

OPTICAL SATURATION IN LASER LIGHT SCATTERING

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(Received 17 September 1968)

Possibilities of observing light scattering from an intense laser beam, whose electric field in well-defined conditions can cause total orientation of the scattering microsystems, are investigated on the basis of a simple classical theory. This saturation of orientation affects the scattered light and should be accessible to measurement in solutions of macromolecules or colloidal particles by usual laser technique, whereas in molecular liquids it cannot be made apparent even if using the focused beam of a strong laser. The measurements under consideration are proposed as a novel and simple method of determining the sign of the optical anisotropy of macromolecules and colloidal particles.

Orientation of anisotropic molecules in the electric field of laser light gives rise to various nonlinear optical processes,^{1,2} including nonlinear changes in Rayleigh light scattering by gases and liquids.³ Recent experiments by Lalanne⁴ with intense laser beams on light scattering in liquids did not yield changes of a nonlinear nature attributable to molecular orientation but showed irregular deviations from linearity due to the occurrence of destructive anomalies^{4,5} in the scattering liquid.

Here, we shall discuss the problem within the framework of classical statistical theory, which

will allow us to define the experimental conditions most advantageous for observing nonlinear scattering due to reorientation as well as total alignment of the microsystems (molecules, macromolecules, or colloidal particles) in the laser field. The latter effect, termed optical saturation, has been shown quite recently by Brewer *et al.*⁶ to play a very important part in the self-trapping of intense laser beams in media. However, in molecular liquids, high optical saturation cannot be achieved without incurring destruction of the substance.^{4,5} But polymers and colloids do admit of a high degree of re-

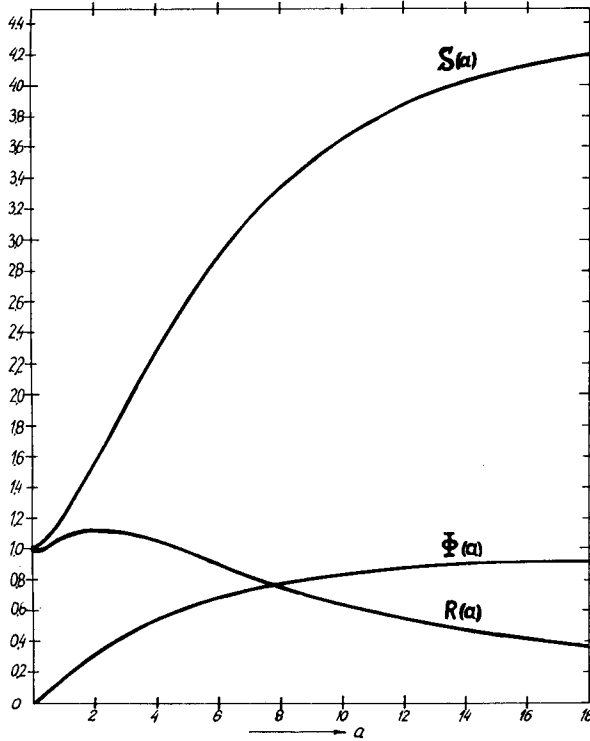


Fig. 1. Orientation functions $\Phi(a)$, $R(a)$ and $S(a)$ calculated and plotted from Eqs. (3)–(5) and (9)–(11) for positive optical anisotropy.

orientation of the macromolecules or particles⁷ which can go over into saturation already at the electric field strengths provided by usual lasers.

