What Makes the Photocatalytic CO₂ Reduction on N-Doped Ta₂O₅ Efficient: Insights from Nonadiabatic Molecular Dynamics

Alexey V. Akimov,† Ryoji Asahi,‡ Ryosuke Jinnouchi,‡ and Oleg V. Prezhdo*‡†

†Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States
‡Toyota Central Research and Development Laboratories, Inc., 41-1 Yokomichi, Nagakute-shi, Aichi 480-1192, Japan

ABSTRACT: Recent experimental studies demonstrated that photocatalytic CO₂ reduction by Ru catalysts assembled on N-doped Ta₂O₅ surface is strongly dependent on the nature of the anchor group with which the Ru complexes are attached to the substrate. We report a comprehensive atomistic analysis of electron transfer dynamics in electroneutral Ru(di-X-bpy) (CO)₂Cl₂ complexes with X = COOH and PO₃H₂ attached to the N-Ta₂O₅ substrate. Nonadiabatic molecular dynamics simulations indicate that the electron transfer is faster in complexes with COOH anchors than in complexes with PO₃H₂ groups, due to larger nonadiabatic coupling. Quantum coherence counteracts this effect, however, to a small extent. The COOH anchor promotes the transfer with significantly higher frequency modes than PO₃H₂ due to both lighter atoms (C vs P) and stronger bonds (double vs single). The acceptor state delocalizes onto COOH, but not PO₃H₂, further favoring electron transfer in the COOH system. At the same time, the COOH anchor is prone to decomposition, in contrast to PO₃H₂, making the former show smaller turnover numbers in some cases. These theoretical predictions are consistent with recent experimental results, legitimating the proposed mechanism of the electron transfer. We emphasize the role of anchor stability, nonadiabatic coupling, and quantum coherence in determining the overall efficiency of artificial photocatalytic systems.

1. INTRODUCTION

Harvesting and transformation of solar energy by artificial photosynthetic complexes⁴⁻⁶ is one of the most important challenges of modern chemistry. The availability of suitable materials⁷⁻¹⁴ that can effectively collect solar photons and transform them into electrical or chemical energy opens attractive prospects to renewable and clean energy supply and production of basic chemicals. In particular, photocatalytic carbon dioxide reduction to low-carbon organic molecules, such as formic acid or carbon monoxide, has been attracting interest of many research groups over the last decades.⁵,¹⁵⁻²⁵ Carbon dioxide capture is also an important technology for air pollution and climate change control.¹⁶,¹⁸ Although the advances in synthesis and experimentation have suggested many practical routes to better materials for CO₂ reduction, the fundamental mechanisms of the processes that occur at different stages of CO₂ reduction are not completely understood. In particular, interactions at the catalyst–substrate interface play one of the most important roles, as has been suggested by numerous studies.²⁴⁻³³ Yet, there is still significant controversy in attributing observed efficiencies to particular atomic-scale mechanisms.

Ru complexes have been utilized for many years in various photoconversion applications, including water splitting.³⁴⁻³⁶ Electricity generation with dye-sensitized solar cells.³⁷⁻⁴⁰ and CO₂ reduction.²³,⁴¹,⁴² In recent experiments of Sato and co-workers⁴¹,⁴² Ru complexes attached to a N-doped Ta₂O₅ (N-Ta₂O₅) substrate have been studied as promising photocatalysts for CO₂ reduction. The experimental observations suggested that anchor groups, which bind Ru complexes to the semiconductor, have a very pronounced effect on the reduction efficiency, as judged by the turnover numbers (TONs). Increasing the number of carboxyl groups in the Ru ligands increases TONs, as demonstrated in a series of Ru complexes: [Ru(bpy)₂(CO)₂]²⁺, [Ru(dcbpy) (bpy) (CO)₂]²⁺, and [Ru(dcbpy)(bpy)(CO)₂]²⁺, where bpy and dcbpy refer to 2,2′-bipyridine and 4,4′-dicyano-2,2′-bipyridine ligands, respectively. Quantum coherence counteracts this effect, however, to a small extent.

Supporting Information

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anchoring groups play a dominating role. However, the fundamental reasons behind these experimental observations are unclear, strongly motivating the need for explicit atomistic computational studies.

In the present work, we report important insights into the photoinduced ET mechanisms, which determine the role of the anchor group. We utilize atomistic nonadiabatic molecular dynamics (NA-MD) in order to obtain a detailed time-domain description of ET in N–Ta$_2$O$_5$ sensitized with Ru complexes. Following our earlier work,

We utilize the electroneutral NAC. We present the rationale for these two opposing the PO$_3$H$_2$ system, in contrast to the trends in the previously intrinsic ET process is faster in the COOH system than in electron-vibrational coupling in the two systems.

