

Cite this: DOI: 00.0000/xxxxxxxxxx

Electronic Supplementary Information (ESI)

Orientalional anisotropy due to molecular field splitting in sulfur 2p photoemission from CS₂ and SF₆ – theoretical treatment and application to photoelectron recoil.

Edwin Kukk,^{*a} Johannes Niskanen,^{*a} Oksana Travnikova,^b Marta Berholts,^c Kuno Kooser,^c Dawei Peng,^b Iyas Ismail,^b Maria Novella Piancastelli,^b Ralph Püttner,^d Uwe Hergerhahn^e and Marc Simon^b

Introduction

We treat the combined effect of spin-orbit interaction and molecular field in the product basis of orbital angular momentum projection m and spin angular momentum projection μ , which constitutes an atomic-problem-in-a-molecule approximation for photoemission. Because the molecular field mixes S 2p orbital states in the molecular frame of reference, we derive the splitting and the formed eigenstates i

$$\psi_i^{\text{mol}} = \sum_{m,\mu} c_{m\mu}^{(i)} \underbrace{Y_1^m(\hat{\mathbf{r}}_{\text{mol}}) 2p(r)}_{=: \phi_m(\mathbf{r}_{\text{mol}})} \chi_{\mu}^{\text{mol}} \quad (1)$$

in this coordinate system, indicated by notion mol. We use $\hat{\mathbf{r}} = \mathbf{r}/r$ and $r = |\mathbf{r}|$ for brevity. Next, using atomic units and following Schmidt¹, we derive the orientation-dependent differential photoemission cross section for solid angle element $d\Omega$ in the direction of the wave vector of the detected electron \mathbf{k}

$$\frac{d\sigma_i}{d\Omega}(R) = 4\pi^2 \alpha k \omega \sum_{\mu} \left| \langle \psi_{\mathbf{k}\mu}^{(-)} | \mathbf{e} \cdot \mathbf{r} | \psi_i^{\text{mol}} \rangle \right|^2, \quad (2)$$

where ω is the photon energy and α the fine structure constant. In the experiment, the polarization \mathbf{e} of the X-ray beam is parallel to \mathbf{k} . We use this direction for the z-axis of the laboratory frame of reference and transform the states ψ_i^{mol} to this coordinate system for calculations. In equation (2) spin projection μ of the detected electron is summed over for spin-insensitive detection. Differential cross section (2) depends on the molecular orientation, characterized by rotation R , which transforms the laboratory frame of reference into the molecular one. In model using the atomic basis, the obtained coefficients $c_{m\mu}^{(i)}$ suffice to define the molecular-orientation-dependence of the cross section for state i together with the Wigner matrix $D^{(1)}(R)$.

^a Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland.

^b Sorbonne Université, CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005 Paris, France.

^c Institute of Physics, University of Tartu, W. Ostwaldi 1, EE-50411 Tartu, Estonia

^d Fachbereich Physik, Freie Universität Berlin, D-14195 Berlin, Germany.

^e Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany.

* To whom correspondence should be addressed: johannes.niskanen@utu.fi, edwin.kukk@utu.fi

Eigenstates in the molecular frame

Whereas the spin-orbit operator for a 2p electron is the same in all frames of reference

$$\hat{H}_{\text{SO}} = \xi \left[\sum_{m,\mu} m\mu a_{m\mu}^{\dagger} a_{m\mu} + \frac{1}{\sqrt{2}} \sum_{m=-1}^0 (a_{m+1,-1/2}^{\dagger} a_{m,1/2} + a_{m,1/2}^{\dagger} a_{m+1,-1/2}) \right],$$

the molecular field operator $\hat{H}_{\text{MF}}^{\text{mol}}$ depends on the system and its frame of reference given by R . For S 2p of the CS₂ molecule we use

$$\hat{H}_{\text{MF}}^{\text{mol}} = \gamma \sum_{m,\mu} (-1)^{|m|+1} a_{m\mu}^{\dagger} a_{m\mu}.$$

In the above, a^{\dagger} and a are the creation and annihilation operators in the *molecular frame*. Parameters ξ and γ are empirical coefficients for the interaction strength. The matrix presentation of these operators for CS₂ read in the (m,μ) basis, ordered as $(-1,-1/2)$, $(-1,+1/2)$, $(0,-1/2)$, $(0,+1/2)$, $(1,-1/2)$, $(1,+1/2)$

$$\mathbf{H}_{\text{SO}}^{\text{mol}} = \xi \begin{bmatrix} 1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & 1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 \end{bmatrix}$$

and

$$\mathbf{H}_{\text{MF}}^{\text{mol}} = \gamma \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

For $\gamma > 0$, the latter operator shifts the $m = \pm 1$ components up in energy by γ and the $m = 0$ down in energy by γ .

