UNUSUAL ISOMERIZATION BEHAVIOR OF ORGANIC SOLUTES
AT THE AQUEOUS-SILICA INTERFACE

by

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DEDICATION

This thesis is dedicated to my family. To my parents for putting up with my endless questions and to my sisters for being my first and favorite friends. And to Addie-dog—thanks for keeping me alive and laughing as I did the work for this thesis. I love you.
The work in this thesis would not have been possible without the advice and support of my advisor, Dr. Robert Walker. He embodies everything I needed in an advisor for my graduate research and I am so grateful for his kind and gracious approach to leading his students. I wouldn’t be here without his support. I also want to thank my graduate committee: Dr. Erik Grumstrup, Dr. Mary Cloninger, Dr. Tim Minton and Dr. Patrik Callis. I’m so grateful for their assistance with research questions and their guidance throughout my graduate career.

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# TABLE OF CONTENTS

1. INTRODUCTION ................................................................................................................................. 1

1.1 Motivation.............................................................................................................................................. 1
1.2 Techniques .............................................................................................................................................. 4
    1.2.1 TIR-TCSPC ................................................................................................................................. 4
    1.2.2 Second Harmonic Generation ..................................................................................................... 7
1.3 Description of the Aqueous-Silica Interface ....................................................................................... 11
1.4 Molecular Isomerization and Twisted Intramolecular Charge Transfer (TICT) States ..................... 13
1.5 Organization of Thesis ........................................................................................................................ 16

Chapter 2: Hindered Isomerization at the Silica-Aqueous Interface: Surface Polarity or Restricted Solvation? ........................................................................................................................................ 16

Chapter 3: Surface Solvation and Hindered Isomerization at the Water-Silica Interface Explored with Second Harmonic Generation ........................................................................................................ 17

Chapter 4: Buried Liquid Interfaces as a Form of Chemistry in Confinement: The Case of 4-dimethylaminobenzonitrile (DMABN) at the Silica-Aqueous Interface .................................................................................... 18

Chapter 5: Isomerization at aqueous silica interfaces and the role of solute structure .......................... 19

1.6 References ............................................................................................................................................. 21

2. HINDERED ISOMERIZATION AT THE SILICA-AQUEOUS INTERFACE: SURFACE POLARITY OR RESTRICTED SOLVATION? ........................................................................................................... 28

Contributions of Authors and Co-Authors .............................................................................................. 28
Manuscript Information Page .................................................................................................................... 29
2.1 Introduction ............................................................................................................................................ 30
2.2 Experimental ......................................................................................................................................... 31
2.3 Results and Discussion ......................................................................................................................... 34
    2.3.1 Time-Resolved Fluorescence at the Silica Interface .................................................................. 34
    2.3.2 Fluorescence of C152 in Frozen Water ..................................................................................... 37
2.4 Conclusions .......................................................................................................................................... 39
2.5 References ............................................................................................................................................ 41

3. SURFACE SOLVATION AND HINDERED ISOMERIZATION AT THE WATER-SILICA INTERFACE EXPLORED WITH SECOND HARMONIC GENERATION ...................................................................... 44

Contributions of Authors and Co-Authors .............................................................................................. 44
TABLE OF CONTENTS CONTINUED

Manuscript Information Page ...........................................................................................................45
3.1 Introduction ................................................................................................................................46
3.2 Experimental ...........................................................................................................................50
3.3 Results and Discussion .........................................................................................................54
3.4 Conclusions ...........................................................................................................................61
3.5 References ............................................................................................................................62

4. BURIED LIQUID INTERFACES AS A FORM OF CHEMISTRY IN CONFINEMENT: THE CASE OF 4-DIMETHYLAMINOBENZONITRILE (DMABN) AT THE SILICA-AQUEOUS INTERFACE ...........................................................................................................66

Contributions of Authors and Co-Authors ................................................................................66
Manuscript Information Page ........................................................................................................67
4.1 Introduction ...........................................................................................................................68
4.2 Experimental Methods ..........................................................................................................74
4.3 Results ...................................................................................................................................79
4.4 Discussion ..............................................................................................................................86
  4.4.1 Strong associations across the silica-aqueous interface impede DMABN photoisomerization ..................................................87
  4.4.2 The silica-aqueous interface sampled by DMABN is more polar than bulk water .............................................................................88
  4.4.3 A combination of surface charge and amino twist are responsible for enhanced SHG intensity in the $S_0-S_1$ transition ........................................................91
4.5 Conclusions ...........................................................................................................................92
4.6 References ............................................................................................................................94

5. ISOMERIZATION AT AQUEOUS-SILICA INTERFACES AND THE ROLE OF SOLUTE STRUCTURE ..................................................................................................................102

Contributions of Authors and Co-Authors ................................................................................102
Manuscript Information Page ........................................................................................................103
5.1 Introduction ...........................................................................................................................104
5.2 Experimental ........................................................................................................................108
5.3 Results and Discussion .........................................................................................................112
5.4 Conclusions ...........................................................................................................................118
5.5 References ............................................................................................................................119

6. CONCLUSIONS .....................................................................................................................122
TABLE OF CONTENTS CONTINUED

6.1 Summary .................................................................................................................. 122
6.2 Future Directions ...................................................................................................... 125
   6.2.1 Other Solutes ............................................................................................... 125
   6.2.2 Other Solvents ............................................................................................. 126
   6.2.3 pH Studies .................................................................................................... 127
6.3 References .............................................................................................................. 128

REFERENCES CITED .................................................................................................... 129
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Lifetimes and amplitudes for C152</td>
<td>37</td>
</tr>
<tr>
<td>3.1 Fluorescence lifetimes and amplitudes of C152 adsorbed to aqueous-hydrophilic and aqueous-hydrophobic silica interfaces as measured by TCSPC</td>
<td>60</td>
</tr>
<tr>
<td>4.1 DMABN spectroscopic properties in various bulk solvents</td>
<td>80</td>
</tr>
<tr>
<td>4.2 Emission lifetime data from DMABN in water at the silica interface collected in a TIR geometry. Uncertainties in life-times are ±0.1 ns and uncertainties in amplitudes are ± 0.04</td>
<td>81</td>
</tr>
<tr>
<td>4.3 Calculated transition wavelengths (in nm) and oscillator strengths (in a.u.) for the S\textsubscript{1} and S\textsubscript{2} transitions in DMABN at different local field strengths (in V/cm) and ground state amine twist angle</td>
<td>90</td>
</tr>
<tr>
<td>4.4 Calculated changes in permanent dipole strength in DMABN at 0 field strength for primary S\textsubscript{2} transition around 290 nm</td>
<td>92</td>
</tr>
<tr>
<td>5.1 Lifetimes and amplitudes from C151 decay in bulk solvents</td>
<td>113</td>
</tr>
<tr>
<td>5.2 Lifetimes and amplitudes from C151 fluorescence decay at various silica-aqueous interfaces</td>
<td>114</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>1.1</td>
<td>Experimental geometry of the TCSPC instrument</td>
</tr>
<tr>
<td>1.2</td>
<td>Experimental geometry of the SHG instrument</td>
</tr>
<tr>
<td>1.3</td>
<td>Structure of the silica surface. Nonlinear optical studies suggest that the silica surface has 2 different types of silanols. One is isolated (red) with a pKa of approximately 8.5. The other is hydrogen bonded to its neighbors (blue) with a lower pKa of approximately 4.5.</td>
</tr>
<tr>
<td>1.4</td>
<td>The structure of DMABN in its ground state (left) and in its excited TICT state (right)</td>
</tr>
<tr>
<td>1.5</td>
<td>The structure of C152 in its ground state configuration (left) and proposed structure of the excited TICT state (right)</td>
</tr>
<tr>
<td>2.1</td>
<td>The structure of C152 in its ground state configuration (left) and proposed structure of the excited TICT state (right)</td>
</tr>
<tr>
<td>2.2</td>
<td>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.</td>
</tr>
<tr>
<td>2.3</td>
<td>TIR-TCSPC traces of saturated (blue) and dilute (red) aqueous solutions of C152. The tail from the 3.52 ns lifetime represents a greater proportional amplitude of the dilute trace, which is evidence for the idea that the cause of that lifetime is an effect that is amplified by the surface</td>
</tr>
<tr>
<td>2.4</td>
<td>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)</td>
</tr>
<tr>
<td>3.1</td>
<td>The structure of C152 in its ground state configuration (left) and excited TICT state (right)</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>3.2</td>
<td>49</td>
</tr>
<tr>
<td>Top: Absorbance spectra of C152 in cyclohexane (blue) and water (red) Bottom: TCSPC decay curves for C152 in water (red) and hexanes (blue)</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>55</td>
</tr>
<tr>
<td>Absorbance of C152 in water (red) and the surface second harmonic spectrum of C152 at the water-silica interface (blue)</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>58</td>
</tr>
<tr>
<td>SHG spectra of C152 at the hydrophilic (blue) and hydrophobic (red) silica interface</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>59</td>
</tr>
<tr>
<td>TIR-TCSPC traces of C152 and the hydrophobic (blue) and hydrophilic (red) silica-aqueous interface</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>72</td>
</tr>
<tr>
<td>The structure of 4-dimethylaminobenzonitrile (left) and proposed structure of its excited TICT state (right)</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>73</td>
</tr>
<tr>
<td>Absorbance of DMABN in water (top) and normalized DMABN fluorescence emission spectra (bottom) in selected solvents</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>79</td>
</tr>
<tr>
<td>TCSPC spectra of DMABN in selected solvents</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>80</td>
</tr>
<tr>
<td>TIR-TCSPC spectra of DMABN at the water-silica interface</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>83</td>
</tr>
<tr>
<td>SH spectrum of DMABN at the water-silica interface</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>84</td>
</tr>
<tr>
<td>Two-photon excitation spectrum of DMABN in aqueous solution. The intensity axis reports DMABN emission recorded at 355 nm</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>84</td>
</tr>
<tr>
<td>SHG spectrum of DMABN at the hydrophobic water-silica interface</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>86</td>
</tr>
<tr>
<td>TIR-TCSPC spectra of DMABN at the hydrophobic water-silica interface</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>105</td>
</tr>
<tr>
<td>Coumarin 151 (top) and Coumarin 152 (bottom)</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>5.2 TCSPC decay traces of C151 dissolved in various bulk solvents</td>
<td>112</td>
</tr>
<tr>
<td>5.3 Fluorescence decay traces of C151 at the aqueous-silica interface with relevant bulk traces also shown</td>
<td>113</td>
</tr>
<tr>
<td>5.4 SHG spectrum (left ordinate, blue crosses) at the silica-aqueous interface and aqueous absorbance (right ordinate, red line) of Coumarin 151</td>
<td>115</td>
</tr>
<tr>
<td>5.5 SHG spectra of C151 taken at the unmodified hydrophilic and the hydrophobic silica interface</td>
<td>117</td>
</tr>
<tr>
<td>6.1 Rhodamine B in its closed-ring spirolactone form (top) and its open, conjugated, fluorescent form (bottom)</td>
<td>126</td>
</tr>
</tbody>
</table>
ABSTRACT

Experiments described in this thesis address the question of how strong association between water molecules and the silica surface alter the solvation and isomerization behavior of adsorbed organic molecules from bulk solution limits. The work was motivated by the hypothesis that the ice-like structure induced by strong hydrogen bonding with the surface silanol groups would restrict solute isomerization. This hypothesis was tested using 2 surface-specific spectroscopic techniques: second harmonic generation (SHG) and time-correlated single photon counting in a total internal reflection geometry (TIR-TCSPC). This work examined two different 7-aminocoumarin dyes (Coumarin 151 and Coumarin 152) and dimethylaminobenzonitrile (DMABN). Coumarin 152 and DMABN both isomerize to form a twisted intramolecular charge transfer (TICT) state upon photoexcitation, whereas Coumarin 151 forms a simple (planar) intramolecular charge transfer state. SHG studies characterized the local solvation environment surrounding adsorbed molecules by providing electronic excitation energies that were compared to bulk excitation energies in different representative solvents. TIR-TCSPC measured the time-resolved emission of adsorbed molecules and quantified a solute’s tendency to form TICT (or ICT) isomers at the aqueous-silica interface. Together, SHG and TIR-TCSPC provide a cohesive description of the local polarity across an aqueous-silica interface and how restricted solvent dynamics change a solute’s photophysical chemistry.

TIR-TCSPC studies reported that both C152 and DMABN are unable to isomerize to TICT states at the aqueous-silica interface, acting as if they were solvated in a nonpolar solvent or in a confined geometry. SHG studies confirm that the aqueous-silica interface is, in fact, more polar than the bulk aqueous limit, strongly implying that the observed effects are dynamic in origin rather than polarity driven. In contrast, studies of C151 show that this solute is largely insensitive to anisotropic, restrictive surface effects. Together results from these three molecules lead us to conclude that adsorption to the strongly associating aqueous-silica interface restricts large amplitude isomerization in organic molecules. Adsorption to less strongly associating interfaces does not cause this restriction. In the event that photo-induced isomerization does not require large amplitude motion, interfacial solvation has little effect on adsorbed solute behavior.
CHAPTER ONE

INTRODUCTION

1.1 Motivation

Every source of reflected light is a surface that creates a distinctive, anisotropic environment where molecular organization and reactivity differ from bulk limits. The unique environment at interfaces is responsible for changing properties such as solvent polarity,\textsuperscript{1-4} solvent viscosity,\textsuperscript{5-7} and solute adsorption\textsuperscript{8-9} dramatically from their bulk solution limits. Because solvent structure and properties are so different at interfaces relative to the isotropic bulk, interfaces can facilitate a variety of chemical reactions and rearrangements. Simple chemical substitutions and additions, such as the Diels-Alder reaction, can see a rate increase by as much as five orders of magnitude at the interface.\textsuperscript{10-12} Solvent properties induced by the interface are also responsible for enhancing structural rearrangements,\textsuperscript{13-16} mediating biological recognition processes,\textsuperscript{17-20} enabling photocatalysis,\textsuperscript{21-22} and even allowing reactions to occur that are not possible in bulk solution.\textsuperscript{23} Despite the knowledge that the interfacial solvation properties differ so significantly from the bulk and are enormously consequential for a variety of chemical processes, buried interfaces between a solid and a liquid or two immiscible liquids have proven quite difficult to study. Even when the properties of both bulk phases composing the interface are known, anticipating surface effects on interfacial structure and organization is not trivial. At the surface, a variety of competing factors including the
affinity of the solute, solvent and surface for each other, the energetics of adsorption and
the hydrogen bonding ability or the surface and solvent will determine the final structure
of interfacial solvent layers as well as that of adsorbed solutes.

For example, at the strongly associating silica-alcohol interface, strong hydrogen
bonding between surface silanols and the solvent alcohol group creates a layer with a
nonpolar solvation environment due to the arrangement of the solvent alkyl tails in an
ordered monolayer adjacent to the interface. Silica surfaces affect nitrile solvent
adsorption similarly, but with opposite effects on interfacial polarity. Acetonitrile at the
silica interface forms a bilayer-like structure that repeats, extending as much as 4 nm into
the surrounding bulk liquid. In contrast to methanol and similar alcohols, however, this
creates a solvation environment even more polar than the bulk solvent alone.

It is worth an interlude here to specify what is meant when polarity and the bulk
static dielectric constant are discussed in this thesis. Polarity is a qualitative descriptor of
the extent of dielectric polarization in a material, where the bulk static dielectric constant
is a descriptor of the average degree of dielectric polarization in a bulk dielectric
material. The dielectric constant is not constant under the influence of an external electric
field, as is true in all of the experiments discussed in this thesis. In this case, the
frequency-dependent dielectric function is given by:

\[
\varepsilon = 1 + \frac{Ne^2}{\varepsilon_0 m} \sum \omega_{i0}^2 \frac{f_i}{\omega_{i0}^2 - \omega^2 - i\omega\gamma_i}
\] (1.1)

Additionally, the dielectric function of water is complicated by its significant hydrogen
bonding network holding neighboring molecules together. It has been shown that the
influence of this hydrogen bonding network is to increase the static dielectric constant of
The experiments described in this thesis describe the importance of the hydrogen bonding network formed between water molecules and the adjacent silica surface, as well as the molecular response to the dielectric environment of this interface. However, from this point forward, I will only refer to the “bulk static dielectric constant”, which for bulk water is known to be $\varepsilon=80$, and disregard the possible effects of the frequency dependence of the dielectric function.

