Progress Report

Ultrafast Optical Studies of Surface Reaction Processes at Semiconductor Interfaces (DE-GE02-91ER14185)

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R. J. Dwayne Miller, P.I.
Department of Chemistry
University of Rochester
Rochester, NY 14627-0216

I. Introduction

Surface photochemistry is currently at the level of fundamental understanding that molecular photophysics and photochemistry was in the 1970s. There is little information on the non-radiative relaxation channels at surfaces, the relative energetics of coupled states, and there is a wide spread in observed reaction rates that makes it difficult to ascertain general features in the laws governing the surface reaction dynamics. The discrepancy in experimental details documenting homogeneous versus heterogeneous processes is largely due to the inherent difficulty in studying surfaces. The DOE funded research has focused on the development of novel non-linear optical methods for the *in situ* study of surface reaction dynamics to fill this void. In particular, the work has concentrated on interfacial charge transfer processes as this is the simplest of all surface reactions, *i.e.*, no bonds are broken and the reaction is derived from nuclear repolarization. For this reason, we have the greatest chance of coming to detailed understanding of this reaction coordinate. Interfacial charge transfer also forms the basis for a number of important solar energy conversion strategies¹⁻⁷ such that a detailed understanding of this process is of primary importance in enhancing our efforts in this area.

This work exploited semiconductor liquid junctions as an optical switch to turn on the surface photochemistry.¹ These systems are extremely efficient at charge separation (photocurrent quantum yield ~1) and can exhibit solar energy conversion efficiencies approaching those of the best solid state devices. In comparison to solid state devices, semiconductor liquid junctions are much simpler to construct. However, the most tantalizing feature of these systems is that theoretically they are capable of attaining nearly 70% solar energy conversion efficiencies.⁸ By comparison, all solid state semiconductor systems are limited to 33%.⁸ The higher potential efficiency of semiconductor liquid junctions is related to the molecular states (rather than a band) that act as the charge acceptors. Due to the discrete nature of these states, it is possible to avoid energy conversion losses in the junction through lattice heating. However, to achieve this goal, interfacial charge transfer must be made sufficiently fast to compete with carrier thermalization. This prospect is related to the "hot carrier" model for fully optimized solar cell performance based on a threshold absorber (e.g., semiconductors).^{8,9} The key question is whether or not interfacial

electron transfer can fundamentally approach time scales comparable to electron thermalization in the solid state. This aspect of the model requires that the charge transfer process occur in the strong coupling or adiabatic limit for electron transfer. This is a highly contested issue.¹⁰ Almost all models for interfacial charge transfer at metal or semiconductor electrodes treat the problem in the weak coupling or non-adiabatic limit.¹¹⁻¹⁴ This treatment is by far the simplest and seems to explain most of the phenomena at electrode surfaces. However, there are theoretical studies which point out that adiabatic coupling should be more prevalent at electrode surfaces than in a solution based on the high donor level density.¹³ There are studies which support this claim¹³ but most evidence favors a weak coupling limit for theoretical modeling. The basic experimental problem is that most of the studies of interfacial charge transfer have concentrated on steady state current measurements in which it is extremely difficult to avoid transport limitations in current measurements¹⁵⁻¹⁷ (*i.e.*, one always measures the slowest rate in steady state measurements). Some competing process invariably limits the current at values lower than the adiabatic (maximum) rate. The only way to access the fastest rate is to do impulsive non-equilibrium experiments and follow the dynamics in the time domain (*e.g.*, T jump, pressure jump, etc.).¹⁸ This work has done precisely that by using optical methods to create a non-equilibrium charge distribution at the surface on a time scale faster than the relevant relaxation rates.

