

Identifying New Mechanisms of Light-Induced Chirality in BPO₄

Dissertation

zur Erlangung des Doktorgrades

an der Fakultät für Mathematik, Informatik und Naturwissenschaften

Fachbereich Physik

der Universität Hamburg

vorgelegt von

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Hamburg

2026

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Abstract

The search for novel strategies for quantum material phase control is one of the key directions in current condensed matter research. In this field, the development of intense ultrashort laser pulses has opened up the possibility of using intense light for material control, paving the way for accessing functionalities beyond equilibrium. On time scales down to the picosecond and femtosecond regimes and with excitation fluences reaching tens of mJ/cm^2 , light pulses have been shown to induce non-equilibrium phase transitions and induce unconventional electronic and magnetic orders, including metal-to-insulator transitions, magnetism, ferroelectricity, and superconductivity. Among these approaches, one intriguing possibility is the accessibility of transient crystal structures through a mechanism based on the anharmonicity of the crystal lattice, known as nonlinear phononics.

Since the initial demonstration in 2011, the number of experimental demonstrations of this protocol has expanded significantly, with a recent addition being light-induced chirality in a solid which is achiral in equilibrium. In the specific case of the large-bandgap insulator BPO_4 , the transient chiral state was shown to emerge upon the resonant excitation of its doubly degenerate in-plane phonon modes with E symmetry. In the context of nonlinear phononics, this phenomenon was explained by anharmonic coupling between two optical phonon modes: the oscillatory motion of the driven E -symmetry modes is rectified into a quasi-static displacement of the out-of-plane B -symmetry modes that induces chirality by breaking all the improper rotation symmetries.

In this thesis, the excitation frequency dependence of the light-induced chirality in BPO_4 was systematically mapped, the result of which expands the insight into the underlying mechanism. This study was enabled by the use of narrowband mid-infrared excitation pulses

with precisely tunable central frequencies, generated by difference frequency generation between chirped near-infrared pulses. Thanks to the greatly enhanced frequency resolution, a significant deviation was found between the experimental frequency dependence and the expectations based solely on the traditional coupling mechanism, pointing to the presence of additional coupling pathways in nonlinear phononics. To explain this discrepancy, several alternative nonlinear coupling terms were considered and their frequency dependencies were extracted. By combining spatiotemporal numerical simulations of phonon polariton propagation with experimental results, the contributions from these different nonlinear coupling terms are disentangled. The analysis revealed that while the traditional mechanism involving two phonons remains the primary driver for on-resonance excitations, a trilinear coupling term, which involves two in-plane E -symmetry phonon modes at different frequencies and one out-of-plane B -symmetry phonon mode, becomes dominant when the excitation frequency is detuned from resonance.

These findings can be extended to other material systems, and provide a quantitative foundation for explaining nonlinear phononic lineshapes in transparent materials. Moreover, the trilinear coupling term opens up new opportunities for lattice control, such as parametric amplification of phonons at finite frequencies.

Zusammenfassung

Die Suche nach neuartigen Strategien zur Manipulation von Phasenzuständen in Quantenmaterialien ist eine der zentralen Richtungen in der aktuellen Festkörperforschung. In diesem Feld hat die Entwicklung intensiver ultrakurzer Laserpulse die Möglichkeit eröffnet, starkes Licht zur Materialkontrolle einzusetzen, was den Weg zu Funktionalitäten jenseits von Gleichgewichtszuständen geebnet hat. Auf Zeitskalen bis in den Pikosekunden- und Femtosekundenbereich und mit Anregungsdichten von bis zu mehreren zehn mJ/cm^2 wurde gezeigt, dass Lichtpulse Nichtgleichgewichts-Phasenübergänge induzieren und unkonventionelle elektronische und magnetische Ordnungen hervorrufen können, darunter Metall-Isolator-Übergänge, Magnetismus, Ferroelektrizität und Supraleitung. Unter diesen Ansätzen ist die Zugänglichkeit transients Kristallstrukturen durch einen Mechanismus, der auf der Anharmonizität des Kristallgitters basiert und als nichtlineare Phononik bekannt ist, eine faszinierende Möglichkeit.

Seit der ersten Demonstration im Jahr 2011 hat sich die Anzahl der experimentellen Nachweise dieses Konzepts der nichtlinearen Phononik erheblich erweitert, wobei eine jüngste Ergänzung die lichtinduzierte Chiralität in einem Kristall ist, der im Gleichgewicht achiral ist. Im spezifischen Fall des Isolators BPO_4 wurde gezeigt, dass der transiente chirale Zustand bei resonanter Anregung einer doppelt entarteten ebenenparallelen Phononmode mit E -Symmetrie entsteht. Im Kontext der nichtlinearen Phononik wurde dieses Phänomen durch eine nichtlineare Kopplung zwischen zwei Phononmoden erklärt: die oszillatorische Bewegung der getriebenen E -Symmetrie-Mode wird gleichgerichtet in eine quasi-statische Auslenkung ebenennormaler B -Symmetrie-Moden, die Chiralität durch das Brechen aller Drehspiegelungssymmetrien, einschließlich Spiegelungen und Inversion, induzieren.

In dieser Dissertation wurde die Abhängigkeit der lichtinduzierten Chiralität in BPO_4 von der Anregungsfrequenz systematisch untersucht, um einen weiteren Einblick in den zugrundeliegenden Mechanismus zu gewinnen. Diese Studie wurde durch den Einsatz von schmalbandigen Anregungspulsen im mittleren Infrarotbereich mit präzise abstimmbaren Zentralfrequenzen ermöglicht, die durch Differenzfrequenzerzeugung zwischen gechirpten Nahinfrarotpulsen erzeugt wurden. Dank der stark verbesserten Frequenzauflösung wurde eine signifikante Abweichung zwischen der experimentellen Frequenzabhängigkeit und den Erwartungen beobachtet, die ausschließlich auf dem traditionellen Kopplungsmechanismus basieren, was auf das Vorhandensein zusätzlicher Kopplungspfade in der nichtlinearen Phononik hindeutet. Um diese Diskrepanz zu erklären, wurden mehrere alternative nichtlineare Kopplungsterme in Betracht gezogen und ihre Frequenzabhängigkeiten extrahiert. Durch die Kombination raumzeitlicher numerischer Simulationen der Ausbreitung von Phononpolaritonen mit experimentellen Ergebnissen wurden die Beiträge dieser verschiedenen nichtlinearen Kopplungsterme voneinander separiert. Die Analyse zeigte, dass der traditionelle Mechanismus, der zwei Phononen umfasst, zwar der primäre Antrieb für resonante Anregungen bleibt. Jedoch wird ein trilinearere Kopplungsterm, der zwei ebenenparallele *E*-Symmetrie-Phononmoden bei unterschiedlichen Frequenzen und eine ebenennormale *B*-Symmetrie-Phononenmode umfasst, dominant, wenn die Anregungsfrequenz von der Resonanz verstimmt ist.

Diese Erkenntnisse lassen sich auf andere Materialsysteme übertragen und bieten eine quantitative Grundlage für die Erklärung spektraler Komponenten der nichtlinearen Phononik in transparenten Materialien. Darüber hinaus eröffnet der trilineare Kopplungsterm neue Möglichkeiten für die Gitterkontrolle, wie beispielsweise die parametrische Verstärkung von Phononen bei endlichen Frequenzen.

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Chapter 1

Introduction: Manipulating Materials with Light Pulses

Controlling electronic and magnetic phases in complex materials and the transitions between them has long been a central topic in condensed matter physics. Traditionally, the manipulation of material phases has been achieved by varying static external conditions, with the most conventional control parameters being temperature, pressure, and electromagnetic field. For a given compound, different ground states are typically observed under varying external conditions, and phase diagrams provide valuable insight into the free energy landscape and the relevant energy scales of interactions within condensed matter systems. In general, phase transitions in materials serve not only as a powerful tool for understanding the connection between macroscopic phenomena and their underlying microscopic mechanisms, but also as a pathway to realizing properties that are ideal for real-world applications.

While static external parameters offer a vast parameter space for exploration, such investigations are inherently limited to equilibrium phases or thermally metastable states, leaving non-equilibrium states and their dynamics largely unexplored. To investigate the out-of-equilibrium properties of materials, ultrafast lasers have emerged as a powerful tool. By generating pulses with durations down to the femtosecond timescale, the ultrafast evolution of material properties under non-equilibrium conditions can be resolved, yielding valuable information regarding the dynamics of collective modes in solids. Furthermore, with

peak electric fields reaching several MV/cm on the ultrafast time scale, it becomes possible to transiently drive materials into regimes inaccessible under static conditions. This intense driving force can also overcome energy barriers between different metastable states on the free energy surface, thereby activating phase transitions. Optical excitation pulses cover a wide frequency range from ultraviolet and visible to near-infrared (NIR) and terahertz (THz), which enables efficient coupling to different degrees of freedom inside the material. For example, visible to NIR light pulses can directly activate electronic transitions in insulators, and mid-infrared (MIR) to THz light pulses can be tuned resonant with infrared-active phonon modes in crystals.

A complete ultrafast pump probe experiment comprises not only the intense optical excitations that drive the materials into non-equilibrium phases, but also the ultrafast probing techniques that detect the transient properties of materials after excitation. Examples of ultrafast probing techniques include time-resolved linear and nonlinear probing [1–4], THz spectroscopy [5], and X-ray scattering and absorption [6]. With these probing methods, it is possible to investigate the properties and dynamics of these out-of-equilibrium states that exist only on ultrafast time scales.

These unique capabilities make the application of ultrafast laser pulses to materials a compelling field of research. To date, various types of photo-induced orders and phase transitions have been identified in condensed matter systems. These include ferroelectricity [1, 7, 8], magnetism [2, 9–11], superconductivity [5, 12–15], metal-to-insulator transitions [4, 16, 17], and the strongly correlated states in the Moiré superlattice of two-dimensional systems [18–21]. Such experiments are instrumental in unraveling the fundamental physics that links microscopic interactions to the macroscopic properties of materials [5, 18, 21–23]. Moreover, they hold potential for real-world technological applications, such as the development of ultrafast, high-density memory devices [1, 24, 25].

The ultrafast optical manipulation of material properties can occur through several distinct pathways. Some representative examples are illustrated in Fig. 1.1, which depicts the time evolution of a solid-state system on its free energy landscape [26]. Weak optical pulses act as a minor perturbation around the ground state. By observing the subsequent relaxation

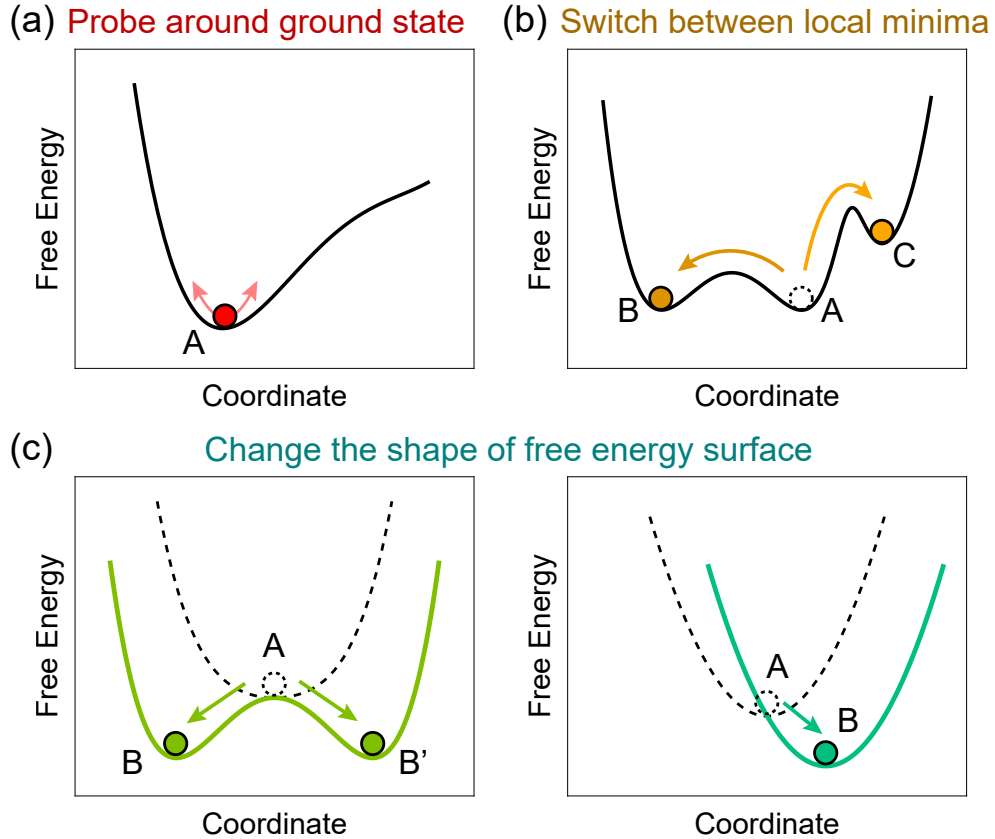


Figure 1.1. Common mechanisms for the optical control of materials. All panels show the free energy or potential as a function of a generalized coordinate in the system, such as phonon displacements or order parameters. **(a)** Under low excitation fluence, the system oscillates around the stable state A and relaxes back to equilibrium. This allows for the probing of collective modes and their couplings near the ground state. **(b)** Strong excitation can drive the system over the energy barrier separating different ground states (e.g., from A to B), or even excite the system into metastable states (e.g., from A to C). **(c)** Intense optical driving can also transiently modify the free energy landscape. This can result in transient spontaneous symmetry breaking (left panel, where B and B' represent two newly-emerged degenerate ground states), or a shift in the potential minimum (right panel, where the ground state is displaced from A to B). Adapted from [26].

dynamics as the system returns to equilibrium, one can extract critical information regarding the nature of the excited collective modes and their mutual couplings (Fig. 1.1a). Stronger excitation pulses can drive the material into entirely new phases. This can be achieved either

by forcing the system to switch between different local minima on the existing free energy surface (Fig. 1.1b), or by transiently modifying the shape of the free energy landscape itself (Fig. 1.1c). Such modifications can produce novel stable states that are inaccessible under equilibrium conditions or substantially shift the position of the potential minimum [4, 26, 27].

In the weak excitation limit, the driven system remains within the linear response regime around its stable state, and the excitation acts as a gentle probe around the ground state. The flexibility of designing and building optical setups enables multiple probing methods, such as time-dependent optical spectroscopy [28], terahertz (THz) emission spectroscopy [9, 29, 30], and X-ray scattering [28, 31]. With these probes, different coherent excitations, including phonons [27, 32], magnons [9, 29], amplitude mode of charge density wave (CDW) materials [28, 33], and Josephson plasma in superconductors [30, 34], have been investigated, covering both charged and chargeless modes. Another recent advance in optical probing technique is ultrafast imaging, which combines the spatial resolution with time-domain spectroscopy [18]. From the spatiotemporal evolution after the line-shaped near-infrared (NIR) excitation, the propagation of different modes inside the material can be probed [18, 19, 35]. Ultimately, the exceptional femtosecond to picosecond temporal resolution of ultrafast laser pulses allows researchers to directly track the real-time dynamics and propagation of such collective modes, offering fundamental insights that are simply inaccessible through conventional equilibrium measurements.

When driven by strong excitation pulses, solid-state systems can switch between different macroscopic phases or even enter novel transient states that cannot exist in thermal equilibrium. Classical examples include: the light-induced insulator-to-metal transition in the correlated insulator VO_2 [36, 37], the switching of phases with entangled spin polarization and electronic band structure in the manganite $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ [16, 38, 39], and the emergence of a light-induced superconducting-like state above the equilibrium transition temperature in the cuprate superconductor $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ from the suppression of the competing "stripe" state [5, 40, 41]. Such strong drives can explore the potential range inaccessible with other methods, and uncover the possible underlying connections between different degrees

of freedom inside the materials.

Another promising avenue for the ultrafast optical control of materials relies on the transient displacement of specific phonon modes. The static analogue to this approach is structural tuning via hydrostatic pressure or uniaxial strain, which are well-established techniques for manipulating material properties [42–44]. While resonantly excited infrared-active phonons generally exhibit harmonic oscillatory motion with zero mean displacement, they can couple nonlinearly to other vibrational modes. This nonlinear coupling exerts a directional force that induces a rectified, quasi-static displacement of the crystal lattice [27, 45, 46]. This paradigm, known as nonlinear phononics, offers a targeted way to dynamically control the crystal structure. To date, nonlinear phononics has been successfully demonstrated in a wide variety of condensed matter systems, enabling the ultrafast control of ferroelectricity [1, 7, 47], magnetism [2], ferroaxial order [24], chirality [48], and metal-to-insulator transitions [4, 17, 49].

Building upon these possibilities, the central focus of this thesis is the exploration of a light-induced chiral state in the achiral solid BPO_4 . Detailed measurements of the excitation frequency dependence of this phenomenon have revealed novel coupling mechanisms within the framework of nonlinear phononics. Chapter 2 provides a comprehensive overview of recent theoretical and experimental progress in the field of nonlinear phononics. It details the underlying physical principles and reviews landmark experimental demonstrations across different solid-state systems. Building on the general basis of nonlinear phononics, Chapter 3 summarizes the previous experiments on light-induced chirality in BPO_4 . Historically, many of the experiments exploring nonlinear phononics protocols have used broadband MIR excitation pulses, which lack the spectral resolution necessary to isolate the individual contributions of closely spaced phonon modes or competing nonlinear coupling pathways. To overcome this limitation, Chapter 4 introduces the design and performance of a frequency-tunable, narrowband MIR source. This custom-built light source is exceptionally well-suited for a precise mapping of the excitation frequency dependence of the light-induced chirality in BPO_4 . Lastly, Chapter 5 presents the experimental results obtained using these narrowband MIR pulses. These findings are discussed alongside detailed simulations of nonlinear

phonon dynamics, which establish a correspondence between the frequency-dependent photosusceptibility and the specific underlying nonlinear coupling mechanisms.

Chapter 2

Nonlinear Control of Phonons in Solids

In the context of nonlinear phononics, the dynamical control of the lattice structure typically proceeds in two steps. First, MIR excitation pulses drive an infrared-active phonon mode, leading to its oscillation. Second, due to the anharmonicity of the lattice, this oscillatory motion induces a rectified displacement along the coordinate of another phonon mode, effectively transforming a zero-mean oscillation into a structural displacement [27]. This process occurs on picosecond or even femtosecond timescales, enabling transient structural control over solids. In this chapter, I will begin by reviewing the linear properties of phonons, including their interaction with electric fields. Next, I will explain how nonlinear coupling potentials influence phonon dynamics, elucidating the core mechanisms of nonlinear phononics. Finally, I will introduce various material systems where nonlinear phononics has been successfully applied to control material properties.

2.1 Linear Response of Optical Phonons

This section presents an overview of the theory of harmonic crystals, starting with the equations of motion for lattice vibrations, defining phonons and their dispersion relations, and then introducing their interactions with optical waves. Finally, I will discuss the formation of phonon polaritons, which arise from the strong coupling between electromagnetic waves and phonon dipoles.

2.1.1 Description of Lattice Vibrations

The potential energy of a crystal includes ion-ion, electron-electron, and electron-ion interactions, which intrinsically couple the electronic and lattice degrees of freedom. However, because electrons are much lighter than ions, their characteristic velocities are substantially higher. This disparity in timescales allows us to decouple and separately treat electronic and ionic motions. When solving the electronic Schrödinger equation, the ions can be regarded as stationary; conversely, when solving the ionic Schrödinger equation, the electrons provide a time-averaged background potential. This framework is known as the Born-Oppenheimer approximation, under which the Hamiltonian of a crystal can be written as [50]

$$H_{\text{ion}} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \mathbf{r}_2, \dots) \quad (2.1)$$

where $\mathbf{r}_i$ are the coordinates of the ions, $\mathbf{p}_i$ are the corresponding momenta, and m_i is the mass of the i -th ion. Provided that the ionic displacements are much smaller than the static interionic spacings, the ionic interaction potential can be approximated as harmonic. Assuming the equilibrium ion positions are $\mathbf{r}_{i,0}$, the first derivative of the potential vanishes: $(\partial V / \partial \mathbf{r}_i)_{\mathbf{r}_{i,0}} = 0$. Omitting the constant energy term at $\mathbf{r}_i = \mathbf{r}_{i,0}$ and denoting the displacement from equilibrium as $\mathbf{u}_i = \mathbf{r}_i - \mathbf{r}_{i,0}$, the Hamiltonian (2.1) can be rewritten as [51, 52]

$$H_{\text{ion}} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j} \mathbf{u}_i^\dagger \mathbf{V}_{ij} \mathbf{u}_j \quad (2.2)$$

where the matrix $\mathbf{V}_{ij}$ can be written as

$$\mathbf{V}_{ij} = \left(\frac{\partial^2 V}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \right)_{\mathbf{r}_{i,0}, \mathbf{r}_{j,0}}$$

In condensed matter physics, the discrete translational symmetry of a crystal is described by a Bravais lattice, where any vector $\mathbf{R}_a$ corresponds to a translation that maps the crystal onto itself. For a crystal containing n ions per unit cell, the global ion index i can be separated into a unit cell index a and a basis index μ indicating the specific ion within that cell. Under this notation, the equilibrium position $\mathbf{r}_{i,0}$ can be decomposed as

$$\mathbf{r}_{i,0} = \mathbf{r}_{a\mu,0} = \mathbf{R}_a + \mathbf{d}_\mu \quad (2.3)$$

where $\mathbf{d}_\mu$ is the relative position of ion μ within the unit cell. Thanks to translational symmetry, the matrix $\mathbf{V}_{ij}$ can be written as [51]

$$\mathbf{V}_{ij} = \mathbf{V}_{a\mu,b\nu} = \mathbf{V}_{\mu\nu}(\mathbf{R}_a - \mathbf{R}_b) \quad (2.4)$$

which leads to

$$H_{\text{ion}} = \sum_a \sum_\mu \frac{\mathbf{p}_{a\mu}^2}{2m_\mu} + \frac{1}{2} \sum_{a,b} \sum_{\mu,\nu} \mathbf{u}_{a\mu}^\dagger \mathbf{V}_{\mu\nu}(\mathbf{R}_a - \mathbf{R}_b) \mathbf{u}_{b\nu} \quad (2.5)$$

This quadratic Hamiltonian can be diagonalized by performing a spatial Fourier transform on the coordinates $\mathbf{u}_{a\mu}$ and momenta $\mathbf{p}_{a\mu}$. Imposing periodic boundary conditions, we define the transformed variables as

$$\mathbf{q}_{\mathbf{k},\mu} = \sqrt{m_\mu} \frac{1}{\sqrt{N}} \sum_a \mathbf{u}_{a\mu} e^{-i\mathbf{k} \cdot \mathbf{R}_a}, \quad \boldsymbol{\pi}_{\mathbf{k},\mu} = \frac{1}{\sqrt{m_\mu}} \frac{1}{\sqrt{N}} \sum_a \mathbf{p}_{a\mu} e^{i\mathbf{k} \cdot \mathbf{R}_a}$$

where $N = N_1 N_2 N_3$ is the total number of Bravais lattice points in the crystal, and

$$\mathbf{k} = \frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3$$

where n_i are integers and $\mathbf{b}_i$ are the primitive reciprocal lattice vectors. Using these Fourier-transformed variables, the Hamiltonian in Eq. (2.5) can be rewritten as

$$H_{\text{ion}} = \sum_{\mathbf{k}} \left[\frac{1}{2} \sum_\mu \boldsymbol{\pi}_{\mathbf{k},\mu}^\dagger \boldsymbol{\pi}_{\mathbf{k},\mu} + \frac{1}{2} \sum_{\mu,\nu} \mathbf{q}_{\mathbf{k},\mu}^\dagger \mathbf{Y}_{\mathbf{k},\mu\nu} \mathbf{q}_{\mathbf{k},\nu} \right] \quad (2.6)$$

with

$$\mathbf{Y}_{\mathbf{k},\mu\nu} = \frac{1}{\sqrt{m_\mu m_\nu}} \sum_{\mathbf{R}} \mathbf{V}_{\mu\nu}(\mathbf{R}) e^{-i\mathbf{k} \cdot \mathbf{R}}$$

This transformation decouples the lattice vibrations for different wavevectors $\mathbf{k}$. Note that the dynamical matrix $\mathbf{Y}_{\mathbf{k},\mu\nu}$ incorporates not only the ion indices μ, ν but also the spatial Cartesian axes (x, y, z) , making it a $3n \times 3n$ positive semi-definite matrix. For each $\mathbf{k}$, we can find its eigenvalues $[\omega_s(\mathbf{k})]^2$ and corresponding eigenvectors $\mathbf{e}_{s,\mu}(\mathbf{k})$ ($s = 1, 2, \dots, 3n$). This allows us to express the Hamiltonian as a sum over independent harmonic oscillators [53]

$$H_{\text{ion}} = \sum_{\mathbf{k}} \sum_s \hbar \omega_s(\mathbf{k}) \left(c_{\mathbf{k},s}^\dagger c_{\mathbf{k},s} + \frac{1}{2} \right) \quad (2.7)$$

with

$$c_{\mathbf{k},s} = \sum_{\mu} \mathbf{e}_{s,\mu}(\mathbf{k}) \cdot \left[\sqrt{\frac{\omega_s(\mathbf{k})}{2\hbar}} \mathbf{q}_{\mathbf{k},\mu} + \frac{i}{\sqrt{2\hbar\omega_s(\mathbf{k})}} \pi_{\mathbf{k},\mu} \right]$$

where $\omega_s(\mathbf{k})$ represents the angular frequency of the given phonon mode.

The quantized collective excitations in Eq. (2.7) are known as phonons. Each phonon is characterized by a crystal momentum $\mathbf{k}$ and a branch index s . In this quantum mechanical description, an excited state of the lattice can be described by the occupation numbers $n_{\mathbf{k},s}$ for each phonon mode. There are always exactly three branches whose frequencies vanish as $\mathbf{k} \rightarrow 0$ (near the Γ point). These are the acoustic phonons, which correspond to the in-phase translation of all ions within a unit cell. The remaining $3(n - 1)$ branches, which have finite frequencies in the long-wavelength limit ($\mathbf{k} \rightarrow 0$), are called optical phonons. In the case of optical phonons, the ions within a unit cell oscillate out-of-phase relative to each other [51, 53, 54]. A representative phonon dispersion relation for a three-dimensional crystal with $n = 2$ atoms per unit cell is illustrated in Fig. 2.1a, where the different acoustic and optical branches are labeled [51].

Another important consideration in three-dimensional crystals is the relationship between the polarization vector $\mathbf{e}_{s,\mu}$ and the wavevector $\mathbf{k}$. For isotropic media, or along high-symmetry directions in crystals, the eigenmodes can be rigorously classified as strictly longitudinal ($\mathbf{e}_{s,\mu} \parallel \mathbf{k}$) or strictly transverse ($\mathbf{e}_{s,\mu} \perp \mathbf{k}$). In general anisotropic crystals, modes pointing in arbitrary directions do not possess purely longitudinal or transverse character [51]. Nevertheless, because the polarization vectors $\mathbf{e}_{s,\mu}$ evolve continuously as $\mathbf{k}$ deviates from high-symmetry axes, the labels "longitudinal" and "transverse" are conventionally retained. Phonons classified this way still predominantly exhibit $\mathbf{e}_{s,\mu} \parallel \mathbf{k}$ and $\mathbf{e}_{s,\mu} \perp \mathbf{k}$ behaviors, respectively [51]. Illustrative schematics depicting the atomic motions for longitudinal acoustic (LA), transverse acoustic (TA), longitudinal optical (LO), and transverse optical (TO) phonons are provided in Fig. 2.1b-e. Here, the red and blue circles represent the two distinct ion types within the diatomic basis.

For the remainder of this chapter, we will primarily adopt a classical description of lattice vibrations. The classical equation of motion corresponding to the Hamiltonian in Eq. (2.5)

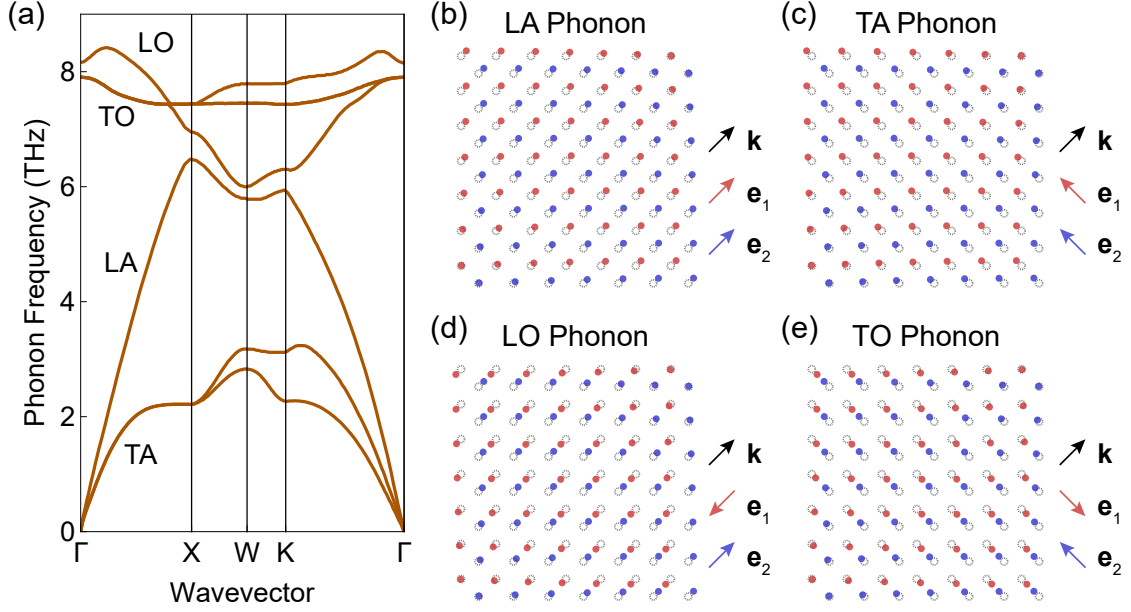


Figure 2.1. Different types of phonons in three-dimensional materials. (a) Phonon spectrum of GaAs, showing three acoustic branches (with $\omega(\mathbf{k}) \sim |\mathbf{k}|$ near the Γ point) and three optical branches (with finite $\omega(\mathbf{k})$ at the Γ point). For certain $\mathbf{k}$ values, some branches are degenerate. Adapted from [55]. (b-e) Schematics of ion motions for LA (b), TA (c), LO (d), and TO (e) phonons. Red and blue circles represent two different ion types, and gray dashed circles indicate their equilibrium positions. $\mathbf{e}_1$ and $\mathbf{e}_2$ are the polarization directions for the red and blue ions, respectively.

is [51]

$$m_\mu \ddot{\mathbf{u}}_{a\mu} = - \sum_b \sum_v \mathbf{V}_{\mu\nu}(\mathbf{R}_a - \mathbf{R}_b) \mathbf{u}_{bv} \quad (2.8)$$

Subject to periodic boundary conditions, Eq. (2.8) admits plane-wave solutions of the form

$$\mathbf{u}_{a\mu}(t) = \Re \left[\frac{A_{\mathbf{k},s}}{\sqrt{m_\mu}} \mathbf{e}_{s,\mu}(\mathbf{k}) e^{i(\mathbf{k} \cdot \mathbf{R}_a - \omega_s(\mathbf{k})t)} \right] \quad (2.9)$$

where $A_{\mathbf{k},s}$ is the complex oscillation amplitude of the respective phonon mode. It is convenient to define

$$Q_{\mathbf{k},s}(\mathbf{R}, t) = \Re \left[A_{\mathbf{k},s} e^{i(\mathbf{k} \cdot \mathbf{R} - \omega_s(\mathbf{k})t)} \right] \quad (2.10)$$

as the real, space- and time-dependent coordinate of the phonon mode $(\mathbf{k}, s)$.

