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Femtosecond dynamics of solvation at the air/water interface

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Abstract

The electronic excited-state solvation dynamics of coumarin 314 (C314) adsorbed at the air/water interface was investigated by femtosecond time-resolved surface second-harmonic generation (TRSHG). This Letter presents the first use of TRSHG to measure solvation dynamics and presents the theoretical basis for monitoring electronic excited-state solvation with TRSHG. The interfacial electronic excited solvation time of C314 was measured to be 790 ± 30 fs. This is close to bulk results and is in agreement with simple dielectric continuum models of solvation and the predictions of molecular dynamics simulations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The physical and chemical properties of interfaces are of great importance to fundamental science, medicine and technology [1–4]. Intrinsic to the interface is the asymmetrical environment experienced by the chemical species at the interface [5,6], whether they are in the form of a solid, or a molecular species as in a gas or liquid, or are interface charges made up of electrons or ions. The solvation dynamics of species within an interfacial environment, although an important aspect of adsorbate–solvent interactions, has been relatively unexplored. For bulk liquids, the measurement and the theory of electronic excited-state solvation has been the focus of many studies [7–12] because of its relevance to chemical processes, such as proton transfer [13] and photo-induced electron transfer reactions in chemical and biological systems [14–16]. The asymmetric interfacial environment has properties that differ from either bulk media in structure [17], composition, and polarity [18,19]. Likewise, the interfacial solvent dynamics can differ from the dynamics in either of the bulk media that define the interface. In this study, the solvation dynamics of coumarin 314 (C314; Fig. 1) at the air/water interface was investigated by time-resolved second-harmonic generation (TRSHG), which is the first use of TRSHG to measure the solvation dynamics at interfaces.

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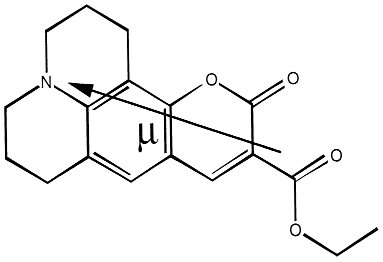

Coumarin 314

Fig. 1. C314. The arrow shows the direction of the permanent dipole moment and the transition dipole moment of the S_0 to S_1 transition.

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 electronic excited-state solvation process for C314 (Fig. 1) in water is illustrated schematically in Fig. 2. The ground state S_0 of C314 has a large permanent dipole moment of 8.2 debye [20]. Water is highly polar and, initially, the water solvent shell is organized around the C314 in a way to minimize the energy of the ground state (lower left). Upon excitation, the dipole moment of C314 instantly increases about 4 debye [21]. However, the water solvent shell is still in a configuration best suited for the less polar ground state (upper left). The solvent shell rapidly reorganizes in reaction to the larger dipole moment of excited state C314, decreasing the energy between the ground and excited states (middle right). The solvation of the excited state is responsible for the large Stokes shift of fluorescence of 30 nm for C314 in bulk water.

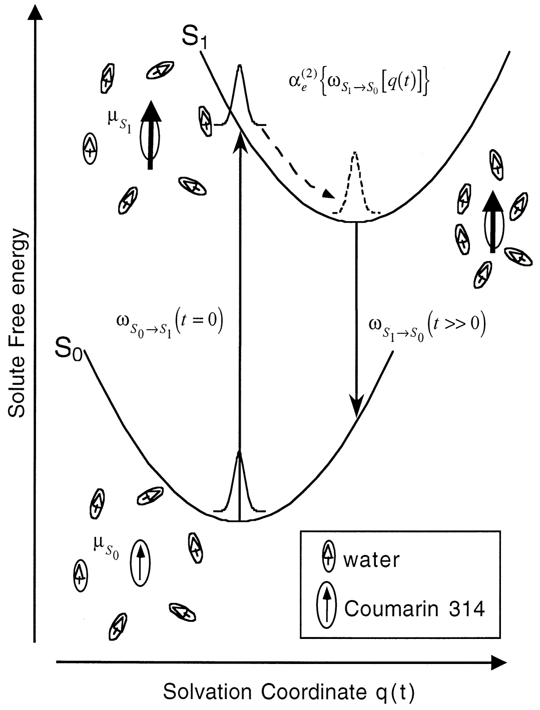

Fig. 2. Schematic of the solvation process.

