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Direct evidence of weakly dispersed and strongly anharmonic optical phonons in hybrid perovskites

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Hybrid organolead perovskites (HOP) have started to establish themselves in the field of photovoltaics, mainly due to their great optoelectronic properties and steadily improving solar cell efficiency. Study of the lattice dynamics is key in understanding the electron-phonon interactions at play, responsible for such properties. Here, we investigate, via neutron and Raman spectroscopies, the optical phonon spectrum of four different HOP single crystals: MAPbBr₃, FAPbBr₃, MAPbI₃, and α-FAPbI₃. Low temperature spectra reveal weakly dispersive optical phonons, at energies as low as 2-5 meV, which seem to be the origin of the limit of the charge carriers mobilities in these materials. The temperature dependence of our neutron spectra shows as well a significant anharmonic behaviour, resulting in optical phonon overdamping at temperatures as low as 80 K, questioning the validity of the quasi-particle picture for the low energy optical modes at room temperature where the solar cells operate.
Over the last few years, halide perovskites have emerged as a promising class of materials for high-performing photovoltaic (PV) cells. The hybrid organolead perovskite (HOP) adopt an ABX$_3$ structure, where A is an organic cation (methylammonium, MA, or formamidinium, FA) and X is an halide (Cl, Br, I) and their optoelectronic properties, as well as easy and cost-effective production (from abundant chemical elements), make HOPs not only attractive for PV applications, but also for light-emitting devices (LEDs) and many other application based on thin films or even single crystals.

Several of the properties responsible for the outstanding performance of hybrid perovskites are connected with electron–phonon interactions, which have been under intense debate. Besides governing their emission line broadening, phonon scattering is among the factors setting a fundamental intrinsic limit to the mobility of charge carriers in these materials. From the inspection of photoluminescence (PL) lineshape broadening in the high-temperature regime of 3D perovskite thin films, it was deduced that carriers scattering is dominated by Fönhlich coupling between charge carriers and longitudinal optical (LO) phonon modes, rather than with acoustic phonons. This was later confirmed from the analysis of elastic constants among different 3D hybrid perovskites. More, optical phonons were shown to play a central role in the slow carrier relaxation in colloidal quantum dots (CQD) of FAPbI$_3$ and FAPbBr$_3$, from the exciton bright triplet to the dark singlet through a second-order process, with strong consequences for CQD brightness and quantum efficiency of CQD light-emitting devices. This mechanism is an alternative to the Rashba effect, which was proposed to lead to an inversion of dark and bright exciton states in CQDs. Further, the potential of perovskite CQDs for hot-carriers solar cell applications has also been stressed; the suppression of the LO relaxation process to longitudinal acoustic (LA) phonons was attributed to a phonon bottleneck effect, and later on related to the anharmonicity of the acoustic modes. Then, a direct measurement of optical phonons branches with the same methodology as for the acoustic modes becomes a necessary step to completely uncover carrier–phonon coupling dynamics and to assess the fundamental intrinsic limit of the mobility of charge carriers in these materials.

HOPs are composed of two sub-lattices: the inorganic sub-lattice, composed of covalently bonded PbX$_3$ octahedra, and the organic sub-lattice consisting of the MA/FA molecular cations inside cuboctahedral perovskite cavities. They have been well documented to undergo a series of crystallographic transitions which differ slightly depending on the organic cation or the halide atoms. It typically goes from the high-temperature cubic phase ($Pm3m$), passing by a tetragonal phase ($I4/mcm$ for MAPbI$_3$ and MAPbBr$_3$) and a orthorhombic phase ($Pnma$ for all compounds except for FAPbI$_3$ where a trigonal phase $P3m1$ has been reported at low temperature) in general, these phase transitions originate from the tilting of the PbX$_3$ cage and the orientational ordering of MA/FA molecules, which is reconstructive for the low-temperature transformation in MA-based compounds. Note that the first-order character of the low-temperature phase transition is less pronounced in FA-based compounds than in MA-based ones. By inducing more complex octahedra tiltings in the perovskite lattice, organic cations may indirectly affect their electronic structure.

