

Theory of nonlinear spectroscopy of quantum magnets

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Two-dimensional coherent spectroscopy (2DCS) is an established method for characterizing molecules and has been proposed in the terahertz regime as a tool for probing exotic excitations of quantum magnets; however, the precise nature of the coupling between pump field and spin degrees of freedom has remained unclear. Here, we develop a general response theory of 2DCS and show how magnetoelectric as well as polarization couplings contribute to 2DCS in addition to the typically assumed magnetization. We propose experimental protocols to probe the presence of polarization couplings, for instance, from exchange-striction or spin-current mechanism, when the electric field couples to quadratic terms in spin operators. We provide example calculations for the paradigmatic twisted Kitaev chain material CoNb_2O_6 and highlight the crucial role of contributions from cross-coupling between polarization and magnetic nonlinear susceptibilities. Our work paves the way for systematic studies of light-matter couplings in quantum magnets and for establishing 2DCS as a versatile tool for probing fractional excitations of exotic magnetic quantum phases.

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I. INTRODUCTION

Spectroscopic measurements are one of the main experimental tools for understanding the microscopic constituents of different forms of matter [1]. In recent years, advances in nonlinear spectroscopy have allowed the measurement of new excitations [2–5] and controlled manipulation of quantum materials [6–9]. Two-dimensional coherent spectroscopy (2DCS), a two-pump probe nonlinear method, is particularly promising as it not only probes intrinsic excitations but also their interactions [10]. 2DCS is well established for studying molecules and proteins [11,12], but recent advances in the generation of terahertz (THz) pulses have allowed the study of excitation energies relevant for quantum materials [13]. 2DCS is well suited for probing quantum magnets with exotic fractionalized excitations [14–23], the latter being hard to detect in linear spectroscopy, as there, they lead to broad continua which could also arise from mundane effects like disorder [24] or thermal smearing [25]. The recent observations of magnon excitations [26] and their interactions [27] in insulating ordered magnets via 2DCS confirm the power of the method, but so far, the microscopic light-matter couplings involved in 2DCS remain unclear to a large extent.

Thus far, numerous theoretical 2DCS studies for quantum magnets [14–23] have solely focused on the nonlinear

magnetization response. However, when considering a free electron coupled to an electromagnetic wave, both electric as well as magnetic components couple. Assuming the free electron to be delocalized on the scale of the Bohr radius, electric coupling even dominates over magnetic coupling by a factor of the inverse fine structure constant $1/\alpha \approx 137$. Of course, the situation is more complex for localized electrons in Mott insulators with only spin excitations at low energy. It is nonetheless pertinent to investigate its contribution to 2DCS because strong intrinsic electrical polarization of spin origin have also been established in quantum magnets [28–35]. Motivated by these considerations, in this work, we provide a microscopic theory of 2DCS of quantum magnets and show that the coupling of the THz field to the intrinsic electric polarization gives an important yet overlooked contribution to the nonlinear response. We discuss the distinct signatures of the electric polarization in 2DCS and how to separate its contribution in experiments. We provide example calculations for a one-dimensional (1D) soluble twisted Kitaev model, motivated by the material CoNb_2O_6 [36–38].

II. SETUP OF 2DCS

First, we introduce the conventionally used protocol for 2DCS [12,14] illustrated in Fig. 1(a), which consists of two consecutive parallel-polarized THz pulses, pumps *A* and *B*, on the sample. For simplicity, we assume the pulses *A* and *B* to be well approximated by δ functions at times $t=0$ and $t=\tau$ for a given orientation

$$\vec{E}(t) = E_0\delta(t)\hat{x} + E_\tau\delta(t-\tau)\hat{x}, \quad (1)$$

$$\vec{B}(t) = B_0\delta(t)\hat{z} + B_\tau\delta(t-\tau)\hat{z}. \quad (2)$$

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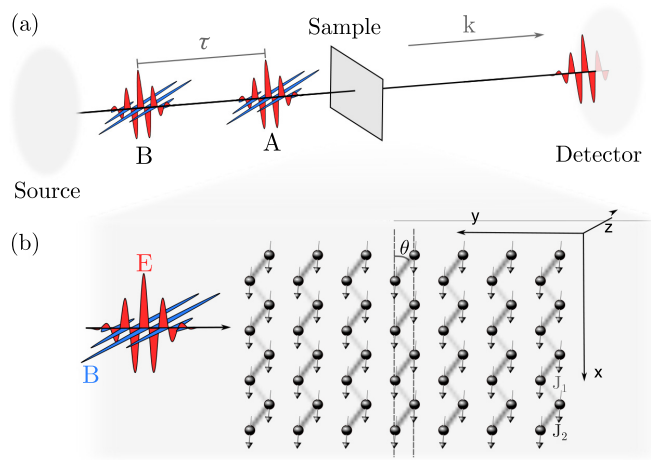


FIG. 1. Setup for 2DCS of quantum magnets. (a) For measuring the nonlinear response, a sample is exposed to two consecutive parallel-polarized pump pulses A and B from a source with propagation vector $\vec{k}$. Interactions with electric $\vec{E}$ and magnetic $\vec{B}$ field components of the pulse induce a nonvanishing polarization as well as magnetization in the sample. The resulting electric field emitted from the sample can be measured in a detector via EOS. (b) We analyze the response of a dimerized twisted Kitaev chain as a candidate quantum magnet realized by the compound CoNb_2O_6 . To exploit the solvable nature of the model, the THz pulse geometry is chosen such that the electric field is aligned with the $\hat{x}$ axis, while the magnetic field is aligned with the $\hat{z}$ axis [18].

While the amplitudes of both pump pulses generally differ, we will consider the same intensities for simplicity (i.e., $E_0 = E_\tau$, $B_0 = B_\tau$). The emitted electric field (amplitude and phase) is measured at a later time $t + \tau$ by electro-optic sampling (EOS) [13,26].

Crucially, we argue that the measured electric field is dominated by dipole contributions not only from the magnetization $M(t)$ but also the polarization $P(t)$ [39], i.e.,

$$E(t) = i[a_E P(t) + b_E M(t)]. \quad (3)$$

The weighting factors a_E, b_E thereby consider sample-specific parameters and geometric properties of the setup. For further details on the derivation, we refer to Appendix A. In general, a_E, b_E can, moreover, be promoted to be frequency dependent to account for different characteristics of the sample at various energies of the emitted field. The emitted magnetic field has an analogous expression; however, it is typically not measured in EOS experiments. Investigating the nonlinear response of the system requires to repeat the experiment two more times with one of the two pump pulses A and B only. Subtracting the two pump-probe measurements from the measurement with both pulses then yields the nonlinear 2DCS response [14].

Next, we relate changes in polarization (and magnetization) to applied pumps with susceptibilities $\chi^{P(n)}$ [and $\chi^{M(n)}$] of different order n using time-dependent perturbation theory [10]. For most cases, the measured signal is dominated by second-order responses in polarization and magnetization

$$P^{\text{NL}}(t + \tau) = \chi_{PP}^{P(2)}(t, t + \tau) E_\tau E_0 + \chi_{MP}^{P(2)}(t, t + \tau) B_\tau E_0 + \chi_{PM}^{P(2)}(t, t + \tau) E_\tau B_0 + \chi_{MM}^{P(2)}(t, t + \tau) B_\tau B_0 + \dots, \quad (4)$$

$$M^{\text{NL}}(t + \tau) = \chi_{PP}^{M(2)}(t, t + \tau) E_\tau E_0 + \chi_{PM}^{M(2)}(t, t + \tau) E_\tau B_0 + \chi_{MP}^{M(2)}(t, t + \tau) B_\tau E_0 + \chi_{MM}^{M(2)}(t, t + \tau) B_\tau B_0 + \dots \quad (5)$$

At a given order n , we obtain a total of 2^{n+1} susceptibilities, with 2^n each corresponding to polarization or magnetization response, respectively. The dots represent higher-order nonlinear response. In most nonlinear spectroscopy experiments, $\chi^{(3)}$ is the generic nonlinear response, but for systems with reduced symmetry, the dominant nonlinear contribution can arise from $\chi^{(2)}$, see Appendix H [26]. In the following, we first focus on the case of dominating $\chi^{(2)}$ responses when the system breaks local symmetries, i.e., for our example of the twisted Kitaev chain, it is the absence of the glide symmetry, as discussed below. We later analyze the case of dominating $\chi^{(3)}$ relevant for systems with glide symmetry.

Most previous theoretical works on quantum magnets have focused on direct interactions between the spin degrees of freedom and the magnetic field of the pulse, thus probing only the magnetic responses like $\chi_{MM}^{M(2)}$ [14–23,40,41]. A step further was recently taken in Ref. [42] studying $\chi_{PP}^{P(2)}$ for the Kitaev quantum spin liquid. Here, our goal is to provide the general response theory of quantum magnets, elucidating the role of all additional contributions to the measurement signal arising from finite polarizations [30,32,43–45]. Polarization of spin systems arises from different microscopic mechanisms [29], and we will concentrate on the (i) exchange-striction (ES) [30,35] or (ii) spin-current (SC)

mechanism [32]. While the first term refers to polarization which can be externally induced via a DC electric field, the second contribution is a result of spin-orbit coupling. The magnitude of ES effects is thereby related to the amount of inversion symmetry breaking in the material which, if present, usually dominates SC effects [29,32,46]. The form of the polarization operator in terms of spin follows from symmetry constraints, e.g., being odd under inversion and even under time reversal, but the precise form and coupling strength is material specific [47]. Below, we discuss the consequences of symmetries by means of a specific example.

III. ISOLATING POLARIZATION CONTRIBUTIONS

In general, 2DCS experiments following the protocol of Fig. 1(a) measure the sum of all different contributions, including the conventionally considered magnetization susceptibility $\chi_{MM}^{M(2)}$, the polarization $\chi_{PP}^{P(2)}$, and also cross-correlations $\chi_{PM}^{M(2)}$ and $\chi_{MP}^{M(2)}$ [plus similar contributions from $\chi_{PP}^{P(2)}$ see Eq. (4)]. Exploiting symmetry properties, we can derive as a key result an experimental protocol to isolate different susceptibilities contained in Eqs. (4) and (5) at second order, which allows us to provide a direct experimental test to

quantify the magnitude of cross-correlations and polarization coupling.

