Charge transfer complexes revisited

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Electron donors such as diethyl ether, benzene, and electron acceptors such as halogens combine to form charge transfer (C–T) complexes. A C–T complex gives a unique absorption band generally in the UV-visible region, which is not present in the spectrum of the donor or the acceptor. A new approach to study a C–T complex is to isolate the complex in the gaseous state and find its occupied orbital energies from UV photoelectron spectroscopy (UVPES), excited states from electron energy loss spectroscopy (EELS) and compare the orbital energies from *ab-initio* molecular orbitals (MO) calculations. Combined use of UVPES, EELS and MO calculations provides a complete molecular description of a C–T complex. Bonding and antibonding orbitals responsible for $h\nu_{C-T}$ absorption in a C–T complex can be identified. In this article we describe this new approach to study C–T complexes.

Atoms combine in a definite proportion to form a molecule. Similarly, two or more molecules can combine to give a new complex molecule. Benesi and Hildebrand[1] discovered this fifty years ago while studying the effect of various solvents on the absorption spectrum of molecular iodine. A solution of benzene and iodine in *n*-heptane gives an absorption band at 268 nm, which is not present in the spectrum of either iodine or benzene. The colour of iodine solution in benzene is pinkish red whereas it is violet in carbon tetrachloride. They attributed this new absorption band due to the formation of an adduct called charge–transfer (C–T) complex. Such complexes are formed between the molecules having capacity to donate electrons (Lewis bases such as diethyl ether, diethyl sulfide, methyl amines, alcohols and benzene) and the molecules having ability to accept the electrons (Lewis acids such as I_2, Br_2, SO_2, BF_3, $AlCl_3$ and $TiCl_4$). Therefore, these adducts were also called electron donor–acceptor (EDA) complexes.

Mulliken[2] was the first to propose a theory of C–T complexes to explain the observation of Benasi and Hildebrand. He used the method of 'valence bond' by considering each member of the complex as an 'atom' and the D–A pair as a diatomic-like molecule. He then wrote a simple diatomic-like wave function for the D–A complex as follows:

$$\psi_N\ (\text{D–A}) = a\psi^0(\text{D–A}) + b\psi^1(\text{D}^+ - \text{A}^-),$$

$$\psi_E\ (\text{D–A}) = a\psi^1(\text{D–A}) + b^*\psi^0(\text{D}^+ - \text{A}^-).$$

After solving these equations, Mulliken showed that $h\nu_{C-T} = E_E - E_N = I_D - E_A + C$. Here D refers to the donor and A refers to the acceptor. ψ_N and ψ_E are wave functions of ground and excited states of the D–A complex. I_D is the ionization energy of the donor and E_A is the electron affinity of the acceptor. This theory was fairly successful in predicting C–T band ($h\nu_{C-T}$). Subsequently, molecular orbital methods have been used to describe D–A complexes. Notable among them is due to Murrel's perturbation approach[3], Dewar's model[4], Fukui *et al.*'s LCAO method[5] and Flurry's LCMO method[6]. While the above EDA bonding models have their own weaknesses and strengths, none of them has considered the complex as a unique entity different from its constituents. In the real sense, the C–T complex is a new entity formed out of the monomers and it can be described using a different set of molecular orbitals. Such an attempt has been made by employing *ab-initio* SCF MO theory considering the C–T complex as a supermolecule[7].

On the experimental side, a large number of C–T complexes have been studied by a variety of spectroscopic methods. Thermodynamic quantities ΔH and ΔS of C–T complexes have also been documented. A monograph on 'Donor–Acceptor Bond' by Gur'yanova, Gol'dstein and Romm[8] gives an excellent account of C–T complexes up to 1975. Even though the formation of a C–T complex is a molecular phenomenon, they have been largely studied in non-polar solvents. Spectroscopic studies of C–T complexes in the gaseous state are extremely rare and only a few systems such as diethyl ether-I_2 have been studied in gaseous state[9,10].

MO description of molecules is valid only in the gaseous state. Molecular orbital energies are obtained from *ab-initio* MO calculations and direct proof of the existence of molecular orbitals came from photoelectron spectroscopy of molecules in gaseous state. D. W. Turner at Imperial College, London, discovered UV photoelectron spectroscopy in 1962 and measured ionization energies of different molecular orbitals in a molecule employing HeI (21.22 eV) photon source[11]. Electronic excitation of molecules employing an electron beam (instead of a photon beam) was also developed during 1960s where excitation energy in the deep ultraviolet region can also be obtained. The method is called electron energy loss spectroscopy (EELS)[12]. Only after the development of UVPES and EELS, quantum-chemical calculations describing molecular orbitals were put to rigorous tests to describe the MOs of a molecule. A large body of UVPES studies of molecules exists in

the literature[13]. Since 1980, we have employed UVPES and EELS to obtain electron states of C–T complexes. While UVPES in conjunction with *ab-initio* MO calculations provides energy levels of occupied valence orbitals, EELS provides C–T band and also the excited states of the complexes. Thus, a complete energy level diagram of a C–T complex molecule can be obtained by the combined use of UVPES, EELS and MO calculations. In this article, we present this new approach to study C–T complexes in gaseous state.

