By process of illumination: Revealing the causes of dramatic anharmonicity in \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) with Raman scattering

Rituraj Sharma,\(^1\) Zhenbang Dai,\(^2\) Lingyuan Gao,\(^2\) Thomas M. Brenner,\(^1\) Lena Yadgarov,\(^1\) Jiahao Zhang,\(^3\) Yevgeny Rakita,\(^1\) Roman Korobko,\(^1\) Andrew M. Rappe,\(^2\) \( \) and Omer Yaffe\(^1\)

\(^1\)Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel
\(^2\)Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

(Dated: January 14, 2020)

Motivated by promising photovoltaic performance, recent works have established halide perovskites as a unique class of semiconductors. Recent evidence links their novel optoelectronic responses to pronounced electron-phonon interactions that stem from strongly anharmonic lattice fluctuations. Here, we reveal the microscopic mechanisms that lead to the strong structural anharmonicity in methylammonium lead iodide (MAPI). Our findings are based on Raman polarization-orientation measurements and first-principles molecular dynamics (MD) across the phase sequence of the crystal. We identify two mechanisms that lead to strong anharmonicity and differ in their temperature dependence. The first is the abrupt breaking of hydrogen bonds, which unlocks the PbI\(_6\) octahedra from the methylammonium molecules. This leads to a phase transition from orthorhombic to tetragonal structure. The second is relaxation movement of the PbI\(_6\) octahedra whose anharmonicity continuously strengthens through both the tetragonal and cubic phases. These strongly anharmonic motions limit phonon lifetimes to the point that the phonon picture breaks down. These conclusions transform our understanding of the structural dynamics of the technologically-relevant tetragonal phase of MAPI, whose anharmonic nature has not been previously demonstrated.

Keywords: Anharmonicity; Hybrid perovskites; \( \text{CH}_3\text{NH}_3\text{PbI}_3 \); Low frequency Raman scattering; molecular dynamics

Methylammonium lead iodide (MAPI, \( \text{CH}_3\text{NH}_3\text{PbI}_3 \)) has emerged as an outstanding absorbing material for photovoltaics, achieving a photo-conversion efficiency of \( > 22\% \).\(^{1,2,3,4,5} \) Additionally, numerous fascinating properties like polar character, light emission, ion migration, low thermal conductivity, etc. make MAPI promising and potentially transformative for several thermooptoelectronic applications.\(^{4,6,7} \) However, the origins of many seemingly contradictory characteristics, such as low mobility but high carrier lifetime, small Urbach energy but many structural defects remain debated.\(^{8,9,10} \) All these anomalous properties of MAPI and related halide perovskites (HPs) are intimately associated with their anharmonic structural dynamics (i.e. phonon-phonon interactions) and mechanical softness.\(^ {11} \) Although HPs appear as crystalline solids in X-ray diffraction,\(^ {11} \) their dielectric response and light scattering properties resemble those of polar liquids.\(^ {12,13} \) This behavior is indicative of strongly anharmonic motions that give rise to local polar fluctuations.\(^ {14,15,16} \)

In light of the above, HPs must be treated beyond the harmonic approximation. Many recent attempts have been made to explain the source of the unique properties of HPs regarding their unusual structural dynamics. Mayers \textit{et al.} explained the unusual optical absorption properties and mobility in HPs through an improved theoretical framework incorporating the effects of high-amplitude anharmonic displacements and nonlinear electron-phonon coupling.\(^ {13} \) Rakita \textit{et al.} explained the low carrier recombination in MAPI as the result of spatial separation of electrons and holes due to spontaneous dielectric polarization.\(^ {17} \) This finding invigorates recent studies that highlight the role of Rashba electronic splitting (due to local or global polarization) in unexpectedly low recombination rates.\(^ {18,19} \) Others focused on the octahedral rotation and reorientation dynamics of the organic molecule to explain self-healing, bandgap fluctuations and ion migration in the HP-1D phase.\(^ {20} \)

Despite the aforementioned extensive body of work, the structural dynamics of MAPI across its phase sequence are still not well understood. This is mainly because of very-low thermal conductivity and high light absorption of MAPI. This combination limits the spectroscopic studies due to incident light-induced thermal damage.\(^ {22} \)

Here, we perform temperature dependent polarization orientation (PO) Raman measurements to study the structural dynamics in MAPI. Sub-band gap excitation at 1064 nm (1.16 eV) is used to overcome the damage due to shorter wavelength excitation. The experimental observations were reproduced using \textit{ab initio} molecular dynamics (AIMD). This allowed us to provide a definitive assignment of the Raman spectral features to real-space atomic motions. We employed this real space analysis to elucidate the microscopic mechanisms governing the strongly anharmonic structural dynamics in MAPI.

