Theory of Stimulated Raman Effect. II

Y. R. SHEN
Department of Physics, University of California, Berkeley, California
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The theory of stimulated Raman scattering using the coupled-wave approach is extended to include the case of polar media, with and without inversion center. Mixed effects of parametric down-conversion and Raman emission may occur. The threshold of the stimulated Raman effect in these media should not be much higher than that in a nonpolar system. The mixed effects of parametric down-conversion and stimulated Raman emission are also considered in purely electronic systems. They may be observable if the Raman transitions have a narrow linewidth.

I. INTRODUCTION

THE theory of stimulated Raman scattering has been discussed by many authors from different points of view.[1] In a previous paper,[1] the coupled-wave approach[2] was used to describe the effect. The incident and the coherently scattered light waves are coupled to the optical phonon waves via the electronic system of the medium. With this approach, many details observed in the experiments on stimulated Raman radiation can be explained. However, by assuming the absence of an infrared electromagnetic (em) wave at the vibrational frequency, we excluded the case of polar media. As a natural extension of the previous paper, the formalism is extended to include the infrared em wave. We shall discuss the generation of Stokes radiation only. In addition, we shall consider possible stimulated Raman effect in a pure electronic system (electronic Raman transitions).

Loudon[3] has investigated stimulated Raman scattering in homopolar and polar crystals from the viewpoint of quantized photon and phonon fields. In particular, he has discussed the scattering mechanism in great detail. For coherent scattering, however, the phases of the fields are generally important. In specifying the number of phonons, information about phases is completely lost. We believe that, with the classical coupled-wave approach, the problem can be solved more generally and more thoroughly. The equivalent approach in quantum theory is by using Glauber's coherent states.[4] We shall not discuss the scattering mechanism in this paper.

The stimulated Raman effect has been observed in many liquids,[5] solids,[6] and gases.[7] In all cases, the medium is nonpolar, and a strong optical vibration of the medium is connected with the Raman transitions. The same effect has not been reported for polar and for pure electronic systems, although spontaneous Raman scattering has been detected in both cases.[8,9] The results of our calculation, however, indicate the possibility of observing stimulated Raman scattering in these systems. If the damping constants for various cases are the same, the gain coefficient for the Stokes generation in polar or in pure electronic systems should be at least of the same order of magnitude as those in the nonpolar molecular systems. The stimulated Raman effect has not been observed in many systems. It is likely that these systems have larger damping constants.

In Sec. II, the general formalism of coupled waves is given. In Secs. III and IV, various cases of a polar medium are considered. It is shown that if the medium lacks an inversion center, mixed effects of parametric down-conversion and stimulated Raman emission may occur, and under certain conditions, may enhance the pure Stokes gain. Finally, in Sec. V, parametric down-conversion and stimulated Raman emission in purely electronic systems are discussed.

II. GENERAL FORMULATION

When the number of photons or phonons present is large, the classical wave description of the photon or phonon fields can be well justified.[10,4] Let us assume for the Stokes generation the presence of four waves, three light waves E_l, E_s, and E_v at ω_l, ω_s, and ω_v ,and a vibra-

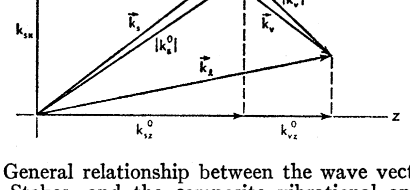

FIG. 1. General relationship between the wave vectors of the laser, the Stokes, and the composite vibrational and infrared electromagnetic waves as stated in Eq. (4).

[1] Y. R. Shen and N. Bloembergen, Phys. Rev. **137**, A1787 (1965), and the references therein.
[2] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. Pershan, Phys. Rev. **127**, 1918 (1962).
[3] R. Loudon, Proc. Phys. Soc. (London), **A82**, 393 (1963); **A275**, 218 (1963).
[4] R. Glauber, Phys. Rev. **130**, 2529 (1963); **131**, 2766 (1963).
[5] G. Eckhardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, D. Weiner, and E. J. Woodbury, Phys. Rev. Letters **9**, 455 (1962); M. Geller, D. P. Bortfeld, and W. R. Sooy, Appl. Phys. Letters **3**, 36 (1963).
[6] G. Eckhardt, D. P. Bortfeld, and M. Geller, Appl. Phys. Letters **3**, 137 (1963).
[7] R. W. Minck, R. W. Terhune, and W. G. Rado, Appl. Phys. Letters, **3**, 181 (1963).
[8] M. V. Hobden and J. P. Russell, Phys. Letters **13**, 39 (1964).
[9] J. T. Hougen and S. Singh, Phys. Rev. Letters **10**, 406 (1963).
[10] E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963).

