Resonance-Enhanced Optical Reorientation of Molecules in Liquids via Intermolecular Interaction

Thai V. Truong[*] and Y. R. Shen[†]

Department of Physics, University of California, Berkeley, California 94720, USA

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Enhanced optical reorientation of molecules in a pure liquid was observed when the optical field was in resonance with the molecular electronic transition. The enhancement comes from photoinduced change in intermolecular interaction. Experimental results agree well with the time-dependent theory based on a mean-field model of intermolecular interaction.

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Optical-field-induced molecular reorientation is a well-known phenomenon in liquids with anisotropic molecules. It results from optical torques created on molecules through interaction of the optical field with induced dipoles on the molecules, and contributes to the optical Kerr effect in liquids. With the input wavelength approaching an electronic transition, resonant enhancement in the molecular polarizability and hence in the reorientation effect are expected. However, this has not taken into account the possibility that orientational interactions between excited-state and ground-state molecules could be different from those between ground-state molecules, providing additional resonant contribution to reorientation. The latter effect should generally be present in liquids and could even be dominating if the molecules are highly anisotropic, but to our knowledge its experimental investigation has never been reported despite the existence of a theoretical description on the subject in the literature [1]. By treating the excited molecules as guests in a host of ground-state molecules, the effect can be seen to be similar to that occurred in dye-doped liquids or liquid crystals [2–4]. Enhancement of optical reorientation by excitation of dye molecules has been observed and studied extensively, and can be understood as the result of photoinduced change in guest/host interactions [1–14]. We describe here an experiment that demonstrates similar enhancement in a pure liquid under resonant excitation. The observed enhancement and dynamics agree well with theory.

We first briefly describe the underlying theory for the effect following the successful model previously developed for dye-doped liquids [1,14,15]. In the current case of pure liquids, linearly polarized optical excitation of the molecules creates a population of oriented molecules in the excited state and a complementary population of oriented "holes" in the ground state. These two populations exert competing torques in reorienting the ground-state molecules, in addition to the direct optical torque exerted on the molecules. If orientational interactions between excited-state and ground-state molecules and between ground-state molecules are different, a net torque on the ground-state molecules will result from the excitation. Considering rod-like molecules, we can describe, as usual, the induced molecular orientations along the optical field in a liquid by the order parameter Q_i, defined as $Q_i = N_i\langle\frac{1}{2}\times(3\cos^2\theta_i - 1)\rangle$, where the subindex $i = g$ or e refers to molecules in the ground or excited state, θ_i is the angle between the field and the molecular long axis, N_i is the density of molecules, and the angular brackets denote the ensemble average. Note that $Q_i = 0$ and N_i, respectively, for completely random and completely aligned molecular distributions. With photoexcitation, the anisotropies Q_i obey the following dynamical diffusion equations [1,14,15]:

$$\frac{\partial Q_e}{\partial t} + \frac{Q_e}{\tau_{De}} = -\frac{Q_e}{\tau_f} + AI(t), \tag{1}$$

$$\frac{\partial Q_g}{\partial t} + \frac{Q_g}{\tau_{Dg}} = +\frac{Q_e}{\tau_f} - AI(t) + BI(t) + \frac{u_{gg}N_gQ_g}{15kT\tau_{Dg}N_t} + \frac{u_{ge}N_gQ_e}{15kT\tau_{Dg}N_t}, \tag{2}$$

with

$$A \equiv \frac{2\beta}{5h\nu}, \qquad B \equiv \frac{4\pi L^2\Delta\alpha'_gN_g}{15kTnc\tau_{Dg}}.$$

