Density-induced heterodyne-amplified rotational dynamics: a new technique for studying orientational relaxation

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Abstract

A new time-domain method, density-induced heterodyne-amplified rotational dynamics (DIHARD), for studying the orientational relaxation of pure or mixed viscous liquids is described. Extremely weak absorption of an excitation pulse produces a density perturbation like that in a thermal lensing experiment. Through translational–rotational coupling, an orientational anisotropy is produced, which is heterodyne detected with a weak probe field. The DIHARD signal appears with the time for the velocity of sound to cross the excitation spot size and decays with the reorientational dynamics of the sample. DIHARD can provide data in situations where laser-excited optical Kerr experiments are difficult to perform. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The orientational relaxation of molecules has been studied extensively to obtain an understanding of dynamics in liquids. Many methods have been used, including NMR [1], light scattering [2], fluorescence depolarization [2], dielectric spectroscopy [3], and optical Kerr effect (OKE) experiments [4]. In this Letter, a new time-domain method, density-induced heterodyne amplified rotational dynamics (DI-HARD), is described. DIHARD is useful in viscous liquids in which laser-induced OKE experiments can fail. The experimental setup is virtually identical to a heterodyne-detected OKE experiment [5], and, therefore, DIHARD can be used to supplement OKE experiments in viscous liquids.

In a DIHARD experiment, a very small fraction of a short excitation pulse is absorbed by the sample, creating a small local temperature increase. The sudden heating launches an acoustic disturbance, which propagates radially outward from the heated spot at the velocity of sound. Once the acoustic disturbance has left the excitation spot, a small decrease in density remains. The spot of decreased density lasts for a time determined by the liquid's thermal conductivity and the spot size. This density change is well known in the context of thermal lensing experiments [6] and has been used to measure extremely weak absorptions as small as 10^{-7} [7].

The density decrease results from a net outward flow of molecules from the heated region. The flow is accompanied by a spatial velocity gradient. A velocity gradient will produce molecular orientational alignment of asymmetrical molecules [8]. This is in essence translational–rotational coupling. The

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resulting orientational anisotropy generates a birefringence, which can be heterodyne detected using a probe beam in the same manner as heterodyne detection of orientational anisotropy induced by the OKE [9]. Creating an optical birefringence through a stress, such as the velocity gradient, has been observed in numerous other contexts, e.g., in flows of viscoelastic fluids [10], in polymers [9], in liquid crystals [11], in glasses [12], and in crystals [13]. While ultrasonic acoustic experiments have been used to measure orientational relaxation [14], this is the first time that the liquid-state translational–rotational coupling effect has been incorporated into a direct time-domain measurement and heterodyne detected.

In the DIHARD experiment, the nature of the observed signal depends on the location of the probe beam relative to the excitation spot. If the probe is placed precisely in the center of the excitation spot, no signal is observed because the molecular alignment is radially symmetric (no orientational anisotropy). If the small probe spot is placed within the excitation spot, but, off center, the signal grows as the acoustic disturbances propagates out of the excitation spot leaving behind the non-propagating density change. The signal then decays with the orientational relaxation dynamics of the sample. If the probe beam is placed well outside of the excitation spot, the signal grows and then decays as the acoustic disturbances passes through the probe spot. Outside the excitation spot, there is no long-lived orientational anisotropy because there is no long-lived density change. The long-lived orientational anisotropy that exists within the excitation spot makes DIHARD distinct from acoustic measurements.

With the probe located within the excitation spot but off center, a substantial long-lived DIHARD signal will be observed if the orientational relaxation time is slow compared to the timescale for the acoustic disturbance to propagate out of the excitation spot. This timescale is also the intrinsic response time of the technique since the signal builds up on this timescale. By making the excitation spot size small (20 μm), the timescale can be 10 ns. Thus, DIHARD is useful for studying relatively slow orientational relaxation. Transient grating OKE (TG–OKE) and heterodyne-detected OKE (HD–OKE) experiments can work well on femtosecond, picosecond, and nanosecond timescales [15]. Like OKE

experiments, DIHARD is sensitive to all contributions to the macroscopic anisotropic polarizability induced in the sample by the excitation process, e.g., contributions from multiparticle polarizability. Given the long timescale of the DIHARD measurement, it is expected that the signal arises virtually exclusively from single particle orientational relaxation.

