Spin-Resolved Electron Spectroscopy of Carbonyl Sulphide

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Introduction

Energy- and angle-resolved photoelectron spectroscopy has been widley used to investigate the structures of atoms, molecules and solid matter as well as the dynamics of photoemission processes. Though, the information that can be obtained with this technique is often incomplete, even when the most simple systems are investigated [1]. Quantum mechanically the photoemission process is described in terms of the wavefunctions for the initial and final states and the Coulomb or dipole transition matrix elements. The determination of all the matrix elements of one physical process is the aim of the so-called complete (or perfect) experiment [2,3]. This definition is clearly model dependent [3].

Different techniques have been introduced to tempt a complete photoionization experiment. Some make use of coincidence between electron and electron [4,5,6] , or electron and fluorescent photon [7,8]. Other take advantage of the properties of polarized atoms [9,10]. The possibility of using spin-resolved electron spectroscopy has been theoretically described by Huang for photoionization [11] and Auger decay [12]. Since then, this technique has been widley used in experiments, see [13,14,15] for example.

Despite the substantial advancements of complete experiment in atomic systems, there have been only very few studies of inner-shell photoionization of molecules beyond intensities and angular distributions [16]. A molecular complete experiment is much more difficult than the determination of matrix elements for atoms, because of the large number of possible outgoing partial waves. Additionally, the molecular environment can influence the core orbitals of the atoms in the molecule. This can lead to the splitting of energy levels due to vibrations, lower than spherical symmetry of the system, etc.

In this work we report on spin polarization measurements of the sulphur 2p photoionization of carbonyl sulphide molecule. Recently, Kukk et al. [17] investigated the sulphur 2p photoionization of OCS molecules by high-resolution, angle-resolved electron spectroscopy. They found that the angular distribution parameter β of the two molecular-field-split components of the sulphur $2p_{3/2}$ line differs significantly at a broad range of photon energies above the 2p threshold. Since the origin of this difference cannot be traced solely by angle-resolved spectroscopy, we measured the spin polarization of the S 2p lines. The analysis of the acquired data is still in progress; some preliminary results will be presented here.

Experiment

The experiment was performed at Beamline 4 at Advanced Light Source (ALS) storage ring. We used circularly and linearly polarized light from the new elliptical polarization undulator (EPU) [18]. The sulphur 2p photoionization was measured for 6 different photon energies, namely 185, 191, 195, 205, 220 and 260 eV. With the chosen setting of the parameters of the beamline, a photon flux of approximately 10^{14} photons/sec and a resolving power $E/\Delta E$

about 1000 was provided. The degree of both circular and linear polarization for all the photon energies was 100% within the experimental errors. The photon beam crossed perpendicularly an OCS effusive gas jet. The kinetic energy of the photoemitted electrons was measured with two Time Of Flight (TOF) spectrometers. Combined with one of the TOF, a spherical Mott polarimeter of the Rice type, operated at 45KV, performed the spin polarization analysis. The instrumental asymmetry of the Mott polarimeter was accounted by combining measurements with positive and negative light helicity [19], changing polarization approximately every 10 min. Due to the substantial loss of signal intensity during the Mott scattering, our experiment considerably benefited from the TOF technique's inherent capability of simultaneous acquisition of all lines in the spectrum.

Results

The sulphur 2p-photoionization spectrum of OCS, as measured with 205 eV circularly polarized photon, is reported in the lower panel of Fig.1 (sum of the spectra with different spin polarization).

