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# Quantum field theory of hyper-Raman scattering in piezoelectric crystals

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The existing theories of hyper-Raman scattering are based on the semiclassical theory of the interaction of electromagnetic radiation with matter. For this reason, a quantum field theory of hyper-Raman scattering of near infrared light by piezoelectric crystals is presented. We establish a unified theoretical framework to describe hyper-Raman scattering of light by nonpolar modes and longitudinal or transverse polar modes. An additional mechanism is found for hyper-Raman scattering from polar modes. In this framework, we derive an analytical, temperature-dependent expression of the hyper-Raman scattering intensity of light. Our theory explains two distinct peaks of hyper-Raman scattering from the split polar modes.

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## I. INTRODUCTION

Raman scattering of light is a powerful tool for determining the properties of elementary excitations in solids.[1–3] Raman scattering involves a two-photon process, in which a photon incident upon solids disappears by creating or annihilating one or several quasiparticles and then another photon emerges with an energy somewhat different from that of the incident photon. However, Raman scattering of light carries several inherent shortcomings. (1) Some excitation modes are inactive in first-order Raman scattering which involves one quasiparticle, while the cross section of second-order Raman scattering which involves two quasiparticles is very weak. (2) The Raman scattering spectrum exhibited by a material is not related to the second-order nonlinear optical properties of the material. A typical example of the second-order nonlinear optical properties is second-harmonic generation, which involves a three-photon process in which two incident photons with the same frequency $\omega$ are coupled nonlinearly into a third photon with double frequency $2\omega$.[4]

To remedy the above difficulties, at the same time several authors[5–7] proposed the idea of hyper-Raman scattering of light. Hyper-Raman scattering is a three-photon process in which a second-order nonlinear medium can convert two incident photons of frequency $\omega$ into one scattered photon at the frequency $2\omega \pm \omega_\kappa$, where $\omega_\kappa$ is the frequency of an elementary excitation of the medium. The first experiment on hyper-Raman scattering was carried out with liquid samples in the year 1965.[8] Subsequently, the selection rules and light intensity expressions for hyper-Raman scattering were obtained.[9,10] In the year 1978, hyper-Raman scattering was employed to investigate the exciton-polariton dispersion curves of CuCl.[11] A recent panorama of hyper-Raman scattering is reviewed in Ref. 12. In particular, this reference treats hyper-Raman scattering by polar modes. More recently,[13] Savasta and Girlanda presented a microscopic theory of hyper-Raman scattering in semiconductors to explain the experiment in Ref. 11. The existing theories of hyper-Raman scattering are based on the semiclassical theory of the interaction of electromagnetic radiation with matter. In the classical theory, hyper-Raman scattering from molecules may be considered as the result of modulation of the hyperpolarizability by molecular vibrations. In the semiclassical theory, the light field is described classically while the medium is described quantum mechanically within the framework of the perturbation approximation. A standard, full quantum mechanical treatment of hyper-Raman scattering seems not to exist. Hyper-Raman scattering of light has become a powerful tool for (i) determining the properties of some elementary excitations in crystalline media and (ii) measuring the second-order nonlinear optical coefficients of crystalline media.

The existing semiclassical theories of hyper-Raman scattering from crystals possess the following deficiencies. (i) There is no unified theoretical framework to describe hyper-Raman scattering of light by nonpolar modes and longitudinal or transverse polar modes. (ii) The fourth-order perturbation theory is used. (iii) The theories depend on concrete models of the electron-lattice interaction. (iv) The quantum many-body effects of light and crystal are not considered. (v) The explanation of the physical mechanism is not intuitive. Therefore, we need to develop a quantum field theory of hyper-Raman scattering of light by crystals to remedy these deficiencies. We mainly consider hyper-Raman scattering of light in the near infrared spectrum of piezoelectric crystals. We establish a unified theoretical framework to describe hyper-Raman scattering of light by nonpolar modes and longitudinal or transverse polar modes. The physical mechanism for nonpolar-mode scattering results from the coupling of the crystal electrons with the lattice vibrations, and it is translated in polarizability theory by the deformation of the electronic wave functions which depend on the nuclear parameters. An additional physical mechanism is found for polar-mode scattering, which stems from the electric-dipole moments of polar modes. In this framework, we derive an analytical, temperature-dependent expression of the hyper-Raman scattering intensity of light. Our theory produces two distinct peaks of hyper-Raman scattering from longitudinal and transverse polar modes.

The remainder of this paper is organized as follows. Section II presents the quantum theory of the noninteracting system. In Sec. III, the author employs the third-order perturbation theory to describe the interaction of light with the crystal. In Sec. IV, we derive the Hamiltonian for hyper-Raman scattering. In Sec. V, the author finds the expression of the hyper-Raman scattering intensity of light. A discussion is given in Sec. VI.

## II. QUANTUM THEORY OF THE NONINTERACTING SYSTEM

The model system under study consists of an incident light field and a piezoelectric crystal. Let us define three conditions for the incident light. The first condition is that the incident light field is a quasimonochromatic field of a central frequency $\omega$. The second condition is that the frequencies of the incident light are far lower than the electronic transition frequencies of the crystal, which lie in the ultraviolet regime of electromagnetic waves. The third condition is that the frequencies of the incident light are much higher than the ionic vibrational frequencies of the crystal, which lie in the far infrared spectrum. In order to meet the latter two conditions, the frequencies of the incident light must be in the near infrared spectrum. When the latter two conditions are met, the incident light can avoid the intrinsic absorption from the electrons and phonons of the crystal and will suffer only the intrinsic scattering by the crystal.

### A. Adiabatic approximation

The crystal consists of a periodic arrangement of $N$ primitive cells in a volume $V$. There are $r$ basis atoms in each cell. An atom is made up of an ion and the valence electrons bonded to the ion. The position of the $j$th ion is determined by the vector $\mathbf{X}_j$, where the ion index $j$ combines the cell index $n$ and the position index $l$ of the basis atom in the cell, i.e., $j=nl$. If $\mathbf{s}_j$ represents the instantaneous displacement of the $j$th ion from its equilibrium position $\mathbf{R}_j$, then $\mathbf{X}_j=\mathbf{R}_j+\mathbf{s}_j$. The spin and spatial coordinates of an electron $i$ bonded to an ion $j$ are denoted by $\sigma_{ji}$ and $\mathbf{x}_{ji}$. Let $\mathbf{r}_{ji}$ denote the relative position vector of the $ji$th electron from the equilibrium position of its nucleus; then we have $\mathbf{x}_{ji}=\mathbf{R}_j+\mathbf{r}_{ji}$. The Hamiltonian $H_C$ of the crystal in the absence of external fields consists of the kinetic energy of all electrons and all ions and the energy associated with all the interactions between these particles, $H_C=H_{el}+H_{ion}+H_{el\text{-}ion}$. The eigenfunctions and eigenvalues of $H_C$ are represented by $\Phi_q(\sigma,\mathbf{r};\mathbf{s})$ and $E_q$, where $q$ represents the set of quantum numbers necessary to specify the crystal, $\sigma$ signifies the set of electronic spin coordinates, $\mathbf{r}$ denotes the set of electronic spatial coordinates, and $\mathbf{s}$ the set of ionic coordinates. In the adiabatic (Born-Oppenheimer) approximation we can adopt a Schrödinger equation for the electrons

$$(H_{el}+H_{el\text{-}ion})\varphi_\iota(\sigma,\mathbf{r};\mathbf{s})=[E_\iota+U_\iota(\mathbf{s})]\varphi_\iota(\sigma,\mathbf{r};\mathbf{s}), \quad (1)$$

where $\iota$ represents the set of quantum numbers necessary to specify the electrons and the electronic wave functions $\varphi_\iota$ contain the ionic displacements as parameters. $U_\iota(\mathbf{s})$ contains no constant term about $\mathbf{s}$ and serves as the potential energy of the ions. Since $U_\iota(\mathbf{s})$ depends slightly on the electronic states $\iota$, we can reasonably suppose that the ions move in the electronic ground state $\iota_0$. If $H_{ion}^*=H_{ion}+U_{\iota_0}(\mathbf{s})$ stands for the effective Hamiltonian of the ions, the movement of the ions follows the equation $H_{ion}^*\chi_v(\mathbf{s})=E_v\chi_v(\mathbf{s})$, where $v$ represents the set of quantum numbers necessary to specify the ions. The wave function of the crystal is the product $\Phi_q(\sigma,\mathbf{r};\mathbf{s})=\varphi_\iota(\sigma,\mathbf{r};\mathbf{s})\chi_v(\mathbf{s})$ and its energy is the sum $E_q=E_\iota+E_v$.

