

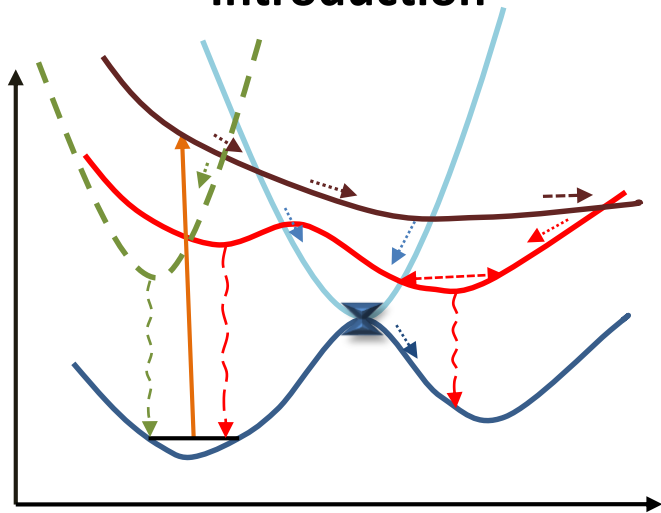


Unravelling Photochemical Mechanisms with Computational Methods

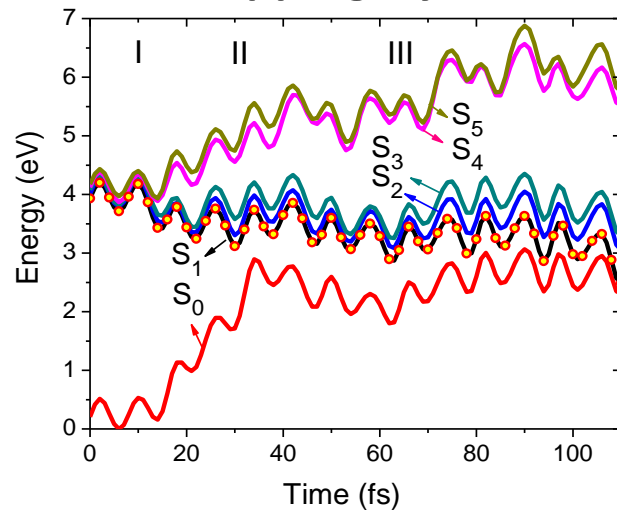
Rachel Crespo-Otero

OUTLINE

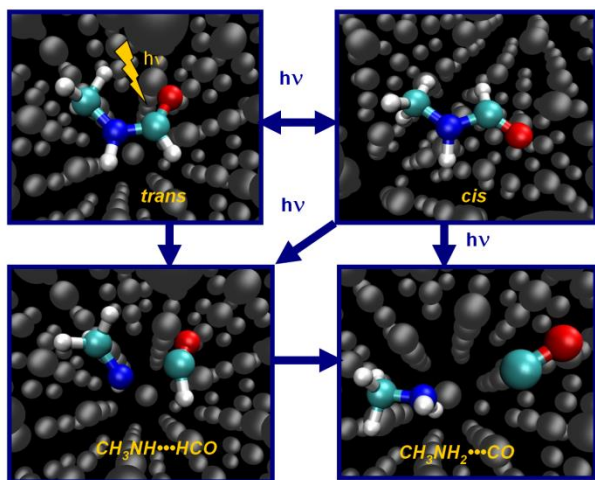
Introduction



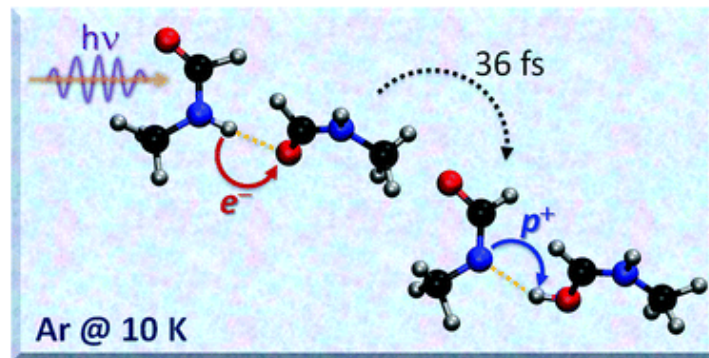
Surface Hopping Dynamics



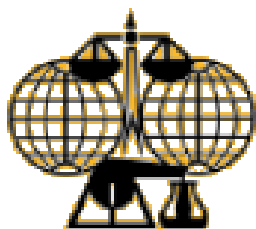
Photodissociation



Excited State Proton Transfer

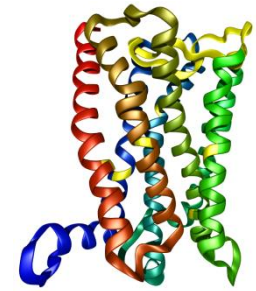
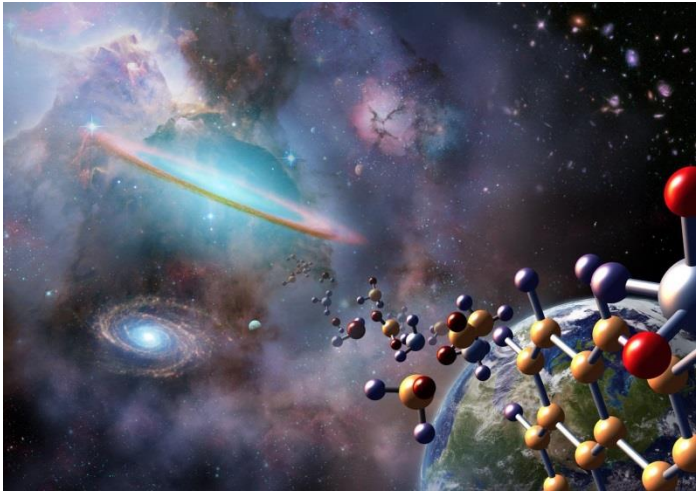


PHOTOCHEMICAL REACTION



IUPAC GOLD BOOK

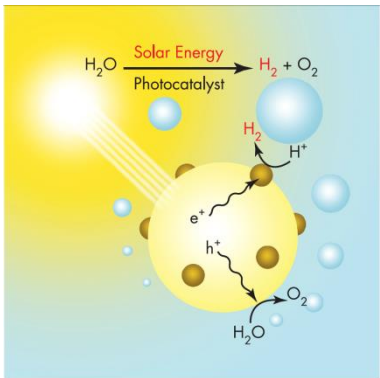
Generally used to describe a chemical reaction caused by absorption of [ultraviolet](#), [visible](#) or [infrared](#) radiation. There are many ground-state reactions, which have photochemical counterparts....



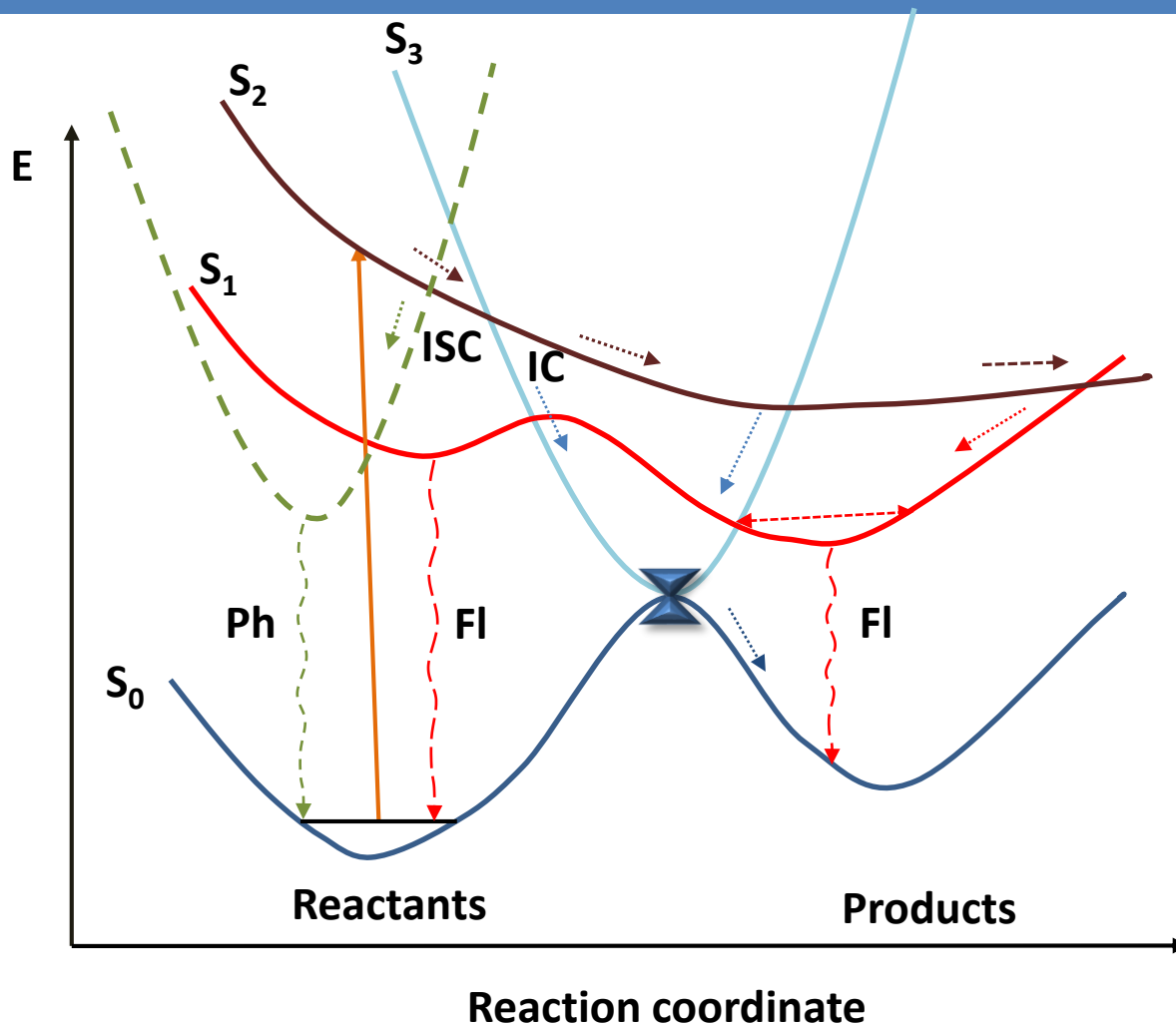
Vision

Modern Technologies

Solar Fuels



PHOTOMECHANISMS



Fl: Fluorescence
Ph: Phosphorescence
ISC: Intersystem crossing
IC: Internal conversion

