

Raman Spectrum of the Organic-Inorganic Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ from First Principles and High-resolution Low-temperature Raman Measurements

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Abstract

We investigate the Raman spectrum of the low-temperature orthorhombic phase of the organic-inorganic halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, by combining first-principles calculations with high-resolution low-temperature Raman measurements. We find good agreement between theory and experiment, and successfully assign each of the Raman peaks to the underlying vibrational modes. In the low-frequency spectral range (below 60 cm^{-1}) we assign the prominent Raman signals at 26, 32, 42 and 49 cm^{-1} to the Pb-I-Pb bending modes with either A_g or B_{2g} symmetry, and the signal at 58 cm^{-1} to the librational mode of the organic cation. Owing to their significant intensity, we propose that these peaks can serve as clear markers of the vibrations of the $[\text{PbI}_3]^-$ network and of the CH_3NH_3^+ cations in this perovskite, respectively. In particular, the ratios of the intensities of these peaks might be used to monitor possible deviations from the ideal stoichiometry of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

1 Introduction

Organic-inorganic lead halide perovskites have emerged as promising new materials for high-performance photovoltaics, enabling solution-processable solar cells with certified power conversion efficiency in excess of 22%.¹⁻⁵ The prototypical halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, abbreviated as MAPbI_3 hereafter, exhibits three polymorphs as a function of temperature.⁶⁻⁸ It crystallizes in an orthorhombic $Pnma$ structure below 162.2 K; between 162.2 and 327.4 K it adopts an $I4/mcm$ tetragonal structure; above 327.4K the system stabilizes in a cubic $Pm\bar{3}m$ structure. MAPbI_3 exhibits a direct band gap of 1.6 eV, and a high absorption coefficient across the visible spectrum.^{9,10} The charge carriers exhibit low effective masses, resulting in relatively high mobilities for solution-processable materials, around $50\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.¹¹⁻¹³ The recombination rate of the carriers is also very low, leading to very long diffusion lengths in the micron scale.¹¹

The vibrational properties of MAPbI_3 and its related compounds have been the subject of

numerous investigations,¹⁴⁻¹⁹ as they underpin electron-phonon interactions,^{11,20,21} dielectric screening,²² heat transport, and elastic properties.²³⁻²⁶ In particular, Raman spectroscopy can be used to identify the symmetry of lattice vibrations,^{27,28} to investigate the temperature and pressure phase diagrams of these systems,²⁹⁻³¹ their degree of crystallinity,³² as well as monitor structural changes in mixed halide perovskites.¹⁷ Raman spectroscopy can also be employed to monitor the stability of halide perovskites during their operation in solar cells.³³ These possibilities provide strong incentives for a detailed characterization of the Raman peaks in these systems.

First-principles calculations along with experiments have shown that the lattice vibrations of MAPbI₃ can be classified into three distinct groups: internal vibrations of the organic MA cations, with frequencies ranging between 300 and 3200 cm⁻¹; libration and spinning modes of these cations, with frequencies in the range 60-180 cm⁻¹; and internal vibrations of the inorganic PbI₃ network, with frequencies below 120 cm⁻¹.^{16,18,34} The character and symmetry of these vibrational modes have been analyzed in detail in Ref. 34. In the same work a large LO-TO splitting of 50 cm⁻¹ was predicted for one of the low-frequency Pb-I stretching modes, and this splitting was confirmed by subsequent experiments.^{20,35}

The Raman and infrared (IR) spectra of MAPbI₃ have been measured by several groups.^{16-19,34-36} In most of the IR experiments the degradation of MAPbI₃ was avoided by keeping the samples protected from moisture. In the case of Raman measurements the experiment is more challenging since the perovskite may also degrade as a result of the thermal stress induced by the laser beam if above-gap excitation is used.^{17,37} The degradation products, such as PbI₂ and MAI, typically yield additional Raman peaks which complicate the spectral assignment.¹⁷ Measuring the Raman spectrum of the low-temperature orthorhombic phase of MAPbI₃ presents an additional experimental challenge of operation at cryogenic temperatures. To the best of our knowledge there is only one reported Raman spectrum of orthorhombic MAPbI₃.^{18,38} The Raman spectrum of the orthorhombic phase of MAPbI₃ was also studied via first-principles calculations, and the results are in good agreement with

experiments.^{16,18,38,39} However, a detailed assignment of each individual peak, including their character and symmetry properties, has not yet been reported.

In order to fill this gap, here we investigate the Raman spectrum of MAPbI₃ in its low-temperature orthorhombic phase. We combine first-principles density-functional perturbation theory calculations in conjunction with high-resolution low-temperature Raman measurements on single crystals. We measure the Raman spectrum of MAPbI₃ at several temperatures from liquid-helium temperature (4 K) up to 150 K, in the spectral range up to 120 cm⁻¹. By comparing our calculated spectrum with these data we succeed in assigning each observed Raman peak. We characterize the peaks using the procedure described in Ref. 34, where the symmetry of each mode was determined via a factor group analysis. In addition we explore the effects of van der Waals (vdW) forces, spin-orbit coupling (SOC), and lattice anharmonicity.

The manuscript is organized as follows: in Sec. 2 we describe the experimental methods and the computational setup. In Sec. 3 we discuss the calculated Raman spectrum of MAPbI₃ and the factor group analysis of the vibrational modes. In this section we also study the sensitivity of the calculated Raman spectrum to vdW interactions, SOC, and anharmonic effects. In Sec. 4 we discuss the measured low-temperature Raman spectrum of MAPbI₃, and in Sec. 5 we compare theory and experiment. In Sec. 6 we summarize our work and offer our concluding remarks.

2 Methods

2.1 Single-crystal preparation and Raman measurements

CH₃NH₃PbI₃ perovskite single crystals were prepared via inverse temperature crystallization.⁴⁰ Typically, 1.3 M CH₃NH₃PbI₃ precursor was prepared by adding 2.3 g lead iodide (PbI₂) and 0.8 g methylammonium iodide (MAI) into 3.85 mL γ -butyrolactone (GBL), heated at 90°C for 2 h with stirring. Then the precursor solution was filtered with syringe

filters (0.22 μm pore size) and transferred to clean containers, which were kept on a stable hot-plate and heated at 130°C for 3 h. Crystals were formed in the bottom of the containers. Finally, the crystals were collected and dried at 60°C in a glovebox for 2 h (see Figure 1).

Raman scattering was excited and collected through a microscope objective, sampling a spot of the order 10^{-6}m diameter, on the surface of a bulk crystal mounted in a coldfinger cryostat. Temperatures quoted relate to the measured coldfinger temperature, and any unshielded thermal radiation will increase the temperature of the surface of the sample measured by the Raman experiment; the more significantly the lower the temperature. To minimise this (unquantified) problem, a ring of oxygen-free high-conductivity (OFHC) copper was lowered on to the top of the sample, bonded to it with a thin layer of vacuum grease. The OFHC copper ring was itself thermally anchored to the coldfinger with copper braid. Raman scattering was conducted in the hole in the centre of the ring. The sample was illuminated with light from a CW Ti:sapphire laser, cleaned by passing it through a diffraction-grating based tunable filter and then linearly polarised using a Glan-Thompson prism. The laser wavelength (830 nm) was chosen to ensure that the photon energy fell below the bandgap of $\text{CH}_3\text{NH}_3\text{PbI}_3$, thereby minimizing material degradation and background photoluminescence signals. The Raman scattered light was also resolved in linear polarisation by a Glan-Thompson prism, dispersed in a triple-grating spectrometer and detected on a silicon CCD.

2.2 Computational setup

We study the normal modes of vibrations in the low-temperature *Pnma* orthorhombic phase of MAPbI_3 . The crystal structure was resolved both by neutron and X-ray diffraction experiments.^{6,7} In this structure the MA cations are fully ordered, therefore the system can be studied using the same computational techniques as for crystalline solids. We calculate structural properties using density functional theory (DFT), and vibrational properties using density functional perturbation theory (DFPT), as implemented in the planewaves

pseudopotential package Quantum ESPRESSO.⁴¹ In a previous work by some of us,⁴² we showed that the two most popular approximations to the exchange-correlation functional, the generalized-gradient approximation of Perdew, Burke and Ernzerhof (PBE),⁴³ and the local density approximation (LDA),⁴⁴ work remarkably well in describing the vibrational properties of MAPbI₃. Based on these findings, here we proceed with the LDA exchange and correlation. The core-valence electron interaction is described by means of norm-conserving pseudopotentials, including 5d semicore states for Pb.⁴⁵ The wavefunctions are represented by planewaves basis sets with a kinetic energy cutoff of 100 Ry, and the Brillouin zone is sampled using a $4 \times 4 \times 4$ Monkhorst-Pack grid. The orthorhombic unit cell of MAPbI₃ is optimized starting from the experimental lattice parameters reported in Ref.⁶. The vibrational eigenmodes and frequencies are computed at the Γ point.

