Chem. Soc. Rev., 1991, **20**, 477–502

Studies of Molecular Interactions in the Vapour Phase by Ultraviolet Photoelectron Spectroscopy: Electronic Structures of Donor–Acceptor Complexes Including Hydrogen Bonded Dimers and van der Waals Molecules†

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1 Introduction

Chemists have been interested in the study of molecular complexes for the past few decades. A proper classification of molecular complexes in terms of the molecular orbitals (MOs) of the electron donor and acceptor units involved in the interaction was first proposed by Mulliken.[1] The strength of interaction in molecular complexes varies anywhere between 65 kJ mol^{-1}, as in strong addition compounds formed between Lewis acids and Lewis bases (*e.g.* BF_3.diethylether, $BH_3.CO$), to thermal energies as in very weak contact pairs or van der Waals molecules (*e.g.* benzene.CCl_4, $Ar.CO_2$). Complexes formed between π-donors (*e.g.* benzene, naphthalene) and σ-acceptors (*e.g.* I_2) as well as those between *n*-donors (*e.g.* ethers and amines) and σ-acceptors fall between these two extremes. Addition compounds between Lewis bases and Lewis acids are also called *n–v* complexes where *v* stands for a vacant-orbital acceptor (*e.g.* BF_3). Hydrogen bonded dimers can also be considered to belong to the n–σ or the π–σ variety of donor–acceptor complexes. Although a large number of donor–acceptor complexes have been investigated by optical spectroscopy and other techniques,[2,3] experimental investigations of their electronic structures were limited until recently. Most of the reports in the literature pertain to electronic spectra obtained primarily in the condensed phase. Information on the orbital energies and the electronic transitions in the vapour phase is, however, necessary to understand properly the electronic structure of molecular complexes. Ultraviolet photoelectron (UVPE) spectroscopy employing HeI or HeII radiation provides a direct means of obtaining the energies of valence orbitals involved in complexation when used in conjunction with results from molecular orbital calculations. *X*-Ray photoelectron spectroscopy, on the other hand, gives information on the core levels which are not perturbed markedly by donor–acceptor interaction; Hillier[4] reviewed the literature in this area a few years ago.

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† Contribution No. 787 from the Solid State and Structural Chemistry Unit.

* To whom correspondence should be addressed.

[1] R. S. Mulliken and W. B. Person, 'Molecular Complexes', Wiley-Interscience, New York, 1969.

[2] L. A. Curtiss and M. Blander, *Chem. Rev.*, 1988, **88**, 827.

[3] C. N. R. Rao, S. N. Bhat, and P. C. Dwivedi, *Appl. Spectrosc. Rev.*, 1971, **5**, 1.

[4] I. H. Hillier in 'Molecular Interactions', ed. H. Ratajczak and W. J. Orville-Thomas, Vol. 2, John Wiley, New York, 1981.

In the last few years, detailed investigations have been carried out on the electronic structures of molecular complexes in the vapour phase by employing UV photoelectron spectroscopy In this article, we present a comprehensive account of the important results from these studies, primarily based on the work carried out in our laboratory The various systems discussed are addition compounds between Lewis acids and Lewis bases (*n–v* complexes), *n–σ* complexes and hydrogen bonded dimers More interestingly, we describe the UV photoelectron spectroscopic studies of van der Waals complexes such as Xe • • • HCl Study of such weak interactions has been made possible by the use of molecular beam techniques[5] Wherever possible, we shall also discuss the electronic transitions in the complexes obtained from vapour phase electron energy loss spectroscopy

2 Experimental Aspects

The UV photoelectron spectroscopic measurement involves the kinetic energy analysis of the photoelectrons ejected from the various orbitals of the sample on impact with HeI or HeII radiation A description of the experimental set-up has been given in a recent article by Westwood[6] in this journal The sample is generally prepared outside and leaked into the spectrometer through a variable leak valve This method is adequate for the study of strong donor–acceptor complexes (*e g* $BF_3 H_2O$) In the case of weak interactions as in van der Waals complexes or some of the hydrogen bonded dimers (*e g* HCl dimer, methanol dimer), it becomes necessary to produce relatively high concentrations of the species in the spectrometer *in situ* by means of a molecular beam One of the important characteristics of a molecular beam relevant in the UVPE experiment is the unidirectional motion with a small velocity dispersion corresponding to low temperatures of relative translational motion Because of the low value of the Knudsen number, clusters are formed in the nozzle and the molecular beam helps to maintain their life time sufficiently long

Procedures are described in the literature for recording the UVPE spectra of strong complexes The sample is generally prepared under vacuum by mixing appropriate amounts of the constituents The complex so prepared is collected in a glass bulb which is then connected directly to the spectrometer For weakly interacting systems one records the spectra with varying compositions of mixtures of the components Seeding techniques (dilution with an inert gas to enhance clustering) are also used in some instances One of the problems encountered in all such studies is that the spectra contain features due to the unreacted constituents along with those of the complex One can obtain the spectra of pure complexes in a few cases (*e g* $BF_3 CH_3OH$) Most of the time, however, it becomes necessary to eliminate the contributions from the component units in order to delineate the features due to the complex The most commonly employed technique is the spectrum stripping procedure[7] Where the spectral

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[5] A Kasntrowitz and J Grey *Rev Sci Instrum* 1951 **22** 328

[6] N P C Westwood *Chem Soc Rev* 1989 **18** 317

[7] J B Peel and G D Willett *J Chem Soc Faraday Trans 2* 1975 **71** 1799

features due to the complex and the free molecules are distinct, the subtraction procedure is rather straightforward. In cases where the features due to the complex are weak, the subtraction procedure has to be carried out with utmost care.

Interpretation of UVPE spectra of molecular species is greatly facilitated by the use of appropriate quantum chemical calculations to yield orbital ordering. While Koopmans' approximation[8] holds good in most instances, enhanced relaxation and correlation effects result in major disagreement between calculated and observed orbital ordering. The usefulness of a particular basis set for calculations depends on the nature of the complex. Smaller basis sets often exaggerate the interaction energy and the eigen values. Expansion of the basis set does not necessarily bring about a significant improvement in the geometry of the complexes. For complexes involving first-row elements, the 3-21G basis set is fairly adequate. For those involving second-row elements, inclusion of *d* and *p* polarization functions becomes necessary. Inclusion of correlation brings the calculated energies close to the experiment, but the orbital ordering is seldom affected.

3 Lewis Acid–Lewis Base Complexes (*n*–*v* Complexes)

Thermodynamics and spectroscopic properties of the strong donor–acceptor (or addition compounds) have been adequately covered in the literature.[9,10] Dissociation energies of these complexes are of the order of 40 kJ mol^{-1} or higher. The large interaction strength of these complexes makes it easy to synthesize them. UVPE spectra of these complexes have been studied in some detail in the last few years and in what follows we shall discuss the complexes formed by BH_3, BF_3, $AlCl_3$, SO_2 and related molecules in detail.

A. Complexes of BH_3.–Borane, BH_3, is one of the simplest vacant orbital acceptors and the UVPE spectra of the complexes formed by BH_3 with NH_3 and CO were reported in the early 1970s by Lloyd and Lynaugh.[11,12] $BH_3.NH_3$ showed three features in the HeI region at 10.3, 13.9, and 17.8 eV. BH_3CO showed bands at 11.9, 14.1, 17.0, and 18.7 eV. The spectra were assigned on the basis of MNDO/2 and INDO calculations by Lloyd and Lynaugh. In these addition compounds, the first UVPE band is due to the highest lying *e* orbital of BH_3. Ionization from this orbital leads to Jahn–Teller splitting giving two peaks in the spectrum. The second band was attributed to the donor–acceptor (B $\cdots$ N or B $\cdots$ C) bond while remaining ionizations were due to the donor orbitals. It was found that on complexation, the 5σ orbital of CO is only slightly stabilized contrary to expectation. This suggests that along with the stabilizing effects

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[8] T. Koopmans, *Physica*, 1933, **1**, 104

[9] E. N. Gur'yanova, I. P. Gol'dshtein, and I. P. Romn, 'Donor Acceptor Bond', Halsted Press, New York, 1975.

[10] 'Molecular Complexes', ed. R. Foster, Vol. 1 and 2, Elek Science, London, 1973.

[11] D. R. Lloyd and N. Lynaugh, *Chem. Commun.*, 1970, 1545.

[12] D. R. Lloyd and N. Lynaugh, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 947.

Table 1 *Vertical ionization energies and assignments of* BH_3 H_2O (*from ref.* 13)

I_i[a] (eV) *from UVPES*	*Orbital energies* (eV) $(-\varepsilon)$	*Assignment*
9.7	11.7	π_{B-H}
10.6	11.8	π_{B-H}
11.8	15.2	$\sigma_{B \cdots O}$
13.2	17.5	n_O
14.4	20.2	$\bar{n}_O$

[a] Vertical ionization energy

arising out of the formation of the $B \cdots C$ σ bond, there is a compensating destabilization due to charge shifts. This charge shift is through the π back donation from the e orbital of BH_3 to the π^* orbital of CO. Lloyd and Lynaugh have also reported[12] the UVPE spectra of substituted amine boranes and $BH_3.PF_3$. The donor lone pair is stabilized by about 3 eV in the amine boranes. While the e orbitals of BH_3 are essentially unperturbed, the a_1 orbital of the donor loses its identity on complexation.

