

An ultraviolet photoelectron spectroscopic study of the H₂S dimer, a van der Waals molecule [☆]

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The ultraviolet photoelectron spectrum of the H₂S dimer shows four features with vertical ionization energies of 9.75, 10.95, 12.37 and 13.69 eV; the adiabatic ionization energies of the first two ionic states are 9.56 and 10.75 eV. Molecular-orbital calculations reveal that the first two features are due to the sulphur lone pairs while the others are due to the π_{SH_2} orbitals. The ground ionic state ($1^2A''$) of the dimer is bound by 0.96 eV and the structure undergoes significant distortion on ionization. The first excited ionic state ($1^2A'$) is repulsive.

1. Introduction

The hydrogen-bonded dimer of H₂O has been extensively studied both theoretically and experimentally [1,2]. The dimer has a C_s structure with an O–H...O distance of 2.98 Å [2]. There are varying estimates of the dissociation energy of the dimer [2], but they are all in the range of 15.1–23.9 kJ mol⁻¹. Based on an ultraviolet photoelectron (UVPE) spectroscopic study, Tomoda et al. [3] reported two vertical ionization energies (IEs) of the H₂O dimer at 12.1 and 13.2 eV due to the non-bonding oxygen lone pairs. Although the difference between the vertical IEs of the monomer and the dimer is small, the difference between the adiabatic IEs is rather large, implying considerable distortion in the dimer geometry on ionization. Configuration-interaction (CI) calculations [4] have indeed shown that the potential minimum of the ground-state dimer ion corresponds to a proton-transferred structure and is far removed from the Franck–Condon region.

Unlike the H₂O dimer, the analogous H₂S dimer has not been investigated in detail. The dissociation energy of the H₂S dimer is 5.9 kJ mol⁻¹ [5] sug-

gesting that it is a van der Waals molecule. Molecular-beam electric-deflection experiments [6] suggest a bifurcated C_{2v} structure for the H₂S dimer, but definitive structural parameters are not known. Quantum-chemical calculations [7,8] predict a C_s structure similar to that of the water dimer. Calculations on the ground ionic state of the H₂S dimer [9,10] show that while the neutral state is a dynamical system with a shallow minimum, the dimer ion has a distinctive energy minimum. The dimer cation could, therefore, involve proton transfer as represented by H₃S⁺...SH⁻. As part of our effort to investigate the electronic structures of van der Waals molecules [11,12], we have studied the photoelectron spectrum of the H₂S dimer by employing molecular-beam photoelectron spectroscopy. The study has enabled us to obtain the ionization energies as well as the dissociation energies of the ionic states, and has also shown that the dimer geometry becomes distorted on ionization.

2. Experimental and computational details

An indigenously designed and fabricated molecular-beam photoelectron spectrometer was used for the investigation. The spectrometer consists of a hemispherical electrostatic analyzer of 154 mm mean

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diameter, a Channeltron electron multiplier and a free jet expansion sample inlet system. A glass nozzle of 0.1 mm diameter was used in the present study and the nozzle stagnation pressure was measured by means of a high-pressure Pirani gauge. H_2S gas prepared in the laboratory was collected in glass bulbs of 1 l capacity at about 1 atm pressure after repeated freeze-pump-thaw cycles. The bulbs were directly connected to the spectrometer through a needle valve. The HeI radiation crosses the molecular beam at 120° and the photoelectrons are directed to the hemispherical sector by an einzel lens. The UVPE spectrum was recorded in the 10–20 Torr stagnation pressure range. Spectra consisting of 1000 data points were acquired by a personal computer. The spectrometer resolution was 50 meV fwhm at 5.3 eV kinetic energy.

Molecular-orbital calculations were carried out at the SCF/6-31G* level with the GAUSSIAN 86 system of programs [13]. Complete geometry optimization was carried out for the neutral ground and the first two ionic states. We have considered only the C_s structures, since all the available calculations point towards this conclusion. For the first two ionic states and for the neutral ground state, single-point calculations at the MP4(SDTQ)/6-31G* level using the SCF/6-31G* geometry were also carried out to yield vertical ionization energies.

