Spin- and angle-resolved spectroscopy of S 2*p* photoionization in the hydrogen sulfide molecule

G. Turri,[1,2] G. Snell,[1,2] B. Langer,[3] M. Martins,[4] E. Kukk,[5] S. E. Canton,[1,2] R. C. Bilodeau,[1,2] N. Cherepkov,[6] J. D. Bozek,[2] A. L. Kilcoyne,[2] and N. Berrah[1]

[1]*Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008, USA*

[2]*Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[3]*Max-Born-Institute, Max-Born-Strasse 2A, 12489 Berlin, Germany*

[4]*Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany*

[5]*Department of Physical Sciences, University of Oulu, P. O. Box 3000, FIN-90014 Oulu, Finland*

[6]*State University of Aerospace Instrumentation, 190000 St. Petersburg, Russia*

(Received 13 March 2004; published 30 August 2004)

Angle- and spin-resolved photoelectron spectroscopy with circularly and linearly polarized synchrotron radiation were used to study the electronic structure of the hydrogen sulfide molecule. A strong effect of the molecular environment appears in the spin-resolved measurements and, although less clearly, in the angular distribution of the sulfur 2*p* photoelectrons. The anisotropy and spin parameters of the three main spectral components have been obtained. The validity of simple atomic models in explaining the results is discussed.

DOI: 10.1103/PhysRevA.70.022515 PACS number(s): 33.60.−q, 29.30.Dn

I. INTRODUCTION

The study of the electronic structure of atoms, molecules, and condensed matter as well as studies of the dynamics of photoemission and the Auger process have been conducted using spin-resolved photoelectron spectroscopy, combined with energy- and angle-resolved spectroscopy. For example, the electronic structures of adsorbates [1], thin films [2], and the magnetic properties of solids [3] have been investigated with this technique. In atoms, spin-resolved measurements have been proved to be a valid alternative to coincidence techniques in order to acquire an expanded data set for the photoionization and Auger decay amplitudes. In particular, for closed shell atoms, the use of the measured values of the cross section, the anisotropy parameter, and the three spin parameters of photoelectrons and Auger electrons, allowed a complete determination of the dynamical quantities, i.e., matrix elements and phase shifts, characterizing the photoionization process to be accomplished [4]. It has been proved recently by Schmidtke *et al.* [5] that for closed shell atoms or atoms with a single electron shell measurements of the cross section and anisotropy parameter together with the three spin polarization parameters of photoelectrons are not always sufficient for the complete experiment since these parameters are not independent. For the case of the spin polarization parameters of molecules, no such dependence has been found so far, because the corresponding analysis is still in its infancy due to the rare spin-resolved studies of molecules found in the literature.

Spin-resolved studies of molecules are rarer in the literature. Only the outer shell photoionization of HI [6] and HBr [7] has been reported in this respect. Recently, we showed how the properties of the inner S 2*p* shell in OCS and H_2S molecules can be investigated by combining spin-resolved and angle-resolved measurements [8].

In this work, we extend the investigation we began in H_2S, by reporting angle-resolved measurements that allowed the anisotropy parameters to be obtained between 180 and 260 eV. In addition, we measured the electron spin polarization of S 2*p* using linearly polarized light.

H_2S is important in geophysics for it plays a main role in the global cycling of sulfur in the Earth atmosphere, and it has been observed in the atmospheres of Venus and other planets, and in the interstellar medium [9]. From a fundamental point of view, the molecular ground state of H_2S has been studied in detail because it shows pronounced localization of vibrations and clustering effects in the rotational structure [9]. Since it is the congener of H_2O, it is a good candidate for implementing wave functions of water. The photoionization of the S 2*p* inner shell in H_2S has been studied both experimentally [8,10] and theoretically [10]. The measured angle-integrated cross sections and energy levels of the residual ion were correctly reproduced within the frame of a simple molecular model [10]. On the other hand, to our knowledge, no spin-resolved or angle-resolved measurements were available in the literature before our recent work [8].

