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Abstract. We have used spin-resolved electron spectroscopy with circularly polarized synchrotron radiation to delineate the electronic structure of the hydrogen sulfide and carbonyl sulfide molecules and their photoemission dynamics. Specifically, inner-shell spin-polarization measurements of the molecular field split components of the S 2p photolines were carried out to reveal effects of the different molecular environments. The validity of simple atomic models to explain the results is discussed.

The photoemission process has been widely studied in atoms. Energy and angle resolved photoelectron spectroscopy has been used alone, or combined with different techniques to acquire an expanded data set [1,2,3,4,5], to investigate the electronic atomic structure as well as the dynamic of the photoemission process itself. When inner-shell photoemission from molecules is considered, the situation is considerably more complex than the atomic case, due to the large number of outgoing partial waves, the influence of the molecular potential on the core level energies, the possibility of creating the ion in a vibrationally excited state, and the lower symmetry of the system. The experimental energy resolution required to resolve these molecular effects is considerably more stringent than that required for atomic measurements. Theoretical treatments similarly require simplifying approximations to make the calculations tenable, sometimes to the detriment of the results.

In this work, we have used for the first time spin-resolved photoelectron spectroscopy to measure the effects of the molecular environment on inner shell photoionization in small molecules. This technique has been successfully used to study photoionization and Auger decay in atoms [6,7,8,9], to investigate the electronic structures of adsorbates [10], thin films [11] and the magnetic properties of solids [12]. For molecules, only the outer shell spin-resolved photoionization of HI [13] and HBr [14] have been reported previously.

We have investigated the direct photoionization of the sulfur 2p shell in carbonyl sulfide (OCS) and hydrogen sulfide (H_2S). Both molecules are of great interest in biology, astrophysics and from a fundamental point of view [15, 16]. The two molecules have different molecular geometries around the sulfur atoms; OCS is linear with a terminal sulfur and H_2S is bent with a central sulfur atom. High-resolution spectroscopy has previously been used to study S2p excitation and ionization in both OCS [17,18,19] and H_2S [17]. In both cases, the non-spherical field induced by the molecular geometry around the sulfur atom removes of the degeneracy of the $S2p_{3/2}$ level resulting in a splitting in the photoelectron spectrum. The magnitude of this molecular field splitting, as well as the angle-integrated photoionization probabilities are well reproduced by a simple molecular model [17,18]. Kukk et al. [19] recently studied the angular distribution of S2p electrons photoemitted from the carbonyl sulfide molecule to probe the effect of the molecular environment. The two molecular field split components of the S $2p_{3/2}$ photoline were found to have different angular distributions, and a semi-empirical atomic model was employed to explain the results. The present study is motivated in part by these previous results, since a comparison between the spin resolved and spin integrated angular distributions can yield additional insight into the effects of the molecular field on inner-shell photoionization.

Spin-resolved sulfur 2p photoelectron spectra were obtained at photon energies between 180 eV and 260 eV, with the S2p threshold at about 170 eV for both molecules [17]. The experiments were performed at the Advanced Light Source using an elliptically polarizing undulator (EPU) at beamline 4.0.2 [20]. A photon flux of approximately 10^{12} photons/sec at a resolving power, E/ΔE, of about 1000 was used. The EPU was set to deliver 100% circularly polarized light. Electron energy analysis was performed using a time-of-flight (TOF) spectrometer, collecting electrons emitted at 45° with respect to the plane of the storage ring, in the plane perpendicular to the photon propagation direction. A spherical Mott polarimeter of the Rice type, operated at 25KV, mounted at the end of the TOF was used to carry out the electron spin polarization analysis [21,22]. The geometry of the experiment was selected to measure the polarization of the spin component of the electrons along the photon propagation direction. Instrumental asymmetries of the Mott polarimeter were negated by reversing the helicity of the photon beam approximately every 10 min and later recombining the results.
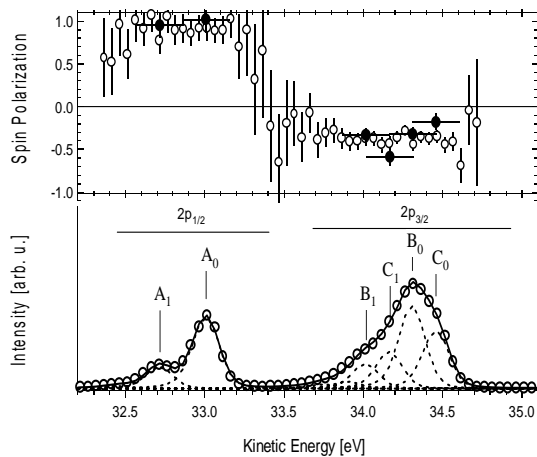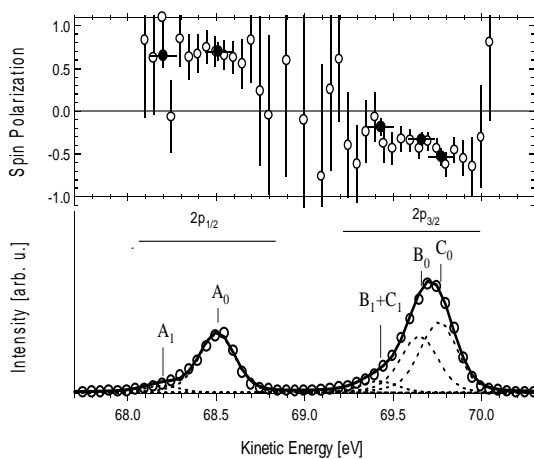
Figure 1. Sulfur 2p photoionization spectrum of OCS measured with 205 eV (a) and H$_2$S measured with 240 eV (b) circularly-polarized light. Bottom: total intensity, the continuous curves are the result of a least-squares fitting procedure. Top: spin polarization, calculated from ● the peak areas and ○ the individual data points.

