Control and design of photochemistry

photoisomerization and excitation energy transfer

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Computational Biomolecular Chemistry

Photo-isomerization

rotation of double bond after photon absorption

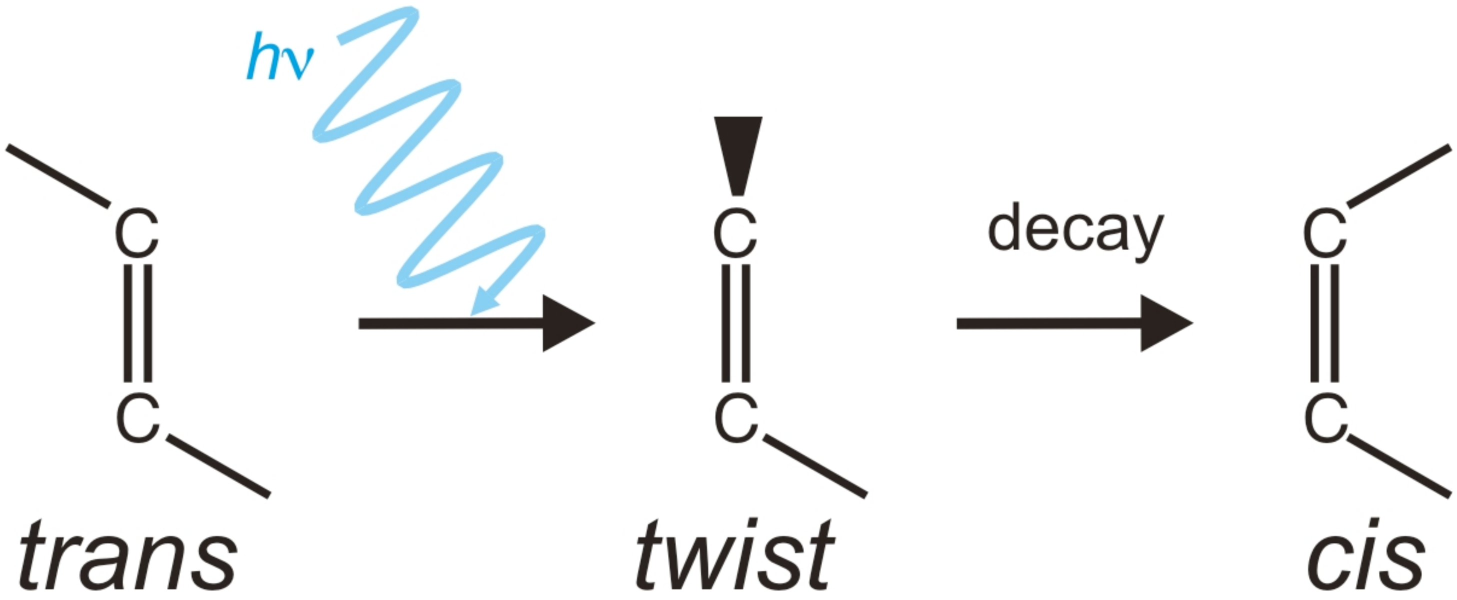

Photo-isomerization

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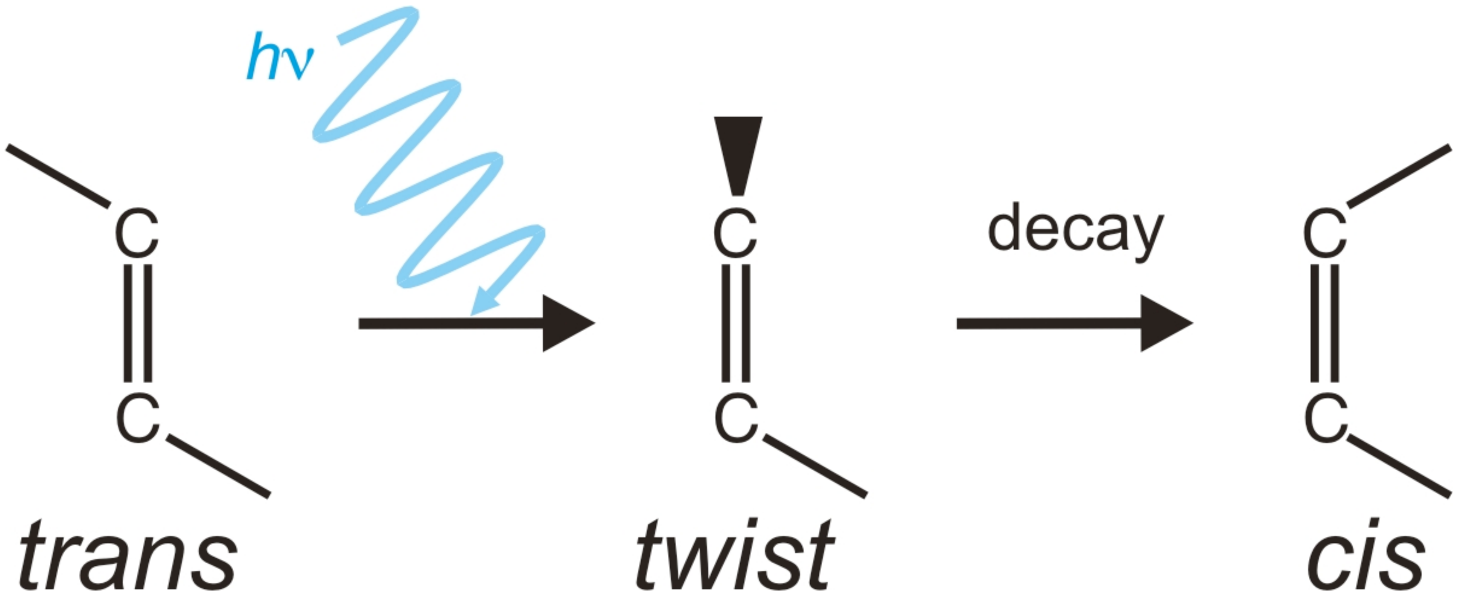
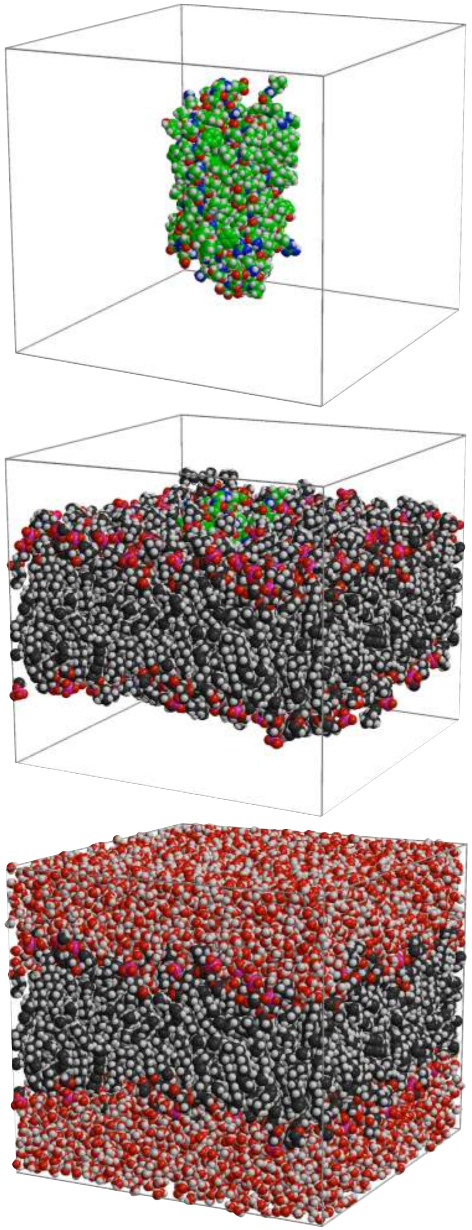


