STUDIES ON SOME ASPECTS OF MOLECULAR COMPLEXES

BHARATI BHATTACHARJEE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

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To

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SHILLONG 793 001
INDIA

AUGUST, 1985

To

MY MOTHER

Phone :
Grams : NEHU

North-Eastern Hill University

Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Department of... Chemistry

Dr. S. N. Bhat

I Certify that the thesis entitled, "STUDIES ON SOME ASPECTS OF MOLECULAR COMPLEXES", submitted by Miss Bharati Bhattacharjee for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She 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

Date : 5th Aug, —

Signature of the Supervisor

Phone :
Grams : NEHU

North-Eastern Hill University

Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Department of... Chemistry

July 15, 1985

This is to Certify that Miss Bharati Bhattacharjee has satisfactorily completed the following Pre-Ph. D. courses, as prescribed by this University:

1. CHEM 608 - BIO-INORGANIC CHEMISTRY
2. CHEM 660 - SOLID STATE CHEMISTRY
3. BASIC FRENCH LANGUAGE
4. SPS 602 - GERMAN LANGUAGE

HEAD

DEPARTMENT OF CHEMISTRY
NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793 003

Head
Department of Chemistry
North Eastern Hill University
Shillong-793003

C O N T E N T S

A C K N O W L E D G E M E N T

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Bharati Bhattacharjee.
(Bharati Bhattacharjee)

CHAPTER I

INTRODUCTION

In this Chapter the general aspects of molecular complexes (including the theories) and some of the spectral and nonspectral methods which are of relevance to the studies, reported in this thesis, and of general interest have been briefly reviewed.

I. 1. ELECTRON DONOR ACCEPTOR SYSTEMS

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 nitro-compounds, 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 ultra-

violet 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 100-400 kJ/mole. The interaction occuring 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 occuring 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's interactions, of definite stoichiometry. (This definition can be extended to hydrogen bonding also). 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

Whenever the molecules interact to form an "associated species", there will be new absorption in electronic/infrared spectral regions or there may be any perturbation of the donor acceptor bonds. So any theory of molecular complexes (EDA systems) should explain satisfactorily the following general features of absorption spectra and energy changes associated with such complex formation.[4]

(i) 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 and in such cases the changes in other physical properties (nonspectral) can be noticed.

(ii) 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.

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

(iv) The enthalpies of formation of molecular complex are of the order of 5-75 kJ/mole. This indicates the weak nature of binding in the ground state of the complex.

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

(vi) 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 wave length (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 electrons. So, iodine absorption shifts to lower wavelength. The molar absorptivity coefficient of complexed iodine may increase or decrease.

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

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

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

An evaluation of the thermodynamic parameters of EDA systems/molecular complexes, such as change in enthalpy, $-\Delta H^{\circ}$, entropy, $-\Delta S^{\circ}$ and standard free energy, $-\Delta G^{\circ}$, occuring on complex formation, provide useful evidence 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]

Hydrogen bonding is an important aspect in the study of the interaction between electron donors and acceptors (i.e. proton acceptors and donors) and it is needless to emphasize the importance of this phenomenon in chemistry.[7-10] As hydrogen bonding is an attractive interaction between two molecules (or between two parts of the same molecule) which requires the presence of a hydrogen atom in the vicinity. So the general term molecular complexes/electron donor-acceptor system include hydrogen bonding (proton acceptor-donor system). Therefore general theory of molecular complexes can be extended to hydrogen bonding also.

I. 3. MULLIKEN'S THEORY OF MOLECULAR COMPLEXES

Electron transfer theory has been developed along two separate lines, namely, Mulliken's[5,11] Charge-transfer theory and Hush's[12] intervalence 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 Chiu[13] has developed a unified molecular charge-transfer theory 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 intervalence 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,[5,11] 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,

$$\underset{\text{I}}{D + A} \longleftrightarrow \underset{\text{II}}{(D,A)} \longleftrightarrow \underset{\text{III}}{(D^{+}\text{-}A^{-})} \longleftrightarrow \underset{\text{IV}}{(D^{-}\text{-}A^{+})}$$

