

The Influence of Surface Hydration on the Interfacial Electron Transfer Dynamics from Rhodamine B into SnO₂

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ABSTRACT

The influence of surface hydration on the time-scales and mechanisms of interfacial electron transfer from rhodamine B into SnO₂ is investigated. We combine molecular dynamics simulations and quantum dynamics propagation of transient electronic excitations to analyze the regulatory role of water molecules affecting the adsorbate-semiconductor interactions and the underlying electronic couplings that determine the electron injection times. The reported results are essential to advance our understanding of interfacial electron transfer dynamics in dye sensitized semiconductor surfaces at the molecule level, including fundamental interactions that affect the efficiency of interfacial electronic processes in dye-sensitized solar cells as well as in a wide range of other technological applications.

Keywords: Quantum Dynamics, Molecular Dynamics, Interfacial Electron Transfer, Rhodamine B, Tin Dioxide

1. INTRODUCTION

Advancing our understanding of interfacial electron transfer (IET) dynamics in dye sensitized semiconductor surfaces is important for a wide range of technological applications, including the development of dye sensitized solar cells (DSSC).¹ Significant efforts in experimental² and computational³ studies have been focused on the characterization of the efficiency and time scales of IET. However, the underlying mechanisms of IET and the influence of hydration on the electron injection time scales remain only partially understood at the molecular level. This paper explores the influence of surface hydration on the IET from Rhodamine B (RhB) into SnO₂.

RhB is an organic chromophore that covalently attaches to semiconductor surfaces by esterification of its carboxylate group (see Fig. 1, top panel). Photoexcitation of RhB adsorbates with visible light (550 nm) leads to IET into the conduction band, as seen for nanocrystalline thin films of In₂O₃, SnO₂ and ZnO.⁴ The observed IET times range from 1.2 ps into In₂O₃ and SnO₂ to 7.0 ps into ZnO (see Fig. 1, bottom panel).⁴ These trends in IET times are similar to those observed for other adsorbates that covalently attach to semiconductor surfaces by esterification of carboxylate groups. For example, Ru-(dcbpy)₂(NCS)₂ [dcbpy= (4,4'-

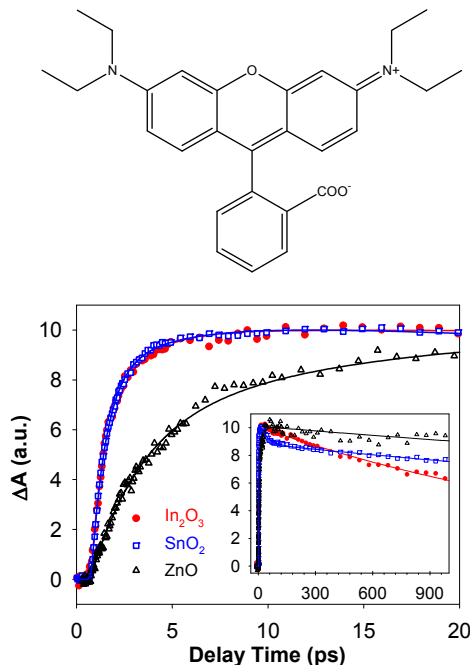


Figure 1. Molecular structure of Rhodamine B (top panel), and comparison of the growth of IR absorption of injected electrons in SnO₂ and other semiconductors (bottom panel).⁴

dicarboxy-2,2'-bipyridine)] (RuN3) injects in ~5 ps when adsorbed onto In₂O₃ and SnO₂,⁵ approximately 30 times faster than when attached to ZnO.⁶ However, the IET dynamics through carboxylate groups can be much faster than observed in these materials, including IET in <100 fs as observed for RuN3 adsorbed onto TiO₂.^{7,8} The longer IET times into SnO₂, when compared to TiO₂, have been attributed to the smaller density of unoccupied states in the conduction band.^{9,10} However, several other factors including surface defects and hydration could also influence the IET times by affecting the strength of the electronic couplings responsible for electron injection. It is, therefore, essential to investigate the underlying IET mechanisms at the detailed molecular level.

Table 2. SnO₂ Lennard-Jones parameters.

