

implies that $F(\xi, \mathbf{r})$ must vanish. In order to show this choose for simplicity a Landau gauge, $\mathbf{A}(\mathbf{r}) = (-yB, 0, 0)$. Then (A1) can be written

$$\int e^{i\mathbf{p} \cdot \xi} e^{im\omega_0 \xi x y} e^{-\frac{1}{2}im\omega_0 \xi x \xi y} F(\xi, \mathbf{r}) d\xi = 0 \quad (\text{A2})$$

by using Eq. (2.18). Form the matrix of (A2) using a plane-wave representation (see Sec. III). Then (A2)

becomes

$$\int e^{i\mathbf{k} \cdot \xi} F_{kk'}(\xi, \mathbf{r}) d\xi = 0, \quad (\text{A3})$$

where $F'(\xi, \mathbf{r})$ is defined by

$$F'(\xi, \mathbf{r}) = e^{im\omega_0 \xi x y} e^{-\frac{1}{2}im\omega_0 \xi x \xi y} F(\xi, \mathbf{r}). \quad (\text{A4})$$

Equation (A3) is now an ordinary Fourier integral and implies that $F'(\xi, \mathbf{r})$ must be zero. According to (A4), this in turn requires that $F(\xi, \mathbf{r})$ must vanish.

Nonlinear Susceptibility Constants and Self-Focusing of Optical Beams in Liquids*

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This paper reports measurements of intensity-induced rotation of the polarization ellipse, and measurements of the self-focusing threshold and its polarization dependence, using an unfocused laser beam in several Raman-active liquids. An attempt was made to determine the nonlinear susceptibility constants in these liquids by correlating these measurements. It is found that the self-focusing formulas for linearly polarized beams are in good agreement with the experiments, but the polarization dependence of the self-focusing threshold disagrees with the corresponding polarization dependence of the nonlinear index changes. A possible explanation for this discrepancy is discussed.

I. INTRODUCTION

IT is assumed in linear optics that a light beam of finite cross section can be represented by a superposition of unbounded plane-wave components propagating in slightly different directions.¹ The presence of optical nonlinearities produced by intense laser beams in a dielectric medium invalidates the principle of superposition. The plane-wave components are no longer independent, but are coupled to each other through the nonlinear polarization terms which bring about transfer of energy among the components.² The nonlinear optical effects of an intense laser beam on the propagation of the beam itself have been considered by several authors;³⁻⁶ they include the intensity-induced rotation of the polarization ellipse,^{5,6} and the intensity-

induced slowing of the plane-wave components, which leads to self-focusing of the laser beam.^{7,8}

This paper discusses some of the nonlinear optical effects which are related to the intensity-dependent changes in the real part of the index of refraction. In Sec. II, a phenomenological description is first given of the self-induced effects of an unbounded plane wave in a medium which is lossless and isotropic in the linear approximation. To describe these effects, a fourth-rank nonlinear susceptibility tensor with three nonzero independent components is introduced. Additional nonlinear effects associated with laser beams of finite cross section are then discussed in Sec. III. Possible ways to determine the susceptibility constants are discussed in Sec. IV and the relations that exist between these susceptibility constants are derived in Sec. V in terms of a simplified physical model.

Section VII reports measurements of intensity-induced rotation of the polarization ellipse associated with an unfocused laser beam in several Raman-active liquids. These measurements were correlated with measurements of self-focusing threshold⁹ to determine the nonlinear susceptibility constants in these liquids.

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¹ See, for example, F. A. Jenkins and H. E. White, *Fundamentals of Optics* (McGraw-Hill Book Company, Inc., New York, 1957), Chap. 12.

² J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, *Phys. Rev.* **127**, 1918 (1962).

³ R. Y. Chiao, E. Garmire, and C. H. Townes, *Phys. Rev. Letters* **13**, 479 (1964).

⁴ V. I. Talanov, *JETP Pis'ma Redaktsiyu* **2**, 218 (1965) [English transl.: *Soviet Phys.—JETP Letters* **2**, 138 (1965)].

⁵ P. D. Maker, R. W. Terhune, and C. M. Savage, *Phys. Rev. Letters* **12**, 507 (1964).

⁶ P. D. Maker and R. W. Terhune, *Phys. Rev.* **137**, A801 (1965).

⁷ M. Hercher, *J. Opt. Soc. Am.* **56**, 563 (1964).

⁸ N. F. Pilipetskii and A. R. Rustamov, *JETP Pis'ma Redaktsiyu* **2**, 88 (1965) [English transl.: *Soviet Phys.—JETP Letters* **2**, 55 (1965)].

⁹ P. L. Kelley, *Phys. Rev. Letters* **15**, 1005 (1965).

It is found that the self-focusing formulas for linearly polarized beams are in good agreement with the experiments, but the polarization dependence of self-focusing threshold disagrees with the corresponding dependence of the nonlinear index changes. A possible explanation for this discrepancy is discussed.

