Femtosecond Optical Kerr Studies on the Origin of the Nonlinear Responses in Simple Liquids

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Abstract—The time-resolved optical Kerr responses of several simple molecular liquids are probed with 65 fs laser pulses. Four dynamically distinct responses associated with the nonlinear susceptibility are observed in every liquid that possesses a permanent anisotropic polarizability. These consist of 1) a slower response ($\tau_{1/e} > 1$ ps) that is commonly identified with diffusive reorientation, 2) an intermediate response ($\tau_{1/e} \sim$ 400–600 fs) that is associated with a translational anisotropy and the resultant intermolecular "interaction-induced" distortion of the molecular polarizability, 3) an ultrafast component exhibiting a rapidly damped ($\tau_{1/e} <$ 170 fs) oscillatory behavior assigned to coherently driven molecular librational motion, and 4) an instantaneous response attributed primarily to the purely electronic hyperpolarizability. In addition, low-frequency intramolecular vibrations accessible to the different Fourier components of the laser pulse are coherently excited, with the time evolution of these normal vibrational coordinates observed directly, superimposed on responses 1)–4). A simple model that specifically includes inertial effects provides an excellent description of the entire temporal profile of the Kerr signal of each liquid investigated. The role of "coherent coupling" effects in the interpretation of optical Kerr data is outlined both experimentally and theoretically.

I. Introduction

RECENT developments in the generation of ultrashort laser pulses [1] have made possible the direct observation of dynamical behavior on the femtosecond time scale, providing information that is complementary to that obtained via frequency domain inelastic light scattering (LS) techniques. In particular, the direct observation of the time domain response functions preserve any inherent temporal ordering which may be compromised by a diffusive relaxation treatment of LS data. In the current study we probe the dynamical behavior of several simple liquids via the time-resolved optical Kerr effect (OKE) with 65 fs FWHM optical pulses, revealing several new aspects of the short time behavior of liquids. A simple model of molecular motion with the explicit inclusion of inertial effects provides an excellent description of the observed temporal profile of the femtosecond time-resolved OKE of each liquid investigated. This analysis, in conjunction with the wealth of information available from LS

experiments and molecular dynamics simulations, enables us to make definitive statements as to the origin and nature of the different responses, both electronic and nuclear.

The dynamical behavior of molecular and atomic liquids has been studied for many years in the frequency domain via Rayleigh and Raman scattering techniques [2]. In the Born–Oppenheimer approximation, the spectrum of the scattered radiation is proportional to the Fourier transform of the time correlation function $\langle [\delta\chi_{ij}(t), \delta\chi_{kl}(t = 0)] \rangle \Gamma(t)$ where the brackets indicate an ensemble average, the $\delta\chi_{ij}$, $\delta\chi_{kl}$ are fluctuations in the bulk linear susceptibility χ_{ij} associated with changes in the nuclear coordinates of the liquid molecules, and $\Gamma(t)$ is the unit step function [3]. When the molecules of the liquid possess an anisotropic molecular polarizability α_{ij}, the LS spectrum will exhibit a sharp Lorentzian line centered at the laser frequency with a width of a few cm^{-1} and causally related to the diffusive (thermal) reorientation of the molecules in the liquid. The intensity in the high-frequency "wings" of the LS spectra, however, is far greater than can be accounted for by simple diffusive reorientation, and the total LS spectrum has been treated in terms of a superposition of the diffusive reorientation contribution and at least one rapidly relaxing (spectrally broad) response [2]. The rapid response is commonly attributed to fluctuations in the α_{ij} induced by intermolecular interactions and exhibits a relaxation time roughly corresponding to the collision period of the liquid [2], [4]. An ultrafast relaxation ($\tau_{1/e} \sim$ 200–300 fs) was not observed in the time domain until subpicosecond laser pulses with durations near the condensed phase collision frequency became available [5], [6]. The actual mechanical origin of this response and the identity of the so-called "second" dynamical variable [2], however, were not further elucidated as a consequence of these observations.

We are aware of at least three proposed physical origins for the polarizability fluctuations that give rise to the high-frequency amplitude of the LS spectra and the subpicosecond laser induced birefringence of polarizable liquids. 1) The intermolecular interactions alluded to above are widely believed to be mechanical collisions and/or induced dipole interactions between nearest neighbor molecules [2], [4]. The relaxation times of these processes are estimated to be on the order of 2–5 × 10^{-13} s. 2) At times less than the collision period, the incremental reorientation rate will be inversely proportional to $I^{1/2}$ where

I is the molecular moment of inertia. This is the "free rotation" or inertial limit [7], [8], with rate constants typically $> 2 \times 10^{12}$ s^{-1} for liquids composed of "small" molecules (i.e., CS_2, benzene, and substituted analogs). 3) Under the influence of laser pulses of duration less than a collision period, the torque experienced by a polarizable molecule will be impulsive and little net alignment of the molecules with respect to the polarization plane of the laser will occur. Instead, the molecules will be induced to librate within a local intermolecular potential or "solvent cage." This dynamical response was originally invoked to explain the high-frequency wings of the LS spectra of liquids [9] and the spectra of filaments formed in CS_2 due to the self-focusing induced by intense laser fields [10]. The rate of this motion will also be inversely proportional to $I^{1/2}$, but because of the constraints imposed upon the motion by the intermolecular potential, should be significantly more rapid than the "free rotation" described above. This rate has been estimated [10] to be on the order of 5×10^{12} s^{-1}.

In order to discriminate between these alternative accounts of the molecular motions involved in the subpicosecond response of polarizable liquids, we have undertaken a study [11]–[13] of the time-resolved OKE. In all liquids studied in which the linear molecular polarizabilities α_{ij} are anisotropic, we observe complex dynamical behavior consisting of three distinct nuclear relaxation processes associated with the correlation function $\langle \alpha_{ij}(t), \alpha_{kl}(t = 0) \rangle$, in addition to a fourth response that is instantaneous on the time scale of our laser pulse. We will show that, in the limit where the laser pulsewidth is small compared to the various material relaxations of the liquid, the use of the unit step function to describe the imposition of the laser-induced anisotropy is inappropriate. The explicit inclusion of inertial effects is necessary [11]–[13] and will be discussed in detail in Section III-B. Similar inertial effects in the CS_2 system have been observed independently by two other groups [14], [15] using transient grating techniques [16]. We have recently demonstrated the necessity of explicitly including a response that is instantaneous on the time scale of the laser pulse in the analysis of the OKE data for several liquids [11]–[13]. The contribution of the "purely electronic" hyperpolarizability to this "instantaneous" response in all liquids studied will be discussed with regard to the "coherent coupling" of the laser pulses used to execute the experiment.

