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### Title

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# Atomic resolution mapping of the excited-state electronic structure of Cu<sub>2</sub>O with time-resolved x-ray absorption spectroscopy

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We have used time-resolved soft x-ray spectroscopy to investigate the electronic structure of optically excited cuprous oxide at the O *K*-edge and the Cu *L*<sub>3</sub>-edge. The 400 nm optical excitation shifts the Cu and O absorptions to lower energy, but does not change the integrated x-ray absorption significantly for either edge. The constant integrated x-ray absorption cross-section indicates that the conduction-band and valence-band edges have very similar Cu 3*d* and O 2*p* orbital contributions. The 2.1 eV optical band gap of Cu<sub>2</sub>O significantly exceeds the one eV shift in the Cu *L*<sub>3</sub>- and O *K*-edges absorption edges induced by optical excitation, demonstrating the importance of core-hole excitonic effects and valence electron screening in the x-ray absorption process.

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## I. INTRODUCTION

Time-resolved spectroscopy from the THz to the vacuum UV has been widely applied to investigate the photophysics and photochemistry of a wide variety of photon-driven phenomena,<sup>1–4</sup> but the complexity of the materials and phenomena being studied often make the interpretation of the experimental results challenging and inconclusive. Theoretical methods also struggle to accurately describe excited electronic states and cannot robustly predict or explain the material properties that determine excited electronic state properties.<sup>5–7</sup> During the rapid development of time-resolved optical techniques a similar growth in synchrotron radiation based soft x-ray spectroscopy has occurred. Soft x-ray spectroscopy has proven to be a powerful method for investigating the equilibrium electronic properties of materials.<sup>8–11</sup> Combining ultrafast laser technology with x-ray synchrotron sources has led to time-resolved soft x-ray spectroscopy methods capable of probing excited-state electronic structure and dynamics with atomic specificity.

Soft x-ray absorption spectroscopy (XAS) has many attributes that make it a powerful tool for investigating electronic structure. XAS allows the decomposition of molecular electronic states into specific contributions from distinct atomic absorptions.<sup>8–11</sup> Copper *L*-edge and oxygen *K*-edge XAS of Cu<sub>2</sub>O represent an excellent case study for demonstrating the power of soft x-ray spectroscopy for characterizing electronic structure.<sup>12–17</sup> The Cu *L*<sub>2,3</sub>-edge interrogates the unoccupied 3*d* density of states,<sup>8</sup> while the oxygen *K*-edge provides a sensitive monitor of the orbital mixing between the unoccupied O 2*p* and the Cu 3*d* electronic states.<sup>17,18</sup> Copper has a formal oxidation state of 1<sup>+</sup> in Cu<sub>2</sub>O, implying a 3*d* (Ref. 10) electronic configuration for the Cu atom, but covalent chemical interactions between oxygen and copper can result in significant deviations from the formal oxidation state. Multi-

ple *ab initio* electronic structure calculations have attempted to determine the 3*d* occupancy of Cu<sub>2</sub>O and characterize the nature of the chemical bonding,<sup>17,19–23</sup> but a consensus conclusion from these studies has not been achieved. The Cu *L*<sub>3</sub>-edge absorption spectrum provides an ideal tool for studying the 3*d* unoccupied density of states, since a full 3*d* shell will result in no *L*<sub>3</sub>-edge white line, as seen for Cu metal. In contrast to this idealized picture, a distinct white line appears in the Cu *L*<sub>3</sub>-edge spectrum of Cu<sub>2</sub>O,<sup>17</sup> providing very strong evidence for a partial vacancy in the Cu 3*d* levels. The strong absorption in the O *K*-edge at the same energy relative to the ionization potential as the unoccupied Cu 3*d* levels<sup>17</sup> further supports this observation and provides an experimental means for characterizing the covalency of the Cu-O interaction.<sup>24–26</sup> Our investigation of optically excited Cu<sub>2</sub>O demonstrates the ability of time-resolved x-ray spectroscopy to characterize electronic excited states, thereby providing information about the charge distribution and covalency of the highest occupied and lowest unoccupied electronic states.

A limited number of time-resolved soft x-ray absorption measurements have been performed.<sup>27–33</sup> The studies of VO<sub>2</sub> by Cavalleri *et al.*<sup>30</sup> deserve mention, since these studies probed the material response to optical excitation with soft x-ray absorption for both of the atomic species in their sample. Our experiment utilizes a similar approach to map out the excited-state electronic structure of Cu<sub>2</sub>O with atomic specificity. The results of our experiment also illustrate key attributes of the valence electronic structure that cannot be accessed with independent applications of either optical or core-hole spectroscopy. This information proves most critical because valence electronic structure dictates the photophysical and photochemical properties of materials. The experiments have been performed on cuprous oxide (Cu<sub>2</sub>O), a widely studied transition metal oxide semiconductor utilized in photovoltaic and photoelectrochemical applications.<sup>34–37</sup> While our experi-

ment specifically addresses the properties of  $\text{Cu}_2\text{O}$ , our experiment also highlights the ability of time-resolved core-hole spectroscopy to characterize the valence excited-state structure in an atom-specific manner. This capability can be applied to an enormous range of molecular and solid-state materials.

