Photoinduced electron transfer processes in dye-semiconductor systems with different spacer groups

Jingrui Li, Haobin Wang, Petter Persson, and Michael Thoss

Citation: *J. Chem. Phys.* **137**, 22A529 (2012); doi: 10.1063/1.4746768

View online: <http://dx.doi.org/10.1063/1.4746768>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v137/i22>

Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

Photoinduced electron transfer processes in dye-semiconductor systems with different spacer groups

Jingrui Li,^{1,2,a)} Haobin Wang,³ Petter Persson,⁴ and Michael Thoss²

¹*Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany*

²*Institute of Theoretical Physics and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 7/B2, D-91058 Erlangen, Germany*

³*Department of Chemistry and Biochemistry, MSC 3C, New Mexico State University, Las Cruces, New Mexico 88003, USA*

⁴*Theoretical Chemistry Division, Chemistry Department, Lund University, Box 124, S-22100 Lund, Sweden*

(Received 23 May 2012; accepted 3 August 2012; published online 23 August 2012)

Photoinduced electron transfer processes in perylene-titanium dioxide dye-semiconductor systems are studied. In particular, the influence of saturated and unsaturated aliphatic spacer groups inserted between the chromophore and the semiconductor substrate is investigated. The study is based on a recently developed method that combines first-principles electronic structure calculations to characterize the dye-semiconductor systems and accurate multilayer multiconfiguration time-dependent Hartree simulations to reveal the underlying nonadiabatic dynamics. The results show that, in agreement with previous experimental studies, the spacer groups may affect the electron transfer dynamics significantly. Furthermore, the influence of electronic-vibrational coupling on the electron transfer dynamics and absorption spectra is discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4746768>]

I. INTRODUCTION

Photoinduced electron transfer (ET) reactions at dye-semiconductor interfaces represent interesting examples of surface ET processes. In particular, the process of electron injection from an electronically excited state of a chemisorbed dye molecule into a semiconductor substrate has been studied in great detail experimentally in recent years.^{1–26} This process represents a key step for photonic energy conversion in nanocrystalline dye-sensitized solar cells.^{2,7,10,27–29} Employing femtosecond spectroscopy techniques, which allow the observation of ultrafast photoreactions in real time, it has been shown that electron injection processes at dye-semiconductor interfaces often take place on an ultrafast subpicosecond timescale.^{3,10,11,17–19,30} Other aspects of ultrafast interfacial ET reactions include the nonequilibrium character of the process, the importance of electronic-nuclear correlation, i.e., nonadiabatic dynamics, the influence of the anchor group on the electron injection dynamics, recombination processes, and the influence of intermediate states localized at the chromophore-substrate interface.

Theoretical study of interfacial ET reactions requires a quantum mechanical description of the overall processes, which includes characterization of the electronic structure of the systems and simulation of the ET dynamics.^{31–34} To this end, a variety of different methods have been developed and employed.^{31,35–69} The electronic structure of dye molecules adsorbed at semiconductor substrates, in particular titanium dioxide, has been studied employing cluster models of nanoparticles^{37,52,55,62,64,65} or the

slab model with periodic boundary conditions to describe an extended surface.^{42–44,47,48,54,57,58,70–72} Information from such electronic structure calculations has been used to determine electronic interfacial coupling strengths. They have provided estimates of femtosecond electron injection rates that are in good agreement with results from ultrafast laser spectroscopy experiments.^{62,71} The dynamics of electron injection at dye-semiconductor interfaces has been studied employing first-principles simulations^{42,44,47,48,52,54,56,58} as well as models based on parametrized Hamiltonians.^{35,36,38–41,46,49,50,53,59–61,63} While the former class of dynamical methods typically use mixed quantum-classical approaches to treat the nuclear dynamics, such as the classical path or Ehrenfest method^{51,58,73} and the surface-hopping approach,^{73–75} the model-based approaches often allow a numerically exact, fully quantum mechanical treatment of the ET dynamics.^{49,60}

Recently, we have developed an approach to study the dynamics of ET in dye-semiconductor systems that combines a first-principles characterization of the systems with an accurate, fully quantum treatment of the dynamics.⁶⁶ This method employs a representation of the Hamiltonian in localized donor and acceptor states. The donor and acceptor states as well as other parameters of the ET Hamiltonian are determined using a partitioning method based on electronic structure calculations. Based on this modeling procedure, the quantum dynamics of the ET process is simulated using the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method.⁷⁶ This approach has been applied to investigate photoinduced interfacial ET processes in different dye-semiconductor systems.^{66–68} Here, we apply this methodology to study ET dynamics in complexes of perylene adsorbed via a carboxylic-acid anchor

^{a)}Present address: Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA.

group at titanium dioxide (anatase) nanoclusters. These systems allow a direct comparison with results from ultrafast laser spectroscopy experiments.^{4,23,62,77–79} Photoinduced ET in these systems has also been studied in great detail theoretically employing a semiempirical model,^{50,53,59,80} thus allowing a comparison with results of our first-principles-based simulations.

In our study, we will especially focus on the influence of spacer groups on the ET dynamics. In particular, we consider the effects of saturated and unsaturated aliphatic spacer groups inserted between the perylene chromophore and the carboxylic-acid anchor group. Employing spacer groups allows to vary the electronic coupling between chromophore and semiconductor substrate and thus to control the ET dynamics. In addition, we investigate the influence of electronic-vibrational coupling on the ET dynamics as well as on the absorption spectrum of the dye-semiconductor systems.

The remainder of this paper is organized as follows. In Sec. II, we outline the theoretical approach including the model Hamiltonian as well as the partitioning method employed to determine the electronic energies and the donor-acceptor coupling matrix elements. Section III presents results for perylene-based dye-semiconductor systems with different spacer group inserted between the perylene chromophore and the carboxylic-acid anchor group. We discuss the dynamics of the electron injection process, the influence of the spacer group and the effects of electronic-vibrational coupling on the ET dynamics and the absorption spectrum. Section IV concludes with a summary.

II. THEORY AND METHODS

To study ET process in dye-semiconductor systems, we have used a methodology developed recently, which combines a first-principles-based model Hamiltonian and accurate quantum dynamical simulations. The methodology has been outlined in detail previously.⁶⁶ Therefore, here we only give a brief summary of the method and some details specific to the application considered in the present work.

A. Electron transfer Hamiltonian

Within the first-principles-based model used here to study ET dynamics in dye-semiconductor systems, the Hamiltonian is represented in a basis of the following localized electronic states which are relevant to the photoreaction: the donor state of the ET process $|\psi_d\rangle$ (which, in the limit of vanishing coupling between the adsorbate and the semiconductor substrate, corresponds to the product of an electronically excited state of the dye and an empty conduction band of the semiconductor) and the (quasi)-continuum of acceptor states of the ET reaction $|\psi_k\rangle$ (corresponding in the zero-coupling limit to the product of the ground state of the adsorbate-cation and a conduction band state of the semiconductor substrate). Thus, the

ET Hamiltonian reads

$$H = T_{\text{nuc}} + |\psi_g\rangle V_g \langle \psi_g| + |\psi_d\rangle V_{dd} \langle \psi_d| + \sum_k |\psi_k\rangle V_{kk} \langle \psi_k| + \sum_k (|\psi_d\rangle V_{dk} \langle \psi_k| + |\psi_k\rangle V_{kd} \langle \psi_d|). \quad (2.1)$$

Here, V_g , V_{dd} , and V_{kk} denote the energies of the electronic ground, donor, and acceptor states, respectively. The off-diagonal matrix elements V_{dk} characterize the donor-acceptor coupling. T_{nuc} is the nuclear kinetic energy operator.

B. Determination of electronic energies and donor-acceptor coupling matrix elements

The parameters of the ET Hamiltonian, Eq. (2.1), are determined from first-principles electronic structure calculations employing a partitioning method. The details of this method, which is motivated by the projection-operator approach of resonant electron-molecule scattering,⁸¹ have been presented previously.⁶⁶ The method employs a partitioning scheme based on electronic structure, in particular, density functional theory (DFT) calculations for a complex of the dye molecule under consideration with a finite TiO_2 cluster. The scheme for defining the localized donor and acceptor states $|\psi_d\rangle$ and $|\psi_k\rangle$ in the Hamiltonian, Eq. (2.1), is based on three steps: (i) a partitioning of the Hilbert space in a donor and acceptor group using a localized basis, (ii) a partitioning of the Hamiltonian according to the donor-acceptor separation, and (iii) a separate diagonalization of the donor and acceptor blocks of the partitioned Hamiltonian. In the present paper, we work within the mean-field single-electron picture. Thus, we identify the effective Hamiltonian with the Fock (or Kohn-Sham) matrix and use the orbitals and orbital energies to represent the corresponding system states and the energies in the partitioning method.

In the first step, the set of (Gaussian-type-of) atomic orbitals of the overall system $\{|\phi_j\rangle\}$ is divided into two groups: the donor group $\{|\phi_j^d\rangle\}$, which comprises the orbitals centered at the atoms of the dye molecule, and the acceptor group $\{|\phi_j^a\rangle\}$, which includes the orbitals centered at the TiO_2 cluster. Since it is advantageous to work with orthogonal orbitals,^{82,83} the set of atomic orbitals of the overall system is orthogonalized according to Löwdin^{84,85}

$$|\tilde{\phi}_n\rangle = \sum_j (\mathbf{S}^{-\frac{1}{2}})_{jn} |\phi_j\rangle, \quad (2.2)$$

where $\mathbf{S}$ denotes the overlap matrix of atomic orbitals, with matrix elements $S_{jj'} = \langle \phi_j | \phi_{j'} \rangle$. The new basis functions obtained ($|\tilde{\phi}_n\rangle$) exhibit a minimal deviation from the original ones in a least-squares sense, and hence, their localization is preserved. In particular, the classification with donor ($\{|\phi_j^d\rangle\}$) and acceptor ($\{|\phi_j^a\rangle\}$) orbitals is still valid.

