

# Photochemistry and Photophysics of Liquid Interfaces by Second Harmonic Spectroscopy

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The study of photochemical and photophysical processes at various liquid interfaces using second harmonic generation methods is described. Among the topics discussed are the dynamics of photoinduced structure changes, the transport of charge across an interface, the rotational motions of interfacial molecules, intermolecular energy transfer within the interface, interfacial photopolymerization, and photoprocesses at a semiconductor/liquid interface.

## I. Introduction. Second Harmonic Generation and Interfaces

The interface, which is that molecularly thin region that separates two bulk media, not only serves as the gatekeeper to control the transfer of chemical species, charges, and energy between the two bulk media that it separates but also has chemical, physical, and biological properties which are different from either bulk medium. Intrinsic to the interface is the asymmetrical environment experienced by the chemical species present at the interface, whether they are in the form of a solid, or a molecular species as in a gas or liquid, or are interface charges made up of electrons or ions. It is this interfacial asymmetry, which is absent in the bulk media, that determines the orientational structure, chemical composition, polarity, and transport properties of the interface. These factors, in turn, determine static properties such as interfacial chemical equilibria, pH, and phases of long chain amphiphiles, as well as the dynamics of molecular motions, energy relaxation, and chemical change.

Although interfaces are of fundamental scientific, technological, environmental, and medical importance,<sup>1,2</sup> it has been difficult to investigate the properties of interfaces at the molecular level. The powerful methods of absorption and emission spectroscopy as well as the analytically powerful vibrational infrared and Raman spectroscopies are generally not applicable to interface studies, in particular not to the liquid interfaces, vapor/liquid, liquid/liquid, and solid/liquid interfaces. The reason for this is that if the molecules of interest are present in the bulk media as well as the interface, then the much larger number of molecules in the bulk will generally overwhelm any optical signal originating from the interface molecules. There are exceptions to these difficulties that permit the use of traditional spectroscopies to be used in some interface studies. Nonetheless, for most situations the traditional spectroscopies are difficult to apply to interface studies, especially liquid interfaces.

An important and relatively new approach to avoiding the dominating effects of the bulk media became feasible with the development of high-power and tunable lasers. With these lasers we have the capability to use nonlinear laser spectroscopies that have the special characteristic of being interface selective. The nonlinear methods that have this interface selectivity are second harmonic and sum frequency generation.<sup>2–15</sup> These second-order processes owe their interface sensitivity to

the fact that they are electric dipole forbidden in centrosymmetric media. Thus, the bulk regions of liquids, gases, amorphous solids, and centrosymmetric crystals will not contribute to the second harmonic or sum frequency signal except in higher order. Although the bulk regions are centrosymmetric, the chemical species at the interface sense the absence of inversion symmetry there. This makes it possible for the interface species to generate a light wave at twice the frequency or at the sum of the frequencies of the light waves that are incident on the sample.

The second harmonic and sum frequency generation can be described in terms of the second-order polarization,  $P^{(2)}$ , induced in the interface by the incident light waves. For second harmonic generation the incident light field  $\vec{E}(\omega)$  at frequency  $\omega$  generates a light wave at  $2\omega$ , whereas sum frequency generation involves two incident light fields,  $\vec{E}(\omega_1)$  and  $\vec{E}(\omega_2)$ , which generate a light field at  $\omega_1 + \omega_2$ . The relationship between the induced polarization  $P^{(2)}$  and the incident fields is given by

$$P^{(2)}(\omega_1 + \omega_2) = \chi_{\omega_1 + \omega_2}^{(2)} E(\omega_1) E(\omega_2) \quad (1)$$

where  $\chi_{\omega_1 + \omega_2}^{(2)}$  is the second-order nonlinear susceptibility, which is determined by the chemical species at the interface. The susceptibility  $\chi^{(2)}$  is a macroscopic quantity that can be related to the molecules that are in the interface, neglecting local field effects, by

$$\chi^{(2)} = N_s \langle \alpha^{(2)} \rangle \quad (2)$$

where  $N_s$  is the interfacial adsorbate density (number per unit area),  $\alpha^{(2)}$  is the molecular second-order polarizability, and the brackets indicate an average over the molecular orientations. When more than one chemical species is contributing significantly to the second harmonic or sum frequency signals, a sum over the density  $N_{s_i}$  and second-order polarizability  $\alpha_i^{(2)}$  for species  $i$  is understood. The electromagnetic SH or SF light wave, which is ultimately detected and analyzed, is directly related to the second-order time derivative of the nonlinear polarization  $P^{(2)}$ , expressed in eq 1.<sup>2</sup>

From measurements of the various parameters that characterize the second harmonic and sum frequency light waves, we obtain information on the molecules at the interface. One such parameter is the signal strength, which is related to the population and chemical composition of the interface. Another is the frequency dependence of the SHG or SFG signals. This quantity yields data on the electronic and vibrational energy levels of the chemical species at the interface. This information

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can then be used to identify chemical species at interfaces. Measurement of the direction of the generated SF or SH light field, i.e., the polarization of the light, yields information on interfacial molecular orientation. Determination of the phase of the SH or SF light with respect to the product of the incident driving fields  $\vec{E}(\omega_1) \vec{E}(\omega_2)$  yields the absolute orientation of the molecule, i.e., is the molecule pointing up vs down (polar alignment). The phase of the SH or SF light can be written as a factor in  $\chi^{(2)}$  as  $|\chi^{(2)}|e^{i\varphi}$ . Lastly, measurements of the time-dependent changes of these parameters make it possible to investigate the dynamics of intramolecular and intermolecular chemical and physical processes at interfaces.

We thus see that SH and SF spectroscopies provide powerful approaches for the investigation of interface properties. This fact is reflected in the large and increasing number of studies in the past decade that have provided new information and insights into equilibrium and dynamic processes occurring at interfaces. These studies cover the gamut of interfaces from gas/liquid, and gas/solid interfaces, to the difficult to access buried liquid/liquid, liquid/solid, and solid/solid interfaces.<sup>4-8</sup> In most of these cases the studies are of equilibrium phenomena, rather than the more experimentally difficult time-dependent processes. Among equilibrium properties there have been SH<sup>4-9,16-24</sup> and SF<sup>14,25-31</sup> orientational structural studies of molecules at various liquid interfaces. The presence of charges at water interfaces, such as long chain ions<sup>33</sup> or ionized silanols<sup>34</sup> ( $-\text{SiOH}$ ) at the silica/water interface, polarizes and orients water molecules up to  $\sim 100$  Å from the interface, depending on electrolyte concentration. At charged electrode/electrolyte interfaces a similar orientational polarization occurs.<sup>8</sup> SHG and SFG investigations of the trans-gauche conformations of long chain hydrocarbon molecules at the air/water interface and the orientation of their tail and head groups have proved to be important probes of the properties of the very large class of insoluble Langmuir monolayers.<sup>14,25-29,35,36</sup> By varying the density of these insoluble long chain molecules at the interface, phase transitions between liquid expanded and liquid condensed states have been observed, which resolved a controversy about the existence of these phases.<sup>26</sup> Fluctuations in the SH signal arising from the fluctuations in density<sup>37</sup> or orientation<sup>38</sup> from an interface spot of less than a 10  $\mu\text{m}$  diameter provided information on the thermal motions of interface clusters and the discovery of a weakly first-order orientational phase transition.

