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Decay channels of core-excited H_2S studied by synchrotron-radiation-excited photoelectron spectroscopy

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The $2p(3a_1)$ to $6a_1$ and $3b_2$ photoexcitation resonance of H_2S has been studied using synchrotron-radiation-excited photoelectron spectroscopy. The overall shape of the measured photoelectron spectrum of H_2S is found to be in close resemblance with the normal Auger-electron spectrum of HCl. The spectrum is assumed to result mainly from the Auger decay in the excited HS molecule taking place after the molecular dissociation of the excited H_2S molecule. The finding is compared with the results of multiconfiguration self-consistent-field calculations [A.N. de Brito and H. Agren, following paper, Phys. Rev. A **45**, 7953 (1992)].

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I. INTRODUCTION

High-resolution photoabsorption spectra of molecules show two kinds of inner-shell resonances in the discrete part of the spectra. Sharp lines represent the core electron excitations to the Rydberg states. Broad structures of lower energy result from the excitation of the core electron to the first empty molecular orbitals. In the hydride molecules these molecular resonances were found to decay via fast dissociation of the molecule followed by the resonance Auger process in the excited fragment. This kind of decay channel was first identified in the photoelectron spectrum of HBr recorded at the $3d \rightarrow \sigma^*$ excitation energy [2]. The HCl $2p \rightarrow \sigma^*$ resonance was also found to decay predominantly by dissociation followed by the electronic decay [3].

In this work we will continue our study of core-excited molecules and extend it to the triatomic H_2S molecule. H_2S is isoelectronic with argon like HCl studied recently by us. With the aid of high-resolution electron spectra recorded at resonance photon energies we will study the decay channels of the core-excited H_2S. On the basis of a simple *semiclassical* model the time scales of the dissociation and the Auger decay are found to be of the same order of magnitude. Details of the electron spectra are used to distinguish the three possible decay channels.

(i) Fast dissociation of both hydrogens into (a) separated atoms and (b) the H_2 molecule, followed by the Auger process in the excited sulfur atom, hereafter referred to as channels 1a and 1b, respectively, or channel 1 when the product of the hydrogen dissociation is not important for the discussion.

(ii) Dissociation of one hydrogen followed by the Auger process in the excited HS molecule (channel 2).

(iii) The Auger process in the excited H_2S molecule before dissociation (channel 3).

Channel 1 should result in the Auger-electron spectrum of excited sulfur atoms. No experimental spectra are available for comparison. Since the atomic calculations are found to reproduce well the experimental Auger transitions [4], they will be used for comparison.

In the case of channel 2 a comparison with the normal Auger-electron spectrum of HCl should show a close resemblance. This is because the excited HS molecule has the same electron configuration as the neutral HCl molecule resulting in analogous Auger transitions. Correspondingly, the normal Auger spectrum of Ar [5] is in a close resemblance to the Auger spectrum of excited Cl atoms obtained after dissociation of the core-excited HCl molecule [3]. The reference spectrum to test if the excited state of H_2S decays via channel 2 is thus the Auger-electron spectrum of HCl [6,7] complemented with the calculated Auger transition rates [8].

High-resoluton photoelectron spectra of H_2S by Adam and co-workers [9,10] are the useful references when testing if channel 3 is a possible decay channel of the core-excited H_2S. This is because the participator and spectator Auger lines of the H_2S molecule should appear at the same energy positions as the outer-shell photoelectron lines and their satellites.

Ab initio molecular orbital calculations are of importance in order to achieve a more deeper understanding on the decay channels of the excited state. The interatomic potential-energy surfaces were obtained by de Brito and Ågren [1] in the companion paper (hereafter referred as paper II) for the ground state and selected excited states of H_2S by multiconfiguration self-consistent-field (MCSCF) calculations. The results of paper II are compared with experimental results.

II. MEASUREMENTS

Earlier photoabsorption measurements of H_2S by Hayes and Brown [11] showed broad structures at the 165–167-eV photon energy region. The energy of the incoming radiation beam was tuned in our measurements across this broad resonance structure. The spectra of emitted electrons were recorded at mean photon energies of 165, 165.5, 166, 166.5, and 167 eV (Fig. 1) using the Laybold-Heraeus electron spectrometer at the Canadian Synchrotron Radiation Facility located at the 1-GeV Aladdin storage ring in Stoughton, Wisconsin [12]. The beam line uses the Grasshopper Mark IV grazing incidence monochromator equipped with a 900-groove/mm holographic grating. The spectra were taken applying a constant 50-eV pass energy in the spectrometer and the monochromator slit width of 50 μm. The spectrometer broadening is thus about 0.3 eV, and the photon bandwidth is about 0.5 eV at the photon energies of the resonance excitations.

