

The dynamics of succinonitrile in the plastic phase by subpicosecond time-resolved optical Kerr effect

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The relaxation kinetics of succinonitrile in the plastic crystalline phase has been investigated between 250 and 320 K by transient optical Kerr effect with femtosecond pulses. Three different noninstantaneous contributions to the signal time profile have been identified. The fastest one is a subpicosecond decay, attributed to the relaxation of the damped librational and torsional vibrations of the molecules. The intermediate decay time, ranging from 4 ps at 323 K to 30 ps at 250 K, is interpreted as due to rotations of the trans molecules about the shortest inertia axis which bring the molecule from one cube diagonal to another. The slowest decay time ranges from 28 ps at 323 K to 190 ps at 250 K and agrees very well with previous measurements with different experimental techniques. This decay is interpreted as due mostly to rotational motions of the gauche molecules jumping from one equilibrium position to another in the unit cell. The activation energy for the two processes is 3.7 and 4.3 kcal/mol, respectively, for the intermediate and slow kinetics.

I. INTRODUCTION

Succinonitrile $\text{NC-CH}_2\text{-CH}_2\text{-CN}$ (SN) is a very flexible molecule which crystallizes, between 233 K and the melting point of 331 K,^{1,2} in a cubic plastic phase characterized by two distinct types of motion of the molecules which form on average the regular cubic lattice:³ the trans-gauche isomerization and the rotation of the molecules about their inertia axes.³ The body-centered-cubic lattice contains two molecules per unit cell, statistically oriented with their central C-C bond along one of the four diagonals of the cube.

Several experimental investigations of the plastic and liquid phases of SN have been performed with different techniques: polarized Raman spectroscopy,² dielectric relaxation,^{4,5} proton⁶ and ¹³C NMR (Ref. 7) studies, depolarized Rayleigh and Brillouin scattering^{3,8-12} and nonlinear optical techniques such as optical Kerr effect (OKE).^{13,14} The first time-resolved OKE experiment was performed on SN by Ho and Alfano,¹⁵ with a few picoseconds resolution, at temperatures ranging between 270 K and the melting point. The results were interpreted in terms of rotational disorder, coupled to the trans-gauche isomerization. These researches have evidenced very different relaxation times, ranging from about 350 to 20 ps, depending upon the temperature and the experimental technique used. A detailed discussion of the data and of their interpretation is given in Ref. 7. We briefly summarize here the fundamental results. Relaxation times ranging from 346 ps at 235.5 K to 86 ps at 273 K were obtained from dielectric measurements.⁴ Since the trans

molecules without dipole moment cannot contribute to the dielectric relaxation, these relatively long times were associated to reorientations of the gauche molecules in the crystal. This rotation requires large cooperative motions of the neighboring molecules to occur, in contrast to rotations of the trans isomer which are much less hindered. From the analysis of the depolarized Rayleigh line two shorter relaxation times (62 and 44 ps at 294 K and 42 and 24 ps at 318 K) were instead obtained.^{8,11} The interpretations given by different authors for these faster times do not agree and their assignment to specific molecular motions is still an open question.

A recent paper¹⁶ reported on the results of a computer simulation of the dynamics of succinonitrile in the plastic phase, made using a simplified four-mass molecular model with three degrees of internal freedom (the torsion about the C-C bond and the two C-C-N bending coordinates) and all degrees of external rotational freedom. The time evolution of the autocorrelation functions of the torsion and of the orientation of the central C-C and of the N-N vectorial distances in the unit cell shows the occurrence of at least three different relaxation times. After a very fast relaxation, due to the internal torsional motion and to librations of the molecules, two additional exponential decays are obtained. The intermediate component is dominated by the rotational motion of the trans isomer about the long molecular axis. The slow component is due to trans-gauche isomerization and to overall jumps of the molecules about the short axes.

In order to check the validity of the simulation and to prove the occurrence of a very fast relaxation time of the order of few ps, predicted by the model, we decided to undertake an experimental investigation of the relaxation processes in the plastic phase of succinonitrile at different tem-

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peratures, by means of time-resolved Kerr effect measurements in the femtosecond time scale. In this paper we report on time-resolved OKE (TROKE) measurements made using high-power 200 fs pulses, which permit us to explore several decades of signal decay, thus offering the unique possibility of observing in the same experiment both fast and slow relaxation mechanisms.

