

Impact of the Organic Cation on the Optoelectronic Properties of Formamidinium Lead Triiodide

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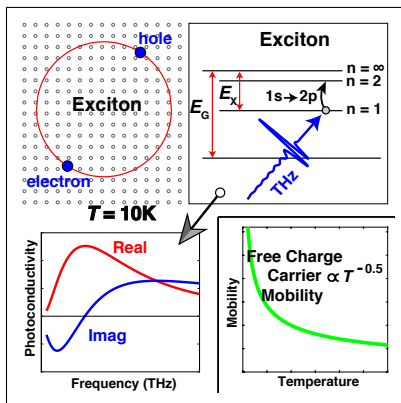
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Abstract

Metal-halide perovskites have proven to be excellent light-harvesting materials in photovoltaic devices whose efficiencies are rapidly improving. Here, we examine the temperature-dependent phonon absorption, exciton binding energy, and band-gap of FAPbI₃ (thin film) and find remarkably different behaviour across the β - γ phase transition compared with MAPbI₃. While MAPbI₃ has shown abrupt changes in the band-gap and exciton binding energy, values for FAPbI₃ vary smoothly over a range of 100 – 160 K in accordance with a more gradual transition. In addition, we find that the charge-carrier mobility in FAPbI₃ exhibits a clear $T^{-0.5}$ trend with temperature, in excellent agreement with theoretical predictions that assume electron-phonon interactions to be governed by the Fröhlich mechanism, but in contrast to the $T^{-1.5}$ dependence previously observed for MAPbI₃. Finally, we directly observe intra-excitonic transitions in FAPbI₃ at low temperature, from which we determine a low exciton binding energy of only 5.3 meV at 10 K.

Graphical TOC Entry



Keywords

FAPbI₃, MAPbI₃, Formamidinium, Charge-carrier mobility, Exciton, Cation, Temperature-dependence, Absorption, Terahertz, Conductivity

Metal-halide perovskites have received an immense amount of interest owing to their potential use as light-absorbing materials in photovoltaic devices. Over recent years, such perovskite solar cells have seen an exciting rise in performance, with current hybrid lead triiodide based devices achieving efficiencies of over 20 %.¹ High charge-carrier mobilities²⁻⁶ combined with long carrier lifetimes⁷⁻¹¹ have been shown to underpin the excellent performance of these materials. In addition, the diversity of deposition techniques, including spin coating,^{12,13} vapour deposition,¹⁴⁻¹⁶ and ink-jet printing,¹⁷ along with a relatively low cost of fabrication, makes metal-halide perovskites both economically and also physically favourable for rapid commercialization.

While the wealth of research into metal-halide perovskites is rapidly growing, most investigations into the fundamental optoelectronic properties have been focused on the prototypical methylammonium lead triiodide perovskite ($\text{MAPbI}_3 = \text{CH}_3\text{NH}_3\text{PbI}_3$). Formamidinium lead triiodide ($\text{FAPbI}_3 = \text{CH}(\text{NH}_2)_2\text{PbI}_3$) on the other hand has received far less attention, perhaps because the choice of the A-cation in the ABX_3 perovskite structure was thought to have a relatively subtle influence on the electronic properties.¹⁸⁻²¹ Here we investigate FAPbI_3 to highlight clear differences with MAPbI_3 in terms of optoelectronic and structural properties, and their dependence on temperature.

The variation in dielectric environment resulting from differences in the choice of A-cation has the potential to influence the Coulomb interactions in hybrid perovskites. As a consequence of such Coulomb interactions, discrete excitonic states may be formed from bound electron and hole pairs at energies below the band gap.^{22,23} Stronger Coulomb interactions in a material lead to a larger exciton binding energy, and also enhance the optical absorption coefficient of the above-gap unbound continuum states for charge carriers.^{22,23} The value of the exciton binding energy E_X in MAPbI_3 has been repeatedly investigated by numerous methods, including absorption onset modelling, photoluminescence quenching, and magneto-absorption, as summarized in Ref. 10. However, reported values vary widely¹⁰ owing to the challenges of directly observing excitonic transitions in these materials. Accurate knowl-

edge of E_X for a range of hybrid perovskites would be highly useful to the development of perovskite solar cells, given that excitons can only contribute to a photocurrent if efficient exciton dissociation is able to occur at the operating temperature of the device.^{24,25}

Intra-excitonic transitions take place upon absorption of low energy photons, typically on the order of a few milli-electron volts. Direct observation of such transitions can therefore be made with light in the terahertz frequency regime ($1 \text{ THz} = 4.1 \text{ meV}$) at low temperature, for which excitonic states persist against thermally induced dissociation. In the absence of an electron-hole population in the conduction and valence band of the hybrid perovskite, terahertz absorption may also result from excitation of lead-halide lattice vibrations.^{26–28} Crucially, the presence of an additional optical pulse in optical-pump terahertz-probe spectroscopy (OPTPS) will photoexcite electrons and holes, allowing a distinction to be made between such vibrational signatures and transitions between excitonic states. OPTPS has therefore been successfully used for the determination of the exciton binding energy in classical inorganic semiconductors such as GaAs-AlGaAs quantum wells.^{29–32} Here, photoexcitation of the semiconductor initially generates a highly non-equilibrium distribution of electrons and holes in the conduction and valence bands, respectively, whose thermalisation occurs on a sub-picosecond timescale, populating exciton states.³³ In OPTPS, a subsequently arriving broadband terahertz pulse (0-15 meV) then probes the presence of excitons through intra-excitonic transitions that predominantly occur between the $1s$ to np states, from whose energy the exciton binding energy can be directly inferred.

