

Simulating photoreaction pathways of TiO_4

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Abstract

60 non-adiabatic molecular dynamics trajectories were run for $\text{Ti}(\text{OH})_4$ starting from vertical excitations into S_1 from ground state molecular dynamics. The rare-event formation of water from $\text{Ti}(\text{OH})_4$ without any physisorbed water was observed in the S_1 excited state, via a hydrogen transfer. The immediate hop back to the ground state after the transfer indicates that the reaction is not well described by transition state theory.

1 Introduction

Hydrogen fuel is considered as one of the future renewable sources for transportation. However, the vast majority of industrial hydrogen is produced from fossil fuels leading to significant carbon dioxide emissions[1]. One promising method is to use titanium dioxide clusters that are able to catalytically split water in the presence of light. The overall process is known to be ultrafast (within 1 ps), making it suitable and important for molecular dynamics simulations from first principles to be conducted; the time scale is small enough to achieve reasonably accurate dynamics with modest computational resources, and ultrafast spectroscopic experiments benefit from mechanistic insights from the simulations.

Kazaryan and coworkers suggest, based on transition state analysis, that photoexcited $\text{Ti}(\text{OH})_4$, representing the smallest possible hydroxylated titanium dioxide cluster, is able to extract a hydrogen from a water molecule upon electronic excitation, producing a $\text{Ti}(\text{OH})_3(\text{OH}_2)$ radical and a OH radical.[2]

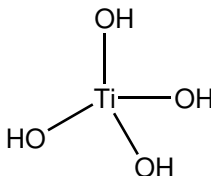


Figure 1: Tetrahedral structure of $\text{Ti}(\text{OH})_4$

Muuronen and coworkers have in contrast performed non-adiabatic molecular dynamics (NAMD) with a hydroxylated $(\text{TiO}_2)_4$ nanoparticle with physisorbed water.[3] By observing the dynamic time evolution of the electron-hole pair, the simulation consistently matches with STM experiments. This analysis using explicit dynamics is not captured in transition state analysis. It was determined that localizing the excited electron and the electron hole were important to catalysis.

We hypothesize that $\text{Ti}(\text{OH})_4$, in the absence of other water molecules, may spontaneously form free water molecules upon electronic excitation. This would be one of the steps of a mechanism for water splitting by $\text{Ti}(\text{OH})_4$. Rather than using the transition state analysis employed by Kazaryan, we choose to employ NAMD similar to Muuronen’s work to capture the non-adiabatic dynamics of this reaction.

2 Methods

2.1 Statement of the Models

Molecular potential energy surfaces (PES) are based on the Born-Oppenheimer (BO) approximation which assumes the separation of the electronic and nuclear degrees of freedom. However, this approximation breaks down whenever two or more electronic states are strongly coupled[4], for example by the nuclear velocity. One method to treat this derivative coupling to nuclear position is the non-adiabatic molecular dynamics (NAMD) within the framework of the time-dependent Schrödinger equation. For each nuclear configuration, \mathbf{R} , the time-evolution of the electronic wavefunction $|\psi(r|\mathbf{R})\rangle$,

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

The time-dependent electronic Hamiltonian is defined as,

$$\hat{H}_{el}(\mathbf{r}|\mathbf{R}(t)) = \hat{T}_e(\mathbf{r}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{ne}(\mathbf{r}|\mathbf{R}(t)) + \hat{V}_{nn}(\mathbf{r}|\mathbf{R}(t)) \quad (2)$$

where \hat{T}_e is the electronic kinetic energy, \hat{V}_{ee} is the electron-electron repulsion, \hat{V}_{ne} is the electron-nucleus attraction, and \hat{V}_{nn} is the nucleus-nucleus repulsion. Meanwhile, the evolution of the nucleus is simply the Newton’s classical equations of motion,

$$\mathbf{F}_j(t) = m_j\ddot{\mathbf{R}}_j(t) \quad (3)$$

where \mathbf{F}_j , m_j , and $\ddot{\mathbf{R}}_j$ denotes the force, the mass, and acceleration, respectively, of the j th nuclei at time t . In the simulation of $\text{Ti}(\text{OH})_4$, the forces are determined with the fewest switches surface hopping (FSSH) method[5] in the basis of the BO states. With the electronic wavefunction,

$$|\Psi(t|\mathbf{R})\rangle = \sum_n c_n(t|\mathbf{R})|\Phi_n(\mathbf{R})\rangle, \quad (4)$$

this can be inserted into the time-dependent Schrödinger equation and yield the time-dependent amplitude vector \mathbf{c} ,

$$i\dot{\mathbf{c}} = (\mathbf{H} - i\mathbf{W}) \mathbf{c} \quad (5)$$

$$W_{mn} = \langle \Phi_m | \frac{\partial}{\partial t} | \Phi_n \rangle \quad (6)$$

