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Observation of dynamic behavior of enhanced optical Kerr effect in light-absorbing liquid

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We observed the dynamic behavior of the optical Kerr phenomenon in the isotropic phase of the liquid crystal, enhanced by the doping of the light-absorbing dye molecules. The system is regarded as a candidate of the Brownian motor, and the newly developed polarization modulation Kerr spectroscopy technique was successfully applied for the light-absorbing sample: The frequency spectra of the molecular orientation were obtained in the vicinity of the isotropic-nematic phase transition temperature. We examined the relaxation behavior as a function of the dye concentration giving the number of liquid crystal molecules dominated by a dye, and the temperature determining the size of the quasidomain of the molecular orientation. The result shows that the critical slowing down of the relaxation is not affected by the dopant, though the magnitude of Kerr constant drastically increases. It is also shown that the change in the elastic coherence length does not affect the enhancement phenomenon. This gives evidence for the idea of the Brownian motor as the mechanism of the enhanced optical Kerr effect.

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I. INTRODUCTION

The enhancement phenomenon of the nonlinear optical effects in light-absorbing liquids attracts a great interest as a model of the Brownian motor and a possible material for the new optical devices. In the early 1990s, Janossy *et al.* found that the doping of a small amount of light-absorbing dye drastically reduced the threshold intensity of the optical Freedericksz transition by two orders of magnitude for the nematic phase of the liquid crystal [1–3]. The enhancement effect was observed later also in the isotropic phase; Paparo *et al.* reported the optical Kerr effect in liquid crystal E63 doped with the dye anthraquinone derivative at a concentration of 0.26% was about 20 times as large as that in pure sample [4]. Muenster *et al.* independently found similar effects, in which the optical Kerr effect with the dye concentration of 0.05% was enhanced by about six times for 4-cyano-4′-pentylbiphenyl [5]. Those phenomena of the increase in the optical nonlinearity are called Janossy effect, and have been investigated by many researchers up to now.

In transparent liquid, the mechanism of molecular reorientation under light exposure is now well understood. The molecules with anisotropic shape rotate so that their main axis of the molecular polarization directs into the external electric field of the polarized laser. Macroscopic birefringence is then derived by their cooperative orientation, and the generated anisotropic index of refraction is proportional to the power of the incident light; namely, the phenomenon is regarded as Kerr effect. The permanent dipoles in molecules cannot follow the electric field at the light frequency and do not contribute to the nonlinear effect. In the enhancement of the optical Kerr constrant, the dye molecules would give additional torque to the liquid crystal since the increased amount of the nonlinear constant is proportional to the density of doped dye molecules, though the mechanism has not been clarified yet.

It was pointed out by Palffy-Muhoray *et al.* that the Janossy effect would be a possible example of the "Brownian motors" [6–8]; Prost *et al.* proposed a mechanism of transporting randomly moving molecules without external forces but spatially or temporally modifying the parameters characterizing the thermal motion of molecules [9]. In the Janossy effect, absorbed light does not exert any optical torque on the liquid crystal molecules but gives light energy to dye molecules constituting a motor rotating molecules *without torque*.

The basic idea of the Brownian motor enhancing the molecular orientation is as follows: The dye molecules spontaneously rotate by thermal fluctuation; under the exposure of the linearly polarized light, the molecules orientated to the electric field are selectively excited. The lifetime of the excited state is in the same order as that of the rotational relaxation time of dye and, therefore, the molecules changing direction from the light polarization to other are almost excited, while those being directed to the polarization are mainly in the ground state. If the interaction between the liquid crystal and dye molecules is different for the excited and the ground states, the orientation of the liquid crystal can be stochastically supported, for example, in cases where the rotating dye in the ground state can take neighboring liquid crystal into the same direction, while one excited does not. Some possible ideas were presented as the microscopic mechanism of the interaction. One is the difference in the angular potential between the ground state of dye and the excited state [10–17] and the other is the difference in the rotational diffusion constant of dye [10–15,17,18]; however, they are still under investigation.

