

Title: Light-induced picosecond rotational disordering of the inorganic sublattice in hybrid perovskites

Authors: Xiaoxi Wu,¹ Liang Z. Tan,² Xiaozhe Shen³, Te Hu,⁴ Kiyoshi Miyata,⁵ M. Tuan Trinh,⁵ Renkai Li,³ R. Coffee,³ Shi Liu,⁶ David A. Egger,⁷ Igor Makasyuk,³ Qiang Zheng,³ Alan Fry,³ J. S. Robinson,³ M.D. Smith⁸, B. Guzelturk¹, H.I. Karunadasa⁸, Xijie Wang,³ X.-Y. Zhu,⁵ Leeor Kronik,⁷ Andrew M. Rappe,² Aaron Lindenberg^{1,4,9*}

Affiliations:

¹ Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

² The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

³ SLAC National Accelerator Laboratory, Menlo Park, CA 94025

⁴ Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

⁵ Department of Chemistry, Columbia University, New York, NY 10027, USA

⁶ Extreme Materials Initiative, Geophysical Laboratory, Carnegie Institution for Science, Washington DC 20015, USA.

⁷ Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

⁸ Department of Chemistry, Stanford University, Stanford, CA 94305, USA

⁹ PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

* To whom correspondence should be addressed. Phone: (650)-725-2640, E-mail: aaronl@stanford.edu

Abstract:

Femtosecond resolution electron scattering techniques are applied to resolve the first atomic-scale steps following absorption of a photon in the prototypical hybrid perovskite methylammonium lead iodide. Following above-gap photo-excitation, we directly resolve the transfer of energy from hot carriers to the lattice by recording changes in the root-mean-square atomic displacements, on ten picosecond time-scales. Measurements of the time-dependent pair distribution function show an unexpected broadening of the iodine-iodine correlation function while preserving the Pb-I distance. This indicates the formation of a rotationally-disordered halide octahedral structure developing on picosecond time-scales. This work shows the important role of light-induced structural deformations within the inorganic sublattice in elucidating the

unique optoelectronic functionality exhibited by hybrid perovskites and provides new understanding of hot carrier – lattice interactions which fundamentally determine solar cell efficiencies.

One Sentence Summary:

Absorption of light in hybrid perovskite solar cells leads to ultrafast large-amplitude deformations of the inorganic sublattice.

Introduction:

As a new prototype material for next generation high-efficiency and low-cost thin film solar cells, methylammonium lead iodide (MAPbI₃) has become a “super star” in the solar cell community since 2010.(1–4) Although perovskite solar cell efficiencies have climbed above the 20% mark,(5, 6) the fundamental working mechanism responsible for these efficiencies and the associated long carrier lifetimes is not understood.(7, 8) MAPbI₃ has an organic-inorganic hybrid structure, where PbI₃[–]-based octahedra compose the fundamental building blocks and MA⁺ cations fill the interstices (Fig. 1). Recent studies probing the unique aspects of charge carrier generation and transport exhibited by these materials have focused on (1) the role of dynamic structural fluctuations, associated with ultrafast changes in local band structure and centrosymmetry, in facilitating charge separation and hindering recombination;(9–13) and (2) the role of the motion of organic cations in screening and protecting carriers from trapping and recombination.(14–19)

Until now, most of the photophysical studies have been based on optical measurements, which probe dipole-allowed electronic transitions with high time resolution but only indirectly probe the nuclear response. Static X-ray and TEM studies have been reported,(20–23) but compete with fast sample degradation.(24, 25) Time-resolved neutron scattering experiments provide specific information on the organic dipole orientation based on spin-magnetic interactions.(26) Compared to X-ray and neutron scattering, electrons interact with nuclei more

strongly and thus facilitate the detection of relatively weak diffuse scattering, from which information about unit cell deformations may be extracted.^(27–29) Here, we report the first direct real-time measurement of the dynamical structural processes that follow absorption of above-gap photons in MAPbI₃ perovskite thin films, using MeV ultrafast electron diffraction (UED). With this technique, we visualize the lattice response associated with the hot carrier-lattice thermalization process, one of the key energy loss channels that determine the efficiency of a solar cell. Furthermore, analysis of the differential pair distribution function (PDF), extracted from the dynamical evolution of the diffraction spectra, reveals that the dominant atomic motion in the inorganic lattice occurs within the iodine octahedra, as manifested in a large amplitude light-induced broadening of the I-I correlation function on picosecond time-scales. Meanwhile, the Pb-I distances are preserved within the signal-to-noise ratio of our measurement. Our observation therefore indicates that above-gap photoexcitation induces significant rotational sublattice disorder of the iodine octahedra, associated with changes of the I-Pb-I bond angles.

Results and Discussion:

The UED experimental setup is illustrated in Fig. 1 and a typical static diffraction image from MAPbI₃ thin film is shown in the inset. The diffraction pattern is composed of a series of concentric rings associated with an ensemble of crystalline grains (~ 50-100 nm in size) with random orientation. After azimuthal integration a plot of diffracted intensity I vs. Q (where $Q_{hkl} = \frac{2\pi}{d_{hkl}}$ is the momentum transfer of the scattered electron) is acquired. The indices of the diffraction peaks are listed in Table S1, and the measured diffraction spectrum is overlaid with the simulated electron diffraction spectrum in the Fig. S1. Our experimental Q -resolution of $\approx 0.17 \text{ \AA}^{-1}$ (determined from measurements on single-crystal gold) is not high enough to resolve all adjacent peaks. We denote the peaks as #1-8 for convenience in the following discussion.

