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Observation of an energy shift in the S $2p_{3/2}$–S $2p_{1/2}$ spin-orbit splitting between x-ray photoelectron and Auger-electron spectra for the H_2S molecule

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The S $2p_{3/2}$–S $2p_{1/2}$ spin-orbit splitting is measured for the free H_2S molecule using both high-resolution x-ray photoelectron spectroscopy (XPS) and high-resolution photon-excited Auger-electron spectroscopy. It is found that the spin-orbit splitting differs in the two experiments by as much as 50 meV. In contrast, the Ar $2p_{3/2}$–Ar $2p_{1/2}$ spin-orbit splitting is practically the same when comparing Auger and XPS data. The origin of the shift for H_2S is discussed with respect to the molecular-field splitting and state interference effects.

The spin-orbit splitting of core levels has been studied using both x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) for almost thirty years.[1] Previously, it was assumed that the spin-orbit splitting of a sublevel remains the same, disregarding the experimental method used to measure it. In fact, spin-orbit splittings obtained from XPS have often been used in the assignment of complex Auger-electron spectra of atoms[2] and of molecules.[3]

For atoms, where high-resolution XPS and high-resolution electron-beam-excited AES studies, as well x-ray emission studies from free molecules, have been available for a long time, any differences in the spin-orbit splitting observed by different techniques have not been reported. In the case of molecules, only a few high-resolution AES studies of core-valence-valence (*CVV*) spectra have been reported. In many cases, e.g., for the hydrogen halides, the existence of overlapping bands also hampers the precise determination of the spin-orbit splitting of the initial core-hole state. From the available data one can conclude that a possible shift between the AES and XPS spin-orbit splittings is small.

The H_2S molecule, however, is very well suited to observe a shift in the S $2p$ spin-orbit splitting between the AES and the XPS. Ionization in the outermost lone pair orbital yields a $1b_1^{-1}\,{}^1B_2$ state that is well isolated in energy from the rest of the singly ionized valence states. This implies that the lowest $1b_1^{-2}\,{}^1A_1$ doubly ionized state is also well separated from the rest of the doubly ionized states, and in the Auger-electron spectrum two well-separated bands corresponding to the $L_{2,3} \rightarrow 1b_1^{-2}\,{}^1A_1$ transitions have been identified.[4]

In order to detect a very small shift between the AES and XPS it is important to avoid possible effects due to drifts, possible charging in the spectrometer, and postcollision interaction in the AES. The experiment should therefore be performed using high-energy monochromatic x rays for the excitation. We have performed the experiments using a photoelectron spectrometer in Uppsala that is provided with a quartz-crystal monochromator for Al $K\alpha$ x rays ($h\nu = 1487$ eV). First, a high-resolution XPS of the spin-orbit-split S $2p$ core photoelectron lines in free H_2S gas was recorded. Subsequently, using the same pressure in the sample compartment and the same monochromatic photon beam as an excitation source, an AES was obtained for the $L_{2,3} \rightarrow 1b_1^{-2}\,{}^1A_1$ bands in free H_2S gas. The sample gas was obtained commercially, with 99.99% purity. The pressure in the gas cell was kept constant at a few mTorr. The results are given in Fig. 1.

In the upper part of Fig. 1, the XPS (excited with monochromatized x rays) of the S $2p_{3/2}$ and S $2p_{1/2}$ photoelectron lines is displayed. The photon-excited AES of the $L_{2,3} \rightarrow 1b_1^{-2}\,{}^1A_1$ bands is displayed below. As can be seen, the vibrational progressions of the bands are resolved in the Auger spectrum. The component peaks in the bands reflect vibrational energy levels in the doubly ionized final state. The spacings agree well with an earlier recording of the AES using electron-beam excitation.[4] The spectra are aligned in such a way that the $v=0$ vibrational component in the $L_3 \rightarrow 1b_1^{-2}\,{}^1A_1$ band coincides with the peak maximum of the S $2p_{3/2}$ photoelectron line. As can be seen, there is a shift of 50 meV when we compare the distance between the $v=0$ components in the $L_3 \rightarrow 1b_2^{-2}\,{}^1A_1$ and $L_2 \rightarrow 1b_1^{-2}\,{}^1A_1$ bands with the distance between the S $2p_{3/2}$ and S $2p_{1/2}$ photoelectron lines. In order to check if this shift could be due to the changing slope of the background observed in the H_2S spectrum, we have made a subtraction of two different slopes for the background in each band in the AES. The result is shown in the lowest part of Fig. 1. No appreciable change in the observed shift of 50 meV can be seen, although the largest possible difference in slope was assumed.

