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Single and multiple photoionisation of H₂S by 40 - 250 eV photons

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Abstract

Multi-electron coincidence measurements on photoionisation of H₂S have been carried out at photon energies from 40 to 250 eV. They quantify molecular field effects on the Auger process in detail and in good agreement with existing theory. Spectra of core-valence double ionisation of H₂S are presented and partially analysed. Auger decays from the core-valence states produce triply charged product spectra with unexplained and surprising intensity distributions. Triple ionisation by the double Auger process from 2*p* hole states shows little effect of the molecular field splitting, but includes a substantial contribution from cascade processes, some involving dissociation in intermediate states. The onset of triple ionisation at the molecular geometry is determined as 61 ± 0.5 eV.

INTRODUCTION

The ionisation of the H_2S molecule by high energy photons can lead to single, double, triple or higher ionisation by direct interaction of a single photon with the valence electrons, but at all photon energies above 170 eV, initial production of a core hole in the $2p$ ($\text{L}_{2,3}$) shell of the S atom is much more probable. Above 235 eV production of a hole in the $2s$ (L_1) shell also occurs. The core-hole states then decay mainly by single or double Auger transitions, in which one or two further electrons are ejected. The single Auger process leading to long-lived H_2S^{++} has been widely studied [1–8], as it produces beautiful vibrationally resolved Auger spectra. It provides one of the earliest examples of the influence of the molecular field on the detailed course of single Auger decay [5, 8, 9], where orbital symmetry plays a key role. In recent experimental and theoretical studies total decay rates of the distinct hole states to all doubly charged states [6] and partial widths for Auger transitions from the different core hole states to the H_2S^{++} ground state have been calculated and compared with experimental observations [6, 8]. All the excited states of H_2S^{++} are dissociative, and their dissociations have also been studied in some detail [10, 11].

In this paper we examine single, double and triple ionisation of H_2S by single photons in the energy range 40 to 250 eV, using an efficient multi-electron coincidence method. We demonstrate directly that single Auger decays from all components of the $2p$ hole states populate both the ground and excited (dissociative) states of the dication, with branching ratios which conform with the symmetry-based restrictions on forming stable ground state ions. Overall, transitions to excited states are at least as intense as decay to the ground state. The experiments show that cascade processes, some involving dissociation in intermediate states, are important in the double Auger decay and also in double photoionisation below the inner shells. Spectra are presented showing the formation and decay of molecular core-valence doubly ionised states (also known as shake-off satellites) with holes in both the $2p$ and valence shells.

EXPERIMENTAL DETAILS

Experiments were carried out using a magnetic bottle time-of-flight (TOF) electron spectroscopy technique, whose working principles have been described before (see, e.g., Ref. [12]

and references therein). Briefly, short (0.3 -10 ns) pulses of monochromatic light from either a laboratory lamp (see, e.g., Ref. [13]) or an electron storage ring intersect an effusive jet of target gas at one end of a magnetic bottle. All ($> 90\%$) of the electrons produced are guided by the inhomogeneous field of a conical permanent magnet and the uniform field of a long solenoid to a distant (ca. 5.6 m in the case of the home laboratory and 2.2 m in the case of the storage ring experiments) detector, where their arrival times relative to the light pulse are recorded. For most of the experiments reported here the light source was beam line U49/2-PGM-2 [14] at the BESSY-II storage ring of the Helmholtz Zentrum, Berlin, where the pulses arrive at intervals of 800.5 ns. Because this period is shorter than the flight times of many electrons, strategies must be adopted to correctly identify the particular pulse on which ionisation occurs in each recorded event. Where one electron from an event is sufficiently fast ($\text{KE} > 24 \text{ eV}$) to arrive in less than 800.5 ns, as is true, for instance of all single Auger electrons, its detection provides an unambiguous identification. In core-hole creation, the exact energy of the photoelectron is also known and location of the corresponding peak in the time spectrum similarly identifies the starting pulse. For multiple ionisation below all inner shells these strategies are not applicable, and we have used a newly developed synchronous chopper [15] which transmits every 15th light pulse, increasing the pulse interval to 12 μs .

Conversion of electron flight times to energies was effected using a calibration from the accurately known Auger spectrum of Xe [16] complemented by the identification of high energy lines from the direct valence ionisation of Xe and of the H_2S molecule.

