Reprinted from JOURNAL OF COLLOID AND INTERFACE SCIENCE, Volume 34, No. 2, October 1970


# Optical Anisotropy Determinations for Rigid Particles from Rayleigh Light-Scattering Measurements at Optical Saturation

STANISŁAW KIELICH

*Institute of Physics, A. Mickiewicz University, Poznań, Grunwaldzka 6, Poland*

Received March 10, 1970; Accepted May 18, 1970

In suspensions of asymmetric particles, nonlinear changes in the intensity components of light scattered in the presence of an intense laser beam or self-induced changes in scattered laser light components are studied for various polarizations of the laser beam. Quantitative analysis is performed for all four intensity components of the scattered light (vertical $V_v$, horizontal $H_h$, and cross components, $V_h$ and $H_v$) for an arbitrary degree of optical reorientation of the particles, with applications extending from weak reorientation to saturation, when all the particles are aligned in the oscillation direction of the electric vector if the beam is linearly polarized or in the propagation direction of the beam if the latter is unpolarized or circularly polarized. For these two limiting cases, simple relations between the variations $\delta V_v$, $\delta V_h$, $\delta H_v$, and $\delta H_h$ for various polarizations of the laser beam are proposed, making possible direct determinations of the sign and value of the optical anisotropy of particles as well as decisions whether they are cigar-like or disk-like in shape. Moreover, the nonlinear variations in the vertical component $V_v$ are shown to depend on the degree of optical reorientation of the particles in the same way as the optical birefringence induced by laser light.

## INTRODUCTION

Investigations of light scattering have at present attained the status of a fundamental, unfailing method for determining the size and shape of macromolecules and colloid particles (1, 2). The general availability of the laser technique in laboratories nowadays has contributed to rendering light scattering an increasingly potent tool in establishing the properties of particles, especially their optical anisotropy and nonlinear deformation (3). The electric vector of a laser beam causes not only partial (weak or intermediate) reorientation[1] of particles in suspension (3) but can moreover achieve their complete orientational ordering—an effect known as saturation of optical reorientation (4). In many a case, optical reorientation of the particles presents advantages as compared to the hitherto applied electric reorientation (5, 6), primarily in experiments on electrically conducting particles (polyelectrolytes, biopolymers, metal colloids).

From a quantitative point of view, the scattered light is commonly described by separating into scattered intensity components with vertically oscillating electric vectors $V_v$, $V_h$, $V_u$ and horizontally oscillating electric vectors $H_v$, $H_h$, $H_u$ (the subscripts $v$, $h$, and $u$ indicate, respectively, that

[1] We use the term "reorientation" (as distinct from natural random orientation and from the weak orienting effect of the probe beam) to denote the angular effect of the external field on the particles. We avoid using the word "ordering," since it can mean a translational as well as an angular change in the natural, random distribution of the spatial and angular coordinates of the particles. Thus, the prefix "re-" indicates the action of a strong external field.

the incident light is vertically polarized, horizontally polarized, or unpolarized (1, 2)).

We assume here that the linear dimensions of the particles are less than the incident wavelength $\lambda = 2\pi c/\omega$ (with $\omega$ the circular oscillation frequency of the wave and $c$ the velocity of light in vacuum) and that they are so rigid as to exhibit only linear optical polarizability $a_{\parallel}^{\omega}$ along their symmetry axis and $a_{\perp}^{\omega}$ perpendicularly to it. It is usual to describe the anisotropy of linear polarizability of an axially symmetric particle by means of the dimensionless parameter:

$$\kappa_{\omega} = (a_{\parallel}^{\omega} - a_{\perp}^{\omega})/3a_{\omega}, \quad [1]$$

where $a_{\omega} = (a_{\parallel}^{\omega} + 2a_{\perp}^{\omega})/3$ is the mean optical polarizability of the particle at frequency $\omega$ of the incident light wave.

For the case of light scattering by randomly oriented small particles we have the well-known formulas (1) (at unit incident intensity, and when observation of the scattered light is performed perpendicularly to the direction of the incident beam):

$$V_v = (\omega/c)^4 \rho a_{\omega}^2 (1 + 4\kappa_{\omega}^2/5),$$
$$V_h = H_v = H_h = (3/5)(\omega/c)^4 \rho a_{\omega}^2 \kappa_{\omega}^2, \quad [2]$$

$\rho$ denoting the mean number density of scattering particles in the medium.

Whereas the vertical component $V_v$ is experimentally apparent in the case of scattering both by isotropic particles and by anisotropic particles, the cross components $V_h$ and $H_v$ as well as the horizontal component $H_h$ appear only in scattering by anisotropic particles. When ellipsoidal particles are small, the components $V_h$, $H_v$, and $H_h$ satisfy the complete Rayleigh-Krishnan reciprocity relation (1, 2).

In the case of light scattering by large particles, the intensity components [2] depend moreover on appropriate form factors (1, 2), which we shall not take into consideration explicitly in this paper.