Complexes of BH_3 with H_2O and H_2S were recently investigated in this laboratory.[13] Extensive molecular orbital calculations have been reported in the literature on $BH_3.H_2O$. While this complex turns out to be stable from theory, experimental investigations are difficult since diborane hydrolyses on contact with water. We have obtained the UV photoelectron spectrum of $BH_3.H_2O$ by passing B_2H_6 through the collision chamber slightly contaminated with water vapour. In Figure 1 we show the UVPE spectra of H_2O and $BH_3.H_2O$. The spectrum of $BH_3.H_2O$ shows bands at 9.7 and 10.6 eV which are not due to either B_2H_6 or H_2O. These bands are assigned to the π_{BH} orbital. The orbital ordering predicted by the SCF/3-21G calculations is in agreement with the experiment. MO calculations yield a binding energy of 94 kJ mol^{-1} for the complex, in which the b_1 orbital of H_2O is involved in bonding. The H_3BO moiety is nearly tetrahedral with an overall symmetry of C_s. In Table 1 we list the experimental ionization energies of $BH_3.H_2O$ along with the assignments. We see that the IE of the oxygen lone pair is 13.2 eV, shifted by 0.6 eV on complexation.

The spectrum of $BH_3.H_2S$ is similar to that of $BH_3.H_2O$. In Figure 1 we have shown the spectra of H_2S and $BH_3.H_2S$. The spectrum of the complex is characterized by a low energy ionization at 9.7 eV lower than the first ionization energies of both B_2H_6 and H_2S. This band is assigned to the π_{BH} orbital of BH_3 although the SCF calculation at the minimum basis set level predicts it to be due to the sulphur lone pair. Since electron density is transferred from H_2S to BH_3 during the formation of the complex, H_2S ionizations should occur at higher energies than in the free molecule. Therefore, the lowest energy ionization can only be due to the π_{BH} orbital of the acceptor. The sulphur lone pair ionization is observed at 11.9 eV (it is at 10.5 eV in free H_2S) and the 12.8 eV band is due to

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[13] T Pradeep, C S Sreekanth, M S Hegde, and C N R Rao, *J Mol Struct*, 1989, **194**, 163

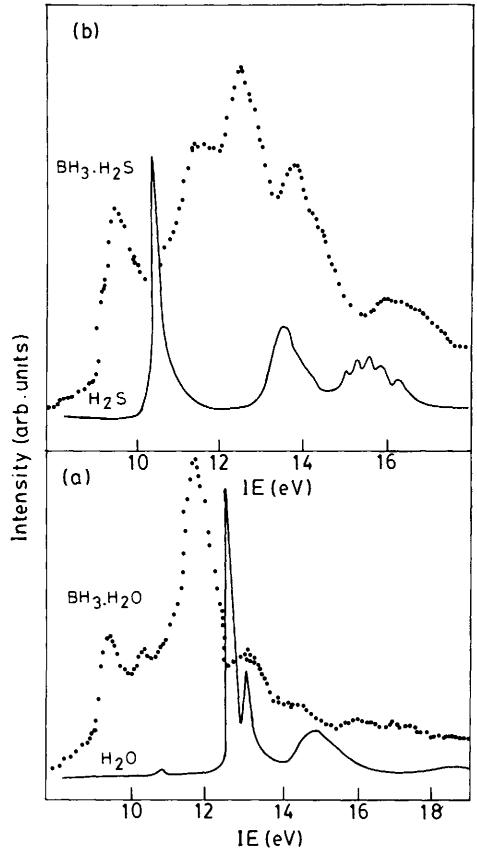

Figure 1 (*a*) HeI *photoelectron spectra of* H_2O *and* $BH_3.H_2O$. (*b*) *Spectra of* H_2S *and* $BH_3.H_2S$ (*from ref.* 13)

the S · · · B dative bond. It is noteworthy that in all the complexes of BH_3 discussed hitherto, the π_{BH} orbitals are the HOMOs. A similar situation obtains with BF_3 complexes (*vide infra*) where the lowest energy ionizations are from n_F orbitals.

UV photoelectron spectra of pyridine boranes[14] are similar to the strong complexes of BH_3 giving the lowest IE features due to the *e* orbitals of BH_3. Assignments made on the basis of MNDO/2 calculations showed that the a_2 and b_2 orbitals of the pyridines are stabilized by 0.9 and 1.4 eV respectively. The spectra show no evidence for π interaction between the pyridine ring and BH_3. The *e* orbitals of BH_3 do not show any splitting, indicating that these are not perturbed to any significant extent on complexation.

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[14] M. A. Weiner and M. Lattman, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 723.

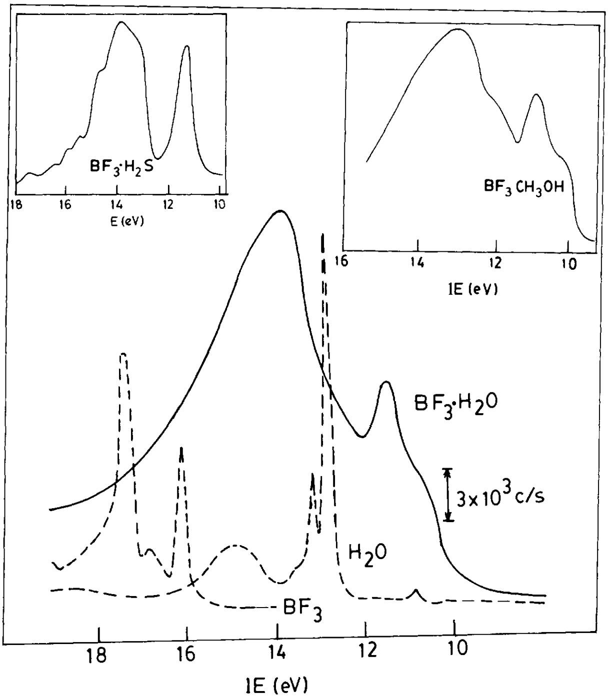

Figure 2 *UVPE spectra of* H_2O, BF_3, *and* $BF_3.H_2O$ (*from ref.* 15). *Spectra of* $BF_3.H_2S$ (*from ref.* 18) *and* $BF_3.CH_3OH$ (*from ref.* 15) *are shown in the insets*

The spectra of BH_3 complexes suggest a simple Lewis acid–Lewis base bonding in these systems. Significant back donation is observed only in the case of $BH_3.CO$. A consequence of donor–acceptor interaction is that the electron density from the donor lone pairs is delocalized to the acceptor unit. The magnitude of the stabilization of the donor lone pair is 1—3 eV. Covalent effects are negligible in determining the shift since the magnitude of the shift is similar for orbitals of varying symmetry.

B. Complexes of BF_3.—UVPE spectra of the strong complexes of BF_3 with H_2O, CH_3OH, $(C_2H_5)_2O$, and CH_3CN have been investigated recently in this laboratory.[15,16] The complexes of BF_3 with H_2O and CH_3OH have interaction energies of the order of 50 kJ mol^{-1} and are completely associated in the vapour phase. Figure 2 shows the photoelectron spectra of BF_3, H_2O, and the $BF_3.H_2O$ adduct. In the same figure, we also show the spectrum of $BF_3.CH_3OH$ for comparison. The spectrum of $BF_3.H_2O$ has characteristic features appearing at

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[15] T Pradeep, C S Sreekanth, and C N R Rao, *J Chem Phys*, 1989, **90**, 4704

[16] M C Durrant, M S Hegde, and C N R Rao, *J Chem Phys*, 1986, **85**, 6356

lower ionization energies than those of H_2O and BF_3. Computations on $BF_3.H_2O$ showed that the b_1 orbital of H_2O is involved in bonding. Based on MO calculations, the observed features have been assigned to the various orbitals as shown in Table 2. A noteworthy aspect is the extensive charge-transfer (of about 0.2 *e*) from the donor to the acceptor resulting in a reorganization of the orbitals and the shifting of the donor and acceptor IEs to higher and lower values respectively. The lowest IE is due to the n_F orbitals. The n_O orbital ionization occurs at 13.4 eV. Rest of the ionizations in the spectrum are due to π_{BF_3} orbitals.

Spectra of $BF_3.CH_3OH$, $BF_3.(C_2H_5)_2O$, and $BF_3.CH_3CN$ show features similar to those of $BF_3.H_2O$. A common feature in all these strong complexes is that the lowest IE is due to the n_F orbital of BF_3. The oxygen non-bonding orbital ionization energy is generally around 13 eV, just as in $BH_3.H_2O$.

One of the very first reports in the literature on the UVPE spectroscopy of donor–acceptor complexes of BF_3 was on the BF_3–amine systems by Lake.[17] These strong addition compounds are completely associated in the gas phase and can be prepared by direct mixing, Lake attributes the lowest ionization in the complexes to the B ••• N dative bond. Spectra of the strong complexes of BF_3 with various donor molecules discussed earlier, however, show that the HOMO in these complexes is that of fluorine. We therefore assign the lowest energy features in the BF_3–amine spectra to the non-bonding fluorine orbitals; the B ••• N and n_N orbital ionizations occur at considerably higher energies.

We shall now discuss the weak complexes of BF_3. SCF/3-21G calculations show that the $BF_3.H_2S$ complex[18] is weak with a binding energy of 22 kJ mol^{-1}. Accordingly the geometries of the component units do not undergo significant changes on complexation. In the optimized C_s structure, the BF_3 unit is nearly planar with a B ••• S distance of 3.0 Å. The spectrum of $BF_3.H_2S$ (inset of Figure 2) shows the first feature due to n_S orbital ionization. Features due to the fluorine lone pair orbitals occur only at 14.2 and 14.8 eV.

