Polarization Dressed Light Propagation in Lead Halide Perovskites

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The ultrafast polarization response to incident light and ensuing exciton/carrier generation are essential to outstanding optoelectronic properties of lead halide perovskites (LHPs). While light propagation is pivotal to optoelectronics and photonics, little is known about this process in LHPs in the vicinity of the bandgap where stimulated emission, polariton condensation, superfluorescence, and photon recycling may take place. Here we develop two-dimensional optical Kerr effect spectroscopy to energetically dissect broadband light propagation and dispersive polarization responses in LHPs. For both hybrid CH₃NH₃PbBr₃ and all-inorganic CsPbBr₃ perovskites, we find strong nonlinear mixing of anisotropically propagating light fields, resulting in an oscillatory polarization response near the bandgap. We quantify dispersion anisotropy and show how nonlinear polarization dynamics vary dramatically with energy. In addition to revealing highly dispersive anisotropic light propagation and strong instantaneous polarizability, this study establishes the origin of ultrafast Kerr responses in single crystal LHPs near the optical bandgap.

LHPs have emerged as an excellent material system for optoelectronics with exceptionally high efficiencies(1). In many of these applications, light propagation right below the bandgap is essential. In LHP nanowire lasers, the lasing modes are known to be red-shifted from excitonic resonances due to efficient coupling to plasmon emission(2). In LHP-based exciton-polariton devices, light-matter coupling red-shifts the hybrid state on the lower polariton branch(3–7). In

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LHP quantum dot superlattices, coherent superfluorescence is red-shifted from incoherent fluorescence(8). Propagation of sub-gap light is known to boost the efficiency of LHP photovoltaic cells and light-emitting devices by the so-called “photon recycling”, i.e., iterative photon emission and re-absorption events(9–12). Light propagation also strongly influences the function of other LHP photonic devices(13–15). A key feature of light propagation near the bandgap is its strong energy dependence, as is obvious from the classic Lorentzian model for the dielectric function near an optical resonance(16). However, most photophysical experiments probing carrier/exciton formation, screening, and scattering, as well as nonlinear optical responses, employ ultrashort laser pulses with inherently low energy resolution. Here, we develop a Fourier-transform based laser spectroscopy technique, 2D-OKE, to investigate light propagation in LHPs directly in the time domain with superior energy resolution near the bandgaps.

The 3rd order nonlinear electric polarization $P^{(3)}$ serves as an in-situ probe of the material’s polarizability and governs the ultrafast macroscopic response to an incident light field. This has been demonstrated in a variety of light-matter interactions, such as OKE and magneto-optical Kerr-effect (MOKE)(17, 18), coherent phonon excitation(19–21), and four-wave mixing phenomena in general(16). OKE has been applied previously to lead halide perovskite crystals; the liquid-like response with excitation far from bandgap has been attributed to phonon disorder(22) and exponential decay response with above gap excitation to polaron formation(23). Interestingly, for excitation energy close to the bandgap in CsPbBr$_3$ at room temperature, time-resolved OKE reveals complex oscillatory features. Such oscillatory responses are often attributed to coherently excited collective-modes, such as phonons(20, 21, 24) or magnons(25, 26), but the strong dependence of the oscillatory frequency on pump photon energy in OKE from CsPbBr$_3$ seems to contradict the coherent phonon interpretation(23). In this work, we unveil a unified source for polarization responses in LHPs, dissect light propagation close to electronic transitions, and discover exceptionally strong nonlinear mixing of anisotropically propagating light fields in LHPs.

**Two-dimensional optical Kerr spectroscopy.** We develop 2D-OKE spectroscopy to probe light propagation and to energetically resolve nonlinear polarization responses in LHPs. In analogy to 2D electronic state spectroscopy(27), we use a phase-stable double pump pulse sequence to implement 2D-OKE, Fig. 1a. A pulse shaper generates a collinear and identical pump pulse pair ($h\nu_1 = 2.25$ eV, 30 fs pulse duration) with the same polarization, a controllable time
delay \( \tau \), and precise phase difference modulated shot by shot. We additionally implement a standard 4-sequence phase cycling scheme to discriminate against incoherent absorption and scattering background, and a rotating frame to increase the pump frequency resolution while maintaining rapid data collection\(^{27, 28}\) (see Methods, Supporting Information 1.2-1.5). Fourier transform with respect to \( \tau \) provides precise pump-energy resolution, particularly near the bandgap where highly dispersive linear and nonlinear optical responses are expected. A successive below-bandgap probe pulse \((h\nu_2 = 1.55 \text{ eV}, 45 \text{ fs pulse duration})\), delayed by time \( t \) with respect to the later pump pulse, monitors the anisotropic 3rd order polarization response by a transient birefringence \( S(t, \tau) \). A balanced detection further discriminates against isotropic transmission changes, e.g. transient absorption. We use solution grown macroscopic single crystal CsPbBr\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) (MAPbBr\(_3\)) with thicknesses in the range of 10 - 800 \( \mu \)m (see Supporting Information 1.1 & Fig. S1).

**Figure 1** Experimental scheme and 1D OKE results. **a**, Experimental Scheme 2D OKE: Two phase-controlled, co-propagating pump pulses induce a nonlinear polarization response while interacting with a time-delayed probe pulse; traced via transient birefringence \( S(t, \tau) \) as a function of pump-pump \( \tau \) and pump-probe delay \( t \). **b**, \( S(t, \tau) \) precisely monitors anisotropy and dispersion of light propagation, dominated by nonlinear \( \chi^{(3)} \) mixing of perpendicular pump field projections \( E_x^p \) and \( E_y^p \) while interacting with - and propagating with respect to - the probe field \( E_y^{pr} \). **c**, Conventional ultrafast OKE in CsPbBr\(_3\) at 295 K. Single pulse (1D) excitation \((h\nu_p = 2.25 \text{ eV})\) exposes polarization dynamics with three distinct frequency regions (circle numbers) in the vicinity of the optical band gap. **d**, Pseudo color (FT amplitude) representation from a moving-window Fourier analysis of the OKE signal in **c**, unveiling a highly nonlinear frequency evolution.

**Fig. 1b** illustrates how time resolved OKE probes light propagation through a crystal with birefringence characterized by an anisotropic refractive index, \( \Delta n_0(\nu) \), as is the case in the
orthorhombic phases of CsPbBr₃ and CH₃NH₃PbBr₃. The pump pulse (red) entering the crystal decomposes into two orthogonal fields with fast (blue) and slow (orange) propagating velocities. The orthogonal pump polarizations and the time-delayed probe pulse non-linearly mix to yield the OKE signal. In addition, the highly dispersive nature near the bandgap is reflected in the pump-probe walk-off due to velocity mismatching and in the temporal spread of the pump pulses due to group velocity dispersion (GVD).

RESULTS

Conventional optical Kerr effect. Before presenting 2D-OKE, we establish the complexity of single pump-pulse (1D) OKE experiments with superior signal-to-noise ratio from the use of balanced detection. The 1D-OKE response from CsPbBr₃ at room temperature with close-to-gap excitation ($h\nu = 2.25$ eV), Fig. 1c, shows a clear oscillatory signal. The initial high frequency response of 5.3 THz is beyond the frequency range of any known lattice mode of this crystal (30–32). We can further exclude stress or photodoping effects that are unable to increase a phonon mode to ~5.3 THz (see SI). Moreover, a time frequency analysis, Fig. 1d, reveals a stark frequency jump from ~5.3 THz to ~2.5 THz (region 2) at ~ 1.5 ps. Our simulations show (Supporting Information 2.2) that such strong phonon-phonon coupling (33, 34) would require parametric down conversion (35, 36) with unprecedented large nonlinear coupling coefficients as compared to those known in other solids (34). The high frequencies ~5.3 THz is also not possible from changes to phonon frequency in the presence of photo-doped carriers (Supporting Information 2.3).