RESULTS

Single ionisation

The photoelectron spectrum for ejection of an $\text{S}2p$ electron from H_2S at $h\nu = 172.6 \text{ eV}$ is shown in Fig. 1. The two main features, near 170.4 and 171.7 eV ionisation energy, correspond to emission of electrons from the $2p_{3/2}$ and $2p_{1/2}$ core-orbitals of the S atom. In the molecular frame a state with the $2p^{-1}$ configuration without spin-orbit splitting would be resolved into the three molecular field split doublet states $^2\text{B}_1$, $^2\text{A}_1$ and $^2\text{B}_2$ from electron holes in the out-of-plane $2p$ orbital and the in-plane $2p$ orbitals which are symmetric and

antisymmetric with respect to the C_2 rotation of the molecule, respectively. In the presence of strong spin-orbit interaction and negligible molecular field splitting, the $2p$ ionized states of H_2S would be $E_{3/2}$ (four-fold degenerate) and $E_{1/2}$ (doubly degenerate). In the C_{2v} symmetry of real H_2S the $E_{3/2}$ term splits into two $E_{1/2}$ states, leaving three Cramers doublets in all, designated as $5e_{1/2}$, $4e_{1/2}$ and $3e_{1/2}$ in order of increasing binding energy. These three doublet states are seen in the spectrum as two components of the $2p_{3/2}$ band with peaks at 170.37 eV and 170.46 eV and the single peak of the $2p_{1/2}$ band at 171.66 eV. The splitting of the two lowest states, measured as 111 meV by Poygin et al. [8], is seen here as a shoulder, but is well resolved in the high resolution photoelectron spectrum at 230 eV photon energy [8]. At our lower photon energy the instrumental resolution (ca. 50 meV) would be sufficient to separate the components, but PCI (post collision interaction) broadens and distorts the peaks.

The three $e_{1/2}$ states seen in the spectrum (cf. Fig. 1) differ by the contribution of the three $2p$ holes. In the bent molecule, the closest approximate correspondence is that of the $5e_{1/2}$ state to a state of 2B_1 symmetry where the remaining unpaired electron is in the out-of-plane $2p$ -orbital. The core hole in the $4e_{1/2}$ state is in the two in-plane $2p$ orbitals while the core hole is essentially equally distributed between the three $2p$ orbitals for the $3e_{1/2}$ state.

There is no sign of vibrational structure in the photolines, although the expected vibrational energy intervals for S-H stretches of 0.3 eV (2500 cm^{-1}) would be easily resolvable. This observation agrees with theoretical predictions [1, 6, 8] that only a small change of equilibrium S-H bond length accompanies $\text{S}2p$ ionisation.

Double ionisation

Our experiments allow several distinct views of the double ionisation of H_2S . At photon energies below the inner shells we can measure valence H_2S^{++} spectra from simple (though both direct and indirect) double photoelectron ejection with relatively good resolution. At energies above 172 eV we can derive selected Auger spectra from decay of each separable component of the $\text{S}2p$ hole states, showing a subset of the same valence dication states. At higher energies Auger effects via the $\text{S}2s$ holes may be visible, and in addition we can obtain core-valence double ionisation spectra, where one electron has departed from the $\text{S}2p$ shell

and one from the valence shell. The same states are also populated by a fast Coster-Kronig transition from an initial S2s hole state. Of these different views, the Auger spectra via S2p holes have been the most intensively studied, and we shall examine them first.

Auger spectra from S2p hole creation

By comparison with classical Auger spectroscopy, coincidence measurements have two great advantages. First, spectra from each component of the inner shell ionisation complex can be extracted separately, whereas in classical one-electron spectra they are overlaid, and secondly the resolution is not limited by the inner-shell hole lifetime (natural width) because energies of both electrons are determined. Unfortunately the second of these advantages is rather vitiated in the present experiments by poor energy resolution for high electron energies in TOF measurements. Nevertheless, structured Auger spectra are obtained, as seen in Fig. 2, where spectra from as nearly as possible pure $5e_{1/2}$, $4e_{1/2}$ and $3e_{1/2}$ hole states, selected from the data of Fig. 1, are presented as (a), (b) and (c).