**Raman scattering across the phase sequence in MAPI**

MAPI crystallizes into an \( ABX_3 \) type perovskite structure, with PbI\(_6\) in corner-sharing octahedral configuration and MA molecule inside the cuboctahedral cavities. It shows two structural phase transitions: orthorhombic (\( o^- \)) to tetragonal (\( t^- \)) at \( T \approx 162 \) K, and tetragonal to cubic...
(c-) at $\approx 327$ K\textsuperscript{12,24}.

To study the various aspects affecting the structural dynamics in MAPI, we perform low-frequency Raman measurements on single crystals oriented along [110] direction (See SI, Fig. S1 for room temperature XRD). Figure 1 shows the unpolarized Raman spectra taken across the phase sequence covering both anti-Stokes and Stokes scattering. The temperature evolution of Raman spectra depicts the phase transitions in accordance with the literature\textsuperscript{25}.

The low-temperature $o$-phase is characterized by sharp Raman peaks, which correspond mainly to harmonic lattice modes\textsuperscript{26}. The $o$-$t$-phase transition is manifested by an abrupt change in the shape of the Raman spectrum, where several sharp peaks of $o$-phase are merged to form an envelope with two distinct peaks at $\approx 28$ and $45$ cm$^{-1}$ (See also SI, Fig. S2). The dramatic merging and broadening of Raman peaks cannot be explained by the normal broadening due to the system-bath interaction\textsuperscript{27}. As temperature increases in the $t$-phase, the peaks further broaden and red-shift due to thermal expansion. The $t$-phase persists up to $\approx 330$ K and evolves to the $c$-phase at 360 K. We note that the peak around $45$ cm$^{-1}$ in the $t$-phase can still be seen in the form of a broad feature in the $c$-phase, and significant broadening of this feature marks the $t$-$c$-phase transition. When the $c$-phase is fully developed, the entire spectrum becomes very broad and appears to be an envelope of the peaks of the $o$-phase. The appearance of such a spectrum is unexpected, as cubic perovskite crystals should not display any single-phonon Raman activity\textsuperscript{28}. The Raman activity is attributed to strong dynamic symmetry breaking in the cubic phase\textsuperscript{15,21,29}. The dynamic symmetry breaking in the $c$-phase is so strong that the spectrum of MAPI resembles the Raman spectrum of a fluid\textsuperscript{30}. To demonstrate this, we compare it to the room-temperature spectrum of benzene (grey curve in the upper panel of Fig. 1). This extraordinary similarity between the Raman spectra of cubic MAPI and benzene reflects the fact that despite the average cubic structure of the crystal, MAPI exhibits stochastic, relaxational motion that has no restoring force\textsuperscript{31}.

**MD mode trajectory analysis of MAPI**

To elucidate the ionic motions that give rise to the Raman spectra, we perform AIMD simulations for all three phases of MAPI and calculate the Raman spectra from the polarizability autocorrelation function as discussed in the methods section. The theoretical spectra of all three phases are displayed above the experimental spectra (blue curves) in Fig. 1. The overall agreement between experimental and calculated Raman spectra, including both peak positions and intensities, is excellent. In the $o$-phase, the distinct peaks are well reproduced, and they merge to form two broad peaks in $t$-phase; in the $c$-phase, a broad spectral continuum emerges and be-

![FIG. 1. Experimental and theoretical low-frequency Raman spectra showing anharmonicity driving structural phase transitions in MAPI.](image-url)
FIG. 2. Mode trajectory analysis for MAPI. Dynamics of PbI$_6$ octahedra and MA molecular motions for (a) Orthorhombic (b) Tetragonal and (c) Cubic phases. The top panel illustrates the unlocking of PbI$_6$ octahedra and MA molecule. In the o-phase, the cage motions are restrained by H-bonds. The o-t-phase transition occurs when the H-bond break, leading to relaxational rotations of the cage along certain directions (shown by circular arrows). In the c-phase, all-axes PbI$_6$ rotations are activated. The middle panel shows the projections of frequency-filtered MD for the three phases. Due to the breaking of H-bonds between the MA molecules and the PbI$_6$ octahedra, the o-phase (a), low-frequency peaks of the octahedra rotational motion are replaced by a broad central feature in the t-phase (b). The weight of this central feature further increases in the c-phase (c), indicating that relaxational motion dominates all other types of motions. The lower panels: Statistics of molecular orientations in the three phases. $\phi$ is the azimuthal and $\theta$ is the polar angle. The molecule is allowed to visit more orientations when it goes from o- to t-phase, indicating the onset of the molecular disorder. The molecular orientations become completely random in the c-phase.