2D-OKE in CsPbBr₃. We now turn to 2D-OKE to establish polarization-dressed light propagation near the bandgap as origin of the oscillatory signal. Figs. 2a and 2c shows the excitation energy ($E_{ex}$) dependent transient birefringence as a function of pump-probe delay $t$ for CsPbBr₃ at $T = 295$ K and 92 K, respectively. The energy-time domain 2D OKE signal (pseudo color) is obtained by the real part of the signal’s Fourier transform (FT) with respect to the pump-pump delay $\tau$ (see Fig. S2 for time-time-domain data). Prominently, the signal exhibits strong oscillatory features decreasing in frequency with increasing $E_{ex}$.

The 2D-OKE in Fig. 2a or 2c exhibits an underlying fan-like superstructure (region 1), showing the strong dependence of oscillatory frequency ($\nu_{OKE}$) on pump photon energy ($h\nu_p$). We quantify
the anti-correlation by carrying out a second Fourier transform with respect to the pump-probe delay $t$. At 295 K, Fig. 2b, the anti-correlation between $v_{OKE}$ and $h\nu_p$ is represented by one dominant branch while at the lower temperature of 92 K, Fig. 2d, multiple branches with different slopes are resolved. As we show below in modeling, the strong anti-correlations of $v_{OKE}$-$h\nu_p$ are signatures of the polarization-dressed light propagation in the highly dispersive and anisotropic region near the bandgap. A particularly revealing feature in the 2D-OKE spectra (Fig. 2a or 2c) is the sudden stop of the fan-like oscillatory superstructure with a bump-like feature (region 2), followed by long-lived low frequency oscillation (region 3). Such sudden change in oscillatory frequency is unphysical for coherent phonons, but is consistent with the dispersive propagation as detailed in the modeling below. Supporting this assignment of light propagation, we find that the probe delay time, $t_1$ (blue markers), when region 2 occurs is proportional to the thickness of the crystal (Fig. S8). Affirming the reliability of the 2D-OKE method based on projection slice...
theorem(27), we show in insets above each panel in Fig. 2 that the $E_{\text{ex}}$-integrated 2D-OKE traces (red) are in excellent agreement with the single pulse excitation 1D-OKE (blue).

2D-OKE in MAPbBr$_3$. The CsPbBr$_3$ crystal at either 295 K or 92 K is in the orthorhombic phase, which is anisotropic and thus birefringent(37). We find that the appearance of oscillatory signatures in 2D-OKE requires the presence of birefringence, as we show for the hybrid CH$_3$NH$_3$PbBr$_3$, which is in the non-birefringent cubic phase at room temperature (295 K) and the birefringent orthorhombic phase below 150 K(38). In the room temperature cubic phase, Fig. 3a, we observe a strong quasi-static Kerr response, which broadens towards the electronic band gap ($E_g \sim 2.32$ eV at 295 K). The signal vanishes towards the bandgap due to a drastic decrease in penetration depth and therefore decreased effective probing volume. The 2D-OKE also unveils an abrupt decay of the Kerr signal, which is averaged out and thus hidden in conventional 1D-OKE experiments due to the lack of energy selectivity (Fig. 3a, upper inset). Fourier transform with respect to pump-probe delay $t$ shows a broad feature peaked at zero frequency. In stark contrast to results at room temperature, 2D-OKE in the low temperature orthorhombic phase ($Pnma$) of CH$_3$NH$_3$PbBr$_3$,
**Fig. 3c**, shows a strong oscillatory signal, which is similar to responses in the orthorhombic phase of CsPbBr$_3$ in **Fig. 2**. Fourier transform of the 2D-OKE with respect to the pump-probe delay $t$, **Fig. 3d**, again reveals the anti-correlation between $\nu_{\text{OKE}}$ and $\nu_{\text{ex}}$ in two apparent branches for CH$_3$NH$_3$PbBr$_3$ in the orthorhombic phase, with $\nu_{\text{OKE}}$ spanning one order of magnitude, from $\sim$ 1 THz to $\sim$ 10 THz.

**Kerr propagation model.** For both CsPbBr$_3$ and CH$_3$NH$_3$PbBr$_3$ in the orthorhombic phase, the exceptionally large spread in frequency and the abrupt decay at $t_1$ are unphysical for coherent phonons or other collective modes. As suggested in early ultrafast four-wave mixing (FWM) studies, light propagation can strongly affect FWM signals and especially 2D spectroscopy line shapes in isotropic media such as dense gases(39, 40), solutions(41) or cubic semiconductors(42). In LHPs, in contrast, anisotropic light propagation seems to play a dominant role. Therefore, we consider electronic polarization and propagating light fields in birefringent single crystals by taking into account the influence of spectral dispersion, static birefringence and nonlinear mixing via the 3$^\text{rd}$ order nonlinear susceptibility $\chi^{(3)}$. We trace the propagation of all three interacting light fields that mix via $\chi^{(3)}$ to produce new polarization components:

$$P_j^{(3)}(t,z) = \epsilon_0 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' \chi_{jklm}^{(3)}(t,t',t'',t''',z) E_k^P(t',z) E_l^P(t'',z) E_m^P(t''',z)$$

with probe field $E^P$, pump fields components $E^P$, vacuum permittivity $\epsilon_0$ and collinear propagation along $z$. To model the instantaneous Kerr response, we set $\chi_{jklm}^{(3)}$ as constants and independent of frequency $\nu$, whereas the equilibrium linear refractive index tensor $n_0(\nu)$ exhibits a strong dispersion near the bandgap and static birefringence $\Delta n_0(\nu)$ in the orthorhombic phase (see Supporting Information 1.6). This includes pump-probe walk-off from group velocity mismatch (group refractive indices: $n^p_g(\nu) > n^p_g$) and the temporal spread of the pump pulses, both due to GVD.

**Isotropic cubic phase.** For cubic ($Pm3m$) CH$_3$NH$_3$PbBr$_3$ at room temperature with $E^P$ parallel to a crystal axis $\hat{y}$, we find that the dominating contribution is the nonlinear mixing term of a single pump pulse with itself via $\chi^{(3)}_{xyxy} E^P_x E^P_y$ while propagating through the depth of the sample, shown in false colors in **Fig. 4a**. To calculate the cumulative field emitted by the local nonlinear polarizations $P_x^{(3)}(z)$ after the sample, we integrate the nonlinear mixing term along...
Figure 4 | Polarization dressed light propagation simulation. 

(a) Spatiotemporal calculation of the instantaneous nonlinear mixing term \( \chi_{xxx}^{(3)} E_x(t', z) E_y^{p}(t',z) \) (false colors) for the isotropic cubic phase. Fields propagate in space \( z \) (top to bottom) and real time \( t' \) (x-axis). At the end of the sample (320 µm), they get partially reflected and propagate in opposite direction. Probe pulse trajectories are shown as green lines. Pump pulse GVD and pump-probe walk-off are clearly resolved by different slopes. 

(b) Corresponding simulated 2D OKE signal (thickness \( d = 835 \) µm, probe polarization \( \phi = 0° \)) in full analogy to the experiments; including double pulse excitation, integrated nonlinear mixing term along each probe pulse trajectory and consecutive signal projections by balanced detection. 

(c) 2D OKE Frequency map from FT of b. Similar to a, b, c, but including both pump and probe birefringence for the orthorhombic phase (thickness \( d = 480 \) µm for f, g; probe polarization \( \phi = 15° \)). Experimental features agree very well with simulated 2D OKE spectrum in e: Main response branch from Fig. 2d (green markers), expected co- and counterpropagating features due to pump birefringence (dashed lines) and probe birefringence (dash-dotted lines).
for signal projections by the balanced detection. Adding a second pump pulse with delay $\tau$ to this simulation (including phase cycling and using a rotating frame) allows for the modeling of the 2D OKE signal (see Supporting Information 1.6). The simulation result in Fig. 4b, reproduces all features of the experimental OKE response in the cubic phase CH$_3$NH$_3$PbBr$_3$ in Fig. 3a. The fan-like OKE response towards the bandgap (region 1) results from the strong GVD and walk-off of each individual nonlinear polarization component, both resolved with an unprecedented meV excitation energy resolution by the 2D-OKE method. The pronounced bump-like feature (region 2) stems from the interference of the pump pulse with itself at the backside of the sample (see Fig. 4a). The 2D frequency map in Fig. 4c is dominated by a broadened zero-frequency feature, in agreement with the experimental frequency map in Fig. 2c.