II. PHENOMENOLOGICAL DESCRIPTION OF THE INTENSITY-DEPENDENT CHANGES IN THE REFRACTIVE INDEX

In a medium with inversion symmetry, the lowest order nonlinear optical effects are those associated with an induced polarization third-order in the electric field strength. Following Maker and Terhune,⁶ the induced polarization \mathbf{P}^{NL} is given by

$$P_i^{NL}(\omega_1) = D\chi_3^{ijkl}(-\omega_1, \omega_2, \omega_3, \omega_4)E_j(\omega_2)E_k(\omega_3)E_l(\omega_4) \times \exp[i(n_2\omega_2 + n_3\omega_3 + n_4\omega_4)z/c], \quad (1)$$

where the summation convention for repeated indices is used. Here $\omega_1 = \omega_2 + \omega_3 + \omega_4$ are the frequencies of the plane-wave components assumed to be propagating along the z axis; $n_{1,2,3,4}$ are, respectively, the linear refractive indices at the frequencies $\omega_{1,2,3,4}$; $E_i^*(\omega) \equiv E_i(-\omega)$ are the complex amplitudes of the electric field strength, regarded as slowly varying functions of distance to account for the nonlinear effects; i, j, k, l are tensor indices; $D=1, 3, \text{ or } 6$ depending on whether three, two, or none of the frequencies are the same; and $\chi_3^{ijkl}(-\omega_1, \omega_2, \omega_3, \omega_4)$ are the components of a fourth-rank nonlinear susceptibility tensor. The frequencies in these components are ordered to indicate their association with the corresponding coordinates. Equation (1) is invariant to the ordering of the various field amplitudes, and the last three frequencies in $\chi_3^{ijkl}(-\omega_1, \omega_2, \omega_3, \omega_4)$ may be permuted at will provided that the corresponding coordinate indices are permuted in the same manner.

Equation (1) describes the generation of new frequency components, and the intensity-dependent changes in the refractive indices for the existing components in a nonlinear medium. This equation must remain invariant to those symmetry operations which transform the medium into itself.¹⁰ Thus the form of the susceptibility tensor is restricted by the symmetry of the medium, and the number of independent nonvanishing components of this tensor may be greatly reduced if the medium possesses high degrees of symmetry.

A. Optical Kerr Effect

Consider two plane-wave components at ω_1 and ω_2 in a medium which is lossless and isotropic in the linear approximation. The nonlinear optical effects at ω_1 induced by the wave at ω_2 can be described in terms of the following nonlinear polarization:

$$P_i^{NL}(\omega_1) = 6\chi_3^{1122}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_i(\omega_1)E_j(\omega_2)E_j^*(\omega_2) \times \exp(in_1\omega_1 z/c) + 6\chi_3^{1212}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_j(\omega_1) \times E_i(\omega_2)E_j^*(\omega_2)\exp(in_1\omega_1 z/c) + 6\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_j(\omega_1)E_j(\omega_1)E_i^*(\omega_2) \times \exp(in_1\omega_1 z/c). \quad (2)$$

This nonlinear polarization can in turn be described as the changes $\delta\mathfrak{K}_1(-\omega_1, \omega_1)$ in the linear susceptibility tensor $\mathfrak{K}_1(-\omega_1, \omega_1)$: These changes are quadratic in the field amplitudes $E_j(\omega_2)$, and are given in component form by

$$\delta\chi_1^{ij}(-\omega_1, \omega_1) = [6\chi_3^{1122}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_k(\omega_2)E_k^*(\omega_2)]\delta_{ij} + [6\chi_3^{1212}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_i(\omega_2)E_j^*(\omega_2) + 6\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)E_j(\omega_2)E_i^*(\omega_2)], \quad (3)$$

where k is a dummy index over which the summation is to be carried out. One observes that the susceptibility tensor $\mathfrak{K}_3(-\omega_1, \omega_1, \omega_2, -\omega_2)$ has in this case three nonzero independent components differing from each other only by the assignment of the frequencies to the coordinates.

The above equations can be used to calculate the optical Kerr effect, namely, the induced birefringence at ω_1 due to an optical field $\mathbf{E}(\omega_2)$,

$$\Delta n = \delta n_{11} - \delta n_{\perp} = (2\pi/n_1)6[\chi_3^{1212}(-\omega_1, \omega_1, \omega_2, -\omega_2) + \chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)]|\mathbf{E}(\omega_2)|^2, \quad (4)$$

where δn_{11} and δn_{\perp} are, respectively, the changes in the refractive index in a direction parallel and perpendicular to the field $\mathbf{E}(\omega_2)$. The optical Kerr constant B_0 follows directly from Eq. (4) and is given by¹¹

$$\frac{1}{2}B_0 = (2\pi/n_1\lambda_1)6[\chi_3^{1212}(-\omega_1, \omega_1, \omega_2, -\omega_2) + \chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)]. \quad (5)$$

The static Kerr effect is a special case of Eq. (4) with the optical field $\mathbf{E}(\omega_2)$ replaced by $2\mathbf{E}(0)$. The corresponding susceptibility constant is designated $\chi_3^{1221}(-\omega, \omega_1, 0, 0)$.

B. Self-Induced Effects

With $\omega_1 = \omega_2 = \omega$, the nonlinear susceptibility tensor $\mathfrak{K}_3(-\omega, \omega, \omega, -\omega)$ describes the effects of an unbounded plane wave upon the propagation of the wave itself. The corresponding nonlinear polarization is directly obtainable from Eq. (1) and is given by

$$P_i^{NL}(\omega) = 3[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + \chi_3^{1212}(-\omega, \omega, \omega, -\omega)] \times E_i(\omega)E_j(\omega)E_j^*(\omega)\exp(in\omega z/c) + 3\chi_3^{1221}(-\omega, \omega, \omega, -\omega)E_j(\omega)E_j(\omega)E_i^*(\omega) \times \exp(in\omega z/c). \quad (6)$$

¹⁰ R. R. Briss, Proc. Phys. Soc. (London) **79**, 946 (1962).