In Figure 3, we have shown the spectra[15] of NO and a mixture of BF_3 and NO. The mixture spectrum has characteristic features of the complex along with those of the free components. The spectrum of the pure complex obtained after stripping is shown in the inset of the same figure. The lowest energy feature is associated with the σ_{NO} orbital ionization followed by those due to the n_F orbitals. The calculated binding energy of the complex is 16 kJ mol^{-1}, much lower than the other BF_3 complexes discussed hitherto. The geometries of the constituents are not affected significantly on complexation. The weakest interaction that has been studied is that between BF_3 and CS_2 wherein calculations show that the strength of the interaction is of the order of thermal energy. The spectrum shows the first feature due to the sulphur lone pair. The fluorine orbitals undergo negligible shift on complexation.

One of the important results of the study of the BF_3 complexes[15] is that the

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[17] R. F. Lake, *Spectrochim. Acta*, 1971, **27A**, 1220.

[18] T. Pradeep, C. S. Sreekanth, M. S. Hegde, and C. N. R. Rao, *Chem. Phys. Lett.*, 1988, **151**, 499.

Table 2 *Vertical ionization energies and assignments of the addition of compounds of* BF_3 *with* H_2O *and* CH_3OH *(from T. Pradeep* et al. *ref.* 15)

$BF_3.H_2O$				
I_v (eV)	*Scaled* (-0.9ε) *orbital energy* (eV)	*MO*	$BF_3.CH_3OH$ I_v (eV)	*Assignment*
10.7	13.9—14.3	$7a''$, $14a'$, $6a''$	10.7	n_F
11.4	14.5—14.8	$13a'$, $12a'$, $5a''$	11.3	n_F
13.4	15.8	$11a'$	12.7	n_O
14.0—16.0	17.1	$4a''$	13.4	π_{BF_3}
–	17.4	$10a'$	—	$\sigma_{B\cdots O}$
–	17.9	$9a'$	—	π_{BF_3}

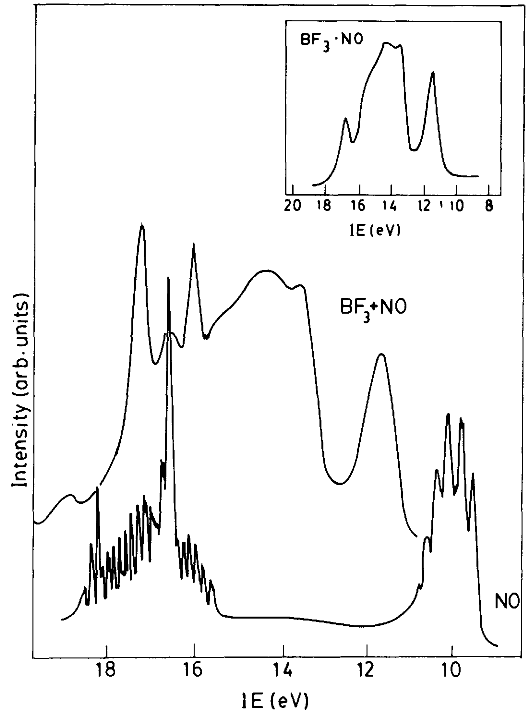

Figure 3 *UVPE spectra of* NO *and a mixture of* NO *and* BF_3. *Spectrum of the* $BF_3.NO$ *complex obtained after stripping is shown in the inset (from ref.* 15)

magnitude of the charge-transfer essentially determines the magnitude of the shift in the ionization energies. The amount of charge-transfer (CT) also determines the interaction strength. In Figure 4 we have plotted the shift in the n_F orbital ionization energies of the complexes against their theoretical binding energies. Although there is no study carried out on the partitioning of the ionization

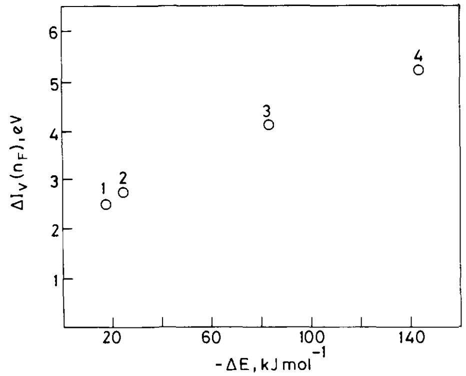

Figure 4 *Plot of the experimentally observed shift in the fluorine lone pair ionization energy, ΔI_v with the theoretical binding energy, ΔE of the* BF_3 *complexes.* (1) $BF_3{\cdot}NO$, (2) $BF_3.H_2S$, (3) $BF_3.CH_3CN$, *and* (4) $BF_3.H_2O$

energy shift (into charge-transfer, electrostatic, polarization, exchange repulsion, *etc.*) of strong electron donor–acceptor complexes, charge-transfer appears to be the most important component.

C. Complexes of $AlCl_3$ and $GaCl_3$.—One of the features of the chemistry of the group III elements is that while BCl_3 is monomeric, the analogous chlorides of Al, Ga, and In are dimeric at ambient temperatures. They become monomers only at elevated temperatures. The experimental stabilization energy[19] of the $AlCl_3$ dimer is 126 kJ mol^{-1}. Al, Ga, and In halides have been studied by variable temperature photoelectron spectroscopy[20,21] and the spectra assigned on the basis of *ab initio* calculations using Gaussian type functions. Experimental as well as theoretical results show that the bridging chlorine orbital IE is higher than in the monomers. The study also suggests the involvement of the metal *d* orbitals in the bonding of the dimers.

Complexes of $AlCl_3$ and $GaCl_3$ with electron donors are stronger than those of BF_3 or BH_3. UVPE spectra of the complexes of $AlCl_3$ and $GaCl_3$ with diethylether and diethylsulphide have been recently examined.[22] In Figure 5 we show the spectrum of the $AlCl_3$.ether complex along with the spectrum of ether. The spectra of the ether complexes are characterized by intense bands around 11 eV. Calculations on the model compound $AlCl_3.H_2O$ show that the first few features in the HeI spectrum are due to chlorine lone pairs followed by the π_{Al-Cl} and σ_{Al-Cl} orbitals. The oxygen lone pairs are predicted to be shifted to rather

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[19] K. Brendhaugen, A. Haaland, and D. P. Novak, *Acta Chem. Scand.*, 1974, **28A**, 45.

[20] M. F. Lappert, J. B. Pedley, G. J. Sharp, and N. P. C. Westwood, *J. Electron Spectrosc.*, 1974, **3**, 237.

[21] M. F. Lappert, J. B. Pedley, G. J. Sharp, and M. F. Guest, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 539.

[22] T. Pradeep, M. S. Hegde, and C. N. R. Rao, *J. Mol. Struct.*, 1991, **247**, 217.

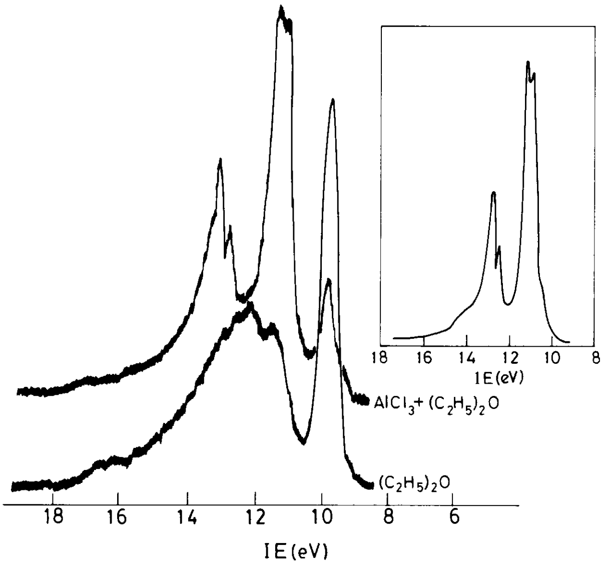

Figure 5 HeI *photoelectron spectra of* $(C_2H_5)_2O$ *and a mixture of* $AlCl_3$ *and* $(C_2H_5)_2O$ *Spectrum of the* $AlCl_3$ $(C_2H_5)_2O$ *complex is shown in the inset* (*from ref* 22)

Table 3 *Vertical ionization energies and assignments of* $AlCl_3$ $(C_2H_5)_2O$ (*from ref* 22)

I_t (eV)	*Scaled* 3-21G* *orbital energy* $(-0\ 9\varepsilon)$ (eV)	*Assignment*
10 5	10 6	n_{Cl}
10 9	10 9	n_{Cl}
11 2	11 0—11 4	n_{Cl}
12 5	12 2	$\pi_{Al\ Cl}$
12 9	12 4	$\pi_{Al\ Cl}$
13 9	13 7	$\sigma_{Al\ Cl}$

high energies The calculations show that as in BF_3 H_2O, the b_1 orbital is involved in bonding In Table 3 we show the assignments of the UVPE spectrum on the basis of calculations carried out on $AlCl_3$ H_2O All the features are due to the chlorine or the Al–Cl orbitals It is noteworthy that the lone pair IEs of the acceptor unit in the complex are shifted to lower values compared to those of the free molecules These shifts are 1 5 and 1 8 eV for $AlCl_3$ and $GaCl_3$ complexes respectively

Spectra of the sulphide complexes of $AlCl_3$ and $GaCl_3$ show that the HOMO is the sulphur lone pair Calculations on the model compound $AlCl_3$ H_2S at 6-31G*, 3-21G*, and 3-21G levels suggest that the first few ionizations are from the n_{Cl} orbitals followed by π_{AlCl} and σ_{AlCl} (with n_S and $\bar{n}_S$ falling in between), a level scheme which is not in agreement with the experiment Such situations are

