Excited-State Coupled Electronic-Structural Dynamics of Molecular Systems with DynEMol

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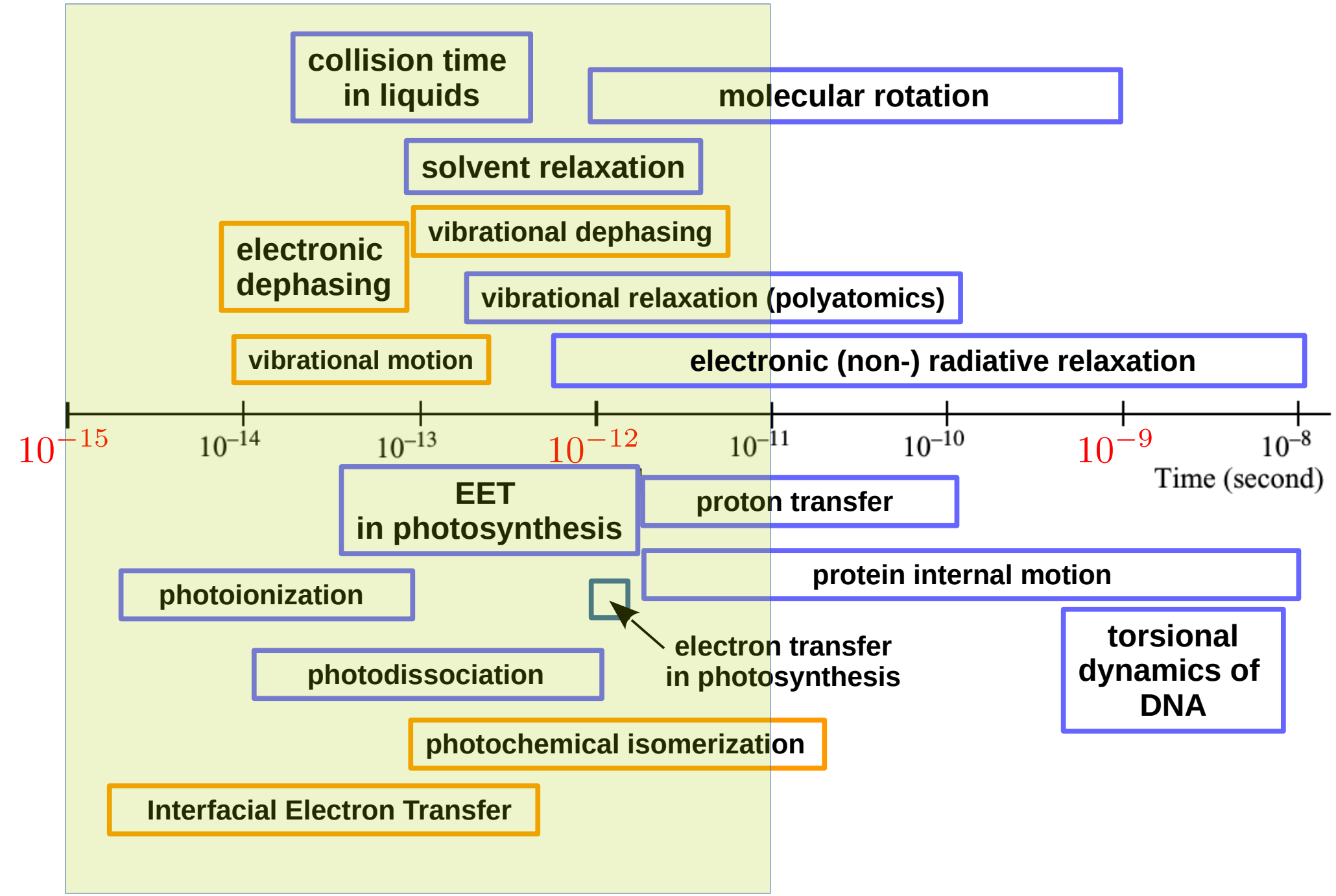


Adapted from G.R. Fleming & P.G. Wolynes, Phys. Today (1990), vol. 43, p. 36

DynEMol
(Dynamics of Electrons in Molecules)

- *Motivation*
  - Self-Consistent Quantum-Classic Method for excited-state dynamics of Molecular and Extended Systems
- *Applications*
  - Intramolecular Vibration Relaxation (IVR)
  - Photoinduced Isomerization
  - Photoinduced Proton Transfer
  - Interfacial Electron Transfer
  - Spin Dynamics Effects

Theoretical Method and Models

Our goal:

Modelling electron quantum dynamics in large molecular systems

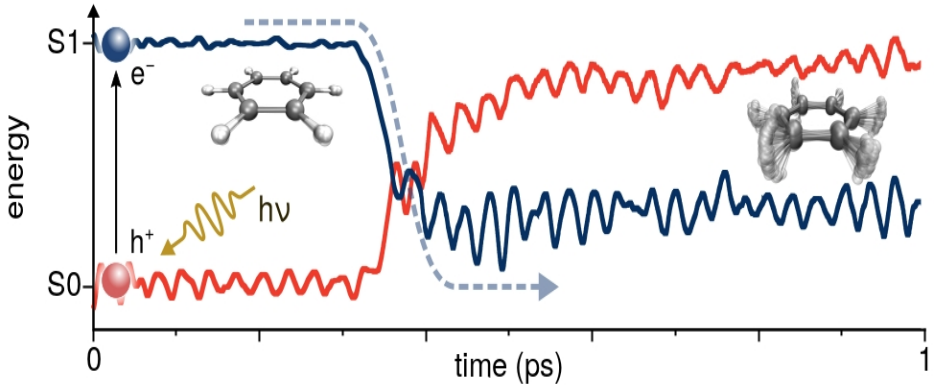
$< 10^2$ atoms	$10^2 - 10^4$ atoms	$\gg 10^4$ atoms
small to medium size	large size	Very large size
First principles Quantum Mechanics Molecular Dynamics	Quantum & Classical regimes	Classical Dynamics
$\tau \lesssim$ few picoseconds	$\tau < 10^2$ picoseconds	$\tau > 10^2$ picoseconds

- Combines:

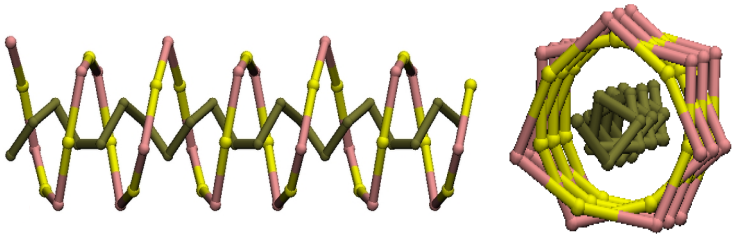
  Molecular Mechanics and tight-binding semi-empirical methods

- Wavepacket propagation of charge excitation

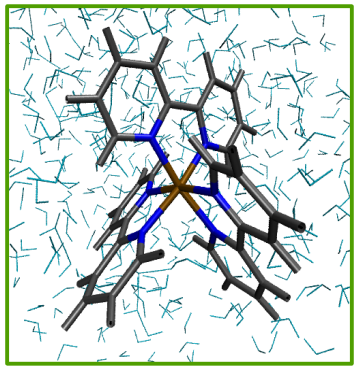
Nonadiabatic Excited-State Dynamics with *Dynemol*



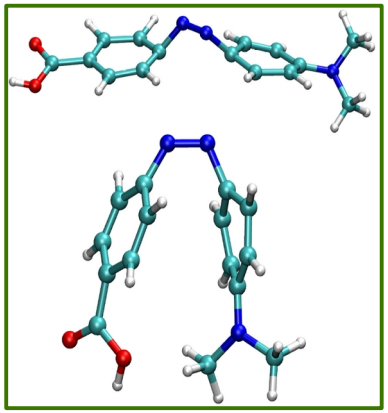
JPC-C 2016, **120**, 27688.



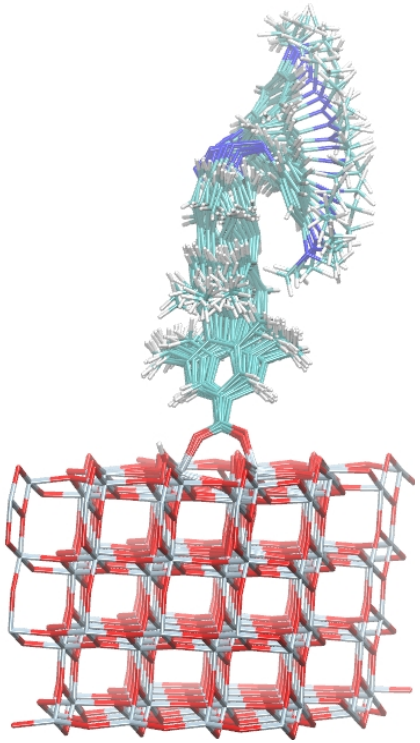
Nano Lett. 2021, 21, 8190.



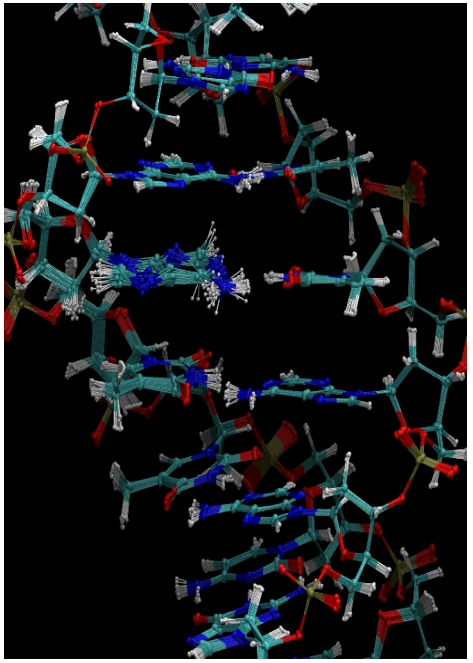
JPC-C 2011, **115**, 15617.



JPC-C, 2016, **120**, 27688.
JPC-L, 2018, **9**, 5926.

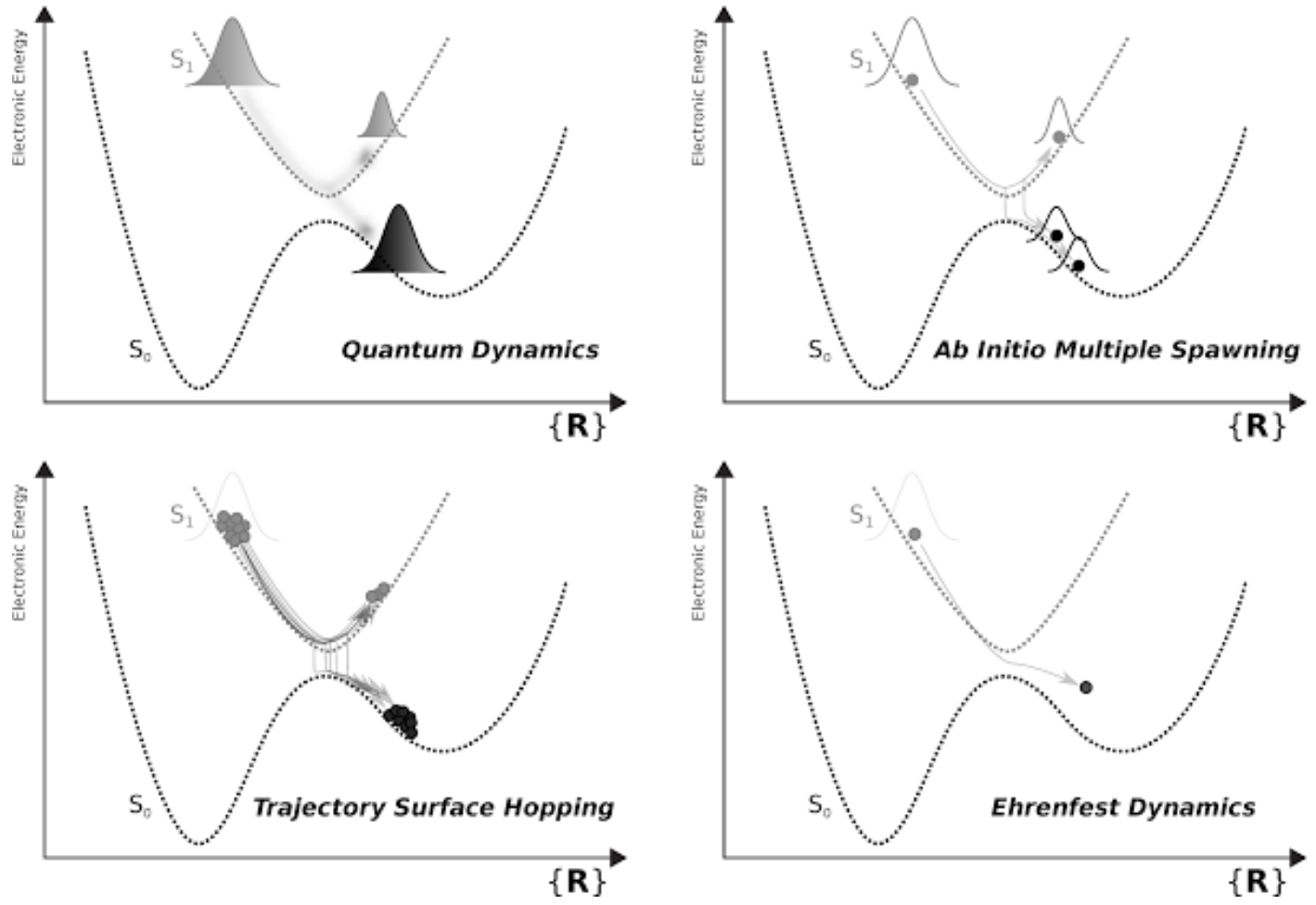


JPC-L, 2015, **6**, 4927.
JPC-C, 2019,**123**, 5692.

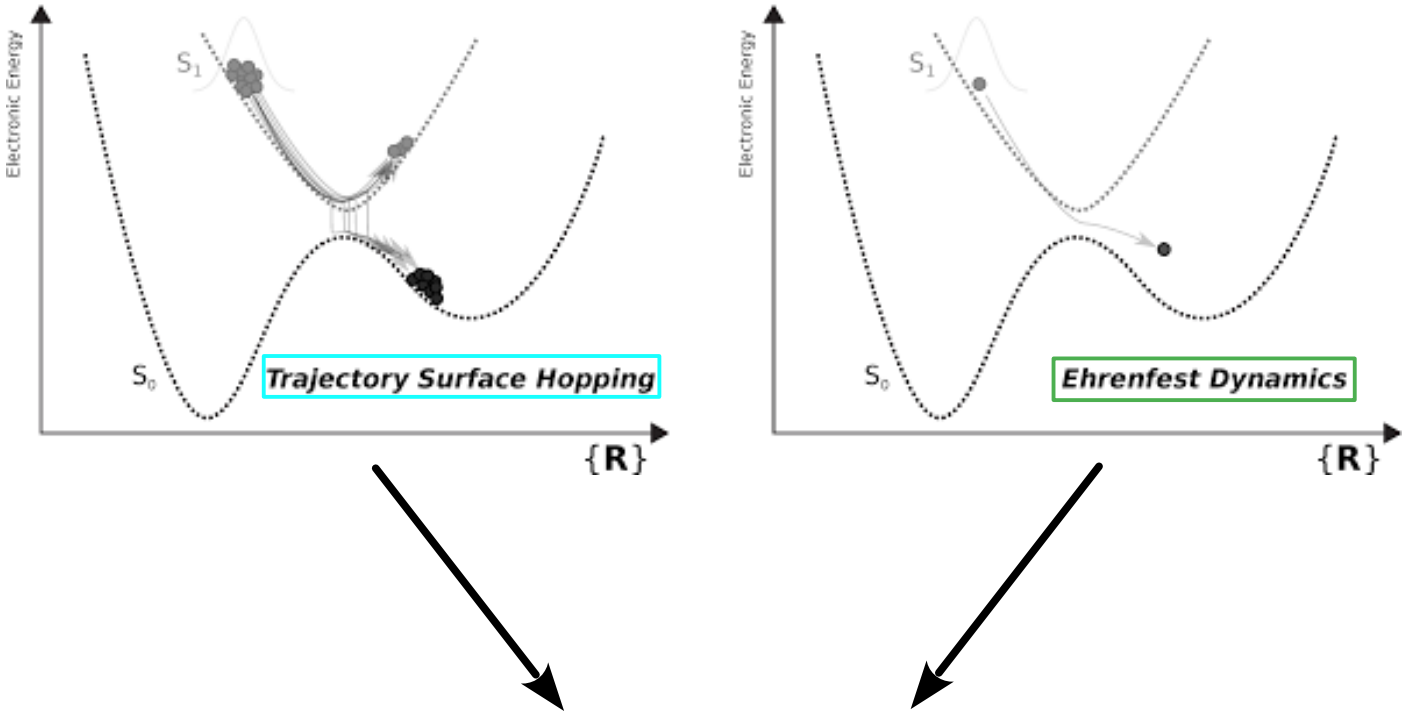


Effects of UV radiation
on DNA strands

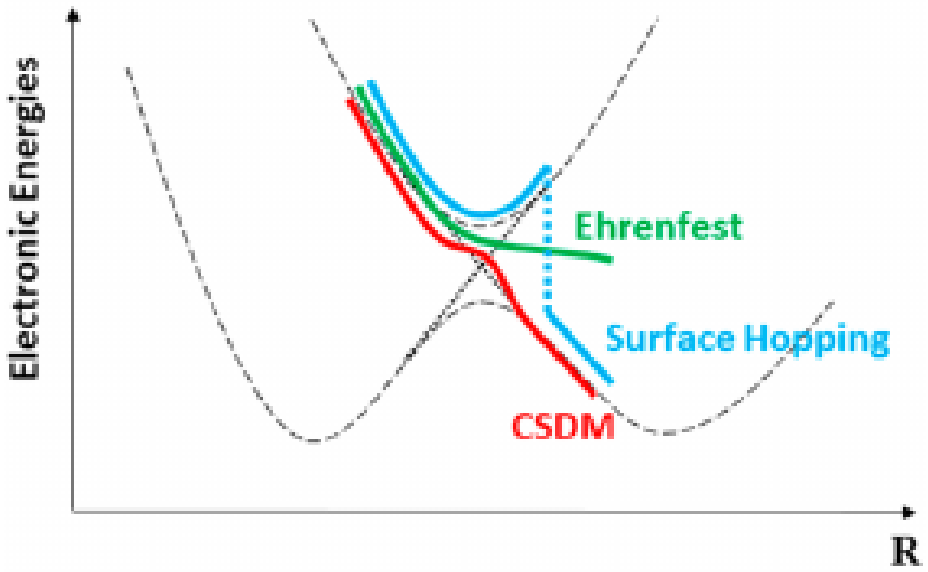
Methodologies of Non-adiabatic Molecular Dynamics