Many electronic states can be involved in a photoreaction

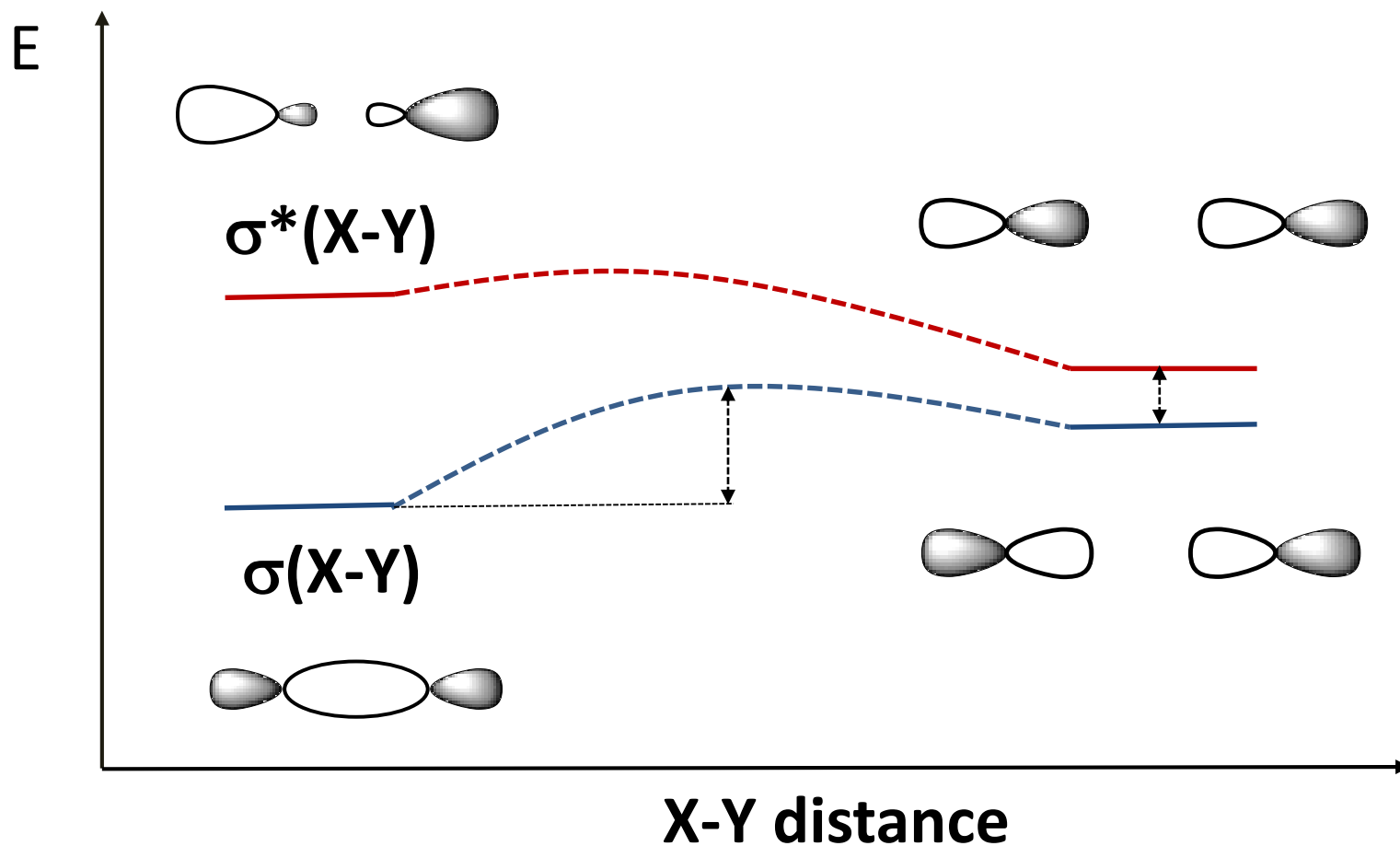
Coupling between nuclear and electronic motions

PHOTOREACTIONS

Reaction barriers are smaller in the excited state

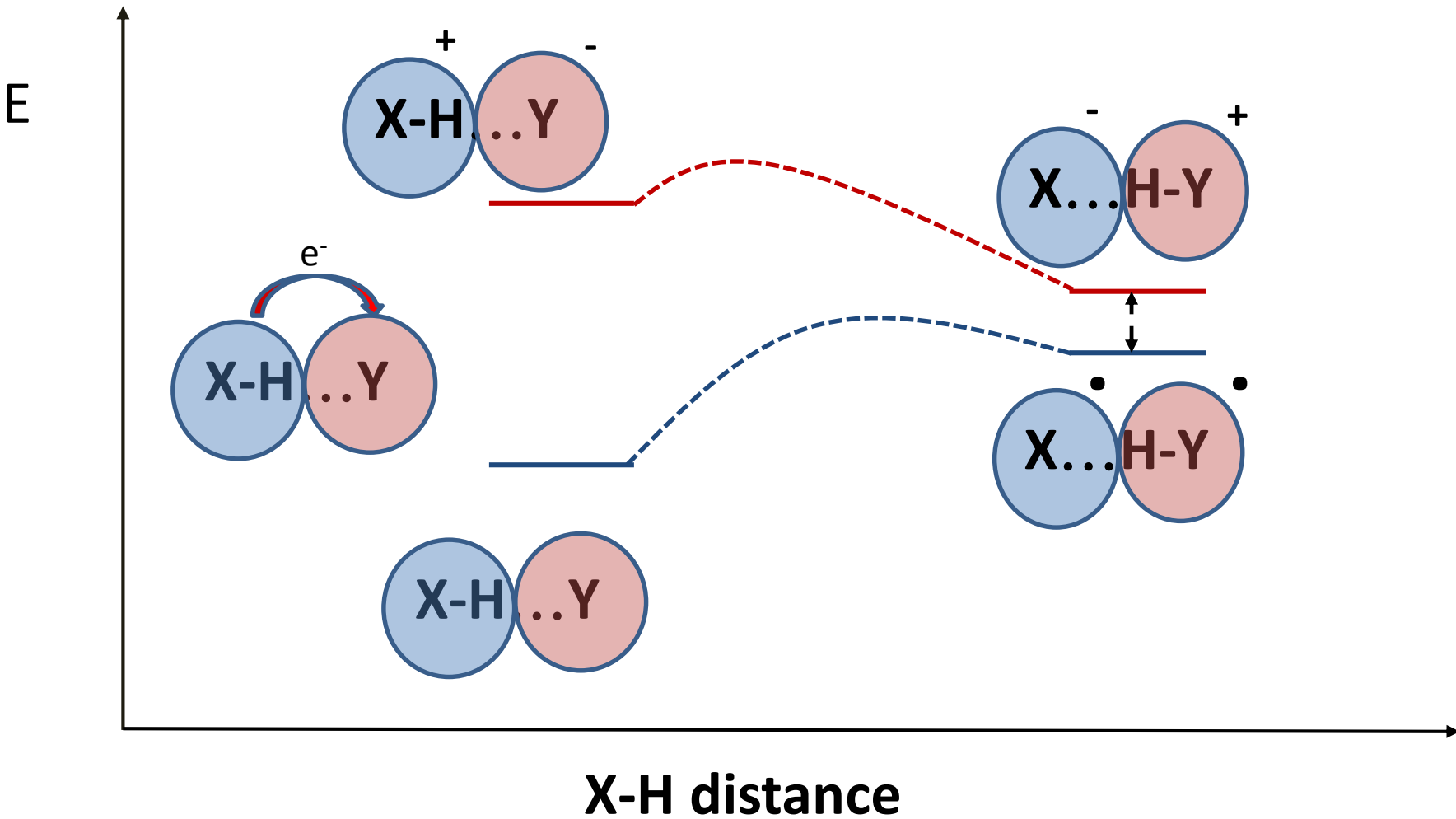
Thermodynamically disfavoured products can be formed

PHOTODISSOCIATION



To reduce the barrier of the reaction in the excited state, an excited state with high X-Y antibonding character can be populated

EXCITED STATE PROTON TRANSFER (ESPT)



Population of Charge Transfer states accelerate PT process in the excited states

EXCITED STATES REACTIONS

Breakdown of the Born-Oppenheimer approximation

Competition between different pathways

Ultrafast!

Photochemical reactions: can we use our chemical intuition?

EXCITED STATES DYNAMICS: SURFACE HOPPING

Time dependent Schrödinger equation

$$\left(i\hbar \frac{\partial}{\partial t} - H_e \right) \varphi(r, R, t) = 0$$

The dynamics of the nuclei is propagated classically on a single Born–Oppenheimer surface at any time.

The nonadiabatic events are simulated by a stochastic algorithm that allows each trajectory to jump to other states during the propagation.

Approximation for the wavefunction

$$\varphi(r, R, t) = \sum_j c_j(t) \Phi_j(r, R(t))$$

EXCITED STATES DYNAMICS: SURFACE HOPPING

$$\left(i\hbar \frac{\partial}{\partial t} - H_e \right) \varphi(r, R, t) = 0$$

Substitute $\varphi(r, R, t) = \sum_j c_j(t) \Phi_j(r, R(t))$

Multiply by Φ_k^* and integrate over the electronic coordinates



Semi-classical time-dependent Schrödinger equation

$$i\hbar \frac{\partial c_k}{\partial t} + \sum_{j=1}^{N_s} \left(i\hbar \sigma_{kj} - H_{kj} \right) c_j = 0$$

The SC-TDSE is solved with standard methods
(Unitary Propagator, Adams Moulton 6th-order, Butcher 5th-order)

Non-adiabatic couplings

$$\sigma_{kj} = \left\langle \Phi_k \left| \frac{\partial \Phi_j}{\partial t} \right. \right\rangle = \mathbf{F}_{kj} \cdot \mathbf{v}$$

Non-adiabatic coupling terms nuclear velocities

Tully, J. Chem. Phys. **93**, 1061 (1990)

EXCITED STATES DYNAMICS: SURFACE HOPPING

Non-adiabatic couplings

$$\sigma_{kj} = \left\langle \Phi_k \left| \frac{\partial \Phi_j}{\partial t} \right. \right\rangle = \mathbf{F}_{kj} \cdot \mathbf{v}$$

Non-adiabatic coupling terms nuclear velocities

$$\mathbf{F}_{kj} = \left\langle \Phi_k \left| \nabla_R \Phi_j \right. \right\rangle$$

H_{ij} elements

$$\left(\{ \Phi_k \} \mid H_{kj} = V_k \delta_{kj} \right) \quad \text{Adiabatic basis}$$

$$\left(\{ \Phi_k^d \} \mid H_{kj} = W_{kj}, \mathbf{F}_{kj} = 0 \right) \quad \text{Diabatic basis}$$

Newton's equations of motion

$$\frac{d^2 \mathbf{R}_m^c}{dt^2} - \frac{\mathfrak{F}_m^c}{M_m} = 0$$

EXCITED STATES DYNAMICS: SURFACE HOPPING

Fewest switches method (Tully)

$$P_{k \rightarrow i} = \max \left[0, \frac{-2\Delta t}{|c_k|^2} \operatorname{Re}(c_k c_i^*) \sigma_{li} \right]$$

(Adiabatic Representation)

Decoherence corrections

Granucci and Persico, J. Chem. Phys. **126**, 134114 (2007)

C. Zhu, S. Nangia, A. W. Jasper, and D. G. Truhlar, J. Chem. Phys. **121**, 7658 (2004).

SURFACE HOPPING: SOME USEFUL REFERENCES

Comparison to other methods

- Cattaneo and Persico, J. Phys. Chem. A **101**, 3454 (1997)
- Worth, Hunt, Robb, J. Phys. Chem. A **107**, 621 (2003)

Comparison between hopping algorithms

- Zhu, A. W. Jasper, and D. G. Truhlar, JCTC **1**, 527 (2005)
- Fabiano, Groenhof, Thiel, Chem. Phys. **351**, 111 (2008)