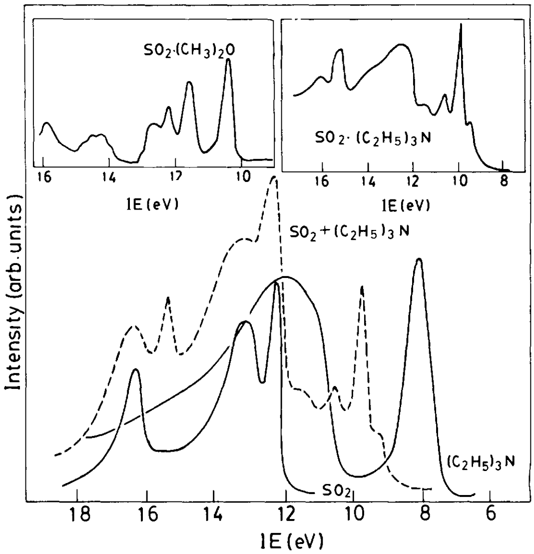

Figure 6 HeI *photoelectron spectra of* SO_2, $(C_2H_5)_3N$, *and a mixture of the two. Spectra of* $SO_2.(C_2H_5)_3N$ *(from ref. 27) and* $SO_2.(CH_3)_2O$ *(from ref. 26) are shown in the insets*

encountered, though not frequently, in molecular photoelectron spectroscopy. This is due to the inability of the basis sets to describe bonding, particularly in complexes involving the second-row elements. A similar situation was encountered in the case of $BH_3.H_2S$ as well.

D. Complexes of SO_2.—Although complexes between SO_2 and amines such as $(CH_3)_3N$ have received considerable attention both in theory and experiment,[23–25] there has been no definitive effort to study experimentally the electronic structure of SO_2 complexes. Bonding in these complexes involve the π^* LUMO of SO_2. Carnovale *et al.*[26] have studied the UVPES of $(CH_3)_2O.SO_2$. Several complexes of SO_2 with the *n* donors, $(CH_3)_3N$, $(C_2H_5)_3N$, $(C_2H_5)_2O$, and $(C_2H_5)_2S$, have been investigated recently in this laboratory.[27] MO calculations show that the donor–acceptor bond is approximately perpendicular to the SO_2 molecular plane in all these complexes.

In Figure 6, we show the photoelectron spectra of $(C_2H_5)_3N$, SO_2, and a mixture of the two. In the inset of the same figure we have given the spectrum of the 1:1 complex obtained after stripping. The spectrum of $(CH_3)_2O.SO_2$, taken from the work of Carnovale *et al.*,[26] is also provided in this figure for purpose of

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[23] W. E. Byrd, *Inorg. Chem.*, 1962, **1**, 672.

[24] S. D. Christian and J. Grundnes, *Nature*, 1967, **214**, 1111.

[25] J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, 1968, **90**, 2234.

[26] F. Carnovale, M. K. Livett, and J. B. Peel, *J. Chem. Phys.*, 1986, **85**, 4304.

[27] T. Pradeep, C. S. Sreekanth, M. S. Hegde, and C. N. R. Rao, *J. Am. Chem. Soc.*, 1989, 111, 5058.

Table 4 *Vertical ionization energies and assignments of* $(CH_3)_3N.SO_2$[a] *(from T. Pradeep* et al. *ref. 27)*

		Calculated MOs	
I_v (eV)	$-\varepsilon$ (eV)	*Character*	*MO*
9.8	10.0	$n_S\ (n_O)$	$21a'$
10.3	11.4	n_O	$12a''$
10.8	11.6	n_N	$20a'$
11.5	11.9	π_{SO}	$11a''$
13.0—13.5	14.4—14.8	$\pi_{CH_2}, \sigma_{CN}, \pi_{CH_2}$	$10a'', 19a', 9a''$
15.0	15.7—15.8	$\pi_{SO}, \pi_{SO}, \sigma_{N \cdots S}$	$18a, 8a'', 17a'$
16.2	16.7, 17.1	π_{CH_2}, π_{CH_2}	$7a'', 16a'$

[a] *The* $(C_2H_5)_3N.SO_2$ *complex gives bands at* 9.5, 9.9, 10.6, 11.5, 13.2, 15.2, *and* 16.0 eV *due to* $n_S(n_O)$, n_O, n_N, π_{SO}, σ_{CN}, $\sigma_{N \cdots S}$ *and* π_{CH_2} *ionizations respectively*

comparison. The spectrum of $(C_2H_5)_3N.SO_2$ shows characteristic bands at 9.5, 9.9, and 10.6 eV. Of these, the first two bands are clearly due to the shifted n_S and n_O respectively. Different features in the spectra of amine–SO_2 complexes are assigned in Table 4. MO calculations show that the binding energy ΔE and the charge-transfer from the donor molecule to SO_2, $\Delta q(SO_2)$, vary with the donor in the order $(CH_3)_3N > (C_2H_5)_2O > (C_2H_5)_2S$. Accordingly, the spectra of the ether and the sulphide complexes show smaller shifts of the ionization energies of the parent units. Calculations on $(CH_3)_2O.SO_2$ at the SCF/3-21G* level show the first ionization at 10.4 eV to be due to the oxygen lone pair of the ether, showing an increase of 0.36 eV on complexation. Calculations overestimate the ionization energy shifts due to higher estimates of the polarity, leading to an overestimation of the electrostatic contribution to the IE shift.

In addition to the *n*-donor–SO_2 complexes, we have investigated the $BF_3.SO_2$ complex, where SO_2 acts as a donor.[27] Calculations at the SCF/3-21G level predict a binding energy of 81.5 kJ mol^{-1} for the complex. The eigen values of this complex are sensitive to the $O \cdots B$ bond length. At the optimized geometry (with a $O \cdots B$ distance of 1.71 Å), the HOMO is the oxygen lone pair. However, at slightly lower $O \cdots B$ distances (1.60 Å), the HOMO is the fluorine lone pair. An examination of the HeI spectrum (Figure 7) shows that the low IE features are associated with the fluorine lone pairs just as in other strong complexes of BF_3 such as $BF_3.H_2O$. We have assigned the different features based on the orbital ordering predicted at this $O \cdots B$ bond length.

Studies of the SO_2 complexes show that the experimental shift in the IE of the lone pair orbital of the donor molecules varies with the binding energy as well as the charge-transfer to SO_2. The dipole moment also varies similarly. In Figure 8 we have shown the plot of the shift in the lone pair IE of the donor against the binding energy as well as the charge-transfer to SO_2. The plot is linear showing the proportionality. This behaviour holds whether SO_2 acts as a donor or as an acceptor. Although the calculations exaggerate the IEs, agreement with the experiments is generally good.

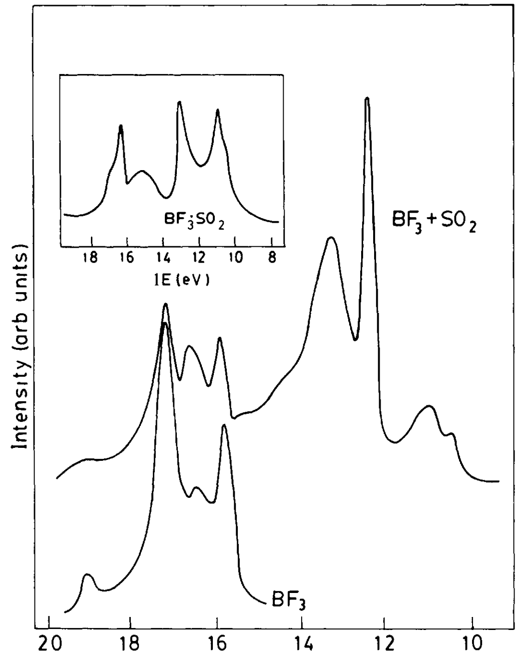

Figure 7 *UV photoelectron spectra of* SO_2 *and a mixture of* SO_2 *and* BF_3. *Spectrum of the complex is shown in the inset (from ref. 27)*

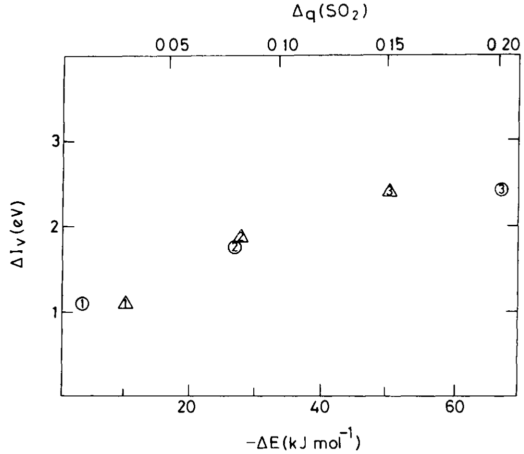

Figure 8 *Plot of the shift in the lone pair orbital ionization energy of the donor,* ΔI_v, *against the binding energy,* ΔE, *of the complex (open circles). Plot of* ΔI_v *against the increase in the Mulliken population of* SO_2, $\Delta q(SO_2)$ *(open triangles) is also shown.* (1) $(C_2H_5)_2S.SO_2$, (2) $(C_2H_5)_2O.SO_2$, and (3) $(C_2H_5)_3N.SO_2$

4 Complexes of Halogens

Compared to the n–v complexes, there have been very few UVPES studies on the n–σ complexes of halogens although a real understanding of such molecular complexes started with halogen–donor complexes.[1] Utsunomiya *et al.*[28] reported the UVPE spectra of complexes of bromine with alkyl amines. These workers have assigned the various features to the shifted donor n_N and the acceptor σ_{4p} and π_{4p} orbitals. While the n_N orbitals show a shift to higher IE, the σ_{4p} and π_{4p} orbitals shift to lower IEs. The results support the charge-transfer mechanism of complex formation. The magnitude of the shifts of the σ_{4p} and the n_N bands are nearly equal and are larger than the π_{4p} band; the π^*_{4p} band shows only negligible shift. This insensitivity of the π^*_{4p} band is explained in terms of the compensation between two effects: the increase in the electron density on bromine and the destabilization of the Br–Br bond. While the former effect destabilizes the orbital, the latter stabilizes it by decreasing the antibonding character.