Electron states of molecules from UVPES

UVPES is a direct experimental method to obtain ionization energies of electron states in atoms and molecules. In this method, HeI photon ($2^1P \rightarrow 1^1S$; 584 Å; 21.22 eV) beam collides with molecules and the valence electrons whose ionization energy is less than 21.22 eV are ionized. According to Einstein's photoelectric effect, $h\nu$ (21.22 eV) $= E_I + E_K$, where E_I is the ionization energy and E_K is the kinetic energy of the photoelectrons. Kinetic energy of the photoelectrons is experimentally determined. Since the photon energy is known, ionization energy can be obtained. According to Koopmans' approximation[14], each ionization energy (E_I) is equal in magnitude and opposite in sign to orbital energy of electrons. Hence, energy of each MO in a molecule can be obtained from UVPES.

We have fabricated UV photoelectron spectrometers[15] in our laboratory. The spectrometer consists of HeI lamp, 180° hemispherical electron energy analyser and electron multiplier to detect electrons. Photoelectron spectra of HCl and H_2O molecules are described here to elucidate the identification of molecular orbitals by UVPES.

Photoelectron spectrum of HCl molecule is given in Figure 1. H–Cl molecule is formed by the overlap of H(1s) and Cl ($3p_x^1$) orbitals and the remaining four electrons of Cl atom in 3p orbital ($3p_y^2$, $3p_z^2$) remain non-bonding. Thus, the lowest ionization energy of HCl molecule should correspond to lone pair orbitals on Cl in HCl and the second ionization energy should correspond to σ_{HCl} bonding orbital. This is what is observed from the UVPES. The first two peaks at 12.75 eV are due to non-bonding Cl (3p) electrons on Cl in HCl and the second set of peaks beginning from 16.2 eV are due to σ_{HCl} bonding electrons. Since two lone pair orbitals are equivalent and they have π-type symmetry, they are split into two peaks due to spin orbit splitting.

Though a single ionization peak is expected for σ_{HCl}, there are several peaks beginning from 16.2 eV. On removal of an electron from σ_{HCl} orbital of HCl, HCl^+ is produced. In the photoionization process, an electron from ground electronic state and ground vibrational state in the neutral molecule is excited to the ground electronic state of HCl^+ ion. Due to Frank–Condon principle, vibrational excited states of HCl^+ are accessible for photoionization. The set of peaks from 16.28 eV to 17.5 eV is the vibrational progression of HCl^+ ion. However, ionization energy of the σ_{HCl} is 16.28 eV.

Excited states from EELS

In this method, a monochromatized electron beam collides with the molecules. Electrons involved in exciting the molecule lose their kinetic energy. The energy loss in the process of excitation is exactly equal to excitation energy. We have fabricated electron energy loss spec-

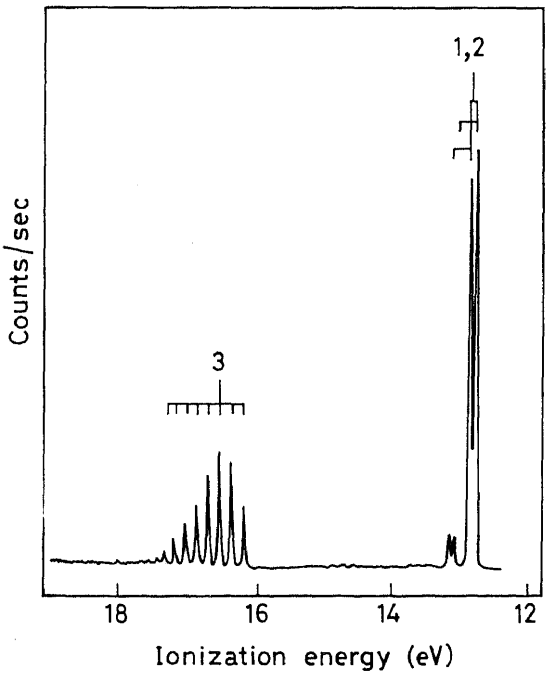

Figure 1. HeI photoelectron spectrum of HCl.

