

## Agreement between Depolarized Rayleigh Scattering and Optical Kerr Effect Induced by *Q*-Switched Laser Waves in Some Liquids

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We report measurements of the optical Kerr effect induced by *Q*-switched laser waves in some liquids, using an original experimental arrangement allowing easy measurements in weak anisotropic liquids. We compared the results obtained by this method to those deduced from our direct measurements of depolarized Rayleigh scattering. It is the first time that a good agreement has been found between these two effects, allowing precise determinations of apparent optical anisotropies.

The discrepancy between the information deduced from the study of the dc Kerr effect and the direct measurements of the depolarized component of the Rayleigh scattering (DRS) is well known.<sup>1</sup> It leads to an ambiguity in the determination of the molecular optical polarizabilities and results in a sometimes excessive multiplicity of the models.<sup>2,3</sup> The experimental evidence by Mayer and Gires<sup>4</sup> of the birefringence (BI) induced by *Q*-switched laser waves, interpreted theoretically by Kielich,<sup>5</sup> could lead to a solution of this problem. In fact, by neglecting the hyperpolarizability in the first approximation, the BI and DRS coming from the same molecular reorientation and redistribution phenomena and free from the slow kinetic disturbances existing in the dc Kerr effect (electrostriction,<sup>6</sup> electrocaloric effect,<sup>7</sup> etc.) should lead to the same results.

If one supposes that molecular reorientation and redistribution are the principal mechanisms of the BI, one can show that a proportionality exists between the BI constant  $B$  and the depolarized scattered intensity  $i$ . In fact, the model of Langevin,<sup>8</sup> adapted to a more accurate evaluation of the polarization energy in the case of the liquids,<sup>9,10</sup> the relation of Lorenz-Lorentz, and the dispersion law of Havelock lead to the formula

$$i_R \propto B_{i,a} \langle E^2 \rangle \beta \quad (1)$$

in which

$$\beta = \frac{n_a(n_R^2 - 1)^4(n_i^2 + 2)}{(n_a^2 - 1)^2(n_i^2 - 1)^2(n_R^2 + 2)^2} \quad ,$$

where the index  $R$ ,  $i$ , or  $a$  refers to the appropriate wavelength  $\lambda$ .  $R$  corresponds to the DRS measurement wavelength,  $i$  to the wavelength of the laser wave inducing the electric field of intensity  $E$ , and  $a$  to the analysis wavelength.  $B$  is

the optical induced birefringence constant given by

$$B = \Delta n_a / \lambda_a \langle E^2 \rangle \quad ,$$

where  $\Delta n_a$  is the anisotropy of the refractive index at wavelength  $\lambda_a$ , and  $\langle E^2 \rangle$  is the mean value of the square of the electric field intensity.

When  $\lambda_i = \lambda_a = \lambda_R$ , the relation (1) takes the simplified form

$$i \propto B \langle E^2 \rangle n / (n^2 + 2) \quad , \quad (2)$$

which can be found from Kielich's works,<sup>5</sup> with the small difference in the exponent of the term  $(n^2 + 2)$  coming from the adapted Langevin model.

When one makes comparative measurements relative to benzene, chosen as a reference, the determination of  $\langle E^2 \rangle$  becomes unnecessary and Eq. (2) is changed to

$$\frac{i}{i_b} = \frac{(B/B_b)n(n_b^2 + 2)}{n_b(n^2 + 2)} \quad , \quad (3)$$

where the index  $b$  refers to the values for benzene.

Except for the corrective term close to unity, one can expect the identity of the BI constants ratio  $B/B_b$  and the depolarized intensities ratio  $i/i_b$ . Unfortunately Paillette's measurements<sup>11</sup> led to an unexpected agreement with the Kerr static effect but not with the DRS experiments.

The discrepancy required further investigations. Following our work concerning the spontaneous anisotropic component of Rayleigh scattering of laser waves and their harmonies,<sup>12</sup> we started a comparative study of the BI and the DRS. The results of this work are given here.