To study the carrier-lattice interaction, we first pumped the perovskite thin film with above-gap 400 nm photons and recorded diffraction images for different time-delays between pump and probe. Snapshots of the time-resolved peak intensities and differential scattering dynamics are plotted in Fig. 2A and Fig. 3 inset respectively. After photo-excitation with 400 nm pump, we observed two clear effects: (1) the relative intensities of all Bragg peaks decrease and (2) the scattering in regions in between the main Bragg peaks increases. As shown in Fig. 2A, the relative intensity drop has a clear Q -dependence: higher-order peaks show larger decreases. Fig. 2C shows that the logarithm of the intensity modulation for a particular Bragg peak depends nearly linearly on the corresponding Q^2 for this Bragg peak, e.g. it follows a Debye-Waller-like dependence: $I(Q,t) \propto \exp\left(-\frac{1}{3}Q^2 \langle u_{RMS}^2(t) \rangle\right)$, where $\langle u_{RMS}^2(t) \rangle$ is the time-dependent mean square displacement of the atoms.(30, 31) The peak intensity decay is correlated with the rise of the lattice temperature (for small changes in diffraction intensity), with a measured time constant of 10 ± 1 ps under $66 \mu\text{J}/\text{cm}^2$ excitation fluence, corresponding to an estimated carrier density of $2.3 \times 10^{19} \text{ cm}^{-3}$ (SI). Photo-excitation at 400 nm generates electrons and holes that first equilibrate at an elevated carrier temperature T_e within hundreds of femtoseconds through carrier-carrier scattering before relaxing to the band edge via carrier-phonon scattering and transferring their excess electronic energy to the lattice.(32, 33) Thus the dynamics of the peak intensity decay tracks the hot carrier cooling time-scale.(31) After ≈ 10 ps, both the carriers and the lattice reach an equilibrium and no further thermalization is observed (Fig. S2D and Fig. S3). From the Q -dependent Bragg peak intensity drop one may extract the photo-induced change in the root-mean-square (RMS, $\sqrt{\langle u_{RMS}^2(t) \rangle}$) displacements, under the assumption of isotropic disorder.(31) Maximum observed RMS displacements are $\approx 0.1 \text{ \AA}$ for temperature jumps of ≈ 8

K (SI), showing that weak photo-excitation induces large structural deformations. From a Debye model, we estimate an effective Debye temperature $\theta_D \approx 60$ K (Table S2), comparable with both experimental values from heat capacity measurements(20) and theoretical calculations(34). To further validate the correspondence between changes in the RMS displacements and lattice temperature, we performed classical molecular dynamics (MD) simulations (see Materials and Methods). Fig. 2D shows that the experimental RMS displacement changes agree well with the results extracted from the force field MD simulations.

To explore explicitly how the band-edge carriers interact with the lattice, we tuned the pump wavelength to 700 nm, close to the band-gap of 760 nm. Contrary to the effects observed under 400 nm excitation, we only observed $< 1\%$ Bragg peak intensity changes even at the highest fluence measured of order $4.3 \times 10^{19}/\text{cm}^2$, just below damage threshold ($\approx 230 \mu\text{J}/\text{cm}^2$) and corresponding to similar carrier densities as measured under 400 nm excitation. This indicates that cold carrier-defect scattering in perovskites leads to negligible lattice heating, which is consistent with reported transport measurements and shows that the dominant heating response comes from hot carrier / phonon coupling.(16, 35, 36)

Analysis based on the Bragg peaks effectively averages over all atoms, with dominant contributions from the Pb and I atoms. More information on the pump-induced structural changes can be obtained by analyzing the scattering in between the main Bragg peaks.(29, 37) Fig. 3 shows that the loss of Bragg peak diffraction intensity leads to a gain in the intensity between peaks. The dynamics of the scattering averaged over different Q regions are plotted in the inset of Fig. 3, showing that low Q scattering ($Q_1 = 2.1 - 2.6 \text{ \AA}^{-1}$ and $Q_2 = 3.8 - 4.1 \text{ \AA}^{-1}$) rises more slowly than higher Q ($Q_3 = 5.1 - 5.3 \text{ \AA}^{-1}$ and $Q_4 = 6.1 - 6.8 \text{ \AA}^{-1}$) in contrast to the Bragg peak dynamics (which show similar time evolution for all peaks, Fig. S5-6 and Table S3). In

order to check if thermal effects and/or heating across the known tetragonal-to-cubic phase transition (typically occurring at temperatures significantly higher than induced here) are playing a role in the observed effects, we carried out temperature dependent x-ray scattering studies of crystalline powders of MAPbI₃, described within the Supplementary Information. These measurements show effects consistent with prior studies (38-40) but not consistent with the differential changes shown in Fig. 3. This indicates that additional optically-induced structural deformations other than pure thermal vibrations are occurring, discussed further below.

From a Fourier transform of the differential diffraction spectrum one may extract the pump-induced change in the pair distribution function (PDF), reflecting changes in local correlations at the atomic-scale (for details see SI). Static PDF analysis on MAPbI₃ based on X-ray scattering studies has been reported showing peaks at $r \approx 3.2$ Å and ≈ 4.6 Å, corresponding to the nearest-neighbor (Pb-I) and (I-I) pairs, respectively.(22) The pump-induced changes in the PDF at different time delays are plotted in Fig. 4. Observed is a clear negative feature at $r \approx 4.6$ Å, the nearest-neighbor I-I distance, along with two positive features on either side. This is an indication of the I-I PDF peak broadening, as a result of variations in the distance between nearest-neighbor iodine ions, which make up the octahedron around each Pb atom. By contrast, no differential PDF signal is observed at $r \approx 3.2$ Å, the nearest Pb-I distance. Taken together, these observations indicate a rotational disordering of the I atoms on a spherical surface around the Pb center within each PbI₆⁴⁻ octahedron. From the peak magnitude of the change in the PDF we estimate a light-induced broadening of the I-I correlation function by ~ 0.1 Å (SI), an amount comparable to its initial intrinsic width, and consistent with the magnitudes estimated from the simple Debye-Waller analysis.

