

# Vibronic Effects in the Ultrafast Interfacial Electron Transfer of Perylene-Sensitized TiO<sub>2</sub> Surfaces

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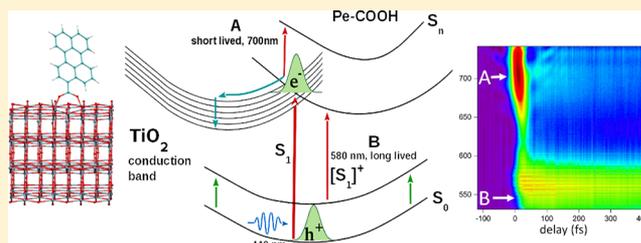
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## Supporting Information

**ABSTRACT:** We combine ultrafast transient absorption (TA) spectroscopy and nonadiabatic quantum dynamics simulations to describe the real-time unfold of vibronic effects on the photoabsorption of TiO<sub>2</sub> anatase sensitized with the (perylene-9-yl)carboxylate dye (Pe-COOH/TiO<sub>2</sub>). The excited state is mapped in time and frequency by ultrafast broadband spectroscopy while atomistic quantum dynamics is used to simulate the self-consistent vibronic effects. The TA map shows the lifetime of the electronic population generated in the S<sub>1</sub> state of the dye and the rise of the absorption D<sub>0</sub>–D<sub>1</sub> of the cation. The theoretical analysis reveals that the electron transfer from perylene into TiO<sub>2</sub> is complete within 20 fs, in agreement with the 12 fs experimental measurement. Because of the structural relaxation produced by the photoinduced electron transfer, the optical gap decreases by 390 meV, in agreement with the D<sub>0</sub>–D<sub>1</sub> transition band. Furthermore, the reorganization energy estimated to be around 220 meV is mostly due to the energy shift of the HOMO level, since the electron transfer occurs in the wide-band limit with little dependence on reorganization energy modes. By assuming the Condon approximation and by making use of the mixed quantum/classical trajectories of the Pe-COOH/TiO<sub>2</sub> system, the absorption spectrum is calculated, and the broad features of the transient absorption spectrum are correlated to excited-state nuclear reorganization effects of the adsorbate dye. The reorganization energy modes are identified by the power spectrum of the velocity autocorrelation function, which shows the occurrence of nonequilibrium modes within the range 1000–1800 cm<sup>-1</sup> as in-plane asymmetric C–C vibrations in the perylene dye. The vibrational modes with the strongest influence on the optical gap contribute to shifting the absorption spectrum up in energy by ~2000 cm<sup>-1</sup>. The overall agreement between theory and experiment reveals the capabilities of both methods to study vibronic effects in molecular and extended systems.



## 1. INTRODUCTION

Nuclear vibrations play an essential role in many energy transfer and charge separation processes.<sup>1–3</sup> In photosynthesis, electronic–vibrational couplings affect the efficiency of energy transfer through the light-harvesting complexes LH2 and LH1.<sup>4–6</sup> In proteins, long-range electron transfer is controlled by structural fluctuations of the medium, which cause the tunneling matrix elements to encompass many alternative pathways, rather than a few dominant paths.<sup>7</sup> At donor–acceptor organic interfaces, vibronic couplings promote the electron–hole pair dissociation by inducing charge delocalization prior to electron transfer.<sup>2,8,9</sup> For dye-sensitized solar cells, in which photoexcited molecular donors inject electrons into the conduction band (CB) of a solid semiconductor electrode, nuclear motion assists electron injection by broadening the electronic coupling between the dye molecule and the

semiconductor band edge<sup>10–12</sup> and by increasing electron transfer pathways.<sup>13–15</sup>

It is usually challenging to identify the fingerprints of nuclear dynamics during interfacial electron transfer (IET) in wide-band dye-sensitized semiconductor surfaces<sup>16,17</sup> because the strong electronic coupling between dye and semiconductor leads typically to ultrafast IET within time scales shorter than vibrational relaxation times,<sup>13,14,18–21</sup> rendering the process to occur far from thermodynamic equilibrium. In general, IET is much faster than homogeneous electron transfer, where the rates are limited by the time scales of solvent reorganization and vibrational energy redistribution. Therefore, the role of

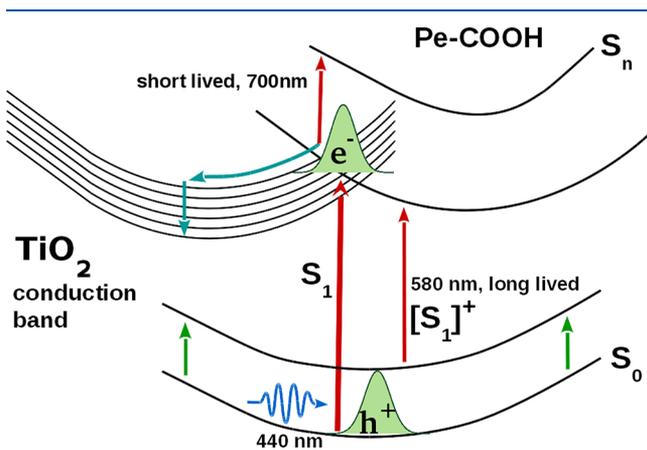
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nuclear dynamics tends to differ in both cases.<sup>2</sup> Here, we combine time-resolved experimental techniques to probe the earliest vibronic relaxation dynamics upon photoexcitation with atomistic modeling of electronic dynamics that accounts for electronic and vibrational coherences.

