Observation of an Anomalous Decay Ratio between the Molecular Field Split Levels in the S 2*p* Core Photoelectron and *LVV* Auger Spectrum of H_2S

S. Svensson, A. Ausmees,* S. J. Osborne, and G. Bray
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

F. Gel'mukhanov and H. Ågren
Department of Physics and Measurement Technology, University of Linköping, S-581 83 Linköping, Sweden

A. Naves de Brito, O.-P. Sairanen, A. Kivimäki, E. Nõmmiste,* H. Aksela, and S. Aksela
Department of Physics, University of Oulu, FIN-90570 Oulu, Finland
and the Finnish Synchrotron Radiation Facility at Max-lab, Box 118, S-22100 Lund, Sweden

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The S $2p_{3/2}$-$2p_{1/2}$ spin-orbit splitting of H_2S has earlier been assigned different values by Auger and x-ray photoelectron spectroscopies. We resolve this apparent ambiguity by presenting very high resolution synchrotron radiation excited Auger and photoelectron spectra, where the molecular field splitting in the "S $2p_{3/2}$" photoelectron line is observed to be 110(5) meV. The difference in spin-orbit splitting is explained in terms of a new strong propensity rule for Auger decay from molecular field split levels. A value of 70(10) meV for the S 2*p* lifetime width in H_2S is also obtained.

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In an earlier report [1] the S $2p_{3/2}$-$2p_{1/2}$ spin-orbit splitting in H_2S was found to be 1.254 eV when measured from the *LVV* Auger electron spectrum, but only 1.201 eV was measured as the energy distance between the peak maxima in a monochromatized Al $K\alpha$ excited x-ray photoelectron spectrum (XPS). Thus a 50 meV shift between the two measurements was observed. The resolution of the XPS [full width at half maximum (FWHM) of 380 meV for the S $2p_{1/2}$ component] did not permit an unambiguous interpretation and two hypothetical explanations were discussed. One was made in terms of an electronic state interference and another in terms of a molecular field splitting of the S $2p_{3/2}$ level. The first explanation was later ruled out by a calculation [2] which predicted that the interference could only shift the S $2p_{3/2}$-$2p_{1/2}$ splitting by 15 meV.

Recently a photoelectron spectrum at somewhat better resolution (FWHM= 322 meV for the S $2p_{3/2}$ photoelectron line) than in Ref. [1] has been reported [3]. In this spectrum a weak ν=1 vibrational component was also reported and, by a Lorentzian or Gaussian fit by the S $2p_{3/2}$ photoelectron line, a lifetime of 185 meV was obtained for the S 2*p* core hole states. However, no splitting of the $2p_{3/2}$ core level was observed.

By using very high resolution electron spectroscopy and synchrotron radiation from an undulator source we have improved substantially the resolution both in the *LVV* Auger and in the S 2*p* core photoelectron spectrum of H_2S. The S $2p_{3/2}$ photoelectron line is resolved into its molecular field split components, thereby, for the first time, allowing us to demonstrate unambiguously the existence of a hitherto unknown anomalous decay ratio between different molecular field split levels. A precise determination of the core hole lifetimes has also been obtained. In addition, a few weak vibrationally excited states are seen in the photoelectron spectrum, originating from the ν_1 mode. In this Letter we will focus on the molecular field splitting and the anomalous decay ratio. This is the deepest core level that has been resolved into molecular field split sublevels.

The experiments were performed at the Finnish beam line (BL51) at the MAX I synchrotron radiation laboratory in Lund, Sweden [4]. The photon resolution at the sulfur edge was calculated by using the measured monochromator resolution, using the same slit size, of 60 meV at the Ar $2p^{-1} \rightarrow 4s$ resonance. Scaling the resolution according to the $E^{3/2}$ (where E is the photon energy) dependence for a PGM gives a monochromator contribution of 40 meV at the S 2*p* absorption edge. The photoelectron spectrometer is an SES-144 hemispherical sector analyzer built in Uppsala [5]. At 10 eV pass energy the electron spectrometer resolution is measured, on the Xe $5p_{3/2}$ photoelectron line, to be 45 meV. The resolution is independent of the kinetic energy of the analyzed electrons. The principal axis of the electron lens of the spectrometer is mounted in the pseudomagic angle relative to the electric vector of the photon beam.