**Birefringent orthorhombic phase.** For CsPbBr$_3$ and CH$_3$NH$_3$PbBr$_3$ in the orthorhombic phase, the key finding is the strong oscillatory signature, which fans out towards the bandgap. In the birefringent crystal, we consider pump field projections on the fast and slow axes with refractive indices $n_x$ and $n_y$, respectively; the birefringence is quantified as $\Delta n_0(\nu) = n_x(\nu) - n_y(\nu)$. The corresponding projections $E^p_x$ and $E^p_y$ propagate with different velocities through the crystal while nonlinearly mixing via $\chi^{(3)}_{xxxyy}E^p_x E^p_y E^p_{y}^*$. The simulation results in Fig. 4d unveil a spatiotemporally oscillating nonlinear mixing term (phase grating) in addition to the effects discussed above for the cubic phase. By further including the birefringence effect of the probe field ($E^{pr}$ rotated from $\hat{y}$ by angle $\phi$) and by a parametrization procedure for the group index mismatch $\Delta n_g(\nu)$ from $t_1$ (see Supporting Information 1.6), the model result in Fig. 4g reproduces the complex 2D-OKE signal of the orthorhombic phase for both materials. Thus, we fully decoded the complex Kerr signals in LHPs: The initial high-frequency oscillatory signal (region 1) is due to the instantaneous nonlinear polarization from propagating pump pulse projections mixing with each other (via $\chi^{(3)}$), traced by a co-propagating probe pulse. The intermediate frequency region 2 stems from the additional spatiotemporal pump interference pattern at the backside of the sample, producing a bump-like structure at the end of high-frequency phase fronts. Lastly, the long lived low-frequency signal (see Figs. 1c, and 2a) is caused by the same effects of the counter-propagating pump reflection (region 3). Additional branches (e.g. upper branch Fig. 4g) originate from additional polarization bands due to significant probe birefringence ($\phi \neq 0$). The two weaker branches in Fig. 2d most likely arise from higher order mixing terms and may contain further structural information.
SUMMARY

The agreement between experimental data and modeling establishes 2D-OKE as a quantitative probe of the highly dispersive and anisotropic light propagation in the vicinity of the bandgaps of CsPbBr3 and CH3NH3PbBr3. We can directly extract absolute values for the group index mismatch $\Delta n_G(\nu)$, Fig. 5a, and dispersive birefringence $\Delta n_0(\nu)$, Fig. 5b, with a precision of $10^{-3}$ in the latter and a wavelength resolution of $\sim 0.5$ nm for any given experimental geometry (see Supporting Information 1.6). We reveal a doubling of the birefringence $\Delta n_0(\nu)$ by cooling to 92 K, indicating anisotropic structural changes within the orthorhombic phase. Thus, we trace how anisotropic light propagation is strongly influenced by position and steepness of the optical bandgap(31), as seen from different dispersion curvatures of group index mismatch and birefringence at 92 K compared to 295 K, even in the same structural phase (Fig. 5). This precise knowledge of polarization dependent group velocities and birefringence is essential to dispersion engineering of polaritons and their degeneracy in Bragg cavities(6, 7, 43) or the design of perovskite nanocrystal lasers(2, 44) and photonic devices(15, 45).

The dominant oscillatory signal in the orthorhombic phase reveals a surprisingly strong and substantial nonlinear effect due to cross polarized (off-diagonal) $\chi^{(3)}$. For comparison, we carry out studies on two polar semiconductors with similar band gaps, the isotropic ZnTe and the birefringent GaSe, both prototype nonlinear optic crystals(46). Whereas the quasi-static signal of ZnTe compares well to the nonlinear response of cubic CH3NH3PbBr3, hints of the oscillatory cross polarized $\chi^{(3)}$ mixing effects in GaSe only occur under very specific phase matching angles.
and with much weaker signal to noise ratio (see Fig. S6). Such dominant nonlinear mixing terms in CsPbBr₃ and CH₃NH₃PbBr₃ mean that intense light fields travel dressed with a nonlinear polarization cloud in the near bandgap region. This adds to the exceptional physical properties of LHPs and confirms their previously suggested applications for nonlinear photonics(45, 47).

Our results provide a unified picture of Kerr-responses near the bandgap of semiconductors in general and LHPs in particular. The 2D method provides meV energy-resolution and fs time-resolution in OKE responses; the resulting 2D-OKE spectral signatures generally contain information about dispersive birefringence, group velocity dispersion, and bandgap absorption. This technique may allow us to distinguish transient birefringence signals of phonons, spin dynamics, or other collective modes, from nonlinear light propagation phenomena in various fields of ultrafast spectroscopy. In the case of LHPs, the contrast in the Kerr responses from CsPbBr₃ and CH₃NH₃PbBr₃ at room temperature for below gap excitation may be dominated by polarization dressed light propagation in different crystallographic phases rather than structural dynamics suggested earlier(22, 23). Moreover, our findings represent a bulk analogy to polarization beats in optical fiber communication, which are used for fast multiplexing via high bandwidth polarization switching(48). Thus LHPs may find applications in integrated photonic devices, e.g., polarization based light modulation or the generation of Kerr-frequency combs in spatially tailored LHP structures, e.g. toroidal microresonators(49). Understanding the Kerr polarization states in LHPs may further pave the way to studies on non-classical states of light in this material class(50).

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**Author contributions.** XYZ, SFM, and PPJ conceived and initiated this work. SFM designed and developed new experimental methods. SFM, PPJ, FW, LH, MC and YL carried out the experimental measurements. LH developed model and carried out 2D-OKE simulations. FW grew the crystals. DMJ, FdA, EM and DM carried out phonon simulation. SFM, LH, FW and PPJ carried out data analysis. SFM and XYZ wrote the manuscript. All authors read and commented on the manuscript.

**Supporting Information.** Methods and Extended Data.

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Polarization Dressed Light Propagation in Lead Halide Perovskites

-- METHODS & EXTENDED DATA --

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1. Methods

1.1. Sample preparation

For the synthesis of CsPbBr₃ single crystals, the precursor solution (0.38 M) was prepared by mixing cesium bromide (CsBr, Aldrich, 99.999%) and lead bromide (PbBr₂, Aldrich, ≥98%) with molar ratio of 1:1 in dimethylsulfoxide (DMSO, EMD Millipore Co., anhydrous ≥99.8%). After being fully dissolved, the solution was titrated with methanol (Alfa, 99.9%) until the yellow-orange precipitate did not re-dissolve. Then it was further stirred at 50 °C until a yellow permanent suspension formed. Before the crystal growth, the precursor solution was filtered by a PTFE filter with 0.22 µm pores. Methanol was used as the anti-solvent for slow vapor diffusion and the crystal growth was quenched when the desired morphology was achieved¹. A similar method was used for the preparation of MAPbBr₃ single crystals². The precursor solution (0.45 M) was formed by adding methylammonium bromide (MABr, Dyesol, 98%) and PbBr₂ with 1:1 molar ratio into N,N-dimethylformamide (DMF, Aldrich, anhydrous 99.8%). A mixture of dichloromethane (CH₂Cl₂, Aldrich, ≥99.5%) and nitromethane (Aldrich, ≥96%) was used as the anti-solvent for MAPbBr₃

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crystal growth. All solid reactants were dehydrated in a vacuum oven at 150 °C overnight and all solvents were used without further purification.

1.2. Experimental design

We developed two-dimensional Kerr effect (2D-OKE) spectroscopy based on three major experimental parts: 1.) A Ti:sapphire regenerative amplifier laser system followed by a home-built noncollinear optical parametric amplifier (NOPA); 2.) A pulse shaper based on a transmissive acoustic optic modulator (AOM); and 3.) Balanced detection setup with single-shot data acquisition (DAQ) fully synchronized to the AOM mask sequence. The latter two experimental parts will be explained in separate Method sections.

