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Laser-Induced Optical Kerr Effect and the Dynamics of Orientational Order in the Isotropic Phase of a Nematogen

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The transient order induced in the isotropic phase of the *N*-(*p*-Methoxybenzylidene)-*p*-butylamine by the plane-polarized electric field of a *Q*-switched laser beam, is experimentally measured and analyzed. Good agreement is found with considerations deduced from the theory of de Gennes. It allows direct measurements of the optical Kerr constant and of the orientational relaxation time in these materials.

The interpretation of the Kerr effect is usually rather complicated; a lot of phenomena such as orientation, redistribution, and perturbation of the electronic cloud of molecules, and also anisotropic striction, joule effect, etc., must be taken into account. The use of inducing laser pulses of 20×10^{-9} sec strongly reduces all slow contributions.[1] Furthermore, the isotropic phase of a nematogen near the nematic-isotropic transition provides a good tool with which to select only the **orientation phenomenon larger than all the others.** de Gennes has given a phenomenological model which can be used to describe this situation.[2] Let us recall the essential features of his theory. Near the transition we can use a Landau-type development of the free energy

$$F = F_0 + \tfrac{1}{2}A Q_{\alpha\beta} Q_{\beta\alpha} + \tfrac{1}{3}B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} - \tfrac{1}{2}\Delta\epsilon^{\lambda\text{ind}}_{\alpha\beta} E^{\lambda\text{ind}}_{\alpha} E^{\lambda\text{ind}}_{\beta} + \tfrac{1}{2}L_1 Q_{\beta\gamma,\alpha} Q_{\beta\gamma,\alpha} + \tfrac{1}{2}L_2 Q_{\alpha\gamma,\gamma} Q_{\alpha\delta,\delta}\,. \tag{1}$$

$Q_{\alpha\beta}$ is the order parameter and can be chosen to equal the anisotropic part of the magnetic susceptibility tensor (because of the weakness of magnetic interactions):

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \tfrac{1}{3}\chi_{\gamma\gamma}\delta_{\alpha\beta}\,. \tag{2}$$

The phase is supposed to suffer from the action of an intense optical electric field at the wavelength λ_{ind}. $\Delta\epsilon^{\lambda\text{ind}}_{\alpha\beta}$ is the anisotropic part of the dielectric permittivity, to first order

$$\Delta\epsilon_{\alpha\beta} = a Q_{\alpha\beta}\,. \tag{3}$$

(This is a general relation linking any couple of symmetric traceless second-order tensors in an isotropic phase.)

A and B are phenomenological constants; B must be different from zero to ensure a first-order transition, but owing to the weakness of the discontinuities such as latent heat and specific-volume change, de Gennes introduces the idea of a second-order transition near the first-order one. A is then expected to vary as $(T - T_c^*)^{\gamma}$, where T_c^* is the second-order temperature transition hindered by the first-order one, T_c. The critical exponent γ is 1 in the mean-field theory.

The dynamical behavior is described according to the thermodynamic theory of irreversible processes; letting

$$R_{\alpha\beta} = \frac{\partial}{\partial t} Q_{\alpha\beta} + Q_{\alpha\beta,\gamma} V_{\gamma} + \omega_{\gamma\alpha} Q_{\gamma\beta} + \omega_{\gamma\beta} Q_{\gamma\alpha}\,,$$

we get

$$\gamma_1 R_{\alpha\beta} = -\frac{\partial F}{\partial Q_{\alpha\beta}} + \frac{d}{dx_{\gamma}}\left(\frac{\partial F}{\partial Q_{\alpha\beta,\gamma}}\right).$$

γ_1 is a viscosity coefficient resembling the orientational viscosity coefficient in the nematic phase.