In an OKE experiment a strong linearly polarized laser pulse creates, via the third-order susceptibility, an anisotropy of the index of refraction that can be probed by a second weak pulse polarized at 45° respect to the pump pulse. This pump–probe technique allows the study of the reorientational motion of molecules directly in the time domain^{17,18} and can be therefore considered as the time-domain counterpart of Rayleigh scattering line-shape analysis. An important advantage of the TROKE technique is that very fast processes, burried in the extreme tail of the Rayleigh wings in a frequency-domain experiment, are instead well detected in time-domain experiments with femtosecond pulses.

It is generally accepted that different mechanisms, due to molecular and electronic responses,^{17–20} contribute to the overall TROKE signal. The fastest process is the deformation of the electronic cloud, whose response can be considered instantaneous on the time scale of our pulses. A second rapid response is due to fluctuations of the molecular polarizability induced by intermolecular interactions. In liquids this process exhibits a relaxation time of the order of the collision period,¹⁸ whereas in solids it is related to the phonon relaxation.²⁰ Additional slower responses are due to rotational motions of the molecules that destroy the out-of-equilibrium orientational distribution.

The most interesting point in the dynamics of SN in the plastic phase is related to the interplay of the intramolecular torsional degree of freedom, leading to the trans–gauche isomerization, and of the molecular rotations as a whole. The large dynamic range, combined to high temporal resolution reached in the experiment reported here, allowed us to identify the different mechanisms which contribute to the relaxation kinetics of SN in the plastic phase.

II. EXPERIMENT AND DATA HANDLING

SN from Merck was purified by repeated sublimations. A large single crystal was grown from the melt and the axes were identified by x-ray diffraction. All measurements were performed with the direction of propagation of the laser beam perpendicular to the 110 plane. A large piece of crystal, 4 mm thick, was placed in a cell whose temperature was controlled by a thermostat with a stability of ± 0.5 °C. The sample was immersed in a matching fluid (decahydronaphthalene) in order to reduce scattering from the crystal faces and to prevent deterioration of surfaces quality. The thickness of the sample was much longer than the length of the overlapping region of the pump and probe beams; any contribution from the index matching fluid to the Kerr signal can then be excluded.

A schematic diagram of the experimental apparatus is

shown in Fig. 1. The 80 ps pulses of a 12 W mode-locked Nd:YAG (Spectra Physics Model 3800) (where YAG denotes yttrium aluminum garnet) are pulse compressed and frequency doubled to 4 ps at 532 nm. The 532 nm beam is actively stabilized (typical averaged power is 900 mW) and is used to synchronously pump a dye laser (Spectra Physics model 3695). The output of the dye laser, consisting of 250 mW at 600 nm and 250 fs pulses, is pulse compressed again to give 100 fs autocorrelation pulses. These pulses are amplified in a three-stages dye amplifier (Quanta Ray PDA1) pumped with half of the frequency-doubled output from a Q-switched 10 Hz Nd:YAG (Quanta Ray DCR3). Half of the amplified pulse (100 μ J peak energy) is focused into a water cell to produce a continuum of white light; the rest is reflected out to the experiment. A component of the continuum is then selected and amplified in a second three-stage amplifier. With this system we have performed both one- and two-color experiments with energies not exceeding 50 μ J/pulse for the pump and 1 μ J/pulse for the probe.

In the TROKE experiment the intense pump pulse, linearly polarized (parallel to the *c* crystal axis), creates an anisotropy of the refractive index that can be probed by a variably delayed weak pulse polarized at 45°. The change in the polarization is detected through crossed polarizers. In our system the 10 Hz signal is fed to a boxcar averager (Stanford sr 265) and digitized. A computer controls the delay line (with a precision of 1 μ m) and reads the signal through IEEE 488 standard interface. Typical outputs are shown in Figs. 2 and 3. The TROKE signal $S(\tau)$ at the delay time τ is obtained by solving analytically the double integral:

$$S(\tau) = \int_{-\infty}^{\infty} I_{\text{probe}}(t - \tau) \times \sin^2 \left[\int_{-\infty}^t R(t - t') I_{\text{pump}}(t') dt' \right] dt, \quad (1)$$

where τ is the time delay between the pump and probe pulses, $R(t)$ is the response function of the system, and I_{probe} and I_{pump} are the intensities of the probe and pump beams, respectively. Assuming that the phase shift between the parallel and the perpendicular components of the probe is small,¹⁷ Eq. (1) becomes

$$S(\tau) = \int_{-\infty}^{\infty} I_{\text{probe}}(t - \tau) \times \left[\int_{-\infty}^t R(t - t') I_{\text{pump}}(t') dt' \right]^2 dt. \quad (2)$$

