

Phonon coherences reveal the polaronic character of excitons in two-dimensional lead halide perovskites

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Hybrid organic–inorganic semiconductors feature complex lattice dynamics due to the ionic character of the crystal and the softness arising from non-covalent bonds between molecular moieties and the inorganic network. Here we establish that such dynamic structural complexity in a prototypical two-dimensional lead iodide perovskite gives rise to the coexistence of diverse excitonic resonances, each with a distinct degree of polaronic character. By means of high-resolution resonant impulsive stimulated Raman spectroscopy, we identify vibrational wavepacket dynamics that evolve along different configurational coordinates for distinct excitons and photocarriers. Employing density functional theory calculations, we assign the observed coherent vibrational modes to various low-frequency ($\lesssim 50\text{ cm}^{-1}$) optical phonons involving motion in the lead iodide layers. We thus conclude that different excitons induce specific lattice reorganizations, which are signatures of polaronic binding. This insight into the energetic/configurational landscape involving globally neutral primary photoexcitations may be relevant to a broader class of emerging hybrid semiconductor materials.

Hybrid organic–inorganic metal halide perovskite quantum-well-like derivatives are of increasing interest due to the presence of strongly bound, stable excitons at room temperature^{1–6}. These excitons are viewed broadly as analogous to those in epitaxial semiconductor quantum wells, which generally feature much lower binding energies. Nevertheless, the distinct ionic character, and the ‘softness’ of the lattice give rise to strong electron–phonon coupling and dynamic disorder effects, which influence the optical and electronic properties of this class of materials^{7–9}, and their consequences on excitonic structure are not thoroughly explored. Thus, there are open questions on the peculiar nature of excitons in these structurally complex materials, which are argued to be in an intermediate regime between extended Wannier excitons in quantum-confined semiconductors and localized excitons in molecular semiconductors¹⁰. We establish here that excitons in two-dimensional (2D) hybrid perovskites are dressed by the ionic lattice leading to the coexistence of multiple excitons with distinct lattice couplings. This has consequences in the formation of biexcitons¹¹, for example, which would have profound implications for the development of light-emitting devices^{12–15}. More generally, our conclusions will shape the detailed description of fundamental excitonic processes—energy transport, population dynamics and quantum dynamics (involving dynamics of many-body couplings and of dephasing dynamics, for example) in 2D hybrid perovskites. Beyond these materials, this knowledge represents an acute contribution to the comprehension of ionic semiconductors with elaborate hybrid lattices^{16,17}.

Unlike excitons in (non-ionic) semiconductor quantum wells, for which the resonances are characterized by sharp, structureless spectral lineshapes, excitons in these materials display a rich spectral structure that depends on the degree of lattice distortion

imposed by the organic cationic ligands^{6,18–27}. To account for this structure, we have invoked a general framework of a delocalized Wannier exciton with binding energy $\sim 200\text{ meV}$ but with substantially large coupling to local lattice vibrations, modelled by four distinct, non-degenerate excitonic transitions, spectrally separated by multiples of 35 meV ⁶. Previously, we hypothesized that polaronic effects play a role in such a rich excitonic spectral structure⁶ ubiquitously observed in 2D perovskites. A direct optical probe of polaronic effects on the nature of excitons would be resonance-Raman spectroscopy²⁸. However, the high photoluminescence background in these materials obscures the relatively weak Raman signal, making such a measurement a practically arduous task. Here, we find direct and unambiguous evidence for this hypothesis by implementing high-resolution resonant impulsive stimulated Raman spectroscopy (RISRS)^{29,30}. We establish polaronic effects on discrete non-degenerate excitonic transitions, evident via distinct coupling to low-frequency phonons. We find that the coupling of carriers to lattice degrees of freedom is stronger than that for excitons in general, which we rationalize by the ionic nature of the crystal. Nevertheless, different excitons with a common ground state and with specific polaronic character coexist in this class of materials.

We focus on two prototypical single-layer perovskite systems, $(\text{PEA})_2\text{PbI}_4$ (PEA = phenylethylammonium) and $(\text{NBT})_2\text{PbI}_4$ (NBT = *n*-butylammonium), which have slightly different structural distortions imposed by the organic cation³¹. The exciton absorption spectrum of $(\text{PEA})_2\text{PbI}_4$ measured at 5 K, is shown in Fig. 1a and the representative crystal structure is depicted in Fig. 1b. The spectrum is characterized by a very well-defined lineshape composed of two dominant transitions at 2.37 and 2.41 eV, labelled A and B, respectively in Fig. 1a, and two additional peaks with the same energy spacing above and below these two main peaks, with