¹¹ M. Born, *Optik* (Julius Springer-Verlag, Berlin, 1933), p. 367.

Transforming $\mathbf{P}^{NL}(\omega)$ and $\mathbf{E}(\omega)$ to a circular representation with $E_{\pm} = (1/\sqrt{2})(E_x \pm iE_y)$, the intensity-dependent changes in the refractive indices for the two senses of circular polarization may be obtained from Eq. (6) and are given by

$$\begin{aligned} \delta n_{+} = (2\pi/n) \{ & 3[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) \\ & + \chi_3^{1212}(-\omega, \omega, \omega, -\omega)] |E_{+}(\omega)|^2 \\ & + 3[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + \chi_3^{1212}(-\omega, \omega, \omega, -\omega) \\ & + 2\chi_3^{1221}(-\omega, \omega, \omega, -\omega)] |E_{-}(\omega)|^2 \} \quad (7a) \end{aligned}$$

$$\begin{aligned} \delta n_{-} = (2\pi/n) \{ & 3[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) \\ & + \chi_3^{1212}(-\omega, \omega, \omega, -\omega)] |E_{-}(\omega)|^2 \\ & + 3[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + \chi_3^{1212}(-\omega, \omega, \omega, -\omega) \\ & + 2\chi_3^{1221}(-\omega, \omega, \omega, -\omega)] |E_{+}(\omega)|^2 \}. \quad (7b) \end{aligned}$$

One observes from Eq. (7) that, for the general case of an elliptically polarized wave, the change in the refractive index is in general different for the two senses of circular polarization. This polarization dependence leads to a rotation of the polarization ellipse¹² of the light wave, as may be shown by combining the two expressions in Eq. (7). Let α be the angle of inclination of the polarization ellipse, measured from the x toward the y axis. Then α is equal to one-half the phase difference between $E_{+}(\omega)$ and $E_{-}(\omega)$, and varies with z as follows:

$$\begin{aligned} \alpha &= \alpha_0 + \frac{1}{2}(\omega/c)(\delta n_{+} - \delta n_{-})z \\ &= \alpha_0 + (\pi\omega/nc)6\chi_3^{1221}(-\omega, \omega, \omega, -\omega) \\ &\quad \times [|E_{-}(\omega)|^2 - |E_{+}(\omega)|^2]z, \quad (8) \end{aligned}$$

where the subscript 0 denotes the initial values at $z=0$.

The intensity-induced rotation described above ceases to have any physical significance both for a linearly polarized wave, and for a perfectly circularly polarized wave. In the former case, $|E_{+}|^2 = |E_{-}|^2 = \frac{1}{2}|\mathbf{E}|^2$, so that the amount of rotation in Eq. (8) is zero identically; in the latter case, the polarization ellipse degenerates into a circle, and so no apparent rotation can be observed. In these two extreme cases, the nonlinear index changes exhibit themselves only through the slowing of the light wave as a function of its own intensity. Thus one obtains from Eq. (7) that the total index change is

$$\begin{aligned} \delta n_{11} = (2\pi/n)3[& \chi_3^{1122}(-\omega, \omega, \omega, -\omega) \\ & + \chi_3^{1212}(-\omega, \omega, \omega, -\omega) \\ & + \chi_3^{1221}(-\omega, \omega, \omega, -\omega)] |\mathbf{E}(\omega)|^2 \quad (9) \end{aligned}$$

for linear polarization, and is

$$\begin{aligned} \delta n_{\pm} = (2\pi/n)3[& \chi_3^{1122}(-\omega, \omega, \omega, -\omega) \\ & + \chi_3^{1212}(-\omega, \omega, \omega, -\omega)] |E_{\pm}(\omega)|^2 \quad (10) \end{aligned}$$

for circular polarization. With a given intensity, the

ratio of the intensity-dependent index change for linear polarization to that for circular polarization is given from the last two equations by

$$\frac{\delta n_{11}}{\delta n_{\pm}} = 1 + \frac{\chi_3^{1221}(-\omega, \omega, \omega, -\omega)}{[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + \chi_3^{1212}(-\omega, \omega, \omega, -\omega)]}. \quad (11)$$

III. SELF-FOCUSING OF LASER BEAMS

So far, in discussing nonlinear optical effects, only unbounded plane waves have been considered. In this section the effects of intensity-dependent index on the diffraction of a beam with finite cross section will be considered. At high beam intensities these effects modify the diffraction and may lead to self-focusing of the laser beam.

