Microscopic dynamics in simple liquids by subpicosecond birefringences

B. I. Greene, P. A. Fleury, H. L. Carter, Jr., and R. C. Farrow

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 28 July 1983)

The transient birefringent responses of three simple liquids (Xe, Ar, and O_2) have been measured using subpicosecond optical pulses. In addition to molecular reorientational dynamic contributions to the birefringence (in O_2), we have directly observed the subpicosecond dynamics arising from electronic and intermolecular interactions (in Xe and Ar). Our results in Xe and Ar constitute the first unambiguous observations of such intermolecular processes in real time. The theoretical connections between such direct observations and the previous indirect, light-scattering studies in the frequency domain are explicated. The importance of intermolecular processes in the subpicosecond dynamics of all dense fluids is noted.

The dynamics of fluid systems for times below 1 ps have traditionally been accessible experimentally only by indirect measurements in the frequency domain, i.e., infrared absorption, or inelastic light, or neutron scattering. In simple liquids such as the rare gases only inelastic light scattering has proven sensitive to the intermolecular interaction processes which exhibit characteristic frequencies in the $10^{12}-10^{13}$-Hz range. For anisotropic molecules, orientational processes are typically much slower and have been successfully examined in both the frequency and time domain, using picosecond optical pulses for the latter.

Recently stable optical pulses shorter than 0.1 ps have become available[1] and have revealed an anomalous transient birefringence response[2-4] in liquid CS_2 with a characteristic relaxation time of approximately 0.28 ps. The similarity of this time to that expected for the duration of intermolecular collisions in a room-temperature dense fluid raised the possibility that intermolecular interactions were responsible in that case.[3] This suggestion was necessarily speculative for CS_2, however, owing to the very large molecular reorientation contribution to its transient birefringence.

We report here the first subpicosecond transient birefringence data on monatomic liquids (Ar and Xe). These results directly demonstrate the purely "intermolecular" contributions to the dynamic anisotropic polarizability. This mechanism is expected to contribute to the transient response of all dense fluids, but has heretofore been ignored in analysis of pulsed optical experiments. We also present subpicosecond birefringence measurements on the simple diatomic liquid O_2, which exhibits substantial and rapid molecular reorientation dynamics, and shows evidence for intermolecular contributions as well.

Dynamics of all three of these simple cryogenic liquids have been studied previously by inelastic light scattering.[5-7] One purpose of the present work has been to elucidate the relationship between the transient birefringent response and the depolarized light scattering spectrum. We shall show that although in principle the two types of experiment measure the same physical processes, direct comparisons of spectral line shapes and temporal birefringence profiles are straightforward only in very limiting situations.

Subpicosecond transient birefringence measurements were performed as previously described.[4] Briefly, pulses 1.8×10^{-13} s full width at half maximum (FWHM) in duration as measured by autocorrelation, centered at 625 nm, are derived from a passively mode-locked colliding-pulsed mode-locked (CPM) dye laser.[1] These pulses are subsequently amplified at a repetition rate of 10 Hz utilizing a four-stage Nd:YAG (yttrium aluminum garnet) pumped-dye-laser amplifier.[8]

The pulses are divided at a beam splitter and sent down separate optical paths. A microprocessor controlled variable delay line is introduced into one optical path. One beam (probe) is attenuated by a factor of 30 relative to the other (pump). The pump and probe pulses are linearly polarized with their polarizations oriented at 45° with respect to each other. The two beams are directed noncollinearly through a 40-cm focal length lens to overlap spatially in the sample. The pump beam is subsequently blocked, while the probe beam is passed through a quarter-wave plate and a polarization analyzer. Signals are detected as probe pulse transmission through the polarization analyzer as a function of time delay between the pump and probe pulses.

Pump-pulse intensities are adjusted to be below the threshold for stimulated scattering or continuum generation for each liquid. Measurements on Xe and O_2 are performed at roughly 10^9 W/cm^2 while the Ar measurements utilize peak power pulses of roughly 10^{10} W/cm^2.