In the first step, we repeated Paillette's experiment with a *Q*-switched ruby laser as inductor ( $\lambda_i = 0.6943 \mu\text{m}$ ;  $P < 10 \text{ MW}$ ). This laser constructed in our laboratory permitted us to freely use either a monocrystal of ruby or a neodymium-glass.

Moreover it had a removable amplifier stage of gain 3. A turning prism (30 000 rpm) aided in the Q-switching. The emission was effected without apparent mode-locking. Pulse duration was approximately 30 nsec. The analysis beam was a helium-cadmium Spectra-Physics laser ( $\lambda_a = 0.4416 \mu\text{m}$ ;  $P \cong \text{mW}$ ). Thus we measured the  $B/B_b$  ratios for some compounds with high anisotropy (see Table I, column a). We noted a rather important difference between Paillette's values<sup>11</sup> and ours, which cannot be explained by our mean error of 15%. So, we did this experiment again with an analysis beam of weaker intensity (laser helium-neon  $\lambda_a = 0.6328 \mu\text{m}$ ;  $P \cong \text{mW}$ ) and an inducting laser wave of  $\lambda_i = 1.06 \mu\text{m}$  ( $P < 10 \text{ MW}$ ) obtained by replacing the monocrystal of ruby in the Q-switched laser described above with a neodymium-glass. We measured with special care the transmission of the infrared wave and we made sure that no induced absorption could exist in the two beams. In all experiments, we set back the inductive power to the minimum value with respect to a correct detection of the phenomenon, in order to reduce self-focusing and other stimulated effects. Each time, we verified that

$$(\Delta I/I)^{1/2} \propto P \text{ for } l \text{ const,}$$

$$(\Delta I/I)^{1/2} \propto l \text{ for } P \text{ const,}$$

where  $\Delta I$  is the induced variation of the analysis signal  $I$ ,  $P$  is the power of the inducing beam, and  $l$  the length of the cell. The data were treated by a least-squares procedure and the slopes of the two lines obtained. The slopes were then used to determine the BI constants. The tests usually linked with this method revealed the significance and the precision of the data (linearity test, correlation coefficient, and estimation of variants).

We never observed, under our experimental conditions, self-focusing, and other stimulated effects. We used, without difficulty, cells of length between 1 and 32 cm inclusive, according to the anisotropy of the compound studied. Four differences may be noted between our apparatus and Paillette's<sup>11</sup>:

(a) The difference of the energy gradients in the inductive wave. We tried to assure the best energetic radial homogeneity of the inducing beam by using a small (3-mm) diameter hole placed near the center of the large ( $\phi$  16-mm) Q-switched laser beam. Our energy gradient is therefore inferior by 12% per mm, where as it attains 33% per mm in the experiments done by Paillette,<sup>11</sup> who used a relatively important part ( $\phi$  3 mm) of a small ( $\phi$  6-mm) Q-switched laser beam with Gaussian intensity distribution.

(b) We used, in front of the analysis photomultiplier, a spath prism which displaced useless analysis light, in order to reduce the noise provoked by the residual light passing through the crossed Glazebrook prisms.

(c) We replaced the polaroids with Glazebrook and Glan prisms, specially sized for the wavelengths used. These permitted us to obtain a better rate of polarization.

(d) We replaced the liquid filters (copper sulfate) by solid filters hoping thereby to attenuate induced parasitic effects in the liquid filters (induced absorption, BI, stimulated effects, etc.).

Our results, reported in Table I (column b), do confirm the values we obtained previously. The disagreement with Paillette's results<sup>11</sup> remains unsolved.

We noticed also that the BI constants of weakly anisotropic liquids are very difficult to measure by these methods, i. e., by using a continuous laser for the analysis beam. The values of the corre-

TABLE I. Comparison between depolarized Rayleigh scattering and optical laser induced birefringence,  $T = 293 \text{ }^\circ\text{K}$ .

