Transient XAS of the Insulating and Metallic States of Vanadium Dioxide

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We revisit the insulator-metal phase transition in VO\textsubscript{2} by measuring the transient X-ray absorption spectroscopy on the picosecond timescale over the entire oxygen pre-edge. We find that the thermal recovery of thin free-standing samples in vacuum is longer than the typical inter-pump-pulse spacing used in previous measurements reported in literature, which can easily drive permanent switching into the metallic phase. By controlling the rate of laser heating, we are able to measure the picosecond dynamics of the insulator-metal phase transition and find good agreement with the equilibrium change. In addition, we find an anomalously large transient change in the photo-excited metallic phase, which we attribute to a broadening of the $\pi^*$ state. Our results show the importance of thermal management in ultrafast measurements of thin free-standing samples in vacuum as well as highlight the interesting physics that can be found in the previously investigated metallic phase of VO\textsubscript{2}.

The insulator-metal phase transition (IMT) in VO\textsubscript{2} is a complex process in which the structure and electronic properties change. At room temperature, VO\textsubscript{2} is insulating with a monoclinic (M\textsubscript{1}) crystal structure. On heating above 338 K it undergoes a first-order insulator-metal phase transition in which the lattice changes to a rutile (R) structure and the conductivity increases by many orders of magnitude. The driving mechanism for this phase transition has been hotly debated, with strong arguments for both the electronic and lattice degrees of freedom as the main force. The fact that light can also trigger the phase transition on the ultrafast timescale has opened the possibility of directly watching how the transition occurs in real time. This new perspective could shed new light on the nature of the transition and a diverse range of ultrafast techniques has been employed and developed in order to study the transition in VO\textsubscript{2}.

Time-resolved soft X-ray absorption (XAS) is a particularly useful technique for studying the phase transition of VO\textsubscript{2}, as it is sensitive to both electronic and structural changes, as well as having element specificity. In particular, the pre-edge absorption features at the oxygen K-edge are amongst the most studied and most understood, with sensitivity to the unoccupied states near the Fermi level\textsuperscript{1,2}. These
features have been used to highlight the role of correlations\textsuperscript{3,4}, to identify the presences of other insulating states\textsuperscript{5}, to suggest evidence for a monoclinic metallic state\textsuperscript{6}, and to image phase separation with a high spatial resolution\textsuperscript{7}. The first time-resolved XAS experiments were performed by Cavalleri and co-workers, first on the picosecond timescale\textsuperscript{8} and later on femtosecond timescales\textsuperscript{9}. However, these experiments covered only a limited range of wavelengths and there have not been subsequent studies in this important spectral region.

In this work, we re-examine the XAS dynamics measured with picosecond time resolution with X-rays generated at a synchrotron. For the first time we can observe transient XAS spectra associated with the insulator-metal transition across the entire oxygen pre-edge. We also report an anomalously large transient change in the transmission of the metallic phase. Our work also highlights the crucial role of heat dissipation, which limits the recovery time of samples between subsequent pump laser pulses.

This places important restrictions on future transient XAS measurements performed in the soft X-ray regime using free electron lasers (FELs), attosecond sources, or time-resolved nanoscale imaging with soft X-Rays.

The oxygen K-edge absorption is shown in Figure 1a for the insulating (300 K) and metallic (360 K) phases measured with 0.1 eV energy resolution. Strong covalent hybridization occurs between the oxygen 2p and vanadium 3d levels\textsuperscript{10} and the main features are well described by the model initially proposed by Goodenough\textsuperscript{11}. In this model, the hybridization of O 2p orbitals with the 3d\textsubscript{xz} and 3d\textsubscript{yz} orbitals, which point in between the ligands, give rise to the π\textsuperscript{*} states. The 3d\textsubscript{z2−r2} and 3d\textsubscript{xy} orbitals, which point towards the ligands, form the α\textsuperscript{*} states, while the relatively nonbonding 3d\textsubscript{xy} orbitals parallel to the rutile c-axis that mediate the V-V bonds form the d\textsubscript{∥} states. During the IMT, the V atoms dimerize along this axis, splitting the d\textsubscript{∥} band into filled bonding and empty antibonding states. In addition, the tilting of these dimers in a zig-zag pattern narrows the π\textsuperscript{*} band, which lifts it above the Fermi level\textsuperscript{12}. Following this model, the first peak in the spectrum at 529 eV corresponds to the π\textsuperscript{*} states, which shows a small red shift on entering the metallic phase as the band crosses the Fermi level and lower-energy transitions can be probed. The second main peak, at 532 eV, corresponds to the α\textsuperscript{*} states, which do not show a significant change. A third peak, at 530.5 eV, is only observable in the insulating phase and corresponds to the unoccupied d\textsubscript{∥} band that is split in the M\textsubscript{1} phase\textsuperscript{1,3,12}. Thus, the insulator-metal phase transition can be tracked through changes in the d\textsubscript{∥} and π\textsuperscript{*} states.