For comparison we have performed the same experiment for Ar. The Ar $2p_{3/2}$ and Ar $2p_{1/2}$ photoelectron lines in atomic argon gas were recorded on the same instrument, and subsequently an AES of the $L_{2,3} \rightarrow 3p^{-2}\,{}^1D_2$ lines was recorded, keeping the conditions in the sample cell constant. The result is shown in Fig. 2. As can be seen, only a very small shift on the order of 5 meV can be observed in this case. The result is also compatible with no shift at all.

Having established the experimental shift between the AES and XPS values for the spin-orbit splitting of the S $2p$ sublevel in H_2S, one might discuss a theoretical explanation. Since the shift exists for the H_2S molecule but seems to be negligible for the Ar atom, one possible explanation would be given by a *molecular-field effect.* The relativistic level scheme, including the molecular-field

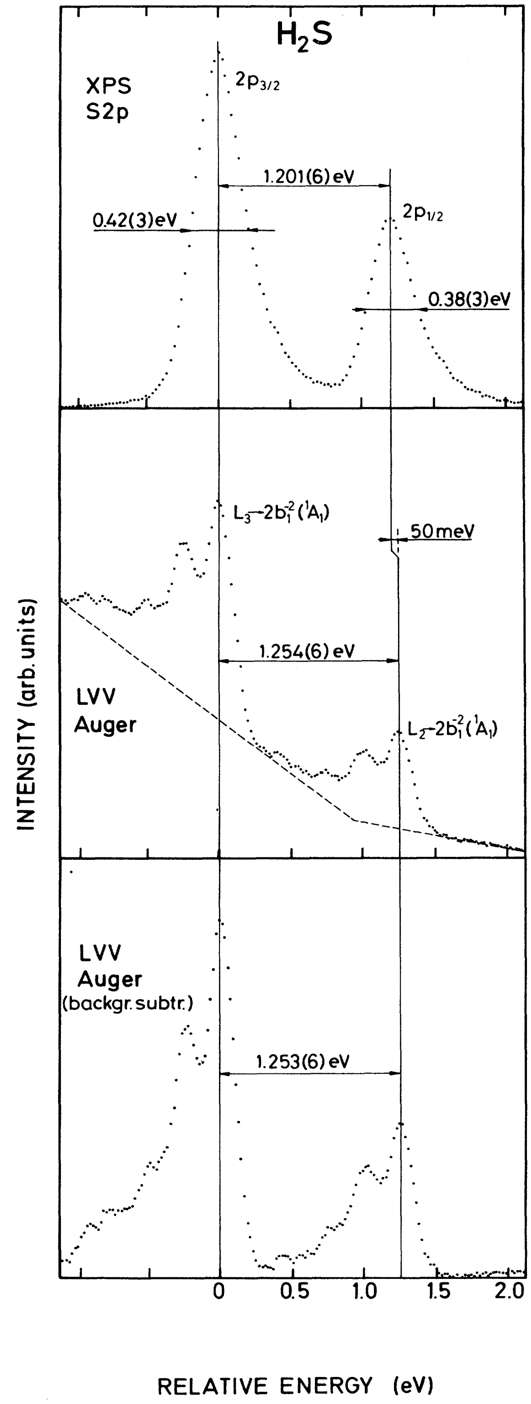

FIG. 1. Top: The monochromatized XPS of the S $2p_{3/2}$ and S $2p_{1/2}$ photoelectron lines in the free H_2S molecule. Middle: A detail of the *LVV* Auger-electron spectrum showing the $L_{2,3} \rightarrow 1b_1^{-2}\,{}^1A_1$ transitions. The spectrum was excited by monochromatized Al $K\alpha$ x rays. The bands show vibrational fine structure corresponding to excitations of the ν_1 mode. Notice that the spin-orbit splitting differs from the uppermost spectrum by 50 meV. Bottom: A background, as indicated by the dotted lines in the middle spectrum, has been subtracted from the Auger-electron spectrum. Notice that the spin-orbit splitting is affected very little by this subtraction.