## II. EXPERIMENTAL METHODOLOGY

We performed our time-resolved studies of optically excited  $\text{Cu}_2\text{O}$  at beamline 6.0.2 at the advanced light source (ALS).<sup>38</sup> The experiment involved optical excitation with  $\sim 100$  fs full width half maximum (FWHM) pulses centered at 400 nm and subsequent probing of laser-induced absorption changes with tunable 60 ps soft x-ray pulses generated by an in-vacuum undulator at a repetition rate of 1.53 MHz. The laser system consists of a cavity-length stabilized Ti:Sapphire oscillator that is synchronized in repetition rate to the 500 MHz RF of the synchrotron storage ring to provide time synchronization. The 800 nm oscillator pulses are amplified in a home-built chirped-pulse regenerative amplifier and a subsequent two-pass amplifier. A grating compressor shortens the pulses to  $\sim 100$  fs which are frequency doubled in a beta-barium borate (BBO) crystal. The resulting 400 nm pulses excite the sample which is then probed by the x-ray pulses provided directly by the synchrotron. The time delay between laser and x-ray pulses is controlled by an electronic phase shifter between the synchrotron's RF and the repetition rate of the oscillator. A similar setup for time-resolved x-ray absorption spectroscopy at the ALS has been described elsewhere.<sup>39</sup>

The x-ray pulses transmitted through the sample are recorded at 2 kHz, while the laser pump pulses are exciting the sample at 1 kHz, generating interleaved data with and without pump pulses present to calculate laser-induced x-ray absorption changes. The x-ray intensity transmitted through the sample was measured by gating the response of an avalanche photodiode (APD) with a boxcar integrator. Zero-time delay is determined with an accuracy of  $\sim 50$  ps by measuring the arrival time of laser and x-ray pulses at the APD with a GHz oscilloscope. The duration of the x-ray pulses of about 60 picoseconds (ps) FWHM determines the time resolution of our measurements. Beamline 6.0.2 uses a variable line spacing grating monochromator with an energy resolution of about 0.3 eV at the O  $K$ -edge and 0.8 eV at the Cu  $L$ -edge to preserve x-ray flux. We performed our experiments with the sample in the monochromatic beam to reduce x-ray induced sample damage.

Soft x-ray measurements require vacuum compatible samples and the design of the 6.0.2 beamline best accommodates x-ray absorption measurements performed in transmission. This necessitates samples of less than 100 nm absorption depth to ensure appreciable soft x-ray transmission. We grew thin film samples of  $\text{Cu}_2\text{O}$  in collaboration with the scientists at EMSL (Environmental and Molecular Sciences Laboratory) at the Pacific Northwest National Laboratory. Cuprous oxide has the advantageous quality that its optical and soft x-ray penetration depths are similar with a sample thickness of roughly 50 nm grown on a  $\text{Si}_3\text{N}_4$  substrate providing reasonable transmission of both optical and x-ray radiation. We used

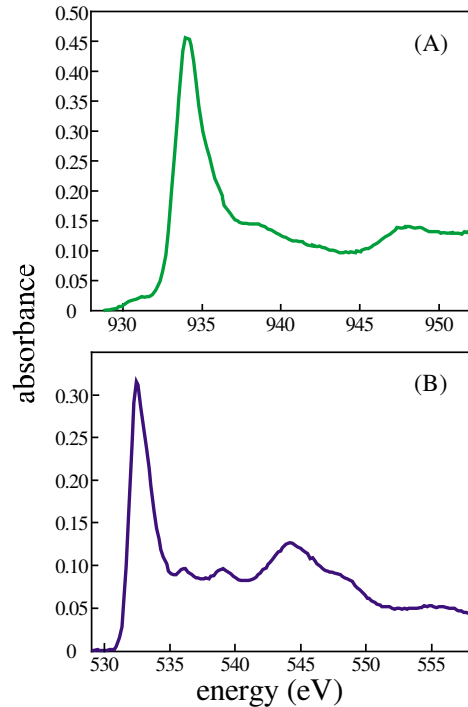


FIG. 1. (Color online) X-ray absorption spectra for the (A) Cu  $L_3$ -edge (—) and the (B) O  $K$ -edge (—). The weak feature roughly 2.8 eV below the cuprous oxide white line results from partial oxidation to cupric oxide.