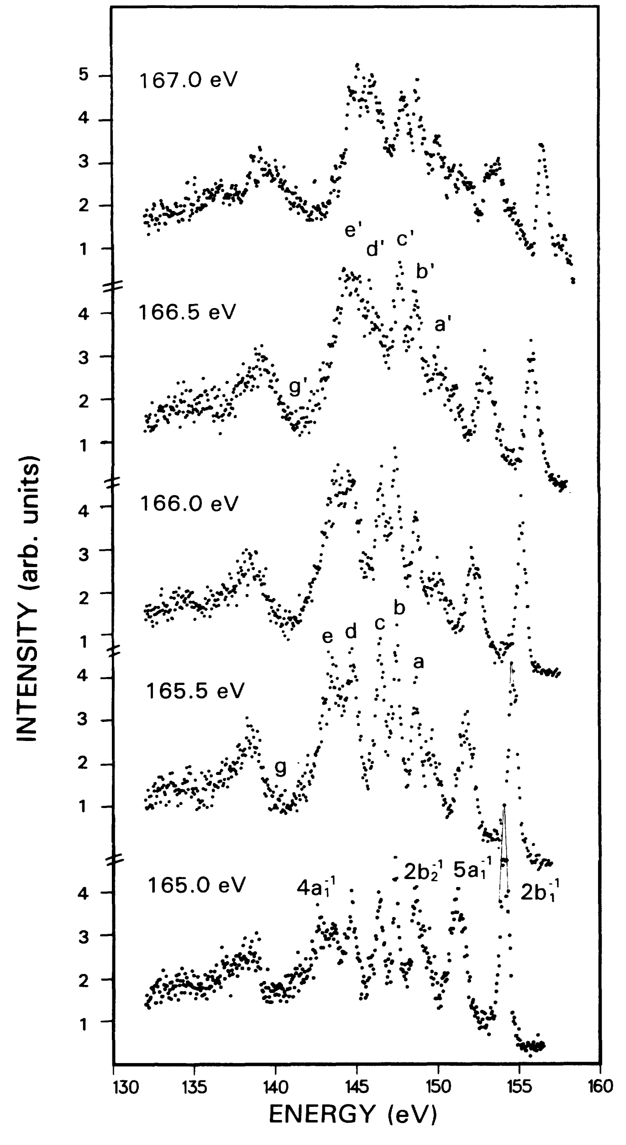

FIG. 1. The ejected electron spectra of H_2S recorded using the mean photon energies of 165, 165.5, 166, 166.5, and 167 eV to excite the $2p_{3/2,1/2}$ $(3a_1)$ electrons to the $6a_1$ and $3b_2$ states. The labels a–g and a'–g' are discussed in text. The photoelectron lines $4a_1^{-1}$, $2b_2^{-1}$, $5a_2^{-1}$, and $2b_1^{-1}$ are labeled in the lowermost spectrum.

In order to study the enhancement of the electron spectra at resonance energies in more detail, the valence-band photoelectron spectrum was also recorded at 125-eV photon energy which is well below the resonance. The shifted and normalized photoelectron spectrum was then subtracted from the spectra taken at resonance energies supposing that the relative intensities of lines originating from direct photoionization do not change essentially between 125- and 165-eV photon energies. This procedure is justified only if the participator Auger decay, which populates the same final states as the valence ionization, is of vanishing importance in the decay of the excited molecular state. Our assumption that this is the case is supported by the results for free atoms which indicate that the participator processes are of minor importance compared to the spectator processes. For instance, the first excited states of Ar decay predominantly (98%) by spectator Auger transitions according to the multiconfiguration Dirac-Fock calculations [13]. The second even stronger evidence is that recent high-resolution experiments do not show any visible contribution due to the participator Auger decay [14].

