

## Electrostatic and Relaxation Effects in Ionization of Intermolecular Complexes

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### Abstract

The shifts in experimental ionization energy (IE) resulting from complexation between the  $(\text{CH}_3)_2\text{O}$  and HF molecules are analysed theoretically with small basis set molecular orbital calculations. Initial state effects are separated according to the Morokuma decomposition procedure which distinguishes electrostatic, polarization and charge transfer contributions. The electrostatic effect, arising from the HF molecule, changes the potential energy of the  $n_{\text{O}}$  electrons on  $(\text{CH}_3)_2\text{O}$ . This is the dominant influence on the observed IE increase of 1.0 eV on complexation. Restricted open-shell calculations allow theoretical comparisons of the electronic relaxation processes which are considered as final state effects. The  $\pi_{\text{F}}$  electrons of hydrogen fluoride experience different relaxation effects in the monomeric and dimeric situations which, with a charge transfer effect, are the main contributions to the observed IE decrease of 1.6 eV on complexation.

### 1. Introduction

The study of weak interactions between atoms, molecules and solids has many facets. The perturbations in experimentally measurable properties resulting from such interactions offer the fundamental data which can be used to characterize the nature of the interactions involved.

During the development of photoelectron (PE) spectroscopic techniques over the last decade (Turner 1970; Rabalais 1977) the main area of application to the study of weak interactions has been in the investigation of adsorbates, both atomic and molecular, on solid surfaces (Lloyd *et al.* 1977).

In the gaseous phase the interactions represented by the formation of dimeric, trimeric and higher clusters have been studied to some extent. The He I PE spectra have been measured for hydrogen-bonded species such as the carboxylic acid dimers (Thomas 1972; Carnovale *et al.* 1980a), as well as some molecular hetero-dimers such as  $(\text{CH}_3)_2\text{O}\cdot\text{HF}$  and  $(\text{CH}_3)_2\text{S}\cdot\text{HF}$  (Carnovale *et al.* 1982) and  $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$  (Carnovale *et al.* 1980b). However, smaller dimers such as  $(\text{H}_2\text{O})_2$ ,  $(\text{HF})_2$  and  $\text{H}_2\text{O}\cdot\text{HF}$  have not yet been studied by this technique. Among weaker interactions, the currently popular van der Waals molecules such as  $\text{Ar}\cdot\text{HF}$  (Keenan *et al.* 1981) have not yet been studied by ionization spectroscopies. This is also the case for the similar interactions occurring in the rare gas matrix isolated atomic and molecular systems (Hallam 1973). With the natural extension of present-day PE techniques it is expected that studies on such systems will be undertaken in the near future.

There has been little theoretical study of the nature of weak interactions as revealed in ionization measurements. As far as the molecular theorist is concerned, the various quantitative procedures defined under the broad umbrella of Hartree-Fock and beyond-Hartree-Fock methods are available for such studies.

Having recently measured the He I PE spectra of the hydrogen-bonded intermolecular complexes  $(\text{CH}_3)_2\text{O}\cdot\text{HF}$  and  $(\text{CH}_3)_2\text{S}\cdot\text{HF}$  (Carnovale *et al.* 1982) and  $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$  (Carnovale *et al.* 1980b), we were interested to perform the minimum basis *ab initio* Hartree-Fock calculations reported here. The main aim of the calculations was to explain the basis of the experimental IE shifts which are the interesting data obtained by a comparison of monomer and dimer spectra.

Hydrogen-bonded complexes have received considerable experimental and theoretical attention, not only because of their fundamental importance as chemical species but, because they are models of more complicated biological systems. Hence the equilibrium geometries of many intermolecular complexes are known from microwave spectroscopy (Buxton *et al.* 1981) and electron diffraction (Derissen 1971) measurements, and studies of monomer-dimer equilibria by various techniques have provided data on the energetics of complexation (Govil *et al.* 1968; Desbat and Lassegues 1979).

## 2. Molecular Orbital Calculations

Molecular orbital (MO) calculations on hydrogen-bonded dimeric systems have not been highly successful because the various limitations inherent in Hartree-Fock methods become apparent when calculating the small total energy differences which represent an energy of dimerization. The calculation of a dimer equilibrium geometry is difficult because the total energy surface is often very shallow for variation in the intermolecular separation.