The new set of orthogonal basis functions is then used to partition the Fock (or Kohn-Sham) matrix from the converged self-consistent field (or DFT) calculation into the two (donor and acceptor) subspaces. The Fock matrix in the orthogonal

basis is given by

$$\tilde{\mathbf{F}} = \mathbf{S}^{-\frac{1}{2}} \mathbf{F} \mathbf{S}^{-\frac{1}{2}}, \quad (2.3)$$

where $\mathbf{F}$ denotes the Fock matrix in the original atomic orbital basis. The Fock matrix can be arranged in the following donor-acceptor block structure:

$$\tilde{\mathbf{F}} = \begin{pmatrix} \tilde{\mathbf{F}}_{dd} & \tilde{\mathbf{F}}_{da} \\ \tilde{\mathbf{F}}_{ad} & \tilde{\mathbf{F}}_{aa} \end{pmatrix}. \quad (2.4)$$

Separate diagonalization of the two (donor and acceptor) blocks of the Fock matrix, $\tilde{\mathbf{F}}_{dd}$ and $\tilde{\mathbf{F}}_{aa}$, and the corresponding transformation of the off-diagonal parts, result in the following prediagonalized block structure:

$$\bar{\mathbf{F}} = \begin{pmatrix} \bar{\mathbf{F}}_{dd} & \bar{\mathbf{F}}_{da} \\ \bar{\mathbf{F}}_{ad} & \bar{\mathbf{F}}_{aa} \end{pmatrix} = \begin{pmatrix} \varepsilon_{d1} & 0 & \cdots & & \\ 0 & \varepsilon_{d2} & \cdots & & \\ \vdots & \vdots & \ddots & & \\ & & & \varepsilon_{a1} & 0 & \cdots \\ & \bar{\mathbf{F}}_{ad} & & 0 & \varepsilon_{a2} & \cdots \\ & & & \vdots & \vdots & \ddots \end{pmatrix}. \quad (2.5)$$

The corresponding donor and acceptor orbitals, which can be denoted as $|\bar{\phi}_n^d\rangle$ and $|\bar{\phi}_n^a\rangle$, are given as the eigenvectors of $\bar{\mathbf{F}}_{dd}$ and $\bar{\mathbf{F}}_{aa}$, respectively. The diagonal blocks of the thus obtained Fock matrix contain the energies of the localized adsorbate states and those of the semiconductor substrate, respectively. The off-diagonal blocks contain the electronic coupling matrix elements between adsorbate and substrate sites. Identifying the donor state $|\psi_d\rangle$ with one of the states $|\bar{\phi}_n^d\rangle$ (based, e.g., on the orbital energy or the transition dipole moment to the ground state) and the acceptor states $|\psi_k\rangle$ with the states $|\bar{\phi}_k^a\rangle$, the electronic energies of donor and acceptor states are given by the corresponding diagonal elements of the prediagonalized Fock matrix (ε_{dn} and $\{\varepsilon_k\}$), while the donor-acceptor coupling matrix elements are given by $V_{dk} = (\bar{\mathbf{F}}_{da})_{nk}$.

The partitioning method discussed above is not limited to dye-semiconductor systems containing a finite semiconductor cluster but can, in principle, also be applied to problems with a dye molecule adsorbed on an extended surface. One possibility is to employ a slab model and electronic structure calculations with periodic boundary conditions. Alternatively, the effect of an infinite semiconductor substrate can also be described using surface Green's function techniques.⁸⁶ Within this method, the effect of the infinite substrate enters via the self-energy. In this paper, we have used a simpler approximate version of this method to mimic the effect of an extended surface. Thereby a constant imaginary part is added to the atomic orbital energies (in the orthogonal basis $\{|\bar{\phi}_k^a\rangle\}$) at the outer atoms of the TiO₂ substrate. In the results presented in Sec. III, a value of 1 eV for the imaginary part has been used. Employing this approach, the interaction of the donor state with the acceptor states is fully characterized by the continuous function

$$\Gamma(\varepsilon) = 2\pi \sum_k |V_{dk}|^2 \delta(\varepsilon - \varepsilon_k), \quad (2.6)$$

which is sometimes also called the energy-dependent decay width of the donor state. It describes the density of states of the semiconductor substrate weighted by the donor-acceptor coupling strength. The details of this method and a practical approach to calculate $\Gamma(\varepsilon)$ are described in Ref. 66.

C. Characterization of nuclear degrees of freedom

To characterize the nuclear degrees of freedom, the partitioning procedure outlined above has to be performed for each nuclear geometry, thus resulting in diabatic potential energy surfaces $V_{ii}(Q)$ and coordinate dependent donor-acceptor coupling matrix elements $V_{dk}(Q)$. Here, we use a compact notation $Q = \{Q_1, Q_2, \dots\}$ to represent the normal modes of nuclear degrees of freedom. If many nuclear degrees of freedom are important, as in the systems considered in this work, such a global characterization of the potential energy surfaces is not feasible. Therefore, in the present paper, we adopt the strategy used in our previous work, where a local low-order polynomial expansion of the diabatic potential matrix elements $V_{ij}(Q)$ around the equilibrium geometry of the neutral ground state is employed. The corresponding vibrational parameters are determined based on electronic structure calculations for the isolated dye, thereby neglecting the coupling to the semiconductor substrate and to the phonons of the semiconductor. Since the ET in the system considered in this paper occurs on an ultrafast timescale, these approximations are expected to be appropriate.

The approach has been described in detail in Ref. 60. Briefly, we perform a vibrational analysis of the isolated dye molecule in the electronic ground state and employ the harmonic approximation for the corresponding potential energy surface,

$$V_g(Q) = \varepsilon_g + \frac{1}{2} \sum_l \Omega_l^2 Q_l^2. \quad (2.7)$$

Here, ε_g denotes the ground-state equilibrium energy (obtained from an electronic structure calculation for the overall dye-semiconductor system) and Ω_l the frequency of the l th normal mode (mass-scaled coordinates and atomic units are used throughout this paper). We assume the donor-acceptor coupling matrix elements V_{dk} to be approximately independent of the nuclear geometry⁸⁷ and expand the potential energy surface of each ET-related diabatic state around the equilibrium geometry of the electronic ground state (denoted by $Q_l = 0$). Taking into account only linear terms in the expansion, we obtain

$$V_{jj}(Q) = V_{jj}(0) + \sum_l \kappa_l^j Q_l + \frac{1}{2} \sum_l \Omega_l^2 Q_l^2. \quad (2.8)$$

Thereby, we have approximated the frequencies by their ground-state values and neglected Dushinsky rotation⁸⁸ of the normal modes. This approximation has been used successfully for describing Franck-Condon and resonance Raman spectra.⁸⁹ It is also employed in the linear vibronic coupling model of conical intersections⁹⁰ and in the Marcus theory of ET.⁹¹

Within the description of the nuclear degrees of freedom employed here, the parameters of the diabatic potential energy surfaces of the donor and acceptor states are obtained from the potential energy functions of the excited state of the neutral dye molecule and the ground state of its cation, respectively. Accordingly, we have

$$V_{dd}(Q) = \varepsilon_d + \sum_l \kappa_l^d Q_l + \frac{1}{2} \sum_l \Omega_l^2 Q_l^2, \quad (2.9a)$$

$$V_{kk}(Q) = \varepsilon_k + \sum_l \kappa_l^a Q_l + \frac{1}{2} \sum_l \Omega_l^2 Q_l^2, \quad (2.9b)$$

where ε_d and ε_k denote the energy of the donor and acceptor states (at the equilibrium geometry of the ground state), respectively, which are obtained from an electronic structure calculation of the overall system. The electronic-vibrational coupling constants κ_l^d and κ_l^a are obtained from the gradients of the excited state of the neutral dye molecule (corresponding to the donor state) and the ground state of the cation of the dye (corresponding to the acceptor states) at the equilibrium geometry of the ground state of neutral dye.

In the results presented below, we will also consider the purely electronic dynamics that is obtained if the nuclear degrees of freedom are frozen at their equilibrium position. The corresponding approximate electronic Hamiltonian is given by

$$H_{\text{elec}} = |\psi_d\rangle \varepsilon_d \langle \psi_d| + \sum_k |\psi_k\rangle \varepsilon_k \langle \psi_k| + \sum_k (|\psi_d\rangle V_{dk} \langle \psi_k| + |\psi_k\rangle V_{kd} \langle \psi_d|). \quad (2.10)$$

D. Observables of interest and dynamical method

Several observables are of interest to analyze heterogeneous ET reactions in dye-semiconductor systems. The ET dynamics is most directly reflected by the time-dependent population of the donor state

$$P_d(t) = \frac{\text{Tr}[e^{-\beta H_{\text{nuc},g}} |\psi_d\rangle \langle \psi_d| e^{iHt} |\psi_d\rangle \langle \psi_d| e^{-iHt}]}{\text{Tr}[e^{-\beta H_{\text{nuc},g}}]}. \quad (2.11)$$

Thereby, we have assumed that the system is initially prepared by an ultrashort laser pulse in the donor state $|\psi_d\rangle$. The initial state of the nuclear degrees of freedom is specified by the Boltzmann operator $e^{-\beta H_{\text{nuc},g}}$ of the nuclear Hamiltonian in the electronic ground state

$$H_{\text{nuc},g} = T_{\text{nuc}} + \frac{1}{2} \sum_l \Omega_l^2 Q_l^2. \quad (2.12)$$

If the coupling to the nuclear degrees of freedom is neglected, i.e., purely electronic dynamics is considered, the time-evolution of the population of the donor state takes the simpler form

$$P_d(t) = |\langle \psi_d | e^{-iH_{\text{elec}} t} | \psi_d \rangle|^2. \quad (2.13)$$