Within the Placzek approximation, the non-resonant Raman intensity I^k of a vibrational mode k with frequency ω_k is given by:²⁷

$$I^k \propto \frac{1}{\omega_k} |\mathbf{e}_i \cdot \bar{\alpha}^k \cdot \mathbf{e}_s|^2, \quad (1)$$

where \mathbf{e}_i and \mathbf{e}_s are the polarization vectors of the incoming and scattered photons, respectively. $\bar{\alpha}^k$ is the Raman tensor associated with this mode, and its components α_{ij}^k in Cartesian coordinates are given by:⁴⁶

$$\alpha_{ij}^k = \frac{\sqrt{\Omega}}{4\pi} \sum_{I,m} \chi_{ij,Im}^{(1)} \frac{v_{k,Im}}{\sqrt{M_I}}. \quad (2)$$

In this equation Ω is the volume of the unit cell, $\chi_{ij}^{(1)}$ is the first partial derivative of the dielectric polarizability χ_{ij} with respect to the displacement of the atom I along the Cartesian direction m , $v_{k,Im}$ is a normalized vibrational eigenmode, and M_I is the atomic mass. The derivatives $\chi_{ij}^{(1)}$ are evaluated via finite differences.⁴⁶

The non-resonant approximation should be adequate in this case, because the laser energy (830 nm) is more than 100 meV away from the absorption edge. In fact, the width of a

Raman resonance curve is determined by the imaginary part of the energy denominator, in a second-order perturbative approach to the description of the scattering. In a band picture this was investigated in detail many years ago for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and the broadening parameters found to be of the order of a few meV for resonances at the $E_0 + \Delta$ gap.^{47,48} In that work the resonance enhancement has fallen by a substantial factor already at 100 meV from the absorption edge, which is similar to the setup used in this manuscript.

The measured Raman spectra are recorded using the HH (horizontal-horizontal) and HV (horizontal-vertical) polarizations of incident light and analyzer. The total Raman intensity is given by $I = I_{\text{HH}} + I_{\text{HV}}$. We calculate each component by taking the isotropic average over crystal orientations:^{49,50}

$$I_{\text{HH}}^k = \frac{1}{\omega_k} \left(a_k^2 + \frac{4b_k^2}{45} \right), \quad I_{\text{HV}}^k = \frac{1}{\omega_k} \frac{3b_k^2}{45}, \quad (3)$$

where

$$a_k = (\alpha_{11}^k + \alpha_{22}^k + \alpha_{33}^k)/3, \quad (4)$$

$$b_k^2 = [(\alpha_{11}^k - \alpha_{22}^k)^2 + (\alpha_{11}^k - \alpha_{33}^k)^2 + (\alpha_{22}^k - \alpha_{33}^k)^2]/2 + 3[(\alpha_{12}^k)^2 + (\alpha_{13}^k)^2 + (\alpha_{23}^k)^2]. \quad (5)$$

Our choice of taking the isotropic average relates to the fact that we could not establish the precise orientation of the crystal with respect to the light polarization, as samples were found to crack following thermal cycling. While we could not resolve the orientation of the crystal, we determine the Raman activity of the normal modes for several orientations of a single crystal of MAPbI_3 , in backscattering geometry. We achieve this by considering the symmetry of the Raman tensors and Eq. 1. We then confirm our predictions by explicitly calculating the Raman spectra for the different backscattering configurations here considered. Our results are presented in Appendix A. In order to investigate the sensitivity of the Raman spectrum to vdW interactions, SOC, and anharmonicity, we correct the vibrational frequencies using the data of our previous work Ref. 42, and we recompute the spectra in each case. We do not correct the eigenmodes as we have already shown that the variations are very small.⁴²

Since different vdW schemes yield similar corrections to the vibrational eigenfrequencies of MAPbI₃, we here focus on the results obtained via the Grimme-D2 approximation.^{51,52} For completeness, we also recalculate IR intensities, using the same method as in Ref. 34.

3 Results and discussion

3.1 Structure

Figure 2 shows a polyhedron-ball-and-stick model of the optimized orthorhombic crystal structure of MAPbI₃. The primitive unit cell contains 48 atoms: 4 Pb atoms, 12 I atoms and 4 MA cations. The Pb and I atoms form a corner-sharing network of octahedra, with the Pb atoms at the centre of each octahedron, and the I atoms at the corners. The MA cations occupy the cavities formed by the PbI₃ network.

The average of the calculated Pb-I bond lengths, and of the apical and equatorial Pb-I-Pb bond angles are 3.19 Å, 158.7° and 149.5°, respectively. These values compare very well with the corresponding experimental values of 3.18 Å, 161.9° and 150.7°, respectively. The average C-N, C-H, and N-H bond lengths in the MA cations are 1.10, 1.06 and 1.45 Å, respectively. Also these values are in good agreement with the corresponding experimental values of 1.1, 1.0, and 1.57 Å, respectively.

3.2 Normal mode analysis

A visual inspection of the calculated eigendisplacements of MAPbI₃ suggests that they can be classified as vibrations of the MA cations, vibrations of the PbI₃ network, or mixed modes. To clarify the nature of the normal modes on more quantitative ground, we perform a decomposition following the procedure of Ref. 34. In this procedure the normal modes are decomposed into rigid rotations of the PbI₃ octahedra, internal vibrations of the inorganic network, rigid modes of the MA cations (including translation, spinning, and libration), and internal vibrations of the cations. The total as well as the partial density of vibrational

states (vDOS) are shown in Figure 3.

The frequencies of the calculated vibrational modes extend up to 3200 cm^{-1} . We observe that the normal modes with frequencies between 300 and 3100 cm^{-1} correspond to pure internal vibrations of the MA cations. In the low-frequency region, the normal modes with frequencies between 140 and 180 cm^{-1} are combinations of librations and translations of the MA cations. The distinct feature at 130 cm^{-1} is associated primarily with MA spinning around the C-N axis. Between 65 and 120 cm^{-1} , the normal modes are either libration/translation modes of the MA cations, or internal vibrations of the PbI_3 network. In contrast, the normal modes appearing below 65 cm^{-1} are found to be dominated by internal vibration of the PbI_3 network. These results are fully consistent with previous work.^{18,34,39}

3.2.1 Symmetry and character of the normal modes

Since the normal modes of MAPbI_3 can be classified as vibrations of the PbI_3 network or vibrations of the MA cations, we study the symmetry of these two families of normal modes using a separate factor group analysis in each case.⁵³⁻⁵⁵

We start with the normal modes of the PbI_3 network. In this case we consider that orthorhombic MAPbI_3 belongs to the $Pnma$ space group. We identify 48 normal modes as vibrations of the PbI_3 network (3 acoustic and 45 optical modes), consistent with the number of Pb and I atoms in the unit cell. The optical modes admit the following symmetry representations: $\Gamma = 7B_{1u} + 6B_{2u} + 7B_{3u} + 5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g} + 7A_u$. Among these representations, the g type (*gerade*, even) contains inversion symmetry, while the u type (*ungerade*, odd) does not. For each of the normal modes we assign the symmetry by checking their transformation under the symmetry operations of each irreducible representation. The resulting assignment is reported in Table 1. In the same table we indicate the character of each mode in terms of Pb-I stretching, Pb-I-Pb bending, and Pb-I-Pb rocking motion.

In the case of the MA cations we identify 4 spinning modes, 20 normal modes which are combinations of translations and librations, and 72 internal vibrations. If we cumulate the

fractions of libration and translation in each mode we obtain a total of 12 translations and 8 librations, consistent with the fact that there are 4 cations in the unit cell. The calculated frequencies of these modes and their character are reported in Table 2.

By performing a visual inspection of the internal vibrations of the MA cations in MAPbI₃, we note that the individual atomic displacements largely resemble those of isolated MA cations. Furthermore we find that the modes of the MA cations appear grouped in quadruples of nearly-degenerate frequencies. This suggests that, while the vibrations of the four MA cations in MAPbI₃ lead to collective vibrations (e.g in-phase and out of phase modes), the inter-cation coupling is small. Based on this observation we proceed to discussing the symmetry and character of the internal vibrations of MA using the isolated cation as a reference. The internal vibrations of an isolated MA cation admit the following symmetry representations: $A_2 + 5A_1 + 6E$, with the E modes being doubly degenerate. By combining the symmetry and character of these normal modes, they can further be described as symmetric or asymmetric CH₃- and NH₃-deformation modes; symmetric C-N stretching modes; symmetric or asymmetric C-H and N-H stretching modes; and asymmetric CH₃-NH₃ rocking modes. This characterization is reported in Table 3. For clarity we report the average frequency of each quadruple of nearly-degenerate modes.

The symmetry of each normal mode dictates its Raman and IR activity.^{27,34,53,56} In the case of the PbI₃ network, the normal modes with A_g , B_{1g} , B_{2g} , and B_{3g} symmetry are predicted to be Raman active, while those with B_{1u} , B_{2u} , and B_{3u} symmetry are predicted to be IR active. None of the modes is at the same time Raman and IR active, since orthorhombic MAPbI₃ is centrosymmetric.²⁷ The A_u modes are expected to be silent.

In the case of the MA cations, our choice of focusing on the individual molecules does not allow us to predict Raman and IR activity by symmetry. Indeed the prediction of which modes will be active requires the use of the symmetries of the complete structure. This analysis was performed in Ref. 57, where the authors showed that the symmetry of these modes can be described as follows: $\Gamma = 14B_{1u} + 10B_{2u} + 14B_{3u} + 14A_g + 10B_{1g} + 14B_{2g} +$

$10B_{3g} + 10A_u$. As for the PbI_3 network, the u modes will be IR active, the g modes will be Raman active, and the A_u modes will be silent. Since our main focus is the vibrational modes of the PbI_3 network, here we do not repeat the symmetry analysis of Ref. 57, and we simply calculate explicitly the Raman and IR intensities of these modes. The data are reported in Table 3.

3.3 Calculated Raman and IR intensities

The calculated Raman and IR intensities of the normal modes of $MAPbI_3$ are reported in Tables 1, 2 and 3. We first discuss our results for the PbI_3 network (Table 1). We note that the calculated Raman intensity of several normal modes with A_g , B_{1g} , B_{2g} , and B_{3g} symmetry are sizeable, while the IR intensities of the same modes are negligible. Similarly, the modes with B_{1u} , B_{2u} , and B_{3u} symmetry exhibit negligible Raman intensities but nonzero IR intensities. The A_u modes do not exhibit any significant Raman or IR intensity. These calculations confirm our predictions in Sec. 3.2.1. A schematic representation of the modes with the largest Raman intensity is shown in Fig. 4; these modes correspond to Pb-I-Pb rocking motion, Pb-I-Pb bending, and Pb-I stretching, respectively.