The electron configuration of H_2S can be written as $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 5a_1^2 2b_1^2$, where the first two orbitals are S1s and S2s, the next three are S2p, $4a_1$ is the inner valence orbital mainly with sulphur 3s character and the last three are the valence orbitals from S3p and H1s. From both high resolution Auger spectra [1–8] and later coincidence measurements [17, 18] we know that the ground state X^1A_1 of H_2S^{++} , reached by $2b_1^{-2}$ double ionisation has its lowest level at 31.66 eV and supports at least four vibrational levels. From the earlier experimental and theoretical work [6–10] we know that Auger decay from the $5e_{1/2}$ component of the $^2P_{3/2}$ state, shown as Fig. 2(a), has a very strong or dominant decay to this stable final state. Nevertheless, the peak in Fig. 2(a) from $5e_{1/2}$ is rather broad (6 eV FWHM) and shows shoulders on the high energy side. The resolution of the apparatus for the ca. 140 eV Auger electrons involved is estimated to be $140/50 = 2.8$ eV, which is considerably less than 6 eV.

Thus it seems highly likely that the $5e_{1/2}$ hole state decays in part to excited states of H_2S^{++} . The calculated energies of the singlet final H_2S^{++} states from Cesar et al. [1] are shown as bars at the base of the figure, and show very close agreement with the positions of features in the experimental spectra. To estimate the branching ratios to the different final states we have fitted the observed spectra by sums of Gaussians of half-width equal to the

instrumental resolution, centred at the energies calculated by Cesar et al. [1], with slight adjustment. First all the calculated energies (cf. tables VI and VII of Ref. [1]) were increased to locate the H_2S^{++} ground state at its experimental position. Then the energies of the two highest singlet states, attributed to $2b_2^{-2}$ and $4a_1^{-1}2b_1^{-1}$ ionisations were each increased by 1 eV to bring them into line with the clear peaks in the spectrum of Fig. 2(a). Apart from a uniform rising background, which was ignored, this approximate procedure yielded very good fits to the spectra with the branching ratios shown in Table I as examples. Because of the non-unique fits and the many approximations enforced by our ignorance of the true state energies and band shapes, besides the poor resolution, the quoted branching ratios are at best only indicative. But they show clearly that while $5e_{1/2}$ decays most strongly by $2b_1^{-2}$ ionisation, it also populates the higher states weakly. Similarly, Auger decays from $4e_{1/2}$ and $3e_{1/2}$ populate the excited states of nascent H_2S^{++} most strongly, but also go to the ground state. The higher excited states are populated less strongly than the lower ones in decays from all components of the $2p$ hole states of H_2S^+ .

A more detailed comparison with the experimental results can be made using newly calculated theoretical spectra of the $5e_{1/2}$, $4e_{1/2}$, and $3e_{1/2}$, components of the $2p$ ionized H_2S molecule shown in Fig. 3 which were obtained as follows. Occupied orbitals were determined with the Hartree-Fock approach using a cc-pVTZ [19] basis set. This orbital set was supplemented with the two S-H-antibonding $6a_1$ and $3b_2$ orbitals obtained from a modified improved virtual orbitals technique [20]. The final states were represented by full configuration interaction (CI) within these valence orbitals and for core ionised states also the $2p$ -type core holes. The Auger electron spectra were calculated as described in Refs. [21] and [6] using the one-centre approximation [22, 23] for Auger transition rates, an effective spin-orbit Hamiltonian [6, 21] for the character of the core ionised states and the moment method of Cederbaum and Tarantelli [24] for the peak positions and widths of the spectral components. The bands that are due to the decay to the electronic final states are represented by Gaussians centred at the relative energy of the final state plus a shift owing to the vibrational relaxation after the excitation process with a width that is also due to vibrational motions within the Auger process. The peak centres, their widths, and shifts and the Auger transition rates for all transitions with a significant contribution to the spectrum are given in Table II. Actually, the widths and shifts of signals that correspond to the transition of different core ionised states to the same final state are slightly

different. However, these differences amount to less than 0.05 eV or 3% for the indicated transitions which is negligible if compared with the approximations within the moment theory. Thus, only average shift and width values are given in Table II. The calculated spectra are shown in Fig. 3. They were obtained by a Gaussian convolution of the complete data set underlying Table II with a FWHM of 2.8 eV corresponding to the experimental resolution of the experiment.