Perylene derivatives have been used as electron donors in a number of IET studies. Perylene exhibits ultrafast IET to TiO<sub>2</sub> in a few tens to a few hundreds of femtoseconds, depending on the nature of the anchor-mediated electronic coupling.<sup>13,19,22–25</sup> Another advantage of perylene is that it has no intramolecular decay channels<sup>13</sup> unlike Ru-based dyes that often undergo fast intersystem crossing,<sup>26</sup> interligand transfer, and localization.<sup>27,28</sup> Moreover, perylene is a suitable system for spectroscopic studies of IET because its absorption spectrum—in the visible—exhibits clearly distinct bands for the ground to first singlet ( $S_0$ – $S_1$ ), for the  $S_1$ – $S_n$ , and for the cationic  $[S_0]^+$ – $[S_1]^+$  (also termed  $D_0$ – $D_1$ ) transitions.<sup>25,29</sup> The decay of the excited-state absorption of neutral perylene ( $S_1$ – $S_n$ ), around 710 nm, can be used as a probe for electron injection.<sup>25</sup> In addition, pump–probe experiments<sup>25,29</sup> have showed that the  $[S_0]^+$ – $[S_1]^+$  absorption peak of the perylene cation, located around 560 nm, has the same time constant, and its rise serves as an independent measurement to probe the electron transfer kinetics, as depicted in Figure 1.



**Figure 1.** Representation of the potential energy surfaces (PES) of the Pe-COOH/TiO<sub>2</sub> system for neutral and cationic states. The photoexcitations  $S_0$ – $S_1$  (ground to first singlet) and  $S_1$ – $S_n$  of the neutral perylene and  $[S_0]^+$ – $[S_1]^+$  (also termed  $D_0$ – $D_1$ ) of the cationic dye are indicated by red arrows, along with their lifetimes. The TiO<sub>2</sub> conduction band (CB) is depicted as a manifold of states. The blue arrows designate electron transfer (ET) channels as well as electronic relaxation. The green arrows indicate the structural relaxation of the neutral  $S_0$  to cationic  $D_0$  ground state as a consequence of ET. The blue wavepacket designates the pump laser excitation.

The IET dynamics of a related dye molecule, (2,5-di-*tert*-butylperylene-9-yl)carboxylic acid (DTB-Pe-COOH), was studied in a vacuum by transient absorption (TA) spectroscopy,<sup>13,22</sup> and electron transfer time constants  $\tau_{\text{IET}} = 13$  and 28 fs were measured for carboxylic acid and phosphonic acid as the respective anchor group. These studies also reported that the linear absorption of perylene in the ground and cationic states is modulated by high-energy vibrational modes. The linear absorption spectrum of the DTB-Pe-COOH/TiO<sub>2</sub> system was later simulated by assuming electron–phonon coupling with a single in-plane C–C stretching mode at 1370

cm<sup>–1</sup>,<sup>30</sup> which is a prominent Franck–Condon active mode in perylene.<sup>31</sup> The effect has yet to be explored by explicit electron–nuclei excited-state quantum dynamics simulations. Here we investigate the dye molecule (perylene-9-yl)carboxylic acid (Pe-COOH) which is considerably smaller than DTB-Pe-COOH and better accessible by theory. This perylene derivative has not been measured previously. We use an improved implementation of TA that employs chirp-free white light and allows direct comparison of optical density changes across the whole spectrum with 25 fs instrument response function for global analysis. For modeling the system, we use a quantum-classical self-consistent method that incorporates nonadiabatic excited-state electronic quantum dynamics into molecular dynamics simulations,<sup>32,33</sup> henceforth designated SC-QMMM (Self-Consistent QMMM).

## 2. EXPERIMENTAL METHODS

Steady-state absorption spectra were measured using a Photon-Control UV–vis fiber spectrometer. Transient absorption spectra were measured with a setup described earlier.<sup>34</sup> The system is based on a 10 kHz regenerative Ti:sapphire amplifier. White light was generated in a 1 mm sapphire window and compressed to a group velocity mismatch of <2 fs across the spectrum by using chirped mirrors (Laser Quantum) and fused silica wedges. The pump pulse at 440 nm was generated by second harmonic generation from the output of a noncollinear parametric amplifier. The instrument response function of the setup is 25 fs. Spectra were recorded using a home-built prism polychromator equipped with a 10 kHz line-scan camera.<sup>35</sup> In the absence of solvent, the regeneration of the oxidized dye occurs within the nanosecond time scale,<sup>36</sup> therefore fast enough to allow for a repetition rate of 10 kHz. Signal analysis has been described in detail elsewhere<sup>34</sup> by fitting spectral data at specific wavelengths to a set of rate equations corresponding to the observed dynamics. The Pe-COOH dye was adsorbed on colloidal anatase TiO<sub>2</sub> films. Preparation of the film and sensitization procedures have been fully described earlier.<sup>34</sup> Briefly, colloidal films on sodium-free thin glass were annealed at 450 °C before being immersed in a 0.1  $\mu\text{M}$  solution of Pe-COOH, 95% toluene and 5% methanol, for 30 min and, thoroughly rinsed five times. Removal of unbound molecules was confirmed by the vanishing fluorescence of the supernatant. The samples were prepared under Ar protection and immediately transferred into a high vacuum chamber, where they remained stable in a high vacuum for days. Minimal bleaching was observed, during the  $\sim 20$  min data acquisition time. After the measurements, an optical microscope was used to check for photobleaching spots, which have not been observed for the Pe-COOH/TiO<sub>2</sub> samples.

