Picosecond Dynamics of a Chemical Reaction at the Air–Water Interface Studied by Surface Second Harmonic Generation

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The dynamics of a chemical reaction at the air–water interface was studied by surface second harmonic generation techniques. Using DODCI (3,3′-diethyloxadicarbocyanine iodide) as example, it was found that the photoisomerization rate was significantly faster at the interface than in the bulk liquid.

Introduction
The inhomogeneous region between a bulk liquid and air, what we call the surface or interface, differs from a bulk liquid in the density and concentration of solvent and solute molecules.1 In addition, the asymmetry in the forces at the interface can produce a net orientation of molecules with respect to the surface normal, unlike the bulk which is isotropic on the average. As a consequence of its composition and structure, the dielectric properties, e.g., polarity, and transport properties, e.g., viscosity, are different from that of the bulk. One manifestation of this is the change in chemical equilibria, such as an acid–base reaction, at the air/water interface.2 Studies of chemical reactions at the air/water interface, as well as various processes at gas/solid and liquid/solid interfaces, have become possible using the nonlinear spectroscopic technique of second harmonic (SHG) or sum frequency (SFG) generation.2–4 The special feature of SH generation is its sensitivity to the asymmetry of an interface located between two centrosymmetric media.5 Just as the static properties of composition, orientational structure, and chemical equilibria can differ, we anticipate that dynamic processes can also differ between the interface and bulk regions of a liquid. In this Letter we report results of picosecond time-resolved studies of a chemical reaction, the photoisomerization of DODCI (3,3′-diethyloxadicarbocyanine iodide) molecules at the air/water interface as well as in the bulk of the same solution. This work follows earlier work where SH detection was used to time resolve the photoinduced melting of a semiconductor surface with femtosecond resolution,6,7 and experiments where the change in the photo signal from an electrode following a potential jump was obtained.8

Results and Discussion
The photoisomerization experiment consisted of exciting \(2 \times 10^4\) M DODCI to S1 with a 532-nm pump pulse of 15-ps duration generated by a mode-locked Nd:YAG laser. To monitor the dynamics following excitation a time-delayed 532-nm probe pulse was used to generate a second harmonic signal from the photoexcited interface. Since the nonlinear susceptibility of the interface is changed by the photoexcitation pulse, the SH signal from the interface is changed and becomes time dependent. The pump and probe pulses arrived at the solution surface at sharply different angles. With this arrangement we determined that the pump pulse (probe blocked) did not produce any second harmonic signal that could pass through the apertures and the monochromator and be detected at the photomultiplier. The pump pulse excites the cis-DODCI from S0 to S1, which then decays back to cis S0 or undergoes a barrier crossing to an intermediate twisted form9 (Scheme I). The twisted form then rapidly decays back to cis S0 or to the trans S1 isomer.10–13 The trans S1 isomer that is formed decays slowly, \(10^8\) s, back to cis S0. It was found, Figure 1, that the SH signal decreased within our experimental resolution of 25 ps and then recovered to a level less than its original value. The observed decrease in SH signal following excitation of DODCI by the pump pulse can result from a smaller nonlinear polarizability of the excited cis S1 DODCI due to the absence of the one photon resonance that contributes to the ground-state S0 nonlinear polarizability. In addition the phases of the ground- and excited-state molecules are likely to be of opposite sign and would thus diminish the SH signal.

At the low DODCI excess of \(3 \times 10^4\) molecules/cm², obtained from surface tension measurements, we assume that local field effects can be neglected. The total nonlinear susceptibility \(\chi^{(2)}_{\text{total}}\) can then be expressed in terms of its linear dependence on the concentrations \(N_i\) (molecules/cm²) and nonlinear polarizabilities \(\alpha_i^{(2)}\) of the molecules in the interface

\[
\chi^{(2)}_{\text{total}} = \sum_i N_i \alpha_i^{(2)}
\]

To extract the kinetics of isomerization in the air/water interface we make the following observations. The SH signal \(I_{\text{SH}}\) generated at time \(t\) after the pump pulse is proportional to the

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Figure 1. Surface second harmonic field, $E_{2u}$, as a function of time following photoexcitation of an aqueous solution containing DODCI ($1.7 \times 10^{-4} \text{ M}$).

The square of the surface nonlinear susceptibility $\chi^{(2)}(t)$, a quantity which is time dependent:

$$I_{2u} \sim |\chi^{(2)}_\text{total}(t)|^2$$

The total nonlinear susceptibility has contributions from the ground-state $S_0$ cis molecules, the excited-state $S_1$ cis molecules, and at some later time the ground-state photoisomer $S_0$ trans. The lifetime in the intermediate twisted form is short compared with the isomerization time and is neglected. We can write the total nonlinear susceptibility

$$\chi^{(2)}_\text{total}(t) = \chi^{(2)}_\text{cis}(t) + \chi^{(2)}_\text{cis}(t) + \chi^{(2)}_\text{trans}(t)$$

Since the ground-state trans photoisomer decays to the ground-state cis isomer on a time scale of milliseconds we can neglect this decay process in our picosecond studies. The only time constant that the signal at long times does not return to its value at negative time is the barrier crossing time $\tau$, which we can define as

$$\tau = 220 \pm 40 \text{ ps}$$

The excited $S_1$ cis form decays as

$$N_{S_0}^{\text{trans}}(t) = N_{S_0}^{\text{trans}}(0)e^{-t/\tau}$$

and the cis $S_0$ increases beyond its population $N_{S_0}^{\text{cis}}(0)$ at the end of the excitation pulse

$$N_{S_0}^{\text{cis}}(t) = (1 - \gamma)N_{S_0}^{\text{cis}}(0)[1 - e^{-t/\tau}] + N_{S_0}^{\text{cis}}(0)$$

where $\gamma$ is the fraction of excited molecules that goes to the ground-state $S_0$ from the intermediate twisted form.

We can use these equations to obtain a simple expression for $\chi^{(2)}_\text{total}(t)$

$$\chi^{(2)}_\text{total}(t) = Ae^{-t/\tau} + B$$

where $A$ and $B$ are constants that contain the nonlinear polarizabilities for the various species, the interfacial concentrations at the end of the pump pulse ($t = 0$), and the distribution factor $\gamma$.

To obtain the bulk dynamics of the DODCI photoisomerization rate is strongly dependent on the specific interactions it has with surrounding solvent molecules. One of the chief factors that controls the isomerization dynamics is the friction that the DODCI molecule experiences as it undergoes a rotation around a bond within its polymethine chain. One interpretation of our results which showed a faster DODCI isomerization rate at the air/water interface than in the bulk water solution is that the friction experienced by DODCI is significantly smaller at the interface than in the bulk liquid. Further experiments to investigate the effect of solvent interactions on the dynamics at the air/water interface are in progress.

Conclusion

We have shown that the DODCI photoisomerization reaction at the air/water interface using a pump/probe method where the probe pulse generated a SH signal at the interface. The isomerization time is $220 \pm 40$ ps at the air/water interface, which is significantly different from its bulk water value of $520 \pm 60$ ps obtained from fluorescence decay measurements. In summary, we have determined the dynamics of a photoisomerization reaction at the air/water interface, and we have shown it to be significantly different from that in the bulk. The faster rate at the interface could indicate a smaller friction for motion along the isomerization coordinates.

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