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Vibrationally resolved states in the HS fragment studied by means of electron-excited Auger spectroscopy

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An autoionization spectrum of the H_2S molecule has been identified from the comparison between the Auger electrons recorded by means of high-resolution electron-beam and monochromatic Al $K\alpha$ exciting sources. Due to the high energy resolution the measured kinetic energies can be used for a precise assignment. Our results support a model of a fast dissociation of the core-excited H_2S^* $(2p)^{-1}(6a_1)^1$ and $(2p)^{-1}(3b_2)^1$ states into core-excited HS^* $(2p)^{-1}(2\pi)^4$ followed by autoionization decay into the HS^+ radical. Vibrational structures are resolved and assigned to the ${}^3\Sigma^-$ and ${}^1\Delta$ final states in the HS^+ radical. No participator Auger process in H_2S^* could be identified. However, contributions from the spectator process in H_2S^* might be present.

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In some hydride molecules core excitation to the low-lying antibonding orbitals has been shown to give rise to fast dissociation of one hydrogen followed by electronic decay in the excited molecular fragment. This type of study was pioneered by Morin and Nenner [1] for the $3d \rightarrow \sigma^*$ excitation in HBr. In a following study Aksela *et al.* [2] reported atomic lines in resonant decay from the $2p \rightarrow \sigma^*$ excitation in HCl. However, they also observed molecular lines originating from the spectator process. Recently, the fast dissociation of H_2S into an excited HS^* fragment after the excitations $2p \rightarrow 6a_1$ and $2p \rightarrow 3b_2$, followed by Auger decay to the HS^+ cation, has been studied both experimentally and theoretically [3,4]. The existence of contributions originating from the Auger process in the excited H_2S before dissociation could, however, not be identified or ruled out by the synchrotron-radiation-induced experiment due to the presence of the direct photoelectron lines in the resonant Auger energy region.

The electron-beam-excited Auger spectrum provides a possibility to resolve this question since in the electron-induced spectrum the direct photoionization lines do not show up. However, in the electron beam excited Auger spectra satellites due to initial-state shakeup may also be present. By comparison to spectra excited by high-energy monochromatic x rays these satellites may be identified. In the present study high-resolution x-ray and electron-induced Auger-electron spectra are presented. The resolution is sufficient to reveal vibrational structure in the electron-beam experiment that can be assigned both to the initial core-excited state and to the final HS^+ states ${}^3\Sigma^-$ and ${}^1\Delta$. No contribution corresponding to the participator Auger electron from the H_2S^* excitation process has been found.

The electron-beam-excited autoionization spectra were recorded in an electron spectrometer developed for high-resolution ultraviolet photoelectron spectroscopy and electron-impact Auger-electron spectroscopy of free molecules [5]. A 1.5-keV electron beam with a typical beam current ≤ 1 mA was used to excite the $2p$ core electron of H_2S molecule. The gas pressure in the source volume was estimated to be about 0.4 Torr. A fixed pass energy of 50 eV was used in the analyzer which is a hemispherical electrostatic type with a mean radius of 144 mm. The autoionization spectrum was calibrated against the H_2S ${}^1A_{1,1/2}(2b_1^{-2})$ (0-0) LVV Auger line at 139.87 eV from Ref. [6]. The x-ray -excited spectrum of H_2S was obtained using a monochromatized Al $K\alpha$ radiation ($h\nu = 1487$ eV) source [7]. This spectrum was calibrated in the same way as the electron induced. The high-purity sample gas was obtained commercially.

