ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 189–196

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

# Studies into the character of electronic coupling in electron transfer reactions

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Received 15 July 1996; revised 4 September 1996; accepted 18 October 1996

## Abstract

Two recent investigations into electron transfer reactions are described. The first study probes solvent effects on intramolecular electron transfer of donor–bridge–acceptor systems. The study compares a molecule which possesses a molecular cleft between the donor and acceptor moiety to one without such a cleft. The influence on the electronic coupling of a solvent molecule between the donor and acceptor is discussed. The second study concerns heterogeneous electron transfer through self-assembled monolayer films on InP electrodes. The data show that the film inhibits oxidation of the semiconductor. Electron tunneling through the film is explored, and the chemical functionalization of the film is shown to modify the charge recombination processes in the electrode. © 1997 Elsevier Science S.A.

*Keywords:* Electron transfer; Photoelectrochemistry; Intramolecular electron transfer; Self-assembled monolayer films

## 1. Introduction

Electron transfer processes are ubiquitous in nature. Many of the fundamental steps in chemical transformations involve electron transfer processes, or at least significant charge rearrangements. The understanding of intramolecular electron transfer processes has evolved to a high degree and studies of such systems are largely responsible for the verification of the Marcus model and its antecedents. In addition, it is possible to design intramolecular electron transfer systems which have desired properties and kinetics. By way of contrast, heterogeneous electron transfer processes are understood primarily at a phenomenological level. Nevertheless, progress is being made and Marcus type models are being successfully applied to these systems as well.

The simple picture of the electron transfer process assumes different timescales for the nuclear and electron motions [1]. In this scheme, the nuclear degrees of freedom of the reactant(s) fluctuate in the medium. When the nuclei reach a configuration where the electronic energies of the reactant and product states are the same, the electron can tunnel from the donor to the acceptor. This nuclear configuration is the "transition state" and (in a nonadiabatic picture) corresponds to the crossing of the potential energy curves of the reactant and product. The probability of electron tunneling is determined by the strength of the electronic interaction between the donor and acceptor moieties, i.e. the electronic coupling $|V|$. When the electronic coupling is weak, the reactant configuration fluctuates through the transition state region many times before tunneling occurs and the product is formed. By contrast, when the electronic coupling is strong, tunneling occurs for nearly every crossing of the transition state. In this latter limit, the reaction rate is controlled by the nuclear motion. This view of the primary electron transfer event is quite successful.

The studies discussed here are well described by the weak coupling regime. In this limit, an expression is found for the electron transfer rate constant $k_{ET}$:

$$k_{ET}=\frac{2\pi}{\hbar}|V|^2\,\mathrm{FCWDS} \qquad (1)$$

where FCWDS is the Franck–Condon weighted density of states [2]. For intramolecular electron transfer, it is common to use a semiclassical approximation, where solvent degrees of freedom are treated classically and the vibrational degrees of freedom are quantized but treated as a single effective mode. In this case, it is found that

$$\mathrm{FCWDS}=\sqrt{\frac{1}{4\pi\lambda_s kT}}\sum_{j=0}^{\infty}\mathrm{e}^{-S}\frac{S^j}{j!}\times\exp\left[-\frac{(\lambda_s+\Delta G^\circ+j\hbar\omega)^2}{4\lambda_s kT}\right] \qquad (2)$$

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*PII* S1010-6030(96)04548-0

where $\lambda_s$ is the solvent reorganization energy, $\Delta G^\circ$ is the Gibbs free energy change of the reaction, $S$ is $\lambda_v/\hbar\omega$, $\omega$ is the frequency of the effective intramolecular mode and $\lambda_v$ is the internal reorganization energy. When the reactant and product states have the same free energy, the total reorganization energy $\lambda_v+\lambda_s$ is the free energy change required for the system to proceed from reactant to product at the equilibrium configuration of the reactant [1–3]. This expression for the rate constant has five parameters: $\Delta G^\circ$, $V$, $\lambda_s$, $\lambda_v$ and $\omega$. In order to test the model, it is important either to characterize these parameters fully or to constrain a subset of them as constant while the other parameters are systematically varied.