The time profiles of I_{probe} and I_{pump} are derived from second- and third-order auto- and cross-correlation traces. These are well fitted, assuming a biexponential shape for the pulses with a fast-rising and a slow-decay profile of the type

$$\begin{aligned} \exp(\alpha_k t) & \text{ for } t < 0, \\ \exp(-\gamma_k \alpha_k t) & \text{ for } t > 0, \end{aligned}$$

where $\gamma > 1$ is an asymmetry parameter and $k = 1$ for the pump and 2 for the probe beam. The best model for the response function $R(t)$ is the sum of three exponential decays plus an instantaneous response:

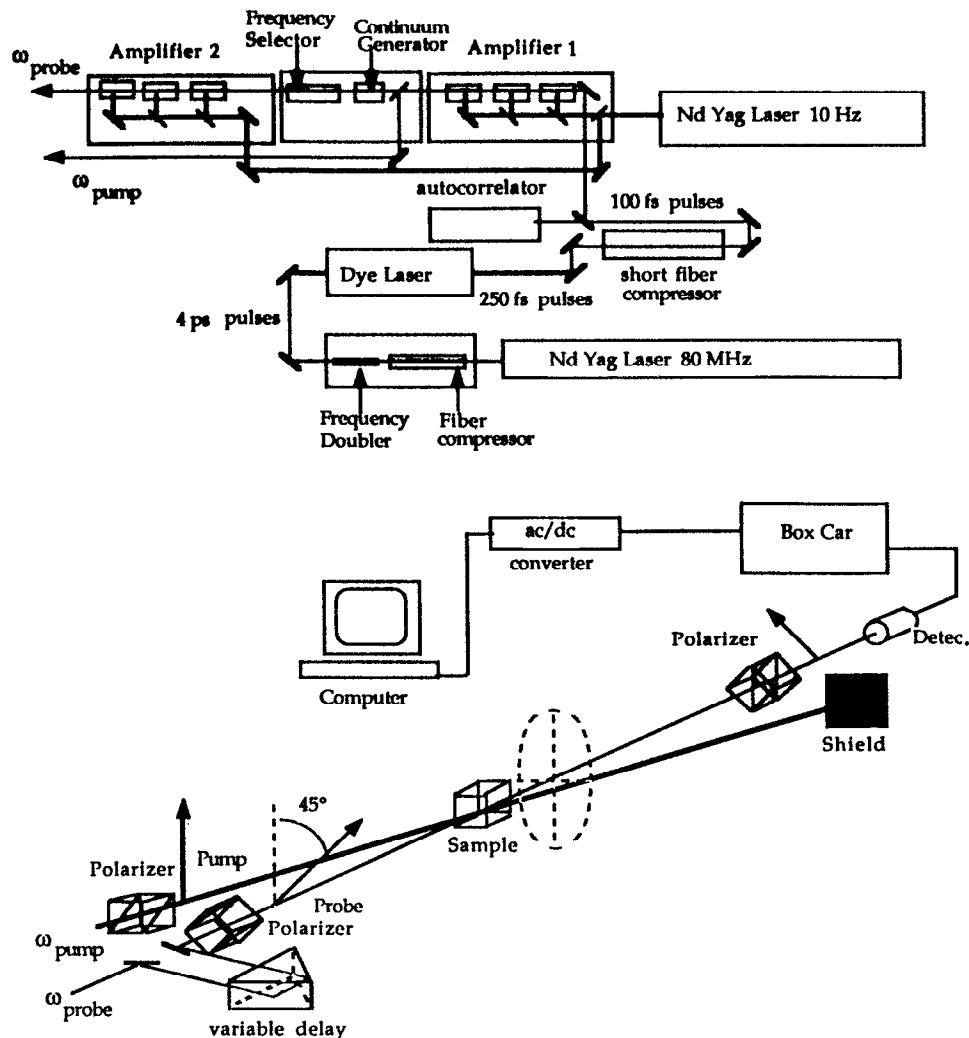


FIG. 1. Schematic drawing of the femtosecond laser system and TROKE experimental setup.