In the ground state the valence electronic configuration of H_2S is $(4a_1^2 2b_2^2 5a_1^2 2b_1^2 6a_1^0 3b_2^0)\,{}^1A_1$. In the high-energy region of the electron-induced H_2S LVV Auger spectrum two different types of processes can create lines with comparable intensity: (1) The lines originating from the decay of the core-excited states $2p \rightarrow 6a_1$ and $2p \rightarrow 3b_2$ giving rise to a singly ionized species; (2) lines originating from the ejection of an electron from a core hole shakeup state, giving rise to a doubly ionized species. The latter process is also referred to as a participator Auger shakeup process. If monochromatized Al $K\alpha$ ($h\nu = 1487$ eV) is used, only the intermediate shakeup state is populated. Therefore, only decay from these states is observable in the high-energy region of the x-ray-induced H_2S LVV Auger spectrum while both processes are observable in the electron-induced spectrum. This is shown in Fig. 1 where we have plotted the x-ray (lower) and the electron-beam (upper) excited spectra.

The structure at 141.37 eV appears in both spectra and hence originates from a participator Auger shakeup process. In the core shakeup photoelectron spectra [8] a state at 15.2 eV above the S $2p_{3/2}$ main line corresponds to the most intense structure and is therefore supposed to be the intermediate state giving rise to the above-mentioned structure. The same final states originating from the sulphur $2p_{3/2}$ core-hole state will then appear at 126.2 eV. At these energies only *CVV* Auger lines involving the $4a_1$ inner valence orbital are present [9]. In the *LVV* Auger spectrum the line corresponding to this state appears with low intensity compared to the lines corresponding to outer valence double hole states. The *LVV* Auger intensity ratio is not reproduced in the participator Auger shakeup spectrum, due to the different intermediate states in these processes.

Figure 2 shows the details of the autoionization region in the electron-induced Auger spectrum. In order to analyze the observed structures which are absent in the x-ray induced spectrum, three different decay channels have to be considered. (1) Fast detachment of both hydrogens followed by ionization in atomic sulphur, referred to as channel 1; (2) dissociation of one hydrogen followed by autoionization decay in the excited HS fragment, channel 2; (3) autoionization in the excited H_2S molecule before detachment, channel 3. Channel 1 is ruled out since, according to the results presented in Ref. [4], there is a potential barrier for symmetric dissociation. Furthermore, the most intense S atomic transitions would appear around 154 eV [3], where no structure is discernible in the experimental spectrum. Channel 2 corresponds to most of the structures observed in this region, as will be discussed below. Using an independent particle picture, channel 3 can be divided into participator and spectator Auger processes [3]. The final ionic state in the first process is a valence hole state whereas in the second it is an excited valence hole state. These final states are also accessible by direct ionization.

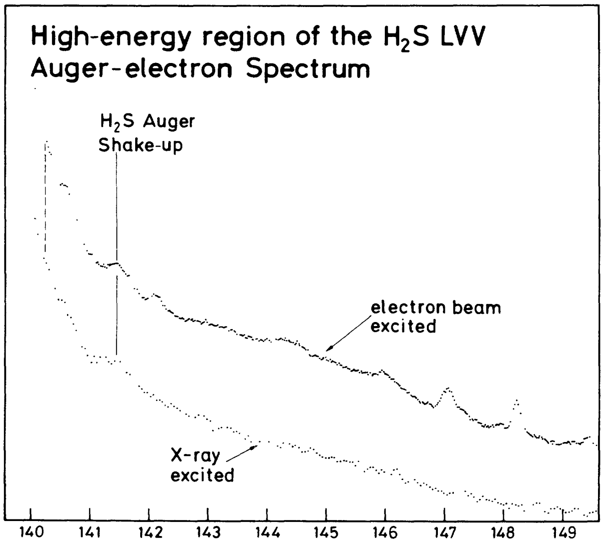

FIG. 1. High-energy region of the H_2S *LVV* Auger-electron spectrum displaying both the x-ray excited (lower) and the electron-beam-excited (upper) spectra. The comparison between the two spectra reveals the structures which are of autoionization origin.

