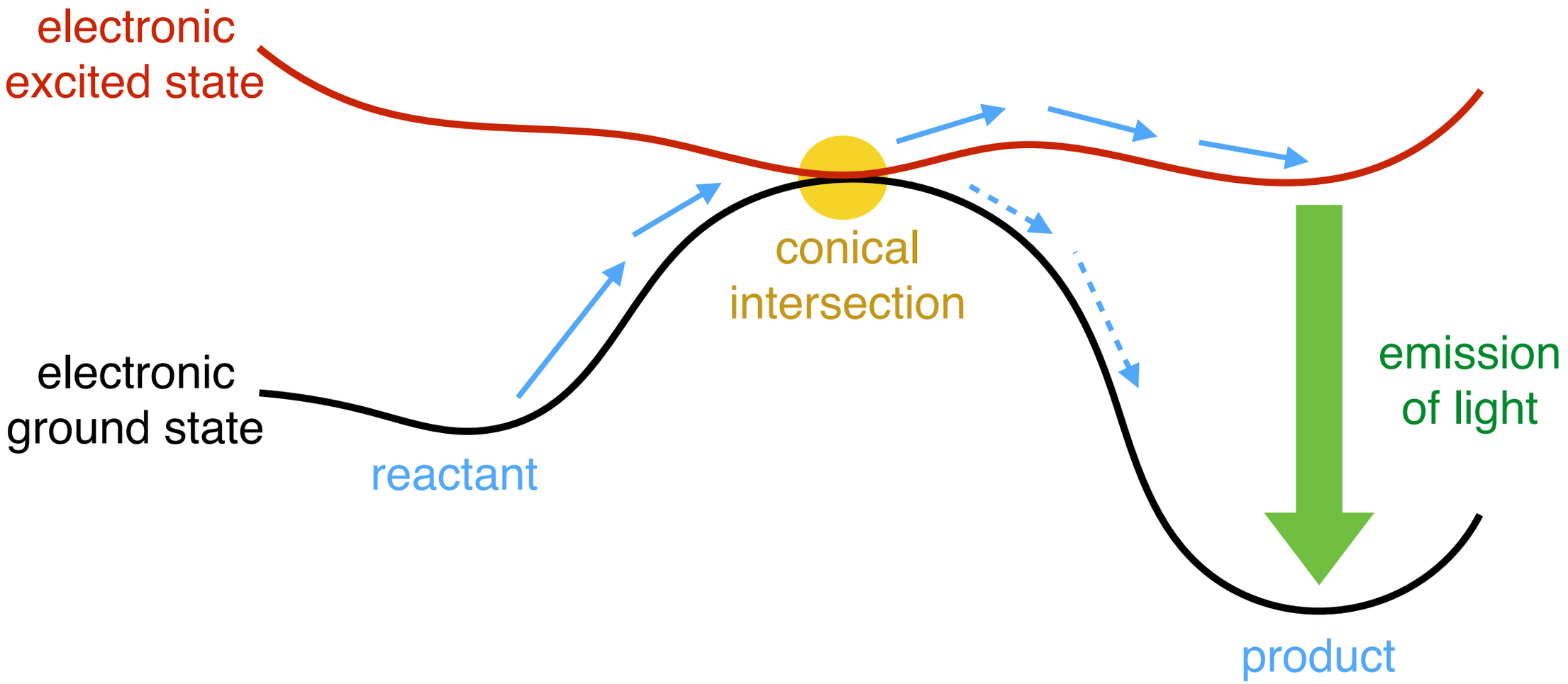
Insights into chemiluminescence from ab initio molecular dynamics simulations and machine learning analysis

Morgane VACHER

What is chemiluminescence?

Definition: Emission of light (luminescence) as the result of a chemical reaction



Chemiexcitation

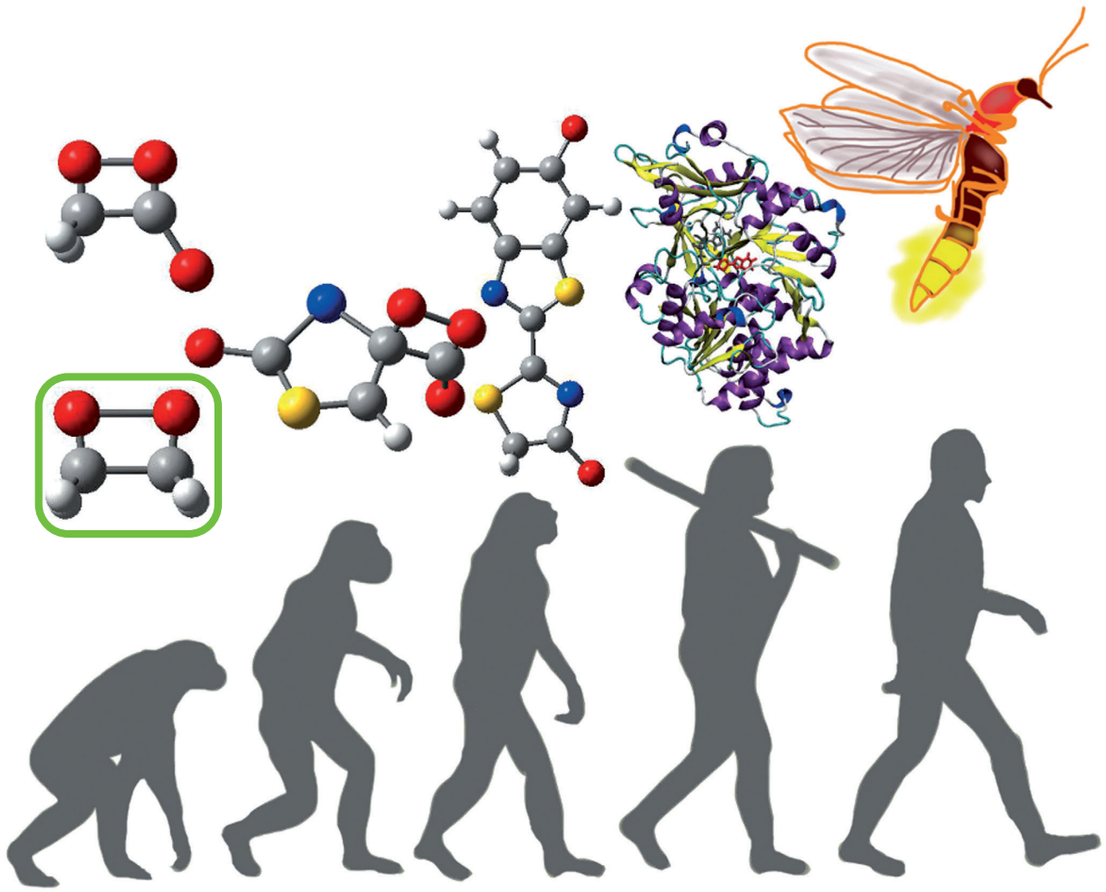
Population of an excited state as the result of a chemical reaction

What is chemiluminescence?

➜ Communication to attract partners, hunting to lure preys, defence to avoid predators

➜ In vivo imaging in medicine, biosensing for environmental polluants, food industry, etc.

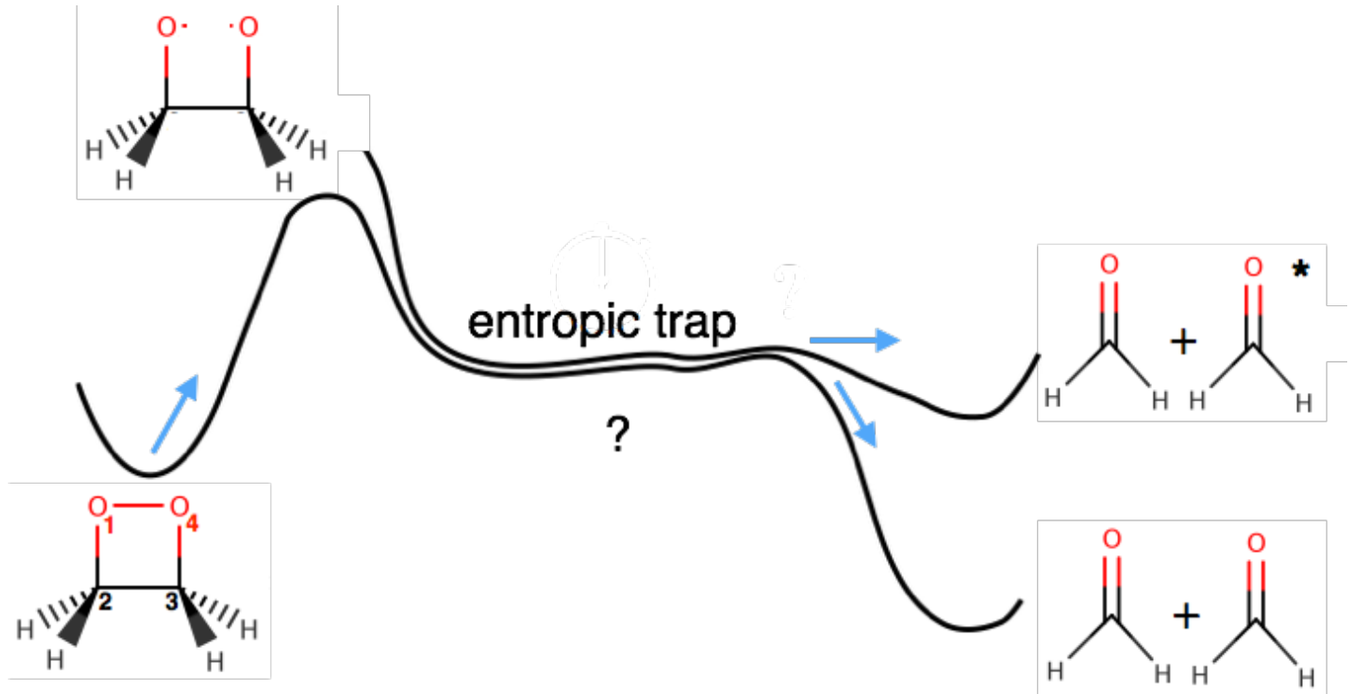
Structures of model compounds



Vacher et al, *Chem. Rev.* **118**, 6927-6974 (2018)

Chemiexcitation in 1,2-dioxetane

Decomposition into fundamental or excited formaldehyde molecules



➜ Yield of triplet excited states > yield of singlet excited sates

➜ Increase in the chemiexcitation yield upon methyl substitution

Vacher et al, *Chem. Rev.* **118**, 6927-6974 (2018)

Adam et al, *J. Am. Chem. Soc.*, **107**,410-416 (1985)

Theoretical approach

Ab initio molecular dynamics simulations

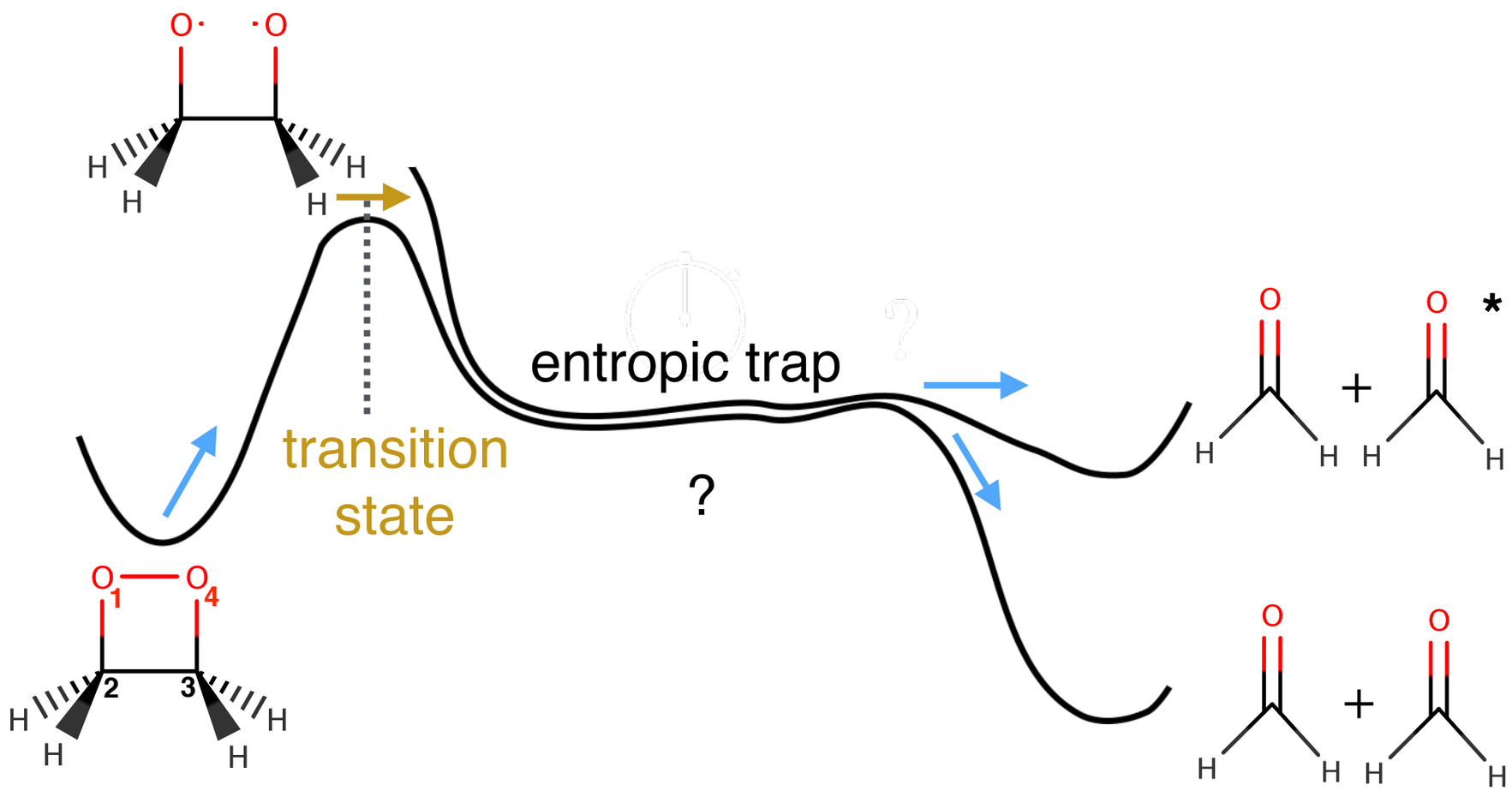
- Born-Oppenheimer dynamics
- non-adiabatic dynamics (surface hopping) including 4 singlet states

Electronic structure method

- CASSCF(12-in-10)
- ANO-RCC-VTZP basis set

Initial conditions

- Transition state geometry with 1kcal/mol kinetic energy in the forward direction
- 150 trajectories sampled from the Wigner distribution (Newton-X package)



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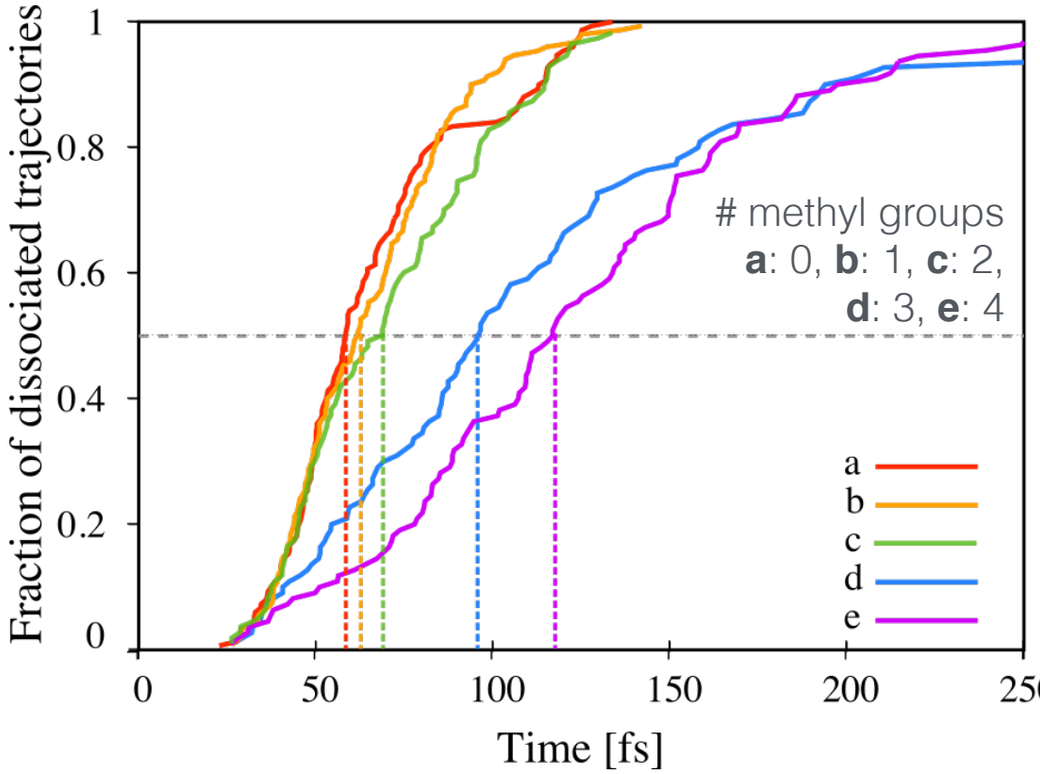
Effect of methyl substitution



➜ Significant increase in the dissociation time scale upon methyl-substitution

➜ Mostly due to a pure mass effect

Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

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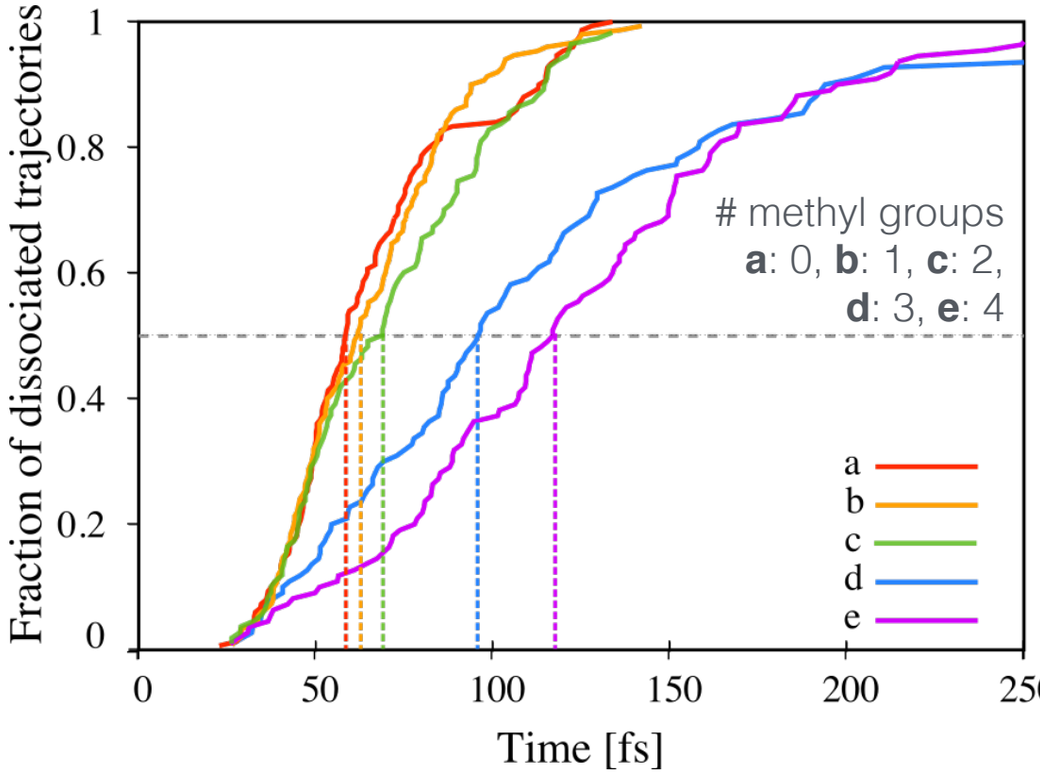
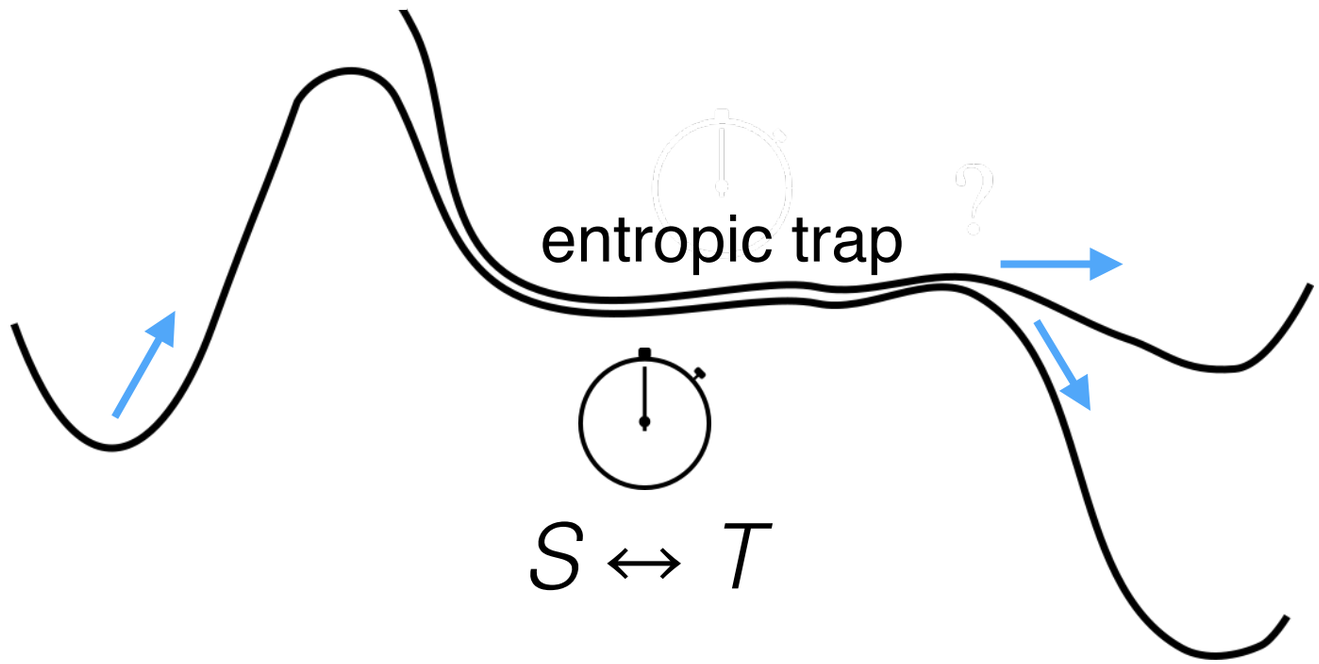
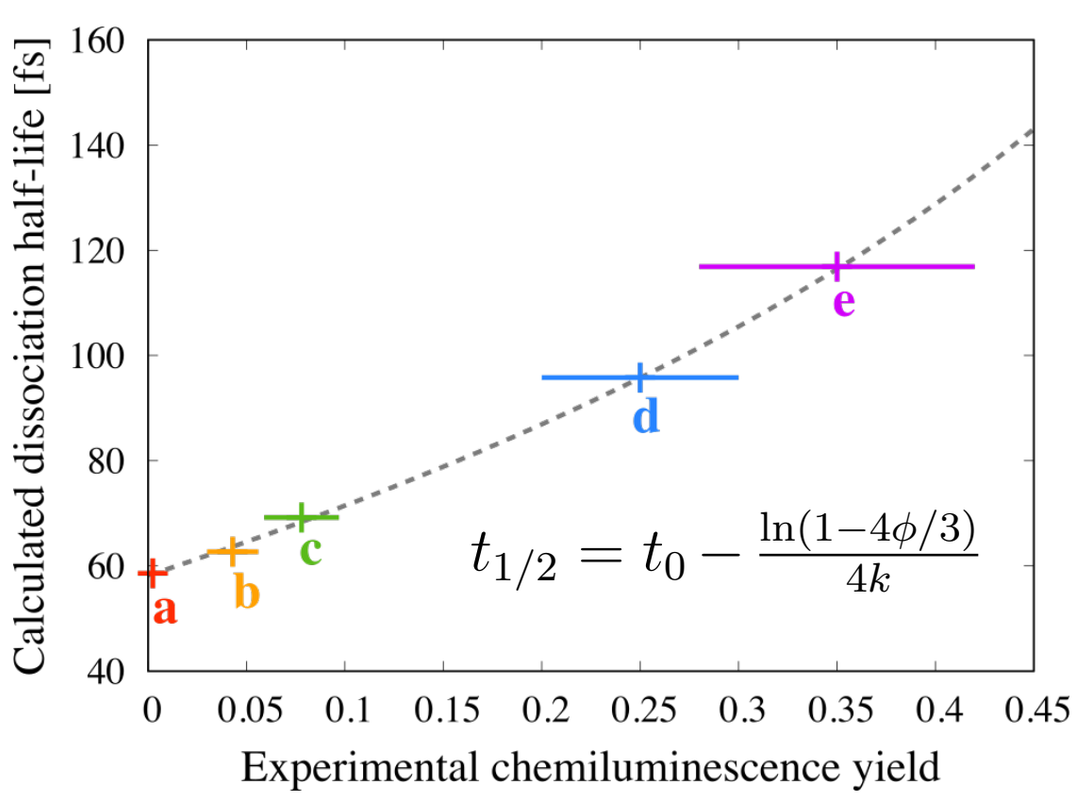




➜ Significant increase in the dissociation time scale upon methyl-substitution

➜ Mostly due to a pure mass effect

➜ The longer the system stays in the entropic trap, the more population is transferred from *S* to *T* and the higher the chemiexcitation yield is.



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machine learning

Can we use **machine learning** algorithms to help the interpretation of AIMD simulations and to extract physical insights?

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Florian Häse

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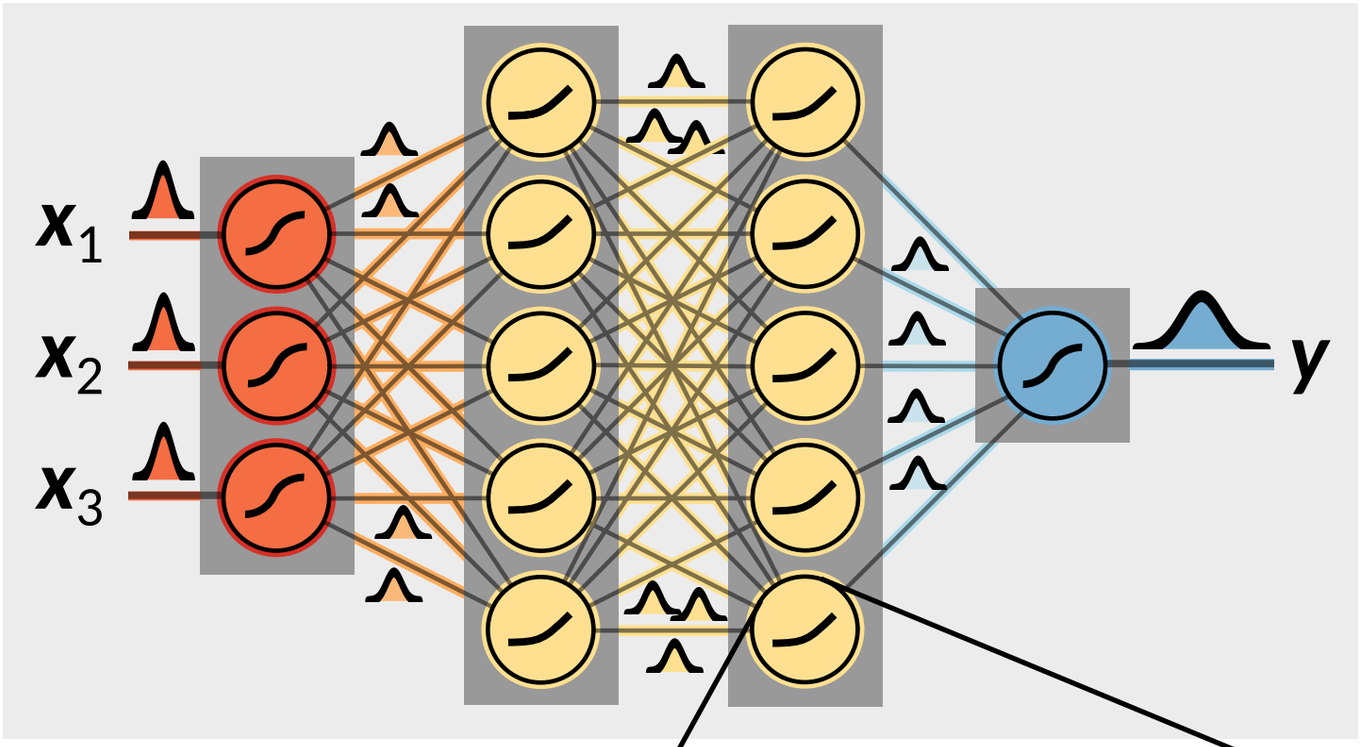
Prediction of dissociation time by ML

Häse, Fdez Galván, Aspuru-Guzik, Lindh and Vacher, *Chem. Science*, **10**, 2298-2307 (2019)

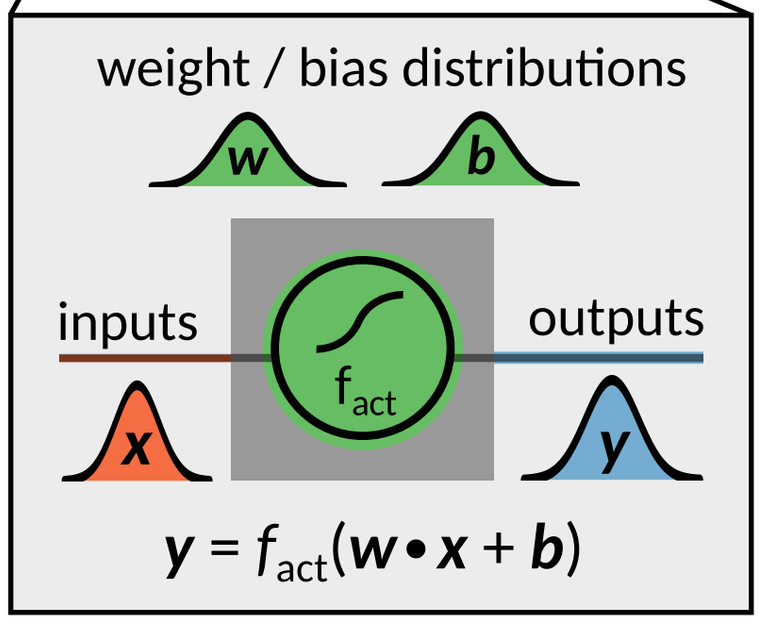
Prediction of dissociation time by ML

BNN1:
initial nuclear
geometry

BNN2:
+ nuclear
velocities



4 layers of 130 neurons
Activation function: Leaky ReLU



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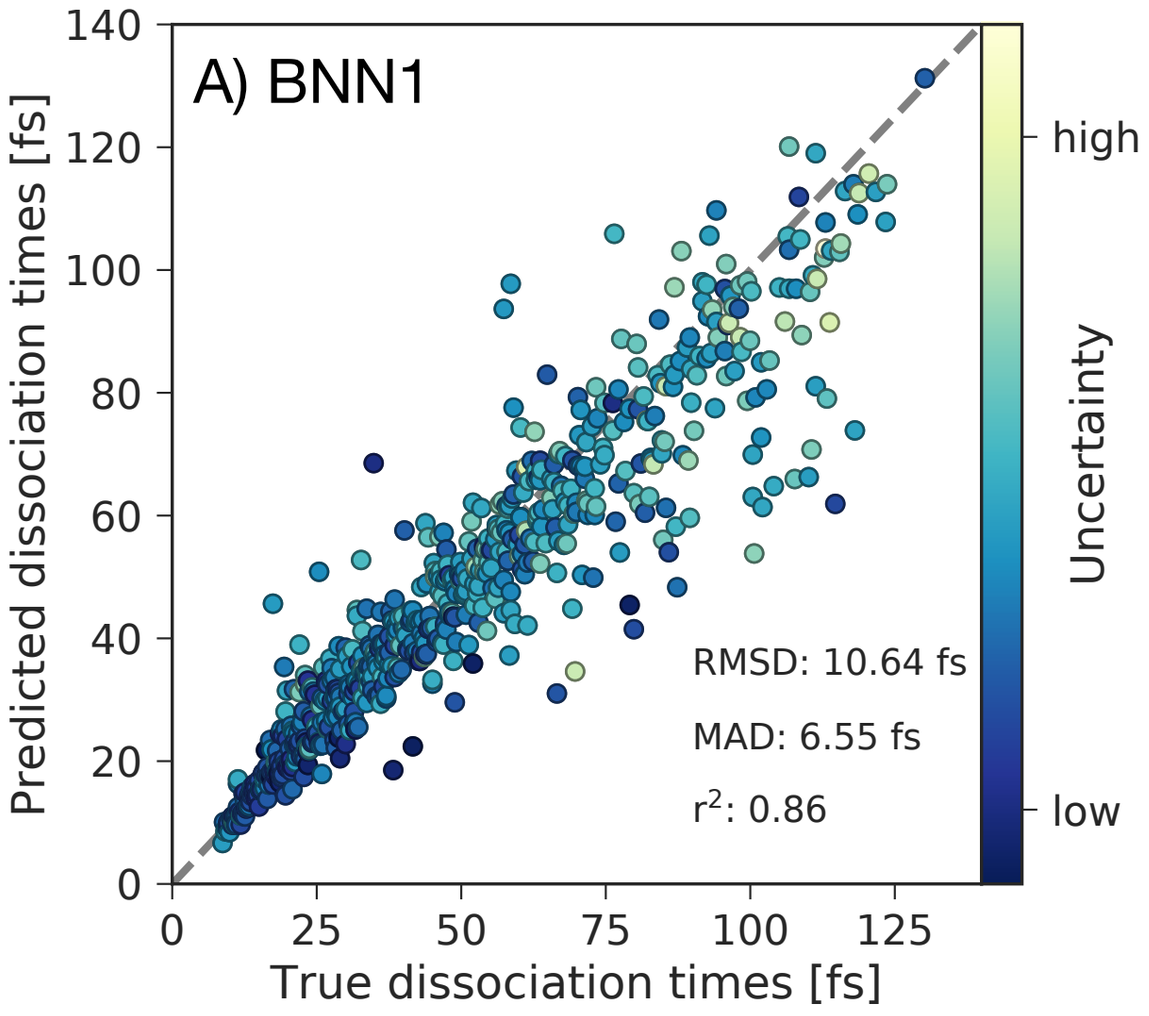
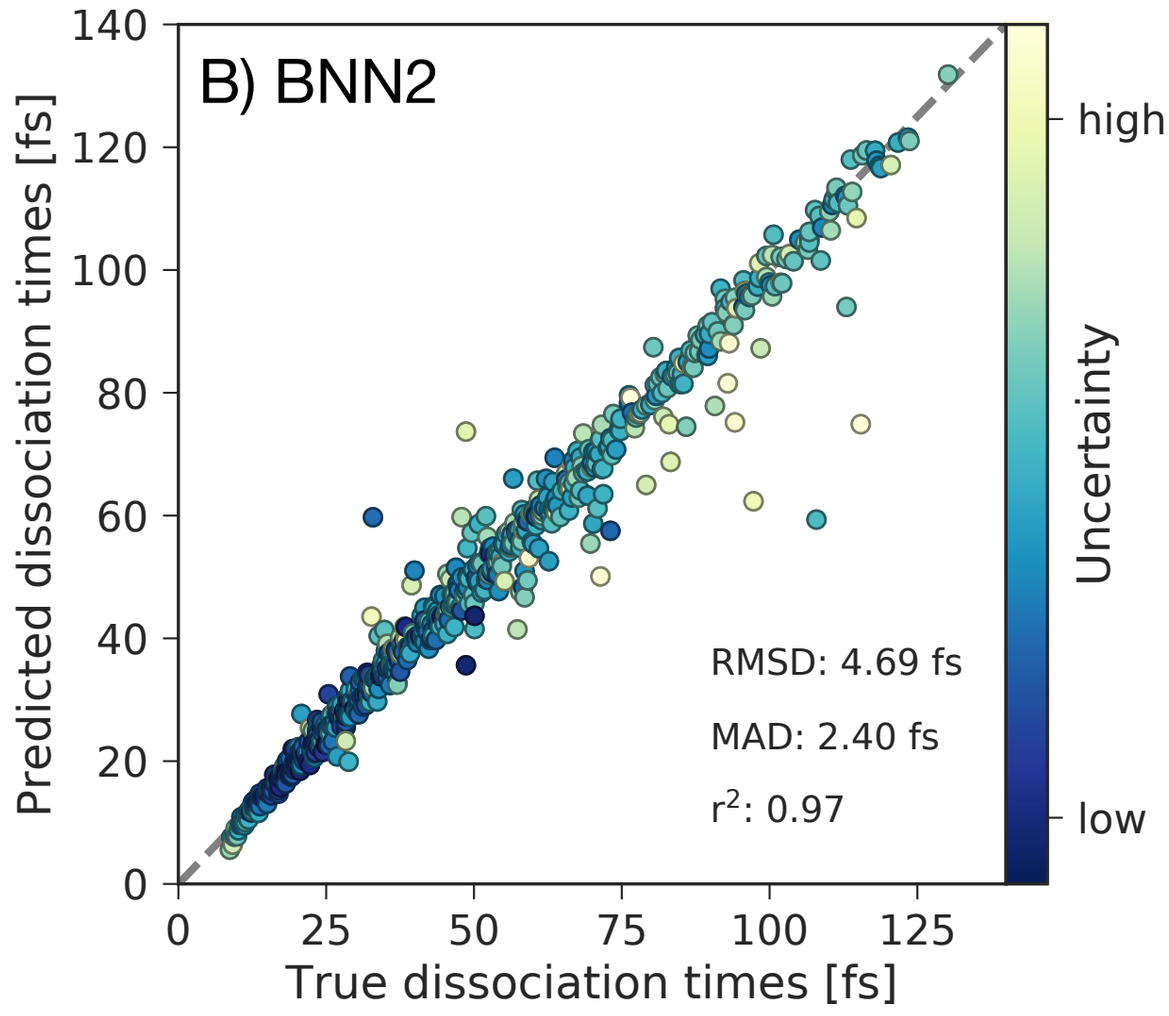
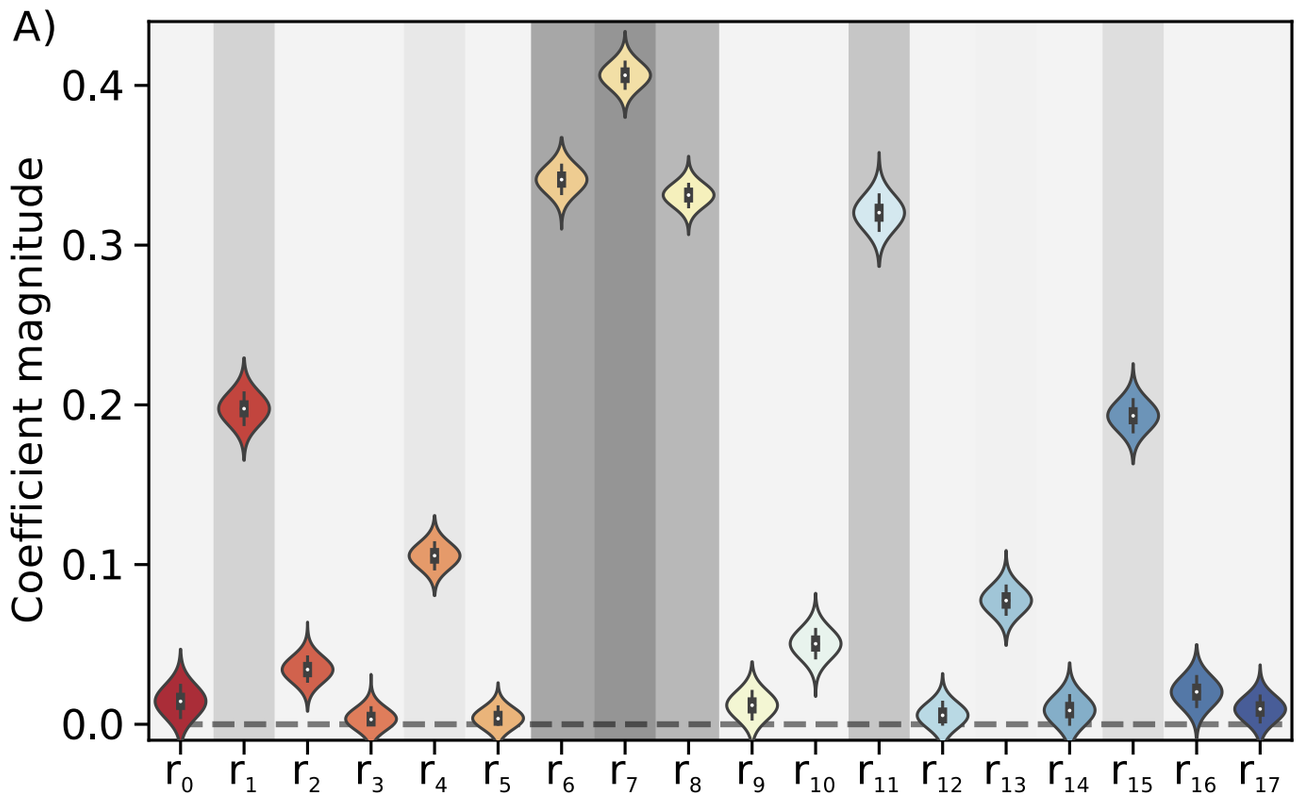