The low-kinetic-energy parts of the spectra taken at the energies of the resonance excitations also contain structures due to the normal Auger transitions originating from the ionizations of the H_2S molecules by second- and higher-order diffracted light and by scattered light in the photon beam. Therefore, the normal Auger spectrum taken at 278-eV photon energy was also normalized and subtracted from the original resonance spectra. There are certain difficulties, however, in the normalization of photoelectron and Auger-electron spectra which may cause some inaccuracies into the final results.

A least-squares fit of Voight functions to the spectra was also carried out using the CRUNCH code [15]. The width and shape of the functions was kept constant during the fitting. The number of functions was chosen to give a best fit. Therefore the results of the fit should not be taken too literally. Only the positions of the sharper lines are reliable. They are given in Table I. The appearance of many other line components only indicates that some extra intensity is left in that part of the spectrum. Positions and intensities of individual nonresolved lines may not have any physical meaning.

III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

Figure 2 (upper part) shows the ejected electron spectrum of H_2S taken at an excitation energy of 165.5 eV after the subtraction of the valence shell photoelectron spectrum and the normal Auger spectrum. No essential

TABLE I. Experimental and theoretical Auger energies of HS*.

Peak[a]	Experimental	Theoretical[b]	State	Dominant[b] configuration
a'	149.3 (3)	151.59	$^3\Sigma^-(p_{1/2})$	$5\sigma^2 2\pi^2$
a	148.1 (3)	150.34	$^3\Sigma^-(p_{3/2})$	$5\sigma^2 2\pi^2$
b'	148.1 (3)	150.14	$^1\Delta(p_{1/2})$	$5\sigma^2 2\pi^2$
c'	147.2 (3)	149.00	$^1\Sigma^+(p_{1/2})$	$5\sigma^2 2\pi^2$
b	147.0 (3)	148.89	$^1\Delta(p_{3/2})$	$5\sigma^2 2\pi^2$
c	146.0 (3)	147.75	$^1\Sigma^+(p_{3/2})$	$5\sigma^2 2\pi^2$
d'	145.3 (6)	147.65	$^3\Pi(p_{1/2})$	$5\sigma^1 2\pi^3$
e'	144.3 (6)	146.36	$^1\Pi(p_{1/2})$	$5\sigma^1 2\pi^3$
d	144.1 (3)	146.40	$^3\Pi(p_{3/2})$	$5\sigma^1 2\pi^3$
e	143.1 (3)	145.11	$^1\Pi(p_{3/2})$	$5\sigma^1 2\pi^3$
g'		141.15	$^1\Sigma^+(p_{1/2})$	$5\sigma^0 2\pi^4$
g		139.90	$^1\Sigma^+(p_{3/2})$	$5\sigma^0 2\pi^4$

[a] As labeled in Fig. 2.

[b] Taken from paper II.

changes were observed between the spectra recorded at 165- and 165.5-eV photon energies. The upper spectrum in Fig. 2 consists of four sharp peaks a–d and broader structures e–g on their low-kinetic-energy side. The sharper peaks were fitted by one to two Voigt functions but several functions were needed to find the best fit to the broader structures. This may indicate that many lines are overlapping or that the width of the lines is broader.

In the one-electron approximation the ground-state electron configuration of H_2S is $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 5a_1^2 2b_1^2 6a_1^0 3b_2^0$. According to the photoabsorption spectrum [11] the excitation of the $3a_1$ core electron to the $6a_1$ molecular orbital takes place at a photon energy of about 165 eV. The excitation to the $3b_2$ orbital is in close proximity, too. Whether the $3a_1^{-1}6a_1^1$ and $3a_1^{-1}3b_2^1$ excited states dissociate fast enough to compete with electronic decay depends on the relationship between the Auger lifetime and the dissociation time.