This work and the optical methods developed during the course of these studies are dedicated to determining the fundamental upper limit to interfacial charge transfer at semiconductor surfaces. In these studies, semiconductor liquid junctions provide a convenient system in which the interfacial charge transfer can be optically initiated. The all-optical approach necessitates that the dynamics of the charge transfer event itself be put in the proper context of the operating photophysical processes at the surface. These are shown in Figure 1 for an n-type semiconductor. As can be seen from this figure, there are at least four dynamical processes that are coupled in determining the overall rate of electron flux across the interface. These are: (1) transport (field accelerated and zero field diffusive transport) to the surface reaction plane; (2) carrier thermalization at the surface; (3) surface state trapping; and (4) interfacial charge transfer. In the limit that interfacial charge transfer approaches strong coupling, the time scale for transport of even field accelerated carriers within the space charge region becomes comparable to the charge transfer dynamics. The transport component needs to be convolved to probes of the carrier population at the surface. The other two dynamical processes, carrier thermalization and surface state trapping, determine the states which ultimately serve as the donor levels to the solution acceptor distribution. In terms of the hot carrier model, these latter two processes compete with direct unthermalized charge transfer. There is a fifth dynamical process which also needs consideration: the solvent modes (ν^{-1}_{eff}) that are coupled to the reaction coordinate. Ultimately, the dynamics of solvent relaxation determine the upper limit to the charge transfer process.¹⁹⁻²⁴ In the strong coupling

limit, the electronic coordinate (between a two state basis) equilibrates faster than the nuclear coordinate. The rate of passage into the product channel at the adiabatic crossing point is determined by the solvent response to the reaction field. These dynamics need to be characterized both for defining the adiabatic limit to charge transfer and to provide a full understanding of the barrier crossing dynamics.

Figure 1. The different photophysical processes are shown for n-type semiconductor interfaces. The surface space charge field separates electron-hole photocarriers and drives the minority hole carrier to within electron tunneling distance to the molecular states at the surface (1). At the surface, the carrier undergoes thermalization of the excess energy gained from field acceleration (2). Once thermalized additional relaxation processes lead to surface state trapping (3). Interfacial charge transfer can occur from any of the hole states during this energy relaxation process. The fundamental upper limit to the interfacial charge transfer dynamics are determined by the solvent relaxation time scales which are treated as an effective bath mode (v_{eff}^{-1}) in this figure.

Different optical techniques have been developed to follow all the above dynamical processes in which a real time view of the charge transfer dynamics at semiconductor surfaces is emerging. These results will be discussed below; the numbers in square brackets refer to papers listed in the Publications Summary.

II. Space Charge Electro-Optic Sampling Studies

The transport of photogenerated carriers to the surface needs to be independently determined. This information is needed to give the arrival times of the carriers at the surface reaction plane and to determine the surface field amplitudes under experimental conditions used for the surface grating studies. In principle, the transport of the carriers can be determined from changes in the surface field amplitude or photovoltage. This point can be understood by considering Poisson's equation for the field,²⁵

$$\Delta E(x,t) = q/\epsilon\epsilon_0 \int_{-\infty}^{\infty} n(x,t) - p(x,t)dx \quad (1)$$

where $n(x,t)$, $(p(x,t))$ is the spatial and temporal distribution of photogenerated electrons (holes) and ΔE is the change in the surface field amplitude. At $t=0$, the spatial distribution of the electrons and holes falls off exponentially from the surface according to the absorptivity (α^{-1} cm) at the excitation wavelength. The surface field acts to drive the minority carrier to the surface and the majority carrier to the bulk. For a surface field value of 2.5×10^5 V/cm, the minority carrier distribution becomes localized to within $10 \text{ \AA}$ ($1/e$ point) of the surface. The overall transport to the surface involves space charge field accelerated motion of the minority carriers photogenerated within the space charge region and diffusive transport of carriers outside this region into the space charge region. This transport component although fast may still affect dynamic issues for electron transfer processes occurring in the picosecond regime. Resolving the carrier transport by the induced field changes requires extremely high time resolution and sensitivity. In principle, this transient field could be detected electronically. However, one would need sub-picosecond ($> \text{THz}$ electrical bandwidth) resolution to acquire it from the voltage rise time (assuming no RC limitations in the semiconductor photoelectrochemical cell). This is clearly not possible and one needs an all optical method to measure these signals. Our approach to this problem has been to use electro-optic sampling to measure the field changes.^{26,27} This technology was originally developed for sampling THz waveforms generated by high speed ($>100 \text{ GHz}$) solid state electronic switches and amplifiers.²⁸ The best time resolution has been attained using an electro-optic "finger" probe in which an electro-optic crystal is used to optically sample the field across a junction - just above the semiconductor. Due to *velocity mismatch*, the best time resolution is nominally 300 femtoseconds. This time resolution is still inadequate. Our approach was to specifically take advantage of the intrinsic electro-optic properties of III-V and II-VI semiconductors. By photoinjecting carriers and monitoring the space charge field amplitude *directly* at the surface, we were able to attain less than 50 femtosecond time resolution to the field changes [3,10]*. The experimental set-up is shown in Figure 2 with representative data shown in Figure 3 for GaAs. The field changes are detected by a change in polarization of the probe caused by the modification of the crystal birefringence through the electro-optic effect. The use of an optically nulled detector (Figure 2) makes this technique extremely sensitive. The high time resolution is due to the fact that the field changes are optically sensed directly where they occur. In this manner, we have completely avoided velocity mismatch problems between the electrical signal and the optical probe. This development has led to the highest possible time resolution through the electro-optic effect. The time resolution is limited only