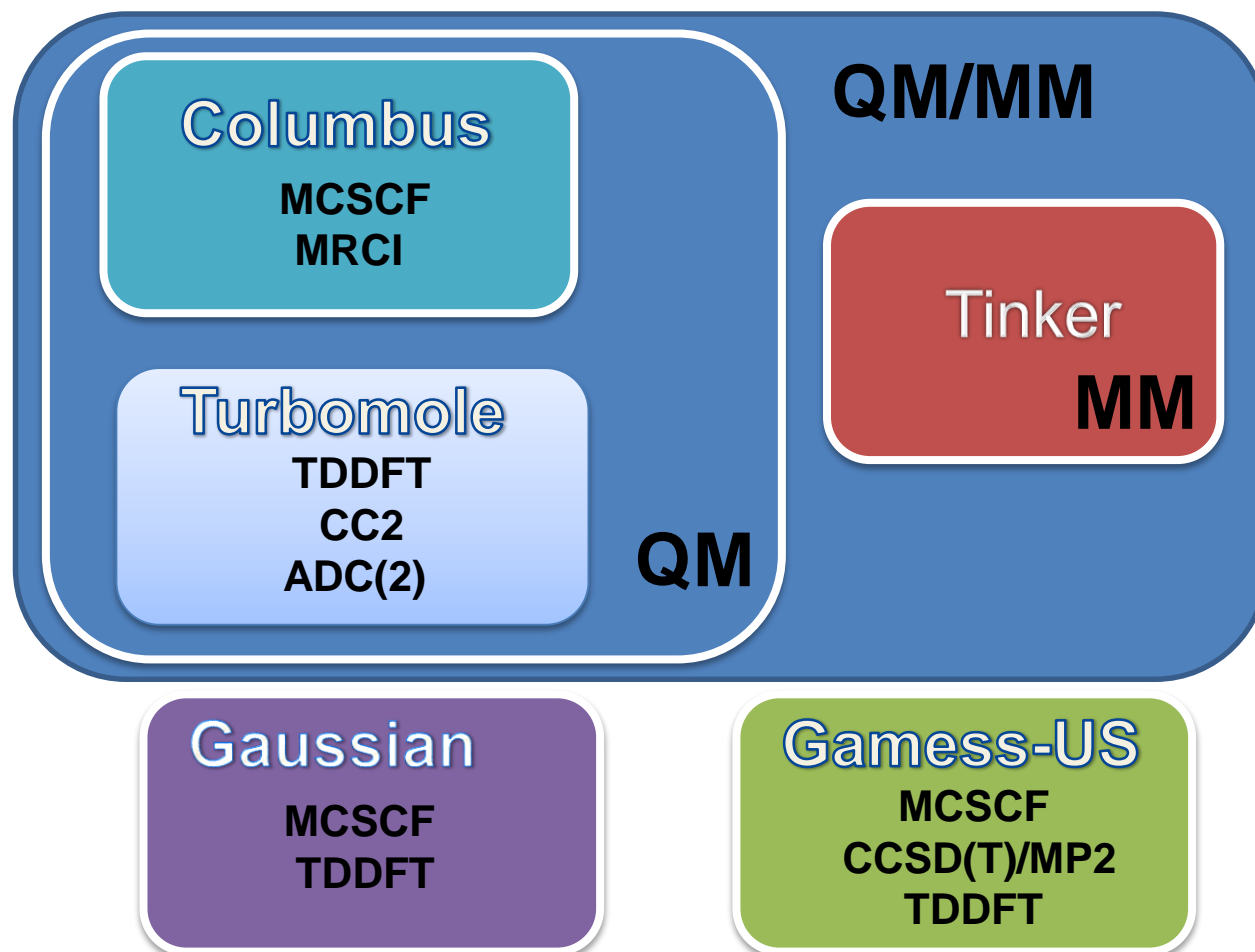
Conceptual background

- Herman, J. Chem. Phys. **103**, 8081 (1995)
- Schwartz, Bittner, Prezhdo, Rossky, J. Chem. Phys. **104**, 5942 (1996)
- Tully, Faraday Discuss. **110**, 407 (1998)
- Schmidt, Parandekar, Tully, J. Chem. Phys. **129**, 044104 (2008)

Surface hopping reviews

- Doltsinis, NIC series, 2002
- Barbatti, WIREs: Comp. Mol. Sci. **1**, 620 (2011)

NEWTON-X: A package for Newtonian dynamics close to the crossing seam



NEWTON-X: A package for Newtonian dynamics close to the crossing seam



Web:

<http://www.newtonx.org>

Wiki:

<https://en.wikipedia.org/wiki/Newton-X>

NX forum at Google:

<https://groups.google.com/forum/?fromgroups#!forum/newtonx>

ELECTRONIC METHODS

Common methods used with Surface Hopping

Multi-Reference Methods

Advantage: Appropriate description of the S_1/S_0 crossing seam region.

Disadvantage: It is challenging to find a stable active state, which can represent all regions of the potential energy surface that can be explored during the dynamics.

CASSCF: Lack of dynamic correlation

MRCI: Too computationally expensive for most applications

ELECTRONIC METHODS

Common methods used with Surface Hopping

Single-Reference Methods

Advantage: Black box methods, they do not require much user intervention, which is very convenient for dynamics simulations.

Algebraic-Diagramatic-Construction ADC(2) : Dynamics is very stable.
(Plasser *et al.* JCTC **10**, 1395 (2014))

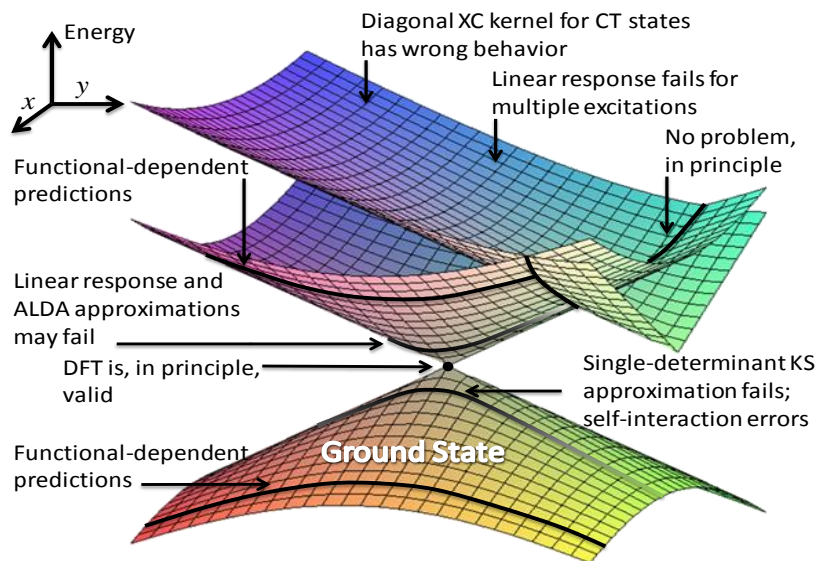
Coupled Cluster to the second order (CC2, RI-CC2): Numerical instabilities close to quasi-degenerate excited states. It seems to provide a proper description of conical interceptions(Tuna *et al.* JCTC **11**, 5758 (2015))

Common methods used with Surface Hopping

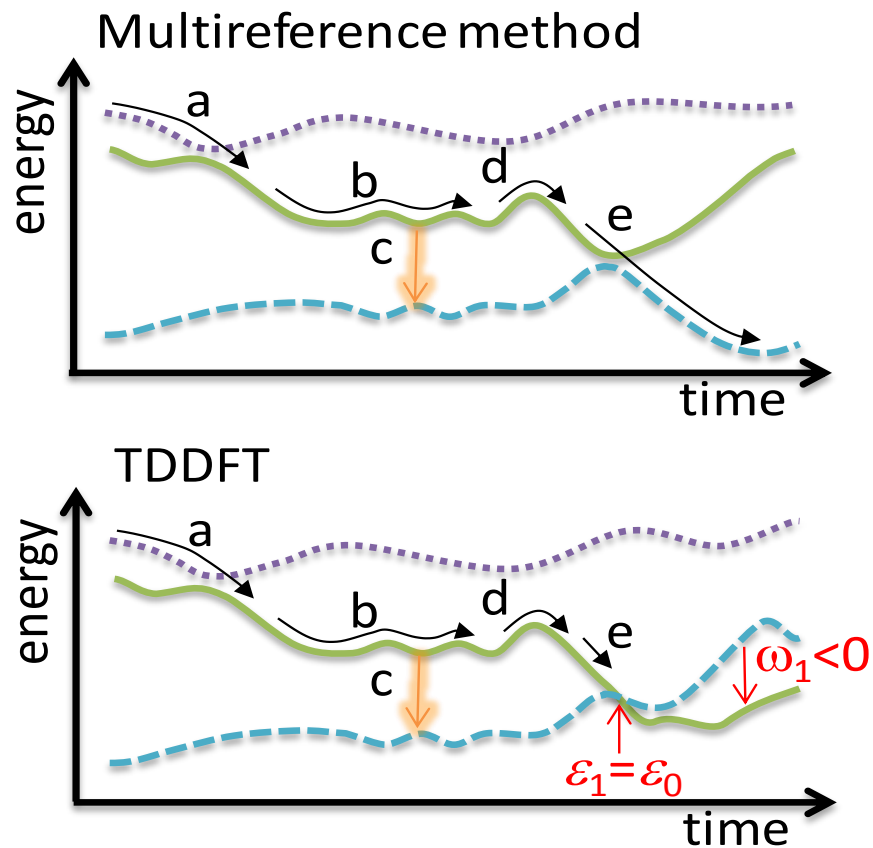
Single-Reference Methods

DFT/TDDFT

Incorrect description
of S_1/S_0 crossing seam

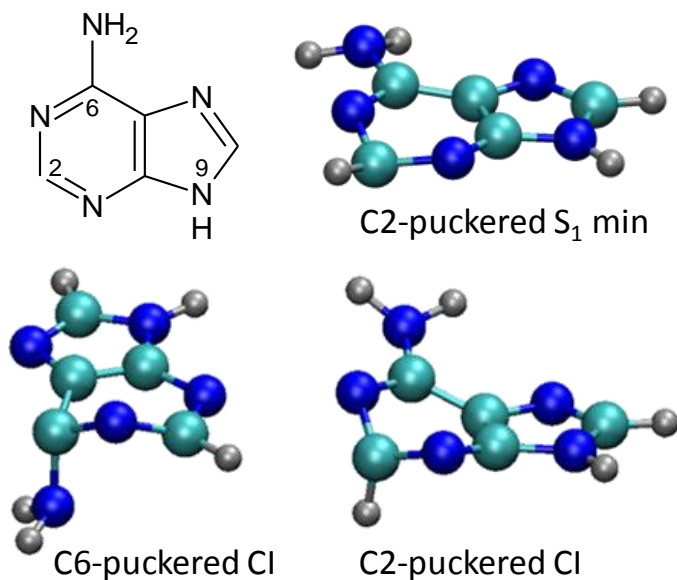


MULTIREFERENCE METHODS vs TDDFT

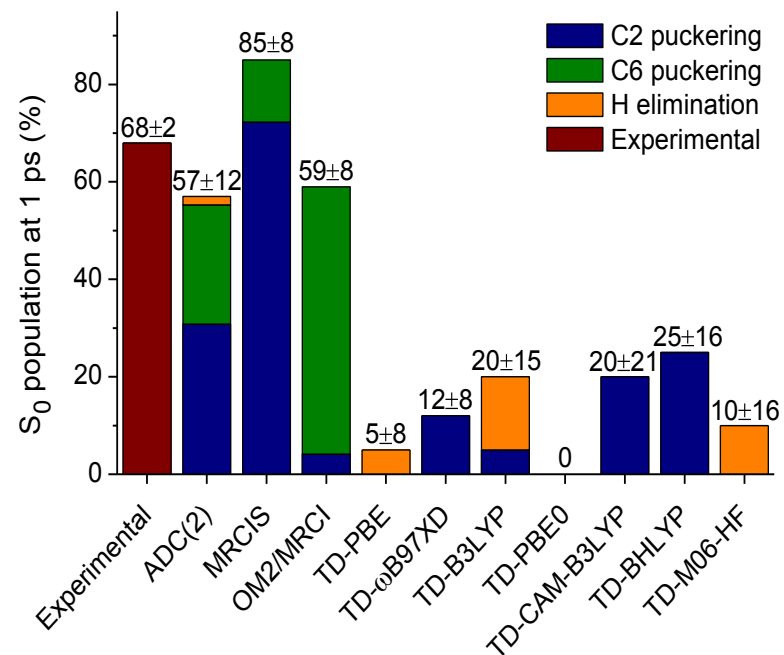


ADENINE: LEVEL OF THEORY

Adenine conical intersections



Population of S_0 at 1 ps



Tested functionals do not explain the photochemistry .
Best results: ADC(2).