2.1.2 Linear Optical Properties of Ionic Crystals

Because optical phonons possess finite frequencies near the Brillouin zone center (long-wavelength limit), they can interact with electromagnetic waves. This interaction determines the infrared optical properties of ionic crystals. Phonon modes that generate a net oscillating electric dipole can couple linearly to the electric field of light and are termed infrared-active. Conversely, phonons that modulate the electronic polarizability of the lattice, thereby participating in inelastic light scattering, are known as Raman-active [56]. The crystal symmetry imposes strict selection rules that govern whether a given phonon mode is infrared-active, Raman-active, or both. In centrosymmetric materials, a phonon is either infrared-active (odd parity) or Raman-active (even parity), but never both. In non-centrosymmetric crystals, however, a single phonon mode can be simultaneously infrared- and Raman-active.

The dynamics of an infrared-active phonon driven by an external electric field $E(t)$ can be phenomenologically described using the Lorentz oscillator model. In this framework, the generalized phonon coordinate $Q_{IR}(t)$ satisfies the equation of motion

$$\ddot{Q}_{IR} + \gamma_{IR}\dot{Q}_{IR} + \omega_{TO}^2 Q_{IR} = Z^* E(t) \quad (2.11)$$

Here, Z^* is the mode effective charge, γ_{IR} is the damping rate, and ω_{TO} is the natural angular frequency of the TO mode. The effective charge is defined as

$$Z^* = v_0 \frac{\partial P_{IR}}{\partial Q_{IR}}$$

where v_0 is the unit cell volume, and P_{IR} is the polarization density corresponding to the phonon displacement Q_{IR} .

When driven by a monochromatic oscillating electric field $E(t) = E_0 e^{-i\omega t}$, the steady-state response of Q_{IR} can be readily obtained from Eq. (2.11) as

$$Q_{IR}(t) = \frac{Z^* E_0 e^{-i\omega t}}{\omega_{TO}^2 - \omega^2 - i\gamma_{IR}\omega} \quad (2.12)$$

which generates a corresponding polarization density

$$P_{IR}(t) = \frac{1}{v_0} \frac{Z^{*2}}{\omega_{TO}^2 - \omega^2 - i\gamma_{IR}\omega} E_0 e^{-i\omega t} \quad (2.13)$$

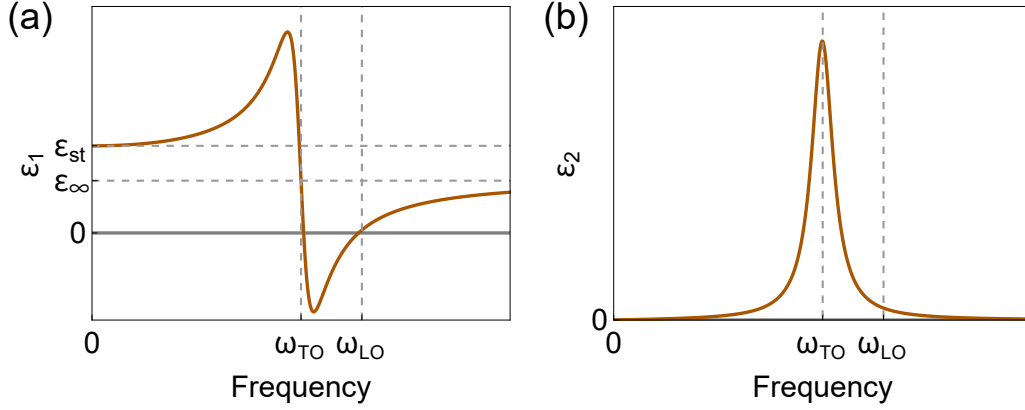


Figure 2.2. Example frequency dependence of the relative permittivity of an ionic crystal with a single infrared-active optical phonon branch. The real part ε_1 and imaginary part ε_2 are shown in (a) and (b), respectively.

In real materials, the total frequency-dependent dielectric permittivity incorporates both the phononic contribution derived in Eq. (2.13) and the background electronic polarizability. For an ionic crystal hosting a single dominant infrared-active optical phonon branch, the relative permittivity in the near-to-mid-infrared spectral range can be expressed as [48, 51]

$$\begin{aligned}\varepsilon_r(\omega) &= \varepsilon_\infty + \frac{1}{\varepsilon_0 v_0} \frac{Z^{*2}}{\omega_{TO}^2 - \omega^2 - i\gamma_{IR}\omega} \\ &= \varepsilon_\infty + (\varepsilon_{st} - \varepsilon_\infty) \frac{\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma_{IR}\omega}\end{aligned}\quad (2.14)$$

where ε_∞ is the high-frequency permittivity (arising from the purely electronic response) and $\varepsilon_{st} = \varepsilon(\omega = 0)$ is the static permittivity. The typical dispersion of the complex permittivity $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is illustrated in Fig. 2.2. The phononic contribution becomes resonantly enhanced when the driving frequency ω approaches the TO phonon frequency ω_{TO} . Near the resonance at $\omega = \omega_{TO}$, the real part ε_1 crosses ε_∞ , and the imaginary part ε_2 exhibits a pronounced peak.

In the absence of free charges and magnetic fields, the macroscopic Maxwell equations governing the electric field inside the dielectric are

$$\nabla \times \mathbf{E} = 0, \quad \nabla \cdot \mathbf{D} = 0 \quad (2.15)$$

where $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$ is the electric displacement field. For a propagating wave with wavevector

$\mathbf{k}$, Eqs. (2.15) simplify to algebraic conditions

$$\mathbf{k} \times \mathbf{E} = 0, \mathbf{k} \cdot \mathbf{D} = 0 \quad (2.16)$$

In the limit of $\gamma_{IR} \rightarrow 0$, the TO phonon mode should have zero $\mathbf{E}$ field and thus $\varepsilon(\omega_{TO}) = \infty$, and the LO phonon mode should have zero $\mathbf{D}$ field and thus $\varepsilon(\omega_{LO}) = 0$. These arguments yield the Lyddane–Sachs–Teller relation [51]

$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon_{st}}{\varepsilon_{\infty}} \quad (2.17)$$

Between the TO and LO frequencies ($\omega_{TO} < \omega < \omega_{LO}$), the real part of the relative permittivity is negative (assuming small damping $\gamma_{IR} \rightarrow 0$). The electromagnetic radiation cannot propagate in the material in this frequency range, known as the Reststrahlen effect.

2.1.3 Phonon Polariton

Next, we consider the co-propagation of electromagnetic waves and phonons. To capture these dynamics, the propagating magnetic field $\mathbf{B}$ must be included in the Maxwell curl equation, namely

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \nabla \times \mathbf{B} = \mu_0 \frac{\partial \mathbf{D}}{\partial t} \quad (2.18)$$

while the divergence equation $\nabla \cdot \mathbf{D} = 0$ remains unchanged. Therefore, the LO phonon is decoupled from the electromagnetic waves with its dispersion flat at $\omega = \omega_{LO}$. The wave equation for the transverse electric field is

$$\nabla^2 \mathbf{E} = \frac{\varepsilon_r}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (2.19)$$

where $c = 1/\sqrt{\varepsilon_0 \mu_0}$ is the speed of light in vacuum. Substituting plane-wave solutions into this wave equation yields

$$\varepsilon_r = \frac{c^2 k^2}{\omega^2} \quad (2.20)$$

In the limit $\gamma_{IR} \rightarrow 0$, Eq. (2.20) yields two distinct dispersion branches [57]

$$\omega_{\pm} = \sqrt{\frac{c^2 k^2 + \varepsilon_{st} \omega_{TO}^2}{2\varepsilon_{\infty}}} \pm \sqrt{\left(\frac{c^2 k^2 + \varepsilon_{st} \omega_{TO}^2}{2\varepsilon_{\infty}}\right)^2 - \frac{c^2 k^2 \omega_{TO}^2}{\varepsilon_{\infty}}} \quad (2.21)$$

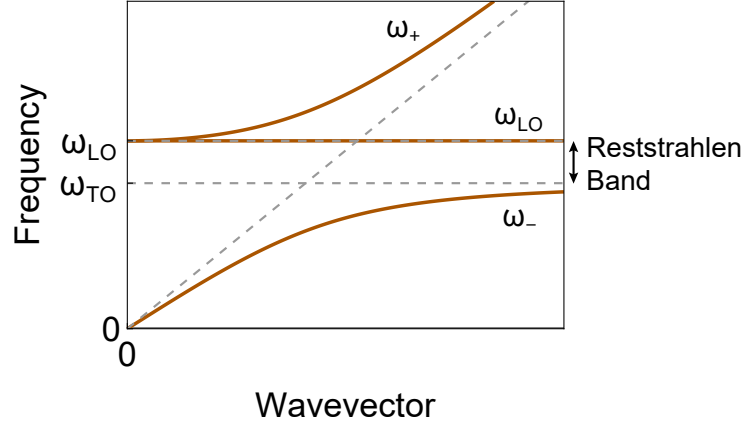


Figure 2.3. Dispersion relation of transverse and longitudinal modes in an ionic crystal.

The transverse modes (polaritons) are labeled $\omega_{\pm}$, and the longitudinal mode (phonon) is labeled ω_{LO} . Dashed lines indicate $\omega = \omega_{TO}$, $\omega = \omega_{LO}$, and $\omega = ck/\sqrt{\epsilon_{\infty}}$. Adapted from [57].

These two branches, denoted ω_{+} and ω_{-} , represent coupled light-matter quasiparticles known as phonon polaritons. They arise from the hybridization between the TO phonons and the photons. The typical dispersion relations for the two polariton branches, along with the uncoupled LO phonon, are schematically depicted in Fig. 2.3. As predicted, a propagation gap exists between ω_{TO} and ω_{LO} , coinciding with the Reststrahlen band. Note that the characteristic photon momentum near the resonance (ω_{TO}/c) is orders of magnitude smaller than the extent of the first Brillouin zone ($\sim \pi/\sqrt[3]{v_0}$). Consequently, over the wavevector range where this strong coupling occurs, the intrinsic dispersion ($\mathbf{k}$ -dependence) of the bare TO and LO phonons is negligible.

2.2 Nonlinear Coupling between Phonons

So far, we have used a harmonic approximation for the lattice potential, and defined phonons as the eigenmodes of this harmonic potential. While this approximation is generally valid for small atomic mode displacements, intense light pulses could induce large-amplitude oscillatory motion of infrared-active phonons, which explores the anharmonic region of the lattice potential. Therefore, to describe intense pulsed excitations, the total lattice potential

energy is expanded beyond the harmonic approximation [58]

$$V = \sum_i \frac{1}{2} \omega_i^2 Q_i^2 - \sum_i Z_i^* Q_i E + V_{anh} \quad (2.22)$$

$$V_{anh} = \sum_{ijk} V_{ijk}^{(2)} Q_i Q_j Q_k + \sum_{ijkl} V_{ijkl}^{(3)} Q_i Q_j Q_k Q_l + \dots \quad (2.23)$$

Note that the mixing between different phonon modes naturally occurs in the anharmonic part, as phonons are defined from the diagonalization of only the harmonic potential. Whether a specific nonlinear coupling term is allowed depends on the crystal's symmetry. In the language of group theory, the symmetry operations of the crystal lattice constitute a group, and every phonon mode transforms according to a specific irreducible representation of this group. The macroscopic potential energy V must be invariant under all symmetry operations of the crystal. Consider a cubic anharmonic coupling term $V = -\alpha Q_i Q_j Q_k$, which exerts a generalized force on mode Q_k

$$F_k = \alpha Q_i Q_j \quad (2.24)$$

Let A_i, A_j, A_k denote the irreducible representations associated with the modes Q_i, Q_j, Q_k , respectively. For this coupling term to be non-zero, the symmetry condition dictates that [27, 59]

$$A_k \subset A_i \otimes A_j \quad (2.25)$$

In other words, if the tensor product $A_i \otimes A_j$ is decomposed into a direct sum of irreducible representations, A_k must be present in that sum. This group theory approach provides a robust and systematic method to identify all symmetry-allowed nonlinear phonon couplings in any given crystal structure.

In the following subsections, I first discuss the lowest-order nonlinear coupling, $Q_1^2 Q_2$. This type of coupling has been the primary mechanism exploited in early nonlinear phononics experiments to drive structural phase transitions [2, 4, 17, 27, 48]. I will then briefly introduce a higher-order coupling term, $Q_1^2 Q_2^2$, which leads to the renormalization of phonon frequencies.

2.2.1 $Q_{IR}^2 Q_R$ Coupling: Transient Phonon Displacement

In centrosymmetric crystals, the total potential energy must have even parity under spatial inversion. Since infrared-active phonons (Q_{IR}) possess odd parity while Raman-active phonons (Q_R) possess even parity, a linear coupling $Q_{IR}Q_R$ is forbidden. The lowest-order allowed anharmonic term coupling must be quadratic in the Q_{IR} coordinate [25, 60]

$$V_\alpha = -\alpha Q_{IR}^2 Q_R \quad (2.26)$$

where the constant α dictates the strength of the nonlinear coupling.

Incorporating this anharmonic potential, the coupled equations of motion for the two phonon modes become [27, 60]

$$\ddot{Q}_{IR} + \gamma_{IR}\dot{Q}_{IR} + \omega_{TO}^2 Q_{IR} = Z^* E(t) + 2\alpha Q_{IR} Q_R \quad (2.27)$$

$$\ddot{Q}_R + \gamma_R \dot{Q}_R + \omega_R^2 Q_R = \alpha Q_{IR}^2 \quad (2.28)$$

where ω_R and γ_R are the natural frequency and the damping rate of the Raman-active mode, respectively. Assuming weak coupling, the amplitude of Q_{IR} scales linearly with the driving field E , while the amplitude of Q_R scales as E^2 . Therefore, to the lowest order, the back-action term $2\alpha Q_{IR}Q_R$ in Eq. (2.27) can be neglected, and the Q_{IR} mode then behaves as a simple driven harmonic oscillator responding to the pump electric field at frequency ω (Fig. 2.4a). When excited by an ultrashort, on-resonance MIR pulse, the coherent oscillations of Q_{IR} will persist for a lifetime of $\sim 1/\gamma_{IR}$ after the pulse departs (Fig. 2.4b).

According to Eq. (2.28), the driving force on Q_R is proportional to Q_{IR}^2 , and it contains a zero-frequency component alongside an oscillating component at 2ω . The rectified component shifts the minimum of the effective potential of Q_R mode, inducing the displacement (Fig. 2.4c). The numerical solution for the temporal evolution of Q_R is shown in Fig. 2.4d, where the dark yellow curve represents the rectified displacement. This directional displacement of the atoms creates a transient structural distortion in the crystal, thereby realizing the optical control of the material's structural phase.

This concept can be naturally extended to non-centrosymmetric systems. In such materials, an intensely driven phonon Q_1 can similarly induce a directional displacement

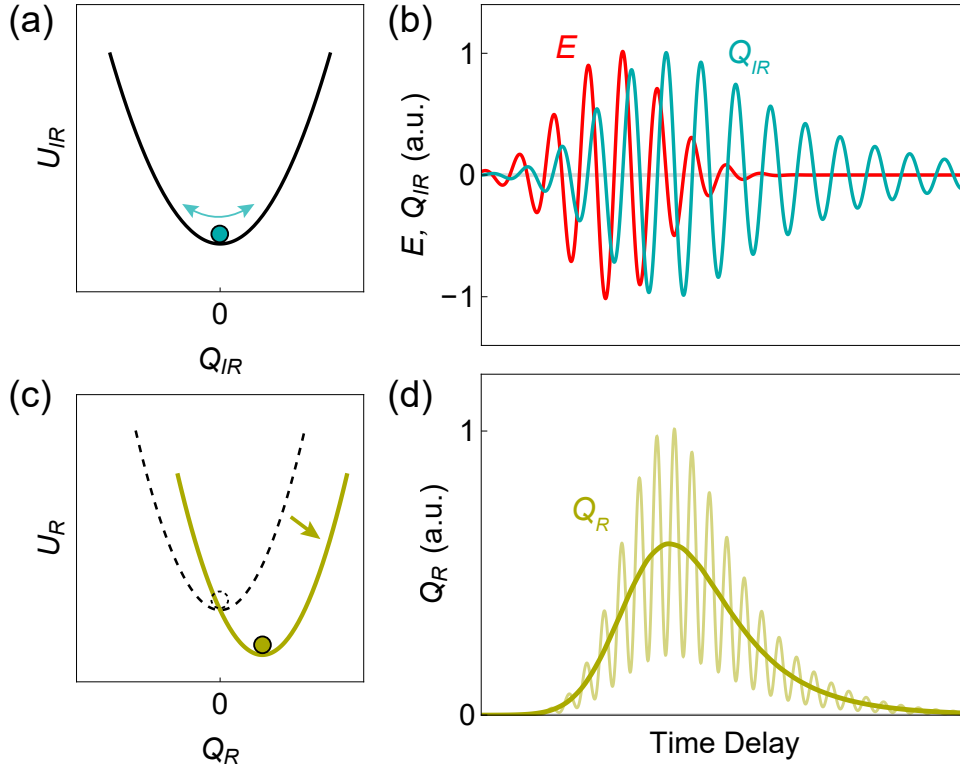


Figure 2.4. Mechanism of the transient displacement of the Q_R mode induced by oscillations of the Q_{IR} mode via $Q_{IR}^2 Q_R$ coupling. (a) Harmonic potential of the infrared-active mode Q_{IR} , which oscillates under the external driving field E . (b) Simulated temporal evolution of E and Q_{IR} . (c) The rectified component of Q_{IR}^2 shifts the minimum of the Q_R potential, thereby displacing the Q_R mode. (d) Numerical solution for the temporal evolution of Q_R . The dark yellow line shows the rectified (low-pass-filtered) component.

onto a second mode Q_2 via a $Q_1^2 Q_2$ coupling, provided the coupling term is permitted by the crystal symmetry.

2.2.2 $Q_{IR}^2 Q_c^2$ Coupling: Renormalization of the Phonon Frequency

In cases where a $Q_{IR}^2 Q_c$ interaction is forbidden by symmetry, fourth-order anharmonic potentials become important. Consider the coupling term [47, 61, 62]

$$U_\beta = -\beta Q_{IR}^2 Q_c^2 \quad (2.29)$$

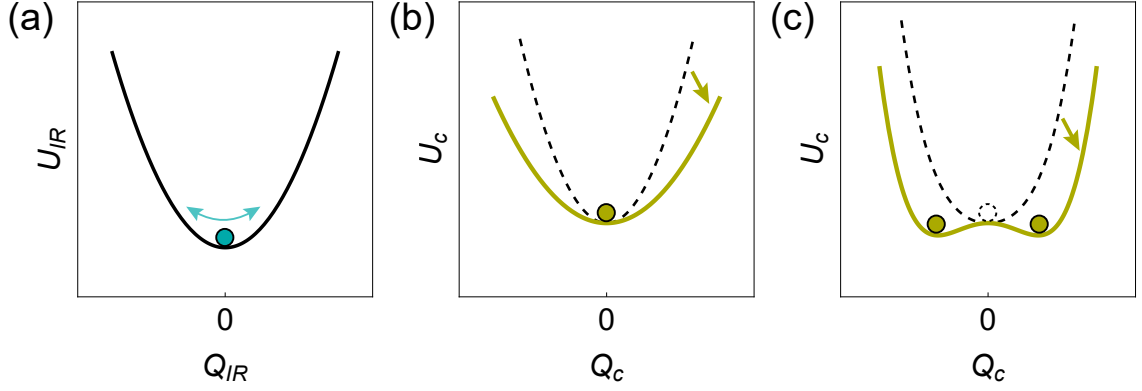


Figure 2.5. Schematics of possible effects of the $Q_{IR}^2 Q_c^2$ nonlinear coupling. (a) Oscillation of the Q_{IR} mode directly driven by the external field E . (b) Softening of the Q_c mode induced by the oscillation of Q_{IR} . (c) New minima at finite Q_c induced by the oscillation of Q_{IR} .

where Q_{IR} is the coordinate of the directly driven infrared-active phonon, Q_c is the coordinate of another phonon, and β defines the coupling strength. The equation of motion for the Q_c mode is

$$\ddot{Q}_c + \gamma_c \dot{Q}_c + \omega_c^2 Q_c = 2\beta Q_{IR}^2 Q_c \quad (2.30)$$

where ω_c and γ_c are the natural frequency and damping rate of the Q_c mode, respectively.

In the presence of a strongly oscillating Q_{IR} mode (Fig. 2.5a), this bi-quadratic coupling does not exert a net directional force on Q_c . Instead, it dynamically renormalizes the effective frequency of the Q_c mode. Averaging over the fast optical cycles of the pump, the effective frequency of the coupled mode shifts to $\omega_{c,\text{eff}} = \sqrt{\omega_c^2 - 2\beta \langle Q_{IR}^2 \rangle}$ (Fig. 2.5b). This transient "softening" (if $\beta > 0$) or "hardening" (if $\beta < 0$) could modify the fluctuations of the Q_c mode represented by $\langle Q_c^2 \rangle$ [47, 62, 63]. In systems where the intrinsic potential of the Q_c mode is highly anharmonic, such as the ferroelectric soft modes in ferroelectric materials [1, 61], a sufficiently large transient softening can lead to an instability ($\omega_{c,\text{eff}}^2 < 0$). This phenomenon creates new energy minima at finite Q_c displacements (Fig. 2.5c), which might trigger a structural phase transition [61].

2.3 Application of Nonlinear Phononics in Different Materials

The true power of nonlinear phononics lies in the complex connection between driven lattice modes, rectified displacements, and structure-dependent macroscopic order parameters in quantum materials. In this section, I will summarize several examples demonstrating the optical control of material phases using nonlinear phononics.

2.3.1 Ultrafast Structural Control in Manganites

The concept of nonlinear phononics was first experimentally demonstrated in the manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, which adopts a distorted perovskite structure in equilibrium [27]. In this experiment, MIR pulses with a fluence of about 2 mJ/cm^2 were tuned to be resonant with an in-plane infrared-active E_u phonon mode at 18.2 THz. Following the excitation, the transient relative reflectivity change ($\Delta R/R$) was probed at an 800 nm wavelength as a function of pump-probe delay (Fig. 2.6a, brown solid curve). A sharp drop in reflectivity was induced by the pump, followed by coherent oscillations at 1.2 THz at longer delays. By Fourier transforming the time-domain signal (Fig. 2.6b, solid curve), this low-frequency oscillation was assigned to a Raman-active E_g phonon mode, which corresponds to rotations of MnO_6 oxygen octahedra in the unit cell (Fig. 2.6b, left inset) [64]. This nonlinear coupling was explained by the cubic anharmonic potential linking the E_u and E_g modes

$$V = -\alpha Q_{E_u}^2 Q_{E_g} \quad (2.31)$$

Under the strong, resonant drive of the MIR electric field, the E_u mode undergoes large-amplitude oscillations at ω_{E_u} . Through the anharmonic coupling defined in Eq. (2.31), the rectified coordinate $Q_{E_u}^2$ exerts a directional force on the E_g coordinate, shifting its potential minimum on a time scale shorter than its natural period. As a result, the E_g mode experiences coherent oscillations at its intrinsic frequency ω_{E_g} around the new potential minimum. This dynamic behavior matches the experimental observations [27].

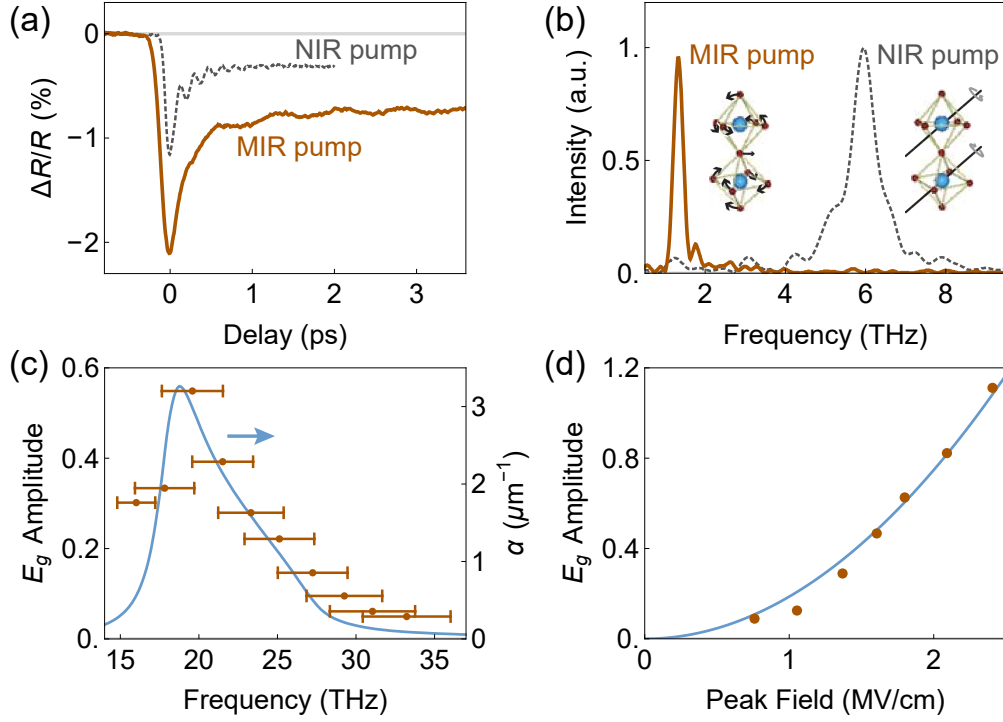


Figure 2.6. Demonstration of the nonlinear phononics concept in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. (a) Light-induced relative reflectivity change $\Delta R/R$ for an 800 nm probe after the MIR excitations at 18.2 THz (brown solid curve) and NIR excitations (gray dashed curve). (b) Fourier transform of the oscillatory signal in (a), showing peaks at different phonon modes for the MIR and NIR cases. (c) Excitation-frequency dependence of the E_g -mode oscillation amplitude (brown dots), resembling the frequency-dependent extinction coefficient (light blue curve) that peaks at the E_u phonon. Error bars indicate the bandwidth. (d) Pump electric-field dependence of the E_g -mode oscillation amplitude at the E_u phonon resonance, showing E^2 scaling (light blue curve). Adapted from [27].

To verify the selectivity of this mechanism, a control experiment utilizing NIR excitation was performed. Unlike the MIR resonant pumping, the NIR excitation predominately launched high-frequency oscillations at 5.8 THz (Fig. 2.6a,b, gray dashed curve), which correspond to the fully symmetric A_{1g} mode (Fig. 2.6b, right inset). This contrast underscores the unique state pathways accessible via direct phonon pumping versus generic electronic excitations. The amplitude of the coherent E_g phonon generally follows the linear absorption profile of the E_u resonance when plotted against the MIR excitation frequency (after correcting

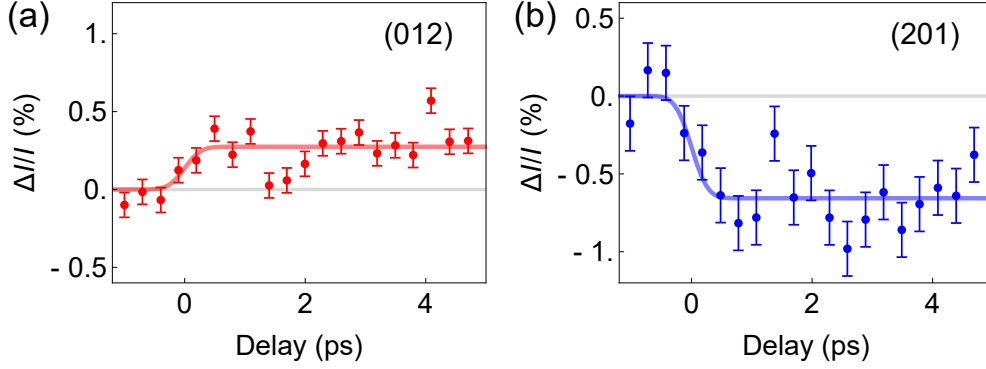


Figure 2.7. First time-resolved X-ray diffraction analysis of nonlinear phononics. Relative changes in scattered intensity from the (012) (a) and (201) (b) lattice reflections in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are plotted as a function of pump-probe delay. Light lines show error-function fits to the data. Adapted from [6].

for Reststrahlen band reflectivity effects, Fig. 2.6c). Additionally, the E_g amplitude scales quadratically with the applied pump electric field at resonance (E^2 , Fig. 2.6d). These two signatures are also consistent with the theoretical model proposed in Eq. (2.31) [27].