The time-resolved XAS measurements were carried out at the FemtoSpeX facility (UE56/1 ZPM) at BESSY II\textsuperscript{13,14}. A 70 nm thick VO\textsubscript{2} thin film was deposited onto a 150 nm thick free-standing Si\textsubscript{3}N\textsubscript{4} membrane, and was maintained under ultra-high vacuum conditions. 800 nm laser pulses of 50 fs duration excited the sample and soft X-rays from the isolated hybrid bunch in the normal multi-bunch pattern were gated to probe the response in transmission with approximately 70 ps temporal and 1 eV spectral resolution. The high spectral bandwidth of the X-ray pulses is designed to increase flux, but reduces the XAS features, which can be seen in the dashed trace in Figure 1b. The light-blue trace in Figure 1b corresponds to the high-resolution spectrum (measured at the UE52-SGM beamline and shown in Figure 1a) after convolution with a 1-eV-width Gaussian function. Despite the relatively low energy resolution, these measurements still represent a factor of four improvement over previous measurements\textsuperscript{8,9}.

The pump laser repetition rate was set to 600 Hz and the sample was cooled to a base temperature of 90 K in order to avoid laser-induced heating. At this reduced pump frequency, the acquired data...
suffer from much lower statistics compared to the usual frequency of 3 kHz at the FemtoSpeX facility. Two X-ray pulses were used to probe the sample. One pulse, the pumped signal, arrives together with the excitation laser with the exact arrival time scanned over a few 100 picoseconds. The second X-ray pulse gives the unpumped signal, in which the X-rays probe the system one round trip of the synchrotron, or 800 ns, before the laser pulse excites the system.

Figure 2a shows three typical transient signals. At a fluence of 4.4 mJ cm$^{-2}$ the transmission at 529 eV decreases, while the transmission at 530.5 eV increases after photo-excitation. These changes are expected for the insulator-metal phase transition. On the hundreds of picoseconds timescale measured here, the initial response is resolution limited and shows no subsequent evolution, suggesting that the phase transition has transformed the whole volume and no subsequent growth of the metallic phase is observed. Interestingly, when the pump fluence is increased to 18 mJ cm$^{-2}$, the response at 530.5 eV changes sign and the transmission decreases in a way that cannot be reconciled with the IMT. This crossover in behaviour is clear from the fluence dependence, shown in Figure 2b. Above a threshold fluence of 3 mJ cm$^{-2}$, the XAS signal shows strong and concomitant changes at both the $d_{∥}$ and $\pi^*$ levels, probed at 530.5 eV and 529 eV, respectively; these signals increase in amplitude until 4.4 mJ cm$^{-2}$. After this point, they begin to decrease, and no transient change is observed at 5 mJ cm$^{-2}$. However, increasing the fluence above this level results in a second signal observed at 530.5 eV, which gradually increases in amplitude, but opposite in sign to the lower-fluence signal.

To understand the nature of these states we plot the full transient change in transmission at the oxygen edge in Figure 2c. The change, when excited with 4.4 mJ cm$^{-2}$ (red line) shows the corresponding decrease and increase in absorption of the $d_{∥}$ and $\pi^*$ states, respectively. This behaviour matches the transition from the insulating M$_{1-}$ to the metallic R-phase, as evidenced by the good agreement between the transient spectrum and the light-red line corresponding to the differential spectrum of the convolved static metallic and insulating spectra from Figure 1a. On the other hand, when the sample is excited with 18 mJ cm$^{-2}$, the transient spectrum shows a negative change in transmission at all photon energies, peaking around 530 eV.

