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Effect of Solute Orientation on Solvation Dynamics at the Air/Water Interface

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The ultrafast solvation dynamics of courmarin 314 (C314) molecules at the air/water interface has been shown to depend on their orientation with respect to the plane of the interface. A pump/second harmonic probe method using femtosecond laser pulses were used to measure the interface solvation dynamics. The pump light was S polarized, i.e., in the interface plane, or P polarized, i.e., in the plane perpendicular to the plane of the interface. The S pumped C314 molecules yielded a solvation time of 820 ± 60 fs, whereas P pumped yielded a solvation time of 1215 ± 90 fs. The interface inhomogeneous broadening on the solvation time scale is due to the differing orientations of C314 at the air/water interface.

Introduction

The solvation dynamics of molecules at a liquid interface, although an important aspect of adsobate−solvent interaction, particularly in charge transfer processes, has been relatively unexplored in contrast to solvation in bulks liquids, which has been extensively studied.[1−6] Information on solvation dynamics in an interfacial region has been obtained for molecules located in micelles suspended in water and at a liquid/solid interface using an evanescent wave method.[7−12] With the development of second harmonic spectroscopy, we have a method that is surface specific and makes possible the study of dynamics at interfaces. We have recently demonstrated that second harmonic generation (SHG) can be used to observe the solvation dynamics of coumarin 314 (C314) at an air/water interface.[13] In this paper we report on our investigation of the effect of solute interface orientation on the dynamics of solvation.

Because the forces experienced by the solute at the interface are asymmetric, the electronic excited state solvation dynamics, as well as the solute transition energies, can depend on the orientation of the solute. It is possible that C314 molecules at the air-water interface that have a large out-of-plane angle θ (horizontal) could be more strongly solvated and therefore red shifted relative to those with a smaller out-of-plane angle θ (vertical). The dynamics of water motion around differently oriented solutes could differ as well.

It has been shown that the asymmetric forces at an interface can have a large effect on the orientational distribution and rotational dynamics of a solute.[14−18] For C314 at the air/water interface the out-of-plane ground-state distribution was measured by the null angle technique.[14] Assuming a narrow distribution of angles the orientation of the $S_0 \rightarrow S_1$ transition axis is found to be peaked at about 80° from the normal.[17] We have used time resolved surface second harmonic generation (TRSHG) to study the rotational motions of C314 at the air/water interface and found that the out-of-plane rotation time (350 ps) was substantially different from the in-plane rotation time (600 ps).[17]

In the present study, the *orientationally dependent* dynamic solvation of C314 at the air/water interface was investigated by time resolved surface second harmonic generation. TRSHG is a form of pump−probe spectroscopy where surface solute molecules are first excited by an optical pump pulse and then monitored by detecting the second harmonic generated by a time-delayed optical probe. The SH signal can be strongly enhanced by being two photon resonant with an electronic transition, in this case the $S_1 \rightarrow S_0$ transition. The strategy to detect orientationally dependent solvation is to excite the $S_0 \rightarrow S_1$ transition of the C314 molecules with either a P or S polarized pump pulse. The photoexcited C314 dipole moment increases by ∼4 D relative to the ground state. The change in the SH probe signal is then monitored as the $S_1 \rightarrow S_0$ transition energy changes as the solvent reorganizes about the excited molecules. Pumping with a P polarized pump will preferentially excite molecules with transitions that are oriented out-of-plane (standing up). Pumping with an S polarized pump will preferentially excite molecules whose transition are oriented more towards the in-the-plane (lying flat) configuration. Different solvation time constants for S and P pumping would indicate orientationally dependent solvent interactions.

While the pump excites solute molecules beyond the surface, the TRSHG technique only monitors the interfacial solute molecules due to the surface specificity of SH, which results from the fact that SH is electric dipole forbidden by symmetry in centrosymmetric bulk media.[19] Only those probe molecules present at the interface where inversion symmetry is broken can contribute to the SH signal.

Solvation describes the influence of the solvent on the relative energies of the electronic states of molecules, which thereby affect the electronic absorption and emission spectra. The ground-state S_0 of coumarin 314 has a large permanent dipole moment of 8.2 D.[20] Water is highly polar, and initially, the neighboring solvent molecules are organized in a way to minimize the energy of the ground state of C314. Upon excitation, the dipole moment of C314 instantly increases by about 4 D.[21] However, the solvent shell is still in a configuration determined by the less polar ground states. Following the photoexcitation, the water rapidly reorganizes in response to the larger dipole moment of excited state C314, thereby decreasing the energy between the ground and excited states.

