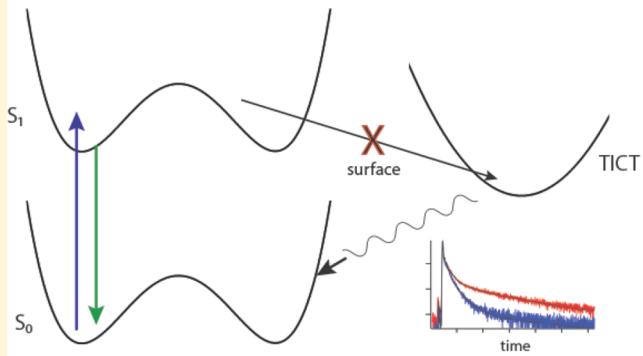


Hindered Isomerization at the Silica/Aqueous Interface: Surface Polarity or Restricted Solvation?

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ABSTRACT: Time-resolved fluorescence measurements performed in a total internal reflection (TIR) geometry examined the photophysical behavior of coumarin 152 (C152) adsorbed to a silica/aqueous interface. Results imply that interfacial C152 has a remarkably different photoisomerization rate compared to its bulk solution value. C152's fluorescence in bulk water is dominated by a short, sub-nanosecond emission lifetime as the solute readily forms a nonemissive, twisted, intramolecular charge transfer (TICT) state. Time-resolved-TIR data from the silica/aqueous interface show that C152 emission contains a contribution from a longer-lived state ($\tau = 3.5$ ns) that matches C152's fluorescence lifetime in nonpolar solvents where a photoexcited TICT state does not form. This long-lived excited state is assigned to C152 solvated in the interfacial region, where strong substrate–solvent hydrogen bonding prevents the aqueous solvent from stabilizing C152's TICT isomer. Similar results are observed for C152 in frozen water, emphasizing the silica surface's ability to restrict solvent mobility and change the interfacial solvation and reactivity from bulk solution limits.



INTRODUCTION

Water's complicated interfacial properties have motivated innumerable studies and sparked considerable debate ever since the first surface-specific, nonlinear, vibrational spectrum of water's aqueous/vapor interface was reported more than two decades ago.^{1–3} With its broad features and characteristic sharp “free-OH” band, water's vibrational structures at aqueous/vapor, liquid/liquid, and solid/liquid interfaces have led researchers to describe surface water as “liquidlike”⁴ or “icelike”⁵ and propose models that identify interfacial populations having specific hydrogen-bonding configurations.^{2,6} Complementing these discoveries, theory and simulations have provided nuanced insight into how surface-altered hydrogen bonding changes water's properties from bulk limits.^{3,7} Despite these concerted efforts, however, very few studies^{8,9} have explored how changes in the water structure and dynamics impact water's ability to solvate the solutes adsorbed to aqueous interfaces.

Interfacial solvation often differs from a solvent's bulk solution limit. In this context, interfacial solvation describes the surface-modified, noncovalent interactions a solute experiences with its surroundings. Eisenthal and co-workers first addressed questions about interfacial polarity, using surface-specific second harmonic generation (SHG) to record effective excitation wavelengths of solutes adsorbed to different liquid/liquid and liquid/vapor interfaces.¹⁰ Shifts in the SHG spectra led the authors to describe interfacial polarity as an average between polarities of the two adjacent phases. Subsequent work by Steel et al. showed that the local dielectric environment of an interface depends sensitively on the solvent

structure, and the polarity across strongly associating interfaces (such as water/1-octanol) is characterized by a low polarity region having an effective dielectric constant of ≤ 2 .^{11,12} Similar results have been reported from silica/n-alcohol interfaces, where strong hydrogen bonding between the surface silanol groups and the first solvent layer effectively transforms the silica surface into a hydrophobic, alkyl-terminated substrate.^{13,14}

EXPERIMENTAL SECTION

Experiments were carried out using a locally constructed time-correlated single photon counting (TCSPC) fluorometer that has been described previously.¹⁵ The output of a Ti:sapphire oscillator (Chameleon, Coherent) was frequency doubled (APE Autotracker), and the 80 MHz repetition rate was attenuated to 4 MHz using an electro-optic modulator (Conoptics model 350-105). Fluorescence emission was collected using a PicoQuant 200 time-to-amplitude converter, and the instrument response function (IRF) was measured using a nonemissive Ludox scattering solution. For bulk solution measurements, the IRF varied between 20 and 50 ps. For total internal reflection (TIR) measurements, a custom-built assembly enabled the excitation pulse to irradiate the interface formed between a hemispherical prism and an aqueous solution at angles beyond the critical angle (61° at 400 nm). Emission was detected at 90° relative to the silica/aqueous interface. The TIR assembly's IRF was ~200 ps. For every experiment, the IRF was deconvoluted from the time-resolved emission histogram, and the resulting trace was then fit to

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one or more single exponential decays. The minimum number of lifetimes required to accurately fit the data was determined using the Akaike information criterion.