* [3,10] refers to papers listed in the Publications Summary.

Figure 2. Reflective electro-optic sampling experimental set up ($\lambda = 590$ nm, $\tau_p = 120$ fs), P - prism, B.S. = beam splitter, Scanner = PZT rapid scanner, $\lambda/2$ = half wave plate, D.L. = delay line, P1,P2 = Glan-Thompson polarizers, B.C. = Babinet compensator, PDA, PDB = photodiodes, DA = differential amplifier. The circularly polarized probe (after the Babinet compensator) samples the field changes induced by the photocarriers injected by the excitation pulse.

Figure 3. Representative electro-optic sampling results [3,10] for GaAs(100). the pulses used in these studies were 120 fs centered at 590 nm. There is a 200 fs rise time which is attributed to hole carrier motion to the surface.

by the highest frequency longitudinal optical phonon of the crystal which for GaAs amounts to an effective electrical bandwidth of 8.55 THz or an intrinsic time resolution of approximately 30-40 femtoseconds.^{26,27} This time resolution is sufficient to follow even ballistic (scatter-free) motion of field accelerated carriers.

The most important insights gained from these studies to date are:

- (1) Field accelerated carriers arrive at the surface with an approximately exponential time dependence of less than 200 femtoseconds. This component

is due to carriers photogenerated within the space charge region and directly determines the space charge field transit time;

- (2) Multi-exponential diffusive transport for carriers photogenerated outside the space charge region occurs on nanosecond time scales for injection levels between 10^{10} - 10^{13} photocarriers/cm². Below 10^{10} /cm², there is no clear delineation between carriers generated within the space charge region and those within a diffusion length. The transport appears multi-exponential over all time scales, although there is still a fast 200 femtosecond component which dominates.

The first point is important as this work demonstrated that a significant fraction of carriers arrive at the surface unthermalized, *i.e.*, this time scale is shorter than currently accepted carrier thermalization rates. (This point will be reexamined in the proposed studies and needs to be re-evaluated based on some preliminary studies of carrier relaxation from our lab.) *This experiment also established the "turn on" time of the surface photochemistry.*

The second observation indicates there is a clear delineation in time scale between the transport of carriers within the space charge region and those generated in the field free region. For typical excitation wavelengths and semiconductor doping levels, approximately half the carriers are generated within the space charge width. These are accelerated to the surface first and form a transient field line which acts as a barrier to further diffusion into the surface region. This aspect of the problem is unique to pulsed studies and needs to be kept in mind in all transient studies of surface reaction processes involving charge carriers. This feature to the transient surface field lines is shown in Figure 4 which is based on earlier Monte Carlo simulations of the carrier

Figure 4. Monte Carlo calculations of the surface field versus distance from the surface (ref. 29) following photocarrier injection (10^{12} photons/cm²) with an excitation pulse centered at 590 nm. Note that within 50 fs, a significant field develops at the edge of the space charge region due to the accumulation of electrons at that point in space (Dember effect). This field line represents a barrier (~ 0.1 eV) to hole diffusion to the surface.

transport.²⁹ Only when the carrier injection is extremely low is the induced coulombic barrier (cusp in Figure 4 at the edge of the space-charge region) less than kT such that it only minimally affects the hole carrier diffusion to the surface.

