ELECTRONIC STRUCTURES OF ELECTRON DONOR–ACCEPTOR COMPLEXES: RESULTS FROM ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY AND MOLECULAR ORBITAL CALCULATIONS*

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ABSTRACT

HeI photoelectron spectra of 1:1 electron donor–acceptor complexes are discussed in the light of molecular orbital calculations. The complexes discussed include those formed by BH_3, BF_3 and SO_2. Some systematics have been found in the ionization energy shifts of the complexes compared to the free components and these are related to the strength of the donor–acceptor bond. HeI spectra of hydrogen bonded complexes are discussed in comparison with results from MO calculations. Limitations of such studies as well as scope for further investigations are indicated.

INTRODUCTION

Spectroscopy, thermodynamics and related aspects of a large variety of electron donor–acceptor (EDA) complexes have been investigated in detail over the past several years [1–4]. The complexes studied span a wide spectrum of interaction energies anywhere from very weak contact pairs to strong addition compounds (n–v complexes), the π–π, π–σ and n–σ complexes with interaction energies in the 10–30 kJ mol^{-1} range falling in between. Although most studies pertain to complexes in solution phase, there have been some studies in the vapour phase, especially of the electronic absorption spectra. Spectral properties of these complexes have generally been explained on the basis of Mulliken's charge-transfer (CT) theory [1] involving ground and excited states formed by a linear combination of no-bond and dative structures. Hydrogen bonding also represents a class of EDA interactions [1]. Thus, the complex between ether and HCl can be treated as an n–σ complex, as can the complex between ether and iodine. Electronic structures of EDA complexes have been

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investigated by a few workers using UV photoelectron spectroscopy (UVPES). Combined with molecular orbital (MO) calculations, orbital ionization energies (IEs) obtained from UVPES provide a direct means of probing the electronic structures of these complexes. Although these investigations have not been as extensive as desirable, the information available to date has been quite instructive and clearly points out the need for further experimentation as well as better theoretical calculations on intermolecular interactions.

In this paper we present the UVPES of EDA complexes as interpreted on the basis of MO calculations, primarily based on the work carried out in our laboratory. The systems to be discussed include the traditional EDA complexes, mainly the strong addition compounds formed between Lewis acids and Lewis bases and some hydrogen bonded complexes.

EXPERIMENTAL AND METHODS OF CALCULATION

UV photoelectron spectroscopic measurements involve the free flow of the species under investigation into the ionization region where it undergoes photoionization on impact with HeI radiation. This method has proved adequate for the study of strong $n-v$ complexes. Cooled sample inlet tubes, effusive nozzles as well as molecular beam techniques are useful for the study of EDA complexes especially if the interaction is weak or moderate. We employed a laboratory-built spectrometer, with a conventional sample inlet system. The main problem faced in these studies relates to the quantitative removal of features due to the free donor and acceptor components. A number of methods of data analysis are being used to isolate the spectrum of the species of interest from a given spectrum of the mixture, the common method being the spectrum stripping procedure [5]. We have generally employed the spectrum stripping procedure in our studies.

Hartree–Fock energies of the complexes were computed in the frame work of the SCF-LCAO-MO methods using the GAUSSIAN 86 program [6] and unless otherwise specified, the 3-21G basis set. Monomer geometries were fully optimized and used as input for the calculations on the complexes.

RESULTS AND DISCUSSION

Donor–acceptor complexes

Historically, complexes of electron donors with halogen acceptors, especially iodine, were the first to be investigated. While the literature abounds with information on the thermodynamics and electronic spectroscopy of such complexes [3], there is little information on their electronic structures as studied by UV photoelectron spectroscopy in the vapour phase. UV photoelectron spectra of bromine with alkylamines [7] show that the lone pair orbitals of the

amine donors were stabilized while the σ and π levels of Br_2 were destabilized as expected from the charge-transfer mechanism. HeI spectra of I_2 complexes of diethyl ether and diethyl sulphide [8] show that the π orbital IEs of I_2 decrease while the n orbital IEs of the donor molecules increase on complexation, consistent with the CT theory.

