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For my parents, my wife, and my son

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List of Abbreviations

ADF	Amsterdam Density Functional
AIMD	*Ab Initio* 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	*p*-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
$<d_{C–N}>$	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
$\Delta\varepsilon$	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
$\langle\lambda\rangle_r$	running average of constraint force
μ	fictitious mass of the electronic degrees of freedom
Λ_{ij}	Lagrange multipliers
$V_{ee}[\rho]$	electron-electron interaction
$V_{ext}[\rho]$	nucleus-electron interaction
$\nu_{ext}(r)$	external potential
ω	vibrational frequency