COMPLEX INTENSITY-DEPENDENT INDEX OF REFRACTION, FREQUENCY BROADENING OF STIMULATED RAMAN LINES, AND STIMULATED RAYLEIGH SCATTERING*

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The intensity-dependent index of refraction was recognized as a generalization of the quadratic Kerr effect early in the development of nonlinear optics.[1] Gires and Mayer[2] and Maker, Terhune, and Savage[3] have demonstrated the effect experimentally. Mayer[2] pointed out that the effect is particularly large in fluids with anisotropic molecules which also have a large dc quadratic Kerr constant. It is the purpose of this note to show that the anisotropic polarizability is a major cause for the frequency broadening of laser light as well as various orders of Stokes and anti-Stokes radiation. These broadening effects were first reported by Stoicheff[4,5] and further studied by Garmire,[6] but have heretofore not received an adequate explanation.

The importance of the quadratic Kerr effect for self-focusing of laser beams and anomalous stimulated Raman gain has recently been demonstrated.[7,8] The effect is also responsible for the stimulated inelastic Rayleigh scattering which has been observed and correctly interpreted by Mash et al.[9] This latter effect as well as the anomalous frequency broadening can be described by a complex "Raman-type" susceptibility.

Consider the motion of an axially symmetric molecule under the influence of the viscous damping in the liquid and the torque exerted on it in the presence of the two light waves; for example, two linear parallel polarized laser components, with real amplitudes E_L and E_L' at frequencies ω_L and ω_L', respectively, with $\omega_L \gg \omega_L - \omega_L' > 0$. The problem is analogous to the motion of a polar molecule under the influence of dc and ac electric fields treated by Debye.[10] The probability for a molecule to have its axis of symmetry in a solid angle element $d\Omega$, making an angle θ with respect to the electric light fields, is given to first order in $(kT)^{-1}$ by

$$f(\Omega, \vec{r}, t)d\Omega = \frac{d\Omega}{4\pi} + \frac{d\Omega}{48\pi kT}(\alpha_\parallel - \alpha_\perp)(-1 + 3\cos^2\theta)$$

$$\times \left\{ |E_L|^2 + |E_L'|^2 + 2\,\text{Re}\frac{E_L E_L'^* \exp[i(\vec{k}_L - \vec{k}_{L'})\cdot\vec{r} - i(\omega_L - \omega_L')t]}{1 - i(\omega_L - \omega_L')\tau_c} \right\}. \tag{1}$$

Here $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal optical polarizabilities of the molecule. The torque exerted by the light fields on a permanent electric dipole moment varies with the light frequency and cannot be followed by the molecular motion. The only frequency-dependent term that has been retained in Eq. (1) varies at the difference frequency $\omega_L - \omega_L'$. This torque is described by a spherical harmonic of the second order whereas the torque on a polar molecule is porportional to $\cos\theta$ or $\sin\theta$. As a consequence, the characteristic time τ_c in Eq. (1) is one-third the time of Debye, characteristic for reorientation of polar molecules. One finds $\tau_c = \zeta/6kT$, where $\zeta = 8\pi\eta a^3$ is the Stokes coefficient for a sphere of radius a rotating in a fluid with viscosity coefficient η.

The anisotropic term in the distribution function (1) leads to an intensity-dependent index of refraction, which contains a dc term and a modulation at $\omega_L - \omega_L'$. First consider the change in index for another light beam at a

frequency ω_S far removed from ω_L and ω_L'. This beam may be polarized parallel or perpendicular to E_L and E_L':

$$\Delta n_{2,\parallel}(\omega_s) = -2\Delta n_{2,\perp}(\omega_s)$$

$$= LM\left\{ |E_L|^2 + |E_L'|^2 \right.$$

$$\left. + \frac{E_L E_L'^* \exp[-i(\omega_L - \omega_L')t]}{1 - i(\omega_L - \omega_L')\tau_c} \right\}, \quad (2)$$

with

$$M = \frac{2\pi\{\alpha_{\parallel}(\omega_s) - \alpha_{\perp}(\omega_s)\}\{\alpha_{\parallel}(\omega_L) - \alpha_{\perp}(\omega_L)\}N_0}{45kTn_0(\omega_s)}. \quad (3)$$