To analyze vibronic effects, we will also consider the absorption spectrum,

$$I(\omega) \sim \frac{\omega}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{\mu\mu}(t), \quad (2.14)$$

which is given by the Fourier transform of the dipole correlation function

$$C_{\mu\mu}(t) = \frac{1}{Z} \text{Tr}[e^{-\beta \hat{H}} [\hat{\mu}(t), \hat{\mu}]]. \quad (2.15)$$

Here, $\hat{\mu}$ denotes the transition dipole operator

$$\hat{\mu} = |\psi_d\rangle \mu_0 \langle \psi_g| + |\psi_g\rangle \mu_0 \langle \psi_d| \quad (2.16)$$

and we have used

$$\hat{\mu}(t) = e^{i\hat{H}t} \hat{\mu} e^{-i\hat{H}t}, \quad Z = \text{Tr}[e^{-\beta \hat{H}}]. \quad (2.17)$$

In Eq. (2.16), we have assumed that the transition dipole operator depends only weakly on the nuclear coordinates (Condon approximation) and direct excitations from the ground state of the dye adsorbate to the conduction band of the semiconductor can be neglected. In the systems considered below, due to the relatively large energy difference between the ground and photoexcited donor states, we can invoke the approximation

$$e^{-\beta \hat{H}} \approx e^{-\beta \hat{H}_{\text{nuc},g}} |\psi_g\rangle \langle \psi_g|, \quad Z \approx \text{Tr}[e^{-\beta \hat{H}_{\text{nuc},g}}], \quad (2.18)$$

which corresponds to a factorized initial state. The extension of the method to simulate quantum dynamics in the condensed phase for a correlated initial state is described in Ref. 92.

To simulate the quantum dynamics, we use the ML formulation⁷⁶ of the MCTDH method^{93–97} in combination with an importance sampling scheme⁹² to describe the thermal initial conditions. The method as well as applications to different reactions in the condensed phase have been described in detail previously.^{49,76,97,98} Here, we only briefly introduce the general idea and give some details specific to the application in this work.

The ML-MCTDH theory⁷⁶ is a rigorous variational method to propagate wave packets in complex systems with many degrees of freedom. In this approach, the wave function is represented by a recursive, layered expansion,

$$|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} \dots \sum_{j_p} A_{j_1 j_2 \dots j_p}(t) \prod_{\kappa=1}^p |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle, \quad (2.19a)$$

$$|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{i_1} \sum_{i_2} \dots \sum_{i_{Q(\kappa)}} B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle, \quad (2.19b)$$

$$|v_{i_q}^{(\kappa, q)}(t)\rangle = \sum_{\alpha_1} \sum_{\alpha_2} \dots \sum_{\alpha_{M(\kappa, q)}} C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, i_q}(t) \prod_{\gamma=1}^{M(\kappa, q)} |\xi_{\alpha_\gamma}^{\kappa, q, \gamma}(t)\rangle, \quad (2.19c)$$

where $A_{j_1 j_2 \dots j_p}(t)$, $B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t)$, $C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, i_q}(t)$, etc., are the expansion coefficients for the first, second, third layers, etc., respectively; $|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle$, $|v_{i_q}^{(\kappa, q)}(t)\rangle$, $|\xi_{\alpha_\gamma}^{\kappa, q, \gamma}(t)\rangle$, etc., are the single particle functions (SPFs) for the first, second,

third layers, etc., respectively. The notations beyond the first layer are as follows. In Eq. (2.19b) $Q(\kappa)$ is the number of (level 2) single particle (SP) groups for the second layer that belong to the κ th (level 1) SP group in the first layer, i.e., there are a total of $\sum_{\kappa=1}^p Q(\kappa)$ second layer SP groups. Continuing along the multilayer hierarchy, $M(\kappa, q)$ in Eq. (2.19c) is the number of (level 3) SP groups for the third layer that belong to the q th (level 2) SP group of the second layer and the κ th (level 1) SP group of the first layer, resulting in a total of $\sum_{\kappa=1}^p \sum_{q=1}^{Q(\kappa)} M(\kappa, q)$ third layer SP groups. Such a recursive expansion can be carried out to an arbitrary number of layers. To terminate the multilayer hierarchy at a particular level, the SPFs in the deepest layer are expanded in terms of time-independent configurations. For example, in the four-layer version of the ML-MCTDH theory, the fourth layer is expanded in the time-independent basis functions/configurations, each of which may still contain several Cartesian degrees of freedom.

Applying the Dirac-Frenkel variational principle,

$$\langle \delta \Psi(t) | i \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle = 0 \quad (2.20)$$

with the functional form in Eq. (2.19), the equations of motion can be obtained as

$$i|\dot{\Psi}(t)\rangle_{L1 \text{ coefficients}} = \hat{H}(t)|\Psi(t)\rangle, \quad (2.21a)$$

$$i|\dot{\underline{\psi}}^{(\kappa)}(t)\rangle_{L2 \text{ coefficients}} = [1 - \hat{P}^{(\kappa)}(t)][\hat{\rho}^{(\kappa)}(t)]^{-1} \langle \hat{H}^{(\kappa)}(t) | \underline{\varphi}^{(\kappa)}(t) \rangle, \quad (2.21b)$$

$$i|\dot{\underline{v}}^{(\kappa,q)}(t)\rangle_{L3 \text{ coefficients}} = [1 - \hat{P}_{L2}^{(\kappa,q)}(t)][\hat{\underline{q}}_{L2}^{(\kappa,q)}(t)]^{-1} \times \langle \hat{\mathcal{H}}_{L2}^{(\kappa,q)}(t) | \underline{v}^{(\kappa,q)}(t) \rangle, \quad (2.21c)$$

$$i|\dot{\underline{\xi}}^{(\kappa,q,\gamma)}(t)\rangle_{L4 \text{ coefficients}} = [1 - \hat{P}_{L3}^{(\kappa,q,\gamma)}(t)][\hat{\underline{q}}_{L3}^{(\kappa,q,\gamma)}(t)]^{-1} \times \langle \hat{\mathcal{H}}_{L3}^{(\kappa,q,\gamma)}(t) | \underline{\xi}^{(\kappa,q,\gamma)}(t) \rangle, \quad (2.21d)$$

...

where the mean-field operators, reduced densities, and projection operators are defined in Ref. 76. For clarity we refer to the top layer as the level one (L1) SP space, the second layer as the level 2 (L2) SP space, etc. The time derivatives in Eq. (2.21), denoted by a overhead dot on the left-hand side of each equation, are meant to be carried out only with respect to the expansion coefficients of a particular layer appeared in that equation. For example, the time derivative in Eq. (2.21a) acts only on the L1 expansion coefficient $A_{j_1 j_2 \dots j_p}(t)$; the time derivative in Eq. (2.21b) is only on the L2 expansion coefficient $B_{i_1 i_2 \dots i_{Q(\kappa)}}^{(\kappa, j_k)}(t)$; etc. Note that for an N -layer version, there are $(N + 1)$ levels of expansion coefficients because the SPFs in the deepest layer need to be expanded in time-independent basis functions/configurations. In this sense, the conventional wavepacket propagation method is a “zero-layer” MCTDH approach.

The inclusion of several dynamically optimized layers in the ML-MCTDH method provides more flexibility in the variational functional, which significantly advances the capabilities of performing wavepacket propagations in complex systems. This has been demonstrated by several applications to quantum dynamics in the condensed phase including many degrees of freedom.^{49,66,68,76,92,98–101} Further development is being pursued to incorporate more general forms of potential energy surfaces as well as to obtain a recursive implementation of the ML-MCTDH with an arbitrary number of layers.^{102,103} The method has also been implemented recently in the Heidelberg MCTDH package.¹⁰⁴

We note that the ML-MCTDH method, as the original MCTDH method, is particularly well suited to accurately simulate the quantum dynamics of ultrafast processes. For longer times more and more single particle functions have to be included in the calculation to achieve convergence, thus making the method less efficient. Considering, for example, electronically nonadiabatic dynamics, where the smallest (electronic) timescale is on the order of a femtosecond, the ML-MCTDH method can be applied efficiently for timescales of a few hundred femtoseconds up to about a picosecond.¹⁰⁵ For processes that take place on an even longer time scale, a rate (kinetic) description is often more appropriate. In this case, one may apply the ML-MCTDH method to calculate the reactive flux correlation function and then obtain the rate constant. Examples for application of the ML-MCTDH method to such processes include the calculation of rates for electron transfer¹⁰⁶ as well as proton transfer¹⁰⁷ reactions.

III. RESULTS AND DISCUSSION

A. Characterization of the systems

The methodology outlined in Sec. II has been applied to study electron transfer reactions in three different dye-semiconductor systems which are depicted in Figure 1. In each system, a bulky $(\text{TiO}_2)_{60}$ cluster is used to model the semiconductor substrate. All dye molecules investigated contain a perylene chromophore group which is directly or indirectly bound to the titanium dioxide substrate via a carboxylic-acid anchor group. To study the influence of spacer groups on the ET dynamics, two different groups, $-\text{CH}=\text{CH}-$ and $-\text{CH}_2-\text{CH}_2-$, were selected and inserted between the perylene chromophore and the carboxylic-acid group, thus resulting in an acrylic-acid and a propionic-acid anchor group. They represent examples for unsaturated and saturated aliphatic spacer groups, respectively. The thus obtained three different dyes are denoted by PeCOOH , $\text{PeCH}=\text{CHCOOH}$, and $\text{PeCH}_2\text{CH}_2\text{COOH}$ in the following. The structure and stability of various binding motifs of carboxylic acid at TiO_2 substrates have been studied, e.g., in Refs. 57 and 70–72. Since the differences of the adsorption energies between the different binding motifs are rather small, it is expected that several binding motifs will coexist.^{69,108} In the present work, we have considered in all cases a bidentate dissociative bridge binding between the adsorbate and the substrate. The proton detached from the carboxylic-acid group is attached to a surface oxygen atom.

