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Giant isotope effect on phonon dispersion and thermal conductivity in methylammonium lead iodide

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Lead halide perovskites are strong candidates for high-performance low-cost photovoltaics, light emission, and detection applications. A hot-phonon bottleneck effect significantly extends the cooling time of hot charge carriers, which thermalize through carrier–optic phonon scattering, followed by optic phonon decay to acoustic phonons and finally thermal conduction. To understand these processes, we adjust the lattice dynamics independently of electronics by changing isotopes. We show that doubling the mass of hydrogen in methylammonium lead iodide by replacing protons with deuterons causes a large 20 to 50% softening of the longitudinal acoustic phonons near zone boundaries, reduces thermal conductivity by ~50%, and slows carrier relaxation kinetics. Phonon softening is attributed to anticrossing with the slowed libration modes of the deuterated molecules and the reduced thermal conductivity to lowered phonon velocities. Our results reveal how tuning the organic molecule dynamics enables control of phonons important to thermal conductivity and the hot-phonon bottleneck.

INTRODUCTION

Organometallic halide perovskites (OMHPs) have attracted considerable attention as candidates for low-cost photovoltaics (1), light emission (2), light and high-energy radiation detection (3–5), and other applications owing to their outstanding optoelectronic properties and solution processability. Despite extensive research, they remain far from being well understood, particularly the role of phonons and organic molecule dynamics on their optoelectronic properties. There is a strong coupling between the dynamics of cation off-centering/orientation in the cage of octahedral and inorganic framework tilting (6–11). However, a full accounting of how the dynamics affects thermal transport and the long-charge carrier lifetimes that help enable high-power conversion efficiencies (12) is still sorely needed (13). The importance of phonons is also highlighted by the observation that a hot-phonon bottleneck prolongs the cooling period of hot charge carriers in lead iodide perovskites (14) and evidence for the role of acoustic-optical phonon up-conversion in controlling this bottleneck (15). Phonons are involved at each stage of the hot carrier thermalization process, and gains in carrier lifetimes can be introduced at each stage of the relaxation process by introducing blocking mechanisms. The initial transfer from the hot carrier energy to the optic phonons is fast, but the transfer of energy from the optic to acoustic phonons [Klemens decay (16)] can be slowed by increasing the gap between the optic and acoustic phonons. The final stage, where heat is propagated away from the hot region, benefits from the ultralow thermal conductivities of lead halide perovskites (17), which is controlled by phonon velocities and scattering rates (18, 19). It was previously suggested that the hot carrier bottleneck can be caused by different mechanisms, including a modified carrier-phonon interaction and large polaron formation coupled with phonon glass characteristics (20, 21). Hence, understanding and controlling the phonon properties in this class of materials is critically important.

The coexistence of several highly anharmonic molecular motions at frequencies near the phonon frequencies is expected to result in multimode coupled dynamics in OMHPs. It was concluded from the temperature-dependent Raman spectroscopy (22) and inelastic x-ray scattering (7) that the dynamic disorder of the methylammonium cation (23) and the inorganic sublattice lead to the anharmonic multimode fluctuations. This behavior results in collective anharmonic polar fluctuations (phonons) or dynamic disorder involving multiple polar vibrational modes. On the basis of first-principles lattice dynamics calculations of the phonon spectrum, Beecher et al. (7) found that the orientations of the methylammonium couple strongly and cooperatively to zone edge phonon instabilities (7).