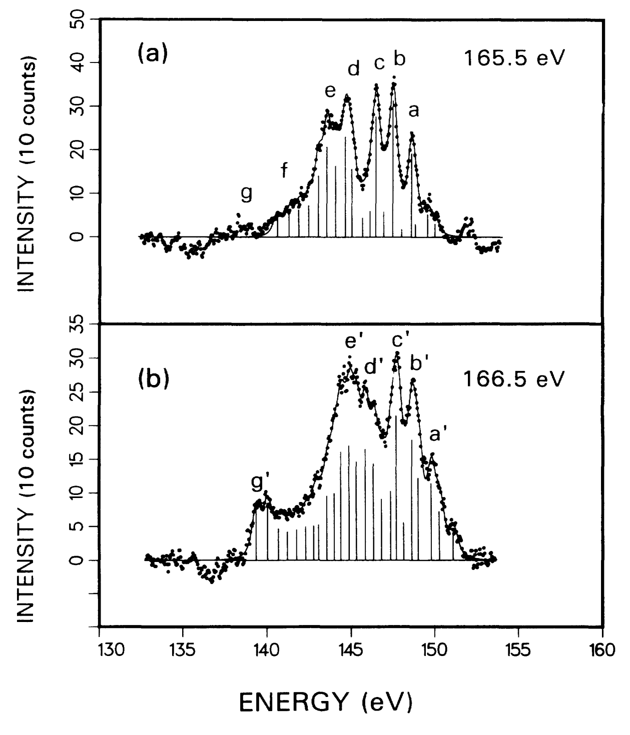

FIG. 2. The ejected electron spectra of H_2S taken at the mean excitation energies of (a) 165.5 eV and (b) 166.5 eV after the subtraction of the valence shell photoelectron spectrum and the normal Auger spectrum. The solid curves and the vertical lines represent the least-squares fits of standard functions to the data points.

The lifetime of the $2p$ core hole of the isoelectronic argon atom is of the order of 5.5 fs. The lifetime was estimated from the measured linewidth of 0.12 eV for the Ar $L_{2,3}MM$ Auger spectrum. As a rough approximation we assumed that the lifetime of a $2p_{H_2S}$ core hole is of the same order of magnitude. Using this lifetime for the $2p_{H_2S}$ core hole we obtained an order of magnitude estimate for the internuclear distance HS-H at the moment of inner-hole relaxation. Using the numerical values of the potential-energy curves of Fig. 9(b) from paper II we calculated that the H atom will have moved 1.5 a.u. in 5.5 fs. The internuclear distance HS-H is thus 3.9 a.u. when the decay takes place. From the same figure of paper II we also noted that the molecule will open its angle. The used semiclassical calculation is rough and only indicates that the electronic decay and the dissociation occur on overlapping time scales.

After dissociation of the H_2S molecule the produced excited HS molecule decays nonradiatively. The transitions from the initial excited configuration $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4 4\sigma^2 5\sigma^2 2\pi^4$ to the final two-hole configurations $5\sigma^0 2\pi^4$, $5\sigma^1 2\pi^3$, or $5\sigma^2 2\pi^2$ are thus taking place. Six possible electronic states are related in $\Lambda\Sigma$ coupling to these final-state configurations: $5\sigma^2 2\pi^2(^3\Sigma^-)$, $5\sigma^2 2\pi^2(^1\Delta)$, $5\sigma^2 2\pi^2(^1\Sigma^+)$, $5\sigma^1 2\pi^3(^3\Pi)$, $5\sigma^1 2\pi^3(^1\Pi)$, and $5\sigma^0 2\pi^4(^1\Sigma^+)$. The normal Auger spectrum of HCl has just the same Auger transitions [6–8]. Energy splittings and relative transition rates are not expected to change considerably on going from HCl to HS*. Close resemblance is thus expected between the Auger spectra of HCl and HS*. The main difference is that in the spectrum of HCl both spin-orbit components $2p_{3/2}$ and $2p_{1/2}$ are ionized simultaneously resulting in two overlapping spectra [6,7], whereas at 165–165.5-eV photon energies the $2p_{3/2}$ electron is predominantly excited in H_2S.

By comparing the spectrum of Fig. 2 (upper part) with the normal Auger spectrum of HCl [6–8] the peaks $a-e$ and g can tentatively be identified to correspond to the transitions to the final states $5\sigma^2 2\pi^2(^3\Sigma^-)$, $5\sigma^2 2\pi^2(^1\Delta)$, $5\sigma^2 2\pi^2(^1\Sigma^+)$, $5\sigma^1 2\pi^3(^3\Pi)$, $5\sigma^1 2\pi^3(^1\Pi)$, and $5\sigma^0 2\pi^4(^1\Sigma^+)$ of HS*, respectively. On the basis of the analogy between HCl and HS* it seems obvious that the main decay channel of the core-excited H_2S is the dissociation of one hydrogen atom followed by the Auger process in the excited HS molecule, referred to as channel 2 in the Introduction. The finding is supported by the results of the MCSCF calculations reported in paper II for the Auger energies of HS*. Calculated absolute energies were found to be 2 eV too large, whereas the relative energies agreed within 0.3 eV. Good agreement indicates that Auger decay takes place in HS*.

