Polar Solvation Dynamics of H₂O and D₂O at the Surface of Zirconia Nanoparticles

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Time-resolved fluorescence-upconversion spectroscopy has been used to study the polar solvation dynamics of H_2O and D_2O at the surface of zirconia (ZrO₂) nanoparticles. While an isotope effect is observed for the solvation dynamics of bulk D_2O , there is no isotope effect on the interfacial solvation dynamics. The interfacial solvation dynamics are the same for H_2O and D_2O and are faster than the bulk solutions. The bulk isotope effect is due to stronger hydrogen bonding in D_2O compared to H_2O , slowing the reorientation of the excited-state dipoles in the bulk D_2O . The lack of isotope effect for the interfacial dynamics is explained in terms of the solvent interacting with the ZrO₂ surface.

I. Introduction

The interaction of liquids with solid surfaces finds application in many different areas of chemistry including chromatography, heterogeneous catalysis, and solar energy harvesting. Despite their ubiquity, little is known about the structure of liquids at solid surfaces and even less is known about dynamical aspects of liquids interacting with solid surfaces. In this paper, we report on the dynamics of H₂O and D₂O molecules interacting with the surface of nanoparticulate ZrO₂.

This system is interesting for several reasons. Among others, it serves as a model for TiO₂. In recent years, dye-sensitized TiO₂ nanoparticles have become a promising medium for the conversion of solar energy into electrical energy in photoelectrochemical cells.¹⁻⁵ Dye sensitization overcomes the large band gap of TiO₂ using an adsorbed molecule to inject the electron from the molecule to the semiconductor. The electron injection time from the adsorbed dye to the semiconductor has been measured to be ultrafast, typically <200 fs, and is similar for the all dye-semiconductor systems that have been measured.^{2,3,6-13} This ultrafast electron injection has been attributed to strong electronic coupling between the dye and conduction band energy levels in the semiconductor. The back reaction from the semiconductor to the solution varies by many orders of magnitude from system to system, and is believed to lie in the Marcus inverted region.^{14–16}

The motion of electrons in solution can be highly sensitive to solvent motion. Indeed, barrierless ultrafast electron-transfer reactions are often determined by the solvation dynamics.^{17,18} Relaxation times for isolated electrons in solution also correlate directly to the ability of the solvent to equilibrate the newly formed charge.¹⁹ The extremely fast electron injection from dye molecules into semiconductor nanoparticles has been attributed to the high density of states in the semiconductor conduction band.²⁰ Though solvent reorganization may not be required for the dye molecule because injection occurs into the conduction band, the nature of the conduction band in the nanoparticles may lead to injection into discrete levels making the electron injection analogous to barrierless electron transfer. Even if injection occurs into a true continuum, solvent motion may be important because it allows electrons to approach the interface. Thus it is important to probe solvent motion at the semiconductor interface.²¹

Solvation dynamics have been studied for a wide range of bulk liquids²² and for some restricted environments. Several experimental techniques have been used to measure solvation dynamics, including time-resolved fluorescence,^{23–25} time-resolved optical Kerr effect,^{26–29} and photon echoes.^{30,31} For all solvents studied there exist two components to the solvation dynamics: an ultrafast, sub-100-fs inertial component and slower diffusive subpicosecond components.³² The solvation dynamics of liquid water have been studied in detail theoretically^{33–37} as well as using ultrafast experimental techniques.^{31,38–41}

The solvation of a solute molecule (or ion) in water has been shown to be bimodal with a Gaussian response at short times, contributing 70%-80% to the total solvation energy, and an exponential response at longer times. These two different responses have been interpreted as different types of solvent motion: an ultrafast, sub-50-fs underdamped component and two slower diffusive components with subpicosecond time constants.

