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Influence of chemical bonds on the lifetime of the molecular-field-split $2p$ levels in H_2S

André Machado Bueno
Institute of Physics, Brasilia University, Caixa Postal 04455, 70910-900 Brasília-DF, Brazil

Arnaldo Naves de Brito*
Laboratório Nacional de Luz Síncrotron, Box 6192, CEP 13084-971, Campinas, Brazil

Reinhold F. Fink,† Margit Bässler, Olle Björneholm, Florian Burmeister, Raimund Feifel, and Catalin Miron‡
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

Stacey L. Sorensen
Department of Synchrotron Radiation Research, Institute of Physics, University of Lund, Box 118, S-221 00 Lund, Sweden

Honghong Wang and Svante Svensson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

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Different lifetime broadenings in molecular-field-split $2p$ core levels in H_2S are predicted theoretically and are identified in an experimental investigation of the S $2p$ Auger electron spectrum. The measurements were performed for the transition to the vibrationally resolved X^1A_1 ground state of H_2S^{2+}. The lifetimes of the $3e_{1/2}$ and $5e_{1/2}$ levels of the $2p$ ionized molecule are found to be 64 and 74 meV, respectively. This unambiguous determination of the lifetime difference of 10 ± 1 meV is only possible as the $4e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$ decay channel that overlaps the $5e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$ channel is practically suppressed in Auger decay in H_2S. The lifetime difference is confirmed by *ab initio* calculations. A theoretical analysis shows that it results from the mutual orientation of the core hole in the intermediate states and the valence electron density in the sulfur $3p$ orbitals. Both are strongly influenced by the chemical bond. Thus the observed effect is the direct result of a fundamental property of molecular electronic structure.

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I. INTRODUCTION

Molecular fields produce interesting splitting effects in core atomic levels. In particular, atomic $2p_{3/2}$ core levels in molecules with less than cubic symmetry are split into two components [1–8]. For the H_2S molecule these levels are designated as $4e_{1/2}$ and $5e_{1/2}$. In this work we consider the question of whether the chemical environment responsible for the splitting in these levels could also affect their lifetime or, to be more specific, their total Auger transition rates. These states show a different spatial distribution of the $2p$ core holes, which is known to have a great influence on the Auger decay rates to particular final states (i.e., partial transition rates). In 1991, the difference in spatial distribution was found indirectly by Svensson *et al.* in a measurement of the spin-orbit splitting between the S $2p_{1/2}^{-1}$ and S $2p_{3/2}^{-1}$ states of the H_2S molecule. Two values differing by about 50 meV were obtained by x-ray photoelectron spectroscopy and by normal Auger decay to the vibrationally resolved X^1A_1 $(2b_1^{-2})$ final state [1]. At this time, it was not possible to resolve the components corresponding to the $2p_{3/2}$ hole states. However, already in 1994 [2] this became possible by synchrotron radiation ionized photoelectron spectroscopy and the levels were shown to differ in energy by about 110 meV. In that study it was also shown that the $4e_{1/2}$ core-hole state decays with a substantially lower probability to the X^1A_1 $(2b_1^{-2})$ final state than the $5e_{1/2}$ state, thus causing an apparent difference in the spin-orbit splitting in the less resolved spectra. The explanation for these changes in the partial Auger decay rates was that each $2p$ molecular split level consists of a different composition of $2p_x$, $2p_y$, and $2p_z$ orbitals and the $L_{2,3}VV$ Auger decay channel is preferred if at least one of the two involved valence orbitals has an orientation parallel to the core orbital [3,9]. The resonant Auger decay of the dissociative core to valence-excited H_2S [10] and the normal Auger-electron spectrum of HCl [11] are two further examples, where substantially different partial Auger transition rates were found experimentally, depending on the molecular-field-split sublevel they originate from.

Now we consider the total decay rate Γ_i of a core-hole state *i*, which is given by the sum of the partial decay rates $[\Gamma_i(a)]$ to all possible final states *a*

$$\Gamma_i=\sum_a \Gamma_i(a). \tag{1}$$

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*Corresponding author. On leave from Institute of Physics, Brasilia University. Fax: +551932874632.
Email address: Arnaldo@lnls.br

†Also at Theoretical Chemistry, University of Lund, Box 124, S-221 00 Lund, Sweden.