Aside from a focus on excitonic effects, the mechanisms determining the charge-carrier mobility in hybrid perovskites have also recently received much scrutiny.^{2,20,34} An understanding of the interactions and scattering processes that limit the mobility of charge-carriers is highly useful, because it can aid the design of novel hybrid perovskites optimized for photovoltaic applications.^{2,34,35} It had recently been shown that the charge-carrier mobility in hybrid lead halide perovskites is mostly governed by Fröhlich³⁶ interactions between longitudinal optical phonons and charge-carriers.²⁰ However, such assertions could potentially be

at odds with the $T^{-1.5}$ temperature dependence of the charge-carrier mobility μ repeatedly observed^{5,37–39} for MAPbI₃. Recent theoretical calculations³⁴ have suggested that in the limit of Fröhlich coupling, the temperature dependence should instead be closer to $\mu \sim T^{-0.5}$. For FAPbI₃, on the other hand, knowledge of the dependence of the charge-carrier mobility on temperature is still outstanding. Here, OPTPS offers a non-contact method to probe the charge-carrier mobility that allows exploration of such intrinsic effects, because the high-frequency AC conductivity spectrum probes the charge-carrier motion on small length scales that are less affected by extrinsic limitations, such as those posed by grain boundaries.

In this study, we utilise OPTPS to explore the photoconductivity and magneto-photoconductivity of FAPbI₃. At low temperature (10 K), we observe direct transitions between the 1s to np excitonic levels, from which we determine a remarkably small exciton binding energy of 5.3 meV. Magneto-OPTPS further reveals that the value of the exciton binding energy increases with magnetic field. Terahertz time domain spectroscopy (TDS) of FAPbI₃ is used to investigate changes in the phonon modes of Pb-I bond vibrations as a function of temperature. The phonon modes of FAPbI₃ show no splitting in the lower temperature phase which is in direct contrast with behaviour observed for MAPbI₃, highlighting differences in crystal structure. We further examine the temperature-dependence of the exciton binding energy and band-gap energy for FAPbI₃ through modelling of the absorption coefficient near the band edge. We observe smooth changes in values with temperature, which contrasts greatly with the discontinuities in the band gap and exciton binding energy typically observed at the orthorhombic-to-tetragonal phase transition in MAPbI₃. In addition, we find that the charge-carrier mobility in FAPbI₃ exhibits a temperature dependence of $T^{-0.5}$, again in contrast with previous observations for MAPbI₃, but in excellent agreement with theoretical expectations for electron-phonon coupling dominated by Fröhlich interactions.

We commenced our study by investigating intra-excitonic transitions between discrete excitonic levels in order to obtain an accurate value of the exciton binding energy in FAPbI₃. Such discrete energy levels are described by the expression $E_n = E_G - E_X/n^2$, where E_G is

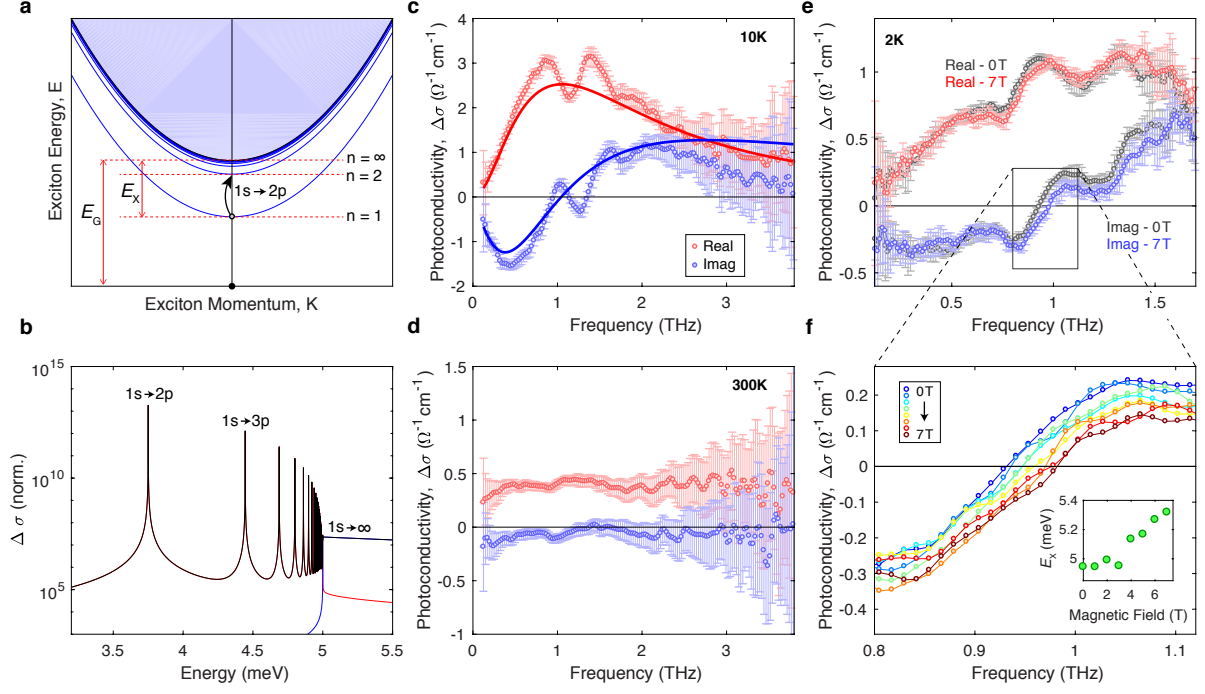


Figure 1: Intra-excitonic transitions in FAPbI₃ measured by photoconductivity spectra. **a** Exciton dispersion relation showing the discrete energy levels of the exciton at energies below the band gap. **b** Modelled photoconductivity spectra shown on a logarithmic scale, calculated from an intra-excitonic model of a 3-dimensional material with minimal broadening ($\Gamma = 1 \mu\text{eV}$; see Supporting Information for details). The bound states are shown as a red line and the continuum states are shown as a blue line, with the total shown in black. **c** and **d** Photoconductivity spectra of FAPbI₃ at 10 K and 300 K respectively. Oscillations in the spectra at 10 K between 0.8 and 1.7 THz are attributed to a modulation of the photoconductivity by phonon modes. Increasing error bars at higher frequencies demonstrate the bandwidth of the measurement. **e** Photoconductivity spectra at a magnetic field of 0 T (grey) and 7 T shown as red and blue for the real and imaginary parts, respectively. The spectrum at 7 T is found to be blue shifted with respect to the spectrum at 0 T. **f** Imaginary part of the photoconductivity spectra, taken at magnetic fields between 0 T (blue) and 7 T (red) in steps of 1 T. The inset in **f** shows the extracted exciton binding energy as a function of magnetic field. Photoconductivity spectra were measured by optical pump terahertz probe spectroscopy (OPTPS) using a 400 nm pump with a fluence of $\sim 10 \mu\text{Jcm}^{-2}$ and a probe delay of 30 ps (**c** and **d**) and 500 ps (**e** and **f**).