The importance of the electrode/aqueous interface has stimulated many SHG and SFG studies. These studies include the effects of applied potential on the SH signal,<sup>4,8,39-41</sup> the adsorption of ions and neutral molecules to the interface,<sup>5,8,42</sup> the symmetry of crystalline metal/aqueous interfaces,<sup>42</sup> and the detection of the two opposite orientations of  $\text{CN}^-$  adsorbed to a platinum electrode.<sup>43</sup> Although we are only considering liquid interfaces in this article, there is a considerable body of important SH and SF work on equilibrium properties of gas/solid interfaces, ranging from metals and semiconductors to insulators, which are available to the reader.<sup>5-8</sup> Just as the methods of SHG and SFG are being widely applied to equilibrium properties, they are also being applied to the study of time-dependent phenomena. Among the many studies are the femtosecond photoinduced melting of silicon,<sup>44</sup> diffusive motions at semiconductor,<sup>45</sup> insulator,<sup>46</sup> metal,<sup>47</sup> and liquid interfaces,<sup>48</sup> photochemistry in Langmuir-Blodgett films<sup>49</sup> and at silica/air,<sup>50</sup> silica/liquid,<sup>51</sup> air/liquid,<sup>52</sup> and liquid/liquid<sup>53</sup> interfaces, rotational motions at air/liquid interfaces,<sup>54</sup> reaction kinetics at electrochemical interfaces,<sup>55,56</sup> and vibrational relaxation.<sup>57,58</sup> Despite this limited description of the research

activities, which are conducted in the many laboratories around the world, it is clear that the study of interfaces by SH and SF methods has contributed to the vitality and resurgence of interface science.

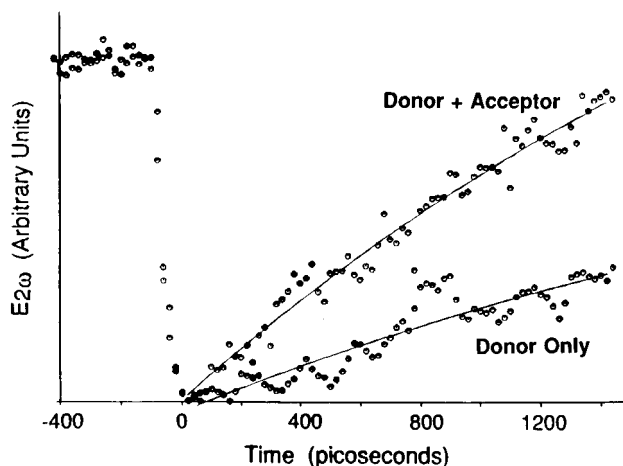
In this article we will restrict the topics to be covered to a narrow but important part of interface chemistry, namely photochemistry and photophysics at liquid interfaces. It is worth noting that liquid interfaces not only are of great scientific interest but also directly impact many areas of medicine and technology. In medicine they are seen in membranes and transport of ions and molecules across membranes. In the electronics industry, they occur in photolithography, for example. They are present in the chemical industry, e.g., oil recovery and liquid phase catalysis, and in the many fields concerned with lubrication. Perhaps the most immediate area where liquid interfaces play a key role is in environmental science. The chemistry, physics, and biology at environmental interfaces play a crucial role in the health and well-being of the world. Thus, we need to increase our understanding of the air/water interface, which constitutes three quarters of the earth's surface, the water/soil interface<sup>59</sup> where pollutants are adsorbed and where most soil biology and chemistry occur, and the atmospheric sciences where the exchange of molecules between the gas phase<sup>60</sup> and the reactive media of aerosols is seen as a key part of atmospheric chemistry.

## II. Photochemistry and Photophysics at Liquid Interfaces

The competing channels for the radiative and nonradiative dissipation of electronic and vibrational energy by excited molecules determine the fate of such species. Whether the molecules of interest are good emitters or degrade their excess energy into heat by its transfer to the surrounding medium depends on these channels. Excited molecules may also utilize the excitation energy to carry out a chemical reaction by the formation or breaking of chemical bonds or by undergoing a structural change. The relative importance of these different pathways for energy decay is often sensitive to the coupling of the photoexcited molecules with the molecules of the surrounding medium, i.e., the solvent in bulk liquid state processes. For example, the polarity of the solvent can affect the energies of the electronic states, their intersections, and the energies and shapes of the potential surfaces and barriers relevant to energy relaxation and chemical changes. In a similar manner the solvent frictional resistance to molecular motions, barrier crossing dynamics, and the reorganization of solvent molecules in the neighborhood of photoexcited molecules can markedly alter the time dependences and quantum yields of the competing pathways for energy decay.

Because the orientational structure, chemical composition, polarity, and friction of an interface are different from the two bulk media that define it, we anticipate in a general way that the photochemistry and photophysics of interfaces have different properties and constitute a separate field from their bulk counterparts. As we shall see from the following discussion, this is indeed the case at liquid interfaces.

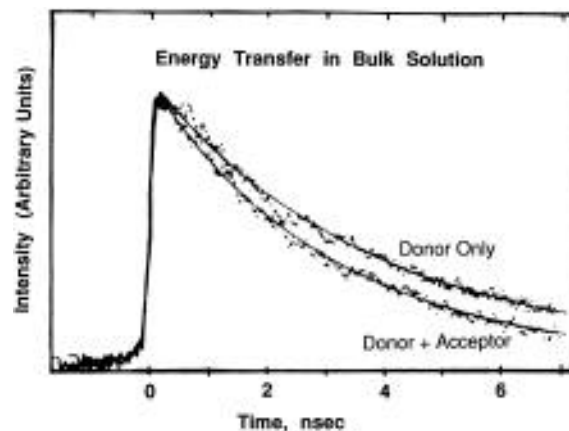
**A. Intermolecular Electronic Energy Transfer.** The transfer of electronic energy between molecules is an important process in photochemistry. It can enhance the efficiency of a photoinduced chemical reaction, as in photosynthesis, or on the other hand be used to protect materials by energy transfer to molecular dopants that dissipate the energy in a nondestructive way. In an interface the photochemical and photophysical transformation of energy can be modified by the lateral transfer of energy among molecules within the interface and by the



**Figure 1.** Amplitude of second harmonic electric field vs time in an energy transfer experiment at the air/water interface. Pump pulse excites Rhodamine 6G at  $t = 0$ . The decay in presence and absence of DODCI acceptor is shown. The solid line for the donor + acceptor transfer is the fit to a 2D Förster energy transfer mechanism. Reprinted with permission from ref 61. Copyright 1989 American Institute of Physics.

exchange of energy between interface and bulk molecules. The competition of energy transfer within the interface and energy transfer out of the interface depends chiefly on the distances separating the donor and acceptor molecules within the interface compared with their separations when one is located in the interface and the other in the bulk. If the transfer mechanism is by a dipole–dipole (Förster) coupling, then the transfer can extend over donor–acceptor distances as large as 100 Å. A short-range exchange transfer, as in triplet–triplet transfer, occurs at distances less than 10–15 Å.

