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**Relaxation kinetics of salol in the supercooled liquid state
investigated with the optical Kerr effect^{a)}**

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The relaxation kinetics of the supercooled liquid salol is investigated using the optical Kerr effect. The Kerr intensity profile versus time is found to decay with two components. The mechanism responsible for this effect is attributed to the nonlinear index of refraction arising from the electronic cloud distortion and molecular reorientational motion of the salol molecules.

The knowledge of the kinetics of the nonlinear index of refraction of liquids can yield fundamental information on the molecular motion in the liquid state.^{1,2} For anisotropic molecules, the dominant mechanisms responsible for the Kerr effect is the electronic cloud distortion and molecular reorientational motion of the molecules.^{3,4,5} The electronic mechanism is temperature independent and is so fast that its time dependence cannot be resolved by picosecond laser techniques. The measurement of the temperature dependence of the Kerr relaxation will yield information on the kinetics of the molecular motion. By measuring the transient response of the optical Kerr effect as a function of temperature, we have separated the electronic and molecular contributions to the nonlinear index of refraction, of the supercooled⁶ liquid—salol⁷ (Phenyl Salicylate). The optical Kerr intensity versus time is found to decay with two distinct components. One component is fast and temperature independent and is attributed to be of electronic origin. The second is relatively slow, temperature dependent, and attributed to be of molecular origin. This is the first direct kinetic measurement delineating the relative effects of electronic and molecular contribution to nonlinear index of refraction. In the past, the relative contributions of the nonlinear index were obtained from steady state temperature dependent measurements^{8,9} or calculated from a combination of careful measurements using different experimental techniques, such as electric field induced second harmonic generation,⁸ third harmonic generation,¹⁰ ellipse rotation,⁵ and the D. C.⁸ and optical Kerr effect.^{11,12}

The experimental setup used to directly measure the relaxation kinetics of the optical Kerr effect has been previously described.^{12,13} An intense 1.06 μm laser with 8 ps duration is used to induce a birefringence of the sample solution which is situated between a pair of crossed polarizers. The birefringence is primarily caused by distorting the electronic cloud and orienting the anisotropic molecules in the liquid through the interaction of the optical field of the laser pulse with the polarizability of the molecules.^{4,11,12} A 0.53 μm pulse of 6 ps duration derived from the second harmonic generation of a 1.06 μm laser pulse is variably delayed

with a prism and is used to probe the time evolution of the induced transitory birefringence.

The salol was the purest grade available from Eastman Kodak Company. The sample was placed in a 1 cm long optical cell and was situated in a glass Dewar with strain free windows. A copper-constantan thermocouple was cleaned and immersed in the sample. The temperature was controlled by flowing cooled nitrogen gas into the Dewar and by surrounding the sample cell holder with heating tape. The sample temperature was controlled to ± 1 C and the temperature gradient across the sample was less than 1 C. Salol can be supercooled to a temperature well below its melting temperature of 42 C.

The Kerr intensity profiles versus time for salol measured at different temperatures are shown in Fig. 1. The salient feature of these curves is the distinct two component decay. At a temperature of 13 C, the decay profile is clearly composed of a slow and a fast exponential decay components. Within experimental error, the fast component is found to be temperature independent whereas the slow component is temperature dependent. The decay of the slow component becomes faster as the sample temperature is increased, merging with the fast component forming a nonexponential decay at the highest temperature (77 C) studied. The risetime of these curves are very fast (~ 5 ps). At a temperature of -10 C the Kerr intensity profile versus time is essentially composed of only the fast component. The decay time of the fast component corresponds to the convolution of laser pulse widths (~ 8 ps). The intensity of the slow component is extremely small because it can not respond significantly to the picosecond pulse excitation.⁴ The decay time of the slow component is estimated to be > 3 ns. With a signal to noise ratio of about 100 to 1, no other component is observed at -10 C.