the energy of the band gap, E_X is the exciton binding energy, and n is a positive integer. Figure 1a illustrates schematically how such excitonic effects modify the dispersion diagram, leading to an exciton-momentum dispersion relation in the two-particle picture as a function of the centre-of-mass momentum, K , of the exciton. Since we use THz photoconductivity

spectroscopy in this study to explore the inter-excitonic resonances, Figure 1b illustrates the expected photoconductivity spectrum of intra-excitonic transitions, calculated for a material with minimal broadening ($\Gamma=1\text{ }\mu\text{eV}$ – see Supporting Information for details). We note that the photoconductivity, $\Delta\sigma$, is related to the change in dielectric function, $\Delta\epsilon$, upon photoexcitation by $\Delta\sigma = -i\epsilon_0\omega\Delta\epsilon$. Therefore, the measurement of $\Delta\sigma$ for the exciton is equivalent to the polarization response caused by the inter-excitonic transitions. Figure 1b reveals sharp lines associated with intra-excitonic transitions ($1s\rightarrow np$), with the lowest energy peak being associated with the $1s$ to $2p$ transition. The oscillator strength of transitions between the $1s$ and np levels decreases rapidly for increasing n , which results in weaker absorption into higher levels from the ground state (see Supporting Information).⁴⁰ As n tends to infinity, the photoconductivity transforms into a pseudo-continuum, and for transition energies above the binding energy, the exciton dissociates into unbound continuum states.

To explore such effects experimentally, we measured the THz photoconductivity spectra of FAPbI₃ at 10 K, where stable excitons are able to persist. Figure 1c shows these data together with a fit for the exciton resonance, given by a sum of Lorentz oscillators with resonant energies $E_{1s-np} = E_X(1 - 1/n^2)$ for transitions between the $1s$ to np states, and assuming a magnitude proportional to the oscillator strength (see Supporting Information for full details). Our use of a recently developed terahertz emitter based on the inverse spin Hall effect^{41–43} here allows for a large spectral bandwidth and therefore clear observation of a resonance near 1 THz, given by the peak in the real part, and a matching zero-crossing in the imaginary part of the photoconductivity. This photoconductivity spectrum of the excitonic resonance in FAPbI₃ is broadened, most likely by a combination of lifetime effects, defects in the crystal and interactions with phonons, such that individual transition lines cannot be resolved. From the full fit based on the modelled $1s$ – np transitions we extract an exciton binding energy of 5.3 meV for FAPbI₃ at 10 K. This value is towards the lower end of the range of values that have been reported for the related MAPbI₃,¹⁰ but it is not atypical for a semiconductor of this bandgap energy.⁴⁴ The additional modulations in the

spectrum at approximately 1 THz and 1.6 THz are attributed to phonon modes that couple to the photoexcited species, as observed previously for MAPbI₃,²⁶ and in agreement with the strong electron-phonon coupling reported for these materials.²⁰

An unambiguous assignment of the observed resonance to excitons requires us to rule out alternative origins. In principle, there is a reasonable possibility that bulk plasmons could produce a resonance in the photoconductivity spectra when these collective free-charge oscillations interact with the boundaries of their containing medium. The resonant frequency of plasmons is proportional to the square-root of the charge carrier density,⁴⁵ therefore, we measured the photoconductivity spectra for different excitation fluences corresponding to different initially generated charge-carrier densities (see Figure S4 in SI). We were unable to discern any significant shift in the resonant frequency as a function of fluence, which verifies that the observed photoconductivity does not originate from a plasmon resonance.

We further find that as we raise the temperature to 300 K, the photoconductivity no longer exhibits a resonance within the observation window (Figure 1d). The disappearance of the resonance is further proof of an excitonic effect, since excitons are expected to dissociate at thermal energies ($300\text{ K} \equiv 26\text{ meV}$) significantly higher than the exciton binding energy. In contrast, a bulk plasmon response would be expected to persist to higher temperatures. We find that instead, the photoconductivity at 300 K (Figure 1d) reflects the Drude response of charge carriers, as observed previously for metal-halide perovskites at room temperature.^{8,26} The Drude model of conductivity applies the principles of kinetic theory to the charge carriers in a material.^{46,47} In contrast with the photoconductivity spectra of excitons, a Drude response is characterised by: (i) a non-zero real component and a zero imaginary component at zero frequency; and (ii) a positive imaginary component maximum at an angular frequency equal to the scattering rate. Therefore, the observed zero imaginary part and constant positive real part across the photoconductivity spectrum derive from a free charge-carrier conductivity response with a scattering rate that lies beyond our measurement bandwidth.