The OKE mechanism for inducing an anisotropy differs depending on whether the excitation pulse is short (large bandwidth) or long (small bandwidth) [5]. For a short pulse, ~ 100 fs, stimulated Raman scattering excites an anisotropic orientational distribution of librations that add to the isotropic thermally excited librations. The librations damp and leave a residual anisotropy because the ensemble average molecular orientation after damping is no longer isotropic. The residual anisotropy decays by orientational relaxation but, there is little amplitude in very slow components. If the pulse is long, ~ 100 ps, the bandwidth is too narrow to excite librations by stimulated Raman scattering, and the anisotropy develops because the $\vec{E}$-field skews the thermal molecular orientational random walk. There is little amplitude developed in relaxation components that are much longer than the pulse duration.

In contrast to OKE experiments, DIHARD produces orientational anisotropy mechanically. It does not depend on stimulated Raman scattering or the intrinsic thermal motions of the sample. Therefore, it is able to generate substantial amplitude in slowly decaying components of orientational relaxation. It is not necessary to use long, very high energy pulses or to use fast switching of high DC voltages to perform time-domain studies of long timescale processes. It is possible to study slow relaxation using the same short excitation pulses and almost the same HD–OKE experimental setups that are used to study fast orientational relaxation.

2. Experimental procedures

The DIHARD experimental setup is basically identical to the experimental setup for a HD–OKE experiment. Since the excitation pulse can produce both the OKE and DIHARD effects, there is an addition to the system which permits either the HD–OKE or the DIHARD signals to be detected sepa-
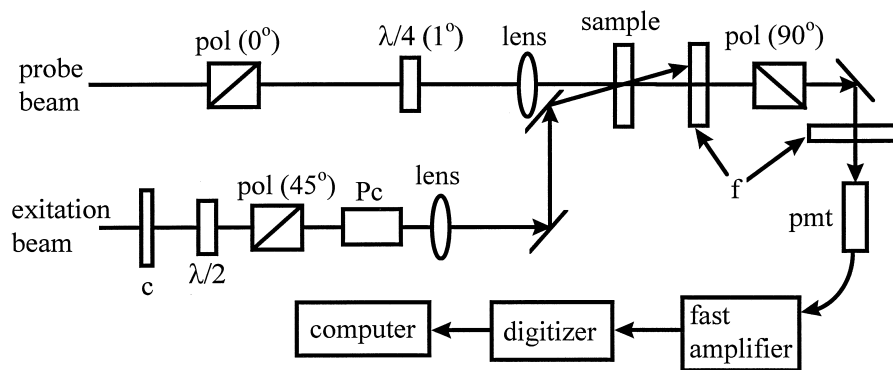
Fig. 1. The experimental setup to perform DIHARD and HD–OKE experiments. pol = polarizer; c = chopper; Pc = Pockel's cell; f = filter; pmt = photomultiplier tube; $\lambda/4$ = quarter-wave plate; $\lambda/2$ = half-wave plate. The probe beam is from a 10 mW 635 nm diode laser. The excitation beam is composed of 100 ps, 50 μJ, 1.06 μm pulses at 1 kHz (or lower) repetition rate from a mode-locked, Q-switched, cavity dumped, Nd:YAG laser.

rately. The experimental setup is shown schematically in Fig. 1.

A 100 ps duration 1.06 μm excitation pulse is produced by a mode-locked Q-switched cavity dumped Nd:YAG laser, which can deliver energies in excess of 1 mJ/pulse at repetition rates of 1 kHz or lower [16]. The excitation pulse is attenuated to produce ∼ 50 μJ at the sample and has a 300 μm spot size. Higher intensities caused a variety of deleterious effects. The excitation beam polarization is at an angle of 45° relative to the probe beam. The excitation beam passes through a Pockel's cell. Switching the voltage of the Pockel's cell (V_{off} to V_{on}) rotates the excitation polarization by 90° ($+45°$ to $-45°$), while still leaving it at a 45° angle relative to the probe beam. The excitation beam is also chopped at half the laser repetition rate to permit noise reduction by subtracting shots with and without the excitation pulse.

A cw beam at 635 nm with 10 mW of power from a diode laser is used as the probe. The probe beam passes through a polarizer oriented at 0° (y axis) and then through a quarter-wave plate at 1° to create a beam with a weak phase-delayed component (x axis), which functions as the local oscillator for heterodyne detection [4]. The probe beam is focused to 150 μm and crossed with the excitation beam at a small angle ($\sim 3°$). The probe then passes through the detection polarizer oriented at 90°. A 1.06 μm absorbing filter and a 635 nm interference transmission filter block stray light from entering the fast photomultiplier tube

(Hamamatsu Model R5600-01) used to detect the signal. The phototube output is pre-amplified using a high-speed amplifier (SRS model #SR240) and digitized by a transient digitizer (EG&G model 9846), which has a maximum resolution of 2 ns per point.

