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Ultrafast Dynamics in the Insulator-to-Metal Phase Transition of Vanadium Dioxide Measured by Attosecond Transient Absorption Spectroscopy

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Abstract: The photoinduced insulator-to-metal phase transition in vanadium dioxide is experimentally investigated by attosecond transient absorption spectroscopy. Ultrafast changes cover a broad ~20-eV-wide spectral range, emphasizing core spectroscopic access and the importance of electron correlation effects.

OCIS codes: (160.0160) Materials; (190.0190) Nonlinear Optics; (300.1030) Spectroscopy, Absorption; (300.6500) Spectroscopy, time-resolved; (300.6560) Spectroscopy, x-ray; (320.7130) Ultrafast processes in condensed matter

The insulator-to-metal phase transition in vanadium dioxide (VO₂) has been subject of extensive scientific investigations throughout the decades, dating back to its discovery in the 1950s [1]. Upon heating above the transition temperature at $T \sim 340$ K, it undergoes both a change in the electronic structure that incorporates a collapse of the insulating bandgap of 0.7 eV towards a metallic filling of electronic states at the Fermi level, as well as a change in its crystallographic structure, moving from an insulating (low T) monoclinic to a metallic (high T) rutile structure. One fascinating aspect of this material is the complex interplay between both lattice and (correlated) electronic degrees of freedom, which even to date poses challenges that make a complete and comprehensive theoretical treatment of the phase transition a difficult task. Some time ago, the question has been raised, whether structural or electronic degrees of freedom are the microscopic driving force of the phase transition [2].

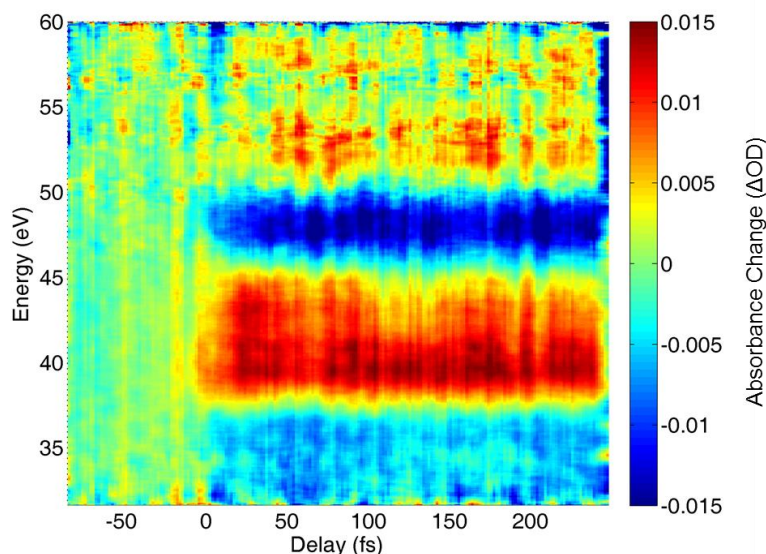


Fig. 1: Measurement of transient changes in the extreme ultraviolet absorption spectrum of VO₂. The transition is probed around the vanadium 3p to 3d resonant excitation at 40 eV, following the pump photoexcitation with a 5-fs-duration (FWHM) few-cycle laser pulse (center wavelength: 760 nm) at ~30 mJ/cm² pump fluence. The instrumental response function has been determined *in-situ* via probing inner-valence transitions in neon, yielding <7 fs temporal resolution.

The goal of the presented experiment is to directly separate the fast electronic degrees of freedom from the slightly slower motion of the lattice via utilizing attosecond transition absorption spectroscopy in ultrathin solid state samples of VO₂. Furthermore, the core spectroscopic fingerprint nature of the associated extreme-ultraviolet (XUV) spectral range will serve as unique probing tool.

Few-cycle 5-fs-duration (FWHM) carrier-envelope-phase stabilized laser pulses are obtained from a commercially available Ti:Sapphire multipass amplifier (Femtolasers, 1.6mJ, 1 kHz), spectrally broadened in a hollow-core fiber, and subsequently compressed with chirped mirrors. These broadband pulses (spanning <600 to 900 nm) are focused to a pump fluence on the order of ~30 mJ/cm². A time-delayed fraction (80%) of the laser pulses is used to drive high-harmonic generation in krypton gas (~ 30 Torr backing pressure), with optimized generation parameters for highest photon flux in the 40 to 50 eV region, yielding close-to-continuous XUV spectra of an attosecond-pulsed light source as the probe. The instrumental response function has been determined *in situ* [3], in parallel to the measurements to the VO₂, via analyzing the coupling dynamics of inner-valence transitions in neon, which yields <7 fs temporal resolution. In order to avoid sample damage and unwanted thermal heating effects in the ~20 nm thin VO₂ samples (supported by a 25 nm thin free-standing membrane of silicon nitride), the laser repetition rate is reduced to 100 Hz for the experiment. Furthermore, a high-speed rotation is utilized to ensure that each subsequent laser pump-probe pulse pair gains access to a fresh spot of the VO₂ sample, rotating it by a little less than 120 degrees in between subsequent shots.