The vibrations corresponding to rigid-body motion of the MA cations with the largest Raman intensity are shown in Fig. 5. These modes correspond to spinning and libration of the cations. The corresponding Raman and IR intensities are reported in Table 2. Also in this case we observe that the modes are either Raman or IR active, but not both, in line with the fact that orthorhombic $MAPbI_3$ is centrosymmetric.

Similar considerations apply to the internal vibrations of the MA cations. The calculated Raman and IR intensities of these modes are reported in Table 3, and a schematic representation of the atomic displacements is shown in Fig. 6.

3.4 Calculated Raman spectrum

The calculated Raman spectrum of MAPbI₃ is shown in Fig. 7. Going from high frequency to low frequency, we first encounter an intense Raman peak at 3048 cm⁻¹, which corresponds to N-H stretching modes with molecular symmetry A₁. The small peak on the right, at 3062 cm⁻¹, is assigned to N-H stretching modes with E symmetry, whereas the small peak on the left, at 3046 cm⁻¹, arises from C-H stretching modes with E symmetry. The Raman peak at 2952 cm⁻¹ originates from a C-H stretching mode with A₁ molecular symmetry.

In the central region of the spectrum in Fig. 7, the peak at 1544 cm⁻¹ is assigned to NH₃ deformation modes with *E* symmetry. The peak at 1419 cm⁻¹ is a NH₃ deformation with A₁ molecular symmetry, whereas the shoulder on the left at 1403 cm⁻¹ arises from CH₃ deformations with E symmetry. Proceeding towards lower frequency, the peaks at 1239 and 906 cm⁻¹ are CH₃NH₃ rocking modes with E symmetry, whereas the peak centered at 1029 cm⁻¹ is assigned to C-N stretching modes with A₁ symmetry. At even lower frequency, there is a small peak at 401 cm⁻¹ which is barely discernible in Fig. 7; this feature corresponds to torsional modes of the MA cations. We emphasize that the present symmetry assignment for the internal vibrations of MA relates to the local symmetry of each cation, as opposed to the symmetry of the entire crystal.

In the low frequency region, we find that the peak at 164 cm⁻¹, showing a significant Raman intensity, and the small peak on its left side, at 152 cm⁻¹, correspond both to librational modes of the MA cations. At lower frequencies, the small feature at 125 cm⁻¹ is assigned to spinning modes of the MA cations. Moving to lower frequencies, we find that the peak at 93 cm⁻¹ stems from librational modes of the MA cations and internal vibrations modes of the PbI₃ network, with B_{3g} and A_g symmetry, respectively. The peak at 74 cm⁻¹ primarily corresponds to librational modes of the MA cations, whereas the peaks at 58 cm⁻¹ and 52 cm⁻¹ are assigned to Pb-I-Pb bending modes with B_{2g} and A_g symmetry, respectively. Further down, the peak at 41 cm⁻¹ arises primarily from Pb-I-Pb bending motion with A_g symmetry, but also comprises a component of Pb-I-Pb bending with B_{2g} symmetry. The

remaining peak at 30 cm^{-1} is attributed to Pb-I-Pb rocking modes with A_g symmetry.

3.5 Sensitivity of calculated Raman spectrum to vdW interactions, SOC, and anharmonicity

Before comparing our calculated Raman spectrum with our experimental data in Sec. 5, we investigate the sensitivity of the calculations to the inclusion of vdW interactions, SOC effects, and anharmonicity.

In a recent work by some of us,⁴² we investigated the role of vdW interactions, SOC, and anharmonicity in the vibrational properties of MAPbI_3 . We found that vdW interactions, relativistic effects, and anharmonic corrections have very little impact on the majority of vibrational modes of this perovskite, and only introduce small corrections to the normal-mode frequencies, Born effective charge tensors, dielectric constant, and IR spectrum. However we also found that the spinning modes of the MA cations carry considerable anharmonicity; in fact anharmonic corrections blueshift the frequencies of these modes by as much as 35 cm^{-1} . The anharmonic shift of the spinning modes has no impact on the IR spectrum, since these modes have almost negligible IR intensities.³⁴

Here we assess the impact of these effects on the Raman spectrum by using the frequency shifts determined in Ref. 42. The Raman spectra computed by including the various corrections are shown in Fig. 8. The bottom line (black) is for the un-corrected spectrum calculated using scalar-relativistic LDA; immediately above we have the spectrum with frequencies corrected by vdW interactions (blue); proceeding upwards we have the spectrum with SOC corrections (red), then SOC and vdW combined together (green); and finally the spectrum with anharmonic corrections (brown).

A close comparison of the spectra reported in Fig. 8 indicates that vdW interactions and SOC tend to shift peaks by $\pm 15 \text{ cm}^{-1}$, but we cannot identify any systematic trend. These variations can be considered to lie within the standard DFT error, and are comparable to the changes expected when using different pseudopotentials. These results reinforce the notion

that vdW interactions do not have any significant impact on the vibrational properties of MAPbI₃, and indicate that interaction between the inorganic PbI₃ network and the MA cations is primarily electrostatic in nature.^{39,42,58,59} Anharmonic corrections lead to similarly small corrections to the frequencies, with the only exception being the spinning modes of MA. The Raman signal of these modes blueshifts from 126 cm⁻¹ to 162 cm⁻¹ (Fig. 8), but the Raman intensity is so small that the effect is barely noticeable.

4 Measured Raman spectra of MAPbI₃

In Fig. 9 we show the Raman spectra acquired for single crystals of MAPbI₃ in the orthorhombic phase. The HV spectrum measured at 4 K shows five peaks between 10 and 70 cm⁻¹, and two small features at 85 cm⁻¹ and 97 cm⁻¹. Additionally, the HH spectrum at 4 K exhibits a further small feature at 9 cm⁻¹. These peaks tend to broaden with increasing temperature, in line with the increasing probability of phonon-phonon scattering, and exhibit a slight redshift of the order of 4 cm⁻¹, which we tentatively attribute to lattice expansion and phonon-phonon interactions. The small peaks at 85 cm⁻¹ and 97 cm⁻¹ are at the detection limit for the experiment, and one plausible explanation for their progressive disappearance as the temperature is raised is that they vanish into the noise as they broaden at higher temperatures.

Importantly there are no new features appearing with increasing temperature, and we do not observe peaks around 94 cm⁻¹ and 110 cm⁻¹, which would indicate the presence of PbI₂.¹⁷ Thus our data indicate that MAPbI₃ is not undergoing degradation during the Raman experiments, and the spectra are representative of the pristine material.

5 Comparison of measured and calculated Raman spectra

In Fig. 10 we compare the HH and HV Raman spectra measured for MAPbI₃ at 4 K with our first-principles calculations. In the calculated spectrum we include anharmonic corrections, following the discussion in Sec. 3.5.

Our calculations nicely reproduce the frequency and relative intensity of almost all the peaks observed in the experiments, for both polarization configurations, except for the measured peak at 142 cm⁻¹. We will come back on this point below. Overall, the good agreement between theory and experiment allows us to proceed with a complete assignment of the measured peaks. Our proposed assignment of the Raman spectrum is indicated in Fig. 10 by the dashed black lines. The measured peak at 9 cm⁻¹ (labelled as ‘0’ in Fig. 10) is assigned to Pb-I-Pb rocking modes with A_g symmetry. The peak at 26 cm⁻¹ corresponds to Pb-I-Pb bending modes with A_g symmetry (1), and the small peak next to it, at 32 cm⁻¹, originates from Pb-I-Pb bending modes with B_{2g} symmetry (2). At slightly higher frequency, the peaks at 42 cm⁻¹ and 49 cm⁻¹ are assigned to Pb-I-Pb bending modes with A_g (3) and B_{2g} (4) symmetry, respectively, whereas the peak at 58 cm⁻¹ corresponds to librational modes of the MA cations (5). At even higher frequency, the peak at 85 cm⁻¹ is assigned to librational modes of the MA cations as well as to Pb-I stretching modes with B_{3g} symmetry (6), whereas the peak at 97 cm⁻¹ stems from Pb-I stretching modes of A_g symmetry (7). In the high-frequency region of the spectrum the small peak at 142 cm⁻¹ (8) is assigned to librational modes of the MA cations. For clarity, these assignments are summarized in Table 4.

Generally speaking, our assignments indicate that the Raman peaks observed below 50 cm⁻¹ in the experiments are internal vibrations of the inorganic PbI₃ network, while above this frequency the features at 58 cm⁻¹ and 142 cm⁻¹ correspond to librational modes of the MA cations, and the peak at 85 cm⁻¹ is a combination of MA libration and internal vibrations of the inorganic network. Owing to the significant Raman intensities of the peaks at 26, 42,

49 and 58 cm^{-1} , the first three of these peaks could be used as markers of the inorganic PbI_3 network, whereas the last one could serve as a fingerprint of the MA cations. Since these assignments are unambiguous, the ratios of the intensities of PbI_3 -related peaks and the MA-related peak could be used to monitor possible deviations from the ideal stoichiometry of MAPbI_3 , for example to check sample purity or detect early signs of degradation.

