# Raman Scattering Signatures of Kitaev Spin Liquids in $A_2IrO_3$ Iridates with $A =$ Na or Li

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We show how Raman spectroscopy can serve as a valuable tool for diagnosing quantum spin liquids (QSL). We find that the Raman response of the gapless QSL of the Kitaev-Heisenberg model exhibits signatures of spin fractionalization into Majorana fermions, which give rise to a broad signal reflecting their density of states, and $Z_2$ gauge fluxes, which also contribute a sharp feature. We discuss the current experimental situation and explore more generally the effect of breaking the integrability on response functions of Kitaev spin liquids.

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*Introduction.*—Frustrated magnetic materials show a wide variety of exotic cooperative quantum phenomena. Frustration can arise when interactions are incompatible with the geometry of the underlying lattice, or as a result of competing interactions. An example of the latter is given by the celebrated Kitaev model [1], which harbors gapless and gapped quantum spin liquids (QSL) states. Only a few known theoretical models to date possess quantum spin-liquid states. Among those the Kitaev model stands out, being exactly solvable in two dimensions (2D). More importantly, it provides valuable insights into the physics of a broader class of spin liquids with Majorana fermions coupled to $Z_2$ gauge fields. There is a number of known integrable generalizations of the model having spin-disordered ground states [2–4], and even its three-dimensional (3D) analogies [5–8].

Because of the simplicity of the Kitaev model Hamiltonian it is likely that its physics can be realized in nature. A number of theoretical proposals suggest that some materials with strong spin-orbit coupling, such as 2D and 3D $A_2IrO_3$ compounds, where $A =$ Na, Li, are possible candidates [9–13]. Because of spin-orbit interactions, the atomic ground state of $Ir^{4+}$ ions is a Kramers doublet, where the spin and the orbital angular momentum are entangled, giving rise to bond-dependent interactions. Since in these compounds the $Ir^{4+}$ ions form either weakly coupled hexagonal layers as in $Na_2IrO_3$ and $\alpha-Li_2IrO_3$, or honeycomb strips with alternating orientation, as in 3D $\beta-$ and $\gamma-Li_2IrO_3$, they might realize the Kitaev model, albeit having extra interactions. While at present all known materials are magnetically ordered at low temperatures, there is evidence that some of them (especially the ones having a 3D structure) are very close to the QSL regime [12,13]. Moreover, residual high energy features of the QSL seem to have been already observed in magnetically ordered systems [14].

The minimal model of $A_2IrO_3$ compounds is the Kitaev-Heisenberg (KH) model, which contains both the anisotropic ferromagnetic Kitaev interaction $J_K$ and the isotropic antiferromagnetic Heisenberg exchange $J_H$. The strength of the interactions in these materials have been estimated by *ab initio* quantum chemistry [15], and by microscopic superexchange calculations [16]. In addition, recent theoretical studies indicate that the QSL phase of the Kitaev model is stable with respect to small Heisenberg perturbations [10,17–19].

Raman scattering is a valuable tool for understanding antiferromagnetically ordered transition metal oxides because its polarization dependence allows us to probe different symmetry properties of the underlying magnetic state [20], e.g., in frustrated triangular antiferromagnets [21,22], and in high-$T_c$ superconductor parent compounds [23–26]. In Mott insulators, the Raman process couples a dynamically induced electron-hole pair with "two-magnon states" which reflect the underlying magnetic phase even if a simple spin wave picture of the low energy excitations is not applicable, e.g., in one-dimensional spin chains [27] and 2D QSLs [28,29]. In general, due to the lack of local order a very weak polarization dependence is conjectured to be one of the key signatures of QSLs [28]. Indeed, recent Raman scattering experiments revealed spin-liquid-like features in the Heisenberg spin $1/2$ kagome-lattice antiferromagnet, Herbertsmithite $ZnCu_3(OH)_6Cl_2$ [30].

