Ultrafast frustration breaking and magnetophononic driving of singlet excitations in a quantum magnet

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Ideal magnetic frustration forms the basis for the emergence of exotic quantum spin states that are entirely nonmagnetic. Such singlet spin states are the defining feature of the Shastry-Sutherland model, and of its faithful materials realization in the quantum antiferromagnet SrCu2(BO3)2. To address these states on ultrafast timescales, despite their lack of any microscopic order parameter, we introduce a nonlinear magnetophononic mechanism to alter the quantum spin dynamics by driving multiple optical phonon modes coherently and simultaneously. We apply intense terahertz pulses to create a nonequilibrium modulation of the magnetic interactions that breaks the ideal frustration of SrCu2(BO3)2, such that previously forbidden physics can be driven in a coherent manner. Specifically, this driving populates a purely magnetic excitation, the singlet branch of the two-triplon bound state, by resonance with the difference frequency of two pumped phonons. Our results demonstrate how light-driven phonons can be used for the ultrafast and selective manipulation of interactions in condensed matter, even at frequencies far from those of the pump spectrum, offering valuable additional capabilities for the dynamical control of quantum many-body phenomena.

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I. INTRODUCTION

Using ultrafast lasers to access all the intrinsic interaction timescales of correlated quantum materials opens a new window on fundamental processes in nonequilibrium many-body physics. Coherent light sources developed to combine ultrafast time structure and high intensity at the appropriate terahertz or infrared (IR) frequencies [1,2] have been used in complex condensed matter to enhance superconductivity [3], drive metal-insulator transitions [4], manipulate multiferroic order [5], and “Floquet engineer” the electronic band structure [6]. This type of dynamical driving, by which different and unconventional static and dynamic properties are conferred on a quantum state, has the potential to reveal many previously hidden or unknown phenomena [7,8].

In ultrafast magnetism, the magnetic field of a light pulse can drive precessional spin dynamics and spin waves in ordered antiferromagnets [9,10], while the electric field can modify the magnetic interactions [11]. Strong lattice excitations have been used to melt magnetic order [12] and to induce spin waves through an effective magnetic field [13]. The concept of magnetophononics, defined as the resonant modulation of magnetic (super)exchange interactions by ultrafast coherent lattice displacements, has to date been discussed only in theory [14]. Although phononic effects observed in ordered magnetic materials have been ascribed in part to exchange interactions [15] or fully to crystal-field effects [16], they remain some orders of magnitude slower than the driving phonons. While the ultrafast manipulation of magnetically ordered phases is developing towards applications in spintronics [17,18], the situation in quantum magnets that lack any magnetic order remains largely unexplored.

In this work we begin the quest to control the properties of nonordered quantum magnetic materials using ultrafast coherent light pulses. The paradigm of ideal frustration is the fundamental ingredient in all of the complex quantum many-body states in magnetism, most of which emerge from rather simple spin Hamiltonians [19]. Its most basic form is geometrical frustration, which has been realized in a wide range of materials hosting antiferromagnetically interacting spins in the triangle-based motifs of the kagome, pyrochlore, Shastry-Sutherland, and other lattices. More complex forms of ideal frustration have been produced using magnetic interactions that are anisotropic in spin or real space, examples including spin ices, SU(N) magnets, and (proximate) Kitaev systems [20]. However, the characteristic properties of the resulting
SrCu$_2$(BO$_3$)$_2$ to display an anomalous spectrum of spin excitations undetectable by the conventional probes of experimental low-lying magnetic excitation (dark blue). The fast component to reveal coherent oscillations associated with the delay time, $t$

the electric field and polarization rotation of the probe as functions of pulse (red) measures the polarization changes. 

(b), (c) Terahertz dipole-active lattice vibrations. A femtosecond near-IR (NIR) probe terahertz pulse (blue) with electric field polarized linearly along the axis of a SrCu$_2$(BO$_3$)$_2$ crystal provides coherent driving of dipole-active lattice vibrations. A femtosecond near-IR (NIR) probe pulse (red) measures the polarization changes. [(b), (c)] Terahertz electric field and polarization rotation of the probe as functions of the delay time, $t$. Inset: Terahertz-driven dynamics after filtering of the fast component to reveal coherent oscillations associated with the low-lying magnetic excitation (dark blue).

ground and excited states, which can include both gapped and gapless quantum spin liquids [21], fractional quasiparticles, topological order, and long-ranged entanglement [20], are often undetectable by the conventional probes of experimental condensed matter. This makes them ideal candidates for ultrafast probing.

For our study (Fig. 1) we choose SrCu$_2$(BO$_3$)$_2$, an archetypal quantum magnetic material whose physics is dominated by local quantum mechanical singlet states [22]. The singlet encapsulates the essence of quantum magnetism, where the fluctuating spin variables combine into both local and global states of especially low energy that have no external magnetic properties [23]. The ideally frustrated geometry of SrCu$_2$(BO$_3$)$_2$ [Fig. 1(a)] realizes a spin model formulated by Shastry and Sutherland specifically for its exact dimer-singlet ground state [24], and if an applied pressure is used to alter the interaction parameters then it undergoes a first-order quantum phase transition (QPT) to a four-site “plaquette” singlet state [25–28]. This ideal magnetic frustration also causes SrCu$_2$(BO$_3$)$_2$ to display an anomalous spectrum of spin excitations and complex phase transitions both in an applied magnetic field [29–31] and as a function of temperature [28].

For the goal of ultrafast modulation of magnetic properties in nonordered materials such as SrCu$_2$(BO$_3$)$_2$, the magnetophononic mechanism is an obvious candidate. Experiments applying static pressure to quantum magnets have created novel ground and excited states [26,32] and have controlled QPTs in both localized [33] and itinerant magnetic systems [34], demonstrating not only the sensitivity of the magnetic interactions to the atomic positions but also the potential for qualitatively new dynamical phenomena. In our study it is important to stress the distinction between magnetophononics, which is a resonant modulation of the magnetic interactions by harmonic phonons [14], and “nonlinear phononics” [35], which exploits the anharmonic potential of large-amplitude phonons. The latter offers a route for combining phonons at their sum and difference frequencies, and the lattice distortions it allows have been applied in ordered magnets to alter their static properties [13]. The former relies on the complex dependence of the magnetic interactions on the periodically varying lattice coordinates to effect a dynamical coupling to the spin sector. We will observe both mechanisms at work in our experiments, but only the magnetophononic mechanism drives the spin sector, and thus our focus lies here.

Nevertheless, modulating an interaction, $J$, at some available phonon frequency, $o_0$, does not constitute control of dynamical properties: a priori there is no match between the energy scales of the dominant IR-active phonon modes and of the elementary magnetic excitations in any material, and we will see that SrCu$_2$(BO$_3$)$_2$ is a case in point. To achieve such frequency matching, we extend magnetophononics to the nonlinear regime, where sums and differences of the available phonon frequencies span a wide energy range, but extremely intense electric fields are required. By using coherent terahertz pulses to drive IR-active phonons in SrCu$_2$(BO$_3$)$_2$ (Fig. 1), we demonstrate experimentally how the leading difference frequency creates a nonequilibrium occupation of the lowest excited singlet state. We establish the theoretical framework for the origin of this phenomenon, in the breaking of ideal magnetic frustration within the driven lattice structure, which we verify by density functional theory (DFT) calculations.

The structure of this article is as follows. In Sec. II we review the properties of SrCu$_2$(BO$_3$)$_2$. In Sec. III we present the results of our ultrafast spectroscopic investigations. Section IV contains a qualitative and quantitative account of the nonlinear magnetophononic phenomena we observe. In Sec. V we discuss the consequences of our findings for the selective static and dynamical control of materials properties both within and beyond quantum magnetism.

II. SHASTRY-SUTHERLAND MODEL AND SrCu$_2$(BO$_3$)$_2$

The Shastry-Sutherland model, for $S = 1/2$ spins with Heisenberg interactions on the two-dimensional orthogonal-dimer network shown in Fig. 2(a) [24], is one of the most intriguing in quantum magnetism. The exact and entirely non-magnetic ground state of singlet quantum dimers is found when the ratio of interdimer ($J^\prime$) to intradimer ($J$) interactions satisfies $\alpha = J^\prime/J \leq 0.675$, above which the QPT occurs to the plaquette-singlet state [25]. It is quite remarkable that this simple model is realized so faithfully in the compound SrCu$_2$(BO$_3$)$_2$ [Fig. 1(a)] [22], with $J$ deter-

FIG. 1. Coherent lattice control in the time domain. (a) An intense terahertz pulse (blue) with electric field polarized linearly along the $\alpha'$ axis of a SrCu$_2$(BO$_3$)$_2$ crystal provides coherent driving of dipole-active lattice vibrations. A femtosecond near-IR (NIR) probe pulse (red) measures the polarization changes. [(b), (c)] Terahertz electric field and polarization rotation of the probe as functions of the delay time, $t$. Inset: Terahertz-driven dynamics after filtering of the fast component to reveal coherent oscillations associated with the low-lying magnetic excitation (dark blue).


triplon bound states (TBSs, blue shaded regions). (b) Low-energy spectrum of SrCu$_2$ (BO$_3$)$_2$ at orthogonal dimers. The localized spin excitations above the singlet ground state (red dimers) are individual triplons (blue dimers) and two-triplon bound states (TBSs, blue shaded regions). (b) Low-energy spectrum of SrCu$_2$ (BO$_3$)$_2$ at $k = 0$. In the spin sector, the singlet two-triplon bound state (STTBS) lies close to the one-triplon excitation, the triplet two-triplon bound state (TTTBS) has a smaller binding energy, and the quintet two-triplon bound state (QTTBS) lies close to the threshold for creating two isolated triplons (energies of the lowest TTTBS and QTTBS taken from Ref. [36]). In the lattice sector, we show the frequencies of the two phonons excited most strongly in our experiment, $\omega_a = 3.80$ THz and $\omega_b = 4.60$ THz. The light blue line and gray shading represent for comparison the amplitude of the pump spectrum [Fig. 3(a)]. [(c), (d)] Lattice-displacement eigenvectors for the phonon modes at $\omega_a$ and $\omega_b$; because both phonons are $E$ symmetric, we show one of the two degenerate modes in each case. $J$ and $J'$ depend on the bond lengths and angles in the superexchange paths involving the Cu, O, and B atoms.

