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Chemical Physics 298 (2004) 213-222

Chemical Physics

www.elsevier.com/locate/chemphys

An initial investigation of S and SH with angle resolved photoelectron spectroscopy using synchrotron radiation

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Received 20 August 2003; accepted 12 November 2003

Abstract

An initial investigation of the photoionization behaviour of S atoms and SH radicals has been made in the gas-phase using angle resolved photoelectron spectroscopy (PES) with radiation from the Elettra synchrotron as the photon source. Angular distributions and relative photoionization cross-sections have been measured for S and SH as a function of photon energy from threshold (~10.3 eV) to 21.64 eV. The ionizations considered are $S^+(^4S) \leftarrow S(^3P)$, $S^+(^2D) \leftarrow S(^3P)$ and $S^+(^2P) \leftarrow S(^3P)$, and $SH^+(X^3\Sigma^-, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$, $SH^+(a^1\Delta, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$ and $SH^+(b^1\Sigma^+, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$.

This study of S and SH follows a recent investigation on atomic oxygen where the feasibility of angle resolved PES measurements on reactive intermediates at the Elettra synchrotron source was demonstrated, and further studies on small molecular radicals were proposed.

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1. Introduction

In recent experiments at the Elettra synchrotron, we have studied atomic oxygen in the gas-phase using angle resolved photoelectron spectroscopy [1]. This work extends these measurements to S and SH.

In the extreme ultraviolet wavelength region, absorption, photoionization and autoionization of sulphur atoms are of fundamental interest for understanding the spectroscopy and photoionization dynamics of openshell atoms. Moreover, due to its relatively high solar abundance, sulphur plays an important role in determining solar and stellar opacities [2,3] and interaction of S atoms with ultraviolet radiation is important in the solar atmosphere [4]. The ground state configuration of S atoms is $1s^2 2s^2 2p^6 3s^2 3p^4$, ³P. Three ionic states arise on $(3p)^{-1}$ ionization from this state: the ⁴S, ²D and ²P at ionization energies of 10.35, 12.21 and 13.40 eV, respectively [5].

There has been considerable theoretical work carried out on the photoionization cross-section of S atoms over a wide photoionization cross-sections for atomic systems with incomplete outer 3p subshells using the continuum Hartree–Fock approximation, and Dill et al. [7] derived expressions for the angular distribution of photoelectrons produced by ionization of open shell atoms including sulphur. The asymmetry parameter, β , as function of photon energy was calculated for each of the three ionic channels resulting from the (3p)⁻¹ ionization of sulphur atoms using both Hartree–Fock and Herman–Skillman wavefunctions for the atom, ion and free electron from threshold up to 60 eV.

Later Manson et al. [8] presented results of calculations of the photoionization cross-sections and angular

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distributions of the outer p subshell of chalcogen and halogen atoms from 13 to 100 eV photon energy, using the continuum Hartree-Fock approximation. In the theoretical work on S atoms [7,8], the general shape of the cross- section for each of the three ionic channels shows a clearly observable Cooper minimum around 40 eV. The calculated asymmetry parameters as a function of photon energy have a small value near threshold, rise rapidly to a maximum then fall to a minimum with negative β values at the Cooper minimum of the crosssection; they subsequently increase smoothly (the S 3p orbital is expected to show a Cooper minimum since the number of nodes in the atomic wavefunction, n - l - 1, is greater than zero). The $(3p)^{-1}$ photoionization crosssection of S atoms has also been calculated at a number of photon energies by Yeh and Lindau [9] using Hartree-Fock-Slater calculations.

Experimentally, a number of studies have been made on S atoms [10–13]. Tondello [10] measured and analysed the absorption spectrum of S in the vacuum ultraviolet region 1830–900 Å (6.77–13.77 eV), below and above the ionization threshold. An attempt to derive the absolute value of the photoionization cross section from the ground state in the 1197–940 Å region (10.36–13.19 eV) was made in this work. Modifications and additions to this spectrum have been made using a similar technique by Sarma and Joshi [11] and, more recently, by Joshi et al. [12]. Subsequently, Gibson et al. [13] studied the photoionization spectrum of atomic sulphur using photoionization mass spectrometry from the ionization threshold, 10.35 to 13.40 eV.

