Electric-field-induced change of the order parameter in a nematic liquid crystal

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We measure optically the increase of quadrupolar order ΔS, induced by a stabilizing electric field E, in the nematic liquid crystal 4'-*n*-pentyl-4-cyanobiphenyl with large positive dielectric anisotropy $\epsilon_a \sim 10$. ΔS shows a linear and a quadratic dependence on E. Both effects are comparable for the largest field $E \sim 3\times 10^5$ V/cm. The linear variation is interpreted as originating from the quenching of *macroscopic* orientational fluctuations, while the quadratic contribution is a superposition of the *microscopic* Kerr effect and of a saturation term due to the macroscopic effect.

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Nematic liquid crystals (NLC's) present quadrupolar ordering around the "director" $\mathbf{n}$ ($\mathbf{n}^2=1$). This ordering is described by the usual traceless tensor [1] $Q_{\alpha\beta}=S(3n_\alpha n_\beta-\delta_{\alpha\beta})/2$ where $0\le S\le 1$ is the order modulus. Macroscopically, a nematic phase presents a dielectric or magnetic susceptibility anisotropy proportional to $\mathbf{Q}$, so that electric or magnetic fields couple at even powers with the nematic order. By applying a field $\mathbf{E}$ along $\mathbf{n}$ on a nematic phase, one can change its ordering. When this coupling is *destabilizing* (for example, negative dielectric or diamagnetic anisotropy) the nematic direction $\mathbf{n}$ rotates at constant S, producing, for instance, the well-known Fréederickz transition [1]. For a *stabilizing* situation (positive dielectric or diamagnetic anisotropy) $\mathbf{n}$ remains fixed but S should increase. This effect has two origins: the well-known Kerr effect, first considered by Hanus [2] for optical fields and later by Fan and Stephen [3] for low-frequency fields, describes the lowest-order *microscopic* coupling, $E_\alpha Q_{\alpha\beta}E_\beta \sim SE^2$, of S with $\mathbf{E}$, *quadratic* in field. The second one, predicted by de Gennes [1], originates from the quenching of *macroscopic* nematic fluctuations and it is *linear* in field. Up to now the Kerr effect of nematic materials has only been observed in their isotropic (I) phase [4,5] where $S=0$. In the nematic (N) phase, a weak fluctuation quenching effect was long ago observed with large magnetic fields [6,7]. Experiments with a large electric field [8] did not lead to conclusive effects. In this paper we experimentally demonstrate for the first time the simultaneous existence of both linear and quadratic changes of S induced by a stabilizing electric field in a strongly anisotropic nematic single crystal.

According to the Landau–de Gennes phenomenological model, the free-energy density f of a NLC can be expanded in powers of S as [5]

$$f=f_0+\tfrac{1}{2}a(T-T^*)S^2-\tfrac{1}{3}bS^3+\tfrac{1}{4}cS^4-\tfrac{1}{5}dS^5 +\tfrac{1}{6}eS^6+\cdots+\tfrac{1}{2}L(\nabla S)^2+\cdots , \quad (1)$$

where the coefficients a, b, c, d, and e are supposed constants, T is the absolute temperature, and T^* is the minimum temperature for the stability of the isotropic phase. $L=[L_1+L_2(1+3\cos^2\theta)/6]$ (Ref. [5]) with L_1, L_2 constants and $\cos\theta=(\nabla S\cdot\mathbf{n})/|\nabla S|$.

In the homogeneous nematic phase, in the absence of an external field, f is minimum for a nonzero order S_0 which minimizes (1). Applying a stabilizing electric field E, S is expected to increase weakly from S_0. $f(S)$ can be written as

$$f(S)=\tfrac{1}{2}(f'')_{S_0}(S-S_0)^2-\frac{1}{3}\left[\frac{\epsilon_{a0}}{4\pi}\right]SE^2 , \quad (2)$$

where $f''=d^2f/dS^2$ and $\epsilon_{a0}=\epsilon_a/S$ is the dielectric anisotropy for $S=1$. The field-induced order variation $\Delta S_K=S-S_0$ is then