The expressions [2] are of a form making possible determinations of the mean polarizability $a_{\omega}$ of the particle or determinations of the square of its optical anisotropy [1]. Hence, investigation of usual Rayleigh scattering provides information only regarding the absolute value $|\kappa_{\omega}|$ of the anisotropy but not regarding its sign. Information as to the sign of the optical anisotropy of the particle can be gained from investigations of light scattering in the presence of saturation of optical reorientation (4) or of electric reorientation (complete alignment) (7).

In this paper, we shall concentrate on certain new procedures of determining the sign and value of the optical anisotropy of asymmetric rigid particles from measurements of nonlinear changes in scattered light intensity. We propose the performing of such measurements by two methods: (1) using a weak probe beam of frequency $\omega$ and, concomitantly, an independently applied intense laser beam of frequency $\omega_L$, and measuring the changes in scattered intensity of frequency $\omega$ caused by the action of the laser beam on the suspension; or (2) using only an appropriately intense laser beam and measuring the self-induced changes in scattered intensity of frequency $\omega_L$. In either method, three cases will be considered: the laser beam can be linearly polarized, circularly polarized, or unpolarized.

## THEORETICAL CONSIDERATIONS

Particles in suspension in an isotropic medium are oriented randomly in the absence of an external field. When the system is acted on by a reorienting agent, the various intensity components of scattered light [2] undergo an increase or reduction according to the shape of the particles and the conditions of the experiment. In our previous paper (3), the reorienting agent was the electric field of a linearly polarized laser beam, and the degree of reorientation caused by it was assumed, for simplicity, as not very considerable, so that the changes in scattered components [2] could still be expressed as a power series in the intensity $I_L$. Here, we shall no longer maintain these restrictions. We shall be considering the laser beam of intensity $I_L$ as polarized vertically ($I_L^v$) or horizontally ($I_L^h$) or as unpolarized ($I_L^u$), and shall accordingly provide the scattered components [2] with a superscript $v$, $h$, or $u$. For instance, $V_h^u$ stands for the *vertical* scattered component obtained with *horizontally* polarized incident light in the presence of strong *unpolarized* laser light. Essentially, we shall be admitting the laser intensity $I_L$ as sufficiently large to produce a high degree of reorientation (alignment) of particles in the medium or even a state of saturation of their optical reorientation (complete alignment). The degree of reorientation for a particle in the optical electric field $\mathbf{E}(\omega_L)$ of a laser wave oscillating at frequency $\omega_L$ and having intensity $I_L = |\mathbf{E}(\omega_L)|^2/2$, is described by the parameter

$$q_L = |a_\parallel^{\omega_L} - a_\perp^{\omega_L}| I_L/2kT, \qquad [3]$$

the value of which depends on the optical anisotropy of the particle, the intensity $I_L$, and the absolute temperature $T$. Weak reorientation, $q_L \ll 1$, occurs when the optical anisotropy $|a_\parallel^{\omega_L} - a_\perp^{\omega_L}|$ is small, the intensity $I_L$ low, or the temperature high. Inversely, strong reorientation, $q_L > 1$, requires a large optical anisotropy of the particle, a high laser intensity, or low temperatures. The results obtained by the previously applied method (3) (the changes in scattered components) will be expressed after Scheludko and Stoylov (6) as relative variations of the scattered components [2], thus, *e.g.*, $\delta V_h^u = (V_h^u - V_h)/V_h$, in each of the three cases. We shall suppose that observation of scattered light is carried out perpendicularly to the direction of propagation of the probe light beam, which is also the propagation direction of the intense reorienting laser beam (the two beams are made to run parallel to each other and along the $z$-axis, Fig. 1). The probe light frequency $\omega$ and laser frequency $\omega_L$ have to differ sufficiently that the experimenter can distinguish light scattered at $\omega$ with respect to the strong laser light $\omega_L$.