## 3. THEORETICAL AND COMPUTATIONAL METHODS

**3.1. Self-Consistent Electron–Nuclear Dynamics.** In the following we summarize the theoretical method, which has been described in detail elsewhere.<sup>11,32,33</sup> The time-dependent Schrödinger equation (TDSE) is solved for the electronic degrees of freedom

$$i\hbar \frac{\partial}{\partial t} |\Psi(\mathbf{r}; t)\rangle = \hat{H}_{\text{el}}(\mathbf{R}_t) |\Psi(\mathbf{r}; t)\rangle \quad (1)$$

where  $\mathbf{r}$  designates the electronic coordinates,  $\mathbf{R}_t \equiv \mathbf{R}(t)$  are the time-dependent nuclear coordinates, and  $\hat{H}_{\text{el}}(\mathbf{R}_t)$  is the time-dependent extended Hückel Hamiltonian for an instanta-

neous molecular configuration. We use the following force field (FF) to describe the nuclear dynamics:

$$V_{\text{GS}}^{\text{MM}}(\{\mathbf{R}\}) = \sum_{\text{bonds}} K_b(\mathbf{R} - \mathbf{R}_0)^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 + \sum_{\text{torsions}} \sum_n C_n(\cos \phi)^n + \sum_{i,j \neq i} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{\mathbf{R}_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{\mathbf{R}_{ij}} \right)^6 \right] + \sum_{i,j \neq i} \frac{q_i q_j}{4\pi\epsilon_0 \mathbf{R}_{ij}} \quad (2)$$

where  $\mathbf{R}$  is the atomic position and  $\mathbf{R}_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$  is the distance between atoms  $i$  and  $j$ , which have fixed partial charges  $q_i$  and  $q_j$ . Likewise,  $\theta$  and  $\phi$  are the angular and dihedral torsional variables. The parameters  $\mathbf{R}_0$  and  $\theta_0$  are the equilibrium bond length and angle;  $K_b$ ,  $K_\theta$  and  $C_n$  are the intramolecular FF parameters, and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the Lennard-Jones parameters. The FF parameters are provided as [Supporting Information](#).

To describe the nonadiabatic nuclear dynamics, we extend the ground-state molecular mechanics to the excited state. That is done by using nonadiabatic Hellmann–Feynman forces in addition to those derived from the ground-state force field potential of eq 2. We assume that the single-particle electron–hole excitation is described by the spinor state  $\Psi = \{\Psi^{\text{el}}, \Psi^{\text{hl}}\}$ , whose components are the wavepackets that describe the excited electron,  $\Psi^{\text{el}}(t)$ , and the hole,  $\Psi^{\text{hl}}(t)$ . The nuclei are described by the classical equations of motion

$$\dot{\mathbf{R}} = \mathbf{P}/M \quad (3)$$

$$\dot{\mathbf{P}} = -\nabla_{\mathbf{R}} \langle \Psi(\mathbf{r}; t) | V(\mathbf{r}, \mathbf{R}) | \Psi(\mathbf{r}; t) \rangle_{\mathbf{r}} \quad (4)$$

as in the Ehrenfest method, where the forces acting upon the nuclei, positioned at  $\mathbf{R}$ , are calculated via the electron–nuclei coupling potential  $V(\mathbf{r}, \mathbf{R})$  averaged over the electron–hole wave function, as designated by the notation  $\langle \dots \rangle_{\mathbf{r}}$ . Therefore, we make the following approximation

$$\langle \Psi(\mathbf{r}; \mathbf{R}, t) | V(\mathbf{r}, \mathbf{R}) | \Psi(\mathbf{r}; \mathbf{R}, t) \rangle_{\mathbf{r}} \approx V_{\text{GS}}^{\text{MM}}(\mathbf{R}) + V_{\text{EH}}[\Psi^{\text{el}}(\mathbf{R}, t), \Psi^{\text{hl}}(\mathbf{R}, t)] \quad (5)$$

by means of which the excited-state interatomic potential is separated as the contribution from the ground-state force field potential,  $V_{\text{GS}}^{\text{MM}}$ , plus a correction that is due to the electron–hole excitation,  $V_{\text{EH}}[\Psi^{\text{el}}, \Psi^{\text{hl}}]$ . The underlying reasoning for this approximation is that  $V_{\text{GS}}^{\text{MM}}$  is produced by all the occupied orbitals that comprise the ground state, and it is, in principle, well described by the force field. Upon the excited state the electron–hole photoexcitation gives rise to a perturbation potential that is a functional of the electron and hole wave functions. This second term is responsible for the coupling between quantum and classical degrees of freedom in the excited state. It is calculated on the fly from the Hamiltonian as

$$V_{\text{EH}}[\Psi^{\text{el}}(\mathbf{R}, t), \Psi^{\text{hl}}(\mathbf{R}, t)] = \text{Tr}[\rho^{\text{EH}}(\mathbf{R}, t)\mathbf{H}(\mathbf{R}_t)] \quad (6)$$

where  $\rho^{\text{EH}} = |\Psi^{\text{el}}\rangle\langle\Psi^{\text{el}}| - |\Psi^{\text{hl}}\rangle\langle\Psi^{\text{hl}}|$  is the electron–hole density matrix. The force produced on atom  $N$  by an e–h excitation is given by

$$\mathbf{F}_N = -\nabla_N V_{\text{EH}}[\Psi^{\text{el}}(\mathbf{R}, t), \Psi^{\text{hl}}(\mathbf{R}, t)] \quad (7)$$

where  $\nabla_N \equiv \nabla_{\mathbf{R}_N}$ . This force is responsible for the electronic back-reaction on the classical degrees of freedom, and it gives rise to adiabatic and nonadiabatic nuclear dynamics effects.<sup>32,33,37</sup> Furthermore, the total energy of the excited system is conserved during the dynamics, which is composed of the overall classical energy of the nuclei (kinetic plus potential) as given by the molecular mechanics formalism and the quantum energy of the excited electron–hole pair  $E_{\text{QM}} = \text{Tr}[\rho^{\text{EH}}\mathbf{H}]$ .

