E-2—Molecular Interactions in Optically Induced Nonlinearities

STANISŁAW KIELICH

Abstract—This is a review of the more important theoretical and experimental results or intensity-dependent refractive index in relation to self-focusing and nonlinear scattering of light in liquids. The part played within the framework of the molecular-statistical theory of these processes by radial and angular molecular correlations, molecular redistribution, various nonlinear polarizations induced by fluctuations of electric fields of neighboring molecular multipoles, and geometrical shape of the molecules, is discussed. Numerical evaluations of the various contributions are given and compared with the available experimental data. It is found that while investigation of optically induced nonlinearities in gases and rarefied substances yields only values of linear and nonlinear optical polarizabilities of atoms or molecules, work on condensed systems yields information on the values of molecular quadrupoles and octupoles as well as on the functions accounting for molecular correlations of various kinds.

The author is with the Department of Molecular Physics, A. Mickiewicz University, Poznań, Grunwaldzka 6, Poland.
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I. INTRODUCTION

TEN years ago linear molecular optics [1] appeared to represent a closed domain. Since then, owing to the rapid progress in laser techniques, this domain has undergone vast developments to a truly unprecedented extent, giving rise to nonlinear molecular optics [2]. While classical optics provided information relating only to the linear optical properties of atoms and molecules, the presently studied interactions between matter and the immensely intense optical fields of laser beams provide valuable data on their nonlinear properties. But the importance of this rapidly developing nonlinear optics is by no means restricted to the novel approach it provides to the electromagnetic properties of isolated atoms and molecules. Essentially, its value resides in the information it provides on their mutual interactions and thus on the molecular structure of matter. These structural

properties become clearly apparent in a number of new and highly remarkable effects such as the self-focusing and self-trapping of intense laser beams [3]-[6] and stimulated Rayleigh, Raman, and Brillouin scattering [6]-[8]. These and various other new effects can be said to depend fundamentally on at least two incontrovertible facts, which are considered in this paper: nonlinear changes in a light refractive index, and nonlinear light scattering processes caused in media by intense laser beams.

A. Nonlinear Refractive Index

The quadratic Kerr effect, which consists of the induction of optical birefringence in a naturally isotropic medium by a strong dc electric field, was explained classically by Voigt and Langevin [1] and has been known for almost a century. Several years before the coming of lasers, Buckingham [9] suggested that optical birefringence could also be induced in an isotropic medium by an intense light beam and would then depend on the light intensity I. The experiment, which can be referred to as the optical Kerr effect, was first performed by Mayer and Gires [10], who employed the laser technique. Paillette [11] carried out measurements in several liquids. This early work confirmed essentially that the primary function was a process of reorientation of anisotropic molecules (Langevin's effect) in the optical field of the light wave, and that molecular correlations of various kinds also contribute [12]. The contribution of third order nonlinear electronic polarizability (Voigt's effect) is generally small [6] and plays a part only in atomic substances or substances composed of molecules that are weakly anisotropic optically [9], [12].

Moreover, the dependence of the refractive index on the light intensity was made apparent experimentally by Maker et al. [13] in measurements of the rotation of the polarization ellipse of light. This intensity-induced rotation was studied recently in more detail by several authors [14]-[16].

A theoretical analysis of a nonlinear refractive index in liquids in relation to self-focusing is due to Hellwarth [17] and Takatsuji [18] who, besides molecular reorientation, took into account molecular redistribution, which is of great importance in substances composed of isotropic molecules [12], [19]. Changes in the refractive index can also be caused by electrostriction [20], [21] and the electrocaloric effect [12]. However, these essentially thermodynamical effects exhibit delay with respect to the optical Kerr effect, and their contribution can be eliminated [6], [14]. The only remaining problem is that of the contribution from nonlinear electronic polarizability. This might be determined, for example, from measurements in the gaseous phase, as has been shown for simple gases [22], [23] or from studies of temperature dependence.

The frequency- and intensity-dependent complex index of refraction in fluids with anisotropic molecules has been discussed by Bloembergen and Lallemand [24] (see also [25]) in relation to stimulated scattering processes, as well as by Herman [26], who analyzed saturation effects in stimulated Rayleigh and Raman scattering.

While self-focusing can be satisfactorily explained by the optical Kerr effect alone [3], [6], [17], the formation of filaments arising from self-trapping of an intense light beam in liquids necessarily involves still other factors. Some new light has recently been shed on this problem, in particular on small-scale trapping, by Shen et al. [27], who consider the role of field-induced phase transitions (see also [28], [29]), by Brewer et al. [30], who considered optical saturation, and by Lugovoy and Prokhorov [31]. Quite recently, Rivoire and Beaudoin [32] showed that these phenomena depend to a large extent on effects of molecular interaction inherent in the optical Kerr effect [12].

B. Nonlinear Light Scattering

In addition to nonlinear refractive index studies, work on the nonlinear scattering of light occurring when a medium is illuminated with an intense laser beam becomes important. Here, the scattered intensity I_S becomes a nonlinear function of the incident intensity I [33]:

$$I_S = S_1 I + S_2 I^2 + S_3 I^3 + \cdots,$$

where the constant S_1 defines the usual (linear) Rayleigh scattering at frequency ω previously much investigated in gases and liquids [1], [34]. The constant S_2 defines nonlinear scattering of the second order, which consists of a first harmonic part due to reorientation of the molecules [33] and of a second harmonic part due to nonlinear polarizability of the second order [35], [36]. The constant S_3 accounts for, among others, third harmonic scattering [37].

Terhune et al. [38], applying laser technique, performed an ingenious experiment making apparent second harmonic light scattering by liquids. Also, Maker [39] succeeded in observing such scattering by compressed methane. Their experiments in conjunction with theoretical considerations [35], [37] showed second harmonic scattering to be highly sensitive to molecular symmetries thus, e.g., to the presence or absence of a center of inversion, whereas linear scattering is almost totally insensitive with respect to this element of symmetry. This led Cyvin et al. [40] to carry out a full discussion of hyperscattering by isolated molecules for all point groups.

In a dense medium, second harmonic scattering is largely dependent on molecular correlations [33]. Bersohn et al. [41], in their recent discussion of the problem, resolved the scattered light intensity into an incoherent, partly due to the individual molecules, and into a coherent, partly due to cooperative scattering of neighboring molecules whose positions and orientations are correlated. Recent detailed studies of the problem by Weinberg [42] and this author [43] for dense media resulted in a considerable role assigned to the electric fields of molecular multipoles, which can cause second harmonic scattering even in liquids with molecules having a center of inversion

[43]. Quite generally, the theory of second harmonic elastic scattering, including angular dependence, can be formulated both in a phenomenological [44] and in a semimacroscopic approach [33], [43].

Lajzerowicz [45] and recently Freund [46] reported observations of second harmonic scattering by angular fluctuations in a system in the immediate vicinity of a critical point, thus opening the domain of critical harmonic scattering of light.

