

Investigating Electron-Phonon Coupling and Re-orientation Effects in Hybrid Lead-Halide Perovskites

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Introduction

Hybrid organic-inorganic lead halide perovskites films are emerging as a promising and inexpensive material for solar cell PVs,¹ with excellent absorption cross-sections which penetrate into the near-IR. Perovskite based devices now have power conversion efficiencies (PCEs) that regularly exceed 15%, and is linked to the $> 1 \mu\text{m}$ carrier diffusion lengths.² Organic lead iodide perovskites take the stoichiometry APbI_3 , where A is an organic cation. In an ideal cubic perovskite crystal structure, the organic cation is caged within an inorganic lattice comprised of a cube of lead cations with an iodide octahedron around each lead cation. Despite a simple chemical structure, hybrid inorganic-organic lead halide perovskites have been shown to be inherently complex materials that support a diverse range of dynamical processes essential to their photovoltaic performance. These phenomena operate over a multitude of timescales and include; organic cation rotation,^{3,4} and octahedral distortions.⁵ Recent studies, however, indicate that static effects such as Rashba splitting in the conduction band, may play a pivotal role.⁶

In this work, we investigate the vibrational dynamics associated with the formamidinium cation ($\text{NH}_2\text{CHNH}_2^+$, FA^+) in formamidinium lead iodide perovskite (FAPbI_3) thin films and elucidate the influence of rotational re-orientation timescale of FA^+ on the photo-physical material properties using two-dimensional vibrational spectroscopy (2DIR). Time-resolved infrared spectroscopy (TRIR) measurements were also used to probe the effect of photo-induced electron and hole charges on the organic cation. In both instances the strong mid-infrared peak centred at 1713 cm^{-1} associated with the C–N antisymmetric stretching vibration of FA^+ was used to probe the inorganic lattice–molecular cation interactions. The experimental studies were carried out at ULTRA at the Central Laser Facility.⁷

Two-Dimensional Infrared Spectroscopy

FAPbI_3 thin films were synthesised modified procedure of a previously reported synthesis.^{7,8} 2DIR data were collected using the Lifetime apparatus in ULTRA,⁹ in a partially collinear geometry, and a 8-step phase cycling scheme. 2DIR measurements were made with pump and probe mid-infrared pulses aligned parallel I_{par} and perpendicular I_{perp} to one another. These data were then used to extract the time-dependent anisotropic and isotropic system responses.

Figure 1 displays isotropic 2DIR spectra for $t_2 = 250 \text{ fs}$. The spectra are dominated by two features; the negative feature centred on the diagonal (black dashed line) at 1713 cm^{-1} corresponds to overlapping ground state bleach (GSB) and stimulated emission (SE) signals associated with the C–N antisymmetric stretch of the FA^+ cation. The positive feature centred at $\omega_3 = 1706 \text{ cm}^{-1}$ is the corresponding excited state absorption (ESA) signal. The GSB/SE and ESA features are predominantly homogeneously broadened, *i.e.* the diagonal and anti-diagonal linewidths are very similar, and they evolve little within the 100 ps measurement window. Centre line slope analysis of the GSB/SE feature showed that the feature's line-shape is almost entirely time-invariant within the noise limit of the experiment, indicating minimal or no spectral diffusion.

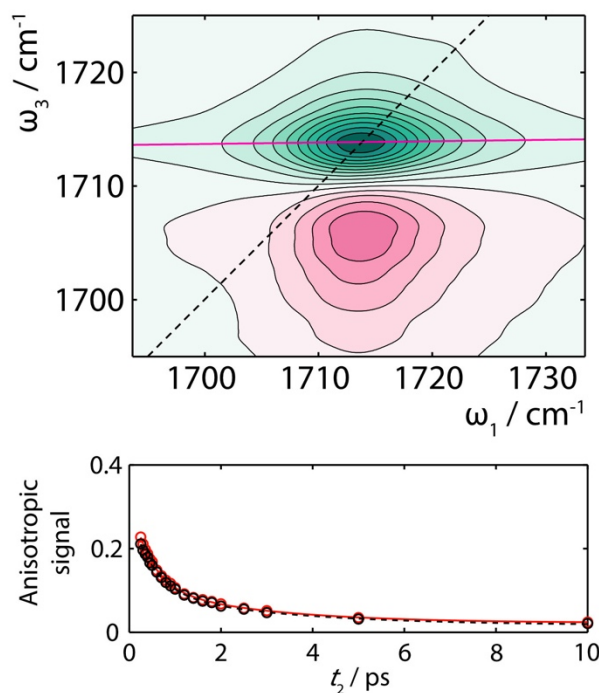


Figure 1 upper panel: Isotropic two-dimensional infrared spectroscopy data for C–N anti-symmetric stretch of FA^+ in FAPbI_3 thin films for $t_2 = 250 \text{ fs}$. The dashed black line indicates the diagonal, and the solid pink line display the fit to the centre line slope associated with GSB/SE feature. Lower panel: Time-dependent anisotropy associated with GSB/SE feature.