Addition compounds or the strong $n-v$ complexes between Lewis acids and Lewis bases have been studied in somewhat greater detail in recent years by employing HeI PE spectroscopy. HeI spectra of addition compounds of BH_3 with NH_3, amines, CO and PF_3 were investigated by Lloyd and Lynaugh [9], who assigned the various bands on the basis of CNDO as well as some ab initio calculations. Generally, the lone pair orbitals of the amines were found to be stabilized due to the increased positive charge on the nitrogen atom; by ~ 3 eV in amine–borane compounds. Shifts are much smaller in $BH_3 \cdot PH_3$, possibly due to back donation. In all these compounds agreement between the calculated and observed ionization energies are good. This is not, however, true of $BH_3 \cdot CO$ where back donation is likely to be much more significant probably requiring a consideration of correlation effects.

We have examined the HeI spectrum of the 1:1 addition compound of BH_3 and H_2S [10]. The prominent features in the spectrum are at 9.7, 11.9, 12.8, 14.1 and 16.6 eV. According to the MO calculations (STO-3G basis set), the highest occupied molecular orbital (HOMO) is the sulphur lone pair with an eigenvalue of 10.1 eV. Since the sulphur lone pair donates electrons, the orbital must stabilize on complexation. It is therefore likely that the first band in the spectrum of the complex at 9.7 eV is due to π_{B-H} orbital ionization. The band at 11.9 eV is assigned to the n_S orbital, the corresponding lone pair IE in free H_2S being 10.4 eV. The band at 12.8 eV is assigned to the $B \cdots S$ dative bond. The next two bands are assigned to π_{S-H} orbitals. These assignments of the orbital IEs of $BH_3 \cdot H_2S$ provide a more rational electronic structure of the complex compared to the earlier ones made strictly in conformity with the calculated level scheme [10].

We could obtain the HeI spectrum of the 1:1 addition compound $BH_3 \cdot H_2O$ [10] by the interaction of B_2H_6 with traces of H_2O in the collision chamber. The spectrum showed features at 9.7, 10.6, 11.8, 13.2 and 14.4 eV. The first two features appear at much lower IEs than those of water (12.6 eV) and B_2H_6 (11.9 eV) and can only be due to the complex (note that there can be no new gaseous product in the reaction of B_2H_6 with H_2O). Based on 3-21G calculations we have assigned the first two features due to the π_{B-H} orbitals and the 11.8 eV band to the σ_{B-O} orbital. Figure 1 compares the orbital energy diagrams of the complexes of BH_3 with H_2O, CO and H_2S, in order to highlight the similarities and differences.

