COUPLING BETWEEN VIBRATIONS AND LIGHT WAVES IN RAMAN LASER MEDIA*

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Since the discovery of coherently stimulated Stokes radiation[1] and anti-Stokes radiation[2] a lively correspondence has developed.[3-8] There are nevertheless a number of salient features in the experimental observations which have not received an adequate explanation. Among these we shall discuss in this note the forward-backward asymmetry of the intensity of the Stokes radiation, the violation of the exact momentum-matching condition for the direction of the anti-Stokes radiation, the frequency shift, the asymmetric line shape, and dark absorption band in the anti-Stokes line.

Consider first the generation of Stokes radiation as a parametric process. The constant laser wave, $E_L \exp(i\vec{k}_L\cdot\vec{r} - i\omega_L t)$, provides a coupling between the Stokes light wave and an optical phonon wave $Q = A_v \exp(i\vec{k}_v\cdot\vec{r} - i\omega_v t)$, with $Q = R(2\rho\omega_v^2)^{+1/2}$. Here Q is the normal vibrational coordinate, R is the change in internuclear distance, ρ the reduced mass density, and ω_v is the frequency, nearly independent of k_v. In the Placzek[9] model, the optical polarizability of the molecule is considered as a linear function of Q, $\alpha = \alpha_0 + (\partial\alpha/\partial Q)_0 Q$. This leads to a time-averaged free energy per unit volume $F = (\partial\alpha/\partial Q) \times N(A_v E_S E_L^* + A_v^* E_S^* E_L)$ due to the coupling between the Stokes wave at frequency $\omega_S = \omega_L - \omega_v$ and the optical phonon with wave vector $\vec{k}_v = \vec{k}_L - \vec{k}_S$. An essential feature of the coupling is that the phonon wave is much more strongly damped than the light waves. One derives the coupled amplitude equations

$$\frac{dE_S}{dz} = N\left(\frac{\partial\alpha}{\partial Q}\right)\left(\frac{i2\pi\omega_S^2}{c^2 k_{Sz}}\right)E_L A_v^*,$$

$$\frac{dA_v^*}{dz} = -\left(\frac{k_v}{\omega_v}\right)\Gamma_{k_v} A_v^* + N\left(\frac{\partial\alpha}{\partial Q}\right)\left(\frac{-ik_v}{2}\right)E_L^* E_S. \quad (1)$$

There are two exponential solutions with gain constants

$$K = \left(-\frac{1}{2}\frac{k_v}{\omega_v}\right)\Gamma_{k_v} \pm \frac{1}{2}\left[\left(\frac{k_v}{\omega_v}\right)^2 \Gamma_{k_v}^{\ 2} + 4\left(\frac{N^2\pi\omega_S^{\ 2}k_v}{c^2 k_{Sz}}\right)\left(\frac{\partial\alpha}{\partial Q}\right)^2 |E_L|^2\right]^{1/2}. \quad (2)$$

The condition

$$\left(\frac{N^2\pi\omega_S^{\ 2}k_v}{c^2 k_{Sz}}\right)^{1/2}\left(\frac{\partial\alpha}{\partial Q}\right)|E_L| \ll \left(\frac{kv}{\omega_v}\right)\Gamma_{k_v}$$

is always satisfied in practice. Expansion of the square root then leads to an amplified mode with essentially pure Stokes character with an amplitude gain constant

$$K_S = \left(\frac{\pi\omega^2}{k_{Sz}c^2}\right)\left\{\frac{N^2(\partial\alpha/\partial R)^2}{2\rho\omega_v \Gamma_{k_v}}\right\}|E_L|^2,$$
$$= -(2\pi\omega_S/k_{Sz}c^2)\,\chi_S''\,|E_L|^2. \quad (3)$$

