

# Decay and dissociation of core-excited OCS studied by X-ray scattering

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## Introduction

The rapid advancement in synchrotron radiation instrumentation in the last few years has led to much progress in the field of molecular core-level spectroscopies. The energy selectivity, which is obtained using monochromatic synchrotron radiation, allows resonant excitation of different types of molecular states. In particular, core excitation of small molecules with repulsive intermediate states has attracted attention. In decay spectra, the dissociation is manifested by the simultaneous presence of molecular and atomic contributions. The core-excited molecule may fragment before de excitation (dissociation channel prior), leading to atomic (or molecular radical) decay lines, or the de-excitation is followed by dissociation (de-excitation channel prior), which leads to broad molecular features. The time for dissociation and the lifetime of the core hole have pronounced effects on line positions, line widths, transition rates, and vibrational fine structures. A fast dissociation results in sharp atomic lines governed by the different dissociation channels involved, while slower dissociation results in broad molecular features. If both molecular and atomic features are observed with similar intensities, the dissociation and the core-hole decay processes occur on the same time scale, i.e. typically in the  $10^{-14}$  s range. The dissociative core-excitation processes have until now been studied in the non radiative deexcitation channel, while no results for the radiative channel has so far been presented. The radiative channel provides new insights owing to the dipole selectivity of the process, and the implementation of local selection rules [1, 2]. This provides a simple way to characterize the dissociated fragments. The lack of experimental data is due to the low fluorescence yields and instrument efficiencies associated with soft X-ray emission (SXE) in the sub-keV energy region which makes the measurements more demanding and intense synchrotron radiation (SR) sources are therefore a prerequisite.

In this work carbonyl sulfide (OCS) has been studied [3]. The OCS molecule has 30 electrons and a linear geometry in the ground state. The corresponding electronic configuration is  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 6\sigma^2 7\sigma^2 8\sigma^2 2\pi^4 9\sigma^2 3\pi^4$ . The  $1\sigma$ ,  $2\sigma$ ,  $3\sigma$ , and  $4\sigma$  orbitals correspond to the S  $1s$ , O  $1s$ , C  $1s$ , and S  $2s$  core levels, respectively, whereas the spin-orbit and molecular-field split S  $2p$  levels are composed of the  $5\sigma$  and  $1\pi$  molecular orbitals. The remaining orbitals are associated with valence levels of mixed atomic character. The OCS molecule belongs to the  $C_{\infty v}$  point group and it has three vibrational modes,  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ . These modes can be characterized as being due to C-S stretching, O-C-S bending, and C-O stretching, respectively. Bending of the molecule lowers the symmetry to the  $C_s$  group. We present high-resolution resonant and nonresonant SXE spectra of carbonyl sulfide near the sulfur  $L_{2,3}$  absorption thresholds to demonstrate a first case of fragmentation in the X-ray scattering process [4]. Recently, it has been discussed whether the lifetime of the sulfur  $L_{2,3} \rightarrow \pi^*$  core-excited states in OCS is long enough to allow a dissociation process to occur before the decay [5, 6].

## Experiment

The experiments were performed at beamline 7.0 at the *Advanced Light Source*, Lawrence Berkeley National Laboratory. The beamline comprises a 98-pole, 5-cm period undulator and a spherical-grating monochromator [7] covering the spectral energy range between 60-1300 eV. The SXE spectra were recorded using a high-resolution grazing-incidence SXE spectrometer [8, 9]. The spectrometer was mounted parallel to the polarization vector of the incident photon beam with its entrance slit oriented parallel to the direction of the incident beam. The pressure in the gas cell was optimized to about 2 mbar for a maximum absorption of photons in the interaction region. The interaction region was viewed by the X-ray spectrometer through a 160 nm thick polyimide window, supported by a polyimide grid and coated with 30 nm of aluminum nitride. During the SXE measurements, the incident photon beam entered the gas cell through a small pinhole of 100  $\mu\text{m}$  diameter and the pressure in the experimental chamber was about  $1 \times 10^{-7}$  Torr due to the outgassing from the pinhole. With 0.30 eV resolution of the