The SH radical is a molecule of environmental importance which plays a role in the ultraviolet photochemistry of several small sulphur-containing compounds which are released into the earth's atmosphere from natural and anthropogenic sources [14]. For example, hydrogen sulphide, carbonyl sulphide and carbon disulphide are released from the earth and its oceans as a consequence of microbiological processes. They react with the hydroxyl radical in the atmosphere to yield SH, which is then oxidized by O_2 and O_3 to SO_2 .

Although SH has been studied with various spectroscopic techniques [15–18] and theoretical methods [19,20], information on its electronic states is still somewhat limited. A multiphoton ionization study of the SH radical in the single photon energy range 4.68-3.91 eV has been performed by Ashfold et al. [15] The observation and partial characterization of three Rydberg states of SD and SH, accessed via 2-photon resonances from the ground state, was achieved in this work. More recently, thirteen Rydberg states converging to the second and third ionic state have been observed and characterised by two-photon resonance enhanced multiphoton ionization spectroscopy and multiphoton ionization photoelectron spectroscopy [21]. Also, the electronic absorption spectrum of SH has been investigated from the near ultraviolet into the vacuum ultraviolet region and several electronic transitions have been identified [16,17].

The adiabatic ionization energies of SH ($X^2\Pi$) to the first five ionic states have been established from HeI vacuum ultraviolet (VUV) photoelectron spectroscopy measurements to an accuracy of ± 0.01 eV [5]. Recently a more accurate determination of the ionization energies to the $X^3\Sigma^{-22}$ and $a^1\Delta$ ionic state [23] from SH $X^2\Pi$ have been achieved by the pulsed field ionization zero electron kinetic energy method.

The ground state electronic configuration of the SH radical is

$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^3$

Photoionization from the valence 2π molecular orbital produces the $X^{3}\Sigma^{-}$, $a^{1}\Delta$ and $b^{1}\Sigma^{+}$ ionic states at adiabatic ionization energies (AIEs), equal to the vertical ionization energies (VIEs), of 10.42, 11.64 and 12.76 eV, respectively [5,22,23]. The potential energy curves of these ionic states are very similar to that of the ground state of the neutral because of the non-bonding S 3p character of the 2π orbital. The removal of one electron from the 5σ shell gives rise to the $A^{3}\Pi$ and $c^{1}\Pi$ ionic states at AIEs of 14.11 and 15.69 eV, respectively [5]. The SH⁺(A³\Pi) \leftarrow SH(X²\Pi) and SH⁺(c¹\Pi) \leftarrow SH(X²\Pi) bands are broad and vibrationally resolved, with the AIE equal to the VIE for both bands. AIE values for these bands are 14.11 and 15.69 eV, respectively [5].

Until now no attempts have been made to measure asymmetry parameters (β) and photoionization crosssections (σ) of either S or SH. The purpose of this present work was to measure angular distribution parameters and relative photoionization cross-sections for the S⁺(⁴S) \leftarrow S(³P), S⁺(²D) \leftarrow S(³P) and S⁺(²P) \leftarrow S(³P) bands and the SH⁺(X³\Sigma⁻, v⁺ = 0) \leftarrow SH(X²\Pi, v'' = 0), SH⁺(a¹\Delta, v⁺ = 0) \leftarrow SH(X²\Pi, v'' = 0) and SH⁺(b¹\Sigma⁺, v⁺ = 0) \leftarrow SH(X²\Pi, v'' = 0) bands as a function of photon energy from threshold (\sim 10.3 eV) to 21.64 eV with the Elettra synchrotron source. This should allow comparison to be made with available calculations.

