

Band-Selective Measurements of Electron Dynamics in VO₂ Using Femtosecond Near-Edge X-Ray Absorption

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We report on the first demonstration of femtosecond x-ray absorption spectroscopy, made uniquely possible by the use of broadly tunable bending-magnet radiation from “laser-sliced” electron bunches within a synchrotron storage ring. We measure the femtosecond electronic rearrangements that occur during the photoinduced insulator-metal phase transition in VO₂. Symmetry- and element-specific x-ray absorption from V2*p* and O1*s* core levels (near 500 eV) separately measures the filling dynamics of differently hybridized V3*d*-O2*p* electronic bands near the Fermi level.

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X-ray measurements on the femtosecond time scale, which combine powerful probes of matter with access to elementary time scales of atomic motion, have to date concentrated almost exclusively on time-resolved diffraction with hard x-ray pulses [1–4]. These early experiments have been enabled primarily by monochromatic ultrafast x-rays from laser-produced plasmas, by femtosecond-laser interaction with relativistic electron-beams [5], and most recently by femtosecond x-ray pulses from a linac [6].

X-ray spectroscopy techniques like near-edge x-ray absorption fine structure (NEXAFS), magnetic circular dichroism (MCD), and extended x-ray absorption fine structure (EXAFS) are important complements to diffraction, probing local electronic, magnetic, and short-range atomic structures with element specificity. A long-standing scientific frontier is their application in time-resolved experiments with femtosecond resolution, to interrogate the dynamics of electronic and magnetic phase transitions in solids or the atomic motions that mediate chemistry within disordered liquids. Yet, because most of the existing femtosecond x-ray sources are not easily tuned, this class of experiments has to date remained an elusive goal.

In this Letter we report on the first demonstration of femtosecond x-ray absorption spectroscopy. Our experiments make use of “laser-sliced” synchrotron pulses, which combine the broad tunability of bending-magnet radiation with the femtosecond time duration of mode-locked lasers [7]. We measure the electronic dynamics in VO₂, a strongly-correlated compound that undergoes an insulator-to-metal phase transition when photo excited with light [8]. Time-resolved near-edge x-ray absorption spectroscopy at the vanadium *L* edge (516 eV) and at the oxygen *K* edge (531 eV) allows separate access to the variously hybridized V3*d* and O2*p* orbitals near the Fermi level.

The photoinduced insulator-to-metal transition in VO₂ is one of a broader class of ultrafast photo-control phe-

nomena in inorganic [9] and organic [10] correlated-electron systems, which are interesting for both basic science and applications [11]. In its low-*T* phase VO₂ has a cell-doubled monoclinic structure and insulating characteristics, resulting from the formation of localized

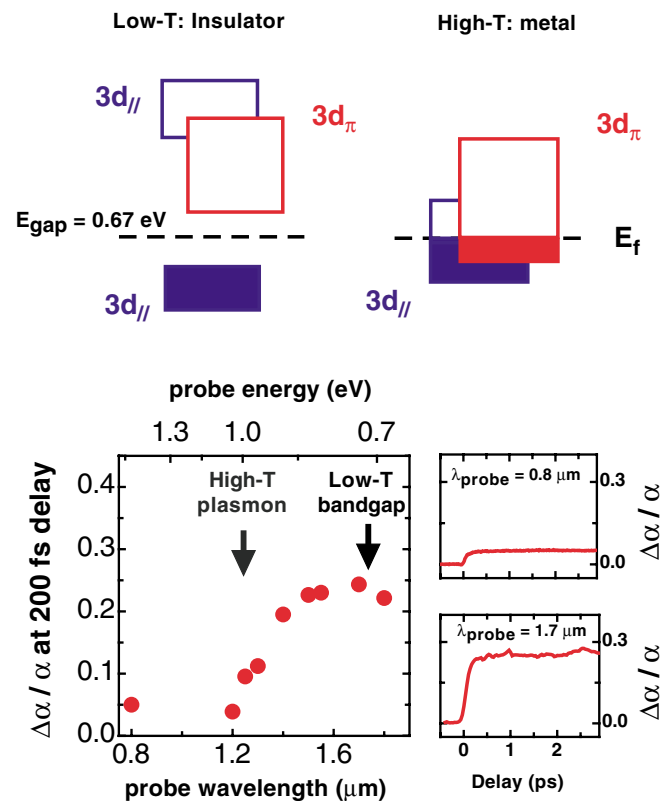


FIG. 1 (color). Top: electronic structure of VO₂ in the equilibrium insulating and metallic phase. Bottom: differential infrared absorption measurements at various wavelengths in the optical band gap region, following excitation with 60 fs pulses at 800 nm.

spin singlets on V^{4+} dimers and by the opening of a Peierls gap. Photo excitation depletes the localized singlet states that form the valence band, injecting electrons into the spatially extended conduction band. As a result of prompt “photo doping,” the structural dimerization rapidly relaxes, and the metallic phase is formed on the 100 fs time scale [3,12].