NON-ADIABATIC COUPLINGS IN NEWTON-X

$$\sigma_{kj} = \left\langle \Phi_k \left| \frac{\partial \Phi_j}{\partial t} \right. \right\rangle = \mathbf{F}_{kj} \cdot \mathbf{v} \quad \mathbf{F}_{kj} = \left\langle \Phi_k \left| \nabla_R \Phi_j \right. \right\rangle$$

Analytical evaluation of \mathbf{F}_{kj}

- MCSCF, MRCI (H. Lischka *et al.* Phys. Chem. Chem. Phys., 3, 664 (2001))

Numerical Evaluation

Finite difference method (S. Hammes-Schiffer and J. C. Tully. J Chem Phys 10, 4657 (1994))

$$\begin{aligned} \sigma_{kj} &\approx \frac{1}{2\Delta t} \left[\left\langle \Phi_k \left(t - \frac{\Delta t}{2} \right) \left| \Phi_j \left(t - \frac{\Delta t}{2} \right) \right. \right\rangle - \left\langle \Phi_k \left(t + \frac{\Delta t}{2} \right) \left| \Phi_j \left(t - \frac{\Delta t}{2} \right) \right. \right\rangle \right] \\ &\approx \frac{1}{4\Delta t} \left[3S_{kj}(t) - 3S_{jk}(t) - S_{kj}(t - \Delta t) + S_{jk}(t - \Delta t) \right] \end{aligned}$$

$$S_{kj}(t) = \left\langle \Phi_k(t - \Delta t) \left| \Phi_j(t) \right. \right\rangle$$

The Newton-X implementation for TDDFT, ADC(2), CC2 is based on approximate CIS wavefunctions.

TDDFT AND TDA: THE CASIDA'S ANSATZ

$$\Phi_K = \sum_o \sum_v C_{ov}^K \Psi_{ov},$$

Energies of the Kohn-Sham orbitals

$$C_{ov}^K = A_K \left(\frac{\varepsilon_v - \varepsilon_o}{\Delta E_K} \right)^{1/2} \underbrace{(X_{ov}^K + Y_{ov}^K)},$$

$$\Delta E_K = V_K - V_0,$$

vectors from linear response

$$Y_{ov}^K = 0 \text{ for TDA}$$

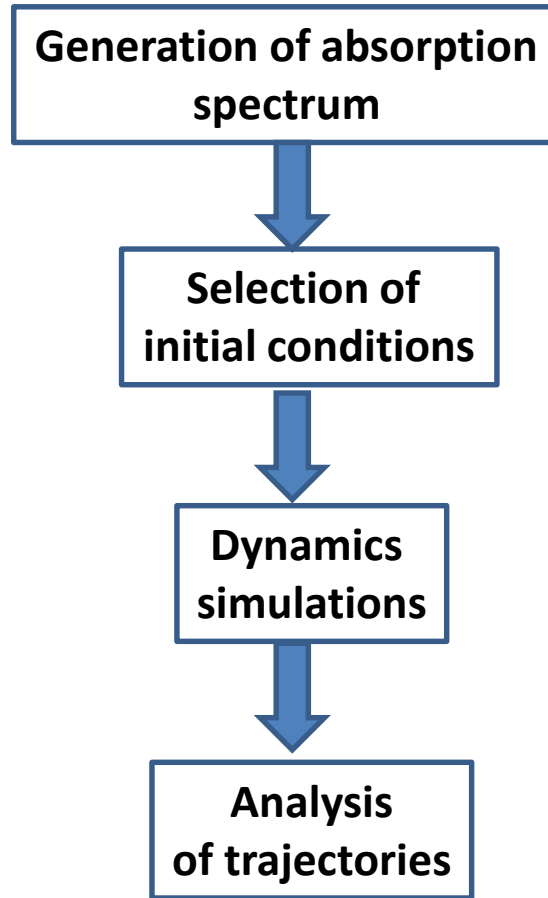
$$A_K = \left(\sum_{o,v} |C_{ov}^K|^2 \right)^{-1/2}, \text{ Normalization factor}$$

Tapavicza E, Tavernelli I, Rothlisberger U. *Phys. Rev. Lett.* 98, 023001 (2007).

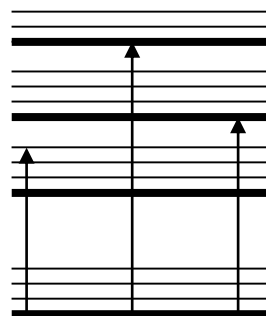
Barbatti M, Pittner J, Pederzoli M, Werner U, Mitrić R, Bonačić-Koutecký V, Lischka H. *Chem. Phys.* 375, 26 (2010).

Plasser, F.; Crespo-Otero, R.; Pederzoli, M.; Pittner, J.; Lischka, H.; Barbatti, M. *J. Chem. Theory Comput.* 10, 1395 (2014).

NAD WITH NEWTON-X



SPECTRA SIMULATIONS AND INITIAL CONDITIONS



Cross Section: $\sigma(E)$

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc\epsilon_0 n_r E} \sum_n^{N_{fs}} \frac{1}{N_p} \sum_l^{N_p} |\chi_{00}(\mathbf{R}_l)|^2 \Delta E_{0,n}(\mathbf{R}_l) f_{0n}(\mathbf{R}_l) \underbrace{g(E - \Delta E(\mathbf{R}_l), \delta_n)}$$

N_p Number of geometries

N_{fs} Number of states

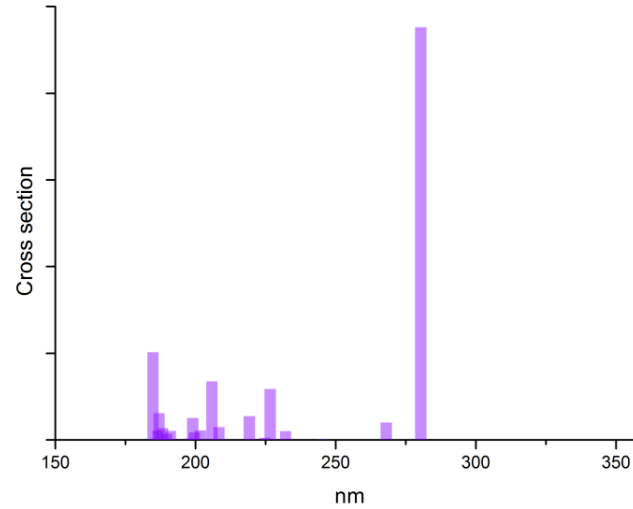
Gaussian or
Lorentzian

$$|\chi_{00}(\mathbf{q})|^2 = \prod_{j=1}^{3N-6} \left(\frac{\mu_j \omega_j}{\pi \hbar} \right)^{1/2} \exp(-\mu_j \omega_j q_j^2 / \hbar)$$

