PHYSICAL REVIEW A VOLUME 17, NUMBER 3 MARCH 1978

Relaxation kinetics of the plastic crystal succinonitrile

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(Received 27 June 1977)

The relaxation kinetics of the optical Kerr effect of succinonitrile [$(CH_2CN)_2$] is measured in the liquid and plastic-crystal phases. The Kerr intensity decay profile of the plastic crystal indicates that more than one relaxation mechanism is operative. The temperature-dependence study of succinonitrile's relaxation time in the plastic-crystal phase yields an activation energy of 2.6 kcal/mole.

The rotational motion of molecules is fundamental to the understanding of molecular interactions in liquids and solids.[1] The reorientational relaxation kinetics of the succinonitrile (SN) molecules [$(CH_2CN)_2$] in the plastic crystal phase has been studied by several techniques, such as dielectric relaxation,[2] nuclear magnetic resonance,[3] and depolarized Rayleigh light scattering.[4] Recently, picosecond laser techniques have become available for directly measuring the subnanosecond time dependence of the optical Kerr effect in liquids.[5,6] This is a powerful technique for obtaining direct kinetic information about the motion of molecules in the condensed state.[6] In this paper, we report the first *direct* measurement of the Kerr relaxation times of SN associated with its rotational motion from the liquid to the plastic crystal phase by measuring the kinetics of the optical Kerr effect using picosecond laser pulses.

For anisotropic molecules in the liquid state, the dominant mechanisms responsible for the Kerr effect in the picosecond region are associated with electronic cloud distortion,[7-9] molecular libration,[10,11] molecular redistribution,[12] and molecular reorientational motion.[6-8] In general, for glasses, polymers, and solids, because of the restrictive motion of the molecule and the available free volume,[13] the Kerr constant associated with molecular orientational motion is either too small to be observed or the relaxation time is too slow to respond to the picosecond laser pulse.[2,8,14,15] However, in the plastic crystal phase, the molecule has a fast rotational degree of freedom due to its "globular" shape.[16] Though the SN molecule is globular in the Timmermans classification,[16] the succinonitrile molecule is not truly spherical in shape. Its plastic phase is related to the guache-trans isomerism.[17,18] The molecular orientational motion in the plastic phase can be described as a series of jumps over barriers between potential energy minima.[15,16] The magnitude of the nonlinear index of refraction change of the Kerr effect of SN in the isotropic liquid and cubic plastic crystal phase is large and has been measured by Bischofberger and Courtens.[19]

A schematic diagram of the experimental setup[5,6] used to directly measure the relaxation kinetics of the optical Kerr effect is shown in Fig. 1. An intense 1.06-μm laser pulse with ~10-ps duration was used to induce the birefringence in the sample which was situated in a Dewar between a pair of crossed polarizers. The birefringence is caused by altering the electronic clouds and the molecular positions in the condensed state through the interaction of the optical field of the laser pulse with the susceptibility of the molecules.[5-12,19] A 0.53-μm pulse of ~8-ps duration derived from the second-harmonic generation of the 1.06-μm pulse was variably delayed with a prism and was used to probe the time evolution of the induced transitory birefringence. The 1.06-μm beam is directed to the sample at an angle of incidence of 3° with respect to the direction of the 0.53-μm beam. The 1.06- and 0.53-μm beams are essentially collinear over the 1-cm-long sample. A dynamic range of

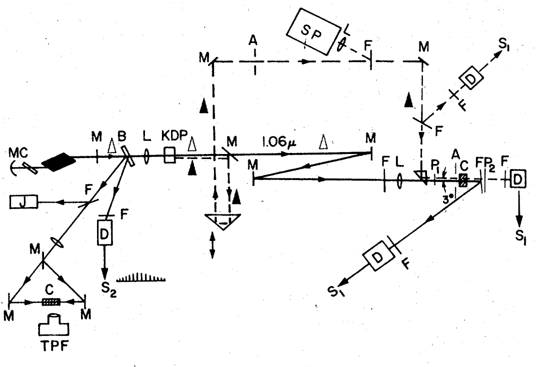

FIG. 1. Experimental setup. The following labeled items are A: aperture; B: beam splitter; C: optical cell; D: photodiode; F: filter; J: energy meter; L: lens; M: dielectric coated mirror; S_1: Tektronix 556 dual beam oscilloscope; S_2: Tektronix 519 oscilloscope; P_1, P_2: HN 22 polarizers, polarized at directions of +45° and −45°, respectively; SP: $\frac{1}{2}$-m Jarrell-Ash spectrometer. The maximum power density for the 1.06-μm laser pulse is about 1 GW/cm^2.