Here N_0 is the number of molecules per cc and n_0 the linear index of refraction. If there are several molecular species present with less than axial symmetry, Eq. (3) is replaced by

$$M = \sum_i \frac{\pi N_i}{45kTn_0(\omega_s)}\left\{(\alpha_{ix} - \alpha_{iy})^{(\omega_s)}(\alpha_{ix} - \alpha_{iy})^{(\omega_L)} + (\alpha_{iy} - \alpha_{iz})^{(\omega_s)}(\alpha_{iy} - \alpha_{iz})^{(\omega_L)} \right.$$

$$\left. + (\alpha_{iz} - \alpha_{ix})^{(\omega_s)}(\alpha_{iz} - \alpha_{ix})^{(\omega_L)}\right\}. \quad (3a)$$

The factor L is a local field correction. In the simple case of a Lorentz cavity it takes the form $L = \{n_0^2(\omega_s) + 2\}^2\{n_0^2(\omega_L) + 2\}^2/81$. The modulated index of refraction will produce side bands around the frequency ω_S, spaced by $\omega_L - \omega_L'$. The spatial dependence has been omitted in Eq. (2). For small $\omega_L - \omega_L'$, momentum matching is generally satisfied if all the light waves move in the same direction. The intensity of the nth side bands around ω_S is given by a Bessel function J_n of complex argument proportional to the time-dependent term in Eq. (2).

Experiments have been carried out to show that light at an arbitrary frequency ω_S can be modulated at $\omega_L - \omega_L'$ in the presence of an anisotropic molecular species. Liquid CS_2 is known to exhibit a large frequency-broadening effect.[4,6,9] This is due to a combination of a large anisotropy in the optical polarizability and a short characteristic time τ_c. A Q-switched ruby-laser pulse was operated with two frequency components ω_L and ω_L', sepa-

rated by 1.6 cm^{-1}, of about equal intensity. The beam was focused into a cyclohexane cell, to which varying amounts of CS_2 were added. Figure 1 shows that pure cyclohexane shows essentially no broadening, while small amounts of CS_2 cause a broadening proportional to its relative concentration. The side bands remain visible to a very high order. There is an additional increase in intensity at 70 and 85 cm^{-1} downward in absolute frequency from the main Stokes line, where higher cyclohexane vibrations at 2920 and 2935 cm^{-1} produce additional Stokes gain. The broadening is asymmetric favoring the lower frequencies. This is connected with the complex nature of the index of refraction in Eq. (2). At the CS_2 concentrations used (15% or less), no stimulated Stokes line of CS_2 was observed. Its broadening characteristics are independent of its Raman properties.

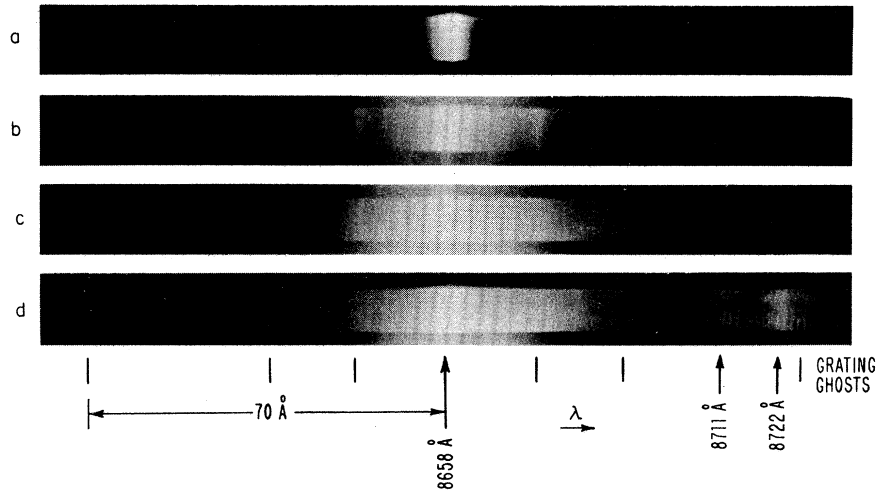The dependence of the frequency broadening on τ_c was also checked. This quantity may

FIG. 1. Frequency broadening of the cyclohexane Stokes line in mixtures of cyclohexane and CS_2. The laser beam contains two components spaced by 1.6 cm^{-1}. (a) Pure cyclohexane, (b) 5% CS_2 by volume, (c) 10% CS_2 by volume, and (d) 15% CS_2 by volume. Consult text for further discussion of these spectra.

be increased by increasing the viscosity. The laser beam with frequencies ω_L and ω_L' and the unbroadened Stokes line ω_S from a pure cyclohexane Raman cell was passed through a second cell 10 cm long in which broadening was produced by toluene. The second cell contained low-viscosity mixtures of 50% CCl_4 (or heptane) and 30% toluene–70% CCl_4, and high-viscosity mixtures of 50% toluene–50% mineral oil and 30% toluene–70% mineral oil. The paraffins and CCl_4 have negligible broadening action. The toluene Stokes components were not stimulated. The broadening of the cyclohexane Stokes beam in these cells is shown in Fig. 2.