The studies described here focus on systems in the nonadiabatic regime and aim to investigate the properties of the electronic coupling, i.e. the $|V|$ parameter. We begin with a review of recent progress in this area, and then we describe two recent investigations into the nature of $|V|$. First, an investigation of the electronic coupling in donor–bridge–acceptor (DBA) molecules is presented. This study compares the electron transfer for two molecules with a similar number of bonds between the donor and acceptor moieties, but with one of the molecules extended and the other having a cleft which is large enough to accommodate small solvent molecules. The influence of solvent in the cleft on the magnitude of $|V|$ is probed by this study. Second, an investigation of heterogeneous electron transfer at the semiconductor/electrolyte interface is explored. This study uses self-assembled monolayer (SAM) films to control the distance between the electrode and the solution redox couple. The film acts as a tunneling barrier whose thickness can be controlled chemically. Comparison of similar systems, in which only the barrier thickness changes, can be used to probe $|V|$.

## 2. Nature of the electronic coupling

Research efforts during the past two decades have mainly focussed on developing a better understanding of the electronic coupling $|V|$ which is a parameter in the nonadiabatic rate expression. Much of the progress in this area has resulted from the synergy of experiment and theory. Below, we briefly review part of this progress, both experimental and theoretical, and identify some major issues which remain outstanding.

The primary focus of the research in this area has been to identify how structural parameters of the system influence the value of the electronic coupling. These studies have proceeded through the use of model systems, such as DBA compounds [4–8], chemically modified proteins [9–11] and chemically modified electrodes [12–16]. For example, numerous studies have characterized the distance dependence of the electronic coupling in DBA compounds and found it to be reasonably described as an exponential dependence (i.e. $|V| \propto \exp(-\beta n/2)$, where $\beta$ is a parameter and $n$ is the number of bonds between the donor and acceptor units) on the shortest "through bond" distance between the donor and acceptor. In contrast, the distance dependence does not always correlate well with the physical distance between the donor and acceptor units [9–11]. Theoretical studies are in agreement with this finding, although they indicate that the exponential dependence is not rigorous. Generally speaking, the distance dependence of the electronic coupling is found to be "softer" than that expected for tunneling through a vacuum. It is typically found to have a decay parameter $\beta$ of 1 per bond for a carbon–carbon bond (or 1.2 Å$^{-1}$), although a range of values (from about 0.4 to 1.3) are predicted [17]. A simple model used to estimate tunneling through a vacuum leads to a sharper distance dependence, $\approx 3.4$ Å$^{-1}$ [11], where the distance is measured through space.

This behavior may be explained using a superexchange, or "through bond", mechanism for the coupling [17–23]. This description, in chemistry, has its origin in the single electron, perturbative treatments of McConnell [18] and Halpern and Orgel [19]. Although modern approaches are considerably more sophisticated and realistic, they maintain much of the character of this early model. The models view the coupling between the donor and acceptor orbitals as being mediated by the orbitals of the intervening atoms which lie between the donor and acceptor. Usually, the models focus on the filled and empty orbitals of the bridge (more strictly, on the orbitals of its cation and anion states). This mechanism results in a softer distance dependence for the electronic coupling between the donor and acceptor when covalent linkages are present than for the case when there is a vacuum between the donor and acceptor. More recently [9e,11,24–28], effort has focussed on determining the influence of couplings mediated across noncovalent structures, e.g. hydrogen bonds, salt bridges and solvent molecules. The theoretical approaches range from simple Hückel models to ab initio based models which incorporate electron correlation effects. Despite important differences between these approaches, they all indicate that "through bond" coupling dominates over "through space" coupling.

Studies in biological systems have focussed largely on the influence of the structural motif of the biological system on the electronic coupling. Empirical models which include the structure of the biomolecule in a realistic manner, known as pathway models, are quite successful when compared with experiments [9–11]. Recent studies in biological systems have focussed on the relative importance of different types of structures, e.g. covalent versus hydrogen bonds, and hydrogen bonded motifs, e.g. $\alpha$-helix versus $\beta$-sheet, for mediating the coupling. Such studies should contribute new general design criteria for electron transfer systems.