The magnetic excitation spectrum of SrCu$_2$(BO$_3$)$_2$, depicted for wave vector $k = 0$ in Fig. 2(b), contains as its lowest mode the “triplon” (singlet-triplet) excitation at $\Delta = 2.9$ meV ($\approx 0.71$ THz), whose dispersion is almost flat in $k$ [37] as a consequence of the ideal frustration. The lattice geometry is also responsible for an anomalously strong binding energy for triplon pairs, with the result that the singlet two-triplon bound state (STTBS), the $S = 0$ branch of this multiplet, appears just above the one-triplon mode, at 3.6 meV ($\omega_{\text{TBS}} = 0.87$ THz). At higher energies, additional discrete and continuum excitations include the triplet ($S = 1$, TTTBS) and quintet ($S = 2$, QTTBS) branches of this bound state.

These modes have been studied by a combination of neutron scattering [38], which targets the triplon and TTTBS, and Raman [39,40], IR [41], and electron spin resonance (ESR) spectroscopies [36], which observe the spectrum at $k = 0$. To date, a detailed explanation for the phonon-assisted coupling of light to the spin excitations observed by Raman and IR remains elusive due to the inherently incoherent nature of these experiments. The interaction ratio in SrCu$_2$(BO$_3$)$_2$, $\alpha = 0.63$, lies close to the QPT of the Shastry-Sutherland model, allowing this transition to be induced under pressure [26]. Recent attention has focused on how the magnetic interactions depend on the geometry of the dimer units [42–44], making SrCu$_2$(BO$_3$)$_2$ a fascinating and timely candidate for exploring ideally frustrated quantum magnetism on ultrafast timescales.

III. ULTRAFAST EXPERIMENT

We perform terahertz-pump, optical-probe spectroscopy using the apparatus of Ref. [45], whose technical specifications are detailed in Appendix A. Our experiments use a single-crystal sample of SrCu$_2$(BO$_3$)$_2$ maintained at 3.5 K ($k_B T \ll \Delta$), a temperature where the ground state is close to the pure singlet state. As represented in Fig. 1(a), intense light pulses [Fig. 1(b)] with spectral content between 2 and 7 THz [Fig. 2(b)] drive the resonant excitation of dipole-active phonon modes [46]. To estimate the external terahertz electric-field strength of the pump, we measured the energy per pulse, beam waist, and pulse duration, also reported in Appendix A, to obtain the value $E_{\text{THz}} = 3.2$ MV cm$^{-1}$, which is comparable to other modern high-intensity sources [47,48]. To probe the driven lattice and spin dynamics, we measured the ultrafast polarization rotation [13], shown in Fig. 1(c), caused by the associated optical birefringence and Faraday effects. These are imprinted on a copropagating NIR pulse (50 fs, wavelength 800 nm) with a variable delay time, $t$, and an analysis of the complete time-frequency response function is presented in Appendix B.

As the inset of Fig. 1(c) makes clear, the picosecond pump pulse creates dynamical oscillations that persist for many tens of picoseconds. We take this observation as an opportunity to establish our use of terminology. It is clear that all of the physical phenomena revealed by ultrafast pulsed driving are transient, in the sense that the stimulus is removed after a very short time (here 1 ps) and the system relaxes back to equilibrium. This relaxation is governed by the characteristic
FIG. 3. Terahertz field-driven lattice and spin dynamics in the frequency domain. (a) Spectral amplitude (blue) of the data of Fig. 1(c) computed for 3.5 ⩽ t ⩽ 20 ps. The primary peaks are (i) $E$-symmetric phonons at 3.80 and 4.60 THz, (ii) a $B_1$-symmetric Raman phonon at 11.6 THz, and (iii) the TBS excitation at $\omega_{\text{TBS}} = 0.87$ THz. The light blue line and gray shading show the spectral amplitude of the driving electric field [Fig. 1(b)]. (b) Spectral amplitude measured at 8 K, where the TBS is absent and the driven dynamics reveal no coherent oscillations at $\omega_{\text{TBS}}$ (inset). (c) Comparison of low-frequency spectra at 3.5 and 8 K. The black dashed line marks the one-triplon gap, $\Delta = 2.9$ meV (0.71 THz), and the red dot $\omega_{\text{TBS}}$ from Raman spectroscopy [39,40]. (d) Temperature dependence of the TBS, normalized to the peak height.

decay times of the multiple eigenmodes of the system, all of which are in principle excited by the wide range of frequencies present in the short pulse. It is during this time that we apply the term “nonequilibrium,” to refer to the situation where the system is in an out-of-equilibrium state, with a nonequilibrium (nonthermal) occupation of the states in the spectrum and the possibility of changes to the eigenergies and eigenstates of this spectrum (i.e., away from their equilibrium properties). In the following we will show that Fig. 1(c) presents a particularly clear separation of timescales, by which the phonon modes driven by the electric field of the terahertz pulse have largely decayed after 20 ps, but the slow oscillation they drove, which is the leading excitation in the magnetic sector, lives far longer. This consequence of the very weak coupling of spins to their environment provides an excellent illustration of our rationale for studying quantum magnetism.

Returning to our experimental observations, in the frequency domain we find coherently excited phonons close to the peak of the pump spectrum [Fig. 3(a)], primarily two of the $E$-symmetric modes measured by IR spectroscopy [46], centered at $\omega_a = 3.80$ and $\omega_b = 4.60$ THz. As noted above, these phonon frequencies lie far above the primary features in the magnetic spectrum. Nonetheless, we observe a striking response precisely at $\omega_{\text{TBS}} = 0.87$ THz [Fig. 3(b)], even though the spectral content of the pump is negligible in this frequency range. In the same way, the feature centered at 11.6 THz lies much higher than the spectral content of the pump, and the appearance of this Raman-active $B_1$ phonon mode in the measured response indicates that nonlinear phonon mixing is allowing sum-frequency excitation processes. In fact this feature constitutes one of the clearest examples of a sum-frequency phonon excitation yet observed, and thus we analyze it in detail in Appendix C, but from the standpoint of magnetophononics it serves only as an indicator of the mechanism for the phenomena we investigate.

Henceforth we refer to the STTBS, whose nonmagnetic ($S = 0$) character makes it the only low-energy mode one may expect to excite strongly with phonons, simply as the TBS. To identify the excitation at 0.87 THz as the TBS, we undertook a number of tests. First we repeated the experiment at 8 K [Figs. 3(b) and 3(c)], where thermal fluctuations cause the triplons to lose their character [49]. While the spectral features of the lattice remain almost unchanged, the magnetic fingerprint of terahertz driving has disappeared. As Fig. 3(d) makes clear, the measured amplitude shows rapid quenching above 5 K, exactly as observed for the TBS in Ref. [39], where this behavior was attributed to strong scattering from thermally excited triplets. The loss of triplon spectral weight at a temperature so anomalously low in comparison with the 34 K gap [Fig. 2(d)] was explained only recently by the massive proliferation of bound and scattering states of two triplons as their energy increases [50], and the exact coincidence of the triplon [49] and TBS decay functions indicates the origin of the behavior we observe in Fig. 3(d) [39]. The reduced lifetime of the $B_1$ phonon in Fig. 3(b) also provides evidence of damping processes due to spin-lattice coupling.

To understand the mechanism driving a purely magnetic excitation, the fact that the spectral content of the pump
contains negligible intensity below 2 THz excludes a direct coupling of light to the TBS, which in any case is not IR active [41]. To probe the indirect origin of the observed spin dynamics, we measure the mode amplitudes as functions of the terahertz electric-field strength. These amplitudes and their uncertainties are extracted from Gaussian fitting as described in Appendix D. The IR phonons display the linear dependence of phonon amplitudes and (b) quadratic dependence of the TBS amplitude on the electric-field strength. (c) Four different pump spectra obtained by filtering of the terahertz beam and labeled by their peak field values in the time domain; dashed lines mark the centroid of each spectral envelope. (d) TBS mode amplitude (colored points), normalized to the square of the peak field, for the four different values of the terahertz pump-frequency centroid in panel (c). Bars mark the noise floor of the extracted signal in each case.