In this work, we make use of the large 2:1 mass ratio of deuterium (D) to hydrogen (H) to probe the hydrogen-related dynamical modes of the organic molecules in methylammonium lead iodide (CH3NH3PbI3) perovskite. Although deuteration only changes the mass density of the lattice marginally, we find using neutron scattering that deuteration results in a large 20 to 50% softening in the longitudinal acoustic (LA) phonons near zone boundaries. This softening of the LA phonons occurs as libration modes of the molecule soften and push down on the zone boundary LA phonons via mode anticrossing. This anticrossing behavior demonstrates the strong coupling between these hydrogen-controlled molecular modes (MMs) and the LA phonons. We also show that this results in a 50% suppression in the already ultralow thermal conductivity (17) owing to a decrease in the propagation velocities of the LA phonons caused by the phonon softening. Last, we use first-principles calculations to show that light- or x-ray–induced lattice expansions/distortions (24, 25) associated with improved performance (24) produce relatively small changes to these phonons, indicating that these phonon properties are likely retained under operating conditions. Our findings highlight the importance of phonon-MM interactions in OMHPs and suggest a route to enhance hot carrier properties by tuning the vibrational transport properties.

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**RESULTS**

**Triple-axis neutron scattering**

Phonon dispersion curves in the cubic phase at 350 K were measured on deuterated methylammonium lead iodide (CD$_3$ND$_3$PbI$_3$) single crystals using the HB3 triple-axis spectrometer at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory (see Materials and Methods). The use of deuterium avoids the large incoherent neutron scattering cross section of hydrogen and allows direct measurements of the phonon dispersion curves. Figure 1 (A to D) shows phonon dispersion data and fits used to determine the dispersion in both transverse and longitudinal geometries along Γ-X and Γ-M plotted in Fig. 1E. The measured transverse acoustic (TA) phonon branches in both directions (lowest branches, Fig. 1E) are in very good agreement with previous measurements made using neutron scattering [Gold-Parker et al. (18) and Ferreira et al. (19)] and x-ray scattering [Beecher et al. (7)] for both protonated crystals [Beecher et al. (7) and Ferreira et al. (19)] and deuterated crystals [Gold-Parker et al. (18)]. The first transverse optic mode (TO$_1$) indicated in black in Fig. 1E along Γ-X appears at a slightly lower energy than observed for protonated crystals measured using inelastic x-ray scattering by Beecher et al. (7). However, this difference is small, and it is determined by fitting the weakest peak in Fig. 1A. The LA phonon branches, on the other hand, show large differences with the measurements on the protonated crystals. The LA phonon at the X point appears about 50% softer (lower frequency) than in the case of the protonated crystal (compare black and purple phonon branches near the X point in Fig. 1E). The LA phonon at the M point is also about 20% softer than in the protonated crystals (right in Fig. 1E). The difference between the protonated (purple) and deuterated (black) LA phonons diminishes toward the zone center (Γ). In the longitudinal Γ-M scan (Fig. 1D), there is also an additional mode around 7 meV just above the softened LA phonon. This mode exhibits only weak dispersion and also shows up to some degree in the other geometries, including in Fig. 1 (A, B, and possibly C), which all suggest a local origin for this mode. This 7-meV mode does not appear in any of the x-ray measurements performed at the same energies on protonated crystals by Beecher et al. (7). However, a mode in CH$_3$NH$_3$PbBr$_3$ was shown to soften from ~11 to ~8 meV upon deuteration (11). In addition, first-principles calculations predict that there should be a strong methylammonium libration mode in CH$_3$NH$_3$PbI$_3$ at about 11 meV (26). Owing to the rocking motion of H atoms, these libration modes should decrease in frequency with the mass increase from D, and they should also appear somewhat localized at the methylammonium molecules. Hence, the 7-meV mode is likely a libration mode of methylammonium that dropped down from higher energies with deuteration. The softening of the LA phonons would then follow from an anticrossing with the libration mode.

**Time-of-flight neutron scattering**

To confirm that the libration mode drops down from around 11 to 7 meV with deuteration, we performed vibrational neutron spectroscopy measurements on protonated (CH$_3$NH$_3$PbI$_3$) and deuterated (CD$_3$ND$_3$PbI$_3$) powders made by grinding down crystals (see Materials and Methods). The powder measurements were made at 5 K in the orthorhombic phase on the VISION time-of-flight instrument at the