A study of the electron states of the n–σ complexes of iodine was carried out in this laboratory.[29] The donors studied were diethylether and diethylsulphide. Figure 9 shows the HeI PE spectra of iodine, diethylether, and the complex. The $\pi_{g_{3/2}}$ and $\pi_{g_{\frac{1}{2}}}$ ionizations are decreased by about 0.2 eV while the n_O orbital IE of ether is increased by 0.9 eV on complexation. Since the sulphide.I_2 complex is stronger than the ether.I_2 complex (the ΔH values are $-37\,\mathrm{kJ\,mol^{-1}}$ and $-16\,\mathrm{kJ\,mol^{-1}}$ respectively), the shifts in the former are greater.

5 Hydrogen Bonded Dimers

A. Dimers of H_2O, NH_3, and H_2S.—Dimers of water and ammonia are by far the two best known examples of hydrogen bonded systems. There have been innumerable reports in the literature on the thermodynamic, spectroscopic, and structural aspects of these dimers.[30] Both the dimers are relatively weak with dissociation energies[2] of about $12\,\mathrm{kJ\,mol^{-1}}$. Conventional photoelectron spectroscopic methods are not adequate to examine the dimers. Using a nozzle beam source, Tomoda *et al.*[31] have studied the UVPES of $(H_2O)_2$ and we show the spectrum in Figure 10. They obtained two ionization energies of the water at dimer 12.1 and 13.2 eV. Both these IEs are due to the lone pair oxygen orbitals. Although the difference between the vertical IEs of the monomer and the dimer is small (0.5 eV) the difference in the adiabatic IEs is large (1.5 eV). This implies that the geometries of the water dimer and the cation are quite different. This was later confirmed by configuration interaction (CI) calculations.[32] These calculations show that the potential minimum of the dimer cation is far removed from the Franck–Condon region, suggesting that the adiabatic IE obtained from UVPES is only an upper estimate.

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[28] U. Utsunomiya, T. Koboyashi, and S. Nagakura, *Chem. Phys. Lett.*, 1976, **39**, 245.

[29] C. S. Sreekanth, M. S. Hegde, and C. N. R. Rao, *Spectrochim. Acta*, 1987, **43A**, 473.

[30] P. Hobza and R. Zahradnik, *Chem. Rev.*, 1988, **88**, 871.

[31] S. Tomoda, Y. Achiba, and K. Kimura, *Chem. Phys. Lett.*, 1982, **87**, 197.

[32] S. Tomoda and K. Kimura, *Chem. Phys.*, 1983, **82**, 215.

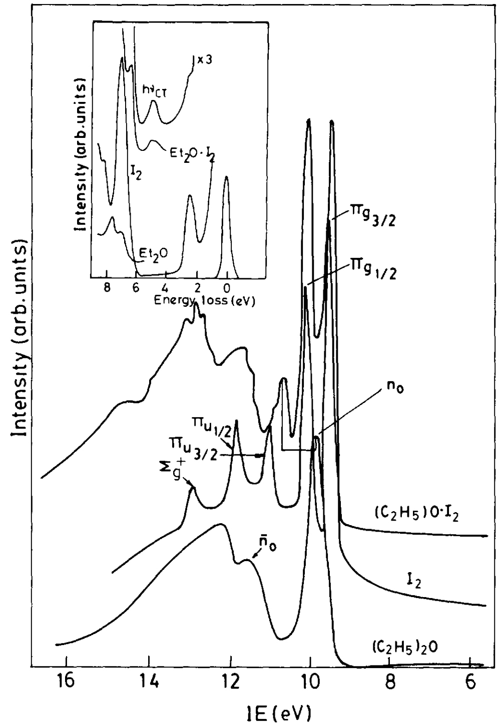

Figure 9 HeI *photoelectron spectra of* I_2, $(C_2H_5)_2O$, *and the* $I_2.(C_2H_5)_2O$ *complex (from ref.* 29). *The electron energy loss spectra of these molecules are shown in the inset (from ref.* 58)

Ab initio MO calculations on the NH_3 dimer favour a classical structure with a linear N–H • • • N linkage,[2] and microwave spectroscopy[33] suggests a non-classical structure. Recent CI calculations of Latajka and Scheiner[34] show that the potential minimum corresponds to the symmetric structure, the linear structure being only $1.6\,kJ\,mol^{-1}$ higher in energy. The photoelectron spectrum[35] of the NH_3 dimer obtained with a pulsed nozzle source shows only one ionization at 10.1 eV due to the lone pair. This implies that the dimer is symmetric, in accordance with the CI calculations.[34] The small value of the dipole moment obtained from the microwave studies may be due to asymmetric van der Waals vibrations.

The dimer stability of H_2S is lower than that of H_2O. Calculations at the SCF/6-31G* level show the binding energy to be only $3.8\,kJ\,mol^{-1}$ (compared to $23.4\,kJ\,mol^{-1}$ for the water dimer).[30] The photoelectron spectra of H_2S at different nozzle stagnation pressures obtained by us recently (Figure 10) shows

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[33] D. D. Nelson, G. T. Fraser, and W. Klemperer, *J. Chem. Phys.*, 1985, **83**, 6201.

[34] Z. Latajka and S. Scheiner, *J. Chem. Phys.*, 1984, **81**, 407.

[35] F. Carnovale, J. B. Peel, and R. G. Rothwell, *J. Chem. Phys.*, 1986, **85**, 6261.

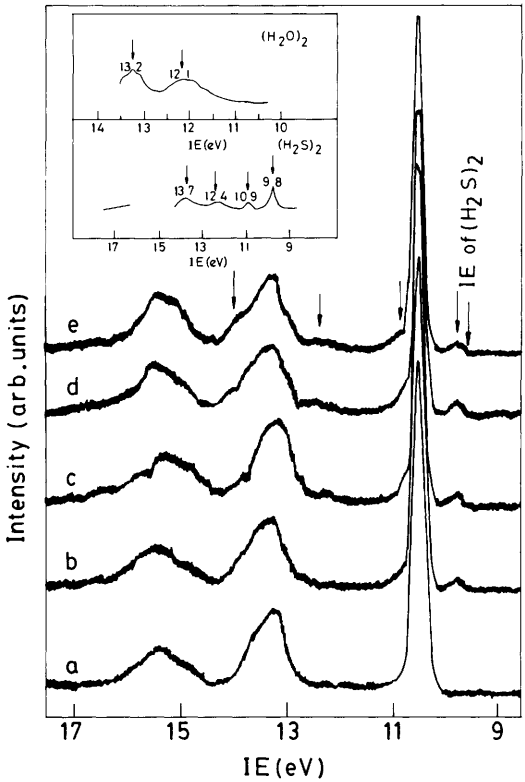

Figure 10 HeI *photoelectron spectra of* H_2S *at different stagnation pressures (from ref.* 36). *The stagnation pressure increases from* (*a*) *to* (*e*). *The spectrum marked* (*a*) *is due to the monomer. The new features due to the dimer are marked by arrows. The spectrum of the* H_2S *dimer is shown as an inset. The spectrum of the* H_2O *dimer (from ref.* 31) *is also shown as an inset. Vertical IEs of the dimers are indicated*

six bands due to the dimer.[36] The adiabatic IE obtained from UVPES (9.56 eV) is close to the photoionization value (9.59 eV).[37] Assignments on the basis of SCF/6-31G* calculations show a simple donor–acceptor interaction in this dimer. The experiment as well as calculations show significant distortion in the dimer geometry on ionization.