Liquids	$B/B_b$ <sup>a</sup>	$B/B_b$ <sup>b</sup>	$B/B_b$ <sup>c</sup>	$B/B_b$ <sup>d</sup>	$B/B_b$ <sup>e</sup>	$i/i_b$ <sup>f</sup>	$B\beta/B_b\beta_b$ <sup>g</sup>	$B\beta/B_b\beta_b$ <sup>h</sup>
Carbon disulfide	7.1	6.6	6.9	5.6	10.45	$7.59 \pm 0.07$	$7.2 \pm 1.3$	10.5
Nitrobenzene		5.3		4.7	7.25	$6.18 \pm 0.06$	$5.6 \pm 0.8$	7.24
Mesitylene	1.6	1.5				$1.58 \pm 0.01$	$1.5 \pm 0.3$	
Toluene	1.3	1.4			2.33	$1.31 \pm 0.01$	$1.3 \pm 0.3$	2.36
Benzene	1	1	1	1	1	1	1	1
Chloroform		0.35			0.45	$0.256 \pm 0.002$	$0.3 \pm 0.1$	0.45
Freon 113			0.25			$0.196 \pm 0.002$	$0.20 \pm 0.04$	
Carbon tetrachloride			0.065		0.128	$0.0447 \pm 0.004$	$0.064 \pm 0.010$	0.128

<sup>a</sup>Experimental relative values of induced birefringence; our work;  $\lambda_i = 0.6943 \mu\text{m}$ ;  $\lambda_a = 0.4416 \mu\text{m}$ .

<sup>b</sup>Experimental relative values of induced birefringence; our work;  $\lambda_i = 1.06 \mu\text{m}$ ;  $\lambda_a = 0.6328 \mu\text{m}$ .

<sup>c</sup>Experimental relative values of induced birefringence; our work;  $\lambda_i = 1.06 \mu\text{m}$ ;  $\lambda_a = 0.5300 \mu\text{m}$ .

<sup>d</sup>Experimental relative values of induced birefringence; see Ref. 4;  $\lambda_i = 0.6943 \mu\text{m}$ ;  $\lambda_a = 0.5000 \mu\text{m}$ .

<sup>e</sup>Experimental relative values of induced birefringence; see Ref. 10;  $\lambda_i = 0.6943 \mu\text{m}$ ;  $\lambda_a = 0.4880 \mu\text{m}$ .

<sup>f</sup>Experimental relative values of depolarized Rayleigh scattering; our work;  $\lambda_R = 0.5461 \mu\text{m}$ .

<sup>g</sup>Values of the mean ratio  $B\beta/B_b\beta_b$  calculated from experimental results a, b, and c.

<sup>h</sup>Values of the mean ratio  $B\beta/B_b\beta_b$  calculated from experimental results e.

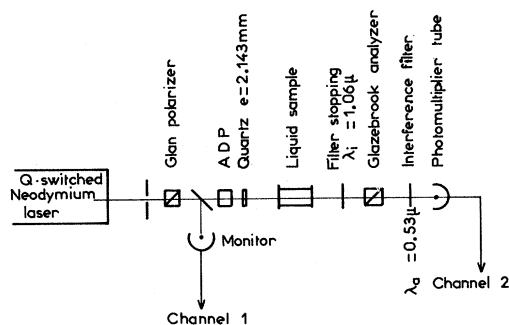


FIG. 1. Experimental arrangement used for detecting optical birefringence induced by  $1.06 \mu\text{m}$  laser pulse and analyzed by its second harmonic,  $0.53 \mu\text{m}$ , generate in ADP crystal. The quartz plate turns the two polarization planes at  $45^\circ$ .

lation coefficient<sup>13</sup> between  $(\Delta I/I)^{1/2}$  and  $P$ , listed in Table II, show perfectly the influence of noise, very weak in general, but becoming important in the case of weekly anisotropic bodies. This Schottky noise, due to residual light passing through crossed Glazebrook polarizers, practically forbids the study of compounds less anisotropic than chloroform.