While the dimerization energy cannot be obtained with high accuracy, such calculations give useful information on the nature or mechanisms of such intermolecular bonding. So Morokuma and coworkers have developed an energy decomposition scheme (Morokuma 1971; Kitaura and Morokuma 1976) which describes the molecular interaction in terms of component contributions from electrostatic (ES), polarization (PL), exchange (EX) and charge transfer (CT) effects. While these workers have looked at the breakdown of the intermolecular energy in these terms, the procedure can also be applied to the shifts in orbital IE resulting from complexation. This has been done in the present study.

Within the linear combination of atomic for molecular orbitals (LCAO-MO) approximation used in the Hartree-Fock self-consistent field (SCF) theory, the four main effects listed above can be described as follows (Kitaura and Morokuma 1976). The ES component of the interaction is the classical electrostatic interaction between occupied MO of the two monomeric species. This only involves potential energy terms and does not result in any mixing of MO. The PL effect is the interaction which causes the mixing between the occupied and vacant MO within each molecule of the dimeric system. There is no movement of electron density between the two molecules due to ES and PL effects, but the individual molecular dipole moments can change under the influence of polarization.

The EX effect involves the interaction between all occupied MO of the dimer system with resulting electron exchange and delocalization between molecules. The CT effect is the interaction which causes intermolecular electron delocalization by

mixing the occupied MO of one molecule with the vacant MO of the other and vice versa. When these definitions are applied within the Hartree-Fock framework they describe almost all of the molecular interaction. The generally small contributions which remain are called the exchange polarization and coupling terms.

The application of the Morokuma decomposition scheme to IE involves the consideration of calculated eigenvalues within the Koopmans (1933) approximation for each of the constrained wavefunctions calculated in the decomposition analysis. The theoretical IE shifts thus obtained can then be regarded as initial state effects in that the comparisons are of the closed-shell wavefunctions of the neutral monomeric and dimeric systems.

By contrast, the corresponding final state effects, which are often considered in theoretical studies of ionization, involve the electronic relaxation process which is excluded in using the Koopmans approximation. Open-shell wavefunctions are required in order to follow the electronic reorganization which follows the creation of a valence MO hole of a particular symmetry within the monomer or dimer system. The  $\Delta$ SCF energy is the difference in total theoretical energies of a closed-shell molecule and its open-shell ground state molecular ion. This gives a theoretical value of the first IE. Such values generally show poor quantitative agreement with the experimental IE due to limitations involved in comparing closed- and open-shell systems. These include the use of different total energy operators for different spin multiplicities, the effects of size and type of basis set used, and the neglect of electron correlation effects. Most of these difficulties are minimized in the present calculations where interest is centred on the differences in energies of the monomer and dimer systems which relate to the shifts in IE observed by experiment.

Table 1. Experimental and theoretical valence ionization energies (eV) of  $(\text{CH}_3)_2\text{O}$  and HF

Experimental		Theoretical <sup>A</sup>		Experimental		Theoretical <sup>A</sup>	
		MO	STO-3G <sup>B</sup>			MO	STO-3G <sup>B</sup> STO-3G <sup>C</sup>
$(\text{CH}_3)_2\text{O}$				HF			
$I_1$	10.04	$2b_1(\text{nO})$	9.08	$I_1$	16.05	$1\pi(\pi_F)$	12.63 15.62
$I_2$	11.91	$6a_1(\sigma_{\text{CO}})$	10.59	$I_2$	19.9	$3\sigma(\sigma_{\text{HF}})$	16.92 19.11
$I_3$	13.43	$4b_2(\sigma_{\text{CH}_3})$	13.13				
$I_4$	14.20	$1a_2(\sigma_{\text{CH}_3})$	14.14				
$I_5$	15.9	$3b_2(\sigma_{\text{CO}})$	15.64				
$I_6$	16.3	$5a_1(\sigma_{\text{CH}_3})$	16.38				
$I_7$	16.7	$1b_1(\sigma_{\text{CH}_3})$	16.67				

<sup>A</sup> Calculation based on experimental molecular geometry.

<sup>B</sup> GAUSSIAN-70 data with the STO-3G minimum basis.

<sup>C</sup> With the augmented STO-3G\* basis as explained in text.

The procedures described above have been used for minimum basis set calculations at the STO-3G level (where each Slater-type orbital is fitted by a linear combination of three gaussian functions), with the GAUSSIAN-70 molecular orbital program (Hehre *et al.* 1973) for the intermolecular complexes  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$ ,  $(\text{CH}_3)_2\text{S} \cdot \text{HF}$  and  $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ . The modified GAUSSIAN-70 algorithms developed can also be used to study larger polymers and clusters in simulating not only gas-phase species but also matrix-isolated species such as small molecules or atomic clusters in rare gas solids.