In Fig. 1 we show the S 2*p* core photoelectron spectrum of H_2S. The energy of the exciting photon beam was 187 eV. The molecular field splitting is clearly observed. Three molecular $E_{1/2}$ states result from the S 2*p* level in H_2S for large spin-orbit interaction. We use the notation $3e_{1/2}$ for the S $2p_{1/2}$ peak and $4e_{1/2}$ and $5e_{1/2}$ for the two components in the S $2p_{3/2}$ photoelectron line.

The line profiles are markedly asymmetric with a tail on the high binding energy side. This asymmetry is due to the postcollision interaction (PCI) at this excitation energy close to the threshold. The shape of a PCI function has been taken from Armen *et al.* [6] and it has been convoluted with a Gaussian representing the monochro-

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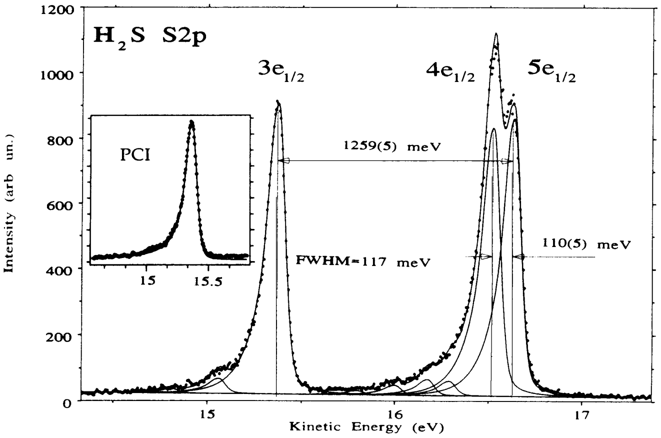

FIG. 1. The S $2p$ core photoelectron spectrum of H_2S. The fitted curves give accurate positions for the main (0→0) $3e_{1/2}$, $4e_{1/2}$, and $5e_{1/2}$ molecular field split relativistic levels. The inset shows the result of a fit of a PCI line profile to the $3e_{1/2}$ core photoelectron line. The lifetime obtained from this fit was 70(10) meV.

mator and spectrometer contribution. The PCI function has been optimized and the resulting functions have been fitted to the spectrum.

A small structure is seen at 314 meV higher binding energy than the $3e_{1/2}$ peak. This energy corresponds rather well to the theoretical fundamental vibrational energy for the ν_1 mode in the core ionized molecule [7]. The relative intensity is ≈5%, which is also in good agreement with the theoretical prediction [7]. A vibrational excitation was also reported in Ref. [3]. However, no discussion of the PCI profile was made in Ref. [3]. The vibrational structure on the $4e_{1/2}$ and $5e_{1/2}$ lines is less obvious due to the overlapping lines. In Table I we summarize the results for the energy positions and intensities.

In Fig. 2 we show the S $2p^{-1} \rightarrow X\,^1A_1(2b_1^{-2})$ Auger electron spectrum excited by 187 eV photons. The electron spectrometer pass energy was set to 10 eV. The resolution in this spectrum is much better than in earlier measurements [1,3,7]. The band at lower kinetic energy must be related to the "S $2p_{3/2}$" core hole and the weaker band at higher kinetic energy to the "S $2p_{1/2}$" core hole [7]. If we sum the intensity in these two bands we find an intensity ratio of around 2.5, which is larger than expected from the statistical ratio. Such a deviation is probably due to differences in the Auger transition probabilities and has been observed earlier for molecules.

