

## Solvent intermolecular polarizability response in solvation

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Polarizability response spectroscopy, a two-color optical Kerr effect method, has been developed and employed to study solvent intermolecular polarizability responses to photoexcited solutes. Here, we report solvent intermolecular polarizability responses in (dipolar) solvation. The time-resolved nonresonant polarizability signals are analyzed in the frequency domain where they are fit to a functional form representing diffusive reorientational, interaction-induced, and librational motions. Diffusive reorientational motion of  $\text{CHCl}_3$  was preferentially driven following photoexcitation of Coumarin 153 while interaction-induced motion was mainly driven in  $\text{CH}_3\text{CN}$  solutions. The mechanism for selective solvent responses involves the relative orientation of the solvent dipole and most polarizable molecular axes and their interaction strength to the solute dipole. © 2003 American Institute of Physics. [DOI: 10.1063/1.1555804]

Solvent plays an important role in chemical reactions by serving at various times as an energy source, a frictional drag, or a bath to stabilize reaction products. Determining the outcome of chemical reactions in liquid phases requires understanding how the solvent participates in activating the process or dissipating kinetic energy. Several theoretical<sup>1–4</sup> and ultrafast experimental approaches have been used to study solvent dynamics in liquids. Pure liquids have been examined by optical Kerr effect (OKE) measurements<sup>5–9</sup> while solvation has been studied by time-resolved fluorescence Stokes shift (TRFSS),<sup>10–12</sup> photon echo<sup>13–16</sup> and other pump-probe<sup>17,18</sup> spectroscopies on femto- and picosecond time scales. Beautiful experiments on small molecule photodissociation have elucidated the spectral density associated with photoproduct vibrational-rotational relaxation to the bath.<sup>19–22</sup> However, despite these advances, our insight into solvent responses in reaction and solvation processes is still incomplete. This stems, in part, from the difficulty of directly probing the solvent responses.

Polarizability response spectroscopy (PORS),<sup>9,23,35,36</sup> employed here in a two-color OKE (i.e. anisotropic Raman) configuration, is used to investigate solvent intermolecular responses to photoexcitation of the solute. In PORS, the pump field is electronically resonant with the solute molecules and off-resonant with solvent while the probe field is electronically off-resonant with both solute and solvent. In the absence of the solute, the solvent molecules are subjected to an ultrashort perturbation by the linearly polarized pump field that drives inter- and intramolecular (vibrational) motions. The subsequent decay of the induced birefringence associated with these solvent molecular motions is monitored by a polarized probe field with sensitivity to the Raman-

active solvent molecular motions measurable in OKE (or dynamic light scattering) experiments.<sup>5–9</sup> These motions are often classified as diffusive reorientational, interaction-induced, librational, and oscillatory (intramolecular vibrational) for symmetric top molecules.

With the addition of a solute that can be electronically excited by the pump field, the solvent molecules experience: (i) a delta function-like perturbation by the linearly polarized pump field and (ii) a step function-like perturbation by the electronically excited solute. Solvent molecules, whose configurations are initially in equilibrium with the ground state solute, will reorganize following photoexcitation. Solvent molecular responses in solution will be different from those of the neat solvent. Therefore, PORS gives information on how solvent molecules respond to photoexcitation of the solute and can do so for strongly interacting reactant-solvent systems. Coumarin 153 (C153) was selected as a solute because its permanent dipole moment increases by  $\sim 8$  D upon photoexcitation, its solvation dynamics have been characterized by TRFSS measurements in several organic solvents<sup>12</sup> and its ground state recovery is much slower ( $\sim 5$  ns) than the nonequilibrium solvent dynamics of interest.<sup>24</sup>

Femtosecond pulses centered at 800 nm and of  $\sim 25$  fs duration were extracted from a home-built cavity-dumped Ti:sapphire oscillator at a 360 kHz repetition rate.<sup>25</sup> The 400 nm second harmonic pump pulse was generated with a 200  $\mu\text{m}$  thick BBO crystal. The setup is identical to that of conventional optical heterodyne detected OKE (OHD-OKE)<sup>6,8,26</sup> except that the pump field is resonant with a C153 electronic transition ( $S_0 \rightarrow S_1$ ); the experiment measures the polarizability (i.e., refractive index) anisotropy of the medium.