In light of the close agreement between experimental and theoretical Raman spectra, we examine the MD trajectories by resolving the specific ionic motions contributing to low-frequency Raman scattering (See Methods). We define the specific ionic motions as stretching, distortion and translational modes as shown in the SI (Figs. S3, S4, S5). MD trajectories filtered for a narrow frequency window are then projected onto these predefined modes in order to construct a spectrally-resolved decomposition of the ionic motions. The weight of each mode as a function of frequency is displayed in Fig. 2 (middle panel). For all three phases, only octahedral distortions and rotations are dominant in the frequency region below 50 cm$^{-1}$. For the o-phase shown in Fig. 2(a), two distinct peaks corresponding PbI$_6$ rotational vibrations are found and an ultra-low-frequency, octahedral rotational motion (5 cm$^{-1}$) is also present. Across the o-t-phase transition, PbI$_6$ rotations (red) change dramatically. The well-resolved features of the o-phase are replaced by a dominant broad feature that is centered around 0 cm$^{-1}$ (i.e. central peak) in the t- and c-phases. This indicates that the harmonic PbI$_6$ vibrations of the o-phase have evolved to relaxational rotations in the t-phase. The weight of this relaxational motion keeps increasing with temperature, and in the c-phase (Fig. 2(c)), it dominates all other types of motions.

The abrupt change in Raman spectra at the o-t-phase...
FIG. 3. Temperature evolution of PO-dependent Raman spectra of MAPI. Contour plots for PO dependence of the Raman spectra of MAPI in parallel configuration for (a) 200 K (tetragonal), (b) 300 K (tetragonal), and (c) 360 K (cubic). The 0° polarization angle is arbitrarily defined and is identical for all measurements. Cross-sections of the contours corresponding to the angular positions (shown by dotted blue and red lines) are also shown above each contour plot (blue and red curves). Strong polarization angle-dependent modulations of the Raman intensity are observed, with dual maxima (180° period) in the tetragonal phase (200 K and 300 K). Intensity modulation shows a 90° period in the c-phase. The PO-dependent measurements reveal an additional spectral feature P2 at ≈ 30 cm$^{-1}$ in the t-phase (blue dashed line indicates angle of maximum intensity of this mode). P2 is hidden in unpolarized Raman due to thermal broadening and modes at the same frequency with different angular dependence. This feature exhibits strong damping and an increase in relative intensity with temperature compared to the features P1 (≈ 28 cm$^{-1}$) and P4 (≈ 45 cm$^{-1}$) in the red curves. The modes giving rise to specific features are shown in the SI. P4 is mostly represented a symmetric distortion in xy plane. Similarly, the hidden feature (P2) is attributed to two equivalently symmetric distortions in different planes (xz, and yz planes).

...transition can be understood on the basis of the interactions between the lattice and the MA molecules. As described in previous works, hydrogen bonding (H-bonds) provides an effective chemical interaction between MA$^+$ cations and the negatively charged [PbI$_3$]$^-$ cages. At low temperatures, the PbI$_6$ cage does not have enough thermal kinetic energy to overcome the H-bonding interactions, and thus PbI$_6$ rotation is vibrational. In other words, the H-bonds provide restoring force to the rotational motion of the PbI$_6$ octahedra. Similarly, the movement of the MA molecule, either translation or rotation, is also restrained by the H-bonds. At higher temperatures, increased PbI$_6$ rotational energy allows the octahedra to break the H-bonding and freeing the movement of the MA molecules. This decoupling between organic cations and inorganic framework enables larger-amplitude motion of both. As a consequence, as can be seen in Fig. 2, the MA molecules are allowed to visit more orientations in t-phase. The weight of the MA translation motion below 50 cm$^{-1}$ also increases in t-phase compared to o-phase (Fig. S4). This “unlocking” phenomenon between molecule and lattice is an important source of anharmonicity in MAPI, in addition to the regular thermal anharmonicity from system-bath interaction. Thus the o-t-phase transition marks the onset of orientational disorder of MA$^+$ ion. We present a cartoon of the octahedral cage for each phase in the top panel of Fig. 3 to illustrate this special “unlocking” phenomenon. It is worth mentioning that this unlocking picture is no longer valid for all-inorganic HPs since there is no H-bond and therefore the change in Raman spectrum at o-t-phase transition is not abrupt but continuous.

Polarization-Orientation Raman of the tetragonal and cubic phase

Having discussed structural rearrangements at the o-t-phase transition, we now turn to investigate the structural dynamics of the t- and o-phases. To that end, we use temperature-dependent, PO Raman spectroscopy (Fig. 3). The details of the experiment are discussed in the methods section. Briefly, the crystal oriented along the [110] direction is excited by plane-polarized laser light having polarization $e_i$. The scattered light is then filtered by another polarizer (analyzer) for polarizations parallel and perpendicular to the incident light. This measurement is repeated after an incremental rotation of the polarization of the incident light.

Figure 3 shows the angular dependence of polarized
Raman spectra for measurements performed at 200 K, 300 K, and 360 K in parallel configuration. It is worth mentioning that the data in Fig. 3 are presented in their raw form without any normalization or baseline correction and the results are completely reversible with temperature. The contour plots show a periodic modulation of the intensities of all the Raman peaks with polarization angle. The data for cross configuration is given in the SI, Fig. S6. The strong and periodic oscillations in intensity are indicative of the long range order of the crystal. In harmonic crystals, the combination of parallel and perpendicular data sets enables the extraction of the symmetry of each observed mode.\cite{37,38} However, since the $t$-and $c$-phases of MAPI are strongly anharmonic, the interpretation of the data is more complex.