II. EXPERIMENTAL

The experiments were performed at 295 ± 1 K with a synchronously pumped antiresonant ring [17] dye laser that produces a continuous train of typically 65–75 fs pulses centered at 633 nm at a repetition rate of 82 MHz and an average power of 15 mW. Assuming a sech^2 pulse shape, the transform-limited FWHM bandwidth is < 180 cm^{-1} with significant Fourier amplitudes over a bandwidth of ~ 350 cm^{-1}. The essential details of the OKE experiment are given in Fig. 1, and have been extensively
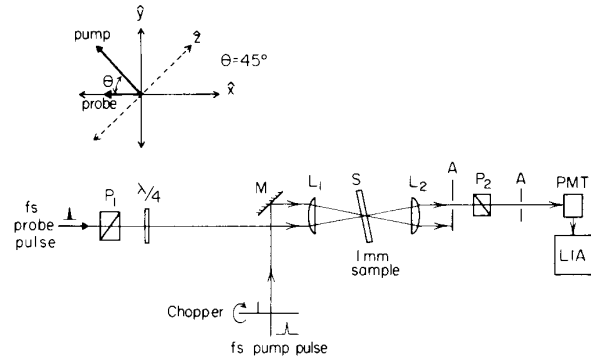

Fig. 1. Schematic diagram of the experimental apparatus. P_1, P_2: crossed Glan–Taylor polarizer pair, $\lambda/4$: mica quarter-wave plate, L_1 and L_2: lenses, S: sample, A: aperture, M: beam steering mirrors, PMT: photomultiplier tube, LIA: lock-in amplifier. The relative pump and probe beam polarizations are shown in the inset with $\theta = 45°$.

documented by previous work in the picosecond [18]–[20] and femtosecond [6], [12], [21] time domains.

In the time-resolved optical Kerr effect, a laser-induced anisotropy of the refractive index, created by the pump pulse, is probed by a variably delayed, weak polarized probe pulse [18], [19]. The change in the polarization state of the probe pulse is detected by the transmission through a crossed polarizer pair (P_1, P_2, Fig. 1) in the probe beam as a function of the time delay between the two pulses. In a conventional (homodyne) Kerr cell, the detected signal scales quadratically with the pump pulse intensity and linearly with the probe intensity [18]. In addition, this signal is quadratic with respect to the impulse response function of the sample. This response function, which we will denote as $R_{ijkl}(t)$, is related to the frequency-dependent, third-order nonlinear susceptibility $\chi_{ijkl}^{(3)}$ through a Fourier transform relationship [22] and in general contains real (dispersive) and imaginary (resonant) contributions [3], [23].

In order to avoid the inherent complexity of analyzing such a signal and render our data linear in the $R_{ijkl}(t)$, optical heterodyne methods are employed in our experimental detection scheme [19], [23]. We derive a local oscillator from the probe pulse in two ways [23], [24]. In the first method, a $\lambda/4$ waveplate positioned between the crossed polarizers of the Kerr cell is oriented with its "fast" axis parallel to the polarization plane of the probe pulse at the sample cell. When the input polarizer (P_1) is rotated $< 1°$, the probe pulse becomes elliptically polarized, while the major axis of polarization remains in the original probe polarization plane. This will introduce a small orthogonal polarization component 90° *out-of-phase* with respect to the probe E field of the homodyne experiment. In the second method, the analyzer polarizer (P_2) is tipped $< 1°$ away from maximum extinction, passing part of the probe pulse which is *in phase* and polarized orthogonal to the probe polarization at the sample. The magnitude of the local oscillator is adjusted to be 30–50× that of the homodyne (crossed polarizer) Kerr signal [24]. Following a previous treatment [23], if we consider the

conventional Kerr signal I_S as arising from an electric field E_S radiated by the sample under the influence of the pump and probe laser fields, the use of a local oscillator field E_{LO} results in a detector signal proportional to

$$I_{LO} + I_S + I_B + \frac{nc}{8\pi} (E_S^* E_{LO} + E_{LO}^* E_S) \qquad (1)$$

where I_{LO} is the local oscillator intensity, I_S is the conventional homodyne Kerr signal intensity, I_B is the intensity due to any background radiation, and $nc/8\pi(E_S^* E_{LO} + E_{LO}^* E_S)$ is the heterodyne term. The local oscillator is adjusted to make the heterodyne term much greater than I_S, and the heterodyne term is separated from I_{LO} and I_B by lock-in detection of the modulated signal [23b]. We note that real and imaginary contributions to E_S associated, respectively, with the imaginary and real parts of $R_{ijkl}(t)$, may be selected [23] by changing the phase of E_{LO}. This will be exploited later when we probe the nature of the signal near zero delay.

III. RESULTS AND DISCUSSION

In the sections that follow, we present the details of the method used in analyzing the optical Kerr data and discuss the implications of the various conclusions that are drawn. Experimental results from several different liquids are presented to emphasize the generality of the relaxation phenomena observed. In the first section, we present a qualitative analysis of the origins of the various responses. In this discussion, a series of halogenated methane derivatives is used to demonstrate the consequences of a permanent polarization anisotropy on the presence or absence of the different nuclear responses. In Section III-B, we present a quantitative analysis of the observed OKE signals using CS_2 and chloroform as prototype examples, with the results generalized to the other liquids studied. In Section III-C, the OKE in liquid benzene is used to demonstrate the role of coherence effects in the current experiments. "Coherent coupling" effects near zero delay are prevalent in the time-resolved degenerate four-wave mixing literature and can have a significant influence on the interpretation of data when both pump and probe pulses overlap in the sample [26]. The different Fourier components of a spectrally broad, ultrashort laser pulse can excite any low-lying vibrational resonances of the sample through a stimulated Raman effect. In Section III-D of this discussion, a direct observation of the temporal evolution of resonantly driven intramolecular vibrational modes is presented for the chlorinated methanes.

A. The Role of Molecular Symmetry

In media which are macroscopically isotropic, there are two contributions [3] to the nonlinear response function $R_{ijkl}(t)$:

$$R_{ijkl}(t) \propto \sigma_{ijkl}(t) + \frac{iV}{2\hbar} \left\langle [\chi_{ij}(t), \chi_{kl}(t = 0)] \right\rangle \qquad (2)$$

where $\sigma_{ijkl}(t)$ is the ensemble-averaged purely electronic hyperpolarizability, and the second term is the ensemble-averaged correlation function [3] of the (complex) bulk linear susceptibility χ_{ij}. The first term is instantaneous on the time scale of the laser pulse and is observed only when the pump and probe pulses are overlapped. The second term contains the contribution of the intra- and intermolecular nuclear motions to the observed relaxation. In the discussion that follows, we will assume that the laser frequency is far below any electronic resonances of the medium and that multiphoton electronic resonances are negligible. Resonant processes, however, may contribute to the OKE signal through the dependence of the χ_{ij} on both the intramolecular (normal mode vibrations) and intermolecular (phonon-like) vibrational modes of the liquid [3]. These vibrations may be coherently driven through a stimulated Raman process by the different Fourier components present in the spectrally broad, ultrashort laser pulse.

