FAST PICOSECOND REORIENTATION IN THE ISOTROPIC PHASE OF NEMATOGENS

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We report the first observation of a fast optical Kerr signal given by nematogens in the isotropic phase, induced by intense mode-locked laser waves. This signal can be attributed to the individual orientational relaxation of molecules inside the highly correlated domains. The relative contribution of this fast relaxation process can be directly measured.

The non-linear optical properties of the isotropic phases of nematic liquid crystals have been intensively studied these last years. More precisely, the transient order induced by plane polarized waves with the use of both Q-switched [1–3] and mode-locked [4] lasers has been investigated. This order can be undoubtedly held as responsible for the non-linear refractive index induced in such materials by the laser optical field. The dynamics of the observed effect, near the isotropic-mesomorphic phase transition, is now well understood. We essentially observe a "slow" response, corresponding to a relaxation time in the range 10^{-9}–10^{-6} sec, which can be attributed to the order parameter fluctuations in De Gennes' phenomenological theory [5], or else, from the microscopic point of view, to orientational fluctuations of domains constituted by highly correlated molecules, the correlation length ξ of which varies with temperature according to the well-known law:

$$\xi \sim (T_c/T - T_c)^{+1/2}.$$

The Fourier transform directly relates this relaxation time τ_s and the linewidth of the sharp component of the Rayleigh scattering five years ago observed by Stinson and Litster [6] with an interferometric device.

Long-range correlations do not prevent local molecular motion from occurring, within a correlated domain. These motions, as in usual isotropic liquids, are probably fast and give rise to a broad Rayleigh wing which appears as a background term in experiments such as Stinson's. In fact, individual motions lead to a broad spectrum of relaxation times with wave vector values greater than $1/\xi$. It is, however, possible to perform spectroscopic studies of these broad components, but the observation is difficult since the main phenomenon is the slow one [7]. Recently, a mean field theory taking account of many relaxation times within the Maier and Saupe approximation has also been derived [8]. In such circumstances, we think that a need for a direct method for probing the local dynamics was clearly demonstrated.

We present here what we believe to be the first observation in the time domain of fast individual reorientation inside the pseudo-nematic domains of liquid crystals in the isotropic phase. It leads to a direct and accurate mea-

surement of the relative importance of the slow and fast phenomena, — a comparison which is rather difficult to perform in Rayleigh scattering experiments which involve two different experimental setups.

We use the optical Kerr effect in the picosecond range [9]. A transient birefringence is induced in the studied compound, placed between two crossed polarizers, by a picosecond laser pulse at λ_{ir} = 1060 nm, giving rise to a time dependent transmission $T(t)$ of the Kerr shutter. An auxiliary picosecond wave at λ_g = 530 nm, delayed by t_0 from the infrared one, is used to analyse the induced birefringence. In this way, the energy of the green light transmitted through the cell appears as the correlation product of the assumed gaussian pulse shape at 530 nm (constant τ_g) and the square of the time dependent transmission $T(t')$, namely:

$$I_g(t_0) = \int_{-\infty}^{+\infty} I_{g,0} \exp\left(-\frac{t'^2}{\tau_g^2}\right)[T(t_0 + t')]^2 dt'. \tag{1}$$

This treatment is equivalent to the ones presented in refs. [10] and [11].

Our experimental setup is deduced from Duguay's one [10]. Plane polarized pulses at 1060 nm, 6–8 psec in duration, are provided by a mode-locked Nd : glass laser. A single pulse is selected by a special Kerr shutter. After amplification, it carries a power of about 500 MW and passes through a 4 cm cell filled with the studied compound and placed between two crossed polarizers. Green pulses are given by second harmonic generation in a 2-cm ADP crystal, mistuned in order to reduce the generation. A special delay element allows the variation of the relative arrival time t_0 of the infrared and green waves at the beginning of the cell in the range 0–5 nsec without any appreciable modification of the superposition of the two beams. This very large range is needed by the long relaxation time of the slow response. The temperature of the cell is carefully controlled and regulated within 10^{-12}°C by electronic devices driven by a Hewlett–Packard 2801-A quartz thermometer. Photon counting techniques give at each laser shot the values of $I_{ir,0}, I_{g,0}$ and $I_g(t_0)$ where $I_{ir,0}$ and $I_{g,0}$ are respectively the energies of the infrared and of the green light pulses before the cell. $I_g(t_0)$ is directly given by eq. (1).