‡Present address: Laboratoire L.U.R.E., Bâtiment 209D, Center Universitaire Paris-Sud, F-91898 Orsay Cedex, France and Laboratoire Francis Perrin of SPAM/DRECAM, CE. Saclay, 91191-Gif-sur-Yvette, Cedex, France.

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In the present work, Γ_i is approximated throughout as the sum of the Auger decay rates, neglecting the minor contribution of x-ray flourescence ($\approx 2\%$).

In the context mentioned above, Gel'mukhanov *et al.* predicted a strong dependence of the lifetime on the $2p^{-1}$ core-hole level [3]. However, a comparison with $2p$-photoelectron spectra showed that the differences in the calculated lifetime widths in Ref. [3] were exaggerated. This disagreement was due to the fact that the precise structure of the molecular-field-split core-hole state was not known at this time. In a careful *ab initio* study Børve [4] showed that an accurate treatment of correlation effects is required to obtain this property correctly. Furthermore, in Ref. [9] a theoretical analysis of the electronic properties of the normal Auger decay rates showed the importance of using proper electronic wave functions if accurate Auger decay rates are desired. In this work again a relatively strong dependence of the core-hole lifetime on the core level (about 25%) was found.

From the experimental point of view the precise measurement of the lifetime of these molecular-field-split core-hole states remains a difficult task. Traditionally, the measurements are based on the photoelectron spectra. The core photoelectron lines in these spectra are broadened by several factors, namely, the exciting photon bandwidth given by the monochromator, the spectrometer contribution that is related to the uncertainty in determining the photoelectron kinetic energy, the lifetime of the initial and the core-hole states. The initial state is the ground state with a lifetime that is many orders of magnitude longer than that of the intermediate state. Thus, after deconvoluting the spectrometer and monochromator contributions the resulting linewidth directly reflects the core-hole lifetime via the Heisenberg uncertainty principle. The difficulty in measuring these lifetime broadenings is that all molecular-field states are populated about equally and the separation of some of these states is of the same order of magnitude as the lifetime broadening. The dertermination of small linewidth differences in nearly overlapping peaks is a very difficult task.

In this paper we apply an alternative method to measure the lifetime of the $2p$ ionized states of H_2S. Instead of using the photoelectron linewidth we use that of the the Auger lines. The main advantage is that in Auger decay only the spectrometer broadening is present. After deconvolution the linewidths reflect, in principle, the sum of the molecular-field-split core-hole width and that of the final doubly ionized state. In the present work, this state is long lived and we can neglect its contribution to the linewidth. In the case of H_2S, it is possible to use this advantage for the decay to the lowest final state as it is vibrationally resolved. Furthermore, the decay of one of the overlapping lines is strongly suppressed.

After the theoretical prediction in Ref. [9] a substantial dependence of the lifetime on the core-hole state was experimentally found by a very careful analysis of the HCl photoelectron spectrum [12]. However, as discussed above, the molecular-field splitting of the $\mathrm{Cl}\,2p_{3/2}^{-1}$ level is rather small compared with the lifetime width of these levels. The substantial overlap of the resulting lines in the spectrum makes it difficult to extract the changes in linewidth although they are comparatively large ($\approx 30\%$).

In the present investigation we use the propensity rule in the Auger decay ratio of the core ionized H_2S molecule. Two separated vibrationally resolved progressions are found in the spectrum, simplifying the experimental determination of differences in the lifetime width of the core levels. The aim of this article is twofold: We want to prove that differences in $2p$ core-hole lifetimes exist in the H_2S molecule and show that the origin of this effect lies in basic properties of the molecular electronic structure. The outline of this article is as follows. After describing theoretical methods and calculations in Sec. II, the experimental techniques and results are presented in Sec. III. We discuss these results in Sec. IV. Finally, concluding remarks are given in Sec. V.

II. THEORETICAL CALCULATIONS

The calculations were performed in a similar way as in Refs. [9] and [13], where further theoretical background may be found. Briefly, the spin-orbit coupling and the molecular-field splitting were described with the method after Børve and co-workers [4–6]. Auger transition rates were calculated with the "one-center approximation" [9,14–17].