In the more viscous mixtures the over-all broadening is less pronounced because of the larger value of $(\omega_L-\omega_L')\tau_c$. At the same time the Fourier components spaced by $\omega_L-\omega_L'$ are not resolved. The broadening becomes quasi-continuous and diffuse. Further experiments on these mixtures are in progress. A temperature variation should also influence η, τ_c, and the broadening.

New frequency components may be created by stimulated Rayleigh scattering.[9] An expression for the nonlinear polarization at a frequency ω_L'', close to ω_L, which is a cubic function of the field amplitudes E_L and E_L'' can be derived from Eqs. (1) and (2):

$$P_{\parallel}^{NLS}(\omega_L'') = n_0(2\pi)^{-1}LM\left[|E_L''|^2E_L'' + \left\{1 + \frac{1}{1+(\omega_L-\omega_L'')^2\tau_c^2} - \frac{i(\omega_L-\omega_L'')\tau_c}{1+(\omega_L-\omega_L'')^2\tau_c^2}\right\}|E_L|^2E_L''\right]. \quad (4)$$

This equation is valid if E_L and E_L'' are parallel. If these fields are polarized at right angles, Eq. (4) is replaced by

$$P_{\perp}^{NLS}(\omega_L'') = n_0(2\pi)^{-1}LM\left[|E_L''|^2E_L'' + \left\{-\frac{1}{2} + \frac{(\frac{3}{4})}{1+(\omega_L-\omega_L'')^2\tau_c^2} - \frac{(\frac{3}{4})i(\omega_L-\omega_L'')\tau_c}{1+(\omega_L-\omega_L'')^2\tau_c^2}\right\}|E_L|^2E_L''\right]. \quad (5)$$

The negative imaginary part of these Raman-type susceptibilities implies exponential gain for ω_L'' $<\omega_L$, proportional to the intensity $|E_L|^2$. The gain is a maximum for $(\omega_L-\omega_L'')\tau_c=1$. The gain per unit length for the perpendicular polarization is $\frac{3}{4}$ of the gain for parallel polarization. This is in agreement with the corresponding spontaneous Rayleigh-scattering cross sections. If the initial
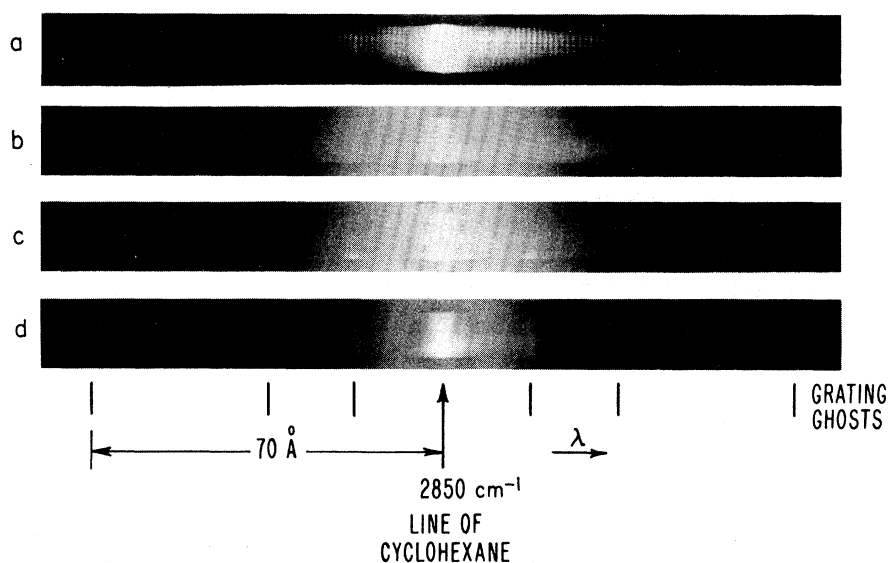
FIG. 2. Frequency broadening of a cyclohexane Stokes beam passing through a 10-cm-long cell containing toluene mixtures of varying viscosity η relative to pure toluene. (a) 50% CCl_4 ($\eta = 1.3$), (b) 50% mineral oil ($\eta = 3$), (c) 70% CCl_4 ($\eta = 1.3$), and (d) 70% mineral oil ($\eta = 7$).