oxygen plasma assisted molecular beam epitaxy (OPA-MBE) to grow the  $\text{Cu}_2\text{O}$  thin films on  $\text{Si}_3\text{N}_4$  substrates, a method previously employed at EMSL to grow nanostructured  $\text{Cu}_2\text{O}$  on  $\text{SrTiO}_3$  substrates.<sup>40,41</sup> We grew the  $\text{Cu}_2\text{O}$  thin films on 200 nm thick  $\text{Si}_3\text{N}_4$  windows supported on 200 micron thick Si wafers. Sample growth was performed in a dedicated UHV chamber that has been described elsewhere.<sup>40,41</sup> A substrate temperature of 600 °C and an  $\text{O}_2$  partial pressure of  $4.6 \times 10^{-6}$  torr provide the optimal growth conditions. These conditions produced a deposition rate of 3 Å per minute and minimized the Cu metal and CuO content of the thin film, as determined by x-ray photoelectron spectroscopy, grazing incidence x-ray diffraction, and Auger electron spectroscopy.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

The copper  $L$ -edge and oxygen  $K$ -edge of the thin film  $\text{Cu}_2\text{O}$  samples appear in Fig. 1. The spectra match the expected results for cuprous oxide with the relatively strong white line indicative of the partial depletion of the copper  $d$  band in  $\text{Cu}_2\text{O}$ .<sup>17</sup> The weak peak 2.8 eV below the main  $\text{Cu}_2\text{O}$   $L_3$  white line results from partial oxidation of the thin film surface to CuO. The energetic separation between the  $\text{Cu}_2\text{O}$  white line and the proposed CuO white line resembles the separation of 2.4 eV found for CuO and  $\text{Cu}_2\text{O}$  by Grioni *et al.*<sup>17</sup> Nachimuthu *et al.*<sup>42</sup> also observed similar oxidation with XAS for cuprous oxide quantum dots grown using OPA-MBE. Our studies focus on transient effects at the Cu  $L_3$ -edge white line at 934 eV and the pre-edge feature at 533 eV for the O  $K$ -edge. This spectral feature has been associated with the O  $2p$  orbitals mixed with the Cu  $3d$  orbitals,<sup>17,24</sup> making it sensi-

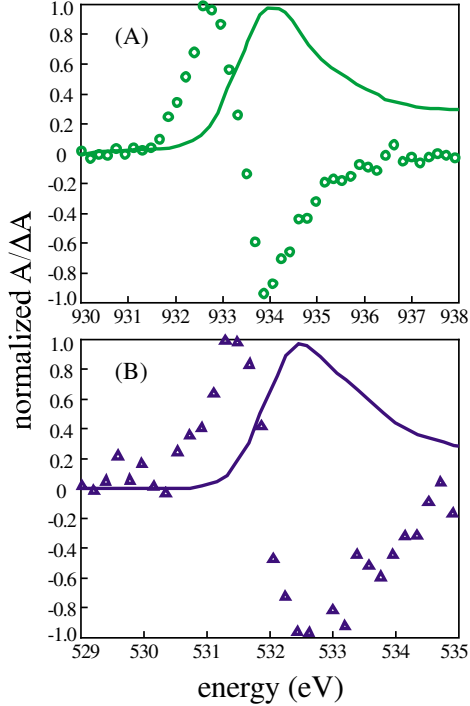


FIG. 2. (Color online) Normalized change in absorption ( $A$ ) induced by optical excitation with 400 nm light collected at a time delay of 70 ps for the (A) Cu  $L_3$ -edge ( $\circ$ ) and the (B) O  $K$ -edge ( $\Delta$ ). For comparison, the normalized ground-state absorption spectra also appear in (A,B).

tive to the covalency of the Cu-O interaction.

We collected both transient spectra at a limited number of time delays and time-resolved kinetics at a limited number of x-ray probe energies. Figure 2 shows the normalized transient absorption spectra collected with a time delay of 70 ps for both the Cu  $L_3$ -edge and the O  $K$ -edge after exciting the sample at 400 nm with an excitation fluence of  $5 - 10 \text{ mJ cm}^{-2}$ . The figure also contains the equilibrium spectra for reference purposes. The maximum change in absorption at the  $L_3$ -edge is  $\sim 5\%$  of the maximum ground state absorption. The difference spectrum looks like the derivation of an absorption peak, consistent with the dominant effect of optical excitation being a shift in spectral weight to lower energy. Within the experimental error in  $\Delta A$  per probed x-ray energy of roughly  $\pm 0.002$ , the Cu  $L_3$ -edge has no integral change in x-ray absorption.