	ϵ (kcal mol ⁻¹)	r_{\min} (Å)
Sn	0.1208	2.8182
O	0.9024	2.9182

Modeling IET in hydrated metal-oxide interfaces is challenging due to the complexity of the systems and the lack of reliable parameters for describing the the adsorbate-semiconductor interactions.¹⁸ For example, force field parameters are available for describing SnO₂ and its interaction with water¹¹ but parameters for describing the interaction of organic molecules covalently attached to SnO₂ surfaces have yet to be reported. In this paper we report force field parameters for modeling SnO₂ surfaces functionalized with RhB adsorbates. The obtained parameters are applied in molecular mechanics simulations in conjunction with the Amber molecular mechanics force field. We model a thermal ensemble of configurations of RhB, covalently attached to hydrated SnO₂, and we analyze the IET time scales as influenced by the distribution of attachment modes available to the adsorbate. Explicit simulations of the IET dynamics are performed and compared to the injection rates estimated by a Golden Rule expression that allows for an approximate description of IET beyond the time scales accessible to explicit molecular dynamics simulations.

Table 1. Lennard-Jones parameters for the interactions of SnO₂ with Amber atom types.

	ϵ (kcal/mol)	r_{\min} (Å)
Sn-Sn	0.0109	4.5959
Sn-O	0.6831	2.6314
O-O	0.3108	3.5306

$$q_{\text{Sn}} = 2.160, q_{\text{O}} = -1.080$$

The paper is organized as follows. First, Sec. 2 introduces the methods and structural models. Then, Sec. 3 presents our results and a discussion on the interpretation of ultrafast spectroscopic data. Concluding remarks are presented in Sec. 4.

2. METHODS

2.1. Sampling of Nuclear Configurations

In order to sample the distribution of configurations available to the RhB adsorbate on SnO₂ surfaces, we have generated an ensemble of thermal configurations. These were obtained by running molecular dynamics (MD) simulations at 300 K, using the molecular dynamics package NAMD.¹² The system was equilibrated for 100 ps and kept at 300 K by using Langevin dynamics with a damping coefficient of 1 ps. Following the equilibration process, a production run of 100 ps generated 100 configurations at 1 ps time step intervals.

The motion of RhB was described using the Amber force field.¹³ The atomic charges have been reparametrized according to the electrostatic potential (ESP) charges obtained by fitting the DFT-B3LYP electrostatic potential, as calculated with the software package Gaussian 03.¹⁴ The SnO₂ charges and non-bonded parameters, including the interactions between the Sn and O atoms on the surface and water molecules, were defined as reported by Bandura *et al.*¹¹ (see Table 1) where they used Coulomb and Lennard-Jones potentials for the pairwise interaction. The Lennard-Jones potential is of the form,

$$V(r) = \epsilon \left[\left(\frac{r_{\min}}{r} \right)^{12} - 2 \left(\frac{r_{\min}}{r} \right)^6 \right], \quad (1)$$

where ϵ is the depth of the well and r_{\min} is the equilibrium distance.

We have also obtained Lennard-Jones parameters for the Sn and O atoms that could be used for the non-bonded interactions between the surface and all Amber atom types (see Table 2). When including hydrating surface waters on the SnO_2 surface, a 0.4 nm thick layer of water molecules was included in the model. The water molecules were described using the TIP3P model.¹⁵

Modeling the bonding upon interaction of the RhB adsorbate with Sn^{4+} ions on the surface and the dynamics of bond formation and breaking in the presence of water is a difficult task. Standard molecular mechanics force fields (*e.g.*, Amber) are limited in this respect since they describe bonds in terms of bound (*e.g.*, harmonic) potentials. Such potentials do not allow for bond breaking processes, constraining the RhB adsorbate to configurations that deviate only harmonically from its minimum energy configuration. In contrast, realistic molecular modeling of hydrated surfaces requires a description of the diffusion of adsorbate molecules on the surface, and sampling a wide range of accessible binding modes, including bridging, chelation and coordination of carboxylate groups to Sn^{4+} surface ions. To overcome these limitations, we describe the adsorbate-surface interactions by treating the oxygen atoms of the carboxylate group as the same atom type as the O^{2-} ions in the SnO_2 host substrate. The total interaction includes the pairwise Lennard-Jones potential and the Coulomb potential for electrostatic interactions based on ESP atomic charges on the carboxylate groups.

