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► To cite this version:

T Marchenko, S Carniato, L Journal, R Guillemin, E Kawerk, et al.. Electron dynamics in the core-excited CS 2 molecule revealed through resonant inelastic x-ray scattering spectroscopy. *Journal of Physics: Conference Series*, 2015, 635 (11), pp.112012 10.1088/1742-6596/635/11/112012 . hal-01266799

HAL Id: hal-01266799

<https://hal.sorbonne-universite.fr/hal-01266799>

Submitted on 3 Feb 2016

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2015 J. Phys.: Conf. Ser. 635 112012

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Electron dynamics in the core-excited CS₂ molecule revealed through resonant inelastic x-ray scattering spectroscopy

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Synopsis We present an experimental and theoretical study of resonant inelastic x-ray scattering (RIXS) in the CS₂ molecule near the S 1s edge. We show that localization of the S 1s core-hole occurs in CS₂ during the RIXS process due to the orientational dephasing of interference between the waves scattering on the two sulfur atoms. Strong evolution of the RIXS profile with the excitation energy far below the first absorption resonance reflects the onset of electron dynamics triggered by a coherent excitation of multiple electronic states..

Excitation of a molecule with a high-energy photon leads to an ultrafast dynamic response involving nuclear and electronic degrees of freedom. Alternatively to the time-resolved measurements using ultrafast laser sources, the nuclear and electron dynamics can be successfully studied in the x-ray energy domain using a technique known as 'core-hole clock' spectroscopy based on core-level excitation and decay [1, 2]. Our previous studies in gas-phase molecules excited at the Iodine L shell [3] show that resonant inelastic x-ray scattering (RIXS) provides information on sub-femtosecond nuclear dynamics in a molecule upon core-hole excitation. To our knowledge, so far there have been no attempts to reveal the electron dynamics in isolated molecules using core-hole clock spectroscopy.

In this study we report on a strong evolution of the RIXS profile with detuning below the first absorption resonance in CS₂ excited at the S 1s shell. The S K_β RIXS spectra of the CS₂ molecule, near the lowest unoccupied molecular orbital resonance 1s→3π_u at ħω=2470.4 eV, were measured at the ID26 beamline of the European Synchrotron Radiation Facility (ESRF) with the high-resolution X-ray spectrometer developed at the Jožef Stefan Institute in Ljubljana [4].

First, we have elucidated the mechanism responsible for the dominant dipole- and symmetry-forbidden transition from the *gerade* Σ_g⁺ electronic ground state to the *ungerade* |2π_g⁻¹3π_u¹Σ_u⁺, Δ_u final state. Violation of the symmetry selection rules occurs due to localization of the S 1s core-hole in CS₂ during the RIXS

process. The reason for the core-hole localization is the orientational dephasing of Young double-slit interference patterns measured in randomly oriented molecules, which is specific to the hard x-ray regime.

Second, a strong evolution of the RIXS profile with the excitation energy tuned down to about 10 eV below the first resonance, is caused by a relative variation of the partial contributions from the different intermediate core-excited states.

Finally, the temporal evolution of the multi-electron wave packet launched by a coherent excitation of multiple electronic states is responsible for the excitation energy dependence of RIXS upon further detuning. Electron dynamics occurs on the characteristic time scale in the attosecond range, determined by the spacing of the coherently excited intermediate states. The RIXS profile is determined by the interplay of the effective scattering duration and the characteristic time of the electron wave packet evolution.

Direct time-resolved measurements of electron dynamics in core-excited molecules require using a short hard x-ray pulse with duration below the core-hole lifetime (~ 1fs), which is so far unavailable. Our study demonstrates the potential of RIXS and core-hole spectroscopy in general, as a promising alternative in application to the studies of electron dynamics in molecules excited at the deep core shells.

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