Now we introduce the index $k$ to symbolize the $i$th electron bonded to the $j$th ion, i.e., $k=ji$. The electronic Hamiltonian is written as

$$H_{el}=-\sum_k \frac{\hbar^2}{2m_e}\nabla_k^2+\frac{1}{8\pi\epsilon_0}\sum_{kk'}{}'\frac{e^2}{|\mathbf{x}_k-\mathbf{x}_{k'}|}, \quad (2)$$

where $\hbar$ is the reduced Planck's constant, $m_e$ is the electronic mass, and $\epsilon_0$ is the permittivity of vacuum. The second term represents the electronic Coulomb interaction and the prime on the sum means excluding $k=k'$. For the electron-ion interaction we put

$$H_{el\text{-}ion}=\sum_k V(\mathbf{r}_k,\mathbf{s}). \quad (3)$$

If in the last equation we set the instantaneous displacements $\mathbf{s}$ of the ions to be zero, Eq. (1) will become

$$(H_{el}+H_{el\text{-}ion})\varphi_\iota(\sigma,\mathbf{r};\mathbf{0})=E_\iota\varphi_\iota(\sigma,\mathbf{r};\mathbf{0}), \quad (4)$$

so that $E_\iota$ gives the energy of the electrons when the ions are in equilibrium. The electronic wave functions $\varphi_\iota(\sigma,\mathbf{r};\mathbf{s})$ that depend on the ionic parameters are deformed relative to $\varphi_\iota(\sigma,\mathbf{r};\mathbf{0})$. Under the one-electron approximation, the wave function of the many-electron system is then separated into the form

$$\varphi_\iota(\sigma,\mathbf{r};\mathbf{s})=f(\sigma)\prod_k \phi_{\mathbf{p}_k n_k}(\mathbf{r}_k,\mathbf{s}), \quad (5)$$

where $f(\sigma)$ is the spin function of the electrons. The space function of a single electron obeys the Hartree equation[14]

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2+V(\mathbf{r},\mathbf{s})-\frac{e}{4\pi\epsilon_0}\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right]\phi_{\mathbf{p}n}(\mathbf{r},\mathbf{s})$$
$$=\varepsilon_{\mathbf{p}n}(\mathbf{s})\phi_{\mathbf{p}n}(\mathbf{r},\mathbf{s}), \quad (6)$$

where $\rho(\mathbf{r})$ stands for the charge density of electrons. This equation describes an electron in a periodic potential consisting of the potential of the lattice ions and the Coulomb interaction of the Hartree approximation, so that $\phi_{\mathbf{p}n}(\mathbf{r},\mathbf{s})$ is a Bloch function that depends on the ionic parameters. $\mathbf{p}$ and $n$ are the wave vector and band index of a Bloch electron. Since the spin does not explicitly appear further, we shall neglect the electronic spin coordinates, so that $\iota=\{\mathbf{p}_k n_k\}$ represents the set of quantum numbers necessary to specify the electronic state. The energy of the electrons is $E_\iota=\Sigma_k\varepsilon_{\mathbf{p}_k n_k}(\mathbf{0})$.

### B. Second quantization of the vibrational and electromagnetic field

One needs to introduce the wave vector $\mathbf{q}$ in the Brillouin zone, which takes $N$ values. Each vibration frequency $\omega_J(\mathbf{q})$ of the lattice represents a normal mode, which is labeled by the two indices $\mathbf{q}$ and $J$. Here $J$ is the branch index of normal modes and will run from 1 to $3r$. Now we use a direct lattice vector $\mathbf{R}_n$ to locate the $n$th cell and introduce a set of normal coordinates $\{Q_J(\mathbf{q})\}$ by

$$s_{nl\alpha}=\sum_{\mathbf{q}J}\frac{1}{\sqrt{Nm_l}}e_{l\alpha}(\mathbf{q}J)Q_J(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_n}, \tag{7}$$

where the index $\alpha=1,2,3$ distinguishes the three rectangular components, the $\mathbf{e}_l(\mathbf{q}J)$ are the orthonormal eigenvectors of lattice vibrations, and $m_l$ is the mass of the $l$th basis ion. If one introduces a reduced dynamical matrix $D_{l\alpha}^{l'\alpha'}(\mathbf{q})$, in the harmonic approximation one can obtain the secular equations

$$\omega_J^2(\mathbf{q})e_{l\alpha}(\mathbf{q}J)=\sum_{l'\alpha'}D_{l\alpha}^{l'\alpha'}(\mathbf{q})e_{l'\alpha'}(\mathbf{q}J). \tag{8}$$

The normal modes are made up of three acoustic branches and $3(r-1)$ optical branches. Only the optical phonons participate in hyper-Raman scattering. The optical vibrations of a crystal fall into two distinct categories, i.e., polar modes and nonpolar modes. Polar modes carry electric-dipole moments and so are active in infrared absorption, whereas nonpolar modes carry no electric-dipole moments and so are infrared inactive. The lattice vibrations are second quantized if we let

$$Q_J(\mathbf{q})=\left[\frac{\hbar}{2\omega_J}(\mathbf{q})\right]^{1/2}(b_{\mathbf{q}J}+b^{\dagger}_{-\mathbf{q},J}), \tag{9}$$

where $b^{\dagger}_{\mathbf{q}J}$ and $b_{\mathbf{q}J}$ are the creation and annihilation operators of the $J$th branch phonons with wave vector $\mathbf{q}$, obey the Bose equal-time commutation relations, and have the explicit time dependence $b_{\mathbf{q}J}(t)=b_{\mathbf{q}J}(0)\exp[-i\omega_J(\mathbf{q})t]$ and $b^{\dagger}_{\mathbf{q}J}(t)=b^{\dagger}_{\mathbf{q}J}(0)\exp[i\omega_J(\mathbf{q})t]$. Then the second-quantized Hamiltonian of lattice vibrations is acquired as

$$H^{*}_{ion}=\sum_{\mathbf{q}J}\hbar\omega_J(\mathbf{q})\left(b^{\dagger}_{\mathbf{q}J}b_{\mathbf{q}J}+\frac{1}{2}\right). \tag{10}$$

Equation (10) represents the Hamiltonian of the system of noninteracting phonons. The eigenstates $|v\rangle$ and eigenvalues $E_v$ of $H^{*}_{ion}$ can be easily acquired as follows:

$$|v\rangle=\prod_{\mathbf{q}J}\left[\frac{1}{\sqrt{v_{\mathbf{q}J}!}}(b^{\dagger}_{\mathbf{q}J})^{v_{\mathbf{q}J}}\right]|0\rangle, \tag{11}$$

$$E_v=\sum_{\mathbf{q}J}\hbar\omega_J(\mathbf{q})\left(v_{\mathbf{q}J}+\frac{1}{2}\right), \tag{12}$$

where $|0\rangle$ is the vacuum state, $v=\{v_{\mathbf{q}J}\}$ represents the set of quantum numbers necessary to specify the vibrational state, and $v_{\mathbf{q}J}=0,1,2,\ldots$.

The electromagnetic field in a piezoelectric crystal is characterized by a single vector potential $\mathbf{A}$, which meets the Coulomb gauge $\nabla\cdot\mathbf{A}=0$. In terms of the creation and annihilation operators $a^{\dagger}_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}$ of linearly polarized photons with wave vector $\mathbf{k}$ and polarization index $\lambda=1$ or 2, the vector potential of the electromagnetic field is expanded as

$$\mathbf{A}(\mathbf{r},t)=\sum_{\mathbf{k}\lambda}\left(\frac{\hbar}{2V\epsilon_0\epsilon\omega_{\mathbf{k}}}\right)^{1/2}\mathbf{e}_{\mathbf{k}\lambda}[a_{\mathbf{k}\lambda}(t)e^{i\mathbf{k}\cdot\mathbf{r}}+a^{\dagger}_{\mathbf{k}\lambda}(t)e^{-i\mathbf{k}\cdot\mathbf{r}}], \tag{13}$$

where $\mathbf{e}_{\mathbf{k}1}$ and $\mathbf{e}_{\mathbf{k}2}$ are the orthogonal unit polarization vectors perpendicular to $\mathbf{k}$. $\omega_{\mathbf{k}}=c|\mathbf{k}|/\sqrt{\epsilon}$ is the photon frequency in the crystal, $\epsilon$ is the linear dielectric function of the crystal, and $c$ is the velocity of light in vacuum. The photon operators obey the Bose equal-time commutation relations and have the explicit time dependence $a_{\mathbf{k}\lambda}(t)=a_{\mathbf{k}\lambda}(0)\times\exp(-i\omega_{\mathbf{k}}t)$ and $a^{\dagger}_{\mathbf{k}\lambda}(t)=a^{\dagger}_{\mathbf{k}\lambda}(0)\exp(i\omega_{\mathbf{k}}t)$. The Hamiltonian of the electromagnetic field is converted into the Hamiltonian of the system of noninteracting photons

$$H_L=\sum_{\mathbf{k}\lambda}\hbar\omega_{\mathbf{k}}\left(a^{\dagger}_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}+\frac{1}{2}\right). \tag{14}$$

The eigenstates $|n\rangle$ and eigenvalues $E_n$ of $H_L$ can be easily acquired as follows:

$$|n\rangle=\prod_{\mathbf{k}\lambda}\left[\frac{1}{\sqrt{n_{\mathbf{k}\lambda}!}}(a^{\dagger}_{\mathbf{k}\lambda})^{n_{\mathbf{k}\lambda}}\right]|0\rangle, \tag{15}$$

$$E_n=\sum_{\mathbf{k}\lambda}\hbar\omega_{\mathbf{k}}\left(n_{\mathbf{k}\lambda}+\frac{1}{2}\right), \tag{16}$$

where $n=\{n_{\mathbf{k}\lambda}\}$ represents the set of quantum numbers necessary to specify the photon state and $n_{\mathbf{k}\lambda}=0,1,2,\ldots$.