The voltage of the Pockel's cell is switched every 500 laser shots, changing the polarization of the excitation beam. The change in excitation polarization inverts the sign of the OKE signal but does not change the sign of the DIHARD signal (see below). The data was averaged in two sets, one with V_{on} and one with V_{off}. Addition of the two sets yields the DIHARD signal, while subtraction gives the OKE signal.

The experiments were performed on dibutylphthalate (DBP) (Aldrich, 99 + % pure). The sample was vacuum distilled to further purify it and remove dust and sealed in a 1 cm glass spectroscopic cell. The sample was placed in a copper block and cooled using a closed-cycle refrigerator. The temperature can be measured to ± 0.1 K.

3. Results

Fig. 2 displays a DIHARD signal taken at 211.8 K with the probe beam within, but off center from, the excitation spot. As can be seen in the figure, there is a fast rise (on the timescale of the figure) and then a slow decay. As discussed above, the DIHARD signal is obtained by adding the data sets
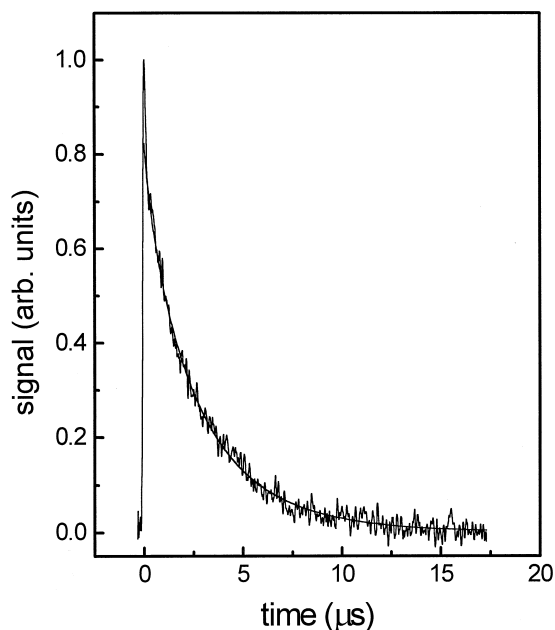
Fig. 2. An example of a DIHARD signal taken on the pure liquid dibutylphthalate at 211.8 K. The decay results from the long timescale dibutylphthalate orientational relaxation. A stretched exponential, $S(t) = \exp[-(t/\tau)^\beta]$ with $\tau = 2.41$ μs and $\beta = 0.84$ was used as a fitting function. At very short time, the presence of the acoustic disturbance causes the fit to miss the data.

taken with V_{on} and with V_{off}. In these experiments, a small amount of CH overtone absorption of the 1.06 μm excitation pulse followed by rapid vibrational relaxation produces the local heating [17,18] that is responsible for the effect. Since the sample is initially isotropic, rotating the excitation polarization does not change the absorption of the excitation pulse or the characteristics of the local heating. Thus the DIHARD signal is independent of the excitation pulse polarization. However, the HD–OKE signal depends on the relative $\vec{E}$-field directions of the excitation and probe beams. Rotating the $\vec{E}$-field by 90°, i.e., from $+45°$ to $-45°$, changes the sign of the HD–OKE signal. In addition to data like those in Fig. 2, as discussed in Section 1, we have observed zero signal when the probe beam is precisely centered on the excitation beam, and we have observed signals with no long-lived decay when the probe is placed well outside of the excitation spot. The absolute sign of the DIHARD signal is dependent on the relative polarization of the probe beam, the position

of the probe spot relative to the pump spot, and the stress optical-coefficient, which may be positive or negative [19].

The rise time (see inset Fig. 3) is consistent with the time required for the acoustic disturbance to leave the excitation spot size at the velocity of sound, ~ 1700 m/s. This same rise time would be seen in a thermal lensing experiment. Great care was taken to test for and avoid a thermal lensing signal. A definitive test was performed to prove that the signal is indeed a heterodyne-detected birefringence.
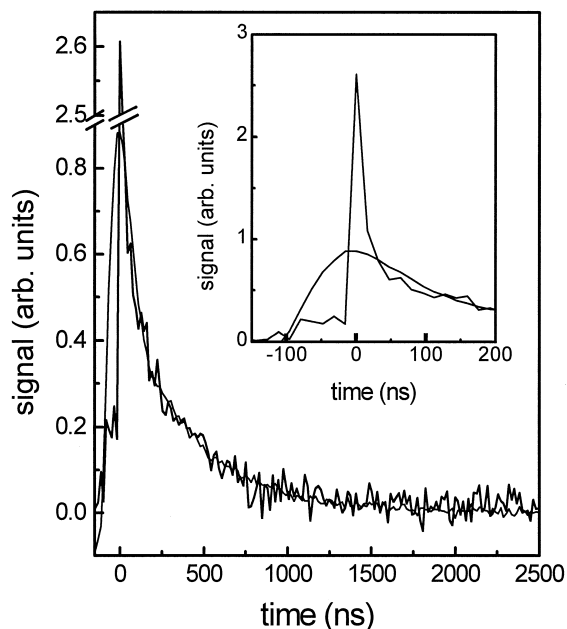