While the molecular cations are not expected to directly contribute to the electronic band structure, they are thought to indirectly influence the electronic band edge states through the induction of distortions in the PbX$_3$ framework. Effective volume in the A-site—which is increasing from K$^+$, Rb$^+$, Cs$^+$ inorganic compounds to MA$^+$ and FA$^{4+}$—is for one affecting the Pb–X elongation. Also, the MA/FA molecules have been suggested to interact with the Pb–X network via hydrogen bonding between the ammonium hydrogens and the halide atoms, perturbing in this way the conduction band minimum, increasing diffusion length and suppressing electron–hole recombination. Therefore, the interplay between the molecular groups and the inorganic network presents itself as an additional factor affecting both in the charge–recombination dynamics and the above-mentioned phonon interactions.

On the other hand, the intrinsic anharmonicity of the perovskite lattice is expected to play a more important role. Lattice dynamic calculations from density functional theory (ab initio atomic-level description) of HOPs is complicated and generally not reliable due to the hybrid nature of these compounds, where molecules perform stochastic motions at ambient temperature. More generally though, the strongly anharmonic character of the lattice dynamics is not taken into account in recent phonon calculations for both inorganic and hybrid compounds. Typically, the lowest energy phonons, related to Pb-halogen vibrations, are found unstable with imaginary mode frequency in almost all available theoretical calculations within the harmonic approximations. It is therefore interesting to rely on frozen-phonon calculations or molecular dynamics to get a first theoretical insight into anharmonic effects.

In this work, we employed both time-of-flight (TOF) and triple-axis (TAS) inelastic neutron scattering (INS) techniques (see Methods) to investigate four different hybrid perovskite single crystals: MAPbBr$_3$, FAPbBr$_3$, MAPbI$_3$, and a-FAPbI$_3$ from now on referred to as MAPB, FAPB, MAPI and FAPI, respectively. Complementary Raman scattering spectroscopy is also used. At low temperatures, well-defined optical phonons are observed. Mode attribution to the respective structural vibrations has been discussed and a comparison has been made between the four compounds. We also find the optical excitations to be very weakly propagating, particularly in MA-based compounds. Moreover, the temperature dependence of the TAS spectra reveals a significant anharmonic behaviour, resulting in optical phonon overdamping at temperatures as low as 80 K. We argue for the importance of the acoustic and optical phonon coupling on the anharmonicity of the lattice.

**Results**

From an experimental perspective, INS allows for direct measurement of the phonon spectrum over the reciprocal space that covers the full Brillouin zone (Fig. 1a, b), thus offering the most complete approach. Raman spectroscopy is also a very powerful and precise technique to measure optical phonons and quasielastic contributions, but restricted to the centre of the Brillouin zone (Γ-point) and limited by specific selection rules. **Room temperature phonon spectra.** In Fig. 2, both room temperature (RT) and low temperature (5 K) TOF and TAS measurements are presented. As a first remark, it is necessary to cool the samples down to the lowest temperature to observe well-defined optical phonon branches. Indeed, the INS spectrum recorded at RT in MAPI shows no well-defined optical phonon modes at any energy range as a result of all modes being overdamped in all momentum points (Fig. 2a). Only low-energy acoustic phonons can be actually identified (see also Supplementary Fig. 1), in agreement with the report of RT acoustic phonons in the same four HOP compounds. Above ~3 meV, the acoustic branches vanish as observed in the broadening of the acoustic branches at the zone boundary in doped MAPbI$_3$ and in MAPbCl$_3$ (ref. 49). The absence of optical phonons at RT is also observed in TAS spectra of the other three systems in the Supplementary Fig. 2, all of which is in line with a previous report on MAPbI$_3$. Accordingly, only a broad
inelastic contribution was observed around 12 meV in MAPB at RT and a tentative attribution of the various phonon modes inside this bundle was only possible through the numerical fitting of the experimental spectrum by a superposition of damped harmonic oscillators (DHOs)\textsuperscript{18}. This is also consistent with the high-temperature Raman spectrum of MAPbBr\textsubscript{3} (vide infra)\textsuperscript{51}. The dispersive optical phonon modes reported at RT by inelastic X-Ray scattering in MAPI and MAPB\textsuperscript{45}, with its broader energy resolution (i.e. ~1.5 meV) and its Lorentzian instrumental shape, are then put into question.