### III. INTERACTION OF LIGHT WITH CRYSTAL

If the crystal and the electromagnetic field were not interacting, the total system would have a Hamiltonian $H_0=H_C+H_L$, which has the eigenstates $\Psi_\alpha(\mathbf{r},\mathbf{s})=\varphi_\iota(\mathbf{r},\mathbf{s})\chi_v(\mathbf{s})|n\rangle$ and the eigenvalues $E_\alpha=E_\iota+E_v+E_n$, where $\alpha=\{\iota v n\}$ represents the set of quantum numbers necessary to specify the noninteracting system. In fact, there is an interaction between the two subsystems, which is described by the Hamiltonian $H_I$. Now, the total system is determined by the Schrödinger equation

$$(H_C+H_L+H_I)\Psi=i\hbar\frac{\partial\Psi}{\partial t}. \tag{17}$$

Let the $\iota$th particle (electron or ion) in the crystal have a charge $q_\iota$ and a mass $m_\iota$, whose position vector is denoted by $\mathbf{r}_\iota$ and whose momentum operator is given by $\hat{\mathbf{p}}_\iota=-i\hbar\nabla_\iota$. The interaction Hamiltonian between the electromagnetic field and the crystal is obtained from the minimal electromagnetic coupling principle as $H_I=H^{(1)}+H^{(2)}$, where

$$H^{(1)}=-\sum_\iota\frac{q_\iota}{m_\iota}\mathbf{A}(\mathbf{r}_\iota)\cdot\hat{\mathbf{p}}_\iota, \tag{18}$$

$$H^{(2)}=\sum_\iota\frac{q_\iota^2}{2m_\iota}\mathbf{A}^2(\mathbf{r}_\iota). \tag{19}$$

The interaction Hamiltonian may be considered as a small perturbation.

We shall suppose that at the initial instant $t=0$, the system is in an eigenstate $\Psi_\beta(\mathbf{r},\mathbf{s})=\varphi_{\iota_0}(\mathbf{r},\mathbf{s})\chi_{v_0}(\mathbf{s})|n_0\rangle$, where $\iota_0$ symbolizes the electronic ground state, $v_0$ denotes the state of lattice vibrations in the absence of electromagnetic field, and $|n_0\rangle=|\{n_{\mathbf{k}\lambda}\}\rangle$ represents the state of incident photons. The perturbation $H_I$ is applied at $t=0^+$, which causes the system to make a transition from the initial state $\Psi_\beta$ to a series of eigenstates $\Psi_\alpha$. Therefore, the general solution of Eq. (17) is a linear superposition of the eigenstates, $\Psi(t)=\Sigma_\alpha c_\alpha(t)\Psi_\alpha e^{-iE_\alpha t/\hbar}$. It is well known that $|c_\alpha(t)|^2$ is the probability of finding the system in the state described by the set $\alpha$ at the instant *t*. $H^{(2)}$ has no effects on the three-photon process being considered. The transition probability due to $H^{(1)}$ will be calculated in the perturbation theory of quantum mechanics in the following. The $(s+1)$-order transition amplitude to any final state $\gamma$ is determined by

$$i\hbar\frac{dc_\gamma^{(s+1)}}{dt}=\sum_\alpha c_\alpha^{(s)}\langle\gamma|H^{(1)}|\alpha\rangle e^{i(E_\gamma-E_\alpha)t/\hbar}, \qquad (20)$$

where $s=0,1,2,\ldots$ and $c_\alpha^{(0)}=\delta_{\alpha\beta}$. In the last equation we can neglect the time dependence of $H^{(1)}$ because $E_\alpha$ already includes the energy of the light field. If the energy spectrum $E_\alpha$ of the system were discrete, the $(s+1)$-order transition probability $|c_\gamma^{(s+1)}|^2$ to a unique final state $\gamma$ would be a good physical quantity.

As we assumed, the energy spectrum of the system is a quasicontinuous photon spectrum near a particular energy $E_\iota$ of the electron subsystem. The transition occurs not on a unique eigenstate of the system but on a set of quasicontinuous eigenstates whose energies $E_\gamma$ are nearly equal to the initial-state energy $E_\beta$. The density of states of the system per unit energy in the vicinity of $E_\gamma=E_\beta$ is equal to the density of photonic states per unit energy around the energy $E=\hbar\omega_{\mathbf{k}}$ per unit solid angle around the direction of wave vector $\mathbf{k}$, which is signified by $\rho(E,\Omega)$, where the solid angle $\Omega$ indicates the direction of wave vector $\mathbf{k}$. Instead of $|c_\gamma^{(s+1)}|^2$, we need to introduce the $(s+1)$-order transition probability per unit time toward a set of quasicontinuous eigenstates $\gamma$, which is then calculated by

$$w^{(s+1)}=t^{-1}\int|c_\gamma^{(s+1)}(t)|^2\rho(E,\Omega)dE_\gamma. \qquad (21)$$

$w^{(s+1)}$ contains all the information about the interaction of light with matter in an $(s+1)$-photon process. $w^{(1)}$ is essential in describing the problem of infrared light absorption, but it can be omitted because the frequencies of the incident light are much higher than the crystal vibrational frequencies. $w^{(2)}$ is fundamental in the treatment of Brillouin and Raman scattering of light, while it can be put aside because we are concerned only with hyper-Raman scattering of light.

The perturbation theory of the third order allows a three-photon indirect transition process originating from $H^{(1)}$. By solving Eq. (20) with the initial conditions $c_\gamma^{(s+1)}(0)=0$, the transition amplitude for the three-photon process can be acquired as

$$c_\gamma^{(3)}(t)=\sum_{\alpha\neq\beta}\sum_{\alpha'\neq\beta}\frac{\langle\gamma|H^{(1)}|\alpha'\rangle\langle\alpha'|H^{(1)}|\alpha\rangle\langle\alpha|H^{(1)}|\beta\rangle}{E_\beta-E_\alpha}\times\left[\frac{e^{i(E_\gamma-E_\beta)t/\hbar}-1}{(E_\beta-E_{\alpha'})(E_\beta-E_\gamma)}-\frac{e^{i(E_\gamma-E_{\alpha'})t/\hbar}-1}{(E_\beta-E_{\alpha'})(E_{\alpha'}-E_\gamma)}-\frac{e^{i(E_\gamma-E_\alpha)t/\hbar}-1}{(E_\alpha-E_{\alpha'})(E_\alpha-E_\gamma)}+\frac{e^{i(E_\gamma-E_{\alpha'})t/\hbar}-1}{(E_\alpha-E_{\alpha'})(E_{\alpha'}-E_\gamma)}\right]. \qquad (22)$$

In comparison with the term conserving the energy $E_\beta=E_\gamma$, the three terms of Eq. (22) with $E_{\alpha(\alpha')}-E_\gamma$ in the denominators are negligible. This is called the rotating-wave approximation. Putting Eq. (22) into Eq. (21), and since the largest contribution to the value of the integral is from the interval surrounding $E_\gamma=E_\beta$, we find the transition probability per unit time for the three-photon process as

$$w^{(3)}=\frac{2\pi}{\hbar}\left|\sum_{\alpha\neq\beta}\sum_{\alpha'\neq\beta}\frac{\langle\gamma|H^{(1)}|\alpha'\rangle}{E_\beta-E_{\alpha'}}\times\frac{\langle\alpha'|H^{(1)}|\alpha\rangle\langle\alpha|H^{(1)}|\beta\rangle}{E_\beta-E_\alpha}\right|^2\rho(E,\Omega). \qquad (23)$$

Here, the states $\alpha$ and $\alpha'$ are intermediate states or virtual states. The state $\alpha$ differs from the initial state $\beta$ by a single photon; the state $\alpha'$ differs from the state $\alpha$ by a single photon too; for the same reason, the final state $\gamma$ differs from the state $\alpha'$ by a single photon; consequently, the final state may differ from the initial one by three photons. Inasmuch as in the frequency region considered there are no electronic transitions between the initial and final states, in the final state $\Psi_\gamma$ the crystal is also in its electronic ground state $\iota_0$. However, electronic transitions between the initial (final) state and the intermediate states are permitted. Therefore, in the intermediate state $\Psi_\alpha$ or $\Psi_{\alpha'}$, $\varphi_\iota$ represents an electronic excited state. The energy is not conserved in transitions from the initial state to the intermediate ones, i.e., $E_\beta\neq E_{\alpha(\alpha')}$.