Notably, for the $t$-phase (Fig. 3a and b), the low-frequency ($<50$ cm$^{-1}$) spectra show modulation of 180° in the PO dependence resulting in two distinct line shapes at 50° and 140° PO angles, denoted by blue and red dotted lines, respectively in Fig. 3. In contrast, the $c$-phase shows a 90° periodicity and both the axes exhibit the same line shape.

The presence of two distinct line shapes in the low-frequency PO Raman of the $t$-phase reflects the anisotropy of the crystal structure.\cite{29} The line shapes have been deconvoluted by fitting the spectra iteratively using a multi-Lorentz oscillator model (details in SI). We identify seven distinct spectral features (labeled as P1-P7). The corresponding widths and positions extracted from the fits are given in Table S1 in SI. In Fig. 3a, we observe that all the spectral features of the 140° lineshape appear in the unpolarized spectrum also (Fig. 1). But the $\approx 30$ cm$^{-1}$ feature (P2, blue curve) appears only at specific angles (50° and 230°). In that sense, it is a hidden feature. With the help of frequency-filtered 200 K MD trajectories, we could assign this feature as a symmetric distortion in the pseudo-cubic $xz$ and $yz$ plane, while the peak P4 is a symmetric distortion in the $xy$ plane, as shown in SI (Fig. S11). Both P2 and P4 reflect the same distortion patterns but in different planes. The comparison between PO data at 200 K (Fig. 3i) and 300 K (Fig. 3j), shows a rapid increase in the relative intensity of P2 with temperature as compared to the features P1 and P4. This suggests a gradual change in structure from the anisotropic $t$-phase towards the isotropic $c$-phase. Remarkably, P2 broadens much more strongly with temperature than P1 and P4 in the similar temperature range (See SI, Table S1). This indicates strong damping of the distortion in the pseudo-cubic $xz$ and $yz$ plane and resembles a soft mode that leads to the phase transition.\cite{28} It becomes completely overdamped when the $t$-$c$-phase transition occurs.

At 300 K, after the $t$-$c$-phase transition is completed, the line shape at the two polarization angles (Fig. 3i) is identical to the line shape of the unpolarized data (Fig. 1). This, in addition to the 90° periodicity in the intensity of both parallel and perpendicular configurations, indicates that the crystal structure is indeed isotropic and cubic on average. However, as discussed earlier, the strong Raman activity indicates that there is a strong dynamic symmetry breaking. According to our fitted line width (See SI), the lifetime of the Lorentz oscillator (P4) becomes extremely short ($\approx 160$ fs) in the cubic phase, which is at least two orders of magnitude less than the lifetime of the standard optical phonon of crystalline silicon.\cite{23} Using the average phonon group velocities reported elsewhere,\cite{23,23} we found that our calculated phonon mean free path is of the order of the cubic MAPI lattice constant ($\approx 7$ Å).\cite{23} This suggests that the standard phonon picture cannot describe the structural dynamics of the crystal.

**Real-space PbI$_6$ rotational motion for $t$-and $c$-phases**

To explain the observed spectral features and to investigate their correlation with the lattice motions at the $t$-$c$-phase transition, we go back to the frequency-filtered MD trajectories. The low-frequency relaxational motion ($\approx 1$ cm$^{-1}$) is further decomposed into four different PbI$_6$ rotations (Fig. S9 and S10 in SI). The rotational motions are separated according to the rotation axis and relative direction. For example, $z$-out means the out-of-phase PbI$_6$ rotation along $z$ axis. Figures 4a-d show the amplitude of the dynamic rotation for different phases, and Table S2 tabulates the equilibrium octahedral tilting angle. Large amplitude rotations are indicative of strongly anharmonic, relaxational motions while a small amplitude is indicative of harmonic, vibrational motion. For the $t$-phase, a large equilibrium tilting angle about the $z$-axis shows that the system is heavily tilted along the $z$ direction, but the amplitude of the dynamic rotation around the $z$-axis is small. In contrast, the equilibrium angles about the pseudo-cubic $x$ and $y$-axis are small, but their corresponding rotation amplitudes are quite significant, revealing strong dynamic processes occur along these two directions. The amplitudes grow even larger as temperature increases from 200 K to 300 K. This indicates that the averaged structures for 200 K and 300 K are indeed tetragonal, and the relaxational rotation happens only around the two short axes of the tetragonal cell. The relaxational PbI$_6$ rotations around the pseudo-cubic $y$ axis and $x$ axis effectively change the local environment of each octahedron in the pseudo-cubic $xz$ and $yz$ plane, respectively, thus damping the restorative motion in these two planes (the feature P2 in Fig. 3). The vibrational motion is further dampened with a larger PbI$_6$ rotation amplitude from 200 K to 300 K. Since in the $t$-phase the amplitude of rotation around the $z$-axis is small, the distortion in the $xy$ plane is not altered and thus the corresponding peak P4 remains sharp and distinct in this range of temperature. In the $c$-phase (Fig. 4i), however, PbI$_6$ rotations along all three axes are activated, and the equilibrated octahedral tilting angles for all three axes are close to zero (a$'a'$a$'$). Interestingly, there is a temporal phase shift between the three out-of-phase rotations (see
FIG. 4. Real-space PbI$_6$ rotational motion for $t$-and $c$-phases. (a) Illustrations of real-space PbI$_6$ rotation motions. (b-d) Time evolution of real-space PbI$_6$ rotation motions for $t$-phase at 200 K (b), 300 K (c) and $c$-phase (d). The legend here represents rotation axis and the relative rotation direction. For example, ‘$x$-out’ represents the out-of-phase rotation along the $x$ axis, and ‘$z$-in’ represents the in-phase rotation along $z$-axis. They are obtained from MD trajectories frequency-filtered to 1 cm$^{-1}$. The black dashed lines represent the equilibrium tilting angle of octahedron. In $t$-phase, ‘$x$-out’ and ‘$y$-out’ rotations have the largest weights, whereas the ‘$z$-in’ and ‘$z$-out’ rotations have negligible amplitudes. In the $c$-phase, all the PbI$_6$ rotation motions are activated, and the equilibrium tilting angle is small for all the three axes.