The other important feature of this work is that the space charge electro-optic sampling method provides a contactless method which is ideal for *in situ* surface studies. Thus we are able to quantify the surface field amplitudes under the same conditions used for the surface grating studies which is an important component to avoiding transport limitations on the time resolution. There have been recent observations of field dependent charge transfer rates (via photoluminescence studies). Ideally, one would like to independently determine the surface field to extract quantitative information from these studies.³⁰ The use of space charge electro-optic sampling to monitor the surface field simultaneously with detection of the photoluminescence decays is an ongoing project and an important application of this spectroscopy.

III. Surface Restricted Grating Studies

This technique takes advantage of the surface space charge field to generate a surface confined population of minority carriers [1,4]. This is a three pulse experiment in which two excitation pulses are crossed at an angle to write a diffraction grating in the form of electron-hole pairs. A third, variably delayed, below band gap probe is used to monitor the carrier population.

Surface grating spectroscopy is an extension of conventional transient grating techniques. The main distinction is the use of the surface fields to attain a surface image of minority carriers. The observable in this experiment is the electron-hole populations through contributions to the phase grating component (Δn). The diffraction efficiency, η , (signal) is given by:

$$\eta = \frac{I_{+1}}{I_0} = \left(\pi \frac{\Delta n}{\lambda} d \right)^2 \quad (2)$$

where:

$$\Delta n = -\frac{Ne^2}{2n\epsilon_0\omega^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] \quad (3)$$

for a Drude model for the carrier intraband transitions. In these expressions d is the grating thickness, $\lambda(\omega)$ is the probe wavelength (radial frequency), m_e^* and m_h^* are the effective electron and hole masses, respectively, N is the number density, and n is the index of refraction. This relationship gives the dispersive contributions of the free carriers due to intraband transitions. There are other contributions as well. The main point is that the grating is sensitive to both electron and hole populations which enables a direct determination of the minority carrier depletion at the surface.

The higher intrinsic sensitivity of grating spectroscopy over conventional two pulse pump/probe methods has enabled this method to achieve sensitivity limits of less than 3×10^{11}

photocarriers/cm². This detection limit is two orders of magnitude lower than pump probe experiments under the same experimental conditions. This sensitivity limit is crucial as it prevents significant screening of the space charge field by the injected carriers. For example, a semiconductor doped at 10¹⁸/cm³ accumulates a surface charge of ~5x10¹² charges/cm². Photoinjection levels of less than 10¹² lead to negligible screening of the space charge field and, as seen from the above studies of the carrier transport, leads to the formation of a surface grating image within a 100 femtosecond time frame. The space charge field redistributes the initial exponentially decaying carrier profile to a surface grating image superimposed on a bulk grating. The surface to bulk signal contrast can be as high as 1:1 (excitation wavelength and N_d dependent). These studies represent the first in which the space charge field is explicitly used to overcome transport limitations on the electron dynamics.

(a) n-GaAs(100) Studies. Being an all optical technique, surface grating spectroscopy permits *in situ* studies of the carrier reaction dynamics. One of the most important semiconductor liquid junctions developed to date is the n-GaAs(100)/(KOH-Se⁻²/Se⁻²)_{aq} contact. This interface was shown to be stabilized against oxidative dissolution and achieved solar energy conversion efficiencies approaching 15%.^{1,35} This was the first surface which showed long-term stable performance. This level of performance was only achieved using high concentrations (1 M) of Se⁻² for the hole carrier acceptor which was thought to kinetically stabilize the surface. The high stability and acceptor concentration is important in these studies as it permitted long signal acquisition times without deleterious degradation of the surface and made the hole carrier reaction rates at the surface pseudo first order. Our first studies of this interface [1-3] showed that the grating signal depended as expected on the carrier populations (via fringe spacing dependence) and the grating decays showed an accelerated decay in the presence of Se⁻². The faster decays in the presence of Se⁻² were shown to arise from interfacial hole transfer by both a Se⁻² concentration dependence (a known hole quencher) and a field bias dependence. The hole transfer was estimated to be less than 30 picoseconds. These studies were prevented from attaining higher time resolution by the relatively long infrared pulses used to probe the grating dynamics. Nevertheless, this information was important and made the key conceptual point that interfacial charge transfer could approach picosecond time scales. It was also found that surface trapping processes could be clearly distinguished from interfacial charge transfer. This signal component appears as a *rise* (increased dispersive component for the near resonant surface state transition at the probe wavelength) rather than a decay in the grating signal.