$$\Delta S_K=\epsilon_{a0}E^2/(12\pi f'') . \quad (3)$$

It is convenient to write $f''=L/\xi^2$, where ξ is the correlation length of the $N-I$ transition. We now introduce the reduced field $|E/E_0|$ where E_0, defined by $\epsilon_{a0}E_0^2=4\pi L/\xi_0^2$, is a molecular electric field and ξ_0 is a molecular length. For a NLC with $\epsilon_{a0}\sim 10$, $L\sim 10^{-6}$ cgs units, and $\xi_0\sim 20$ Å, E_0 is $\sim 1.7\times 10^6$ V/cm. Equation (3) then becomes

$$\Delta S_K=\frac{L}{3f''\xi_0^2}\left|\frac{E}{E_0}\right|^2=c_K\left|\frac{E}{E_0}\right|^2=\left[\frac{\xi}{\xi_E}\right]^2 S_0 , \quad (4)$$

where $\xi_E=\xi_0(3S_0)^{1/2}|E_0/E|=\xi_c|E_0/E|$ is the usual electric coherence length [1]. As L appears in the definition of E_0, the reduced Kerr constant c_K also depends on L, while the absolute Kerr coefficient in (3) depends only on f''. For a second-order nematic-isotropic transition, c_K is $\sim S_0^{-2}$. The Kerr effect is *microscopic* because f describes the microscopic interactions.

In the absence of an electric field, thermally induced *macroscopic* angular fluctuations of $\mathbf{n}$, i.e., on wavelengths larger than ξ, also decrease S (Ref. [1]). By quenching these macroscopic fluctuations with a stabilizing field one can expect an increase of order, linear in field, as

$$\Delta S_1 = \frac{k_B T S_0^{1/2} L^{1/2}}{4\pi K_3^{1/2} \xi_0} \left[\frac{1}{K_1} + \frac{1}{K_2} \right] \left| \frac{E}{E_0} \right| = c_1 \left| \frac{E}{E_0} \right| = c_1 \frac{\xi_c}{\xi_E} , \quad (5)$$

where K_i $(i=1,2,3)$ are the curvature elastic constants. The order of magnitude of c_l is $\sim(4\pi)^{-1} S_0^{-5/2}$. Linear and quadratic effects compare when $|E'| \sim E_0/10 = 1.7\times10^5$ V/cm, or $\xi_E \sim 10\xi_0$. E' is experimentally accessible. On the other hand, for the same NLC with $\chi_a \sim 10^{-7}$, the corresponding magnetic field $H' \sim 1.7\times10^6$ G is more difficult to achieve.

The quenching of macroscopic fluctuations with a stabilizing electric field contributes to ΔS not only as a linear term but also at higher orders in field. This comes from the dependence of ϵ_a and K_i on S, implicit in (5), which becomes, at second order,

$$\Delta S_1 \sim c_1 \left| \frac{E}{E_0} \right| - \frac{5}{2} \frac{c_l^2}{S_0} \left| \frac{E}{E_0} \right|^2 = c_1 \left| \frac{E}{E_0} \right| + c_{lq} \left| \frac{E}{E_0} \right|^2 . \quad (6)$$

The negative c_{lq} is a saturation effect. One can estimate a saturation field $|E_s| = 2S_0|E_0|/5c_l$. The total induced order ΔS from a stabilizing field is

$$\Delta S \sim c_l |E/E_0| + c_q |E/E_0|^2 , \quad (7)$$

where $c_q = c_{lq} + c_K$. Because of the saturation, the total quadratic effect is expected to be smaller than the simple Kerr effect.

To observe ΔS we measure the change Δl in the optical path difference of a uniform nematic cell, with **n** perpendicular to the surface electrodes ("homeotropic" alignment). The electric field **E** is parallel to the director **n**. Calling $\epsilon'_\parallel, \epsilon'_\perp$ the optical dielectric anisotropies parallel and perpendicular to **n**, the eigenvalues of the dielectric constants are, at first order in S

$$\epsilon'_\parallel = \epsilon'_{\rm iso} + \tfrac{2}{3}\epsilon'_{a0} S = n_e^2 , \quad (8a)$$

$$\epsilon'_\perp = \epsilon'_{\rm iso} - \tfrac{1}{3}\epsilon'_{a0} S = n_0^2 , \quad (8b)$$

where n_0, n_e are the ordinary and extraordinary refractive indices, $\epsilon'_{\rm iso} = (\epsilon'_\parallel + 2\epsilon'_\perp)/3$, and ϵ'_{a0} is the optical dielectric anisotropy in the perfectly aligned nematic phase. A measurement of the field-induced birefringence variation should then give ΔS.