In MAPbI₃, we find that the time-scale for the change in the PDF (27 ± 8 ps) is significantly slower than the Bragg peak intensity drop (10 ± 1 ps) for a carrier density of $2.3 \times 10^{19}/\text{cm}^3$. Additionally, this time-constant is observed to be excitation intensity dependent, with faster effects observed for higher carrier density (inset of Fig. 4A). These discrepancies in rates, along with the observed deviations from simple Debye-Waller-like responses at low Q , suggest that the origin of the observed rotational disordering is not merely due to thermally activated processes. Further support for this statement comes from our MD simulations. The equilibrium change in PDF, ΔG , calculated from molecular dynamics trajectories at 300 K and 325 K shows that pure isotropic thermal fluctuations are unlikely to cause such large selective broadening of the I-I PDF peak (Fig. 4B). The MD calculations, in contrast, show similar broadening of both Pb-I and I-I peaks and predict changes in the I-I PDF peak significantly smaller than observed experimentally. Similar results were obtained for MD simulation temperatures up to 400 K (Fig. S9). We estimate the additional fluctuation required to explain the experimental results by adding post hoc random displacements to our MD trajectories and calculating the resulting PDFs. We add independent normally distributed displacements of magnitude 0.1 Å to iodine atoms in directions perpendicular to Pb-I bonds, and find good agreement with experimental PDF in both the shape and the amplitude (Fig. 4A). The 0.1 Å I displacement also agrees with the broadening of the I-I correlation function estimated above from the experimental PDF analysis. This implies that light preferentially excites volume-preserving distortions of I₆ cages (e.g. deviations of the I-Pb-I bond angle) around the Pb center in each PbI₆⁴⁻ octahedron. Additional contributions may come from tilting of adjacent octahedra. From the magnitude of the experimentally or theoretically estimated displacements, this corresponds to an angular deviation of a few degrees, comparable to that estimated theoretically in reference (11) We carried out similar time-resolved

PDF analysis on gold polycrystalline films, which exhibits a simple homogeneous lattice heating response upon photo-excitation, and observed isotropic broadening responses at all nearest-neighbor distances, confirming the validity of our PDF analysis (Fig. S10).

Conclusion:

We conclude by briefly discussing the significance of and the physical mechanisms for the observed changes in the PDF. Recent studies have emphasized the role of structural fluctuations in reducing effective bimolecular recombination constants in the hybrid perovskites, typically in reference to the freely reorienting organic dipoles, e.g. MA^+ , and their coupling to the inorganic lattice.^(11, 19) Our work shows that one should consider not only the organic molecules but also the contribution from the inorganic lattice, and in particular the structural deformations induced by absorption of a photon. Indeed, the iodine-iodine correlation peak broadens by an amount comparable to its intrinsic width (under excitation conditions corresponding to temperature jumps of < 10 K). Considering that these distortions are localized within each octahedron and our UED experiment averages over all unit cells in the sample, the extracted I-I broadening is likely an underestimate of the local motions near an excited carrier.

The MD simulations demonstrate that equilibrium thermal activation cannot explain the observed distortion. From the fact that no clear Pb-I correlation change was observed even after ~ 200 ps (Fig. S11), we further conclude that the observed effect is not due to non-equilibrated thermal excitation (e.g. preferential excitation of I before eventually coupling to Pb). This indicates that the distortions of the I ions likely arise from electronic excitation and are frozen within the I sublattice. A light-induced hydrogen bond breaking mechanism between MA^+ and I^- has recently been hypothesized with respect to photo-enhanced lattice expansion, H migration via the Bourgoïn-Corbett mechanism, and ferroelectric response in the hybrid perovskites.^{(14,}

41–43) The observation that the I-sublattice distortion stabilizes faster under higher pump fluence (inset of Fig. 4 A) and only occurs under above-gap excitation is consistent with the presence of an activation barrier for the distortion, where higher carrier temperatures help to overcome the barrier faster. The observed dominant motion of the iodine is also consistent with previous predictions that I ions have the smallest hopping barriers among the intrinsic defect species, and that ionic transport processes may be light-enhanced; (44–46) but we emphasize that on the short times probed here all observed effects are reversible at the 180 Hz repetition rate of the experiment and do not lead to full ionic hops. Future studies under lower excitation density (closer to 1 sun illumination) that probe the observed short time ionic displacements and their dependence on sample morphology may help to explain morphology-dependent device performance. Finally, this light-enhanced local disorder provides a source for the structural reorganizations that underlie light-induced changes in dielectric constant (19, 47) and the dynamical symmetry breaking required for proposed Rashba effects and other photo-induced changes in band structure.(9, 11, 13) From these perspectives, whereas structural fluctuations may facilitate charge separation and ion transport, these also depend upon the carrier generation process, which further softens the lattice and makes it even more vulnerable to deformation.

Materials and Methods:

Ultrafast Electron Diffraction

The UED experimental setup is illustrated in Fig. 1 and is similar as reported elsewhere. (31, 37, 48) The output of a multipass amplified Ti:sapphire laser is split into two paths: one is doubled to 400 nm as the pump and the other is tripled for the electron pulse generation. Alternatively, for 700 nm pump excitation, the pump beam is first frequency converted using an optical parameter amplifier. The electron pulses are accelerated to 3.7 MeV with 300 fs (FWHM,

estimated by N-body simulation for ~ 120 fC/pulse) duration in the SLAC Ultrafast Electron Diffraction (UED) facility(47). Electron pulses were focused onto the MAPbI₃ films at normal incidence with ~ 300 μ m diameter and the diffracted electrons were detected by a red phosphor screen and captured by an EMCCD. The pump beam with 40 fs (FWHM) duration was spatially overlapped with the electron beam on the sample with incident angle of $\sim 3^\circ$ and diameter of ~ 400 μ m. The pump beam and the electron probe beam are phase locked and synchronized at 180 Hz. The delay between the pump and probe pulses are controlled by a translational stage. All data discussed above are taken on fresh samples without observable sample degradation. At the highest fluence investigated and after several hours of photo-excitation, some evidence for degradation and production of PbI₂ (Supplementary Information, Fig. S15, peak 4 of PbI₂) was observed, which was used as a monitor of the sample stability.