tional wave Q_v at ω_v, with frequencies satisfying the relation $\omega_l=\omega_s+\omega_v$. These four waves are coupled and governed by the wave equations

$$\begin{aligned}
&\nabla^2E_l-(\epsilon_l/c^2)\frac{\partial^2}{\partial t^2}E_l \\
&\qquad=(4\pi/c^2)\frac{\partial^2}{\partial t^2}[\lambda_1Q_vE_s+\lambda_2E_vE_s],\\
&\nabla^2E_s-(\epsilon_s/c^2)\frac{\partial^2}{\partial t^2}E_s \\
&\qquad=(4\pi/c^2)\frac{\partial^2}{\partial t^2}[\lambda_1Q_v{}^*E_l+\lambda_2E_v{}^*E_l],\\
&\nabla^2E_v{}^*-(\epsilon_v{}^*/c^2)\frac{\partial^2}{\partial t^2}E_v{}^* \\
&\qquad=(4\pi/c^2)\frac{\partial^2}{\partial t^2}[\lambda_2{}^*E_sE_l{}^*+\lambda_3{}^*Q_v{}^*],\\
&\nabla^2Q_v{}^*+\left[\omega_0{}^2Q_v{}^*+2\Gamma\frac{\partial}{\partial t}Q_v{}^*+\frac{\partial^2}{\partial t^2}Q_v{}^*\right]\Big/\beta \\
&\qquad=(1/\beta)[\lambda_1E_l{}^*E_s+\lambda_3E_v{}^*].
\end{aligned}\tag{1}$$

Γ is the phenomenological damping constant for the vibrational wave. All waves are assumed to be linearly polarized so that the coupling constants are scalar. The coupling constant λ_1 for the nonlinear coupling between light and vibrational waves can be described classically in terms of the Placzek model[11]

$$\lambda_1=N(\partial\alpha/\partial Q_v)_0$$

where N is the number of atoms (or molecules) per unit volume, and $(\partial\alpha/\partial Q_v)_0$ is the rate of change of the optical polarizability with respect to the normal coordinate Q_v. The coupling constant λ_2 is the nonlinear susceptibility of the medium which couples the three light waves. It is nonvanishing only in media lacking an inversion center. The quantum-mechanical expressions for both λ_1 and λ_2 can be derived in the usual way with the electronic system quantized.[1,12] The light wave and the vibrational wave at ω_v are coupled directly. The strength of their coupling, or the magnitude of λ_3, depends on the properties of the normal vibration, such as the degree of ionization, etc. For a strictly infrared-inactive vibration, the coupling constant λ_3 vanishes.

We assume that the laser power remains more or less a constant in the medium. Then the equation for E_l can be eliminated. The remaining set of equations is linearized, and the solution takes the form

$$\begin{aligned}
&E_s\sim\exp[i(\mathbf{k}_s\cdot\mathbf{r}-\omega_st)],\\
&E_v\sim\exp[i(\mathbf{k}_v\cdot\mathbf{r}-\omega_vt)],\\
&Q_v\sim\exp[i(\mathbf{k}_v\cdot\mathbf{r}-\omega_vt)],
\end{aligned}\tag{2}$$

with

$$\begin{aligned}
&E_l=\mathcal{E}_l\exp[i(\mathbf{k}_l\cdot\mathbf{r}-\omega_lt)],\\
&\mathbf{k}_l=\mathbf{k}_s{}'+\mathbf{k}_v{}',\\
&k_s{}''=k_v{}'';
\end{aligned}$$

k' and k'' being the real and the imaginary parts of k. The propagation constant k_s is obtained from the determinant

$$\begin{vmatrix}
-k_s{}^2+\omega_s{}^2\epsilon_s/c^2 & (4\pi\omega_s{}^2/c^2)\lambda_1\mathcal{E}_l & (4\pi\omega_s{}^2/c^2)\lambda_2\mathcal{E}_l\\
-\lambda_1\mathcal{E}_l{}^*/\beta & -(\mathbf{k}_l-\mathbf{k}_s{}^*)^2+(\omega_0{}^2-\omega_v{}^2+i2\omega_v\Gamma)/\beta & -\lambda_3/\beta\\
(4\pi\omega_v{}^2/c^2)\lambda_2{}^*\mathcal{E}_l{}^* & (4\pi\omega_v{}^2/c^2)\lambda_3{}^* & -(\mathbf{k}_l-\mathbf{k}_s{}^*)^2+\omega_v{}^2\epsilon_v{}^*/c^2
\end{vmatrix}=0,\tag{3}$$

where the Stokes frequency ω_s, and the transverse component of its wavevector, $(k_{sx}{}^2+k_{sy}{}^2)^{1/2}$, are regarded as independent variables; the boundary of the medium is assumed to be perpendicular to the z axis.

With k_s determined, the problem is essentially solved. If all the coupling terms (off-diagonal terms) were zero, the six roots of Eq. (3) would simply be the propagation constants for the free E_s, E_v, and Q_v waves, travelling forward and backward in the medium. However, owing to coupling between waves, these propagation constants are no longer the same as those for the free waves, the amount of change depending on the coupling strength. Also the eigenwaves are now composite waves with mixed character.