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 transfered from donor to acceptor and in IV, from acceptor to 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 wave function for the ground state of complex, ψ_N, can be expressed as a linear combination of the wave functions of the 'no-bond' structure, ψ_0, and the dative structure, ψ_1, neglecting the contribution of the ionic structures, $(D^- — A^+)$

$$\psi_N = a^* \psi_0(D....A) + b\psi_1(D^+ — A^-) \quad ...I.1.$$

A corresponding excited state of the complex can be represented by the wave function, ψ_E,

$$\psi_E = a^* \psi_1 (D^+ — A^-) - b^* \psi_0(D,A) \quad ...I.2.$$

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 structure

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 functions which are normalised. 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:

$$W_N = W_o - \frac{(H_{01} - W_0 \cdot S_{01})^2}{(W_1 - W_0)} \quad \ldots \text{ I. 3.}$$

and

$$W_E = W_1 + \frac{(H_{01} - W_1 \cdot S_{01})^2}{(W_1 - W_o)} \quad \ldots \text{ I. 4.}$$

where,

$$W_0 = \int \psi_o H \psi_o \, d\tau$$

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

$$H_{01} = \int \psi_o H \psi_1 \, d\tau$$

$$S_{01} = \int \psi_o \psi_1 \, d\tau$$

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

$$h\nu_{CT} = I_D - (E_A + E_C + W_0) + X_E - X_N \quad \ldots \text{I.5.}$$

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

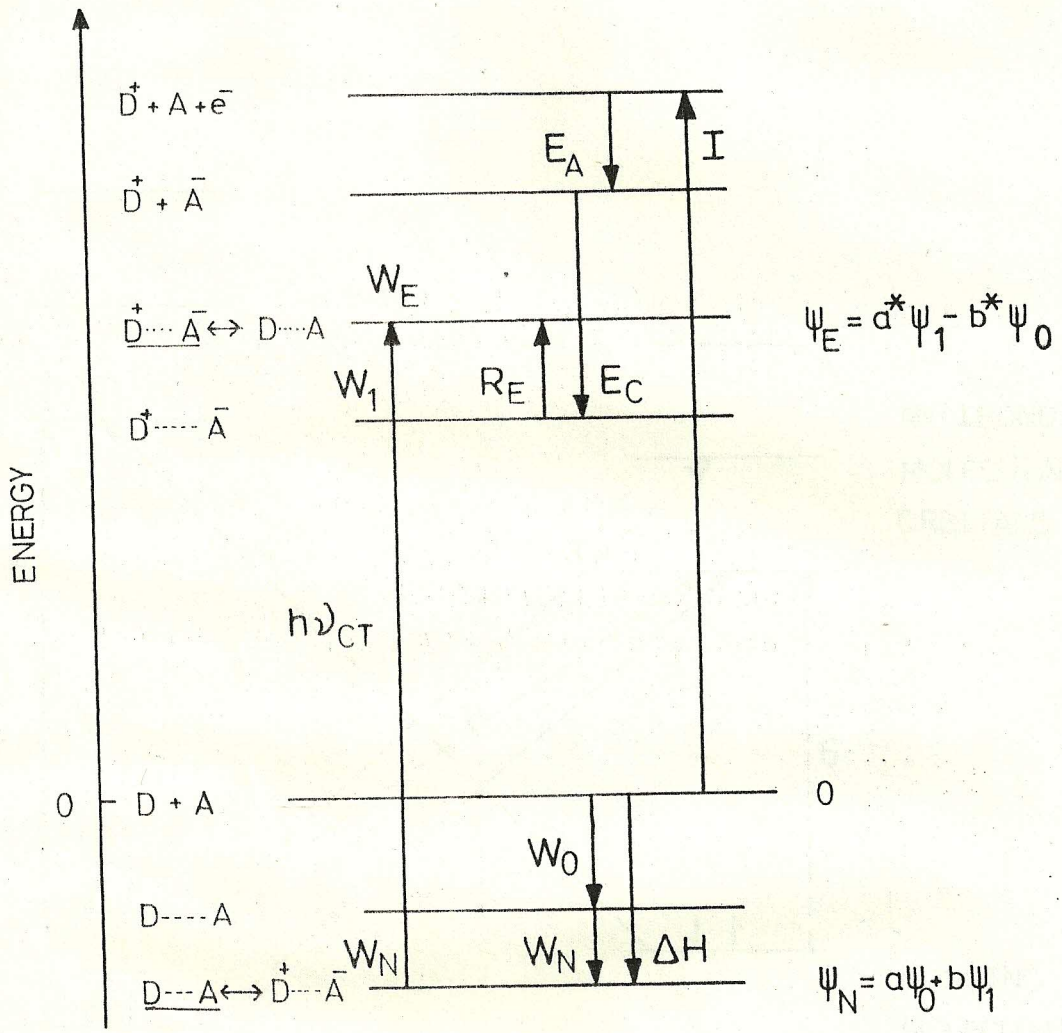

Fig. I. 1. Schematic Energy Level Diagram showing Various Contributions.