Due to the interactions of solvent molecules with the surface, one would expect the dynamics at interfaces to differ from bulk solution. While the dynamics in bulk solutions have been measured extensively, there are only few reports of measurements at surfaces. Yanagimachi et al.42 studied solvation dynamics of 1-butanol at silica surfaces. While the shorter solvent relaxation time components could not be resolved due to the >60 ps time-resolution of their instrument, the longer time components increased for the interfacial butanol and the solvent appeared to be influenced a substantial distance from the interface. Bessho et al.⁴³ explored fluorescence decays from 1,8-anilino-8-naphthalenesulfonic acid at the water-heptane interface. Like Yanagimachi et al., the polar solvent response observed was also slower at the interface than in bulk. Using time-resolved optical Kerr effect measurements, Fourkas and co-workers44,45 have probed liquid dynamics in porous silicate sol-gel glasses. They demonstrate that for weakly wetting solvents, such as CS₂ and CH₃I, the dynamics of the molecules at the surface are slowed and determined by geometric confinement. However, for more interacting solvents such as acetonitrile the dynamics are influenced by molecular interactions with the

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surface. Recently, we have used ultrafast time-resolved fluorescence techniques to probe the motion of water in reverse micelles^{41,46–49} where we have shown that the water motion inside the reverse micelles is significantly slowed compared to the bulk solutions.

Compared to experimental studies, even fewer models exist for solvent dynamics at any kind of liquid interface.⁵⁰⁻⁵² Chandra et al.⁵³ have developed a time-dependent density functional theory to predict polarization relaxation at the solidliquid interface. They find that while the polarization is smaller at the interface, the relaxation occurs at a faster rate than the bulk relaxes. Ursenbach et al.⁵⁰ have developed a model for water at the surface of a silicon single crystal. Their results show that the vibrational modes of water molecules at the surface are virtually unchanged from their bulk values. However, they suggest that ultrafast motions of the interfacial solvent, occurring on the time scale of molecular vibrations, may impact interfacial electron transfer. Benjamin has simulated the dynamics of water at liquid/liquid interfaces. His molecular dynamics calculations predict little change in the water dynamics at the interface and that as close as one monolayer away from the interface, the dynamics are completely bulklike.⁵¹ Using molecular dynamics calculations, Hartnig et al.54 have simulated water motion within model polar and nonpolar cylindrical pores. In nonpolar pores, reduced hydrogen bonding at the surface results in a translational motion and dipolar motion that is faster than bulk water. However, in polar pores, generated by adding surface charges to the model system, the translation motion and dipolar relaxation times are longer than bulk. Using molecular dynamics calculations, Shinto et al.55 have modeled the response of water at NaCl surfaces. While their simulations show that the water diffusivity is reduced at the surface, they also observe a strong perturbation to the hydrogen-bonding network for solvent molecules at the solid surfaces.

Recently, we studied the solvation dynamics of a 95:5% (v/ v) water/acetone mixture at the ZrO₂ surface.⁵⁶ The interfacial solvent response we observed displayed two subpicosecond diffusive components with the relaxation times similar to that of bulk solution. However, the relative amplitude corresponding to the shorter component was significantly larger for the ZrO₂ solution than the bulk solution, which led to a faster average solvation response for molecules at the ZrO₂ surface. Several questions were generated from this study, such as (i) how does the minuscule acetone component affect the observed dynamics at the surface of ZrO_2 nanoparticle, and (ii) at the surface, do the dynamics depend on the solvent used for the measurements? Is the result universal, that is, would other systems display the same response? To address these and other issues, we report the solvation dynamics of pure H₂O and D₂O at the surface of ZrO₂ nanoparticles. The dynamics are measured for the bulk solutions also in order to compare with the dynamics at the surface of ZrO₂ nanoparticles.

II. Experimental Methods

The ZrO₂ particle solutions were prepared following the previously published synthetic methods for the synthesis of TiO₂ nanoparticles.^{6,57} Briefly, 200 mg of Zr(IV) isopropoxide (Aldrich) was dissolved into 25 mL of 2-propanol (Fisher Scientific, 99.9%). This solution was slowly added (3 mL/min) to 200 mL of acidified H₂O (with 1.2 mL of concentrated HNO₃) at 1 °C under N₂ (air was previously removed from the solution by boiling for 5 min). Milli-Q quality water (18.2 M Ω cm resistivity) was used to avoid impurities in the final ZrO₂ sample. After stirring for 3–4 h the solvent was removed by rotary

evaporation at a temperature lower than 40 °C. The resulting white powder was dried under vacuum overnight. KOH was placed in the desiccator to help remove the excess HNO₃. The ZrO₂ particle radius measured 3.8 ± 0.5 nm via dynamic light scattering (DynaPro-MSTC, Protein Solutions). For the solvation dynamics measurements, we estimate the concentration of nanoparticles in the solution was 1×10^{-3} M. Coumarin 343 (C343, Exciton), was used as a probe molecule without further purification. The dye concentration was 3×10^{-4} M. At these relative concentrations it is unlikely that multiple dye molecules adsorb on a single nanoparticle. At higher relative concentrations of dye to nanoparticle, that is, up to ~20 dye molecules per nanoparticle, the absorption spectra were significantly altered. We discuss these results briefly.