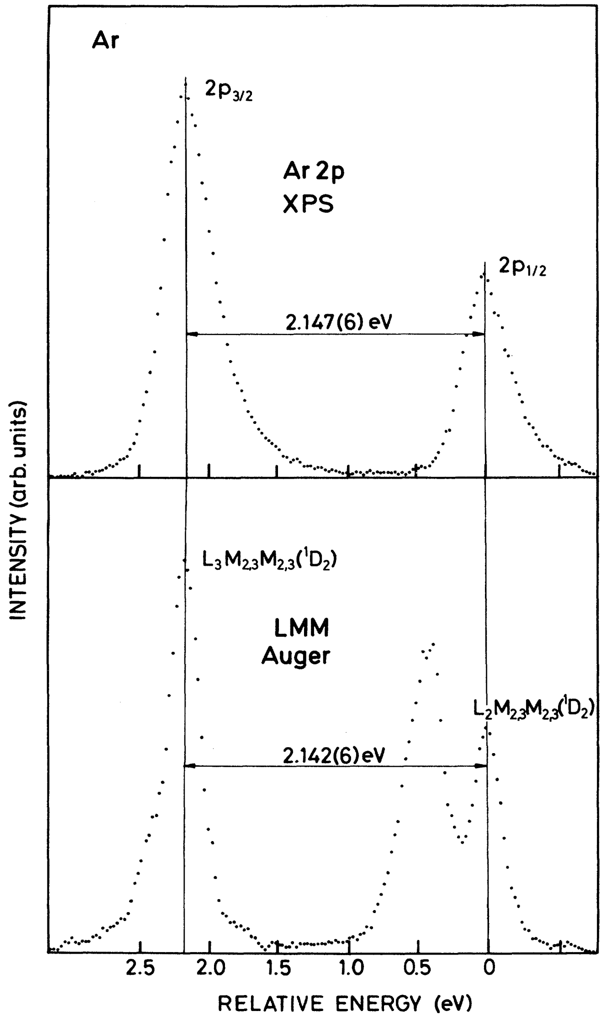

FIG. 2. Top: The monochromatized XPS of the Ar $2p_{3/2}$ and Ar $2p_{1/2}$ photoelectron lines in the argon atom. Bottom: A detail of the $L_{2,3}M_{2,3}M_{2,3}$ Auger-electron spectrum of argon showing transitions to the ${}^1D_2$ final state.

splitting of the core levels, is given in Fig. 3. The atomic S $2p_{1/2}$ core level is correlated to a level of $E_{1/2}$ symmetry and the S $2p_{3/2}$ core level is split into two levels of $E_{1/2}$ symmetry in the presence of the molecular field. Thus, the core orbitals are split into molecular orbitals. This effect is small and the splitting of the two levels that are correlated to the S $2p_{3/2}$ core level has been calculated by Cesar and Ågren[5] to be ca. 80 meV in the case of H_2S. The small difference in linewidth (full width at half maximum) of the S $2p_{1/2}$ core photoelectron lines in the uppermost part of Fig. 2 indicates that this calculated splitting has the correct order of magnitude. Molecular-field splittings of core levels have been observed in the Xe 4*d* photoelectron spectra of the xenon fluorides.[6] Since the Auger transitions involve these molecular-field-split core levels, there could be a shift between the XPS-observed and the Auger-observed spin-orbit splitting, as indicated in Fig. 3. However, in order to explain a shift of 50 meV