Finding eigenvectors and eigenvalues of the effective interaction Hamiltonian matrix $\mathbf{H}^{\text{mol}} = \mathbf{H}_{\text{SO}}^{\text{mol}} + \mathbf{H}_{\text{MF}}^{\text{mol}}$ results in eigenenergies and respective eigenstates (coefficients $c_{m\mu}^{(i)}$) in the molecular frame. By fitting the spin-orbit splitting for SF₆ with $\gamma = 0$, we obtained $\xi = 0.806$ eV, which we consider a constant in terms of chemical environment. For CS₂ further fitting with this ξ value fixed resulted $\gamma = 0.102$ eV.

We checked the results of this semiempirical method with those of Kosugi and co-corkers² for the OCS molecule with the $2p_{3/2}$

splitting of 0.145 eV. We obtained $\gamma \approx 0.117$ eV by fitting, and evaluated the square of the respective nonzero expansion coefficient $c_{0\mu}$. These σ -character values of 0.426 (states labeled $2p_{1/2, \pm 1/2}$), 0.574 (states labeled $2p_{3/2, \pm 1/2}$) and 0 (states labeled $2p_{3/2, \pm 3/2}$) match well with those of Kosugi *et al.* who obtained 0.433, 0.567 and 0, respectively². For the pure spin-orbit-coupled case these numbers are $1/3$, $2/3$ and 0, respectively.

Cross section as a function of molecular orientation

An orbital or a spin state in the molecular frame can be presented as a linear combination of states in the laboratory frame using the appropriate Wigner $D^{(j)}$ matrix for rotation R , which transforms the laboratory frame basis vectors to those of the molecular frame¹. In the direct product basis this transformation follows

$$\phi_m(\mathbf{r}_{\text{mol}})\chi_{\mu}^{\text{mol}} = \hat{D}^{(1)}(R)\phi_m(\mathbf{r})\hat{D}^{(1/2)}(R)\chi_{\mu}.$$

In particular, for a spin state

$$\chi_{\mu}^{\text{mol}} = \sum_{\mu'} \chi_{\mu'} D_{\mu'\mu}^{(1/2)}(R),$$

and for the spherical harmonics of the p orbitals

$$Y_1^m(\hat{\mathbf{r}}_{\text{mol}}) = \sum_{m'} Y_1^{m'}(\hat{\mathbf{r}}) D_{m'm}^{(1)}(R).$$

We evaluate the transition matrix elements in the laboratory frame, in which the polarization vector is oriented along the z -axis. This choice yields a convenient form $\mathbf{e} \cdot \mathbf{r} = \hat{\mathbf{z}} \cdot \mathbf{r} = r_z = z = \sqrt{4\pi/3} Y_1^0(\hat{\mathbf{r}})r$. In this particular experiment, electron detection takes also place in the direction of the z -axis to yield the wavefunction for the emitted electron¹

$$\psi_{\mathbf{k}, \mu}^{(-)}(\mathbf{r}) = \frac{1}{\sqrt{k}} \sum_{l, q} i^l e^{-i\Delta_l} Y_l^q(\hat{\mathbf{k}}) Y_l^q(\hat{\mathbf{r}}) R_{\varepsilon l}(r) \chi_{\mu},$$

where $\mathbf{k} = k\hat{\mathbf{z}}$ ($k = |\mathbf{k}|$) is the wave vector with kinetic energy $\varepsilon = k^2/2$, and the phase shift Δ_l originates from the shape of the potential.

The transition operator and electron detection in the experiment are spin-independent which makes each transition matrix element decompose to a spatial part and a spin part

$$\begin{aligned} \langle \psi_{\mathbf{k}, \mu}^{(-)} | z \otimes \mathbb{1} | \psi_i^{\text{mol}} \rangle &= \sum_{m, \mu_1} c_{m\mu_1}^{(i)} \underbrace{\langle \psi_{\mathbf{k}, \mu}^{(-)} | z | \phi_m^{\text{mol}} \rangle}_{=: T_m} \langle \chi_{\mu} | \mathbb{1} | \chi_{\mu_1}^{\text{mol}} \rangle \\ &= \sum_m T_m \sum_{\mu_2, \mu_1} c_{m\mu_1}^{(i)} D_{\mu_1 \mu_2}^{(1/2)} \langle \chi_{\mu} | \chi_{\mu_2} \rangle, \end{aligned}$$

where T_m is used for the spatial part. We drop χ in the notation for laboratory-frame spin ket and carry out the summation over the two possible spin projections μ in (2) to describe the cross section

in a spin-insensitive experiment. With the prefactor $C_1 = 4\pi^2 \alpha k \omega$