B. F. E. Curchod, U. Rothlisberger, and I. Tavernelli. ChemPhysChem 2013, 14, 1314-1340



CSDM = Coherent Switches with Decay of Mixing



J. Chem. Theory Comput. 2020, 16, 3464−3475

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 16 22 OCTOBER 2004

Coherent switching with decay of mixing: An improved treatment of electronic coherence for non-Born–Oppenheimer trajectories

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Implementation of Coherent Switching with Decay of Mixing into the SHARC Program

Yinan Shu,[⊥] Linyao Zhang,[⊥] Sebastian Mai, Shaozeng Sun,* Leticia González,* and Donald G. Truhlar*

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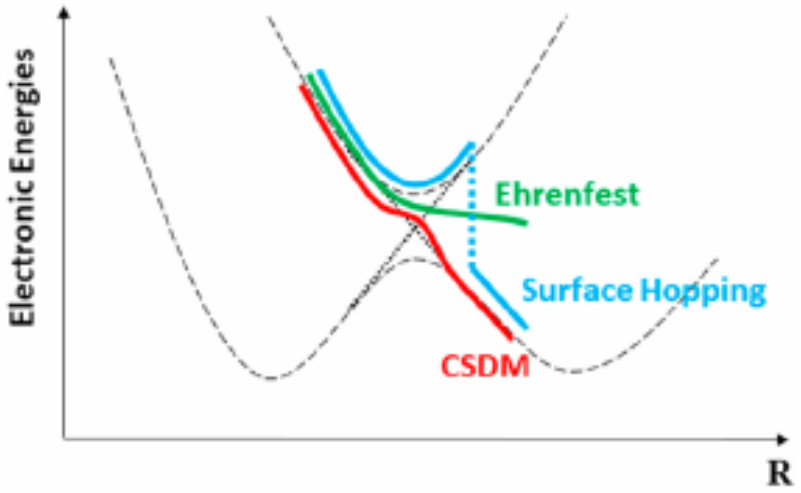
CSDM = Coherent Switches with Decay of Mixing



Trajectory-Based Dynemol Method

Hybrid Quantum-Classical Dynamics:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(r,R,t) = \left[\frac{\hbar^2}{2m}\nabla_r^2 + \frac{\hbar^2}{2M}\nabla_R^2 + V(r,R)\right]\Psi(r,R,t)$$

➔ Coherent quantum dynamics for the electrons:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(r;R,t)\right\rangle = \hat{H}_{el}(R(t))\left|\Psi(r;R,t)\right\rangle \quad , \quad \Psi(r;R,t) = \text{electronic wavepacket}$$

$$\Downarrow$$

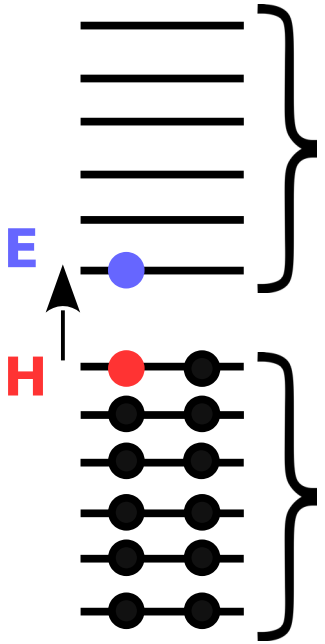
$$\frac{d}{dt}C_n + \sum_m C_m\langle\phi_n|\frac{d}{dt}\phi_m\rangle + \frac{i}{\hbar}\mathcal{E}_n C_n = 0 \qquad \langle\phi_n|\frac{d}{dt}\phi_m\rangle = \dot{\mathbf{R}}\cdot\mathbf{d}_{nm}$$

➔ Classical dynamics for the nuclei:

$$\begin{aligned}\dot{R}_N &= P_N/M_N \ , \\ \dot{P}_N &= -\nabla_N U[R,\Psi(r)]\end{aligned}$$

Classical Nuclear Dynamics in the ES

Ehrenfest Method: $M\ddot{\mathbf{R}} = -\nabla_{\mathbf{R}}\langle\Psi(\mathbf{r};\mathbf{R},t)|V(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r};\mathbf{R},t)\rangle_{\mathbf{r}}$



unoccupied

occupied

$$\langle\Psi(\mathbf{r};\mathbf{R},t)|V(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r};\mathbf{R},t)\rangle_{\mathbf{r}} \approx V_{gs}^{FF} + V_{eh}^{QM}\left[\Psi^{el}(t), \Psi^{hl}(t)\right]$$

$$V_{gs}^{FF} = \sum_{bonds} K_b(R-R_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{torsions}\sum_{n=0}^{5} C_n(cos\phi)^n$$

$$+ \sum_{i,j\neq i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \sum_{i,j\neq i}\frac{q_j q_i}{4\pi\epsilon_o R_{ij}}$$

*In this case we keep the charges q_i and q_j fixed.

Classical Nuclear Dynamics in the GS

Molecular Mechanics-Quantum Mechanics

$$M\ddot{\vec{R}} = -\nabla_{\vec{R}}\, V_{gs}^{FF} - \nabla_{R_A}\, V_{eh}^{QM}$$

$$\begin{aligned} V_{gs}^{FF} &= \sum_{bonds} K_b(R - R_o)^2 + \sum_{angles} K_\theta(\theta - \theta_o)^2 + \sum_{torsions} \sum_{n=0}^{5} C_n(cos\phi)^n \\ &+ \sum_{i,j\neq i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \sum_{i,j\neq i} \frac{q_j q_i}{4\pi\epsilon_o R_{ij}} \end{aligned}$$

*In this case we keep the charges q_i and q_j fixed.

Quantum-Classical Coupling

From $V_{eh}^{QM}\left[\Psi^{el}(t),\Psi^{hl}(t)\right] = Tr\left[\rho^{eh}\mathbf{H}\right] = \sum_n \mathcal{E}_n \rho_{nn}^{eh}$

$\mathbf{F}_A^{eh} = -\nabla_{R_A} V_{eh}^{QM}$

Total force (AD + NA) between atom pair A and B,

in the **Extended Hückel formalism**, is

$$\mathbf{F}_{AB} = -2\sum_{a\in A}\sum_{b\in B}\langle f_b|\nabla f_a\rangle \times \left\{\sum_n \rho_{nn}^{eh}\left(\chi_{ab}-\mathcal{E}_n\right)Q_b^n Q_a^n + \sum_{m>n}\mathbb{R}\left(\rho_{nm}^{eh}\right)\left[\left(\chi_{ab}-\mathcal{E}_m\right)Q_a^n Q_b^m + \left(\chi_{ba}-\mathcal{E}_n\right)Q_b^n Q_a^m\right]\right\}$$

the extended Hückel hamiltonian is given by $H_{ab} = \chi_{ab} S_{ab}$,

with $\chi_{ab} \equiv K_{ab}\dfrac{h_a + h_b}{2}$.

Adiabatic states: $HQ_n = \mathcal{E}_n S Q_n$

JPCC 2016, **120**, 27688.

Coherent Switches with Decay of Mixing (CSDM)

- Hybrid quantum-classical hamiltonian:

$$\mathrm{H} = \mathrm{T} + \left\{ V^{GS} + \langle \Psi | \mathbf{H}^{eh} | \Psi \rangle \right\} = T + V^{GS} + V^{QM}$$

- Adiabatic representation: $\mathbf{H}^{eh}|\phi\rangle = \varepsilon|\phi\rangle$, $|\Psi\rangle = \sum_i C_i|\phi_i\rangle$, $\mathrm{V}^{QM} = Tr\left[\rho \mathbf{H}^{eh}\right]$

- Electronic density matrix: $\rho = |\Psi\rangle\langle\Psi|$

$$\boxed{\dot{\rho} = \dot{\rho}\Big|_{\mathrm{Coh}} + \dot{\rho}\Big|_{\mathrm{Decoh}}}$$

- Conservation of energy for the hybrid hamiltonian: $\dot{H} = \dot{T} + \dot{V} = 0$

$$T = \sum_N \frac{\vec{P}_N \cdot \vec{P}_N}{2M_N} \Longrightarrow \dot{T} = \sum_N \frac{\vec{P}_N}{M_N} \cdot \dot{\vec{P}}_N = \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N$$

$$V = V^{GS} + Tr\left[\rho \mathbf{H}^{eh}\right] \Longrightarrow \dot{V} = \dot{V}^{GS} + \dot{V}\Big|_{Coh} + \dot{V}\Big|_{Dech}$$

Coherent Switches with Decay of Mixing (CSDM)

$$\dot{V}^{QM} = \dot{V}\big|_{\rm Coh} + \dot{V}\big|_{\rm Dech} = \sum_i \dot{\rho}_{ii} E_i + \sum_i \rho_{ii} \dot{E}_i$$

$$= \sum_i \left\{ \dot{\rho}_{ii}\big|_{\rm Coh} + \dot{\rho}_{ii}\big|_{\rm Dech} \right\} E_i + \sum_i \rho_{ii} \dot{E}_i$$

$$= \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\rm Coh} E_i + \sum_i \rho_{ii} \dot{E}_i}_{\dot{V}\big|_{\rm Coh}} + \underbrace{\sum_i \dot{\rho}_{ii}\big|_{\rm Dech} E_i}_{\dot{V}\big|_{\rm Dech}}$$

- Conservation of energy for the hybrid hamiltonian: $\dot{H} = \dot{T} + \dot{V} = 0$

$$\dot{\mathbf{H}} = \sum_N \vec{v}_N \cdot \left(\dot{\vec{P}}_N\big|_{\rm Coh} + \dot{\vec{P}}_N\big|_{\rm Dech} \right) + \dot{V}^{GS} + \dot{V}\big|_{\rm Coh} + \dot{V}\big|_{\rm Dech} = 0$$

$$= \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\rm Coh} + \dot{V}^{GS} + \dot{V}\big|_{\rm Coh} \right\} + \left\{ \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\rm Dech} + \dot{V}\big|_{\rm Dech} \right\} = 0$$

Mean-Field Ehrenfest Method

- Coherent electronic dynamics:

$$\dot{V}\big|_{\mathrm{Coh}} = \sum_i \rho_{ii}\dot{E}_i + \sum_i \dot{\rho}_{ii}\big|_{\mathrm{Coh}} E_i$$

$$= \sum_N \vec{v}_N \cdot \left\{ \rho_{ii}\nabla_N E_i - \sum_{i\neq j} 2\mathbb{R}\left[\rho_{ij}\right] E_i \vec{d}_{ij}^{N} \right\}$$

$$\dot{U} = \sum_N \vec{v}_N \cdot \nabla_N U$$

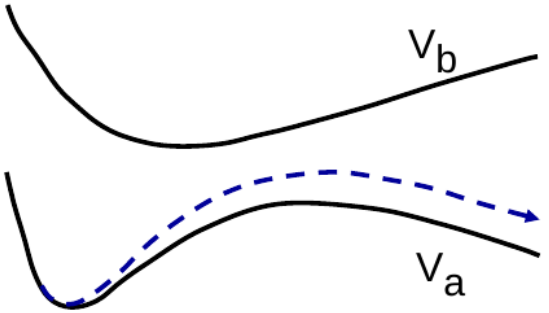
- Ehrenfest Mean-Field Force

$$\vec{F}_N^{\mathrm{Ehrenfest}} = -\nabla_N V^{QM} = -\rho_{ii}\nabla_N E_i + \sum_{i\neq j} 2\mathbb{R}\left[\rho_{ij}\right] E_i \vec{d}_{ij}^{N}$$

- Energy conservation:

$$\sum_N \vec{v}_N \cdot \left\{ \vec{F}_N\big|_{\mathrm{Coh}} + \nabla_N V^{GS} + \nabla_N V^{QM} \right\} = 0$$

$$\vec{F}_N\big|_{\mathrm{Coh}} = -\nabla_N V^{\mathrm{GS}} - \nabla_N V^{QM}$$

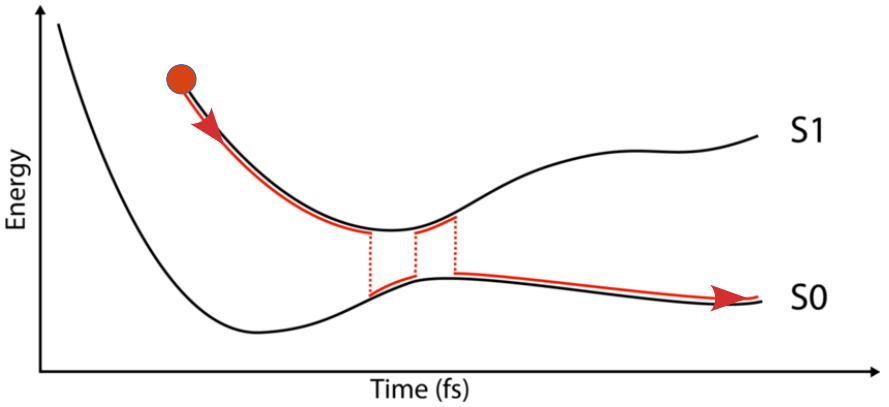


Fewest Switches Surface Hopping (FSSH)

- Surface Hopping Force

$$\vec{F}_N^{FSSH} = -\nabla_{R_N} \langle \phi_k | \hat{H} | \phi_k \rangle = -\nabla_{R_N} E_k(\{\vec{R}\})$$

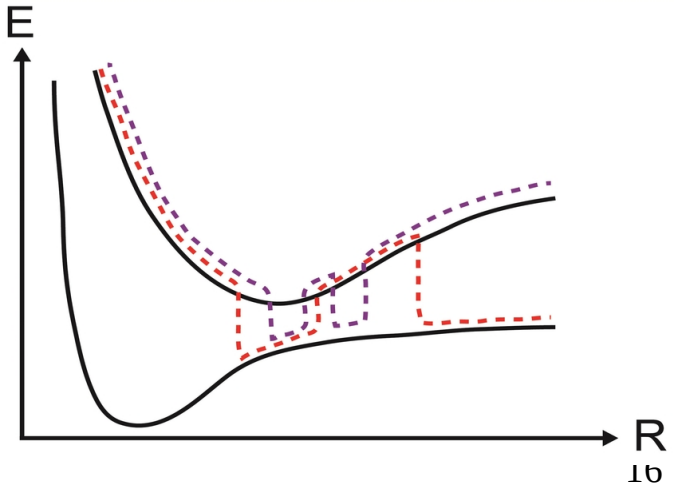
$$\vec{F}_N = -\nabla_N V^{\mathrm{GS}} - \nabla_N E_k(R)$$



- Fewest Switches transition probability:

$$\frac{d\rho_{kk}}{dt} = -\sum_{i \neq k} 2\mathbb{R}\left[\rho_{ik}\right] \left(\sum_N \vec{v}_N \cdot \vec{d}_{ik}^N \right) = \sum_{i \neq k} \dot{\rho}_{ik}$$

$$P_{k \to i} = \max\left(0, -\frac{\dot{\rho}_{ik} dt}{\rho_{kk}}\right)$$



- Nuclear velocity rescaling due to transition $k \to i$

$$\sum_N \frac{\vec{P}_N^2}{2M_N} + E(\phi_k) = \sum_N \frac{\vec{P'}_N^2}{2M_N} + E(\phi_i)$$

Coherent Switches with Decay of Mixing (CSDM)