Traditional fluorescence experiments in bulk liquids have related the time evolution of the solvent to the Stokes shift response function[1−3]

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$$C(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)} \quad (1)$$

where the $\omega(0)$, $\omega(\infty)$, and $\omega(t)$ frequencies correspond to the fluorescence emission maxima of the solute molecule immediately after excitation, at equilibrium, and at intermediate times as the transition energy evolves as the solvent relaxes.

There have been several measurements of the solvation dynamics in bulk water using conventional time-resolved fluorescence methods. Measurements using 7-dimethylamino-coumarin-4-acetate yielded bi-exponential decays with time constants of $\tau_1 = 160$ fs and $\tau_2 = 1.2$ ps, with an amplitude weighted average solvation time of $\langle\tau_s\rangle = 860$ fs.[4] Measurements using coumarin 343 yielded time constants of $\tau_1 = 250$ fs and $\tau_2 = 960$ fs, with an amplitude weighted average solvation time of $\langle\tau_s\rangle = 610$ fs.[5] More recent measurements on C343 with better time resolution beyond our instrument resolution show an additional sub 100 fs component.[6] C343 is structurally very similar to C314 having the ethyl ester group in C314 replaced by a carboxylic acid group.

There are two possible methods to relate $C(t)$ to experimental measurements of the time dependent SH signal. A sequence of SH measurements of $\chi^{(2)}(t)$ taken at many wavelengths could be used to spectrally reconstruct the time dependent SH spectrum and extract $\omega(0)$, $\omega(\infty)$, and $\omega(t)$ to compute $C(t)$ directly. In the second method a single probe wavelength is selected for which $\chi^{(2)}(t)$ is directly proportional to $C(t)$. This linear wavelength method relies on a linear relationship between the magnitude of the SH response at the chosen wavelength and the solvation coordinate (see Figure 2 of ref 13). The linear wavelength procedure has been shown to work very well yielding bulk solvation kinetics within 10−20% of the spectral reconstruction method.[4,22]

Theory

Elements of the theory of the measurement of interfacial electronic excited state solvation dynamics by time-resolved second-harmonic generation (TRSHG) have been presented previously.[9] The second harmonic signal field generated at the interface is proportional to the square root of the experimentally measured intensity, $E(2\omega) = \sqrt{I(2\omega)}$. The SH field is proportional to the induced second order nonlinear polarization, $E(2\omega) \propto P^{(2)}(2\omega)$. The SH polarizations with components i, j, and k, referring to the laboratory axes, can be written as the probe electric field acting twice multiplied by the second-order nonlinear susceptibility,

$$P_i(2\omega;t) = \chi_{i,j,k}(2\omega,\omega,\omega;t)E_j(\omega)E_k(\omega) \quad (2)$$

where the subscripts i, j, k are determined by the polarization of the analyzed SH and probe fundamental. The surface second-order nonlinear susceptibility tensor for an ensemble of solutes at the air/water interface can be expressed as[17,19]

$$\chi^{(2)}{}_{ijk}(eq) = N\sum\langle T^{ijk}_{lmn}\alpha^{(2)}_{lmn}(\omega,\theta)\rangle \quad (3)$$

where T^{ijk}_{lmn} is the direction cosine matrix that transforms the laboratory frame (i, j, k) into the molecular frame (l, m, n), N is the number density of molecules at the interface, $\alpha^{(2)}_{lmn}(\omega,\theta)$ is the interfacial molecular hyperpolarizability for the l, m, n axes, and $\langle\ \rangle$ denotes the orientational ensemble average. The hyperpolarizability depends on the probe frequency ω and the out-of-plane angle θ (there is no dependence on the in-plane angle ϕ because of in plane isotropy). The transition dipole moment of the solute is taken to be the reference axis of the molecule (see Figure 1 of ref 17).

