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Orientation of Colloid Particles in Laser Optical Fields and Its Effect on Light Scattering by Colloids

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A simple theory of nonlinear scattered light intensity variations due to orientation of colloid particles in the optical electric field of laser beams is proposed. On the example of the depolarization ratio, these variations are shown to be so considerable as to provide a source of information, by easy measurements, on the size and shape of the particles as well as the sign of their optical anisotropy.

INTRODUCTION

Previously (1, 2), molecules by undergoing orientation in the optical field of a laser beam were shown to cause nonlinear changes in the scattered light intensity. In molecular gases (1) and liquids (2) these variations are small but accessible to experimental detection by present laser techniques, which provide light beams of sufficiently high intensity. It is our aim here to show that colloidal particles in suspension undergo considerable optical orientation giving rise to such strong variations of the scattered light intensity as to be accessible to observation even with the use of a low-power laser.

The replacement of a dc or ac electric (3–7) or magnetic (1, 3, 5) field by an electric laser field as orienting factor can present various advantages by eliminating, for example, certain electrical effects which perturbate the optical measurements. In the experimental study of different optical nonlinearities of colloidal systems (optical birefringence, nonlinear optical activity, and dichroism, etc.), parametric lasers will prove particularly useful as their power, though small, suffices for producing measurable effects whereas the light they emit can be easily tuned to a wavelength for which the colloid exhibits transparency. Here, we shall propose a concise theory leading to a simple formula for the nonlinear change in depolarization ratio making possible numerical evaluations of the variations to be expected in gold and silver aqueous colloids.

THEORETICAL

Let us consider an isotropic medium of dielectric permittivity ϵ_0 containing in suspension ellipsoidal particles of volume v having permittivities ϵ_1, ϵ_2, ϵ_3 along the three principal axes. Assume a light wave incident on the system, with weak intensity $I_1 = E_{01}^2/2$ and carrying an electric field $\mathbf{E}_1 = \mathbf{E}_{01} \cos \omega_1 t$ oscillating at frequency ω_1 and inducing in the particles a dipole moment $\mathbf{m}$ oscillating at the same frequency. If the particle's linear dimensions are small as compared with the light wavelength ($2r < \lambda/\pi n$), the induced dipole moment component can be written in the form

$$m_\sigma^{\omega_1} = v g_{\sigma\tau}^{\omega_1} E_{1\tau}, \qquad [1]$$

with the polarizability tensor $g_{\sigma\tau}^{\omega_1}$ at frequency ω_1 (per unit volume) having the principal values (3, 9)

$$g_i^{\omega_1} = \frac{(\epsilon_i^{\omega_1} - \epsilon_0^{\omega_1})\epsilon_0^{\omega_1}}{4\pi[\epsilon_0^{\omega_1} + (\epsilon_i^{\omega_1} - \epsilon_0^{\omega_1})L_i]}, \qquad [2]$$

where the L_i ($i = 1, 2, 3$) are parameters of shape of the particle ($L_1 + L_2 + L_3 = 1$).

Assume moreover another light beam of light intensity $I_2 = E_{02}^2/2$ incident on the scattering system, its rapidly oscillating (at

frequency ω_2) electric field $\mathbf{E}_2 = \mathbf{E}_{02} \cos \omega_2 t$ causing orientation of the colloid particles. In the field of this light beam, the particles gain the potential energy (1)

$$u(\Omega, \mathbf{E}_2) = -\tfrac{1}{2} v g_{\sigma\tau}^{\omega_2} E_{2\sigma} E_{2\tau}, \qquad [3]$$

where the principal values of the polarizability tensor $g_{\sigma\tau}^{\omega_2}$ of the particle at frequency ω_2 are given by Eq. [2] on the substitution therein of ω_1 by ω_2.

The intensity of light scattered by the system (of number density ρ of the particles) can be approximately expressed by the dipole scattering tensor (1)

$$I_{\sigma\tau}^{S} = \frac{\rho}{c^4} \int \overline{\frac{d^2 m_\sigma}{dt^2} \frac{d^2 m_\tau}{dt^2}}^{t} f(\Omega, I_2)\, d\Omega, \qquad [4]$$

where

$$f(\Omega, I_2) = \frac{\exp\left\{-\dfrac{u(\Omega, I_2)}{kT}\right\}}{\displaystyle\int \exp\left\{-\frac{u(\Omega, I_2)}{kT}\right\} d\Omega} \qquad [5]$$

is a function of the statistical orientation of the particles in the presence of strong light (intensity I_2), and $u(\Omega, I_2)$ is the time-averaged potential energy of Eq. [3], i.e., $u(\Omega, I_2) = \overline{u(\Omega, \mathbf{E}_2)}^{t}$ for optical frequencies ω_2.

