

## Ultraviolet photoelectron spectroscopy of the hydrogen bonded hetero-dimer $\text{H}_2\text{S} \cdots \text{HCl}$ \*

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**Abstract**—The HeI photoelectron spectrum of the hydrogen bonded hetero-dimer  $\text{H}_2\text{S} \cdots \text{HCl}$  shows two vertical ionization energies at 10.91 and 12.16 eV. *Ab initio* MO calculations reveal that these features are due to the sulphur and chlorine lone pair ionizations respectively. Results show that while the ground ionic state is repulsive the first excited ionic state is strongly bound. The photoelectron spectrum of the diethyl sulphide  $\cdots \text{HCl}$  complex is similar to that of  $\text{H}_2\text{S} \cdots \text{HCl}$

### INTRODUCTION

ULTRAVIOLET photoelectron spectroscopy (UVPES) has been used extensively for the study of electron states of molecular complexes, hydrogen bonded dimers and van der Waals molecules [1]. The complex between  $\text{H}_2\text{O}$  and  $\text{HCl}$  is one of the simple examples of hydrogen bonded hetero-dimeric species. Extensive experimental investigations have been carried out on this dimer to yield its structural and spectroscopic properties [2–4]. Theoretical calculations have also been performed on this dimer [5]. The complex has a fairly large interaction energy, the binding energy at the MP2/6-31G(2*d*, *p*) level being 27.6 kJ mol<sup>-1</sup>. The H–O  $\cdots$  H bond is nearly linear, with a hydrogen bond length of 3.22 Å. The electronic structure of  $\text{H}_2\text{O} \cdots \text{HCl}$  has not been studied experimentally. However, there are reports on the HeI photoelectron spectra of the complexes of  $\text{HCl}$  with dimethylether [6] and diethylether [7]. The oxygen lone pair is stabilized by ~0.6 eV and the chlorine lone pair is destabilized by ~0.8 eV on dimer formation. While the electrostatic effect is responsible for the shift in the ether orbitals, charge transfer and electronic relaxation cause the shift of the chlorine lone pair.

The analogous hydrogen bonded dimer,  $\text{H}_2\text{S} \cdots \text{HCl}$ , has not been investigated in detail. The dimer has a *C<sub>s</sub>* structure with a linear S  $\cdots$  H–Cl distance of 3.809 Å [8]. The geometries of the constituents do not undergo any significant change on hydrogen bond formation. The binding energy of the complex is 20.7 kJ mol<sup>-1</sup> at the MP2/6-31G(2*d*, *p*) level. The dispersion energy contribution to the interaction energy is much larger than in  $\text{H}_2\text{O} \cdots \text{HCl}$ . As part of our effort to investigate the electronic structures of weak molecular complexes and hydrogen bonded molecules [9–12], we have studied the photoelectron spectrum of  $\text{H}_2\text{S} \cdots \text{HCl}$  by using a molecular beam photoelectron spectrometer. It was our intention to see whether there is any proton transfer in the ionic states. The study has enabled us to obtain the first two ionization energies of the dimer as well as the dissociation energies of the ionic states. We see that while the ground ionic state is repulsive the first excited ionic state is strongly bound. We have also studied the diethyl sulphide  $\cdots \text{HCl}$  complex for comparison.

### EXPERIMENTAL

The photoelectron spectra were measured with a double chamber photoelectron spectrometer fabricated indigenously for the study of weak molecular interactions [13]. Briefly, the spectrometer consists of a nozzle source, a 154 mm mean diameter hemispherical analyser, a channeltron detector and a data acquisition system. Glass nozzles of two different diameters (0.15 and 0.10 mm) were used in the experiment. Laboratory made  $\text{HCl}$  and  $\text{H}_2\text{S}$  gases subjected to repeated freeze–pump–thaw cycles were collected in glass bulbs at about 1 atm pressure. Gas mixtures of

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different compositions were prepared in a vacuum line and were collected in glass bulbs and they were connected to the spectrometer through a variable leak valve. A high pressure Pirani gauge monitors the stagnation pressure behind the nozzle. The UVPE spectrum was studied in the 10–20 Torr stagnation pressure range. The monomer spectra were obtained at the lowest stagnation pressure. The spectrometer resolution was 50 meV for 5.3 eV kinetic energy electrons. Each spectrum consisted of 1000 data points acquired by a personal computer.