The ultrashort laser pulses (energy of 0.8 mJ, center wavelength 800 nm, duration of 30 fs, and a repetition rate 10 kHz) were delivered by a Ti:sapphire regenerative amplifier (modified KMLabs Wyvern). These amplified and compressed pulses were split to serve as pump and probe pulses. The major part was used for frequency conversion in a homebuilt NOPA, which is a one stage BBO-based OPA pumped by the second harmonic of the fundamental pulse (center wavelength of 400 nm). The output of the NOPA was optimized for a center wavelength of 550 nm (photon energy of 2.25 eV) and a broad spectrum expanding partly beyond the bandgap of CsPbBr3 (~ 2.35 eV), spanning over 55 nm (230 meV) in full width (see Fig. S3).

The pulse energy incident on the sample was 35 ± 5 µJ per pump pulse pair after double pulse generation with the pulse shaper and traversing through a motorized delay stage, focusing optics and polarization optics (broadband waveplate and broadband thin film polarizer). Active dispersion compensation by the pulse shaper was optimized in order to achieve a pulse duration of 30 fs (per single pump pulse), as verified by frequency-resolved optical gating. The probe beam was focused to a diameter of 30 µm under normal incidence and attenuated to a pulse energy of less than 200 nJ on the sample. The pump beam was overlapped with the probe focus under a small angle < 5° with respect to the probe beam. The pump beam diameter of 160 µm on the sample was chosen to be significantly larger than the probe beam focus to ensure a homogeneous lateral excitation profile.
For the 1D-OKE excited by a single pump pulse (Figs. 1c,d, S9 and S10), the pulse shaper was bypassed, and the NOPA was optimized for more narrow band spectra with central wavelength of 550 nm (photon energy of 2.25 eV, pulse duration < 30 fs) with spectral widths of < 25 nm.

1.3. Pulse and phase shaping

In contrast to previous probe energy resolved OKE, excitation energy resolved 2D-OKE requires a double pulse excitation scheme. To accomplish this, we generated double pulses from the NOPA output pulse by using an AOM based visible pulse shaper (PhaseTech QuickShape Visible). The phase shaper utilizes the first order diffraction from an acoustic wave, which is used as a phase mask. The phase mask pattern was generated by an arbitrary waveform generator (AWG). The AWG output signal was synchronized to the arrival of the femtosecond laser pulse at the AOM. After each laser shot the next mask of a pre-defined mask sequence was send to the AOM. The phase of each spectral component in the pulse can be modified independently, thereby allowing the creation of double pulses with arbitrary relative phases. Compared to interferometer-based double pulse generation, the use of a pulse shaper exhibits several advantages.

First, compared to a mechanical delay stage the pump-pump delay \( \tau \) can be controlled more precisely, without mechanical jitter, and much faster on a shot-to-shot basis. This enables a rapid scan approach to avoid laser drifts within one full pump-pump delay scan. Even with phase cycling, where every pump-pump delay step consists of 4 different AOM phase masks (see below), in our experiments, a typical pump-pump delay mask sequence of 904 sequences (226 delays) was acquired in 90.4 ms due to single shot detection. Within this time frame (<100 ms) thermal fluctuations of the NOPA and regenerative amplifier are negligible.

Second, the possibility of phase cycling is a unique advantage of using a pulse shaper. Due to the collinear propagation and parallel polarization of the two pump pulses \( E_1^P \) and \( E_2^P \), it is important to separate the nonlinear 2D signals resulting from a coherent interaction of \( E_1^P \) and \( E_2^P \) from linear and single-pump signals (e.g. transient absorption, scattering or OKE caused be \( E_1^P \) and \( E_2^P \) separately). This was achieved by phase cycling, which is implemented by subtracting two signals \( S(\tau, \Delta \phi = 0) - S(\tau, \Delta \phi = \pi) \) at the same pump-pump delay \( \tau \), where \( \Delta \phi \) is the phase
difference between the to pump pulses. We used the following 4-sequence phase cycling scheme, which is common in 2D spectroscopy4:

\[
\bar{S} = S(\phi_1 = 0, \phi_2 = 0) - S(\phi_1 = 0, \phi_2 = \pi) + S(\phi_1 = \pi, \phi_2 = \pi) - S(\phi_1 = \pi, \phi_2 = 0). 
\]

Additionally, we added a rotating frame with frequency \(\omega_F\) by an additional phase factor \(e^{-i\tau\omega_F}\), which reduced the number of sampling points and increased the frequency resolution in the frequency window of interest\(^4,5\). Both rotating frame and phase cycling was automatically implemented by the commercial phase shaper control software (PhaseTech QuickControl).

Importantly, we carefully excluded artifacts related to phase cycling and rotating frame by performing a single pulse excitation (1D) experiment for every 2D-OKE data set. In the single pulse excitation case, we use exactly the same optical path through the phase shaper to account for dispersion and divergence effects. The only difference is the AOM mask sequence, which is simply used as a 5 kHz chopper (masks “1” and “0”). No phase cycling or rotating frame is applied in this chopper mode. The 1D pump-probe delay \(\Delta \tau\) is introduced by a conventional mechanical delay stage. As required, for all 2D-OKE data sets, the \(E_{\text{ex}}\)-integrated transient birefringence signal agrees with the single pulse excitation (1D-OKE) signal (see Figs. 2 and 3).

1.4. 2D Data analysis and experimental parameters

To extract the excitation frequency dependence of the observed transient birefringence, we perform a Fourier transform (FT) of the 2D data set along the pump-pump delay \(\tau\) as commonly employed in Fourier transform infrared (FTIR) spectroscopy and 2D electronic spectroscopy: Our collinear pump-pump geometry based on a pulse shaper allows for simultaneous phase matching of rephasing and non-rephasing electronic coherences and therefore adds up the corresponding signal contributions\(^6\). We obtain the oscillatory birefringence as a function of photon energy by taking the real part of the FT with respect to the pump-pump delay \(\tau\), as shown in Figs. 2a,c and 3a,c. The perfect agreement of the excitation energy integrated 2D-OKE and the equivalent single pulse excitation experiment (1D-OKE), e.g. in Fig. 2a (top trace), fully validates the consistency and absence of systematic artifacts of the here presented 2D-OKE methodology (projection slice theorem)\(^6\).
We can now treat each horizontal line cut of constant excitation energy $E_{ex}$ as a third order nonlinear polarization response as a function of pump-probe delay $t$. To obtain the OKE frequency spectrum, we thus perform a second FT along the pump-probe axis $t$ and take its absolute value (= amplitude) as we would do for every oscillatory spectrum. Accordingly, this procedure results in the 2D frequency maps showing the correlation between excitation energy and OKE modulation frequency in Figs. 2b,d and 3b,d.

In order to gain optimized energy resolution along the excitation energy axis, experimentally we set the rotating frame (e.g. to 500 THz; 2.07 eV), such that the observation window is centered around the excitation spectrum (e.g. 550 THz; 2.27 eV), see e.g. Fig. S3a,b. The 100 THz width of the accessible frequency window is set by the pump-pump delay step size of 5 fs. The frequency resolution is determined by the maximum pump-pump delay, which was set to 2000 fs.

1.5. Balanced detection

In order to detect small changes in the anisotropic transmission, resulting from transient birefringence, we implemented a balanced detection scheme. Our balanced detection enables the observations of very small ($\sim 10^{-4}$) changes in the ellipticity or linear polarization of the ultrashort probe pulse (pulse duration of 30 fs, center wavelength 800 nm) while discriminating against isotropic or unpolarized transmission changes. Therefore, isotropic pump-induced changes such as transient absorption or scattering effects were highly suppressed and did not contribute to the pump probe signal. Further, the phase cycling of the two pump pulses discriminates against incoherent effects.

The balanced detection consists of broadband waveplate and Wollaston prism followed by a focusing lens and two identical fast Si-photodiodes. The Wollaston prism spatially separates two orthogonal components of the probe beam; one component parallel and one component perpendicular to the pump pulse polarization. The photo currents corresponding to these two projections are separately single-shot resolved detected on the two identical photodiodes. For small polarization changes the relative difference between signal $\Delta l/l_0 = (l_1 - l_2)/(l_1 + l_2) = \sin (\Gamma)$ scales linear with the phase shift $\Gamma$ between the two electric field polarization components. Depending on the waveplate, this corresponds either to a change in ellipticity or change in linear polarization (polarization rotation angle) for a quarter-wave plate (QWP) or half-wave plate.
(HWP), respectively. The single shot difference signal $\Delta I(t, \tau, \phi_1, \phi_2)$ was digitized and acquired at a 10kHz rate in conjunction with the corresponding pump-pump-pulse sequence. Here $t$ is the pump-probe delay, $\tau$ is the pump-pump delay, and $\phi_1, \phi_2$ are the phases of the pump pulse sequence.