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**Fig. 1. Inelastic neutron scattering measurements of phonons in protonated (CH$_3$NH$_3$PbI$_3$) and deuterated (CD$_3$ND$_3$PbI$_3$) methylammonium lead iodide.** (A to D) Energy scans measured on a triple-axis spectrometer (HB3) at fix points in momentum, Q, with fits used to determine the phonon dispersion curves. (E) Summary of phonon dispersion measured on both deuterated and protonated crystals (7, 18, 19). r.l.u., reduced lattice units.
Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory (see Materials and Methods). Higher temperature measurements were attempted but were inconclusive owing to the large multi-phonon background. The large incoherent cross section of hydrogen dominates the inelastic neutron scattering for the protonated crystal, and this provides a measure of the vibrational density of states (Fig. 2A). Deuterium has a much stronger coherent neutron scattering cross section. In this case, the vibrational density of states is approximated by summing the powder averaged data over momentum transfers (Fig. 2B). A comparison of the inelastic peaks for protonated and deuterated powders in Fig. 2 reveals the shift of several peaks to lower energies with deuteration, as expected. In

Fig. 2. Vibrational spectrum of protonated and deuterated powders measured on a time-of-flight spectrometer (VISION) at 5 K. (A) Protonated (CH3NH3PbI3) and (B) deuterated (CD3ND3PbI3) powders.

Fig. 3. Thermal properties of deuterated and protonated methylammonium lead iodide. (A) Thermal diffusivity (α) measurements on protonated and deuterated crystals show a significant lowering with deuteration in both the tetragonal and cubic phases. (B) Heat capacity at constant pressure (Cp) measured in the deuterated crystal showing the transition. (C) Thermal conductivity calculated from the heat capacity and thermal diffusivity using κ = ραCp. (D) Low-temperature heat capacity shows transition to orthorhombic phase, and the inset plot of Cp/T3 peaks at 5.8 K.
particular, there is a strong peak around 12.5 meV that shifts to around 8.5 meV. These energies are somewhat higher than the shift from 11 to 7 meV expected in the cubic phase at 350 K, but this is not unexpected because the modes are typically stiffer in the lower temperature phases. Hence, an anticrossing with an MM that drops down to ~7 meV with deuteration appears to be the source of the large softening of the LA phonons near the zone boundaries. The absence of H-mode peaks in the deuterated measurement verifies >99.985% deuteration, which was also established by nuclear magnetic resonance (NMR) spectroscopy (fig. S1).

The observed zone boundary softening of the LA phonons (Fig. 1E) causes a substantial fraction of the LA phonon density of states to have a reduced group velocity (27), which would tend to lower the LA phonon contribution to thermal conductivity. However, such large changes in the phonon dispersion curves can also change the phase space for the allowed three-phonon scattering processes controlling thermal conductivity (28, 29), making thermal transport difficult to predict from a simple inspection of the dispersion curves.

**Thermal properties measurements**

To explore the effect of deuteration on the thermal transport, thermal conductivity (\(\kappa\)) was determined experimentally for protonated (CH\(_3\)NH\(_3\)PbI\(_3\)) and deuterated (CD\(_3\)ND\(_3\)PbI\(_3\)) crystals using laser flash measurements of the thermal diffusivity (\(\alpha\)) combined with specific heat (\(C_P\)) measurements using the relationship \(\kappa = \alpha C_P\), where \(\rho\) is density (see Materials and Methods). The thermal diffusivity measurements made between 303 and 373 K (Fig. 3A), which include both tetragonal and cubic phase regions, show that the thermal diffusivity is about 50% lower for the deuterated crystal for both phases. The specific heat measurements shown in Fig. 3B confirm the 327 K transition from the tetragonal to cubic phase and enable a calculation of the thermal conductivity shown in Fig. 3C. The ultralow thermal conductivity of the protonated crystal of about 0.51 W m\(^{-1}\) K\(^{-1}\) at 335 K is in very good agreement with the value of 0.5 W m\(^{-1}\) K\(^{-1}\) reported by Pisoni et al. (17) for CH\(_3\)NH\(_3\)PbI\(_3\) at 300 K. The value for the deuterated crystal of 0.29 W m\(^{-1}\) K\(^{-1}\) is significantly lower than the protonated crystal and is actually comparable to some of the lowest values ever recorded for a single crystal at ambient conditions (30).

