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Y. R. Shen

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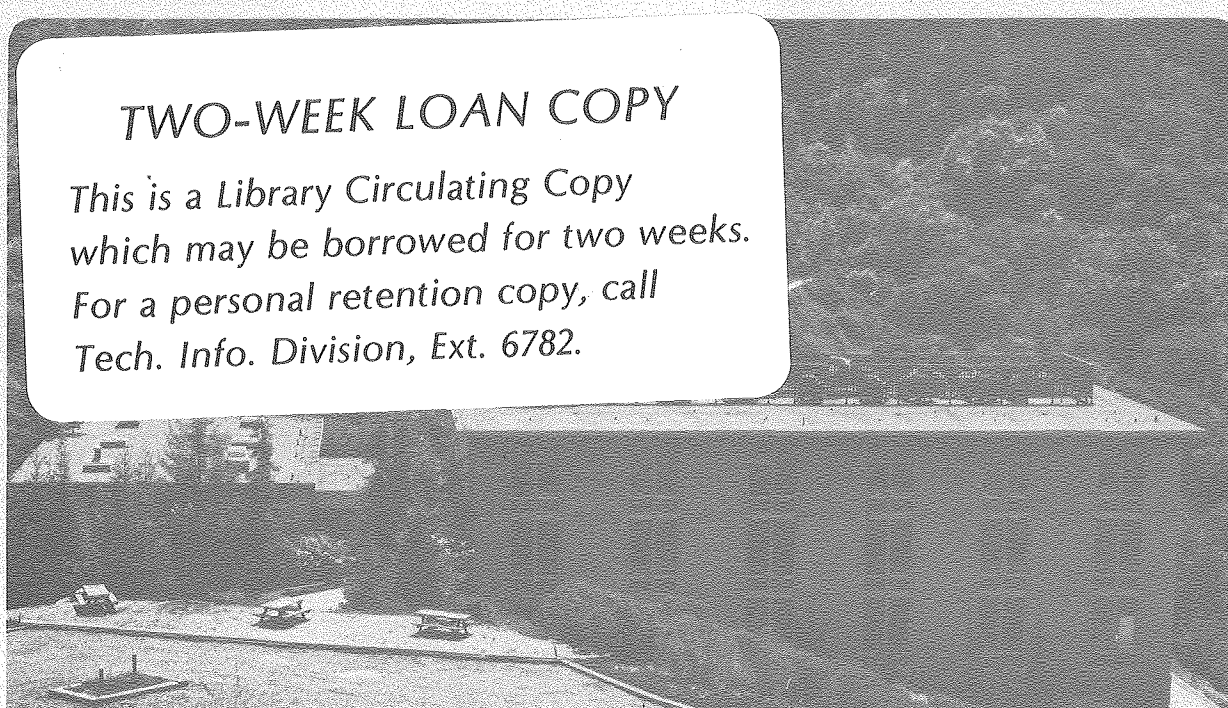

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A NOTE ON TWO-PHONON COHERENT ANTISTOKES RAMAN SCATTERING

Y. R. Shen

Department of Physics
University of California
Berkeley, California 94720

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

ABSTRACT

Difference-frequency mixing of two pump waves can in principle excite two coherent phonon waves via the parametric process. Only when the phonon excitation is small, can the nonlinear susceptibility of two-phonon coherent antiStokes Raman scattering be described as proportional to the product of two Raman tensors.