A SH investigation has been carried out on the long-range Förster energy transfer at the air/water interface between Rhodamine 6G (Rh6G) as the donor and the cyanine dye DODCI as the acceptor.<sup>61</sup> The SH signal generated by the molecules in the interface is dominated by the ground state Rh6G molecule. This is because of a resonance enhancement of the Rh6G ground state nonlinear polarizability at the wavelength (532 nm) of the probe pulse. The decay of photoexcited Rh6G molecules back to their ground states due to excited state relaxation processes including intermolecular energy transfer to the acceptor DODCI molecules was monitored by the SH light generated by a probe pulse time delayed with respect to the pump pulse. In the absence of deactivation by energy transfer to acceptor molecules, the photoexcited Rh6G molecules decay back to their ground states in 3.1 ns, as determined by the SH measurements. When acceptor molecules are present, the SH signal recovers faster by a factor of 3. The more rapid decay in the presence of the DODCI is attributed to the additional pathway for relaxation provided by the Förster energy transfer mechanism. The SH kinetics did not depend on the interface density of Rh6G at the low concentrations used, which indicates that excited donor to ground state donor transfer was not important in the Rh6G–DODCI energy transfer process. The factor of 3 increase in the decay of interfacial photoexcited Rh6G due to energy transfer to DODCI is quite different from the 15% increase in the bulk Rh6G decay due to energy transfer to DODCI in the bulk. The lifetime of bulk Rh6G in the absence of the DODCI acceptor was 3.7 ns. The considerably greater energy transfer in the interface is consistent with the larger donor–acceptor distances in the bulk liquid (~130 Å) compared with the much smaller donor–acceptor separations at the interface (50–100 Å). It is the relatively strong adsorption of DODCI to the interface that is responsible for the smaller

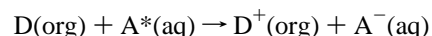
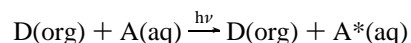


**Figure 2.** Effect of the addition of the acceptor DODCI on the fluorescence decay of the donor Rh6G in bulk aqueous solution. Donor-only solid line is fit to an exponential decay, and the donor + acceptor solid line is fit to a 3D Förster energy transfer model.

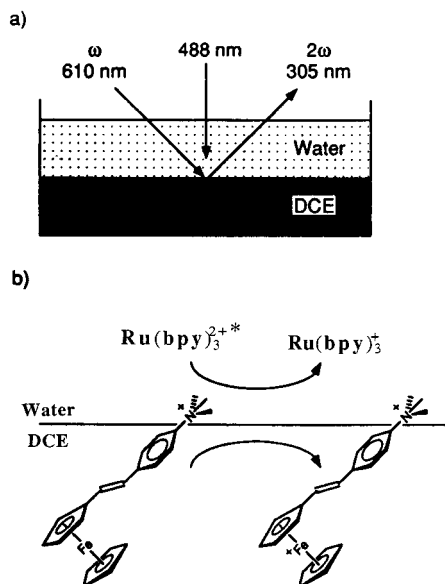
donor–acceptor separation at the interface than in the bulk solution. Because of the low bulk donor and acceptor concentrations, the transfer of energy between interface and bulk molecules can be neglected.

Having established by these SH experiments that there is significant energy transfer within the interface, the question of whether the transfer is “two-dimensional” or not can be posed. If one compares as a first approximation the kinetics based on a two-dimensional vs a three-dimensional Förster transfer model for the interface, it is found that the parameters used to fit the data to the 2D model are more reasonable than for the 3D model. However, the effects on the kinetics of the assumption in the Förster model of a random distribution of donor–acceptor orientations must be more closely examined. It would appear in a rough approximation that the kinetics obtained from the 2D and 3D formulations of the Förster model, which assumes random orientations and random donor–acceptor separations, is dominated by the  $1/R^6$  distance dependence of the donor–acceptor interactions, and not the orientational dependence. Although these ideas suggest that the Förster model is a plausible first approximation, a more complete treatment of what appears to be a two-dimensional energy transfer process is needed.

**B. Excited State Electron Transfer at a Liquid/Liquid Interface.** To achieve the efficient conversion of reactants into products, it is necessary to block the recombination of the product molecules. One way to do this is to take advantage of the asymmetry of an interface. By selecting reactants and an interface such that the product molecules preferentially separate into different bulk phases, one can markedly reduce the recombination reaction. This has been done in an oxidation–reduction reaction<sup>62,63</sup> and in photoinitiated electron transfer reactions<sup>64–66</sup> at an organic liquid/water interface, where the electron donor is soluble in the organic bulk phase only and the acceptor is soluble in the water phase only. When the molecules are in their ground electronic states, the oxidation–reduction potentials of the electron donor–acceptor pair cannot effect an electron transfer reaction. However, on excitation of the acceptor molecule the reaction can be initiated. Schematically,



Because the electron transfer reaction requires the overlap of donor and excited acceptor wave functions, the reacting pair must be close to each other (<10–15 Å). The reaction is therefore restricted to the liquid/liquid interface region. The

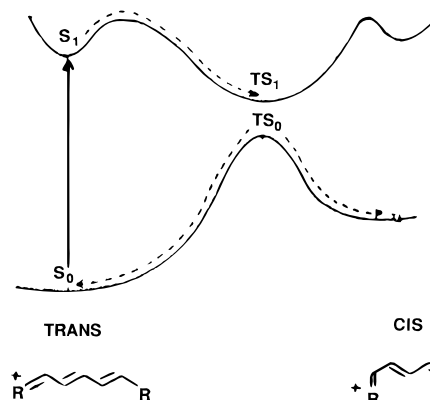


**Figure 3.** (a) SHG experiment for monitoring the photoinduced electron transfer reaction from a 1+ ferrocene derivative to photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  at a water/dichloroethane interface. (b) Schematic representation of the photoinduced electron transfer at a water/dichloroethane interface. Reprinted from ref 66.