3. Results and discussion

In fig. 1, we show the photoelectron spectra of H_2S in the 10–20 Torr stagnation pressure range. Each spectrum is normalized to the intensity of the 1^2B_1 band. Spectrum (a), due to the H_2S monomer, shows vertical IEs at 10.48, 13.25 and 15.35 eV due to 1^2B_1 , 1^2A_1 and 1^2B_2 states, respectively [14]. As the stagnation pressure increases, the spectrum becomes more complex with the appearance of new features. The first band at 9.75 eV appears distinctly at a lower IE than that of the monomer and is the most intense among the new features. The feature at 12.37 eV is similarly distinct. In addition to these two distinct bands, we observe the emergence of two shoulders at about 10.95 and 13.69 eV by the side of the 1^2B_1 and 1^2A_1 bands of the monomer. All these four features are marked by vertical lines in fig. 1. We con-

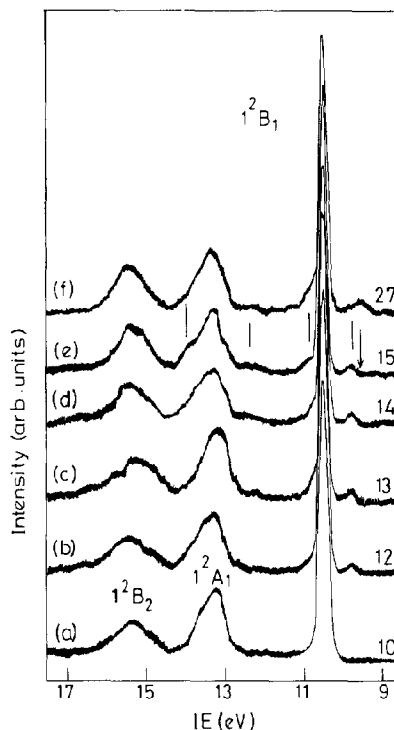


Fig. 1. Hel photoelectron spectra of H_2S in the 10–20 Torr nozzle stagnation pressure range. Stagnation pressures (in Torr) are indicated. In spectrum (a) due to the monomer, band assignments are shown. Different features of the dimer are marked by vertical lines. An arrow indicates the adiabatic IE of the dimer. The spectrum recorded at a stagnation pressure of 27 Torr shows the presence of higher clusters.

sider these features to be due to the H_2S dimer on the basis of the following considerations: (i) The nozzle stagnation pressure is lower than that used in the investigations of the H_2S dimer with comparable nozzle dimensions reported in the literature [6,15]. At this pressure, the concentration of higher clusters would be very small. (ii) The adiabatic IE corresponding to the first feature is 9.56 eV which is close to the photoionization value of 9.59 eV reported for the H_2S dimer [15]. Within the experimental uncertainty (± 0.05 eV), we found no evidence for the trimer (IE=9.47 eV). It, therefore, appears that all the other ionizations would also be due to the dimer since the experimental conditions remain the same during a single sweep. (iii) The new features shifted to lower IEs when the stagnation pressure was increased above 25 Torr, suggesting the formation of

larger clusters. Below this pressure range, an increase in the stagnation pressure only increased the intensity of the features ascribed to the dimer.

While the first and the third features are distinct, we could delineate the other features of the dimer by employing the spectrum-stripping procedure [16]. The stripping was carried out with a large number of spectra of the monomer-dimer mixture and the results were identical. In fig. 2, we show a typical stripped spectrum where the vertical ionization energies are also indicated. The four vertical IEs of the dimer obtained by us are 9.75, 10.95, 12.37 and 13.69 eV, and the adiabatic IEs for the first two bands are 9.56 and 10.75 eV. We are not sure of the spectral contours of the fifth and sixth bands due to difficulties faced in subtracting the overlapping monomer band. From the intensities of the monomer and dimer bands, we estimate the dimer concentration in the expansion to be $\approx 1\%$ using the expression given by Tomoda and Kimura [17].