SI, Fig. S9), meaning that at one time, the significant rotation occurs only about one axis while for the other two axes, rotational amplitudes are quite small. This leads to instantaneous $t$-phase structures formed along different directions. Thus, along with the identification from PO Raman shown in Fig. 3c, AIMD also confirms that the cubic phase we observe is indeed the dynamical sampling of the low symmetry phases along different orientations. This slow dynamical symmetry breaking process leads to the occurrence of Raman activity in the $c$-phase violating group theory predictions. The residual feature at $\approx 45$ cm$^{-1}$ (Fig. 3c) remains due to the dynamic symmetry breaking. We hypothesize that this feature is a degenerate combination of P2 and P4 from the $t$-phase. The turning-on of the $z$-out relaxational rotation strongly damps the motion of this mode resulting in its drastic broadening. The all axis rotational relaxation also explains the transition from 180° to 90° intensity modulation in PO Raman in the parallel configuration (Fig. 3b and c), since all three directions are now degenerate. Therefore, apart from the abrupt structural rearrangements at the $o$-$t$-phase transition, the all-axes PbI$_6$ relaxational rotation is another important source of anharmonicity that increases continuously with temperature. Importantly, our analysis clearly reflects the highly anharmonic behavior of the $t$-phase. This contradicts the 0 K phonon dispersion computations which do not display negative frequencies.$^{[7][11]}$

| Phase          | Equilibrium octahedral tilting angle |
|----------------|-------------------------------------|
|                | $x$  | $y$  | $z$  |
| Tetragonal (200 K) | 3.65 | 2.18 | 24.66 |
| Tetragonal (300 K) | 7.55 | 4.49 | 24.20 |
| Cubic          | 4.94 | 1.66 | 2.96  |

In conclusion, we elucidate the detailed mechanisms of the strongly anharmonic structural dynamics of MAPI. We show how the atomic motion and phase sequence is dominated by temperature-activated relaxational motion of the PbI$_6$ octahedra and MA molecules. Furthermore, we identify two distinct mechanisms that lead to this relaxational motion. The first is an abrupt unlocking of the H-bonds at the $o$-$t$-phase transition that enables the rotation of MA molecules in PbI$_6$ cages leading to large amplitude anharmonic motions. The second is the continuous overdamping of the PbI$_6$ rotational modes throughout the $t$-and $c$-phases. This also explains the liquid-like
relaxational behavior and reflects the breakdown of the phonon picture in HPs.

METHODS

Experimental methods

High quality, MAPI single crystals were grown at room temperature using the Anti-solvent method as discussed elsewhere. The crystallographic orientation the crystal was determined using powder X-ray diffraction (XRD) (See SI, Fig. S1). Raman experiments were performed on the same face for which XRD was obtained.

Low frequency micro-Raman scattering measurements were performed in a customized set-up fitted with a confocal microscope and optical cryostat (Janis, USA) evacuated to $10^{-5}$ Torr. 1064 nm line from an Nd:YAG laser was guided into a x50/0.42 NA, C-coated IR objective, using a 90/10 volume holographic grating (VHG) beam splitter (Ondax Inc., USA) in a backscattered configuration. The polarization of the beam was maintained using fixed Glan-Laser polarizers in the incident and scattered beam path. A motorized $\lambda/2$ wave plate controls the direction light polarization of with respect to the sample. An achromatic $\lambda/2$ wave plate rotates $0^\circ$ or $45^\circ$ relative to the polarizer to filter the scattered radiation parallel or cross-polarization directions. Two 90/10 VHG notch filters (each having OD >4 rejection with a spectral cut off $\pm 7$ cm$^{-1}$ around 1064-nm) discard the Rayleigh-scattered light. The scattered beam is then imaged onto the entrance slit of a 1 m focal length spectograph (Horiba FHR-1000), dispersed by a 950 lines/mm grating onto a liquid N$_2$ cooled InGaAs detector (Symphony II, Horiba).