An ultrafast insulator-to-metal transition is clearly evidenced by the femtosecond infrared absorption measurements reported in Fig. 1, measured in pump-probe geometry with 800 nm femtosecond-laser excitation of VO_2 films (50–200 nm thick) on Si_3N_4 windows (200 nm thick). Above a threshold fluence of 3 mJ/cm^2 a steplike increase in the absorption coefficient below 1 eV was observed. Formation of the metallic state is thus indicated by (1) appearance of a near-1 eV plasma edge and by (2) collapse of the semiconducting band gap at 0.67 eV. Above 10 mJ/cm^2 , the changes in the optical properties were independent of excitation level and saturated over a broad fluence range, extending to the damage threshold of 50 mJ/cm^2 . Such saturated dependence on the excitation fluence rules out mere carrier excitation as an explanation for the observed dynamics and is rather indicative of an ultrafast insulator-to-metal transition, as concluded in previous experiments [3,13,14].

Beyond the identification of the metallic product phase, the dynamics within this complex electronic structure cannot be exhaustively addressed with infrared spectroscopy alone. In fact, the response at visible and near-infrared wavelengths is primarily sensitive to the joint density of

band gap states and to the collective response of the electronic plasma. The variously hybridized valence states of VO_2 can instead be distinguished with near-edge x-ray absorption spectroscopy. Because of dipole selection rules, $3d$ -symmetry bands are selectively probed by measuring x-ray absorption from the $V2p$ core levels near 516 eV. The $V3d_{\pi}$ band, which derives from strong mixing between $V3d$ and $O2p$ orbitals [15], is instead most visible at the $O1s$ resonance (530 eV) [13]. An exhaustive discussion of the signatures of the VO_2 electronic structure in the optical and x-ray absorption spectra can be found in Refs. [13,15]. Static XAS spectra from the thin-film samples used in our experiments are shown in the upper part of Fig. 2, where blue and red are used to highlight transitions from the $V2p$ and $O1s$ into the unoccupied $V3d_{\parallel}$ and $V3d_{\pi}$ states (see also Ref. [14] for details on these static XAS measurements).

Time-resolved x-ray absorption measurements were performed with femtosecond pulses of synchrotron radiation, generated by laser modulation of the electron-bunch energy within a wiggler (see experimental setup in Fig. 2). The modulated time slice of the electron bunch was spatially separated from the main orbit in the radiating bending magnet, where the electron beam energy was dispersed along the radius of the storage ring. Femtosecond radiation was thus emitted off axis by the bending magnet, with a characteristic spectrum extending from the THz to the hard x-ray region. The femtosecond pulses of synchrotron radiation, focused onto the VO_2 sample with a toroidally bent silicon mirror, were spatially selected using a slit in the