The quantum mechanical wavepackets that describe the electron–hole excitations are herein written in terms of adiabatic molecular orbitals  $\{\phi\}$  as  $|\Psi(t)\rangle = \sum_n C_n(t) |\phi_n(\mathbf{R}_t)\rangle$ . They evolve according to the time-dependent Schrödinger equation (TDSE), written for the adiabatic expansion coefficients  $C_n(t)$  as

$$\frac{dC_n}{dt} + \sum_m C_m \langle \phi_n | \dot{\phi}_m \rangle = -\frac{i}{\hbar} \mathcal{E}_n C_n \quad (8)$$

where  $\langle \phi_n | \dot{\phi}_m \rangle$  is the nonadiabatic coupling term. For short time slices  $\delta t$ , the instantaneous eigenvalue equation  $\mathcal{H}^{(j)} |\phi_n^{(j)}\rangle = \mathcal{E}_n^{(j)} |\phi_n^{(j)}\rangle$  is used to generate a locally diabatic basis, where  $\mathcal{H}^{(i)} \equiv \mathcal{H}(j\delta t)$ . Formally equivalent to eq 8, the overall time evolution is obtained as

$$|\Psi(t_{j+1})\rangle = \prod_{j=0} \mathcal{U}(t_{j+1}, t_j) |\Psi(t_0)\rangle \quad (9)$$

where

$$\mathcal{U}(t_{j+1}, t_j) = \mathcal{U}_{\text{NA}}(t_{j+1}, t_j) \mathcal{U}_{\text{AD}}(t_j) \quad (10)$$

is the time-evolution operator within the time slice,<sup>11</sup> which is comprised an adiabatic ( $\mathcal{U}_{\text{AD}}$ ) part

$$\mathcal{U}_{\text{AD}} |\Psi(t_j)\rangle = \sum_n C_n(t_j) \exp[-i\mathcal{E}_n^{(j)} \delta t / \hbar] |\phi_n^{(j)}\rangle \quad (11)$$

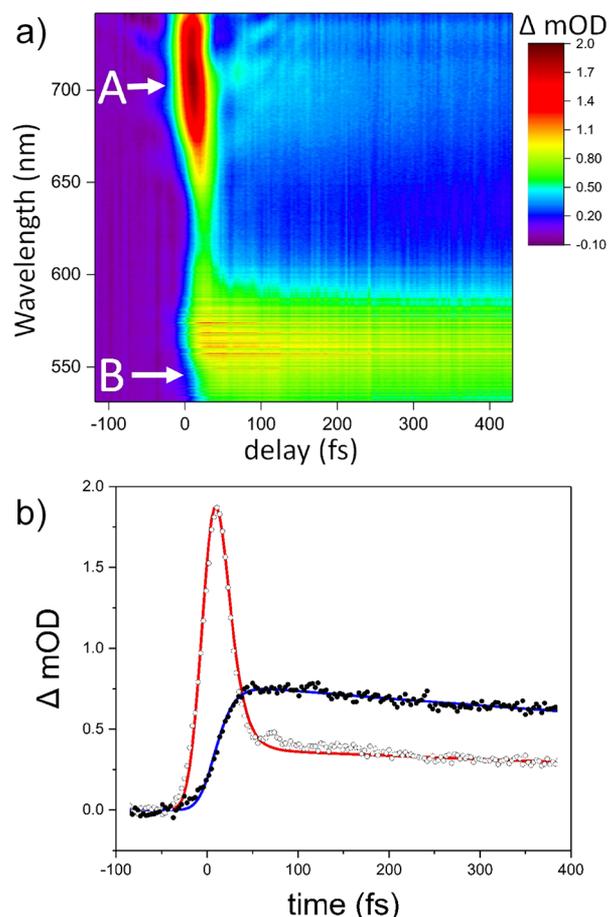
and a nonadiabatic ( $\mathcal{U}_{\text{NA}}$ ) coupling term

$$\mathcal{U}_{\text{NA}} = \sum_{n,m} \Omega_{n,m} |\phi_m^{(j+1)}\rangle \langle \phi_n^{(j)}| \quad (12)$$

where  $\Omega_{n,m} = \langle \phi_m^{(j+1)} | \dot{\phi}_n^{(j)} \rangle \approx \delta_{n,m} + \langle \dot{\phi}_m^{(j)} | \phi_n^{(j)} \rangle \delta t$ . The term  $\Omega_{n,m}$  can be calculated directly by using the instantaneous eigenstates at successive time slices.

## 4. EXPERIMENTAL RESULTS

Figure 2a shows the transient absorption (TA) map of the P-COOH/TiO<sub>2</sub> sample after excitation at 440 nm. It shows the excited-state absorption of the neutral ( $S_1$ ) and cationic ( $[S_1]^+$ ) perylene that is formed upon IET. The short-lived excited-state absorption band has its maximum around 710 nm (indicated by A). The measured cation absorption band is broad and centered around 570 nm (indicated by B), stretching up to 700 nm where it overlaps with the excited-state absorption. The TA map shows that the excited-state population that is generated in  $S_1$  decays while the signal due to the cation absorption rises. It should be noted that the white-light probe pulse is compressed using chirped mirrors and the group velocity mismatch between the signal at A and at B has been measured to be below 2 fs. Transients are extracted from the map at positions A (hollow dots) and B (full dots), shown in Figure 2b. The time resolution of 25 fs together with the precisely known time-zero is sufficient to extract a 12 fs

