Ultrafast Heterodyne Infrared Nano-Imaging of Polaron Dynamics in Lead Halide Perovskites

Jun Nishida[1], Peter T. S. Chang[1], Jiselle Ye[2,3], Prachi Sharma[2,3], Sean E. Shaheen[2,3], and Markus B. Raschke[1]

1. Department of Physics, Department of Chemistry, and JILA, University of Colorado, Boulder, CO 80309, USA

2. Department of Electrical, Computer, and Energy Engineering, and Department of Physics, University of Colorado, Boulder, CO 80309, USA

3. Renewable and Sustainable Energy Institute, University of Colorado, Boulder, CO 80303, USA

E-mail: jun.nishida@colorado.edu

Abstract: Ultrafast heterodyne infrared nano-imaging has been developed to reveal nanoscale heterogeneity of polaron formation, dynamics, and polaron-cation coupling in lead halide perovskites, with real space-time mapping of elementary electron-phonon coupling underlying their optoelectronic response.

1. Introduction

Lead halide perovskites exhibit remarkable photovoltaic performance, characterized by long carrier lifetime and extraordinary defect tolerance. The highly dynamical lattice of the perovskites is believed to play a key role by forming a large polaron (Fig. 1A), which arises from electron-phonon coupling across multiple unit cells and stabilizes the photoinduced carriers. On the other hand, the perovskite films are known to be spatially non-uniform in their optoelectronic response, yet the fundamental origin of such disorder, particularly in relation to the elementary electron-phonon coupling, has remained elusive.

Here, we develop ultrafast heterodyne infrared nano-imaging [1] to provide access to the full spatio-temporal-spectral response dynamics and apply to a triple cation perovskite film [2] to reveal its polaron dynamics on the nanoscale. By directly probing the pump-induced mid-infrared "polaron absorption" (Fig. 1B) with nanometer spatial resolution [3], we resolve the heterogeneity in the polaron formation and its dynamics on the picosecond scale. By taking advantage of the combined spatial, temporal, and spectral resolution, we also probe a nano-localized transient molecular vibrational response that signifies the coupling between polaron and molecular cations. We thus characterize the nanoscale disorder in perovskites from the perspective of the fundamental electron-phonon coupling, the control of which is critical for the engineering of perovskite-based optoelectronic devices.

2. Ultrafast heterodyne infrared nano-imaging system

Fig. 1C shows the schematic of our ultrafast heterodyne infrared nano-imaging and -spectroscopy system [1]. The optical pump and mid-infrared probe pulses are collinearly focused to a metallic tip apex in an atomic force

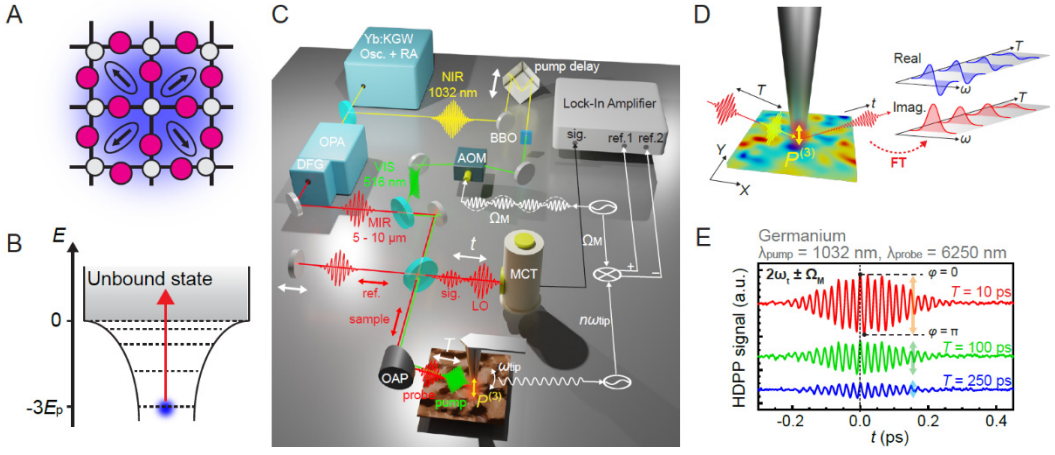

Fig. 1: A. Large polaron formation in a lead halide perovskite. **B.** Optical transition associated with strong-coupling polaron absorption. **C.** Schematic of ultrafast heterodyne infrared nano-imaging system. **D.** Optical heterodyne detection of the near-field pump-probe signal yields spatio-temporal-spectral resolution. **E.** Near-field heterodyne pump-probe interferogram acquired on a germanium reference sample.

microscope, inducing a nanoscale pump-probe signal [4]. The near-field pump-probe signal is interfered with a reference pulse for heterodyne detection, implementing phase and spectral resolution (Fig. 1D, 1E) and also eliminating contributions arising from the uncontrolled interference of the near-field signal with the far-field background scatter [5].