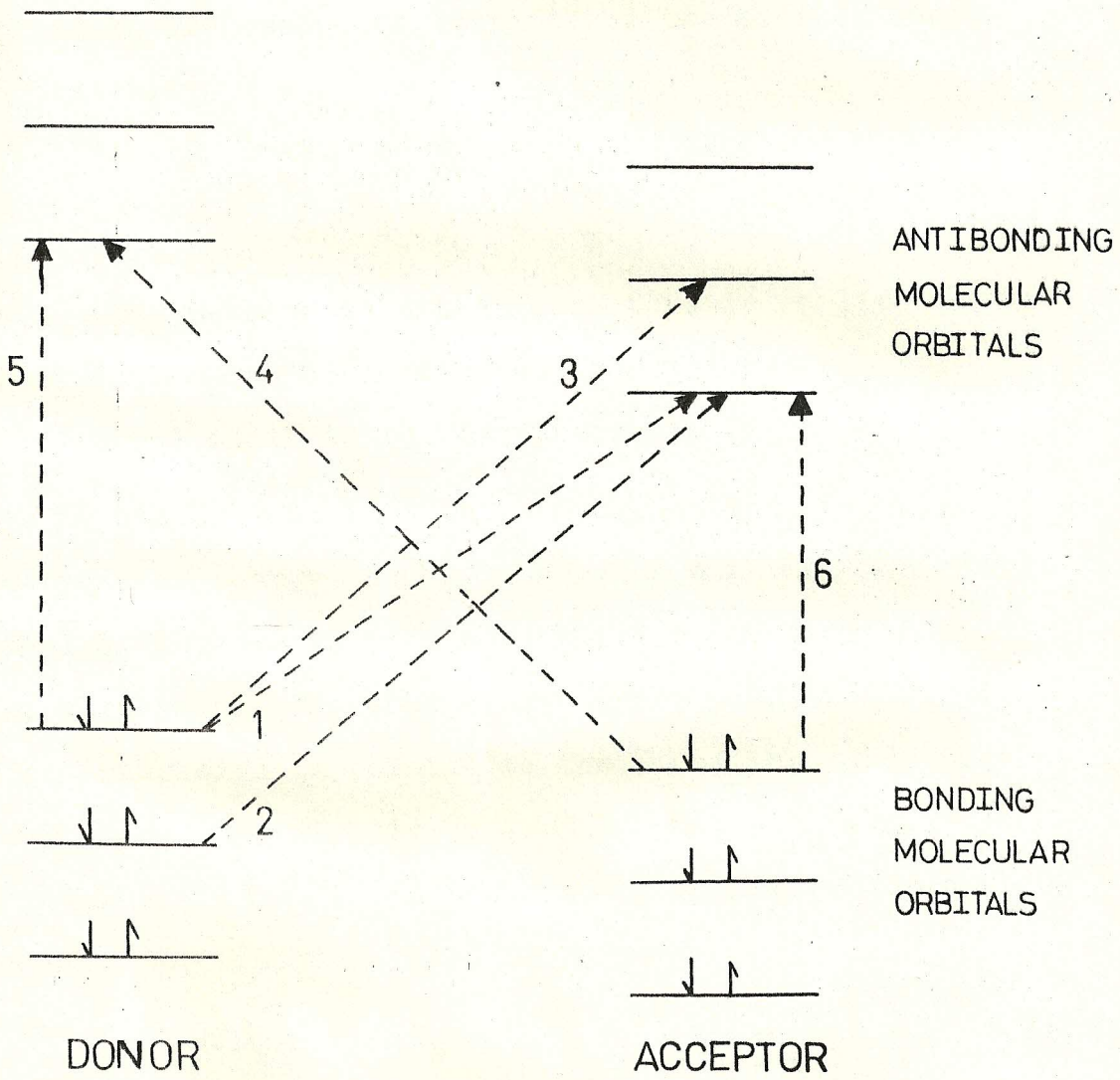

Fig. I. 2. Schematic Diagram showing Electronic Excitation:

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.

where I_D is the ionization potential of donor, E_A, is the electron affinity of the acceptor, E_C, is the Coulombic energy between $D^+ — A^-$ and $D^- — A^+$, W_O is the no-bond energy and 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 absorption 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 $h\nu_{CT} = I_D - E_A - \Delta + [-2\beta^2/(I_D - E_A - \Delta)]$. In the case of aromatic hydrocarbon-iodine systems, Briegleb[14] has shown that

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

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

$$\beta_o = H_{01} - W_o S_{01} \quad \text{and} \quad \beta_1 = H_{01} - W_1 S_{01}$$

When $h\nu_{CT}$ was plotted against I_D, Briegleb[14] 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).

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

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, Tanka and Nagakura[15] have derived the following equation for such strong complexes

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

It is now realized that linearity between $h\nu_{CT}$ and I_D is not universal rule,[15-17] since with the change of donor, the other factors such as the overlap integral vary as well.[16] A number of workers have correlated $h\nu_{CT}$ values with I_D for

the interaction of a related series of donors with an acceptors and the results of such correlations are summarized by Rao, Bhat and Dwivedi.[18]

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. The 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 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

$$f = \frac{2.303\, mc^2}{\pi e^2 W_0} \int \epsilon_v \delta v$$

$$= 4.318 \times 10^{-9} \int \epsilon_v \delta v$$

$$\cong 4.32 \times 10^{-9} \epsilon_{max} \overline{\Delta\tilde{\nu}}_{\frac{1}{2}} \qquad \ldots \qquad \ldots \text{ I.10.}$$

where $\Delta\tilde{\nu}_{\frac{1}{2}}$ 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, M^2_{VN}. The oscillator

strength, f, and electronic transition dipole, $\mathcal{M}_{VN}$, are related by,

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

or, $$\mathcal{M}_{VN} = 0.0958 \left[\frac{\int \epsilon \, d\nu}{\bar{\nu}} \right]^{\frac{1}{2}}$$

$$\approx 0.0958 \left[\frac{\epsilon_{max} \cdot \Delta\bar{\nu}_{\frac{1}{2}}}{\bar{\nu}} \right]^{\frac{1}{2}} \quad \ldots \text{ I.12.}$$

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.[19-21] Umeyama et al[22] 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[13] has 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 ($a \gg b$), and hence to the ground state stability. So the term "molecular complex" rather than "Charge-transfer" or electrostatic complex (or Electron Donor-Acceptor Systems) seems to be reasonable to represent the 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.[23-27] 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.[21] Fukui[28] used linear combination of atomic orbitals of the donor and acceptor for representing the molecular orbital of the complex. Guryanova et al[23] briefly summarized 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 other words, the interaction energies in the ground state are small compared with the transition energies to the 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

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

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 Huckel treatment, $D_i = \alpha + \beta x_i$, where α is the coulomb integral, β is the resonance integral and x_i is the Huckel 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,

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

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-donors- 6 -

Table I. 1.

Classification of Donors and Acceptors

Number of Electron	Function Type	Donor Type		Acceptor Type	
		Structures	Examples	Structure	Examples
Odd	Free	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, AlX_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	<10
2. π-σ	Benzene + I_2; Phenanthrene + I_2	5-20
3. π-π	Naphthalene + sym-trinitrobenzene.	5-20
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.

acceptor complexes and the n-donor- σ-acceptor complexes may exist as $\alpha:\alpha$ or as 1:1 complexes; the $\alpha:\alpha$ complexes are generally found in solid state and the 1:1 complexes in solution and vapor 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 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[23]:

$$-\frac{\Delta H}{\mu_{DA}} = \frac{h\nu_{CT}}{er} \cdot \frac{1}{a^2\left(1 + \frac{a}{b} S_{01}\right)\left[1 + \frac{b^2}{a^2} + \frac{(b^*)^2}{(a^*_I)^2}\right]} = \frac{h\nu_{CT}}{erA} \quad \ldots\ldots\ldots\ldots\ldots \text{I.15.}$$

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

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[24] assumed that $b^2 \ll a^2$ and $(b^*)^2 \ll (a^*)^2$ and derived the equation