On the right-hand side the imaginary part of the Raman susceptibility χ_S'' has been introduced. This quantity can also be calculated for a model in which the electronic and vibrational levels of the molecules are quantized.[10] The two methods are entirely equivalent. A detailed proof will be given elsewhere. It is important to note that the damping of the phonon wave will, in general, be a function of its wave number. The damping is caused predominantly by interaction with acoustical phonons via anharmonic elastic forces and crystalline imperfections. One may expect, on the basis of general considerations of available volume in momentum space, that a phonon with a shorter wavelength will be somewhat more heavily damped. Therefore the gain for a Stokes wave in the forward direction, proportional to $\Gamma^{-1}(k_L - k_S)$, will be somewhat larger than the gain in the backward direction, proportional to $\Gamma^{-1}(k_L + k_S)$. A difference of a few percent in the "nonlocal" damping should be sufficient to give a large forward-backward ratio of the intensities. The suggestion that the forward-backward asymmetry is caused by the extremely short duration (~10^{-11} sec) of the traveling light pulse may be discounted on two grounds. The observed spectral width of the laser pulse is too narrow to admit such a short burst and this mechanism cannot account for the wide variation of forward-backward ratio in different substances.

Turning now to the question of generation of anti-Stokes light, we should consider simultaneously three waves, optical phonons, Stokes, and anti-Stokes light coupled parametrically by the laser field. Since the optical phonons are strongly damped, the system of equations can be reduced to a coupling between the light waves only. The considerations of Zeiger et al.[5] should therefore lead to the same results as those derived with the aid of complex Raman-type susceptibilities. The omission of the phonon damping led Zeiger et al. to a distinction between the two cases. The coupled amplitude equations between the waves at the Stokes frequency $\omega_S = \omega_L - \omega_v - \Delta\omega$ and the anti-Stokes frequency $\omega_a = \omega_L + \omega_v + \Delta\omega$ take the form

$$dE_S/dz = \lambda_{SS}E_S + \lambda_{Sa}E_a^* e^{i\Delta kz},$$

$$dE_a^*/dz = \lambda_{aS}E_S e^{-i\Delta kz} + \lambda_{aa}E_a^*, \qquad (4)$$

with

$$\lambda_{SS} = +(2\pi i\omega_S^2/c^2k_{Sz})\chi_S|E_L|^2 - \alpha_S,$$

$$\lambda_{aa} = -(2\pi i\omega_a^2/c^2k_{az})\chi_a^*|E_L|^2 - \alpha_a,$$

$$\lambda_{Sa} = +(2\pi i\omega_S^2/c^2k_{Sz})(\chi_S\chi_a^*)^{1/2}E_L,$$

$$\lambda_{aS} = -(2\pi i\omega_a^2/c^2k_{az})(\chi_S\chi_a^*)^{1/2}E_L^{*2}.$$

Here $\Delta k = 2k_L - k_S - k_a$ is the momentum mismatch in the z direction of the laser beam as shown in Fig. 1, α_S and α_a are loss coefficients due to linear absorption and scattering at ω_S and ω_a, repectively, $\chi_S = \chi_S'(\Delta\omega) + i\chi_S''(\Delta\omega)$ is the complex Raman susceptibility at ω_S, $\chi_a = \chi_a'(\Delta\omega) + i\chi_a''(\Delta\omega)$ is the complex Raman susceptibility at ω_a. These susceptibilities follow from a quantum mechanical calculation[10] or from the coupling coefficients with the optical phonons [compare, e.g., Eq. (1)]. It should be emphasized that the real part of the Raman susceptibility also contains a contribution from nonresonant terms not necessarily involving the nuclear vibrations

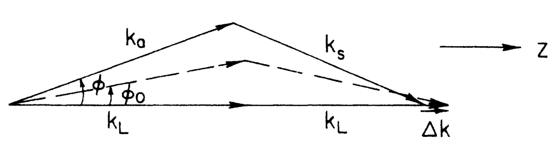

FIG. 1. Wave-vector diagram in the case of momentum mismatch $\Delta\vec{k} = 2\vec{k}_L - \vec{k}_S - \vec{k}_a$. The matching condition is satisfied in the x-y plane. The dashed arrows show the case of perfect matching. The angular deviation $\varphi - \varphi_0$ can be determined from the relationship $\cos\varphi = \cos\varphi_0 - \Delta k/2k_L$. A typical order of magnitude is $\varphi - \varphi_0 \sim 10^{-2}$ radian.