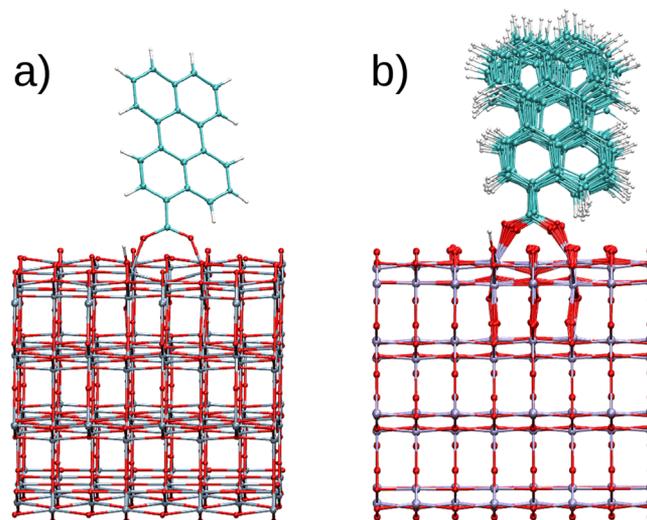


**Figure 2.** (a) Measured transient absorption (TA) map of Pe-COOH adsorbed on TiO<sub>2</sub> in a high vacuum after excitation at 440 nm. (b) Fit curves and transient absorption signal extracted from the map in (a) at position A (hollow dots and red line) and at position B (full dots and blue line).

time constant in the decay of the excited state and in the rise of the cation signal. The long-lived signal observed at B is due to the very broad cation absorption. The cation experimental signal was fit at 545 nm, slightly below the maximum, to minimize contributions from excited state absorption at early times. The decay of the long-lived cation signal is identical at all wavelengths.

## 5. SIMULATION RESULTS

**5.1. System Preparation.** The present Pe-COOH/TiO<sub>2</sub> model system consists of the dye molecule (perylene-9-yl)carboxylic acid (Pe-COOH) bound to the (101) surface of anatase TiO<sub>2</sub> by the carboxyl group in a bidentate bridging geometry, as shown in Figure 3. The exposed surface of anatase colloids is predominantly formed of {101} faces, as reported in experimental<sup>38</sup> and theoretical<sup>39</sup> studies. In fact, DFT total energy calculations together with the Wulff construction method show that for naturally occurring anatase crystals the most stable {101} faces constitute more than 90% of the exposed crystal surface. The binding of the carboxylic group to nanostructured anatase has been investigated for several configurations<sup>40,41</sup> on clean and hydrated surfaces. Although not the strongest binding mode, the bridging bidentate geometry is considered a prototypical binding mode, which provides stability against water and robust electronic coupling

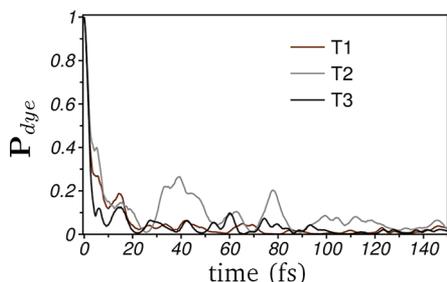


**Figure 3.** (a) Optimized geometry of the Pe-COOH/TiO<sub>2</sub> system. (b) Sample snapshots of the structure obtained during molecular mechanics simulations performed with the system in contact with a Nosé–Hoover thermostat at 300 K, evidencing that the structure remained rather rigid while in contact with the thermostat.

between dye and substrate.<sup>24</sup> In the model system, all the nuclei comprising the dye adsorbate as well as 30 nuclei of the TiO<sub>2</sub> cluster close to the anchoring site are allowed to evolve through molecular mechanics. The other nuclei of the TiO<sub>2</sub> cluster remain constrained to their optimized positions during classical and excited-state nonadiabatic dynamics. For describing the interfacial electron transfer, the electronic degrees of freedom of all atoms of the Pe-COOH/TiO<sub>2</sub> system, free and constrained, are treated as quantum mechanical. Before performing excited-state quantum dynamics simulations, the model system was thermalized. First we performed molecular mechanics simulations in the ground state, with time steps  $\delta t = 0.1$  fs, keeping the system in contact with a Berendsen thermostat at 300 K until the molecular structure of the whole dye/TiO<sub>2</sub> system was stabilized. Then, additional molecular mechanics simulations were performed with the system in contact with a Nosé–Hoover thermostat at 300 K. Snapshots of the system are shown in Figure 3b, evidencing that the dye structure remained rather rigid while in contact with the thermostat. A cutoff radius for electrostatic interactions of 50 Å was used. After thermalization, the positions and velocities of the atoms were used to initiate the nonadiabatic quantum simulations. The photoexcited system was prepared in the S<sub>1</sub> state of the Pe-COO moiety, assuming instantaneous photoexcitation. The coupled quantum/classical method for dynamics of electrons in molecules (DynEMol<sup>42</sup>) was used for nonadiabatic self-consistent quantum-classical simulations with a time step of  $\delta t = 0.02$  fs for both electrons (QM) and nuclei (MM).

Yet before quantum dynamics simulations the extended Hückel Hamiltonian was parametrized to describe the frontier orbitals {H-1, HOMO, LUMO, L+1} of the isolated Pe-COOH dye molecule in the optimized geometry, as detailed in the Supporting Information. No further adjustments were made for the subsequent quantum dynamics simulations.

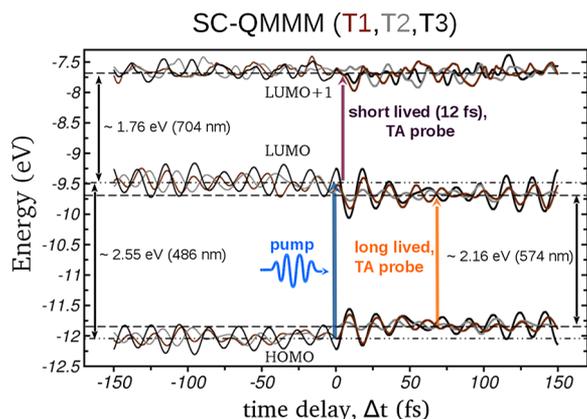
**5.2. Quantum Dynamics Results.** In the following we present data for three independent trajectories {T1, T2, T3} prepared as outlined above. Beginning with Figure 4, we show time-dependent survival probabilities ( $P_{\text{dye}}$ ) for the photo-