Molecular Dynamic Simulation

Classical molecular dynamics (MD) simulations were performed on an $8 \times 8 \times 8$ pseudocubic super-cell of MAPbI₃ (6144 atoms, one formula unit in each pseudocubic unit cell) with the LAMMPS code.(49) We used the force field developed by Mattoni *et al.*,(50) which was shown to provide an accurate description of temperature-dependent lattice expansion and orthorhombic-to-tetragonal phase sequences of MAPbI₃. The good agreement between simulations and experiments as shown in Fig. 2C on the changes in RMS displacements at different temperatures, along with the agreement of the calculated bond lengths, RMS displacements (Table S5) and Pb-I and I-I PDF peak widths (Fig. 4B) with literature values,(22, 51) further confirm the validity of the MD simulations. Starting from 300 K, using a Nosé-Hoover thermostat we increased the simulation temperature in 5 K steps to mimic experimental temperature jumps. At each temperature, we first equilibrated the system, using an *NPT* ensemble and ≈ 500 ps simulation

time, and then performed a 20 ps *NVT* production run to extract the structural data; the time step in all cases was set to 0.5 fs.

Perovskite Thin Film Growth

Thin films of lead halide perovskite (~40 nm) were prepared by thermal evaporation of methylammonium iodide (MAI) and PbCl₂ in high vacuum (base pressure < 10⁻⁵ Pa). The materials were co-deposited onto a TEM grid supported by a 20 nm carbon film. The partial pressure of MAI was maintained at ~2 x 10⁻³ Pa during evaporation. The substrate was at room temperature during growth and each sample was post-annealed in MAI atmosphere at 370 K for 15 minutes. The deposition rate of PbCl₂ was ~0.5 nm/min, as monitored by a quartz-crystal microbalance. (1) PbI₂ thin films are spin coated on 50 nm SiN windows. Each diffraction image frame was accumulated over 540 electron pulses (3s) and at each pump-probe time delay 3 image frames were taken. In addition to the time-resolved diffraction images taken with pump and probe pulses at certain given time delay, we also recorded the static diffraction images at each delay position without pump irradiation, which is utilized as a reference for sample damage.

References:

1. M. Liu, M. B. Johnston, H. J. Snaith, Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*. **501**, 395–8 (2013).
2. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*. **338**, 643–7 (2012).
3. A. Mei *et al.*, A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science*. **345**, 295–298 (2014).
4. H. Zhou *et al.*, Interface engineering of highly efficient perovskite solar cells. *Science*. **345**, 542–546 (2014).
5. W. S. Yang *et al.*, High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*. **348**, 1234–1237 (2015).
6. M. Saliba *et al.*, A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nat. Energy*. **1**, 15017 (2016).

- 1 7. G. Xing *et al.*, Long-range balanced electron- and hole-transport lengths in organic-
2 inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science*. **342**, 344–7 (2013).
- 3 8. T. M. Brenner *et al.*, Hybrid organic—inorganic perovskites: low-cost semiconductors
4 with intriguing charge-transport properties. *Nat. Rev. Mater.* **1**, 15007 (2016).
- 5 9. T. Etienne, E. Mosconi, F. De Angelis, Dynamical Origin of the Rashba Effect in
6 Organohalide Lead Perovskites: A Key to Suppressed Carrier Recombination in
7 Perovskite Solar Cells? *J. Phys. Chem. Lett.* **7**, 1638–1645 (2016).
- 8 10. O. Yaffe *et al.*, Local polar fluctuations in lead halide perovskite crystals. *Phys. Rev. Lett.*,
9 **118**, 136001 (2017).
- 10 11. C. Motta *et al.*, Revealing the role of organic cations in hybrid halide perovskite
11 $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nat. Commun.* **6**, 7026 (2015).
- 12 12. S. Liu *et al.*, Ferroelectric Domain Wall Induced Band-Gap Reduction and Charge
13 Separation in Organometal Halide Perovskites. *J. Phys. Chem. Lett.* **6**, 693–699 (2015).
- 14 13. F. Zheng, L. Z. Tan, S. Liu, A. M. Rappe, Rashba spin-orbit coupling enhanced carrier
15 lifetime in $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nano Lett.* **15**, 7794–7800 (2015).
- 16 14. M. Coll *et al.*, Polarization Switching and Light-Enhanced Piezoelectricity in Lead Halide
17 Perovskites. *J. Phys. Chem. Lett.* **6**, 1408–1413 (2015).
- 18 15. J. M. Frost *et al.*, Atomistic origins of high-performance in hybrid halide perovskite solar
19 cells. *Nano Lett.* **14**, 2584–2590 (2014).
- 20 16. X. Y. Zhu, V. Podzorov, Charge Carriers in Hybrid Organic-Inorganic Lead Halide
21 Perovskites Might Be Protected as Large Polarons. *J. Phys. Chem. Lett.* **6**, 4758–4761
22 (2015).
- 23 17. J. Ma, L. W. Wang, Nanoscale charge localization induced by random orientations of
24 organic molecules in hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nano Lett.* **15**, 248–253 (2015).
- 25 18. A. J. Neukirch *et al.*, Polaron stabilization by cooperative lattice and cation rotations in
26 hybrid perovskite materials. *Nano Lett.* **16**, 3809–3816 (2016).
- 27 19. W. Nie *et al.*, Light-activated photocurrent degradation and self-healing in perovskite
28 solar cells. *Nat. Commun.* **7**, 11574 (2016).
- 29 20. N. Onoda-Yamamuro, T. Matsuo, H. Suga, Calorimetric and IR spectroscopic studies of
30 phase transitions in methylammonium trihalogenoplumbates (II)†. *J. Phys. Chem. Solids*.
31 **51**, 1383–1395 (1990).
- 32 21. T. J. Jacobsson, L. J. Schwan, M. Ottosson, A. Hagfeldt, T. Edvinsson, Determination of
33 Thermal Expansion Coefficients and Locating the Temperature-Induced Phase Transition
34 in Methylammonium Lead Perovskites Using X-ray Diffraction. *Inorg. Chem.* **54**, 10678–
35 10685 (2015).
- 36 22. J. J. Choi, X. Yang, Z. M. Norman, S. J. L. Billinge, J. S. Owen, Structure of
37 methylammonium lead iodide within mesoporous titanium dioxide: Active material in
38 high-performance perovskite solar cells. *Nano Lett.* **14**, 127–133 (2014).
- 39 23. D. Li *et al.*, Size-dependent phase transition in methylammonium lead iodide perovskite
40 microplate crystals. *Nat. Commun.* **7**, 11330 (2016).