Our calculations provide a rather surprising conclusion that the intrinsic ET process is faster in the COOH system than in the PO$_3$H$_2$ system, but its role is less than that of faster ET. Our analysis suggests that quantum coherence favors electron back-reaction on the nuclear dynamics. We use the results of the NA-MD calculations to analyze and compare the ET dynamics in both energy levels and NAC, for each point along the trajectories. The electronic structure information is subsequently used to perform NA-MD simulations within the classical path approximation that neglects electronic structure, respectively. The MM part is used to produce well-thermalized and sufficiently long ground state molecular dynamics (MD) trajectories. The EHT gives the electronic structure, including both energy levels and NAC, for each point along the trajectories. The electronic structure information is subsequently used to perform NA-MD simulations within the classical path approximation that neglects electron back-reaction on the nuclear dynamics. We use the results of the NA-MD calculations to analyze and compare the ET dynamics in the COOH and PO$_3$H$_2$ systems.

2.2. Molecular Structure and Dynamics. The molecular models used in the present work are depicted in Figure 2. Following the stability considerations, we assume that Ru complexes are bound via two anchor groups. The hydroxyl groups of the N–Ta$_2$O$_5$ surface binding the anchors are chosen to minimize distortion of the adsorbate. Because of different flexibility of the anchors, the resulting bound complexes differ in relative orientation of the Ru complex and substrate. Although the coordination mode can, in principle, affect the nonadiabatic couplings and electronic energy levels of a system, this effect is rather minimal for our complexes. As we have demonstrated in the previous work, both mono- and bidentate coordination of the PO$_3$H$_2$ anchor result in practically indistinguishable pDOS. For the COOH anchor, the bidentate binding may create defect states. However, the presence of such states will only enhance charge transfer to COOH complex. As we will show below, defects will not change the qualitative results obtained in this work. We used a 10% doped cluster of Ta$_2$O$_5$, which is close to the 8.9% nitrogen content in the experiments.

In view of the need for expensive evaluation of electronic structure at each point of the MD trajectories, we utilize a minimal N–Ta$_2$O$_5$ cluster, yet sufficiently large to adequately represent the surface. Molecular structures as well as MD trajectories are computed using our implementation of the rigid-body molecular dynamics (RB-MD), with highly accurate and stable qTerec algorithm.

The coordinates of

N–Ta$_2$O$_5$ acts as a chromophore by absorbing light, which excites electrons and promotes them from the occupied valence band (VB) levels to the unoccupied conduction band (CB) levels. The photoexcited electrons can be injected from the N–Ta$_2$O$_5$ subsystem to the lowest or next lowest unoccupied molecular orbitals (LUMO or LUMO+1) of the Ru catalyst anchored on the surface, as long as the energy of the acceptor states is below the energy of the donor states (Figure 1, right). The injected electron is used in the CO$_2$ reduction reactions.

In our recent work,

we investigated the electronic structure of Ru complexes attached to the pure Ta$_2$O$_5$ substrate with OH, COOH, and PO$_3$H$_2$ anchors. We found that the alignment of the energy levels in Ta$_2$O$_5$ and Ru complexes was not favorable for the ET to occur, because the acceptor level was higher in energy than the donor level (Figure 1, left). N-Doping was suggested as one of the most critical factors making the ET possible. Recent, yet unpublished data of Jinnouchi et al. confirm the calculation results. The authors showed that the CB edge is shifted toward more positive energies, when Ta$_2$O$_5$ is doped with N atoms. The atomistic origin of such shift was attributed to electrostatic effects due to the dipole created by the N–O layer in the doped material.

In the present work, we take the previously developed methodology to the state-of-the-art level, by performing NA-MD simulations. The approach combines classical molecular mechanics (MM) and extended Hückel theory (EHT) to compute nuclear dynamics and electronic structure, respectively. The MM part is used to produce well-thermalized and sufficiently long ground state molecular dynamics (MD) trajectories. The EHT gives the electronic structure, including both energy levels and NAC, for each point along the trajectories. The electronic structure information is subsequently used to perform NA-MD simulations within the classical path approximation that neglects electron back-reaction on the nuclear dynamics. We use the results of the NA-MD calculations to analyze and compare the ET dynamics in the COOH and PO$_3$H$_2$ systems.
the optimized geometries of the two complexes are presented in the Supporting Information.

In the RB-MD, one constrains arbitrary degrees of freedom via grouping specific atoms in united fragments. The nuclear dynamics of the system is then described in terms of translations and rotations of the rigid bodies into which the system is partitioned. In the limiting case, a single atom can be considered a rigid fragment with fully degenerate rotational degrees of freedom. Currently, we focus solely on the role of the anchor, and therefore, treat the entire Ru complex and the cluster representing the N–Ta2O5 surface as two distinct rigid fragments. The anchor groups are fully flexible at the atomistic level. Hence, the Ru-complex/N–Ta2O5 system with the COOH is composed of 8 fragments, 6 of which are the atoms of two COO groups, and the PO3H2 system is composed of 12 fragments, 10 of which are the atoms of two PO4H2 groups. The geometry of the N–Ta2O5 cluster and Ru complexes are taken from our previous calculations64 performed using the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06). The interactions between all rigid bodies are computed based on the explicit-atoms universal force field, UFF.65 As any other force fields, UFF would predict the structures of Ru complex and N–Ta2O5 to be different from the DFT-optimized structures. The rigid-body approach helps us to avoid any spurious effects due to structural differences. At the same time, the all-atomic description of the anchor groups allows us to focus on the ET dynamics through the anchors and to reveal the factors that stem only from their nature.