The signal between 3-4.4 mJ cm$^{-2}$ can be identified as the transient photo-induced insulator-metal transition. However, while thresholds in the region of 4 mJ cm$^{-2}$ are common for the driven transition at room temperature$^{15}$, they shift to higher values when the sample is cooled$^{16}$. This points to a significant heating contribution to the signal, which has been previously identified on free-standing thin films$^{17,18}$. To determine the role played by laser-induced heat, we plot both the transmitted intensity of the pumped and unpumped channels at a delay of ± 400 ps as a function of fluence in Figure 3. At a positive delay of 400 ps, both channels present an abrupt change in transmission when the fluence reaches a critical value (see Figure 3a). This transition occurs for lower fluences in the pumped channel than in the unpumped one. On the contrary, the change occurs at the same fluence in both channels at negative 400 ps delay, as seen in Figure 3b. This shows that the quasi-equilibrium properties of the sample have changed due to the presence of the pump.

To demonstrate that this change is due to heat accumulation driving an equilibrium insulator-metal transition, we perform optical pump-probe measurements on the same samples under similar experimental conditions. Figure 3c shows the transient optical response at 600 nm. At low fluences (light-red line), the response of the monoclinic phase can be observed, easily identified from the coherent phonons oscillations of the M$_{1-}$-phase. Note that at this fluence we do not observe an XAS signal (Figure 2b), as the lattice and electronic structure has not changed. At 5.8 mJ cm$^{-2}$ (red line) the
phonon signal is strongly suppressed, indicative of the transient insulator-metal phase transition\textsuperscript{19,20}. In this region, the transient XAS response shows the features associated with the insulator-metal transition. At high fluence (dark-red line), the pump-probe trace changes dramatically and corresponds to the transient response of the metallic phase, characterized by a sharp spike-like change in optical transmission near zero time delay\textsuperscript{20}. The small differences in threshold fluence between the data sets are due to the difference in laser repetition rate, which was 500 Hz for the optical data, compared to 600 Hz for the X-rays. This enables slightly more time for the sample to recover, and therefore slightly reduced temperature increases for the same fluence.

We now turn to examine the nature of the photo-excited metallic state. Previous transient XAS experiments have also shown rapid changes in the metallic phase of VO\textsubscript{2}\textsuperscript{17}. However, these were recorded at the vanadium M-edge, which is less well understood and harder to interpret. To understand these dynamics we focus on the π\textsuperscript{+} states. Figures 4a, b show, schematically, how the band structure and corresponding XAS signal change, due to the equilibrium IMT. The pre-edge absorption shifts to lower energy as the π\textsuperscript{+} states lower in energy due to new states appearing in the insulating gap, and the X-rays probe the states near the Fermi level. Figures 4c, d show two possible scenarios for the dynamics in the metallic state. If the response were purely electronic (c), resulting from an increase in the electronic temperature, previously filled states below the Fermi-level would be de-populated, while states above the Fermi-level, would become partially occupied. This should modify the absorption in a small region at the start of the pre-edge. Below the initial edge, the absorption should increase, as X-rays can now probe the lower-energy depopulated states. Likewise, a small region above it should show a decrease in absorption because of increased Pauli-blocking. However, we do not observe such a bi-polar feature in our data at 18 mJ cm\textsuperscript{-2}. Alternatively, the bandwidth of the π\textsuperscript{+} states could continue to broaden in the metallic phase, as occurs during the insulator-metal transition\textsuperscript{12}. This would result in an increase in absorption well above the Fermi level, as the top of the conduction band increases in energy. This broadening is consistent with the fact that the lattice continues to harden above T\textsubscript{c}\textsuperscript{21}. Interestingly, spectral weight is not conserved in this region, which could also imply that this phenomenon results from an increase in hybridization with oxygen 2p and vanadium 3d levels. However, further measurements and theoretical calculations are required in order to fully understand these dynamics.

We note that the long recovery times measured here are not intrinsic to VO\textsubscript{2}, but a result of the type of sample and the vacuum conditions. The time scale for the heat deposited by the laser pulse to dissipate is set by the temperature gradient generated in the sample. In absorbing samples, light can only penetrate a few hundred nanometers. Therefore, thick samples can have temperature gradients on this length scale. This results in recovery times of order 1 ns for thermal diffusivities of order 10\textsuperscript{-5} m\textsuperscript{2}s\textsuperscript{-1}. However, for thin, free-standing samples, which are thinner than the absorption length, there is no thermal gradient into the depth of the material. As a result, heat transport can only occur in the transverse direction. The thermal gradient in the transverse plane is set by the pump spot size, which is of order a few hundreds of microns for X-ray or electron diffraction experiments. This results in recovery times that are six orders of magnitude longer, i.e., in the millisecond regime, and leads to substantial temperature rises if the repetition rate of the pump laser is too high.