### 3. Calculations on $(\text{CH}_3)_2\text{O} \cdot \text{HF}$

The GAUSSIAN-70 calculations on  $(\text{CH}_3)_2\text{O}$ , HF and  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  at the STO-3G level show a particular basis set effect which must be accounted for in the present studies on IE. For molecules such as these with single covalent bonds, the Koopmans approximation is reasonably accurate in that the distribution of calculated eigenvalues agrees well with the spread in measured IE displayed in the valence PE spectrum. While this is true individually for  $(\text{CH}_3)_2\text{O}$  and HF it is less accurate for the  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex. The quantitative agreement between theoretical and experimental IE differs for  $(\text{CH}_3)_2\text{O}$  and HF so, when the monomer IE are considered together, the GAUSSIAN-70 Koopmans order is incorrect. The relevant data for calculations made at the experimental geometries of  $(\text{CH}_3)_2\text{O}$  and HF are given in Table 1. We see here that the STO-3G IE underestimate the experimental values by a mean of 0.4 eV for  $(\text{CH}_3)_2\text{O}$  and a mean of 3.6 eV for HF. The STO-3G basis is clearly performing badly for the fluorine atom in comparison with the carbon and oxygen atoms. This can be corrected by extending the basis set for the fluorine atom in order to obtain a better matching of the experimental and theoretical IE of hydrogen fluoride. It was found that the addition of 1s, 2s and 2p STO, each of exponent 1.5, provided the necessary shift in IE. This can be seen in Table 1 to underestimate the hydrogen fluoride experimental IE by a mean of 0.5 eV. This augmented basis set, represented as STO-3G\*, was used in all subsequent calculations on HF and  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$ .

Table 2. Experimental and theoretical valence ionization energy shifts (eV) for  $(\text{CH}_3)_2\text{O}$  and HF in  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex

ES, electrostatic contribution; PL, polarization contribution; EX, exchange contribution; CT, charge transfer contribution

Experi- mental <sup>A</sup>		MO <sup>B</sup>	ES	Theoretical		CT	Total <sup>C</sup>
				PL	EX		
<b><math>(\text{CH}_3)_2\text{O}</math></b>							
$\Delta I_1$	1.00	$3b_1(n_O)$	1.02	-0.26	0.00	0.46	1.16
$\Delta I_2$	1.01	$9a_1(\sigma_{CO})$	1.24	-0.17	-0.35	0.45	1.24
$\Delta I_3$	0.8	$5b_2(\sigma_{CH_3})$	0.60	-0.05	0.00	0.20	0.79
$\Delta I_6$	0.5	$1a_2(\sigma_{CH_3})$	0.45	0.04	0.00	0.15	0.69
$\Delta I_7$	0.6	$3b_2(\sigma_{CO})$	0.71	-0.07	0.01	0.29	0.93
$\Delta I_8$	0.6	$8a_1(\sigma_{CH_3})$	0.72	-0.05	-0.48	0.23	0.47
$\Delta I_9$	0.6	$1b_1(\sigma_{CH_3})$	0.66	-0.07	0.00	0.28	0.85
<b>HF</b>							
$\Delta I_{4,5}$	-1.6	$2b_1, 4b_2(\pi_F)$	-0.56	-0.05	0.00	-0.32	-1.38
$\Delta I_{10}$	—	$7a_1(\sigma_{HF})$	-0.71	-0.08	0.56	-0.30	-0.68

<sup>A</sup> The IE are numbered for the  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex, with the shift calculated as  $\text{IE}(\text{complex}) - \text{IE}(\text{monomer})$ .

<sup>B</sup> The MO are numbered for the  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex, with approximate description in parentheses.

<sup>C</sup> The total theoretical shift also includes the exchange polarization and coupling contributions.