IV. THEORY: FRUSTRATION BREAKING

A. Analysis

We now establish the physical framework for the nonlinear magnetophononic phenomenon we have created. Qualitatively, the lattice displacements due to any phonon excitation alter the instantaneous magnetic interactions [Fig. 5(a)]. To analyze this situation we express the Hamiltonian of the driven system as

\[ H = H_0 + H_H + V_{ph} + H_{ph-Em} + H_D, \]  

where \( H_0 \) is the Hamiltonian of the undriven system, \( H_H \) represents the Hamiltonian of the pump field, \( V_{ph} \) is the interaction of the pump field with the lattice, \( H_{ph-Em} \) describes the interaction of the phonons with the electronic medium, and \( H_D \) is the interaction of the magnetic moments with the lattice. This form of the Hamiltonian is a generalization of the work of others in which the contributions of the phonons and the electronic medium are added in a perturbative manner. The detailed form of each term will depend on the specific system under consideration.
where $H_0$ is spin independent and

$$H_I = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J' \sum_{\langle \langle ij \rangle \rangle} \vec{S}_i \cdot \vec{S}_j$$  \hspace{1cm} (2)$$

is the Shastry-Sutherland model at equilibrium. $\vec{S}_i$ is a spin-1/2 operator located on the Cu$^{2+}$ ion at site $i$, $J$ and $J'$ are the magnetic interactions depicted in Fig. 2(a), and $\langle \langle ij \rangle \rangle$ and $\langle \langle ij \rangle \rangle$ denote respectively pairs of sites on intra- and interdimer bonds. $V_{ph}$ is the phonon potential and $H_{ph-Em} = \sum_m \mu_m q_m E_{THz}$, the dipole coupling between the lattice and the terahertz light, is the term driving the excitation of IR-active phonon modes. The action of the coherent lattice deformation due to all of these phonon modes, $q_i = \sum_m q_m$, in modulating the magnetic interaction parameters causes additional coupled spin-phonon terms to enter the Hamiltonian, which we collect in $H_0$. To separate the phonon modulation terms in $H_I$, it is convenient to perform a Taylor expansion of the magnetic interactions, $J$ and $J'$, in powers of the simultaneously driven coherent IR phonon coordinates, which we denote as $q_m, q_n, \ldots$. Denoting an arbitrary interaction term as $\tilde{J}$, we obtain

$$\tilde{J}(q_m, q_n, \ldots) = \tilde{J}(0) + \frac{\partial \tilde{J}}{\partial q_m} |_{q_m=0} q_m + \frac{\partial^2 \tilde{J}}{\partial q_m \partial q_n} |_{q_m, q_n=0} q_m q_n + \ldots$$  \hspace{1cm} (3)$$

where the first term is part of $H_I$ and the higher terms make clear the direct dependence of the additional contributions on the oscillating phonon coordinates.

Both the key features of our experiment become clear immediately in a minimal model with only two harmonic IR phonons, i.e., $q_i = q_a + q_b$, where $q_a$ and $q_b$ are vectors of normal-mode coordinates with cosinusoidal time structures at respective frequencies $\omega_a$ and $\omega_b$. The $q_i^2$ terms appearing in the second line of Eq. (3) lead to spectral components at frequencies $2\omega_a, \omega_a + \omega_b$, $2\omega_b$, 0, and $\omega_a - \omega_b$. These quadratic terms provide the leading nonlinear mechanism that allows a very wide range of spin excitation energies to be
addressed using the sum and difference frequencies of driven IR phonons, whose frequency range may be more restricted.

The second key feature is that the unconventional physics of the Shastry-Sutherland model, and by extension of SrCu₂(BO₃)₂ at equilibrium, relies on the ideal frustration of the spin correlations between dimers. The term \( S_i \cdot S_j \) acting on a single dimer is an eigennonoperator and when acting between dimers it is exactly canceled by a second \( S_i \cdot S_j \) term with equal size (\( J' \)) and effectively opposite sign [Fig. 2(a)]. However, the excited phonons driving the lattice out of equilibrium cause frustration breaking in the magnetic sector, in the form of a finite interdimer coupling, \( \Delta J_{12} = J'_1(q_m, q_n, \ldots) - J'_2(q_m, q_n, \ldots) \) (and similarly for \( \Delta J_{34}, \Delta J_{56}, \) and \( \Delta J_{78} \)), that connects nearest-neighbor dimers [Fig. 5(a)]. This has the immediate effect of allowing two qualitatively new types of physical process that are forbidden at equilibrium.

To make these most transparent, we reexpress the bond-operator description may be found in Ref. [59]. Treating the singlets as a scalar term gives conventional leading-order triplet processes of the form

\[
H_D = \sum_i \left[ \Delta J_{12} \left( t_{1,i}^{+} t_{2,i+1}^{+} + t_{1,i} t_{2,i+1} \right) + \Delta J_{34} \left( t_{3,i}^{+} t_{4,i+1}^{+} + t_{3,i} t_{4,i+1} \right) + \Delta J_{56} \left( t_{5,i}^{+} t_{6,i+1}^{+} + t_{5,i} t_{6,i+1} \right) + \Delta J_{78} \left( t_{7,i}^{+} t_{8,i+1}^{+} + t_{7,i} t_{8,i+1} \right) \right] + \text{H.c.,}
\]

where the full set of eight inequivalent \( J' \) bonds is shown in Fig. 12 in Appendix G. This may be contrasted with the explicit treatment for SrCu₂(BO₃)₂ at equilibrium in Ref. [38], where all of these bilinear triplet terms vanish. The first term in each bracket describes the propagation of existing triplon excitations between dimers, relieving their strict localization, although the high-frequency oscillation of \( \Delta J' \) does not allow any quasistatic changes of the flat triplon bands.

The second term in Eq. (4) describes two-triplon creation on neighboring dimer pairs, i.e., the direct excitation of the TBS from the singlet quantum ground state (\( |\psi\rangle \)). While the triplon pairs are created initially on adjacent dimers, on the timescale of the spin system they will optimize their relative localization, which depend on the effective charges (\( Z_{\text{eff}} \)), the transmission coefficients (\( \beta_m \)), and the reduced masses of the phonon modes, which we deduce from the maximum displacements \( \delta_u = 0.04 \text{ Å} \), \( \delta_b = 0.17 \text{ Å} \) calculated following Appendix A. From Eq. (5) we compute as a function of time the net atomic displacement due to the two leading phonon modes, \( q_d = q_a + q_b \), obtaining the result shown in Fig. 5(c).

B. Lattice dynamics and density functional theory

We perform two types of quantitative calculation within this framework. To model the nonlinear effects of the driven phonons, we follow Refs. [35,60] by considering \( H_D(q_m, q_n) \) as a dynamic perturbation through the coupling term \( H_{\text{em} \rightarrow \text{ph}} \) in Eq. (1). In our experiments (Sec. III), two different IR-active phonon modes show the strongest driving. Labeling these by \( a \) and \( b \), their equations of motion are

\[
\ddot{q}_a + \gamma_a q_a + \omega_a^2 q_a = -B_a E_{\text{THz}}(t),
\]

\[
\ddot{q}_b + \gamma_b q_b + \omega_b^2 q_b = -B_b E_{\text{THz}}(t),
\]

where \( \omega_a = 3.80 \text{ THz} \) and \( \omega_b = 4.60 \text{ THz} \) are the experimental phonon frequencies, \( \gamma_a = 0.02 \text{ THz} \), \( \gamma_b = 0.03 \text{ THz} \) are their respective damping rates (Appendix B), and \( E_{\text{THz}} \) is the external terahertz driving field taken from experiment [Fig. 1(b)]. \( B_b \) and \( B_b \) are the dipolar coupling constants, which depend on the effective charges (\( Z_{\text{eff}} \)), the transmission coefficients (\( \beta_m \)), and the reduced masses of the phonon modes, which we deduce from the maximum displacements \( \delta_u = 0.03 \text{ Å} \), \( \delta_b = 0.17 \text{ Å} \) calculated following Appendix A. From Eq. (5) we compute as a function of time the net atomic displacement due to the two leading phonon modes, \( q_i = q_a + q_b \), obtaining the result shown in Fig. 5(c).

In the initial step of our calculations we used this procedure to refine \( U \), deducing that \( U = 11.4 \text{ eV} \) yields the magnetic interactions \( J = 7.24 \text{ meV} \) (84.0 K) and \( J' = 4.28 \text{ meV} \) (49.7 K), in good agreement with experimental findings [38] and giving a coupling ratio \( \alpha = 0.592 \) for the equilibrium lattice structure. We then extended these methods to estimate the phonon-induced modulation of the magnetic interaction parameters by computing the temporal evolution of the frustration-breaking terms, \( \Delta J'(t) \). For this we evaluated the magnetic interactions in a dense sequence of different “frozen phonon” configurations of the lattice. Each atom in the SrCu₂(BO₃)₂ structure was displaced by \( q_{im} \), where \( q_{im} \) is the instantaneous displacement amplitude of excited phonon mode \( m \), \( \bar{u}_{im} \) denotes the set of normal-mode vectors taken from Ref. [46], and we restricted our calculations to \( m = a, b \) with \( \omega_a = 3.80 \text{ and } \omega_b = 4.60 \text{ THz} \). The displacements of the atoms from equilibrium reduce the lattice symmetry, as represented in Fig. 5(a), and hence require more complex calculations of more interaction parameters in a larger unit cell, as detailed in Appendix G.

In Fig. 5(b) we show the four different interdimer interaction parameters (\( J'_1, J'_2, J'_6, J'_8 \)) neighboring each vertical spin dimer as functions of the largest scalar phonon displacement amplitude, \( q_{im} \), whose maximum value is \( \delta_b \). We stress that the parameters (\( J'_5, J'_6, J'_7, J'_8 \)), which we do not show, are different
from \((J'_1, J'_2, J'_3, J'_4)\) for these specific members of the \(E\)-symmetric phonon doublets, but are interchanged with them for the other member of the doublet. Figure 5(b) shows that, while the phonon-induced variations in \(J_1\) and \(J_2\) are almost quadratic, the interactions \(J'_{1...4}\) all have significant linear components. These result in large values of the frustration-breaking difference interactions, \(\Delta J'\), well in excess of 10 K (i.e., reaching 20–30 % of \(J'\) by this estimate).