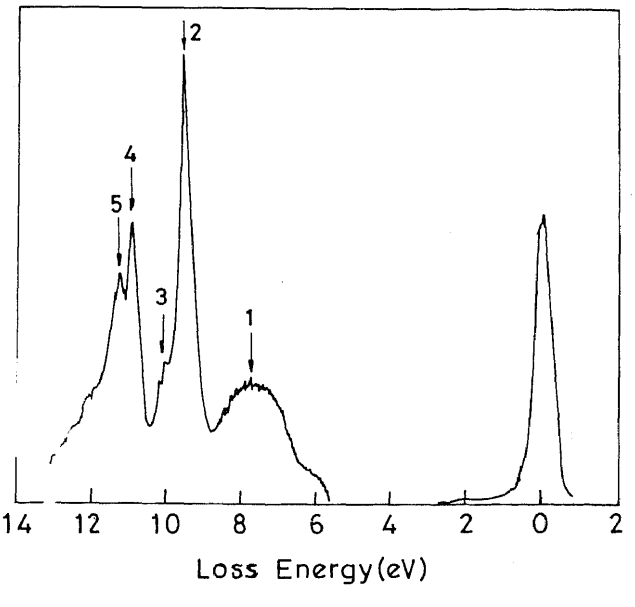

Figure 2. Electron energy loss spectrum of HCl.

trometers for molecules[16]. Electron energy loss spectrum of HCl in the gaseous state is given in Figure 2. Not only do the electrons get excited to antibonding MOs, they can also get excited to atomic levels of chlorine which are called Rydberg states. Transitions are assigned based on quantum defect calculation[17]. A complete energy level diagram can now be drawn knowing occupied molecular orbitals from UVPES and excited states from EELS, which is shown in Figure 3. Notice that all the energy levels are with reference to zero energy scale. Atomic orbital energies of H(1s) at –13.6 eV, Cl(3p) at –13 eV and the MO energies of n_{Cl} (–12.75 eV), σ_{HCl} (–16.2 eV) are obtained from UVPES experiments. From the excitation energies obtained from EELS, σ^*_{HCl}, 4p and 4d Rydberg states are fixed. Thus, UVPES and EELS give a complete energy level diagram starting from energy levels of atoms. It is interesting to see that the two lone pairs Cl ($3p_y$, $3p_z$) in the MO diagram have essentially remained at the same level as that in Cl atom true to the meaning of non-bonding orbitals. Cl ($3p_x$) and H(1s) bonding orbitals have shifted to –16.2 eV in the HCl molecule. Such a simple description of the MOs is not possible in the case of polyatomic molecules. Therefore, it is essential to employ quantum mechanical methods to obtain energies of molecular orbitals.

MO calculations

Ab-initio MO calculations have been generally successful in predicting the geometry, orbital energies, dipole moment, vibrational frequencies, binding energy and many others properties of molecules.

Many *ab-initio* MO programs have been developed and among them, Gaussian system of programs by Pople[18] and his co-workers are widely used. These Gaussian programs (latest being Gaussian-96) are commercially available. Input to these programs is a Z matrix, which specifies the atoms forming the molecule and their relative positions, namely, the distances and angles with each other. Optimization of geometry is carried out to obtain a minimum energy structure.

MO calculations of H_2O with 6-31G* basis set, for example, give five distinct sets of orbital energies at –13.55 eV, –15.52 eV, –19.37 eV, –36.61 eV and –556 eV. From the coefficients of the atomic orbitals of oxygen and hydrogen, the highest occupied orbital at –13.55 eV has O($2p_x$) character and π symmetry. The second orbital at –15.52 eV lies in the H–O–H plane and has σ-type symmetry. The third orbital is due to σ_{OH} at –19.37 eV. The fourth orbital at –36.61 eV is due to O(2s). The orbital at –556 eV is due to O(1s), not participating in bonding with H(1s). This is the delocalized electron description of H_2O molecule from *ab-initio* MO calculations.

UVPES of H_2O shown in Figure 4 gives peaks at 12.61, 14.74 and 18.51 eV corresponding to π-type O(2p) nonbonding orbital (n_O (1)), σ-type O(2p), ((n_O(2)) and σ_{OH} orbitals. O(2s) is observed at 32.5 eV when higher energy photon is used in the UVPES experiment. O(1s) of H_2O in vapour phase is observed around 545 eV