MO calculations were carried out at the 6-31G\* level using the GAUSSIAN 86 system of programs [14]. Calculations were carried out on the ground neutral and the ionic states. In our calculations, the geometries of both the dimer and the monomer were fully optimized. For the dimer, we have considered the  $C_s$  structure since both experimental and theoretical studies point toward this conclusion.

## RESULTS AND DISCUSSION

In Fig. 1, we show the HeI photoelectron spectra of a mixture of  $H_2S$  and HCl in the 10–20 Torr nozzle stagnation pressure range. Each spectrum is normalized to the intensity of the HCl  $^2\pi$  band at 12.8 eV. The spectrum marked a is due to a neat mixture showing bands at 10.48, 13.25 and 15.35 eV due to  $H_2S$  and 12.80 and 16.3 eV due to HCl. The bands of  $H_2S$  are due to  $^2B_1$ ,  $^2A_1$  and  $^2B_2$  in order of increasing ionization energy (IE) [15]. The bands at 12.80 and 16.3 eV are due to HCl corresponding to the  $^2\pi$  and  $^2\Sigma$  states respectively. As the stagnation pressure increases, we see the emergence of two bands at 10.9 and 12.1 eV. These new bands are attributed to the  $H_2S \cdots HCl$  dimer on the basis of the following considerations. (1) The nozzle stagnation pressure is much smaller than that used in other investigations. At this pressure, the concentration of the

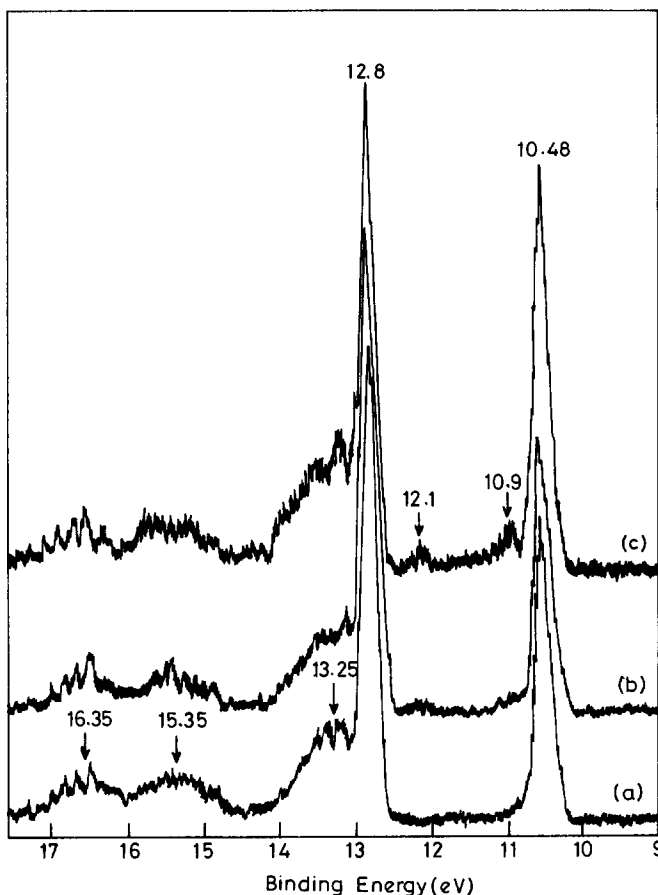


Fig. 1. HeI photoelectron spectra of a mixture of  $H_2S$  and HCl at three stagnation pressures. New features due to the  $H_2S \cdots HCl$  hetero-dimer are indicated by arrows.

