Taylor, V. C. A., Tiwari, D., Duchi, M., Donaldson, P. M., Clark, I. P., Fermin, D. J., & Oliver, T. A. A. (2019). Investigating Electron-Phonon Coupling in Formamidinium Lead Iodide Perovskite Using Ultrafast Laser Spectroscopy. In *18th International Conference on Nanotechnology, NANO 2018* (Vol. 2018-July). [8626311] (IEEE International Conference on Nanotechnology (IEEE-NANO)). IEEE Computer Society. <https://doi.org/10.1109/NANO.2018.8626311>

Peer reviewed version

License (if available):
Other

Link to published version (if available):
[10.1109/NANO.2018.8626311](https://doi.org/10.1109/NANO.2018.8626311)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the accepted author manuscript (AAM). The final published version (version of record) is available online via IEEE at <https://doi.org/10.1109/NANO.2018.8626311> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

Investigating Electron-Phonon Coupling in Formamidinium Lead Iodide Perovskite Using Ultrafast Laser Spectroscopy

V.C.A. Taylor,^{1,2} D. Tiwari,¹ M. Duchi,¹ P.M. Donaldson,³ I.P. Clark,³ D.J. Fermin^{1,2} and T.A.A. Oliver^{1,2*}

¹ School of Chemistry, University of Bristol, UK, *email: tom.oliver@bristol.ac.uk

² Bristol Centre for Functional Nanomaterials, University of Bristol, UK, ³ Central Laser Facility, Science and Technology Facilities Council, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot, UK

Abstract—The high charge carrier mobilities of hybrid inorganic-organic lead halide perovskites has previously been linked to ferroelectric domain formation due to alignment of organic cations within films. [1], [2] Our two-dimensional infrared ultrafast spectroscopy studies reveal that organic cations re-orient within several picoseconds, and therefore ferroelectric domain formation is very unlikely and unable to account for the observed long carrier lifetimes.[3] Complimentary time-resolved infrared measurements examined the electron-phonon coupling in the conduction band. Analysis of the spectral line shapes indicates that carriers form polarons within the instrument response.

I. INTRODUCTION

Hybrid organic-inorganic lead halide perovskites films are finding prominence as the photoactive layer in optoelectronic devices, [4] due to low associated production costs and remarkable power conversion efficiencies (> 15%) despite the significant spatial disorder on nanometer to micron length scales. Perovskites also possess other key properties necessary for photovoltaic materials such as excellent absorption cross-sections that penetrate into the near-infrared part of the electromagnetic spectrum, > 1 μm carrier diffusion lengths, and tunable bandgaps. [5] The precise interactions that give rise to these desirable properties, however, remains unclear. Organic lead iodide perovskites take the chemical formula XPbI_3 , where X is a small organic cation. The 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 complex materials that support a plethora of dynamical processes essential to their photovoltaic performance. These phenomena operate over a multitude of timescales and include; organic cation rotation, [6] and octahedral distortions.[7] Several studies indicate that the interaction of dipoles between adjacent organic cations leads to macroscopic orientation and facilitates chaperoning of nascent carriers, and reducing carrier recombination rates. [1], [2]

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.

II. METHODS

FAPbI_3 thin films were synthesised using modified previously reported procedure.[8] X-ray diffraction measurements confirmed the perovskite samples were present in their cubic phase. Samples were freshly prepared prior to ultrafast measurements and rastered throughout experiments.

2DIR measurements were performed using the LIFETIME spectrometer at the Rutherford Appleton Laboratory. [9] Broadband mid-infrared ultrafast pump and probe laser pulses (central frequency = 1720 cm^{-1}) were used for the mixed time-frequency domain measurements. [10] 2DIR correlation spectra for many values of the waiting time, t_2 . Measurements were performed with pump and probe pulses aligned parallel (I_{para}) and perpendicular (I_{perp}). The time-dependent anisotropic response of the perovskite sample was generated via:

$$R(t_2) = (I_{\text{para}} - I_{\text{perp}})/(I_{\text{para}} + 2I_{\text{perp}}). \quad (1)$$

TRIR experiments were performed at the University of Bristol using an established spectrometer. [3] 760 nm pump-pulses were chosen to excite perovskite samples just above the FAPbI_3 bandgap, and the broadband mid-infrared pulses were centred at 1725 cm^{-1} .

III. RESULTS AND DISCUSSION

Two-dimensional infrared spectra were dominated by two main features (see Fig. 1(a) for $t_2 = 250\text{ fs}$): a negative feature centered on the diagonal (black dashed line) of the frequency-frequency correlation spectrum. This signal arises from overlapping ground state bleach (GSB) and stimulated emission (SE) pathways associated with the C–N antisymmetric stretching vibration of the FA^+ cation. A positive signal is also evident at $\omega_1 = 1713$, $\omega_3 = 1706\text{ cm}^{-1}$, and is the corresponding excited state absorption (ESA) signal. The spectral line shapes associated with the GSB/SE and ESA

Fig. 1 (a) Isotropic 2DIR data for C-N antisymmetric stretch of FA^+ in FAPbI_3 thin films for $t_2 = 250$ fs. The dashed black line indicates the diagonal of 2D spectrum. (b) Time-dependent anisotropic response associated with GSB/SE feature.

features in 2DIR spectra were broadly time-independent and homogeneously broadened.