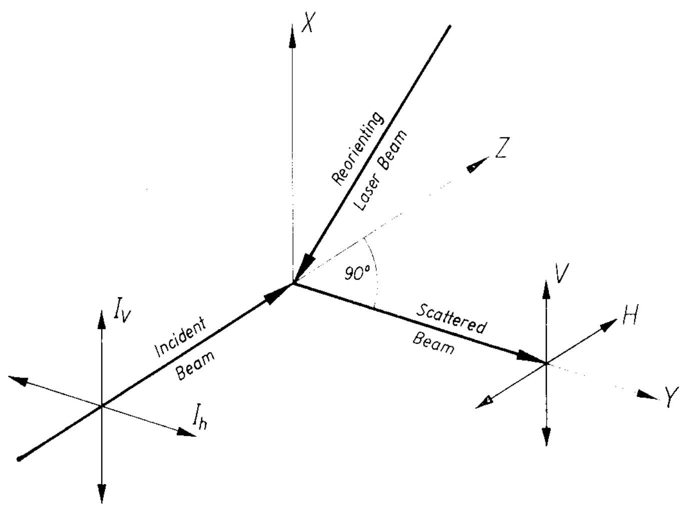


FIG. 1. The probe beam is supposed to propagate along the $z$-axis with electric vector $\mathbf{E}(\omega)$ oscillating in the $xy$-plane (the direction of electric oscillations is assumed to define the direction of polarization of light). The $yz$-plane, in which the probe ray and scattered ray lie, defines a horizontal plane in which observation of the scattered light is supposed to be performed at an angle of 90° to the incident probe beam. $I_v$ and $I_h$ are intensities of, respectively, vertically and horizontally polarized incident probe light. $V$ and $H$ are, respectively, the vertical and horizontal components of the scattered light. The intense laser beam of intensity $I_L$ which causes the reorientation of scattering particles can be chosen to propagate in any direction, so as to provide the most favorable conditions for observation.

*a. Vertically Polarized Laser Wave.* In the case when the laser beam causing reorientation of the particles is vertically polarized with intensity $I_L^v$, the scattered light intensity components [2] undergo variations which are given by the following formulas:

$$\delta V_v^v(1 + 4\kappa_\omega^2/5) = 4\kappa_\omega \Phi(\pm q_L^v) + 8\kappa_\omega^2[Q(\pm q_L^v) + T(\pm q_L^v)]/5, \quad [4]$$

$$\delta V_h^v = \delta H_v^v = -Q(\pm q_L^v), \quad [5]$$

$$\delta H_h^v = -T(\pm q_L^v), \quad [6]$$

involving certain reorientation functions defining the degree of optical reorientation of the particles (we omit the $v$ and $L$ at $q$):

$$\Phi(\pm q) = [3L_2(\pm q) - 1]/2, \quad [7]$$

$$Q(\pm q) = [15L_4(\pm q) - 15L_2(\pm q) + 2]/2, \quad [8]$$

$$T(\pm q) = [30L_2(\pm q) - 15L_4(\pm q) - 7]/8. \quad [9]$$

The generalized Langevin functions of even order have the following shape for all values of $q$ (4):

$$L_2(\pm q) = \mp 1/2q \pm 1/[2q^{1/2}I(\pm q)],$$
$$L_4(\pm q) = 3/4q^2 \pm (2q \mp 3)/[4q^{3/2}I(\pm q)], \quad [10]$$

and are plotted in Fig. 2. The integrals[2]

$$I(\pm q) = \exp(\mp q)\int_0^{\sqrt{q}} \exp(\pm t^2)\, dt \quad [11]$$

have been tabulated numerically (8–10).

In Eqs. [4]–[11], the upper "plus" sign is for particles with positive optical anisotropy, $a_\parallel^\omega - a_\perp^\omega > 0$. This is the case of cigar-like particles. The lower "minus" sign is for negative optical anisotropy, $a_\parallel^\omega - a_\perp^\omega < 0$, *i.e.*, for disk-like particles. The reorientation functions [7]–[9] are plotted in Fig. 3, where the shape of their dependence on the parameter $q$ is seen to be different for the two kinds of particles. Indeed, $\Phi(+q)$ and $T(+q)$ are always positive and tend steeply to the limiting value $+1$, whereas $\Phi(-q)$ and $T(-q)$ are negative in the entire range of variability of $q$ and tend to the limiting values $-0.5$ and $-0.875$, respectively. The function $Q(+q)$ for small $q$ is negative but undergoes an inversion in sign at $q = 4.6$, when it becomes positive and tends to the value $+1$ at saturation. The function $Q(-q)$ is positive for all values of $q$. These analytical properties of the reorientation functions enable us to form conclusions as to the shape of the scattering particles, *i.e.*, they make it

[2] Integrals of the form $\int_0^x \exp(t^2)\, dt$ up to $x = 10$ are tabulated in reference 10. Integrals $\int_0^x \exp(-t^2)\, dt = (\sqrt{\pi}/2)\,\mathrm{erf}(x)$ are given by the tabulated error function.

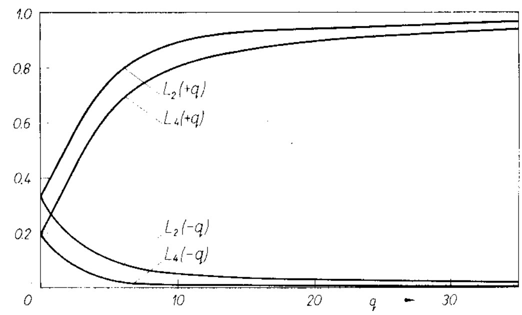


FIG. 2. Even Langevin functions [10], in their dependence on $q$.