2. Experimental

The experiments reported here were undertaken on beam-line 4.2 R of the Circularly Polarized Beamline at the Elettra Synchrotron Light Source (Trieste). From the synchrotron source, the radiation passes to the electron spectrometer via a monochromator, which covers the photon energy range 5–35 eV. The photoelectron spectrometer used in this work has been specifically designed to study reactive intermediates with photoelectron spectroscopy using synchrotron radiation and has been described in detail previously [24,25]. Briefly, it consists of an ionization chamber, a three element lens assembly, a 10 cm mean radius hemispherical analyser and a channeltron detector. It can be rotated around the axis of linear polarization of the photon beam in the range $\theta = 0^{\circ}$ to $\theta = 73.5^{\circ}$, allowing the angular distributions of photoelectrons to be studied.

Photoelectron (PE) spectra were recorded in the constant pass energy mode, by scanning the voltage on a lens which accelerates (or decelerates) the photoelectrons before they enter the analyser.

In this work, S atoms and the SH radicals were produced by the following consecutive reactions:

 $F + H_2 S \rightarrow SH + HF$

 $\mathrm{F} + \mathrm{HS} \rightarrow \mathrm{S} + \mathrm{HF}$

The room temperature rate constants for the above reactions are 1.33×10^{-10} and 2.01×10^{-10} cm³ molecule⁻¹ s⁻¹, respectively [26]. To obtain a high F-atom yield, fluorine atoms were produced by flowing 5% F_2 in helium through a microwave discharge at 2.45 GHz in the side arm of a glass inlet system [27], with an inner inlet system which is the inlet used for the target molecules (in this case H₂S). In order to avoid attack of the glass system by the fluorine atoms produced by the discharge, the inner surface of the tube was coated with a thin layer of teflon, while the discharge cavity was positioned on an alumina section of the inlet system to prevent melting of the teflon due to heating from the discharge [27]. The intensities of the bands in the experimental PE spectra were normalized by the photon flux and then by the transmission correction of the spectrometer. The transmission function of the spectrometer, for electrons of different initial electron kinetic energy, was determined by measuring the intensity of the helium $(1s)^{-1}$ photoelectron band at different photon energies. The intensity of the helium $(1s)^{-1}$ band was measured in the VUV photon energy range used and then it was normalised using the absolute photoionization cross-section of helium in this range [28]; finally the normalized intensity was plotted as function of the electron kinetic energy. This curve was used to correct the experimental PE spectra for the transmission of the spectrometer.

The degree of linear polarisation (P = 1) of the radiation was well established [29]. The asymmetry parameter (β) was measured for S and SH radicals at selected photon energies and over a photon energy range, by recording PE spectra at two different angles (0° and 54°44′) at each photon energy (at 54°44′ the measured intensity is proportional to the total photoionization cross-section, independent of β); the β parameter was then calculated from

 $\beta = (R-1),\tag{1}$

where $R = I_0/I_{54^\circ 44'}$ is the ratio of the experimental intensities at these two angles, after applying the above corrections.