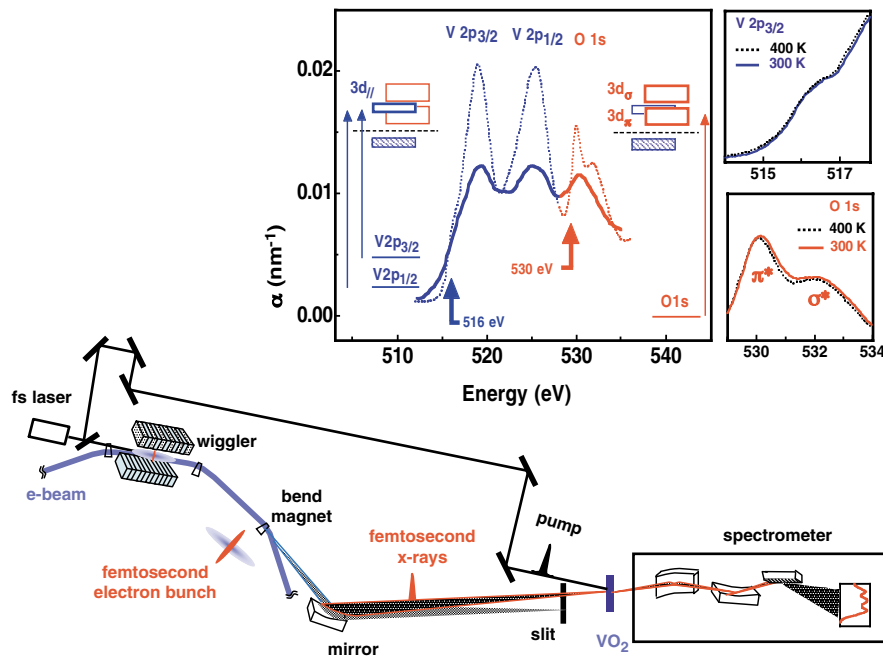


FIG. 2 (color). Top: static soft x-ray absorption of VO_2 at the $V2p$ and $O1s$ absorption resonances. The high-resolution spectra were collected at beam line 6.3.2 of the ALS with 100 meV resolution. High-resolution x-ray absorption changes across T_c are reported. Bottom: experimental setup for femtosecond XAS experiments.

image plane of the bend-magnet source. A flat-field imaging spectrometer was used to disperse the transmitted soft x rays after the sample, generating femtosecond spectra between 100 eV and 800 eV with a resolution of 4 eV at 500 eV.

The femtosecond x-ray-absorption response, measured on the rising edge of the two resonances (see arrows in Fig. 2) is reported in Fig. 3(a). At the $V2p_{3/2}$ edge, a prompt increase in absorption was observed immediately after photo excitation, recovering within a few picoseconds. At the $O1s$ resonance, the absorption coefficient was also initially observed to increase, synchronously with that at the $V2p_{3/2}$ resonance. Enhanced $O1s$ absorption at 530 eV was followed by bleaching and by relaxation on the same few-picosecond time scale as the signal at the 516 eV $V2p_{3/2}$ edge. Our interpretation of the data, schematically illustrated in Fig. 3(b), considers two main effects: (1) valence band filling/rearrangements and (2) dynamic shifting of the core levels.

First, laser photo doping depletes the d -symmetry valence band, populating the $3d_{\pi}$. Band gap collapse follows immediately, leaving the electrons in a transient, hot Fermi distribution with $T_e \gg T_l$. As a third step, electrons thermalize with the lattice within a few picoseconds. In the hot-electron metal, the broad $3d_{\pi}$ band remains overpopulated by the tail of the distribution, while the narrower $3d_{\parallel}$ band has still lower electron occupancy than at equilibrium. For a rigid band structure and no shift in the core levels, a prompt increase in absorption at the $V2p$ edge and bleaching at the $O1s$ resonance is expected, with a decay time of a few picoseconds. In the data, the $V2p_{3/2}$ absorption promptly increases and indeed remains higher than at equilibrium for a few picoseconds, as expected from the above considerations. Note that the subpicosecond transients reported in Fig. 3(a) are related to the nonequilibrium photo-doping process, and the signal is larger than either the thermally induced changes or those observed at longer time delays, after electron-hole thermalization [14]. Thus, the increased absorbance at 516 eV can be reconciled with hole photo doping into the $3d_{\parallel}$ band. On the other hand, filling and shifting of the valence bands alone does not explain the dynamics at the $O1s$ edge, where a simple bleaching (decreased absorbance) would be expected.

Second, photo excitation into the $3d_{\pi}$ band transiently increases the valency of the O^{2-} anion, reducing that of the V^{4+} cation. This effect can be as high as 0.25 electrons/ O^{2-} anion and 0.5 holes/ V^{4+} cation for 50% photo doping estimated for the 25 mJ/cm² used in the experiments. This valence-charge unbalance likely results in a dynamic shift of the $O1s$ core level toward lower binding energy, while the $V2p$ states shift toward higher binding energy. Thus, a blueshift of the vanadium L edge and a redshift of the oxygen K edge are expected immediately after excitation, driving x-ray absorption at