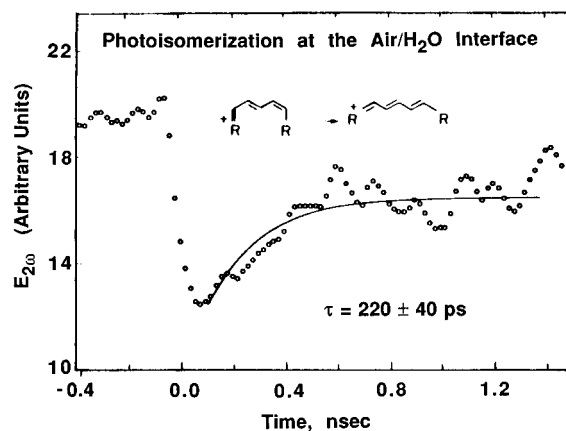
techniques used to study these photoinitiated reactions were measurements of the photocurrent,<sup>64,65</sup> and to more directly probe the reaction at the interface SHG was used.<sup>66</sup> In the SHG experiments the bulk liquids used were the immiscible liquids, water and 1,2-dichloroethane (DCE). The organic soluble donor was a ferrocene derivative, *trans*-1-ferrocenyl-2-[4-(trimethylammonio)phenyl]ethylene tetraphenylborate,  $1^+ \text{--} \text{BH}_4^-$ . The water-soluble acceptor is tris(2,2'-bipyridyl)ruthenium(II) chloride [ $\text{Ru}(\text{bpy})_3^{2+} \cdot 2\text{Cl}^-$ ]. The SH signal is due chiefly to the ferrocene derivative because of its greater nonlinear polarizability compared with the  $\text{Ru}(\text{bpy})_3^{2+}$  acceptor. On excitation of the  $\text{Ru}(\text{bpy})_3^{2+}$  using an argon laser at 488 nm, there is reaction of  $\text{D}(\text{org})$  with  $\text{A}^*(\text{aq})$  at the interface. The increase in SH signal following the electron transfer reaction is attributed to the resonant enhancement of the second-order polarizability of the ferrocene derivative in its oxidized state  $\text{D}^+(\text{org})$ . The slow rise time of  $13 \pm 4$  s in the SH signal is thought to reflect a diffusion-controlled reaction, i.e. the motion of the donor and excited acceptor molecules to the interface where they can react. The  $20 \pm 4$  s decay of the SH signal after its  $13 \pm 4$  s reaction rise time can be due to several processes. They include back-reaction, lateral diffusion out of the laser probe area, and desorption of  $\text{D}^+(\text{org})$  from the interface. Stimulated by this study, we anticipate further work on this system and on other electron-donor pairs and other interfaces.

### C. Dynamics of Structural Changes in Excited Molecules.

(i) *Barrier Crossing Isomerization.* The photoexcitation of the cyanine dye 3,3'-diethyloxadiazocyanine iodide (DODCI), from its *trans* ground state structure to its lowest excited singlet state, results in a rapid barrier crossing that takes the molecule to an intermediate twisted conformation,  $\text{TS}_1$ , which then crosses over to a vibrationally hot ground state *trans* or *cis* form of the molecule.<sup>67-69</sup> The dynamics in the bulk has been obtained from pump and time-resolved fluorescence measurements.<sup>52,69</sup> The decay of the initially excited singlet state is known to be dominated by the barrier crossing, at least in bulk water, where the fluorescence decay time has been found to be 520 ps.<sup>52,69</sup> In the DODCI experiment at the air/water interface a decay time of 220 ps was obtained.<sup>52</sup> Because the polarity of the air/water interface is lower than that in the bulk aqueous solution, it is



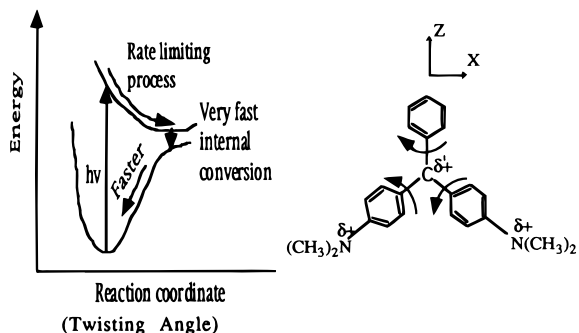
**Figure 4.** Potential energy diagram,  $S_0 \rightarrow S_1$  photoexcitation, and relaxation pathways for the photoisomerization of the cyanine dye (DODCI). The kinetics are determined by the barrier crossing from  $S_1$  to the intermediate twisted conformation,  $\text{TS}_1$ . The dashed line indicates possible radiationless decay pathways. Reprinted from ref 52.



**Figure 5.** Second harmonic field,  $E_{2\omega}$ , as a function of time following photoexcitation of the cyanine dye DODCI at an air/water interface. Reprinted from ref 52.

expected, based on bulk solvent polarity effects, that the reaction barrier at the interface is larger than in the bulk liquid. The increase in barrier height would increase the decay time at the interface, not decrease it as was observed. It is therefore likely that the more rapid isomerization at the air/water interface is due to a smaller friction along the isomerizing coordinate at the interface than in the bulk medium.

Further evidence that the friction is playing a key role in causing the interface dynamics to be faster than the bulk dynamics is seen from studies of several aqueous-methanol solutions containing the cyanine dye. Measurements of the bulk dynamics at bulk methanol volume fractions of 0%, 10%, 20%, 30%, and 100% yielded the slower decay constants 520, 690, 730, and 930 ps, respectively, as the methanol concentration increased. The slower kinetics in the bulk solution as the methanol concentration increased is attributed to the increase in the barrier height due to the lower polarity of the methanol solutions. It should be noted that the viscosity of neat methanol is lower than that of neat water, indicating that the slower rate in methanol is not due to an increased friction. At the interface of the 0%, 10%, and 20% solutions the kinetics became faster, yielding decay times of 220, 135, and 96 ps, respectively. Although these results suggest that the friction along the isomerization coordinate is smaller at the air/solution interface than in the bulk solution, the contribution of the barrier to the interface kinetics is not known from these experiments.



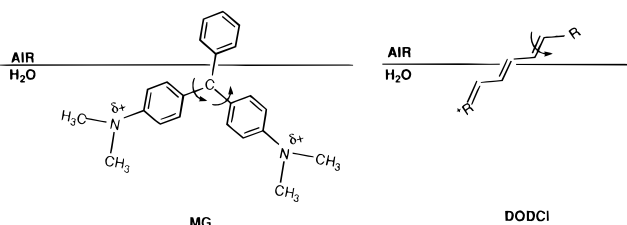
**Figure 6.** Malachite green structure and potential energy diagram for the excitation and photoisomerization dynamics. The kinetics is due to the twisting motion of the aromatic moieties on the barrierless excited energy surface.

In addition to the effects of barrier height and friction on the interface kinetics, there is the issue of molecular aggregation at interfaces and its effects on excited state relaxation. In the bulk it is found that molecular aggregation generally results in more rapid excited state decay because of new channels for energy decay. Typically, the dye molecules more readily aggregate in water because of the hydrophobic parts of the dye molecules. Consequently, the dye molecules would favor the monomer form, i.e. less association in less polar solvents such as the alcohols. If interface aggregation was responsible for the shortening of the DODCI lifetime relative to the bulk solution lifetime, then it would be expected that the interface lifetime would become longer on addition of the aggregate-breaking methanol molecules to the system. The SH measurements showed that the interface lifetime became shorter when methanol was at the interface, which suggests that interface aggregation is not a dominant factor in the interface dynamics.