Fig. 3. A comparison of DIHARD and HD–OKE experiments taken under identical conditions on dibutylphthalate at 222.7 K This temperature was selected for the comparison because the HD–OKE signal was still strong enough to observe yet the decay was slow enough to measure with DIHARD. The curve with less noise is the DIHARD data. After short times, the decays are identical, demonstrating that DIHARD measures the same orientational relaxation as a conventional OKE experiment. The inset shows the short time behavior. The rising edges differ because of the different mechanisms that prepare the molecular orientational anisotropy. The HD–OKE data has a large spike around $t = 0$ because of the electronic optical Kerr effect caused by the response of the electrons to the excitation pulses. In the DIHARD data, the delay between $t = 0$ and the peak of the signal and the characteristics of the rising edge of the signal are determined by the time required for the velocity of sound to cross the excitation spot size (300 μm).

While the DIHARD signal is not sensitive to the excitation polarization, since it is heterodyne detected, the signal should be sensitive to a phase shift in the probe local oscillator. A symmetrical rotation of the quarter-wave plate relative to the probe beam's axis of polarization changes the projection of the local oscillator from the $+x$ axis to the $-x$ axis, which is identical to a 180° phase shift of the local oscillator. Shifting the local oscillator phase 180° by rotation of the quarter-wave plate caused the signal to invert, just as such a shift inverts a HD–OKE signal. A thermal lens signal depends on a change in focusing or direction of the probe. It is insensitive to the optical phase of the probing light since a phase shift leaves all other characteristics of the experiment unchanged. Therefore, it is possible to rule out thermal lensing as the cause of the signal shown in Fig. 2. (Any contamination of a DIHARD signal from thermal lensing can be removed by taking two data sets, one with the local oscillator phase shifted by 180° relative to the other and subtracting the data sets. Since the DIHARD signal is inverted and the thermal lensing signal is not, the subtracted sets yield the DIHARD signal only. This procedure is being used in studies to be reported subsequently.)

The decay of the signal in Fig. 2 is the long timescale orientational relaxation of DBP at 211.8 K. In principle, the decay could be due to thermal conductivity. Given the spot size of 300 μm and the thermal conductivity of liquids like DBP [20], the timescale for the signal to decay by thermal conductivity is milliseconds, which is orders of magnitude longer than the observed decay.

DBP is very viscous at room temperature and becomes increasingly so below room temperature where it supercools. As the temperature is decreased, the slowest components of the orientational relaxation become virtually impossible to observe using the experimental apparatus in the HD–OKE configuration. At high temperatures, where HD–OKE works well, the DIHARD method does not have sufficient time resolution to observe even the slowest components of the orientational relaxation because of the limitation produced by the excitation spot size used in these experiments. However, there is a range of temperatures in which both experiments give good signals. To demonstrate that DIHARD does, in fact, measure the same dynamics as the HD–OKE, Fig. 3 shows data taken with DIHARD and HD–OKE at 222.7 K. The data sets were taken under the same conditions. As can be seen from the figure, the decays are identical while the rise times differ (see inset). The DIHARD signal has a significantly better signal-to-noise ratio. The HD–OKE rise time is determined by the instrument response, in this case the electrical response of the phototube/transient digitizer. The DIHARD rise time is slower, determined by the excitation spot size and the velocity of sound.