Besides the above-mentioned effects of elastic harmonic scattering, nonelastic scattering effects of the Raman type can be investigated [38], in which, in general, n photons of frequency ω are incident on the molecule. The latter, on making a transition from quantum state k to l at frequency ω_{kl} then scatters a photon of frequency $\omega_n = n\omega \pm \omega_{kl}$. Such processes have to be dealt with by quantum-mechanical methods [35]–[37], [47]. Investigation of these nonelastic scattering processes lays the foundations of a new nonlinear Raman spectroscopy, permitting closer insight into the finer details of molecular structure than was previously possible by linear Raman spectroscopy [48].

In this paper, we shall discuss the molecular statistical aspects of induced nonlinearities within the framework of a uniform theory, taking into account various radial and angular molecular correlations, molecular redistribution processes, and nonlinear polarizabilities induced by the electric fields of molecular multipoles. Particular attention will be given to the fact that molecular correlations not only modify significantly the considered effects on transition from the rarefied to the dense phase, but in some cases are the sole source of such effects. For the sake of simplicity, we shall restrict our considerations to dense isotropic optically transparent media in the absence of dispersion and absorption.

II. Intensity-Dependent Refractive Index of Liquids

A. General Theory

We consider a dense homogeneous medium of volume V, isotropic in the absence of external fields. When acted on by the electric field $E(t)$ of a light wave of high intensity, the medium becomes optically anisotropic and nonlinear, and the change in its optical permittivity tensor is given by [19]

$$n_{\sigma\tau} - n\,\delta_{\sigma\tau} = \{n_2^{i*}\,\delta_{\sigma\tau}\,\delta_{\nu\rho} + \lambda B_\lambda(\delta_{\sigma\nu}\,\delta_{\tau\rho} - \tfrac{1}{3}\delta_{\sigma\tau}\,\delta_{\nu\rho})\}\overline{E_\nu E_\rho} \tag{1}$$

where n stands for the intensity-independent part of the refractive index for wavelength λ, and the bar for a time average over many cycles of the macroscopic electric field $E(t)$.

The quantity n_2^{i*} accounts for nonlinear changes of the isotropic kind in the tensor $n_{\sigma\tau}$ due to electrostriction and third order nonlinearity. The optical Kerr effect constant B_λ, which accounts for anisotropic changes in

the tensor $n_{\sigma\tau}$ is of the form

$$B_\lambda = \frac{3}{2n\lambda}\left(\frac{n^2 + 2}{3}\right)^4 B \tag{2}$$

where B consists in general of a part B_{NL} resulting from nonlinear polarizability of the molecules and a part B_R resulting by molecular reorientation. As to the part with B_{NL}, we shall refrain from considering it here since it depends but slightly on the molecular correlations. We rather shall concentrate on the constant B_R, which in general is given by [19]

$$B_R = \frac{2\pi}{45kTV}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N}\left(3\frac{\partial m_\alpha^{(p)}}{\partial E_\beta}\frac{\partial m_\alpha^{(q)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha}\frac{\partial m_\beta^{(q)}}{\partial E_\beta}\right)\right\rangle \tag{3}$$

with $\mathbf{m}^{(p)}$ denoting the dipole moment induced by the electric field in the pth molecule of the medium, and the brackets denoting a statistical average in the absence of external fields when the system is at thermodynamical equilibrium at temperature T.

Once we chose the Y-axis as direction of propagation of the linearly polarized light beam, with electric vector $\mathbf{E}$ oscillating in the Z direction ($E_X = E_Y = 0$), (1) leads to the following expressions for the changes in refractive index in the two directions perpendicular to the beam:

$$n_{XX} - n = (n_2^{i*} - \tfrac{1}{3}\lambda B_\lambda)\overline{E_Z^2} \tag{4}$$

$$n_{ZZ} - n = (n_2^{i*} + \tfrac{2}{3}\lambda B_\lambda)\overline{E_Z^2}. \tag{5}$$

Note that the Kerr constant B_λ increases the value of n_{ZZ} but simultaneously decreases that of n_{XX}, and that the variation $n_{XX} - n$ can be negative if $n_2^{i*} < \lambda B_\lambda$, as is the case in liquids like CS_2 or $C_6H_5NO_2$ [20], [21]. This circumstance can be expected to affect the self-focusing and self-trapping of beams in such liquids, where by (4) and (5) it can result in a noncircular cross section of the autocollimation filament.

Obviously, on considering (4) and (5), the optical birefringence induced in the medium

$$n_{ZZ} - n_{XX} = \lambda B_\lambda \overline{E_Z^2} \tag{6}$$

does not depend on the electrostrictive effect contained in the contribution of n_2^{i*}.

The ratio of absolute changes in refractive index

$$\frac{n_{ZZ} - n}{n_{XX} - n} = \frac{3n_2^{i*} + 2\lambda B_\lambda}{3n_2^{i*} - \lambda B_\lambda} \tag{7}$$

depends simultaneously, in general, on n_2^{i*} and B_λ. On neglecting the effects of electrostriction and nonlinear polarizability ($n_2^{i*} = 0$), the ratio of (7) takes the value -2 in accordance with Langevin's theory of molecular orientation.

B. Angular Molecular Correlations

Proceeding to discuss the optical Kerr constant in the form (3), we shall first consider the simplest molecular statistical model where the linear polarizabilities of the molecules given by the tensor $\alpha_{\alpha\beta}$ remain unaffected by

interactions. In this 0th approximation we have

$$m_\alpha^{(p)} = \alpha_{\alpha\beta}^{(p)} E_\beta \qquad (8)$$

and the constant (3) can be split into a part [9]

$$B_R^{(0)} = \frac{2\pi\rho}{45kT} \{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\} \qquad (9)$$

describing the system (of number density $\rho = N/V$) in the absence of all correlations, when the molecules have principal polarizabilities α_1, α_2, α_3, and a part [9], [12]

$$B_R^{(A)} = \frac{2\pi\rho^2}{45kTV} \sum_{s,t=1}^{3} \alpha_s \alpha_t$$

$$\cdot \iint (3 \cos^2 \theta_{st}^{(pq)} - 1) g^{(2)}(\tau_p, \tau_q) \, d\tau_p \, d\tau_q \qquad (10)$$

describing the system with pairwise correlations taken into account by way of the binary distribution function $g^{(2)}(\tau_p, \tau_q)$ of a pair of molecules p, q at configurations τ_p, τ_q, with principal axes s, t subtending an angle $\theta_{st}^{(pq)}$.

