

## II.G.2 Real-Time Atomistic Simulation of Light Harvesting and Charge Transport for Solar Hydrogen Production

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### Objectives

Develop novel approaches for studying photo-induced electron-nuclear dynamics in nanoscale materials and investigate excited state processes in photovoltaic and photocatalytic systems for solar hydrogen production.

### Technical Barriers

Theoretical and computational approaches are needed, capable of accurate description of non-equilibrium electron-nuclear dynamics, including nuclear quantum effects, and applicable to systems composed of hundreds of atoms.

### Abstract

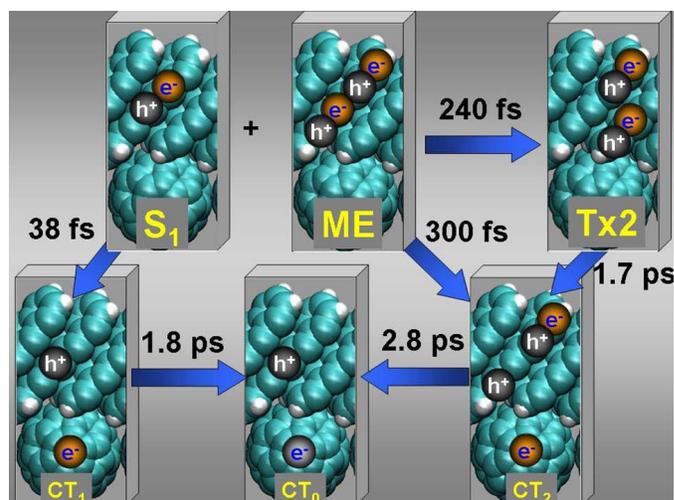
The growing need for renewable, clean and abundant energy sources constitutes one of the highest priority problems of the humankind. If a small fraction of the Sun energy can be accumulated and transformed into a convenient form, the problem can be solved. Therefore, search for novel photovoltaic and photocatalytic materials is an actively developing field of chemistry. Rational design of solar materials requires thorough understanding of the charge separation and photochemical processes, in competition with charge recombination and energy losses to heat. Many key steps occur on ultrafast timescales and are best understood by direct non-equilibrium time-domain simulation. I will present the non-adiabatic molecular dynamics (NA-MD) approach for studying quantum dynamics of solar energy nanoscale materials. The recent implementation of NA-MD within the open-source package, PYXAID, will be introduced.<sup>1,2</sup> Then, two important applications will be considered.<sup>3,4</sup>

### Progress Report

#### Sub Topic 1: Non-adiabatic dynamics of singlet fission in organic photovoltaic materials

The first application focuses on the dynamics of singlet fission (SF) and charge transfer (CT) at a pentacene/ $C_{60}$  photovoltaic heterojunction.<sup>4</sup> In the early works on singlet fission the mechanism involving optically dark multi-exciton (ME) state has been proposed. According to the scheme, initially prepared singly excited state,  $S_1$ , the natural product of direct photoexcitation, is gradually transformed in otherwise inaccessible ME state. The existence of the ME state has later been confirmed experimentally, however it was found that decay of  $S_1$  and accumulation of ME states are not directly correlated. The coherent mechanism of the SF has been suggested, according to which both ME and  $S_1$  configurations are excited simultaneously, as the components of a true wavefunction of multielectron Hamiltonian. In our work we have performed atomistic time-domain NA-MD simulations to better understand the nature of the SF process.