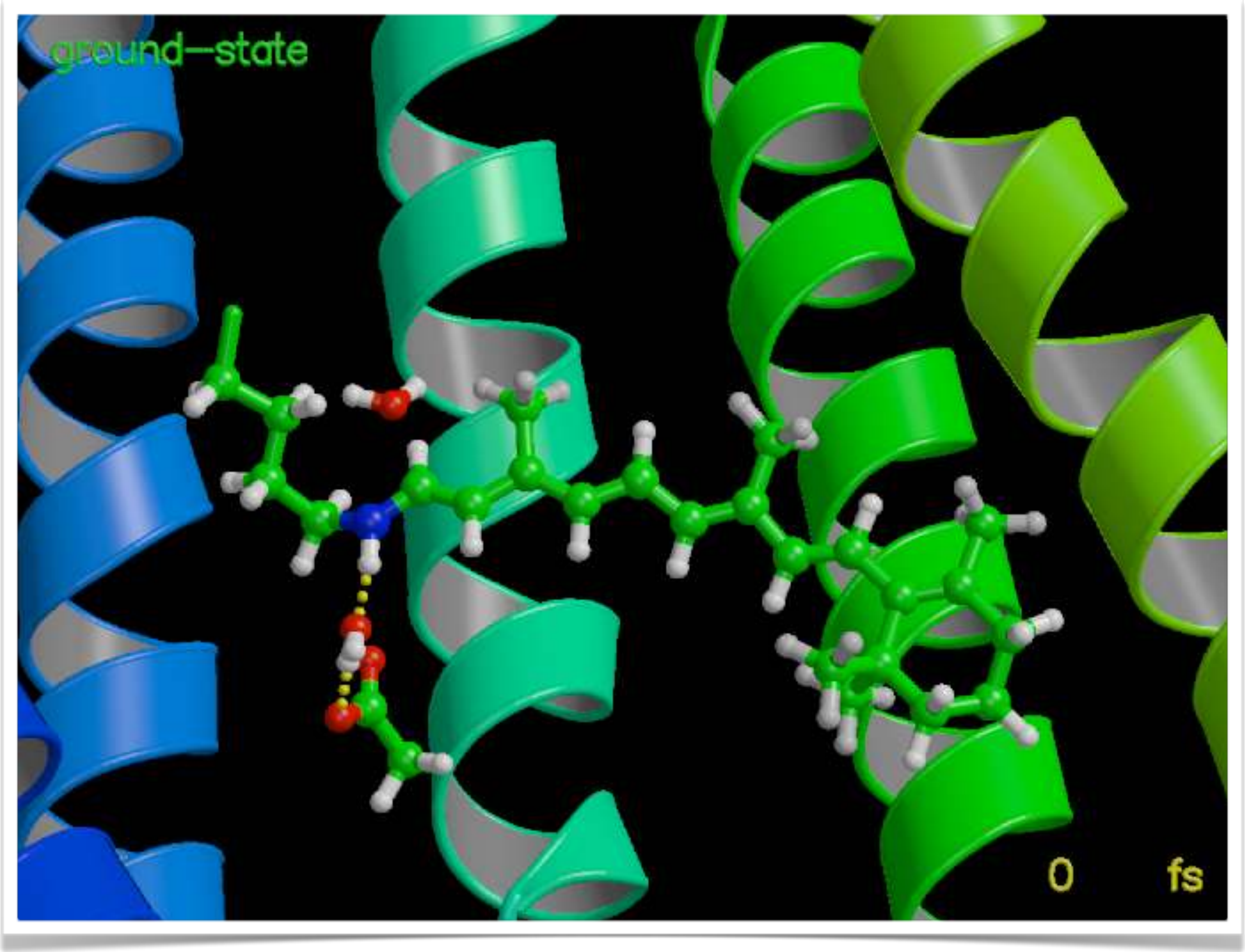
ubiquitous in photo-biology, e.g. :