We optimize the COOH and PO3H2 systems by several rounds of simulated annealing. Each round consists of 100–200 cycles. Each cycle consists of a short MD simulation (1–100 fs), followed by resetting all linear and angular momenta of moving rigid fragment to zero. Initial annealing rounds utilize 0.1 fs integration timesteps. The subsequent rounds utilize larger, 1 fs, integration timesteps. Once the system is annealed until the heat production is negligible, we thermalize the system by running a 25 ps MD simulation in the NVT ensemble with the target temperature of 278 K. Temperature is maintained by the Nose-Hoover chain thermostat48,50 of length 3. The 25 ps thermalization period is followed by the 5 ps production run. The obtained trajectories are used to compute coordinate-dependent vibronic Hamiltonians needed for NA-MD simulations.

### 2.3. Electronic Structure

The electronic structure calculations are performed using our implementation of the semiempirical EHT method.51–55 EHT utilizes a minimal basis set of atomic s, p, and d orbitals. The matrix elements of the electronic Hamiltonian, H_{\text{io}} are defined as (\hat{H}_{\text{io}})_{ij} = K_{ij}((I_i + I_j)/2)S_{ij} where I_i and I_j are the atomic orbital energies, routinely set to negative of the valence state ionization potentials; K_{ij} is a proportionality factor that may, in principle, depend on orbital types, and S_{ij} is the overlap of atomic orbitals.

The use of EHT is essential for efficient computations with the systems of interest: the N–Ta2O5 cluster contains many Ta atoms, each contributing many electrons and orbitals. Thus, the electronic structure calculations quickly become expensive even for small clusters. Keeping in mind that such calculations must be done for many configurations along the MD trajectory, and that NAC matrices must be computed as well, the computational expenses become unfeasible for standard ab initio or DFT methods. At the same time, the tight-binding theories, including EHT, are well-known for capturing essential physics,13,14,18,19,20,40,46 which makes them reliable and transparent for qualitative analysis of chemical phenomena.

Although EHT is a well-defined tight-binding method, it lacks explicit electrostatic effects.66 The effects can be included in a more elaborate self-consistent charge version67–69 or using a configuration-interaction approach,69 but the costs would increase by at least an order of magnitude due to the need for self-consistency iterations or multiple configurations, respectively. Therefore, in the present work we choose to develop an effective parametrization that would capture the shift of the CB minimum level in N-doped Ta2O5, placing this level above the acceptor levels of the Ru complexes.

For the EHT parametrization, we utilize a set of three Ru complexes with different anchor groups, as well as moderate-size N–Ta2O5 clusters. The parametrization includes variation of the orbital energies, I_{ij}, the proportionality constants, K_{ij}, and the atomic orbital exponents.

The parametrization is performed to reproduce the absolute values of the frontier occupied and unoccupied orbitals in all four training systems. The target values for the conduction band minimum (CBM) and valence band maximum (VBM) of N–Ta2O5 are taken from the experiment: The values reported from ultraviolet photoelectron spectroscopy (UPS)65 and those measured electrochemically in solution,65,66,70,71 are close to each other. The HOMO/LUMO energy levels of the Ru complexes obtained in our earlier HSE06 calculations44 are used as the reference values. Ideally, the target values should be obtained from experimental measurements. However, such data are not available for the Ru(di-X-bpy) (CO)2Cl complexes used in the present work. At the same time, the values for other complexes such as (Ru(dpbbpy) (bpy)) (CO)2Cl71 agree well with the corresponding HSE06 results. However, we observe a systematic difference in these values, on the order of 0.2 eV. This difference is used as a correction to adjust the computed HOMO/LUMO levels of Ru(di-X-bpy) (CO)2Cl to estimate the expected experimental values. These corrected energies are used in our EHT parametrization as the reference values. Table 1 summarizes the frontier orbital energy levels of the training set system computed with the optimized EHT parameters and the corresponding reference values. The optimized EHT parameters are provided in the Supporting Information, section A. Further we shall discuss the orbitals of our primary interest: the LUMO levels of the Ru complexes and the CBM of the N–Ta2O5.

The agreement in the absolute values of the computed and target CBM levels of the N–Ta2O5 cluster is very good, thanks to the sufficient number of degrees of freedom used in the parametrization. The agreement in the absolute values for the three Ru complexes is satisfactory, showing some deviations from the corresponding target values for the OH and COOH systems. The deviations are modest. More importantly, the absolute values are less critical for our purposes. What matters the most, is that the two main qualitative features are captured well. First, the EHT calculations reproduce the monotonous increase of the energy levels in a series COOH < PO4H2 < OH, which is also observed for the adjusted HSE06 values. Second, the CBM energy of the N–Ta2O5 cluster is higher than the LUMO (and also LUMO+1, for COOH) energy levels of isolated Ru complexes. Proper energy level alignment, reproduced by EHT, is essential for making the interfacial ET possible. We emphasize again that this favorable energy level alignment originates from the N-doping of Ta2O5, and it is not observed in pure Ta2O5.