In order to make possible the study of compounds of very weak anisotropy, we designed the experimental setup shown in Fig. 1. The infrared inducing beam ( $\lambda_i = 1.06 \mu\text{m}$ ) of a Q-switched neodymium laser, polarized vertically by a Glan polarizer, generates in the ammonium dihydrogen phosphate (ADP) crystal an analysis harmonic wave ( $\lambda_a = 0.53 \mu\text{m}$ ) of horizontally polarized light. The quartz, cut perpendicularly to the optical axis, has a carefully chosen thickness of  $2.143 \text{ mm}$ , and directs the polarization planes of the two waves at  $45^\circ$  from each other. A Glazebrook prism, crossed with the green wave, works as an analyzer. The intensity of the analysis signal and its short duration make it possible to study weak anisotropy easily. The resulting signals ( $\Delta I$ ) are proportional to the fourth power of the inducing intensity ( $P$ ) as

Table II. Mean values of the correlation coefficient (Ref. 13) between  $(\Delta I/I)^{1/2}$  and  $P$  with the experimental arrangements  $\lambda_i = 1.06 \mu\text{m}$ ,  $\lambda_a = 0.6328 \mu\text{m}$  and  $\lambda_i = 0.6943 \mu\text{m}$ ,  $\lambda_a = 0.4416 \mu\text{m}$ .

Liquid	Correlation coefficient	
	$r^2$	
Carbon disulfide	0.85	
Nitrobenzene	0.93	
Mesitylene	0.93	
Toluene	0.92	
Benzene	0.90	
Chloroform	0.66	

shown in Fig. 2. The results we obtained (Table I, column e) confirm our previous measurements in the case of carbon disulfide and show a large difference with Paillette's in the case of carbon tetrachloride.

Next, we undertook direct measurements of DRS using Bothorel's method<sup>14</sup> and Q-switched laser waves and their harmonics.<sup>12</sup> We added to our own measurements values already obtained<sup>15</sup> with a photometer<sup>16</sup> constructed in our laboratory. These results are reported in Table I, column f. In column g (Table I) one finds the mean values of  $B\beta/B_b\beta_b$  obtained from our results a, b, and c.

Table I, column h gives the values of the same ratio obtained from Paillette's results.<sup>11</sup>

Taking into account the experimental errors, there is a rather good agreement between our BI and DRS values. As far as we know, it is the first time such an agreement has been found. Two conclusions can be drawn:

First, for liquids strongly anisotropic, the agreement obtained demonstrates that the molecular reorientation phenomenon, proportional to the optical anisotropy, is preponderant.

Second, in the case of carbon tetrachloride, the slight disagreement noticed between BI and DRS appears to be due to the hyperpolarizability,<sup>17</sup> which intervenes only in the BI. This phenomenon, too often exaggerated, has limited importance in light of the redistribution<sup>18,19</sup> preponderant here.

So, with the use of a simple model, based upon a simple hypothesis of internal field, it allows a rather precise determination of the apparent optical anisotropies. It seems to prove that the values obtained by the dc Kerr effect cannot be considered, at the present time, for the deter-