Bulk samples for comparison with the particle suspension were prepared from high-purity H_2O (Milli-Q filtered, 18.2M Ω cm) and D_2O (99.5%, Aldrich). To study the solvent effect on the dynamics at the surface of ZrO₂, we have attempted to make the samples in acetonitrile, ethanol, and 2-propanol but the ZrO₂ did not remain suspended well with these solvents.

The fluorescence upconversion spectrometer used in these experiments has been described in detail previously.⁴¹ Briefly, a mode-locked Ti:sapphire laser produced output pulses centered at 820 nm, with a duration of 160 fs, at 100 MHz repetition rate, and energies of 6.5 nJ/pulse. Frequency doubled laser pulses served to excite the sample, while the residual fundamental light was used to gate the sample fluorescence in a nonlinear BBO crystal. The sum frequency of the fluorescence and the gate pulse was detected as a function of the time delay between excitation and gate pulses. The polarization of the pump and gate pulses is kept at the magic angle to eliminate effects from rotational diffusion. The upconverted signal passed through a monochromator and was detected with a photomultiplier tube. Signals were collected via photon counting interfaced to a computer. Samples were circulated with a peristaltic pump fitted with PTFE tubing.

Data were collected at nine different wavelengths from 455 to 575 nm at 15 nm intervals. The data were fit to a multiexponential function using an iterative—reconvolution fit program with the cross-correlation of the pump and gate pulses as the instrument response function. From these fits, time-resolved fluorescence spectra were reconstructed. The time correlation function, C(t),

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

where v(t), v(0), and $v(\infty)$ are the peak of the fluorescence spectra at time = t, instantaneously, and at equilibrium, respectively, was calculated using the peak position of the reconstructed fluorescence spectra fitted to log-normal line shapes.

Time-resolved fluorescence anisotropy measurements were made for the dye in the ZrO_2 and bulk solutions to quantify dye adsorption to the nanoparticle surface. These measurements were analyzed were via

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)}$$
(2)

where $I_{||}(t)$ and $I_{\perp}(t)$ are the time-dependent intensities of the upconverted fluorescence with the polarization of the pump and probe pulses parallel and perpendicular to each other, respectively. The initial anisotropy was ~0.4 for all samples, showing that initially they are completely isotropic.



Figure 1. (a) Absorption and (b) emission spectra for C343 in bulk H_2O (---), bulk D_2O (---), ZrO_2 in H_2O (--), and ZrO_2 in D_2O (---).

Absorption spectra were recorded with a Cary 2400 UVvis-NIR spectrophotometer. Fluorescence spectra were measured with a home-built fluorometer.

III. Results and Discussion

Sample Characterization. Before time-resolved solvation dynamics measurements were made, samples were characterized via several different methods. First, the steady-state absorption and emission spectra of C343 were measured in bulk H₂O and D₂O, and H₂O/ZrO₂ and D₂O/ZrO₂ samples. These spectra of C343 are shown in Figure 1. Clearly, both the absorption and the emission spectra of C343 in the ZrO₂ solutions shift significantly to longer wavelength compared to the bulk solutions. While the absorption spectra for C343 in the ZrO₂ sample are slightly broader than the bulk samples, the shapes of the emission spectra remain largely unchanged. Part of the red shifting observed for the absorption spectra is most likely due to a difference in the dye's oxidation state. That is, in the acidic ZrO₂ solutions, the dye is found in its neutral form whose spectrum peaks near 458 nm in aqueous solution compared to the peak at 427 nm for the C343 anion in aqueous solution.⁴⁶

The red shift in the steady-state spectra of C343 for the ZrO_2 solutions implies that the environment sensed by the dye in the ZrO_2 solutions differs from bulk solution. Similar red shifts in steady-state spectra have been observed for virtually every dye-sensitized semiconductor system that has been probed. For example, Cherepy et al.² observed a red shift in the absorption and emission spectra of a cyanine dye complexed to the ZrO_2 nanoparticles. They attributed this red shift to the presence of a charge transfer state for the cyanine dye complexed to ZrO_2 in analogy to the cyanine dye complexed to TiO_2 . Martini et al.^{6,58} have also measured red shifts in the absorption spectrum of 9-anthracenecarboxylic acids on TiO_2 and ZrO_2 . They hypothesize that the shifts in the absorption spectra reflect

changes in the polarization energies of the dye's ground and excited electronic state from the interaction of the dye with the particle.