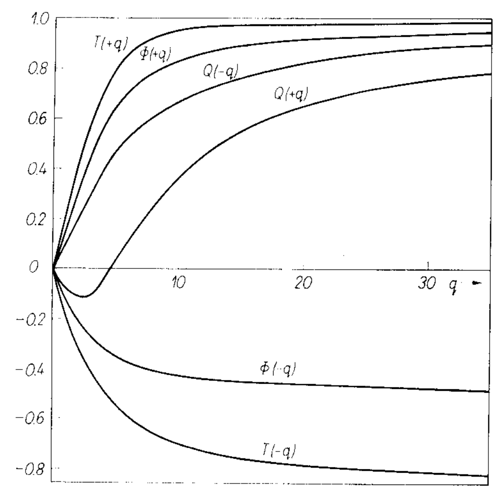


FIG. 3. Reorientation functions [7]–[9], describing the degree of alignment of the particles *versus* the parameter $q$.

possible to decide whether the particles we are dealing with resemble rods or disks.

*b. Horizontally Polarized Laser Wave.* In the case when the laser beam is polarized horizontally with electric oscillations along the $y$-axis, we obtain in place of [4]–[6] the following formulas:

$$\delta V_v^h(1 + 4\kappa_\omega^2/5) = -\kappa_\omega(2 + \kappa_\omega)\Phi(\pm q_L^h) + 3\kappa_\omega^2[Q(\pm q_L^h) + T(\pm q_L^h)]/5, \quad [12]$$

$$\delta V_h^h = \delta H_h^h = -Q(\pm q_L^h), \quad [13]$$

$$\delta H_v^h = -T(\pm q_L^h). \quad [14]$$

The reorientation functions appearing above are given by Eqs. [7]–[9] with $q$ replaced by the parameter $q_L^h$ defined by Eq. [3] with $I_L = I_L^h$. The expressions [12] and [14] still remain valid in the case when the laser beam is incident perpendicularly to the plane of observation (along the $x$-axis, Fig. 1) with its electric vector $\mathbf{E}(\omega_L)$ oscillating parallel to the observed scattered light (along the $y$-axis). If, however, $\mathbf{E}(\omega_L)$ oscillates parallel to the propagation direction of the probe beam ($z$-axis), expression [12] remains unchanged but in place of [13] and [14] we now have:

$$\delta V_h^h = -T(\pm q_L^h), \quad [13a]$$

$$\delta H_v^h = \delta H_h^h = -Q(\pm q_L^h). \quad [14b]$$

We note from Eqs. [12] and [13] that whereas in the case of Eq. [5] the variations in cross components were equal to each other (as in the case of scattering by free particles given by Krishnan's reciprocity relation [2] $H_v = V_h$), they are by no means equal in the case of horizontally polarized laser light. Krishnan's relation is not fulfilled in the cases [13$a$] and [14$b$] either.

*c. Unpolarized Laser Wave.* In the case of an unpolarized laser beam, of intensity $I_L^u = I_L^v + I_L^h$, the scattered light components [2] exhibit the following nonlinear variations:

$$\delta V_v^u(1 + 4\kappa_\omega^2/5) = -\kappa_\omega(2 + \kappa_\omega)\Phi(\mp q_L^u) + 3\kappa_\omega^2[Q(\mp q_L^u) + T(\mp q_L^u)]/5, \quad [15]$$

$$\delta V_h^u = -T(\mp q_L^u), \quad [16]$$

$$\delta H_v^u = \delta H_h^u = -Q(\mp q_L^u). \quad [17]$$

The reorientation functions are still given by Eqs. [7]–[9]; however, we have to take $q = -q_L^u/2$. As a consequence of this, we have here an interchange in sign, so that now particles with positive optical anisotropy are accounted for by the upper "minus" sign, and particles with negative anisotropy by the lower "plus" sign. This interchange in sign is due to the circumstance that unpolarized laser light reorients the particles with their symmetry axis along the propagation direction of the laser light wave, which is at the same time that of the optical axis of the birefringence induced in the medium. Prolate ellipsoidal particles (positive anisotropy) will align themselves with their longer axis (symmetry axis) in the propagation direction, *i.e.*, perpendicular to the plane of oscillations of the electric vector of the laser wave (this plane then contains the two shorter axes of the particle). Oblate ellipsoidal particles (negative anisotropy) will reorient in a manner to bring their shorter axis (symmetry axis) into line with the propagation direction and their longer axes into the oscillation plane. These considerations, as well as Eqs. [15]–[17], remain valid for the case of circularly polarized laser light of intensity $I_L^c = I_+ + I_-$, with $I_+$ and $I_-$ denoting, respectively, the intensities for the two senses of circular polarization of light.

From the expressions [16] and [17], Krishnan's relation is not fulfilled for the case of an unpolarized laser beam propagating parallel to the probe beam ($z$-axis), and it would not be fulfilled for an unpolarized laser beam propagating in the direction of observation of scattered light. On the other hand, in the case of an unpolarized laser beam incident perpendicularly to the plane of observation (along the $x$-axis), Krishnan's relation is fulfilled, since now instead of the expressions [15]–[17] we obtain expressions of the form [4]–[6] on changing the upper subscripts from $v$ to $u$ and putting $q_L^v = -q_L^u$.