24. C. Xiao *et al.*, Mechanisms of Electron-Beam-Induced Damage in Perovskite Thin Films Revealed by Cathodoluminescence Spectroscopy. *J. Phys. Chem. C*. **119**, 26904–26911 (2015).
25. H. Yuan *et al.*, Degradation of Methylammonium Lead Iodide Perovskite Structures through Light and Electron Beam Driven Ion Migration. *J. Phys. Chem. Lett.* **7**, 561–566 (2016).
26. A. M. A. Leguy *et al.*, The dynamics of methylammonium ions in hybrid organic-inorganic perovskite solar cells. *Nat. Commun.* **6**, 7124 (2015).
27. R. Srinivasan, V. A. Lobastov, C.-Y. Ruan, A. H. Zewail, Ultrafast electron diffraction (UED): A new development for the 4D determination of transient molecular structures. *Helv. Chim. Acta*. **86**, 1763–1838 (2003).
28. R. P. Chatelain, V. R. Morrison, B. L. M. Klarenaar, B. J. Siwick, Coherent and incoherent electron-phonon coupling in graphite observed with radio-frequency compressed ultrafast electron diffraction. *Phys. Rev. Lett.* **113**, 235502 (2014).
29. V. R. Morrison *et al.*, A photoinduced metal-like phase of monoclinic VO₂ revealed by ultrafast electron diffraction. *Science*. **346**, 445–448 (2014).
30. A. M. Lindenberg *et al.*, Atomic-scale visualization of inertial dynamics. *Science*. **308**, 392–5 (2005).
31. E. M. Mannebach *et al.*, Dynamic Structural Response and Deformations of Monolayer MoS₂ Visualized by Femtosecond Electron Diffraction. *Nano Lett.* **15**, 6889–6895 (2015).
32. A. D. Wright *et al.*, Electron–phonon coupling in hybrid lead halide perovskites. *Nat. Commun.* **7**, 6050–6051 (2016).
33. Y. Yang *et al.*, Observation of a hot-phonon bottleneck in lead-iodide perovskites. *Nat. Photonics*. **10**, 53–59 (2015).
34. J. Feng, Mechanical properties of hybrid organic-inorganic CH₃NH₃BX₃ (B = Sn, Pb; X = Br, I) perovskites for solar cell absorbers. *APL Mater.* **2**, 81801 (2014).
35. T. M. Brenner *et al.*, Are Mobilities in Hybrid Organic-Inorganic Halide Perovskites Actually “high”? *J. Phys. Chem. Lett.* **6**, 4754–4757 (2015).
36. H. T. Yi, X. Wu, X. Zhu, V. Podzorov, Intrinsic Charge Transport across Phase Transitions in Hybrid Organo-Inorganic Perovskites. *Adv. Mater.* **28**, 6509–6514 (2016).
37. T. Chase *et al.*, Ultrafast electron diffraction from non-equilibrium phonons in femtosecond laser heated Au films. *Appl. Phys. Lett.* **108**, 41909 (2016).
38. T. Baikie *et al.*, Synthesis and crystal chemistry of the hybrid perovskite (CH₃NH₃)PbI₃ for solid-state sensitised solar cell applications. *J. Mater. Chem. A*. **1**, 5628 (2013).
39. F. Brivio *et al.*, Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide. *Phys. Rev. B*. **92**, 144308 (2015).
40. P.S. Whitfield *et al.*, Structures, phase transitions and tricritical behavior of the hybrid perovskite methyl ammonium lead iodide. *Sci. Rep.* **6**, 35685 (2016)
41. Y. Zhou *et al.*, Giant photostriction in organic–inorganic lead halide perovskites. *Nat.*

- Commun.* **7**, 11193 (2016).
42. D. A. Egger, L. Kronik, A. M. Rappe, Theory of Hydrogen Migration in Organic-Inorganic Halide Perovskites. *Angew. Chemie - Int. Ed.* **54**, 12437–12441 (2015).
 43. S. Liu, F. Zheng, I. Grinberg, A. M. Rappe, Photoferroelectric and Photopiezoelectric Properties of Organometal Halide Perovskites. *J. Phys. Chem. Lett.* **7**, 1460–1465 (2016).
 44. Y. Deng, Z. Xiao, J. Huang, Light-induced self-poling effect on organometal trihalide perovskite solar cells for increased device efficiency and stability. *Adv. Energy Mater.* **5**, 1500721 (2015).
 45. C. Eames *et al.*, Ionic transport in hybrid lead iodide perovskite solar cells. *Nat. Commun.* **6**, 7497 (2015).
 46. D. W. deQuilettes *et al.*, Photo-induced halide redistribution in organic–inorganic perovskite films. *Nat. Commun.* **7**, 11683 (2016).
 47. E. J. Juarez-Perez *et al.*, Photoinduced Giant Dielectric Constant in Lead Halide Perovskite Solar Cells. *J. Phys. Chem. Lett.* **5**, 2390–2394 (2014).
 48. S. P. Weathersby *et al.*, Mega-electron-volt ultrafast electron diffraction at SLAC National Accelerator Laboratory. *Rev. Sci. Instrum.* **86**, 73702 (2015).
 49. S. Plimpton, Fast Parallel Algorithms for Short – Range Molecular Dynamics. *J. Comput. Phys.* **117**, 1–19 (1995).
 50. A. Mattoni, A. Filippetti, M. I. Saba, P. Delugas, Methylammonium Rotational Dynamics in Lead Halide Perovskite by Classical Molecular Dynamics: The Role of Temperature. *J. Phys. Chem. C.* **119**, 17421–17428 (2015).
 51. C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* **52**, 9019–38 (2013).
 52. J. Yin *et al.*, Interfacial charge transfer anisotropy in polycrystalline lead iodide perovskite films. *J. Phys. Chem. Lett.* **6**, 1396–1402 (2015).
 53. L.-M. Peng, Electron Scattering Factors of Ions and their Parameterization. *Acta Crystallogr.* **54**, 481–485 (1998).
 54. L. M. Peng, G. Ren, S. L. Dudarev, M. J. Whelan, Robust Parameterization of Elastic and Absorptive Electron Atomic Scattering Factors. *Acta Crystallogr. Sect. A Found. Crystallogr.* **52**, 257–276 (1996).
 55. B. J. Siwick *et al.*, An Atomic-Level View of Melting Using Femtosecond Electron Diffraction. *Science.* **302**, 1382–1385 (2003).
 56. M.I. Saidaminov *et al.*, High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. *Nat. Commun.* **6**, 7586 (2015).