In order for the number of unknowns to equal the number of relations, we must add the equations of conservation of mass and momentum. However, considerable simplifications can be suggested by the following arguments: (i) In the range where the Kerr effect is E^2 dependent, the third-order term may be neglected. More exactly, in our experiments $\langle P_2^0 \cos\theta\rangle_{\text{av.}}$ was always smaller than $10^{-5}\times\langle P_2^0\cos\theta\rangle_{\text{av.}}$ in the nematic phase. It is then sure that $\tfrac{1}{3}BQ^3 \ll \tfrac{1}{2}AQ^2$. (ii) The objective rate of change of $Q_{\alpha\beta}$ contains two types of contributions: The first is due to the variation in the orientational order in the laboratory frame, and the second to the background fluid motion. We can drop out this last one, noting that it is of second order. As stressed by de Gennes, doing that, we neglect subtle coupling with fluctuations, which could perhaps be of some importance.[3]

The aligning field extends over a finite region; but, as long as the coherence length $\xi = (L/A)^{1/2}$ (L is some mean value of L_1 and L_2, because we only need an order of magnitude; $\xi \sim 100$ Å[2]) is small in comparison with the dimensions of that region, the gradient effects at the boundaries are quite negligible. Another effect taking place at the boundaries is the striction; as long as the fluid may be considered incompressible,[4] we can ignore it.

With the help of these considerations, the equation can be reduced to

$$\gamma_1 \frac{\partial Q_{\alpha\beta}}{\partial t} = -A Q_{\alpha\beta} + \tfrac{1}{2} a^{\lambda_{\text{ind}}} (E_\alpha E_\beta \tfrac{1}{3} E^2 \delta_{\alpha\beta}) . \tag{4}$$

The integral solution can be written

$$Q_{\alpha\beta}(t) = \frac{a^{\lambda_{\text{ind}}}}{2\gamma_1} \int_{-\infty}^{t} \exp\left(\frac{(t'-t)A}{\gamma_1}\right) \times [E_\alpha(t') E_\beta(t') - \tfrac{1}{3} E^2(t') \delta_{\alpha\beta}] \, dt' . \tag{5}$$

To arrive really at the experimental level we still need a few calculations. The wave inducing the order propagates in a damping medium; on the other hand, the order is revealed by a low-power beam, polarized at 45° of the inducing one. Let λ_{ana} be the wavelength of the analyzing beam; β be the absorption coefficient of the inducing beam; $\tau = \gamma_1/A$ be the orientational relaxation time; $B^{\lambda_{\text{ind}}, \lambda_{\text{ana}}} = a^{\lambda_{\text{ana}}} a^{\lambda_{\text{ind}}} / 4\epsilon_0 n_{\lambda_{\text{ana}}} A_{\lambda_{\text{ana}}}$ be the optical Kerr constant. ($n_{\lambda_{\text{ana}}}$ being the refractive index of the isotropic phase at the wavelength λ_{ana}). $\Psi_e - \Psi_o$ is the phase difference between ordinary and extraordinary analyzing waves emerging from the cell, l is length of the cell. Then

$$\tfrac{1}{2}(\Psi_e - \Psi_o)(t, l) = \tfrac{1}{2}\Pi \, \frac{1 - e^{-2\beta l}}{\beta} \, B^{\lambda_{\text{ind}}, \lambda_{\text{ana}}} \times \int_{-\infty}^{t/\tau} E^2(t') \exp\left(\frac{t'-t}{\tau}\right) d(t'/\tau) . \tag{6}$$

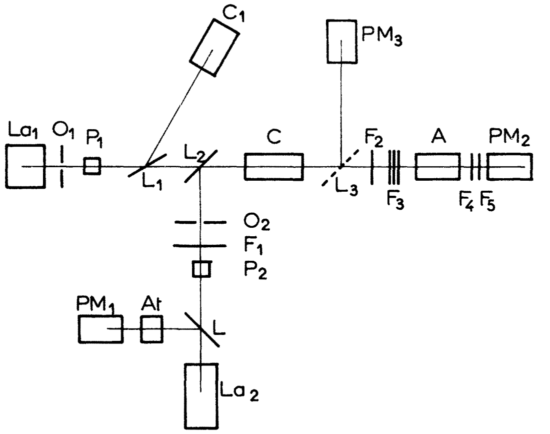

FIG. 1. Experimental setup: La$_1$, Q-switched neodymium glass laser; La$_2$, He-Ne laser, Spectra Physics 125A; C$_1$, photocell Compagnie de Télégraphie sans Fil C.P.A. 1143; PM1 and PM2 photomultiplier tubes, Radiotechnique XP1002; PM3 photomultiplier tube, Radiotechnique 150CVP; C, liquid cell, $l = 102.2 \pm 0.1$ mm; P_1, Glan prism; P_2 and A, Glazebrook prisms; L, L$_1$, L$_2$, and L$_3$, glass plates; O$_1$, pinhole 0, 3 mm; O$_2$, pinhole 0, 2.5 mm; F_1 and F_3, Metallisations et Traitements Optiques filter athervex Ta; F_2, Metallisation et Traitements Optiques filter athervex T; F_4, Metallisations et Traitements Optiques filter 580C; F_5, interference filter, $\lambda = 0.6340\,\mu$, $\Delta\lambda = 0.0080\,\mu$, $\tau = 0.24$; At, Polaroid HN22.