PORS measurements were performed at a series of C153 concentrations in a variety of solvents. In contrast to the PORS signals from the neat solvents, the PORS signals from the solutions are primarily negative in amplitude with a long decay component. Results for  $\text{CHCl}_3$  are shown in Fig. 1(A). The data are corrected for pump beam attenuation by solving a system of equations for Beer's law absorption using several concentration-dependent measurements in each solvent—this

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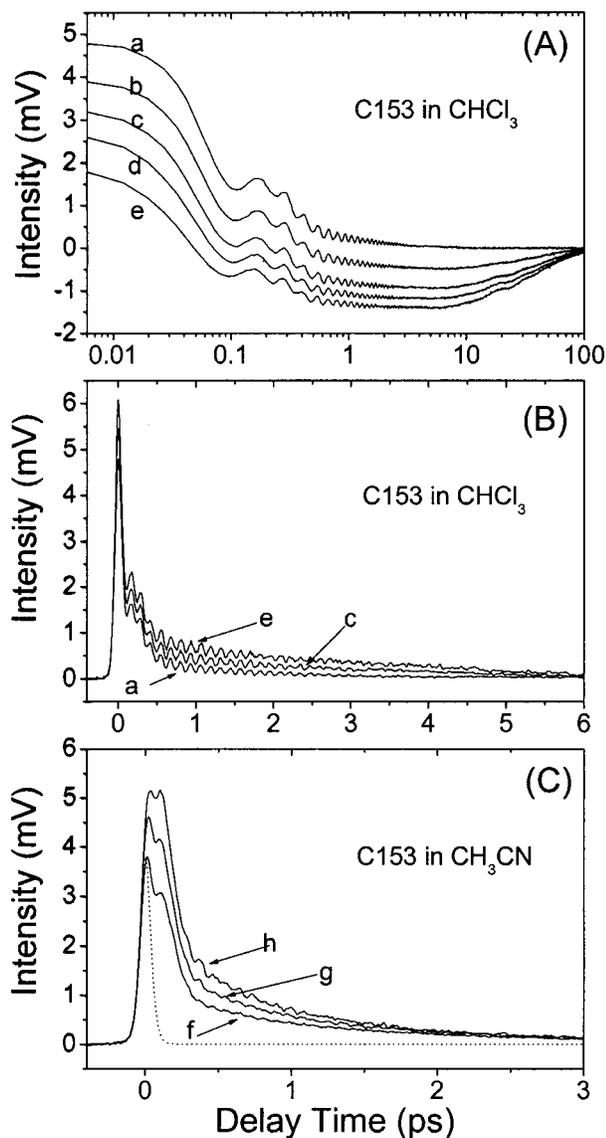


FIG. 1. (A) Two-color PORS signals for different concentrations of C153 in  $\text{CHCl}_3$  corrected for pump pulse absorption. a: neat  $\text{CHCl}_3$ ; b: 0.419 mM; c: 0.899 mM; d: 1.318 mM; e: 1.789 mM. (B)  $S'(t_d)$  in  $\text{CHCl}_3$ . (C)  $S'(t_d)$  in  $\text{CH}_3\text{CN}$ . f: neat  $\text{CH}_3\text{CN}$ ; g: 0.707 mM; h: 1.331 mM. Note the different timescales in the panels. All measurements were performed at room temperature ( $18^\circ\text{C}$ ). The dotted curve in (C) is a representative pump-probe cross-correlation. The pump-probe beam overlap was adjusted to begin at the front surface of the solution and extends approximately  $200\ \mu\text{m}$  into the 1 mm path length flow cell. The FWHM of the cross-correlation obtained from the electronic response of a pure  $\text{CCl}_4$  sample yields an 85 fs Gaussian; significant group velocity mismatch contributes to the width.

allows quantitative comparison of pure solvent and solution responses. The long-time decay of the negative signal is fit with an exponential function. While the magnitude of the negative signals increase with concentration, the decay time only depends on the solvent;  $\tau=36.9\ \text{ps}$  in  $\text{CHCl}_3$  and  $\tau=21.4\ \text{ps}$  in  $\text{CH}_3\text{CN}$ . These results and analogous measurements in a wide range of solvents<sup>23,27,36</sup> are in excellent agreement with C153 rotational reorientational times.<sup>28</sup> Since the PORS signal reflects the change in polarizability (or index of refraction) anisotropy with pump-on versus pump-off, this amounts to measuring the polarizability anisotropy difference of the solution with the solute in  $S_1$  ver-

sus  $S_0$ . The refractive index anisotropy of the photoexcited solution is negative compared to the isotropic ground state system because the refractive index of the photoselected distribution is reduced. From the Kramers–Kronig relation, diminishment of the absorption due to photoexcitation also decreases the resonances' contribution to the wavelength-dependent index of refraction.