Laser Raman spectroscopy, pioneered by Sergio Porto, has been most valuable for study of two-phonon Raman scattering. The high sensitivity of the technique allows the probing of details in the two-phonon scpectra.[1] More recently, coherent antiStokes Raman scattering (CARS) (or coherent Raman spectroscopy in general) has been developed.[2] It has been suggested that the latter technique can yield as much (or more) information as (than) the conventional Raman scattering technique. This follows from the general conviction that the third-order nonlinear susceptibility governing CARS should be proportional to the product of two Raman matrix elements (or in the off-resonance case, proportional or nearly proportional to the Raman cross-section). The classical description of one-phonon CARS is as follows: The incoming laser waves at ω_1 and ω_2 beat in the crystal to create a coherent phonon wave at $\omega_1 - \omega_2 \simeq \omega_{phonon}$, which in turn coherently scatters the laser beam at ω_1 to generate an antiStokes wave at $\omega_a = 2\omega_1 - \omega_2$. Questions now arise on how the two-phonon CARS should be described. Does the beating of the pump waves at ω_1 and ω_2 create simultaneously two coherent phonon waves, and then the two phonon waves interact simultaneously with the wave at ω_1 to generate the antiStokes output? Or is the phonon wave generated actually a coherent two-phonon bound-state wave?[4] Which phonon relaxation time would the time-delayed CARS measure?[5] If both the existence of two-phonon bound states and the simultaneous creation of two coherent phonon waves are not likely, does it mean that the correspondence between spontaneous Raman scattering and CARS breaks down in the two-phonon or multiphonon cases? Then, will the two-phonon CARS be observable? Although CARS has been well developed in recent years, no experimental observation of two-phonon CARS has ever been reported.

To answer these questions, we consider as an example the two-phonon Raman transition represented by the diagram in Fig. 1a. The corresponding Raman cross-section derived from the perturbation calculation is

$$\sigma_{ij} \propto |R_{ij}(\omega_2,\omega_1)|^2$$

$$R_{ij}(\omega_2,\omega_1) = \sum_{\alpha,\beta,\gamma} \frac{\langle g|r_i|\gamma\rangle}{\omega_2 - \omega_\gamma}\left[\frac{\langle\gamma|\vec{f}\cdot\hat{e}_{Q1}|\beta\rangle\langle\beta|\vec{f}\cdot\hat{e}_{Q2}|\alpha\rangle}{\omega_1 - \omega_\beta - \omega_{ph2}} + \frac{\langle\alpha|\vec{f}\cdot\hat{e}_{Q2}|\beta\rangle\langle\beta|\vec{f}\cdot\hat{e}_{Q1}|\alpha\rangle}{\omega_1 - \omega_\beta - \omega_{ph1}}\right]\frac{\langle\alpha|r_j|g\rangle}{\omega_1 - \omega_\alpha} \; . \tag{1}$$

Here, R_{ij} is the Raman tensor with the subindices i and j denoting the polarization states of $\vec{E}_1$ and $\vec{E}_2$, $\langle g|$, $\langle\alpha|$, $\langle\beta|$, and $\langle\gamma|$ are electronic states of the system, $\hat{e}_{Q1}$ and $\hat{e}_{Q2}$ are the polarization unit vectors of the phonon fields Q_1 and Q_2, and $\vec{f}\cdot\hat{e}_{q\lambda}Q_\lambda$ is the electron-phonon interaction Hamiltonian with Q_λ proportional to the phonon creation operator at $\omega_{ph,i}$. If we treat emission and absorption of two phonons as transitions to and from a two-phonon state of the system respectively, then it can be shown by third-order perturbation calculation that the Raman tensor is related to the Raman susceptibility as[7]

$$\chi^{(3)}_{ijji}(\omega_2 = \omega_1 - \omega_1 + \omega_2) \propto |R_{ij}(\omega_2,\omega_1)|^2. \tag{2}$$

A similar derivation yields the relation $\chi^{(3)}_{ijk\ell}(\omega_a = \omega_1 + \omega_1 - \omega_2) \propto R_{ij}(\omega_a,\omega_1)R_{k\ell}(\omega_1,\omega_2)$ governing the CARS process represented by Fig. 1b. Thus, it seems that two-phonon CARS should be observable as long as σ_{ij} is sufficiently large.