1.6. Kerr propagation model
We simulate the induced 3rd order nonlinear polarization $P^{(3)}_j(t,z)$ according to the general definition shown in the main paper. The spatial and temporal evolution of all 3 interacting fields are calculated on a time-space grid with one dimensional spatial slices of $\Delta z = 500 \text{ nm}$ ($z_i = 0 \ldots d$) and time resolution of $\Delta t' = 10 \text{ fs}$. The coarse spatial resolution (for the sake of computational efficiency) is responsible for the minor phase artifacts in Figs. 4b,c and f.g. The pump-pump and pump-probe delay steps $\Delta \tau$ and $\Delta t$, respectively, are chosen similar to the experimental parameters: $\Delta \tau = 7 \text{ fs}$ ($t = 0 \ldots 2 \text{ ps}$) and $\Delta t = 15 \text{ fs}$ ($t = -0.2 \ldots 8.5 \text{ ps}$). We assume that the fields are not depleted by the nonlinear process and that the polarization components $P^{(3)}_j(t,z)$ emit a nonlinear signal field $E^{NL}(t,z)$ at every slice $z$, which then co-propagates with the probe field. The transmitted probe field $E^{pr}$ and integrated nonlinear field $E^{NL}$ is then projected on two polarization detection directions given by a half-wave plate and a Wollaston prism via Jones calculus. The difference of two projected intensities finally delivers the simulated 2D-OKE signal $S(t, \tau)$.

To model the 3rd order nonlinear polarization dominated by the instantaneous electronic response, all $\chi^{(3)}$ components were assumed to be independent of frequency $\nu$, which corresponds to a $\delta(t - t') \delta(t' - t'' \delta(t'' - t''')$ temporal response function. For normal incidence on the (101) crystal surface, the orthorhombic space group ($Pnma$) of both MAPbBr$_3$ and CsPbBr$_3$ permits Kerr signals from $\chi^{(3)}_{xxxx}, \chi^{(3)}_{yyyy}, \chi^{(3)}_{xyxy} = \chi^{(3)}_{xxyy} = \chi^{(3)}_{xyyx}$ and $\chi^{(3)}_{yxyy} = \chi^{(3)}_{yyxy} = \chi^{(3)}_{yxyx}$ (Ref.1). The allowed off-diagonal tensor elements of $\chi^{(3)}$ were assumed to be of same magnitude (in arb. u.), while diagonal elements had to be assumed 5 times larger to reproduce the experimental 2D-OKE features.

*Fit to experimental data*
To fit the Kerr propagation simulation to our experimental data and to obtain the quantitative fit parameters shown in Fig. 5, we developed the following parametrization procedure:

First, $t_1$ is extracted from the phase-discontinuity observed in the imaginary part of experimental energy-time signal (see Fig. S15; results shown as blue diamonds in Figs. 2a,c). $t_1$ corresponds to the specific pump-probe delay, when the probe pulse cannot catch up with the pump components within the sample thickness $d$ (see Fig. 1b). From this we can derive the group index mismatch $\Delta n_g(\nu)$. The period of the oscillating off-diagonals mixing terms, e.g. $\chi^{(3)}_{xxyy} E_x^p(t', z) E_y^c(t', z)$ in Fig. 4d, is governed by the pump-birefringence $\Delta n_0(\nu)$. The observed oscillatory 2D-OKE peak signal (e.g. Fig. 2b,d) is given by the integration along the probe propagation trajectories (green lines Fig. 4d) and thus is additionally affected by $\Delta n_g(\nu)$. By fitting our model both to $t_1$ (blue diamonds in Fig. 2a,c) and to the oscillatory 2D-OKE main branch (green broken line in Fig. 4g), we extract consistent values for $\Delta n_0(\nu)$ and $\Delta n_g(\nu)$. An additional contribution from the birefringence at probe frequencies (when the probe field is not perfectly polarized aligned along a crystal axis, $\phi \neq 0$), can be fitted to the occurrence of a second (upper), higher-frequency 2D-OKE branch, e.g. in Fig. 2d. A probe polarization angle of $\phi \approx 15^\circ$ was found to reproduce the experimental data very well (see Fig. 4d-g).

For the 92 K results in Figs. 4 and 5, the refractive and group index at the probe wavelength along the fast axis was set to 1.85 and 2.05, respectively, with a birefringence of 0.112. For the 300 K results, the refractive and group index was set to 1.85 and 2.00, respectively, with a birefringence of 0.053. The comparatively large value of birefringence are required to account for the secondary high frequency branch observed experimentally in Fig. 2d. The fast axis refractive index $n_x$ at 2.1 eV was assumed to be 1.97 and 1.94 for 92 K and 300 K, respectively, while the dispersion at higher frequencies $n_0(\nu)$ and birefringence $\Delta n_0(\nu)$ is defined by the fitting procedure explained above. The calculations for the isotropic case in Figs. 4a-c, are based on the fast axis refractive index $n_x$ given above.

1.7. Time-Frequency analysis

We conduct time-frequency analysis of 1D-OKE using a short-time Fourier transform (STFT), which is available in MATLAB as a standard function. In STFT, a transient is split into windows of constant width, and a fast Fourier transform (FFT) is applied to each window. By specifying
window width and overlap, we achieve a time-resolved frequency analysis of the 1D-OKE frequency evolution. In Fig. 1d, the window size was 60 data points and the window overlap was set to 59 data points.

2. Extended data analysis

2.1. Fluence dependence

As the long data acquisition time of the 2D-OKE experiments does not allow for a reliable fluence dependence measurement series, we investigated both the initial oscillatory high frequency response (region 1) and the consecutively low frequency oscillations (region 2) as a function of pump fluence in a 1D-OKE experiment. The fluence dependence at room temperature, Fig. S10, clearly unveils the linear dependence of both regions on the excitation fluence. This confirms a third order nonlinear polarization as source of the transient birefringence signal and is thus consistent with an OKE response.

In a scenario where the oscillatory OKE response results from coherent lattice oscillations, the only phonon-phonon coupling mechanism suitable to this fluence dependence is based on a linear-square coupling term and a parametric down-conversion type of coupling\(^9,10\). We can exclude this scenario by a coupled anharmonic oscillator model and by calculating the impact of photodoping or strain in the next sections.

2.2. Coupled oscillator model excluding parametric phonon decay

In this section, we present a model of coherently coupled phonons to exclude to phononic origin of the OKE oscillations at 5.3 and 2.65 THz as shown in Fig. 1c,d. We describe the coupling of a strongly-damped high-frequency fully-symmetric \(A_g\) mode to a weakly-damped low-frequency mode of arbitrary symmetry. Our model is fully consistent with a previously described approach for the parametric coupling of the anharmonic \(A_g\) mode in bismuth\(^9,10\). The harmonic part of the potential energy of the two phonons, \(V_h\), is given by

\[
V_h = \frac{\Omega_1^2}{2} Q_1^2 + \frac{\Omega_2^2}{2} Q_2^2
\]
where $Q_1$ and $Q_2$ are the normal mode coordinates (or amplitudes) of the initial 5.3 THz and the target mode given in $\text{Å}\sqrt{\text{amu}}$, where amu is the atomic mass unit. $\Omega_1$ and $\Omega_2$ are the respective eigenfrequencies given in $2\pi$ THz.