As a first step, the nonrelativistic electronic energy of the ground state, the intermediate states, and the final states were calculated at the equilibrium bond distance and angle of the H_2S ground state (2.53 a_0 and 91.96°, respectively) [18]. The correlation consistent polarized valence triple zeta basis set after Dunning and co-workers [19,20] was used. In order to allow for a better description of the core orbitals, the (15s9p2d1f) basis at the sulfur atom was only weakly contracted to (13s8p2d1f). In C_{2v} symmetry the orbitals occupied in the H_2S ground state are $1a_1$, $2a_1$ (the S $1s$ and S $2s$ orbitals), the sulfur $2p$ orbitals ($1b_2$, $3a_1$, and $1b_1$), and the valence orbitals $4a_1$, $2b_2$, $5a_1$, and $2b_1$. They were obtained by the restricted Hartree-Fock (RHF) method. A modified improved virtual orbitals method [13] was used to determine the unoccupied valence orbitals $6a_1$ and $3b_2$.

The nonrelativistic energies and wave functions of the states were calculated by a valence configuration interaction (VCI) approach in which all excitations from the occupied to the virtual valence orbitals were allowed (ground and final states). Furthermore, one core hole was introduced in the $2p$ orbitals (core ionized state). These wave functions were used in the one-center approximation method [14–17] to obtain the Auger transition rates from the singly positive core ionized states to the doubly positive final states. In the one-center approximation calculation the spin-orbit-averaged radial Auger transition integrals after Chelkowska and Larkins [16] were employed. Thus, this method, applied to the argon atom, gives 1/2 for the ratio of all Auger transition rates from the $2p_{1/2}$ and $2p_{3/2}$ core-hole states. The lifetime of a nonrelativistic intermediate state was obtained by the sum of the transition rates to all final states. I.e., the calculated lifetime widths contain only the dominating Auger decay channel and neglect other decay channels like x-ray fluorescence.

The quality of these energies has been shown to be generally sufficient for a correct description of the relative final-

TABLE I. Calculated properties of the nonrelativistic core ionized states of H_2S: $2p$ ionization potentials of the H_2S molecule as calculated with different *ab initio* approaches ϵ (method). Total and partial Auger transition rates Γ and Γ (final state), respectively, in μa.u. (1 μa.u.$=2.72116\times10^{-5}$ eV). $n_{occ}(3p_\parallel)$ is the occupation number of the $3p$ valence orbital in the core-excited state, which has the same orientation as the core-hole orbital.

State	$1b_1^{-1}$	$1b_2^{-1}$	$3a_1^{-1}$
ϵ(SCF) (eV)	170.411	0.049 [a]	0.032 [b]
ϵ(VCI) (eV)	177.824	0.111 [a]	0.097 [b]
ϵ(MCCEPA) (eV)	170.525	0.186 [a]	0.133 [b]
ϵ(MCPF)[c] (eV)	170.555	0.183 [a]	0.138 [b]
$\Gamma(\mu$a.u.)	3326.6	1825.6	2565.2
$\Gamma(X^1A_1)(\mu$a.u.)	715.4	19.8	19.4
$n_{occ}(3p_\parallel)$	1.96	1.22	1.47

[a] Energy difference $\epsilon(1b_2)-\epsilon(1b_1)$.

[b] Energy difference $\epsilon(1a_1)-\epsilon(1b_1)$.

[c] MCPF(v+cv+c;5≤occ(L)≤7) level after Ref. [4].

TABLE II. Calculated ionization potentials ϵ, core-hole densities, total and partial Auger transition rates of the relativistic H_2S core-ionized states.

Core-hole state	$3e_{1/2}$	$4e_{1/2}$	$5e_{1/2}$
ϵ	171.436	170.286	170.172
$c[1b_1^{-1}]^2$	0.278	0.013	0.709
$c[1b_2^{-1}]^2$	0.378	0.542	0.081
$c[3a_1^{-1}]^2$	0.344	0.445	0.211
$\Gamma(\mu$a.u.)	2497.63	2174.65	3045.07
Γ(meV)	67.96	59.18	82.86
$\Gamma(X^1A_1)(\mu$a.u.)	213.0	28.7	512.9

