J. Phys. Chem. 1988, 92, 4579-4580

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

E. V. Sitzmann and K. B. Eisenthal*

Department of Chemistry, Columbia University, New York, New York 10027 (Received: May 31, 1988)

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.

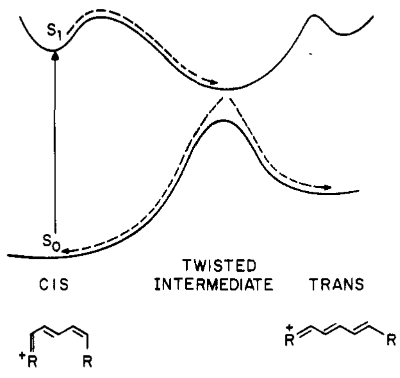
Introduction

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.[3-14] The special feature of SH generation is its sensitivity to the asymmetry of an interface located between two centrosymmetric media.[3,15] 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,[16] and experiments where the change in the SH signal from an electrode following a potential jump was obtained.[17]

Results and Discussion

The photoisomerization experiment consisted of exciting 2 × 10^{-4} M DODCI to S_1 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 S_0 to S_1, which then decays back to cis S_0 or undergoes a barrier crossing to an intermediate twisted form[18] (Scheme I). The twisted form then rapidly decays back to cis S_0 or to the trans S_0 isomer.[18-21] The trans S_0 isomer that is formed decays slowly, 10^{-3} s, back to cis S_0. 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 S_1 DODCI due to the absence of the one photon resonance that contributes to the ground-state S_0 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.

SCHEME I



At the low DODCI excess of 3 × 10^{13} molecules/cm^2, 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/cm^2) and nonlinear polarizabilities $\alpha_i^{(2)}$ of the molecules in the interface

$$\chi^{(2)}_{\text{total}} = \sum_i N_i \alpha_i^{(2)} \qquad (1)$$

To extract the kinetics of isomerization in the air/water interface we make the following observations. The SH signal $I_{2\omega}$ generated at time t after the pump pulse is proportional to the

---

[1] Adamson, A. W. *Physical Chemistry of Surfaces*, 3rd ed.; Wiley: New York, 1976, and references cited therein.

[2] Bhattacharyya, Kankan; Sitzmann, E. V.; Eisenthal, K. B. *J. Chem. Phys.* **1987**, *87*, 1442.

[3] Shen, Y. R.; *J. Vac. Sci. Technol. B* **1985**, *3*, 1464. Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984; Chapter 25.

[4] Marowsky, G.; Gierulski, A.; Dick, B. *Opt. Commun.* **1985**, *52*, 339.

[5] Richmond, G. L. *Langmuir* **1986**, *2*, 132.

[6] Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacone, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350.

[7] Casassa, M. P.; Woodward, A. M.; Stephenson, J. C.; King, D. S. *J. Chem. Phys.* **1986**, *85*, 6235.

[8] Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597.

[9] Zhu, X. D.; Shen, Y. R. *Phys. Rev. B* **1987**, *35*, 3047.

[10] Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45, 52.

[11] Allara, D. L.; Swalen, J. D. *J. Phys. Chem.* **1982**, *86*, 2700.

[12] Murphy, D. V.; Von Raben, K. V.; Chen, T. T.; Owen, J. F.; Chang, R. K.; Laube, B. L. *Surf. Sci.* **1983**, *124*, 529.

[13] Corn, R. M.; Romagnoli, M.; Levenson, M. D.; Philpott, M. R. *Chem. Phys. Lett.* **1984**, *106*, 30.

[14] Voss, D. F.; Nagumo, M.; Goldberg, L. S.; Bunding, K. A. *J. Phys. Chem.* **1986**, *90*, 1834.

[15] Bloembergen, N.; Pershan, P. S. *Phys. Rev.* **1962**, *128*, 606.

[16] Shank, C. V.; Yen, R.; Hirliman, C. *Phys. Rev. Lett.* **1983**, *51*, 900.

[17] Shannon, V.; Koos, D. A.; Robinson, J. M.; Richmond, G. L. *Chem. Phys. Lett.* **1987**, *142*, 323.

[18] Rulliere, C. *Chem. Phys. Lett.* **1976**, *43*, 303.

[19] Rentsch, S.; Grummt, U. W.; Khetchinashwili, D. *Laser Chem.* **1987**, *7*, 261.

[20] Magde, D.; Windsor, M. W. *Chem. Phys. Lett.* **1974**, *27*, 31.

[21] Fleming, G. R.; Knight, A. E. W.; Morris, J. M.; Robbins, R. J.; Robinson, G. W. *Chem. Phys. Lett.* **1977**, *49*, 1.