One possible explanation for this effect suggested by Martini et al.⁵⁸ is that the dye is influenced by an image dipole formed in the semiconductor. To assess the validity of this argument, we have calculated the potential due to the molecule at the surface of the ZrO₂ particle both with and without an image dipole.⁵⁹ We approximate the dipole as the sum of equal but opposite charges separated by a distance estimated by the structure of the dye⁶⁰ to yield the known ground and excited-state dipole moments.⁶¹ Because the positions selected for the charges comprising the dipole are somewhat arbitrary, we change only the magnitude of the charges, not their positions, to change the dipole magnitude. Then, using the formalism presented by Jackson⁵⁹ to describe the potential due to the dipole and its image will be

$$\Phi = \sum_{i=1}^{2} \frac{1}{\epsilon_{i}} \left(\frac{q_{i}}{R_{1}^{i}} + \frac{q'_{i}}{R_{2}^{i}} \right)$$
(3)

where q is the charge of in the material, q' is the image charge, at distance R_1^i and R_2^i from the charge and image charge, respectively. The summation is over the individual charges comprising the dipole. The image charge, q' is given by

$$q' = \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_1 + \epsilon_2}\right) q \tag{4}$$

where ϵ_1 and ϵ_2 are the dielectric constant of the water, 78,⁶² and ZrO₂, 13.5,⁶³ respectively. In cylindrical coordinates, $R_1{}^i = \sqrt{\rho^2 + (d_i^2 - z^2)}$ and $R_2{}^i = \sqrt{\rho^2 + (d_i^2 + z^2)}$, where d_i is the distance of the charge from the interface. In the absence of the image dipole, the potential due to the dye's dipole is given by

$$\Phi = \frac{q_1}{\epsilon R_1} + \frac{q_2}{\epsilon R_2} \tag{5}$$

where *q* is the charge, ϵ is the dielectric constant of water, and *R* is the distance from the charge. We calculated the potential due to the ground- and excited-state dipole moments assuming that the ground- and excited-state dipole moments of C343 are 10.41 and 15.70 D.⁶¹ A plot of the potential as a function of distance from the interface is shown in Figure 2. This plot shows that the image dipole generates changes peak-to-peak potential distance by only ~4% for both ground and excited states. However, the largest deviation in the potential occurs near the interface. Thus, it is possible that the image dipole could lead to an overall red shift of the steady-state spectra.

The relative concentration used for the solvation dynamics measurements reported here yields an average of <1 dye molecule/particle. However, because many dye sensitization studies employ a significantly higher relative concentration, we have probed the steady-state absorption and emission, and time-resolved emission spectra as a function of the relative dye concentration. To avoid effects due to the concentration of dye in solution, we varied relative dye/particle concentration by changing the nanoparticle concentration in solution while the dye concentration was kept constant. In Figure 3, absorption spectra of C343 are shown as a function of ZrO₂ nanoparticle concentration, the absorption spectra are significantly blue shifted. As the particle concentration is



Figure 2. Electric potential as a function of distance from the interface for the ground (heavy lines) and excited (light lines) states of Coumarin 343 at the water $-ZrO_2$ interface. Solid lines represent calculations including the image dipole, and dashed lines are without the image dipole.



Figure 3. Absorption spectra of C343 in H_2O with various ZrO_2 nanoparticle concentrations.

increased, the dye's spectrum shifts to longer wavelength. However, unlike smooth shifts we have observed for other varying environments,⁴¹ these spectra also display significant changes in the spectral shape.