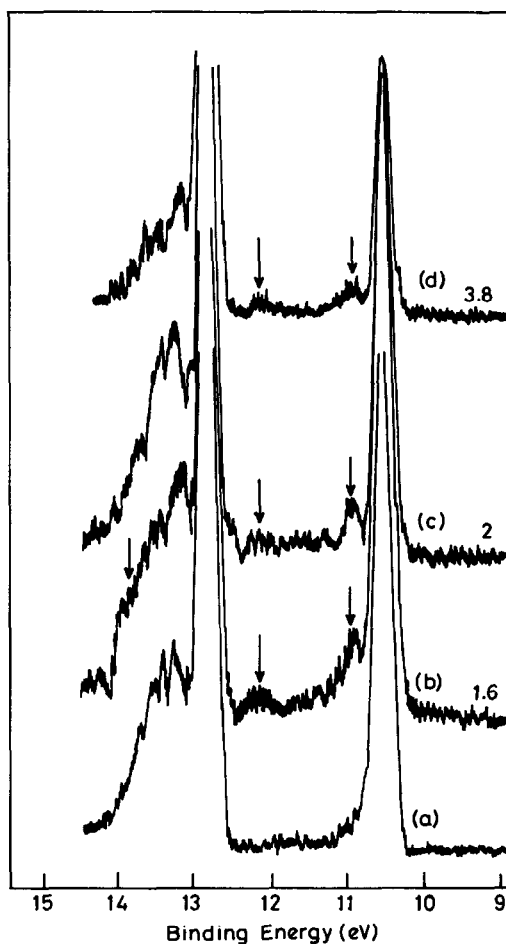


Fig. 2. HeI photoelectron spectra of mixtures of  $\text{H}_2\text{S}$  and  $\text{HCl}$  at different compositions. Curve a is due to a 1:1 mixture. New features are indicated by arrows.

higher clusters would be rather small. (2) As the stagnation pressure was increased above 25 Torr, the new features shifted to still lower IEs, suggesting the formation of heavier clusters. (3) The IEs of the new features are not due to  $(\text{HCl})_2$  [10] or  $(\text{H}_2\text{S})_2$  [11]. The only other possible species in the expansion is the hetero-dimer between the two, namely  $\text{H}_2\text{S} \cdot \cdot \text{HCl}$ . We show an expanded spectrum of the mixture in Fig. 2, which depicts the spectra of mixtures of different compositions at the same stagnation pressure. The intensity ratio of the  $n_{\text{Cl}}$  band of  $\text{HCl}$  at 12.8 eV to the  $n_{\text{S}}$  band of  $\text{H}_2\text{S}$  at 10.48 eV is a measure of their relative concentrations. This ratio was varied from 1.6 to 3.8 (curves b–d), but the new features remained the same. Thus, we conclude that the features with

Table 1. Vertical ionization energies, calculated orbital energies and assignments of the  $\text{H}_2\text{S} \cdot \cdot \text{HCl}$  hetero-dimer

Calculated MOs (SCF/6-31G*)			
$I_v$ (eV)	$\epsilon$ (eV)	MO	Character
10.91	10.83	$14a'$	$n_{\text{S}}$
12.16	12.67	$13a'$	$n_{\text{Cl}}$
	12.68	$4a''$	$n_{\text{Cl}}$
—	13.97	$12a'$	$\pi_{\text{SH}_2}$
—	16.78	$3a''$	$\pi_{\text{SH}_2}$
—	16.84	$11a'$	$\sigma_{\text{HCl}}$

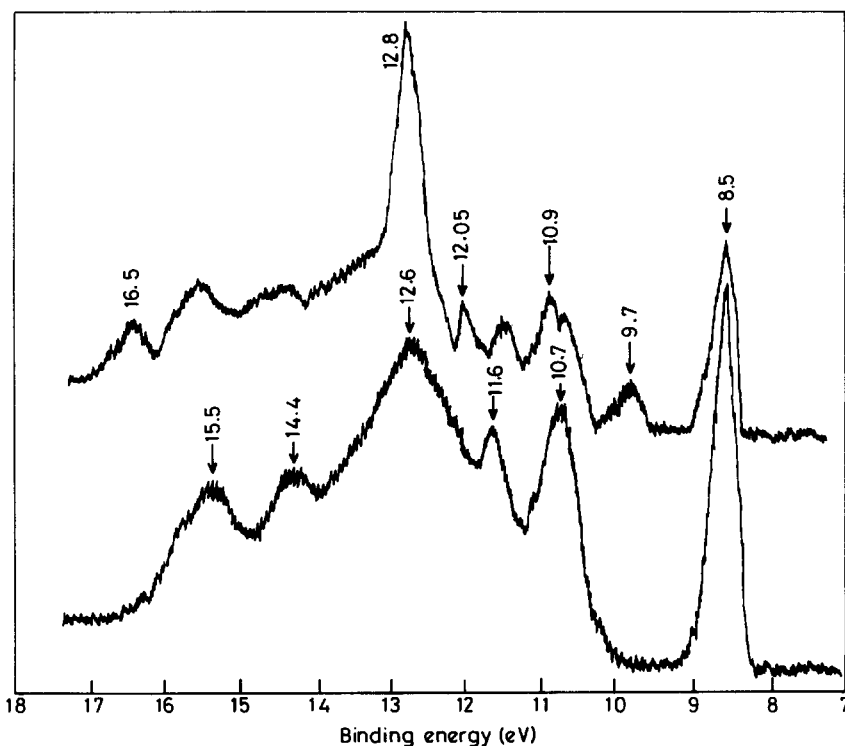


Fig. 3. HeI photoelectron spectra of  $(\text{C}_2\text{H}_5)_2\text{S}$  and a mixture of  $(\text{C}_2\text{H}_5)_2\text{S}$  and HCl. The spectrum of the mixture shows the presence of additional features due to the hetero-dimer,  $(\text{C}_2\text{H}_5)_2\text{S} \cdots \text{HCl}$ .

vertical IEs of 10.91 and 12.16 eV are due to the  $\text{H}_2\text{S} \cdots \text{HCl}$  hetero-dimer. The adiabatic IEs corresponding to these features are 10.50 and 11.76 eV respectively.