The probability for three-photon transitions given by Eq. (23) involves the matrix element of $H^{(1)}$ between two states. To treat these matrix elements, we may separate the ions from the electrons in the interaction Hamiltonian (18) and write

$$H^{(1)}=\frac{e}{m_e}\sum_{ji}\mathbf{A}(\mathbf{x}_{ji})\cdot\hat{\mathbf{p}}_{ji}-\sum_j\frac{Z_l(\mathbf{r})e}{m_l}\mathbf{A}(\mathbf{X}_j)\cdot\hat{\mathbf{P}}_j, \qquad (24)$$

where $\hat{\mathbf{p}}_{ji}$ represents the momentum operator of an electron *i* bonded to an ion *j*, $\hat{\mathbf{P}}_j$ is the momentum operator of the *j*th ion, and $Z_l(\mathbf{r})$ is the net charge number of the *l*th basis ion, which depends on the coordinates of all electrons because the valence electrons participate in the chemical bonding among atoms. The wavelength of a near infrared light wave is about 30 000 Å, and this is much larger than a typical lattice constant (5 Å, say). The variation of the potential vector $\mathbf{A}$ in the dimensions of an atom and a cell can be neglected. Therefore, we may replace the arguments of the potential vector $\mathbf{A}$ in Eq. (24) by the equilibrium positions $\mathbf{R}_j$

of the ions. This is called the dipole approximation. Thereby, the interaction Hamiltonian (24) becomes

$$H^{(1)}=-\sum_j \mathbf{A}(\mathbf{R}_j)\cdot\left[-\sum_i \frac{e}{m_e}\hat{\mathbf{p}}_{ji}+\frac{Z_l(\mathbf{r})e}{m_l}\hat{\mathbf{P}}_j\right], \qquad (25)$$

where the summation over $i$ is on the electrons bonded to the ion $j$.

The probability for three-photon transitions involves the matrix element of $H^{(1)}$ between two states. If we employ Eq. (5), we may acquire a general relation between the matrix elements of the position vector of an electron and of its momentum operator,[15]

$$\langle\varphi_{\iota'}|\hat{\mathbf{p}}_k|\varphi_\iota\rangle=m_e i\omega_{\mathbf{p}'_k n'_k,\mathbf{p}_k n_k}\langle\varphi_{\iota'}|\mathbf{r}_k|\varphi_\iota\rangle, \qquad (26)$$

where $\omega_{\mathbf{p}'_k n'_k,\mathbf{p}_k n_k}=(\varepsilon_{\mathbf{p}'_k n'_k}-\varepsilon_{\mathbf{p}_k n_k})/\hbar$ is the Bohr transition frequency. The conservation of energy requires that $\omega_{\mathbf{p}'_k n'_k,\mathbf{p}_k n_k}=\pm\omega_{\mathbf{k}}$. We can also derive a general relation between the matrix elements of the displacement vector of an ion and of its momentum operator,

$$\langle\chi_{v'}|\hat{\mathbf{P}}_j|\chi_v\rangle=\pm i\omega_{\mathbf{k}}m_l\langle\chi_{v'}|\mathbf{s}_j|\chi_v\rangle. \qquad (27)$$

Under the dipole approximation, for the $j$th atom in the crystal we may write:

$$-\sum_i \frac{e}{m_e}\hat{\mathbf{p}}_{ji}+\frac{Z_l(\mathbf{r})e}{m_l}\hat{\mathbf{P}}_j=\pm i\omega_{\mathbf{k}}\left[-e\sum_i \mathbf{r}_{ji}+Z_l(\mathbf{r})e\mathbf{s}_j\right],$$

where the $-$ sign corresponds to the annihilation of a photon and the $+$ sign to its creation. The expression in brackets obviously represents the dipole moment operator of the $j$th atom. It is more convenient to introduce the electronic dipole moment operator of the $j$th atom by $\mathbf{m}_j=-e\Sigma_i\mathbf{r}_{ji}$ and the ionic dipole moment operator of the $j$th atom by $\mathbf{M}_j=Z_l(\mathbf{r})e\mathbf{s}_j$. Putting Eq. (13) into Eq. (25) and utilizing the relation $\mathbf{E}=-\partial\mathbf{A}/\partial t$, the interaction Hamiltonian (25) reduces to

$$H^{(1)}=-\sum_j \mathbf{E}(\mathbf{R}_j)\cdot(\mathbf{m}_j+\mathbf{M}_j), \qquad (28)$$

where the electric field $\mathbf{E}(\mathbf{R}_j)$ is given by

$$\mathbf{E}(\mathbf{R}_j)=-\sum_{\mathbf{k}\lambda} i\left(\frac{\hbar\omega_{\mathbf{k}}}{2V\epsilon_0\epsilon}\right)^{1/2}(-a_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{R}_j}+a^\dagger_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{R}_j})\mathbf{e}_{\mathbf{k}\lambda}. \qquad (29)$$

Equation (28) tells us that the Hamiltonian of interaction of light with a crystal consists of photon-electron and photon-phonon interactions.

## IV. HAMILTONIAN FOR HYPER-RAMAN SCATTERING

The probability for three-photon transitions given by Eq. (23) can give all the details of hyper-Raman scattering of light by crystals. To expound these details, we need to derive the Hamiltonian for hyper-Raman scattering. Hyper-Raman scattering corresponds to indirect transitions of three photons due to the interaction Hamiltonian $H^{(1)}$, which is given by Eq. (28) under the dipole approximation. Since the crystal being investigated has a negligible effect on optical rectification, an obverse three-photon process involves the simultaneous annihilation of two fundamental-frequency photons and then the creation of a double-frequency photon. We have marked the system's initial state as $|\beta\rangle=|\iota_0\rangle|v_0\rangle|n_0\rangle$, where $|n_0\rangle=|\{n_{\mathbf{k}\lambda}\}\rangle$. For spontaneously hyper-Raman scattering of light, the system's initial state should contain no double-frequency photons. This requirement is naturally satisfied for a quasimonochromatic incident light. The transition probability in Eq. (23) is not zero only if the system's final state is of the form $|\gamma\rangle=|\iota_0\rangle|v''\rangle|n''\rangle$, where

$$|n''\rangle=|n_{\mathbf{k}\lambda}-1,n_{\mathbf{k}'\lambda'}-1,n_{\mathbf{k}''\lambda''}+1,\ldots\rangle \qquad (30)$$

signifies the photonic eigenstate in the system's final state, the modes $\mathbf{k}\lambda$, $\mathbf{k}'\lambda'$ refer to fundamental-frequency photons, and the mode $\mathbf{k}''\lambda''$ refers to double-frequency photons. The fundamental-frequency photons in different modes have approximately the same frequency $\omega$.

The final state may be reached through transitions from the initial state to two intermediate states. (1) The action of the annihilation operator $a_{\mathbf{k}\lambda}$ on the initial state $|\beta\rangle$ yields the first intermediate state $|\alpha\rangle=|\iota\rangle|v\rangle|n\rangle$ where $|n\rangle=|n_{\mathbf{k}\lambda}-1,n_{\mathbf{k}'\lambda'},\ldots\rangle$. The energy difference between the initial and intermediate states is calculated as

$$E_\beta-E_\alpha=E_{\iota_0}-E_\iota+E_{v_0}-E_v+\hbar\omega\approx-\hbar(\omega_{\iota 0}-\omega),$$

where $\omega_{\iota 0}=(E_\iota-E_{\iota_0})/\hbar$ is the electronic transition frequency and the vibrational energy difference is omitted because $|E_v-E_{v_0}|\ll\hbar(\omega_{\iota 0}-\omega)$. (2) The action of the annihilation operator $a_{\mathbf{k}'\lambda'}$ on the intermediate state $|\alpha\rangle$ leads to the second intermediate state $|\alpha'\rangle=|\iota'\rangle|v'\rangle|n'\rangle$ where $|n'\rangle=|n_{\mathbf{k}\lambda}-1,n_{\mathbf{k}'\lambda'}-1,\ldots\rangle$ and next the action of the creation operator $a^\dagger_{\mathbf{k}''\lambda''}$ on the intermediate state $|\alpha'\rangle$ gives rise to the final state $|\gamma\rangle$. The energy difference between the initial and intermediate states is found as $E_\beta-E_{\alpha'}\approx-\hbar(\omega_{\iota'0}-2\omega)$. On the other hand, we must consider an inverse three-photon process, which consists of the annihilation of a double-frequency photon and then the simultaneous creation of two fundamental-frequency photons. The contribution of the inverse three-photon process to the transition probability in Eq. (23) is null because the system's initial state $|\beta\rangle=|\iota_0\rangle|v_0\rangle|n_0\rangle$ contains no double-frequency photons. Nevertheless, the inverse three-photon process makes the same contribution as the obverse three-photon process to the hyperpolarizability of a crystal to be introduced in the following.