3. Polaronic heterogeneity in a lead halide perovskite

We study a triple cation perovskite (Fig. 2A), $[(FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}]Pb(I_{0.83}Br_{0.17})_3$, as a highly stable model system of the perovskites. Fig. 2B shows conventional far-field visible-pump/mid-infrared-probe decay profiles with pronounced dependence on the pump fluence, suggesting that the observed carrier dynamics are dominated by the second and higher order carrier recombination. For a given fluence, we acquire pump-probe spectra (Fig. 2C), demonstrating the peak-like structure around 1100-1200 cm^{-1} with tail on the high-frequency side, consistent with the spectral response expected for polaron absorption [3]. The time evolution of the spectral line shape signifies increasing polaron size as the pump-probe waiting time is increased. Fig. 2D shows a spatio-temporal mapping of such polaron absorption by ultrafast heterodyne infrared nano-imaging, demonstrating the heterogeneity both in polaron formation and polaron recombination dynamics [2]. To further characterize the disordered nature of the coupling between the photoinduced carriers and perovskite lattice, we measure a transient vibrational response arising from the coupling between polaron and molecular cation at the nanoscale (Fig. 2E). The spatial variation in the transient vibrational peak position (Fig. 2F) demonstrates the non-uniform charge-cation coupling, suggesting that the observed heterogeneity in polaron absorption likely relates to the disorder in the dynamical lattice elasticity [6].

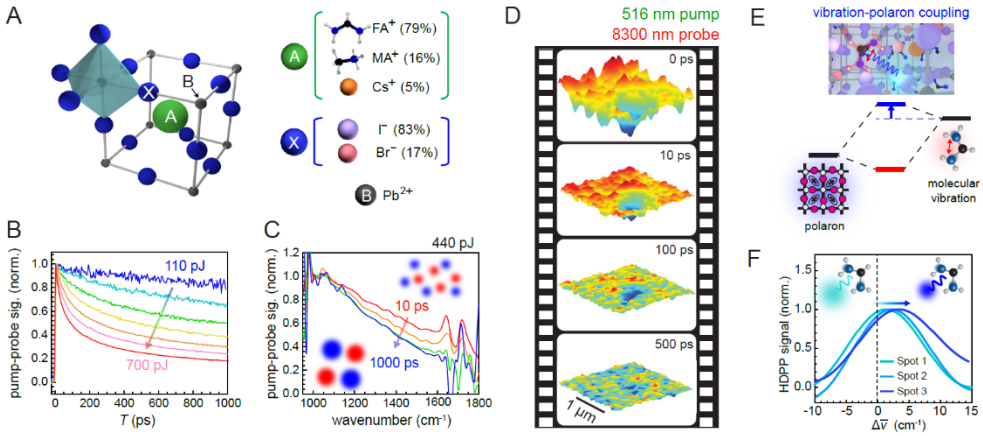

Fig. 2: A. Triple cation perovskite FAMACs. **B.** Far-field pump-probe decay profiles with different pump fluences. **C.** Pump-probe spectra acquired with the pump energy of 440 pJ at different pump-probe timings. The evolution of the line shape over time is consistent with increasing size of the polaron. **D.** Ultrafast heterodyne infrared nano-imaging of polaron absorption, signifying the heterogeneity in polaron formation and its recombination dynamics. **E.** CN anti-symmetric stretch mode of a FA cation couples to a photoinduced polaron, resulting in the blue shift in the vibrational resonance. **F.** Transient vibrational resonance resolved at different spots, suggesting the spatial variation in the cation-polaron coupling.

4. Conclusions

In this work, we establish ultrafast heterodyne infrared nano-imaging as a tool to characterize the heterogeneity in polaron dynamics, as well as an enabling method for transient vibrational nano-spectroscopy which reveals disordered charge-lattice coupling. The technique is generally applicable to address disorder in electron-phonon coupling, which has been identified in a variety of systems including two-dimensional materials and superconductors.

5. References

[1] J. Nishida et al., "Ultrafast heterodyne infrared nano-imaging: resolving quantum dynamics in space, time, and energy," submitted.
[2] J. Nishida et al., "Ultrafast nano-imaging of polaron dynamics in a lead halide perovskite," submitted.
[3] K. Munson et al., "Dynamic Disorder Dominates Delocalization, Transport, and Recombination in Halide Perovskites," Chem., 4, 2826 (2018).
[4] S. A. Dönges et al., "Ultrafast Nanoimaging of the Photoinduced Phase Transition Dynamics in VO_2," Nano. Lett., 16, 3029 (2016).
[5] A. J. Sternbach et al. "Artifact Free Time Resolved Near-Field Spectroscopy," Opt. Express 25, 28589 (2017).
[6] J. Nishida et al., "Heterogeneous Cation-Lattice Interaction and Dynamics in Triple-Cation Perovskites Revealed by Infrared Vibrational Nanoscopy," ACS Energy Lett., 5, 1636 (2020).