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Femtosecond M$_{2,3}$-Edge Spectroscopy of Transition-Metal Oxides: Photoinduced Oxidation State Change in $\alpha$-Fe$_2$O$_3$

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ABSTRACT: Oxidation-state-specific dynamics at the Fe M$_{2,3}$-edge are measured on the sub-100 fs time scale using tabletop high-harmonic extreme ultraviolet spectroscopy. Transient absorption spectroscopy of $\alpha$-Fe$_2$O$_3$ thin films after 400 nm excitation reveals distinct changes in the shape and position of the 3p → valence absorption peak at $\sim$0.57 eV due to a ligand-to-metal charge transfer from O to Fe. Semiempirical ligand field multiplet calculations of the spectra of the initial Fe$^{3+}$ and photoinduced Fe$^{2+}$ state confirm this assignment and exclude the alternative d→d excitation. The Fe$^{2+}$ state decays to a long-lived trap state in 240 fs. This work establishes the ability of time-resolved extreme ultraviolet spectroscopy to measure ultrafast charge-transfer processes in condensed-phase systems.

SECTION: Spectroscopy, Photochemistry, and Excited States

Time resolved X-ray absorption spectroscopy is a powerful tool for probing the electronic structure of short-lived states because of the element, oxidation state, and spin state specificity of core-to-valence transitions. With the advent of third-generation synchrotrons and free-electron lasers, photoinduced nuclear and electronic dynamics of transition-metal complexes have been studied on picosecond to femtosecond time scales. First-row transition metals are generally probed using X-ray absorption spectroscopy. Transient absorption spectroscopy of $\alpha$-Fe$_2$O$_3$ thin films confirms the assignment and excludes the alternative d→d excitation. The Fe$^{2+}$ state decays to a long-lived trap state in 240 fs. This work establishes the ability of time-resolved extreme ultraviolet spectroscopy to measure ultrafast charge-transfer processes in condensed-phase systems.

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HHG allows a full spectrum to be collected at once, as in an acquisition time of 3.5 h. The XUV continuum produced by the observed transient signal. Data from three identical samples 104 photons/0.1 eV/sec (Figure 2A).

...both even and odd harmonics to be produced. The average pulse. Beyond the semi-in...collected from one sample before there is a data acquisitions, and approximately 2000 transient spectra are required due to the short penetration depth of the probe beam. The 3 mm sample is raster-scanned between 2 s pump/probe data acquisitions, and approximately 2000 transient spectra are collected from one sample before there is a ~10% reduction in the observed transient signal. Data from three identical samples are averaged to create the transient spectra, for a total data acquisition time of 3.5 h. The XUV continuum produced by HHG allows a full spectrum to be collected at once, as in an energy-dispersive beamline. The spectrometer is calibrated using the first- and second-order absorption peaks of Xe gas. To minimize the effect of pump light scattering onto the CCD, difference spectra at time t are recorded in comparison to a spectrum taken at ~500 fs. The chirp of the XUV probe pulse is not expected to be significant on the time scales presented here.

The ground-state XUV absorption of the α-Fe2O3 film is shown in Figure 2B, with major and minor peaks at 57.5 and 53.7 eV, respectively. This spectrum is an excellent match for that of a hematite single crystal measured using a synchrotron source, and electron diffraction was used to confirm the sample phase (see the Supporting Information). Static M2,3-edge spectra of first-row transition metals have been discussed in detail and are calculated using a semiempirical ligand field multiplet model with the atomic charge, ligand field symmetry and strength, and a screening parameter as the only inputs. Briefly, the Fe11+ cation in the octahedral ligand field of the surrounding O2− anions has a ground-state electronic configuration of 6A1 (Figure 3). In the absence of spin–orbit coupling, only two 3p → 3d transitions are allowed by spin and dipole selection rules, leading to the two observed absorption features. Unlike the 2p → 3d transition in L2,3-edge absorption, spin–orbit coupling effects at the M2,3-edge are weak and effectively only broaden the two peaks. The simulated spectrum shown in Figure 2B, calculated using the program CTM4XASS5 with the ligand field parameters of Berlasso et al., is an excellent match to the experimental spectrum. The absolute peak position determined from this calculation is approximate, and the energy axis is therefore shifted by ~1.7 eV.