Clearly, a detailed quantitative analysis of Raman scattering in a spin liquid is called for, not least because the experimental task of diagnosing QSLs remains a challenge. In this Letter, we report on our theoretical study of inelastic Raman scattering in a QSL, which is done in the framework of the Kitaev-Heisenberg model, and in the limit of small Heisenberg exchange [10]. Given the difficulty of neutron scattering experiments with compounds hosting iridium ions [31], our study may be of special interest for the $A_2IrO_3$ series. The central result of this Letter is the identification of signatures of quasiparticle fractionalization, a hallmark of topologically ordered phases, in the dynamical Raman scattering response. To leading order in the Heisenberg exchange, and in the Majorana fermion density of states, we obtain the dominant contributions to the response $I(\omega) = I_K(\omega) + I_H(\omega)$. Here, $I_K(\omega)$ originates from the Kitaev exchange, and $I_H(\omega)$ is the result of the Heisenberg perturbation. Our approximation amounts to taking the ground state of the integrable Kitaev model as the ground state of the KH model. However, the calculation of the response goes a step beyond integrability by including contributions to the Raman response that arise from integrability-breaking Heisenberg terms.

In the remainder of the Letter, after introducing the KH model, we present the derivation of the Raman vertex. We then outline the calculation of $I_K$ and $I_H$, and discuss their characteristic features. We close with remarks on the relevance of our results to a broader class of Hamiltonians and observables.

*The model.*—The Hamiltonian of the KH model reads

$$\hat{\mathcal{H}} = -J_K \sum_{\langle ij\rangle_a} \hat{\sigma}_i^a \hat{\sigma}_j^a + J_H \sum_{\langle ij\rangle} \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j, \tag{1}$$

which reduces to the original Kitaev model for $J_H = 0$. As shown in Kitaev's seminal work, the model can be solved exactly in this limit by representing the spin-1/2 operators $\hat{\sigma}_i^a$ in terms of four Majorana fermions $\hat{b}_i^x, \hat{b}_i^y, \hat{b}_i^z$, and $\hat{c}_i$ such that $\hat{\sigma}_i^a = i\hat{c}_i\hat{b}_i^a$, which satisfy the anticommutation relations, $\{\hat{b}_i^a, \hat{b}_j^{a'}\} = 2\delta_{ij}\delta_{a,a'}$, $\{\hat{c}_i, \hat{c}_j\} = 2\delta_{ij}$, and $\{\hat{c}_i, \hat{b}_j^a\} = 0$. For our purposes it is convenient to introduce complex bond fermions $\hat{\chi}^\dagger_{\langle ij\rangle_a} = (\hat{b}_i^a - i\hat{b}_j^a)/2$, by combining two $\hat{b}$ Majorana operators on adjacent sites. The Kitaev contribution in Eq. (1) then takes the form

$$\hat{\mathcal{H}}_K = iJ_K \sum_{\langle ij\rangle_a} \hat{u}_{\langle ij\rangle_a} \hat{c}_i \hat{c}_j, \tag{2}$$

where bond operators $\hat{u}_{\langle ij\rangle_a} = i\hat{b}_i^a\hat{b}_j^a = 2\hat{\chi}^\dagger_{\langle ij\rangle_a}\hat{\chi}_{\langle ij\rangle_a} - 1$ are constants of motion for $\hat{\mathcal{H}}_K$, i.e., $[\hat{\mathcal{H}}_K, \hat{u}_{\langle ij\rangle_a}] = 0$. The Hilbert space in which $\hat{\mathcal{H}}_K$ acts can now be decomposed into the gauge $|F\rangle$ and matter $|M\rangle$ sectors. We denote the ground state of $\hat{\mathcal{H}}_K$ by $|0\rangle = |F_0\rangle \otimes |M_0\rangle$, in which $\hat{u}_{\langle ij\rangle_a}|F_0\rangle = +1|F_0\rangle$; i.e., we replace the bond operators by their ground-state eigenvalues $+1$. The Kitaev part of the Hamiltonian then assumes a quadratic form in Majorana fermions $\hat{c}_i$, and can be diagonalized. To this end, we first combine two Majorana $\hat{c}$ fermions from two sublattices in the unit cell to form a complex fermion (a matter fermion) $\hat{f}_{\mathbf{r}} = (\hat{c}_{A,\mathbf{r}} + i\hat{c}_{B,\mathbf{r}})/2$. After a Fourier transform, followed by a Bogoliubov transformation $\hat{f}_{\mathbf{q}} = \cos\theta_{\mathbf{q}}\hat{a}_{\mathbf{q}} + i\sin\theta_{\mathbf{q}}\hat{a}^\dagger_{-\mathbf{q}}$, the Hamiltonian of Eq. (2) in the ground-state flux sector is diagonalized $\hat{\mathcal{H}}_0 = \hat{\mathcal{H}}_{K,F_0} = \sum_{\mathbf{q}}|s_{\mathbf{q}}|(2\hat{a}^\dagger_{\mathbf{q}}\hat{a}_{\mathbf{q}} - 1)$, where $s_{\mathbf{q}} = J_K(1 + e^{i\mathbf{q}\cdot\mathbf{n}_1} + e^{i\mathbf{q}\cdot\mathbf{n}_2})$, and $\tan 2\theta_{\mathbf{q}} = -\mathrm{Im}[s_{\mathbf{q}}]/\mathrm{Re}[s_{\mathbf{q}}]$. The primitive lattice vectors $\mathbf{n}_1$, $\mathbf{n}_2$ are shown in Fig. 1. The ground state of the matter sector $|M_0\rangle$ is defined by the condition that $\hat{a}_{\mathbf{q}}|M_0\rangle = 0$ for all $\mathbf{q}$, and the ground-state energy $E_0 = -\sum_{\mathbf{q}}|s_{\mathbf{q}}|$.