3. Results and discussion

Test experiments were carried out in Southampton in order to determine the optimum pressures and mixing distance above the photon beam, to be used in the experiments at Elettra, which maximise the intensities of the second and third photoelectron bands of SH at 11.64 and 12.76 eV AIE, corresponding to the ionizations $SH^+(a^1\Delta, v^+=0) \leftarrow SH(X^2\Pi, v''=0)$ and $SH^+(b^1\Sigma^+, v''=0)$ $v^+ = 0$ \leftarrow SH(X² Π , v'' = 0), and the second and third photoelectron bands of S at 12.21 and 13.40 eV IE, corresponding to the ionizations $S^+(^2D) \leftarrow S(^3P)$ and $S^+(^2P) \leftarrow S(^3P)$ [5]. The following conditions were found to be the optimum for production of both S and SH: a mixing distance above the photon beam of 2 cm, with the inner-inlet system used for H₂S longer than the outer inlet system by about 2 mm, and the partial pressures of H_2S and $F_2(5\%)/He$ measured on an ionization gauge positioned on the wall of the ionization chamber of 2.4×10^{-7} and 4.6×10^{-6} mbar, respectively. The PE spectra recorded at a photon energy of hv = 21.64 eV with synchrotron radiation and at two different angles with respect to the polarization axis of the photon source ($\theta = 0^{\circ}$ and $\theta = 54^{\circ}44'$) of the products of the $F + H_2S$ reaction are shown in Figs. 1(a) and (b) with the assignment of the major features indicated. These spectra show sharp bands at 11.64 and 12.76 eV, which are the second and third bands of SH, and sharp bands at 12.21 and 13.40 eV which are the second and third bands of S atoms. The sharp band at ≈ 10.5 eV arises from overlap of the first band of S atoms at 10.35 eV, and the first band of SH at 10.42 eV as well as a small contribution from the first band of residual H₂S at 10.48 eV [5]. Bands associated with F and F₂ were also observed in the spectra [30,31], as well as a small contribution from SF₂ which is a secondary reaction product [32] (see Figs. 1 and 2). The vibrationally resolved band of SH at 14.11 eV AIE is the fourth band of SH (the $SH^+(a^3\Pi) \leftarrow SH(X^2\Pi)$ ionization). Unfortunately, the fifth band of SH (the SH⁺($c^{1}\Pi$) \leftarrow SH(X² Π) ionization) AIE 15.69 eV, was not observed because it was to weak and overlapped with the first band of F_2 .

In Fig. 2(b), an expanded version of the composite band at ≈ 10.5 eV is shown. It clearly shows two maxima. Deconvolution of this band into two Gaussians was performed and the fitted Gaussians were centred at 10.36 ± 0.02 and 10.45 ± 0.03 eV. These energies are in agreement with the known energies of the S⁺(⁴S) \leftarrow S(³P) and SH⁺(X³\Sigma⁻) \leftarrow SH(X²\Pi) ionizations at 10.35 and 10.42 eV, respectively. The small contribution of the H₂S⁺(X²B₁) \leftarrow H₂S(X¹A₁) ionization at 10.48 eV is



Fig. 1. Photoelectron spectra recorded at hv = 21.64 eV for the reaction F + H₂S at a mixing distance of 2 cm above the photon beam (a) at an angle (θ) with respect to the polarization axis of the photon source of 0°, and over the ionization energy range 10.0–17.5 eV, and (b) at two angles $\theta = 0^{\circ}$ and 54°44′ and over the ionization energy range 10.0–14.7 eV. (The photon energy was set to 21.22 eV at Elettra but, after calibration of the monochromator, the actual photon energy was 21.64 eV.)

included in the band centred at 10.45 eV. This is consistent with a slightly larger full-width-at-half-maximum (FWHM) of the second fitted Gaussian compared to the first Gaussian. The values obtained from the fit are FWHM₁ = 72 ± 3 meV and FWHM₂ = 95 ± 3 meV for the first and second Gaussian, respectively.

The broad band on the low energy side of the $S^+(^2P) \leftarrow S(^3P)$ ionization at 13.40 eV ionization energy in Fig. 2(a) is mainly due to the presence of un-reacted H_2S , along with SF_2 produced by secondary reactions. Confirmation of the presence of SF_2 can be easily obtained from the observation of the first two vibrational components of the first band of SF_2 on the low ioniza-



Fig. 2. (a) Photoelectron spectrum recorded at hv = 21.64 eV at $\theta = 0^{\circ}$ for the reaction F + H₂S at a mixing distance of 2 cm above the photon beam. Estimated contributions from SF₂ (first and second bands) and H₂S (second band) are shown. (The asymmetry parameter of the first vibrational component of the 4th band of SH at 14.11 eV IE has been measured as (1.04 ± 0.39) at hv = 21.64 eV.) (b) Deconvolution of the band shown in (a) at ≈ 10.4 eV ionization energy into two Gaussian components. The band centred at 10.36 eV is the first band of S atoms (S⁺(⁴S) \leftarrow S(³P)) whereas the band at 10.45 eV contains contributions from the first band of SH (SH⁺(X³\Sigma⁻) \leftarrow SH(X²Π)) and from the first band of H₂S (see text for further details).

tion energy side of the sharp band at ≈ 10.5 eV (1st AIE of SF₂ 10.08 eV) [32] (see Fig. 2(a)). The spectra obtained are in good agreement with those previously recorded in Southampton by Dunlavey et al. [5] with a Hel radiation source.