Traditional fluorescence experiments in bulk liquids have related the time evolution of the solvent to the Stokes shift response function [7–9],

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

where $\omega(0)$, $\omega(\infty)$, and $\omega(t)$ are the optical frequencies that correspond to the fluorescence emission maxima of the solute molecule immediately after the photon is adsorbed ($t = 0$ in Fig. 2), at the time when the solute and solvent have reached equilibrium ($t \gg 0$ in Fig. 2), and at intermediate times t, as the solute transition energy is evolving as the solvent relaxes (upper curve in Fig. 2). $C(t)$ is related to the solvation coordinate $q(t)$ in Fig. 2 [22].

It is difficult to use conventional time-resolved fluorescence spectroscopy to measure interfacial electronic excited-state solvation because, in general, the fluorescence signal from solute within the bulk easily overwhelms the interfacial fluorescence. Time-resolved fluorescence techniques can typically be used only when the probe is so insoluble that it is present chiefly at the interface or confined to a restricted geometry with a very small bulk volume [6,23,24]. Time-resolved fluorescence has been used to measure the solvation dynamics of oil in water micelles [25] and water in oil reverse micelles [26]. Occasionally one of the bulk media has a favorable index of refraction to allow the fluorescence to be probed by total internal reflectance (TIR) [23,27]. TIR fluorescence spectroscopy has been used to measure the solvation dynamics of coumarin 460 (C460) at the 1-butanol/sapphire interface [27]. It was found that the solvation dynamics of C460 at 1-butanol/sapphire interface is slower than in bulk 1-butanol [27]. Although TIR provides important results, it is not rigorously surface specific because the evanescent wave probes hundreds of molecular layers ($\geqslant 500$ Å) beyond the surface, regardless of the angle of incidence.

The surface specificity of the SH signal gives TRSHG a great advantage over other spectroscopic methods sensitive to solvation. Second-harmonic (SH) signal is generated only by the chosen interfacial adsorbate (see Refs. [1,2] for reviews of SH spectroscopy). There is no interference from the bulk solute, since SH is electric dipole forbidden by symmetry in isotropic bulk media [1,2]. Only those probe molecules present at the interface where inversion symmetry is broken can contribute to the SH signal.

TRSHG has been used to study molecular dynamics of molecules at the air/quartz [28] and the liquid/quartz [29] interfaces. Rotational relaxation has been studied at the air/water interface [30,31] as well as processes like energy transfer and photoisomerization [32] among others. Recently we have used TRSHG to study the rotational motions of C314 at the air/water interface [30], which is the same system as the solvation studies in this Letter. Because both the out-of-plane (350 ps) and in-plane (600 ps) rotation times, as well as the 4.5 ns ground-state recovery time of C314 at the air/water interface, all occur on a longer timescale [30], it is possible to separate these processes from that of the much more rapid solvation dynamics.

There have been several measurements of the solvation dynamics in bulk water using conventional time-resolved fluorescence. In general, the decay of $C(t)$ was found to be bi-exponential. Measurements using 7-dimethylaminocoumarin-4-acetate yielded 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 [10]. Measurements using C343 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 [11]. More recent measurements on C343 with better time resolution show an additional sub-100 fs component [12]. C343 is structurally very similar to C314. The ethyl-ester group in C314 is replaced with a carboxylic acid group in C343.

2. Second-harmonic detection of interfacial excited-state solvation

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.

While the pump may excite solute beyond the surface, the technique only monitors the solute in the surface layer due to the surface specificity of SH. The SH signal is strongly dependent on being two-photon resonant with either the ground-state or the excited-state solute molecules. The strategy to detect electronic excited-state solvation is to excite the $S_0 \rightarrow S_1$ transition of the C314 molecules with a pump pulse and then monitor the change in SH probe signal as the $S_1 \rightarrow S_0$ transition energy changes with solvation.

