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Production of neutral high-Rydberg fragments via inner-shell excitation and field ionization detection in the CO_2 molecule

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Keywords: synchrotron radiation, high-Rydberg states, K edges, CO_2 molecule

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Atoms and molecules have long-living metastable states with lifetimes which are considerably longer than those of ordinary excited states. In particular, the excited states having an electron in a high-Rydberg (HR) orbital and energy below the first ionization potential (IP) belong to those long-living states. Their lifetimes are expected to rise proportionally to n^3 [1], where n is the principal quantum number. Recently Kivimäki *et al.* [2, 3] have discovered a new class of the mechanisms of the photon-induced fragmentation, namely recapture processes to Rydberg states by detection of the field ionized TOF mass spectra of neutral high-Rydberg fragments after inner-shell C1s and S2p core excitations and ionization of the CH_4 and SF_6 molecules, exploiting a combined soft x-ray excitation with pulsed field ionization and ion time-of-flight (TOF) spectrometry. These measurements showed that core ionization of small molecules with a photon energy just above the 1s or 2p ionization potentials leads to ultrafast photoelectron recapture processes where the photoelectron is pushed back to high-Rydberg orbital of the molecular ion. Then, neutral high-Rydberg fragments can be created together with ions after subsequent dissociation processes. Those fragments may also be produced following resonant Auger decay after core–excitation.

In the present study we have studied the production of neutral high-Rydberg fragments and their intensities in the CO_2 molecule after inner-shell C1s and O1s core excitations and ionization, using soft x-ray excitation with pulsed field ionization and ion TOF spectroscopy. The experiments were carried out at the Gas Phase Photoemission beamline at the Elettra synchrotron radiation facility exploiting the TOF mass spectrometer that was modified for pulsed field ionization measurements [2]. The experimental set-up also allows the measurements of the yields of neutral HR fragments, ions, and of the photoelectron-photoion coincidence spectra.

First of all, we have measured the NEXAFS spectra by recording total ion yields (TIY) at both the C1s and O1s inner-shell edges without field ionization. In the second step, we have switched on field ionization and measured the sum (or total yield) of HR fragments and energetic photons (THRY). Figure 1 shows the example patterns of total ion yield and HR fragments+VUV photons yield recorded in CO_2 at the O1s edge in the photon energy range of 538-543.8 eV. Both yields are normalized to the photon flux and scaled to have the same intensity at the lowest energy resonance. In Figure 1, the THRY resembles the TIY only over the 3pσ/4sσ and 4pσ/5sσ resonances. But around the ionization energy (IP~541.3 eV) very strong peak occurs that can be attributed to the production of neutral fragments in the HR states by recapture processes where the photoelectron is pushed back to HR orbital of the molecular ion [2]. Recapture processes lead to the population of val^{-2} HR^1 states, whose dissociation can then yield neutral fragments in HR states. In order to identify particular HR fragments, the TOF spectra have been measured at the selected energies using field ionization. The HR fragments with the energy sufficiently close to the IP entered the first stage of the TOF spectrometer. Then, they were ionized by a pulsed electric field and pulled into the spectrometer. Ions produced in that way were detected using the MCP detector mounted at the end of the drift tube; their flight times allowed the identification of the initial neutral HR fragments. The mass spectra of neutral HR fragments revealed high intensity peaks due to atomic fragments C(HR) and O(HR).

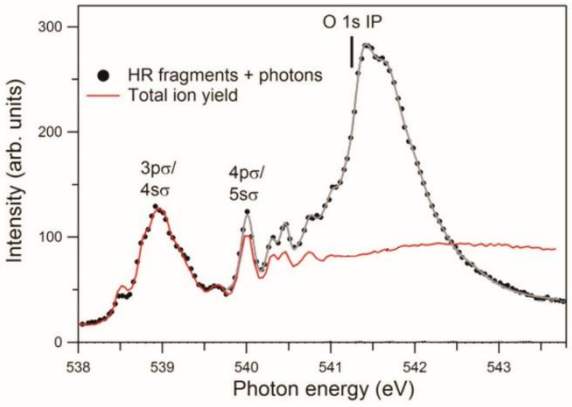

Figure 1. The HR fragment and ion yields measured at the O 1s edge of the CO_2 molecule.

Acknowledgments: Part of this work was performed during the Short Term Scientific Mission supported by the COST Action CM1204 (XLIC).

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