The deuterated low-temperature specific heat shown in Fig. 3D exhibits the expected 162-K transition between the tetragonal and orthorhombic phases. The shape of the curve is in good agreement with the measurements of Fabini et al. (31) on protonated crystals except for a slight difference at low temperatures. A plot of \(C_P/T^3\) (inset in Fig. 3D) results in a peak at \(T_{\text{max}} = 5.8\) K for our deuterated crystal compared to \(T_{\text{max}} = 5.92\) K found for CH\(_3\)NH\(_3\)PbI\(_3\) (32). The slight shift to lower temperatures is consistent with the phonon softening because this will result in more modes being occupied at low temperatures. Additional differential scanning calorimetry (DSC) measurements show that the tetragonal to cubic transition is about 4 K lower in the deuterated crystal, further confirming the effect of isotope exchange (fig. S2).

**First-principles calculations**

To determine if the LA phonon softening with deuteration is changed by the lattice expansion/distortions or nonequilibrium electronic distributions induced by light (24, 25) and/or x-ray excitations in previous measurements (7), we performed first-principles calculations of the M- and X-point LA phonon under several conditions (see Materials and Methods). The cubic and distorted structures are shown in Fig. 4 (A and B). The distorted structure was created by imposing displacements corresponding to the R\(_{TA}\) mode (the unstable mode with largest frequency magnitude) in a 2 × 2 × 2 supercell of the cubic phase, followed by structural relaxation. A 1.4% uniform lattice expansion (24) was chosen to simulate the possible lattice expansion induced by x-rays. As shown in Fig. 4C, the effect of the 1.4% lattice expansion (24) of both the cubic phase and the distorted structure resulted in negligible changes in the LA phonons at both the M and X points.

The distortion, which makes the identification of M and X points only approximate, has an effect of stiffening the X-point LA and slightly softening the M-point LA. The largest effect is seen with a 0.75-eV Fermi smear (i.e., occupation of the electronic states with an electronic temperature of 0.75 eV), which is meant to simulate the effect of a nonequilibrium hot electron distribution. The impact of the hot electron distribution is to soften the LA phonons further. Hence, these results rule out an x-ray–induced stiffening of the LA phonons as an alternative explanation for the observed difference between the neutron (on deuterated) and x-ray (on protonated) measured LA phonons in Fig. 1, because the effect goes in the wrong direction. This also suggests that LA phonon softening may result from both deuteration and nonequilibrium hot electrons, which may
These results reveal how coupling between molecular and lattice dynamics enables control of the phonon properties important to thermal transport and, by extension, to the phonon bottleneck effect (14) and hot carrier lifetimes (32) in OMHPs.

**MATERIALS AND METHODS**

**Methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) single-crystal growth**

Lead (II) acetate trihydrate (99%) was purchased from Alfa Aesar. All other materials used in CH$_3$NH$_3$PbI$_3$ growth were purchased from Sigma-Aldrich. The single crystals of CH$_3$NH$_3$PbI$_3$ were prepared by a modified cooling-induced crystallization method. Details of single-crystal growth can be found in our previous work (33).

**Deuterated methylammonium lead iodide (CD$_3$ND$_3$PbI$_3$) single-crystal growth**

For deuteration, the starting materials were either synthesized or purchased from Sigma-Aldrich. To prepare CD$_3$ND$_3$, methylamine anhydrous gas ≥98% was dissolved in D$_2$O. The lead (II) acetate trihydrate (99%) was dissolved in D$_2$O three times for an exchange reaction and subsequently dried in a vacuum oven for several hours. The deuterated hydroiodic acid (DI) [57% (w/w) aqueous solution] was synthesized [adopted from (34)] by a reaction between hypophosphorous acid–d$_3$ solution 50 weight % in D$_2$O, 98 atomic % D, and potassium iodide (KI) at 170°C. As a product of the reaction, the deuterated hydroiodic acid vapor was condensed and collected (34). Single crystals of CD$_3$ND$_3$PbI$_3$ were prepared from deuterated precursors similar to CH$_3$NH$_3$PbI$_3$ growth method. Single crystals were rinsed with diethyl ether–d$_{10}$ for three times and vacuum-dried at room temperature before the measurements.