The ionization energy region 9.600–15.200 eV was recorded using 23 different photon energies from 13.205 to 21.640 eV. A step size of 0.20 eV was used from hv = 13.205 eV to hv = 16.420 eV and a step size of 0.40 eV was used from hv = 16.420 eV to hv = 18.494 eV; PE spectra were also recorded at hv = 21.640 eV. All spec-

tra were recorded at two angles, $\theta = 0^{\circ}$ at $\theta = 54^{\circ}44'$, with respect to the polarization axis of the photon source. Due to significant variations in the intensities of the 12.21 eV band (second band of S) and the 11.64 eV band (second band of SH) with photon energy, the ionization energy region 11.500-12.400 eV was re-examined by recording a new series of 21 PE spectra with photon energies from hv = 13.205 eV to hv = 13.411 eV, with a smaller step size of 0.01 eV. A strong sharp band was observed in the PE spectra recorded at photon energies above 12.5 eV, due to ionization of helium by second order radiation. In this photon energy region second order radiation can ionize helium (IE = 24.58eV [33]) with consequent emission of electrons. This helium $(1s)^{-1}$ band was used as internal check for the correction factor applied for the evaluation of the asymmetry parameter for the observed bands of S and SH. Indeed, with the procedure used, β was always obtained as 2.00, within experimental error, for this helium $(1s)^{-1}$ band. In practice, for the measurements of angular distribution it is important to make sure that the efficiency of the analyser does not change when the spectrometer is rotated. The biggest contribution to the change of the efficiency of the analyser comes from small misalignments between the axis of rotation and the direction of the photon beam. This contribution is minimised by adjusting, after each rotation of the spectrometer, the direction of the photon beam in such a way as to maximise the signal coming from the detector and the current measured by the photodiode on the opposite side of the ionization chamber of the spectrometer from the direction of the photon beam. However, to quantify this contribution for all the angle resolved experiments a correction factor is evaluated at each set of experiments by measuring the intensity of bands at $\theta = 0^{\circ}$ and at $\theta = 54^{\circ}44'$, usually at 21.22 eV photon energy, from a sample (usually Ar) where the asymmetry parameter is well established. From the comparisons between the calculated asymmetry parameter and the known asymmetry parameter, the correction factor was determined. Then, at each photon energy, the asymmetry parameter can be calculated for an S or SH band using Eq. (1) with this correction factor, and relative photoionization cross-sections can be evaluated by integrating the area of the bands at $\theta = 54^{\circ}44'$. This has been carried out to give the plots shown in Figs. 3-8.

Inspection of existing angular distribution and relative cross-section (σ) measurements for H₂S [34–36], indicates that for the S photoelectron bands arising from a $(3p)^{-1}$ ionization, the angular distribution parameter (β) plotted as function of photon energy is expected to show an initial increase, a maximum at ≈ 25 eV and a minimum at ≈ 40 eV, the Cooper minimum, whereas the σ -plot is expected to show a regular decrease from threshold, the shallow Cooper minimum at $\approx 40 \text{ eV}$ and

Fig. 3. Plots of the asymmetry parameter (β) as a function of photon energy over the range hv = 13.0-21.0 eV, for the first three photoelectron bands of S atoms. (b) includes β values for the first band of H₂S measured at different photon energies in [34], denoted with the symbol (*) in the figure.