In Fig. 2, we present the time-resolved OKE transients for a series of chlorinated methane derivatives. This series of curves demonstrates dramatically the effect of the permanent polarizability anisotropy on the Kerr signal. The OKE signal for the highly symmetric CCl_4 molecule (lower curve), which possesses an isotropic linear polarizability, is dominated by an instantaneous response attributable to the purely electronic hyperpolarizability. In addition, this curve exhibits a slight exponential asymmetry at positive delays, with oscillations clearly evident and persisting for several picoseconds. These oscillations result from the coherent excitation of the CCl_4 Raman modes at 218 and 314 cm^{-1} and will be discussed in more detail later.

The OKE signals for the less symmetrical $CHCl_3$ and CH_2Cl_2 molecules (upper curves) also have prominent contributions from the electronic hyperpolarizability near zero delay, but exhibit a complicated temporal profile at positive time delay. We have decomposed the OKE signal of these liquids into *four* dynamically distinct components (cf. Section III-B) that appear common to all liquids composed of anisotropic molecules. These components include 1) diffusive reorientation, which accounts for the OKE intensity at probe delays > 1.5 ps; 2) an intermediate component with an exponential time constant in the range 400–600 fs; 3) an ultrafast component ($\tau_{1/e} < 170$ fs) that accounts for the prominent shoulder in the upper curves of Fig. 2; and 4) a response that is instantaneous on the time scale of the laser pulse and is well represented by a scalar multiple of the laser pulse autocorrelation function. Oscillations arising from the 262 cm^{-1} Raman active vibration are also evident in the $CHCl_3$ data, superimposed on the responses described above. In the discussions that follow, we will refer to the different responses, in the order presented above, as 1) diffusive, 2) intermediate, 3) ultrafast, and 4) instantaneous.

In discussing the physical origin of the subpicosecond relaxations, it is useful to cite earlier experimental [4], [25] and theoretical [2] work on the dynamics of molecular motion and intermolecular interactions. Xe, like CCl_4, is highly symmetric and possesses a large elec-
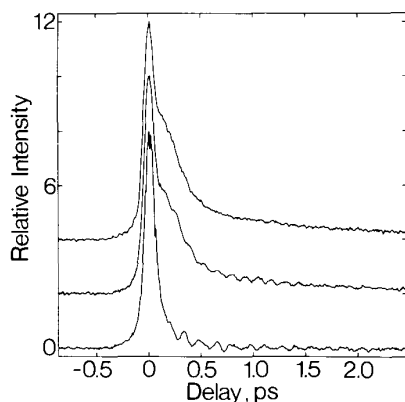
Fig. 2. Optical Kerr signals for the liquids CH_2Cl_2, $CHCl_3$, and CCl_4 (top to bottom).

Fig. 3. (a) Optical Kerr signal for neat CS_2 together with tail matched theoretical response for the diffusive orientation component, $\tau_i = 1.61$ ps. (b) Logarithmic plot of the difference of the two curves given in (a). The straight line corresponds to a time constant of 426 fs.

tronic polarizability. The Kerr response of liquid Xe has been measured using 150 fs FWHM laser pulses [25] and, like CCl_4, is found to consist of a prominent instantaneous (pulse-limited) component plus a small (< 10 percent) exponentially decaying response ($\tau_{1/e} \sim 450$ fs) at positive delay. Similar results were observed for liquid Ar, with the amplitude of the exponentially decaying component $\sim 30\times$ smaller than in liquid Xe due to the decreased polarizability of Ar. Since the rare gas atomic liquids possess no permanent polarization anisotropy, this noninstantaneous signal component is believed to arise from an anisotropy associated with transient distortions of the atomic polarizability. These are the "interaction-induced" (or "collision-induced") effects described in the LS and molecular dynamics literature [2], [3] that have recently been invoked as a possible origin of the subpicosecond response in CS_2 [6]. In the atomic liquids, this effect must originate in deviations from the average equilibrium internuclear separation, and thus is associated with a *local translational anisotropy* in the liquid [27]. In LS experiments, a translational anisotropy arises from microscopic density fluctuations in the fluid, while in OKE experiments, this anisotropy is field induced and will decay on the time scale of the density fluctuations.

The time-resolved OKE of liquid O_2 is qualitatively very different from that of liquid Xe and Ar. Specifically, the O_2 data of [25] (Fig. 3) reveals a distinct shoulder on an "instantaneous" response with a $1/e$ relaxation time of <200 fs, in addition to a longer (>1 ps) small amplitude relaxation apparently originating in diffusive orientational motion. We infer the presence of an intermediate lifetime component by inspection. These features are similar to those of the $CHCl_3$ and CH_2Cl_2 data of Fig. 1 and, if the difference in time resolution between the two experiments is taken into account, the O_2 OKE data are almost identical to the chlorobenzene data recently reported [12], [13]. O_2, in contrast to the atomic species, does possess a permanent polarization anisotropy and should, therefore, exhibit relaxations causally related to molecular orientational motions. Most molecular dynamics simulations of orientational motions reveal effects due
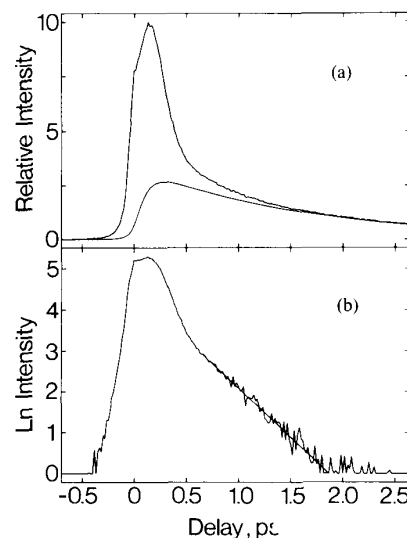
to inertial reorientation at times less than or equal to the condensed phase collision frequency [28]. These effects, which appear to be librational in nature [28], will not be observed in liquids composed of species with spherically symmetric linear polarizabilities.