(ii) *Barrierless Isomerization.* One way to separate the effects of the barrier from that of friction on the reaction dynamics is to select a molecule for which the photoisomerization involves no barrier; i.e., the reaction occurs on a barrierless potential energy surface. To further assist in removing the effects of the potential surface on the dynamics, it is important to select a molecule whose isomerization kinetics, as determined from bulk studies, shows that the dynamics is not strongly dependent on polarity. This will minimize changes in the reaction potential energy surface at the interface due to polarity differences between the interface and bulk regions of the solution. One such molecule is the triphenylmethane dye malachite green (MG). In its ground electronic state the aromatic rings are arranged in a propeller-like geometry about the central carbon to which they are bonded.<sup>70</sup> On photoexcitation to its lowest excited singlet state it was found in bulk liquid studies that the relaxation back to the ground state was strongly dependent on the viscosity of the solvent.<sup>70–76</sup> The current model for the isomerization reaction involves the synchronous motion on a barrierless excited potential surface of the aromatic rings from a more twisted initial conformation toward a flatter excited state conformation.<sup>76–80</sup> The ground state recovery time is determined by the motion on the excited surface, the relaxation on the vibrationally hot ground state being much faster. Studies of the isomerization in bulk water established a time constant of about 0.7 ps.<sup>70</sup> At the air/water interface a time constant of 1.9 ps was obtained using SHG.<sup>53</sup> This result is rather interesting in showing that the process is slower at the air/water interface than in the bulk solution, which is the reverse of what was found for the cyanine dye discussed previously. The issue to be addressed is how the friction at the air/water interface can be apparently higher for the triphenylmethane dye MG yet lower for the cyanine dye DODCI.

One way to investigate the frictional resistance experienced by the isomerizing MG molecule is to change the interface. Using this approach, the air above the bulk water was replaced by an alkane (octane or pentadecane) liquid, forming an alkane/water interface, which contains MG molecules.<sup>53</sup> The effect of the change in friction on the isomerization at the alkane/water interface relative to the air/water interface depends on which part of the MG molecule projects into the air or alkane phase and how the water structure and thus friction in the water side of the interface are altered by replacing the air bulk phase with the liquid alkane phase. On the basis of chemical considerations, one expects the more hydrophobic phenyl ring to project into the air or alkane part of the interface and the charged anilino moieties to be located in the polar, solvating, water side of the interface. This expectation is supported by the significantly greater adsorption of MG to the alkane/water interface than to the air/water interface,<sup>53</sup> a result which is consistent with an attractive interaction between the nonpolar phenyl moiety and the alkane phase. With the phenyl groups projecting into the alkane phase and the anilino groups projecting into the water phase, one would anticipate that the twisting of these different moieties in the course of the isomerization reaction would be sensitive to the frictional properties of the phases in which they are located. At the octane/water interface the isomerization time was found to be  $3.0 \pm 0.4$  ps, which is an increase of only 50% above the air/water result. The change appears to be small considering the fact that the twisting of the phenyl group should experience significantly more frictional resistance in the alkane phase than in the air. However, we do not know how far the phenyl group projects into the air side of the air/water interface. At the octane/water interface, however, the phenyl group is thought to significantly project into the octane phase because of the much greater MG adsorption to the octane/water interface than to the air/water interface. In comparing the air/water and octane/water interfaces, we furthermore do not know to what extent the water structure is changed by the liquid alkane making contact with the water phase rather than air. On the basis of computer simulations of the air/water and various alkane/water interfaces, it appears that the water structure at these interfaces is similar.<sup>81–86</sup> This theoretical finding is consistent with the relatively small change in dynamics that is found from the SH studies at the air/water and octane/water interfaces.

To address the issue of the effects of the alkane on the structure of the alkane/water interface and thereby the MG isomerization, another alkane/water interface was investigated, namely the pentadecane/water interface.<sup>53</sup> The MG orientation and population were found to be the same at the pentadecane/water interface as at the octane/water interface, which indicates that the time-averaged MG interactions and the interfacial structures are similar at the two interfaces. The isomerization at the pentadecane/water interface was found to be  $3.6 \pm 0.3$  ps. This represents only a 20% increase in the isomerization time constant compared with octane/water, despite the roughly sixfold increase in the pentadecane bulk viscosity relative to that of bulk octane. This result is surprising if one accepts the inferences based on the orientation and population measurements that the structures of the two interfaces are similar and that the phenyl group of MG projects into the alkane phase. Based on these inferences, the twisting motions of the phenyl group should be very sensitive to the alkane interface frictional resistance. The relatively small difference between octane/water and pentadecane/water interfaces suggests that the twisting of the phenyl group of MG is not important in the isomerization dynamics. On the basis of this observation, it is proposed that



**Figure 7.** Schematic of orientations and isomerizing motions of malachite green (MG) and DODCI at an air/water interface. The isomerizing motions of MG take place on water side of interface and those of DODCI on the air side.

it is the twisting of the charged anilino groups that determines the dynamics, a conclusion that is contrary to the heretofore generally accepted model that the synchronous motions of all three aromatic groups are required in the isomerization process. The proposed dominance of the anilino motions in the kinetics explains the similar time constants for the two alkane/water interfaces because the anilino groups are located on the water side of the interface in both cases.

Returning now to the observations that MG and DODCI display opposite behavior in their air/water interface vs bulk dynamics, it is suggested that the interface location and orientation of the parts of the adsorbed molecule involved in the isomerization motions have to be considered to understand the experimental findings. The SH measurements of the DODCI orientation indicate that it is similar to MG, yielding a geometry with one end of the molecule pointing toward the air phase with a tilt of about  $45^\circ$  to the interface normal. The DODCI isomerization involves the motion of one end of the cyanine dye about its methylene bonds. Because part of DODCI projects into the air side, which is a region of lower water density, and therefore smaller frictional resistance, it is anticipated that the isomerization at the interface will preferentially involve motions on the air side rather than the water side of the interface. The frictional resistance to the isomerization motion is thus lower at the interface than in the higher density homogeneous bulk region, resulting in the more rapid dynamics at the interface.