**Powder sample preparation**

For powder preparation, some of the single crystals grown were ground to a fine powder using a porcelain mortar and pestle. The procedure was done in a glove box to prevent surface contamination by humidity adsorption.

**DISCUSSION**

In summary, we have investigated the impact of doubling the mass of hydrogen (deuteration) on the phonon dispersion and thermal transport properties of methylammonium lead iodide perovskite. Although the TA phonons are mostly unaffected by deuteration, the LA phonons soften by as much as a factor of 2 near the zone boundaries. This softening far exceeds what would be expected based solely on the change in the mass density (frequency scale as the inverse square root of mass and $\sqrt{\rho_{\text{protonated}}}/\sqrt{\rho_{\text{deuterated}}} = 0.9952$). This giant softening is attributed to a strong coupling of the zone edge LA phonon to libration modes of the methylammonium molecule that depend strongly on the mass of hydrogen. Observed consequences of this isotope exchange include a 50% reduction in the already ultralow thermal conductivity and slow carrier relaxation kinetics. Further, these results reveal how coupling between molecular and lattice dynamics enables control of the phonon properties important to thermal transport and, by extension, to the phonon bottleneck effect (14) and hot carrier lifetimes (32) in OMHPs.

**Femtosecond pump-probe transient absorption spectroscopy**

To check whether deuteration changes the hot carrier lifetime, initial ultrafast transient absorption measurements (see Materials and Methods) were performed on both deuterated and protonated crystals under identical ambient conditions at room temperature. A 50-fs pump pulse centered at 500 nm was used to excite carriers well above the band gap for both samples, while an ultrashort broadband white-light continuum (480 to 1100 nm) was used as probe. The pump-induced change in absorption spectrum shown in Fig. 5 (A and B) was acquired as a function of time delay for both protonated and deuterated crystals. The decays of the peak bleaching signal are compared in Fig. 5D. In the deuterated sample, a much slower carrier relaxation was observed compared to the protonated crystal, which warrants further investigation into the potential enhancement of hot carrier bottleneck effects by deuteration.

**Fig. 5. Transient absorption spectra for protonated and deuterated methylammonium lead iodide.** The intensities are given as minus the log of the difference in absorption with and without pump (−ΔOD) as a function of wavelength and time delay for the (A) protonated (CH$_3$NH$_3$PbI$_3$) and (B) deuterated (CD$_3$ND$_3$PbI$_3$) single crystals. (C) Decay of the strongest bleaching signals (symbols) for both crystals with their two-exponential fitting results (lines) showing carrier relaxation kinetics.
NMR spectroscopy of deuterated methylammonium lead iodide (CD$_3$ND$_3$PbI$_3$)

The synthesized CD$_3$ND$_3$PbI$_3$ was characterized using $^{13}$C NMR spectroscopy obtained on a Varian VNMRS 500 NMR spectrometer at 23°C in dimethylformamide-d$_7$ (DMF-d$_7$), and inverse-gated decoupling with pw = 90 and a recycle delay of 60 s were used. The peaks around 164, 35, and 29 ppm are from the deuterated DMF-d$_7$ solvent (see fig. S1). The peaks around 25 ppm are from the methyl carbon in CD$_3$ND$_3$PbI$_3$. The multiple splits of the peaks demonstrated the success of preparing deuterated perovskite, CD$_3$ND$_3$PbI$_3$, because a proton-decoupled carbon spectrum will not remove coupling to deuterium and proton due to different spin (s = 1/2 for proton; s = 1 for deuterium). This is supported by the time-of-flight inelastic neutron scattering comparing both deuterated and protonated powders samples (Fig. 2), because there are no hydrogen peaks in the deuterated measurements. The inelastic scattering intensity, which scales as the neutron cross section divided by mass, is about 23 times stronger for H than for D, making a sensitive test for any hydrogen contamination in the deuterated material. From the neutron spectroscopy, we estimate that there is less than 0.00015 H per D in the deuterated crystal.