Assuming molecules p and q to have orientations ω_p, ω_q and to be at mutual distance r_{pq}, we can write in a satisfactory approximation [49]:

$$g^{(2)}(\tau_p, \tau_q) = g(r_{pq}) \exp\left\{-\frac{w(r_{pq}, \omega_p, \omega_q)}{kT}\right\}, \qquad (11)$$

where $g(r_{pq})$ is the well-known radial distribution function and $w(r_{pq}, \omega_p, \omega_q)$ the potential energy of orientational interaction of molecules p and q. By using (11), we are able to calculate the contribution from the angular correlations (10) for various molecular correlations of the dispersional, inductional, and orientational kinds [12], [49]. In particular one notes that if the distribution function (11) is independent of angular correlations, the contribution (10) vanishes.

C. Molecular Redistribution.

With increasing condensation of the medium, the dipole moments (8) induced in the molecules cease to have the same constant value in every phase of thermal motion, and the statistical translational fluctuations [50], [51] related to this fact cause the molecules to have the following effective polarizabilities [12], [49]:

$$\frac{\partial m_\alpha^{(p)}}{\partial E_\beta} = \alpha_{\alpha\beta}^{(p)} - \sum_{q=1}^{N} \alpha_{\alpha\gamma}^{(p)} T_{\gamma\delta}^{(pq)} \alpha_{\delta\beta}^{(q)}$$

$$+ \sum_{q=1}^{N} \sum_{r=1}^{N} \alpha_{\alpha\gamma}^{(p)} T_{\gamma\delta}^{(pr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rq)} \alpha_{\eta\beta}^{(q)} - \cdots, \qquad (12)$$

where the tensor of dipole–dipole interaction is given by

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5}(3r_{pq\alpha}r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}), \qquad p \neq q.$$

On inserting the full expansion (12) into (3), we get by unweighted averaging over all possible orientations of the axially symmetric molecules (terms linear in the interaction tensor $T_{\alpha\beta}$ vanish, and the lowest approximation yielding nonzero terms is that of the second order):

$$B_R^{(2)} = \frac{8\pi\rho}{45kT} \left\{ \left(9\alpha^4 + \frac{28}{5}\alpha^2\delta^2 + \frac{2}{3}\alpha\delta^3 + \frac{67}{225}\delta^4\right) R_6^{(2)} \right.$$

$$\left. + 9\alpha^2\left(\alpha^2 + \frac{14}{45}\delta^2\right) R_6^{(3)} \right\} \qquad (13)$$

with $\delta = (2\alpha_3 - \alpha_1 - \alpha_2)/2$ denoting the anisotropy of the molecule and $R_6^{(2)}$ a parameter of paired radial correlations ($n = 6$) [49]:

$$R_n^{(2)} = \rho \int r_{pq}^{-n} g(r_{pq}) \, d\mathbf{r}_{pq} \qquad (14)$$

while the parameter of triple (three-molecule) radial correlations is of the form

$$R_6^{(3)} = \frac{\rho^2}{V} \iiint \{3(\mathbf{r}_{pr}\cdot\mathbf{r}_{rq})^2$$

$$- r_{pr}^2 r_{rq}^2\} r_{pr}^{-5} r_{rq}^{-5} g(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) \, d\mathbf{r}_p \, d\mathbf{r}_q \, d\mathbf{r}_r. \qquad (15)$$

Above, $g^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)$ is the ternary distribution function of three molecules having positions $\mathbf{r}_p$, $\mathbf{r}_q$, $\mathbf{r}_r$.

The contribution (13) is particularly interesting, since it does not vanish even if the anisotropy of the isolated molecule is zero $\delta = 0$. In other words, as a result of translational fluctuations, an assemblage of mutually correlating atoms or isotropic molecules has a nonzero effective optical anisotropy [49]; this is the source of optical birefringence in CCl_4 and similar liquids [12], [19].

On closer inspection it is apparent that on inserting into (3) the first approximation of the expansion (12) with subsequent statistical averaging involving a distribution function of the type (11), containing the energy of dipole interaction [49]

$$w(r_{pq}, \omega_p, \omega_q) = \mu_\alpha^{(p)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(q)} \qquad (16)$$

one gets to within paired correlations

$$B_R^{(1)} = \frac{16\pi\delta\mu^4\rho}{225k^3T^3}\left(\alpha^2 + \frac{4}{15}\alpha\delta + \frac{1}{5}\delta^2\right) R_9^{(2)}, \qquad (17)$$

where μ is the molecule's permanent dipole moment.

This contribution (17) is significant since for dipolar molecules with negative anisotropy δ, it is negative. A reduction in Kerr constant has also been obtained quite recently by Takatsuji [18] for a nonpolar liquid of two parallel orienting molecules.

Numerical calculations of the contributions (13) and (17) imply numerical calculations of the parameters (14) and (15). This can indeed be performed in full with sufficient accuracy for real gases [49], but calculations of (15) involve the use of Kirkwood's "superposition approximation" for $g^{(3)}$. Restricting ourself to paired correlations for a liquid we can recur to the approximate model of hard spheres of diameter d, i.e., when [51]

$$g(r_{pq}) = \begin{cases} 0 & \text{for } r_{pq} < d, \\ 1 & \text{for } r_{pq} > d, \end{cases}$$

which together with (14) yields

$$R_n^{(2)} = \frac{4\pi\rho}{n-3}\left(\frac{\pi}{6v}\right)^{(n-3)/3} \qquad (18)$$

TABLE I

A COMPARISON OF THE THEORETICALLY CALCULATED VALUES OF B_R (IN 10^{-12} ESU) AND THE VALUES FOUND BY REFERRING TO EXPERIMENTAL RESULTS [11]

Liquid	$B_R^{(0)}$, eq. (9)	$B_R^{(1)}$, eq. (17)	$B_R^{(2)}$, eq. (13)	B_R^{theor}	B_R^{exp}, eq. (2)
Carbon tetrachloride	0	0	1.32	1.32	0.07
Chloroform	0.28	−0.08	0.92	1.13	0.21
Carbon disulphide	6.36	0	5.45	11.39	3.83
Benzene	1.65	0	2.00	3.53	0.49
Toluene	2.12	−0.54	2.24	3.82	1.11
Nitrobenzene	3.05	−1.64	3.26	4.67	3.25

for $n \geq 4$ where $v = \pi d^3/6$ is the volume of the molecule.

From Table I, one sees that the theoretical values obtained for B_R recurring to the approximation (18) for $\rho v = 0.6$ are considerably larger than those obtained using experimental data (especially in the case of CCl_4). It would seem that these divergences are due to the omission up to this point of still other molecular factors and of the contributions of triple and quadruple correlations, rather than to the approximate nature of the model (18). These multimolecular correlations have been taken into account by Hellwarth [17] when calculating the influence of molecular redistribution on the nonlinear refractive index of liquids. Further on, we shall discuss some other factors yielding nonzero contributions to B_R even in the approximation of paired correlations.