We shall present here the spin polarization and the angular distribution of the three most intense components of the S 2*p* photoelectron spectrum as measured by photoionization of H_2S with linearly and circularly polarized light. It should be noted that the use of circularly rather than linearly polarized light affects only the geometry of the experiment when angular distributions are concerned, whereas it changes the dynamics of the spin polarization of the photoelectrons. The two mechanisms, known as "spin transfer" and "dynamical polarization," are responsible for the spin polarization in case of circularly and linearly polarized light, respectively [11,12]; different parameters describe the spin polarization in these two cases. Conversely, the same parameter, namely, the anisotropy parameter, characterizes the angular distribution of the photoelectrons in the cases of linearly and circularly polarized light. We use the dipole approximation, plausible in our experimental conditions, to describe the photon-atom interaction.

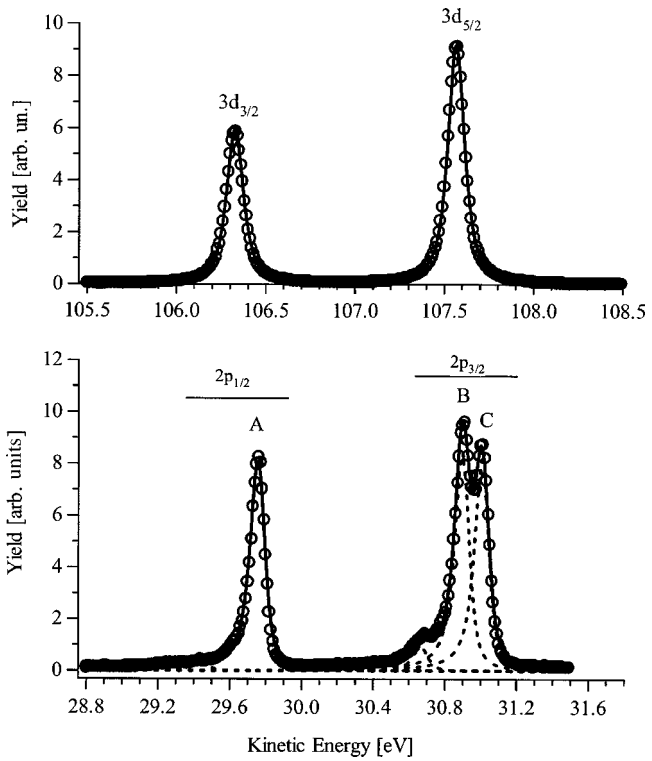

FIG. 1. Photoionization spectrum of Kr 3*d* (top) and S 2*p* shell of H_2S (bottom) as measured at the magic angle with 200 eV linearly polarized light. The continuous and dashed curves are the result of a least-squares fitting procedure. Lines labeled *A*, *B*, and *C* in the bottom panel are associated with the H_2S ion in its ground vibrational state.

II. EXPERIMENTAL SETUP

All the measurements reported in this work were performed at the Advanced Light Source in Berkeley (CA). Two different experimental apparatuses were used.

The angular distributions were measured at beamline 10.0.1, using the Scienta SES 200 high-resolution electrostatic analyzer. Photoelectron spectra were obtained at eight different photon energies between 180 eV and 260 eV, with the S 2*p* threshold in H_2S at about 170 eV [10]. The beamline was set to have about 50 meV photon resolution; in this condition, a photon flux of 10^{12} photons/s, 100% linearly polarized, was delivered to the sample. The Scienta analyzer was operated at 50 meV resolution; thus an overall 70 meV instrumental (analyzer plus photon) broadening was expected. Spectra were measured at four different angles, namely, 0, 54.7° (magic angle), 65°, and 80°. In order to account for possible variations of the efficiency of the Scienta analyzer operating at different orientations, a gas mixture of H_2S and Kr, rather than pure H_2S, was used in the experiment. The Kr 3*d* photoelectron lines with well known anisotropy parameter [13] were measured together with the H_2S S 2*p* photolines, and were used in the calibration of the data. As an example, we report in Fig. 1 the spectra that we measured at the magic angle with 200 eV linearly polarized light. In the upper panel, the Kr 3*d* photoionization spectrum is shown. The peak areas were obtained by applying a least squares fitting procedure to the experimental spectra (full line in the figure). Voigt functions were used, and the value of 88 meV [14] of the natural width of the Kr 3*d* hole was imposed in the fitting procedure. The lower panel of Fig. 1 shows the S 2*p* photoionization spectrum. As discussed in previous investigations [8,10] the shape of the S 2*p* photoelectron spectrum is determined by three factors: spin-orbit splitting of the 2*p* hole, vibrational excitations in the residual ion, and molecular field splitting of the S $2p_{3/2}$ hole. The last results from the breaking of the spherical symmetry of the *p* electrons by the molecular field having C_{2v} symmetry, which removes the degeneracy of the states with different projections of orbital angular momentum along the C_{2v} axis. The most intense transitions are associated with the ion in its ground vibrational state [10,15], and only these will be considered in this paper (lines *A*, *B*, and *C* in Fig. 1). To resolve the different components of the peaks, we applied a least squares fitting procedure to the experimental spectra (full and broken lines in Fig. 1) utilizing asymmetric Voigt functions. Asymmetric distortion of the line shape due to postcollisional interaction was included using the method of van der Straten [16]. Previously determined values of the lifetime width (70 meV), vibrational period (300 meV), and molecular field splitting (110 meV) [10,15] were used in the fit. The values of the Gaussian width as returned by the fit, about 65–75 meV, are in good agreement with the expected instrumental broadening.

