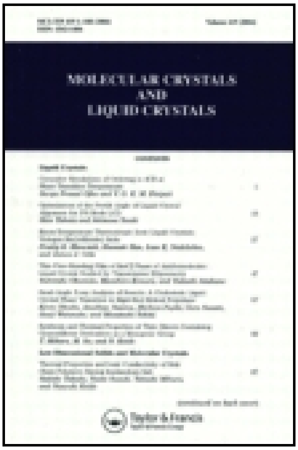

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Direct Observation of Picosecond Reorientation of Molecules in the Isotropic Phases of Nematogens

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Direct Observation of Picosecond Reorientation of Molecules in the Isotropic Phases of Nematogens

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We present here an experimental investigation of individual molecular movements inside the isotropic phase of nematogens, by means of Optical Kerr Effect techniques. They give rise to a fast response of amplitude C_F in the picosecond range, which is evidenced. Its time constant is evaluated and compared to that of molecules prefigurating liquid crystals but showing no nematic phase. Moreover, we present in the case of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA), the first direct measurement of the ratio C_F/C_S, where C_S is the amplitude of the well known slow response, induced by the order parameter fluctuations.

INTRODUCTION

The molecular movements inside the isotropic phase of nematogens have been intensively studied these last years, both theoretically and experimentally. The most important one can be attributed, from a microscopic point of view, to the collective reorientation of strongly correlated molecules inside a pseudo nematic domain, or, in the De Gennes phenomenological theory, to the fluctuations of the order parameter.[1] This movement gives rise to a sharp central peak in Rayleigh scattering spectra[2,3] and to an exponentially decreasing signal with a time constant τ_S up to one microsecond in optical Kerr effect measurements.[4–6]

Besides this collective reorientation, there still exists individual molecular movements[7] inside the domains, with a correlation time τ_F which we expect to be much shorter than τ_S and not to exhibit any critical behavior versus temperature near the isotropic ⇄ nematic transition.

Since such movements involve individual molecules, it seemed interesting to evidence them and, in case of success, to compare them to those of some molecules prefigurating liquid crystals but showing no nematic phase.

Rayleigh scattering or optical Kerr Effect set-up are available to observe both the slow and fast fluctuations described above. In fact, scattering spectra allowing a measurement of τ_F for MBBA have been recently published by Amer and Al.[8] But such a technique does not allow to exhibit, on the same spectrum, both the slow and fast responses, since the latter involves spectroscopic devices whereas the first needs a high resolution Fabry–Perot interferometer. Then, the measurement of the relative amplitude C_F/C_S of the two responses is fairly hazardous, since it is derived from the comparison of two spectra, provided by two different set-up. On the other hand, concerning the measurement of both τ_F and C_F/C_S, optical Kerr Effect in the picosecond range, associated with photon counting techniques, seems to be a necessary complement to Rayleigh scattering as it will be shown by the following description of our experimental set-up.

EXPERIMENTAL SET-UP

It is deduced from Duguay's one[9] and shown on Figure 1. The optical Kerr effect is induced in the cell C by a plane, vertically polarized wave at 1060 nm given by a Nd^{3+}/glass laser, mode-locked by an Eastman Kodak 9740 solution. The cavity round trip is about 6 nsec.

Pulse selection is performed by a fast Kerr shutter driven by the mode-locked oscillator. An amplifier (gain about 30) increases the energy of the single pulse up to a few millijoules.

The infrared pulse passes through the cell C, filled with the studied liquid dielectric, and placed between two crossed polarizers P_1 and P_2. Green pulses at 530 nm are given by a 2 cm KDP crystal, slightly mistuned so as to reduce their intensity. The infrared field at 1060 nm is linearly polarized at 45° to P_1, whereas the green field at 530 nm is parallel to P_1.

Photocells D_3, D_4 and photomultiplier tubes D_1, D_2, associated with Tektronix 1 GHz scope and photon counting devices, measure the energies of infrared and green pulses and allow the control of the single pulse selector.