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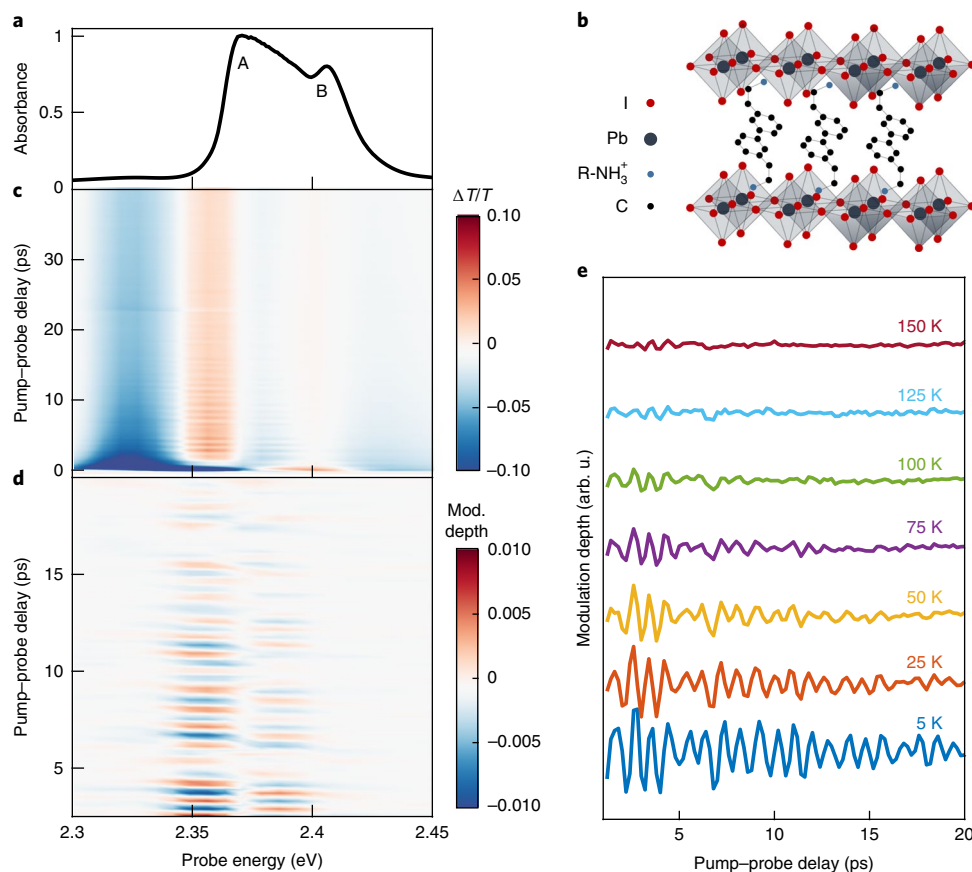


Fig. 1 | Impulsive coherent vibrational dynamics of $(\text{PEA})_2\text{PbI}_4$. **a**, Absorption spectrum measured at 5 K. **b**, Schematic of the lattice structure of $(\text{PEA})_2\text{PbI}_4$ (see Supplementary Section 1 for X-ray diffraction data). **c**, The time-resolved differential transmission spectrum measured at 5 K and with a pump photon energy of 3.06 eV. **d**, Oscillatory components of the time-resolved differential transmission spectrum, obtained by subtracting the population dynamics (empirically approximated as twelfth-order polynomials) from the transient spectrum in **c**. **e**, Temperature-dependent cuts of the oscillatory response obtained by binning transient maps such as that displayed in **d** around a probe energy of 2.35 eV.

much lower oscillator strength⁶. We have carried out transient absorption measurements by pumping into the conduction band at 3.06 eV, shown in Fig. 1c. These excitation conditions generate an initial hot charge-carrier density. The spectra and dynamics follow the reported trends dominated by carrier thermalization and exciton-screening mechanisms^{32,33}. During the first picosecond, the differential transmission spectrum is composed of a strong negative feature across the A band and a positive feature at the B band. This lineshape is characteristic of a superposition of excitation-induced shift and broadening of the excitonic transition by many-body interactions along with the bleach of higher lying electronic states³⁴. In a few picoseconds, the positive signal corresponding to the ground-state bleach gains in intensity, indicating carrier thermalization into the A exciton. The spectrum still contains the signatures of pump-induced spectral shifts induced by the substantial photocarrier population over picosecond time windows. The low-energy negative feature below 2.3 eV can be attributed to the excited-state absorption from the exciton to multi-particle states¹¹.

In addition to the population dynamics, we observe a periodic modulation of the differential transmission signal, particularly strong in the spectral region that corresponds to absorption of exciton A. The oscillatory components can be clearly seen after subtracting the population dynamics at all detection energies as shown in Fig. 1d. We identify these as the signatures of coherent phonons generated via RISRS induced by the ultrashort pump pulse²⁹. When the duration of the pulse is much shorter than the period of

Raman-active low-frequency vibrations, Raman interactions generate an impulsive force on the lattice driving its coherent motion²⁹. This modulates the permittivity at the frequency of the lattice motion, which can be detected as the oscillatory component of the differential transmission signal.

As shown in Fig. 1e, at higher temperatures the coherent oscillations not only dephase faster due to phonon-phonon scattering³⁵, but they also exhibit reduced modulation depth. The latter can be attributed to the presence of strong dynamic disorder, especially above 100 K as we have demonstrated previously¹¹. We focus only on the coherent phonon dynamics at 5 K in the rest of the manuscript because the conclusions that we draw by analysing the vibrational coherences under resonant excitation at low temperature are relevant over the entire range up to room temperature, as we have established that the same excitonic spectral structure persists over this range^{6,11}. The full temperature-dependent dataset is presented in Supplementary Figs. 2 and 3.

By Fourier-transforming the measured oscillatory response in Fig. 1 along the pump-probe time axis, we obtain a RISRS spectrum. We identify six vibrational modes that we label M1–M6, with peak energies reported in Table 1. The peaks display well-defined Lorentzian lineshapes with full-width at half-maximum ≤ 0.33 meV, as shown by the fit in Fig. 2a.

