Ultrafast evolution and transient phases of a prototype out-of-equilibrium Mott-Hubbard material

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Lantz et al.1, report a transient non-thermal phase in V2O3 following photoexcitation with femtosecond pulses of light at 800 nm arising from both the paramagnetic insulating (PI) and paramagnetic metallic (PM) phases of V2O3. The transient state is said to be stabilised by lattice distortion due to an overpopulation of the a1g electronic orbital. This is observed through a hardening of the A1g coherent phonon mode by 14% from the value observed in Raman measurements at equilibrium. We have repeated the optical measurements, performed on the paramagnetic metallic phase, on several different samples and found no evidence for light-induced phonon hardening. Raman and time-domain signals are found to be in good agreement. Instead, we find that the equilibrium A1g mode frequency is sample dependent, with values spanning 0.6 THz in the three samples measured. Our results show that V2O3 does not undergo any anomalous photo-induced phase transition and that the excited state is most likely a thermal one.

The data shown in Fig. 1 comes from a single crystal of the PM phase of V2O3. The samples were ground and polished using grinding disk papers and polishing cloths with diamond suspension down to 3 µm to give a (001) surface normal. The room temperature lattice parameters of a = 4.9535(5) Å and c = 14.0043(4) Å were measured. A sharp first-order insulator–metal phase transition at 165 K, often resulting in the crystal shattering, shows that our samples are of high quality and correspond to stoichiometric V2O3.

Experiments were carried out in an optical cryostat held at 200 K. In order to reproduce the experimental conditions reported in Ref. 1, the pump–probe measurements were performed in a cross-polarised geometry at near normal incidence, and the pump fluence was set to 8 mJ cm−2. One significant difference in our measurement is that we use a broadband optical probe and frequency-resolve detection, which provide greater sensitivity to the phonon oscillation. Figure 1a shows the wavelength dependence of the transient optical response after correcting for the chirp of the white light probe. The response is similar to that observed by Ref. 1 with a spike-like feature near t = 0 and coherent oscillations over a slowly varying background. The response is similar at all wavelengths, but the relative strength of the peak and oscillation amplitude changes for different wavelengths. In order to obtain the phonon frequency, we averaged a 100-nm section of the wavelength data, centred at 600 nm, to produce a single time trace. Figure 1b shows a zoom of the transient, together with a time dependent fit to the transient data, which resulted in a central frequency of 7.41 ± 0.01 THz (247 cm−1). In addition, we remove the background by differentiating the transient response, as performed by Ref. 2, which acts as a complex low-pass filter for the slow dynamics. A fast Fourier transform (FFT) of the result was then calculated, after excluding the range close to the spike at t = 0. The resulting FFT is shown in Fig. 1c. A Lorentzian fit to the FFT gives a central frequency of 7.51 ± 0.01 THz (250 cm−1). The discrepancy in frequency obtained from the two methods of analysis of the same data is larger than the error reported by the fitting algorithm in either case. This shows that the main error in determining the mode frequency arises from how the background is processed. We determine the frequency of the mode to be 7.46 ± 0.05 THz by using the mean and standard deviation of the two fit results. This frequency is significantly slower than 8 THz, the response observed in Ref. 1.

Raman measurements were also performed on the same sample at room temperature. Here, a small red shift can be expected due to the thermal induced softening of the mode, i.e., we expect it to be slightly lower in frequency than the data recorded at 200 K. The data were recorded in an unpolarised backscattering geometry with a 785-nm laser, and the results are also plotted in Fig. 1c. The Raman measurements are in good agreement with previous reports in the literature3,4, again attesting to the good quality of our crystals. We used a multi-Lorentzian fit and linear background to extract the central frequency of the Raman mode and a value of 7.39 ± 0.03 THz. Again, this value can change if the background function is also modified, and the true error will be larger than the value reported by the fit. However, even with this lower bound, the Raman and time-domain

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frequencies obtained can be considered the same, to within the combined error bars. Therefore, we conclude that light does not induce a significant blue shift.

In order to investigate the discrepancy further, we performed a range of fluence-dependent measurements on different samples of stoichiometric V$_2$O$_3$ and at different fluences. Samples 1 and 2 were grown and polished by our collaboration at John Hopkins University using the methods described above. The data from other samples were acquired at facilities in our lab at ICFO. We show these data only for the purpose of showcasing the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
D.M.M., A.R.A. and L.V. built the time-domain experimental setup, measured the static Raman data and analysed the data under the supervision of S.W. S.M.K. grew and characterised the static properties of the V2O3 single crystals studied. S.W. wrote the paper and coordinated the project.

Additional information
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Competing interests: The authors declare no competing interests.

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