

Photoinduced electrical conductivity and photorefraction in a nematic liquid crystal

E. V. Rudenko and A. V. Sukhov

*Institute of Problems of Mechanics, Russian Academy of Sciences,
117526 Moscow, Russia*

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A new mechanism for an optical nonlinearity of nematic liquid crystals is predicted theoretically. It has also been implemented experimentally. It involves a reorientation of the axis of the liquid crystal caused by the field of the spatially nonuniform charge of photoinduced carriers. This mechanism is three orders of magnitude stronger than the direct orientational mechanism.

It is well known that liquid crystals, primarily the nematics, can be reoriented easily by relatively weak electric fields¹ (1–100 esu). These fields can be optical fields.² If so, the reorientation leads to an extremely large, orientational, cubic, optical nonlinearity of the medium.

On the other hand, it is equally as well known that optical radiation in a medium, which has a photoinduced conductivity and in which the intensity dependence of the concentration of photoinduced carriers is more or less local (e.g., photorefractive crystals), can generate spatially nonuniform space-charge fields³ which are *much stronger than the optical wave itself*.

We are naturally led to ask whether a field of the same sort could be excited by electromagnetic radiation in a liquid crystal (a nematic) and whether such fields could be utilized to write orientational gratings of the refractive index in the medium. In this letter we are reporting a study of this question.

A key issue here is thus the following: Can a nematic liquid crystal have a photoconductivity with a carrier concentration high enough, and with an intensity dependence of this concentration local enough, that the Debye length of the carriers is much smaller than the length scale of the variations in the intensity (in practice, on the order of a few microns).

Since the information on photoinduced changes in the electrical conductivity of nematics is rather scanty,^{4,5} we decided to consider the following possibility. Many laser dyes in polar solvents (such as the nematic liquid crystal 5CB, which we used) are known⁶ to be subject to reversible heterolytic dissociation. The mechanisms underlying this effect involve the very different acidities of the ground state and the excited state of the dye molecule, which make possible either protolytic reactions or complex formation with solvent molecules, accompanied by a heterolytic dissociation of the complex after it undergoes a transition to the ground state. The kinetics of these effects is rather involved and has received little study. We have therefore restricted the present study to simply an empirical attempt to observe a photoinduced conductivity.

Specifically, we learned that when a weak solution (on the order of 10^{-4} M) of

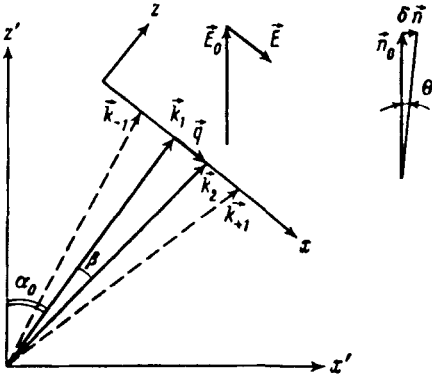


FIG. 1. Experimental geometry for the observation of self-diffraction.

rhodamine 6G (R6G) in the nematic liquid crystal 5CB is illuminated by an extremely low-power ($10\text{--}100\text{mW/cm}^2$) beam from an argon laser (with a wavelength $\lambda = 0.4880\ \mu\text{m}$), the conductivity of the solution increases reversibly by a factor of more than 10 and reaches $\sigma = 1.5 \times 10^3\ \text{s}^{-1} = 1.5 \times 10^{-9}\ \text{S/cm}$. A detailed study of the mechanism for the observed photoinduced conductivity lies outside the scope of the present study, so we will simply point out two aspects of the phenomenon here. First, the dependence of σ on the light intensity I is $(\sigma - \sigma_d) \propto I^{1/2}$, where the subscript d specifies the dark conductivity of the mixture. Second, the dependence of the conductivity on the concentration of the solution does not have a percolation limit at low R6G concentrations. This result indicates that the conductivity is of an ion drift nature, rather than, say, an exchange nature.