state energies [13,17,21,22]. This is not the case for the intermediate, core-ionized states, which are strongly influenced by the spin-orbit splitting of the $2p$ shell. The actual form of the wave functions is further highly dependent on the molecular-field splitting. However, the VCI approach is not expected to reproduce the relative energies of the ground, the three intermediate, and the lowest final states sufficiently accurately to allow for conclusive predictions. In order to obtain quantitatively correct nonrelativistic energies, we applied the multiconfiguration coupled electron pair (MCCEPA) program [23] in a similar manner as e.g., in Refs. [9] or [12]. For that purpose the RHF wave functions of these states were used as reference wave functions for the MCCEPA method. In all calculations excitations from all occupied orbitals were allowed. For reasons of numerical stability, the core-hole states were set up only from electronic configurations that have at least one hole in the $2p$ core orbitals [4,9]. Table I shows the obtained nonrelativistic $2p$ ionization energies using different calculational methods. Our best values (MCCEPA) are very similar to the most accurate numbers given in the extensive investigation of the core ionization of H_2S by Børve [4]. The MCCEPA energies were used for the determination of the relativistic (spin-orbit including) wave functions and energies that are described below.

Now we turn to the problem of including the spin-orbit splitting. Recently, advanced four component relativistic codes [24–26] have been used for this purpose, but much less demanding effective spin-orbit Hamiltonian approaches have been shown to provide similarly accurate results and furthermore important insight into details of the electronic structure [3,4,7,9]. In this work we use the latter approach, in the formulation given in Ref. [9]. Thus, the effective spin-orbit coupling operator

$$H_{SO}=\zeta_{SO}\hat{\mathbf{l}}\hat{\mathbf{s}} \tag{2}$$

is added to the Hamiltonian, where $\hat{\mathbf{l}}$ and $\hat{\mathbf{s}}$ are the orbital- and spin-angular-momentum operators, which act only on the sulfur $2p$ orbitals. ζ_{SO} is the known spin-orbit coupling parameter of the S $2p$ orbital ($\zeta_{SO}=-0.800$ eV) [2]. The solutions of this Hamiltonian may be obtained by using the calculated energies of the three nonrelativistic S $2p$ ionized states [$\epsilon(1b_1^{-1})$, $\epsilon(1b_2^{-1})$, and $\epsilon(3a_1^{-1})$] [27] in the equation

$$\begin{pmatrix} \epsilon(1b_1^{-1}) & \frac{1}{2}\zeta_{SO} & \frac{1}{2}\zeta_{SO} \\ \frac{1}{2}\zeta_{SO} & \epsilon(1b_2^{-1}) & \frac{1}{2}\zeta_{SO} \\ \frac{1}{2}\zeta_{SO} & \frac{1}{2}\zeta_{SO} & \epsilon(3a_1^{-1}) \end{pmatrix} \mathbf{c}_i=E_i\mathbf{c}_i . \tag{3}$$

The results of Eq. (3) are called ''relativistic'' in the following. The eigenvalues of this equation give the energies of the relativistic $3e_{1/2}$, $4e_{1/2}$, and $5e_{1/2}$ states—these include both spin-orbit and molecular-field splitting. The corresponding relativistic wave functions are given by the eigenvectors $\mathbf{c}_i$ multiplied with e.g., $\{\Psi[1b_1\alpha], i\Psi[1b_2\alpha], -\Psi[3a_1\beta]\}$ [9], where the $\boldsymbol{\Psi}[\varphi]$'s represent the respective nonrelativistic wave functions with a hole in the spin orbital φ. The Auger decay rate of the ith relativistic state is calculated from [9]

$$\Gamma_{r,i}=\sum_{\varphi=1b_1,1b_2,3a_1} c_i[\varphi]^2\Gamma_{nr}[\varphi], \tag{4}$$

where $\Gamma_{nr}[\varphi]$ is the nonrelativistic total Auger transition rate of the state with a core hole in the orbital φ. In the following text these squared coefficients in Eq. (4) are designated ''$2p$ core-hole densities.'' The relativistic energies, core-hole densities and Auger transition rates are collected in Table II. The good agreement of the calculated energy difference between the $4e_{1/2}$ and $5e_{1/2}$ hole states (114 meV) with the experimental value of Svensson *et al.* [2] (110±5 meV) supports the adequacy of the present approach to describe the core-hole states.