FIG. 1. The three dye-semiconductor complexes investigated: (a) $\text{PeCOOH}-(\text{TiO}_2)_{60}$, (b) $\text{PeCH=CHCOOH}-(\text{TiO}_2)_{60}$, and (c) $\text{PeCH}_2\text{CH}_2\text{COOH}-(\text{TiO}_2)_{60}$.

The structures of the three investigated dye-semiconductor systems were obtained according to the following protocol:⁶² (i) The local structure of the interface between the TiO_2 cluster and the various sensitizers was optimized using a smaller $(\text{TiO}_2)_5(\text{H}_2\text{O})_5$ cluster model.

In this step, relaxation of the local surface environment including the substrate atoms in the vicinity of the adsorbate was allowed in the optimization. (ii) The $(\text{TiO}_2)_{60}$ cluster was optimized. (iii) The structure of dye-semiconductor interface obtained in step (i) is adopted at the surface of the

optimized $(\text{TiO}_2)_{60}$ cluster. The geometry optimization was performed using DFT with the PW86 exchange functional and the PW91 correlation functional¹⁰⁹ together with a Slater-type orbital valence single-zeta basis set as well as large frozen cores implemented in the ADF package.¹¹⁰ It is noted, that the $(\text{TiO}_2)_{60}$ cluster employed in the present study is considered as a model for a small nanoparticle and not an extended surface. The dependence of the geometric and electronic structure of TiO_2 clusters on their size as well as the difference to extended TiO_2 surfaces is discussed in detail in Ref. 65.

The electronic structure calculations of the investigated dye-semiconductor systems were carried out with DFT using the GAUSSIAN 03 package¹¹¹ with the B3LYP functional¹¹² and a split-valence basis set with large effective core potentials¹¹³ describing the core electrons. Here, a Gaussian-type orbital valence double-zeta (VDZ) basis set was used to describe all atoms, except that an additional diffuse sp shell for oxygen is included in the basis set in order to allow a realistic description of the negative ions in the nanocrystals with significant ionic character. This method, denoted by B3LYP/VD(T)Z, has proved capable to give good results in describing the electronic structure of systems comprising organic adsorbates on TiO_2 surfaces.⁴³

The characterization of the nuclear degrees of freedom of the isolated dye molecules, which includes geometry optimization in the electronic ground state of the neutral molecule, determination of the corresponding normal modes as well as the calculation of the energy gradients along the normal modes in the first electronically excited state and the ground state of the cation, were performed with DFT using the TURBOMOLE package¹¹⁴ with the B3LYP functional and the TZV(P) basis set.

B. Energy-level scheme, donor-acceptor separation, and coupling matrix elements

To discuss the donor-acceptor partitioning, we first consider the energy-level scheme. Figure 2 shows energies of the molecular orbitals (MOs) of the overall dye- TiO_2 complexes as well as those of the donor and acceptor orbitals obtained from the partitioning procedure for the three systems investigated. For each system, the MO-energies (shown in the middle panel of the corresponding subfigure) exhibit a dense level structure with a valence and a conduction band separated by a bandgap. In addition, for each system there is one isolated level in the bandgap, which is the highest occupied molecular orbital (HOMO) of the overall complex. The calculated value for the bandgap is 3.1 eV, which is somewhat smaller than experimental value (3.4 eV (Ref. 115)) for anatase TiO_2 nanoparticles.

The partitioning procedure results in donor and acceptor orbitals that are localized in the adsorbate and the $(\text{TiO}_2)_{60}$ substrate, respectively. The energy-level scheme of the acceptor orbitals shows a structure very similar to that of the isolated $(\text{TiO}_2)_{60}$ cluster.⁶² In all systems considered, a single energy level located in the bandgap is obtained. The orbital of this energy level is localized in the adsorbate, and, therefore, results within the partitioning procedure in a donor or-

bit, which is associated with the HOMO of the corresponding isolated dye molecule. The energy of this donor level is very close to the energy of the HOMO in the complex, indicating almost negligible interaction with the substrate. This is corroborated by the fact that the overlap of this donor orbital with the HOMO of the complex is larger than 0.99.

The energies of the orbitals that correspond to the lowest unoccupied orbitals of the dye, on the other hand, are located in the conduction band of TiO_2 in all systems considered. As a consequence, these levels are dissolved in the dense manifold of conduction-band levels of TiO_2 . In the dynamical calculations discussed below, we have chosen the lowest donor orbital in the conduction band, which corresponds to the LUMO of the isolated dye molecule, as the donor state $|\psi_d\rangle$. The TD-DFT calculations for the isolated dye molecules indicate that the first excited state of perylene corresponds almost exclusively to the HOMO-LUMO excitation.^{62,116} Therefore, the use of the LUMO as a model for the excited state is well justified in these systems.

An important parameter for the ET process is the energy of the donor state relative to the conduction-band minimum of TiO_2 . For PeCOOH-TiO_2 and PeCH=CHCOOH-TiO_2 , the energy of the donor state is close to the conduction-band minimum, while it is well above the conduction-band minimum in $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$. This result can be rationalized by the coupling strength between the chromophore and the substrate for the different anchor groups (carboxylic acid, acrylic acid, and propionic acid): The coupling via the propionic-acid anchor group is significantly weaker and results in a higher donor level as compared to both carboxylic-acid and acrylic-acid bridge.

The local character of the frontier orbitals for the investigated systems and the resemblance between them and the corresponding orbitals (HOMO and LUMO) of the isolated dye molecules are illustrated in Figures 3 and 4, respectively. The comparison shows that the localized orbital associated with the HOMO is almost identical to the HOMO of the corresponding isolated dye molecule and also to the HOMO of the complex (data not shown), thus indicating that this orbital has negligible interaction with the TiO_2 substrate. On the other hand, all acceptor orbitals are localized in the TiO_2 substrate (data not shown). For both $\text{PeCOOH-(TiO}_2)_{60}$ and $\text{PeCH=CHCOOH-(TiO}_2)_{60}$, the localized orbital associated with the LUMO of the isolated dye molecule, which constitutes the donor state of the ET reaction, shows noticeable contribution at the anchor bridge. For $\text{PeCH=CHCOOH-(TiO}_2)_{60}$, the localized orbital associated with the LUMO of the isolated dye molecule shows also pronounced contribution at the spacer group $-\text{CH=CH}-$. In contrast, in $\text{PeCH}_2\text{CH}_2\text{COOH-(TiO}_2)_{60}$, the localized orbital which is associated with the LUMO of $\text{PeCH}_2\text{CH}_2\text{COOH}$ is almost completely localized in the perylene chromophore.

Another key parameter for ET reactions is the strength of the donor-acceptor coupling. Figure 5 shows the modulus of the donor-acceptor coupling matrix elements V_{dk} for the three systems (note that the scale of the V_{dk} -axis for $\text{PeCH}_2\text{CH}_2\text{COOH-(TiO}_2)_{60}$ is different to that for the other two systems). The first-principles-based models result in a distribution of donor-acceptor coupling matrix elements V_{dk}

FIG. 2. Energy-level schemes of the investigated dye-semiconductor complexes: (a) PeCOOH , (b) PeCH=CHCOOH , and (c) $\text{PeCH}_2\text{CH}_2\text{COOH}$ adsorbed at the $(\text{TiO}_2)_{60}$ substrate. From left to right in each subfigure: energy levels of the donor orbitals (obtained from the partitioning procedure) which are localized in the adsorbate, energy levels of the overall complex, and energy levels of the acceptor orbitals (obtained from the partitioning procedure) which are localized in the semiconductor substrate. The selected donor state $|\psi_d\rangle$ as well as the correlations among some energy levels relevant for the ET reaction are indicated.

that exhibits a rather complex structure. The overall strength of the donor-acceptor coupling varies for the three systems. Thereby, the major effect is caused by the spacer group. The system with the perylene chromophore bound to the substrate directly via the carboxylic-acid anchor group shows the strongest donor-acceptor coupling, while the donor-acceptor coupling for the system containing the unsaturated $-\text{CH=CH}-$ spacer group between the perylene chromophore and the carboxylic-acid anchor group is slightly weaker. The donor-acceptor coupling for the system containing the saturated $-\text{CH}_2\text{CH}_2-$ spacer group between the perylene chromophore and the carboxylic-acid anchor group, on the other

hand, is significantly weaker than that of the other two systems. This is in accordance with previous studies^{53,69} and the different character of the donor orbitals in the various systems as discussed above.