The apparatus we used for spin-resolved measurements has been described elsewhere [8,11], and only a few details will be given here. The measurements were performed at the elliptically polarizing undulator beamline 4.0.2 [17] which was set to deliver alternatively linearly and circularly polarized light (100% polarization), at a resolving power $E/\Delta E$ of about 1000. In these conditions, a photon flux of approximately 10^{12} photons/s was delivered on the H_2S sample. An electron time-of-flight (TOF) detector combined with a spherical Mott polarimeter of the Rice type, operated at 25 KV, carried out the spin-resolved analysis. The geometry of the experiment was selected to measure the polarization of the spin component of the electrons along the photon propagation direction and for electrons emitted in the plane perpendicular to the photon propagation direction and at 45° with respect to the horizontal plane. Instrumental asymmetries of the Mott polarimeter were eliminated by rotating the light polarization by 90° (from horizontal to vertical) when linearly polarized light was used, and by inverting the helicity of the circularly polarized light, approximately every 10 min. The appropriate data files were later recombined to give the final results. Figure 2 depicts a typical spectrum measured with 210 eV linearly polarized light. The spin-unresolved photoelectron spectrum, measured with a second regular electron TOF analyzer (without a Mott detector), is shown in the bottom frame of the figure, corresponding to the sum of spectra measured with vertically and horizontally polarized light. In the middle panel, the spectra of electrons with spin parallel (empty squares) and antiparallel (full triangles) are shown. Data have been converted from flight time to kinetic energy and grouped at intervals of 50 meV. The spectra were analyzed using the same fit technique we employed for the angle-resolved spectra (full and broken