As it was shown in our previous work,44 the donor and acceptor energy level alignment present in free components (unbound Ru complex and substrate) is well preserved in the bound systems. Nonetheless, this effect needs explicit verification, especially when a new parameter set is developed. To verify that the alignment is preserved in the bound complexes, we compute the projected density of state (pDOS) for each system, shown in Figure 2. We project the DOS on the sets of atoms that constitute the Ru complex together with the anchor and the N–Ta2O5 substrate. The results are shown in Figure 3. One can observe that there are two unoccupied acceptor levels (LUMO and LUMO+1) below the N–Ta2O5 CBM in the COOH system (Figure 3a), and there is only one such level (LUMO) in the PO4H2 system (Figure 3b). The energy level alignment in the bound systems is consistent with that in the unbound components, suggesting that the present parametrization is suitable for modeling the ET dynamics in the bound system.

Table 1. LUMO/CBM Energy Levels for the Ru-(di-X-bpy) (CO)2Cl Complexes and N–Ta2O5 Used in Parameterization

<table>
<thead>
<tr>
<th>system</th>
<th>computed, eV</th>
<th>HSE06 (*)</th>
<th>experiment (**), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = COOH</td>
<td>−3.79</td>
<td>−3.58</td>
<td></td>
</tr>
<tr>
<td>X = PO4H2</td>
<td>−3.51</td>
<td>−3.52</td>
<td></td>
</tr>
<tr>
<td>X = OH</td>
<td>−3.33</td>
<td>−2.92</td>
<td></td>
</tr>
<tr>
<td>N–Ta2O5</td>
<td>−2.78</td>
<td>−2.8**</td>
<td></td>
</tr>
</tbody>
</table>
2.4. Nonadiabatic Molecular Dynamics. To carry out nonadiabatic ET simulations, we utilize the PTXAXID code\(^{70,71}\) designed for modeling of NA-MD in nanoscale systems. In the NA-MD simulations, we first solve the time-dependent Schrödinger equation (TD-SE), \(i\hbar (\partial \Psi / \partial t) = H \Psi\), where \(H = T_{\text{nuc}} + H_{\text{el}}\) is the total Hamiltonian of the system. The overall electron–nuclear wave function, \(\Psi\), is represented as a superposition of electronic basis states, \(|i\rangle\), weighted by the time-dependent coefficients, \(c_i(t)\): \(\Psi = \sum c_i(t)|i\rangle\). The electronic basis states \(|i\rangle\) can, in principle, be chosen arbitrarily. In the present work, we utilize a set of Slater determinants\(^{70,71}\) constructed from the adiabatic MOs of the bound Ru-catalys/N–Ta_2O_5 complexes. The TD-SE in the basis of electronic states reduces to the semiclassical TD-SE: \(i\hbar (d \Psi / dt) = \sum_i (H_{\text{vib}})_{ij} c_j(t),\) where \(H_{\text{vib}}\) is the vibronic (electron–nuclear) Hamiltonian, defined in terms of state energies, \(E_i\) and NAC for pairs of states, \(D_{ij} = \langle i | (\partial / \partial t) | j \rangle\), as following: \((H_{\text{vib}})_{ij} = E_{ij} - i\hbar D_{ij}\). The energies \(E_i\) are computed by diagonalizing the electronic EHT Hamiltonian: \(H_{\text{el}}C = \text{SCE}\), where \(C\) is the matrix of MO-LCAO coefficients and \(S\) is the matrix of AO overlaps. The energies and NAC needed to construct the vibronic Hamiltonian are computed in our composite MD/EHT scheme, described in previous sections.

Solution of the semiclassical TD-SE does not account for detailed balance, allowing barrier-less access to high-energy states from any arbitrary initial state. The electron–vibrational energy relaxation taking place during the ET process is mistreated, and thermodynamic equilibrium cannot be achieved in the long-time limit. To remedy this problem, we use the obtained coefficients, \(c_i(t)\), only as auxiliary quantities for the fewest switches surface hopping (FSSH) NA-MD algorithm\(^{72}\). In the FSSH, a swarm of trajectories is propagated, and each trajectory may diffuse in the Hilbert space of electronic basis states included in the model. The hopping probabilities depend on the semiclassical TD-SE amplitudes, \(c_i(t)\), as well as on the NAC between source and target states, \(D_{\text{source,target}}\). The averaging over all stochastic realizations of the FSSH trajectories and over all initial conditions (different starting configurations) yields SH populations of different states: \(P(t) = \langle N_{\text{source}}(t)/N_{\text{target}}(t)\rangle\), where \(\langle \rangle\) denotes thermal averaging. For more details on the NA-MD method and its trajectory surface hopping implementation, we refer the reader to the original works\(^{70–72}\) and related review papers.