The calculated spectra in Fig. 3 show essentially the same features as the experimental ones (cf. Fig. 2). Thus, the assignments given in the figure and in Table II are a reliable basis for the interpretation of the spectra. The most intense feature is the broad peak between 30 and 40 eV ionisation energy which corresponds to transitions that lead to two holes in the upper valence orbitals ($2b_1$, $5a_1$, and $2b_2$) with dominating $S3p$ character.

The most obvious deviation between experiment and theory is found in the high ionisation energy part of the $4e_{1/2}$ decay spectrum. In the calculated spectrum this part is about a factor of two more intense than the low energy part while in the experimental spectrum the count rate is essentially constant between 30 and 40 eV ionisation energy. Additionally, for the decay of the $4e_{1/2}$ core hole state, the intensity of the low ionisation energy is more dominant in the calculated spectrum than in the experimental counterpart. Finally, the weak structure at about 43 eV ionisation energy is not resolved in the calculated spectrum of the $4e_{1/2}$ decay. These differences may be explained by a 10-30% admixture of $5e_{1/2}$ decay to the $4e_{1/2}$ spectrum in Fig. 2(b) and by a 5-10% admixture of $4e_{1/2}$ decay to the spectrum in Fig. 2(a). Furthermore, the calculated intensities at the present level of theory are known to deviate by 5-10% from the experimental data [21] due to limitations of the method used.

The assignments of the most intense structures in Fig. 3 and the corresponding data in Table II show that double valence configurations with singlet and triplet coupled holes are about equally important for the spectrum. It should be noted that the assignments of the final states to single configurations become rather ambiguous with increasing ionisation energy as the amount of these configurations decreases rapidly. In this energy regime the density of states becomes rather large and only a part of the actual configurations is represented with the present configurational space.

Double ionisation below the inner shells

At photon energies where no inner shell hole creation is possible, double ionisation may still be both direct and indirect, because superexcited singly ionised states exist above the lowest double ionisation energy and may be involved as intermediates. The direct pathway produces two electrons which share the excess energy as a continuous distribution, whereas indirect double ionisation produces a structured distribution. The two contributions can be partially distinguished in our data because the electron pair distributions are measured, and indirect pathways almost always produce one electron of low energy in the range 0 to 5 eV. Fig. 4 shows two spectra taken at 100 eV photon energy, and two from laboratory measurements at 40.8 eV [18] for comparison. In each case we show one spectrum excluding pairs containing a low energy electron and one spectrum selecting such pairs. The marked difference in intensity distribution, seen at both photon energies, is attributed to the strong contribution from singly ionised intermediate states decaying preferentially to excited dication states rather than to the 1A_1 ($2b_1^{-2}$) ground state. The resolution in these valence double ionisation spectra is better than in the Auger spectra (cf. Fig. 2) but individual excited states cannot be distinguished. This is mainly because the bands are almost structureless, in accord with the states' dissociative nature, and may also be partly due to band congestion, as valence photoionisation produces both triplet and singlet states whereas the Auger effect in light atoms populates singlets predominantly. On the other hand our present calculations indicate that the $2p$ hole Auger decay in H_2S populates singlet and triplet final states with comparable intensity (cf. Fig. 3).

Core-valence double ionisation spectra

At photon energies of 230 eV and above double ionisation may produce states with one hole in the $S2p$ shell and one in the valence shell; such states may also be called "shake-off satellites". We show three spectra of this kind in Fig. 5. In the present case of H_2S , as for most other molecules studied so far [26–30], the core-valence spectrum bears a very close resemblance to the ordinary photoelectron spectrum [31] shifted to about 20 eV above the inner shell edge and doubled by the core-hole spin-orbit splitting. The correspondence allows us to identify the main bands involving $^2P_{3/2}$ cores as follows: at 192.4 eV, $S2p^{-1}2b_1^{-1}$; at

195.3 eV, $S2p^{-1}5a_1^{-1}$; at 197 eV, $S2p^{-1}2b_2^{-1}$; at 206.5 eV bands arising from $S3s^{-1}$, i.e. $4a_1^{-1}$. The two lower spectra in Fig. 5 are from direct double ionisation to the states shown, while the uppermost spectrum, (c), comes from initial production of a $S2s$ hole followed by its Auger decay. It is perhaps not surprising on grounds of overlap that when there is an initial hole in $S2s$, the core-valence states deriving their intensity from emission of a $S3s$ electron are relatively favoured, as clearly seen in the spectra. As in other cases [26–30] it seems that the singlet-triplet splitting is small, so with rare exceptions only a single band is seen for each configuration.