Studies on model organic systems have investigated how the structure and symmetry of the molecular orbitals can influence the electronic coupling. Some work [6,29] has found the orbital and state symmetry of the donor and acceptor to effect the coupling 10-fold or more [6]. Much work has focussed on the influence of the bridge configuration on the electronic coupling, e.g. the "all-trans" effect [12,21,30]. These studies reveal the sensitivity of the coupling to the overlap of the bridge orbitals with one another. More recent studies [17] of bridge effects have focussed on the interference of different coupling pathways, and indicate that the interference effects can lead to a softer (harder) distance dependence when the interference is constructive (destructive). These studies are theoretical and await detailed testing, although the predictions are consistent with extensive studies of norbornane bridged molecules.

Studies of intermolecular electron transfer show that the solvent can mediate the electronic coupling. Early studies by Miller [31] in glasses indicated the distance dependence of the electronic coupling to be well described as exponential with $\beta$ values of 1.1–1.4 Å$^{-1}$. More recent work by Gould and co-workers [25] indicates that solvent molecules lying between the donor and acceptor can mediate the electronic coupling.

Electron transfer studies on electrode systems have produced similar results. Studies which use thioalkane layers [13–15] as an insulating barrier have probed the distance dependence of the electron transfer. Recent studies on gold electrodes give a distance dependence for the electron transfer which is similar to that found for intramolecular systems and glasses, i.e. 0.9–1.2 Å$^{-1}$. A study on Si electrodes [12] has shown that ordered monolayer films provide more efficient electron transfer than disordered films. This finding is qualitatively in accordance with the all-trans rule.

Despite the successes of the past two decades, fundamental questions remain in this area. First, the relative importance of electron mediated coupling (via empty orbitals of the bridging unit) as compared to hole mediated coupling (via filled orbitals of the bridging unit) has not been addressed by experiment [11,22]. Second, criteria must be found for determining how the nature of the interaction between orbitals effects the coupling. Although extensive work has been done on systems with covalent linkages, work on hydrogen bonded linkages [28] and solvent mediated coupling [24–27,31] is in its nascent stages. Third, the effect of symmetry constraints and vibronic coupling in augmenting symmetry forbidden electronic coupling needs to be more widely addressed [6,29]. Fourth, the effect of the energy gap between the donor and acceptor orbitals and the bridge orbitals should be investigated in a systematic manner [22,31,32]. Lastly, all of the issues described and outlined treat the electronic coupling as a static property of the system; however, in a solvent or a protein the electronic coupling could vary with fluctuations in the environment. Although some theoretical work [33] has addressed this issue, it has not been explored experimentally.

The work described below begins to address some of these important issues. The studies on intramolecular electron transfer are designed to investigate the relative importance of "through bond" pathways for the coupling as compared to "through solvent" pathways. The studies of heterogeneous electron transfer are aimed at understanding how the energetics of the acceptor (the semiconductor valence band) effects the electronic coupling.

## 3. Intramolecular electron transfer

A large number of workers have investigated electron transfer in unimolecular systems. These studies have clearly delineated the importance of molecular properties and provided direct tests for the adequacy of Eq. (1) in describing the kinetics. Prominent studies are those of Miller and co-workers [7,20], who demonstrated the presence of the inverted regime in electron transfer and have more recently investigated the important role of nuclear tunneling. The studies of Paddon-Row and co-workers [4] and others [5,7] on DBA systems with rigid bridges provide a clear test of the distance dependence of the electron transfer. The studies of Zimmt and co-workers [6] have investigated the influence of donor and acceptor state symmetry on the electronic coupling. In cooperation with these and other experimental studies, theoretical progress has focussed on the calculation of electronic couplings for DBA systems [17–23] and the use of semiempirical models to describe electronic couplings in complex systems [10,11]. Although this and other work demonstrates important progress in this area, much remains to be understood.