Subsequent studies explored various methods of generating subpicosecond infrared (1.8 μm) pulses. Considerable effort was spent attaining these pulses via difference mixing which should have increased the signal by a factor of four. However, the increase in signal was offset by the poorer detector response and pulse noise. A four pulse upconversion method was employed

which dramatically improved the signal to noise.³⁶ With this approach, the diffracted IR signal (long pulse) is upconverted by summing with a visible pulse in a non-linear crystal. The signal is then detected in the visible where detectors are much more sensitive. Most important, the upconversion process itself acts to gate the detector. In this manner, the four-pulse grating sequence isolates the signal both spatially and temporally which greatly reduces the background noise. Representative results are shown in Figures 5 and 6 [4,8]. The most important feature to note is that there is a 20% decay component of 1-2 picoseconds, the amplitude of which depends on Se^{2-} concentration. In the absence of Se^{2-} , under identical conditions, we observe a delayed rise in the signal due to surface state trapping as previously surmised from signal amplitudes. Further, the fast decay component in the presence of Se^{2-} shows the expected bias dependence, *i.e.*, the initial decay is reduced in amplitude and becomes longer as the junction is biased towards flat band (decreased surface hole concentration). These new findings demonstrate that charge transfer at surfaces can approach the adiabatic limit and compete with surface state trapping. These are important conceptual points which are in line with the hot carrier hypothesis, *i.e.*, interfacial charge transfer dynamics can be competitive with carrier thermalization.*

Figure 5. Surface grating studies for n-GaAs(100)/(KOH- Se^{2-}) junction. ($\lambda_{\text{ex}} = 590 \text{ nm}$, $\lambda_p = 1.053 \mu\text{m}$) The excitation conditions were $5 \times 10^{17} \text{ cm}^{-3}$ (KOH- Se^{2-})_{aq} for a crystal doped $2 \times 10^{18} \text{ cm}^{-3}$. There is a rapid 1-2 picosecond component ($A = 0.2$) which is observed only in the presence of Se^{2-} . This component is superimposed on the background grating due to the electron population and residual hole carriers.

*See further discussion of this point in the Proposed Studies.

Figure 6. Surface grating studies of n-GaAs(100) in the absence of Se^{2-} . The experimental conditions are the same as for Figure 5. Rather than a decay, a rise in the grating signal delayed with respect to $t=0$ is observed which is attributed to surface state trapping.

(b) Si Liquid Junctions. The above studies are for a chemisorbed redox couple which should show the fastest interfacial charge transfer dynamics. An important question is whether weakly bound physisorbed outer sphere redox couples can likewise show appreciable electronic coupling. Following the lead of Lewis and coworkers^{37,38} we have investigated the interfacial charge transfer dynamics at silicon interfaces [11]. The silicon interfacial studies are important as it is possible to prepare surfaces with extremely low surface recombination velocities. This opens up the possibility of studying slower interfacial electron transfer processes. By contrast, in the case of GaAs, the extremely fast surface state trapping severely restricts the dynamic range that can be studied at this interface. The Si interface permits the study of outer sphere redox couples such as ferrocene/ferrocenium (Fc/Fc^+) and derivatives.³⁹ Microwave conductivity measurements have been performed on n-type Si under high injection conditions which measure the surface recombination velocities.³⁷ These studies found no appreciable difference with and without dimethylferrocene (DFc) hole acceptors ($S_{\text{et}} < 40 \text{ cm/sec}$). This result is expected based on the nuclear activation barrier for hole transfer to DFc at this surface. The energetics of the interface are shown in Figure 7 for a ferrocene redox couple, assuming a reorganization energy of 0.75 eV. The most important point to note from this figure is that the Fc^+ electron acceptor distribution is nearly perfectly poised for electron transfer. From the acceptor distribution overlap, electron transfer should be significantly faster than hole transfer at this interface. Surface recombination velocity measurements are rate limited by the slowest step and are not sensitive to the difference in