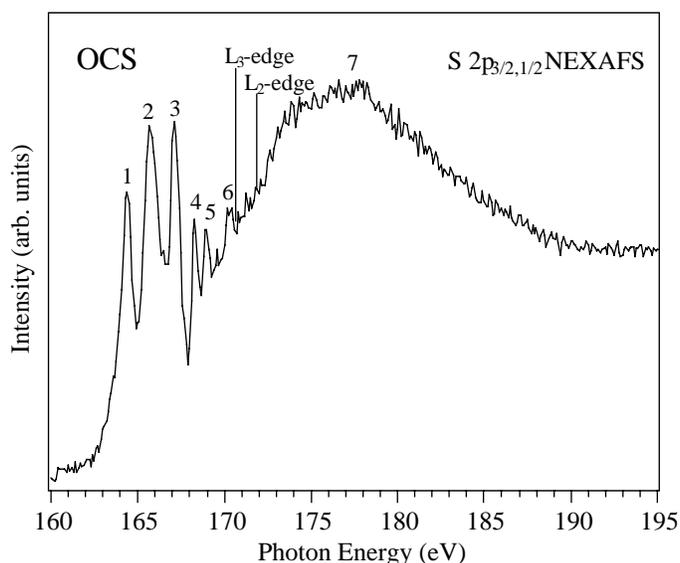
monochromator of the beamline, a near-edge X-ray absorption (NEXAFS) spectrum of sulfur was measured using the photocurrent from an electrode situated inside the gas cell where the incident photon beam entered the gas cell through a 100 nm thick silicon nitride window. The spectra were normalized to the incident photon flux using a gold mesh in front of the gas cell. The bandwidth of the synchrotron light during the sulfur, carbon, and oxygen emission measurements was set to 0.2 eV, 0.7 eV, and 1.1 eV, respectively. The resolution of the X-ray emission spectrometer is estimated to be 0.2 eV, 0.7 eV and 0.8 eV, respectively.

## Results and Discussion

### S 2p X-ray absorption spectrum

Figure 1 shows a NEXAFS spectrum measured in the region of the S  $L_{2,3}$ -edges used as a reference for the SXE measurements. The spectrum consists of three strong resonance peaks followed by a weaker Rydberg series, and a shape resonance structure in the continuum, just above the ionization thresholds, presumably with multielectron excitations superimposed.

The positions of the indicated  $L_{2,3}$ -edges are based on experimental photoelectron data [10]. The first peak in the NEXAFS spectrum is solely excitation from the  $2p_{3/2}$  ( $L_3$ ) channel which is also the case for peak number 5, while the remaining peaks are mixtures of excitations from both channels [5]. Peak number 6 has contributions from many Rydberg levels converging to the ionization potential. The fine structure of the Rydberg energy region is complicated due to the role of intermediate coupling. The 2p spin-orbit splitting creates a double-peak structure in the sulfur SXE spectra of the OCS molecule when the excitation is tuned to the mixed states (such as peaks 2,3 and 4) or the shape resonance.



**Fig. 1:** A NEXAFS spectrum measured at the sulfur  $L_{2,3}$ -edges used as a reference for the emission measurements.