The experimental evidence for self-focusing of a laser beam has come most notably from studies of the laser-induced damage in glasses,⁷ where the damage appears in the form of long, thin filaments along the lens axis; and from studies of stimulated Raman emission in liquids, where the existence of anomalous gain can be reconciled only by recognizing the formation of high-intensity filaments in the laser beam.^{13,14}

The self-focusing effect of a laser beam can be readily understood in the approximations of geometrical optics.⁹ For liquids, the refractive index usually increases with intensity (see Sec. V). Because of the nonuniform intensity distribution inherent with a beam of finite cross section, the intensity-dependent index of refraction causes different parts of the beam to propagate with different phase velocities. A lens effect is thus produced whereby the rays move toward the region of higher intensity and further increase the intensity there. This increase in intensity is accompanied by a reduction in the effective beam diameter, which continues until it is limited by other factors. A threshold exists for the onset of self-focusing as this effect must overcome the spreading of the beam due to diffraction. Chiao, Garmire and Townes³ have predicted that a light beam may be self-trapped at any arbitrary diameter and will thus not spread. They have further predicted that this self-trapping occurs at a critical power level which is independent of the beam diameter. While it is not yet understood which factors determine the size of the observed high-intensity filaments, the distance required for the establishment of these filaments should depend very little on the terminal filament size if the beam is reduced in diameter by an appreciable factor. This distance has been referred to as the self-focusing length l , and is related to the input laser power, P , through

¹³ G. Bret and G. Mayer, in *Proceedings of the International Conference on the Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966), p. 180.

¹⁴ P. Lallemand and N. Bloembergen, *Phys. Rev. Letters* **15**, 1010 (1965).

¹² In Refs. 5 and 6, the term "vibrational ellipse" instead of "polarization ellipse" is used. The polarization ellipse is discussed in M. Born and E. Wolf, *Principles of Optics* (The Macmillan Company, New York, 1959), p. 24.

the following relation^{9,15}:

$$P^{1/2} = P_{cr}^{1/2} + A/l \quad (12)$$

where

$$A = \frac{1}{4}n(a^2/f)(c/n_2)^{1/2}. \quad (13)$$

Here n_2 is related to the index change in Eq. (9), $\delta n_{11} = (n_2/2)|E|^2$; P_{cr} is the critical power for self-trapping with a linearly polarized beam,³

$$P_{cr} = 5.763\lambda^2 c / 16\pi^3 n_2; \quad (14)$$

a is the radius of the beam; and f is a parameter introduced to account for deviations of the beam from an equiphase Gaussian intensity profile, $f=1$ for such a Gaussian beam.

Equations (12) and (13) are derived for linearly polarized beams only; they have been verified experimentally by direct observation of the evolution of beam trapping,¹⁶ and by analyzing the length-dependent threshold data¹⁵ for stimulated Raman emission. According to these equations, the plot of $P^{1/2}$ versus $1/l$ for various materials should yield straight lines, and the critical power for self-trapping should be obtainable from the vertical intercept of these straight lines. The results thus obtained are in gross agreement with the values of critical power in Eq. (14) calculated from the optical Kerr constants¹⁷ for a number of liquids. The effect of one- and two-photon absorption has been considered, and also found to be in agreement with the experiments.¹⁸

Despite the general agreement noted above for the self-focusing effect of a laser beam, many aspects of this effect remain to be explained. In their direct observation of beam trapping, Garmire *et al.*¹⁶ have observed the presence of what may be called small-scale trapping superimposed upon large-scale trapping. The former appears in the form of a multiplicity of small high-intensity filaments, whereas for the latter the entire beam is trapped as a unit. Both types of trapping appear to have the same threshold, but exhibit different dynamic properties as a function of the incident laser power. It is not at all understood why the beam does not focus as a unit, and which factors determine the final size of these high-intensity filaments. The state of polarization of the filaments has been studied by McClung¹⁹ and co-workers; with the input laser beam approximately circularly polarized, the filaments were found to be linearly polarized, but with random orientation. It is possible that this depolarization effect results from the difficulty in obtaining and maintaining

a perfectly circularly polarized beam, and from the difference between the index changes for the two senses of circular polarization. Note however that the theoretical treatment to date has dealt primarily with the steady-state solutions for linearly and circularly polarized beams. The transient behavior associated with a linearly polarized beam has been discussed very recently by Brueckner and Jorna²⁰; but no work on the general case of elliptical polarization has been reported. The interpretation of the polarization data on self-focusing thus remains an open question.

IV. DETERMINATION OF THE NONLINEAR SUSCEPTIBILITY CONSTANTS

To determine the three susceptibility constants defined in the earlier section, a set of three independent measurements are required. Since these measurements are necessarily to be made with light beams of finite cross section, they may be obscured by the self-focusing effect of the laser beam. It will be assumed in the following that measurements can be made at intensity levels high enough for the medium to exhibit the nonlinear effect under study, and at the same time well below the threshold for self-focusing so that the beam emerges from the nonlinear medium without appreciable changes in its intensity distribution.

It follows from Eq. (8) that a measurement of intensity-induced rotation yields the sign and magnitude of the susceptibility constant $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$. A measurement of the optical Kerr effect and its frequency dependence will give determination of the linear combination

$$[\chi_3^{1212}(-\omega, \omega, \omega, -\omega) + \chi_3^{1221}(-\omega, \omega, \omega, -\omega)].$$

Thus separate determination of both constants

$$\chi_3^{1212}(-\omega, \omega, \omega, -\omega) \quad \text{and} \quad \chi_3^{1221}(-\omega, \omega, \omega, -\omega)$$

is possible by correlating these two measurements.

The above measurements involve the relative slowing of one polarization component with respect to another. An apparent way of determining $\chi_3^{1122}(-\omega, \omega, \omega, -\omega)$ is to measure the absolute slowing of the light beam as a function of its own intensity. This measurement can in principle be performed with conventional interferometer techniques, but may actually be quite difficult because of the lack of a reference-beam traversing the same path in the nonlinear medium. To avoid beam distortion due to self-focusing, one must work at a power level well below the threshold for self-focusing. This implies that the shift will be much less than one fringe; no measurement of the kind has been reported.