This relation contains two unknowns which can be determined separately. Let us sum the equation on both sides over time; we get

$$\int_{-\infty}^{+\infty} \tfrac{1}{2}(\Psi_e - \Psi_o)\, dt = \tfrac{1}{2}\Pi B^{\lambda_{\text{ind}}, \lambda_{\text{ana}}} \left(\frac{1 - e^{-2\beta l}}{\beta}\right) \times \int_{-\infty}^{+\infty} E^2(t) \, dt . \tag{7}$$

Thus, knowing the absorption coefficient, we can measure the Kerr constant independently of any kinetic consideration. Then it is possible to perform the convolution with the experimental curve $E^2(t)$. Adjusting the relaxation time, we can check the theoretical model. The results are expected to be quite similar to those given by the study of the light-scattering spectrum,[4] but obtained by a more direct method.

The experimental setup is described in Fig. 1. The inducing electric field (IR) is given by a Q-switched neodymium glass laser ($\lambda = 1.06\ \mu$m,

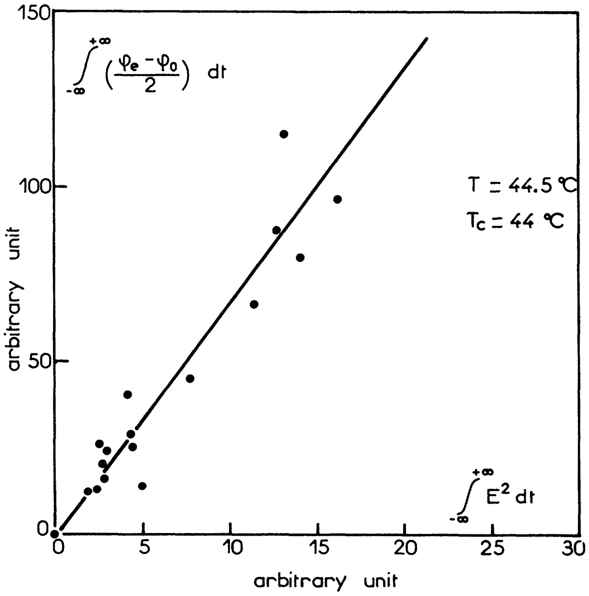

FIG. 2. Linear dependence of $\int_{-\infty}^{+\infty} \frac{1}{2}(\Psi_e - \Psi_o) dt$ upon $\int_{-\infty}^{+\infty} E^2(t) dt$ for various laser pulse energies. Temperature: 44.5 °C.

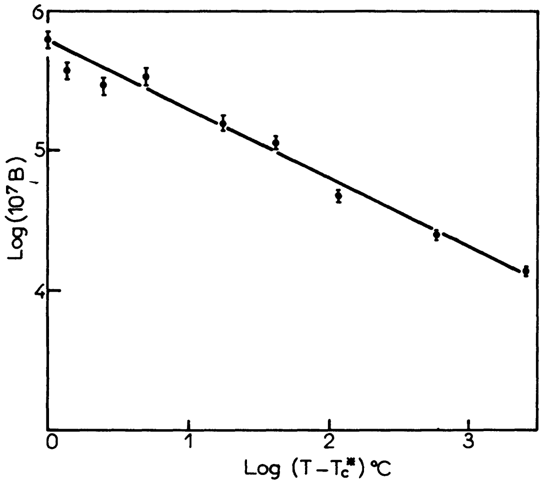

FIG. 3. Logarithmic plot of the optical Kerr constant B esu ($\lambda_{\text{ind}} = 1.06\ \mu$; $\lambda_{\text{ana}} = 0.6328\ \mu$m) vs temperature referred to the critical temperature T_c^*. These results are dependent upon the reference values. $B^{\lambda_{\text{ind}} = 106 \mu\text{m}; \lambda_{\text{ana}} = 0.6328 \mu\text{m}} = 83 \times 10^{-9}$ esu, and $T_c^* = 43$ °C.