For all experiments, cuvettes and experimental assemblies were rinsed with methanol and deionized (DI) water (Millipore, 18.2 Ω), then soaked in a bath of 50/50 sulfuric/nitric acid for no less than an hour, and rinsed with DI water before use. TIR-TCSPC spectra used fused silica hemispheres from SPI Optics, and bulk TCSPC spectra were taken in quartz Starna cuvettes.

Most experiments in this work used saturated aqueous solutions of coumarin 152 (C152) (Figure 1). C152 was purchased from Exciton

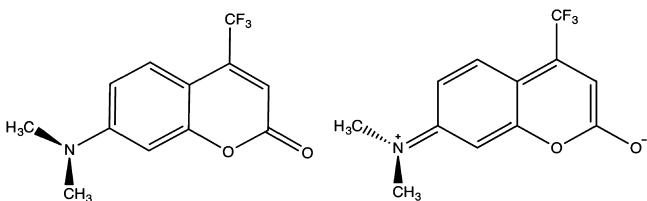


Figure 1. C152 in ground-state configuration (left) and the proposed structure of the excited TICT state (right).

and used as received. The photophysical behavior of C152 has been examined in detail both experimentally and computationally.^{16,17} Several properties of this solute make it an attractive probe of the local solvation environment: well-defined absorption/emission behavior, photostability, and insensitivity to local viscosity. In most solvents, C152 emission is characterized by a single exponential decay, simplifying the interpretation of C152 fluorescence in chemically complex environments. In polar protic solvents, C152 photoexcitation leads to rapid formation of a nonradiative, twisted intramolecular charge transfer (TICT) state and a correspondingly short (≤ 1 ns) emission lifetime. Structures of C152's ground state and excited TICT state are shown in Figure 1. Less polar solvents such as alkanes cannot stabilize the TICT state. As a result, C152 has a longer fluorescence lifetime (~ 3.5 –4 ns) in these low dielectric environments.

Saturated solutions were made by allowing DI water and excess C152 to equilibrate with stirring at 50 °C overnight and then filtering the excess dye from the solution before use. At room temperature, the concentration of an aqueous solution saturated with C152 is approximately 6 μ M. In the experiments presented here, the molecules were excited at 396 nm, the peak absorption wavelength of C152 in aqueous solution, and the emission monochromator was set to collect at either 525 nm, the peak fluorescence emission wavelength in room temperature water, or 505 nm, the fluorescence emission peak of C152 in ice. In aqueous solution, C152's emission is characterized by a short, sub-nanosecond lifetime (0.47 ns), whereas in nonpolar solvents, C152's emission lifetime is markedly longer (3.5 ns in alkanes) (Figure 2).

For time-resolved fluorescence experiments conducted in a TIR geometry, the incident beam passes through the higher index-fused silica prism at an angle of approximately 65.5° relative to the surface normal; the resulting evanescent wave propagates ~ 150 nm into the aqueous solvent conferring pseudosurface specificity to the measurements.

RESULTS

Experiments used TCSPC in a TIR geometry to measure the time-resolved emission of C152 adsorbed at a silica/aqueous ($\text{pH} = 5.9$) interface. In bulk water, $>98\%$ of the time-resolved fluorescence signal from C152 can be fit to a lifetime of 0.47 ns. A small but measurable fraction of C152's emission fits to a much longer lifetime (4.02 ns) that has been assigned previously to dimers in solution.¹⁵ For TIR measurements carried out at the silica/aqueous interface, the fluorescence decay from a saturated C152 solution is best fit with two lifetimes: a short 0.47 ns lifetime assigned to C152 in bulk

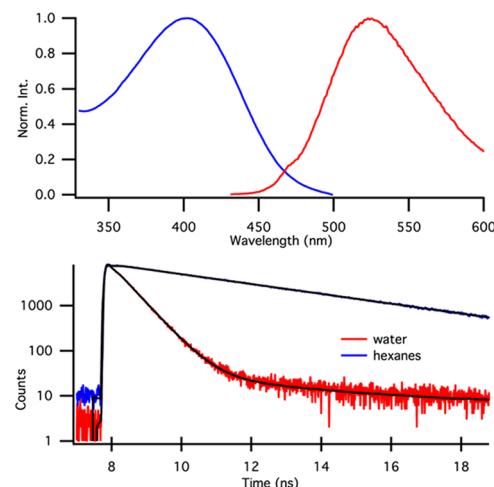


Figure 2. Top: Absorbance (blue) and fluorescence (red) spectra of a saturated solution of C152 in water. Bottom: TCSPC decay curves for C152 in water and in hexanes.