An alternative but less satisfactory way of determining $\chi_3^{1122}(-\omega, \omega, \omega, -\omega)$ is to measure the threshold for self-focusing. Physically, this follows from the fact that self-focusing action results from the *relative*

¹⁵ C. C. Wang, Phys. Rev. Letters **14**, 344 (1966).

¹⁶ E. Garmire, R. Y. Chiao, and C. H. Townes, Phys. Rev. Letters **16**, 347 (1966).

¹⁷ G. Mayer and F. Gires, Compt. Rend. **258**, 2039 (1964); M. Paillette, *ibid.* **242**, 264 (1966).

¹⁸ C. C. Wang and G. W. Racette, Appl. Phys. Letters **8**, 256 (1966).

¹⁹ F. J. McClung, in Proceedings of the 1966 International Quantum Electronics Conference, Phoenix, Arizona, 1966 (unpublished). IEEE J. Quant. Electron. **QE2**, Nos. 8, 9 (1966).

²⁰ K. A. Brueckner and S. Jorna, Phys. Rev. Letters **17**, 78 (1966).

slowing induced by the nonuniform intensity distribution over the beam cross section. However, the values of $\chi_3^{122}(-\omega, \omega, \omega, -\omega)$ thus obtained may be quite uncertain because of the uncertainties that exist in the present understanding of the self-focusing action.

In addition to the above difficulties, measurements of nonlinear optical effects have always been complicated by the unknown spatial and temporal variations in the intensity of the laser beam. It has been observed that¹³ the presence of multiple temporal modes enhances the nonlinear index changes. When the total laser intensity is distributed over a number of statistically independent temporal modes, it can be shown that the nonlinear index changes are enhanced by a factor which approaches 2 as the number of such modes increases. This multimode effect is similar to that observed in the second-harmonic-generation experiments.²¹

V. ANALYSIS OF A SIMPLIFIED PHYSICAL MODEL

The nonlinear index changes in liquids have been discussed in terms of a simplified physical model,²² which assumes a system of noninteracting molecules. According to this model, the index changes may be due to reorientation of molecules with anisotropic polarizabilities; due to the nonlinear electronic polarizability arising from the distortion of the electron cloud in the molecules; and due to electrostriction giving rise to macroscopic density changes in the medium. This description is appropriate for dilute gaseous systems, in which interaction of molecules can be neglected; but it may often be a poor approximation for liquids, as in the liquid state molecules are usually distorted and may form structures,²³ thus exhibiting behavior different from isolated molecules.²⁴

It has been observed^{14,25} that molecular reorientation is the dominant mechanism in determining the intensity-dependent index changes in liquids. Measurements of the optical Kerr effect¹⁷ indicate that the susceptibility constants in Eq. (5) are of the order of 10^{-13} to 10^{-12} esu in liquids with anisotropic molecules, whereas they are the order of 10^{-15} esu or less in gases composed of molecules with isotropic polarizabilities. In liquid CCl_4 , whose molecules have the symmetrical tetrahedral structure and thus isotropic polarizabilities in the gaseous state, the observed susceptibility constants are of the order of 10^{-14} esu; it is believed that this effect results from the distortion of molecules due to molecular interactions in liquids.

²¹ A. Ashkin, G. D. Boyd, and J. M. Dziedzic, *Phys. Rev. Letters* **11**, 14 (1963).

²² Ya. B. Zel'dovich and Yu. P. Raizer, *JETP Pis'ma Redaktsiyu* **3**, 137 (1966) [English transl.: *Soviet Phys.—JETP Letters* **3**, 86 (1966)].

²³ J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), p. 302.

²⁴ A. D. Buckingham and M. J. Stephen, *Trans. Faraday Soc.* **53**, 884 (1957).

²⁵ Y. R. Shen, *Phys. Letters* **20**, 378 (1966).

In liquids with nonpolar molecules, the model of molecular reorientation predicts that both the optical and static Kerr effects arise from the alignment of anisotropic polarizabilities; as a result, they are approximately equal in these liquids. In dipolar liquids, the static Kerr effect may also be due to interaction with the permanent electric-dipole moments; but the optical Kerr effect does not. This is because the torque exerted on the permanent electric-dipole moments by the optical fields varies at the optical frequency, and so cannot be coupled to the much slower molecular motion. It follows that the static Kerr effect may be much larger than the optical Kerr effect in dipolar liquids.

The electrostrictive effect is characterized by a relatively long time constant, as it propagates at the sound velocity ($\sim 10^5$ cm/sec). In liquids, the electrostrictive contribution is estimated to be of the order of 10^{-13} esu in the steady state³; but its effectiveness may be reduced significantly because of the short durations typical of *Q*-switched pulse lasers.²⁴ In the normal dispersion range, the electronic contribution to the components of χ_3 should be comparable to those giving rise to third-harmonic generation⁶; it is of the order of 10^{-15} esu, and thus can be neglected in the following discussion.