To isolate specific contributions to the response, one can superimpose measurement outcomes of several experimental runs with different parameters. Here, we consider inverting the $\vec{E}$ field of the probe pulses, as achieved by inverting the direction of pulse propagation or by sample rotation, see Appendix C, resulting in modified polarization $P^{\text{NL}}(t|\vec{E}, \vec{B})$ and magnetization $M^{\text{NL}}(t|\vec{E}, \vec{B})$ compared with previously measured quantities $P^{\text{NL}}(t|\vec{E}, \vec{B})$ and $M^{\text{NL}}(t|\vec{E}, \vec{B})$. Note, due to the sign change, all components linear in the inverted $\vec{E}$ field pick up a global sign, and the combination of measurements provides access to

$$\begin{aligned} P_{\parallel}^{\text{NL}}(t) &\equiv (P^{\text{NL}}(t|\vec{E}, \vec{B}) + P^{\text{NL}}(t|-\vec{E}, \vec{B}))/2 \\ &= \chi_{PP}^{(2)}(t-\tau, t)E_{\tau}E_0 + \chi_{MM}^{(2)}(t-\tau, t)B_{\tau}B_0 + \dots, \end{aligned} \quad (6)$$

$$\begin{aligned} P_{\times}^{\text{NL}}(t) &\equiv (P^{\text{NL}}(t|\vec{E}, \vec{B}) - P^{\text{NL}}(t|-\vec{E}, \vec{B}))/2 \\ &= \chi_{MP}^{(2)}(t-\tau, t)B_{\tau}E_0 + \chi_{PM}^{(2)}(t-\tau, t)E_{\tau}B_0 + \dots \end{aligned} \quad (7)$$

Equivalent relations can also be formulated for the magnetization $M_{\parallel/\times}^{\text{NL}}$, see Appendix C. The absence of polarization couplings would lead to a vanishing $P_{\times}^{\text{NL}}$, although $P_{\parallel}^{\text{NL}}$ would be finite due to the purely magnetic contribution. However, for experimental verification, we need to study the combination of measurement signals, see Eq. (3). For this, it is required to analyze the behavior of a_E and b_E under inversion of the pulse propagation geometry. Overall, the mapping respects the parity symmetry of electrodynamics. Recalling the vector (pseudovector) like properties of $\vec{E}, \vec{P}$ ($\vec{M}$) being parity odd (even) requires b_E to flip sign after inverting the $\vec{E}$ field, while a_E remains unaltered. Superimposing the different measurement outcomes with opposite $\vec{E}$ -field directions, $E(t|\vec{E}, \vec{B}) = i[a_E P(t|\vec{E}, \vec{B}) - b_E M(t|\vec{E}, \vec{B})]$ and $E(t|\vec{E}, \vec{B})$ yields

$$\begin{aligned} E_{\text{sym}}^{\text{NL}}(t) &= (E^{\text{NL}}(t|\vec{E}, \vec{B}) + E^{\text{NL}}(t|-\vec{E}, \vec{B}))/2 \\ &= i[a_E P_{\parallel}^{\text{NL}}(t) + b_E M_{\times}^{\text{NL}}(t)], \end{aligned} \quad (8)$$

$$\begin{aligned} E_{\text{asym}}^{\text{NL}}(t) &= (E^{\text{NL}}(t|\vec{E}, \vec{B}) - E^{\text{NL}}(t|-\vec{E}, \vec{B}))/2 \\ &= i[a_E P_{\times}^{\text{NL}}(t) + b_E M_{\parallel}^{\text{NL}}(t)]. \end{aligned} \quad (9)$$

Crucially, as the symmetric response $E_{\text{sym}}^{\text{NL}}(t)$ only contains terms involving a polarization component, thus, a nonvanishing response serves as a direct indicator for finite polarization coupling in a material, see Appendix C for details.

IV. EXAMPLE RESPONSE FOR KITAEV CHAIN MATERIAL

While our previous statements apply for general quantum magnets independent of, e.g., their dimensionality, we next analyze the response for a paradigmatic quasi-1D example. For this, we examine the twisted Kitaev spin chain (TKSC) as a minimal model of the compound CoNb_2O_6 reduced to a single zigzag chain [37,38], see Fig. 1(b). While the

material exhibits a nonaligned local and crystal axes [18,38], our minimal model neglects this subtlety but is meant to serve as a soluble example to illustrate the distinct coupling contributions. Since the minimal model is based on the symmetry properties of CoNb_2O_6 [37], the qualitative features of the signal are expected to remain similar, even though additional crystallographic details like interchain effects are neglected. The presence of magnetoelectric couplings in CoNb_2O_6 have been reported experimentally [34]. However, the details of their effects on the 2DCS response have not yet been investigated. In our model, interactions are governed by

$$H_{\text{TK}} = - \sum_{i=1}^{L/2} [J_1 \tilde{\sigma}_{2i-1}(\theta) \tilde{\sigma}_{2i}(\theta) + J_2 \tilde{\sigma}_{2i}(-\theta) \tilde{\sigma}_{2i+1}(-\theta)]. \quad (10)$$

Here, we define a rotated basis for the spin- $\frac{1}{2}$ variables to simplify notation, i.e., $\tilde{\sigma}_i(\theta) = \cos(\theta)\sigma_i^x + \sin(\theta)\sigma_i^y$. Also, J_1, J_2 denote positive ferromagnetic exchange couplings, which in the presence of finite dimerization can be of different strengths, e.g., as a result of an externally applied electric field [42,48,49]. Further, H_{TK} is exactly solvable via Jordan-Wigner mapping to spinless fermions. The ground-state phase diagram interpolates between two canted Ising ferromagnetic phases orientated along the $\hat{x}$ or $\hat{y}$ axes via tuning the zigzag angle θ [18,19,50].

To use the exact solubility, we chose the geometry of the spectroscopic setup such that the linearly polarized THz pulse propagates against the $\hat{y}$ direction, i.e., $\vec{k} \propto -\hat{y}$. We emphasize that our considerations above do not depend on these specific choices of the geometry. The $\vec{E}$ field points along $\hat{x}$, and magnetic field components are in the $\hat{z}$ direction, see Fig. 1(b). For this setup, the magnetic field couples directly via $M^z B^z$. Coupling the spin system to the electric field via $E^x P^x$, however, requires a nonzero polarization of the system.

For this, we identify microscopic polarizations in terms of spin operators. First, finite polarization of the sample can result from ES, if the system breaks inversion symmetry about the bond center. Second, polarization can emerge spontaneously in the system through the SC mechanism which is most pronounced in materials with strong spin-orbit coupling [32,43,46,51], thus also suitable for CoNb_2O_6 . For our TKSC Hamiltonian in Eq. (10), both contributions take the following forms:

$$P_{\text{ES}}^x \propto \sum_{i=1}^{L/2} (\tilde{\sigma}_{2i-1}(\theta) \tilde{\sigma}_{2i}(\theta) - \tilde{\sigma}_{2i}(-\theta) \tilde{\sigma}_{2i+1}(-\theta)), \quad (11)$$

$$P_{\text{SC}}^x \propto \sum_{i=1}^L (-1)^i \sin(\theta) (\sigma_i^y \sigma_{i+1}^x - \sigma_i^x \sigma_{i+1}^y). \quad (12)$$

Here, we omitted material-specific constants related to the amount of symmetry breaking due to dimerization as well as the magnitude of spin-orbit coupling. In practice, the precise coupling constants can be determined in different ways: The relevant couplings can be (i) extracted from complementary experimental data on the magnetoelectric properties of the sample, for example, the linear response; (ii) taken as variational parameters, which are tuned in theory simulations to match a given experimental measurement output; or (iii) computed from *ab initio* calculations on a given sample material. To highlight the signatures arising from polarization,

magnetization, or cross-coupling terms, we consider in the following the exemplary case where all effects contribute equally, i.e., setting all coupling constants to unity. While not universally true, typically, ES dominates over the polarization, resulting from SC effects in systems of broken inversion symmetry [29,46]. The functional form of the coupling enables us to compute the response of the system within the formalism of nested commutators, i.e., for the magnetic susceptibilities

$$\chi_{MM}^{M(2)}(t, t + \tau) \equiv -\theta(t)\theta(\tau)[[M^z(t + \tau), M^z(\tau)], M^z(0)] \quad (13)$$

and similar for polarization and all cross-couplings contributing to the polarization $P^{\text{NL}}(t)$ and magnetization $M^{\text{NL}}(t)$ response of Eqs. (4) and (5), see Appendix B.

V. SECOND-ORDER RESPONSE

First, we concentrate on the second-order response with polarization originating from ES. A nonzero P_{ES}^x will arise if inversion symmetry about the bond center is broken. To get a dominating $\chi^{(2)}$, we need to analyze the symmetries of our model. For $J_1 = J_2$, the system has glide symmetries $G_y = T_c e^{i\pi/2 \sum_i \sigma_i^y}$ and $G_x = T_c e^{i\pi/2 \sum_i \sigma_i^x}$, with T_c the translation operator by half a unit cell [37]. Since the ground state preserves G_x , it acts trivially on it. The coupling terms P_{ES}^x and M^z are odd under G_x , implying that even-order susceptibilities vanish [18] (see Appendix H). To obtain a nonzero $\chi^{(2)}$ response, we hence assume finite dimerization ($J_1 \neq J_2$) in the system, which explicitly breaks the glide symmetry. Dimerization could thereby result from a finite DC electric field applied to the system [42,48,49], or glide symmetry could be intrinsically broken in the material [44,52].

In Fig. 2, we show results for $J_2 = 1.5J_1$ comparing the measurement signals for a pure magnetic 2DCS response as calculated in previous works $\chi_{MM}^{M(2)}$ (a) and against the total response $\chi_{\text{total}}^{(2)}$ including electric field coupling obtained from Eq. (3) via ES P_{ES}^x at second order (b). To allow for a comparison of both results, we assume equal weights for polarization and magnetization, i.e., $a_E = b_E = 1$, and set all unknown coupling constants to order unity. Interestingly, we observe clear qualitative differences between both responses; for example, additional features for negative frequencies ω_τ can be attributed to cross-coupling terms. A more quantitative comparison is depicted in Figs. 2(c) and 2(d) with high-symmetry cuts in frequency space. Both the response of vanishing frequency ($\omega_t = 0$) and the diagonal response ($\omega_\tau = \omega_t$) show no characteristic features in the usually considered magnetic channel $\chi_{MM}^{M(2)}$. In contrast, contributions arising from ES (red lines) in Figs. 2(c) and 2(d) show three distinct peaks. The different signals refer to nonrephasing and THz rectification (TR) signals and can be understood from the spinon band structure [14,19,21,26], see Appendix I.