The value of 5.3 meV we determine for the low-temperature phase of FAPbI₃ is smaller than that proposed previously from temperature-activated PL intensity measurements (18 meV).⁴⁸ However, the temperature-dependence of the PL intensity is also influenced by variations in trap-mediated charge-carrier recombination^{37,49} and in bimolecular charge-carrier recombination²³ which results in a complex temperature-dependence that is difficult to decouple from effects attributable solely to exciton dissociation. In addition, the value we determine is somewhat lower than that derived from magneto-absorption measurements.⁵⁰ However, since such techniques rely on an accurate extrapolation of binding energies to zero magnetic field,^{50–52} we also explore here how the low-temperature photoconductivity resonance changes with magnetic field. Numerical variational calculations on hydrogenic systems in arbitrary magnetic fields performed by Aldrich and Greene⁵² predict a rise in the exciton binding energy with increasing B-field, which has indeed been observed in inorganic semiconductors such as GaAs.³² Accurate modelling of the magneto-absorption of the exciton is therefore required for the deduction of the exciton binding energy from this method,^{50–52} with differences between the theoretical and actual dependence of the exciton binding energy on magnetic field resulting in errors in the estimation of the zero-field exciton binding energy. As a direct measure of how the exciton binding energy of FAPbI₃ changes in a moderate magnetic field between 0 T and 7 T, we exploit OPTPS to observe the excitonic resonance energy as a function of magnetic field. Figure 1e shows the photoconductivity spectra of FAPbI₃ in the presence of a magnetic field of 0 T shown in grey, and 7 T shown in red for the real and blue for the imaginary parts. The spectrum at 7 T is blue shifted with respect to the spectrum at 0 T. Zooming in on the imaginary component at the zero conductivity crossover point near 1 THz, Figure 1f demonstrates clearly the increasing resonant frequency as the magnetic field is increased in 1 T steps from 0 T to 7 T. The inset shows the increase in exciton binding energy deduced from fits based on the modelled 1s–np transitions to the data. While we do find an increase in exciton binding energy with magnetic field, the magnitude of the increase is of a significantly smaller extent than calculations would predict.^{51,52} We therefore suggest

that the discrepancy between the theoretically expected and the experimentally observed dependence of the exciton binding energy on the magnetic field is the reason for the elevated exciton binding energy suggested for FAPbI₃ from magneto-absorption experiments.

One way by which hybrid perovskites differ from classical inorganic semiconductors is by exhibiting a plethora of structural phase transitions at different temperatures. However, while the structural phases of MAPbI₃ and their transition temperatures are well established, the picture for FAPbI₃ is far less clear.^{53–58} An important starting point for structural calculations is an accurate knowledge of the energy of phonon modes of a material’s lattice structure. We therefore use absorption spectra at terahertz frequencies to investigate the phonon modes in FAPbI₃ as a function of temperature, and contrast our findings with what is observed in MAPbI₃.

Table 1: Reported crystal phases of FAPbI₃ and MAPbI₃. While a consensus of the crystal phases of MAPbI₃ has been reached, a unified picture of the crystal phases of FAPbI₃ is still outstanding. Note[†] that Chen *et al.*⁵⁶ reported different phase transition temperatures for heating and cooling.

	α -phase		β -phase		γ -phase	Ref.
FAPbI ₃	$P3m1$ Trigonal	$\leftarrow 150\text{ K} \rightarrow$	$P3$ Trigonal	$\leftarrow 100\text{ K} \rightarrow$	-	53
	$Pm\bar{3}m$ Cubic	-	-	-	-	54
	$Pm\bar{3}m$ Cubic	$\leftarrow 285\text{ K} \rightarrow$	$P4/mbm$ Tetragonal	$\leftarrow 140\text{ K} \rightarrow$	$P4/mbm$ Tetragonal	55
	$Pm\bar{3}m$ Cubic	$\leftarrow 290 - 350\text{ K}^\dagger \rightarrow$	$P6_3/mmc$ Hexagonal	$\leftarrow 100 - 175\text{ K} \rightarrow$	$P6_3/m$ Hexagonal	56
	$Pm\bar{3}m$ Cubic	$\leftarrow 280\text{ K} \rightarrow$	$P4/mbm$ Tetragonal	$\leftarrow 140\text{ K} \rightarrow$	$P4bm$ Tetragonal	57
MAPbI ₃	$Pm\bar{3}m$ Cubic	$\leftarrow 327.4\text{ K} \rightarrow$	$I4/mcm$ Tetragonal	$\leftarrow 162.2\text{ K} \rightarrow$	$Pnma$ Orthorhombic	58

To illustrate the inconsistencies in the literature on the phase transitions between the α , β and γ (high to low-temperature) phases of FAPbI₃ we present in Table 1 details of previously reported structures. The structural phases of MAPbI₃ and the transition temperatures are

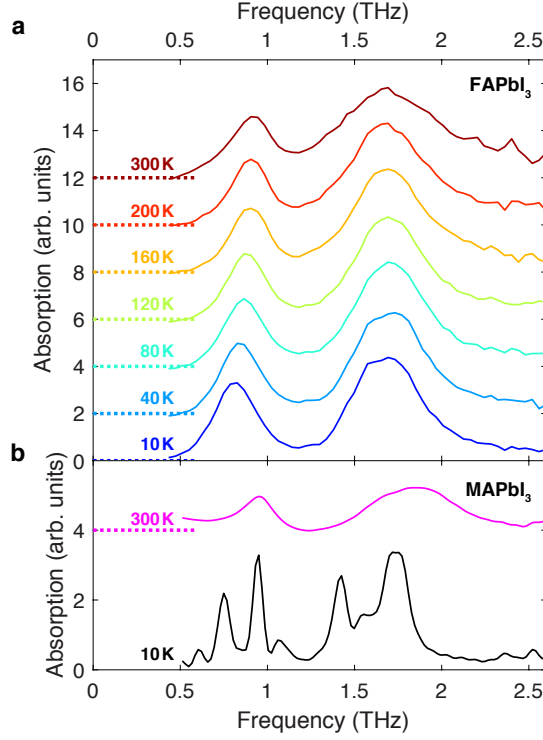


Figure 2: Lead-iodide phonon absorption spectra. **a** Absorption spectra of FAPbI₃ at terahertz frequencies for different temperatures. The two peaks at approximately 0.8–0.9 and 1.65 THz are attributed to Pb-I vibrations. The dashed lines show the offsets by which each spectrum has been shifted for clarity. **b** Absorption spectra of MAPbI₃ at 10 K and 300 K at terahertz frequencies. In contrast to FAPbI₃, the lead-halide phonon modes of MAPbI₃ split into 4 modes at low temperature.^{27,28} The absorption, α_{Abs} was calculated from the measured transmission, T using the expression $\alpha_{\text{Abs}} = -\ln(|T|)$.