After formation, the core-valence states decay by Auger emission to produce triply ionised H_2S . The core-valence spectra shown in Fig. 5, are extracted from the coincidence data as the energies of the two slower electrons in triple electron emission, as this yields cleaner spectra than selection of the same states from electron pairs where the fastest of the three electrons has been missed.

Double ionisation via $S2s$ hole creation

The photoline for ionisation of a $S2s$ electron is found as a featureless, broad and weak band at 235.0 eV. Its width derives mainly from a very short lifetime towards Coster-Kronig decay in which the $2s$ hole is initially filled by a $2p$ electron. The subsequent Auger emission of a valence electron gives rise to the core-valence states shown in Fig. 5 and discussed above. While that pathway is dominant, a small fraction of the intensity decays by capture of one valence electron and ejection of another to form the valence doubly ionised states. The spectrum produced in this way (not shown) is of very low intensity but seems to differ substantially from those produced by Auger emission from the $2p$ holes states. The ground and lower valence states of H_2S^{++} are barely detectable, and the most highly populated states lie in the 50 eV region, apparently dominated by ejections from the $S3s$ orbitals.

Triple ionisation

The onset of triple ionisation of H_2S is at about 60 eV, so it should in principle be possible to obtain a complete triple ionisation spectrum at 100 eV photon energy, particularly with use of the chopper for unambiguous energy determination. Unfortunately the cross-section

seems to be too low at this energy to produce a spectrum above the noise level in our experiments. Triple ionisation is clearly observed in double Auger decay of the $S2p$ hole states and in single Auger decay from the core-valence states produced at higher photon energy. No stable H_2S^{3+} ions have been reported in mass spectra, so all the accessible states are assumed to be dissociative.

Triple ionisation spectra from double Auger decay of $S2p^{-1}$ hole states

In the double Auger process, the emission of two valence electrons can be considered as a separate step after creation of the initial core hole. As in double photoionisation, both direct and indirect (cascade) pathways can be distinguished. The direct process is envisaged as a simultaneous emission of the two electrons producing a continuous distribution of the excess energy shared between them. The cascade process produces a structured electron spectrum because superexcited doubly-charged states are formed as short-lived intermediates. Some intermediate states dissociate before the final (third) electron is ejected, so the spectrum shows autoionisation from a dissociation fragment, usually a superexcited atom, as discussed below.

Fig. 6 is a coincidence map showing part of the distribution of electron triples involving decay of the $S2p^{-1}$ state complex. Horizontal lines at different vertical positions correspond to formation of final states of H_2S^{3+} . The strong vertical intensity concentrations are the $2p_{1/2}$ and $2p_{3/2}$ photolines. At summed energies $E_1+E_2+E_3$ above 110 eV, distinct vertical lines are due to autoionisation from superexcited fragments produced by dissociation in intermediate ionised states. Spectra of the final triply charged products can be extracted by summation along horizontal lines in different zones of the distribution. Fig. 7 shows spectra extracted from two zones, one corresponding to the decay from the whole of $^2P_{3/2}$, the other to decays involving the autoionizing fragments. Because of dissociation in the intermediate states, the autoionizations give access to parts of the repulsive potential energy surfaces of H_2S^{3+} at binding energies below the energy range of vertical transitions at the molecular geometry. From the data of Fig. 7 we deduce a triple ionisation energy for H_2S at the molecular geometry of 61 ± 0.5 eV, while its triply ionised dissociation products can be reached at an energy of 53 eV.

It might be expected that as in normal Auger decay, the molecular field splitting of

the core hole states should also influence the double Auger process. In fact triple ionisation spectra taken in coincidence with photoelectrons corresponding to the $5e_{1/2}$ and $4e_{1/2}$ components of $2p_{3/2}$ are identical in shape. There is a significant difference in relative intensity, however, as the triple ionisation spectrum from $5e_{1/2}$ is distinctly weaker than that from $4e_{1/2}$. The overall ratio of single to double Auger decay, including all Auger electrons, appears to be about 15:1 from $5e_{1/2}$ but 10:1 from $4e_{1/2}$.