We now comment on the intensity of the Raman peak at 142 cm^{-1} , which we assigned to MA librational and translational modes. As can be seen in Fig. 10, our calculations yield an intensity which is significantly larger than in experiments. We notice that Brivio et al.¹⁸ also reported an overestimation of the intensity of this Raman peak by calculations. In a previous work by some of us,³⁴ we performed a similar comparison between theory and experiment for IR spectra, and we also found that our calculations significantly overestimate the IR intensity of the same peak. Therefore it seems that we consistently overestimate the Raman and IR activity of the MA librational/translational modes. The origin of this discrepancy remains unclear. A possible explanation may be that vdW interactions, SOC, and anharmonicity may affect the Raman intensities of these modes (as opposed to their frequencies). However, it has previously been shown that vdW effects and SOC lead to only small changes to the IR intensities,⁴² and anharmonic renormalization of the intensities can be ruled out on the grounds of molecular dynamics simulations which yield results similar to ours.¹⁶ Another possible explanation may be lifetime broadening effects, as suggested by Brivio et al.¹⁸ However, Druzicki et al.⁶⁰ measured the inelastic neutron scattering (INS) spectrum of orthorhombic MAPbI_3 , and found that these modes exhibit considerable intensities, therefore ruling out lifetime broadening effects.

One possibility which is left out of this analysis is the combination of anharmonicity and quantum nuclear quantum effects,⁶¹ which is not captured by the present work and by the MD simulations of Ref. 16. A thorough investigation of this aspect will require path-integral molecular dynamics simulations,⁶² which are computationally prohibitive for a system as complex as MAPbI_3 .

6 Conclusions

In summary, we carried out first-principles calculations in conjunction with high-resolution low-temperature Raman measurements to investigate the Raman spectrum of the low-temperature orthorhombic phase of MAPbI₃. The good agreement between measured and calculated Raman peaks allowed us to perform a complete assignment of the main peaks observed in the experiments, including the symmetry and character of each normal mode.

We found that the Raman spectrum of MAPbI₃ extends up to 3200 cm⁻¹, and can be partitioned into three distinct regions: internal vibrations of the MA cations (300-3200 cm⁻¹); libration/translation and spinning of the organic cations (60-180 cm⁻¹), and internal vibrations of the PbI₃ network (0-60 cm⁻¹). For the comparison with experiments we focused on the low-frequency region. Here we found that the Raman peaks observed below 50 cm⁻¹ correspond to internal vibrations of the inorganic PbI₃ network, while the peaks at 58 cm⁻¹, 85 cm⁻¹, and 142 cm⁻¹ correspond to librational modes of the MA cations (the peak at 85 cm⁻¹ also containing a component of PbI₃ vibrations). Our complete assignment is summarized in Table 4 and Fig. 10.

The Raman peaks P_1 , P_3 , P_4 , P_5 (at 26, 42, 49, and 58 cm⁻¹) are intense and well separated, therefore they could be used as markers for monitoring of the MAPbI₃ structure and stoichiometry. In particular, the P_1 , P_3 , and P_4 peaks can clearly be identified with vibrations of the PbI₃ network, while the P_5 peak comes from the MA cations. Therefore we suggest that the ratios of the intensities P_1/P_5 , P_3/P_5 , and P_4/P_5 could be used to monitor the PbI₂/MAI ratio in the system, for example to detect deviations from the ideal stoichiometry or to monitor degradation.

We observed a discrepancy between theory and experiment for the P_8 peak, which corresponds to librational/translational modes of MA. In this case the calculations yield too strong a Raman intensity, and the effect is analogous to what was previously observed for IR spectra.³⁴ We ruled out vdW effects, SOC, and anharmonicity as the origin of this discrepancy, and we proposed that path-integral MD simulations might be necessary to clarify

this aspect.

Overall we reported the first complete assignment of the symmetry and character of the main Raman peaks of orthorhombic MAPbI₃ in the low-frequency range. We hope that the present study will serve as a solid framework for future characterization of this important organic-inorganic perovskite.

Acknowledgement

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Appendix A

The Raman tensors of the orthorhombic MAPbI₃ (*Pnma*) have the following symmetries,

$$\bar{\alpha}(A_g) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, \bar{\alpha}(B_{1g}) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\bar{\alpha}(B_{2g}) = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, \bar{\alpha}(B_{3g}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$$

Making use the symmetry of the Raman tensors and Eq. 1 of the main text (this is, $I^k \propto \frac{1}{\omega_k} |\mathbf{e}_i \cdot \bar{\alpha}^k \cdot \mathbf{e}_s|^2$), we predict the Raman activity of the normal modes for several orientations of a single crystal of MAPbI₃, in backscattering geometry $\mathbf{k}_i(\mathbf{e}_i, \mathbf{e}_s)\mathbf{k}_s$, with $\mathbf{k}_i = -\mathbf{k}_s$. \mathbf{k}_i and \mathbf{k}_s are the directions of the propagation vectors of the incoming and scattered photons, respectively, and \mathbf{e}_i and \mathbf{e}_s are their corresponding polarisation vectors. The backscattering geometries here considered and the predicted Raman activity of the normal modes are shown in Table 5.

To confirm our predictions, we explicitly calculate the Raman intensities of the normal modes by solving Eq. 1 for the following backscattering geometries $x(yy)\bar{x}$, $x(yz)\bar{x}$, $y(xx)\bar{y}$ and $y(xz)\bar{y}$. With the resulting Raman intensities, we calculate the corresponding Raman spectra, and our results are shown in Fig. 11c,d. In this figure, we also compare the spectra with the calculated Raman spectra using the isotropic average, and with experiment.

As one can see, the A_g normal modes observed in the calculated Raman spectra using the isotropic average (Fig. 11b), exhibit nonzero Raman intensities in the backscattering geometries $x(yy)\bar{x}$ and $y(xx)\bar{y}$. On the contrary, the B_{1g} , B_{2g} and B_{3g} normal modes observed in Fig. 11b, vanish in these backscattering configurations. These observations are in line with our symmetry-based predictions. In the case of the calculated Raman spectra for the configurations $x(yz)\bar{x}$ and $y(xz)\bar{y}$ (Fig. 11c), we observe that the B_{3g} and B_{2g} normal modes show nonzero Raman intensities, respectively, whereas the A_g modes do not. This result is

also in line with our symmetry-based predictions.

As one can see, the calculated Raman spectra of Fig. 11b,c strongly depend on the backscattering configuration. This analysis reveals that, while the geometry modifies the intensity of the peaks as expected, the intensity of the peak P_8 remains large irrespective of the geometry.

Overall, the results presented in this Appendix could be useful to experimentalists for characterising the Raman spectra of orthorhombic MAPbI_3 measured on a single crystal, and to demonstrate the symmetry of the lattice vibrations in this system.

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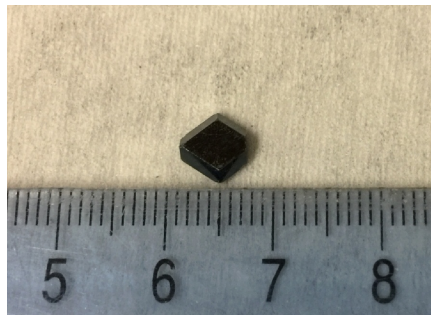


Figure 1: Optical photograph of a typical $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal obtained in this synthesis.

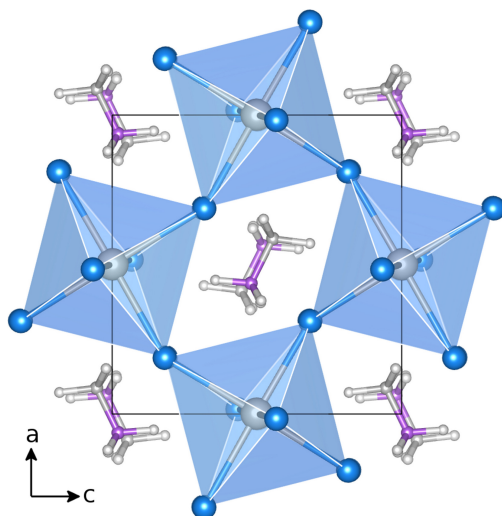


Figure 2: Polyhedron-ball-and-stick model of the optimized structure of the low-temperature orthorhombic phase of MAPbI_3 , viewed across the ac plane of the unit cell. The unit cell is indicated by the black lines. The Pb and I atoms are in grey and blue, respectively, whereas the C, N, and H atoms of the MA cations are in grey, purple, and white, respectively.

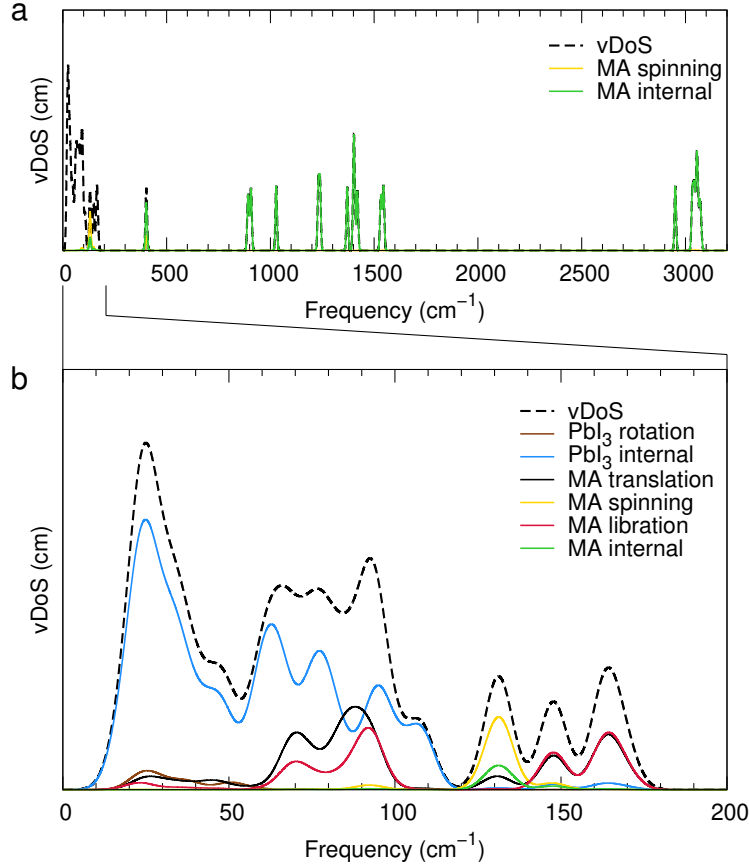


Figure 3: (a) Calculated total and partial vibrational density of states (vDOS) of the low-temperature orthorhombic phase of MAPbI₃. (b) Detail of the vDOS in the low frequency region. The dashed black curve indicates the total vDOS. The vibrational modes are decomposed into rigid rotations and internal vibrations of the PbI₃ octahedra (brown and blue curves, respectively), and into translation (solid black curve), spinning (yellow curve), and libration (red curve) of the MA cations, and internal vibrations (green curve) of these cations. A Gaussian smearing of 5 cm⁻¹ has been applied to all curves.