Liquid samples are condensed into a 3-cm path length cell from the highest quality commercially available gases.[9] Temperatures are regulated to be within 0.5 deg of the normal boiling points of Ar, Xe, and O_2; 87.5, 166, and 90 K, respectively.

Figure 1 shows both the logarithmic and linear birefringent response of liquid Xe convoluted with the experimental probe autocorrelation function (dotted curve). Two contributions to the response are evident: one is indistinguishable from the experimental resolution and the
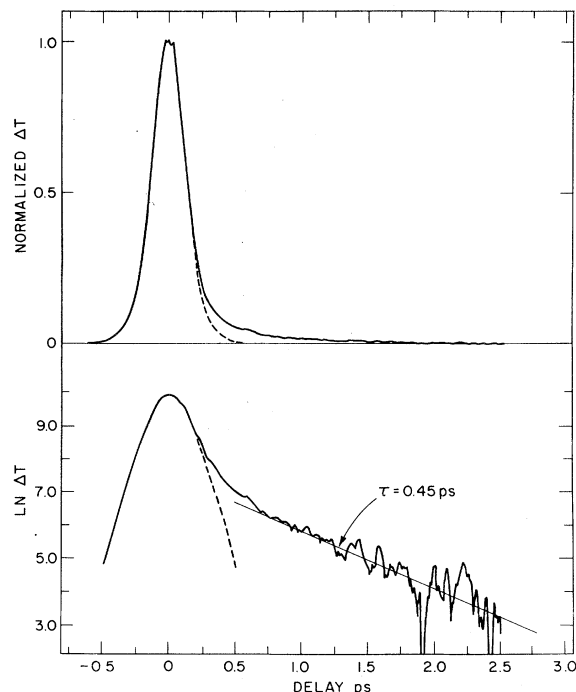
FIG. 1. Liquid xenon: Normalized incremental transmission ΔT vs probe pulse delay (top). Semilogarithmic plot of data (bottom). The instrumental response is shown as a dashed line. A single exponential fit yields the 0.45-ps decay shown.

second shows a characteristic relaxation time of 0.45 ps. As argued below, the former is attributed to electronic polarizability whose characteristic response time is much faster than τ_{pump}, while the latter arises from intermolecular interactions which have been shown to cause a depolarized exponential wing in the light scattering spectrum[6] of characteristic frequency 14 cm^{-1}.

Figure 2 shows data for liquid argon, which is qualitatively very similar to Xe, although the effect is approximately 30 times smaller. Note that for both Ar and Xe the rising edge of the birefringent response is indistinguishable in shape from the instrumental response. The
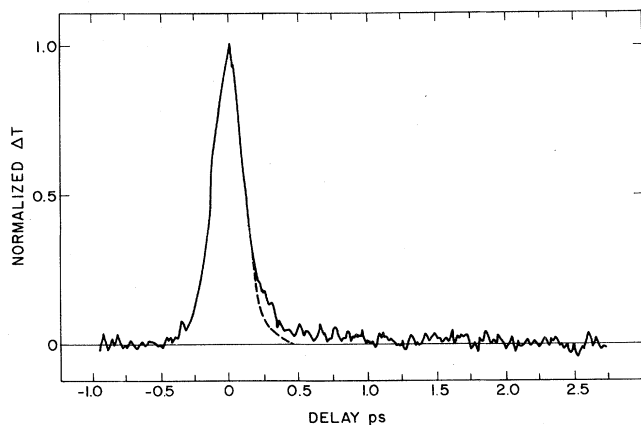
result for O_2 is markedly different in several respects from the monatomic fluids.