0022-3654/88/2092-4579$01.50/0

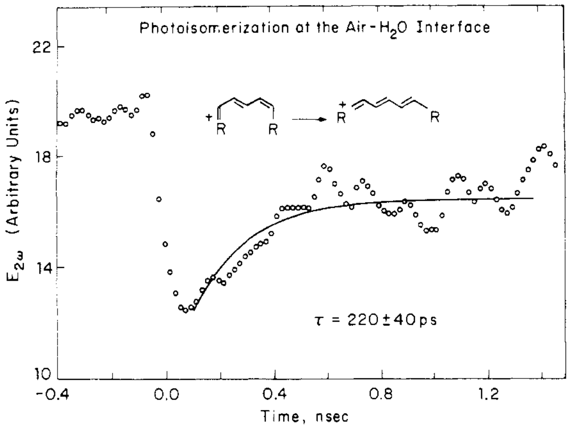


Figure 1. Surface second harmonic field, $E_{2\omega}$, as a function of time following photoexcitation of an aqueous solution containing DODCI (1.7×10^{-4} M).

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

$$I_{2\omega} \sim |\chi^{(2)}_{\text{total}}|^2 \qquad (2)$$

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

$$\chi^{(2)}_{\text{total}}(t) = \chi^{(2)}_{S_0}(\text{cis})(t) + \chi^{(2)}_{S_1}(\text{cis})(t) + \chi^{(2)}_{S_0}(\text{trans})(t) \qquad (3)$$

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 is the barrier crossing time τ. The excited S_1 cis form decays as

$$\mathcal{N}^{\text{cis}}_{S_1}(t) = \mathcal{N}^{\text{cis}}_{S_1}(0)e^{-t/\tau} \qquad (4)$$

The trans S_0 isomer builds in as

$$\mathcal{N}^{\text{trans}}_{S_0}(t) = \gamma \mathcal{N}^{\text{cis}}_{S_1}(0)[1 - e^{-t/\tau}] \qquad (5)$$

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

$$\mathcal{N}^{\text{cis}}_{S_0}(t) = (1 - \gamma)\mathcal{N}^{\text{cis}}_{S_1}(0)[1 - e^{-t/\tau}] + \mathcal{N}^{\text{cis}}_{S_0}(0) \qquad (6)$$

where γ is the fraction of excited molecules that goes to the trans ground-state S_0 from the intermediate twisted form.

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

$$\chi^{(2)}_{\text{total}}(t) = Ae^{-t/\tau} + B \qquad (7)$$

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 γ. In order to obtain the isomerization time τ we first take the square root of the SH signal since the SH signal is proportional to the square of the nonlinear susceptibility $|\chi^{(2)}_{\text{total}}(t)|^2$. By this procedure we obtain an isomerization time of 220 ± 40 ps. It is to be noted that the signal at long times does not return to its value at negative times, that is, its value at times before the pump pulse excites the sample. This is due to the fact that all of the molecules initially excited have not yet returned to the cis ground-state S_0. At the longest times we have measured (~2 ns) the interface is composed of the long-lived (~10^3 s) trans photoisomers in their ground-state S_0 trans, and the remainder are cis ground-state molecules. By the time of the next pump/probe pulse sequence, 0.1 s later, we find that the trans ground-state molecules have decayed to the lower cis ground-state form, yielding the same system measured by the earlier pump/probe pulses.

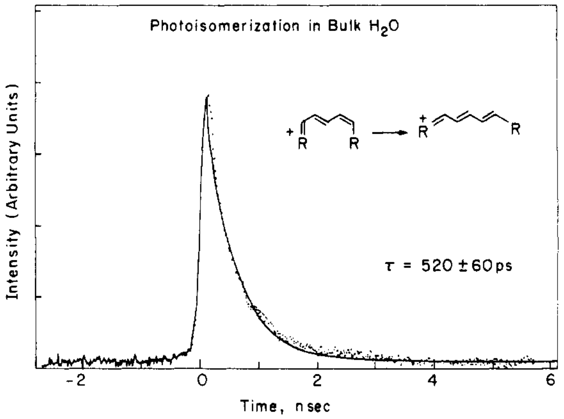


Figure 2. Fluorescence decay of DODCI (1.7×10^{-4} M) in water.

To obtain the bulk dynamics of the DODCI photoisomerization we have carried out experiments on the same solution that we used for the SH interfacial experiments. The decay from the photoexcited S_1 cis singlet state is measured by focusing the fluorescence from S_1 cis onto the slit of a picosecond streak camera, Figure 2. The decay time is determined by the isomerization rate since this is the fastest decay channel from S_1. To ensure that rotational motions of the photoexcited DODCI were not affecting the observed decay we used a polarizer set at 54.7° to the pump polarization direction. The decay time we found for DODCI in water was 520 ± 60 ps. This value is in reasonable agreement with earlier measurements[20] that yielded a value of 570 ps.

It is known from bulk studies that the DODCI photoisomerization rate is strongly dependent on the specific interactions it has with surrounding solvent molecules.[18-21] 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 effects of friction, the counterion, and DODCI–DODCI interactions on the dynamics at the air/water interface are in progress.

Conclusion

We have determined the dynamics of the cis–trans photoisomerization reaction of DODCI 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 ± 40 ps at the air/water interface, which is significantly different from its bulk water value of 520 ± 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.

Acknowledgment. We gratefully acknowledge the National Science Foundation, the Air Force Office of Scientific Research, and the donors of Petroleum Research Fund, administered by the American Chemical Society, for their support, and Alonso Castro for his help with the surface tension measurements.