The SH signal field generated at the interface is proportional to the square root of the experimentally measured intensity, $I(2\omega) = \sqrt{E(2\omega)}$. The SH field is proportional to the induced second-order non-linear polarization, $E(2\omega) \propto P^{(2)}(2\omega)$. The SH polarizations with components i, j, and k can be written as the probe electric field acting twice times the second-order non-linear polarizability,

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

where the subscripts i, j, k are determined by the polarization of the analyzed SH and probe fundamental. All spectral dynamics are included in this tensor. The surface second-order non-linear susceptibility tensor for a ground-state ensemble of C314 at the air/water interface can be expressed as [1]

$$\chi_{ijk_g}^{(2)}(eq) = N_g \Sigma \langle T_{lmn}^{ijk} \rangle_g\, \alpha_{lmn_g}^{(2)}\,, \tag{3}$$

where T_{lmn}^{ijk} is the direction cosine matrix that transforms the laboratory frame (i,j,k) into the molecular frame (l,m,n), N_g is the number of ground-state molecules at the surface at equilibrium, $\alpha_{lmn_g}^{(2)}$ is the molecular hyperpolarizability for the l,m,n axes and $\langle\ \rangle$ denotes the orientational ensemble average.

The number of non-zero hyperpolarizability elements $\alpha_{lmn}^{(2)}$ contributing to Eq. (3) is determined by the symmetry of the molecule and its electronic structure. 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. In this case there is only one non-zero hyperpolarizability element for ground state, $\alpha_g^{(2)}$, and the excited state, $\alpha_e^{(2)}$ which we found to be experimentally supported by the previous observation that $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$ are equal for C314 at the air/water interface [30]. The orientational dynamics of C314 at the air/water interface occur two orders of magnitude slower than solvation [30], so for any experimentally chosen susceptibility $\chi_{ijk}^{(2)}$ the orientational average is constant in time. The average over all possible orientations at the interface can be made implicit. For brevity, the indices associated with the tensorial nature of both $\chi^{(2)}$ and $\alpha^{(2)}$ will be dropped.

For negative time delays, ($t < 0$, i.e., probe arrives before the pump), the total SH susceptibility of the molecules is simply its equilibrium ground-state susceptibility,

$$\chi^{(2)}(t<0) = \sigma_g N_0 \alpha_g^{(2)}\,, \tag{4}$$

where N_0 is the number of interfacial solute molecules per unit area, $\alpha_g^{(2)}$ is the ground-state molecular hyperpolarizability, and σ_g is a constant appropriate for the ground-state orientational average.

After excitation by the pump, the susceptibility becomes time dependent,

$$\chi^{(2)}(t) = \sigma_g N_g \alpha_g^{(2)} + \sigma_e N_e \alpha_e^{(2)}(t)\,, \tag{5}$$

where N_e is the number of molecules excited by the pump, N_g the number of remaining ground states ($N_g = N_0 - N_e$), $\alpha_e^{(2)}(t)$ is the *time-dependent* excited-state molecular hyperpolarizability, and σ_e is a constant appropriate for the excited-state orientational average. Since the ground-state recovery is up to three orders of magnitude slower than solvation [30], N_g and N_e can be taken to be constant.

The spectral dependence of the resonant part of the ground-state hyperpolarizability $\alpha_g^{(2)}$, on the fundamental laser frequency (ω) and the second harmonic (2ω) is given by [18,19]

$$\alpha_g^{(2)} \propto \sum_k \frac{\mu_{S_0 \rightarrow k}\, \mu_{k \rightarrow S_1}\, \mu_{S_1 \rightarrow S_0}}{\left(\omega_{S_0 \rightarrow k} - \omega + \mathrm{i}\Gamma_{S_0 \rightarrow k}\right)\left(\omega_{S_1 \rightarrow S_0} - 2\omega + \mathrm{i}\Gamma_{S_1 \rightarrow S_0}\right)}\,, \tag{6}$$

where μ_{ij} is the transition dipole matrix element between the states i and j, ω_{ij} is the transition frequency between states i and j, and Γ_{ij} is the line width for the transition. The frequencies ω and 2ω are determined by the probe laser and are not varied. For C314, the only resonant quantity in the denominator is the SH transition at 2ω between S_0 and S_1, $\omega_{S_0 \to S_1}$. Since solvent reorganization only occurs for the excited states, the transition energy $\omega_{S_0 \to S_1}$ for the ground state does not change and the hyperpolarizability $\alpha_g^{(2)}$ is constant in time.