W_{mn} is the nonadiabtic coupling of the two BO states m and n . A random number is generated to determine whether the molecule will hop between one state to another. If the switch is accepted, the total energy of the system is conserved by scaling the momenta in the direction of the non-adiabatic coupling vector. Otherwise for nuclear dynamics, the forces are computed where $\mathbf{F}_j = -\frac{\partial E_m(\mathbf{R})}{\partial \mathbf{R}_j}$ and then, the leapfrog Verlet algorithm is used to propagate the nuclei,

$$\mathbf{P}(t_{i+1/2}) = \mathbf{P}(t_{i-1/2}) + \mathbf{F}(t_i)\Delta t \quad (7)$$

$$\mathbf{Q}(t_{i+1}) = \mathbf{Q}(t_i) + \mathbf{M}^{-1}\mathbf{P}(t_{i+1/2}) \quad (8)$$

where \mathbf{P} , \mathbf{Q} , and \mathbf{M} are the nuclear momentum, postion, and mass tensor, respectively.

2.2 Computational Details

The simulation of $\text{Ti}(\text{OH})_4$ was computed on TURBOMOLE v7.2[6] to sample the water splitting mechanism of $\text{Ti}(\text{OH})_4$. The initial structures are generated using ground state ab initio molecular dynamics (AIMD) with PBE0[7] functional and def2-SVP basis set[8]. At initial velocities of 2200K and 3200K, 30 trajectories were computed at each temperature using 1 fs timestep (40 a.u.). Each trajectory ran for a total of 250 fs. At every 85 fs, the coordinates of the $\text{Ti}(\text{OH})_4$ were extracted to run NAMD simulations with time-dependent density functional theory and FSSH starting in the S_1 state, simulating a vertical excitation. The same PBE0[7] functional and def2-SVP basis[8] were used. The NAMD simulations ran until the systems hopped to the S_0 ground state and the nonradiative excited state lifetime was determined by the log-linear regression of the excited state population defined as,

$$\rho_{11}^{\text{av}}(t) = \frac{1}{N_{\text{ensemble}}} \sum_{k \in \text{ensemble}} n_k(t) \quad (9)$$

where $n_k = 0$ means the simulation is at the ground state and $n_k = 1$ is at the excited state. The trajectories were visualized with the MOLDEN package.

3 Results

A total of 60 NAMD simulations were performed and out of the 60, only 7 trajectories revealed the formation of water. Of these trajectories, only one showed a complete dissocia-

tion of water from the $\text{Ti}(\text{OH})_4$ cluster as seen in Fig 3. The overall reaction is shown in Fig 2. There is a hydrogen transfer in this reaction, which with the electronic rearrangement produces a $\text{Ti}=\text{O}$ double bond and a water molecule.

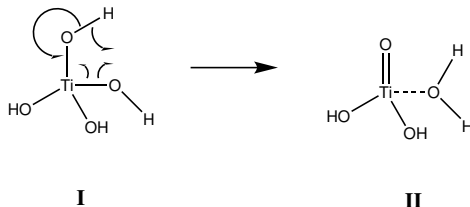


Figure 2: Reaction mechanism observed for $\text{Ti}(\text{OH})_4$ (I) to form water(II).

For the trajectory that produced a free water molecule, the water formation and split from $\text{Ti}(\text{OH})_4$ took a total of 516 fs. The water appeared when the OH stretch became vibrationally active and the hydrogen atom transfer from the OH ligand to another OH ligand from Fig 3. This suggested that the vibrational nuclear degrees of freedom to be mainly responsible for the excited states deactivation.

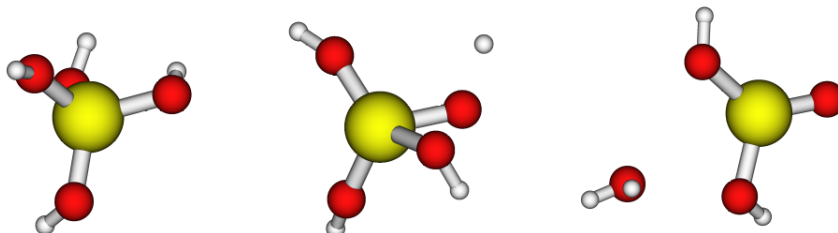


Figure 3: Snapshots of the $\text{Ti}(\text{OH})_4$ simulation taken at 0 fs (left), 392 fs (middle), and 516 fs (right).