We have studied the HeI spectra of $n-v$ type adducts of BF_3 with H_2O, CH_3OH, $(C_2H_5)_2O$ and CH_3CN; in addition, we have also examined the spectra of complexes of BF_3 with NO and H_2S [11–13]. Figure 2 shows the HeI
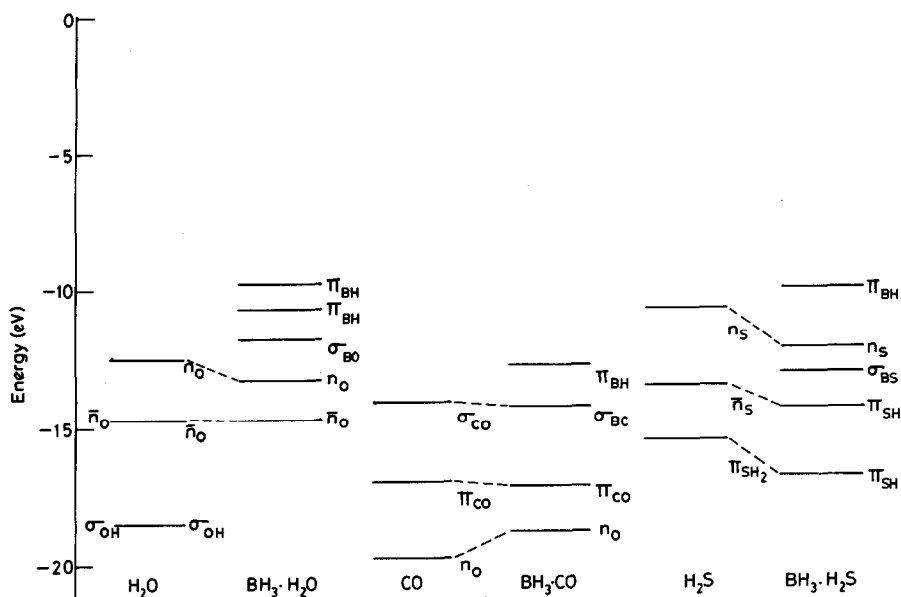
Fig. 1. Correlation diagram of the experimental vertical ionization energies of complexes of BH_3 with H_2O, CO and H_2S. Note that the dissociation energies of the complexes decrease in the same order.
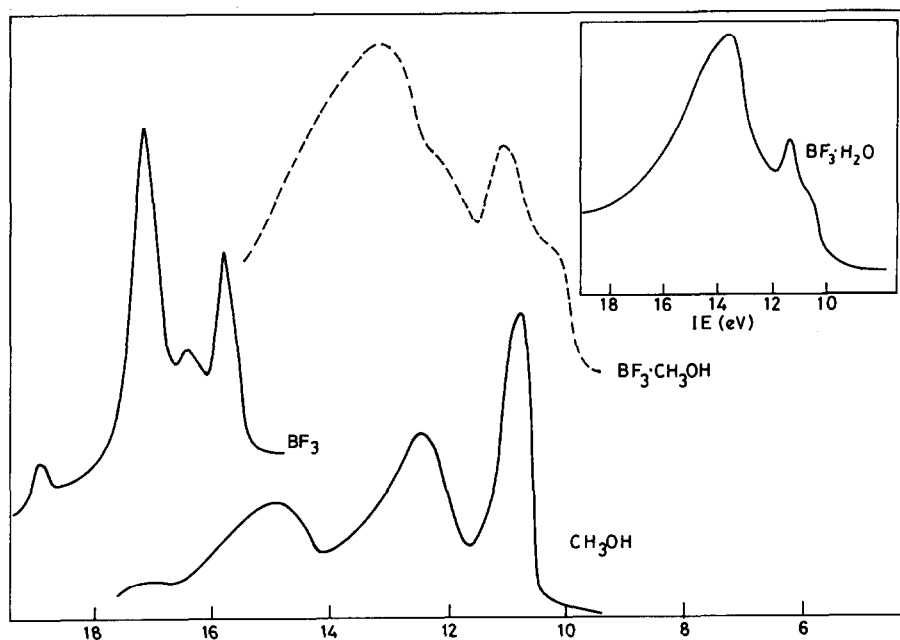

Fig. 2. HeI spectra of BF_3, CH_3OH and $BF_3 \cdot CH_3OH$. In the inset the HeI spectrum of $BF_3 \cdot H_2O$ is shown.

spectra of the adducts of BF_3 with CH_3OH and H_2O along with the spectra of free BF_3 and CH_3OH. The spectra of the addition compounds show features distinctly different from those of the free donor and acceptor molecules. Thus, the spectrum of $BF_3 \cdot CH_3OH$ shows no band in the region where BF_3 has its characteristic features. Furthermore, there are new features not present in the spectra of the free donor molecules including some at ionization energies lower than those of the donors. The dissociation energy of the $BF_3 \cdot H_2O$ complex obtained from MO calculations (3-21G basis) is 144 kJ mol^{-1}. Table 1 lists the various vertical IEs along with assignments based on the orbital ordering obtained from the MO calculations on $BF_3 \cdot H_2O$. The spectrum of $BF_3 \cdot (C_2H_5)_2O$ is similar to that of $BF_3 \cdot CH_3OH$ giving rise to the lowest IE features due to n_F orbital ionizations. The spectrum of $BF_3 \cdot CH_3CN$ shows bands at 10.9, 11.6, 13.4, 14.3 and 15.3 eV of which the first four arise from n_F orbital ionizations. The feature at 15.3 eV is partially attributable to σ_{BN} orbital ionization. This dative bond ionization energy is comparable to that of the $BF_3 \cdot (C_2H_5)_2O$ adduct (15.9 eV).