$$R(t) = R_{cl}(t) + R_{mol}(t) \\ = \delta(t) + \sum_i (a_i/T_i) \exp(-t/T_i), \quad (3)$$

where $i = 1, 2, 3$, T_i is the relaxation time of the i th decay component, and $\delta(t)$ is the delta function. The preexponential factors a_i are parameters connected to the polarizability and concentration of the active species and to the probability of their contribution to the process.

III. RESULTS AND DISCUSSION

The decay of the OKE signal has been measured in the temperature range 250–320 K. At all temperatures the experimental curves are correctly reproduced by a response function consisting of the superposition of three exponentials, associated to three different decay processes $D(T_1)$, $D(T_2)$, and $D(T_3)$, together with an instantaneous response. In order to show the occurrence of three distinct relaxation times, two decay profiles measured at 273 K, with different time resolution, are shown in Figs. 2 and 3. We recall that all decay times considered below are orientational relaxation times, which are twice the measured signal decay times.

The fastest process $D(T_1)$ is characterized by subpicosecond relaxation times. The T_2 times for the intermediate $D(T_2)$ process range from 4 ps at 323 K to 30 ps at 250 K, and those for the slow $D(T_3)$ decay process vary from 28 ps at 323 K to 190 ps at 250 K. The relaxation times T_1 , T_2 , and T_3 are collected in Table I for some representative temperatures between 250 and 320 K. In Table I we report also the ratio a_2/a_3 between the coefficients of Eq. (3) for the two processes $D(T_2)$ and $D(T_3)$, which gives the relative weight of the two relaxation mechanisms.

In the computer simulation,¹⁶ the relaxation time T_1 is interpreted as an average relaxation time of the low-frequency vibrations of the crystal, including both molecular librations and torsional oscillations. The intramolecular torsion about the central C–C bond is a very soft vibration, with frequency lower than 100 cm^{-1} .²¹ A strong coupling between librational and torsional degrees of freedom then occurs, making the distinction between intra- and intermolecular motions meaningless.

Our experimental data confirm this interpretation. In the TROKE experiment, the strong femtosecond pump pulses coherently excite the low-frequency librational and torsional modes of the molecules. In liquids the short life-

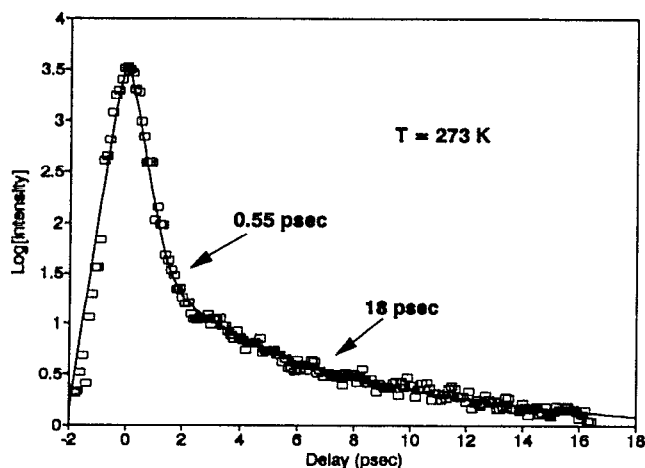


FIG. 2. TROKE signal decay in the first 16 ps of SN at 273 K. \square , experimental; —, fit from Eq. (4).

time of the local structure surrounding the molecules causes a very effective damping of such vibrations and, consequently, a fast decay of the TROKE signal. Times of a few hundred femtoseconds have actually been observed in several molecular liquids.^{19,22} A similar situation occurs in a plastic crystal like SN, where the relaxation process is induced by the fast rearrangement of the local cage, coupled to the interaction with the acoustic phonons. The determination of the time constant of the very fast process $D(T_1)$ is complicated by the strong instantaneous response due to the electronic hyperpolarizability. However, once the shape of the excitation and probe pulses have been determined by auto- and cross-correlation in a KDP crystal, the decay time is estimated with reasonable accuracy by a deconvolution procedure. The $D(T_1)$ decay appears to be exponential in the entire temperature range within experimental errors; the corresponding T_1 times are plotted in Fig. 4 as a function of the temperature. The shorter time of 400 ± 100 fs measured at 315 K is longer than the minimum time resolution (250 fs) of our experimental setup, obtained by measuring the

TABLE I. Decay times in ps at selected temperatures and corresponding a_2/a_3 ratios.