Lack of dispersion in momentum space. In order to be able to observe sharp optical phonon features, recording neutron spectra at 5 K (Fig. 2b–f) is necessary as cooling down to the lowest temperature substantially reduces phonon damping. In MA-based HOP compounds, the phonons are typically resolution-limited in energy at 5 K, whereas in FA-based systems the phonon features remain broad even at 5 K (see e.g. Fig. 3a–h). Showing relatively broad peaks that apparently represent scattering from a bundle of modes, it should be emphasized that the INS technique is incapable of detecting a specific phonon dispersion in such closely packed optical modes which might overlap. However, this experimental limit depends greatly on the instrumental energy resolution which is very much improved for cold neutron spectrometers (see Fig. 3 caption).

Having said that, one observes that all phonon modes (or mode bundles) show little to no dispersion as summarized in Fig. 4 for MAPB, suggesting a localized character in real space.
Fig. 3 Low-temperature optical phonon spectra. Triple-axis spectrometer (TAS) neutron spectra measured at 5 K, at the R Bragg reflection (1/2, 1/2, 3/2) of a, b MAPB, c, d MAPI, f at the M point (5/2, 1/2, 0) of FAPB and g at the R point of FAPI. For each compound, each row shows the measurements either using a thermal (a, c, e) or a cold (b, d, f) neutron instrument, with the exception of FAPI only using cold TAS (g). The energy resolution using TAS varies considerably with experimental conditions and the neutron energies. It is broader on thermal instrument (1–3 meV from 0 to 40 meV energy transfer) than on cold neutron instruments (0.2–0.4 meV from 0 to 15 meV energy transfer). The experimental TAS data (black scatter points) are fitted (full red line) with a sum of damped harmonic oscillators and are presented with a removed constant background. Individual fitted peaks are labelled (filled-coloured area). h Comparison of the Raman scattering responses above (170 K) and below (20 K) the orthorhombic-tetragonal transition. Error bars (sometimes smaller than the symbol size) represent one standard deviation.
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MAPbCl3 (ref. 53) does not show any sharp features in clear
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peaks, as we observed for MA-based HOP, can only be accounted
sharpness of the measured peaks. Energy resolution-limited
incoherent scattering, some information can be obtained from the

However, we need to temper this observation. Indeed, as
pointed out in Supplementary Note 1, the neutron intensities
correspond to the sum of coherent and incoherent cross-sections.
In case of incoherent scattering, the phonon momentum
information is lost. As hydrogen atom has a large incoherent
scattering length, the phonon peaks involving hydrogen would
roughly correspond to the incoherent cross-section. In contrast,
the phonon peaks from the PbX3 cage are related to the coherent
cross-section, which typically corresponds to the lowest energy
bundle a (as discussed below) showing as well no dispersion (see
e.g. the TOF data in MAPI, Fig. 2b). Furthermore, even for
incoherent scattering, some information can be obtained from the
sharpness of the measured peaks. Energy resolution-limited
peaks, as we observed for MA-based HOP, can only be accounted
for by dispersionless phonons even for incoherent scattering. It is
interesting to compare our data with the neutron scattering
studies of HOP powder samples where the q dependence is also
lost by averaging over all orientational directions. It appears that
the powder sample spectra of MAPB52 and MAPI53 also show
sharp phonon modes at the same energy than in our experiments,
suggesting once more the dispersionless nature of these phonon
modes. The neutron powder sample spectrum observed in
MAPbCl3 (ref. 53) does not show any sharp features in clear
contrast with MAPI, suggesting again that optical phonons
exhibit no dispersion in MA-based HOPs.

It should be further stressed that the lowest energy mode at
5 meV in MAPB52 is found at the same position in protonated and
deuterated samples, showing that it is not related to a molecular
vibration. The lowest energy mode is therefore necessarily
associated to the coherent neutron cross-section, corroborating
the lack of dispersion in MA-based HOPs of the lowest frequency
modes. In contrast, the observation of broader phonons modes in
FA-based HOPs (see below) may question the dispersionless
nature in FAPB and FAPI (for instance, the modes above ~7 meV
in Fig. 3e–g involving molecular vibrations). Indeed, the origin of
broader phonon peaks can be either due to a larger damping or
related to moderately dispersive phonons in FA-based HOP.