By varying t_0, we can have a direct access to the short times dynamics of the optical Kerr effect. Fig. 1 shows
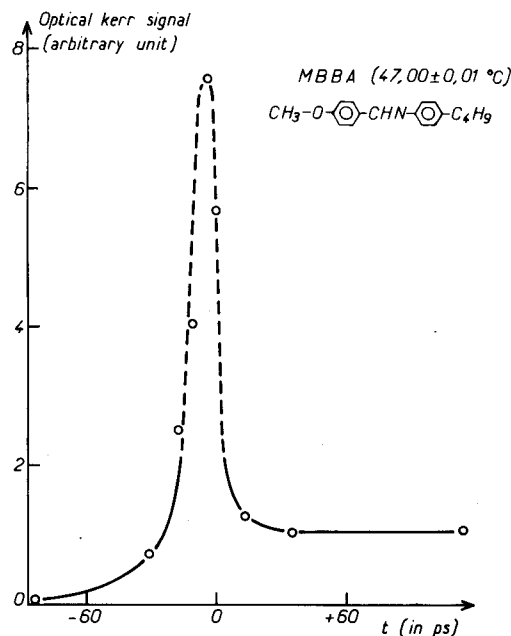

Fig. 1. ○ experimental optical Kerr signal given by MBBA at (47.00 ± 0.01)°C. ‒‒‒‒ computer curve with the values δ_{ir} = 7 psec, δ_g = 5 psec, τ_F = 5 psec, β = 5.1 psec·cm^{-1}. The time origin is the one of the computed curve.

a typical experimental result obtained with p-methoxy-benzilidene-p-n-butylaniline (MBBA) at the temperature $T = 47.00 \pm 0.01°C$. Two relaxation rates can be easily distinguished. The slow one gives a flat curve experimentally checked up to 5 nsec. Longer delays are not easily obtained with the setup we are currently using, but previous work [2] gave a relaxation rate of about 110 nsec for MBBA at 47°C. The fast one corresponds to a rather symmetrical curve ~15 psec wide.

These experimental results can be well explained if we assume the presence of two rather different relaxation times inside the medium: a slow one (relaxation time τ_s in the nanosecond range) and a fast one (relaxation time τ_f in the picosecond range). This purely phenomenological treatment does not take into account the unknown microscopic nature of the fast molecular motions inside the domain. In this case, and for an input laser pulse with a gaussian shape of characteristic time τ_{ir} one has:

$$I_{ir}(t, z) = I_{ir,0} \exp \left| -(t - zn_{ir}/c)^2/\tau_{ir}^2 \right|. \tag{2}$$

The time dependent non-linear refractive index is simply given by the theory of the linear response:

$$\Delta n(t, z) = (2\pi/n_g)B_{or}I_{ir,0} \sum_{k=s,f} (C_k/\tau_k) \int_{-\infty}^{t} \exp \left| -(t' - zn_{ir}/c)^2/\tau_{ir}^2 \right| \exp(-\alpha_{ir}z) \exp \left| -(t - t')/\tau_k \right| dt', \tag{3}$$

where B_{or} is an orientational, temperature dependent constant proportional to the square of the optical anisotropy of the molecule, n_g the refractive index at the wavelength λ_g and α_{ir} the absorption coefficient of the material at λ_{ir}. C_k is a constant already introduced in ref. [8].

Eq. (3) can be written:

$$\Delta n(z, t) = (2\pi/n_g)B_{or}I_{ir,0}$$

$$\times \sum_{k=s,f} (C_k/\tau_k)\exp(+\tau_{ir}^2/4\tau_k^2)\exp[-(t - zn_{ir}/c)]\{1 + \mathrm{erf}[(t - zn_{ir}/c - \tau_{ir}^2/2\tau_k)/\tau_{ir}]\} \tag{4}$$

which can be considered as the generalised form for two relaxation mechanisms of eq. (6) in ref. [9]. It is then possible to perform the calculation for many different values of t_0 of the time dependent transmission $T(t_0 + t)$ which can be written:

$$T(t_0 + t) = \int_0^l (d\phi/dz)_{(z, zn_g/c+t_0+t)} \exp(-\alpha_g z/2)dz \tag{5}$$

with $(d\phi/dz)_{(z,t)} = (2\pi/\lambda_g)\Delta n(z, t)$ and where α_g is the absorption coefficient at $\lambda_g = 530$ nm and l the length of the cell. Eq. (5) can be written as:

$$T(t_0 + t) = \int_0^l \frac{2\pi^{5/2}}{\lambda_g n_g} I_{ir,0}\tau_{ir}\exp[-(\alpha_{ir} + \tfrac{1}{2}\alpha_g)z]$$

$$\times \sum_{k=s,f} \frac{C_k}{\tau_k} \exp\left(+\frac{\tau_{ir}^2}{4\tau_k^2}\right) \exp\left(-\frac{t + t_0 + \beta z}{\tau_k}\right) \left\{1 + \mathrm{erf}\left(\frac{t_0 + t + \beta z - \tau_{ir}^2/2\tau_k}{\tau_{ir}}\right)\right\} dz, \tag{6}$$

where we have introduced the parameter $\beta = (n_g - n_{ir})/c$ taking into account the dispersion of the refractive index. The values of the refractive index of MBBA, at 47.00°C have been deduced from the literature [12]. A linear extrapolation has been used for the temperature dependence. A development of the form

$$n_\lambda^2 = C_1\lambda^2 + C_2 + C_3\lambda^{-2} + C_4\lambda^{-4}$$

allows the calculation of the refractive index at 1060 nm. We obtained the following values: n_g = 1.624 ± 0.001; n_{ir} = 1.425 ± 0.004. This correction cannot be neglected. The velocity mismatch between the infrared and green pulses can amount to ~20 psec in a 4 cm cell filled with nematogen molecules. Consequently, the picosecond pulses become broadened because of the very important dispersion, the red components moving to the leading edge and the blue to the tailing one of the pulse envelope. Computer calculations, performed with different values of the dispersion, clearly show the increase of the width of the optical Kerr signal with β.

α_{ir} and α_g have been measured at each temperature, directly on the sample using the infrared and green picosecond pulses. The obtained value of α_{ir} at 47°C for MBBA is 16.4 ± 0.8 m^{-1}. There is no appreciable attenuation of the green wave at this temperature. It only becomes measurable for temperatures in the vicinity of the clearing point of the material.

By putting eq. (6) into eq. (1), we can perform the calculations of $I_g(t_0)$ for different values of t_0. The value of τ_{ir}, 7 ± 1 psec, is a mean value obtained from two-photon fluorescence measurements performed on the single pulse. The value of τ_s has been derived from optical Kerr effect measurements in the nanosecond range previously achieved in our laboratory [2,4]. τ_g has been experimentally measured from an auxiliary optical Kerr measurement performed on CS_2 using the value τ_{CS_2} = 2.1 ± 0.3 psec, recently obtained with 1.2 psec pulse width [13]. We found τ_g = 5 ± 1 psec.

Comparison of computer calculations and experimental results leads to a relaxation time τ_f not larger than 5 psec, which can be of the same order of magnitude as the one recently reported for benzene [11]. A more accurate determination cannot be performed because of the well-known fluctuations in the duration of the mode-locked pulses. The corresponding frequency with $\Delta\nu_f = 1/2\pi\tau_f \sim 1$ cm^{-1} is also of the same order than the experimental one reported by Amer [7] (in the range 3.5—5.5 cm^{-1}).

Moreover, this comparison allows the determination of the ratio C_f/C_s. We found: C_f/C_s = (1.7 ± 0.3) × 10^{-3} for MBBA at the temperature 47°C. Such a result cannot be directly obtained from Rayleigh scattering experiments because of the large difference between the bandwidths of the two lorentzian spectra. Only an indirect information can be deduced from the results of two different experimental setups (high-resolution Fabry—Perot interferometer and spectrometer).

Similar results, reported in fig. 2, have been obtained with a second nematogen molecule NEMATEL 105** (see the formula in fig. 2).

We have also checked the temperature dependence of both amplitude and time constants of the fast relaxation. Experimental results are shown in fig. 3.

The important point is that in spite of a large experimental uncertainty which is usual in this kind of experiments, the two parameters *do not show a critical behavior* as T decreases near T_c.

It is well known that an electronic hyperpolarisability contribution to the total non-linear refractive index exists [14]. This distortion can play an important role in self-phase modulation or self-trapping experiments, but only in the cases of solid materials [15], isotropic atoms and molecules [16] and viscous liquids [17].

In materials with large orientational Kerr constants (CS_2, nitro-benzene, etc.) experimental work leads to the conclusion that the orientation is dominant in the picosecond range [18]. Nematogens must be, of course, included in that case because of the very important anisotropy of their first-order polarizability***. We believe that the main part of the observed effect must be attributed to individual, optical field induced, molecular orientation.