5×10^3 in intensity was measured. The relaxation time extracted from the Kerr intensity decay profile corresponds to an overall reorientational motion of the molecules. This relaxation time is a combination of the reorientations about the individual axes of the molecules, just like the relaxation time obtained from the depolarized Rayleigh wing linewidth.[20] The measured relaxation time is more strongly weighted by the reorientation about the axis which is associated with the largest polarizability change upon orientation. The activation energy deduced from the temperature dependence of the measured relaxation time is an overall weighted average. Picosecond-laser single-shot technique[21] was also applied to measure the relaxation time. The results were similar except the available dynamic range of the decay profile was reduced by an order of magnitude due to the dynamic range of the PAR optical multichannel analyzer I.

The SN was obtained from the Eastman Kodak Co. Single crystals of SN were grown by using the Bridgman-Stockbarger technique.[18] The plastic crystal phase is between −40 to +57 °C.[2,3,15] The SN crystal melts at about 56 ± 1 °C. Depending on the rate of cooling, the freezing temperature of the liquid SN occurs between 57 to 50 °C. A 1-cm-long crystal was cut in the $(1\bar{1}0)$ plane which was perpendicular to the propagation direction of the laser beam. The SN crystal was situated in a 1-cm-long optical cell containing decane liquid for index matching. The geometry of the crystal related to the directions of the laser fields is shown in Fig. 2. The cell was placed in a glass Dewar with strain-free windows. The Kerr effect on the windows and decane was measured to be negligible. A copper-Constantan thermocouple was cleaned and immersed in the cell. The temperature was changed by adjusting the flow rate of cooled-nitrogen gas into the Dewar and by applying voltage to a heater tape which surrounded the sample cell holder. The temperature was controlled to within one degree. The SN crystal occasionally damaged when the power density of 1.06-μm laser beam exceeded 1 GW/cm^2. This limited the signal to noise ratio. In order to minimize the formation of defects in the crystal during a temperature-dependent experiment, the relaxation-time measurements were performed in a series from low to high temperature.

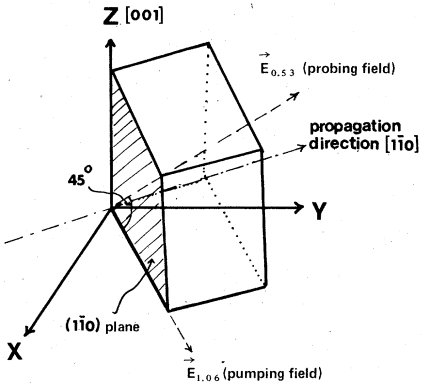

FIG. 2. Geometry of the SN crystal orientation for the optical Kerr effect. The dashed-dotted line is the propagation direction $(1\bar{1}0)$ of the orienting 1.06 μm and the probing 0.53 μm beams. The dashed lines are the polarization directions of the electric field of the orienting and probing laser pulses.