Here, τ_{De} and τ_{Dg} denote the rotational diffusion times for the excited and ground-state molecules, respectively, in the absence of molecular correlation, τ_f is the relaxation time from the excited state to the ground state, $AI(t)$ is the rate of excitation by optical pump intensity $I(t)$ that creates the oriented population in the excited state and the oriented holes in the ground state, Q_e/τ_f describes relaxation from excited to ground state (assuming no change in molecular orientation), and $BI(t)$ results from the direct optical torque exerted on the ground-state molecules. The last two terms in Eq. (2) describe the torques on the ground-state molecules by the oriented ground-state and excited-state populations, respectively, with u_{ij} being the mean-field potential of orientational coupling between i and j-type molecular species, and $N_t = N_g + N_e$. Other parameters in the equations are the absorption coefficient β, the photon energy $h\nu$, the Lorentz local-field factor $L = (n^2 + 2)/3$, the anisotropy in the ground-state molecular polarizability $\Delta\alpha'_g$, the temperature T, the refractive index n, the Boltzman constant k, and the light speed in vacuum c. The two terms proportional to Q_g/τ_{Dg} in Eq. (2) can be combined into a single term of the form Q_g/τ_g on the left of the equation with $\tau_g = \tau_{Dg}T/(T - T^*)$ and $T^* = u_{gg}/15k$, knowing that $N_t \approx N_g$. If T approaches T^*, the orientational dynamics of the ground-state molecules would slow down drastically. This is the well-known critical slowing down behavior of liquid crystalline materials [16]. Because $N_e \ll N_g$, we have neglected perturbation on Q_e due to torques exerted on the excited-state molecules in Eq. (1).

Consider the case where the pump pulse is much shorter than all the relevant relaxation times. The solution of Eqs. (1) and (2) is readily found, with $t = 0$ being when the pump is essentially over

$$Q_e(t, z) \simeq +A\Phi(z)e^{-t/\tau_{Qe}}, \tag{3}$$

$$\begin{aligned} Q_g(t, z) \simeq {} & -RA\Phi(z)e^{-t/\tau_{Qe}} + (R-1)A\Phi(z)e^{-t/\tau_g} \\ & + B\Phi(z)e^{-t/\tau_g}, \end{aligned} \tag{4}$$

where

$$\begin{aligned} \Phi(z) &\equiv \left[\int_{-\infty}^{\infty} I(t)dt\right]e^{-\beta z}, \\ \tau_{Qe} &\equiv (1/\tau_{De} + 1/\tau_f)^{-1}, \\ R &\equiv \frac{(T^* u_{ge}/T u_{gg}) + (\tau_{Dg}/\tau_f)}{(T^*/T) + (\tau_{Dg}/\tau_{De}) + (\tau_{Dg}/\tau_f) - 1}. \end{aligned}$$

Here z measures the propagation of the excitation beam into the material. The first two terms on the right-hand side of Eq. (4) describe the ground-state anisotropy created by resonant excitation, while the last term describes anisotropy created by direct optical torque. We can define an enhancement factor as

$$\begin{aligned} \eta(t) &= Q_g(t, A)/Q_g(t, A = 0) \\ &= 1 + (A/B)[Re^{-t(1/\tau_{Qe} - 1/\tau_g)} + (R - 1)] \\ &\simeq 1 + (A/B)(R - 1) \quad \text{for} \quad t \gg \tau_{Qe} \quad \text{if} \quad \tau_{Qe} \ll \tau_g. \end{aligned} \tag{5}$$

A value different than 1 for $\eta(t \to \infty)$ signifies an enhancement to the reorientation effect due to excitation. This is determined by the parameter R, which provides a measure of the difference in the interactions between excited-state–ground-state and ground-state–ground-state molecules. If they are the same, then $u_{ge} = u_{gg}$, $\tau_{De} = \tau_{Dg}$, and $R = 1$, and the reorientation effect due to excitation via intermolecular interaction should vanish, as can be seen in Eq. (4), leading to $\eta(t \to \infty) = 1$. Using the approximation $T \simeq T^*$ and $\tau_{Dg} \ll \tau_f$, which is the experimental case we have studied, we find

$$R \simeq (u_{ge}/u_{gg})(\tau_{De}/\tau_{Dg}). \tag{6}$$

We have assumed in the above model a single excited state. This is a good approximation if relaxation among excited states is much faster than the various other relaxations described in the model and we ignore the early dynamics in our discussion. Such a case is what we have experimentally investigated. We used 4-pentyl-4-cyanobiphenyl (5CB) (Sigma-Aldrich) in the isotropic liquid phase as our sample. It is known that excited 5CB monomers bond with neighbors to form excimers in a time scale of 100–200 ps, and even in the steady state under constant excitation, the excited monomer comprises only 10% of the total excited population [17]. Therefore, if we focus only on the dynamics after a few hundred ps, we can treat the excited-state population as a single molecular species, representing mainly the excimers.