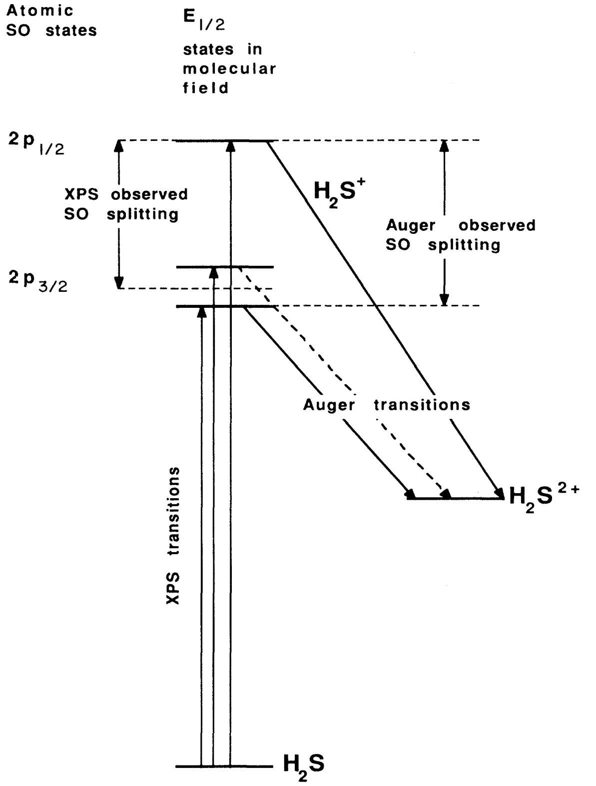

FIG. 3. A schematic illustration of the energy levels and transitions involved in the Auger and XPS experiments on H_2S.

in the present case one has to assume that the Auger transition from one of the $E_{1/2}$ states that are correlated to the S $2p_{3/2}$ core level is more or less quenched (see Fig. 3). This could be explained by a very large difference in angular dependence of the Auger-electron emission or a strong propensity rule.

Another possible explanation is offered by a *state interference*[5,7] in the AES. This explanation has been put forth by Cesar and Ågren.[5] The phenomenon of vibrational interference has been known for a long time in AES. Due to the finite lifetime of the initial core-hole states in the Auger-electron transition interference phenomena can be observed in the vibrational progressions in AES spectra. Extensive calculations and experimental investigations have been reported on this phenomenon.[4,8,9] However, in a recent theoretical investigation by Cesar and Ågren, the interference phenomenon in AES is extended to interference between separate electronic states. This results in a shift of the lines in the AES and also in a change in the vibrational progressions. In addition, the shape of the vibrational progression is affected with an apparent broadening of the $v=1$ state in the $L_2 \rightarrow 1b_2^{-2}\ ^1A_1$ band (see Fig. 1). In a pilot study, a shift of about 15 meV is found for H_2S by Cesar and Ågren. This does not explain the present shift, but it is of the correct order of magnitude. The state interference depends strongly on the distance between the spin-orbit split levels and therefore only a very small, unobservable, effect of about 1 meV is calculated in the case of argon,[5] as also observed in Fig. 2.

In conclusion we have found a 50-meV shift between the XPS and AES spin-orbit splitting of the S $2p$ sublevels in H_2S. In the case of Ar, the corresponding experimental shift is negligible. An explanation of the shift in terms of molecular-field splitting and state interference has been discussed. A difference of this order of magnitude between the XPS and AES values for the spin-orbit splitting of core levels will have consequences for the assignment of complex partly vibrationally resolved Auger-electron spectra of molecules, since the vibrational splitting in the bands is often of the same order of magnitude as the shift indicated in this paper. In the case of overlapping vibrational bands, this might shift the assignment of states with at least one vibrational quantum number.

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