well established, and there is generally good agreement with the parameters shown in the last line of Table 1. However, the table highlights a large spread in reported structures for FAPbI₃, with some sort of consensus only existing for the cubic high-temperature α -phase. In addition to the determination of structural phases for bulk FAPbI₃, other studies have reported on the structural phases of nanocrystals, with the nanocrystal form of FAPbI₃ taking a cubic form at room temperature.⁵⁹ For FAPbI₃, the phase transitions between both the α - β and β - γ phases appear to occur over a large temperature region (> 50 K), which has been attributed to the non-trivial reorganisation of atoms owing to the lack of a group-subgroup relation between space groups of the phases, and also the different temperature-dependent rotational

dynamics of the FA cation, compared to the MA cation.^{55,56,60} Upon the transition from the high-temperature, high-symmetry α -phase to the β -phase, the symmetry is lowered by the introduction of Pb-I octahedra tilting. The transition from the β -phase to the low-temperature γ -phase is accompanied by a freezing of the cations in random orientations.⁵³ Interchanging the cation between MA and FA therefore has a significant impact on the structural properties of the material. As we show below, such changes may also affect the optical properties, as evident from differences in the phonon modes and optical absorption.

The dark terahertz transmission, T , of a FAPbI₃ thin film was measured by terahertz time-domain spectroscopy (see Experimental Details below). Absorption, α_{Abs} , was calculated from the measured transmission using the expression $\alpha_{\text{Abs}} = -\ln(|T|)$. Figure 2a reveals two phonon modes at approximately 0.85 THz and 1.65 THz for FAPbI₃, which we attribute to vibrations of the Pb-I bonds, in analogy with MAPbI₃.²⁶⁻²⁸ We find that in FAPbI₃, these modes are largely unchanged over the temperature range from 10 K to 300 K, despite the up to two phase transitions occurring over that range, i.e. from the low-temperature γ -phase to the β -phase between 100 K and 175 K and potentially on to the α -phase near 290 K.^{55,56} There is only a small shift in the lowest frequency mode, from 0.8 THz at low temperature, to 0.9 THz at room temperature. In contrast, Figure 2b shows the absorption of phonon modes in MAPbI₃, which change significantly between 10 K and 300 K, that is, the two high-temperature phonon modes observed in the β -phase split into four phonon modes in the γ -phase.^{27,28} Such differing behaviour can be attributed to the link between the dynamics of the Pb-I octahedra and the orientation of the organic cation.⁶¹ In the two high-temperature phases of MAPbI₃ (α and β) both tumbling (rapid reorientation of the C-N axis) and twisting (rotation about the C-N axis) of the MA cation are possible, however only twisting is possible in the γ phase.^{62,63} The low-temperature rotational dynamics of the FA cation have been explored to a much lesser extent. Carignano *et al.* have performed molecular dynamic simulations of FAPbI₃, and found that at high temperatures (450 K) FA rotations about the N-N axis and orthogonal to the N-N axis are possible. On lowering the

temperature from 450 K to 300 K, the FA cation mobility reduces and rotations are nearly all about the N-N axis.⁶¹ While at lower temperatures the rotational freedom of MA in MAPbI₃ is significantly reduced, the FA cation in FAPbI₃ appears to be less affected.⁶⁴ In addition, FA cations have a larger effective ionic radius than MA cations, which results in FAPbI₃ having a larger unit cell than MAPbI₃.⁵⁴ In general, we conclude that the differences between FAPbI₃ and MAPbI₃ in terms of the temperature-dependent phonon mode spectra most likely derives from the different dynamics of the FA and MA cations in the lead-iodide cage.

The magnitude of the dipole moments carried by the chosen A-cation could potentially influence the polarizability of the perovskite.⁶⁵ Any changes in the dielectric function will have an effect on charge-carrier screening and therefore the exciton binding energy. To observe the effect of structural changes with temperature on the exciton binding and band gap energy, we measured the reflection (R) and transmission (T) spectra of FAPbI₃ between 4 K and 300 K, using a Fourier transform infrared spectrometer with the sample mounted in a gas exchange cryostat (see Experimental Details below). Reflection-transmission spectra were converted to absorption coefficient spectra ($\alpha(E)$) using $\alpha = -(1/d) \ln(T/(1 - R))$, where d is the thickness of the FAPbI₃ film.

Figure 3a presents the resulting absorption coefficient spectra of FAPbI₃ as a two dimensional colour map versus temperature and energy. Outside of the phase transition region between ~ 100 K and 160 K, the absorption onset generally blue shifts with increasing temperature in both the high- and low-temperature phases. This general trend in band gap energy with temperature is similar to what has been observed for MAPbI₃^{20,37} but is in contrast with the typical behaviour for III-V inorganic semiconductors, such as GaAs.⁶⁶

To extract values for the band gap energy and exciton binding energy, the absorption spectrum has to be modelled to include both electronic transitions between electron-hole continuum and bound excitonic states, as illustrated earlier in Figure 1a. Elliott developed a theory on the intensity of optical absorption by excitons,²² which has previously been

applied to model the absorption onset for MAPbI₃.^{23,67,68} Here we apply this theory for FAPbI₃ to determine the band gap (Figure 3c) and the exciton binding energy (Figure 3d) as a function of temperature (see SI for a full description of the fitting function used). An example fit of Elliott’s expression to the absorption onset at one temperature (4 K) is shown in Figure 3b. We note that unlike for MAPbI₃, which at low temperature has been found to exhibit a sharp peak below the gap as a result of absorption into bound excitonic states,^{23,67} FAPbI₃ only exhibits a much weaker enhancement. Our fits of Elliott’s expression to the absorption onset show that the lack of a pronounced excitonic peak for FAPbI₃ at 4 K is not the result of increased broadening, but rather derives from a low value of the exciton binding energy, in agreement with the low-energy excitonic resonance we observed in our OPTP measurements discussed above.