The induced birefringence of the Kerr effect^{4,11} can be described by the equation

$$\Delta n(t) = \Delta n^e(t) + \Delta n^o(t), \quad (1)$$

where $\Delta n^e(t)$ and $\Delta n^o(t)$ denoted the electronic and molecular reorientational contributions, respectively. The electronic (*e*) and molecular (*o*) parts, $\Delta n^i(t)$, are given by the equations

$$\Delta n^i(r, t) = \frac{n_2^i}{\tau_i} \int_{-\infty}^t E_0^2(r, t') \exp \frac{-(t-t')}{\tau_i} dt', \quad (2)$$

where $i = e$ or o , n_2^i is the change to the nonlinear index of

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refraction through electronic cloud distortion, n_2^e is the change of nonlinear index of refraction from molecular reorientational motion, and τ_e , τ_o are the relaxation time of electronic and reorientational processes, respectively. Estimates of τ_e in most media lie in the range from 10^{-14} to 10^{-16} s and τ_o is longer than 10^{-12} s.^{4,12,13,14,15,16}

The transmitted signal of the probe 0.53 μm pulse through the Kerr gate at a delay time τ is

$$I_s(\tau) = \int_{-\infty}^{\infty} I_{2\omega}(t-\tau) \sin^2 \frac{1}{2} \delta\phi(t) dt, \quad (3)$$

and

$$\delta\phi(t) = \frac{2\pi L}{\lambda} \Delta n(t), \quad (4)$$

where L is the length of the sample cell, λ is the wavelength of the probe light, and $\delta\phi$ is the phase retardation

in the sample. Using Eqs. 2, 3, and 4 the magnitudes n_2^e and n_2^o are computed from the experimental measurements of the transmission of the probe 0.53 μm light pulse at different times, from the input power of the exciting 1.06 μm pulse, and from the relaxation times: τ_e and τ_o . The table lists the calculated values of n_2^e and n_2^o at different temperatures. The value of n_2^o of carbon disulfide ($\sim 2 \times 10^{-11}$ esu)^{5,12} is used as the standard to obtain the absolute values shown in the table. In the calculations, n_2^e is assumed to be independent of temperature and the envelope of the laser pulse is assumed to be exponential.