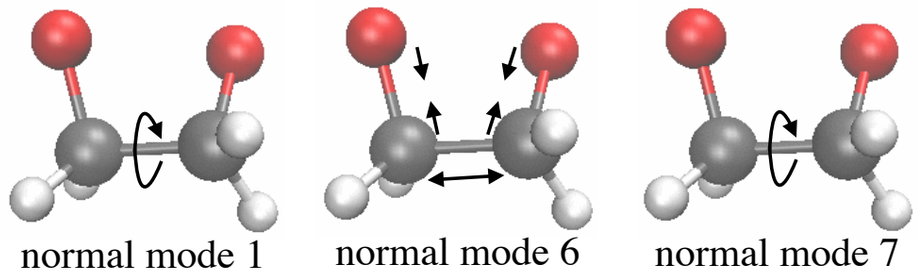


➜ Accurate predictions of the dissociation times of 1,2-dioxetane

Häse, Fdez Galván, Aspuru-Guzik, Lindh and Vacher, *Chem. Science*, **10**, 2298-2307 (2019)

Analysis of the trained BNN - part 1





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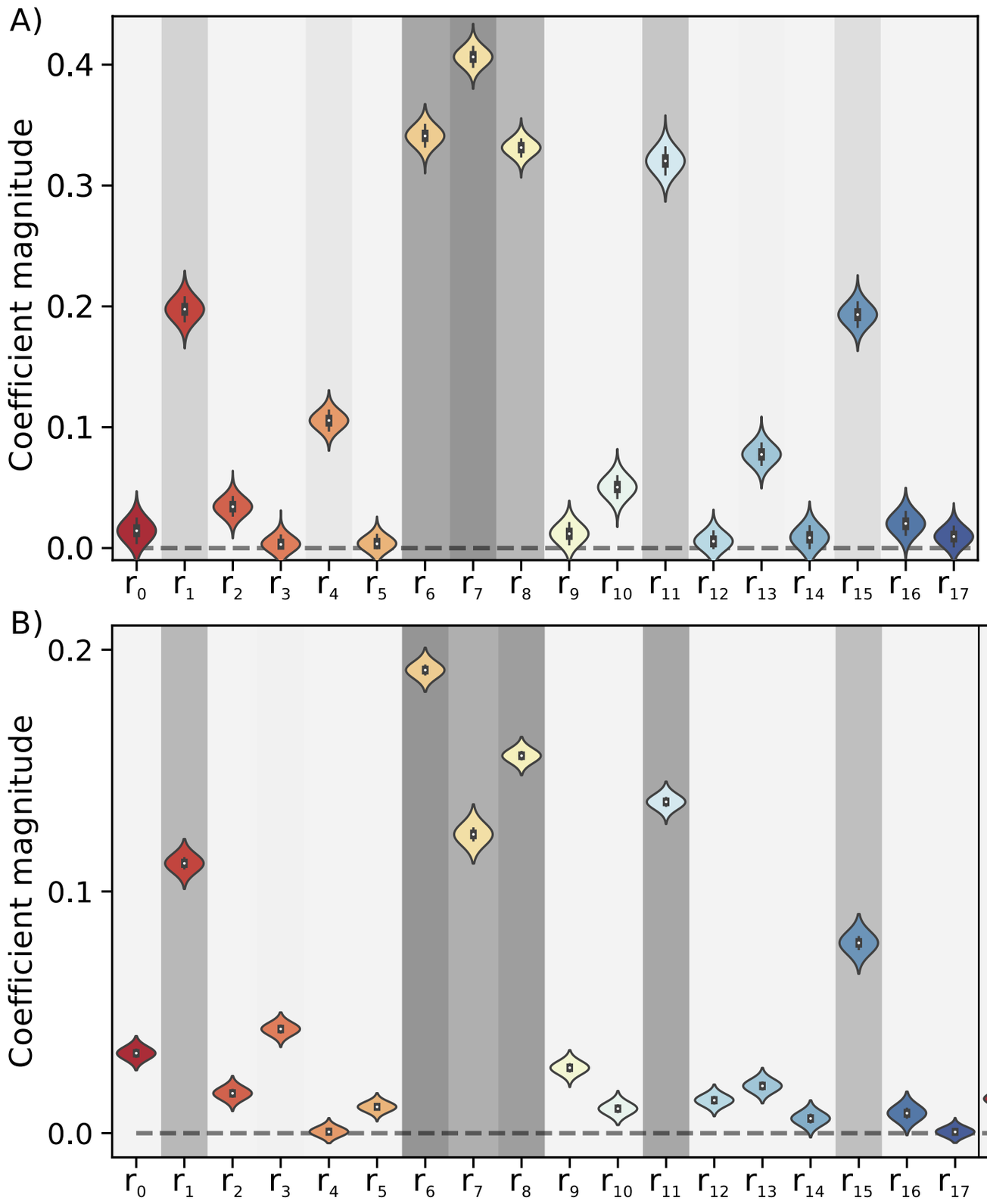

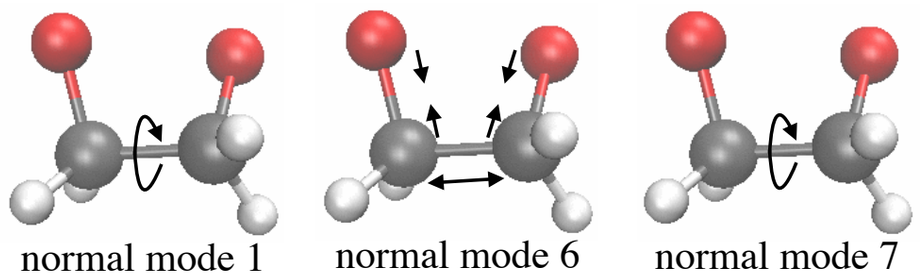

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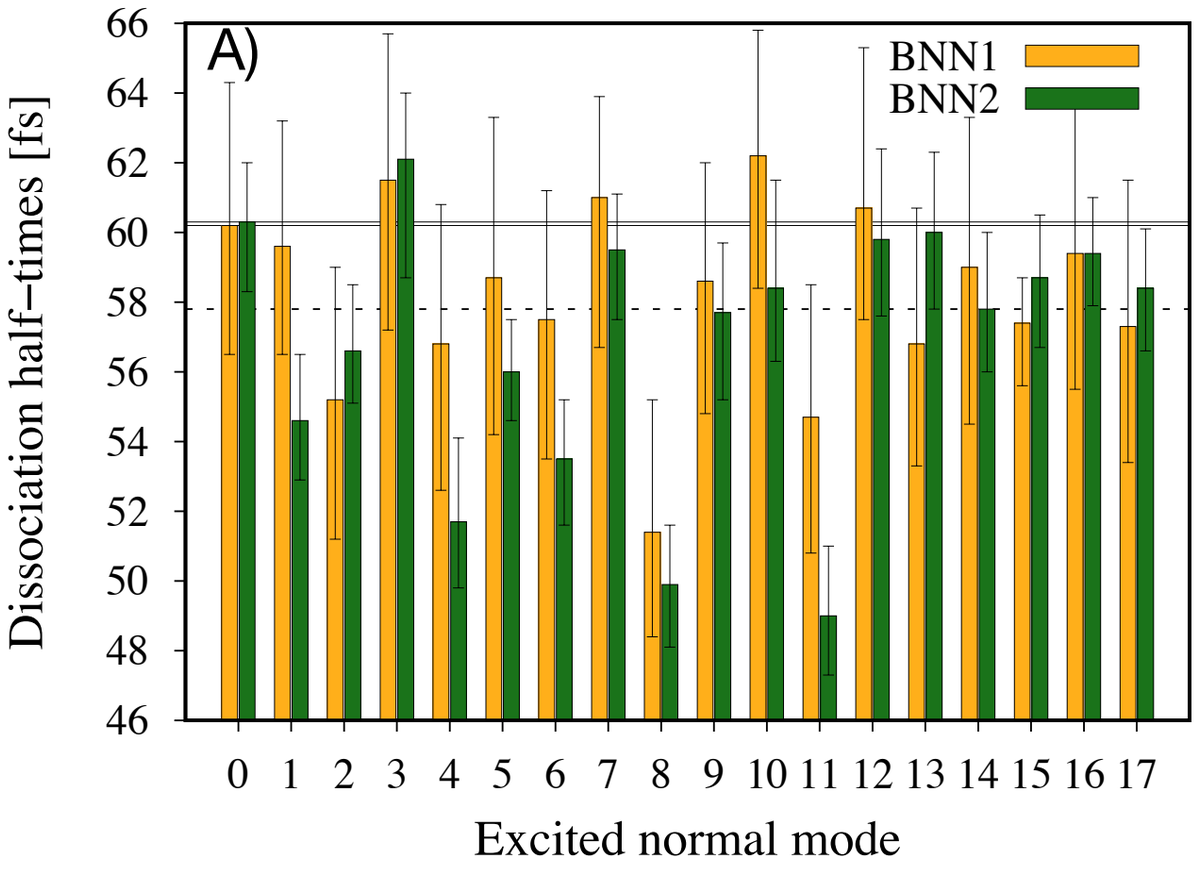
Analysis of the trained BNN - part 2

- Predictions of dissociation times for vibrational excited states



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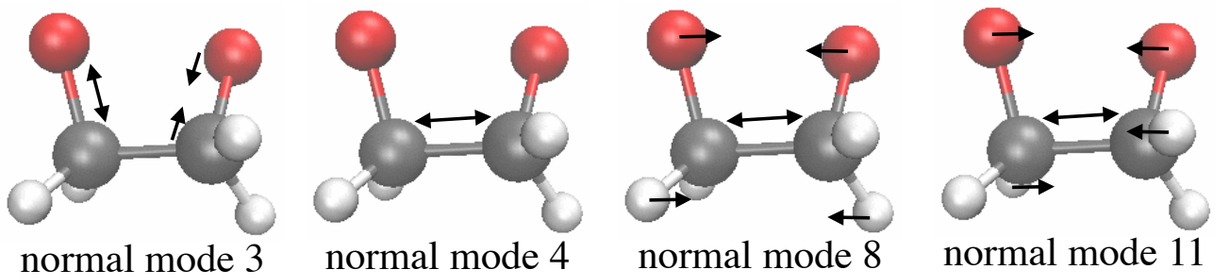

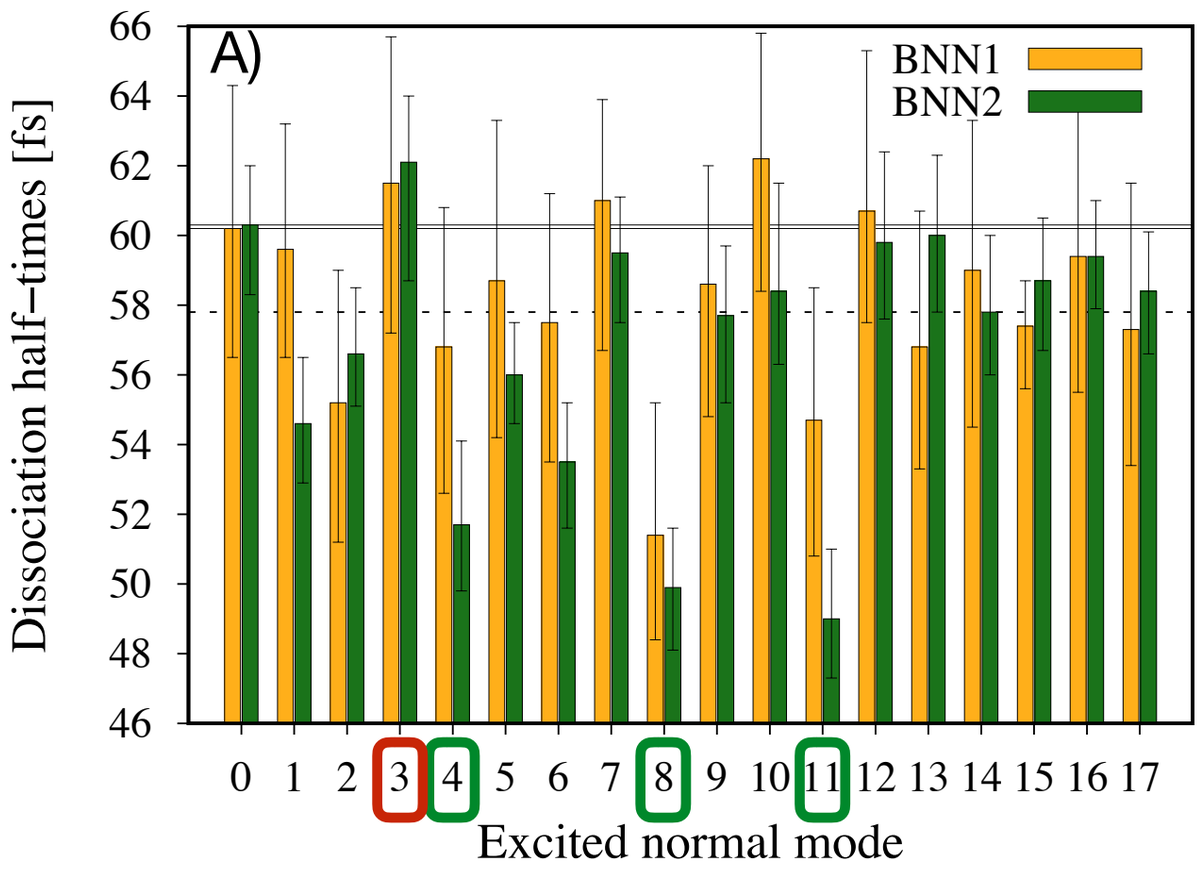

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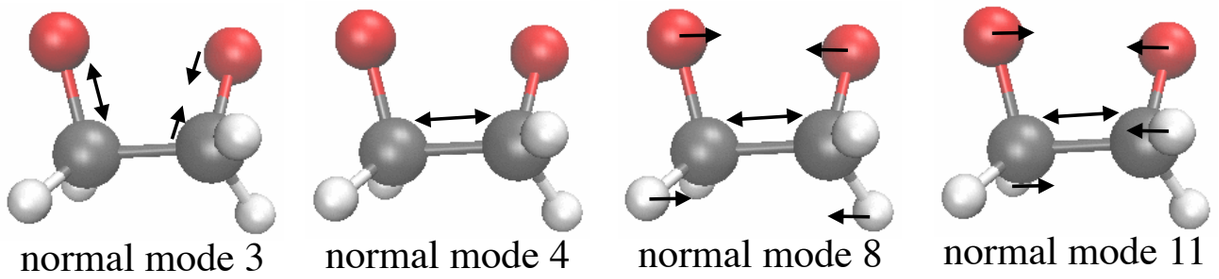

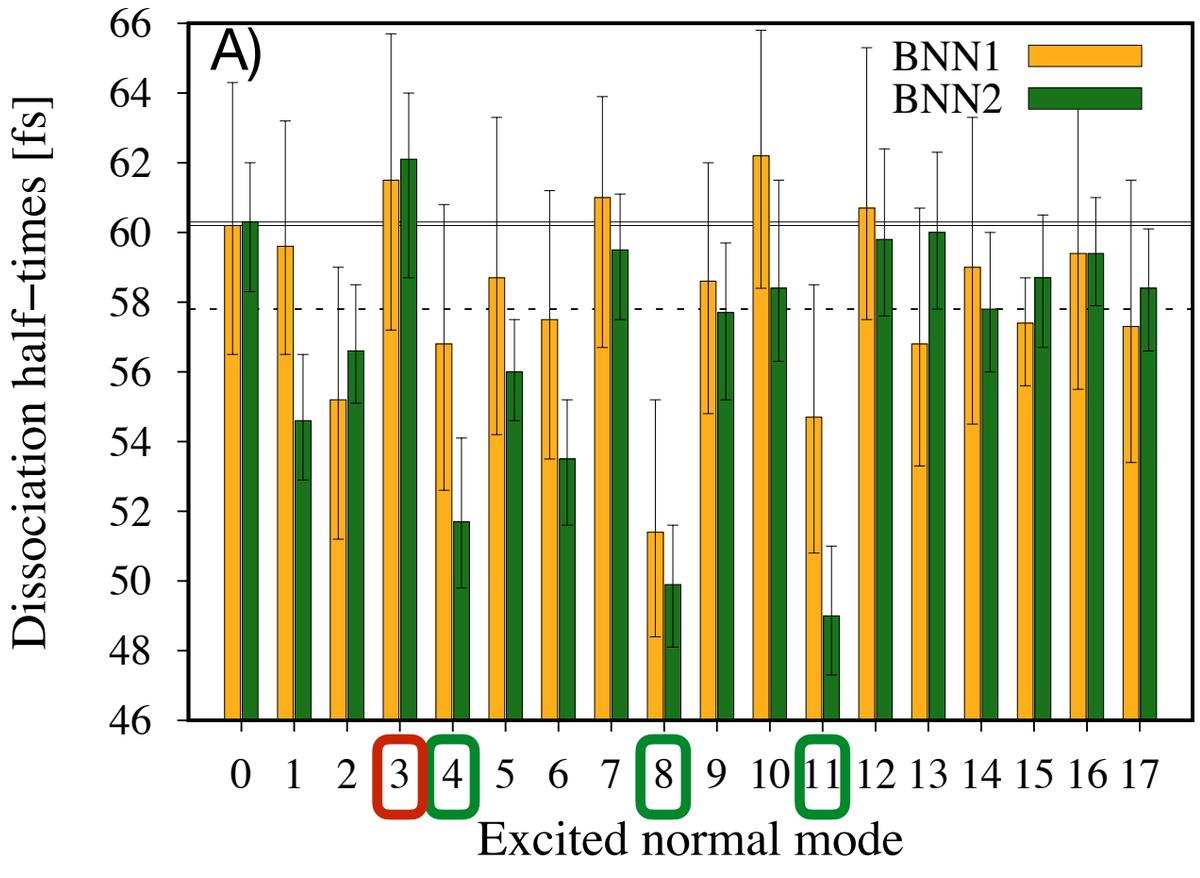

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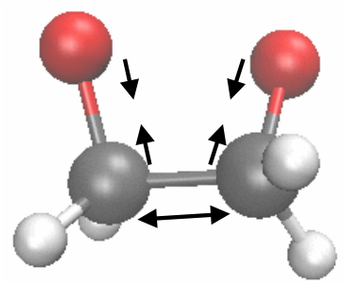
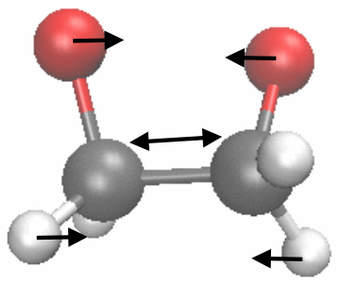
Interpretation of the trained BNN

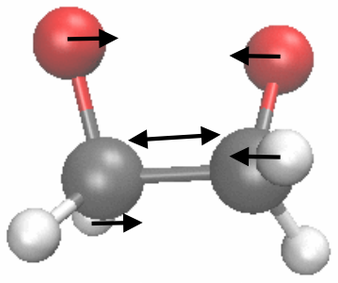
➜ Correlation between nuclear coordinates and dissociation times



normal mode 6



normal mode 8



normal mode 11

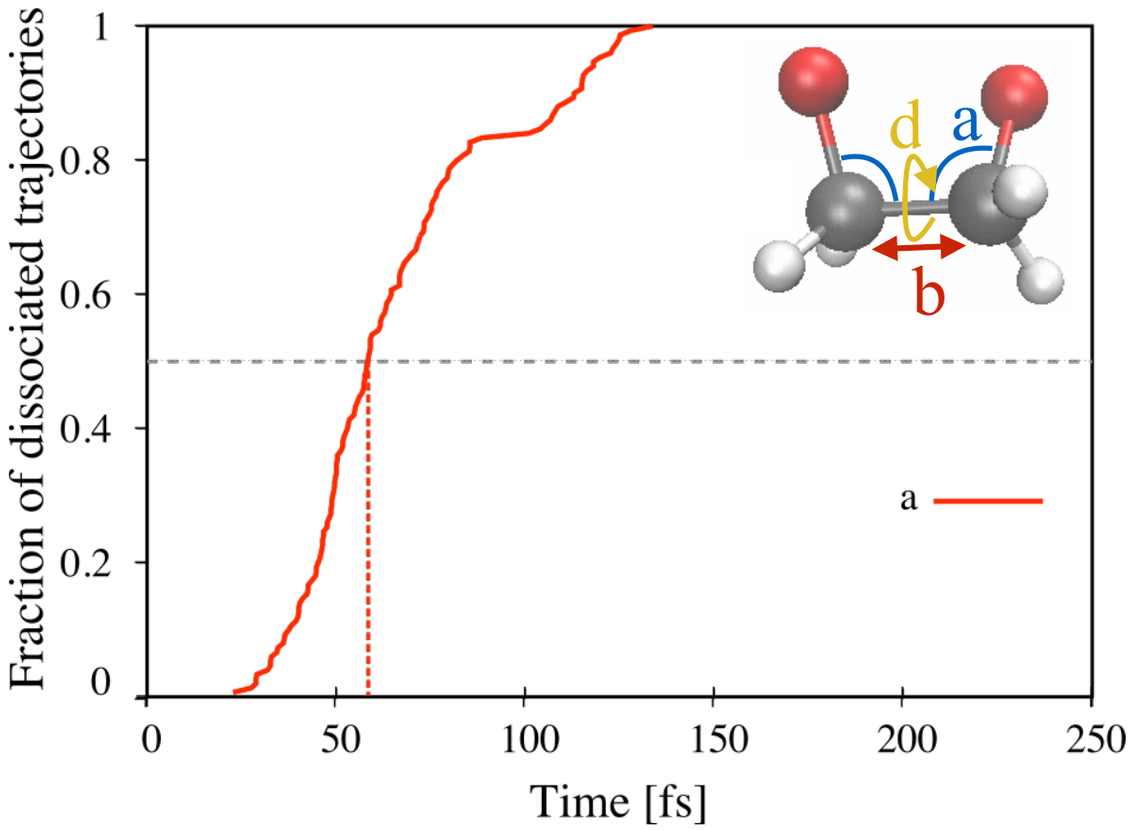
… related to empirical rules known today as:

- octet rule
- relation between bond order and bond length
- orbital hybridisation / valence shell electron pair repulsion (VSEPR) model

This is chemistry !

Häse, Fdez Galván, Aspuru-Guzik, Lindh and Vacher, *Chem. Science*, **10**, 2298-2307 (2019)

“Frustrated” dissociations



➜ Dissociation time scale
between t = 25 fs and t = 140 fs
half-time of 59 fs

Vacher et al, *J. Chem. Theory Comput.*, **13** (6), 2448-2457 (2017)

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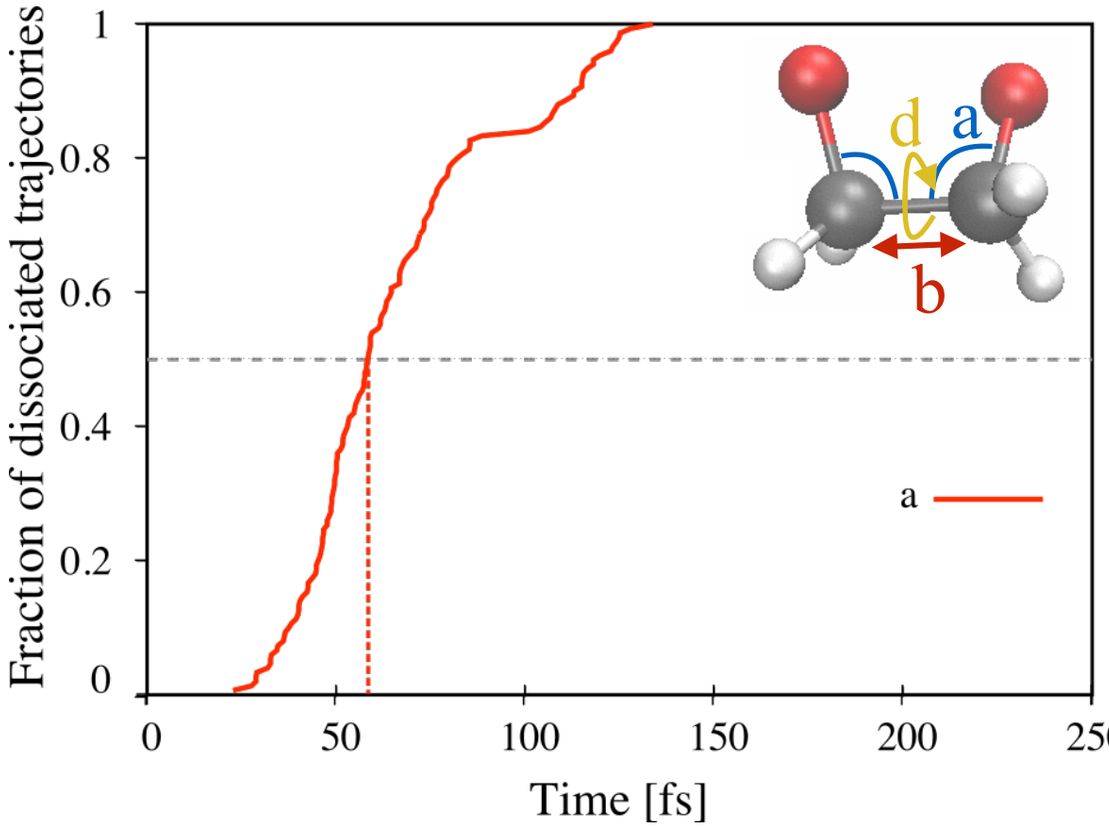

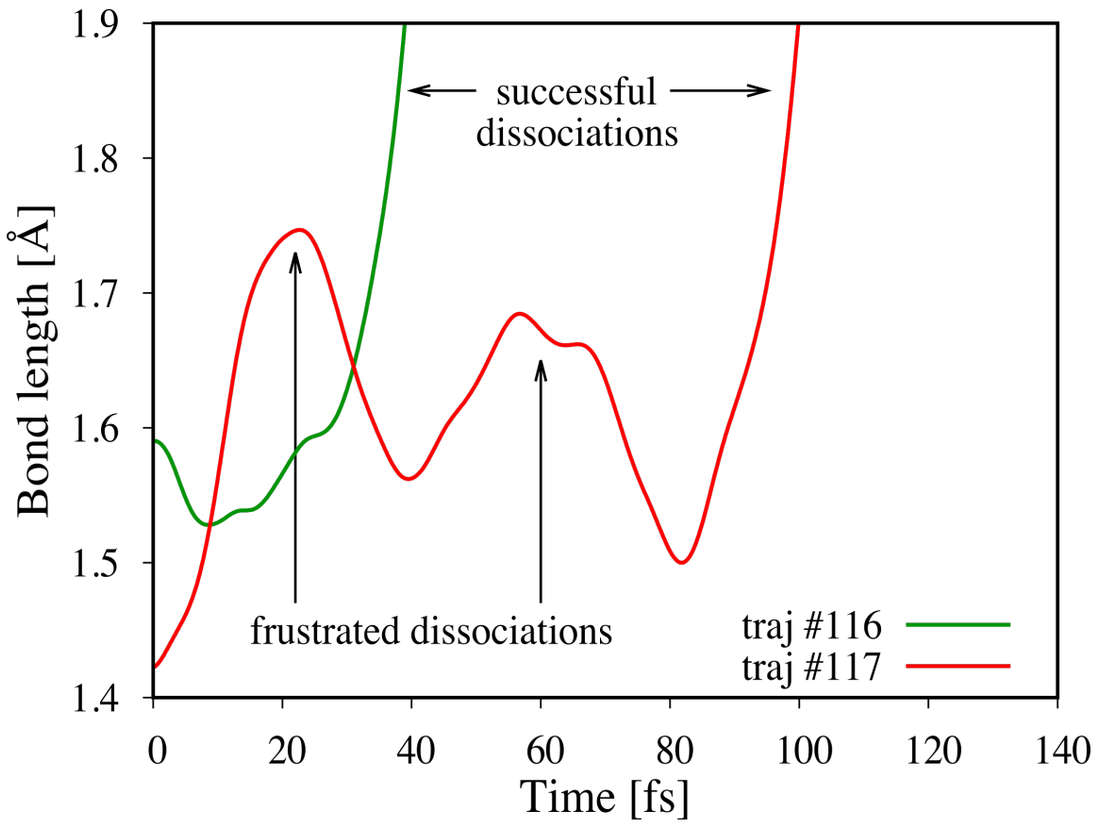

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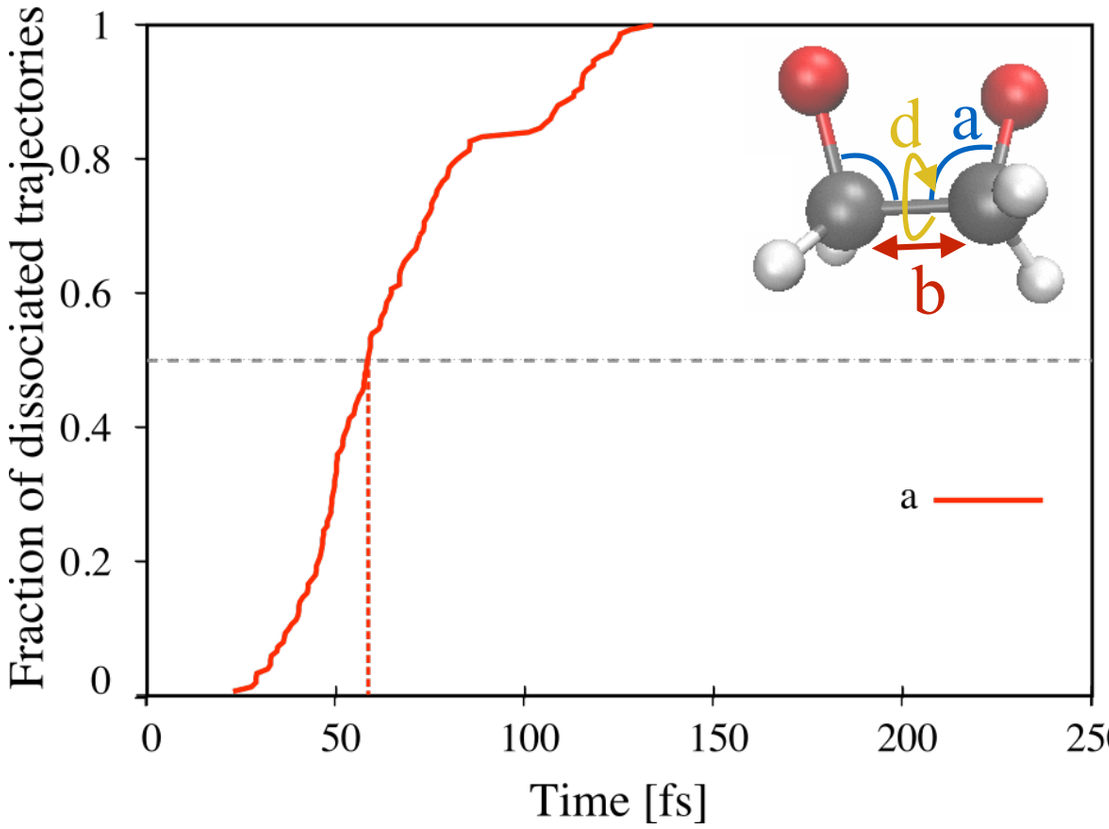

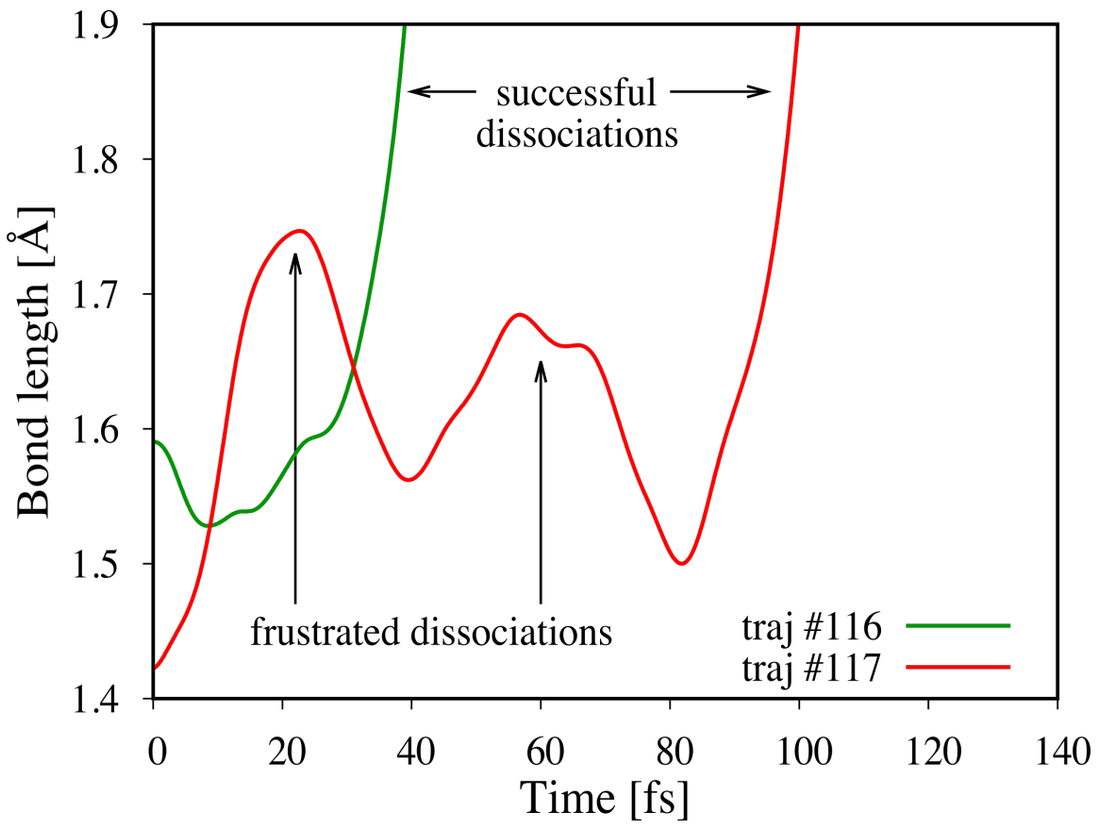

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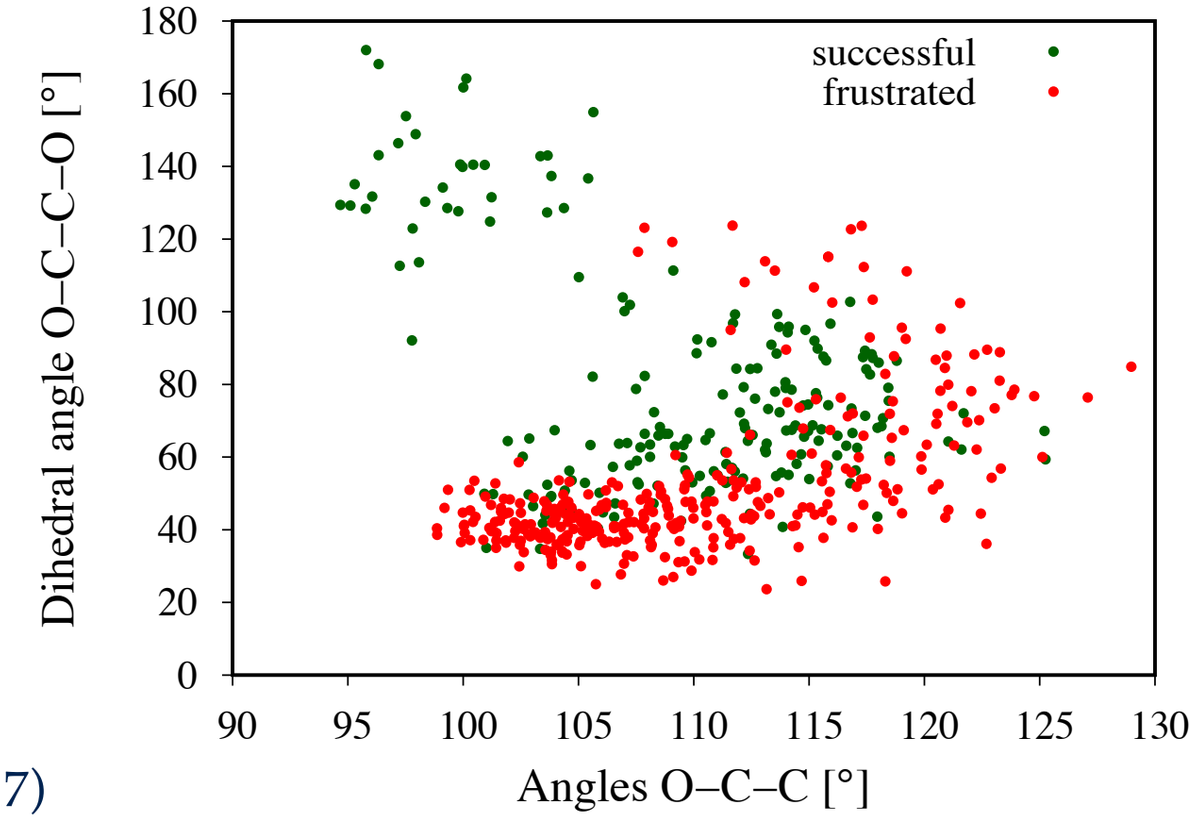