The observation of dispersionless phonon is opposed to what
has been previously predicted using density functional perturba-
tion theory in the frozen-phonon approximation in MA-based
HOPs25,45, where dispersive phonon branches were computed. It
is worth to emphasize that this lack of dispersion concerns both
longitudinal and transverse optical phonons. For FA-based HOP,
due to the large broadening still observed at low temperature,
slight phonon dispersion associated to crossing of branches inside
the three bundles cannot be completely ruled out.

Raman scattering spectroscopy has been performed as well in the
MAPB single crystal as a control experiment (see Methods). Figure 5
shows the comparison of the low-temperature (20 K) spectra of
MAPB, between INS on a thermal instrument and Raman scattering
(that agrees with a previous Raman scattering report54). Raman
spectra are recorded at very low q, whereas the INS experiments are
measured at a Bragg peak position Q = (0, 0, 2), both are therefore
probing optical phonons at the Γ point in the Brillouin zone. The
energy positions of the optical phonon modes here identified from
INS and Raman are consistent, especially the Raman mode bundles
around 5, 12 and 18 meV (inset). However, the modes below 9 meV
are significantly broader and less intense in INS than in Raman
scattering. This may be attributed to a poorer energy resolution
in INS for thermal TAS (1–2 meV) as compared to Raman
(0.125 meV) as well as to the different scattering efficiency between
both techniques. Figure 2 shows as well that each optical phonon
mode can be defined by almost the same energy for any Q-point of
the Brillouin zone, although mode broadening related to instru-
mental resolution is more important for neutron scattering than for
Raman scattering.

Optical phonons in the orthorhombic phase. Systematic low-
temperature INS experiments were performed with medium- and
high-energy resolutions from, respectively, thermal and cold
beams (see Methods). The optical phonon spectra (obtained at
either the M point or R point) for all four compounds are pre-
sent in Fig. 3. Each compound studied undergoes structural
distortions at low temperature, giving rise to atomic super-
structures at either or both the M and R points. At low tem-
perature, phonon spectra have been recorded at both momentum
points. As no noticeable difference can be observed between these
spectra (related to the lack of dispersion of the phonon modes), we
here report the phonon spectrum measured at the R point for
most compounds, except for FAPB, where it is shown at the
M point (see also Supplementary Fig. 3). As already stated, a
series of prominent optical phonon bundles of modes are
observed at different energy ranges. Each phonon mode is usually
accounted for by a DHO. Therefore, a model with a sum of
DHs convoluted by the spectrometer energy resolution is used to describe the neutron spectra, including a constant background (see Methods). The neutron spectra of Fig. 3 have been fitted using Eq. (1) and the obtained phonon energies are summarized in Table 1.

For a first analysis, we define three energy ranges where the different optical modes are located. These modes have been arbitrarily labelled as low (2–10 meV), medium (10–20 meV) and high (>20 meV). More specifically, in MAPB we find a low-energy mode at 5 meV; an intense peak at 11.6 meV followed by two smaller shoulders at 13.5 and 16.9 meV; and relatively broader bands at 23.2, 27.2 and 36.6 meV (Fig. 3a, b). These results match well with a previous INS experiment on an MAPB powder sample.

Similarly in MAPI, we obtained two low-energy modes at 2.3 and 3.8 meV, an intense peak centred at 11.7 meV surrounded by two smaller shoulders at 10.8 and 12.8 meV followed by two bundles at 15.5 and 18.3 meV and at higher energy range, other ones at 23.5, 28.5 and 38.3 meV (Fig. 3c, d). These again are directly comparable with previous INS studies and where two additional small modes in the 2–5 meV range (~3.1 and ~4.3 meV) were reported.