In line with the above analyses, the matrix elements of the third-order perturbation in Eq. (23) are evaluated as follows:

$$\sum_{\alpha\neq\beta}\sum_{\alpha'\neq\beta}\frac{\langle\gamma|H^{(1)}|\alpha'\rangle}{E_\beta-E_{\alpha'}}\frac{\langle\alpha'|H^{(1)}|\alpha\rangle\langle\alpha|H^{(1)}|\beta\rangle}{E_\beta-E_\alpha}=\langle n''|\langle v''|H_{3p}|v_0\rangle|n_0\rangle, \qquad (31)$$

where we have introduced the interaction Hamiltonian $H_{3p}$ for three-photon indirect transitions, which is defined by

$$H_{3p}=-\sum_{j,j',j''}\sum_{\alpha,\alpha'}\frac{2\langle\iota_0|\mathbf{E}(\mathbf{R}_j)\cdot(\mathbf{m}_j+\mathbf{M}_j)|\alpha'\rangle\langle\alpha'|\mathbf{E}(\mathbf{R}_{j'})\cdot(\mathbf{m}_{j'}+\mathbf{M}_{j'})|\alpha\rangle\langle\alpha|\mathbf{E}(\mathbf{R}_{j''})\cdot(\mathbf{m}_{j''}+\mathbf{M}_{j''})|\iota_0\rangle}{\hbar^2(\omega_{\iota'0}-2\omega)(\omega_{\iota0}-\omega)},\tag{32}$$

where the prefactor 2 accounts for the two equal contributions from the obverse and inverse three-photon processes. The triad $\mathbf{E}(\mathbf{R}_j)\mathbf{E}(\mathbf{R}_{j'})\mathbf{E}(\mathbf{R}_{j''})$ contains only the $a^{\dagger}_{\mathbf{k}''\lambda''}a_{\mathbf{k}'\lambda'}a_{\mathbf{k}\lambda}$ and $a^{\dagger}_{\mathbf{k}\lambda}a^{\dagger}_{\mathbf{k}'\lambda'}a_{\mathbf{k}''\lambda''}$ terms. In calculating the summation over the intermediate states $\alpha$ and $\alpha'$, we can employ the closure relations for the vibrational eigenstates $v,v'$ and for the photonic eigenstates $n,n'$, for example,

$$\sum_{v}|v\rangle\langle v|=1,\quad \sum_{n}|n\rangle\langle n|=1.\tag{33}$$

Consequently, the interaction Hamiltonian $H_{3p}$ can be cast into the standard form,

$$H_{3p}=-\frac{2}{3}\sum_{j,j',j''}\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s}):\mathbf{E}(\mathbf{R}_j)\mathbf{E}(\mathbf{R}_{j'})\mathbf{E}(\mathbf{R}_{j''}),\tag{34}$$

where $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})$ is a third-rank tensor and represents the hyperpolarizability due to virtual transitions of the valence electrons in the electromagnetic field. The hyperpolarizability $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})$ accounts for the bonding among the three atoms $j$, $j'$, and $j''$ through valence electrons and contains all the information of a lattice of interacting ions. When $j=j'=j''$, the hyperpolarizability $\mathbf{P}^{(2)}_{jjj}(\omega,\mathbf{s})$ reduces to the second-order nonlinear atomic polarizability. In what follows, we consider only the bonding of the atom $j=nl$ with the nearest-neighbor atoms $j'=nl'$ and $j''=nl''$. In other words, we consider only the bonding among the atoms in the same cell.

The hyperpolarizability is defined by

$$\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})=\frac{3}{\hbar^2}\sum_{\iota,\iota'}\frac{\langle\iota_0|(\mathbf{m}_j+\mathbf{M}_j)|\iota'\rangle\langle\iota'|(\mathbf{m}_{j'}+\mathbf{M}_{j'})|\iota\rangle\langle\iota|(\mathbf{m}_{j''}+\mathbf{M}_{j''})|\iota_0\rangle}{(\omega_{\iota'0}-2\omega)(\omega_{\iota0}-\omega)}.\tag{35}$$

The hyperpolarizability originates from a simple physical mechanism. Under the influence of the electromagnetic field, the charge center of the electron shell of an atom shifts relative to that of its nucleus and hence an electric dipole moment $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s}):\mathbf{E}(\mathbf{R}_j)\mathbf{E}(\mathbf{R}_{j'})$ is induced in the two bonding atoms $j$ and $j'$, which interacts with the $j''$th atom through the electric field $\mathbf{E}(\mathbf{R}_{j''})$.

### A. Hyper-Raman scattering of light by nonpolar modes

This subsection concerns hyper-Raman scattering of light by nonpolar modes. It is well known that nonpolar modes carry no ionic dipole moments $\mathbf{M}_j$. Nonpolar-mode scattering is due to the electronic dipole moments $\mathbf{m}_j$ in Eq. (35), so that the ionic dipole moments $\mathbf{M}_j$ in Eq. (35) are omitted. The $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})$ in this case is given by

$$\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})=\frac{3}{\hbar^2}\sum_{\iota,\iota'}\frac{\langle\iota_0|\mathbf{m}_j|\iota'\rangle\langle\iota'|\mathbf{m}_{j'}|\iota\rangle\langle\iota|\mathbf{m}_{j''}|\iota_0\rangle}{(\omega_{\iota'0}-2\omega)(\omega_{\iota0}-\omega)}.\tag{36}$$

It is desirable to explicitly express the matrix element of the electronic dipole moment operator of the $j$th atom between the electronic states $\iota'$ and $\iota$,

$$\langle\iota'|\mathbf{m}_j|\iota\rangle=\int\varphi^{*}_{\iota'}(\mathbf{r},\mathbf{s})\left(-e\sum_{i}\mathbf{r}_{ji}\right)\varphi_{\iota}(\mathbf{r},\mathbf{s})d\mathbf{r}.\tag{37}$$

As shown, the wave functions of valence electrons depend on the ionic coordinates. Although the matrix element involves two different states of a valence electron, the integration over valence electrons in Eq. (37) brings a nonzero contribution to the matrix element. Thereby, the matrix element $\langle\iota'|\mathbf{m}_j|\iota\rangle$ depends on the ionic displacements $\mathbf{s}$ and so does the hyperpolarizability $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})$. Since the acoustic modes do not participate in hyper-Raman scattering, the ionic displacements $\mathbf{s}$ here refer to the optical vibrations.

The hyperpolarizability $\mathbf{P}^{(2)}_{jj'j''}(\omega,\mathbf{s})$ can be expanded in a power series of $\mathbf{s}$,

$$\mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})=\mathbf{P}^{(2)}_{ll'l''}(\mathbf{0})+\delta_1\mathbf{P}^{(2)}_{jj'j''}(\mathbf{s}),\tag{38}$$

$$\delta_1\mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})=N^{-1/2}\sum_{j_1}\mathbf{B}_{jj'j''j_1}\cdot\mathbf{s}_{j_1}+\frac{1}{2}\sum_{j_1j_2}\mathbf{s}_{j_1}\cdot\mathbf{B}_{jj'j''j_1j_2}\cdot\mathbf{s}_{j_2}+\cdots.\tag{39}$$

Here $\mathbf{P}^{(2)}_{ll'l''}(\mathbf{0})$ is the hyperpolarizability in the equilibrium configuration of the lattice. $\delta_1\mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$ is the variation in the hyperpolarizability $\mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$ due to deformation of the electronic wave functions and $\mathbf{B}_{jj'j''j_1}$ and $\mathbf{B}_{jj'j''j_1j_2}$ are the fourth- and fifth-rank tensors computed at the equilibrium positions of the ions. In Eq. (39), the first-order term gives rise to a one-phonon hyper-Raman scattering; the second-order term leads to a two-phonon hyper-Raman scattering.