Time-resolved X-ray diffraction provided direct evidence of the rectified atomic displacement of the E_g mode induced by the resonant pumping of the E_u mode [6]. As illustrated in Fig. 2.7, a step-like change in the scattered X-ray intensity was observed for both the (012) and (201) lattice Bragg reflections. This change confirms the transient structural displacement of the E_g coordinate following the ultrafast MIR excitation.

Because the distortions of the oxygen octahedra significantly impact the electronic and magnetic ground states in perovskites, this nonlinear phononic mechanism offers a versatile tool for controlling phases in perovskite materials [4, 42, 49]. One example is the light-induced melting of charge order in the related manganite $\text{Pr}_x\text{Ca}_{1-x}\text{MnO}_3$. In that material, resonant MIR excitation transiently drives a specific lattice distortion that is energetically unfavorable for the charge-ordered phase [17, 46].

2.3.2 Other Examples of Material Control with Nonlinear Phononics

Since the demonstration of nonlinear phononics in manganites [27], the concept has been extended to other materials where different types of nonlinear coupling potential exist. Fig. 2.8 summarizes several examples where the nonlinear coupling potentials beyond $Q_1^2 Q_2$ play a role in material control.

In Ref. [1], an infrared-active phonon mode at 19 THz in the ferroelectric LiNbO₃ was resonantly excited with intense MIR pulses and used to control the ferroelectricity in this system. The subsequent dynamics of the electric polarization P were tracked using time-resolved (heterodyne) SHG measurements [1]. The measured polarization dynamics shows a transient excursion through zero into a reversed polarization state (Fig. 2.8a, right panel). Denoting Q_P as the ferroelectric soft mode, and Q_{IR} as the directly driven phonon (Fig. 2.8a, left panel), this ultrafast polarization reversal can be qualitatively understood using the potential [61]

$$V(Q_P, Q_{IR}) = \frac{1}{4}\omega_P^2 \left(-Q_P^2 + \frac{1}{2}Q_P^4 \right) + \frac{1}{2}\omega_{IR}^2 Q_{IR}^2 + \kappa Q_{IR}^2 Q_P^2 \quad (2.32)$$

At equilibrium, this potential exhibits two degenerate minima at $Q_P = \pm 1$, representing the two stable, oppositely polarized states. For weak excitation where $\kappa \langle Q_{IR}^2 \rangle < 1$, the effective potential retains its double-well shape with the minima displaced symmetrically inward to $Q_P = \pm \sqrt{1 - \kappa \langle Q_{IR}^2 \rangle}$. However, under sufficiently intense excitation where $\kappa \langle Q_{IR}^2 \rangle \geq 1$, the energy barrier at the origin is completely suppressed, and the potential transiently transforms into a single well centered at $Q_P = 0$. Therefore, the polarization can be pushed to zero with strong excitation of the Q_{IR} mode. Whether a complete switching to the opposite ferroelectric domain occurs after the pump depends sensitively on the system's dynamics, and theoretical modeling suggests that the purely transient reversal observed experimentally can be explained by τ_{IR} being comparable to ω_P^{-1} [61, 65].

The framework of nonlinear phononics is not restricted to lattice-lattice interactions, with one prominent frontier being the resonant optical excitation of magnons mediated by nonlinear spin-phonon interactions [3, 66–69]. In ErFeO₃, two orthogonal infrared-active phonons, the B_{ua} mode polarized along the a axis and the B_{ub} mode polarized along the b

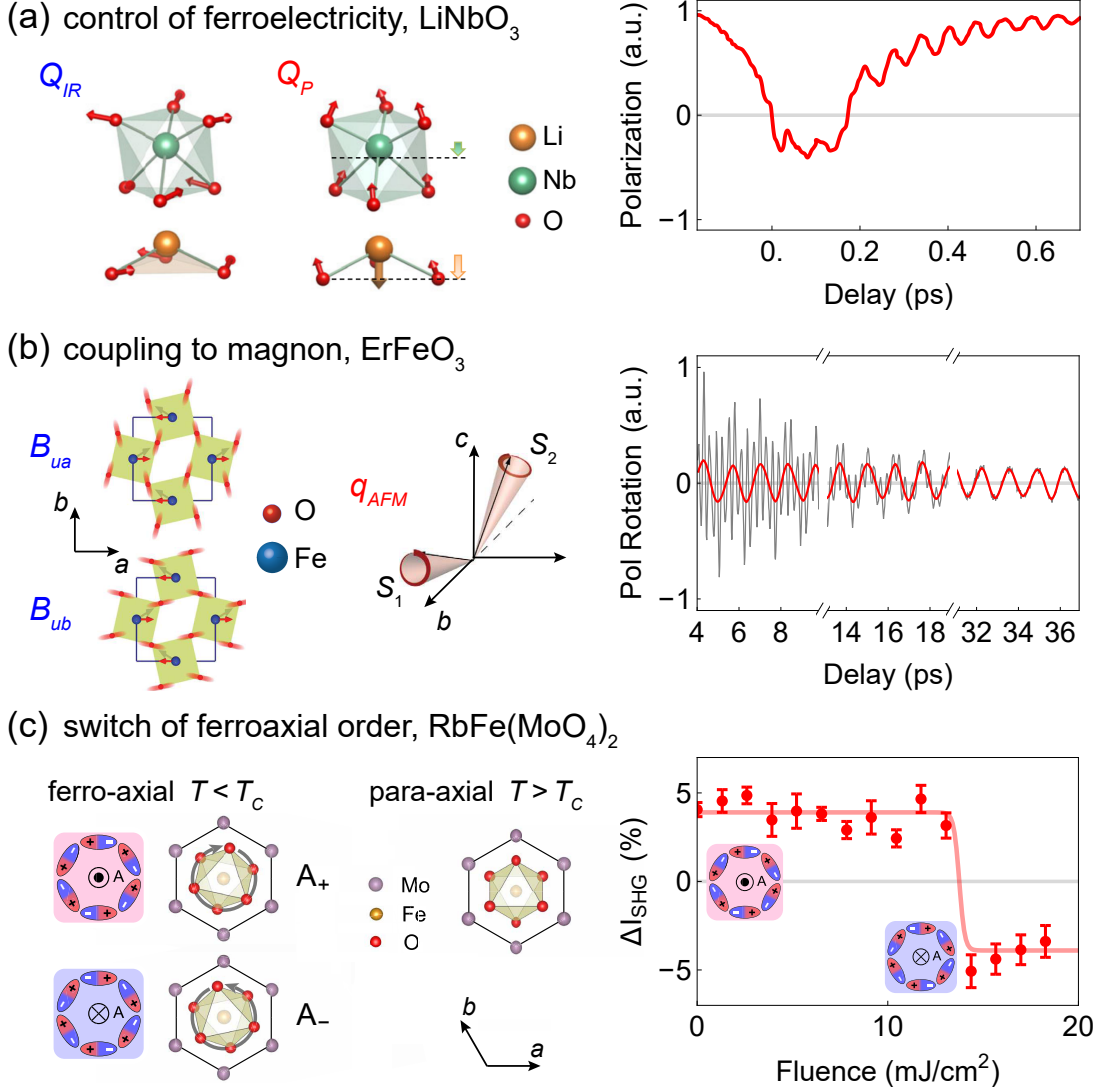


Figure 2.8. Additional examples of material control with nonlinear phononics. (a) The polarization of LiNbO_3 transiently reverses after MIR excitation. The dynamics can be explained by the nonlinear coupling potential $Q_{IR}^2 Q_P^2$, where Q_{IR} is the driven mode and Q_P is the polarization. Adapted from [1]. (b) In ErFeO_3 , through the nonlinear interaction between two phonons Q_{ua}, Q_{ub} and the magnon q_{AFM} , the magnon oscillation can be activated by the optical excitation of phonons. Adapted from [3]. (c) In $\text{RbFe}(\text{MoO}_4)_2$, the axial phonon mode Q_A can be displaced by the potential $(\mathbf{Q} \times \mathbf{E})_c Q_A$, where $\mathbf{E}$ is the MIR electric field and $\mathbf{Q}$ is the driven mode, resulting in an all-optical switching of the ferroaxial state. Adapted from [24].

axis (Fig. 2.8b, left panel), can be simultaneously driven by an appropriately polarized MIR pump pulse. These two orthogonal lattice displacements, Q_{ua} and Q_{ub} , couple to the c -axis magnetization M_c via a nonlinear potential [3]

$$V = i\alpha (Q_{ua}Q_{ub}^* - Q_{ua}^*Q_{ub}) M_c \quad (2.33)$$

In Ref. [3], the MIR excitation pulse was linearly polarized at an angle of 45° relative to the a and b axes, effectively driving both modes simultaneously. Because the intrinsic resonant frequencies of the Q_{ua} and Q_{ub} phonons are slightly non-degenerate (16.17 THz and 17.03 THz, respectively), a relative phase difference occurs between the two oscillations, and an effective magnetic field along the c axis is produced. Because the quasi-antiferromagnetic magnon mode (q_{AFM}) entails small dynamical changes of the magnetization vector predominantly along the c axis (Fig. 2.8b, left panel), it couples forcefully to the phonons as dictated by Eq. (2.33). Such coupling is evidenced by the Faraday rotation measurements, where the time-domain traces revealed a long-lived component oscillating at the frequency of the q_{AFM} magnon frequency (red curve in Fig. 2.8b, right panel).

A recent addition to the phases controllable by nonlinear phononics is ferroaxial order. This phase is characterized by a rotational texture that hosts vertices of electric dipoles [24, 70, 71], and the corresponding order parameter can be written as $\mathbf{A} = \mathbf{r} \times \mathbf{p}$, where $\mathbf{r}$ is the position vector and $\mathbf{p}$ is the local dipole. When cooling below $T_C \approx 190$ K, $\text{RbFe}(\text{MoO}_4)_2$ transitions from a high-symmetry paraaxial phase to a ferroaxial phase with two distinct domain types, denoted A_+ and A_- (Fig. 2.8c, left panel). These two domains correspond to a net ferroaxial order parameter $\mathbf{A}$ parallel or antiparallel to the c axis. The order parameter $\mathbf{A}$ is conjugate to a generalized field

$$\mathbf{F}_A = \mathbf{Q} \times \mathbf{E} \quad (2.34)$$

where $\mathbf{E}$ represents the electric field of the driving MIR pulse, and $\mathbf{Q}$ is the lattice displacement associated with the driven infrared-active phonon. In Ref. [24], circularly polarized MIR pulses at 24 THz propagating along the c axis are used to resonantly drive the two degenerate infrared-active modes spanning the ab plane and generate a static unidirectional effective field $\mathbf{F}_A$. Such quasi-static force enables an all-optical switching of ferroaxial domains for

the excitation fluence above $I_{th} \approx 14 \text{ mJ/cm}^2$ (Fig. 2.8c, right panel). The direction of switching can be controlled by the handedness of the pump light.

Chapter 3

Light-Induced Chirality in BPO₄

In Chapter 2, the nonlinear interaction between light pulses and optical phonons in solids was introduced, outlining the principles and experimental techniques of nonlinear phononics. In this chapter, I will focus on the specific phenomenon investigated in this thesis: light-induced chirality in the achiral solid BPO₄. I will begin by defining chirality in condensed matter systems, followed by an introduction to the experimental demonstration of the light-induced chiral state in BPO₄.

3.1 Chirality in Solids

3.1.1 Chiral Materials

An object is considered chiral if its mirror image cannot be superimposed onto the original object through any combination of translations and rotations. Chirality is crucial not only in the study of the optical properties of materials but also in the chemical and biological behavior of molecules [72, 73]. A prominent example of a chiral crystal is α -quartz, which can exist in either left- or right-handed structures, characterized by atomic spirals within its unit cell (Fig. 3.1a) [74, 75]. The left- and right-handed forms of α -quartz are mirror images of one another.

In chiral materials, circularly polarized electromagnetic waves of opposite handedness propagate at different speeds and experience different losses, phenomena known as circular

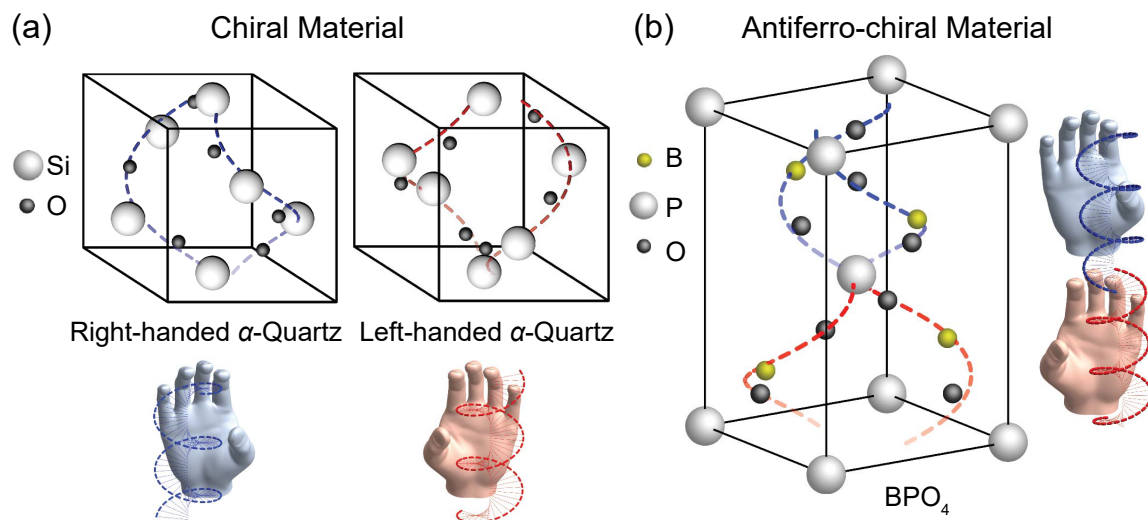


Figure 3.1. Example crystal structures of chiral and antiferro-chiral materials. (a) The structure of the chiral crystal α -quartz in its left- and right-handed forms. The two structures are exact mirror images of each other. (b) The structure of the antiferro-chiral crystal BPO_4 , which contains both left- and right-handed fragments within a single unit cell. Adapted from [48].

birefringence and circular dichroism, respectively. Circular birefringence causes the polarization plane of linearly polarized light to rotate as it travels through a chiral medium, which can be quantified by rotary power, defined as the rotation angle of the polarization plane divided by the thickness of the material. This effect is also known as optical activity, and the resulting rotation of the polarization plane has a magnitude and sign independent of the incident polarization angle. This polarization rotation serves as a sensitive probe for detecting the chiral state of a material [76, 77]. For instance, α -quartz exhibits a rotary power of approximately 0.22 rad/mm at a wavelength of 760 nm [78].

3.1.2 Antiferro-chiral Materials

In chiral crystals such as α -quartz, the handedness is determined during crystal growth. Once formed, this handedness cannot be switched without melting and recrystallizing the solid [79]. This fundamental limitation motivates the search for alternative materials whose

chirality can be dynamically controlled by external drives.

Antiferro-chiral materials represent a specific class of achiral systems that contain both left- and right-handed structural sub-units within a single unit cell, with an example being BPO_4 (Fig. 3.1b). Because these two oppositely handed fragments perfectly compensate for each other, the crystal remains macroscopically achiral. However, if the balance between the two fragments is broken, a nonzero overall chirality can be induced. This underlying structural property opens up the possibility of dynamically controlling the macroscopic chirality of antiferro-chiral materials using external perturbations, such as optical excitation [48] or mechanical strain [80].

Remarkably, the B -symmetry phonon modes in BPO_4 involve atomic displacements that lift the degeneracy between the left- and right-handed fragments, transforming the material into a ferri-chiral state (Fig. 3.2) [48]. Upon a nonzero displacement of the B -symmetry modes, the crystal symmetry of BPO_4 is reduced, and the point group changes from $\bar{4}$ (achiral) to 2 (chiral). The handedness of this induced macroscopic chirality is determined directly by the sign of the B -mode coordinate Q_B .

3.2 Light-Induced Chiral State in BPO_4

An ideal method for inducing a coherent displacement of the Q_B mode in BPO_4 is to employ the principles of nonlinear phononics discussed in Chapter 2. In the following sections, I will first outline the form of the nonlinear coupling potential. I will then summarize the experimental characterization of the relevant phonon modes and review the recent demonstration of light-induced chirality in BPO_4 .

3.2.1 Nonlinear Phonon Coupling Form

As established in Chapter 2, a transient displacement of a B -symmetry mode can be generated through a nonlinear coupling term of the form $Q_1^2 Q_B$, where Q_1 represents an infrared-active phonon mode directly driven by a mid-infrared (MIR) pump pulse. In BPO_4 , crystal symmetry permits coupling between the Q_B mode and the doubly degenerate E -symmetry

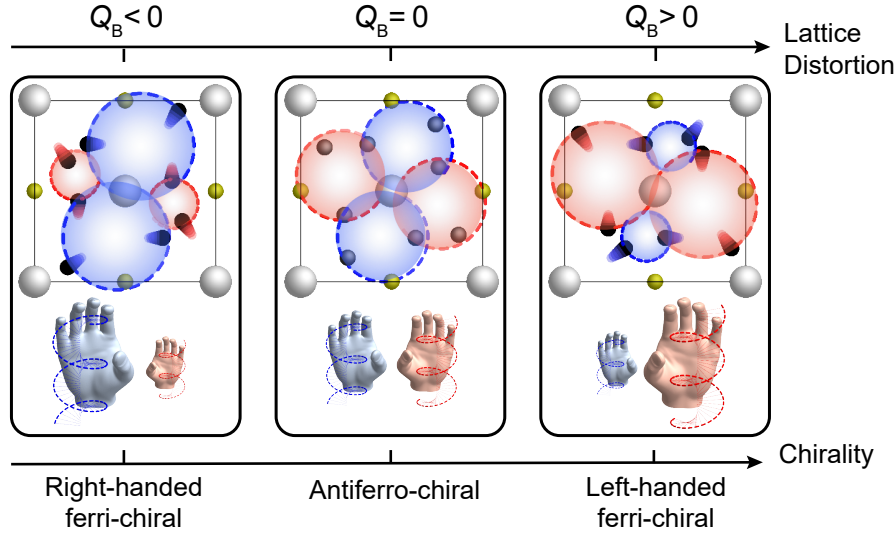


Figure 3.2. Connection between the B -mode coordinate Q_B and chirality in BPO_4 . If $Q_B \neq 0$, the balance between the left- and right-handed chiral fragments in BPO_4 is broken. As a result, the material becomes chiral, with the resulting handedness dictated by the sign of Q_B . Adapted from [48].

phonon modes, $Q_{E,a}$ (along the crystal a -axis) and $Q_{E,b}$ (along the b -axis). This coupling potential takes the form [48]

$$U = -\alpha \left(Q_{E,a}^2 - Q_{E,b}^2 \right) Q_B - \alpha' Q_{E,a} Q_{E,b} Q_B \quad (3.1)$$

where α and α' are nonlinear coupling coefficients.

For MIR excitation pulses polarized exclusively along either the crystal a - or b -axis, the second term $-\alpha' Q_{E,a} Q_{E,b} Q_B$ vanishes, simplifying the analysis [48]. According to the coupling potential in Eq. (3.1), exciting $Q_{E,a}$ versus $Q_{E,b}$ produces opposite driving forces for the Q_B displacement. Consequently, the induced chirality is expected to reverse its handedness when the pump polarization changes between the a -axis and the b -axis.

3.2.2 The BPO_4 Optical Phonon Spectrum

The parameters of the E -symmetry phonon modes were extracted from the THz-to-MIR optical-response measurements of BPO_4 , performed with Fourier-transform infrared spectroscopy (FTIR) in a normal-incidence reflection geometry.

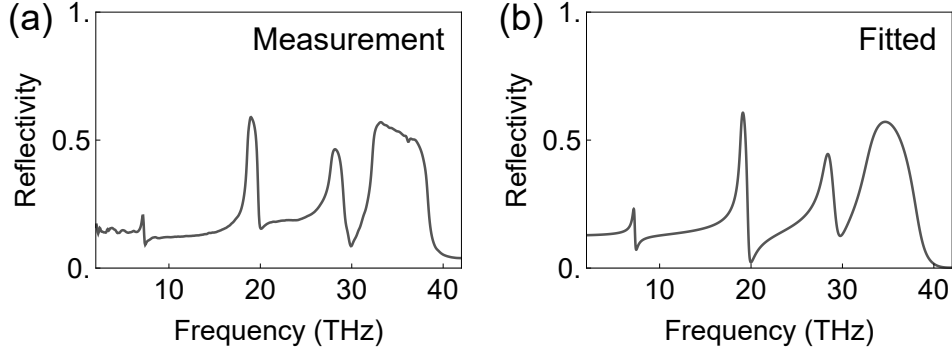


Figure 3.3. Frequency-dependent reflectivity measurement on the (001)-cut BPO_4 crystal. (a) The FTIR experimental results. (b) Fit to the experimental results. Adapted from [48].

Phonon	$\omega_{TO,i}/(2\pi)$ (THz)	$\omega_{LO,i}/(2\pi)$ (THz)	$\gamma_{E,i}/(2\pi)$ (THz)
$E(1)$	7.2	7.4	0.24
$E(2)$	18.9	20.3	0.33
$E(3)$	28.2	30.5	0.96
$E(4)$	32.8	37.0	2.0

Table 3.1. Fitted parameters for the four E -symmetry phonon modes. The corresponding experimental data and the fit curve are displayed in Fig. 3.3. Adapted from [48].

For a (001)-cut crystal, the transverse electric field of normally incident light couples exclusively to the in-plane E -symmetry phonons. The measured reflectivity spectrum is shown in Fig. 3.3a. These data can be effectively modeled using a dielectric permittivity function comprising four Lorentzian phonon oscillators (as introduced in Eq. (2.14) of Chapter 2)

$$\varepsilon(\omega) = \varepsilon_{\infty} + \varepsilon_{\infty} \sum_{i=1}^4 \frac{\omega_{LO,i}^2 - \omega_{TO,i}^2}{\omega_{TO,i}^2 - \omega^2 - i\gamma_{E,i}\omega} \quad (3.2)$$

The corresponding best fit is shown in Fig. 3.3b. The extracted transverse optical (TO) frequencies $\omega_{TO,i}$, longitudinal optical (LO) frequencies $\omega_{LO,i}$, and scattering rates $\gamma_{E,i}$ for the four E -symmetry phonons are summarized in Table 3.1. The high-frequency relative permittivity ε_{∞} is determined to be 2.70.

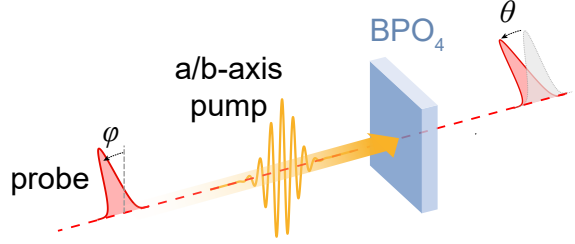


Figure 3.4. Schematic of the pump-probe experimental setup. The MIR excitation pulse is linearly polarized along either the crystal a - or b -axis. A near-infrared (NIR) pulse then probes the transient state by measuring the induced polarization rotation θ as a function of the incident probe polarization angle φ . Adapted from [48].

Besides these four E -symmetry phonons, we also consider all four B -symmetry phonons in BPO_4 . Their intrinsic frequencies from first-principles calculations are shown in Table C.1 in Appendix C.

3.2.3 Inducing Chirality with Light

In Ref. [48], a broadband MIR excitation pulse was tuned to resonate with the $E(2)$ phonon mode at 18.9 THz. The transiently induced chiral state was then detected by measuring the polarization rotation of a linearly polarized 800 nm probe pulse (Fig. 3.4). Specifically, the polarization rotation angle θ was recorded as a function of both the incident probe polarization angle φ and the pump-probe time delay.

The measured polarization rotation θ for a 360° sweep of the incident angle φ , for optical phonon excitation along the a axis, is plotted in Fig. 3.5a. The angular dependence can be decomposed into two distinct contributions: an isotropic optical activity ρ , which is independent of the incident probe polarization, and a linear birefringence contribution, which stems from the birefringence-induced refractive index difference Δn and exhibits a four-fold rotational symmetry. The overall polarization rotation angle can thus be expressed as [48]

$$\theta(\varphi) = A_1 \rho + A_2 \sin(4\varphi - \gamma_0) (\Delta n)^2 \quad (3.3)$$

where A_1 and A_2 are proportionality coefficients independent of φ , and γ_0 defines the orientation of the principal birefringence axes. This theoretical relation matches the

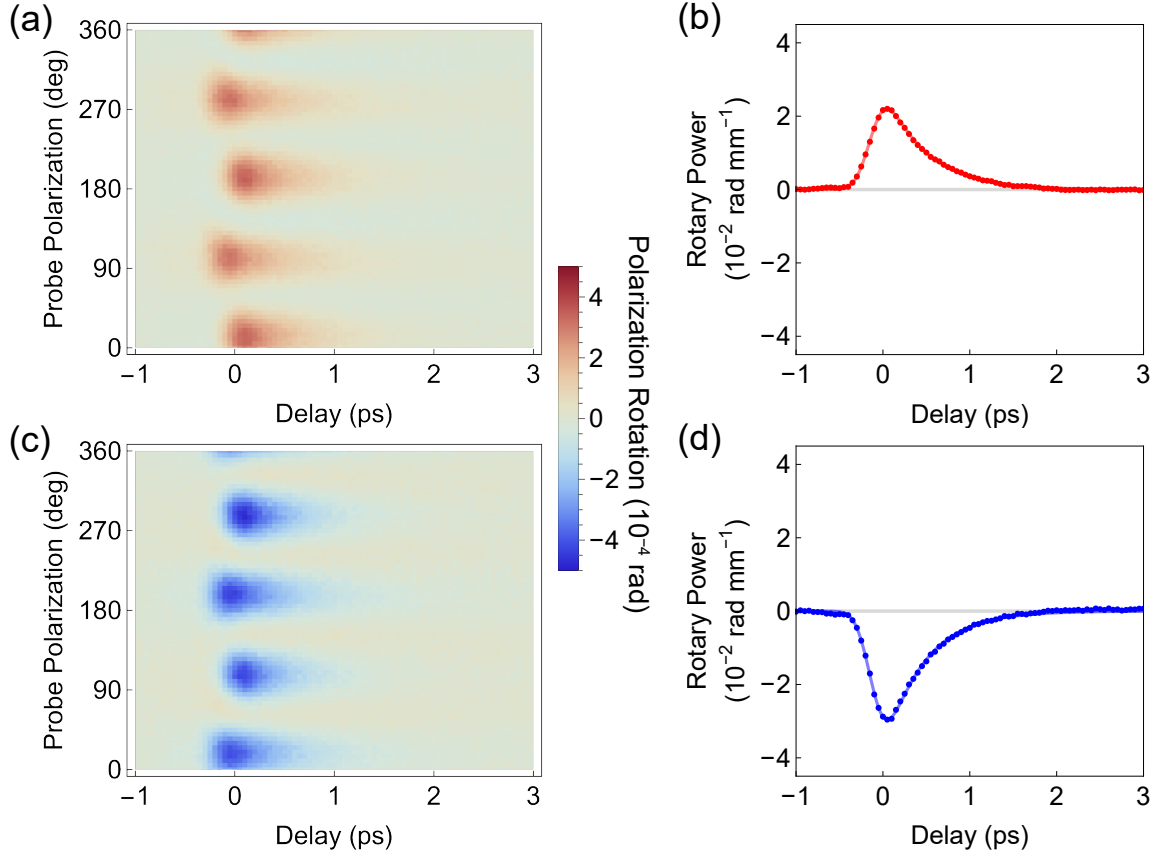


Figure 3.5. Time-resolved polarization rotation in BPO_4 induced by broadband MIR excitation of the $E(2)$ phonon mode. (a) Pump-probe delay dependence of the polarization rotation for a -axis excitation, measured at various incident probe polarizations. (b) Transient rotary power extracted from the data in (a), accounting for the finite penetration depth of the excitation pulses. (c,d) Analogous measurements and extracted rotary power for b -axis excitation. Adapted from [48].

experimental measurements shown in Fig. 3.5a. By averaging the rotation signal over all incident probe angles φ , the purely chiral optical activity ρ can be isolated. The transient rotary power, extracted in this way, is displayed in Fig. 3.5b. It decays over several picoseconds, a timescale significantly longer than the ~ 200 fs duration of the MIR excitation pulse [48].

When the pump polarization is rotated from the a -axis to the b -axis, both the B -mode displacement Q_B and the resulting optical activity are expected to reverse their signs, as

suggested by the nonlinear coupling potential in Eq. (3.1). This prediction is confirmed by the b -axis excitation data shown in Fig. 3.5c,d, which display a transient rotary power of comparable magnitude but opposite sign relative to the a -axis excitation (Fig. 3.5a,b).

The experiments in Ref. [48] have introduced a new phenomenon, light-induced chirality, into the family of nonlinear phononics and paved the way for further experiments. In the following chapters, the light-induced chiral state in BPO_4 serves as an example system to study the underlying coupling mechanisms involved in the nonlinear phononic control of materials.