$W \simeq 0.3$ J, $\delta t = 30 \times 10^{-9}$ sec). The Q-switched mode is obtained with the use of a rotating prism (400 rotations/sec). No mode selection is performed inside the optical cavity and, in spite of some irregularities in the spike shape (as the one shown in Fig. 3), partial mode locking of the pulse was never evidenced in our experiments. The use of attenuating filters permitted the reduction of the Nd-glass laser power in order to avoid self-trapping and stimulated effects. The Glan polarizer P1 defines the direction of the electric field at 45° from the vertical. The glass plate L1 gives a reference beam that is sent to the photo cell C1. The transmission of the inducing infrared wave is measured at each temperature by the photomultiplier tube PM3. The values are always compared to the ones measured at weak power (Beckman DK2A spectrophotometer). Stimulated Raman scattering was never observed in our work performed with a multimode structure of the laser wave. We also tried to assure the best energetic radial homogeneity of the inducing beam by using a small (3-mm diam) hole placed near the center of the large (16-mm diam) Q-switched laser beam. This gives an energy gradient smaller than 12% per mm. The beam of the helium-neon laser La_2 ($\lambda = 0.6328\ \mu$m, $P = 60 \times 10^{-3}$ W) is vertically polarized by the Glazebrook prism P_2, reflected by L_2, and partly depolarized in the cell C, when, and only when, the IR beam induces the uniaxial order. The direction of the analyzer A is horizontal, so that the photomultiplier tube PM_2 gives a signal proportional to $I \sin^2 \frac{1}{2}(\Psi_e - \Psi_0)$ (where I is the intensity of the analyzing wave). The light source La_2 has nonnegligible fluctuations and we measured its intensity for each laser shot with the use of the glass plate L, the attenuator At, and the photomultiplier tube PM1.

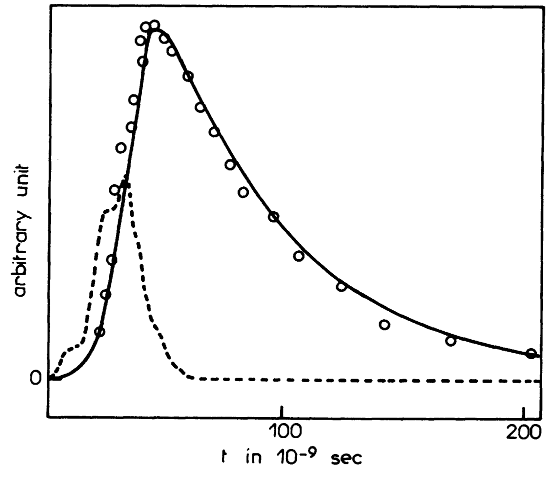

FIG. 4. Comparison between a convoluted optical Kerr curve and the experimental one (circles). The incident laser pulse is represented by the dashed line Temperature: 48.1 °C.

The nematogen we have studied is the p-methoxy benzilidene-pn-butylaniline (MBBA). We have

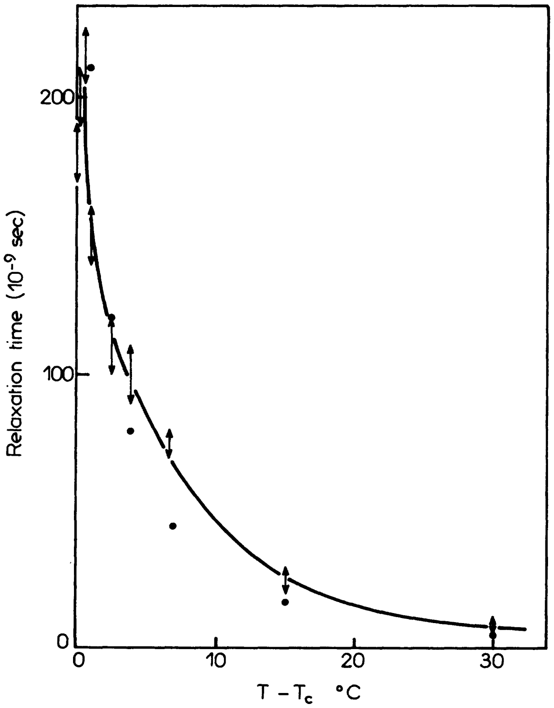

FIG. 5. Relaxation time vs temperature referred to the transition one $T_c = 44$ °C: ↕: our experimental points; the circles correspond to values calculated from Ref. 3.