VI. THIRD-ORDER RESPONSE

Next, we explore signatures of SC polarizations in 2DCS. We assume that inversion symmetry is preserved such that

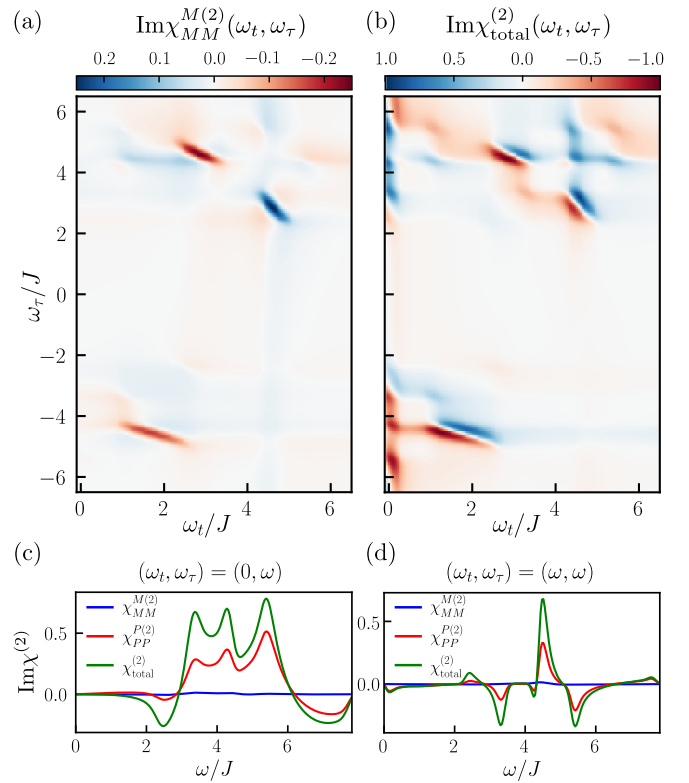


FIG. 2. Second-order response of a dimerized TKSC. We compare the imaginary part of (a) the pure magnetic response $\chi_{MM}^{M(2)}$ against (b) the total response $\chi_{\text{total}}^{(2)} = \chi_{MM}^{M(2)} + \chi_{PM}^{M(2)} + \chi_{MP}^{M(2)} + \chi_{PP}^{P(2)} + \chi_{MM}^{P(2)} + \chi_{PM}^{P(2)} + \chi_{MP}^{P(2)} + \chi_{PP}^{P(2)}$, including interactions with the electric field via ES at second order. (c) and (d) High-symmetry cuts through the 2D frequency space (ω_t, ω_τ) indicate additional signatures in the measurement response from electric and cross-coupling terms, absent in the pure magnetic response. (c) Along the ω_τ axis ($\omega_t = 0$), we can discriminate a vanishing response for magnetic-only coupling against nontrivial spectra of the polarization $\chi_{PP}^{P(2)}$ (red) and total response $\chi_{\text{total}}^{(2)}$. (d) Qualitatively similar results are found for diagonal cuts of the frequency plane ($\omega_t = \omega_\tau$). Characteristic signatures in the spectrum are present in pure polarization response $\chi_{PP}^{P(2)}$ and even amplified in the total response $\chi_{\text{total}}^{(2)}$. The magnetic response $\chi_{MM}^{M(2)}$ is featureless on comparable scales. For comparison of polarization and magnetization contributions, we consider equal geometric factors $a_E = b_E$. All results are derived for finite dimerization ($J_2 = 1.5J_1$) and number of sites $L = 220$.

P_{ES}^x vanishes and the response results from P_{SC}^x . As discussed above, for unbroken glide symmetry ($J_1 = J_2$), even-order susceptibilities vanish because G_x and inversion about the bond center act trivially on the ground state of the system, while the couplings M^z and P_{SC}^x are odd under G_x and bond inversion, respectively. Therefore, the leading contribution to the nonlinear response arises at third order. Analogously to the structure of the second-order expression, the third-order response for polarization and magnetization contains eight different terms each, for details, see Appendix B. Results for $\chi^{(3)}$ are shown in Fig. 3. We emphasize that, while the pure magnetic contribution $\chi_{MMM}^{M(3)}$ results mostly in broad features, see Fig. 3(a), coupling to the electric pump field via polarization P_{SC}^x adds sharp peaks to the spectrum, see Fig. 3(b).

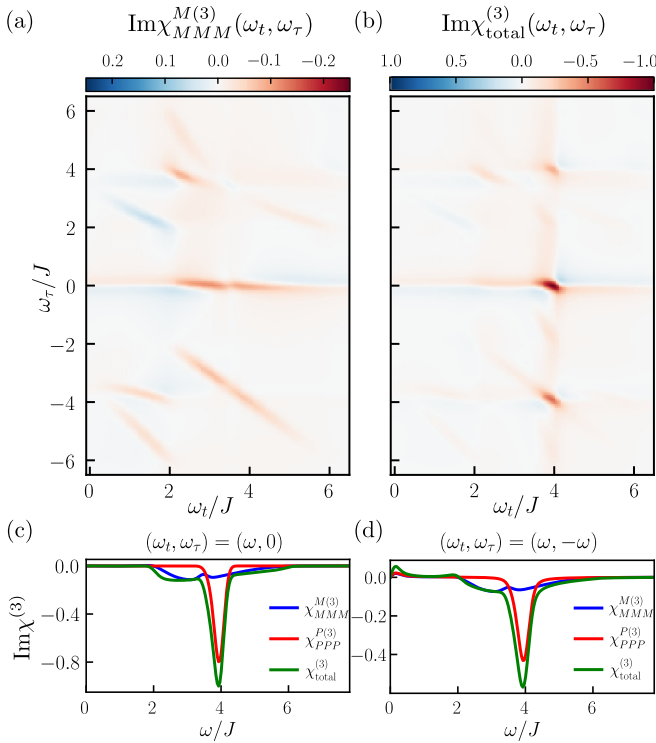


FIG. 3. Third-order nonlinear response of undimerized TKSC. (a) and (b) Comparison between the leading-order contribution to the nonlinear response of an undimerized ($J_1 = J_2$) TKSC. We contrast the imaginary part of response expected from (a) pure magnetic coupling $\chi_{MMM}^{(3)}$ (see Appendix B) against (b) the total response including all possible interactions with polarization P_{SC} arising from SC effects. The latter adds sharp features to the otherwise diffuse signatures. Note the different scales of color bars in (a) and (b). (c) and (d) Comparison along the (c) horizontal ($\omega_\tau = 0$) and (d) anti-diagonal ($\omega_t = -\omega_\tau$) reveals sharp peaks in the pure polarization response $\chi_{PPP}^{(3)}$ (see Appendix B; redlines) that are also reflected in the total signal (green line). For comparison of polarization and magnetization contributions, we consider equal weighting factors $a_E = b_E$.

Quantitative comparisons are best visualized in horizontal (c) and anti-diagonal (d) line cuts. Both show sharp resonance signals from pure electric coupling $\chi_{PPP}^{(3)}$, also clearly reflected in the total signal $\chi_{total}^{(3)}$, including cross-coupling terms. The different signals can be identified as pump-probe and rephasing contributions, and their intensities can be inferred from the spinon band structure, see Appendix I.

Our observations are expected to hold more generally. The coupling of a magnetic field to a spin system via a Zeeman term is not constrained by the symmetries of the underlying model. As a result, the purely magnetic response is expected to probe the full quasiparticle spectrum. For our exactly solvable model with free spinon excitations, this gives rise, for example, to broad features along the anti-diagonal, reflecting the finite spinon bandwidth. The infinite lifetime of the excitations is, moreover, encoded in sharp features of the signal along the diagonal direction [14]. In contrast, polarization couplings are directly tied to the symmetry properties of the model. Consequently, the associated spectral response is subject to selection rules, such that only specific parts of the spectrum can be accessed.

VII. DISCUSSION AND OUTLOOK

We have argued that 2DCS of quantum magnets not only probes the nonlinear magnetization but also polarization response as well as cross-coupling contributions. On the one hand, the hitherto overlooked polarization terms complicate the interpretation of experimental signatures, but we have provided protocols to quantify the role of polarization couplings. Concretely, a nonzero symmetric contribution with inverted $\vec{E}$ field provides direct evidence for the presence of magneto-electric couplings. In light of these contributing susceptibilities, it would be important to revisit previous theoretical calculations [14–23, 40, 41], e.g., whether signatures of nontrivial braiding statistics can still appear in the total 2DCS signal [20]. On the other hand, the direct coupling of 2DCS to the polarization opens avenues for probing quantum magnets. Once 2DCS experiments become more widely accessible, an optimized experimental protocol would consist of understanding the type and strength of polarization coupling in simpler, well-established experiments, e.g., linear response, before using the obtained information together with 2DCS probes to investigate in detail effects of, e.g., braiding statistics or quantum geometry in the material. A favorable way to thereby obtain large 2DCS signals in experiment could consist of exploring materials with large magnetoelectric couplings like multiferroic hexagonal manganites [53] or recent van der Waals magnets [54].

2DCS has been for a long time a powerful method for understanding complex molecules, and we hope that our work helps to establish it as a versatile tool for elucidating exotic excitations of quantum magnets.

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All authors contributed to conception, execution and write-up of this project [55].

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are openly available [55].

APPENDIX A: EMITTED FIELD IN TERMS OF POLARIZATION AND MAGNETIZATION

In this Appendix, we discuss our arguments for Eq. (3) in the main text by explicitly expressing the emitted electric field in terms of polarization and magnetization of a source. To derive this relation, we first emphasize that the emitted electromagnetic field can, in standard fashion, always be expanded into contributions arising from different spatial moments, as carried out in several textbooks [39,56]. Typically, the dominant contributions are given by electric and magnetic dipole radiation, which macroscopically create a natural link to the electric polarization and magnetization of the material. Depending on the limit of interest, i.e., the near-field or far-field approximation, the precise form of the relation between the emitted field and the source generally differs in its prefactors and phase information; the overall relation between the emitted field, polarization, and magnetization, however, is general.

