Coherent Control of Nuclear Motion Driving Charge and Spin Ordering in Molecular and Extended Solids

John H. Burke Literature Seminar November 11, 2020

An important direction in information technology is achieving ultrafast, all-optical switching between bit states. This could be achieved with materials that undergo photoinduced phase transitions from insulating to metallic phases. Peierls transitions are examples of such phase transitions, wherein nuclear displacement results in a metal-insulator transition accompanied by charge/spin ordering. Ultrashort laser pulses may initiate these phase transitions, which proceed on ultrafast (subpicosecond) timescales. The uncertainty principle states that the shorter a laser pulse, the broader its energy spectrum. As a result, the pulse may overlap spectrally with several vibronic transitions, exciting a coherent superposition of vibrational states (phonons) which oscillate as a wavepacket on the electronically excited state potential energy surface. Double-pulse excitation schemes enable coherent control of vibrational wavepackets: the wavepackets created by two pulses may interfere with each other, resulting in enhancement or suppression of the coherent oscillations, depending on the time delay between the pulses and the period of the vibrational mode. The Peierls transition is driven by electron-phonon coupling: nuclear displacement drives large changes in electronic structure. Therefore, coherent control of the nuclear motion may allow some control over the photoinduced phase transition. Photoinduced phase transitions may be studied with pump-probe techniques: a laser pulse (the pump) excites the system, and the ensuing dynamics are monitored by a probe pulse. The probe may be spectral (UV/Vis/NIR reflectivity, photoemission) or structural (diffraction). Coherent control may be afforded by using a double-pulse excitation scheme, i.e. pump-pump-probe. In this presentation, I will draw examples which utilize diverse probes on diverse systems to answer 1) what mechanistic information can pump-pump-probe measurements provide? and 2) can coherent control of nuclear motion control the dynamics of photoinduced phase transitions?

Coherent control experiments can provide mechanistic information, as well as influence the dynamics themselves. By enhancing or suppressing coherent vibrations with double-pulse excitation in potassium tetracyanoquinonedimethane (K[TCNQ]), Rich and Frontiera[1] demonstrated control over the amount of excited state and high-temperature phase formed. K[TCNQ], an organic charge transfer molecular crystal, exhibits 1D stacks of TCNQ radical anions, which above 398 K are evenly spaced and antiferromagnetically coupled. At 398 K, the system undergoes a spin-Peierls transition, resulting in dimerization of the TCNQ anions and diamagnetic behavior at low temperatures. The vis/NIR reflectivity

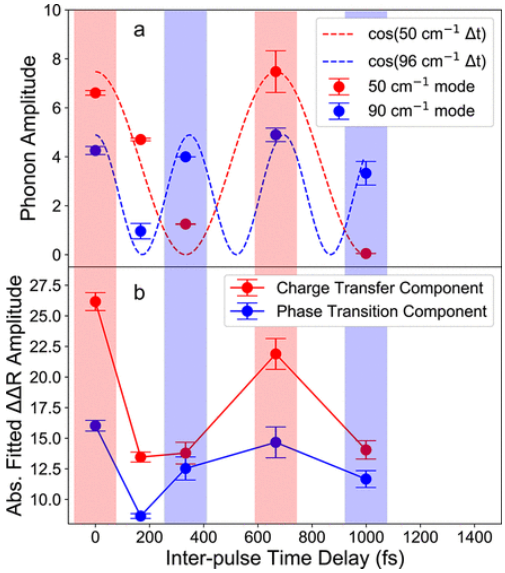

Figure 1: Coherent control of vibrations controls excited state populations in K[TCNQ]. **a)** Amplitude of oscillations and **b)** amplitude of exponential fits of transient reflectivity signal as a function of pump-pump delay. Figure from Ref.[1]

spectrum features a charge transfer (CT) absorption at 1 eV (1240 nm). This transition optically transfers an electron from one TCNQ anion to another, which destabilizes the diamagnetic phase and initiates a phase transition to the antiferromagnetic phase. Okamoto and coworkers[2,3] used pump-probe transient reflectivity to study this system, and found the timescales of the photoinduced phase transition and phase recovery to be >180 fs and 1.8 ps, respectively. Furthermore, the transient reflectivity signal was modulated by coherent oscillations of 50 and 90 cm^{-1}. The coherent control experiments by Rich and Frontiera[1] helped elucidate the role of these phonons. By using two pump pulses, and varying the time delay Δt_{12} between them, the authors could enhance or suppress the oscillations. Remarkably, they found that the populations of the CT state and the antiferromagnetic phase correlated with coherent phonon amplitudes of the 50 and 90 cm^{-1} modes, respectively, as demonstrated in **Figure 1**. Therefore, these pump-pump-probe measurements determined the functional role of these coherences, as well demonstrated the use of coherent control of vibrations to control the yield of electronic excited states.