- Decoherence effect on the electronic dynamics:

$$\sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Dech}} + \dot{V}\big|_{\text{Dech}} = 0$$

$$\tau_{ik} = \frac{\hbar}{|E_i - E_k|}\left(1 + \frac{C}{E_{kin}}\right)$$

- Define *Pointer State* "k" , so that

$$C_i \longrightarrow C_i e^{-\Delta t/(2\tau_{ik})}, \qquad i \neq k$$

$$C_k \longrightarrow \frac{C_k}{|C_k|}\left[1 - \sum_{i\neq k}|C_k|^2\right]^{1/2}$$

$$\dot{\rho}_{ii}\big|_{\text{Dech}} = -\frac{\rho_{ii}}{\tau_{ik}} < 0\ , \qquad i \neq k$$

$$\dot{\rho}_{kk}\big|_{\text{Dech}} = \sum_{j\neq k}\frac{\rho_{jj}}{\tau_{jk}} > 0\ ,$$

Decay of Mixing

- *Pointer State* switch (analogous to FSSH):

$$P_{ik} = \max\left(0, -\frac{\dot{\rho}_{ik}dt}{\rho_{ii}}\right)$$

$$\dot{\rho}_{ik} = 2\mathbb{R}\left[\rho_{ik}\right]\left(\sum_N \vec{v}_N \cdot \vec{d}^N_{ik}\right)$$

Coherent Switches with Decay of Mixing (CSDM)

- Decoherence effect on the electronic dynamics:

$$\sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Dech}} + \dot{V}\big|_{\text{Dech}} = 0 \quad \Rightarrow \quad \sum_N \vec{v}_N \cdot \dot{\vec{P}}_N\big|_{\text{Dech}} = \sum_{i\neq k} \frac{\rho_{ii}}{\tau_{ik}} (E_i - E_k)$$

$$\begin{aligned} \dot{V}\big|_{\text{Dech}} &= \sum_i \dot{\rho}_{ii}\big|_{\text{Dech}} E_i \\ &= \sum_{i\neq k} \dot{\rho}_{ii}\big|_{\text{Dech}} E_i + \dot{\rho}_{kk}\big|_{\text{Dech}} E_k \\ &= -\sum_{i\neq k} \frac{\rho_{ii}}{\tau_{ik}} (E_i - E_k) \end{aligned}$$

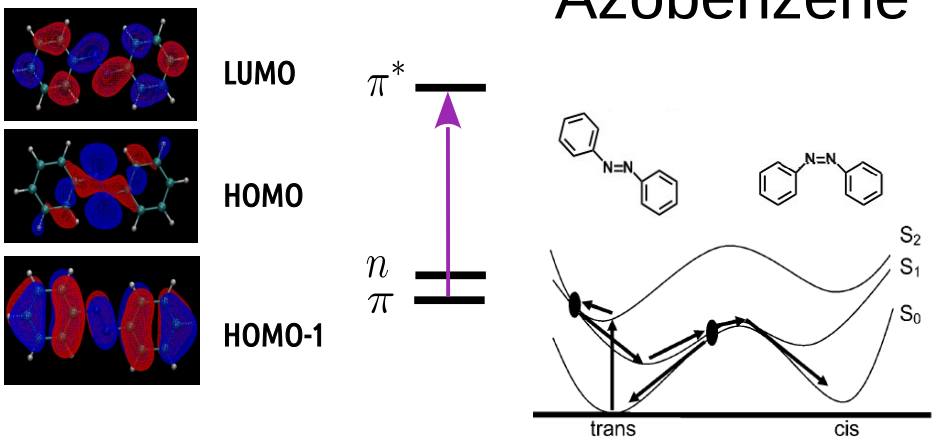
- Decoherent force:

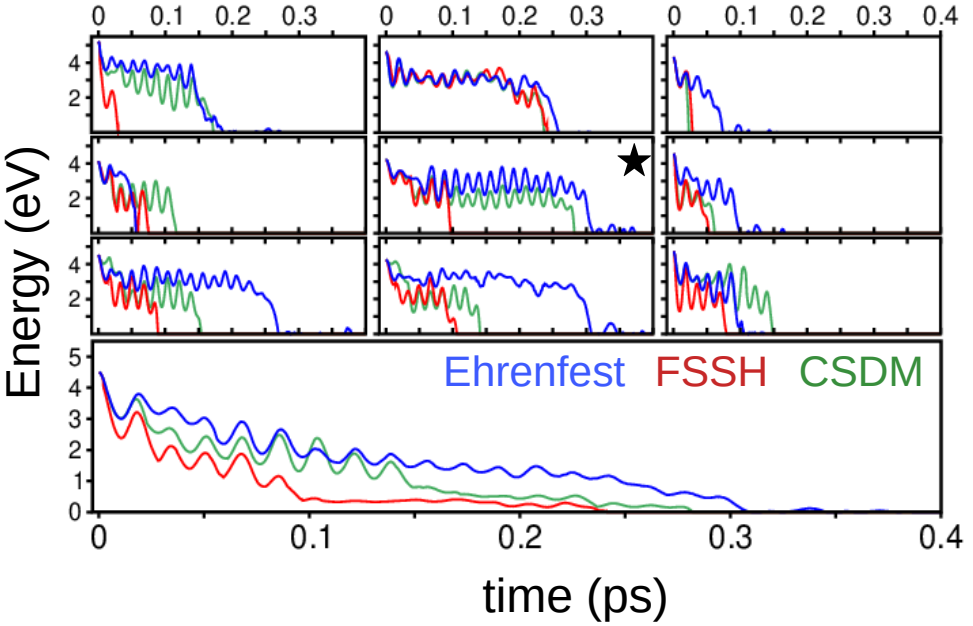
$$\vec{F}_N\big|_{\text{Dech}} = \sum_{i\neq k} \frac{\rho_{ii}}{\tau_{ik}} \frac{(E_i - E_k)}{(\sum_N \vec{v}_N \cdot \hat{s}_{ik}^N)} \hat{s}_{ik}^N$$

- Total force on atom N:

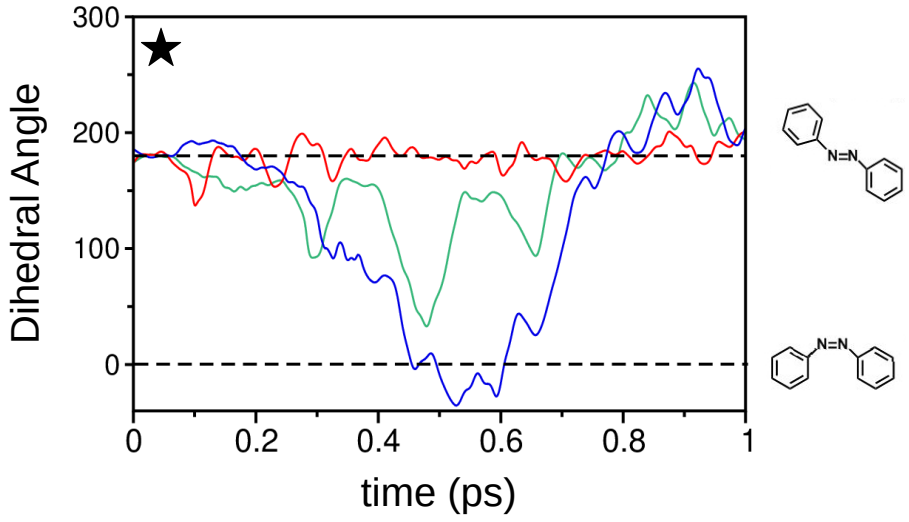
$$\vec{F}_N = \vec{F}_N\big|_{\text{Coh}} + \vec{F}_N\big|_{\text{Dech}} = -\nabla_N V^{\text{GS}} - \nabla_N V^{QM} + \vec{F}_N\big|_{\text{Dech}}$$

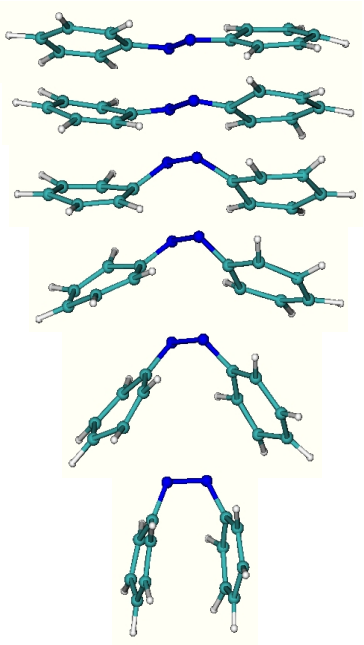
Azobenzene



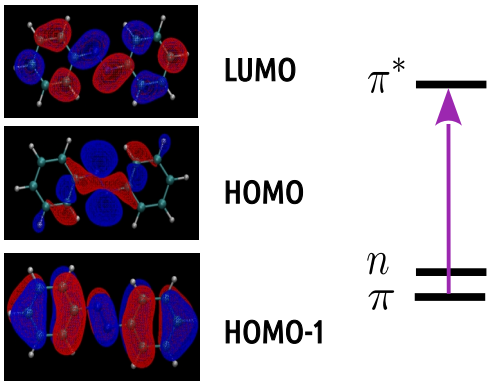


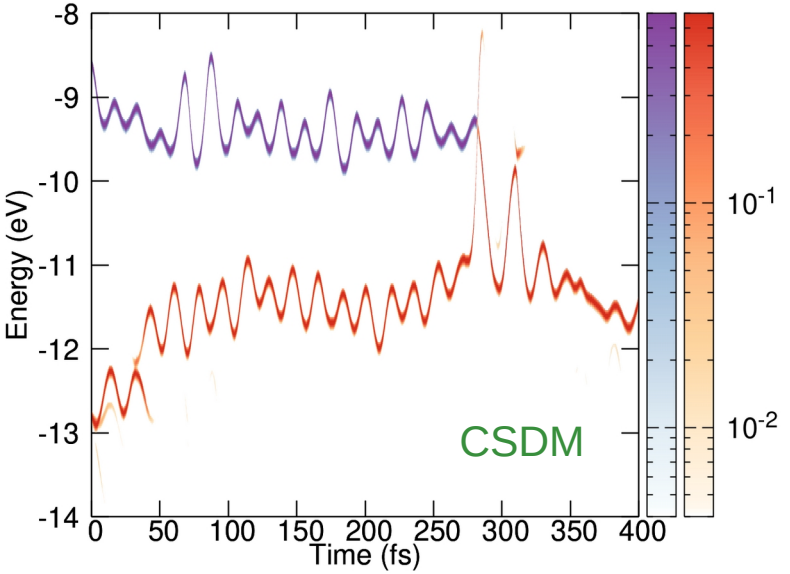
- Photo induced isomerization of Azobenzene:



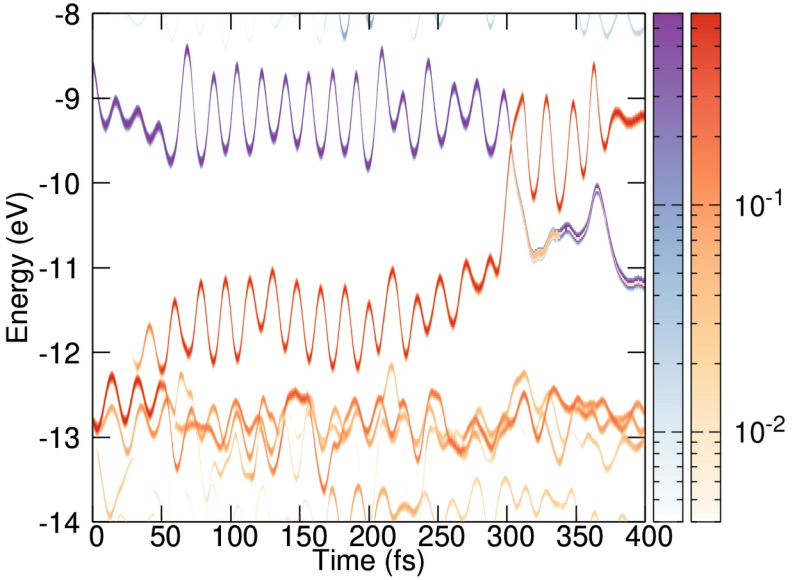


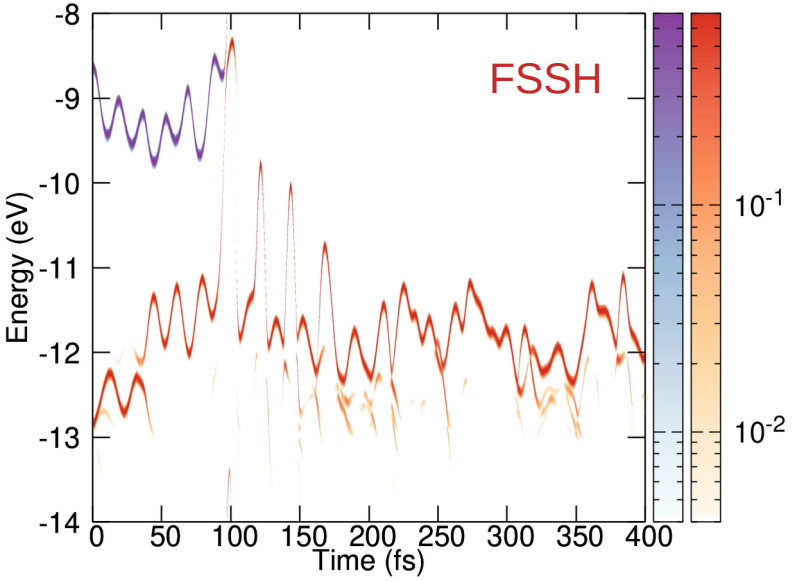
Azobenzene





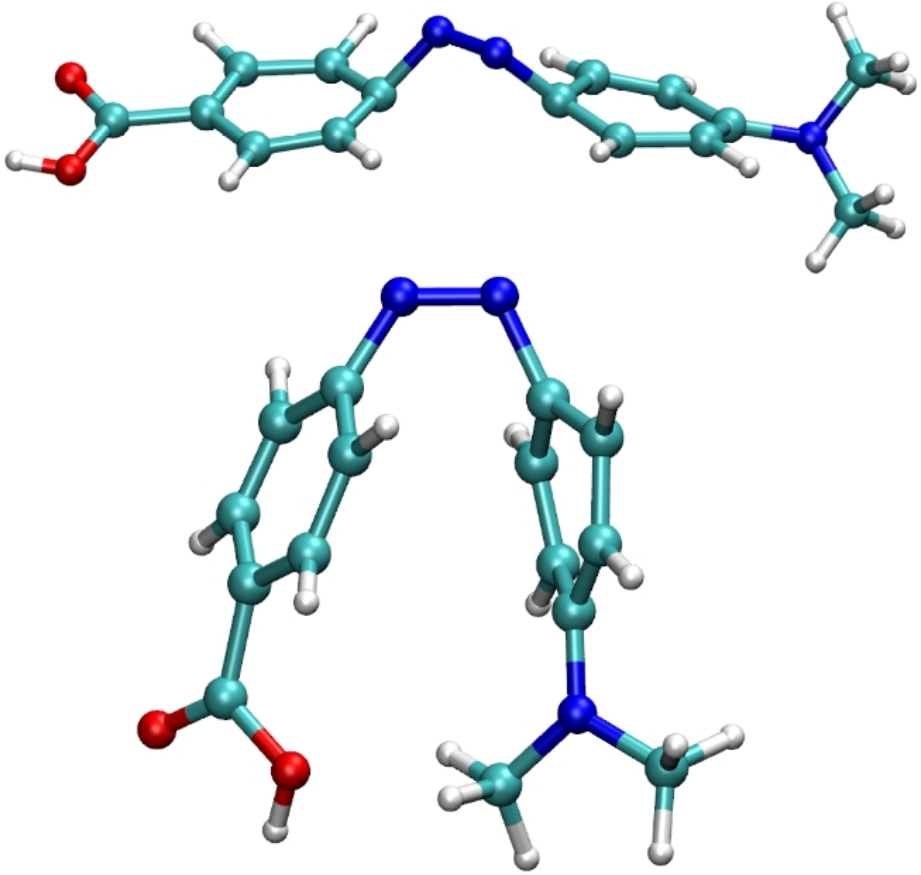
Ehrenfest

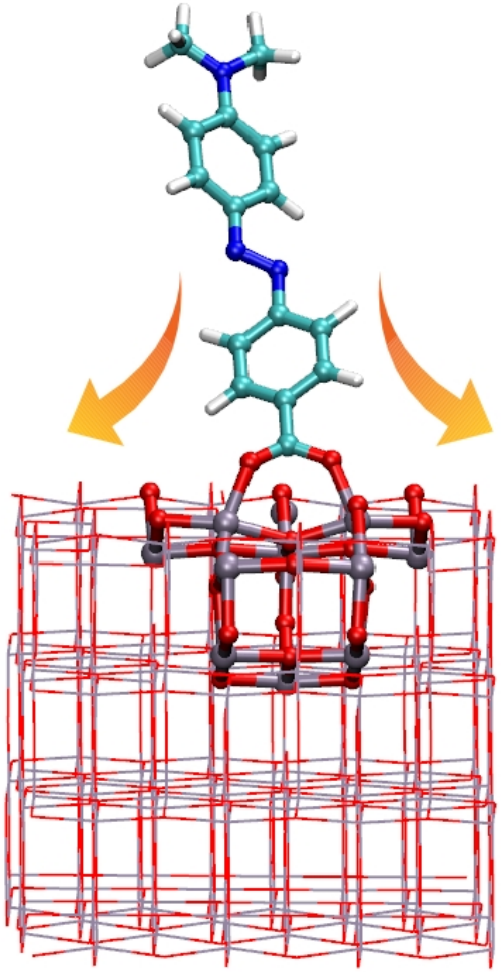




Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

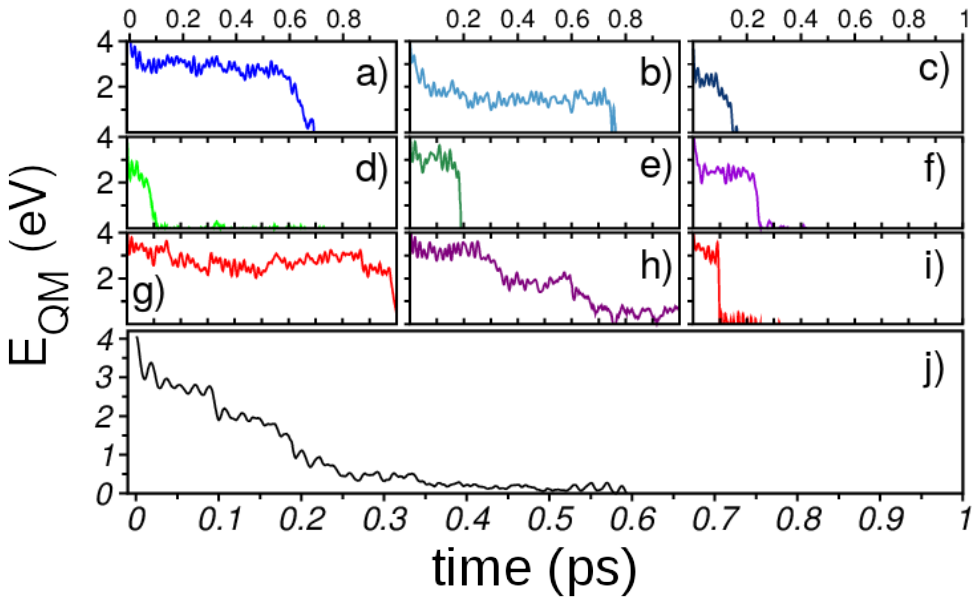
Push-Pull AZO compounds and Dye Sensitizers