The excited state hyperpolarizability $\alpha_e^{(2)}(t)$, however, is *not* constant in time, because the $S_1 \to S_0$ transition energy for the excited molecules depends on the solvation coordinate $q(t)$, $\omega_{S_1 \to S_0}(q(t))$. As the water reorganizes around the excited-state dipole of C314, the transition frequency $\omega_{S_1 \to S_0}(q(t))$ changes in time. The time-dependent hyperpolarizability $\alpha_e^{(2)}$ is given by

$$\alpha_e^{(2)}(t) \propto \sum_k \frac{\mu_{S_1 \to k}\, \mu_{k \to S_0}\, \mu_{S_0 \to S_1}}{\left(\omega_{S_1 \to k} - \omega + \mathrm{i}\Gamma_{S_1 \to k}\right)\left(\omega_{S_0 \to S_1}(q(t)) - 2\omega + \mathrm{i}\Gamma_{S_0 \to S_1}\right)} . \tag{7}$$

Note that initially at $t = 0$, before any solvation takes place, the microscopic hyperpolarizabilities are equal in magnitude but opposite in sign, $\alpha_e^{(2)} = -\alpha_g^{(2)}$ for the two-state model.

There are two possible methods to relate $C(t)$ to experimental measurements of $\chi^{(2)}(t)$ in Eq. (5). A sequence of 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. This method is experimentally tedious. Alternately, it is possible to choose to make a measurement of $\chi^{(2)}(t)$ at a single wavelength where $\chi^{(2)}(t)$ is directly proportional to $C(t)$. This linear wavelength method [9,33] relies on a linear relationship between the magnitude of the spectra at the chosen wavelength and the solvent coordinate $q(t)$. The spectra for solvent coordinate q can be correlated to the equilibrium spectra with the solvent polarity parameter $E_t(30)$ [9] and the linear wavelength predicted from the equilibrium data.

The air/liquid and liquid/liquid interfaces do not have the static polarity that correspond to either bulk media that border the interface [18,19]. SH experiments have shown that the solvent polarity parameter of the interface is the average of the polarity parameters of the bulk media, at least for the several interfaces studied [18,19]. The air/water interface was found to be less polar than bulk water, having a polarity close to bulk butyl ether. While the absorbance maximum of C314 is 448 nm in bulk water, the interface absorbance maximum is predicted to be 417 nm [18,19]. We have measured the fluorescence spectra of C314 as a function of polarity, and have found from these spectra that 420 nm is a wavelength that allows us to use a single wavelength to follow the solvation dynamics. Hence by pumping at 420 nm and probing at 840 nm, $\chi^{(2)}(t)$ can be taken to be proportional to $C(t)$. Furthermore, by pumping slightly to the red of the origin, there should be no contribution of vibrational relaxation to the dynamics.

3. Experimental

The probe molecule chosen for this study was C314 (Fig. 1). C314 was obtained commercially (Acros) and used without further purification. All solution concentrations were measured by UV/VIS spectroscopy. The solution pH was 6.5. All experiments were performed at 23°C.

C314 is a water-soluble ester that is surface active. It was found from surface tension measurements that the surface excess of C314 did not exceed 5×10^{13} molecules/cm^2 at the bulk saturation concentration of 30 μM. Experiments were typically run at a 26 μM bulk concentration to maximize signal. No change in dynamics was observed with 14 μM bulk concentration. This indicates that energy transfer and dimerizations were not factors in these experiments. C314 is ideal for SH spectroscopy using femtosecond Ti:Sapphire lasers because the electronic origin provides a strong two-photon resonance enhancement to the SH from an 840 nm fundamental probe. C314 has an extinction coefficient of 45000 L/Mcm, which allows for substantial excitation by a low-power pump.