The anisotropic response ($R(t_2)$) for the GSB/SE in 2DIR spectra are shown in the lower panel of Figure 1. These data were fit to a biexponential decay with an offset, which returned $470 \pm 50 \text{ fs}$ and $2.8 \pm 0.5 \text{ ps}$ time constants ($R^2 > 0.999$), with associated normalised exponential pre-factors of 65% and 29%, and an offset corresponding to 6% of the total amplitude. Our 2DIR anisotropy measurements and MD simulations indicate that the barrier to rotational re-orientation and sampling various faces of the lead-iodide lattice must be small relative to room temperature to explain the observed decay in $R(t_2)$ towards zero within 10 ps. This means, that the FA^+ moieties are unlikely to form ferroelectric domains with phenomenologically significant lifetimes, contrary to prior experimental and theoretical studies.^{10,11} Such results echo the findings of previous 2DIR investigations of methylammonium cations in lead iodide perovskite films.^{4,12}

Time-Resolved Infrared Spectroscopy

Time-resolved infrared (TRIR) measurements, specifically near-IR pump and mid-infrared probe, were also performed for FAPbI_3 thin films to investigate the role of the formamidinium cations in the conduction band, or evidence for any vibration-intraband coupling. Our 760 nm pump, broadband mid-infrared probe data are displayed in Figure 2. Each TRIR spectra is dominated by two positive features; a sharp positive peak feature

centred at 1718 cm^{-1} , attributed to a molecular vibration, and a broad diffuse feature that spans all probe frequencies. The latter has previously been assigned to electronic intra-band transitions within the conduction band.^{13,14} The sharp feature at 1718 cm^{-1} in our TRIR data has a similar line shape to the ground state FTIR spectrum, but is blue-shifted by 5 cm^{-1} , and notably has one third the intensity of the intra-band feature. Negative features at the ground state central frequency associated with the C–N anti-symmetric stretching vibration are seemingly absent from our TRIR spectra, counter to our expectations based on typical TRIR line shapes.

We rationalize these observations as follows: 760 nm pump photons generate charge-carriers either in the form of free carriers or localized polarons.^{13–16} This results in an increased internal electric field in the perovskite thin film and changes the electrostatic environment surrounding the FA^+ molecular cation, compared to the valence band ground state. This nascent field perturbs the vibrational potential associated with the C–N anti-symmetric stretching FA^+ vibration, and shifts the associated fundamental frequency, *i.e.* inducing a transient vibrational Stark shift. In addition, the vibrational transition dipole moment of the C–N anti-symmetric stretch vibration in the conduction band is enhanced significantly compared to the unperturbed vibration in the valence band. Such enhanced vibrational cross-sections has been observed for thin polymer films, where the oscillator strength associated with vibrational transitions is enhanced by orders of magnitude, making them comparable to those typically associated with electronic states.^{15–17}

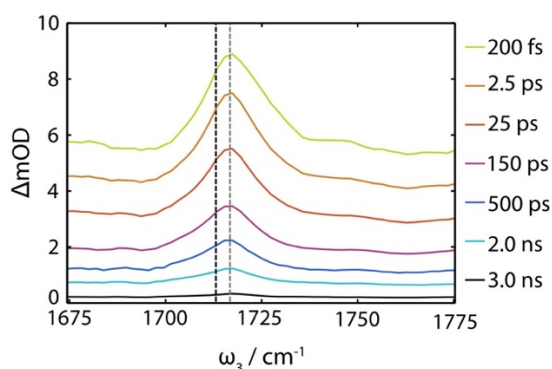


Figure 2 TRIR spectra of FAPbI_3 thin films for 760 nm excitation at the stated waiting times. The dashed black line indicates the central frequency associated with the ground state FA^+ anti-symmetric stretching vibration (1713 cm^{-1}), whereas the dashed grey line highlights the shifted transient vibrational feature centred at 1718 cm^{-1} .

Conclusions

Two-dimensional infrared spectroscopy was used to determine $470 \pm 50\text{ fs}$ and $2.8 \pm 0.5\text{ ps}$ time constants for the rotational reorientation time scales associated with the formamidinium cation inside FAPbI_3 thin films. Our results rule out the existence of long-lived (anti-) ferroelectric domains in FAPbI_3 . Based on our results, the observed power conversion efficiencies, and carrier recombination rates¹⁰ of FAPbI_3 cannot be explained by (anti-) ferroelectric domain formation, and are most likely explained by large polaron formation,¹⁸ as evidenced by the line shapes in our TRIR data, or Rashba splitting.⁶

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