B. Dimers of Carboxylic Acids.—The formic acid dimer is an example of a classic type of hydrogen bonding characterized by the cyclic structure and the high values of the association constant as well as the association enthalpy. Carboxylic acid dimers were the first hydrogen bonded systems studied by UVPE spectroscopy. By cooling the ionization region of the spectrometer, Thomas[38] obtained the spectra of homo- and hetero-dimers of carboxylic acids. The spectra

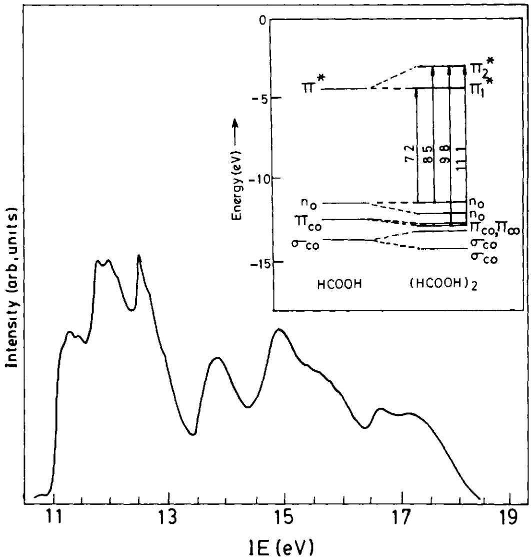

Figure 11 HeI *spectrum of formic acid dimer* (*from ref.* 40). *A partial energy level scheme of the dimer constructed using the UVPES and EELS data is shown in the inset of the figure* (*from ref.* 62)

showed IE shifts of less than 0.5 eV on complexation. While the IEs of the electron donor unit increased, those of the acceptor decreased. The UVPE spectrum of formic acid dimer has also been studied by Tomoda *et al.*[39] and Carnovale *et al.*[40] The results from these studies are similar in the energy range below 16.5 eV. In Figure 11 we show the spectrum of the formic acid dimer obtained by Carnovale *et al.*[40] using a nozzle source incorporated into a double chamber UVPE spectrometer. The dimer is characterized by features at 11.3, 12.0, 12.6, and 12.7 eV of which the first two are due to the *n* levels and the others to the π levels. An analysis of the spectrum shows strong σ–σ interaction leading to the splitting of the IEs (up to 1.1 eV). The σ–σ interaction essentially arises from a through-space mechanism; the π–π interaction seems to be weak. The study by Tomoda *et al.*[39] gives the lowest estimate of the dissociation energy of the ground state dimer ion to be 1.0 ± 0.1 eV. Assignments of the bands in the UVPE spectrum of formic acid dimer as listed in Table 5.

Carnovale *et al.*[41] have studied the HeI spectra of the dimers of acetic and trifluoroacetic acids as well as the hetero-dimer between the two. The results

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[36] T. Pradeep and C. N. R. Rao, *Chem. Phys. Lett.*, in press.

[37] H. F. Prest, W.-B. Tzeng, J. M. Brom, Jr., and C. Y. Ng, *J. Am. Chem. Soc.*, 1983, **105**, 7531.

[38] R. K. Thomas, *Proc. R. Soc. London Ser. A.*, 1972, **331**, 249.

[39] S. Tomoda, Y. Achiba, K. Nomoto, K. Sato, and K. Kimura, *Chem. Phys.*, 1983, **74**, 113.

[40] F. Carnovale, M. K. Livett, and J. B. Peel, *J. Chem. Phys.*, 1979, **71**, 255.

[41] F. Carnovale, T. H. Gan, and J. B. Peel, *J. Electron Spectrosc.*, 1980, **20**, 53.

Table 5 *Vertical ionization energies and assignments of formic acid dimer (from ref.* 40)

	Calculated MOs[a]	
I_v (eV)	$-\varepsilon$ (eV)	*MO*
11.3	11.9	$10b_u$
12.0	12.6	$10a_g$
12.6	12.4	$2a_u$
12.7	12.7	$2b_g$
13.9	14.3	$9b_u$
15.0	15.5	$9a_g$
15.5	16.2	$1b_g$
15.6	16.4	$1a_u$
16.0	17.4	$8a_g$
16.7	18.3	$8b_u$
17.2	18.6	$7a_g$
17.5	19.6	$7b_u$

[a] MOs were computed using 4-31G basis set. The eigen values were multiplied by an empirical factor of 0.92

show appreciable resonance interaction between the in-plane monomer orbitals in the homo-dimer. In the hetero-dimer, a net transfer of electron density from CH_3COOH to CF_3COOH is observed. Inductive influences are transmitted through the hydrogen bond bridges.

C. Alcohol and Amine Dimers.—The methanol dimer has an enthalpy of association comparable to that of the water dimer.[2] UVPE spectra of methanol and ethanol dimers have been recently studied by us, employing a double chamber UVPE spectrometer.[42] The spectrum of methanol dimer is characterized by bands at 11.2, 11.9, 13.0, and 13.4 eV. The first two are due to the lone pairs of the donor and the other two are due to the corresponding orbitals of the acceptor. The spectrum of methanol dimer reported by Tomoda and Kimura[43] showed an adiabatic IE of 9.8 eV, while the appearance potential from photoionization[44] is 10.3 eV. We suspect that the first band of the methanol dimer obtained by Tomoda and Kimura may have a significant contribution from the HeI_β ionization of the $\tilde{n}_O$ orbital of the monomer. The adiabatic IE observed by us is 10.7 eV, giving a dissociation energy of 0.3 eV for the ground state dimer ion in agreement with the photoionization study. The spectrum of the ethanol dimer is similar, but shows fewer features. The prominent bands are at 10.7, 11.2, 12.8 and 14.4 eV.

Quantum chemical calculations[42] on the SCF/3-21G level on the dimer of dimethylamine showed the N–H $\cdots$ N hydrogen bond to be weaker than the O–H $\cdots$ O bond in the methanol dimer. The UVPE spectra of dimethylamine recorded at different nozzle stagnation pressures[42] have provided the features of $[(CH_3)_2NH]_2$. The characteristic features of this dimer are at 8.3, 10.0, and

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[42] T. Pradeep, M. S. Hegde, and C. N. R. Rao, *J. Mol. Spectrosc.*, in press.

[43] S. Tomoda and K. Kimura, *Chem. Phys.*, 1983, **74**, 121.

[44] K. D. Cook, G. G. Jones, and J. W. Taylor, *Intern. J. Mass Spectrom. Ion Phys.*, 1980, **35**, 273.

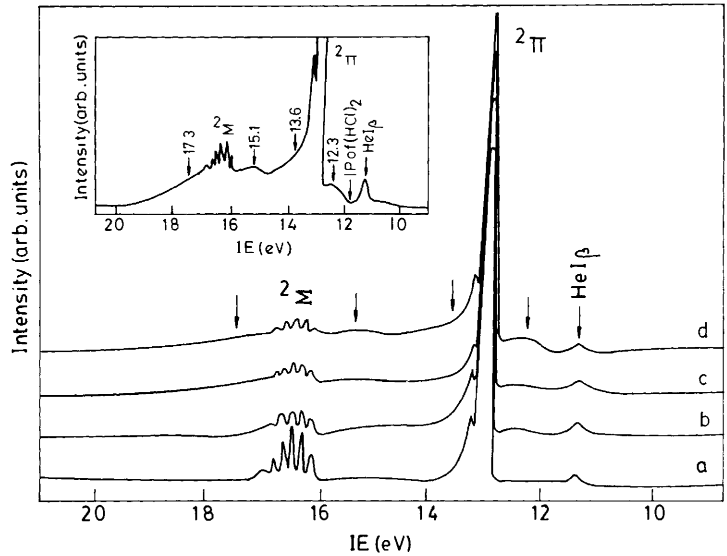

Figure 12 HeI *photoelectron spectra of* HCl *at different stagnation pressures* (*from ref.* 49). *The stagnation pressure increases from* (*a*) *to* (*d*). *The spectrum marked* (*a*) *is due to the monomer. The dimer features are marked by arrows. Note the* HeI$_\beta$ *feature. The inset shows an enlarged spectrum, truncated for clarity*

11.1 eV. The first two bands are due to n_N orbitals and the last one is due to a σ_{CN} orbital. The lone pair IEs of the monomers undergo an average shift of 1 eV on dimerization.

D. HCl Dimer.—Dimers of hydrogen halides constitute the simplest class of hydrogen bonded systems. A high resolution rotational–vibrational spectroscopic study of the HCl dimer[45] suggests a nearly orthogonal structure with rapid tunnelling between the equivalent forms. The zero-point centre of mass separation is 3.797 Å and the zero-point dissociation energy[46] is 5.2 kJ mol^{-1}. A large number of MO calculations have also been performed on the dimer.[47,48] The electronic structure of hydrogen chloride dimer has been studied recently. In Figure 12 we show the HeI spectrum of HCl at different nozzle stagnation pressures.[49] As the pressure increases, new features due to the dimer start gaining in intensity. The appearance potential of $(HCl)_2$ determined from the UVPE spectrum is 11.9 eV, remarkably close to the photoionization value (11.91 eV).[50]

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[45] N. Ohashi and A. S. Pine, *J. Chem. Phys.*, 1984, **81**, 73.

[46] A. S. Pine and B. J. Howard, *J. Chem. Phys.*, 1986, **84**. 590.

[47] M. J. Frish, J. A. Pople. and J. E. Del Bene, *J. Phys. Chem.*, 1985, **89**, 3664.

[48] A. Karpfen, P. R. Bunker, and P. Jensen, *Chem. Phys.*, 1991, **149**, 299 and the references cited therein.

[49] T. Pradeep and C. N. R. Rao, *J. Chem. Phys.*, in press.

[50] P. W. Tiedemann, S. L. Anderson, S. T. Ceyer, T. Hiroka. C. Y. Ng, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, 1979, 71, 605.