In all practical cases, the coupling between the Stokes wave E_s and the vibrational and infrared waves Q_v and E_v is small. Consequently, all the Stokes waves have propagation constants only slightly different from that of the free Stokes wave, $k_s{}^0=(\omega_s{}^2\epsilon_s{}'/c^2)^{1/2}$. If one of the Stokes waves has a negative $k_s{}''$, we have the result of stimulated Stokes generation. Let

$$\begin{aligned}
&k_{sx}{}'=k_{lx}-k_{vx}{}',\\
&k_{sy}{}'=k_{ly}-k_{sy}{}',\\
&k_{sx,y}{}'=k_{sx,y}{}^0,\quad k_{vx,y}{}'=k_{vx,y}{}^0,\\
&k_{sz}=k_{sz}{}^0+\Delta K=k_{lz}{}^0-k_{vz}{}^*,\\
&k_{vz}{}^*=k_{vz}{}^0-\Delta K,\\
&k_{sz}{}''=k_{vz}{}''.
\end{aligned}\tag{4}$$

The corresponding vector relations are shown in Fig. 1.

[11] G. Placzek, *Marx Handbuch der Radiologie*, edited by E. Marx (Academische Verlagsgesellschaft, Leipzig, Germany, 1934), 2nd ed., Vol. VI, Part II, pp. 209–374.

[12] N. Bloembergen and Y. R. Shen, Phys. Rev. **133**, A37 (1964).

We are interested in the solution with

$$|\Delta K| \ll k_{vz}^0, k_{sz}^0. \quad (5)$$

Substituting Eq. (4) into Eq. (3), and neglecting $(\Delta K)^2$ in the diagonal terms, we find

$$(-\Delta K+i\alpha_s)(\Delta K+D/2k_{vz}^0\beta)(\Delta K+F/2k_{vz}^0-i\alpha_v)$$
$$+\Lambda_1(\Delta K+F/2k_{vz}^0-i\alpha_v)-\Lambda_2(\Delta K+D/2k_{vz}^0\beta)$$
$$+\Lambda_3(-\Delta K+i\alpha_s)-\Lambda_{123}=0, \quad (6)$$

where

$$\alpha_s=\omega_s^2\epsilon_s''/2k_{sz}^0c^2,$$
$$\alpha_v=\omega_v^2\epsilon_v''/2k_{vz}^0c^2,$$
$$D=\omega_0^2-\beta k_v^{02}-\omega_v^2+i2\omega_v\Gamma,$$
$$F=(\omega_v^2-k_v^{02}c^2/\epsilon_v')(\epsilon_v'/c^2),$$
$$\Lambda_1=(\pi\omega_s^2/c^2k_{sz}^0k_{vz}^0\beta)|\lambda_1E_l|^2,$$
$$\Lambda_2=(4\pi^2\omega_s^2\omega_v^2/c^4k_{sz}^0k_{vz}^0)|\lambda_2E_l|^2,$$
$$\Lambda_3=(\pi\omega_v^2/c^2k_{vz}^{02}\beta)|\lambda_3|^2,$$
$$\Lambda_{123}=(4\pi^2\omega_s^2\omega_v^2/c^4k_{sz}^0k_{vz}^{02}\beta)\lambda_1(\lambda_2^*\lambda_3+\lambda_2\lambda_3^*)|E_l|^2.$$

Among the three roots of Eq. (6), only those satisfying Eq. (5) are of interest. Further approximation can be made for the physical problems encountered. We assume that the vibrational wave is highly damped such that

$$|D/2k_{vz}^0\beta| \gg \Lambda_1^{1/2}, \quad \alpha_s. \quad (7)$$

This assumption is often well satisfied for optical phonon waves, and consequently a perturbation approach can be used. A complete solution of the problem requires of course the solution of all roots in Eq. (3). In addition, the waves must satisfy various boundary

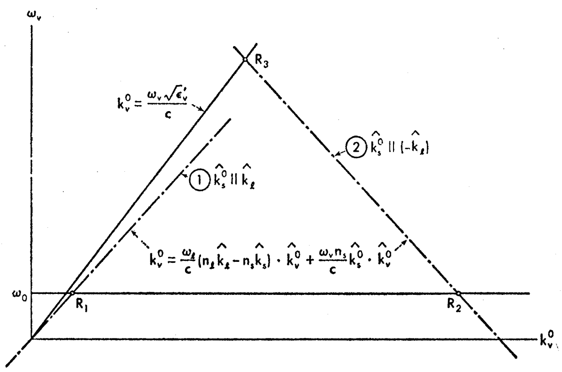

FIG. 2. Dispersion relations illustrating coupling between Stokes, vibrational, and infrared em waves for Case A. The coupling between E_v and Q_v is weak. The momentum matching condition Eq. (8) is given by the dashed lines (——–——) (1) and (2) for the Stokes beams parallel and antiparallel to the laser beam, respectively. The lines intersect the dispersion curve (——) for E_v and Q_v waves at the resonant points R_1, R_2, and R_3, where the Stokes gain is close to a maximum. At R_2, the Stokes wave is coupled to a purely vibrational wave; the coupling to the infrared em wave can be ignored. At R_3, the Stokes wave is coupled to a purely infrared em wave; the coupling to the vibrational wave can be ignored.