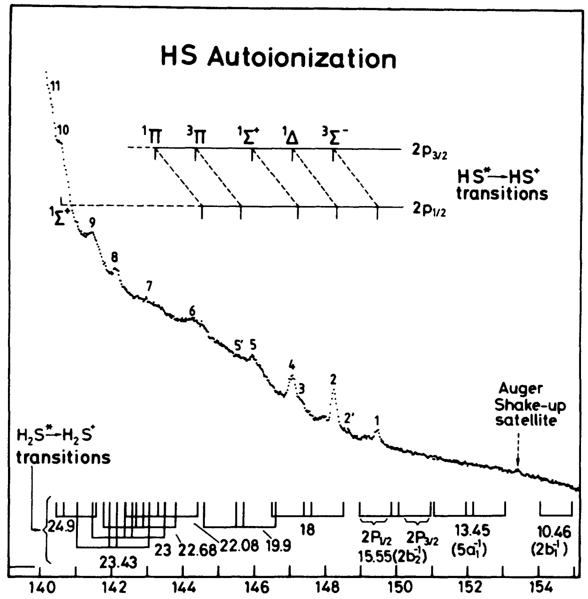

FIG. 2. Electron-induced autoionization of H_2S. The energy positions for transitions described as channel 2 in the text are indicated at the top of the figure and for channel 3 at the bottom.

In order to assign the observed structures in the spectrum presented in Fig. 2 we consider channels 2 and 3. The predicted energy positions of lines originating from channel 3 are shown in the bottom of Fig. 2. They were obtained by subtracting the valence ionization energies [9] from the core-excitation energies reported in the photoabsorption spectrum of H_2S [10]. Each singly ionized valence state would correspond to four lines in the energy region of the autoionization spectrum originating from the decay of the $(2p_{1/2})^{-1}(6a_1)^1$; $(2p_{1/2})^{-1}(3b_2)^1$; $(2p_{3/2})^{-1}(6a_1)^1$ and $(2p_{3/2})^{-1}(3b_2)^1$ core-excited states (also referred to as $L^*_{\mathrm{II,III}}$) to the respective valence hole states. They are indicated as fourfold lines at the bottom of Fig. 2. The resolution in the present experiment is high enough to make an assignment based on energies. As can be seen from Fig. 2 the predicted energy positions do not match the peaks observed in the spectrum. Furthermore, no lines are observed in the region where the participator transitions, corresponding to the final singly ionized valence holes $(2b_1)^{-1}$, $(5a_1)^{-1}$, and $(2b_2)^{-1}$ would appear. These arguments rule out channel 3 as responsible for most of the observed structures.

The excitation of a core electron from an atomic S $2p$ orbital in the H_2S molecule to a $6a_1$ or $3b_2$ orbital results in antibonding excited states that may dissociate to the

$(3\sigma^1 2\pi^4)\,^2\Sigma^+$ and $(1\pi^3 2\pi^4)\,^2\Pi$ states of the core-excited HS fragment. A detailed study of this dissociation process in terms of potential-energy surfaces was presented in Ref. [4]. After dissociation, autoionization in the excited HS radical takes place and six electronic states, in the $\Lambda\Sigma$ coupling scheme, can be populated: $(5\sigma^2 2\pi^2)\,^3\Sigma^-$, $(5\sigma^2 2\pi^2)\,^1\Delta$, $(5\sigma^2 2\pi^2)\,^1\Sigma^+$, $(5\sigma^1 2\pi^3)\,^3\Pi$, $(5\sigma^1 2\pi^3)\,^1\Pi$, and $(5\sigma^0 2\pi^4)\,^1\Sigma^+$. In Fig. 2 transitions from each of the intermediate $2p_{1/2}$ and $2p_{3/2}$ core-excited states to these final valence hole states are indicated. Peaks number 1, 2, 3, 4, 5, 6, 7, and 10 can be identified as such transitions. It is interesting to note that lines number 1, 2, and 3 clearly show fine structure. We will discuss these lines in more detail below. The energy positions and assignments are reproduced in Table I together with previous results obtained from multiconfiguration self-consistent-field calculations [4] and from the synchrotron radiation excited autoionization spectrum [3].