We note that the Hamiltonian $\hat{\mathcal{H}}_K$ defined in Eq. (2) acts in the enlarged Hilbert space, and has a local $Z_2$ gauge invariance. The fermionic spectrum can thus be enumerated by the configurations $\{\phi_{\hexagon}\}$ of $Z_2$ fluxes on hexagons; here $\phi_{\hexagon} = \prod_{\langle ij\rangle\in\hexagon} u_{ij}$ is a product of bond variables. The fermionic ground state lives in the flux-free sector, i.e., when $\phi_{\hexagon} = +1$ on all hexagons. The physical states $|\Psi_{\mathrm{phys}}\rangle = \hat{P}|\Psi\rangle$ are defined using a projector $\hat{P} = \frac{1}{2}\hat{P}'[1 + (-1)^{N_\chi}(-1)^{N_f}]$, where $\hat{P}'$ is the sum of all operators which change bond fermion numbers in an inequivalent way [2], and $N_{\chi/f}$ denote bond or matter fermion number operators. For a given state the total parity of $N_\chi + N_f$ is always even and is a conserved quantity, whereas the parity of the corresponding bond or matter sectors can change as a result of a gauge transformation. In the remainder we use the property that for a large class of operators, namely, those that do not change the bond fermion number, the matrix elements in projected and unprojected states are the same [32–34].

Upon addition of small nonzero Heisenberg exchanges to the Hamiltonian ($J_H \neq 0$), the Kitaev QSL states remain stable, with ultra-short-ranged (nearest neighbor only) spin correlations replaced by exponentially decaying ones [10,17]. We assume in the following that $\lambda = J_H/J_K \ll 1$ and take into account the Heisenberg terms, perturbatively.

*Raman operator.*—We derive the Raman vertex operator along the lines of the Loudon-Fleury approach [35,36]. The vertex is given by the photon-induced superexchange, which for the KH model, contains two contributions $\hat{\mathcal{R}} = \hat{\mathcal{R}}_K + \hat{\mathcal{R}}_H$ (the counterpart of the Loudon-Fleury vertex for the Heisenberg model)

$$\hat{\mathcal{R}} = \sum_{\langle ij\rangle_a} (\hat{\boldsymbol{\epsilon}}_{\mathrm{in}} \cdot \mathbf{d}_a)(\hat{\boldsymbol{\epsilon}}_{\mathrm{out}} \cdot \mathbf{d}_a)(K_K \hat{\sigma}_i^a \hat{\sigma}_j^a + K_H \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j), \tag{3}$$

where $\mathbf{d}_a$ denote lattice vectors, and $\hat{\boldsymbol{\epsilon}}_{\mathrm{in/out}}$ are polarization vectors of the incident or outgoing photons. The constants $K_K \propto J_K$ and $K_H \propto J_H$, hence, $\lambda = K_H/K_K \ll 1$.

The Raman response of the KH model (1) is related to the Fourier transform $I(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} iF(t)$ of the correlation function $iF(t) = \langle \hat{\mathcal{R}}(t)\hat{\mathcal{R}}(0)\rangle$, where the average is taken with respect to the ground state $|\Psi_0\rangle$ of the KH Hamiltonian, and the operators $\hat{\mathcal{R}}(t)$ are given in their