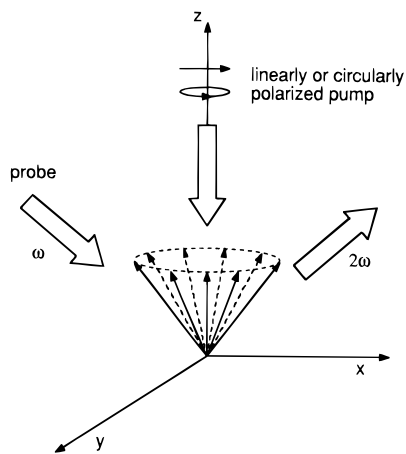
For MG it is the motions of the anilino groups, located on the water side of the air/water interface, that determine the isomerization dynamics. Thus, the parts of the MG and DODCI molecules involved in the isomerizing motions are sampling very different regions of the air/water interface. The DODCI is proposed to be experiencing the lower frictional resistance on the air side of the interface, in contrast with MG for which the isomerizing motions occur on the water side of the interface. The observation that the MG dynamics is slower at the air/water interface than in the bulk aqueous solution is attributed to greater frictional resistance in the water side of the air/water interface. The greater resistance at the interface could reflect the differences in the orientational structure of water next to MG at the interface compared with the orientation of water molecules next to MG in the bulk solution. In addition, the twisting motions of the anilino groups on photoexcitation of MG at the interface could result in an increased friction due to the forcing of the surrounding water molecules into higher energy orientations than are required in the bulk solution. Similarly, an increased friction associated with an overall change in the equilibrium orientation and positions of the MG isomer at the interface could be a factor. In any event we can understand from the MG and DODCI studies that different frictional effects at the same interface are possible and can result in apparently opposite effects.

Unlike the air/water and alkane/water interfaces the solid/liquid interface, in particular the silica/water interface, offers

the possibility of specific interactions of the adsorbed MG molecules with the  $-\text{SiOH}$  and  $-\text{SiO}^-$  groups of the silica.<sup>51,53</sup> Using SHG methods, the isomerization time was found to be longer (5.5 ps) than in the air/water and alkane/water interfaces.<sup>53</sup> The slower dynamics could be due to specific MG-silica interactions as well as an increase in the interface friction due to increased water structure, as suggested in fluorescence studies of other organic molecules near the silica/water interfaces.<sup>87,88</sup> Further experiments, e.g. variation of pH, electrolyte concentration, and temperature, as well as the use of related molecules which are also sensitive to friction, are needed to separate the different contributions to the dynamics at this interface. Related studies based on the fluorescence of MG at the silica/water interface at higher concentrations using a total internal reflection geometry (100 nm penetration depth) showed that there were slow, concentration-dependent components in the observed kinetics.<sup>89</sup> The connection between the fluorescence and SH results has not been established, in part due to the different concentrations and possible aggregate effects in the different experiments. The contributions of aggregates as well as specific interactions of MG with silica could be an important factor in SH studies of MG at the silica/ether interface.<sup>51</sup> The kinetics show a much slower isomerization time (40 ps) than is expected for bulk ether. Once again further work on liquid/solid interfaces is needed to separate the effects of friction, specific interactions, and possible aggregation at high concentration on the dynamics of energy relaxation and excited state structure changes.

**D. Molecular Rotation and Friction at Interfaces.** Measurements of orientational relaxation have proven to be an important way to investigate the frictional forces exerted against molecular motions in bulk liquids. On the basis of the isomerization studies discussed in the previous section, it is clear that some way to probe the interfacial solvent forces that exert a drag on molecular motions at interfaces would be of value. The use of transient absorption and fluorescence techniques, which have been shown to be very useful in studies of motions in bulk liquids, is generally not applicable to interface studies. The reason for this is that the interface is usually masked by the absorption or fluorescence of bulk molecules. Exceptions to the difficulties imposed by bulk molecules can be circumvented if the fluorescing or absorbing molecules of interest have a negligible bulk population. One way to avoid the bulk population contribution is to covalently bind a fluorescent probe molecule to a water-insoluble surfactant.<sup>90</sup> This ensures a reasonable population of the probe at the air/water interface and a negligible population in the bulk solution. The limitation of this method is that it is only the hindered rotational motions of a bound moiety that can be examined and not the free rotations of an unattached molecule. In addition, it is restricted to interfaces where the binding molecules are themselves excluded from the bulk media. Another approach<sup>91</sup> that has been used, and has provided very interesting results, is one where the adsorption of the probe molecule to the interface is so strongly favored that only a very small bulk concentration ( $10^{-8}$ – $10^{-9}$  M) is needed to achieve a detectable interface population. Under these conditions the fluorescence originating from the bulk molecules can be neglected. Unfortunately, this approach, though of value, is not general.

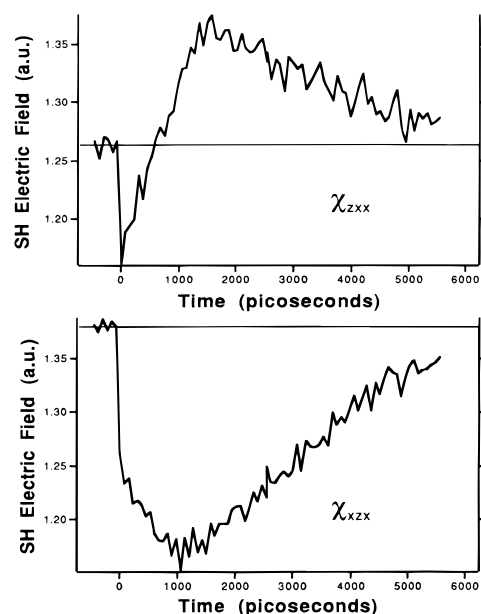
Unlike the exceptions just noted, it is possible by SHG and SFG to directly probe molecular rotational motions in the interface, even when there is a large population of the molecules in the bulk solution.<sup>54</sup> The approach used for interface rotational studies is fundamentally the same as that for bulk studies. A polarized pump pulse of short duration excites preferentially



**Figure 8.** Schematic of SH experiment for measuring interfacial molecular reorientation dynamics. The arrows show one tilt angle of the orientational distribution of the molecular transition dipoles before photoexcitation. Reprinted from ref 54.

those molecules whose transition moments are oriented along the incident field direction. This photoselection process perturbs the distribution of molecular orientations. Unlike bulk solutions, where the orientational distribution is isotropic before photoexcitation, at an interface the ground state molecules already have an anisotropic orientational distribution; i.e., the molecules are tilted out of the interface plane in some preferred orientations. The exciting pulse disturbs this equilibrium ground state orientational distribution by burning a hole in it and also by producing a nonequilibrium orientational distribution of excited molecules. Following excitation the interface ground state molecules reorient to fill the hole created in their equilibrium orientational distribution, and the excited molecules reorient toward whatever their equilibrium orientational distribution in the interface is. The equilibrium excited state orientation can be the same as that of the ground state; i.e., they can have the same average molecular tilt angle. Alternatively, the ground and excited state molecules can have different orientations because of the change in charge distribution (dipole moment, etc.) on excitation.