$$\begin{aligned} \frac{d\sigma_i}{d\Omega}(R) &= C_1 \sum_{\mu} \left| \langle \psi_{\mathbf{k}, \mu}^{(-)} | z \otimes \mathbb{1} | \psi_i^{\text{mol}} \rangle \right|^2 \\ &= C_1 \sum_{\mu} \left| \sum_m T_m \sum_{\mu_1, \mu_2} c_{m\mu_1}^{(i)} D_{\mu_2 \mu_1}^{(1/2)}(R) \langle \mu | \mu_2 \rangle \right|^2 \\ &= C_1 \sum_{\mu} \left(\sum_m T_m \sum_{\mu_2, \mu_1} c_{m\mu_1}^{(i)} D_{\mu_2 \mu_1}^{(1/2)}(R) \langle \mu | \mu_2 \rangle \right)^* \\ &\quad \times \left(\sum_{m'} T_{m'} \sum_{\mu'_2, \mu'_1} c_{m'\mu'_1}^{(i)} D_{\mu'_2 \mu'_1}^{(1/2)}(R) \langle \mu | \mu'_2 \rangle \right) \\ &= C_1 \sum_{m, m'} T_m^* T_{m'} \sum_{\mu_1, \mu'_1} c_{m\mu_1}^{(i)*} c_{m'\mu'_1}^{(i)} \sum_{\mu_2, \mu'_2} D_{\mu_2 \mu_1}^{(1/2)*}(R) D_{\mu'_2 \mu'_1}^{(1/2)}(R) \\ &\quad \times \underbrace{\sum_{\mu} \langle \mu_2 | \mu \rangle \langle \mu | \mu'_2 \rangle}_{=: \delta_{\mu_2 \mu'_2}} \\ &= C_1 \sum_{m, m'} T_m^* T_{m'} \sum_{\mu_1, \mu'_1} c_{m\mu_1}^{(i)*} c_{m'\mu'_1}^{(i)} \underbrace{\sum_{\mu_2} D_{\mu_1 \mu_2}^{(1/2)}(R^{-1}) D_{\mu_2 \mu'_1}^{(1/2)}(R)}_{=: \delta_{\mu_1 \mu'_1}} \\ &= C_1 \sum_{\mu_1} \sum_{m, m'} T_m^* T_{m'} c_{m\mu_1}^{(i)*} c_{m'\mu_1}^{(i)} \\ &= C_1 \sum_{\mu_1} \left(\sum_m T_m^* c_{m\mu_1}^{(i)*} \right) \left(\sum_{m'} T_{m'} c_{m'\mu_1}^{(i)} \right) \\ &= C_1 \sum_{\mu} \left| \sum_m T_m c_{m\mu}^{(i)} \right|^2. \end{aligned}$$

Previous considerations yield spatial transition matrix element

$$\begin{aligned} T_m &= \langle \psi_{\mathbf{k}, \mu}^{(-)} | z | \phi_m^{\text{mol}} \rangle \\ &= \sqrt{\frac{4\pi}{3k}} \sum_{l, q, m'} i^{-l} e^{i\Delta_l} \int R_{\varepsilon, l}^*(r) 2p(r) r^3 dr \\ &\quad \times \underbrace{Y_l^q(\hat{\mathbf{z}}) \int Y_l^q(\hat{\mathbf{r}}) Y_1^0(\hat{\mathbf{r}}) Y_1^m(\hat{\mathbf{r}}) d\hat{\mathbf{r}}}_{=: G_{qm}^l} \\ &\quad \times D_{m'm}^{(1)}(R). \end{aligned}$$

In this equation it is necessary that $m' = q$ and $l = 0, 2$ for the Gaunt integral G_{qm}^l to be nonzero. Moreover, only $q = 0$ gives a nonzero $Y_l^q(\hat{\mathbf{z}})$. Thus

$$T_m = \frac{D_{0m}^{(1)}(R)}{\sqrt{k}} \underbrace{\sum_{l=0,2} (2l+1) \sqrt{\frac{3}{4\pi}} \begin{pmatrix} 1 & 1 & l \\ 0 & 0 & 0 \end{pmatrix}^2}_{=: C_2} i^{-l} e^{i\Delta_l} \int R_{\varepsilon, l}^*(r) 2p(r) r^3 dr,$$

where the dependence on rotation R is contained by the single Wigner matrix element $D_{0m}^{(1)}(R)$. The summation over l gives an

energy-dependent factor, marked here C_2 , that accounts for both s-waves and d-waves but is independent of R , m , μ and i . We note that the initial state splitting is negligible compared to ε , and therefore it is reasonable to use the same partial-wave radial functions for each transition.

Based on these calculations, the R -dependent differential cross section in this particular experimental geometry reads

$$\frac{d\sigma_i}{d\Omega}(R) = 4\pi^2\alpha\omega \sum_{\mu} \left| \sum_m C_2 D_{0m}^{(1)}(R) c_{m\mu}^{(i)} \right|^2. \quad (3)$$

Furthermore, owing to the aforementioned independencies of C_2 , the probability of electron detection from one-electron state i of a molecule oriented by R is proportional to

$$\sigma_i^{\text{rel}}(R) = \sum_{\mu} \left| \sum_m D_{0m}^{(1)}(R) c_{m\mu}^{(i)} \right|^2. \quad (4)$$

This relative orientational function measures the projection of the initial state i on the $Y_1^0(\hat{\mathbf{r}})$ in laboratory frame of reference.

Notes and references

- 1 V. Schmidt, *Electron Spectrometry of Atoms using Synchrotron Radiation*, Cambridge University Press, Cambridge, UK, 1997.
- 2 N. Kosugi and T. Ishida, *Chemical Physics Letters*, 2000, **329**, 138–144.