We shall keep only the first-order term. Owing to translation symmetry, the expansion coefficient $\mathbf{B}_{nl,nl',nl'',n_1l_1}$ is a function only of the relative cell indices $n_2 = n_1 - n$, i.e., $\mathbf{B}_{nl,nl',nl'',n_1l_1} = \mathbf{B}_{ll'l''l_1}(n_2)$. When the ionic displacements $\mathbf{s}_j$ are given by Eq. (7) with $J$ being an optical branch index of normal modes, the hyperpolarizability increment $\delta_1 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$ can be rewritten as follows:

$$\delta_1 \mathbf{P}^{(2)}_{nl,nl',nl''}(\mathbf{s}) = N^{-1} \sum_{\mathbf{q}J} \mathcal{P}^{(2)}_{1,ll'l''}(J,\mathbf{q}) Q_J(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n}, \tag{40}$$

$$\mathcal{P}^{(2)}_{1,ll'l''}(J,\mathbf{q}) = \sum_{n_2 l_1} m_{l_1}^{-1/2} \mathbf{B}_{ll'l''l_1}(n_2) \cdot \mathbf{e}_{l_1}(\mathbf{q}J) e^{i\mathbf{q}\cdot\mathbf{R}_{n_2}},$$

where $\mathbf{R}_{n_2} = \mathbf{R}_{n_1} - \mathbf{R}_n$. It is more useful to introduce a quantity $\mathcal{P}^{(2)}_1(J,\mathbf{q}) = \Sigma_{ll'l''} \mathcal{P}^{(2)}_{1,ll'l''}(J,\mathbf{q})$, which is the electronic component of the hyper-Raman tensor.

### B. Hyper-Raman scattering of light by polar modes

There are two mechanisms responsible for hyper-Raman scattering of light by polar modes. In mathematical terms, the first mechanism is due to the interaction Hamiltonian (28) without $\mathbf{M}_j$. Therefore, the theory developed in Sec. IV A also applies to the first mechanism of hyper-Raman scattering of light by polar modes. In physics, the first mechanism results from the coupling of the crystal electrons with the lattice vibrations, and it is translated into polarizability theory by the deformation of the electronic wave functions which depend on the ionic displacements. Now we need to establish a quantum theory to interpret the second mechanism of hyper-Raman scattering of light by polar modes. The starting point of the theory is that, when we consider the polar vibrations of the lattice, the electrons of the crystal move in an equilibrium configuration of the lattice. Therefore, we employ the electronic wave functions, which do not depend on the ionic displacements, i.e., $\varphi_\iota(\mathbf{r},\mathbf{0})$. Since polar modes carry electric-dipole moments, which are characterized by the ionic-dipole moments $\mathbf{M}_j$, now in Eq. (35) we should keep only one ionic-dipole moment $\mathbf{M}_j$ and two electronic-dipole moments $\mathbf{m}_j$. In this method, one derives an additional variation in the hyperpolarizability due to the electric-dipole moments of polar modes,

$$\delta_2 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s}) = \frac{9}{\hbar^2} \sum_{\iota,\iota'} \frac{\langle \iota_0|\mathbf{M}_j|\iota'\rangle\langle \iota'|\mathbf{m}_{j'}|\iota\rangle\langle \iota|\mathbf{m}_{j''}|\iota_0\rangle}{(\omega_{\iota'0} - 2\omega)(\omega_{\iota 0} - \omega)}. \tag{41}$$

Then, the development of the theory is parallel to the formulation established in Sec. IV A. Using the expression $\mathbf{M}_j = Z_l(\mathbf{r}) e \mathbf{s}_j$ and the expression (7) of $\mathbf{s}_j$ in Eq. (41), we can also cast $\delta_2 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$ in the form of Eq. (40):

$$\delta_2 \mathbf{P}^{(2)}_{nl,nl',nl''}(\mathbf{s}) = N^{-1} \sum_{\mathbf{q}J} \mathcal{P}^{(2)}_{2,ll'l''}(J,\mathbf{q}) Q_J(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n}, \tag{42}$$

$$\mathcal{P}^{(2)}_2(J,\mathbf{q}) = \sum_{ll'l''} \mathcal{P}^{(2)}_{2,ll'l''}(J,\mathbf{q}) = 9\sqrt{N} e Z_J \boldsymbol{\xi}_J(\mathbf{q}) \mathbf{T}_J / \hbar^2 \omega^2. \tag{43}$$

Here $\boldsymbol{\xi}_J(\mathbf{q})$ is a unit polarization vector of optical mode $Q_J(\mathbf{q})$ and $Z_J$ is the effective charge number of optical mode $J$ defined by

$$Z_J \boldsymbol{\xi}_J(\mathbf{q}) \mathbf{T}_J = \sum_{ll'l''} \frac{Z_l' \mathbf{e}_l(\mathbf{q}J) \mathbf{T}_{l'l''}}{\sqrt{m_l}},$$
$$\mathbf{T}_{l'l''} = \sum_{\iota,\iota'} \frac{\omega^2 \langle \iota'|\mathbf{m}_{j'}|\iota\rangle\langle \iota|\mathbf{m}_{j''}|\iota_0\rangle}{(\omega_{\iota'0} - 2\omega)(\omega_{\iota 0} - \omega)}. \tag{44}$$

Under the decoupling approximation we have introduced the effective charge number of the $l$th basis ion by $Z_l' = \langle \iota_0|Z_l|\iota_0\rangle$ and because of translational invariance $\mathbf{T}_{l'l''}$ is independent of the cell indices $n'$ and $n''$. By Eq. (44) we have also introduced a tensor $\mathbf{T}_J$ associated with the $J$th mode. The effective charge number $Z_J$ defined in this way is zero for all nonpolar modes. $\mathcal{P}^{(2)}_2(J,\mathbf{q})$ is the ionic component of the hyper-Raman tensor. Note that the matrix element $\langle \iota_0|\mathbf{M}_j|\iota'\rangle$ or $\langle \iota_0|Z_l|\iota'\rangle$ does not vanish because $Z_l(\mathbf{r})$ depends on the coordinates of all electrons.

A polar mode that carries electric-dipole moments generates a macroscopic electric field in the crystal. The electric field modifies the hyperpolarizability of the crystal and thereby produces a hyperpolarizability increment $\delta_2 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$. This is the second-order nonlinear electro-optic effect or the Pockels effect. Therefore, the second mechanism of hyper-Raman scattering arises from the second-order nonlinear electro-optic effect produced by the macroscopic electric field related to a polar mode.

### C. A general case

The above two subsections can be united into a general case when the hyper-Raman active modes may be nonpolar modes or polar modes. The total variation in the hyperpolarizability among three atoms $j$, $j'$, and $j''$ due to optical vibrations of a lattice is given by $\delta \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s}) = \delta_1 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s}) + \delta_2 \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s})$, where the second term is absent for nonpolar modes. It will be helpful to introduce the total variation in the hyperpolarizability of the $n$th cell by

$$\delta \mathbf{P}^{(2)}_n(\mathbf{s}) = \sum_{ll'l''} \delta \mathbf{P}^{(2)}_{nl,nl',nl''}(\mathbf{s})$$
$$= N^{-1} \sum_{\mathbf{q}J} \mathcal{P}^{(2)}(J,\mathbf{q}) Q_J(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_n}, \tag{45}$$

where $\mathcal{P}^{(2)}(J,\mathbf{q}) = \mathcal{P}^{(2)}_1(J,\mathbf{q}) + \mathcal{P}^{(2)}_2(J,\mathbf{q})$ is the total hyper-Raman tensor. The Hamiltonian for hyper-Raman scattering is defined by

$$H_{hR} = -\frac{2}{3} \sum_{j,j',j''}{}' \delta \mathbf{P}^{(2)}_{jj'j''}(\mathbf{s}) \vdots \mathbf{E}(\mathbf{R}_j) \mathbf{E}(\mathbf{R}_{j'}) \mathbf{E}(\mathbf{R}_{j''}), \tag{46}$$

where the prime on the summation symbol means $j = nl$, $j' = nl'$, and $j'' = nl''$.

We may replace the arguments of the electric field $\mathbf{E}$ in Eq. (46) by the direct lattice vectors $\mathbf{R}_n$. When one substitutes Eq. (45) into Eq. (46) and uses the expression (9) for $Q_J(\mathbf{q})$ and the expression (29) for $\mathbf{E}(\mathbf{R}_n)$, the Hamiltonian $H_{hR}$ for hyper-Raman scattering is second quantized below:

$$H_{hR} = \sum_{\mathbf{q}J} \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \lambda\lambda'}} V_{\lambda\lambda'}(\mathbf{k},\mathbf{k}';\mathbf{q}J)(a^\dagger_{\mathbf{k}+\mathbf{k}'+\mathbf{q},\lambda'} a_{\mathbf{k}'\lambda} a_{\mathbf{k}\lambda} - a^\dagger_{\mathbf{k}\lambda} a^\dagger_{\mathbf{k}'\lambda} a_{\mathbf{k}+\mathbf{k}'-\mathbf{q},\lambda'})(b_{\mathbf{q}J} + b^\dagger_{-\mathbf{q},J}), \tag{47}$$

$$V_{\lambda\lambda'}(\mathbf{k},\mathbf{k}';\mathbf{q}J) = -i\left[\frac{2\hbar\omega_{\mathbf{k}+\mathbf{k}'\mp\mathbf{q}}\omega_{\mathbf{k}'}\omega_{\mathbf{k}}}{\omega_J(\mathbf{q})\epsilon_2\epsilon_1^2}\right]^{1/2}\left(\frac{\hbar}{2V\epsilon_0}\right)^{3/2} \times \boldsymbol{\mathcal{P}}^{(2)}(J,\mathbf{q}) : \mathbf{e}_{\mathbf{k}+\mathbf{k}'\mp\mathbf{q},\lambda'}\mathbf{e}_{\mathbf{k}'\lambda}\mathbf{e}_{\mathbf{k}\lambda}, \tag{48}$$