Figure 7. Energetics for Si/MeOH interfaces with ferrocene/ferrocenium (Fc/Fc^+) redox couples. This figure assumes a reorganization energy of 0.75 eV. Within the range of acceptable reorganization energies from 0.5 - 1 eV, the electron-acceptor distribution overlap for electron transfer is significantly larger than that for hole transfer (from ref. 39).

the capture cross section for electron and hole transfer. This point and the rationalization of the slow hole transfer for DFc in terms of the nuclear activation barrier was made earlier by Lewis.¹⁰ This problem is one example where surface grating studies have an important role to play in understanding surface reaction dynamics. Under low injection, surface grating studies can differentiate between electron and hole transfer dynamics by exploiting the effects of the space charge field on the surface concentration of electron and hole carriers.

Surface grating studies of n-type Si(100) found no significant effect of dimethylferrocene on the carrier depletion dynamics, in agreement with earlier studies. In contrast, studies of p-type Si(100) under the same injection conditions found significantly faster grating decays in the presence of ferrocenium relative to the control. (The decays in the absence of Fc^+ are determined solely by transport parallel to the surface which washes out the grating image. This feature of the decay was verified by a fringe spacing dependence.) These results are shown in Figure 8. Because of the large fraction of carriers generated outside the space charge field in silicon ($\alpha^{-1} \sim 10^{-4}$ cm at λ_{ex}), more detailed modeling is needed to extract the electron capture cross sections. A direct determination of the carrier transport using electro-optic sample is not possible for silicon as this crystal is not electro-optic. On a preliminary basis, this work has found electron capture velocities approaching 10^3 cm/sec ($[\text{Fc}^+]$ in the 0.1 M range) which implies near adiabatic cross sections, assuming the concentration of Fc^+ is unperturbed by the surface. The most important aspect of this work is that it illustrates the huge effect the energetics (2-3 orders of magnitude) can

Figure 8. Surface grating studies for p-Si(100)/Fc⁺(0.1 M) in MeOH ($\lambda_{\text{ex}} = 532 \text{ nm}$, $\lambda_p = 1.064 \mu\text{m}$). The decays are significantly faster than the control without Fc⁺ under low photocarrier injection. At higher injection and surface field screening, the grating decays are identical and are determined by carrier transport parallel to the surface.

have on the transfer dynamics. This part of the problem is well understood but it is generally difficult to separate the slower kinetics that are limited by nuclear activation barriers from faster processes. Unless the reorganization energy is exactly half the semiconductor band gap and the maxima in the acceptor distributions coincide with the band edges, it will be impossible to have both the hole and electron transfer processes occur under barrierless conditions. This difficulty in part accounts for the wide range of reported charge transfer rate constants. The use of space charge field accumulation of the minority carrier population at the surface, as illustrated in this work, is one way to separate these processes. Studies along these lines should provide a systematic method to separate the energetics of the problem and determine intrinsic electronic coupling parameters.

(c) InP Studies. A collaborative effort was initiated with Carl Koval's group at the University of Colorado at Boulder. His group has completed an exhaustive study of steady state electrochemical studies of supra-band edge acceptors with p-InP (100) interfaces.⁴⁰⁻⁴¹ Studies along these lines have been used to argue that the interfacial electron transfer involves hot electrons. However, to be sure the quantum yields of supraband edge acceptors can be attributed to hot carrier processes, it is important to directly resolve the interfacial electron transfer dynamics. Given the sensitivity of these surfaces to preparation, a collaborative project exploiting both groups' expertise is essential.