From the dependence of the band gap energy on temperature (Figure 3c) we can clearly discern a region between 100 K and 160 K (shaded grey) over which a change from the γ -phase to the β -phase occurs. This transition temperature range agrees well with that deduced from previous XRD measurements.^{55,56} We note that the change in bandgap energy at the phase transition we observe here for FAPbI₃ is markedly different from that previously reported for MAPbI₃^{23,37} which typically displays a sharp discontinuity in band gap of the order of 100 meV. In contrast, the change in bandgap energy between the β and γ phases in FAPbI₃ is remarkably smooth, occurring over a wide temperature range (\sim 60 K) and only leading to a downshift of \sim 20 meV with increasing temperature. This contrasting behaviour in terms of band-gap changes at the phase transition of FAPbI₃ and MAPbI₃ is likely to arise from the difference in molecular dynamics of the organic cations already mentioned above. It has been suggested that for MAPbI₃, reorientation of the dipole (tumbling of C-N axis) completely freezes out once the low-temperature γ -phase is entered. However, some degree of dipole reorientation (about the N-N axis) is preserved in FAPbI₃ both in the β and γ phases near the transition temperature,⁶⁰ which will lead to the much more gradual change in optical properties we report here.

The other parameter obtained from fits of Elliott’s theory to the band edge is the exciton binding energy, shown in Figure 3d as a function of temperature. In the low temperature γ -phase, the exciton binding energy is approximately constant with a value near 8 meV. Over the phase transition from the γ to β -phase (beginning at 100 K through to 160 K), a steady decline in the exciton binding energy occurs. The exciton binding energy continues to decrease with increasing temperature throughout the β -phase, reaching a value of 2.4 meV at room temperature. We recently extracted the exciton binding energy for MAPbI₃²³ through an identical method of Elliott fitting of the absorption onset, and note two main differences with the data reported here for FAPbI₃. The first is, that the overall value of the binding energy for FAPbI₃ is generally lower by a factor of 2–3 than for MAPbI₃ across the temperature range. The second is that while both FAPbI₃ and MAPbI₃ exhibit a near constant value of the exciton binding energy in the γ -phase, the behaviour around the phase transition is markedly different. For MAPbI₃, a sharp decrease in binding energy by approximately 5 meV has been found to occur over a very narrow temperature range.²³ However, here we observe that there is no sudden discontinuity in the exciton binding energy for FAPbI₃ (Figure 3d) but rather a gradual decrease over a broad temperature range. The absence of discontinuities in the band gap and exciton in FAPbI₃ and the presence of discontinuities in MAPbI₃ suggests a different nature of the phase transition, and is attributed to differences in the dynamics and structural influence of the FA and MA cations on FAPbI₃ and MAPbI₃, respectively. We note that these observations for the exciton binding energy are in agreement with temperature-dependent measurements of the dielectric permittivity of FAPbI₃, which was found to change smoothly across the phase transition.⁵⁵ The inherent dependence of the exciton binding energy on the inverse of the square of the dielectric permittivity¹⁰ is therefore reflected in the differences in the nature of the phase transition, and the associated changes in polarizability of the material.

We note that the value we extract for the exciton binding energy at low temperature is slightly higher for the Elliott approach compared with that determined from terahertz spec-

troscopy (OTPT). We suggest that these slight discrepancies may arise from the difficulties in obtaining a satisfactory fit of Elliott’s theory to the absorption onset over a sufficiently wide energy range.^{23,68} As we have shown recently, Elliott’s theory does not account for the possible presence of multiple electronic transitions, non-parabolic bands and an energy dependence of the associated matrix elements.²³ As a result, the shape of the free (uncorrelated) continuum-state absorption may deviate from the square-root dependence on energy above the gap. As we discuss in more detail in the Supporting Information, for FAPbI₃, these deviations seem to cause a slight up-shift in the value of the exciton binding energy extracted from the Elliott approach.