For the most part, the solvent has been found to influence the reaction through its impact on the energetics, i.e. solvation of the reactant and product states, and reorganization energy. This role is quite important as readily seen from Eq. (2), where the free energy change and the reorganization energy appear in the argument of the exponential term. Although these solvent effects are well understand on a conceptual level, accurate theoretical modeling of the energetics and the reorganization energies is lacking. The role of solvent in the dynamics of electron transfer reactions is of more recent interest. For reactions which occur in the adiabatic limit, considerable work on the role of solvent dynamics has been performed [34]. This regime is not discussed here. Rather, the focus of this work is on systems in the nonadiabatic, or weakly coupled, regime. Recent work in our laboratories [24] and others [25] has explored the ability of solvent to mediate the electronic coupling between donor and acceptor moieties.

Fig. 1 shows two molecules which have been investigated in our studies. Species 1 has an extended structure with seven

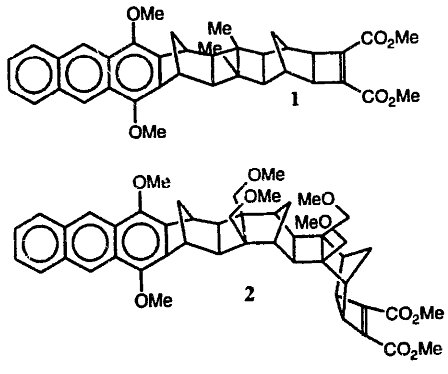

Fig. 1. Molecular structures for the "linear" system 1 and the "C-clamp" system 2.

bonds between the donor and acceptor. Species **2** has the same donor and acceptor, but with nine bonds between them. If the electronic coupling is dominated by through bond interactions, then the degree of electronic coupling in **2** would be expected to be lower than in **1**, because fewer bonds separate the donor and acceptor groups in the latter. In addition, **2** has more gauche linkages in its bridge, which should decrease the magnitude of the coupling relative to **1**. However, the through space distance between donor and acceptor is shorter for species **2** ( $\approx 7.1$ Å) than for species **1** ( $\approx 11.5$ Å). Our work characterizes the competition between these two alternative "pathways" for the electronic coupling and the way in which they are influenced by the nature of the solvent.

Recently, we investigated the nature of the coupling between the donor and acceptor in three solvents: acetonitrile, dimethylacetamide and benzonitrile [24]. The value of the electronic coupling was obtained by measuring the temperature dependence of the electron transfer rate and analyzing the data according to Eq. (1), in which the reorganization energies and free energies were modeled. This procedure is nontrivial because of the number of parameters and their interdependence; however, the focus of these studies is the comparison of the electronic coupling of the two species rather than its absolute value. Although the absolute value of the electronic coupling can vary by a factor of two, or even three, with changes in the parameters of the model, the ratio of the couplings obtained for **2** with those for **1** do not change significantly [26]. The best fit values for the electronic couplings in species **1** were found to be 15 $\text{cm}^{-1}$ in acetonitrile, 14 $\text{cm}^{-1}$ in dimethylacetamide, and 13 $\text{cm}^{-1}$ in benzonitrile, whereas those in species **2** were found to be 21 $\text{cm}^{-1}$ in acetonitrile, 15 $\text{cm}^{-1}$ in dimethylacetamide and 64 $\text{cm}^{-1}$ in benzonitrile. The electronic coupling for species **2** in benzonitrile is anomalously high by a factor of three to four.

The model proposed to account for this increased coupling has the benzonitrile moiety located in or near the molecular cleft (jaws of the C-clamp) where its $\pi$ system can mediate the electronic coupling. Fig. 2 illustrates the type of interaction envisioned. Although the experiments provide no direct evidence about the placement or distribution of the solvent, some circumstantial evidence is available. The energy of the donor emission band red shifts with increasing polarity and polarizability of the solvent. The red shift is the same for both compounds, **1** and **2**, which indicates that there is little difference in the solvation of the anthracene moiety between the extended and cleft structures. NMR studies of **1** and **2** in MCH-D14/$C_6D_6$ detected aromatic solvent within the cleft of **2**. However, the observed shifts could not be interpreted as arising from a single well-defined solvent geometry. Because of the nonspecific nature of the interaction, i.e. no directed hydrogen bonds, such behavior is not surprising. Lastly, the hypothesis is supported by theoretical calculations of the electronic coupling for these systems [27], with and without a solvent molecule in the cleft. These theoretical studies find the electronic coupling to depend strongly on whether a benzonitrile molecule is located within the molecular cleft and how it is positioned relative to the donor and acceptor moieties, as opposed to outside the cleft. In contrast, theoretical studies on the linear compound **1** find no dependence of the electronic coupling on the location of solvent molecules. These observations suggest that the cleft is accessible to the solvent and that the aromatic system of benzonitrile is important in determining the electronic coupling.