Nonlinear index

T(C)	13	25	40	47	62	77
$n_2^o (\times 10^{-12} \text{ esu})$	58	46	37	32	25	19

$n_2^e = 3 \times 10^{-12}$ esu

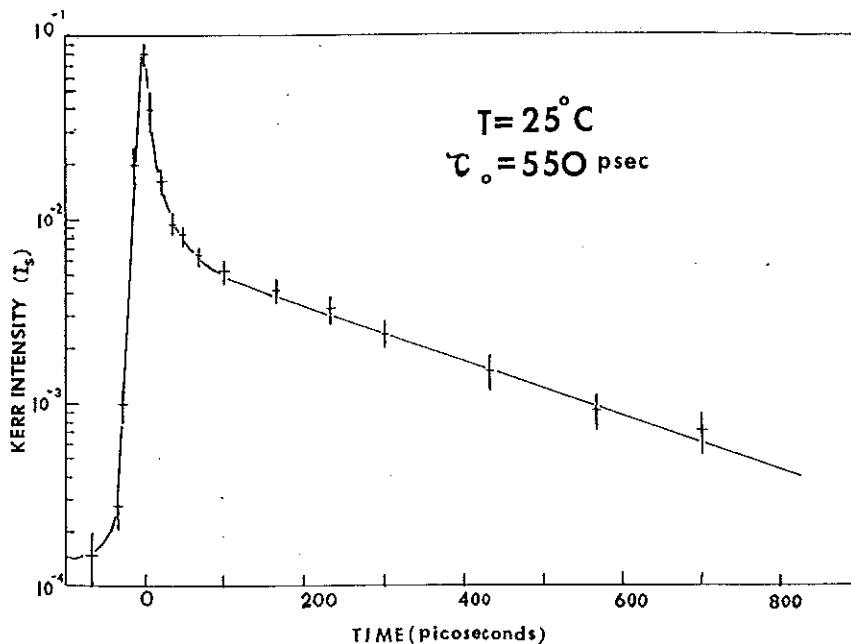
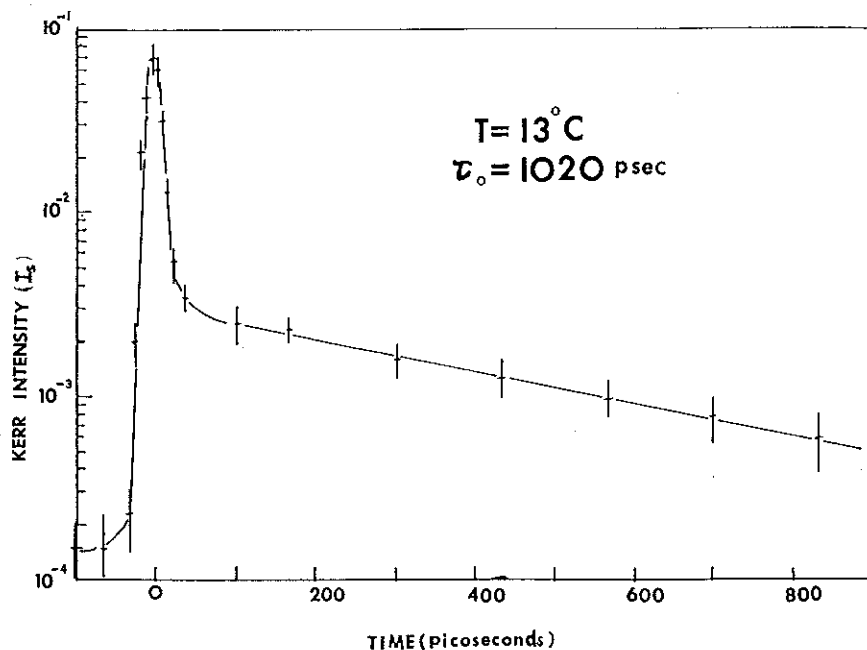


FIG. 1. Decay profiles of optical Kerr effect of salol at various temperatures. The vertical axis is the intensity of the transmitted 0.53 μm light pulse in arbitrary unit and the horizontal axis is the delay time in picoseconds. The zero time is arbitrary. (a) 13, (b) 25, (c) 47, (d) 77 C.