Consider an assemblage of N axially symmetric microsystems, small compared with the light wavelength λ , on which an intense laser beam is incident along the y axis with electric vector $\mathbf{E}_L = \mathbf{E}_0 e^{-i\omega_L t}$ oscillating along the z axis at frequency ω_L . If observation of the scattered light is along the x axis, the scattered intensity components with oscillations, respectively, along the z and y axis result as follows:

$$I_z = \rho\alpha^2(2\pi/\lambda)^4 \{1 + 4\kappa\Phi(a) + \frac{4}{3}\kappa^2 S(a)\} I_L, \quad (1)$$

$$I_y = \rho\alpha^2(2\pi/\lambda)^4 \frac{3}{5}\kappa^2 R(a) I_L. \quad (2)$$

(These formulas are derived as in Refs. 3 and 7.) Above, V is the scattering volume, $\rho = N/V$ the number density of microsystems of mean optical polarizability $\alpha = (\alpha_{||} + 2\alpha_{\perp})/3$ and anisotropy of polarizability $\kappa = (\alpha_{||} - \alpha_{\perp})/3\alpha$ ($\alpha_{||}$ and α_{\perp} are polarizabilities parallel and perpendicular to the symmetry axis), whereas the orientation functions

$$\Phi(a) = \frac{1}{2} \langle 3 \cos^2 \vartheta - 1 \rangle_{I_L}, \quad (3)$$

$$R(a) = \frac{15}{2} \langle \cos^2 \vartheta - \cos^4 \vartheta \rangle_{I_L}, \quad (4)$$

$$S(a) = \frac{5}{4} \langle 9 \cos^4 \vartheta - 6 \cos^2 \vartheta + 1 \rangle_{I_L}, \quad (5)$$

define the degree of orientation of the microsys-

tems in the laser field \mathbf{E} . The statistical average $\langle \rangle_{I_L}$ in the presence of laser light of intensity $I_L = \mathbf{E}_L \mathbf{E}_L^*$ is, by classical Boltzmann statistics

$$\langle \cos^{2n} \vartheta \rangle_{I_L} = \frac{\int_0^\pi \cos^{2n} \vartheta \exp(a \cos^2 \vartheta) \sin \vartheta d\vartheta}{\int_0^\pi \exp(a \cos^2 \vartheta) \sin \vartheta d\vartheta}, \quad (6)$$

ϑ being the angle between the microsystem's symmetry axis and the vector \mathbf{E}_L , and

$$a = (3\alpha\kappa/2kT)I_L = [(\alpha_{||} - \alpha_{\perp})/2kT]I_L \quad (7)$$

is a dimensionless parameter of orientation of the microsystem.

On substituting $-a^{1/2} \cos \vartheta = t$ into Eq. (6) and integrating per partes, we obtain the formula:

$$\langle \cos^{2n} \vartheta \rangle_{I_L}^{\pm} = \pm [2|a|^{1/2} I(\pm a)]^{-1} \mp [(2n-1)/2|a|] \langle \cos^{2n-2} \vartheta \rangle_{I_L}^{\pm}, \quad (8)$$

which contains integrals of the form

$$I(\pm a) = \frac{1}{2} e^{\mp |a|} \int_{-|a|^{1/2}}^{|a|^{1/2}} \frac{|a|^{1/2}}{|a|^{1/2} \mp t} e^{\pm t^2} dt, \quad (9)$$

the upper and lower signs relating to positive and negative optical anisotropy (thus, $\alpha_{||} - \alpha_{\perp} > 0$ as in CS_2 , and $\alpha_{||} - \alpha_{\perp} < 0$ as in C_6H_6). The general formula (8) leads to

$$\langle \cos^2 \vartheta \rangle_{I_L}^{\pm} = \pm [2|a|^{1/2} I(\pm a)]^{-1} \mp (+1/(2|a|)), \quad (10)$$

$$\langle \cos^4 \vartheta \rangle_{I_L}^{\pm} = \pm \frac{(2|a| \mp 3)}{4|a|^{3/2} I(\pm a)} + \frac{3}{4|a|^2}. \quad (11)$$

The orientation function (3) defines, e.g., saturation of optical Kerr effect⁶ and has been tabulated by O'Konski *et al.*⁸ for positive anisotropy and plotted by Shah⁹ for negative anisotropy. Figure 1 shows graphs of the functions (3)–(5) calculated from Eqs. (9)–(11) for positive anisotropy, for which the integral $I(+a)$ has been tabulated.^{6,8}