Calculations were carried out at the SCF/6-31G\* level on the  $\text{H}_2\text{S} \cdots \text{HCl}$  dimer. In the optimized geometry, the  $\text{S} \cdots \text{H}-\text{Cl}$  linkage is nearly linear, with an  $\text{S} \cdots \text{H}$  distance of 3.005 Å. The geometrical parameters of the constituents have not changed by any significant extent on complexation. In the optimized geometry, the  $b_1$  orbital of  $\text{H}_2\text{S}$  is involved in bonding. Koopmans' IE for the HOMO ( $14a'$ ) is 10.83 eV, corresponding to the in-plane sulphur lone pair. The calculated vertical IE for the  $1^2A'$  ground ionic state is 9.1 eV at the  $\Delta\text{SCF}$  level. Although there is a considerable difference between the experimental and the  $\Delta\text{SCF}$  values, the calculated vertical IE would come very close to the experimental value once correlation is included, as shown in the case of the  $\text{H}_2\text{S}$  dimer [11]. An estimate of the adiabatic IE for this state could not be obtained since the structure undergoes dissociation to  $\text{H}_2\text{S}^+$  and HCl. The experimental first vertical IE is very close to Koopmans' IE. We assign the first feature with a vertical IE of 10.91 eV to the  $1^2A'$  state. The sulphur lone pair is stabilized by 0.43 eV from the free  $\text{H}_2\text{S}$  value as a result of hydrogen bonding. The magnitude of stabilization is similar for the  $\text{H}_2\text{S}$  dimer, where the value is 0.27 eV.

Koopmans' IE for the second orbital is 12.67 eV due to the chlorine lone pair. The second chlorine lone pair is very close in energy (12.68 eV). Koopmans' IEs of the dimer may be compared with the HCl monomer (12.93 eV), where the chlorine lone pairs are degenerate. The theoretical value of the destabilization is 0.25 eV, while the experimental shift is 0.64 eV. The magnitude of destabilization is comparable to similar hydrogen bonded molecules such as the HCl dimer [10]. We assign the second photoelectron feature at 12.16 eV to this orbital. The experimental vertical IEs, orbital energies and assignments are listed in Table 1. The results support an electron donor-acceptor interaction in the dimer, leading to the splitting of the donor and acceptor IEs to higher and lower values respectively.

Using the UVPES data, we have calculated the dissociation energies of the ionic states from the equation  $D = D_0 + IE_0 - IE_1$ , where  $D$  and  $D_0$  are the dissociation energies of the ionic and the neutral states, respectively, while  $IE_0$  is the adiabatic IE of the state to which the ionic state dissociates and  $IE_1$  is that of the ionic state in question. Although there is no estimate of the dissociation energy of the complex, we can assume it to be close to that of similar complexes. Taking a dissociation energy of 0.06 eV for the ground neutral state [which is close to the values for  $(\text{H}_2\text{S})_2$  and  $(\text{HCl})_2$ ] and adiabatic IEs of 10.46 and 12.75 eV for  $\text{H}_2\text{S}$  and  $\text{HCl}$  respectively, it turns out that the  $1^2A'$  state is repulsive. The dissociation energy of the  $2^2A'$  state (with respect to  $\text{H}_2\text{S}$  and  $\text{HCl}^+$ ) is 1.05 eV.

The photoelectron spectrum of the diethyl sulphide  $\cdots \text{HCl}$  hetero-dimer is similar to that of  $\text{H}_2\text{S} \cdots \text{HCl}$ . In Fig. 3 we give the spectra of diethyl sulphide and a mixture of  $\text{HCl}$  and diethyl sulphide. The spectrum of the mixture shows the presence of two new features due to the hetero-dimer. These features, at 9.7 and 12.0 eV, are due to the hetero-dimer and can be assigned to the  $n_{\text{S}}$  and  $n_{\text{Cl}}$  orbitals respectively.

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