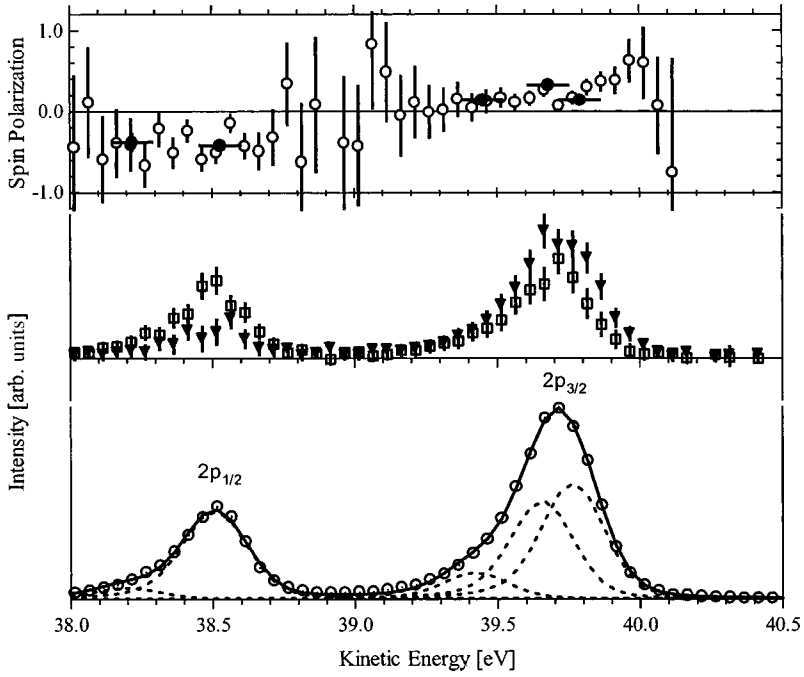

FIG. 2. S 2*p* photoionization spectra as measured with 210 eV linearly polarized light. Bottom: total intensity; the continuous curves are the result of a least-squares fitting procedure. Middle: spin-resolved spectra (spin parallel □ and antiparallel ▼ to the photon propagation). Top: spin polarization, calculated from the peak areas ●and the individual data points ○.

lines in the lower panel); values of about 200 meV for the Gaussian width were given by the fits at the different measured photon energies. The areas of the peaks obtained from the fitting procedure were used to determine the spin polarization for the individual photoelectron lines. Additionally, we performed a single-channel analysis [11], where the spin polarization was determined for each point of the spectrum. The results of the two methods are compared in the top panel of Fig. 2 (full and empty circles, respectively) and demonstrate good agreement. The error bars of the spin polarization values in the figure include both statistical and systematic errors.

III. RESULTS

A. Angular distributions

When photoionization from unoriented molecules is considered within the dipole approximation, the angular distribution of the photoelectrons is expressed by the same formulas that apply to the photoionization of atoms. If linearly polarized light is used, then

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta\text{-}1)\right], \qquad (1)$$

θ being the angle between the light polarization vector and the photoelectron direction, σ the total (angle-integrated) cross section, and β the so-called anisotropy parameter. As in the atomic case, σ is the sum of squares of dipole matrix elements, and β is expressed through the products of the matrix elements and cosine functions of the phase shift differences characterizing the photoionization process. For molecules a larger (in principle infinite) number of partial waves is allowed for the electron in the continuum, and σ and β can have quite complicated analytical expressions. In practice, however, the number of partial waves contributing substantially to the photoionization process is usually restricted to the values $l \leqslant 5$.

For inner molecular shells, one may think of introducing atomic or atomiclike models to describe them. Using an atomic model is a valid approximation in the case of the H_2S molecule, because of the localized nature of the S 2*p* core orbitals and the absence of shape resonances around the L_{23} sulfur edge [18]. In H_2S, the sulfur atom is in the closed shell configuration of argon, and the photoionization cross section for the 2*p* levels of second row elements depends only weakly on the nuclear charge. Thus calculations for the 2*p* shell of Ar in [19] will be compared to the experimental results in this paper.

We show in the lower part of Fig. 3 the anisotropy parameters that we measured at different photon energies for lines *A*, *B*, and *C* (asterisks, full circles, and empty circles, respectively), as compared with the Ar calculation (full line). At all the investigated photon energies, lines *A* and *C* show the same values of β, whereas line *B* has systematically a slightly higher value of β at lower photon energies. It is interesting to notice that a similar behavior has been qualitatively reported by Kukk *et al.* in OCS [20]. The discrepancy between theory and experiment is not that large, and can be related either to the difference between the free Ar atom and the S in the Ar configuration, or to the molecular environment. If the unresolved *B*+*C* doublet is considered, depicted in the top panel of Fig. 3, the calculations are in a very good agreement with the experimental result. As we showed in our previous paper [8], and will show in the next section, the spin polarization of the photoelectrons is also correctly reproduced by the Ar calculations when lines *B* and *C* are not resolved, indicating that the effects of the molecular environment vanish when the experiment is somehow integrating over the different orientations of the angular momenta. Thus, the fact that the anisotropy parameter of line *A* is the same as line *B* rather than as lines *B*+*C* would suggest some influ-