This project involved a short-term visit by the student who conducted the electrochemical studies. His role was to construct and do the preliminary diagnostics on the liquid junction cell to ensure that the surface preparations used for the electrochemical measurements and the time domain studies were identical and reproducible. He worked closely with one of the P.I.'s students and was involved in all aspects of the transient studies. We were successful in obtaining reasonable grating signals, and electro-optic studies are forthcoming. The grating decays were found to be extremely fast, *i.e.*, completely decayed with no long-lived components in less than 200 picoseconds. On a preliminary basis, we did observe faster decays in the presence of the supraband edge acceptors. However, this work needs to be conducted with better quality optical cells and a host of background controls to unambiguously correlate the kinetics to the supraband edge acceptor. This collaborative project is ongoing and is part of the proposed future studies.

IV. Optical Kerr Effect Studies of the Solvent Response Function

Under barrierless conditions, the charge transfer dynamics are determined by the nuclear relaxation along the reaction coordinate. This dynamic process represents the upper limit to the electron transfer rate constant.¹⁹⁻²⁴ This motion is normally assumed to be the highly damped diffusive solvent modes which can be estimated from the longitudinal relaxation time (τ_L) of the solvent ($\tau_L \approx \epsilon_0/\epsilon_s \tau_D$; where τ_D is the Debye relaxation time determined from dielectric measurements). Recently, it has been pointed out by Maroncelli and Fleming that, at the reaction saddle point for charge transfer, the non-diffusive librations of the solvent (inertial response) play the dominant role in the solvent relaxation. There is now a great deal of support for this insightful hypothesis. Water represents the fastest solvent for charge transfer and was used for construction of the GaAs liquid junctions. The question is how fast can water respond to the charge transfer reaction field.

This question can be answered using Optical Kerr Effect spectroscopy.⁴² Without getting into the details, the basic idea is that a short laser pulse creates an intense transient field in the medium. This field creates a torque on the molecules through the induced polarization (Raman effect) that leads to a partial alignment of the molecules and a change in the material birefringence. The response time of the solvent to the field can be monitored by following the sample birefringence using polarization sensitive detection of the probe. The experiment casts out all the frequency-components of the solvent that lie within the laser bandwidth. The amplitudes of the coupling coefficients of the different frequency components to the charge transfer coordinate need to be determined separately from dynamic Stokes shift measurements or MD simulations.¹⁹⁻²⁴ Results for water using 30 femtosecond pulses are shown in Figures 9 and 10. In Figure 9, both the time domain response and frequency distribution of the response are shown [5]. This signal has had the electronic contribution removed by heterodyne detection of the probe (out-of-phase component) and a Fourier filtering procedure. Figure 10 shows the in-phase detected heterodyne

Figure 9. Optical Kerr Effect studies of water. Out-of-phase heterodyne detected time domain results in which the electronic contribution has been removed. The inset shows the Fourier transform which gives the distribution of components in the water response. The components above 300 cm^{-1} are the sub 100 fs librational motions. The 170 cm^{-1} peak is due to the "breathing" mode of the dominant pentamer structure in the hydrogen bonded network of water molecules. Overdamped shear motions (60 cm^{-1}) and diffusive components represent the features below 100 cm^{-1} .

Figure 10. In-phase heterodyne detected OKE water response (raw data). The inset shows the expanded view of the long-time dynamics. The diffusive relaxation is clearly biexponential.

signal. There are two important features in the data. First, the nuclear response shows the classic inertial lag, but the lag is only 15 femtoseconds. The signal peaks at 15 femtoseconds after $t=0$. This finding represents the highest time resolution attained to date on the water response.⁴³ This response is due to the high frequency librational motions in the intermolecular modes of liquid water. The rapid decay in the signal is due to nuclear dephasing of the impulsively excited modes with an underdamped mode due to hindered longitudinal (non-diffusive) translational modes of the water spectrum showing up as a secondary oscillation (or the 170 cm^{-1} peak in the frequency distribution). These non-diffusive motions constitutes the inertial response of water. These results are strikingly similar to the MD simulations of water which calculate that this fast librational motion should be the dominant relaxation phase. The above dynamical information can also be obtained through frequency domain depolarized light scattering studies of water.⁴⁴ The second important feature is the multi-exponential tail in the response which is due to diffusive (net rms Brownian displacements) motions of water. This response could be fit to two exponential components of 500 femtoseconds and 1.7 picoseconds (inset to Figure 10). The 500 femtosecond component is in good agreement with dielectric predictions for longitudinal diffusive relaxation. The clearly multi-exponential behavior is expected for associated liquids²⁴ but could not have been resolved for water with any other current method.