The TRSHG setup to detect electronic excited-state solvation dynamics is a pump–probe geometry similar to the one described in Ref. [30] (Fig. 2). Briefly, a regeneratively amplified Ti:Sapphire laser (Clark MXR) was used to generate pulses of about 100 fs duration, 1 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 1 m f.l. lens to a 1 mm diameter spot size at the interface, and directed to the sample at an angle 70° from normal. 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 attenuater, and then focused onto the sample by a 1 m f.l. lens to a 1 mm spot diameter. The probe incidence angle was close to 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. Care was taken choosing optics that did not substantially temporally broaden either the pump and the probe beams. The sum-frequency cross-correlation of the probe and pump from the neat air/water interface was recorded before each solvation pump–probe experiment.

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 (Jarrell Ash) and detected by a photomultiplier tube (R4220P, Hammatsu). The signal from the PMT was averaged by a box-car-gated integrator (SRS) with a typical effective time constant of 300 ms. Laser stability was excellent ($< 1\%$ shot to shot) so that shot-to-shot normalization was not necessary. The box-car signal was digitized by a computer A/D board (National Instruments) and the SH was recorded as a function of pump-delay by the computer (Apple Macintosh). Typically 40 data sets were averaged at each pump polarization.

A shallow Teflon beaker was used to contain the C314 solution. This beaker was rotated at 1 rpm with the probe spot 1 cm off axis in order to minimize any heating or other photoinduced process in the pump/probe region of the surface. No sample degradation was observed. The measured kinetics did not change upon reduction of power by 50%.

4. Results and discussion

The TRSHG measured dynamics of electronic excited-state solvation of 26 μM C314 at the air/water interface is shown in Fig. 3. The 420 nm pump was s-polarized. The $\chi^{(2)}_{xzx}$ susceptibility element was selected by polarizing the 840 nm probe 45° with respect to normal and detecting the s-polarized component of the second harmonic. The normalized $\chi^{(2)}_{xzx}$ SH electric field at 420 nm is plotted versus pump delay. The dashed line is a fit to a single exponential plus baseline giving a solvation decay time of $\tau_s = 790 \pm 30$ fs. The baseline represents the remaining contribution of the ground states to the SH. Because the change in the SH signal does not recover to half of its maximum value, the fully solvated excited state is still partially two-photon resonant with the probe. The data did not yield a better fit with a bi-exponential decay function. The sum-frequency cross-correlation of the pump and the probe with FWHM = 180 fs is shown to illustrate the temporal resolution.

Note that while the presence of air on one side of C314 may change the polarity of the interface and the static Stokes shift, air itself does not solvate in response to the increased dipole moment of C314. Hence in this case, the dynamics are due solely to water solvation. The air/water interface is not necessarily the most general result; a liquid/liquid interface having two polarizable liquids adjacent to it could be expected to have more complex dynamics.

The air/water solvation time of $\tau_s = 790$ is substantially similar to the longer component (or average values) of 690–880 fs previously measured in bulk water. Unlike bulk water, only one solvation component greater than