In the next example, it is shown how coherent control of vibrational motion can directly affect the bandgap of a material. The system for which this is demonstrated is $DyTe_3$. The crystal structure of this inorganic extended solid features 2D layers of Te ions in the ac plane. The Te ions are arranged in a square, with their $5p_{x/z}$ orbitals constituting the valence orbitals. At high temperatures, the system is metallic, but at ~310 K two of the four Te ions in the unit cell are displaced along the c axis, distorting the square of Te ions to a diamond shape. This opens up a band gap along the k_z direction in the electronic band structure.[4–6] Angle-resolved photoemission spectroscopy is able to probe the band structure of materials by mapping the energy and momenta of electrons. Rettig *et al.*[7] used this technique to observe the photoinduced phase transition in $DyTe_3$. Upon excitation of the low temperature phase, carriers are excited to the conduction band which lies above the Fermi energy, E_F. Within 200 fs, the band gap closes, indicating a phase transition to the metallic phase. However, the band gap then reopens and closes periodically at frequencies of 58 cm^{-1} (1.75 THz) and 73 cm^{-1} (2.2 THz), due to modulation by coherent phonons. Using double pulse excitation, Rettig *et al.*[7] exhibited coherent control over these phonon modes. As shown in **Figure 2a**, the peak position of the valence band is modulated by coherent phonons. Varying the time delay between the two pump pulses allows for

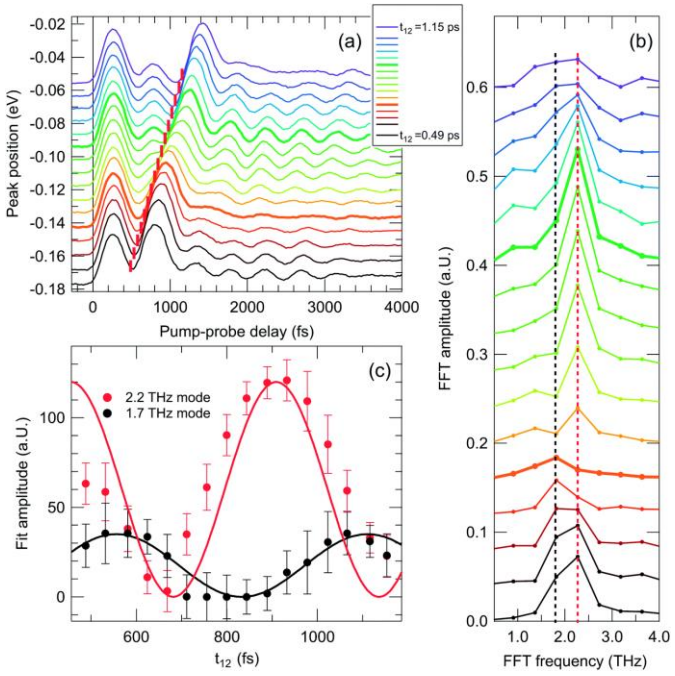

Figure 2: Coherent control of vibrations controls modulations of valence band edge in $DyTe_3$. **a)** Double-pulse excitation transient ARPES of $DyTe_3$ showing valence band peak position energy as a function of pump-probe delay for different pump-pump delays (t_{12}). Red rectangle marks arrival time of second pump pulse. **b)** Fast Fourier transform spectra of traces in **2a** after 2 ps. **c)** Peak FFT amplitudes for the 2 phonon modes as a function of pump-pump delay. Figure from Ref.[7]

enhancement or suppression of the modes, as evidenced by the fast Fourier transform (FFT) spectra shown in **Figure 2b** and the peak FFT amplitudes as a function of pump-pump delay in **Figure 2c**. Ultimately, this example demonstrates how coherent control of nuclear motion can be used to control the electronic structure of a material.

In summary, for photoinduced phase transitions where nuclear motion drives electronic changes, coherent control of phonons offers an attractive means of affecting the dynamics. The double-pulse excitation transient ARPES experiments of Rettig *et al.*[7] demonstrated control over modulations in the band gap by coherent control of phonons in $DyTe_3$. The double-pulse excitation transient reflectivity measurements of Rich and Frontiera[1] allowed them to determine the mechanistic role of coherent phonons in the photoinduced dynamics of K[TCNQ], and furthermore allowed them to control the population of the intermediate excited state and antiferromagnetic phase by controlling the phonon amplitudes. While these two examples demonstrate clear effects of coherent control of phonons on the photoinduced phase transitions, they are limited in their applicability and novelty by their lack of control over the outcome of the reaction. While Rich and Frontiera were able to affect the excited state populations by enhancing or suppressing coherent phonons, the lifetimes, identities, and pathways of the accessed excited states remained the same. An interesting direction would be to demonstrate divergent dynamics affected by coherent control. Researchers should search for a system where the dynamics of the photoinduced phase transition could be changed to access an intermediate phase with different charge/spin ordering by enhancing or suppressing a particular coherent vibration. This would have technologic relevance as ultrafast, all-optical switching in a 3-state system.

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