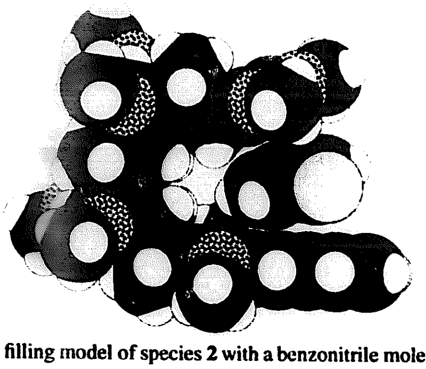

Fig. 2. Space filling model of species **2** with a benzonitrile molecule located in the cleft.

Recently, we have begun to investigate a series of alkylbenzene solvents and benzene/methylcyclohexane mixtures to ascertain the role of the aromatic system in the electron transfer. These studies monitor the kinetics by fluorescence decay of the locally excited state using the time-correlated single photon counting method [35]. In all of these solvents, we observe biexponential relaxation of the locally excited state for **2**. Fig. 3 shows a fluorescence decay curve for **2** in cumene on the left and a kinetic model for the process on the right. The fluorescence decay curve represents the population decay of the locally excited state (LE). For the case when back electron transfer $k_{\text{back}}$ from the charge transfer state CT to the LE state is slow, the fluorescence decay should be single exponential, as observed in the more polar solvents acetonitrile, benzonitrile and dimethylacetamide [24]. The observation of biexponential kinetics, however, is consistent with relaxation involving charge transfer from the LE state to the CT state $k_{\text{for}}$, and back electron transfer to regenerate the LE state species, i.e. equilibration in the excited state. Such relaxation kinetics has been observed in other intramolecular electron transfer systems [36], and assigned to this type of kinetic scheme. Using this kinetic model and knowledge of the decay rate for the locally excited state ($k_f = 0.51 \times 10^8\ \text{s}^{-1}$), it is possible to obtain both the forward $k_{\text{for}}$ and back $k_{\text{back}}$ electron transfer rates, and hence $\Delta G$ for the electron transfer.

The electron transfer rate constants were determined for **2** in a series of solvent systems at 298 K. These data are plotted versus $\Delta G$ for the reaction in Fig. 4. The open symbols correspond to mixtures of benzene and methylcyclohexane (MCH) which range from 20% benzene/80%MCH to neat benzene. The filled symbols are data for benzene, cumene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, mesitylene, and 1,3,5-triisopropylbenzene. Most of these data lie on a smooth curve. The line is a simple fit to the semiclassical

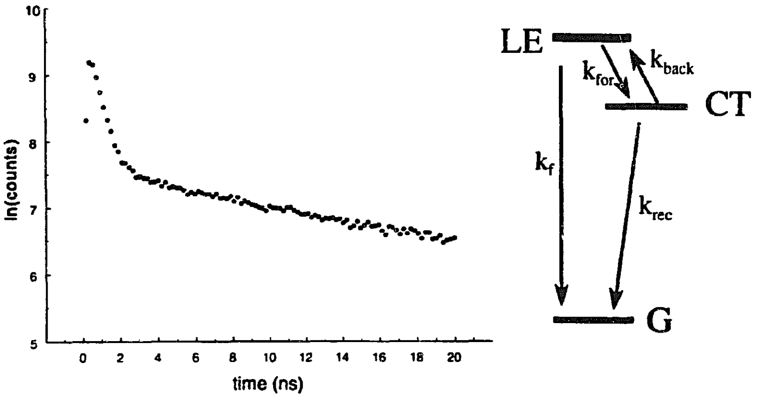

Fig. 3. Fluorescence decay curve for **2** in cumene at 298 K on the left and the scheme used to interpret the fluorescence kinetics on the right.