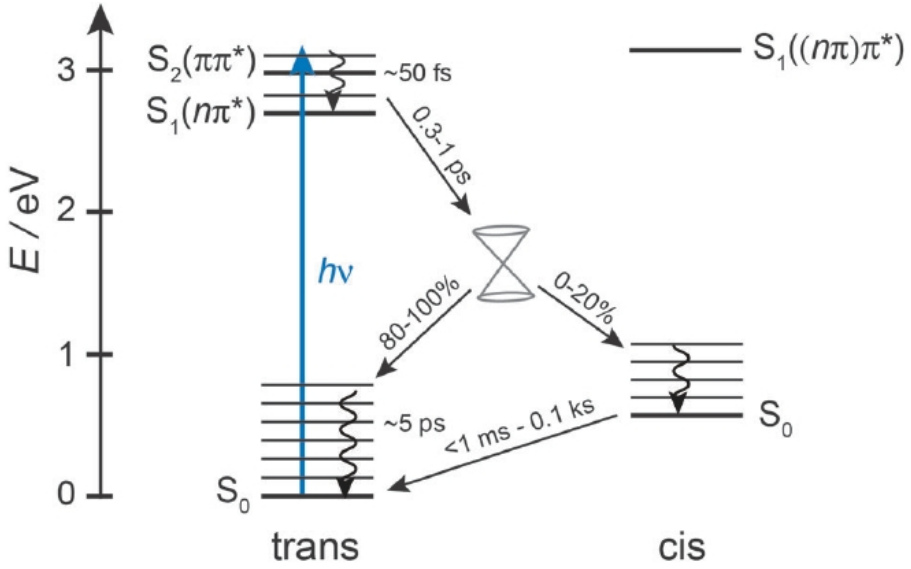




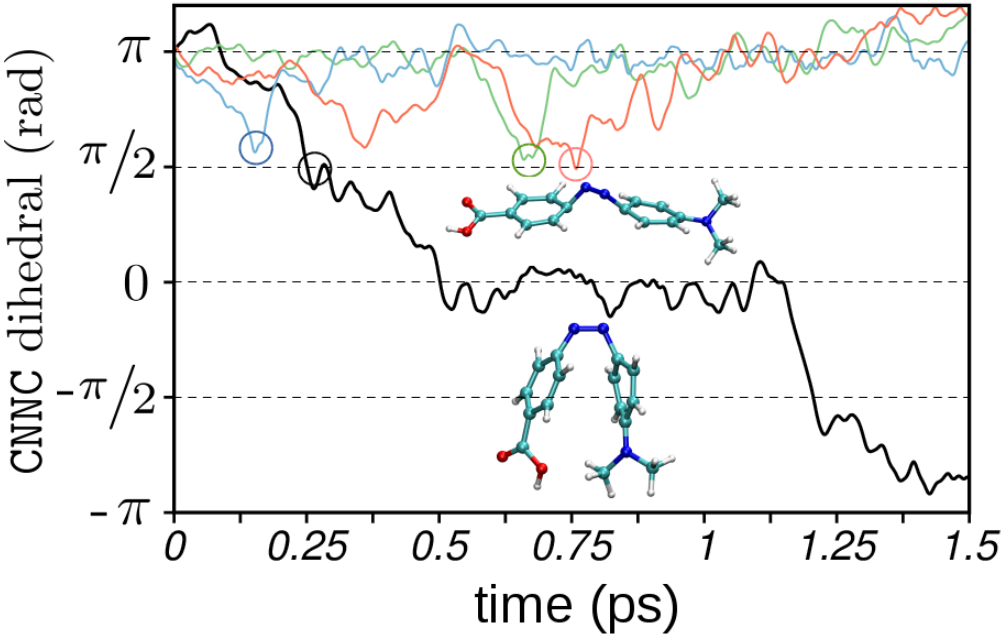
JPC Lett., 2018, **9**, 5926.

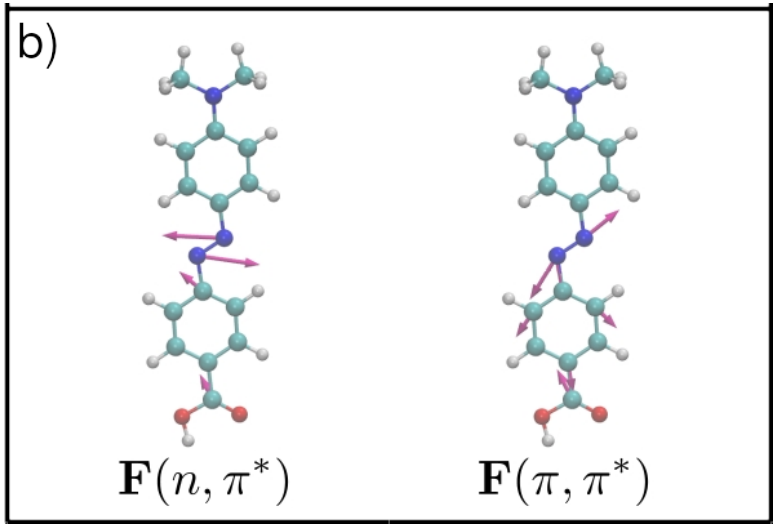
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



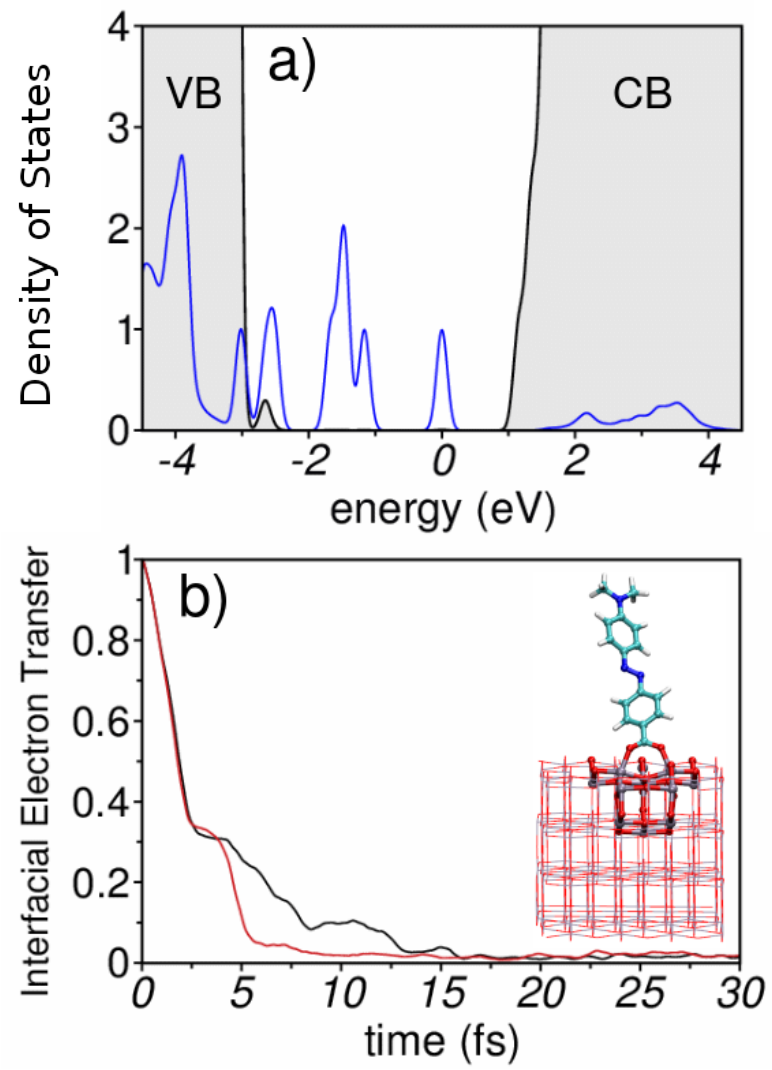


Vauthey et al.,PCCP, 2018,7254



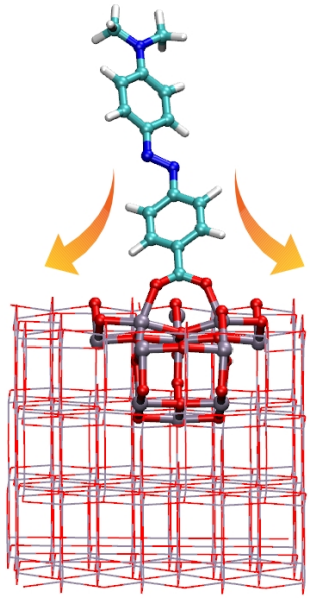


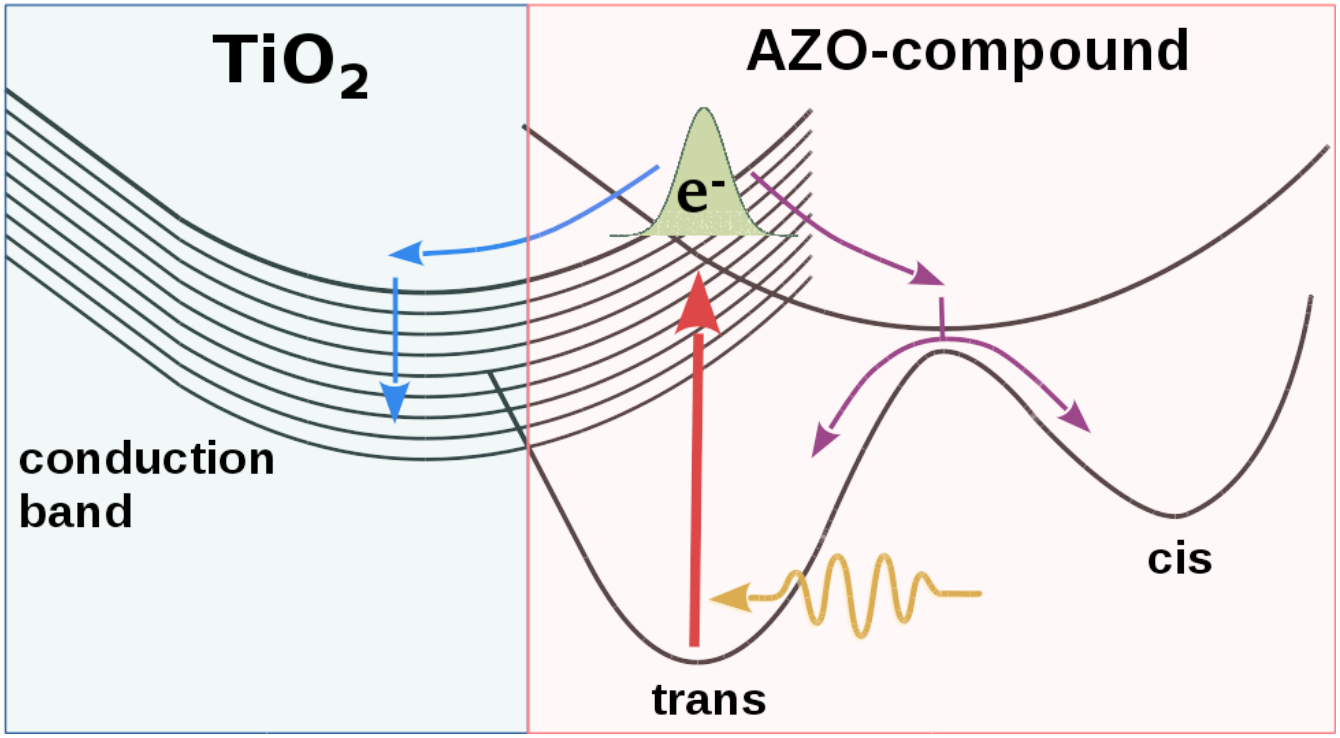
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