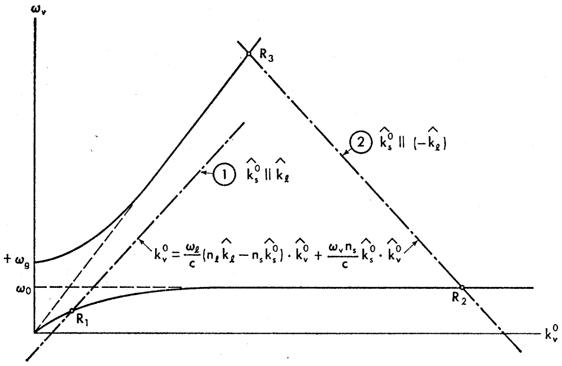

FIG. 3. Dispersion relations illustrating coupling between Stokes, vibrational, and infrared em waves for case B. The coupling between E_v and Q_v is strong and gives rise to a forbidden gap ω_g. Assume $n_l > n_s$. The Stokes wave parallel to the laser beam is coupled to a composite E_v-Q_v wave as shown by the resonant point R_1. For resonant points R_2 and R_3, the Stokes wave is coupled to a purely vibrational wave and to a purely infrared em wave, respectively.

conditions. In this paper, however, we are only interested in the gain coefficient of the Stokes wave.

The coupling between E_s, E_v, and E_v can be illustrated by the dispersion curves in Figs. 2 and 3. They show, respectively, the cases where the coupling between E_v and Q_v is less and comparable or larger than the linewidths of the coupled modes. In Fig. 2, the λ_3 coupling is effective in admixing E_v and Q_v waves only in the immediate vicinity of the intersection of the two branches. In Fig. 3, a forbidden gap appears as a result of strong coupling between E_v and Q_v.[13] The two waves are thoroughly mixed in the curved region of the two branches. For each direction of the wave vector $\mathbf{k}_s$, the relation between k_v^0 and ω_v is a straight line given by the requirements of energy conservation $\omega_v=\omega_l-\omega_s$ and the momentum conservation

$$k_v^0=|\mathbf{k}_l-\mathbf{k}_s^0|=(\omega_l/c)(n_l\hat{k}_l^0-n_s\hat{k}_s^0)$$
$$\cdot\hat{k}_v^0+\omega_v(n_s\hat{k}_s^0\cdot\hat{k}_v^0/c), \quad (8)$$

where n_l and n_s are the indices of refraction for the em waves at ω_l and ω_s, and $\hat{k}$'s are unit vectors. By specifying the frequency ω_v or ω_s, we specify a point on the line. The effective coupling between the Stokes wave E_s and the infrared and vibrational waves E_v and Q_v is expected to be the strongest at the resonant points R where the line intersects the dispersion curve, i.e., the frequency ω_v coincides with a resonant mode. The Stokes gain would then be a maximum. If the intersecting point is in the region where the admixing between E_v and Q_v is negligible, the Stokes gain would come essentially from coupling between E_s and pure E_v or Q_v waves.

In the following sections, we shall discuss quantitatively the two special cases corresponding to Figs. 2 and 3.

[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

III. CASE A. Λ_1 OR/AND $\Lambda_2 \gtrsim \Lambda_3$

The small λ_3 coupling means that Fig. 2 applies. Consider first the case where ω_v is close to the vibrational mode, but the phase mismatch from the infrared em mode is large $(|k_v^{02}-(\omega_v^2\epsilon_v/c^2)|\gg 0)$, so that $|F|/2k_{vz}^0 \gg \Lambda_v^{1/2}$, $\Lambda_3^{1/2}$. With the approximations suggested by this inequality and by Eq. (7), the root of Eq. (6) for the positive Stokes gain is

$$\Delta K_s = i\alpha_s + [2k_{vz}^0\beta\Lambda_1/D] - [2k_{vz}^0\Lambda_2/(F-i2k_{vz}^0\alpha_v)] - [4\beta k_{vz}^0\Lambda_{123}/D(F-i2k_{vz}^0\alpha_v)]. \quad (9)$$

In a medium with an inversion center,[13a] the constant λ_2 vanishes so that $\Lambda_2=\Lambda_{123}=0$. Equation (9) reduces to that with coupling of Stokes and pure vibrational waves only[1]:

$$\Delta K_s = i\alpha_s + 2k_{vz}^0\beta\Lambda_1/D. \quad (10)$$

The maximum Stokes gain appears at Re$D=0$ (corresponding to the resonant point R on the vibrational branch), and takes the form

$$-\mathrm{Im}\Delta K_s = -\alpha_s + k_{vz}^0\beta\Lambda_1/\omega_v\Gamma. \quad (11)$$