D. Nonlinearities Due to Molecular Fields

In a dense medium, there generally exist very strong microscopic electric fields of electric multipoles, causing nonlinear polarization of the molecules and thus modifying the tensor of their effective polarizability in accordance with the following expansion [49]:

$$\frac{\partial m_\alpha^{(p)}}{\partial E_\beta} = \alpha_{\alpha\beta}^{(p)} + \beta_{\alpha\beta\gamma}^{(p)}F_\gamma^{(p)} + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}^{(p)}F_\gamma^{(p)}F_\delta^{(p)} + \cdots , \quad (19)$$

where $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are tensors of nonlinear polarizability of the second and third order, respectively [52], [53].

To begin with, let us consider a molecule as acted on by the field of dipoles of its neighbors [49]:

$$F_\alpha^{(p)} = -\sum_{q=1}^{N} T_{\alpha\beta}^{(pq)}\mu_\beta^{(q)}. \quad (20)$$

We get by (3), with regard to (11), (16), and (19) for paired correlations:

$$B_R^\mu = \frac{4\pi\mu^2\rho}{3375kT}\left\{10\delta\gamma + 81\beta^2 + \frac{12\mu}{kT}\delta_\beta\right\}R_6^{(2)} \quad (21)$$

where $\beta = (\beta_{113} + \beta_{223} + \beta_{333})/3$ and $\gamma = \gamma_{\alpha\alpha\beta\beta}/5$ are the mean nonlinear polarizabilities (the anisotropic parts of $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ have been neglected).

The electric field produced at the center of molecule p by the quadrupoles of its neighbors in the medium is of the form [49]:

$$F_\alpha^{(p)} = \frac{1}{3}\sum_{q=1}^{N} T_{\alpha\beta\gamma}^{(pq)}\theta_{\beta\gamma}^{(q)} \quad (22)$$

$\theta_{\alpha\beta}$ being the quadrupole moment tensor, and $T_{\alpha\beta\gamma}$ the dipole–quadrupole interaction tensor.

By means of (19) and (22) we derive from the general formula (4), to within paired correlations of axially symmetric molecules having a quadrupole moment θ,

$$B_R^\theta = \frac{16\pi\rho}{63kT}\delta\gamma\theta^2 R_8^{(2)}. \quad (23)$$

One notes that the contributions (21) and (23) can also be negative if the molecular anisotropy δ is negative, thus decreasing the final values of B_R.

If the molecules have electric octupoles given by the tensor $\Omega_{\alpha\beta\gamma}$, they will give rise to an electric field [49]

$$F_\alpha^{(p)} = -\frac{1}{15}\sum_{q=1}^{N} T_{\alpha\beta\gamma\delta}^{(pq)}\Omega_{\beta\gamma\delta}^{(q)} \quad (24)$$

and by (3) and (19) we get for the tetrahedral molecules:

$$B_R^\Omega = \frac{128\pi\rho}{35kT}\beta_{123}^2\Omega_{123}^2 R_{10}^{(2)}. \quad (25)$$

In order to make numerical evaluations of these contributions one has to know the values of β and γ (but these are known only for several molecules [52], which are not considered in Table I) as well as those of θ and Ω, which can be determined by various methods [54], [55].

E. The Role of Molecular Shape

Throughout our preceding considerations, the molecules though optically anisotropic were tacitly assumed to be geometrically spheric. Now, as a matter of fact, the effect of reorientation of molecules in an ac electric field depends strongly on their shape. The influence of geometrical shape on B_R is most conveniently calculated by using the ellipsoidal Lorentz or Onsager–Scholte model [56], leading to the following expression if short range statistical correlations are neglected in (3):

$$B_R = \frac{2\pi\rho}{45kT}\{(\alpha_1^* - \alpha_2^*)^2 + (\alpha_2^* - \alpha_3^*)^2 + (\alpha_3^* - \alpha_1^*)^2\}. \quad (26)$$

Above, α_1^*, α_2^*, and α_3^* denote principal effective polarizabilities of the molecule.

TABLE II

OPTICAL KERR CONSTANT B_R(IN 10^{-12}) CALCULATED FOR THE ELLIPSOIDAL LORENTZ AND ONSAGER–SCHOLTE MODELS

Liquid	Without Field Anisotropy eq. (9)	Lorentz Ellipsoidal eqs. (26), (27)	Onsager–Scholte eqs. (26), (28)
Carbon disulphide	6.30	3.21	3.75
Benzene	1.65	0.62	0.92
Acetone	0.29	0.15	0.25
Toluene	2.12	0.90	3.66
Chloroform	0.28	0.07	0.09
Chlorobenzene	2.20	0.75	1.16
Nitrobenzene	3.05	0.97	1.53
Bromobenzene	1.58	0.37	0.82
Fluorobenzene	0.81	0.34	0.82
Pyridine	1.64	0.86	2.20

With the ellipsoidal Lorentz model, the sth principal effective polarizability is [49]:

$$\alpha_s^* = \left\{1 + \frac{n^2 - 1}{n^2 + 2}(3L_s - 1)\right\}\alpha_s \qquad (27)$$

where L_s is a parameter of shape of the ellipsoid ($L_1 + L_2 + L_3 = 1$). For a sphere $L_1 = L_2 = L_3 = 1/3$ and the anisotropy of the local field $3L_s - 1$ vanishes making the effective polarizability (27) identical with that of the isolated molecule, while (26) reduces to (9).

The Onsager–Scholte model leads to the following effective polarizability for the molecule [49]:

$$\alpha_s^* = \frac{\left(\frac{3n^2}{n^2 + 2}\right)abc\alpha_s}{[n^2 + (1 - n^2)L_s]abc - 3(n^2 - 1)(1 - L_s)L_s\alpha_s} \qquad (28)$$

with a, b, c, $\cdots$, the semiaxes of an ellipsoidal cavity whose dimensions in Onsager's model are taken equal to those of the anisotropic molecule immersed in a continuous medium of refractive index n.

Table II shows that the Lorentz local field anisotropy strongly decreases the B_R values of all liquids, whereas the Onsager–Scholte model in some cases (C_5H_5N) yields a considerable increase and in others ($C_6H_5NO_2$) a decrease in B_R. Simultaneous consideration of molecular shape in accordance with either model, and of short range correlations, is liable to lead to satisfactory agreement with experiment.

III. THE ROLE OF MOLECULAR CORRELATIONS IN SECOND HARMONIC DEPOLARIZATION

We shall refrain here from discussing in detail the general theories of second harmonic scattering developed elsewhere [33], [41]–[44] for dense media, and shall but review the important part played by molecular correlations in the depolarization ratio that is defined (for vertically polarized incident light [43]) as

$$D_{2\omega} = \frac{4C - A}{6C + 9A} \qquad (29)$$

where in the absence of dispersion and absorption we have

$$A = \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{\partial^2 m_\alpha^{(p)}}{\partial E_\beta \, \partial E_\beta} \frac{\partial^2 m_\alpha^{(q)}}{\partial E_\gamma \, \partial E_\gamma} \right\rangle \qquad (30)$$

$$C = \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{\partial^2 m_\alpha^{(p)}}{\partial E_\beta \, \partial E_\gamma} \frac{\partial^2 m_\alpha^{(q)}}{\partial E_\beta \, \partial E_\gamma} \right\rangle . \qquad (31)$$

We now have to take into account the nonlinear polarization induced in the molecules by a strong laser field. In the absence of molecular fields we can write, instead of (8),

$$m_\alpha^{(p)} = \alpha_{\alpha\beta}^{(p)}E_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma}^{(p)}E_\beta E_\gamma + \cdots . \qquad (32)$$

The constants (30) and (31) have been discussed in the above approximation by Bersohn et al. [41] for various molecular symmetries [40]. Here, we shall draw attention to two cases of peculiar interest not discussed in [41].

