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Synchrotron excitation – field ionization studies of high-Rydberg fragments produced after inner-shell ionization of small molecules

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Synopsis We have studied the production of neutral high-Rydberg (HR) fragments in small molecules after inner-shell excitation and ionization. Such fragments were ionized using a pulsed electric field and resulting ions were mass-analyzed with an ion time-of-flight (TOF) spectrometer. As an example, the results obtained at the C 1s ionization threshold of the methane molecule will be discussed.

A small molecule usually fragments if one of its inner-shell (or core) electrons is promoted to an unoccupied molecular or Rydberg orbital or is completely removed from the molecule. This is because electronic states with an inner-shell hole typically decay through Auger transitions, whose two-hole final states are unstable in most molecules. The molecule then breaks up, yielding in general both ionic and neutral fragments.

In the present study, we have constructed an experimental set-up that allows us to detect neutral fragments in high-Rydberg (HR) states and determine their identities. It combines soft x-ray excitation with pulsed field ionization (PFI) and ion TOF spectroscopy. The experiment exploits PFI with high electric fields (of the order of kV/cm). A special feature of our apparatus is that field ionization of HR fragments occurs in a region that is separated from their place of creation. Therefore the measurements can be performed in the usual multi-bunch operation mode of a synchrotron light source.

Previous neutral particle-photoion coincidence experiments of the CH_4 molecule [1] revealed that the production of metastable H atoms hugely increases just above the C 1s ionization potential. There the so-called post collision interaction between a slow photoelectron and a subsequently emitted fast Auger electron can induce recapture processes, where the slow C 1s photoelectron is pushed back to a HR orbital of the molecular ion. The present experiments (figure 1) show that all possible HR fragments – not only H(HR) – can be created after subsequent dissociation processes. The C(HR) and H(HR) fragments dominate the spectrum, but molecular fragments CH_n(HR), n=1-3, and H_2(HR) were also observed. The findings are rationalized in comparison with the results of Auger electron-ion coincidence experiments [2,3]. The large intensity of the C(HR) fragments can be explained if they result from recapture processes after double Auger decay, whereas CH_3(HR), CH_2(HR) and H_2(HR) could mostly be created in recapture processes after single Auger decay.

We have performed similar experiments at the C 1s and O 1s edges of the CO_2 molecule, and at the S 2p edge of the SF_6 molecule.

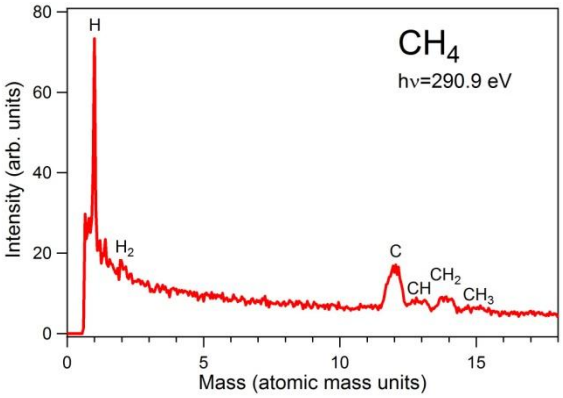

Figure 1. The ion-mass spectrum of field-ionized HR fragments of the CH_4 molecule measured just above the C 1s ionization potential.

References

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