Computational methods

We employ the autocorrelation function approach to compute Raman activities where we relate the Raman spectral weight at frequency $\omega_0$ to the dynamical autocorrelations of the polarizability tensor. The polarization of the beam can be computed as:

$$I_{ij} \propto \omega_0^2 \int \langle \alpha_{ij}(\tau) \alpha_{ij}(t+\tau) \rangle e^{-i\omega_0 \tau} d\tau$$

Here, $i(j)$ represents the polarization component of the incident (scattered) light, $\omega_0$ is the frequency of the phonon mode $\nu$, and $\alpha_{ij}$ is the polarizability tensor. The polarizabilities of selected structures are obtained from the ab-initio molecular dynamics (AIMD) trajectory, and we employ the Wiener-Khintchine’s theorem to calculate the autocorrelation functions. The computation details of running AIMD and getting polarizabilities are summarized in SI.

We calculate frequency-filtered trajectories by first performing a Fourier transform on the real-space MD trajectories from $t$ to $\omega$, and then filter the $\omega$-space trajectories within a frequency window $\Delta \omega$, and finally perform an inverse Fourier transform back to $t$. The whole procedure is expressed as:

$$\tilde{R}_{\text{filtered}}(t;\omega_0) = \mathcal{F}^{-1} \left[ \Theta (\omega - (\omega_0 - \Delta \omega)) \Theta (-\omega + (\omega_0 + \Delta \omega)) \mathcal{F} \left[ \tilde{R}(t) \right] \right]$$

In addition, we establish a basis of modes that can fully describe atomic motions, including Pb-I stretching, PbI$_6$ distortion, PbI$_6$ rotation, Pb off-center motion, and MA molecular translation (we take the molecule as a unit, see SI). We project the frequency-filtered trajectories onto this basis via the following equation:

$$W_{\omega_0} = \frac{1}{N_\tau} \sum_{t} \frac{\tilde{R}_{\text{filtered}}(t;\omega_0) \cdot \tilde{u}}{| \tilde{R}(t;\omega_0) |^2}$$

With the weight $W_{\omega_0}$ of each component, we can tell the specific motions corresponding to the Raman spectral weight at frequency $\omega_0$.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Tsachi Livneh (NRC) for fruitful discussions, Dr. Ishay Feldman (WIS) for performing X-Ray diffraction measurements and Dr. Lior Segev (WIS) for developing the Raman software. R. S. acknowledges FGS-WIS for financial support. O. Y. acknowledge funding from: ISF (1861/17), BSF (grant No. 2016650), ERC (850041 - ANHARMONIC), Benoziyo Endowment Fund, Ilse Katz Institute, Henry Chanoch Krener Institute, Soref New Scientists Start up Fund, Carolito Stiftung, Abraham & Sonia Rochlin Foundation, E. A. Drake and R. Drake and the Perlman Family. Z. D. and L. G. acknowledge support from the US National Science Foundation, under grant DMR-1719353. J. Z. acknowledges support from a VIEST Fellowship at the UPenn. A. M. R. acknowledges support from the Office of Naval Research under Grant N00014-17-1-2574. The authors acknowledge computational support from the High-Performance Computing Modernization Office.

REFERENCES

* These authors contributed equally
\[ \text{rappe@sas.upenn.edu} \]
\[ \text{omer.yaffe@weizmann.ac.il} \]
\[ \text{T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, Nat. Rev. Mater. 1, 15007 (2016)} \]
\[ \text{M. Grätzel, Acc. Chem. Res. 50, 487 (2017)} \]
By process of illumination: Revealing the causes of dramatic anharmonicity in CH$_3$NH$_3$PbI$_3$ with Raman scattering

Rituraj Sharma$^1$, Zhenbang Dai$^2$, Lingyuan Gao$^2$, Thomas M. Brenner$^1$, Lena Yadgarov$^1$, Jiahao Zhang$^2$, Yevgeny Rakita$^1$, Roman Korobko$^1$, Andrew M. Rappe$^2$, Omer Yaffe$^1$

$^1$Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel
$^2$Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