Figure 1. Diagram of the XUV transient absorption instrument. High harmonics are generated in a semi-infinite gas cell with a two-color driving field (1.5 mJ, 35 fs at 800 nm + 20 μJ, 60 fs at 400 nm). Residual 800/400 nm light is blocked with a total of 1.2 mm Al filters. The Ne pressure in the gas cell is 100 Torr (1.3 × 104 Pascals). The XUV beam is refocused onto the sample with a gold-coated toroidal mirror in grazing incidence, and the transmitted beam is diffracted from a concave variable line-spacing grating onto an array CCD. The sample is pumped at 400 nm with a 3 μJ, 80 fs pulse. Beyond the semi-infinite gas cell, the instrument is under vacuum (~10−6 Torr).

Figure 2. (A) Absolute XUV photon flux collected at the detector after passing through 14 nm thick α-Fe2O3 on 100 nm Si3N4. The use of odd and even harmonics produces excellent spectral coverage with sufficient flux for absorption spectroscopy, with an average of 2.6 × 104 photons/0.1 eV/sec from 47.5 to 67.5 eV. (B) Ground-state XUV absorption of a 14 nm thick α-Fe2O3 thin film. Black: experimental spectrum. Red line and sticks: ligand field multiplet simulation. See the Supporting Information for a discussion of the line broadening and Fano line shape.
to match the major peak position at 57.5 eV. The calculated stick spectrum is broadened, as described in the Supporting Information. All simulated spectra in this work use identical energy-axis shifting and broadening. In Figure 2A, the vertical axis of the simulated spectrum is shifted and scaled to best match the experimental result and account for a baseline of nonresonant absorption.

Photoexcitation of the $\alpha$-Fe$_2$O$_3$ film with 3 $\mu$J, 400 nm, 80 fs pulses causes a change in the shape of the M$_{\text{L}}$$_3$-edge spectrum indicative of the excited-state electronic structure (Figure 4A). Immediately after photoexcitation, the transient spectrum is characterized by a negative feature at 57.5 eV caused by depopulation of the ground state and three excited-state peaks at 52.9, 54.6, and 55.8 eV. Over the next 1 ps, the 55.8 eV peak increases and blue shifts, while the negative feature at 57.5 eV decays to $\sim$25% of its initial magnitude. No further spectral evolution is observed for delay times as long as 100 ps. Given the pump power of 3 $\mu$J, spot size of 150 $\mu$m fwhm, and optical density at 400 nm of 0.5, it is estimated that one pump photon is absorbed per 20 Fe atoms. No significant change was seen in the spectra or kinetics at 1 $\mu$J/pulse. Kinetic traces at absorption energies of 54.6, 56.4, and 57.4 eV are shown in Figure 4B. Because of the spectral overlap of the transient features, a global fit is performed on the full 2-D data set using the program GLOTARAN. An excellent match to the experimental data is obtained by using a two-state sequential model ($A \rightarrow B$) with a time constant (1/$k$) of 240 $\pm$ 30 fs, convoluted with an 88 $\pm$ 3 fs Gaussian instrument response function (IRF). Errors are the standard deviation of the mean from four data sets on fresh samples. The two evolution-associated spectral components identified by the fit are shown in Figure 4C, with the time evolution of each component shown in the inset.

The electronic structure of the short-lived initial photoexcited state is determined by comparing the experimental initial excited-state spectrum with simulated spectra of the possible LMCT and d–d excited states. Figure 5A shows simulated XUV absorption spectra of the $^6T_1$ Fe$^{2+}$ state that would be formed from a LMCT transition and the $^4T_1$ Fe$^{3+}$ state that would be formed from a d–d transition, calculated using the ligand field multiplet method described above. For consistency, all of the input parameters to the simulation except for the oxidation and spin state are identical to those used for the $^6A_1$ Fe$^{3+}$ ground state in Figure 2B. The simulated spectrum of the LMCT state is red-shifted from that of the ground state, with two large peaks at 56.2 and 54.6 eV and a small peak at 52.2 eV. Core-level spectra of reduced species (Fe$^{2+}$) are red-shifted from their oxidized counterparts (Fe$^{3+}$), and the $\sim$2.5 eV shift is consistent with that observed in an electron energy-loss spectroscopy (EELS) study of the Fe$^{2+/3+}$ M$_{\text{L}}$$_3$-edge of a series of iron-containing minerals. A red shift in Fe absorption upon photoreduction was also observed via picosecond time-resolved X-ray absorption spectroscopy at the Fe K-edge of dye-sensitized $\gamma$-Fe$_2$O$_3$ nanoparticles.