As shown in Figure 3, the absorption spectra show a dramatic change with dye concentration. At low relative concentration (fewer than one dye molecule per nanoparticle) the absorption spectrum reflects the spectrum of the protonated dye in bulk solution. As the relative dye concentration increases, an additional spectral feature appears to the blue of the original dye absorption peak. This shoulder grows with increasing relative concentration eventually dominating the spectrum. This behavior is reminiscent of H-aggregation.⁶⁴ In contrast to the dramatic spectral shifts observed for the absorption spectrum, the steadystate emission spectra vary only slightly over the extensive relative concentration range. It appears that excitation into the "aggregate" band yields emission from the monomer, or, at least, emission that is indistinguishable from the monomer emission. In contrast, the time-resolved fluorescence Stokes shift displays significantly faster relaxation for the high relative dye concentration than the low concentration. This large, fast red shift depends on the relative concentration of dve molecules on the surface. Thus, while we cannot verify unequivocally, these results indicate that the time-resolved behavior observed at high relative concentration of dye on the nanoparticle surface, that is >40 molecules per particle, arises from energy transfer within the aggregated molecules. Thus, all our solvation dynamics experiments were conducted in the range where statistics predict

 TABLE 1: Fit Parameters for Time-Resolved Anisotropy

 Measurements^a

sample	α	au (ps)
bulk H ₂ O	0.37	83
bulk D ₂ O	0.37	75
ZrO ₂ in H ₂ O	0.34	5700
ZrO ₂ in D ₂ O	0.35	5200

^{*a*} Error bars are $\pm 10\%$.

a low probability for finding more than one dye molecule adsorbed to any given nanoparticle to ensure that the dynamics measured reflect solvent motion rather than complications from aggregation.

We used time-resolved fluorescence anisotropy to measure whether the dye adsorbed to the ZrO₂ particles. Time-resolved fluorescence anisotropy was therefore measured for each different solution of C343. The rotational correlation times are obtained from multiexponential fits to the data, and the fitting parameters are given in Table 1. The rotational correlation time for the dye in H₂O agrees well with the literature values for the bulk water.⁴¹ While the viscosity of D₂O is higher than that for H₂O, the emission anisotropies measured here for H₂O and D₂O were, within experimental error, the same. In contrast, the large increase in the rotation time for C343 in the ZrO₂/H₂O solution (4 ns) as well as in the ZrO₂/D₂O solution (5 ns) indicates that the dye adsorbs to the surface of the nanoparticles. If the dye were free in the ZrO₂ solution, it should display a rotational correlation time that is the same as for the bulk solution. The presence of nanoparticles in solution is insufficient to slow the molecular rotation time. In aqueous SiO₂ nanoparticle suspensions, r(t) for the dye is indistinguishable from bulk solution because the dye does not adsorb to the negatively charged surface of the silica particles. This shows that mere presence of the nanoparticles in solution is insufficient to change the rotational correlation time and that the C343 dye adsorbs strongly to the ZrO₂ particle surface.

In the studies reported here, the C343 molecule does not inject electrons into the conduction band of ZrO_2 , because the excited-state redox couple of C343 lies below the conduction band edge of ZrO_2 .⁵⁶ Evidence for the unfavorable electron injection can be seen from the fluorescence intensity, which increases for the dye in the ZrO_2 solutions compared to the bulk solutions. If the dye injected electrons into the ZrO_2 solution, the fluorescence quantum yield, hence the intensity, should decrease substantially. Thus, in contrast to C343 on TiO_2 ,³ the excited-state dynamics for C343 on ZrO_2 solution reflect the solvation dynamics rather than electron injection.

Solvation Dynamics, The solvation dynamics of H₂O and D₂O at the surface of the ZrO₂ nanoparticles and in bulk solutions were measured. Fluorescence decays from which the time-resolved fluorescence spectra were generated were normalized to the steady-state spectrum at 5 ps. No additional Stokes shift was observed beyond 5 ps for the longer time scans, hence there was no additional contribution to the solvation dynamics on a longer time scale. Figure 4 displays the time-correlation function for bulk H₂O and H₂O at the surface of ZrO₂ while Figure 5 shows the time-correlation function for bulk D₂O and D₂O at the surface of ZrO₂. All solvation dynamics parameters for these samples are given in Table 2. In all these solutions, the decays fit well to a biexponential function characterized by three different time scales.²⁵ First, we calculate the inverse of the decay rate or the "initial" time constant, τ_0 ,

$$\tau_0^{-1} = a_1 \tau_1^{-1} + a_2 \tau_2^{-1} \tag{6}$$



Figure 4. Normalized time-correlation function, C(t), displaying the dynamic response for C343 in bulk H₂O (\blacktriangle) and at the surface of ZrO₂in H₂O (\blacklozenge). Points are the experimental data and lines are fits to the data via $\sum_i a_i \exp(-t/\tau_i)$. Values for the fits are given in Table 2.