where $V^*_{\lambda\lambda'}(\mathbf{k},\mathbf{k}';\mathbf{q}J) = -V_{\lambda\lambda'}(\mathbf{k},\mathbf{k}';-\mathbf{q},J)$ and the minus and plus signs correspond to the Stokes and anti-Stokes scattering events respectively. $\epsilon_1$ and $\epsilon_2$ denote the relative permittivities of the crystal at the fundamental frequency $\omega_{\mathbf{k}}$ or $\omega_{\mathbf{k}'}$ and the double frequency $\omega_{\mathbf{k}+\mathbf{k}'\mp\mathbf{q}}$, respectively. The Hamiltonian $H_{hR}$ given by Eq. (47) describes the obverse process of two correlated fundamental photons scattered by an optical phonon into a second-harmonic photon and the related inverse process. Since the incident light is a quasimonochromatic field, we have to make sums over all possible modes $\mathbf{k}\lambda$, $\mathbf{k}'\lambda'$, and $\mathbf{q}J$. Notice that the two fundamental photons have the same polarization index $\lambda$ while the polarization index $\lambda'$ of the second-harmonic photon may be different from that of the incident photons.

## V. HYPER-RAMAN SCATTERING INTENSITY OF LIGHT

As we said, the transition probability per time unit for a three-photon process given by Eq. (23) contains all the information about the interaction of light with matter in the three-photon process. Substituting Eq. (31) into Eq. (23) one gets an explicit expression of the transition probability

$$w^{(3)} = \frac{2\pi}{\hbar}|\langle n''|\langle v''|H_{3p}|v_0\rangle|n_0\rangle|^2\rho(E,\Omega). \tag{49}$$

In this section we shall use Eq. (49) to calculate the hyper-Raman scattered intensity of light. To this end, the Hamiltonian $H_{3p}$ in Eq. (49) is replaced with the Hamiltonian $H_{hR}$ for hyper-Raman scattering as given by Eq. (47). The state $|v_0\rangle$ in Eq. (49) is a pure many-mode number state given by Eq. (11) and therefore far from thermal equilibrium. However, the crystal is in a thermal equilibrium state characterized by a certain temperature $T$ before the system makes transitions. The crystal in thermal equilibrium must occupy every eigenstate $|v_0\rangle$ with a definite probability. The distribution of probability over eigenstates obeys Boltzmann's law,

$$\rho(v_0) = \frac{\exp(-E_{v_0}/k_BT)}{\mathrm{Tr}\exp(-H^*_{ion}/k_BT)}, \tag{50}$$

where $k_B$ is the Boltzmann constant and Tr denotes the trace. $H^*_{ion}$ and $E_{v_0}$ are given by Eqs. (10) and (12), respectively. If we take the thermal average over all the initial states $|v_0\rangle$ with weight factors $\rho(v_0)$, Eq. (49) becomes

$$w_{hR} = \frac{2\pi}{\hbar}\sum_{v_0}\rho(v_0)|\langle n''|\langle v''|H_{hR}|v_0\rangle|n_0\rangle|^2\rho(E,\Omega). \tag{51}$$

In the following, $\mathbf{k}''$ and $\omega_2 = c|\mathbf{k}''|/\sqrt{\epsilon_2}$ represent the wave vector and frequency of a second-harmonic photon. $w_{hR}$ stands for the hyper-Raman scattering probability of a second-harmonic photon per unit time into a unit solid angle around the direction $\mathbf{k}''$. We have to evaluate the density of states $\rho(E,\Omega)$ per unit energy around the energy $E$ per unit solid angle around the direction $\mathbf{k}''$, since this $\rho$ appears in Eq. (51). Employing the relation $E = \hbar\omega_2$, we acquire

$$\rho(E,\Omega) = (V/8\pi^3c^3\hbar)\epsilon_2^{3/2}\omega_2^2. \tag{52}$$

The Hamiltonian $H_{hR}$ for hyper-Raman scattering as given by Eq. (47) describes all possible scattering events of a quasimonochromatic incident light. For simplicity, we now consider a particular scattering configuration, in which an incident plane light wave propagates along a wave vector $\mathbf{k}$ with a polarization index $\lambda$, a scattering optical vibration wave travels along a wave vector $\mathbf{q}$ with a branch index $J$, and hence the scattered second-harmonic light runs along a wave vector $\mathbf{k}'' = 2\mathbf{k} \pm \mathbf{q}$ with a polarization index $\lambda'$. Further, one makes a prescription that the polarization vector $\mathbf{e}_{\mathbf{k}\lambda}$ of the incident plane light is along the $\alpha$th Cartesian coordinate while the polarization vector $\mathbf{e}_{\mathbf{k}''\lambda'}$ of the scattered second-harmonic light points to the $\beta$th one. Consistent with this scattering configuration, we abolish the sums in Eq. (47) and obtain the Hamiltonian for a particular hyper-Raman scattering event as

$$H_{hR} = V_{\lambda\lambda'}(\mathbf{k},\mathbf{k};\mathbf{q}J)(a^\dagger_{2\mathbf{k}+\mathbf{q},\lambda'}a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda} - a^\dagger_{\mathbf{k}\lambda}a^\dagger_{\mathbf{k}\lambda}a_{2\mathbf{k}-\mathbf{q},\lambda'}) \times (b_{\mathbf{q}J} + b^\dagger_{-\mathbf{q},J}), \tag{53}$$

where Eq. (48) reduces to

$$V_{\lambda\lambda'}(\mathbf{k},\mathbf{k};\mathbf{q}J) = -i\left[\frac{2\hbar\omega_{2\mathbf{k}\pm\mathbf{q}}\omega_{\mathbf{k}}^2}{\omega_J(\mathbf{q})\epsilon_2\epsilon_1^2}\right]^{1/2}\left(\frac{\hbar}{2V\epsilon_0}\right)^{3/2}\mathcal{P}^{(2)}_{\alpha\alpha\beta}(J,\mathbf{q}). \tag{54}$$

Since we have idealized the incident laser light as a single-mode laser light, the corresponding eigenstate of the Hamiltonian of the light field reads

$$|n_0\rangle = |n_{\mathbf{k}\lambda}\rangle = \frac{1}{\sqrt{n_{\mathbf{k}\lambda}!}}(a^\dagger_{\mathbf{k}\lambda})^{n_{\mathbf{k}\lambda}}|0\rangle, \tag{55}$$

where the photon number $n_{\mathbf{k}\lambda} \gg 1$. Obviously the photonic initial state contains no double-frequency photons, such that

$a_{\mathbf{k}''\lambda'}|n_0\rangle=0$. After the system makes transitions, the photonic eigenstate is specified by $|n''\rangle=a^{\dagger}_{\mathbf{k}''\lambda'}|n_{\mathbf{k}\lambda}-2\rangle$. The phononic eigenstate in the system's initial state is written as $|v_0\rangle=|v_{\mathbf{q}J},v_{\mathbf{q}'J'},\ldots\rangle$, which is still given by Eq. (11). After the system makes transitions, the phononic eigenstate takes the form

$$|v''\rangle=|v_{\mathbf{q}J}\pm 1,v_{\mathbf{q}'J'},\ldots\rangle,$$

where the plus and minus signs refer to the Stokes and anti-Stokes scattering events, respectively.

The formula (51) and the subsequent expressions provide us with all the elements necessary for the calculation of the hyper-Raman scattering probability of second-harmonic photons per unit time into an infinitesimal solid angle $d\Omega$ around the direction $\mathbf{k}''$:

$$w_{hR}d\Omega=\frac{\sqrt{\epsilon_2}\omega_2^3}{16\pi^2c^5\epsilon_1\epsilon_0^3\omega_J(\mathbf{q})}\frac{n_{\mathbf{k}\lambda}-1}{n_{\mathbf{k}\lambda}}[\mathcal{P}^{(2)}_{\alpha\alpha\beta}(J,\mathbf{q})I_0]^2 \times d\Omega\begin{cases}\overline{v}_{\mathbf{q}J}+1 & \text{for a Stokes line,}\\ \overline{v}_{\mathbf{q}J} & \text{for an anti-Stokes line.}\end{cases} \tag{56}$$

The second-harmonic photons suffering from hyper-Raman scattering have the frequencies $\omega_2=2\omega_{\mathbf{k}}\mp\omega_J(\mathbf{q})$, where the minus and plus signs refer to the Stokes and anti-Stokes lines, respectively. $\overline{v}_{\mathbf{q}J}$ is the mean value of the phonon number $v_{\mathbf{q}J}$ in an active optical mode $\mathbf{q}J$ defined by

$$\overline{v}_{\mathbf{q}J}=\frac{1}{\exp[\hbar\omega_J(\mathbf{q})/k_BT]-1}. \tag{57}$$

We have introduced the intensity of the incident plane wave by

$$I_0=\frac{n_{\mathbf{k}\lambda}\hbar\omega_{\mathbf{k}}}{V}\frac{c}{\sqrt{\epsilon_1}}. \tag{58}$$

The component $\mathcal{P}^{(2)}_{\alpha\alpha\beta}(J,\mathbf{q})$ of a hyper-Raman tensor associated with an active mode characterizes the ability of a crystal to scatter a second-harmonic light and so is completely determined by the crystal properties.