The main property of interest is the core-hole density, which is pictorially the product of the core-hole orbital or—to be more precise—spinor with its complex conjugate. It is a purely real three-dimensional function. These densities

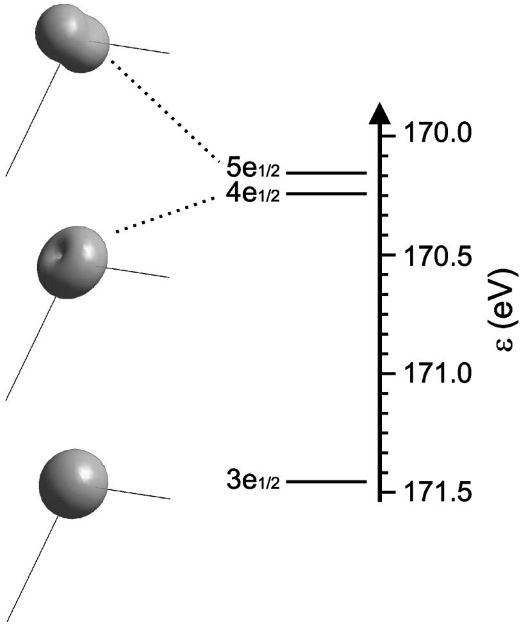

FIG. 1. Core-hole densities and relative energies of the $3-5e_{1/2}$ states of the $2p$-ionized $\mathrm{H_2S}$ molecule.

are shown in Fig. 1, where also the relative energies of the corresponding relativistic states are given.

III. EXPERIMENT

A. Setup

$\mathrm{H_2S}$ was produced by reacting 20% sulfuric acid with iron (II)sulfide (Aldrich, 99%)

$$\mathrm{FeS(s)+H_2SO_4(l)\rightarrow H_2S(g)+FeSO_4(l)}. \tag{5}$$

The gas production system was evacuated and a cold finger was used to trap the water coming from the sulfuric acid mixture. The gas purity was checked by valence photoelectron spectra. During the runs no contaminants were found.

The measurements were performed at the undulator beam line I411 of the MAX II storage ring in Lund, Sweden [28,29]. The incoming photons had an energy of 260 eV. At this energy the $2p$ electrons were ionized with an excess energy of about 100 eV, which causes almost negligible line broadening due to post collision interaction (PCI) effects [30,31]. An appropriate monochromator slit as well as low gas pressure were chosen to limit the ionization rate to keep the inhomogeneous electric field generated by the ions so small that its retardation of the electrons causes only an insignificant line broadening [32,33]. Auger electrons were collected in a Scienta SES 200 analyzer, at the pseudo-magic-angle (54.7°). The total spectrometer broadening was 28 meV according to valence test measurements performed using low excitation energy, where the photon bandwidth is negligible. Although this spectrometer broadening can be determined accurately, we have confirmed by a trial-and-error process that the difference in lifetime of core-hole molecular-field-split levels is not sensitive to the spectrometer broadening. The lifetime difference was the same, whether the spectrometer broadening with a value much less than and much greater than the true value was used in the fit. Thus the fitted value of the lifetime broadening is independent of the fixed experimental parameters used in the fit. We will come to this point later in the text in more detail.

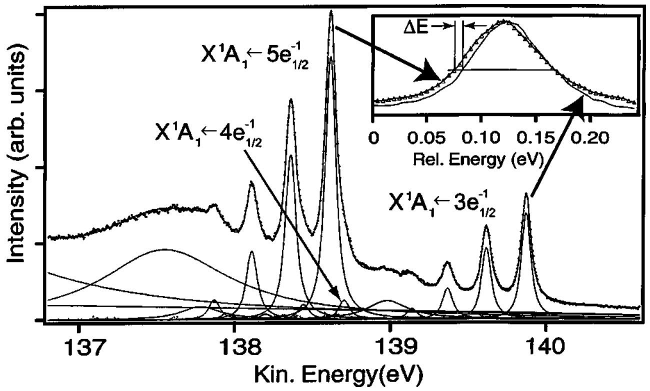

FIG. 2. The high-kinetic-energy part of the $L_{2,3}VV$ Auger spectrum of $\mathrm{H_2S}$ showing the $2p^{-1}\rightarrow X^1A_1(2b_1^{-2})$ transitions.