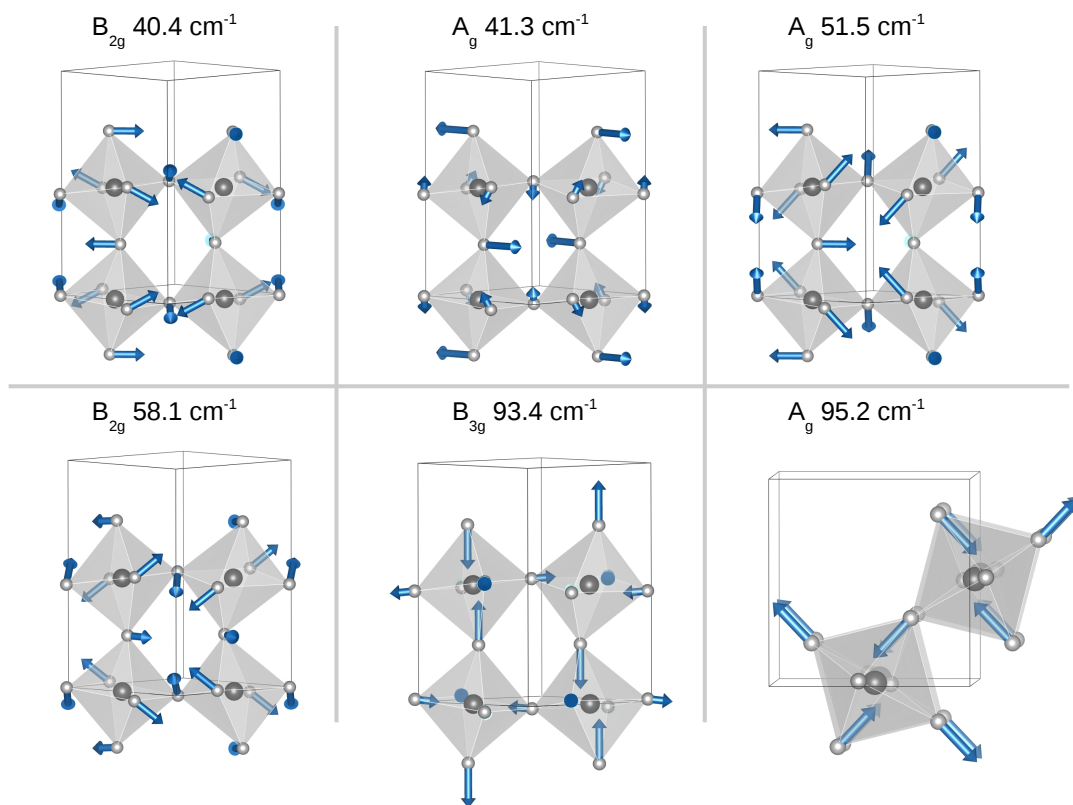


Figure 4: Schematic representation of the most important Raman-active modes of the PbI_3 -network in MAPbI_3 . The MA cations, whose contribution to the Raman intensity is negligible, are not shown for clarity. The symmetry and calculated frequency of each normal mode is indicated at the top of the each panel, and the solid black lines indicate the unit cell.

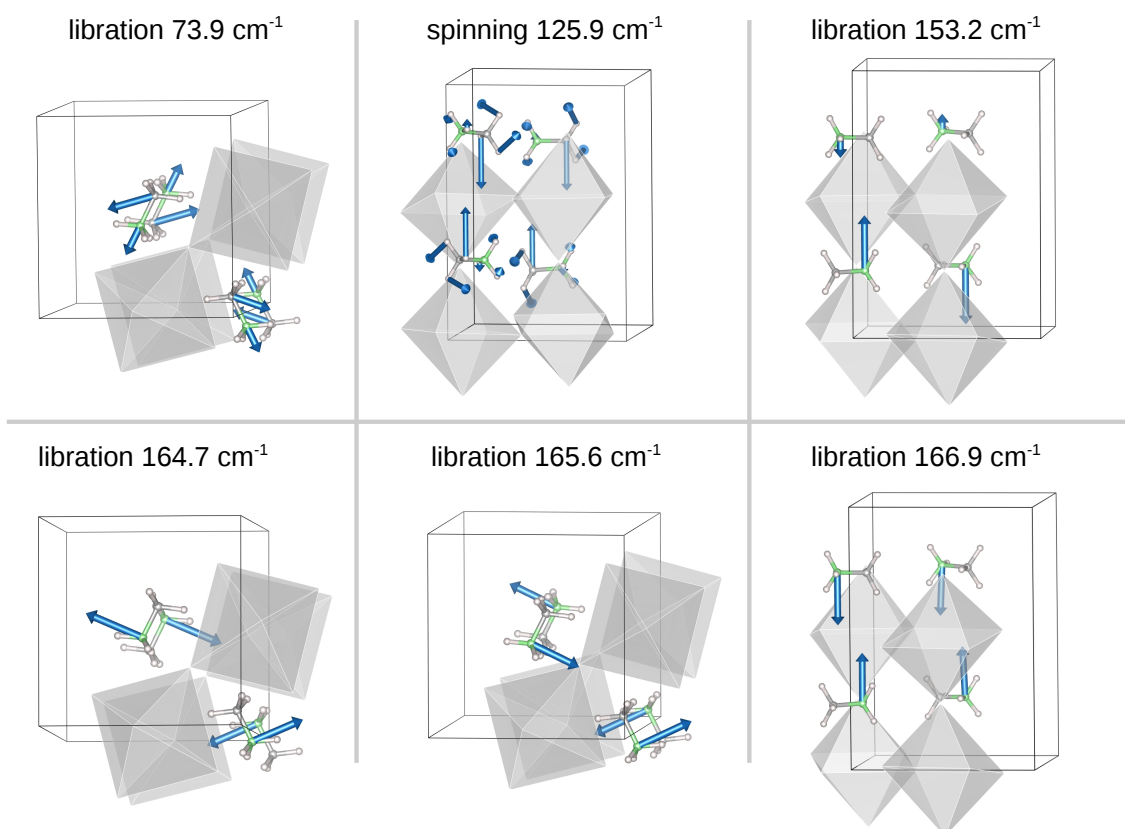


Figure 5: Schematic representation of the libration/translation and spinning modes of the MA cations with the largest calculated Raman intensities. For clarity we only show the octahedra without the Pb and I atoms, and in the librational modes only the displacements of the C and N atoms are indicated by arrows. The character and frequency of each mode is reported at the top. We note that all these modes also include a component of rigid translation of the cations.