When the relation:

$$L_{IR,1} + L_{IR,2} = L_{G,1} + 2L_{G,2}$$

is fulfilled, the two pulses reach the Kerr cell at nearly the same time. The optical Kerr signal at 530 nm is detectable by the photomultiplier tube D_5 associated with photon counting techniques.

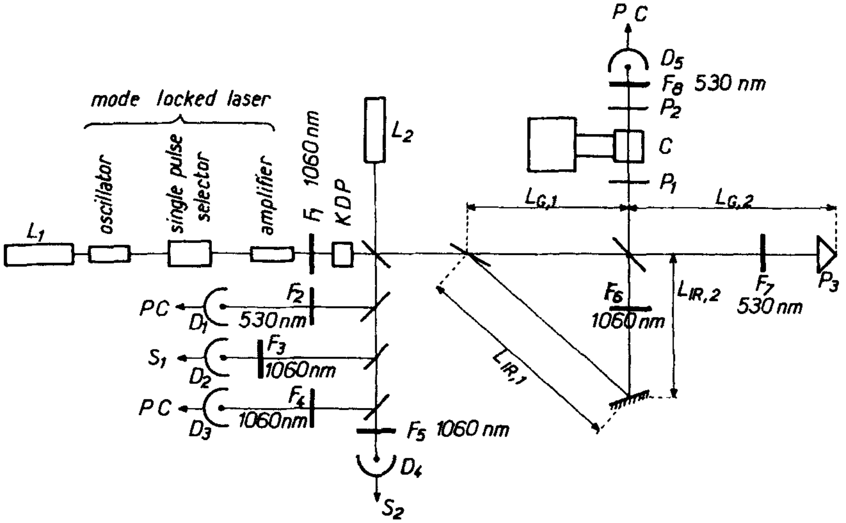


FIGURE 1 Experimental arrangement

L_1, L_2:	He–Ne laser 1 mW
F_1, F_3, F_4, F_5, F_6:	interference fieters 1060 nm
F_2, F_7, F_8:	interference fieters 530 nm
P_1, P_2:	polaroïd HN 22
P_3:	prism
D_1, D_2, D_5:	photomultiplier tubes
D_3, D_4:	photocells

Thus, when varying the position of P_3, we can set the delay t_0 between the infrared and green pulses at the beginning of the cell, to values in the range 0–5 nsec, with an uncertainty $\Delta t_0 \leq 1$ psec. Then, when plotting the optical Kerr signal $S(t_0)$ versus t_0, we get a curve where the short response gives rise to a sharp peak, above a flat background corresponding to the slow response in the nematic compounds. Of course, the latter is missing in the case of the molecules which do not show any nematic phase.

Since the duration of the mode-locked pulses is several picoseconds, we cannot expect, by such means, a very accurate measurement of τ_F. But the important fact is that, contrary to Rayleigh scattering, we can directly deduce from the curve $S(t_0)$ a fairly accurate value of the ratio C_F/C_S.

THE PHYSICS OF THE PROBLEM

Let us now consider the physical treatment of the problem.

Let be $I_{IR}(z, t)$ the shape of the infrared pulse

$I_G(z, t)$ the shape of the green pulse

α_{IR} the absorption rate of the compound at $\lambda_{IR} = 1060$ nm

α_G	the absorption rate of the compound at $\lambda_G = 530$ nm
n_{IR}	the refractive index of the compound at $\lambda_{IR} = 1060$ nm
n_G	the refractive index of the compound at $\lambda_G = 530$ nm
l	the length of the Kerr cell.

The transient birefringence induced by the infrared pulse in a nematic compound is given by[7]

$$\Delta n_{(z,t)} = (2\Pi/n_G)B\left\{\int_{-\infty}^{t}[C_S\exp(-(t-t')/\tau_S) + C_F\exp(-(t-t')/\tau_F)] \times I_{IR}(z,t')\exp(-\alpha_{IR}z)\,dt'\right\} \tag{1}$$

Where B is a function of the polarizability of the molecule, proportional to its optical anisotropy. For a compound showing no nematic phase, $C_S = 0$.