Silica-solvent interfaces have been the subject of intense study and scientific debate, and few buried interfaces have received more attention than the silica-aqueous interface. 71% of the Earth’s surface is water, and 59% of the solid crust is made up of silica, or silicon dioxide ($\text{SiO}_2$). Together, these statistics mean that approximately 42% of the planet’s surface is an aqueous-silica interface. Additionally, fused silica glassware and the use of silica gel chromatography columns mean that solute behavior at silica-liquid interfaces has important consequences for many areas of chemical functionality. Despite the ubiquity of this interface and its importance in a variety of fields, almost none of the work studying this interface has looked at anything other than the structure of the surface-associated water molecules. While understanding this interfacial structure is certainly important, understanding how surface-altered solvent structure and organization change the solvation properties of water is more important. In this context, solvation describes the noncovalent interactions that a solute experiences with its surroundings, and these solvation properties will control solute orientation, conformation and reactivity. Water’s unique hydrogen bonding ability makes it nature’s solvent of choice; since surfaces can affect solvation properties, sometimes in nonintuitive ways, understanding
how the solvation properties of interfacial water differ from those in bulk solution is critical for understanding solution phase surface chemistry.

Work described in this thesis examined how surface induced changes at the aqueous-silica interface dramatically altered the isomerization tendencies of adsorbed solutes. Specifically, time-resolved emission and resonance enhanced second harmonic generation (SHG) were used to measure whether or not solutes known to isomerize in bulk aqueous solution isomerized in the same manner when adsorbed to the aqueous-silica interface and to characterize the local solvation environment sampled by the adsorbed solutes. Results show that while the silica-aqueous interface is polar, molecules with large amplitude excited state isomerizations experience a solvation environment that cannot stabilize this isomerization, leading to spectroscopic results that make the interface appear nonpolar.

1.2 Techniques

Buried interfaces are difficult to study because any response from molecules at the surface is overwhelmed by that from those in the adjacent bulk solution. Thus, in order to see signal from surface molecules experimental methods must be able to discriminate signals arising from the bulk molecules from those coming from surface species.

1.2.1 TIR-TCSPC

Total internal reflection (TIR) spectroscopy is one of the most common methods used to study surface chemistry. TIR geometries can be used for most optical
spectroscopy techniques including fluorescence, infrared absorption, and Raman scattering by exploiting the total internal reflection that occurs when a light propagating through a medium with a higher refractive index reflects off of a surface at an angle greater than the critical angle. When light is incident on such an interface at an angle greater than its critical angle, all of the light will be reflected back on itself, rather than propagating along the path of its incident vector. This property derives from Snell’s law for the reflection of light that states:

\[ n_1 \sin \theta_1 = n_2 \sin \theta_2 \]  

(1.2)

where \( n_1 \) and \( n_2 \) are the refractive indices for the materials at the interface and \( \theta_1 \) and \( \theta_2 \) are the angles of incidence and transmission of the light beam incident on the surface. In order to create a TIR condition, \( n_1 \) must be greater than \( n_2 \). In this case, we can solve for the critical angle by setting:

\[ \sin \theta_1 = \frac{n_2}{n_1} \sin \theta_2 \]  

(1.3)

As the angle of reflection, \( \theta_2 \), reaches 90°, \( \sin \theta_2 = 1 \), and we solve for the critical angle, \( \theta_c \):

\[ \sin \theta_c = \frac{n_2}{n_1} \]  

(1.4)

While TIR spectroscopy is selectively sensitive to surface species, TIR techniques are not uniquely surface sensitive. Even at angles above the critical angle, light impinging on a surface creates a local electric field, also known as an evanescent wave, propagates into the adjacent medium with its field strength decaying exponentially as a function of distance. Depending on the system’s critical angle and the wavelength of the incident light, the evanescent wave in a TIR geometry will propagate into the adjacent
bulk material ~50-500 nm. Although this condition does not confer absolute surface specificity to any TIR technique, any experiment carried out under total internal reflection conditions will necessarily be more sensitive to surface species than any bulk measurement. This sensitivity is enhanced further if TIR methods are being used to study surface active species.

In the experiments described in this work, I have coupled a TIR experimental geometry with a time-resolved fluorescence technique known as time-correlated single photon counting (TCSPC). TCSPC experiments use an ultrafast laser pulse to excite a material, and then count the fluorescent photons that are emitted as a function of time after excitation. This procedure creates a histogram of photons per unit time which can be fit to a sum of exponential decays (equation 1.4) to determine the fluorescence lifetimes of the molecules being excited:

\[ I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i} \]  

(1.5)

where \( A_i \) is the amplitude of the \( i \)th fluorescent lifetime, \( t \) is time since excitation and \( \tau_i \) is the \( i \)th fluorescent lifetime. Fitting parameters are optimized with a least squares fit. Knowledge of the fluorescence lifetimes of a molecule gives information about that molecule’s environment and photophysical properties.\(^{32}\)

To perform the TCSPC experiments described in this work, a Coherent Chameleon mode-locked, tunable Ti:sapphire oscillator with a wavelength range of 680-1080 nm and an 80 MHz repetition rate and ~2W average power was coupled to an APE autotracker to convert the fundamental beam into the necessary wavelength using either a second or third harmonic crystal. The second harmonic output was in the range of 350-
520 nm and the third harmonic output was between 230-350 nm, with 50-200 mW power dependent on wavelength. The beam out of the autotracker was sent into an optoacoustic modulator (Conoptics Model 350) to reduce the repetition rate from 80 to 4 MHz. Fluorescent photons were collected with a Picoquant PicoHarp 300 detector with a FluoTime 200 software interface.

![Figure 1.1: Experimental geometry of the TCSPC instrument](image)

1.2.2 Second Harmonic Generation

The second technique used in the experiments in this work is resonance enhanced second harmonic generation or SHG spectroscopy. As a second order nonlinear optical spectroscopy, SHG is inherently surface specific.

Nonlinear optical effects were first reported in 1961, soon after the discovery of the first ruby laser. The effects were explained by expanding the expression for the linear optical polarization, $P(t) = \varepsilon_0\chi^{(1)}E(t)$, in a power series in electric field strength,
as linear polarization could no longer account for the consequences of illumination with intense, coherent optical radiation, like a laser:

\[ P(t) = \varepsilon_0 \left[ \chi^{(1)}E(t) + \chi^{(2)}(t)^2 + \chi^{(3)}(t)^3 + \cdots \right] \quad (1.6) \]

The second order nonlinear optical polarization, \( P^{(2)} \), is the origin of second order nonlinear optical effects, and from the expansion above is equal to the second order nonlinear optical susceptibility times the incident electric field squared: \( P^{(2)}(t) = \varepsilon_0 \chi^{(2)}(t)^2 \). The second order nonlinear optical susceptibility, \( \chi^{(2)} \), is a third rank tensor so by definition, \( \chi^{(2)}_{ijk} = -\chi^{(2)}_{i-j-k} \), a statement which can only be true in a spatially isotropic material if \( \chi^{(2)} = 0 \). Thus, the only systems which will have a nonzero second order nonlinear optical susceptibility are those with an inherent anisotropy, such as interfaces. This property of \( \chi^{(2)} \) enables detection of signal from molecules at intrinsically anisotropic interfaces to the exclusion of signal arising from the adjacent centrosymmetric bulk materials.

When two laser beams having different frequencies (i.e. \( E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c. c. \)) are incident on a medium with a non-zero nonlinear susceptibility, substitution into the expression for the second order nonlinear polarization, assuming real-valued field amplitudes (i.e. \( E_1 E_1^* = E_1^2 \)), gives:

\[ P^{(2)}(t) = \varepsilon_0 \chi^{(2)} \left[ (E_1^2 e^{-i(2\omega_1)t} + E_2^2 e^{-i(2\omega_2)t} + c. c.) + 2E_1 E_2 (e^{-i(\omega_1 + \omega_2)t} + e^{-i(\omega_1 - \omega_2)t} + c. c.) + 2(E_1^2 + E_2^2) \right] \quad (1.7) \]

The frequency components in the equation above comprise the signals from 3 different second order nonlinear optical techniques: SHG, sum frequency generation (SFG) and
difference frequency generation (DFG). The static electric fields produced are another second order nonlinear polarization effect known as optical rectification.\textsuperscript{34-35}

Of these second order optical nonlinear effects, two are the most useful for interface spectroscopy: second harmonic generation and sum frequency generation. Second harmonic generation spectroscopy (SHG) uses two incident photons of frequency $\omega$ to generate a single resultant second harmonic (SH) photon of frequency $2\omega$, and is typically performed with incident photons in the visible region, generating photons in the ultraviolet. When either the incident or the generated second harmonic light is resonant with an electronic transition of the interfacial molecules, the SH signal experiences a large resonant enhancement, making SHG well-suited to study the electronic structure of interfacial molecules and materials.

Sum frequency generation (SFG) is similar in principle to SHG. In SFG, 2 photons of frequencies $\omega_1$ and $\omega_2$ combine to give a single photon of frequency $\omega_3$, where $\omega_3 = \omega_1 + \omega_2$. A typical SFG experiment uses incident beams in the visible and infrared (IR) regions to generate a sum frequency (SF) photon. When the IR frequency is resonant with a vibrational transition of the interfacial molecules, enhancement of the SF signal will occur, allowing detailed structural information about the interfacial molecules to be gathered. SFG requires that 2 pulsed laser beams overlap at the sample in both time and space, as well as necessitating that at least one medium making up the interface be transparent to both visible and IR light. These technical constraints limit the utility of SFG when studying buried interfaces. As the experiments in this thesis were interested exclusively in the buried silica-aqueous interface, and SHG provides a complementary
electronic spectroscopy technique to fluorescence, SHG was used preferentially to vibrational SFG.

Not only is $\chi^{(2)}$ surface specific due to its behavior with respect to inversion, elements in the $\chi^{(2)}$ tensor are also molecularly specific. The $\chi^{(2)}$ tensor has 2 components, a resonant (R) and a nonresonant (NR) piece:

$$\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_{R}$$

(1.8)

The nonresonant part of this tensor in the experiments described in this thesis was simple and could be fit to a constant. The resonant portion of $\chi^{(2)}$ is the orientational average over the molecular hyperpolarizability multiplied by the total number of surface molecules:

$$\chi^{(2)}_{R} = N(\beta_{i,j,k})$$

(1.9)

where $\beta$ is given by: $\beta = \frac{A}{\omega_0 - \omega - i\Gamma}$. In this equation, $A$ is a constant related to the one- and two-photon absorption resonances of the surface molecules, $\omega_0$ is the resonant frequency of the transition, $\omega$ is the frequency of the incident light, and $\Gamma$ is the linewidth associated with the transition. When collecting SHG spectra, the data is fit with equations 1.8 and 1.9 in order to determine the linewidth and central wavelength of the resonance.

In order to collect SHG spectra, a Coherent Libra-HE Ti:sapphire chirped pulse regenerative amplifier (1 kHz repetition rate, 3.3 W average power, 801 nm, 85 fs pulses) was used, coupled to an optical parametric amplifier (Coherent OPerA Solo, FWHM 10 nm) to create the wavelengths needed to perform SHG experiments. If necessary, neutral density filters were used to reduce the intensity of the light to less than 4 mW. The beam from the OPA was focused on the sample, then the fundamental beam was filtered out of
the reflected light and the SH photons were collected by a photomultiplier tube (PMT),
coupled to a monochrometer to discriminate the relevant wavelengths.

Figure 1.2: Experimental geometry of the SHG instrument

1.3 Description of the Aqueous-Silica Interface

In 1994, the first spectroscopic description of the structure of the aqueous-silica
interface was published by Ron Shen’s group at Berkeley. This description was based on
SFG experiments that probed the OH stretches of interfacial water molecules. This study reported 2 prominent peaks in the SFG spectrum of the aqueous-silica interface:
one at 3200 cm$^{-1}$, which corresponds to the coupled OH stretch of a tetrahedrally
coordinated water molecule, indicating ordered (ice-like) water molecules, and one at
3400 cm$^{-1}$, which is an asymmetric stretch whose intensity correlates with the degree of
disorder in the water layers. The relative intensities of these two peaks can give a rough
approximation of ordering in the water molecules being studied. The 1994 study
concluded that at all pH values, interfacial water layers at the silica surface have bonds
that correspond to both ordered and disordered water structures. This result was
consistent with findings from molecular dynamics simulations available at the time.
As more accurate and specific surface spectroscopy methods became available and the ability to analyze complex spectroscopic data became routine, there were several groups that disagreed with Shen’s original assignment of the silica-aqueous spectrum to bulk water-like and ice-like components.\textsuperscript{39-41} These comments led to a controversy about the structure of the interfacial water layers at the aqueous-silica interface that continues to this day.\textsuperscript{42-45} While there remains no consensus on the absolute assignment of the vibrational SFG bands at the aqueous-silica interface, all researchers agree that the presence of a charged silica interface leads to a high degree of anisotropy across the interfacial region.\textsuperscript{44, 46}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{silica_surface.png}
\caption{Structure of the silica surface. Nonlinear optical studies\textsuperscript{47} suggest that the silica surface has 2 different types of silanols. One is isolated (red) with a pKa of approximately 8.5, The other is hydrogen bonded to its neighbors (blue) with a lower pKa of approximately 4.5.}
\end{figure}

The surface layer of fused, amorphous silica is characterized by silanol and siloxide groups, with a density of approximately 5 groups per nm\textsuperscript{2} although this number will vary depending on how a sample has been processed and its exposure history.\textsuperscript{48-49} The surface chemistry of the aqueous-silica interface is dominated by the dissociation reaction:

\[SiOH + OH^- \rightarrow SiO^- + H_2O\] 

(1.10)
The point of zero charge (PZC) at the silica surface falls between pH 2 and 3.\textsuperscript{47, 50-51} When the silica surface is in contact with an aqueous solution at a higher pH, some surface silanols will be deprotonated to form siloxides. Above a pH of approximately 10, no more silanols will be deprotonated. When the silica surface has a higher concentration of negative charges and therefore a greater surface electric field, it is known to orient water molecules more strongly. However, even at neutral or weakly charged surfaces, strong hydrogen bonding interactions between water molecules and the silica surface aligns water dipoles for as much as 15 Å into the bulk.\textsuperscript{46, 51-54} There is also consensus that this strong association between the silica and its associated interfacial molecules significantly slows water reorientation dynamics,\textsuperscript{44, 46} and a single study that suggested the same is true for solutes adsorbed at the interface.\textsuperscript{55}

1.4 Molecular Isomerization and Twisted Intramolecular Charge Transfer (TICT) States

Work described in this thesis examines how the anisotropy found at silica interfaces changes a solute’s photoisomerization properties. Following photon absorption, an excited solute will be surrounded by solvent organized in a way to minimize the solute’s ground state energy. Solvent reorganization to stabilize the solute’s new excited state electronic structure will require $10^{-14} - 10^{-11}$ seconds depending on the solvent.\textsuperscript{56-58} During this time, a solute’s emission red-shifts and – depending on details of solute structure and surrounding environment – the photo-excited solute may isomerize. While there are many different forms of excited state geometries, a particularly common structure is the charge transfer (CT) state, where an electron is transferred from an electron donating part of the molecule to an electron accepting part of the molecule or supramolecular structure. This
photoinitiated electron transfer process is the fundamental basis of photosynthesis and a host of technological innovations, particularly in the area of solar energy conversion.\(^{59}\)

A particularly interesting case of photoexcited electron transfer is that of the twisted intramolecular charge transfer or TICT state. In the creation of a TICT state, an electron donor and an electron acceptor within the same molecule fully separate a set of radical ion pairs across the molecule by twisting some portion of that molecule by 90° relative to the plane of the molecule. In all of the cases discussed in this thesis, this involves an amine group shifting from a pyramidal geometry in the ground state to a 90° twisted structure in the excited TICT state.