A. Reduction to Two Susceptibility Constants

Almost all models for Raman and Rayleigh type scattering processes involve the assumption that these processes are describable in terms of real symmetric polarizability tensors. These same processes are associated with the intensity-dependent indices of refraction. It follows from this assumption that the tensor $\delta\chi_1^{ij}(-\omega_1, \omega_1)$ in Eq. (3) is symmetric in its indices *i, j*. Thus

$$\chi_3^{1212}(-\omega_1, \omega_1, \omega_2, -\omega_2) = \chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2),$$

leaving $\chi_3^{1222}(-\omega_1, \omega_1, \omega_2, -\omega_2)$ to be the only other independent component of $\chi_3(-\omega_1, \omega_1, \omega_2, -\omega_2)$. Except when noted to the contrary, this equality will be assumed throughout this paper.

To determine this reduced set of two susceptibility constants, one notes that a measurement of intensity-induced rotation still yields the value of $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$. But a measurement of the optical Kerr effect is now redundant and can thus be dispensed with. As before, a measurement of the absolute slowing of the light beam, or a measurement of the threshold for self-focusing will then give determination of $\chi_3^{1222}(-\omega, \omega, \omega, -\omega)$.

B. Molecular Reorientation and Reduction to One Susceptibility Constant

With the assumption that $\chi_3^{1212}(-\omega, \omega, \omega, -\omega) = \chi_3^{1221}(-\omega, \omega, \omega, -\omega)$ the ratio of the refractive

index changes in Eq. (11) is simplified to

$$\frac{\delta n_{11}}{\delta n_{\pm}} = 1 + \frac{\chi_3^{1221}(-\omega, \omega, \omega, -\omega)}{\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + \chi_3^{1221}(-\omega, \omega, \omega, -\omega)}. \quad (15)$$

If the index changes are due to molecular reorientation only, it can be shown²² that this ratio of the refractive index changes should be 4, and the corresponding ratio of $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$ should be 3 for all liquids. On the other hand, if the index changes are due to electrostriction only, the ratio of the refractive index changes should be unity so that $\chi_3^{1221}(-\omega, \omega, \omega, -\omega) = 0$ and $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221}) = 0$. In either case, it follows that the number of independent susceptibility constants is reduced to one.

With a dc or low-frequency field applied, it has been found in a number of liquids that, when the electrostrictive contribution is suppressed, the ratio $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$ is close to 3, but with deviations outside the experimental error.²⁶ This indicates that the simple model of molecular reorientation is approximately valid for $\chi_3(-\omega, \omega, 0, 0)$. One expects that this simple model should also be approximately valid for $\chi_3(-\omega, \omega, \omega, -\omega)$ in liquids; however, no experimental work on the ratio $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$ for $\chi_3(-\omega, \omega, \omega, -\omega)$ has been reported.

In terms of the simple model of molecular reorientation, the effect of finite relaxation times has been considered by Bloembergen and Lallemand.²⁷ These authors derived the following expression for the frequency dependence of the susceptibility constants in Eq. (2):

$$F = \frac{1}{2} \left[1 + \frac{1}{1 - i(\omega_1 - \omega_2)\tau} \right], \quad (16)$$

where τ is the relaxation time for molecular reorientation ($\sim 10^{-11}$ sec). Here the first term arises from the dc change in the refractive index, and the second term from modulation of the index at the difference frequency, $|\omega_1 - \omega_2|$, in the medium. The latter term is important only when the response of the medium is faster than the difference frequency. Thus when $|\omega_1 - \omega_2| \ll 1/\tau$, $F = 1$ and the corresponding susceptibility constants in Eqs. (2) and (6) are equal. But when $|\omega_1 - \omega_2| \gg 1/\tau$, $F = \frac{1}{2}$ and the corresponding susceptibility constants differ by a factor $\frac{1}{2}$.

In the measurements of optical Kerr constants¹⁷ to be discussed in Sec. VII, the two frequencies are in the optical region with the difference frequency much larger than the inverse of the relaxation time for molecular reorientation. This model then predicts that $\chi_3^{1221}(-\omega_1, \omega_1, \omega_1, -\omega_1) = 2\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)$.

²⁶ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 7, p. 109.

²⁷ N. Bloembergen and P. Lallemand, *Phys. Rev. Letters* **16**, 81 (1966).

Independently of the sharp dispersion described in Eq. (16), the susceptibility constant $\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)$ is also expected to show small dispersion due to electronic resonances. This part of the frequency dependence is comparable to that of the susceptibility constant $\chi_3^{1221}(-\omega_1, \omega_1, 0, 0)$.

VI. EXPERIMENTS

The experiments were performed with the unfocused output near 6940 Å from a Q-switched ruby laser. The laser beam provided a peak power of 2 MW and was found to contain two nearly diffraction-limited spots approximately equal in intensity and each about (0.1 ± 0.02) cm in diameter. Usually, this laser radiation was emitted in a single sharp line less than 0.02 cm^{-1} in width; but on occasions a second line with less than 20% relative intensity and displaced 0.45 cm^{-1} from the first was also observed.

In the measurements of intensity-induced rotation of the polarization ellipse, the experimental arrangement was very much similar to that described in Ref. 5 with the exception that an unfocused rather than a focused beam was used. It was observed that the amount of induced rotation was linearly proportional to the laser intensity at low intensities, but began to level off as the threshold for self-focusing was reached. Only data taken in the linear range were used to deduce the susceptibility constants.