The pump-SH probe method was used to investigate the molecular reorientational dynamics of Rhodamine 6G (Rh6G) at the air/water interface.<sup>54</sup> A 532 nm picosecond pump pulse excited the Rh6G. The interface rotations of the ground and excited molecules were monitored by detecting the SH signal generated by a weaker time delayed 532 nm picosecond probe pulse. The time dependence of the SH signal was found to be dependent on the polarization of the incident light and on the polarization component of the SH light selected by an analyzer located in front of the detector. This polarization dependence means that the different susceptibility elements  $\chi_{ijk}^{(2)}$  have different kinetics. The  $j$  and  $k$  subscripts represent the projection of the incoming fundamental field along the laboratory  $j$  and  $k$  axes, and  $i$  represents the projection of the SH field along the  $i$  laboratory axis. If the time dependence in the SH signal was due only to a change in the ground and excited state populations then the kinetics of the different elements  $\chi_{ijk}^{(2)}$  would have been the same. To minimize any contribution of orientationally dependent intermolecular energy transfer, the interface concentration was kept low ( $<4 \times 10^{12}$  molecules/cm<sup>2</sup>). For this population range the observed SH kinetics did not change when the interface population was doubled, demonstrating that energy transfer can be neglected. In Figure 9 the time dependence of the  $\chi_{ijk}^{(2)}$  components obtained from measurements of the amplitude of the SH electric fields is shown. After the initial, instrument limited drop in the SH signal, the kinetics for the



**Figure 9.** Time dependence of different polarization elements,  $\chi_{ZXX}^{(2)}$  and  $\chi_{XZX}^{(2)}$ , obtained in photoexcitation pump-SH probe experiment for Rhodamine 6G at the air/water interface.  $Z$  is the laboratory axis normal to the interface, and  $X$  is an axis in the plane of the interface. Reprinted from ref 54.

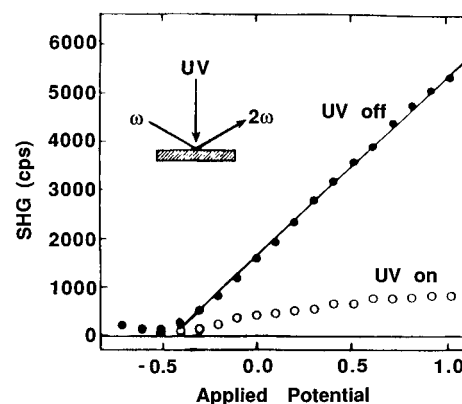
$\chi_{ZXX}^{(2)}$  and  $\chi_{XZX}^{(2)}$  components are seen to be very different, where  $Z$  is the normal to the interface and  $X$  is parallel to the interface. The initial drop in the SH signal is due to the smaller amplitude of the nonlinear polarizability of the excited state molecule relative to that of the ground state molecule at the probe wavelength. The observation that  $\chi_{ZXX}^{(2)}$  increases in  $\sim 1.5$  ns to a value that is greater than its value at negative times, when all molecules were in their ground states, suggests that the excited molecules are reorienting toward an equilibrium orientation different from that of the ground state molecules. Although the amplitude of the nonlinear polarizability tensor  $\alpha_{S_1}^{(2)}$  of the excited state is smaller than that of the ground state  $\alpha_{S_0}^{(2)}$ , the contributions of the excited molecules in their new orientations make a greater contribution to  $\chi_{ZXX}^{(2)}$  than do the ground state molecules in their equilibrium orientations. For  $\chi_{XZX}^{(2)}$ , on the other hand, the SH signal continues to decrease after the immediate drop to a minimum value in about 1.2 ns. This result indicates that the rotations of the ground and excited molecules to their preferred orientations further decrease their contributions to  $\chi_{XZX}^{(2)}$ . The subsequent decrease in  $\chi_{ZXX}^{(2)}$  from its maximum value, and increase in  $\chi_{XZX}^{(2)}$  from its minimum value, are associated with the decay of the excited state populations in 3–4 ns.

The orientational perturbation produced by a photoexciting pump pulse results in ground and excited state rotational motions that can be described in terms of out-of-plane motions, i.e., changes in the molecular tilt angles, and in terms of rotational motions in the plane of the interface. If the pump light is linearly polarized, then the in-plane rotational motions seek to relax the anisotropy caused by the pump light being polarized along an in-plane axis, for example the  $X$  axis. Molecules that have their transition moments along the  $X$  axis are preferentially excited. This in-plane photoselection transforms what was an in-plane isotropic interface into an in-plane anisotropic one. The out-of-plane rotations seek to restore the ground state molecules to an equilibrium distribution in their polar angles and similarly to bring the excited molecules to their equilibrium polar angle distribution. One way to separate the in-plane from out-of-

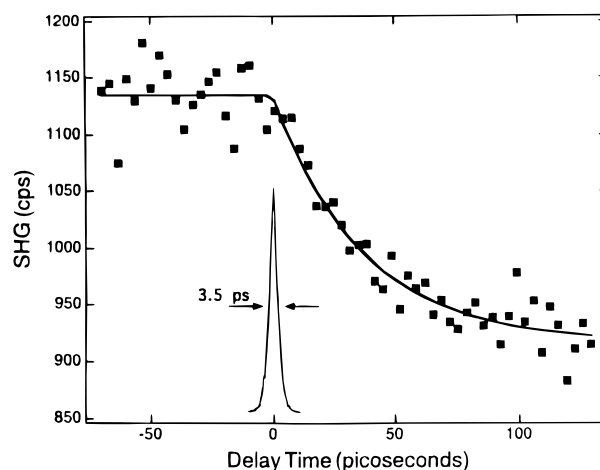
plane orientational relaxation motions is to use a circularly polarized pump pulse that is incident normal to the interface. Because there is equal likelihood of excitation by the circularly polarized pump light of all molecules irrespective of their orientation with respect to the in-plane axes, no in-plane anisotropy is induced in the interface molecular orientations. The only photoinduced anisotropy is with respect to the molecular tilt orientation. Thus, the observed kinetics should depend only on out-of-plane rotations, i.e. those motions that change the tilt angles. The results showed that the kinetics is the same using linearly or circularly polarized light for both the  $\chi_{ZZX}^{(2)}$  and  $\chi_{ZZX}^{(2)}$  components. These somewhat surprising findings indicate that the observed orientational relaxations are due to out-of-plane and not in-plane molecular motions. Whether this is due to an in-plane relaxation that is faster than can be resolved with 15 ps laser pulses, or whether the particular pump-SH probe geometry used is relatively insensitive to the polarization of the pump light, is not known. The out-of-plane orientation relaxation data indicate a reorientation time of about 400–500 ps. However, it should be noted that a model calculation, e.g., rotational Brownian motion in an orienting force field normal to the interface, or a computer simulation is needed to properly extract the parameters of the orientational relaxation. Nonetheless, it appears for Rhodamine 6G that the time scale for orientational relaxation is noticeably longer in the interface than in bulk water where the measured rotational relaxation time is 200 ps.<sup>92</sup> The rotational motion of Rhodamine 6G, which is a positively charged rigid molecule, should be determined by the friction in the higher density water side of the interface. On the basis of these considerations, we conclude that the frictional resistance is greater at the air/water interface than in bulk water for interface motions that occur in the water side of the interface. This inference is consistent with the slower isomerization dynamics of MG observed at the air/water interface relative to that in bulk water. It is of interest to note that the ratio in the air/water interface dynamics relative to bulk water is comparable in the MG isomerization, roughly a factor of 2–3 (1.9/0.7), and in the rotation of Rhodamine 6G, where it is roughly a factor of 2–3 (500/200).