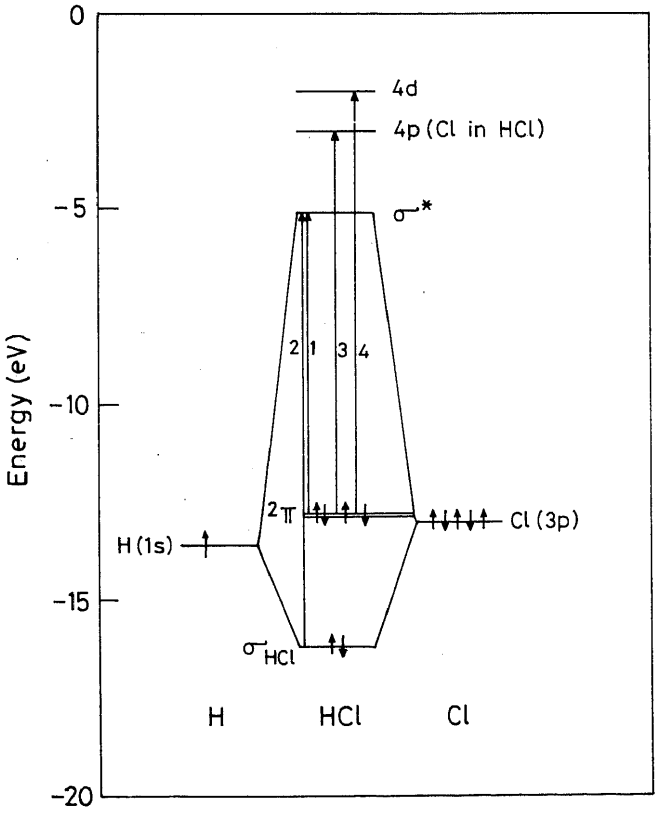

Figure 3. Energy level diagram of HCl molecule.

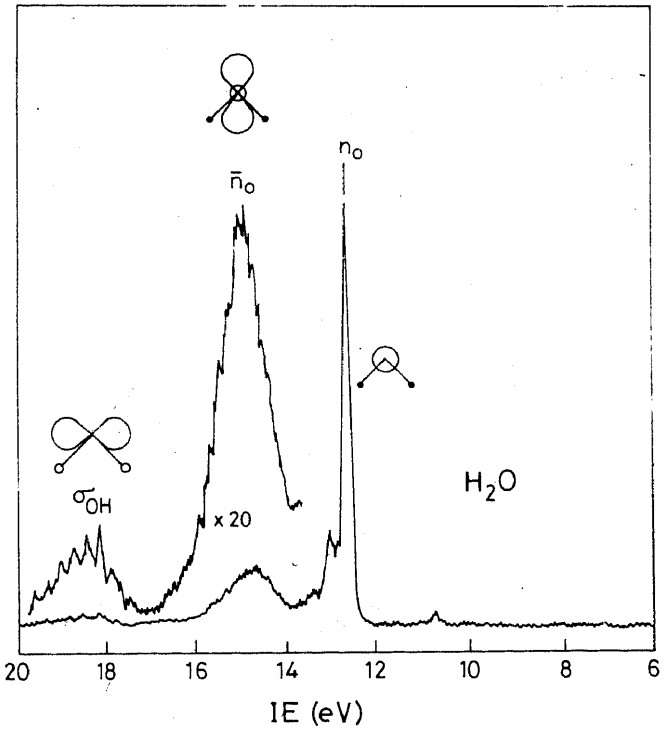

Figure 4. HeI photoelectron spectrum of H_2O molecule.

from X-ray photoelectron spectroscopy. Thus, orbital energies from MO calculations are close to the observed values by photoelectron spectroscopy.

Electron energy loss spectrum of H_2O molecule in Figure 5 shows excitation bands at 7.31, 9.64, 10, 10.58, 11.04 and 11.54 eV. First excitation band at 7.31 eV (169 nm) is assigned to π-type O(2p) to 3s (σ^*) and it is deep inside the UV region. Higher transitions are due to O(2p) to O(3p), O(3d), O(4s), O(4p) and such Rydberg (atomic-like) transitions[17]. A complete energy level diagram of H_2O based on UVPES and EELS is drawn in Figure 6 starting from two hydrogen atoms and one oxygen atom. Thus, the 6 valence electrons of oxygen and two valence electrons from two hydrogen atoms are occupied in four molecular orbitals. The two lone pairs on oxygen are non-equivalent in H_2O molecule. A similar approach can be followed to obtain energy level diagram of a C–T complex molecule starting from a donor and an acceptor.