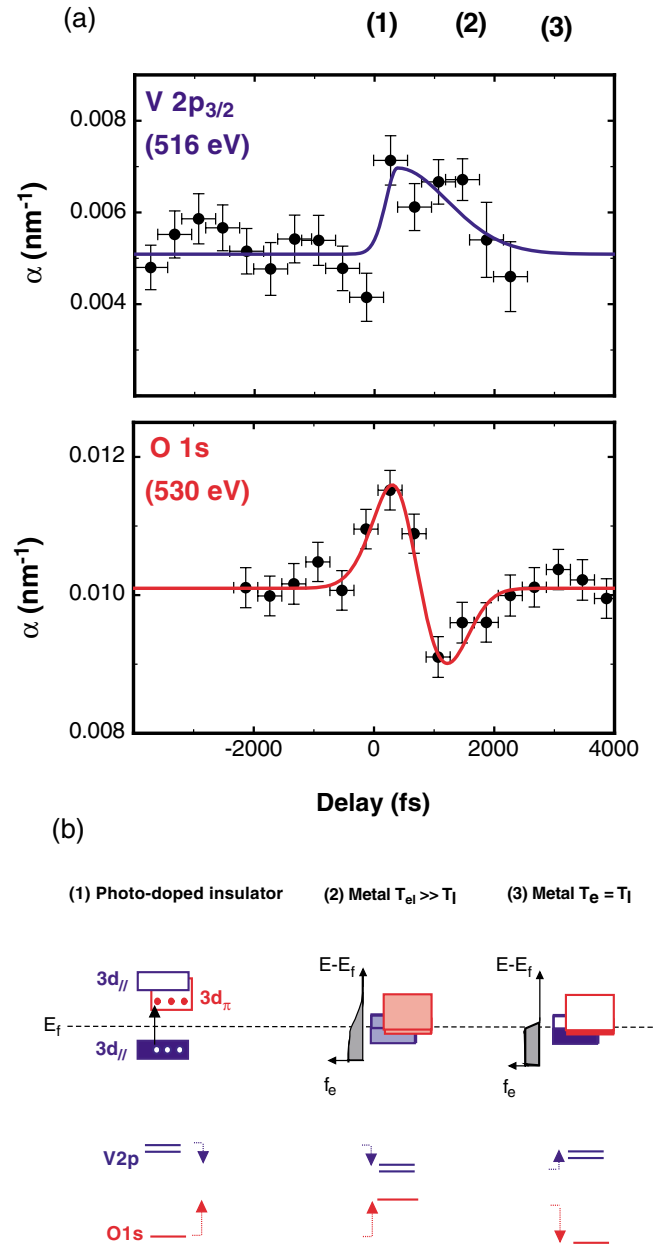


FIG. 3 (color). (a) Femtosecond XAS measurements at the $V2p$ and $O1s$ resonances. Vertical error bars represent one standard deviation of the photon counting distribution. Horizontal error bars reflect the long-term drift in the delay between laser pump and x-ray probe pulses measured via cross correlation with visible femtosecond synchrotron pulses [7]. Solid lines are guides to the eye. (b) Illustration of the photo-induced rearrangement of electronic population between the $3d$ -symmetry valence band and the mixed $3d_{\pi}$ orbitals. (1 left) Photoexcitation results in (2 middle) a collapse of the band gap, the creation of a nonequilibrium electron distribution, and an increase (decrease) of the $V2p$ ($O1s$) binding energies due to transient charge transfer from V^{4+} anions to O^{2-} anions. (3 right) Transient core-level shifts recover as the hot electron distribution thermalizes with the lattice, reestablishing the valency of the equilibrium metal.

516 eV and at 530 eV in the opposite directions as non-equilibrium band filling. The shift of the $V2p$ core levels is expected to be relatively small when compared to the 4 eV resolution of our experiments. This can be estimated by noting the small binding-energy differences for different oxides of vanadium, amounting to few hundred meV for valency changes of one full electron/cation in V_2O_3 versus VO_2 [16]. On the other hand, measurements of the $O1s$ binding energy in SiO_2 and ZrO_2 reveal large shifts for subtle differences in ionicity of the chemical bonding, despite a nominal O^{2-} valency in both cases [17].

Significant improvement in our understanding of all these processes will also result from future experiments with increased x-ray flux, where entire x-ray absorption spectra with femtosecond time resolution will be measured. Approximately one-thousand-fold increase in the femtosecond x rays will result in the future by using undulator radiation and by increasing the laser repetition rate [18]. Second, for experiments that rely on dense photo excitation, time-resolved core-level x-ray photo emission should be performed as a complement to femtosecond NEXAFS experiments.

In summary, we have reported on femtosecond x-ray-absorption spectroscopy experiments, made possible by the use of a femtosecond laser to manipulate the electron energy distribution within a synchrotron storage ring. By comparing the response of photo-excited VO_2 at two absorption edges, we can separate the electronic dynamics within selected bands of different orbital symmetries. The tunability of bending-magnet radiation allows for femtosecond x-ray spectroscopy in the soft x-ray region below 1 keV, which is important for studies of transition metal oxides (L edges of metals and K edge of oxygen) and organics (K edge of carbon). Tunability of ultrafast x-ray pulses will, with appropriate flux increases, make possible new science in the areas of ultrafast magnetic phenomena, chemical dynamics at surfaces, in the gas phase, or in liquids [19–21].

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