The first two features are due to the shifted n_{Cl} orbitals. The bands at 15.1 and 17.3 eV are due to the σ_{HCl} orbitals. Experimental as well as theoretical results show that the ionic state geometry is significantly different from that of the neutral dimer. As a result of the interaction, 0.005 *e* is transferred from the proton acceptor to the donor which results in a reorganization of the orbitals. The UVPE spectrum shows considerable interaction between the σ orbitals while the π interaction is marginal. The optimized structure of the ground ionic state is nearly cyclic without any proton transfer, unlike in the case of the water dimer.[32]

E. Hydrogen Halide Complexes with Electron Donors.—Complexes of hydrogen halides are the simplest hydrogen bonded hetero-dimeric species. The UVPE spectrum of dimethylether.HCl was reported sometime ago by Carnovale *et al.*[51] Calculations at the SCF/STO-3G level showed that the first ionization to be from the oxygen lone pair followed by the chlorine lone pairs. These features appear at 10.6 and 11.8 eV in the spectrum. The shifts are brought about by an inductive transfer of electron density of about 0.05 *e* from $(CH_3)_2O$ to HCl. Hydrogen bond formation increases the IE of the n_O orbital by 0.6 eV and decreases that of π_{Cl} by 1.0 eV. The spectrum of diethylether.HCl[52] is similar but the shifts are smaller, consistent with the lower value of the dissociation energy of the complex. The n_O orbital is shifted only by 0.2 eV and the π_{Cl} orbitals by 0.8 eV on complex formation. SO_2.HCl showed only small shifts in the IEs.[27]

Using a pinhole inlet system Carnovale *et al.*[53] studied the UVPES of the HF complex with dimethylether and dimethylsulphide. The hydrogen bond stabilizes the n_O and n_S orbitals by 1.0 and 0.8 eV respectively in these complexes; the destabilization of the π_F orbitals is 1.6 and 1.2 eV respectively. While the dominant factor for the shift of the donor orbitals is electrostatic, for the π_F orbitals it is charge-transfer and electronic relaxation. The calculated charge-transfer is 0.6 and 0.5 *e* for the ether and the sulphide complexes.

UVPE spectra of hydrogen bonded complexes generally support the donor–acceptor picture of hydrogen bonding. Charge-transfer accompanying hydrogen bonding, and electrostatic relaxation following ionization are the dominant factors in determining the shift.[54] Interaction between the in-plane σ orbitals is greater while the π–π interaction is marginal.

6 Electronic Transitions in Molecular Complexes

In order to obtain a complete picture of the electronic structure of molecular complexes it would be necessary to have information on the electronic transitions besides orbital energies. One of the important characteristics of the weak donor–acceptor complexes of the n–σ, π–σ, or π–π varieties is the occurrence of a new band in the electronic absorption spectrum due to the charge-transfer transition.

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[51] F Carnovale, M K Livett, and J B Peel, *J Am Chem Soc*, 1980, **80**, 569

[52] T Pradeep and C N R Rao, *J Mol Struct*, 1990, **224**, 21

[53] F Carnovale, M K Livett, and J B Peel, *J Am Chem Soc*, 1982, **104**, 5334

[54] J B Peel, *Aust J Phys*, 1982, **35**, 651

Besides such new bands, the absorption maxima of the individual components also get shifted considerably on complexation.[1,10,55,56] The electronic absorption spectra of such donor–acceptor complexes have been studied in the vapour phase,[3,10] but by and large these studies have been limited to the visible and near ultraviolet regions. Many of the electronic transitions of donor and acceptor molecules as well as some of the charge-transfer excitations fall in the vacuum UV region and conventional optical spectroscopy is generally not adequate to study them. Electron energy loss spectroscopy (EELS) is useful for the study of the electronic transitions of complexes in the vapour phase since the entire range from visible to vacuum UV is accessible by this technique. Here, we briefly summarize some of the EELS results on complexes obtained in this laboratory.

The charge-transfer band in the I_2.diethylether complex is known to occur at 250 nm.[57] In such complexes the visible band of I_2 at 520 nm undergoes blue-shift on complexation.[3,57] The EEL spectrum of $I_2.(C_2H_5)_2O$ shown in Figure 9 not only has the well-known CT band at 4.91 eV but also demonstrates the occurrence of the blue-shifted 520 nm band [58] of I_2. Furthermore, we see that the 180 nm band of I_2 also undergoes a blue-shift on complexation. The position of the two blue-shifted I_2 bands are at 2.75 and 7.95 eV (450 and 156 nm), respectively, in the complex. The diethylether.Br_2 complex [58] shows the CT band at 6.2 eV. Although a distinct blue-shift of the visible band of Br_2 was not observed, the blue-shifted vacuum UV band is seen at 9.0 eV. The magnitude of the blue-shift of Br_2 is comparable to that of the I_2 complex. The trimethylamine.I_2 complex [58] shows a CT band at 4.82 eV.

In Figure 13, we show the EEL spectrum [13] of $BH_3.H_2S$ along with the spectra of B_2H_6 and H_2S. Electronic transitions of B_2H_6 and H_2S are well known in the literature.[59,60] The characteristic transitions of the complex falls in the vacuum UV region at 6.1, 8.7, and 10.5 eV due to π–π^*, n–π^*, and σ–σ^* excitations respectively. Based on these transition energies, we have fixed the energies of the unoccupied orbitals and by making use of the UVPES data, constructed the complete MO level scheme of this complex (see the inset of Figure 13). Electronic transitions of $BH_3.CO$, $BF_3.H_2O$, and $BF_3.H_2S$ have also been studied by EELS.[13,16,18] Results from the EELS studies have been used to construct the MO level schemes of these complexes as well.

EEL spectra of the dimers of $AlCl_3$ and $FeCl_3$ have been recently reported in the vapour phase.[61] The spectrum of $AlCl_3$ recorded at 320 K showed a unique feature due to the dimer at 7.2 eV. The spectrum of Fe_2Cl_6 recorded at 420 K showed the first feature at 4.6 eV due to the ligand–metal charge-transfer transition. The next band at 6.2 eV has been assigned to an n–σ^* transition. The remaining bands have the same origin as of the monomer.

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[55] C. N. R. Rao, 'Ultraviolet and Visible Spectroscopy', Butterworths, London, 1975.

[56] S. Nagakura, *Excited States*, 1975, **2**, 322.

[57] C. N. R. Rao, G. C. Chadurvedi, and S. N. Bhat, *J. Mol. Spectrosc.*, 1970, **33**, 554.

[58] P. V. Kamath, M. S. Hegde, and C. N. R. Rao, *J. Phys. Chem.*, 1986, **90**, 1990.

[59] E. Blum and G. Herzberg, *J. Phys. Chem.*, 1937, **41**, 91.

[60] T. Pradeep and M. S. Hegde, *Spectrochim. Acta*, 1988, **44A**, 883.

[61] T. Pradeep and C. N. R. Rao, *J. Mol. Spectrosc.*, 1990, **130**, 453.

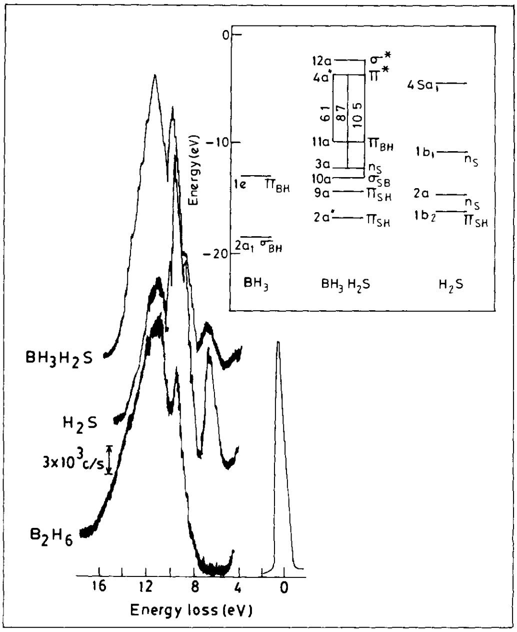

Figure 13 EEL *spectra of* B_2H_6, H_2S, *and* BH_3 H_2S (*from ref* 13) *The energy level scheme of the complex is shown in the inset The observed electronic transitions are indicated*

EEL spectra of some of the SO_2 complexes have been studied[27] Only $(C_2H_5)_3N$ SO_2 shows a charge-transfer like transition at 4 2 eV, corresponding to the 4 4 eV band in the optical absorption spectrum[23] The other bands in the spectrum of this complex are due to the shifted SO_2 transitions Diethylether and diethyl sulphide adducts of SO_2 show similar EEL spectra The observed bands have been assigned to the various transitions based on the experimental orbital energies from UVPES and the LUMO ordering from MO calculations

Electronic transitions of the formic acid dimer were for the first time studied recently by employing EELS[62] The spectrum of formic acid studied at different nozzle stagnation pressures revealed four features due to the dimer at 7 2, 8 5, 9 8, and 11 1 eV The first two are due to n–π^* and the last two are due to π–π^* excitations Based on this study, a partial energy level scheme of the dimer (shown in the inset of Figure 11) has been constructed

7 NO and NO_2 Dimers

NO and NO_2 readily form dimers UVPE spectra of the NO dimer and clusters have been studied by Carnovale *et al*[63] The spectrum of $(NO)_2$ consists of two

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[62] T Pradeep and C N R Rao *J Chem Soc Chem Commun* 1989 1019
[63] F Carnovale J B Peel and R G Rothwell *J Chem Phys* 1986 **84** 6526

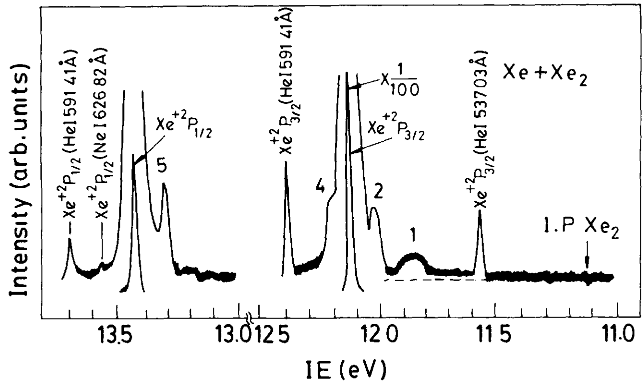

Figure 14 HeI *photoelectron spectrum of a mixture of* Xe *and* Xe_2 (*from Dehmer and Dehmer ref* 74). *The spectrum is truncated to show the weak dimer features*

bands due to the $^2A_1$ and $^2B_2$ states separated by 1.9 eV, close to the theoretical value of 2.11 eV. The band separation increases to 2.4 eV in higher clusters, close to the condensed NO value.[64] The $v' = 0$ corresponding to the ground ionic state of $(NO)_2$ is observed at 8.77 eV, in close agreement with other studies.[65,66] The dimer of NO_2 has been studied by several workers.[67–71] A many-body Greens function calculation[72] of the IEs is in agreement with the experimental data.