To see this, we generalize the derivation discussed in Ref. [57] and first obtain a general wave equation for the electric field from Maxwell's equations. Inserting Ampère's law into Faraday's law yields [39]

$$\nabla(\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\mu_0 \frac{\partial \vec{J}}{\partial t} - \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}. \quad (\text{A1})$$

Furthermore, assuming charge neutrality in the system causes the first term to vanish according to Gauss's law, i.e.,

$$\nabla^2 \vec{E} - \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial \vec{J}}{\partial t}. \quad (\text{A2})$$

With this, we have obtained the standard wave equation relating the emitted electric field $\vec{E}$ to a source current $\vec{J}$. To connect $\vec{E}$ with the polarization $\vec{P}$ and magnetization $\vec{M}$, we must address which currents arise from the latter. Generally, a time-dependent polarization and a spatially varying magnetization induce a total current $\vec{J} = \partial_t \vec{P} + \nabla \times \vec{M}$. Hence, we find

$$\nabla^2 \vec{E} - \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2} + \mu_0 \nabla \times \frac{\partial \vec{M}}{\partial t}. \quad (\text{A3})$$

While this relation holds on general grounds, it is convenient to simplify the dependence in Eq. (A3) by making further assumptions regarding the functional forms of $\vec{P}(\vec{r}, t)$, $\vec{M}(\vec{r}, t)$, and $\vec{E}(\vec{r}, t)$. First, we assume that all quantities can be decomposed into a spatially and temporally slowly varying part and a rapidly oscillating part. Additionally, we fix a propagation direction $\vec{k}_{\text{sig}} \parallel \hat{z}$, i.e.,

$$\vec{E}(\vec{r}, t) = \vec{E}_{\text{sig}}(z) \exp(ik_{\text{sig}}z - i\omega_{\text{sig}}t). \quad (\text{A4})$$

Similar relations are assumed for $\vec{P}(\vec{r}, t)$ and $\vec{M}(\vec{r}, t)$. Moreover, in the near-field regime, all fields are expected to be in phase [39]

$$\vec{M}(\vec{r}, t) = \vec{M}_0 \exp(ik_{\text{sig}}z - i\omega_{\text{sig}}t), \quad (\text{A5})$$

$$\vec{P}(\vec{r}, t) = \vec{P}_{\text{sig}}(z) \exp(ik_{\text{sig}}z - i\omega_{\text{sig}}t). \quad (\text{A6})$$

For simplicity, we assume that the magnetization amplitude is position independent. Inserting Eqs. (A4)–(A6) into Eq. (A3), while neglecting rapidly oscillating terms and applying the dispersion relation $c = \omega_{\text{sig}}/k_{\text{sig}}$, we find

$$-2ik_{\text{sig}} \frac{\partial \vec{E}_{\text{sig}}(z)}{\partial z} = \mu_0 \omega_{\text{sig}}^2 \vec{P}(z) - \mu_0 \omega_{\text{sig}} \vec{k}_{\text{sig}} \times \vec{M}_0. \quad (\text{A7})$$

Assuming Δk to be the wave vector mismatch between the radiated field and the polarization, such that $\vec{P}(z) = \vec{P}_0 \exp(i\Delta kz)$, we obtain the solution by integrating the above differential equation over the interval $0 < z < l$

$$\vec{E}_{\text{sig}} \sim i\omega_{\text{sig}}l \left(\omega_{\text{sig}} e^{i\Delta kl/2} \text{sinc}(\Delta kl/2) \vec{P}_0 - \frac{1}{k_{\text{sig}}} \vec{k}_{\text{sig}} \times \vec{M}_0 \right). \quad (\text{A8})$$

In the case discussed in the main text, $\vec{M}_0$, $\vec{P}_0$, and $\vec{k}_{\text{sig}}$ form an orthogonal basis. This allows us to sum the individual contributions from magnetization and polarization without additional cross-terms. Furthermore, fixing a specific measurement position for the emitted electric field motivates the definition of geometric factors a_E and b_E , such that

$$E_{\text{sig}} = i(a_E P + b_E M). \quad (\text{A9})$$

We emphasize that relaxing certain assumptions is expected to modify Eq. (A9). For example, when transitioning from the near-field to the far-field approximation, the source fields and the emitted electric field are no longer expected to be in phase. Instead, a retardation effect occurs, which would enter Eq. (A9) and may require the parameters a_E and b_E to be complex. For more general problem settings, determining a_E and b_E can, in fact, be very challenging. Nevertheless, we emphasize once more that the overall structure—where both magnetization and polarization contribute to the response—remains independent of the specific details of the system.

APPENDIX B: SUSCEPTIBILITIES FROM NESTED COMMUTATORS

To define the response of the quantum magnet to the external pump pulses, we consider a time-dependent perturbation of the system Hamiltonian H by the electromagnetic field

$$H(t) = H + \sum_i a_i(t) X_i. \quad (\text{B1})$$

Here, $a_i(t)X_i$ includes polarization coupling to the electric field, i.e., $\vec{E}(t) \cdot \vec{P}$, and magnetization coupling to magnetic field components, i.e., $\vec{B}(t) \cdot \vec{M}$. The response of the system to the drive can be quantified by the evolution of a set of characteristic observables $\{O_\ell\}_\ell$. From response theory [10], we know that the evolution of such an observable O is associated with a set of susceptibilities $\chi^{O(n)}$ of different orders n , i.e.,

$$\begin{aligned} \Delta O(t) = & \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} ds_1 \cdots ds_n \sum_{i_1, \dots, i_n} \chi_{i_1, \dots, i_n}^{O(n)}(t - s_1, \dots, t - s_n) \\ & \times a_{i_1}(s_1) \cdots a_{i_n}(s_n). \end{aligned} \quad (\text{B2})$$

Retaining a causal structure, moreover, implies the condition of $\chi^{O(n)}$ being non-zero only if $t \geq s_1 \geq \dots \geq s_n$. The summation indices thereby run over all perturbations to the Hamiltonian $\{X_i\}$. For the scenario studied in the main text of having two perturbing fields ($\vec{E}$ and $\vec{B}$), this implies $i_1, \dots, i_n \in \{P, M\}$. We can therefore have two kinds of susceptibilities in the first order, four in the second order, and eight in the third order. Using the delta-like properties of the pump sequence in Eq. (1) yields first- and second-order contributions

$$\Delta O^{(1)}(t) = \chi_M^{O(1)}(t)B_0 + \chi_M^{O(1)}(t - \tau)B_\tau + \chi_P^{O(1)}(t)E_0 + \chi_P^{O(1)}(t - \tau)E_\tau, \quad (\text{B3})$$

$$\begin{aligned} \Delta O^{(2)}(t) = & \chi_{MM}^{O(2)}(B_0)^2 + \chi_{MM}^{O(2)}(B_\tau)^2 + \chi_{MM}^{O(2)}B_\tau B_0 \\ & + \chi_{PP}^{O(2)}(E_0)^2 + \chi_{PP}^{O(2)}(E_\tau)^2 + \chi_{PP}^{O(2)}E_\tau E_0 \\ & + \chi_{PM}^{O(2)}E_0 B_0 + \chi_{PM}^{O(2)}E_\tau B_\tau + \chi_{PM}^{O(2)}E_\tau B_0 \\ & + \chi_{MP}^{O(2)}B_0 E_0 + \chi_{MP}^{O(2)}B_\tau E_\tau + \chi_{MP}^{O(2)}B_\tau E_0. \end{aligned} \quad (\text{B4})$$

Here, we suppressed the temporal dependence in the susceptibilities in Eq. (B4) for simpler presentation of the individual contributions. The temporal arguments can, however, be deduced from the associated field components, see Eq. (B2), i.e., the last contribution to Eq. (B4) with all arguments reads $\chi_{MP}^{O(2)}(t - \tau, t)B_\tau E_0$. Note that this especially implies that the first two contributions to Eq. (B4) couple to the same susceptibility $\chi_{MM}^{O(2)}$, however, evaluated at different times. Computing the linear response is achieved by setting the intensity of one pump pulse to zero, i.e., $B_\tau = E_\tau = 0$ for ΔO_A or $B_0 = E_0 = 0$ for ΔO_B . The nonlinear part of the response is now given by the difference

$$\Delta O^{\text{NL}}(t) = \Delta O(t) - \Delta O_A(t) - \Delta O_B(t). \quad (\text{B5})$$

The latter only contains terms where fields evaluated at both pumping times $t = 0$ and $t = \tau$ show up simultaneously. At second order, this results in the responses for polarization and magnetization specified in Eqs. (4) and (5). At third order, the polarization and magnetization responses read

$$\begin{aligned} P^{(3)}(t + \tau) = & \chi_{PPP}^{P(3)}(t, t + \tau, t + \tau)E_\tau(E_0)^2 + \chi_{PPP}^{P(3)}(t, t, t + \tau)(E_\tau)^2E_0 + \chi_{PPM}^{P(3)}(t, t, t + \tau)(E_\tau)^2B_0 \\ & + \chi_{PPM}^{P(3)}(t, t + \tau, t + \tau)E_\tau E_0 B_0 + \chi_{PMP}^{P(3)}(t, t + \tau, t + \tau)E_\tau B_0 E_0 + \chi_{PMP}^{P(3)}(t, t, t + \tau)E_\tau B_\tau E_0 \\ & + \chi_{MPP}^{P(3)}(t, t + \tau, t + \tau)B_\tau(E_0)^2 + \chi_{MPP}^{P(3)}(t, t, t + \tau)(B_\tau)E_\tau E_0 + (M, B) \leftrightarrow (P, E), \end{aligned} \quad (\text{B6})$$

$$\begin{aligned} M^{(3)}(t + \tau) = & \chi_{MMM}^{M(3)}(t, t + \tau, t + \tau)B_\tau(B_0)^2 + \chi_{MMM}^{M(3)}(t, t, t + \tau)(B_\tau)^2B_0 + \chi_{MMP}^{M(3)}(t, t, t + \tau)(B_\tau)^2E_0 \\ & + \chi_{MMP}^{M(3)}(t, t + \tau, t + \tau)B_\tau B_0 E_0 + \chi_{MPM}^{M(3)}(t, t + \tau, t + \tau)B_\tau E_0 B_0 + \chi_{MPM}^{M(3)}(t, t, t + \tau)B_\tau E_\tau B_0 \\ & + \chi_{PMM}^{M(3)}(t, t + \tau, t + \tau)E_\tau(B_0)^2 + \chi_{PMM}^{M(3)}(t, t, t + \tau)E_\tau B_\tau B_0 + (P, E) \leftrightarrow (M, B). \end{aligned} \quad (\text{B7})$$

The first two contributions to Eq. (B6) contain only interactions with the E -field component of the pump and can hence be denoted as the purely electric response of the system at third order. Similarly, the first two terms of Eq. (B7) denote purely magnetic third-order response. Purely magnetic respectively electric contributions are compared with the total signal in Fig. 3.

To make quantitative predictions about the response, we are left to compute the susceptibilities $\chi^{O(n)}$ from the perturbations to the Hamiltonian $\{X_i\}$. This can be done using a generalized Kubo's formula

$$\chi_{X_1 X_2}^{O(2)}(t, t + \tau) = \frac{i^2}{L} \theta(t) \theta(\tau) \langle [[X_2(t + \tau), X_1(\tau)], O(0)] \rangle. \quad (\text{B8})$$

Generalizations to higher-order susceptibilities can be obtained by enlarging the nested commutator of Eq. (B8) to more operators.