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

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

An important feature of weak attractive interactions (molecular complexes/hydrogen bonding) in solution is that at ordinary temperatures, only a fraction of the molecules are generally associated. At equilibrium, while a certain number of new complexes are continuously broken, due to the kinetic energy of motion of the interacting molecules. The formation of molecular complexes, hydrogen bonds 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.[29] This

properties include the absorption of ultra-violet or visible radiation, vapor pressure, dielectric constant, refractive index, conductometric titrations, viscosity, surface tension, etc.[23,29-34] Recently valuable information have been obtained from calorimetry,[35-37] Gas-liquid Chromatography,[29,38-40] ultracentrifugation,[41] fluorescence measurement,[42-44] solubility method,[45] constant activity method,[46] microwave spectroscopy,[47-50] double diffusion uv-method, vibrational spectroscopy,[51-55] Raman spectroscopy,[56-60] picosecond spectroscopy,[61-64] nuclear magnetic resonance,[65-71] electron spin resonance,[72,73] positron annihilation life time measurements,[74] dielectric and dipole moment measurements,[75-76] NQR spectroscopy,[77,78] chemical dynamics,[79] Mossbauer spectroscopy,[80,81] Mass spectrometry,[82-84] Overhauser effects,[85.86] optical dichroism of single crystals,[87-90] magnetic circular dichroism,[91] X-ray and neutron diffraction studies,[92-96] electrical and optical properties of solid molecular complexes,[93,97-105] magnetic properties of molecular complexes,[92,106-111] phase transition and phase diagram,[112-117] cyclic voltametry,[118-121] ultrasonic interferrometry,[122-125] differential thermal analysis.[126] The contributions of Tamres and coworkers[127-135] in understanding the nature of interactions of molecules in vapor phases and contact charge transfer complexes, Nagakure and coworkers on exciples,[136] Kuroda and others on PES/ESCA,[137-140] Matsunaga and coworkers[141] on the studies of charge transfer and

proton transfer processes, Muralikrishna and coworkers[79,142-159] in using CT complexes in analytical studies, Bhowmik and coworkers[160-169] in the effect of solvents on spectra and thermodynamics of charge-transfer complexes, Plusinski and coworkers[170] on detection of charge transfer complexes in solution by the method of isosbestic points and recently photo-acoustic spectroscopy,[171] Radiotracer techniques,[172] polarographic techniques,[172a,b] stopped flow technique[168] are also being used in the study of molecular interactions. In addition, theoretical studies on molecular complexes are also being carried out.[172-180] Such studies will undoubtebly be very useful in understanding the nature of 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 vapor phases as well.[181] 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,

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

a thermodynamic equilibrium constant, K, is obtained:

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

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

where $[D]$, $[A]$ and $[DA]$ represent the equilibrium concentration of donor, acceptor and complex and $[D]_0$ and $[A]_0$ 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.[182-184] When the concentration of donor is very much in excess of that of acceptor ($D \gg A$), (or vice versa) then $([D]_0 - [AD])$ can be replaced by $[D]_0$ in the above equation. Expressing the concentration of the complex in terms of experimentally measureable absorbance ($[DA] = O.D./\epsilon.l.$) the above equation (I.19) can be rewritten as,

$$\frac{[A]_0.l}{O.D.} = \frac{1}{K.\epsilon}.\frac{1}{[D]_0} + \frac{1}{\epsilon} \quad \ldots \text{I.20.}$$

This is the original Benesi-Hildebrand equation.[182] Even-though, 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 and summarized by Rao et al[18] as well as by Foster[32a] 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.[185] The arguments in favour of above ideas are :-

(i) 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 $K.\epsilon$ can be determined from spectral measurements restricted to the dilute solution region, the resolution of the product $K.\epsilon$ 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.[186-188] Thus, in studies of complexes for which K is considerably less than 1 M^{-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 signifi-

cantly different from those of infinite dilution.[189] 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.[190-191] In addition, there may be higher order (n:m) complexes at higher donor/acceptor concentrations.[192-193]

(ii) 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.[194] So, doubts have been raised on the validity of optically determined values of K and ϵ (from $K\epsilon$), particularly in the case of weak molecular complexes.[195]

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 non-spectral methods (such as solubility, vapor pressure, refractive index, dielectric constant and dipole moment,[196-200] viscosity measurement,[201] surface tension,[33,34] colligative

property,[202,203] 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.[204] Thus, if spectral and non-spectral methods are employed conjunctively, accurate information can be obtained about both the spectra and energetics of molecular complexes. In addition, it is to be noted that the same technique can not be used under all conditions. Although it is mentioned in the literature that the stoichiometry of the complex can be determined by the continuous change method[205] or by the molar ratio method,[206] these methods using the measurements of physical properties like uv-vis radiation absorption etc. are not much helpful when either, the interaction between the molecules is so weak that there is only slight perturbation in the spectra of the interacting molecules, or when complex formed dissociates to give ions in polar media.[207] Under such circumstances one can determine the stoichiometry of such ionizable complexes either by making use of any convenient non-spectral method or by measuring the electrical conductivities of the solutions in a suitable media.