Even in a medium with no inversion center, the Λ_2 term is still negligible if the frequency ω_v is sufficiently far away from the infrared mode such that $|F|\gtrsim\omega_v^2/c^2$. This can be seen as follows. The nonlinear susceptibility λ_2 is of the order of 10^{-8} to 10^{-9} from data on second harmonic generation. It may become anomalously large only when one or more of the frequency components approaches an electronic resonance. The constant λ_1 is related to the resonant Raman susceptibility χ_s'' by $\lambda_1^2=2\omega_v\Gamma\chi_s''$,[1] which is typically $\lambda_1^2\approx 10^{-11}\omega_v\Gamma$. Take $\lambda_2=5\times10^{-9}$, $\omega_v=10^{13}$ sec^{-1}, and $\Gamma=5\times10^{10}$ sec^{-1}. The ratio of the Λ_2 term to the Λ_1 term in Eq. (9) turns out to be

$$|(D/2k_{vz}^0\beta)\Lambda_2/[(F/2k_{vz}^0)-i\alpha_v]\Lambda_1| \cong 6\times10^{-3}|D/c^2|/|F|. \quad (12)$$

Usually, we have $\beta<10^{-5}c^2$. The ratio is much smaller than 1 if $|F|\gtrsim|D/c^2|$. This is true for resonant points R on the vibrational branch, but sufficiently away from the branch crossing point so that $|D|=2\omega_v\Gamma$ and $|F|\gtrsim\omega_v^2/c^2$. There, even the Λ_{123} term in Eq. (9) is negligible. The coupling constant λ_3 is related to the forbidden gap ω_g by $4\pi\lambda_3^2\cong[(\omega_0+\omega_g)^2-\omega_0^2]$. For the present case, since $|D/2k_{vz}^0\beta|^2\gg\Lambda_3$, we have $\lambda_3\ll(\omega_v\Gamma)^{1/2}$. The ratio of the Λ_3 term to the Λ_1 term in Eq. (9) is

$$|\Lambda_{123}/[(F/2k_{vz}^0)-i\alpha]\Lambda_1| = 4(\Lambda_1\Lambda_2\Lambda_3)^{1/2}/|(F/2k_{vz}^0)-i\alpha_v|\Lambda_1 \cong 0.08(\omega_v^2/c^2|F|)[\lambda_3/(\omega_v\Gamma)^{1/2}]. \quad (13)$$

Therefore, for $|F|\gtrsim\omega_v^2/c^2$, the Λ_{123} term is also negligible. The amplitude ratio of E_s, E_v, and Q_v for the composite wave corresponding to the eigenvalue ΔK_s of Eq. (9) can easily be found, but is too lengthy to be reproduced here. The wave has mostly Stokes character, but has a slight admixture of vibrational character, and a much smaller portion of infrared em character.

When R on the vibrational branch moves towards the branch crossing point, the factor $|F|$ gets smaller, and the Λ_{123} term first becomes relatively more important. It helps the Stokes gain whenever F is negative. If $|F|$ becomes so small that $|F|\lesssim\Lambda_1^{1/2}$, or if the resonant point R is on the infrared em branch, the assumption for deriving Eq. (9) no longer holds. There are now two eigenvalues from Eq. (6), both of which may give positive Stokes gain

$$\Delta K_{s\pm} = -(\tfrac{1}{2}a)\pm\tfrac{1}{2}[a^2-4b]^{1/2}, \quad (14)$$

where

$$a = -i(\alpha_s+\alpha_v)+(F/2k_{vz}^0)-(\Lambda_1-\Lambda_2-\Lambda_3)/(D/2k_{vz}^0\beta),$$
$$b = -i\alpha_s[(F/2k_{vz}^0)-i\alpha_v]+\Lambda_2 - \{\Lambda_1[(F/2k_{vz}^0)-i\alpha_v]+i\alpha_s\Lambda_3-\Lambda_{123}\}/(D/2k_{vz}^0\beta).$$

If the frequency ω_v is far away from the vibrational mode, such that $|\Lambda_1/(D/2k_{vz}^0\beta)|\ll|(F/2k_{vz}^0)-i\alpha_v|$, we have essentially the case of parametric down-converters.[14] The problem reduces to one with coupling between E_s and E_v only since the coupling to the vibrational mode can be neglected. With previous numerical values for the variables, the gain coefficient for this case is comparable with the Stokes gain given by Eq. (11). The gain can be higher if ω_v is in the immediate vicinity of the branch crossing point because then the coupling between E_v and Q_v also affects the gain. However, for the resonant point R in this region, we must have an anisotropic medium with $n_l<n_s$ because of the dispersion in the index of refraction. In a cubic crystal, we have $n_l\approx n_s$; the point R always appears to the right of the branch crossing point.