T (K)	T_1	T_2	T_3	a_2/a_3
313	0.35 ± 0.1	5 ± 0.5	28 ± 1	0.5
295	0.37	11	44	0.5
273	0.55	18	70	0.4
251	1	24	180 ± 15	0.3

Kerr response from a H_2O cell. The measured T_1 times are affected by large experimental errors (see Fig. 4), which are particularly relevant at high temperatures; a detailed discussion of their temperature dependence is then impossible. However, their increase with decreasing temperature is a clear indication of the onset of long-range order which reduces the cage fluctuations.

The relaxation times T_2 (lower trace) and T_3 (upper trace) are plotted in Fig. 5 as a function of temperature. From their plot in a log scale vs the inverse temperature shown in Fig. 6, we have determined the values of 3.7 and 4.3 kcal/mol, respectively, for the activation energies of the corresponding decay processes.

According to the computer simulation,¹⁶ the intermediate decay process $D(T_2)$ is controlled by rotations of the trans molecules about their long inertia axis. A schematic drawing of the 90° rotations, which bring a molecule from one diagonal of the cube to another, is shown in Fig. 7. The rotation of the trans isomer around the long axis, besides involving the smallest moment of inertia, is less hindered than all other possible rotations of the gauche and trans isomers. During the rotation the N atoms remain practically fixed at the center of two opposite faces of the cube as can be seen from Fig. 7. In all other rotations the motion implies instead large displacement of the end groups. These results of the computer simulation are fully compatible with our experimental data. The ratio a_2/a_3 of Table I, which measures the efficiency of the intermediate $D(T_2)$ with respect to the slow $D(T_3)$ process, increases from 0.3 at 251 K to 0.5

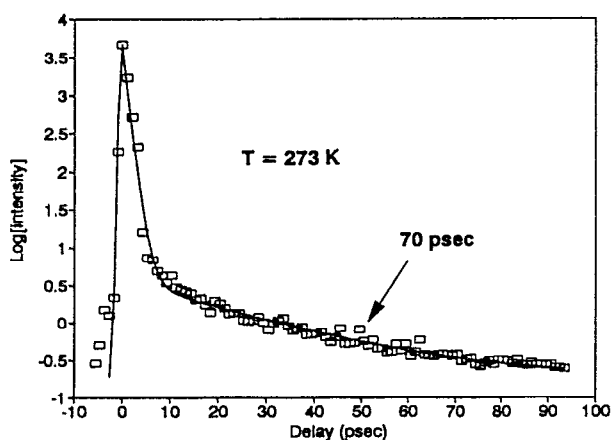


FIG. 3. Long-range decay of the TROKE signal at 273 K. \square , experimental; —, fit from Eq. (4).

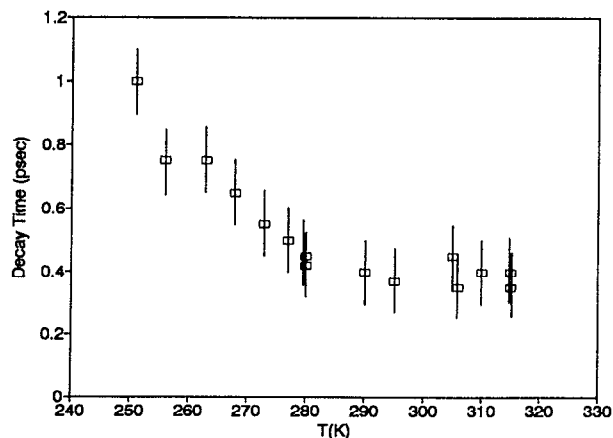


FIG. 4. Temperature variation of the T_1 decay time. Above 290 K the decay times are within the instrumental resolution.