The intermolecular distance  $R(\text{O} \cdots \text{H})$  in the  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex has not been determined experimentally so, allowing for the fact that Hartree-Fock calculations cannot give a reliable value for this parameter, an estimated value is used in the calculations described here. Because minimum basis calculations generally show

some collapse in the intermolecular bond, an  $R(O \cdots H)$  value of 1.9 Å was chosen as it represents a slightly larger value than that found in various geometry optimization calculations. In the present work an equilibrium value of 1.72 Å was obtained with the STO-3G\* basis and a value of 1.67 Å with a 4-31G basis. In both of these calculations, which involved fixed experimental geometries for the  $(CH_3)_2O$  and HF moieties, the minimum energy geometry involved a planar  $C_2OHF$  skeleton. Other calculations (Hinchliffe 1978) on  $(CH_3)_2O \cdot HF$  have involved optimization of  $R(H-F)$ , as well as  $R(O \cdots H)$ , giving  $R(O \cdots H)$  values of 1.61 Å for a 6-31G basis and 1.73 Å for an extended basis.

By using the Morokuma decomposition procedure to give the various constrained wavefunctions for the  $(CH_3)_2O \cdot HF$  complex, comparison with the monomer  $(CH_3)_2O$  and HF wavefunctions within the Koopmans approximation leads to a description of the theoretical IE shifts resulting from complexation in terms of ES, PL, EX and CT effects. The results are given in Table 2. These show that the total theoretical IE shifts are dominated by the ES contributions. In the case of the  $(CH_3)_2O$  moiety they can be regarded as virtually the entire contribution since there is approximate cancellation of the smaller PL and CT effects. As well, the calculated ES shifts show good agreement with the experimental values. However, the PL and CT effects are of reasonable size, as can be gauged by the changes in dipole moment under polarization and the changes in local atomic charges under both PL and CT effects for the electrically neutral  $(CH_3)_2O$  and HF moieties. These are listed in Table 3. So the PL effect slightly increases the dipole moment of each monomer in the complex with electron density moving onto oxygen and fluorine resulting in negative IE shift contributions for the  $n_O$  and  $\pi_F$  MO. The CT effect moves a total of 0.055 of an electron from  $(CH_3)_2O$  to HF resulting in a positive contribution to the IE shift of  $n_O$  and a negative contribution for the  $\pi_F$  MO. The other interaction contributions are responsible for a further 0.002 of an electron shift onto hydrogen fluoride as indicated by the total charges given in Table 3.

**Table 3. Theoretical dipole moments and atomic charges for  $(CH_3)_2O$  and HF and their changes on complexation as  $(CH_3)_2O \cdot HF$**

$\mu$  (in Debye units) and  $q$  (in proton charge units) refer to total values for monomer and complex.  $\Delta\mu$  and  $\Delta q$  are the changes in  $\mu$  and  $q$  resulting from PL, EX and CT effects on complexation. For  $q$  and  $\Delta q$  the subscripts refer to atoms C, H and O in  $(CH_3)_2O$  and H and F in HF

	$\mu/\Delta\mu$	$q_C/\Delta q_C$	$q_H/\Delta q_H$	$q_O/\Delta q_O$	$\mu/\Delta\mu$	$q_H/\Delta q_H$	$q_F/\Delta q_F$
	$(CH_3)_2O$				HF		
Monomer	1.276	-0.054	0.060	-0.252	2.000	0.255	-0.255
PL	0.196	-0.001	0.006	-0.037	0.109	0.026	-0.026
EX	—	-0.001	0.000	0.001	—	0.012	-0.012
CT	—	0.003	0.000	0.046	—	-0.055	0.000
Complex	—	-0.052	0.061	-0.267	—	0.274	-0.331

However, for hydrogen fluoride Table 2 indicates that the ES contribution is only a fraction of the total calculated IE shift, with the total calculated shifts also falling short of the experimental values by reasonable amounts. The other initial state contributions mentioned earlier contribute a total of -0.45 eV to the  $\pi_F$  IE shift indicating some deviation from the simple picture consisting only of ES, PL and CT effects. The remaining difference between theoretical and experimental IE shifts

arises from effects associated with electronic relaxation (ER), which are expected to be more significant for HF orbitals than  $(\text{CH}_3)_2\text{O}$  orbitals.

The ER effect involves the movement of electron density towards the valence hole created by ionization. If the valence hole is highly localized, as in the case of the  $n_{\text{O}}$  or  $\pi_{\text{F}}$  MO, a relatively large electronic rearrangement is expected resulting in a large relaxation energy. Delocalized MO are expected to show smaller relaxation energies associated with ionization.

