We present a study that uses a technique extending upon high harmonic spectroscopy, which is generated as a function of photoexcitation pump fluence to probe the resulting time-resolved electronic dynamics of the insulator-to-metal phase transition in VO$_2$ [1]. When heated to above ~343 K, VO$_2$ experience a complete atomic rearrangement of the crystal lattice structure from a monoclinic insulator (M$_1$ phase) to a metallic rutile crystalline structure (R phase). When initiating this IMT via photoexcitation, the pathways are even more complex. After photoexcitation, the ultrashort pulse immediately excited electrons creating the M$^*$ state. With sufficient pump energy, the periodic lattice of the M$_1$ phase can transition completely into the R phase. If there is insufficient energy, after a few hundred femtoseconds, the excited photodoped electrons in the M$^*$ state relax into a pseudothermal state in which the thermalized photodoped populations have the same chemical potential (M$^{*,b}$ state). After about a picosecond, the M$^{*,b}$ state then transitions into a long-lived metastable monoclinic metallic $\mathcal{M}$ state. If the pumping fluence is between these two thresholds, a final metallic mixed state of rutile and monoclinic is produced (R + $\mathcal{M}$). So far, only Morrison et al. have reported the existence of the monoclinic metallic $\mathcal{M}$ state [2].

We track the IMT dynamics in VO$_2$ by measuring the yield of an intraband harmonic, requiring a conduction band with an anharmonic band structure. A mid-infrared laser pulse (drive) at 10 $\mu$m is used to drive high harmonic generation (HHG) from a 100 nm thick, epitaxial VO$_2$ sample [3]. The sample is photoexcited with a 50 fs, 1.5 $\mu$m laser pulse (pump) to initiate the IMT. The production of the fifth harmonic of the HHG driver is recorded as a function of time delay between the pump and drive for various fluences as presented in Fig. 1(a).

The observed changes in the harmonic yield correlate with the state transitions in the pumped VO$_2$. Immediately after optical excitation, regardless of pump fluence, a drop in HHG yield is observed, corresponding to the M$^*$ state of the VO$_2$. If the pump fluence is very low, the harmonic yield returns to nearly the same level, indicating the system returns to its initial state, with no new metastable states created. Once enough pump fluence is applied, after the initial drop in harmonic yield, an increase in yield is observed after ~300 fs corresponding to the relaxation to the M$^{*,b}$ pseudothermal state. The VO$_2$ then further relaxes over a picosecond time period to the metastable metallic monoclinic $\mathcal{M}$ state, characterized by an almost, but not complete, recovery in harmonic yield. If there is sufficient pump fluence, a complete suppression of the harmonics indicating that the VO$_2$ has completely transitioned to the metallic R state. Between these two thresholds, a mix of the long-lived $\mathcal{M}$ and R states is reached. Complementary measurements of a transmitted IR probe pulse at 1.7 $\mu$m show no indication of a revival in transmittance as shown in Fig. 1(b). By using both the harmonic yield and its time evolution, we are able to distinguish the various states in VO$_2$, and thereby track, in real-time, the IMT dynamics. The dynamics we see are in good agreement with previous UED experiments [2]. We see the double time constant feature in the change in HHG yield corresponding to a transition time for the M$^*$ $\rightarrow$ M$^{*,b}$ transition of 291 $\pm$ 100 fs and the M$^{*,b}$ $\rightarrow$ $\mathcal{M}$ transition of 1.4 $\pm$ 0.4 ps.

As this technique is simple and easy to implement, we expect that our time-resolved HHG spectroscopy technique can be easily extended to other strongly correlated materials and solids. This opens the path to study how materials evolve and transition to other exotic phases under different conditions such as high pressure, high temperature, and photoexcitation.