If the above description is correct, the same $\chi^{(3)}_{ijk\ell}(\omega_a = \omega_1 + \omega_1 - \omega_2)$ for two-phonon CARS should be obtainable from the picture of interaction of light with phonon waves. The wave equations for the optical fields $\vec{E}_1(\omega_1)$, $\vec{E}_2(\omega_2)$, and $\vec{E}_a(\omega_a)$ and the phonon fields $\vec{Q}_1(\omega_I)$ and $\vec{Q}_2(\omega_{II})$ in the steady-state case are

$$(\nabla^2 + \frac{\omega_1^2}{c^2}\epsilon_1)\vec{E}_1 = -\frac{4\pi\omega_1^2}{c^2}\vec{P}_1^{NL}(\omega_1)$$

$$(\nabla^2 + \frac{\omega_2^2}{c^2}\epsilon_2)\vec{E}_2 = -\frac{4\pi\omega_2^2}{c^2}\vec{P}_2^{NL}(\omega_2)$$

$$(\nabla^2 + \frac{\omega_a^2}{c^2}\epsilon_a)\vec{E}_a = -\frac{4\pi\omega_a^2}{c^2}\vec{P}_a^{NL}(\omega_a)$$

$$[\omega_{ph,1}(\frac{1}{i}\nabla) - \omega_I - i\Gamma_1]Q_1 = F_1(\omega_I)$$

$$[\omega_{ph,2}(\frac{1}{i}\nabla) - \omega_{II} - i\Gamma_2]Q_2 = F_2(\omega_{II}). \tag{3}$$

Here, $\omega_{ph,1}(\frac{1}{i}\nabla)$ and $\omega_{ph,2}(\frac{1}{i}\nabla)$ are functional operators which operating on $\exp(i\vec{q}\cdot\vec{r})$ will yield the phonon dispersion relations $\omega_{ph,1}(\vec{q})$ and $\omega_{ph,2}(\vec{q})$. The nonlinear polarizations $\vec{P}^{NL}$ and the generalized forces $\vec{F}$ can be obtained from perturbation calculations[3] and can be written as

$$\vec{P}_1^{NL}(\omega_1) = \overleftrightarrow{\xi}_{12,\alpha} \cdot Q_1 Q_2 \vec{E}_2 + \overleftrightarrow{\xi}_{12,\beta} \cdot Q_2 Q_1 \vec{E}_2$$

$$+ \overleftrightarrow{\xi}_{1a,\alpha} Q_1^* Q_2^* \vec{E}_a + \overleftrightarrow{\xi}_{1a,\beta} \cdot Q_2^* Q_1^* \vec{E}_a \propto e^{-i\omega_1 t}$$

$$\vec{P}_2^{NL}(\omega_2) = \overleftrightarrow{\xi}_{2,\alpha} \cdot Q_1^* Q_2^* \vec{E}_1 + \overleftrightarrow{\xi}_{2,\beta} \cdot Q_2^* Q_1^* \vec{E}_1 \propto e^{-i\omega_2 t}$$

$$\vec{P}_a^{NL}(\omega_a) = \overleftrightarrow{\xi}_{a,\alpha} Q_1 Q_2 \vec{E}_1 + \overleftrightarrow{\xi}_{a,\beta} \cdot Q_2 Q_1 \vec{E}_1 \propto e^{-i\omega_a t}$$

$$\vec{F}_1(\omega_I) = \overleftrightarrow{\xi}_{Q11} : Q_2^* \vec{E}_1 \vec{E}_2^* + \overleftrightarrow{\xi}_{Q12} Q_2^* \vec{E}_a \vec{E}_1^* \propto e^{-i\omega_I t}$$

$$\vec{F}_2(\omega_{II}) = \overleftrightarrow{\xi}_{Q21} : Q_1^* \vec{E}_1 \vec{E}_2^* + \overleftrightarrow{\xi}_{Q22} : Q_1^* \vec{E}_a \vec{E}_1^* \propto e^{-i\omega_{II} t} \qquad (4)$$

where $\omega_a = 2\omega_1 - \omega_2$ and $\omega_I + \omega_{II} = \omega_1 - \omega_2$. The coefficients $\overleftrightarrow{\xi}$'s can be derived from the perturbation calculations using the interaction Hamiltonians