In the measurements of self-focusing threshold both for circularly and for linearly polarized beams, the corresponding threshold for stimulated Raman emission was taken as the threshold for self-focusing.¹⁵ Photographic observations indicated that more than half of the beam appeared trapped as the threshold was exceeded. The circular polarization was obtained through use of mica quarter-wave plate properly oriented with the aid of a gas laser. The quarter-wave plate was believed to be sufficiently accurate so that the counter-rotating circular component was down to about 1% in relative intensity. Experiments with another quarter-wave plate which converted about 95% of the total intensity into one circular component and the rest into the other gave the same threshold results within experimental accuracy.

The intensity profile of the laser beam used has been studied experimentally, and an appropriate average was taken to relate the intensity to the measured power of the laser beam. For the measurements reported in this paper, the over-all accuracy of the measured values is believed to be $\pm 25\%$ relative to each other, and $\pm 50\%$ on an absolute basis.

VII. RESULTS AND DISCUSSIONS

The values of $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$ in several Raman-active liquids have been derived from measurement of intensity-induced rotation of the polarization ellipse, and are tabulated in Table I. They are found to be

TABLE I. Measured values of the nonlinear susceptibility constants in several Raman-active liquids. The results are expressed in esu. For a discussion of other units, see R. W. Minck, R. W. Terhune, and C. C. Wang, Proc. IEEE 54, 1357 (1966).

Liquid	Rotary-power measurements ^a $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$ (10^{-14} cm ³ /erg)	Self-focusing measurements ^{b, c} $[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + 2\chi_3^{1221}(-\omega, \omega, \omega, -\omega)]$ (10^{-14} cm ³ /erg)	$\chi_3^{1221}(-\omega, \omega, \omega, -\omega)^{c, d}$		Kerr-Effect measurements ^{e, f} $2\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)$ (10^{-14} cm ³ /erg)
			$\chi_3^{1122}(-\omega, \omega, \omega, -\omega)$	$\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$	
CS ₂	34	47		2.6	38
Nitrobenzene	23	31		2.9	26
Toluene	8	11		2.7	9
Benzene	6.5	9		2.6	4
CCl ₄	0.9	1.2		3.0	0.5

^a $\lambda(\omega) = 6940 \text{ \AA}$.

^b Deduced from the critical power P_{cr} for self-trapping with a linearly polarized beam. With $\lambda(\omega) = 6940 \text{ \AA}$, $P_{cr} = 15, 22, 57, 76,$ and 600 kW for CS₂, nitrobenzene, toluene, benzene, and CCl₄.

^c The equality $\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2) = \chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2)$ has been assumed in this table.

^d Deduced from columns (a) and (b).

^e Deduced from measurements of optical Kerr constants in Ref. 17; $\lambda(\omega_1) = 4880 \text{ \AA}$ and $\lambda(\omega_2) = 6940 \text{ \AA}$.

about ten times higher than the values obtained by Maker *et al.*⁵ Note, however, that their relative values for CS₂ and CCl₄ are in excellent agreement with ours. It is possible that the apparent discrepancy arises from the uncertainties associated with the focused beam used in their experiments.²⁸ Also included in Table I are the values of $[\chi_3^{1122}(-\omega, \omega, \omega, -\omega) + 2\chi_3^{1221}(-\omega, \omega, \omega, -\omega)]$ deduced from the critical power for self-trapping with a linearly polarized beam. The values for the ratio $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$ are then obtained from the above two sets of measurements, and are found to be close to 3 for all liquids.

As has been noted earlier, the model of molecular re-orientation predicts that the ratio $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$ is 3. However, considering all the uncertainties involved in deducing this ratio from our experiments, it is surprising that this ratio came out to be close to 3 in all liquids. Thus it appears that the self-focusing formulas in Eqs. (12)–(14) for linearly polarized beams are in good agreement with the experiments; but the agreement may be in part due to compensation among the various sources of error discussed in the previous sections.

The last column in Table I lists the values of $[\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2) + \chi_3^{1122}(-\omega_1, \omega_1, \omega_2, -\omega_2)]$ deduced in accordance with Eq. (5) from the data of Mayer *et al.*¹⁷ on optical Kerr constants. With

$$\chi_3^{1221}(-\omega_1, \omega_1, \omega_2, -\omega_2) = \chi_3^{1122}(-\omega_1, \omega_1, \omega_2, -\omega_2),$$

the measurements of optical Kerr constants can be used as a cross check on our measurements of intensity-induced rotation. The dispersion of these optical Kerr constants was not available from these authors, but should be comparable to the dispersion of $\chi_3^{1221}(-\omega, \omega, 0, 0)$, which they found to vary from a few percent in benzene and toluene to as much as 25% in CCl₄ over the range $\omega_2 \leq \omega \leq \omega_1$ used in their exper-

²⁸ Very recently, the intensity-induced rotation associated with an unfocused laser beam was also reported by McWane and Sealer, Appl. Phys. Letters 8, 278 (1966). Of the five Raman-active liquids listed in Table I in the present paper, only CS₂ was investigated by these authors. For CS₂, the value of $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$ deduced from their result is about twice the value reported in this paper; however, their threshold value is about five times higher than other published results in Refs. 16 and 18.

iments.²⁹ When correction is made for dispersion, the values of these coefficients for CS₂, nitrobenzene, and toluene are found in good agreement with our corresponding values of $\chi_3^{1221}(-\omega, \omega, \omega, -\omega)$ deduced from measurements of intensity-induced rotation. For benzene and CCl₄, however, the two values disagree. We have also observed that out threshold data in benzene are likewise different from theirs.¹³ We have been unable to explain this discrepancy.

