# Ultrafast Photoinduced Energy and Charge Transfer - Supplementary

## Information

ARTICLE

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# Decomposing Electronic and Lattice Contributions in Optical Pump – X-ray Probe Transient Inner-Shell Absorption Spectroscopy of CuO - Supplementary Information

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**Sample preparation** Copper sheet metal is cut to size and the surface roughened with sand paper to create better adhesion of the CuO film grown on the Cu substrate. This is followed by cleaning with micro-soap, acetone and ethanol in this order. The samples are then transferred to a furnace and heated to 500°C for 15 minutes in normal atmosphere. During this procedure, the sample surface oxidizes, creating a layer of CuO.[1–3] After cooling, the sample is gently wiped with an ethanol-soaked lint-free tissue. The heating-cooling-wiping cycle is repeated a total of five times. While the exact value for the final CuO film thickness is unknown, it is large compared to the ~43 nm probing depth of the X-rays (see below), as no significant count rate fluctuations are observed while raster-scanning the sample.

**Time-resolved XAS** Inside the vacuum system, the pump and probe beams are combined by reflecting the laser beam off a mirror with a hole in the center that allows the X-rays to pass through. Spatial pump-probe overlap is achieved by performing knife-edge scans for both beams using a photodiode with carbon tape attached along horizontal and vertical directions, providing straight edges in both dimensions. The laser pointing is adjusted with a piezo-actuator controlled mirror mount to coincide with the X-rays. The X-ray and laser focus spot sizes are $180 \times 80\,\mu m^2$ and $\sim 250 \times 200\,\mu m^2$ (horizontal × vertical, FWHM), respectively, ensuring that the probed sample area is homogeneously excited. Larger laser spot sizes would unnecessarily increase the total deposited energy (mJ) per shot at a given excitation fluence (mJ/cm$^2$), leading to additional sample heating and, potentially, damage (see below). The laser spot sizes were approximately the same for both laser colors. Temporal pump-probe overlap is adjusted using a biased photodiode with 30 ps

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response time and a digital oscilloscope with 1 GHz bandwidth and 10 GS/s sample rate.

The ALS was operated in multi-bunch mode with 2 ns bunch-to-bunch spacing. Thus, individual TFY spectra have pump-probe delays of $\Delta t_N = t_N - t_0 = \Delta t_0 + 2\,\text{ns} * (N\text{-}1)$, where $\Delta t_0$ is the pump-probe delay of the first X-ray pulse after the laser pulse and $N$ = 1,2,3,… indicates the $N^{th}$ X-ray pulse following the laser pulse. The minimum pump-probe delay is set to $\Delta t_0 = (150\pm30)$ ps for all measurements presented here. The simultaneous recording of trXAS spectra from an extended X-ray pulse train enables the concurrent capture of dynamics across hundreds of nanoseconds, while for delays <2 ns, the pump-probe delay $\Delta t_0$ is varied by a programmable, electronic delay line. Excited state spectra ("pumped") are compared to ground state reference spectra ("unpumped") by creating difference spectra for each pump-probe delay, $\Delta\text{trXAS}(\Delta t) = \text{trXAS}_{\text{pumped}}(\Delta t) - \text{trXAS}_{\text{unpumped}}$. Any given pumped spectrum is compared to an unpumped spectrum stemming from the same ALS electron bunch, but acquired one round-trip (656 ns) before laser excitation. This procedure ensures minimum impact of bunch-to-bunch variations in the ALS fill pattern on the ΔtrXAS spectra. Long-term variations of the bunch fill pattern are accounted for using bunch current monitor data supplied by the ALS. Additionally, photon energy dependent variations of the average incident X-ray flux are monitored via a gold mesh placed in the X-ray beam downstream from the last beamline optic.

The main reason for raster scanning the sample during data acquisition is to avoid thermally induced conversion of CuO to $Cu_2O$, which is particularly noticeable when pumping with 355 nm pulses. High temperatures in conjunction with low partial pressures of oxygen lead to a CuO to $Cu_2O$ phase transition.[4,5] The effect is more pronounced in the 355 nm measurement, most likely due to the smaller penetration depth of 355 nm light compared to 532 nm photons,[6] which leads to higher transient surface temperatures under UV exposure (see section 4 of the main text). The scan speed is chosen such that upon recording of an XAS spectrum on an already laser-scanned sample area, no contributions from the intense $Cu_2O$ white line at 532.5 eV (Fig. 1a) is detected. Note that the scanning procedure is essential to avoid artifacts due to overlapping transient features from CuO and $Cu_2O$.[7]

**Selection of pump laser fluences** The 1.8 mJ/cm² fluence for 355 nm excitation is chosen such that the average laser excitation density within the probed volume is expected to be approximately comparable to that for 532 nm and 4.8 mJ/cm². This estimate takes into account the wavelength dependent reflectivities (11.3% and 9.9%, measured independently) and absorbances (1/e penetration depths 21.2 nm and 124.5 nm[2,6]) of the 355 nm and 532 nm pump pulses, respectively, as well as the X-ray penetration and escape depths at the angles of incidence (0˚) and detection (~82±8˚). The 1/e X-ray penetration depth undergoes significant changes around the absorption edge from 320 nm below (<528 eV) to 180 nm above (>543 eV) the edge.[8] For simplicity, the latter value (180 nm) is used as the average penetration depth for the incoming X-rays while the former (320 nm) is used for the 1/e escape depth of the X-ray fluorescence. Multiplying the two exponential decay functions that describe the X-rays entering and escaping the CuO sample and including the entrance and detection angles, leads to an effective 1/e X-ray probing depth of 43 nm. According to this estimate, the excitation densities within the probed volume for 355 nm and 532 nm pump pulses are comparable for a pump fluence ratio $F_{532\text{ nm}}/F_{355\text{ nm}} = 1.9^{+1.9}_{-0.4}$. The range of this value is relatively large due to the large angular acceptance of the X-ray fluorescence detector. It includes, in particular, the experimental ratio of 4.8 mJ/cm² / 1.8 mJ/cm² = 2.7.

## References


1 L. De Los Santos Valladares, D. H. Salinas, A. B. Dominguez, D. A. Najarro, S. I. Khondaker, T. Mitrelias, C. H. W. Barnes, J. A. Aguiar and Y. Majima, *Thin Solid Films*, 2012, **520**, 6368–6374.
2 D. Tahir and S. Tougaard, *Journal of Physics: Condensed Matter*, 2012, **24**, 175002.
3 Y. S. Gong, C. Lee and C. K. Yang, *Journal of Applied Physics*, 1995, **77**, 5422–5425.
4 S. Poulston, P. M. Parlett, P. Stone and M. Bowker, *Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films*, 1996, **24**, 811–820.
5 M. Heinemann, B. Eifert and C. Heiliger, *Physical Review B*, 2013, **87**, 115111.
6 W. K. C. Yung, B. Sun, Z. Meng, J. Huang, Y. Jin, H. S. Choy, Z. Cai, G. Li, C. L. Ho, J. Yang and W. Y. Wong, *Scientific Reports*, 2016, **6**, 39584.
7 S. Neppl, J. Mahl, A. S. Tremsin, B. Rude, R. Qiao, W. Yang, J. Guo and O. Gessner, *Faraday Discussions*, 2016, **194**, 659–682.
8 CuO - X-ray attenuation length, http://henke.lbl.gov/optical_constants/atten2.html, (accessed 28 November 2018).