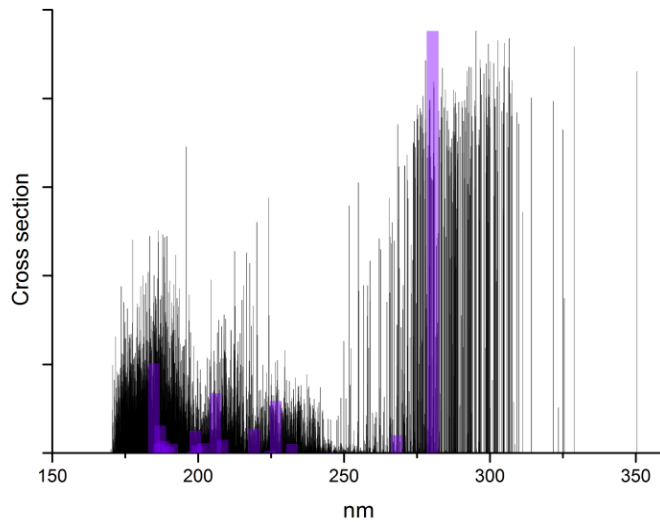
Wigner distribution

SPECTRA SIMULATIONS AND INITIAL CONDITIONS

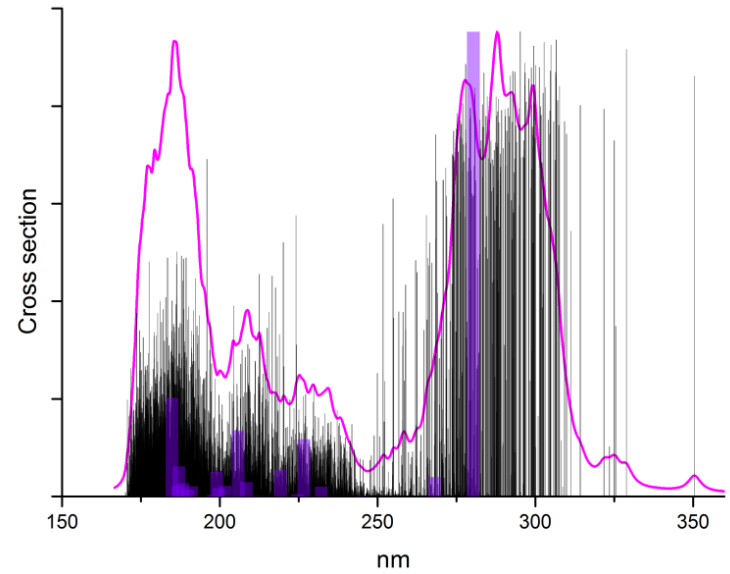
Equilibrium Geometry



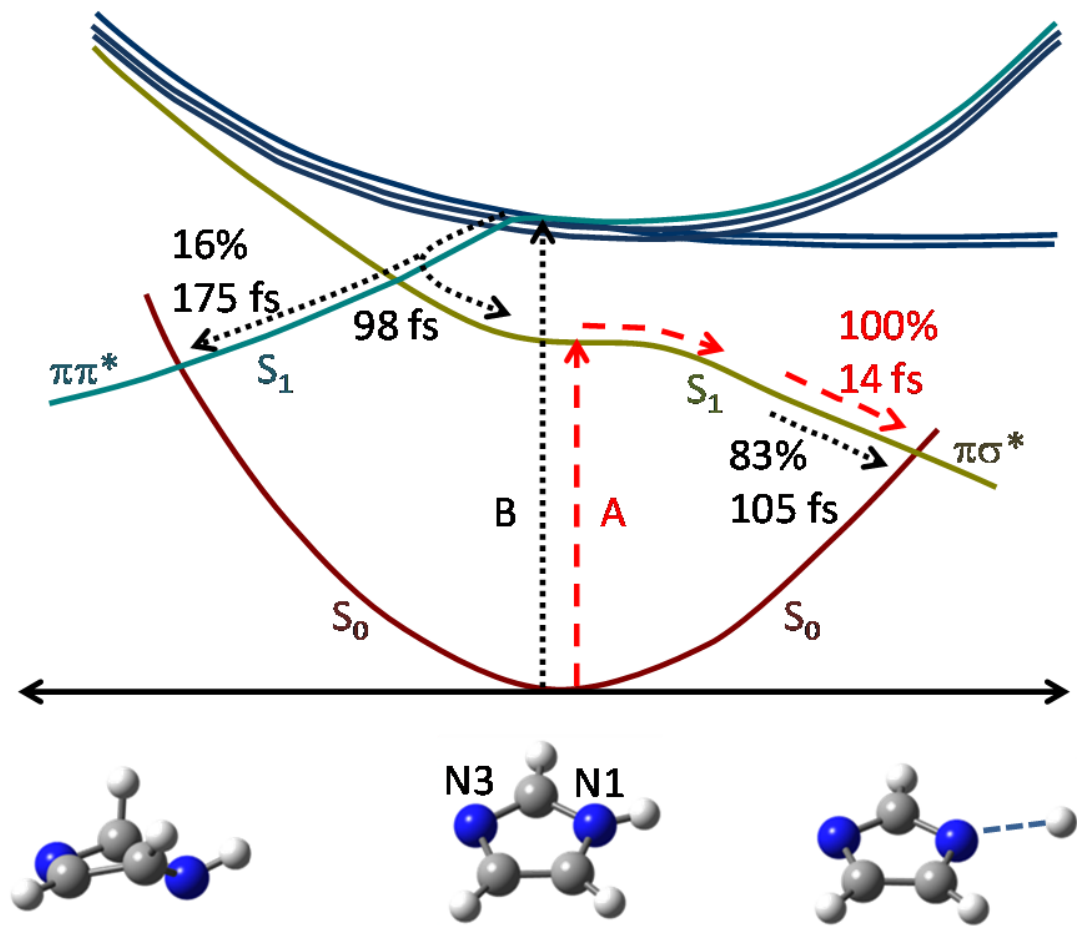
Wigner Distribution



Spectrum



IMIDAZOLE: DYNAMICS

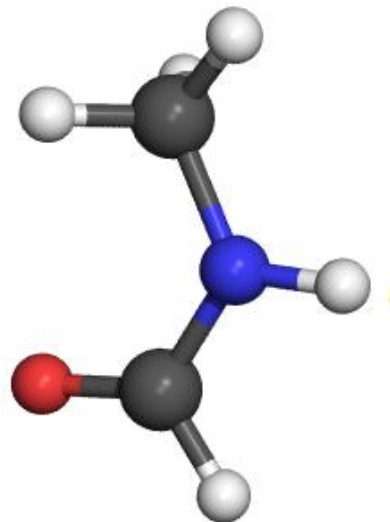


Window A
 pump: 240 nm
Window B
 pump: 201 nm

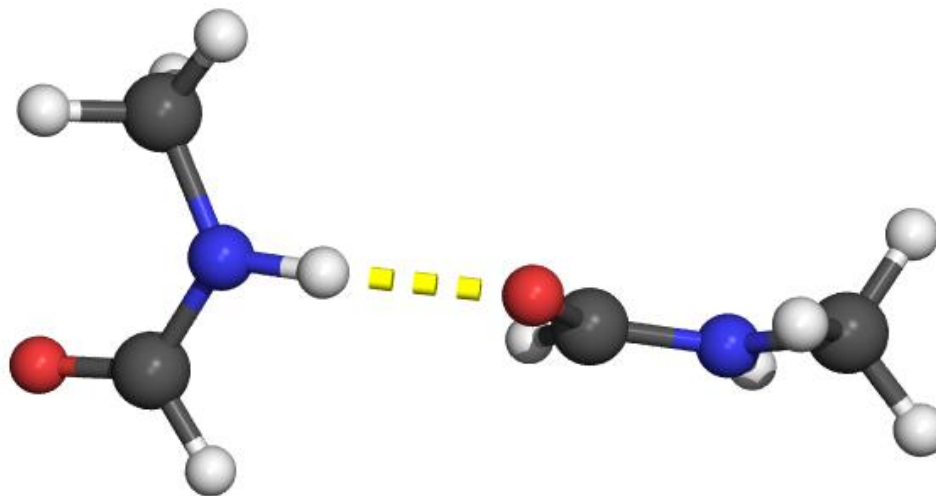
TDDFT (B3LYP/TZVP+mod)

The mechanism depends on the initial excitation

N-METHYLFORMAMIDE PHOTOCHEMISTRY



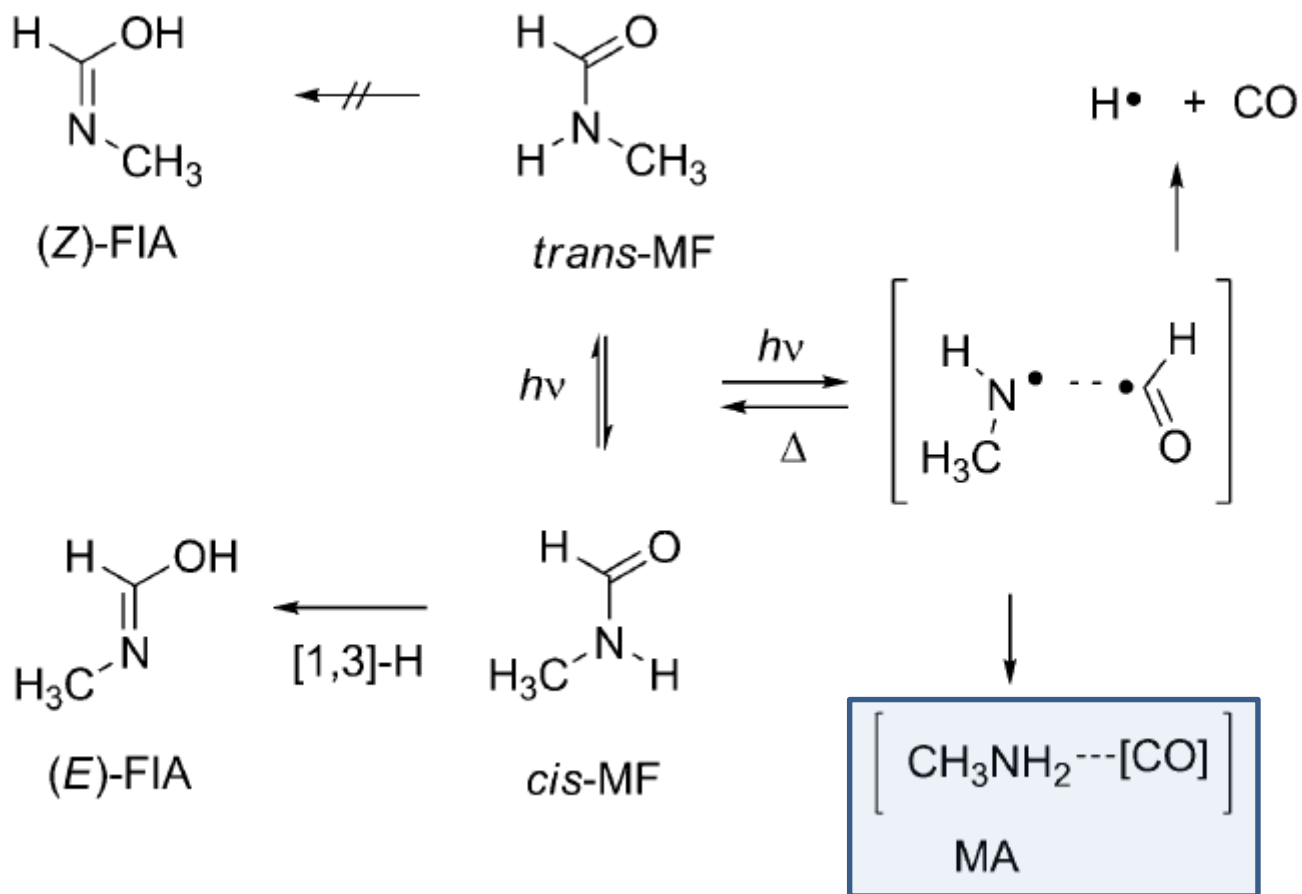
Monomer



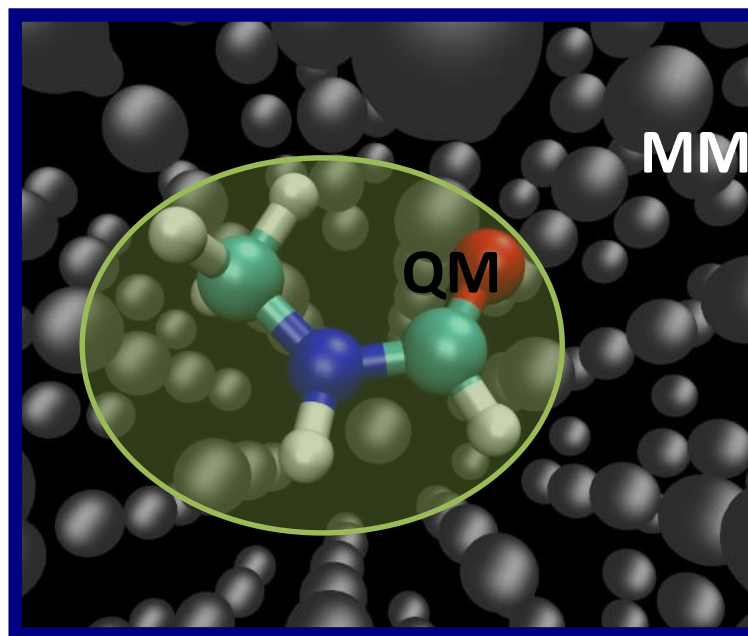
Dimers

N-METHYLFORMAMIDE: MONOMER

Argon matrix



N-METHYLFORMAMIDE: QM/MM SIMULATIONS



Gas phase dynamics:

SA-3-CASSCF(10,8)/6-31G(d,p)

Matrix conditions:

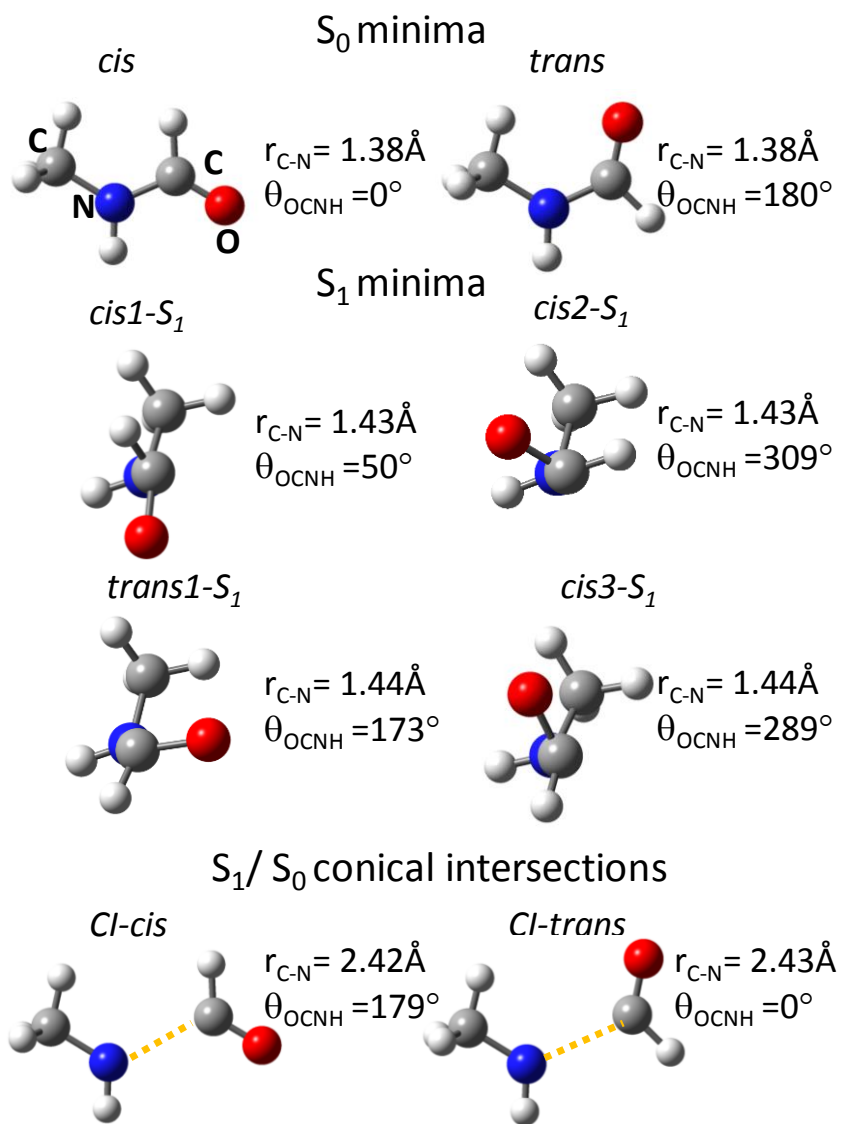
QM (NMF): SA-3-CASSCF(10,8)/6-31G(d,p)