The HeI spectrum of the 1:1 adduct of BF_3 and NO [13] shows the first feature at 11.4 eV is due to the valence orbital of NO (compared to 10 eV in free NO). The calculated dissociation energy of the complex (3-21G basis) is 16 kJ mol^{-1}, a value much lower to that of the addition compounds of BF_3 with $(C_2H_5)_2O$ and CH_3CN. The fluorine orbitals in $BF_3 \cdot NO$ are shifted by 2.5 eV compared to free BF_3, unlike in $BF_3 \cdot H_2O$ and such complexes where the shifts are much larger. Table 2 lists the calculated orbital energies with the observed ionization energies of the $BF_3 \cdot NO$ complex. We have also studied the HeI spectra of $BF_3 \cdot H_2S$ and $BF_3 \cdot CS_2$ where the interaction energies are close to thermal energy. In $BF_3 \cdot H_2S$, the first two features at 11.6 and 13.4 eV are associated with the sulphur orbitals (n_S and π_{SH} respectively); the n_S orbital IE of the complex is higher than the free H_2S value. The σ_{BS} IE is observed at 16.1 eV. MO calculations show that the complex is stable, though much weaker

TABLE 1

Occupied orbital energies and assignments of a few addition compounds of BF_3

$BF_3 \cdot H_2O$			$BF_3 \cdot CH_3OH$ I_v (eV)	$BF_3 \cdot (C_2H_5)_2O$ I_v (eV)
I_v (eV)	Scaled (0.9ϵ) STO-3G energy	Assignment		
10.7	9.9–10.1	n_F	10.7	9.9
11.4	10.3–10.8	n_F	11.3	10.6
13.4	13.0	n_O	12.7	12.6
14.0–16.0	13.7	π_{BF_3}	13.4	14.0
	14.1	σ_{CO}		15.9
	16.5	π_{BF_3}		16.5

TABLE 2

Occupied orbital energies and assignments of $BF_3 \cdot NO$

I_v (eV)	Scaled (0.9ϵ) energy (3-21G)	MO character
11.4	11.4	σ_{NO}
13.4	15.6	n_F
14.2	15.9	π_{NO}
15.3	16.1–16.4	n_F
16.8	16.3	π_{NO}
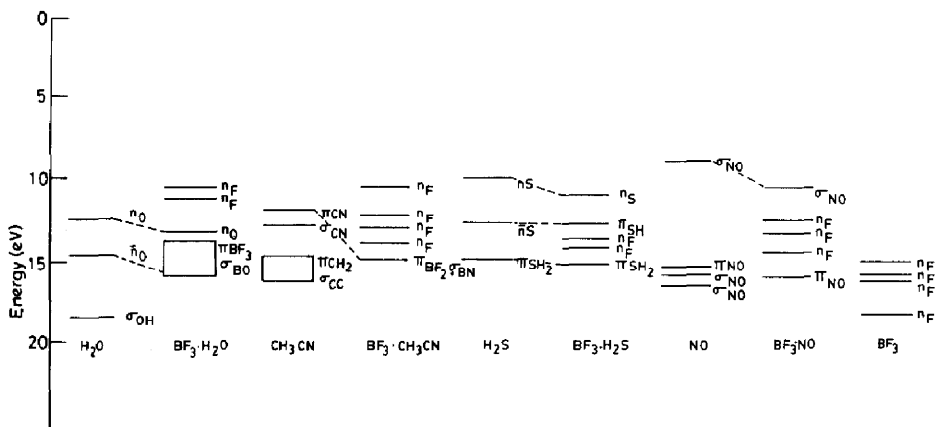
Fig. 3. Correlation diagram of experimental vertical ionization energies of a few complexes of BF_3 with the free components.

than $BF_3 \cdot H_2O$. MO calculations however show that the dissociation energy of $BF_3 \cdot CS_2$ is very low (2 kJ mol^{-1}). Accordingly, the HeI spectrum of the complex shows only slight shifts in the ionization energies compared to those of the component molecules.

Figure 3 compares the orbital energy diagrams of a few complexes of BF_3 in order to highlight certain systematics. The most important feature that emerges from the study is that the magnitude of the shift in the fluorine orbital ionization energy of BF_3 in the 1:1 complex depends on the strength of the donor–acceptor interaction (Table 3). Thus, the shifts are large in the addition compounds of BF_3 with H_2O, CH_3OH, $(C_2H_5)_2O$ and CH_3CN, and rather small in the weak complexes $BF_3 \cdot NO$ and $BF_3 \cdot H_2S$. It is close to zero in the contact pair $BF_3 \cdot CS_2$. This observation clearly indicates that the shift in the n_F orbital IE is determined by the magnitude of the electron donation by the donor which in turn also determines the dissociation energy of the complex (Table 3).