First a clearly asymmetric birefringent response is observed in O_2 (Fig. 3). The rise of the signal is seen to occur more rapidly than its subsequent decay. This is to be expected as the medium's dominant response time becomes comparable to or longer than the laser pulse width. The sample response thereby reflects an integration of the pump pulse energy. By numerical modeling, a rough fit to the data yields a short-time exponential decay constant of ~ 0.2 ps. Although a long-time tail is evident (>1.0 ps) we have not been able to fit its behavior quantitatively.

These times are close to those extracted from depolarized light scattering spectra[7] which exhibit two characteristic relaxation frequencies. The high-frequency tail exhibits a characteristic frequency of 30—40 cm^{-1} (~ 0.15 ps) while the low-frequency central peak shows a half-width of ~ 5—7 cm^{-1} (~ 1 ps). Thus both the light scattering spectra and our time-dependent birefringence data are consistent with two time domains in the dynamic response of liquid oxygen. In the simplest approximations[6] the characteristic times for molecular reorientation (τ_R) and intermolecular interactions (τ_I) are given by

$$\tau_R = \frac{\eta V}{kT} , \qquad (1)$$

$$\tau_I^{-1} = 3 \left[\frac{E}{m\sigma^2} \right]^{1/2} \left[\frac{kT}{E} \right]^{1/2} \left[1 + \left[\frac{2\sigma^3\rho}{m} \right]^2 \right] = \omega_I , \qquad (2)$$

where η is the shear viscosity, V the molecular volume, ρ the mass density, m the molecular mass, σ and E the Lennard-Jones length and potential energy parameters, respectively. Using the parameter values for liquid O_2 from Ref. 11, we estimate $\tau_R \simeq 2.1$ ps and $\tau_I \simeq 0.19$ ps.

However, despite the close coincidence of these times with those observed in our experiments we do not believe that it is correct to simply associate the shorter with intermolecular interactions and the longer with molecular reorientations. As recent molecular-dynamics[10,11] simula-
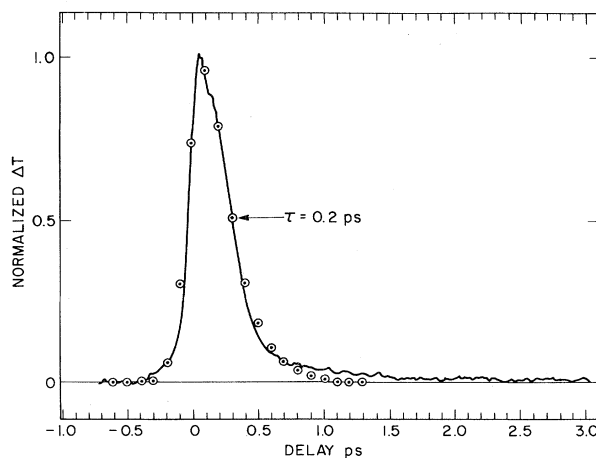

FIG. 2. Liquid argon: Normalized incremental transmission ΔT vs probe pulse delay. The instrumental response is shown as a dashed line.

FIG. 3. Liquid oxygen: Normalized incremental transmission ΔT vs probe pulse delay. A numerically modeled response assuming 0.18-ps Gaussian laser pulses and a 0.20-ps single exponential decay is indicated by circles (○).

tions on liquid O_2 have shown, both time scales are evident in both the "reorientational" and the "collision-induced" correlation functions. That is, the intermolecular interactions are manifest in the reorientation dynamics and vice versa. Therefore, the clear appearance of two well-separated time scales in both the birefringence and the light scattering experiments does not correspond to a clearly separable identification of the microscopic processes responsible.