We deduce the transparency induced in the Kerr cell at $\lambda_G = 530$ nm, namely:

$$T(t) = (2\Pi/\lambda_G)\int_0^l \Delta n_{(z,\,zn_G/C+t)}\exp(-\alpha_G z/2)\,dz \tag{2}$$

If we assume a delay t_0 between the infrared and green pulses, the light transmitted through the cell is given by the convolution product:[10]

$$S(t_0) = \int_{-\infty}^{+\infty} I_G(t_0 - t')T^2(t')\,dt' \tag{3}$$

We have assumed I_{IR} and I_G to be Gaussian:

$$I_{IR}(z,t) = I_{IR,0}\exp[-(t - zn_{IR}/C)^2/\tau_{IR}^2]$$
$$I_G(z,t) = I_{G,0}\exp[-(t - zn_G/C)^2/\tau_G^2]$$

Then Eq. (1) becomes:

$$\Delta n_{(z,t)} = (2\Pi/n_G)BI_{IR,0}\sum_{K=S,F}(C_K/\tau_K)\exp(\tau_{IR}^2/4\tau_K^2) \times \exp[-(t - zn_{IR}/C)\tau_K]\{1 + \mathrm{erf}[(t - zn_{IR}/C - \tau_{IR}^2/2\tau_K)/\tau_{IR}]\} \tag{1 bis}$$

and Eq. (2) can be written:

$$T(t) = (2\Pi^{5/2}/\lambda_G n_G)I_{IR,0}\tau_{IR}B\int_0^l \exp[-(\alpha_{IR} + \alpha_G/2)z] \times \sum_{K=S,F}(C_K/\tau_K)\exp(\tau_{IR}^2/4\tau_K^2)\exp[-(t + \beta z)/\tau_K] \times \{1 + \mathrm{erf}[(t + \beta z - \tau_{IR}^2/2\tau_K)/\tau_{IR}]\}\,dz \tag{2 bis}$$

where $\beta = (n_G - n_{IR})/C$.

We have computed the curves $S(t_0)$. The data are τ_{IR}, τ_G and, for each compound, τ, α_{IR}, α_G, β or rather βl which is the delay due to the dispersion of the material between the green and infrared pulses at the end of the cell when $t_0 = 0$.

τ_{IR} was measured in our laboratory by means of two photon fluorescence techniques. We have used an average value:

$$\tau_{IR} = (7 \pm 1) \text{ psec.}$$

τ_G was deduced from the comparison between the experimental curve $S(t_0)$ for CS_2 and the computed one, with the value $\tau = (2.1 \pm 0.3)$ psec, recently published.[10] We have found:

$$\tau_G = (5 \pm 1) \text{ psec.}$$

We have measured the transmission of the studied compounds at each temperature, for the green and infrared pulses. We have found α_G to be negligible compared to α_{IR}, except in the vicinity of the clearing point of the material.

The studied compounds are shown in the Table I.

The refractive index of MBBA is deduced from its values in the visible range, already published.[11] n_{IR} is calculated using a development of the form $n_\lambda^2 = C_1\lambda^2 + C_2 + C_3\lambda^{-2} + C_4\lambda^{-4}$. The temperature dependence of n_G and n_{IR} is assumed to be linear. Under these conditions, we have found $\beta l = 19.6$ psec. for MBBA at 47°C. This cannot be neglected: the velocity mismatch between the infrared and green pulses is responsible for the broadening of the signal $I_G(t_0)$, as it is clearly evidenced by computer calculations performed with increasing values of βl.

Computed values of $I_G(t_0)$ versus t_0 for three values of the relaxation time τ_F and for $C_S = 0$ are shown on Figure 2.