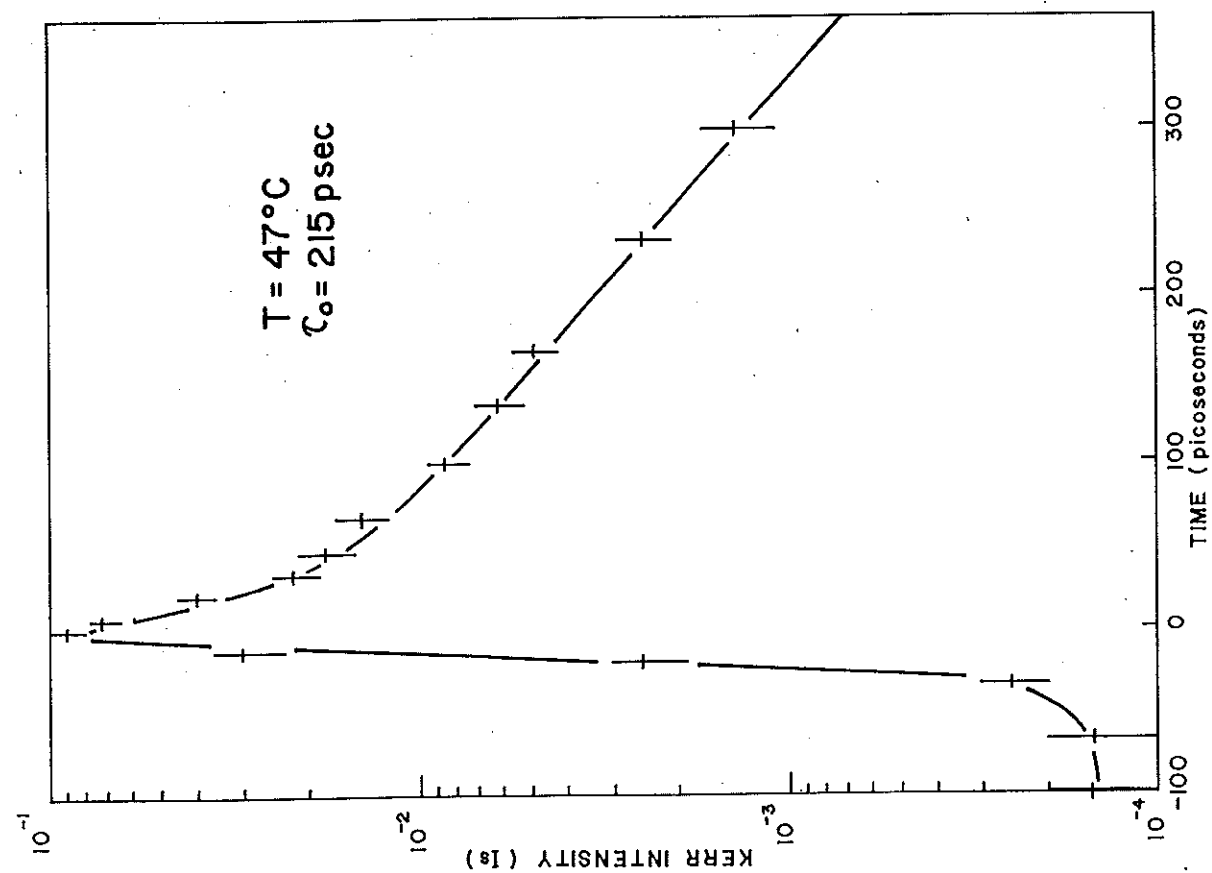