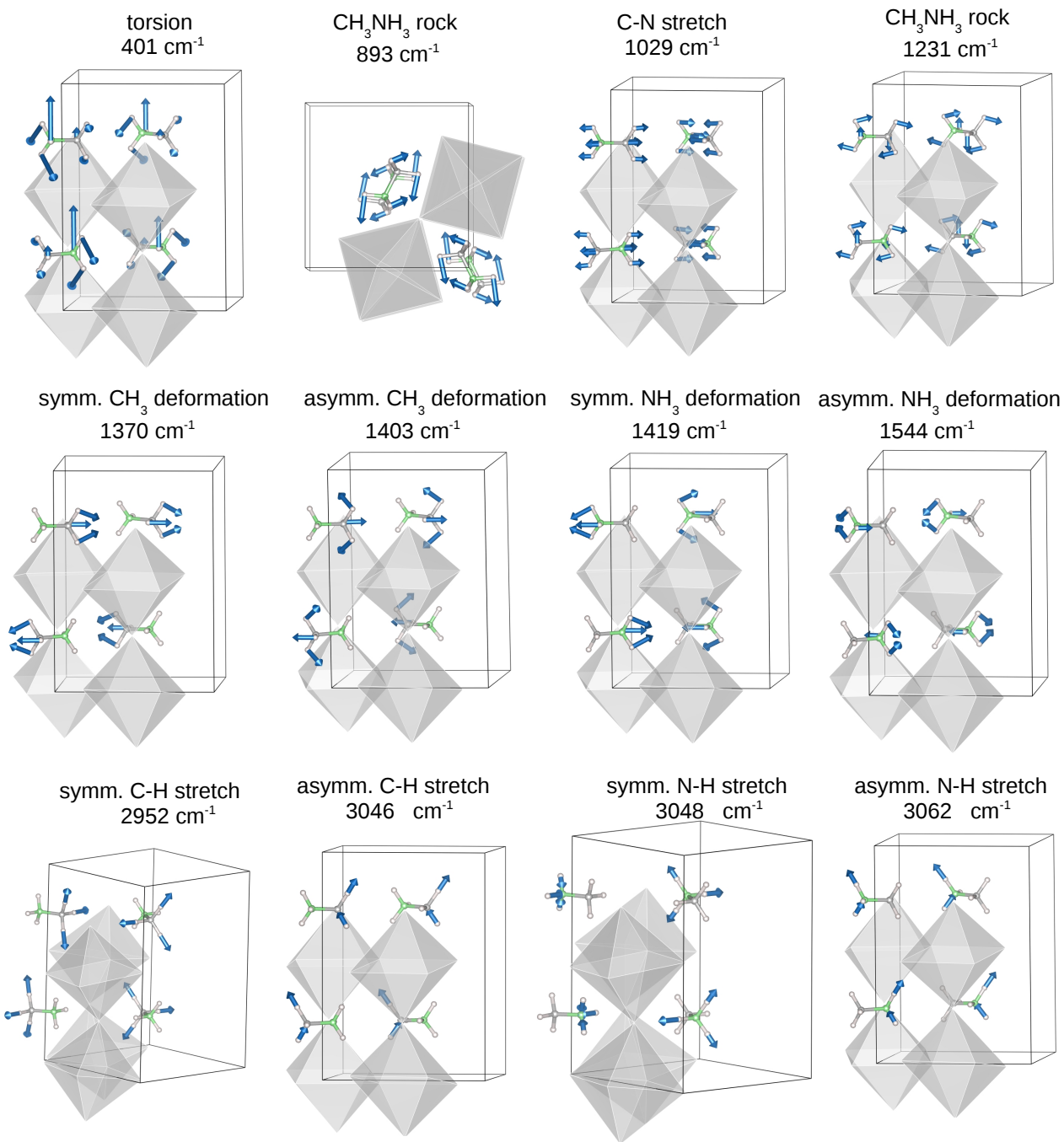


Figure 6: Schematic representation of the internal vibrations of the MA cations in MAPbI_3 . For each set of normal modes reported in Table 2, we show a schematic representation of the mode with the largest Raman intensity. The mode character and frequency are given at the top of each panel.

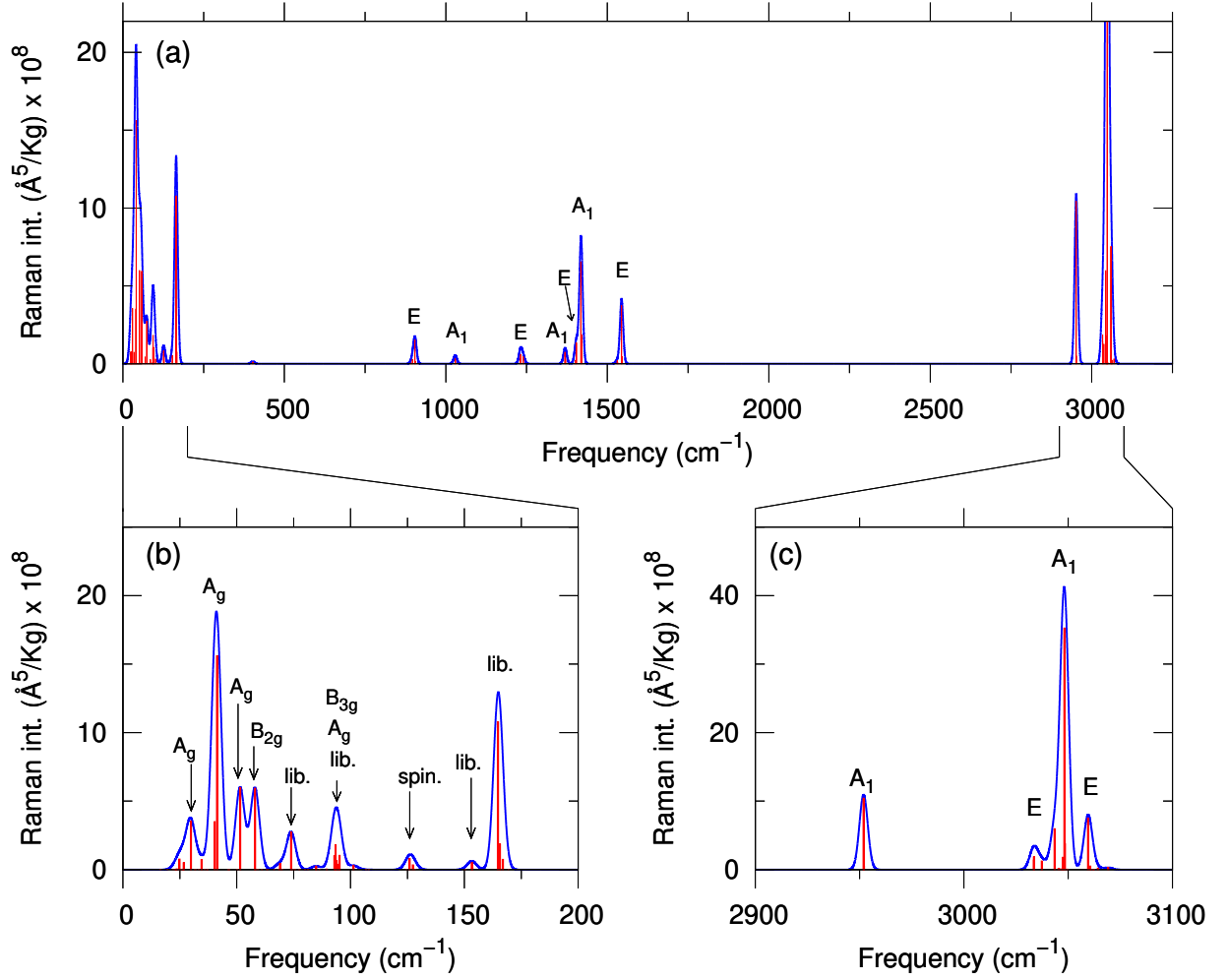


Figure 7: (a) Calculated Raman spectrum of MAPbI₃ in the orthorhombic structure. (b), (c) Details of the calculated Raman spectrum in the low and high-frequency regions, respectively. The red sticks indicate the calculated Raman intensities of the normal modes, obtained as $I^k = I_{\text{HH}}^k + I_{\text{HV}}^k$. The blue line is computed by applying a Gaussian broadening of 2 cm^{-1} to the discrete spectrum. For clarity we only indicate the symmetry of the normal modes with the largest Raman intensities.

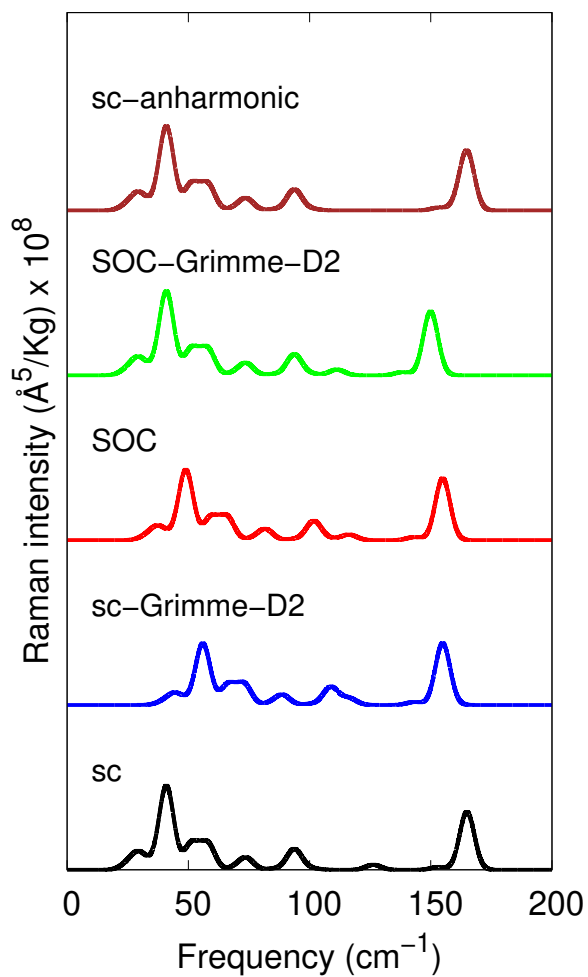


Figure 8: Comparison of the Raman spectra of the orthorhombic MAPbI_3 calculated using scalar-relativistic LDA (black) with the spectra obtained after including corrections from vdW interactions (blue); SOC (red); vdW interactions in combination with SOC (green); anharmonicity (brown).

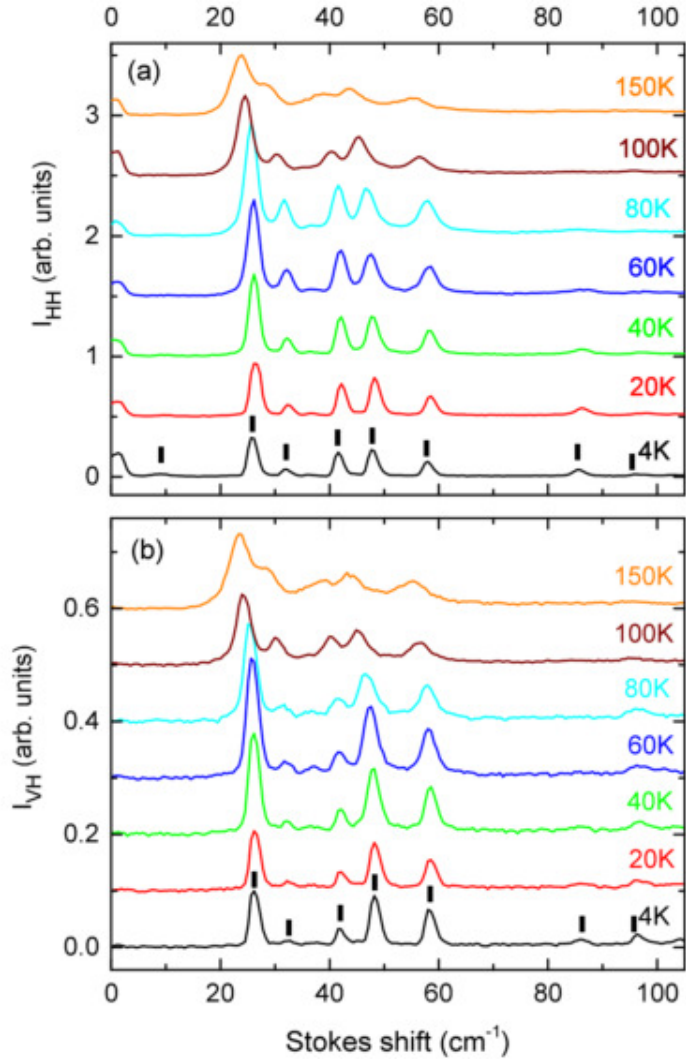


Figure 9: Raman spectra for a single crystal of MAPbI_3 , measured in backscatter geometry from the (100) plane, using a 830 nm laser polarized (a) parallel (HH) or (b) perpendicular (HV) to the polarization of the scattered light. Spectra acquired at different temperatures are shifted vertically for clarity.