MM (Argon matrix) : OPLSAA force field

- 3 states
- Maximum Simulation time: 2000 fs
- Total of 400 trajectories

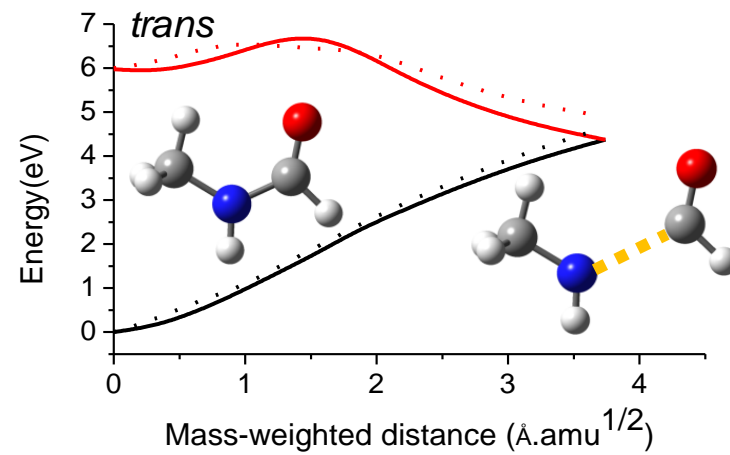
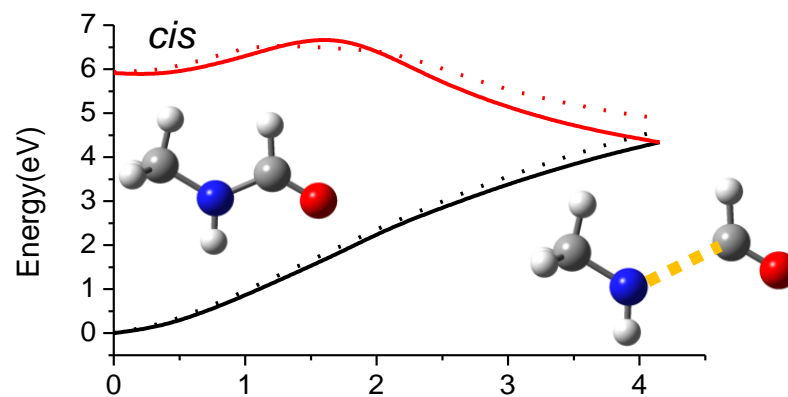
Active Space: $n(O)$, σ_{CN} , σ_{CN}^* , σ_{CH} , σ_{CH}^* , 2π , π^*

N-METHYLFORMAMIDE: CONICAL INTERSECTIONS



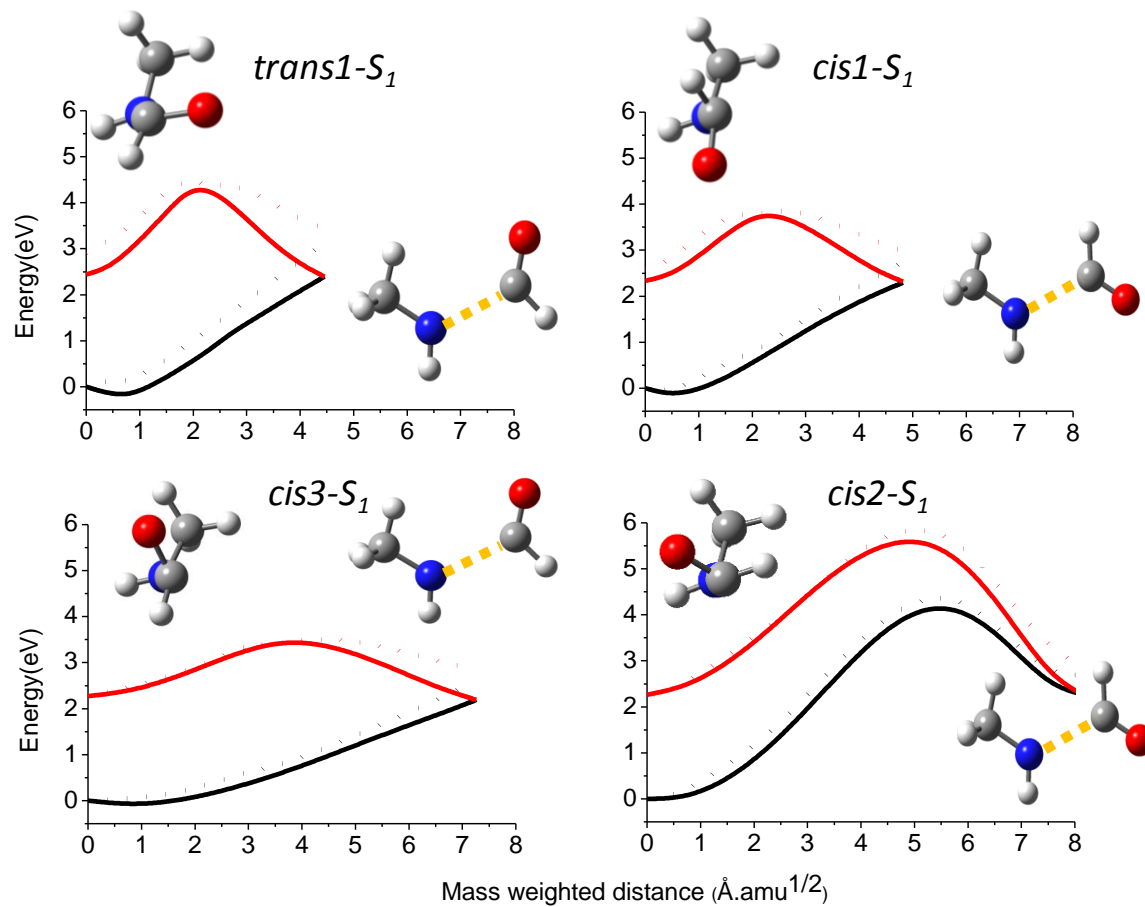
Structures optimized at SA-3-CASSCF(10,8)/6-31G(d) level of theory

N-METHYLFORMAMIDE:



dots: MS-CASPT2
line: CASSCF

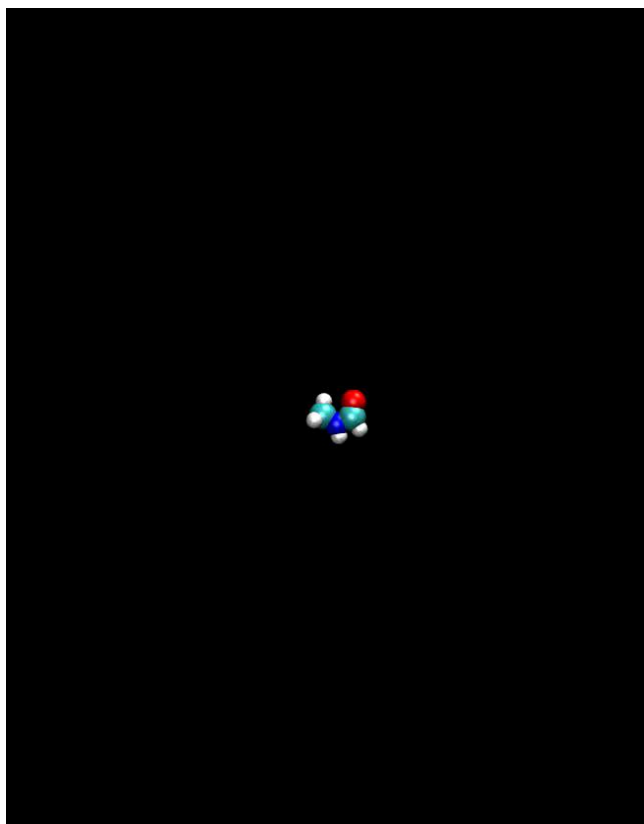
N-METHYLFORMAMIDE:



dots: MS-CASPT2
line: CASSCF

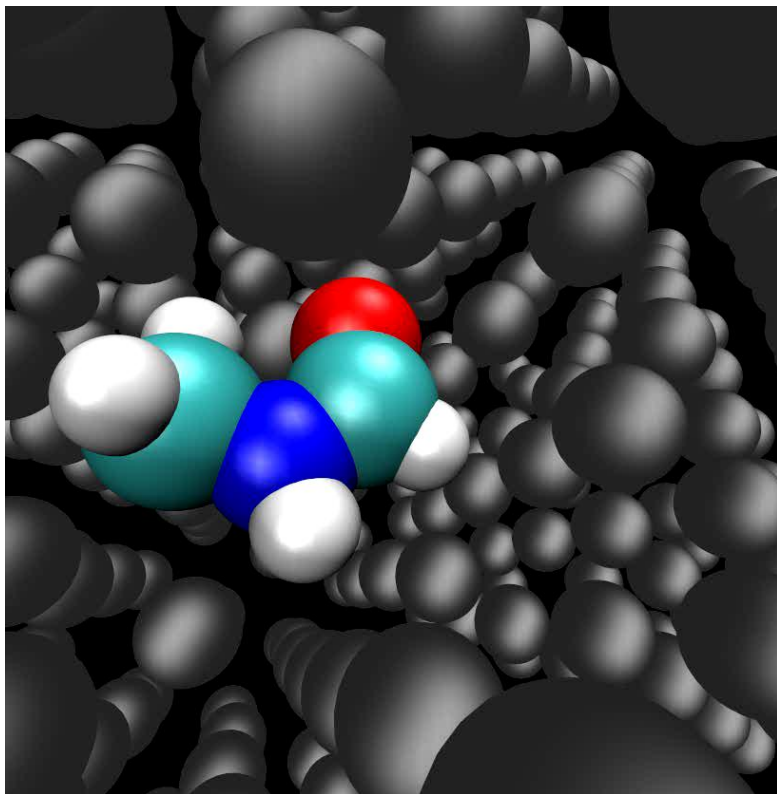
N-METHYLFORMAMIDE: GAS PHASE

First step in the photo-mechanism: C-N dissociation



SA-3-CASSCF(10,8)/6-31G(d,p)