In this paper, we examine the possibility of the idea of the Brownian motor from the viewpoint of the cooperative motion of molecules, which is characteristically seen in complex soft fluids. We focused our attention to the dynamic behavior of the optical Kerr effect especially near the phase transition temperature, where the susceptibility of the system

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for the external field diverges drastically, and the coherence length of the random molecular motion extends over the light wavelength due to the cooperative molecular dynamics. The self-organization of molecules under the strong thermal noise is a remarkable feature of soft condensed materials and we consider it is worth investigating the enhancement phenomenon in detail, especially in the vicinity of the critical point, where random thermal motion plays a more important role.

We investigated the dynamic behavior of the optical Kerr effect (OKE) and observed the orientational relaxation at various temperatures and dye concentrations, especially in the vicinity of phase transition and in a wide dye concentration region where the coherence length exceeds the mean distance between dye molecules.

The measurement was carried out by a newly developed optical Kerr spectroscopy system that enables the observation of the optical Kerr phenomenon in the light-absorbing medium with high-time resolution near the phase transition point. In Sec. II the used sample and the principle of our measurement system are described and in Sec. III the measurement data are shown in samples with different dye concentrations.

II. EXPERIMENT

A. Sample

We chose as our liquid crystal sample 4-cyano-4′-pentylbiphenyl (5CB) whose behavior near the phase transition has been thoroughly studied and which possesses chemical stability against the exposure of strong laser beam. The sample was purchased by Merck and used without further purification. The doped dye was 1-amino-anthraquinone purchased from WAKO Pure Chemical Industries. The dye has a broad light absorption band around the peak wavelength of 470 nm and does not show conformation deformation (trans-cis isomerization), unlike the azo dye derivatives. The dye concentration in the sample was varied in the range of 0–0.05 wt %. The sample was held in a glass cell and placed in a temperature-controlled oven within the accuracy of ±0.1 °C. The measurement temperature range was from $\Delta T=0.8$ K to 5 K, where ΔT is the temperature difference apart from the critical temperature.

B. Experimental system

The measurement was conducted with original optical Kerr effect spectroscopy system, the detail of which was described in our previous paper [19] and here we give a brief account. The light source to induce the molecular orientation was frequency-doubled Nd: yttrium aluminum garnet (YAG) laser with the power of 0.4 W oscillating at 532 nm, and the probe laser to pick up the optical anisotropy was a He-Ne laser (17 mW) at 632.8 nm. Two laser beams are aligned coaxially with a dichroic mirror and are incident to the sample cell. The wavelength of the pump laser is within the absorption band of the dye 1-amino-anthraquinone, while that of probe laser is outside it and the absorption of the probe laser is negligibly small. The feature of the system is that we applied a continuous wave (cw) laser as the pump laser instead of conventionally used pulse lasers with much higher peak power [1,2,4,5] as well as the polarization modulation method.

The electric field of the linearly polarized pump laser induces the molecular orientation in the sample parallel to the light polarization giving the birefringence $\Delta n=n\|-n\perp$, where $n\|,n\perp$ denote a refractive index parallel and perpendicular to the polarization of the pump laser, respectively. The ensemble of the liquid molecules changes its orientational order without average torque. The incident probe laser is modified slightly elliptically and focused by a lens to 56 μm, and the change in the birefringence through the propagation in the sample is analyzed. The polarization of the pump laser is periodically modulated between ±45° with respect to the main axis of probe laser by electro-optical modulator. The laser is focused by a lens to 50 μm diameter and incident to the sample during the period of several tens of μs, in which the sample temperature increases only by 0.01 K. The sample is then kept without the laser radiation for several seconds and the sample cools down to the initial temperature. We can obtain the relaxation spectra of the optical Kerr effect by sweeping the frequency of the polarization modulation, which is swept in the range of 50 K–10 MHz. The laser is repeatedly radiated and the averaged signal is obtained by a digital oscilloscope.