Anharmonic coupling between different phonons is allowed, when their product contains the fully symmetric representation of the system, which, for orthorhombic CsPbBr$_3$, is the $A_g$ representation. For a coherently-excited $A_g$ mode, this leaves nonlinear coupling terms of the type

$$V_{ni} = cQ_1Q_2^2$$

in cubic order of the phonon amplitude, where $Q_1 \equiv Q_{A_g}$, and $c$ is the linear-quadratic coupling coefficient given in $\text{eV}/(\text{Å}\sqrt{\text{amu}})^3$. This is fundamentally different from the nonlinear phonon couplings that have been intensively studied in recent years in the context of ionic Raman scattering, in which a coherently-excited infrared (IR)-active phonon scatters by a Raman (R)-active phonon. This type of interaction is described by a quadratic-linear $Q_{IR}^2Q_{R}$ (Refs. 11,12) or trilinear $Q_{IR,1}Q_{IR,2}Q_{R}$ (Ref. 13) coupling and cannot be used to reproduce the temporal signal obtained in this work.

Here, we model the hypothetical excitation of the initial mode via a stimulated Raman scattering process, which can be described by the potential

$$V_R = \varepsilon_0 R Q_1 E^2(t)$$

where $\varepsilon_0$ is the static dielectric constant, $R$ is the frequency-dependent Raman tensor of the $A_g$ mode, and $E(t)$ is the electric field of the incoming laser pulse. The pump pulse $E(t)$ can be modeled as $E(t) = E_0 \exp\left\{-\frac{(t-t_0)^2}{[2(\tau/\sqrt{8 \ln2})^2]}\right\} \cos(\omega_0 t + \phi_{\text{CEP}})$, where $\tau$ is the full width at half maximum pulse duration, $\omega_0$ is the center frequency of the laser pulse, and the carrier-envelope phase $\phi_{\text{CEP}}$ can be chosen to be zero without loss of generality\(^\text{14}\. The resulting system of coupled differential equations is
\[ \ddot{Q}_1 + \kappa_1 \dot{Q}_1 + \Omega_1^2 Q_1 = \varepsilon_0 R E^2(t) + c Q_2^2 \quad (S1) \]
\[ \ddot{Q}_2 + \kappa_2 \dot{Q}_2 + (\Omega_2^2 + c Q_1) Q_2 = 0 \quad (S2) \]

Here, \( \kappa_1 \) and \( \kappa_2 \) are the damping coefficients of the initial and the target mode, respectively. As the initial mode is excited via impulsive excitation, its amplitude depends on the square of the electric field, which is proportional to the fluence \( F \): \( Q_1 \propto E^2 \propto F \). The \( c Q_2^2 \) term in Eq. (S1) is the back-action of the coupled target mode, which can be assumed to be negligible due to the strong damping of the initial mode. The \( c Q_1 \) term in Eq. (S2) dynamically modifies the frequency of the secondary \( (Q_2) \) mode, and for a resonance condition \( \Omega_1 = 2 \Omega_2 \), the secondary mode gets excited through parametric amplification\(^9,15\). The amplitude \( Q_2 \) is linearly dependent on the amplitude of the parametric drive \( c Q_1 \), and therefore we would expect a linear dependence on the fluence \( Q_2 \propto Q_1 \propto F \) consistent with our experimental fluence dependence (Fig. S10 and S11b).

We list the parameters that we used for Eqs. (S1) and (S2) in table ST1. Note that, in order to reproduce a similar 1D-OKE signal through nonlinear phonon coupling (see simulation results in Fig. S11), the value of the coupling coefficient that we have to assume here \( \approx \text{eV}/(\text{Å} \sqrt{\text{amu}})^3 \) is two to four orders of magnitude higher than common ground state values found in bulk dielectrics \( \approx \text{meV}/(\text{Å} \sqrt{\text{amu}})^3 \) (Ref. \(^{12}\)). Such strong anharmonic coupling would be unprecedented and reminiscent of a macroscopic phase transition. We therefore exclude anharmonically coupled phonons as source for the observed oscillatory OKE signal in the orthorhombic phase in both CsPbBr\(_3\) and MAPbBr\(_3\).

**Table ST1.** Parameters used in the evaluation of Eqs. (S1) and (S2).

| Parameter | Value |
|-----------|-------|
| \( \Omega_1 \) / \( 2\pi \) | 5.3 THz |
| \( \Omega_2 \) / \( 2\pi \) | 2.65 THz |
| \( \kappa_1 \) | 5.3 THz |
| \( \kappa_2 \) | 0.75 THz |
| \( R \) | 100 Å\(^2\)/√amu |
2.3. Impact of photodoping and strain on lattice modes

We carried out first principles simulations on both CsPbBr3 and MAPbBr3 to gain insight into the effect of photodoping and structural deformation/stress on the perovskite phonon modes. We started by considering the perovskites in their orthorhombic phase, considering their neutral and positively charged state, the latter corresponding to the presence of a photogenerated hole. For these systems we calculated the relaxed atomic positions and cell parameters, see results in Fig. S12. As one may notice, for both CsPbBr3 and MAPbBr3 addition of a charge hole to the cell system leads to a contraction of lattice parameters (and associated bond lengths), consistent with previous results. The effect of added electrons should be even smaller, based on previous analyses, so we did not consider it here. The measured lattice contraction refers to that one could expect at very high charge density, as we here consider the extreme case of one positive charge per orthorhombic unit cell (4 formula units).

We then investigate the effect of this lattice contraction on the calculated phonon modes. The simulated IR spectra of both CsPbBr3 and MAPbBr3 are reported for the neutral case in Fig. S13. While the phonon spectrum of CsPbBr3 has a highest accessible frequency of 146 cm⁻¹ (4.38 THz), the spectrum of MAPbBr3 extends up to ~3300 cm⁻¹ (98.9 THz) due to modes of the organic cations. Here we focus on the low energy region common to both perovskites. The spectra are dominated by Br-Pb-Br bending and Pb-Br stretching modes, which are coupled in MAPbBr3 to librational modes of the methylammonium cation. By inserting a positive charge into the system, the frequencies shift in all cases to higher energies. As an example, the highest CsPbBr3 phonon mode at 146 cm⁻¹ shifts to 155 cm⁻¹ (4.65 THz). Similarly, for MAPbBr3 the highest mode related to the inorganic framework shifts from 181 to 188 cm⁻¹ (5.63 THz). See Table ST2 for more details.

Table ST2. Calculated phonon frequencies (cm⁻¹) CsPbBr3 and MAPbBr3 in their neutral and positive charge state.
Table ST2. Phonon frequencies (cm\(^{-1}\)) in neural (NEU) and hole-doped (POS) CsPbBr\(_3\) and MAPbBr3