Heisenberg representation. After switching to the interaction representation treating $\hat{\mathcal{H}}_H$ as the interaction, the correlation function assumes the form

$$F(t) = -i\langle 0|T_K[\hat{\mathcal{R}}(t)\hat{\mathcal{R}}(0)e^{-i\int_{C_K}\hat{\mathcal{H}}_H(t')dt'}]|0\rangle, \quad (4)$$

where time-ordering $T_K$ and the integral are calculated along the Keldysh contour (with the Heisenberg term adiabatically switched on and off at $t \to -\infty$). Note that the expectation value is taken with respect to the ground state $|0\rangle$ of the Kitaev Hamiltonian Eq. (2). Starting from Eq. (4) we perturbatively compute the response by expanding the exponent in powers of $\lambda = J_H/J_K$; see Supplemental Material [37]. To leading order in $\lambda$, and neglecting long-range correlations of the Majorana fermions containing higher order terms in density of states, we obtain two dominant contributions to the response $F(t) \approx F_K(t) + F_H(t)$.

First, let us consider the Raman response of the unperturbed Kitaev model, $iF_K(t) = \langle 0|T[\hat{\mathcal{R}}_K(t)\hat{\mathcal{R}}_K(0)]|0\rangle$, here $T$ denotes the standard time ordering. In terms of the quasiparticle operators $\hat{a}_{\mathbf{q}}$ which diagonalize the flux-free Hamiltonian (2), the Raman operator is given by

$$\hat{\mathcal{R}}_K = \sum_{\mathbf{q}}\{(h'_{\mathbf{q}}\cos 2\theta_{\mathbf{q}} - h''_{\mathbf{q}}\sin 2\theta_{\mathbf{q}})\hat{a}^\dagger_{\mathbf{q}}\hat{a}_{\mathbf{q}} + i(h'_{\mathbf{q}}\sin 2\theta_{\mathbf{q}} + h''_{\mathbf{q}}\cos 2\theta_{\mathbf{q}})\hat{a}^\dagger_{\mathbf{q}}\hat{a}^\dagger_{-\mathbf{q}} + \text{H.c.}\}, \quad (5)$$

where $h'_{\mathbf{q}}$ and $h''_{\mathbf{q}}$ denote the real and imaginary parts of $h_{\mathbf{q}} \equiv K\sum_{a=1}^{3}(\hat{\epsilon}_{\text{in}}\cdot\mathbf{d}_a)(\hat{\epsilon}_{\text{out}}\cdot\mathbf{d}_a)e^{i\mathbf{q}\cdot\mathbf{n}_a}$ with $\mathbf{n}_0 = (0,0)$ and $\mathbf{n}_1, \mathbf{n}_2$ defined in Fig. 1. Then

$$I_K(\omega) = 4\pi\sum_{\mathbf{q}}\delta(\omega - 4|s_{\mathbf{q}}|)(\text{Im}[h_{\mathbf{q}}s^*_{\mathbf{q}}]/|s_{\mathbf{q}}|)^2. \quad (6)$$

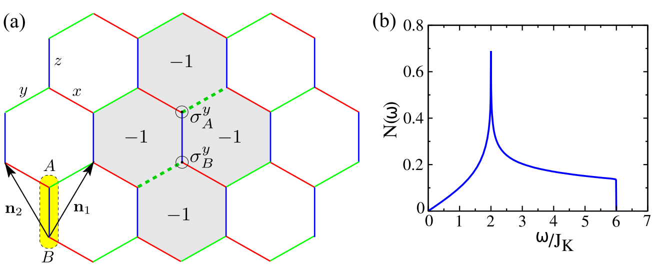


FIG. 1 (color online). A honeycomb lattice is shown in panel (a). Shaded yellow region indicates the unit cell with two sites $A$ and $B$. Three inequivalent nearest-neighbor bonds $x, y, z$, are shown in red, green, and blue. The problem of calculating the Raman response in the presence of Heisenberg terms can be mapped onto a local quantum quench, where four adjoining $Z_2$ fluxes, shown as gray hexagons, are inserted. The contribution from the nearest-neighbor $\sigma^y_{A\mathbf{r}}\sigma^y_{B\mathbf{r}}$ interactions along the $z$ bond, which flips the sign of the link variables is shown as green dashed bonds. Panel (b) displays the density of states $N(\omega)$ of Majorana fermions in the ground state flux sector.