A. Tetrahedral Molecules

One such case is that of tetrahedral molecules for which, in the ground state, $\beta_{\alpha\beta\beta} = 0$ and the constant A vanishes in the approximation of (32), while C is nonzero and is given by

$$C = 6N\beta_{123}^2 + \rho^2 \iint \beta_{\alpha\beta\gamma}^{(p)}\beta_{\alpha\beta\gamma}^{(q)}g^{(2)}(\tau_p, \tau_q) \, d\tau_p \, d\tau_q. \qquad (33)$$

One sees that here the depolarization ratio (29) takes the value 2/3, while for liquid CCl_4 one has experimentally a value close to 1/3 [38]. This result is highly significant since, notwithstanding the fact that statistical correlations are inherent in (33) by way of $g^{(2)}$, the ratio $D_{2\omega}$ is, nevertheless, a constant quantity independent of density and temperature. It is readily shown that by taking into account the effect of molecular redistribution in the discussion of (30) and (31) one gets nonvanishing C as well as A constants, resulting in the following relation [43]:

$$D_{2\omega} = \frac{2}{3}\frac{1 + \tfrac{76}{5}\alpha^2 R_6^{(2)}}{1 + \tfrac{118}{5}\alpha^2 R_6^{(2)}}. \qquad (34)$$

The contribution $\alpha^2 R_6^{(2)}$ from molecular redistribution decreases the 2/3 value by about 15 percent. But a decrease of 50 percent is required in order to have agreement with the experimental data. As shown by Weinberg [42] and this author [43], this can be achieved by taking into account the effect of the electric field of molecular octupoles (24), which causes additional nonlinear polarization:

$$\frac{\partial^2 m_\alpha^{(p)}}{\partial E_\beta \, \partial E_\gamma} = \beta_{\alpha\beta\gamma}^{(p)} + \gamma_{\alpha\beta\gamma\delta}^{(p)}F_\delta^{(p)} + \cdots . \qquad (35)$$

Including both this effect and molecular redistribution in the calculation of the constants (30) and (31), one obtains the depolarization ratio of tetrahedral molecules in the form:

$$D_{2\omega} = \frac{2}{3} \frac{1 + \frac{76}{5} \alpha^2 R_6^{(2)} + \frac{14}{9} \left(\frac{\gamma}{\beta_{123}}\right)^2 \Omega_{123}^2 R_{10}^{(2)}}{1 + \frac{118}{5} \alpha^2 R_6^{(2)} + \frac{28}{3} \left(\frac{\gamma}{\beta_{123}}\right)^2 \Omega_{123}^2 R_{10}^{(2)}}. \quad (36)$$

Inserting here the data for CCl_4: $\alpha = 10.5 \times 10^{-24}$ cm^3, $\beta_{123} = 0.35 \times 10^{-30}$ ESU [38], $\gamma = 12 \times 10^{-36}$ ESU [52], and recurring to the approximation (18) for $\rho v = 0.6$, accordance with experiment is obtained [38] if the octupole moment is taken as equal to $\Omega = 15 \times 10^{-34}$ ESU. Weinberg [42], not considering molecular redistribution, obtained a value for Ω about twice as large.

B. Quadrupolar Molecules with a Center of Inversion

Isolated molecules having a center of inversion cannot produce second harmonic scattering because in their case the components $\beta_{\alpha\beta\gamma}$ vanish. Nevertheless, if they possess a permanent quadrupole moment, they become deprived of their center of inversion as a result of nonlinear polarization in the electric fields of other quadrupoles [(22)], in accordance with the expansion (35). Hence, a dense medium consisting of centrosymmetric quadrupolar molecules is apt to produce second harmonic scattering defined by the constants [43]:

$$A = \frac{25}{3}\gamma^2\Theta^2 N R_8^{(2)} \quad (37)$$

$$C = 5\gamma^2\Theta^2 N R_8^{(2)} \quad (38)$$

where we have neglected the anisotropy of the tensor $\gamma_{\alpha\beta\gamma\delta}$. The above expressions, when inserted into (29), lead to a depolarization ratio of 1/9. It is worth mentioning in this respect that Terhune et al. [38] observed weak second harmonic scattering from a liquid of trans-dichloroethylene, which is centrosymmetric, twenty times weaker than from the cis isomer, which lacks a center of inversion.

IV. Conclusions

From what has been said, the part played by molecular correlations in nonlinear optical effects is not only that of a source of numerical corrections modifying the "gas values," since these correlations can in certain cases be the source of the effects as such. An example of this is found in the existence of temperature-dependent optical Kerr effect in liquids with optically isotropic molecules as a result of molecular redistribution [(13) for $\delta = 0$]. The same effect also decreases the depolarization ratio of second-harmonic scattering in accordance with experimental data [(34)]. In liquids of tetrahedral molecules a further decrease in $D_{2\omega}$ as well as the occurrence of a Kerr effect can result by fluctuations of the electric fields of octupoles causing nonlinear polarization of the molecules [(25) and (36)]. Clearly, in the absence of molecular correlations, these effects do not occur. It is moreover noteworthy that, while molecular redistribution as calculated with the radial correlation function yields an increase in B_R [(13)], a decrease in B_R will result on taking into account angle-dependent correlations [e.g., by (17)].

Values of the correlation parameters (14) and (15), as

calculated with the approximation (18), can moreover be determined from other effects, such as linear light scattering [49] or electric polarization in liquids [51], [57]. Along these lines, we can gain more detailed information concerning the nature and shape of the paired, triple, and multimolecular correlation functions, which are of essential meaning to the statistical mechanics of liquids [58]. To this aim, it would be most useful to investigate the phenomena under consideration in multicomponent systems, for which for example the optical Kerr constant can be expanded in a power series in the mole fractions x [19]:

$$B = \sum_i x_i B_i + \sum_{ij} x_i x_j B_{ij} + \sum_{ijk} x_i x_j x_k B_{ijk} + \cdots \quad (39)$$

where the first term describes the additive properties of the ideal mixture, while the subsequent terms account for deviations from additivity due to various paired, triple, etc. molecular correlations. The study of these deviations from additvity will thus provide information on the binary $g_{ij}^{(2)}$, ternary $g_{ijk}^{(3)}$, $\cdots$ correlation functions inherent in the coefficients B_{ij}, B_{ijk}, $\cdots$ of the expansion (39).