|          | CsPbBr\(_3\) | MAPbBr3 |
|----------|--------------|---------|
|          | NEU | POS | NEU | POS |
| 11,16    | 20,48 | 20,81 | 18,34 |
| 17,66    | 22,87 | 23,62 | 21,18 |
| 21,66    | 23,04 | 26,4 | 24,51 |
| 23,02    | 24,03 | 28,46 | 25,22 |
| 25,24    | 24,72 | 28,86 | 25,69 |
| 26,31    | 25,02 | 29,04 | 27,46 |
| 27,44    | 26,12 | 31,01 | 30,53 |
| 27,65    | 28,14 | 32,4 | 32,34 |
| 28,17    | 31,55 | 33,54 | 33,9 |
| 29,06    | 32,6 | 36,27 | 36,2 |
| 29,78    | 32,93 | 39,96 | 39,67 |
| 30,13    | 34,02 | 40,15 | 40,26 |
| 32,11    | 34,94 | 41,23 | 43 |
| 32,3     | 37,2 | 44,23 | 44,41 |
| 33,7     | 39,94 | 45,46 | 47,86 |
| 34,73    | 41,77 | 45,68 | 48,9 |
| 35,96    | 45,4 | 47,22 | 49 |
| 36,77    | 46,82 | 47,99 | 52,3 |
| 39,85    | 47,94 | 48,42 | 53,15 |
| 40,41    | 49,26 | 52,2 | 53,95 |
| 40,44    | 49,46 | 53,18 | 56,53 |
| 43,69    | 51,44 | 55,54 | 56,73 |
| 44,21    | 51,86 | 56,72 | 59,03 |
| 44,57    | 54,75 | 57,05 | 59,53 |
| 45,48    | 55,64 | 57,9 | 59,96 |
| 45,57    | 57,33 | 59,83 | 60,38 |
| 51,53    | 59,82 | 64,66 | 60,76 |
| 52,1     | 61,31 | 71,21 | 65,94 |
| 55,81    | 61,41 | 73,91 | 72,05 |
| 56,68    | 65,8 | 75,85 | 75,72 |
| 57,41    | 69,89 | 76,47 | 84,19 |
| 58,51    | 71,48 | 78,38 | 88,74 |
| 60,31    | 71,76 | 79,87 | 89,46 |
| 60,36    | 74,48 | 81,53 | 95,54 |
| 61,8     | 76,66 | 82 | 96,28 |
| 62,34    | 76,85 | 85,02 | 97,14 |
| 62,9     | 81,91 | 87,44 | 98,39 |
| 63,17    | 88,48 | 88,6 | 99,25 |
| 63,57    | 88,87 | 90,13 | 100,35 |
| 63,62    | 90,11 | 91,1 | 101,4 |
| 65,81    | 91,96 | 92,65 | 103,71 |
| 68,57    | 96,22 | 94,06 | 104,74 |
| 70,6     | 98,07 | 97,7 | 105,97 |
|     |      |      |      |      |
|-----|------|------|------|------|
| 71,04 | 102,81 | 100,6 | 111,92 |
| 75,96 | 103,33 | 102,51 | 113,47 |
| 79,41 | 103,86 | 109,17 | 119,55 |
| 79,49 | 104,86 | 109,38 | 119,91 |
| 81,6  | 119,5  | 112,68 | 120,96 |
| 83,14 | 119,94 | 115,85 | 121,3  |
| 83,31 | 120,75 | 119,09 | 123,49 |
| 91,2  | 121,15 | 121,27 | 124,96 |
| 112,76 | 135,35 | 125,42 | 136,45 |
| 113,35 | 145,72 | 126,4  | 136,59 |
| 114,32 | 146,05 | 127,18 | 139,15 |
| 137,32 | 150,2  | 129,01 | 140,22 |
| 141,28 | 152,13 | 129,28 | 142,47 |
| 145,85 | 154,88 | 129,7  | 147,19 |
|       | 133,25 | 149,61 |
|       | 141,1  | 149,84 |
|       | 150,21 | 152,66 |
|       | 151,81 | 155,94 |
|       | 152,67 | 156,87 |
|       | 154,15 | 158,08 |
|       | 155,5  | 160,46 |
|       | 167,69 | 172,84 |
|       | 173,07 | 179,72 |
|       | 176,91 | 182,34 |
|       | 179,96 | 186,23 |
|       | 180,96 | 188,38 |
|       | 300,81 | 297,32 |
|       | 303,62 | 297,47 |
|       | 303,64 | 299,91 |
|       | 304,88 | 300,71 |
|       | 903,9  | 901,67 |
|       | 904,16 | 902,5  |
|       | 904,81 | 902,97 |
|       | 905,12 | 906,35 |
|       | 910,48 | 907,69 |
|       | 912,74 | 909,29 |
|       | 913,99 | 910,07 |
|       | 914,52 | 910,25 |
|       | 1004,49 | 1012,94 |
|       | 1005,11 | 1013,39 |
|       | 1005,31 | 1013,58 |
|       | 1005,52 | 1013,78 |
|       | 1237,69 | 1236,72 |
|       | 1238,35 | 1237,61 |
|       | 1238,95 | 1238,59 |
|       | 1239,11 | 1239,05 |
|       | 1246,35 | 1245,04 |
|       | 1246,54 | 1245,55 |
|       |       |       |
|-------|-------|-------|
| 1246,74 | 1246,33 |
| 1247,39 | 1247,43 |
| 1390,53 | 1393,48 |
| 1391,83 | 1393,75 |
| 1392,16 | 1394    |
| 1392,66 | 1394,54 |
| 1438,42 | 1435,55 |
| 1438,86 | 1436,47 |
| 1439,54 | 1437,64 |
| 1440,68 | 1439,22 |
| 1441,67 | 1439,53 |
| 1442,59 | 1440,27 |
| 1444,21 | 1441,11 |
| 1444,64 | 1441,52 |
| 1474,27 | 1474,25 |
| 1476,55 | 1476,61 |
| 1479,47 | 1479,08 |
| 1481,76 | 1480,77 |
| 1550,96 | 1556    |
| 1552,12 | 1557,1  |
| 1552,7  | 1557,57 |
| 1553,18 | 1558,48 |
| 1578,49 | 1579,14 |
| 1581,32 | 1582,33 |
| 1586,32 | 1587,4  |
| 1587,8  | 1588,79 |
| 2972,56 | 2980,78 |
| 2973,04 | 2981,05 |
| 2973,1  | 2981,6  |
| 2973,82 | 2981,89 |
| 3068,03 | 3077,03 |
| 3068,34 | 3077,14 |
| 3069,49 | 3078,89 |
| 3070,02 | 3079,68 |
| 3071,92 | 3079,99 |
| 3072,53 | 3080,35 |
| 3077,33 | 3087,22 |
| 3078,02 | 3088,37 |
| 3079,83 | 3090,36 |
| 3080,07 | 3090,36 |
| 3081,52 | 3090,6  |
| 3082,49 | 3091,19 |
| 3098,15 | 3099,15 |
| 3098,78 | 3100,03 |
| 3115,63 | 3117,32 |
| 3118,45 | 3119,47 |
| 3190,23 | 3247,08 |
| 3191,98 | 3250,87 |
These shifts are small considering the experimental observations and are likely not consistent with a photodoping mechanism being responsible for the observed high-frequency oscillatory Kerr response.

We thus investigated whether stress and structural deformation could induce a shift towards higher frequencies. We used in this case a simple cubic model of CsPbBr$_3$ and we compressed one Pb-Br bond recalculating the associated vibration frequencies and energy variation. As one may notice from Fig. S14 to have a 50% highest frequency increase (light dashed lines) one needs to significantly compress the Pb-Br bond with an energy penalty of ~0.2 eV. Clearly, this situation is highly unlikely as this energy is comparable to the calculated formation enthalpy of typical lead-halide perovskites$^{18}$. We can therefore dismiss both dynamic strain or photodoping effects as sources for large phonon frequency shifts.

**Computational Details.** The orthorhombic APbBr$_3$ perovskites were simulated with a 1x1x1 unit cell containing 4 formula units (20 and 48 atoms). All calculations have been carried out using the Quantum Espresso program package$^{19}$ along with the PBE functional$^{20}$. Electron–ion interactions were described by scalar relativistic (SR) ultrasoft pseudopotentials with electrons from N, and C 2s2p, H 1s, Pb 6s6p5d, Cs 4s4p4d and Br 4s4p electrons explicitly included in the calculations. A 2x2x2 k-point mesh for sampling the Brillouin zone was used$^{21}$. Calculations were performed using plane wave cutoffs of 25 and 200 Ry for expansion of the wave function and density, respectively, while for variable cell calculations and for calculations in the presence of the field 50 and 400 Ry cutoffs are used. For the simulation of the structural compression we adopt a cubic CsPbBr3 unit cell, we carried out a variable cell geometry optimization using a cutoffs of 50/400 Ry along with a 4x4x4 k-points grid. DFT-D2 dispersion interactions have been included in the calculation$^{22}$. From the relaxed cell we constrained one Pb-Br at different bond lengths and we relax all the other atoms keeping the relaxed cell parameter fixed. On these optimized geometries a phonon calculation has been performed at the same level of theory.
3. **Extended data figures**

![Sample characterization](image)

**Fig. S1 Sample characterization.** Optical images (a,b) and diffraction patterns (c,d) of CsPbBr$_3$ and MAPbBr$_3$ single crystals. Scale bars are 1 mm. The single-crystal X-ray diffraction (SCXRD) was collected at room-temperature and 180 K for CsPbBr$_3$ and MAPbBr$_3$, respectively. The clear optical morphology and single crystalline nature indicate the high quality of the crystals.
**Fig. S2| Time-time domain data.** Time-time domain raw data from 2D-OKE. Displayed signals $S(t, \tau)$ are retrieved after 4-sequence phase cycling scheme (see Methods). Therefore, each data pixel consists of 4 pump-pump-probe experiments with distinct pump-pump phase. Before time-zero (negative slope) straight lines are single-pump OKE contributions from phase-cycling imperfections due to small laser drifts during hours of data acquisition. All data correspond to the 2D-OKE signals shown in the main paper: a, CsPBr$_3$ at 295 K. b, CsPBr$_3$ at 92 K (Fourier window function superimposed for $\tau > 1800$ fs). c, MAPBr$_3$ at 295 K. d, MAPBr$_3$ at 104 K.
Fig. S3 | Low temperature 2D-OKE incl. excitation energy spectrum. 