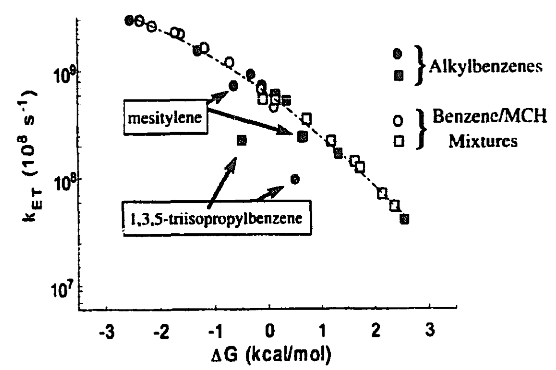

Fig. 4. Forward (●,○) and backward (■,□) electron transfer rates as a function of the Gibbs free energy change for compound **2** in a series of alkylbenzenes and benzene/methylcyclohexane mixtures.

model given in Eq. (1). The fit assumes that the reorganization energies and electronic coupling do not change through this series of similar solvents. The data which lie below the curve correspond to the triply substituted benzenes: mesitylene and 1,3,5-triisopropylbenzene. The lower rate constants observed for these two solvents can be rationalized as arising from their distribution of bulky alkyl groups, which inhibits the approach of the aromatic nucleus to the cleft in **2**. This explanation is consistent with the expectation that the aromatic system can enhance the electronic coupling when it lies between the donor and acceptor moieties. i.e. in or along the cleft. For 1,3,5-triisopropylbenzene the steric bulk around the benzene ring prohibits its access to the cleft, and decreases the electronic coupling and hence the rate constant. This effect is also observed for mesitylene, but here it is much smaller in magnitude, presumably related to the difference between the size of the methyl and propyl groups. An alternative explanation for the discrepancies observed can be given by a change in the reorganization energy through the solvent series. Studies of the rate constants as a function of temperature should help to clarify which of these two explanations is most appropriate.

The studies discussed here probe the influence of solvent on nonadiabatic intramolecular electron transfer processes. In addition to its important influence on the free energy and the reorganization energy of the electron transfer, the solvent may also play a role in mediating the electronic coupling between the donor and acceptor moieties.

## 4. Heterogeneous electron transfer

Compared to intramolecular electron transfer, the understanding of heterogeneous electron transfer processes is crude, despite its enormous technological importance. Although the transport of redox species to an electrode interface is relatively well understood, the nature of the electron transfer event and its dependence on electrode properties, interfacial properties and molecular properties is poorly understood [37]. Recent work in this laboratory has exploited the ability to create ordered monomolecular films through self-assembly to prepare well-defined interfaces for study of electron transfer. The ability to control the chemistry and structure of the interface is essential to understanding interfacial processes, because only with a high level of control can the properties of the system be varied in a systematic manner.

Although work on SAMs has focussed largely on the preparation of films on metal surfaces and insulators [38], some work has been performed on semiconductor substrates, in particular GaAs [39] and Si [12,40]. Recent work [41] by our group has demonstrated the formation of alkanethiol films on InP (both *n*-doped and *p*-doped). InP is a direct band gap (1.35 eV) semiconductor which has found broad use in optoelectronics. The structure of the films have been characterized through a variety of surface spectroscopies. To summarize these findings, the films are observed to form with the thiol near the interface and the alkanes further away (Fig. 5). The nature of the bonding has not been identified, although

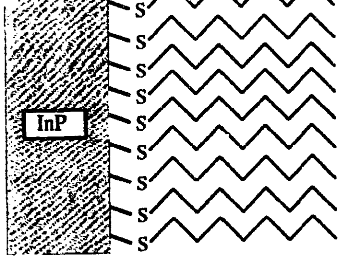

Fig. 5. Idealized view of the self-assembled monolayer (SAM) structure.