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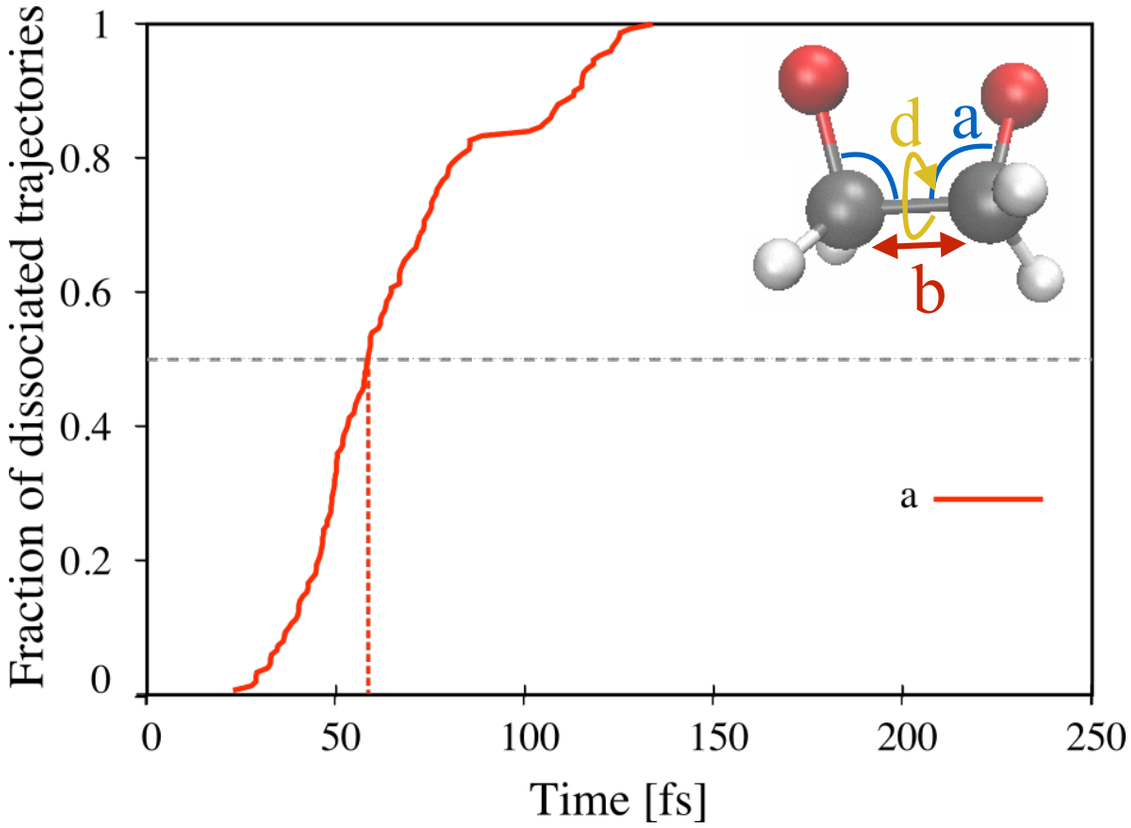

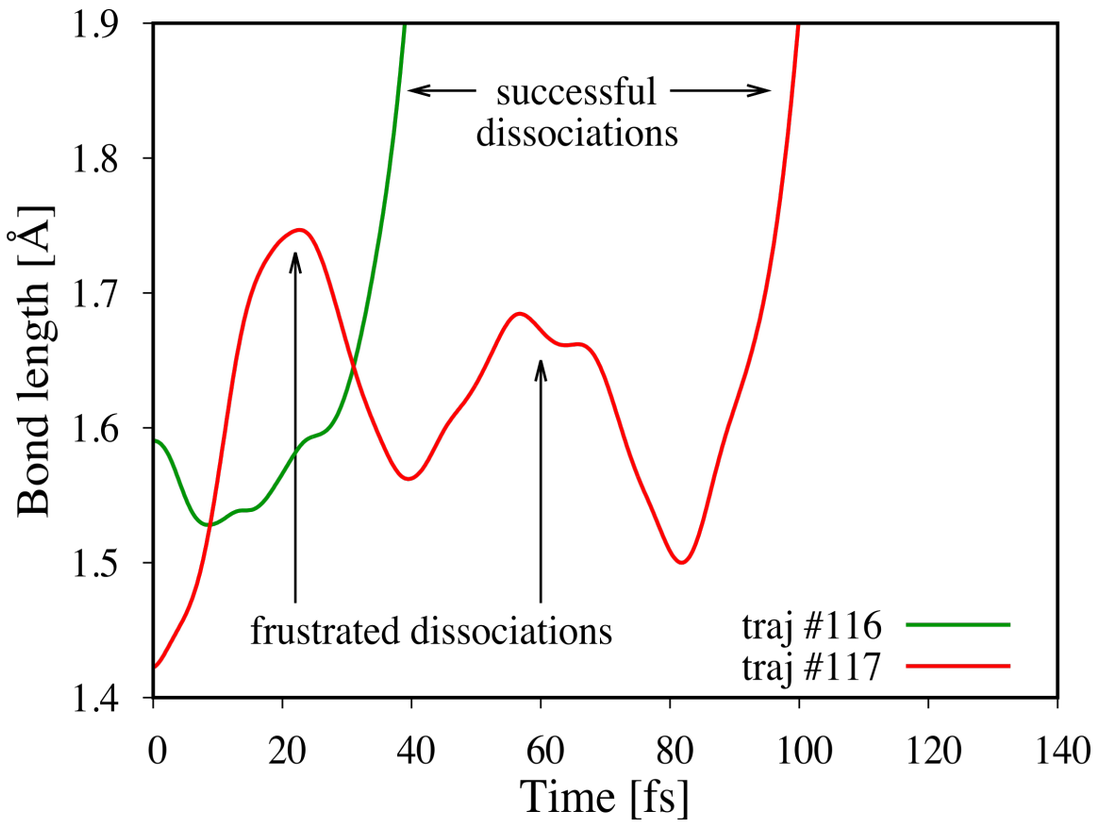

➜ Dissociation time scale

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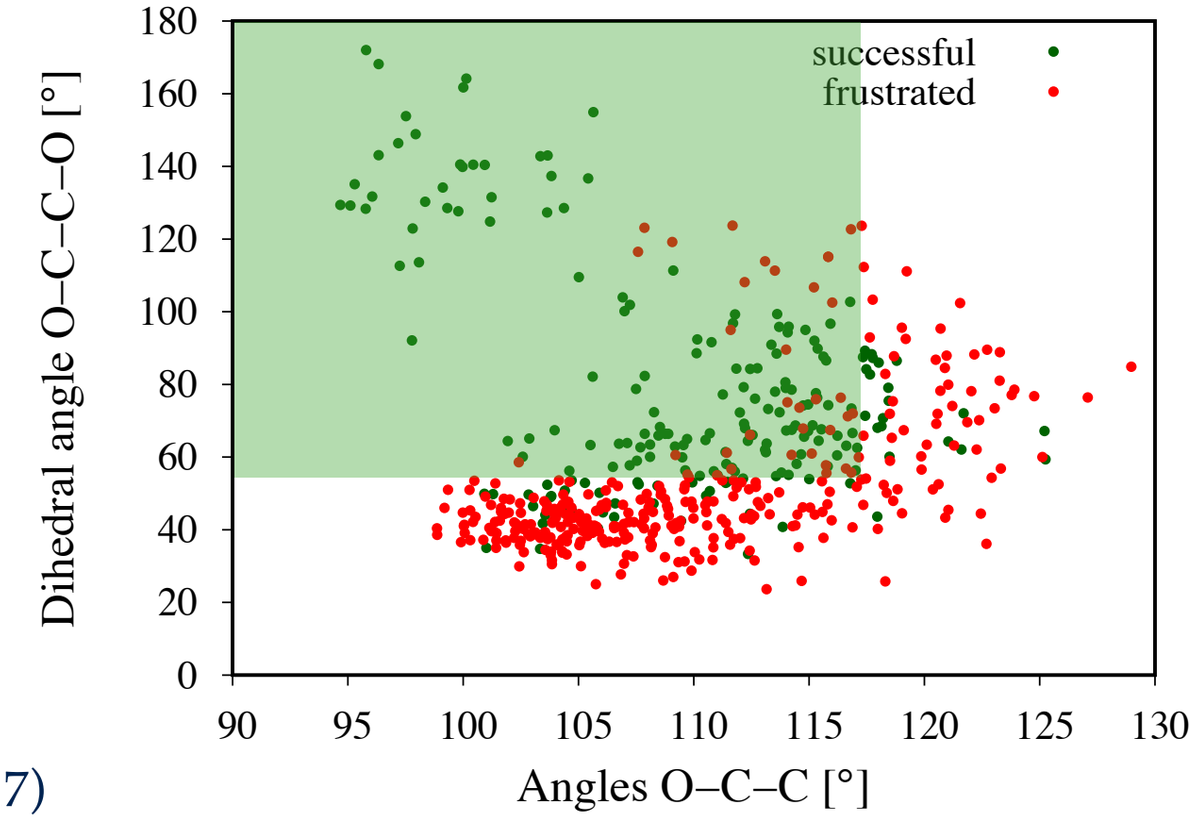
half-time of 59 fs

➜ Geometrical conditions necessary

O-C-C-O dihedral > 55°

O-C-C angle < 117°



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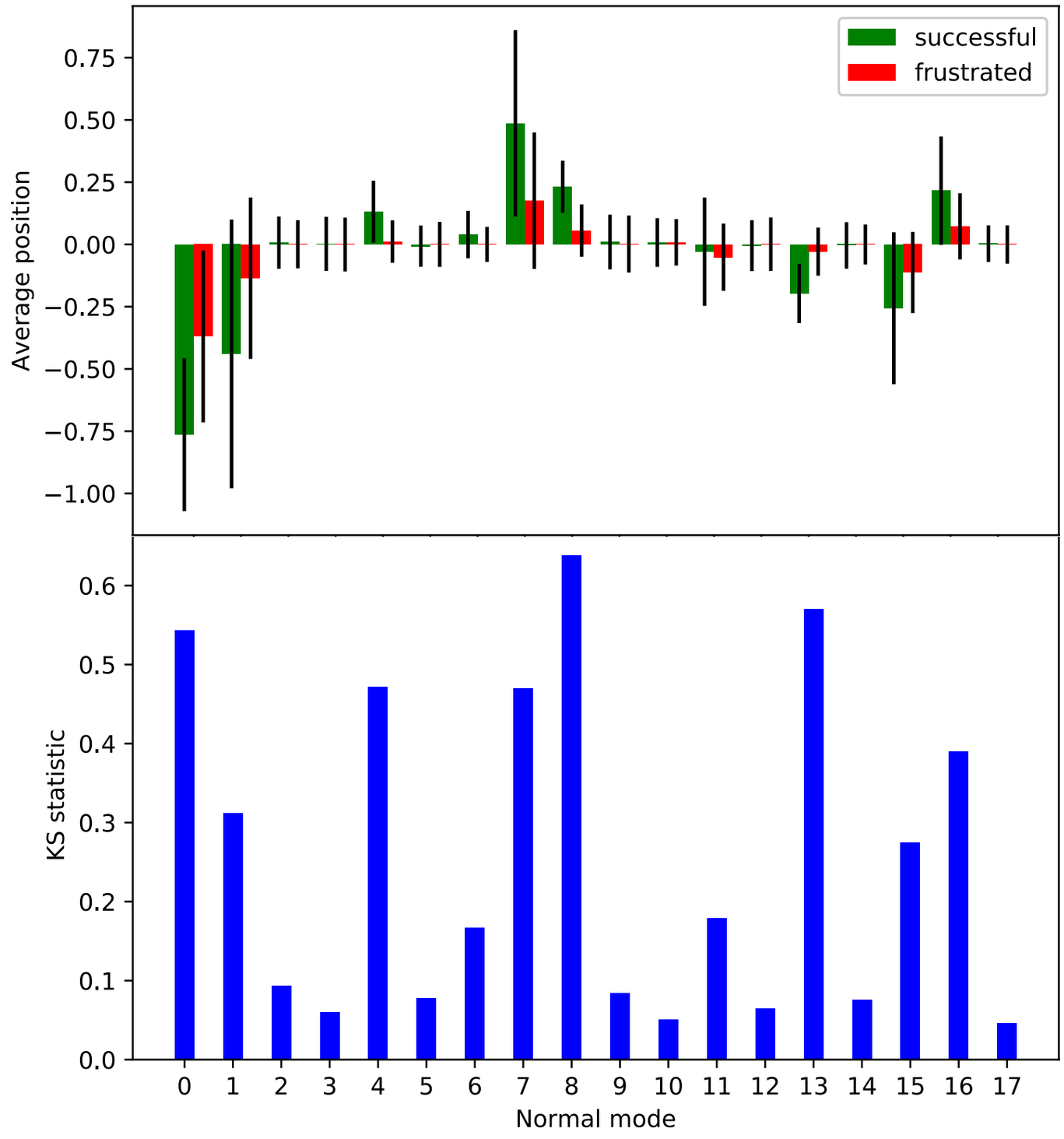

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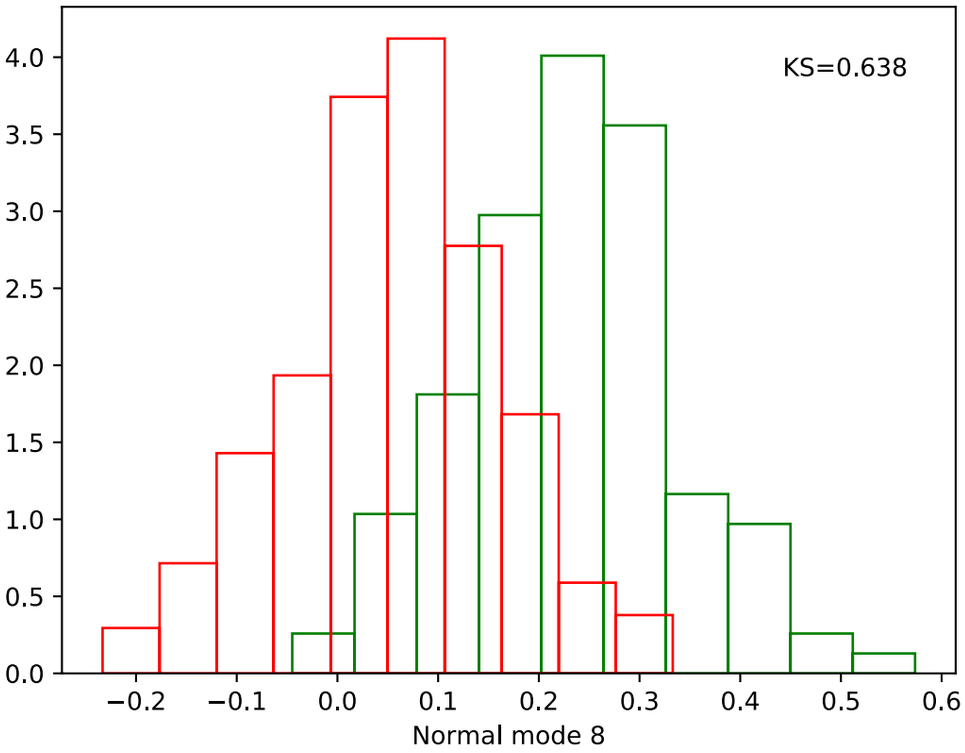

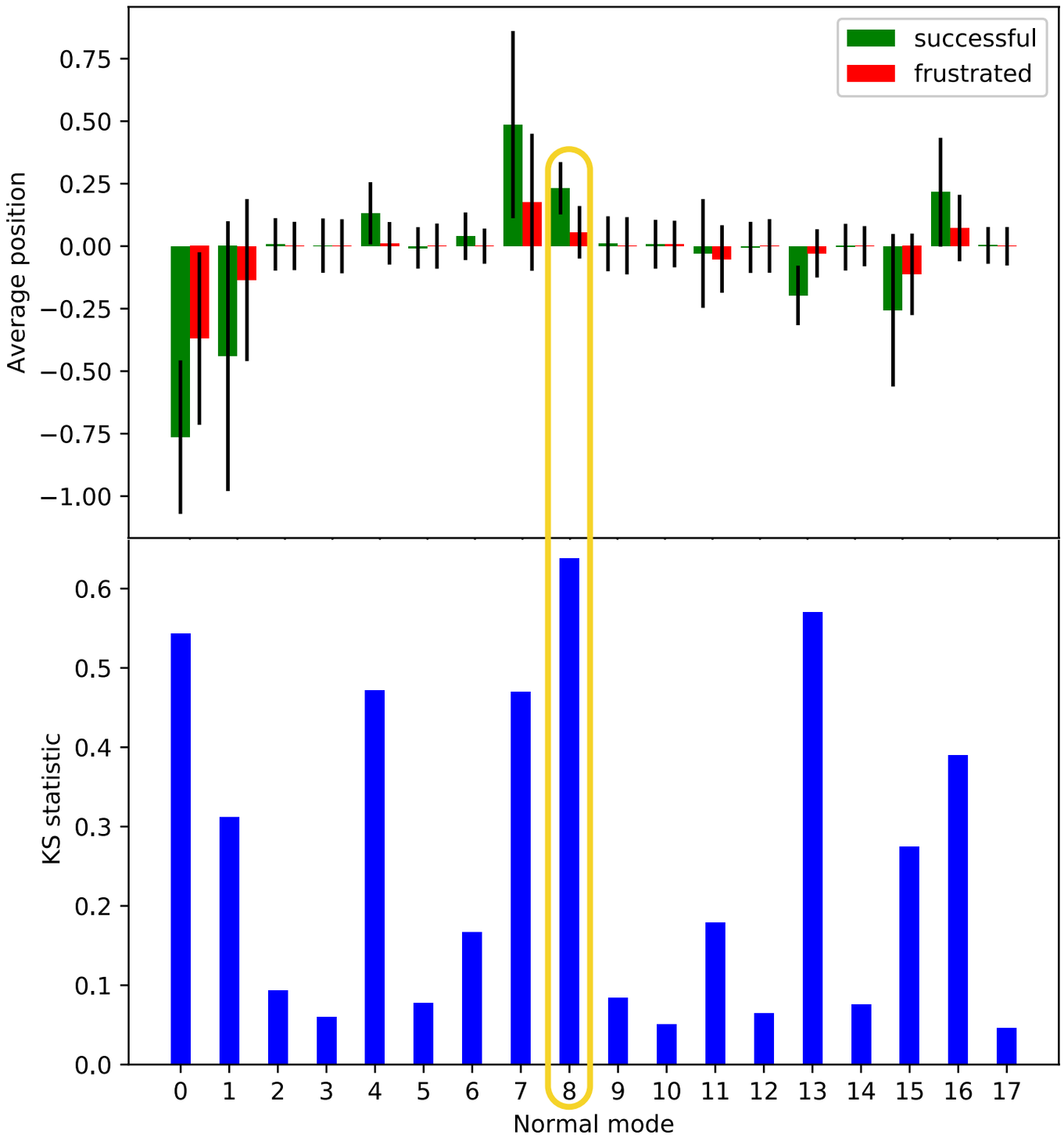

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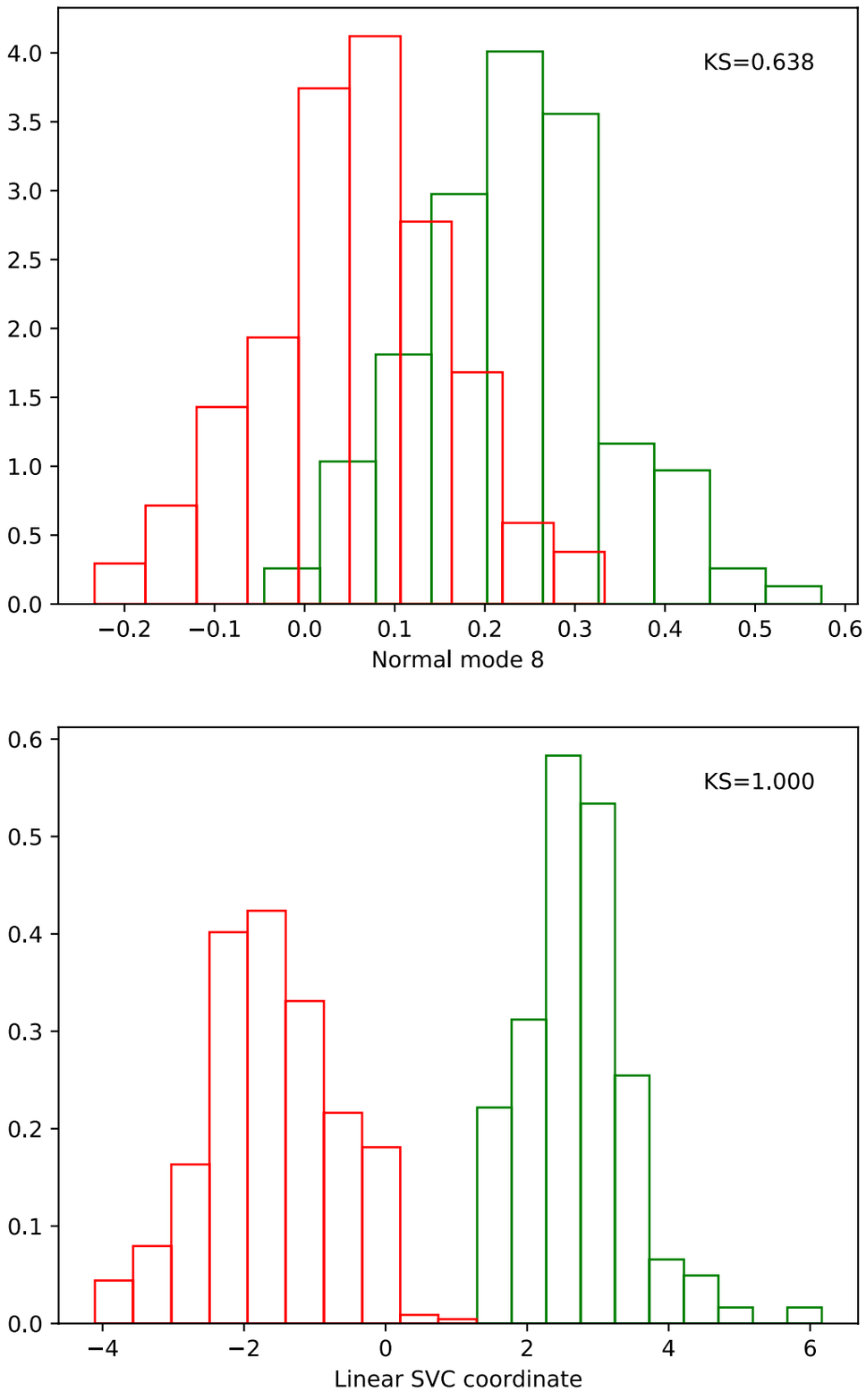

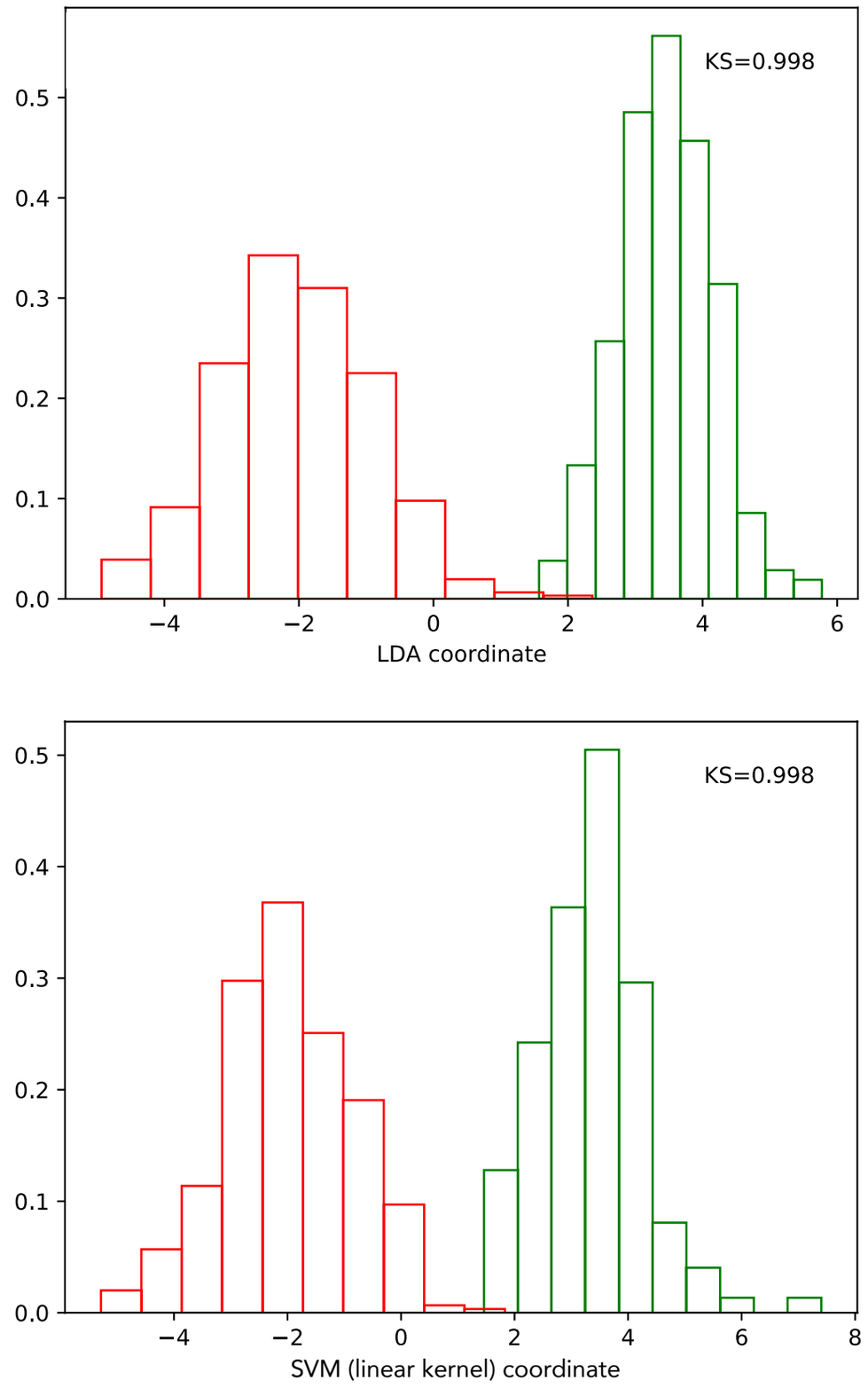

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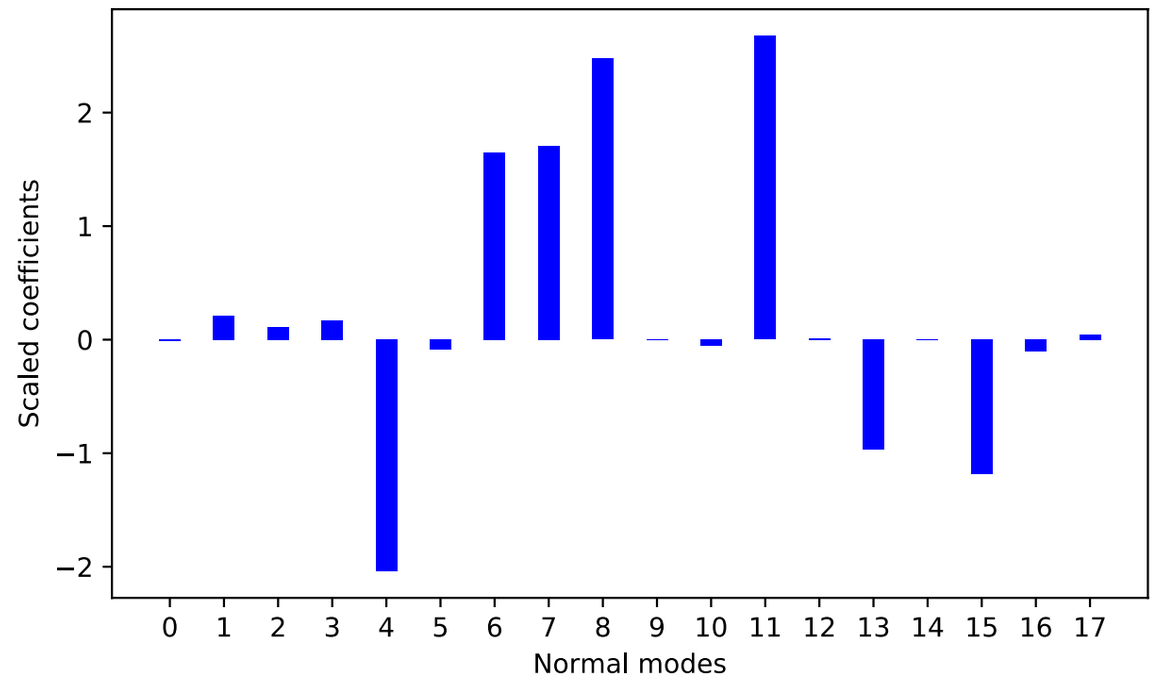

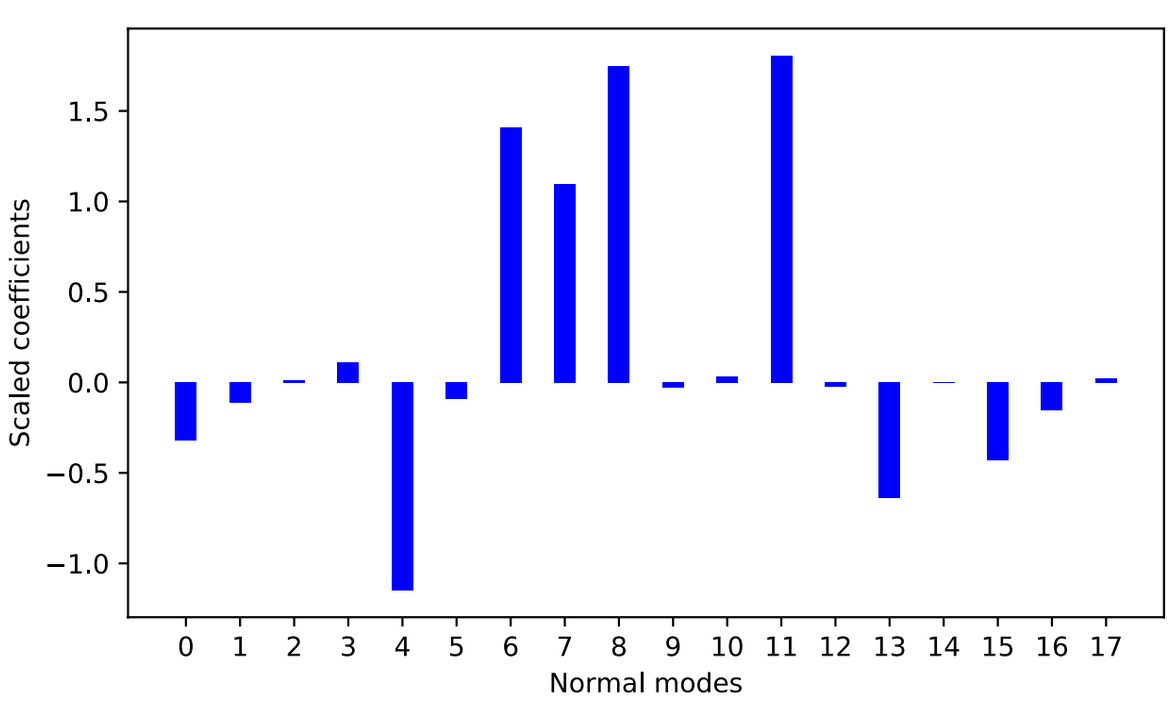

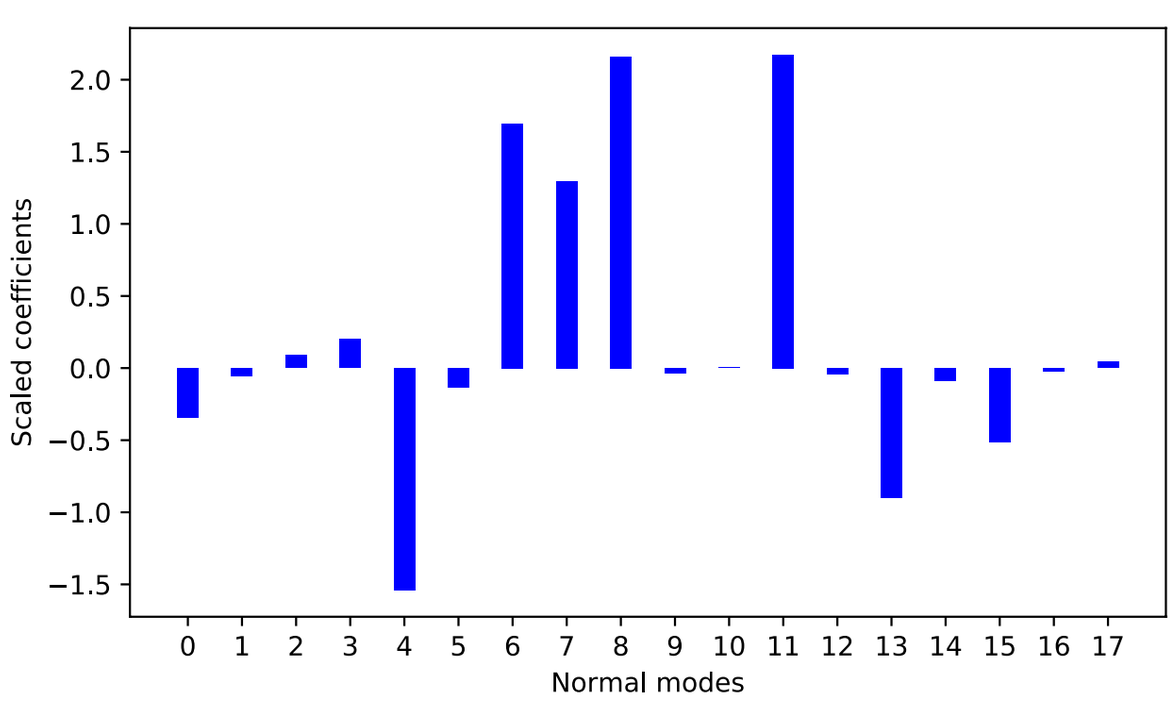

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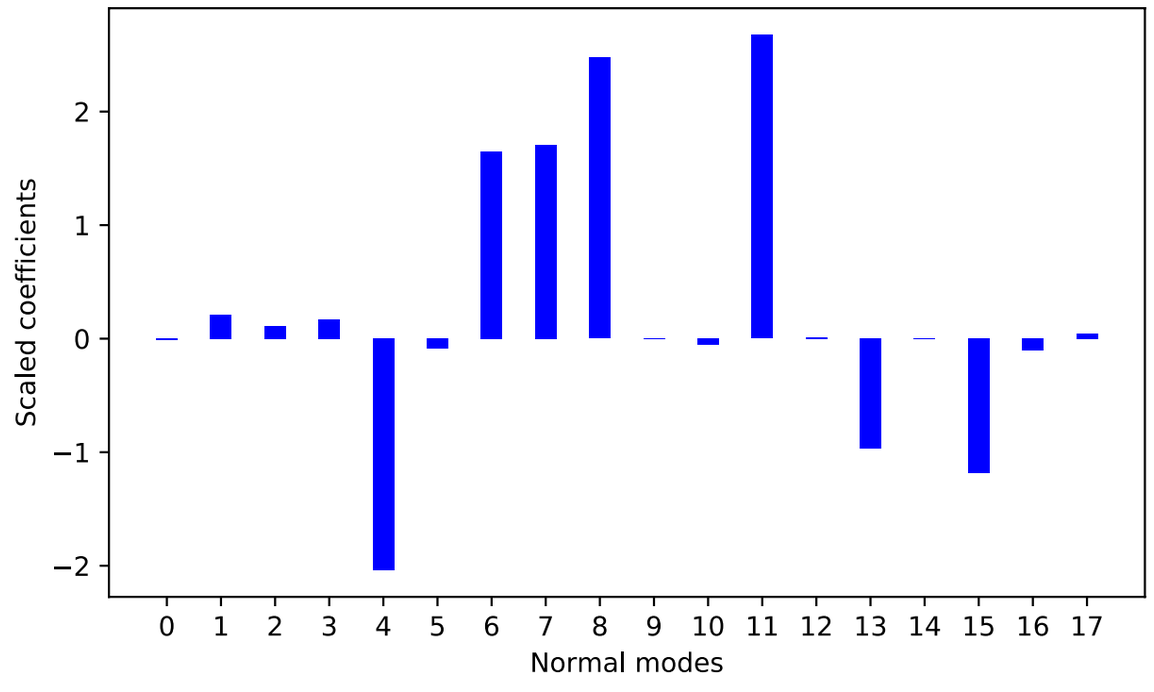
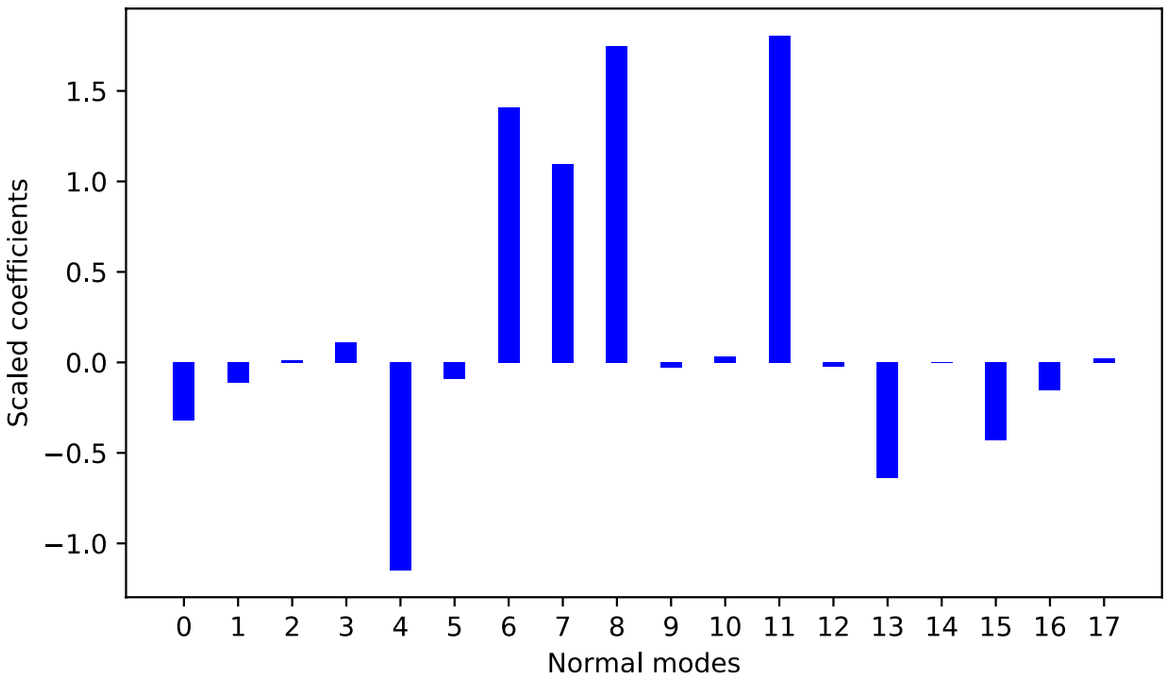
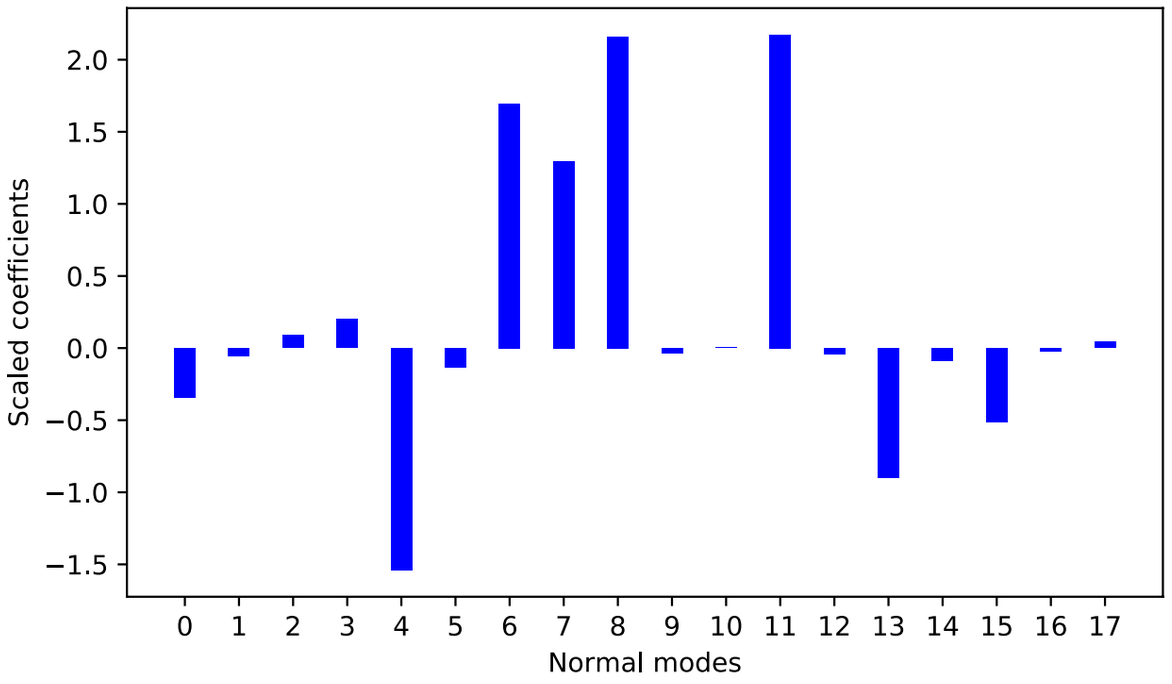
“Frustrated” dissociations - revisited