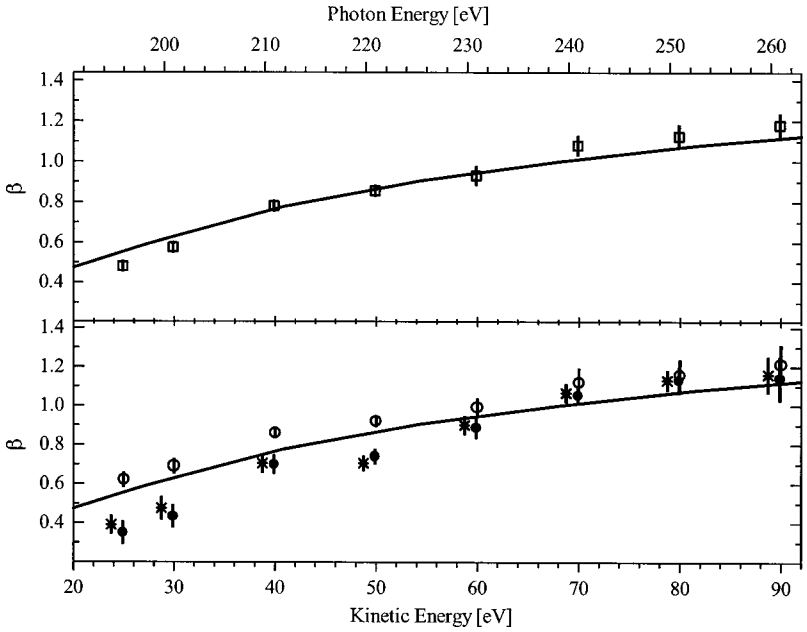

FIG. 3. Anisotropy parameter as a function of the photoelectron kinetic energy. Experimental points are for the ground vibrational state of ($*=A$)S $2p_{1/2}$ and ($\bullet=B, \circ=C$) molecular field split S $2p_{3/2}$ in the lower panel, and for the unresolved doublet $2p_{3/2}(\square)$ in the upper panel. Full lines are calculations for Ar $2p$ photoionization.

ence of molecular effects, although such effects are relatively small.

B. Spin polarizations

As for the angular distribution, it is possible to show [21] that the spin polarization of the photoelectrons emitted from unoriented molecules is described by the same formulas valid in atoms. In the properly chosen geometry of our experiment, they take the simple forms

$$P_{\mathrm{circ}} = -\frac{A + \gamma/2}{1 + \beta/4}(\varepsilon) \tag{2}$$

for circularly polarized light ($\varepsilon = \pm 1$ for the photon helicity), and

$$\mathrm{P_{lin}} = \frac{\eta}{1 + \beta/4} \tag{3}$$

for linearly polarized light. In our notation, a positive spin polarization means that the electron is preferentially emitted with its spin antiparallel to the photon propagation direction. We are using here the notation of the spin parameters (A, γ, η) introduced by Cherepkov [21]; different notations have been used by Huang [12] and Heinzmann [22]. Like the anisotropy parameter β, the three spin parameters A, γ, and η are combinations of the matrix elements and phase shifts characterizing the photoionization process. Thus the same considerations about the complexity of their analytical forms and the validity of the atomic approximation that we draw for β in the previous section do apply, and we shall compare

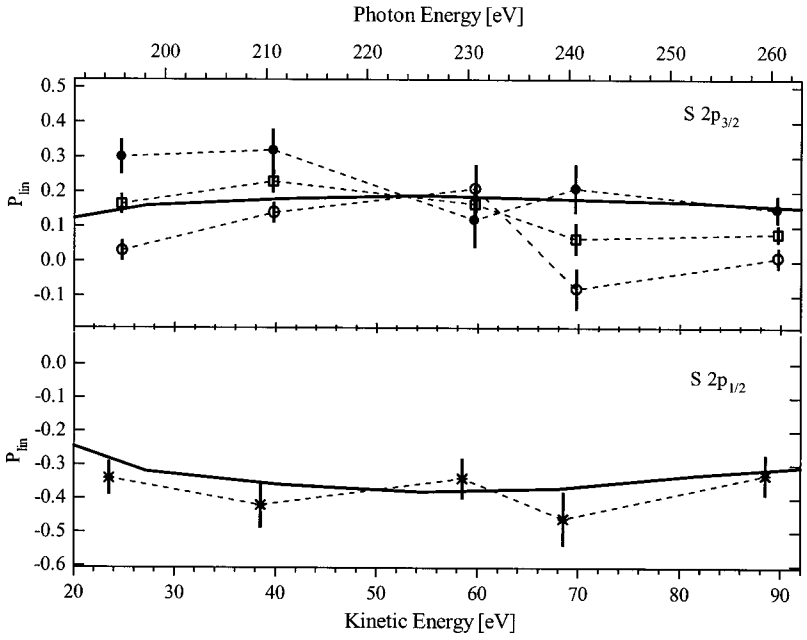

FIG. 4. Spin polarization as a function of the photoelectron kinetic energy as measured with linearly polarized light. Experimental points are for the ground vibrational state of ($*=A$)S $2p_{1/2}$, lower panel, and ($\bullet=B, \circ=C$) molecular field split S $2p_{3/2}$ and unresolved doublet $2p_{3/2}(\square)$, upper panel. Full lines are calculations for Ar $2p$ photoionization.