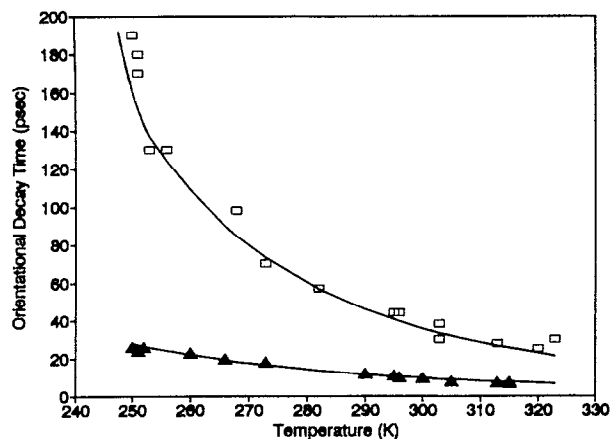


FIG. 5. Temperature variation of the T_2 (\blacktriangle) and T_3 (\square) decay times.

at 313 K and parallels the trend with T of the relative abundance of the trans form estimated from Raman spectra.² Furthermore, as shown by the plot of Fig. 6, the activation energy of 3.7 kcal/mol for the $D(T_2)$ process is lower than that of the $D(T_3)$ decay. Both arguments support thus the conclusion that the less-hindered rotation of the trans molecules about the long axis (spinning motion) is responsible for the $D(T_2)$ decay process.

The decay profile of $D(T_3)$ has values comparable to those obtained previously by TROKE,¹⁵ by dielectric measurements^{4,5} and by the analysis of depolarized Rayleigh wings.^{3,10,23} The T_3 time increases exponentially as the transition to the stable ordered phase is approached. From dielectric measurements it reaches 346 ps at 235.5 K and tends to infinity at the transition temperature. In the ordered crystalline phase the molecules are all in the gauche configuration and cannot jump from one equilibrium position to another. In the plastic phase these jumps are possible only if assisted by the cooperative motions of the neighboring molecules, since they involve large displacements of the CN end

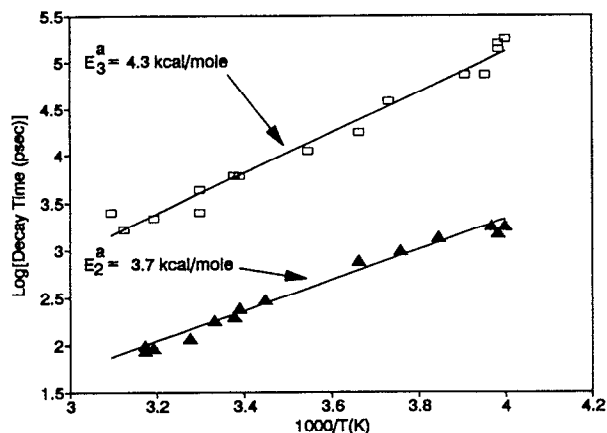


FIG. 6. Log plot of T_2 (\blacktriangle) and T_3 (\square) decay times as a function of $1/T$. The corresponding activation energies are marked in the figure.

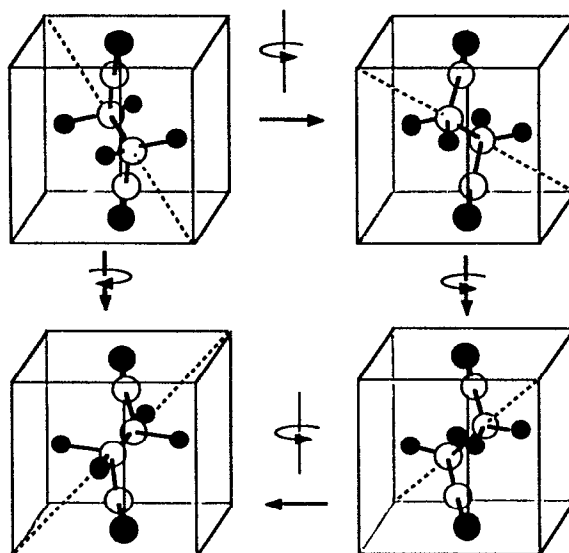


FIG. 7. The four possible orientations of a trans molecule along the diagonals of the cubic unit cell. 90° rotation about the long inertia axis brings the molecule from one equilibrium position to another.