III. OPTICAL KERR PHENOMENON IN DYE-DOPED ISOTROPIC PHASE OF LIQUID CRYSTAL

As described in the former section, the newly developed system has an experimental advantage quite effective for the investigation of the dye-induced enhancement of the optical Kerr effect. We can distinguish the contribution of the induced optical anisotropy due to the Kerr effect and the thermal lens caused by the light absorption in the sample: The thermal effect causes the monotonous change of the signal intensity, while the Kerr signal follows the periodical modulation of the laser polarization. Another advantage is that the temperature increase is suppressed within 0.05 K throughout the experiment even for the sample with highest dye concentration, and therefore, we can determine the optical Kerr constant at very close to the isotropic-nematic phase transition temperature T_c; the orientational relaxation spectra were successfully observed just above the phase transition temperature.

A major matter to be investigated in this experiment is an examination of whether the mechanism of the enhancement is attributed to the Brownian motor phenomenon. The Brownian motor is driven by the random thermal fluctuation and can be realized by introducing, for example, the periodical anisotropic or asymmetric potential to the Brownian particles. In a possible model of the Kerr enhancement, the periodical modulation is achieved by the spontaneous rotation of the dye molecules due to the thermal fluctuation. The lifetime of the excited state of dye is 307 ps while the typical time constant of its rotational relaxation is 490 ps [12]. They are in the same order, which is reasonable to support this physical model.

The remarkable feature of the Brownian motor is that the microscopic behavior of each molecule constituting the system is dominated by the random thermal noise and, therefore, the characteristic time constant of the enhanced phenomenon is still determined as that required for the molecules to achieve the equilibrium state under the stochastic process.

Another behavior expected for the Brownian motor is the critical phenomena near the phase transition. The amplitude of the thermal fluctuation drastically increases near the second order phase transition, while the typical time constant and the spatial scale characterizing the fluctuation also diverge in the power law of $\Delta T = T - T^*$, where T^* is the critical temperature. The sample of 5CB undergoes a weak first order transition from isotropic to nematic phase at $T_c = 35$ °C and the virtual critical temperature is by 0.8 K below T_c: T^* is accurately determined by the high-resolution dynamic light scattering measurement [20] as the critical temperature, where the relaxation time of the rotational orientation diverges. The enhancement effect, if dominated by the Brownian motor, would also show the similar anomaly such as the critical slowing down and the coarsening of the spatial pattern of the fluctuation in the order parameter.

Along this line, we carried out the observation of the optical Kerr phenomenon, paying attention to its dynamic aspect and the temperature dependence. The molecules in the isotropic phase of liquid crystal take a finite time to rotate into the direction of the external electric field. We examined whether the excess Kerr constant brought about by the dye doping also shows a similar relaxation spectrum. We assumed that the enhanced constant would also show the same relaxation if the mechanism of the enhancement is still dominated by the rotational Brownian motion of liquid crystal molecules.

In addition, we observed the temperature dependence of the orientational relaxation especially near the phase transition temperature to examine if the enhanced amount of Kerr constant also shows the critical slowing down. The authors' interest is on the mechanism of the interaction between the dye and liquid crystal to enhance the laser-induced molecular orientation. We investigated the role of the quasidomain of the molecular orientation temporally generated by the thermal fluctuation.

A. Static aspect of Kerr effect

It is known that the coherence length of the orientational order in the isotropic phase critically increases towards T^*. The decrease in the free energy due to the cooperative orientational order overcomes the contribution of the thermal fluctuation to the random orientation in the lower temperature range: The size of the quasidomain in the isotropic phase then grows, in which the liquid crystal molecules direct cooperatively and share the information on the ensemble orientational order.

First, we examined the effect of the critical phenomenon on the static aspect of the enhancement of the Kerr constant. The temperature was swept towards the phase transition temperature and the spatial size of the quasidomain of the orientational order was changed. Some samples with different dye concentration were prepared so that we could change the ratio between the number of dye molecules and that of quasidomain. Here, we roughly estimate the actual spatial size of the domain and the ratio of dye in liquid crystal. According to de Gennes's theory [21], the coherence length ξ of the orientational order is given by

$$\xi = \xi_0 (T/T^* - 1)^{-1/2}, \tag{1}$$

where ξ_0 is a constant and often given as the molecular length. The number of liquid crystal molecules n_Q included in a domain is then given by

$$n_Q = (T/T^* - 1)^{-3/2}. \tag{2}$$

On the other hand, the number of molecules assigned to a dye is given as the molar concentration.