Chapter 4

Generation of Narrowband Mid-Infrared Pulses

The experiments described in Chapter 3 were performed using broadband MIR pulses with a full width at half maximum (FWHM) of approximately 5 THz [48]. These broadband pulses obscure information about the efficiency of inducing the chiral state at slightly off-resonant frequencies. Furthermore, when multiple phonon modes are clustered within a narrow frequency range, the broadband MIR pump pulses cannot resolve their individual responses [81]. A deeper understanding of the nonlinear phonon coupling can be gained by using excitation pulses with a narrower bandwidth. This chapter introduces the principles behind a table-top narrowband MIR source and presents the generation of MIR pulses with FWHM bandwidths of 1 to 1.5 THz and tunable central frequencies [82–84]. These narrowband pulses are ideally suited for mapping the detailed pump-frequency dependence of light-induced effects driven by nonlinear phononics, such as light-induced chirality.

4.1 Generation of Intense Mid-Infrared Pulses

MIR pulses are typically generated via nonlinear optical processes driven by 800 nm pulses from a Ti:sapphire femtosecond amplifier system. First, optical parametric amplification (OPA) produces NIR pulses with tunable wavelengths. Then, two NIR pulses of slightly

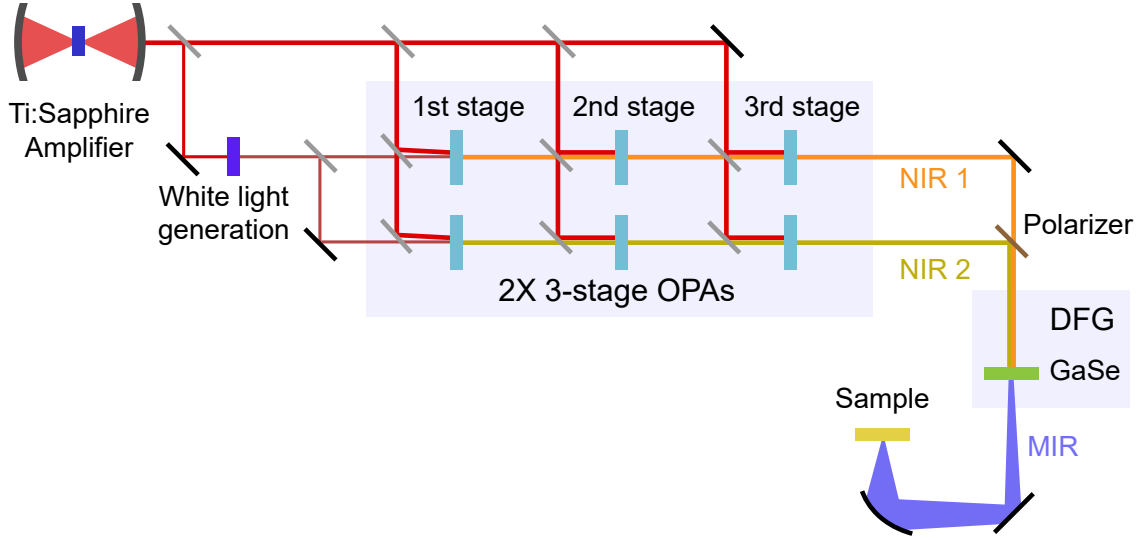


Figure 4.1. Schematic of the broadband MIR generation setup. NIR pulses at 1530 and 1390 nm are generated in two three-stage OPAs and mixed in the DFG crystal to generate the MIR pulse at $15\ \mu\text{m}$.

different wavelengths are mixed in a difference-frequency generation (DFG) process to generate the MIR pulses. Figure 4.1 illustrates the schematic of a broadband MIR generation setup. Within this thesis, we used an amplifier system delivering pulses with the duration of $\sim 75\ \text{fs}$ and pulse energy of $\sim 6.5\ \text{mJ}$ at a repetition rate of $1\ \text{kHz}$.

During the OPA process, 800 nm pump pulses are combined in a beta-barium borate (BBO) crystal with a white-light continuum, which is generated by focusing a portion of the 800 nm light into a sapphire plate to exploit high-order nonlinear effects. The white light serves as a seed for the amplification of the signal pulses. Simultaneously, a third beam (idler beam) is generated. The frequencies of these three beams are constrained by energy conservation

$$\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}} \quad (4.1)$$

High conversion efficiency in the OPA process is achieved by satisfying the phase-matching condition [58]

$$\vec{k}_{\text{pump}} = \vec{k}_{\text{signal}} + \vec{k}_{\text{idler}} \quad (4.2)$$

In the present setup, type-II phase matching is employed in the OPAs. The target output

frequency of the signal beam is selected by tuning the angle of the BBO crystal, which controls the phase-matching condition. In practice, to achieve high overall conversion efficiency, an OPA typically consists of multiple amplification stages, where the amplified signal from the preceding stage seeds the subsequent one. As depicted in Figure 4.1, each NIR beam is generated by a three-stage OPA: the first stage uses a non-collinear geometry, while the final two stages use collinear geometries. The resulting NIR pulses typically have an energy of $\sim 750 \mu\text{J}$ and a duration of $\sim 120 \text{ fs}$.

In the next step, these two NIR beams are spatially and temporally overlapped in a DFG crystal to generate their difference frequency in the MIR spectral range. The two requisite NIR beams can be the signal and idler outputs from a single OPA, or alternatively they can be the signal beams from two independent OPAs (as shown in Figure 4.1). Although the two-OPA approach requires a more complex optical setup, it allows the frequencies of the two NIR beams to be tuned completely independently. Furthermore, if the same white-light continuum is split to seed both OPAs, the resulting MIR pulses will be carrier-envelope phase (CEP) stable [83, 85].

Several key factors determine the conversion efficiency of the DFG process. First, since DFG is a second-order nonlinear optical effect, a crystal with a large second-order susceptibility $\chi^{(2)}$ is highly desirable. Second, because the maximum achievable field strength inside the crystal is restricted by optical damage, materials with a high damage threshold are preferred. Third, the DFG crystal must be transparent at both the NIR pump and the target MIR frequencies. Lastly, in addition to the energy conservation condition $\omega_{\text{MIR}} = \omega_1 - \omega_2$ (where ω_1 and ω_2 are the frequencies of the two NIR pulses), the phase-matching condition $\vec{k}_{\text{MIR}} = \vec{k}_1 - \vec{k}_2$ is crucial. The spatial scale over which phase matching is roughly maintained is quantified by the coherence length l_c , defined as [58]

$$l_c = \frac{\pi}{|\Delta\vec{k}|} \quad (4.3)$$

where $\Delta\vec{k} = \vec{k}_{\text{MIR}} - (\vec{k}_1 - \vec{k}_2)$. The coherence length dictates the maximum thickness of the DFG crystal. If the crystal is thicker than l_c , MIR radiation generated at different positions within the crystal will destructively interfere, reducing the overall output.

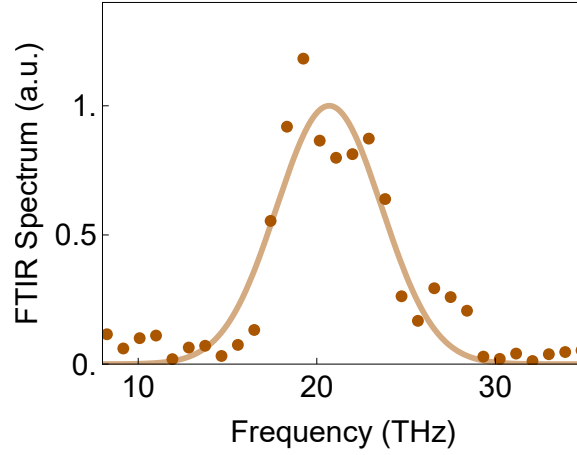


Figure 4.2. Representative FTIR spectrum of a broadband MIR pulse. The central frequency is 20 THz and the bandwidth is 6 THz.

A conventional choice for the DFG crystal is the semiconductor GaSe, which has been widely employed to generate MIR pulses at frequencies above 16 THz. Typically, type-II phase matching is utilized, and optimal phase matching is achieved by rotating the crystal to adjust the incidence angle with respect to the optical axis. A representative Fourier-transform infrared (FTIR) spectrum of a broadband MIR pulse generated in GaSe is displayed in Figure 4.2. In this example, the pulse features a FWHM bandwidth of roughly 6 THz and a pulse energy of 6 μJ .

4.2 The Principle of Bandwidth Control

The fundamental concept behind generating narrowband MIR pulses is illustrated in Figure 4.3, which displays the time-frequency diagram for the two interacting NIR pulses [82, 83, 86]. In this representation, only frequency components that are present at the same time can mix nonlinearly and generate their corresponding difference frequency. The resulting MIR bandwidth can then be estimated as $\Delta\Omega = \Omega_1 - \Omega_2$, where Ω_1 and Ω_2 denote the maximum and minimum difference frequencies between the interacting temporal slices, respectively.

As depicted in Figure 4.3a, when the incident NIR pulses are Fourier-transform limited, all frequency components arrive at the crystal simultaneously. Consequently, they all mix

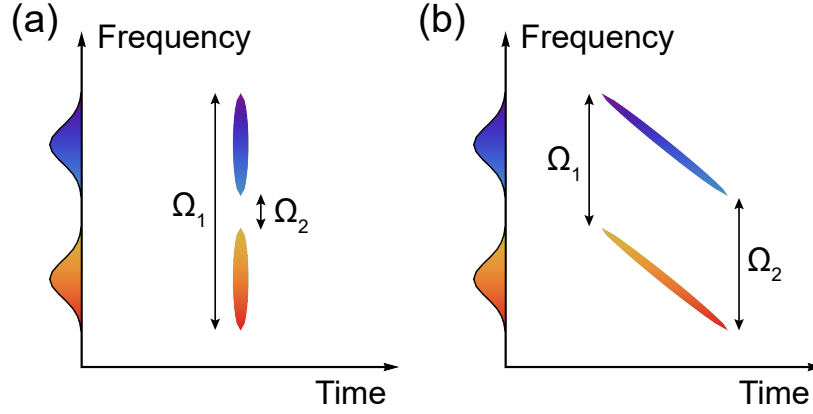


Figure 4.3. Illustration of MIR bandwidth control via DFG between chirped NIR pulses. (a) DFG between two transform-limited NIR pulses. The bandwidth of the generated MIR pulse is given by $\Delta\Omega = \Omega_1 - \Omega_2$. (b) DFG between two NIR pulses with identical chirp. The bandwidth is significantly compressed since $\Omega_1 \approx \Omega_2$. Adapted from [83].

together, yielding a broad MIR spectrum. To compress the MIR bandwidth, a linear chirp is introduced to both NIR pulses. As illustrated in Figure 4.3b, when the chirps of the two NIR pulses are identical, their instantaneous difference frequency remains constant across the entire temporal envelope of the pulses. This persistent frequency difference directly results in a narrowband MIR spectrum. Ideally, the generated MIR pulse is itself transform-limited, with its temporal duration determined by the duration of the two stretched NIR pulses.

A distinct advantage of chirped-pulse DFG is that, within limits set by the center frequencies and bandwidths of the two NIR pulses, MIR frequency tunability can be achieved by tuning the optical delay, without the need to adjust the OPA wavelengths. As shown in Figure 4.4, scanning the relative time delay between the two chirped NIR pulses shifts the frequency components that temporally overlap. Consequently, a single frequency component in the first pulse mixes with different frequency components in the second pulse depending on the delay. In our experiments, modifying the DFG delay allows for a typical frequency tuning range of ± 2 THz around the central frequency, ultimately limited by the available bandwidth of the NIR pulses [82, 87]. To access MIR frequencies outside of this scanning range, one must tune the output wavelength of one or both of the OPAs.

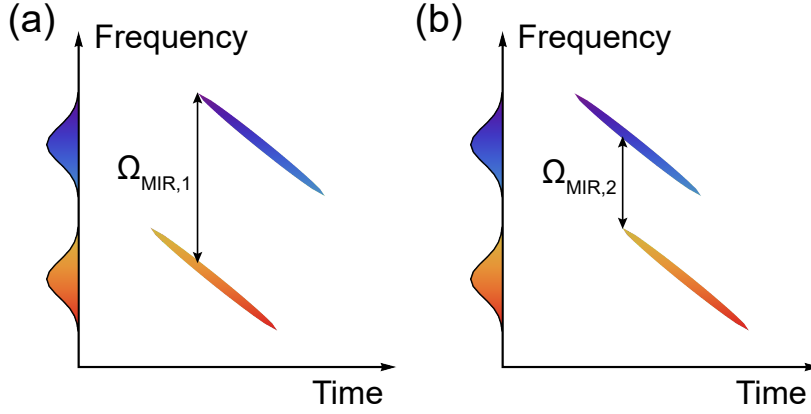


Figure 4.4. Frequency tunability of the chirped-pulse DFG technique. By tuning the relative time delay between the two NIR pulses away from zero, a higher (a) or lower (b) MIR frequency can be generated. Adapted from [84].

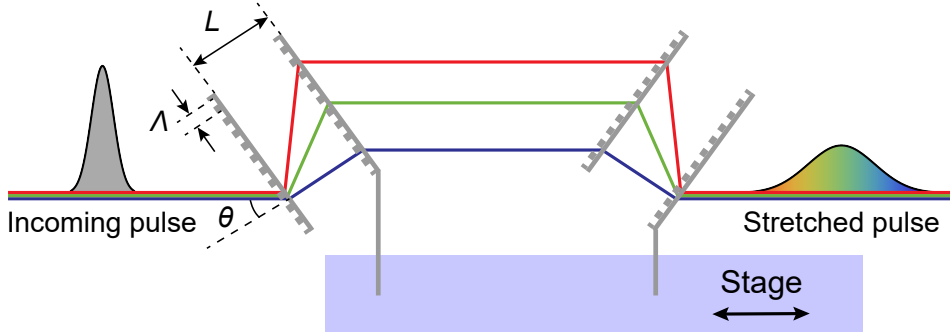


Figure 4.5. Illustration of the stretcher composed of two grating pairs. Light paths colored from red to blue represent decreasing NIR wavelengths.

In our experiments, the chirp of the NIR pulses is controlled using optical stretchers composed of transmission grating pairs. The operating principle of the stretcher is shown in Figure 4.5. By diffracting off the gratings, different wavelength components travel different optical path lengths, thereby accumulating different amounts of group delay. To ensure that all spectral components recombine into a collinear beam at the exit, the incidence angle must be identical for all gratings, and the spacing L between the gratings must be equal for both pairs. The introduced group delay dispersion (GDD) is given by [84]

$$\text{GDD}(\omega_0) = -\frac{4\pi^2 m^2 c}{\omega_0^3 \Lambda^2} \left[1 - \left(-m \frac{2\pi c}{\omega_0 \Lambda} - \sin \theta \right)^2 \right]^{-3/2} L \quad (4.4)$$

where ω_0 represents the central angular frequency of the NIR pulse, Λ is the grating period, m denotes the diffraction order, and c is the speed of light. Assuming initially transform-limited Gaussian pulses, the output pulse duration t_{out} scales with the input duration t_{in} according to

$$t_{\text{out}} = t_{\text{in}} \sqrt{1 + \left(\frac{\text{GDD}(\omega_0)}{t_{\text{in}}^2} \right)^2} \quad (4.5)$$

Under the condition $|\text{GDD}(\omega_0)| \gg t_{\text{in}}^2$, this expression simplifies to

$$t_{\text{out}} = \frac{|\text{GDD}(\omega_0)|}{t_{\text{in}}} \quad (4.6)$$

Therefore, when $t_{\text{out}} \gg t_{\text{in}}$, the duration of the stretched NIR pulse is directly proportional to $\text{GDD}(\omega_0)$, and thus to the grating spacing L . Consequently, one can smoothly tune the pulse duration simply by simultaneously displacing one grating in each pair.

A complete schematic of the narrowband MIR generation setup is presented in Figure 4.6. After the NIR pulses pass through the stretchers, their resulting temporal profiles are characterized using a second-harmonic-generation frequency-resolved optical gating (SHG-FROG) apparatus [82, 88]. Based on these measurements, the grating spacing is fine-tuned to achieve the desired chirp. Subsequently, the two chirped NIR pulses are focused onto the DFG crystal at a small crossing angle ($< 1^\circ$) to generate the desired narrowband MIR pulses.

The DFG crystal in this narrowband MIR generation setup can be either an organic crystal (for MIR pulses with frequencies from 4 to 18 THz) [81, 84, 89] or the semiconductor GaSe (for MIR pulses with frequencies above 16 THz) [81]. The results for the narrowband MIR pulses generated from GaSe, which is used in the pump-probe measurements of light-induced chirality in BPO₄, will be introduced in the next section. The similarities and differences of the narrowband MIR pulses generated in organic crystals are covered in Appendix A.

4.3 Narrowband Mid-Infrared Pulses from GaSe

The primary motivations for employing optical stretchers with GaSe are purely to compress the MIR bandwidth and to enable frequency tunability via delay lines. By simply guiding the

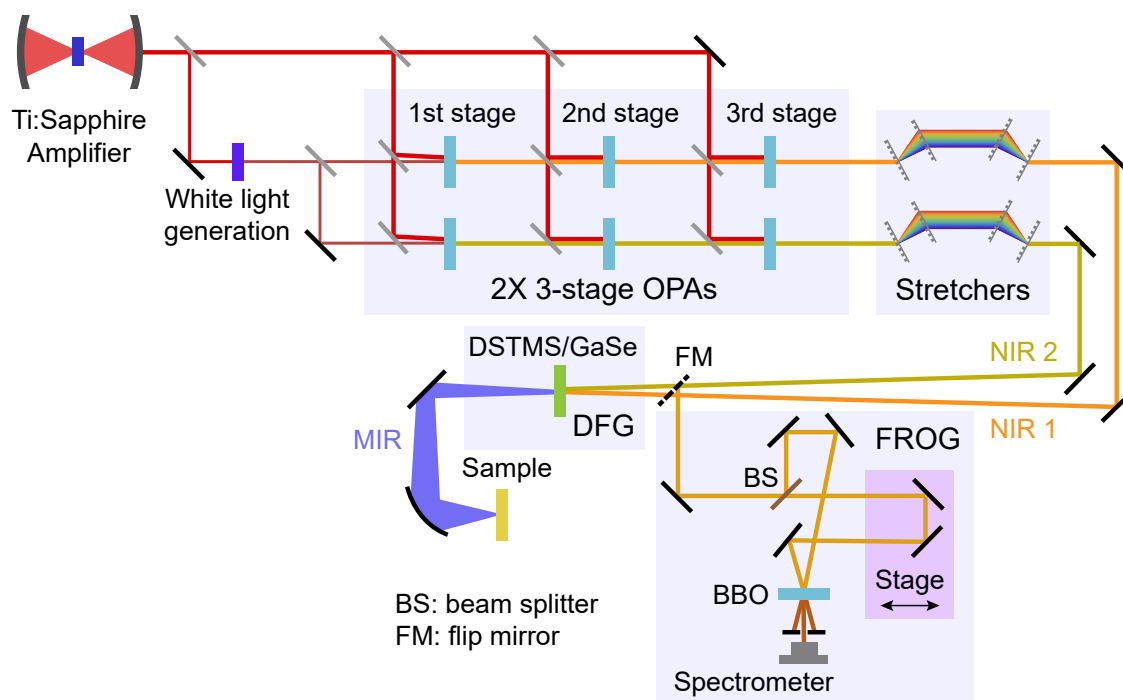


Figure 4.6. Schematic of the narrowband MIR generation setup. The grating stretchers induce chirp in the NIR pulses, and their resulting durations are measured with SHG-FROG. The two chirped NIR pulses are then mixed in the DFG crystal, producing the narrowband MIR pulse.

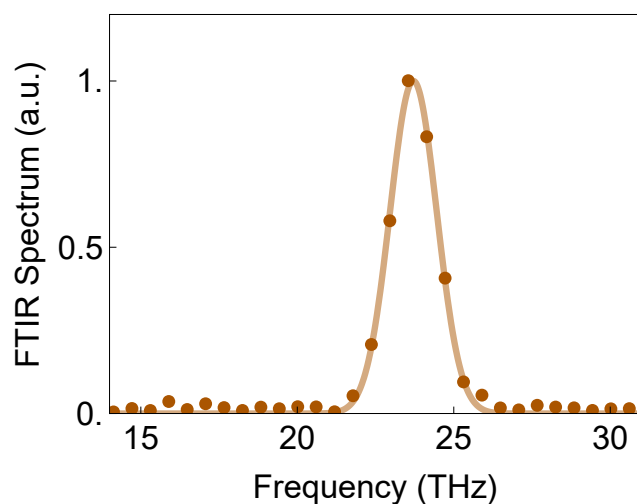


Figure 4.7. Representative FTIR spectrum of a narrowband MIR pulse generated in GaSe. The central frequency is 23.7 THz and the bandwidth is 1.7 THz.

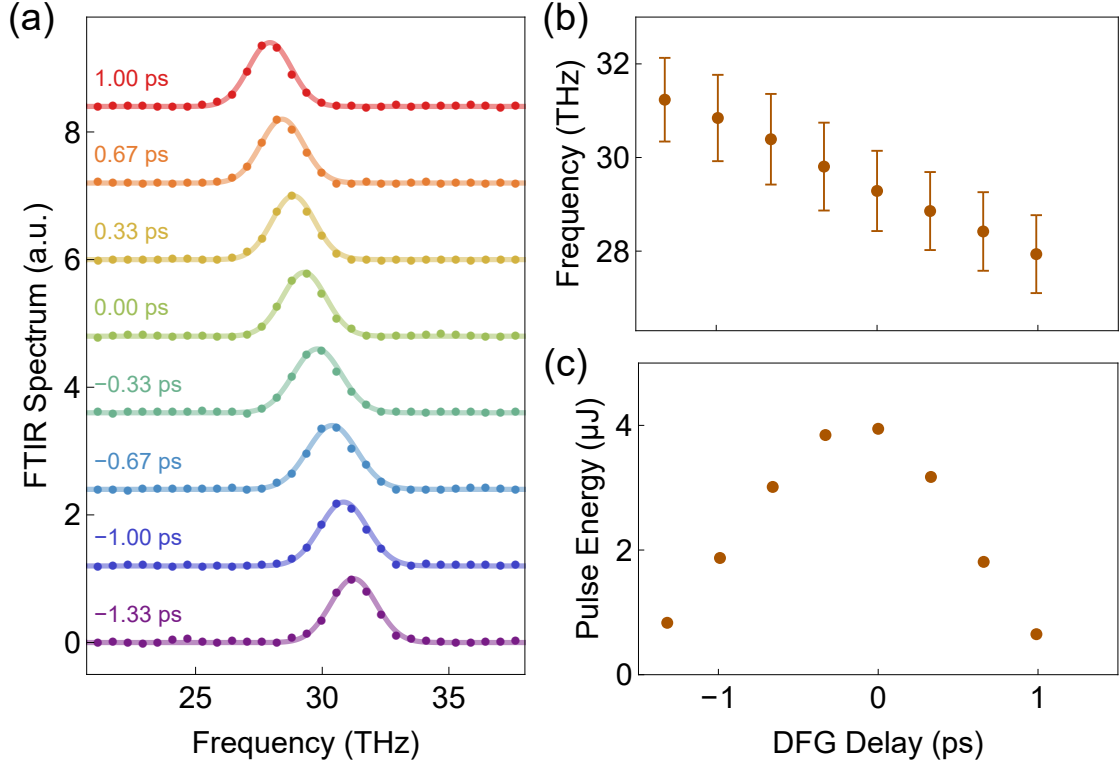


Figure 4.8. Frequency tunability of chirped-pulse DFG in GaSe. (a) FTIR spectra for different DFG delays. Colors from red to violet indicate increasing frequencies. (b) Central frequencies as a function of DFG delay corresponding to the spectra in (a). The error bars represent the bandwidth. (c) MIR pulse energy as a function of DFG delay corresponding to the spectra in (a).

chirped NIR pulses into the standard DFG section of the broadband MIR generation setup, one can produce narrowband MIR pulses at frequencies above 16 THz. This process utilizes type-II phase matching, meaning the two interacting NIR beams are orthogonally polarized. The phase-matching condition is then tuned by adjusting the tilt angle of the GaSe crystal. Figure 4.7 displays a typical MIR spectrum generated in GaSe using two chirped NIR pulses, each with a duration of 600 fs. The resulting MIR pulse possesses an energy of $\sim 5 \mu\text{J}$, a central frequency of 23.7 THz, and a narrow FWHM bandwidth of 1.7 THz.

As illustrated in Figure 4.8, continuous frequency tuning by scanning the relative DFG delay works well in GaSe, offering a tuning range of roughly 4 THz (see Figure 4.8b). Because GaSe is transparent across this entire high-frequency region (> 16 THz), the bandwidth of

the generated spectra remains narrow and uniform across different DFG delays, as evidenced by the error bars in Figure 4.8b. Furthermore, the delay-dependent MIR power from GaSe exhibits a Gaussian-like profile (Figure 4.8c). This behavior is consistent with the theoretical expectation that the generation efficiency is directly proportional to the temporal overlap of the two chirped NIR Gaussian pulses [87].

Chapter 5

Excitation Frequency Dependence of Light-Induced Chirality in BPO₄

In Ref. [48], light-induced chirality in BPO₄ was demonstrated only under broadband MIR excitation resonant with the $E(2)$ phonon at 18.9 THz. Based on symmetry principles, the same mechanism is predicted to also occur for the excitation of other E -symmetry phonon modes. Due to their larger mode effective charges, the higher-frequency E -symmetry phonon modes ($E(3)$ at 28.2 THz and $E(4)$ at 32.8 THz) are expected to yield a stronger light-induced chiral response. Furthermore, detailed frequency-dependent measurements could provide important insights into the potential nonlinear coupling mechanisms that contribute to light-induced chirality in BPO₄.

Using the narrowband tunable MIR source introduced in Chapter 4, we carefully mapped the excitation frequency dependence of the light-induced chiral state in BPO₄. This set of experiments revealed fine structures that could not be observed with the earlier broadband MIR source [48]. To account for these new, excitation frequency-dependent experimental features, additional nonlinear coupling terms that contribute to light-induced chirality must be included alongside the two-phonon mixing term $Q_E^2 Q_B$ from Eq. (3.1).

In this chapter, I will first summarize the experimental results, and then introduce possible additional phonon coupling mechanisms. Finally, I will provide theoretical explanations based on a combination of experimental results and numerical simulations. The main results

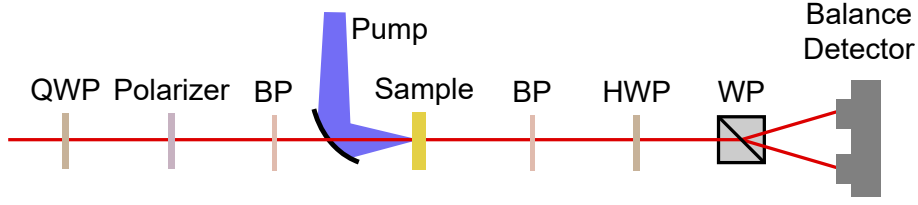


Figure 5.1. The optical setup for probing the transient chirality in BPO_4 . The probe incident angle is controlled by a polarizer behind the quarter waveplate, and the probe polarization rotation is measured via balanced detection. QWP: quarter waveplate, HWP: half waveplate, BP: 808/5 nm bandpass filter, WP: Wollaston prism.

of this chapter are summarized in a recent manuscript [90].

5.1 Excitation-Frequency-Dependent Measurements

5.1.1 Experimental Setup

The sample used in our experiments was prepared using the method described in Appendix B. The sample was excited with the tunable narrowband MIR source introduced in Fig. 4.6, using a FWHM of about 1.5 THz, and was probed with linearly polarized pulses at 800 nm. The principle behind probing the transient chirality in BPO_4 is the same as in Ref. [48] (see also Chapter 3), where the time-dependent polarization rotation θ was measured for a 360° sweep of the polarization angle φ of the incident probe.

The optical setup of the probe path is shown in Fig. 5.1. A quarter-wave plate first converts the linearly polarized probe pulses into circular polarization, and a downstream polarizer then sets the incident polarization angle φ . The latter transforms the initially linearly polarized probe pulses from the laser system into circularly polarized light, ensuring that the probe power remains constant across different incident polarization angles φ . The polarization rotation θ is measured using a combination of a half waveplate, a Wollaston prism, and a balance detector composed of two photodiodes. For each probe polarization, the two diodes are re-balanced through a motorized tuning of the fast axis angle of the half waveplate, under the condition that the excitation pulses are blocked. Two identical bandpass

filters (with a center wavelength of 808 nm and a bandwidth of 5 nm) were placed before and after the sample to filter out the time-resolved response from the Pockels effect, which gives rise to sidebands in the probe spectrum.

The pump pulse train in the setup is optically chopped at a frequency of 500 Hz, i.e. at half the laser repetition rate. As a result, the balance detector receives pulsed signals from pump-on and pump-off conditions alternately. After passing through a boxcar integrator, the signal is sent to a data acquisition card connected to a computer, where the integrated signal size of each electric pulse is recorded and the polarization rotation is calculated.

5.1.2 Extraction of Photosusceptibility

For a given excitation fluence, the probe polarization rotation θ is measured as a function of the probe incident polarization angle φ . Fig. 5.2a,c shows the complete dataset for the probe polarization dependence at excitation frequency of 33.3 THz and fluence of 11 mJ/cm². The detected polarization rotation θ was fitted with Eq. (3.3), accounting for both the isotropic optical activity ρ and the four-fold component arising from the photo-induced birefringence Δn .

