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Accelerating the photocatalytic water splitting in catalyst-dye complexes

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Citation

Shao, Y. (2021, February 24). *Accelerating the photocatalytic water splitting in catalyst-dye complexes*. Retrieved from <https://hdl.handle.net/1887/3147173>

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Author: Shao, Y.

Title: Accelerating the photocatalytic water splitting in catalyst-dye complexes

Issue date: 2021-02-24

Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes

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Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes

Ph.D. thesis, Leiden University

Cover and Bookmark designed by Yang Shao

Printed by PRINTSUPPORT4U || www.printsupport4u.nl

This research was financed by the Chinese Scholarship Council (Grant No. 201606450019) and Leiden University. The use of supercomputer facilities at SURFsara was sponsored by NWO Physical Sciences, with financial support from the Netherlands Organization for Scientific Research (NWO) in the context of the NWO Solar to Products program (project number 733.000.007).

Accelerating the Photocatalytic Water Splitting in Catalyst–Dye Complexes

PROEFSCHRIFT

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof.dr.ir. H. Bijl,
volgens besluit van het College voor Promoties
te verdedigen op woensdag 24 februari 2021
klokke 13:45 uur

door

Yang Shao

geboren te Shandong, China
in 1990

Promotiecommissie

Promotor: Prof. dr. Huub J. M. de Groot

Copromotor: Dr. Francesco Buda

Overige leden: Prof. dr. Hermen S. Overkleeft (Leiden University)

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Prof. dr. Sandra Luber (University of Zurich)

For my parents, my wife, and my son

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List of Abbreviations

ADF	Amsterdam Density Functional
AIMD	<i>Ab Initio</i> Molecular Dynamics
APT	Concerted Atom-Proton Transfer
BO	Born-Oppenheimer approximation
BOMD	Born-Oppenheimer Molecular Dynamics
bpy	2,2'-bipyridine
CB	Conduction Band
CFF	Consistent Force Field
CHARMM	Chemistry at HARvard Macromolecular Mechanics
COSMO	Conductor-like Screening Model
CPMD	Car-Parrinello Molecular Dynamics
cy	<i>p</i> -cymene
DCACP	Dispersion-Correcting Atom-Centered Potential
DFT	Density Functional Theory
DFT-MD	DFT-based Car-Parrinello Molecular Dynamics
DS-PEC	Dye-Sensitized Photoelectrochemical Cell
DSSC	Dye-sensitized Solar Cells
EPT	Concerted Electron-Proton Transfer
ET	Electron Transfer
FMD	Free Molecular Dynamics
FS	Final State
GEA	Gradient Expansion Approximation
GGA	Generalized Gradient Approximation
GTH	Goedecker-Teter-Hutter
HEC	Hydrogen-Evolving Catalyst
HOMO	Highest Occupied Molecular Orbital
IEM	Ion Exchange Membrane
IS	Initial State
I₂M	Oxo-oxo Coupling
KS	Kohn-Sham
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MD	Molecular dynamics
NCAP	Nonadiabatic Conversion by Adiabatic Passage
NDI	2,6-diethoxy-1,4,5,8-diimide-naphthalene
NPT	Isothermal-isobaric Ensemble

NVT	Canonical Ensemble
OEC	Oxygen Evolving Center
OPBE	OPTX-Perdew-Burke-Ernzerhof
OPTX	Handy's Optimized Exchange
PBC	Periodic Boundary Conditions
PBE	Perdew-Burke-Ernzerhof
PCET	Proton-Coupled Electron Transfer
PEC	Photoelectrochemical Cell
PEM	Proton Exchange Membrane
PSI	PhotoSystem I
PSII	PhotoSystem II
PV-E	PV-Electrolysis
PT	Proton Transfer
PV	Photovoltaics
SOMO	Singly Occupied Molecular Orbital
TD-DFT	Time-Dependent Density Functional Theory
TIP₃P	Transferable Intermolecular Potential with 3 Points
TS	Transition State
TZP	Triple-Zeta Polarized Basis Set
VDOS	Vibrational Density of States
VMD	Visual Molecular Dynamics
WNA	Water Nucleophilic Attack
WOC	Water Oxidation Catalyst

List of Symbols

A	pre-exponential frequency factor
d_{C-N}	C–N bond length
d_{C-N_ini}	C–N bond length of the initial intermediate
d_{C-N_fin}	C–N bond length of the final intermediate
$\langle d_{C-N} \rangle$	time-averaged C–N bond length
e	Euler's number
η	overpotential
$E[\rho]$	ground state energy
$E_{xc}[\rho]$	exchange-correlation functional
E_{tot}	total bonding energy
ΔE_{SOMO}	energy difference between molecular orbitals
ΔE_{int}	energy difference between intermediates
$\Delta \epsilon$	excitation energy around the transition state
f	oscillator strength
$g(r)$	radial distribution function
ΔG^*	activation free energy barrier
ΔG^o	thermodynamic driving force
ΔG	free energy change
ΔG_{calc}	calculated free energy change
ΔG_{exp}	experimentally measured free energy change
h	Planck constant
$J[\rho]$	classical Coulomb interaction
k	reaction rate
k_B	Boltzmann constant
ϕ_i	Kohn-Sham orbital
$n(r)$	coordination number
r	O...O distance
R	Universal gas constant
$\rho(\mathbf{r})$	electron density
S	total spin angular momentum
$2S+1$	spin multiplicity
T	thermodynamic temperature
$T[\rho]$	kinetic energy
σ	standard deviation
θ	dihedral angle
θ_{ini}	dihedral angle of the initial intermediate

θ_{fin}	dihedral angle of the final intermediate
$\langle \theta \rangle$	time-averaged dihedral angle
λ	constraint force
$\langle \lambda \rangle$	time-averaged constraint force
$\langle \lambda \rangle_{\text{r}}$	running average of constraint force
μ	fictitious mass of the electronic degrees of freedom
Λ_{ij}	Lagrange multipliers
$V_{\text{ee}}[\rho]$	electron-electron interaction
$V_{\text{ext}}[\rho]$	nucleus-electron interaction
$v_{\text{ext}}(\mathbf{r})$	external potential
ω	vibrational frequency