To mimic our experiment, we superposed the phonon normal modes to obtain \(q_t = q_a + q_b\) [Fig. 5(c)] at 285 time points in steps of 0.035 ps, in order to span 10 ps. The corresponding frustration-breaking interaction parameters, \(\Delta J'_{12}\) and \(\Delta J'_{34}\) [Fig. 5(d)], show a strong and in-phase oscillation controlled largely by \(q_b\). In the frequency domain, this density of time steps reproduces well-resolved peaks at both the low frequency of the TBS peak and the intermediate frequency of the driven phonons. Even at the harmonic level we model, the IR phonons excited by the terahertz pump [Fig. 5(e)] create a nonlinear modulation of the interaction parameters [through Eq. (3)] with a rich spectrum [Fig. 5(f)]. This spectrum includes significant weight at the frequency \(\omega_0 - \omega_a\), whose resonance with the TBS [inset, Fig. 5(e)] ensures large values of the matrix element for two-triplon creation, \(\langle TBS | \Delta J'(\omega \hat{J}_1 \hat{J}_2, j) \rangle\), and hence the strong nonequilibrium population of this purely magnetic excitation that we report in Figs. 3(a) and 3(c).

V. DISCUSSION

Ideal frustration of magnetic interactions is the core attribute that leads quantum spin systems to form entirely unconventional and exotic phases, although some of the most fundamentally novel properties (such as fractional excitations, topological order, and entanglement) often remain largely hidden from conventional experimental probes. In this context, a static breaking of ideal frustration is often regarded as trivial, merely removing the properties that make the system special; in \(\text{SrCu}_2(\text{BO}_3)_2\), a static \(\Delta J'\) would restore triplon propagation, destabilize the bound states, and favor the nearby phase of long-ranged antiferromagnetic order [25]. However, the dynamical frustration breaking we effect means that the static and equilibrium state of ideal frustration is retained, excluding most of these more trivial hallmarks and thereby offering an alternative route to the selective and controlled investigation of certain hidden properties.

While much has been made of “controlling quantum systems” on ultrafast timescales, we stress that ultrafast processes in magnetic materials have to date been restricted in large part to destroying, modulating the magnitude, or switching the direction of an ordered moment [10,12,16]. Here we have solved two further fundamental problems on the route to ultrafast dynamical control. The first is the coupling of light to a quantum magnet with no magnetic order. As a lattice-based route, magnetophotonics achieves such coupling both universally, meaning for all forms of interaction in condensed matter—but “hidden” the resulting unconventional order may be, or how “forbidden” a process may be, in experiments performed at equilibrium—and in an intrinsically resonant manner. The second is the frequency-matching problem by which the light-driven pump (the phonons) can be tuned to the target (magnetic) excitations, and for this purpose our second-order nonlinear variant of magnetophotonics allows a universal extension of lattice control to very low (phonon difference) and high (phonon sum) frequencies.

At the conceptual level, by periodic driving of a quantum system one may expect to achieve state control, population control, or spectral control, all of which are covered in the term “Floquet engineering” [6]. In the true Floquet regime, where the frequency of the light far exceeds the system frequencies, driving causes no significant modification of the basis states (very little energy is transferred), but induces phase-coherent superpositions of these states that can have dramatically different properties. When the light frequency resonates with a system transition, the high available laser intensities allow one to achieve strongly nonequilibrium state populations, raising the prospect of driving a nonequilibrium Bose condensation in suitable systems. While these processes may alter the spectrum of the system as a secondary effect, a direct modulation of the system parameters can be achieved in one of two ways. A simple situation would be the opposite limit to \(\text{SrCu}_2(\text{BO}_3)_2\), where slow phonons in a material with high magnetic energies give linear control of the parameters. However, magnetophonic driving at the resonant frequencies of the spin system offers the clearest potential for unconventional dynamical phenomena, including qualitatively different types of hybrid spin-phonon state, engineering of the spin and phonon energies, and strong mutual feedback effects on state populations [64].

In \(\text{SrCu}_2(\text{BO}_3)_2\) we have achieved control in the form of creating a significant nonequilibrium population of a target excited state. However, this population was not sufficient, at our available electric fields, to cause a detectable modification of the TBS energy. In the limit exemplified by \(\text{SrCu}_2(\text{BO}_3)_2\), where the phonons are much faster than the spin excitations and thus resonant driving is caused by a rather weak second-harmonic component, we have not yet been able to alter the TBS or triplon energies directly. However, considering the many different phonon normal modes and frequencies available in \(\text{SrCu}_2(\text{BO}_3)_2\), it is clear that such dynamical driving presents a wide variety of highly specific control channels for different interactions in the atomic structure, in stark contrast to the universal alterations effected by conventional static control channels, such as an applied pressure or magnetic field. Here we recall also that the pulsed nature of the experimental driving, while essential for heat control in the sample, implies that all of the phenomena observed will be long-lived transients constituting an approximation to the true nonequilibrium states of the driven system.

As a more general route to nonresonant interaction control, Fig. 5(g) indicates for the example of a driven \(q_b\) phonon how the method of driving IR-active phonons in the harmonic regime can cause a strong increase in the instantaneous ratio of the spatially averaged interactions, \(\alpha = J'/J\). While recent experimental [43] and theoretical [44] studies have highlighted the role of the “pantograph” phonon [42] in modulating \(\alpha\), this \(A_1\)-symmetric mode, found at 6.1 THz in Raman measurements, cannot be excited coherently in the same way as IR phonons. Because the phonons are so much faster than the magnetic interactions, the important quantity is the time average of \(\alpha(q_b)\) in Fig. 5(g), whose rise with \(q_b\) indicates
the prospect, at still higher electric fields, of a driven, dynamical approach to the static QPT into the plaquette phase of SrCu$_2$(BO$_3$)$_2$, i.e., with no frustration-breaking effects on long timescales. Although it represents the effect of only a single phonon, Fig. 5(g) suggests that the dynamical approach to controlling $\alpha$ is clearly comparable in range with hydrostatic pressure techniques [26,31]; indeed our current studies, which were not optimized for this purpose, indicate a high potential for achieving significantly stronger static effects by further increasing the terahertz field strength and by tailoring of the excited phonon modes.

Beyond the primary superexchange interactions ($J$ and $J'$), further terms in the modulated spin Hamiltonian can also produce spin excitations that are normally weak or forbidden. SrCu$_2$(BO$_3$)$_2$ has Dzyaloshinskii-Moriya (DM) interactions [36], which are small (3% of $J$), but are important in applied magnetic fields, including to create topological states [38]. The driving of symmetry-breaking IR phonons also creates dynamical antisymmetric spin interactions directly analogous to the modulation of $J$ and $J'$. In SrCu$_2$(BO$_3$)$_2$, our experiments demonstrate no discernible role for driven DM interactions, because the one-triplon excitation process ($\Delta S_{\text{tot}} = 1$) at 0.71 THz should be excited by the same difference-frequency envelope as the TBS, but clearly no feature is visible above the detection threshold at this frequency in Fig. 3(c). More generally, however, one may use selective nonlinear IR phonon driving to manipulate both the symmetric and antisymmetric magnetic interactions in systems such as skyrmion lattices and chiral spin liquids, where both couplings play an essential role.

In summary, we have demonstrated coherent light-driven spin dynamics in a purely quantum magnetic system. By the resonant excitation of phonons and their nonlinear mixing to span a very wide (sum and difference) frequency range, our experimental protocol meets the intrinsic challenge of spin-phonon frequency matching. We have applied it to SrCu$_2$(BO$_3$)$_2$ and achieved the selective excitation of the singlet branch of the two-triplon bound state without exciting individual triplons. We have shown theoretically how this process occurs, once the driven phonons relieve the ideal magnetic frustration, and have performed DFT calculations to estimate the magnitude of the interaction modulation. Our results open an additional time dimension for exploring quantum magnetic phenomena that to date have been probed only by quasistatic stimuli, and because it uses the lattice as its medium our method is applicable without restriction to all the exotic spin states available in quantum magnetic materials. In view of ongoing technical progress at all the frontiers of magnetic frustration, and have performed DFT calculations in Fig. 6(a) [45]. The output of a 20-mJ, 55-fs, 800-nm Ti:sapphire laser was used to drive an optical parametric amplifier (OPA), which provides ultrashort, multi-millijoule pulses [65]. Single-cycle terahertz pulses were generated by optical rectification, using a crystal of DAST (4-N,N-dimethylamino-4’-N-methyl-stilbazolium tosylate, from Rainbow Photonics), of the OPA signal at 1.5 $\mu$m. The OPA pulse energy of 3.2 mJ gave a NIR pump fluence at the crystal surface of approximately 5 mJ cm$^{-2}$. Three low-pass filters, two with a 20-THz cutoff frequency and one with 10 THz, were used after the terahertz generation step to block the residual OPA beam, and gave an extinction ratio for the pump in excess of 105. For the pump pulses, an additional high-pass filter with a cutoff of 4.2 THz was used to drive the primary IR-active phonons while ensuring a negligible spectral weight at the frequency of the leading magnetic modes [Fig. 3(a)]. To select the four different pump pulses shown in Fig. 4(c), we used respectively a 2-THz low-pass filter, a 3-THz bandpass filter, a 4.2-THz high-pass filter coupled with a 6-THz low-pass filter, and a 6-THz bandpass filter.