The behavior seen in the cryogenic liquid series Xe, Ar, and O_2 appears isomorphic to that observed in the chlorinated methane series CCl_4, and $CHCl_3$ and CH_2Cl_2. On going from systems with anisotropic to isotropic polarizabilities, both the ultrafast relaxation (associated with the prominent shoulder at probe delays <300 fs) and the slower ($\tau_{1/e} > 1$ ps) exponentially decaying component vanish. It may thus be concluded that these two responses are associated with orientational motions of the molecules. We suggest, therefore, that the prominent ultrafast relaxation [response 3] in the time-resolved OKE of the room temperature liquids we have studied is due to the rapidly damped libration (also referred to as "rocking" [10] or hindered rotation) of molecules within a solvation structure that is fixed on the time scale of the laser pulse. This solvation structure defines the intermolecular potential in which the molecules/atoms must move. Furthermore, if we assume that the intermediate lifetime response observed in liquids composed of anisotropic molecules ($\tau_{1/e} \sim 300$–600 fs) does correlate with the exponentially decaying component present in CCl_4 and the atomic liquids, then this response may be associated with the translational anisotropy and corresponding "interaction-induced" effects described above. Solvent motions on the time scales of these two relaxations have been invoked [29] to describe the high-frequency viscoelastic properties of the n-alkanes near 300 K. For the purposes of this analysis, we neglect any coupling between these two dynamical variables [2].

B. Analysis of the Kerr Response

The transmission of the Kerr cell for our optical heterodyne detection scheme is given by [18]

$$T(\tau) = \int_{-\infty}^{\infty} I_{\text{probe}}(\tau - t)\left\{1 + \sin\left[\phi(t)\right]\right\} dt \quad (3)$$

where τ is the time delay between the two pulses, I_{probe} is the probe pulse intensity, and $\phi(t)$ is the time-dependent phase shift induced in the Kerr active sample by the pump pulse intensity $I_{\text{pump}}(t)$. The phase shift $\phi(t)$ is related to the induced anisotropy in the refractive index Δn by

$$\phi(t) = \frac{\omega L}{c} \Delta n(t) \quad (4)$$

where L is the interaction length, ω is the laser frequency, and c is the speed of light. When the dynamical responses of the liquid occur on separable time scales [2], the effective $\Delta n(t)$ may be expressed as a linear superposition of dynamically independent contributions:

$$\Delta n(t) = \sum_m \Delta n_m(t)$$
$$= \sum_m \int_{-\infty}^{\infty} I_{\text{pump}}(t') r_m(t - t') dt' \quad (5)$$

where $r_m(t)$ represents the mth contribution to the third-order dielectric response function $R_{ijkl}(t)$ of the sample when the OKE is represented as a transient four-wave mixing process [3], [23], [26]. On substituting (4) and (5) into (3), we obtain the equation actually used in the data analysis:

$$T(\tau) = \sum_m \int_{-\infty}^{\infty} G_0^{(2)}(t) r_m(\tau - t) dt \quad (6)$$

where $G_0^{(2)}(t)$ is the zero background laser pulse intensity autocorrelation. In obtaining (6), we used the approximation that $\sin x \sim x$ for small x, and recognized that the constant term in (3) is not detected when chopping the pump beam.

In recent preliminary communications [11]–[13], we have noted the inability of the diffusion approximation [30], [31] to account for the short-time dynamical behavior observed in the OKE of room temperature liquids CS_2, chlorobenzene, and nitrobenzene. It was proposed [11]–[13] that both the delay in the signal rise and the width of the observed transient could be explained by inclusion of an inertial term in the equation of motion for the nuclear contribution to the birefringence. This inclusion recognizes that the induced anisotropy is not instantaneously imposed on the molecular liquid when the laser pulse is sufficiently shorter than the various relaxation modes of the sample. This conclusion has been independently proposed [14] in explication of a similar lag in a transient grating study of CS_2.

The effects of inertial motion were invoked to describe early depolarized light scattering spectra [9], [32] and the spectra of filaments formed from the self-focusing of intense laser pulses [10] in liquid CS_2. These workers treated the orientation of the condensed phase molecules with respect to the polarized radiation field as a linear driven oscillator described by the equation of motion:

$$I\frac{d^2\delta\theta}{dt^2} + \xi\frac{d\delta\theta}{dt} + \mu\delta\theta = F(t) \quad (7)$$

where $\delta\theta$ is the angle induced between the laser electric field and the principle axis of the molecular polarizability tensor, I is the molecular moment of inertia, ξ is the microscopic friction, μ is the elastic force constant of an harmonic potential, and $F(t)$ is the generalized forcing function. The form of the observed response function $\delta\theta(t)$ depends upon the relative magnitudes of the coefficients of (7) as well as the details of the forcing function, and has been evaluated by the Green's function method [33].

The equation of motion for the birefringence induced by an arbitrarily shaped laser pulse I_{pump} was derived from (7) and applied to filament spectra [10] in CS_2 in the form

$$I/\mu\frac{d^2\Delta n_i}{dt^2} + \xi/\mu\frac{d\Delta n_i}{dt} + \Delta n_i = n_{2i}I_{\text{pump}}(t') \quad (8)$$

where n_{2i} is the ith contribution to the nonlinear refractive index n_2. All of the noninstantaneous field-driven responses are associated with nuclear motions through the correlation function $\langle \chi_{ij}(t), \chi_{kl}(0) \rangle$ and therefore may not be capable of instantaneously following our femtosecond laser pulses. The solution to (8) in the overdamped limit is

$$\Delta n_i(t) = \frac{n_{2i}\beta_i}{(I/\mu)^{1/2}} \int_{-\infty}^{t} \sinh\left[(t - t')/\beta_i\right]$$
$$\cdot \exp\left[-(t - t')/\tau_i\right] I_{\text{pump}}(t') dt' \quad (9)$$

where

$$\tau_i = \frac{2I}{\xi}; \quad \beta_i = 2\left[(\xi/I)^2 - 4(\mu/I)\right]^{-1/2}$$

and naturally accounts for this behavior by including the physically required "quadratic lag" while maintaining the exponential diffusive character at long times. Equation (9) reduces to the diffusion result [31] in the limit of small β_i and is used to model the exponentially decaying components of the OKE response [responses 1) and 2)].

The solution to (8) in the underdamped limit is

$$\Delta n_i(t) = \frac{n_{2i}\beta_i}{(I/\mu)^{1/2}} \int_{-\infty}^{t} \sin\left[(t - t')/\beta_i\right]$$
$$\cdot \exp\left[-(t - t')/\tau_i\right] I_{\text{pump}}(t') dt'. \quad (10)$$

This equation describes the oscillatory motion of a molecule in a potential well defined by the surrounding solvent structure and is used to model response 3), the ultrafast (but noninstantaneous) component of the OKE signal attributed to librational motion. The period of oscillation is given by $2\pi\beta_i$.