The Kerr intensity decay profiles versus time of SN measured at different temperatures are shown in Fig. 3. The prompt response curve of liquid CS_2 (the reorientational relaxation time[22] is about 1.8 ps) is shown in Fig. 3(a). After 20 ps away from the peak, the time slope for the decay profile is 2.5 ps. Therefore, the smallest reorientational relaxation time that can be reasonably extracted[23] from the data is ~8 ps. In Fig. 3(a), the picosecond-laser Kerr technique[5,23] cannot resolve the contributions to the nonlinear index of refraction change due to the electronic cloud distortion, molecular librations, molecular redistribution, and molecular reorientational motion.[7,8,11] It has been argued[7(c),8] that the primary mechanisms for the Kerr effect in condensed matter arises from electronic and reorientational motion of molecules. This point can be challenged in some cases. To obtain the molecular reorientational relaxation time (τ^K) of SN, the equation[5(a)] $A\exp[-2(t-27)/\tau^K]+B$ which describes time dependence of the Kerr intensity profile for $t \geq 27$ ps is used to fit the data. The parameter A is a constant to fit the data at $t=27$ ps, and the parameter B denotes the background light level originating from the leakage of the probe 0.53-μm light through the polarizers. The Kerr intensity decay profile of liquid SN at 57 °C is shown in Fig. 3(b). The slope of this curve 27 ps away from the peak, is about twice as slow as that of the CS_2 prompt curve. The reorientational relaxation time is 11 ± 4 ps at 57 °C.

The reorientation relaxation time of the molecules for the different experimental methods in the diffusion and large jump limit can be expressed by[6(a),24] $\tau_l = \tau_0/l(l+1)$ and $\tau_l = \tau_0$, respectively, where τ_l is the measured relaxation time for the particular experimental technique which measures the kinetics of the lth rank of susceptibility tensor, and τ_0 is the time interval during which the molecules stay in the local equilibrium positions. In the analysis of the experimental data[6(a)] from the optical Kerr effect ($l=2$), light scattering ($l=2$), and dielectric relaxation ($l=1$) for various liquids,