Analogously with OKE,<sup>6</sup> the PORS signal can be written as a convolution of the molecular response function,  $R(t) = \sigma(t) + r(t)$ , where  $\sigma(t)$  is the electronic and  $r(t)$  the nuclear response of the solute–solvent system with the laser intensity cross-correlation function,  $G_0^{(2)}$ . A reduced PORS signal is obtained by subtracting the solute reorientational component,

$$S'(t_d) = \int dt G_0^{(2)}(t) \cdot R(t-t_d) - \int dt G_0^{(2)}(t) \cdot [A \cdot e^{-(t-t_d)/\tau} \cdot H(t-t_d)], \quad (1)$$

where  $A$ ,  $\tau$ , and  $H(t)$  are the amplitude and decay time constant of the solute reorientational motion, and a Heaviside step function, respectively. These results are shown in Figs. 1(B) and 1(C) for  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$ , respectively. When compared with the PORS signal from the neat solvent,  $S'(t_d)$  includes the additional solvent molecular responses to photoexcitation of C153. Equation (1) assumes that the solute reorientational dynamics are Markovian. However, the fast solvent dynamics observed in the OKE response of the pure liquids in Fig. 1 occur on a range of timescales and are not instantaneously sampled. Therefore,  $S'(t_d)$  embodies the non-Markovian dynamics exhibited in the solute–solvent interaction as well as polarizability anisotropy of the bulk non-interacting solvent.

The polarizability susceptibility,  $\text{Im}\{D(\omega)\}$ , is the imaginary part of the Fourier transform of  $S'(t_d)$  divided by the Fourier transform of the cross-correlation function<sup>8</sup> giving the spectrum of solvent molecular responses. Polarizability susceptibilities calculated from  $S'(t_d)$  transients are shown in Figs. 2(A) and 2(B). In both cases, the amplitude of the susceptibilities increases with solute concentration. As the concentration increases, the total number of solvent molecules interacting with the solute molecules increases though the number of solvent molecules per solute remains unchanged (i.e. dilute solution assumption, the number density is approximately  $10^4$  solvents per solute). Thus, the increase of the susceptibility with increasing concentration is due to the greater number of solvent molecules coupled to solutes.

The susceptibility changes in the low frequency region ( $0\sim 250\ \text{cm}^{-1}$ ) are quite different in  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$ . As shown in Fig. 2, the change in  $\text{CHCl}_3$  is the growth of the lowest frequency feature near  $2\ \text{cm}^{-1}$  while in  $\text{CH}_3\text{CN}$  the amplitude of nearly the entire low frequency region increases without large changes in the overall shape. The frequencies of various components are observed to increase and will be discussed in a full account of this work.<sup>27</sup> The high frequency peaks in Figs. 2(A) and 2(B) correspond to intramolecular vibrational modes of  $\text{CHCl}_3$  ( $\sim 260\ \text{cm}^{-1}$ , Cl–C–Cl bending) and  $\text{CH}_3\text{CN}$  ( $\sim 380\ \text{cm}^{-1}$ , methyl/cyano bending). While there is no significant change in the vibrational mode