Diethyl ether-I_2 C–T complex

Diethyl ether–iodine $[(C_2H_5)_2O–I_2]$ is a typical C–T complex. The complex gives a C–T band at 249 nm. Formation of this complex is described by the transfer of electrons from highest occupied oxygen lone pair in ether molecule to the antibonding σ^* (σ_u) of I_2 molecule. Heat of formation of this complex is 4.3 kcal/mole. Even though this complex has been studied extensively, several questions remained unanswered. They are (a) what is the geometry of the complex? What are the donor and acceptor orbitals involved in the bonding? What are the bonding and antibonding orbitals involved in the absorption of $h\nu_{C-T}$? Where are the electron states of the complex molecule *vis-à-vis* electron states of their monomers? HeI UVPES, EELS and MO calculations have given answers to these questions. In Figure 7, we show HeI UVPES of $(C_2H_5)_2O$, I_2 and their complex. Just as in H_2O, there are two lone pairs of electrons on oxygen of ether molecule, $n_O(1)$ and $n_O(2)$ at 9.6 eV and 11.1 eV respectively. $n_O(1)$ is a π-type lone pair on oxygen and $n_O(2)$ is the σ-type lone pair in the C–O–C plane. Ionization energy of σ_{C-C}, σ_{CH}, σ_{C-O} of ether occurs in the range 12–16 eV. UVPES of I_2 molecule gives two peaks due to π_g (split due to spin orbit splitting), two peaks due to π_u and a single peak due to σ_g of I_2. The MOs of I_2 are shown in the inset of the figure. Upon complexation, iodine orbitals are shifted to lower ionization energy while the lone pair orbitals of oxygen in diethyl ether are shifted to higher ionization energies as shown in the diagram. Such an unambiguous assignment has been possible from *ab-initio* MO calculations[19]. The MO calculations showed that the optimized geometry of the molecule has C_{2V} symmetry (Figure 8). Calculations at the MP2/3-21G* level gave an interaction energy of 4.5 kcal/mol agreeing well with the experimental value of 4.3 kcal/mol. From the coefficients of atomic orbitals, we have confirmed the ordering of the molecular orbitals. Accordingly, the σ-type lone pair orbital on oxygen of ether, $n_O(2)$ is bonding with σ_u of I_2 and not the highest occupied π-type $n_O(1)$

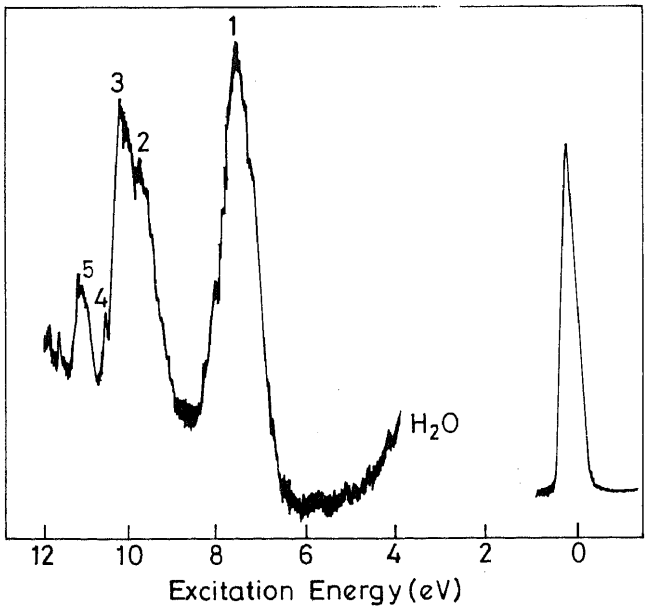

Figure 5. Electron energy loss spectrum of H_2O.

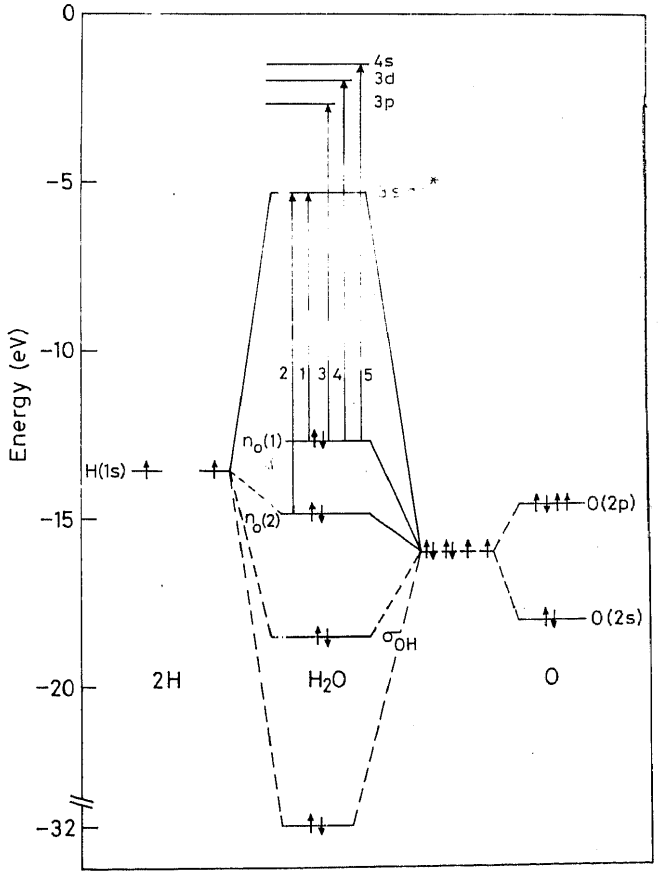

Figure 6. Electron states of H_2O molecule.