The MD simulations cell included a 2.0×1.9 nm slab of the SnO_2 rutile crystal structure, including 4 layers of Sn^{4+} ions, with periodic boundary conditions (Fig. 1). The model of a semi-infinite surface was constructed by including a vacuum spacer between slabs, extending the cell dimensions to 50 Å in the direction [110] of the SnO_2 crystal. The RhB adsorbate was covalently attached to the surface, with the carboxylate linker bridging between two adjacent pentacoordinated Sn^{4+} ions on the surface (110). Figure 2 shows representative configurations for RhB covalently attached to SnO_2 .

2.2. Simulations of IET

The time-propagation of the electronic excitations was based on a tight-binding model Hamiltonian gained from the semi-empirical extended Hückel method (eH). We first solved the time-independent Schrödinger equation in the basis set of Slater-type atomic orbitals (AOs) $|\chi_i\rangle$,

$$\mathbf{H}\mathbf{Q}^q = E_q \mathbf{S}\mathbf{Q}^q, \quad (2)$$

where \mathbf{H} represents the extended Hückel Hamiltonian matrix, \mathbf{S} is the atomic orbital overlap matrix, \mathbf{Q}^q are the expansion coefficients of the molecular orbitals,

$$|q\rangle = \sum_i Q_i^q |\chi_i\rangle, \quad (3)$$

and E_q are the corresponding eigenvalues. The initial state is expanded as a linear combination of the molecular orbitals,

$$|\Psi(0)\rangle = \sum_q C_q |q\rangle = \sum_q \sum_i C_q Q_i^q |\chi_i\rangle. \quad (4)$$

Most initial states were defined as excited electronic states of the adsorbate that resulted from allowed optical transitions in the UV/Vis region. These are states with significant electronic coupling with the semiconductor conduction band.

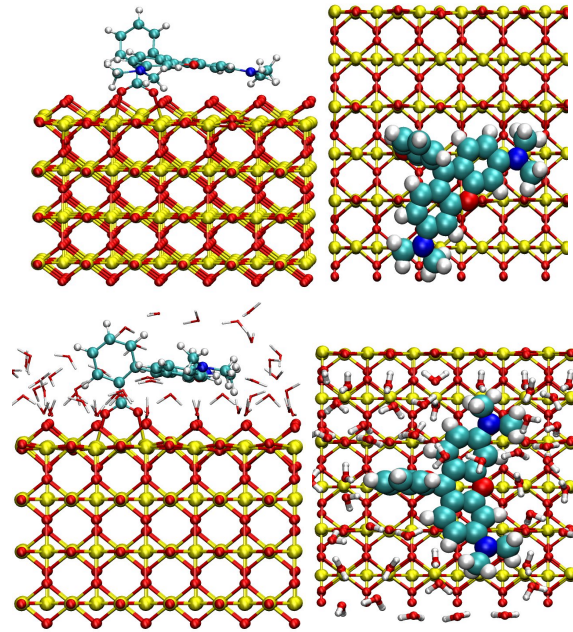


Figure 2. Representative configurations of rhodamine B on dry (top panels) and hydrated (bottom panels) SnO_2 surfaces (110), viewed from the side (left) and top (right), respectively. Note the monolayer of H_2O screening the interactions between RhB and the SnO_2 (110) surface (bottom left panel).

The time-evolved wavefunction was obtained by propagating the initial state as follows,

$$|\Psi(t)\rangle = e^{-(i/\hbar)\hat{H}t}|\Psi(0)\rangle, \quad (5)$$

where

$$|\Psi(t)\rangle = \sum_i \sum_q C_q Q_i^q e^{-(i/\hbar)E_q t} |\chi_i\rangle, \quad (6)$$

and

$$|\Psi(t)\rangle = \sum_i B_i(t) |\chi_i\rangle, \quad B_i(t) = \sum_q C_q Q_i^q e^{-(i/\hbar)E_q t}. \quad (7)$$

Finally, the time-evolved electronic wavefunction was projected onto the atomic orbitals of the molecular adsorbate to obtain the survival probability,

$$P(t) = \left| \sum_i^{ads.} \sum_j^{all} B_i^*(t) B_j(t) S_{ij} \right|, \quad (8)$$

where the summation over i runs through the atomic orbitals of the adsorbate, and the summation over j runs through the complete basis.

$P(t)$ describes the probability that the photoexcited electron remains in the adsorbate molecule at time t after the photoexcitation of the system. The IET times dynamics were obtained from the analysis of $P(t)$ averaged over the sampled nuclear configurations obtained from molecular dynamics trajectories. Our simulations of IET are therefore based on the complete ensemble of configurations of the system obtained from MD simulations of SnO₂ (110) surfaces functionalized with RhB (dry, or hydrated with water molecules). It is important to note that the electron dynamics does not include nuclear motion during the simulation.