Triple-axis inelastic neutron scattering

We measured the low-energy phonon dispersion curves in deuterated crystals (CD$_3$ND$_3$PbI$_3$) using an HB3 triple-axis spectrometer at the HFIR of the Oak Ridge National Laboratory. The spectrometer was operated with filtered fixed final neutron energy of 14.7 meV with horizontal collimation 48′:40′:40′:120′. The crystal was mounted using a vanadium holder in the (HHL) plane in a furnace and heated to 350 K, which is above the transition to the high-temperature cubic phase. Vanadium is used for holders because of its incoherent neutron scattering cross section. For the transverse phonons from $\Gamma$ to X, we measured along $Q = [2, 2, L]$, and for the transverse phonons from $\Gamma$ to M, we measured along $Q = [H, H, -L]$. The longitudinal modes from $\Gamma$ to X were measured along $Q = [0, 0, 2 + L]$, and for the longitudinal modes from $\Gamma$ to M, we measured along $Q = [2 + H, 2 + H, 0]$.

Time-of-flight inelastic neutron scattering

We measured the vibrational density of states over a wide energy range on both protonated (CH$_3$NH$_3$PbI$_3$) and deuterated (CD$_3$ND$_3$PbI$_3$) powders using the VISION instrument (35) at the SNS of the Oak Ridge National Laboratory. VISION is an inverted geometry instrument with a usable dynamic range of 0 to 600 meV and an energy resolution of 1 to 1.5%. Incident energy determination uses the time-of-flight method, and a curved crystal analyzer (PG002) is used for final neutron energy selection. Because of the instrument geometry, VISION produces effectively a vibrational spectrum averaged over the Brillouin zone, with the averaging improving with increasing energy. For our measurements, the samples (powders) were placed in 6-mm vanadium sample holder and slits were adjusted to restrict illumination to the sample volume to increase the signal-to-background ratio. The powders were sealed in the sample holders in a dry helium box. The excellent thermal conductivity of helium at low temperature ensures that the powder sample temperature is uniform and close to that read by the temperature sensor. Datasets were collected at 5 K and at room temperature.

Thermal diffusivity measurements

A Netzsch MicroFlash LFA 457 system was used to obtain thermal diffusivity of the samples. The measurement follows ASTM 1461 on flash diffusivity. A 1.06-μm Nd:YAG (neodymium-doped yttrium aluminum garnet; Nd:Y$_3$Al$_5$O$_{12}$) is used to deposit a heat pulse onto the sample surface. An InSb (3 to 5 μm) infrared (IR) detector is used to record the temperature rise from the opposite surface. Because the samples are partially transparent in the IR region, both surfaces were coated with 100-nm gold and a graphite spray to increase emissivity. For the irregular sample geometry, a 6-mm-diameter SiC holder was used and the gaps between the sample edges and circular holder were filled by a black clay. An aluminum foil that has an opening matching the shape of the sample was placed on top of the sample to make sure that the IR detector only measured temperature rise from the sample and not from the clay and sample holder. The measurements were carried out in ultrahigh-purity argon purge gas with a flow rate of 100 ml/min. Three measurements at each set point were conducted from 303 to 373 K. Near the tetragonal to cubic transition between 313 and 343 K, 5-K steps were used, while 10-K steps were used outside of this range. Thermal diffusivity was calculated using the Cowan method with pulse-width correction.