The optical activity contribution to the polarization rotation, $\bar{\theta}[a \text{ or } b \text{ axis}]$, for either a - or b -axis excitation can be extracted by averaging over all probe incident polarization angles φ . The corresponding rotary power $\rho[a \text{ or } b \text{ axis}]$ is then calculated from $\bar{\theta}[a \text{ or } b \text{ axis}]$ by dividing it by the penetration depth at the excitation frequency (Fig. 5.2b,d). Due to the crystal symmetry [48], the rotary power reverses its sign for the two different excitation axes, and the average rotary power is defined as

$$\rho = \frac{\rho[a \text{ axis}] - \rho[b \text{ axis}]}{2} \quad (5.1)$$

Fig. 5.3 displays time traces of ρ for several excitation frequencies. All of these time traces can be fitted with the product of a step-like function and a single exponential decay

$$\rho(t) = A \left(1 + \operatorname{erf} \left(\frac{t - t_0}{s} \right) \right) e^{-t/\tau} \quad (5.2)$$

where s represents the rise time of the signal and τ is the decay constant. While s is

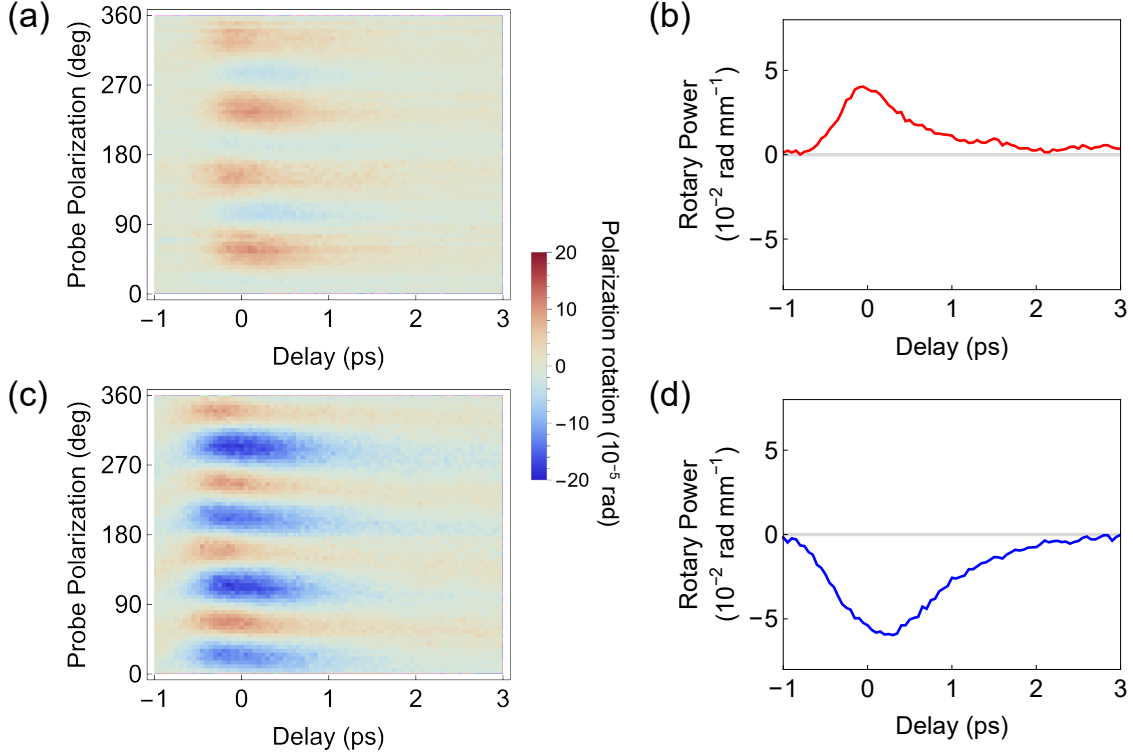


Figure 5.2. Time-resolved polarization rotation measurements in BPO₄ following narrowband MIR excitation at 33 THz. (a) Time-delay-dependent polarization rotation for *a*-axis excitation at various probe incident polarizations. **(b)** Time-delay-dependent rotary power extracted from the data shown in (a), accounting for the finite penetration depth of the excitation pulses. **(c,d)** Same as (a,b) but for *b*-axis excitation.

primarily determined by the pump pulse duration, τ is mainly determined by the lifetime of the *E*-symmetry phonon modes.

For each excitation frequency, the time trace of the rotary power was measured at multiple pump fluences. For a given excitation fluence I , the rotary power $\rho_{\max}$ at the peak of the time-delay-dependent response was extracted from the fit using Eq. (5.2). Fig. 5.4 illustrates the relationship between $\rho_{\max}$ and I for several narrowband MIR excitation frequencies. All datasets can be fitted with a linear relationship

$$\rho_{\max} = \chi I \quad (5.3)$$

where the slope χ denotes the photosusceptibility. This linear dependence is consistent with

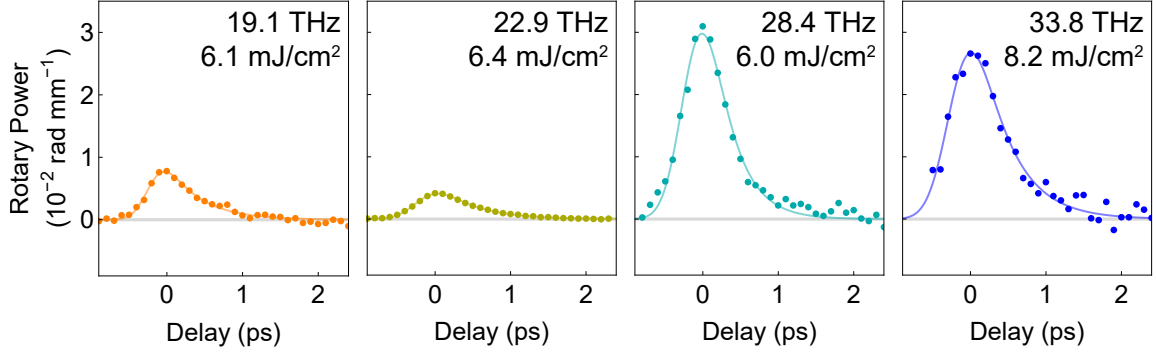


Figure 5.3. Representative time-delay-dependent rotary power signals in BPO₄ after narrowband MIR excitation. The labels in each panel indicate the excitation frequency and fluence. All time traces can be fitted with a product of a step-like function and an exponential decay (light curves).

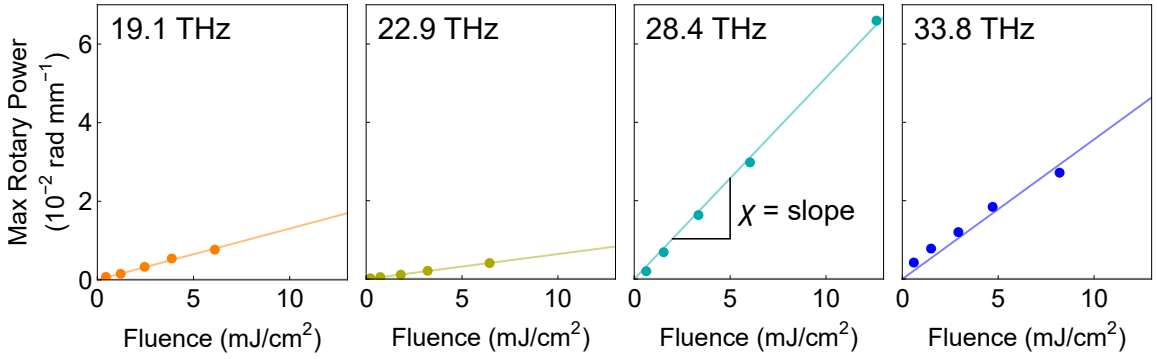


Figure 5.4. Representative fluence-dependent measurements of the maximal rotary power in BPO₄ after narrowband MIR excitation. The labels in each panel indicate the excitation frequency. The photosusceptibility χ is defined as the slope of the linear fit (light lines).

the nonlinear phononics mechanism described in Eq. (3.1), which predicts that the optical activity is proportional to the Q_B displacement. This displacement, in turn, is proportional to the square of the excitation peak electric field E^2 . In the following sections, we will use χ to quantify the efficiency of each excitation frequency.

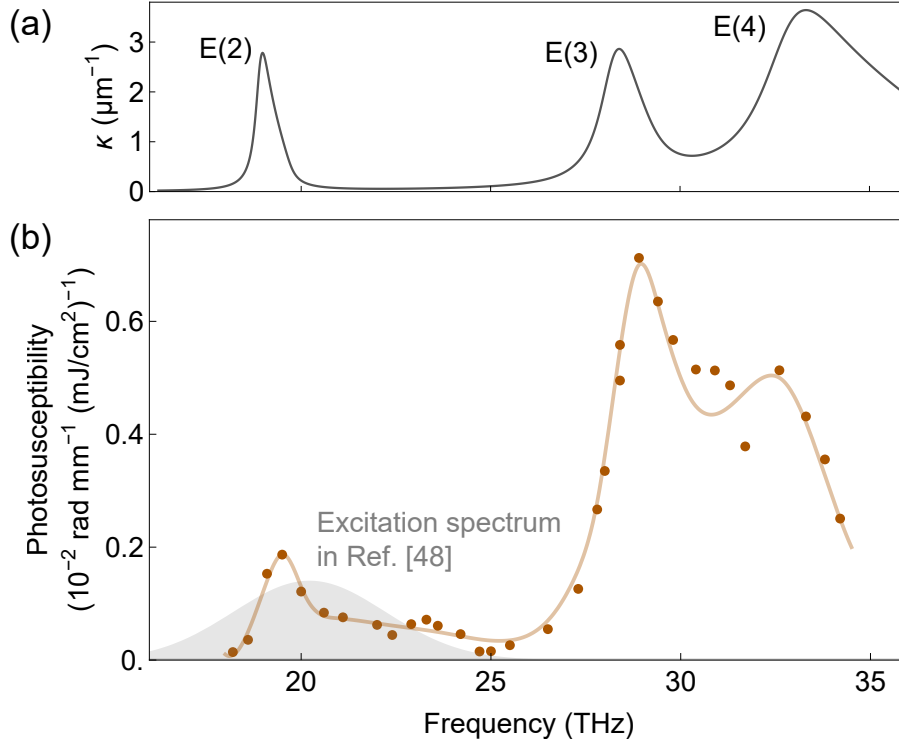


Figure 5.5. Excitation frequency dependence of light-induced chirality in BPO₄. (a) Extinction coefficient of BPO₄ in the MIR range for light propagating along the crystal *c*-axis. The three peaks correspond to the three *E*-symmetry phonon modes. (b) Photosusceptibility as a function of excitation frequency. Brown dots represent experimental results, and the light brown curve is a guide to the eye. The excitation spectrum used in Ref. [48] is indicated by gray shading.

5.1.3 Comparison to Frequency-Dependent Extinction

Based on the nonlinear phononics theory featuring a two-phonon $Q_E^2 Q_B$ -type coupling, the driving force on the *B*-symmetry modes is proportional to Q_E^2 , which is effective only for resonant excitation. Hence, the frequency-dependent photosusceptibility would be expected to closely follow the extinction coefficient (Fig. 5.5a) [4, 25, 45, 46, 48, 60].

The measured frequency dependence of the photosusceptibility over the frequency range of the three *E*-symmetry phonons (*E*(2), *E*(3), and *E*(4)) is shown in Fig. 5.5b. Clear deviations of the photosusceptibility from the frequency-dependent extinction coefficient are

observed, particularly in the frequency intervals between different E -symmetry modes, i.e. between 20 THz and 24 THz, and around 30 THz. These deviations suggest the presence of additional coupling pathways beyond the two-phonon mixing mechanism $Q_E^2 Q_B$. It is worth noting that this observation was only made possible by the reduced pump bandwidth of the narrowband MIR source. The larger bandwidth of the previous broadband MIR excitation (Fig. 5.5b, gray shading) would have smeared out these fine features.

5.2 Additional Nonlinear Coupling Mechanisms

In this section, we explore three corrections beyond the traditional nonlinear coupling term $Q_{E,i}^2 Q_B$. First, as suggested by G. Khalsa et al. [91], two additional coupling terms emerge when considering the nonlinear interaction between the MIR driving field and the B -symmetry phonons: the electro-phononic term $Q_{E,i} E Q_B$, which describes the mixing between the E -symmetry mode oscillations $Q_{E,i}$ and the MIR electric field E to displace Q_B ; and the pure electric coupling $E^2 Q_B$, which is well known as stimulated Raman scattering for visible and NIR excitations [92, 93]. Additionally, a three-phonon mixing of the form $Q_{E,i} Q_{E,j} Q_B$, where $Q_{E,i}$ and $Q_{E,j}$ represent two non-degenerate E -modes polarized along the same a or b -axis, can induce a Q_B displacement [25, 45]. With these nonlinear coupling terms, the lattice potential energy relevant to the experimental scheme can be written as

$$V = \sum_i \frac{1}{2} \omega_{E,i}^2 (Q_{E,i,a}^2 + Q_{E,i,b}^2) - \sum_i Z_{E,i}^* (Q_{E,i,a} E_a + Q_{E,i,b} E_b) + \sum_k \frac{1}{2} \omega_{B,k}^2 Q_{B,k}^2 + V_{anh} \quad (5.4)$$

$$V_{anh} = \sum_{i,k} \alpha_{i,k} (Q_{E,i,a}^2 - Q_{E,i,b}^2) Q_{B,k} + \sum_{i,k} \delta_{i,k} (Q_{E,i,a} E_a - Q_{E,i,b} E_b) Q_{B,k} + \sum_k \zeta_k (E_a^2 - E_b^2) Q_{B,k} \\ + \sum_{i < j, k} \kappa_{ij,k} (Q_{E,i,a} Q_{E,j,a} - Q_{E,i,b} Q_{E,j,b}) Q_{B,k} \quad (5.5)$$

where $\omega_{E,i}$ and $\omega_{B,k}$ are the eigenfrequencies of E - and B -symmetry phonons, respectively, $Z_{E,i}^*$ are the effective charges of the E -symmetry modes, $\alpha_{i,k}$, $\delta_{i,k}$, ζ_k , and $\kappa_{ij,k}$ are coupling coefficients, and the subscripts a and b denote the crystal axes. Schematic representations of the coupling pathways leading to a Q_B displacement via these four mechanisms are compared in Fig. 5.6.

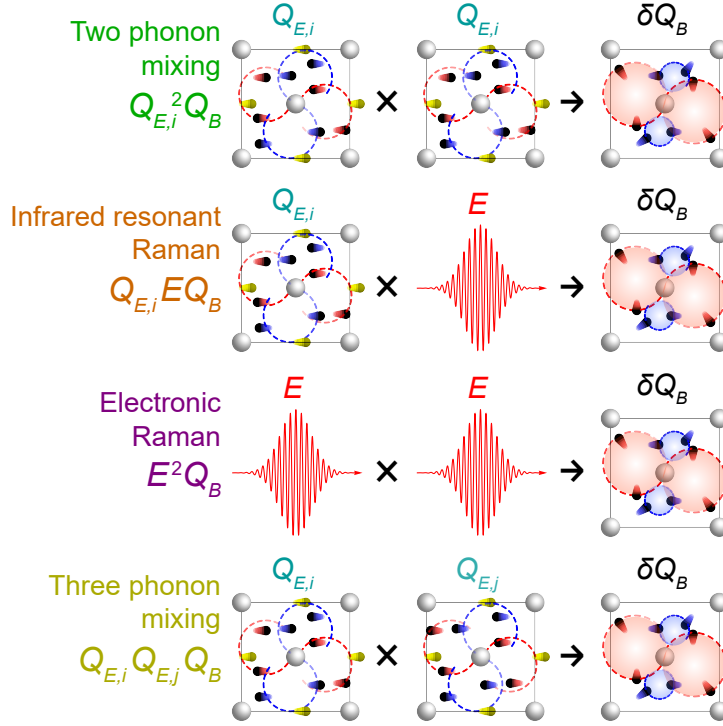


Figure 5.6. Schematics of four possible pathways that can lead to light-induced chirality in BPO_4 . From top to bottom, the mechanisms are two-phonon mixing $Q_{E,i}^2 Q_B$, infrared resonant Raman $Q_{E,i} E Q_B$, electronic Raman $E^2 Q_B$, and three-phonon mixing $Q_{E,i} Q_{E,j} Q_B$. In each pathway, the mixing of E -mode oscillations ($Q_{E,i}$) and/or the MIR electric field (E) induces a displacement of the B -mode, denoted by δQ_B .

5.2.1 Electro-Phononic Coupling and Pure Electric Coupling

In Ref. [91], the first three terms of Eq. (5.5) are introduced as distinct Raman-like scattering mechanisms. The second and third terms can be conceptually derived from the first term by substituting one or both $Q_{E,i}$ coordinates in the $Q_{E,i}^2 Q_B$ expression with the MIR electric field E . Since the electric field E couples linearly to the E -symmetry modes $Q_{E,i}$, the $Q_{E,i} E Q_B$ and $E^2 Q_B$ coupling terms automatically satisfy the required symmetry conditions.

The first term, $Q_{E,i}^2 Q_B$ (corresponding to the phononic or ionic Raman term in Ref. [91]), has been the primary focus of most previous studies on nonlinear phononics [4, 25, 48, 60]. In BPO_4 , the oscillation of the E -symmetry mode $Q_{E,i}$ induces a displacement of the B -symmetry mode Q_B . Because this Q_B displacement is proportional to $\langle Q_{E,i}^2 \rangle$, the term is

only prominent when the MIR excitation is resonant with the corresponding E -symmetry phonon (Fig. 5.7b, green curves). Furthermore, since $\langle Q_{E,i}^2 \rangle$ is strictly non-negative, the induced effect from a specific E -mode will maintain a consistent sign across all excitation frequencies.

The second term, $Q_{E,i}EQ_B$ (corresponding to the infrared resonant Raman term in Ref. [91]), provides another effective driving force on the B -symmetry phonon [91, 94]. Unlike the purely nonlinear phononic term, which is rooted in lattice anharmonicity, the electro-phononic coupling term originates from the coupling between the effective charge of the E -symmetry mode and the displacement of the B -symmetry modes. Since the resulting Q_B displacement is proportional to $\langle Q_{E,i}E \rangle \sim A_{Q,i}A_{MIR} \cos(\varphi_{Q,i} - \varphi_{MIR})$, the magnitude of the effect depends not only on the oscillation amplitudes $A_{Q,i}$ (of $Q_{E,i}$) and A_{MIR} (of E), but also on their phase difference $\varphi_{Q,i} - \varphi_{MIR}$. As illustrated by the blue curves in Fig. 5.7a, this phase difference is near zero for excitation frequencies below the phonon resonance, increases to approximately $\pi/2$ exactly at resonance, and approaches π as the pump frequency is increased further. Hence, the net force on the B -symmetry phonon flips sign when the excitation frequency crosses the intrinsic frequency of the E -symmetry mode, yielding a bipolar frequency dependence (Fig. 5.7b, orange curves). This behavior indicates that the $Q_{E,i}EQ_B$ mechanism is most effective for slightly off-resonance excitations, in contrast to the $Q_{E,i}^2Q_B$ mechanism, which peaks at phonon resonances.

The third term, E^2Q_B (corresponding to the electronic Raman term in Ref. [91]), is typically dominant in frequency ranges far from any phonon resonances and is often referred to as stimulated Raman scattering [92, 93, 95–97]. The force on the B -mode induced by this mechanism is proportional to $\langle E^2 \rangle$. Since its frequency dependence arises solely from the frequency-dependent transmission of the excitation pulse at the material surface, this term does not have a strong frequency dependence (Fig. 5.7b, purple curve).

5.2.2 Three-Phonon Mixing

The fourth term, $Q_{E,i}Q_{E,j}Q_B$, where $E(i)$ and $E(j)$ are two non-degenerate E -modes, describes a three-phonon mixing mechanism [25, 45]. It can be conceptualized by allowing

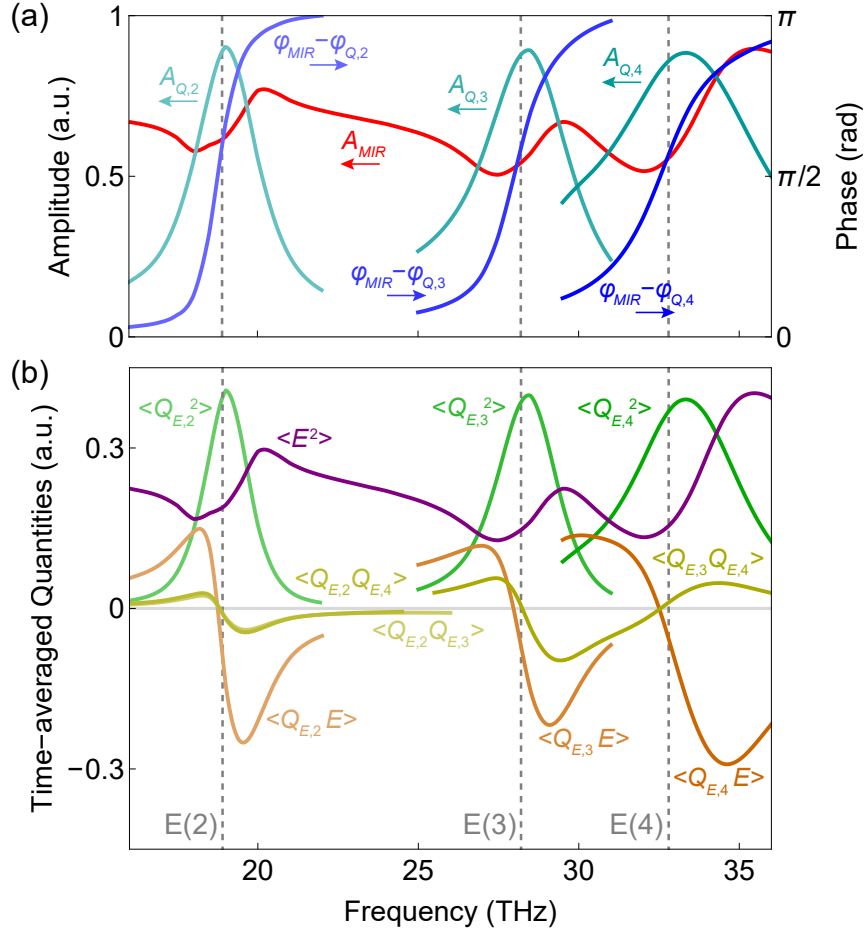


Figure 5.7. Frequency dependence of the four nonlinear coupling mechanisms. (a) Excitation frequency dependence of the electric field oscillation amplitude A_{MIR} (red curve), the E -mode oscillation amplitude $A_{Q,i}$ (cyan curves), and their relative phase difference $\varphi_{Q,i} - \varphi_{MIR}$ (blue curves) at the sample surface. (b) Excitation frequency dependence of the time averages of $Q_{E,i}^2$ (green curves), $Q_{E,i}E$ (orange curves), E^2 (purple curves), and $Q_{E,i}Q_{E,j}$ (yellow curves). These quantities are proportional to the excitation frequency dependence of the B -mode displacement resulting from $Q_{E,i}^2 Q_B$, $Q_{E,i}E Q_B$, $E^2 Q_B$, and $Q_{E,i}Q_{E,j} Q_B$ coupling terms, respectively. Vertical dashed lines indicate the intrinsic E -mode frequencies.

the two E -modes in the traditional $Q_{E,i}^2 Q_B$ potential to be distinct. Like the $Q_{E,i}^2 Q_B$ term, it also originates from lattice anharmonicity. Although the intrinsic frequencies of the $E(i)$ and $E(j)$ modes are different, their driven oscillations ($Q_{E,i}$ and $Q_{E,j}$) will both

follow the frequency of the external MIR pulse. Consequently, a quasi-static B -mode displacement remains possible. The dispersive force on the Q_B modes is proportional to $\langle Q_{E,i} Q_{E,j} \rangle \sim A_{Q,i} A_{Q,j} \cos(\varphi_{Q,i} - \varphi_{Q,j})$. Because the relative phase $\varphi_{Q,i} - \varphi_{MIR}$ shifts from 0 to π as the excitation frequency crosses the intrinsic frequency of $Q_{E,i}$ from below (Fig. 5.7a, blue curves), the phase difference between the two modes, $\varphi_{Q,i} - \varphi_{Q,j}$, behaves distinctively. Assuming $\omega_i < \omega_j$, $\varphi_{Q,i} - \varphi_{Q,j}$ is close to zero when the excitation frequency is either below ω_i or above ω_j , but drops to approximately $-\pi$ in the interval between ω_i and ω_j . In other words, the induced effect flips sign when the excitation frequency crosses the intrinsic resonance of the first E -symmetry phonon, and flips back upon crossing the second one. These features produce the frequency dependence illustrated by the yellow curves in Fig. 5.7b. Overall, the quasi-static Q_B displacement driven by this mechanism is most efficient for excitation frequencies situated between two different E -symmetry phonons, provided that the frequency spacing between these phonons is comparable to their linewidths.

5.3 Theoretical Discussions

In the previous section, we discussed the key physics of several nonlinear coupling mechanisms that may contribute to the light-induced chirality in BPO_4 . To establish a connection between the experimental observations and these nonlinear coupling terms, we combine numerical simulations of phonon-polariton propagation with first-principles calculations of the nonlinear coupling coefficients and optical response. Then, we group the terms with the same excitation frequency dependence together, define the summed gyration coefficient for each term, and fit these coefficients to the experimental data.

5.3.1 Numerical Simulations

Upon the optical excitation, the electric field E of the excitation pulse and the E -mode oscillations $Q_{E,i}$ co-propagate inside the material, forming the phonon polariton. Note that the electric dipoles of B -symmetry phonons are along the c direction of the crystal, and therefore do not interact linearly with the electric field E of the excitation pulse along a or b

axis. Hence, the reason to consider phonon polariton in this scenario is very different from the previous work [7] where propagated phonon polariton is from the coupling between the electric field and the displaced mode. To gain information about the spatiotemporal evolution of the B -mode displacement Q_B driven by each of the above coupling terms, we performed numerical simulations that account for phonon-polariton propagation inside the material. Specifically, we solve the time- and space-dependent coupled equations for the E -modes Q_E and the electric field E [57]

$$\frac{\partial^2 Q_{E,i}}{\partial t^2} + \gamma_{E,i} \frac{\partial Q_{E,i}}{\partial t} + \omega_{E,i}^2 Q_{E,i} = Z_{E,i}^* E \quad (5.6)$$

$$\frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \left(\varepsilon E + \sum_i \beta_{E,i} Q_{E,i} \right) \quad (5.7)$$

alongside the equation describing the nonlinear coupling to the B -modes Q_B

$$\begin{aligned} \frac{\partial^2 Q_{B,k}}{\partial t^2} + \gamma_{B,k} \frac{\partial Q_{B,k}}{\partial t} + \omega_{B,k}^2 Q_{B,k} = \\ \pm \left[\sum_i \alpha_{i,k} Q_{E,i}^2 + \sum_i \delta_{i,k} Q_{E,i} E + \zeta_k E^2 + \sum_{i<j} \kappa_{ij,k} Q_{E,i} Q_{E,j} \right] \end{aligned} \quad (5.8)$$

The detailed simulation methods are outlined in Appendix D. Using the nonlinear coupling coefficients obtained from first-principles calculations (Table C.2 in Appendix C), we simulate the pump-frequency dependence of the $Q_{B,k}$ displacement for various B -modes (Fig. 5.8).

The induced geometric chirality in BPO_4 is linear in the B -modes and quadratic in the E -modes, and the related optical activity can be calculated as [48, 90]

$$\rho = \sum_k \frac{\partial \rho}{\partial Q_{B,k}} Q_{B,k} + \frac{1}{2} \sum_{i,j} \frac{\partial^2 \rho}{\partial Q_{E,i} \partial Q_{E,j}} Q_{E,i} Q_{E,j} \quad (5.9)$$

where the optical activity coefficients $g_{B,k} = \partial \rho / \partial Q_{B,k}$, $g_{E,ii} = \partial^2 \rho / \partial Q_{E,i}^2 / 2$, and $g_{E,ij} = \partial^2 \rho / (\partial Q_{E,i} \partial Q_{E,j})$ can be estimated from first-principles calculations (see Appendix C for details).

The frequency-dependent photosusceptibilities for all the four coupling mechanisms are shown in Fig. 5.9. The contributions from the pure phononic couplings, namely

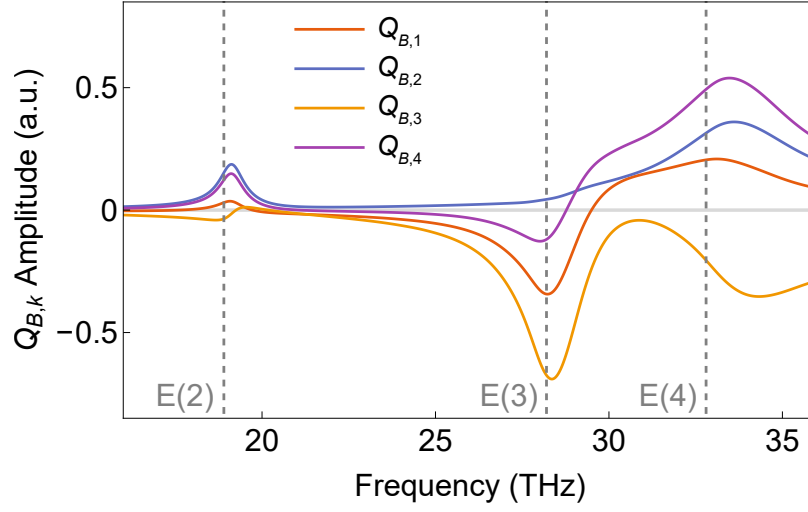


Figure 5.8. Simulated frequency dependence of the displacements of different B -modes $Q_{B,k}$. All the four nonlinear coupling terms in Eq. (5.5) are considered, with the coupling coefficients obtained from first-principles calculations.

the two-phonon interaction $Q_{E,i}^2 Q_B$ and the three-phonon interaction $Q_{E,i} Q_{E,j} Q_B$, are of similar size, because they correspond to anharmonicities of lattice potential with the same order. Meanwhile, the optical activity directly from the oscillating E -modes, $g_{E,ii} Q_{E,i}^2$ and $g_{E,ij} Q_{E,i} Q_{E,j}$ (Fig. 5.9 top panel, dashed lines), has a similar frequency dependence and is of similar size as the corresponding pure phononic terms (Fig. 5.9 top panel, solid lines). The similar frequency dependence comes from the fact that both optical activity directly from the oscillating E -modes and the pure phononic couplings contribute a rotary power proportional to the time averages $\langle Q_{E,i}^2 \rangle$ or $\langle Q_{E,i} Q_{E,j} \rangle$. At the same time, the contribution from the infrared resonant Raman term $Q_{E,i} E Q_B$ is at least one order of magnitude smaller, and the contribution from the electronic Raman term $E^2 Q_B$ is even smaller (Fig. 5.9 bottom panel). Consequently, our subsequent discussions will focus exclusively on the purely phononic terms, while neglecting the two Raman terms that involve direct coupling to the drive electric field. A more detailed discussion about the relative size of different nonlinear coupling terms is presented in Appendix E.