The essence of subsections ($a$)–($c$) is resumed in the following statement[3]: Krishnan's relation is fulfilled when the optical axis of the anisotropy induced in the suspension by laser light is perpendicular to the plane of observation, but is not fulfilled if the induced optical axis lies in the plane of observation (thus, e.g., along the incident probe or scattered ray).

For particles of low optical anisotropy one is justified in omitting terms in $\kappa_\omega^2$ in Eqs. [4], [12], and [15]. With satisfactory accuracy, the following simple formulas now express the relative changes in vertical components:

$$\delta V_v^v = \pm 4 \mid \kappa_\omega \mid \Phi(\pm q_L^v), \qquad [4a]$$

$$\delta V_v^h = \mp 2 \mid \kappa_\omega \mid \Phi(\pm q_L^h), \qquad [12a]$$

$$\delta V_v^u = \mp 2 \mid \kappa_\omega \mid \Phi(\mp q_L^u), \qquad [15a]$$

where $\mid \kappa_\omega \mid$ is the absolute value of the optical anisotropy [1].

## APPLICATIONS AND DISCUSSION

The Langevin functions [10] are plotted in Fig. 2 for arbitrary values of $q$. In practice, however, it is often useful to know these functions for very small and very large values of $q$, for example, for $q \ll 1$ and $q \geqq 10$. We shall consider the two cases separately:

*a. Weak Reorientation.* If reorientation of particles is not very considerable ($q \ll 1$), the Langevin functions [10] can be expanded in the power series:

$$L_2(\pm q) = 1/3 \pm 4q/45 + 8q^2/945 \mp \cdots,$$
$$L_4(\pm q) = 1/5 \pm 8q/105 + 16q^2/1575 \mp \cdots, \qquad [18]$$

so that the reorientation functions [7]–[9] can be written in a satisfactory approximation as:

$$\Phi(\pm q) = \pm 2q/15 + 4q^2/315 \mp \cdots,$$
$$Q(\pm q) = \mp 2q/21 + 4q^2/315 \pm \cdots, \qquad [19]$$
$$T(\pm q) = \pm 4q/21 + 4q^2/315 \mp \cdots.$$

Taking only the term linear in $q$, we obtain with regard to Eqs. [4a], [12a], and [15a] the following relations:

$$\delta V_v^v/q_L^v = -2\delta V_v^h/q_L^h = 2\delta V_v^u/q_L^u = 8 \mid \kappa_\omega \mid/15. \qquad [20]$$

Consequently, at weak reorientation of the particles, investigation of nonlinear changes in vertical components [20] provides information regarding only the absolute value $\mid \kappa_\omega \mid$ of the optical anisotropy. An unequivocal decision as to the sign of the anisotropy is reached from investigations of nonlinear changes in the horizontal and cross components, since by Eqs. [5], [6], [13], [14], [16], and [17] we get in a linear approximation the relations:

$$2\delta V_h^v/q_L^v = 2\delta H_v^v/q_L^v = -\delta H_h^v/q_L^v = 2\delta V_h^h/q_L^h = 2\delta H_h^h/q_L^h = -\delta H_v^h/q_L^h = -2\delta H_v^u/q_L^u = -2\delta H_h^u/q_L^u = +\delta V_h^u/q_L^u = \pm 4/21, \qquad [21]$$

where $+4/21$ is for positive optical anisotropy (cigar-like particles) and $-4/21$ is for negative anisotropy (disks).

*b. Complete Alignment.* When reorientation of the particles is very considerable, as is the case if $q \geqq 10$, the Langevin functions

[3] The fact was established by Krishnan for scattering by colloidal suspensions of graphite sols in the presence of an intense magnetic field. (Cited by us from the paper of S. P. Tewarson and Vachaspati, *Kolloid-Z. Z. Polym.* **213**, 131 (1966), as Krishnan's papers were not available in the original.)

[10] are given by the asymptotic expressions:

$$L_2(+q) = 1 - 1/q + O(1/q^2),\quad L_4(+q) = 1 - 2/q + O(1/q^2), \qquad [22]$$

$$L_2(-q) = 1/2q + O(1/q^2),\quad L_4(-q) = 3/4q^2 + O(1/q^2). \qquad [23]$$

If reorientation of all the particles attains saturation ($q \to \infty$, optical saturation), the Langevin functions [22] tend to a maximal value of 1; so do the reorientation functions [7]–[9]:

$$\Phi(+\infty) = Q(+\infty) = T(+\infty) = 1. \qquad [24]$$

On the other hand, the Langevin functions [23] tend to 0 at $q \to \infty$ and the reorientation functions [7]–[9] take the following limiting values:

$$\Phi(-\infty) = -1/2, \qquad Q(-\infty) = 1, \qquad T(-\infty) = -7/8. \qquad [25]$$