Results for OCS obtained with 205 eV photon circularly polarized light are given in Fig. 1a. The spin unresolved photoelectron spectrum is shown in the bottom frame of the figure, corresponding to the sum of spectra measured with left and right circularly polarized light. Data have been converted from flight time to kinetic energy and grouped at intervals of 50 meV. The shape of the S 2p photoelectron spectrum is determined by three factors: the spin-orbit splitting of the S 2p hole, vibrational excitations in the residual ion, and molecular field splitting of the S $2p_{3/2}$ hole. The latter results from the breaking of the spherical symmetry of the p electrons by the axial molecular field, which removes the degeneracy of the states with different projections of orbital angular momentum along the molecular axis. . 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.1a) utilizing asymmetric Voigt functions to account for post-collisional effects. Previously determined values of the lifetime width (65 meV), vibrational period (279 meV), and molecular field splitting (145 meV) [19] were used in the fit. The areas of the peaks obtained from the fitting procedure were used to determine the spin polarization for the individual photoelectron lines as described below. Additionally, we performed a single channel analysis [9], 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.1a (full and empty circles respectively) and are in good agreement. The error bars of the spin polarization values in the figure include both statistical and systematic errors.

Spin-orbit, vibrational and molecular field splittings also determine the S-2p photoionization spectra of H_2S. We report in Fig. 1b the results we obtained at 240 eV photon energy, with the same notation as in Fig. 1a. The values of the vibrational splitting (about 300 meV), molecular field splitting (110 meV) and S 2p lifetime width (70 meV) from [17,18] were used in the fits of the spectra to extract peak areas. In the following discussion of the results we shall concentrate on transitions leading to the ground vibrational state of the ion, labeled as A_0, B_0 and C_0 in Fig. 1.

The angular distribution of photoelectrons with definite spin orientation can be expressed by five parameters, namely the total cross section σ, the anisotropy parameter β, and three parameters related to the spin polarization A, γ and η. We are adopting the notation used by Cherepkov [23, 24]. Different notations have been used by Huang [25] and Heinzmann [7]. In the geometry of our experiment, the spin polarization takes the simple form [24]:

$$P = \frac{\eta\, S_1 - (A + \gamma/2)\, S_3}{1 + \beta/4} \tag{1}$$

where S_1, S_3 are the Stokes parameters of the incident photons. In an unoriented molecule, the initial state is a linear combination of orbitals with different orbital angular momenta, and an infinite number of partial waves are allowed for the electrons in the continuum. In order to explore the effects of the molecular environment, we start by describing the process within a simple atomic model.
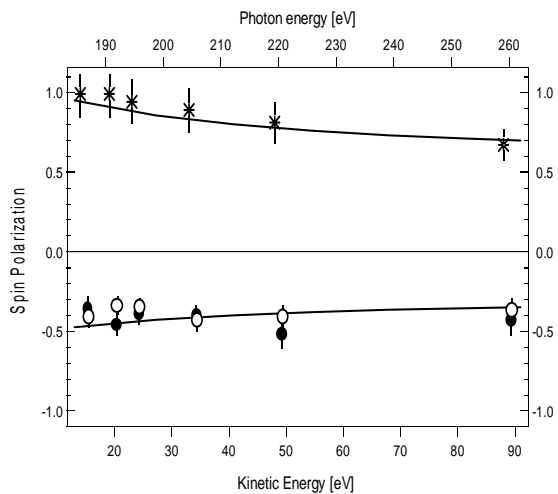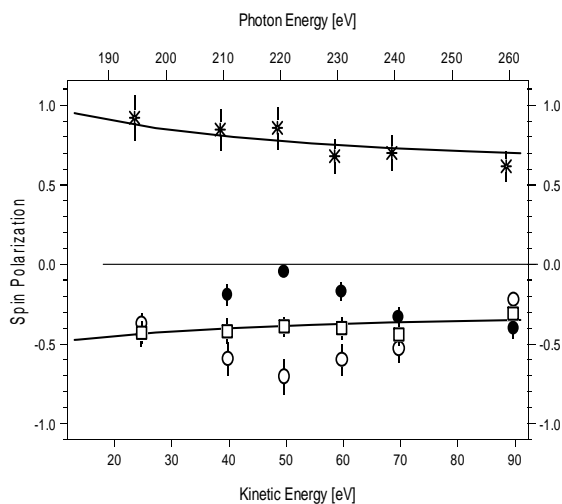
Figure 2. Spin polarization of the S 2p photoelectrons as a function of (circularly polarized) photon energy in OCS (a) and H_2S (b). Experimental points are for the ground vibrational state of the (*=A_0) S $2p_{1/2}$, and (• = B_0, ○ = C_0) molecular field split S $2p_{3/2}$. The spin polarization of the (□) sum of the S $2p_{3/2}$ lines is also reported for H_2S. Full lines are calculations for Ar-2p photoionization.

Using an atomic model to compare with our results is a valid approximation in this case because of the localized nature of the S 2p core orbitals. The photoionization cross section for the 2p levels of second row elements depend only weakly on the nuclear charge, therefore calculations for Ar can be used as an approximation. The spin polarization of the three S 2p lines as a function of the photon energy are compared with the Ar 2p photoionization calculations previously published by Cherepkov [23] in Fig. 2a and Fig. 2b for OCS and H_2S respectively.

In the case of S $2p_{1/2}$ photoionization, giving rise to line A_0, which is a single non-degenerate level and therefore can not be split by the molecular field, the spin polarization is correctly reproduced for both molecules by the atomic calculation. The situation is very different for the S $2p_{3/2}$ lines B_0 and C_0. The atomic model seems to correctly reproduce the spin polarization of the lines B_0 and C_0 in OCS, but not those of H_2S which deviate from one another over a wide energy range. However, if the unresolved (B_0+C_0) lines are considered (empty squares in Fig. 2b), then again the Ar calculations are able to reproduce the spin polarization of the lines in H_2S.

Interesting similarities can be observed when considering the values of the anisotropy coefficients of lines A_0, B_0 and C_0, as measured by Kukk et al. [19] in OCS. The anisotropy coefficient of the unresolved B_0+C_0 doublet is still correctly reproduced in the 195 - 300 eV photon energy range using the same calculation employed for the spin polarization of Ar. On the contrary, the difference in the anisotropy coefficients of lines B_0 and C_0 can not be explained by an atomic model and is instead attributed to the molecular environment. The anisotropy coefficients of line A_0 have not been published by Kukk et al., anyway no experimental evidence of any molecular effect has been reported [19]. Furthermore, there are no published values of anisotropy coefficients of lines A_0, B_0 and C_0 for H_2S. Thus, from the measured values of the spin polarization in H_2S, and the anisotropy coefficients and the spin-polarization in OCS, it appears that the effects of the molecular environment vanish when the experiment integrates over the different orientations of the 2p angular momentum, restoring the spherical symmetry. This behavior is coherent with the strong atomic character of the S-2p orbital in these molecules as well as the absence (or low oscillator strength) of shape resonances above the L_{23} sulfur edge [15,26].

On the contrary, the different molecular structure is clearly reflected in the spin polarization of the B_0 and C_0 lines. A difference in the two molecules is expected on the basis of simple geometrical considerations. Because of the different geometry, the ligand field split levels are characterized by different quantum numbers. As a result, transitions to the states B_0 and C_0 obey different selection rules, which leads to a difference in the behavior of all parameters.

In summary, spin-resolved electron spectroscopy and circularly polarized light were used to measure the spin polarization of S 2p electrons from OCS and H_2S for the first time. Differences in the electron spin polarization for the molecular field split S $2p_{3/2}$ lines of H_2S but not in OCS highlight the sensitivity of this differential technique to the molecular field.

ACKNOWLEDGMENTS

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