Next, we obtain the leading contribution to the Raman response arising from the Heisenberg exchange $iF_H(t) = \langle 0|T[\hat{\mathcal{R}}_H(t)\hat{\mathcal{R}}_H(0)|0\rangle$. A typical term in $\hat{\mathcal{R}}_H$, e.g., on the $z$ bond, contains operators $\propto \hat{\sigma}^x_{A,\mathbf{r}}\hat{\sigma}^x_{B,\mathbf{r}} + \hat{\sigma}^y_{A,\mathbf{r}}\hat{\sigma}^y_{B,\mathbf{r}}$. The spin operator written in terms of Majorana fermions, e.g. $\hat{\sigma}^a_{A,\mathbf{r}} = ic_{A,\mathbf{r}}(\chi_{\langle A,\mathbf{r};B,\mathbf{r}+\mathbf{n}_a\rangle_a} + \chi^\dagger_{\langle A,\mathbf{r};B,\mathbf{r}+\mathbf{n}_a\rangle_a})$, creates a matter fermion $\hat{c}_i$, and changes bond fermion number $\chi$, which corresponds to flipping of the sign of two $Z_2$ fluxes on the plaquettes sharing the bond (here the corresponding bond is of the $x$ or $y$ type). The combined effect of these terms in $\hat{\mathcal{R}}_H$ is to insert four fluxes around the $z$ bond at site $\mathbf{r}$; see Fig. 1. The $Z_2$ fluxes have to be annihilated by the corresponding term in the other Raman operator in $iF_H(t)$ in order to have a nonzero expectation value with respect to $|0\rangle$. Consequently, the Heisenberg Raman response $F_H$ can be decomposed into a sum over individual bonds $F_H(t) = \sum_{a=x,y,z}\sum_{\mathbf{r}} F_{H,a}(\mathbf{r},t)$. Below, we focus on contributions from the $z$ bond (contributions from the $x$ and $y$ bonds can be obtained by symmetry).

The correlator $F_{H,z}(\mathbf{r};t)$ contains two types of matrix elements, $\langle\hat{\sigma}^x(t)\hat{\sigma}^x(t)\hat{\sigma}^x(0)\hat{\sigma}^x(0)\rangle$, and the off-diagonal ones $\langle\hat{\sigma}^x(t)\hat{\sigma}^x(t)\hat{\sigma}^y(0)\hat{\sigma}^y(0)\rangle$. The corresponding correlators are denoted as $F^{xx}(t)$ and $F^{xy}(t)$. The former can be calculated without projection onto the physical states. However, the off-diagonal term conserves the flux sector, but *changes* the number of bond fermions, $\hat{\chi}$; thus, one has to use the projectors in the calculation of $F^{xy}(t)$ [2,41]; see Supplemental Material for details [37].

The calculation of the Heisenberg contribution of the correlator can be cast in the form of a local quantum quench, along the lines of the calculation of the dynamical spin correlations in the Kitaev model [32,42]. The Raman response can be expressed entirely in terms of matter fermions acting in the ground-state flux sector $|F_0\rangle$, subjected to the time-dependent local potential $\hat{V}$,

$$F^{xx}_{H,z}(\mathbf{r},t) = -i\langle M_0|e^{it\hat{\mathcal{H}}_0}e^{-it(\hat{\mathcal{H}}_0+\hat{V}_{\mathbf{r}})}|M_0\rangle,$$
$$F^{xy}_{H,z}(\mathbf{r},t) = -i\langle M_0|e^{it\hat{\mathcal{H}}_0}e^{-it(\hat{\mathcal{H}}_0+\hat{V}_{\mathbf{r}})}c_{A,\mathbf{r}}c_{B,\mathbf{r}}|M_0\rangle. \quad (7)$$

Here, the Hamiltonian $\hat{\mathcal{H}}_0 + \hat{V}_{\mathbf{r}}$ differs from $\hat{\mathcal{H}}_0$ in the sign of the Majorana hopping for the two $y$ bonds attached to sites $(A,\mathbf{r})$ and $(B,\mathbf{r})$. The locally perturbed Hamiltonian belongs to the sector with four extra fluxes shown in Fig. 1(a). The problem is now reduced to the one of a local quantum quench, where the ground state $|M_0\rangle$ of $\hat{\mathcal{H}}_0$ is time evolved with a different Hamiltonian $\hat{\mathcal{H}}_0 + \hat{V}_{\mathbf{r}}$. Note that in the calculation of dynamic spin correlators in the Kitaev model, $\hat{V}_{\mathbf{r}} \propto \hat{f}^\dagger_{\mathbf{r}}\hat{f}_{\mathbf{r}}$ assumes the form of a local on-site potential [42], which is switched on at $t = 0$. Here we have a four-flux rather than two-flux quench and the expression for $\hat{V}_{\mathbf{r}}$ in terms of complex bond fermions is complicated. The correlators can be evaluated numerically using