We are interested in the dynamics of population transfer from the donor states localized on N–Ta_2O_5 to the acceptor states of the Ru complexes. This goal determines the choice of the model space of electronic basis states (the active space). The classification of electronic states of the combined Ru-complex/N–Ta_2O_5 systems as either donor or acceptor is based on the analysis of the pDOS shown in Figure 3. The COOH system contains two Ru-complex levels below the N–Ta_2O_5 CB (Figure 3a). These are the LUMO and LUMO+1 states of the bound complex. These are electron acceptor states. In the case of the PO_3H_2 system, there is only one state below the CB of N–Ta_2O_5 (Figure 3b). Thus, only LUMO is assigned as an acceptor state.
For this system. For both systems we choose a set of states localized on $N^−Ta_2O_5$. LUMO$^+$ through LUMO$^+$ + $m$ ($n = 3$ for COOH and $n = 2$ for PO$_3$H$_2$; $n + m = 10$) to act as donor states. These states span approximately a 1 eV energy window above the CBM of $N^−Ta_2O_5$. They include the CB edge states and a portion of the quasi-continuous part of DOS in the region where the DOS shows the high-density peak (see Figure 3). The initial excitations to even higher energy levels would be appropriate for modeling intraband relaxation in $N^−Ta_2O_5$, rather than for interfacial ET we study.

NA-MD simulation provides the total survival probability for a system to remain in any of the donor states after a time delay, $t$:

$$P_{\text{donor}}(t) = \sum_{m,n+m} P_{n+m}(t).$$

The computed probability is averaged over initial excitations to all considered donor states. The wave function isosurfaces of the acceptor and lowest donor states in the COOH and PO$_3$H$_2$ system are shown in Figure 4. One can observe a distinct difference in the localization of the orbitals, consistent with an intuitive assumption about the nature of donor and acceptor states. We should note, however, that this localization can become less pronounced as a result of dynamical disorder. One then would observe a notable mixing of the defined donor and acceptor states in instantaneous snapshots. Nonetheless, the distinctive features of the donor and acceptor states remain valid during the course of MD.

3. RESULTS AND DISCUSSION

3.1. Electron Transfer Dynamics. The results of NA-MD calculations are presented in Figure 5. First, we compare the population transfer dynamics without effects of electronic decoherence (Figure 5a). The initial relaxation shows weak Gaussian character, which is typical for quantum processes. The Gaussian component decays when quantum dynamics develops to encompass multiple states. The rest of the relaxation follows the exponential decay law. We determine the ET time to be 530 fs for the COOH system and 5.50 ps for the PO$_3$H$_2$ system. The ET occurs on much shorter time scale in the COOH system. In the fully coherent FSSH description, population transfer is governed by NAC and energy gap between donor and acceptor states. The energy gap magnitudes are very similar in the COOH and PO$_3$H$_2$ systems, as it follows from Table 1. We, therefore, conclude that the major reason leading to very distinct intrinsic efficiencies of the ET in these systems is disparity of the NAC magnitudes.

The fully coherent scheme is known to underestimate transition times of slow processes, because it lacks the important decoherence effects stemming from system-bath interactions. The results in Figure 5a are valid only for a hypothetic system, in which the electronic subsystem is isolated from the bath of quantum vibrations. We use it to demonstrate the dominant role of NAC in determining the qualitative trends in ET for complexes attached with different anchors. To obtain quantitative results for transitions happening on picosecond and longer time scales, it is important to include decoherence effects into NA-MD. We utilize the decoherence-induced surface hopping method. The results are presented in Figure 5b.

As expected, nonadiabatic dynamics that includes decoherence shows slower ET. The decay curves follow exponential law with practically absent Gaussian component. The time scales obtained for the COOH and PO$_3$H$_2$ systems are 7.50 and 56.7 ps, respectively. The time scale for the COOH system agrees reasonably well with the experimentally measured value of 12 ± 1 ps. The experimentally measured time scale for the PO$_3$H$_2$ system is not available. Judging by the results for the COOH

![Figure 5. Decay of the total population of donor ($N^−Ta_2O_5$) states. Results for COOH and PO$_3$H$_2$ anchors are present: (a) without decoherence and (b) with decoherence.](image)