Addition compounds of SO_2 have been a subject of investigation for the past

TABLE 3

Some important features of BF$_3$ complexes

Electron donor	Experimental shift in the fluorine orbital ionization energy $\Delta I_v(n_F)$ (eV)	Calculated (3-21G) dissociation energy $-\Delta E$ (kJ mol^{-1})
H$_2$O	5.2	144
CH$_3$CN	4.3	82
NO	2.5	16
H$_2$S	1.7	22
CS$_2$	0.4	2

TABLE 4

Occupied orbital energies and assignments of (CH$_3$)$_3$N·SO$_2$

I_v (eV)	Calculated (3-21G) MOs	
	$-\epsilon$ (eV)	Character
9.8	10.06	$n_S(n_O)$
10.3	11.36	n_O
10.8	11.58	n_N
11.5	11.89	π_{SO}
13.0–13.5	14.36–14.75	$\pi_{CH_2}, \sigma_{CN}, \pi_{CH_2}$
15.0	15.70–15.79	$\pi_{SO}, \sigma_{SO}, \sigma_{NS}$

several years. The HeI spectrum of (CH$_3$)$_2$O·SO$_2$ complex was reported by Carnovale et al. [14] who assigned the various bands based on STO-3G, 3-21G and other calculations. These workers found that the effect of complexation is to increase the ionization energies of the ether moiety by ~ 0.4 eV and to decrease the SO$_2$ IEs by ~ 0.9 eV. We have investigated [15] the HeI spectra of a few complexes of SO$_2$ with several electron donors as well as of complexes where SO$_2$ acts as an electron donor via the oxygen as in SO$_2$·BF$_3$ and SO$_2$·HCl.

The 1:1 complex between (CH$_3$)$_3$N and SO$_2$ shows characteristic features at 9.8, 10.3, 10.8 and 11.5 eV. Table 4 lists the assignments of the UVPES bands of (CH$_3$)$_3$N·SO$_2$. Our calculations give a dissociation energy, ΔE, of 62 kJ mol^{-1} and the increase in the Mulliken population of SO$_2$, Δq(SO$_2$), of 0.15 which is comparable to that reported by Sakaki et al. [16]. The HeI spectrum of (C$_2$H$_5$)$_3$N·SO$_2$ is very similar to that of (CH$_3$)$_3$N·SO$_2$. HeI spectra of these two amine–SO$_2$ complexes reveal that the ionization energies of the donor and the acceptor are shifted considerably due to complexation. In the case of (CH$_3$)$_3$N·SO$_2$, the n_N orbital of the amine is stabilized by 2.4 eV while the n$_S$(n$_O$) orbital of SO$_2$ is destabilized by 2.7 eV. In the case of (C$_2$H$_5$)$_3$N·SO$_2$,

the shifts are slightly larger; the shifts of n_N and $n_S(n_O)$ are 2.5 and 3.0 eV respectively, indicating a slightly higher strength of the donor–acceptor interaction.

Studies on the HeI spectra of $(C_2H_5)_2O \cdot SO_2$ and $(C_2H_5)_2S \cdot SO_2$ complexes also reveal the relation between the strength of the donor–acceptor interaction and the shift in the lone pair IE of the donor. Thus, in the ether complex n_O (ether) orbital IE is 11.4 eV compared to 9.6 eV of free ether. In the sulphide complex the n_S orbital IE is 9.7 eV, 1.1 eV higher than that of free sulphide. The calculated $S \cdots O$ and $S \cdots S$ distances are 2.40 and 3.32 Å respectively. The sulphide complex has considerably lower dissociation energy than the ether complex.

Figure 4 shows the experimental orbital energy level scheme for the $SO_2 \cdot$ donor complexes. In general, the shift in the IE of the lone pair orbital of the donor molecule, ΔI_v, in these complexes varies monotonically with the magnitude of the donor–acceptor interaction; the increase in the Mulliken population of SO_2, $\Delta q(SO_2)$, and the dipole moment (μ) also vary in the same direction. This is true whether SO_2 acts as an electron donor or as an acceptor. The main conclusions from our investigations of SO_2 complexes are summarized in Table 5.

Fig. 4. Correlation diagram of the experimental vertical ionization energies of the complexes of SO_2 with the free components.