One usually observes the hyper-Raman scattering intensity $I_2$ of light at a large distance $R$ from a crystal. The $w_{hR}d\Omega$ given by Eq. (56) also expresses the number of second-harmonic photons hyper-Raman scattered per time unit into an infinitesimal solid angle $d\Omega$ around the direction $\mathbf{k}''$. By multiplying Eq. (56) by $\hbar\omega_2$, we obtain $I_2R^2d\Omega=\hbar\omega_2w_{hR}d\Omega$. $I_2R^2d\Omega$ represents the energy of second-harmonic light scattered per second into a solid angle $d\Omega$ around the direction $\mathbf{k}''$ and is acquired as

$$I_2R^2d\Omega=\frac{\sqrt{\epsilon_2}\hbar\omega_2^4}{16\pi^2c^5\epsilon_1\epsilon_0^3\omega_J(\mathbf{q})}[\mathcal{P}^{(2)}_{\alpha\alpha\beta}(J,\mathbf{q})I_0]^2 \times d\Omega\begin{cases}\overline{v}_{\mathbf{q}J}+1 & \text{for a Stokes line,}\\ \overline{v}_{\mathbf{q}J} & \text{for an anti-Stokes line.}\end{cases} \tag{59}$$

As the reduced Planck constant $\hbar$ appears in the above expression, hyper-Raman scattering of light is a quantum effect. Equation (59) shows that the distance dependence of the intensity $I_2$ is an inverse square law. The intensity $I_2$ corresponds to a scattered second-harmonic light analyzed in the $\beta$ direction, which is induced by an incident radiation polarized in the $\alpha$ direction. The intensity $I_{2S}$ of a Stokes line of frequency $\omega_2=2\omega-\omega_J(\mathbf{q})$ is associated with an optical phonon creation in hyper-Raman scattering. The intensity $I_{2A}$ of an anti-Stokes line of frequency $\omega_2=2\omega+\omega_J(\mathbf{q})$ is associated with an optical phonon annihilation in hyper-Raman scattering. The temperature dependence of $I_{2S}$ is different from that of $I_{2A}$. By taking account of the expression (57) for the mean phonon number $\overline{v}_{\mathbf{q}J}$, we thus obtain

$$I_{2A}/I_{2S}=\left[\frac{2\omega+\omega_J(\mathbf{q})}{2\omega-\omega_J(\mathbf{q})}\right]^4\exp[-\hbar\omega_J(\mathbf{q})/k_BT]. \tag{60}$$

Equation (60) gives the ratio of the intensities of the Stokes and anti-Stokes lines for a definite temperature.

The hyper-Raman scattering of light mentioned above is spontaneous. As known, the spontaneously Raman scattering intensity of light is directly proportional to the intensity $I_0$ of an incident light. However, as shown in Eq. (59), the spontaneously hyper-Raman scattering intensity of light is directly proportional to the square of the incident intensity $I_0$. It is interesting to inspect the hyper-Raman scattering spectrum of light by polar modes. A polar vibration mode that carries electric-dipole moments produces a lattice polarization, and again the polarization generates a macroscopic electric field. The polar-vector representation is threefold degenerate for the cubic symmetry groups. The effect of the macroscopic field in cubic crystals is to lift the group-theoretical degeneracy of polar modes, producing a nondegenerate longitudinal vibration, which lies at a higher frequency than the doubly degenerate transverse vibrations. The modes thus produce two distinct peaks in the hyper-Raman spectrum. The simplest cubic piezoelectric crystals possess the zinc blende structure like GaP, which has a single threefold polar mode. The above results deduced from Eq. (59) agree well with the known experimental results.[12] However, the variation of Eq. (60) with temperature will be verified in an experiment.[16]

## VI. SUMMARY AND DISCUSSION

The earlier theories of hyper-Raman scattering possess the following shortcomings: (1) the theories are semiclassical in nature, (2) fourth-order perturbation theory is used, and (3) the theories lack universality. In contrast our theory possesses the following advantages. (1) We present a quantum field theory of hyper-Raman scattering of light by crystals. Our theory can also be generalized to molecular media. (2) We employ third-order perturbation theory. Now we explain why our theory is so much simpler than a semiclassical theory. In the semiclassical theory, the interaction of light with a crystal is only a photon-electron interaction but there is an electron-phonon interaction, so that hyper-Raman scattering is a four-photon process. In the first process, an incident photon creates a virtual electron-hole pair. In the second process, the electron (or hole) emits or absorbs a phonon. In the third process, another incident photon creates the second virtual electron-hole pair. In the fourth process, the second-harmonic photon arises in the recombination of the pairs. In the semiclassical theory, the scattering process in a crystal is represented by means of four electronic transitions induced by photons and phonons, which requires the use of fourth-order perturbation theory. In our theory, the Hamiltonian of the interaction of light with a crystal consists of photon-electron and photon-phonon interactions but there is no electron-phonon interaction, so that hyper-Raman scattering is a three-photon process. In the first process, an incident photon creates a virtual electron-hole pair and another incident photon emits or absorbs a phonon. In the second process, the second photon creates the second virtual electron-hole pair. In the third process, the second-harmonic photon arises in the recombination of the pairs. In our theory, the scattering process in a crystal is represented by means of three electronic transitions induced by photons and phonons, which requires the use of only third-order perturbation theory. Our theory is independent of any concrete model of electron-phonon interaction and therefore has a certain generality. (3) We establish a unified theoretical framework to describe hyper-Raman scattering of light by nonpolar modes and longitudinal or transverse polar modes. In this framework, photons and phonons are described by second-quantized field theory while electrons are depicted by classical quantum mechanics, because electrons play an auxiliary role. By comparison our theory possesses a clear physical picture and is strongly systematic.

The properties of the scattered radiation of principal interest are the frequency, polarization, and intensity. The determination of frequency depends on the frequencies of the incident laser light and the hyper-Raman active mode. Much of the detailed work in the present paper concerns the intensity of the scattered light. However, we never touch upon the polarization of the scattered light. In general the polarization of the scattered light is different from that of the incident beam. The polarization direction of the scattered light is very difficult to determine theoretically. Our discussion also does not relate to the type of piezoelectric crystal. In general our theory applies to isotropic piezoelectric crystals. For uniaxial and biaxial piezoelectric crystals some correction is made. Uniaxial and biaxial crystals are birefringent crystals. When a beam of polarized light travels in an arbitrary direction through a birefringent crystal it is split into two perpendicularly polarized components with different velocities. This also applies to scattered light. In the biaxial case the basic polar modes are all nondegenerate by group theory and the macroscopic electric field cannot produce any additional mode splittings.

Now we summarize the approximations made in the present paper. The author initially assumes that the incident light is a quasimonochromatic field of central frequency $\omega$, which is consistent with quantum field theory. In quantum field theory, the electromagnetic field is a many-mode field and the quantized Hamiltonian of the field contains a sum over all such modes. However, in Sec. V the author idealizes the incident laser light as a single-mode laser light. In this case, the sum in the Hamiltonian can be abolished and the calculation is much simpler. In Sec. II, the author uses the adiabatic approximation to separate the motion of valence electrons from that of lattice ions. Afterwards, the one-electron approximation is employed to solve the Schrödinger equation of the many-electron system and the harmonic approximation is utilized to reduce the coupled motion of lattice ions. In Sec. III, we use the rotating-wave approximation to find the transition probability per unit time in a three-photon process and use the dipole approximation to derive the effective interaction Hamiltonian of light with a crystal. Within these constraints all the calculations have been carried out correctly, but these constraints on the theory have to be kept in mind.

To sum up, we have established a quantum field theory of hyper-Raman scattering of light by piezoelectric crystals. Our theory can produce an additional physical mechanism of hyper-Raman scattering of light by polar modes, which arises from the second-order nonlinear electro-optic effect of polar modes. We have developed a unified theoretical framework to describe hyper-Raman scattering of light by nonpolar modes and longitudinal or transverse polar modes. In this framework, we find the ratio of the intensities of the Stokes and anti-Stokes lines for hyper-Raman scattered light and observe two distinct peaks of hyper-Raman scattering from the split polar modes.

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