The optical thickness difference Δl of the cell is related to its geometry as [9]

$$\Delta l = d n_0 \{ [1 - n_e^{-2} \sin^2\alpha_i]^{1/2} - \cos[\sin^{-1}(n_0^{-1} \sin\alpha_i)] \} , \quad (9)$$

where α_i is the angle of incidence (Fig. 1). Shining linearly polarized light at 45° of the incidence plane one can produce ordinary and extraordinary waves, which will interfere when changing α_i. The intensity of the emerging light behind an analyzer is $I = I_0 \sin^2(\delta/2)$, where $\delta = 2\pi\Delta l/\lambda$ is the phase difference, I_0 is the incoming beam intensity, and λ is the wavelength of light. We obtain ΔI from δ by measuring I at the cell output. ΔS is finally calculated from Eqs. (8) and (9).

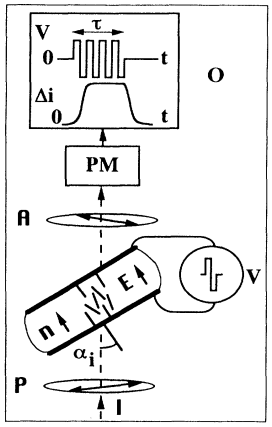

FIG. 1. Experimental setup for birefringence measurements in a high electric field. *P*: polarizer; *A*: analyzer; PM: photomultiplier; *O*: oscilloscope with the burst ac electric field pulse *V* and the light signal Δi.

The NLC cell is made with two indium tin oxide transparent glass electrodes. They are silane coated to induce homeotropic orientation. The thickness of the cell is fixed around $d \sim 7$ μm by Mylar spacers. The experiments are performed on nematic 5CB (4′-*n*-pentyl-4-cyanobiphenyl) chosen for its large dielectric anisotropy. The cell is filled at room temperature and is enclosed in an oven whose temperature stability is ~ 10 mK. The ensemble is placed on a rotating stage, below a polarizing microscope. **n** is oriented at 45° with respect to the crossed polarizer and analyzer. The cell is tilted compared to the measuring light beam for maximum birefringence sensitivity (Fig. 1). λ is 546 nm, fixed by an interference filter. E has a maximum intensity of 3×10^5 V/cm. Such high electric fields could give sample heating. A typical 1-K heating was measured [8] with a dc electric field $\sim 10^5$ V/cm. To prevent heating we use a burst pulsed ac electric field, with a few positive and negative half-period square waves (Fig. 1) of high enough frequency (~ 100 kHz) to avoid ionic effects. The pulse lasts $\tau \sim 10$–100 μs with a time interval $T \sim 10$ sec. With such $\tau/T < 10^{-5}$, heating is expected to be negligible. The pulses are produced by a wideband amplifier of 1-μs response time, of maximum output voltage ± 200 V. I is measured by the photocurrent i of a photomultiplier. The transient variation $\Delta i(t)$ during the pulse is recorded on a digital oscilloscope.

To calibrate d, we measure $\Delta l(\alpha_i)$ with a compensator for $0° < \alpha_i < 45°$ by tilting the stage in the absence of field. From $\Delta l(\alpha_i)$ and the knowledge [10] of n_0, n_e, we calculate d, fitting the data to within 3%. The same measurement is made for two other points of the cell to check parallelism. We measure the maximum i_0 at the top of the interference fringes. We fix α_i at the $i = i_0/2$ position to obtain maximum sensitivity. We apply $E = V/d$

across the cell, and record $\Delta i(t)$ during the E pulse. We observe a weak transient signal $\Delta i(t)$ which increases within a few μs and becomes constant during the pulse. After the pulse, $\Delta i(t)$ relaxes down to zero within a few μs. $\Delta i(t)$ does not change when $E(t)$ changes its sign. The short observed relaxation time is the signature of an S variation at constant $\mathbf{n}$. We interpret $\Delta i(t)$ as the optical effect of $\Delta S(E)$. We check that after each measurement the photocurrent in the absence of field relaxes down to its initial value. This ensures that there is no visible temperature change nor degradation of the NLC. We measure now only the stabilized $\Delta i(t)$ value after its growth during one pulse, i.e., the stabilized transient value $\Delta i(E)$. Superimposed to it, we do observe fluctuations giving an "order" noise $\delta(\Delta S)\sim\pm 0.03$. For each E we accumulate the signals of 2^8 pulses to decrease $\delta(\Delta S)$ down to ± 0.002.