All the structure cannot be identified to be due by the decay channel 2. Especially around f and on the high-energy side of peak a we see some extra intensity. The first one appears at the position of the $4a_1$ photoelectron line of H_2S and the satellite structure accompanying it and the second one at the position of the $2b_2$ photopeak. The $4a_1$ photoelectron satellite structure of H_2S was proposed by Adam, Cauletti, and Piancastelli [9] to be due to the interaction between a single-hole configuration with excited configuration having two holes in outer valence orbitals and one electron in an unoccupied orbital. If the excited H_2S molecule decays directly by participator Auger decay (excited electron taking part in the Auger decay) the photopeak intensities would increase. Satellite intensities would be enhanced in the case of spectator Auger decay (the excited electron remaining as a spectator during the Auger decay). Due to great difficulties in the subtraction of the photoelectron spectrum obtained off resonance from the resonance spectrum, it is extremely hard to be sure about the intensity enhancement in Fig. 2. If our guesses are real, however, there would be a competing decay channel for the dissociation: the Auger process in the excited H_2S molecule before dissociation (referred to as channel 3 in the Introduction). Alternatively the extra structure might be due, not to pure molecular contribution, but a superposition of dissociative molecular structures with varying energies. This contribution, however, seems to be of minor importance since the main sharp peak structure clearly appears at the energy region where no H_2S photoelectron or satellite lines have been observed. Thus, as already pointed out above, the dissociation of one hydrogen atom followed by Auger decay in the excited fragment is obviously the main decay channel of the excited state in question.

In order to find out if the simultaneous dissociation of two hydrogens followed by Auger decay (channel 1) gives any contribution into the experimental spectrum, the Auger process in excited sulfur atom was also considered. The $2p_{3/2}^5 3p^5 \rightarrow 2p_{3/2}^6 3p^3$ Auger decay in S^* has a rich fine structure since we are dealing with an open-shell atom. Energies of these transitions fall in the kinetic-energy region of 145–158 eV according to our multiconfiguration Dirac-Fock (MCDF) calculations carried out with the code of Grant [16]. The $2b_1$, $5a_1$, and $2b_2$ photoelectron lines in the resonance spectra (Figs. 1 and 2) appear at the same kinetic-energy region with the expected atomic lines. We cannot see, however, any clear extra structure around these photoelectron lines besides the HS* lines. Furthermore, when increasing the photon energy, the kinetic energies of photopeaks decrease by the same amount but the kinetic energies of sulfur Auger lines should remain the same. By comparing the spectra taken at various excitation energies, no lines obeying such a behavior were found at the energy region of the main photopeaks. We thus conclude that if there exists such a decay channel where simultaneous dissociation of both hydrogens is followed by Auger decay, it will be extremely weak. As already pointed out above, the diffuse contribution due to dissociative molecules has not been ruled out.

An inspection of the spectrum taken at 166.5-eV photon energy (lower part of Fig. 2) shows that the peaks a, b, and c are shifted to higher kinetic energy by 1.2 eV. In the lower figure they are labeled by a', b', and c'. The shift corresponds the energy difference between the spin-orbit components $2p_{3/2}$ and $2p_{1/2}$. Peak d is not resolved in the lower spectrum of Fig. 2 because it overlaps with the broad low-kinetic-energy structure. A clear increase in the intensity of the broad structure takes place in going from the upper spectrum to the lower spectrum of Fig. 2. The background overlapping with the main peaks is also increasing. Even the main peaks in the lower spectrum are most probably due to the decay channel 2 after the excitation of a $2p_{1/2}$ electron; competing channels may be present. Their contribution may be somewhat higher at 166.5 eV than at 165.5 eV.