8 van der Waals Molecules

Extensive investigations of the thermodynamic and spectroscopic aspects of weak interactions carried out in recent years have enabled us to understand properly the nature of van der Waals molecules. By combining an UVPE spectrometer with an appropriate molecular beam source, it is possible to study the electronic structures of these systems. Such studies reveal the nature of the ionic states at large internuclear separations.

Noble gas dimers are an important class of van der Waals molecules. The UVPE spectrum of Xe_2 reported by Dehmer and Dehmer[73,74] showed four peaks at 11.85, 12.02, 12.21, and 13.31 eV corresponding to the $A^2\Sigma^+{}_{\frac{1}{2}u}$, $B^2\pi_{3/2g}$, $B^2\pi_{\frac{1}{2}g}$, and $C^2\pi_{\frac{1}{2}u}$ states of the dimer ion. The $C^2\pi_{3/2u}$ state falling in between is

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Table 6 *Vertical ionization energies and dissociation energies of the ionic states of noble gas dimers (from ref. 75)*

	Ar_2		Kr_2		Xe_2	
State	*IE*[a] (eV)	*Dissociation energy* (eV)	*IE*[a] (eV)	*Dissociation energy* (eV)	*IE*[a] (eV)	*Dissociation energy* (eV)
$A^2\Sigma^+_{(1/2)u}$	15.55	1.33	13.76	1.15	11.85	1.03
$B^2\Pi_{(3/2)g}$	15.67	0.14	13.90	0.16	12.02	0.18
$C^2\Pi_{(3/2)u}$	–	–	–	–	–	–
$B^2\Pi_{(1/2)g}$	–	–	–	–	12.21	*b*
$C^2\Pi_{(1/2)u}$	15.87	0.10	14.57	0.14	13.31	0.19

[a] Vertical ionization energy [b] This state is repulsive

not observed in the spectrum (Figure 14). The ionic states of Xe_2 were supposed to be bound through polarization forces, but the dissociation energies of some of the ionic states are indeed very high (up to 1.03 eV). By fitting the UVPE band corresponding to the ground ionic state to the calculated Franck–Condon distribution, an optimum potential has been determined for the ground ionic state. Calculations show the inadequacy of the Morse function to describe the potential curve at larger internuclear separations. The spectra taken at increased stagnation pressures showed the presence of Xe clusters. The IEs decrease to that of solid Xe (9.7—9.8 eV) in the clusters.

Photoelectron spectra of Ar_2 and Kr_2 have also been studied by Dehmer and Dehmer.[75] Stability of the ionic ground state of the noble gas dimers are in the order, $Ar_2 > Kr_2 > Xe_2$. Excited ionic states of all the dimers have similar stabilities. Some of the important features of the UVPES of noble gas dimers are listed in Table 6. Just as in Xe_2, the Morse function is inadequate to describe the Rg^+ground states. Since many of the excited neutral states would have potential curves similar to those of the ground ionic states, the inadequacy of the Morse function has to be borne in mind while constructing the potential curves.

The UVPE spectrum of Xe ··· HCl has been examined using a nozzle expansion of the gas mixtures.[76] Xe ··· HCl has a van der Waals minimum of 339 cm^{-1} at a large internuclear separation.[77] The centre of mass separation[78] is 4.29 Å. The spectrum of Xe + HCl mixtures using a nozzle source is shown in Figure 15. The spectrum with an effusive nozzle is shown in the inset of the same figure. In the spectrum at high stagnation pressures, features attributable to the Xe ··· HCl van der Waals molecule manifest themselves. These features marked a, b, c, d, and e in the figure have been assigned to the $^2\Pi$(HCl), $^2\Sigma$(Xe), $^2\Pi_{3/2}$(Xe), $^2\Pi_{\frac{1}{2}}$(Xe), and $^2\Sigma$(HCl) respectively. The excited ionic states are found to be bound.

The UVPE spectrum of $(N_2)_2$ reported by Carnovale *et al.*[79] shows vertical IEs which are lower than the monomer by 0.3 ± 0.1 eV. The dimer features are at

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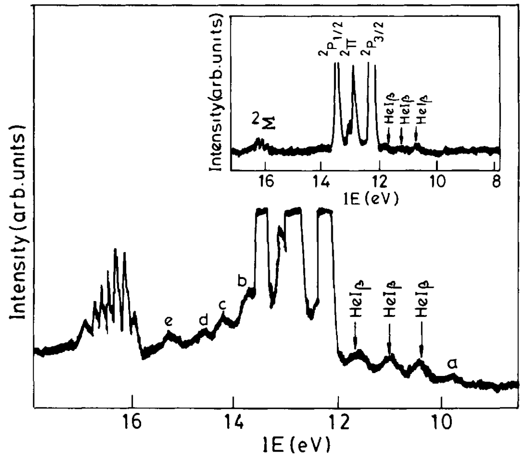

Figure 15 HeI *photoelectron spectrum of a mixture of* Xe *and* HCl (*from ref.* 76). *Features due to the van der Waals molecule* Xe ••• HCl *are marked* (*a*), (*b*), (*c*), (*d*), and (*e*). *Note the weak* HeI_β *features. The spectrum obtained at a lower stagnation pressure* (*inset*) *is due to a mixture. The spectra are truncated to show the weak features due to the van der Waals molecule*

15.2 and 16.7 eV and the spectrum shows 1:1 correspondence with the monomer. The spectral features (band widths and shapes) of N_2 dimer are same as those of N_2 clusters. This implies that the ionization chromophore of N_2 clusters is $(N_2)_2$. The shift of IEs to lower values is due to the electronic relaxation in a dielectric medium. The dimer ion formed in the ionization of N_2 clusters is different for each valence band, a linear $^2\Sigma_u^+$ for the first band, a rectangular $^2B_{2u}$ for the second band and linear $^2\Sigma_u^+$for the third band. The dimer ion states are strongly bound. In the case of Ar clusters,[80] the ionization chromophore is not the dimer but higher clusters. For very small clusters the trimer ion is relevant, while for heavier clusters as well as for condensed Ar the chromophore is Ar_{13}.

Photoelectron–photoion coincidence (PEPICO) spectroscopy has been used in the past few years to obtain UVPE spectra of van der Waals molecules. In this method one measures the ion mass in coincidence with the photoelectron kinetic energy. Early studies by this technique were carried out on Xe_2 and Xe_3[81,82] and the appearance potential of Xe_3 was found to be 11.30 ± 0.05 eV. As the cluster size increases, the appearance potential moves closer to the adiabatic IE. PEPICO studies of noble gas dimers and clusters,[83,84] Ar.CO,[85] $(CO)_2$,[86] and

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$(CO)_3$[86] have provided the estimates of the life times of the ionic states apart from the precise values of the appearance potentials

9 Concluding Remarks

The spectroscopic results discussed in the previous sections should clearly bring out how ultraviolet photoelectron spectroscopy provides valuable information related to the electronic structures of molecular complexes when interpreted in the light of appropriate molecular orbital calculations UVPES results obtained on molecular complexes are generally in agreement with theoretical predictions with only a few instances where Koopmans' approximation breaks down In most of the weakly interacting systems, the electrostatic interactions seem to determine the IE shifts, relaxation effects being negligible [87,88] Most of the UVPES studies hitherto have been limited to Lewis acid–Lewis base complexes (*n–v* complexes) and hydrogen bonded dimers A lot more can be done with *n*–σ complexes There has been no study of π–σ (*e g* benzene I_2) and π–π (*e g* naphthalene or benzene with trinitrobenzene or TCNE) complexes, although these were some of the first complexes investigated by optical spectroscopy and other techniques

In hydrogen bonded complexes, relaxation effects play an important role in deciding the IE shifts UVPE spectra of such complexes are consistent with the donor–acceptor model of the hydrogen bond The systems studied show considerable σ–σ interaction but only weak π–π interaction In a few of the systems studied (H_2O and H_2S dimers), significant proton transfer is observed in the ionic states

PE spectroscopy has been a useful probe to examine the potential curves at larger internuclear separations In such cases, the adiabatic IE obtained may not correspond to the potential minimum Large differences between the experimental and theoretical adiabatic IEs are not uncommon Poor Franck–Condon factors make the potential minimum inaccessible

PE studies combined with Franck–Condon simulations have shown the inadequacy of the Morse potential to describe the ionic states This would mean that these potentials are unreliable for the neutral excited states as well, since the nature of the potential curves are similar Dissociation energies of many of the ionic states of van der Waals molecules are rather large, contrary to expectations

There is a need to conduct studies directed towards obtaining vibrational fine structures of the ionic states Studies with mass selected species would be advantageous since most studies on van der Waals molecules are conducted by monitoring the stagnation pressure dependence of the monomer/mixture spectrum Such studies can also give valuable thermodynamic information UVPES data are yet to be used to obtain information on the excited state surfaces of molecular complexes

Acknowledgements The authors thank the Council of Scientific and Industrial Research, New Delhi, for support

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