B. Experimental results and fits

In Fig. 2 we show the high-kinetic-energy part of our experimental $L_{2,3}VV$ Auger-electron spectrum of $\mathrm{H_2S}$. Between 139.9 eV and 139.1 eV kinetic energy there are four vibrational peaks corresponding to the transitions $3e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$. From 138.6 to 137.2 eV we can see the $5e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$ transitions. The figure also shows the results of our fitting procedure, which was done by fitting Voigt functions convoluted with a PCI function [34] with an asymmetry parameter of 0.059 units [30,31]. The Gaussian width of the Voigt function was fixed to be the known analyzer broadening ($\mathrm{FWHM}=28$ meV). For the two transitions mentioned above, only the four highest-kinetic-energy peaks were considered explicitly in the fitting procedure. Higher H-S stretching vibrational levels were fitted to a common broader peak for each of the transitions. Our improved resolution and the small PCI contribution (compared with previous studies [2]) allows us to identify the presence of the weak $4e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$ transitions (indicated in Fig. 2), which have not been previously observed. This component was fitted to a series of vibrational peaks with the width determined by the statistically significant $5e_{1/2}$ decay. A background based partially on previous work [2] was used. It was composed of three functions: one linear, and two broad Voigt functions convoluted with the same PCI function.

In Table III, we show the fitting results for the energies, intensities (areas), and widths of the peaks due to the $X^1A_1(2b_1^{-2})$ vibrational levels. In Table IV the average fitted lifetime widths of the $3e_{1/2}$ and $5e_{1/2}$ core-hole states are presented. In order to get the best possible values we averaged the three independently-fitted widths from the transition $3e_{1/2}$ $(v=0)$ to $X^1A_1(2b_1^{-2})$ $(v=0,\ 1,\ 2)$ weighted by the vibrational transition intensity. A similar procedure was repeated for the $5e_{1/2}$ transitions. We obtained a 10 meV change in the width well beyond our error bar (1 meV). The values extracted from the fit to the $3e_{1/2}$ and $5e_{1/2}$ decay states differ by 10 meV. Since the model peak profiles in-

TABLE III. Energies, intensities, and widths of the $H_2S^+(2p^{-1}) \rightarrow X^1A_1$ transitions.

Auger Transition	E_{kin} (meV)[a]	Vibrational components			
			E_{kin} (meV)[b]	Intensity[c]	Width (meV)
$3e_{1/2} \rightarrow X^1A_1(2b_1^{-2})$	0	$\nu=0$		1.00	63 ± 2
		$\nu=1$	-255 ± 2	0.67	64 ± 2
		$\nu=2$	-503 ± 2	0.29	70 ± 2
		$\nu=3$	-730 ± 2	0.10	70 ± 2
		band	-890 ± 7	0.18	
$4e_{1/2} \rightarrow X^1A_1(2b_1^{-2})$	-1167 ± 5	$\nu=0$		1.00	
		$\nu=1$	-259 ± 5	0.79	
		$\nu=2$	-502 ± 5	0.29	
		$\nu=3$	-752 ± 5	0.35	
$5e_{1/2} \rightarrow X^1A_1(2b_1^{-2})$	-1257 ± 2	$\nu=0$		1.00	73 ± 2
		$\nu=1$	-254 ± 2	0.63	74 ± 2
		$\nu=2$	-502 ± 2	0.26	76 ± 2
		$\nu=3$	-742 ± 3	0.07	78 ± 3
		band	-830 ± 8	0.05	

[a] Relative kinetic energy with respect to the $3e_{1/2} \rightarrow X^1A_1(2b_1^{-2}, \nu=0)$ peak.

[b] Relative kinetic energy with respect to the $\nu=0$ peak of the band.

[c] Relative intensity (peak area) with respect to the $\nu=0$ peak of the band.

clude an identical Gaussian broadening this difference can only be attributed to the lifetime broadening. The error bar was obtained from comparison of different fitting strategies where, for example, the background was represented in different ways. In all these fitting procedures the difference in width was not smaller than 10 meV. Apart from the best fitting strategy presented here, several other strategies were investigated including obviously too large or too small spectrometer contributions (20 meV and 40 meV, instead of 28 meV). Furthermore, the fitting has been done independently on the three most intense vibrational components of the $3e_{1/2} \rightarrow X^1A_1(2b_1^{-2})$ and $5e_{1/2} \rightarrow X^1A_1(2b_1^{-2})$ transitions. As the determined lifetime width difference between the $3e_{1/2}$ and $5e_{1/2}$ core-ionized states remained almost constant in all strategies we have confidence for this value to be 10 ± 1 meV.