To properly discern the nature of coupling and to assign the observed energies to specific lattice vibrations, we calculated the vibrational normal modes of $(\text{PEA})_2\text{PbI}_4$ by using density functional theory (DFT) within the harmonic approximation. This (almost)

Table 1 | Assignment of the resonant impulsive stimulated Raman spectrum of (PEA)₂PbI₄ and (NBT)₂PbI₄

Mode	Measurement (meV)	Calculation (meV)	λ (meV)	Mode assignment
(PEA) ₂ PbI ₄				
M1	2.57 ± 0.01	3.18	0.609	Octahedral twist along one of the two pseudocubic axes of the inorganic sheet
M1'	—	3.93	0.94	Octahedral twist along one of the two pseudocubic axes of the inorganic sheet ^a
M2	4.38 ± 0.01	4.51	5.21	Octahedral twist and Pb–I–Pb bending
M3	4.89 ± 0.02	4.51	3.49	Pb displacement and Pb–I–Pb bending
M4	5.22 ± 0.06	—	—	— ^b
M5	5.41 ± 0.02	5.34	4.54	Pb–I–Pb bending and P–I stretching
M6	5.75 ± 0.01	5.86	4.78	Scissoring of Pb–I–Pb angle
(NBT) ₂ PbI ₄				
N1	3.10 ± 0.01	2.93	0.76	Octahedral twist along one of the two pseudocubic axes of the inorganic sheet
N2	5.42 ± 0.02	5.38	4.42	Octahedral twist along one of the two pseudocubic axes of the inorganic sheet
N3	6.06 ± 0.01	5.97	16.29	Octahedral twist orthogonal to the inorganic sheet
N4	6.52 ± 0.15	6.60	8.69	Scissoring of Pb–I–Pb angle
N5	7.31 ± 0.19	7.37	0.12	Scissoring of Pb–I–Pb angle

Experimental vibrational energies from the spectrum in Fig. 2, and normal-mode energies obtained from DFT calculations, along with the mode assignment. ^aMode M1' is predicted by calculation but is not discernible experimentally. ^bMode M4 is measured experimentally but not predicted by calculation.

parameter-free computational approach represents the current state-of-the-art in the simulation of the vibrational spectroscopic response of solid-state materials including hybrid perovskites^{35–38}. The calculations do not yield negative vibrational frequencies at the Γ point, further indicating that the crystalline structure used to model PEA₂PbI₄ is a real minimum of the potential energy surface (PES; the full list of computed vibrational frequencies is reported in Supplementary Section 5).

The electron–phonon coupling is estimated by displacing the crystalline structure along the normal mode (Q_i) and evaluating the corresponding variation of the single-particle electronic bandgap (E_g). For each normal mode Q_i in the energy region of interest, we find a linear relationship between the displacement and the bandgap (that is, linear electron–phonon coupling regime) and calculate the relaxation energy λ_i as^{39,40}:

$$\lambda_i = \left(\frac{\partial E_g}{\partial Q_i} \right)^2 (4\alpha_i)^{-1} \quad (1)$$

where α_i is the curvature of the ground-state PES along the Q_i normal mode of vibration. Among all normal modes below 8 meV, our calculations identify a few with frequency similar to those showed in Fig. 2a and associated with sizable relaxation energy (a few millielectronvolts); that is, coupled to bandgap excitations. In Table 1, we compare the experimental vibrational frequencies with those obtained from DFT, together with the corresponding relaxation energies and a description of the characteristic atomic displacements. The agreement between calculation and measurement is remarkable, especially considering the inherent difficulty in computing normal-mode vibrations at such low frequency, where anharmonic effects can play a significant role⁴¹. The lattice motion corresponding to each of these modes is pictographically represented in Fig. 2b, and is also available in animated files in the Supplementary Information. We have further verified the present results against calculations including spin–orbit coupling and found close agreement with the results in Table 1 (see Supplementary Table 2).

As previously demonstrated in other lead halide hybrid materials, the identified modes in this energy range correspond to the motion

of the lead iodide network^{38,42,43}. All of the modes have contributions from rotation of the octahedra along the two pseudocubic axes lying within the inorganic sheet. With increasing energy, we also find additional contributions from the I–Pb–I bendings and I–Pb stretching or octahedral rotations orthogonal to the inorganic sheets (represented as the scissoring mode), indicative of the larger stiffness of these coordinates. The nature and energy of some of these modes are strikingly similar to those reported for 3D perovskites based on experimental^{7,42,43} as well as theoretical³⁸ investigations.

To further generalize the experimental findings and provide further validation for the theoretical methodology, we also investigated polycrystalline films of (NBT)₂PbI₄. Figure 2c shows the integrated RISRS spectrum when the sample is photo-excited at 3.06 eV. We observe five modes with full-width at half-maximum ≤ 0.29 meV, distinct from the case of (PEA)₂PbI₄, but again in very close agreement with the DFT predictions (see Table 1). All of the modes appear to be shifted to higher energies, possibly due to the stiffening of the lattice induced by the octahedral distortions ubiquitous in the low-temperature phase of (NBT)₂PbI₄³¹. Similarly to the case of (PEA)₂PbI₄, we can assign the observed modes to the octahedral twist along or perpendicular to the inorganic sheet as well as the scissoring of the Pb–I–Pb angle (see Fig. 2d for diagrammatic representation of the vibrations). Additional data on this material are presented in Supplementary Figs. 8 and 9.