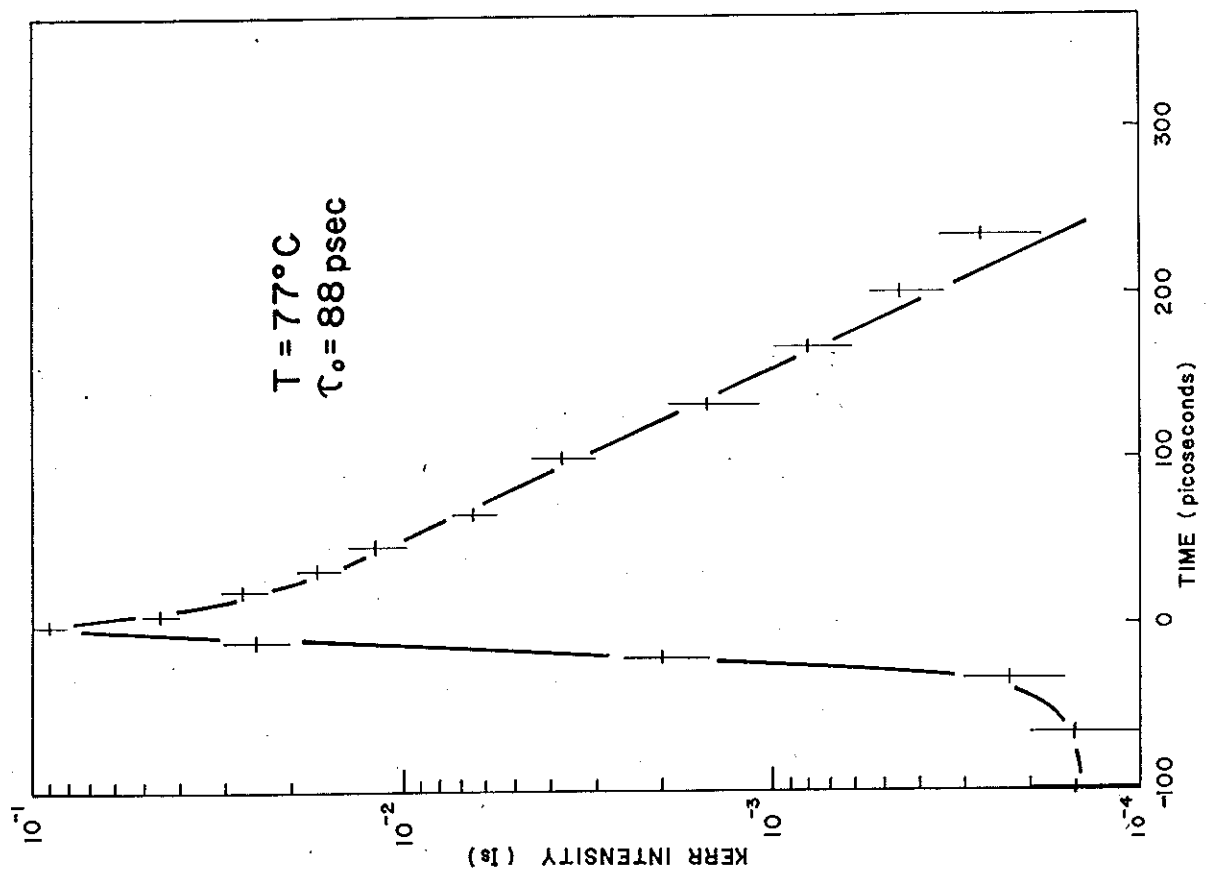