Lehmann representation. To this end, we introduce a basis $|\lambda\rangle$ of many-body eigenstates of the Hamiltonian $\hat{\mathcal{H}}_0 + \hat{V}_{\mathbf{r}}$. We denote the corresponding energy as $E_\lambda$ and the ground-state energy of $\hat{\mathcal{H}}_0$ as $E_0$, and obtain

$$I^{xx}_{H,z}(\omega) = 2\pi \sum_\lambda \delta(\omega - \Delta_\lambda)|\langle M_0|\lambda\rangle|^2,$$
$$I^{xy}_{H,z}(\omega) = 2\pi \sum_\lambda \delta(\omega - \Delta_\lambda)\langle M_0|\lambda\rangle\langle\lambda|\hat{c}_{A,\mathbf{r}}\hat{c}_{B,\mathbf{r}}|M_0\rangle, \quad (8)$$

where $\Delta_\lambda = E_\lambda - E_0$. Note that nonvanishing contributions arise only from the excited states $|\lambda\rangle$ having the same parity as the ground state $|M_0\rangle$ of matter fermions. We evaluate numerically the dominant contributions $I^{[0]}_H(\omega), I^{[2]}_H(\omega)$ arising from the zero and two-particle processes; details are relegated to the Supplemental Material [37].

*Results.*—The Raman response, shown in Fig. 2, is markedly different from known strongly polarization-dependent behavior seen in the two-magnon response of antiferromagnetically ordered systems [20–23]. In fact, the characteristic features of the overall weakly polarization-dependent response $I(\omega)$ can be related either to the flux, or to the Majorana fermion sector: First, a strong polarization-independent Kitaev contribution $I_K(\omega)$ reflects the Majorana fermion density of states in the ground state flux sector; see Fig. 1(b). It shows a linear onset at low energies, a sharp band edge at $12J_K$, and a dip at $4J_K$ due to the van Hove singularity. Second, a weaker Heisenberg contribution is related to flux excitations, e.g., $I_H(\omega) = 0$ for $\omega < \Delta_F$ with the flux gap $\Delta_F$ which is the difference in ground-state energy of the zero- and four-flux sector. It has a characteristic polarization dependence with a simple overall intensity dependence on the relative angle $\theta$ between incoming and outgoing photons as shown in the inset of Fig. 2. It arises because the Heisenberg perturbation belongs to a different irreducible representation of the lattice translation group than both the Kitaev Hamiltonian and its QSL ground state [28]. A striking feature is a sharp peak at the energy of the four-flux gap $\Delta_F = 0.446J_K$ originating from the zero-particle contribution (the overlap between ground states); see Eq. (8). This is a clear signature of the flux excitation in the *isotropic* gapless QSL ($J^x_K = J^y_K = J^z_K$). Note that usually sharp lines in Raman scattering are attributed to optical phonons that appear at different energy scales [20]. In addition, $I_H(\omega)$ has a broad response in energy reflecting the two-particle density of states of matter fermions propagating in the background of four fluxes.

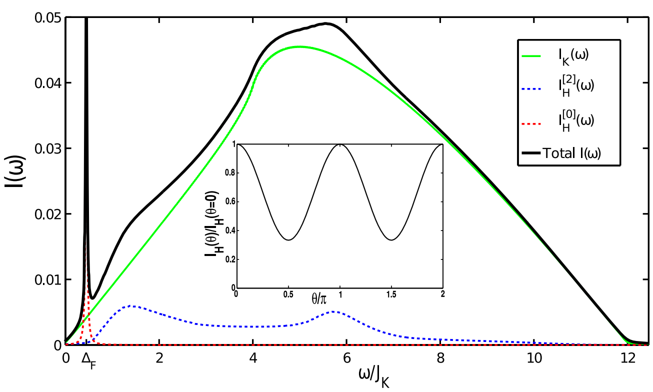


FIG. 2 (color online). The Raman response $I(\omega)$ (black curve) and its separate contributions (here $J_K = 10J_H$). The Kitaev contribution $I_K(\omega)$, shown in green, is independent of the photon polarization and shows characteristic features of the matter fermion density of states, including the linear onset at low energies and the band edge at $12J_K$, note an additional factor of 2 in Eq. (6). The van Hove singularity at $2J_K$ is seen as a small dip at $4J_K$ (due to a discontinuity of the derivative). The zero and two-particle responses, $I^{[0]}_H(\omega)$ and $I^{[2]}_H(\omega)$, of the Heisenberg contribution are shown in blue and red (dashed line), respectively. A $\delta$-function peak occurs at the four flux gap $\Delta_F = 0.446J_K$, while the frequency dependence of the two-particle contribution reflects the local two-particle density of states in the presence of four fluxes. The overall polarization dependence of $I_H(\omega)$ on the relative angle $\theta$ between incoming and outgoing photons is shown in the inset. Accordingly, $I_K(\omega)$ only has contributions from the doublet $E_g$-symmetry component, while $I_H(\omega)$ has both $A_{1g}$ and $E_g$.