TABLE 5

Some important features of SO$_2$ complexes

	$-\Delta E^a$ (kJ mol^{-1})	$\Delta q(SO_2)^a$	ΔI_v^b (eV)	μ^a (D)
Donor				
(CH$_3$)$_3$H	62	+0.15	2.4	6.4
(C$_2$H$_5$)$_2$O	26	+0.08	1.8	6.0
(C$_2$H$_5$)$_2$S	3	+0.03	1.1	5.5
Acceptor				
BF$_3$	82	−0.16	3.7	7.6
HCl	31	−0.06	0.1	6.3

^{a}3-21G calculations. ^{b}Experimental values.

Hydrogen bonded dimers

Although vibrational spectra, thermodynamics and other aspects of hydrogen bonded dimers have been investigated extensively, studies of the vapour phase UV photoelectron spectra of these systems have been limited. We shall examine some of the important results of these studies related to their electronic structures. The HeI photoelectron spectrum of water dimer [17] shows the first two vertical IEs at 12.1 and 13.2 eV, with a threshold IE of 11.1 eV suggesting that the ground-state dimer cation geometry differs considerably from that of the neutral dimer. Ab initio configuration interaction (CI) calculations [18] show that the dimer cation may be represented as an H$_3$O$^+$···OH$^•$ complex. The neutral dimer, with a shallow potential minimum shows a wide Franck–Condon region. The large difference in the geometries of the neutral dimer and its cation as well as the wide Franck–Condon region of the initial dimer seem to be responsible for the large difference between the threshold and vertical IEs. Furthermore, the observed threshold IE is still 0.5 eV higher than the adiabatic value which cannot be observed due to the small Franck–Condon factor. The HeI spectrum of NH$_3$ dimer [19] shows a single IE at 10.1 eV due to the near equivalent nitrogen lone pair orbitals of NH$_3$ subunits. This implies that the dimer is symmetric, a conclusion also supported by detailed CI calculations [20].

Carboxylic acid dimers have been a subject of active investigation both by theory and experiment. HeI spectra of formic acid recorded at fairly high pressures [21, 22] show characteristic features of the dimer. The spectrum shows considerable interaction of the monomer based states of σ symmetry, but little interaction of the π states. The σ splitting arises mainly from through space interaction. In Table 6, we compare the first few important IEs of the formic acid dimer with the orbital energies obtained from HAM/3 and ab initio 4-31G calculations [21]. The HAM/3 method involves a diffuse removal of half an

TABLE 6

Comparison of experimental vertical ionization energies with the ab initio (3-21G) and HAM/3 eigenvalues for formic acid dimer [24]

I_v (eV)	HAM/3[a]	3-21G (0.92ϵ)	Character
11.3	11.50	11.92	n_O
12.0	11.98	12.56	n_O
12.6	12.68	12.44	π_{C-O}
12.7	12.70	12.69	π_{C-O}
13.9	13.97	14.29	σ_{C-O}
15.0	14.65	15.46	σ_{C-O}
15.5	15.86	16.16	π_{C-O}
15.6	15.89	16.36	π_{C-O}

[a]For 0.66 e diffusely removed.

electron giving rise to lower IEs than the monomer. The values listed in Table 6, obtained by increasing the diffusely increased charge to 0.66 e for the dimer, show fair agreement with the observed values. The 4-31G values are scaled by an empirical factor of 0.92. The calculations are generally satisfactory, but do not take into account correlation effects which could separate the n and π states further apart than the theoretical predictions. HeI spectra of the dimers of acetic an trifluoroacetic acids and the mixed dimer between the two have also been studied using a high pressure nozzle inlet system [23]. The spectra are consistent with the SPINDO calculations. In the case of acetic and trifluoroacetic acid dimers the calculations show considerable resonance interaction between the in-plane monomer orbitals. SPINDO calculations on the mixed dimer overestimate the IE shifts following dimerization.

HeI spectra of the complexes of HF with $(CH_3)_2O$ and $(CH_3)_2S$ [24] show that the hydrogen bond stabilizes the non-bonding electrons of the donor atom by 1.0 and 0.8 eV respectively. It appears that the electrostatic effects play a major role in determining the strength of the complex. The observed IEs are in fair agreement with the results from the STO-3G, 4-31G and other calculations. The charge-transfer accompanying complexation and electronic relaxation following the ionization seem to cause the lowering IEs of the π_F orbitals (by 1.6 eV in the case of ether and 1.2 eV in the case of sulphide). Neglect of electronic relaxation effects is found to have no influence on the spectral assignments of these systems based on Koopmans approximation.