➜ In-phase planarisation motion of the two formaldehyde moieties







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Take home messages

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- Machine learning algorithms are able to predict accurately a specific outcome quantity of AIMD simulations. In order to make accurate predictions, the models evidence empirical rules that are, today, part of the common chemical knowledge.

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- Machine learning techniques are also helpful to analyse and further interpret the results produced by the AIMD simulations.

- This paves the way for new conceptual insights in chemistry where machine analysis would provide a source of inspiration for us.

Acknowledgements

Ignacio Fdez. Galván

Roland Lindh

Florian Häse

Alan Aspuru-Guzik

Anders Brakestad
Hans Karlsson
Hannes Gustafsson

Thank you!

UPPSALA UNIVERSITET

HARVARD UNIVERSITY

UNIVERSITY OF TORONTO

Chimie Et Interdisciplinarité Synthèse, Analyse, Modélisation

CEISAM

UMR CNRS 6230

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Theoretical methods

time-dependent Schrödinger equation $$i\hbar\frac{\partial\Phi}{\partial t} = \hat{H}\Phi$$

molecular Hamiltonian $$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{U}$$

clampled-nucleus Hamiltonian $$\hat{H}_{el}(\mathbf{r};\mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{U}(\mathbf{r};\mathbf{R})$$

For any given value of *R*, $$\hat{H}_{el}\psi_i(\mathbf{r};\mathbf{R}) = E_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

electronic eigenstates

electronic eigenvalues

Born representation: $$\Phi(\mathbf{r},\mathbf{R},t) = \sum_i^\infty \chi_i(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$

nuclear function

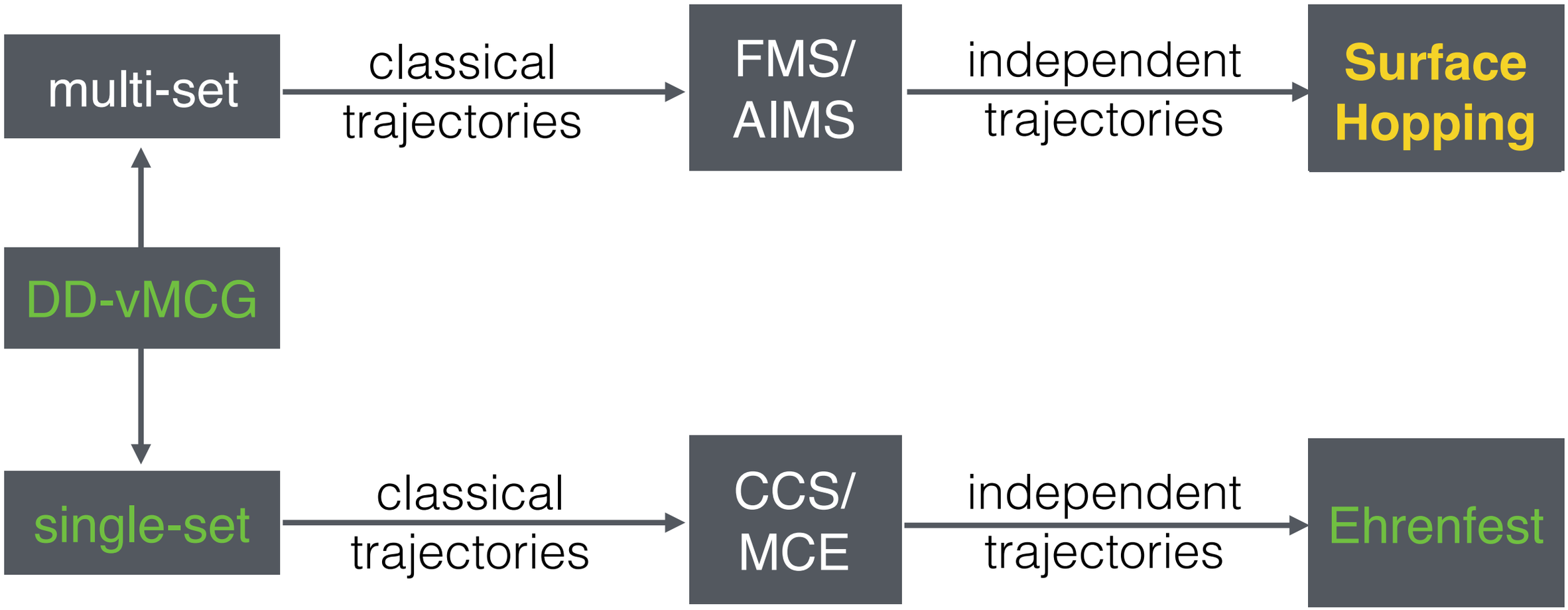
non-adiabatic coupling

$$\hat{\Lambda}_{ij} = \frac{1}{2M}(2F_{ij} + G_{ij})$$

$$F_{ij} = \langle\psi_i|\nabla\psi_j\rangle = \frac{\langle\psi_i|(\nabla\hat{H}_{el})|\psi_j\rangle}{E_j - E_i}$$

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + E_j]\chi_j - \sum_i^\infty \hat{\Lambda}_{ji}\chi_i$$

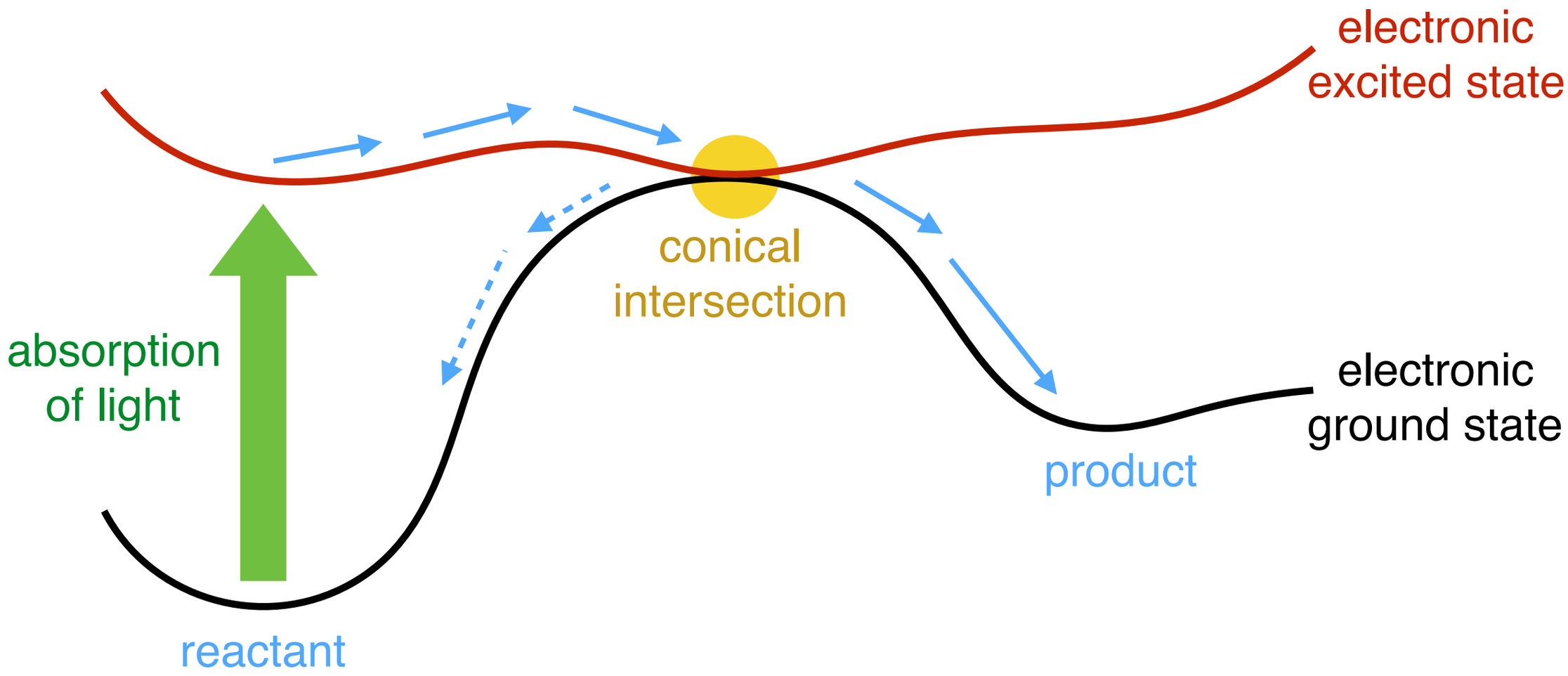
On-the-fly non-adiabatic methods



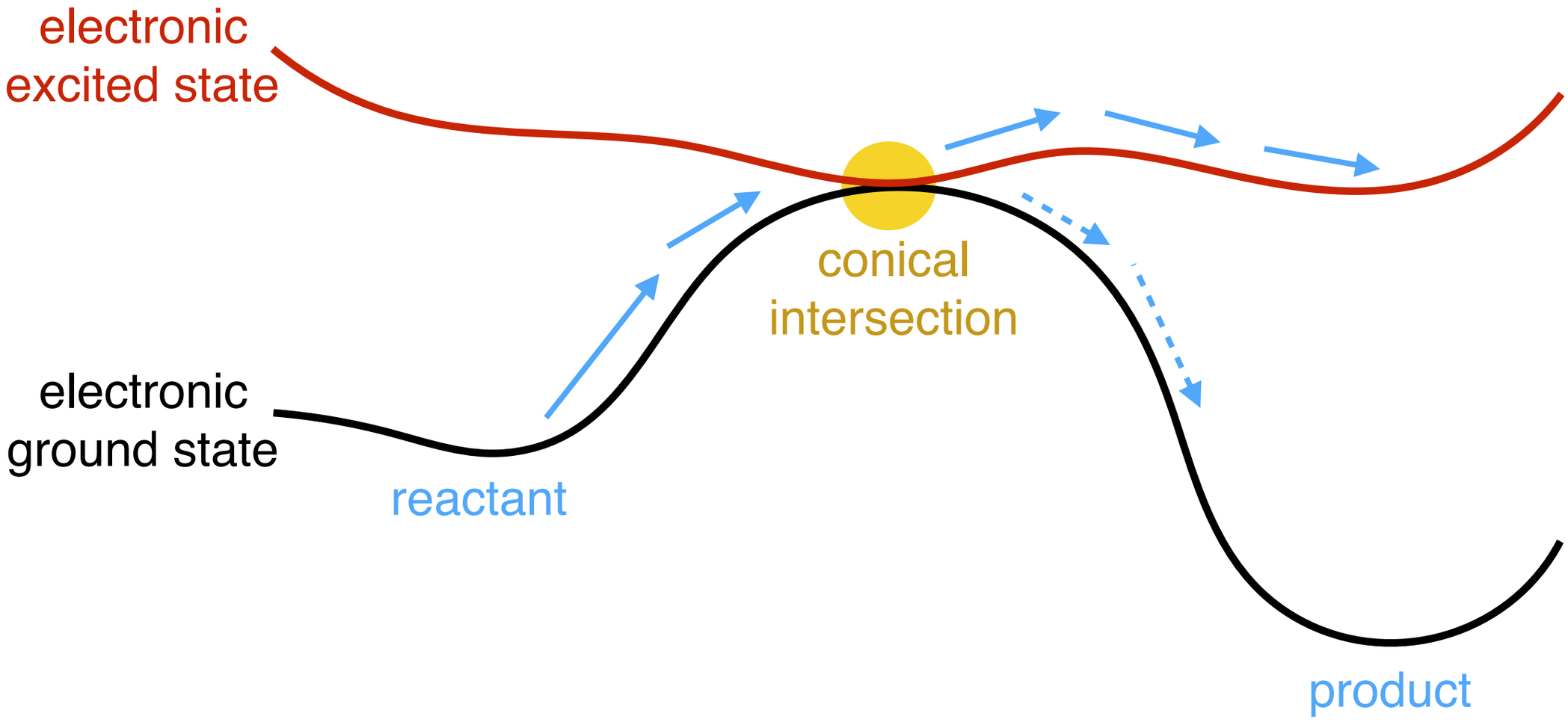
DD-vMCG: direct dynamics variational multi-configuration Gaussian.
FMS: full multiple spawning and **AIMS**: ab initio multiple spawning.
CCS: coupled-coherent states and **MCE**: multi-configurational Ehrenfest.

Vacher et al, *Theor. Chem. Acc.* (2014) **133**, 1505
Vacher et al, *Theor. Chem. Acc.* (2016) **135**, 187

What is chemiluminescence?



What is chemiluminescence?

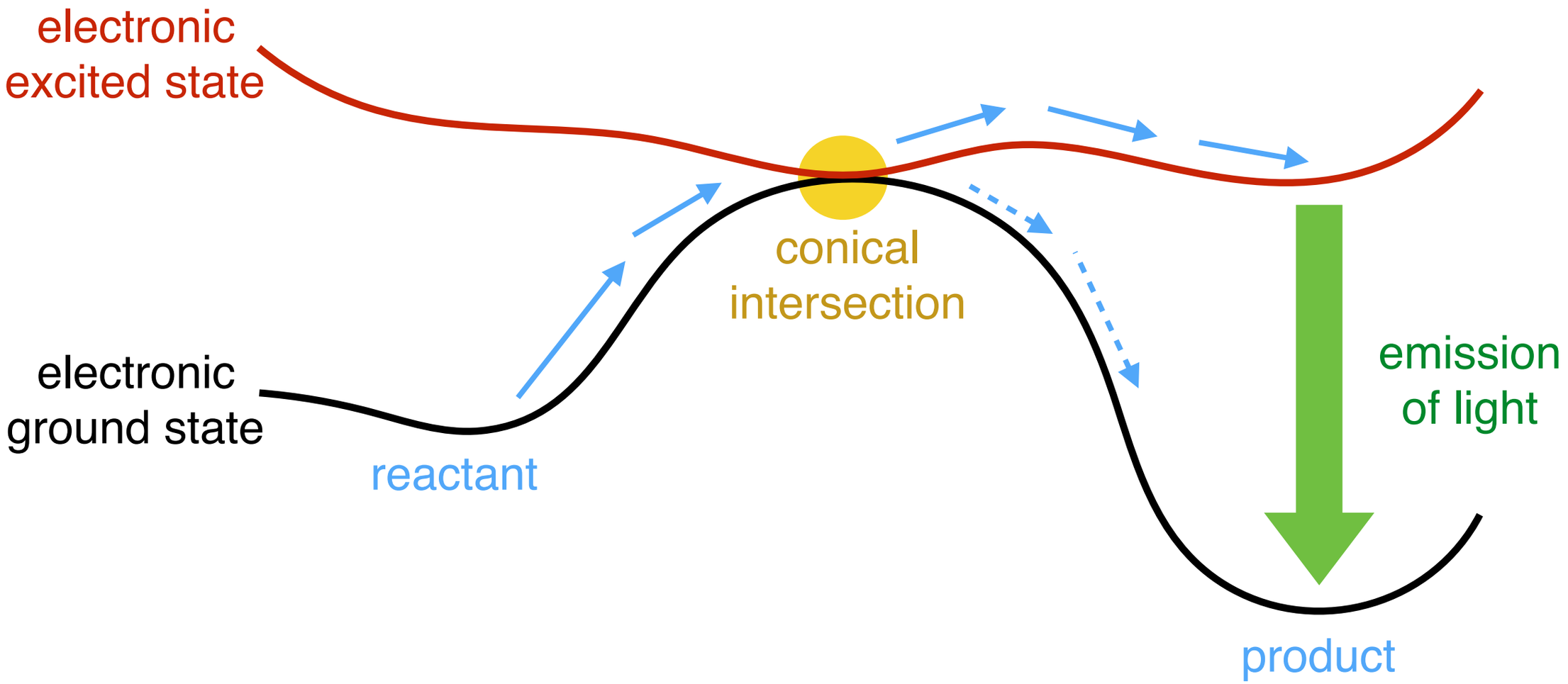


Chemiexcitation

Population of an excited state as the result of a chemical reaction

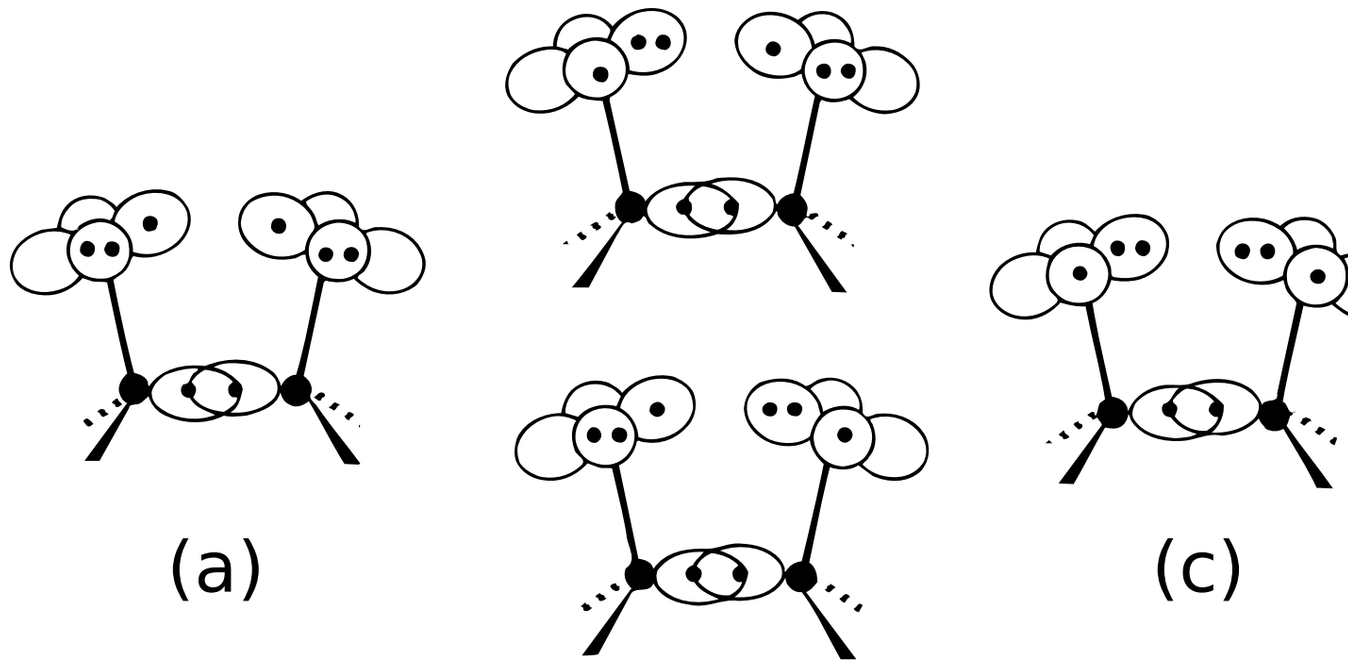
What is chemiluminescence?

Definition: Emission of light (luminescence) as the result of a chemical reaction



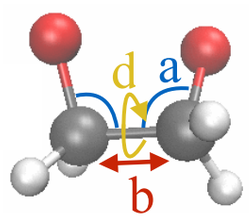
Chemiexcitation

Population of an excited state as the result of a chemical reaction

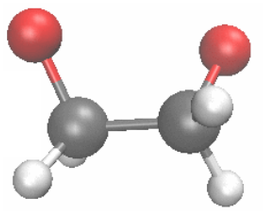


(a) (b) (c)

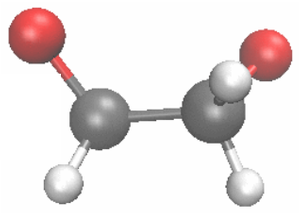
Dissociation of 1,2-dioxetane



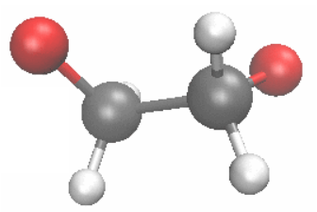
t=0 fs



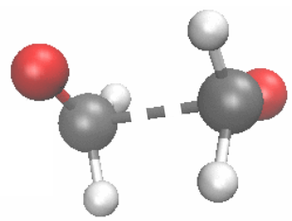
t=37.3 fs



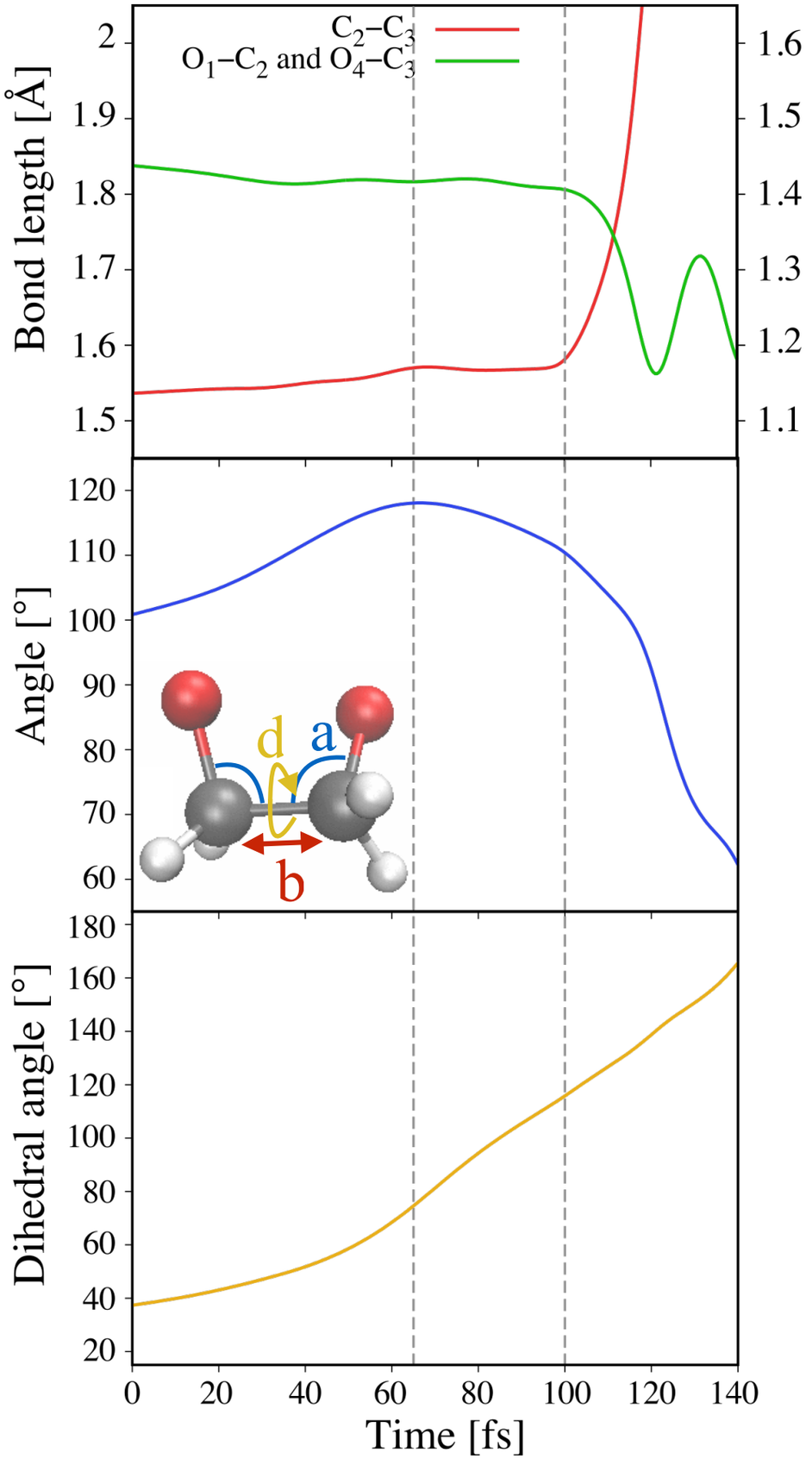
t=65.3 fs



t=104.5 fs

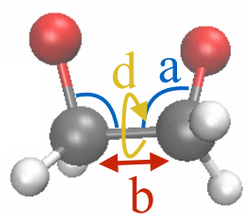


t=120.0 fs

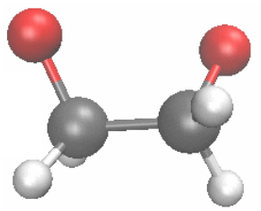


Vacher et al, *J. Chem. Theory Comput.*, **13** (6), 2448-2457 (2017)