SUPPORTING INFORMATION

1. Computation details:

We perform Born-Oppenheimer AIMD with the Quantum-ESPRESSO code. A $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing four formula units of MAPI is chosen. We use the PBE31 functional and the Tkatchenko-Scheffler scheme for dispersive interactions. A $3 \times 3 \times 2$ k-point grid is used, and the plane-wave cutoff energy is 50 Ry. The DFT total energy is converged to $10^{-7}$ Ry/cell. Spin-orbit coupling is not taken into account, as it does not affect the structural properties of lead-halide perovskites. To compare with experiments, AIMD on MAPI was performed at 77 K, 200 K, 300 K, and 500 K, corresponding to orthorhombic, tetragonal, and cubic phases. We choose 500 K for the simulation of cubic phase to make it more distinguishable from the tetragonal phase. This temperature is well above the transition temperature, and the perovskite structure can be maintained well in our AIMD simulation. The time step of AIMD is 1 fs, and we equilibrate the systems with a velocity-rescaling thermostat (rescale every 10 steps) for 10 ps. We run another 30 ps to obtain a converged autocorrelation function. To obtain the Raman spectra, density functional perturbation theory (DFPT) with a denser $6 \times 6 \times 4$ k-point grid is used to calculate the polarizability at a time interval of 100 fs.

2. Fitting Procedure

We have used the imaginary part of the damped Lorentz oscillator model to simulate the Raman scattering data. The experimentally measured Raman scattering spectrum is expressed as eq. S1

$$I_{\text{exp}}(\nu, \nu_i, \Gamma_i) = c_{BE}(\nu) \left( \sum_{i=1}^{n} c_i \frac{|\nu| \nu_i |\Gamma_i|^2}{\nu^2 + (\nu^2 - \nu_i^2)^2} \right)$$

where $\nu$ is the spectral shift, $\nu_i$ and $\Gamma_i$ are respectively the resonance energy and damping coefficient of the Lorentz oscillators and $c_i$ are unitless fitting parameters for the intensities of the Lorentz oscillator components. The spectral shift $\nu$, the parameters $\nu_i$ and $\Gamma_i$ are in wavenumber units. The approximate lifetime of the phonons can be calculated as $\tau = \frac{1}{2 \pi c \Gamma_i}$, where $c$ is the speed of light. The prefactor $c_{BE}(\nu)$ accounts for the thermal population from the Bose-Einstein distribution. The Stokes signal is proportional to $1+n$, and the anti-Stokes signal is proportional to $n$, with $n$ being the Bose-Einstein distribution. The Bose-Einstein prefactor is written as eq. S2

$$c_{BE}(\nu) = \begin{cases} n + 1 & \nu_0 \geq 0, \\ n & \nu_0 < 0. \end{cases}$$

We remove the spectral artifacts from the notch filter around 0 cm$^{-1}$, and fitted the Stokes scattering with equation S1 using fitting parameters $c_i$; $\nu_i$ and $\Gamma_i$. Numerical fitting was carried out in the customized MATLAB code and Igor Pro 8.

To fit the parallel polarization orientation (PO) data of the tetragonal phase, we have identified seven peaks. Peaks P1 and P4 appear only angle 140° and P2 appears only at 50°. Peaks P3, P5, P6 and P7 remain common for all PO angles. The data at both 50° and 140° angles are separately fitted to find the positions and widths of the peaks. Thereafter, the obtained parameters were fixed to fit the entire PO dependence, keeping only the intensity of modes ($c_i$) as variable. To fit the higher temperature, cubic data, the Raman modes are further softened and damped to produce a good overall fit containing the central peak. Then the same technique was applied to fitting the intensities of the PO as in the tetragonal phase. The same parameters for all the seven peaks were fixed to fit the cross data. The calculated $\Gamma_i$ values were used to calculated the lifetime of the Raman modes.
TABLE S1. **Fit position and width parameters from fits to the polarization dependent Raman data sets for each temperature measured.** These parameters were held constant for all polarization angles and both analyzer configurations, except for P2, which is only present in the parallel configuration.