![Figure 6. Visualization of the NACs between unoccupied orbitals of $N^−Ta_2O_5$ and Ru complex attached via either COOH anchor (a) or PO$_3$H$_2$ anchor (b). NAC values at noninteger points are interpolated from the values at integer-valued x and y coordinates.](image)
The situation is different for the PO₃H₂ system (Figure 6b). Here, we observe only a single ET channel, between the LUMO acceptor state and the LUMO+1 donor state. Most importantly, the average magnitudes of the couplings are almost an order of magnitude smaller than those in the COOH system. The coupling between LUMO and LUMO+1 is on the order of 30 meV. This channel promotes faster electron transfer in the COOH system compared to those in PO₃H₂. As it follows from the NAC definition, NAC characterizes wave function sensitivity to nuclear motion. One may expect larger couplings for the PO₃H₂ anchor, since the group is more flexible due to sp³ hybridization of the central P atom, whereas COOH is more rigid due to sp² hybridization of the C atom. However, nuclear motion is not the determining factor. pDOS of the COOH system (Figure 3) shows that both LUMO and LUMO+1 contain notable contributions from the central C atom of the COOH anchor, because the anchor is conjugated to the ligand π-system. Thus, motion of the COOH group strongly affects the acceptor wave functions and the donor–acceptor NAC. On the contrary, pDOS of the PO₃H₂ system shows little contribution of anchor orbitals to the only acceptor state (LUMO). Therefore, motions of the PO₃H₂ group do not affect the acceptor wave function notably, leading to smaller NAC.

3.3. Role of Quantum Coherence. The role of quantum coherence in natural and artificial light-harvesting is receiving significant attention. To fully characterize ET dynamics in the COOH and PO₃H₂ systems, we have analyzed decoherence properties of these complexes. Using the optical response function formalism, we compute decoherence functions (Figure 7a). These functions show how quickly electronic coherences are destroyed due to interactions with phonons. Frequent “observation” or “measurement” of the electronic state of the system by the vibrational environment forces the system to collapse onto one of its eigenstates, causing decoherence. Therefore, fast decoherence may “return” the system to its initial electronic state, slowing down electronic transitions. On the contrary, when the system evolves as a coherent superposition of several states, electronic transitions are accelerated. The decoherence function quantifies the rate with which the system looses its memory about the past, and hence shows how frequently the system is “returned” to its original state by the environment-induced fluctuations. We observe that coherence decays faster in the COOH system than in the PO₃H₂ system, as seen in the decoherence functions (Figure 7a). The ET is faster in the system with the COOH anchor. Moreover, the ratio of the ET times changes little, leading to the conclusion that the only role of decoherence is the reduction of the ET rates. Coherence effects do not alter the qualitative trends observed across the different systems. Hence, one expects that the trends can be explained by the NAC magnitudes.

3.2. Role of Nonadiabatic Coupling. As it has been conjectured in the previous section, the NAC should be larger in the COOH system. In order to verify this hypothesis, we compute the 2D maps showing the time-averaged NAC magnitudes for all pairs of orbitals in the considered range (Figure 6). The quantities are computed as \( \langle |\langle H_{\alpha\beta} \rangle |^2 \rangle \rangle \), where \( T \) is the number of steps in the MD trajectory, \( \langle \rangle \) denotes the time averaging.

The COOH system (Figure 6a) exhibits strong coupling of the LUMO+1 and LUMO+2 levels, with the magnitude of ca. 300 meV. This large coupling realizes an efficient population transfer from the lowest donor (LUMO+2) state to the upper acceptor (LUMO+1) level. One can also observe that there is a secondary channel for the exciton relaxation via a direct coupling between the LUMO+2 state and the LUMO+4−LUMO+6 states. This channel promotes faster electron relaxation to the lowest donor state (LUMO+2), and therefore facilitates the interfacial ET. These couplings are smaller than those between LUMO+1 and LUMO+2, on the order of 20−50 meV, but are still much larger than the couplings with other states, except for couplings between sequential LUMO+n and LUMO+n+1 states. The secondary channel is visualized on the 2D map as green off-diagonal areas. Visualization of the isosurfaces of the LUMO+4, 5, 6 orbitals (see Supporting Information, section B) indicates that the orbitals are mostly localized on the N−Ta₂O₅ cluster, and are partially delocalized to the Ru complex, providing a possible explanation of the notable coupling.

The situation is different for the PO₃H₂ system (Figure 6b). Here, we observe only a single ET channel, between the LUMO acceptor state and the LUMO+1 donor state. Most importantly, the average magnitudes of the couplings are almost an order of magnitude smaller than those in the COOH system. The coupling between LUMO and LUMO+1 is on the order of only 20−30 meV.

The 2D maps clearly show the regions of strong coupling between higher-lying orbitals. As seen in pDOS of Figure 3, states localized on the Ru-complex are in resonance with higher-lying CB states of N−Ta₂O₅. As a result, the orbitals are mixed and strongly coupled to each other. Therefore, a high-energy excitation will lead to fast ET to the Ru complex via these intraband couplings.

It is important to explain the fundamental reasons leading to large NACs in the COOH system compared to those in PO₃H₂. As it follows from the NAC definition, NAC characterizes wave function sensitivity to nuclear motion. One may expect larger couplings for the PO₃H₂ anchor, since the group is more flexible due to sp³ hybridization of the central P atom, whereas COOH is more rigid due to sp² hybridization of the C atom. However, nuclear motion is not the determining factor. pDOS of the COOH system (section B of the Supporting Information) shows that both LUMO and LUMO+1 contain notable contributions from the central C atom of the COOH anchor, because the anchor is conjugated to the ligand π-system. Thus, motion of the COOH group strongly affects the acceptor wave functions and the donor–acceptor NAC. On the contrary, pDOS of the PO₃H₂ system shows little contribution of anchor orbitals to the only acceptor state (LUMO). Therefore, motions of the PO₃H₂ group do not affect the acceptor wave function notably, leading to smaller NAC.