then a slow increase. The first bands of S, SH and H₂S are expected to be very similar in their β and σ plots as they all correspond to ionization from a S 3p lone-pair orbital. Comparisons of the measured asymmetry parameters as a function of photon energy for the three ionization channels resulting from the $(3p)^{-1}$ photoionization of S derived from this work with results of the angular distribution Hartree-Fock calculations of Dill et al. [7] have been made over the photon energy range 10-22 eV. These calculations [7] used LS coupling and were based on an angular momentum transfer expansion for the differential photoionization cross-section. Dill et al. [7] showed that the three ionic channels resulting from photoionization of $S(^{3}P)$ should show significantly different behaviour from each other when plotted as function of photon energy, in contrast to identical behaviour expected in the Cooper-Zare model [37]. In Fig. 3, the three different angular distribution plots are shown as a function of photon energy and comparison with the results of Dill et al. [7] is presented in Fig. 4. As can be seen in Fig. 4, the experimental results obtained in this work are in reasonable agreement

1.0 0.5 0.0 (b) S⁺(²D) ← S(³P -0.5 -1.0 2.5 -2.0 1.5 1.0 0.5 0.0 S⁺(²P) S(³P) (c) -0.5 -1.0 14 19 20





Fig. 4. Asymmetry parameters for S atoms plotted as a function of photon energy and compared with the results of Dill et al. [7]: (a) for the first S atom band, $S^+(^4S) \leftarrow S(^3P)$, (b) for the second S atom band, $S^+(^2D) \leftarrow S(^3P)$, and (c) for the third S atom band, $S^+(^2P) \leftarrow S(^3P)$.





Fig. 5. Plots of the asymmetry parameter (β) as a function of photon energy over the range hv = 13.0-18.5 eV, for the first three photoelectron bands of SH. (b) includes β values for the first band of H₂S measured at different photon energies in [34], denoted with the symbol (*) in the figure.

with the results of the calculations [7] for the $S^+({}^4S) \leftarrow S({}^3P)$ and $S^+({}^2D) \leftarrow S({}^3P)$ ionization channels, but are in poorer agreement for the $S^+({}^2P) \leftarrow S({}^3P)$ ionization. However, for all three ionizations data points are required to higher photon energy than the range covered in this work (notably in the 25–50 eV region) for a more detailed comparison between experiment and theory. Fig. 3(b) also shows data points taken from [34] for the first band of H₂S. This shows reasonable agreement with the S atom results of this work but again more H₂S data points are required for a more meaningful comparison.

Fig. 5 shows similar β -plots for the first three bands of SH, with Fig. 5(b) again showing the available data for the first band of H₂S from [34]. No previous measurements or calculations of the β -parameter as a function of photon energy have been made for SH. However, as with the S-atom data, more data points are required notably at higher photon energy. Also, it should be borne in mind that, as stated earlier, the first band of SH contains a small contribution from H₂S and this will contribute to Fig. 5(a).



Fig. 6. (a) Relative cross-sections for the $S^+({}^4S) \leftarrow S({}^3P)$ band in the photon energy region 13.205–18.494 eV. The maximum observed at 13.30 eV corresponds to excitation to unresolved $[3s^2 3p^3 ({}^2P) \text{ nd}] {}^3P$ Rydberg states. (b) Relative cross-sections for the $S^+({}^2D) \leftarrow S({}^3P)$ band in the photon energy region 13.205–13.412 eV. The resonances present in the region 13.205–13.350 eV have been assigned to excitations to $[3s^2 3p^3 ({}^2P) \text{ nd}] {}^3P$ Rydberg states which are part of a series which converges to the third ionization limit at 13.400 eV.

In Figs. 6 and 7 the relative photoionization crosssections for the first three S atom bands are plotted as a function of photon energy in the energy region 13.0–21.7 eV. In Fig. 6(b), the relative cross-section of the second S atom band, the $S^+(^2D) \leftarrow S(^3P)$ ionization, is plotted as function of the photon energy in the interval 13.20– 13.80 eV. As can be seen, this plot shows clear structure in the region 13.205–13.350 eV. The observed maxima can be assigned to excitation to ³P Rydberg states derived from [3s² 3p³ nd] configurations accessed from the $3s^23p^4$ ³P ground state. These Rydberg states are parts of a series which converges to the third ionization limit at 13.400 eV [12,13].

