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Raman scattering using vortex light

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ABSTRACT

We re-examine the theory of Raman scattering in cubic crystals. The unconventional vector potential of vortex light leads to new selection rules. We show that in this novel optical process, (a) silent phonon modes become active and (b) scattering tensors change for ordinary Raman active phonon modes. Calculation based on a simplified model shows that the vortex Raman scattering intensity can be comparable with that of ordinary Raman process.

1. Introduction

Light can carry both spin angular momentum (SAM) and orbital angular momentum (OAM) [1]. SAM determines the polarization direction of the beam while OAM describes its spatial profile. Laguerre–Gaussian (LG) beams are one family of light beams with non-zero OAM. LG beams have helical phase fronts, and a phase singularity near the beam center leads to vanishing intensities. Today, LG beams can be readily produced [2], and similar helical profiles have been realized in other forms of waves [3–6]. The existing studies of the interaction between vortex light and matter include optical tweezers [7–10], the rotational Doppler effect [11,12], and others [13]. As suggested by many authors [14], OAM is not just a property of the beam but rather an intrinsic property of photons. This opens the possibility of spectroscopic applications. However, due to the smallness of single atoms, atomic transitions have not been realized. The lack of experimental confirmation of atomic transitions may also be explained by the fact that [15] the interactions between vortex light and electronic degrees of freedom are higher order effects.

In solids, the electronic wave functions extend over the entire interaction volume and electrons can “see” the whole profile of the vortex light. In this manuscript, we present the first study of Raman processes using vortex light. The discussion is focused on high symmetry cubic crystals. We analyze and tabulate the Raman tensors for the forward scattering geometry with vortex light and show that two effects are expected: (a) additional Γ_2 phonons and (b) a new scattering cross section dependence on polarization for Γ_3 phonons (Fig. 2). The relative intensity of vortex Raman is also studied. The scattering intensity is shown to be comparable with that of the ordinary Raman process.

This paper is arranged as follows: Section 2 gives the general theory of light scattering. Parallel discussions of Raman scattering using both ordinary light and vortex light are presented in Sections 3 and 4. The results of Raman tensor analysis are tabulated for cubic crystals. A calculation of the scattering intensity is also presented. Section 5 shows the experimental implementations. Discussions are given in Section 6.

2. General discussion of light scattering intensity

In a light scattering process, the total scattering intensity is given by

$$I_{mn} = \frac{2^7\pi^5}{3^2c^4} I_0(\nu_0+\nu_{mn})^4 \sum_{\rho,\sigma} |(\alpha_{\rho\sigma})_{mn}|^2 \tag{1}$$

m, n are indices for vibrational states and ρ, σ are indices for the incident and scattered photons. The polarizability α is related to the initial, final and intermediate vibrational states through the following relation:

$$(\alpha_{\rho\sigma})_{mn} = \frac{1}{2\pi\hbar}\sum_r \left[\frac{(M_\rho)_{rn}(M_\sigma)_{mr}}{\nu_{rm}-\nu_0} + \frac{(M_\rho)_{mr}(M_\sigma)_{rn}}{\nu_{rn}+\nu_0}\right] \tag{2}$$

$(M_\rho)_{mn}$ is the transition matrix between vibrational levels m and n, in the presence of the *radiation operator* $\hat{\mathbf{m}}_\rho$:

$$(M_\rho)_{mn} = \int \Psi_r^* \hat{\mathbf{m}}_\rho \Psi_m \, d\tau \tag{3}$$

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The vibrational wave function Ψ_m, under Born–Oppenheimer approximation, can be expressed as $\Psi_m = \Psi_{gi} = \Theta_g(\xi, Q)\phi_i^g(Q) \equiv |g>|gi>$ where Θ and ϕ are the electronic and vibrational states, respectively. Therefore, the transition matrix $(M_\rho)_{mn}$ can now be written explicitly as

$$(M_\rho)_{mn} = (M_\rho)_{gi,ev} = \int (\Theta_e \phi_v^e)^* \hat{\mathbf{m}}_\rho (\Theta_g \phi_i^g)\, d\xi\, dQ \equiv \int (\phi_v^e)^* [\hat{\mathcal{M}}_\rho(Q)]_{g,e} (\phi_i^g)\, dQ \tag{4}$$

where the *electronic transition moment* $\mathcal{M}$ is defined. Θ depends on the vibrational states Q thus $\mathcal{M}$ can be expressed in Q using Taylor expansion:

$$(\hat{\mathcal{M}}_\rho)_{g,e} = (\hat{\mathcal{M}}_\rho)^0_{g,e} + \sum_{a,s} \frac{h^a_{es} Q_a}{\Delta E_{e,s}} (\hat{\mathcal{M}}_\rho)^0_{g,e} \tag{5}$$

The zeroth order term $(\hat{\mathcal{M}}_\rho)^0_{g,e}$ corresponds to the processes without phonon generation or annihilation. The summation is over all vibrational states a and all excited electronic states s but not for states e. Putting all the terms together, the polarizability α becomes

$$(\alpha_{\rho\sigma})_{gi,gj} = A + B \tag{6a}$$

$$A = \frac{1}{h} \sum_{ev} \left(\frac{1}{\nu_{ev,gi} - \nu_0} + \frac{1}{\nu_{ev,gi} + \nu_0} \right) \{ (\hat{\mathcal{M}}_\rho)^0_{g,e} (\hat{\mathcal{M}}_\sigma)^0_{g,e} < gj|ev > < ev|gi > \} \tag{6b}$$

$$B = \frac{1}{h} \sum_{ev} \left(\frac{1}{\nu_{ev,gi} \pm \nu_0} \right) \sum_{s,a} \frac{h^a_{es}}{\Delta E_{es}} \{ (\hat{\mathcal{M}}_\rho)^0_{g,e} (\hat{\mathcal{M}}_\sigma)^0_{g,s} < gj|ev > < ev|Q_a|gi > + \cdots \} \tag{6c}$$

The term A does not involve changes in vibrational states while term B does. They correspond to Rayleigh and Raman scatterings respectively. The Raman term includes both Stokes and anti-Stokes components. Both ordinary and resonant Raman processes can be discussed in this framework but only the non-resonant case is shown in this work. In the following sections, comparisons between Raman scattering using ordinary light and vortex light will be presented.