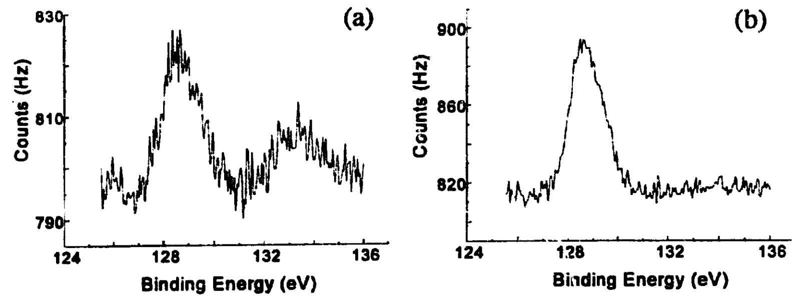

Fig. 6. XPS data for the 2p core level of phosphorous. A is an InP electrode which has been oxidized by exposure to electrolyte solution and B is an InP electrode coated with a SAM which protects it from oxidation.

no shift in the 2p core level of phosphorous is observed. The films appear to be quite compact (as judged from contact angle measurements) and the film thickness is consistent with that expected from consideration of the chain length (as judged from ellipsometry). Present characterization efforts are on infrared studies which should probe the tilt of the alkane chains with respect to the surface normal and the degree of order in the films, and the use of fluorescence quenching experiments to investigate the defects in the film.

The studies described below explore redox chemistry at electrode interfaces which have been coated with thiol based monomolecular films. Work in this area has focussed largely on SAM modified gold electrodes [13–15]. These studies found that the current through such structures occurs by electron tunneling through the film, resulting in relatively slow kinetics [14]. The distance dependence observed for the electron transfer is exponential with a decay parameter of about 1 per $CH_2$. Miller and co-workers [15] have used the gold systems to explore detailed features of the electron transfer and its modeling. These studies represent the first stages of the ability to investigate electron transfer at interfaces in a controlled manner.

Recently, we have explored the electron transfer between the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple and InP electrodes. The use of this redox couple in conjunction with bare InP electrode surfaces results in the formation of an oxide layer [42] on the surface of the electrode which can inhibit charge transfer. The presence of a SAM acts to stabilize the interface and inhibit the formation of an oxide. Fig. 6 demonstrates this effect for *p*-InP electrodes by analyzing the XPS data for the 2p core level of phosphorous. For both spectra, 0.008 coulombs of charge was transferred between the electrode and a 0.08 M $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ solution at a voltage of 0.35 V versus SCE. For Fig. 6A, the InP surface did not contain a monolayer film. The formation of an oxide peak is observed at 4 eV higher binding energy. For Fig. 6B, a SAM overlayer with 16 methylene units was present on the electrode surface and only the 2p core level of phosphorous is observed. This stabilization of the interface allows electron transfer studies, which are not complicated by oxidation processes, to be performed in this system.

The electron transfer between *n*-InP (dopant density of $10^{18}$ $cm^{-3}$) and $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ was explored by measuring the photocurrent as a function of the thickness of the insulating film [16]. The thickness of the film was varied by changing the number of methylene units in the alkane chain, i.e. layers ranging from octanethiol to hexadecanethiol. The distance dependence for the electron transfer is exponential, but is observed to be softer than that observed on gold electrodes (a decay parameter of 0.52 per $CH_2$ rather than 1.0 per $CH_2$). Much effort has been made to ensure that the softer distance dependence is not caused by poor film quality and other experimental conditions; however, these cannot yet be unequivocally ruled out. In principle, the photocurrent depends on the concentration of the photogenerated holes and the reductant—the latter is present in large excess and should be constant. The material has a high surface recombination velocity which should act to stabilize the hole concentration at the surface as the level of the photocurrent changes; however, this remains to be verified experimentally. See Ref. [16] for further discussion of these issues.