To estimate the behaviour of the absolute photoionization cross-section for the three ionic states of sulphur,



Fig. 7. Relative photoionization cross-sections for the first three bands of S atoms in the photon energy region 13.0–18.5 eV. (b) includes σ values for the first band of H₂S measured at different photon energies in [38], denoted with the symbol (*) in the figure.

the integrated area of each band was estimated at a photon energy of 16.7 eV, an energy at which the total photoionization cross-section has been calculated by Yeh and Lindau [9] as 18.2 Mb, using Hartree-Fock-Slater calculations. While for the second and third bands, corresponding to the $S^+(^2D) \leftarrow S(^3P)$ and the $S^+(^2P) \leftarrow S(^3P)$ ionizations, the integrated areas could be easily measured, for the first S atom band, the $S^+({}^4S) \leftarrow S({}^3P)$ ionization, that strongly overlaps with the first band of SH, the result of the double-Gaussian deconvolution shown in Fig. 2(b) was used. The contribution of the first H₂S band at 10.48 eV is included with the first band of SH in the second Gaussian band and it does not affect the calculated intensity of the first S band, which corresponds to the first fitted band. As a result, the intensity ratios of the first three bands of S atoms, were measured at an angle of 54°44', as (6.2 ± 1.0) :10: (5.7 ± 0.5) at 16.7 eV. The relatively high experimental uncertainty of the first band relative intensity is due to overlap of the first S atom band with the first bands of SH and H₂S, as stated earlier. In order to estimate the absolute cross-sections for these ionizations at 16.7 eV, the total areas of these bands were normal-



Fig. 8. Relative photon ionization cross-sections for SH plotted as a function of photon energy (a) for the second band of SH in the photon energy region 13.205–18.494 eV, and (b) for the first three bands of SH in the photon energy region 13.0–18.5 eV. (b,2) includes σ values for the first band of H₂S measured at different photon energies in [38], denoted with the symbol (*) in the figure.

ized to the total cross-section of the $(3p)^{-1}$ ionization of 18.2 Mb, calculated by Yeh and Lindau [9].

Once this had been done, the experimental results could be used to estimate the photoionization cross-section at 13.8 eV, an energy at which the total photoionization cross-section has been determined in an experimental study of the absorption spectrum of S atoms. In this investigation, Tondello [10] determined the photoionization cross-section over the energy region investigated, 10.3–13.8 eV. In the photon energy region

12.8–13.8 eV, which overlaps with the photon energy region investigated in the present work, the photoionization cross-section decreases regularly from 90 to 79 Mb. At 13.8 eV, values for the photoionization crosssections of the first two bands of atomic S could be obtained from the plots made in the present study, whereas the photoionization cross-section for the third band was obtained by extrapolation of the plot shown in Fig. 7(c) to lower energy. This gave estimates of the photoionization cross-section for the first three bands of S atoms at 13.8 eV, which when summed gave a total photoionization cross-section of 58 Mb, which can be compared with the photoionization cross-section value determined in Tondello's [10] work of 79 Mb. Given the approximations involved, most notably that the total photoionization cross-section in the present work has been referenced to the photoionization cross-section calculated at 16.7 eV by Hartree-Fock-Slater calculations [9], it is not surprising that only moderate agree-

ment is obtained. Nevertheless, this comparison indicates there is a clear need for a direct measurement of the photoionization cross-section of atomic sulphur in the vacuum ultraviolet region, most notably above the third ionization energy of 13.4 eV, i.e., at photon energies which include all three ionic states arising from the $(3p)^{-1}$ ionization.

