 (1969).

90. R.A. Zingaro, C.A. Vanderwerf and J. Kleinberg, J. Am. Chem. Soc., 73, 88 (1951).

91. S.B. Shah and A.S.N. Murty, J. Phys. Chem., 79, 322 (1975).

92. R.M. Bixon and G. Gileadi, J. Phys. Chem., 84, 715 (1980).

93. H. Cheung and M. Tamres, J. Phys. Chem., 81, 1367 (1977).

94. H. Hayakawa and S. Namakura, Bull. Chem. Soc., Japan, 50, 566 (1977).

95. R.H. Stokes, J. Am. Chem. Soc., 76, 1988 (1954).

96. F.G.K. Baulke, R. Bertran and K. Case, J. Electroanal Chem. Interfacial Electro. Chem., 32, 247 (1971).

97. H. Kuroda and H. Akamatu, Bull. Chem. Soc., Japan, 35, 1604 (1962).

98. H.B. Friedrich and W.B. Person, J. Chem. Phys., 44, 2161 (1966).

99. J.L. Wood in "Spectroscopy and Structure of Molecular Complexes", Plenum Press, London, 1973. Chapter IV.

100. a) J. Yarwood, "Annual Reports C. Royal Society of Chemistry, London, 1979, Chapter IV.

b) C. Baker, P. L. James and J. Yarwood, Faraday Discussions of Faraday Society, 188 (1978).

100. c) C. Baker, P.L. James and J. Yarwood in "Protons and ions involved in Fast Dynamic Phenomena" Elsevier Scientific Pub. Co., Amsterdam, 1978.

101. M. Tamres, J. Chem. Edn., 45, 221 (1968).