Figure 2 shows the measured variations of $\Delta S(E)$ for two different temperatures. In both cases, $\Delta S(E)$ presents a linear and a quadratic part. For $\Delta T = T_{NI} - T = 3.8$ K, where T_{NI} is the N-I transition temperature, curve β shows a dominant linear part even at high-field values. For $\Delta T = 0.1$ K, α shows a larger quadratic part, which is dominant for the high field. Qualitatively, both linear and quadratic parts of ΔS become stronger approaching T_{NI}. We fit the experimental data on the form (7). To define E_0, we take typical values [11] $\xi_0 = 18$ Å, $L = 10^{-6}$ dyn, and $\epsilon_{a0} = 20$, i.e., $E_0 = 1.32\times 10^6$ V/cm. The solid lines in Fig. 2 show the best fit of $\Delta S(E)$. The fit gives $c_l = 0.42\pm 0.02$ for $\Delta T = 0.1$ K and $c_l = 0.15\pm 0.01$ for $\Delta T = 3.8$ K. To calculate the corresponding theoretical values from (5) we interpolate $K_i(T)$ and $\epsilon_a(T)$ for $\Delta T = 3.8$ K from the experimental data [12,13] while we extrapolate them for $\Delta T = 0.1$ K (Table I). The absolute accuracy on K_i is [12] $\sim 5\%$, and on ϵ_a it is [13] $\sim 3\%$. The resulting error on c_l is $\sim 8\%$, while near T_{NI} this error becomes $\sim 15\%$ due to extrapolation. We calculate, finally, $c_l = 0.37 \pm 0.06$ and $c_l = 0.14\pm 0.01$, respectively, in good agreement with the experiments.

We can now compare the electric-field linear order increase with the previously measured values obtained on 7CB with a magnetic field [6,7]. $H = 1.2\times 10^5$ G used in Ref. [6] corresponds for 5CB to $E \sim 1.2\times 10^4$ V/cm $\ll 3 \times 10^5$ V/cm used in our experiment. They measured a linear $\Delta S \sim 10^{-3}$ for their maximum H for $\Delta T \sim 3.8$ K, while we obtain $\sim 1.3\times 10^{-3}$ for the corresponding E. The agreement of 5CB measurements for small E with the magnetic-field measurements on 7CB is reasonably good.

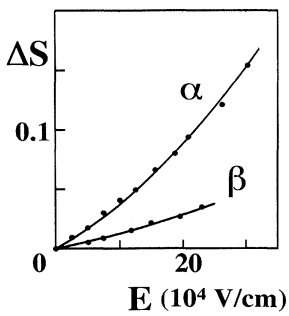

FIG. 2. Order increase ΔS induced by a stabilizing electric field $\mathbf{E}\|\mathbf{n}$ in the nematic liquid crystal 5CB, for $T = T_{NI} - 0.1$ K (α) and $T = T_{NI} - 3.8$ K (β).

TABLE I. Elastic constants K_i ($i = 1,2,3$) in units of 10^{-7} dyn and dielectric anisotropy ϵ_a of 5CB from Refs. [12,13].

$T_{NI} - T$ (K)	K_1	K_2	K_3	ϵ_a
0.1	2.0±0.2	1.0±0.1	2.1±0.2	7.2±0.3
3.8	3.8±0.2	2.1±0.1	4.6±0.2	9.7±0.3