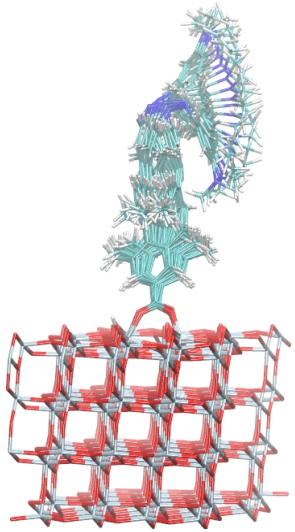


Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

Push-Pull AZO compounds and Dye Sensitizers







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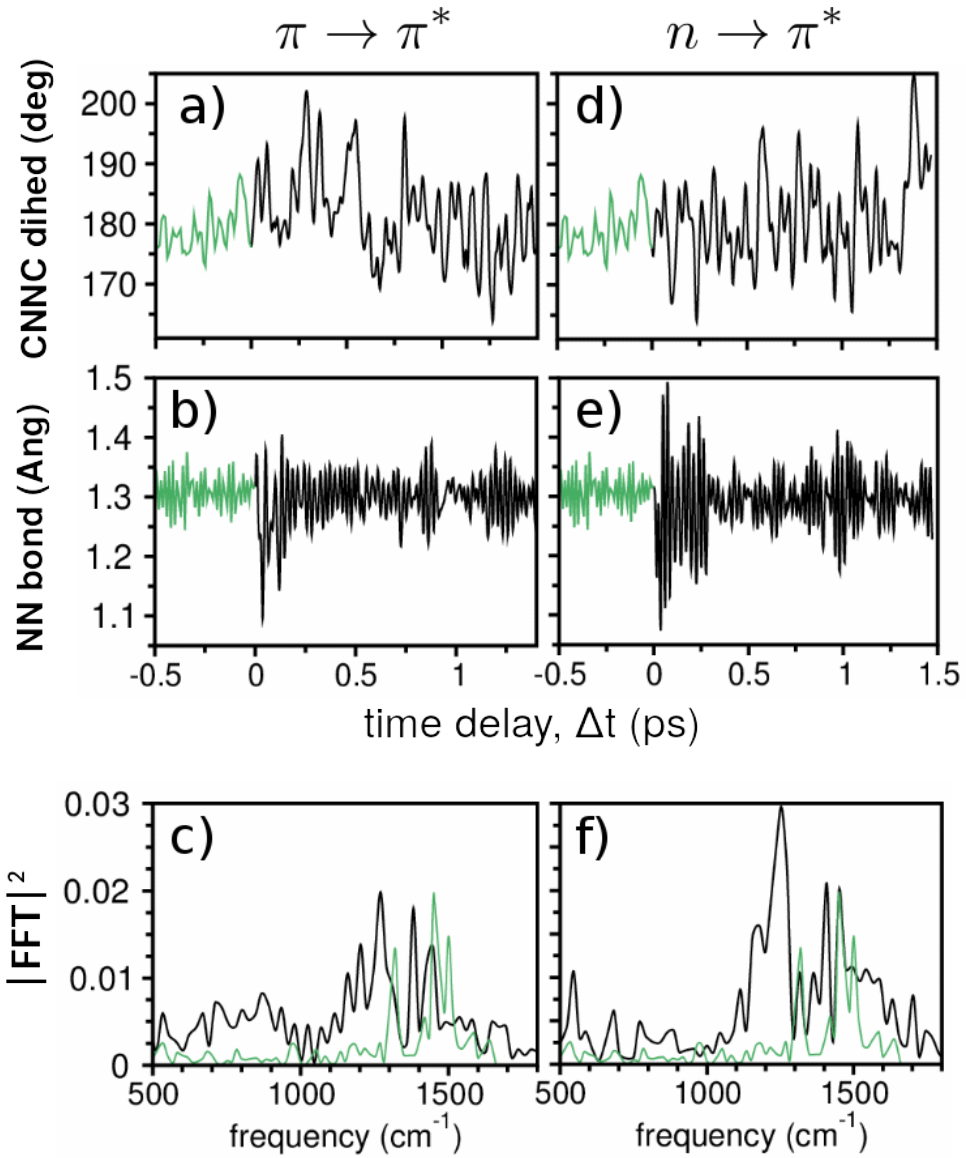
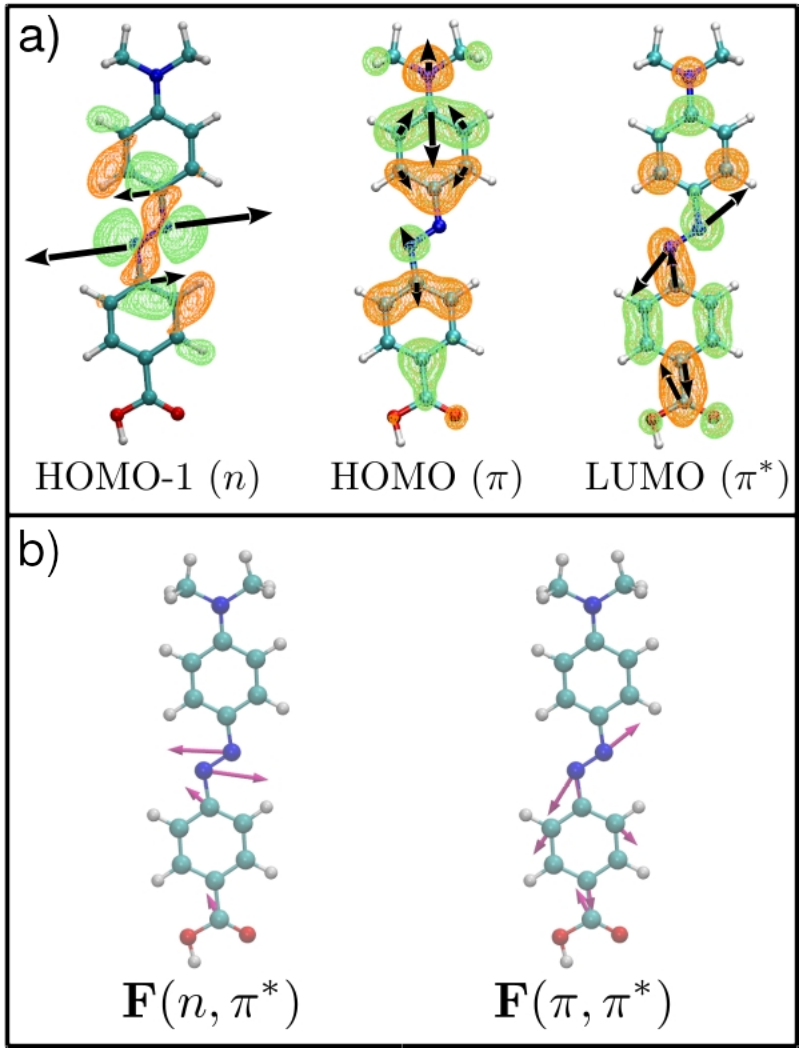
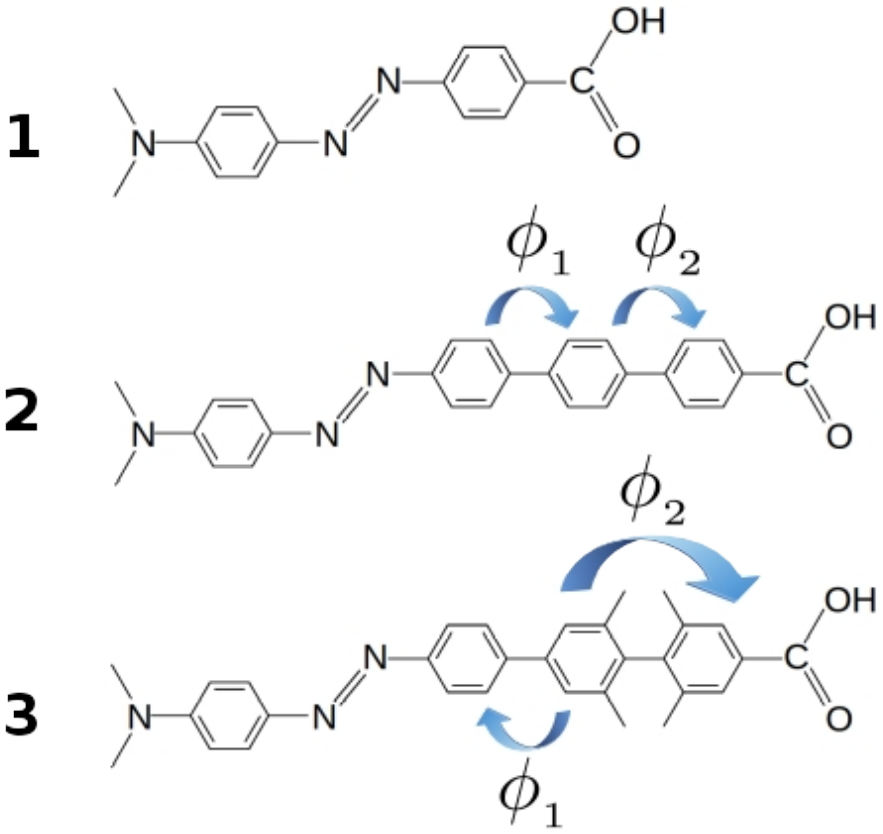
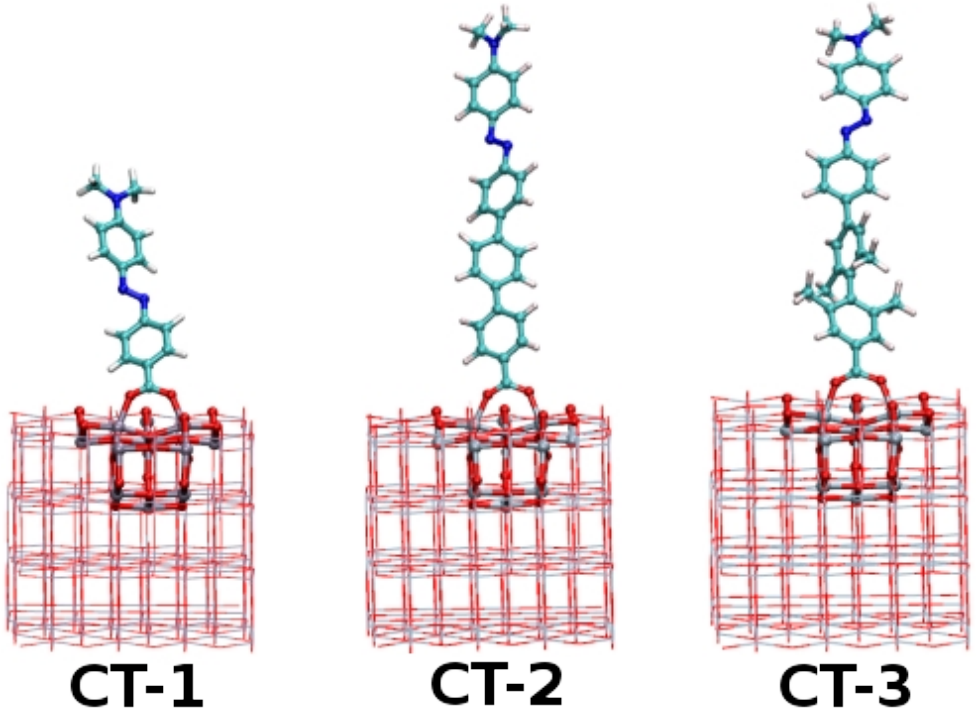
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics





Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



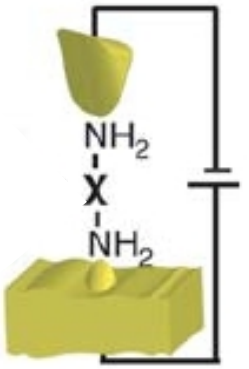


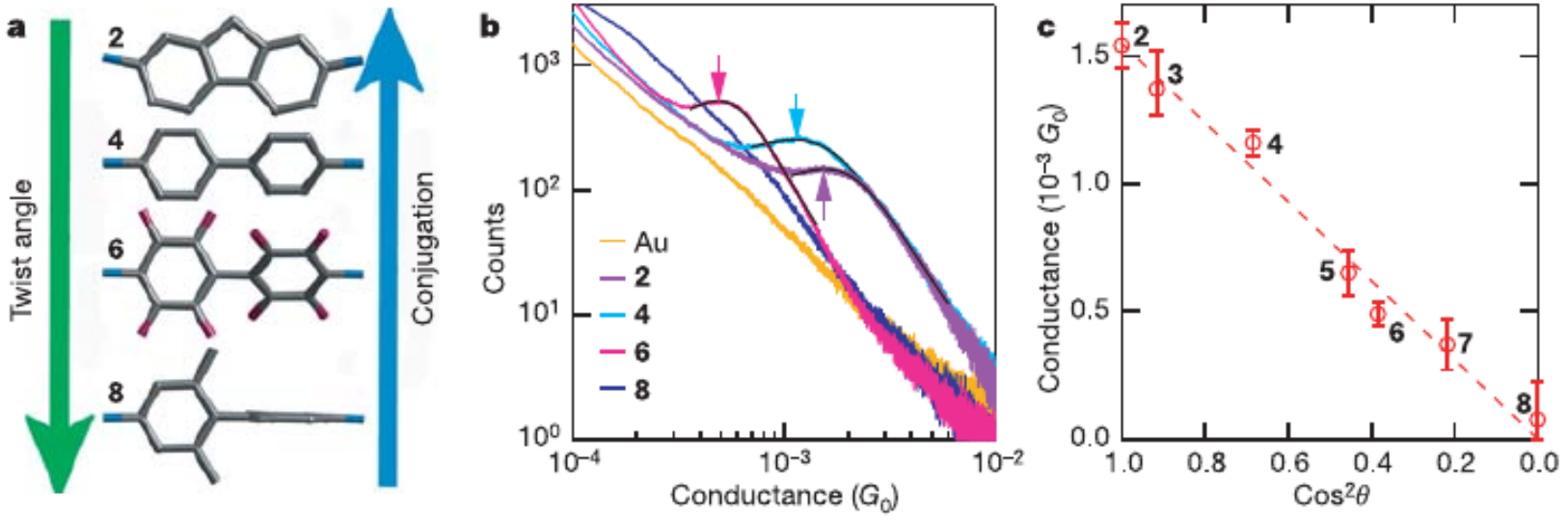
J. Phys. Chem. C, 2019

nature Vol 442|24 August 2006|doi:10.1038/nature05037

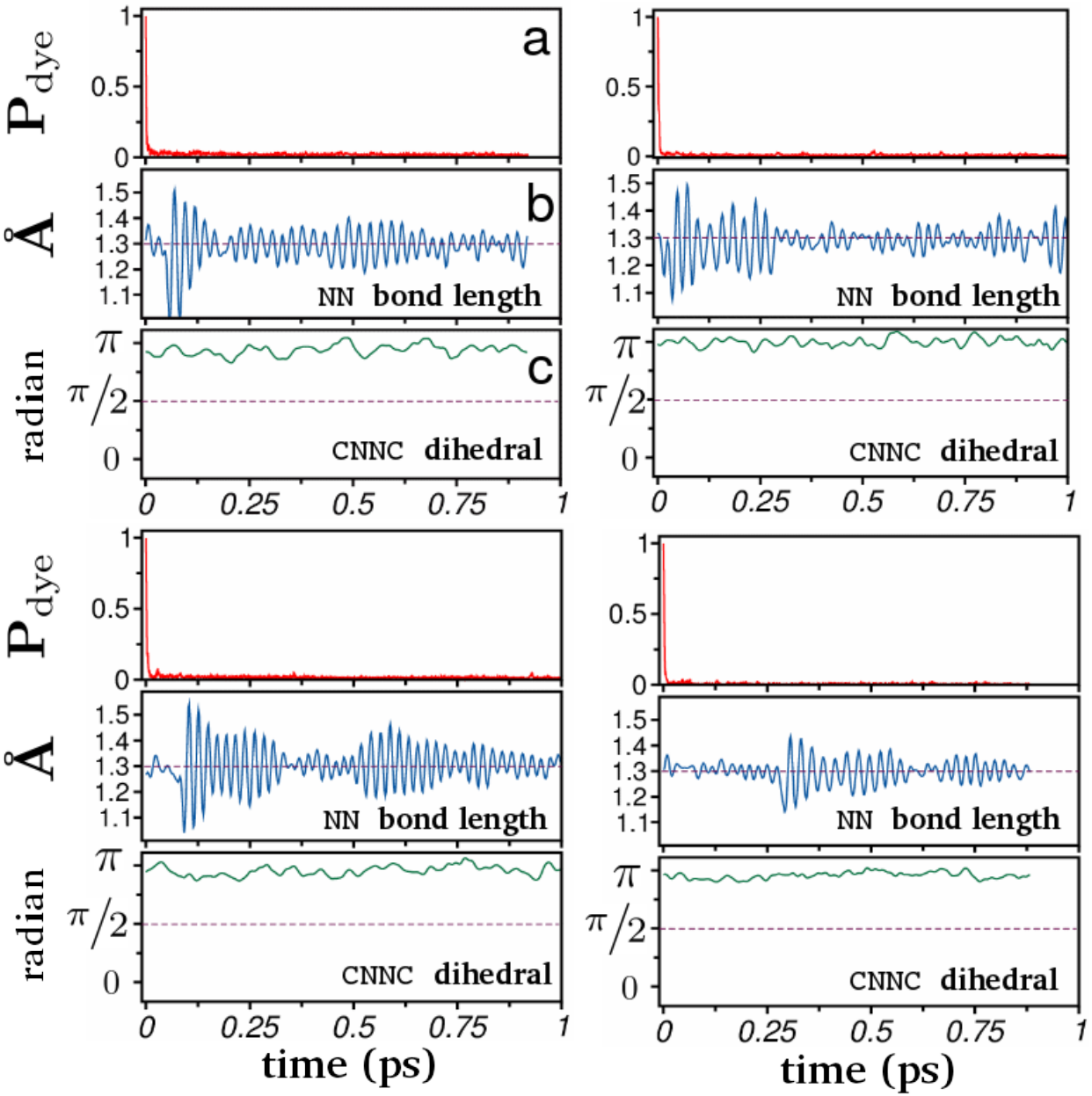
Dependence of single-molecule junction conductance on molecular conformation

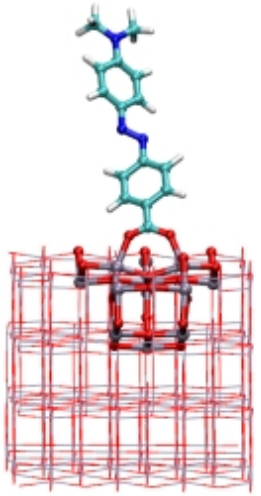
Latha Venkataraman[1,4], Jennifer E. Klare[2,4], Colin Nuckolls[2,4], Mark S. Hybertsen[3,4] & Michael L. Steigerwald[2]





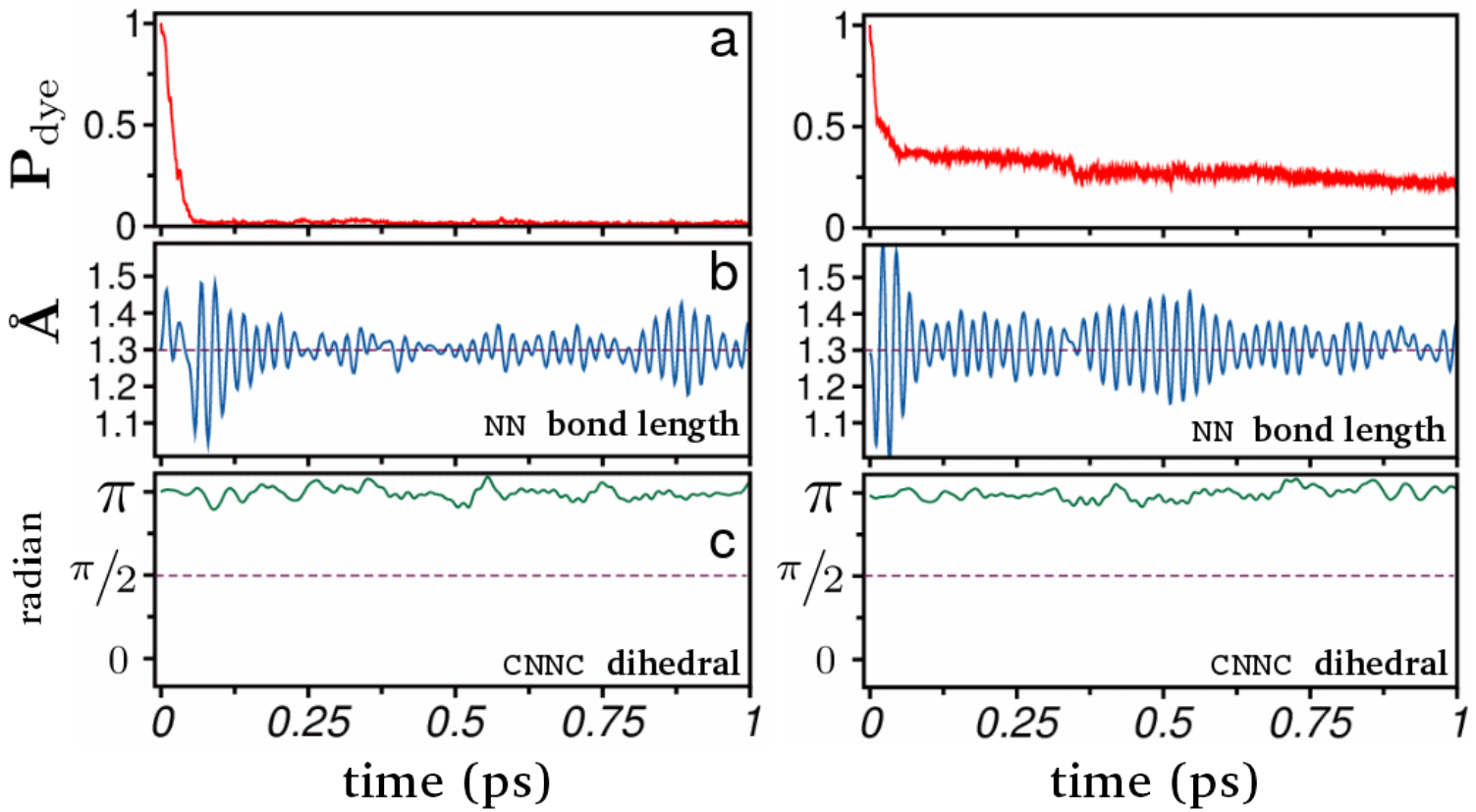
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics