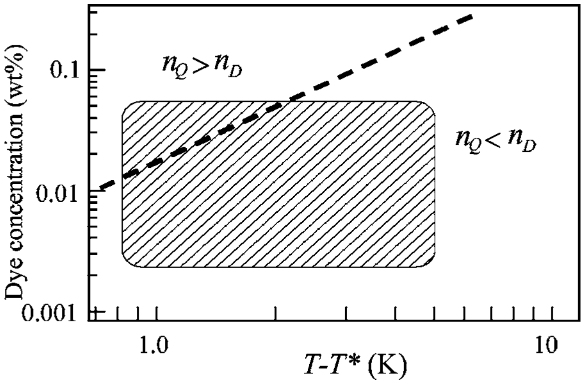

FIG. 1. The relation between the number of liquid crystal molecules included in a quasidomain n_Q and the number assigned for single dye molecule n_D, shown against the temperature and dye concentration. The dashed line represents $n_Q = n_D$ and the hatched area is the region of the present experiment, covering both the conditions of dye-rich ($n_Q > n_D$, left upper) and dye-poor ($n_Q < n_D$, right lower).

Figure 1 schematically shows the relation between n_Q and n_D, the number of liquid crystal molecules assigned for single dye molecule, as a function of the temperature and the dye concentration. The temperature range of the present experiment is $0.8\ \mathrm{K} < T - T^* < 5\ \mathrm{K}$, which inversely corresponds to $8000 > n_Q > 500$. On the other hand the dye concentration was changed in the range of $0.0025\ \mathrm{wt}\,\% < c < 0.05\ \mathrm{wt}\,\%$, which gives n_D of $36\,000 > n_D > 2000$. The dashed line with the gradient 3/2 shows the relation of $n_D = n_Q$ and the hatched area is the region experimentally examined in this study, which covers both conditions of $n_Q > n_D$ and $n_Q < n_D$.

First, we show the temperature and concentration dependence of the optical Kerr constant in Fig. 2. A linearly polarized laser oscillating at 532 nm with the power of 400 mW is employed as the pump light and the optical Kerr effect is measured at the fixed polarization modulation frequency of 100 kHz. In the temperature range of the experiment, the relaxation frequency of the orientational relaxation is above 500 kHz, and the optical Kerr constant at 100 kHz can be approximately regarded as the low frequency limit.

The critical divergence in the optical Kerr constant B in the isotropic phase of liquid crystals can be written as $B \sim (T - T^*)^{-1}$, also for the case of the dye-doped samples. In

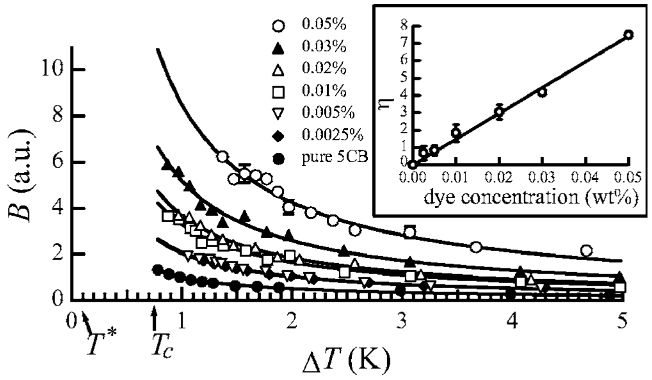

FIG. 2. The static optical Kerr constant for various dye concentrations in 0–0.05 wt % plotted against the temperature down to T^*. The solid curves are the fitting of $B \propto (T-T^*)^{-1}$. The inset shows the dye concentration dependence of the enhancement factor $\eta(c)$ of the optical Kerr constant.

addition, B also depends on the dye concentration. According to the previous study [5], we introduce here the enhancement factor η as $\eta(c)=B(c)/B(0)-1$, where $B(c)$ is the Kerr constant at the dye concentration c, and the factor can be regarded constant in a wide range of concentration. The enhancement factor was obtained as the zero-frequency limit of the spectroscopic measurement, the detail of which is described in the next section. The result is shown against the dye concentration in the inset of Fig. 2. The enhancement factor shows proportional increase to the concentration as reported in the previous study [5]. As shown, our system of cw laser Kerr spectroscopy can detect the enhancement phenomenon with a satisfactory sensitivity.