The pump pulse excites an orientational subset of molecules from the interfacial anisotropic orientational distribution, thereby altering the orientational average in eq 4. The probability that a specific ground-state orientation is excited is related to the square of the pump electric field projected onto the solute transition dipole moment. The probe SH susceptibility at time t is given by

$$\chi^{(2)}{}_{i,j,k}(\Theta;t) = (N - N_e)\sum\langle T^{ijk}_{lmn}\alpha^{(2)}_{lmn_g}(\omega,\theta)\rangle_{g(PorS)} + N_e\sum\langle T^{ijk}_{lmn}\alpha^{(2)}_{lmn_e}(\omega,\theta;t)\rangle_{e(PorS)} \quad (4)$$

The right hand term in eq 4 contains all of the polarization dependent excited state solvation dynamics. The orientational average selected by the pump is denoted by "P" or "S" in the orientational average. The number density of excited molecules is N_e and the total number density of adsorbates is N. The C314 does not reorient nor decay on the time scale of excited-state solvation, which means that the orientational distribution and N_e are constant.[17] The change in SH with solvation is due to the change in resonance of S_1-S_0 with the second-harmonic light, which reduces the magnitudes of the hyperpolarizability $\alpha^{(2)}_{lmn_e}(\omega,\theta;t)$.

If the adsorbate molecule has uniaxial symmetry, there is only one microscopic hyperpolarizability element in the ground and excited states, and the macroscopic elements $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zxx}$ have the same orientational average. Previous measurements show that the orientational and solvation dynamics for C314 at the air/water interface are the same for these two elements, i.e., $\chi^{(2)}_{xzx} = \chi^{(2)}_{zxx}$.[13,17] Since the only strong SH resonance enhancement for C314 is the two photon resonance of the ground S_0 and lowest excited state S_1, we make the approximation that C314 is a two level system. Furthermore, we make the approximation that the C314 has uniaxial symmetry where the hyperpolarizability elements are $\alpha^{(2)}_{\zeta\zeta\zeta_g}(\omega,\theta)$ for ground state and $\alpha^{(2)}_{\zeta\zeta\zeta_e}(\omega,\theta;t)$ for the excited state.

The second harmonic spectral line shape can be expressed by perturbation theory assuming a simple phenomenological pure dephasing function. The excited-state hyperpolarizability $\alpha^{(2)}_{\zeta\zeta\zeta_e}(\omega,\theta;t)$ is time dependent because the $S_1 \rightarrow S_0$ transition energy $\omega_{eg}(\theta;t)$ changes as the water reorganizes around the excited state dipole. The hyperpolarizability is given by,

$$\alpha^{(2)}_{\zeta\zeta\zeta_e}(\omega,\theta;t) \propto \frac{\mu_{ge}\sigma_e}{(\omega_{eg}(\theta;t) - 2\omega + i\Gamma_{ge})} \quad (5)$$

where μ_{ge} is the transition dipole matrix element between the ground and excited state, Γ_{ge} is the line width for the transition, and σ is a collection of time independent terms. Initially the hyperpolarizabilities are equal in magnitude but opposite in sign, $\alpha^{(2)}_e = -\alpha^{(2)}_g$.

Experimental Section

Coumarin 314 was obtained commercially (Acros) and used without further purification. The 30 μM C314−water solution was at pH 6.5 and the temperature at 23 °C, which is the same as the experimental conditions in the previous report.[13] The water was doubly distilled and dionized.

The TRSHG setup is similar to the one described in refs 9 and 10. A regeneratively amplified Ti:Sapphire laser (Clark MXR) was used to generate pulses of about 100 fs duration, 1