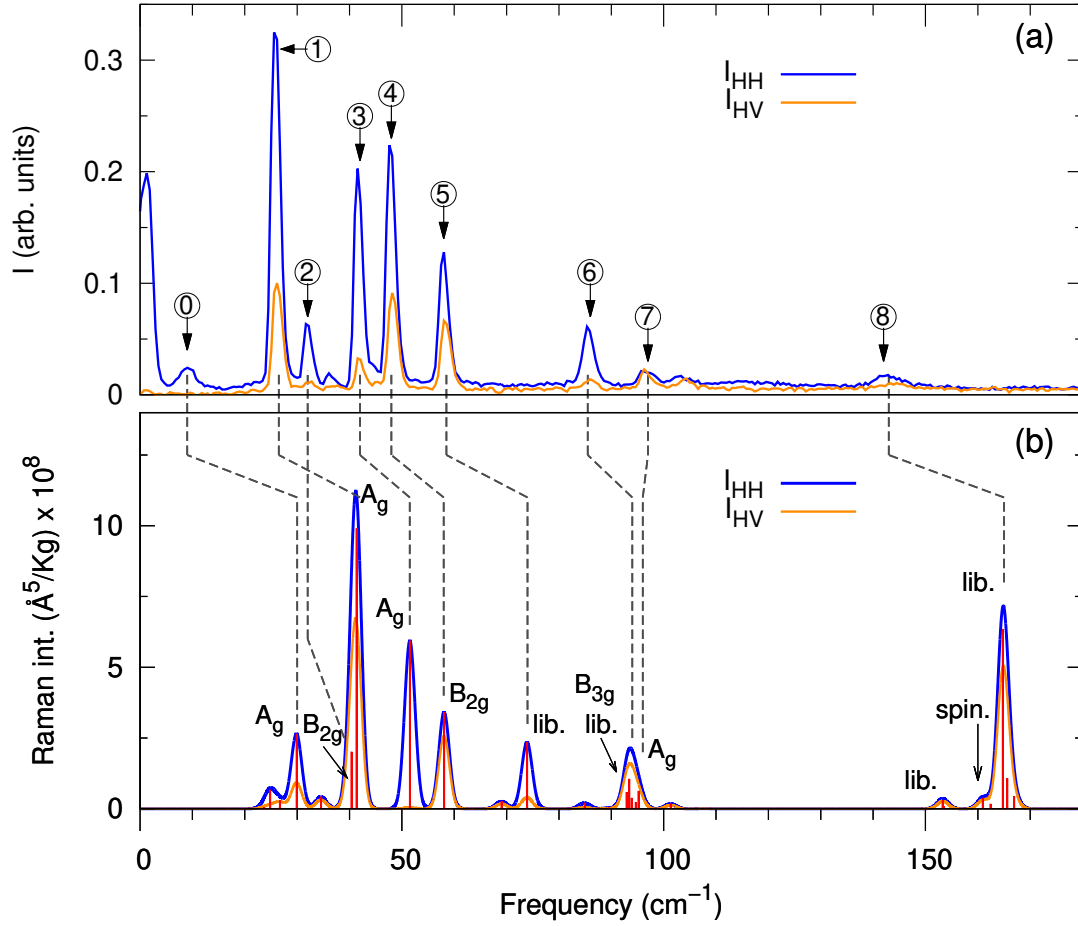


Figure 10: Comparison between the measured (a) and calculated (b) Raman spectra of MAPbI₃ in the orthorhombic structure. The experimental spectra are recorded at 4 K. In both panels the data for the HH and HV configurations are shown in blue and orange, respectively. The red sticks in (b) indicate the calculated Raman intensities for the HH configuration, I_{HH} . The dashed grey lines indicate the tentative assignment of the Raman peaks observed in experiment. In the calculated spectra we used a Gaussian smearing of 1.0 cm^{-1} .

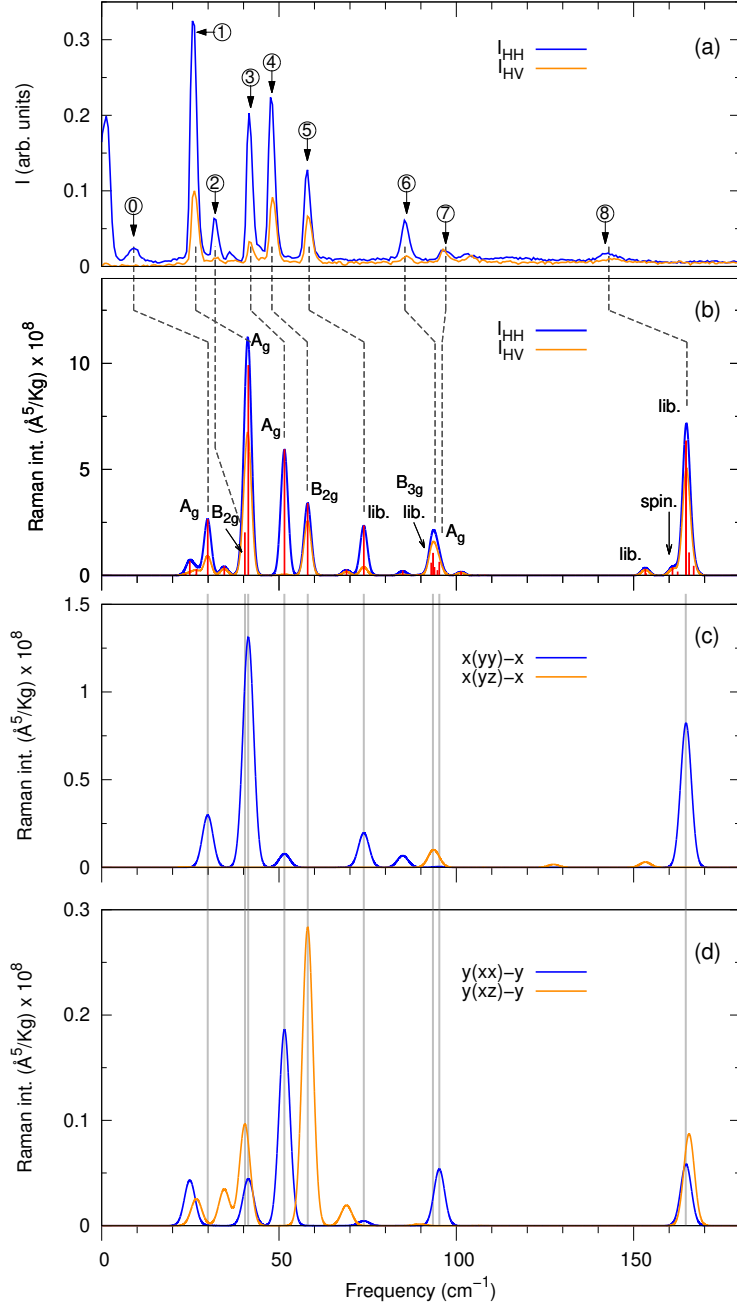


Figure 11: Measured and calculated Raman spectra of orthorhombic MAPbI_3 . (a) Measured Raman spectra at 4 K, in HH and HV backscattering polarisation configurations. (b) Calculated Raman spectra in HH and HV polarisation configurations, using the isotropic average (see Methods for further details). (c) Calculated Raman spectra for the backscattering geometries $x(yy)\bar{x}$ and $x(yz)\bar{x}$. (d) Calculated Raman spectra for the backscattering geometries $y(xx)\bar{y}$ and $y(xz)\bar{y}$. Panels (a) and (b) are the same as Fig. 10. The vertical light grey lines are guides to the eye, to indicate the frequencies of the normal modes with the highest Raman intensities in (b).

Table 1: Symmetry, character, frequency, and predicted Raman activity of the calculated vibrational modes of the PbI_3 network in MAPbI_3 . We also report the calculated IR intensity for completeness. The labels ‘R’ and ‘IR’ indicate modes which are expected to be Raman active or IR active by symmetry. We also report the Raman and IR intensities calculated from first principles. Whenever the Raman or IR intensity is not indicated, the corresponding value is smaller than $0.1 \times 10^8 \text{ \AA}^5/\text{Kg}$ or $0.1 \text{ (D/\AA)}^2/\text{Kg}$, respectively.