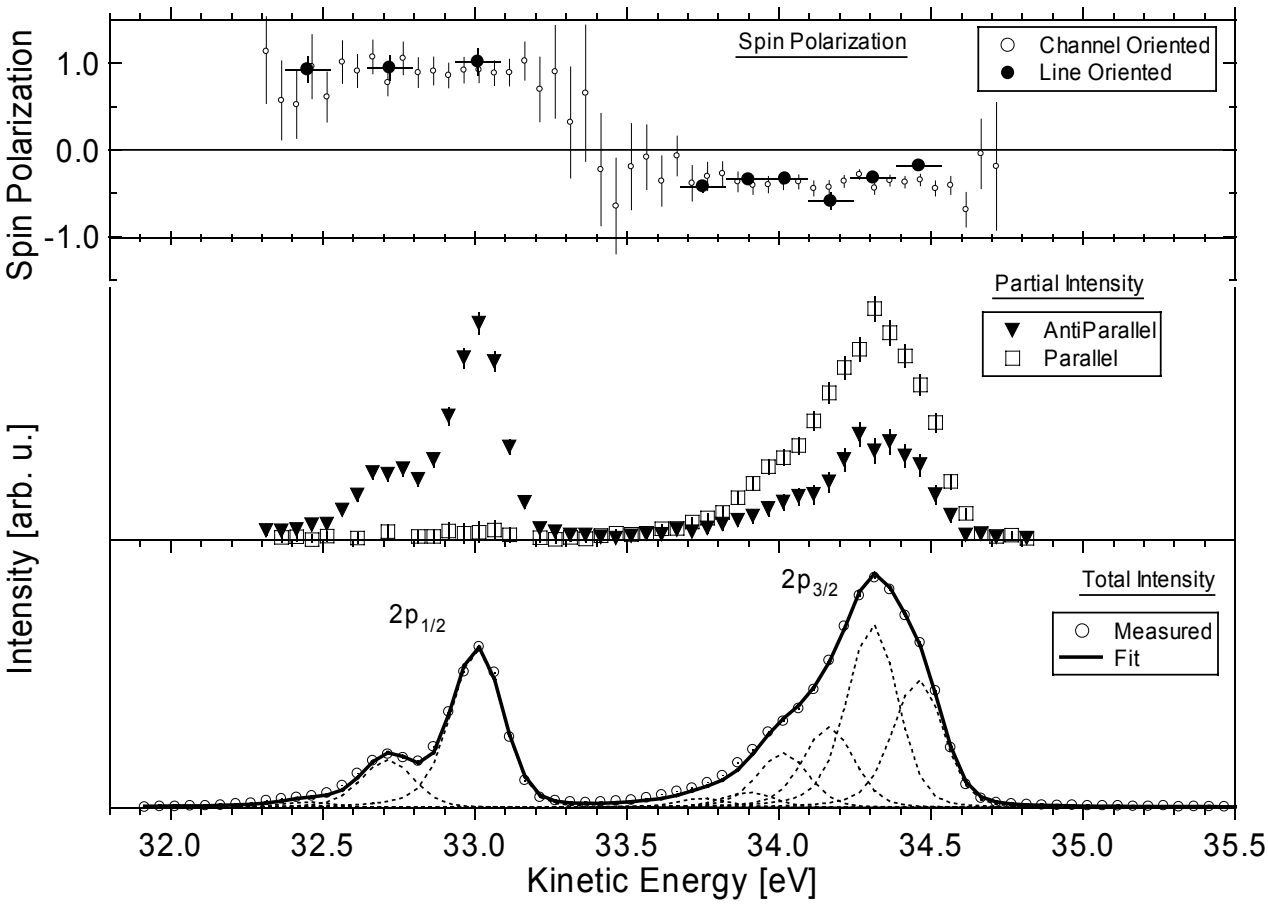

Fig.1: Sulphur 2p-photoionization spectrum of OCS molecule, as measured with 205 eV circularly-polarized photon. (bottom) Total Intensity, the continuous curves are the result of a least-squares fitting procedure. (middle) Spin-Separated Intensity. (up) Spin Polarization. See text for details.

As described in details by Kukk et al. [17] the spectrum can be completely understood in terms of spin-orbit, vibrational and molecular field split. Within the resolution of our experiment, the two spin-orbit components are easily resolved; in order to solve the vibrational and molecular field splitting, we applied a least-squares fitting procedure, using asymmetric Voight profiles.

We applied two different techniques to extract the spin polarization from our data. The areas of

the different peaks, as returned by the fitting procedure, were used to obtain the polarization of the different components of the spectrum. This technique has been referred as a "Line-Oriented" analysis [15]. Alternatively, we applied a "Channel-Oriented" analysis, where the spin polarization has been calculated for each point of the photoemission spectra. The results of the two methods are reported in the top panel of Fig.1, showing good agreement. Using the values obtained with the latter analysis, we deduced the spin separated spectra [14], which correspond to the spectra that a "perfect" Mott polarimeter (i.e. with no instrumental asymmetry, and Sherman function equal to1) would measure in case of completely circularly polarized light. These spectra are reported in the middle panel of Fig.1.

Both the spin-orbit components show strong spin-polarization. Conversely, the vibrational and the molecular splitting show minor effect on the spin polarization at this photon energy. The polarization of the three states of the $2p_{1/2}$ peak is $+0.95 \pm 0.15$, i.e. these states are almost completely spin-polarized. This is reflected in the vanishing of the $2p_{1/2}$ peak in the spin separated spectrum associated with electron spin parallel to the photon spin. The states associated with the $2p_{3/2}$ peak show slightly different polarization values out of the error bars. The different sign in the spin polarization of the two spin-orbit states qualitatively agree with the fact that the polarization of the 2p photoionization line should vanish when the spin-orbit structure is not resolved.

Conclusion

Whereas the most of the analysis has to be done, the few preliminary results seem to be encouraging. The investigated transitions show strong spin polarization, which makes them very suited for spin resolved technique. The agreement of the results obtained by using different analysis techniques confirms the consistency of the investigation.

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