However, the pattern of the ER is likely to differ for the complexed dimeric state compared with the uncomplexed monomeric state, depending on the electric polarizability of the complexing molecule. Hence, the larger and more highly polarizable  $(\text{CH}_3)_2\text{O}$  moiety is expected to lose more electron density to a valence-hole state of  $\text{HF}^+$  than would the smaller and less polarizable HF to a valence hole of  $(\text{CH}_3)_2\text{O}^+$ . Hence, the HF ionizations should show more significant ER energy contributions to the total IE shift between monomer and complex.

Table 4. Theoretical relaxation energies (eV) for ionization of  $(\text{CH}_3)_2\text{O}$  and HF monomers and  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex

MO	KA( $-\epsilon$ ) <sup>A</sup>	$\Delta\text{SCF}^{\text{B}}$	ER <sup>C</sup>	MO	KA( $-\epsilon$ ) <sup>A</sup>	$\Delta\text{SCF}^{\text{B}}$	ER <sup>C</sup>
$(\text{CH}_3)_2\text{O}$				$(\text{CH}_3)_2\text{O} \cdot \text{HF}$			
$2b_1(n_{\text{O}})$	9.08	7.23	1.85	$3b_1(n_{\text{O}})$	10.24	8.42	1.82
$6a_1(\sigma_{\text{CO}})$	10.59	9.22	1.37	$9a_1(\sigma_{\text{CO}})$	11.83	10.61	1.22
$4b_2(\sigma_{\text{CH}_3})$	13.13	12.66	0.47	$5b_2(\sigma_{\text{CH}_3})$	13.91	13.41	0.50
$1a_2(\sigma_{\text{CH}_3})$	14.14	13.74	0.40	$2b_1(\pi_{\text{F}})$	14.25	11.62	2.63
$3b_2(\sigma_{\text{CO}})$	15.64	15.11	0.53	$4b_2(\pi_{\text{F}})$	14.25	11.66	2.59
$5a_1(\sigma_{\text{CH}_3})$	16.38	15.99	0.39	$1a_2(\sigma_{\text{CH}_3})$	14.83	14.39	0.44
$1b_1(\sigma_{\text{CH}_3})$	16.67	16.21	0.46	$3b_2(\sigma_{\text{CO}})$	16.57	15.92	0.65
HF				$8a_1(\sigma_{\text{CH}_3})$	16.85	16.50	0.35
$1\pi(\pi_{\text{F}})$	15.62	13.25	2.37	$1b_1(\sigma_{\text{CH}_3})$	17.53	16.95	0.58
$3\sigma(\sigma_{\text{HF}})$	19.11	17.73	1.38	$7a_1(\sigma_{\text{HF}})$	18.44	17.61	0.83

<sup>A</sup> The Koopmans approximation with molecular eigenvalues.

<sup>B</sup> Difference between total energies of ion and molecule.

<sup>C</sup> The difference  $\text{KA}(-\epsilon) - \Delta\text{SCF}$ .

The valence-hole open-shell GAUSSIAN-70 calculations incorporated the Roothaan (1960) restricted open-shell total energy operator for the doublet spin states represented by a single determinantal wavefunction. When the valence hole is in the uppermost occupied orbital of a given symmetry, the Hartree-Fock procedure can be regarded as giving a suitable variational energy which is a minimum. When the valence hole is not uppermost among the occupied orbitals of the appropriate symmetry, the excited ion state which it represents can only be obtained by applying a constraint to the calculation. A suitable constraint, which also assists with the convergence problems which plague calculations of this type, is to optimize the overlap of the valence-hole orbital with the closed-shell orbital on which it is based. The convergence difficulties referred to are much greater for valence-hole calculations than core-hole calculations due to the higher density of orbitals of the same symmetry in the vicinity of the valence-hole orbital.

The calculation procedure involves using the closed-shell wavefunction as the starting point. The chosen valence hole is created and the iterative relaxation open-shell calculation proceeds. The valence-hole orbital is monitored at each iteration and constrained by an orbital transformation within its symmetry block to a maximum overlap with the appropriate closed-shell orbital. In this procedure the valence hole can be regarded as frozen while the other doubly occupied orbitals are allowed to relax to a minimum energy configuration.