$$\mathcal{H}_{eR} = - e\vec{r} \cdot (\vec{E}_1 + \vec{E}_2 + \vec{E}_a) + \text{complex conjugate (c.c.)}$$

$$\mathcal{H}_{ep} = \vec{f} \cdot (\vec{Q}_1 + \vec{Q}_2) + \text{c.c.}$$

for electron-radiation and electron-phonon coupling respectively. We find in particular, for the process in Fig. 1b,

$$(\xi_{a,\alpha})_{ij}(\omega_a,\omega_1) = \sum_{\alpha,\beta,\gamma} \frac{\langle g|r_i|\gamma\rangle\langle\gamma|\vec{f} \cdot \hat{e}_{Q1}|\beta\rangle\langle\beta|\vec{f} \cdot \hat{e}_{Q2}|\alpha\rangle\langle\alpha|r_j|g\rangle}{(\omega_a - \omega_\gamma)(\omega_1 + \omega_{ph,2} - \omega_\beta)(\omega_1 - \omega_\alpha)}$$

cont'd

$$(\xi_{a,\beta})_{ij}(\omega_a,\omega_1) = \sum_{\alpha,\beta,\gamma} \frac{<g|r_i|\gamma><\gamma|\vec{f}\cdot\hat{e}_{Q2}|\beta><\beta|\vec{f}\cdot\hat{e}_{Q1}|\alpha><\alpha|r_j|g>}{(\omega_a-\omega_\gamma)(\omega_1+\omega_{ph,1}-\omega_\beta)(\omega_1-\omega_\alpha)}$$

$$(\xi_{Q11})_{ij}(\omega_2,\omega_1) = (\xi_{Q21})_{ij}(\omega_2,\omega_1)$$

$$= \sum_{\alpha,\beta,\gamma} \frac{<g|r_i|\gamma>}{\omega_2-\omega_\gamma}\left[\frac{<\gamma|\vec{f}\cdot\hat{e}_{Q1}|\beta><\beta|\vec{f}\cdot\hat{e}_{Q2}|\alpha>}{\omega_1-\omega_{ph,2}-\omega_\beta} + \frac{<\gamma|\vec{f}\cdot\hat{e}_{Q2}|\beta><\beta|\vec{f}\cdot\hat{e}_{Q1}|\alpha>}{\omega_1-\omega_{ph,1}-\omega_\beta}\right]\frac{<\alpha|r_j|g>}{\omega_1-\omega_\alpha}$$

$$(\xi_{Q12})_{ij}(\omega_a,\omega_1) = (\xi_{Q22})_{ij}(\omega_a,\omega_1)$$

$$= [(\xi_{a,\alpha})_{ij} + (\xi_{a,\beta})_{ij}](\omega_a,\omega_1). \quad (5)$$

If the phonons are highly damped so that they can be considered as localized, we can write

$$Q_1Q_2 = [F_1(\omega_I)Q_2 + Q_1F_2(\omega_{II})]/D^*$$

$$Q_2Q_1 = [Q_2F_1 + F_2Q_1]/D^*$$

$$D^* = (\omega_{ph,1}+\omega_{ph,2}) - (\omega_I+\omega_{II}) - i(\Gamma_1+\Gamma_2). \quad (6)$$

Substitution of these expressions into Eq. (4) yields

$$(P_a^{NL})_i = D^{*-1}\{[(\xi_{a,\alpha})_{ij}(\xi_{Q11})_{k\ell}(Q_2^*Q_2 + Q_1Q_1^*) \qquad \text{cont'd}$$

$$+ (\xi_{a,\beta})_{ij}(\xi_{Q11})_{k\ell}(Q_2Q_2^* + Q_1^*Q_1)]E_{1j}E_{1k}E_{2\ell}^*$$

$$+ [(\xi_{a,\alpha})_{ij}(\xi_{Q22})_{k\ell}(Q_2^*Q_2 + Q_1Q_1^*)$$

$$+ (\xi_{a,\beta})_{ij}(\xi_{Q11})_{k\ell}(Q_2Q_2^* + Q_1^*Q_1)]E_{1j}E_{ak}E_{1\ell}^*\}. \tag{7}$$