![Figure 1.4: The structure of DMABN in its ground state (left) and in its excited TICT state (right)](image)

The first reports of TICT state formation were for a push-pull aromatic solute, 4-dimethylaminobenzonitrile (DMABN), the subject of chapter 4 of this thesis. In 1962, a paper was published describing DMABN’s anomalous dual fluorescence in polar solvents.\(^{60}\) This discovery spawned a host of theories about the origins of DMABN’s behavior,\(^{61-68}\) but in 1973 the first of a series of papers was published describing what became known as the TICT hypothesis for DMABN’s fluorescence signature.\(^{69-71}\) On the
basis of strong experimental and computational evidence, the TICT hypothesis has become the accepted explanation for DMABN’s dual fluorescence, and the solute remains the prototypical donor-acceptor TICT compound due to its simple structure and well-understood photophysics.\textsuperscript{59}

In the years since the discovery of the TICT state in DMABN, the existence of TICT states in several classes of well-known fluorescent dyes has been postulated on the basis of their photophysical behavior and the highly dipolar nature of their excited states. In particular, the existence of a TICT state in the set of 7-aminocoumarin dyes has been the subject of much debate.\textsuperscript{72-79} The generally accepted conclusion is that in coumarin dyes with strong electron donors (e.g. alkyl amines) in the 7-position and strong electron acceptors on the opposing ring, polar solvents can stabilize a charge transfer state following photoexcitation.\textsuperscript{80} The CT state can be either planar – described as a simple intramolecular charge transfer or ICT conformation – or twisted (TICT). Two different 7-aminocoumarin solutes are studied in this thesis. Coumarin 152 (7-(Dimethylamino)-4-(trifluoromethyl)-1-benzopyran-2-one) has a tertiary amine in the 7-position and is thought to form a TICT state in polar solvents. Coumarin 151 (7-amino-4-(trifluoromethyl)-1-benzopyran-2-one) is the closely related primary amine and forms a simple planar ICT state. These different pathways have important consequences for each solute’s excited state photophysical behavior.

Coumarin 152 (C152), the subject of chapters 2 and 3 of this work, is a member of the 7-aminocoumarin family with a dimethylamino group in the 7-position and a –CF\textsubscript{3}
group and an ester on the opposing ring, which provide optimal charge transfer characteristics for the formation of a TICT state. Because the coumarin TICT state is non-fluorescent, it changes the photophysical behavior of C152 in noticeable and distinct ways. As C152 is dissolved in solvents of greater polarity, formation of the TICT state becomes more allowed. With increased TICT character in the excited state, more molecules decay through the non-fluorescent decay pathway opened by the TICT state. This effect shortens the fluorescence lifetime and causes the fluorescence to red-shift relative to dye molecules solvated in less polar environments. The solvatochromism caused by the TICT state in C152 allows the dye to be used as a fluorescent indicator of the polarity of its solvation environment.

Figure 1.5: The structure of C152 in its ground state configuration (left) and proposed structure of the excited TICT state (right)

1.5 Organization of Thesis

Chapter 2: Hindered Isomerization at the Silica-Aqueous Interface: Surface Polarity or Restricted Solvation

Chapter 2 presents data from TIR-TCSPC studies of Coumarin 152 dye at the aqueous-silica interface. At this interface, the solvatochromic C152 dye molecule shows
a fluorescent spectral signature reminiscent of the molecule dissolved in a nonpolar bulk solution. This result is unexpected given that the polarity of water is high, as is that of silica. These results are discussed in the context of C152’s excited state photoisomerization into a TICT state. A nonpolar solvent’s inability to solvate this highly dipolar state is the basis for the spectral signatures in that medium, so we conclude that some aspect of C152’s solvation at the aqueous-silica interface is preventing this isomerization following photoexcitation. Since a truly nonpolar region at the aqueous silica interface is unlikely, we hypothesized that possibly the strong association of the water molecules to the silica surface was creating a solvent cage restricting C152 isomerization.

This hypothesis was supported with TCSPC data from C152 dissolved in an ice matrix, which displayed a similar fluorescence signature to C152 at the aqueous-silica interface, despite having a bulk static dielectric constant greater than that of bulk water.

Chapter 3: Surface Solvation and Hindered Isomerization at the Water-Silica Interface Explored with Second Harmonic Generation

Chapter 3 continues the line of inquiry begun in Chapter 2. SHG spectra of C152 at the aqueous-silica interface show that in its ground state C152 experiences a polar environment, lending support to the theory that the unusual fluorescence results observed at the same interface are the result of confined water structure and not that of a genuine interfacial nonpolar region.

To test if the strong association between water and the silica surface was, in fact, responsible for C152’s unexpected behavior, we disrupted hydrogen bonding at the
interface by rendering the silica surface hydrophobic through reaction with
dichlorodimethylsilane. At this hydrophobic silica-aqueous interface, C152 molecules
showed a lifetime similar to C152 dissolved in a polar organic solvent like methanol.
SHG results confirm that this hydrophobic interface is less polar than that made by
unmodified hydrophilic silica; the hydrophobic silica-aqueous interface also shows a
spectral signature reminiscent of C152 dissolved in a polar organic solvent in SHG
spectra. These results implicate the strong, ordered hydrogen bonding network between
water and silica as the instigator of C152’s hindered photoisomerization to a TICT state
at the aqueous-silica interface.

Chapter 4: Buried Liquid Interfaces as a Form
of Chemistry in Confinement: The Case of 4-
dimethylaminobenzonitrile (DMABN) at the
Silica-Aqueous Interface

Chapter 4 presents data that tests the generality of the hypothesis set out in
Chapters 2 and 3, namely that hydrogen bonding networks at the aqueous-silica interface
impede TICT formation. The new solute that is the subject of these experiments, 4-
dimethylaminobenzonitrile or DMABN, is the earliest and classic example of TICT
chemistry as noted in Section 1.4. TIR-TCSPC data from DMABN at the aqueous-silica
interface are consistent with C152 studies and indicate the DMABN is unable to
isomerize into its TICT at this interface. Both TIR-TCSPC and SHG spectra at the
hydrophobic silica-aqueous interface with DMABN show that removing the hydrogen
bonding network enables the solute to once again form a TICT state following
photoisomerization. SHG studies show that at this hydrophobic interface DMABN, like
C152, samples a slightly less polar environment than molecules at the hydrophilic interface.

SHG studies of DMABN at the hydrophilic aqueous-silica interface confirm that DMABN in its ground state is experiencing a bulk static dielectric constant consistent with that of water. However, SHG spectra show the presence of an unexpected and large peak that is not seen in bulk absorbance spectra. With the help of semi-empirical computations, this feature is assigned to the $S_0 \rightarrow S_1$ transition of DMABN. In order for a transition to have a strong $\chi^{(2)}$ response, the transition in question must be both 1- and 2-photon absorption allowed. In the case of DMABN, the $S_0-S_1$ transition is only very weakly allowed in 1-photon absorption experiments, although its 2-photon absorption cross section is more significant. However, semi-empirical and DFT calculations predict that in the presence of strong electric fields at the surface, the relative oscillator strengths of the $S_1$ and $S_2$ transitions can flip, explaining the dramatic intensity seen for this transition in the surface SHG spectra. These studies also lend a generality to the theory that we posited about surface association via hydrogen bond networks restricting TICT formation.

Chapter 5: Isomerization in Coumarin 152 and Coumarin 151 at the Water-Silica Interface: Effect of Primary vs. Tertiary Amines

Chapter 5 is a comparative study of Coumarin 151 and 152 at the aqueous-silica interface. C151 has the same molecular structure as C152, except in the 7-position it has a primary amine instead of the tertiary dimethyl amine found in C152. This change in structure means that C151 does not form an excited TICT state because its primary amine
is not a strong enough electron donor. Instead, C151 forms a planar ICT state which involves an isomerization of a much smaller magnitude than that required to form the TICT state in C152. These studies showed that even though C151 forms an excited state with a significant dipole, its spectral response is unchanged from those in bulk water by adsorption at the aqueous-silica interface. This led us to conclude that it is the large-amplitude isomerization in C152 and DMABN that is hindered at the silica-aqueous interface.
1.6 References


73. Nad, S.; Kumbhakar, M.; Pal, H., Photophysical properties of coumarin-152 and
coumarin-481 dyes: Unusual behavior in nonpolar and in higher polarity solvents.

Effects on the Absorption and Emission of 7-Aminocoumarins. *J Lumin* 1994, 59 (6),
369-375.

Effect on the Photophysical Properties of 7-Aminocoumarin Derivatives. *J Phys Chem-
Us* 1993, 97 (18), 4704-4707.

76. Cave, R. J.; Burke, K.; Castner, E. W., Theoretical Investigation of the Ground
and Excited States of Coumarin 151 and Coumarin 120. *The Journal of Physical
Chemistry A* 2002, 106 (40), 9294-9305.

77. Cave, R. J.; Castner, E. W., Time-Dependent Density Functional Theory
Investigation of the Ground and Excited States of Coumarins 102, 152, 153, and 343. *The

78. Rettig, W.; Klock, A., Intramolecular Fluorescence Quenching in
Aminocoumarines - Identification of an Excited-State with Full Charge Separation. *Can J
Chem* 1985, 63 (7), 1649-1653.

79. Rechthaler, K.; Kohler, G., Excited-State Properties and Deactivation Pathways of

80. Corrie, J. E. T.; Munasinghe, V. R. N.; Rettig, W., Synthesis and fluorescence
properties of substituted 7-aminocoumarin-3-carboxylate derivatives. *J Heterocyclic
Chem* 2000, 37 (6), 1447-1455.
CHAPTER TWO

HINDERED ISOMERIZATION AT THE SILICA/AQUEOUS INTERFACE: SURFACE POLARITY OR RESTRICTED SOLVATION?

Contribution of Authors and Co-Authors

Manuscript in Chapter 2:

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 Contributions: Collected and analyzed all experimental data and authored manuscript

Co-Author: Robert A. Walker

 Contributions: Assisted with data analysis and edited manuscript
CHAPTER TWO

HINDERED ISOMERIZATION AT THE SILICA/AQUEOUS INTERFACE: SURFACE POLARITY OR RESTRICTED SOLVATION?

2.1 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. 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 ‘liquid-like’, ‘ice-like’, and/or propose models that identify interfacial populations having specific hydrogen bonding configurations. Complementing these discoveries, theory and simulations have provided nuanced insight into how surface-altered hydrogen bonding changes water’s properties from bulk limits. Despite these concerted efforts, however, very few studies have explored how changes in water structure and dynamics impact the water’s ability to solvate 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, non-covalent interactions a solute experiences with its surroundings. Eisenthal and coworkers 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.\textsuperscript{86} Shifts in 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. reported that an interface’s local dielectric environment depends sensitively on solvent structure, and polarity across strongly associating interfaces (such as water/1-octanol) is characterized by a low polarity region having an effective dielectric constant of $\leq 2$.\textsuperscript{2,87} Similar results have been reported from silica/$n$-alcohol interfaces where strong hydrogen bonding between surface silanol groups and the first solvent layer effectively transforms the silica surface into a hydrophobic, alkyl terminated substrate.\textsuperscript{7,26}

### 2.2 Experimental

Experiments were carried out using a locally-constructed TCSPC fluorometer that has been described previously.\textsuperscript{9} 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 was measured using a non-emissive Ludox scattering solution. For bulk solution measurements, the IRF was between 20 and 50 ps. For TIR measurements, a custom-built assembly enabled the excitation pulse to irradiate the interface formed between a hemispherical prism and 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 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 DI water (Millipore, 18.2Ω), 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.

![Figure 2.1: The structure of C152 in its ground state configuration (left) and proposed structure of the excited TICT state (right)](image)

Most experiments in this work used saturated aqueous solutions of Coumarin 152 (C152). (Figure 2.1) Coumarin 152 was purchased from Exciton and used as received. C152’s photophysical behavior has been examined in detail both experimentally and computationally. Several properties of this solute make it an attractive probe of local solvation environment: well-defined absorption/emission behavior, photostability, and an
insensitivity to local viscosity. In most solvents, C152 emission is characterized by a single exponential decay, simplifying 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 2.1. 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.

Figure 2.2: 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.

Saturated solutions were made by allowing DI water and excess C152 to equilibrate with stirring at 50°C overnight and then filtering excess dye from the solution before use. At room temperature, the concentration of an aqueous solution saturated with C152 is approximately 6 µM. In the experiments presented here, 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-ns lifetime (0.47 ns), while in nonpolar solvents, C152’s emission lifetime is markedly longer (3.5 ns in alkanes). (Figure 2.2)

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 surface normal; the resulting evanescent wave propagates ~150 nm into the aqueous solvent conferring pseudo-surface specificity to the measurements.

2.3 Results

2.3.1 Time-Resolved Fluorescence at Silica Interface

Experiments used time correlated single photon counting in a total internal reflection (TIR) geometry to measure the time-resolved emission of a coumarin solute adsorbed to a silica/aqueous (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.\(^9\) For TIR measurements carried out at the silica/aqueous interface, the fluorescence decay from a saturated C152 solution is best fit with 2 lifetimes: a short, 0.47 ns lifetime assigned to C152 in bulk solution and a longer lifetime of 3.52 ns assigned to C152 adsorbed to the surface. (Figure 2.3) Normalized
amplitudes for 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 two (~3 µM) leads to no change in lifetimes but the longer lifetime contributes twice as much (0.27) to the overall emission decay data. This result supports assignment of the long-lived monomers adsorbed to the silica/aqueous interface.\textsuperscript{85}

Figure 2.3: TIR TCSPC traces of saturated (blue) and dilute (red) aqueous solutions of C152. The tail from the 3.52 ns lifetime represents a greater proportional amplitude of the dilute trace, which is evidence for the idea that the cause of that lifetime is an effect that is amplified by the surface.

Data in Figure 2.3 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: 1) the local dielectric constant at the silica/aqueous interface is significantly less than $\varepsilon = 78.0$ experienced in bulk solution, and/or 2) water’s restricted motion or ‘ice-like’ character at the
silica/aqueous interface prevents interfacial solvent from stabilizing 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, findings presented here are among the first reported examples of how surface-mediated solvation in aqueous systems changes 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 ($\varepsilon \sim 2$). While interfacial polarity is expected to be less than that of bulk water based on prior experiments, alkane-like properties at a hydrophilic silica/aqueous interface are not expected. Unlike strongly associating organic solvents such as methanol, 1-butanol, and others, water does not have a ‘hydrophobic piece’ that can organize at a surface to form a locally non-polar region with alkane-like solvation. 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. 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 surface potentials at the silica/aqueous (pH ~6) interface > 75 mV in the low ionic strength limit. Over a distance of 2 nm, this surface potential will create fields > $10^6$ V/cm.
In 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 ‘ice-like’ water at silica-aqueous interfaces. Experiments and simulations create conflicting narratives about ice’s static dielectric constant relative to bulk water, but both theory and experiment show unequivocally that water reorientation dynamics at hydrophilic surfaces slow significantly from bulk limits. In vibrational spectroscopy experiments, highly structured water at a silica/aqueous interface is observed as a single broad feature centered at relatively low frequency (3100 cm\(^{-1}\)), very similar to the vibrational Raman spectrum of bulk ice.

<table>
<thead>
<tr>
<th></th>
<th>(A_1^a)</th>
<th>(\tau_1) (ns)(^b)</th>
<th>(A_2^a)</th>
<th>(\tau_2) (ns)(^b)</th>
</tr>
</thead>
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<td>0.50</td>
<td>≤ 0.02</td>
<td>4.02</td>
</tr>
<tr>
<td>TIR water (saturated)</td>
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<td>0.47</td>
<td>0.13</td>
<td>3.52</td>
</tr>
<tr>
<td>TIR water (dilute)</td>
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<td>0.47</td>
<td>0.27</td>
<td>3.52</td>
</tr>
<tr>
<td>ice</td>
<td>0.85</td>
<td>0.71</td>
<td>0.15</td>
<td>7.47</td>
</tr>
</tbody>
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\(^a\)Amplitude uncertainties are ±0.02. \(^b\)Lifetime uncertainties are ±0.15 ns.

Table 2.1: Lifetimes and amplitudes for C152

2.3.2 Fluorescence of C152 in Frozen Water

To test the viability of these explanations for C152’s long emission lifetime at the silica aqueous interface - reduced polarity vs. 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 2.4) While the structure of the ice matrix was not characterized explicitly in this work, we assumed that ice had an I-h structure given temperature and ambient pressure considerations.

Figure 2.4: 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)

Approximately 85% of the fluorescence emission from C152 in ice can be fit to a lifetime assigned to cold, bulk water (.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 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 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 non-polar based on comparison to bulk solvent studies, 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 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.