Theoretical calculations on the H_2S dimer [9,10] generally assume a C_s structure in which the a_1 -orbital of the proton acceptor is involved in bonding. Calculations at the SCF/6-31G* level, however, reveal that this C_s structure is 1.4 kJ mol^{-1} higher in energy than the other possible C_s structure where the b_1 -orbital is involved in bonding with a binding energy of 3.8 kJ mol^{-1} . The latter structure is the same as that proposed by Frisch et al. [8] who obtained a binding energy of 3.8 kJ mol^{-1} at the SCF/6-31+G(d) level with a hydrogen-bond length of 3.18 \AA . The geometries of the constituents undergo neg-

ligible change on complexation. Frisch et al. [8] obtain a binding energy of 6.0 kJ mol^{-1} at the MP4/6-31+G(d) level, and this reduces to 3.4 kJ mol^{-1} when the zero-point energy is included.

Theoretical calculations of Fernandez et al. [9] and Ortiz [10] suggest that the adiabatic IE of the ground ionic state of the H_2S dimer corresponds to the complex between the H_3S^+ cation and HS radical resulting from the proton transfer. The adiabatic IE, calculated by many-body perturbation theory and electron-propagator theory [10], is 9.49 eV , in agreement with experiment. The calculated vertical IE, at the same level of theory for the C_s structure, is 10.12 eV [10] while the $\Delta\text{MP2}/6\text{-}31\text{G}^*$ value is 10.04 eV [9]. The difference between the experimental and calculated vertical IEs is higher for the other dimer geometries. Our calculations at the SCF/6-31G* level give a Koopmans' IE of 10.22 eV for the HOMO ($4a''$). This orbital is due to the sulphur in-plane non-bonding orbital of the proton donor. The ΔSCF vertical ionization energy is 8.99 eV for the $1^2A''$ ground ionic state. By including correlation, the ΔSCF value becomes close to experiment. The values at the ΔMP2 , ΔMP3 and ΔMP4 levels are 9.60 , 9.59 and 9.59 eV , respectively. We assign the first band in the UVPE spectrum at 9.75 eV to this state.

Koopmans' IE for the second orbital ($14a'$) obtained by us is 10.69 eV , and this is due to the out-of-plane lone-pair orbital of the proton acceptor. The calculated vertical IEs at the ΔSCF , ΔMP2 , ΔMP3 and ΔMP4 levels are 9.43 , 10.05 , 10.04 and 10.03 eV , respectively, for the $1^2A'$ state. The second band in the UVPE spectrum at 10.95 eV is assigned to this state.

Ionizations of the H_2S dimer occurring above 11 eV are all from the π_{SH_2} orbitals. We list the various vertical ionization energies, orbital energies and assignments in table 1. We see that the n_s orbital of the proton donor is destabilized by 0.73 eV and the corresponding orbital of the proton acceptor is stabilized by 0.47 eV on hydrogen-bond formation. The π_{SH_2} orbitals also behave similarly, destabilized by 0.88 eV in the case of proton donor and stabilized by 0.44 eV in the case of proton acceptor. Our SCF/6-31G* calculations predict two additional ionizations in the HeI region due to the π_{SH_2} orbitals at 16.14 and 16.60 eV (table 1). These two features are indeed present in the stripped spectrum at 15.07 and

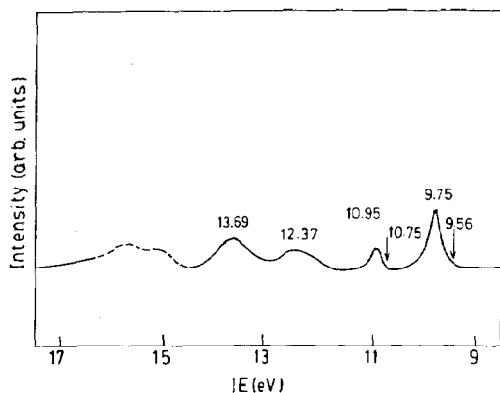


Fig. 2. HeI photoelectron spectrum of the H_2S dimer obtained by spectrum stripping.