For the measurement of properties dependent on the pump strength, the terahertz electric field was tuned by three wire-grid polarizers. Peak electric fields were reached by tight focusing of the terahertz beam using three parabolic mirrors [65]. To estimate the electric-field strength of the pump pulses shown in Fig. 1, we apply the formula [66]

$$E_{\text{TBS}} = \sqrt{\frac{z_0E_p4\sqrt{\ln 2}}{\pi \sqrt{\pi/2} w^2 \tau_{\text{FWHM}}}},$$

where $z_0$ is the vacuum impedance and we measured (i) the terahertz energy per pulse, $E_p = 0.8 \mu$J, using a calibrated terahertz energy meter (Gentec THZ12D3S-VP-D0); (ii) the beam waist, $w = 92 \mu$m, obtained by a Gaussian fit of the beam profile [Fig. 6(b)], which was measured with a microbolometric terahertz camera (NEC IRV-T0830); (iii) the pulse duration, $\tau_{\text{FWHM}} = 0.21$ ps, obtained from the FWHM

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**Appendix A: Experiment**

Single crystals of SrCu$_2$(BO$_3$)$_2$ were grown using an optical floating-zone furnace (FZ-T-10000-H-IV-VP-PC, Crystal System Corp., Japan) with four 300-W halogen lamps as the heat source. The growth rate was 0.25 mm/h, with both feeding and seeding rods being rotated at approximately 15 rpm in opposite directions to ensure the homogeneity of the liquid: an argon atmosphere with 20% oxygen was maintained at 5 bars during growth. The high structural quality and orientation of the resulting single crystal were confirmed by x-ray diffraction and the high magnetic quality (absence of impurities) by susceptibility measurements. The crystal was cut using a diamond wire saw and cleaved along the $ab'$ plane to give a sample of dimensions $1 \times 3 \times 0.24$ mm$^3$ that was used for the experiments.

The terahertz-pump and optical-probe setup is shown in Fig. 6(a) [45]. The output of a 20-mJ, 55-fs, 800-nm Ti:sapphire laser was used to drive an optical parametric amplifier (OPA), which provides ultrashort, multi-millijoule pulses [65]. Single-cycle terahertz pulses were generated by optical rectification, using a crystal of DAST (4-N,N-dimethylamino-4’-N-methyl-stilbazolium tosylate, from Rainbow Photonics), of the OPA signal at 1.5 $\mu$m. The OPA pulse energy of 3.2 mJ gave a NIR pump fluence at the crystal surface of approximately 5 mJ cm$^{-2}$. Three low-pass filters, two with a 20-THz cutoff frequency and one with 10 THz, were used after the terahertz generation step to block the residual OPA beam, and gave an extinction ratio for the pump in excess of 105. For the pump pulses, an additional high-pass filter with a cutoff of 4.2 THz was used to drive the primary IR-active phonons while ensuring a negligible spectral weight at the frequency of the leading magnetic modes [Fig. 3(a)]. To select the four different pump pulses shown in Fig. 4(c), we used respectively a 2-THz low-pass filter, a 3-THz bandpass filter, a 4.2-THz high-pass filter coupled with a 6-THz low-pass filter, and a 6-THz bandpass filter.

For the measurement of properties dependent on the pump strength, the terahertz electric field was tuned by three wire-grid polarizers. Peak electric fields were reached by tight focusing of the terahertz beam using three parabolic mirrors [65]. To estimate the electric-field strength of the pump pulses shown in Fig. 1, we apply the formula [66]

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of the Gaussian envelope fitting the temporal intensity waveform of the terahertz pump [Fig. 6(c)], which was taken as the square of the electric field measured at the sample position by electro-optic sampling in a 200-μm-thick (110) GaP crystal with a 50-fs, 800-nm gating pulse obtained as a fraction of the Ti:sapphire beam. Our estimated electric-field strength, \( E_{\text{THz}} = 3.2 \text{ MV cm}^{-1} \), is similar to other values in recent literature [47,48].

The gating pulse was used to probe the ultrafast pump-induced polarization dynamics of the sample, which were measured by splitting the probe beam into two orthogonal components with a Wollaston prism. The terahertz electric field of the pump was polarized in the sample plane along the direction perpendicular to the optical table. The polarization of the probe relative to the sample was offset by 45° from the pump polarization. All measurements were performed in a He cryostat, which allowed a minimum sample temperature of 3.5 K to be reached.

For a quantitative analysis of the effect of \( E_{\text{THz}} \) on the sample, the peak polarization, \( P_m \), induced by the terahertz pulse resonant with a generic phonon mode, \( m \), is [3]

\[
P_m = \frac{\sigma_1(\omega_m)}{\omega_m} E_{\text{THz}}, \tag{A2}
\]

where \( \omega_m \) is the angular frequency and \( \sigma_1(\omega_m) \) the optical conductivity of the driven phonon. The polarization arises from the modulation of the dipole moment of the crystal, \( P_m = n_d \delta \mu_m \mu_m \), where \( \delta \mu_m = e | \sum_i \mu_{im} Z_{\text{eff}} | \) is the magnitude of the charge displacement due to phonon mode \( m \), \( \mu_{im} \) is the normalized vector of displacements of each atom, \( i \), in phonon mode \( m \), \( Z_{\text{eff}} \) are the Born effective charges of each atom, \( n_d \) is the number of dipoles per unit volume, and \( \delta_m \) is the maximum displacement coordinate of the phonon. The driving field, \( E_{\text{THz}} = \beta_m E_{\text{THz}} \) in Eq. (A2), is the effective electric field inside the sample acting on the phonon [66], where \( \beta_m = 1 - R_m \) is determined by the reflectivity at frequency \( \omega_m \).

To illustrate the estimation of the \( \delta_m \) values induced by the terahertz electric field, we take the example of the 4.60-THz phonon mode, which is the strongest single feature of the driven response (Fig. 3) and is labeled \( m = b \) in Sec. IV. Thus we use \( \omega_b = 2\pi \times 4.6 \times 10^{12} \text{ s}^{-1} \), \( \sigma_1(\omega_b) = 137\Omega^{-1} \text{ cm}^{-1} \) from Ref. [46], \( n_d = V^{-1} \) with \( V = 5.71 \times 10^{-22} \text{ cm}^{-3} \) the volume of the unit cell, and the value \( \mu_b = 0.6e \) taken from our DFT calculations (below). The bandwidth of the external terahertz field, approximately 2.7 THz FWHM [Fig. 3(a)], is large compared to the linewidth of the phonon mode [0.1 THz FWHM, Fig. 4(c)], and by accounting for the reflection of the external field [Fig. 4(c)] we estimate \( \beta_b \simeq 0.02 \). Thus we deduce a maximum displacement of \( \delta_b = 0.17 \text{ Å} \), which is comparable to that estimated in SrTiO\(_3\) [58].

### APPENDIX B: TIME-FREQUENCY ANALYSIS OF TERAHERTZ-DRIVEN DYNAMICS AND MODE SYMMETRIES

Figure 7 reports the temporal profile and frequency content measured for the terahertz pump pulse [Fig. 7(a)] and the resulting polarization rotations induced in the SrCu\(_2\)(BO\(_3\))\(_2\) sample at 4 K [Fig. 7(b)]. The spectral decomposition was computed using a Hamming sliding-window fast Fourier transform. It is clear that the distribution of frequencies in the terahertz pump pulse [Fig. 7(a)] causes not only a direct resonant driving of \( E \)-symmetric, IR-active phonons but also a less direct, nonlinear driving of \( B_1 \)-symmetric, Raman-active phonons at higher frequencies [Figs. 7(b) and 7(c)]; for this the low-temperature point group, \( D_{2d} \) (space group \( I42m \)), permits the excitation of \( B_1 \) (\( C \subset E \times E \)) phonons by the...
composition of two $E$-symmetric phonons. Similarly, the magnetic excitation from the singlet ground state to the TBS mode can be interpreted as a resonance driven by the difference-frequency harmonic components of the $E$-symmetric phonons shown in Figs. 7(d) and 7(e). The TBS [Fig. 7(f)] also has $B_1$ symmetry, as determined by Raman spectroscopy [39,40], indicating that its driving relies on the same symmetry composition ($B_1 \subseteq E \times E$). We comment that, because both the singlet ground state and the TBS are nonmagnetic ($S = 0$), the origin of the polarization rotation measured in SrCu$_2$(BO$_3$)$_2$ must lie in lattice (birefringence) effects, which are clearly enhanced by the spin-lattice coupling.