The time-dependent anisotropic response for the GSB/SE is displayed in Fig. 1(b) and fit to a biexponential function (plus offset). This analysis returned 470 ± 50 fs and 2.8 ± 0.5 ps time constants ($R^2 > 0.999$), revealing that the formamidinium cation re-orient rapidly within the lead iodide lattice, meaning that the barrier to rotation must be very small compared to thermal energy at room temperature. Consequentially this means that the organic cations are unlikely to align for any meaningful length of time and form ferroelectric domains, counter to prior experimental and theoretical reports. [1], [2] Our observations are reminiscent of those made for lead-iodide perovskites incorporating smaller methylammonium cations. [6]

TRIR experiments explored the response of the formamidinium cations in the conduction band. These data are displayed in Fig. 2. Each spectrum is dominated by two positive features. The first is a sharp peak at 1718 cm^{-1} and thus attributed to a molecular vibration. This vibrational transient is festooned on a broad feature that spans all probe frequencies, with the latter assigned to electronic intra-band transitions within the conduction band. We do not observe any negative features associated with “bleaching” pathways as expected in typical TRIR line shapes. We rationalize this observation based on the following: 760 nm light generates electrons and holes in the form of either free carriers or polarons. This increases the internal electric field of the perovskite thin film and perturbs the electrostatic environment surrounding FA cations. In turn, this modulates the vibrational potential and shifts the associated vibrational frequency-inducing a vibrational Stark effect. We infer that the vibrational transition dipole moment associated with the anti-symmetric C-N stretching vibration in the conduction band is also enhanced significantly such that it dwarfs any negative

Fig. 2 TRIR spectra of FAPbI_3 thin films for 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 centered at 1718 cm^{-1} .

signals and has a comparable cross-section to the underlying electronic intra-band transient. Such observations are consistent with polaron formation inside thin semi-conducting films. As the TRIR line shape doesn’t evolve between $200 \text{ fs} \geq t_2 \geq 3 \text{ ns}$, we infer that charge-carriers immediately take the form of polarons in our perovskite thin films.

ACKNOWLEDGMENTS

TAAO acknowledges the Royal Society for financial support through the award of a University Research Fellowship (UF1402310) and research grant (RG160046). DJF and DT were supported by EPSRC (EP/L017792/1). VCAT and MD acknowledge EPSRC for Ph.D. studentships (EP/G036780/1). Access to LIFETIME at the Rutherford Appleton Laboratory was awarded by STFC (Application 16230050).

REFERENCES

- [1] A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X.-H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed, and O. M. Bakr, “Formamidinium Lead Halide Perovskite Crystals with Unprecedented Long Carrier Dynamics and Diffusion Length,” *ACS Energy Lett.*, vol. 1, pp. 32–37, Jul. 2016.
- [2] J. M. Frost and A. Walsh, “What Is Moving in Hybrid Halide Perovskite Solar Cells?,” *Acc. Chem. Res.*, vol. 49, pp. 528–535, Mar. 2016.
- [3] V. C. A. Taylor, D. Tiwari, M. Duchi, P. M. Donaldson, I. P. Clark, D. J. Fermin, and T. A. A. Oliver, “Investigating the Role of the Organic Cation in Formamidinium Lead Iodide Perovskite Using Ultrafast Spectroscopy,” *J. Phys. Chem. Lett.*, vol. 9, pp. 895–901, Feb. 2018.
- [4] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, “Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites,” *Science*, vol. 338, pp. 643–647, 2012.
- [5] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, “Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber,” *Science*, vol. 342, pp. 341–344, Oct. 2013.
- [6] A. A. Bakulin, O. Selig, H. J. Bakker, Y. L. A. Rezus, C. Müller, T. Glaser, R. Lovrincic, Z. Sun, Z. Chen, A. Walsh, J. M. Frost, and T. L. C. Jansen, “Real-Time Observation of Organic Cation Reorientation in Methylammonium Lead Iodide Perovskites,” *J. Phys. Chem. Lett.*, vol. 6, pp. 3663–3669, Sep. 2015.
- [7] A. N. Beecher, O. E. Semonin, J. M. Skelton, J. M. Frost, M. W. Terban, H. Zhai, A. Alatas, J. S. Owen, A. Walsh, and S. J. L. Billinge, “Direct Observation of Dynamic Symmetry Breaking above Room Temperature in Methylammonium Lead Iodide Perovskite,” *ACS Energy Lett.*, vol. 1, pp. 880–887, Oct. 2016.
- [8] D. Tiwari and D. J. Fermin, “Textured PbI_2 photocathodes obtained by gas phase anion replacement,” *Electrochimica Acta*, vol. 254, pp. 223–229, 2017.

[9] P. M. Donaldson, G. M. Greetham, D. J. Shaw, A. W. Parker, and M. Towrie, "A 100 kHz Pulse Shaping 2D-IR Spectrometer Based on Dual Yb:KGW Amplifiers," *J. Phys. Chem. A*, vol. 122, pp. 780–787, Jan. 2018.

[10] T. A. A. Oliver, "Recent advances in multidimensional ultrafast spectroscopy," *R. Soc. Open Sci.*, vol. 5, p. 171425, Jan. 2018.