In FAPB, we note a broader central feature dominating the medium-energy range (Fig. 3c, f), while three distinct bundles can be identified at 5.5, 13.1 and 22.2 meV. These results on FAPB are in line with the ones observed in MAPB, although much broader phonon bundles are systematically observed in FAPB compared to the more numerous (and narrower) modes that appear for MAPB. These two compounds share the same space group (Pna2₁) at low temperature although the static structural distortions characteristic of the orthorhombic phase are smaller in FAPB. This may be connected to a different dynamics of the FA cation and its coupling to the perovskite lattice, by comparison to the MA cation (vide infra).

Finally, in FAPI—a sample requiring specific procedures and a proper storage to avoid the transformation to its yellow non-perovskite δ-phase at high temperature before cooling and, therefore, scarcely studied at such a low temperature in the literature—we could only perform measurements on the 4F2 cold neutron spectrometer (Fig. 3g). Nevertheless, in the accessible energy range, we detect large optical phonons at 3.9, 9.8 and ~5.1 meV. PL studies on single CQDs have identified exciton side-bands at 3.2, 7.8 and 15.4 meV, which match rather well with our TAS results on FAPI. The intermediate mode seemingly exhibits a slight discrepancy, but as reported in ref. 20, it undergoes temporal fluctuations under high-energy excitation, and is roughly spread between 7.5 and 12.5 meV. Again, our TAS results on FAPI show a significantly broad profile, as in FAPB.

According to nuclear magnetic resonance (NMR) measurements, the broader nature of the optical modes of FA-based compounds, compared to their MA-based counterparts, may be attributed to the fact that the FA reorientation in FA-containing materials is faster than that of MA in the MA-based perovskite, despite the fact that FA is larger than MA. This has an impact on the charge carriers lifetime in these compounds. In addition, the acoustic density of states is located at lower energy in FA-based compounds as compared to the MA based, thus leading to enhanced scattering between acoustic and optical phonons and related increased anharmonicity.

Table 1: Energies of the optical phonon modes measured at 5 K by inelastic neutron scattering (INS) and 20 K by Raman scattering.

| Energy (meV) | Mode character          | MAPB INS | Raman INS | MAPI INS | FAPB INS | FAPI INS |
|-------------|-------------------------|----------|-----------|----------|----------|----------|
| Low (0–5)   | PbX₃ rocking and bending| 5.1      | 4.1       | 4.8      | 5.1      | 5.5      | 3.9      |
| Medium (10–20) | PbX₃ stretching       | 11.6 | 11.9  | 12.6  | 13.5  | 10.8 ± 0.3 | 11.7 | 12.8 | 13.1 | 9.8 ± 0.3 |
| High (>20)  | Molecular librations   | 23.2 | 21.8   | 23.5  | 28.5 ± 0.6 | 22.2 |

Phonon lines (or bundles of modes for INS) are fitted by a sum of damped harmonic oscillators. Energies are given in meV. The error bars of the phonon energies obtained from the fit of INS spectra are 0.1–0.2 meV unless stated otherwise. The error bars of the phonon energies obtained from Raman scattering are 0.05 meV for low energy, 0.2 meV for the medium-energy range and 0.4 meV for the high-energy range. Mode characters are indicated as they are discussed in the main text.
spectroscopic measurements on MA\textsubscript{59} and, as a result, ascribe the observed side-bands to LO phonon modes related to bending (3.5 meV) and stretching (15 meV) motion of the PbI\textsubscript{3} cage, and to rigid-body motions of FA cations (11 meV). As far as the mode at \textasciitilde 37 meV is concerned, there is a consensus that it originates from organic molecular vibrations\textsuperscript{55,60,61}, although there is a debate about the exact nature of the involved atomic motions. Park et al.\textsuperscript{60} describe MA vibrations involving MA wagging, MA rotation and MA – MA stretch. Quartì et al.\textsuperscript{61}, as well as Druzbicki et al.\textsuperscript{55}, suggest a torsional MA vibration (also called disrotatory vibrations) that involves the terminal NH\textsubscript{3} and CH\textsubscript{3} moieties, which is also in line with the vibrational mode found near 300 cm\textsuperscript{−1} (i.e. 37.2 meV) in isolated MA calculations\textsuperscript{61,62}.