**APPENDIX C: TERAHERTZ-DRIVEN NONLINEAR PHONON DYNAMICS**

Our results [Sec. III] demonstrate that the resonant dynamic distortion of the lattice in response to intense and coherent terahertz excitation creates nonlinear channels for the transfer of energy to both magnetic and phononic modes. The phenomenon of sum-frequency ionic Raman scattering has been investigated recently in both experiment [35,60] and theory [67], and our results include its clearest observation to date. To describe the driven nonlinear lattice dynamics that we observe, we consider two IR-active phonons with normal coordinates $q_b$ and $q_c$, with corresponding frequencies $\omega_b$ and $\omega_c$, and a Raman-active phonon with coordinate $q_R$ and frequency $\omega_R$. By discarding terms quadratic in $q_R$, on the assumption that the amplitude of the Raman mode will be much smaller than that of the IR modes driven by the terahertz pump ($|q_{bc}| \gg |q_R|$), the minimal lattice potential to cubic order (i.e., lowest anharmonic order) is

$$V(q_b, q_c, q_R) = \frac{1}{2} \omega^2_b q^2_b + \frac{1}{2} \omega^2_c q^2_c + \frac{1}{2} \omega^2_R q^2_R + [c_{bb,R}q^2_b + c_{bc,R}q bq_c + c_{cc,R}q^2_c]q_R,$$

(C1)

where the $c$ coefficients specify the leading nonlinear coupling terms between the IR and Raman phonons. The equation of motion for a generic terahertz-driven, IR-active phonon mode, $m$, takes the form

$$\ddot{q}_m + \gamma_m \dot{q}_m = -\frac{\partial [V - B_m q_mE_{THz}(t)]}{\partial q_m},$$

(C2)

with $\gamma_m$ the damping rate and $B_m$ the dipole coupling constant introduced in Eq. (5). For a phonon that is Raman-active but not IR-active, the driving term is only $\partial V/\partial q_R$. The coherent terahertz-driven lattice dynamics are then described in the time domain from Eq. (C2), to leading order in $q_R$, by the coupled differential equations

$$\ddot{q}_b + \gamma_b \dot{q}_b + \omega^2_b q_b = -B_b E_{THz}(t),$$

(C3)

$$\ddot{q}_c + \gamma_c \dot{q}_c + \omega^2_c q_c = -B_c E_{THz}(t),$$

(C4)

$$\ddot{q}_R + \gamma_R \dot{q}_R + \omega^2_R q_R = -[c_{bb,R}q^2_b + c_{bc,R}q bq_c + c_{cc,R}q^2_c].$$

(C5)

Clearly Eq. (C5) for the Raman phonon describes a damped harmonic oscillator driven by terms quadratic in the IR-active

FIG. 7. Time-frequency terahertz-driven dynamics. (a) Terahertz pump electric-field amplitude. (b) Pump-induced polarization modulation in SrCu$_2$(BO$_3$)$_2$ at 4 K. In (a), the color contours around $t = 0$ are based on the full width at half maximum (FWHM) isoline of the amplitude. In (b), the blue circles indicate the frequencies of the $E$-symmetric IR-active phonon modes that are pumped directly, where our measured values of 3.80, 4.27, 6.75, and 7.00 THz match within the experimental error with those of Ref. [46], whereas the 4.60-THz mode we measure is tabulated there as 4.75 THz. Green circles show the frequencies of $B_1$-symmetric modes at 8.57 and 11.7 THz [46] that are not IR active but are excited by sum-frequency processes, which are expected to involve respectively the $E$-symmetric IR-active phonon modes that are pumped directly, where our measured values of 3.80, 4.27, 6.75, and 7.00 THz match within the experimental error with those of Ref. [46], whereas the 4.60-THz mode we measure is tabulated there as 4.75 THz. Green circles show the frequencies of $B_1$-symmetric modes at 8.57 and 11.7 THz [46] that are not IR active but are excited by sum-frequency processes, which are expected to involve respectively the $E$-symmetric IR-active phonons shown in Figs. 7(d) and 7(e). The TBS mode can be interpreted as a resonance driven by the difference-frequency harmonic components of the $E$-symmetric phonons shown in Figs. 7(d) and 7(e). The TBS [Fig. 7(f)] also has $B_1$ symmetry, as determined by Raman spectroscopy [39,40], indicating that its driving relies on the same symmetry composition ($B_1 \subseteq E \times E$). We comment that, because both the singlet ground state and the TBS are nonmagnetic ($S = 0$), the origin of the polarization rotation measured in SrCu$_2$(BO$_3$)$_2$ must lie in lattice (birefringence) effects, which are clearly enhanced by the spin-lattice coupling.
phonon displacements, resulting in sum-frequency excitation processes. The effectiveness of this driving then depends on the proximity of the combinations $2\omega_b$, $2\omega_c$, and $\omega_b + \omega_c$ (and indeed $\omega_c - \omega_b$) to $\omega_R$.

The clearest example in Fig. 7(b) is the $B_1$ Raman mode with frequency $\omega_R = 11.7$ THz and damping $\gamma_R = 0.2$ THz [Fig. 7(c)]. The two terahertz-pumped $E$-symmetric phonons marked by the asterisks have parameters $\omega_b = 4.60$ THz, $\gamma_b = 0.03$ THz and $\omega_c = 7.00$ THz, $\gamma_c = 0.10$ THz. Figure 8(a) shows the temporal evolution of $q_b$ and $q_c$ calculated from Eqs. (C3)–(C5) using the experimental terahertz pump field. As expected from the respective phonon frequencies, the Raman coordinate, $q_R$, is dominated by coherent oscillations at frequency $\omega_b + \omega_c$ [Fig. 8(c)], confirming the sum-frequency ionic Raman mechanism. The phenomenon is equally clear in the frequency domain, where the Fourier amplitudes of the measured and calculated dynamics are compared in Fig. 8(c).

Because the amplitude of $q_R$ varies linearly with each individual amplitude $q_b$ or $q_c$ [Eq. (C5)], it should scale quadratically with the terahertz field strength, as Fig. 8(d) confirms. We note again that all the phonon frequencies used in our analysis are the experimental values obtained from our pump-probe measurement, which with one exception match the Fourier transform infrared (FTIR) spectroscopy measurements of Ref. [46] to within the experimental uncertainties; as a result of this match, we took all the phonon damping parameters ($\gamma_m$) from Ref. [46]. The exception was the phonon frequency $\omega_b = 4.60$ THz, found at 4.75 THz by FTIR spectroscopy, where our measured value gave a significantly better account of the $B_1$ Raman frequency we observed at 11.58 THz. A similar analysis can be performed for the $B_1$ phonon mode at 8.57 THz, with driving by $\omega_b$ combined with the IR-active phonon at $\omega_a = 3.80$ THz [both marked by blue diamonds in Fig. 7(b)].

APPENDIX D: FITTING OF PHONON AND TBS MODES

The amplitudes of the $\omega_a$ and $\omega_b$ phonon modes shown in Fig. 4(a), and of the TBS mode shown in Fig. 4(b), were determined together with their uncertainties by a Gaussian fitting procedure in the frequency domain. Figure 9 shows the spectral peaks of the TBS mode, and of the two phonon modes, for a range of values of the peak electric field of the terahertz pump pulse, with the Gaussian fits shown as dashed black lines. In fitting a Gaussian function, $G(a, \omega_0, w)$, to these peaks, the only free parameter was the peak amplitude, $a$, whereas the center frequency, $\omega_0$, and the Gaussian width, $w$, were fixed for every peak. The amplitudes and their uncertainties were then determined by the least-squares Gaussian fit method [68].

The nonlinear dependence of the TBS amplitude on the terahertz electric-field strength can be also be read from
FIG. 9. Extraction of mode amplitudes. Spectral amplitude computed for the interval $1.9 \leq t \leq 14.4$ ps and shown for a range of terahertz pump field strengths with an added vertical offset. (a) TBS. (b) Phonon $\omega_a$. (c) Phonon $\omega_b$. Short-dashed black lines show fits to a Gaussian function, $G(a, \omega_0, w)$, with the amplitude $a$ as a free parameter. The center frequency ($\omega_0$) and Gaussian width (standard deviation, $w$) parameters for the TBS are $\omega_0 = 0.87$ THz and $w = 0.06$ THz, for phonon mode $a$ are $\omega_0 = 3.77$ THz and $w = 0.06$ THz, and for phonon mode $b$ are $\omega_0 = 4.60$ THz and $w = 0.07$ THz.

Fig. 9(a), by comparing it with the linear dependence of $\omega_a$ in Fig. 9(b). Both modes have comparable amplitudes at the maximum terahertz electric field, making clear the much faster decrease in the TBS amplitude at lower field strengths.

APPENDIX E: DEPENDENCE ON POLARITY OF THE TERAHERTZ PUMP FIELD

As Fig. 4(b) shows, the amplitude of the phonon-driven TBS excitation is proportional to the square of the driving electric field of the terahertz pump pulse. A further important test of our observations and modeling is therefore to invert the polarity of this field, as represented in Fig. 10(a). To implement this sign inversion experimentally, we rotate the crystal for terahertz generation by 180° and compare the driven dynamics of the polarization-rotation signals. The results in the time domain are shown in Figs. 10(b)–10(e). Because the $E$-symmetric (IR-active) phonon modes are excited directly, the carrier-envelope phase of the terahertz pump is imprinted onto them and Figs. 10(c) and 10(d) confirm a phase shift of 180°. By contrast, the dynamics of the TBS [Fig. 10(b)] are invariant on changing the electric-field polarity, fully consistent with a quadratic driving mechanism. The dynamics of the Raman-active phonon at 11.6 THz, presented in Appendix C, are similarly insensitive to the change of polarity [Fig. 10(e)], as expected of a sum-frequency process. We note that perfect inversion of the IR phonon signals, and perfect overlap of the TBS and Raman phonon signals, are actually obtained for a time shift of $-20$ fs in the $E(\rightarrow)$ signal. This can be attributed to the fact that rotation of the terahertz generation crystal may produce a small time delay in the event of an inhomogeneity in its thickness (20 fs corresponds to approximately 6 μm in vacuum).