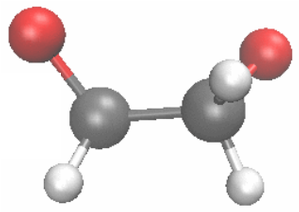
Dissociation of 1,2-dioxetane



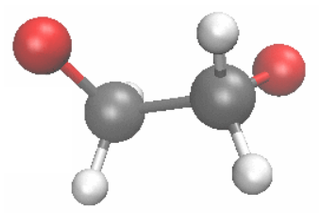
t=0 fs



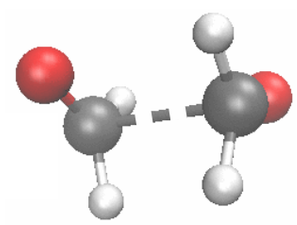
t=37.3 fs



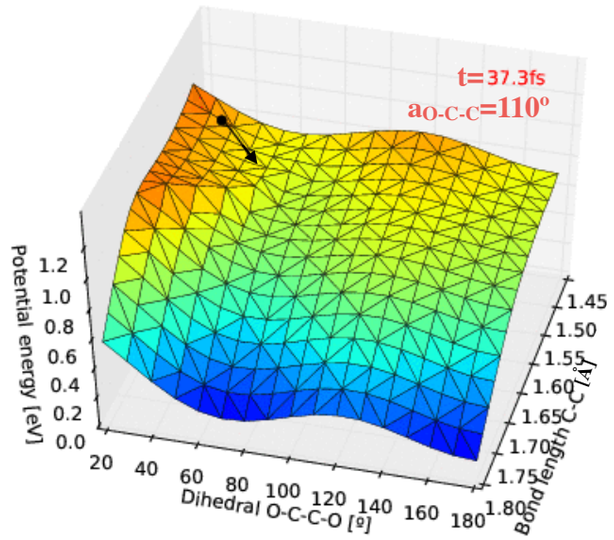
t=65.3 fs

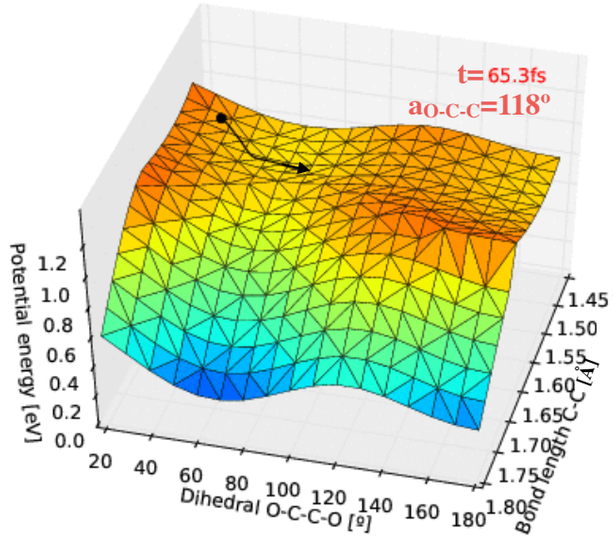


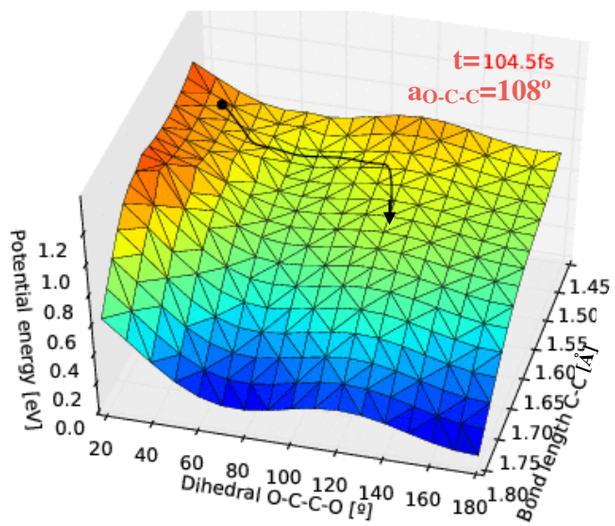
t=104.5 fs

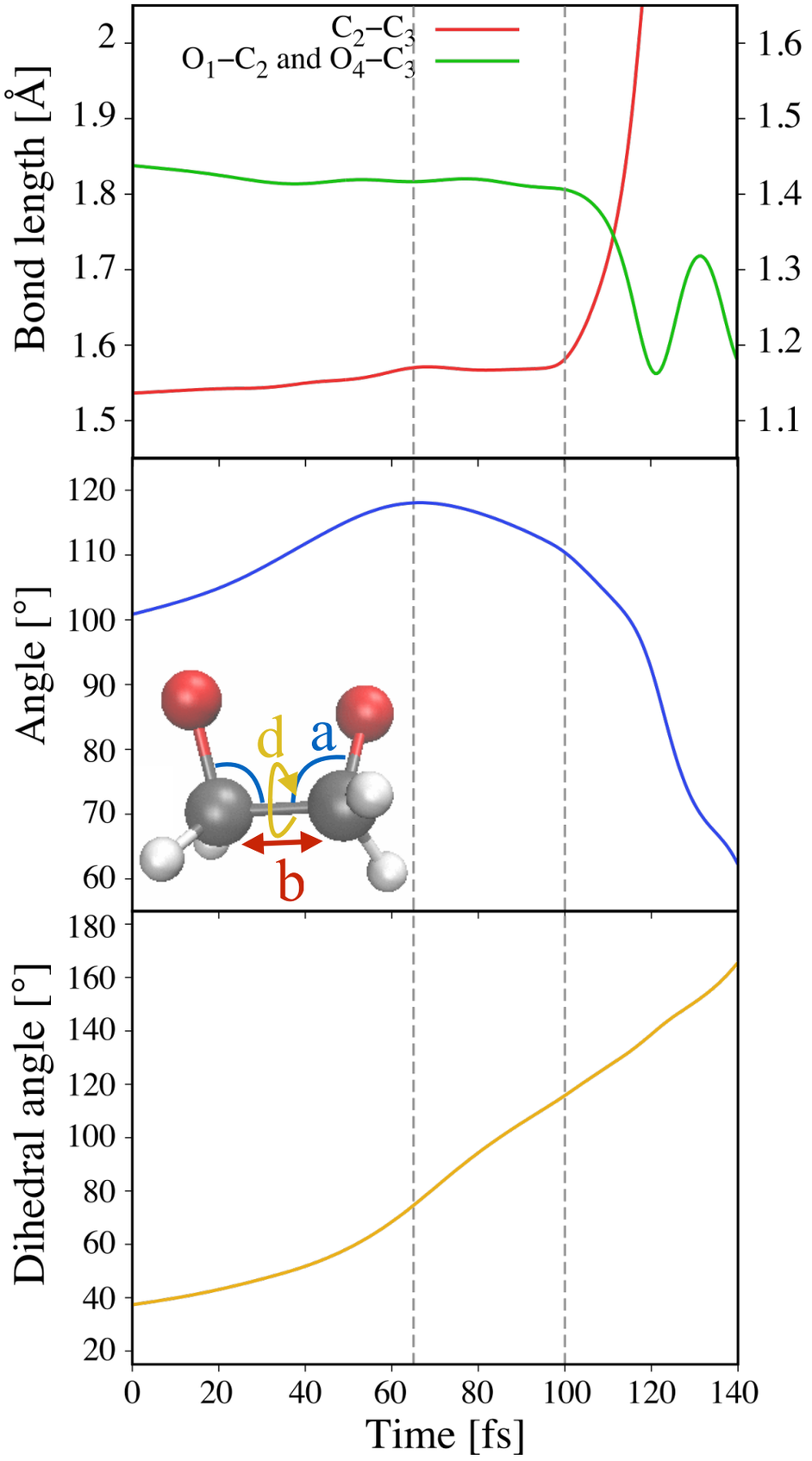


t=120.0 fs



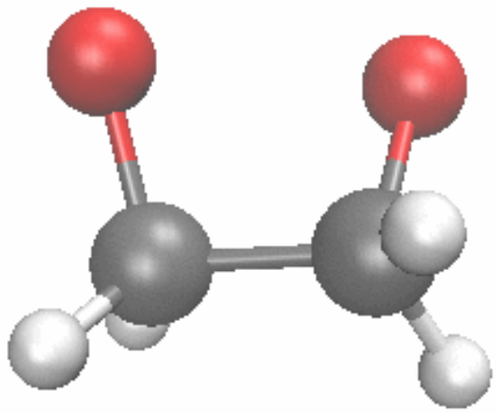


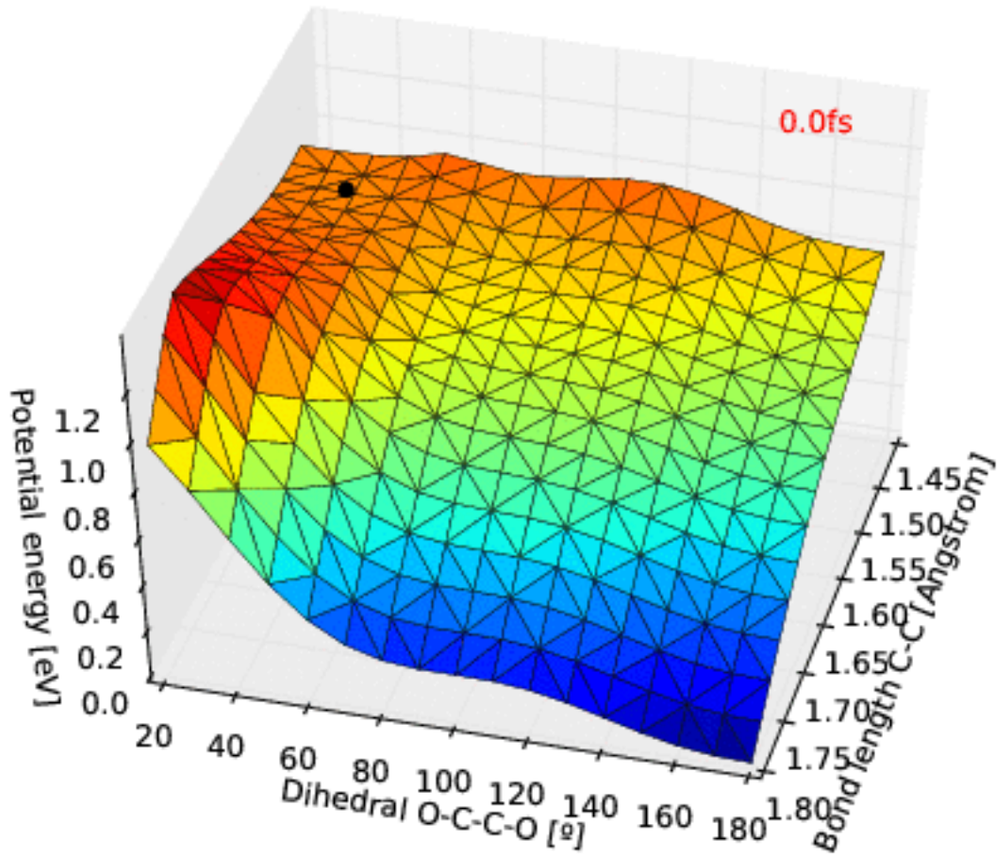


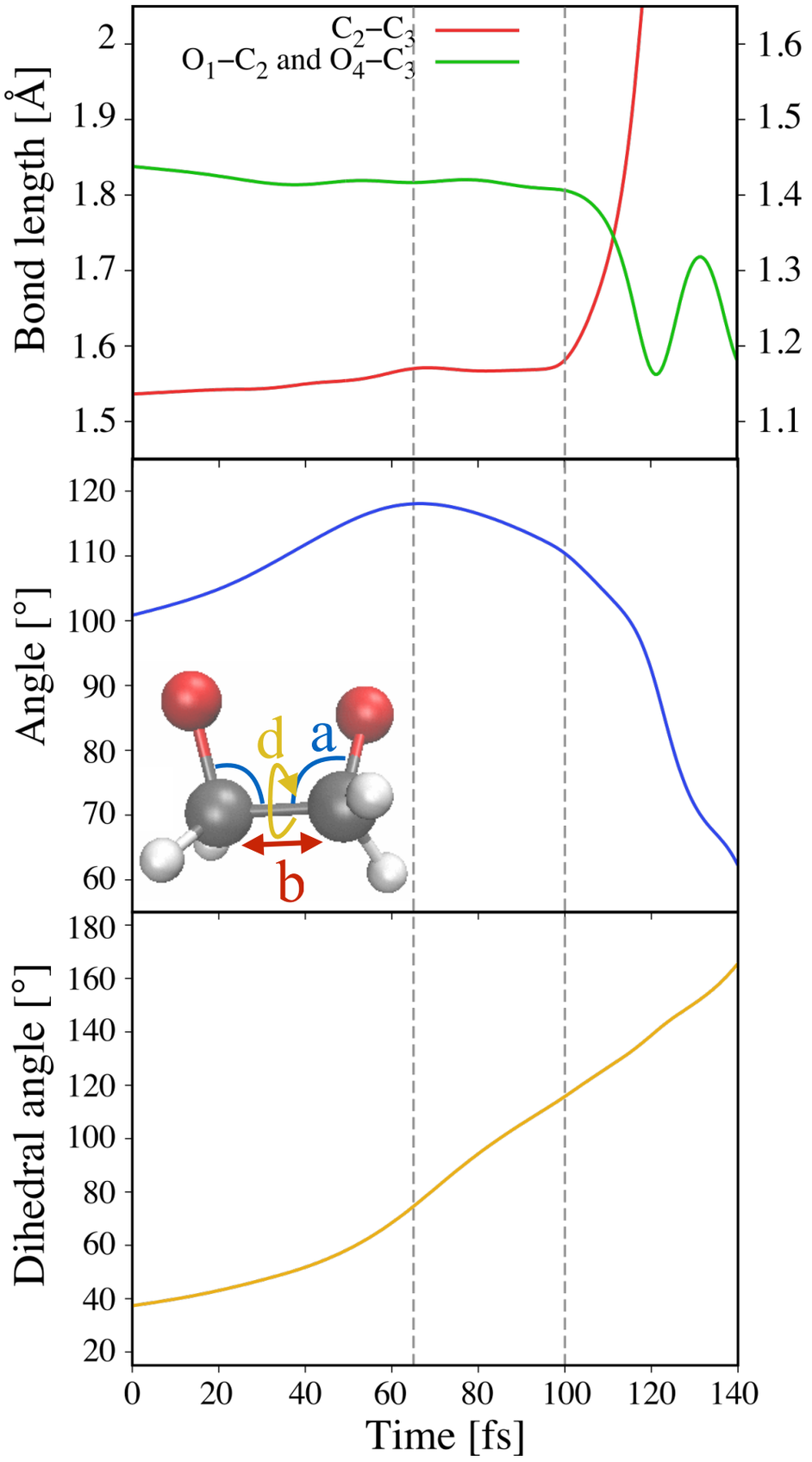


Vacher et al, *J. Chem. Theory Comput.*, **13** (6), 2448-2457 (2017)

Dissociation of 1,2-dioxetane







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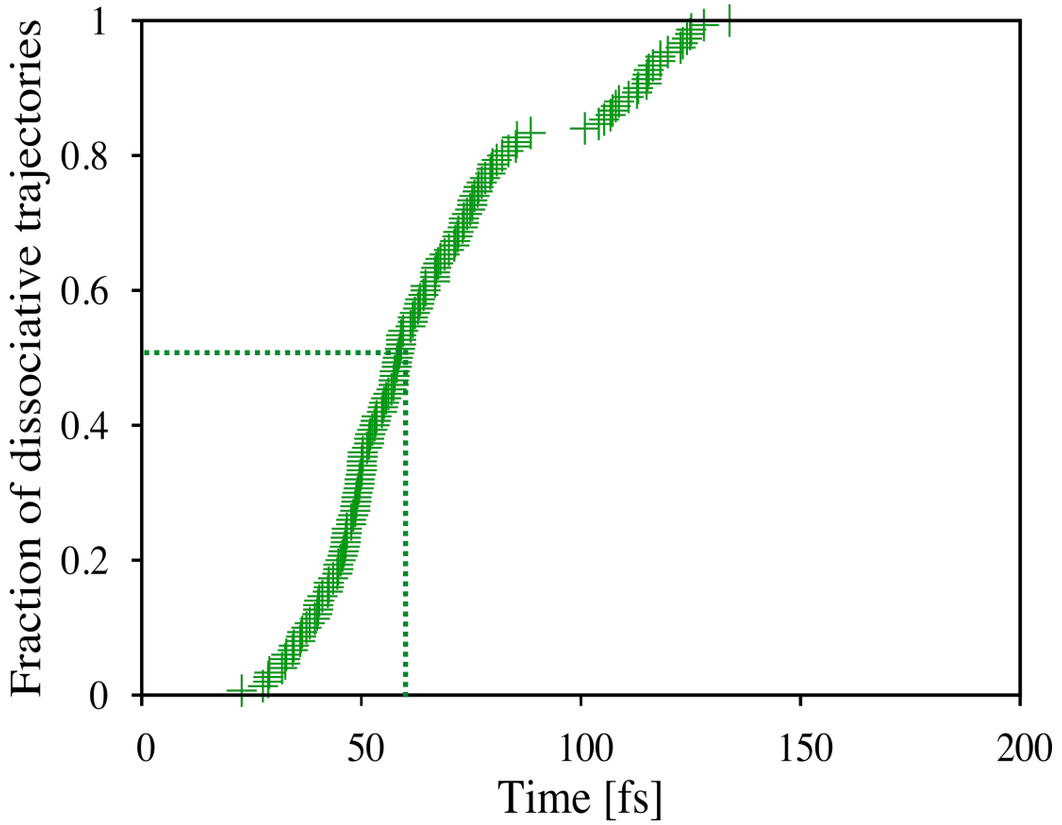

➜ Dissociation time scale
between t = 25 fs and t = 140 fs
half-time of 59 fs

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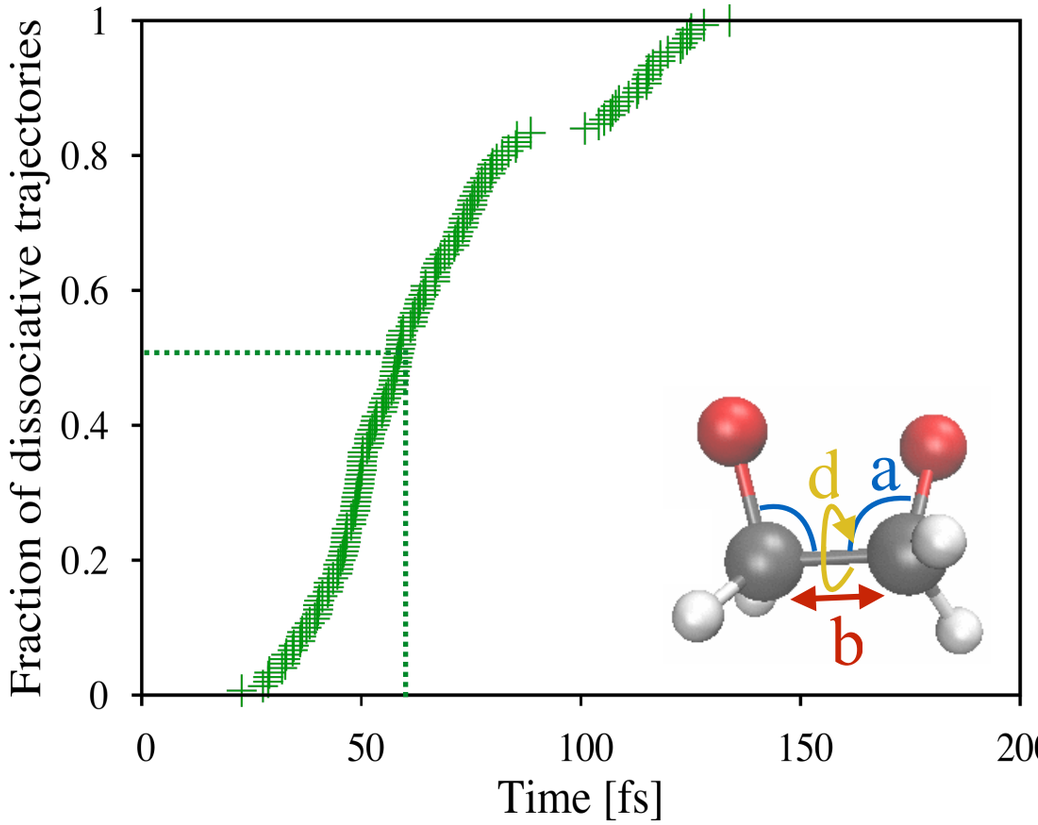
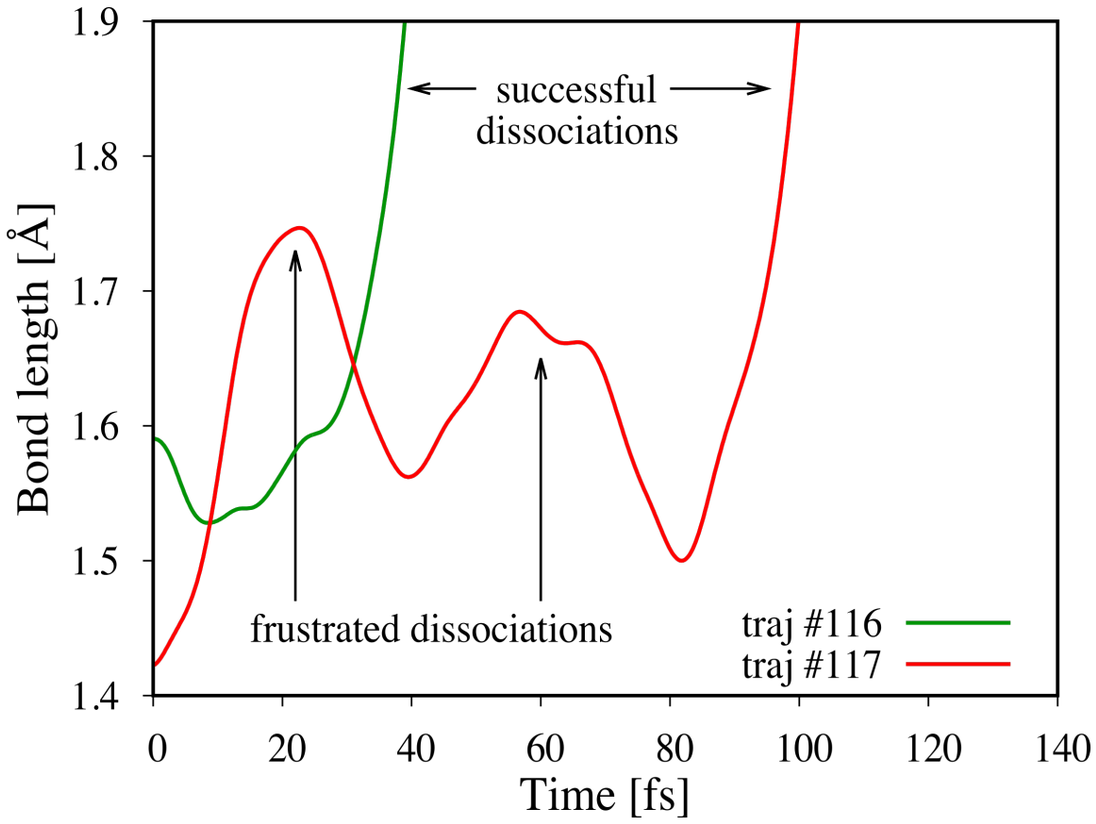
Dissociation of 1,2-dioxetane





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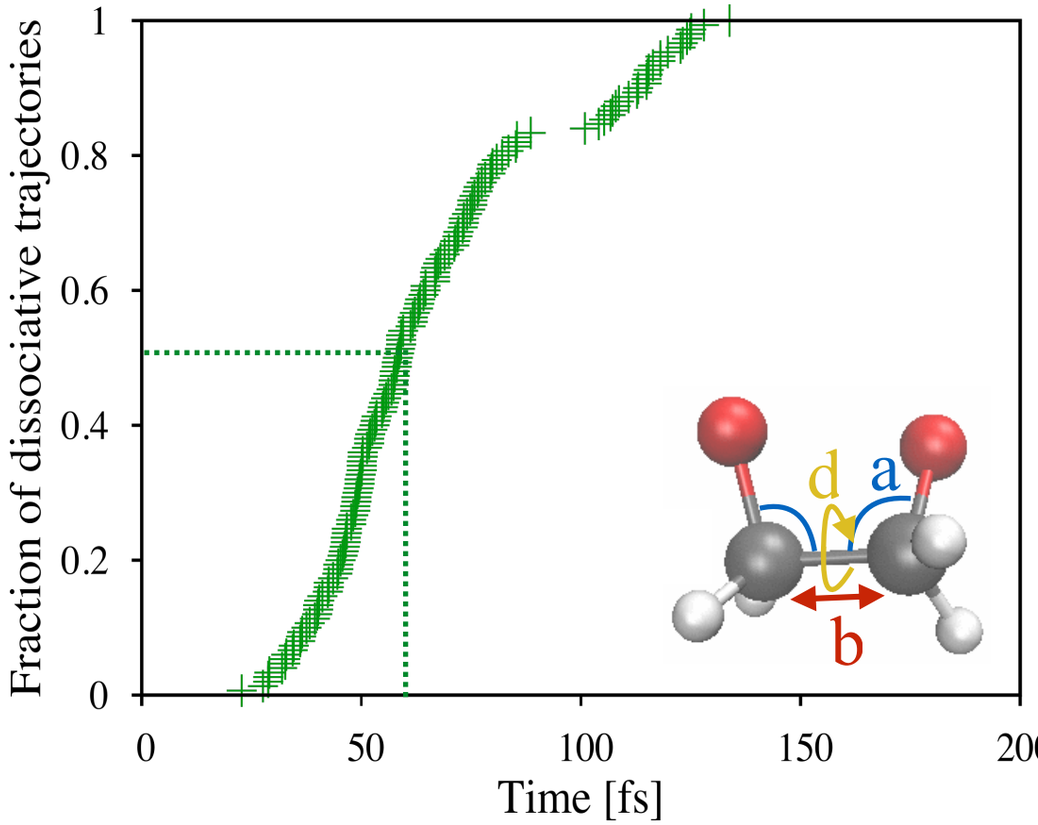
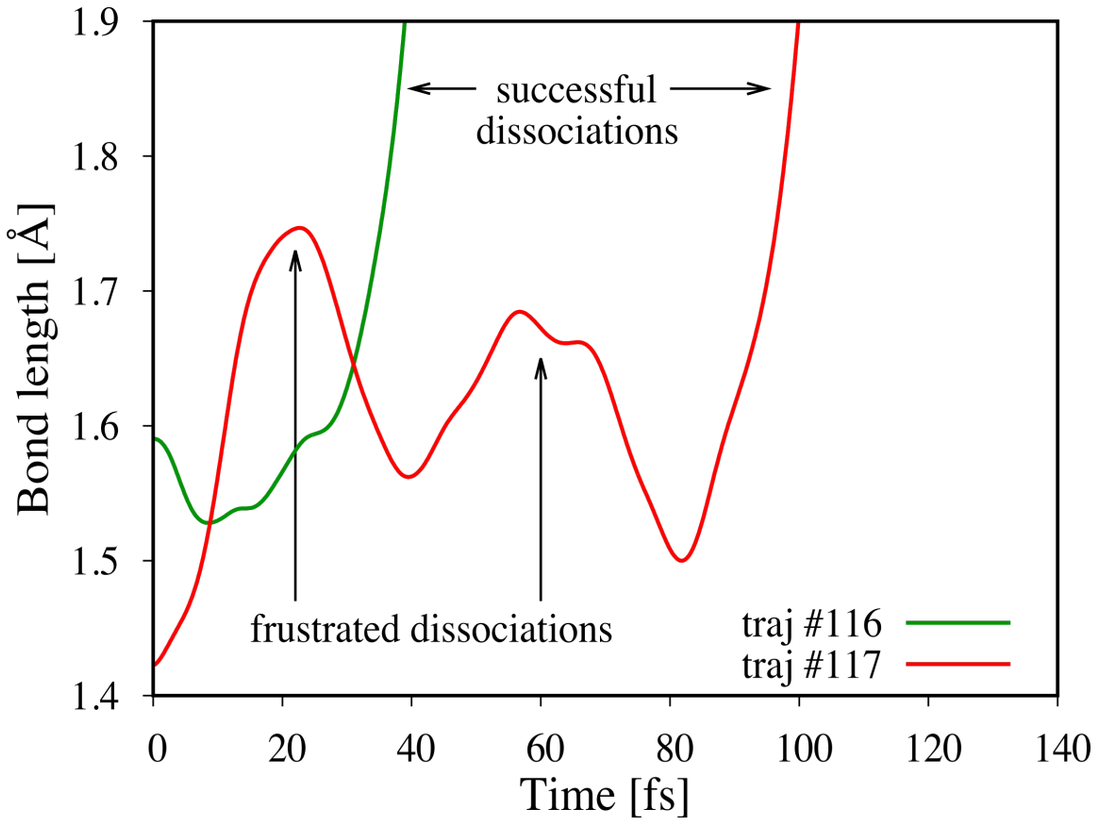
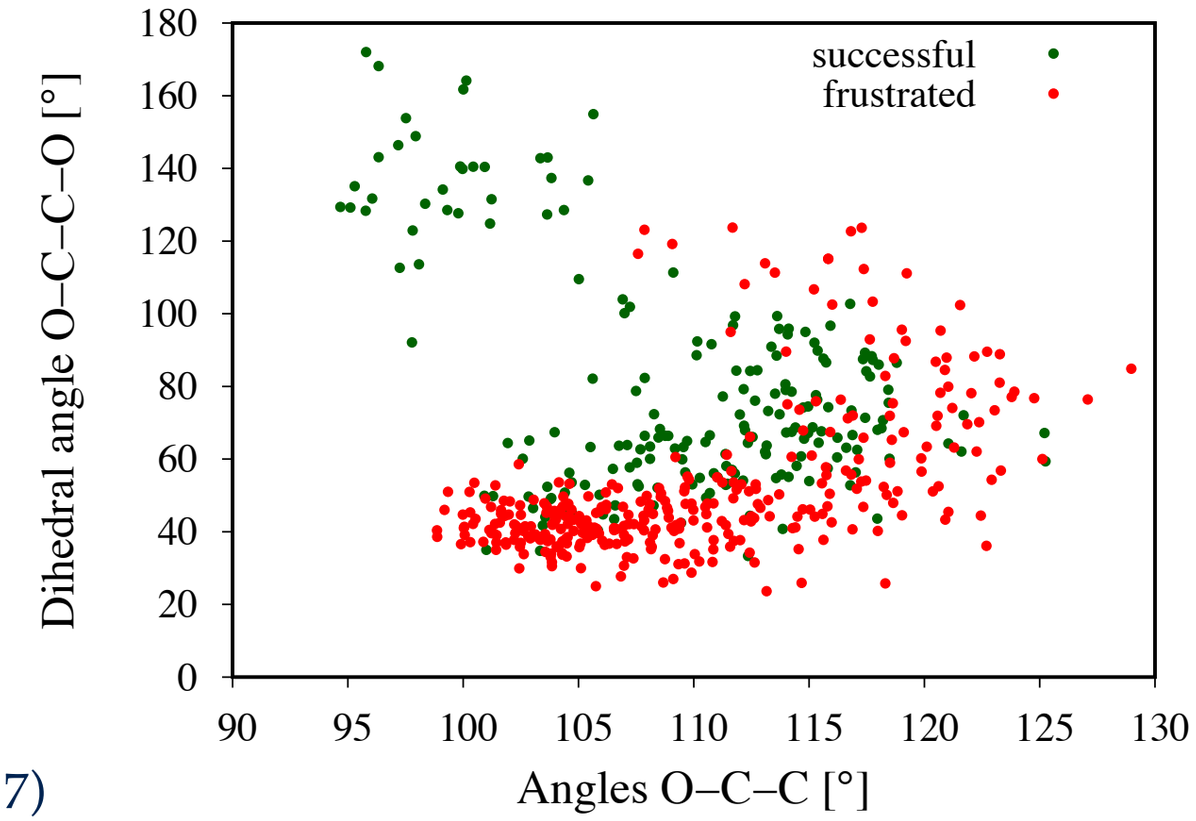




➜ Dissociation time scale
between t = 25 fs and t = 140 fs
half-time of 59 fs

➜ Geometrical conditions necessary



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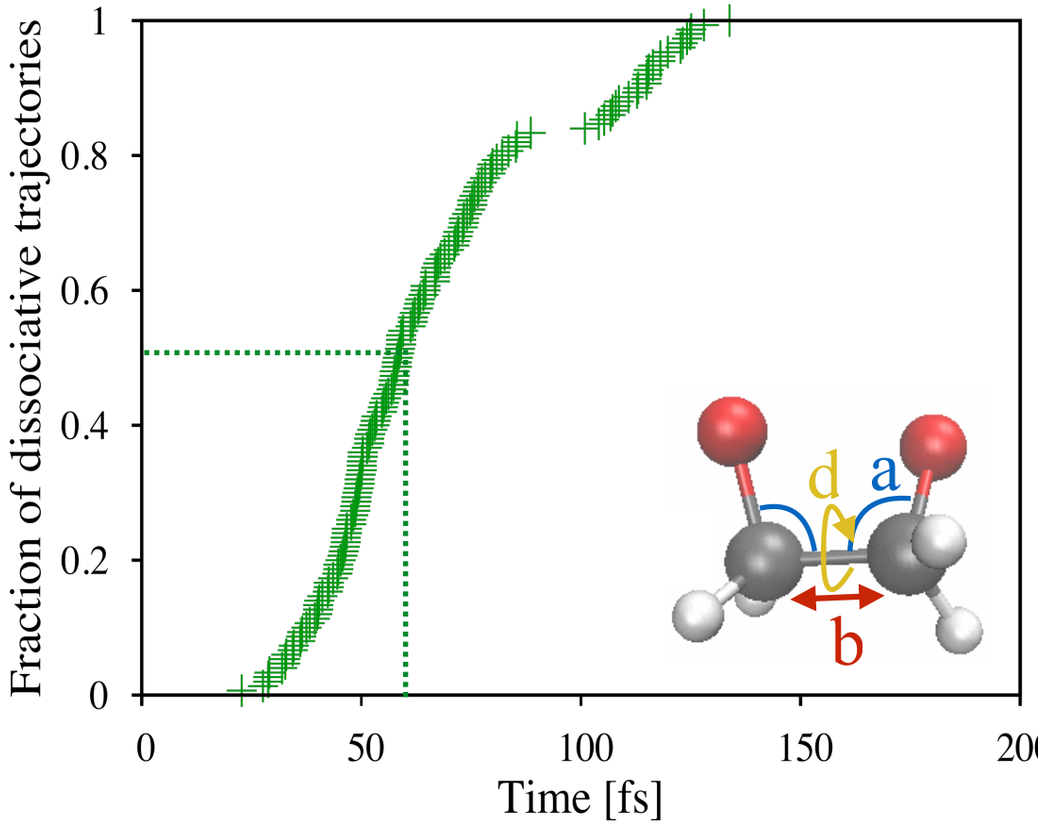
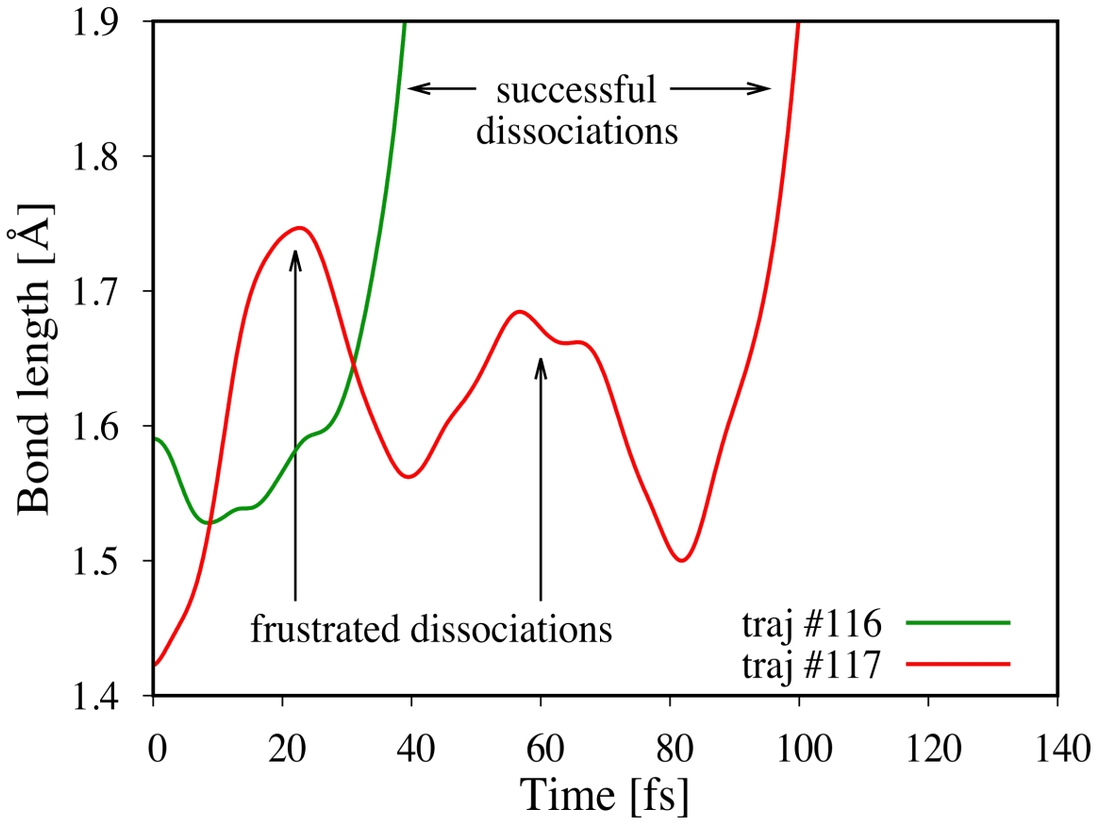
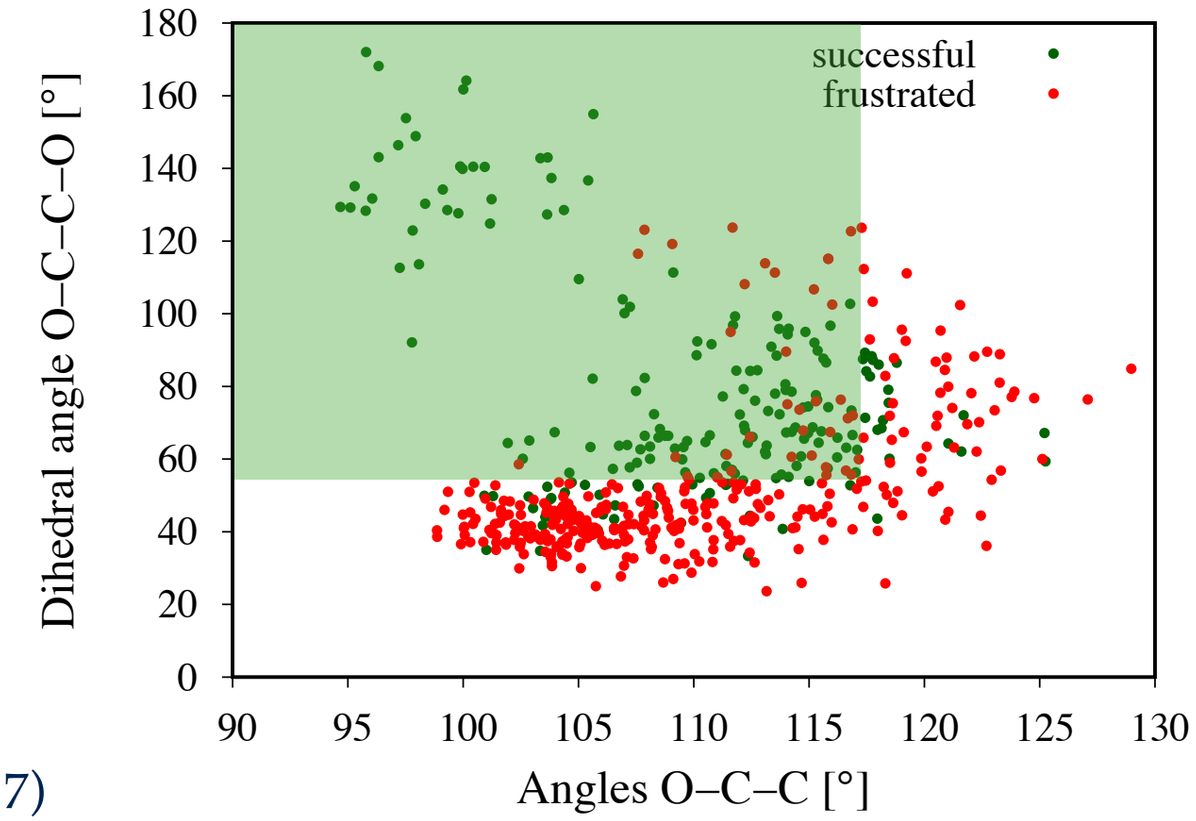




➜ Dissociation time scale
between t = 25 fs and t = 140 fs
half-time of 59 fs

➜ Geometrical conditions necessary
O-C-C-O dihedral > 55°
O-C-C angle < 117°



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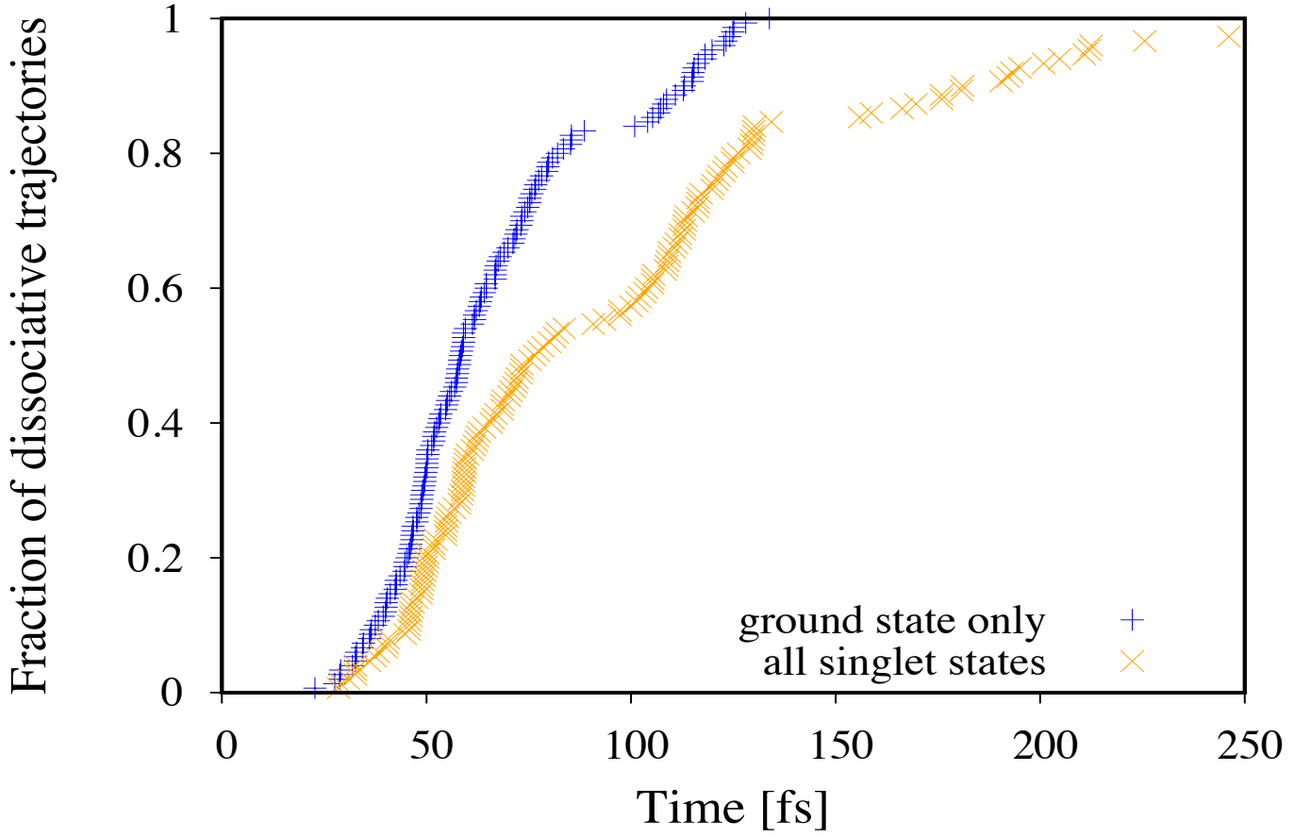
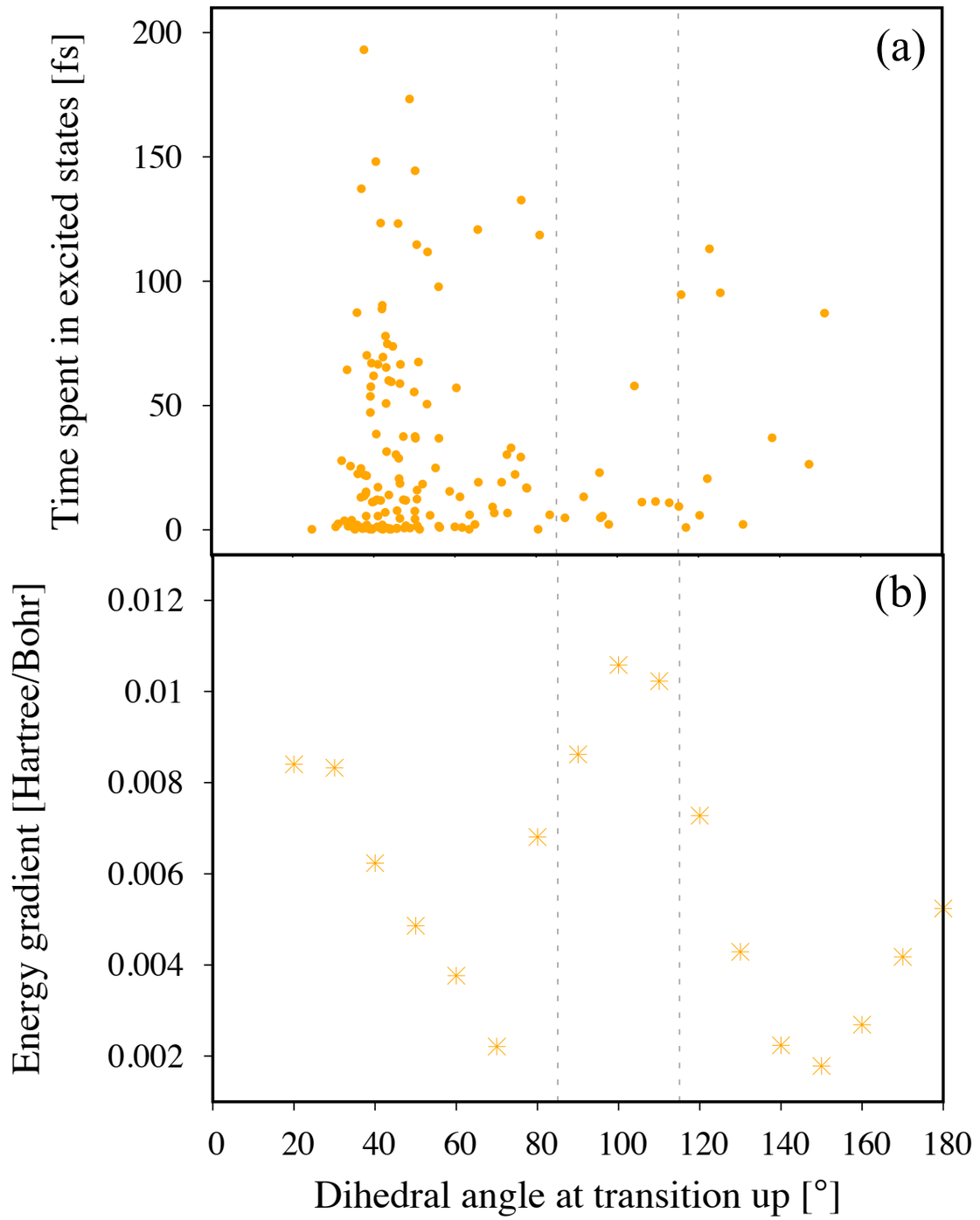
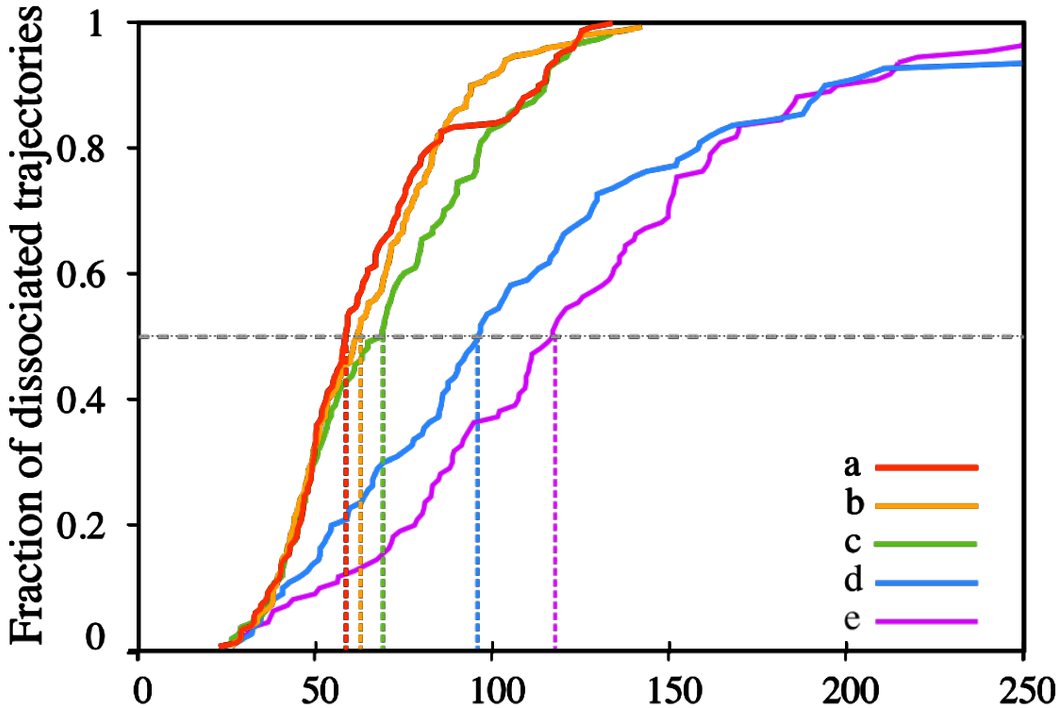
…with surface hopping dynamics