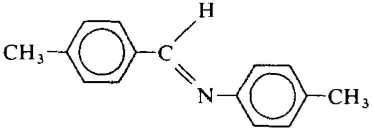
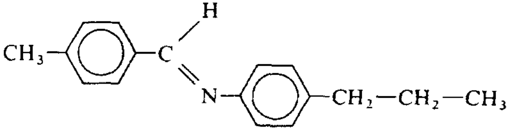
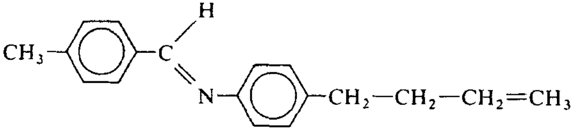
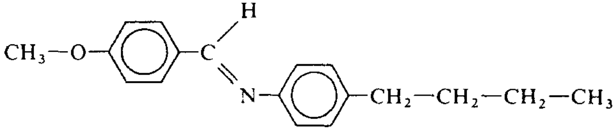
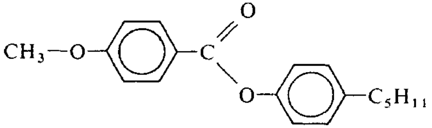
In order to deduce from the experimental curves an estimation of τ_F, we have plotted the variations of the full width at half maximum of the computed curves versus τ_F (Figure 3).

RESULTS

Experimental results obtained with the different compounds we have studied are shown on Figures 4, 5, 6, 7, 8. The flat background, corresponding to the reorientation of pseudo-nematic domains, is clearly evidenced on Figure 7 (MBBA).

We note that, in all the cases, the sharp peaks due to individual molecular reorientation have a fairly constant width, considering the uncertainty upon τ_{IR} and τ_G. The corresponding relaxation time, which cannot be

TABLE I

Molecular structure	Name	Melting point (°C)	Temperature range of the melting point (°C)
	*p*-methylbenzilidene- *p*-methylaniline (MMA) or (1-1)	91.5	no nematic phase
	*p*-methylbenzilidene- *p*-*n*-propylaniline (MPA) or (1-3)	50.7	no nematic phase
	*p*-methylbenzilidene- *p*-*n*-butylaniline (MBA) or (1-4)	16.5	no nematic phase
	*p*-methoxybenzilidene- *p*-*n*-butylaniline (MBBA) or (1-0-4)	20.0	20.0 ↔ 42.5
	*p*-methoxybenzoate- *p*-*n*-pentylbenzene (NEMATEL 105)	29.0	29.0 ↔ 42.4

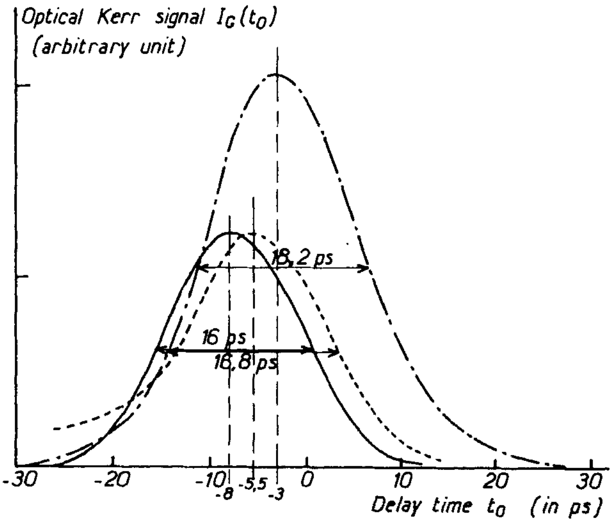


FIGURE 2 Computed values of $I_G(t_0)$ versus t_0 for three values of the relaxation time. $\tau_G = 5$ psec; $\tau_{IR} = 7$ psec; $\beta l = 19.6$ psec.
———, $\tau_F = 2$ psec; – – – –, $\tau_F = 5$ psec; —·—·—, $\tau_F = 10$ psec.