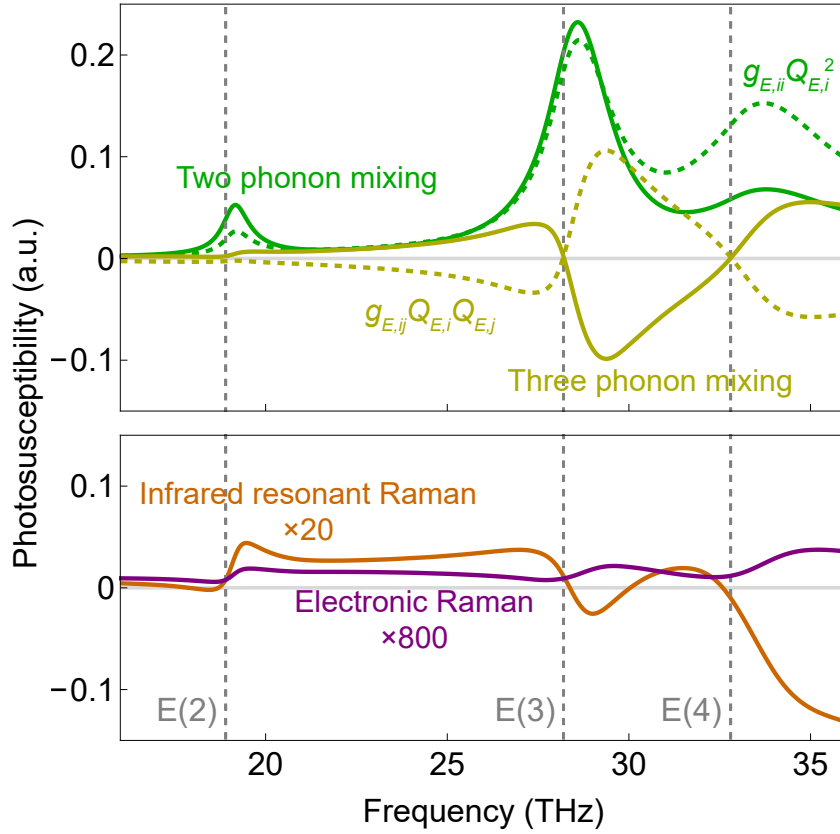


Figure 5.9. Simulated frequency dependence of the rotary power from different pathways. The optical activity from B -mode displacement related to two-phonon mixing (green solid curve), infrared resonant Raman (orange solid curve), electronic Raman (purple solid curve), and three-phonon mixing (yellow solid curve) coupling terms, as well as the excitation frequency dependence of the optical activity quadratically dependent on the E -modes, $g_{E,ii}Q_{E,i}^2$ (green dashed curve) and $g_{E,ij}Q_{E,i}Q_{E,j}$ (yellow dashed curve), are shown. The coupling coefficients are obtained from first-principles calculations.

5.3.2 Fit to Experimental Results

The simulations of the chirality-induced rotary power were based on nonlinear coupling coefficients and optical activity coefficients obtained from first-principles calculations. However, quantitative deviations between theory and experiment are unavoidable, as first-principles calculations necessarily involve approximations in the exchange-correlation functional and are performed under idealized structural conditions. In addition, the experiments may be affected

by defects and sample inhomogeneity, which are beyond the scope of the first-principles calculations. Importantly, while the nonlinear phononic coupling coefficients are associated only with low-energy excitations on the scale of approximately 80 meV, corresponding to the MIR frequency range, the gyration coefficients are governed by electronic transitions on the scale of several eV, corresponding to the NIR to visible frequency range. The first-principles results for the gyration coefficients are therefore expected to be less accurate than those for the nonlinear phononic coupling coefficients. A reasonable strategy is thus to allow the optical activity coefficients to vary around their first-principles values, thereby fitting the experimental data more reliably.

The experimentally measured optical rotary power contains inseparable contributions both from the rectified displacements of different B -modes and from the quadratic dependence of the oscillating E -modes. As a result, the measured data does not uniquely constrain all components of the gyration coefficients. Hence, we group together different pathways with the same excitation frequency dependence, which leads to the following form of the rotary power

$$\rho = \pm \left[\sum_i A_i \langle Q_{E,i}^2 \rangle + \sum_{i < j} K_{ij} \langle Q_{E,i} Q_{E,j} \rangle \right] \quad (5.10)$$

where $\langle \cdots \rangle$ is the time average, and the coefficients A_i and K_{ij} are the weighted summation of the gyration coefficients from different pathways with the same frequency dependence, defined as

$$A_i = \sum_k \frac{\alpha_{i,k}}{\omega_{B,k}^2} \frac{\partial \rho}{\partial Q_{B,k}} + \frac{1}{2} \frac{\partial^2 \rho}{\partial Q_{E,i}^2} \quad (5.11)$$

$$K_{ij} = \sum_k \frac{\kappa_{ij,k}}{\omega_{B,k}^2} \frac{\partial \rho}{\partial Q_{B,k}} + \frac{\partial^2 \rho}{\partial Q_{E,i} \partial Q_{E,j}} \quad (5.12)$$

In the fitting procedure, with the goal of matching the frequency-dependent photosusceptibility with the rotary power given by Eq. (5.10), the free parameters are the summed coefficients A_i and K_{ij} . Because the experiments span the frequency range of the $E(2)$, $E(3)$, and $E(4)$ phonons, we employ six fitting parameters: A_2 , A_3 , A_4 , and K_{23} , K_{24} , K_{34} .

Fig. 5.10 shows the best fit of the model (black solid line) to the experimental results (black dots), revealing good agreement. The individual contributions from the terms

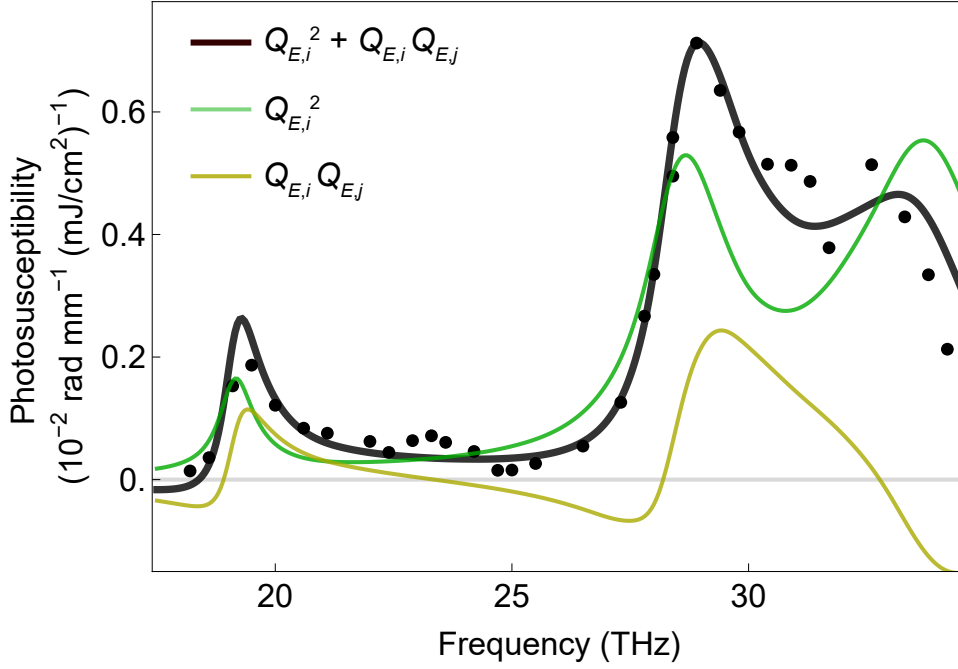


Figure 5.10. Decomposition of the photosusceptibility into contributions from different coupling mechanisms. Experimental data (black dots) are shown together with the fit (black curve) based on Eq. (5.10), where the total gyration coefficients A_i and K_{ij} are fitting parameters. The green and yellow curves represent the contributions from the terms proportional to $\langle Q_{E,i}^2 \rangle$ and $\langle Q_{E,i}Q_{E,j} \rangle$, respectively.

proportional to $\langle Q_{E,i}^2 \rangle$ and $\langle Q_{E,i}Q_{E,j} \rangle$ are plotted as green and yellow curves, respectively, highlighting the frequency ranges at which each of the two components is dominant. Table 5.1 shows the first-principles values and the fitted values of the ratio $|K_{ij}|/\sqrt{|A_i A_j|}$ for different E -symmetry modes, which characterize the relative size of the terms proportional to $\langle Q_{E,i}^2 \rangle$ and $\langle Q_{E,i}Q_{E,j} \rangle$. The similar size of K_{ij} and A_i within roughly one order of magnitude is consistent with the fact that the two-phonon and three-phonon mechanisms share the same order of lattice anharmonicity, and underscores the importance of considering both mechanisms in the fitting.

The model that includes only the $Q_{E,i}^2$ contributions cannot fully explain the measurement results, because it shows maximal responses only at resonance. The introduction of the additional $Q_{E,i}Q_{E,j}$ contributions is crucial to resolve this discrepancy, because their specific

Quantity	First-Principles Result	Fitted Result
$ K_{23} / \sqrt{ A_2 A_3 }$	0.22	2.14
$ K_{24} / \sqrt{ A_2 A_4 }$	1.62	3.99
$ K_{34} / \sqrt{ A_3 A_4 }$	2.59	2.72

Table 5.1. The ratio $|K_{ij}| / \sqrt{|A_i A_j|}$ obtained from first-principles calculations and fitting to experimental data.

frequency dependence shifts the maxima in photosusceptibility away from the exact phonon resonances, in agreement with the experimental observations. At phonon resonances, the light-induced chirality effect is dominated by the terms proportional to $\langle Q_{E,i}^2 \rangle$ ($g_{E,ii} Q_{E,i}^2$ and two-phonon mixing), whereas at frequencies a few phonon linewidths away from the resonances of multiple E -symmetry phonons, the terms proportional to $\langle Q_{E,i} Q_{E,j} \rangle$ ($g_{E,ij} Q_{E,i} Q_{E,j}$ and three-phonon mixing) become dominant.

Chapter 6

Conclusions and Outlook

Light has long served as a tool for probing the equilibrium properties of materials through spectroscopic techniques [98]. The advent of ultrafast pulsed lasers has expanded the scope of optical spectroscopies in two fundamental ways. First, pulse durations have been reduced to the picosecond, femtosecond, and even attosecond regimes, allowing time-resolved spectroscopy to capture fast dynamics near equilibrium [99–101]. Second, the high peak electric fields of intense ultrafast pulses offer unique possibilities for driving materials away from equilibrium, transforming the role of light in solids from a passive spectator to an active manipulator [26, 102]. Today, ultrafast laser systems combined with nonlinear optical frequency conversion enable the generation of intense excitation pulses across a broad spectral range, from terahertz and infrared to visible and ultraviolet frequencies. This capability enables the resonant excitation and detection of a wide variety of elementary excitations across different energy scales within materials [103–106]. Chapter 1 reviewed representative experiments that use ultrafast lasers to control and probe non-equilibrium phenomena in solids, highlighting the opportunities offered by ultrafast pump-probe techniques.

A promising route for manipulating materials with laser pulses is to break specific structural symmetries and induce transient lattice distortions through optical phonon excitation. This form of structural control can be achieved through lattice anharmonicity, where the oscillation of a directly driven infrared-active phonon is rectified into a quasi-static directional displacement of secondary phonon modes [25, 27, 60]. This phenomenon is generally

referred to as nonlinear phononics. Chapter 2 introduced its fundamental principle, including the linear response of optical phonons, nonlinear phonon-phonon coupling arising from anharmonic lattice potentials, and different pathways by which phonons can be connected to different types of order in materials [1, 2, 4, 17, 24, 48]. These examples highlight how resonant vibrational excitation can be translated into quasi-static changes of structure and order, providing a general framework for material engineering with light.

Within this broader framework, this thesis focuses on light-induced chirality in the achiral crystal BPO_4 . Chapter 3 introduced this material as an antiferro-chiral crystal: its left- and right-handed structural sub-units within the unit cell compensate in equilibrium, while a suitable symmetry-breaking displacement of B -symmetry phonons can make the crystal transiently chiral. In this system, the two-phonon mixing mechanism converts the oscillation of a driven E -symmetry phonon into the rectified displacement of the B -symmetry phonon modes, thereby breaking the balance between the two opposite handednesses in the unit cell. The first observation of light-induced chirality was achieved in BPO_4 [48], which established the phenomenon through time-resolved measurements of the optical activity induced by broadband mid-infrared excitation.

This and other earlier nonlinear phononics experiments were mostly performed using broadband mid-infrared excitation [1, 4, 27, 48]. While such few-cycle pulses drive lattice motion with very high peak electric fields, their large bandwidth obscures off-resonant contributions and may average over nearby phonon resonances. As a result, measurements with broadband excitations cannot determine whether a response is governed only by the resonantly driven phonon or whether additional nonlinear pathways are also involved. This unresolved question defined the experimental requirement for the thesis. Chapter 4 introduced a frequency-tunable narrowband mid-infrared source [82, 83], which enables the excitation frequency to be scanned across the mid-infrared phonon spectrum with sufficient resolution.

Chapter 5 returned to the question posed by the earlier broadband experiment on light-induced chirality in BPO_4 . If the light-induced chirality were solely governed by the two-phonon mixing mechanism, its excitation-frequency dependence would be expected to closely follow the linear extinction spectrum. However, the measured photosusceptibility

showed pronounced features between phonon resonances. These features can be understood by recognizing that the same mid-infrared excitation pulse can simultaneously drive oscillations of two non-degenerate phonon modes. Through a three-phonon mixing potential, the product of these two oscillations can generate a rectified force on a third phonon coordinate, producing a transient displacement in the same sense as conventional nonlinear phononics. By comparing the data with phonon-polariton simulations and first-principles estimates of the nonlinear coupling coefficients and optical responses, it was shown that such three-phonon mixing pathways must be included together with the two-phonon mixing mechanism. These observations extend nonlinear phononics beyond strictly resonant excitation, and demonstrate that off-resonant three-phonon interactions can be quantitatively important.

Taken together, the results of this thesis establish light-induced chirality in BPO_4 as a model case for excitation-frequency-resolved studies of nonlinear phononics. The new findings extend the demonstration the light-induced chirality in BPO_4 into the investigation of the underlying pathways by which the chiral state is produced. In this view, the excitation-frequency dependence becomes a spectroscopic observable that contains information about distinct nonlinear coupling channels. This perspective should be useful whenever several phonon modes lie close in frequency or when multiple symmetry-allowed interactions can produce the same macroscopic order parameter.

These findings suggest several directions for future work. First, optical rotation measurements are highly sensitive to the emergence of chirality, but they do not directly identify the microscopic atomic displacement pattern. Time-resolved structural probes, especially ultrafast X-ray diffraction, could provide complementary information by resolving the displacements of different chiral-symmetry-breaking modes after excitation [6]. Such measurements would extend the microscopic interpretation developed here and clarify how different phonon branches cooperate to generate the macroscopic chiral response.

A second direction is to extend the three-phonon mixing mechanism to other material systems. A particularly intriguing extension would be to search for the mixing between three modes of distinct symmetries. In such cases, symmetry can forbid the usual two-phonon mixing pathways between any two of the three phonon modes while allowing a genuine

three-phonon mixing interaction, so that the third mode is displaced only when the other two modes are driven simultaneously [107]. This would provide a particularly clean route for isolating three-phonon-mixing nonlinearities.

The most promising experimental implementation would use two independently-tunable narrowband pump sources, each resonant with one of the two driven modes. Such a scheme could realize non-degenerate three-phonon mixing and may even enable parametric amplification of a third phonon mode at finite frequency [108]. More broadly, multi-mode excitation would make nonlinear phononics a more flexible form of structural control, where the transient state can be selected by pairs of excitation frequencies rather than by isolated resonances. It will be interesting to explore this strategy in other systems controllable with nonlinear phononics, including perovskites [4, 49, 109], magnetic systems [32, 110–112], and ferroelectric materials [1, 113]. From this perspective, light-induced chirality serves as a model case for a broader goal: using tailored ultrafast excitation fields to reveal and control the multidimensional nonlinear energy landscape of quantum materials.

Appendix A

Narrowband Mid-Infrared Pulses from DSTMS

In Chapter 4 of the main text, we discussed the MIR pulse generation in the semiconductor nonlinear crystal GaSe. One major limitation of GaSe is its strong absorption band below 16 THz, limiting its utility for generating low-frequency MIR pulses. Conversely, organic nonlinear crystals, such as 4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) and 4-N,N'-dimethylamino-4'-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS), have exceptionally high nonlinear optical coefficients and are transparent at lower frequencies. This makes them ideal for generating low-frequency MIR pulses, typically between 4 and 18 THz [81, 84, 89]. When adapting a setup from semiconductor emitters to organic crystals, several unique material properties must be considered to optimize the MIR generation:

1. **Phase Matching and Tunability:** In DSTMS, DFG relies on type-0 phase matching, in which the two incoming NIR beams and the generated MIR beam are all polarized along the same crystallographic axis. Because the target MIR frequency is significantly lower than the NIR pumps, the rigorous phase-matching condition can be closely approximated by velocity matching

$$n_{THz} = n_g \quad (\text{A.1})$$

where n_{THz} is the refractive index of the generated MIR light, and $n_g = c/(d\omega/dk)$

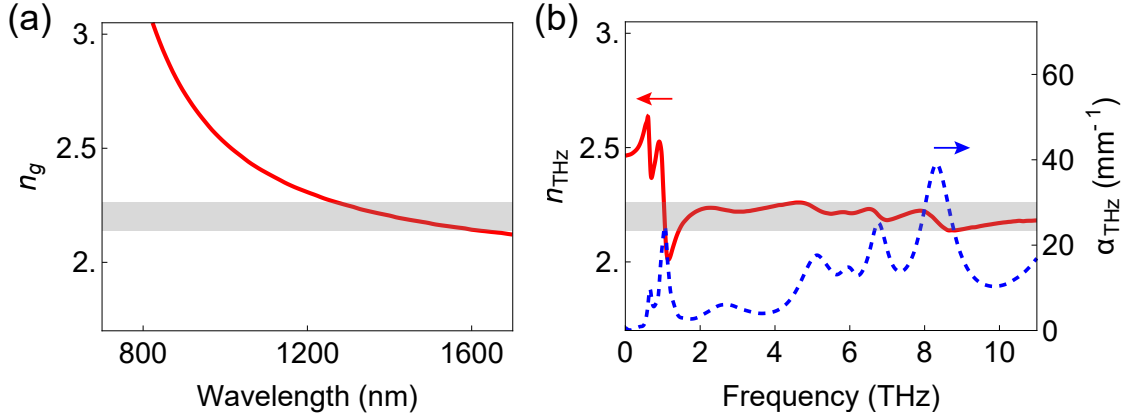


Figure A.1. Optical properties of DSTMS in the NIR and MIR ranges. (a) Wavelength dependence of the group index n_g for NIR beams. (b) Frequency dependence of the refractive index n_{THz} and absorption coefficient α_{THz} for MIR beams. The gray areas indicate the ranges where the phase-matching condition $n_{THz} = n_g$ can be satisfied. Adapted from [114].

is the group index evaluated at the central frequency of the NIR driving beams. Comparing the NIR group index and the MIR refractive index curves in Figure A.1 reveals that to efficiently generate MIR frequencies between 2 and 11 THz, the central wavelength of the NIR pumps must lie between 1300 and 1550 nm [114, 115]. Consequently, to continuously satisfy this index-matching condition while varying the desired MIR output frequency, one must independently tune the wavelengths of both NIR beams. This necessitates the use of two separate OPAs. In our experiments, the small crossing angle between the two NIR pulses ($< 1^\circ$) provides an additional degree of freedom for fine-tuning the phase matching, maximizing the output power for the desired MIR frequency [116, 117]. By employing these optimization strategies, the coherence length l_c for the DFG process can exceed 0.5 mm [114].

2. **Suppression of Optical Rectification:** Besides its utility for DFG, DSTMS is also highly efficient at generating broadband terahertz transients via optical rectification (OR), a process driven by intra-pulse difference-frequency mixing among the broad spectral components of a single NIR pulse. In a DFG configuration using transform-limited pulses, this spontaneous OR competes strongly with the desired inter-pulse

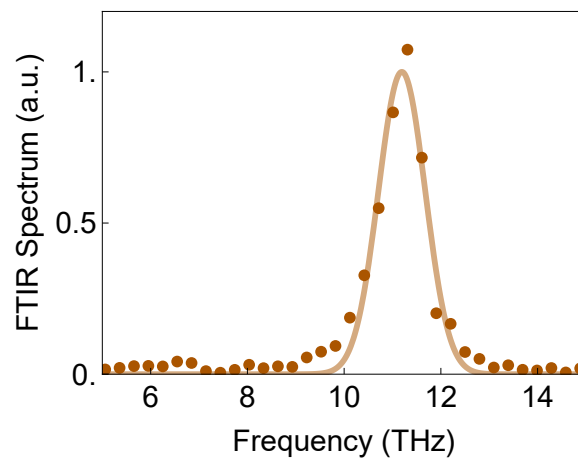


Figure A.2. Representative FTIR spectrum of a narrowband MIR pulse generated in DSTMS. The central frequency is 11.2 THz and the bandwidth is 1.1 THz.

DFG process. This competition depletes the available NIR pump power and can distort the NIR spectrum, hindering efficient MIR generation. To resolve this issue, the OR process must be suppressed by limiting the instantaneous bandwidth of the NIR pump pulses. Therefore, when driving DFG in DSTMS, strongly chirping the NIR pulses serves a dual purpose: it controls the bandwidth of the generated MIR pulse, and suppresses OR, ensuring efficient energy conversion into the MIR pulse [82].

3. **Intrinsic Absorption Features:** DSTMS exhibits numerous phonon-absorption peaks throughout the low-terahertz frequency range, as shown by the blue dashed curve in Figure A.1b [114]. Due to these resonances, the DFG efficiency fluctuates dramatically depending on the target MIR frequency. Furthermore, this strong, frequency-dependent absorption can distort the spectral shape of the generated MIR pulses.
4. **Damage Threshold:** The melting point of organic crystals such as DSTMS is much lower than that of inorganic nonlinear crystals. Consequently, the optical damage threshold is often dictated by average-power heating rather than peak-field effects [84]. This necessitates careful optimization of the NIR spot size at the crystal to avoid thermal damage.

Figure A.2 illustrates a typical MIR spectrum generated by mixing two chirped NIR

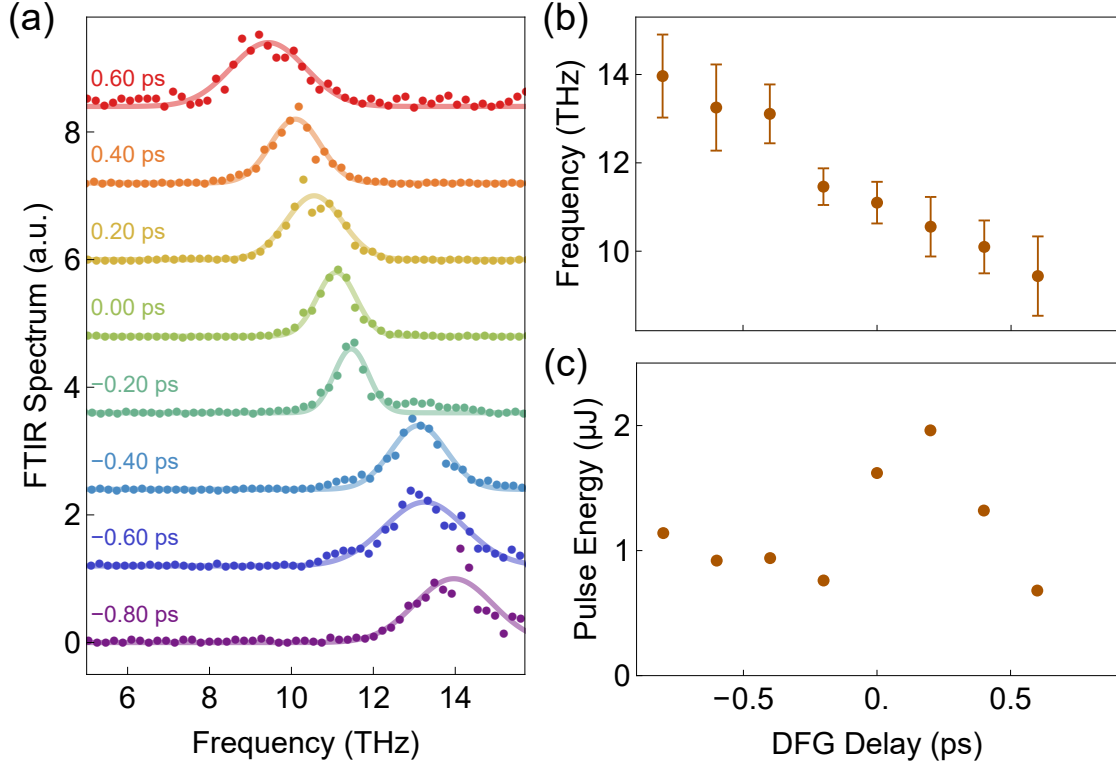


Figure A.3. Frequency tunability of chirped-pulse DFG in DSTMS. (a) FTIR spectra for different DFG delays. Colors from red to violet indicate increasing frequencies. (b) Central frequencies as a function of DFG delay corresponding to the spectra in (a). The error bars represent the bandwidth. (c) MIR pulse energy as a function of DFG delay corresponding to the spectra in (a).

pulses in a DSTMS crystal with a thickness of approximately $500\ \mu\text{m}$. Each of the stretched NIR driving pulses carries an energy of $\sim 550\ \mu\text{J}$ and is chirped to a duration of $\sim 600\ \text{fs}$. Their central wavelengths are set to $1415\ \text{nm}$ and $1485\ \text{nm}$. The NIR beams are focused to a spot with a diameter of $\sim 2.5\ \text{mm}$ at the crystal position. Under these conditions, the generated MIR pulse yields an energy of $\sim 3\ \mu\text{J}$, a central frequency of $11.2\ \text{THz}$, and an exceptionally narrow FWHM bandwidth of $1.1\ \text{THz}$.

An experimental demonstration highlighting the frequency tunability of the chirped-pulse DFG setup using DSTMS is summarized in Figure A.3. By varying the delay between the two chirped NIR pulses, the central frequencies of the output MIR pulses can be tuned over a range of nearly $5\ \text{THz}$ (see Figure A.3b). Importantly, the bandwidth of most generated

pulses remains close to ~ 1 THz, as indicated by the error bars. As shown in Figure A.3c, the output MIR pulse energy as a function of DFG delay does not follow a simple single-peaked Gaussian profile. A prominent dip near 12 THz corresponds to a known absorption peak in DSTMS [118]. Additionally, the measured spectra at delays of 0.2 ps, -0.6 ps, and -0.8 ps exhibit distorted line shapes that deviate from an ideal Gaussian profile, and the spectra at -0.2 ps and 0 ps exhibit unusually narrow linewidths. These anomalous spectral features are likely related to the frequency-dependent absorption profile of the DSTMS crystal itself [114, 118]. In summary, this strong frequency-dependent absorption complicates the optimization of DFG in DSTMS and makes the generation of sufficient pulse energy at certain MIR frequencies extremely challenging [117].

Appendix B

Sample Preparation

Polycrystalline BPO_4 powder was synthesized from high-purity H_3BO_3 (99.9995%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (99.998%) powders, before being ground, pelletized, and sintered. Single crystals were grown from this powder using a Li_2MoO_4 flux via the top-seeded solution growth technique in a platinum crucible at up to 975 °C. After homogenization, the melt was slowly cooled down, resulting in the growth of high-quality BPO_4 single crystals [119].

These crystals were characterized by X-ray diffractometry and oriented with an optically flat (001) surface using focused ion beam milling. Xenon ions were accelerated at 30 kV with a beam current of 2.5 mA for the surface orientation. To reduce roughness, the sample was finally milled at grazing incidence with a beam current of 200 nA. The thickness of the sample used in this experiment was approximately 200 μm .

Appendix C

First-Principles Calculations

We performed first-principles calculations based on density functional theory (DFT) to investigate the phonon excitation spectrum, anharmonic lattice-coupling coefficients, and optical response of BPO₄. We used the Vienna Ab initio Simulation Package (VASP) 6.6 DFT implementation [120–122], together with the Phonopy software package [123] for the phonon calculations. Our calculations employed pseudopotentials constructed within the projector augmented-wave (PAW) method [124]. Specifically, we used the default pseudopotentials for B ($2s^2 2p^1$), P ($3s^2 3p^3$), and O ($2s^2 2p^4$), and treated the exchange-correlation potential within the generalized gradient approximation (GGA) [125]. Lastly, following Ref. [126], we employed local field corrections in the framework of the Bethe-Salpeter equation [127, 128] atop the many-body GW quasiparticle framework [129, 130].

After convergence checks, we used a $(7 \times 7 \times 5)$ Monkhorst–Pack [126] k -point mesh for sampling the Brillouin zone and a plane-wave energy cutoff of 700 eV as the final numerical settings for the structural relaxations and phonon calculations. The self-consistent calculations were iterated until the change in total energy was converged to within (10^{-8}) eV. All phonon-mode and anharmonic-coupling-constant calculations were performed in a $(2 \times 2 \times 2)$ conventional cell of BPO₄.