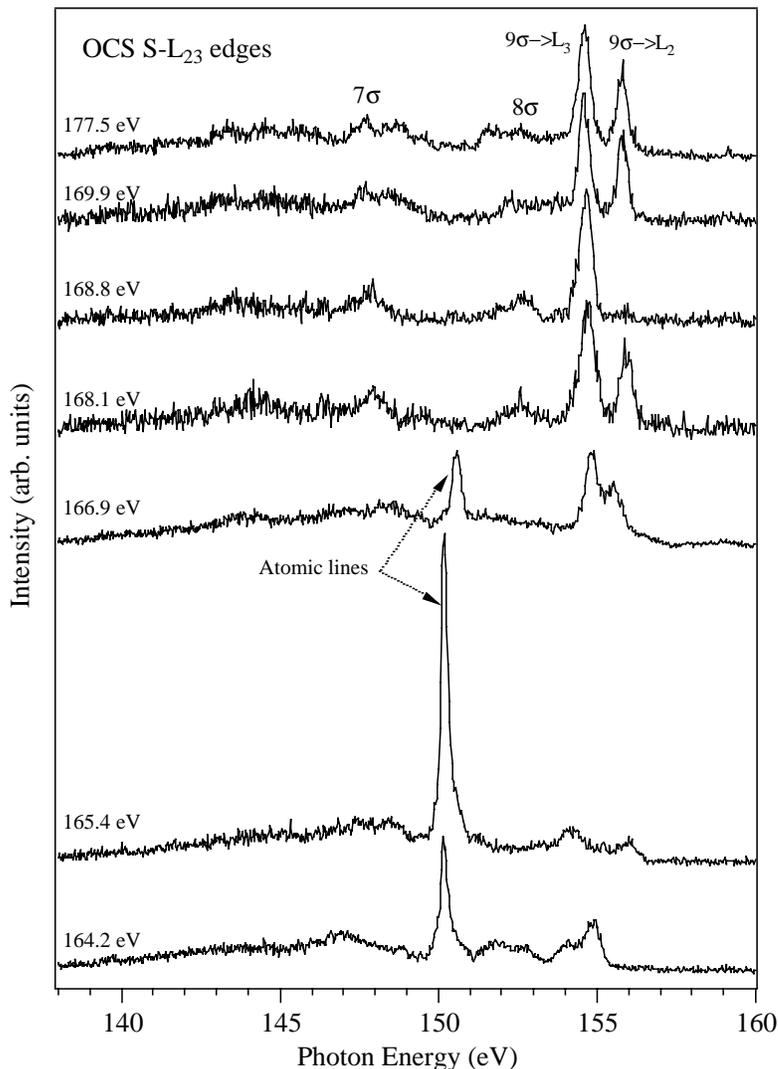
### S 2p X-ray emission spectra

Figure 2 shows a series of experimental sulfur  $L_{2,3}$  SXE spectra on a photon energy scale. The spectra were resonantly excited at the absorption peaks, denoted by the numbers 1 through 7 in Fig. 1. The spectral shape changes substantially when going from the nonresonant and Rydberg excited topmost four spectra to the  $\pi^*$  and  $\sigma^*$  excited spectra. In the latter spectra the emission peaks are substantially more vibrationally broadened and the peaks also appear at somewhat lower energy due to the screening effect of the spectator electron. The larger screening resulting from a spectator electron in the first unoccupied MO's ( $\pi^*$  or  $\sigma^*$ ) than from an electron in a Rydberg orbital is most apparent in the third spectrum from the bottom (excited at 166.9 eV). This excitation energy corresponds to two transitions,  $2p_{3/2} \rightarrow 4s$  and  $2p_{1/2} \rightarrow \sigma^*$ . In the emission spectrum the  $2p_{3/2}^{-1} 4s \rightarrow 9 \sigma^{-1} 4s$  transition results in a narrow peak with a small spectator shift, whereas  $2p_{1/2}^{-1} \sigma^* \rightarrow 9 \sigma^{-1} \sigma^*$  transition yields a broader feature with a larger spectator shift. The narrow intense atomic line at a photon energy of 150.2 eV in Fig. 2 shows up when the incident photons are tuned to the second absorption peak at 165.4 eV, whereas another atomic line at 0.4 eV higher emission energy (150.6 eV) is observed when exciting to the third absorption peak at 166.9 eV. The atomic lines completely disappears at the higher excitation energies where the incident photon energy is tuned to Rydberg states. The atomic lines have a width of 0.26 eV, which can be attributed to the instrumental spectrometer resolution (of about 0.2 eV) and the natural lifetime broadening (20-40

meV) of the sulfur  $L_{2,3}$  core-hole [11]. The  $9\sigma \rightarrow L_{2,3}$  double-peak feature at about 155 eV photon energy reflects the spin-orbit splitting of the  $L$ -shell excitation. Peaks No. 2, 3, 4, 6, and 7 (165.4, 166.9, 168.1, 169.9 and 177.5 eV) are due to excitations from both the  $L_3$  and  $L_2$  core levels. In these cases the filling up of the core levels by an electron from a single valence orbital results in two peaks.

It has been shown from angle-resolved ion-yield experiments that the OCS molecule induces a bending vibrational mode for the  $\pi^*$  excitations and that the dominating dissociation mechanism involves the breakup of the OC-S bond and the production of CO and S fragments at an angle of about 130 degrees [5, 6]. Thus, when an electron is placed in the  $\pi^*$  orbital, the potential energy is lowered by the bending motion, which can be understood as a Renner-Teller vibronic coupling effect [12, 13]. The atomic lines in the resonant SXE spectra can be considered as the result of a competition between the dissociation and the decay channels.