The calculated ER energies for monomeric  $(\text{CH}_3)_2\text{O}$  and HF are listed in Table 4 as the IE decreases, represented by the difference between the Koopmans approximation IE and the  $\Delta\text{SCF}$  energy for each valence-hole state. Because of the reasonable size of each relaxation energy the  $\Delta\text{SCF}$  theoretical IE are much further from the experimental values than the Koopmans approximation IE. This is because the minimum basis set gives eigenvalues which are relatively high, in contrast to an extended basis set for which the eigenvalues generally have magnitudes exceeding the experimental IE. For both  $(\text{CH}_3)_2\text{O}$  and HF the more localized  $n_{\text{O}}$  and  $\pi_{\text{F}}$  orbitals show the higher ER energies, while the highly delocalized  $\sigma_{\text{CH}_3}$  orbitals of  $(\text{CH}_3)_2\text{O}$  show the smallest ER energies. As well, the  $6a_1(\sigma_{\text{CO}})$  orbital of  $(\text{CH}_3)_2\text{O}$  which is mostly located on oxygen, and the  $3\sigma(\sigma_{\text{HF}})$  orbital of HF which is also relatively localized, show sizeable relaxation energies.

Table 5. Experimental and theoretical valence ionization energy shifts (eV) for  $(\text{CH}_3)_2\text{O}$  and HF in  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex

Experi- mental <sup>A</sup>		MO <sup>B</sup>	Theoretical		Total <sup>E</sup>
			KA <sup>C</sup>	ER <sup>D</sup>	
(CH <sub>3</sub> ) <sub>2</sub> O					
ΔI <sub>1</sub>	1.00	3b <sub>1</sub> (n <sub>O</sub> )	1.16	0.03	1.19
ΔI <sub>2</sub>	1.01	9a <sub>1</sub> (σ <sub>CO</sub> )	1.24	0.15	1.39
ΔI <sub>3</sub>	0.8	5b <sub>2</sub> (σ <sub>CH<sub>3</sub></sub> )	0.79	-0.03	0.76
ΔI <sub>6</sub>	0.5	1a <sub>2</sub> (σ <sub>CH<sub>3</sub></sub> )	0.69	-0.04	0.65
ΔI <sub>7</sub>	0.6	3b <sub>2</sub> (σ <sub>CO</sub> )	0.93	-0.12	0.81
ΔI <sub>8</sub>	0.6	8a <sub>1</sub> (σ <sub>CH<sub>3</sub></sub> )	0.47	0.04	0.51
ΔI <sub>9</sub>	0.6	1b <sub>1</sub> (σ <sub>CH<sub>3</sub></sub> )	0.85	-0.12	0.73
HF					
ΔI <sub>4,5</sub>	-1.6	2b <sub>1</sub> ,4b <sub>2</sub> (π <sub>F</sub> )	-1.38	-0.24	-1.62
ΔI <sub>10</sub>	—	7a <sub>1</sub> (σ <sub>HF</sub> )	-0.68	0.55	-0.13

<sup>A</sup> As in Table 2.

<sup>B</sup> As in Table 2.

<sup>C</sup> The total initial state shift from Table 2.

<sup>D</sup> The total final state shift obtained from Table 4 as  $\text{ER}(\text{monomer}) - \text{ER}(\text{complex})$ .

<sup>E</sup> Sum of KA and ER terms.

The comparison with the corresponding ER energies for the  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  complex can be made from the data in Table 4. The theoretical ER energy contributions to the IE shifts associated with complexation are given in Table 5 as the difference between the calculated ER for the dimer and associated monomer ionizations. Table 5 also contains the experimental and theoretical initial state effects from Table 2, allowing the determination of the total theoretical estimates of the IE shifts.

#### 4. Calculations on $(\text{CH}_3)_2\text{S}\cdot\text{HF}$ and $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$

The augmented STO-3G\* basis set used for the GAUSSIAN-70 calculations on  $(\text{CH}_3)_2\text{S}\cdot\text{HF}$  consisted of additional 1s, 2s and 2p STO, each of exponent 1.5, on fluorine. The geometry optimization involved keeping the  $(\text{CH}_3)_2\text{S}$  and HF monomers at their experimental geometries and resulted in a non-planar equilibrium conformation for the complex. An out-of-plane angle of  $67^\circ$  between the  $\text{S}\cdots\text{H}-\text{F}$  line and the C-S-C plane was determined with an  $R(\text{S}\cdots\text{H})$  distance of 2.26 Å. Calculations with a 4-31G basis set also produced a non-planar equilibrium geometry and an  $R(\text{S}\cdots\text{H})$  distance of 2.34 Å. Further calculations, both closed and open shell, on the complex, which is hence of  $C_s$  symmetry, were carried out at the STO-3G\* minimum energy geometry. The resulting theoretical IE shifts associated with complexation and the contributions of ES, PL, EX, CT and ER effects are given in Table 6 where they are compared with the corresponding experimental values (Carnovale *et al.* 1982).

