

Creation of high valency iron molecule with high intensity ultrashort X-ray pulse

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The use of 3rd and 4th generation radiation sources in studies on the structure of complex systems have been always associated with concern about the deleterious influence of the incident beam on the target sample undermining feasibility of intact system characterization. Profiting from the high peak brightness of the pulsed X-ray sources without losing the sought information is possible in the so called *probe-before-destroy* approach where shortening of the X-ray pulse duration to tens of femtoseconds allows to probe the system before the damage occurs. The radiation damage is typically regarded as the Coulomb explosion and it occurs on time scales of more than 50 fs. It has been, however, shown to be much faster when one considers the electronic structure modification.

In this work a Fe(CN)₆/H₂O solution was irradiated using an X-ray free-electron laser (XFEL) with 30 fs-short X-ray pulses of photon energy 7200 eV (88 eV above the Fe *K*-edge binding energy) and of different photon fluxes changed from 5.8×10³⁰ to 2.4×10³² photon/(s×cm²). For each photon flux the Fe *K*β emission spectra were recorded in shot-to-shot mode with an X-ray spectrometer based on the von Hamos geometry equipped with an InSb(444) crystal and a CS-PAD 140K detector.

Increasing the photon flux caused a shift of the Fe *K*β emission spectral curve to higher energies and a decrease of the main line's intensity. Analysis of the electronic processes in the studied material showed that this effect originated from outer-shell ionization of the metal site done predominantly by the photoelectrons and Auger electrons released from the oxygen atoms.

In this study Fe(CN)₆ complex in aqueous solution was irradiated with an XFEL beam which lead to multiple ionization of Fe atoms and rupture of the Fe-C bonds. The applied element-specific X-ray emission spectroscopy allowed observation of this process at 30 fs time scale when the atoms preserved the structure integrity but the system possessed no longer bonds between Fe and C, effectively creating a unique high valence state on the Fe site.

Acknowledgments: Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. W. Błachucki and J. Sá wish to acknowledge the Polish Ministry of Science and Higher Education for support from the budget allocations for science for years 2016-2019 within the IDEAS PLUS II project of number IdPII2015000164. J. Szlachetko acknowledges National Science Centre, Poland (NCN) for partial support under grant no. 2015/19/B/ST2/00931.