solution and a longer lifetime of 3.52 ns assigned to C152 adsorbed to the surface (Figure 3). Normalized amplitudes for

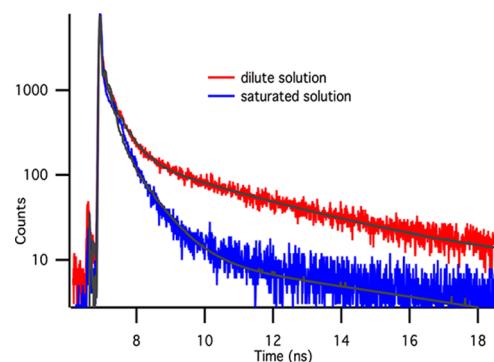


Figure 3. TIR TCSPC traces of saturated (blue) and dilute (red) aqueous solutions of C152. The tail from the 3.52 ns lifetime comprises a larger relative amplitude in data from the more dilute solution.

the short and long lifetimes are 0.87 and 0.13, respectively. Repeating the same experiment with a C152 solution that has been diluted by a factor of 2 ($\sim 3 \mu\text{M}$) leads to no change in lifetimes, but the longer lifetime contributes twice as much (0.27) to the overall emission decay data (Figure 3). This result supports the assignment of the long-lived monomers adsorbed to the silica/aqueous interface (Table 1).⁹

Data in Figure 3 imply that the interfacial solvation environment cannot readily stabilize C152's nonradiative TICT state, effectively making the interfacial region appear nonpolar. Two possible explanations can rationalize this result:

Table 1. Lifetimes and Amplitudes for C152

	A_1^a	τ_1 (ns) ^b	A_2^a	τ_2 (ns) ^b
bulk water	≥ 0.98	0.50	≤ 0.02	4.02
TIR water (saturated)	0.87	0.47	0.13	3.52
TIR water (dilute)	0.73	0.47	0.27	3.52
ice	0.85	0.71	0.15	7.47

^aAmplitude uncertainties are ± 0.02 . ^bLifetime uncertainties are ± 0.15 ns.

(1) the local dielectric constant at the silica/aqueous interface is significantly less than $\epsilon = 78.0$ experienced in bulk solution and/or (2) water's restricted motion or "icelike" character at the silica/aqueous interface prevents the interfacial solvent from stabilizing the C152's TICT state, thus inhibiting isomerization. Comparison of TIR data with results from C152 solvated in bulk ice suggests that both effects contribute to the observed behavior, although restricted solvent motion appears to play a more important role. More importantly, the findings presented here are among the first reported examples of how surface-mediated solvation in aqueous systems changes the solute reactivity from bulk solution limits.

A longer emission lifetime from C152 adsorbed to the silica/aqueous interface is consistent with the solute being solvated in solvents less polar than water and might suggest that the silica/aqueous interface has a local dielectric constant approaching that of alkanes ($\epsilon \approx 2$). Although interfacial polarity is expected to be less than that of bulk water based on prior experiments,^{10,18,19} alkane-like properties at a hydrophilic silica/aqueous interface are not expected. Unlike strongly associating organic solvents such as methanol, 1-butanol, and others that form nonpolar interfacial regions, water does not have a "hydrophobic piece" that can organize at a surface to form a locally nonpolar region with alkane-like solvation.^{9,13,20} Radial distribution functions describing water adjacent to silica surfaces show enhanced densities and well-defined long-range ordering that extends up to 2 nm into the liquid.^{7,21} Such a high density of aligned dipoles would be expected to enhance, not diminish, water's permittivity. These arguments are bolstered by surface wetting and electrokinetic measurements that calculate the surface potentials at the silica/aqueous ($\text{pH} \approx 6$) interface to be greater than 75 mV in the low ionic strength limit.^{22,23} Over a distance of 2 nm, this surface potential will create fields $>10^5 \text{ V/cm}$.