- photosynthesis
  - bacteriorhodopsin
- light sensing
  - rhodopsin, phytochromo, photoactive yellow protein, ...

photoisomerization in bacteriorhodopsin

observe while it happens in MD simulations



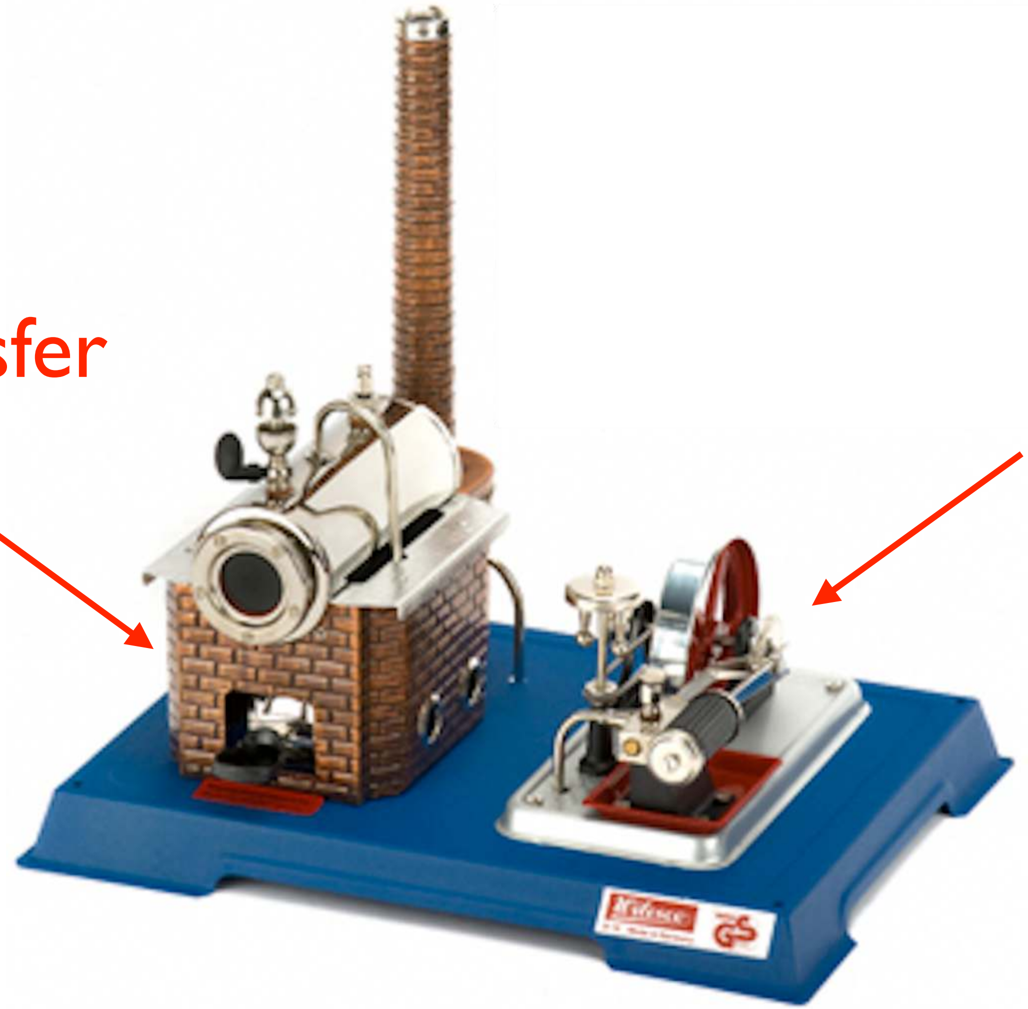


Our ultimate goal

artefical molecular machines

energy transfer

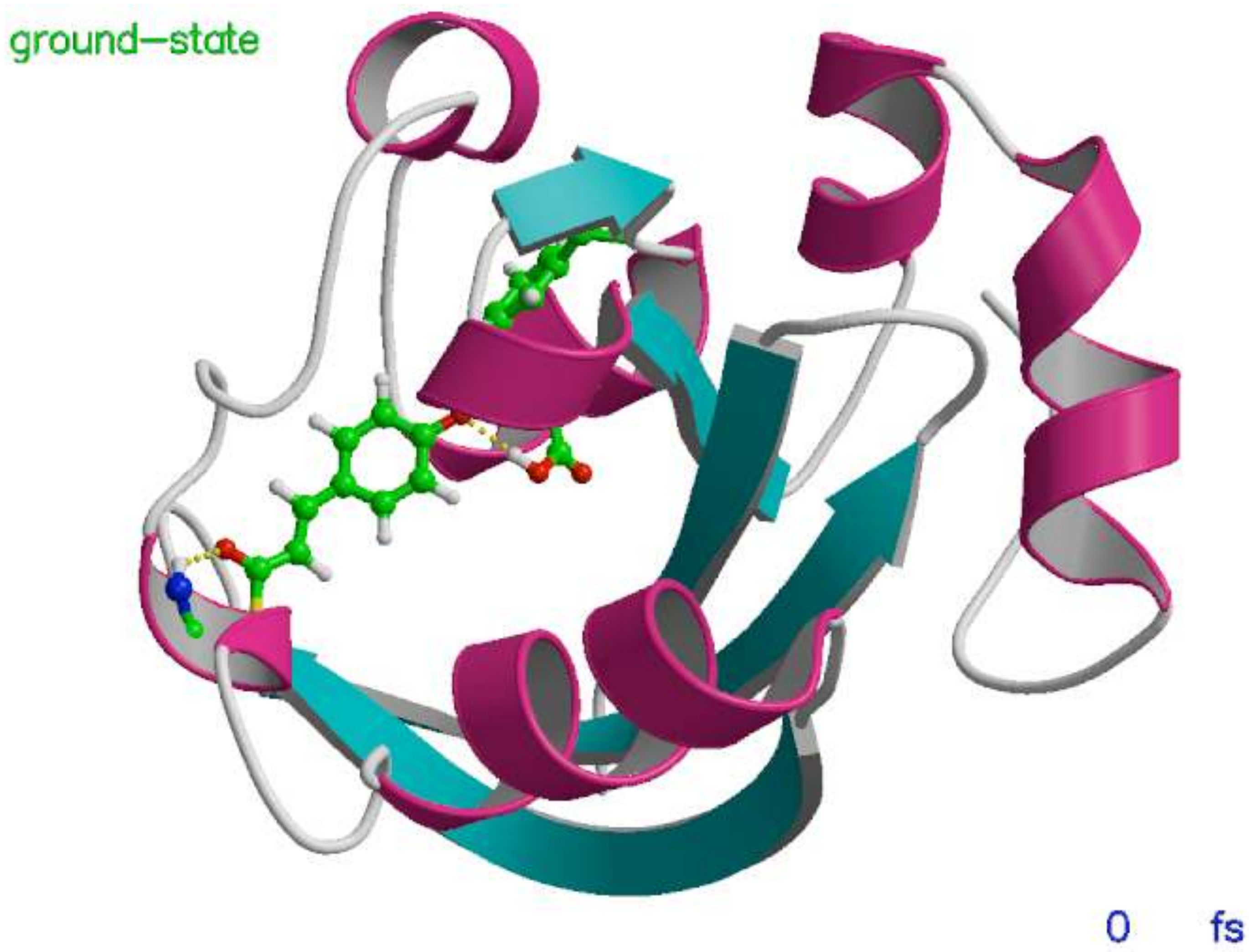
isomerization



Get inspired by nature