A detailed calculation of the DIHARD signal as a function of time and probe beam position will be presented in a future publication. The nature of the calculation is as follows. The thermal and density changes that are a consequence of absorptive heating of a liquid for a Gaussian laser spot have been calculated using the Navier–Stokes equation in connection with thermal lensing [21,22]. The Navier–Stokes equation is evaluated numerically. The solution to the Navier–Stokes equation yields the change in density and temperature caused by absorption of the laser beam as functions of time and position. From the density changes, the flow velocity for each location at a given time is calculated. For non-spherical molecules, their orientation will be coupled to a flow velocity gradient through the differential equation [8,23],

$$\dot{\overline{Q}}(\vec{r},t) = -\Gamma_0 \overline{Q}(\vec{r},t) + \Lambda \frac{\partial \overline{v}(\vec{r},t)}{\partial y}, \qquad (1)$$

where $\overline{Q}(\vec{r},t)$ is an ensemble average of the orientational density, i.e., it defines the extent to which there is an orientational anisotropy. Γ_0 is the ensemble averaged orientational relaxation frequency, Λ is the rotational-shear coupling strength, and $\overline{v}(\vec{r},t)$ is the average net velocity of particles at position r and time t. Eq. (1) is solved numerically using the Navier–Stokes results. Since the initial heating of the sample is radially symmetric, the velocity gradient will be radially outward from the center of the excitation spot. Thus, the direction of the molecular alignment will be along a vector from the excitation spot center to the probe spot center.

Eq. (1) is comprised of two terms; the first term decreases the anisotropy through orientational relaxation. As written, the relaxation is a single exponential decay, but any form of the relaxation can be

incorporated. The second term increases the anisotropy from a flow-induced alignment. At very low viscosities, Γ_0 is very large, therefore, no substantial orientational alignment will develop because molecules will randomize their orientation faster then the velocity gradient aligns them. At very high viscosities, Γ_0 approaches zero thus a signal will build up as long as the velocity gradient is present. So the total signal amplitude will be independent of viscosity for high viscosity. This is in contrast to the OKE performed with a fixed pulse duration. As the viscosity becomes high, the signal in the slow relaxation components will tend to zero. At intermediate viscosity, there is a competition between the two terms causing $\overline{Q}(\vec{r},t)$ to range from 0 to $\overline{Q}(\vec{r},t)_{max}$, its maximum value. We observe this behavior experimentally. For low viscosity, no DIHARD signal was observed; HD–OKE experiments still produce strong signal levels. We have observed strong DIHARD signals in DBP just above the glass transition temperature while the HD–OKE signal was undetectable on the long timescale of the DIHARD signal.

4. Discussion

The DIHARD signal is detected in a manner which is identical to the detection in a HD–OKE experiment. The signal in both experiments depends on inducing an orientational anisotropy and observing the orientational anisotropy through the molecular anisotropic polarizability. However, the manner in which the orientational anisotropy is produced is fundamentally different. In the DIHARD experiment, the anisotropy is induced mechanically. The mechanism depends on very weak absorption by the sample, as in a thermal lensing experiment. The absorption leads to molecular displacements, and, through translational–rotational coupling, orientational alignment. This mechanical mechanism does not depend on the molecular anisotropic polarizability to produce the alignment. In an OKE experiment, the excitation $\vec{E}$-field induces a dipole and that dipole, in turn, interacts with the $\vec{E}$-field to produce a torque on the molecule. The alignment process depends on the square of the molecular anisotropic polarizability. In a HD–OKE experiment the over all signal depends on the cube of the molecular anisotropic polar-

izability. For liquids in which the molecular anisotropic polarizability is relatively small, DIHARD may have an advantage since the signal is only linear in the molecular anisotropic polarizability. In addition, as discussed above, pulsed laser excitation OKE experiments are poor for generating significant amplitude in the very slow components of orientational relaxation in viscous liquids.

In the experiments presented above, very weak overtone absorption by the bulk liquid of 1.06 μm light was used to produce the local heating responsible for the DIHARD signal. Other wavelengths, including visible wavelengths [17], can be used to excite vibrations of a pure liquid. It should also be possible to use two photon electronic absorption, if it is followed by rapid radiationless relaxation, to produce the necessary local heating. Another possibility is to electronically excite a very low concentration solute, such as malachite green, which undergoes rapid radiationless relaxation. If the solute is in sufficiently low concentration, the signal will come from the bulk liquid, which will not be perturbed by a sufficiently low concentration solute. It may also be possible to study the orientational dynamics of a solute with DIHARD, whether it is used for excitation or not. If the probe wavelength is tuned very near a solute electronic absorption, the tremendous increase in the polarizability should enable the solute to be selectively observed [24]. It may be possible to align large molecules, such as DNA, which are difficult to align with the OKE. Small solvent molecules will relax much faster than the macromolecules, so that the slow dynamics of the large molecules may be observable.

DIHARD is useful for examining relatively slow orientational dynamics. The longest timescale is restricted by thermal diffusion out of the initially heat spot. However, if the excitation spot size is increased, the rise time increases linearly with the spot size but the timescale for thermal diffusion increases as the square of the spot size. Therefore, exceedingly slow orientational relaxation can be measured in the time domain using a large excitation spot size.

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