**a, b,** Low temperature 2D-OKE signal of CsPbBr$_3$ at 92 K in energy-time and energy-frequency domain, respectively. The upper bound of the oscillatory response at ~2.35 eV indicates the bandgap edge and its steep absorption feature; consistent with temperature dependent photoluminescence and absorption studies (Ref. 24). The pump-pulse spectrum (right-hand side) clearly shows that this upper bound of the 2D-OKE is not related to a lack of pump photons with energies above the bandgap. 

**c, d,** Same as **a,b,** but for MAPbBr$_3$ at 104 K. Clearly, the 2D-OKE feature precisely pinpoints the optical band gap at 2.29 eV (Ref. 24) despite the much broader excitation energy spectrum (right-hand side).
Fig. S4| Line cuts for specific excitation energies (CsPbBr₃). a, b, Time-frequency domain 2D-OKE at 295 K (as in Fig. 2a) and corresponding line cuts for fixed excitation energies, respectively. The time domain traces in b are vertically offset for clarity. The excitation energy-integrated 2D-OKE (red line) agrees well with the single pulse excitation (grey line). Small modulation for $t < 0$ results from the replica at 2.1 eV, which is caused by imperfect phase cycling in conjunction with the rotating frame. c, Corresponding Fourier transforms of the line cuts in b. Already in these few line cuts a significant frequency shift is prominent. The dominant high-frequency feature sits on top of a smaller low-frequency modulation.
Fig. S5: Line cuts for specific excitation energies (MAPbBr₃). a, b, Time-frequency domain 2D-OKE at 295 K (as in Fig. 3a) and corresponding line cuts for fixed excitation energies, respectively. The time domain traces in b are vertically offset for clarity. The window-like Kerr feature is fully consistent with previous below-gap 1D-OKE studies. The spike at the end of the window-like feature results from the dispersed pump-pulse mixing with its reflection at the backside of the sample. c, Corresponding Fourier transforms of the line cuts in b. The spike leads to small ripples observed for frequencies up to 5 THz; also visible in Fig. 3b.
Fig. S6| Comparative 2D-OKE in ZnTe and GaSe at 295 K. a, 2D-OKE of the isotropic (cubic) semiconductor ZnTe with a bandgap of 2.25 eV. We clearly find a similar non-oscillatory Kerr-response as in the cubic phase MAPbBr₃. The curvature of the ZnTe feature is less pronounced, consistent with the lower refractive index dispersions in ZnTe (Ref. 23). b, 2D-OKE frequency spectrum of a. c, 2D-OKE of the birefringence (hexagonal) semiconductor GaSe with bandgap at 2.03 eV (Ref. 23). The GaSe birefringence of $\Delta n_H \approx 0.2$ at 1.95 eV (Ref. 25) is one order of magnitude higher than $\Delta n_0$ of LHPs close to the band gap as derived in this work. Nevertheless, only under specific phase matching angles, an oscillatory signal similar to orthorhombic phase perovskites was observed. This comparison highlights the robustness and the strength of the oscillatory signal from polarization dressed light propagation in LHPs. d, 2D-OKE frequency spectrum of c. The features between 3-6 THz show mild similarities to the correlation branches in the 2D frequency maps of orthorhombic LHPs.
Fig. S7 | Thickness dependence. a, c, e, 2D-OKE signal of CsPbBr$_3$ at 295K for different thicknesses of 450 µm, 240 µm, 75 µm, respectively. b, d, f, corresponding constant excitation energy cuts to visualize the temporal width of the main oscillatory signal. Signal width as a function of thickness for $E_{ex} = 2.29$ is given in Fig. S8.
Fig. S8 | Thickness dependence for 2.29 eV excitation energy. a, 2D-OKE width as a function of single crystal CsPbBr$_3$ thickness at 295 K. For an arbitrary cut at constant excitation energy of 2.29 eV, the duration of the main 2D-OKE feature scales linearly with the thickness. This demonstrates that 2D-OKE traces the nonlinear polarization by light propagation along the full propagation path through the sample.
**Fig. S9 | Consistency of 1D-OKE and 2D-OKE.** **a,** Pump-energy resolved Fourier transform of 2D-OKE on CsPbBr$_3$ at 295K. As the pump excitation energy decreases from the bandgap, the OKE modulation frequency increases with excitation energy from 3.5 THz to 7.0 THz. The dotted line indicates that at an excitation energy of 2.25 eV the corresponding dominating OKE frequency is 5.2 THz. **b,** **c** The Fourier transform and 1D-OKE trace of CsPbBr$_3$ with a narrowband excitation centered at 2.25 eV, respectively. The initial high-frequency response in **c** corresponds to the broad peak centered at 5.3 THz in **b.** Note that **a,** and **b,** share the same frequency axis. The close match between the dotted line (5.2 THz) and the solid line (5.3 THz) emphasizes the consistency of 1D- and 2D-OKE.
**Fig. S10 | Fluence-dependent 1D-OKE in CsPbBr₃ at 295K.**

a. The raw data taken with pump fluences of 191, 127, 64, 32, and 13 µJ/cm². The incoherent contribution is shown with gray-broken traces (single-exponential decay). b. The coherent contribution to the OKE trace, taken by subtracting the incoherent part in a from the respective raw trace. The gray shaded regions indicate areas in which the high-frequency and low-frequency phonon contributions are separated. The red markers indicate the maximum in the gray shaded regions, the blue markers indicate the minimum in the same regions. c. The Fourier transform (FT) of the raw data shown in a. The blue and red markers indicate the maximum FT amplitude of the respective gray shaded regions. d. The maxima of the peaks in c plotted against pump fluence. As shown, both the higher frequency and lower frequency features scale linearly with fluence. This confirms a third order nonlinear polarization as source of the transient birefringence signal.
Fig. S11 | Model simulation of coherent phonon-phonon coupling and comparison to 1D-OKE signal in CsPbBr₃ at 295 K. a, Schematic illustration of parametric decay; b, Excitation fluence dependence of the oscillatory OKE signal extracted from time domain data in Fig. S10b. Blue-circles: the 5.3 THz feature (region 1); red circles: the 2.6-1.6 THz feature (region 2). The lines are linear fits. c, Simulation results from Eqs. (S1) and (S2) of the time-evolution of the coherent coupling of a 5.3 THz (blue) to a 2.65 THz (red) mode. d, The simulated coherent phonon trace (red) can be fitted to rough agreement with experimental result from Fig. 1c (black), but this would require an unprecedented high anharmonic coupling constant $c$ in Eqs. (S1) and (S2).
Fig. S12 | Optimized structures and lattice parameters. a) CsPbBr$_3$ and b) MAPbBr$_3$ in their neutral (left) and positive (right) charge states along with calculated cell parameters (Å). Different views are reported in upper (along c axis) and lower (along the a axis) panels.
Fig. S13 | Simulated IR spectra. For CsPbBr$_3$ and MAPbBr$_3$ perovskites in the low frequency range.
Fig. S14 | Energy variation (a, eV) and calculated highest phonon frequency (b, cm⁻¹) for cubic CsPbBr₃ subjected to compression of a single Pb-Br bond (Å).
**Fig. S15 | Phase discontinuity.** The phase discontinuity (even more apparent in the here shown imaginary parts of the 2D-OKE signals of Fig. 2) is used to determine the excitation frequency dependent stop $t_1(\nu)$ of the high-frequency feature (region 1) for CsPbBr$_3$ a, at 295 K and b, at 92 K.
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