Varying the thickness of the monolayer film changes the average distance between solution species and the electrode, but does not significantly modify the free energy of the reaction or the reorganization energies (see Refs. [16] and [43]). Given that the concentrations of the redox species and the photogenerated holes are fixed, the softer distance dependence would result from a change in the electronic coupling for these systems as compared to the gold systems. Beratan et al. [10a] have shown that the electronic coupling should depend on the relative energy of the donor state to the mediating orbitals of the bridge (for this system the alkane chains), and this phenomenon is consistent with the observations. The valence band of the InP, from which the photocurrent is generated, lies further from the vacuum level than does the Fermi level of gold. Consequently, the valence band lies closer in energy to the HOMO orbitals of the bridge. Further studies are being performed to better characterize the hole concentration at the interface and explore the physical reason for the softer distance dependence.

By tethering a redox active species to the end of the alkane chain, its location can be controlled and issues related to defects in the film become less important. To this end, we have begun to prepare films which are functionalized. Fig. 7 shows band gap emission decays for InP treated with different thiol derivatives. The top curve C8 corresponds to octanethiol, Am corresponds to *N*-acetyl-4-aminophenoxyl, Me corresponds to 4-methylphenoxyl and Me3 corresponds to

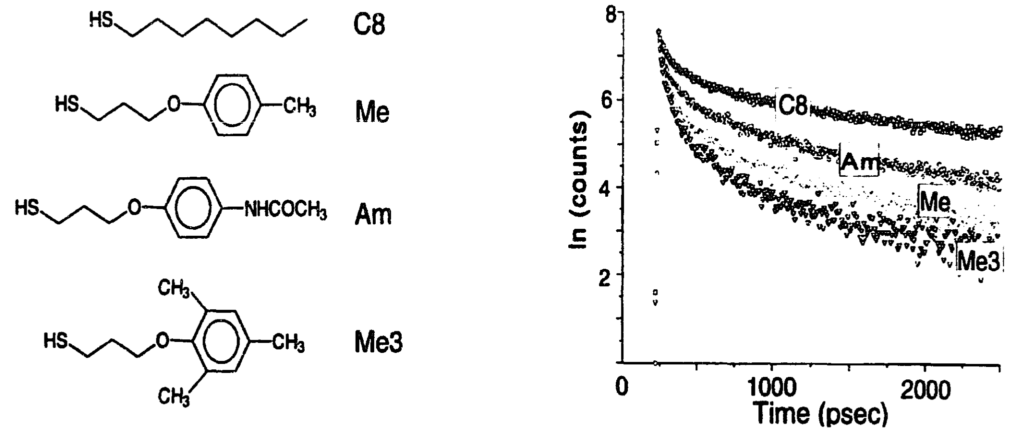

Fig. 7. Fluorescence decay curves of the InP bandgap emission for different surface treatments.

2,4,6-trimethylphenoxyl. The different functionalities are seen to effect the fluorescence decay characteristics of the electrode. The quenching of the fluorescence correlates well with the expected change in redox potential of the phenoxyl moiety [44]. This quenching may result from two different effects. First, the substitutent may effect the energetics of InP surface electronic states and hence the recombination of electron–hole pairs at the interface. Second, the substituent effect could result from the phenoxy group acting as a recombination center for electron–hole pairs, i.e. the phenoxy moiety is first oxidized by photogenerated holes and then recombines with an electron from the solid. This latter process would involve electron tunneling through the layer to the electrode. Studies are presently underway to distinguish between these two possible mechanisms. These investigations show that chemical control of interfacial electrode properties allows the electrochemical behavior to be explored in a systematic manner.

## 5. Conclusions

Progress in our understanding and the ability to model and design electron transfer systems has exploded over the past decade. Nevertheless, a detailed understanding of electronic coupling and molecular design features for its optimization remains an important avenue of study. The work described above is two-fold. First, a new mechanism is probed for donor/acceptor coupling that is mediated by the solvent. Second, electron transfer is probed in heterogeneous systems with the aim of elucidating the distance dependence of the electron transfer.

## Acknowledgements

This work was supported in part by the Department of Energy, Division of Chemical Sciences (DE-FG02-89ER14062) and by the National Science Foundation (CHE-9416913 and CHE-9206765).

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