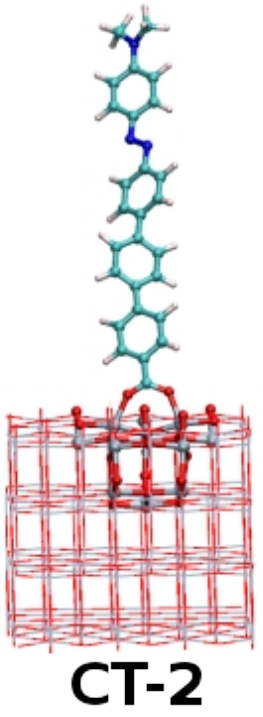




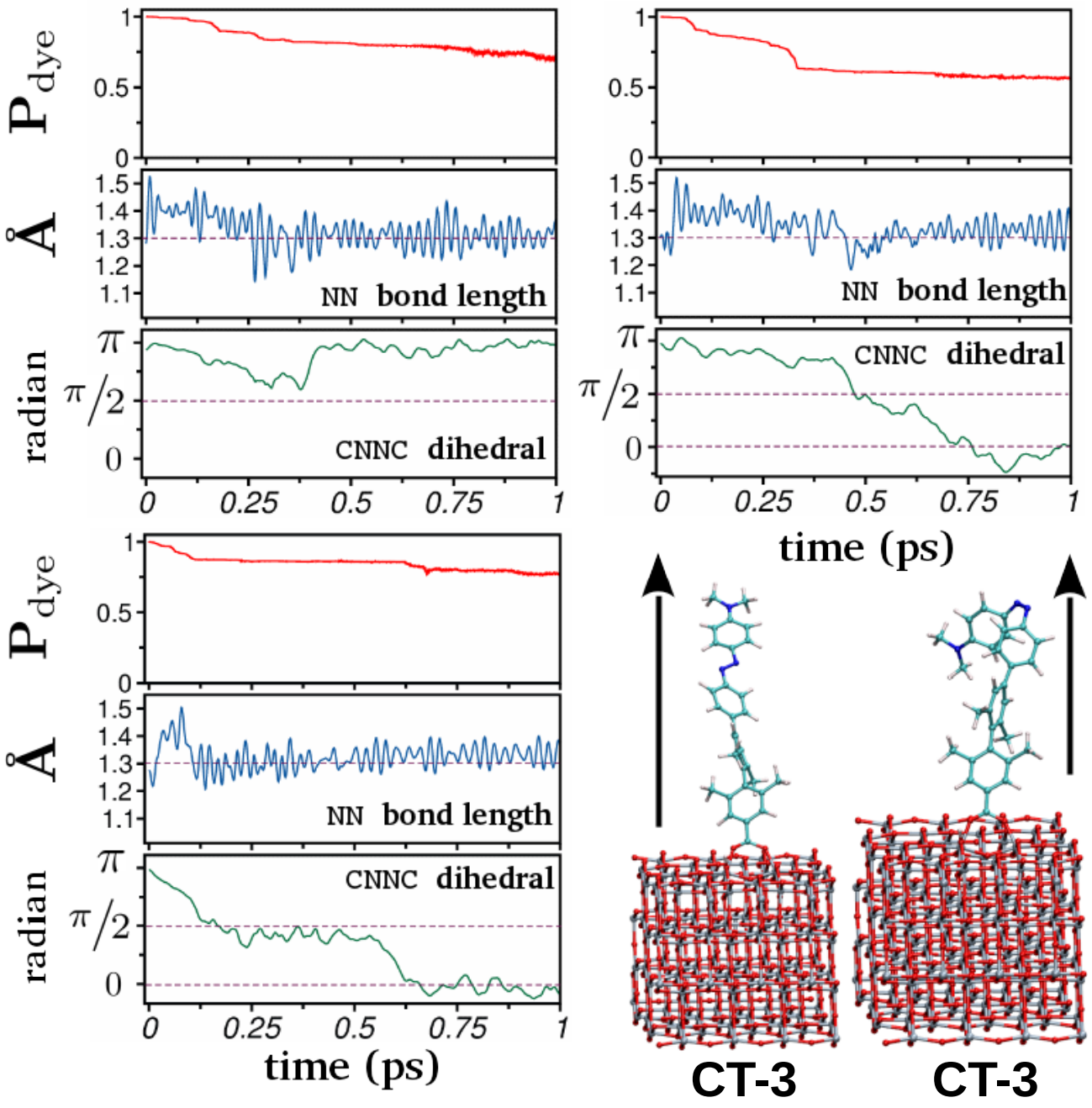
CT-1

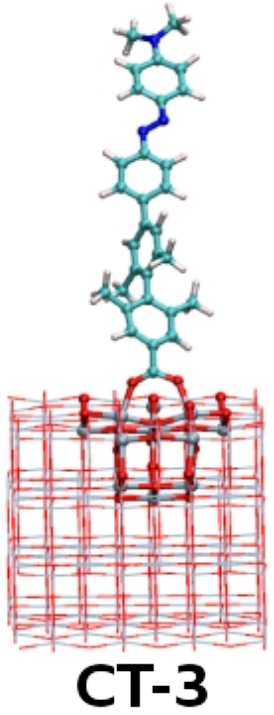
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



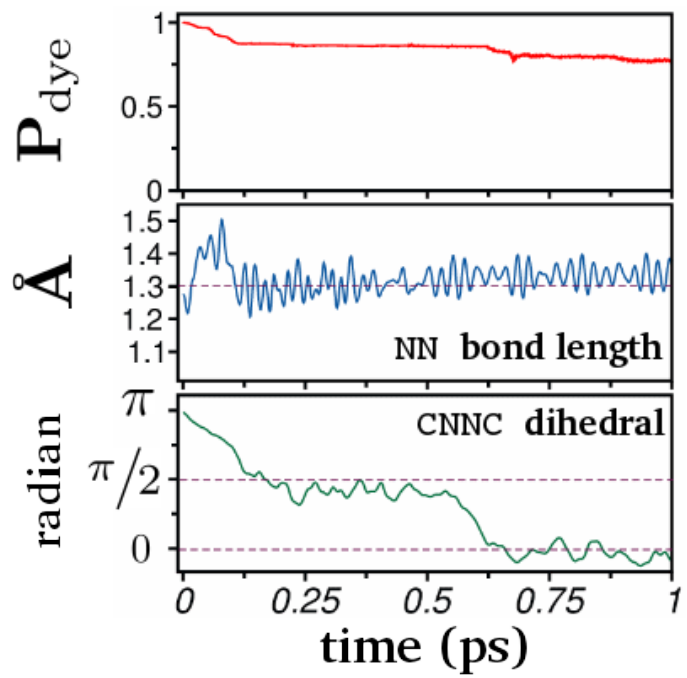


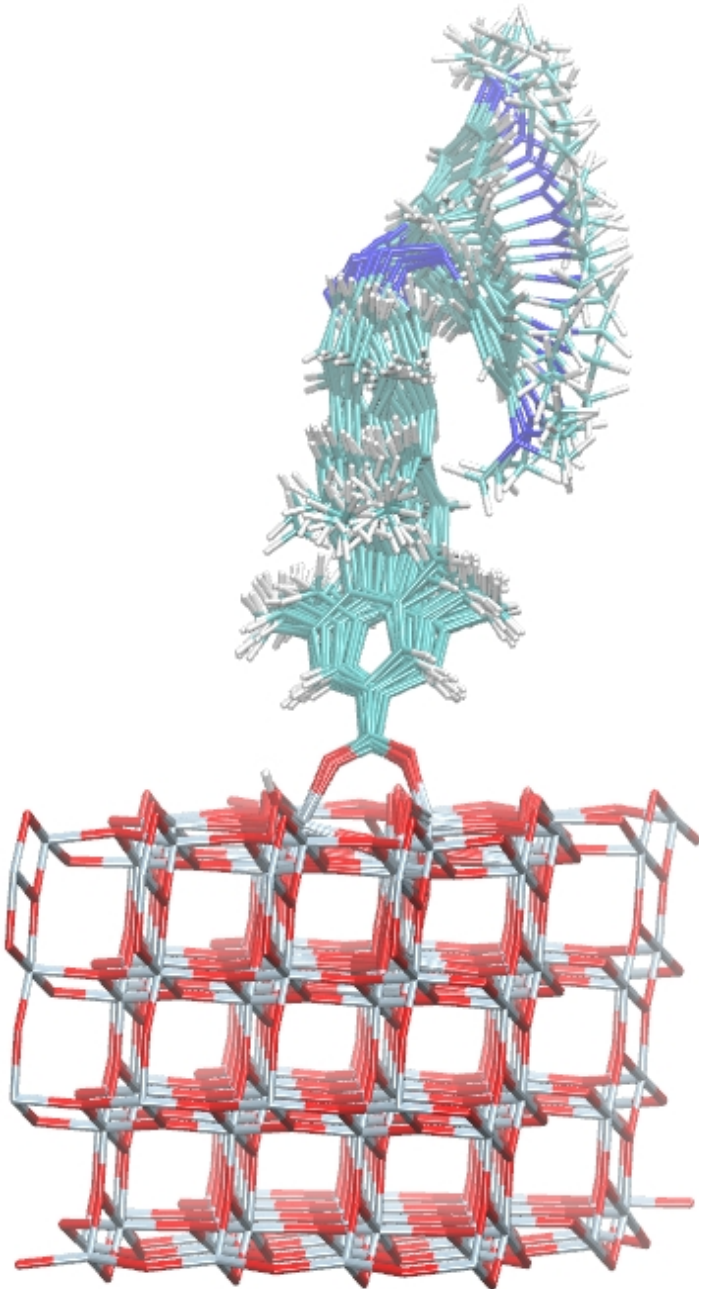
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics





Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics





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CAPES

fapesc
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Laboratório Nacional de Computação Científica
UNIDADE DE PESQUISA DO MCTI

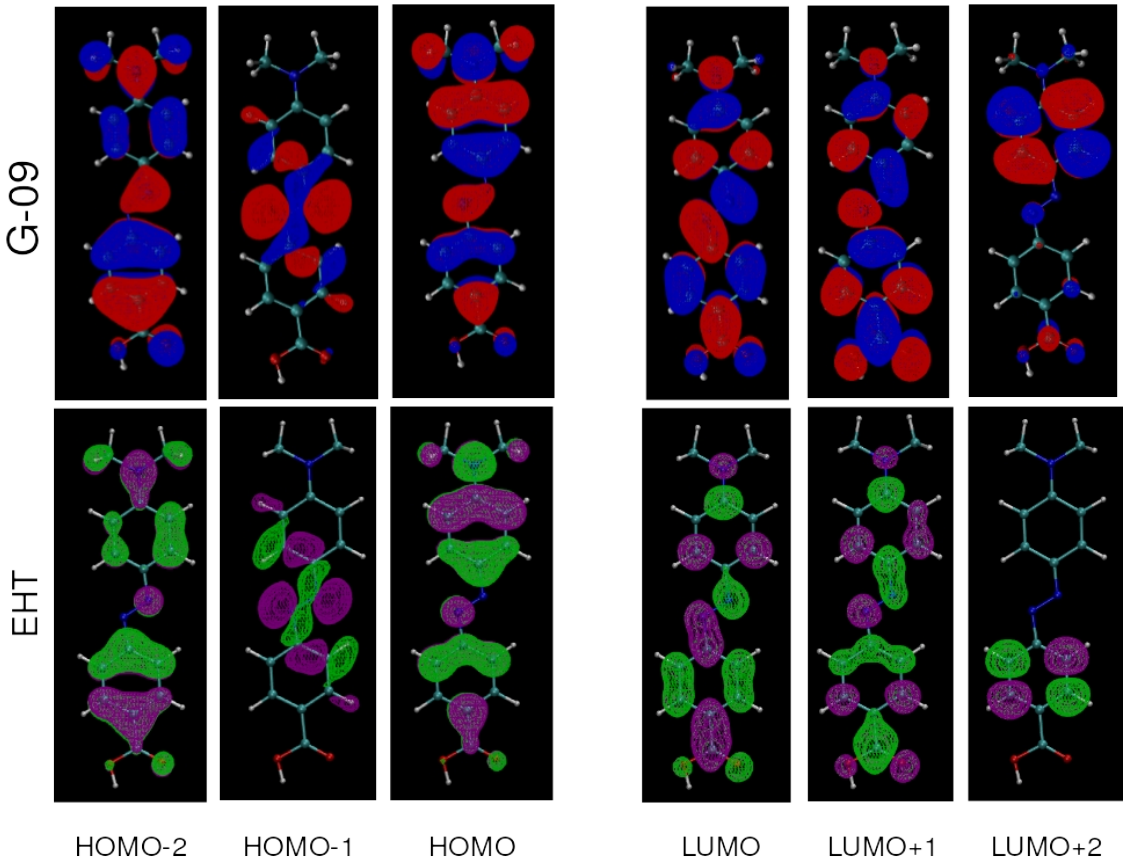
INCT INE
Instituto Nacional de Eletrônica Orgânica

Summary: Coherent Switches with Decay of Mixing (CSDM)

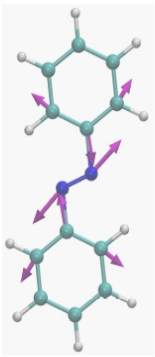
Advantages of the CSDM method:

- CSDM combines Mean-Field Ehrenfest and Fewest Switches Surface Hopping;
- No discontinuities in nuclear momentum (due to non-adiabatic hops);
- Total energy is naturally conserved;
- Includes electronic decoherence effects in Mean-Field Ehrenfest;
- Decoherence is weaker at strong coupling regions, allowing for vibronic effects.

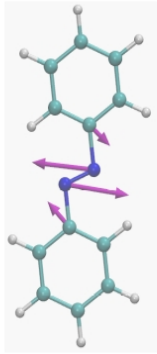
Nonadiabatic Molecular Mechanics with Charge Transfer and Excitation Dynamics



Frontier Orbitals	DFT/B3LYP/6-31G(d)	DynEMol-EHT
LUMO - HOMO	3.14	2.97
HOMO - [HOMO-1]	0.81	0.67
LUMO - [HOMO-1]	3.78	3.63
[LUMO+1] - LUMO	1.70	1.81



$\mathbf{F}(\pi, \pi^*)$



$\mathbf{F}(n, \pi^*)$

Extended Hückel Tight-binding

Extended Hückel theory to ***account for the chemical bonding***:

$$H_{ab}^{EHT} = K_{ab}\ S_{ab}\ \frac{h_a + h_b}{2}$$

Atomic Orbitals: Slater-type orbitals (STO)

$$f_a^{STO}(\vec{r} - \mathbf{R}_A(t)) = (\zeta_a)^{n+1/2} \sqrt{\frac{1}{(2n)!}}\ r^{n-1}\ \exp\left[-\zeta_a r\right]\ Y_{lm}(\theta, \varphi)$$

Overlap Matrix:
$$\begin{cases} S_{ab} = \delta_{ab}\ , & A = B \\ S_{ab}(t) = \langle\ f_a(\mathbf{R}_A(t))\ |\ f_b(\mathbf{R}_B(t))\ \rangle\ , & A \neq B \end{cases}$$

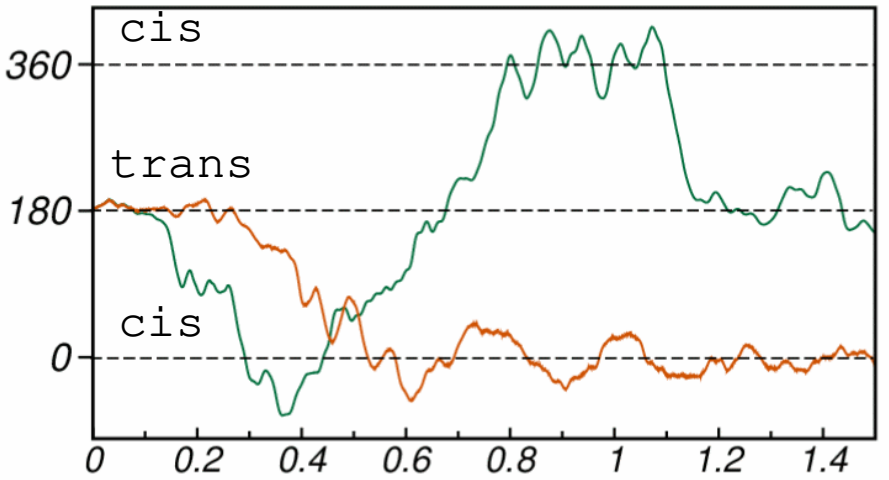
Sensitive to molecular geometry, short range couplings: cutoff = 12 Å.

