Local Fields as a Probe for Non-Adiabatic Carrier-Phonon Dynamics

S Neb[1], D Shin[2], F Burri[1], M Hollm[1], E de Vos[1], D A Kuznetsov[3], C R Müller[3], A Fedorov[3], S A Sato[4,5], A Rubio[5,6], U Keller[1], and L Gallmann[1]

[1]*Department of Physics, ETH Zurich, Zürich, Switzerland*
[2]*Gwangju Institute of Science and Technology, Gwangju, South Korea*
[3]*Department of Mechanical and Process Engineering, ETH Zurich, Zürich, Switzerland*
[4]*Department of Physics, Tohoku University, Sendai, Japan*
[5]*Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany*
[6]*Center for Computational Quantum Physics (CCQ), Flatiron Institute, New York NY, USA*
Contact Email: gallmann@phys.ethz.ch

We use attosecond transient absorption spectroscopy (ATAS) to study non-adiabatic carrier-lattice interactions in a titanium carbide ($Ti_3C_2T_x$) MXene at the atomic scale. Local field effects (LFEs) act as a sensitive probe for modulations by coherent phonons with carrier, site and orbital specificity. Our experiments revealed that electrons lagged lattice oscillations by 32±8 fs, whereas holes responded almost instantaneously (7 ± 7 fs). The observed lag represents a breakdown of the Born–Oppenheimer approximation.

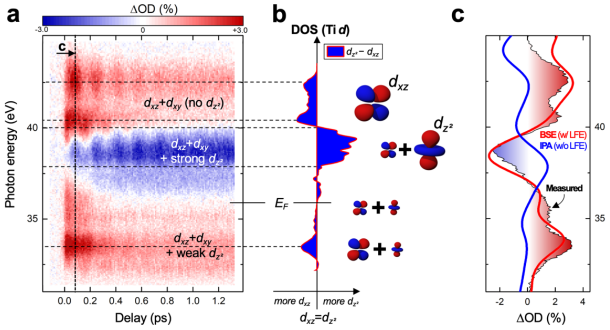

Figure 1: Local field effects reveal fingerprint of atomic-scale electron-phonon coupling. a) Transient absorption spectrogram with modulation of optical density by 6 THz A_{1g} phonon mode. b) Orbital-resolved contributions to signal. c) Comparison of independent-particle approximation (IPA), which does not capture local field effects, and Bethe-Salpether equation (BSE) calculations with experiment

We performed a combined experimental and theoretical study providing insights into LFEs primarily modified by near-infrared (NIR) excited coherent A_{1g} phonons. The Ti $3p$ shallow-core level serves as an optimal probe for LFEs, enabling us to resolve the interplay between distinct d-orbitals during coherent A_{1g} phonon oscillations. The energy region covered by our experiments below the Fermi level corresponds to a mixture of d_{xz} and d_{z^2} orbitals, while higher-energy levels exhibit almost pure d_{z^2} and fully pure d_{xz} states (see Figure 1).

We solve the Bethe-Salpeter Equation (BSE) at an elevated electron temperature of 1000 K, incorporating lattice elongations obtained via Ehrenfest dynamics in time-dependent density functional theory (TDDFT) following NIR excitation. This approach successfully reproduces the measured changes in optical density (ΔOD). However, agreement with experiment is only achieved when LFEs are included in the BSE, whereas the independent particle approximation (IPA) completely fails to capture our observations.

Our study not only demonstrates the capability of ATAS to probe the LFEs in an element-specific manner but also showcases their sensitivity to phononic fingerprints even in individual d-orbitals with excellent theoretical agreement.

The understanding of the investigated carrier-lattice interactions is essential for material optimizations for many applications as they govern the energy transfer in materials and ultimately set limits in microelectronics. We believe that our approach can also be applied to other materials.