Unlike the usual cases, $\vec{P}_a^{NL}$ here still depends on the phonon fields, and does not have the usual form

$$(P_a^{NL})_i = \chi_{ijk\ell}^{(3)}(\omega_a = \omega_1 + \omega_1 - \omega_2)E_{1j}E_{1k}E_{2\ell}^*$$

$$+ \chi_{ijk\ell}^{(3)}(\omega_a = \omega_1 + \omega_a - \omega_1)E_{1j}E_{ak}E_{1\ell}^*. \tag{8}$$

However, if Q_λ and Q_λ^* are treated as phonon creation and annihilation operators, and $(Q_\lambda Q_\lambda^* + Q_\mu^* Q_\mu)$ is replaced by the expectation value $<Q_\lambda Q_\lambda^* + Q_\mu^* Q_\mu>$, then when the phonon occupation numbers of Q_1 and Q_2 are essentially zero, we have $<Q_\lambda Q_\lambda^* + Q_\mu^* Q_\mu> = 1$. In this case, Eq. (8) is again valid and

$$\chi_{ijk\ell}^{(3)}(\omega_a = \omega_1 + \omega_1 - \omega_2) = [(\xi_{a,\alpha})_{ij} + (\xi_{a,\beta})_{ij}](\xi_{Q11})_k\ /D^*$$

$$\propto R_{ij}(\omega_a,\omega_1)R_{k\ell}(\omega_1,\omega_2). \tag{9}$$

This expression of $\chi_{ijk\ell}^{(3)}(\omega_a = \omega_1 + \omega_1 - \omega_2)$ is in fact exactly the same as the one derived earlier from the third-order perturbation calculation treating emission and absorption of two phonons as transitions to and from a two-phonon state. Physically, this is not surprising since in the latter case, it has been implicitly assumed that the system is always in the ground state with zero phonon.

Strictly speaking, the generation of two phonon waves by the beating of $\vec{E}_1$ and $\vec{E}_2$ in the medium is a parametric amplification process starting from phonon noise or spontaneous parametric phonon emission. If the amplification gain is large, $\langle Q_\lambda Q_\lambda^* + Q_\mu^* Q_\mu \rangle$ may be very much larger than 1. Then, the result in Eq. (9) is no longer valid. From Eq. (3), the growth of the amplitudes $\mathcal{Q}_1$ and $\mathcal{Q}_2$ of the phonon fields Q_1 and Q_2 is described by the coupled equations

$$(\beta_1 \frac{\partial}{\partial z} + i\Delta\omega_1 + \Gamma_1)\mathcal{Q}_1 = i\, \overleftrightarrow{\xi}_{Q11} : \vec{\mathcal{E}}_1 \vec{\mathcal{E}}_2^* \mathcal{E}_2^*$$

$$(\beta_2 \frac{\partial}{\partial z} - i\Delta\omega_2 + \Gamma_2)\mathcal{Q}_2^* = -\, i\, \overleftrightarrow{\xi}_{Q11}^* : \vec{\mathcal{E}}_1^* \vec{\mathcal{E}}_2 \mathcal{E}_1 \qquad (10)$$

assuming negligible pump depletion of $\vec{E}_1 = \vec{\mathcal{E}}_1 e^{i(k_1 z - \omega_1 t)}$ and $\vec{E}_2 = \vec{\mathcal{E}}_2 e^{i(k_2 z - \omega_2 t)}$. We have also assumed $Q_1 = \mathcal{Q}_1 e^{i(q_1 z - \omega_I t)}$, $Q_2 = \mathcal{Q}_2 e^{i(q_2 z - \omega_{II} t)}$, $\Delta\omega_1 = \omega_{ph,1}(q_1) - \omega_I$, $\Delta\omega_2 = \omega_{ph,2} - \omega_{II}$, $\beta_1 = \frac{\partial}{\partial q_1}\omega_{ph,1}(q_1)$, $\beta_2 = \frac{\partial}{\partial q_2}\omega_{ph,2}(q_2)$, and $q_1 + q_2 = k_1 - k_2$. The solution of Eq. (10) with Q_1 and Q_2 treated as classical waves is