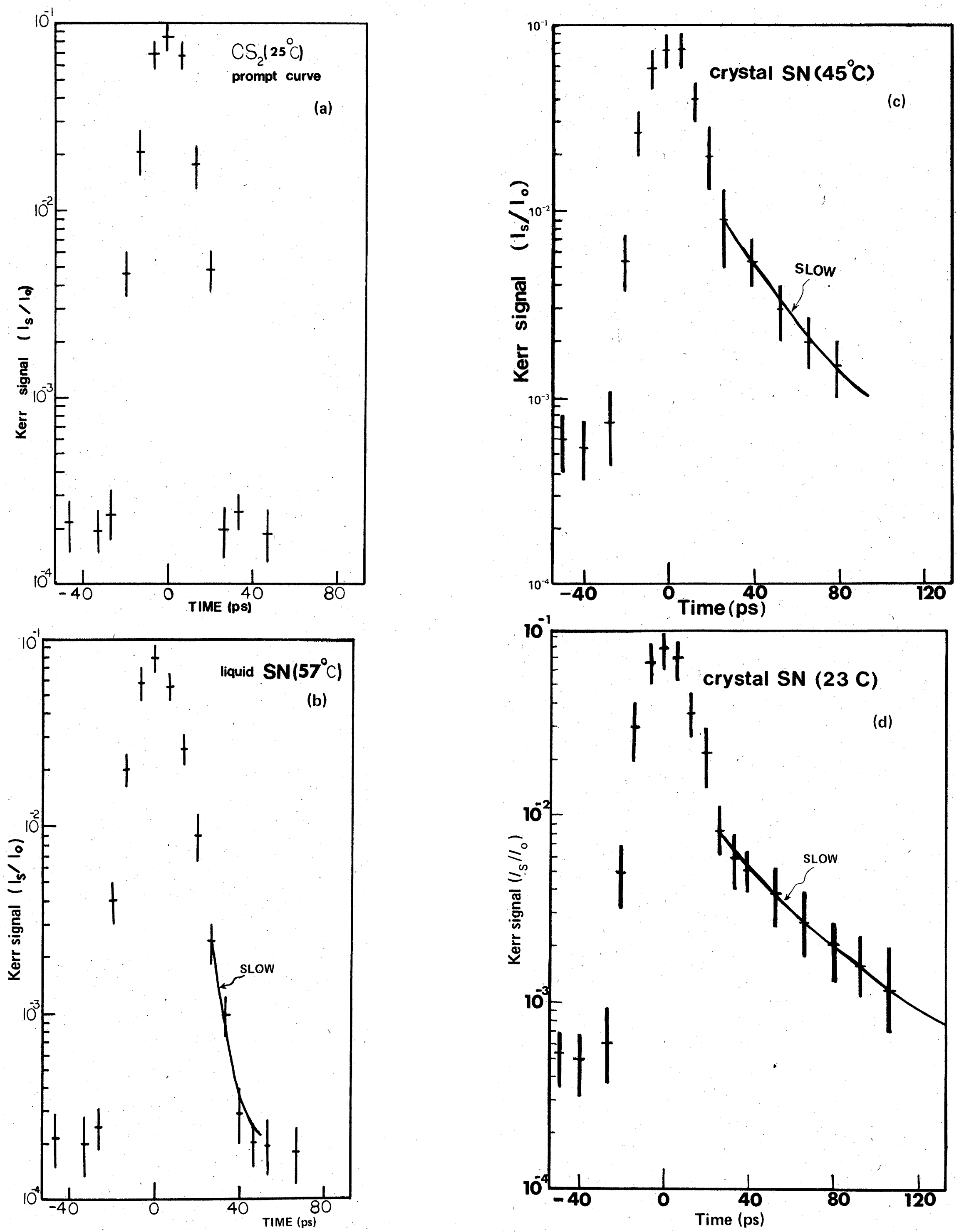

FIG. 3. Decay profile of the transmitted Kerr signal at various temperatures. I_s is the Kerr transmitted signal through the gate, and I_0 is the signal through the gate with the polarizers axes set parallel. The horizontal axis is the delay time measured in picoseconds. The zero time is arbitrary. Each data point is the average of four to six laser shots. The solid lines are fitted to the following equations due to the molecular relaxation process. (a) Prompt CS_2 gate response curve; (b) liquid SN at 57 °C, $I(t)/I_0 = 2.2\times10^{-3}\exp[-\frac{2}{11}(t-27)] + 2\times10^{-4}$; (c) plastic crystal SN at 45 °C, $I(t)/I_0 = 9\times10^{-3}\exp[-\frac{2}{45}(t-27)] + 6\times10^{-4}$; (d) plastic crystal SN at 23 °C, $I(t)/I_0 = 8\times10^{-3}\exp[-\frac{2}{64}(t-27)] + 5\times10^{-4}$. The intensity of the pump 1.06-μm laser beam was reduced by 10 times for the CS_2 prompt curve.

the ratio τ_1/τ_2 has been shown to lie between 1.1 to 1.5. This analysis suggests that the rotational motion of small molecules is probably characterized by either jumps of intermediate size or more likely by a distribution of jump angles.[6(a)] Comparing the relaxation times of the liquid SN from the Kerr effect with the dielectric relaxation ($\tau_1 = 18$ ps at 59 °C and $\tau_1 = 14$ ps at 74 °C[25]), the ratio τ_1/τ_2 is in reasonable agreement with the above discussion.

The decay profiles of the transmitted Kerr signal of the SN plastic crystal at 45 °C and 23 °C are shown in Figs. 3(c) and 3(d), respectively. The nonsingle exponential decay clearly indicates that different mechanisms are operative[6-8,10,11]—the fast component arises from the electronic cloud distortion and molecular librational motion, and the slow component arises from the molecular reorientational motion. At 23 °C the ratio of the peak transmitted signal of the fast to slow component is estimated to be about 5 to 1. Within the experimental error, there is no noticeable temperature dependence to the fast component decay. Its shape is very close to that of the prompt CS_2 curve. We have assumed the fast component is essentially temperature independent in this experiment. The relaxation time of the slow component tail at 23 °C is 64 ±20 ps which is in good agreement with the measurements from other techniques [τ(dielectric relaxation)(23 °C) = 82 ps,[2] or 64 ps,[25] and τ(depolarized Rayleigh scattering) = 59 ps (25 °C),[4(c)] 40 ps (19 °C),[4(a)] 71 ps (23 °C)[4(b)]]. The relaxation time at 45 °C is 45 ± 15 ps. In Fig. 4, the relaxation times of slow component tail versus the inverse of temperature is compared with the relaxation times obtained by other techniques. The salient feature of these curves is the sudden jump of the relaxation time at the liquid-to plastic crystal phase transition temperature. The activation energy estimated from the temperature dependence of the optical Kerr effect in the plastic phase is 2.6 ±0.7 kcal/mole. This value is in good agreement with the value obtained from the dielectric relaxation in the temperature range of this experiment [$E = 2.5$ kcal/mole (Ref. 2) and $E = 2.1$ kcal/mole (Ref. 25)] and is slightly lower than the activation energy obtained from the depolarized Rayleigh wing scattering [$E = 3.8$ kcal/mole (Ref. 4(b))]. The activation energy in the liquid state is about 3 kcal/mole.[4(b)] This suggests that the gauche-trans isomerization barrier in the plastic phase is similar to the overall barrier in the liquid state.