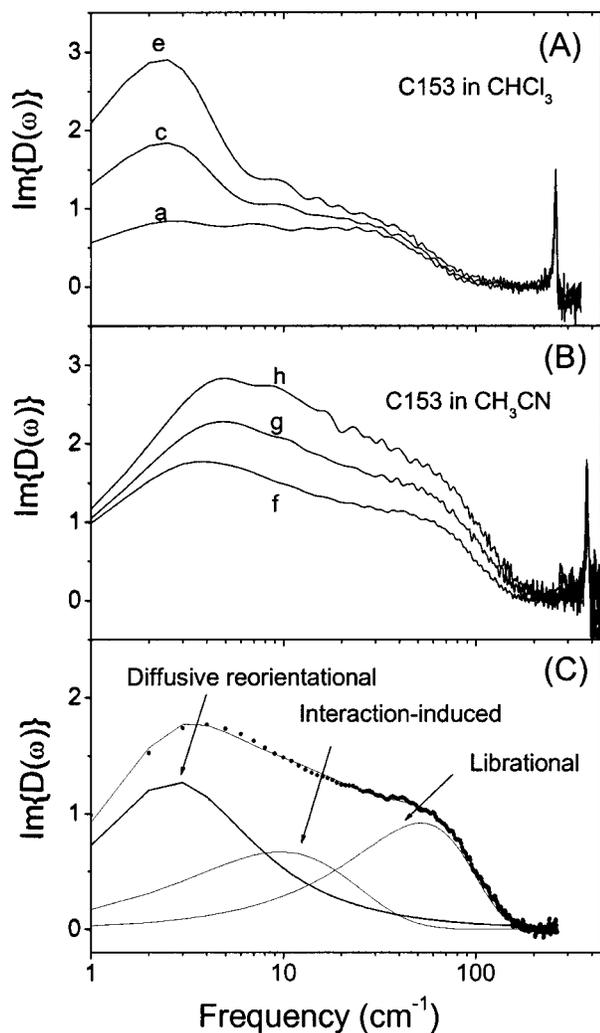


FIG. 2. Polarizability susceptibilities calculated from the  $S'(t_d)$  transients. (A) a: neat  $\text{CHCl}_3$ ; c: 0.899 mM; e: 1.789 mM. (B) f: neat  $\text{CH}_3\text{CN}$ ; g: 0.707 mM; h: 1.331 mM. (C) Lineshape analysis of the low frequency polarizability susceptibility of neat  $\text{CH}_3\text{CN}$ . All parameters are determined by nonlinear least squares fitting and areas under the fitted curves are calculated. Three solvent modes are shown. Note common frequency scale.

of  $\text{CHCl}_3$ , the amplitude of the  $\text{CH}_3\text{CN}$  vibrational mode increases indicating that the dipolar perturbation of this IR-active mode is also involved in the total solvation response. The polarizability anisotropy of liquids composed of symmetric top molecules decays through translational and orientational motions. More quantitative information about the solvent responses is obtained from lineshape analysis. One representation is given by<sup>8</sup>

$$\text{Im}\{D(\omega)\} = a_d \cdot \frac{\omega}{(\omega - \omega_d) + 1/\delta^2} + a_0 \cdot \omega \cdot \exp\left(-\frac{\omega}{\omega_0}\right) + a_g \cdot \left[ \exp\left(-\frac{(\omega - \omega_g)^2}{2 \cdot \sigma^2}\right) - \exp\left(-\frac{(\omega + \omega_g)^2}{2 \cdot \sigma^2}\right) \right], \quad (2)$$

where the first, second, and third terms represent diffusive reorientational, interaction-induced, and librational responses, respectively.<sup>8</sup> Diffusive reorientation and libration are primarily orientational; diffusive reorientation is an individual molecular motion while libration is a collective mo-

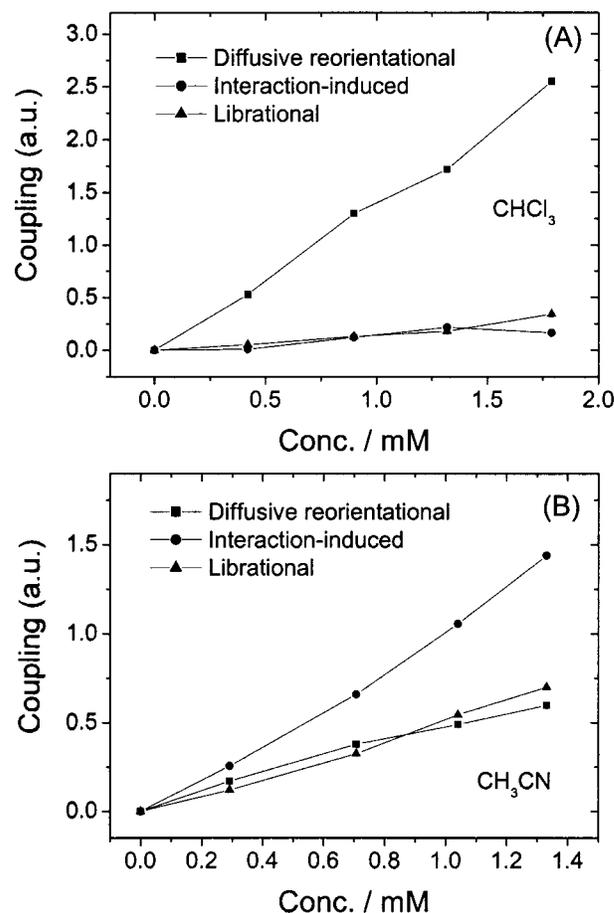


FIG. 3. Plot of the normalized areas under the fitted curves,  $([Area_{\text{solution}} - Area_{\text{solvent}}]/Area_{\text{solvent}})$  against concentration: (A) in  $\text{CHCl}_3$  and (B) in  $\text{CH}_3\text{CN}$ . See the text for details.

tion. The interaction-induced response has a center-of-mass translation dependence.