In the experiment to probe $Q_e(t)$ and $Q_g(t)$, we used the pump/probe polarization spectroscopy technique. We probed linear dichroism and birefringence induced by a linearly polarized pump beam through the change of the complex refractive index

$$\Delta n(t) = \frac{4\pi L^2}{3n} \sum_{i=g,e} (\Delta\alpha'_i + i\Delta\alpha''_i)Q_i(t). \tag{7}$$

Here the local-field factor and polarizability anisotropy pertain to the probe wavelength. With l being the sample thickness, the signals from the induced dichroism and birefringence are, respectively,

$$\begin{aligned} S_d(t) &\propto \int_0^l (4\pi L^2/3n)[\Delta\alpha''_e Q_e(t, z) + \Delta\alpha''_g Q_g(t, z)]dz, \\ S_b(t) &\propto \int_0^l (4\pi L^2/3n)[\Delta\alpha'_e Q_e(t, z) + \Delta\alpha'_g Q_g(t, z)]dz. \end{aligned} \tag{8}$$

They can be found separately using the experimental arrangement sketched in Fig. 1. With the pump polarization along $\hat{y}$, the probe polarization along $\hat{x} + \hat{y}$, and the analyzer (without the quarter-wave plate) at small angles $\pm\gamma$ away from $-\hat{x} + \hat{y}$, we can obtain $S_d(t)$ from the difference of the two measurements. Inserting the quarter-wave plate with its fast axis along $\hat{x} + \hat{y}$ and carrying out similar

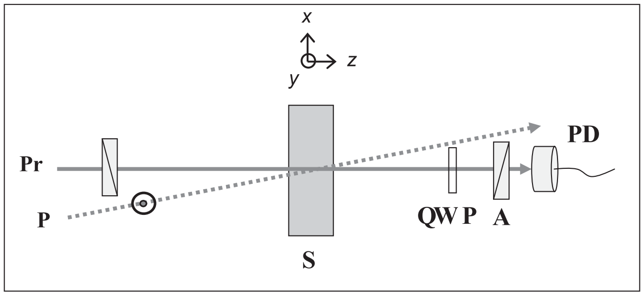

FIG. 1. Schematic of the experiment setup. Pr: probe beam; P: pump beam; S: sample; QWP: removable quarter-wave plate for the probe beam; A: analyzer; PD: photodetector.

measurements allows the determination of $S_b(t)$. Details were described in Refs. [18,19].

We used in our experiment a 15-ps pulsed Nd:YAG laser/wavelength-tunable optical parametric system to produce pump and probe beams. The resonant pump was set at 339 nm just inside the lowest absorption band of 5CB. The absorption coefficient was measured to be 29 cm^{-1}. The probe was set at 1064, 633, and 532 nm. Pump and probe beams had energies of 11 and 2 mJ per pulse, and diameters of 2 and 1 mm, respectively. The isotropic sample was housed in a flow cell, and maintained at $T = 52\,^\circ\mathrm{C}$.

For better illustration of experimental consistency, we first measured the relaxation times, τ_{Qe} and τ_g, of the excited and ground states separately. With the probe set at 532 nm, we have $\Delta\alpha''_g = 0$ and $S_d(t) \propto \int_o^l \Delta\alpha''_e Q_e(t,z)dz \propto B\exp(-t/\tau_{Qe})$ if we ignore the early time evolution. Figure 2(a) shows the measured data. For $t > 500$ ps, we found a single-exponential decay with $\tau_{Qe} = 1.01 \pm 0.08$ ns. An independent fluorescence measurement (data not shown) yielded an excited-state lifetime $\tau_f = 18 \pm 2$ ns, which agrees with the measured value of Ref. [17]. We then have $\tau_{\mathrm{De}} = 1.07 \pm 0.1$ ns. To find the ground-state rotational relaxation time τ_g, we set the pump off-resonance at 1064 nm and the probe at 532 nm. With $A = 0$, and ignoring the early dynamics, we have $S_b(t) \propto \int_o^l \Delta\alpha'_g Q_g(t,z)dz \propto B\exp(-t/\tau_g)$. The experimental result displayed in Fig. 2(b) can be fit by a single-exponential decay with $\tau_g = 14$ ns for $t > 500$ ps, in good agreement with that reported in Ref. [20]. Knowing $T^* = 34.2\,^\circ\mathrm{C}$ [21], we find the intrinsic rotational diffusion time of 5CB to be $\tau_{\mathrm{Dg}} = 760 \pm 65$ ps.