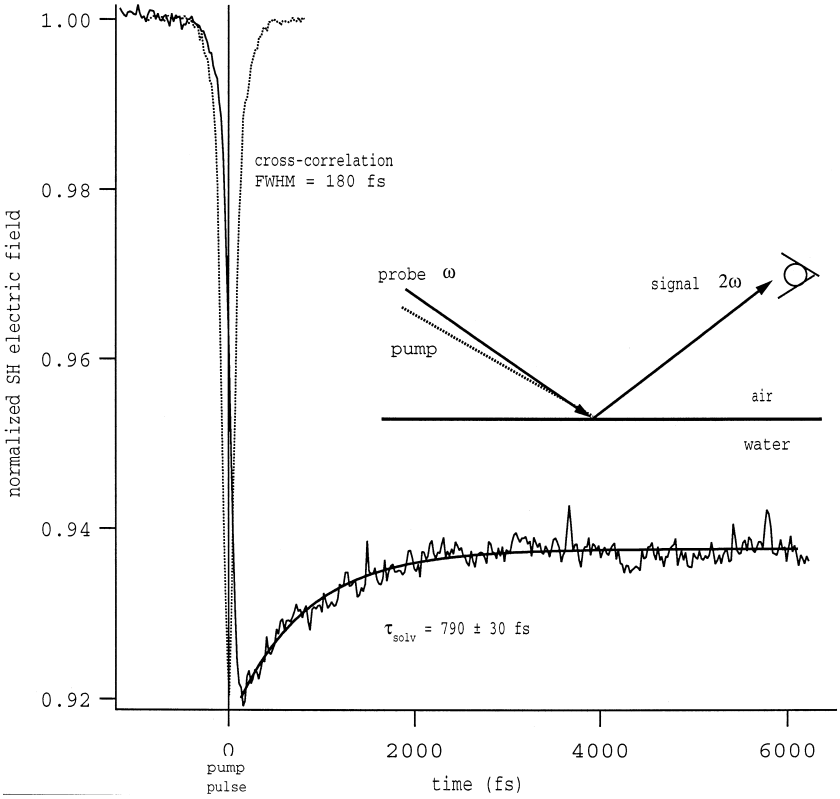

Fig. 3. Dynamics of electronic excited-state solvation of C314 at the air/water interface. The probe was at 840 nm. The pump was at 420 nm. The dashed line is a fit to a single exponential giving a decay time of 790 ± 30 fs. The sum-frequency cross-correlation of the pump and the prove with FWHM = 180 fs is shown to illustrate the temporal resolution.

100 fs is observed; the temporal resolution of this experiment was not adequate to measure the sub-100 fs inertial component [12].

The measured solvation time of $\tau_s = 790$ fs is in reasonable agreement with the simple dielectric continuum model (DCM) that predicts the bulk solvation time to be equal to the longitudinal dielectric relaxation time of bulk water, $\tau_l = 590$ fs [10,34]. One possibility for the agreement to the bulk prediction is that the solvation depends on long-range as well as short-range interactions of the solute with the solvent, an interpretation that is also supported by static measurements of interface polarity [18,19]. Here we consider short-range interactions to mean interactions with the first solvent shell, whereas long-range interactions are from the second shell to infinity. From the static polarity studies it was found that the interface polarity value, for a range of water interfaces (air/water, chlorobenzene/water 1,2-dichloroethane/water, and heptane/water), could be accurately predicted from measurements of the bulk polarites on either side of a given interface. It was proposed therefore that a significant part of the solute–solvent interactions (~ 70%) extended from the second solvent shell and beyond. The reason that we use the bulk longitudinal relaxation time of water and not that for surface water, which may be considerably longer, is based on the experimental polarity results and because the interactions involve large solute dipole–solvent interactions. The precise number of shells that contribute significantly to the long-range interactions is not known. The equivalence of the bulk water and air/water solvation times is also supported by molecular dynamics studies which indicate that the bulk and surface dynamic response is nearly identical because the solvent shell of the surface solute is nearly identical to the bulk solute [34,35].

The similarity of the C314 interfacial air/water and bulk water solvation times, in contrast to the differing C460 bulk 1-butanol and 1-butanol/sapphire interfacial solvation times [27], could be due to the very different effects of an air/liquid interface compared with a solid/liquid interface. This is especially important when the surface of the solid, which in this case is sapphire, can hydrogen bond with the solvent molecules of the liquid. It has been proposed that solvation in alcohols depends strongly on the dynamics of the alcohol hydrogen bond network, which could be stabilized at the 1-butanol/sapphire interface by the surface hydroxy groups of sapphire [27]. Unlike 1-butanol at the sapphire surface, water molecules at the air/water interface cannot hydrogen bond with the air-phase.

Experiments are currently underway using SH probes at longer wavelengths that are resonant with the final solvated excited state. Preliminary results show a time-dependent solvation at longer wavelengths, indicating that the solvation of the excited state continues to be responsible for the observed dynamics.

5. Conclusion

The electronic excited-state solvation dynamics of C314 adsorbed at the air/water interface was investigated by femtosecond TRSHG. The use of TRSHG to measure solvation dynamics was demonstrated and the theoretical basis for monitoring electronic excited-state solvation with TRSHG was discussed. The interfacial excited-state solvation time of C314 was measured to be 790 ± 30 fs. This is substantially similar to solvation results in bulk water and is in approximate agreement with simple dielectric continuum models and molecular dynamics simulations.

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