Working from the values of σ given above, we can easily estimate the carrier concentration n^\pm and the Debye length r_D . Specifically, we have $\sigma \approx \mu^\pm en^\pm = D^\pm e^2 n^\pm / k_b T$. Here e is the charge of a proton, μ and D are respectively the mobilities and diffusion coefficients of the positive and negative ions which form, and $k_b T$ is the temperature in energy units. We can find an upper estimate of the value of D for the ions which form, as the self-diffusion coefficient of the nematic liquid crystal (we are ignoring the slight anisotropy of the latter): $D \approx 3 \times 10^{-6}\ \text{cm}^2/\text{s}$. We thus find the lower estimate $n^\pm \geq 4 \times 10^{13}\ \text{cm}^{-3}$ and the upper estimate $r_D = (4\pi e^2 n^\pm / k_b T \epsilon)^{-1/2} \leq 6 \times 10^{-5}\ \text{cm}$. Here ϵ is the static dielectric constant of the nematic liquid crystal. We thus see that the carrier concentration is sufficient for writing gratings with a spatial period $\geq 6\ \mu\text{m}$ ($qr_D \ll 1$, where q is the wave number of the grating). Let us calculate the space-charge field which would be expected during illumination of a sample by an interference pattern of two waves, $I = I_0 [I + m \sin(qx)]$ (Fig. 1). The balance equations for the ions are

$$\partial n^\pm / \partial t + \gamma n^+ n^- + D^\pm \Delta n^\pm + \mu^\pm (\mathbf{E} \cdot \nabla) n^\pm = \alpha I(\mathbf{r}). \quad (1)$$

There are some points to be noted here. First, we are assuming, in accordance with Ref. 6, that pairs of singly charged ions form by a monomolecular mechanism. Second, we must be clear about just what is meant by "carrier recombination." From the standpoint of the formation of space charge, recombination is any process which eliminates a mobility ion (not necessarily a charge). For light ions, a suitable process

might be solvation by molecules of the nematic liquid crystal (linear recombination). However, we are dealing here with the heavy R6G ions, whose mobility should not be particularly affected by solvation by 5CB molecules. We thus assume that the only process of importance which eliminates ions from forming space charge is the actual quadratic recombination of these ions. The rate constant for the latter process can be estimated easily in the diffusion approximation: $\gamma = D^{\pm} e^2 / k_b T \epsilon$. The ratio of terms on the left side of (1) describing recombination and the diffusion–drift movement of carriers is then $(qr_D)^{-2} \gg 1$ in order of magnitude and can be ignored. We are thus led directly to a local nature (as mentioned above) of the relationship between the intensity and the carrier concentration:

$$\partial n^{\pm} / \partial t + \gamma n^+ n^- = \alpha I(\mathbf{r}). \quad (2)$$

The current density in the sample is described by

$$\mathbf{j}/e = D^+ \nabla n^+ - D^- \nabla n^- + \mathbf{E}(\mu^+ n^+ + \mu^- n^- + \sigma_d/e). \quad (3)$$

A steady-state solution of system (2), (3) in the approximation $qr_D \ll 1$ can be constructed easily by perturbation theory; see, for example, Ref. 3. In the zeroth approximation, the conditions of electrical neutrality on the average give us $n^+ = n^- = [\alpha I(\mathbf{r})/\gamma]^{1/2}$. For the steady-state value of the space-charge field we have, assuming $\mathbf{j} = 0$,

$$\mathbf{E} = \frac{mk_b T}{e} q \mathbf{v} \frac{\sigma - \sigma_d \gg \sigma}{\sigma} \cos(qx), \quad (4)$$

$$\mathbf{v} = (D^+ - D^-)/(D^+ + D^-), \quad \sigma - \sigma_d = (\mu^+ + \mu^-)(\sigma I_0/\gamma)^{1/2}.$$

Expression (4) is completely analogous to the so-called diffusion field in a photorefractive crystal⁶ in the case of a photoinduced electron–hole conductivity. Since the reorientation of a nematic is quadratic in the field, in contrast with the case of a photorefractive crystal, to obtain a reorientation grating with the same q as that of the interference pattern, we must also apply a uniform static field to the sample; this was done experimentally (Fig. 1). The calculations of the amplitude of the orientation grating and of the diffraction efficiency η for a Raman–Nath self-diffraction of waves $E_{1,2}$ into the $\pm l$ th diffraction peak are completely routine,^{1,2} so we skip ahead to their results:

$$n = \left\{ \frac{\epsilon_a \epsilon_{a0} \sin \alpha_0 \cdot E_0}{I + \epsilon_{a0} E_0^2 / 2\pi K q^2} \frac{L}{\lambda n_e} \frac{mk_b T v}{e K q} \frac{\sigma - \sigma_d \gg \sigma}{\sigma} \right\}^2. \quad (5)$$

Here $\epsilon_{a,0}$ are the anisotropies of the dielectric constant at the frequency of the light and at zero frequency, respectively; α_0 is the angle through which the waves are refracted in the crystal (we assume $\beta \ll \alpha_0$; Fig. 1); L is the thickness of the homeotropic sample of nematic liquid crystal (100 μm); K is the Frank constant (the single-constant approximation); and n_e is the refractive index for the extraordinary wave.