$$\mathcal{Q}_1 = C_{11} e^{\gamma_+ z} + C_{12} e^{\gamma_- z} \qquad \text{cont'd}$$

$$Q_2^* = C_{21}e^{\gamma_+ z} + C_{22}e^{\gamma_- z}$$

$$\gamma_\pm = \tfrac{1}{2}\left\{- (i\Delta\omega_1 + \Gamma_1)/\beta_1 + (i\Delta\omega_2 - \Gamma_2)/\beta_2 \pm \left[\left(\frac{i\Delta\omega_1 + \Gamma_1}{\beta_1} + \frac{i\Delta\omega_2 - \Gamma_2}{\beta_2}\right)^2 + \frac{4|\overleftrightarrow{\xi}_{Q11} \cdot \vec{\mathcal{E}}_1\vec{\mathcal{E}}_2^*|^2}{\beta_1\beta_2}\right]^{\frac{1}{2}}\right\} \tag{11}$$

where the coefficients C_{ij} can be determined from Eq. (10) and the boundary conditions $Q_1(0)$ and $Q_2(0)$ at $z = 0$. To take into account the phonon noise or spontaneous phonon emission, an appropriate constant driving term should be inserted in the right hand side of each equation in Eq. (10), and the solution should be accordingly modified. It is seen that γ_+ can have a positive real part if $\Gamma_1/\beta_1 + \Gamma_2/\beta_2$ is sufficiently small, and then the phonon waves can grow exponentially. Consequently, following Eq. (4) and neglecting the ordering of Q_1 and Q_2 and the $\exp(\gamma_- z)$ terms, we obtain

$$\vec{P}_a^{NL}(\omega_a) = (\overleftrightarrow{\xi}_{a,\alpha} + \overleftrightarrow{\xi}_{a,\beta})C_{11}C_{21}^*\vec{\mathcal{E}}_1 e^{(\gamma_+ + \gamma_+^*)z + ik_a z - i\omega_a t} \tag{12}$$

which is of course different from Eq. (8) with $E_a = 0$. In the limit of large Γ_1/β_1 and Γ_2/β_2, corresponding to highly localized phonons, however, the general solution here again leads to the expression of $\vec{P}_a^{NL}(\omega_a)$ in Eq. (8) (with $E_a = 0$).

The above case of parametric amplification of Q_1 and Q_2 is only of academic interest for phonons of high frequenices since under normal circumstances, those phonons are always highly damped. For low-frequency phonons, magnons or plasmons, parametric amplification is however quite possible. One-photon parametric excitations of magnons and plasmons are in fact fairly well known.[8,9] With appropriate symmetry and strong enough pump fields, two-photon parametric excitations should in principle also occur. That parametric amplification will modify the dependence of $\vec{P}_a^{NL}(\omega_a)$ on $\vec{E}_1$ and $\vec{E}_2$ can actually also happen in one-phonon CARS. In that case, a sufficiently strong pump field $\vec{E}_1(\omega_1)$ can lead to parametric excitation and amplification of $\vec{E}_2(\omega_2)$ and $Q(\omega_{ph})$ with $\omega_1 - \omega_2 = \omega_{ph}$.

In summary, we have shown that if the phonons are not highly excited, both the ordinary perturbation calculation and the phonon wave approach yield a nonlinear susceptibility $\chi^{(3)}_{ijk\ell}(\omega_a = \omega_1 + \omega_1 - \omega_2)$ for two-phonon CARS proportional to the product of two Raman tensors. The result needs modification only when parametric excitation and amplification become important. Two-phonon Raman lines can be as sharp and strong as one-phonon Raman lines,[6] and should therefore be observable. From our derivation here, we expect that the time-delayed CARS signal should decay exponentially with a time constant given by $2(\Gamma_1 + \Gamma_2)$.