groups. As the temperature decreases and the number of gauche molecules increases, these large-scale rotations became more and more difficult and thus the relaxation time increases. The strong increase of T_3 with decreasing temperature confirms therefore that the $D(T_3)$ process is dominated by the tumbling motion of the molecules. As shown by Ivanov,²⁴ the reorientational times depend in general on the rank l of the susceptibility tensor probed in the experiment; in particular, $\tau_l = \tau/l(l+1)$ for a purely diffusive process, while $\tau_l = \tau$ for reorientations which happen through large jumps. As already observed,¹⁵ dielectric measurements depend on a vectorial quantity, while optical scattering techniques are based on a second-rank tensor. A ratio 3 to 1 should then be expected between our decay times and those of Ref. 4 in the case of diffusive motion, while they should coincide in the large jumps limit. The ratio of the two sets of data ranges between 1 and 1.2, thus proving that the $D(T_3)$ process is dominated by jumps of the molecules from one equilibrium position to another. Trans-gauche isomerization and rotations of the trans isomers about the short inertia axes contributes also to this regime in our experiments. In the liquid phase at 330 K dielectric relaxation measurements give a reorientational time of 16 ps,⁴ while a value of 11 ps was obtained by TROKE,¹⁵ with a ratio of 1.6.

Moreover, the activation energy of 4.3 kcal/mol estimated from the plot of Fig. 6 for the $D(T_3)$ process is slightly higher than the value (3.8 kcal/mol) obtained from depolarized Rayleigh wing scattering,²⁵ and is in very good agreement with the value of 4.7 kcal/mol obtained from dielectric relaxation.^{4,7} The small difference in the activation energy can be explained, beside the experimental uncertainty, by considering that dielectric relaxation is only affected by the motion of the gauche isomer.⁴ Other previous experiments^{5,6,13,15} gave lower values for the activation energy

ranging between 2.1 and 3 kcal/mol; all these experiments, however, cover a smaller temperature range than that of the present work and of Ref. 4. In addition, such low values for the activation energy seem to be hardly compatible with the value of 3.6 kcal/mol measured for the liquid phase of SN.⁶

It is also of interest to compare our results to those obtained with ¹³C NMR.⁸ In this comparison it must be taken into account that NMR is only sensitive to local properties while OKE, like other optical techniques, measures also long-range properties.^{20,25} We notice that the relaxation times T_2 of our intermediate $D(T_2)$ decay process becomes comparable to NMR correlation times approaching the melting point while the NMR results are rather similar to the relaxation times T_3 of the slow $D(T_3)$ decay process at low temperatures. In this last technique the experimental parameters are sensitive to carbon atom motions and the values of effective rotational correlation times are the weighted average of all possible rotations. The different behavior of the decay times measured at low and at high temperatures in NMR and TROKE experiments is then consistent with the fact that the percentage of trans isomer increases with temperature.² The intermediate $D(T_2)$ process, due to the rotation along the long axis of the trans isomer, will contribute more at higher temperature than at lower temperature in ¹³C NMR experiments.

From the assumption of a response function of the form given in Eq. (3) we can estimate the contributions of the three individual dynamics to the nuclear part of the third-order susceptibility: they result to be in the order 1:11:18, going from T_1 to T_3 process at 273 K. At the same temperature the overall nuclear part and the purely electronic part of the third-order susceptibility are in the ratio 1:7.5.

In summary, we can describe the dynamics of SN in the plastic phase as due to three distinct mechanisms. The fast relaxation is due to the decay of the heavily damped low-frequency librational and torsional oscillations coherently excited by the strong femtosecond pulses. This dynamics is essentially similar to that observed in several molecular liquids. Moreover, the increase up to the picosecond range of the decay time T_1 when the temperature is lowered near the order-disorder transition is a clear indication of increasing long-range order, i.e., of "crystallinity" of solid SN. The intermediate time T_2 is attributed to rotations about the long molecular axis: considerations on the steric properties of the

trans and gauche isomers lead to the conclusion that this motion is peculiar of the trans molecules. The slow decay T_3 is due to the tumbling motion of both the isomers rotating about the short axes. These last two dynamics resemble very closely those observed in liquids. We finally stress that our conclusions are consistent with the finding of a recent computer simulation of succinonitrile plastic phase.

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