APPENDIX C: SELECTION PROTOCOL FOR RESPONSE FUNCTIONS

As emphasized in the main text, the measurement response of the 2DCS protocol of Fig. 1(a) generically contains a superposition of different coupling contributions, including terms from correlations of one component of the electromag-

netic pulses as well as cross-correlations between electric and magnetic components. In the following, we outline protocols that allow us to differentiate between different contributions of the response. We show how to quantify the amount of polarization coupling in the system. We will highlight the consequences of (i) spatial inversion of the propagating THz pulse and (ii) rotation of the sample on the measurement outcome.

1. Inverting the propagation direction of the THz pulse

The general strategy will be to invert the sign of the electric field and to superimpose the measurement outcomes of the direct and inverted fields. This can be achieved by inverting the direction of pulse propagation, i.e., $\vec{k} \rightarrow -\vec{k}$. For the field components, spatial inversion is reflected in a mapping of the vector $\vec{E} \rightarrow -\vec{E}$, while for the pseudovector, it is $\vec{B} \rightarrow \vec{B}$. The induced polarization $P^{\text{NL}}(t | -\vec{E}, \vec{B})$ and magnetization $M^{\text{NL}}(t | -\vec{E}, \vec{B})$ for the new geometry obtain a minus sign in each component, where $\vec{E}$ appears at odd orders. In case of a dimerized chain, the leading-order contribution to the nonlinear response appears at second order, and only cross-correlations are affected by the changes in the experimental setup. The individual contributions can hence be isolated by feasible superposition of results according to Eqs. (6) and (7). By reversing the direction of pulse propagation, also the sign

of measured electric field will flip $E^{\text{NL}} \rightarrow -E^{\text{NL}}$. Considering how the measured electric field adds up from induced polarization and magnetization

$$E^{\text{NL}}(t|\vec{E}, \vec{B}) = i[a_E P^{\text{NL}}(t|\vec{E}, \vec{B}) + b_E M^{\text{NL}}(t|\vec{E}, \vec{B})], \quad (\text{C1})$$

we conclude that a_E, b_E transform as $a_E \rightarrow a_E$ and $b_E \rightarrow -b_E$. This results in an altered measured response

$$\begin{aligned} E^{\text{NL}}(t|\vec{E}, \vec{B}) \\ = i[a_E P^{\text{NL}}(t|\vec{E}, \vec{B}) - b_E M^{\text{NL}}(t|\vec{E}, \vec{B})]. \end{aligned} \quad (\text{C2})$$

Thus, adding and subtracting Eqs. (C1) and (C2) yields the symmetric and antisymmetric response in Eqs. (8) and (9). Explicitly writing out the symmetric component

$$\begin{aligned} E_{\text{sym}}^{\text{NL}}(t) &= i[a_E P_{\parallel}^{\text{NL}}(t) + b_E M_{\times}^{\text{NL}}(t)] \\ &= i[a_E (\chi_{PP}^{P(2)}(t - \tau, t) E_{\tau} E_0 + \chi_{MM}^{P(2)}(t - \tau, t) B_{\tau} B_0) \\ &\quad + b_E (\chi_{MP}^{M(2)}(t - \tau, t) B_{\tau} E_0 \\ &\quad + \chi_{PM}^{M(2)}(t - \tau, t) E_{\tau} B_0)]. \end{aligned} \quad (\text{C3})$$

From Eq. (C3), all the response functions on the right-hand side have a polarization operator appearing in the subscript, superscript, or both. This implies that $E_{\text{sym}}^{\text{NL}}$ would vanish if the P operator for the system vanishes. Thus, this protocol tells us whether the system would couple to an electric field.

2. Rotating the sample

A similar result can be obtained by rotation of the sample by 180° around the axis aligned with the magnetic field. While this leaves the magnetic and electric field components unaltered, the relative orientation between pulse and sample are modulated. We denote the spatial axes of real space by $\{x_r, y_r, z_r\}$ and that of the sample by $\{x_s, y_s, z_s\}$. When rotating the sample, this maps $\{x_s, y_s, z_s\} \rightarrow \{-x_s, -y_s, z_s\}$. While this leaves the magnetization pointing along the rotation axis untouched, the polarization response gets inverted. As a result, the couplings transform as $E^x, P^x \rightarrow -E^x, P^x$ and $B^z, M^z \rightarrow B^z, M^z$. This yields the same response as expected from an inversion of the propagation direction of the pulse propagation discussed above.

APPENDIX D: JORDAN-WIGNER TRANSFORMATION

To compute the 2DCS response of the TKSC, we derive the diagonal version of the Hamiltonian as well as magnetization and polarization operators. This can be achieved by an exact mapping from spins to spinless fermions via Jordan-Wigner transformation. The perturbation operators commute with the parity operator, and hence, we can solve the system in the sector of even parity containing the ground state [18,51,52,58]

$$\sigma_i^+ \equiv \frac{1}{2}(\sigma_i^x + i\sigma_i^y) = c_i \exp\left(i\pi \sum_{j=1}^{i-1} c_j^\dagger c_j\right), \quad (\text{D1})$$

$$\sigma_i^z = 1 - 2c_j^\dagger c_j. \quad (\text{D2})$$

The Hamiltonian in the fermionic basis is given by

$$\begin{aligned} H_{\text{TK}} &= - \sum_{i=1}^{L/2} [J_1 (e^{i2\theta} c_{2i-1}^\dagger c_{2i}^\dagger + c_{2i-1}^\dagger c_{2i}) \\ &\quad + J_2 (e^{-i2\theta} c_{2i}^\dagger c_{2i+1}^\dagger + c_{2i}^\dagger c_{2i+1}) + \text{H.c.}], \end{aligned} \quad (\text{D3})$$

and we use the mapping to momentum space via Fourier transform

$$c_{2j-1} = \sqrt{\frac{2}{L}} \sum_k e^{-ikj} a_k, \quad c_{2j} = \sqrt{\frac{2}{L}} \sum_k e^{-ikj} b_k, \quad (\text{D4})$$

with $k = 2\pi n/L$ and $n = -(\frac{L}{2} - 1), -(\frac{L}{2} - 3), \dots, (\frac{L}{2} - 1)$. The discrete k values have been chosen to account for antiperiodic boundary conditions in the even-parity sector. The Hamiltonian takes the form

$$H_{\text{TK}} = \sum_k [B_k a_k^\dagger b_{-k}^\dagger + A_k a_k^\dagger b_k - A_k^* a_k b_k^\dagger - B_k^* a_k b_{-k}], \quad (\text{D5})$$

where $A_k = -(J_1 + J_2 e^{ik})$ and $B_k = J_2 e^{i(k-2\theta)} - J_1 e^{i2\theta}$. Writing the Hamiltonian in Bogoliubov-de Gennes (BdG) form

$$\begin{aligned} H_{\text{TK}} &= \sum_{k>0} \psi_k^\dagger \Gamma_k \psi_k, \quad \text{with} \\ \Gamma_k &= \begin{pmatrix} 0 & 0 & S_k & P_k + Q_k \\ 0 & 0 & P_k - Q_k & -S_k \\ S_k^\dagger & P_k^\dagger - Q_k^\dagger & 0 & 0 \\ P_k^\dagger + Q_k^\dagger & -S_k^\dagger & 0 & 0 \end{pmatrix}, \end{aligned} \quad (\text{D6})$$

where we introduced the spinor notation $\psi_k^\dagger = (a_k^\dagger, a_{-k}, b_k^\dagger, b_{-k})$ and $S_k = -(J_1 + J_2 e^{ik})$, $P_k = -i(J_1 + J_2 e^{ik}) \sin(2\theta)$, $Q_k = -(J_1 - J_2 e^{ik}) \cos(2\theta)$ allows for a direct diagonalization of the form

$$H_{\text{TK}} = \sum_{k>0} [l_k (\alpha_k^\dagger \alpha_k - \alpha_{-k}^\dagger \alpha_{-k}) + \lambda_k (\beta_k^\dagger \beta_k - \beta_{-k}^\dagger \beta_{-k})]. \quad (\text{D7})$$

Here, we have defined l_k and λ_k as

$$l_k = \sqrt{\xi_k - \sqrt{\xi_k^2 - \tau_k^2}}, \quad \lambda_k = \sqrt{\xi_k + \sqrt{\xi_k^2 - \tau_k^2}}, \quad (\text{D8})$$

where $\xi_k = |P_k|^2 + |Q_k|^2 + |S_k|^2$ and $\tau_k = |P_k^2 - Q_k^2 + S_k^2|$. Examples for the resulting band spectrum and the associated density of states (DOS) are shown in Fig. 4 for the cases of undimerized ($J_2 = J_1$ upper panel) and dimerized ($J_2 = 1.5J_1$ lower panel) chains.

Similarly, we can express the magnetization and polarization operators in the basis of free fermions. The magnetization operator is given by

$$M^z = \frac{1}{2} \sum_{i=1}^L \sigma_i^z = \frac{1}{2} \sum_{i=1}^L (c_i c_i^\dagger - c_i^\dagger c_i), \quad (\text{D9})$$

which can be expressed in BdG form as

$$M^z = \sum_{k>0} \psi_k^\dagger \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \psi_k. \quad (\text{D10})$$

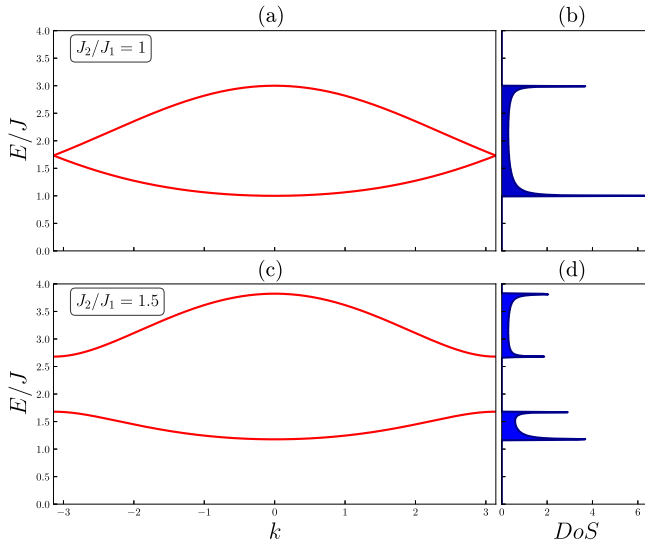


FIG. 4. Band spectrum of H_{TK} . We show the (a) dispersion and (b) DOS for an undimerized ($J_2 = J_1$) TKSC with two-site unit cell. (c) Dimerization ($J_2 = 1.5J_1$) results in a gap opening between the individual bands and (d) the emergence of two additional peaks in the corresponding DOS.