Let us furthermore assume for simplicity that the incident light propagates along the laboratory Y-axis, its electric vector $\mathbf{E}_1$ oscillating in the direction of observation of scattered light (X-axis). We assume that the strong light beam is propagating in any direction of the (horizontal) XY-plane, with the electric vector $\mathbf{E}_2$ oscillating along the (vertical) Z-axis. With the preceding experimental array, and assuming moreover that the particles have the symmetry of rotation ellipsoids $\epsilon_1 = \epsilon_2 \neq \epsilon_3$ and $L_1 = L_2 \neq L_3$, we obtain by [1]–[5] for the vertical and horizontal components of scattered light intensity, respectively (see Appendix),

$$V_h = V_h^{\omega_1} \sum_{n=0}^{\infty} a_n v^n y_{\omega_2}^n I_2^n, \qquad [6]$$

$$H_h = H_h^{\omega_1} \sum_{n=0}^{\infty} b_n v^n y_{\omega_2}^n I_2^n, \qquad [7]$$

where the intensity components in the absence of intense light have been defined in the well-known manner:

$$V_h^{\omega_1} = H_h^{\omega_1} = \frac{\rho v^2}{15} \left(\frac{\omega_1}{c}\right)^4 (g_3^{\omega_1} - g_1^{\omega_1})^2 I_1. \qquad [8]$$

The numerical coefficients of the expansions [6] and [7] are

$$a_n = \frac{15}{n!(2n+3)(2n+5)} - \sum_{k=1}^{n} \frac{a_{n-k}}{k!(2k+1)}; \qquad [9]$$

$$b_n = \frac{15}{n!(2n+1)(2n+3)(2n+5)} - \sum_{k=1}^{n} \frac{b_{n-k}}{k!(2k+1)}. \qquad [10]$$

The quantity

$$y_{\omega_2} = \frac{g_3^{\omega_2} - g_1^{\omega_2}}{2kT} \qquad [11]$$

is an orientation parameter of the particle in an intense optical field E_2.

By eqs. [6] and [7], we obtain the following expression for the depolarization ratio of light scattered in the presence of an intense laser beam of intensity I_2:

$$D_h = \frac{V_h}{H_h} = \sum_{n=0}^{\infty} D_h^{(n)} I_2^n, \qquad [12]$$

where

$$D_h^{(n)} = c_n v^n y_{\omega_2}^n \qquad [13]$$

is the depolarization coefficient for n^{th} order scattering, and

$$c_n = \frac{15}{n!(2n+3)(2n+5)} - \sum_{k=1}^{n} \frac{15 c_{n-k}}{k!(2k+1)(2k+3)(2k+5)}. \qquad [14]$$

APPLICATIONS AND DISCUSSION

In the absence of intense light ($I_2 = 0$), the equality [8] is fulfilled as in the case of linear scattering by molecules. If the colloidal scatterer is acted on by light of high intensity I_2, we have by [6] and [7] the

TABLE I

CALCULATED VALUES OF $D_h^{(n)}$ ($n = 1, 2, 3$) FOR GOLD AND SILVER PARTICLES IN WATER

Colloid		g_1	g_3	$\frac{D_h^{(1)}}{v} \times 10^{-12}$	$\frac{D_h^{(2)}}{v^2} \times 10^{-24}$	$\frac{D_h^{(3)}}{v^3} \times 10^{-36}$
Gold in water	a)	0.588	0.975	1.37	1.25	0.78
	b)	0.513	1.891	4.87	15.82	35.03
Silver in water	a)	0.477	0.704	0.80	0.43	0.16
	b)	0.427	1.082	2.31	3.57	3.76

following relative nonlinear variations of vertical and horizontal components:

$$\frac{V_h - V_h^{\omega_1}}{V_h^{\omega_1}} = \sum_{n=1}^{\infty} a_n v^n y_{\omega_2}^n I_2^n, \qquad [15]$$

$$\frac{H_h - H_h^{\omega_1}}{H_h^{\omega_1}} = \sum_{n=1}^{\infty} b_n v^n y_{\omega_2}^n I_2^n, \qquad [16]$$

which can be negative or positive, according to the sign of the molecular orientation parameter [11].