Table 6. Experimental and theoretical valence ionization energy shifts (eV) for  $(\text{CH}_3)_2\text{S}$  and HF in  $(\text{CH}_3)_2\text{S}\cdot\text{HF}$  complex

Experi- mental <sup>A</sup>		MO <sup>A</sup>	ES <sup>A</sup>	PL <sup>A</sup>	Theoretical			KA <sup>B</sup>	ER <sup>B</sup>	Total <sup>B</sup>
					EX <sup>A</sup>	CT <sup>A</sup>				
(CH <sub>3</sub> ) <sub>2</sub> S										
$\Delta I_1$	0.8	15a'(n <sub>s</sub> )	0.89	-0.13	-0.12	0.36	0.98	0.00	0.98	
$\Delta I_2$	0.3	14a'(σ <sub>CS</sub> )	0.75	-0.10	-0.06	0.28	0.86	-0.06	0.80	
$\Delta I_3$	0.3	7a''(σ <sub>CS</sub> )	0.51	-0.05	0.00	0.21	0.67	-0.03	0.64	
$\Delta I_4$	0.1	6a''(σ <sub>CH<sub>3</sub></sub> )	0.35	0.04	0.00	0.11	0.54	-0.09	0.45	
$\Delta I_7$	0.5	4a''(σ <sub>CH<sub>3</sub></sub> )	0.39	0.02	0.00	0.13	0.57	-0.04	0.53	
$\Delta I_8$	0.5	12a''(σ <sub>CH<sub>3</sub></sub> )	0.38	0.02	-0.01	0.12	0.56	-0.04	0.52	
$\Delta I_9$	0.0	11a''(σ <sub>CH<sub>3</sub></sub> )	0.40	0.02	-0.03	0.13	0.57	-0.03	0.54	
HF										
$\Delta I_{5,6}$	-1.2	13a',5a''(π <sub>F</sub> )	-0.23	-0.08	0.00	-0.34	-0.84	-0.38	-1.22	
$\Delta I_{10}$	—	10a''(σ <sub>HF</sub> )	-0.29	-0.04	-0.01	-0.34	-0.68	-0.16	-0.84	

<sup>A</sup> As in Table 2.

<sup>B</sup> As in Table 5.

For the calculations on  $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$  an augmented STO-3G\* basis set was required, in that, as for the case of HF, the HCl eigenvalues were badly positioned in an STO-3G basis calculation. The addition of 1s, 2s and 2p STO, each of exponent 1.4, to the Cl atom, stabilized the valence MO of HCl by an average of 0.8 eV. This gave the desired correlation between the experimental IE and calculated eigenvalues for the  $(\text{CH}_3)_2\text{O}$  and HCl monomers considered together.

Geometry optimization calculations on the  $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$  complex produced a non-planar equilibrium conformation of  $C_s$  symmetry. When the monomeric moieties were fixed at their experimental geometries, the complex geometry was found to have an out-of-plane angle of  $34^\circ$  and an intermolecular separation  $R(\text{O}\cdots\text{H})$  of 1.54 Å. By comparison, other calculations (Hinchliffe 1978) assuming a planar  $\text{C}_2\text{OHCl}$  skeleton gave  $R(\text{O}\cdots\text{H})$  equilibrium distances of 1.46 Å for an STO-3G basis, 1.68 Å for a 4-31G basis and 1.97 Å for an extended basis. These results clearly indicate the basis set dependence of the calculated intermolecular distance. Consequently an  $R(\text{O}\cdots\text{H})$  distance set at 1.9 Å was used in further STO-3G\* calculations on the complex with an out-of-plane angle of  $34^\circ$ . The resulting



theoretical IE shifts associated with complexation and the contributions of ES, PL, EX, CT and ER effects are given in Table 7 where they are compared with the corresponding experimental values (Carnovale *et al.* 1980b).