This thesis embodies the results of studies on molecular complexes/hydrogen bonding by using the above mentioned

less familiar methods — conductometry, viscometry, in addition to the usual [illegible] infrared spectroscopy.

I. 6. OUTER AND INNER COMPLEXES

When the donor and acceptor molecules interact to form a complex, the ground state of the complex which depends largely on the coulombic interaction between the components is influenced markedly by the dielectric constant of the medium. In some n-donor-σ-acceptor complexes, the new bonds which are formed are loosened due to environmental assistance and transform to the 'dissociative' inner complex, due to the rupture of the bond. In the presence of non-ionizing solvents, the two ions formed by the rupture of the σ bond will be together (ion pair); while in an ionizing solvent they are separated out. Mulliken[5,11,208] has compared the "dissociative" and "associative" donor acceptor interactions/ reactions in detail. The 'associative' mode helps to form the 'outer complex' while the dissociative mode to "inner complex". In the presence of a strong environmental conditions, the activation energy for the transformation of the outer to inner complex decreases. If the environmental influence is sufficiently strong, the inner complex may be the stable form. The kinetic study of transformation of outer complex to inner complex helps in understanding the

nature of interaction and the effect of environmental influence on the transformation.[209-217]

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[218]; such donor and acceptor species are ionic. Gutmann and co-workers[219] had demonstrated that conductometry/conductometric titration can be used to study the formation of such complexes. In addition to this, the stoichiometry of such ionizable complex can be determined conductometrically. (ref. 220-226).

I.8. VISCOMETRIC STUDIES ON MOLECULAR COMPLEXES AND HYDROGEN BONDING

When molecules interact to form complexes the physical properties of the new species formed will be different (however small it may be) from those of the reacting molecules. So in principle one can study the "interaction" between the molecules by noting the change in any of the properties, e.g. viscosity of the systems under different conditions. The viscosities of the "binary" and "ternary"

systems will be different from those of calculated (i.e. using additivity rules) values and the deviation is an indication of interaction between the molecules. It has been pointed out that viscometric method can be used to obtain the equilibrium constant of complex-hydrogen bonding directly,[227-242]

I. 9. INFRARED SPECTRA OF SOLID MOLECULAR COMPLEXES

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.[253] 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, generally apparent in the infrared spectra of the adducts.

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[254] have carried out systematic and exhaustive investigations on measurement and interpretation of vibrational spectra of molecular complexes. Similarly Haque and co-workers,[255] Wood et al,[256] Devlin et al[257] made

significant contribution in understanding the nature of interaction between molecules by vibrational spectroscopy.

The Charge-transfer complexes are of interest and are being studied in all branches of chemistry. Tamres[258] had listed the general areas of recent research (experimental) on charge-transfer complexes:

1. Vapor phase charge-transfer complexes.
2. Solvent effects on charge-transfer complexes.
3. Pressure effects on charge-transfer complexes.
4. Contact charge-transfer complexes.
5. Excited state properties of charge-transfer complexes.
6. Electrical, optical and magnetic properties of charge-transfer complexes.
7. Structure of solid charge-transfer complexes.
8. PES/ESCA studies of molecular complexes.
9. Polarised absorption spectral studies of single crystals.
10. Charge-transfer complexes of polymers.
11. Optically active charge-transfer complexes.
12. Charge-transfer complexes of biological interest involving carcinogenic compounds, drug receptors.
13. Charge-transfer complexes in analysis, chromatographic separation, catalysis.

14. Charge-transfer complexes involving donors with multiple sites, species which behave either as donors or acceptors.
15. Charge-transfer complexation for estimating electron affinity of acceptors.
16. Reaction intermediates involving CT complexes.
17. 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 may have occurred by oversight or error in judgement.

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