The spectrum taken at 166-eV photon energy displays the same main peaks as the spectrum taken at 165.5 eV, only the background level is somewhat larger. In going to the spectrum obtained with 167-eV photons, the background becomes even more pronounced, though the same peaks as at 166.5 eV are clearly resolved. The increase of the broad structure and the background with increasing photon energy can be seen when inspecting the spectra of Fig. 1.

IV. DISCUSSION

Measured ejected electron spectra at $3a_1 \rightarrow 6a_1$ and $3a_1 \rightarrow 3b_2$ resonances were found to indicate that the main decay channel of the excited state would be the dissociation of one hydrogen atom followed by the Auger process in the excited HS molecule (channel 2). MCSCF calculations for the potential energy of the excited state also indicate the existence of a dissociative channel which leads to an excited HS molecule (paper II). MCSCF calculations predict a strong dissociative character for the $3a_1^{-1} 6a_1^1$ state. The presence of a crossing between this state and the $3a_1^{-1} 3b_2^1$ state lying inside the ground-state Franck-Condon region is, furthermore, predicted to lead to the dissociation of one hydrogen also at the $3a_1 \rightarrow 3b_2$

resonance. The experimental finding is thus supported by MCSCF calculations. Even stronger evidence of the existence of channel 2 is the good agreement between experimental and calculated Auger energies of HS*.

Due to the spin-orbit splitting, there are separate curves for the $2p_{1/2}$ and $2p_{3/2}$ hole states at the distance of 1.2 eV from each other. In a relativistic coupling scheme, including the molecular-field effect, the S $2p_{1/2}$ couples with the $3a_1$ molecular orbital to form a state of $E_{1/2}$ symmetry, the S $2p_{3/2}$ couples with the $1b_1$ and $1b_2$ molecular orbitals to form two states of $E_{1/2}$ symmetry splitted by 0.1 eV. Due to the molecular-field splitting a broadening of the lines would be expected if the $E_{1/2}$ states correlated to the $1b_1$ and $1b_2$ orbitals is excited instead of the $E_{1/2}$ state correlated to the $3a_1$ orbital. However in a recent study [17] no broadening was observed in the Auger decay. Instead, a shift of 50 meV between the x-ray photoelectron and Auger-electron spectra was observed. In the present resonant Auger spectra, due to the presence of overlapping lines, it is difficult to establish whether or not there is a small shift in the HS Auger decay. For simplicity we shall consider only the spin-orbit splitting. The excited state related first with the $2p_{3/2}$ and then with the $2p_{1/2}$ spin-orbit component may thus be reached when photon energy is increased. The $2p_{3/2}$ spin-orbit component is clearly predominated in the upper spectrum and the $2p_{1/2}$ component in the lower spectrum of Fig. 2. Our spectrum obtained at 164.5-eV photon energy does not display the peaks a,b,c, etc. but only a somewhat increased background level. This may indicate that at this excitation energy one just starts to reach the lowest-energy surface. The peaks a,b,c, etc. appear at 165 eV for the first time, and only the $2p_{3/2}$ component is present until 166.5 eV where the $2p_{1/2}$ component clearly shows up. The spectral behavior is in good agreement with the calculated excitation and dissociation energies (paper II), if the calculated values are expected to refer to the $2p_{3/2}$ component and the $2p_{1/2}$ component is expected to lie 1.2 eV above it.

According to the MCSCF calculations (paper II) the dissociation of both hydrogens followed by the Auger decay in the excited sulfur atom can take place with small probability. The major part of the Franck-Condon region was, however, predicted to end up within the nondissociative region of the potential-energy surface. Since no sharp peaks besides the ones related to channel 2 are visible in experiment, the existence of channel 1 is not confirmed by experiment. On the contrary, the experiment obviously contains some broad structures with varying strength as a function of photon energy. This is because the few peaks (Table I) could not cover all the existing intensity but a wide variety of peaks had to be included when fitting the spectra. As pointed out in paper II, such a behavior might result from a superposition of dissociative molecular spectra. Time-dependent quantum calculations are, however, needed in order to achieve a more deeper understanding on the phenomena.

From the experimental point of view, it is not possible to distinguish the decay channels in more detail with the use of electron spectroscopy. This is because the peak structure is smearing out due to the overlap of different transitions, making the identification less reliable. Ion-yield spectra recorded at different photon energies would be very helpful in further understanding of the decay channels of the excited states of H_2S.

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