### 2.4 Conclusions

Time resolved fluorescence measurements of C152 adsorbed to the silica/aqueous (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 are
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, results described in this communication represent one of the first reported examples of how surface modified solvent properties affect 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.
2.5 References


CHAPTER THREE

SURFACE SOLVATION AND HINDERED ISOMERIZATION AT THE WATER/SILICA INTERFACE EXPLORED WITH SECOND HARMONIC GENERATION

Contribution of Authors and Co-Authors

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Co-Author: Robert A. Walker
Contributions: Assisted with data analysis and edited manuscript
CHAPTER THREE

SURFACE SOLVATION AND HINDERED ISOMERIZATION AT THE WATER/SILICA INTERFACE EXPLORED WITH SECOND HARMONIC GENERATION

3.1. Introduction

Water’s complicated behavior at surfaces has attracted significant attention since the first nonlinear spectroscopic study of water’s interfacial vibrational structure was published in the early 1990s. In parallel, numerous studies of organic solvents at interfaces have shown that surfaces can significantly change the organization and properties of adjacent liquids from bulk solution limits. For example, nonlinear optical experiments examining the silica-methanol interface showed conclusively that this interface is characterized by a distinctly nonpolar solvation region where the effective dielectric constant is ~2 (compared to methanol’s bulk static dielectric constant $\varepsilon = 32.7$). Molecular dynamics simulations and complementary vibrational studies suggest that at the silica-methanol interface, solvent density is significantly reduced within ~1 nm of the interface, and the interfacial methanol solvent molecules create a bilayer-type structure where methyl groups in adjacent methanol solvent layers adopt anti-parallel orientation. This organization creates an alkane-like sheet adjacent to the interface with a correspondingly low dielectric environment. Analogous results have been reported for the silica-acetonitrile interface.
Water’s extended long range ordering at surfaces and strong, directional hydrogen bonding raise similar questions about how anisotropic water structure impacts water’s ability to solvate solutes at interfaces. Studies of structure and dynamics at water-air and water-quartz interfaces have sparked considerable debate as to the dielectric environment, pH and structural ordering of interfacial water rather than leading to a definitive consensus. 41, 89-90, 101-102 Despite considerable interest in the structure of interfacial water layering, however, surprisingly little work has considered the effect of water’s unique structure at silica interfaces on the solvent’s ability to solvate adsorbed solutes. 82-83, 103 In this context, the term solvation refers explicitly to noncovalent interactions between an adsorbed solute and its surrounding solvent. These interactions can be either nonspecific such as those described by polarizable continuum models or specific such as the localized, directional interactions including hydrogen bonding and other dipole-dipole attractions. 104-107

A recent report examining the time resolved emission of Coumarin 152 (C152), a solvatochromic fluorescent dye, adsorbed at the silica-aqueous (pH 5.9) interface suggested that the adsorbed solute sampled a distinctly nonpolar solvation environment. 108 Specifically, fluorescence lifetimes measured from the silica-aqueous interface in a total internal reflection (TIR) geometry showed that C152 had a long-lived contribution more typical of C152 solvated in non-polar solvents such as alkanes or carbon tetrachloride. Coumarin 152 (Figure 3.1) derives its solvatochromic behavior from the +4 D change in dipole 72-73
Figure 3.1: The structure of C152 in its ground state (left) and excited TICT state (right)

formation of a twisted intermolecular charge transfer (TICT) state upon photoexcitation. The TICT state can only be solvated in polar dielectric environments.\textsuperscript{74, 80} Stabilization of the TICT state by polar solvents leads to a much shorter fluorescence lifetime and a red shift in the fluorescence spectrum relative to C152’s behavior in nonpolar media (Figure 3.2).\textsuperscript{73}

Given that water and silica are both polar materials, the existence of a ‘nonpolar’ fluorescence lifetime at the silica-aqueous interface is surprising. Two possible explanations for this behavior were proposed: 1) the effective dielectric permittivity at the aqueous-silica interface was reduced from its value in bulk water of 80.4, consistent with reports from studies of water in confined spaces\textsuperscript{90} or 2) strong hydrogen bonding between water and the silica substrate restricted interfacial water’s mobility so that solvent molecules at the surface could not reorganize around photoexcited C152 to stabilize the TICT state, leading to a longer fluorescence lifetime.\textsuperscript{109-110}

Additional studies in the same report measured the fluorescence behavior of C152 frozen in an ice matrix and reported lifetimes consistent with the
Figure 3.2: Top: Absorbance spectra of C152 in cyclohexane (blue) and water (red). Bottom: TCSPC decay curves for C152 in water (red) and in hexanes (blue)

interfacial TIR measurements. These data implied that either confinement or restricted solvation dynamics prevented C152 from isomerizing into a nonradiative TICT state upon photoexcitation and bolstered an explanation that solvation at silica-aqueous interfaces was controlled largely by immobilized solvent.

Interpretation of TIR time-resolved fluorescence measurements is hampered, however, by ambiguity about the solutes being excited. Given that fluorescence is not intrinsically surface specific and that the evanescent field of incident light propagates ~150 nm into the adjacent aqueous phase in the TIR geometry used in previous studies, one cannot definitively correlate observed responses to solutes directly adsorbed to the solid-liquid interface. In order to
resolve whether or not the silica-aqueous interface is truly nonpolar (with a low effective static dielectric constant) or if interfacial solvation is due to restricted solvent motion, experiments must be able to discriminate responses from solutes in the interfacial region from those originating in the adjacent, isotropic bulk.

Data presented below report resonance enhanced second harmonic generation (SHG) spectra from C152 molecules adsorbed to the silica-water interface. Results show that C152’s effective excitation wavelength at the silica-aqueous interface is similar to that in bulk aqueous solution, supporting the idea that solvation at the silica-aqueous interface is characterized by a high permittivity but restricted solvent mobility. SHG is intrinsically sensitive only to molecules subject to the anisotropy induced by an interface within the electric dipole limit.\textsuperscript{111-113} Furthermore, SHG and time resolved fluorescence data acquired from C152 molecules adsorbed to a hydrophobic silica-water interface show a local dielectric environment similar to what one would expect if interfacial solvation were described by averaged contributions from the adjacent phases. Taken together, resonance enhanced SHG spectroscopy and time-resolved fluorescence measurements illustrate that strong solvent-substrate association can conspire to create conflicting pictures of equilibrium and dynamic solvation.

3.2 Experimental

Laser grade Coumarin 152 was purchased and used as received from Exciton. Water used in the experiments was nanopure, from a Millipore filtration system, resistivity of 18.2 MΩ. Silica slides and experimental assemblies were
rinsed with methanol and DI water then soaked in a bath of 50/50 sulfuric/nitric acid for no less than one hour, and rinsed with DI water and dried under nitrogen before use. Experiments described in this work used saturated solutions of Coumarin 152 in water, that were made by combining excess C152 and water and allowing the solution to equilibrate with stirring overnight at 50°C. The solutions were filtered to remove excess dye before use. At room temperature, the concentration of C152 in a saturated aqueous solution is approximately 6 $\mu$ M. SHG spectra were collected from Kel-F sample chambers containing saturated C152 solution in contact with fused silica slides (Structure Probe, Inc.). For TIR-TCSPC measurements, a custom-built assembly was made from Kel-F sample chambers containing saturated aqueous C152 solution in contact with fused silica prisms (ISP Optics, Inc.), which allowed the excitation pulse to irradiate the interface formed between a hemispherical prism and an aqueous solution at angles greater than the critical angle (61° at 400 nm). Sample chambers, coumarin solutions, silica slides and prisms were allowed to equilibrate for at least an hour before being used in experiments.

Silica slides (Structure Probe, Inc.) and prisms (ISP Optics, Inc.) were functionalized with a solution of dimethyldichlorosilane in THF to create hydrophobic surfaces. Silica substrates were cleaned as described above and allowed to sit in the silane solution at 30°C for 36 hours. Once removed from the silane solution, silica slides and prisms were first washed with toluene, then methanol and finally tested with water to verify that the surface was hydrophobic.
To collect TIR-TCSPC spectra, 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 non-emissive Ludox scattering solution. 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 one or more single exponential decays. The minimum number of lifetimes required to accurately fit the data was determined using the Akaike information criterion.

In order to collect SHG signal from surface molecules, the coherent output from a tunable, amplified Ti:sapphire pumped optical parametric amplifier (OPA) at frequency \( \omega \) is focused on the surface and creates a polarization of the surface molecules at \( 2\omega \). The intensity of the collected second harmonic signal is proportional to the square of the second order polarizability, denoted as \( P^{(2)} \):

\[
I(2\omega) \propto |P^{(2)}(2\omega)|^2
\]  

(3.1)

where \( P^{(2)} = |\chi^{(2)}E(\omega_1)E(\omega_2)| \). In the case of second harmonic generation, the incident beam is of a single frequency and \( \omega_1 = \omega_2 \). The surface specificity of SHG, along with all second order nonlinear optical techniques, derives from \( \chi^{(2)} \), the second order nonlinear susceptibility. \( \chi^{(2)} \) is a rank 3 tensor consisting of 27 matrix elements; in centrosymmetric systems, the requirement that \( \chi^{(2)}_{ijk} = \chi^{(2)}_{-i,-j,-k} \) means that no second harmonic response will originate from an isotropic
solution within the electric dipole approximation. At an interface where symmetry is broken, elements of the $\chi^{(2)}$ tensor can take on non-zero values, dependent on the identity of the molecules at the interface. $\chi^{(2)}$ is composed of a non-resonant (NR) piece and a resonant (R) piece:

$$\chi^{(2)} = \chi_{NR}^{(2)} + \chi_{R}^{(2)}$$  \hspace{1cm} (3.2)

The non-resonant portion of the $\chi^{(2)}$ tensor is usually simple and can be fit to a single value whereas the resonant contribution is more complicated. The resonant portion of $\chi^{(2)}$ is equal to the number of molecules on the surface multiplied by the orientational average over the molecular hyperpolarizability ($\beta$) of the adsorbed molecules:

$$\chi_{R}^{(2)} = N \langle \beta_{i.j,k} \rangle$$, where $\beta$ is given by:

$$\beta = \frac{A}{\omega_0 - \omega - i\Gamma}$$  \hspace{1cm} (3.3)

In this expression for $\beta$, $A$ is a constant related to the transition dipole moment of the electronic resonance being examined, $\omega_0$ is the resonant frequency of the transition, $\omega$ is the frequency of the incident light, and $\Gamma$ is the linewidth associated with the transition.

In cases where the interface under investigation carries a surface charge, the second harmonic spectral lineshape can be influenced by some non-resonant elements of the $\chi^{(3)}$ tensor, which makes equation (3.2) take the form:

$$\chi_{\text{total}}^{(2)} \propto \chi^{(2)} + (\chi_1^{(3)} + i\chi_2^{(3)}) \Phi(0)$$  \hspace{1cm} (3.4)

where $\Phi(0)$ is the interfacial potential and both elements of the $\chi^{(3)}$ tensor are purely real.\textsuperscript{114-115} Collected second harmonic spectra are fit with equations (3.2), (3.3) and (3.4) to determine the linewidth and the center of the resonant peak.
Resonance-enhanced SHG spectra were acquired from an experimental assembly that has been described previously. Briefly, ~3.3W from a Ti:Sapphire regenerative amplifier (Libra-HE, Coherent, 85 fs pulses, 1 kHz repetition rate, 801 nm) was coupled to a visible optical parametric amplifier (Coherent OPerA Solo, fwhm 10 nm) and focused on the sample. If necessary, incident visible light was attenuated to below 4 mW with neutral density filters before it reached the sample. Second harmonic signal was collected using a photomultiplier tube and photon counting electronics. Data from each individual wavelength was collected over 3-5 separate 10s intervals, background corrected and then averaged. Typically, up to 300 counts were measured on resonance during a 10 sec. acquisition.

### 3.3 Results and Discussion

Figure 3.3 shows the second harmonic spectrum of C152 at the silica/aqueous interface. Also included on the opposite ordinate is C152’s absorbance spectrum in bulk water. The SHG data show clearly that the surface spectrum experiences a bathochromic shift relative to the spectrum in bulk water, with the resonance center at the surface measuring 405 nm, 7 nm higher than the absorbance peak at 398 nm. This result includes the $\chi^{(3)}$ term in Eq. 4 above with an assumed surface potential of 70-80 mV given an unbuffered, pH = 6 aqueous solution. (Omitting the $\chi^{(3)}$ contribution changes the calculated excitation wavelength maximum by less than 1.5 nm.)
According to C152’s well-characterized solvatochromic behavior, a red-shifted spectrum implies solvation in a more polar dielectric environment. This result at the water-silica interface is consistent with experiments and calculations predicting that water molecules immobilized in a solid ice matrix can also create a more polar dielectric environment than that found in liquid water. Under the influence of dipole ordering introduced by the solid structure, ice’s dielectric constant is reported to be between 78.2 and 107, depending on the ice structure and temperature. (Pure water has a dielectric constant of 80.4 at room temperature.)

Both experimental and computational results have suggested that water molecules within 10 Å of a silica surface experience a hexagonal ordering analogous to water molecules frozen in a solid state. The alignment of dipoles at the surface induces the coumarin to display spectroscopic evidence of a
more polar static, dielectric environment at the surface than in bulk. At the silica-
aqueous interface, all of the water dipoles are aligned in the same direction for the
first 2-3 solvent layers.\textsuperscript{46, 54} We propose that this anisotropic solvent dipole
ordering leads to a local permittivity greater than that of an isotropic arrangement
of the same solvent in bulk solution. Given these considerations, the fluorescence
signatures reported in Chapter 2 are unlikely to originate from any sort of non-
polar environment (with an effective alkane-like static dielectric constant).
Instead, since the SHG spectrum of the silica-aqueous interface indicates that the
molecular dipoles of water are highly arranged under the influence of hydrogen
bonds to the silica surface with a high static dielectric constant, a more likely
explanation for the long lifetime in C152 fluorescence is that restricted solvent
reorientation dynamics are too slow to enable formation of C152’s nonradiative
TICT state. Taken together, the SHG data imply a very polar static environment
but the TIR (and bulk ice) fluorescence measurements suggest slower dynamic
solvation than found in bulk solution. These results are not surprising given
interfacial water rotational correlation times reported to be as much as 40 times
slower at the surface than in bulk solution.\textsuperscript{109-110}

At the silica-aqueous interface, time-resolved fluorescence spectra of C152 show
a very long fluorescence lifetime, generally resulting from C152 solvated in nonpolar
solvents such as alkanes. Since the SHG results presented here confirm that the silica-
aqueous interface is indeed polar, we conclude that the fluorescence results derive from
restricted solvation at the interface and not from any reduction in the interfacial static
polarity. Furthermore, if this description is accurate, we expect that disrupting the ability of water to hydrogen bond to the silica surface will cause the static solvation environment sampled in SHG experiments and the time-dependent solvation interactions probed by TIR-time resolved fluorescence to be more consistent with each other.

In order to disrupt the strong ordering effects of the silica surface on adjacent water structure and dynamics, we functionalized silica slides with a dimethylsilane to create nonpolar, methyl terminated silica surfaces, and performed SHG and TIR-TCSPC measurements of C152 adsorbed to this hydrophobic silica-water boundary. Figure 3.4 shows the SHG spectrum of C152 adsorbed to the hydrophobic silica-aqueous interface. The same SHG spectrum of C152 adsorbed to the hydrophilic silica-aqueous interface first shown in Figure 3.2 is reproduced for comparison. At the hydrophobic-aqueous aqueous interface, C152’s SHG spectrum shows strong resonance enhancement with an excitation wavelength maximum of 389 nm, considerably blue-shifted from the 405 nm measured at the unmodified hydrophilic silica-aqueous surface and from the 398 nm measured in bulk aqueous solution. This hydrophobic silica-aqueous excitation wavelength is consistent with a local solvation environment similar to that found in bulk polar organic solvents such as ethyl acetate and acetone. Furthermore, this result is also consistent with expectations that a hydrophobic surface and a polar solvent would create an interfacial solvation environment that reflected averaged contributions from the two phases.
The SHG spectrum acquired from this hydrophobic-aqueous interface is broader than that measured at the unmodified silica-aqueous interface, with a linewidth of 26 nm compared to 19 nm at the hydrophilic interface. This spectral broadening usually indicates a heterogeneous solvation environment. The fact that the linewidth for C152 at the unmodified silica interface is narrower than that at the hydrophobic interface implies that the unmodified silica-water interface exhibits some degree of order that prevents further inhomogeneous broadening relative to what is observed at the hydrophobic interface.