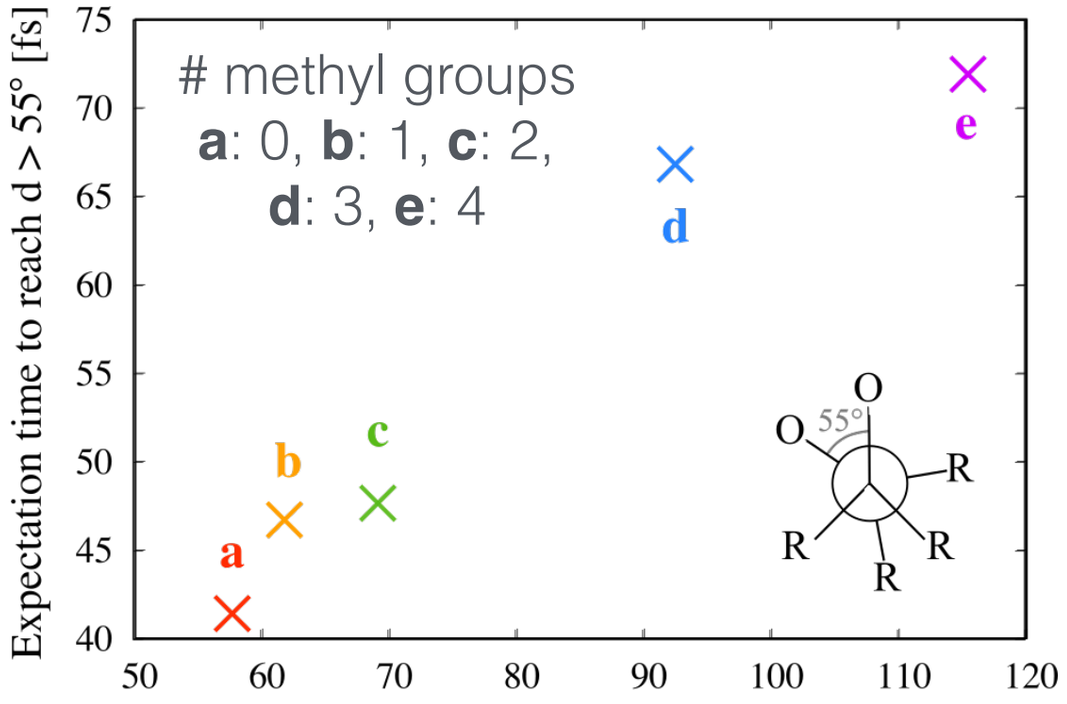


➜ The singlet excited states participate as well in the trapping of the molecule



Effect of methyl substitution

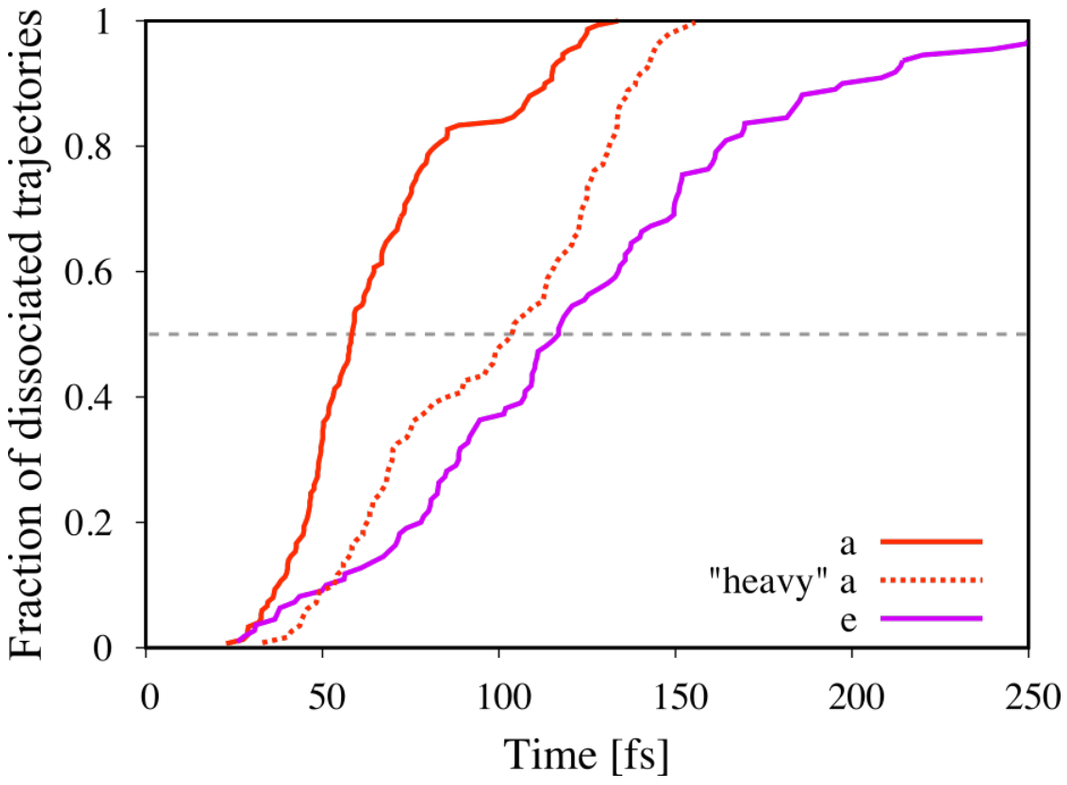




➜ Significant increase in the dissociation time scale upon methyl-substitution

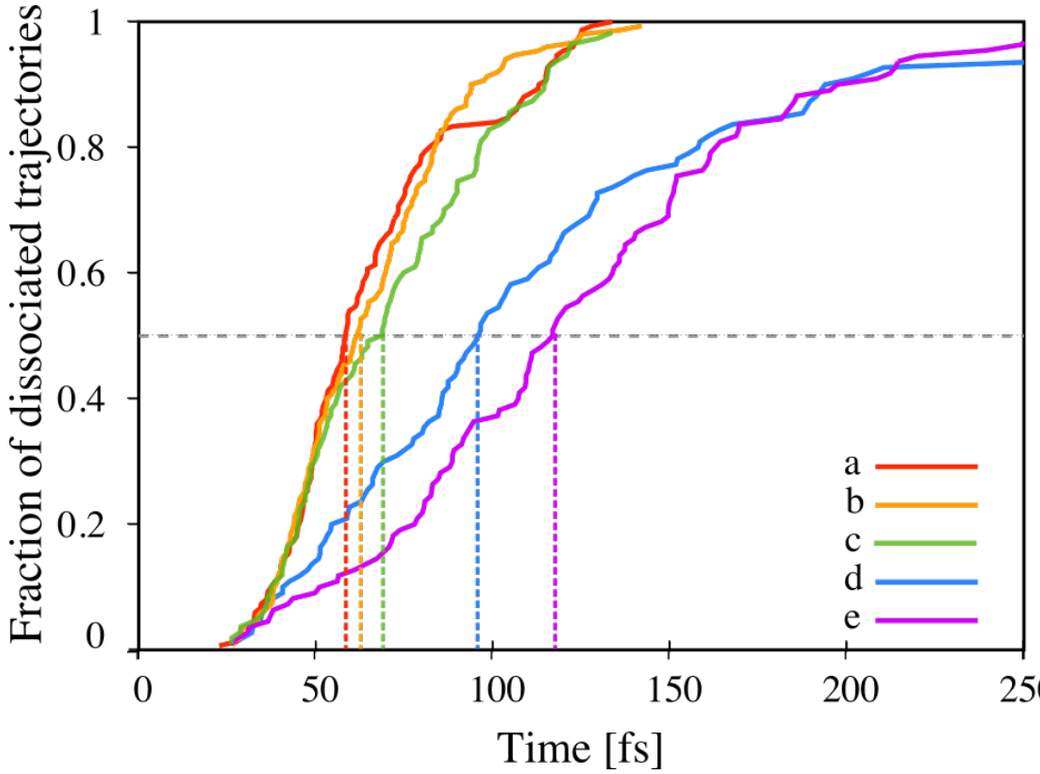
➜ Mostly due to a pure mass effect

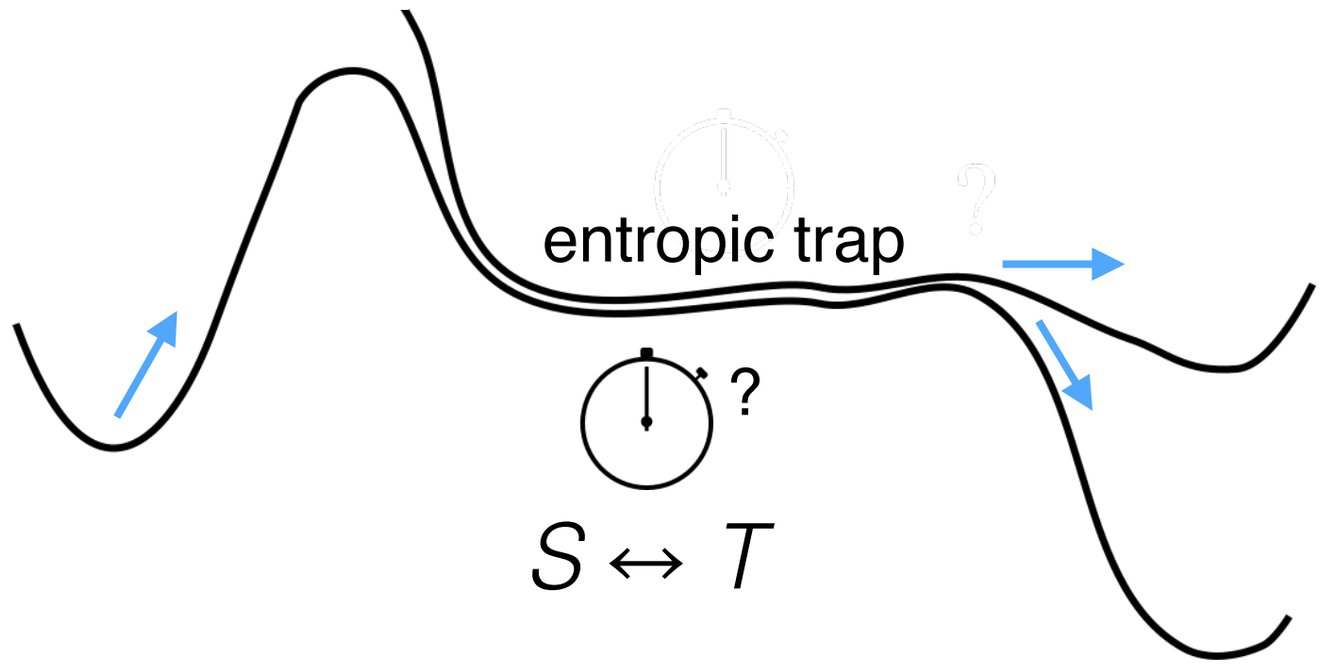
➜ Rotation around the O-C-C-O dihedral angle slowed down



Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution

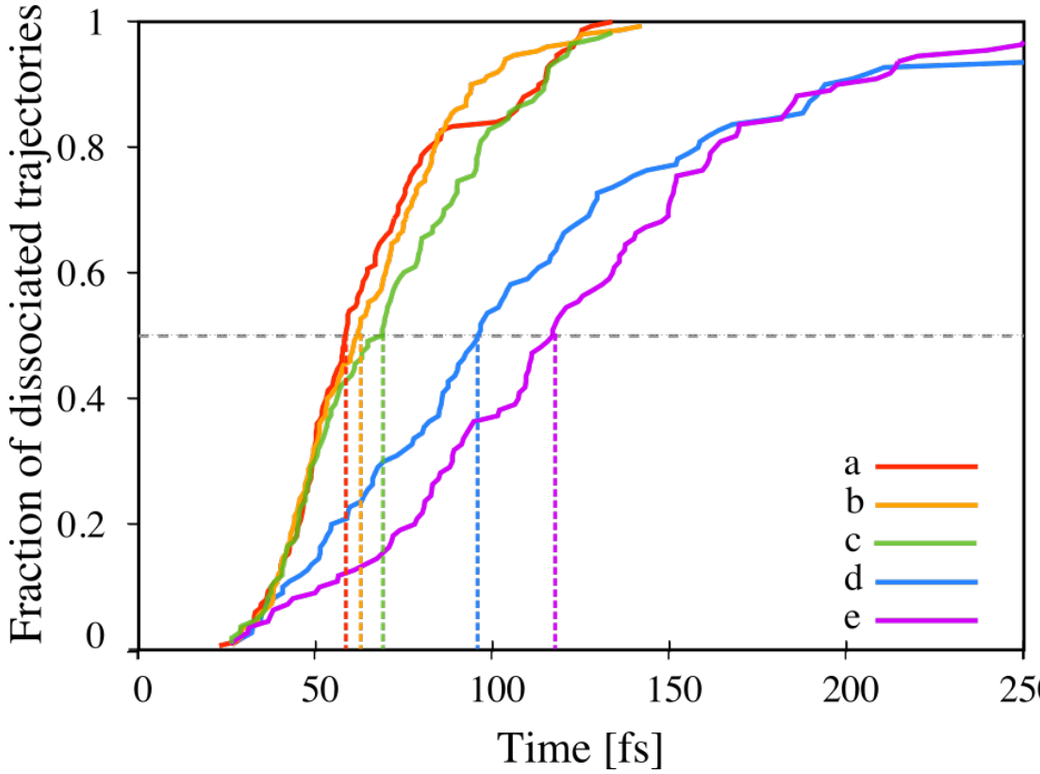


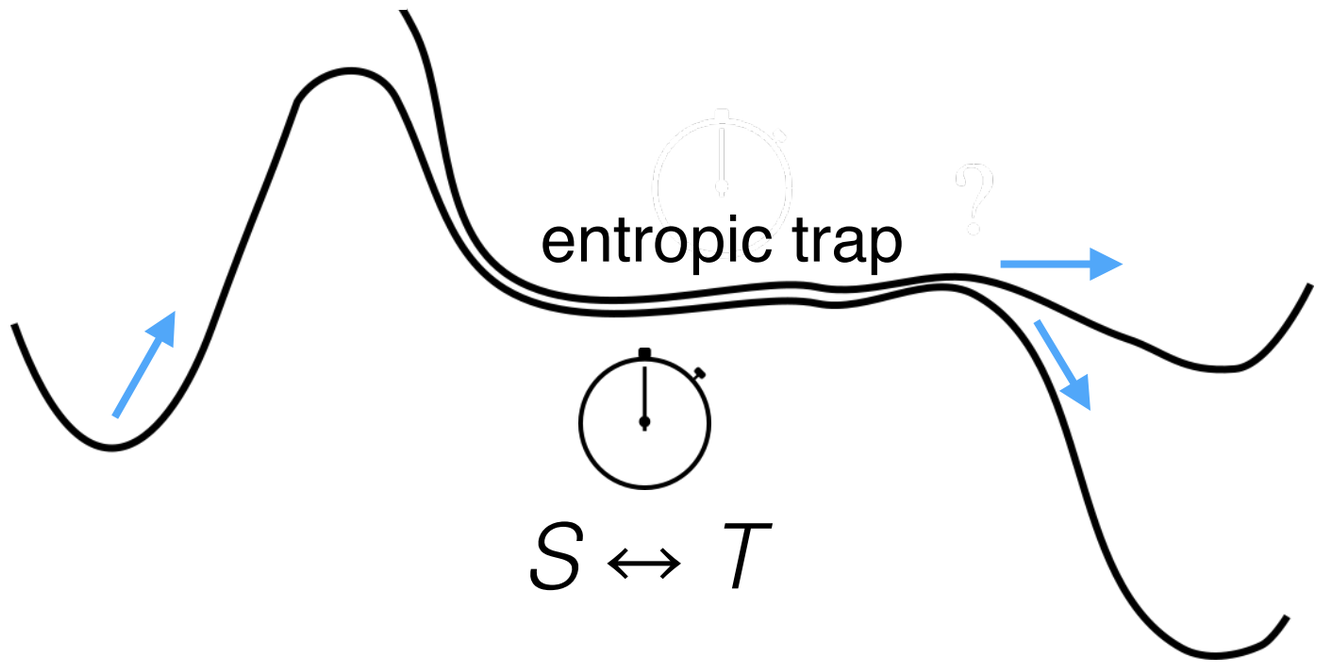


➜ The longer the system stays in the entropic trap, the more population is transferred from *S* to *T* and the higher the chemiexcitation yield is.

Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution





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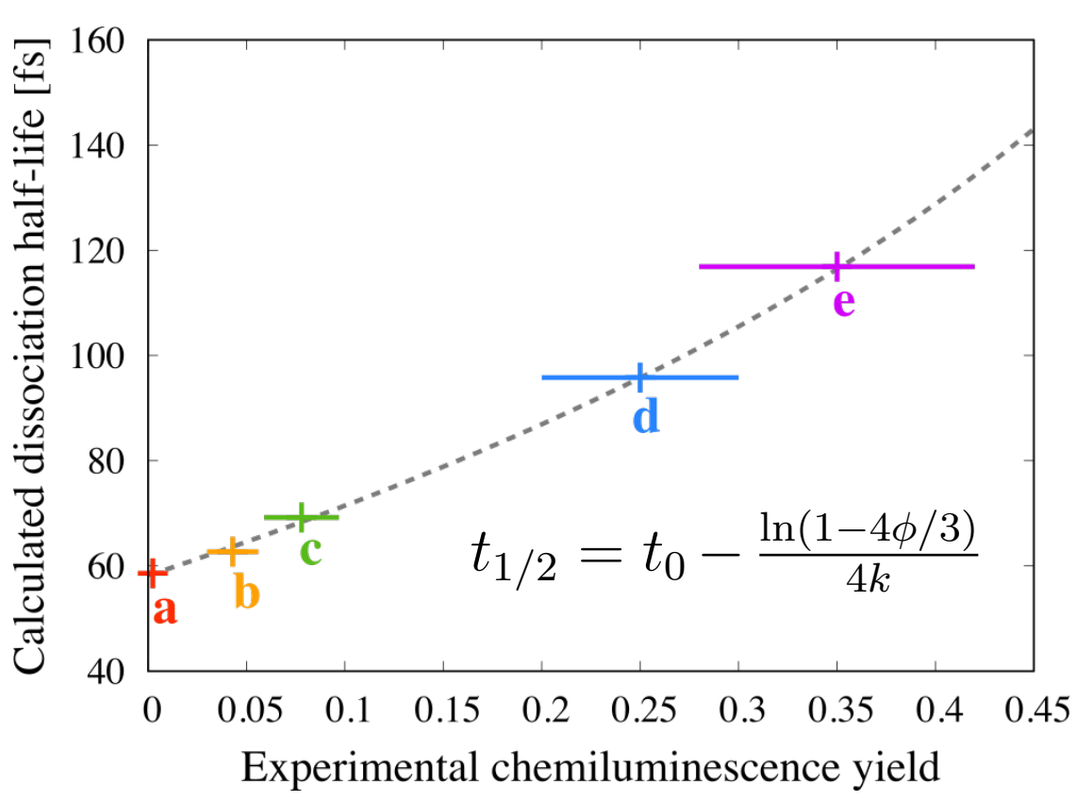

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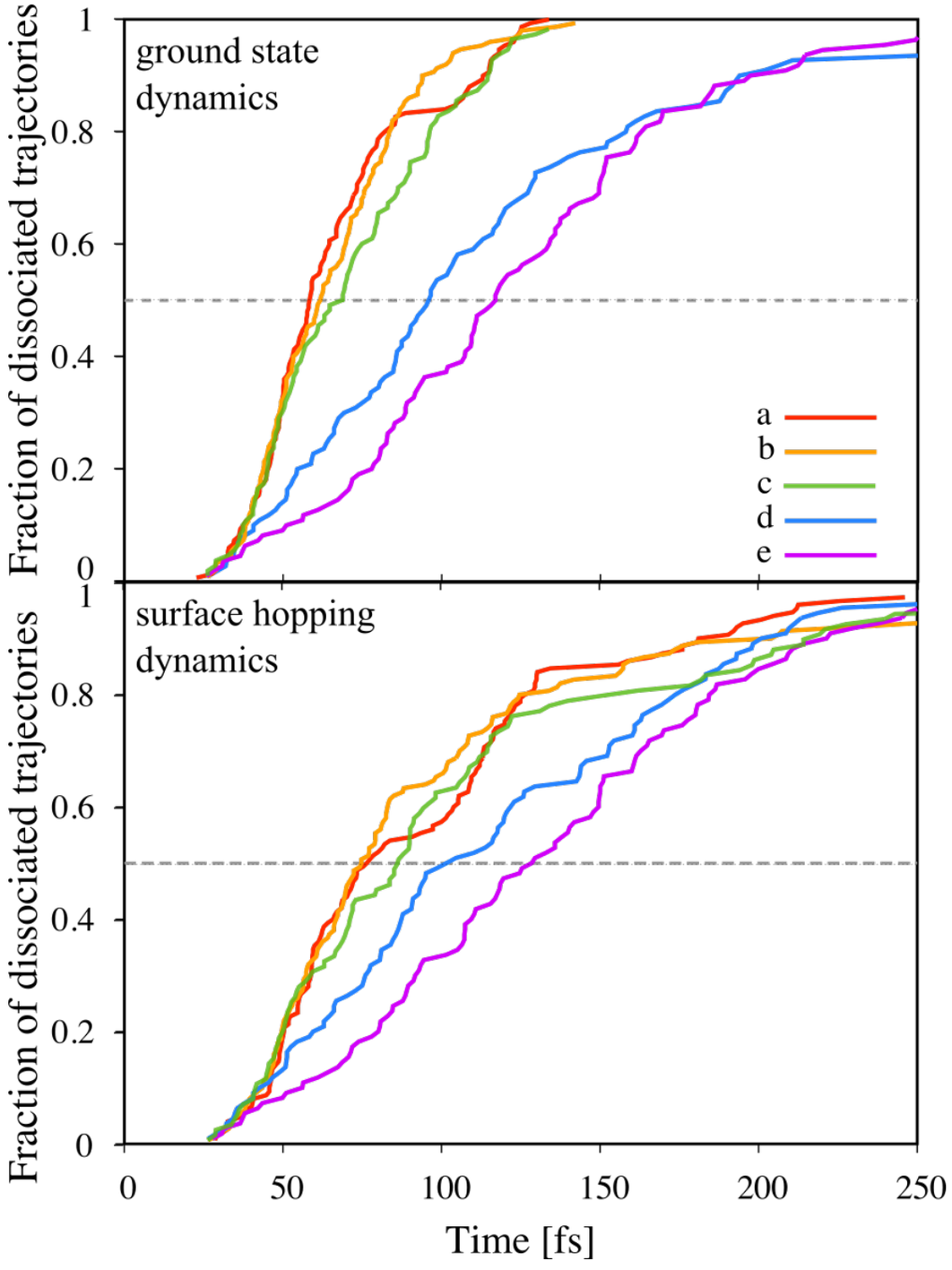
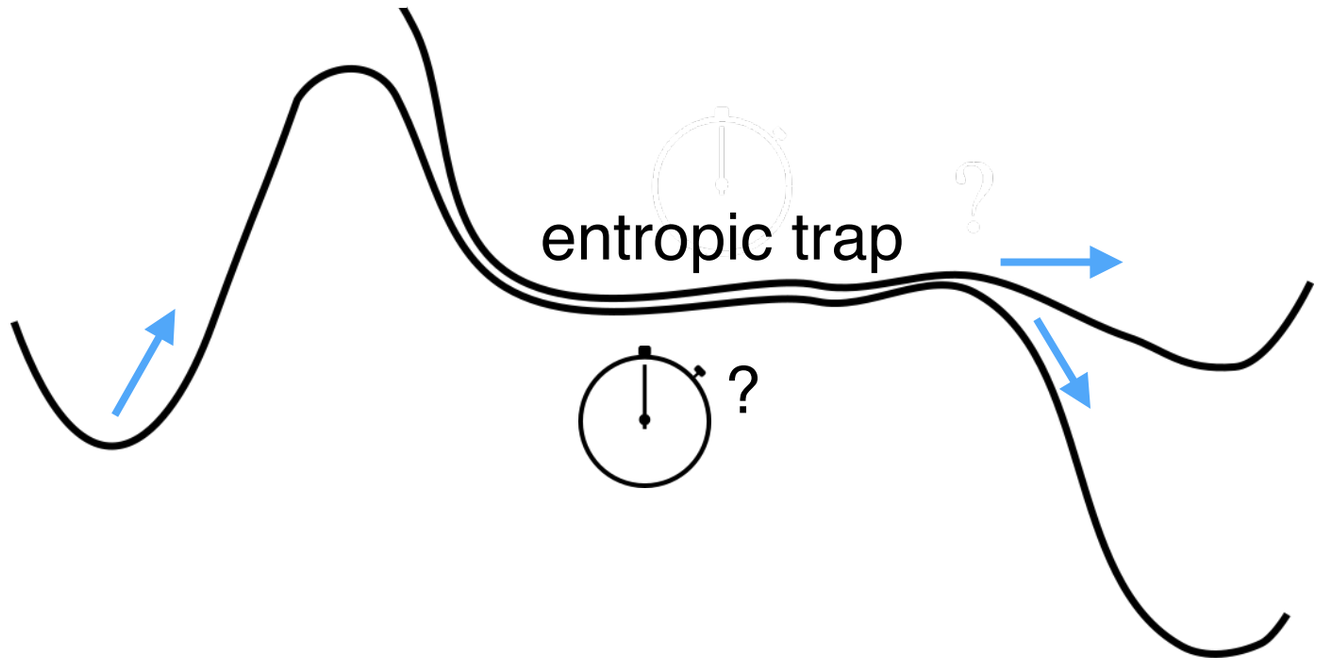
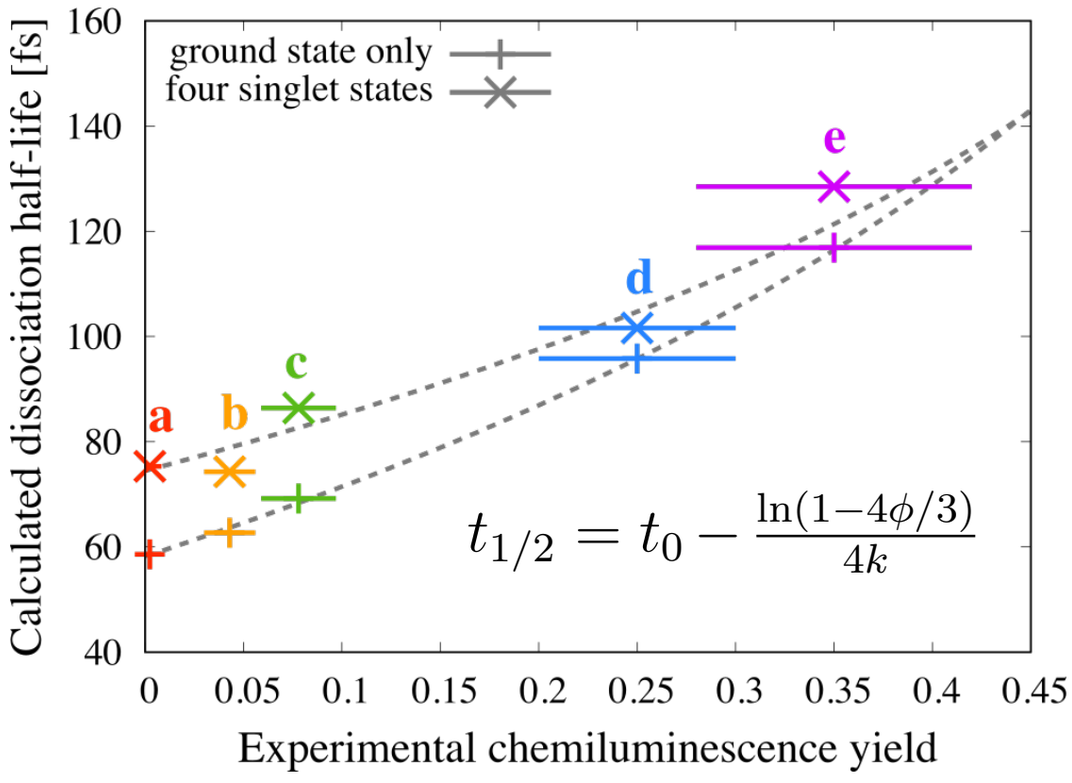
Effect of methyl substitution







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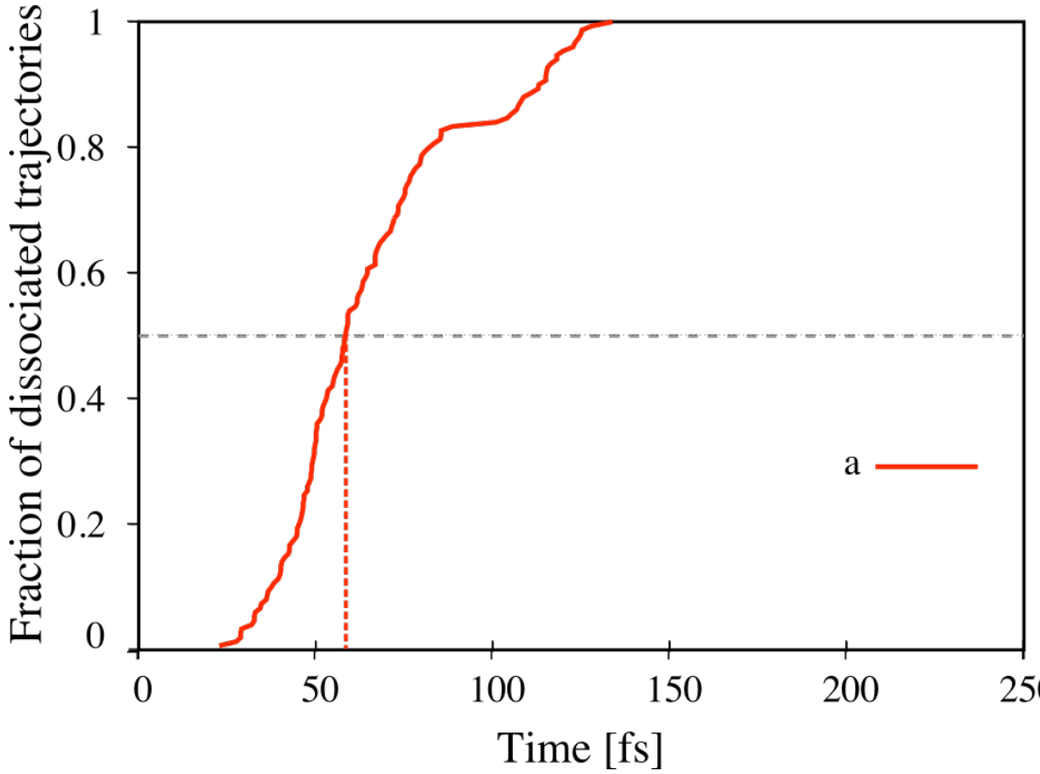
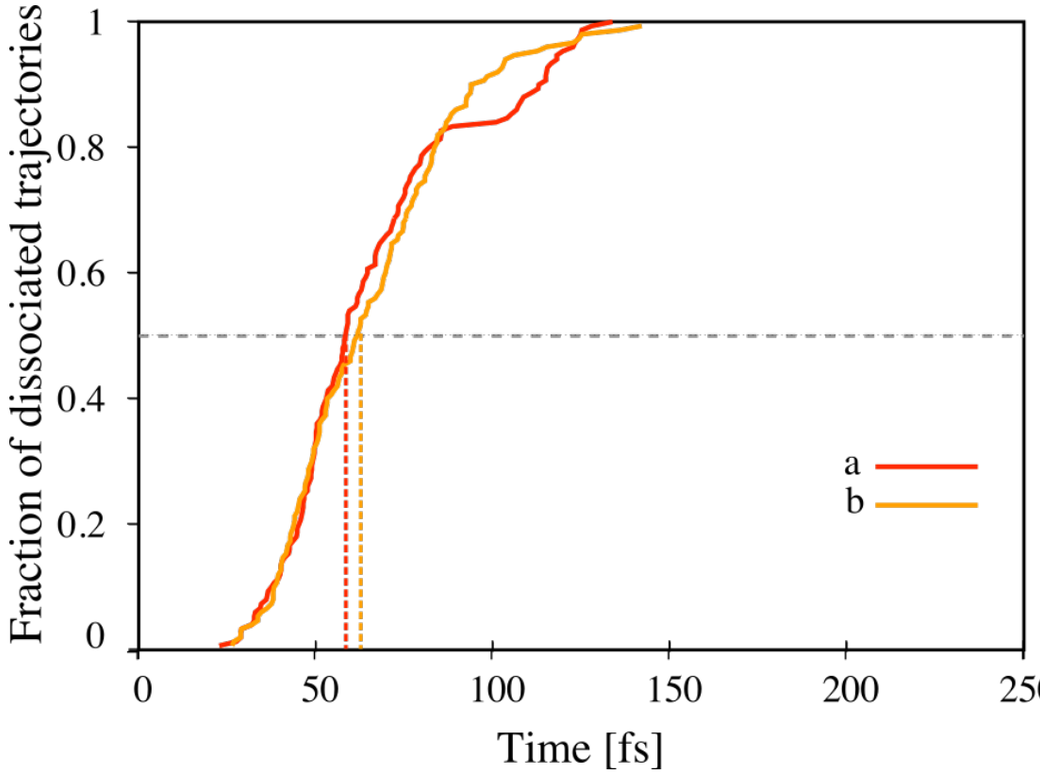
Effect of methyl substitution



methyl groups
a: 0, **b**: 1, **c**: 2,
d: 3, **e**: 4

Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution



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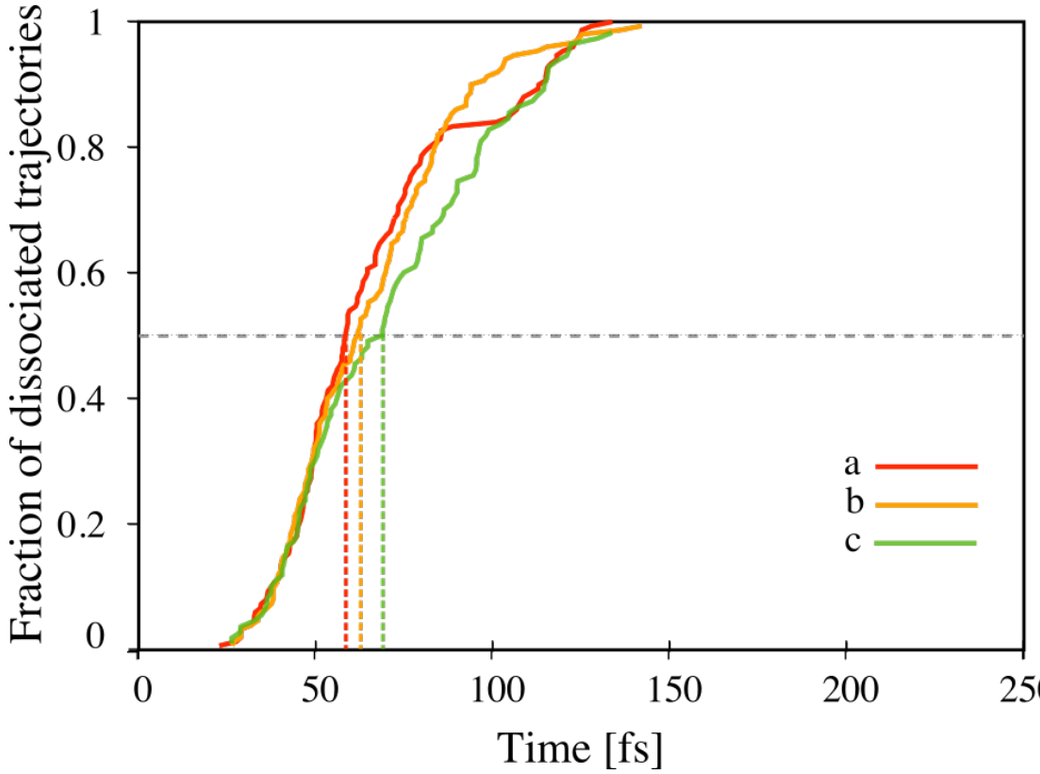
Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution



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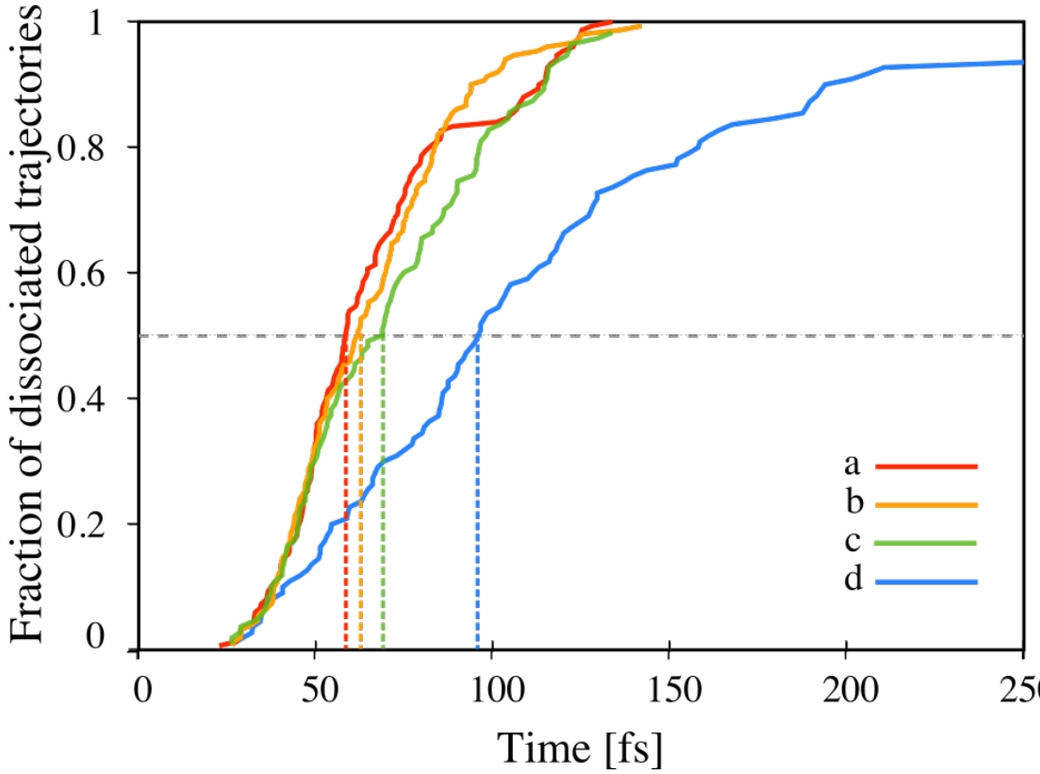

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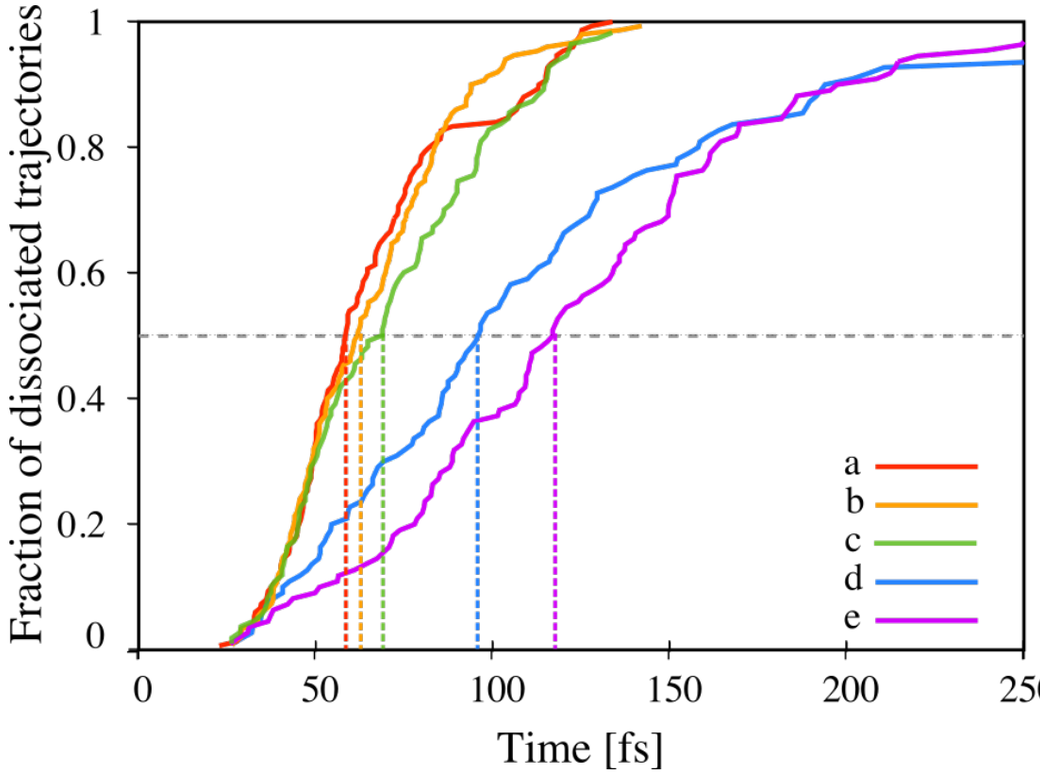
Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution

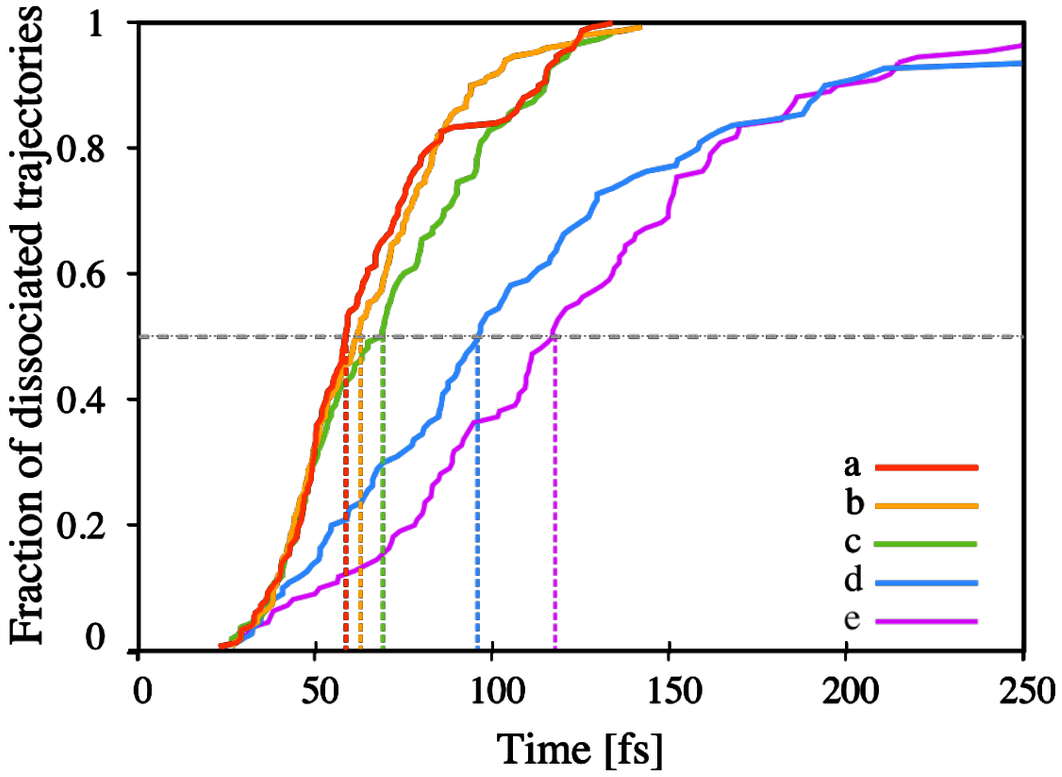


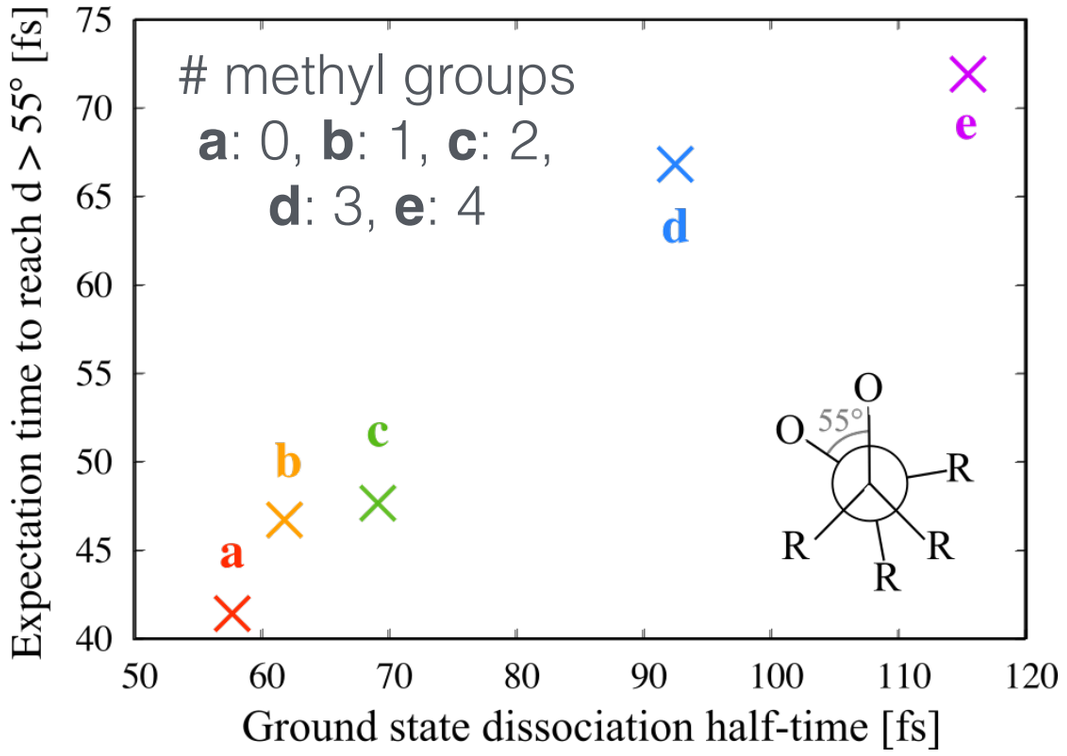
methyl groups
a: 0, **b**: 1, **c**: 2,
d: 3, **e**: 4

➜ Significant increase in the dissociation time scale upon methyl-substitution

Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution

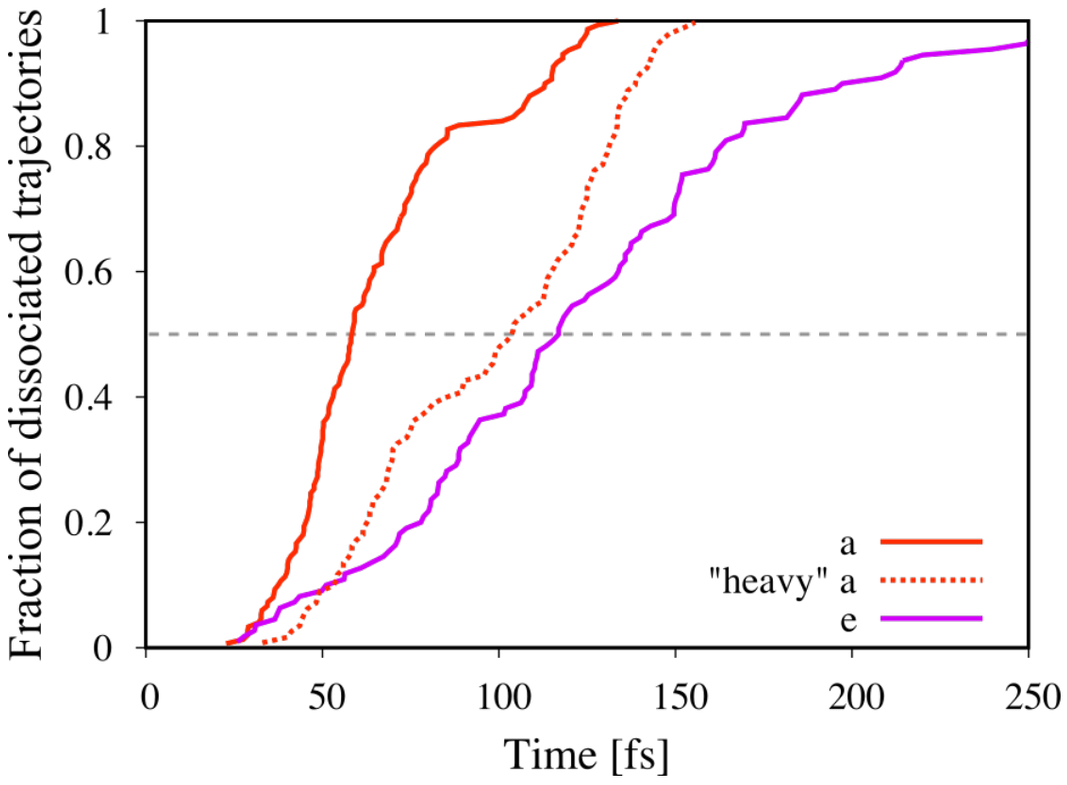




➜ Significant increase in the dissociation time scale upon methyl-substitution

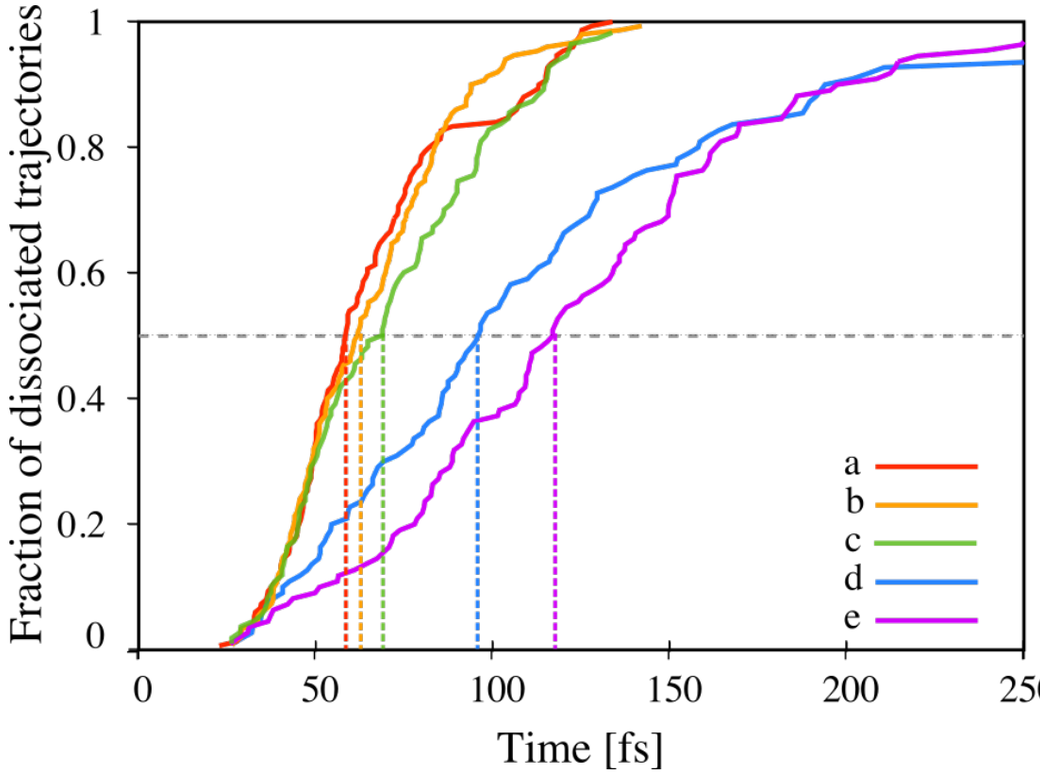
➜ Mostly due to a pure mass effect

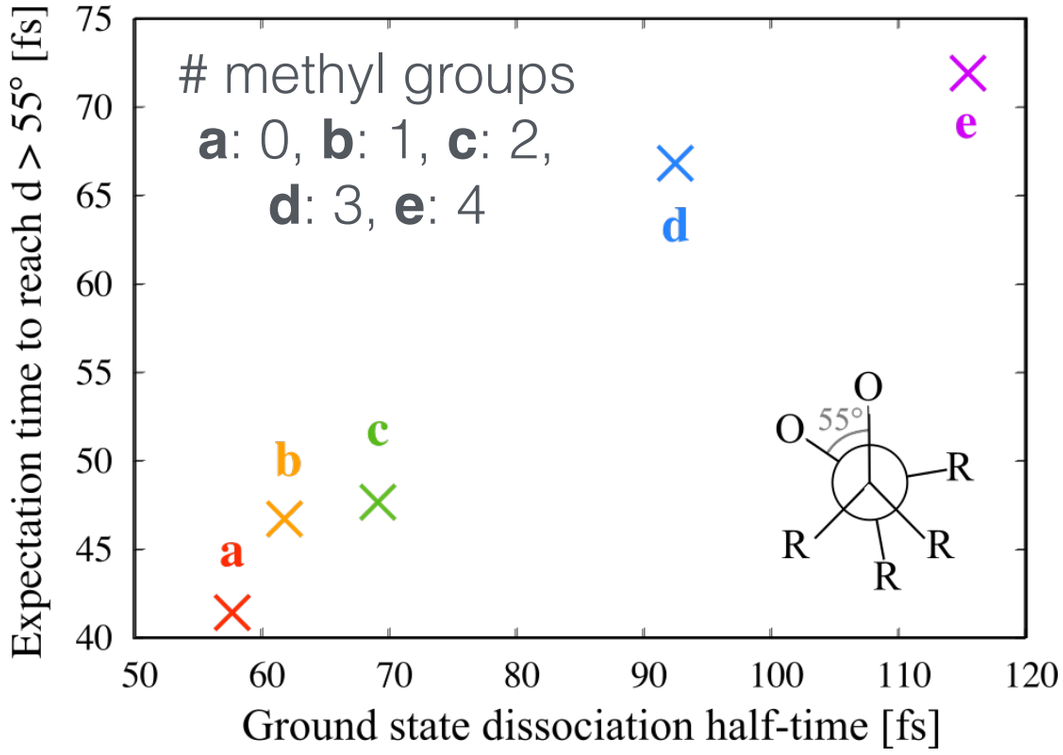
➜ Rotation around the O-C-C-O dihedral angle slowed down



Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution



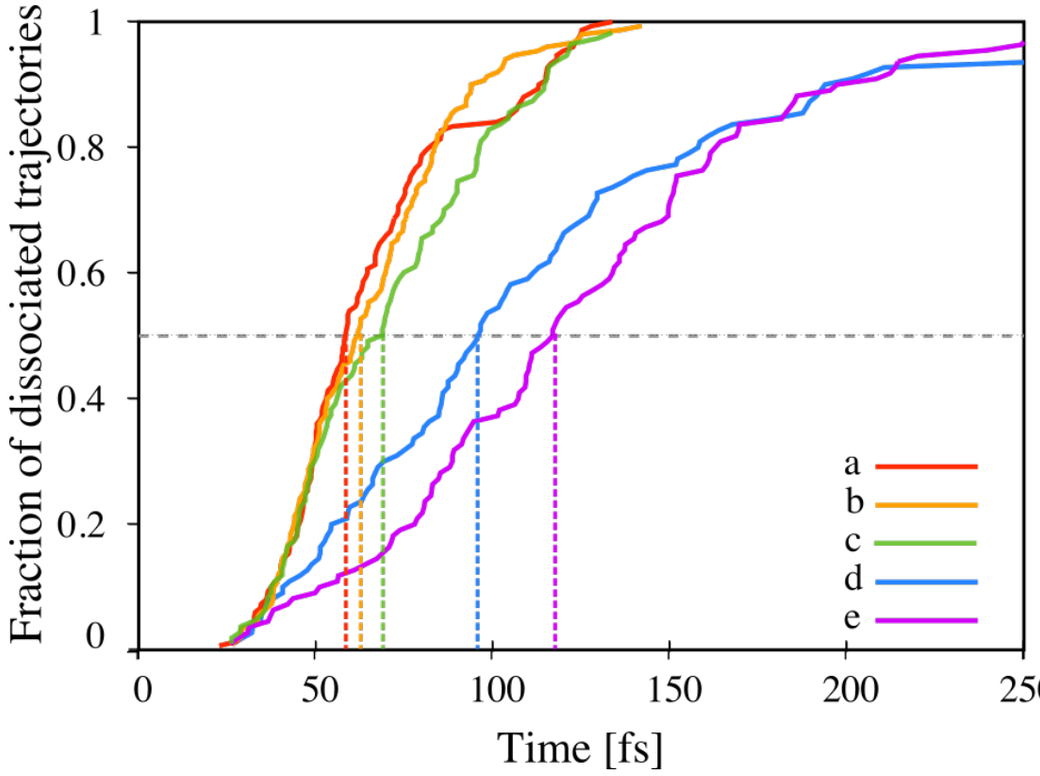


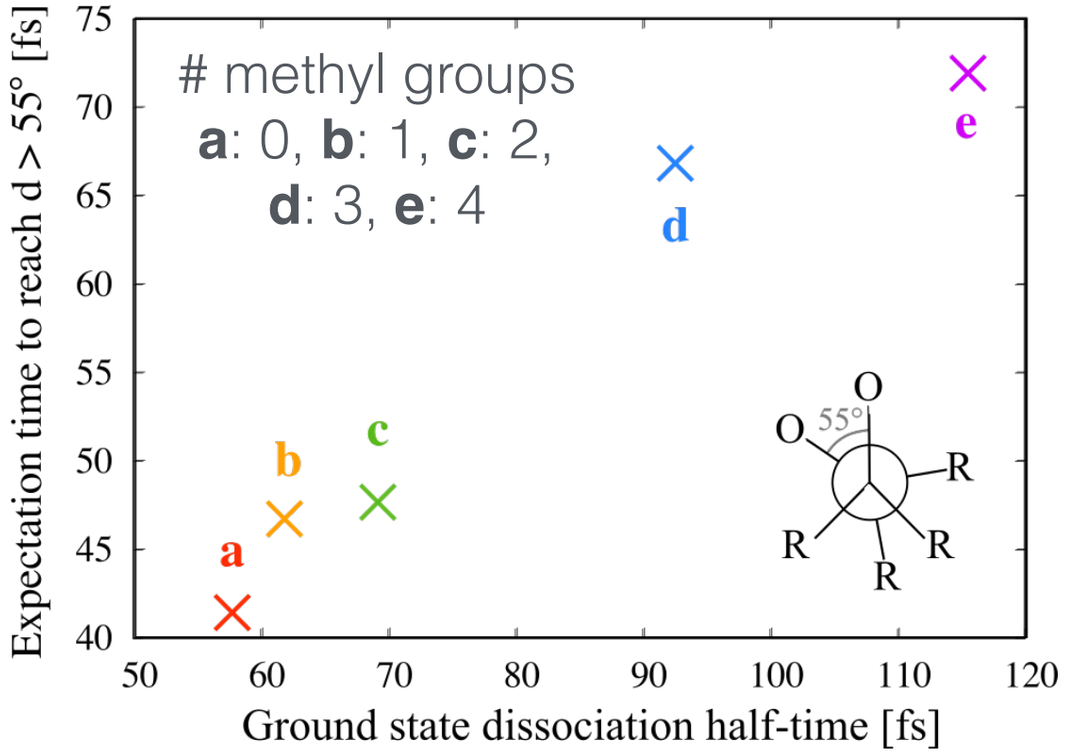
➜ Significant increase in the dissociation time scale upon methyl-substitution

➜ Rotation around the O-C-C-O dihedral angle slowed down

Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Effect of methyl substitution

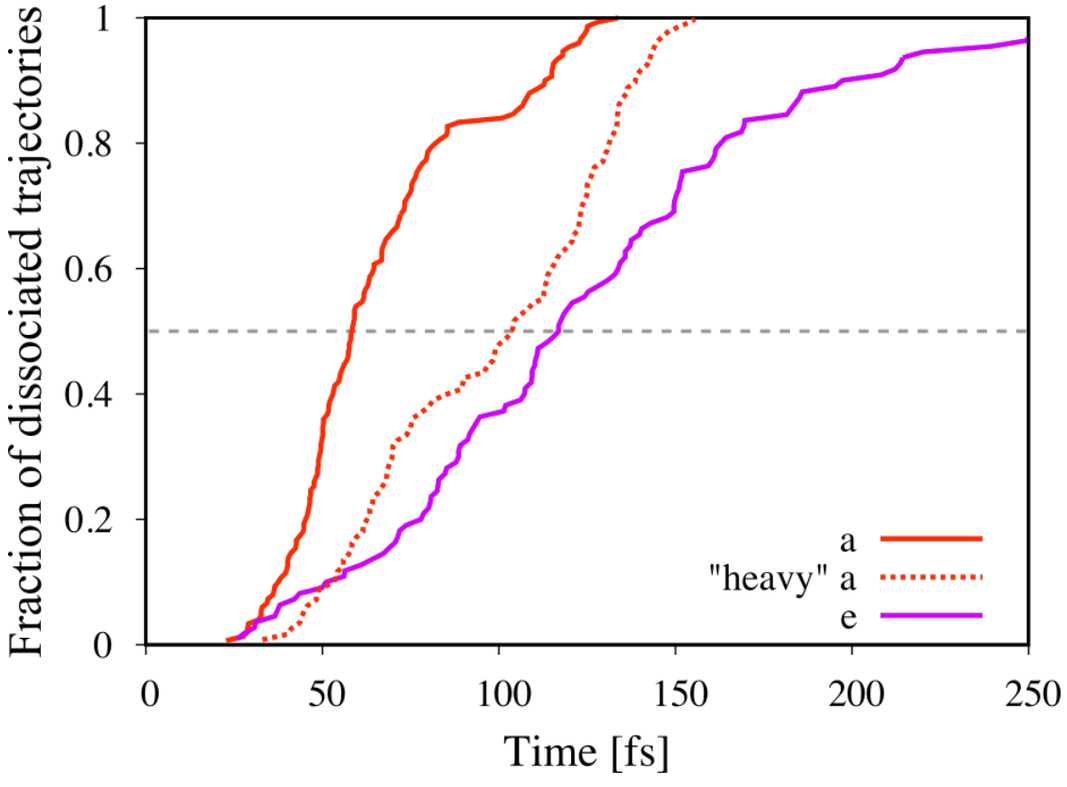




➜ Significant increase in the dissociation time scale upon methyl-substitution

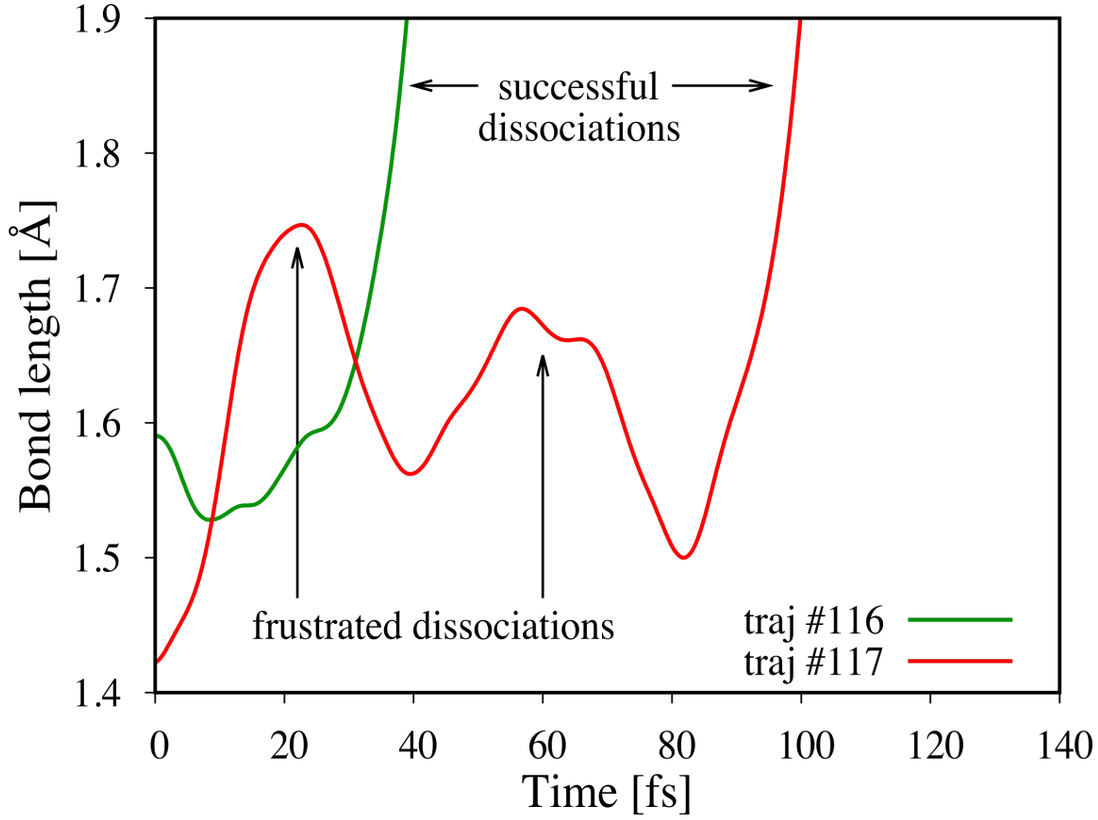
➜ Rotation around the O-C-C-O dihedral angle slowed down

➜ Partly due to a pure mass effect



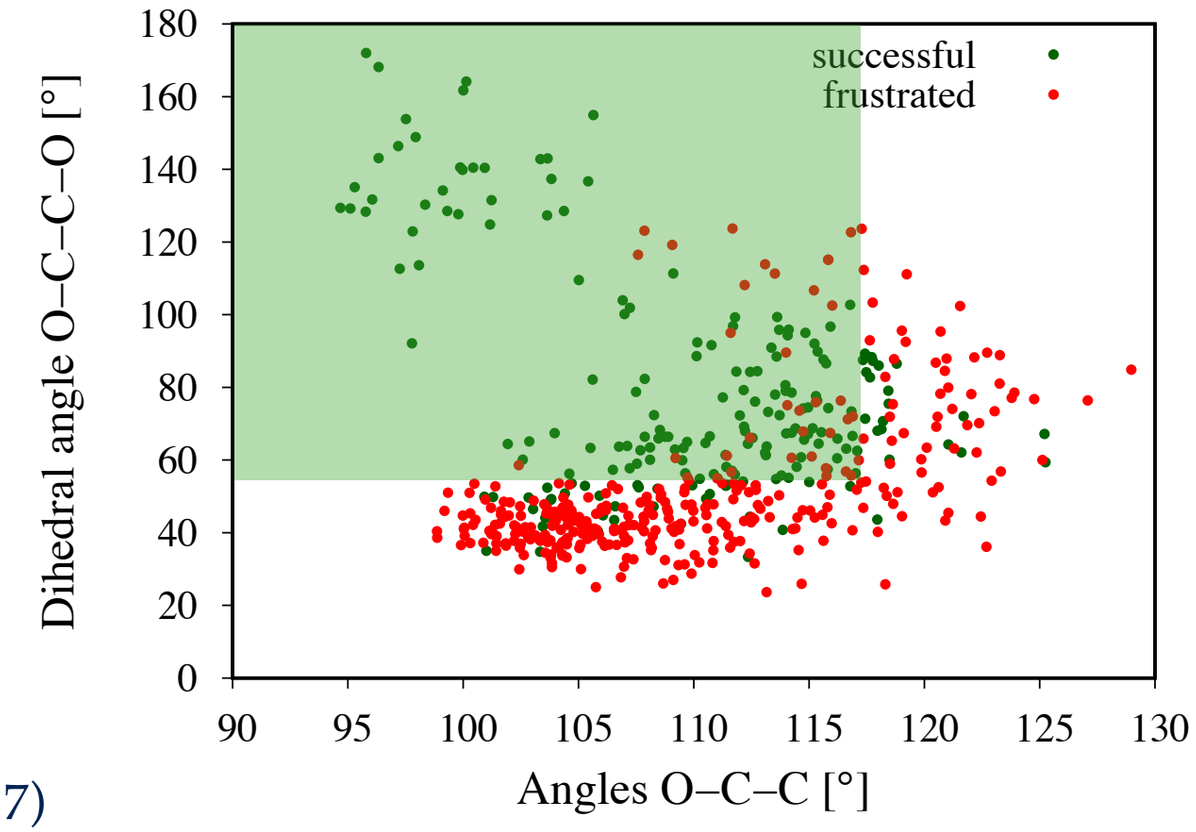
Vacher et al, *J. Phys. Chem. Letters*, **8** , 3790-3794 (2017)

Finding relevant nuclear coordinate



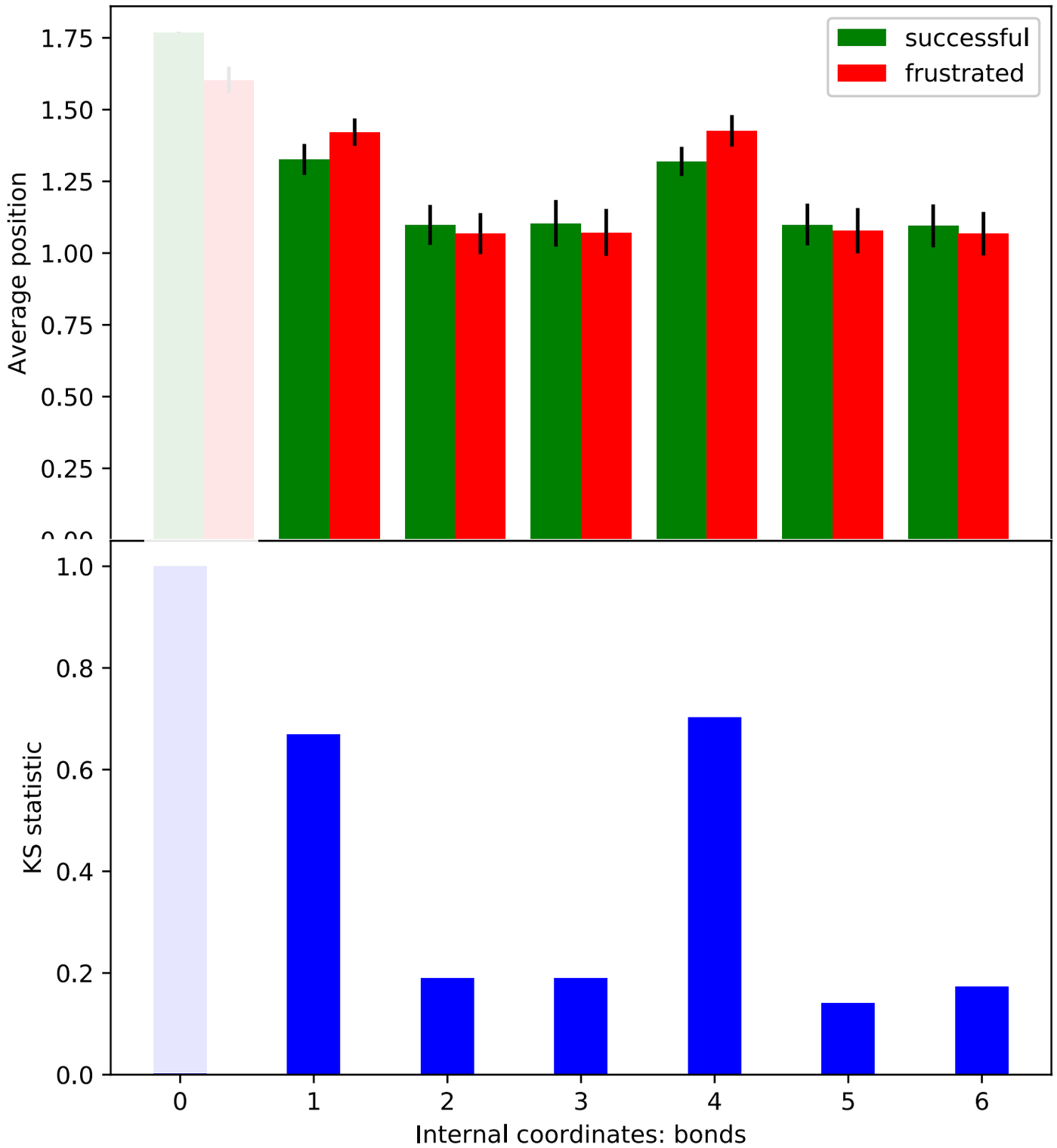
Geometrical conditions necessary to escape the entropic trap:

- O-C-C-O dihedral > 55°
- O-C-C angle < 117°

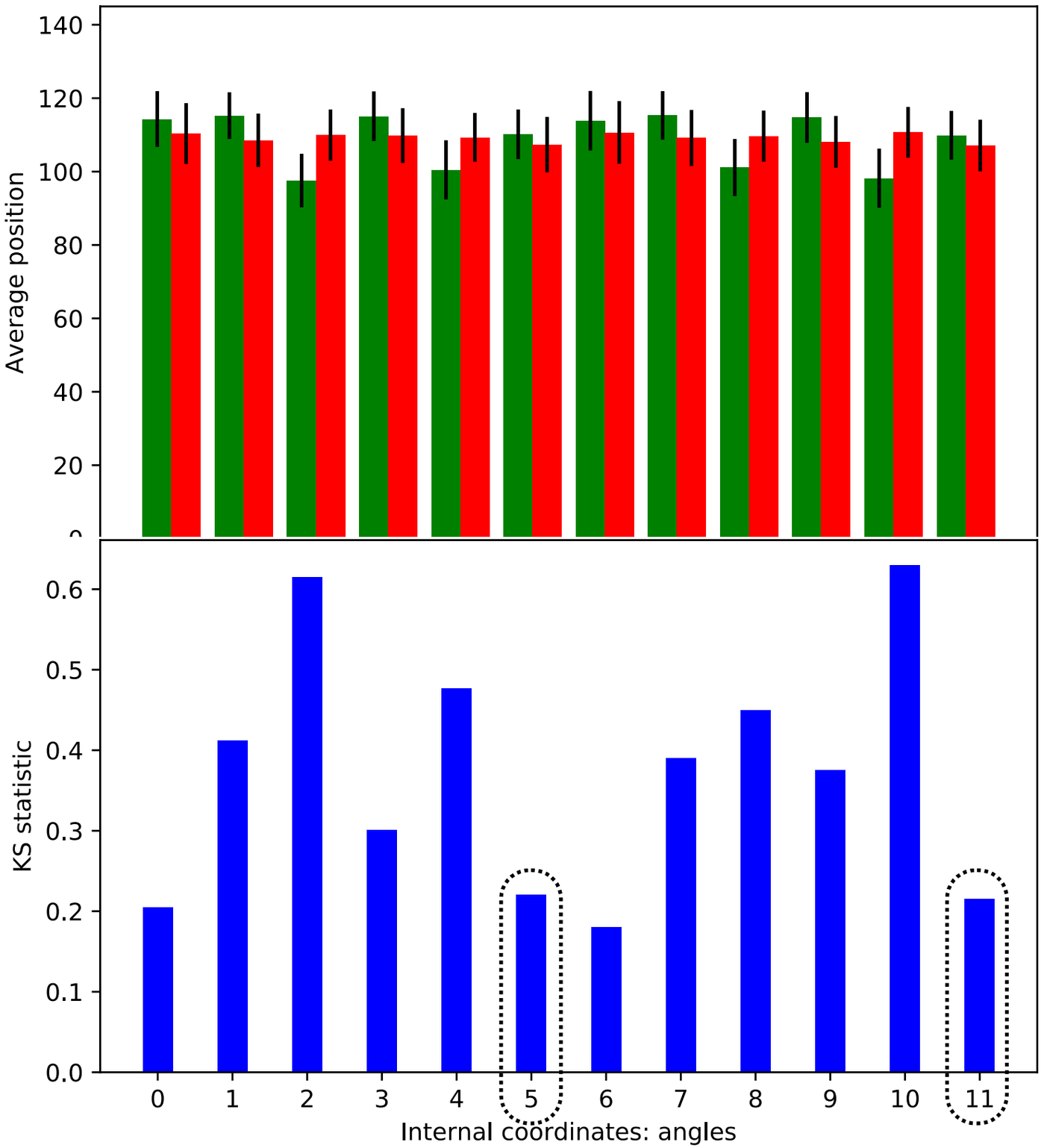


Vacher et al, *J. Chem. Theory Comput.*, **13** (6), 2448-2457 (2017)

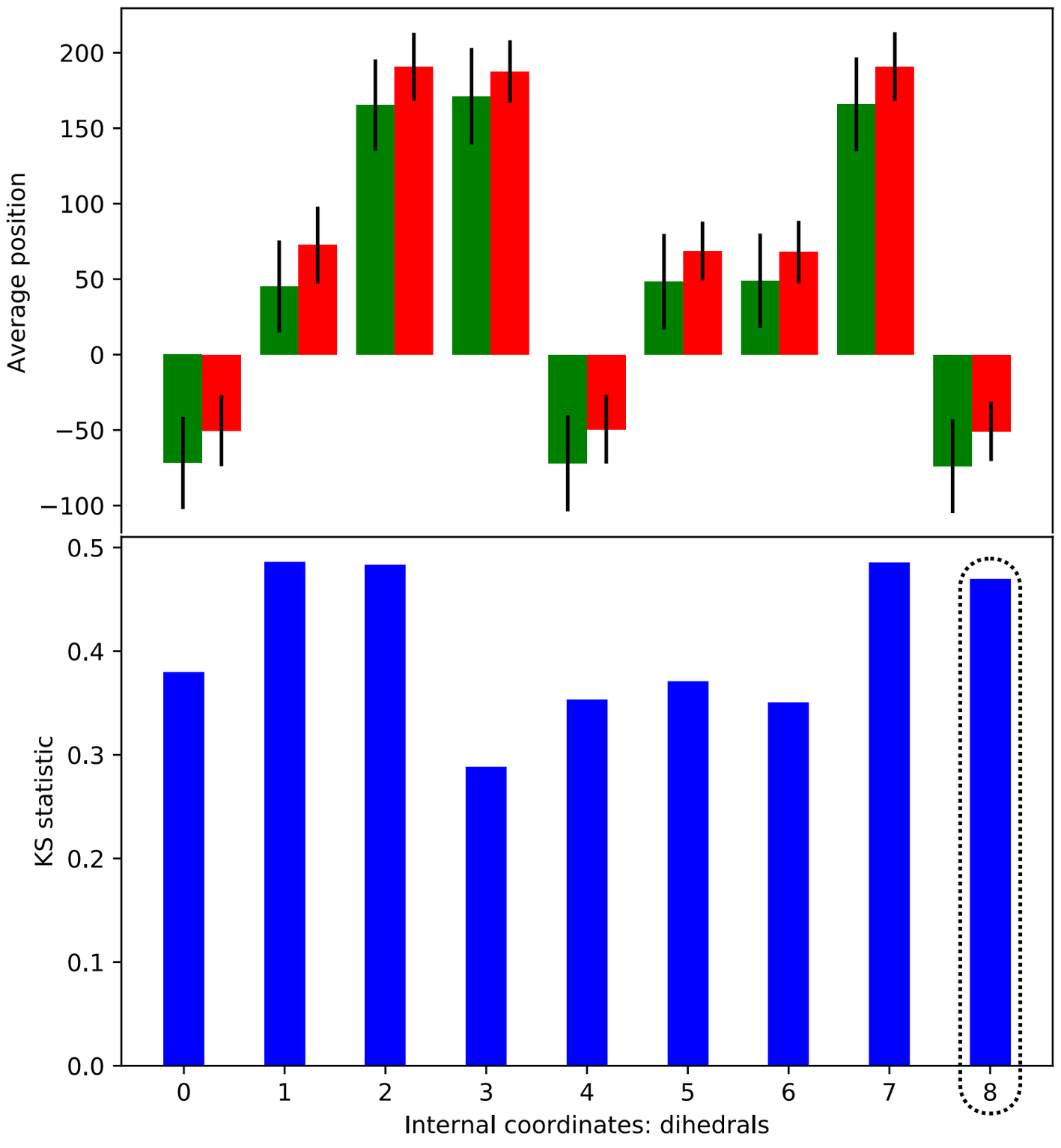
Finding relevant nuclear coordinate



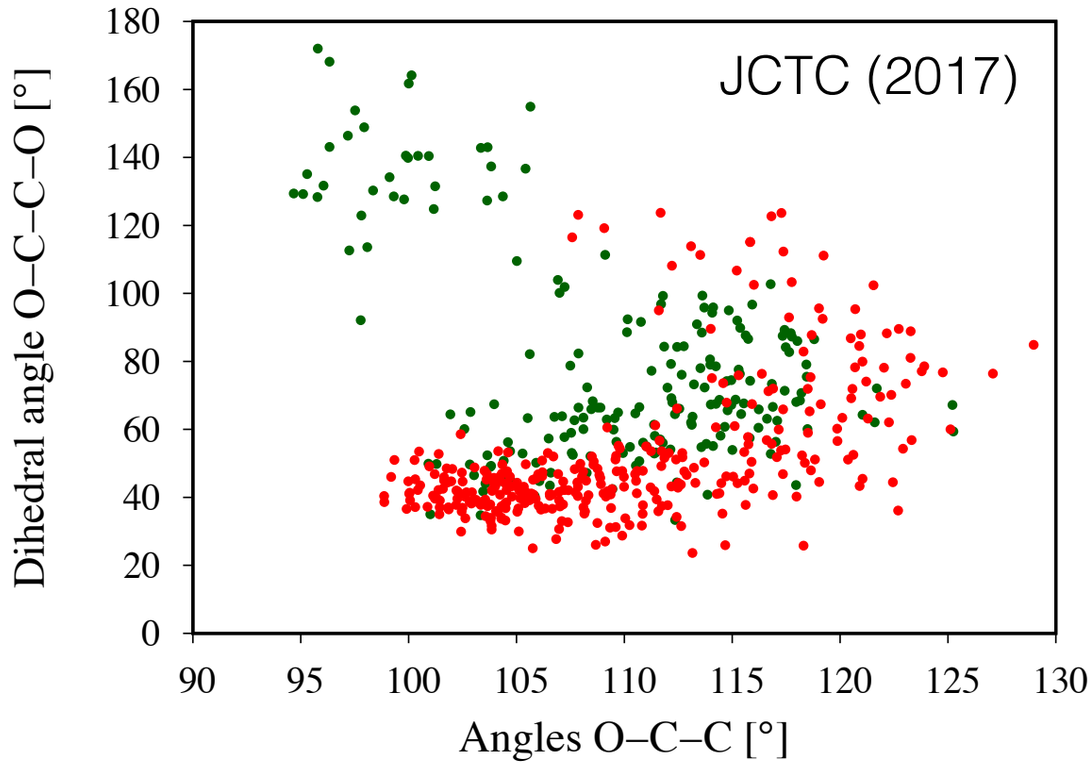
Finding relevant nuclear coordinate



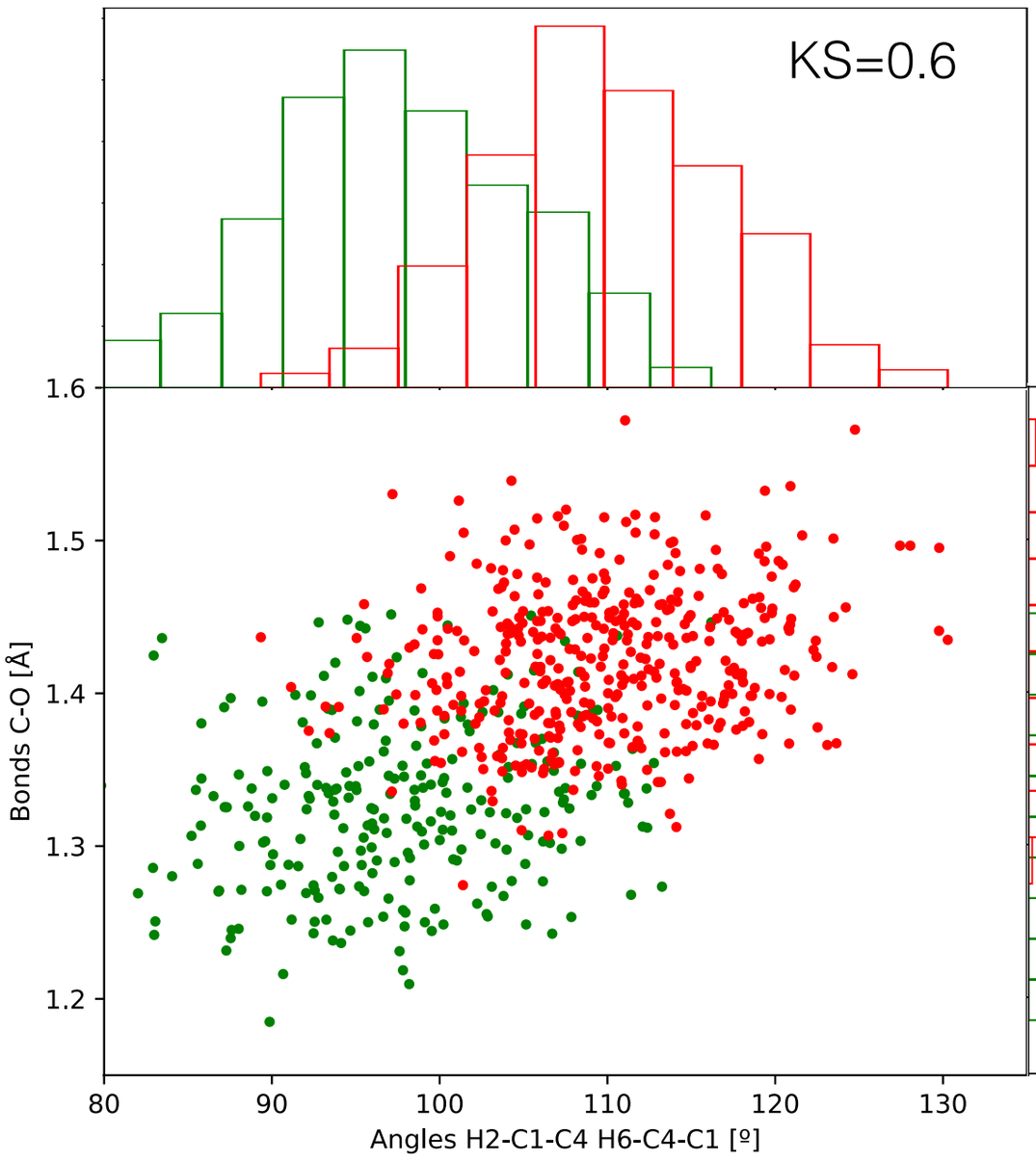
Finding relevant nuclear coordinate

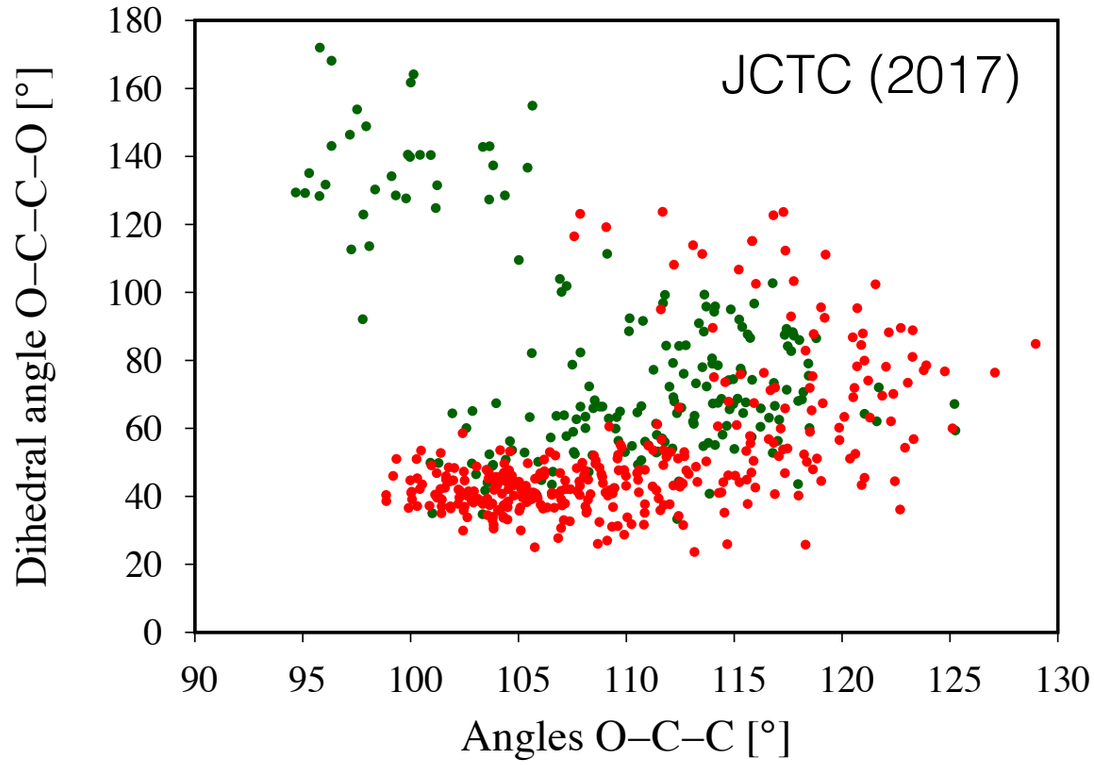


Finding relevant nuclear coordinate

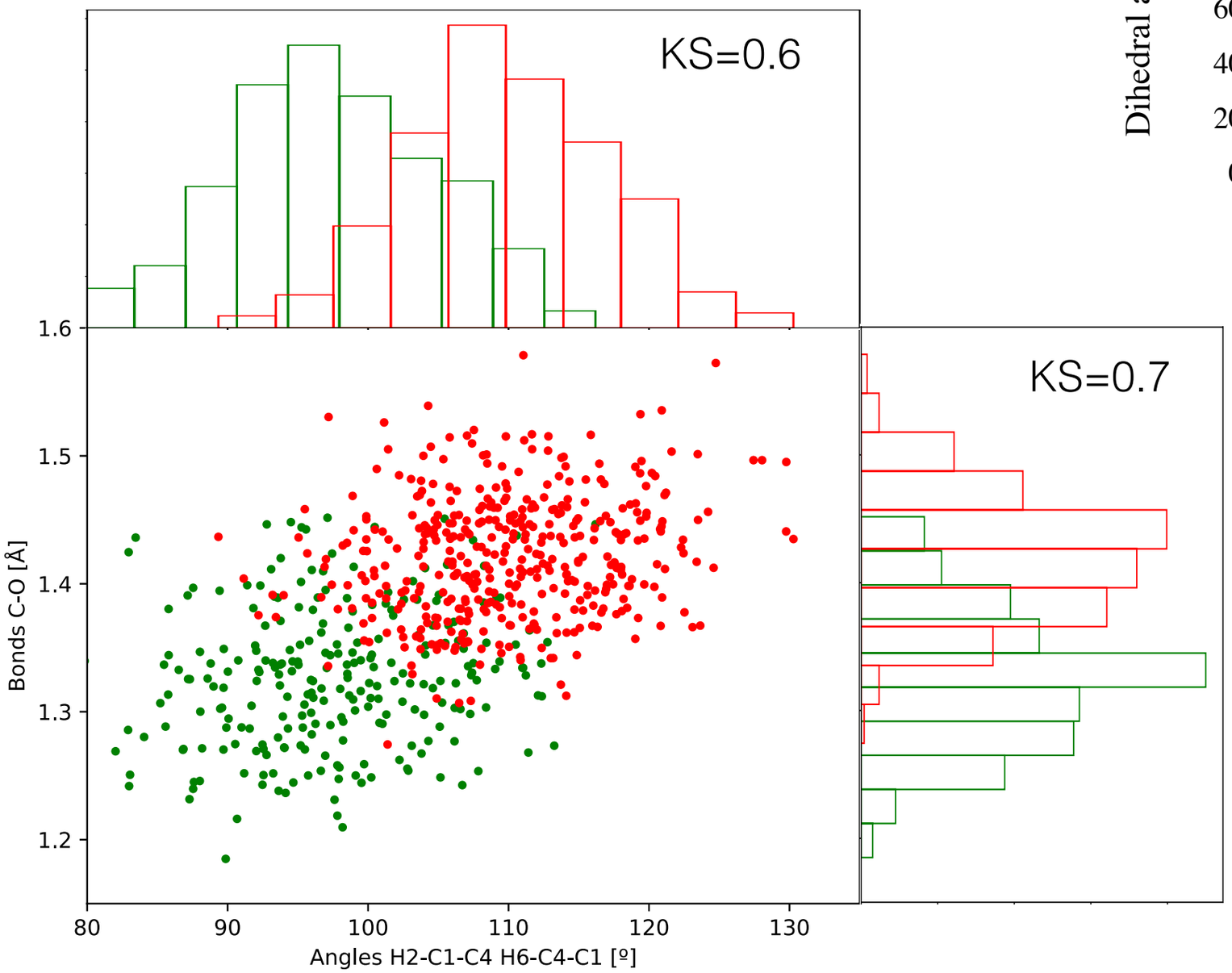


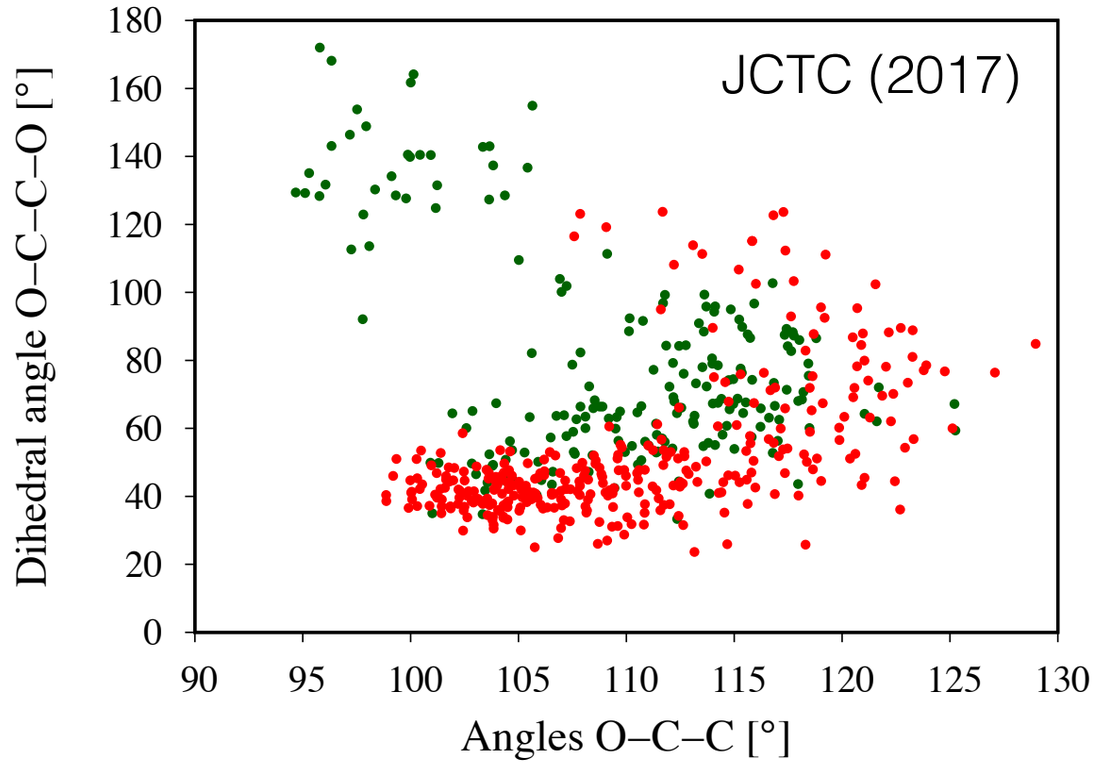
Finding relevant nuclear coordinate





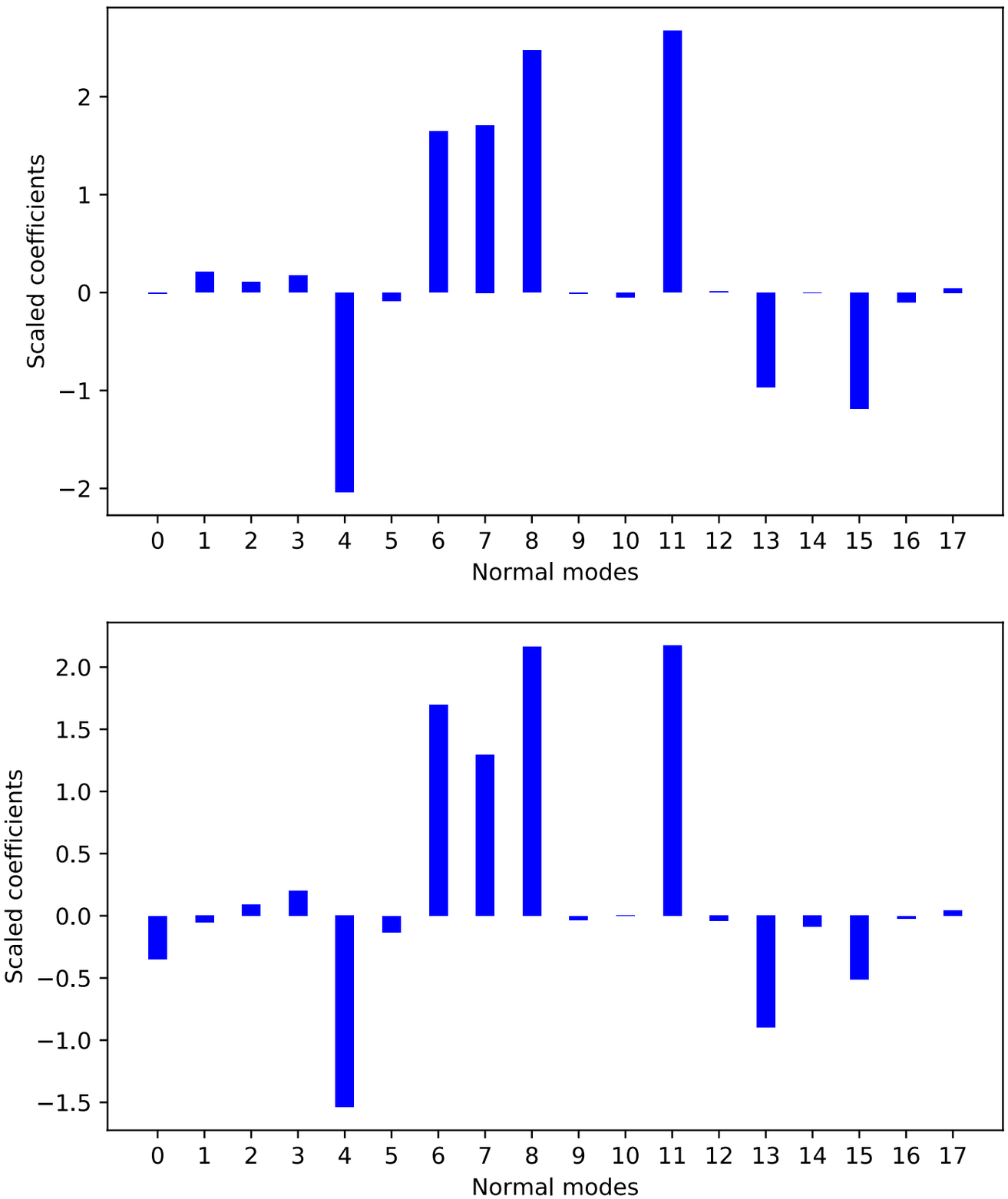
Finding relevant nuclear coordinate

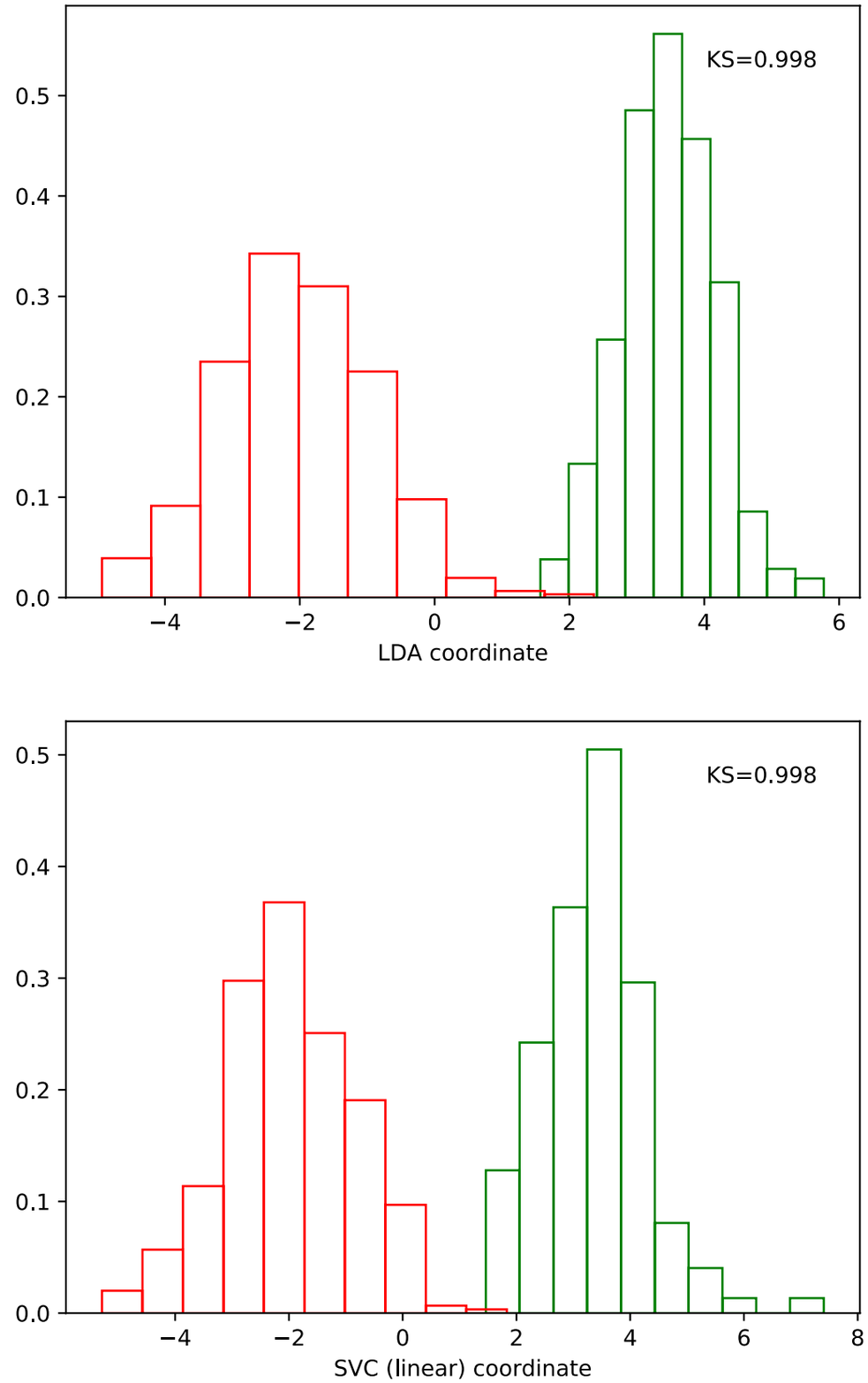




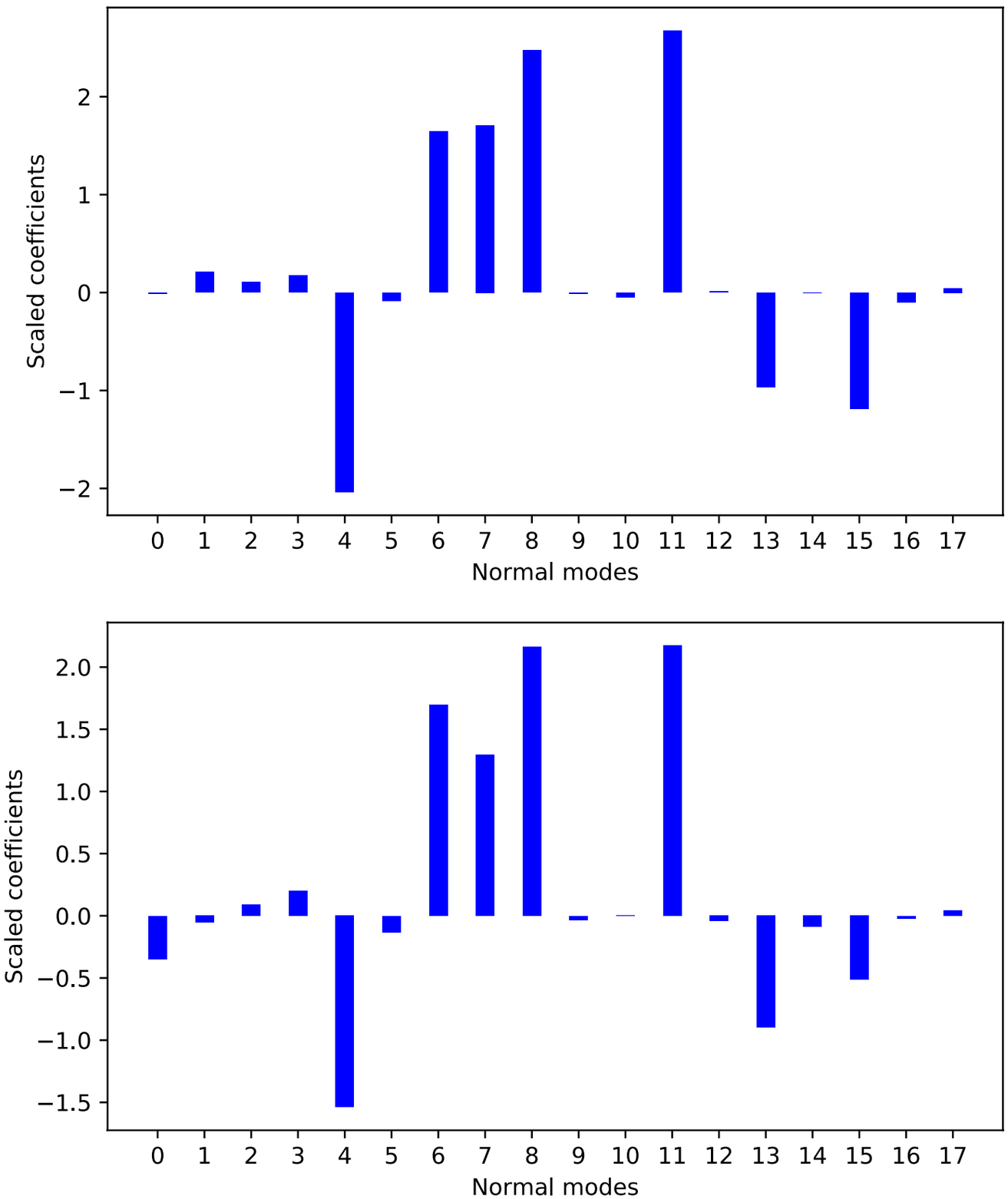
➜ Can machine learning identify a nuclear coordinate that distinguishes better between frustrated and successful dissociations?

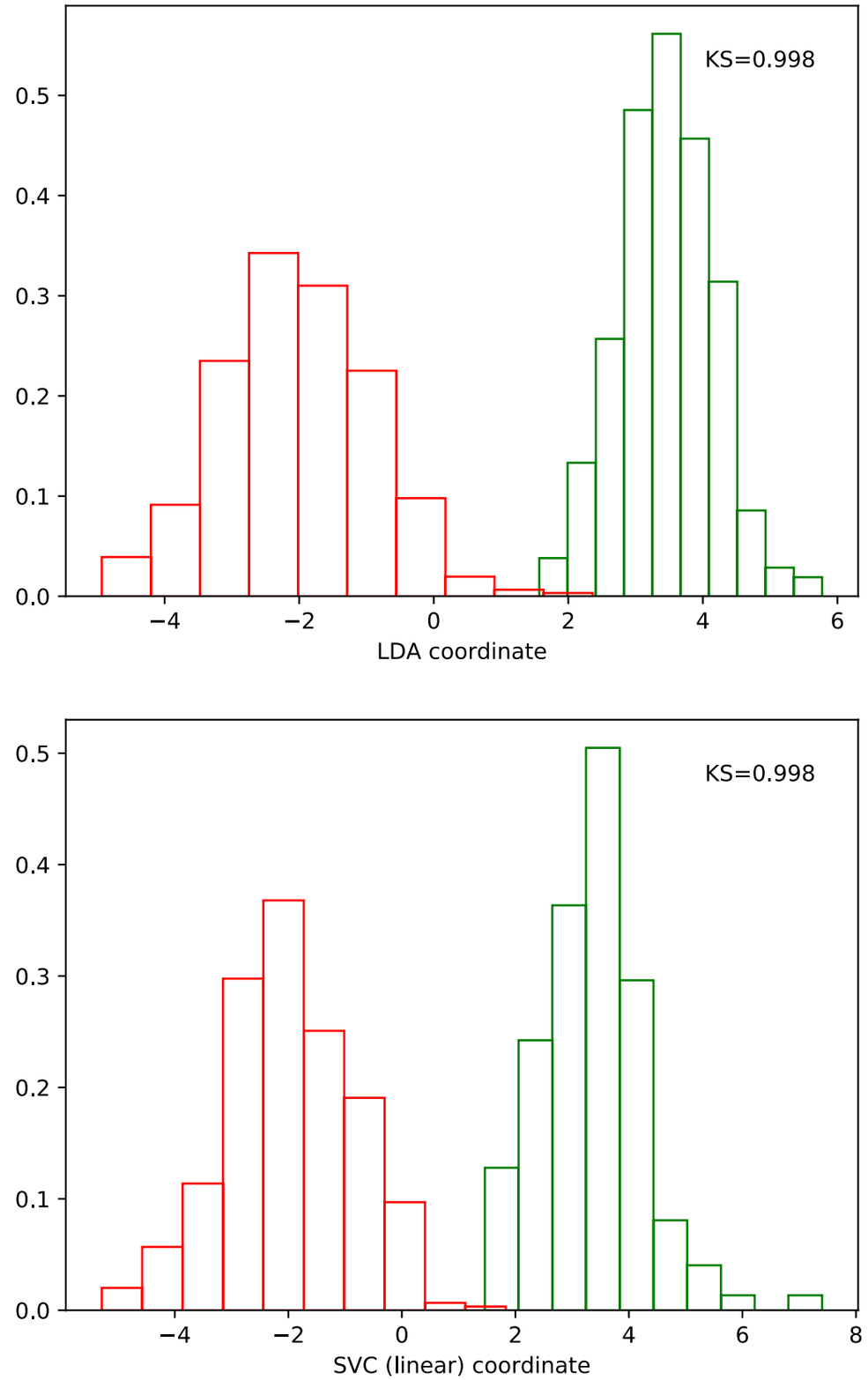
Finding relevant nuclear coordinate





Finding relevant nuclear coordinate





➜ in-phase planarisation of the two formaldehyde moieties