Acknowledgments:

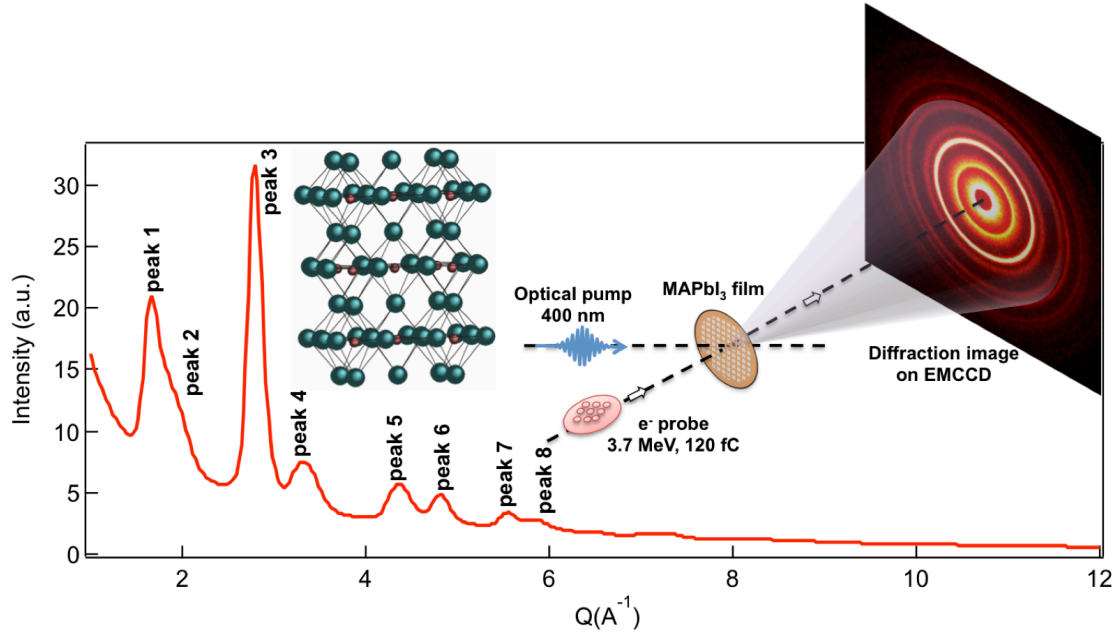
Funding: This work was supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. The UED source was supported in part by the DOE BES Scientific User Facilities Division and SLAC UED/UEM program development fund. X.Y.Z. acknowledges the US Department of Energy, Office of Science - Basic Energy Sciences, Grant ER46980 for supporting the growth of the hybrid perovskite samples used in this study. L.Z.T acknowledges support of the Office of Naval Research, under grant number N00014-14-1-0761. A.M.R. acknowledges support of the Office of Naval Research, under grant number N00014-12-1-1033. D.A.E. and L.K. were supported by the Austrian Science Fund (FWF): J3608-N20 and by a research grant from Dana and Yossie Hollander, in the framework of the WIS Alternative sustainable Energy Initiative. T.H. acknowledges support from the Precourt Institute for Energy Sciences. H.I.K. thanks the Alfred P. Sloan Foundation for support. M. D. S. is supported by an NSF Graduate Research Fellowship (DGE-114747). Part of this work was performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under award ECCS-1542152.

Author contributions: X. W., X. S., T. H., R. L., R. C., I. M., Q. Z., A. F., J. S. R., X. W. and A. L. carried out the UED experiment. X. W., K. M., M. T. T., M.S., B.G., H.K. and X.-Y. Z. led the sample growth, x-ray, and optical characterization experiments. L. Z. T., D. A. E., L. K. and A. M. R. carried out the theory and simulations. X. W. and A. L. performed data analysis and wrote the manuscript with input from all authors.

Competing interests: The authors declare no competing interests.

Additional information: Correspondence and requests for materials should be addressed to A.L.

1 **Figures:**



2

3 **Fig. 1.** Radial diffraction intensity plot as a function of scattering vector Q . Center inset: Atomic-
4 scale structure of MAPbI₃ with tetragonal phase and I4cm space group (Dark green sphere
5 denotes I and red sphere denotes Pb. N, C and H are not shown). Right inset: Schematic of
6 femtosecond transmission electron diffraction setup with optical pump and electron probe,
7 showing also the recorded 2-dimensional diffraction image of the MAPbI₃ perovskite thin film.