Figure 7. Decoherence functions (a) and spectral densities (b) of the COOH (green lines) and PO₃H₂ (red lines) systems computed using fluctuation of the gap between appropriate donor and acceptor states.
in the PO$_3$H$_2$ system. The computed decoherence times for the two main transitions LUMO+2 $\rightarrow$ LUMO+1 (in COOH) and LUMO+1 $\rightarrow$ LUMO (in PO$_3$H$_2$) are ca. 30 and 105 fs, respectively.

The observed trends in both NAC and decoherence are caused by the same factors, namely, anchor motions and delocalization of donor and acceptor orbitals onto anchor. One may assume that the COOH anchor, being a planar and more rigid than the PO$_3$H$_2$ can induce smaller structural fluctuations than the more flexible PO$_3$H$_2$ group. In our previous study,$^{44}$ we found that the fluctuation of the tilt angle of these Ru complexes relative to the substrate plane are, in fact, comparable to each other. The structural fluctuation analysis suggests that there would be no notable difference in decoherence times due to differences in motion of the two complexes.

The structural dynamics is not the direct factor that affects decoherence times. Similar to our analysis of NAC in their relation to orbital-resolved pDOS, it is the response of the energy gap fluctuation to the structural changes that matters the most. There are situations when structural correlations may decay very rapidly, whereas coherence can still persist for a long time.$^{92}$ To understand the origins of faster decoherence in the COOH system, we analyze the autocorrelation function (ACF) of the energy gap fluctuation, $\langle \delta E_{AD}(t) \delta E_{AD}(0) \rangle$, where A and D denote the acceptor and donor states, respectively. The Fourier transform of the ACF reveals the frequencies of the gap fluctuation (Figure 7b). Generally, the higher the frequency of such fluctuations, the faster the decoherence, because the wave functions corresponding to the two energy levels would build up a larger phase difference.

The results shown in Figure 7b indicate that the donor–acceptor energy gap fluctuation occurs with a smaller frequency in the PO$_3$H$_2$ system than in the COOH. In accord with our explanation above, this result suggests that decoherence in the COOH occurs faster than in the PO$_3$H$_2$ system. The atomistic origins for this effect are twofold. First, the LUMO state in the PO$_3$H$_2$ system does not have any notable contribution of anchor orbitals. Thus, motion of the PO$_3$H$_2$ anchor does not affect the orbital energies as much as motion of the COOH anchor does. We observe the same reason that made NAC smaller in the PO$_3$H$_2$ system than in the COOH complex. Second, the vibrations of the aromatic C–C bond connecting the Ru complex and the COOH anchor are faster than the vibrations of the analogous aliphatic P–C bond in the PO$_3$H$_2$ system: both because of a larger force constant for the C–C bond as compared to the P–C bond, and due to a smaller atomic mass of the C atom as compared to the P atom. The faster vibration leads to a more rapid evolution of the wave function phase for each energy level, and to faster accumulation of the phase difference for the energy level pair.

Faster decoherence in the COOH system should decelerate ET more than in the PO$_3$H$_2$ complex. This effect is achieved in our simulations, indeed: the deceleration ratio for the COOH can be defined as $\tau_{\text{COOH}} = \tau_{\text{decoherence(COOH)}} / \tau_{\text{no-decoherence(COOH)}} = 14.15$, the analogously defined deceleration ratio for the PO$_3$H$_2$ system is $\tau_{\text{PO3H2}} = 10.31$. Inclusion of decoherence favors faster dynamics in the PO$_3$H$_2$ system. However, the effect is relatively small. On the other hand, the effects due to differences in NACs are significantly more pronounced: the ratio of the averaged NACs between the donor and acceptor levels of the two systems reaches the order of 10. Overall, ET is notably faster in the COOH system.

### 3.4. Implications to the ET in the COOH and PO$_3$H$_2$ Systems

The conclusions from our calculations are in formal contrast with the previous experimental measurements,$^{38}$ which report an opposite trend: Our calculations predict the COOH anchor to be more efficient than PO$_3$H$_2$, whereas the experimental TONs are larger for the PO$_3$H$_2$ system. Our results address only one factor affecting the overall efficiency of the photocatalytic CO$_2$ reduction. Structure of the catalyst surface is the most likely reason for the discrepancy. It has been known from other studies that molecules attached via the COOH anchor are very sensitive to conditions such as pH and solvent.$^{25,26}$ It is easier for the system with the COOH anchor to detach from the substrate, partially because the final anion forms an extended aromatic system, stabilizing the dissociation product. There is no such stabilization for the PO$_3$H$_2$ anchor. The PO$_3$H$_2$ system is more stable,$^{24,25}$ leading to a larger surface coverage and, hence, higher TONs. Finally, the reduction potential of CO$_2$ is greater than that of almost any other organic system found in a photocatalytic cell. The electron injected into the Ru complex can reduce the COOH group. We attribute the larger TONs observed experimentally in the PO$_3$H$_2$ system to higher stability and effective surface coverage, and to smaller extent of self-reduction.