IV. DISCUSSION

The theoretical results clearly predict substantially different partial and total Auger transition rates for the nonrelativistic states. In prior work [3,9] it has been established that partial $L_{2,3}VV$ Auger transition rates are large, if the core hole points in the same direction as the atomic orbital $3p$ contribution of at least one of the valence holes. The nonrelativistic partial Auger transition rates to the $H_2S^{2+}X^1A_1(2b_1^{-2})$ final state in Table I show exactly this behavior. The relative orientations of the core and valence holes are obviously parallel for the $1b_1^{-1}$ intermediate state and orthogonal for the $3a_1^{-1}$ and $1b_2^{-1}$ states. Accordingly, the nonrelativistic total Auger decay rates (i.e., the sum over the partial Auger transition rates to all possible final states) are big for high occupation numbers of the $3p$ orbital with the same orientation as the $2p$ core hole [3,9]. We have calculated the occupation numbers with a Mulliken population analysis and included them in Table I.

TABLE IV. Experimental and theoretical lifetime widths of the $3e_{1/2}$ and $5e_{1/2}$ core-hole states of H_2S^+.

Core-hole state	Experiment (meV)	Theory (meV)
$3e_{1/2}$	64 ± 2	68
$5e_{1/2}$	74 ± 2	83

For the relativistic core holes the situation is a bit more complex, as the spin-orbit interaction—the clearly dominating effect for the energetical structure of the $2p$ ionized levels—blurs the orientation of the core holes. This blurring is almost complete for the $2p_{1/2}$ hole state $3e_{1/2}$ (see Table II and Fig. 1), but the splitting of the $2p_{3/2}$ level in the $4e_{1/2}^{-1}$ and $5e_{1/2}^{-1}$ states opens an opportunity to generate some core-hole orientation. The splitting can be understood on the basis of differences in the energies of the nonrelativistic $2p$ ionized states [See Eq. (3)]. Børve and Thomas [7] found that differences in the occupation of the $3p$ atomic orbitals of the core-hole atom are the main reason for these energy differences in PH_3 and PF_3. The mechanism may be simply stated in the following way: A low population of a $3p$ atomic valence orbital in one particular direction causes electrons in the $2p$ orbital with the same orbital orientation to experience a reduced repulsion. One could argue that the same is also true for electrons in the other $2p$ orbitals, but the Coulomb interaction of p orbitals with the same direction is much bigger than that of orbitals with different directions. Thus the ionization potential increases with decreasing population of the valence p orbitals with the same direction. The occupation numbers of the $3p$ valence orbitals in the $2p$ ionized H_2S molecule (Table I) show exactly this trend.

In the nonrelativistic case, both the total Auger transition rates, as well as the core-hole state splittings are mostly determined by the occupation of the sulfur $3p$ atomic orbitals, which are the valence atomic orbitals with the biggest contribution to the chemical bond in the molecule. This is responsible for the observed lifetime dependence of the relativistic states. We want to point out that the reason for the $3p$ atomic orbital occupation differences is a characteristic effect of chemical bonds on electronic structure: The chemical bonds in the molecular plane cause electrons in the in-plane $3p$ orbitals to be shared between the sulfur and the hydrogen atoms. Furthermore, the positive interference of the S $3p$ and H $1s$ orbitals decreases the amplitude of the bonding orbitals at the sulfur atom even more [9].

There is another possible reason for the observed difference in the total Auger transition rates. As the $2p_{1/2}$- and $2p_{3/2}$-hole states have different energies, the corresponding Auger-continuum wave functions have different forms that influence the total decay rate. However, the size of this effect is expected to be small. According to the tabulated Auger decay integrals of Chen, Larkins, and Crasemann [35] the lifetimes of argon $2p_{3/2}^{-1}$ are only about 0.4% bigger than those of the $2p_{1/2}^{-1}$ states. In the experimental work of Köppe *et al.* [36] the lifetime of the $2p_{3/2}^{-1}$ state in argon is reported to be $7\pm10\%$ bigger than the $2p_{1/2}^{-1}$ state. In Ref. [12] the average of the experimental lifetimes of the two $2p_{3/2}^{-1}$ states of HCl was found to be 87 ± 12 meV, whereas the lifetime of the $2p_{1/2}^{-1}$ state was 84 ± 9 meV. These results indicate that a statistically significant difference between the core-hole lifetime of the different j values does not exist in $2p$ core-hole states. But even if this difference was 7% as claimed by Köppe *et al.* for the argon atom [36], the H_2S difference of 16% would be surprisingly high. Nevertheless, it should be noted that the experimental data alone do not provide an unambiguous proof of the interpretation of the lifetime differences as a result of the core-hole orientation and the valence electron distribution. For such a proof the lifetime of the $4e_{1/2}^{-1}$ state would be required.