In concluding, it may be worth stating once more that although the permanent electric dipoles (and higher moments) of molecules do not participate directly in purely optical effects, they nevertheless do contribute to these effects indirectly in sufficiently dense media by way of the correlation functions and by way of their electric fields, which induce nonlinear polarization in neighboring molecules, also in the absence of externally applied fields. Hence, the nonlinear optical processes accompanying the propagation of intense laser light in liquids are largely dependent on the electrical properties and the structure of the molecules as well as on the nature and amount of their mutual interactions. Obviously the present preliminary stage attained by this domain does not as yet permit to draw far reaching conclusions, but it can surely be said to provide a basis for the nonlinear molecular optics now undergoing rapid development, whence interesting results are to be expected with regard to the nonlinear properties of atoms and molecules and their mutual correlations in dense media.

V. Final Remarks

Molecular correlations are apparent to a greater or lesser extent not only in the phenomena previously cited but moreover in the stimulated scattering processes reviewed recently by Bloembergen [7] as well as Akhmanov and Khokhlov [59], and in other optical nonlinearities [59] probably including frequency shifts in self-focused light [60], [61]. These correlations predictably play a very important part in the nonlinear changes in electric and magnetic susceptibilities induced in liquids by strong laser light [12], [62] (as yet unobserved effects, though it is worth noting that recently variations of the absolute refractive index of liquids have been measured [63], [64]). Recent attempts [65] to detect nonlinear changes in the

ratio of depolarization of scattered laser light due to optical molecular reorientation and angular correlations [66] have not as yet led to unambiguous results because of laser-produced shock waves [57] and dielectric breakdown [68] at high intensities of the beam. Moreover, molecular correlations play a part in nonlinear phenomena, which can be induced optically in gyrotropic media [69], [70], namely nonlinear optical activity [59], [71], inverse Faraday effect [72], and light intensity-dependent Faraday effect [71].

Those of the above-mentioned nonlinear optical processes which have up to this point not proved accessible to detection in atomic or molecular substances can be predicted to be readily accessible to observation in macromolecular and colloidal ones, where (like the already measured effect of electric saturation [73]) optical saturation should be easily achievable [74]–[76]. However, in such substances, nonlinear optical processes will depend more strongly on the size, shape, and anisotropy of the macromolecules or particles [75], [76]. Significantly, in molecular liquids, the optical Kerr constants are in agreement with experiment [11] if angular correlations are included in the calculations [77].

REFERENCES

[1] M. Born, *Optik*. Berlin: Springer, 1933.
M. V. Volkenshteyn, *Molekularnaya Optika (Molecular Optics)*. Moscow: Gostekhizdat, 1951.

[2] S. A. Akhmanov and R. V. Khokhlov, *Problemy Nyelineynoy Optiki*. Moscow: WINJTJ, Akad. Nauk. USSR, 1964.
N. Bloembergen, *Nonlinear Optics*. New York: Benjamin, 1965.
P. N. Butcher, *Nonlinear Optical Phenomena*. Columbus: Ohio State University Press, 1965.
W. M. Fayn and Ya. I. Khanin, *Kwantovaya Radiofizika*. Moscow: Soviet Radio, 1965.

[3] E. Garmire, R. Y. Chiao, and C. H. Townes, "Dynamics and characteristics of the self-trapping of intense light beams," *Phys. Rev. Letters*, vol. 16, pp. 347–349, February 1966.

[4] R. W. Minck, R. W. Terhune, and C. C. Wang, "Nonlinear optics," *Appl. Opt.*, vol. 5, pp. 1595–1612, October 1966.

[5] S. A. Akhmanov, A. P. Sukhorukov, and R. V. Khokhlov, "Self-focussing and diffraction of light in nonlinear media," *Usp. Fiz. Nauk*, vol. 93, pp. 19–70, September 1967.

[6] Y. R. Shen and Y. J. Shaham, "Self-focussing and stimulated Raman and Brillouin scattering in liquids," *Phys. Rev.*, vol. 163, pp. 224–232, November 1967.

[7] N. Bloembergen, "The stimulated Raman effect," *Am. J. Phys.* vol. 35, pp. 989–1023, November 1967.

[8] V. S. Starunov, "Investigation concerning the spectra of thermal and stimulated molecular light scattering in liquids," *Tr. Fiz. Inst.* Akad. Nauk USSR, vol. 39, pp. 151–218, 1967.

[9] A. D. Buckingham, "Birefringence resulting from the application of an intense beam of light to an isotropic medium," *Proc. Phys. Soc.*, vol. B 69, pp. 344–349, February 1956.

[10] G. Mayer and F. Gires, "Action of an intense light beam on the refractive index of liquids," *Compt. Rend. Acad. Sci.* (Paris), vol. 258, pp. 2039–2042, February 1964.

[11] M. Paillette, "Measurements of Kerr effect induced by an intense light wave," *Compt. Rend. Acad. Sci.* (Paris), vol. 262, pp. 264–267, January 1966.

[12] S. Kielich and A. Piekara, "A statistical-molecular theory of electric, magnetic and optical saturation phenomena in isotropic dielectric and diamagnetic media," *Acta Phys. Polon.*, vol. 18, pp. 439–472, May 1958.
S. Kielich, "Optically induced birefringence," *Acta Phys. Polon.*, vol. 30, pp. 683–707, October 1966.

[13] P. D. Maker, R. W. Terhune, and C. M. Savage, "Intensity dependent changes in the refractive index of liquids," *Phys. Rev. Letters*, vol. 12, pp. 507–509, May 1964.
P. D. Maker and R. W. Terhune, "Study of optical effects due to an induced polarization third order in the electric field strength," *Phys. Rev.*, vol. 137, pp. A801–A818, February 1965.

[14] C. C. Wang, "Nonlinear susceptibility constants and self-

focussing of optical beams in liquids," *Phys. Rev.*, vol. 152, pp. 149–152, December 1966.

[15] P. D. McWane and D. A. Sealer, "New measurements of intensity-dependent changes in the refractive index of liquids," *Appl. Phys. Letters*, vol. 8, pp. 278–279, June 1966.

[16] F. Shimizu, "Study of the intensity dependent refractive index in liquids," *J. Phys. Soc. Japan*, vol. 22, pp. 1070–1077, April 1967.

[17] R. W. Hellwarth, "Effect of molecular redistribution on the nonlinear refractive index of liquids," *Phys. Rev.*, vol. 152, pp. 156–165, December 1966.

[18] M. Takatsuji, "Effect of angular correlation on nonlinear index of liquids," *Phys. Rev.*, vol. 165, pp. 171–177, January 1968.