Very recently, Sato et al. synthesized the electroneutral COOH and PO$_3$H$_2$ systems, and evaluated their photocatalytic activities.$^{93}$ Contrary to the previously reported results for [Ru(dcbpy)(bpy)(CO)$_2$]$^{2+}$ and [Ru(dpbbpy)(bpy)(CO)$_2$]$^{2+}$, they found that an initial TON of CO$_2$ reduction using [Ru(dcbpy)(CO)$_2$Cl$_2$] was about three times larger than that using [Ru(dpbbpy)(CO)$_2$Cl$_2$], which is consistent with the present theoretical prediction. In addition, they observed that the COOH system was deactivated after 15 h, suggesting instability of the catalyst surface.

Intrinsic properties of the COOH anchor suggest that the complexes attached with this group should be more efficient in an ideal environment. This conclusion agrees with other simulations$^{31}$ that report faster ET in systems attached with the COOH anchor compared to the PO$_3$H$_2$ anchor. Additional evidence supporting our conclusion can be inferred from the existing experimental works. For example, Mulhern et al.$^{94}$ showed that electrons are injected approximately twice as efficiently from chalcogenorhodamine dyes anchored to TiO$_2$ via carboxylate linkages than via phosphonate linkages. Bae et al.$^{35}$ reported larger steady-state photocurrents in RuL$_3$ complexes attached to TiO$_2$ with the COOH anchor as opposed to the analogous molecules attached with the PO$_3$H$_2$ anchor. The photocurrent can be linked to ET rates directly, whereas TONs values can be affected by the surface coverage and other factors. Higher stability of the PO$_3$H$_2$ anchor in contrast to that of COOH is also suggested by the direct calculations of the binding energy, although the effect may depend on the choice of the surface plane.$^{48}$

### 4. CONCLUSIONS

We have reported nonadiabatic dynamics studies of ET in the prototypical Ru(di-X-bpy)(CO)$_2$Cl$_2$/N–Ta$_2$O$_5$ complexes for photocatalytic CO$_2$ reduction. We have investigated the role the anchor groups, X = COOH and PO$_3$H$_2$, play in determining the efficiencies of these systems. Our calculations show notably faster ET in the COOH system compared to PO$_3$H$_2$. The computed ET time scales in the COOH and
Overall, decoherence slows down ET by an order of magnitude.

The results of our calculations indicate that the COOH anchor is intrinsically more efficient than PO$_3$H$_2$. This conclusion is supported by the existing computational and experimental data indicating that the COOH system is in good agreement with the experimentally measured value of 12 ± 1 ps.

We suggest that the experimentally observed TONs are not necessarily indicative of faster or slower ET dynamics at the fundamental ET mechanisms and highlights the importance qualitative trends, despite the method's simplicity. We expect the qualitative conclusions to hold for more elaborate methodologies.

Quantum coherence counteracts NAC; however, NAC plays a more important role. Electronic decoherence in the COOH system is faster than that in PO$_3$H$_2$, 30 and 105 fs, respectively. Overall, decoherence slows down ET by an order of magnitude. At the same time, it decelerates ET only slightly more in the COOH complex than in the PO$_3$H$_2$ complex, having only a small effect on the ratio of the ET times in the two systems.

The observed trends in the NAC and decoherence rates are both explained by sensitivity of the acceptor state wave functions to motion of the anchor groups. This sensitivity is analyzed using orbital-resolved pDOS. The frontier level of the PO$_3$H$_2$ system contains no contribution from the anchor. On the contrary, the acceptor states in the COOH system contain a notable fraction of orbitals of the C atom of the COOH anchor group, leading to larger NAC and smaller decoherence times.

We suggest that the experimentally observed TONs are not necessarily indicative of faster or slower ET dynamics at the semiconductor/Ru-complex interface. Other factors are likely to play a notable role. Existing experimental data indicate that effective surface coverage may be one of such factors. The coverage in the COOH system is likely to be lower due to dissociation of the anchor-surface bond and reduction of the COOH anchor by the photogenerated charges. The possibility of the latter process is supported by our electronic structure calculations, showing a notable localization of the acceptor state electron density on COOH. The reported comprehensive, time-domain, atomistic analysis of the photoinduced dynamics establishes the fundamental ET mechanisms and highlights the importance of anchor stability, nonadiabatic transitions and quantum coherence in artificial photocatalysis.

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### REFERENCES


### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07454.

Optimized EHT parameters and orbital-resolved pDOSs (PDF)

Geometry of COOH system (XYZ)

Geometry of PO$_3$H$_2$ system (XYZ)

### AUTHOR INFORMATION

Corresponding Author

*prezhdo@usc.edu*

Notes

The authors declare no competing financial interest.