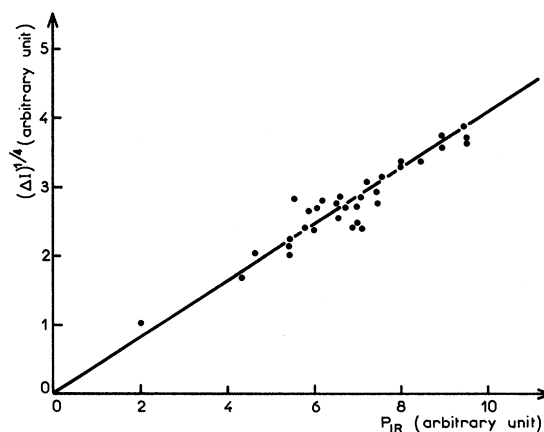


FIG. 2. Experimental curve showing the dependence  $(\Delta I)^{1/4} \propto P_{IR}$  between birefringence signal  $\Delta I$  and inducing power  $P_{IR}$  for carbon tetrachloride (length of cell:  $32 \text{ cm}$ ) and with the experimental arrangement described Fig. 1.

mination of optical anisotropies. There is no doubt that one or more effects, not related to the re-orientation and redistribution phenomena, rise to disparities in this case. New theoretical work on the dc Kerr effect, such as that recently published

by Hellwarth,<sup>1</sup> is of great importance.

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## Origin of Bound States of He<sup>3</sup> Atoms on Free Superfluid He<sup>4</sup> Surfaces

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An approximate theory of the motion of a He<sup>3</sup> atom in the vicinity of a superfluid He<sup>4</sup> surface is presented. The theory predicts a bound state of the He<sup>3</sup> atom in the vicinity of the surface, in accord with experimental results. The theoretical value for the energy of this state (measured with respect to the He<sup>4</sup> chemical potential) is within 35% of the experimentally determined value.

### I. INTRODUCTION

The existence of bound states of He<sup>3</sup> atoms on free superfluid He<sup>4</sup> surfaces was first proposed by Andreev<sup>1</sup> in order to explain the observed drop<sup>2-4</sup> in the surface tension of dilute solutions of He<sup>3</sup> in He<sup>4</sup> at low temperatures. Andreev did not, however, explain the existence of these surface states. Recently Lekner<sup>5</sup> has derived, using the variational principle, a simple one-dimensional Schrödinger equation governing the motion of a single He<sup>3</sup> atom near a free He<sup>4</sup> surface at zero temperature. Assuming a plane surface in the  $x$ - $y$  plane, he took a trial wave function of the form  $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = [\psi(z_1)/n^{1/2}(z_1)] \times \psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ . Here  $\vec{r}_1$  is the coordinate of the He<sup>3</sup> atom and  $\vec{r}_2, \vec{r}_3, \dots, \vec{r}_N$  are the coordinates of  $N-1$  He<sup>4</sup> atoms.  $\psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is the ground-state wave function for  $N$  He<sup>4</sup> atoms with a surface in the  $x$ - $y$  plane, and  $n(z)$  is the number density associated with  $\psi_0$ . Application of the variational principle give the equation

$$\frac{d^2\psi(z)}{dz^2} + [\lambda - U(z)]\psi(z) = 0 \quad (1)$$

for  $\psi(z)$ . The effective potential  $U(z)$  is given by

$$U(z) = \left(1 - \frac{m_3}{m_4}\right)t(z) + n^{-1/2}(z)\frac{d^2n^{1/2}(z)}{dz^2}. \quad (2)$$

$(\hbar^2/2m_4)t(z)$  is the kinetic energy per particle in pure He<sup>4</sup>, the bulk of the He<sup>4</sup> atoms being located at  $z > 0$ .  $m_3$  and  $m_4$  are the masses of He<sup>3</sup> and He<sup>4</sup> atoms, respectively. The surface-energy levels  $\epsilon_s = (\hbar^2/2m_3)\lambda$  are measured with respect to the chemical potential in pure bulk He<sup>4</sup>.

Equation (1) was not solved by Lekner, although he did point out that  $U(z)$  can have an attractive region if  $t(z)$  and  $n(z)$  decrease monotonically as the surface is approached from the bulk. In this paper we show that the asymptotic values of  $U(z)$  far from the surface can be determined exactly. Then we construct a simple analytic form for  $U(z)$  by interpolating between these values and solve numerically