The mode effective charges and dielectric response, including optical activity, were calculated using the LOPTICS settings of VASP, together with the approaches described in Refs. [126, 131]. To achieve convergence of the optical properties, we increased the k -point

Phonon	$\omega_{E,i}/(2\pi)$ (THz)	$Z_{E,i}^*$ (e/u ^{1/2})	Phonon	$\omega_{B,k}/(2\pi)$ (THz)	$Z_{B,k}^*$ (e/u ^{1/2})
$E(1)$	7.0	0.1	$B(1)$	15.8	0.9
$E(2)$	18.1	0.8	$B(2)$	17.7	0.4
$E(3)$	28.3	1.2	$B(3)$	28.1	1.1
$E(4)$	32.2	1.4	$B(4)$	31.5	1.5

Table C.1. Eigenfrequencies and mode effective charges for E - and B -symmetry phonons obtained from first-principles calculations.

Phonon	$\alpha_{2,k}$	$\alpha_{3,k}$	$\alpha_{4,k}$	$\delta_{2,k}$	$\delta_{3,k}$	$\delta_{4,k}$	ζ_k	$\kappa_{23,k}$	$\kappa_{24,k}$	$\kappa_{34,k}$
	[10 ⁻³ eV/(u ^{3/2} Å ³)]			[10 ⁻³ e/(u Å)]			[(e/√u)/(V/m)]	[10 ⁻³ eV/(u ^{3/2} Å ³)]		
$B(1)$	-8	158	-140	-13	43	48	-2.5×10^{-12}	83	-81	257
$B(2)$	-40	-12	-255	23	-43	-66	-2.2×10^{-12}	-55	-94	-18
$B(3)$	17	897	372	14	85	17	-0.5×10^{-12}	360	215	1066
$B(4)$	-106	256	-1284	27	23	14	3.2×10^{-12}	147	-497	779

Table C.2. Nonlinear coupling coefficients $\alpha_{i,k}$, $\delta_{i,k}$, ζ_k , $\kappa_{ij,k}$ for different B -phonons $B(k)$, obtained from first-principles calculations. The coefficients are defined in Eq. (5.5), and the indices i, j label the E -phonons.

mesh to $(128 \times 128 \times 82)$ and used 1000 empty states.

Our first-principles investigation started from the tetragonal unit cell of BPO₄. We first determined the DFT equilibrium volume of this cell, obtaining $V_{\text{cell}} = 131.6 \text{ \AA}^3$, with $a = b = 4.43 \text{ \AA}$ and $c = 6.71 \text{ \AA}$. The relaxed atomic equilibrium positions were found at the Wyckoff sites B (2d), P (2a), and O (8g), with oxygen coordinates (0.132, 0.258, 0.127). We then calculated the relevant phonon eigenfrequencies and mode-effective charges, which are listed in Table C.1. Subsequently, we computed the coupling constants defined in Eq. (5.5), which are listed in Table C.2.

Finally, we computed the changes in the antisymmetric parts of the dielectric tensor induced by lattice distortions along the coordinates of the four transiently displaced B -

Quantity	Unit	Value
$g_{B,1}$	$\text{rad mm}^{-1}\text{u}^{-1/2}\text{\AA}^{-1}$	-0.351
$g_{B,2}$	$\text{rad mm}^{-1}\text{u}^{-1/2}\text{\AA}^{-1}$	0.661
$g_{B,3}$	$\text{rad mm}^{-1}\text{u}^{-1/2}\text{\AA}^{-1}$	-0.325
$g_{B,4}$	$\text{rad mm}^{-1}\text{u}^{-1/2}\text{\AA}^{-1}$	-0.204
$g_{E,22}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	0.009
$g_{E,33}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	0.129
$g_{E,44}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	0.164
$g_{E,23}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	0.132
$g_{E,24}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	-0.164
$g_{E,34}$	$\text{rad mm}^{-1}\text{u}^{-1}\text{\AA}^{-2}$	-0.125

Table C.3. Phonon-amplitude-dependent changes of the rotary power, $g_{B,k}$ from B -symmetry phonons and $g_{E,ii}, g_{E,ij}$ from E -symmetry phonons, obtained with first-principles calculations.

symmetry modes and the combined displacements of pairs of E modes. The resulting gyration coefficients, as defined in Eq. (5.9), are listed in Table C.3.

Appendix D

Methods of Numerical Simulations Considering Polariton Propagation

To determine the frequency dependence of different nonlinear coupling terms, we performed spatiotemporal simulations of the electric field and phonon dynamics inside the material, explicitly accounting for polariton propagation. Here, the methods and primary results of the numerical simulations are introduced.

D.1 Solving Coupled Equations for Phonon Polaritons

Denoting z as the propagation direction, we define the spatial domain $0 < z < 150 \mu\text{m}$ as the BPO₄ sample, matching the actual sample thickness used in our experiments.

Inside the sample ($0 < z < 150 \mu\text{m}$), the MIR electric field couples linearly to the dipoles of the E -symmetry modes in the ab -plane, leading to the formation of phonon polaritons. For a phonon polariton propagating along the c -axis (normal to the sample surface), the coupled equations governing the E -mode coordinates $Q_{E,i}$ and the electric field E are given by [57]

$$\frac{\partial^2 Q_{E,i}}{\partial t^2} + \gamma_{E,i} \frac{\partial Q_{E,i}}{\partial t} + \omega_{E,i}^2 Q_{E,i} = Z_{E,i}^* E \quad (\text{D.1})$$

$$\frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \left(\varepsilon E + \sum_i \beta_{E,i} Q_{E,i} \right) \quad (\text{D.2})$$

where c is the speed of light in vacuum, ε is the high-frequency dielectric constant, $\gamma_{E,i}$ represents the damping coefficients, $\omega_{E,i}$ denotes the intrinsic phonon frequencies, and $Z_{E,i}^*$ and $\beta_{E,i}$ are the effective charges and dipole coupling constants of the phonons, respectively. The parameters of the E -symmetry phonons are calculated from the FTIR results in Table 3.1.

Outside the sample ($z < 0$ or $z > 150 \mu\text{m}$), the spatiotemporal evolution of the electric field E satisfies

$$\frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} \quad (\text{D.3})$$

The initial condition for the simulation is defined by a Gaussian pulse propagating along the $+z$ direction outside the sample. At the initial time, the electric field is

$$E(z, t_{\text{init.}}) = E_0 \exp\left[-(z-z_0)^2/(c\tau_d)^2\right] \sin\left(\frac{\omega_0 z}{c}\right) \quad (\text{D.4})$$

where τ_d is proportional to the excitation pulse duration, and ω_0 is its central frequency. To match the duration of the MIR pump used in our experiments, we set $2\sqrt{\ln 2}\tau_d = 600$ fs. To ensure that the pulse is completely outside the sample at $t = t_{\text{init.}}$, the initial center coordinate z_0 must satisfy $z_0 < -3c\tau_d$.

Representative numerical results for the time- and space-dependent electric field E and the E -mode coordinates $Q_{E,i}$ are shown in Fig. D.1a,d and Fig. D.1b,e, respectively. Results are presented for excitation resonant with the $E(4)$ phonon (33 THz) and for excitation slightly off resonance from the $E(4)$ phonon (31 THz). Compared with on-resonance excitation, both E and $Q_{E,4}$ penetrate deeper into the sample for off-resonance excitation.

After obtaining the solutions for E and $Q_{E,i}$, we evaluate their nonlinear coupling to the B -symmetry modes $Q_{B,k}$. Based on the coupling potential in Eq. (5.5), the equation of motion for $Q_{B,k}$ can be written as

$$\begin{aligned} \frac{\partial^2 Q_{B,k}}{\partial t^2} + \gamma_{B,k} \frac{\partial Q_{B,k}}{\partial t} + \omega_{B,k}^2 Q_{B,k} = \\ \pm \left[\sum_i \alpha_{i,k} Q_{E,i}^2 + \sum_i \delta_{i,k} Q_{E,i} E + \zeta_k E^2 + \sum_{i < j} \kappa_{ij,k} Q_{E,i} Q_{E,j} \right] \end{aligned} \quad (\text{D.5})$$

where $\gamma_{B,k}$ and $\omega_{B,k}$ are the damping coefficients and intrinsic frequencies of the B -modes, respectively. The frequencies of the B -symmetry phonons and the nonlinear coupling

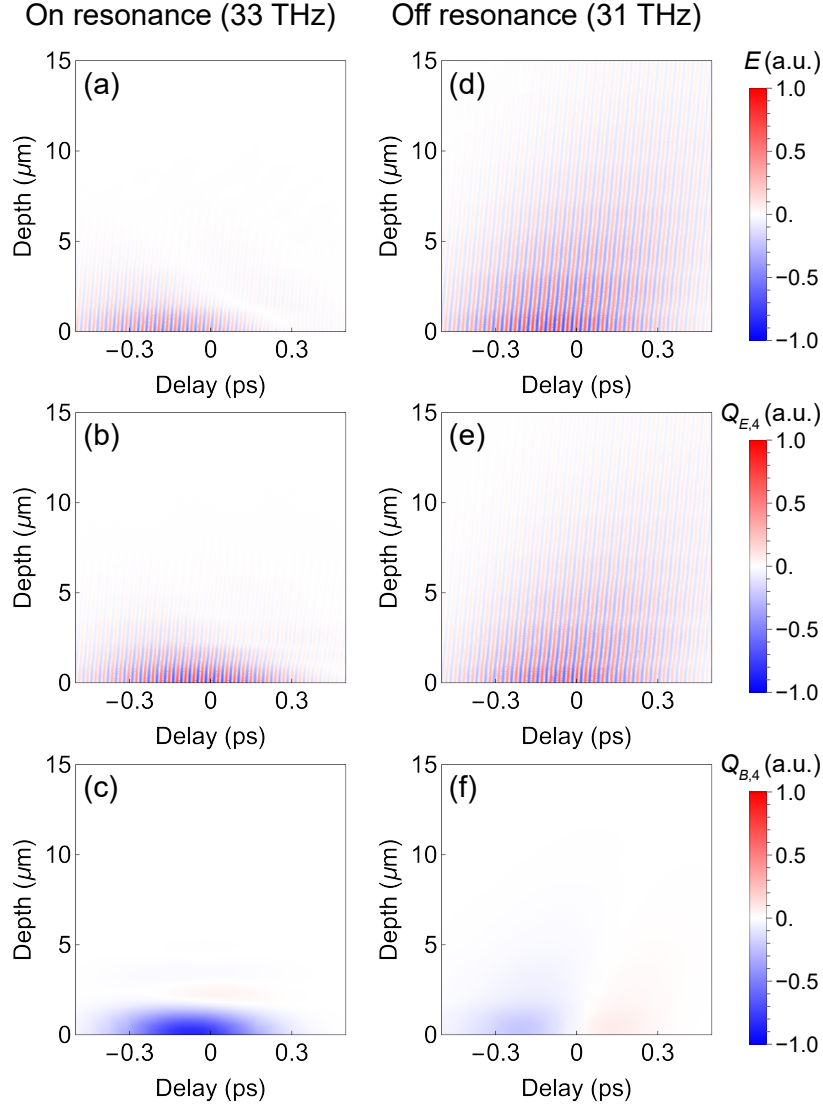


Figure D.1. Representative spatiotemporal simulation results for phonon-polariton propagation inside BPO₄. (a) Electric field E inside the material from on-resonance excitation at 33 THz. (b) E -mode oscillation $Q_{E,4}$ inside the material from on-resonance excitation at 33 THz. (c) B -mode displacement $Q_{B,4}$ inside the material from on-resonance excitation at 33 THz. The result is low-pass filtered in the time domain such that only the quasi-static displacement is preserved. (d-f) Same as (a-c) but for off-resonance excitation at 31 THz.

coefficients are taken from the first-principles calculation results in Tables C.1 and C.2. The overall sign on the right-hand side of Eq. (D.5) is determined by the choice of pump

polarization axis. Here, the linear dipole moments of the B -symmetry modes are not included in the wave equation, because for our chosen cut of BPO_4 , these dipoles are oriented along the crystal c -axis (parallel to the wave propagation direction) and thus do not couple linearly to the transversely propagating electric field. Examples of the simulated $Q_{B,k}$ displacements are shown in Fig. D.1c,f. These are derived from the E and $Q_{E,i}$ fields shown in Fig. D.1a,b and Fig. D.1d,e, respectively, and are then low-pass filtered in time to remove the rapidly oscillating components that cannot be resolved in our experiments.

D.2 Extraction of Optical Activity

After obtaining the B -symmetry mode displacement $Q_{B,k}$, the resulting rotary power ρ at each sample position can be calculated as

$$\rho(z, t) = \sum_k \left(\frac{\partial \rho}{\partial Q_{B,k}} \right) Q_{B,k}(z, t) + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \rho}{\partial Q_{E,i} \partial Q_{E,j}} \right) Q_{E,i}(z, t) Q_{E,j}(z, t) \quad (\text{D.6})$$

where the coefficients $g_{B,k} = \partial \rho / \partial Q_{B,k}$ for the B -phonons and $g_{E,ii} = \partial^2 \rho / \partial Q_{E,i}^2 / 2$, $g_{E,ij} = \partial^2 \rho / (\partial Q_{E,i} \partial Q_{E,j})$ for the E -phonons are again extracted from first-principles calculations (Table C.3). To determine the macroscopic signal observed by the NIR probe, we note that the probe pulse propagates through the sample with a velocity of $c/\sqrt{\epsilon_\infty}$ (the speed of light inside the medium at NIR wavelengths). The overall polarization rotation θ experienced by the probe is computed by integrating the local rotary power along these propagation lines [48], yielding

$$\theta(t) = \int_0^{150 \mu\text{m}} \frac{1}{\sqrt{\pi} \tau_p} \int_{-\infty}^{\infty} e^{-t'^2/\tau_p^2} \rho \left(z', t + \frac{z'}{c/\sqrt{\epsilon_\infty}} + t' \right) dt' dz' \quad (\text{D.7})$$

Here, the integration over t' accounts for the finite duration τ_p of the probe pulse, while the integration over z' sums the contributions from all longitudinal layers of the sample. Simulated pump-probe time traces from the contributions related to $Q_{E,i}$, including $g_{E,ii} Q_{E,i}^2$ and $g_{E,ij} Q_{E,i} Q_{E,j}$ terms, and $Q_{B,k}$, including $g_{B,k} Q_{B,k}$ terms, are presented in Fig. D.2 and Fig. D.3, respectively.

The maximal rotary power ρ_{max} extracted from the simulation is defined as the peak rotary power at the sample surface across all time delays. An example of the depth-dependent

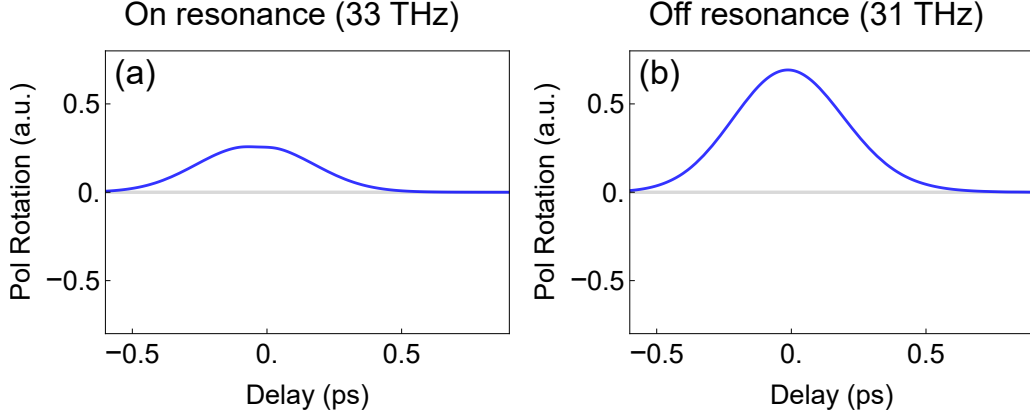


Figure D.2. Representative simulated pump-probe time traces of probe polarization rotation resulting from the E -modes, considering $(\partial^2 \rho / \partial Q_{E,i}^2 / 2) Q_{E,i}^2$ and $(\partial^2 \rho / \partial Q_{E,i} \partial Q_{E,j}) Q_{E,i} Q_{E,j}$ terms. The results are obtained by applying the numerical integration to the results in Fig. D.1. (a) Time-dependent polarization rotation for on-resonance excitations at 33 THz, considering the finite duration of the probe pulses. (b) Same as (a) but for off-resonance excitations at 31 THz.

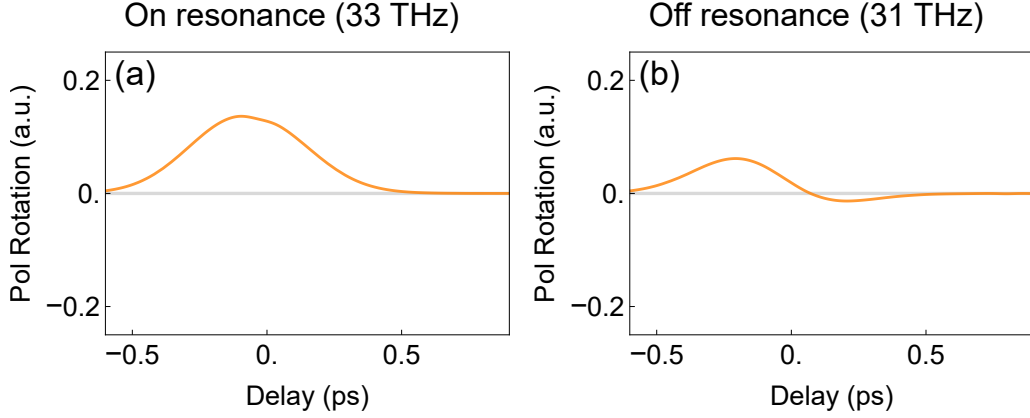


Figure D.3. Representative simulated pump-probe time traces of probe polarization rotation resulting from the B -modes, considering $(\partial \rho / \partial Q_{B,k}) Q_{B,k}$ terms. The results are obtained by applying the numerical integration to the results in Fig. D.1. (a) Time-dependent polarization rotation for on-resonance excitations at 33 THz, considering the finite duration of the probe pulses. (b) Same as (a) but for off-resonance excitations at 31 THz.

contribution to the maximal polarization rotation angle $\theta_{\max}$ is shown in Fig. D.4. As the

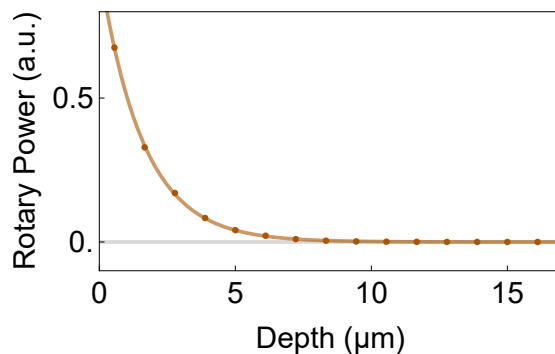


Figure D.4. Representative depth-dependent contribution to the rotation angle in BPO_4 . The brown dots are extracted directly from the simulation, and the light brown curve represents the exponential fit.

pump pulse penetrates into the sample, the induced rotary power decays approximately exponentially, with a characteristic decay length similar to the penetration depth at the excitation frequency. Consequently, the maximal rotary power at the surface can also be approximated by dividing the total maximal polarization rotation angle by this penetration depth. This is also how the maximal rotary power is obtained from the experimentally measured rotation angle (see Section 5.1.2 for details).

Appendix E

Comparison of Nonlinear Coupling Coefficients from First-Principle Calculations

Here, I compare the relative sizes of different nonlinear coupling pathways, with the coupling coefficients taken from first-principles calculations (Table C.3). Two methods are used: the numerical simulations based on the methods introduced in Appendix D, and the ratios between different nonlinear coupling terms.

E.1 Numerical Simulation Results

By combining the spatiotemporal simulation of the electric field and phonon motions with the coupling coefficients from first-principles calculations, we compare the contributions from different coupling mechanisms. The contribution from a given nonlinear coupling pathway can be calculated by retaining only the corresponding term on the right-hand side of Eq. (5.8).

Following the same numerical integration procedure illustrated in Fig. D.3, Fig. E.1 shows the separated contributions to the simulated pump-probe time trace from the four nonlinear coupling pathways, $Q_{E,i}^2 Q_B$, $Q_{E,i} E Q_B$, $E^2 Q_B$, and $Q_{E,i} Q_{E,j} Q_B$. Both on-

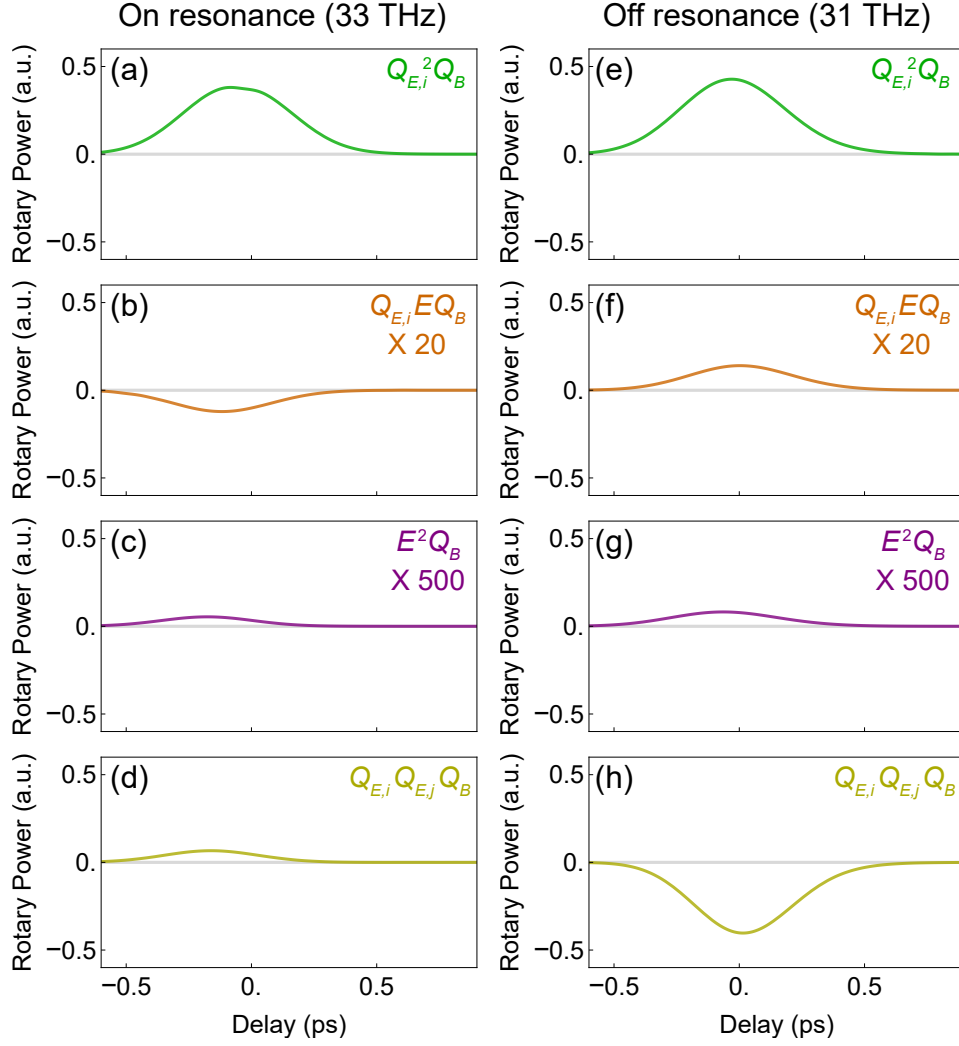


Figure E.1. Comparison of contributions from different nonlinear coupling pathways, combining numerical simulations and first-principles calculations. (a-d) Simulated time-delay dependence of rotary power from $Q_{E,i}^2 Q_B$ (a), $Q_{E,i} E Q_B$ (b), $E^2 Q_B$ (c), and $Q_{E,i} Q_{E,j} Q_B$ (d) coupling terms for on-resonance excitations at 33 THz. **(e-h)** Same as (a-d) but for off-resonance excitations at 31 THz.

resonance excitation at 33 THz (Fig. E.1a-d) and off-resonance excitation at 31 THz (Fig. E.1e-h) are considered. For on-resonance excitation, the $Q_{E,i}^2 Q_B$ mechanism is dominant. For off-resonance excitation, the $Q_{E,i}^2 Q_B$ contribution is much smaller, and the $Q_{E,i} Q_{E,j} Q_B$ mechanism also contributes significantly to the overall signal. Theoretically, these two purely phononic contributions share the same microscopic origin, namely lattice anharmonicity,

and therefore naturally have comparable coupling coefficients. Since the bandwidths of the $E(3)$ and $E(4)$ phonons are similar to their frequency spacing, the $Q_{E,i}^2 Q_B$ and $Q_{E,i} Q_{E,j} Q_B$ mechanisms are expected to produce signals of similar magnitude. At the same time, however, the contributions from nonlinear pathways involving the electric field, namely $Q_{E,i} E Q_B$ and $E^2 Q_B$, are orders of magnitude smaller than those from the purely phononic pathways.

The above analysis can be extended to the full MIR frequency range covered in our experiments, yielding the full excitation frequency dependence of the four nonlinear coupling terms to Q_B , as shown in Fig. 5.9 in the main text. The conclusion that the Raman mechanisms contribute much less to polarization rotation than the purely phononic mechanisms holds for the full MIR frequency range covered in our experiments.

E.2 Ratios of Coupling Coefficients

The relative magnitudes of the contributions from different nonlinear coupling terms stem from the relative magnitudes of the corresponding coupling coefficients. It is therefore desirable to compare these coupling coefficients directly using the results from first-principles calculations. However, because the coefficients $\alpha_{i,k}$, $\delta_{i,k}$, ζ_k have different dimensions, extra care is required when comparing them directly. Since δ/α has the dimension of Q_E/E and ζ/α has the dimension of $(Q_E/E)^2$, it is natural to consider the oscillation amplitudes $A_{Q,i}$ (of $Q_{E,i}$) and A_{MIR} (of E). At phonon resonance $\omega_0 = \omega_{E,i}$, the ratio $A_{Q,i}/A_{MIR}$ reaches its peak value

$$\left(\frac{A_{Q,i}}{A_{MIR}} \right)_{\omega_0=\omega_{E,i}} = \frac{Z_{E,i}^*}{\omega_{E,i} \gamma_{E,i}} \quad (\text{E.1})$$

Therefore, we can use the dimensionless quantities

$$\frac{\delta_{i,k}}{\alpha_{i,k}} \left(\frac{\omega_{E,i} \gamma_{E,i}}{Z_{E,i}^*} \right), \quad \frac{\zeta_k}{\alpha_{i,k}} \left(\frac{\omega_{E,i} \gamma_{E,i}}{Z_{E,i}^*} \right)^2 \quad (\text{E.2})$$

to quantify the relative magnitudes of $\delta_{i,k}$ and ζ_k with respect to $\alpha_{i,k}$. As summarized in Tables E.1 and E.2, the absolute values of $\delta_{i,k}/\alpha_{i,k}(\omega_{E,i}\gamma_{E,i}/Z_{E,i}^*)$ are mostly smaller than 0.06, and the absolute values of $\zeta_k/\alpha_{i,k}(\omega_{E,i}\gamma_{E,i}/Z_{E,i}^*)^2$ are mostly smaller than 0.002. Therefore, we can conclude that the coefficients $\delta_{i,k}$ and ζ_k are much smaller than $\alpha_{i,k}$, in the

	$E(2)$	$E(3)$	$E(4)$
$B(1)$	0.053	0.026	-0.052
$B(2)$	-0.019	0.329	0.039
$B(3)$	0.028	0.009	0.007
$B(4)$	-0.009	0.008	-0.002

Table E.1. Dimensionless ratios $\delta_{i,k}/\alpha_{i,k}(\omega_{E,i}\gamma_{E,i}/Z_{E,i}^*)$ for different E -modes $E(i)$ and B -modes $B(k)$, calculated from first-principles results.

	$E(2)$	$E(3)$	$E(4)$
$B(1)$	-0.0015	0.0006	-0.0018
$B(2)$	-0.0003	-0.0067	-0.0009
$B(3)$	0.0001	0.00002	0.0001
$B(4)$	-0.0001	0.0005	0.0003

Table E.2. Dimensionless ratios $\zeta_k/\alpha_{i,k}(\omega_{E,i}\gamma_{E,i}/Z_{E,i}^*)^2$ for different E -modes $E(i)$ and B -modes $B(k)$, calculated from first-principles results.

	$E(2), E(3)$	$E(2), E(4)$	$E(3), E(4)$
$B(1)$	2.33	-2.42	1.73
$B(2)$	-2.51	-0.93	-0.59
$B(3)$	2.92	2.70	1.85
$B(4)$	0.89	-1.35	1.36

Table E.3. Dimensionless ratios $\kappa_{ij,k}/\sqrt{|\alpha_{i,k}\alpha_{j,k}|}$ for different E -mode pairs $E(i), E(j)$ and B -modes $B(k)$, calculated from first-principles results.

sense of these derived dimensionless quantities. This order-of-magnitude reduction in the coupling coefficients $\delta_{i,k}$ and ζ_k leads directly to the small contributions of the $Q_{E,i}EQ_B$ and E^2Q_B terms to light-induced chirality in BPO₄.

On the other hand, the comparison between $\alpha_{i,k}$ and $\kappa_{ij,k}$ is relatively straightforward because they have the same units. The ratios $\kappa_{ij,k}/\sqrt{|\alpha_{i,k}\alpha_{j,k}|}$ are summarized in Table E.3 and are generally of order unity. This observation explains why the simulated $Q_{E,i}^2 Q_B$ and $Q_{E,i} Q_{E,j} Q_B$ contributions are comparable in magnitude.