e.g. photo-isomerization in photoactive yellow protein

learn & mimic the effect of the protein environment



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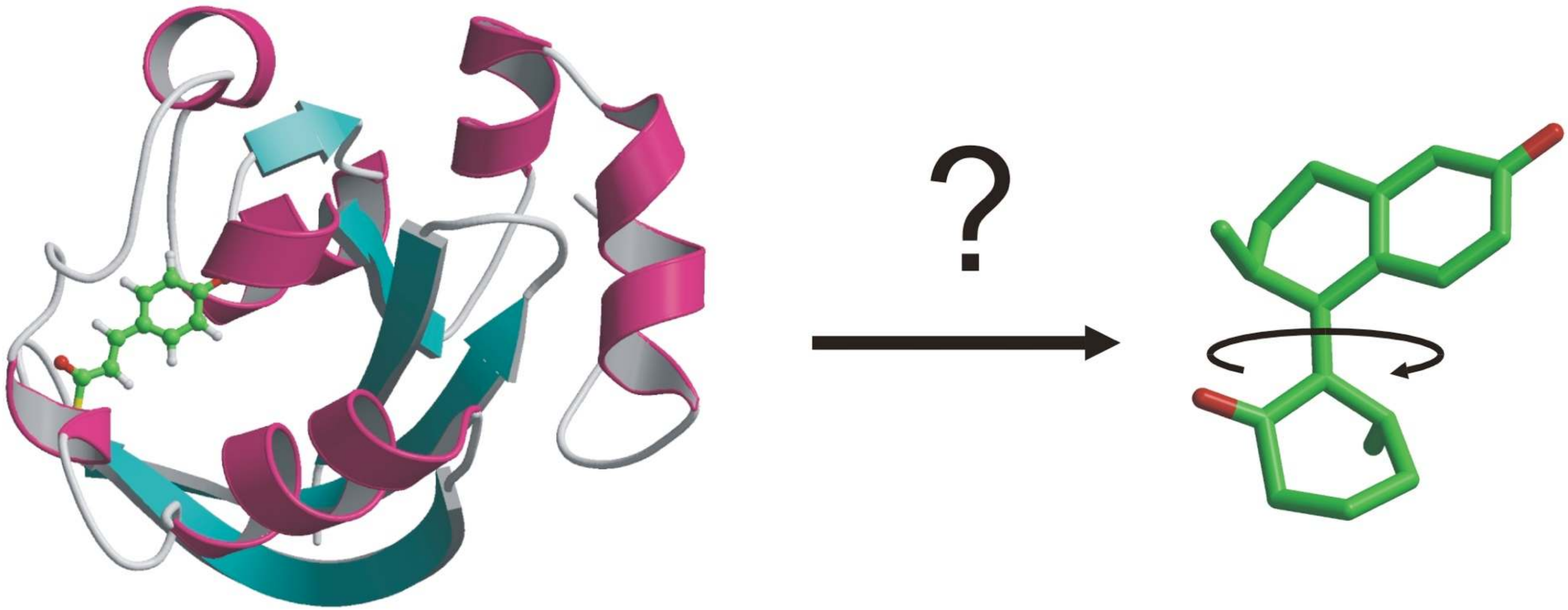


however....

still too complex, even in our simulations

Reducing complexity in MD simulations

maximally correlated motion in trajectory $(\mathbf{x}(t))$

find vector $\mathbf{a} \in R^{3N}$ that correlates with observable $f(t)$

$$p_a(t) = [\mathbf{x}(t) - \langle \mathbf{x} \rangle] \cdot \mathbf{a}$$

observable

quantum yield, energy gap, lifetime, ...

maximize Pearson coefficient

$$R = \frac{\mathrm{cov}(f, p_a)}{\sigma_f \sigma_a}$$

reducing dimensionality: basis

normal modes: eigenvectors of Hess matrix

principal components: eigenvectors of covariance matrix

$$C_{ij} = \langle (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \rangle$$