The XUV absorption spectrum of the lowest-energy Fe$^{3+}$ d–d excited state (4$T_2$) is calculated to have a minor peak at 53.0 eV and major peaks at 58.8 and 63.8 eV (Figure 5A). Higher-energy d–d excited states such as 6$T_2$ are calculated to have spectra similar to that of the 4$T_1$ state, with a prominent absorption feature at around 64 eV. This net blue shift upon crossover from high to low/intermediate spin has been predicted for a range of 3d transition metals, and a similar effect has been observed in the L$_3$-edge spectrum of the spin-crossover compound $\left[\text{Fe(tren}(\text{py})_3)\right]^+$. Note that these simulations do not take into account possible structural distortions resulting from the excitation.

Figure 3. Diagram of initial and final states in the M$_{\text{L}}$$_3$-edge (3p $\rightarrow$ 3d) absorption of octahedral Fe$^{3+}$. Electron–electron repulsion splits the 3p$^3$3d$^1$ ground state and 3p$^3$3d$^3$ core–hole excited state into the atomic multielectron states 6S, 4G, and so forth, which are further split by the ligand field. In an octahedral field, the absorption of a photon transforms as the symmetry operation 1$T_1$, resulting in two spin- and dipole-allowed transitions. Spin–orbit coupling further splits and mixes the states (not shown in this diagram), effectively broadening these two transitions to produce the spectrum shown in Figure 2B.

Figure 4. (A) XUV transient absorption spectra of $\alpha$-Fe$_2$O$_3$ after excitation at 400 nm. Spectra are binned by 0.1 eV and smoothed using a 0.5 eV running boxcar average. (B) Kinetic traces at 54.6, 56.4, and 57.4 eV. Points are experimental data, and solid lines are from the global fit. (C) Evolution-associated spectra of the initial and final excited states obtained from a global fit using a two-state sequential ($A \rightarrow B$) model, convoluted with a Gaussian IRF. (Inset) Population of each state versus time. The fit identifies a time constant (1/$k$) of 240 $\pm$ 30 fs and an IRF of 88 $\pm$ 3 fs.
Simulated difference spectra (excited state – ground state) of the LMCT and d–d excited states are shown in Figure 5B, along with the experimental difference spectrum of the initial excited state determined by the global fit. The simulated LMCT difference spectrum is an excellent match to the experimental initial excited-state difference spectrum, with similar shape and peak-to-peak spacing. On the other hand, the shape of the simulated d–d difference spectrum is qualitatively very different from that of the observed spectrum, most notably in the positive feature from 60 to 70 eV that is absent in the experiment.

The 240 fs time constant for conversion of the initial LMCT state to the final trap state is consistent with a reported ∼300 fs (instrument-response-limited) decay to a low-lived state observed with visible-light transient absorption spectroscopy of α-Fe₂O₃ nanoparticles and thin films after 400 nm excitation. This fast decay was assigned as hot electron relaxation, band filling, and/or band gap shrinkage. The long-lived state was attributed to trapping at either Fe³⁺ oxygen-relaxation, band excitation. This fast decay was assigned as hot electron relaxation, band filling, and/or band gap shrinkage. The long-lived state was attributed to trapping at either Fe³⁺ or Fe²⁺ oxygen-relaxation, band electronic state. Ab initio simulations of the XUV spectra of possible trap states are ongoing and will be the subject of a future publication.

In conclusion, we have demonstrated the power of high-harmonic M₃⁺-edge transient absorption spectroscopy to measure ultrafast photoinduced oxidation state changes in solid-state transition-metal systems. The strong oscillator strengths of the 3p → 3d transitions, electronic-state-specific peak shapes, and ultrafast time resolution make this an attractive alternative to synchrotron- and free-electron laser-based sources. Charge-transfer processes are central to photovoltaic and photocatalytic materials, and the ability to observe the flow of electrons in real time using a tabletop source will open up new possibilities in inorganic chemistry and materials science.

**REFERENCES**


**AUTHOR INFORMATION**

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