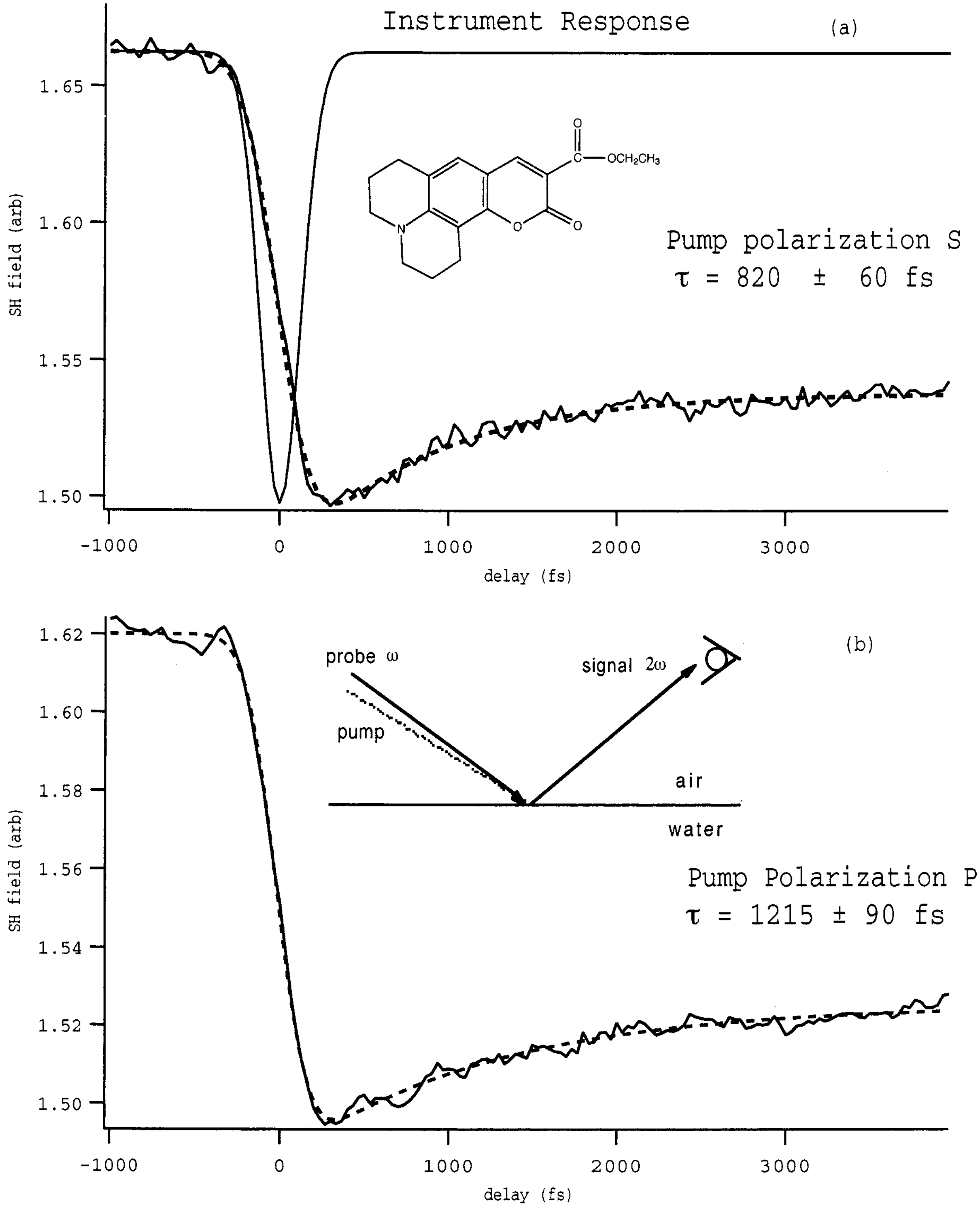

Figure 1. Orientational dependent dynamics of electronic excited-state solvation of coumarin 314 at the air-water interface for 840 nm probe (SH at 420), $\chi^{(2)}_{xzx}$ element. The pump was at 420 nm. (a) Pump polarization S (in-plane). The normalized change in SH field is plotted vs pump delay. The line through the data is a fit to a single exponential giving a decay time of 820 ± 60 fs. (b) Pump polarization P (out-of-plane). The normalized change in SH field is plotted vs pump delay. The line through the data is a fit to a single exponential giving a decay time of 1215 ± 90 fs.

mJ energy at 840 nm, and at a repetition rate of 1 Khz. The pump excitation light at 420 nm was obtained by frequency doubling the fundamental. A 500 nJ pump pulse was focused by a 20 cm focal length lens to a 500 μm diameter spot size at the interface. The pump intensity was at all times well below saturation. A half-wave plate followed by a quarter wave plate (both zero-order quartz at 420 nm) were used to control the polarization. The linear polarizations were verified to be better than 300:1.