IV. CASE B. $\Lambda_3\gg\Lambda_1$, Λ_2

Figure 3 applies when $\Lambda_3\gtrsim|\omega_v\Gamma/k_{vz}\beta|^2$. Again we are interested in finding the Stokes gain near resonant points. For $|F|/2k_{vz}^0$, $|D|/2k_{vz}^0\beta\gg\Lambda_1^{1/2}$, $\Lambda_2^{1/2}$, the root of Eq. (6) corresponding to the positive Stokes gain is

$$\Delta K_s = i\alpha_s + (1/\gamma_+\gamma_-)\{\Lambda_1[(F/2k_{vz}^0)-i\alpha_v] - \Lambda_2(D/2k_{vz}^0\beta)-\Lambda_{123}\}, \quad (15)$$

where

$$\gamma_\pm = \{-[D+\beta F-i2k_{vz}^0\beta\alpha_v] \pm[(D-\beta F+i2k_{vz}^0\beta\alpha_v)^2 - 16k_{vz}^0\beta^2\Lambda_3]^{1/2}\}/4\beta k_{vz}^0,$$
$$\gamma_+\gamma_- = \{D[F-i2k_{vz}^0\alpha_v]+4k_{vz}^{02}\beta\Lambda_3\}/4\beta k_{vz}^{02}.$$

Equation (13) shows that the maximum Stokes gain

[13a] *Note added in proof*. In a medium with an inversion center, a transverse vibrational mode is Raman-inactive from symmetry consideration. This means that Λ_1 also vanishes. In general, however, we can have $\Lambda_1\neq0$ if the mode is not purely transverse.

[14] R. H. Kingston, Proc. I. R. E. (Inst. Radio Engrs.) **50**, 472 (1962), N. M. Kroll, Phys. Rev. **127**, 1207 (1962).

occurs near the points where

$$\mathrm{Re}(\gamma_+\gamma_-)=\mathrm{Re}\{D[F-i2k_{vz}{}^0\alpha_v]+4k_{vz}{}^{0^2}\beta\Lambda_3\}=0. \quad (16)$$

This is just the dispersion equation (ω_v versus $k_v{}^0$) for the two branches of the dispersion curve in Fig. 3. The solutions of Eqs. (8) and (16) therefore correspond to the resonant points R. The gain at these resonant points is given by

$$-\mathrm{Im}\Delta K_{sr}=-\alpha_s+\{k_{vz}{}^0\beta\Lambda_1+[(\omega_v\Gamma\alpha_v+k_{vz}{}^0\beta\Lambda_3)(4k_{vz}{}^0\Lambda_2/F^2)]-2\Lambda_{123}\beta k_{vz}{}^{0^2}/F\}\times 1/[\omega_v\Gamma+(\omega_v\Gamma\alpha_v+k_{vz}{}^0\beta\Lambda_3)(4k_{vz}{}^{0^2}\alpha_v/F^2)]. \quad (17)$$

The true maximum gain for a fixed direction of Stokes waves is of course obtained by maximizing the imaginary part of ΔK_s in Eq. (15) subject to Eq. (8), but is expected to be close to that of Eq. (17). Because of the strong dispersion of the E_v-Q_v wave (Fig. 3), both the Stokes frequency and the Stokes gain change with the propagating direction of the Stokes wave. Unfortunately, there is no simple analytic expression for the phenomenological damping constant $\Gamma(\omega_v)$ as a function of the frequency ω_v. It is therefore difficult to predict quantitatively how the gain varies with the Stokes direction.

In a medium with an inversion center, Eq. (17) becomes

$$-\mathrm{Im}\Delta K_{sr}=-\alpha_s+\{k_{vz}{}^0\beta\Lambda_1/[\omega_v\Gamma+(4k_{vz}{}^0\alpha_v/F^2)(\omega_v\Gamma\alpha_v+\beta k_{vz}{}^0\Lambda_3)] \quad (18)$$

Loudon has discussed this case using the quantized-field picture.[3] He has obtained essentially the same result as Eq. (18), which shows that the Stokes gain is reduced by coupling between vibrational and infrared em waves. Assume resonant points R on the lower branch of Fig. 3. For Stokes waves in the backward direction (antiparallel to the laser beam), the point R always appears on the part of the dispersion curve which has nearly pure vibrational character. We have $|F/2k_{vz}{}^0|^2\gg\Lambda_3$, α_v, and Eq. (18) reduces to the form of Eq. (11). As the Stokes wave gradually approaches the forward direction, the resonant point R now corresponds to a wave with more and more infrared em character. The factor $|F|$ gets smaller, and hence the Λ_3 coupling term becomes relatively more important in reducing the Stokes gain. The Stokes frequency ω_s also increases accordingly, while the damping constant $\Gamma(\omega_v)$ often increases with decrease of ω_v. Therefore, the Stokes gain close to the forward direction would appear to be smaller than that in the backward direction. For Stokes waves very close to the forward direction, the straight line of Eq. (18) may even fail to intersect the dispersion curve to give a resonant point if