In our work we develop a minimalistic model that is capable of describing singlet fission and charge transfer in the pentacene/ $C_{60}$  heterojunction. The model includes six types of states – single pentacene exciton ( $S_1$ ), pentacene multiexciton (ME), pair of coupled triplets ( $Tx2$ ) – a predecessor of a charge-multiplied state, and three types of charge transfer between heterojunction components ( $CT_0$ ,  $CT_1$ , and  $CT_2$ ). With the minimalistic set of these diabatic states we propose a comprehensive kinetic scheme that yields electron transfer timescales in agreement with experimental observations. The kinetic scheme is parameterized by energy levels of participating states and by the non-adiabatic

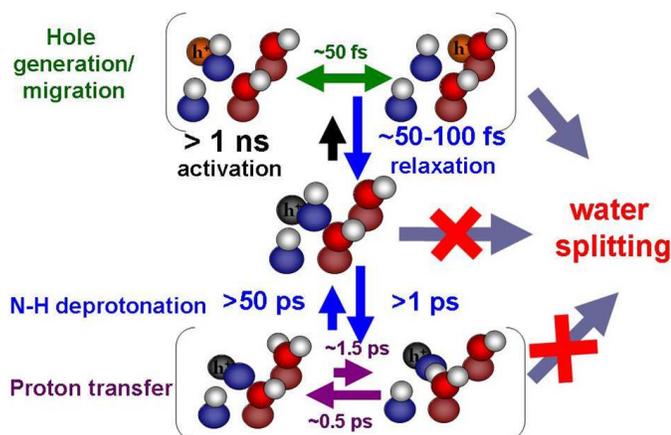


coupling between each their pair. The energy levels of the states are chosen on the basis of judicious examination of comprehensive experimental and theoretical data. For singly-excited states they agree with our DFT calculations, while for doubly excited states the differences are substantial, pointing to importance of electrostatic and exchange-correlation interaction, which are absent at the level of single Slater determinants. The non-adiabatic couplings are computed explicitly using NA-MD approach and real time TD-DFT simulations. These calculations indicate that the coupling between  $S_1$  and ME states is negligible, making them effectively decoupled from each other. As a result, the ME state can not be populated by a decay of  $S_1$  state, supporting the hypothesis of the coherent mechanism of SF.

By direct examination, we find that alternative kinetic schemes fail to reproduce the timescales of one or more kinetic processes. This implies some restrictions on the order and difference of the involved energy levels, helping us to resolve some inconsistencies among the available experimental and theoretical results. On the basis of analysis of the energy levels and the magnitudes of non-adiabatic couplings, we propose that the intermediate doubly-excited states of charge-transfer character are crucially important for dissociation of the ME state into a pair of coupled triples, Tx2. Without the corresponding intermediate states, the direct coupling between ME and Tx2 is vanishing and singlet fission can not proceed efficiently. The model predicts that the SF efficiency relies strongly on the availability of the intermediate states and on its competition with the CT processes.

### Sub Topic 2: Non-adiabatic dynamics of holes in photocatalytic water splitting

The second application concerns photocatalytic water splitting at GaN semiconductor. Photochemical water splitting is a promising avenue to sustainable, clean energy and fuel production. Gallium nitride (GaN) and its solid solutions are excellent photocatalytic materials; however, the



efficiency of the process is low on pure GaN, and co-catalysts are required to increase the yields.

We present the first time-domain theoretical study of the initial steps of photocatalytic water splitting on a GaN surface. Our state-of-the-art simulation technique, combining NA-MD and time-dependent density functional theory (TD-DFT), allows us to characterize the mechanisms and timescales of the evolution of the photogenerated positive charge (hole) and the subsequent proton transfer at the GaN/water interface. The calculations show that the hole loses its excess energy within 100 fs and localizes primarily on the nitrogen atoms of the GaN surface, initiating a sequence of proton transfer events from the surface N-H group to the nearby OH groups and bulk water molecules. Water splitting requires hole localization on oxygen rather than on nitrogen, necessitating non-adiabatic transitions uphill in energy on pure GaN. These transitions occur infrequently, resulting in low yields of the photocatalytic water splitting observed experimentally. We conclude that efficient co-catalysts should favor localization of the photogenerated hole on oxygen-containing species at the semiconductor/water interface.

### Future Directions

We will investigate novel, promising materials for solar hydrogen production, and will continue developing efficient theoretical and computational approaches for this purpose.

### Publication list (including patents) acknowledging the DOE grant or contract

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