The solid line shows the linear relation between η and c and the proportional coefficient agrees well with the results given by Shen *et al.* [5]. Figure 3 shows the enhancement factor plotted against the temperature difference ΔT for each concentration. The dashed curve in the figure divides the region of $n_Q > n_D$ (left upper) and $n_Q < n_D$ (right lower). We can examine the enhancement effect under both conditions: $n_Q > n_D$ at $\Delta T < 2$ K for the concentration of $c = 0.05$ wt % and $n_Q < n_D$ at $\Delta T > 1.5$ K for 0.03 wt %, for example. As shown, the enhancement factor is constant as a function of temperature even if the quasidomain of molecular orientation grows with decreasing temperature and exceeds the volume assigned for single dye molecule. It suggests that the enhancement phenomenon is not affected by the coherence length of the elasticity with respect to the orientational order in liquid crystals. The mechanism of the enhancement seems not to be based on the elastic interaction between the dye and liquid crystal molecules, though its dynamic behavior is still dominated by the Brownian motion driven by the thermal fluctuation even in the vicinity of the phase transition temperature.

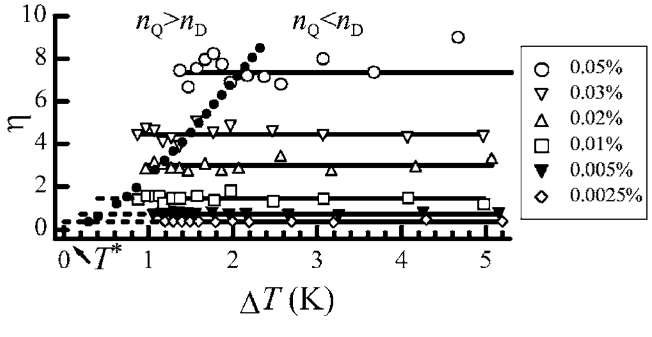

FIG. 3. The enhancement factor of the optical Kerr constant in various dye concentrations plotted as a function of the temperature down to T^*. The dashed curve divides the region of $n_Q > n_D$ (left upper) and $n_Q < n_D$ (right lower).

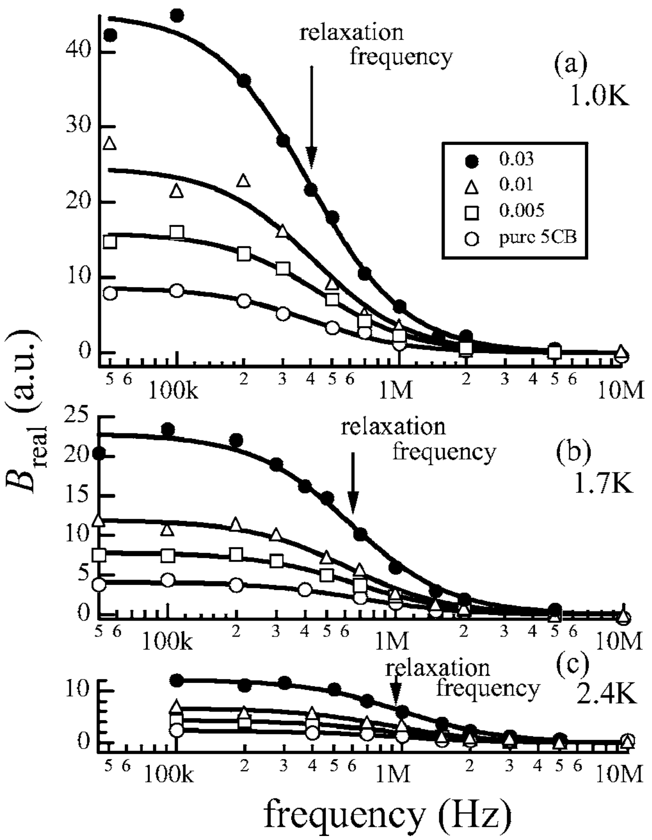

FIG. 4. Frequency spectra of the real part of the optical Kerr constant obtained at (a) $\Delta T = 1$ K, (b) 1.7 K, and (c) 2.4 K.