2.3. Estimation of IET Rate

For some adsorbate/semiconductor systems the electron transfer dynamics is too slow to be simulated explicitly, using the methodology described in Sec. 2.2. In such cases, we are limited to approximate estimations of the rate^{16,17} as given by the Golden Rule of Perturbation Theory. According to such a method, the IET is approximated by a single exponential relaxation,

$$P(t) = P(0)e^{-t/\tau_{IET}}, \quad (9)$$

with characteristic time $\tau_{IET} = \hbar/\gamma$ estimated from the broadening γ of the initially populated state in the photoexcited adsorbate molecule, due to coupling with the conduction band:

$$\gamma = \sum_i p_i |E_d - \varepsilon_i|, \quad (10)$$

where p_i is the population of the i^{th} orbital with energy ε_i and

$$E_d = \sum_i p_i \varepsilon_i, \quad (11)$$

is the energy of the initial state. The broadening is thus obtained from the projection of the adsorbate donor state onto the total density of states.

3. RESULTS

Figure 3 shows the average time-dependent electronic populations $P(t)$ of RhB sensitizers covalently attached to SnO₂-rutile surfaces (110), after instantaneous excitation of RhB with visible-light (550 nm). The calculations involve explicit quantum dynamics simulations of the ensuing electronic relaxation, including inhomogeneous broadening as averaged over a thermal ensemble of 100 configurations.

Figure 3 shows that the electron injection in both dry and hydrated SnO₂ surfaces involves biexponential relaxation dynamics,

$$P(t) = c_1 e^{-t/\tau_1} + c_2 e^{-t/\tau_2}, \quad (12)$$

with sub-ps (τ_1) and ps (τ_2) times, reported in Table 3. The sub-ps times (τ_1) for dry and hydrated surfaces are predicted to be 92 fs and 116 fs, respectively. The longer (ps) times (τ_2) for dry and hydrated surfaces are predicted to be 0.9 ps and 1.4 ps, respectively. The distribution of injection times is shown in Fig. 4. The injection dynamics in hydrated surfaces is significantly slower, partially due to the effect of the monolayer of bound water molecules directly attached to the SnO₂ surface (see Fig. 2). Such a monolayer separates the RhB adsorbate from the surface, reducing its electronic coupling with the SnO₂ surface.

Considering that hydrolysis might break the ester bonds that covalently bind RhB to SnO₂, we have also analyzed the IET from physisorbed RhB molecules that are only hydrogen bonded to SnO₂ surfaces. The average injection time calculated for such configurations is 135 ps, two orders of magnitude longer than the experimental value 1.2 ps.⁴ In addition, no exchange of adsorbate molecules between the surface and the solvent was observed during the course of 100 ps of molecular dynamics simulations. These results indicate that the 1.2 ps time observed by ultrafast spectroscopy can only result from adsorbate RhB molecules that are covalently attached to SnO₂.

Table 3 compares the average IET times (τ_1 and τ_2) obtained from explicit simulations to the single relaxation time (τ_{IET}) obtained by using the Golden Rule. It is shown that the Golden Rule predicts injection times that are an order of magnitude shorter than 1.2 ps time observed by ultrafast spectroscopy. In contrast, the explicit quantum dynamics simulations predict IET times (τ_2) that are in closer agreement with the experimental 1.2 ps transfer time, particularly when analyzing IET in hydrated surfaces.

Figure 4 analyzes the correlation between the IET times obtained from explicit quantum dynamics simulations, for 100 configurations of RhB covalently attached to dry and hydrated SnO₂ (110) surfaces, and those IET times estimated according to the Golden Rule expression. Perfect agreement between both methods would position all of the data points on the line indicating linear correlation. Figure 4 shows that with the exception of the small fraction of adsorbates that inject in less than 50 fs, the Golden Rule expression systematically underestimates the IET transfer times when compared to those obtained from explicit quantum dynamics simulation.

We have also analyzed the IET times from RhB physisorbed to hydrated SnO₂ surfaces. We found that the injection time estimated according to the Golden Rule expression is 222±70 fs in complete disagreement with calculations based on explicit quantum dynamics simulations.