The polarization operator through the SC mechanism can be expressed in a similar fashion

$$P_{\text{SC}}^x = \sum_j (-1)^j \gamma \sin(\theta) (\sigma_j^y \sigma_{j+1}^x - \sigma_j^x \sigma_{j+1}^y) \\ \propto \sum_{j=1}^{L/2} 2i \sin(\theta) (c_{2j-1}^\dagger c_{2j} + c_{2j-1} c_{2j}^\dagger - c_{2j}^\dagger c_{2j+1} - c_{2j} c_{2j+1}^\dagger), \quad (\text{D11})$$

$$P_{\text{SC}}^x \propto \sum_{k>0} \psi_k^\dagger \begin{pmatrix} 0 & 0 & R_k & 0 \\ 0 & 0 & 0 & R_k \\ R_k^\dagger & 0 & 0 & 0 \\ 0 & R_k^\dagger & 0 & 0 \end{pmatrix} \psi_k, \quad (\text{D12})$$

with $R_k = -2i\gamma \sin(\theta)(1 + e^{ik})$.

The polarization operator through the ES mechanism can be found by calculating the change of the Hamiltonian due to variation of the external electric field $P = \frac{\partial H_{\text{TK}}}{\partial E_{\text{dc}}}$ [42,49]. Once we absorb the DC electric field in rescaled exchange interactions, we obtain

$$P_{\text{ES}}^x = g \sum_{i=1}^{L/2} [\tilde{\sigma}_{2i-1}(\theta) \tilde{\sigma}_{2i}(\theta) - \tilde{\sigma}_{2i}(-\theta) \tilde{\sigma}_{2i+1}(-\theta)]. \quad (\text{D13})$$

The corresponding spinor formulation of expression in Eq. (D13) can be obtained by setting $J_1 = -g$ and $J_2 = g$ in Eq. (D6).

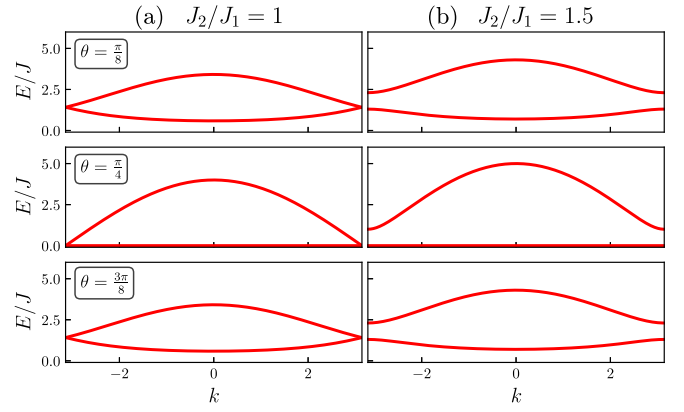


FIG. 5. Band spectra for a dimerized and undimerized TKSC. We plot the fermionic band spectrum obtained for H_{TK} diagonalizing the Hamiltonian in the space of free fermions. For (a) undimerized ($J_2 = J_1$) respectively (b) dimerized ($J_2 = 1.5J_1$) chains, we show band structures for zigzag angles $\theta = \{\frac{\pi}{8}, \frac{\pi}{4}, \frac{3\pi}{8}\}$. Both cases show similar characteristics in terms of the minimal excitation energies of the lower band, i.e., critical behavior with a flat gapless band at $\theta = \frac{\pi}{4}$. Effects of finite dimerization in (b) are, however, finite energy gaps between both fermionic bands.

APPENDIX E: PHASE DIAGRAM AND ENERGY SPECTRUM

As discussed in the main text, we consider the example of a TKSC [51,52]

$$H_{\text{TK}} = - \sum_{i=1}^{L/2} (J_1 \tilde{\sigma}_{2i-1}(\theta) \tilde{\sigma}_{2i}(\theta) + J_2 \tilde{\sigma}_{2i}(-\theta) \tilde{\sigma}_{2i+1}(-\theta)). \quad (\text{E1})$$

Here, L denotes the number of sites in the system, and $J_1, J_2 > 0$ are the ferromagnetic exchange couplings. The notation $\tilde{\sigma}_i(\theta) = \cos(\theta)\sigma_i^x + \sin(\theta)\sigma_i^y$ indicates a rotated basis of Pauli matrices. The Hamiltonian is solved exactly by mapping spins to free fermions (see main text). The excitations in the system are hence described by dressed-domain wall or spinons. Diagonalizing the fermionic Hamiltonian with a two-site unit cell yields the band spectra depicted in Figs. 5(a) and 5(b) for the cases of undimerized ($J_2 = J_1$) respectively dimerized ($J_2 = 1.5J_1$) chains. We plot the band structure for different values of the zigzag angle $\theta \in \{\frac{\pi}{8}, \frac{\pi}{4}, \frac{3\pi}{8}\}$. While we find a finite energy gap for $\theta = \frac{\pi}{8}, \frac{3\pi}{8}$, the theory at $\theta = \frac{\pi}{4}$ is critical and characterized by a flat gapless band. Interestingly, finite dimerization in the chain does not qualitatively change the characteristics of the overall energy gap; instead, it only causes a gap opening between both fermionic bands at the edges of the Brillouin zone, see Fig. 5(b). Extracting the energy gap ΔE , i.e., the minimal excitation energy for the lower fermionic band, as a function of θ and dimerization $\frac{J_2}{J_1}$, we find that the ground-state phase diagram of our system contains two distinct ferromagnetic phases orientated along the $\hat{x}$ respectively $\hat{y}$ directions. By tuning the zigzag angle θ of our chain, we can tune through the different phases, as emphasized in Fig. 6. Both ferromagnetic phases are separated by gapless lines in phase space at zigzag angles $\theta = \frac{\pi}{4}, \frac{3\pi}{4}$. As already indicated in Fig. 5, we find that finite dimerization

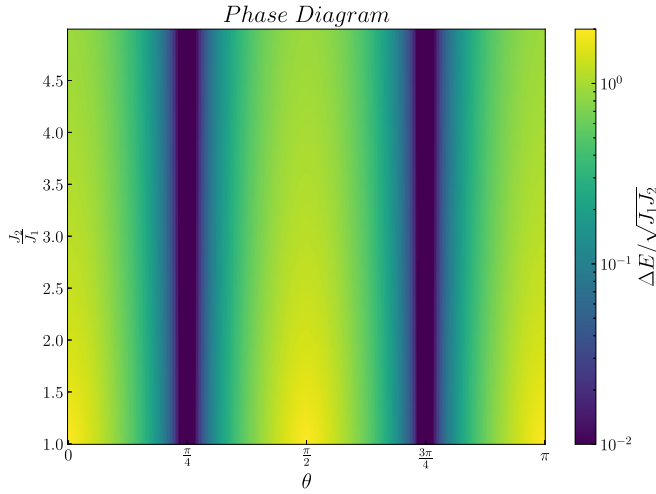


FIG. 6. Ground-state phase diagram of H_{TK} . We show the excitation gap ΔE in the model as a function of zigzag angle θ and dimerization J_2/J_1 . We identify critical lines in the phase diagram at $\theta = \frac{\pi}{4}$ and $\theta = \frac{3\pi}{4}$. Apart from that, the model exhibits ferromagnetic order oriented along the $\hat{y}$ direction for $\frac{\pi}{4} < \theta < \frac{3\pi}{4}$. For all other values of θ , we find ferromagnetism along the $\hat{x}$ direction. Notably, we find that changes in the dimerization do not result in gap closing and hence only smoothly transform the ground state.

in the chain does not change the overall character of the ground state, as changes in $\frac{J_2}{J_1}$ do not lead to gap closing. The ground state is thus given by a smooth deformation of the corresponding $\hat{x}$ - or $\hat{y}$ -polarized product states.

APPENDIX F: INDIVIDUAL CONTRIBUTIONS TO THE NONLINEAR SPECTROSCOPY RESPONSE

In the main text, we have emphasized that the total response measured in 2DCS experiments is added up from various contributions resulting from all different combinations of polarization and magnetization couplings. Here, we will focus on second-order contributions, which usually dominate the experimental response. In general, all second-order terms

are given by a functional form [10]

$$\chi_{XY}^{O(2)}(t, t + \tau) = \frac{i^2}{L} \theta(t) \theta(\tau) \langle [[Y(t + \tau), X(\tau)], O(0)] \rangle, \quad (F1)$$

where all operators O, X, Y represent either polarization P^x or magnetization M^z terms. The response spectrum is obtained from Eq. (F1) by performing a Fourier transformation in both the time delay for the second pump pulse τ as well as the evolution time t , see Appendix G for a precise definition. For the example of CoNb_2O_6 with inversion symmetry breaking, these operators are given by standard Zeeman coupling for magnetization $M^z = \sum_i \sigma_i^z$ and a polarization operator given by ES

$$P_{ES}^x \propto \sum_{i=1}^{L/2} (\tilde{\sigma}_{2i-1}(\theta) \tilde{\sigma}_{2i}(\theta) - \tilde{\sigma}_{2i}(-\theta) \tilde{\sigma}_{2i+1}(-\theta)), \quad (F2)$$

with $\tilde{\sigma}_i$ as defined for the Hamiltonian in Eq. (E1). We show all four contributions included in the polarization response in Fig. 7 and all contributions to the magnetization response in Fig. 8. It is worth noting that, while being computed individually, the shown contributions are not separately measurable in experiment. Conventional 2DCS experiments will always measure the electric field emitted by the sample using EOS. The latter is given by the sum of all terms shown in Figs. 7 and 8 weighted by the corresponding field strength and geometric factors assigned to the different terms, see main text. Applying, however, the symmetry protocol discussed in the main manuscript allows us to, moreover, access symmetric and antisymmetric combinations given by

$$\begin{aligned} \chi_{\text{sym}}^{(2)}(t - \tau, t) &= \chi_{PP}^{P(2)}(t - \tau, t) + \chi_{MM}^{P(2)}(t - \tau, t) \\ &+ \chi_{MP}^{M(2)}(t - \tau, t) + \chi_{PM}^{M(2)}(t - \tau, t), \quad (F3) \end{aligned}$$

$$\begin{aligned} \chi_{\text{asym}}^{(2)}(t - \tau, t) &= \chi_{MP}^{P(2)}(t - \tau, t) + \chi_{PM}^{P(2)}(t - \tau, t) \\ &+ \chi_{MM}^{M(2)}(t - \tau, t) + \chi_{PP}^{M(2)}(t - \tau, t), \quad (F4) \end{aligned}$$

representing the response for the case of equal geometric factors $a_E = b_E = 1$ and all field strengths of the THz pulse set to 1. Results for the response spectra $\chi_{\text{sym}}^{(2)}(\omega_t, \omega_\tau)$ and $\chi_{\text{asym}}^{(2)}(\omega_t, \omega_\tau)$ are shown in Figs. 9(a) and 9(b).

