



## Time - resolved x - ray absorption spectroscopy of ferrioxalate using a laser plasma source and microcalorimeter detectors

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Fine structure in x-ray absorption structure in a region from just before to a few hundred eV after x-ray absorption edges contains element-specific information such as bond length, oxidation state, and coordination number. We have performed measurements of transient x-ray absorption on aqueous solutions of ammonium ferrioxalate with picosecond time resolution using a table-top apparatus, focusing on this fine structure. Although it is well known that photolysis of ferrioxalate leads to reduction of Fe(III) to Fe(II), along with ligand dissociation, the mechanism is still controversial. The two proposed mechanisms differ according to whether oxalate ligand to Fe(III) electron transfer occurs before or after breakage of an Fe-O bond between Fe and oxalate. The ferrioxalate sample is photoexcited by 1 mJ pulses of 400 nm light synchronized to the x-ray pulses. We generate broadband, sub-picosecond x-ray pulses by focusing 50 fs pulses of 800 nm light onto a water jet. X-rays are collected and focused onto a sample jet via a polycapillary optic, which stretches the x-ray pulses by 2 ps.

Transmitted x-rays are detected with a 240 pixel TES microcalorimeter array operating at 75 mK. Calibration x-rays from a fluoresced target of mixed transition metals are incident upon the array simultaneously with the science x-rays. At low count rates, the array is capable of 5 eV FWHM resolution at 7 keV. At typical experimental rates of 25 counts per second per pixel, the system achieves about 8 eV resolution. There is additional apparent resolution degradation due to a non-gaussian component in the detector lineshape. Nonetheless, these resolution levels are sufficient for the described measurements. Typical ferrioxalate spectra contain approximately 108 counts. Our results impose new constraints on the dynamic behavior of ferrioxalate and we discuss the implications of these constraints on the pathways of the Fe(III) to Fe(II) photoreaction.

To verify the capabilities of our novel x-ray absorption instrument we took spectra of a series of reference compounds. Because these are some of the first x-ray transmission measurements with microcalorimeters, we performed a series of static transmission measurements on iron reference samples to assess our ability to determine absolute and relative edge locations. In static measurements, we show that we can clearly resolve edge shifts among Fe metal, FeO, and Fe<sub>2</sub>O<sub>3</sub> and that the absolute edge locations are correct. Furthermore, we accurately reproduce a static spectrum for ferrioxalate obtained by our team at the Canadian Light Source.

Our laboratory-based time-resolved X-ray absorption apparatus is also capable of x-ray emission measurements. We have started work towards time-resolved emission spectroscopy, beginning with static emission spectra of different iron containing compounds, showing that our apparatus can resolve differences in the K Alpha and K Beta lineshapes due to differences in spin and oxidation state.

The attached figure shows a schematic of the laboratory-based time-resolved X-ray absorption apparatus.