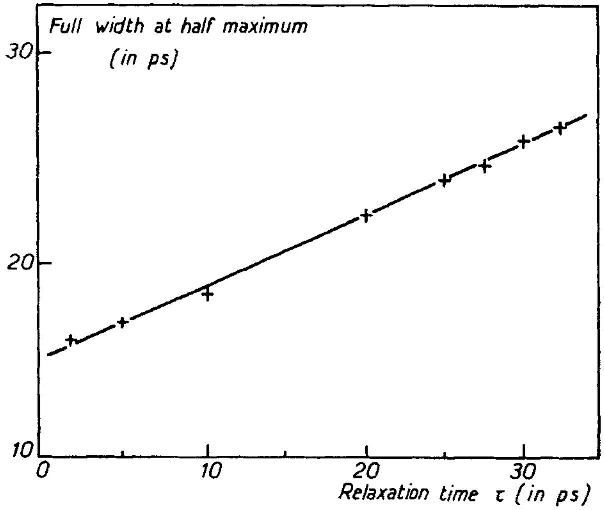


FIGURE 3 Variations of the full width at half maximum versus relaxation time τ_F. $\tau_G = 5$ psec; $\tau_{IR} = 7$ psec; $\beta l = 19.6$ psec.

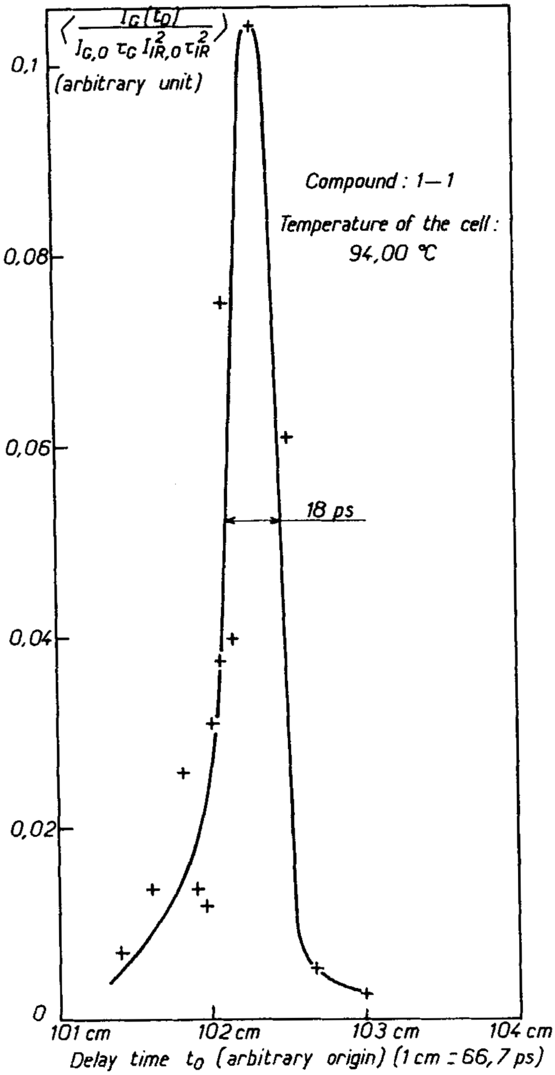


FIGURE 4 Intensity of the optical Kerr signal versus delay time for compound 1-1. Temperature 94°C.