The SHG data show clearly that C152 adsorbed to the hydrophobic silica-aqueous interface samples a less polar environment, indicating that disrupting the strong substrate-solvent interactions diminishes the local polarity. The consequences of this disrupted interfacial solvent structure on C152’s
isomerization can also be observed in the TIR-TCSPC measurements shown in Figure 3.5. These experiments were performed using hemispherical silica prisms that had been functionalized with dimethylsilane in the same manner as the silica slides used for SHG experiments. Also shown in Figure 3.5 for comparison is the time-resolved fluorescence from C152 adsorbed to the hydrophilic silica-aqueous interface.

![Figure 3.5: TIR-TCSPC traces of C152 at the hydrophobic (blue) and hydrophilic silica-aqueous interface (red)](image)

As previously reported, for a saturated solution of C152 in water at the unmodified silica-aqueous interface, two fluorescence lifetimes are seen—87% of the decay corresponds to C152 solvents in contact with bulk water with a lifetime of 0.47ns and 13% from solutes in contact with the silica surface with a lifetime of 3.52ns. The longer lifetime is similar to C152’s single, ~4 ns lifetime in
nonpolar media. At the hydrophobic silica-aqueous interface, fluorescence decays cannot be fit with less than 3 lifetimes. 72% of the decay still derives from C152 solutes dissolved in bulk water solution, with a lifetime of .45ns. 4% of the decay fits to a longer fluorescence lifetime of 4.25ns, either from solutes held by hydrogen bonds at defects in the hydrophobic surface layer, or from molecules completely excluded from water by the nonpolar molecules on the silica surface. The third lifetime seen at this interface composes 24% of the total decay and corresponds to a new lifetime of .93ns, typically attributed to C152 in a polar, hydrogen bonding solvent similar to methanol. These results are summarized in Table 3.1. Considering the structure of the hydrophobic silica-aqueous interface, this additional lifetime is sensible. The silica surface is composed of a layer of terminal methyl groups and the interfacial water solvent is expected to diminish in density and to be considerably less ordered.  

<table>
<thead>
<tr>
<th></th>
<th>A₁</th>
<th>t₁ (ns)</th>
<th>A₂</th>
<th>t₂ (ns)</th>
<th>A₃</th>
<th>t₃ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic silica</td>
<td>72%</td>
<td>0.45</td>
<td>4%</td>
<td>4.25</td>
<td>24%</td>
<td>0.93</td>
</tr>
<tr>
<td>Hydrophilic silica</td>
<td>87%</td>
<td>0.47</td>
<td>13%</td>
<td>3.52</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 3.1 Fluorescence lifetimes and amplitudes of C152 adsorbed to aqueous-hydrophilic and aqueous-hydrophobic interfaces as measured by TIR-TCSFCP. Lifetime data assigned to bulk solvated solutes are reported as A₁ and A₂.

The additional lifetime also makes the SHG and TIR-TCSFCP results from the hydrophobic interface much more internally consistent relative to the apparently conflicting findings from the hydrophilic interface. The SHG results at the hydrophobic silica interface indicate a dielectric environment similar to that of
bulk acetone (\(\varepsilon=20.7\)), while the time-resolved fluorescence data indicate a polar, protic solvation environment similar to that of methanol.

### 3.4 Conclusions

The results presented in this work create a more nuanced picture of water’s solvation properties at hydrophilic and hydrophobic silica-aqueous interfaces. Previous results indicated that solute isomerization was impeded at hydrophilic silica-aqueous interfaces and implied that the interface had distinctive nonpolar character. Resonance enhanced SHG spectra of adsorbed C152 show that the hydrophilic silica-aqueous interface is, in fact, characterized by a strong local dielectric constant. The restricted solute isomerization, then, likely reflects slower solvent reorientation dynamics resulting from strong water-silica association. Disrupting these solvent-substrate interactions leads to static and dynamic interfacial solvation properties that more closely mirror each other.
3.5 References


82. Richmond, G. L., Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chem Rev* 2002, 102 (8), 2693-2724.


CHAPTER FOUR

BURIED LIQUID INTERFACES AS A FORM OF CHEMISTRY IN CONFINEMENT:
THE CASE OF 4-DIMETHYLAMINOBENZONITRILE AT THE
SILICA-AQUEOUS INTERFACE

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Contributions: Collected and analyzed experimental data and authored manuscript

Author: Marshall T. McNally
Contributions: Collected second harmonic data

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Contributions: Assisted in performing computational calculations and analysis. Assisted in editing manuscript.

Co-Author: Robert A. Walker
Contributions: Assisted with data analysis and edited manuscript
CHAPTER FOUR

BURIED LIQUID INTERFACES AS A FORM OF CHEMISTRY IN CONFINEMENT:

THE CASE OF 4-DIMETHYLAMINOBENZONITRILE AT

THE SILICA-AQUEOUS INTERFACE

4.1 Introduction

Chemical reactivity at buried liquid interfaces differs from bulk solution limits in ways that affect processes as diverse as biological recognition\(^{17-20}\) and photocatalysis.\(^{21-22}\) These effects arise from a surface’s ability to change solvent phase stability criteria,\(^{124-125}\) as well as solvent polarity\(^{1-4}\) and viscosity.\(^{5-7}\) As a result, chemical transformations such as simple substitution reactions and Diels-Alder additions can see rate constants change by as much as five orders of magnitude or more.\(^{10-12}\) Surface-mediated solvent properties also facilitate structural rearrangements\(^{13}\) and enable reactions not possible in bulk solution.\(^{23}\)

Of particular interest is solute isomerization at liquid-solid,\(^{14-15}\) and liquid-liquid\(^{16}\) interfaces. Isomerization reactions are important mediators of protein structure-function relationships, and isomerization also plays an important role controlling conducting polymer properties and pharmacological activity.\(^{126-128}\) While surface effects on solution phase surface-chemistry are clear, anticipating these effects a priori is not trivial. Results presented in this work show that aqueous-silica interfaces slow photoisomerization of adsorbed solutes in a way similar to that of solutes in confinement. This effect is attributed to strong hydrogen bonding between the interfacial solvent and silica substrate,
creating an effective cage-like environment that restricts large amplitude solute motion
despite the fact that local dielectric properties should promote isomerization.

Interfacial properties of liquids, especially at strongly associating buried
interfaces have proven challenging to categorize. In alcohols, strong hydrogen bonding
between surface silanols and the solvent creates a non-polar region that extends a
nanometer or more away from the interface due to ordering of the non-polar hydrocarbon
tails.3, 24, 85 This effect is apparent for silica surfaces in contact with methanol where the
first two solvent layers adopt an antiparallel structure creating reduced solvent density
and an alkane-like static dielectric environment.7, 9, 25 Silica has similar effects on nitrile
solvent organization but with different consequences. At a hydrophilic silica surface,
acetonitrile adopts a repeating bilayer type structure that extends more than 4 nm into the
bulk liquid and the local solvation environment appears even more polar than bulk
solution limits.27

Silica’s surface properties including its isoelectric point, acidity and surface
composition can vary depending on the material’s processing and history,129-131 but in
general, silica surfaces are generally quite acidic with a point of zero charge at
approximately pH = 2.051,132, and studies have shown that silica functions much more
effectively as a hydrogen bond donor rather than a hydrogen bond acceptor.104 As a
result, silica’s effect on an adjacent solvent must consider both localized, directional
forces (e.g. hydrogen bonding) as well as more general Coulomb and dipolar interactions
and the constraints that come with a restricted dynamic surface structure.
Recent studies have reported that the silica-aqueous interface impedes isomerization of a coumarin solute, 7-(dimethylamino)-4-trifluoromethylchromen-2-one, or coumarin 152 (C152). In polar protic solvents, C152 is thought to form a nonradiative twisted, intramolecular charge transfer (TICT) state upon photoexcitation. This isomerization shortens C152’s radiative lifetime from ~3.5 ns (in nonpolar solvents) to ≤1 ns in solvents such as methanol and water. Total internal reflection, time-resolved fluorescence measurements carried out with C152 adsorbed to the silica-aqueous interface show that surface C152 has a lifetime similar to that in alkanes.

Water – unlike methanol – cannot form a nonpolar solvation region at the hydrophilic silica – aqueous interface, and surface specific second harmonic generation experiments showed clearly that the silica-aqueous interface is (slightly) more polar than bulk solution. This paradox was reconciled by proposing that strong hydrogen bonding between water and the silica surface restricts solvent motion and its ability to stabilize C152’s TICT state, although the adsorbed solute cavity still experiences strong internal electric fields (i.e. high polarity).

To test this idea that solvent-substrate interactions across the aqueous-silica interface can impede solute isomerization, we applied the methods described above to examine the photophysical behavior of N,N-dimethylaminobenzonitrile (DMABN) adsorbed to the silica-aqueous interface. DMABN was chosen, in part, because of its extensively characterized isomerization following photoexcitation. While some questions linger about the exact nature of C152’s solvent-dependent excited state...
structure,\textsuperscript{76-77} a broad consensus of researchers believe that DMABN forms an emissive TICT state in protic and aprotic polar solvents.

4-dimethylaminobenzonitrile (DMABN) (Figure 4.1) first attracted attention in 1962 in a report by Lippert et al. that described the solute’s anomalous dual fluorescence in polar solvents.\textsuperscript{134} DMABN exhibits 2 fluorescence emission bands; the first, termed the locally excited (LE) or 1L\textsubscript{b} fluorescence band, is not sensitive to solvent polarity and appears around 350 nm in all solvents. The second fluorescence band, the anomalous or 1L\textsubscript{a}, is strongly solvatochromic and appears between 440 and 520 nm, depending on solvent polarity (Figure 4.2b). Since the first report of DMABN’s dual fluorescence, the nature of the 1L\textsubscript{a} band has been the subject of intense discussion. Lippert and co-workers first assigned the 1L\textsubscript{a} fluorescence band of DMABN to a solvent stabilized inversion of excited state energies that would lower the energy of the excited state producing the long wavelength fluorescence below the energy of the locally excited state whence the typical short wavelength emission derives. Given the highly dipolar nature of the excited state, this inversion can only happen in polar solvents that stabilize charge separation on the excited molecule.

This explanation was abandoned after further experimental evidence, and other researchers have since proposed alternate explanations for the dual fluorescence of DMABN, including a solvent exciplex,\textsuperscript{61-62} dimer excitation,\textsuperscript{63} a pseudo-Jahn Teller (PJT) effect,\textsuperscript{135} and a twisted intramolecular charge transfer (TICT) state.\textsuperscript{69} In recent years, other geometries of a charge-transfer state, including a planar intramolecular
charge transfer state\textsuperscript{64-65} (PICT), a rehybridized intramolecular charge transfer state\textsuperscript{66-68} (RICT), and a wagged intramolecular charge transfer state\textsuperscript{136} (WICT) have all been proposed on the basis of energy calculations and experiments, but the TICT state explanation has the broadest body of experimental support. DMABN is the prototypical model of the donor-acceptor twisted charge-transfer reaction because its early discovery and simple molecular structure allow its photophysics to be well understood\textsuperscript{59, 69, 137-138}.

In the work presented below, we examine the photophysical behavior of DMABN adsorbed to aqueous-silica interfaces. TIR-TCSPC measurements show that photoexcited DMABN at the strongly associating aqueous-silica interface does not decay through its TICT state, as would be expected in bulk aqueous solution. Instead, TIR time-resolved emission measurements show that adsorbed DMABN relaxes with a lifetime more characteristic of the LE state implying a locally nonpolar solvation environment. To test the local dielectric environment at the aqueous-silica interface, we employed resonance enhanced SHG to measure the effective excitation wavelength of adsorbed DMABN.
Interestingly, SHG spectra showed strong resonance enhancement at 340 nm, a wavelength corresponding to the $S_0 - S_1$ transition that is only very weakly observed in absorbance and fluorescence excitation spectra. In contrast, the strongly allowed $S_0 - S_2$ transition

Figure 4.2 Absorbance of DMABN in water (top) and normalized DMABN fluorescence emission spectra (bottom) in selected solvents.

commonly used to photoexcite DMABN (at 290 nm) showed only a very weak NLO response. Electronic structure calculations suggest that these observations are consistent with both a distorted DMABN ground state geometry and strong local electric fields perturbing adsorbed DMABN’s ground state electronic structure. Taken together, results
from experiments and calculations illustrate how surface induced changes in solvent structure can fundamentally change a solute’s reactivity from bulk solution limits.

4.2 Experimental Methods

4-dimethlyaminobenzonitrile was purchased from Sigma Aldrich and used as received. Water used in the experiments was nanopure, from a Millipore filtration system and had a resistivity of 18.2 MΩ. Silica substrates and experimental assemblies were rinsed with methanol and DI water then soaked in a bath of 50/50 sulfuric/nitric acid for no less than one hour, and rinsed with DI water and dried under nitrogen before use. SHG spectra were collected from Kel-F sample chambers containing aqueous DMABN solution in contact with fused silica slides (Structure Probe, Inc.). For TIR-TCSPC measurements, a custom-built assembly was made from Kel-F sample chambers containing aqueous DMABN solution in contact with fused silica hemispheres (ISP Optics, Inc.), that allowed the excitation pulse to irradiate the interface formed between a hemispherical prism and an aqueous solution at angles greater than the critical angle (65° at 290 nm). Sample chambers, DMABN solutions, and silica slides/prisms were allowed to equilibrate for at least an hour before being irradiated.

Silica slides (Structure Probe, Inc.) and prisms (ISP Optics, Inc.) were functionalized according to previously published methods\(^3,119\) with a solution of dichlorodimethylsilane in toluene to create hydrophobic surfaces. These samples were created to test the role that silica hydrogen bonding played in controlling DMABN isomerization. Fresh silica substrates were cleaned as described above and allowed to sit in a 3% silane solution at 130°C for 36 hours. This procedure reliably leads to water
contact angles of 100°. Once removed from the silane solution, silica slides and prisms were first washed with toluene, then methanol and finally tested with water to verify that the surface was hydrophobic. Slides were used within 24 hours of silanization to ensure consistency of the monolayer.

To collect TCSPC spectra, 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 non-emissive Ludox scattering solution. In bulk solution, the IRF is between 20-50 ps. For TCSPC in a total internal reflection (TIR) geometry, 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 one or more single exponential decays:

\[ I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i} \]  

where \( A \) is the amplitude of the fluorescence lifetime, \( t \) is time since the excitation pulse and \( \tau \) is the fluorescence lifetime. The minimum number of lifetimes required to accurately fit the data was determined using the Akaike information criterion.\(^{139}\)

In order to collect SHG signal from surface molecules, the coherent output from a tunable Ti:Sapphire-pumped optical parametric amplifier (OPA) (Coherent, OPerA Solo) at frequency \( \omega \) is focused on the surface and creates surface polarization at frequency \( 2\omega \). SH data were acquired using a \( P_{2\omega}P_\omega \) polarization scheme. The intensity of the collected
second harmonic signal is proportional to the square of the second order polarizability, denoted as $P^{(2)}$:

$$I(2\omega) \propto |P^{(2)}(2\omega)|^2$$  \hspace{1cm} (4.2)

where $P^{(2)} = |\chi^{(2)} E(\omega_1) E(\omega_2)|$ for a generalized second order nonlinear polarization.

In the case of second harmonic generation $\omega_1 = \omega_2$. The surface specificity of SHG, along with all second order nonlinear optical techniques, derives from $\chi^{(2)}$, the second order nonlinear susceptibility. $\chi^{(2)}$ is a rank 3 tensor consisting of 27 matrix elements; in centrosymmetric systems, the requirement that $\chi^{(2)}_{i,j,k} = \chi^{(2)}_{-i,-j,-k}$ means that, within the electric dipole approximation, no second harmonic response will originate from an isotropic solution, as the only way to make the equality above true is for $\chi^{(2)}$ to equal zero. At an interface where symmetry is broken, elements of the $\chi^{(2)}$ tensor can take on non-zero values. $\chi^{(2)}$ is composed of a non-resonant (NR) piece and a resonant (R) piece:

$$\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_{R}$$  \hspace{1cm} (4.3)

The non-resonant portion of the $\chi^{(2)}$ tensor is often fit to a single value whereas the resonant contribution is more complicated. The resonant portion of $\chi^{(2)}$ is equal to the number of molecules at the surface multiplied by the orientational average over the molecular hyperpolarizability ($\beta$) of the adsorbed molecules:

$$\chi^{(2)}_{R} = N \langle \beta_{i,j,k} \rangle,$$  \hspace{1cm} (4.4)

where $\beta$ is given by: $\beta = \frac{A}{\omega_0 - \omega - \alpha}$.