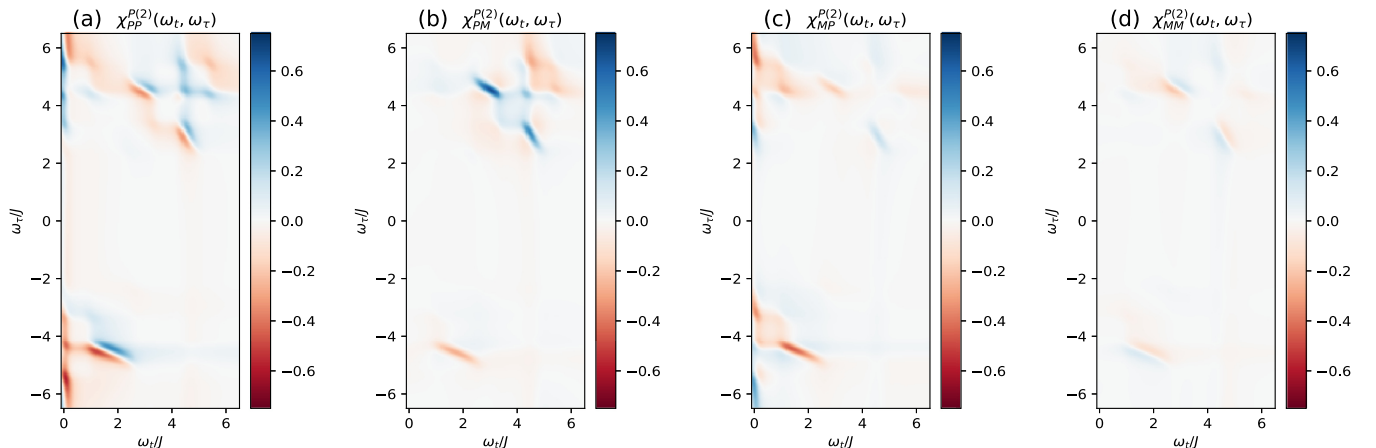


FIG. 7. Polarization response. We show the imaginary part of all contributions to the polarization response at second order including (a) the purely electric response, (b) and (c) cross-coupling contributions, and (d) the magnetic response.

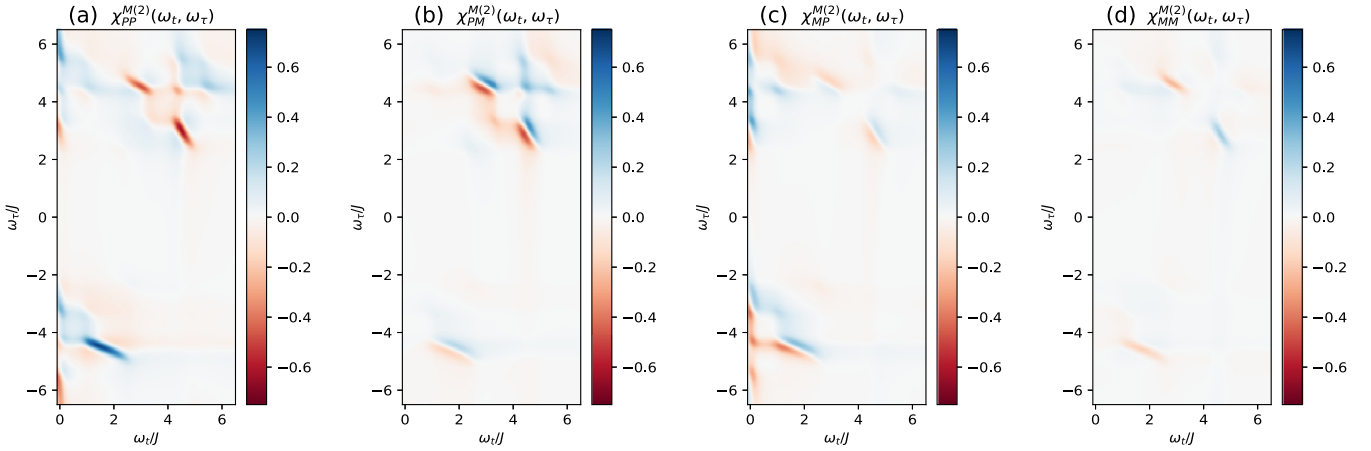


FIG. 8. Magnetization response. We show the imaginary part of all terms contributing to the magnetization response at second order including (a) the purely electric response, (b) and (c) cross-coupling contributions, and (d) the magnetic response.

APPENDIX G: FOURIER TRANSFORM

The datasets are obtained by evolving the system for time $t = 160/J$ and $\tau = 160/J$. We set $J = 1$ for our simulations and calculate the response functions at time intervals of $\Delta t = \Delta\tau = 0.4/J$. Therefore, we have $N^2 = 400^2$ points in the dataset. We then perform a discrete inverse Fourier transform to obtain Fourier components. For the second-order response functions, we have

$$\chi^{(2)}(\omega_t, \omega_\tau) = \frac{1}{N^2} \sum_{t, \tau} \chi^{(2)}(t, t + \tau) e^{i(\omega_t t + \omega_\tau \tau)}. \quad (\text{G1})$$

Here, the summation runs over all time steps $t, \tau \in \{0, \Delta t, \dots, (N-1)\Delta t\}$. As demonstrated in Eqs. (B6) and (B7), we can have two distinct limits in the third order. The corresponding Fourier components are given by

$$\chi^{(3,1)}(\omega_t, \omega_\tau) = \frac{1}{N^2} \sum_{t, \tau} \chi^{(3)}(t, t + \tau, t + \tau) e^{i(\omega_t t + \omega_\tau \tau)}, \quad (\text{G2})$$

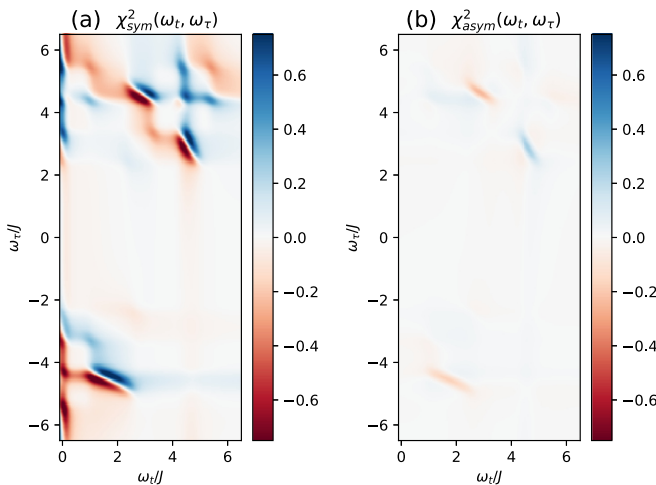


FIG. 9. Symmetric and antisymmetric channel for radiated electric field. We show the imaginary part of dominant second-order susceptibilities (a) $\chi_{sym}^{(2)}$ and (b) $\chi_{asym}^{(2)}$ contributing to the electric field emitted by the sample.

and

$$\chi^{(3,2)}(\omega_t, \omega_\tau) = \frac{1}{N^2} \sum_{t, \tau} \chi^{(3)}(t, t, t + \tau) e^{i(\omega_t t + \omega_\tau \tau)}. \quad (\text{G3})$$

Assuming the strengths of δ peaks at $t = 0$ and $t = \tau$ to be equal in the perturbing signal, see Eqs. (1) and (2), we can define $\chi^{(3)}(\omega_t, \omega_\tau)$ by adding the above two contributions

$$\chi^{(3)}(\omega_t, \omega_\tau) = \chi^{(3,1)}(\omega_t, \omega_\tau) + \chi^{(3,2)}(\omega_t, \omega_\tau). \quad (\text{G4})$$

APPENDIX H: SYMMETRY CONSIDERATIONS

As we will demonstrate in the following, a lot of information about the different susceptibilities can be deduced from symmetry properties of the Hamiltonian. For the undimerized case ($J_2 = J_1$), the Hamiltonian respects inversion symmetry along a bond center $\mathcal{I}$ as well as two glide symmetries $G_x = T_c \circ e^{i\pi/2 \sum_j^L \sigma_j^x} = T_c \circ \bigotimes_j (i\sigma_j^x)$ and $G_y = T_c \circ e^{i\pi/2 \sum_j^L \sigma_j^y} = T_c \circ \bigotimes_j (i\sigma_j^y)$. Here, T_c denotes translation by one lattice site. The two distinct ferromagnetic phases of the model, shown in Fig. 6, can thereby be distinguished via symmetry breaking of one of the glide symmetries. While, for example, the ground state of the $\hat{x}$ -ferromagnetic phase transforms trivially under $\mathcal{I}$ and G_x , it breaks G_y [18]. To analyze the response of the system, it is furthermore necessary to study the transformation properties of both polarization as well as the magnetization couplings under these symmetries.

1. Transformation properties of H_{TK} and P_{ES}^x

To analyze the transformation properties of H_{TK} in Eq. (E1) and P_{ES}^x in Eq. (F2) under glide symmetry G_x , it is useful to determine how $\tilde{\sigma}_i(\theta) = \cos(\theta)\sigma_i^x + \sin(\theta)\sigma_i^y$ transforms. We find $\tilde{\sigma}_i(\theta) \mapsto G_x^{-1} \tilde{\sigma}_i(\theta) G_x = \tilde{\sigma}_{i+1}(-\theta)$. This confirms that H_{TK} in fact transforms trivially under G_x , while P_{ES}^x accumulates a minus sign from the transformation. Conclusions for transformation with respect to G_y follow the same strategy and yield the same symmetry properties.