Figure 1 shows the threshold data for CS₂ with both linearly and circularly polarized beams. Similar threshold data were also obtained for nitrobenzene, toluene, and benzene. One observes that the linear relation in Eq. (12) is satisfied for both linearly and

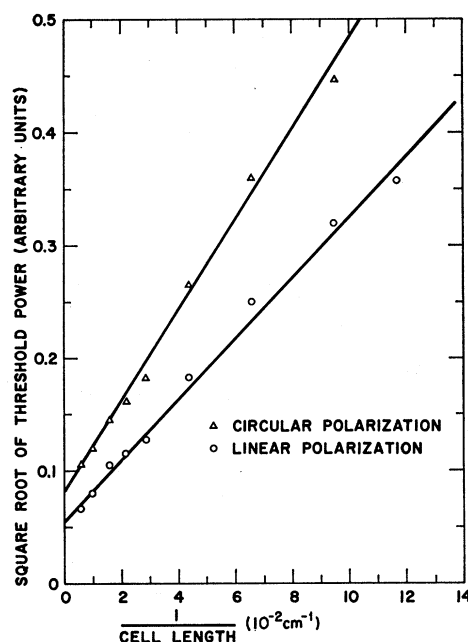


FIG. 1. Plot of the square root of the threshold power for self-focusing in CS₂ as a function of the inverse of the cell length with both linearly and circularly polarized beams.

²⁹ The large dispersion in CCl₄ according to these authors disagrees with the tabulated result in Landolt-Börnstein (Springer-Verlag, Berlin, 1962), Vol. II-8, p. 5-859. The latter indicates a dispersion of only a few percent.

circularly polarized beams. The ratio of the slopes of these two straight lines was found to be about the same as the corresponding ratio of the vertical intercepts of these lines. The threshold ratios between circularly and linearly polarized beams were determined from the vertical intercept of these lines, and were found to be, respectively, 2.00, 1.66, 1.60, and 1.50 for CS₂, nitrobenzene, toluene, and benzene. For CCl₄, our maximum available laser power was insufficient to permit similar measurements with a circularly polarized beam.

It has been suggested²² that the above threshold ratios should be identified with the corresponding ratios of the index changes in Eq. (11). It then follows that the observed threshold ratios of 2.0 to 1.5 would correspond to a range of values from 1.0 to 0.5 for the ratio $\chi_3^{1221}/(\chi_3^{1122} + \chi_3^{1221})$. These are the ratios which we determined in Table I to be close to 3. Thus it appears that discrepancy exists between the results

deduced from the observed ratios of self-focusing threshold, and the results deduced jointly from measurements of intensity-induced rotation and measurements of self-focusing threshold for a linearly polarized beam. However, we feel that the results deduced from measurements of intensity-induced rotation and measurements of self-focusing threshold with a linearly polarized beam are probably correct. Since uncertainties exist both in theory and in experiment for the self-focusing effect of a circularly polarized beam, it is not clear if the ratio of self-focusing threshold is to be identified with the corresponding ratio of the index changes.

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Effect of Molecular Redistribution on the Nonlinear Refractive Index of Liquids*

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An expression for the static nonlinear dielectric constant of a nonpolar liquid is derived which takes into account the reorientation and local spatial redistribution of molecules in the presence of a strong electric field. This result is used to calculate the nonlinear index of refraction of various lossless liquids at "optical" frequencies which are much higher than molecular reorientation rates. From this nonlinear index, we obtain estimates of the optical power required to initiate self-focusing in a liquid over periods so short that macroscopic density changes do not have time to take place. This situation is commonly approached in experiment. The theory predicts that the effects of molecular redistribution, hitherto not considered, will be generally as important as the widely considered effects of molecular reorientation, and will in fact dominate the nonlinear index of many symmetric and nearly symmetric molecules. Furthermore, the results suggest that some purely symmetric molecules, such as SiBr₄, may exhibit self-focusing in liquid as readily as do some commonly studied asymmetric molecules, such as nitrobenzene. The calculation proceeds from classical statistical mechanics with the aid of a variational principle that is valid for arbitrary density. In the low-density limit our results reflect only molecular reorientation and reduce to those of Debye and others. The accuracy of the results depends mainly on the accuracy of Kirkwood's "superposition approximation" in representing three- and four-particle correlation functions in liquids. Since the accuracy of this approximation is at present unknown, nonlinear index data may prove useful in checking it. As a by-product of our investigation, we have proven that the Clausius-Mossotti expression gives a lower bound for the dielectric constant of a fluid in which the two-particle correlation function is a function only of the interparticle spacing and approaches a constant at large spacing. Molecular redistribution must also play a role in induced birefringence (ac and dc Kerr effects), especially for symmetric molecules. However, the present treatment is limited to waves of a single linear polarization, and does not cover the Kerr effect.

I. INTRODUCTION

THE self-focusing of optical beams and the effects of this self-focusing on stimulated Raman scattering and other nonlinear effects have been studied in a variety of liquids.¹⁻⁶ The nonlinear index of re-

fraction which causes self-focusing has been attributed to electrostrictive effects and to the reorientation of asymmetric molecules (ac Kerr effect) in the strong optical fields; the electronic nonlinearities are presumed

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