[19] S. Kielich, "Light intensity dependence of the refractive index of non-dissipative media by a semi-macroscopic approach," *Proc. Phys. Soc.*, vol. 90, pp. 847–858, March 1967. Also "On the relation between nonlinear refractive index and molecular light scattering in liquids," *Chem. Phys. Letters*, vol. 2, pp. 112–116, June 1968.

[20] Y. R. Shen, "Electrostriction, optical Kerr effect and self-focussing of laser beams," *Phys. Letters*, vol. 20, pp. 378–380, March 1966.

[21] S. Kielich, "Optically induced birefringence calculated from light scattering data of liquids," *Phys. Letters*, vol. 24A, pp. 383–385, March 1967.
B. Kasprowicz and S. Kielich, "On nonlinear changes in refractive index of liquids due to electrostriction and electrocaloric effect," *Acta Phys. Polon.*, vol. 31, pp. 787–790, April 1967.

[22] L. L. Boyle, A. D. Buckingham, R. L. Disch, and D. A. Dunmur "Higher polarizability of the helium atom," *J. Chem. Phys.*, vol. 45, pp. 1318–1323, August 1966.

[23] W. G. Rado, "The nonlinear third order dielectric susceptibility coefficients of gases and optical third harmonic generation," *Appl. Phys. Letters*, vol. 11, pp. 123–125, August 1967.

[24] N. Bloembergen and P. Lallemand, "Complex intensity-dependent index of refraction, frequency broadening of stimulated Raman lines, and stimulated Rayleigh scattering," *Phys. Rev. Letters*, vol. 16, pp. 81–84, January 1966.

[25] S. Kielich, "On the effect of a strong oscillating electric field on the refractive index of isotropic media," *Acta Phys. Polon.*, vol. 31, pp. 689–713, April 1967.

[26] R. M. Herman, "Saturation effects in stimulated Rayleigh wing scattering," *Phys. Rev.*, vol. 164, pp. 200–206, December 1967.

[27] Y. R. Shen, M. Y. Au Yang, and M. L. Cohen, "Theory of self-trapped filaments of light," *Phys. Rev. Letters*, vol. 19, pp. 1171–1174, November 1967.

[28] K. Grob and M. Wagner, "Equations of Ginzburg–Landau type in nonlinear optics," *Phys. Rev. Letters*, vol. 17, pp. 819–821, October 1966.

[29] M. J. Freiser and R. J. Joenk, "Enhancement of self-trapping by cooperative phenomena; application to liquid crystals," *Phys. Letters*, vol. 24A, pp. 683–684, June 1967.

[30] R. G. Brewer, J. R. Lifsitz, E. Garmire, R. Y. Chiao, and C. H. Townes, "Small-scale trapped filaments in intense laser beams," *Phys. Rev.*, vol. 166, pp. 326–331, February 1968.
T. K. Gustafson, P. L. Kelley, R. Y. Chiao, and R. G. Brewer, "Self-trapping in media with saturation of the nonlinear index," *Appl. Phys. Letters*, vol. 12, pp. 165–168, March 1968.

[31] V. N. Lugovoy and A. M. Prokhorov, "On a possible explanation of small-scale trapping filaments," *Zh. Eksperim. i Teor. Fiz.,Pis'ma*, vol. 7, pp. 153–155, March 1968.

[32] G. Rivoire and J. L. Beaudoin, "Température et seuil d'obtention des raies Stokes et anti-Stokes en effet Raman stimulé," *J. Phys.*, vol. 29.

[33] S. Kielich, "Classical theory of nonlinear molecular light scattering," *Bull. Soc. Amis Sci. Lettres Poznan*, ser. B, vol. 17, pp. 43–58, 1962–63. Also "Light scattering by an intense light beam," *Acta Phys. Polon.*, vol. 25, pp. 85–99, January 1964.

[34] J. Cabannes, *La Diffusion Moléculaire de la Lumière*. Paris: Les Presses Universitaires de France, 1929.
I. L. Fabelinskiy, *Molekularnoye Rassieyaniye Svyeta* (Molecular Light Scattering). Moscow: Glavnaya Redaktsiya Fiziko-Matematicheskoy Literatury, 1965.

[35] S. Kielich, "Nonlinear light scattering by molecules without a centre of inversion," *Bull. Acad. Sci. Sér., Math. Astron. Phys.*, vol. 12, pp. 53–60, January 1964.

[36] R. Bersohn, "Scattering of optical harmonics by macromolecules," *J. Am. Chem. Soc.*, vol. 86, pp. 3505–3507, September 1964.

[37] S. Kielich, "Influence of a strong optical electric field on the molecular scattering of light," *Physica*, vol. 30, pp. 1717–1724, 1964. Also "Theory of molecular light scattering in the presence of an intense light beam," *Acta Phys. Polon.*, vol. 26, pp. 135–154, July 1964.

[38] R. W. Terhune, P. D. Maker, and C. M. Savage, "Measurement of nonlinear light scattering," *Phys. Rev. Letters*, vol. 14, pp. 681–684, April 1965.

[39] P. D. Maker, "Nonlinear light scattering in methane," *Physics of Quantum Electronics*. New York: McGraw-Hill, 1966.

[40] S. J. Cyvin, J. E. Rauch, and J. C. Decius, "Theory of hyper Raman effects (nonlinear inelastic light scattering): Selection rules and depolarization ratios for the second order polarizability," *J. Chem. Phys.*, vol. 43, pp. 4083–4095, December 1965.

[41] R. Bersohn, Yoh-Han Pao, and H. L. Frisch, "Double-quantum light scattering by molecules," *J. Chem. Phys.* vol. 45, pp. 3184–3198, November 1966.

[42] D. L. Weinberg, "Temperature-dependence, orientation correlation, and molecular fields in second-harmonic light scattering from liquids and gases," *J. Chem. Phys.*, vol. 47, pp. 1307–1313, August 1967.

[43] S. Kielich, "Second harmonic light scattering by dense isotropic media," *Acta Phys. Polon.*, vol. 33, pp. 89–104, January 1968.

[44] V. L. Strizhevsky and V. M. Klimenko, "Three-photon scattering of light in an isotropic medium," *Zh. Eksperim. i Teor. Fiz.*, vol. 53, pp. 244–253, July 1967.

[45] J. Lajzerowicz, "Second-harmonic generation by random media: 'Critical opalescence' at certain solid-solid phase transitions," *Solid State Commun.*, vol. 3, pp. 369–370, November 1965.

[46] I. Freund, "Critical harmonic scattering in NH_4Cl," *Phys. Rev. Letters*, vol. 19, pp. 1288–1291, November 1967. "Harmonic scattering and critical point correlations in NH_4Cl," *Chem. Phys. Letters*, vol. 1, pp. 551–554, January 1968.

[47] S. Kielich, "Non-linear processes to result from multipole interaction between molecules and electromagnetic fields," *Proc. Phys. Soc.*, vol. 86, pp. 709–725, 1965. "Multi-harmonic molecular light scattering in liquids," *Chem. Phys. Letters*, vol. 1, pp. 441–442, December 1967.