We now return to the vibrational coherences observed in (PEA)₂PbI₄ to demonstrate contrasting coupling of the lattice to the two most intense excitonic transitions A and B, and also to photocarriers. Figure 3a shows the excitation profiles of modes M1 and M2 plotted along with the linear absorption spectrum. Due to the resonant excitation, the RISRS driving the coherent lattice motion is enhanced for those ground-state vibrational coherences that are strongly coupled to the electronic transitions^{29,44}. This is clearly observed as a monotonic increase of the intensity of both the modes in the excitation spectra when the excitation energy is tuned to higher energies into the carrier continuum, at pump energies ≥ 2.56 eV. The photon flux at each excitation energy is kept constant to directly correlate the mode intensity to the absorption cross-section. The full beating maps and integrated spectra corresponding to these excitation conditions are presented in Supplementary Figs. 4 and 5.

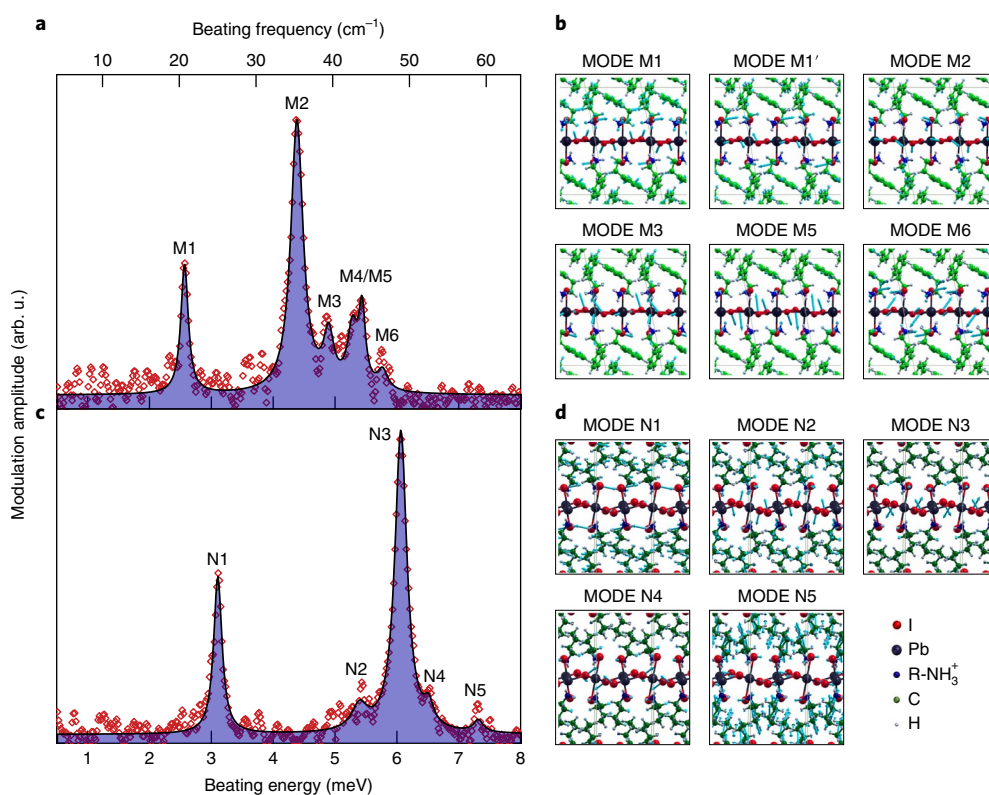


Fig. 2 | Integrated resonant impulsive stimulated Raman spectrum of $(\text{PEA})_2\text{PbI}_4$ and $(\text{NBT})_2\text{PbI}_4$ at 5 K and associated phonon modes. **a, c, Fourier-transform spectrum of the oscillatory components such as those displayed in Fig. 1d, and integrated over all of the detection energies probed in Fig. 1 for $(\text{PEA})_2\text{PbI}_4$ and $(\text{NBT})_2\text{PbI}_4$ respectively. The pump energy is tuned to 3.06 eV. The continuous line with blue shade is a fit to a function composed of six and five Lorentzian components respectively. **b, d**, Diagrammatic representations of the vibrational modes obtained via DFT calculations. The black spheres at the centre of the octahedra represent the Pb ions, while the red spheres represent the iodine. The green structures represent the organic cations—PEA in **b** and NBT in **d**. The cyan arrows represent the motion of each of the ions within the lattice.**

In Fig. 3b,d,f,h, we show the 2D beating maps, which represent the probe-energy-resolved Raman spectra, obtained by Fourier-transforming the dynamics at all of the detection energies for each of the excitation energies marked by shaded regions in Fig. 3a. We display two spectra resulting from pumping into the continuum at 3.06 and 2.67 eV (Fig. 3b,d, respectively), one spectrum resulting from pumping exciton B (Fig. 3f) and one exciting exciton A (Fig. 3h). Figure 3c,e,g,i shows the integrated spectra across all of the detection energies. The raw pump–probe data and cuts corresponding to these pumping conditions are presented in Supplementary Figs. 10–12.