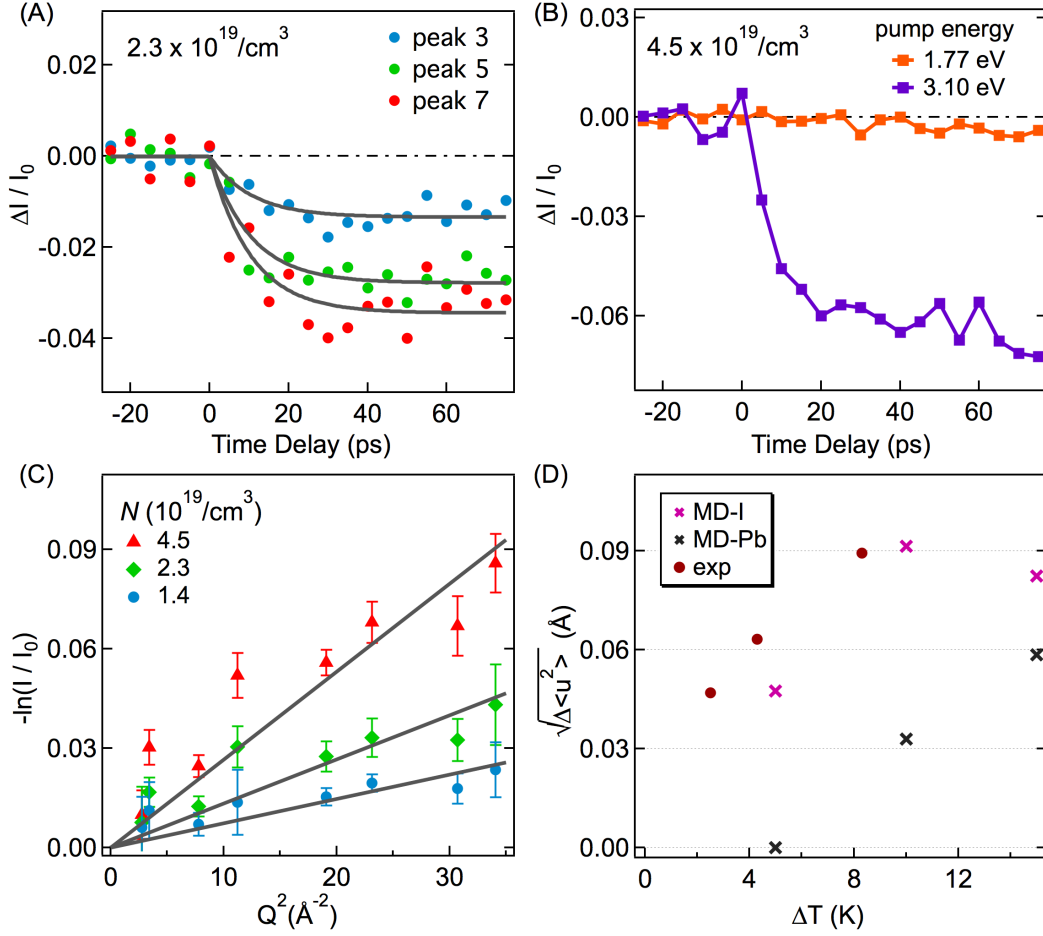


Fig. 2. Time-dependent changes in Bragg peak intensities and associated RMS displacements

(A) Peak intensity dynamics for different diffraction peaks showing Q -dependent peak intensity decay with similar time constants. Excitation is at 400 nm and corresponding to carrier density of $2.3 \times 10^{19} / \text{cm}^3$. The solid curves are global fits. Global fitting results for other peaks are plotted in Fig. S7. (B) Comparison of peak #7 decay between 400 nm and 700 nm pump with similar photo-induced carrier density. (C) Semi-log plot of intensity change (signal averaged over the delay range 40 ~ 75 ps as a function of the squared scattering factor (Q^2)) for different excitation densities, showing a Debye-Waller-like response corresponding to an increase in the RMS displacements of the atoms. The solid lines are linear fits with y-intercept forced to 0. (D)

Comparison between experimental and theoretical RMS ($\sqrt{\langle u_{RMS}^2 \rangle}$ in Å) displacements at different temperatures (ΔT is referenced to room temperature).