Triple ionisation spectra from Auger decay of core-valence states

In studies of triple ionisation of OCS and CS₂ via core-valence intermediate states [29, 30] we have discovered that orbital hole identities tend to be preserved in such triple ionisations, and we might expect the same thing to happen in H₂S. The observed spectra, Fig. 8, are less easy to interpret. When the initial state assigned as $2p^{-1}2b_1^{-1}$ decays, it leaves the triply charged products in a well-defined state or group of states between 65 and 70 eV, with a sharp onset, a peak at 67.4 eV and a weak tail to higher energy. From $2p^{-1}5a_1^{-1}$, however, a much broader distribution of final states is produced, stretching from 57 eV to 70 eV with a peak at 65.6 eV. The greater breadth may be related to a wider range of nuclear motion in the intermediate state, but as $5a_1$ is at higher energy than $2b_1$, it is hard to understand why the peak has moved down. From the broad band of core-valence states including $2p^{-1}2b_2^{-1}$ a broad band of triple ionisation is produced, again with no increase in peak energy. Most surprising of all is that when the intermediate state is $2p^{-1}4a_1^{-1}$ there is again almost no shift in the peak triple ionisation energy, which goes up only to 69.4 eV. This +2 eV shift relative to the first band is miniscule when compared with the energy difference between the $2b_1$ and $4a_1$ orbitals in the neutral molecule, of 12.5 eV. At this stage we can only point out that the attribution of single configurations to the states involving inner-valence orbitals is a gross simplification; mixed configurations are certainly involved and may affect the dynamics significantly.

Dissociative ionisation with fragment autoionisation

In valence double ionisation and in double Auger triple ionisation we observe the autoionisation of fragment species, often leading to below threshold double (or triple) ionisation, as

already seen by earlier techniques in H_2S [17]. The atomic autoionisations produce sharp low energy lines in the electron spectra, as shown in Fig. 9. Most of the autoionising species can be identified as neutral superexcited S atoms [32–34], as indicated in the figure. One exception is the strong peak at about 0.03 eV, which was tentatively ascribed to HS^* in an earlier work [17].

If the intermediates responsible for formation of S^* atoms are created by Auger emission of one electron after initial hole formation, they (the intermediates) must be doubly charged and would have to dissociate into $\text{S}^* + 2\text{H}^+$. Alternatively, the intermediates might be singly charged, if they can be formed by soft X-ray emission from the core-hole state. Although this must be a very minor channel, the near identity of autoionisation spectra produced in valence double ionisation and in Auger triple ionisation does suggest the existence of common intermediates.

DISCUSSION AND CONCLUSIONS

Molecular field effects on the normal Auger process following $2p$ electron ionisation, which operate through effects of orbital symmetry, are clearly seen in the branching to different final doubly charged states. The same effects seem likely to be the cause of substantial differences in the ratios of single to double Auger decay from the different molecular-field split core hole levels. These effects have received considerable theoretical attention, and the present new experimental results are in good accord with the theoretical predictions. Triple ionisation (double Auger) seems to be less affected by the distinction between molecular-field split components, possibly because no H_2S orbitals are degenerate, so every triple ionisation involves at least two valence orbitals.

The formation of core-valence doubly ionised states (or shake-off satellites) in H_2S has not been treated theoretically before, so the present identification of bands seen in the spectra with particular configurations remains empirical. Nevertheless, unless the attributions are very surprisingly erroneous, the Auger decay patterns from the CV states present a notable enigma. Why do some of the highest energy CV states, where inner valence electrons have been removed, decay to low energy states of the triply charged ions rather than to high energy states with retention of orbital occupancy?

The energies of the Auger electrons emitted in decay of the core-valence states are lower

than those of the main single Auger lines, and fall exactly in the range where Poygin et al. [8] observed resolved satellite peaks in photoionisation at 230 eV. They attributed them to formation of atomic or diatomic dissociation products, and it now seems possible from our results that such products are indeed formed, but in triple ionisation by intermediacy of the core-valence states.

Spectra of triple ionisation itself, either to nascent states of molecular H_2S or to its dissociation products, are presented here for the first time. We hope that our results will soon stimulate theoretical efforts to explain the systematic features uncovered. One aspect is the importance of cascade processes in molecular double Auger, with dissociation of the intermediate states and autoionisation from the fragments. This complex process offers a redoubtable challenge to theory.