transition is at 6.9 eV. Due to C–T complex formation, the $n_O(1)$ and $n_O(2)$ are shifted to higher ionization energies and the orbitals of I_2 are shifted to lower ionization energies, which are determined by UVPES. From MO theory, the bonding orbitals are $n_O(2)$ of ether and σ_u of I_2. Position of the first excited state of the complex should lie 4.9 eV above the shifted n_O of ether after complexation. The first excited state of the complex is also the same level to which the $\pi_g \rightarrow \sigma_u$ type of transition in the complex should occur which is at 2.7 eV. Thus, σ_u of the complex is uniquely fixed. The figure illustrates that C–T complex is formed from the donor and acceptor orbitals and it is a new molecule. The bonding and antibonding orbital pairs are clearly defined and the transition from the bonding to antibonding level corresponds to the C–T band. If the C–T band was due to charge transfer from highest occupied lone pair from ether $n_O(1)$ to σ_u of I_2 as proposed by Mulliken, the C–T band should have occurred at about 3.5 eV but no such band is observed experimentally.

To test this methodology, diethyl sulphide–I_2 C–T complex has been studied and in Figure 11, UVPES of this complex is shown. It is clear that the I_2 orbital energies are stabilized and lone pair orbital energies of sulphur are destabilized. From MO calculations of $(C_2H_5)_2S$–I_2 complex[19], it is π-type lone pair electron on S that interacts with σ_u of I_2. The optimized geometry is shown in Figure 8. The molecule has C_s symmetry. The C–T band is at 4.2 eV and indeed, the excitation energy from the shifted π-type lone pair, $n_S(1)$, to the shifted σ_u of I_2 is 4.2 eV as shown in the energy level diagram of complex shown in Figure 12. Again, the C–T band is due to excitation of the electron from bonding to antibonding orbital of the C–T complex.

We have studied $(C_2H_5)_2O$–Cl_2 and $(C_2H_5)_2O$–Br_2, and found that bonding is between σ-type of oxygen lone pair of oxygen with σ_u of Cl_2 and Br_2 in the case of diethyl ether. But in the case of $(C_2H_5)_2S$–Br_2 complex,

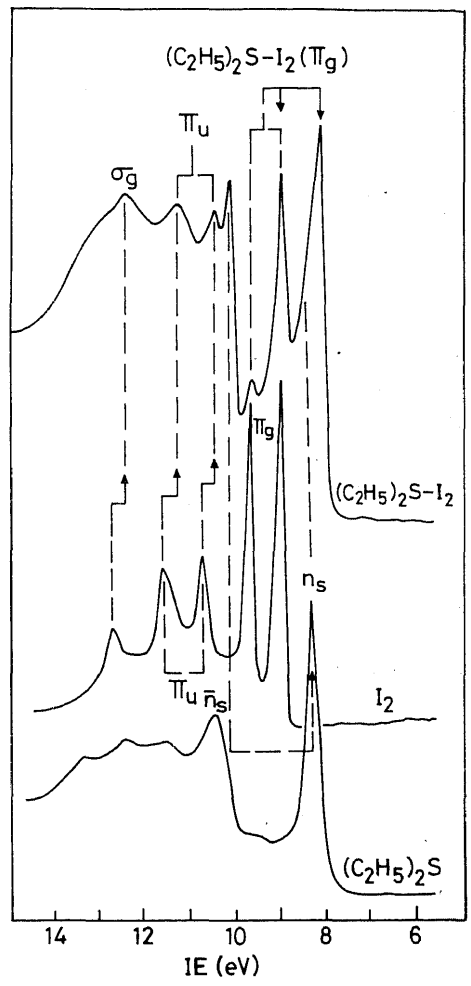

Figure 11. UVPES of diethyl sulphide, I_2 and their C–T complex.

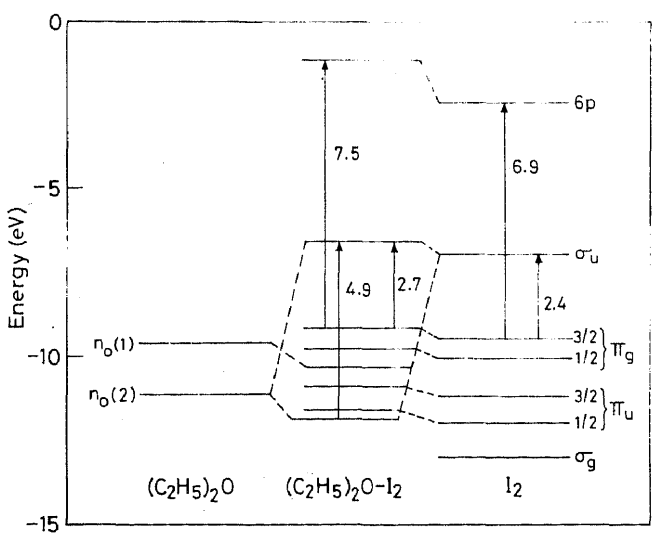

Figure 10. Electron states of ether, I_2 and their C–T complex.

