

Directly measuring the coupling of solvent intermolecular modes in solvation

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Abstract. Resonant pump off-resonant probe OKE spectroscopy was performed to study the coupling of solvent molecular modes to photoexcitation of the solute. The intermolecular solvent modes of a range of polar and polarizable solvents including CHCl_3 and CH_3CN are coupled in distinct to the electronic excitation of Coumarin 153.

1. Introduction

Polarization response spectroscopy (PORS), a resonant pump off-resonant probe optical Kerr effect (two-color OKE) spectroscopy, was employed to investigate the coupling of solvent molecular modes to photoexcitation of the solute. In this spectroscopy, the pump field is electronically resonant with the solute and off-resonant with solvent and the probe field is electronically off-resonant with both solute and solvent. The pump field (i) excites the solute and (ii) induces solvent molecular motions. The induced solvent motions are coherently driven as a result of their coupling to the new electronic structure resulting from photoexcitation of the solute. The modes observed in OKE experiments of symmetric top (non-hydrogen bonded) solvents can be classified by the symmetry of the motion into diffusive reorientational, interaction-induced, librational, and intramolecular oscillatory motions. Diffusive reorientation is an individual molecular orientational motion occurring on a picosecond time scale. Interaction-induced is translational motion arising from molecular density fluctuations. Libration is a hindered molecular rotation in the intermolecular potential.[1] These solvent modes, which are Raman-active, can couple in a mode-specific manner to the photoexcitation of the solute. Related experiments have been reported that have concentrated on determining all tensor elements of $\chi^{(3)}$ [2, 3] as opposed to establishing the molecular couplings as in the present case.

2. Experimental Methods

Femtosecond pulses centered at 800 nm and of ~ 25 fs duration were generated from a home-built cavity-dumped Ti:Sapphire oscillator.[4] The 400 nm second harmonic pump pulse was generated with a 200 μm thick BBO crystal. The FWHM of the cross-correlation obtained and fitted to a Gaussian temporal profile was ~ 85 fs including group velocity mismatch. Coumarin 153 (C153) was used as a solute molecule because its solvation dynamics have been characterized in

several organic solvents[5] and does not exhibit a transient absorption of the 800 nm probe pulse. The chemical perturbation results from a large change in dipole moment from ~ 6 D to ~ 14 D upon photoexcitation.[6]

3. Results and Discussion

Two-color OKE measurements were performed with different concentrations of C153 in CHCl_3 and CH_3CN (and other solvents) as shown in Fig.1. The negative long decay component due to the reorientational motion of C153 was fit with an exponential function and subtracted to obtain “reduced” PORS transients. The reduced PORS signals measured in solutions of varying solute concentrations were normalized by taking into account the pump intensity attenuation by C153 absorption. Polarizability susceptibilities shown in the center panels of Fig. 1 are the imaginary part of the Fourier transformation of reduced PORS transients divided by Fourier transformation of the cross-correlation function. The low frequency region ($0 \sim 250 \text{ cm}^{-1}$) contains information on diffusive reorientational, interaction-induced, and librational motions.

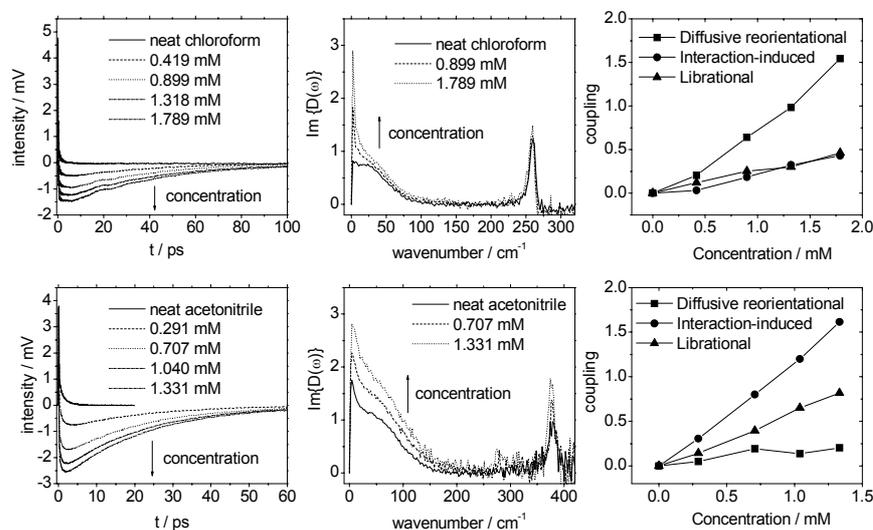


Fig. 1. Two-color OKE signals of C153 in CHCl_3 or CH_3CN (left panels), polarizability susceptibilities (center panels) and coupling $((\text{Area}_{\text{solution}} - \text{Area}_{\text{solvent}})/\text{Area}_{\text{solvent}})$ (right panels) are plotted in CHCl_3 (upper panels) and CH_3CN (lower panels).

The amplitudes in the low frequency region increase with solute concentration reflecting enhancement of the solvent motions. The enhancement in CHCl_3 and CH_3CN is quite different indicating that the solvent modes in each solvent are coupled to the photoexcitation of C153 in distinct ways. A peak near 0 wavenumbers grows greatly in CHCl_3 with solute concentration while in CH_3CN the overall shape looks the same but the amplitude and width of the low frequency region increase. The peaks in higher frequency region in Fig.1 correspond to intramolecular vibrational modes of CHCl_3 (260 cm^{-1}) and CH_3CN (380 cm^{-1}) observed in the measurement. There appears to be no significant change in the CHCl_3 vibrational mode but that of CH_3CN may be increasing.

More detailed information on which solvent motions are strongly coupled to the photoexcitation of the solute is obtained by lineshape analysis. The low frequency region is assumed to be described by terms that represent diffusive reorientational, interaction-induced, and librational motions.[7] All parameters are determined by nonlinear least square fitting. Areas under the fitted curves are calculated and coupling plotted against the concentration as shown in Fig. 1. In CHCl_3 , the diffusive reorientational motion is strongly coupled to the changed electronic structure of C153 in S_1 while in CH_3CN , the interaction-induced motion is strongly coupled showing that solvent specificity of the interaction.

PORS is complementary to time-resolved fluorescence Stokes shift and photon echo spectroscopies. The PORS approach does not depend on chromophore fluorescence[5] and will be applied to photodissociation with non-emissive reaction products. It is better suited to examine strongly interactive solute-solvent systems than echo methods. [8]

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