The spin-orbit splitting of the core-excited states measured at the $^3\Sigma^-$ final state is 1.22 eV. This value is in good agreement with that obtained for the core-hole spin-orbit splitting, viz. 1.25 eV [6]. In a previous study, we reported a difference of 50 meV between the spin-orbit splitting measured by x-ray photoelectron spectroscopy and by Auger electron spectroscopy for H_2S [11]. Whether there is a corresponding shift in HS is difficult to access since there is an overlap between the lines assigned to the $L^*_{\rm II}\to{}^1\Delta$ and $L^*_{\rm III}\to{}^3\Sigma^-$ transitions.

Although the majority of the peaks observed in Fig. 2 can be associated to the decay in HS the weak structure 2′ may be assigned to the spectator Auger process in H_2S. Structure 2′ corresponds to the transition from the $(2p_{1/2})^{-1}(6a_1)^1$ to a $(4a_1)^{-1}$ correlation satellite state described in Ref. [9]. Line number 8 and the broad structure numbered 7 may also have a contribution from the spectator Auger decay to $(4a_1)^{-1}$ valence correlation satellite at 23 eV. It should be noted that the $^1\Pi(2p_{3/2})$ state from HS also falls under structure 7. Lines number 9 and 11 correspond to participator Auger shakeup processes, as discussed above.

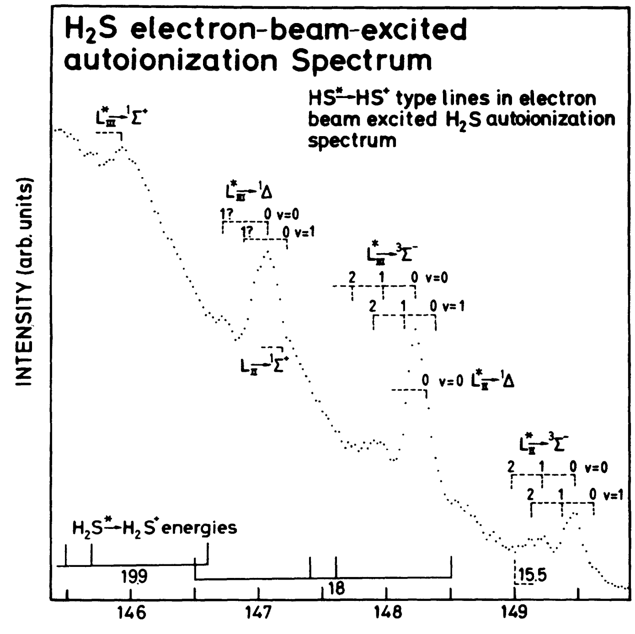

FIG. 3. Detail of the H_2S electron-beam-excited autoionization spectrum. Tentative vibrational assignment is indicated as dashed lines above the spectrum.

In Fig. 3 we present a detail of the autoionization spectrum discussed above. Vibrational structures are clearly discernible in the $L^*_{\rm II,III}\to{}^3\Sigma^-$ and in the $L^*_{\rm III}\to{}^1\Delta$ transitions. A tentative vibrational assignment is given in the figure. It should be pointed out that the decay is occurring in an excited molecular fragment after dissociation and therefore it is expected that vibrationally excited states are populated in the intermediate state. In the energy region of the outermost band, $L^*_{\rm II}\to{}^3\Sigma^-$, the Auger decay from undissociated H_2S would correspond to a participator process and no such lines are observed in the spectrum; cf. Fig. 2. Furthermore, the relative intensity

TABLE I. Experimental and theoretical HS^+ Auger energies (eV).