Table 1
Vertical ionization energies, orbital energies and assignments of the H₂S dimer

I_v^{a1} (eV)	Calculated MOs		
	$-\epsilon$ (eV)	MO	character
9.75	10.22	4a''	π_S
10.95	10.69	14a'	π_S
12.37	13.31	13a'	π_{SH_2}
13.69	13.80	12a'	π_{SH_2}
–	16.14	11a'	π_{SH_2}
–	16.60	3a''	π_{SH_2}

^{a1} Vertical ionization energy.

15.71 eV, but we are not entirely certain of these two features due to errors involved in subtracting the mixture spectrum in the vicinity of the 1²B₂ band of the monomer.

Geometry optimization at the SCF/6-31G* level for the 1²A'' state shows considerable distortion from that of the neutral dimer. The hydrogen-bond length is 2.31 Å and the two monomer units are nearly perpendicular, but there is little change in the geometry of the constituent units. The calculated adiabatic IE (8.82 eV) of the 1²A'' state is lower than the experimental value (9.56 eV) by 0.74 eV. The difference between the adiabatic and vertical IEs of the H₂S monomer is 0.02 eV [14,18] and increases to 0.2 eV in the dimer. This difference is not as large as in the H₂O dimer where the value is 1.5 eV [3]. This observation suggests that, although the dimer structure undergoes significant distortion on ionization, it may not be as large as in the H₂O dimer.

A theoretical estimate of the adiabatic IE for the

1²A' state could not be obtained since geometry optimization calculations do not yield a stable minimum. The structure seems to undergo dissociation into H₂S⁺ and H₂S.

Based on 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; 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. Taking a dissociation energy of 0.061 eV for the ground neutral state [5] and an adiabatic IE of 10.46 eV for H₂S [18], we find that the dissociation energy of the 1²A'' state (with respect to H₂S⁺ and H₂S) is 0.96 eV. The dissociation energy obtained by Prest et al. [15] using photoionization data is 0.92 eV. Although this value is close to the bond dissociation energies of some of the van der Waals dimer ions [11], it is considerably lower than the value of 1.7 eV reported for the H₂O dimer ion [3]. The vertically ionized point is, however, 0.77 eV lower than the dissociation limit just as in the H₂O dimer, suggesting that ionic-state surfaces in the Franck–Condon region of these dimers are possibly similar. Unlike the 1²A'' state, the 1²A' state is repulsive. In table 2, we have listed the adiabatic IEs, vertical IEs and the dissociation energies of two ionic states of the H₂S dimer. The results show the importance of correlation effects in estimating the ionization energies. Apart from the changes in the relaxation energy accompanying complexation [19], correlation effects also appear to be dominant in determining the IE shifts in such weakly hydrogen-bonded systems.

Table 2
Adiabatic IEs, vertical IEs and dissociation energies of the first two ionic states of the H₂S dimer

State	Adiabatic IE (eV)		Vertical IE (eV)						Dissociation energy (eV)
	expt.	Δ SCF	expt.	Δ SCF	Δ MP2	Δ MP3	Δ MP4	EPT/MBPT ^{c)}	
1 ² A''	9.56 ^{a)}	8.82 ^{b)}	9.75	8.99 ^{b)}	9.60 ^{c)}	9.59	9.59	10.12	0.96
1 ² A'	10.75	– ^{d)}	10.95	9.43	10.05	10.04	10.03	–	– ^{f)}

^{a)} Value from the photoionization study of Prest et al. [15] is 9.59 eV.

^{b)} The adiabatic and vertical IEs calculated by Fernandez et al. [9] at the SCF/6-31G* level are 8.80 and 9.41 eV, respectively.

^{c)} The Δ MP2/6-31G* value of Fernandez et al. [9] is 10.04 eV.

^{d)} The structure undergoes dissociation into H₂S and H₂S⁺ and a stable minimum was not observed.

^{e)} Calculated by Ortiz [10] using electron-propagator theory and many-body perturbation theory.

^{f)} This state is repulsive.

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