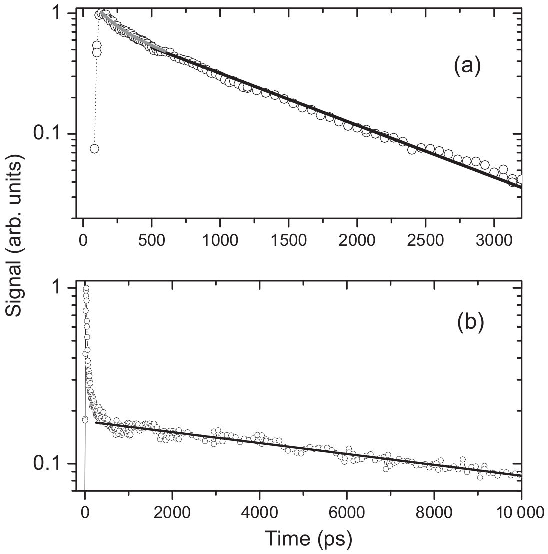

FIG. 2. (a) Photoinduced dichroism, $S_d(t)$, observed with pump wavelength at 339 nm and probe at 532 nm. Solid black line is a single-exponential fit of the decay from 500 ps on. Gray line is a biexponential fit of the entire decay. (b) Photoinduced birefringence, $S_b(t)$, measured with pump wavelength at 1064 nm and probe at 532 nm. Solid black line is a fit with a single-exponential decay.

Figure 3 shows the observed time evolution of the birefringence, with the pump pulse at 339 nm and the probe pulse at three different wavelengths 532, 633, and 1064 nm. Again, let us focus on the time range >500 ps after the pump pulse. The decays in all cases can be fit very well by $S_b(t)$ in Eq. (8) with the help of Eqs. (3) and (4) using $\Delta\alpha'_e/\Delta\alpha'_g$ as the fitting parameter (A, B, and R can be determined, as described below). They consist of two exponential components with decay times $\tau_{Qe} = 1.01$ ns and $\tau_g = 14$ ns, determined from independent measurements mentioned earlier. Beyond several ns, $Q_e \to 0$ and the decay becomes single-exponential, governed by the last two terms of $Q_g(t)$ in Eq. (4), one from intermolecular interaction and the other from optical torque. As seen from Eqs. (5) and (8), the ratio of the signal $S_b(t, A)$ at such large t to the expected signal that comes from the optical torque alone, $S_b(t, A = 0)$, should yield the enhancement factor $\eta(t \to \infty)$. However, $S_b(t, A = 0)$ cannot be separately measured from $S_b(t, A)$ if the pump is in the absorption region. We must deduce $S_b(t, A = 0)$ from comparison with the reference signal $S_b^{\mathrm{ref}}(t)$ obtained at the same probe wavelength, but with a nonabsorbing pump wavelength,

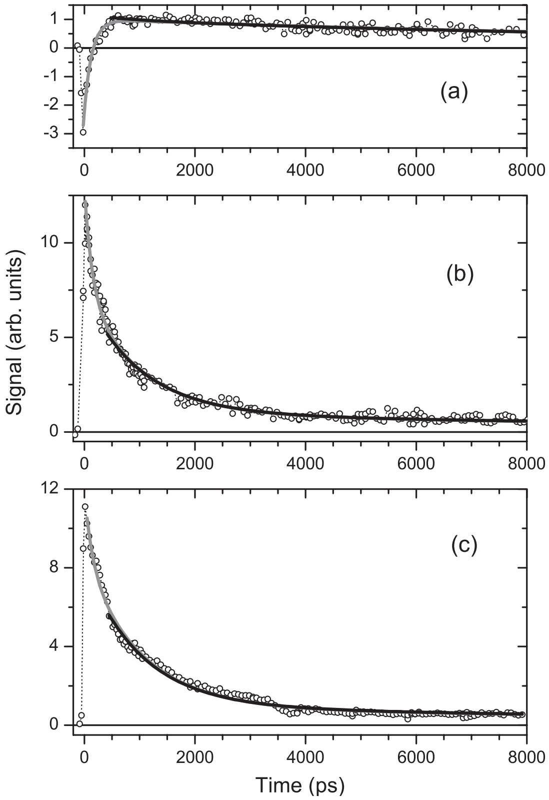

FIG. 3. Photoinduced birefringence, $S_b(t)$, observed with pump wavelength at 339 nm and probe wavelength at (a) 532 nm, (b) 633 nm, and (c) 1064 nm. Solid black lines are biexponential fits of the decays from 500 ps on. Gray lines are triexponential fits of the entire decays.