In the present spectrum as many as four vibrational components can be observed in each of the bands. Because of the PCI at this low excitation energy the Auger lines are asymmetric on the high kinetic energy side. Because of the background it is very difficult to fit a PCI profile to the Auger spectrum. In order to estimate the linewidths we have fitted asymmetric Voigt profiles and a reasonable background to the spectrum. The results are shown in Fig. 2 and in Table I. As can be seen, the linewidths in this spectrum, 115 meV, are comparable to those in Fig. 1. This is expected since in the core electron spectrum the Doppler contribution is negligible due to the low kinetic energy, whereas in the case of the Auger the Doppler broadening is 27 meV. Thus in both cases the linewidth is dominated by the inherent linewidths.

In order to get information on the lifetime of the S $2p$ core hole state we, as discussed above, made a fit of a PCI function convoluted with a Gaussian total instrument line profile which has an FWHM of 60 meV. The lifetime width was optimized in a least squares procedure giving an estimate of 70(10) meV. This value is considerably smaller than the value of 185 meV given in Ref. [3], where the fit was made on the S $2p_{3/2}$ photoelectron line, which is broadened by the $4e_{1/2}$-$5e_{1/2}$ splitting. Our result seems reasonable considering the lifetime of the Ar $2p$ core levels [8], the theoretical value of 54 meV given by Krause and Oliver [9], and also the lifetimes recently estimated for S $2p$ core excited Rydberg states in H_2S [10].

From Figs. 1 and 2 an unambiguous explanation can be given for the 50 meV shift between the XPS and Auger

TABLE I. Binding and kinetic energies of the photoelectron and Auger lines, respectively, relative to the most intense $2p_{1/2}$ component. Energies and intensities of the vibrational components are given relative to the ν=0 line.

	Photoelectron spectrum				Auger spectrum				
Level	E_b (meV)	Vibrational components			Auger transition	E_k (meV)	Vibrational components		
		Energy (meV)		Intensity			Energy (meV)		Intensity
$3e_{1/2}$	0		ν=0	1	$3e_{1/2} \rightarrow X\,^1A_1(2b_1^{-2})$	0		ν=0	1
		+314(9)	ν=1	≤0.05			251	ν=1	0.6
		+600(30)	ν=2	≤0.01			508	ν=2	0.3
							739	ν=3	0.2
$4e_{1/2}$	-1149		ν=0	0.95(7)					
		+340(50)	ν=1	≤0.05					
$5e_{1/2}$	-1259		ν=0	0.93(7)	$5e_{1/2} \rightarrow X\,^1A_1(2b_1^{-2})$	-1261		ν=0	1
		+340(50)	ν=1	≤0.05			255	ν=1	0.6
							506	ν=2	0.2
							768	ν=3	0.1

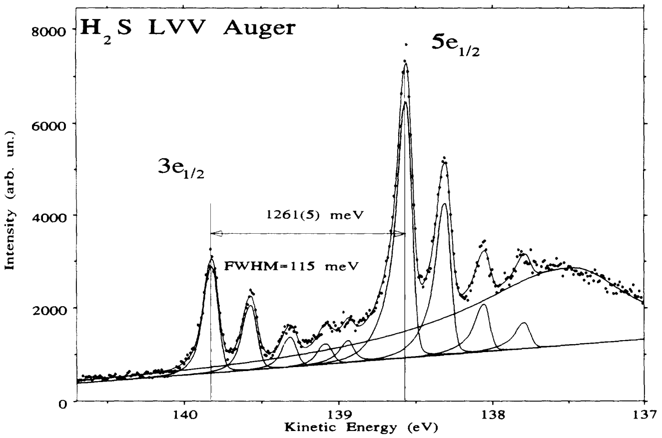

FIG. 2. Part of the $L_{2,3}VV$ Auger spectrum of H_2S showing the S $2p^{-1} \rightarrow X\,^1A_1(2b_1^{-2})$ transitions. The vibrational energies are due to the vibrationally excited $X\,^1A_1(2b_1^{-2})$ final state. The difference in energy between the 0→0 transitions fits with the energy difference between the $3e_{1/2}$ and $5e_{1/2}$ orbital energies.