**Figure 4.** Survival probability of the photoexcited electron in the Pe-COO moiety ( $P_{\text{dye}}$ ) as a function of time for the independent trajectories {T1, T2, T3}.

excited electron in the Pe-COO moiety. For the independent trajectories, the simulation results describe an IET that is complete within 20 fs, in agreement with the aforementioned TA measurements that yield an IET time of 12 fs. It has been reported, though, that perylene derivatives with longer saturated spacer groups exhibit a slower electron injection as compared to short conjugated groups.<sup>13,20,24</sup>

To further explain the TA map of Figure 2, we analyze the behavior of the frontier molecular orbitals {HOMO, LUMO, LUMO+1} of the Pe-COO dye as a function of time. Figure 5



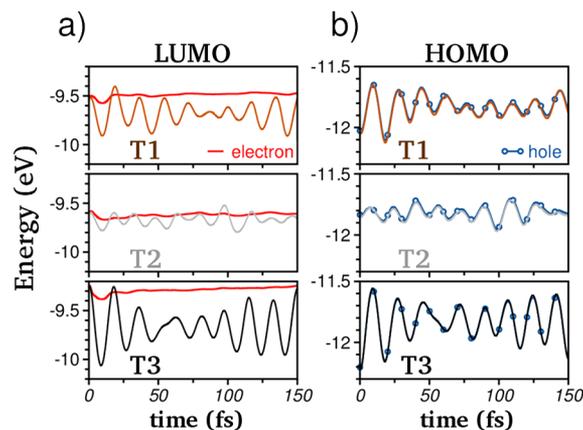
**Figure 5.** Frontier molecular orbitals {HOMO, LUMO, LUMO+1} of the Pe-COO moiety calculated on the fly for trajectories {T1, T2, T3} with the SC-QMMM method.

presents the energy of such frontier MOs calculated on the fly with the SC-QMMM method for trajectories {T1, T2, T3}. It reveals that the ultrafast IET produces a structural relaxation in the dye that reduces the HOMO–LUMO gap by  $\sim 390$  meV, that is, from  $\sim 2.55$  eV (486 nm) to  $\sim 2.16$  eV (574 nm). The mean energy of the LUMO+1 orbital, however, is not appreciably affected by the electron transfer throughout the simulations. Thus, in regard to the TA map, we can initially associate the HOMO–LUMO gap of  $\sim 486$  nm to the  $S_0$ – $S_1$  pump photoexcitation at 440 nm. A more direct comparison is provided ahead by calculating the absorption spectrum of the pump pulse. In addition, the short-lived excited state absorption peak ( $S_1$ – $S_n$ ) observed around 710 nm in the TA map can be associated with the LUMO–[LUMO+1] gap of  $\sim 704$  nm of the neutral perylene, and finally, the  $D_0$ – $D_1$  absorption band around 570 nm in the TA map matches the HOMO–LUMO gap of  $\sim 574$  nm obtained after IET. The fact that the three independent trajectories evince the same behavior corroborates the analysis. Moreover, despite the

large-amplitude oscillations displayed by the molecular orbitals in Figure 5, the standard deviation of the total energy ( $E = \sum_{\text{atoms}} E_{\text{MM}} + E_{\text{QM}}^{\text{EH}}$ ) is  $\sim 6$  meV during the simulations, and its drift is  $\sim 25$  meV after 150 fs (Figure S4).

## 6. DISCUSSION

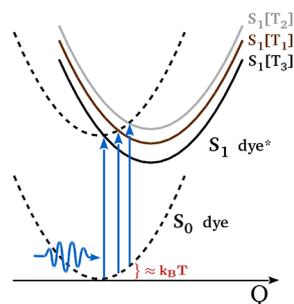
Thus, we can draw some conclusions about the reorganization energies involved in the electron transfer process. We conclude that the intramolecular reorganization energy of the overall photoinduced ET process should be associated mostly to the energy shift  $\delta E_{\text{HOMO}} \approx 0.19$  eV, which is produced by the  $S_0$ – $S_1$  transition in the dye. The reasons are the following: (1) the photoexcited electron wavepacket spends effectively  $t < 10$  fs in the LUMO of the Pe-COO moiety, as evinced by Figure 4; (2) its energy,  $E_{\text{el}} = \text{Tr}[\hat{H}\rho_{\text{el}}]$ —described by the red curve in Figure 6a—remains approximately constant throughout the



**Figure 6.** Energies of the LUMO and HOMO orbitals upon photoexcitation for the independent trajectories {T1, T2, T3}. In addition, average energy of the electron (red) and hole (blue) wavepackets.

electron transfer  $\text{dye}^*/\text{TiO}_2 \rightarrow \text{dye}^+/\text{TiO}_2^-$ ; (3) the hole, otherwise, remains closely associated with the HOMO of the dye, as shown in Figure 6b; and (4) the overall gain of nuclear energy  $\Delta E_{\text{MM}}$  varies around 0.22 eV for the sampled trajectories. These values are in qualitative agreement with calculations reported elsewhere which range through 0.3 eV,<sup>38</sup> 0.22 eV,<sup>43</sup> and 0.18 eV<sup>30,44</sup> based on static *ab initio* methods. Thus, because of the ultrafast electron transfer, the LUMO gets depopulated well before the structural relaxation of the dye is complete, hindering it to contribute to the reorganization energy. Moreover, the graphs of Figure 6a, which show the energy of the photoexcited electron compared to the energy of the LUMO, evidence that the electron transfer occurs in the wide band limit,<sup>13</sup> with little influence by reorganization energy modes. Upon photoexcitation the reorganization energy is converted into kinetic and potential energies of the nuclei. Therefore, based on the data of the mixed quantum/classical dynamics as well as Figure 6, the intramolecular reorganization effect is described schematically in Figure 7 for initial conditions corresponding to each of the trajectories {T1, T2, T3}.