In the cases of the free-carrier excitations, we observe identical vibrational coherences with the dominant signal at modes M1 and M2. While the resonant excitation of exciton A reveals predominant coupling to mode M2, excitation of exciton B displays a strikingly different vibrational spectral structure. As evident in Fig. 3g, we observe more intense signals at modes M6 and M4 along with diminished intensity of mode M2. These observations suggest rather distinct lattice couplings exhibited by each of the exciton states. Another important observation from the beating maps is the non-uniformity of the amplitude across the detection energy axis for different excitation energies. For instance, the free-carrier excitation beating maps reveal dominant signal only at the detection energies around the exciton A absorption resonance. The amplitude spectrum has a characteristic dual-peaked lineshape with a dip at the peak energy of exciton A⁴⁵, indicated by dashed lines in the beating maps. Importantly, there is no notable signal at the energy of exciton B, which is indicated by dotted lines. The only exception

to this is the case shown in Fig. 3f, where most of the signal is present around the energy of exciton B. These data correspond to resonant excitation of exciton B, and establish that the vibrational coherences associated with this transition differ to those due to exciton A, as well as those generated by photocarriers. We employ this intriguing observation as the key evidence in this work to differentiate the polaronic character of each of the excitons and that of free-carrier excitations.

We now discuss the nature of the observed lineshapes by comparing the amplitude spectra obtained by taking horizontal cuts of the probe-energy-resolved beating maps from different cases in Fig. 4. We first consider exciton A in Fig. 4a and exciton B in Fig. 4b. Given that M2 and M6 are the dominant vibrational modes in these two cases, we plot the amplitude spectra taken at those energies. The lineshapes in Fig. 4a are indicative of vibrational wavepacket dynamics often observed in molecular systems^{44,45}, where the energy of exciton A is modulated by the motion of a vibrational wavepacket along the a real-space vibrational coordinate associated with the coherently excited phonon. The dual-peaked lineshape and the π phase shift at the peak energy (not shown here but displayed in Supplementary Section 4) is clearly indicative of such dynamics, where the detection energies around the exciton peak display the most prominent oscillations. The observed lineshape can be reproduced using a simple harmonic oscillator model involving two electronic states, which are defined by their respective PESs. The PES minimum of the excited state is displaced along one of the vibrational normal coordinates due to electron–phonon coupling. Impulsive optical excitation generates a vibrational