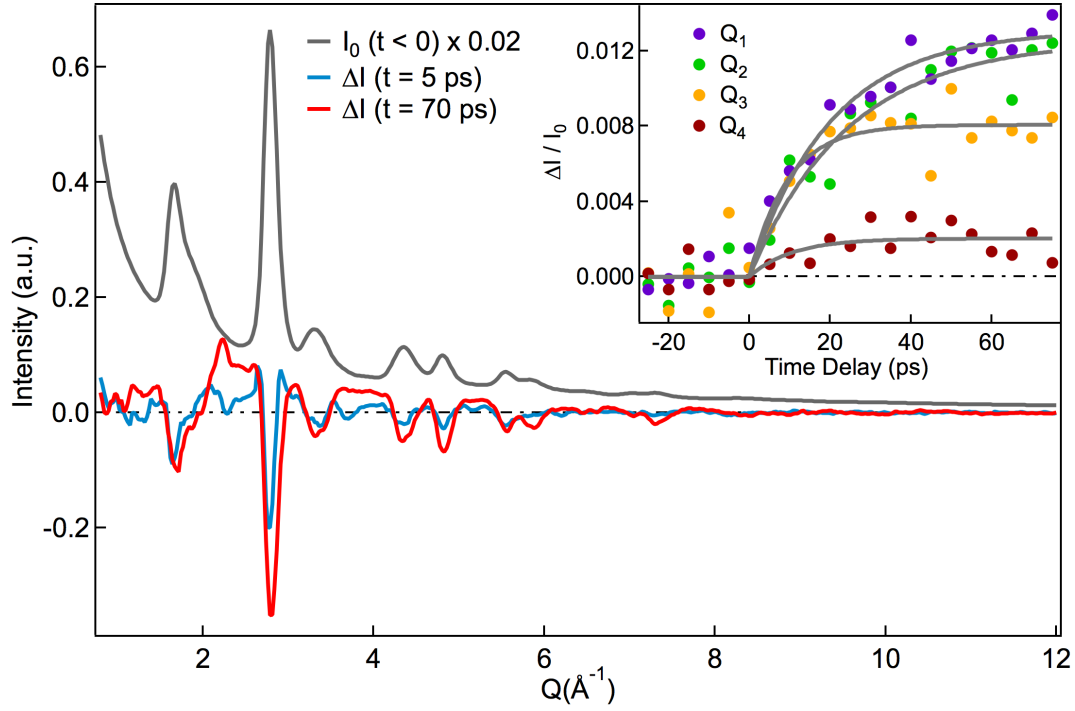


Fig. 3. Static and differential radial diffraction spectra at different time delays. Differential radial diffraction spectrum at $t = 5$ ps and 70 ps with photo-excited carrier density of $2.3 \times 10^{19}/\text{cm}^3$. Inset: time evolution of scattering integrated over four different Q ranges: $Q_1 = (2.1 - 2.6 \text{ Å}^{-1})$, $Q_2 = (3.8 - 4.1 \text{ Å}^{-1})$, $Q_3 = (5.1 - 5.3 \text{ Å}^{-1})$, $Q_4 = (6.1 - 6.8 \text{ Å}^{-1})$. The solid curves are single exponential fits to each Q range with time constants of $20 (\pm 2)$ ps, $25 (\pm 5)$ ps, $9 (\pm 3)$ ps and $11 (\pm 7)$ ps from low Q to high Q , respectively.

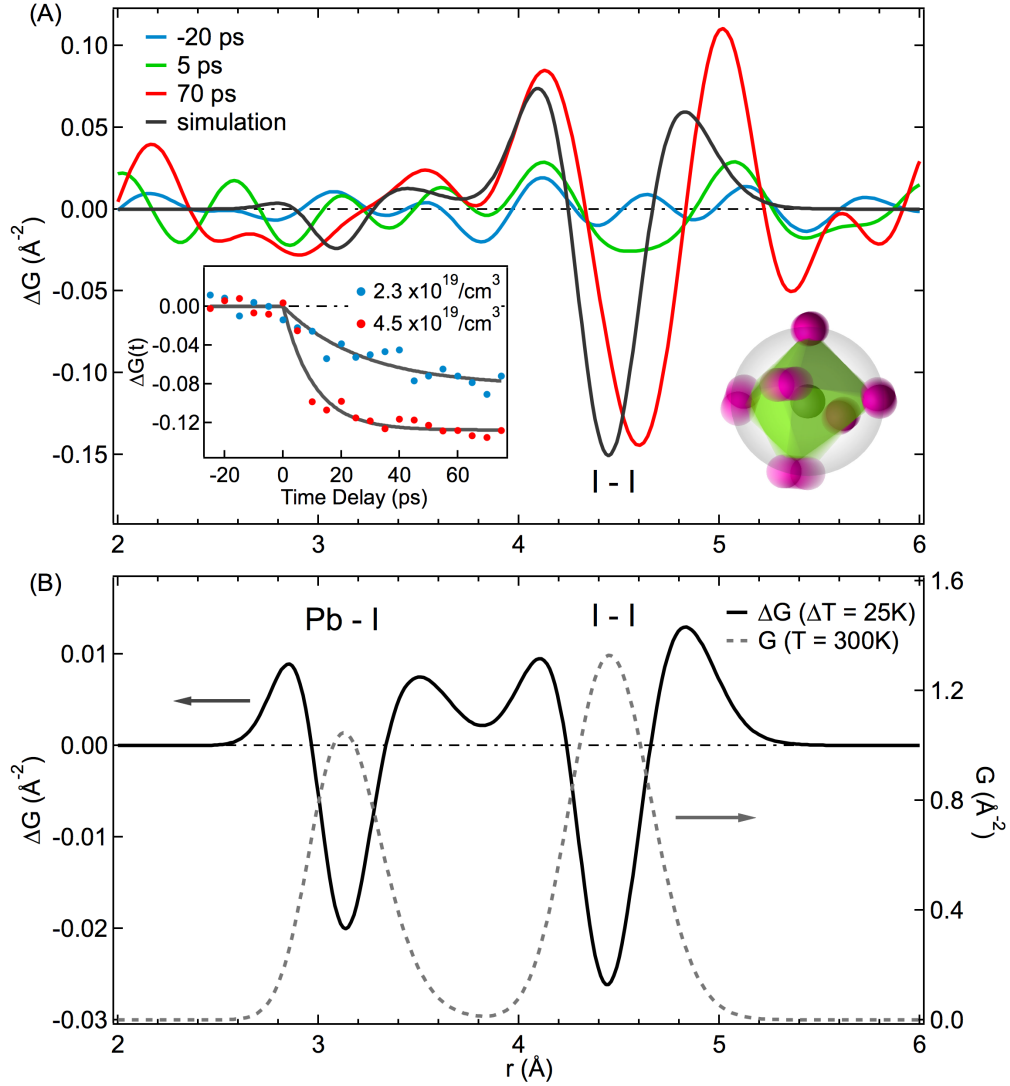


Fig. 4 Comparison between experimental and calculated differential PDF. (A) Differential PDF at different delay times with $4.5 \times 10^{19}/\text{cm}^3$ carrier density. The black curve in the main panel is the calculated difference PDF from molecular dynamics simulations equilibrated at temperatures 300 K and 325 K ($\Delta T = 25$ K), with additional fluctuations of iodine atoms 0.1 Å in magnitude, to simulate the photoactivation (see text for details). Left inset shows the time-dependent PDF dynamics at $r = 4.6 (\pm 0.1)$ Å corresponding to the I-I atomic distance under two excitation densities as noted in the figure. The solid curves in the left inset are single exponential fits. Right inset is an illustration of the proposed I rotational disorder in one PbI_6 octahedron. (B) Calculated

1 PDF (solid) at room temperature (300 K, left axis) and calculated difference PDF (dashed) from
2 molecular dynamics simulations equilibrated at temperatures 300 K and 325 K, without
3 additional fluctuations, corresponding to pure thermal activation.

4 **Supplementary Materials:**

5 Supplementary text

6 Fig. S1-S21

7 Tables S1-S5