A comparison of the experimental and theoretical lifetimes (Table IV) is not trivial as the calculated absolute lifetimes generally exceed measured values (See, e.g., Ref. [9] and references therein). Thus, a comparison of relative lifetimes is more feasible. The theoretical results show a 22% increase of the lifetime from $3e_{1/2}$ to $5e_{1/2}$ compared with a $16\pm2\%$ increase from the experiment.

The calculated and experimental data may be compared in one more respect. In Table V we show the calculated relative partial Auger transition rates to the ground state of H_2S^{2+} i.e., the S $2p\rightarrow X$ Auger transition rates divided by the $5e_{1/2}\rightarrow X$ ones. These are compared with the relative experimental partial transition rates, which were obtained from the corresponding peak areas in the spectrum. The theoretical and experimental data are equivalent if the photoionization cross sections for ionization of the three $2p$ core-hole states are about equal. According to Ref. [2] this is a reasonable assumption. Due to the higher photoelectron energy in the present study, we can assume that this is also true in our case. The calculated numbers agree with the experimental ones within the experimental error.

Finally we want to mention that the relative intensity distributions of the $H_2S^{2+}X^1A_1$ vibrational states (5th column in Table III) also depend on the intermediate state. This may be due to the lifetime differences again, which are known from lifetime-vibrational interference theory to affect the intensity distributions. Another very reasonable explanation is that the potential energy surfaces of the intermediate states depend on the core-hole state. The observed difference of the vibrational intensity distribution is small. However, as in the analysis of $2p$ photoelectron spectra it is generally assumed [5,6,11] that the vibrational profiles resulting from different intermediate states are identical. Our results indicate that this assumption is mostly but not strictly correct.

TABLE V. Relative intensities of the transitions from the three intermediate states $3e_{1/2}$, $4e_{1/2}$, and $5e_{1/2}$ to the $X^1A_1(2b_1^{-2})$ final state. The experimental intensities are the sum of the transition intensities to the vibrational sublevels (0-0), (0-1), (0-2), and (0-3). The theoretical intensities are obtained from the calculation of the partial transition rates.

Auger transition	Relative intensities	
	Experiment	Theory
$3e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$	0.42 ± 3	0.42
$4e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$	0.09 ± 3	0.06
$5e_{1/2}\rightarrow X^1A_1(2b_1^{-2})$	1.00	1.00

V. CONCLUSION

We have observed a difference in the lifetime of the $3e_{1/2}$ and $5e_{1/2}$ $2p^{-1}$ levels in the H_2S molecule by investigating the band widths of vibrationally resolved final states in the Auger decay spectrum. We explain this difference to be due to the nonspherically-symmetric valence electron distribution, which is mainly a result of the existence of chemical bonds. Thus, the lifetime dependence of different core-hole states is one example of the possibility to observe electronic structure properties by Auger-electron spectroscopy.

For core electron spectroscopy, there are several fundamental reasons why the difference of lifetimes of core-hole states with a core-hole that is localized at the same atom is of interest.

1. It is well known that the spectra obtained from these states are strongly influenced by the lifetimes as a determining factor of the spectral widths. But, as no further information on this was available, in almost all preceding studies [5,6,11], it has been assumed that the lifetime widths of $2p$ core-ionized states are the same for the different $2p$ ionized states in a given molecule.

2. As the total Auger decay rates contain interesting information about the relative orientation of the valence electron density and core-holes, they can provide information about the electronic structure of the investigated species.

3. Core-hole lifetime was shown to be a key feature in the spectroscopy of dissociative core-excited states, which is a powerful tool to study nuclear motion in molecules on the femtosecond time scale [37–41]. In fact, the lifetime of core-excited states is used in these cases as a spectroscopic probe of ultrafast nuclear dynamics. The existence of lifetime differences could be used to precisely time these dynamical processes.

4. Molecular quasialignment may be probed by excitations to bound, core-excited states with linearly polarized light, which would be an important application of this effect.

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