Anharmonic behaviour of lattice dynamics. As mentioned above, anharmonicity of the hybrid halide perovskite lattice is expected to play a considerable role in electron–phonon interactions. In Fig. 6 we show the temperature behaviour of the INS optical phonon spectra of the four compounds, up to 120 K. The anharmonicity manifests already at low temperatures well below RT, where optoelectronic devices and solar cells are usually operating. The increased phonon damping is observed in Fig. 6 above \textasciitilde 30 K, together with an increase of the low-energy quasi-elastic signal and a reduced phonon intensity. The weaker phonon intensity upon warming corresponds to a decrease of the phonon Debye–Waller factor, meaning the increase of atomic mean displacements. However, consistent DHO fitting of the temperature data has also proven difficult due to the strong anharmonic behaviour. These effects lead to a rather quick overdamping of certain phonon modes at temperatures as low as 80 K, making it difficult to properly assign the exact contribution of each phonon mode to the overall spectra at higher temperatures.

**Discussion**

The low-temperature INS (and Raman) optical phonon spectra in our four HOP single crystals reveal a number of characteristic features down to very low energy. It is now accepted that carriers scattering in HOPs is dominated by Fröhlich coupling between charge carriers and optical phonon modes. This phonon scattering is believed to be the key fundamental factor in establishing the intrinsic limit of the charge carriers mobility. More specifically, it has been recently suggested that this limit is set by the lower-energy LO modes (3–20 meV)\textsuperscript{58}. Therefore, the observed presence of such modes, common in all four compounds, seems to be the reason for the relatively low mobilities compared to classical inorganic semiconductors like Si and GaAs. Nevertheless, our experimental study clearly indicates that a missing ingredient of current attempt to reproduce the observed temperature dependence of charge carriers mobilities in HOPs is related to the underlying harmonic or quasi-harmonic assumptions of phonon modelling. Defining optical phonons as well-defined quasi-particles above 80–100 K is actually questionable according to the present experimental observations. Therefore, the apparent discrepancy between the experimental acoustic-like temperature dependence of carriers mobilities and the expected dominant process (Frohlich interaction) may be an unexpected consequence of the HOPs lattice softness.

Three different energy ranges have been identified in the spectra and gathered the modes or bundles of modes for each compound in three categories (a, b and c), as can be seen in Fig. 3. The following conclusions are drawn from our experimental data and based on earlier literature. Modes in the low-energy range (below 10 meV) are associated with vibrations of the PbX\textsubscript{3} network, mainly rocking and bending. As for the intermediate energy range, between 10 and 20 meV, a series of mutually coupled modes are observed which arise from both the organic and inorganic sub-lattices and, therefore, show a highly
that contain I− as opposed to Br−. Likewise, there is a significant decrease in energy in the medium/high-energy bundles when coming from MA-based compounds to FA ones. Reminding that the phonon energy is generally proportional to the square root of the inverse of atomic mass \(E \propto 1/\sqrt{M}\) and that FA+ and I− are heavier than MA+ and Br−, respectively, we can conclude that such trends agree with the attribution regarding the origin of the respective modes (see Supplementary Note 2). Actually, the relative shifts observed here, i.e., lower energy in FA+ and I−-based compounds when comparing with MA+ and Br−, are also consistent with the smaller elastic constants obtained in our previous INS study15.

In 3D hybrid perovskites, substantial interactions between the organic and Pb-halogen neighbouring networks are typically expected; however, besides being located in low-energy range, the optical lattice excitations measured here appear to be basically non-propagating (Figs. 2 and 4), exhibiting nearly no dispersion in the Brillouin zone, and thus contradicting existing reports on phonon simulations based on the harmonic approximation. Similarly to phonon modes in thermoelectric clathrates64, strong anharmonic phonon–phonon scattering processes may lead to a series of anticrossings flattening phonons dispersions. For instance, this strong hybridization between phonons would typically involve rattling of the organic molecule within the PbX cage. Furthermore, rattling phonon modes are generally associated with anharmonicity and lower thermal conductivities65,66 as it has been discussed through a crystal–liquid duality of HOPs67.