The complexity of the OKE signals at short times is evident in the data of Fig. 2. We will now describe the procedure used to extract meaningful physical parameters from the measured temporal signals. The data are treated within the assumptions of (5), that is, the net material response is given by the sum of the individual responses. CS_2 and $CHCl_3$ will be used as working examples, but the procedure outlined has been successfully applied to all liquids we have investigated thus far.

The time constant for diffusive reorientation is easily extracted from semi-log plots of the data when sufficiently long time windows are used. Long scans are necessary to eliminate contributions from the faster decays, and we typically require that the curve be linear over four time constants. The analysis of shorter scans systematically underestimates this decay time. Of equal importance is the establishment of an accurate baseline since small baseline errors give rise to significant errors in the measured lifetime [6b]. A typical 10 ps scan of the OKE in CS_2 demonstrating these points is given in [13, Fig.]. The analysis of numerous such curves results in a diffusive reorientation time for CS_2 of 1.61 ± 0.05 ps.

Having established the reorientation time, its contribution is then removed from the Kerr signal by tail matching and subtracting the two curves. This procedure is illustrated for CS_2 in Fig. 3. The upper curve of Fig. 3(a) is the OKE signal for neat CS_2, with the lower curve generated according to (9) with $\tau_i = 1.61$ ps. (The particular choice of β_i affects only the rising edge of the response and is not significant at this point in the analysis [34].) The logarithmic plot of the residual curve given in Fig. 3(b) exhibits a markedly nonexponential decay with the tail region well described by an exponential time constant of 426 fs. This intermediate lifetime component has not been observed previously in the dynamical response of CS_2 nor has its presence been deduced from frequency domain studies.

Fig. 3 unambiguously establishes the existence of *three noninstantaneous responses* in the Kerr signal of CS_2. We have recently reported similar results for the OKE signals of nitrobenzene and chlorobenzene [12], [13] and have now observed three noninstantaneous responses in numerous molecular liquids [35]. Thus, when the instantaneous electronic response is included, *four distinct dynamical responses have been observed in all liquids composed of anisotropic molecules* thus far investigated. As discussed in Section III-A, the intermediate component appears analogous to the "interaction-induced" responses observed in cryogenic atomic liquids [25], and is under current investigation.

In accordance with (6), the net OKE response for a liquid composed of anisotropic molecules is represented by the sum of these three individual responses, together with an instantaneous response that is represented by a scalar multiple of the measured laser pulse autocorrelation. Fig. 4 gives the results of this analysis for the specific cases of CS_2 and $CHCl_3$. As is evident, the experimental data (dots) are very well reproduced in terms of (6) (solid
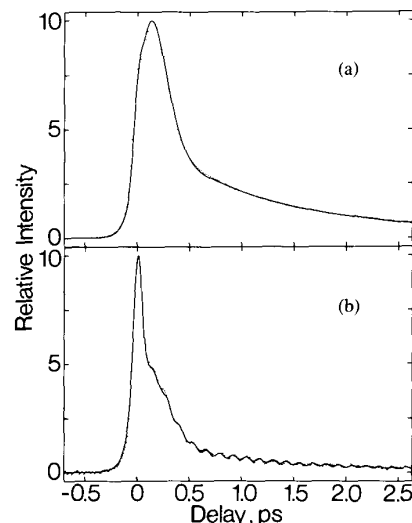

Fig. 4. Optical Kerr signals for (a) CS_2 and (b) $CHCl_3$ (dots) shown together with theoretical best fits (solid) generated in accordance with the model described in the text.

curves) for both liquids in spite of their dramatically different appearance. The theoretical curves of Fig. 4 are given again in Fig. 5 decomposed into their respective component curves. The oscillatory component arising from an intramolecular Raman resonance at 262 cm^{-1} has been suppressed in the case of $CHCl_3$ for clarity.

In obtaining the theoretical curves of Figs. 4 and 5, the time constants for the two exponentially decaying components were fixed at the values obtained from the linear least squares analysis described above, with the instantaneous component represented by a scalar multiple of the laser pulse autocorrelation function. Because the leading edge of the two slower responses is buried under the larger amplitude instantaneous and librational components, it is difficult to independently determine a β_i value for each [34]. Reasoning that the magnitude of the inertial effect should be similar for all of the noninstantaneous nuclear responses, we have set the values of all three β_i's equal [36]. Thus, the only fitting parameters used are the τ_i and β_i values for the ultrafast librational component and the three independent component amplitudes. These parameters were varied in an iterative fashion to obtain the curves of Figs. 4 and 5. We note that the noninstantaneous responses are generated from (9) and (10) using the measured laser pulse autocorrelation at the experimentally determined zero delay with no arbitrary shifting of either the individual components or the net response. This puts rather stringent restrictions on the possible values of the various parameters, especially with respect to the ultrafast librational component.

The τ_i values of the noninstantaneous responses used in obtaining the theoretical curve for CS_2 are 140 fs, 450 fs, and 1.61 ps with corresponding amplitudes of 0.38, 0.138, and 0.192, respectively. A β_i value of 150 fs was used for each component in accordance with the above discussion. The instantaneous component is represented
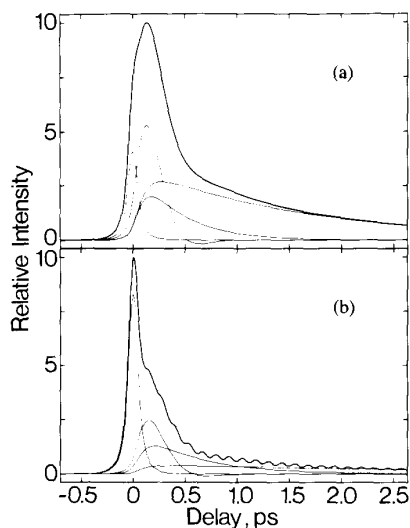
Fig. 5. The theoretical curves of Fig. 4 given with their respective component curves. See text for details.

by a scalar multiple of the measured laser pulse autocorrelation with an amplitude of 0.29. For $CHCl_3$, the time constants are 165 fs, 550 fs, and 2.0 ps with amplitudes of 0.192, 0.10, and 0.03, respectively, with a β_i value of 170 fs. For the intramolecular Raman contribution, $\beta_i = 20.2$ fs, corresponding to a frequency of 262 cm^{-1}, with a damping rate (τ_i) of 2.0 ps. The amplitude of the instantaneous component is 0.65. The significance of each specific parameter for the different liquids will be presented elsewhere [35]. At this time, we will concentrate on the general features that appear common to all liquids.

In both liquids, the ultrafast librational component accounts for a significant fraction of signal intensity at probe delays < 300 fs. Consequently, the theoretical curves are extremely sensitive to the τ_i and β_i parameters that determine the form of this response. In particular, for all liquids thus far investigated, the underdamped solution of (8) [(9)] accounts for the signal width and peak position of the ultrafast component, as well as the rapid decay following the signal maximum. Neither the diffusional result [11]–[13] nor the overdamped solution to (8) [(9)] can reproduce this short time behavior.