In Fig. 6(a), the relative photoionization cross-section of the first S atom band is plotted as a function of the photon energy in the interval 13.205–18.494 eV. In this figure the maximum at 13.30 eV corresponds to excitation to the [3s² 3p³ (²P) nd] ³P Rydberg states seen in Fig. 6(b), recorded with a smaller photon energy increment. The general behaviour of the photoionization cross-sections for the first three ionizations of sulphur atoms are shown in Fig. 7. In this figure it can be seen that except for the resonance at 13.30 eV, already assigned to excitation to $[3s^2 3p^3 (^2P) nd]^3 P Rydberg states, at least two other small$ maxima are seen at 14.96 and 15.37 eV. These probably correspond to excitation to $[3s^{1} 3p^{4} (^{4}P) np]^{3}D/^{3}P/^{3}S$ or $[3s^1 3p^4 (^2P) np] ^3D/^3P/^3S$ states accessed from the $3s^2 3p^4$ (³P) state. However, because of the step-size used to record these spectra (0.20 eV) and the limited number of data points, assignment of these features will only be achieved when spectra of the type shown in Figs. 6 and 7 are recorded over a wider photon energy range and with a smaller step-size.

Figs. 8(a) and (b) show plots of relative photoionization cross-sections for the first three bands of SH. They show similar overall behaviour to that observed for the equivalent plots for S atoms (Fig. 7) and H₂S [34], but, as with the S atom plots, need to be recorded over a wider photon energy range with a smaller stepsize. Figs. 7(b) and 8(b,2) also include the experimental photoionization cross-section for the first band of H₂S as a function of photon energy, taken from [38], for comparison.

This initial study of S and SH has shown that PES studies on short lived species of this type are possible using synchrotron radiation, and angular distribution and relative cross-section measurements can be made. For SH, the results obtained are new and no calculations of σ or β as a function of photon energy are available with which the results obtained can be compared. For S atoms no previous measurements of this type have been made but, calculations are available of σ and β as a function of photon energy [6–8]; however, the measurements need to be extended over a wider photon energy range and should be recorded with a smaller step-size to allow a more detailed comparison to be made. For example, investigation of the structure shown in Fig. 6(b) at higher resolution should allow the Fano profiles of the observed bands to be investigated. Also, it would be valuable to put the relative cross-section plots obtained in this work for S atoms on an absolute scale. This should be possible as the photoionization cross-section of the first band of H₂S as a function of photon energy is known in the 10.0-60.0 eV region from dipole (e, e+ion) coincidence spectroscopy [38] and at some selected wavelengths in the vacuum ultraviolet region from photoionization measurements [39]. For example, the photoionization cross-section of the first band of H₂S has been measured at 16.7 and 21.22 eV as 17.65 and 9.30 Mb, respectively [38]. Therefore, if spectra were recorded of the reaction $F + H_2S$ under conditions which converted all the H₂S to S atoms (with negligible subsequent reactions, e.g., SF_2 production), and the spectrum of H_2S was then recorded with the F_2 /He discharge turned off with all the other experimental conditions unchanged, then the cross-section of the S bands can be determined from the known cross-section of the first H₂S band at the photon energy used. Experiments of this type are proposed.

4. Conclusions

In this initial investigation on S and SH with synchrotron radiation, the angular distribution parameters and relative photoionization cross-section for the $S^+(^4S) \leftarrow S(^3P)$, $S^+(^2D) \leftarrow S(^3P)$ and $S^+(^2P) \leftarrow S(^3P)$ ionizations and the $SH^+(X^3\Sigma^-, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$, $SH^+(a^1\Delta, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$ and $SH^+(b^1\Sigma^+, v^+ = 0) \leftarrow SH(X^2\Pi, v'' = 0)$ ionizations have been evaluated as a function of photon energy from threshold to 21.64 eV, using radiation from the Elettra synchrotron as the photon source. The results obtained have been compared, where available, with previous experiments and calculations. Further experiments are proposed to extend these measurements to higher photon energies.

Acknowledgements

The authors are grateful to the Reactive Intermediates RTN EC Network, EPSRC and the Leverhulme Trust for support of this work. The authors also acknowledge support from Dr. N. Zema and Dr. S. Turchini and the staff of the POLAR beamline at Elettra.

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