Our analysis of Raman response relies on the stability of the Kitaev QSL with respect to the addition of small Heisenberg exchanges (note that the latter is believed to be small in the proposed Kitaev model realizations in iridates). We expect that for small Heisenberg couplings, the features which we find are robust, being only somewhat renormalized by nonlocal fluctuations, such as the ones originating from the dynamics of the fluxes generated by the Heisenberg exchange (or disorder, which is present in real materials). Crucially, there is a window of parameters where the features which we find should be observable, thus making Raman scattering an important experimental tool for diagnosing Kitaev QSLs.

*Discussion.*—The calculation of the Heisenberg contribution $I_H(\omega)$ to the Raman response is equivalent to a nonequilibrium problem with a sudden insertion of four fluxes. The Raman vertex of the Kitaev model does not change the flux sector, but the integrability breaking contribution due to Heisenberg interactions does. The latter takes the form of a quantum quench which generates an unusual sharp $\delta$-function component in the response.

In general, we expect that for Kitaev-like models the calculation of the correlation functions $\langle\hat{O}(t)\hat{O}(0)\rangle$, whose operators $\hat{O}$ change the flux sector, can be mapped to a local quantum quench for Majorana fermions by exploiting selection rules and by eliminating flux degrees of freedom as pioneered for the spin correlation function in the original Kitaev model [32]. This is true, for example, for the calculation of spin correlations in generalizations of the honeycomb model to higher dimensions [5–8,12] (or possibly even to different classes [2–4]). At low temperatures the response is mainly determined by the low energy matter fermions; e.g., depending on the Fermi surface topology, a singular behavior may appear. Overall, while a QSL might be stable with respect to sufficiently weak integrability-breaking interactions, the change in response functions can be remarkable, revealing basic properties of the underlying phase by connecting otherwise orthogonal sectors of the emergent gauge flux.

In conclusion, we have shown that Raman scattering renders visible both flux and Majorana fermion excitations potentially relevant to iridates. It thus presents a valuable tool for diagnosing topological quantum states.