The difference spectrum can be approximated by a sum of a positive amplitude Gaussian representing the excited-state absorption and a negative Gaussian representing the ground-state bleach. The Gaussian lineshape reflects the x-ray monochromator resolution and energetic inhomogeneity in the thin film. The limited signal-to-noise of the measurement does not warrant a more sophisticated lineshape analysis. The excited-state absorption maximum shifts to lower energy by  $1.1 \pm 0.2 \text{ eV}$  relative to the cuprous oxide Cu  $L_3$ -edge white line. The O  $K$ -edge spectrum shows similar behavior to the Cu spectrum discussed above and appears in Fig. 2(B). Like the transient Cu  $L_3$ -edge, the O  $K$ -edge transient signal shifts to lower energy by  $1.0 \pm 0.2 \text{ eV}$ . For the O  $K$ -edge, the integral bleach signal exceeds the integral excited-state absorption by roughly

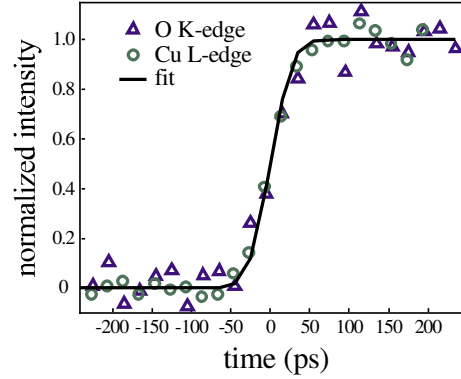


FIG. 3. (Color online) Time-resolved scan monitoring the increase in absorption at the peak of the induced absorption for the ( $\circ$ ) Cu  $L_3$ -edge (932.8 eV) and the ( $\Delta$ ) O  $K$ -edge (531.4 eV) as a function of time delay between laser pump and x-ray probe. We fit the data to an error function with a 62 ps FWHM, consistent with the ALS x-ray pulse duration.

10%, but the standard deviation in the signal also equals 10%, so we have not observed a statistically meaningful change in the integrated absorption. The maximum change in absorption at the O  $K$ -edge equals  $\sim 4\%$  of the maximum ground state absorption, similar to the change seen for the Cu  $L_3$ -edge.

We also monitored the time dependent change in x-ray absorption at 932.7 eV, the peak in the difference spectrum for the Cu  $L_3$ -edge, and at 531.5 eV, the peak in the difference spectrum for the O  $K$ -edge. The resulting data appears in Fig. 3. These measurements and transient spectra collected at time delays other than 70 ps, indicate that the normalized transient spectrum does not change on the time-scales accessible to the measurement. Both scans exhibit the same dynamics and have been fit with an error function. The derivative of the error function provides the Gaussian pulse width of 62 ps FWHM equal to the x-ray pulse duration at the ALS,<sup>39</sup> This demonstrates, as expected, that the relaxation dynamics occurring in the valence and conduction bands occur too quickly to be resolved within the experimental time resolution of  $\sim 60 \text{ ps}$ ,<sup>43</sup> Excited state recombination in Cu<sub>2</sub>O occurs on the nano to microsecond time scale depending on crystallographic purity,<sup>43</sup> thus our measurement observes the excited-state electronic structure following carrier relaxation to the valence and conduction band edges.

The shift of the absorption edge to lower energy conforms to expectation since the optical laser depopulates the valence band and populates the conduction band. However, the magnitude of the absorption edge shift of 1.1 eV at the Cu edge and 1.0 eV at the O edge induced by laser excitation is significantly smaller than the cuprous oxide band gap of 2.1 eV.<sup>43</sup> The inequality of these numbers demonstrate that the electronic relaxation associated with valence excitation to the conduction band differs from the electronic relaxation that accompanies core-hole excitation to the conduction band.

The transient spectrum provides further information about the excited-state electronic structure in cuprous oxide. The lack of an integrated change in the Cu  $L_3$ -edge and the O  $K$ -edge represents the most interesting experimental observation. This provides evidence that the Cu  $3d$  and O  $2p$  orbital contributions to the conduction-band edge strongly resemble the

orbital contributions to the valence-band edge. If the valence-band edge had a much stronger or weaker  $3d$  character than the conduction-band edge, the Cu  $L_3$ -edge would be expected to have a net increase or decrease in absorption, but this has not been observed experimentally.

#### IV. CONCLUDING REMARKS

We have used time-resolved soft x-ray spectroscopy to investigate the electronic structure of optically excited cuprous oxide at the O  $K$ -edge and the Cu  $L_3$ -edge. While optical excitation shifts both edges to lower energy, the integrated x-ray absorption does not change. We interpret this observation as an indication that the conduction-band and valence-band edges have very similar Cu  $3d$  and O  $2p$  orbital contributions. Our work demonstrates the ability of time-resolved x-ray spectroscopy to characterize the chemical bonding in excited states, making it a useful tool for characterizing the electronic excited states of photovoltaic and photocatalytic materials.

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