B. Dynamic behavior of orientational relaxation in dye-doped isotropic phase of liquid crystal

Next, we examine the dynamic behavior of the relaxation of the enhanced molecular orientation. In the isotropic phase of liquid crystal, 5CB, the relaxation spectrum of the molecular orientation is known to obey the single Debye type and the frequency dependence of the Kerr constant is described as

$$B(\omega) = B_0/(1 + i\omega\tau), \tag{3}$$

where ω is the angular frequency of the polarization modulation of the external electric field induced by the laser and τ is the relaxation time, which depends on the temperature in the form of

$$\tau = \tau_0(T/T^* - 1)^{-1} \tag{4}$$

in the vicinity of the critical temperature. Figure 4 shows the

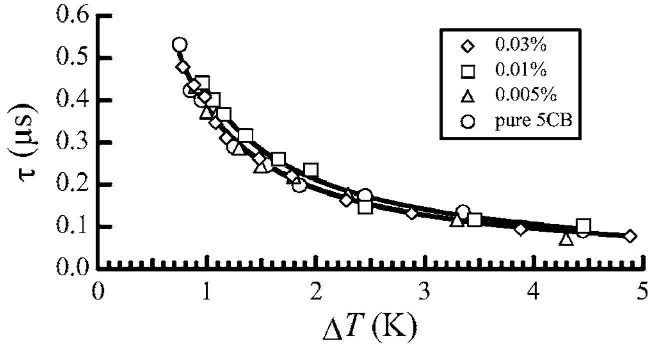

FIG. 5. The relaxation times plotted against the temperature for each concentration. The solid curves show the theoretical curves of $\tau=\tau_0(T/T^*-1)^{-1}$, giving the same constant of $\tau_0=1.2$ ns.

concentration dependence of the real part of relaxation spectrum obtained at (a) 1 K, (b) 1.7 K, and (c) 2.4 K. The solid curves are the best fitting of the single relaxation of Eq. (3), which well reproduces the experimental results at any concentration. In addition, the relaxation frequency, which is derived from the fitting and shown as arrows in the figure, and the spectrum shape are independent of the existence of dye molecules, though the amplitude of B increases as described in detail in the former section.

The relaxation times are plotted against the temperature for each concentration in Fig. 5. All the data points are plotted on the universal theoretical curve of Eq. (4) with a unique value of $\tau_0=1.2$ ns. As shown, the relaxation time, which is the typical time constant of the cooperative rotational Brownian motion, is not affected by the doping of the dye molecules. The enhanced amount of the optical Kerr constant is also dominated by the Brownian motion driven by the thermal fluctuation. The relaxation time can be understood as the time required for the liquid molecules constituting a quasidomain to share the information on the molecular orientation through the diffusion process; the relaxation time can be given in the diffusion type equation of $\tau=\xi^2/D$, where $D=\xi_0^2/\tau_0$ is the diffusion constant of the information. The present result is evidence supporting the assumption that the enhancement of the Kerr effect is a model of the Brownian motor.

The idea of the Brownian motor as the origin of the dye-induced optical Kerr effect was proposed by Paparo *et al.* [10,22], in which the rotational friction between the dye and liquid crystal molecules changes for the ground state and excited dye. The results of the present experiment support these conclusions from the viewpoint that the enhanced molecular orientation is still dominated by the random Brownian motion and the dye molecules apparently introduce the additional anisotropic potential to liquid crystals.

In conclusion, we successfully observed the static and dynamic aspect of the optical Kerr effect enhanced by the doping of light-absorbing dye molecules. From the spectroscopic measurement of the orientational relaxation, the rotational motion of liquid crystal is found to be dominated by the Brownian motion. Further study would be required, therefore, to reveal the detail of the origin of this interesting phenomenon and examine its application to the industrial use.

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