In conclusion, we have directly shown that fast molecular orientation can occur inside pseudo-nematic domains, in spite of the very strong correlations between molecules. The observations of such movements, in Rayleigh scattering experiments, remains difficult: the slow orientation gives the main contribution; the fast one a background term with an intensity 10^3-10^4 times smaller. The two contributions cannot be measured with the same

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** Nematel 105 has been synthetised by J.C. Dubois at the Thomson—CSF Laboratories. Its nematic—isotropic transition occurs at 42.0±0.1°C.

*** Depolarized Rayleigh scattering investigations lead to the values of (29.0 ± 0.5) × 10^{-24} cm^3 and (20.5 ± 0.5) × 10^{-24} cm^3 of the first-order polarisability anisotropy of non-correlated molecules of MBBA and Nematel 105 [19].

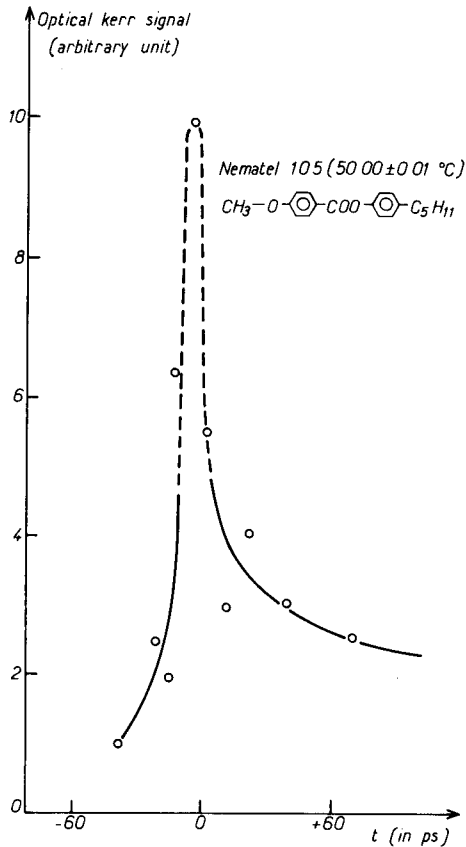Fig. 2. ○ experimental optical Kerr signal given by Nematel 105 at 50.00 ± 0.01°C. − − − computer curve with the values $\delta_{ir} = 7$ psec, $\delta_g = 5$ psec, $\tau_f = 5$ psec, $\beta = 5.1$ psec.cm^{-1}. The time origin is the one of the computer curve.
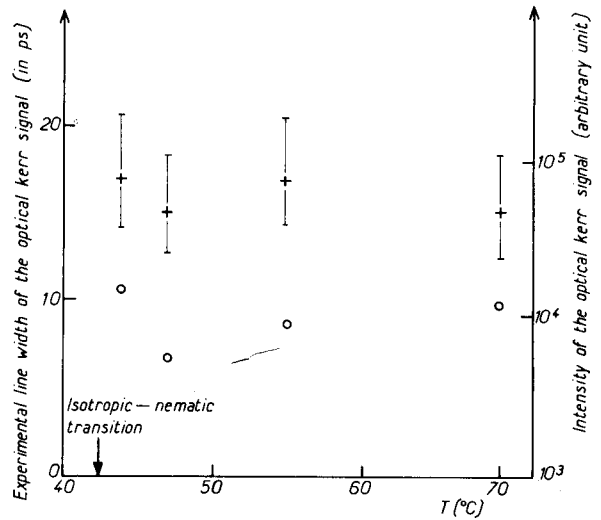
Fig. 3. + experimental line width of the optical Kerr signal given by MBBA as a function of temperature; $\delta_{ir} \sim 7$ psec, $\delta_g \sim 5$ psec. ○ experimental intensity of the optical Kerr signal given by MBBA as a function of temperature. Temperature of the transition isotropic ⇌ nematic of MBBA: 42.50 ± 0.01°C.

experimental setup. A totally opposite situation occurs when picosecond laser pulses are used in Optical Kerr investigations; the fast reorientation appears as the most important term, the slow one giving a flat background. The ratio of the two contributions can be directly obtained from only one investigation. Direct investigations of individual dynamics inside highly correlated species are then possible, not only in the isotropic phase of nematogens, but also in properly oriented nematic and smectic A for instance. These studies are now in progress in our laboratories.

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