such as the one presented in Fig. 2(b). Both originating from direct optical torque, the ratio of the two is given by: $S_b(t, A = 0)/S_b^{\mathrm{ref}}(t) = B\Phi(1 - e^{\beta l})/(B^{\mathrm{ref}}\Phi^{\mathrm{ref}}\beta l)$, with $B/B^{\mathrm{ref}} = (L^2\Delta\alpha'_g/n)/(L^2\Delta\alpha'_g/n)^{\mathrm{ref}}$. From the known refractive index dispersion of 5CB [22] and the measured S_b^{ref} [Fig. 2(b)], Φ, Φ^{ref}, β, and l, we can find $S_b(t, A = 0)$ with the pump at 339 nm. We then found $\eta(t \rightarrow \infty) = S_b(t, A)/S_b(t, A = 0) = 17$, with a 30% error resulting from uncertainty in our measurements of Φ and Φ^{ref}.

Thus we have observed a significant enhancement in optical reorientation of ground-state molecules due to interaction with excited molecules. From the known values of the parameters [22] in the expressions for A and B in Eq. (2), with $N_g = 2.39 \times 10^{21}\ \mathrm{cm}^{-3}$, we find $A = 2.0 \times 10^{19}\ (\mathrm{J\,cm})^{-1}$ and $B = 8.8 \times 10^{17}\ (\mathrm{J\,cm})^{-1}$. Then, with $\eta(t \rightarrow \infty) = 17$, Eq. (5) yields $R = 1.7$, and with $\tau_{De}/\tau_{Dg} = 1.4$, we find from Eq. (6), $u_{ge}/u_{gg} \simeq 1.2$. The result here shows that ground-state–ground-state and ground-state–excited-state interactions of the molecules are not very different. Presumably the change in the electronic wave function of the 5CB molecule upon excitation is spent mostly on forming the excimer state and leaves little to enhance its interaction with the ground-state molecules significantly (though the larger volume of the excimer should contribute to a decrease in rotational diffusion and thus an increase in the ratio τ_{De}/τ_{Dg}). Although $R > 1$ is essential for enhancement, the large enhancement we observed is mainly due to $A/B \gg 1$. Compared with the dye-doped case, A is much larger because the density of molecules under polarized excitation is much larger. This should be generally true for pure liquids when the pump wavelength is on a strong absorption band. On the other hand, in the dye-doped case, the intermolecular interaction between dye and 5CB molecules could increase by a factor of 5 upon dye excitation [14]; strengthening of specific chemical interactions, particularly hydrogen bonding, has been found to be the likely cause for the change [9,13].

We briefly discuss the early dynamics ($t \approx 0$ to 500 ps) shown in Figs. 2 and 3 that involve both monomers and excimers of excited molecules. The excited-state anisotropy is expected to follow a biexponential decay from the two molecular species [23]. As seen in Fig. 2(a), the early part of the time evolution of the excited-state dichroism can indeed be fitted well by a biexponential decay with $\tau' = 140$ ps and $\tau_{Qe} = 1.01$ ns (shown in gray). This additional decay component of $Q_e(t)$ should create an extra decay component with the same decay time τ' in $Q_g(t)$ and the overall anisotropy signal. The satisfying triexponential fit of the decays in Figs. 3(a)–3(c) (shown in gray), with the prescribed values of decay constants τ', τ_{Qe}, and τ_g, indicates that the model is reasonable. The negative signal in the early part of the time evolution in Fig. 3(a) comes from the negative polarizability anisotropy of the monomer species.

In summary, we have shown in 5CB liquid that resonant excitation can greatly enhance optical reorientation of molecules. This happens when the interaction between excited molecules and ground-state molecules is stronger than the interaction between ground-state molecules. The enhancement increases with increase of the resonant oscillator strength. The effect described here should be common in many liquids.

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[*] Present address: Biological Imaging Center, Beckman Institute, California Institute of Technology, Pasadena, CA 91125, USA.

[†] To whom correspondence should be addressed. yrshen@calmail.berkeley.edu

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