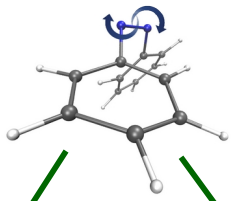
Y_{ml}	=	Spherical Harmonics;
K_{ab}	=	Wolfsberg-Helmholz coupling parameter
h_a, h_b	$\approx$	Valence State Ionization Potentials (VSIPs)
ζ	=	constant related to the effective charge of the nucleus

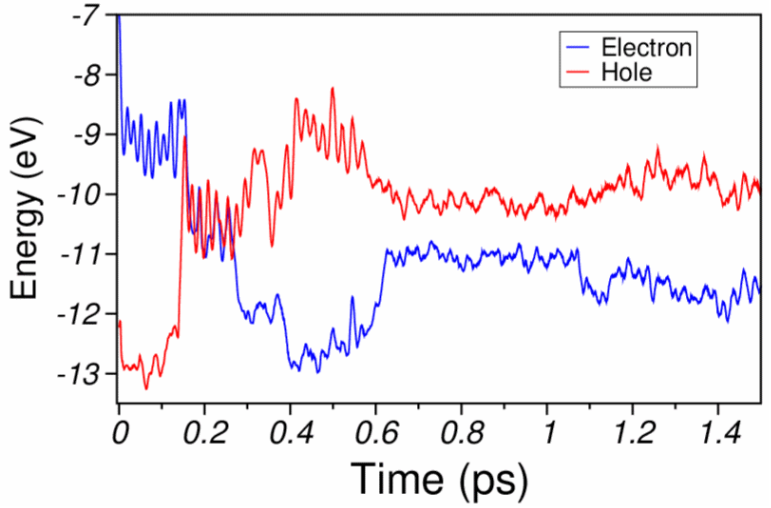
*Optimize EHT semiempirical parameters

Azobenzene in Methanol solution

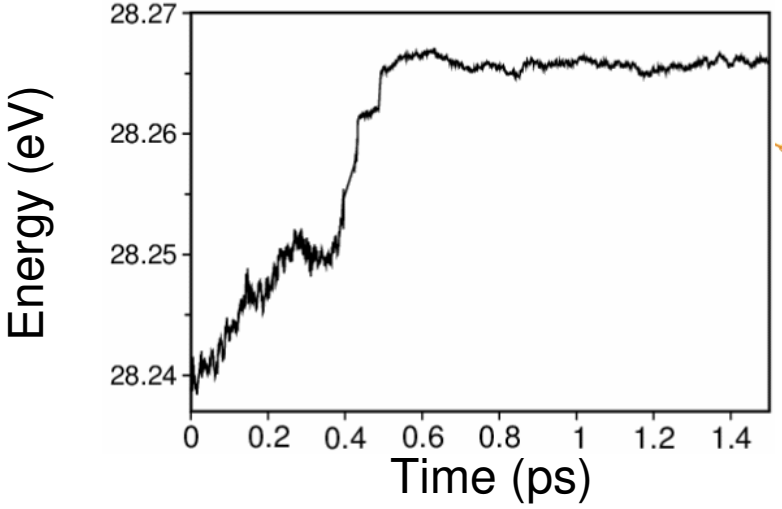
CNNC dihedral angle

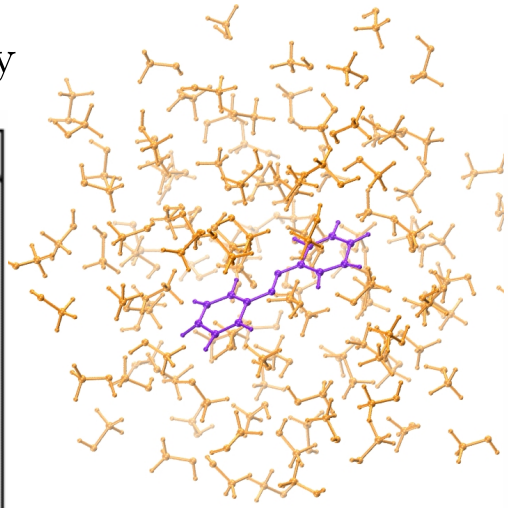




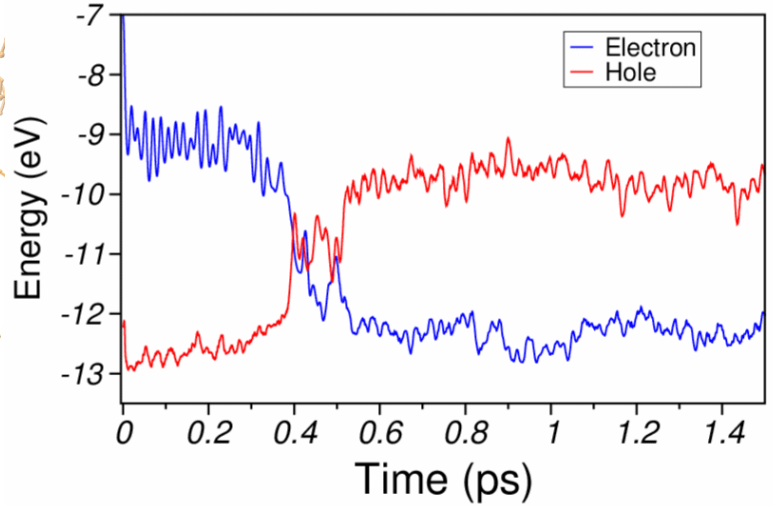


Total Quantum-Classical Energy



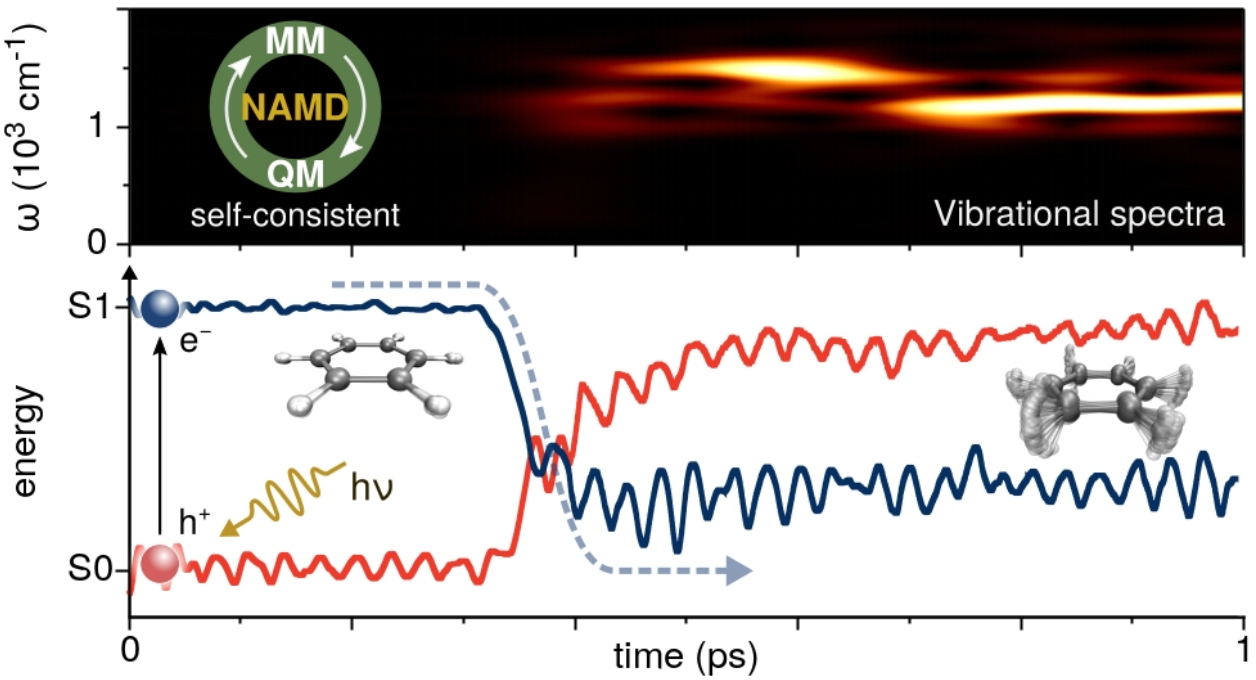


QM-MM simulation



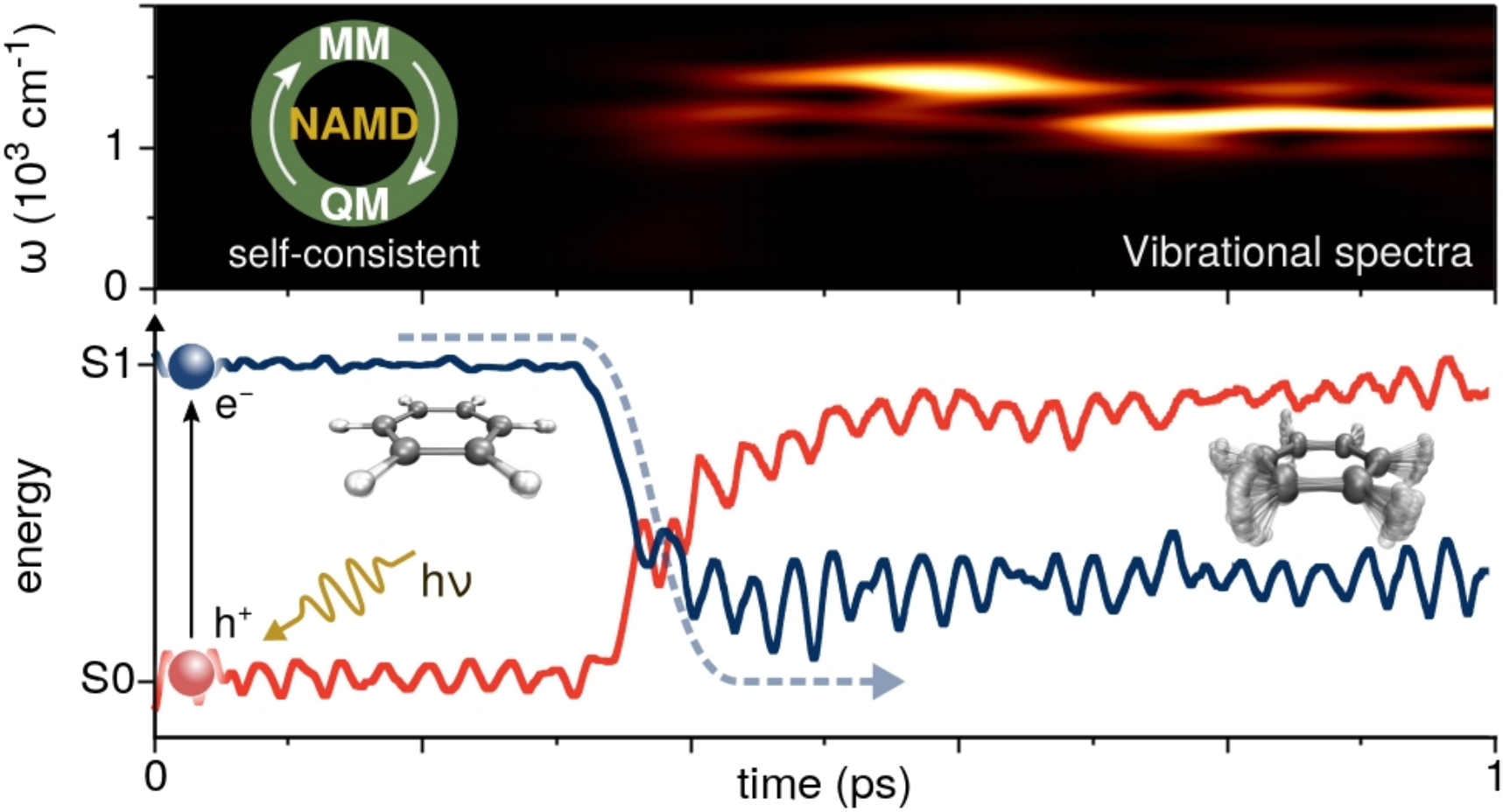
DynEMol Method

Dynamics of Electrons in Molecules
A Semi-empirical MO method for Large Scale Electronic Quantum Dynamics



DynEMol: tools for studying Dynamics of Electrons in Molecules.
https://github.com/lgcrego/Dynemol

Benzene – Intramolecular Vibrational Relaxation (IVR)



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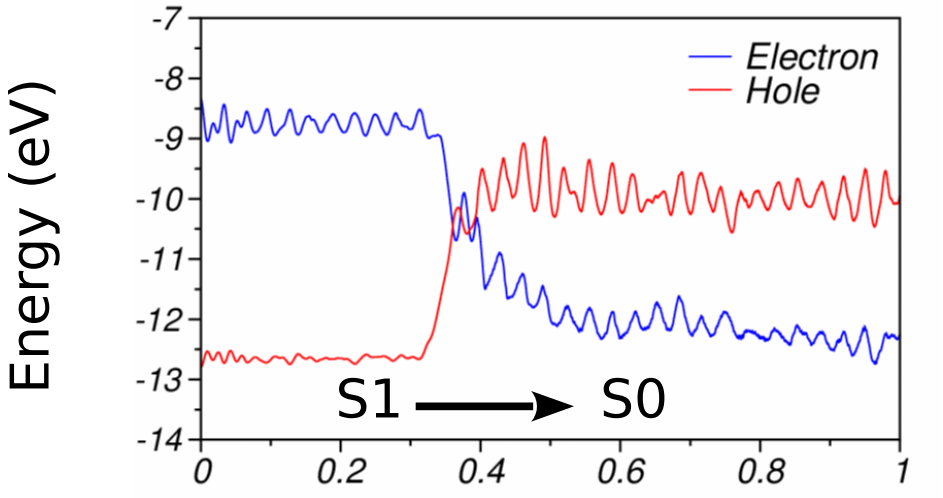
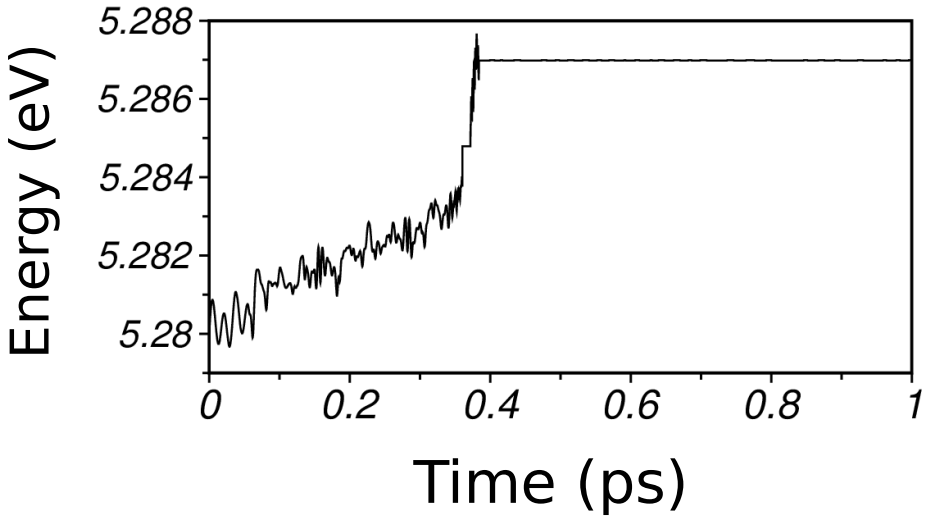
Benzene: Energy balance in Vibrational Relaxation