While the anharmonicity of halide perovskites leads to low-frequency acoustic phonons, characteristic of a soft lattice19, it occurs for optical phonons through an overdamped behaviour over the entire Brillouin zone at RT, and weakly dispersing branches at low temperature. The overriding anharmonic character of optical phonons specific to halide perovskites is most probably an important missing link for a proper account of the leading Fröhlich carrier–phonon interaction for this class of soft semiconductors. The size of the cation and the nature of the halogen are additional features known to strongly influence the softness of the lattice19. They also have a direct impact on the damping of the optical modes. Therefore, this suggests that the coupling between acoustic and optical phonons may play a role in the harmonicity of the lattice, besides non-linear coupling between optical phonons.

The lack of dispersion of such low optical modes overlapping with the upper part of the acoustic phonon dispersions is expected to be at the origin of several specific physical properties of HOPs. We first note a significant anharmonic behaviour that manifests itself in phonon overdamping at temperatures well below the ones used for operating optoelectronic devices and solar cells. Therefore, the current modelling of charge carriers mobilities based on a quasi-particle picture for low-energy optical lattice modes is questionable. Together with an apparent correlation between lattices softness (i.e. elastic constants) and optical phonon energy/frequency, our results point to the influence of acoustic and optical phonon coupling on the harmonicity of the lattice and the Fröhlich interaction between charge carriers and optical phonons. Moreover, this coupling occurs as well in the anharmonicity of the upper part of the acoustic phonon branches.

In conclusion, we present here an extensive comparison of optical phonon excitations in four different HOP compounds. INS and complementary Raman scattering measurements revealed various features of the low-temperature phonon spectra, which we have assigned to possible structural vibrations. The dispersionless nature of these optical modes is a first characteristic feature of HOPs. The optical phonons overdamping upon warming for temperatures as low as ~80 K demonstrate the strong anharmonicity in these materials. We believe that the following experimental report could serve as a solid base in future theoretical calculations and modelling for improved mode assignment and understanding of the electron–phonon interactions, especially for FA-based compounds where measurements of their optical phonon spectrum have been lacking.

**Fig. 7** Main phonon bundles comparison. We illustrate the relative energy positions of the optical phonon bundles \(a, b\) and \(c\), between MAPB, FAPB, MAPI and FAPI. The figure highlights an obvious influence of the molecular and/or the halide component on the respective vibrational modes and the associated optical phonon energy.
Neutron wavelength of cold TAS goes from ~0.2 to 0.4 meV for an energy transfer ranging from 0 to 3 of the main text correspond to the polarized spectra (i.e. scattered light // [100] directions [001] and [110] were within the horizontal plane, except for FAPB which were mounted in a scattering plane such that the high symmetry reciprocal polarization was parallel to the [110] direction and the results shown in Figs.2 and parallel to the [001]-cubic crystallographic direction of the sample. The incident spectra have been obtained in the backscattering geometry with the incident light 647 nm was tightly focused into the sample with a ×100 objective. In order to avoid under an optical microscope and a T64000 Jobin-Yvon double pass diffractometer onto a vanadium sheet also results in additional incoherent elastic scattering.

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172 and https://doi.org/10.5291/ILL-DATA.TEST-2912, respectively. The rest of the data request.

Data availability

Data collected on IN12 and IN5 are available at https://doi.org/10.5291/ILL-DATA.7-02-172 and https://doi.org/10.5291/ILL-DATA.TEST-2912, respectively. The rest of the data that support the findings of this study is available from the corresponding authors upon request.

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Raman scattering spectroscopy

Raman scattering in MAPb has been performed under an optical microscope and a T64000 Jobin-Yvon double pass diffractometer working with 18000 trts/mm gratings. The radiation of a krypton laser emitting at 647 nm was tightly focused into the sample with a ×100 objective. In order to avoid photo-induced effects, the incident power was always kept lower than 2 mW. The spectra have been obtained in the backscattering geometry with the incident light parallel to the [011]-cubic crystallographic direction of the sample. The incident polarization was parallel to the [110] direction and the results shown in Figs. 2 and 3 of the main text correspond to the polarized spectra (i.e. scattered light // [110]).