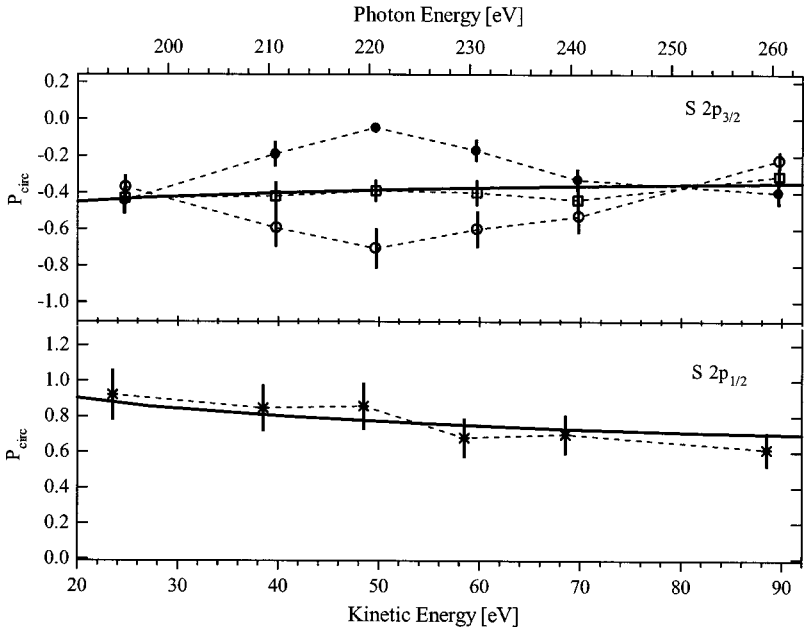

FIG. 5. Same as Fig. 4, as measured with circularly polarized light.

our results with the spin polarization calculated for Ar by Cherepkov.

If the anisotropy parameter is known, measuring the spin polarization of the photoelectron with linearly and circularly polarized light will allow η and $(A+\gamma/2)$ to be obtained from formulas (2) and (3). However, to obtain independently the values of A and γ, the spin component of the electron along its propagation direction should be measured, which requires a more sophisticated experimental setup, like the use of a Wien filter.

We report (with the same notation as in Fig. 3) the spin polarization of lines A, B, C, and the unresolved doublet $B+C$ (empty squares) in Figs. 4 and 5, as we measured it with linearly and circularly polarized light, respectively, together with the Ar calculations. For both polarizations of the light, the spin polarization of lines B and C is different over a broad range of photon energies, whereas the variations for the unresolved doublet are smoother. The Ar calculations can correctly reproduce the experimental results of line A and the unresolved doublet, whereas they fail to describe the single lines B and C. This is analogous to what we observed in carbonyl sulfide with circularly polarized light [8]. By comparing Fig. 3 with Figs. 4 and 5, it is clear that the effects of the molecular environment on lines B and C are much more evident in the spin polarization than in the angular distribution. This can be understood on the basis of some qualitative considerations. In general, the spin polarization parameters, as well as the β parameter, are not very sensitive to the details of the atomic potential or to the many-electron correlations. However, occasionally in molecules, contrary to atoms, one or more of the dipole matrix elements or phase shifts can vary sharply in some energy region (as in the σ^* shape resonances in CO or N_2 molecules), making some of the parameters different from the corresponding atomic ones. That can more strongly affect the spin polarization of photoelectrons, which depends on all the parameters, than the angular distributions that depends on one parameter, namely, β, only.

From the measured values of β, P_{lin}, and P_{circ}, we obtained the values of η and $A+\gamma/2$ summarized in Table I.