Any response describable by (10) is characterized by a frequency and a damping rate, and thus should have a corresponding band in the LS spectrum. For CS_2, with a β_i value of 150 fs and a damping rate of 140 fs, such a band would be expected at 35.4 cm^{-1} with a 37.9 cm^{-1} FWHM bandwidth and, in the spontaneous LS spectrum, should appear in the Rayleigh "wing." A stimulated Raman gain technique that is capable of observing near-zero-frequency resonances has revealed [37] a weak band in the low-frequency spectrum of liquid CS_2. This band, centered at 35 cm^{-1} with a bandwidth of 40 cm^{-1} FWHM, exhibits almost precisely the frequency and bandwidth extracted from our time domain measurements. This observation confirms the description of the ultrafast component

at room temperature in terms of a *strongly damped periodic motion*, and the absence of any such component in liquids composed of rare gas atoms or isotropic molecules implies that its origin lies in *molecular librational motion*.

This response is a bulk material resonance arising from the short-range structure of the liquid. In an OKE experiment utilizing ultrashort laser pulses, an ensemble of oscillators is coherently excited by the different Fourier components of the pulse (through a stimulated Raman process [10], [37]; cf. Section III-D). The damping rate $1/\tau_i$ of (10) is most likely associated with the *loss of coherence* of these oscillators and therefore is best referred to as a *dephasing rate*. The most probable origin of this dephasing is the dynamic nature of the local potential, arising from high-frequency density fluctuations correlated with the condensed phase "collision" frequency. This damping rate should therefore exhibit a strong dependence on temperature. We point out, at this time, the distinction between the librational motion discussed here and the "free-rotation" or inertial limit often invoked in discussion of LS and molecular dynamics data. Specifically, libration refers to the oscillatory motion of a molecule in the potential defined by its nearest neighbors and, as such, is a resonance phenomena. A "free rotation" between collisions will exhibit no such resonance. Preliminary discussions of the molecular motion in liquids attempted to describe the transient responses in terms of a nonresonant overdamped motion [13], [14], but the inadequacy of this overdamped description with regard to the ultrafast component is now evident.

The correspondence between our data and frequency domain data for this low-frequency mode, however, is readily available only for the case of neat CS_2 [37]. For nitrobenzene in particular, our data predict a low-frequency band associated with librational motion at 55.8 cm^{-1}, a much higher frequency than in the case of CS_2. Similar predictions concerning the low-frequency stimulated Raman gain spectrum can be made on the basis of our results for benzene, the monohalogenated benzene derivatives, and the chlorinated methanes [35]. Since this feature should be absent in the light scattering spectrum of any liquid composed of species possessing an isotropic linear polarizability, these conclusions may be tested against LS data on such liquids.

C. The Electronic Response and the Role of Coherence

In the preceding discussions, we have referred to the instantaneous signal contribution in terms of the purely electronic hyperpolarizability σ_{ijkl} of (2). However, it is necessary to consider the possible role of coherence effects in the detected signal near zero time delay when the pump and probe pulses are temporally as well as spatially overlapped. The dominant contribution to the nonlinear dielectric susceptibility responsible for the OKE is nonresonant and real; therefore, the reality of the heterodyne term in (1) requires the use of an out-of-phase local oscillator ($\hat{E}_{LO} \propto i\hat{E}_{probe}$). This may be understood follow-

ing a previous treatment of the laser-induced birefringence [23].

The laser-induced birefringence of the sample generates an electric field component phase shifted by 90° and polarized orthogonal to the input polarization of the probe field. In the four-wave mixing representation, the detected signal intensity $I(\tau)$ using a phase shifted local oscillator is given by [26]

$$I(\tau) = \gamma(\tau) + \rho_1(\tau) + \rho_2(\tau). \tag{11}$$

The $\rho_1(\tau)$ and $\rho_2(\tau)$ describe the "coherent" signal contribution observed when $|\tau| \leq \Delta t_{\text{pulse}}$, while $\gamma(\tau)$ describes the incoherent material response. The latter is independent of the spectral phase of the laser pulses and, for $|\tau| \geq \Delta t_{\text{pulse}}$, can be attributed soley to the correlation function of the linear molecular polarizabilities ($\langle \alpha_{ij}(t), \alpha_{kl}(0) \rangle$) as discussed in the previous sections. Explicitly,

$$\gamma(\tau) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |E_2(t - \tau)|^2 |E_1(t')|^2$$
$$\cdot R_{ijkl}^{\text{Re}}(t - t') \, dt' \, dt \tag{12a}$$

$$\rho_1(\tau) = \text{Re} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_2^*(t - \tau) E_1(t) E_1^*(t')$$
$$\cdot E_2(t' - \tau) R_{ijkl}^{\text{Re}}(t - t') \, dt' \, dt \tag{12b}$$

and

$$\rho_2(\tau) = \text{Im} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_2^*(t - \tau) E_1(t) E_1^*(t')$$
$$\cdot E_2(t' - \tau) R_{ijkl}^{\text{Im}}(t - t') \, dt' \, dt. \tag{12c}$$

The $E_2(t - \tau)$, $E_1(t)$ are the complex field amplitudes of the probe and pump waves, respectively, while $R_{ijkl}^{\text{Re}}(t - t')$ and $R_{ijkl}^{\text{Im}}(t - t')$ are the real and imaginary contributions to the nonlinear response function described earlier.

The discussion of [26a] applies to each signal contribution, except that the roles of the real and imaginary parts of $R_{ijkl}(t - t')$ in the integrands of (12) are interchanged. We note that the $\rho_{1,2}(\tau)$ terms are linear in $R_{ijkl}(t - t')$ and therefore contain contributions from both the instantaneous and noninstantaneous components [26a]. The notable aspects of these signal contributions are that for $\hat{E}_{LO} \propto i\hat{E}_{\text{probe}}$, the $\rho_1(\tau)$ and $\rho_2(\tau)$ terms are, respectively, symmetric and antisymmetric in the time delay (12). Conversely, when $\hat{E}_{LO} \propto \hat{E}_{\text{probe}}$ (the in-phase local oscillator), the real and imaginary parts of $R_{ijkl}(t - t')$ appear in $\rho_2(\tau)$ and $\rho_1(\tau)$, $\gamma(\tau)$, respectively, and the symmetries are effectively reversed. In this case, the discussion of [26a] applies rigorously.