$$n_l\approx n_s<n_v(1+4\pi\lambda_3{}^2/\omega_0{}^2\epsilon_v{}')^{1/2}$$

as in the case of cubic crystals. In noncubic crystals, the line may still intersect the dispersion curve as long as n_l is sufficiently different from n_s.[3] It would intersect the upper branch in Fig. 3 if $n_l<n_s$, and the lower branch if $n_l>n_s$. To see how strongly the Λ_3-coupling affects the gain in this case, we assume a forbidden gap $\omega_g=\omega_0/10$. Assume also $n_l>n_s$, and for a resonant point $|F|=\frac{1}{2}\omega_v{}^2/c^2$, $\omega_v=2\omega_0/3$, $\omega_v/\Gamma=200$, and $\alpha_v=10^{-5}\omega_v/c$. We find from Eq. (18)

$$-\mathrm{Im}\Delta K_{sr}\cong-\alpha_s+[k_{vz}{}^0\beta\Lambda_1/\omega_v\Gamma(1+0.005)],$$

which shows that the effect of the Λ_3 term in Eq. (18) is small. It becomes more important for smaller $|F|$, larger ω_g and larger α_v.

In a medium which lacks an inversion center, the Stokes gain at the resonant points is given by Eq. (17). Assuming the same numerical values for the variables λ_1, λ_2, ω_v, and Γ as in Sec. III, we find that the ratios of the Λ_2 and the Λ_{123} terms to the Λ_1 term in Eq. (17) are still given by Eqs. (12) and (13). For $|F|\gtrsim\omega_v{}^2/c^2$, the Λ_2 term is again negligible. For Stokes waves travelling in the backward direction, the Λ_{123} term would also be negligible if $|F|\geqq\omega_v{}^2/400c^2$ for a resonant point R on the lower branch of the dispersion curve. The Stokes gain reduces essentially to that of Eq. (11), since physically the Stokes wave is now coupled to a nearly pure vibrational wave. For Stokes waves in the forward direction, the Λ_{123} term may become comparable to the Λ_1 term. The ratio of the two terms is $\frac{1}{2}$ if we assume $|F|=\frac{1}{2}\omega_v{}^2/c^2$, $\omega_g=\omega_0/10$, and $\omega_v=2\omega_0/3$. The denominator of Eq. (17) is still approximately equal to $\omega_v\Gamma$ as has been shown earlier. When the resonant point R is on the lower branch of the dispersion curve, we have a negative F, and hence a positive contribution to the Stokes gain from the Λ_{123} term in Eq. (17). For R on the upper branch, the Λ_{123} term contributes negatively. In the above cases, the corresponding exponentially growing eigenwave has mostly Stokes character, a small portion of mixed E_v and Q_v waves being dragged along. The amount of E_v and Q_v admixture in the eigenwave can be calculated easily. However, a qualitative estimate can readily be obtained from the position of R on the dispersion curve.

We have assumed $|F/2k_{vz}{}^0|\gg\Lambda_1{}^{1/2}$. If the resonant point R on the dispersion curve corresponds to a nearly pure infrared em mode, the quantity F becomes so small that $|F/2k_{vz}{}^0|\lesssim\Lambda_1{}^{1/2}$. Equation (14) and the related discussion in the previous section again apply to the case. In particular, the vibration wave can be neglected if ω_v is far away from the vibrational mode such that $|D/2k_{vz}{}^0\beta|\gg|2k_{vz}{}^0\Lambda_3/F|$. We then have the case of parametric down-converters. If $\alpha_s\approx\alpha_v$, the exponentially growing eigenwave contains nearly equal amounts of E_s and E_v waves. The gain coefficient is a function of the nonlinear susceptibility λ_2 coupling the E_s and E_v waves. It increases anomalously when the infrared frequency ω_v approaches a narrow electronic resonance as we shall now discuss.

V. PARAMETRIC DOWN-CONVERSION AND STIMULATED ELECTRONIC RAMAN EFFECT

Consider the case of coupling of three waves E_l, E_s, and E_v, the vibrational wave being neglected. The medium can be regarded as a pure electronic system. Assuming E_l constant, we obtain the coupled equations, for E_s and E_v as follows:

$$\nabla^2 E_s-(\epsilon_s/c^2)\frac{\partial^2}{\partial t^2}E_s =(4\pi/c^2)\frac{\partial^2}{\partial t^2}[\lambda_2 E_l E_v^*+\chi_s|E_l|^2E_s],$$
$$\nabla^2 E_v^*-(\epsilon_v^*/c^2)\frac{\partial^2}{\partial t^2}E_v^* =(4\pi/c^2)\frac{\partial^2}{\partial t^2}[\lambda_2^* E_l^* E_s+\chi_v^*|E_l|^2E_v^*], \quad (19)$$

where we have included the third-order nonlinear susceptibilities χ_s and χ_v. The quantum-mechanical expression of these nonlinear susceptibilities can also be derived in the usual way.[12] Because of the typical resonance dispersion, χ_s and λ_2 become complex and anomalously large as the frequency ω_v approaches an electronic resonance. Exactly on resonance, the magnitudes of their imaginary parts are inversely proportional to the half width Γ of the resonance transitions.