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FIG. 1. Photoelectron spectrum of the $S2p$ levels taken at 172.6 eV photon energy. The small sharp peak at 172.39 eV ionisation energy is probably an artefact. The $^2P_{1/2}$ peak (171.66 eV) is broader than either component of the $^2P_{3/2}$ complex because of the stronger PCI (post collision interaction) effect at the lower photoelectron energy.

TABLE I. Branching in Auger decay from $H_2S\ 2p^{-1}$ hole states to single-configuration final states of H_2S^{++} . Energies have been rounded. All intensities are relative to the transition from $5e_{1/2}$ to $2b_1^{-2}$ and all arise from approximately the same number of initial photoionisation events, as in Fig. 2.

Energy (eV)	Ionisation	$5e_{1/2}$	$4e_{1/2}$	$3e_{1/2}$
32	$2b_1^{-2}$	100	42	51
34	$5a_1^{-1}2b_1^{-1}$	47	47	63
36	$2b_2^{-1}2b_1^{-1}$	54	45	54
37.5	$5a_1^{-2}$	16	19	23
39	$2b_2^{-1}5a_1^{-1}$	17	49	60
44	$2b_2^{-2}$	21	21	21
51	$4a_1^{-1}2b_1^{-1}$	9	7	9

FIG. 2. Selected Auger spectra showing states of H_2S^{++} populated from distinct levels within the $\text{S}2p$ hole spectrum: (a) spectrum from $5e_{1/2}$ taken as a 50 meV wide slice on the rising edge centred at 170.37 eV (cf. Fig. 1); (b) from (mainly) $4e_{1/2}$ at 170.46 eV and (c) from $3e_{1/2}$ at 171.66 eV. The three curves are on a common intensity scale, but (b) and (c) are offset vertically by 1400 and 2200 counts respectively for clarity. Each of the three spectra is extracted in coincidence with 100 000 photoelectron emission events, so the intensities are strictly comparable. This was done by adjusting the widths of the slices taken in (b) and (c), which were thus both slightly less than 50 meV. The single configuration energies indicated above the spectra are from Cesar et al. [1] with adjustments as described in the text.

FIG. 3. Calculated Auger spectra of the spin-orbit components of the 2p ionised H_2S^{++} molecule: (a) shows the spectrum of the $5e_{1/2}$, (b) that of the $4e_{1/2}$, and (c) that of the $3e_{1/2}$ component. Both triplet and singlet states are shown for all the configurations where they arise.

FIG. 4. Double ionisation spectra of H_2S taken at 40.8 eV ((a) and (b)) and 100 eV ((c) and (d)). The lower spectrum of each set has been derived by excluding electron pairs where one electron is of low energy ($< 5\text{eV}$), while the upper spectra have been derived by selecting only such pairs. Spectra b), c) and d) are offset vertically by 200, 500 and 700 counts respectively for clarity.

FIG. 5. Core-valence spectra of H_2S showing states where one electron is missing from the $2p$ orbital and one from a valence orbital. (a) at 230 eV photon energy; (b) overall spectrum at 250 eV displaced upwards by 800 counts; (c) spectrum at 250 eV in coincidence with photoelectrons from the $2s^{-1}$ photoline, with local background removed by subtracting a spectrum extracted in exactly the same way in coincidence with a section of the (flat) photoelectron spectrum adjacent to the $2s^{-1}$ peak and of equal width.

FIG. 6. Distribution of intensity in coincident electron triples from H₂S at 172.6 eV photon energy. The origin of the different features is explained in the text.

FIG. 7. Triple ionisation spectra of H_2S at 172.6 eV, extracted from Fig. 6. (a) for E_3 less than 0.7 eV, corresponding mainly to fragment autoionisations; (b) for E_3 between 2.0 and 2.2 eV, corresponding to the $^2P_{3/2}$ photoline. The spectra are on a common vertical scale, but (b) is displaced upwards by 100 counts.

FIG. 8. Triple ionisation spectra of H_2S from single Auger decay of the core-valence doubly ionised states seen in Fig. 5. (a) from the states between 192 and 194 eV, assigned as $2p^{-1}2b_1^{-1}$; (b) from states between 195 and 196 eV, assigned as $2p^{-1}5a_1^{-1}$; (c) from states between 196 and 200 eV, thought to involve a mixture of configurations; (d) from states between 204 and 210 eV, thought to involve $2p^{-1}4a_1^{-1}$ ionisation. All the curves are on a common intensity scale with appropriate zero-level displacements; i.e. spectra b), c) and d) are offset vertically by 230, 420 and 700 counts respectively for clarity.