In order to set the stage for comparing light scattering and transient birefringent results we shall expand below the earlier results of Hellwarth,[12] Ho and Alfano,[13] and Sala and Richardson.[14] The appropriate expression for the transient transmission of a Kerr gate in the configuration used in our experiments is

$$T(t)\alpha \int_{-\infty}^{\infty} I_s(t'-t)[1+\sin\phi(t')]dt' , \qquad (3)$$

where ϕ is the phase shift introduced by the nonlinear birefringence and $I_s(t)$ is the time-dependent probe pulse intensity.[15] In the usual crossed polarizer configuration $(1+\sin\phi)$ is replaced by $\sin^2\frac{1}{2}\phi$ in (3).[16]

The physical processes usually considered to contribute to $\phi(t)$ are (a) electronic and (b) molecular reorientational anisotropic polarizabilities. The former is typically regarded as instantaneously responsive, relative to pump or probe pulse durations, and the latter is usually assumed to relax with an exponential (Debye-Stokes-Einstein) time dependence characterized by Eq. (1). More generally in-

termolecular contributions should, of course, be included as well.

Formally we may express these as

$$\phi(t)=\frac{L}{c}\omega_1\delta n(t) , \qquad (4)$$

where ω_1 is the optical field frequency, L the sample length, and c the velocity of light. Thus

$$\delta n(t)=\sum_i \int_{-\infty}^{t} I_p(t')r_{ijkl}^i(t-t')dt' , \qquad (5)$$

where I_p is the pump pulse intensity and $r_{ijkl}^i(t)$ is the contribution to the third-order nonlinear response function from the ith process.[12] For example $r_{ijkl}(t)$ for molecular reorientation is usually expressed[13] as $r^R(t)$ $=(n_2^R/\tau_R)e^{-t/\tau_R}$, and for electronic response as $r^e(t)=n_2^e\delta(t)$. More generally $r_{ijkl}(t)$ is expressible as[12]

$$r_{ijkl}(t)=\frac{iV}{2\hbar}\Gamma(t)\langle[X_{ij}(t),x_{jk}(0)]\rangle , \qquad (6)$$

where $\Gamma(t)$ is the unit step function, [ ] is the commutator, and $\langle\ \rangle$ denotes the ensemble average. As Hellwarth has shown[12] the Fourier transform of $r_{ijkl}(t)$ is directly related to the spectrum of scattered light $S(\omega)$:

$$S(\omega)=\mathrm{Im} r_{ijkl}(\omega) . \qquad (7)$$

Combining Eqs. (3)—(6) gives

$$T(t)= \int_{-\infty}^{\infty} I_s(t-t') \left\{ 1+\sin\left[\left[\frac{\omega L}{c} \right] \sum_i \int_{-\infty}^{t'} I_p(t'')r_{ijkl}^i(t'-t'')dt'' \right] \right\}dt' . \qquad (8)$$

Comparison of Eqs. (7) and (8) makes it clear that the relation between the transient birefringent response and the light scattering spectrum is quite complex in the general case. Of course the same caveats regarding identification of time scales with specific microscopic processes discussed following Eq. (2) apply to light scattering.

In particular extraction of characteristic response times from measured $T(t)$ is simple only in a few limiting situations. Indeed, as shown convincingly by Sala and Richardson,[14] even when the electronic response is instantaneous and the molecular reorientational is described by simple exponential relaxation τ_R, the shape of $T(t)$ can vary markedly depending on the relative sizes of n_2^e and n_2^R as well as τ_p/τ_R (the ratio of pulse width to reorientational relaxation time). The extraction of line-shape information from $T(t)$ is even more difficult. Because the sample's dynamic information, represented by $r_{ijkl}(t)$ is contained within the kernel of the integral in Eq. (8), the best one can do is to assume forms for $r(t)$ and numerically integrate Eq. (8) for comparison with the experimental $T(t)$. Alternatively, if light scattering spectra are available over the entire frequency regime, Eq. (7) can be Fourier transformed to give $r(t)$ from which $T(t)$ could be obtained for comparison with direct time measurements.