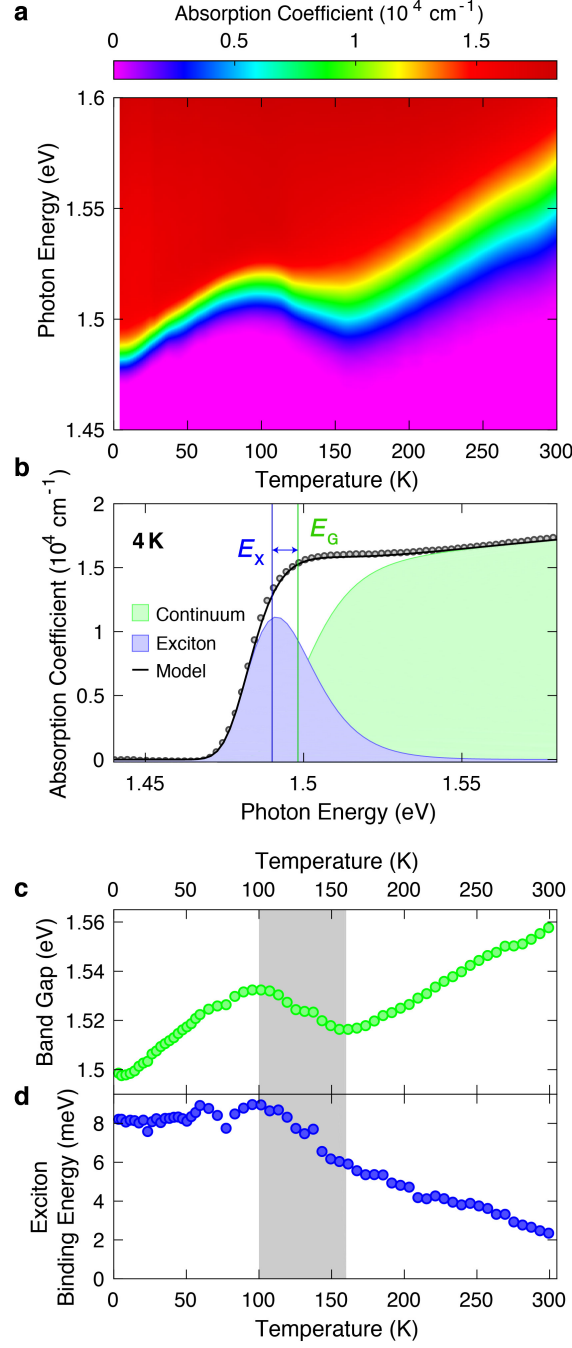


Figure 3: Absorption coefficient of FAPbI₃ at optical frequencies. **a** Temperature-dependent absorption spectra of FAPbI₃ displayed as a two dimensional colour map. **b** Absorption spectrum at 4 K, measured by Fourier transform infrared (FTIR) spectroscopy. Experimental data are shown as grey circles and a fit based on Elliott's theory is shown as a solid black line. Contributions to the absorption coefficient from bound excitonic and continuum states are displayed by shaded blue and green areas, respectively. The vertical green line shows the band gap energy, E_G and the difference between blue and green vertical lines is the exciton binding energy, E_X . **c** and **d** show the band gap and exciton binding energy extracted from such fits to the absorption spectra. The grey area displays the region of the observed β - γ phase transition of FAPbI₃ between 100 K and 160 K.

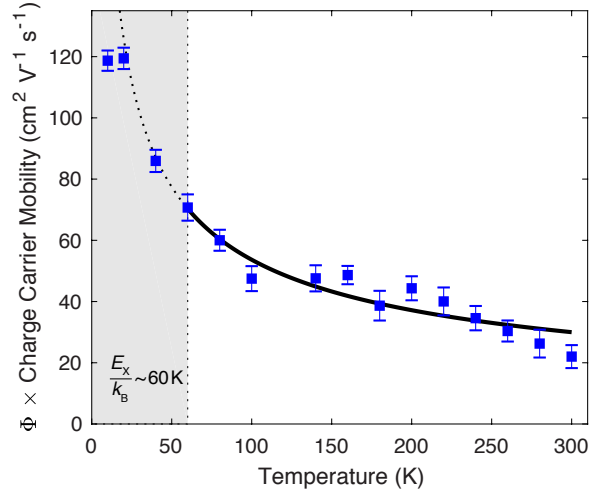


Figure 4: Effective charge carrier mobility $\Psi\mu$ as a function of temperature for a thin film of FAPbI₃. Here, μ is the charge-carrier mobility, and Ψ the photon-to-free-charge branching ratio, which is expected to decrease from a high-temperature value of 1 when the temperature is lowered below the value of $E_X/k_B \sim 60$ K and excitons become thermally stable. The solid line shows a fit of $\mu \propto T^w$ to the data for temperatures 60 K and above. A power-law behaviour with an exponent of $w = -0.53$ is found, in agreement with predictions³⁴ based on charge-carrier interactions with polar optical-phonons.²⁰

Another electronic parameter that underpins the operation of solar cells is the charge-carrier mobility. For charge carriers to be extracted in a photovoltaic device, charge mobilities need to be sufficiently high such that within the carrier lifetime the charges are able to reach the electron and hole transport layers.¹¹ Terahertz photoconductivity measurements are an excellent choice for studying the charge carrier mobility of a material as the method does not rely on electrical contacts that would otherwise complicate the measurement.

The mechanisms limiting the mobility of charge-carriers in metal halide perovskites are a subject of much current debate. While some hybrid perovskites can still show dependences on extrinsic factors, such as electron scattering off grain boundaries and defects, it has recently been argued that high-performing materials such as MAPbI₃ and FAPbI₃ are nearing the limit of what is intrinsically achievable.² An analysis of the temperature-dependent emission line broadening in MAPbI₃ and FAPbI₃²⁰ further revealed that Fröhlich interactions between charge-carriers and longitudinal optical (LO) phonons are the dominant intrinsic mechanism limiting charge-carrier motion. Such a mechanism qualitatively agrees with the

strong increase observed in the charge-carrier mobility of MAPbI₃ as the temperature is lowered.^{5,37–39} However, such measurements have consistently yielded^{5,37–39} a dependence of the charge-carrier mobility μ on temperature T according to $\mu \propto T^w$ with $w = -1.5$. This experimentally determined value of the exponent w for MAPbI₃ does not agree with the value of ~ -0.5 proposed recently³⁴ as a suitable high-temperature approximation to the charge-carrier mobility expected according to Hellwarth and Biaggio⁶⁹ when Fröhlich interactions dominate.

To assess whether such discrepancies also manifest themselves in FAPbI₃, we used OPTP to measure the effective charge carrier mobility as a function of temperature for FAPbI₃ (see Methods and Supporting Information for experimental details). Figure 4 shows the resulting data together with a best fit to $\mu \propto T^w$ over the temperature-range 60–300 K, which yields a value of $w = -0.53$, very close to what would theoretically be expected for MAPbI₃ when subject to Fröhlich interactions.³⁴ We note that this fit excluded data points below 60 K, as excitonic effects may become more dominant here ($k_b \times 60 \text{ K} \leq 5.3 \text{ meV}$) and hence measurements of the effective charge-carrier mobility no longer fully reflect the values of the charge carrier mobility in the material (see SI). To indicate this, the dashed line is extrapolated from the fit, at temperatures below 60 K.

Our results thus reveal that the discrepancy between the theoretically expected and experimentally determined temperature-dependence of the charge-carrier mobility for MAPbI₃ is not a universal feature of lead-iodide perovskites. For FAPbI₃, excellent agreement with the dependence expected for halide perovskites is obtained, suggesting that a Fröhlich picture of charge-carrier interactions with phonons is fully appropriate. While we cannot conclusively determine here the reasons for the discrepancy between theory and experiments observed in MAPbI₃, we propose that they may lie in issues with phase retention observed in MAPbI₃. Experiments have repeatedly shown that thin films of MAPbI₃ may have remnant domains that contain regions of different crystallographic structure.⁷⁰ For example, additional photoluminescence features in the low-temperature orthorhombic phase below

160 K have been attributed to the presence of remnant tetragonal domains over a relatively large temperature range.⁷⁰ Such regions could represent barriers to charge-carrier motion, whose prevalence depends on the material temperature, leading to a deviation from the intrinsic behaviour expected from Fröhlich interactions alone. For FAPbI₃, on the other hand, such minority-phase inclusions have been shown to be absent,²⁰ and hence the expected^{34,69} temperature-dependence of $\mu \propto T^{-0.5}$ is indeed observed.