At $a = 0$ we have $\Phi(a) = 0$ and $R(a) = S(a) = 1$, whence Eqs. (1) and (2) reduce to the well-known results for linear light scattering¹⁰:

$$I_z^0 = \rho\alpha^2(2\pi/\lambda)^4 (1 + \frac{4}{3}\kappa^2) I_L, \quad (12)$$

$$I_y^0 = \rho\alpha^2(2\pi/\lambda)^4 \frac{3}{5}\kappa^2 I_L. \quad (13)$$

In the limiting case at $a \rightarrow \infty$, the orientation functions (3)–(5) become $\Phi^+(\infty) = 1$, $R^+(\infty) = 0$, $S^+(\infty) = 5$ for positive and $\Phi^-(\infty) = -1/2$, $R^-(\infty) = 0$, $S^-(\infty) = 5/4$ for negative anisotropy.

With regard to the shape of $R(a)$ in Fig. 1, one sees that quite generally, as I_L increases, the component I_y (which is the only component depolarizing the scattered light) at first increases slightly and then decreases to zero as optical saturation is approached. This permits to state that experimental studies of nonlinear changes in depolarization,⁴ which are insignificant, are by no means advantageous, particularly in molecular liquids.

Accordingly, experiments ought to be set up in a manner to measure the vertical component I_z , which by Eqs. (1) and (12) undergoes the following, considerable change:

$$\frac{I_z - I_z^0}{I_z^0} = \frac{20\kappa\Phi(a) + 4\kappa^2[S(a) - 1]}{5 + 4\kappa^2} \quad (14)$$

For low anisotropies ($\kappa < 0.1$), one can neglect small κ^2 terms in the preceding formula, leading to the rather interesting result

$$(I_z - I_z^0)/I_z^0 = 4\kappa\Phi(a), \quad (15)$$

which establishes a direct link between the change in vertical component of scattered light and the orientation function $\Phi(a)$ defining Kerr's effect.^{6,8}

For the case of optical saturation, Eqs. (14) and (15) reduce to:

$$\left(\frac{I_z - I_z^0}{I_z^0}\right)_{a \rightarrow \infty}^+ = \frac{20\kappa + 16\kappa^2}{5 + 4\kappa^2} \approx 4\kappa, \quad (16)$$

for positive anisotropy, and to

$$\left(\frac{I_z - I_z^0}{I_z^0}\right)_{a \rightarrow \infty}^- = \frac{-10\kappa + \kappa^2}{5 + 4\kappa^2} \approx -2\kappa, \quad (17)$$

for negative anisotropy.

Equations (14)–(17) are important relationships inasmuch as they allow us to determine not only the value of the optical anisotropy but, in the first place, its sign. The latter cannot be derived from experiments on linear light scattering, which in accordance with Eqs. (12) and (13) depends on the square of the anisotropy. Thus, we have here a new method of determining the sign of the optical anisotropy of microsystems.

Since the optical anisotropy of molecules is not large ($\alpha_{\parallel} - \alpha_{\perp}$ being of the order of 10^{-24} cm³), the achievement of optical saturation in molecular liquids would demand the use of a laser field of 10^5 esu. Such strong fields cause optical breakdown, or

other anomalies detrimental to the liquid,^{4,5} before saturation is reached. The situation is entirely different in polymer and colloid solutions, where microsystems about 100 Å in size present optical anisotropies of at least 10^{-18} cm³, permitting to attain optical saturation at electric fields strengths of as little as 10^2 esu. Thus, in macromolecular and colloidal substances, not only nonlinear changes in scattered intensity^{3,7} but also saturation scattering can be measured by recurring to usual laser technique accessible in most laboratories.

The author thanks Professor C. T. O'Konski, Professor R. M. Herman, and Dr. J. R. Lalanne for their interesting and fruitful discussions on the present topics while staying at this Department. Thanks are also due to K. Flatau, M.Sci., for the English version.

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