In the case $\hat{E}_{LO} \propto i\hat{E}_{\text{probe}}$ (12), the contribution of the purely electronic hyperpolarizability σ_{ijkl} to both the $\gamma(\tau)$ and $\rho_1(\tau)$ terms will be significant [26b]. In particular, to the extent that the σ_{ijkl} may be represented by a product of delta functions [3], its contribution to $\gamma(\tau)$ and $\rho_1(\tau)$ will be equal, each being a scalar multiple of the intensity

autocorrelation function of the laser $G_0^{(2)}(\tau)$ and independent of the phases of the electric field envelopes of the pump and probe pulses [28b]. We expect the antisymmetric $\rho_2(\tau)$ term to be small since the laser frequency is far from any molecular resonance ($R_{ijkl}^{\text{Im}} \sim 0$) and our laser pulses are nearly transform limited [26a]. Thus, $\gamma(\tau)$ is always $\geq \rho_1(\tau)$ for $|\tau| \leq \Delta t_{\text{pulse}}$. It is therefore inappropriate to attribute the signal at $|\tau| \leq \Delta t_{\text{pulse}}$ purely to mutual scattering of the pump and probe pulses off a laser-induced phase or amplitude grating (the $\rho_1(\tau)$ and $\rho_2(\tau)$ terms, respectively).

In order to investigate the nature of the signal at time delays within the laser pulsewidth, the OKE transients have been detected using both in-phase and out-of-phase local oscillators derived from the probe beam. The upper trace of Fig. 6 gives the OKE signal for neat benzene detected with an out-of-phase local oscillator of intensity $50 \times$ that of the homodyne signal. The time constant in the exponentially decaying tail of the response ($\tau > 1.5$ ps) is two times that measured in the tail of the homodyne OKE, as is expected [38] for a signal linear in the response function $R_{ijkl}(t)$. The detected signal magnitude is $> 12 \times$ that of the homodyne experiment, while the use of an in-phase local oscillator of equal intensity results in an OKE signal for neat benzene of the same magnitude as the homodyne signal, confirming that the real part of the nonlinear susceptibility dominates the response. This in-phase heterodyne signal (Fig. 6, lower) exhibits a small antisymmetric signal component near zero time delay corresponding to the $\rho_2(\tau)$ term of (12c). We have investigated the OKE signals with varying amounts of phase noise in the laser pulses (deviations from transform limit) and have verified that the antisymmetric component in the in-phase experiment, in fact, can become quite large when the pulse deviates significantly from the transform limited time–bandwidth product. Conversely, the OKE signal obtained with out-of-phase detection is relatively insensitive to the coherence properties of the laser pulses used.

We have noted a dramatic pulsewidth dependence in the amplitude of the instantaneous signal contribution of all liquids studied. This dependence does not appear explicable in terms of coherence effects alone. When laser pulses of FWHM > 200 fs are used, the OKE transient does not appear to exhibit a signal component that follows the pulse autocorrelation [12]. Previous OKE experiments on liquid CS_2, using mutually coherent 150 fs FWHM laser pulses in an identical detection scheme [7], failed to reveal any symmetric, instantaneous signal component corresponding to the $\rho_1(\tau)$ term. In this regard, a method for removing the contribution of the $\rho_1(\tau)$ term from the detected heterodyne signal is necessary in order to independently observe the instantaneous signal contribution due to the $\gamma(\tau)$ term. When nondegenerate probe pulses are employed, the symmetric grating term $\rho_1(\tau)$ vanishes [38] and any instantaneous signal component must arise from the $\gamma(\tau)$ term. Such experiments are in progress and, in conjunction with the heterodyne experiments of Fig. 6 which also have been completed for the chlorinated meth-
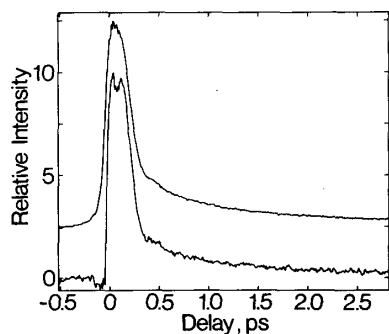
Fig. 6. Optical Kerr signals for neat benzene detected with out-of-phase (upper) and in-phase (lower) local oscillators. The lower trace has been expanded six times for clarity.

Fig. 7. Optical Kerr signal for neat CCl_4 shown together with theoretical best fit generated in accordance to the model described in the text. Inset is expanded three times vertically.

anes, monohalogenated benzenes, and CS_2, will be the subject of a forthcoming paper [39].

D. Resonantly Driven Intramolecular Vibrations

In Section III-B, we discussed the contribution of bulk material resonances which are *intermolecular* in origin to the observed OKE relaxation. In addition, we have observed oscillations arising from *intramolecular* normal mode vibrations in the OKE signals of several methane derivatives. In particular, these oscillations are evident in the data of CCl_4 and $CHCl_3$ given in Fig. 2.

The equation of motion [40] for a resonantly driven generalized harmonic vibrational coordinate $Q(t)$ is

$$\frac{\partial^2 Q_i(t)}{\partial^2 t} + \frac{2}{\tau_i}\frac{\partial Q_i(t)}{\partial t} + \omega_{oi}^2 Q_i(t) = F(t) \qquad (13)$$

where $F(t)$ is the generalized forcing function into which the intensity profile of the laser pulse and all the relevant constants associated with the strength of the Raman transition are absorbed, and the explicit frequency dependence of the pulse is suppressed. ω_{oi} is the undamped characteristic frequency of the oscillator and τ_i is the damping rate. The underdamped solution to (13) for an arbitrarily shaped driving function is

$$Q_i(t) = \int_{-\infty}^{t} \sin\left[\omega_i(t - t')\right]$$
$$\cdot \exp\left[-(t - t')/\tau_i\right] F(t')\, dt' \qquad (14)$$

with the resulting oscillating polarization density [40], [41] given by

$$P_{Qi}(t) = \frac{\partial \alpha}{\partial Q_i} Q_i(t) \hat{E}. \qquad (15)$$

When the system is driven by an ultrashort laser pulse, any material vibrations having a period greater than temporal width of the laser pulse may be resonantly (and coherently) excited by the different Fourier components of that pulse through a stimulated Raman process. Equation (15) predicts an oscillating polarization density whose time dependence is given by that of (14). In an OKE experiment, this oscillating polarization density is detected
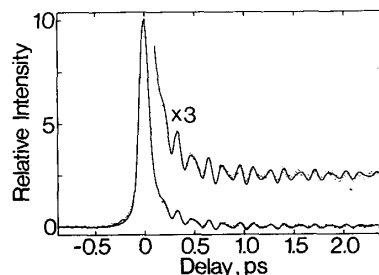
through its effect on the polarization of a second variably delayed probe pulse. Hence, the current experiment is a time-resolved analog of Raman-induced Kerr effect spectroscopy (RIKES [42]). In every case, the observed frequencies correspond precisely to those of the lowest frequency Raman active modes [43], and thus represent the direct observation of the temporal evolution of these intramolecular vibrational coordinates.