For an extended substrate, the donor-acceptor coupling is characterized by the decay-width function $\Gamma(\varepsilon)$ given by Eq. (2.6). The results for $\Gamma(\varepsilon)$, depicted by the solid blue lines in Figure 5, show significant structures. For the system without spacer group, the details of the structures of $\Gamma(\varepsilon)$ are somewhat different from the results of our previous study.⁶⁷ In particular, in the previous study the maximum of $\Gamma(\varepsilon)$ at $\varepsilon_k \approx -2$ eV was more pronounced and the maximum close to

FIG. 3. Selected localized adsorbate orbitals (as obtained from the partitioning procedure) of the investigated systems (a) $\text{PeCOOH}-(\text{TiO}_2)_{60}$, (c) $\text{PeCH}=\text{CHCOOH}-(\text{TiO}_2)_{60}$, and (e) $\text{PeCH}_2\text{CH}_2\text{COOH}-(\text{TiO}_2)_{60}$ that are associated with the HOMO of corresponding isolated dye molecules (b) PeCOOH , (d) $\text{PeCH}=\text{CHCOOH}$, and (f) $\text{PeCH}_2\text{CH}_2\text{COOH}$.

the energy of the donor state, ε_d , appeared only as a shoulder. This difference is presumably related to the different binding mode considered (monodentate molecular versus bidentate dissociative binding). The bidentate binding motif results also in the additional peak at $\varepsilon_k \approx -4$ eV, which is caused by an orbital localized at a titanium atom bonded to the

FIG. 4. Selected localized adsorbate orbitals (as obtained from the partitioning procedure) of the investigated systems (a) $\text{PeCOOH}-(\text{TiO}_2)_{60}$, (c) $\text{PeCH}=\text{CHCOOH}-(\text{TiO}_2)_{60}$, and (e) $\text{PeCH}_2\text{CH}_2\text{COOH}-(\text{TiO}_2)_{60}$ that are associated with the LUMO of corresponding isolated dye molecules (b) PeCOOH , (d) $\text{PeCH}=\text{CHCOOH}$, and (f) $\text{PeCH}_2\text{CH}_2\text{COOH}$.

dye molecule. The trend of the overall chromophore-substrate coupling strength represented by $\Gamma(\varepsilon)$ is in accordance with previous studies,⁵³ where the value of the coupling strength was fitted to reproduce experimental results for the absorption spectrum. The results obtained from our first-principles

FIG. 5. Modulus of donor-acceptor electronic coupling matrix elements V_{dk} (discrete lines) and the decay-width function $\Gamma(\varepsilon)$ (continuous line) of (a) $\text{PeCOOH}-(\text{TiO}_2)_{60}$, (b) $\text{PeCH}=\text{CHCOOH}-(\text{TiO}_2)_{60}$, and (c) $\text{PeCH}_2\text{CH}_2\text{COOH}-(\text{TiO}_2)_{60}$. For each system, the red vertical line indicates the energy of the donor state ε_d .

calculations are in very good agreement with these previous semiempirical results for the systems $\text{PeCOOH}-(\text{TiO}_2)_{60}$ and $\text{PeCH}=\text{CHCOOH}-(\text{TiO}_2)_{60}$ (note that there is a factor of two difference in the definition of $\Gamma(\varepsilon)$ between Eq. (2.6) and Ref. 53). For the system $\text{PeCH}_2\text{CH}_2\text{COOH}-(\text{TiO}_2)_{60}$ with the saturated anchor group, however, our first-principles results are significantly smaller than the semiempirical results. This results in a longer ET time, which is in better agreement with experiment (see below).

C. Electron transfer dynamics and influence of spacer groups

The ET dynamics of the three systems were simulated based on the first-principles model outlined in Sec. II. Thereby, the donor state and all localized acceptor states associated with unoccupied orbitals of the isolated semiconductor cluster were included in the simulation. We first consider the influence of the spacer groups on the ET dynamics. To this end, we employ a purely electronic model, Eq. (2.10), where the nuclear degrees of freedom are frozen at their equilibrium geometry.

Figure 6 shows the dynamics of the population of the donor state for all systems. The decay of the population re-

FIG. 6. Population dynamics of the donor state after photoexcitation in the investigated systems PeCOOH-TiO_2 (black lines), $\text{PeCH}=\text{CHCOOH-TiO}_2$ (red lines), and $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ (blue lines). Shown are results obtained for the finite $(\text{TiO}_2)_{60}$ cluster (thick lines) and for the model of an infinite TiO_2 surface (thin lines). All results are obtained for a purely electronic model, i.e., neglecting electronic-vibrational coupling.

flects the injection of the electron from the chromophore into the (quasi-)continuum of acceptor states in the TiO_2 substrate. All systems exhibit an ultrafast initial decay of the population of the donor state. The timescale of this initial decay as well as the character of the long-time dynamics depend on the specific system. In PeCOOH-TiO_2 and $\text{PeCH}=\text{CHCOOH-TiO}_2$, the population of the donor state decays within a few femtoseconds to a value of about 0.1, while the injection process in $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ is significantly slower. These findings can be rationalized by the energy-level structure and the donor-acceptor coupling strength discussed in Sec. III B. As shown in Figures 2 and 5, the position of the donor level with respect to the conduction-band minimum and the strength of the donor-acceptor coupling are both very similar in the dye-semiconductor systems PeCOOH-TiO_2 and $\text{PeCH}=\text{CHCOOH-TiO}_2$. This results in similar ET dynamics in these two systems. In $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$, on the other hand, the donor-acceptor coupling is much weaker resulting in a significantly slower injection dynamics.

Following the ultrafast decay, the results for PeCOOH-TiO_2 and $\text{PeCH}=\text{CHCOOH-TiO}_2$ show pronounced oscillatory structures. In $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$, due to the smaller chromophore-surface coupling, these oscillations are less pronounced and occur on a longer time scale. The oscillatory structures are a result of the finite TiO_2 cluster considered and are caused by the reflection of the electronic wavepackets at the boundary of the TiO_2 cluster. This is demonstrated by the thin lines in Fig. 6, which show the corresponding results for an extended TiO_2 substrate modeled by including absorbing boundary conditions as discussed in Sec. II B. The results for the extended TiO_2 substrate follow those for the finite TiO_2 cluster for short times. For longer times, however, they do not exhibit oscillation and decay to zero, thus reflecting a complete electron injection process.

Traditionally, ET processes have been characterized by a single rate constant. Thereby, different concepts can be employed. In Table I, we compare the Golden-Rule rate $\Gamma(\varepsilon_d)$ for the ET process to the long-time limit rate constant $k = -\lim_{t \rightarrow +\infty} \dot{P}_d(t)/P_d(t)$ and to the τ_{e-1} time, by which the

TABLE I. Characteristic times of the electron injection processes in the investigated systems. The definition of the different time scales is given in the text. All data are given in fs.

Adsorbate	PeCOOH	PeCH=CHCOOH	PeCH ₂ CH ₂ COOH
Finite (TiO ₂) ₆₀ cluster			
τ_{e-1}	5.2	6.4	43.2
Extended TiO ₂ surface			
τ_{e-1}	5.8	6.4	47.4
k^{-1}	5.0	5.9	47.2
$(\Gamma(\epsilon_d))^{-1}$	5.3	5.8	47.3
Previous studies finite TiO ₂ cluster (Ref. 62)			
$\tilde{\tau}$	5	6	33
Experiments (Refs. 23 and 62)	13	10	57

population of the donor state has decayed to a value of e^{-1} . While the former rate concepts can only be defined for the extended TiO₂ substrate, the τ_{e-1} time can also be obtained for the finite TiO₂ cluster. The results for the different rates show very good agreement, indicating that for an extended TiO₂ substrate the ET process can be approximately characterized by a single rate constant.

The ET dynamics is influenced by the adsorption geometry of the dye at the TiO₂ cluster. This becomes apparent when comparing the results of the present study, where a bidentate binding motif is considered, to that of the monodentate binding considered in our previous study⁶⁷ for the system PeCOOH-TiO₂. The bidentate adsorption geometry facilitates a faster ET process ($\tau_{e-1} \approx 6$ fs) compared to the monodentate binding ($\tau_{e-1} \approx 9 - 16$ fs).⁶⁷

The ET time constants obtained in the present work are also in rather good agreement with previous studies,⁶² where the electron injection rate for the investigated systems was characterized based on the lifetime broadening of the donor state (cf. Table I) as well as with the semiempirical studies mentioned above⁵³ and with first-principles studies of Troisi *et al.*⁷¹ Significant deviations to the latter two studies occur for the system with the longest ET time, PeCH₂CH₂COOH-TiO₂, where the present time-dependent studies based on a first-principle description show a better agreement with experimental results.

We finally compare the ET time scales obtained in the present study to experimental results from transient absorption spectroscopy in ultrahigh vacuum.^{23,62} Table I shows that the overall trend of the ET timescale

$$\begin{aligned} \tau(\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2) &> \tau(\text{PeCOOH-TiO}_2) \\ &\approx \tau(\text{PeCH=CHCOOH-TiO}_2) \end{aligned}$$

is in agreement with the experimental results. However, for all systems considered, the injection rates obtained from experimental studies are somewhat slower than the theoretical results. In view of the fact that the details of the systems considered in the experimental and theoretical investigations dif-

fer, e.g., in the TiO₂ substrate and additional side groups at the chromophore, the agreement is rather good.

In summary, the theoretical simulations of the ET dynamics for different spacer groups show, in agreement with experimental results, that saturated aliphatic spacer groups result in a slower ET dynamics and thus act as an insulator for electron transport from the chromophore to the substrate. Unsaturated aliphatic spacer groups, on the other hand, provide a molecular wire for electrons and have little influence on the ET time. This finding is in accordance with previous studies on photoinduced ET in self-assembled molecular layer at surfaces^{117,118} as well as electron transport in molecular junctions.¹¹⁹

D. Influence of electronic-vibrational coupling on ET dynamics and absorption spectrum

An important mechanism in ET reactions is the coupling of the electron to the nuclear degrees of freedom. Previous theoretical studies of heterogeneous ET in dye-semiconductor systems show that electronic-vibrational coupling may have a significant effect on the ET dynamics, in particular, if the donor state is located close to the conduction band minimum.^{48,49,60} Experimental studies for perylene-based dye molecules bound via phosphonic acid anchor groups to TiO₂ revealed vibrational structures in femtosecond pump-probe spectra, which were interpreted as a steplike electron injection process.¹¹

To study the influence of vibronic effects, we consider as an example the system PeCH₂CH₂COOH-TiO₂, which among the systems considered has the longest ET time. The other two systems investigated have electron transfer times of less than 10 fs and, therefore, vibronic effects are expected to be less important.