MATRIX EFFECTS: QM/MM

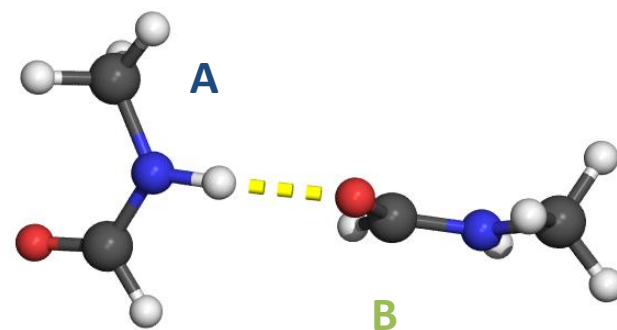
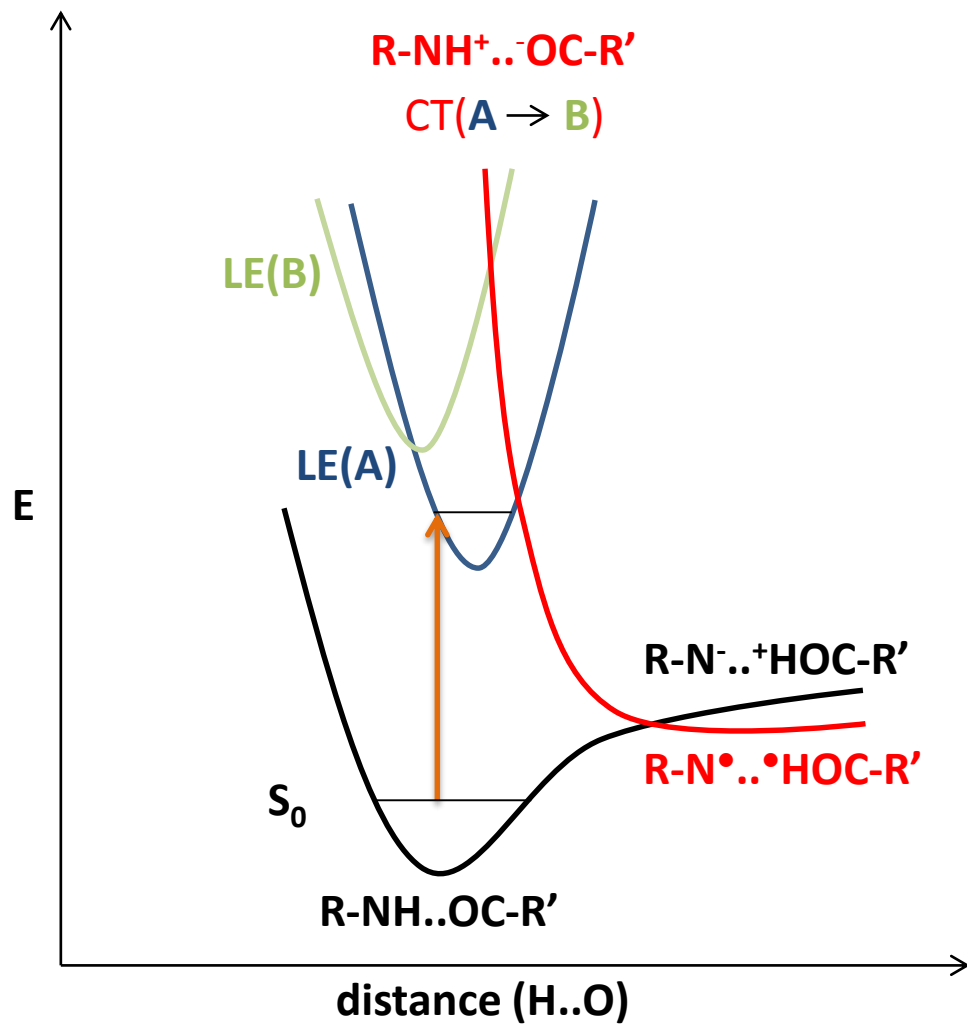


QM (NMF): SA-3-CASSCF(10,8)/6-31G(d,p)
MM (Argon matrix) : OPLSAA force field

Photo-mechanism

- 1.) C-N photo -dissociation
- 2.) Hydrogen transfer
- 3.) $\text{CH}_3\text{NH}_2 \dots \text{CO}$ complex

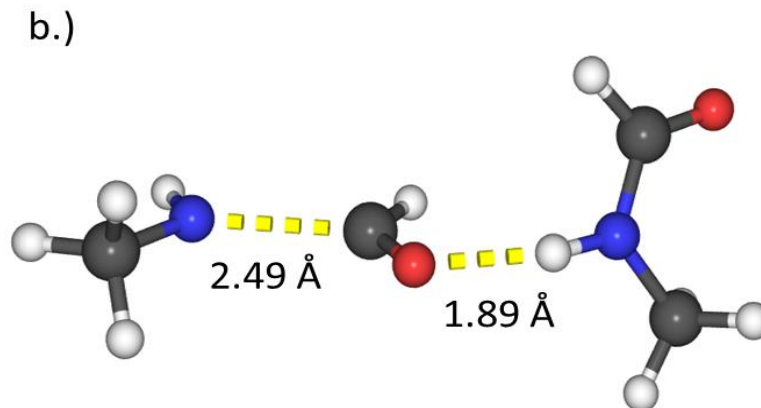
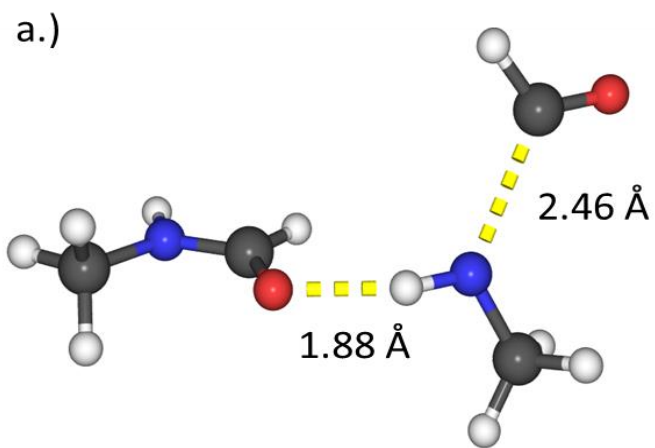
PROTON TRANSFER MECHANISM



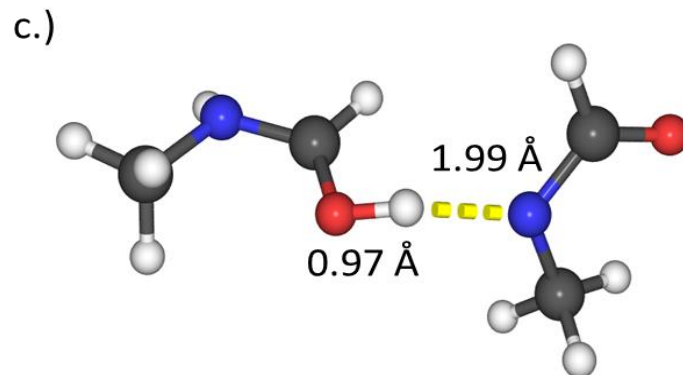
This mechanism protects biomolecules from UV-irradiation

S_0/S_1 CROSSING GEOMETRIES

C-N dissociation

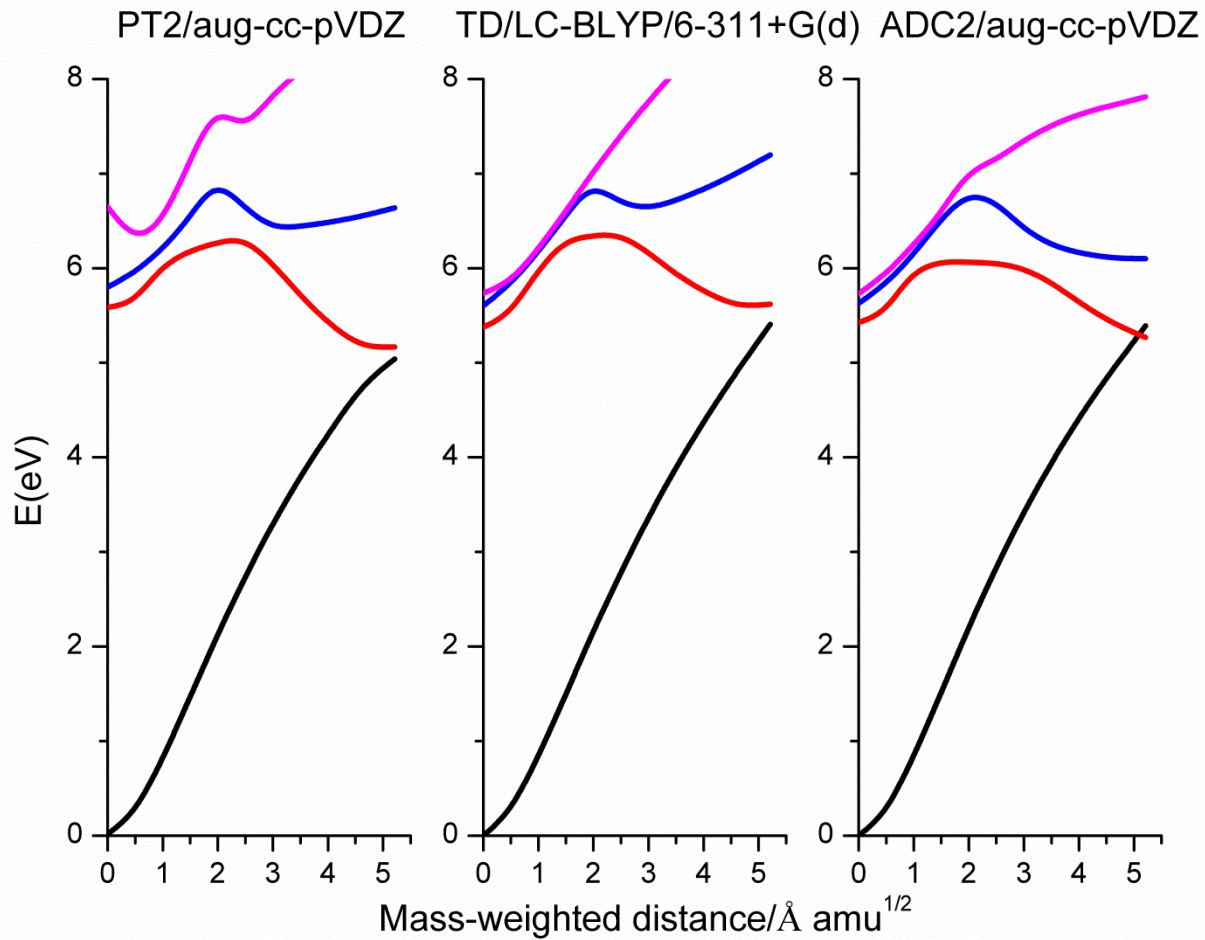


Proton Transfer

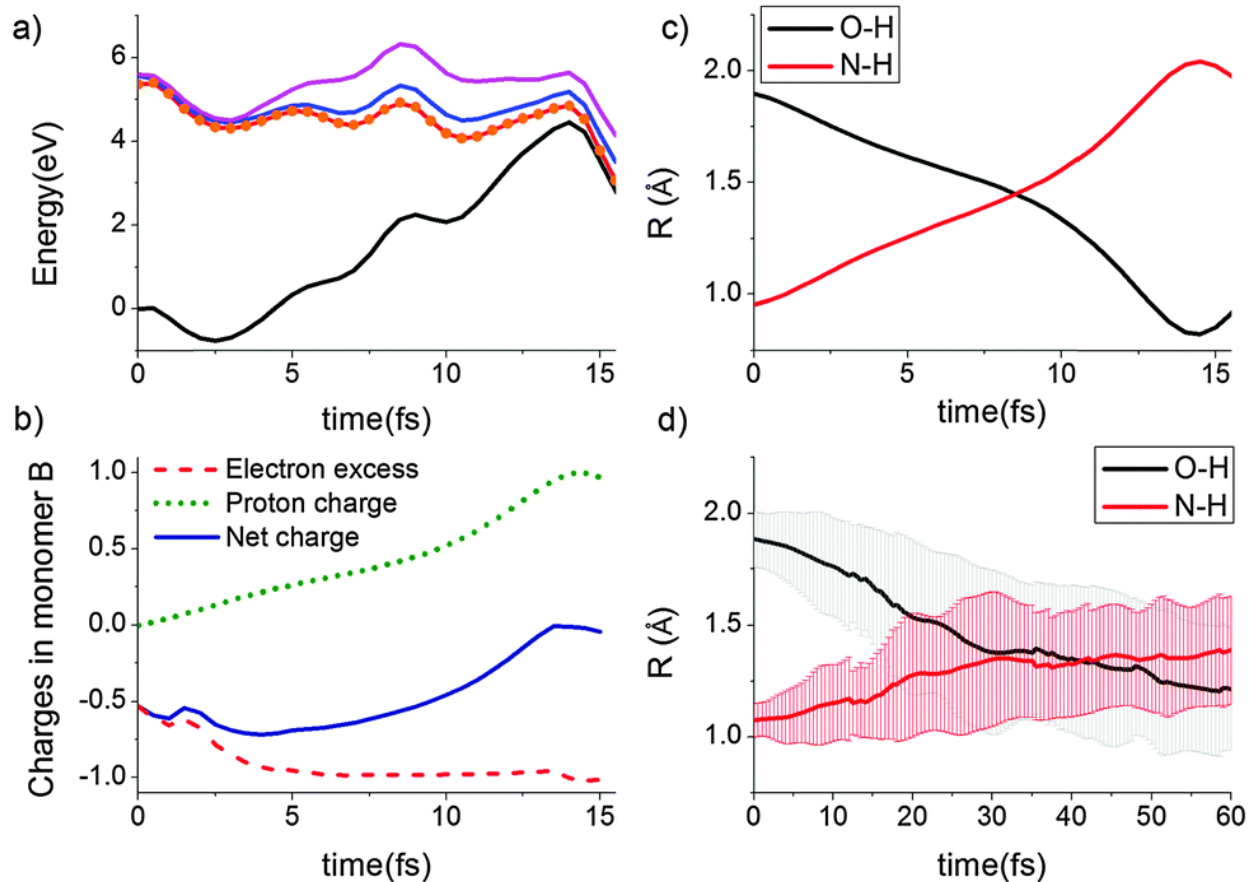


TD/LC-BLYP($\mu=0.2$)/6-311+G(d)