In this expression for $\beta$, $A$ is a constant related to the transition dipole moment and the two photon polarizability\(^\text{36}\) of the electronic resonance being examined, $\omega_0$ is the
resonant frequency of the transition, \( \omega \) is the frequency of the incident light, and \( \Gamma \) is the linewidth associated with the transition.

When surfaces are charged (as is the case for silica in contact with Millipore water, pH = 5.8), the second harmonic spectral lineshape can be influenced other contributions to the nonlinear polarization, namely elements of the \( \chi^{(3)} \) tensor, that modify equation (4.2) take the form:

\[
\chi_{\text{total}}^{(2)} \propto \chi^{(2)} + (\chi_1^{(3)} + i\chi_2^{(3)})\Phi(0)
\]  

(4.5)

Here \( \Phi(0) \) is the interfacial potential and both elements of the \( \chi^{(3)} \) tensor are purely real.\(^{114-115}\) Collected second harmonic spectra are fit with equations (4.3), (4.4) and (4.5) to determine the linewidth and the center of the resonantly enhanced transition wavelength.

Resonance-enhanced SHG spectra were acquired from an experimental assembly that has been described previously.\(^8-9\) Briefly, \(~3.3\)W from a Ti:Sapphire regenerative amplifier (Libra-HE, Coherent, 85 fs pulses, 1 kHz repetition rate, 801 nm) pumped a visible optical parametric amplifier (Coherent OPerA Solo, fwhm 10 nm) and focused on the sample. If necessary, incident visible light was attenuated to < 10 mW with neutral density filters before it reached the sample. Second harmonic data were collected using a photomultiplier tube and photon counting electronics. Data from each individual wavelength were collected over 3-5 separate 10s intervals, background corrected and then averaged. Typically, up to 300 counts were measured on resonance during a 10 sec. acquisition.
One and two-photon fluorescence excitation spectra were collected using a Horiba Fluorolog-3 fluorescence spectrometer using 50uM aqueous solutions of DMABN. Fluorescence was collected at the LE peak at 355 nm, and the excitation wavelength was scanned from 500nm to 700nm. Excitation and emissions slits were 5nm wide. No additional effort was made to correct the two photon excitation spectrum to account for a quadratic dependence on incident power. Self-absorption may account for anomalously narrow linewidths.

Semiempirical calculations employed the INDO/S program of Ridley and Zerner,\textsuperscript{140} which is a spectroscopically calibrated semiempirical MO method, was used in the present study. The program was modified to include the electrostatic effects of surrounding charges and for constant fields, and has been used in numerous studies to provide insight into spectroscopic properties of molecules similar to DMABN.\textsuperscript{141-144} The potentials and fields were added to the appropriate elements of the Fock matrix as described by Theiste.\textsuperscript{141} The resulting self-consistent field equations were solved, followed by configuration interaction (CI). We have used 196 singly excited configurations for CI, arising from the transitions between the 14 highest occupied and the 14 lowest unoccupied MOs. The Mataga—Nishimoto formula was used to calculate two-center electron-electron repulsion integrals. The overlap weighting factors were 1.267 and 0.585, respectively. Results for relative state energies, intensities, and polarizations were insensitive to changes in the number of configurations.

TD-DFT computations were carried out for the lowest 3 singlet states of DMABN for all 119 functionals listed on the Gaussian.com website using Gaussian 09\textsuperscript{145} on a
Colfax CX2450-N4 2U Server with 4 16-core AMD Opteron 6376 CPUs, 256 gb ram, and 12 tb of disk. Geometry optimization of DMABN was carried out with B3LYP/6-31g(dp) with all heavy atoms in a planar configuration. To obtain qualitative behavior, the effect of twisting the DMA group was done by holding the rotating the group rigid. Single point computations were done with constant external fields applied using the “field” keyword.

4.3 Results

This work was motivated by a hypothesis proposing that solutes adsorbed to the strongly associating aqueous-silica interface sample a constrained, polar environment much like what a solute might experience if it were confined in a polar or ionic material with limited opportunity for intramolecular motion.¹⁴⁶

![Figure 4.3 TCSPC spectra of DMABN in selected solvents](image)
To test this hypothesis time-resolved emission data were measured from DMABN adsorbed to an aqueous-silica interface using TIR-TCSPC. Figure 4.3 shows time-resolved fluorescence from DMABN in bulk solvents. In solvents where the TICT state is accessible but poorly stabilized, DMABN emission is characterized by a single lifetime decay that varies between 1.7 ns in methanol and 3.5 ns in less polar, aprotic solvents such as THF. In aqueous solution, the observed behavior of DMABN emission depends strongly on the wavelength used to collect the emission. Emission from DMABN’s S$_1$ LE state (collected at shorter wavelengths ($\leq$ 370 nm) shows dual lifetimes with $\sim$85% of

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<th>$\lambda_{exc}$ (nm)</th>
<th>$\lambda_{em,LE}$ (nm)</th>
<th>$\lambda_{em,TICT}$ (nm)</th>
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<th>$A_1$</th>
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Table 4.1 DMABN spectroscopic properties in selected bulk solvents

Figure 4.4 TIR-TCSPC spectra of DMABN at the water-silica interface
the emission characterized by a very short lifetime ($\leq 0.1$ ns) and 15% of the emission having a much longer, 3.2 ns lifetime. This short lifetime is faster than can be resolved by our TCSPC assembly and is also consistent with time resolved emission from nonpolar solvents that cannot stabilize TICT state formation.

At wavelengths corresponding to TICT emission ($\geq 450$ nm), $\geq 98\%$ of DMABN emission in water has a lifetime of 0.3 ns. DMABN emission data from the TICT state in representative solvents are shown in Table 4.1. All bulk solution data measured in this work compare favorably to values reported previously.\textsuperscript{135,147} Figure 4.4 shows time-resolved emission from DMABN adsorbed to an aqueous-silica interface acquired using TIR-TCSPC. The TIR data show emission from adsorbed DMABN decays with a single exponential lifetime faster than can be resolved unambiguously by our instrument ($\leq 0.1$ ns, 94%) with only 6% of the emission coming from a putative TICT state ($\tau_{\text{TICT}} = 0.3$ ns). (Table 4.2)

<table>
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<th>$A_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$</th>
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<td>0.04</td>
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<tr>
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<td>2.16</td>
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</tr>
<tr>
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<td>0.12</td>
</tr>
<tr>
<td>Water/hydrophobic silica interface + 420 LP filter</td>
<td>0.31</td>
<td>0.71</td>
<td>2.04</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 4.2 Emission lifetime data from DMABN in water at the silica interface collected in a TIR geometry. Uncertainties in lifetimes are $\pm 0.1$ ns and uncertainties in amplitudes are $\pm 0.04$.

The longer lifetime component is assigned to those DMABN solutes that are not adsorbed to the interface but nevertheless excited by the evanescent field that extends $\sim 175$ nm into bulk solution. (For reference, DMABN emission in bulk aqueous solution
shown in Figure 4.3 is reproduced in Figure 4.4.) This result suggests that DMABN adsorbed to the aqueous-silica interface does not isomerize after photo-excitation or, equivalently, that the silica surface and surrounding water impedes TICT state formation. To test this idea further, we acquired time-resolved spectra using a 420 nm long pass filter so that only TICT emission was being detected. With the 420 LP filter in place, the majority (96%) of the measured emission had a 0.31 ns lifetime matching the bulk solution TICT data with 4% of the emission characterized by a 2.16 ns lifetime. Taken together, TIR results demonstrate clearly that the aqueous-silica interface impedes DMABN isomerization.

Given that DMABN TICT-state formation appears restricted at the aqueous-silica interface, questions arise about the local polarity experienced by adsorbed DMABN solutes. TICT-state formation is less likely in nonpolar solvents such as cyclohexane where excited state emission is dominated by relaxation from the LE state back to the ground state. (Figure 4.2) To assess adsorbed DMABN’s local dielectric environment, we measured the solute’s resonance-enhanced SHG spectrum. Figure 4.5 shows a surprising result. SHG data were acquired across the wavelength region 280-370 nm, and the spectrum shows the expected $S_0 \rightarrow S_2$ excitation peak at 316 nm, red-shifted ~ 10 nm from its peak in bulk water. More surprisingly, this spectrum is dominated by a strong resonance at 342 nm that we assign to the $S_0 \rightarrow S_1$ transition. This feature is very weak or absent in most absorption and fluorescence excitation spectra. When this feature does appear in bulk solution absorbance spectra, it usually does so at wavelengths between 317 and 321 nm depending on solvent polarity.\textsuperscript{148}
The red shift of both resonances in the SHG spectrum implies that adsorbed DMABN experience a polar environment, a result that is consistent with previously reported studies of coumarin isomerization. This issue is addressed further in the discussion section where semi-empirical calculations show that DMABN’s excitation wavelength depends sensitively on both the magnitude of the electric field inside of the solute cavity and structural deformation in the form of a twist about the amine nitrogen-ring carbon bond.

A molecule’s second order hyperpolarizability depends on the product of its one and two photon absorption cross sections. To confirm that the observed long wavelength feature in the SH spectrum is consistent with the $S_0\rightarrow S_1$ transition, we collected a 2-photon fluorescence excitation spectrum of DMABN dissolved in water. Figure 4.6 shows the 2-photon excitation spectrum of DMABN in aqueous solution. Both the $S_0\rightarrow S_1$ and the $S_0\rightarrow S_2$ transitions are clearly visible at (bulk solution) wavelengths of 325 and 280 nm, respectively, confirming the assignment of the $S_0\rightarrow S_1$ transition.
Figure 4.6 Two-photon excitation spectrum of DMABN in aqueous solution. The intensity axis reports DMABN emission recorded at 355 nm.

observed in the SHG spectrum. In order to test strong associations between the silica substrate and adjacent aqueous solvent were responsible for adsorbed DMABN’s paradoxical behavior, we functionalized silica slides with dichlorodimethylsilane to create a methyl-terminated surface. Previously reported nonlinear optical studies

Figure 4.7 SHG spectrum of DMABN at the hydrophobic water-silica interface
proposed that hydrophobic solid surfaces limit the degree of water ordering to only the first solvent layer and that the first layer of water has a significant population of dangling -OH bonds.\textsuperscript{149}

Figure 4.7 shows an SHG spectrum of DMABN at the hydrophobic silica-water interface, with data from Figure 4.5 superimposed for comparison. DMABN adsorbed to the aqueous-hydrophobic interface again shows two features, but now both have significantly less intensity and the short wavelength, \( S_0 \rightarrow S_2 \) transition has comparable intensity to the longer wavelength \( S_0 \rightarrow S_1 \). We attribute the reduced intensity to a smaller number of adsorbed DMABN solutes. Interestingly, the \( S_0 \rightarrow S_1 \) peak also appears in this spectrum at a slightly longer wavelength (347 nm) relative to the hydrophilic interface (342 nm), while the \( S_0 \rightarrow S_2 \) resonance peak shifts from 310 nm to 294 nm, similar to its absorbance wavelength in bulk methanol.

Figure 4.8 shows TIR-TCSPC data from the same system (acquired at the aqueous TICT emission wavelength of 520 nm). The time-resolved emission is dominated by a single exponential decay having an emission lifetime of 0.3 ns, consistent with DMABN emitting from a TICT state in bulk aqueous solution. This result stands in marked contrast to results from the aqueous-hydrophilic interface where the dominant contribution to the time resolved emission was assigned to emission from the LE state. (Figure 4.4).

These results are supported by polarization dependent SHG measurements designed to measure the relative orientation of adsorbed solutes. Assuming a single dominant element in the \( \chi^{(2)} \) tensor, molecular orientations can be calculated by
measuring second harmonic emission as a function of the incident field polarization. Fitting these data following previously published methods\textsuperscript{150-151} leads to calculated orientations of 54° for species contributing to the 340 nm transition and 33° for the 310 nm species. These results compare favorably with fluorescence data taken from DMABN molecules adsorbed in zeolites, that showed DMABN molecules without room to twist into the TICT excited state still show two spectral bands with different fluorescence signatures.\textsuperscript{146}

![Figure 4.8 TIR-TCSPC spectrum of DMABN at the hydrophobic water-silica interface](image)

**Figure 4.8 TIR-TCSPC spectrum of DMABN at the hydrophobic water-silica interface**

### 4.4 Discussion

From the SHG and TIR-TCSPC results presented above, three important findings need to be addressed:

1. DMABN solutes adsorbed at the hydrophilic water-silica interface are unable to isomerize into their excited TICT state.

2. The silica-water interface appears polar based on the solvatochromic shifts of the DMABN’s electronic resonances in SHG spectra at the water-silica interface.
3. DMABN adsorption to the silica substrate enables the S₀—S₁ transition to acquire significant intensity in the resonant SHG spectrum. Rendering the substrate hydrophobic suppresses intensity from the long wavelength S₀—S₁ transition.

4.4.1 Strong associations across the silica-aqueous interface impedes DMABN photoisomerization.

Assessing the ability of strong solvent-substrate associations to restrict solute isomerization was the primary goal of these studies. The time-resolved fluorescence results presented in Figure 4.4 strongly support the conclusion that adsorption to strongly associating water-silica interface prevents DMABN isomerization to a TICT state. In nonpolar solvents where a TICT state cannot be stabilized, DMABN fluorescence is faster than can be resolved clearly with our TCSPC assembly. (Table 4.1 and Figure 4.3) The same behavior is observed for DMABN adsorbed to the silica-aqueous interface. (Table 4.2 and Figure 4.4) In bulk aqueous solution, emission from the TICT state has a 0.31 ns lifetime and that lifetime only lengthens in other, less polar solvents. Previous reports have attributed slower isomerization rates at strongly associating interfaces to surface-induced changes in local solvent viscosity.⁵⁻⁷ At silica-aqueous interfaces surface specific vibrational spectra show that strong hydrogen bonding between the water and the surface silanols groups leads to an ice-like structure in the adjacent solvent.⁵⁴ If the lone pair of adsorbed DMABN’s amine serves as a hydrogen bond acceptor and if the hydrogen bond network at the surface is both strong and rigid, then one would reasonably expect TICT state formation from photoexcited DMABN to be slowed and correspondingly fast relaxation from the LE state. Disrupting this strong, surface induced
hydrogen bonding by rendering the surface hydrophobic enables DMABN solvation to return to bulk solution limits, even for those solutes directly influenced by interfacial anisotropy. These results lead us to propose that adsorbates adsorbed to the planar silica/aqueous interface behave as if they were in confinement.

4.4.2 The silica-aqueous interface sampled by DMABN is more polar than bulk water.

DMABN exhibits bathochromic behavior, with an \((S_0-S_2)\) absorbance wavelength that shifts from 283 to 293 nm as solvent polarity increases from that of alkanes \((\varepsilon = 2)\) to that of water \((\varepsilon = 80)\). (Table 4.1, Figure 4.2) This behavior is common for dipolar solutes having a larger dipole in the excited state than in the ground state. A solute’s solvatochromic properties have been used in SHG measurements to examine interfacial solvent polarity as a function of solvent structure and substrate composition.\(^2,8\) DMABN has a measured ground state dipole moment of 6.2 D and a calculated excited TICT state dipole of 16.5 D.\(^{152}\) While resonance-enhanced SHG intensity depends on DMABN’s hyperpolarizability and not its linear absorption cross section, for aromatic solutes having a combination of “push-pull” ligands, these two properties have been shown to track each other.\(^{153-155}\) Despite the solvatochromic evidence for a polar interface, we do not observe the expected corresponding behavior in the SHG intensities for the \(S_1\) and \(S_2\) resonances.