The vibrational frequencies Ω_l and the corresponding electronic-vibrational coupling constants $\kappa_l^{d/a}$ in the donor and acceptor states have been determined for all 117 vibrational normal modes of the isolated dye molecule PeCH₂CH₂COOH as described in Sec. II C. For the l th normal mode, the electronic-vibrational coupling constants are related to reorganization energies via

$$\lambda_l^d = \frac{(\kappa_l^d)^2}{2\Omega_l^2}, \quad (3.1a)$$

$$\lambda_l^a = \frac{(\kappa_l^a)^2}{2\Omega_l^2}, \quad (3.1b)$$

which are associated with transitions from the electronic ground state to the excited state and the cation of PeCH₂CH₂COOH, respectively. The reorganization energy for the ET process for the l th normal mode, which corresponds to the transition from the excited state of the chromophore to the cation, is given by

$$\lambda_l^{\text{ET}} = \frac{(\kappa_l^d - \kappa_l^a)^2}{2\Omega_l^2}. \quad (3.1c)$$

FIG. 7. Reorganization energies of the intramolecular modes of $\text{PeCH}_2\text{CH}_2\text{COOH}$ associated with (a) the transition from the ground to the electronically excited state and (b) the ET transition.

The corresponding total reorganization energies are given by the sum $\Lambda^{d/a/ET} = \sum_l \lambda_l^{d/a/ET}$. The calculated frequencies and reorganization energies for the donor state and the ET transition are depicted in Figure 7. It is seen that the electronic-vibrational coupling is distributed over a rather large number of vibrational modes. The overall reorganization energies obtained are $\Lambda^d = 0.188\text{eV}$, $\Lambda^a = 0.096\text{ eV}$, and $\Lambda^{ET} = 0.040\text{ eV}$ for the donor state, the acceptor state, and the ET transition, respectively. These values for the reorganization energies suggest a moderate electronic-vibrational coupling with respect to excitation but rather weak coupling to the ET process.

We first consider the influence of the vibrational degrees of freedom on the absorption spectrum. The absorption spectrum of $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ at $T = 300\text{ K}$ has been simulated according to Eq. (2.14) employing absorbing boundary conditions and including all 117 vibrational normal modes of $\text{PeCH}_2\text{CH}_2\text{COOH}$. The spectrum depicted in Figure 8 exhibits pronounced vibronic structures. The first maximum of the spectrum (marked “0”) corresponds predominantly to the $0 \rightarrow 0$ transition. The structures marked by “1,” “2,” and “3” can be assigned to contribution from several vibrational modes as described in Table II. These modes, which are depicted in Figure 9, have significant reorganization energies for excitation, λ_l^d , while their reorganization energies with respect to ionization and, in particular, to ET are rather small. The structures at higher energies, e.g., the broad peak at about

FIG. 8. Absorption spectrum of $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$.

$25\,000\text{ cm}^{-1}$, are due to $0 \rightarrow n$ ($n > 1$) transitions of the above mentioned modes as well as combinations of transitions involving several modes.

The absorption spectra of similar perylene-based systems adsorbed at TiO_2 substrates in solution have been studied experimentally and analyzed in detail based on a semiempirical model previously.⁵³ Overall, the result of our first-principle based calculations is in good agreement with the experimental results. In contrast to the simulated spectrum, however, the experimental spectrum exhibits its maximal value not at the $0 \rightarrow 0$ transition but at higher energies. This difference is presumably related to the fact that the vibrational parameters for our model have been obtained for the isolated dye molecule, thereby neglecting the influence of the binding to the TiO_2 substrate on the vibrational frequencies and vibronic coupling constants. Furthermore, the experiments were carried out in solution and the systems have additional side groups. In contrast to the previous analysis,⁵³ which was based on a single vibrational mode, our study indicates that the vibronic structures in the absorption spectrum are related to several vibrational modes (cf. Table II).

Next, we analyze the influence of electronic-vibrational coupling on the ET dynamics in $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$. Figure 10(a) shows the dynamics of the donor state (solid line) in this system employing all 117 modes of $\text{PeCH}_2\text{CH}_2\text{COOH}$ and a finite cluster model for the TiO_2 substrate. In addition, the results obtained within a purely electronic model (dashed lines), i.e., neglecting electronic-vibrational coupling, is depicted. The comparison shows that the coupling to the vibrational degrees of freedom results in a

TABLE II. Classification of vibronic structures in the absorption spectrum of $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ (Figure 8). Listed are the approximate energy difference between each vibronic structure and the $0 \rightarrow 0$ transition, the frequencies of the corresponding vibrational modes as well as their reorganization energies with respect to excitation, ionization and ET, respectively. All data are given in cm^{-1} .

	$\Delta\omega$	Ω	λ^d	λ^{ET}
1	333	305	53	10
		360	79	6
2	1390	1325	341	39
		1389	171	19
3	1612	1602	486	65

FIG. 9. Vibrational normal modes that are associated with the vibronic structures in the simulated absorption spectrum (Figure 8). The frequencies of the modes are (a) 305 cm^{-1} , (b) 360 cm^{-1} , (c) 1325 cm^{-1} , (d) 1389 cm^{-1} , and (e) 1602 cm^{-1} .

shorter period and a damping of the amplitude of the oscillations related to recurrences of the electronic wavepacket. However, there is only little influence on the initial ET dynamics and the ET timescale. The results obtained for an extended TiO_2 substrate, depicted in Figure 10(b), show even less influence of the vibronic coupling on the dynamics of

FIG. 10. Population dynamics of the donor state after photoexcitation in $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$. Shown are results obtained for (a) a finite $(\text{TiO}_2)_{60}$ nanocluster and (b) for a model of an extended TiO_2 substrate. Both results with vibronic coupling (solid lines) and without vibronic coupling (dashed lines) are depicted.

the ET process. These results indicate that vibronic coupling in $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ has negligible direct influence on the ET dynamics. At first glance, this appears to be in contradiction to the observed pronounced vibronic structures in the absorption spectrum. However, as discussed above (cf. Figure 7), the system exhibits significant reorganization energies with respect to excitation but only small electronic-vibrational coupling with respect to the ET transition, thus resulting in significant vibronic effects in excitation but negligible influence on the ET dynamics.

To validate the stability of this finding with respect to variations of the vibronic parameters, we have performed studies where the first-principles-based reorganization energies were scaled to larger values as described in Table III. The results depicted in Figure 11 demonstrate that the finding of negligible vibronic effects on the dynamics of the donor state holds true if the reorganization energies are increased up to a factor of two. For even larger couplings, the results exhibit oscillatory structures in the ET dynamics related to electronic-vibrational coupling to high-frequency modes. An example is the result obtained for model III (thick solid line in Figure 11(b)), where the reorganization energy for excitation was increased by a factor of four, while keeping the reorganization energy for ionization constant. The thus obtained model exhibits a rather large reorganization energy with

TABLE III. Total reorganization energies with respect to excitation (Λ^d), ionization (Λ^a), and ET (Λ^{ET}) of the first-principles-based model as well as the models considered in Figure 11, where the reorganization energies were increased by scaling factors. All data are given in eV.

Model	Λ^d	Λ^a	Λ^{ET}	Legend in Figure 11
First-principles-based model	0.188	0.096	0.040	Thin solid lines in both (a) and (b)
I	0.376	0.192	0.079	(a) Thick dashed line
II	0.751	0.385	0.158	(a) Thick solid line
III	0.751	0.096	0.358	(b) Thick solid line
IV	0.188	0.385	0.084	(b) Thick dashed line

respect to ET. Since a difference of more than a factor of two to the first-principles-based values of the reorganization energies is unlikely, we conclude that the finding of negligible influence of electronic-vibrational coupling on the dynamics of the donor state is robust.

FIG. 11. Population dynamics of the donor state after photoexcitation in model systems for $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$ with increased electronic-vibrational coupling in comparison with the dynamics of the original, first-principles-based model (thin solid lines). The models are defined in Table III. Shown are (a) results, where reorganization energies with respect to excitation, ionization, and ET for all modes are scaled by a factor of 2 (model I, thick dashed line) and 4 (model II, thick solid line), respectively, and (b) results, where the excitation reorganization energy (model III, thick solid line) and the ionization reorganization energy (model IV, thick dashed line) for all modes are scaled by a factor of 4, respectively. All results are obtained for an extended TiO_2 substrate.

IV. CONCLUDING REMARKS

In this paper, we have studied the quantum dynamics of heterogeneous ET processes in perylene- TiO_2 dye-semiconductor systems focusing on the influence of spacer groups. In the investigated systems, different spacer groups are inserted between the perylene chromophore and the carboxylic-acid anchor group, resulting in dye-semiconductor systems with perylene anchored to the TiO_2 substrate via carboxylic-acid, acrylic-acid, or propionic-acid anchor group. The ET dynamics in these systems have been simulated employing a method developed previously, which combines a model based on first-principles electronic structure (DFT) calculations and accurate quantum dynamical simulations using the ML-MCTDH method.

The results show that the electron injection in the three systems investigated occurs on an ultrafast time scale which ranges from a few femtoseconds to a few tens of femtoseconds. The dynamics is significantly influenced by the spacer groups. In particular, carboxylic-acid and acrylic-acid anchor groups provide a stronger donor-acceptor coupling, which extends the π -system of the planar perylene chromophore and results in ET injection processes which are significantly faster than in the system with the nonplanar propionic-acid anchor groups. The time scales obtained in our theoretical study are in rather good agreement with experimental results and are in most cases in accordance with previous theoretical treatments based on rate concepts or semiempirical models. In a more general context, our findings obtained for a specific example show that saturated aliphatic spacer groups result in a slower ET dynamics and thus act as an insulator for electron transport from the chromophore to the substrate. Unsaturated aliphatic spacer groups, on the other hand, provide a molecular wire for electrons and have little influence on the ET time.