**E. Charge Dynamics at an Electrolyte/Semiconductor Interface.** It is the array of photochemical and photophysical processes that occurs at a liquid electrolyte/semiconductor electrode interface which determines the efficiency of various energy conversion schemes. The ultrafast processes involved in the generation of charges in the bulk and near surface regions of the semiconductor, the transport of the charges (holes or electrons) to the interface, and the oxidation or reduction reactions with neutral or ionic species at the interface are the key steps that require investigation. A number of SHG studies<sup>93–98</sup> and other optical studies<sup>99–104</sup> including transient absorption, fluorescence, resonance Raman, photoluminescence, electrooptic sampling, transient grating measurements, and STM studies<sup>105,106</sup> have been carried out on electrolyte/semiconductor systems. Because of the abundance of semiconductor/electrolyte interfaces, the complexity of the charge generation process, charge transport to the interface, charge transfer to adsorbates, and subsequent interface recombination reactions, there remain many questions concerning the dynamics of these various processes.

Picosecond time-resolved SHG has been used to investigate the n-TiO<sub>2</sub> semiconductor electrode/electrolyte interface following UV photoexcitation of the semiconductor.<sup>97</sup> The origin of the SH signal in the presence or absence of UV photoexcitation is the excess charge density in the space charge layer. The space charge electric field polarizes the TiO<sub>2</sub> crystal near



**Figure 10.** SHG signal as a function of applied potential from a n-TiO<sub>2</sub> electrode with (open circles) and without (filled circles) UV irradiation on a TiO<sub>2</sub>/electrolyte interface. Reprinted from ref 97.

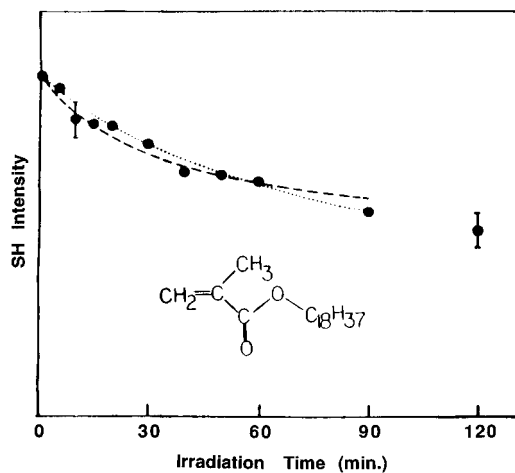


**Figure 11.** Time-dependent measurement of the transport of photo-generated holes to the n-TiO<sub>2</sub> electrode/electrolyte interface in a photoexcitation of n-TiO<sub>2</sub>-SH probe experiment. The solid line gives an exponential fit of 36 ps. The sharp peak shows the instrument response. Reprinted from ref 97.

the electrode interface, destroying the centrosymmetry of the crystal in this region and resulting in what is referred to as electric field induced second harmonic generation. We thus see that SHG can be a useful and perhaps unique probe of the interface electric field. Following photoexcitation a decrease in the SH signal was observed and attributed to the photo-generated holes that migrate to the interface. The increased hole density at the interface reduces the interface electrostatic field and thus the magnitude of the electric field induced second harmonic signal. The observed exponential decay of the SH signal in repeated experiments yielded an average time constant of 25 ps, which is thought to be the time for the transport of the photogenerated holes to the interface from a distance of about 20 nm. This distance is estimated from the n-TiO<sub>2</sub> absorption coefficient at the UV excitation wavelength. The hole transit time is not found to be significantly dependent on pH or solution composition. From this data an average surface hole drift velocity is estimated and found to differ from bulk hole velocities. The recovery of the SH signal takes 3–4 ns and is attributed to removal of the excess photogenerated holes by electrochemical charge transfer and interface electron-hole recombination. Although many questions remain, this application of SHG is one example of the power of this approach to the study of electrode/liquid interfaces.

**F. Photopolymerization at the Air/Water Interface.** Photopolymerization of monolayers composed of monomer molecules is a subject of considerable interest because of its





**Figure 12.** SHG intensity vs irradiation time for UV polymerization of octadecyl methacrylate monomer (ODMA). The data can be fitted by both first-order (—) and second-order (---) kinetics. Reprinted with permission from ref 107. Copyright 1986 American Institute of Physics.

relevance to the preparation of microelectronic surfaces in microlithography, as well as interest in the fundamental science of polymerization in the restricted environment of an interface. Second harmonic generation is well-suited to monitor the kinetics of interface polymerization directly. It has the important feature of being a nondestructive probe of the polymerization process. Monolayers of the monomer octadecyl methacrylate were spread at the air/water interface, UV irradiated, and the polymerization reaction time monitored by SHG using a nanosecond 532 nm incident probe source.<sup>107</sup> The kinetics of the polymerization is controlled by the concentration of free radicals generated by the UV light and by chain termination reactions. The relative importance of these processes determines the kinetic rate law for the observed polymerization reaction. The photopolymerization kinetics was found to extend over two or more hours, and it was found that it could be fit to different rate laws. Whether the process is a first- or second-order reaction, or possibly of order  $3/2$ , has not been resolved yet. In any case the applicability of SHG to study this important interface photochemical reaction is very nicely demonstrated by these experiments.

### III. Summary

The focus of this paper has been the application of second harmonic spectroscopy to the study of photochemical and photophysical processes at liquid interfaces. The response of an interface to a controlled perturbation, most commonly a photoexciting pulse of light, can be selectively followed in time using SHG or SFG methods. The competition among the various chemical and physical pathways for degrading the excess energy delivered by the exciting pulse is an important and forefront research area that can be investigated using the high-power, time resolution, and frequency tunability of available lasers. The key feature that makes SHG and SFG such powerful interface methods is their surface sensitivity, unlike traditional absorption, emission, and scattering spectroscopies, which generally have dominating contributions from the bulk regions of the material. Because of its intrinsic asymmetry and molecularly thin dimension, interfaces have different chemical and physical properties. The transport of charge across an interface, the dynamics and efficiency of photoinduced structure changes, the rotational motions of interfacial molecules, the diffusion of energy within the interface, the process of photo-

polymerization at an interface, and the photogeneration of holes and their migration and quenching at a semiconductor/liquid interface are among the SH studies of interface photochemistry and photophysics discussed in this article.

As more laboratories direct their resources to the application of nonlinear spectroscopy to the ground and excited state chemistry and physics of interfaces, we anticipate significant advances in our understanding of interface phenomena and the discovery of new effects.

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