Our samples are of similar thicknesses to that used by Cavalleri and coworkers\textsuperscript{8,9}. However, the base temperature for those measurements was room temperature, and the laser fluence and repetition rate were significantly higher. As a result, we believe that the initial pioneering measurements on the
phase transition in VO$_2$ were in fact performed on the photoexcited metallic state and did not reflect the dynamics of the insulator-metal transition.

In conclusion, we have found conditions in which the insulator-metal transition can be measured at a reasonable repetition rate and provided the first measurement of the transient XAS spectra of the insulator-metal transition across the oxygen pre-edge. We have also observed that the metallic response shows an interesting response, which may be the result of a broadening of the $\pi^*$ states. Managing heating was key to these measurements, but will be a serious challenge for future experiments that require strong laser excitation and high repetition rates, as required for attosecond spectroscopy in which the number of photons per pulse generated in the soft X-ray region is low. This suggests that FEL measurements in the soft X-ray regime, which typically operate at much lower repetition rates, will play a stronger role in this field.

Figures

**Figure 1 X-ray transmission spectra of VO$_2$ at the oxygen $K$-edge.** (a) Static, high-resolution spectra measured at low and high temperatures show the absorption peaks corresponding to the $\pi^*$, $d_{\parallel}$ and $\sigma^*$ bands. The $\pi^*$ shifts to lower energy and $d_{\parallel}$ state is lost due to the closing of the band gap. The $\sigma^*$ states do not show a significant change. (b) The low temperature XAS spectra measured with $\sim$1 eV resolution at the FemtoSpex beamline (dashed line) compared to the low temperature data in (a) convolved with a 1 eV energy resolution. The discrepancy is likely due to different backgrounds in the two measurement techniques.
Figure 2 Transient XAS changes. (a) The time traces of the d|| (530.5 eV) and π* (529 eV) states show the corresponding positive and negative responses when pumped with low fluence. At high fluence the d|| signal presents a change of sign with respect to the insulator-metal transition. (b) Above the threshold of 3 mJ cm\(^{-2}\), the amplitude of the signal of both states increase with fluence until it reaches 4.4 mJ cm\(^{-2}\). After this point, they decrease until no significant change is observed at 5 mJ cm\(^{-2}\). A signal with opposite sign can be seen when the fluence is further increased. (c) The transient spectra at the oxygen K-edge when pumped with 4.4 mJ cm\(^{-2}\) (red line) and 18 mJ cm\(^{-2}\) (purple line) at positive 400 ps delay. The light-red line corresponds to the calculated differential static spectra in Figure 1a convolved with a spectral resolution of 1 eV.

Figure 3 Heat dissipation in the sample. (a) Transmitted intensity measured in the pumped and unpumped channels of the diode for positive delays. A transient signal is observed only in the pumped channel for a threshold fluence of 3 mJ cm\(^{-2}\). An abrupt change in transmission occurs in the unpumped channel above 4.4 mJ cm\(^{-2}\), and the difference signal is reduced. The small difference between the traces at low fluence is due to a small offset in the data acquisition settings in the two channels. (b) At negative time delays, the transmission change is observed in both channels at the same fluence, suggesting the sample has been heated into the metallic state. (c) The 800 nm pump, 600 nm probe traces measured in equivalent conditions. For low pump fluences (2.2 mJ cm\(^{-2}\)), the oscillations of the M\(_1\)-phase phonon modes can be observed, indicating the sample is monoclinic. At higher fluences (5.8 mJ cm\(^{-2}\)) the phonons are suppressed, as expected for the transient insulator-metal transition. Above 8 mJ cm\(^{-2}\), the sample shows a clear offset at negative delays and the transient response of the metallic phase\(^{30}\), indicating the sample has been heated above the insulator-metal transition.
Figure 4 Photo-excited metallic state X-ray spectra. (a) Schematic of the density of states (DOS) probed by soft X-rays (SXR) in the insulating state. For simplicity only the $\pi^*$ states are considered. Absorption first occurs into the unoccupied states, which are separated from the Fermi level by the band-gap. When the metallic state is formed, the $\pi^*$ states move below the Fermi energy and the XAS absorption occurs for lower energies. (c) A hot electronic state reduces the occupation of states below the Fermi level and increases it above, resulting in an increase in absorption at low photon energies and a decrease for higher photon energies. (d) Band broadening enables more absorption at higher photon energies without shifting the start of the absorption process, which is compatible with the spectral changes reported in Figure 2c at 18 mJ cm$^{-2}$.

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