We have also studied the influence of electronic-vibrational coupling on the ET dynamics and the absorption spectrum of the dye-semiconductor system with the longest injection time, $\text{PeCH}_2\text{CH}_2\text{COOH-TiO}_2$. In the absorption spectrum, electronic-vibrational coupling results in pronounced vibronic structures. Extending previous theoretical studies on the basis of a semiempirical model with a single reaction mode,⁵³ our first-principles-based simulations including all vibrational modes of the chromophore demonstrate that the vibronic structures in the absorption spectrum are caused by several vibrational modes. The nonadiabatic dynamical simulations show, on the other hand, only little direct effect of electronic-vibrational coupling on the ET dynamics. This is, in particular, the case for systems adsorbed on an extended TiO_2 substrate. In simulations employing a finite TiO_2 cluster, the coupling to the vibrational degrees of freedoms results in a dephasing of electronic coherence effects. The minor importance of vibronic effects in the systems considered are related to the fact that the reorganization energy of the perylene chromophore with respect to ET, i.e., the transition from the electronically excited state of neutral perylene to the ground state of the perylene cation, is rather small.

In the present work, we have employed a model based on a single-electron description, which captures electron-electron interaction only on the mean-field level. The

ML-MCTDH method, employed to simulate the dynamics, has recently been extended to describe many-body electron correlation effects using the second quantization representation of Fock space.¹²⁰ This opens the possibility to study charge transfer dynamics beyond the single-electron picture, which is an interesting topic for future research. The inclusion of electron correlation effects is expected to be particularly important in systems where hole transport is involved¹²¹ or molecular adsorbates on metal surfaces.^{118,122}

ACKNOWLEDGMENTS

We thank Ralph Ernstorfer, Sten Lunell, and Ivan Kondov for helpful discussions. The generous allocation of computing time by the computing centers in Erlangen (RRZE), Munich (LRZ), and Jülich (JSC) is gratefully acknowledged. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) through the DFG-Cluster of Excellence Munich-Centre for Advanced Photonics and a research grant (M.T.), the Swedish Research Council (P.P.), and the Knut and Alice Wallenberg Foundation (P.P.), and the National Science Foundation CHE-1012479 (H.W.).

- ¹J.-E. Moser and M. Grätzel, *Chem. Phys.* **176**, 493 (1993).
- ²A. Hagfeldt and M. Grätzel, *Chem. Rev.* **95**, 49 (1995).
- ³J. M. Rehm, G. L. McLendon, Y. Nagasawa, K. Yoshihara, J.-E. Moser, and M. Grätzel, *J. Phys. Chem.* **100**, 9577 (1996).
- ⁴B. Burfeindt, T. Hannappel, W. Storck, and F. Willig, *J. Phys. Chem.* **100**, 16463 (1996).
- ⁵I. B. Martini, J. Hodak, G. V. Hartland, and P. V. Kamat, *J. Chem. Phys.* **107**, 8064 (1997).
- ⁶H. N. Ghosh, J. B. Asbury, Y. Weng, and T. Lian, *J. Phys. Chem. B* **102**, 10208 (1998).
- ⁷J. Wachtveitl, R. Huber, S. Spörlein, J.-E. Moser, and M. Grätzel, *Int. J. Photoenergy* **1**, 153 (1999).
- ⁸R. Huber, S. Spörlein, J.-E. Moser, M. Grätzel, and J. Wachtveitl, *J. Phys. Chem. B* **104**, 8995 (2000).
- ⁹F. Willig, C. Zimmermann, S. Ramakrishna, and W. Storck, *Electrochim. Acta* **45**, 4565 (2000).
- ¹⁰J. B. Asbury, E. Hao, Y. Wang, H. N. Ghosh, and T. Lian, *J. Phys. Chem. B* **105**, 4545 (2001).
- ¹¹C. Zimmermann, F. Willig, S. Ramakrishna, B. Burfeindt, B. Pettinger, R. Eichberger, and W. Storck, *J. Phys. Chem. B* **105**, 9245 (2001).
- ¹²N. A. Anderson, E. Hao, X. Ai, G. Hastings, and T. Lian, *Chem. Phys. Lett.* **347**, 304 (2001).
- ¹³G. Ramakrishna, H. N. Ghosh, A. K. Singh, D. K. Palit, and J. P. Mittal, *J. Phys. Chem. B* **105**, 12786 (2001).
- ¹⁴G. Ramakrishna and H. N. Ghosh, *J. Phys. Chem. A* **106**, 2545 (2002).
- ¹⁵J. Kallioinen, G. Benkö, V. Sundström, J. E. I. Korppi-Tommola, and A. P. Yartsev, *J. Phys. Chem. B* **106**, 4396 (2002).
- ¹⁶K. A. Walters, D. A. Gaal, and J. T. Hupp, *J. Phys. Chem. B* **106**, 5139 (2002).
- ¹⁷R. Huber, J.-E. Moser, M. Grätzel, and J. Wachtveitl, *J. Phys. Chem. B* **106**, 6494 (2002).
- ¹⁸J. Schnadt, P. A. Brühwiler, L. Patthey, J. N. O'Shea, S. Södergren, M. Odelius, R. Ahuja, O. Karis, M. Bäessler, P. Persson, H. Siegbahn, S. Lunell, and N. Mårtensson, *Nature (London)* **418**, 620 (2002).
- ¹⁹R. Huber, J.-E. Moser, M. Grätzel, and J. Wachtveitl, *Chem. Phys.* **285**, 39 (2002).
- ²⁰K. Takeshita, Y. Sasaki, M. Kobashi, Y. Tanaka, S. Maeda, A. Yamakata, T. Ishibashi, and H. Onishi, *J. Phys. Chem. B* **107**, 4156 (2003).
- ²¹N. A. Anderson and T. Lian, *Annu. Rev. Phys. Chem.* **56**, 491 (2005).
- ²²V. V. Matyilitsky, M. O. Lenz, and J. Wachtveitl, *J. Phys. Chem. B* **110**, 8372 (2006).
- ²³R. Ernstorfer, L. Gundlach, S. Felber, W. Storck, R. Eichberger, and F. Willig, *J. Phys. Chem. B* **110**, 25383 (2006).
- ²⁴L. Dworak, V. V. Matyilitsky, and J. Wachtveitl, *ChemPhysChem* **10**, 384 (2009).
- ²⁵D. Stockwell, Y. Yang, J. Huang, C. Anuso, Z. Huang, and T. Lian, *J. Phys. Chem. C* **114**, 6560 (2010).
- ²⁶H. Némec, J. Rochford, O. Taratula, E. Galoppini, P. Kužel, T. Polvka, A. P. Yartsev, and V. Sundström, *Phys. Rev. Lett.* **104**, 197401 (2010).
- ²⁷B. O'Regan and M. Grätzel, *Nature (London)* **353**, 737 (1991).
- ²⁸A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.* **33**, 269 (2000).
- ²⁹M. Grätzel, *Nature (London)* **414**, 338 (2001).
- ³⁰G. Benkö, J. Kallioinen, J. E. I. Korppi-Tommola, A. P. Yartsev, and V. Sundström, *J. Am. Chem. Soc.* **124**, 489 (2002).
- ³¹W. R. Duncan and O. V. Prezhdo, *Annu. Rev. Phys. Chem.* **58**, 143 (2007).
- ³²I. Kondov, V. Vallet, H. Wang, and M. Thoss, *J. Phys. Chem. A* **112**, 5467 (2008).
- ³³O. V. Prezhdo, W. R. Duncan, and V. V. Prezhdo, *Acc. Chem. Res.* **41**, 339 (2008).
- ³⁴N. Martsinovich and A. Troisi, *Energy Environ. Sci.* **4**, 4473 (2011).
- ³⁵S. Ramakrishna and F. Willig, *J. Phys. Chem. B* **104**, 68 (2000).
- ³⁶Å. Petersson, M. A. Ratner, and H. O. Karlsson, *J. Phys. Chem. B* **104**, 8498 (2000).
- ³⁷P. Persson, R. Bergström, and S. Lunell, *J. Phys. Chem. B* **104**, 10348 (2000).
- ³⁸S. Ramakrishna, F. Willig, and V. May, *Phys. Rev. B* **62**, 16330 (2000).
- ³⁹S. Ramakrishna, F. Willig, and V. May, *J. Chem. Phys.* **115**, 2743 (2001).
- ⁴⁰M. Schreiber, I. Kondov, and U. Kleinekathöfer, *J. Lumin.* **94**, 471 (2001).
- ⁴¹S. Ramakrishna, F. Willig, and V. May, *Chem. Phys. Lett.* **351**, 242 (2002).
- ⁴²W. M. Stier and O. V. Prezhdo, *J. Phys. Chem. B* **106**, 8047 (2002).
- ⁴³P. Persson, S. Lunell, and L. Ojamäe, *Chem. Phys. Lett.* **364**, 469 (2002).
- ⁴⁴W. M. Stier and O. V. Prezhdo, *Israel J. Chem.* **42**, 213 (2002).
- ⁴⁵P. Persson, R. Bergström, L. Ojamäe, and S. Lunell, *Adv. Quantum Chem.* **41**, 203 (2002).
- ⁴⁶S. Ramakrishna, F. Willig, V. May, and A. Knorr, *J. Phys. Chem. B* **107**, 607 (2003).
- ⁴⁷L. G. C. Rego and V. S. Batista, *J. Am. Chem. Soc.* **125**, 7989 (2003).
- ⁴⁸W. M. Stier, W. R. Duncan, and O. V. Prezhdo, *Adv. Mater.* **16**, 240 (2004).
- ⁴⁹M. Thoss, I. Kondov, and H. Wang, *Chem. Phys.* **304**, 169 (2004).
- ⁵⁰L. Wang and V. May, *J. Chem. Phys.* **121**, 8039 (2004).
- ⁵¹W. R. Duncan and O. V. Prezhdo, *J. Phys. Chem. B* **109**, 365 (2005).
- ⁵²L. G. C. Rego, S. G. Abuabara, and V. S. Batista, *J. Chem. Phys.* **122**, 154709 (2005).
- ⁵³L. Wang, R. Ernstorfer, F. Willig, and V. May, *J. Phys. Chem. B* **109**, 9589 (2005).
- ⁵⁴W. R. Duncan, W. M. Stier, and O. V. Prezhdo, *J. Am. Chem. Soc.* **127**, 7941 (2005).
- ⁵⁵P. Persson and M. J. Lundqvist, *J. Phys. Chem. B* **109**, 11918 (2005).
- ⁵⁶W. R. Duncan and O. V. Prezhdo, *J. Phys. Chem. B* **109**, 17998 (2005).
- ⁵⁷M. Nilsing, P. Persson, and L. Ojamäe, *Chem. Phys. Lett.* **415**, 375 (2005).
- ⁵⁸S. G. Abuabara, L. G. C. Rego, and V. S. Batista, *J. Am. Chem. Soc.* **127**, 18234 (2005).
- ⁵⁹L. Wang, F. Willig, and V. May, *J. Chem. Phys.* **124**, 014712 (2006).
- ⁶⁰I. Kondov, M. Thoss, and H. Wang, *J. Phys. Chem. A* **110**, 1364 (2006).
- ⁶¹K. L. Sebastian and M. Tachiya, *J. Chem. Phys.* **124**, 064713 (2006).
- ⁶²P. Persson, M. J. Lundqvist, R. Ernstorfer, W. A. Goddard III, and F. Willig, *J. Chem. Theory Comput.* **2**, 441 (2006).
- ⁶³K. K. Liang, C.-K. Lin, H.-C. Chang, M. Hayashi, and S. H. Lin, *J. Chem. Phys.* **125**, 154706 (2006).
- ⁶⁴I. Kondov, H. Wang, and M. Thoss, *Int. J. Quantum Chem.* **106**, 1291 (2006).
- ⁶⁵M. J. Lundqvist, M. Nilsing, P. Persson, and S. Lunell, *Int. J. Quantum Chem.* **106**, 3214 (2006).
- ⁶⁶I. Kondov, M. Čížek, C. Benesch, H. Wang, and M. Thoss, *J. Phys. Chem. C* **111**, 11970 (2007).
- ⁶⁷J. Li, M. Nilsing, I. Kondov, H. Wang, P. Persson, S. Lunell, and M. Thoss, *J. Phys. Chem. C* **112**, 12326 (2008).
- ⁶⁸J. Li, I. Kondov, H. Wang, and M. Thoss, *J. Phys. Chem. C* **114**, 18481 (2010).
- ⁶⁹F. Ambrosio, N. Martsinovich, and A. Troisi, *J. Phys. Chem. C* **116**, 2622 (2012).
- ⁷⁰A. Vittadini, F. P. Rotzinger, A. Selloni, and M. Grätzel, *J. Phys. Chem. B* **104**, 1300 (2000).
- ⁷¹N. Martsinovich and A. Troisi, *J. Phys. Chem. C* **115**, 11781 (2011).
- ⁷²E. Mosconi, A. Selloni, and F. de Angelis, *J. Phys. Chem. C* **116**, 5932 (2012).
- ⁷³O. V. Prezhdo, W. R. Duncan, and V. V. Prezhdo, *Prog. Surf. Sci.* **84**, 30 (2008).
- ⁷⁴J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).