Excitation Energy

$$E^{el} = \sum_n \mathcal{E}_n(t)|C_n^{el}(t)|^2$$

$$E^{hl} = \sum_n \mathcal{E}_n(t)|C_n^{hl}(t)|^2$$



Total Quantum-Classical Energy

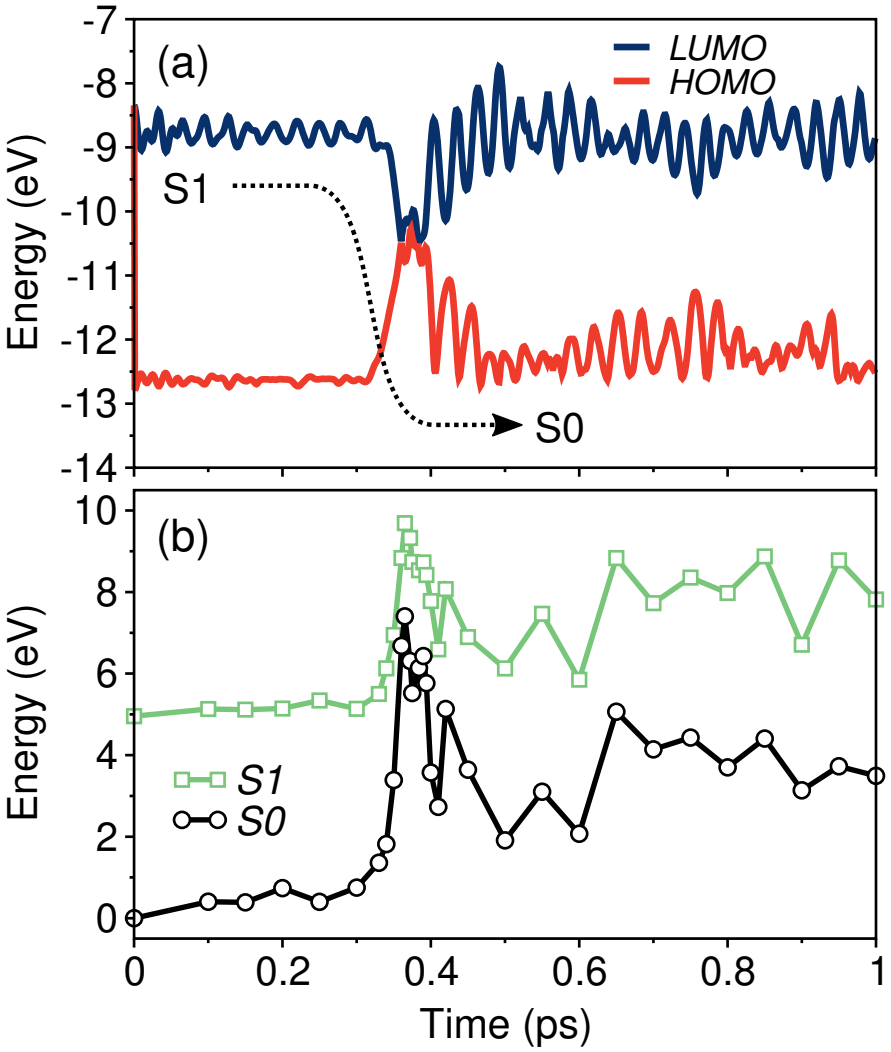
$\delta t = 0.005\text{fs}$

$$E_{S1} \longrightarrow E_{S0}$$

$$E_{MM} + E_{QM} = K + V_{gs}^{FF} + Tr\left[\rho^{eh}\mathbf{H}\right] \qquad E_{MM} = K + V_{gs}^{FF}$$

Benzene – Intramolecular Vibrational Relaxation (IVR)

Check: comparisson with high-level theory



→ EHT-MM-Ehrenfest

→ CASSCF(6,6)/6-31G*

(performed with Gaussian-09)

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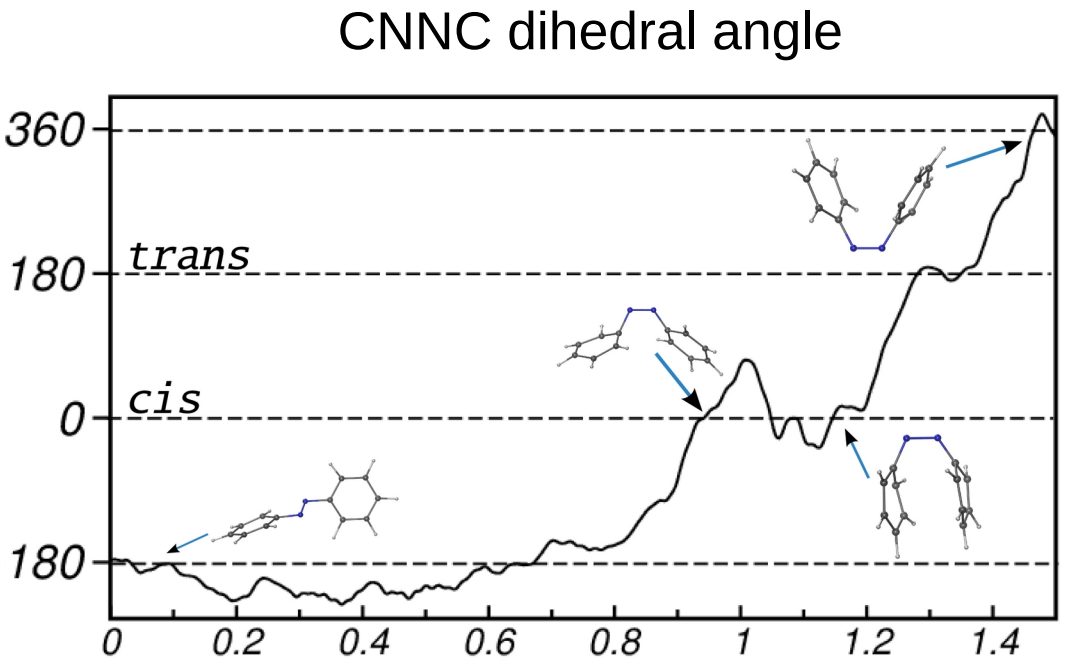
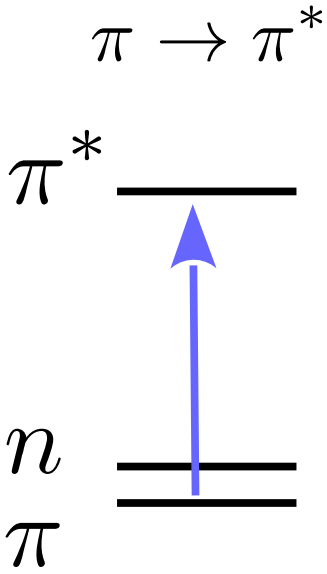
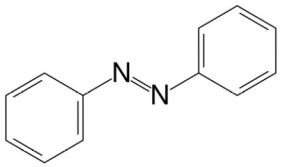
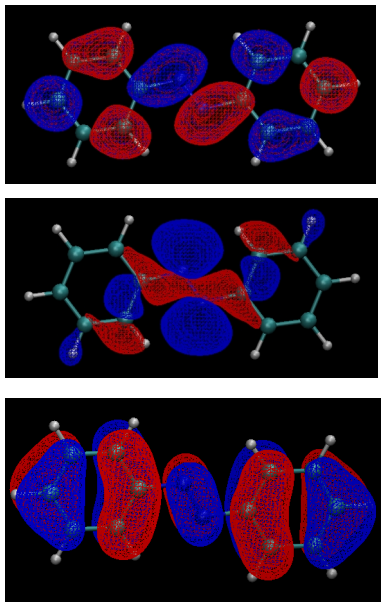
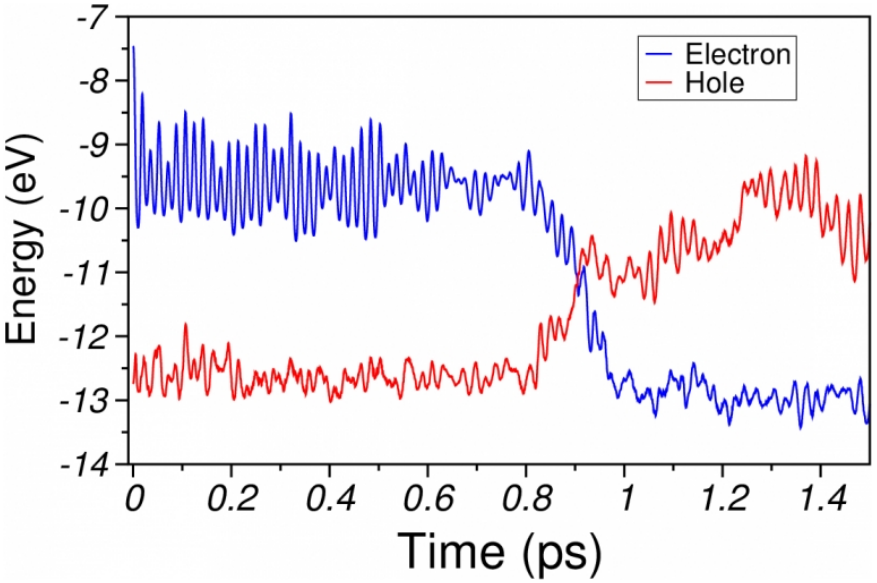
Azobenzene – Photoinduced Isomerization

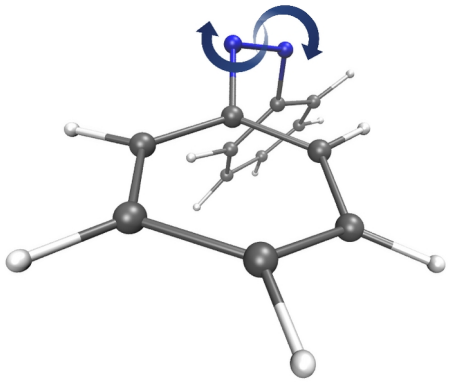












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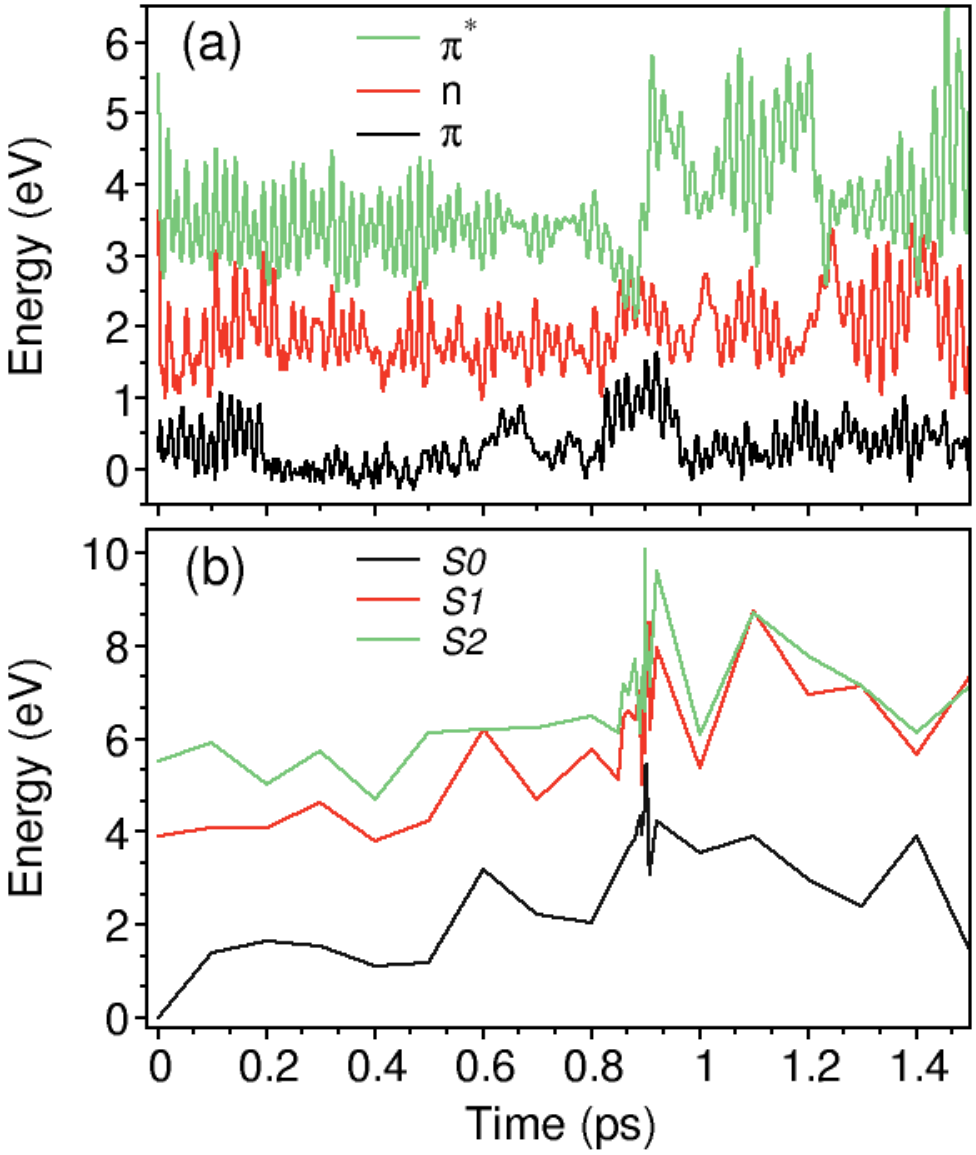
Azobenzene – Photoinduced Isomerization

Check: comparisson with high-level theory



→ EHT-MM-Ehrenfest

$\delta t = 0.005\text{fs}$

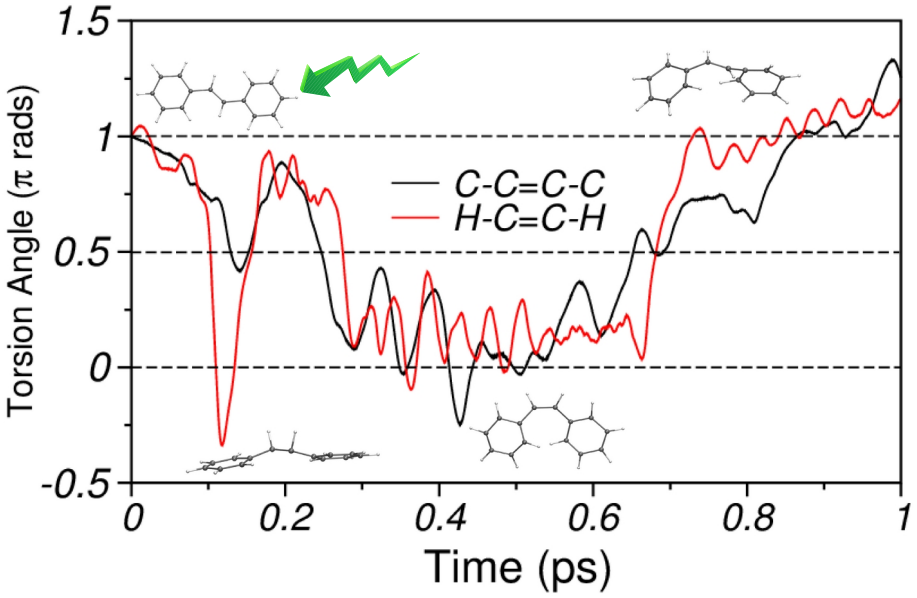
run time $\sim$ 12h on a 16 core CPU

→ CASSCF(14,12)/6-31G*

Concerted Photoisomerization of Stilbene

the *trans→cis* torsion

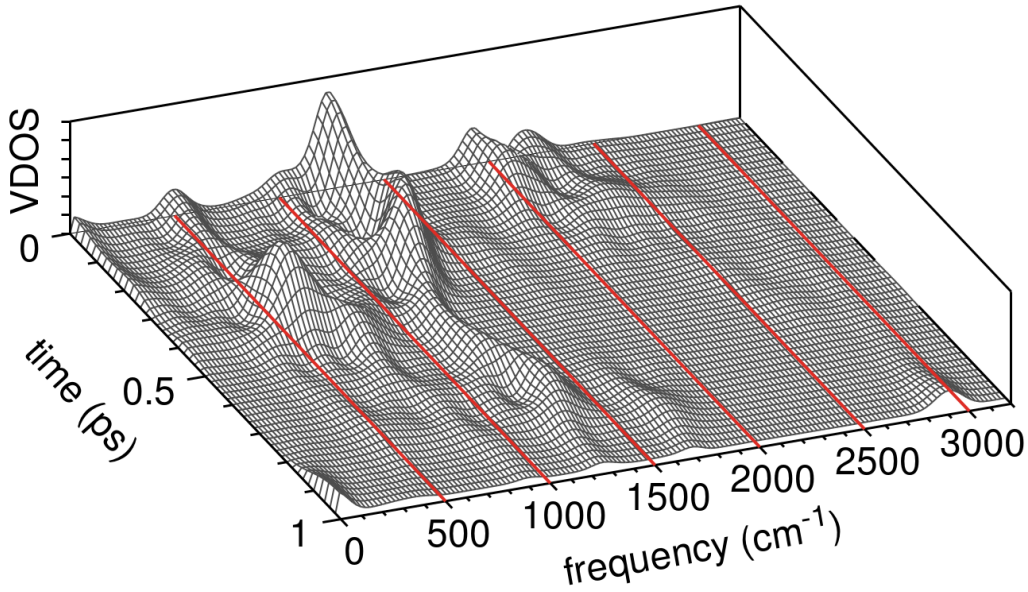
H-C=C-H dihedral drives the C-C=C-C isomerization



Time-dependent Vibrational Spectra

$$C_v(t) = \frac{\sum_i m_n \vec{v}_n(0) \cdot \vec{v}_n(t)}{\sum_i m_n \vec{v}_n(0) \cdot \vec{v}_n(0)}$$

$$g_\tau(\omega, t) = \left| \int_{t_0}^{t_f} C_v(t') \exp\left[-\frac{(t'-t)^2}{2\tau^2} \right] e^{-i\omega t'} \, dt' \right|$$



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