Figure 5. Normalized time-correlation function, C(t), displaying the dynamic response for C343 in bulk D₂O (\blacktriangle) and at the surface of ZrO₂ in D₂O (\blacklozenge). Points are the experimental data and lines are fits to the data via $\sum_i a_i \exp(-t/\tau_i)$. Values for the fits are given in Table 2.

 TABLE 2: Fit Parameters for Solvation Dynamics

 Measurements

	$\Delta \nu$		τ_1		τ_2	$ au_0$	<i>t</i> _{1/e}	$\langle \tau_{\rm s} \rangle$
sample	(cm^{-1})	α_1	(ps)	α_2	(ps)	(ps)	(ps)	(ps)
bulk water	800	0.34	0.07	0.66	0.63	0.17	0.40	0.44
water/acetone ^a	700	0.32	0.14	0.68	0.68	0.30	0.44	0.51
bulk D ₂ O	500	0.18	0.06	0.82	1.01	0.26	0.81	0.84
$ZrO_2 + water$	150	0.73	0.09	0.27	0.64	0.12	0.14	0.24
$ZrO_2 + water/acetone^a$	260	0.77	0.15	0.23	0.66	0.18	0.20	0.27
$ZrO_2 + D_2O$	190	0.63	0.06	0.37	0.56	0.09	0.12	0.25

^a Results from Pant and Levinger.⁵⁶

where a_1 , and a_2 are the relative amplitudes, and τ_1 , and τ_2 are the corresponding relaxation times. This time constant, τ_0 , reflects short time behavior of the dynamics. Second, we use the time required to reach 1/e (0.368) of the original amplitude, which represents the overall relaxation time. Finally, we calculate the average solvation time, $\langle \tau_s \rangle$,

$$\langle \tau_{\rm s} \rangle = a_1 \tau_1 + a_2 \tau_2 \tag{7}$$

characterizing the long time component of our data.

Before comparing the dynamics of bulk D_2O with the dynamics of D_2O at the surface of ZrO_2 , we discuss the solvation dynamics for the bulk H_2O and D_2O . Our measurements of solvation dynamics for the liquid H_2O and D_2O (Table 2) are in good agreement with the literature values,^{31,38–41,65} though

the time resolution for these measurements precluded full resolution of the solvation dynamics inertial component. A significant isotope effect is observed for the longer solvation time component in D_2O . The structure of D_2O is reported to be more ordered and stable with stronger hydrogen bonding than H_2O .⁶⁶ Thus, the hydrogen-bond making and breaking processes are slower in D_2O than in H_2O , leading to slower motions and consequently slower solvation dynamics in D_2O . Further, the substantial isotope effect in the solvation dynamics of D_2O can simply reflect the increased mass hence the larger moment of inertia of D_2O compared to H_2O .

Though the static dielectric constant and the index of refraction of H₂O and D₂O are almost the same,⁶⁷ dynamical parameters such as the Debye relaxation time, τ_D , are different.⁶⁸ Like bulk H₂O, the solvation time correlation function for D₂O reveals two time components. The shorter relaxation times for both solvents are similar and most likely reflect a degree of inertial behavior.37 However, the longer time component for D2O is significantly larger than bulk H₂O. This leads to a larger solvation time for D₂O. Barbara and co-workers⁶⁵ report timeresolved fluorescence Stokes shift measurements using C343 in H₂O and D₂O. Their results showed the solvation dynamics were approximately 30% slower in D₂O than in H₂O, essentially what is predicted from a dielectric continuum model and the kinetic isotope effect. Das et al.69 have reported that the solvation dynamics of D₂O are a factor of 1.2 slower than H₂O when confined to the interior of reverse micelles. Using the technique of resonance heterodyne optical Kerr effect, Zolotov et al.⁷⁰ have measured the isotope effect for D₂O compared to H₂O. Their results agree well with the effect of isotopic substitution on the Debye relaxation time. They attributed the results to a specific solvation due to the formation and breaking of an intermolecular solute-solvent hydrogen bond. Using ultrafast near-infrared pump/variable wavelength probe transient absorption spectroscopy of the solvated electron, Kimura et al.¹⁹ have reported that a small isotope effect exists for the longitudinal relaxation time in water.