Various papers have studied vibronic effects on the photoabsorption spectrum of perylene-based dyes, with good results.<sup>30,45–47</sup> Usually, the methods made use of vibrational modes calculated *a priori* for the isolated molecule in the optimized geometry, instead of considering the actual nuclear



**Figure 7.** Scheme of PES describing the intramolecular reorganization effect for initial conditions corresponding to each of the trajectories {T1, T2, T3}.  $Q$  represents a generalized coordinate.

dynamics that unfolds during the structural relaxation. This is indeed a good approximation for rigid molecules like perylene, but it can fail for flexible structures. In a more general approach, it is possible to use mixed quantum/classical dynamics to investigate vibrational effects on the optical spectrum. Such dynamics methods have been applied to compute the IR and Raman spectra of molecules, liquids and solids.<sup>48–50</sup>

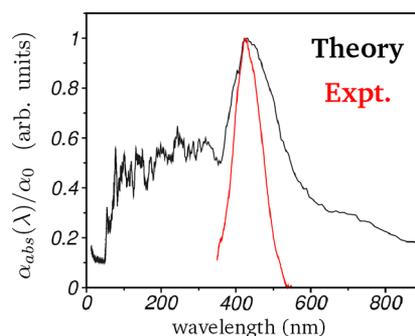
Provided the Condon approximation is valid, so that the dipole moment operator does not depend on position, it is possible to obtain the absorption coefficient as<sup>30,51</sup>

$$\alpha_{\text{abs}}(\omega) = \frac{4\pi\omega n_{\text{mol}}}{3\hbar c} |d_{\text{eg}}|^2 \text{Re} \int_0^{\infty} e^{i(\omega - \omega_{\text{eg}}(t))t} \langle \chi_{\text{g}0}^{(e)} | \chi_{\text{g}0}^{(e)}(t) \rangle dt \quad (13)$$

where  $n_{\text{mol}}$  is the volume density of the absorbing dye with the factor 1/3 introduced for orientational average. The autocorrelation function  $\langle \chi_{\text{g}0}^{(e)} | \chi_{\text{g}0}^{(e)}(t) \rangle$  is obtained by solving the time-dependent Schrödinger equation for the nuclear motion on the electronic excited PES (represented by  $\chi_{\text{g}0}^{(e)}(t)$ ), with the initial condition  $|\chi_{\text{g}0}^{(e)}(t=0)\rangle = |\chi_{\text{g}0}\rangle$ . However, instead of using the phonon autocorrelation function in eq 13, we apply the following approximation to calculate the absorption of the pump pulse. We employ the normalized velocity autocorrelation function (VACF) of the nuclei comprising the dye molecule

$$C_{\text{vv}}^{\text{dye}}(t) = \frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle v^2(0) \rangle} \quad (14)$$

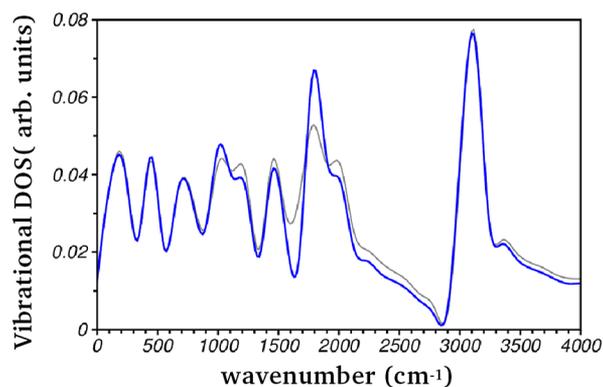
calculated upon photoexcitation. For a harmonic oscillator coupled to a bath with memory, both the velocity and position autocorrelation functions have the same vibrational dephasing time ( $T_2$ ),<sup>52</sup> but the former is better suited for numerical applications that require spectral analysis. This simplification is consistent with the Condon principle and has the benefit of taking into account all the vibrational modes. As for  $\omega_{\text{eg}}(t)$ , we use the time-dependent HOMO–LUMO gap calculated in the ground state—before the pump pulse—which oscillates around 2.55 eV in Figure 5. Following this procedure, we calculate  $\alpha_{\text{abs}}(\lambda)/\alpha_0 = \mathcal{D}(\lambda)/\lambda$ , with  $\alpha_0 = 8\pi^2 n_{\text{mol}} |d_{\text{eg}}|^2 / (3\hbar)$  and  $\mathcal{D} = \text{Re} \int [\exp(i[\omega - \omega_{\text{eg}}]t)] C_{\text{vv}}^{\text{dye}}(t) dt$ . Figure 8 shows the calculated absorption coefficient and the experimental UV–vis spectrum of the pump pulse, both normalized at their peak heights. First, we observe the very good agreement between peak positions around 440 nm, better indeed than in the comparison with the mean HOMO–LUMO gap of  $\sim 486$  nm (2.55 eV), shown in Figure 5. We attribute the cause of



**Figure 8.** Measured UV–vis absorption spectrum (red) of the Pe-COOH/TiO<sub>2</sub> system for the pump laser at 440 nm in comparison to the simulated absorption spectrum (black). Both curves are normalized at their peak heights.

this shift to the oscillations of the optical gap  $\omega_{\text{eg}}(t)$ , whose Fourier spectra are shown in Figure 10. On the other hand, the width of the simulated spectrum is approximately twice that of the experimental one. This discrepancy can be ascribed, in addition to the approximations described above, to the short time domain used for calculating VACF and  $\alpha_{\text{abs}}$ —although the vibrational dephasing time of VACF is much shorter than the simulation time—and to deficiencies of the FF used in the underlying MM simulations.