The OKE signal for neat CCl_4 induced by 75 fs FWHM laser pulses is reproduced in Fig. 7. The curve is dominated by a prominent central peak that closely follows the laser pulse autocorrelation with the oscillatory nature clearly evident at longer times. A Fourier transform of the data of Fig. 6 gives a frequency spectrum with two distinct peaks centered at 218 and 314 cm^{-1}. These frequencies correspond precisely to those of the ν_2 and ν_4 modes of the CCl_4 molecule [43]. The solid curve of Fig. 6 is obtained by the procedure outlined in previous sections; however, because CCl_4 possesses an isotropic polarizability, all relaxations associated with orientational motion (including librations) are absent. The net response consists of a sum of four terms in (6): an instantaneous signal component represented by the laser pulse autocorrelation with an amplitude of 0.80, two resonantly driven vibrational terms whose time dependence is given by (14), and finally, a small rapidly decaying component exhibiting an ~ 200 fs time constant is required to account for the asymmetry of the central feature at positive delay. This latter component appears to be analogous to the exponential relaxation observed in the Kerr responses of a diatomic molecular and rare gas atomic liquids at low temperatures, as was discussed earlier. The oscillatory portion of this curve is very well described by the superposition of these two sinusoidals, with the best fit obtained using a damping rate of 1.30 ps for each. Thus, the oscillatory behavior in the Kerr response of CCl_4 represents a direct observation of the independent temporal evolution of the ν_2 and ν_4 normal vibrational coordinates of CCl_4, coherently excited by the ultrashort laser pulse.

Several recent studies [44]–[46] have revealed oscillatory behavior in time domain experiments that are qualitatively similar to those reported here. These experiments have been performed on both absorbing [44] and nonabsorbing [45]–[46] media with the specific technique and

measured quantity different in each case. Our technique, utilizing heterodyne detection, is linear in the $R_{ijkl}(t)$ and thus measures directly the temporal evolution and dephasing rate of the accessible vibrational modes, with no contribution from cross terms that would arise from a quadratic dependence on the impulse response function.

IV. CONCLUSIONS

We have experimentally resolved the optical Kerr signal of several liquids into dynamically distinct responses. Four such responses are evident in the OKE of every liquid investigated that is composed of molecules possessing a permanent polarizability anisotropy. Of these, one is associated with the electronic hyperpolarizability and is instantaneous on the time scale of the laser pulse, with the remaining three arising from intermolecular nuclear motions.

Of the nuclear responses, two are absent in liquids composed of atoms or isotropic molecules and, for symmetry reasons, must be associated with orientational motions of the molecules. The slower, exponentially decaying component ($\tau_{1/e} < 1$ ps) can be unambiguously identified with the orientational diffusion process. The ultrafast component ($\tau_{1/e} < 170$ fs) exhibits a rapidly damped oscillatory behavior that is characteristic of librational motion. The correspondence of our experimental data at probe delays <200 fs to a simple model for the librational motion of a molecule in a locally harmonic potential is striking. We recognize that this librational motion is Raman active [37] and indicative of local structure in the liquid [47] on the time scale of ~200 fs.

The third, noninstantaneous Kerr response exhibits an intermediate time constant ($\tau_{1/e} = 300$–600 fs) and is believed to correlate with the small amplitude, exponentially decaying component present in the OKE signals of rare gas atomic liquids, as well as that in liquid CCl_4. Isolated atomic species possess a rigorously isotropic linear polarizability. Any nonresonant, noninstantaneous response necessarily arises from the interatomic interactions that break this symmetry. The exponentially decaying, intermediate lifetime component observed in the OKE of the anisotropic molecular liquids, as well as the exponential component present in the OKE of liquid CCl_4, is therefore associated with this "interaction-induced" anisotropy.

Finally, every liquid investigated exhibits a pronounced "instantaneous" response that follows the intensity profile of the laser pulse autocorrelation. This response, in general, is composed of contributions from the purely electronic hyperpolarizability and from "coherence" effects that arise from the scattering off laser-induced gratings. While the current results cannot quantitatively ascertain the relative importance of these two contributions, several considerations indicate that the primary contribution to the observed signal near $\tau = 0$ is the incoherent contribution of the electronic hyperpolarizability.

The experimental OKE signals are treated as a super-

position of the various individual component responses with the overall response being well described in terms of a simple conceptual model that accounts for the observed inertial lag of the three nuclear responses. The temporal evolution of any coherently excited intramolecular Raman modes (accessible through the bandwidth of our femtosecond dye laser) are treated as independently evolving dynamical responses within the harmonic approximation generally applied to molecular normal-mode vibrations.

This simple treatment, in which no coupling between the various dynamical responses is considered, is found to be generally applicable to all liquids investigated to date and provides a useful working description of the various molecular motions that occur on the subpicosecond time scale. The similarity of the dynamical responses of these simple molecular liquids is striking, and indicates that the equations of motion for molecules in these liquids adhere to the principle of corresponding states, as has been noted previously [4], [48]. The differences in the component amplitudes and time constants provide important insights into the local intermolecular potentials, the microscopic friction, and the interrelationship between these parameters and the ultrafast dynamics. We have treated the case of molecular motion in an harmonic potential for the sake of simplicity and recognize that intermolecular potentials are, in general, not harmonic. A detailed comparison of the current experimental results to molecular dynamics simulations should prove useful in evaluating the dynamical consequences of the detailed intermolecular potential. In a forthcoming paper [49], we discuss these considerations with specific regard for the CS_2 system and the behavior of the different responses upon dilution in inert alkane solvents.

Note Added in Proof: The analysis of the Raman active intermolecular librational response recently has been extended to include the effects of inhomogeneous broadening that arise from the distribution of molecular environments in the disordered liquid systems [49], [50]. If the inhomogeneity is described by a Gaussian distribution of frequencies, the response function in the integrand of (10) will be of the form

$$\exp\left\{-\left[\alpha_i(t - t')\right]^2/2\right\} \cdot \exp\left[-(t - t')/\tau_i\right]$$
$$\cdot \sin\left[(t - t')/\beta_i\right]$$

where α_i is related to the width of the inhomogeneous distribution. Destructive interference between the different frequency components of the coherently excited ensemble of oscillators provides the dominant contribution to the decay of the detected signal; however, the homogeneous (exponential) damping term remains significant and should not be neglected. The effect of inhomogeneous broadening in the damping of the librational response recently has been recognized by others [51].

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