checked that it presents no intrinsic absorption at the analyzing wavelength, therefore thermal lens effects, noticeable over distances of 10 cm, were never observed in our experiments. Owing to the intense diffusion of light, a strong damping is observed near the transition. At each temperature it was measured with a thermopile and taken into account when calculating the phase difference. The informations given by PM1, C1, and PM2 were simultaneously displayed on a dual-beam scope (Fairchild 777), equipped with a Polaroid camera. We have prepared two computer programs adapted to the experiment. The first one allows the calculations of

$$\int_{-\infty}^{+\infty} \tfrac{1}{2}(\Psi_e-\Psi_o)dt, \quad \int_{-\infty}^{+\infty} E^2(t)\,dt ,$$

and their ratio, with due care to the corrections of transmission. The second one allows the calculation of the convolution product, written on the right-hand side of Eq. (6). This calculation is compared with the experimental curve $\frac{1}{2}(\Psi_e-\Psi_o)(t)$ on the screen of a storage oscilloscope, then both curves are traced by the computer.

Figure 2 shows the linear dependence of $\int_{-\infty}^{+\infty} \frac{1}{2}(\Psi_e-\Psi_o)\,dt$ upon $\int_{-\infty}^{+\infty} E^2(t)\,dt$ for various pulse energies.

Figure 3 shows the thermal variation of the optical Kerr constant of MBBA. At each temperature we have checked the E^2 dependence on integral form (7). The values are relative to the one of benzene taken as $B^{\lambda_{\text{ind}},\lambda_{\text{ana}}}=83\times10^{-9}$ esu [(1)]; $\lambda_{\text{ind}}=1.06$ μm; $\lambda_{\text{ana}}=0.6328$ μm. They follow the law

$$B=\frac{k}{(T-T_c^*)^\gamma},$$

with $\gamma=0.5\pm0.1$, and $k=(330\pm10)\times10^{-7}$ esu. For $T_c=44$ °C, $T_c^*\simeq 43$ °C. Once the experimental cell was sealed, the temperature transition was found to be quite stable within 4×10^{-2} °C.

The optical Kerr effect is about three times weaker than the static one.[5] On the other hand, the critical exponent γ is comparable to the one given in static Kerr-effect investigations[5,6] and strongly contrasts with the one obtained by Rayleigh scattering and magnetic and flow birefringence.[4,7] Intensity of integrated depolarized Rayleigh-scattering measurements made in our laboratory[8] essentially confirm the results published by Litster and Stinson. Although the orientation correlations are strongly predominant, optical Kerr effect and Rayleigh scattering do not lead to the same results. Such a discrepancy cannot be explained at this time.

Figure 4 shows an example of the comparison between a convoluted curve and the experimental one. We think that it is a good check of the relation (6). Such a satisfactory agreement was found on the 50 convolutions we have performed. This agreement shows that, except in a very short range near the transition, the dynamics of reorientation are relatively simple and can be correctly described with the use of only one exponential function as is done in our theoretical treatment. The resulting variation of the relaxation time is given in Fig. 5. The shortest time measurements allowed were determined by irregularities in the inducing pulse, thus they corresponded to times significantly smaller than 20×10^{-9} sec. The values obtained are comparable to those given by Rayleigh-linewidth investigations, although not exactly the same. We note near the transition point a saturation of the relaxation time value and if our accuracy allows such an observation, a small decrease quite near T_c. Let us point at last, that to correctly perform the determinations near the transition, we have used lower incoming ir energies ($W\simeq10^{-2}$ J). At higher energies more complicated phenomena occur; for instance, the time duration of the effect (which can reach 10^{-6} sec) depends on the incoming power of the inducing wave.

This work will be now extended (i) theoretically, by research on the physical explanation of the unexpected thermal variation of static and optical Kerr constants and (ii) experimentally, by new investigations of the optical Kerr effect in a very short range near the transition points of other nematogens.

We wish to thank Professor P. G. de Gennes for many fruitful discussions about this work and the still open questions it asks.

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