Completely aligned cigar-like particles, with regard to [24] and [25] as well as to [1]–[6] and [12]–[17], yield the following variations in scattered components:

$$\delta V_v^{\,v} = -2\delta V_v^{\,h} = 4\delta V_v^{\,u} = 4|\kappa_\omega|, \qquad [26]$$

$$\delta V_h^{\,v} = \delta H_v^{\,v} = \delta H_h^{\,v} = \delta V_h^{\,h} = \delta H_h^{\,h} = \delta H_v^{\,h} = \delta H_v^{\,u} = \delta H_h^{\,u} = -1, \qquad [27]$$

$$\delta V_h^{\,u} = 7/8.$$

Completely aligned disk-like particles yield:

$$\delta V_v^{\,v} = -2\delta V_r^{\,h} = \delta V_v^{\,u} = 2|\kappa_\omega|, \qquad [28]$$

$$\delta V_h^{\,v} = \delta H_v^{\,v} = \delta V_h^{\,u} = \delta H_v^{\,u} = \delta H_h^{\,u} = \delta H_h^{\,h} = \delta V_h^{\,h} = -1, \qquad [29]$$

$$\delta H_h^{\,v} = \delta H_v^{\,h} = 7/8.$$

On inspection of Eqs. [26] and [28] one sees that, as was the case for weak reorientation (relations [20]), investigation of the vertical components at optical saturation makes possible the determination of the absolute value $|\kappa_\omega|$ only. But the study of optical saturation of variations in cross and horizontal scattered components $\delta V_h^{\,u}$, $\delta H_v^{\,h}$, and $\delta H_h^{\,v}$ which, as seen from Eqs. [27] and [29], differ in sign for cigar-shaped and diskshaped particles, enables us to determine the shape of the particles and the sign of their optical anisotropy. Lalanne and Bothorel [11] proposed a laser method of rapid measurements of these anisotropic components, which, however, in molecular liquids, revealed no well-defined nonlinear variations.

Optical saturation of the other components appearing in Eqs. [27] and [29] is a source of no information, since the relative variations amount to $-1$ for cigars and disks alike.

Similar results for the variations $\delta V_v^{\,\infty}$, $\delta H_v^{\,\infty} = \delta V_h^{\,\infty}$, and $\delta H_h^{\,\infty}$ caused by electric saturation have been recently derived by Stoylov and Sokerov (7) for needle-like colloid particles.

*c. Relation to Optically Induced Birefringence.* It is interesting to note that the nonlinear changes in vertical scattered components in the form of Eqs. [4*a*], [12*a*], and [15*a*] are defined by the reorientation function $\Phi(\pm q)$, which at the same time defines the optical birefringence induced in a colloidal medium by strong laser light (3, 12). In fact, the reorientation function $\Phi(\pm q)$ in the form [7] with Langevin function $L_2(\pm q)$ given by [10] represents a special case (particularized to nondipolar particles) of the Kerr effect reorientation function discussed by O'Konski *et al.* (8) for cigar-shaped particles, by Shah (9) for disk-like ones, and by Yoshioka *et al.* (10) for both cases.

In a medium, strong laser light induces optical birefringence, and the refractive index now takes different values according to the direction in the medium. Supposing the laser wave to propagate along the $z$-axis (Fig. 1), the nonlinear changes in refractive indices measured with the probe light in various directions, for laser light polarized vertically (along the $x$-axis), are obtained in the form (12):

$$\delta n_{xx}^{v} = -2\delta n_{yy}^{v} = -2\delta n_{zz}^{v} = \pm(4\pi/n)\rho a_\omega |\kappa_\omega| \Phi(\pm q_L^{\,v}); \qquad [30]$$

for laser light polarized horizontally (along the $y$-axis) as:

$$\delta n_{yy}^{h} = -2\delta n_{xx}^{h} = -2\delta n_{zz}^{v} = \pm(4\pi/n)\rho a_{\omega} \mid \kappa_{\omega} \mid \Phi(\pm q_L{}^{h}); \quad [31]$$

and, for unpolarized or circularly polarized laser light as:

$$\delta n_{zz}^{u} = -2\delta n_{xx}^{u} = -2\delta n_{yy}^{u} = \pm(4\pi/n)\rho a_{\omega} \mid \kappa_{\omega} \mid \Phi(\mp q_L{}^{u}). \quad [32]$$

Here $n$ is the index in the absence of strong laser light.

By Eqs. [30] and [31], the optical birefringence induced in the medium by intense laser light, vertically polarized, results in the form:

$$\delta n_{xx}^{v} - \delta n_{yy}^{v} = \pm(6\pi/n)\rho a_{\omega} \mid \kappa_{\omega} \mid \Phi(\pm q_L{}^{v}), \quad [33]$$

or for horizontally polarized laser light:

$$\delta n_{yy}^{h} - \delta n_{xx}^{h} = \pm(6\pi/n)\rho a_{\omega} \mid \kappa_{\omega} \mid \Phi(\pm q_L{}^{h}), \quad [34]$$

provided that the probe light beam employed for measuring the birefringence also propagates along the $z$-axis (Fig. 1).