The experiment which was carried out corresponds precisely to the geometry in Fig. 1. Two unfocused single-mode beams, with a total intensity $\leq 200 \text{ mW/cm}^2$ from

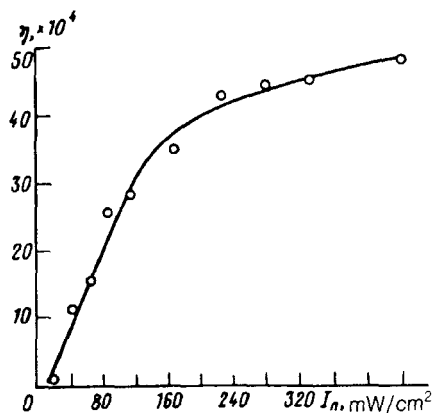


FIG. 2. Diffraction efficiency versus the total intensity of the waves. $E_0=186$ V/cm, $\beta=1.4 \times 10^{-2}$ rad.

an argon laser, intersected in a homeotropic sample consisting of a mixture of 5CB and R6G (0.75mM). Qualitatively, the results can be summarized as follows: The self-diffraction described above was observed only when e waves were incident obliquely on the sample. This circumstance rules out any mechanism for the formation of an ϵ grating other than a reorientation of the axis. Furthermore, this self-diffraction was observed only in the presence of a static external field, which was applied to the sample by means of transparent electrodes at the nematic-glass interfaces. This result is evidence that the spatially nonuniform field which causes the reorientation is also a static field. We studied the functional dependences $\eta(I_0)$ (at a constant $m=0.6$), $\eta(q^{-2})$, and $\eta(E_0^2)$. The first of these, shown in Fig. 2, is linear at small values of I_0 and reaches saturation at $\sigma \gg \sigma_d$. The second is also linear (Fig. 3a). The third (Fig. 3b) is linear at small voltages across the cell, and it increases sharply as the threshold for the Fréedericksz transition is approached ($\epsilon_{d0} < 0$). We see that all three of these functional dependences support expression (5). From the absolute value $\eta \approx 0.2$ we

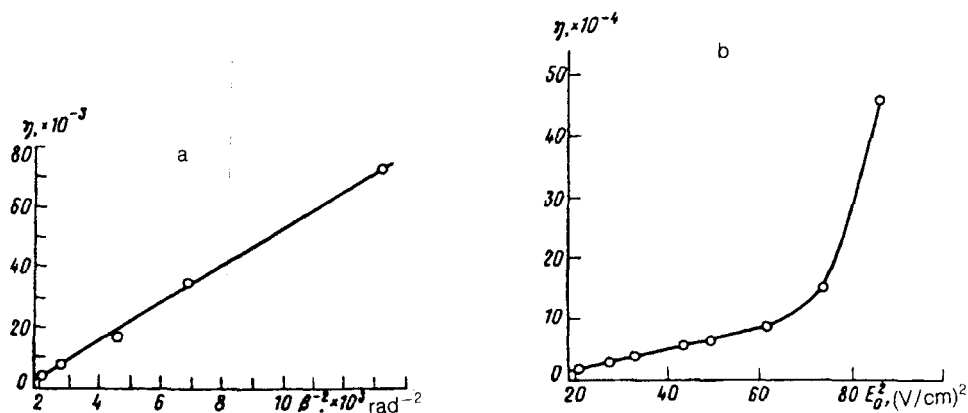


FIG. 3. a— η versus β^{-2} at $E_0=140$ V/cm and $I_0=205$ mW/cm²; b— η versus E_0^2 at $I_0=95$ mW/cm² and $\beta=1.4 \times 10^{-2}$ rad.

easily find the estimate $\nu \approx 0.02$; i.e., the mobilities of the carriers of the different signs are essentially equal in this mixture. Accordingly, there is the possibility of an increase in the nonlinearity by yet another one or two orders of magnitude in an optimum mixture.

In summary, there is every reason to believe that these experiments have revealed a photorefractive orientation mechanism for nonlinearity of nematic liquid crystals which is comparable in terms of the intensities required to the mechanisms operating in solid photorefractive crystals and that this mechanism is more than three orders of magnitude better than the "direct" orientational nonlinearity of nematic liquid crystals.²

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