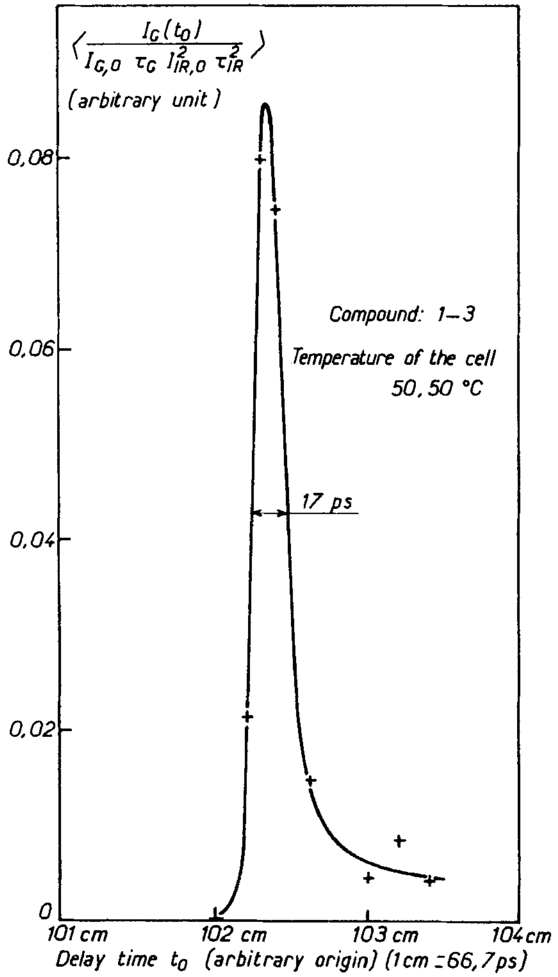


FIGURE 5 Intensity of the optical Kerr signal versus delay time for compound 1-3. Temperature 50.50°C.

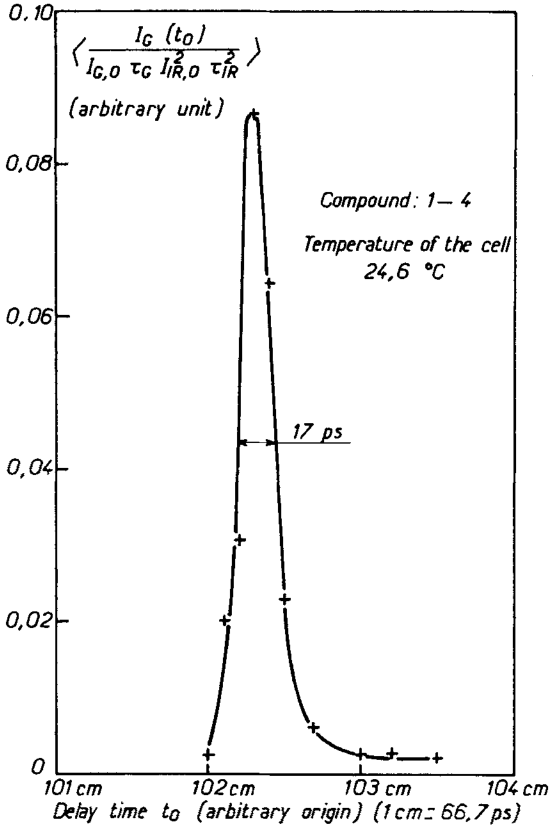


FIGURE 6 Intensity of the optical Kerr signal versus delay time for compound 1-4. Temperature 24.6°C.