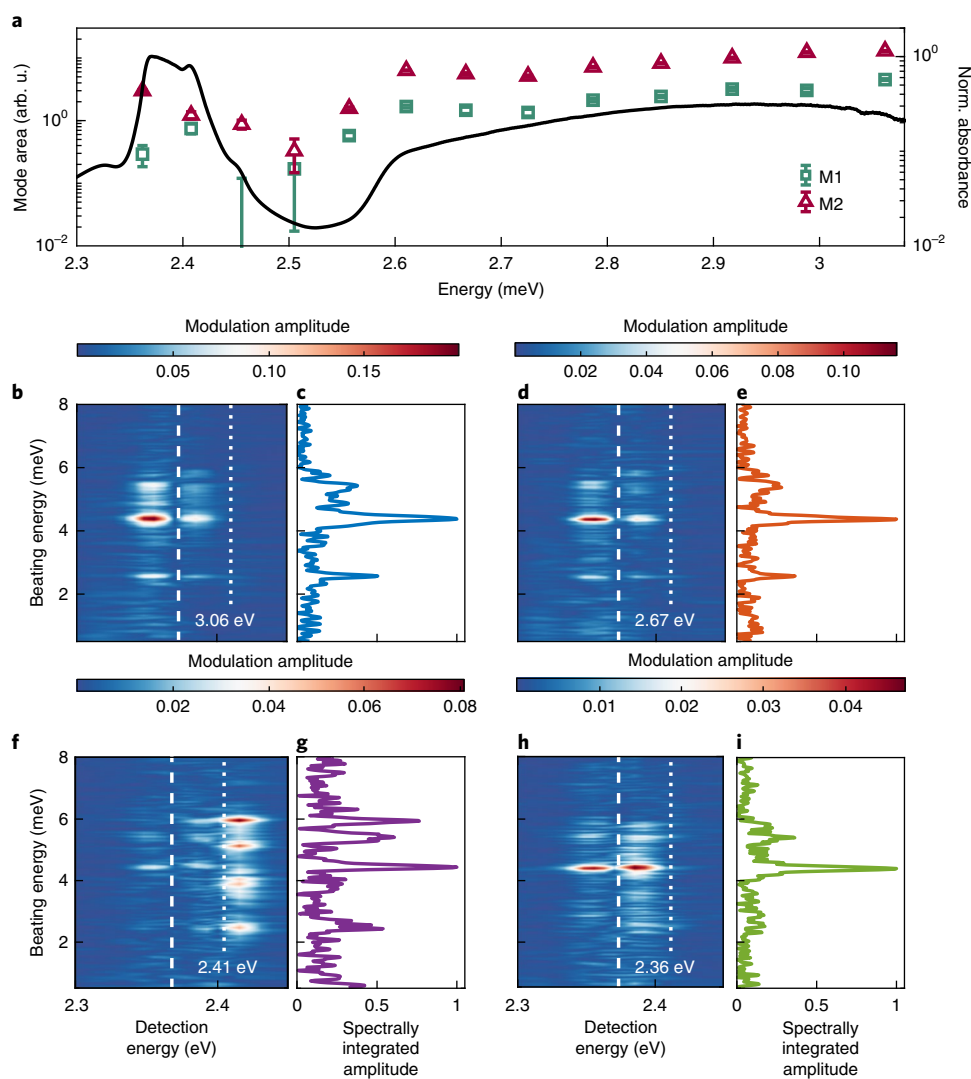


Fig. 3 | Pump wavelength dependence of the resonant impulsive stimulated Raman spectra of $(\text{PEA})_2\text{PbI}_4$ at 5 K. **a**, Excitation profiles of modes M1 and M2 as defined in Fig. 2 (represented as symbols indicated in the key), plotted with the linear absorption spectrum. The error bars represent statistical error arising from noise in the beating spectra. **b,d,f,h**, Beating spectra as a function of detection (probe) energies. Probe-energy-integrated vibrational spectra are also shown in **c,e,g,i**. The pump energies are 3.06 eV (**b,c**), 2.67 eV (**d,e**), 2.41 eV (**f,g**) and 2.36 eV (**h,i**). The dashed and dotted lines over the beating maps indicate the peak energies of excitons A and B respectively, as defined in Fig. 1a.

wavepacket, which oscillates along the PESs. The effect of these vibrational degrees of freedom on the permittivity can be computed as described in ref. 46. A detailed description of this model and the results of such simulations are given in the Supplementary Section 3. The observed dynamics are a consequence of the displacement of the PES of the excited state perceived via spectator lattice modes and thus are indicative of polaronic effects^{47,48}. We can compare the relative displacement (Δ) of the PES in the excited state across each of the normal-mode coordinates. The Raman cross-section is proportional to $\Delta^2\omega^2$, with $\hbar\omega$ being the phonon energy, and thus the analysis of relative intensities of each of the modes at different pump energies provides a representation of the complex excited-state landscape in $(\text{PEA})_2\text{PbI}_4$, as depicted schematically in Fig. 4c. By pumping exciton A, we can infer that its PES is displaced strongly along the normal coordinate defined by the phonon at M2, with a relatively more limited displacement along all of the other coordinates, as represented by the blue PES shown in Fig. 4c. The absence of any modulation at the energy of exciton B in this case suggests the relative immunity of exciton

B to the wavepacket dynamics only along the coordinate defined by the normal mode M2. This is duly supported by the amplitude spectra shown in Fig. 4b, where the M6 mode also modulates the exciton B transition strongly. We may infer that the PES of exciton B is displaced along both M2 and M6 axes as represented by the green PES in Fig. 4c.

We highlight that the PES associated with exciton A is also displaced, albeit slightly, along the coordinate axis associated with M1, as evident from the amplitude spectra shown in Fig. 4d and represented schematically in Fig. 4f. The PES of photocarriers (Fig. 4f), on the other hand, shows much more significant displacement along both M1 as well as M2, which can also be observed in the relatively higher intensity for these modes when the pump is tuned to the carrier continuum (see Fig. 3). This suggests that the photocarrier induces substantially larger lattice reorganization than the two excitons. This can be rationalized by considering the ionic nature of the perovskite lattice, which is subjected to stronger Coulomb potential in the presence of charged photoexcitations⁴⁹, in contrast to a globally neutral excitonic quasi-particle.