FIG. 9. Spectra of low energy electrons, (a) in triple ionisation of H_2S by the double Auger effect starting from a $^2P_{3/2}$ hole created at 172.6 eV photon energy; (b) in double ionisation of H_2S at 40.8 eV photon energy. The curves are on the same vertical scale, but curve (b) is offset naturally by a strong low-energy background caused mainly by secondary electrons generated by surface collisions in the spectrometer. The line identities marked on the figure are from Penent et al. [32].

TABLE II. Auger transition rates (Γ), peak shifts (ΔE), peak widths (σ), peak centres in terms of double ionisation energies ($\langle E \rangle$), terms, leading configurations and their contribution to the wavefunction according to the calculations described in the text.

	Γ (10^{-6} au)			ΔE	σ	$\langle E \rangle$	term	%	leading configuration
sum	$3e_{1/2}$	$4e_{1/2}$	$5e_{1/2}$	(eV)	(eV)	(eV)			
736	208	28	500	-0.15	0.44	31.65	1A_1	90	$(2b_1^{-2})$
962	296	200	466	-0.36	1.04	32.61	3B_1	91	$(5a_1^{-1}2b_1^{-1})$
596	184	125	288	-0.44	1.22	34.23	1B_1	92	$(5a_1^{-1}2b_1^{-1})$
696	227	187	282	-0.37	1.98	35.57	3A_2	94	$(2b_2^{-1}2b_1^{-1})$
415	135	109	172	-0.39	1.99	36.47	1A_2	95	$(2b_2^{-1}2b_1^{-1})$
557	191	240	127	-0.71	2.06	37.61	1A_1	89	$(5a_1^{-2})$
536	194	266	76	-0.59	1.88	38.36	3B_2	95	$(2b_2^{-1}5a_1^{-1})$
327	119	163	45	-0.58	1.81	40.20	1B_2	92	$(2b_2^{-1}5a_1^{-1})$
306	87	20	199	-0.73	2.34	43.25	3B_1	54	$(4a_1^{-1}2b_1^{-1})$
207	76	106	24	-0.67	3.73	43.60	1A_1	86	$(2b_2^{-2})$
136	38	3	96	-0.88	2.87	45.63	1B_1	58	$(2b_2^{-1}5a_1^{-1}2b_1^{-1}3b_2^1)$
220	76	98	46	-0.93	2.53	47.28	3A_1	57	$(4a_1^{-1}5a_1^{-1})$
88	25	7	56	-0.94	3.06	48.68	3B_1	61	$(2b_2^{-1}5a_1^{-1}2b_1^{-1}3b_2^1)$
165	62	88	16	-0.94	3.74	50.16	3B_2	59	$(4a_1^{-1}2b_2^{-1})$
76	21	1	53	-1.21	3.56	49.95	1B_1	44	$(2b_2^{-1}5a_1^{-1}2b_1^{-1}3b_2^1)$
85	29	38	18	-1.23	3.46	50.64	3A_1	61	$(2b_2^{-1}5a_1^{-2}3b_2^1)$
155	52	61	42	-1.12	3.09	51.33	1A_1	45	$(4a_1^{-1}5a_1^{-1})$
231	65	10	156	-0.84	2.44	51.73	1B_1	48	$(4a_1^{-1}2b_1^{-1})$
80	27	32	22	-1.28	3.63	53.69	1A_1	29	$(4a_1^{-1}5a_1^{-1})$
84	31	44	8	-1.43	4.18	56.38	1B_2	38	$(4a_1^{-1}2b_2^{-1})$
101	38	54	9	-1.34	4.80	57.90	1B_2	41	$(4a_1^{-1}2b_2^{-1})$
70	23	22	25	-1.38	4.53	61.12	1A_1	47	$(4a_1^{-1}2b_2^{-1}5a_1^{-1}3b_2^1)$
118	40	43	36	-1.71	5.29	66.24	1A_1	39	$(2b_2^{-2}5a_1^{-2}3b_2^2)$