State	Dominant configuration	Theoretical[a]	Experimental electron induced	Experimental[b] photoinduced	Peak number
$^3\Sigma^-(p_{1/2})$	$(5\sigma)^2(2\pi)^2$	149.47	149.47[2]	149.3[3]	1
$^1\Delta(p_{1/2})$	$(5\sigma)^2(2\pi)^2$	148.02	148.2[1]	148.1[3]	2
$^3\Sigma^-(p_{3/2})$	$(5\sigma)^2(2\pi)^2$	148.22	148.25[2]	148.1[3]	2
$^1\Sigma^+(p_{1/2})$	$(5\sigma)^2(2\pi)^2$	146.88	147.22[4]	147.2[3]	3
$^1\Delta(p_{3/2})$	$(5\sigma)^2(2\pi)^2$	146.77	147.09[2]	147.0[3]	4
$^1\Sigma^+(p_{3/2})$	$(5\sigma)^2(2\pi)^2$	145.63	146.00[2]	146.0[3]	5
$^3\Pi(p_{1/2})$	$(5\sigma)^1(2\pi)^3$	145.53	145.7[1]	145.3[6]	5′
$^1\Pi(p_{1/2})$	$(5\sigma)^1(2\pi)^3$	144.24	144.6[1]	144.3[6]	6
$^3\Pi(p_{3/2})$	$(5\sigma)^1(2\pi)^3$	144.28	144.37[3]	144.1[3]	6
$^1\Pi(p_{3/2})$	$(5\sigma)^1(2\pi)^3$	142.99	143.3[1]	143.1[3]	7
$^1\Sigma^+(p_{1/2})$	$(5\sigma)^0(2\pi)^4$	139.03	140.5[1]		10
$^1\Sigma^+(p_{3/2})$	$(5\sigma)^0(2\pi)^4$	137.78			

[a] Values taken from Ref. [4]. A shift of −2.12 eV was added to the calculated energies.

[b] Values taken from Ref. [3].

of such a process compared to spectator Auger decay is much smaller in Ar[12]. The vibrational energy spacings for the outermost band are given in Table II. From the difference between the 0-0 and 1-0 transitions the vibrational spacing in the excited HS fragment can be estimated to be 0.13 eV. This value is smaller than that observed in the isoelectronic HCl Auger spectrum (0.32 eV) [13] and also smaller than obtained from the calculated potential curve for dissociated HS using the harmonic approximation (0.37 eV). A possible explanation for this discrepancy lies in the dynamics of the dissociation process. The HS fragment may emit the electron before the dissociation is completed and the shallower shape of the potential curve along the dissociation path will give smaller vibrational spacings. Another possibility is that interference between the different short-lived vibrational states shifts the energy position of the spectral lines.

The first vibrational spacing in the $^3\Sigma^-$ state, which we measured to be 0.25 eV from Table II, can be compared with the value of 0.3 eV obtained in Ref. [14] by measuring the fluorescence produced when H_2S is excited at 22.34 eV. The small difference between the measured vibrational spacing can be due to the above-described state interference effects.

The results obtained in this work support the previous assignment in terms of fast dissociation of the core-excited H_2S^* into core-excited HS^* followed by autoionization decay into HS^+ molecular fragment. Vibrational structures have been resolved and a tentative assignment is proposed. The presence of hot bands in the spectrum indicates that vibrationally excited states in HS^* are populated. The time scales of dissociation and autoionization processes may be comparable. This complicates the assignment of the observed vibrational structures. Further investigations are needed to clarify this point, for instance, by analyzing the corresponding spectrum of D_2S. No participator resonance Auger decay in H_2S^* could be identified, but a weak contribution from the spectator process in H_2S^* might be present.

TABLE II. Vibrational energies of HS^+ radical cation.

Vibrational transition[a]	Relative energy (eV)
1-0	0
0-0	0.13
1-1	0.25
0-1	0.38
1-2	0.49
0-2	0.62

[a] The notation v-v' designates the relative energy position of the line assigned to the transition $HS^*(v)$ to $HS^+(v')$.

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