The take-home message from this study is that water has relaxation components in the 10 femtosecond to picosecond range. Based on the amplitude of the relaxation energy associated with the librational motions (re: MD calculations),²¹ the 10 femtosecond time scale associated with these solvent modes is more than sufficient to drive interfacial charge transfer reactions in competition with carrier relaxation in the solid state. This fast charge transfer will only pertain to photoinduced charge transfer in which the carrier is isoenergetic with a molecular acceptor (under barrierless conditions), and the electronic mixing of states is in the adiabatic limit. With respect to the GaAs studies, it appears that either the coupling is not truly adiabatic for an aqueous interface or the solvent response is significantly altered at the interface. This latter possibility will be explored in the proposed studies. The other possibility is that a significant fraction of the hole transfer dynamics still have not been resolved. This possibility will also be pursued. However, it should be kept in mind that the overall reaction is essentially a bimolecular process and the electronic density of states mismatch across the interface is expected to reduce the electron transmission probability, *i.e.*, the hole carrier has more filled valence band states (phase space) in the semiconductor than suitable Se^{-2} states in the liquid half space of the reaction coordinate. This part of the problem needs to be modeled explicitly. In view of this consideration, picosecond charge transfer times are approaching adiabatic coupling regimes if not representative of this condition. The surface grating studies illustrate how efficient this process can be; whereas the

water relaxation studies suggest that the interfacial charge transfer can in principle be an order of magnitude faster yet.

V. Summary

A multifaceted approach has been taken to arrive at a real time view of interfacial charge transfer processes at single crystal surfaces. The experimental studies have been involved in the development of two new surface spectroscopies (surface electro-optic sampling and grating spectroscopies) with an unprecedented combination of time resolution and sensitivity to achieve this goal. This work, along with the dynamic studies of the water response function, is beginning to give a complete picture for the operating dynamics at GaAs interfaces. The overall story is summarized in Figure 11. Assuming bulk studies of carrier relaxation hold at surfaces, this figure illustrates that a significant fraction of the carriers are undergoing interfacial transitions prior to thermalization. A direct observation of the carrier thermalization at the surface is needed to solidify this statement. The single most important fundamental lesson learned from this work is that interfacial charge transfer processes can occur in the picosecond range which is consistent with strong electronic coupling between molecular states within the Helmholtz layer and the electrode band states. Given the highly damped nature of the molecular wavefunctions ($\beta \sim 0.9 \text{ \AA}^{-1}$), this condition was not obvious for a solvated state at an electrode interface.^{16,17} This work needs to be extended to physisorbed outer sphere reagents such as the ongoing studies of Si and InP to determine whether this phenomena holds in general (in the absence of a nuclear barrier, *i.e.*, for optimally poised redox couples).

Figure 11. Summary. The transport of the minority carrier distribution to the surface from within the space charge region occurs within 200 fs as determined from electro-optic sampling. Surface grating studies have found 1-2 picosecond hole depletion components at the surface attributable to interfacial hole transfer. The solvent barrier crossing dynamics have sub 100 fs to ps components as determined from OKE studies.

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Personnel

Carl Bonner, graduate student, 1989
M.S. Howard University, B.S. Howard University 1982
AT&T Research Associate, 1985-1989
Expected Completion Date: June 1994

Dong Wang, graduate student, 1989
B.S. Fudan University
Expected completion date: 1994
Current Position: Senior Scientist, TCI Corporation

Dr. Joseph Buontempo, postdoctoral student
Ph.D. 1992 University of Rochester
Thesis Advisor: Stuart Rice
Current Position: Senior Scientist, NALCO Chemical Company

Steven Palese, graduate student 1988
B.S., University of Rochester 1987
Partial Support: industrial donations
Expected Completion Date: June 1994

Sabrina Diol, graduate student 1994
B.S., Stevens Institute of Technology 1992

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