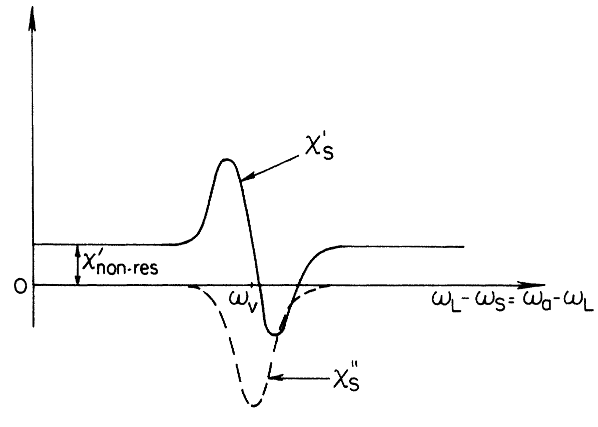

FIG. 2. Variation of Raman susceptibility with frequency $\omega_v + \Delta\omega$ near resonance ($\Delta\omega \sim 0$). Since ω_S increases from right to left on the frequency scale, χ_S' appears inverted in agreement with the negative value of χ_S''.

(Fig. 2). Also note that, in general, $\lambda_{Sa} \neq \lambda_{aS}^*$.

The solution of the set of coupled waves is the linear combination of the exponentials with complex gain constants

$$K_S = K + i\tfrac{1}{2}\Delta k,$$

$$K_a = K - i\tfrac{1}{2}\Delta k,$$

$$K = \tfrac{1}{2}(\lambda_{aa} + \lambda_{SS}) \pm [\tfrac{1}{4}(\lambda_{aa} - \lambda_{SS} + i\Delta k)^2 + \lambda_{aS}\lambda_{Sa}]^{1/2}. \qquad (5)$$

If the dispersion in the linear absorption and the nonlinear coupling is ignored, $\alpha_S = \alpha_a$ and $(\omega_S^2/k_{Sz})\chi_S = (\omega_a^2/k_{az})\chi_a^*$, the gain constant K becomes

$$K = -\alpha \pm [(2\pi\omega_S^2/c^2k_{Sz})\chi_S|E_L|^2\Delta k - \tfrac{1}{4}\Delta k^2]^{1/2}. \qquad (6)$$

For the case of exact momentum matching, $\Delta k = 0$, one finds $K_a = K_S = -\alpha$. There is no gain either at ω_S or ω_a. This result should be compared with that of Garmire, Pandarese, and Townes,[3] who considered the coupling between Stokes and anti-Stokes radiation at $\Delta k = 0$ and $\Delta\omega = 0$. It is incorrect to say that the Stokes wave is first created and subsequently absorbed while anti-Stokes light is generated. For $\Delta k = 0$ there is indeed a dark ring in the Stokes radiation, but there is also no anti-Stokes light for exact momentum matching. This situation is well known in parametric amplifier theory, where absence of gain exists if neither sideband is suppressed.

The bright anti-Stokes light cones are generated by an offset from the exact momentum matching. Simultaneously there may be an offset in frequency $\Delta\omega$ from exact resonance. The real part of the Raman susceptibility plays an essential role. Consider the wave with positive gain by writing out the real part of K given by Eq. (6):

$$\mathrm{Re}K = -\alpha + 2^{-1/2}\{(2\pi\omega_S^2/c^2k_{Sz})\chi_S'(\Delta\omega)|E_L|^2\Delta k - \tfrac{1}{4}(\Delta k)^2 \pm [((2\pi\omega_S^2/c^2k_{Sz})\chi_S'(\Delta\omega)|E_L|^2\Delta k - \tfrac{1}{4}(\Delta k)^2]^2 + [(2\pi\omega_S^2/ck_{Sz})\chi_S''(\Delta\omega)|E_L|^2\Delta k)^2]^{1/2}\}^{1/2}. \quad (7)$$