C-N DISSOCIATION IN THE DIMER



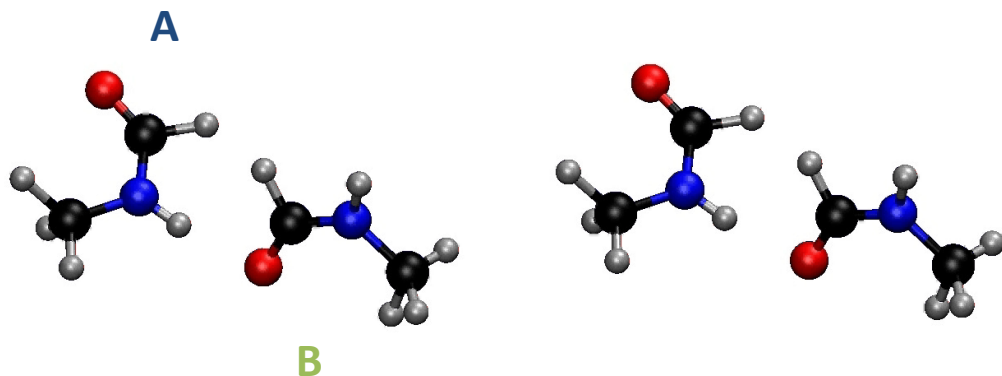
A TYPICAL TRAYECTORY



72 % of the trajectories deactivated through the ESTP mechanism

N-METHYLFORMAMIDE: THE DIMER

Experiments: The dimer does not dissociate under same irradiation conditions



Proton transfer mechanism protects the dimer from photo-dissociation

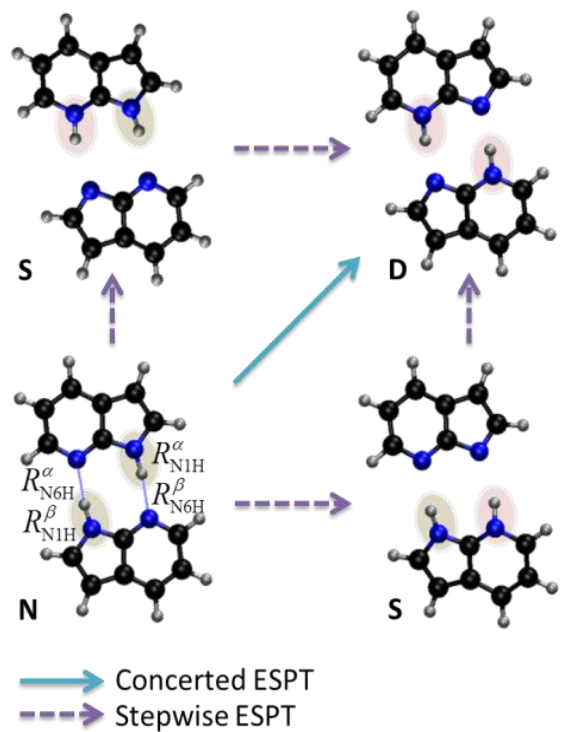
Proton-transfer is faster than C-N dissociation (50 fs vs 400 fs).

Orange → Green

TDDFT/LC-BLYP($\mu=0.2$)/6-311+G(d)

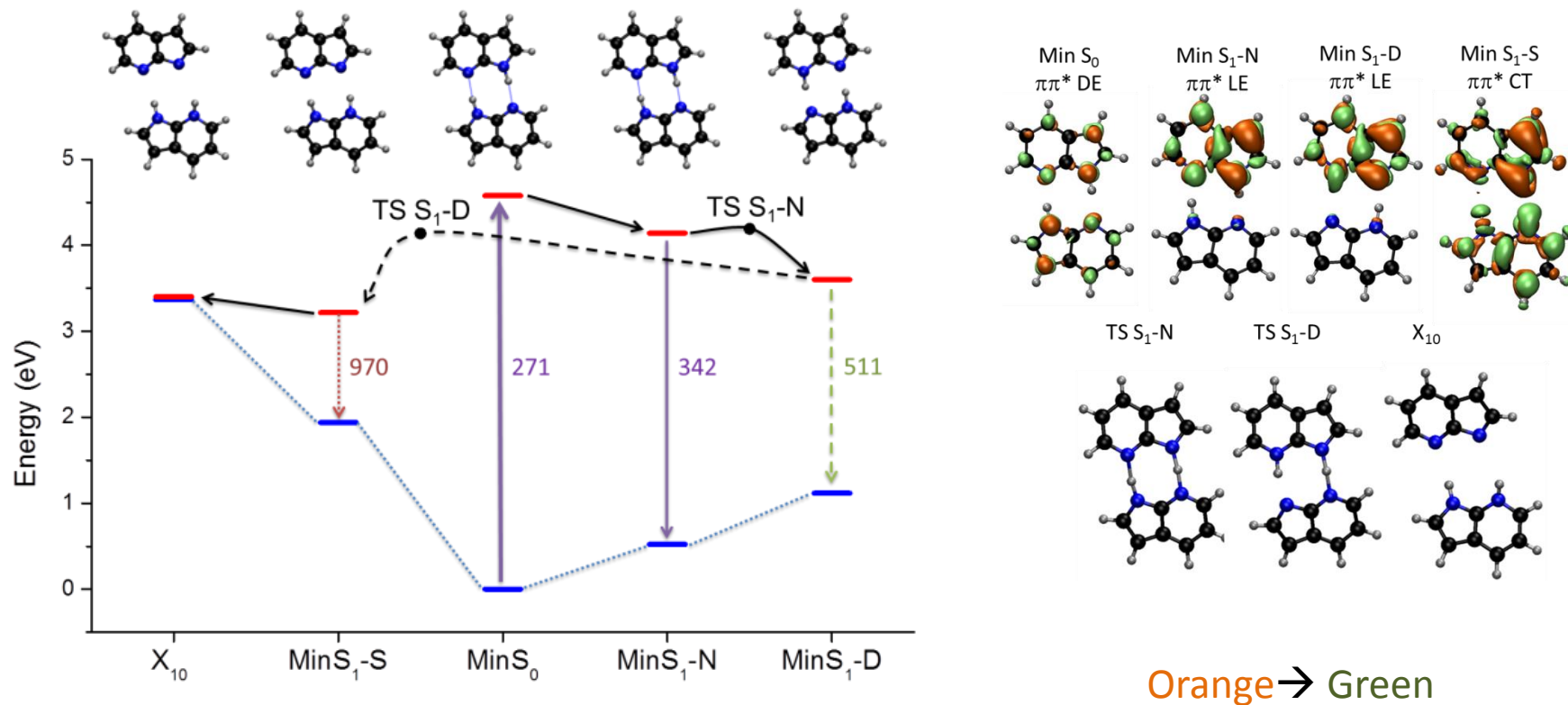
DOUBLE PROTON TRANSFER IN ... DIMERS

7-Azaindole (7AI) dimer: Concerted vs Stepwise ESPT



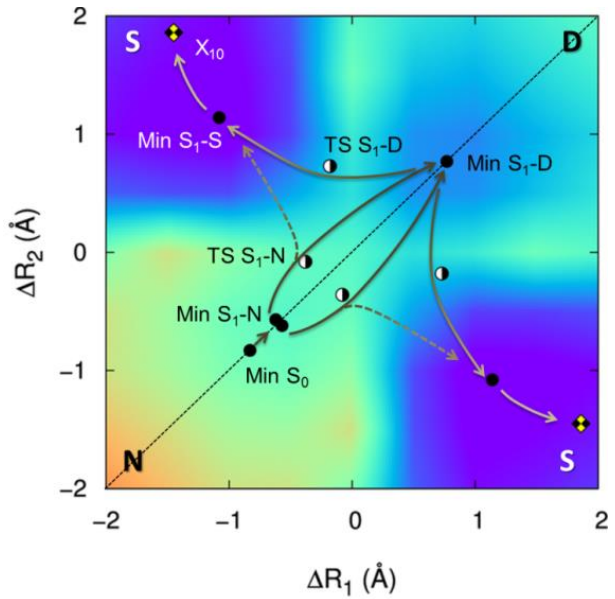
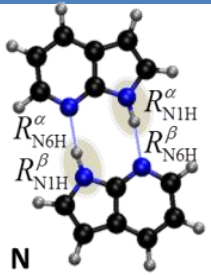
CONCERTED MECHANISM

RI-CC2/TZVP



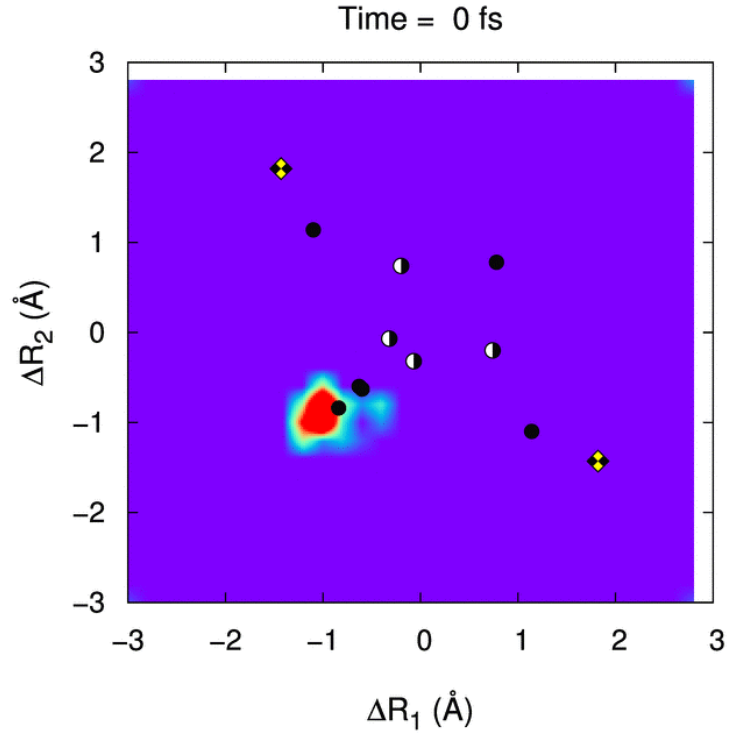
Most electronic methods fail to provide a balanced description of the different regions of the excited state.

DOUBLE PROTON TRANSFER IN ... DIMERS



RI-CC2/TZVP

Low energy window (4.1 ± 0.1 eV)



ADC(2)/SV(P)

DPT: 80%, SPT: 15%, MPT: 5%

CONCLUSIONS

- Surface Hopping is very useful to explore photochemical mechanisms.

- Be careful before starting running long NAD dynamics simulations. Make sure that the level of theory is appropriate!



ACKNOWLEDGMENTS

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Newton-X team

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Susanne Ulrich (University of Georgia)

Nawee Kugnwan (University of Chiang Mai)

Michael Dommett (Queen Mary University of London)



Queen Mary
University of London