Table 7. Experimental and theoretical valence ionization energy shifts (eV) for  $(\text{CH}_3)_2\text{O}$  and HCl in  $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$  complex

Experi- mental <sup>A</sup>		MO <sup>A</sup>	ES <sup>A</sup>	PL <sup>A</sup>	Theoretical EX <sup>A</sup>	CT <sup>A</sup>	KA <sup>B</sup>	ER <sup>B</sup>	Total <sup>B</sup>
$(\text{CH}_3)_2\text{O}$									
$\Delta I_1$	0.6	15a'(n <sub>O</sub> )	0.85	-0.15	-0.07	0.45	1.01	0.12	1.13
$\Delta I_4$	0.4	14a'( $\sigma_{\text{CO}}$ )	0.90	-0.10	-0.25	0.42	0.97	0.27	1.24
$\Delta I_5$	0.4	6a''( $\sigma_{\text{CH}_3}$ )	0.53	-0.02	0.00	0.20	0.74	-0.06	0.68
$\Delta I_6$	0.4	5a''( $\sigma_{\text{CH}_3}$ )	0.41	0.04	0.00	0.14	0.66	-0.07	0.59
$\Delta I_8$	0.6	4a''( $\sigma_{\text{CO}}$ )	0.60	-0.04	0.00	0.28	0.84	-0.13	0.71
$\Delta I_9$	0.5	11a'( $\sigma_{\text{CH}_3}$ )	0.59	-0.02	0.14	0.22	0.91	-0.09	0.82
$\Delta I_{10}$	0.4	10a'( $\sigma_{\text{CH}_3}$ )	0.58	-0.03	0.25	0.26	0.89	0.00	0.89
HCl									
$\Delta I_{2,3}$	-1.0	13a',7a''( $\pi_{\text{Cl}}$ )	-0.34	-0.11	0.00	-0.19	-0.79	-0.10	-0.89
$\Delta I_7$	-1.0	12a'( $\sigma_{\text{HCl}}$ )	-0.51	-0.05	-0.22	-0.18	-0.86	-0.04	-0.90

<sup>A</sup> As in Table 2.

<sup>B</sup> As in Table 5.

## 5. Discussion and Conclusions

For each of the three intermolecular complexes considered in the present study, comparisons of the experimental and calculated IE shifts associated with complexation show generally good agreement. For the  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{S}$  moieties, the ES effect of HF or HCl approaching and forming the hydrogen bond is the dominant influence on the increases in IE of all the valence orbitals. While the effect of CT is reasonable for the more localized orbitals of  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{S}$ , it is partly cancelled by the PL effects. The ER energies associated with ionization are also quite large for these localized orbitals, but the differences in ER energies for the uncomplexed and complexed forms are very small.

By comparison the IE shifts on complexation of the HF and HCl moieties require a more detailed description. The experimental IE shifts for the  $\pi$  valence orbitals are the largest obtained in the PE measurements, indicating that while these orbitals are not participating directly in the hydrogen-bond formation, they are considerably influenced by the approach of the highly polarizable  $(\text{CH}_3)_2\text{O}$  or  $(\text{CH}_3)_2\text{S}$  moieties. The ES effect of this approach represents only 20–35% of the total IE shift. While  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{S}$  are reasonably polar their dipole character is relatively diffuse in relation to the highly localized  $\pi$  orbitals of HF or HCl.

The CT effect contributes 20–30% of the IE shift, being largest for the  $(\text{CH}_3)_2\text{S} \cdot \text{HF}$  complex and least for the  $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$  complex, completely in accord with expectations based on the relative polarizabilities of  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{S}$  and the relative electronegativities of fluorine and chlorine.

The calculated ER energies associated with the  $\pi$  ionizations are very large for  $\pi_{\text{F}}$ , averaging 2.6 eV, but still considerable for  $\pi_{\text{Cl}}$ , averaging 0.7 eV. The ER contributions to the IE shift on complexation are similarly large for  $\pi_{\text{F}}$  being 15% and 30% of the total respectively for  $(\text{CH}_3)_2\text{O} \cdot \text{HF}$  and  $(\text{CH}_3)_2\text{S} \cdot \text{HF}$ . For  $\pi_{\text{Cl}}$  ER

contributes only 10% to the total IE shift in  $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ . These results show the trends expected in terms of the larger polarizability of  $(\text{CH}_3)_2\text{S}$  and the lower electronegativity of chlorine.

For each complex the total calculated IE shift for the  $\pi$  ionizations is in good agreement with the experimental data. This also suggests that the determination of the location of the  $\pi$  ionizations in the PE spectra of the complexes (Carnovale *et al.* 1982) has been reasonably accurate.

Despite the limitations inherent in small basis set Hartree-Fock calculations, and despite the difficulties conferred by the size of the intermolecular complexes considered in the present study, it has been found that the effects of complexation observed in the PE spectra of these species are adequately explained by the MO calculations undertaken.

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