The rest of the trajectories did not undergo any reaction in the excited state before hopping back to the ground state. The decay is plotted in fig 4.

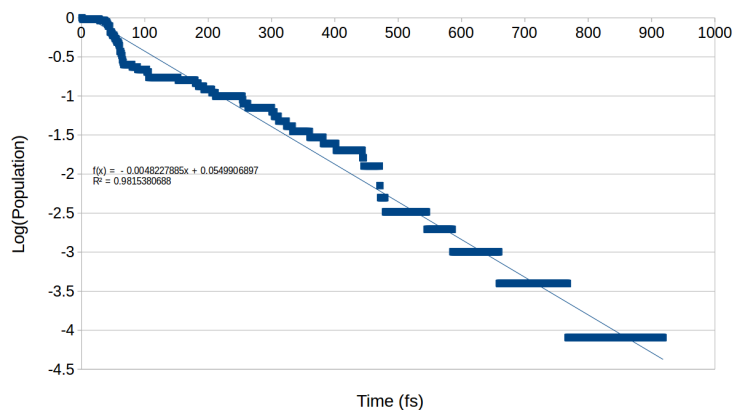


Figure 4: NAMD simulation of $\text{Ti}(\text{OH})_4$ starting at the S_1 state Franck-Condon geometry that show the nonradiative excited state lifetime by the natural log-linear regression of the excited state population.

In Fig 4, the population analysis of the 60 NAMD simulations starting from the S_1 state Franck-Condon geometry with random nuclear velocities showed that the nonradiative excited state lifetime is approximately 207 fs.

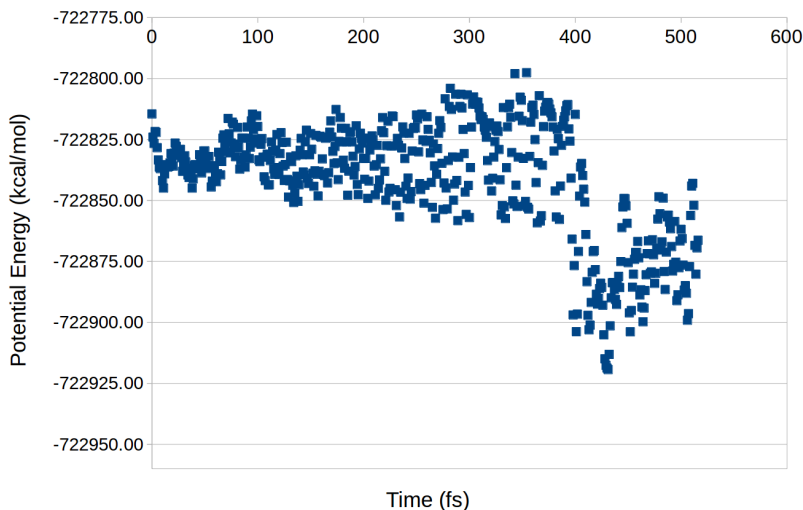


Figure 5: The potential energy of the $\text{Ti}(\text{OH})_4$ system transitioning between the S_1 excited state and the S_0 ground state.

In Fig 5, the transition from the S_1 state to the S_0 state is approximately a difference of 25 kcal/mol. This transition appears to happen at approximately 400 fs. Prior to the transition is the vibrationally active OH stretch beginning at approximately 300 fs. This relative energy difference captured from the NAMD simulation appears to match fairly close to the CCSD(T) relative potential energies of the reaction of H_2O with $\text{Ti}(\text{OH})_4$ at the excited state[2] which is approximately 34 kcal/mol.

Due to the small number of trajectories, the population analysis for the products of photo-excitation of $\text{Ti}(\text{OH})_4$ is skewed. 1 in 10 trajectories is observed to form water, but only 1 in 60 trajectories forms a free water molecule.

4 Conclusions

In summary, our NAMD simulation of $\text{Ti}(\text{OH})_4$ demonstrate a rare-event mechanism for the formation of a free water molecule upon photo-excitation to the S_1 state. The formation of water molecules is more frequent, and may be the more important reaction pathway. Analysis suggests that the nonradiative transition from the S_1 to S_0 state mainly depends on the nuclear velocity in their vibrational motion. In addition, the transfer of hydrogen appears to only happen in the excited states and not in the ground state. This transfer leads to the formation of water and to an immediate non-radiative transition from the S_1 excited state to the S_0 ground state.

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