Figure 1 depicts the main result of the measurement. The XUV spectral range covers the vanadium M_{2,3} edge (3p core initial state) that occurs in VO₂ at 39 eV [4]. At energies close to this value, a dipole-allowed resonant excitation into empty 3d states around the Fermi level is possible. A prompt rise at this energy (39 eV and above) is apparent from the data, which supports an ultrafast collapse of the band gap as recently discussed in the literature [5]. Furthermore, transient changes are apparent over a much wider spectral region, spanning from below 35 eV to above 50 eV. The most prominent feature is a strong increase in absorbance (10 to 15 mOD) spanning 40 to 45 eV, and an equally strong decrease in absorbance at higher energies in between 47 and 50 eV. A weaker decrease in absorbance (5 mOD) can also be seen at energies below 38 eV. At the highest energies (>50 eV) within the probed spectral window, a weak increase in absorbance just above the noise level can be observed. The enhanced noise in this region is due to the fact that the employed XUV high-harmonic photon flux was reduced at these energies. Each spectral region appears to support an absorbance change established within the first ~25 fs, which subsequently stays constant over the whole range scanned up until ~250 fs.

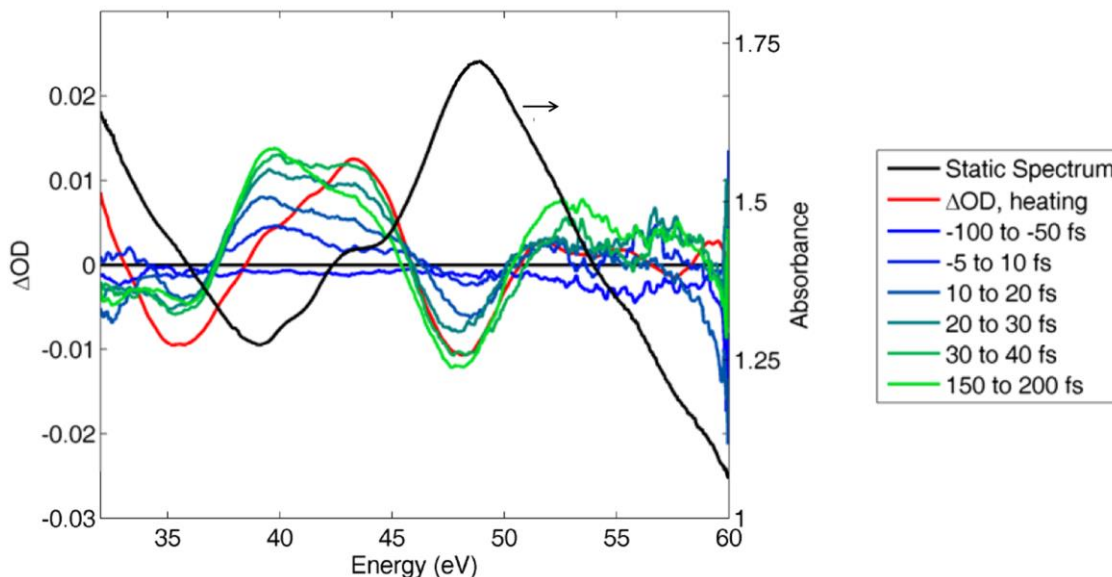


Fig. 2: The XUV spectroscopic fingerprint of the absorbance changes (left axis scale) in VO₂. The NIR photoinduced changes (blue to green curves) are compared to changes upon heating the sample above the transition temperature (red curve). The ground-state static spectrum is also shown (black curve) with absolute optical densities shown (right axis scale). The legend further denotes the temporal delay regions over which of the photoinduced absorbance changes have been averaged, respectively. The data shown reflects the transient response as plotted in Fig. 1.

In order to more quantitatively discuss the different spectral regions, selected temporal lineouts are shown in Figure 2, along with changes of the XUV absorbance upon heating of the VO₂ sample. In addition, also the static absorption response around the vanadium M_{2,3} edge is shown. Especially at energies 43 eV and above, it is striking to see that the photoinduced transient changes match the thermally induced changes almost perfectly after only 20 to 30 fs. On the other hand, for instance at 40 eV, the photoinduced response clearly rises and converges to higher magnitudes than are seen for the thermally induced response. These findings suggest that a non-thermal metallic phase could be at play, which is also supported by findings in recent literature [5], establishing a monoclinic metallic phase as an intermediate photoinduced phase that is triggered by the fast motion of electrons/holes, which only later is stabilized into the rutile metallic phase by the delayed motion of the heavier ions. Furthermore, the presence of hot carriers upon photoexcitation is also expected to contribute to the measured absorption changes.

In general, the occurrence of transient changes across a very broad (~20 eV) spectral range emphasizes the fact that mechanisms such as Pauli state opening/blocking alone cannot explain all details of the observed transients. The energy span is clearly beyond the accessible range of the single-photon excitation spectrum of the pump pulses that are being used. Instead, a more likely scenario for their explanation involves multi-electron correlation effects of the strongly interacting vanadium 3p and 3d orbitals, as well as core-level screening effects. The latter would manifest as spectrally shifting features of the static absorbance spectrum. The importance of core-level shifts and their connection to electronic and lattice degrees of freedom have also been discussed in the literature [4].

In conclusion, ultrafast attosecond transient absorption spectroscopy measurements in VO₂ have been presented at unprecedented temporal resolution (< 7 fs instrumental response function). Most importantly, the spectroscopic access to a broad spectral range, covering the vanadium 3p level, and the combined study of the heating-induced and the time-resolved photoinduced spectral response allows for a careful comparison to advanced theoretical interpretations in the future. This finally highlights the fact that the technique of attosecond transient absorption spectroscopy is fit for analyzing and disentangling structural and electronic degrees of freedom when studying the complex class of strongly correlated materials.

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