In conclusion, our temperature dependent studies of FAPbI₃ have revealed significant differences in the optoelectronic properties in comparison with MAPbI₃. We directly observed intra-excitonic transitions in FAPbI₃ from which we determined the exciton binding energy to be 5.3 meV at 10 K, which is at the low end of the spectrum of reported values for MAPbI₃. We further examined how parameters critical to the operation of photovoltaic cells, such as the exciton binding energy, band gap, vibrational properties and charge-carrier mobilities vary with temperature and across phase transitions. We found that, in contrast to MAPbI₃, the band gap and exciton binding energy varies smoothly over a range of 100–160 K at the β to γ phase transition in FAPbI₃. Such absence of clear discontinuities for FAPbI₃ most likely results from the rotational freedom of the FA dipole moment being reduced only gradually upon entry into the γ phase, whereas in MAPbI₃, MA dipole rotation is frozen out abruptly over a narrow temperature range. We also demonstrated that such structural changes manifest themselves in the IR phonon signatures associated with the lead-halide sublattice vibrations. The two phonon modes observed in the β phase are largely unchanged for FAPbI₃ upon entry into the γ phase, while for MAPbI₃, a splitting into four phonon modes is observed. Finally, we revealed that the charge-carrier mobility in FAPbI₃ exhibits a clear $T^{-0.5}$ trend with temperature, in excellent agreement with theoretical predictions for halide perovskites whose electron-phonon interactions are governed by the Fröhlich mechanism, but in contrast to the $T^{-1.5}$ dependence previously observed for MAPbI₃. The contrasting temperature-dependent behaviour of excitons, phonons, electronic transitions and charge-carrier mobilities in MAPbI₃ and FAPbI₃ highlight the impact of cation substitution not

only on the structure of the perovskite but also on its optoelectronic properties.

Experimental Details

FAPbI₃ thin film fabrication by vapour-deposition

Formamidinium lead triiodide thin films were fabricated using thermal co-evaporation in a vacuum chamber. We used a dual-source evaporation system (Kurt J. Lesker), with PbI₂ and FAI as precursors. Formamidinium iodide powder was obtained from Dyesol and PbI₂ beads from Alfa Aesar. The PbI₂ and FAI precursors were heated in separate crucibles until each of the precursors evaporated. During evaporation the pressure in the chamber stayed at approximately 10⁻⁶ mbar. For FAI the evaporation temperature was 150 °C, and PbI₂ was evaporated at 300 °C. The quartz substrates were mounted above the sources so that the vapours condensed on to the substrates and an FAPbI₃ film formed. The deposited films were annealed on a hotplate at 170 °C for 1 min to ensure that they were in the desired perovskite phase of FAPbI₃. We previously confirmed and reported that this deposition method results in smooth, uniform FAPbI₃ thin-films.¹⁶ The samples used in this study are from the same batch growth as that reported by Borchert et al.,¹⁶ whose study provides a detailed characterisation of the material including X-ray diffraction measurements, performance in photovoltaic cells, atomic force microscopy images of the surface, scanning electron microscopy images, UV/VIS and near-IR absorption spectra and PL lifetimes.

Terahertz time-domain spectroscopy (TDS)

Terahertz time domain spectroscopy (TDS) was used to measure the absorption of phonon modes in FAPbI₃ and MAPbI₃. With TDS, the output of an amplified laser system with 30 fs pulses at a repetition rate of 5 kHz with a central wavelength of 800 nm and an average power of 4 W is split into two beam paths: a probe beam; and a gate beam. Terahertz

pulses are generated by the inverse-spin Hall effect.^{41–43} Terahertz pulses are detected by electro-optic sampling using a 0.2 mm thick GaP(110) crystal, Wollaston prism and a pair of balanced photodiodes. Temperature-dependent TDS measurements were performed using a cold-finger cryostat (Oxford Instruments). By measuring FAPbI₃ on a quartz substrate and taking reference measurement of a quartz substrate, we can obtain the terahertz transmission in the time domain.

Optical pump terahertz probe spectroscopy (OPTPS)

Optical pump terahertz probe spectroscopy (OPTPS) was used to measure the photoconductivity of FAPbI₃. OPTPS extends the TDS technique to allow measurement of a sample in the photoexcited state. A schematic of the OPTPS setup is provided in Supporting Information. In OPTPS, the sample is photoexcited by an optical pump, and after a short time delay is probed with a terahertz pulse. The generation and detection of the terahertz pulse is the same as in the TDS method detailed above. Transformation from the change in transmission with photoexcitation to photoconductivity is detailed in Supporting Information. Magneto-photoconductivity measurements were measured by magneto-OPTPS, which is the same as OPTPS but conducted in the presence of a magnetic field (Oxford Instruments Spectromagnet). For magneto-OPTPS, terahertz pulse were generated using optical rectification using a ZnTe crystal and were detected using a ZnTe crystal. Further experimental details have been detailed previously.³²

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to determine the absorption coefficient spectra of FAPbI₃. Temperature-dependent reflectance transmission measurements of FAPbI₃ were performed using a FTIR spectrometer (Bruker Vertex 80v) with the sample mounted in a gas exchange cryostat (Oxford Instruments OptistatCF2). A tungsten halogen lamp was used as the illumination source, with a CaF₂ beamsplitter and a silicon detector.

Acknowledgement

The authors gratefully acknowledge support from the Engineering and Physical Sciences Research Council (EPSRC) through Projects EP/P033229/1, EP/P006329/1 and EP/L024667/1). J.B. is supported through a studentship by the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics (EP/L01551X/1).

Supporting Information Available

Details of Optical-Pump Terahertz-Probe Spectroscopy set-up. Details of photoconductivity of intra-excitonic transitions. Analysis of photoconductivity measured by OPTPS. Determination method of charge-carrier mobility from OPTPS. Extraction of exciton binding energy from fitting of the absorption edge. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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