[48] J. Brandmüller, "Laser Raman spectroscopy—I. Linear Raman effect," *Naturwissenschaften*, vol. 54, pp. 293–297, 1967.

H. W. Schrötter, "Laser Raman spectroscopy—II. Nonlinear effects," *Naturwissenschaften*, vol. 54, pp. 607–612, 1967.

[49] S. Kielich, "Role of molecular interaction in anisotropic light scattering by liquids," *J. Chem. Phys.*, vol. 46, pp. 4090–4099, May 1967. Also "Theory of optical anisotropy of unlike interacting molecules," *J. Phys.*, vol. 29, 619–630, July 1968.

[50] J. Yvon, "Recherches sur la Théorie Cinétique des liquides," in *Actualités Scientifiques et Industrielles*. Paris: Hermann Cie, 1937.

[51] J. G. Kirkwood, "On the theory of dielectric polarization," *J. Chem. Phys.*, vol. 4, pp. 592–601, September 1936.

[52] A. D. Buckingham and B. J. Orr, "Molecular hyperpolarizabilities," *Quart. Rev.*, vol. 21, pp. 195–212, February 1967.

[53] S. Kielich, "Optical linear and nonlinear properties of atoms and molecules," *J. Phys.*, vol. 28, pp. 519–534, July 1967.

[54] Krishnaji and V. Prakash, "Evaluation of molecular quadrupole moment," *Rev. Mod. Phys.* vol. 38, pp. 690–709, October 1966.

[55] D. E. Stogryn and A. P. Stogryn, "Molecular multipole moments," *Mol. Phys.*, vol. 11, pp. 371–393, October 1966.

[56] C. J. F. Böttcher, *Theory of Electric Polarization*. New York: Elsevier, 1952.

[57] S. Kielich, "Multipolar theory of dielectric polarization in dense mixtures," *Mol. Phys.*, vol. 9, pp. 549–564, June 1965.

[58] T. L. Hill, *Statistical Mechanics*. New York: McGraw-Hill, 1956.

G. H. A. Cole, *The Statistical Theory of Classical Simple Dense Fluids*. Oxford: Pergamon Press, 1967.

[59] S. A. Akhmanov and R. V. Khokhlov, "New results in non-linear optics," *Usp. Fiz. Nauk*, vol. 95, pp. 231–247, May 1968.

[60] R. G. Brewer, "Frequency shifts in self-focused light," *Phys. Rev. Letters*, vol. 19, pp. 8–10, July 1967.

F. Shimizu, "Frequency broadening in liquids by a short light pulse," *Phys. Rev. Letters*, vol. 19, pp. 1097–1100, November 1967.

[61] A. C. Cheung, D. M. Rank, R. Y. Chiao, and C. H. Townes, "Phase modulation of Q-switched laser beams in small-scale filaments," *Phys. Rev. Letters*, vol. 20, pp. 786–789, April 1968.

[62] S. Kielich, "Opticostriction and optically induced electric anisotropy," *Physica*, vol. 34, pp. 586–588, April 1967. Also "Electric and magnetic anisotropy induced in nonabsorbing media by an intense laser beam," *Acta Phys. Polon.*, vol. 32, pp. 405–419, September 1967.

[63] A. P. Veduta and B. P. Kirsanov, "Variation of the refractive index of liquids and glasses in the strong field of a ruby laser," *Zh. Eksperim i Teor. Fiz.*, vol. 54, pp. 1374–1379, May 1968.

[64] M. Paillette, "Experimental study of the intensity dependent variations of the absolute refractive index in liquids," presented at the 1968 International Quantum Electronics Conf., Miami, Fla., paper J-10; Abstract in *IEEE J. Quantum Electronics*, vol. QE-4, p. 350, May 1968.

[65] J. R. Lalanne and P. Bothorel "Fast measurements of molecular optical anisotropy with a pulsed ruby laser," *Compt. Rend. Acad. Sci.* (Paris), vol. 263, pp. 693–696, September 1966.
J. R. Lalanne, "Rayleigh depolarized scattering anomaly presented by certain liquids placed in the path of an intense pulsed laser beam," *Compt. Rend. Acad. Sci.* (Paris), vol. 265, pp. 1181–1184, November 1967.

[66] S. Kielich, "Nonlinear change in light depolarization ratio due to optical molecular reorientation effect," *Phys. Letters*, vol. 25A, pp. 153–154, July 1967.

[67] C. E. Bell and J. A. Landt, "Laser-induced high-pressure shock waves in water," *Appl. Phys. Letters*, vol. 10, pp. 46–48, January 1967.

[68] M. W. Dowley, K. B. Eisenthal, and W. L. Peticolas, "Laser-produced dielectric breakdown in liquids with resulting absorption of a secondary light beam," *Phys. Rev. Letters*, vol. 18, pp. 531–533, April 1967.

[69] S. Kielich "Frequency- and spatially variable electric and magnetic polarizations induced in nonlinear media by electromagnetic fields," *Acta Phys. Polon.*, vol. 29, pp. 875–898, June 1966.

[70] S. A. Akhmanov and V. I. Zharikov, "On nonlinear optics of gyrotropic media," *Zh. Eksperim. i Teor. Fiz., Pisma*, vol. 6, pp. 644–648, September 1967.

[71] S. Kielich, "Natural and magneto-optical rotation in the presence of an intense light beam," *Phys. Letters*, vol. 25A, pp. 517–518, October 1967.

[72] P. S. Pershan, J. P. van der Ziel, and L. D. Malmstrom, "Theoretical discussion of the inverse Faraday effect, Raman scattering, and related phenomena," *Phys. Rev.*, vol. 143, pp. 574–583, March 1966.

[73] C. T. O'Konski, K. Yoshioka, and W. H. Orttung, "Electric properties of macromolecules—IV. Determination of electric and optical parameters from saturation of electric birefringence in solutions," *J. Phys. Chem.*, vol. 63, pp. 1558–1565, 1959.

[74] F. Kaczmarek, "Application of a high power ruby laser beam for studying propagation phenomena of light in various dielectric media," *Acta Phys. Polon.*, vol. 32, pp. 1003–1022, December 1967.

[75] G. A. Askaryan, "Nonlinearity of media due to induced deformation of atoms, molecules and particles," *Zh. Eksperim. i Teor. Fiz, Pisma.*, vol. 6, pp. 672–674, September 1967.

[76] S. Kielich, "Strong optical nonlinearities in colloidal systems," *Chem. Phys. Letters*, vol. 1, pp. 675–677, April 1968. "Linear and nonlinear light scattering in colloidal media," *J. Colloid Interface Sci.*, vol. 27, pp. 432–441, July 1968.

[77] B. Kasprowicz and S. Kielich, "Numerical calculations of optical Kerr constant for several liquids," *Acta Phys. Polon.*, vol. 33, pp. 495–498, March 1968.