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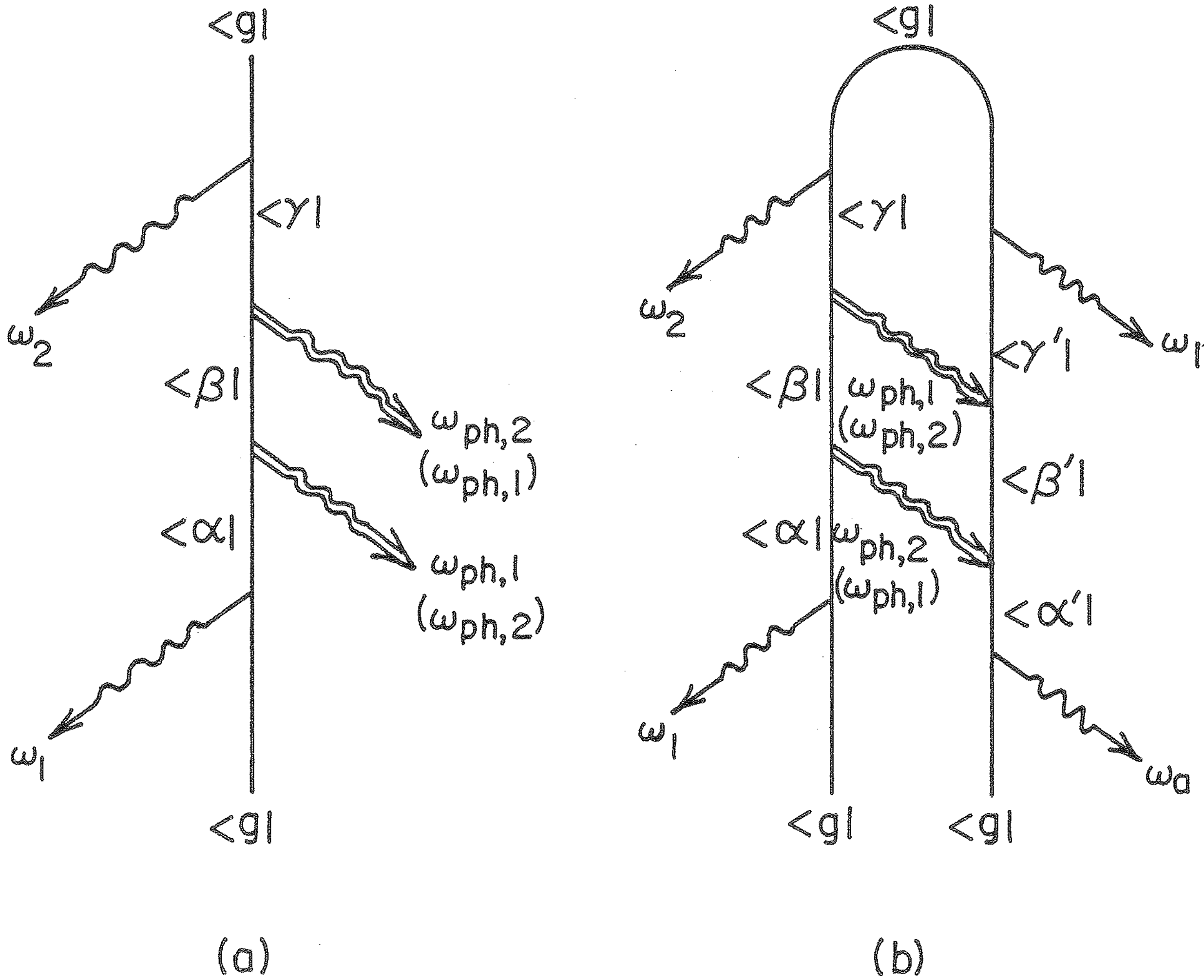
Figure Caption

Fig. 1. Diagrams describing (a) two-phonon Raman scattering, and (b) two-phonon coherent antiStokes Raman scattering.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