Isotope effects have been observed in solvation dynamics for solvents other than water. Pal et al.⁷¹ have investigated the deuterium isotope effect on the solvation dynamics of aniline using the dynamic Stokes shift method. They found a slower solvation dynamics for the deuterated aniline than for normal aniline and explained the isotope effect as due to the presence of intermolecular hydrogen bonding. Using femtosecond fluorescence upconversion, Shirota et al.⁷² found the solvation dynamics to be slower for deuterated solvent than for normal methanol.

The isotope effects in D₂O solvent motion have been explained via theory and simulations as well as experiments. Schwartz and Rossky have modeled the H_2O and D_2O response to the solvated electron.^{35,37,73} Their calculations mirror experimental results. That is, the fastest, underdamped, "inertial" response and the slowest solvent response are largely unaffected by isotopic substitution. However, the intermediate time response, ~ 1 ps, corresponding largely to rotational motion, displays the expected \sim 30% isotope effect. They explain the missing isotope effect in the fastest dynamics as due to translational motion that would be less strongly influenced than rotational motions. In contrast, Fonseca and Ladanyi⁷⁴ have shown via molecular dynamics simulations that the fast inertial type component of solvation in methanol is slowed upon isotopic substitution and attribute this to the free rotation of the hydroxyl hydrogen about the CO bond. Svishchev and Kusalik⁷⁵ have also used molecular dynamics simulations to show that both short as well as long time components of dielectric relaxation process in water become slower on isotopic substitution of the hydrogen by the deuterium or tritium atoms. Recently, Nandi et al.⁷⁶ have predicted solvation dynamics using molecular hydrodynamic theory. In particular, they find that the longer time component in D_2O is slower than that in the H_2O . Thus, calculations would predict isotope effects in both the short and long time response of the liquid.

The interfacial dynamics differ from the bulk dynamics in several ways. First, all of the solvation dynamics data show that the molecules at the ZrO₂ surface move faster than they do in the bulk solutions (see Table 2). Second, while the two subpicosecond time components comprising the interfacial solvent response are the same, if not shorter, than the corresponding components in bulk solutions the relative amplitude of the shorter component dominates the interfacial dynamics. This leads all three characteristic time responses, τ_0 , $t_{1/e}$, and $\langle \tau_s \rangle$, to be shorter by at least a factor of 2 for surface solvent molecules than for the corresponding bulk solution. Third, the overall fluorescence Stokes shift displayed by the dye adsorbed to the particle surface is considerably smaller than the shift observed in bulk solvent. This implies that the solvation energy is reduced for the dye adsorbed to the ZrO2 surface and that the extent of molecular motion of the water molecules is smaller than in bulk. Previously, we reported similar results for 95:5% water: acetone solutions.⁵⁶ The results for water solutions reported here show that the presence of 5% acetone, by volume, in our previous work plays only a minor a role in the measured interfacial and bulk water dynamics. The solvation dynamics for bulk acetone/water and neat water virtually identical for both bulk and at the surface of ZrO₂. Finally, we observe no isotope effect for the solvation dynamics at the surface of ZrO₂. Surprisingly, all three characteristic time responses, τ_0 , $t_{1/e}$, and $\langle \tau_s \rangle$, are essentially the same for both H₂O and D₂O at the ZrO₂ surface.