Heat capacity measurements

Specific heat capacity measurements were performed in a Quantum Design Physical Property Measurement System. To inspect the first-order phase transitions, data obtained using large thermal pulses were analyzed with the single-slope method provided by Quantum Design. This yields isolated heating/cooling curves, and a thermal hysteresis of less than 2 K was observed across both structural transitions. Above 210 K, the thermal grease Apiezon H was used, and Apiezon N grease was used below 210 K.

DSC measurements

DSC was performed on powder sample using a TA (thermal analysis) DSC Q20 instrument operated at a scanning rate of 5°C min$^{-1}$ under an N$_2$ atmosphere. The temperature scale was calibrated using an indium (In) standard (T$_m$ = 156°C).

First-principles calculations

Calculations were carried out using Density Functional Theory with the Perdew-Burke-Ernzerhof Generalized-Gradient Approximation corrected for solids (PBEsol) (36) for the exchange-correlation functional, and the Projector Augmented Wave (PAW) method (37), as implemented in the Vienna Ab initio Simulation Package (VASP) (38–40). The PAW potential used in the calculations for Pb includes semicore 5d electrons. The energy cutoff for the plane wave basis was set to 520 eV, and relaxation calculations were carried out with a gamma-centered k-point mesh of 6 × 6 × 6 for the pseudo-cubic structure (7) and 2 × 2 × 2 for the distorted structure in the 2 × 2 × 2 supercell. A tolerance of 10$^{-6}$ eV was applied in the electronic minimizations, and a force tolerance of 5 × 10$^{-3}$ eV/Å was applied in the structure relaxations. The phonon frequencies at M and X points were calculated using a 2 × 2 × 2 supercell with density functional perturbation theory (DFPT), as implemented in VASP. The phonon frequencies were then averaged among three inequivalent M points and X points of the pseudo-cubic structure. To simulate the impact of x-ray on the structures, several different structure configurations were considered and fully relaxed before performing the DFPT calculations: (i) the pseudo-cubic structure, (ii) the pseudo-cubic structure with 1.4% expansion, (iii) the distorted structure induced by the phonon instability at R point, and (iv) the distorted structure with 1.4% expansion. The choice of the orientation of the
MA molecules along the <100> direction of the cubic unit cell in the model structures was made following earlier work by Frost et al. (41), where it is shown that this choice is preferred at 300 K in ab initio molecular dynamics. The results for phonon frequencies in the pseudo-cubic structure are in good agreement with previous calculations (7).

**Femtosecond pump-probe transient absorption spectroscopy**

The laser consisted of a 20-fs, 76-MHz Ti:Sapphire oscillator (Mantis-5E, Coherent) that seeded a regenerative amplifier (RegA 9050 m, Coherent). The amplifier generated 50-fs, 6-μJ pulses centered at 800 nm with a 250-kHz repetition rate, which was then split into pump and probe beams. The pump beamline was then fed into a visible optical parametric amplifier (OPA 94350, Coherent). The output beam from the OPA, centered at 500 nm, passed through a delay stage before being directed to the sample. The probe beamline was used to generate a white light continuum (480 to 1100 nm). A 800-nm notch filter was then used to block the fundamental mode from the seed laser. The detectable wavelength for the current setup was therefore from 480 to 780 nm. After being reflected from the sample surface, the probe was sent into a spectrometric charge-transporting cavity (CCT-10, Princeton Instruments) and the pump-induced change in absorbance was monitored as a function of a time delay between pump and probe. The change of absorbance, ΔOD, was calculated using the following equation

\[
-\Delta OD = \log[I_{pr}(\lambda)]_{ON} - \log[I_{pr}(\lambda)]_{OFF}
\]

where \(I_{pr}(\lambda)\) is the intensity of the probe at a given wavelength λ, and "ON" and "OFF" stand for the presence and absence of the pump pulse, respectively (42). Each point on the transient spectral map was obtained by covering over 50 exposures at a given delay position. All the measurements were performed under the same pump fluence. The samples were at ambient environment with a constant nitrogen flow over the surface to minimize the effect of the degradation. No detectable degradation was observed over the duration of the measurements.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/31/eaaz1842/DC1

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