We discuss now the quadratic effect. We measure from the experimental fitting $c_q = 1.1\pm 0.1$ for $\Delta T = 0.1$ K and $c_q = 0.28\pm 0.07$ for $\Delta T = 3.8$ K. We calculate now c_K and c_{lq} from (4) and (6). For f'' we first take from the literature [4] the Landau–de Gennes coefficients up to 4th order in the isotropic phase (Table II). We find $c_q = c_{lq} + c_K = -1.3 + 2.6 = 1.3\pm 0.2$ for $\Delta T = 0.1$ K and $c_q = -0.11 + 1.11 = 1.0\pm 0.2$ for $\Delta T = 3.8$ K. The agreement between experimental and calculated values is good enough near T_{NI}. Far from T_{NI}, the calculated c_q is ~ 3 times larger than the measured one. Such a deviation is due to the insufficient fourth-order approximation in the free-energy expansion. We fit now the $S_0(T)$ data [12,14] to 6th order. As the data of Ref. [12] were normalized using the absolute values of Ref. [14], we use both sets of data in the fitting procedure. The coefficients obtained from this fitting are given in Table II. Using these data, we recalculate $c_q = c_{lq} + c_K = -1.3 + 2.5 = 1.2\pm 0.2$ for $\Delta T = 0.1$ K and $c_q = -0.11 + 0.32 = 0.21 \pm 0.03$ for $\Delta T = 3.8$ K. These values are now in good agreement with the experimental values. The reduced Kerr coefficient c_K is thus strictly calculable from (4) in the nematic phase of a NLC. For 5CB the reduced Kerr coefficient is $c_K = 2.5\pm 0.2$ for $\Delta T = 0.1$ K and $c_K = 0.32\pm 0.03$ for $\Delta T = 3.8$ K. We compare our data in the nematic phase with the Kerr constant c_{Ki} from the literature [4] in the isotropic phase, i.e., $c_{Ki} = 3.8$ for $\Delta T = 0.1$ K and $c_{Ki} = 1.4$ for $\Delta T = 3.8$ K. Near T_{NI} the effect is of the same order of magnitude ($\Delta S_K \sim 3|E/E_0|^2$) in both phases. Below T_{NI} in the nematic phase the Kerr effect is much smaller than in the isotropic phase because the nematic phase is more "rigid."

The model assumes that the decrease of S due to mac-

TABLE II. Coefficients of the free-energy expansion in powers of S for 5CB from Ref. 4 and recalculated from Refs. [12] and [14], in 10^7 ergs/cm^3. Note that, because the expansion of f in powers of S is not orthogonal, one cannot compare the coefficients of the first set with the truncated three first terms of the second set.

Source	a	b	c	d	e
Ref. [4]	0.13±0.01	1.6±0.2	3.9±0.3	0	0
Refs. [12,14]	0.14±0.01	1.6±0.1	6.0±0.3	18.9±0.9	32.8±1.6

roscopic fluctuations is small enough to be considered as a perturbation. Our experimental results show a good agreement with the model. In fact, for our maximum reduced field ~ 0.23 we measure $\Delta S_I = 0.04$, which remains an acceptable perturbation of $S_0 = 0.34$ close to T_{NI}.

In principle, our experiment, made on a homogeneous sample, can only give information on the uniform free-energy expansion coefficients through f''. In the isotropic phase there exist data [11,15] which also imply f'', namely the coherence length $\xi^2(T) = L/f''$. Taking L from the K_i data [12], with the approximated relation [16] $K_i \sim 2LS^2$, we can estimate $\xi(T)$ from our f'' data. We find $\xi = 47 \pm 5$ Å for $\Delta T = 0.1$ K and $\xi = 17 \pm 2$ Å for $\Delta T = 3.8$ K. The correlation length just below T_{NI} is smaller than the isotropic one just above, $\xi_I = 88 - 105$ Å, as qualitatively expected. There are no available data for ξ in the nematic phase in the literature to be compared with our results.

In conclusion, we have observed the increase of order induced by a stabilizing electric field in a nematic liquid crystal. We find a linear order variation for small fields, and a quadratic dependence for larger fields. The linear part of $\Delta S(E)$ is described by the de Gennes model of macroscopic fluctuations quenching, while the quadratic part is described by the microscopic Landau–de Gennes model, as opposed to a saturation from the macroscopic effect. We have then been able to separate the *macroscopic* from the *microscopic* contribution to the order-parameter increase. As discussed in Ref. [7], this behavior should be very general for systems undergoing an order-disorder transition, but the nematic-isotropic transition is the only system up to now where a change of order from the microscopic coupling with an external field and from the quenching of macroscopic fluctuations of the phase of the order parameter, has been simultaneously demonstrated.

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