As noted above, numerous studies have shown how surface-induced anisotropic solvent structure changes solvent polarity from bulk solution limits. The details of these changes depend upon solvent structure and substrate-solvent interactions. For example, hydrogen bonding between silica and alcohols creates an alkane-like interfacial polarity,
even when the solvent is methanol. In contrast, the local polarity at both silica-cyclohexane and silica-acetonitrile interfaces is greater than bulk solution limits.

Recent discoveries imply that the local interfacial dielectric environment at the silica-aqueous interface depends sensitively on the details of substrate-solvent interactions. DMABN data support this conclusion. The main feature in every bulk solution absorption spectrum of DMABN, regardless of polarity, is the \( S_0 \rightarrow S_2 \) transition, seen at \( \sim 290 \) nm. In less polar solutions, the \( S_0 \rightarrow S_1 \) peak is also clearly evident – albeit weakly – between 317 and 321 nm depending on solvent polarity. Most calculations and experiments have supported the hypothesis that the \( S_0 \rightarrow S_2 \) transition proceeds along the charge transfer pathway, so in bulk solution, the intensity of the \( S_0 \rightarrow S_1 \) peak decreases with increased solvent polarity as the \( S_2 \) transition becomes more and more stabilized and represents a larger percentage of the absorption spectrum’s total integrated intensity. Furthermore, the \( S_0 \rightarrow S_1 \) transition that is not observable in absorption or 1-photon fluorescence excitation spectroscopy is expected to appear at \( \sim 320 \) nm in polar solvents. SHG data show this wavelength to be 342 nm for DMABN adsorbed to the silica aqueous interface. Wavelengths for both transitions of adsorbed DMABN, \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \), are redshifted from bulk aqueous limits leading us to conclude that the local polarity experienced by adsorbed solutes is more polar than bulk aqueous solution.

An interesting effect to consider is the role that surface charge may play in controlling the local environment. Several reports show that the static polarity of ices are greater than that of water. However, at the experimental pH (pH = 5.8), silica carries a partial negative charge. Over the short distances intrinsic to an interface, this
charge together with a polar solvent can create strong electric fields on the order of \( \sim 10^6 \) V/cm and higher. Semi-empirical calculations show that the \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) transition wavelengths are affected both by local electric fields and by conformational distortions. (*Vide infra.*) Table 4.3 reports how calculated \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) wavelengths change as a function of local electric field. Given these considerations – surface-induced ice-like structure in the solvent and strong local electric fields created by the partially charged

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Table 4.3. Calculated transition wavelengths (in nm) and oscillator strengths (in a.u.) for the \( S_1 \) and \( S_2 \) transitions in DMABN at different local field strengths (in V/cm) and ground state amine twist angle.
surface – we have several plausible mechanisms that can explain the observed solvatochromic shifts observed in DMABN’s SHG spectrum. The fact that only one of these transitions returns to more bulk-like limits when the surface is rendered hydrophobic implies that surface charge plays less of a role in creating the high polarity solvation environment at the silica/aqueous interface.

4.4.3 A combination of surface charge and amino twist are responsible for enhanced SHG intensity in the $S_0$–$S_1$ transition.

A previous report has proposed that DMABN may already assume partial charge transfer character in its solvated ground state.\(^\text{161}\) When the amine on DMABN is in its gas phase equilibrium structure (with both methyl groups $60^\circ$ below the ring plane), $F_{01}$ and $F_{02}$, the oscillator strengths for the $S_1$ and $S_2$ transitions, respectively, are calculated to be .027 and .596 using ZINDO. As the amine group begins to rotate around the ring carbon-N axis however, $F_{02}$ diminishes monotonically, while $F_{01}$ first increases and then decreases. (Table 4.3)

Furthermore, changes in rotation angle are accompanied by pronounced changes in the permanent dipole. Table 4.4 summarizes these effects for the zero external field condition. Changes in oscillator strengths and excitation wavelengths become even more pronounced in the presence of an external field. With a static field of $-5.14 \times 10^7$ V/cm, the $S_0$–$S_1$ transition wavelength red-shifts more than 100 nm with changing twist angle.

These changes in dipole also lead to changes in $S_0$–$S_1$ and $S_0$–$S_2$ transition wavelengths. With surface potentials at the silica-aqueous interface estimated to be on the order of 30-50 mV (at a pH of 6.0)\(^\text{47}\) and with surface charge effects converging to bulk
Twist Angle & Delta Dipole (D) 

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</tr>
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<td>90°</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 4.4: Calculated changes in permanent dipole strength in DMABN at 0 field strength for primary $S_2$ transition around 290 nm

solution (neutral) limits on the order of 1-2 nm, local electric fields can be $\geq 10^6$ V/cm. Consequently, we anticipate that local gradients in interfacial potential are capable of significantly affecting adsorbed DMABN’s ground and excited state electronic structure. While the effects of local potential and geometric deformation cannot be decoupled from one another, we expect that both play a role in DMABN’s unexpected nonlinear susceptibility.

4.5 Conclusions

Second harmonic and surface fluorescence spectra of DMABN at the water-silica interface show that DMABN molecules adsorbed at this interface experience an environment that prevents them from accessing their excited TICT state which has dramatic effects on its surface spectra. When the silica surface is modified by the addition of a hydrophobic silane layer, the effects seen at a surface capable of hydrogen bond donation modulate to resemble those seen when DMABN is dissolved in a polar organic
solvent. Energy structure calculations show that surface potential and twisting of the amine group in DMABN may contribute to the unique second harmonic spectrum of DMABN at both the hydrophobic and hydrophilic silica interfaces.
4.6 References


98


CHAPTER FIVE

ISOMERIZATION AT AQUEOUS-SILICA INTERFACES
AND THE ROLE OF SOLUTE STRUCTURE

Contribution of Authors and Co-Authors

Manuscript in Chapter 5:

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Contributions: Collected and analyzed experimental data and authored manuscript

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Contributions: Collected second harmonic data

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Contributions: Assisted with data analysis and edited manuscript
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Isomerization reactions are among the simplest chemical transformations that involve structural and bond rearrangements. Isomerization serves as the simplest model for RRKM (Rice-Ramsperger-Kassel-Marcus) descriptions of molecular reaction pathways and encompasses a variety of changes to molecular structure. Common isomerization reactions include cis-trans isomerization about a double bond, molecular rearrangements and intramolecular charge transfer reactions. In the limit that isomerization leads to intramolecular charge separation, reaction rates depend sensitively on the solute’s local environment. In higher polarity solvents that can stabilize the charge separation, this reaction proceeds as much as 10x faster than in nonpolar media.

Another factor that can affect isomerization is confinement. Reactions such as cis-trans trans isomerization or twisted intramolecular charge transfer (TICT) state formation involve a reorientation of functional groups about a bond. Such large amplitude motions in solution require that a solute’s surrounding solvation shell be sufficiently mobile to accommodate significant solute volume changes, especially at the solute’s transition state. Confinement restricts solute motion so that even if local polarity is likely to stabilize isomerization in the excited state, steric constraints restrict isomer formation. A study looking at confined catalysts showed that confinement can be used to
discriminate by polarity of adsorbate, allowing reactions that occur at confined catalytic sites to be selective by the polarity of the substrate. In experiments that have studied isomerization in confinement, longer emissive lifetimes and broader absorption bands have been observed from molecules that undergo cis-trans isomerizations, such as stilbenes and some organic dye molecules.

Figure 5.1: Coumarin 151 (top) and Coumarin 152 (bottom)

Recently, several reports have shown that solute isomerization at the strongly associating, planar aqueous-silica interface is restricted with adsorbed solutes behaving as if they experience confinement. Specifically, time resolved emission from two different solutes known to form TICT states upon photo excitation in polar solvents behave as if they were in nonpolar environments when adsorbed to aqueous-silica boundaries. The two solutes, Coumarin 152 (C152) and 4-dimethylaminobenzonitrile (DMABN), have well characterized photophysical properties that depend sensitively on
the local dielectric properties, and only polar solvents can stabilize the charge separation found in the TICT isomer. For DMABN adsorbed to the aqueous-silica interface, time resolved fluorescence shows emission out of the non-TICT or locally excited state, even though independent resonant enhanced second harmonic generation experiments show that the interface is measurably more polar than even bulk aqueous solution.

The experiments described below were designed to explore further the effects that strong associations between a substrate and solvent have on adsorbed solute isomerization. Specifically, a solute was chosen that does not require a large change in solvation volume as it forms its photoexcited isomer. 7-aminocoumarins with alkyl substituents on the amino group, i.e. Coumarin 152 (C152), have a radiationless deactivation pathway in polar solvents not seen in coumarins with a primary amine in the 7-position, such as Coumarin 151 (C151) (Figure 5.1). This radiationless deexcitation pathway is attributed to TICT state formation, where a charge from the amino group is transferred to the C=O moiety on the pyrone ring and the alkyl amino group twists 90° relative to the plane defined by the benzopyrone rings. This phenomenon is only possible due to the electron donating alkyl amine groups and is therefore not observed from aminocoumarin dyes with primary amines. Coumarin 151 is closely related to C152, but has a primary rather than a tertiary amine in the 7-position. C151 and C152 share several similarities: both show strong solvatochromic behavior due to the large (positive) change in dipole that occurs upon photoexcitation (+2.81 D for C151, +4.13 for C152) and both have time dependent emission behavior that is extremely sensitive to both solvent polarity and hydrogen bonding.
However, whereas C152 forms a TICT isomer in polar, protic solvents following photoexcitation, C151 simply isomerizes to a planar ICT state where the excited solute has both amine protons in the plane of the molecule and the amine nitrogen assumes $sp^2$ hybridization character. These differences lead to very different time-resolved emission from these two solutes that serves as a sensitive indicator of local solvation behavior.

In order to more specifically understand solute isomerization behavior at the interface, we examined the photophysical behavior of Coumarin 151 at the aqueous-silica interface. ICT formation does not require large amplitude, intramolecular motion nor does it require extensive solvent rearrangement. Given the hypothesis that strong solvent-substrate interactions restrict solute dynamics and impede solute photoisomerization, C151 should show very little change in its photophysical behavior relative to bulk aqueous solution when adsorbed to aqueous-silica interfaces. Time resolved emission experiments presented below support this hypothesis. Fluorescence lifetimes of C151 adsorbed to an aqueous-silica interface differ very little from C151 lifetimes in bulk aqueous solution. Independent SHG measurements show the aqueous-silica interface to still be very polar, similar to what has been reported in the C152 and DMABN studies.\textsuperscript{108, 171} Model calculations performed to estimate solute volume in its ground state structure, transition state geometry and excited state structure support the hypothesis that a flexible solute solvation volume is just as critical to promoting isomerization reactions as the local dielectric environment.

Results from these and prior studies provide clear benchmarks for emerging models seeking to describe chemical reactivity at buried interfaces.\textsuperscript{172-174}
anisotropic forces in between two phases strongly influence some reactions (e.g. TICT formation) but appear to have very little effect on others (e.g. planar ICT formation). We anticipate that these findings will provide grist for the mill in the general area of condensed phase theory and surface science for years to come.

5.2 Experimental

Laser grade Coumarin 151 was purchased and used as received from Aldrich. Water used in the experiments was nanopure, from a Millipore filtration system, resistivity of 18.2 MΩ. Silica slides and experimental assemblies were rinsed with methanol and DI water then soaked in a bath of 50/50 sulfuric/nitric acid for no less than one hour, and rinsed with DI water and dried under nitrogen before use. Experiments described in this work used saturated solutions of Coumarin 151 in water, that were made by combining excess C151 and water and allowing the solution to equilibrate with stirring overnight at 50°C. The solutions were filtered to remove excess dye before use. At room temperature, the concentration of C151 in a saturated aqueous solution is approximately 6 µM. SHG spectra were collected from Kel-F sample chambers containing saturated C151 solution in contact with fused silica slides (Structure Probe, Inc.). For TIR-TCSPC measurements, a custom-built assembly was made from Kel-F sample chambers containing saturated aqueous C151 solution in contact with fused silica prisms (ISP Optics, Inc.), which allowed the excitation pulse to irradiate the interface formed between a hemispherical prism and an aqueous solution at angles greater than the critical angle (61° at 400 nm). Sample chambers, coumarin
solutions, silica slides and prisms were allowed to equilibrate for at least an hour before being used in experiments.

Silica slides (Structure Probe, Inc.) and prisms (ISP Optics, Inc.) were functionalized with a solution of dimethyldichlorosilane in THF to create hydrophobic surfaces. Silica substrates were cleaned as described above and allowed to sit in the silane solution at 30°C for 36 hours. Once removed from the silane solution, silica slides and prisms were first washed with toluene, then methanol and finally tested with water to verify that the surface was hydrophobic.

To collect TIR-TCSPC spectra, 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 non-emissive Ludox scattering solution. 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 one or more single exponential decays. The minimum number of lifetimes required to accurately fit the data was determined using the Akaike information criterion.

In order to collect SHG signal from surface molecules, the coherent output from a tunable, amplified Ti:sapphire pumped optical parametric amplifier (OPA) at frequency $\omega$ is focused on the surface and creates a polarization of the surface
molecules at $2\omega$. The intensity of the collected second harmonic signal is proportional to the square of the second order polarizability, denoted as $P^{(2)}$:

$$I(2\omega) \propto |P^{(2)}(2\omega)|^2$$

(5.1)

where $P^{(2)} = |\chi^{(2)}(E(\omega_1)E(\omega_2))|$. In the case of second harmonic generation, the incident beam is of a single frequency and $\omega_1 = \omega_2$. The surface specificity of SHG, along with all second order nonlinear optical techniques, derives from $\chi^{(2)}$, the second order nonlinear susceptibility. $\chi^{(2)}$ is a rank 3 tensor consisting of 27 matrix elements; in centrosymmetric systems, the requirement that $\chi^{(2)}_{i,j,k} = 0$ means that no second harmonic response will originate from an isotropic solution within the electric dipole approximation. At an interface where symmetry is broken, elements of the $\chi^{(2)}$ tensor can take on non-zero values, dependent on the identity of the molecules at the interface. $\chi^{(2)}$ is composed of a non-resonant (NR) piece and a resonant (R) piece:

$$\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_R$$

(5.2)

The non-resonant portion of the $\chi^{(2)}$ tensor is usually simple and can be fit to a single value whereas the resonant contribution is more complicated. The resonant portion of $\chi^{(2)}$ is equal to the number of molecules on the surface multiplied by the orientational average over the molecular hyperpolarizability ($\beta$) of the adsorbed molecules:

$$\chi^{(2)}_R = N\langle \beta_{i,j,k} \rangle$$

where $\beta$ is given by:

$$\beta = \frac{A}{\omega_0 - \omega - i\Gamma}$$

(5.3)
In this expression for $\beta$, $A$ is a constant related to the transition dipole moment of the electronic resonance being examined, $\omega_0$ is the resonant frequency of the transition, $\omega$ is the frequency of the incident light, and $\Gamma$ is the linewidth associated with the transition.

In cases where the interface under investigation carries a surface charge, the second harmonic spectral lineshape can be influenced by some non-resonant elements of the $\chi^{(3)}$ tensor, which makes equation (5.2) take the form

$$\chi_{\text{total}}^{(2)} \propto \chi^{(2)} + (\chi_1^{(3)} + i\chi_2^{(3)}) \Phi(0)$$

(5.4)

where $\Phi(0)$ is the interfacial potential and both elements of the $\chi^{(3)}$ tensor are purely real.\textsuperscript{114-115} Collected second harmonic spectra are fit with equations (5.2), (5.3) and (5.4) to determine the linewidth and the center of the resonant peak.

Resonance-enhanced SHG spectra were acquired from an experimental assembly that has been described previously.\textsuperscript{8-9} Briefly, ~3.3W from a Ti:Sapphire regenerative amplifier (Libra-HE, Coherent, 85 fs pulses, 1 kHz repetition rate, 801 nm) was coupled to a visible optical parametric amplifier (Coherent OPerA Solo, fwhm 10 nm) and focused on the sample. If necessary, incident visible light was attenuated to below 4 mW with neutral density filters before it reached the sample. Second harmonic signal was collected using a photomultiplier tube and photon counting electronics. Data from each individual wavelength was collected over 3-5 separate 10s intervals, background corrected and then averaged. Typically, up to 300 counts were measured on resonance during a 10 sec. acquisition.
C151 emission in solution depends sensitively on solvent polarity. Figure 5.2 shows TCSPC traces from C151 dissolved in solvents selected to represent a range of static dielectric constants as well as both polar protic (methanol) and polar aprotic (acetonitrile) limits. Table 5.1 shows lifetimes and amplitudes from the traces displayed in Figure 5.2. C151 decay in nonpolar solvents can be fit to two lifetimes, 1.05 ns and 1.62 ns. In every other non-aqueous polar solvent C151 decays with single lifetimes between 5.2 and 5.3 ns. In water, C151 decays with a single lifetime of 4.57 ns. These lifetimes agree with data previously reported by Nad and Pal. The long lifetimes observed in polar solvents has been attributed to ICT formation following photoexcitation. Nonpolar solvents cannot stabilize the ICT isomer.