Part of the fundamental beam served as the probe beam. The probe was sent through a half-wave plate−polarizer attenuator and then focused onto the sample by a 20 cm focal length lens to a 400 μm spot diameter. Both the pump and the probe were directed to the sample at an angle 70° from normal. The pump and probe beams were separated by a small angle, approximately 5°, to ensure maximum temporal resolution. The polarization of the probe and the setting of the analyzer could be varied to select the desired tensor element of $\chi^{(2)}$. A colored long-wave pass glass filter was placed in the probe beam immediately before the sample to block any spurious source of SH. A polarizer was used to analyze the SH signal of the desired element of $\chi^{(2)}$. Finally, a colored short-wave pass glass filter was used to block any remaining fundamental, and the SH was focused into a $^1/_4$ m monochromator, detected by a photomultiplier tube (R4220P, Hammatsu), and signal averaged by a computerized system.[13,17] Typically 40 data sets were averaged at each pump polarization.

Results and Discussion

The orientation dependent excited-state solvation dynamics of 30 μM coumarin 314 at the air/water interface for the $\chi^{(2)}{}_{xzx}$ element probed at 840 nm (SH at 420 nm) are shown in Figure 1. The normalized change in SH field is plotted vs. pump delay. The top curve (dotted) shows the decay for S-polarized pumping. The line through the data is a fit to a single exponential giving a decay time of 820 ± 60 fs. The bottom curve (dashed) shows the decay for P-polarized pumping. The line through the data is a fit to a single exponential giving a decay time of 1215 ± 90 fs. The sum frequency cross correlation of the pump and the probe having a fwhm = 180 fs is shown to illustrate the temporal resolution.

Two physical processes that could result in differing S and P polarized pumped TRSHG solvation dynamics are the following. First, the static electronic transition energies of C314 could depend on the out-of-plane orientation of C314 at the air/water interface. The center frequency of the SH excited state spectral line shape (given by $\alpha^{(2)}_{\zeta\zeta\zeta_e}(\omega,\theta;t)$ in eqs 3−5 will depend on whether the pump was S or P polarized. It is possible that the more vertical (P pumped) excited state C314 molecules could be blue shifted in comparison to the more horizontal (S pumped) molecules. If we consider a dipole oriented parallel (in-plane) to a dielectric with one oriented closer to the perpendicular (out of plane) then in the continuum dielectric description the parallel dipole would be at lower energy than the more perpendicular oriented dipole. Because the observed dynamics is dependent on where in the spectral envelope the dynamics is being monitored the S and P pumped molecules could yield different solvation time constants. We calculate that a shift of only 5 nm between the S and P pumped spectral envelopes would be sufficient to account for the different solvation times.

A second physical process that could be responsible for the observed difference in the S vs P pumped solvation dynamics measured at 840 m would be differing motions of the water molecules surrounding the “in-plane” vs “out-of-plane” oriented coumarin molecules. This would imply that the solvation motions of the water solvated around the more horizontal (S pumped) distribution of C314 are faster in comparison to the more vertical (P pumped) distribution. However, this possibility seems to be less likely than differing excited state spectra causing a difference in the S and P pumped dynamics. Solvation dynamics are due to solvent-solvent interactions and bulk measurements do not strongly depend on the probe solute.[4,5] Furthermore second harmonic measurements of interfacial solvatochromism suggest that the solvation effect is long range, which if applicable to the interface solvation dynamics would suggest that the solvent motions of the water molecules beyond the first shell are of major importance in the dynamics.[23] Thus the water motions responding to the change in the C314 dipole moment would be similar for the in vs. out of plane molecules. We thus attribute the difference in the S pumped and P pumped solvation dynamics to a shifting of the spectral envelopes of the S vs P pumped molecules.

Conclusion

An orientational dependence of excited-state solvation dynamics of coumarin 314 (C314) adsorbed at the air/water interface was observed by femtosecond time-resolved surface second harmonic generation. The second harmonic response to excited state solvation was measured for the probe fundamental at 840 nm with two pump polarizations (S and P). The more horizontally oriented S pumped distribution solvation decay time was 820 ± 60 fs. The more vertically oriented P pumped distribution solvation decay time was 1215 ± 90 fs. The results indicate that the solvation environments of C314 at the air/water interface depend on the out-of-plane orientation of C314 or equivalently that the S0→S1 spectrum is inhomogeneously broadened on the solvation time scale due to the different C314 orientations at the air/water interface.

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