Bibliography

- [1] R. Mankowsky, A. von Hoegen, M. Först, and A. Cavalleri, “Ultrafast reversal of the ferroelectric polarization”, *Physical Review Letters* **118**, 197601 (2017).
- [2] A. S. Disa, M. Fechner, T. F. Nova, B. Liu, M. Först, D. Prabhakaran, P. G. Radaelli, and A. Cavalleri, “Polarizing an antiferromagnet by optical engineering of the crystal field”, *Nature Physics* **16**, 937 (2020).
- [3] T. F. Nova, A. Cartella, A. Cantaluppi, M. Först, D. Bossini, R. V. Mikhaylovskiy, A. V. Kimel, R. Merlin, and A. Cavalleri, “An effective magnetic field from optically driven phonons”, *Nature Physics* **13**, 132 (2017).
- [4] M. Rini, R. Tobey, N. Dean, J. Itatani, Y. Tomioka, Y. Tokura, R. W. Schoenlein, and A. Cavalleri, “Control of the electronic phase of a manganite by mode-selective vibrational excitation”, *Nature* **449**, 72 (2007).
- [5] D. Fausti, R. Tobey, N. Dean, S. Kaiser, A. Dienst, M. C. Hoffmann, S. Pyon, T. Takayama, H. Takagi, and A. Cavalleri, “Light-induced superconductivity in a stripe-ordered cuprate”, *Science* **331**, 189 (2011).
- [6] M. Först, R. Mankowsky, H. Bromberger, D. M. Fritz, H. Lemke, D. Zhu, M. Chollet, Y. Tomioka, Y. Tokura, R. Merlin, et al., “Displacive lattice excitation through nonlinear phononics viewed by femtosecond x-ray diffraction”, *Solid State Communications* **169**, 24 (2013).
- [7] M. Henstridge, M. Först, E. Rowe, M. Fechner, and A. Cavalleri, “Nonlocal nonlinear phononics”, *Nature Physics* **18**, 457 (2022).

- [8] T. Nova, A. Disa, M. Fechner, and A. Cavalleri, “Metastable ferroelectricity in optically strained SrTiO_3 ”, *Science* **364**, 1075 (2019).
- [9] C. J. Allington, C. A. Belvin, U. F. Seifert, M. Ye, T. Tai, E. Baldini, S. Son, J. Kim, J. Park, J.-G. Park, et al., “Distinct optical excitation mechanisms of a coherent magnon in a van der waals antiferromagnet”, *Physical Review Letters* **134**, 066903 (2025).
- [10] A. Disa, J. Curtis, M. Fechner, A. Liu, A. Von Hoegen, M. Först, T. Nova, P. Narang, A. Maljuk, A. Boris, et al., “Photo-induced high-temperature ferromagnetism in YTiO_3 ”, *Nature* **617**, 73 (2023).
- [11] T. F. Nova, A. Cartella, A. Cantaluppi, M. Först, D. Bossini, R. V. Mikhaylovskiy, A. V. Kimel, R. Merlin, and A. Cavalleri, “An effective magnetic field from optically driven phonons”, *Nature Physics* **13**, 132 (2017).
- [12] H. Chu, M.-J. Kim, K. Katsumi, S. Kovalev, R. D. Dawson, L. Schwarz, N. Yoshikawa, G. Kim, D. Putzky, Z. Z. Li, et al., “Phase-resolved higgs response in superconducting cuprates”, *Nature Communications* **11**, 1793 (2020).
- [13] M.-J. Kim, S. Kovalev, M. Udina, R. Haenel, G. Kim, M. Puviani, G. Cristiani, I. Ilyakov, T. V. de Oliveira, A. Ponomaryov, et al., “Tracing the dynamics of superconducting order via transient terahertz third-harmonic generation”, *Science Advances* **10**, eadi7598 (2024).
- [14] R. Matsunaga, Y. I. Hamada, K. Makise, Y. Uzawa, H. Terai, Z. Wang, and R. Shimano, “Higgs amplitude mode in the bcs superconductors $\text{Nb}_{1-x}\text{Ti}_x\text{N}$ induced by terahertz pulse excitation”, *Physical Review Letters* **111**, 057002 (2013).
- [15] K. Katsumi, M. Nishida, S. Kaiser, S. Miyasaka, S. Tajima, and R. Shimano, “Near-infrared light-induced superconducting-like state in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_y$ studied by c-axis terahertz third-harmonic generation”, *Physical Review B* **107**, 214506 (2023).

- [16] T. Li, A. Patz, L. Mouchliadis, J. Yan, T. A. Lograsso, I. E. Perakis, and J. Wang, “Femtosecond switching of magnetism via strongly correlated spin–charge quantum excitations”, *Nature* **496**, 69 (2013).
- [17] V. Esposito, M. Fechner, R. Mankowsky, H. Lemke, M. Chollet, J. M. Glowia, M. Nakamura, M. Kawasaki, Y. Tokura, U. Staub, et al., “Nonlinear electron-phonon coupling in doped manganites”, *Physical Review Letters* **118**, 247601 (2017).
- [18] R. Xiong, Y. Guo, C. Qin, F. Yin, T. Wang, S. L. Brantly, J. Qi, J. Zhou, Z. Zhang, M. Erdi, et al., “Propagating neutral modes in an intervalley coherent state”, *arXiv preprint arXiv:2507.18770* (2025).
- [19] T. Xie, S. Xu, Z. Dong, Z. Cui, Y. Ou, M. Erdi, K. Watanabe, T. Taniguchi, S. A. Tongay, L. S. Levitov, et al., “Long-lived isospin excitations in magic-angle twisted bilayer graphene”, *Nature* **633**, 77 (2024).
- [20] R. Xiong, J. H. Nie, S. L. Brantly, P. Hays, R. Sailus, K. Watanabe, T. Taniguchi, S. Tongay, and C. Jin, “Correlated insulator of excitons in WSe₂/WS₂ moiré superlattices”, *Science* **380**, 860 (2023).
- [21] Y. Wang, J. Choe, E. Anderson, W. Li, J. Ingham, E. A. Arsenault, Y. Li, X. Hu, T. Taniguchi, K. Watanabe, et al., “Hidden states and dynamics of fractional fillings in twisted MoTe₂ bilayers”, *Nature* **641**, 1149 (2025).
- [22] M. H. Michael, E. Demler, and P. Lee, “Parametrically amplified josephson plasma waves in YBa₂Cu₃O_{6+x}: evidence for local superconducting fluctuations up to the pseudogap temperature T^* ”, *arXiv preprint arXiv:2505.03358* (2025).
- [23] D. De Santis, A. G. Salvador, N. Bazhan, S. Erne, M. Prüfer, C. Guarcello, D. Valenti, J. Schmiedmayer, and E. Demler, “Momentum-resolved two-dimensional spectroscopy as a probe of nonlinear quantum field dynamics”, *arXiv preprint arXiv:2509.25147* (2025).
- [24] Z. Zeng, M. Först, M. Fechner, D. Prabhakaran, P. Radaelli, and A. Cavalleri, “Photo-induced nonvolatile rewritable ferroaxial switching”, *Science* **390**, 195 (2025).

- [25] A. S. Disa, T. F. Nova, and A. Cavalleri, “Engineering crystal structures with light”, *Nature Physics* **17**, 1087 (2021).
- [26] A. De La Torre, D. M. Kennes, M. Claassen, S. Gerber, J. W. McIver, and M. A. Sentef, “Colloquium: nonthermal pathways to ultrafast control in quantum materials”, *Reviews of Modern Physics* **93**, 041002 (2021).
- [27] M. Först, C. Manzoni, S. Kaiser, Y. Tomioka, Y. Tokura, R. Merlin, and A. Cavalleri, “Nonlinear phononics as an ultrafast route to lattice control”, *Nature Physics* **7**, 854 (2011).
- [28] A. Zong, P. E. Dolgirev, A. Kogar, E. Ergeçen, M. B. Yilmaz, Y.-Q. Bie, T. Rohwer, I.-C. Tung, J. Straquadine, X. Wang, et al., “Dynamical slowing-down in an ultrafast photoinduced phase transition”, *Physical Review Letters* **123**, 097601 (2019).
- [29] U. F. Seifert, M. Ye, and L. Balents, “Ultrafast optical excitation of magnetic dynamics in van der waals magnets: coherent magnons and bkt dynamics in NiPS₃”, *Physical Review B* **105**, 155138 (2022).
- [30] D. Nicoletti, M. Rosenberg, M. Buzzi, M. Fechner, Y. Liu, S. Nakata, B. Keimer, R. A. Vitalone, D. N. Basov, P. E. Dolgirev, et al., “Enhanced coherent terahertz emission from critical superconducting fluctuations in YBa₂Cu₃O_{6.6}”, *Physical Review X* **15**, 041036 (2025).
- [31] S. Gerber, S.-L. Yang, D. Zhu, H. Soifer, J. Sobota, S. Rebec, J. Lee, T. Jia, B. Moritz, C. Jia, et al., “Femtosecond electron-phonon lock-in by photoemission and x-ray free-electron laser”, *Science* **357**, 71 (2017).
- [32] A. von Hoegen, R. Mankowsky, M. Fechner, M. Först, and A. Cavalleri, “Probing the interatomic potential of solids with strong-field nonlinear phononics”, *Nature* **555**, 79 (2018).
- [33] J. Demsar, K. Biljaković, and D. Mihailovic, “Single particle and collective excitations in the one-dimensional charge density wave solid K_{0.3}MoO₃ probed in real time by femtosecond spectroscopy”, *Physical Review Letters* **83**, 800 (1999).

- [34] Y. Laplace and A. Cavalleri, “Josephson plasmonics in layered superconductors”, *Advances in Physics: X* **1**, 387 (2016).
- [35] Z. Bi and L. Fu, “Excitonic density wave and spin-valley superfluid in bilayer transition metal dichalcogenide”, *Nature Communications* **12**, 642 (2021).
- [36] A. Cavalleri, T. Dekorsy, H. H. Chong, J.-C. Kieffer, and R. W. Schoenlein, “Evidence for a structurally-driven insulator-to-metal transition in VO₂: a view from the ultrafast timescale”, *Physical Review B* **70**, 161102 (2004).
- [37] P. Baum, D.-S. Yang, and A. H. Zewail, “4d visualization of transitional structures in phase transformations by electron diffraction”, *Science* **318**, 788 (2007).
- [38] M. Fiebig, K. Miyano, Y. Tomioka, and Y. Tokura, “Sub-picosecond photo-induced melting of a charge-ordered state in a perovskite manganite”, *Applied Physics B* **71**, 211 (2000).
- [39] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, “Photoinduced insulator-to-metal transition in a perovskite manganite”, *Physical Review Letters* **78**, 4257 (1997).
- [40] J. Fink, E. Schierle, E. Weschke, J. Geck, D. Hawthorn, V. Soltwisch, H. Wadati, H.-H. Wu, H. A. Dürr, N. Wizen, et al., “Charge ordering in La_{1.8-x}Eu_{0.2}Sr_xCuO₄ studied by resonant soft x-ray diffraction”, *Physical Review B* **79**, 100502 (2009).
- [41] M. Fujita, H. Goka, K. Yamada, and M. Matsuda, “Competition between charge- and spin-density-wave order and superconductivity in La_{1.875}Ba_{0.125-x}Sr_xCuO₄”, *Physical Review Letters* **88**, 167008 (2002).
- [42] H. Sun, M. Huo, X. Hu, J. Li, Z. Liu, Y. Han, L. Tang, Z. Mao, P. Yang, B. Wang, et al., “Signatures of superconductivity near 80 K in a nickelate under high pressure”, *Nature* **621**, 493 (2023).
- [43] T. Li, S. Deng, H. Liu, and J. Chen, “Insights into strain engineering: from ferroelectrics to related functional materials and beyond”, *Chemical Reviews* **124**, 7045 (2024).

- [44] Y. Liu, E. K. Ko, Y. Tarn, L. Bhatt, J. Li, V. Thampy, B. H. Goodge, D. A. Muller, S. Raghu, Y. Yu, et al., “Superconductivity and normal-state transport in compressively strained $\text{La}_2\text{PrNi}_2\text{O}_7$ thin films”, *Nature Materials*, 1 (2025).
- [45] D. M. Juraschek, M. Fechner, and N. A. Spaldin, “Ultrafast structure switching through nonlinear phononics”, *Physical Review Letters* **118**, 054101 (2017).
- [46] V. Esposito, M. Fechner, R. Mankowsky, H. Lemke, M. Chollet, J. M. Glowia, M. Nakamura, M. Kawasaki, Y. Tokura, U. Staub, et al., “Nonlinear electron-phonon coupling in doped manganites”, *Physical Review Letters* **118**, 247601 (2017).
- [47] M. Fechner, M. Först, G. Orenstein, V. Krapivin, A. Disa, M. Buzzi, A. Von Hoegen, G. De La Pena, Q. Nguyen, R. Mankowsky, et al., “Quenched lattice fluctuations in optically driven SrTiO_3 ”, *Nature Materials* **23**, 363 (2024).
- [48] Z. Zeng, M. Först, M. Fechner, M. Buzzi, E. Amuah, C. Putzke, P. Moll, D. Prabhakaran, P. Radaelli, and A. Cavalleri, “Photo-induced chirality in a nonchiral crystal”, *Science* **387**, 431 (2025).
- [49] A. D. Caviglia, R. Scherwitzl, P. Popovich, W. Hu, H. Bromberger, R. Singla, M. Mitrano, M. C. Hoffmann, S. Kaiser, P. Zubko, et al., “Ultrafast strain engineering in complex oxide heterostructures”, *Physical Review Letters* **108**, 136801 (2012).
- [50] D. Griffiths, *Introduction to quantum mechanics* (Cambridge University Press, 2017).
- [51] N. Ashcroft and N. Mermin, *Solid state physics* (Cengage Learning, 2011).
- [52] C. Kittel and P. McEuen, *Introduction to solid state physics* (Wiley, 2018).
- [53] A. Altland and B. Simons, *Condensed matter field theory*, Cambridge books online (Cambridge University Press, 2010).
- [54] C. Kittel, *Quantum theory of solids* (Wiley, 1963).
- [55] G. Petretto, S. Dwaraknath, H. PC Miranda, D. Winston, M. Giantomassi, M. J. Van Setten, X. Gonze, K. A. Persson, G. Hautier, and G.-M. Rignanese, “High-throughput density-functional perturbation theory phonons for inorganic materials”, *Scientific Data* **5**, 1 (2018).

- [56] M. Fox, *Optical properties of solids*, Vol. 3 (Oxford university press, 2010).
- [57] K. Huang, “Lattice vibrations and optical waves in ionic crystals”, *Nature* **167**, 779 (1951).
- [58] R. Boyd, *Nonlinear optics*, Electronics & Electrical (Academic Press, 2003).
- [59] M. Dresselhaus, G. Dresselhaus, and A. Jorio, *Group theory: application to the physics of condensed matter* (Springer Berlin Heidelberg, 2007).
- [60] R. Mankowsky, M. Först, and A. Cavalleri, “Non-equilibrium control of complex solids by nonlinear phononics”, *Reports on Progress in Physics* **79**, 064503 (2016).
- [61] T. Mertelj and V. Kabanov, “Comment on “ultrafast reversal of the ferroelectric polarization””, *Physical Review Letters* **123**, 129701 (2019).
- [62] N. Taherian Hosseinabadi, “Multidimensional phononics in driven $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ”, PhD thesis (Staats-und Universitätsbibliothek Hamburg Carl von Ossietzky, 2025).
- [63] N. Taherian, M. Först, A. Liu, M. Fechner, D. Pavicevic, A. von Hoegen, E. Rowe, Y. Liu, S. Nakata, B. Keimer, et al., “Probing amplified josephson plasmons in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ by multidimensional spectroscopy”, *npj Quantum Materials* **10**, 54 (2025).
- [64] M. Abrashev, A. Litvinchuk, M. Iliev, R. Meng, V. Popov, V. Ivanov, R. Chakalov, and C. Thomsen, “Comparative study of optical phonons in the rhombohedrally distorted perovskites LaAlO_3 and LaMnO_3 ”, *Physical Review B* **59**, 4146 (1999).
- [65] R. Yusupov, T. Mertelj, V. V. Kabanov, S. Brazovskii, P. Kusar, J.-H. Chu, I. R. Fisher, and D. Mihailovic, “Coherent dynamics of macroscopic electronic order through a symmetry breaking transition”, *Nature Physics* **6**, 681 (2010).
- [66] M. Fechner, A. Sukhov, L. Chotorlishvili, C. Kenel, J. Berakdar, and N. Spaldin, “Magnetophononics: ultrafast spin control through the lattice”, *Physical Review Materials* **2**, 064401 (2018).

- [67] D. Afanasiev, J. Hortensius, B. Ivanov, A. Sasani, E. Bousquet, Y. Blanter, R. Mikhaylovskiy, A. Kimel, and A. Caviglia, “Ultrafast control of magnetic interactions via light-driven phonons”, *Nature Materials* **20**, 607 (2021).
- [68] D. M. Juraschek, P. Narang, and N. A. Spaldin, “Phono-magnetic analogs to opto-magnetic effects”, *Physical Review Research* **2**, 043035 (2020).
- [69] K. Wang, K. Ren, Y. Hou, Y. Cheng, and G. Zhang, “Magnon–phonon coupling: from fundamental physics to applications”, *Physical Chemistry Chemical Physics* **25**, 21802 (2023).
- [70] S. Bhowal and N. A. Spaldin, “Electric toroidal dipole order and hidden spin polarization in ferroaxial materials”, *Physical Review Research* **6**, 043141 (2024).
- [71] H. Yokota, T. Hayashida, D. Kitahara, and T. Kimura, “Three-dimensional imaging of ferroaxial domains using circularly polarized second harmonic generation microscopy”, *npj Quantum Materials* **7**, 106 (2022).
- [72] J. Gal, “Molecular chirality in chemistry and biology: historical milestones”, *Helvetica Chimica Acta* **96**, 1617 (2013).
- [73] V. Prelog, “Chirality in chemistry”, *Science* **193**, 17 (1976).
- [74] B. L. Feringa and R. A. Van Delden, “Absolute asymmetric synthesis: the origin, control, and amplification of chirality”, *Angewandte Chemie International Edition* **38**, 3418 (1999).
- [75] M. Nespolo and A. H. Benahsene, “Symmetry and chirality in crystals”, *Applied Crystallography* **54**, 1594 (2021).
- [76] E. Plum, J. Zhou, J. Dong, V. Fedotov, T. Koschny, C. Soukoulis, and N. Zheludev, “Metamaterial with negative index due to chirality”, *Physical Review B* **79**, 035407 (2009).

- [77] P. Stephens, F. Devlin, J. Cheeseman, M. Frisch, O. Bortolini, and P. Besse, “Determination of absolute configuration using ab initio calculation of optical rotation”, *Chirality: The Pharmacological, Biological, and Chemical Consequences of Molecular Asymmetry* **15**, S57 (2003).
- [78] C. Hurlbut Jr and J. L. Rosenfeld, “Monochromator utilizing the rotary power of quartz”, *American Mineralogist: Journal of Earth and Planetary Materials* **37**, 158 (1952).
- [79] T. Matsuura and H. Koshima, “Introduction to chiral crystallization of achiral organic compounds: spontaneous generation of chirality”, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **6**, 7 (2005).
- [80] Z. Zeng, M. Först, M. Fechner, X. Deng, A. Cavalleri, and P. Radaelli, “The piezochiral effect”, arXiv preprint arXiv:2510.21674 (2025).
- [81] B. Liu, M. Först, M. Fechner, D. Nicoletti, J. Porras, T. Loew, B. Keimer, and A. Cavalleri, “Pump frequency resonances for light-induced incipient superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ”, *Physical Review X* **10**, 011053 (2020).
- [82] B. Liu, H. Bromberger, A. Cartella, T. Gebert, M. Först, and A. Cavalleri, “Generation of narrowband, high-intensity, carrier-envelope phase-stable pulses tunable between 4 and 18 thz”, *Optics Letters* **42**, 129 (2016).
- [83] A. Cartella, T. F. Nova, A. Oriana, G. Cerullo, M. Först, C. Manzoni, and A. Cavalleri, “Narrowband carrier-envelope phase stable mid-infrared pulses at wavelengths beyond $10\text{ }\mu\text{m}$ by chirped-pulse difference frequency generation”, *Optics Letters* **42**, 663 (2017).
- [84] B. Liu, “Controlling superconductivity using tailored thz pulses”, PhD thesis (Universität Hamburg, 2020).
- [85] A. Sell, A. Leitenstorfer, and R. Huber, “Phase-locked generation and field-resolved detection of widely tunable terahertz pulses with amplitudes exceeding 100 MV/cm ”, *Optics Letters* **33**, 2767 (2008).

- [86] K.-H. Hong, J.-H. Kim, Y. H. Kang, and C. H. Nam, “Time–frequency analysis of chirped femtosecond pulses using wigner distribution function”, *Applied Physics B* **74**, s231 (2002).
- [87] A. PICANO, “Narrowband phonon pumping for the investigation of light-induced superconductivity”, MA thesis (Politecnico di Milano, School of Industrial and Information Engineering, 2018).
- [88] R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbügel, B. A. Richman, and D. J. Kane, “Measuring ultrashort laser pulses in the time-frequency domain using frequency-resolved optical gating”, *Review of Scientific Instruments* **68**, 3277 (1997).
- [89] E. Rowe, B. Yuan, M. Buzzi, G. Jotzu, Y. Zhu, M. Fechner, M. Först, B. Liu, D. Pontiroli, M. Riccò, et al., “Resonant enhancement of photo-induced superconductivity in K_3C_{60} ”, *Nature Physics* **19**, 1821 (2023).
- [90] Y. Zhu, A. Vanderhaegen, Z. Zeng, M. Först, M. Fechner, C. Putzke, P. J. W. Moll, D. Prabhakaran, P. Radaelli, and A. Cavalleri, “Three-phonon mixing as a source of light-induced chirality”, arXiv preprint arXiv:2606.31356 (2026).
- [91] G. Khalsa, N. A. Benedek, and J. Moses, “Ultrafast control of material optical properties via the infrared resonant raman effect”, *Physical Review X* **11**, 021067 (2021).
- [92] L. Dhar, J. A. Rogers, and K. A. Nelson, “Time-resolved vibrational spectroscopy in the impulsive limit”, *Chemical Reviews* **94**, 157 (1994).
- [93] R. Merlin, “Generating coherent thz phonons with light pulses”, *Solid State Communications* **102**, 207 (1997).
- [94] E. A. Mashkovich, K. A. Grishunin, R. M. Dubrovin, A. K. Zvezdin, R. V. Pisarev, and A. V. Kimel, “Terahertz light–driven coupling of antiferromagnetic spins to lattice”, *Science* **374**, 1608 (2021).

- [95] A. M. Weiner, D. Leaird, G. P. Wiederrecht, and K. A. Nelson, “Femtosecond pulse sequences used for optical manipulation of molecular motion”, *Science* **247**, 1317 (1990).
- [96] S. Fahy and R. Merlin, “Reversal of ferroelectric domains by ultrashort optical pulses”, *Physical Review Letters* **73**, 1122 (1994).
- [97] J. Shi, C. Heide, H. Xu, Y. Shen, M. Henstridge, I. Sedwick, A. Mangu, X. Peng, S. Zhang, M. Trigo, et al., “Nonresonant raman control of ferroelectric polarization”, *Advanced Materials* **37**, e10524 (2025).
- [98] O. Stenzel, *Light–matter interaction: a crash course for students of optics, photonics and materials science*, UNITEXT for Physics (Springer International Publishing, 2022).
- [99] W. Denk, J. H. Strickler, and W. W. Webb, “Two-photon laser scanning fluorescence microscopy”, *Science* **248**, 73 (1990).
- [100] M. C. Fischer, J. W. Wilson, F. E. Robles, and W. S. Warren, “Invited review article: pump-probe microscopy”, *Review of Scientific Instruments* **87** (2016).
- [101] P. Agostini and L. F. DiMauro, “The physics of attosecond light pulses”, *Reports on Progress in Physics* **67**, 813 (2004).
- [102] C. Bao, P. Tang, D. Sun, and S. Zhou, “Light-induced emergent phenomena in 2d materials and topological materials”, *Nature Reviews Physics* **4**, 33 (2022).
- [103] A. Subedi, “Light-control of materials via nonlinear phononics”, *Comptes Rendus. Physique* **22**, 161 (2021).
- [104] M. Koch, D. M. Mittleman, J. Ornik, and E. Castro-Camus, “Terahertz time-domain spectroscopy”, *Nature Reviews Methods Primers* **3**, 48 (2023).
- [105] C. Winterfeldt, C. Spielmann, and G. Gerber, “Colloquium: optimal control of high-harmonic generation”, *Reviews of Modern Physics* **80**, 117 (2008).
- [106] M. Chini, K. Zhao, and Z. Chang, “The generation, characterization and applications of broadband isolated attosecond pulses”, *Nature Photonics* **8**, 178 (2014).

- [107] O. Kovalenko, R. Dubrovin, R. Pisarev, A. Kimel, A. Kalashnikova, and R. Mikhaylovskiy, “Nonlinear phononics in rare-earth orthoferrites”, *Physical Review Materials* **10**, 034408 (2026).
- [108] D. M. Juraschek, D. S. Wang, and P. Narang, “Sum-frequency excitation of coherent magnons”, *Physical Review B* **103**, 094407 (2021).
- [109] Z. Zhang, J. Zhang, Z.-J. Liu, N. S. Dahod, W. Paritmongkol, N. Brown, A. Stollmann, W. S. Lee, Y.-C. Chien, Z. Dai, et al., “Discovery of enhanced lattice dynamics in a single-layered hybrid perovskite”, *Science Advances* **9**, eadg4417 (2023).
- [110] B. Ilyas, T. Luo, A. von Hoegen, E. Viñas Boström, Z. Zhang, J. Park, J. Kim, J.-G. Park, K. A. Nelson, A. Rubio, et al., “Terahertz field-induced metastable magnetization near criticality in FePS₃”, *Nature* **636**, 609 (2024).
- [111] B. Ilyas, T. Luo, H. Ning, E. V. Bostrom, A. von Hoegen, J. Park, J. Kim, J.-G. Park, A. Rubio, and N. Gedik, “Coherent terahertz control of metastable magnetization in FePS₃”, *arXiv preprint arXiv:2510.16993* (2025).
- [112] Z. Zhang, F. Y. Gao, Y.-C. Chien, Z.-J. Liu, J. B. Curtis, E. R. Sung, X. Ma, W. Ren, S. Cao, P. Narang, et al., “Terahertz-field-driven magnon upconversion in an antiferromagnet”, *Nature Physics* **20**, 788 (2024).
- [113] M. Kwaaitaal, D. G. Lourens, C. S. Davies, and A. Kirilyuk, “Disentangling thermal birefringence and strain in the all-optical switching of ferroelectric polarization”, *Scientific Reports* **14**, 24956 (2024).
- [114] M. Jazbinsek, U. Puc, A. Abina, and A. Zidansek, “Organic crystals for thz photonics”, *Applied Sciences* **9**, 882 (2019).
- [115] G. Montemezzani, M. Alonzo, V. Coda, M. Jazbinsek, and P. Günter, “Running electric field gratings for detection of coherent radiation”, *Journal of the Optical Society of America B* **32**, 1078 (2015).

- [116] T. Satoh, Y. Toya, S. Yamamoto, T. Shimura, K. Kuroda, Y. Takahashi, M. Yoshimura, Y. Mori, T. Sasaki, and S. Ashihara, “Generation of mid-to far-infrared ultrashort pulses in 4-dimethylamino-n-methyl-4-stilbazolium tosylate crystal”, *Journal of the Optical Society of America B* **27**, 2507 (2010).
- [117] E. Rowe, “Resonant enhancement of light induced superconductivity in K_3C_{60} ”, PhD thesis (Universität Hamburg, 2024).
- [118] U. Puc, T. Bach, P. Günter, M. Zgonik, and M. Jazbinsek, “Ultra-broadband and high-dynamic-range thz time-domain spectroscopy system based on organic crystal emitter and detector in transmission and reflection geometry”, *Advanced Photonics Research* **2**, 2000098 (2021).
- [119] P. J. Moll, “Focused ion beam microstructuring of quantum matter”, *Annual Review of Condensed Matter Physics* **9**, 147 (2018).
- [120] G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set”, *Computational Materials Science* **6**, 15 (1996).
- [121] G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals”, *Physical Review B* **47**, 558 (1993).
- [122] G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”, *Physical Review B* **54**, 11169 (1996).
- [123] A. Togo, “First-principles phonon calculations with phonopy and phono3py”, *Journal of the Physical Society of Japan* **92**, 012001 (2023).
- [124] G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method”, *Physical Review B* **59**, 1758 (1999).
- [125] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple”, *Physical Review Letters* **77**, 3865 (1996).
- [126] X. Wang and Y. Yan, “Ab initio theory of optical activity in α -quartz in the gw-bethe-salpeter-equation framework”, *Physical Review Letters* **136**, 186901 (2026).

- [127] G. Onida, L. Reining, and A. Rubio, “Electronic excitations: density-functional versus many-body green’s-function approaches”, *Reviews of Modern Physics* **74**, 601 (2002).
- [128] M. Rohlfing and S. G. Louie, “Electron-hole excitations and optical spectra from first principles”, *Physical Review B* **62**, 4927 (2000).
- [129] M. S. Hybertsen and S. G. Louie, “Electron correlation in semiconductors and insulators: band gaps and quasiparticle energies”, *Physical Review B* **34**, 5390 (1986).
- [130] L. Hedin, “New method for calculating the one-particle green’s function with application to the electron-gas problem”, *Physical Review* **139**, A796 (1965).
- [131] X. Wang and Y. Yan, “Optical activity of solids from first principles”, *Physical Review B* **107**, 045201 (2023).