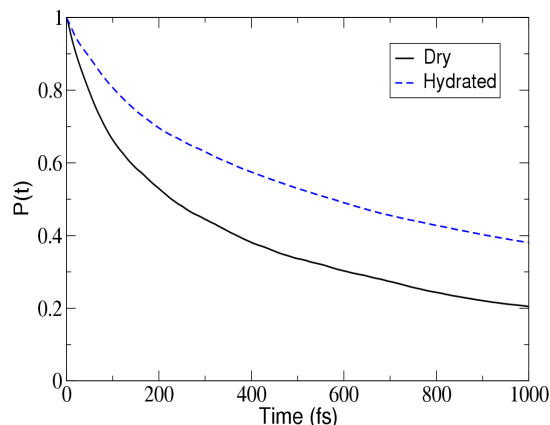


Figure 3. Time-dependent electronic populations $P(t)$ of RhB sensitizers covalently attached to dry (black) and hydrated (blue) SnO₂-rutile surfaces (110), after instantaneous excitation of RhB with visible-light (550 nm).

Table 3. Comparison of IET times [in fs] from RhB into dry and hydrated SnO₂-rutile (110) surfaces, as estimated by explicit quantum dynamics simulations for the biexponential relaxation (τ_1 and τ_2) and with the Golden Rule single exponential (τ_{IET}) approximation.

	Dry	Hydrated
τ_1 (c_1)	92 (0.403)	116 (0.246)
τ_2 (c_2)	895 (0.597)	1411 (0.754)
τ_{IET}	72	79

4. CONCLUSIONS

Fully atomistic models of RhB adsorbed on SnO₂-rutile (110) surfaces provided fundamental insight on the IET times, including the effect of surface hydration, after photoexcitation of the RhB with visible light. We conclude that the interfacial electron injection involves a biexponential relaxation dynamics, with sub-ps and ps time components.

The sub-ps time components for dry and hydrated surfaces are predicted to be 92 fs and 116 fs, respectively, as characterized by explicit simulations of quantum dynamics of IET. The (ps) time component results from a large fraction of the ensemble having injection times of 1.4 ps in hydrated surfaces, and 0.9 ps in dry surfaces. Hydration slows down the injection dynamics, mostly due to the effect of a monolayer of water molecules directly attached to

the SnO₂ surface. The monolayer of water separates the adsorbate from the surface reducing its electronic coupling with the SnO₂ host substrate.

We conclude that the electron injection from RhB molecules physisorbed to the SnO₂ surface is at least 2 orders of magnitude slower than when RhB is covalently attached by esterification of the carboxylate group. Therefore, the observation of electron injection by ultrafast spectroscopy in 1.2 ps must result from IET in hydrated surfaces where RhB is covalently attached to SnO₂. We also predict that it should be possible to observe IET in the sub-ps (100-200 fs) time scale in dry SnO₂ surfaces (e.g., under ultra-high vacuum conditions).

Finally, we conclude that calculations of IET times based on the Golden Rule approximation can often underestimate the IET times leading to significant errors.

5. ACKNOWLEDGEMENTS

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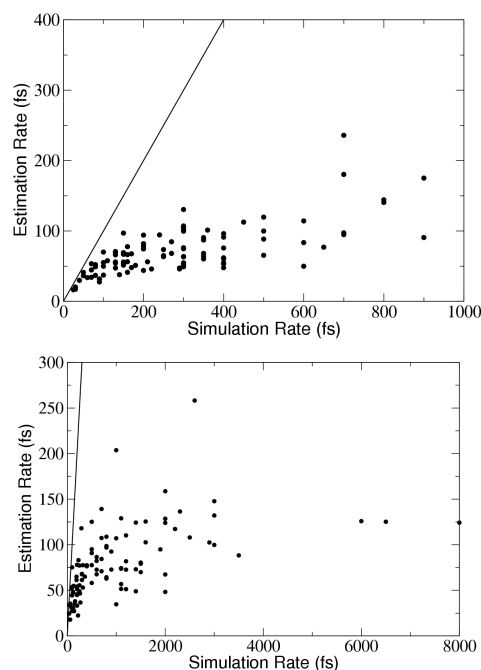


Figure 4. Correlation between IET times obtained from explicit quantum dynamics simulation of electron injection from RhB into SnO₂ surfaces (x axis), and according to the Golden Rule expression (y axis) for dry (top) and hydrated (bottom) surfaces. The black trace corresponds to linear correlation.

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