From Eq. [32], since unpolarized or circularly polarized light induces anisotropy with the optical axis lying in the propagation direction of the intense laser light wave, no birefringence is apparent if the probe beam is made to propagate in the same direction ($z$-axis). For the induced birefringence to be measurable, the measuring beam has to propagate along the $x$-axis or $y$-axis, which is the case if it is perpendicular to the intense laser beam employed for inducing the birefringence. Experimentally, however, such measurements are not effective, because the active optical path where the medium is rendered birefringent is restricted to the diameter of the laser beam.

With regard to Eqs. [30]–[32], we have the following ratios:

$$\delta n_{xx}^{v}/\delta n_{xx}^{u} = -2\Phi(\pm q_L{}^{v})/\Phi(\mp q_L{}^{u}),$$
$$\delta n_{yy}^{h}/\delta n_{yy}^{u} = -2\Phi(\pm q_L{}^{h})/\Phi(\mp q_L{}^{u}), \quad [35]$$

which at optical saturation as given by Eqs. [24] and [25] take the values 4 for cigar-like particles and 1 for disk-like ones. Thus, the relations [35] can also be said to permit some determinations of particle shape.

Laser-induced birefringences [33] and [34] and the ratios [35] have hitherto been investigated only in molecular liquids and solutions, where, obviously, optical reorientation is rather weak, though sufficient for recording in an approximation linear in $q$ (13).

Laser technique makes it possible to induce optical birefringence without applying electrodes—a circumstance of considerable advantage in anisotropy studies on biopolymers and colloids, since in this way we avoid the destructive phenomena (electrophoresis, electric conductivity, dielectric breakdown) which accompany the use of a dc electric field. Moreover, in addition to optical birefringence, an intense laser beam induces nonlinear changes in the angle of rotation of the polarization plane[4] of optically active substances (14), as already observed by Tinoco (15) in poly($\gamma$-benzyl glutamate) in ethylene dichloride under the influence of a dc electric field.

*d. Self-Induced Variations.* In the preceding sections, we have been considering the experimental setup when light scattered at frequency $\omega$ underwent a change owing to reorientation of scattering asymmetric particles in suspension by the electric field of an intense laser beam of different frequency $\omega_L$. Obviously, it is also feasible to consider the variant when a laser beam is used alone. If the beam is not very intense, its light will undergo usual Rayleigh scattering on the randomly oriented particles. If, however, it is sufficiently strong, it will cause "self-induced" reorientation of the particles; the scattering medium as a whole then becomes anisotropic and nonlinear, meaning that the

[4] The relative change in optical rotation angle $\Theta$ due to intense laser light (circularly polarized or unpolarized) is $\delta\Theta = \kappa_g{}^{\omega}\Phi(\mp q_L)$, where $\kappa_g{}^{\omega} = (g_{\parallel}{}^{\omega} - g_{\perp}{}^{\omega})/(g_{\parallel}{}^{\omega} + 2g_{\perp}{}^{\omega})$ denotes the gyration anisotropy of the particle (14).

intensity of light scattered at frequency $\omega_L$ becomes a nonlinear function of the incident intensity $I_L$ of the laser beam. In the case when this beam is vertically polarized, the observable changes in scattered components are:

$$\delta V_v(1 + 4\kappa_{\omega_L}^2/5) = 4\kappa_{\omega_L}\Phi(\pm q_L^v) + 8\kappa_{\omega_L}^2[Q(\pm q_L^v) + T(\pm q_L^v)]/5, \quad [36]$$

$$\delta H_v = -Q(\pm q_L^v), \quad [37]$$

with $\kappa_{\omega_L}$ now denoting the optical anisotropy of the particle at laser frequency $\omega_L$.

In the case when the beam is polarized horizontally, one will measure only the following variations of the two, mutually equal components:

$$\delta V_h = \delta H_h = -Q(\pm q_L^h). \quad [38]$$

Finally, if the beam is unpolarized, the measurable changes in scattered light components are:

$$\delta V_u(1 + 7\kappa_{\omega_L}^2/5) = -\kappa_{\omega_L}(2 + \kappa_{\omega_L})\Phi(\mp q_L^u) + 3\kappa_{\omega_L}^2 Q(\mp q_L^u)/5, \quad [39]$$

$$\delta H_u = -Q(\mp q_L^u). \quad [40]$$

The expressions [36]–[40], like those of subsections (*a*) and (*b*), are applicable to both weak reorientation and self-induced optical saturation.

*e. Experimental Prospects.* The laser technique is now generally accessible in physicochemical laboratories (16). This paves the way for the program of rapid and easy experimental studies of light scattering by colloid systems proposed in this paper. Clearly, in choosing the laser source for the reorientation of particles in suspensions, one will have to provide for a laser pulse of sufficiently long duration, so that alignment of particles can become steady (the so-called relaxation time of birefringence $\tau_B$ (3, 17) relevant for the optical orientation of particles is one-third of Debye's dielectric relaxation time, $\tau_D = 3\tau_B$). For moderately bulky macromolecules and particles of about 100 Å in size, the birefringence relaxation time ranges (17) from $10^{-6}$ to $10^{-8}$ sec, permitting the use of pulsed lasers with a pulse duration of $10^{-4}$–$10^{-7}$ sec and high power wave conveying an electric field strength of at least 100 esu (or as much as $10^4$ esu (16) in the focused beam). Since the optical anisotropy of small particles 100 Å in size is of the order of $10^{-18}$ cm$^3$, the reorientation parameter [3] is of order $q_L = 10^{-5} I_L$ permitting the optical saturation of the reorientation functions plotted in Fig. 1 by means of a laser beam with intensity $I_L$ of the order $10^5$–$10^6$ esu.