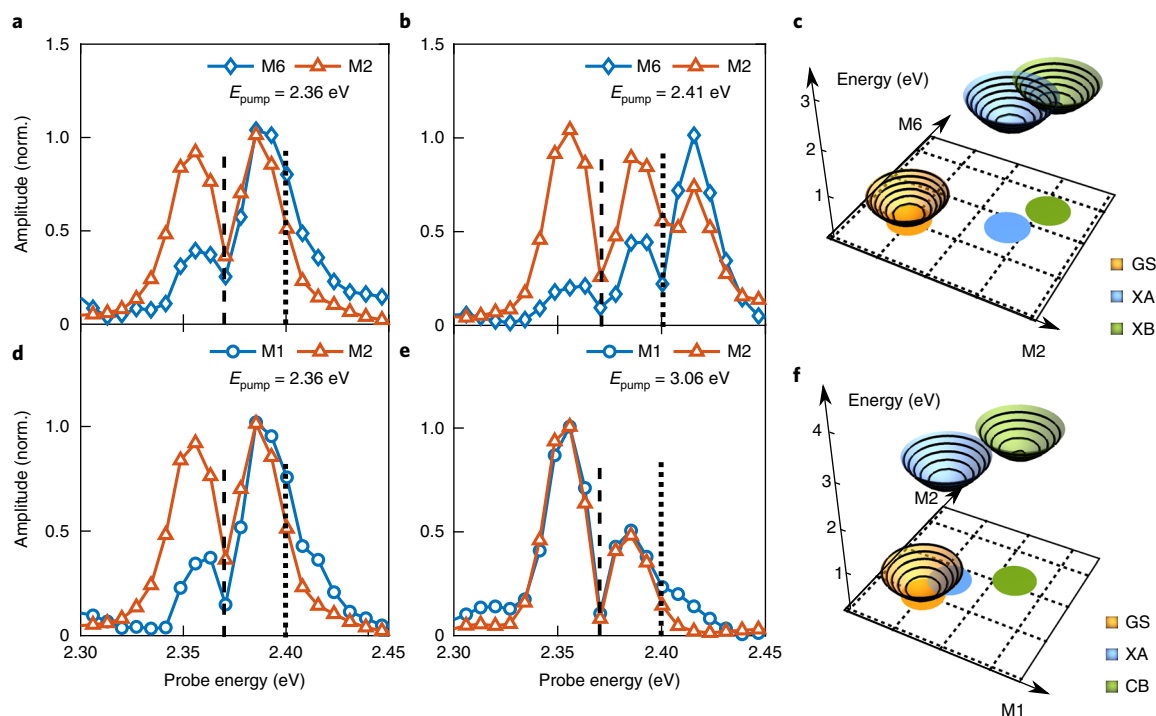


Fig. 4 | Consequences of the wavepacket dynamics in $(\text{PEA})_2\text{PbI}_4$ at 5 K. a, b, Amplitude spectra of M2 and M6 modes when the pump energy is resonant with exciton A at 2.36 eV (**a**) and with exciton B at 2.41 eV (**b**). **c,** Configuration-space representation of the harmonic potentials of the ground state (GS), exciton A and exciton B. **d, e,** Amplitude spectra of M1 and M2 modes when the pump energy is resonant with exciton A at 2.36 eV (**d**) and with the carrier continuum at 2.41 eV (**e**). **f,** Configuration space representation of the harmonic potentials of the ground state (GS), exciton A (XA, displaced predominantly along M2 coordinates) and the free carriers (CB, with strong and approximately equal displacement along M1 and M2 coordinates).

An important question is whether the modes reported in Table 1 are primarily sourced by the lattice reorganization around the hole or the electron. According to equation (1), the relaxation energy is calculated from the change in the single-particle bandgap (E_g) when the atomic positions are displaced along the coordinates of the various normal modes Q_i . Using the same protocol, we can track the variations in the bandgap that are due to a shift in the valence or in the conduction-band edge to assess hole and electron polaron relaxation energies, respectively. The obtained dimensionless electron–phonon couplings for holes and electrons in $(\text{PEA})_2\text{PbI}_4$ and $(\text{NBT})_2\text{PbI}_4$, listed in Supplementary Table 1, clearly demonstrate that for $(\text{PEA})_2\text{PbI}_4$, M1', M2, M5 and M6 contribute to the formation of hole polarons, while M1 and M3 contribute to the formation of electron polarons. On the other hand, for $(\text{NBT})_2\text{PbI}_4$, all vibrational modes are more strongly coupled to holes than electrons. The fact that changes in the electronic structure induced by reorganization of the lattice are more pronounced for the valence band edge is not surprising. The valence band is indeed primarily composed by antibonding combination of $5p$ atomic orbitals from iodine and $6s$ orbitals from lead. Thus, any change in the relative distance and orientation of the lead and iodine ions, as induced by displacement along the inorganic lattice vibrational modes, is expected to significantly affect the wavefunction overlap and Pb–I hybridization, hence energy, of the valence band. By comparison, the conduction-band edge is instead mostly composed by $6p$ orbitals of lead. It does, therefore, not come as a surprise that mode M3 in $(\text{PEA})_2\text{PbI}_4$ couples more strongly to the conduction band, as this mode is associated with the displacement of Pb ions within the PbI_6 octahedron, and that a change along this coordinate should strongly affect the atomic overlap among the $6p$ orbitals of lead.

Our analysis highlights the complex landscape encountered by charge carriers before they relax to the excitonic states, scanning across different lattice configurations. We have already

demonstrated that the exciton–phonon coupling can be tuned by the nature of the organic cation and the thickness of the quantum well^{6,50}. In the context of the growing number of custom-designed organic molecules that are being developed to template the 2D hybrid perovskite for optoelectronics, our observation garners fundamental importance to establish the optimum relaxation pathway following charge-carrier injection. We consider that the type of quantitative development of the relevant PESs is a challenging but fundamentally important task for large-scale molecular dynamics simulations that capture accurately the non-adiabatic quantum dynamics implied by this work^{48,51}.

Lastly, we have unambiguously demonstrated the presence of multiple distinct excitonic transitions separated by 35 meV⁶. Our observation of vastly different spectral structures in the resonant vibrational excitation spectra effectively rules out their previous assignments to vibronic progressions²⁶. It also establishes substantial and importantly distinct polaronic character of each of the excitons. We consider that this observation strongly suggests the role of polaronic binding as at least part of the origin of the spectral fine structure, which we have considered in ref. ⁶. This was initially motivated by a simple estimate of the polaron binding energy that was consistent with the energy splitting of 35 meV within the fine structure. We highlight that the origin of the fine structure can be rigorously established only via a detailed theoretical treatment that would predict the full excitonic dispersion and that includes spin–orbit coupling effects³², exchange interactions^{22,24,53}, many-body correlations¹¹ and, based on our current observation, non-negligible yet complex polaronic effects⁵⁴.