laser beam contains two frequency components ω_L and ω_L', there are of course also new Fourier components created on the anti-Stokes side of ω_L by parametric interaction. We have observed this frequency broadening of the laser beam around ω_L itself on CS_2 and other liquids. The analysis of the coupling between the various light waves proceeds in principle along the same lines as for the stimulated Raman effect. The actual situation is further complicated by the self-focusing effect. The stimulated Rayleigh scattering can, however, account qualitatively for the diffuse broadening of light beams exhibited by the toluene samples in Fig. 2. It also accounts for the fact that the light components observed by us are preferentially broadened to the low-frequency side. Stoicheff[4] has, however, reported preferential broadening to higher frequencies on higher order Stokes and anti-Stokes lines.

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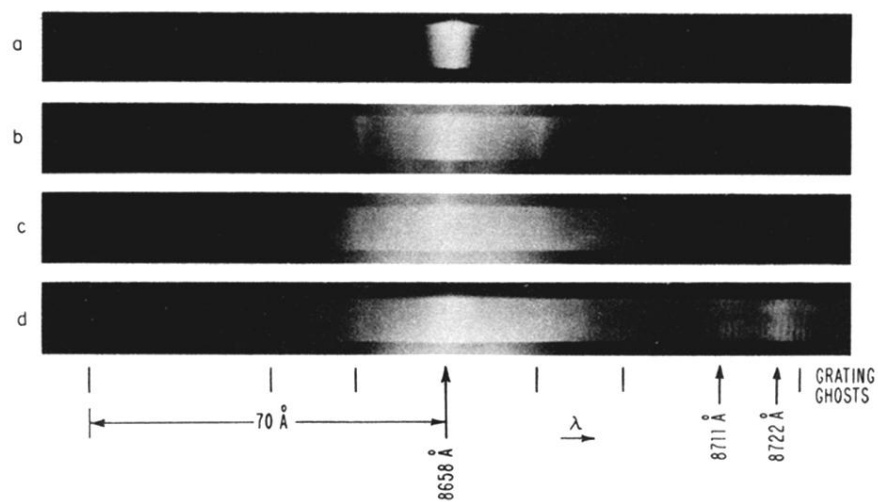
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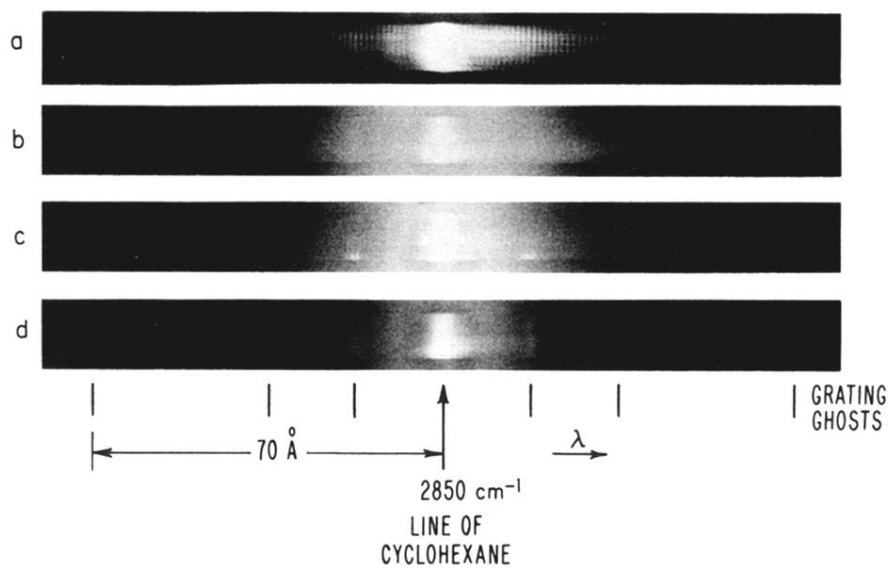FIG. 2. Frequency broadening of a cyclohexane Stokes beam passing through a 10-cm-long cell containing tolu-ene mixtures of varying viscosity η relative to pure toluene. (a) 50% CCl_4 ($\eta = 1.3$), (b) 50% mineral oil ($\eta = 3$), (c) 70% CCl_4 ($\eta = 1.3$), and (d) 70% mineral oil ($\eta = 7$).