In the case of the liquid rare gases, light scattering spectra may be quantitatively described by

$$\mathrm{Im} r(\omega)=e^{-\omega/\omega_I} , \qquad (9)$$

where values ω_I are 14 cm^{-1} for xenon[5] and 24 cm^{-1} for argon.[6] This corresponds to a Lorentzian (rather than exponential) dependence of $r_{ijkl}(t)$ on time. The observed $T(t)$ for argon and xenon should contain two terms arising from

$$\int_{-\infty}^{t'} I_p(t'') \left[n_2^e\delta(t'-t'')+n_2^I\omega_I \frac{1+i(t'-t'')\omega_I}{1+(t'-t'')^2\omega_I^2} \right]dt'' . \qquad (10)$$

Although as Hellwarth has argued the ratio n_2^e/n_2^I can be obtained from frequency integrals of Raman spectra, we do not have at present quantitatively reliable values for these ratios. Furthermore, even for xenon which has the largest signal for $T(t)$ the experimental signal-to-noise ratio (in Fig. 1) is not sufficient to provide a quantitative test of the temporal line shape. The characteristic time scale of 0.45 ps evident in Fig. 1 corresponds to a frequency of 11.8 cm^{-1}. This is quite close to the measured value $\omega_I=14$ cm^{-1} obtained by inelastic light scattering,[6] and

provides strong support for the identification of intermolecular polarizability as the physical mechanism responsible for the "long-time" response in $T(t)$ for xenon. From our transient birefringent data (0.18-ps pump pulse) we determine the ratio of n_2^e/n_2^I in xenon to be ~ 9.5.

In conclusion we have presented the first direct observations in real time of intermolecular processes in simple dense fluids. A formalism for relating dynamic physical processes to observed transient birefringent response has been elucidated and compared to light scattering spectral information. In liquid argon and xenon these comparisons verify the dominant role of intermolecular interaction dynamics on transient optical response. In liquid oxygen even though two time scales are clearly observed the contributions from intermolecular interaction and individual molecular reorientation could not be separately determined. Nevertheless, the ubiquitous nature of intermolecular processes in the short-time dynamics of both monatomic and polyatomic fluids has been clearly demonstrated and must be taken into account in future studies of such systems.

[1]R. L. Fork, B. I. Greene, and C. V. Shank, Appl. Phys. Lett. 38, 671 (1981).

[2]J. M. Halbout and C. L. Tang, Appl. Phys. Lett. 40, 765 (1982).

[3]B. I. Greene and R. C. Farrow, J. Chem. Phys. 70, 4779 (1982).

[4]B. I. Greene and R. C. Farrow, Chem. Phys. Lett. 98, 273 (1983).

[5]P. A. Fleury, W. B. Daniels, and J. M. Worlock, Phys. Rev. Lett. 27, 1493 (1971).

[6]P. A. Fleury, J. M. Worlock, and H. L. Carter, Phys. Rev. Lett. 30, 591 (1973).

[7]J. Bruining and J. H. R. Clarke, Chem. Phys. Lett. 31, 355 (1975).

[8]R. L. Fork, C. V. Shank, and R. T. Yen, Appl. Phys. Lett. 41, 223 (1982).

[9]Mass spectral analysis of our xenon samples indicated upper limits on oxygen and nitrogen concentrations of 0.01%.

[10]B. M. Ladanyi, J. Chem. Phys. 78, 2189 (1983).

[11]D. Frenkel and J. P. McTague, J. Chem. Phys. 72, 2801 (1980).

[12]R. W. Hellwarth, Progress in Quantum Electronics (Pergamon, New York, 1977), Vol. 5, pp. 1—68.

[13]P. P. Ho and R. R. Alfano, Phys. Rev. A 20, 2170 (1979).

[14]K. Sala and M. C. Richardson, Phys. Rev. A 12, 1036 (1975).

[15]E. P. Ippen and C. V. Shank, Appl. Phys. Lett. 26, 92 (1975).

[16]E. E. Wahlstrom, Optical Crystallography, 5th ed. (Wiley, New York, 1979), p. 169.