There exist plausible explanations for the faster solvation dynamics, smaller solvation energy, and missing isotope effect we observe at the ZrO_2 surface. The smaller solvation energy is most likely due to several different effects in concert. First, the nanoparticle surface blocks the part of the dye molecule, so the relative number of solvent molecules surrounding the C343 molecule is smaller than the number surrounding it in the bulk solution. Thus fewer solvent molecules would respond to the new electric field leading to smaller solvation energy. A simple geometric calculation of the total number of water molecules surrounding the C343 molecule shows that approximately 12.5 water molecules are in the first solvation shell. If each water molecule contributed the same amount to the overall Stokes shift, then the observed Stokes shift for C343 adsorbed on the ZrO₂ surface would lead us to conclude that the molecule is solvated by at most four water molecules. Geometrically, it is impossible for the surface to block that much of the dye molecule. However, spectroscopic measurements of the related molecule, coumarin 151 (C151) show that a single water molecule located near the cyclic ester functionality of the molecule is responsible for a large fraction of the Stokes shift.⁷⁷ If C343 behaves similarly to C151, then the overall Stokes shift would be smaller because the C343 attaches to the nanoparticle via this group. Thus, the semiconductor would block the position for the water molecule that causes the most significant portion of the Stokes shift. Additionally, our image dipole calculation shows that the potential due to the molecule and its image differs most dramatically in the region where the molecule attaches to the particle. Thus, the ZrO₂ particle not only blocks the position

of the water that is important for stabilizing the dye molecule, it also perturbs the electronic environment in which the dye sits.

An additional effect may contribute to the reduced overall Stokes shift. One way to reduce the overall Stokes shift would be for the water molecules at the surface to be prealigned. If the water molecules are close to the position required to solvate the dye's excited state then we would anticipate a smaller degree of reorientation leading to a smaller Stokes shift. It is most likely that a combination of all three effects, that is, the partial blocking of the dye's solvation shell, prealignment of the surface water, and the image dipole lead to the overall smaller solvation energy for the dye at the particle surface.

We feel that the most plausible reason for the faster response and missing isotope effect at the surface is that the hydrogen bonding is disrupted allowing water to move more freely than it does in bulk solutions. The ZrO₂ solutions are slightly acidic and the point of zero charge for ZrO₂ is near pH = $7.^{78}$ As a result, the surface chemistry is most likely modified from the standard O–Zr(O)–O moiety to O–Zr(OH)–O (O–Zr(OD)– O) in the H₂O(D₂O) solutions. Thus, the solvation dynamics probe H₂O(D₂O)–OH(OD) interactions rather than interactions with surface O atoms. If the interfacial water forms weaker hydrogen bonds with the surface OH(D) groups than it does with itself, then it could reorient more quickly. Furthermore, interfacial motion could reflect librational motion of the surface hydroxyls in addition to surface water motion.

Prealignment of the surface water and a reduced solvation shell could also potentially shorten the relaxation time. Prealignment could reduce the solvation response; because the extent of the motion would be smaller, the time for the motion to occur would be shorter. A smaller number of water molecules in the dye's solvation shell could also lead to a shorter relaxation time if collective motion were responsible for the observed relaxation. However, neither of these effects can account for the missing isotope effect. Therefore, the shorter solvation times measured at the particle surface cannot be solely due to these effects.

The intermolecular structure of water at the particle surface and near the dye could be perturbed by the presence of the dye molecule. Since the dipole moment of the dye molecule points toward the nanoparticle, it is aligned with the anticipated orientation of water at the surface, assuming that the ZrO_2 is hydroxylated. Thus the presence of the dye could disrupt the normal water surface structure causing the water to align relative to the dye rather than the surface. While this means that the dynamics we measure could be significantly different from the dynamics in the absence of the dye molecule, this result is inconsequential for comparison with electron injection by the C343 into the semiconductor because it is only dye sensitization that makes electron injection possible. Thus the solvation dynamics reported here are most relevant for comparison with electron injection into the semiconductor particles.

In summary, we have measured the solvation dynamics for H_2O and D_2O both in bulk solution and at the surface of nanoparticulate ZrO_2 using the time-resolved fluorescence Stokes shift technique. For bulk solutions, the dynamics follow the anticipated behavior.^{38,65} The dynamics at the particle surface depart from bulk behavior in several different ways. First, the solvation dynamics at the surface of the nanoparticles are faster than dynamics in bulk solution. Additionally, dynamics at the surface show no isotope effect. Finally, the overall Stokes shift for the probe dye molecule at the surface is smaller than in bulk solution. These results suggest that the hydrogen-bonding

network normally found in these solutions is substantially disrupted at the particle surface. Further experiments are currently underway to probe the universality of these results for other surfaces, other solvents and pH values.

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