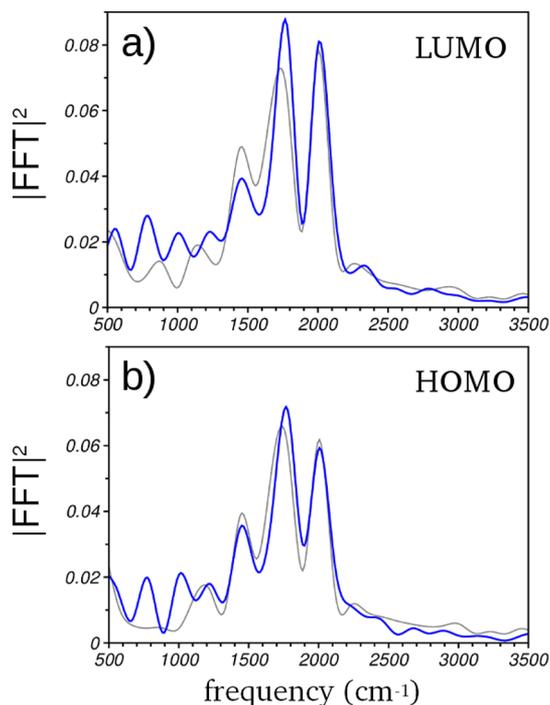
We can use the power spectrum of the mass-weighted VACF to obtain the vibrational modes (vibrational density of states, VDOS). Figure 9 shows the VDOS of the Pe-COO dye moiety



**Figure 9.** Vibrational density of states (VDOS) of the Pe-COO dye moiety calculated for the ground-state dynamics (gray) and for the excited-state SC-QMMM dynamics (blue) evince effects of vibrational reorganization due to the photoinduced IET process. Results include trajectories {T1, T2, T3}.

calculated from the mixed quantum/classical dynamics simulations. In thermal equilibrium each peak of the mass-weighted VDOS of a harmonic system should have the same intensity; however, anharmonic effects and nonequilibrium mode occupation alter the intensity and position of the peaks.<sup>48</sup> Thus, by comparison of the VDOS calculated for the ground-state molecular dynamics (gray) with that for the excited-state SC-QMMM dynamics (blue), it is possible to identify the intramolecular nonequilibrium vibrational modes excited by photoexcited IET. The biggest differences between the two spectra consist of a suppression of modes around 1600  $\text{cm}^{-1}$  and a concentration of modes around 1800  $\text{cm}^{-1}$ . Such frequencies are associated with various in-plane C–C asymmetric modes of the perylene dye (shown in Figure

S10). Moreover, the frequencies within this spectral region are the most strongly coupled to the LUMO and HOMO levels of the attached dye, as evidenced by the power spectrum of the time-dependent energies of these orbitals, shown in Figure 10.



**Figure 10.** (a) Power spectrum of the LUMO energy level before photoexcitation (gray) and after photoexcitation (blue), averaged over trajectories {T1, T2, T3}. (b) Likewise for the HOMO energy level.

They contribute to the width of  $\alpha_{\text{abs}}(\omega)$  as well as to the shift of its peak from 486 to 440 nm. Interestingly, the large peak viewed in Figure 9 at  $3100\text{ cm}^{-1}$ , associated with the C–H stretching mode, is not present in the graphs of Figure 10. Finally, these results should be viewed with the caveat that the frequency values are overestimated by the force field.

## 7. CONCLUSIONS

This paper combined ultrafast transient absorption (TA) spectroscopy with nonadiabatic quantum dynamics simulations to reveal in real time the vibronic effects of the photoinduced interfacial electron transfer (IET) of  $\text{TiO}_2$  anatase sensitized with the (perylene-9-yl)carboxylate dye (Pe-COOH/ $\text{TiO}_2$ ). The TA map obtained with the broadband pump–probe technique allowed the extraction of a 12 fs time constant for the photoinduced IET by measuring simultaneously—and independently—the lifetime of the electronic population generated in the  $S_1$  state of the dye and the rise of the absorption  $D_0$ – $D_1$  of the cation. The self-consistent quantum/classical dynamics simulations revealed that the electron is completely transferred to the conduction band of the  $\text{TiO}_2$  semiconductor within 20 fs. Furthermore, because of the structural relaxation produced by the photoinduced electron transfer the optical gap decreases by 390 meV, from 484 to 576 nm, in agreement with the measured  $D_0$ – $D_1$  transition band. It is shown that the reorganization energy, estimated to be  $\sim 220$  meV, is mostly due to the energy shift of the HOMO level, since the electron transfer occurs in the wide-band limit with

little dependence on reorganization energy modes. By assuming the Condon approximation and by making use of the mixed quantum/classical trajectories of the Pe-COOH/ $\text{TiO}_2$  system, the absorption spectrum of the pump pulse is calculated and compared to the UV–vis spectrum, revealing that the peak positions match closely, whereas the simulated peak is twice as broad. The reorganization energy modes are identified by the power spectrum of the autocorrelation function, which shows the occurrence of nonequilibrium modes within the region  $1000$ – $1800\text{ cm}^{-1}$ . The vibrational modes with the strongest influence on the optical gap, located within the spectral range  $1500$ – $2000\text{ cm}^{-1}$ , contribute to shifting the absorption spectrum up in energy by  $\sim 2000\text{ cm}^{-1}$ . In conclusion, the overall agreement between theory and experiment produced a detailed description of the photo-induced heterogeneous electron transfer in the perylene/ $\text{TiO}_2$  system, revealing the capabilities of both methods to study vibronic effects in molecular and extended systems.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b02106.

Parametrization of the quantum method and electronic structure of the Pe-COOH/ $\text{TiO}_2$  system and molecular mechanics force field parametrization (PDF)

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### Notes

The authors declare no competing financial interest.

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