For the photoionization of a p atomic shell, the anisotropy and the spin parameters satisfy the simple relations

$$\beta(2p_{1/2}) = \beta(2p_{3/2}), \quad \eta(2p_{1/2}) = -2\eta(2p_{3/2}),$$
$$\gamma(2p_{1/2}) = -2\gamma(2p_{3/2}), \quad A(2p_{1/2}) = -2A(2p_{3/2}). \tag{4}$$

We can then discuss the validity of such an approximation by

TABLE I. Spin parameters for the ground vibrational state of the S $2p_{1/2}(A)$ and the molecular field split S $2p_{3/2}(B,C)$ as measured at different photon energies.

	Line A		Line B		Line C	
Photon Energy (eV)	η	$A+\gamma/2$	η	$A+\gamma/2$	η	$A+\gamma/2$
195	−0.37(0.07)	1.01 (0.20)	0.33 (0.08)	−0.48(0.12)	0.03 (0.03)	−0.43(0.08)
210	−0.49(0.09)	1.00 (0.17)	0.38 (0.08)	−0.22(0.08)	0.17 (0.04)	−0.72(0.13)
220		1.01 (0.17)		−0.06(0.03)		−0.87(0.14)
230	−0.42(0.08)	0.83 (0.14)	0.15 (0.10)	−0.21(0.07)	0.26 (0.09)	−0.75(0.13)
240	−0.58(0.10)	0.89 (0.15)	0.27 (0.09)	−0.42(0.08)	−0.10(0.08)	−0.68(0.12)
260	−0.43(0.08)	0.79 (0.14)	0.19 (0.05)	−0.51(0.10)	0.01 (0.04)	−0.29(0.06)

TABLE II. Comparison between the spin parameter η and the anisotropy parameter for the ground vibrational state of the S $2p_{1/2}(A)$ and the unresolved doublet $2p_{3/2}$ $(B+C)$ at different photon energies.

Photon energy (eV)	$\beta(A)$	$\beta(B+C)$	$\eta(A)$	$-2\eta(B+C)$
195	0.39 (0.05)	0.48 (0.03)	−0.37(0.07)	−0.37(0.07)
210	0.71 (0.05)	0.78 (0.03)	−0.49(0.09)	−0.55(0.08)
230	0.90 (0.05)	0.93 (0.05)	−0.42(0.08)	−0.41(0.13)
240	1.07 (0.05)	1.08 (0.05)	−0.58(0.10)	−0.17(0.12)
260	1.16 (0.10)	1.18 (0.06)	−0.43(0.08)	−0.21(0.07)

checking the first two equalities for lines A and the unresolved $B+C$. The values are reported in Table II.

It can be seen that the agreement for the anisotropy parameters is good at higher photon energies, whereas the second relation in (4) is satisfied only at lower photon energies. Again, the deviations from the simple atomic model more strongly affect the spin than the angular distribution parameter. The η parameter in atoms is more sensitive to changes in the phase shifts rather than in the matrix elements of the photoionization process, whereas β is sensitive to both. Thus the deviations from the simple atomic behavior that we observe at different photon energies would suggest a deviation of both the phase shifts and the matrix elements from such a model.

IV. CONCLUSIONS

We have measured the angular distribution and the dynamical spin polarization of the photoelectrons from the photoionization of the S $2p$ shell in H_2S molecule using linearly polarized light. The anisotropy parameter and the η and $A+\gamma/2$ spin parameters were obtained at different photon energies. We observed much stronger molecular effects on the electron spin polarization than on the angular distributions. When the measurements do not resolve the molecular field structure introduced by the symmetry breaking of the molecule, then a simple atomic model describes the photoionization process to a good approximation. For a better understanding of the effects of the molecular field on the spin polarization of photoelectrons, a further theoretical study is necessary with the molecular field included into the calculation.

ACKNOWLEDGMENTS

This work has been funded by DOE, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Divisions. The ALS is supported by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We would like to thank E. Arenholz, A. Young, and B. Rude for their support at the ALS beamlines 4.0.1 and 10.01. E.K. acknowledges financial support from the Research Council for the Natural Sciences of the Academy of Finland. N.A.C. acknowledges financial support from the DFG-RFBR, Grant No. 03-02-04015.

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