It has been suggested in the case of bulk lead halide perovskites that polaronic effects shield the photo-generated carriers from lossy scattering pathways involving defects, longitudinal optical phonons or Auger-like processes^{9,55}. We identified a diminished polaronic

character of excitons that can potentially enhance the multi-particle scattering processes. Intriguingly, in our earlier work on the multi-dimensional spectroscopy of $(\text{PEA})_2\text{PbI}_4$, we observed signatures of bound biexcitons with different binding energies for AA and BB, with additional evidence that A excitons also experience repulsive interactions¹¹. The consequences of the nature of the excitonic structure on these many-body physics are clearly critical in the context of, for example, biexciton lasing^{12,15}.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/10.1038/s41563-018-0262-7>.

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Author contributions

F.T., D.A.V.-C., I.B. and A.R.S.K. carried out transient absorption measurements. F.T. and D.A.V.-C. performed the analysis of the experimental data. C.Q. performed ab initio calculations. D.C. synthesized the samples. A.P. supervised the sample

preparation activity, D.B. supervised the ab initio calculations, and C.S. and A.R.S.K. supervised the ultrafast spectroscopy activity. A.R.S.K. and C.S. conceived the project. All authors contributed to the redaction of the manuscript. F.T. and D.A.V.-C. are to be considered first co-authors, and C.S. and A.R.S.K. corresponding co-authors.

Competing interests

The authors declare no competing interests.

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Methods

Sample preparation. For the preparation of (PEA)₂PbI₄ thin films (PEA = phenylethylammonium), the precursor solution (0.25 M) of (PEA)₂PbI₄ was prepared by mixing (PEA)I (Dyesol) with PbI₂ in a 1:1 ratio in *N,N*-dimethylformamide. For example, 62.3 mg of (PEA)I and 57.6 mg of PbI₂ were dissolved in 500 μ l of dimethylformamide (anhydrous, Sigma Aldrich). The thin films were prepared by spin-coating the precursor solutions on fused-silica substrates at 4,000 r.p.m., 30 s, followed by annealing at 100 °C for 30 min. The extensive structural characterization of these films is reported in our earlier works^{6,11}.

Ultrafast differential transmission measurements. Differential transmission spectroscopy measurements were performed using an ultrafast laser system (Pharos Model PH1-20-0200-02-10, Light Conversion) emitting 1,030-nm pulses at 100 kHz, with an output power of 20 W and pulse duration of ~220 fs. Experiments were carried out in an integrated transient absorption/time-resolved photoluminescence commercial set-up (Light Conversion Hera). Pump wavelengths in the spectral range 360–2,600 nm (see Supplementary Fig. 13 for typical pump excitation spectra) were generated by feeding 10 W from the laser output to a commercial optical parametric amplifier (Orpheus, Light Conversion), while 2 W are focused onto a sapphire crystal to obtain a single-filament white-light continuum covering the spectral range ~490–1,050 nm for the probe beam. When higher-energy probe light was required, a blue white-light continuum was similarly obtained by using the second harmonic of the laser output instead. The probe beam transmitted through the sample is detected by an imaging spectrograph (Shamrock 193i, Andor Technology) in combination with a multichannel detector (256 pixels, 200–1,100-nm wavelength sensitivity range). Energy densities used spanned 25 to 1,100 nJ cm⁻², but most of the measurements were carried out at 215 nJ cm⁻² with a typical spot diameter of 1.9 mm estimated at the 1/*e*² plane. Beating maps and integrated spectra corresponding to these fluences are presented in Supplementary Figs. 6 and 7. All measurements were carried in a vibration-free closed-cycle cryostat (Montana Instruments). We disclose that we observed a slow degradation of the sample over long exposure to the laser light. Such a process, also widely reported for 3D perovskites, appears to be reversible and can be slightly negated by photo-exposing the sample for an hour before the experiment. While the extent of degradation is not substantial enough to make the observed trends unreliable, the shape of the excitation spectrum should nevertheless be considered only as

qualitative. Nevertheless, we consider that the comparison of excitation spectrum for different modes is rigorous.

DFT calculations. The present calculations are based on the harmonic approximation, which solely relies on the availability of realistic crystallographic models that, in the present case, are provided by established X-ray diffraction measurements^{11,31,56}. The crystalline model is relaxed using the van der Waals-corrected DFT-D2 method. The Hessian matrix of the forces is then calculated on the fully relaxed structure and diagonalized to obtain the vibrational frequencies. The calculations have been performed by adopting periodic boundary conditions and a localized atomic basis set as implemented in the CRYSTAL17 program⁵⁷. The computational set-up consists of double split quality basis sets that include polarization, along with the Perdew–Burke–Ernzerhof functional for the description of the exchange–correlation⁵⁸. An automatic 4 × 4 × 1 sampling of the first Brillouin zone was selected⁵⁹, where the less dense sampling is related to the direction associated with the inorganic-sheet stacking, in the reciprocal lattice. The Grimme-D2 approach was included, to improve the description of the atomic forces between the organic cations. The SCF accuracy has been increased to 10¹⁰ Hartree, to obtain accurate interatomic forces. This computational set-up has already been tested for the parental CH₃NH₃PbI₃ perovskite in ref. ³⁵ and resulted in DFT vibrational spectra in excellent agreement with the experimental data available.

Data availability

The experimental data and analysis material that support the findings of this study are available in the Scholarly Materials And Research @ Georgia Tech repository (SMARTech), <https://smartech.gatech.edu>.

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