Larger particles require more time to reorient, so that lasers with millisecond light pulses will have to be used (16). Reorientation of very large particles, *e.g.*, of biological origin, will demand continuously operating lasers, of power not excessively large but providing an electric field strength sufficient for complete alignment of the particles. Thus, in collagen, TMV, poly($\gamma$-benzyl glutamate), and other large particles, the reorientation parameter [3] being of the order of $(10^{-1}$–$10^{-2})I_L$ is high enough to allow complete optical alignment with the electric fields of the light beams of strong, continuously operating gas and molecular lasers (16).

Although the theory of nonlinear Rayleigh light scattering proposed in this paper is strictly applicable to particles of dimensions not exceeding $\lambda/20$ and does not hold for very large particles, it nevertheless can be applied with satisfactory accuracy to larger particles owing to the fact that the reorientation functions [7]–[9] introduced by us define relative changes in scattered components which are but weakly dependent on particle size. The effect of size on the reorientation functions becomes more strongly apparent for still larger particles or for particles of the order of the applied light wavelength. Indeed, nothing stands in the way of extending our theory to the case of very large particles in a manner to include form factors, as done in the usual Rayleigh scattering (1, 2); the results, though, are mathematically involved and not well legible (6). It would rather seem that at this stage of nonlinear light-scattering studies, the degree of approximation maintained here may prove sufficient to enable us to grasp the essence of the new phenomenon. It is our hope that these studies will develop rapidly, since they lead in a simple way to knowledge of the sign and value of the optical anisotropy as well as of the shape of macromolecules and particles permitting comparisons with data obtained by previously employed methods (1, 2, 17, 18).

ACKNOWLEDGMENT

The author wishes to thank K. Flatau, M.Sc., for his stimulating discussions while the paper was being translated into English.

REFERENCES

1. Sadron, Ch., *J. Polymer Sci.* **12,** 69 (1954).
2. Kerker, M., *Ind. Eng. Chem.* **60,** 30 (1968).
3. Kielich, S., *J. Colloid Interface Sci.* **27,** 432 (1968); *ibid.* **28,** 214 (1968) and references therein.
4. Kielich, S., *Appl. Phys. Lett.* **13,** 371 (1968).
5. Wippler, C., and Benoit, H., *Makromol. Chem.* **13,** 7 (1954); Jennings, B. R., and Jerrard, H. G., *J. Chem. Phys.* **44,** 1291 (1966).
6. Scheludko, A., and Stoylov, S., *Kolloid Z. Z. Polym.* **199,** 36 (1964); Stoylov, S., *Collect. Czech. Chem. Commun.* **31,** 2866, 3052 (1966).
7. Stoylov, S., and Sokerov, S., *Bulg. Acad. Sci. Commun. Chem.* **2,** 191 (1969).
8. O'Konski, C. T., Yoshioka, K., and Orttung, W. H., *J. Phys. Chem.* **63,** 1558 (1959).
9. Shah, M. J., *J. Phys. Chem.* **67,** 2215 (1963).
10. Matsumoto, M., H. Watanabe, H., and Yoshioka, K., *Sci. Pape. Coll. Gen. Educ. Univ. Tokyo* **17,** 173 (1967).
11. Lalanne, J. R., and Bothorel, P., *C. R. Acad. Sci., Paris, Sér. B* **263,** 693 (1966); Lalanne, J. R., *C. R. Acad. Sci., Paris, Sér. B* **265,** 1181 (1967).
12. Kielich, S., *J. Colloid Interface Sci.* **33,** 142 (1970).
13. Paillette, M., *C. R. Acad. Sci., Paris,* **262,** 264 (1966); also Thèse, Paris, 1969.
14. Atkins, P. W. and Woolley, R. G., *J. Chem. Soc., A* **1969,** 515; Kielich, S., *Opt. Commun.* **1,** 129 (1969).
15. Tinoco, I., Jr., *J. Am. Chem. Soc.* **81,** 1540 (1959).
16. Haught, A. F., *Ann. Rev. Phys. Chem.* **19,** 343 (1968); Kaczmarek, F., *Postpy Fiz.* **20,** 201 (1969).
17. O'Konski, C. T., *Encycl. Polym. Sci. Technol.* **9,** 551 (1968); Krause, S., and O'Konski, C. T., *Biopolymers* **1,** 503 (1963).
18. Stoylov, S., *Advan. Interface Colloid Sci.* (1970).