Comparing the intensity ratio of the atomic line to the molecular background in the three lowest SXE spectra shown in Fig. 2, one can conclude the presence of dissociation for all three, but to different extents. The dissociation time,  $t_d$ , can be estimated with the simple formula;  $t_d = -\tau \ln(1-n)$ , where  $\tau$  is the core-hole lifetime and  $n$  is the ‘molecular fraction’ [14]. Here, a larger molecular fraction corresponds to a longer dissociation time and we assume the SXE yield to be the same for the molecule and the fragment. The first spectrum (164.2 eV),  $L_3 \rightarrow \pi^*$  excitation, shows an atomic peak that contributes to about 15 % of the total intensity. If we assume the core-hole lifetime to be 22 fs (30 meV core-level width), a dissociation time of about 40 fs is found. In the second spectrum (165.4 eV) where there is a mixture of excitations from both the  $L_2 \rightarrow \pi^*$  and  $L_3 \rightarrow \sigma^*$  channels, the molecular fraction is smaller than for the first spectrum. This indicates a steeper potential path for  $\sigma^*$  than for  $\pi^*$  dissociation. Thus, the dissociation time is also smaller, about 30 fs. In the third spectrum (166.9 eV), the atomic contribution is still significant, however, in this case dissociation only occur from the  $L_2^{-1} \sigma^*$  intermediate state, and the  $L_3^{-1} 4s$ , which is also excited, only result in a molecular contribution. The estimated dissociation time is about the same as in the first spectrum (about 40 fs). At higher excitation energies, i.e., for ionization as well as core excitation to Rydberg states, the atomic contribution completely disappears.



**Fig. 2:** A series of X-ray emission spectra of the S  $L_{2,3}$  excitations of OCS.

## Summary

We show the first evidence of molecular dissociation prior to de-excitation in resonant soft X-ray emission. Resonant and nonresonant *L*-shell X-ray emission spectra for sulfur in the carbonyl sulfide molecule were measured by the use of monochromatic synchrotron radiation. In the case of S *L*-shell excitation to the  $\pi^*$  and  $\sigma^*$  orbitals a strong competition is observed between de-excitation and dissociation resulting in atomic-like lines in the SXE spectra. The line shapes of the molecular features in those spectra are also strongly affected by the dissociative character of the core-excited states.

## References

- [1] H. M. O'Bryan, H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).
- [2] H. Jones, N. F. Mott and H. W. B. Skinner, Phys. Rev. **45**, 379 (1934).
- [3] M. Magnuson, J. Guo, C. S  the, J.-E. Rubensson, J. Nordgren, P. Glans, L. Yang, P. Salek and H.   gren; Phys. Rev. A, in press.
- [4] Some very sharp lines in the broad band electron-excited X-ray sulfur emission spectrum of SF<sub>6</sub> was tentatively assigned atomic origin. However, no mechanism could be identified since energy tuning was not available; see H.   gren, J. Nordgren, L. Selander, C. Nordling, and K. Siegbahn, Physica Scripta **18**, 499 (1978).
- [5] V. Brems, B. M. Nestmann, S. D. Peyerimhoff, Chem. Phys. Lett. **287**, 255 (1998).
- [6] P. Erman, A. Karawajczyk, E. Rachlew, M. Stankiewicz and K. Yoshiki-Franz  n; Phys. Rev. A **56**, 2705 (1997).
- [7] T. Warwick, P. Heimann, D. Mossessian, W. McKinney and H. Padmore; Rev. Sci. Instr. **66**, 2037 (1995).
- [8] J. Nordgren and R. Nyholm, Nucl. Instr. Methods A **246**, 242 (1986).
- [9] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J. E. Rubensson and N. Wassdahl, Rev. Sci. Instr. **60**, 1690 (1989).
- [10] C. J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn and K. Siegbahn, J. Elec. Spec. **1** (1972/73).
- [11] K. C. Prince, M. Vondracek, J. Karvonen, M. Cereno, R. Camilloni, L. Avaldi and M. de Simone, J. Electr. Spec., in press.
- [12] Jun-ichi Adachi, Nobuhiro Kosugi, Eija Shigemasa and Akira Yagishita; J. Chem. Phys. **107**, 4919 (1997).
- [13] G. Herzberg; *Molecular Spectra and molecular structure*, Lancaster press, inc., New York, 1945, and references therein.
- [14] A. N de Brito, A. N. de Brito, O. Bj  rneh  lm, J. S. Neto, A. B. Machado, S. Svensson, A. Ausmees, S. J. Osborne, L. J. Saethre, H. Aksela, O.-P. Sairanen, A. Kivim  ki, E. Nommiste and S. Aksela; J. Mol. Struct. (Theochem) **394**, 135 (1997).

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