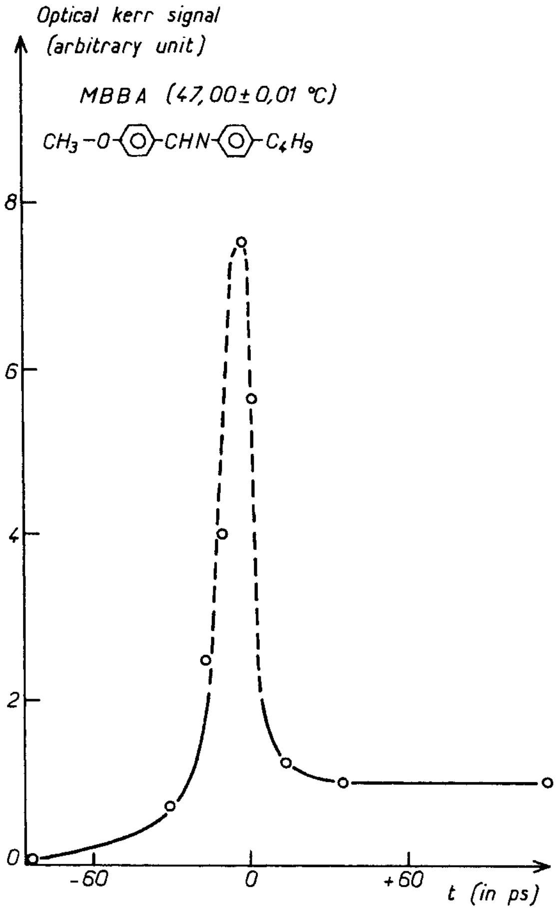


FIGURE 7 Intensity of the optical Kerr signal versus delay time for compound MBBA. Temperature 47°C.

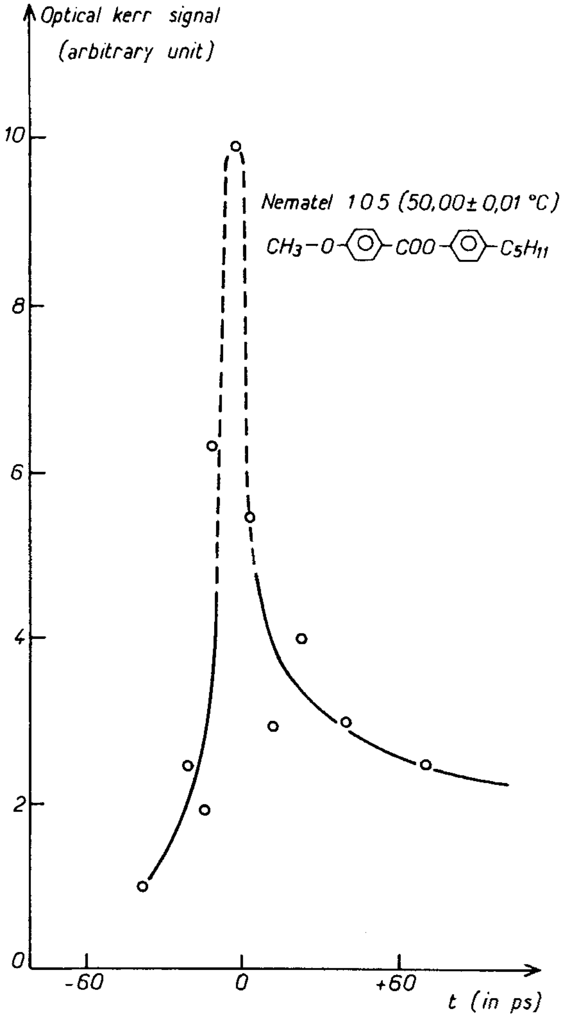


FIGURE 8 Intensity of the optical Kerr signal versus delay time for compound NEMATEL 105. Temperature 50°C.

deduced accurately, is not larger than 5 psec. This suggests that the individual molecular reorientation movements involved have the same kinetics whether the molecules are strongly correlated or not.

We have performed the measurement of the ratio C_F/C_S in the case of MBBA, by comparing the experimental curve (Figure 7) to the theoretical one, computed with $\tau_F = 3$ psec and $\tau_S = 100$ nsec. The latter was deduced from an earlier experiment performed in our laboratory.[5] We have found $C_F/C_S = (1.7 \pm 0.3) \cdot 10^{-3}$. One could dispute such a result, since only an estimation of τ_F has been achieved. In fact, we have shown its influence on the value of C_F/C_S is not significant, at least in the range 1–5 psec.

CONCLUSION

We have achieved the first observation, in the time domain, of individual molecular movements inside the pseudo-nematic domains of the isotropic phase of nematogens and compared their correlation time with those of the nearest molecules showing no nematic phase. Moreover we have experienced the possibility of a direct measurement of the ratio C_F/C_S: this should improve our knowledge of the molecular interactions responsible for the liquid crystal structure.

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