An example of fitting Eq. (2) to the pure solvent data is shown in Fig. 2(C). Plots of the areas under the fitted curves versus concentration (not shown here) show that libration is the dominant response in both solvents.<sup>27</sup> In neat  $\text{CHCl}_3$ , the contributions for librational, diffusive reorientational and interaction-induced responses are 60%, 21%, and 19%, respectively while those in neat  $\text{CH}_3\text{CN}$  are 65%, 20%, and 15%, respectively. INM simulations evaluating the rotational and translational contributions to the polarizability anisotropy for  $\text{CH}_3\text{CN}$  show that diffusive reorientation and libration give the largest contribution while the interaction-induced contribution is small.<sup>3</sup> These findings are in good agreement with the present results.

Figures 3(A) and 3(B) show the differences between areas under the fitted curves of the solution data sets and those of the neat solvent divided by areas of the fitted curves of the neat solvent plotted against the concentration. This quantity reflects the coupling of a given solvent response to the solute dipolar perturbation relative to the neat solvent by eliminating the bulk solvent contribution and normalizing to the solvent properties (e.g., density of states, motion-dependent polarizability) that affect the magnitude of a given response in the measurement. Zero slope denotes no coupling to the solute dipolar perturbation while a steeply sloped dependence denotes strong coupling. In  $\text{CHCl}_3$ , diffusive reorientational

motion is preferentially driven while interaction-induced motion is driven in CH<sub>3</sub>CN.

These frequency-selective solvent responses can be understood by considering interactions between the solute and solvent molecules and between solvent molecules before and after photoexcitation of C153. The dipole moment of C153 changes from 6.98 to 14.9 D, rotates by  $\sim 10^\circ$ , and its static polarizability changes from 23.4 to 35.7 Å<sup>3</sup> upon photoexcitation ( $S_0 \rightarrow S_1$ ).<sup>4,12,29,30</sup> The solute-solvent and solvent-solvent interaction energies can be estimated from<sup>31</sup>

$$U = -\frac{1}{r^6} \left\{ \frac{2\mu_1^2\mu_2^2}{3kT(4\pi\epsilon_0)^2} + \frac{\mu_1^2\alpha_2 + \alpha_1\mu_2^2}{(4\pi\epsilon_0)^2} + \frac{3\alpha_1\alpha_2}{2(4\pi\epsilon_0)^2} \frac{E_1^I E_2^I}{(E_1^I + E_2^I)} \right\}, \quad (3)$$

where  $r$  is the distance between centers of mass of the molecules being considered. In Eq. (3), the first, second, and third terms are the electrostatic (dipole-dipole), induction (dipole-induced dipole), and dispersion energies (induced dipole-induced dipole), respectively, and  $\mu$ ,  $\alpha$ , and  $E^I$  are the permanent dipole moment, static polarizability, and ionization energy. The first and second terms in Eq. (3) are the Boltzmann weighted average energies for two freely rotating molecules. For nonspherically symmetric molecules, the  $\alpha_1$ 's in the third term are orientationally averaged quantities. The interaction energies are calculated using previously reported values for  $\mu$ ,  $\alpha$ , and  $E^I$ .<sup>4,12,30,32,33</sup> The dispersion interaction between ground state C153 and CHCl<sub>3</sub> is nearly twice as large as the dipole-dipole energy and the dispersion interaction between CHCl<sub>3</sub> molecules is dominant. However, the dipole-dipole energy becomes dominant upon electronic excitation of C153. Therefore, since the most polarizable axes in CHCl<sub>3</sub> are perpendicular to the permanent dipole moment, the solvent molecules near the solute will reorganize such that orientational motion is preferentially driven. On the other hand, the dipole-dipole interaction is always dominant between CH<sub>3</sub>CN molecules and between C153 and CH<sub>3</sub>CN. However, since the dipole-dipole interaction between excited C153 and CH<sub>3</sub>CN is 4.5 times as large as that between ground state C153 and CH<sub>3</sub>CN and the absence of an orientational term in the interaction suggests preferential coupling to translational/interaction-induced motion, i.e., local density increase of the CH<sub>3</sub>CN solvent about the excited solute. This idea agrees with the solvation model of Berg.<sup>34</sup>

The key finding is that the susceptibility associated with the solute-solvent interaction reflects specific solvent molecular responses and is not simply related to the bulk solvent susceptibility. Therefore, short of having performed a molecular dynamics simulation with a polarizable solvent, the measured reactant-solvent interactions that reflect the orientation of the solvent dipole and most polarizable axis suggest the solvent-specific molecular responses to a solute dipolar perturbation that are observed.

The PORS approach complements other ultrafast spectroscopies (e.g., TRFSS and photon echo) in examining reactant-solvent interactions. It is expected that PORS will allow measurement of the solvent response to photodissociation and charge transfer reactions, even when the photopro-

ducts are non-fluorescent. Extension to three-pulse PORS, giving two-dimensional solvent response information, will be reported elsewhere.

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