Experimental data fitting

The experimental TAS spectra can be described by a sum of phonon terms on top of a flat background (BG). Each phonon is typically accounted for by a DHO. The neutron spectra can then be described by the following expression:

\[ I(Q, \omega) = BG + \sum_j \left( -\frac{h\omega}{k_B T} \right)^2 \int \frac{d^4 \mathbf{p}}{(2\pi)^3} \left( \frac{\omega_j}{(\omega^2 - \omega_j^2)^2 + (\omega_j \Gamma_j)^2} \right) \]

where \( \omega \) represents the energy, \( \Gamma_j \) the damping and \( F(\mathbf{Q}) \) the dynamical structure factor of the \( j \)-th phonon. The number of modes depends on how many peaks are visible. The prefactor of DHOs is the phonon population factor. This full scattering function, \( I(Q, \omega) \), is next convoluted by the 4D spectrometer resolution function of the instrument as explained in ref. 68, and used to fit the experimental data. The presence of several phonon lines in a given phonon bundle would have the effect to increase the damping when fitted by a DHO due to the energy resolution function.

Methods

Sample preparation

Single crystals of four different hybrid lead halide perovskites have been grown by the inverse temperature crystallization method (see Supplementary Note 3). The perovskite compounds are MAPbBr\(_3\), (MAPB), FAPbBr\(_3\), (FAP), MAPbI\(_3\), (MAPI), and a-FAPbI\(_3\), (FAPI). MA and FA stand for MA and FA molecules, respectively. All single crystals of typical size of 200 mm\(^2\) for all compounds (except for FAP where only a volume of ~50 mm\(^3\) could be achieved) were synthesized at the Institut des Sciences Chimiques de Rennes (ISCR).

INS spectroscopy

INS measurements were conducted using both triple-axis spectrometers (TAS) and time-of-flight spectrometers (TOF). On all TAS instruments, monochromators and analysers were made from the 002 reflection of pyrolytic graphite (PG). Cold (below ~15 meV) and thermal TAS have been used to cover the full energy range of the phonon spectrum in the three hybrid lead halide perovskites: MAPbI\(_3\), MAPI, MAPbF\(_3\), and a-FAPbI\(_3\). The energy resolution of cold TAS goes from ~0.2 to 0.4 meV for an energy transfer ranging from 0 to 3 meV. For the thermal TAS (1T) it goes from ~1 to 3 meV for an energy transfer ranging from ~0 to 40 meV.

In MAPI, mapping of the phonon spectrum has been performed using the TOF instrument INS at the Institut Laue-Langevin (ILL) in Grenoble with an incident neutron wave vector of \( \mathbf{k}_i = 1.55 \) Å\(^{-1}\) utilized with a beryllium (Be) filter to remove high-order neutrons in the beam. In addition for the measurement on IN12, a velocity selector was used to remove neutrons with high-order harmonics from the incident beam. At the thermal TAS 1T at LBL, a constant final neutron wave vector of \( \mathbf{k}_f = 2.662 \) Å\(^{-1}\) was used with a pyrolytic graphite filter to remove neutrons with high-order harmonics. The energy resolution of cold TAS goes from ~0.2 to 0.4 meV for an energy transfer ranging from 0 to 15 meV. For the thermal TAS (1T) it goes from ~1 to 3 meV for an energy transfer ranging from ~0 to 40 meV.

Data availability

Data collected on IN12 and IN5 are available at https://doi.org/10.5291/ILL-DATA.7-02-172 and https://doi.org/10.5291/ILL-DATA.TEST-2912, respectively. The rest of the data that support the findings of this study is available from the corresponding authors upon request.
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Author contributions
P.B., C.K. and J.E. conceived and supervised the project; A.C.F. and P.B. performed the INS experiments at LBL SACLAY and ILL Grenoble with support from A.L.; S.R. and J.O. participated in the INS experiments at ILL as the local contacts for IN12 and IN5, respectively; A.C.F. and P.B. analysed the neutron data; B.H. and B.R. performed the Raman scattering experiments and analysed the Raman data; S.P. synthesized the perovskite single crystal samples with support from S.C.; J.E. contributed to the analysis and discussion of the results. A.C.F., P.B. and J.E. wrote the manuscript with further contributions from all authors. All authors contributed to this work, read the manuscript and agree to its contents.

Competing interests
The authors declare no competing interests.

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