For each direction of momentum mismatch Δk, one can find a frequency offset $\Delta\omega$ to give maximum gain in that direction. For each eigenvalue one should calculate the partial anti-Stokes character of the wave. In this manner point(s) for optimum anti-Stokes gain may be found in the (Δk, $\Delta\omega$) plane. Consider, for example, the direction for which $\Delta k = (8\pi\omega_S^2/c^2k_{Sz})\chi_S'(\Delta\omega)|E_L|^2$. In this direction the anti-Stokes character is near fifty percent. The gain is equal to $-\alpha + (8^{1/2}\pi\omega_S^2/c^2k_{Sz}) \times |E_L|^2(\chi_S'\chi_S'')^{1/2}$ and the threshold is first exceeded for a frequency offset $\Delta\omega = \sqrt{3}\Gamma_v$. A detailed analysis of Eq. (7) shows the following features.

(1) The anti-Stokes intensity for the direction of exact momentum matching is zero.

(2) The anti-Stokes intensity is maximum for an angular deviation which is proportional to the power density of the laser beam and to the nonlinear susceptibility. Under suitable circumstances, if the nonresonant part of χ_S' is small, a doubling of the anti-Stokes rings may occur due to emission at positive and negative values of Δk. Important deviations from momentum matching are observed in all liquids.[11] In calcite Δk appears to be small, presumably because of a small value of $|\chi_S||E_L|^2$ in this case. The experimental procedure[8] to "extrapolate to infinite focal length" has no theoretical foundation. The variation of direction with focal length is probably caused by a variation of the intensity of the laser beam when different lenses are used.

(3) The frequency spectrum of the anti-Stokes line has an asymmetric shape, due to mixing of the effects of the real and imaginary part of the Raman susceptibility. Its center of gravity is displaced towards lower or higher frequencies depending on whether χ_{nonres} is positive or negative (Fig. 2). If the threshold is lowest for directions with $\Delta k > 0$ and $\Delta\omega < 0$, but an only slightly higher threshold exists for directions with $\Delta k < 0$ and $\Delta\omega > 0$, a dark band may appear in the anti-Stokes line near the frequency for which $\chi' = 0$. This effect has been reported by Stoicheff[4] and Terhune.[11]

(4) For large momentum mismatch the amplified wave has essentially pure Stokes character. In principle there is always a slight admixture at the anti-Stokes frequency which "drags along" with the Stokes wave. In the forward direction the ratio of the intensity of Stokes to anti-Stokes radiation should be given by

$$I(\omega_a)/I(\omega_S) \simeq (4\pi^2\omega_S^4/c^4k_{Sz}^2)|\chi_S|^2|E_0|^4/(2k_L - k_S - k_a)^2.$$

This anti-Stokes intensity in the forward direction may be observable.

A straightforward extension of the theory of coupled light waves of Armstrong, Bloembergen, Ducuing, and Pershan,[12] to include the effects of the imaginary part of the nonlinear susceptibilities,[13] is capable to account for many details observed in Raman laser media. A manuscript intended for publication in the Physical Review is in preparation, which will contain a more detailed treatment of coupling between waves including higher order anti-Stokes and Stokes waves, as well as a detailed quantum mechanical calculation of the nonlinear Raman susceptibilities.

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[1]Gisela Eckhardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, D. Weiner, and E. J. Woodbury, Phys. Rev. Letters 9, 455 (1962).

[2]R. W. Terhune, Bull. Am. Phys. Soc. 8, 359 (1963).

[3]E. Garmire, F. Pandarese, and C. H. Townes, Phys. Rev. Letters 11, 160 (1963).

[4]B. P. Stoicheff, Phys. Letters 7, 186 (1963).

[5]H. J. Zeiger, P. E. Tannenwald, S. Kern, and R. Herendeen, Phys. Rev. Letters 11, 419 (1963).

[6]G. Eckart, 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]R. Chiao and B. P. Stoicheff, Phys. Rev. Letters 12, 290 (1964).