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[1] A. Yu. Kitaev, Ann. Phys. (Berlin) **321**, 1 (2006).
[2] H. Yao, S.-C. Zhang, and S. A. Kivelson, Phys. Rev. Lett. **102**, 217202 (2009).
[3] M. Barkeshli, H.-C. Jiang, R. Thomale, and X.-L. Qi, arXiv:1405.1780.
[4] A. Vaezi, Phys. Rev. B **90**, 075106 (2014).
[5] S. Mandal and N. Surendran, Phys. Rev. B **79**, 024426 (2009).
[6] E. K.-H. Lee, R. Schaffer, S. Bhattacharjee, and Y. B. Kim, Phys. Rev. B **89**, 045117 (2014).
[7] I. Kimchi, J. G. Analytis, and A. Vishwanath, arXiv:1309.1171.
[8] M. Hermanns and S. Trebst, Phys. Rev. B **89**, 235102 (2014).
[9] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. **102**, 017205 (2009).
[10] J. Chaloupka, G. Jackeli, and G. Khaliullin, Phys. Rev. Lett. **105**, 027204 (2010).
[11] Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, and P. Gegenwart, Phys. Rev. Lett. **108**, 127203 (2012).
[12] T. Takayama, A. Kato, R. Dinnebier, J. Nuss, and H. Takagi, arXiv:1403.3296.
[13] K. A. Modic *et al.*, Nat. Commun. **5**, 4203 (2014).
[14] Z. Alpichshev, F. Mahmood, G. Cao, and N. Gedik, arXiv:1405.1793.
[15] V. M. Katukuri, S. Nishimoto, V. Yushankhai, A. Stoyanova, H. Kandpal, S. Choi, R. Coldea, I. Rousochatzakis, L. Hozoi, and J. van den Brink, New J. Phys. **16**, 013056 (2014); S. Nishimoto, V. M. Katukuri, V. Yushankhai, H. Stoll, U. K. Roessler, L. Hozoi, I. Rousochatzakis, and J. van den Brink, arXiv:1403.6698.
[16] Y. Sizyuk, C. Price, P. Woelfle, and N. B. Perkins, arXiv:1408.3647.
[17] S. Mandal, Subhro Bhattacharjee, K. Sengupta, R. Shankar, and G. Baskaran, Phys. Rev. B **84**, 155121 (2011).
[18] J. Reuther, R. Thomale, and S. Trebst, Phys. Rev. B **84**, 100406 (2011).
[19] R. Schaffer, S. Bhattacharjee, and Y. B. Kim, Phys. Rev. B **86**, 224417 (2012).
[20] Thomas P. Devereaux and Rudi Hackl, Rev. Mod. Phys. **79**, 175 (2007).
[21] Natalia Perkins and Wolfram Brenig, Phys. Rev. B **77**, 174412 (2008).
[22] Natalia B. Perkins, Gia-Wei Chern, and Wolfram Brenig Phys. Rev. B **87**, 174423 (2013).
[23] Andrey V. Chubukov and David M. Frenkel, Phys. Rev. Lett. **74**, 3057 (1995); Phys. Rev. B **52**, 9760 (1995).
[24] G. Blumberg, P. Abbamonte, M. V. Klein, W. C. Lee, D. M. Ginsberg, L. L. Miller, and A. Zibold, Phys. Rev. B **53**, R11930 (1996); G. Blumberg, M. Kang, M. V. Klein, K. Kadowaki, and C. Kendziora, Science **278**, 1427 (1997).
[25] C.-C. Chen, C. J. Jia, A. F. Kemper, R. R. P. Singh, and T. P. Devereaux, Phys. Rev. Lett. **106**, 067002 (2011).
[26] F. Kretzschmar, B. Muschler, T. Bohm, A. Baum, R. Hackl, Hai-Hu Wen, V. Tsurkan, J. Deisenhofer, and A. Loidl, Phys. Rev. Lett. **110**, 187002 (2013).
[27] M. Sato, H. Katsura, and N. Nagaosa, Phys. Rev. Lett. **108**, 237401 (2012).
[28] O. Cepas, J. O. Haerter, and C. Lhuillier, Phys. Rev. B **77**, 172406 (2008).
[29] Wing-Ho Ko, Zheng-Xin Liu, Tai-Kai Ng, and Patrick A. Lee, Phys. Rev. B **81**, 024414 (2010).
[30] D. Wulferding, P. Lemmens, P. Scheib, J. Roder, P. Mendels, S. Chu, T. Han, and Y. S. Lee, Phys. Rev. B **82**, 144412 (2010).
[31] S. K. Choi, R. Coldea, A. N. Kolmogorov, T. Lancaster, I. I. Mazin, S. J. Blundell, P. G. Radaelli, Yogesh Singh, P. Gegenwart, K. R. Choi, S.-W. Cheong, P. J. Baker, C. Stock, and J. Taylor, Phys. Rev. Lett. **108**, 127204 (2012).
[32] G. Baskaran, S. Mandal, and R. Shankar, Phys. Rev. Lett. **98**, 247201 (2007).
[33] A. J. Willans, J. T. Chalker, and R. Moessner, Phys. Rev. Lett. **104**, 237203 (2010).
[34] A. J. Willans, J. T. Chalker, and R. Moessner, Phys. Rev. B **84**, 115146 (2011).
[35] P. A. Fleury and R. Loudon, Phys. Rev. **166**, 514 (1968).
[36] B. S. Shastry and B. I. Shraiman, Phys. Rev. Lett. **65**, 1068 (1990).
[37] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.113.187201, which includes Refs. [38–40], for details.
[38] K. S. Tikhonov, M. V. Feigel'man, and A. Yu. Kitaev, Phys. Rev. Lett. **106**, 067203 (2011).
[39] V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, and A. H. Castro Neto, Rev. Mod. Phys. **84**, 1067 (2012).
[40] J. P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems* (MIT Press, Cambridge, MA, 1985).
[41] F. L. Pedrocchi, S. Chesi, and D. Loss, Phys. Rev. B **84**, 165414 (2011).
[42] J. Knolle, D. L. Kovrizhin, J. T. Chalker, and R. Moessner, Phys. Rev. Lett. **112**, 207203 (2014).