APPENDIX F: TERAHERTZ-PUMPED NEAR-INFRARED TRANSMISSION MODULATION

To demonstrate that ultrafast electronic processes, such as the displacive excitation of phonons [52], are not involved in the terahertz generation mechanism of the coherent phonons and TBS modes we observe, we have performed terahertz-pump, NIR-probe spectroscopy to measure the transient transmission modulation, $\Delta T/T$. Working under the same experimental conditions as for the measurements in Fig. 1(c), we measured the terahertz-induced NIR $\Delta T/T$ at a photon energy of 1.55 eV and show the results as a function of the pump-probe time delay in Fig. 11. The transient transmission can monitor the presence of ultrafast terahertz-induced carrier generation, which would appear as a peak at very short times, but the observed dynamics show no signature of such processes. Instead the $\Delta T/T$ dynamics show only a slow decrease of the sample transmission upon terahertz irradiation. In solids with impurity states or in narrow-gap insulating systems, an intense terahertz pulse can generate carriers through impact ionization or tunneling processes [57,69], whose dynamics are confined to the duration of the terahertz pump pulse (i.e., a few picoseconds). Carrier excitation can generate vibrational or spin modes through a displacive process if the excitation dynamics are shorter than half an oscillation period of the mode [53,54]. However, the measured $\Delta T/T$ is not compatible with this scenario: no free carriers
FIG. 10. Pump polarity inversion. (a) Representation of two terahertz pump pulses with inverted electric-field polarities, \( E^+ \) and \( E^- \). [(b)–(e)] Comparison of the dynamics of the magnetic and lattice modes for these two pump polarities.

are excited and therefore it is self-evident that displacive excitations play no role in the phenomenon we have observed. Taken together with the evidence presented in Sec. III, this result further reinforces the magnetophononic mechanism.

The \( \Delta T/T \) dynamics shown in Fig. 11 can be fitted by a single exponential with a time constant of \( \tau = 8.3 \) ps (solid blue line), and thus can be ascribed to a slight increase in temperature arising from the relaxation of lattice phonons.

One may estimate the maximum increase in temperature due to terahertz irradiation as being less than 1 K, based on the low-temperature specific heat of 5 J mol\(^{-1}\) K\(^{-1}\) [70]. The decrease of the NIR transmission with increasing temperature is consistent with the fact that the steady-state NIR transmission decreases by approximately 50% upon heating from 4 to 300 K.

APPENDIX G: PHONON MODULATION OF MAGNETIC INTERACTIONS

We have performed a hierarchy of DFT calculations in order to obtain quantitative estimates of the effects of the driven IR phonons on the magnetic system in SrCu\(_2\)(BO\(_3\))\(_2\).

1. DFT calculations at equilibrium

First we used QUANTUM ESPRESSO [61] to compute the total lattice and magnetic energies of SrCu\(_2\)(BO\(_3\))\(_2\) at equilibrium. For these calculations we worked in the structural unit cell of the system, which is tetragonal and contains 44 atoms (of which 8 are Cu atoms) in two “Shastry-Sutherland” layers. The electron-ion interactions were modeled using pseudopotentials from the curated SSSP library [71,72]. The plane-wave cutoff was set at 750 eV (6000 eV for the charge density) and for sampling of the Brillouin zone we used a \( 6 \times 6 \times 6 \) \( k \)-point grid. Structural relaxation was continued until each component of the force acting at every atom was less than 0.0025 eV/Å and the pressure (defined as \( 1/3 \text{Tr}[ \sigma ] \), with \( \sigma \) being the stress tensor) was below 0.5 kbar. These parameters ensure errors smaller than 1 meV/atom within the total energy and, more importantly, smaller than 1 K on the magnetic interactions (which depend only on total-energy differences, and thus converge faster and better than do the total values). By comparing the energies of different spin configurations computed with the same relaxed structure, we fixed the value of the effective Hubbard term to \( U = 11.4 \) eV by reproducing the interaction parameters \( J = 84.0 \) K and \( J' = 49.7 \) K [63]. The lattice parameters we obtain for this value of \( U \), the \( T = 0 \) DFT + \( U \) structure, agree with the measured low-temperature structure of SrCu\(_2\)(BO\(_3\))\(_2\) [73] to within 1% for the \( a \) and \( b \) axes and 3% for the \( c \) axis. The Born effective charges, \( Z_{\text{eff}} \), used in Sec. III to estimate the maximum displacements, \( \delta_m \), were computed for the system in the antiferromagnetic configuration using the PHONON module of QUANTUM ESPRESSO and the PBE functional [62].

2. DFT calculations for frozen phonons

In order to extend our DFT calculations to include the nonequilibrium atomic configurations in the presence of lattice excitations, we first made a phonon symmetry analysis of the different interatomic paths. From this we deduced that the most general magnetic state in the presence of a phonon distortion \( q_i \) is characterized by ten different interaction parameters in the unit cell, two values of \( J(q_i) \) and eight of...
interdimer interaction terms, $J$, every normal mode of the lattice, the system has two different values of the intradimer interaction, $J$, phonon modes measured in experiment [Fig. 7(a)], according to the normal coordinates of the strongest two structures obtained by systematic displacement of all atoms.

An arbitrary "frozen" configuration of the phonons in SrCu$_2$(BO$_3$)$_2$. Red dots represent the $S = 1/2$ spins at the Cu$^{2+}$ sites in SrCu$_2$(BO$_3$)$_2$. For every normal mode of the lattice, the system has two different values of the intradimer interaction parameters.

We performed total-energy calculations for the lattice supercells in each of the two layers of the structural unit cell (a total of 32 magnetic sites) required to obtain enough independent spin configurations to determine all 11 unknown parameters.

$J'(q_i)$, as shown in Fig. 12. To compute this number of unknown parameters, it is necessary to work on a $2 \times 2 \times 1$ supercell, meaning to use four of the basic magnetic unit cells of SrCu$_2$(BO$_3$)$_2$. In these supercell calculations we reduced the $k$-point grid to $2 \times 2 \times 3$, and verified that this sampling density provided essentially equivalent results.

We performed total-energy calculations for the lattice structures obtained by systematic displacement of all atoms according to the normal coordinates of the strongest two phonon modes measured in experiment [Fig. 7(a)], $q_a$ at $\omega_a = 3.80$ THz and $q_b$ at $\omega_b = 4.60$ THz. While it is possible to include many more of the phonons observed in Appendix B, here we have focused rather on optimizing our treatment of the time and frequency domains. For each distorted structure, we computed the electronic ground state as a function of the displacement amplitudes of the two phonons and for 11 different configurations of up- ($S_\uparrow = 1/2$) and down-oriented spins ($S_\downarrow = -1/2$), from which we obtained 11 linearly independent equations in order to determine all the interaction parameters in the system. This process is represented in Table I for one set of 11 spin configurations in layer 1 of Fig. 12 and the corresponding equations are

\begin{align}
E(1) &= E_0 + 4J_1 + 4J_2 - 6J'_1 - 2J'_2 - 6J'_3 - 6J'_4 - 6J'_5 - 6J'_6 - 6J'_7 - 2J'_8, \\
E(2) &= E_0 + 4J_1 + 4J_2 - 2J'_1 - 6J'_2 - 6J'_3 - 6J'_4 - 6J'_5 - 6J'_6 - 2J'_7 - 6J'_8, \\
E(3) &= E_0 + 6J_1 + 6J_2 - 4J'_1 - 6J'_2 - 6J'_3 - 8J'_4 - 8J'_5 - 6J'_6 - 6J'_7 - 4J'_8, \\
E(4) &= E_0 + 2J_1 + 2J_2 - 4J'_1 - 6J'_2 - 2J'_3 - 4J'_4 - 4J'_5 - 2J'_6 - 6J'_7 - 4J'_8, \\
E(5) &= E_0 + 4J_1 + 4J_2 - 6J'_1 - 6J'_2 - 6J'_3 - 2J'_4 - 6J'_5 - 2J'_6 - 6J'_7 - 6J'_8, \\
E(6) &= E_0 + 4J_1 + 4J_2 - 6J'_1 - 6J'_2 - 2J'_3 - 6J'_4 - 2J'_5 - 6J'_6 - 6J'_7 - 6J'_8, \\
E(7) &= E_0 + 6J_1 + 6J_2 - 8J'_1 - 6J'_2 - 6J'_3 - 4J'_4 - 4J'_5 - 6J'_6 - 6J'_7 - 8J'_8, \\
E(8) &= E_0 - 2J_1 - 2J_2 - 6J'_1 - 6J'_2 - 6J'_3 - 6J'_4, \\
E(9) &= E_0 - 2J'_1 - 6J'_2 - 6J'_3 + 2J'_4 - 2J'_5 - 6J'_6 - 2J'_7 - 2J'_8, \\
E(10) &= E_0 - 2J'_1 - 2J'_2 - 6J'_3 - 2J'_4 + 2J'_5 - 6J'_6 - 6J'_7 - 2J'_8, \\
E(11) &= E_0 - 2J_1 - 2J_2 - 4J'_1 - 4J'_2 - 2J'_3 - 4J'_4 - 2J'_5 - 4J'_6 - 4J'_7 - 2J'_8. 
\end{align}
The extraction of the magnetic interaction parameters is by its nature a statistical exercise, because different spin configurations lead to different local spin densities in the DFT wave function, which cause subtle differences in the results for the effective $J$ and $J'$ parameters. We benchmark the accuracy of our statistics by testing the magnetic interactions at equilibrium (i.e., $q_a$ and $q_b = 0$) with 100 different spin configurations and performing a least-squares regression analysis. As we show in Table II, our results are fully consistent with the equilibrium $J$ and $J'$ values. The resulting statistical error on $J'$ is 0.4 K. $E_0$ in Eqs. (G1) is a large constant that captures all of the nonmagnetic contributions to the calculation and cancels from the equations determining the magnetic interaction parameters.