[9]G. Placzek, Marx-Handbuch der Radiologie (Akademie Verlagsgesellschaft, Leipzig, Germany, 1934),

Vol. VI, Pt. 2, pp. 209-374.
[10]N. Bloembergen and Y. R. Shen, Phys. Rev. 133, A37 (1964).
[11]B. P. Stoicheff (private communication); R. W. Hellwarth (private communication); R. W. Terhune, Bull. Am. Phys. Soc. 9, 236 (1964).
[12]J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).
[13]N. Bloembergen, Proc. IEEE 51, 124 (1963); Proceedings of the Third International Symposium on Quantum Electronics, Paris, February, 1963 (Dunod, Paris, France, 1964), p. 1501

INTENSITY-DEPENDENT CHANGES IN THE REFRACTIVE INDEX OF LIQUIDS

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In this paper we wish to report measurements of some of the changes in the real part of the index of refraction for monochromatic light which are proportional to the light intensity. In the accompanying analysis of the effect, for elliptically polarized light in isotropic centrosymmetric materials, it is shown that in addition to a polarization-independent change in velocity, a rotation of the axes of the vibrational ellipse as a function of distance occurs. Observation of this rotation, such as reported here, provides a very sensitive technique for measuring the magnitude and sign of the coefficients involved. This rotational effect is not to be confused with the Faraday effect or optical activity. It is more closely related to the second-order Kerr and Cotton-Mouton effects, which involve dc fields, and are special cases of the interaction between two frequency components. Such an interaction, however, leads in isotropic centrosymmetric materials to birefringent rather than rotary effects.

The effect which usually determines the intensity-dependent index of refraction can be described in terms of an induced nonlinear polarization of third order in the electric field strength.[1] The Fourier component of this nonlinear polarization at frequency ω, $\mathrm{Re}\vec{P}^{NL}$, which is induced by a plane wave at frequency ω traveling in the z direction can be represented as follows[2]:

$$P_i^{NL} = [AE_i(\vec{E}^*\cdot\vec{E}) + \tfrac{1}{2}BE_i^*(\vec{E}\cdot\vec{E})] \times \exp(-i\omega t + in\omega z/c), \qquad (1)$$

where the electric vector of the light wave is $\vec{\epsilon}(\omega, z) \equiv \mathrm{Re}[\vec{E}\exp(-i\omega t + in\omega z/c)]$, n is the refractive index at frequency ω, and A and B are complex constants. Here, $\vec{E}$ is regarded as a slowly varying function of z as a result of the nonlinearities. In a lossless medium, A and B are real and when ω is far from all resonances, $A \cong B$. Transforming $\vec{P}^{NL}$ and $\vec{E}$ to a circular representation with $E_+ \equiv (E_x + iE_y)/\sqrt{2}$ and $E_- \equiv (E_x - iE_y)/\sqrt{2}$, it can be shown that in a lossless medium, the nonlinearity leads only to the following changes in the refractive indices for the two senses of circular polarization:

$$\delta n_+ = (2\pi/n)[AE_+E_+^* + (A+B)E_-E_-^*],$$

$$\delta n_- = (2\pi/n)[AE_-E_-^* + (A+B)E_+E_+^*]. \qquad (2)$$

From the above, one can readily verify that the index changes for plane and for circularly polarized light are different. Let α be defined as the angle of inclination of the vibrational ellipse of the elliptically polarized radiation, measured from the x toward the $+y$ axis. Then α is equal to one half the phase difference between E_+ and E_- and varies with z as follows:

$$\alpha = \alpha_0 + \tfrac{1}{2}(\omega/c)(\delta n_+ - \delta n_-)z$$

$$= \alpha_0 + (\pi\omega/cn)B(E_-E_-^* - E_+E_+^*)z. \qquad (3)$$

The direction of rotation is determined by the sign of B and the handedness of the ellipticity.

Figure 1 is a schematic diagram of the experimental arrangement used. A giant pulsed ruby laser providing in the sample a 16-mJ pulse with a 40-nsec halfwidth was used. The mica eighth-wave plate was oriented so that the electric vector of the laser beam bisected the angle between its fast and slow axes. The laser beam was brought to a focus in the middle of a one-meter-long liquid cell with windows selected for minimum birefringence. A right-angle Rochon prism separated the output beam into two components plane-polarized parallel to the fast and