3. Raman effect for ordinary light

Ordinary radiation from lasers can be described as plane waves. The vector potential of a plane wave propagating in the z direction can be written as

$$\mathbf{A} = A_0(\alpha \hat{e}_x + \beta \hat{e}_y) e^{-i\omega t + ikz} + c.\,c.$$

αor β determines the polarization of the photon with $\alpha^2 + \beta^2 = 1$. They are real numbers for linearly polarized light. The light-matter interaction can be put in the form of $e/m(\mathbf{A}\cdot\mathbf{p})$ and this leads to the explicit form of radiation operator $\hat{\mathbf{m}}_\rho$:

$$\hat{\mathbf{m}} = [A_0(\alpha \hat{e}_x + \beta \hat{e}_y)\cdot\mathbf{p}] e^{-i\omega t + ikz} + c.\,c. \tag{7}$$

The first component that is associated with $e^{-i\omega t}$ corresponds to photon absorption and its complex conjugate corresponds to photon emission. In the dipole approximation, the factor e^{ikz} is dropped. The non-vanishing terms in Eq. (6c) correspond to Raman active phonon modes. To have a non-vanishing intensity requires $h^a_{e,s}$, $(\mathcal{M}_\rho)_{g,e}$ and $(\mathcal{M}_\sigma)_{g,s}$ to be non-zero, a condition that can be satisfied when

$$\Gamma_a \otimes \Gamma_\rho \otimes \Gamma_\sigma \ni \Gamma_1$$

Γ_a, Γ_ρ and Γ_σ are irreducible representations of the phonon, the incident photon and the scattering photon, respectively. Raman tensors give the relative intensities of the same phonon in different scattering geometries. It has been shown that the Raman tensors are Clebsch–Gordon coefficients [16].

4. Raman effect for vortex light

Laguerre–Gaussian (LG) functions are a set of solutions of the Maxwell's equations in the paraxial approximation [14]. Mathematically, a LG beam is described by Laguerre polynomials with a Gaussian envelop. The vector potential of a LG beam in the Lorentz-gauge is [17,18]:

$$\mathbf{A}_{l,p} = A_0(\alpha \hat{e}_x + \beta \hat{e}_y) \sqrt{\frac{2p!}{\pi(|l| + p)!}} \frac{w_0}{w(z)} L_p^{|l|}\left(\frac{2\rho^2}{w^2(z)}\right) \left(\frac{\sqrt{2}\rho}{w(z)}\right)^{|l|} e^{il\phi - i\omega t + ikz} + c.\,c.$$

$L_p^{|l|}(x)$ are generalized Laguerre polynomials; l is the azimuthal index and it is sometimes referred to as the "topological charge"; p is the radial index. ρ is the radial distance from the center axis of the beam; ϕ is the azimuthal angle; z is the axial distance from the waist. w_0 is the waist size; $w(z)$ is the radius at which the field amplitude drop to 1/e of their axial values. $p=0$ is chosen to simplify the analysis. The radiation operator $\hat{\mathbf{m}}_\rho$ for a LG beam is therefore:

$$\hat{\mathbf{m}} = \left[A_0(\alpha \hat{e}_x + \beta \hat{e}_y) \sqrt{\frac{1}{\pi|l|!}} \frac{w_0}{w(z)} L^{|l|} \left(\frac{2\rho^2}{w^2(z)}\right) \left(\frac{\sqrt{2}\rho}{w(z)}\right)^{|l|} e^{il\phi - i\omega t + ikz} \right] \cdot\mathbf{p} + c.\,c. \tag{8}$$

The term e^{ikz} can be neglected in the dipole approximation. In what is remaining, the part related to $e^{-i\omega t}$ is associated with photon absorption and it transforms according to $(\alpha x + \beta y)\rho^l e^{il\phi} \equiv (\boldsymbol{\rho}\cdot\hat{\epsilon}_I)\rho^l e^{il\phi}$; the complex conjugate part related to $e^{i\omega t}$ is associated with photon emission and it transforms according to $(\alpha x + \beta y)\rho^l e^{-il\phi} \equiv (\boldsymbol{\rho}\cdot\hat{\epsilon}_S)\rho^l e^{-il\phi}$.

4.1. Selection rules

Same as in the case for ordinary Raman process, the non-vanishing matrix elements for Raman scattering with a LG beam requires

$$\Gamma_a \otimes \Gamma_\rho \otimes \Gamma_\sigma \ni \Gamma_1$$

Γ_a, Γ_ρ and Γ_σ are the irreducible representations of the phonon, incident photon and scattered photon, respectively. The Raman tensor is written in the form of $P_{\alpha\beta\gamma\delta}(\Gamma_j^\sigma)$. Full index Γ_j^σ is needed to denote the jth branch of the σth phonon instead of single index a. Similarly, the single indices ρ and σ are replaced by (α, β) and (γ, δ) to represent wave vector and polarization direction of incident and