Next, we analyze the transformation properties under inversion along a bond center $\mathcal{I}$. To this end, it is convenient to label the sites symmetrically using indices $i \in \{-\frac{L}{2}, \frac{L}{2}\}$. As a

result, inversion along the center bond, linking sites 0 and 1, takes $\tilde{\sigma}_i \mapsto I^{-1}\tilde{\sigma}_i I = \tilde{\sigma}_{-i+1}$

$$\begin{aligned}
 I^{-1}H_{\text{TK}}I &= -I^{-1}\sum_{i=-L/4}^{L/4}[J_1\tilde{\sigma}_{2i-1}(\theta)\tilde{\sigma}_{2i}(\theta) \\
 &\quad + J_2\tilde{\sigma}_{2i}(-\theta)\tilde{\sigma}_{2i+1}(-\theta)]I \\
 &= -\sum_{i=-L/4}^{L/4}[J_1\tilde{\sigma}_{-2i+2}(\theta)\tilde{\sigma}_{-2i+1}(\theta) \\
 &\quad + J_2\tilde{\sigma}_{-2i+1}(-\theta)\tilde{\sigma}_{-2i}(-\theta)] \\
 &= -\sum_{j=-L/4}^{L/4}[J_1\tilde{\sigma}_{2j+1}(\theta)\tilde{\sigma}_{2j+2}(\theta) \\
 &\quad + J_2\tilde{\sigma}_{2j}(-\theta)\tilde{\sigma}_{2j+1}(-\theta)] = H_{\text{TK}}. \quad (\text{H1})
 \end{aligned}$$

Thus, H_{TK} is invariant under I for all J_2/J_1 , and the same holds for P_{ES}^x .

2. Transformation properties of P_{SC}^x

As we will emphasize in the following, the different form of

$$P_{\text{SC}}^x = \gamma \sum_i^L (-1)^i \sin(\theta) (\sigma_i^y \sigma_{i+1}^x - \sigma_i^x \sigma_{i+1}^y) \quad (\text{H2})$$

compared with P_{ES}^x leads to different transformation properties [32]. Under G_x , the P_{SC}^x operator transforms trivially, i.e.,

$$\begin{aligned}
 G_x^{-1}P_{\text{SC}}^x G_x &= \gamma \bigotimes_j (-i\sigma_j^x) T_c^{-1} \sum_i^L (-1)^i \sin(\theta) \\
 &\quad \times (\sigma_i^y \sigma_{i+1}^x - \sigma_i^x \sigma_{i+1}^y) T_c \bigotimes_j (i\sigma_j^x) \\
 &= \gamma \bigotimes_j (-i\sigma_j^x) \sum_i^L (-1)^i \sin(\theta) \\
 &\quad \times (\sigma_{i+1}^y \sigma_{i+2}^x - \sigma_{i+1}^x \sigma_{i+2}^y) \bigotimes_j (i\sigma_j^x) \\
 &= \gamma \sum_i^L (-1)^{i+1} \sin(\theta) (\sigma_{i+1}^y \sigma_{i+2}^x - \sigma_{i+1}^x \sigma_{i+2}^y) \\
 &= P_{\text{SC}}^x.
 \end{aligned}$$

Under inversion I , the polarization P_{SC}^x , however, flips sign

$$\begin{aligned}
 I^{-1}P_{\text{SC}}^x I &= \gamma I^{-1} \sum_{i=-L/2}^{L/2} (-1)^i \sin(\theta) (\sigma_i^y \sigma_{i+1}^x - \sigma_i^x \sigma_{i+1}^y) I \\
 &= \gamma \sum_{i=-L/2}^{L/2} (-1)^i \sin(\theta) (\sigma_{-i+1}^y \sigma_{-i}^x - \sigma_{-i+1}^x \sigma_{-i}^y) \\
 &= -\gamma \sum_{j=-L/2}^{L/2} (-1)^j \sin(\theta) (\sigma_j^y \sigma_{j+1}^x - \sigma_j^x \sigma_{j+1}^y) \\
 &= -P_{\text{SC}}^x.
 \end{aligned}$$

TABLE I. Symmetry properties. Transformation properties of undimerized Hamiltonian H_{TK} and coupling terms M^z , P_{ES}^x , and P_{SC}^x under the symmetries I , G_x , G_y . Entries denote the eigenvalues ξ under transformation $O \mapsto U^{-1}OU = \xi O$.

$\backslash O$	H_{TK}	M^z	P_{ES}^x	P_{SC}^x
I	+1	+1	+1	-1
G_x	+1	-1	-1	+1
G_y	+1	-1	-1	+1

A summary of all symmetry properties of Hamiltonian H_{TK} , polarization operators P_{SC}^x and P_{ES}^x , as well as magnetization coupling M^z is shown in Table I.

3. Even-order susceptibilities for undimerized system

As emphasized before, both the Hamiltonian H_{TK} and the ground state of the system $|0\rangle$ respect inversion symmetry. For both ferromagnetic phases, there is, moreover, one glide symmetry which is preserved by H_{TK} and $|0\rangle$, while the other glide symmetry gets spontaneously broken by the ground state. Thus, we can always find a combined symmetry transformation $U \equiv G_\alpha \circ I$ which leaves H_{TK} and $|0\rangle$ invariant. According to Table I, the coupling terms M^z , P_{ES}^x , and P_{SC}^x are, however, odd under U . Applying this symmetry transformation to even-order susceptibilities as, for example, the second-order contribution $\chi_{XY}^{(2)}$ from Eq. (F1), we find

$$\begin{aligned}
 \chi_{XY}^{(2)}(t, t + \tau) &= \frac{i^2}{L} \theta(t) \theta(\tau) \langle 0 | U [[U^{-1}Y(t + \tau)U, \\
 &\quad \times U^{-1}X(\tau)U], U^{-1}O(0)U] U^{-1} | 0 \rangle \\
 &= \frac{i^2}{L} \theta(t) \theta(\tau) \\
 &\quad \times \langle 0 | [[-Y(t + \tau), -X(\tau)], -O(0)] | 0 \rangle \\
 &= -\chi_{XY}^{(2)}(t, t + \tau),
 \end{aligned}$$

where we used the fact that U commutes with the time evolution of the operators $X, Y, O \in \{M^z, P_{\text{ES}}^x, P_{\text{SC}}^x\}$ in the Heisenberg picture governed by H_{TK} and applied the transformation properties of Table I. As a result, all even-order susceptibilities are expected to vanish if H_{TK} respects glide symmetries as well as inversion. As discussed in the main text, we can explicitly break the glide symmetry of the model by considering finite dimerization ($J_2 \neq J_1$), which will result in finite contributions to the nonlinear response at second order.

4. Second-order susceptibilities for dimerized system

If we take $P = P_{\text{SC}}$ even for the dimerized system, all second-order susceptibilities with a polarization index vanish. That $\chi_{PP}^{(2)}$, $\chi_{MP}^{(2)}$, $\chi_{PM}^{(2)}$, and $\chi_{MM}^{(2)}$ must vanish follows from symmetry arguments. As shown before, P_{SC} is odd under I , while M^z and the ground state transform trivially under I . Thus, any susceptibility with P_{SC} appearing an odd number of times vanishes. This can be demonstrated explicitly

$$\begin{aligned}
 \chi_{MM}^{(2)}(t, t + \tau) &= \frac{i^2}{L} \theta(t) \theta(\tau) \times \langle 0 | [M(t + \tau), M(\tau)], P(0) \rangle \\
 &= \frac{i^2}{L} \theta(t) \theta(\tau) \times \langle 0 | I [[I^{-1}M(t + \tau)I,
 \end{aligned}$$

$$\begin{aligned}
& \times I^{-1}M(\tau)I, I^{-1}P(0)I]I^{-1}|0\rangle \\
& = \frac{i^2}{L}\theta(t)\theta(\tau)\langle 0|[[M(t+\tau), M(\tau)], -P(0)]|0\rangle \\
& = -\chi_{MM}^{P(2)}(t, t+\tau),
\end{aligned}$$

Similarly, we can show $\chi_{PP}^{P(2)}$, $\chi_{MP}^{M(2)}$, and $\chi_{PM}^{M(2)}$ vanish.

It remains to show $\chi_{PP}^{M(2)}$, $\chi_{MP}^{P(2)}$, and $\chi_{PM}^{P(2)}$ vanish. As checked by analytic calculation, when expressed in the eigenbasis of the Hamiltonian, time evolved P_{SC} is antidiagonal, and M^z has vanishing diagonal terms. When such matrices are substituted in the nested commutator formulas for $\chi_{PP}^{M(2)}$, $\chi_{MP}^{P(2)}$, and $\chi_{PM}^{P(2)}$, the resulting matrix has a vanishing diagonal. Taking the expectation value over the ground state involves summing over those diagonal entries that correspond to negative energies. Since all the diagonal entries are zero, this implies that the response functions vanish.

This is not the case for $P = P_{ES}$. Hence, we used $P = P_{ES}$ for second-order calculations in the main text.

APPENDIX I: HIGH-SYMMETRY CONTRIBUTIONS TO NONLINEAR RESPONSE SIGNAL

In this Appendix, we explain the high-symmetry cuts shown in Figs. 2 and 3. The three peaks in Figs. 2(c) and 2(d) reflect the distinct spinon pair excitations possible [19]

(see Fig. 4). The diagonal peaks and those along the ω_τ axis correspond to nonrephasing and TR signals, respectively [14,21,26]. The latter arise from signals oscillatory only in τ , with ω_τ acting as the pump frequency and ω_t as the detection frequency. The broad spectrum due to pure magnetic contribution in Figs. 3(c) and 3(d) emerges from excitations with both spinons in the same band. The electric field coupling introduces sharp peaks to the total response as it excites spinon pairs with spinons from different bands and the two-spinon DOS peaks for such an excitation. The peaks along the antidiagonal being oscillatory in $t - \tau$ are perfectly rephasing as the phase acquired in time t is perfectly canceled by τ . They correspond to the spinon-echo signal [14,26,59]. The signal along the horizontal axis oscillates only in t and with ω_τ and ω_t as pumping and detecting frequency, respectively, can be considered a pump-probe signal [14,26]. The perfectly rephasing signal arises from the terms $\sin[\lambda_k(\tau - t)]$ and $\sin[l_k(\tau - t)]$ from $\chi_{MMM}^{M(3)}$ and $\sin[(\lambda_k + l_k)(\tau - t)]$ from $\chi_{PPP}^{P(3)}$, whereas the terms responsible for pump-probe signal are $\sin(\lambda_k t)$ and $\sin(l_k t)$ from $\chi_{MMM}^{M(3)}$ and $\sin[(\lambda_k + l_k)t]$ from $\chi_{PPP}^{P(3)}$, all of which have k -dependent coefficients. At second order, the TR signal peaks result from terms $\cos[(\lambda_k + l_k)\tau]$, $\cos(2l_k\tau)$, and $\cos(2\lambda_k\tau)$, and nonrephasing signals are a consequence of terms $\cos[(\lambda_k + l_k)(\tau + t)]$, $\cos[2l_k(\tau + t)]$, and $\cos[2\lambda_k(\tau + t)]$ associated with $\chi_{PP}^{P(2)}$.

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