Probing strongly correlated electron dynamics on extreme timescales

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Abstract. We use sub-10 fs laser pulses in the visible and near IR region of the spectrum in order to probe the dynamics of photo-induced phase transitions on their characteristic timescales. We present results from two different cases: the 1D organic Mott insulator ET-F$_2$TCNQ and the more complex, colossal magneto-resistive manganite, Pr$_{0.7}$Ca$_{0.3}$MnO$_3$. For the former, we find that the melting of the Mott state takes 20 fs, a timescale which is dictated by the electron tunnelling time, $\hbar/t$. In comparison, the dynamics of the manganite show coupling to a 14 THz structural mode and a high frequency 30 THz mode, which we assign as an orbiton, a collective electronic excitation.

1. Introduction
Correlated materials are ones in which electron-electron interactions play a dominate role in determining the physical properties of the system. The simplest case is that of a Mott insulator, where the onsite electron-electron interaction energy, $U$, is greater than the kinetic energy term, $t$, arising from electrons tunneling from site-to-site and inhibits conduction. When a prompt change of filling occurs due to laser excitation, the system can be expected to respond on a timescale which is commensurate with the electron tunnelling time, $\hbar/t$. In this case, the change in the system is expected to respond on a timescale which is commensurate with the electron tunnelling time $\hbar/t$, i.e. the time needed for an electron to move from an occupied site to the newly created vacant site.

In many correlated materials the electronic degree of freedom is often coupled to other parameters, such as the lattice, spin and orbit, which makes the response of the system more complicated than that of the simple case above. In this paper, we demonstrate the response of a simple Mott insulator and show that the electron tunneling time dictates the dynamics. We also show how the coupling to other degrees of freedom is apparent in the response of a colossal magneto-resistive (CMR) manganite.
Both measurements are achieved by using short pulse lasers to probe the materials on their characteristic timescale.

2. ET-F₂TCNQ: A 1D Mott insulator

ET-F₂TCNQ is a mixed stack 1D organic Mott insulator. Electrons are localized along 1D chains of ET molecules due to onsite electron-electron interaction energy, $U = 1.5$ eV, being bigger than the electron tunneling energy, $t = 200$ meV. This opens an energy gap between the fully occupied lower Hubbard band and the empty upper Hubbard band, with an energy given by $E_{\text{gap}} = U - 4t = 0.7$ eV. This results in a sharp peak in the reflectivity at $0.7$ eV ($1.7$ µm) for light is polarized along the direction of the chains and corresponds to the charge transfer excitation $\{\text{ET}^+, \text{ET}^+\} \rightarrow \{\text{ET}^0, \text{ET}^{2+}\}$.

Previous time-resolved studies on ET-F₂TCNQ have focused on the long timescale behavior and observed the formation of a metallic state which is inferred by the collapse of the charge transfer resonance and a Drude-like response at long wavelengths [2].

In order to probe the melting of the Mott state the dynamics of the charge transfer excitation needs to be probed on a timescale which is shorter than the electron tunneling time $\hbar/t = 20$ fs. This presents a serious technological challenge as this is close to a single optical cycle at these wavelengths. To this end we use a recently developed near-IR optical parametric amplifier (OPA) which generates pulses with a spectrum spanning 1.2 to 2.1 µm which are compressed to 9.1 fs by a deformable mirror [3].

The output of the OPA was split to provide degenerate pump and probe pulses. The pump fluence was $3.5$ mJ cm$^{-2}$, which approximately corresponds to an excitation of 1 in 4 ET molecules. The time resolved change in reflectivity was spectrally resolved in a monochrometer, allowing the response of the charge transfer peak to be measured. The change in reflectivity grew linearly with pump fluence for low pump powers, with non-linear growth occurring when more than 4% of the ET molecules are excited. The signal size saturates when more than 7% of the sites were photodoped.

![Figure 1](image1.png)

**Figure 1.** The normalized photoinduced change in reflectivity of ET-F₂TCNQ at 1.4 µm compared to the normalized change in transmission of a carbon nanotube thin film. ET-F₂TCNQ shows a 20 fs delay in the signal rise.

Figure 1 shows the normalized time resolved change in reflectivity at 1.4 µm and is compared with the change in transmission of a carbon nanotube thin film at the same wavelength. This measurement demonstrates that the rise of the ET-F₂TCNQ signal is delayed by approximately 20 fs with respect to the carbon nanotube at the half rise point. This verifies the picture that the delocalization of charges exhibit a bottleneck timescale which is comparable to the tunneling time of the electrons.

3. CMR manganite Pr$_{0.7}$Ca$_{0.3}$MnO$_3$

The response of the manganites is more complex due to coupling between multiple degrees of freedom. This is best demonstrated by the fact that insulator to metal transition can be triggered by changing the electronic state through photodoping [4], as well as directly controlling a specific structural mode of the material [5]. In addition, very recently, it has been shown that control over the structural mode can also control the orbital ordering of the material [6].
Figure 2. The photoinduced change in reflectivity at 660 nm at 77 K (left) with optic phonons modulations at 14 THz and at 300 K (centre) with modulations due to orbitons at 30 THz.

Figure 2 shows the time resolved change in reflectivity at 77 K, where the ground state is antiferromagnetic insulator and at 300 K where it is paramagnetic insulator. Pump probe measurements were taken with sub 10-fs pulses at visible wavelengths to probe the charge transfer resonance in this material. Figure 2 also shows the Fourier transform of the background subtracted oscillations from both temperatures.

The response of the low temperature phase shows coupling to a structural mode at 14 THz. This mode corresponds to distortions of the oxygen octahedra which are known to alter the conductivity of the material.

In the high temperature phase higher frequency oscillations are observed at 30 THz. This mode is higher than that of the optic phonons found in this material and we assign it to the controversial collective electronic d-d excitation, or orbiton. [7-9].

4. Summary
We have shown that ultrafast response of a material is dictated by the nature of its ground state. The electronic Mott insulator, ET-F₂TCNQ, has a delayed response of 20 fs after photodoping due to the electron tunnelling time. The response of the CMR manganite, Pr₀.₇Ca₀.₃MnO₃ is slower, showing coupling to multiple degrees of freedom, such as optic phonons associated with bandwidth changes in the low temperature phase, and high frequency collective electronic excitations corresponding to orbital excitations.

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