Figure 5.2: TCSPC decay traces of C151 dissolved in various bulk solvents

An important point to note when assessing data in Table 5.1 is the extreme lifetime difference between C151 in aqueous solution and in cyclohexane. If C151 motion at the
Table 5.1: Lifetimes and amplitudes from C151 fluorescence decay in bulk solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( A_1 )</th>
<th>( \tau_1 ) (ns)</th>
<th>( A_2 )</th>
<th>( \tau_2 ) (ns)</th>
<th>( \chi^2 )</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>.59</td>
<td>1.620</td>
<td>.41</td>
<td>1.047</td>
<td>1.008</td>
<td>2.02</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>1</td>
<td>5.323</td>
<td>.14</td>
<td>1.101</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1</td>
<td>5.244</td>
<td></td>
<td>1.020</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>1</td>
<td>5.332</td>
<td></td>
<td>1.029</td>
<td>32.7</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>4.566</td>
<td></td>
<td>1.082</td>
<td>80.1</td>
<td></td>
</tr>
</tbody>
</table>

aqueous-silica interface were restricted, one would expect to observe a faster fluorescence decay from C151 in the TIR data. Figure 5.3 shows TIR emission from C151 adsorbed to the aqueous-silica interface. Adsorbed C151 decays with a single lifetime of 4.51 ns, unchanged from its bulk water lifetime within the error of the instrument (Figure 5.3). This result stands in marked contrast to previously reported data from C152 and DMABN where adsorption to the aqueous-silica introduces a new decay pathway consistent with the adsorbed solute’s inability to isomerize.

Figure 5.3: Fluorescence decay traces of C151 at the aqueous-silica interface with relevant bulk traces also shown
In prior work, disrupting the strong hydrogen bonding interactions between interfacial water molecules and surface silanol groups enabled adsorbed solutes to behave more like they were in bulk solution. To test what effects – if any – water-silica interactions have on C151 isomerization, the silica prism used in the TIR-TCSPC experiments was functionalized with a dichlorodimethylsilane layer to create a non-polar methyl layer at the silica-aqueous interface. C151 adsorbed to the aqueous-hydrophobic silica interface showed 2 emission lifetimes, one attributed to molecules in contact with the hydrophobic methyl layer and the other to C151 solutes dissolved in the bulk solution. The bulk lifetime, comprising 72% of the decay amplitude, is consistent with bulk solution measurements at 4.55 ns. The second lifetime was 3.51 ns. This shorter lifetime is difficult to interpret, as it does not correspond to C151 fluorescence decay in any known solvent, regardless of solvent polarity, viscosity, or hydrogen bonding. We propose that this lifetime originates from a local environment that affects C151 ICT formation without changing the interfacial polarity. Importantly, this result emphasizes the dangers of assuming that interfacial solvation and reactivity can be represented as a weighted average of two limiting behaviors.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic silica TIR</td>
<td>1</td>
<td>4.513</td>
<td></td>
<td></td>
<td>0.972</td>
</tr>
<tr>
<td>Hydrophobic silica TIR</td>
<td>.72</td>
<td>4.548</td>
<td>.28</td>
<td>3.509</td>
<td>1.204</td>
</tr>
</tbody>
</table>

Table 5.2: Lifetimes and amplitudes of C151 fluorescence decay at various silica-aqueous interfaces
The resonance-enhanced second harmonic generation (SHG) spectrum taken of C151 at the aqueous-silica interface aligns well with the absorbance spectrum of C151 in bulk water (Figure 5.4). The peak of the SHG spectrum is at 364 nm; the peak absorbance in bulk water is at 367 nm. To within experimental uncertainty, these numbers are functionally equivalent. The SHG spectrum has a much narrower linewidth than the bulk absorbance spectrum—27 nm vs 63 nm—a result consistent with other reported SHG spectra. The resonant SHG spectrum illustrates that C151 adsorbed to the aqueous-silica interface experiences a polar, strong hydrogen bonding solvation environment very similar to bulk water.

Figure 5.4: SHG spectrum (left ordinate, blue crosses) at the silica-aqueous interface and aqueous absorbance (right ordinate, red line) of Coumarin 151

Given similarities in both the SHG and TCSPC data between C151 adsorbed to the aqueous-silica interface and in bulk solution, we also measured the resonantly enhanced SHG spectrum of C151 adsorbed to the aqueous-hydrophobic silica interface. As described above, TCSPC data from this system showed an unusual 3.51 ns lifetime that did not correspond to any known lifetime from bulk solution measurements raising
the question about the local polarity sampled by C151 at this surface. SHG data are shown in Figure 5.5. Superimposed on the C151 SHG spectrum at the aqueous-hydrophobic silica interface is the C151 spectrum from the aqueous-hydrophilic silica interface (reproduced from Figure 5.4). At the hydrophobic silica interface, C151 shows a maximum in its SHG spectrum at 366 nm, virtually unchanged from hydrophilic silica result. The only significant difference between the spectra at the hydrophobic and hydrophilic silica interfaces is the linewidth—32 nm at the hydrophobic interface, 5 nm wider than at the hydrophilic interface. This result suggests more inhomogeneous broadening at the aqueous-hydrophobic silica interface. We expect that in the absence of strong, directional hydrogen bonding opportunities provided by the surface silanol groups, correspondingly greater disorder in the interfacial water organization will lead to more heterogeneity in adsorbed C151’s environment. This difference in linewidth notwithstanding, the important result from the SHG measurements is that the polarity experienced by C151 at the aqueous-hydrophilic silica and aqueous-hydrophobic silica interfaces is effectively the same, meaning that differences observed in the TIR-TCSPC data likely owe their origins to differences in solvation dynamics.

Collectively, both the TIR-TCSPC and SHG results of C151 at the silica-aqueous interface suggest that despite any ordering of the water due to hydrogen bonding to the silica surface, C151 solutes at the interface do not experience a significantly different environment than in bulk water solution. These findings support the hypothesis that isomerization reactions requiring very small intramolecular structural rearrangements are
Figure 5.5: SHG spectra of C151 taken at the unmodified hydrophilic and the hydrophobic silica interfaces

largely insensitive to structural constraints imposed by the surrounding environment.

Results also stand in stark contrast to the behavior of Coumarin 151’s tertiary amine analog, Coumarin 152, that experiences significant restriction in its ability to isomerize at the interface, resulting in dramatic spectral differences between solutes dissolved at the aqueous-silica interface and in bulk water. We believe that this difference between these otherwise similar molecules has to do with the reaction coordinate required for each to form its excited state isomer. C152 isomerizes into a TICT state upon photoexcitation, where C151, not having the electron donating ability on its primary amine to form a TICT state, isomerizes into a planar ICT excited state. C151’s isomerization from pyramidal amine to one in the plane of the rest of the molecule requires a much smaller solvent volume than the TICT isomerization, where C152’s alkyl amine group goes from pyramidal in the ground state to a 90° twist relative to the molecular plane. Because of
the significant solvent ordering due to hydrogen bonding between the water molecules and the silanols at the interface, C152 is unable to complete this isomerization at the aqueous-silica interface due to strong geometric restriction. C151, with its much smaller excited state isomerization, is not restricted by solvent organization at the interface, and therefore displays the same solvation behavior at the silica-aqueous interface as it does in bulk solution.

5.4 Conclusions

Coumarin 151 solutes at the aqueous-silica interface do not experience a solvation environment significantly different than in bulk water. This result is in contrast to that of the closely-related Coumarin 152, where molecules adsorbed at the interface show time resolved fluorescence that implies a nonpolar environment. This result is attributed to the difference in excited state isomerization behavior between C151 and C152. C152 isomerizes into an excited TICT state, an isomerization that requires significant free solvent volume. In contrast, C151 isomerizes into a planar ICT state upon photoexcitation, a change that does not require as significant solvent volume as the isomerization in C152. This difference in isomerization behavior, the result of replacing the primary amine in C151 with the tertiary amine in C152, causes different behavior in the spectra of the two molecules at the aqueous-silica interface.
5.5 References


174. Okuno, Y.; Ushirogata, K.; Sodeyama, K.; Tateyama, Y., Decomposition of the fluoroethylene carbonate additive and the glue effect of lithium fluoride products for the
6.1 Summary

Work presented in this thesis examined how adsorption at the strongly associating silica-aqueous interface impacted the ability of several organic molecules to isomerize in their excited states. Several linear and nonlinear electronic spectroscopic techniques were utilized to understand the interfacial environment in which these molecules were adsorbed, and from there, infer information about the excited state dynamics of the adsorbed solutes and give insight into solvent structure and dynamics at the silica-aqueous interface.

Initial studies focused on time-resolved fluorescence spectra of Coumarin 152 (C152) adsorbed to the aqueous-silica interface. These spectra showed that C152 at this interface shows fluorescence behavior very similar to solutes that are dissolved in bulk nonpolar solutions. These results were interpreted in light of the strong association between the silica and the water molecules at the interface which imposes a geometric order on the surface-associated water molecules. This solvent order at the interface means that the surface waters are unable to reorganize to stabilize the twisted intramolecular charge transfer (TICT) state after photoexcitation and that this order imposes a limited solvent volume for the solute to isomerize. This hypothesis about solvent structure and association preventing solutes from isomerizing following photoexcitation was supported by fluorescence studies of C152 inside an ice matrix. Inside a structured ice matrix, C152
solute also show a fluorescence lifetime similar to that seen in bulk nonpolar solution and at the silica-aqueous interface.

Chapter 3 used second harmonic generation (SHG) to confirm that the silica-aqueous interface is indeed polar. Given that confirmation, we functionalized a silica surface to remove its ability to hydrogen bond by adding a dichlorodimethylsilane monolayer to that surface. When C152 is adsorbed to this hydrophobic silica-aqueous interface, its fluorescence signature once again shows that it can access its excited TICT state. This result supports the hypothesis that strong hydrogen bonding and water ordering is responsible for C152’s inability to isomerize at the aqueous-silica interface. At the hydrophilic silica-aqueous interface, there is a marked distinction between ground and excited state behavior, which is caused by C152’s inability to isomerize following photoexcitation when water molecules are strongly ordered by the interface. When we disrupt the ability of the silica surface to order the water molecules adjacent to it by removing its ability to hydrogen bond, the environment indicated by both ground and excited state behavior merges to a similar intermediate polarity limit.

Chapter 4 describes the studies done on 4-dimethylaminobenzonitrile (DMABN) in order to expand the hypotheses formulated to explain the behavior of C152 at the silica-aqueous interface to a more general class of organic molecules with large-amplitude excited state isomerizations. DMABN is the oldest and most well-known example of TICT chemistry, with dual emissive states, so we took SHG and TIR-TCSPC spectra of it at the aqueous silica-interface. Its time-resolved fluorescence at the surface is missing any evidence of TICT formation, as the results from prior studies with C152
would suggest. The TICT emission returns when hydrogen bonding is disrupted by adhering a hydrophobic monolayer to the silica surface, which is also predicted from the C152 studies. Unexpectedly, the SHG spectrum of DMABN at the aqueous-silica interface shows a second electronic resonance that is not immediately evident in bulk absorption spectra of the molecule. This second peak is rationalized with the help of semi-empirical calculations that show that strong electric fields caused by the surface can enhance the intensity of the $S_0—S_1$ transition dramatically, giving the spectrum seen from DMABN adsorbed to the aqueous-silica interface.

Chapter 5 describes the studies done on another molecule in the 7-aminocoumarin family, Coumarin 151 (C151). C151 is structurally similar to C152, but with a primary amine in the 7-position where C152 has a tertiary dimethyl amine group. This structural difference means that C151 does not form a TICT state upon photoexcitation, rather, it forms a planar intramolecular charge transfer (ICT) state. The same sets of SHG and TIR-TCSPC experiments were performed on C151 as on C152 and DMABN to examine the effect of the surface on a much smaller amplitude isomerization event. C151 shows nearly identical spectroscopic behavior at the aqueous-silica surface as in bulk aqueous solution, indicating that only large amplitude isomerizations are restricted at the interface.

Together the experiments described in this thesis represent a detailed investigation of how surface properties can influence molecular isomerization behavior, which has a significant impact on those molecules’ reactivity at that interface. Since the surface restricts the formation of excited states with a significant geometric change from the ground state, these results were interpreted as a form of chemistry in confinement, similar
to that which might occur inside a zeolite or molecular pore. Understanding how the reactivity of molecules is changed by adsorption to an interface is important for many areas of chemistry from chromatography to environmental geochemistry.

6.2 Future Directions

While these experiments represent new and important discoveries into the surface chemistry of organic molecules, there remain several avenues of investigation prompted by the results in this thesis that have not yet been investigated. The remaining questions inspired by this work fall into 3 general areas: other solutes, other solvents, and effect of pH.

6.2.1 Other Solutes

The work in this thesis examined coumarin dyes and a substituted aniline molecule, but there are several other classes of organic molecules that are also capable of large amplitude isomerizations. A particularly interesting example of TICT chemistry is Rhodamine B (Figure 6.1). Rhodamine B has a closed-ring spirolactone that can be opened by hydrogen ions. In its closed form, it exists in a TICT state that is colorless and nonfluorescent. When it is opened by acid, conjugation extends over the whole molecule, and it turns bright pink and highly fluorescent. Given the propensity of the surface to inhibit TICT formation, an interesting application of the results of this thesis would be to place a basic (colorless, TICT) solution of Rhodamine B adjacent to the silica surface and see if and to what extent the surface rejects the TICT state and makes the molecules adhered to the surface fluorescent again. This concept is supported by an offhanded
Figure 6.1 Rhodamine B in its closed-ring spirolactone form (top) and its open, conjugated, fluorescent form (bottom)

mention in a paper from 1982, which stated that their rhodamine solutions could not be left in their silica cuvettes for long before taking a spectrum, as contact with the walls of the cuvette tended to turn the solution pink.$^{175}$

6.2.2 Other Solvents

The work described in this thesis is concerned only with the aqueous-silica interface but there are many other solvents that have interesting interactions with silica surfaces that warrant examination. It is known that the strong association of alcohols to the silica surface creates a nonpolar region adjacent to the interface where the hydrogen bonded hydroxyl groups align the attached alkyl tails.$^{6, 25, 104, 119}$ In this thesis, we look at the effect of creating a hydrophobic surface to prevent association with water, but to my
knowledge, this surface has not been explored in terms of the solvation of organic solutes in solvents other than water. In particular, do alcoholic solvents adjacent to a hydrophobic silica surface also align with their alkyl tails attracted to the silica and their hydroxyl groups forming an ordered, high polarity region adjacent to the interface, or do they interact by another means? Understanding how different solvents interact with the silica surface and what that means for molecules solvated therein is important particularly for chemical separations and chromatography.

6.2.3 pH Studies

Most of the earliest work examining water structure at silica-aqueous interfaces noted that the spectral peaks corresponding to ordered (i.e. ice-like) and disordered water changed their relative intensities as an effect of changing the pH of the water solution. Specifically, in low and high pH solutions that create a more strongly charged silica surface, the intensity of the ordered, ice-like peak was larger than in the solutions of more neutral pH. Given that the central premise of this thesis is that ordering of water molecules as a result of association with the silica surface interferes with molecular isomerization, investigation of surfaces with different degrees and structures of water ordering is an obvious next step. Additionally, changing the pH of the water solution in contact with the silica surface will also affect the surface charge and corresponding electric field on the silica surface. The computational results presented in chapter 4 attest to the importance of the surface field in determining molecular reactivity at the interface, so a systematic study of the effect of the pH of the aqueous solution provides a convenient way to experimentally test those computational conclusions.
6.3 References


Farkas, J. B. Foresman, and D. J. Fox Gaussian 09, Revision A.02, Wallingford CT, 2016.