By [12], the nonlinear change in depolarization ratio due to the effect of intense light is

$$\Delta D_h = D_h - D_h^{(0)} = \sum_{n=1}^{\infty} D_h^{(n)} I_2^n. \qquad [17]$$

By [13] in the absence of intense light $D_h^{(0)} = 1$, as in the case of molecular scattering. Since according to Eqs. [13] and [14]

$$D_h^{(1)} = \frac{2}{7} v y_{\omega_2}, \qquad D_h^{(2)} = \frac{8v^2}{147} y_{\omega_2}^2, \qquad D_h^{(3)} = \frac{80v^3}{11319} y_{\omega_2}^3, \cdots, \qquad [18]$$

the nonlinear change in depolarization ratio [17] is positive when the orientational parameter [11] is positive, and vice versa. Consequently, investigation of the changes in depolarization ratio can be a source of information regarding not only the size and shape of the particles but also the sign of their optical anisotropy.

According to Gans (9), gold and silver colloid particles are elongated ellipsoids, with semiaxis ratios ranging from 0.77 to 0.57; the parameters of shape are, respectively,

a) $L_1 = L_2 = 0.365, \quad L_3 = 0.270;$

b) $L_1 = L_2 = 0.4, \quad L_3 = 0.2.$

Table I gives the values of $g_1 = g_2$ and g_3 calculated from Eq. [2] for $\lambda = 6500$ Å as well as those of $D_h^{(n)}/v^n$ calculated from Eq. [13], with the use of the preceding data.

Assuming 300 Å as mean diameter for a gold particle and recurring to Eqs. [17] and [18] and the values in Table I, we obtain for case (*a*) ($L_1 = 0.365$, $L_3 = 0.27$):

$$\Delta D_h^{Au} = 1.9 \times 10^{-5} I_2 + 2.5 \times 10^{-10} I_2^2 + 2.2 \times 10^{-15} I_2^3 + \cdots \qquad [19]$$

For the sake of comparison, we refer to the values resulting for molecules of CS_2 and C_6H_6:

$$\Delta D_h^{CS_2} = 0.3 \times 10^{-10} I_2 + 7.7 \times 10^{-22} I_2^2 + 1.2 \times 10^{-32} I_2^3 + \cdots, \qquad [20]$$

$$\Delta D_h^{C_6H_6} = -0.2 \times 10^{-10} I_2 + 2.5 \times 10^{-22} I_2^2 - 0.2 \times 10^{-32} I_2^3 + \cdots. \qquad [21]$$

Hence, for gold colloid in water the variations ΔD_h are seen to be 10^6 times larger than for strongly anisotropic molecular liquids. Such large variations should become observable at a moderate intensity $I_2 \geqq 100$ esu of the laser beam.

Also, from Eqs. [17] and [19], one sees that total orientation of the particles (optical saturation) can be achieved in colloid solutions by applying an optical field of $E < 10^3$ esu, which can be easily done by present laser techniques (see Appendix).

Our considerations can be extended on the basis of earlier papers (3–10) to arbitrary conditions of observation (variation in the angle of observation, and the like) and to scattering particles of arbitrary size and shape.

APPENDIX

On the assumption that the particles have the symmetry of rotational ellipsoids, the

polarizability tensor can be written as follows:

$$g_{\sigma\tau} = g_1\delta_{\sigma\tau} + (g_3 - g_1)k_\sigma k_\tau , \quad [A1]$$

where **k** is the unit vector in the direction of the symmetry axis of the particle, and k_σ, k_τ are its components in the laboratory reference system X, Y, Z.

By inserting Eqs. [1] and [A1] jointly into Eq. [4], and on introducing the notation $I^S_{zz}(xx) = V_h$ and $I^S_{yy}(xx) = H_h$, we obtain

$$V_h = 15V_h^{\omega_1} \int (\mathbf{kx})^2(\mathbf{kz})^2 f(\Omega, I_2)\, d\Omega, \quad [A2]$$

$$H_h = 15H_h^{\omega_1} \int (\mathbf{kx})^2(\mathbf{ky})^2 f(\Omega, I_2)\, d\Omega, \quad [A3]$$

where **x**, **y**, **z** are unit vectors along the axes X, Y, Z of the laboratory frame of coordinates, and the components $V_h^{\omega_1}$ and $H_h^{\omega_1}$ are defined by Eq. [8]. Denote by ϑ the angle between the axis of symmetry of the particle and the laboratory Z-axis. Then

$$\mathbf{kx} = \sin\vartheta\cos\varphi, \qquad \mathbf{ky} = \sin\vartheta\sin\varphi, \qquad \mathbf{kz} = \cos\vartheta, \quad [A4]$$

φ being the azimuth in the XY-plane.