| Peak label | $\omega$ (cm$^{-1}$) | $\Gamma$ (cm$^{-1}$) | $\omega$ (cm$^{-1}$) | $\Gamma$ (cm$^{-1}$) | $\omega$ (cm$^{-1}$) | $\Gamma$ (cm$^{-1}$) |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| P1         | 30.0            | 15.0            | 25.0            | 18.0            | 23.0            | 24.0            |
| P2         | 37.5            | 25.8            | 36.0            | 39.0            | -               | -               |
| P3         | 39.5            | 13.4            | 38.5            | 34.5            | -               | -               |
| P4         | 45.8            | 5.1             | 44.1            | 7.5             | 44.0            | 33.0            |
| P5         | 67.5            | 26.9            | 64.3            | 38.0            | 64.0            | 40.0            |
| P6         | 92.7            | 33.6            | 99.0            | 44.0            | 100.0           | 45.0            |
| P7         | 127.9           | 48.2            | 131.0           | 56.0            | 132.5           | 56.2            |
FIG. S1. Room temperature XRD of MAPI single crystals.
FIG. S2. Raman spectra acquired near the orthorhombic-tetragonal phase transition.
FIG. S3. Complete definition lattice modes. The preliminary classifications shown in the legend of Figure 2 are as follow: mode 1, 2, 3, and 4 belong to “Rotation”, mode 5-30 belong to “Distortion”, and mode 31, 32, 33, 34, 35, and 36 belong to “Stretching”. Here, we can see that mode 27 and 28 are equivalent, and they have the same distortion pattern as mode 30.
FIG. S4. Mode projection for molecular translations along different directions for 77 K (a), 300 K (b) and 500 K (c). (d) Summation of projections below 50 cm\(^{-1}\) for different temperatures. It can be seen that at 77 K, the molecular translation for the low-frequency range (0 - 50 cm\(^{-1}\)) in every direction has the lowest weight because of the “locking” of hydrogen bond formed between MA and \([\text{PbI}_6]\) lattice. At tetragonal phase (300 K), this coupling is “unlocked” such that the weight of molecular translation increases. In cubic phase (500 K), since \(\text{PbI}_6\) rotation totally dominates the low-frequency range, the relative weight of overall molecular translation has a slightly decrease. But we also notice the consistent increase in y axis from t- to c-phase. This is because lattice constant is the shortest in tetragonal phase for pseudo-cubic cell (not the simulation cell), which sterically restrict its motion at tetragonal phase. When transitioning into cubic phase, all the three axes are equivalent so that the weight of y axis can continue increasing.

FIG. S5. Illustration of the 4 MA molecular translation modes (H atoms are omitted for clarity). Similar patterns can be defined for other directions.
FIG. S6. Temperature evolution of PO dependent Raman spectra of MAPI. Contour plots for PO dependence of the Raman spectra of MAPI in cross configuration for (a) 200 K, (b) 300 K and (c) 360 K. The 0° polarization angle is arbitrarily defined and is identical for all measurements. Cross sections of the contours corresponding to the angular positions shown by dotted lines are also shown at the top of each contour. Strong polarization angle dependent modulation of the Raman intensity is observed with 90° period.

FIG. S7. Fitting of tetragonal phase Raman spectra using a multi Lorentz oscillator. Left and right panels show seven Lorentz fits to the experimental data at temperatures 200 K and 300 K using equation S1.
FIG. S8. Fitting of cubic phase Raman spectra using multi Lorentz oscillator at 360 K using equation S1.

FIG. S9. The fluctuation of the square of PbI$_6$ rotation in a randomly selected time domain. All the equilibrium tilting angles have been subtracted for clarity. We can see that there is a temporal phase shift between the three out-of-phase rotations, meaning that at one time, the significant rotation occurs only along one axis while for the other two axes, rotational amplitudes are quite small. This leads to instantaneous, tetragonal structures formed along different directions, and it shows what we observe as cubic phase is indeed the dynamical sampling of t-phase along different orientations.
FIG. S10. Illustration of the possible PbI$_6$ rotation modes in our simulated supercell. In general, PbI$_6$ rotation can happen along x, y, and z axis, and between two layers, the rotation can be either in-phase or out-of-phase. However, due to the size limitation of our simulated cell, only out-of-phase rotation can happen along the pseudo-cubic x and y axis, whereas both in-phase and out-of-phase rotation can occur along z axis. The possible two types of rotation about z axis can be understood easily since there are two independent layers along z-axis for our supercell. However, for the pseudo-cubic x and y axis, which are the diagonals for a $\sqrt{2} \times \sqrt{2} \times 2$ supercell, the two-layers are interrelated. For example, A and B iodine atoms shown here are the images of each other. If atom A moves downward (-z), the B also has to move downward (-z). The similar argument can apply to other iodine atoms involved in a PbI$_6$ rotation mode. Thus, we can see that the only possible PbI$_6$ rotation mode along pseudo-cubic x and y axis is out-of-phase rotation.

FIG. S11. Assignment of low frequency peaks in PO measurement. The frequency window is 0.5cm$^{-1}$ in order to distinguish the closely lying peaks. The peak at $\approx 45$ cm$^{-1}$ (P4) is mostly represented by mode 30, which is a symmetric distortion mode in xy plane. The hidden mode at $\approx 30$ cm$^{-1}$ (P2), is mostly represented by mode 27 and mode 28, which are two equivalently symmetric distortions in different planes (pseudocubic xz, and yz planes). The distortion patterns of both the peaks are the same but in different planes. For the peak at $\approx 28$ cm$^{-1}$ (P1), we can see that the motions are even more convoluted, so it’s hard to identify a specific motion for it. However, if we look at the modes 5-16 which have relative large weight, we can find that they all fall into the same pattern where each octahedron is shrinking on one side and expanding on the other side, so these kinds of asymmetric distortion could contribute to P2. On the other hand, we also notice that modes 17-20 are of large weight, and their motions can be classified as PbI$_6$ rotation for two octahedrons and symmetric distortion for the other two octahedrons in the supercell. Therefore, this kind of motion could be another source.