- ⁷⁵C. F. Craig, W. R. Duncan, and O. V. Prezhdo, *Phys. Rev. Lett.* **95**, 163001 (2005).
- ⁷⁶H. Wang and M. Thoss, *J. Chem. Phys.* **119**, 1289 (2003).
- ⁷⁷L. Gundlach, R. Ernstorfer, and F. Willig, *Appl. Phys. A* **88**, 481 (2007).
- ⁷⁸J. M. Szarko, A. Neubauer, A. Bartelt, L. Socaci Siebert, F. Birkner, K. Schwarzbach, T. Hannappel, and R. Eichberger, *J. Phys. Chem. C* **112**, 10542 (2008).
- ⁷⁹A. Neubauer, J. M. Szarko, A. Bartelt, R. Eichberger, and T. Hannappel, *J. Phys. Chem. C* **115**, 5683 (2011).
- ⁸⁰D. Tsvilin and V. May, *Chem. Phys.* **338**, 150 (2007).
- ⁸¹W. Domcke, *Phys. Rep.* **208**, 97 (1991).
- ⁸²I. V. Kurnikov and D. N. Beratan, *J. Chem. Phys.* **105**, 9561 (1996).
- ⁸³M. Galperin, S. Toledo, and A. Nitzan, *J. Chem. Phys.* **117**, 10817 (2002).
- ⁸⁴P.-O. Löwdin, *J. Chem. Phys.* **18**, 365 (1950).
- ⁸⁵I. Mayer, *Int. J. Quantum Chem.* **90**, 63 (2002).
- ⁸⁶Y. Xue and M. A. Ratner, *Phys. Rev. B* **68**, 115406 (2003).
- ⁸⁷This corresponds to the Condon approximation, which is often employed in the ET systems and is expected to be valid for the relatively rigid systems considered in this paper.
- ⁸⁸F. Dushinsky, *Acta Physicochim. URSS* **7**, 551 (1937).
- ⁸⁹A. B. Myers, *Chem. Rev.* **96**, 911 (1996).
- ⁹⁰*Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).
- ⁹¹R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).
- ⁹²H. Wang and M. Thoss, *J. Chem. Phys.* **124**, 034114 (2006).
- ⁹³H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).
- ⁹⁴U. Manthe, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **97**, 3199 (1992).
- ⁹⁵M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).
- ⁹⁶H.-D. Meyer and G. A. Worth, *Theor. Chem. Acc.* **109**, 251 (2003).
- ⁹⁷H.-D. Meyer, F. Gatti, and G. A. Worth, *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* (Wiley-VCH, Weinheim, 2009).
- ⁹⁸M. Thoss and H. Wang, *Chem. Phys.* **322**, 210 (2006).
- ⁹⁹H. Wang and M. Thoss, *J. Phys. Chem. A* **107**, 2126 (2003).
- ¹⁰⁰M. Thoss, W. Domcke, and H. Wang, *Chem. Phys.* **296**, 217 (2004).
- ¹⁰¹H. Wang and M. Thoss, *Chem. Phys. Lett.* **389**, 43 (2004).
- ¹⁰²U. Manthe, *J. Chem. Phys.* **128**, 164116 (2008).
- ¹⁰³U. Manthe, *J. Chem. Phys.* **130**, 054109 (2009).
- ¹⁰⁴O. Vendrell and H.-D. Meyer, *J. Chem. Phys.* **134**, 044135 (2011).
- ¹⁰⁵R. Borelli, M. Thoss, H. Wang, and W. Domcke, *Mol. Phys.* **110**, 751 (2012).
- ¹⁰⁶H. Wang, D. E. Skinner, and M. Thoss, *J. Chem. Phys.* **125**, 174502 (2006).
- ¹⁰⁷I. R. Craig, M. Thoss, and H. Wang, *J. Chem. Phys.* **135**, 064504 (2011).
- ¹⁰⁸R. Luschinetz, J. Frenzel, T. Milek, and G. Seifert, *J. Phys. Chem. C* **113**, 5730 (2009).
- ¹⁰⁹J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986); **45**, 13244 (1992).
- ¹¹⁰C. Fonseca Guerra, J. G. Snijders, G. te Velde, and E. Baerends, *J. Theor. Chem. Acc.* **99**, 391 (1998); G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, and T. J. Ziegler, *Comput. Chem.* **22**, 931 (2001); E. J. Baerends, J. A. Autschbach, A. Bacrces, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, L. Fan, T. H. Fischer, C. Fonseca Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, M. Graning, F. E. Harris, P. van den Hoek, H. Jacobsen, G. van Kessel, F. Kootstra, E. van Lenthe, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, and T. Ziegler, ADF2002.03, SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, see <http://www.scm.com>.
- ¹¹¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision E.01, Gaussian, Inc., Wallingford, CT, 2004.
- ¹¹²C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988); A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ¹¹³P. Durand and J.-C. Barthelat, *Theor. Chim. Acta* **38**, 283 (1975); Y. Bouteiller, C. Mijoule, M. Nizam, J.-C. Barthelat, J. P. Daudey, M. Péliissier, and B. Silvi, *Mol. Phys.* **65**, 295 (1988).
- ¹¹⁴R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).
- ¹¹⁵C. Kormann, D. W. Bahnemann, and M. R. Hoffmann, *J. Phys. Chem.* **92**, 5196 (1988).
- ¹¹⁶T. M. Halasinski, J. L. Weisman, R. Ruiterkamp, T. J. Lee, F. Salama, and M. Head-Gordon, *J. Phys. Chem. A* **107**, 3660 (2003).
- ¹¹⁷H. Hamoudi, S. Nepl, P. Kao, B. Schüpbach, P. Feulner, A. Terfort, D. L. Allara, and M. Zharnikov, *Phys. Rev. Lett.* **107**, 027801 (2011).
- ¹¹⁸F. Blobner, P. B. Coto, F. Allegretti, M. Bockstedte, Ö. Rubio-Pons, H. Wang, D. L. Allara, M. Zharnikov, M. Thoss, and P. Feulner, *J. Phys. Chem. Lett.* **3**, 436 (2012).
- ¹¹⁹J. C. Cuevas and E. Scheer, *Molecular Electronics: An Introduction to Theory and Experiment* (World Scientific, Singapore, 2010).
- ¹²⁰H. Wang and M. Thoss, *J. Chem. Phys.* **131**, 024114 (2009).
- ¹²¹A. Decker, S. L. Suraru, Ö. Rubio-Pons, E. Mankel, M. Bockstedte, M. Thoss, F. Würthner, T. Mayer, and W. Jaegermann, *J. Phys. Chem. C* **115**, 21139 (2011).
- ¹²²J. C. Tully, *Annu. Rev. Phys. Chem.* **51**, 153 (2000).