We now choose the direction of oscillations of the intense light beam as parallel to the Z-axis; hence, by [A1], the potential energy [3] of the particle time-averaged over a period of oscillations of the optical field becomes

$$\overline{u(\Omega, E_2)}^t = -\tfrac{1}{2}\, v[g_1 + (g_3 - g_1)\cos^2\vartheta]I_2. \quad [A5]$$

This is the correct time-averaged potential energy for insertion into the distribution function [5], which describes the system at thermodynamical equilibrium with the electric field. In the present case, we obtain

$$f(\vartheta, I_2) = \frac{\exp\,(vy_{\omega_2}I_2\cos^2\vartheta)}{2\pi\displaystyle\int_0^\pi \exp\,(vy_{\omega_2}I_2\cos^2\vartheta)\sin\vartheta\, d\vartheta}. \quad [A6]$$

Hence, orientation of particles can be caused not only by a dc field or an alternating field but by a field oscillating at optical frequencies as well (11). Obviously, the permanent electric dipoles of the particles are unable to keep pace with the rapid oscillations of the light field, and their potential energy (which is a linear function of the field) vanishes on time-averaging. Thus, in an optical field, orientation of particles occurs only by way of their ellipsoid of polarizability.

Since we are interested in the change in scattering of a weak light beam of frequency ω_1 due to orientation of the scattering particles in the field of an intense laser beam of frequency ω_2, we naturally ask when does this orientation keep pace with the changes in the difference $\omega_1 - \omega_2$ between the oscillation frequencies of the two light beams and whether thermal equilibrium can be established at each instant of the cycle (12). In a quadratic approximation, the problem can be solved within the framework of Debye's relaxation theory (12–14); this leads to a characteristic relaxation time of anisotropic reorientation τ_c amounting to $\frac{1}{3}$ of the Debye relaxation time, $\tau_D = 3\tau_c$. At $(\omega_1 - \omega_2)\tau_c \ll 1$ the conditions demanded by small colloid particles are fulfilled, whereas at $(\omega_1 - \omega_2)\tau_c \gg 1$ the particles cannot follow the time variation. Quite recent experiments on the propagation of a strong laser beam in colloid solutions have made apparent the optical orientation of gold colloid particles in suspension in water (15).

As we see from Eq. [A6], the distribution function of rotationally symmetric particles depends only on the angle ϑ, so that with regard to Eq. [A4] we can write the components [A2] and [A3] as follows after averaging over all possible values of the azimuth φ:

$$V_h = 15\tfrac{1}{2}\, V_h^{\omega_1}\langle\cos^2\vartheta - \cos^4\vartheta\rangle_{I_2}, \quad [A7]$$

$$H_h = 15\tfrac{1}{8}\, H_h^{\omega_1}\langle 1 - 2\cos^2\vartheta + \cos^4\vartheta\rangle_{I_2}, \quad [A8]$$

where we have denoted the statistical mean value in the presence of light of intensity I_2 as follows:

$$\langle\cos^{2k}\vartheta\rangle_{I_2} = 2\pi\int_0^\pi \cos^{2k}\vartheta\, f(\vartheta, I_2)\sin\vartheta\, d\vartheta. \quad [A9]$$

Expanding in a power series the exponential factors appearing in the distribution function [A6],

$$\exp\,(v y_{\omega_2} I_2 \cos^2\vartheta) = \sum_{n=0}^{\infty} \frac{1}{n!} v^n y_{\omega_2}^n I_2^n \cos^{2n}\vartheta \quad [A10]$$

and recurring to the formula

$$\int_0^{\pi} \cos^{2m}\vartheta \sin\vartheta\, d\vartheta = \frac{2}{2m+1}, \quad [A11]$$

we can rewrite [A9] as follows:

$$\langle \cos^{2k}\vartheta \rangle_{I_2} = \frac{\sum_{n=0}^{\infty} \frac{v^n y_{\omega_2}^n I_2^n}{n![2(k+n)+1]}}{\sum_{n=0}^{\infty} \frac{v^n y_{\omega_2}^n I_2^n}{n!(2n+1)}}. \quad [A12]$$

Inserting the preceding values for $k = 0, 1, 2$ into Eqs. [A7] and [A8] we immediately get the components V_h and H_h in the form [6] and [7].

Going over to the limiting case of optical saturation (total orientation of particles), we find it more convenient to refrain from using the series expansion [A10] and to represent [A9] in integral form instead:

$$\langle \cos^{2k}\vartheta \rangle_{I_2} = \frac{\int_{-\sqrt{s}}^{\sqrt{s}} t^{2k} e^{t^2}\, dt}{\int_{-\sqrt{s}}^{\sqrt{s}} e^{t^2}\, dt}. \quad [A13]$$

This form is also convenient for tabulation; $s = v y_{\omega_2} I_2$ and $\sqrt{s}\cos\vartheta = t$.

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