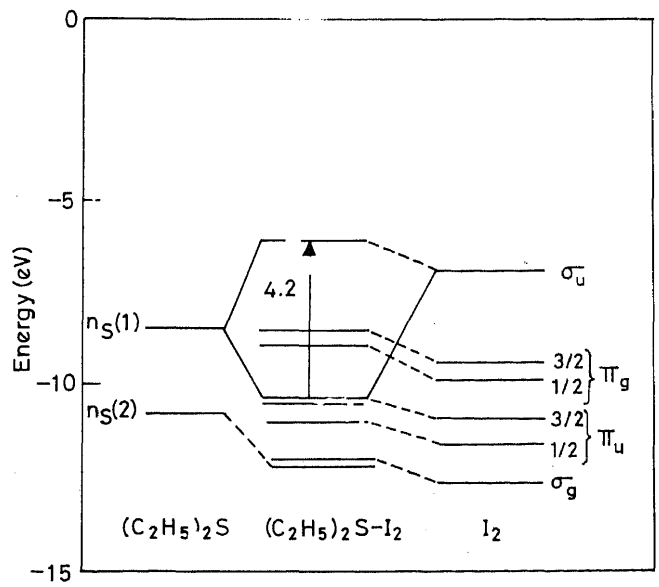

Figure 12. Electron states of diethyl sulphide–I_2 complex.

bonding is between π-type sulphur lone pair with σ_u of Br_2. Thus, in general, donors containing S, the highest occupied lone pair on sulphur that is bonding with σ^* of I_2, Br_2, Cl_2.

Strength of the C–T complexes formed is reflected in the amount of shifts in the ionization energies of MOs of donors and acceptors. Higher the strength, higher is the shift. Amines NH_3, CH_3NH_2, $(C_2H_5)_3N$ are also good donors where N has one lone pair electron. Unlike in the case of O and S containing ligands, bonding between amine and halogen is simple. Interaction is between the lone pair on nitrogen with σ_u of halogen[21].

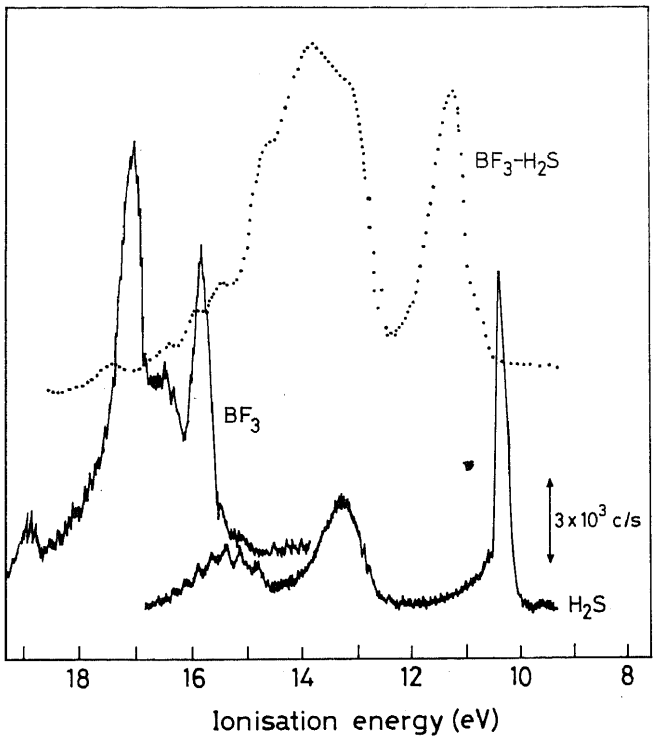

Figure 13. HeI UVPES of BF_3, H_2S and their complex.

Complexes with BF_3 and $TiCl_4$

BF_3 and $TiCl_4$ are Lewis acids. H_2O, H_2S, $(C_2H_5)_2O$ and all such Lewis bases combine with BF_3 to form 1 : 1 molecular complexes[22]. Photoelectron spectra of BF_3, H_2S and H_2S–BF_3 are shown in Figure 13. An entirely new set of MOs is formed on complexation[23]. Similar studies on the complexes of SO_2 with amines have been reported by us[24]. $TiCl_4$ is found to form 1 : 2 addition complexes with diethyl ether and diethyl sulphide[25]. $TiCl_4$ is a tetrahedral molecule. Nearly octahedral type of molecule is formed when reacted with diethyl ether. Geometry of the complexes formed is shown in Figure 14 *a* and *b*. Here again, the σ-type lone pair of oxygen in ether is interacting with Ti whereas π-type $n_s(1)$ of S interacts with Ti. UVPES and EELS of these complex molecules have been studied and the electron energy level diagrams have been obtained as shown in Figure 14 *c*.