Mode no.	Symm.	Character	Active	Freq. (cm^{-1})	Raman intensity ($\text{\AA}^5/\text{Kg}) \times 10^8$	IR intensity ($\text{(D/\AA)}^2/\text{Kg}$)	Mode no.	Symm.	Character	Active	Freq. (cm^{-1})	Raman intensity ($\text{\AA}^5/\text{Kg}) \times 10^8$	IR intensity ($\text{(D/\AA)}^2/\text{Kg}$)
1	B_{1u}			0.0			25	A_g	Pb-I-Pb bend	R	41.3	15.6	
2	B_{2u}			0.0			26	B_{1u}	Pb-I-Pb bend	IR	46.1		0.5
3	B_{3u}			0.0			27	B_{3g}	Pb-I-Pb bend	R	46.7		
4	A_u	Pb-I-Pb bend	silent	16.5			28	B_{3u}	Pb-I-Pb bend	IR	50.3		1.5
5	B_{2u}			19.6			29	A_g	Pb-I-Pb bend	R	51.5	6.0	
6	B_{1u}	Pb-I-Pb rock	IR	22.1		0.2	30	B_{2g}	Pb-I-Pb bend	R	58.1	5.9	
7	B_{1g}	Pb-I-Pb rock	R	22.9		0.4	31	B_{2u}	Pb-I stretch	IR	58.2		7.2
8	B_{3u}	Pb-I-Pb bend	IR	23.3			32	A_u	Pb-I stretch	silent	61.1		
9	A_u	Pb-I-Pb rock	silent	23.4		0.2	33	B_{1u}	Pb-I stretch	IR	61.1		16.2
10	B_{3g}	Pb-I-Pb rock	Raman	23.6			34	B_{3u}	Pb-I stretch	IR	63.2		16.4
11	A_g	Pb-I-Pb rock	R	24.8			35	A_u	Pb-I stretch	silent	63.5		
12	A_u			25.6	0.8		36	B_{2u}	Pb-I stretch	IR	66.4		10.6
13	A_u	Pb-I-Pb rock	silent	26.5			41	B_{1u}	Pb-I-Pb bend	IR	74.7		0.2
14	B_{2u}	Pb-I-Pb rock	IR	26.6		0.4	42	B_{3u}	Pb-I-Pb bend	IR	75.5		0.1
15	B_{1u}			26.6		0.1	43	A_u	Pb-I-Pb bend	silent	77.4		
16	B_{2g}	Pb-I-Pb rock	R	26.7			44	B_{2u}	Pb-I-Pb bend	IR	77.6		0.9
17	A_g	Pb-I-Pb rock	R	29.9	0.5		45	B_{1u}	Pb-I-Pb bend	IR	79.9		0.9
18	B_{2u}	Pb-I-Pb bend	IR	31.6	3.6		46	B_{3u}	Pb-I stretch	IR	81.2		0.4
19	B_{3u}	Pb-I-Pb rock	IR	31.9		1.8	53	B_{3g}	Pb-I stretch	R	93.4	1.8	
20	B_{3u}	Pb-I-Pb rock	IR	33.4		1.6	54	B_{1g}	Pb-I stretch	R	93.9	0.7	
21	B_{2g}	Pb-I-Pb bend	R	34.6	0.7	0.1	56	A_g	Pb-I stretch	R	95.2	1.0	
22	B_{1u}	Pb-I-Pb rock	IR	36.0		1.4	58	B_{1g}	Pb-I stretch	R	101.3	0.3	
23	B_{1g}	Pb-I-Pb bend	R	37.1			59	B_{2g}	Pb-I stretch	R	106.8		
24	B_{2g}	Pb-I-Pb rock	R	40.4	3.5		60	B_{3g}	Pb-I stretch	R	108.0		

Table 2: Character, frequency, and calculated Raman intensity of the vibrational modes corresponding to the rigid-body motion of the MA cations in MAPbI₃. We also report the IR intensities for completeness. We distinguish spinning, libration, and translations based on the decomposition shown in Fig. 2. Modes of mixed character correspond to vibrations where the contribution of different components have similar weights in Fig. 2. Whenever the Raman or IR intensity is not indicated, the corresponding value is smaller than $0.1 \times 10^8 \text{ \AA}^5/\text{Kg}$ or $0.1 \text{ (D/\AA)}^2/\text{Kg}$, respectively.

Mode no.	Character	Frequency (cm^{-1})	Raman intensity ($\text{\AA}^5/\text{Kg}) \times 10^8$	IR intensity [(D/\AA) ² /Kg]	Mode no.	Character	Frequency (cm^{-1})	Raman intensity ($\text{\AA}^5/\text{Kg}) \times 10^8$	IR intensity [(D/\AA) ² /Kg]
37	libr/transl	68.5			61	spin	124.7		1.0
38	libr/transl	69.0	0.4		62	spin	125.9	0.8	
39	libr/transl	69.9			63	spin	127.4	0.3	
40	libr/transl	73.9	2.7		64	spin	128.6		
47	translation	84.8		3.2	65	libr/transl	150.3		8.6
48	libr/transl	84.9	0.2		66	libr/transl	153.2	0.5	
49	translation	86.3		1.9	67	libr/transl	153.5	0.1	
50	libr/transl	89.6			68	libr/transl	164.7	10.8	
51	libr/transl	92.9	1.0		69	libr/transl	165.6	1.9	
52	libr/transl	93.3		0.2	70	libr/transl	165.9		9.8
55	libr/transl	94.7	0.4		71	libr/transl	166.9	0.7	
57	libr/transl	95.3			72	libr/transl	169.3		1.1

Table 3: Symmetry, character, frequency, and Raman intensity of the internal vibrations of the MA cations in MAPbI₃. We also report the calculated IR intensities for completeness. The frequencies and intensities are averaged over nearly-degenerate modes. Whenever the Raman or IR intensity is not indicated, the corresponding value is smaller than $0.01 \times 10^8 \text{ \AA}^5/\text{Kg}$ or $0.1 \text{ (D/\AA)}^2/\text{Kg}$, respectively.

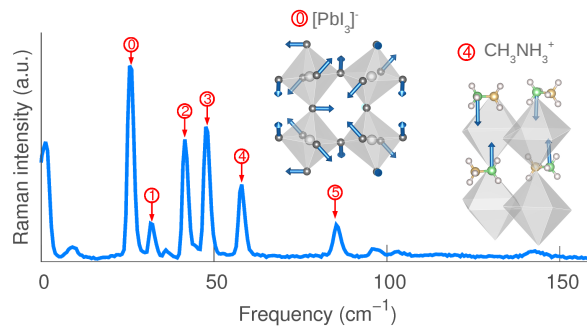
Mode no.	Molecular Symmetry	Character	Frequency (cm ⁻¹)	Raman intensity (Å ⁵ /Kg)×10 ⁸	IR intensity [(D/Å) ² /Kg]
73–76	A ₂	sym. Torsion	401	0.1	0.4
77–80	E	asym. CH ₃ NH ₃ rock	893	0.2	9.3
81–84	E	asym. CH ₃ NH ₃ rock	906	0.8	6.3
85–88	A ₁	sym. C–N stretch	1029	0.3	0.5
89–92	E	asym. CH ₃ NH ₃ rock	1231	0.5	0.6
93–96	E	asym. CH ₃ NH ₃ rock	1239	0.4	0.3
97–100	A ₁	sym. CH ₃ deformation	1370	0.5	0.8
101–108	E	asym. CH ₃ deformation	1403	0.8	2.4
109–112	A ₁	sym. NH ₃ deformation	1419	4.2	4.5
113–116	E	asym. NH ₃ deformation	1533	0.1	3.0
117–120	E	asym. NH ₃ deformation	1544	2.1	1.6
121–124	A ₁	sym. C–H stretch	2952	10.9	0.2
125–128	E	asym. C–H stretch	3035	1.4	21.8
129–132	E	asym. C–H stretch	3046	6.2	103.2
133–136	A ₁	sym. N–H stretch	3048	40.9	16.5
137–144	E	asym. N–H stretch	3062	8.6	115.4

Table 4: Proposed assignment of the main peaks in the Raman spectrum of MAPbI₃ acquired at 4 K. The peak labels correspond to those in Fig. 10(a).

Peak label	Frequency (cm ⁻¹)	Symmetry	Description
<i>P</i> ₀	9	A _g	Pb-I-Pb rock
<i>P</i> ₁	26	A _g	Pb-I-Pb bend
<i>P</i> ₂	32	B _{2g}	Pb-I-Pb bend
<i>P</i> ₃	42	A _g	Pb-I-Pb bend
<i>P</i> ₄	49	B _{2g}	Pb-I-Pb bend
<i>P</i> ₅	58		libration/translation
<i>P</i> ₆	85	B _{3g}	Pb-I stretch and libration/translation
<i>P</i> ₇	97	A _g	Pb-I stretch
<i>P</i> ₈	142		libration/translation

Table 5: Predicted Raman activity of the normal modes in orthorhombic MAPbI₃, for several backscattering geometries. x , y , and z denote the [100], [010] and [001] crystallographic directions in the orthorhombic unit cell of MAPbI₃, respectively. y' , z' , x'' and z'' indicate the [011], [0 $\bar{1}$ 1], [101] and [$\bar{1}$ 01] crystallographic directions, respectively. **R** denotes nonzero Raman activity.

Backscattering geometry	Normal Mode Symmetry			
	A_g	B_{1g}	B_{2g}	B_{3g}
$x(yy)\bar{x}$	R			
$x(zz)\bar{x}$	R			
$x(yz)\bar{x}$				R
$x(y'y')\bar{x}$	R			R
$x(z'z')\bar{x}$	R			R
$x(y'z')\bar{x}$	R			
$y(xx)\bar{y}$	R			
$y(zz)\bar{y}$	R			
$y(xz)\bar{y}$			R	
$y(x''x'')\bar{y}$	R		R	
$y(z''z'')\bar{y}$	R		R	
$y(x''z'')\bar{y}$	R			



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