S $2p_{1/2}$-$2p_{3/2}$ splitting observed in Ref. [1]. In Fig. 3 we give a level scheme with the relative energies of the observed lines and Auger transitions, as obtained from the curve fitting on the spectra in Figs. 1 and 2. From Fig. 3 it is clear that the observed 50 meV difference in spin-orbit splitting observed in Ref. [1] must be explained by the relativistic energy level scheme. The splitting between the $4e_{1/2}$ and $5e_{1/2}$ photoelectron lines is 110(5) meV. This can be compared to the value of 80 meV from an estimation using a nonrelativistic calculation [2]. The difference between the most prominent Auger peaks in the two bands of Fig. 2 coincides, within the error limits, with the difference in energy between the $3e_{1/2}$ and $5e_{1/2}$ photoelectron lines. No energy difference in the Auger spectrum coincides with the $3e_{1/2}$ and $4e_{1/2}$ photoelectron lines. If a transition from the $4e_{1/2}$ core hole state to the $X\,^1A_1$ state in the doubly ionized ion existed, it should be resolved in the spectrum of Fig. 2. In the unresolved XPS one observed the S $2p_{3/2}$ energy as the average between the $4e_{1/2}$ and $5e_{1/2}$ energies. Since the latter lines have a distance of 110 meV in the present spectrum, the unresolved splitting will be roughly 110/2 = 55 meV different from the S $2p$ spin-orbit splitting observed in a resolved spectrum, in agreement with the earlier value of 50 meV [1].

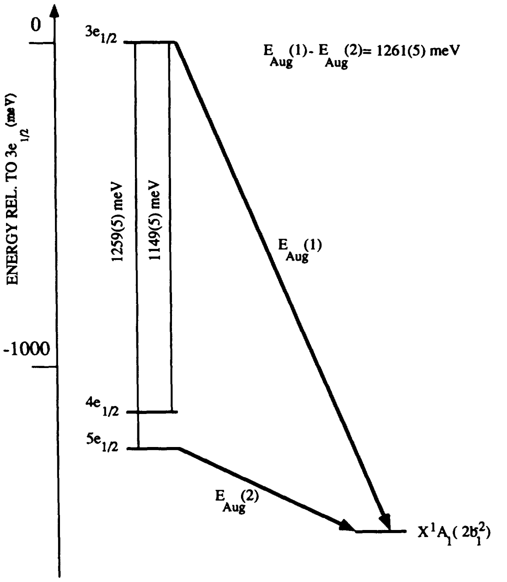

FIG. 3. A schematic view of the levels and observed transitions.

We consider the cases where the spin-orbit splitting is much larger than the molecular field splitting ($\Delta_{\text{SO}} \gg \Delta_M$). For the H_2S molecule the $2p^{-1}$ level is split by the molecular field into three sublevels, $2p_x^{-1}$, $2p_y^{-1}$, and $2p_z^{-1}$ with energies $E(1b_1)$, $E(1b_2)$, and $E(3a_1)$ using C_{2v} point group notation. These energies were computed at different levels of approximation of multiconfigurational self-consistent field theory in Ref. [7], giving splittings on the order of a few tens of meV. The wave function for the $3e_{1/2}$, $4e_{1/2}$, and $5e_{1/2}$ levels caused by the simultaneous action of the molecular field V_M and the spin-orbit interaction V_{SO} can be written as

$$\Psi = A\Psi(3/2, \pm 3/2) + B\Psi(3/2, \mp 1/2) \tag{1}$$

pertaining to $4e_{1/2}$ and $5e_{1/2}$ ("$2p_{3/2}$") levels and

$$\Psi^{\pm} = \Psi(1/2, \pm 1/2) \tag{2}$$

for the $3e_{1/2}$ level. Here $\Psi(J, M_J)$ is the atomic wave function and J and M_J are the quantum numbers for the total angular momentum and its projection, respectively. The function in (2) experiences no splitting and can be discarded here. Solving the secular equation,