Equation (19) shows that the E_s and E_v waves are coupled by the λ_2 terms. In a medium with an inversion center, we have $\lambda_2=0$, and hence the two waves are not coupled. The pure Stokes wave is given by

$$E_s\sim\exp[i(\mathbf{k}_s\cdot\mathbf{r}-\omega_s t)], \quad (20)$$

where

$$\mathbf{k}_s=\mathbf{k}_s^0+\mathbf{\Delta K},\quad k_s^0=(\omega_s^2\epsilon_s'/c^2)^{1/2},$$
$$\Delta K\cong\gamma_s\equiv(\omega_s^2/2k_{sz}^0c^2)[i\epsilon_s''+4\pi\chi_s|E_l|^2].$$

The Stokes gain is

$$g_s\equiv-\mathrm{Im}\gamma_s=(\omega_s^2/2k_{sz}^0c^2)(i\epsilon_s''-4\pi\chi_s''|E_l|^2), \quad (21)$$

where $\chi_s''=\mathrm{Im}\chi_s$ is a negative quantity, which has its absolute maximum inversely proportional to Γ when ω_v is at the electronic resonance.

Crystals doped with rare-earth ions may possess narrow electronic states in the infrared range. Elliot and Loudon[15] have shown that for spontaneous Raman scattering, the probability of electronic Raman transitions in these systems can be equal to or better than that of vibrational Raman transitions in a molecular system. Then, for stimulated Raman effect, the Stokes gain in an electronic system can also be equal to or larger than that in a molecular system if the corresponding attenuation or damping factors are the same.

In systems lacking an inversion center, the nonlinear susceptibility λ_2 does not vanish. Assuming wave solutions with wave-vector relations Eq. (4), we find

$$(\Delta K)^2+(\gamma_s-\gamma_v)(\Delta K)-(\gamma_s\gamma_v-\Lambda_2)=0, \quad (22)$$

where

$$(\Delta K)\ll k_{vz}^0,$$
$$\gamma_v=(\omega_v^2/2k_{vz}^0c^2)[\epsilon_v^*-(k_v^{0 2}c^2/\omega_v^2)+4\pi\chi_v^*|E_l|^2].$$

The solutions are

$$\Delta K_\pm=\tfrac{1}{2}\{(\gamma_s-\gamma_v)\pm[(\gamma_s+\gamma_v)^2-4\Lambda_2]\}^{1/2}, \quad (23)$$

with the corresponding amplitude ratio

$$E_s/E_v=(2\pi\omega_s^2/k_{sz}^0c^2)\lambda_2E_l/(\gamma_s-\Delta K_\pm). \quad (24)$$

If the waves are linearly mismatched such that

$$k_v^{0 2}=(k_l-k_s^0)^2\neq\omega_v^2\epsilon_v'/c^2 \quad\text{and}\quad |\gamma_v|\gg\Lambda_2^{1/2},$$

Eq. (23) can be approximated by

$$\Delta K_\pm=\gamma_v^s\mp[\Lambda_2/(\gamma_s+\gamma_v)]. \quad (25)$$

The eigenwave corresponding to ΔK_+ has mostly Stokes character with a gain coefficient $(-\mathrm{Im}\Delta K_+)$. This gain reduces to Eq. (21) when the linear mismatch is so large that the Λ_2 term in Eq. (25) can be neglected, as is the case where E_s and E_v are essentially decoupled.

For a fixed Stokes frequency, the waves can be linearly matched for a special Stokes direction. If, in addition, the infrared frequency ω_v is exactly on a narrow electronic resonance, both χ_s and λ_2 attain their resonant values and χ_v can be neglected. Equation (23) then reduces to

$$\Delta K_\pm\cong-\tfrac{1}{2}i[g_s\pm(g_s^2+4\Lambda_2)^{1/2}]. \quad (26)$$

If $\Lambda_2\gg g_s^2$, Eq. (26) becomes

$$\Delta K_\pm\cong-i[(\pm\sqrt{\Lambda_2}+\tfrac{1}{2}g_s)\pm(g_s^2/4\sqrt{\Lambda_2})].$$

This is the case of parametric down-conversion where the gain is mostly due to direct coupling between E_s and E_v. Since the gain is larger than g_s, the process is also likely to take place.

VI. CONCLUSION

Spontaneous Raman transitions in polar systems (GaP)[8] and in electronic systems ($PrCl_3$)[9] have been reported. They involve some sharp, intense peaks of half widths of several cm^{-1}, denoting a value of Γ nearly the same as that of a pure vibrational wave in some nonpolar systems in which the stimulated Raman effect has been detected. It is concluded that if the laser and the Stokes waves have sufficient transparency in such media, the stimulated Raman effect is likely to be observed.

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[15] R. J. Elliot and R. Loudon, Phys. Letters 3, 189 (1964).