The HeI spectrum of the $(CH_3)_2O \cdot HCl$ complex [25] has also been studied. The IEs of n_O of the donor increases by 0.6 eV while that of HCl decreases by 1.0 eV on hydrogen bonding. The σ_{CH_3} IEs are increased by 0.4 eV and of σ_{CO} by 0.7 eV. MO calculations indicate that the shifts arise from an inductive transfer of electron density of about 0.05 e from the ether to HCl. The stabili-

zation of the n_O orbital of the ether results from a through-space inductive effect associated with the hydrogen bond.

We studied the HeI PE spectrum of $(C_2H_5)_2O \cdot HCl$ complex. Figure 5 shows the HeI spectra of HCl, $(C_2H_5)_2O$, and a mixture of the two (the inset shows the spectrum of the 1:1 heterodimer obtained after stripping). The experimentally observed IEs are listed in Table 7 along with the orbital assignments based on MO calculations. The eigenvalues of the complex are sensitive to the $O \cdots H$ bond length, just as in the case of the $(CH_3)_2O \cdot HCl$ complex [25]. We have found the eigenvalues of $BF_3 \cdot SO_2$ complex [15] to be similarly sensitive to the length of the donor–acceptor bond. At the optimized geometry of $(CH_3)_2O \cdot HCl$, the HOMO is one of the nearly degenerate π_{Cl} orbitals. An examination of the HeI spectrum shows, on the other hand, that the first band is associated with n_O ionization. While at shorter $O \cdots H$ distances (1.50–1.60
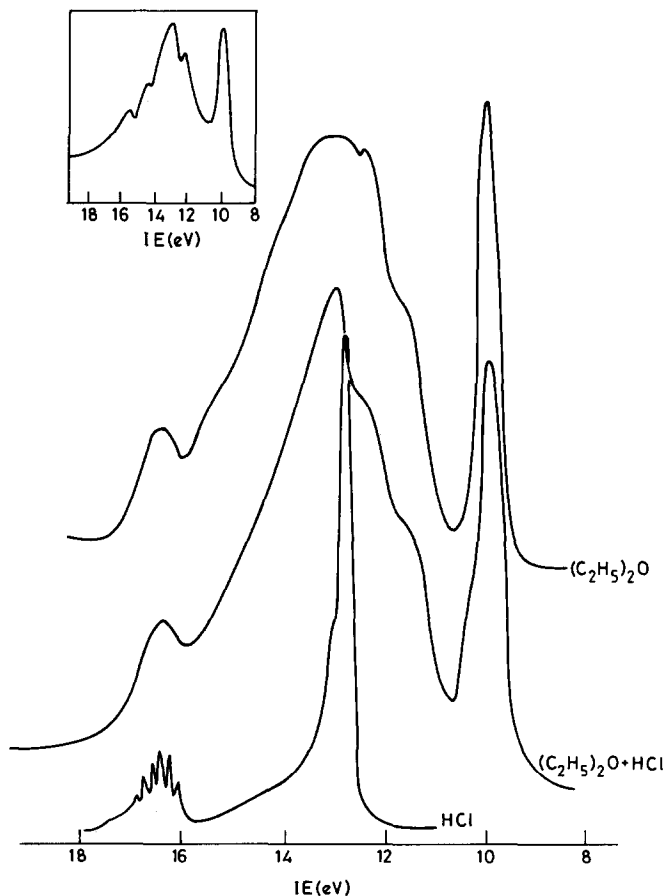

Fig. 5. HeI spectra of $(C_2H_5)_2O$, HCl and a mixture of $(C_2H_5)_2O$ and HCl. The spectrum of the pure heterodimer obtained after stripping is shown in the inset.

