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Ultrafast carrier interactions in metal-halide perovskites probed with two-dimensional electronic spectroscopy

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Abstract. We use 2D electronic spectroscopy with sub-10-fs resolution to probe carrier-carrier scattering in perovskites. We report excitation-density dependent thermalization times below 100-fs. Strong coupling with excitonic states further reveals sub-bandgap states with low oscillator strength.

Fundamental understanding of the excited state processes in a semiconductor requires insights into the initial carrier-carrier interactions after photo-excitation. In band-like semiconductors, such thermalization and cooling processes provide information on band structure and carriers properties, which are relevant for transport and recombination in applications. Recently, the class of hybrid lead-halide perovskite semiconductors has gained attention due to the reported disruptive efficiencies in solution-processed solar cells, exceeding 20%. Low apparent defect densities give rise to internal luminescence yields above 70% and sharp absorption edges. [1,2] Cooling of thermal carrier distributions in hybrid lead halide perovskites has been studied with pump-probe spectroscopy. Cooling timescales of ~300 fs were reported, which were discussed to arise from carrier-phonon scattering [3,4].

Here we report 2D electronic spectroscopy (2DES) with sub-10 fs resolution on metal-halide perovskites, which directly probes the carrier interactions leading to a thermal carrier distribution. First, we study the hybrid metal-halide perovskite $CH_3NH_3PbI_3$, which is commonly used in perovskite solar cells. Immediately after formation of an excited state population, we resolve a bleach signal along the diagonal, which follows the shape of the pump spectrum (Fig. 1a). Over the initial 100 fs, this distribution rapidly broadens in energy while the energy equilibrates amongst the carriers (Fig. 1b). Bleach signals arise now also above the diagonal, which indicates that some photo-excited carriers initially excited near the band edge gained energy. At longer time delays (>300 fs) our data reaches the cooling regime (Fig. 1c), providing a full picture of the thermalization and cooling dynamics in hybrid perovskites [5].

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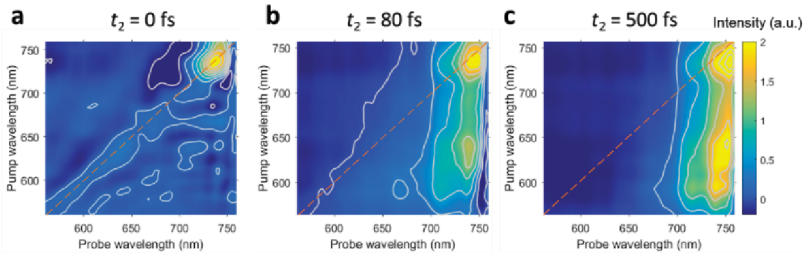

Fig. 1. (a) – (c) 2DES maps for waiting times t_2 of (a) 0 fs, (b) 80 fs and (c) 500 fs for an excitation density of $2x10^{18}$ cm^{-3} at 1 kHz repetition rate. Initially, a non-thermal carrier energy distribution is excited. After undergoing carrier-carrier scattering, carriers form a thermalized distribution with a temperature higher than the lattice. Through carrier-phonon scattering, the carriers subsequently cool down until they reach an equilibrium with the lattice temperature.

We extract the bleach kinetics for several energies along the diagonal of the 2DES map for a quantitative analysis (Fig. 2a). From exponential fits, we obtain characteristic carrier thermalization times from 8 to 85 fs with a strong dependence on excess energy (Fig. 2b). Faster scattering rates are found for carriers at higher energies above the band edge, in agreement with an approximately parabolic band dispersion near the band minima. Further, we observe a dependence of thermalization times on photo-excited carrier density. We conclude that thermalization occurs dominantly via carrier-carrier scattering at the investigated fluences. The reported thermalization times set the limit for carrier mobilities in lead-halide hybrid perovskites to 400 cm^2/Vs at carrier densities lower than $2x10^{18}$ cm^{-3}.

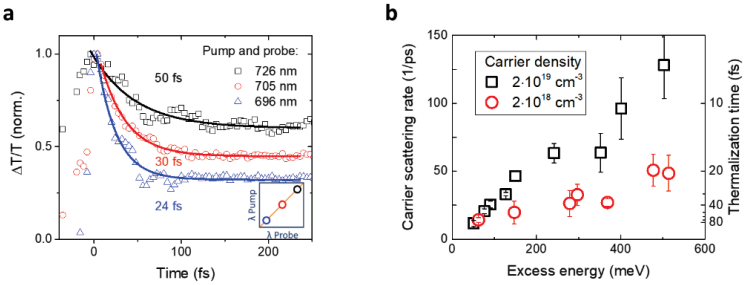

Fig. 2. (a) Pump wavelength dependence of the kinetics of the diagonal peaks in the 2DES maps at an excitation density of $2x10^{19}cm^{-3}$. The shorter the pump wavelength, the faster the diagonal decays. (b) Carrier scattering rate vs. excess energy over the bandgap at 1.63 eV. The scattering rates increase with excess energy and show a fluence dependence.

Interactions between photo-excited charges can further lead to renormalization of the electronic states, and the formation of bound electron-hole pairs in materials with strong Coulomb interactions. For this, we turn to the metal-halide perovskite $CH_3NH_3PbBr_3$, in which excitonic states form with binding energy around 50 meV, stronger compared to the previous case. At early times after excitation the 2DES map shows a bleach at the exciton energy of λ_{Probe} = 525 nm, which is slightly broadened

along the diagonal (Fig. 3), indicating low inhomogeneous disorder in the system. We further find photo-induced absorption (PIA) signals above and below the diagonal at λ_{Probe} = 510 nm and λ_{Probe} = 540 nm.

We extract kinetics of the PIA and bleach signals to distinguish between optical Stark effect and bandgap renormalization processes. Unexpectedly, we further find a strong broadening of the excitonic bleach along the pump axis for all time delays. We interpret this signal as a coupling between excitonic states and low oscillator strength sub-gap states, which so far could not be observed in linear absorption. Our results provide insights into a potential origin of the sharp optical band edges and low apparent defect densities in these emerging semiconductor materials.

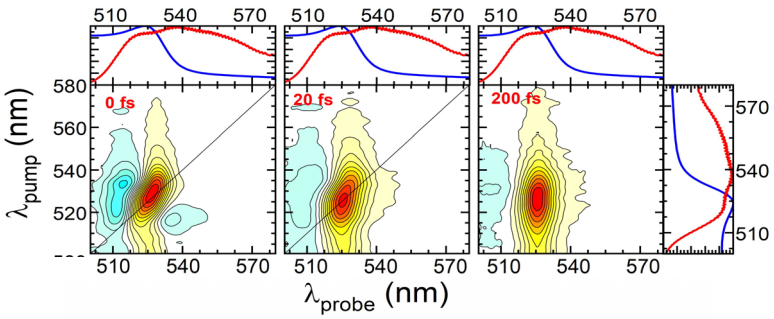

Fig. 3. 2DES maps for $CH_3NH_3PbBr_3$ thin films at an excitation density of $5x10^{17}cm^{-3}$ at 0, 20 and 200 fs. The dynamics of the width of the bleach signal along and across the diagonal suggest fast dephasing times and low inhomogeneous broadening. The exciton bleach signal is strongly broadened along the pump axis, also at pump wavelengths below the excitonic resonance.

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