Future trends

With all these advances in MO calculations, occupied energy levels of complex molecules are predicted reasonably well but excited state energies are difficult to predict accurately. Accurate prediction of charge transfer excitation energy has not yet been possible

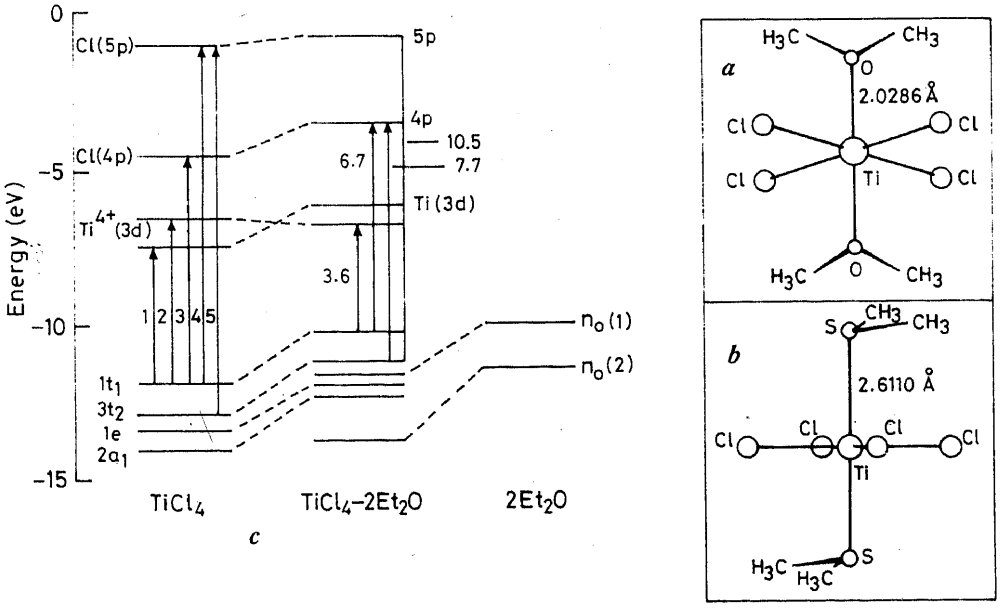

Figure 14. (*a*) and (*b*) optimized geometry of $TiCl_4$ complexs. (*c*) Electron states of $TiCl_4$–2 $(C_2H_5)_2O$ complex.

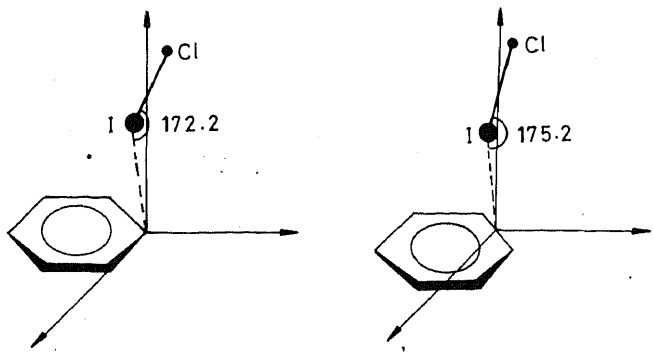

Figure 15. Optimized geometry of C_6H_6-ICl complex.

except by Mulliken's empirical method. Benzene–iodine C–T complex was studied 50 years ago but energy levels of C_6H_6–I_2 have not been obtained by UVPES, EELS or MO calculations so far. This is because interaction energy is small and the complex dissociates before it is brought to the photon beam collision chamber in the UVPES experiment. It is essential to have a nozzle expansion cell where beams of benzene and I_2 molecules are brought and made to collide with HeI photon. However, we have studied C_6H_6–ICl complex recently. The optimized geometry of the complex is shown in Figure 15. MO calculations show that bonding is between centre of a C–C π bond or one of the carbon and the σ_u of ICl.

Electronic excitation by EELS is a versatile experimental technique and the method is much less used mainly because of non-availability of commercial instruments. Relative intensities of excitation peaks, electron impact excitation cross-section of molecules have not been studied. UVPES and EELS coupled with MO calculation is also an ideal subject of basic research. High resolution UVPES and EELS coupled with higher level MO calculations would provide more insight on the bonding in molecules.

Photoelectron–photoion mass spectrometric study would give mass of the complex molecule directly. Almost no study of obtaining mass of a C–T complex molecule exists in the literature. Primary mass peak of the complex molecule followed by the fragments of the molecular ion would give direct information on the dissociation characteristics of C–T complexes.

Conclusions

UVPES, EELS and MO calculations of typical C–T complexes have shown that they are new molecules formed out of monomers. Complete electron energy level diagram of a C–T complex can be obtained by this combination of experiments and theory. Electron states involved in the C–T excitation have been determined in typical C–T complexes and the method is general enough to study a large number of C–T complexes in gaseous state.

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