FIG. 1. (Continued).

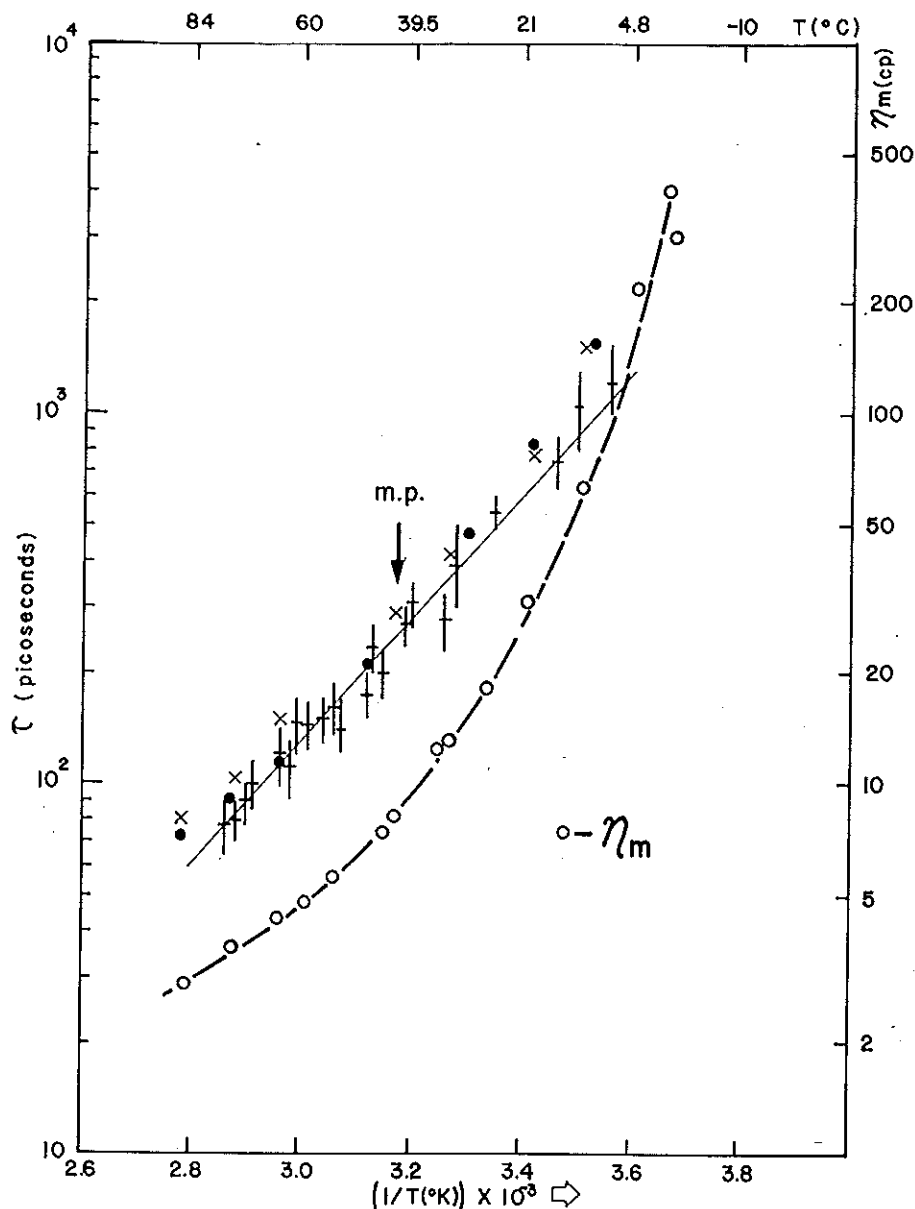


FIG. 2. The orientational relaxation time and viscosity versus $1/T$. +; optical Kerr effect, the lifetimes are doubled¹² from the decay profiles of Fig. 1. •, x: inverse of the depolarized Rayleigh wing linewidth from Refs. (17) and (7), respectively. o: measured viscosity from standard tables.^{17,18}

In accordance with the theories of Buckingham⁸ and Keilich³ the values of $\tau_2(T)$ measured at different temperatures follows a $1/T$ dependence.

In Fig. 2, the measured viscosity η_m ,^{17,18} the relaxation time of the slow component (τ_0) of the optical Kerr effect, and the inverse of the depolarized Rayleigh wing linewidth^{7,17} of salol are plotted versus $1/T$. There is no discontinuity in the slope of the Kerr lifetimes as salol is supercooled through its melting temperature. The lifetime decreases approximately exponentially as $1/T$. The Kerr relaxation times of the slow components from 7 to 77 C follows the Arrhenius behavior^{19,20,21}

$$\tau(T) = A \exp(E/RT), \quad (5)$$

where A is a proportionality constant ($\sim 3.4 \times 10^{-15}$ s) from data fitting and E is the potential barrier for molecules transiting from their original equilibrium positions to its new positions. The activation energy E of salol calculated from the Kerr effect measurements is 7.5 ± 0.5 kcal/mol, close to the activation energy = 5.6

kcal/mole calculated from viscosity measurements above the melting temperature. The Kerr relaxation times and the inverse of the depolarized Rayleigh wing linewidth measurements^{7,17} are in good agreement with each other over this temperature range. The temperature dependence of the Kerr relaxation time data reasonably fits the viscosity data above the melting temperature; but, below the melting temperature the measurements diverge rapidly. Therefore, Debye's equation²² of molecular rotational relaxation time in a liquid

$$\tau(T) = V\eta_m(T)/KT, \quad (6)$$

cannot be used to describe the temperature variation studied. It is apparent from Fig. 2 that the viscosity of salol does not follow a simple Arrhenius behavior below the melting temperature. This is a common characteristic of supercooled liquids which has been attributed to the progressive restriction of the different rotational degrees of freedom of the molecules with decreasing temperature.²³ These results suggest an ansatz that

the Kerr relaxation data measures the rotational kinetics associated with a particular rotational degree of freedom of the salol molecules whose motion may only contribute partly to the overall measured viscosity of the supercooled liquid.

In conclusion, the Kerr relaxation kinetics of salol has been measured at different temperatures. The temperature variation of reorientational relaxation time τ_r increases exponentially as $1/T$ following an Arrhenius behavior. No discontinuity is noticed at the melting point or in the supercooled region. Two distinct components of the Kerr decay profile are observed. From the temperature dependences of these components, the mechanisms responsible for the fast and slow components are attributed to the electronic and molecular reorientational parts of nonlinear refractive index, respectively. This is the first clear observation delineating the electronic and molecular contributions of the nonlinear index of refraction.

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