$$(H_0 + V_M + V_{\text{SO}})\Psi = E\Psi, \tag{3}$$

the A and B coefficients are obtained for the $4e_{1/2}$ and $5e_{1/2}$ levels analytically in terms of $E(1b_1)$, $E(1b_2)$, and $E(3a_1)$, and corresponding Auger matrix elements can be evaluated. At degeneracy between $E(1b_2)$ and $E(3a_1)$ the analytical expression for Ψ implies a complete quenching of the decay from the first of the two "$2p_{3/2}$" components. Even when degeneracy is absent one component still dominates. This can be referred to the fact that only the $2p_x$ function from Ψ gives a significant contribution to the Auger matrix element. This is due to the orientation of the final $2b_1^{-2}$ state along the x axis. As a result the Auger transition from the $4e_{1/2}$ hole state is strongly depressed because the $2p_x$ contribution to the $\Psi(4e_{1/2})$ function is small in comparison with the $5e_{1/2}$ function.

The numerical results using molecular field splittings of Ref. [7] are given in Table II. As seen in the table, when molecular field splitting amounts to tens of meV only one

TABLE II. Calculated vertical ionization potentials $E(^2B_1)$, $E(^2A_1)$, and $E(^2B_2)$ in eV obtained at different computational levels from Table IV in Ref. [7], relative Auger energies $E(5e_{1/2}) - E(4e_{1/2})$ in eV, and branching ratio $I(4e_{1/2})/I(5e_{1/2})$. The spin-orbit splitting has not been taken into account when calculating the ionization potentials.

$E(^2B_1)$	$E(^2A_1)$	$E(^2B_2)$	$E(5e_{1/2})-E(4e_{1/2})$	$I(4e_{1/2})/I(5e_{1/2})$
170.87	170.93	170.91	0.035	0.03
170.69	170.74	170.71	0.029	0.11
170.89	171.05	171.09	0.122	0.01
170.35	170.44	170.44	0.06	0

Auger peak from the initial $4e_{1/2}$ and $5e_{1/2}$ levels emerges with significant intensity. Table II displays intensity ratios obtained from different calculation schemes. The intensity ratio $I(4e_{1/2})/I(5e_{1/2})$ depends on two factors, the energy gap between the $4e_{1/2}$ and $5e_{1/2}$ states and the energy splitting between the $^2B_2$ and $^2B_1$ states. Therefore, the intensity ratio is not monotonous with the energy gap. However, in all calculation schemes essentially only one Auger line is anticipated. Because of the near degeneracy of these levels vibronic (nonadiabatic) coupling can be of relevance. However, state interference effects for the decay from these levels do not alter the qualitative picture obtained. A full account of the present derivation will be given elsewhere [11].

In a series of beautiful studies from the Canadian Synchrotron Radiation Facility at SRC in Wisconsin it has been shown that relativistic splitting can be resolved, at lower binding energies for several molecules, including the important cases of HI [12] and HBr [13]. The molecular field splitting observed for the core photoelectron lines was used to reinterpret the complex Auger spectra [14–16] associated with the decay of the core holes. In Refs. [12,13] it was concluded that a complete reinterpretation should be made concerning the Auger spectra. However, as was pointed out in Ref. [14], the new interpretation of the HI was not consistent. From the present results it is clear that one of the key factors in this issue is the understanding of the propensity rules in Auger transitions from molecular field split levels and of the vibronic coupling. A new revision of the data has to be made and further theoretical work is also urgent.

In conclusion, we have for the first time partly resolved the S 2p photolines into all the spin-orbit and molecular field split levels. The splitting between the $4e_{1/2}$ and $5e_{1/2}$ core levels was measured to be 110(5) meV and the lifetime of the S 2p levels is 70(10) meV. The Auger spectrum shows an anomalous ratio for the decay from the $4e_{1/2}$ and $5e_{1/2}$ levels; only the decay from the $5e_{1/2}$ level is observed. This effect has been explained by a new propensity rule that applies for molecular field split core levels.

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[*] On leave from Institute of Physics, Estonian Academy of Sciences, Tartu, Estonia.

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