By contrast, water's restricted mobility at a silica surface—also apparent in simulations—would limit the solvent's ability to promote C152 photoisomerization. Such behavior is similar to what one expects in solid matrices composed of polar materials and would be consistent with reports of "icelike" water at silica/aqueous interfaces.²⁴ Experiments and simulations create conflicting narratives about the static dielectric constant of ice relative to bulk water,^{25,26} but both theory and experiment show unequivocally that water reorientation dynamics at hydrophilic surfaces slows significantly from bulk limits.²⁷ In vibrational spectroscopy experiments, highly structured water at a silica/aqueous interface is observed as a single broad feature centered at a relatively low frequency (3100 cm^{-1}), very similar to the vibrational Raman spectrum of bulk ice.²

To test the viability of these explanations for C152's long emission lifetime at the silica aqueous interface—reduced polarity versus slow solvation dynamics—we measured the steady-state fluorescence excitation and emission and the time-resolved fluorescence from solutions of C152 in frozen water (Figure 4). Although the structure of the ice matrix was not characterized explicitly in this work, we assumed that ice had an I-h structure, given the temperature and ambient pressure considerations.

Approximately, 85% of the fluorescence emission from C152 in ice can be fit to a lifetime assigned to cold, bulk water (0.71 ns) in coexistence with ice, with the remaining decay intensity described by a fluorescence lifetime of 7.47 ns. We assign this long-lived contribution to the total fluorescence decay to

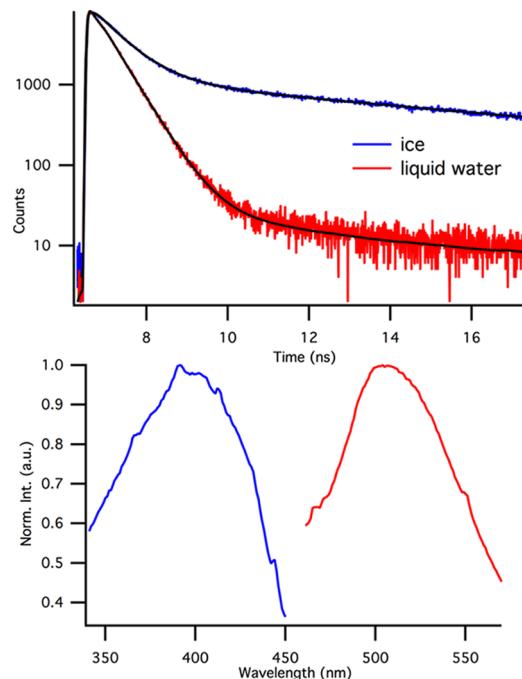


Figure 4. Time-resolved fluorescence spectra of C152 in ice and liquid water at room temperature (top). Excitation (blue) and emission (red) spectra of C152 in ice (bottom).

coumarin solutes unable to form the TICT state. Interestingly, the steady-state fluorescence spectrum of C152 also changes when trapped in ice, with the peak emission wavelength shifting from 525 nm in liquid water to 504 nm in ice. C152's fluorescence excitation maximum in ice (396 nm) remains unchanged from that in liquid water.

Comparing the data from the C152 time-resolved emission at the silica/water interface to C152 behavior in bulk ice shows that although the C152 molecules adsorbed to the silica surface experience an environment that appears more nonpolar, based on comparison to bulk solvent studies,^{12,14} in fact, the results are consistent with solutes "trapped" in a local environment unable to accommodate changes in properties associated with photoexcitation. What remains to be determined is whether or not complementary behavior is observed in the excitation spectra of adsorbed C152. This question is currently being addressed with surface-specific SHG measurements and will be the subject of a future report.

CONCLUSIONS

Time-resolved fluorescence measurements of C152 adsorbed to the silica/aqueous ($\text{pH} = 5.9$), solid/liquid interface show the emergence of a 3.52 ns lifetime that is significantly longer than the C152's emission lifetime in bulk aqueous solution (0.47 ns). Concentration-dependent amplitudes for these long and short lifetimes support the long lifetime emission originating from adsorbed monomers that are unable to rapidly isomerize and form a TICT state. The origin of this behavior may result from a local dielectric environment at the silica/aqueous interface that is less polar than bulk water or from interfacial water's restricted motion caused by strong solvent–substrate interactions. Comparative time-resolved fluorescence experiments performed with C152 solvated in bulk ice imply that slower water reorientation dynamics at the silica/aqueous interface is more likely responsible for C152's

unusual behavior at the strongly associating silica/aqueous interface.

Regardless of the origin of C152's behavior at the silica/water interface, the results described in this communication represent one of the first reported examples of how surface modified solvent properties affect the surface isomerization/reactivity. Given the importance of silica/water interfaces in chemical techniques such as chromatography as well as in environmental applications, this result motivates further study to understand the response of organic solutes that are influenced by interfacial asymmetry.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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