TABLE 7

Occupied orbital energies and assignments of diethyl ether·HCl complex

I_v (eV)	Calculated (3-21G) MOs	
	$-\epsilon$ (eV)	Character
9.8	11.47	n_O
12.0	12.00,12.01	π_{Cl}
13.5	13.04–14.27	n_O, π_{CH_3}
14.3	14.54–15.29	σ_{CC}, π_{CH_3}
15.6	15.89	σ_{HCl}

Å) π_{Cl} is the HOMO, at longer $O \cdots H$ distances (1.85–1.95 Å) n_O becomes the uppermost occupied orbital. Since a shorter $O \cdots H$ distance would not be consistent with the experimental spectrum, we used a distance of 1.90 Å for the final calculation keeping all other values the same as the optimized geometry. This $O \cdots H$ distance is also close to the experimental value found in hydrogen bonded complexes of HCl. Assignments based on such a calculation show that the π_{Cl} and σ_{HCl} ionization energies are lowered by 0.8 and 0.6 eV on hydrogen bond formation; the n_O ionization is increased by 0.2 eV. The HeI spectrum of the $SO_2 \cdot HCl$ complex [15] referred to earlier (see Table 5) shows features at 12.3, 12.6, 13.0, 13.4 and 14.5 eV assigned to n_{Cl}, $n_S(n_O)$, n_O, n_O and σ_{HCl} orbital ionizations, respectively.

CONCLUDING REMARKS

There is little doubt that HeI PE spectroscopy of 1:1 EDA complexes has provided considerable insight into their electronic structures when interpreted in the light of MO calculations. Hitherto, studies have been essentially restricted to n–v type addition compounds. There is considerable scope for investigating the vapour phase UVPES of π–σ and n–σ complexes of halogens formed with π and lone pair donor molecules as well as π–π complexes such as TCNE-aromatics and trinitrobenzene-aromatics. We hope to undertake these studies soon. There is a need for studies employing better resolution in order to resolve the ionizations from closely lying orbitals.

UVPE spectra of the complexes discussed in this paper have all been interpreted on the basis of MO calculations. The agreement obtained between experimental IEs and the eigenvalues from theory depends on the type of calculation. In general, the agreement obtained from ab initio calculations is quite satisfactory. How good a particular basis set is, however, depends on the nature of the complex under investigation. The validity of assignments based on orbital IEs from MO calculations are sometimes questionable, since the Koopmans approximation breaks down in certain instances. In the case of weak

interactions, the orbitals show negligible mixing on adduct formation [26] and the effects of complexation on the IEs are dominated by electrostatic effects. In such cases electronic relaxation effects are negligible and the PE spectral assignments based on the Koopmans approximation are truly valid.

The Morokuma decomposition scheme of partitioning the interaction energy [27] can also be applied to separate the electrostatic, exchange, polarization and charge-transfer components of the ionization energy shifts associated with complexation. Calculations on $(CH_3)_2O \cdot HF$, $(CH_3)_2S \cdot HF$ and $(CH_3)_2O \cdot HCl$ complexes [28] have shown that for the $(CH_3)_2O$ and $(CH_3)_2S$ moieties, the electrostatic effect of the approaching HF or HCl molecule is the dominant factor in determining the shift. In the case of π_F and π_{Cl} ionizations, electrostatic relaxation and charge-transfer effects seem to play an important role. It is noteworthy that in weak to medium hydrogen bonds, the electrostatic term dominates the interaction energy, charge transfer becoming important only in strong hydrogen bonded complexes [29].

In weakly interacting systems, the adiabatic IEs may not correspond to the minimum of the potential energy surface. Thus, in the $1^2A''$ state of the H_2O dimer [17], there is a large difference between the experimentally observed adiabatic IE and that obtained from theory. The potential minimum is not observed in the experiment probably because of the poor Franck–Condon factor. There is considerable scope for studies of weak interactions as in van der Waals complexes by combined use of UVPES and theoretical calculations. To date, there are hardly any reports on this most interesting topic. Dehmer and Dehmer [30, 31] have reported the photoelectron spectra of Ar_2, Kr_2 and Xe_2 and determined the dissociation energies of the bound excited states of these dimer cations. The observed dissociation energies were significantly higher than those predicted from theory. The dimer of N_2 has been studied by Carnovale et al. [32] by HeI spectroscopy. The first vertical IE of the dimer is 0.4 eV lower than the monomer, the spectral features of higher clusters being similar to those of the dimer. It would be most worthwhile to study other van der Waals complexes such as $Ar \cdot HCl$ and $Ar \cdot CO_2$ by UVPES.

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