3. DFT calculations with driven phonons

To model our experiment, in Figs. 13(a) and 13(b) we show the vectors, meaning the ensembles of atomic displacements, of the two primary IR-active phonons excited by the terahertz pump ($\omega_a = 3.80$ and $\omega_b = 4.60$ THz). We performed DFT calculations of the magnetic interactions in the presence of phonon oscillations for each phonon separately, as shown in Figs. 13(c)–13(h), and with both phonons superposed, as we show in the time series illustrated in Fig. 5(d). Considering first the individual phonons, we observe that the intradimer interactions, $J_1(q_{a,b})$ and $J_2(q_{a,b})$, have a largely quadratic dependence on $q_{a,b}$ for both phonons [Figs. 13(c) and 13(d)], suggesting that out-of-plane O atomic motions cause the predominant effects on these parameters. By contrast, most of the interdimer interactions, $J'_1(q_{a,b})$, show strong linear as well as quadratic contributions [Figs. 13(e) and 13(f)] that depend both on the interaction pathway in question and on the combination of in- and out-of-plane atomic motions. It is clear that all four difference parameters, $\Delta J'_1(q_{a,b})$, $\Delta J'_3(q_{a,b})$, $\Delta J'_6(q_{a,b})$, and $\Delta J'_8(q_{a,b})$, have strong linear contributions [Figs. 13(g) and 13(h)] that allow an efficient driving of two-trigonal processes by the IR-active phonon oscillations (Sec. IV).

For the purposes of creating nonlinear magnetophononic phenomena in SrCu$_2$(BO$_3$)$_2$, the strongest modulation of the $\Delta J'_1(q_{a,b})$ interactions is produced by the 4.60-THz phonon [Fig. 13(b)]. This is due largely to the fact that its maximum terahertz-induced phonon displacement, $\delta_b = 0.17$ Å (Sec. III), is significantly greater than that of the other phonons (at 3.80 THz we estimated the displacement $\delta_a = 0.04$ Å). These maximum displacements are included in the calculations shown in Fig. 5, where we have computed the phonon-induced modulation of the magnetic interaction parameters as a time series based on the pulse durations of our experiment. For this calculation, we computed 285 points covering 10 ps with a time resolution of 0.035 ps, which accessed both the high- and low-frequency regimes to a sufficient degree that we obtained well-resolved results for all features, in particular the TBS peak.

Finally, we comment that an average over all our computed values of $J$ and $J'$ indicates that the averaged coupling ratio, $\tilde{\alpha}(q_{a,b}) = \tilde{J}/\tilde{J}$, increases as a function of $q_{a,b}$ for both phonon modes. This leads to the results shown in Fig. 5(g) and to the possibility of driving the static QPT of the spin system into the plaquette phase by using the ultrafast driving of IR phonons to increase the time-averaged coupling ratio.

| Configuration No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|-------------------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|
| Magnetic site     |   |   |   |   |   |   |   |   |   |    |    |    |    |    |    |    |
| 1                 | −1 | −1 | 1 | −1 | −1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | −1 | −1 | −1 |
| 2                 | −1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 3                 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 4                 | −1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 5                 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 6                 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 7                 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 8                 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 9                 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 10                | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |
| 11                | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 | −1 | −1 |

| Interaction | $J_1$ (K) | $J_2$ (K) | $J'_1$ (K) | $J'_2$ (K) | $J'_3$ (K) | $J'_4$ (K) | $J'_5$ (K) | $J'_6$ (K) | $J'_7$ (K) | $J'_8$ (K) |
|-------------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|
| Strength    | 83.2      | 83.6      | 48.5       | 48.7       | 47.5       | 47.4       | 48.1       | 48.1       | 48.9       | 48.7       |
FIG. 13. Phonon displacement vectors and calculated magnetic interaction parameters in SrCu$_2$(BO$_3$)$_2$. (a) Atomic motions in the normal mode ($q_a$) of the lattice at $\omega_a = 3.80$ THz. (b) As in panel (a) for $q_b$ at $\omega_b = 4.60$ THz. We comment that these phonon modes are not symmetric between the $a'$ and $b'$ axes [Fig. 1(a)], but that their doublet counterparts within each $E$-symmetric manifold restore this symmetry. [(c), (d)] Intradimer interactions, $J_1$ and $J_2$, shown as functions of the phonon displacement amplitudes. [(e), (f)] Interdimer interactions, $J'_1$, ..., $J'_8$. [(g), (h)] Differences, $\Delta J'_{12}$, $\Delta J'_{34}$, and $\Delta J'_{56}$, between pairs of interdimer interaction parameters. The parameters shown in panels (c)–(f) were obtained using 11 spin configurations and, after verification of their systematic evolution, were centered on the results of Table II.

[1] P. Salén, M. Basini, S. Bonetti, J. Hebling, M. Krasilnikov, A. Y. Nikitin, G. Shamulov, Z. Tibai, V. Zhaunerchyk, and V. Goryashko, Phys. Rep. 836-837, 1 (2019).
[2] D. Nicoletti and A. Cavalleri, Adv. Opt. Photonics 8, 401 (2016).
[3] M. Mitrano, A. Cantaluppi, D. Nicoletti, S. Kaiser, A. Perucchi, S. Lupi, P. Di Pietro, D. Pontiroli, M. Riccò, S. R. Clark, D. Jaksh, and A. Cavalleri, Nature (London) 530, 461 (2016).
[4] A. D. Caviglia, R. Scherwitzl, P. Popovich, W. Hu, H. Bromberger, R. Singla, M. Mitrano, M. C. Hoffmann, S. Kaiser, P. Zubko, S. Gariglio, J.-M. Triscone, M. Först, and A. Cavalleri, Phys. Rev. Lett. 108, 136801 (2012).
[5] T. Kubacka, J. A. Johnson, M. C. Hoffmann, C. Vicario, S. de Jong, P. Beaud, S. Grübel, S.-W. Huang, L. Huber, L. Patthey, Y.-D. Chuang, J. J. Turner, G. L. Dakovski, W.-S. Lee, M. P. Minister, W. Schlotter, R. G. Moore, C. P. Hauri, S. M. Koohpayeh, V. Scagnoli et al., Science 343, 1333 (2014).
[6] T. Oka and S. Kitamura, Annu. Rev. Condens. Matter Phys. 10, 387 (2019).
[54] F. Giorgianni, M. Udina, T. Cea, E. Paris, M. Caputo, M. Radovic, L. Boie, J. Sakai, C. W. Schneider, and S. L. Johnson, Commun. Phys. 5, 103 (2022).

[55] H. Yamakawa, T. Miyamoto, T. Morimoto, T. Terashige, H. Yada, N. Kida, M. Suda, H. M. Yamamoto, R. Kato, K. Miyagawa, K. Kanoda, and H. Okamoto, Nat. Mater. 16, 1100 (2017).

[56] A. T. Tarekegne, H. Hirori, K. Tanaka, K. Iwaszczuk, and P. U. Jepsen, New J. Phys. 19, 123018 (2017).

[57] S. Hubmann, G. V. Budkin, M. Urban, V. V. Bel’kov, A. P. Dmitriev, J. Ziegler, D. A. Kozlov, N. N. Mikhailov, S. A. Dvoretsky, Z. D. Kvon, D. Weiss, and S. D. Ganichev, J. Infrared, Millimeter, Terahertz Waves 41, 1155 (2020).

[58] M. Kozina, M. Fechner, P. Marsik, T. van Driel, J. M. Glownia, C. Bernhard, M. Radovic, D. Zhu, S. Bonetti, U. Staub, and M. C. Hoffmann, Nat. Phys. 15, 387 (2019).

[59] B. Normand and C. Rüegg, Phys. Rev. B 83, 054415 (2011).

[60] A. A. Melnikov, K. N. Boldyrev, Y. G. Selivanov, V. P. Martovitskii, S. V. Chekalin, and E. A. Ryabov, Phys. Rev. B 97, 214304 (2018).

[61] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo et al., J. Phys.: Condens. Matter 29, 465901 (2017).

[62] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[63] G. Radtke, A. Sauli, H. A. Dabkowska, B. D. Gaulin, and G. A. Botton, Phys. Rev. B 77, 125130 (2008).

[64] M. Yarmohammadi, M. Krebs, G. S. Uhrig, and B. Normand, Phys. Rev. B 107, 174415 (2023).

[65] F. Giorgianni, J. Sakai, and S. Lupi, Nat. Commun. 10, 1159 (2019).

[66] H. G. Roskos, M. D. Thomson, M. Kreß, and T. Löffler, Laser Photonics Rev. 1, 349 (2007).

[67] D. M. Juraschek and S. F. Maehrlein, Phys. Rev. B 97, 174302 (2018).

[68] D. S. Sivia and J. Skilling, Data Analysis: A Bayesian Tutorial, 2nd ed. (Oxford University Press, Oxford, UK, 2006).

[69] T. Kampfrath, K. Tanaka, and K. A. Nelson, Nat. Photonics 7, 680 (2013).

[70] A. N. Vasil’ev, M. M. Markina, A. V. Inyushkin, and H. Kageyama, JETP Lett. 73, 633 (2001).

[71] G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet, and N. Marzari, npj Comput. Mater. 4, 72 (2018).

[72] G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet, and N. Marzari, A Standard Solid State Pseudopotentials (SSSP) library optimized for precision and efficiency (Version 1.1, data download), Mater. Cloud Arch.2018.0001/v4 (2020), https://archive.materialscloud.org/2018.0001/v3.

[73] C. Vecchini, O. Adamopoulos, L. C. Chapon, A. Lappas, H. Kageyama, Y. Ueda, and A. Zorko, J. Solid State Chem. 182, 3275 (2009).