We also measured the relaxation times of SN at different crystal orientations by rotating the crystal around the $[1\bar{1}0]$ and $[001]$ axes at room temperature. Within the experimental error, the measured relaxation times are roughly the same with respect to the different orientation axes of the crystal. We need to improve the accuracy in order to determine if the reorientation about the different axes may have different relaxation times. In this experiment, we are most likely measuring a weighted average relaxation time about the different axes. The reorientational nonlinear refractive index n_2^0 of SN at 25 °C is estimated to be about 2×10^{-12} esu by comparing the magnitude of the Kerr effect of SN with that of CS_2 ($n_2(CS_2) = 2\times10^{-11}$ esu (Ref. 5)). In this estimation, the response time of the transmitted Kerr signal of SN has been taken into account. In the plastic crystal phase of SN, the contribution to the nonlinear index of refraction (n_2) from the fast relaxation processes (electronic cloud distortion and molecular libration) are estimated to be of the same order of magnitude as the orientational contribution. The total nonlinear index of refraction which has been measured by the Kerr effect using a 30-ns pulse from Q-switched ruby laser[19(b)] is 2.5×10^{-12} esu.

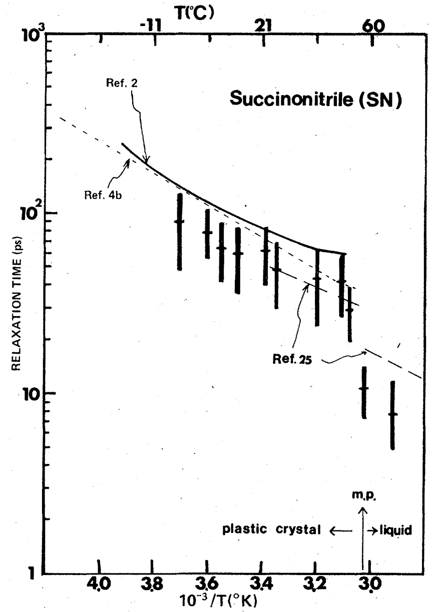

FIG. 4. Reorientational relaxation time of SN vs the inverse of the temperature. +: optical Kerr effect data; dotted line: best-fit curve from depolarized Rayleigh scattering [Ref. 4(b)]; dashed line: best-fit curve from dielectric relaxation (Ref. 25); and solid line: best-fit curve from dielectric relaxation (Ref. 2).

In summary, we have directly measured the Kerr relaxation times of SN molecules in the liquid and plastic crystal states at different temperatures. The relaxation kinetics is due to different mechanisms—a fast relaxation process (electronic cloud distortion and molecular libration motion) and a slow relaxation process (molecular reorientational motion). The activation energy in the plastic crystal state is 2.6 ± 0.7 kcal/mole. The relaxation time in the plastic crystal at room temperature about different crystal axes are the same within the experimental error.

ACKNOWLEDGMENTS

We thank Paul Wang of the Polytechnic Institute of New York and Jeff Steiner for helpful discussions and measurements of the x-ray diffraction pattern. This research was supported in part by grants from NSF DMR 73-02392-A02 and CUNY FRAP. One of us (R.R.A.) is grateful to the Alfred P. Sloan Fellowship Foundation for financial support.

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