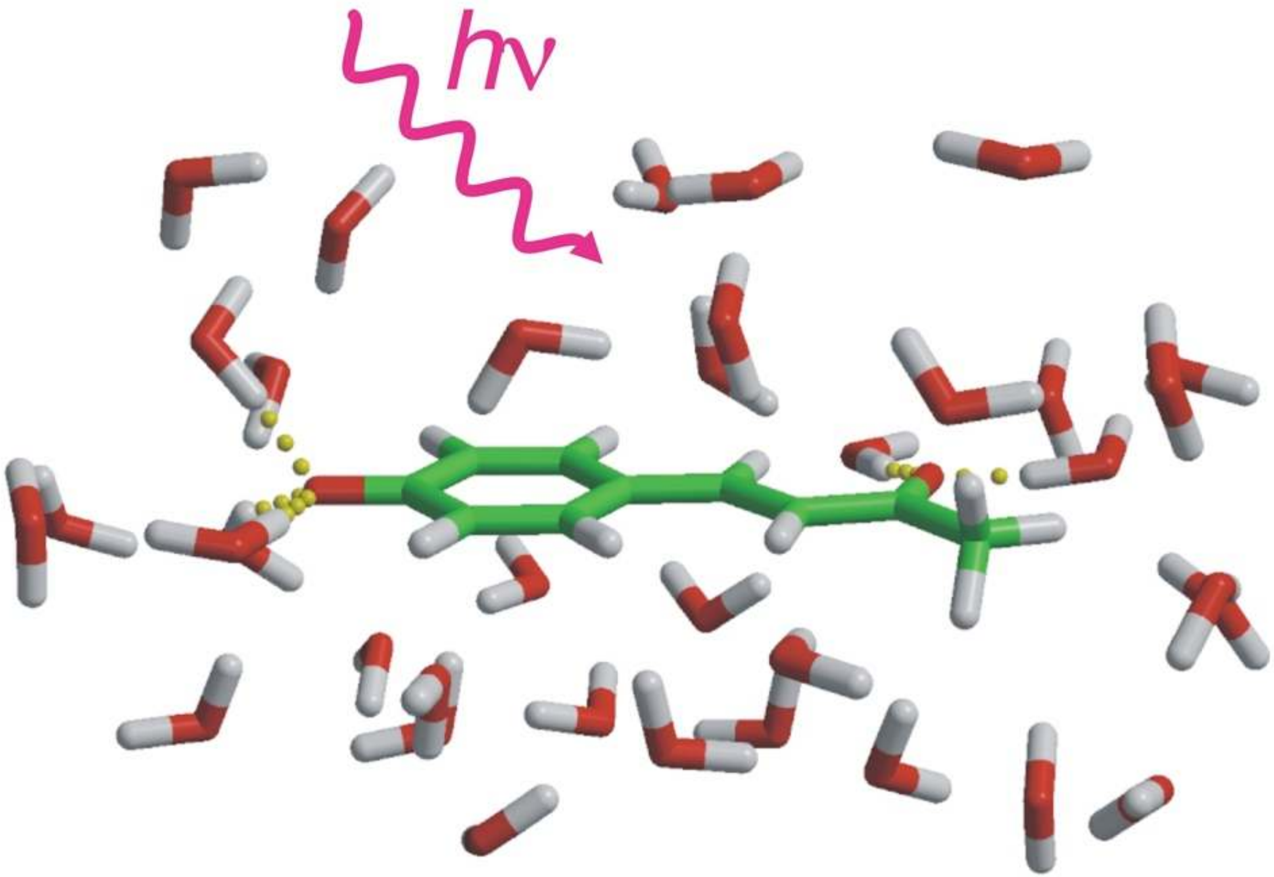
Simpler model systems

photo-isomerization in isolation and solution

lower complexity

systematic improvement of theory

high quality experimental data



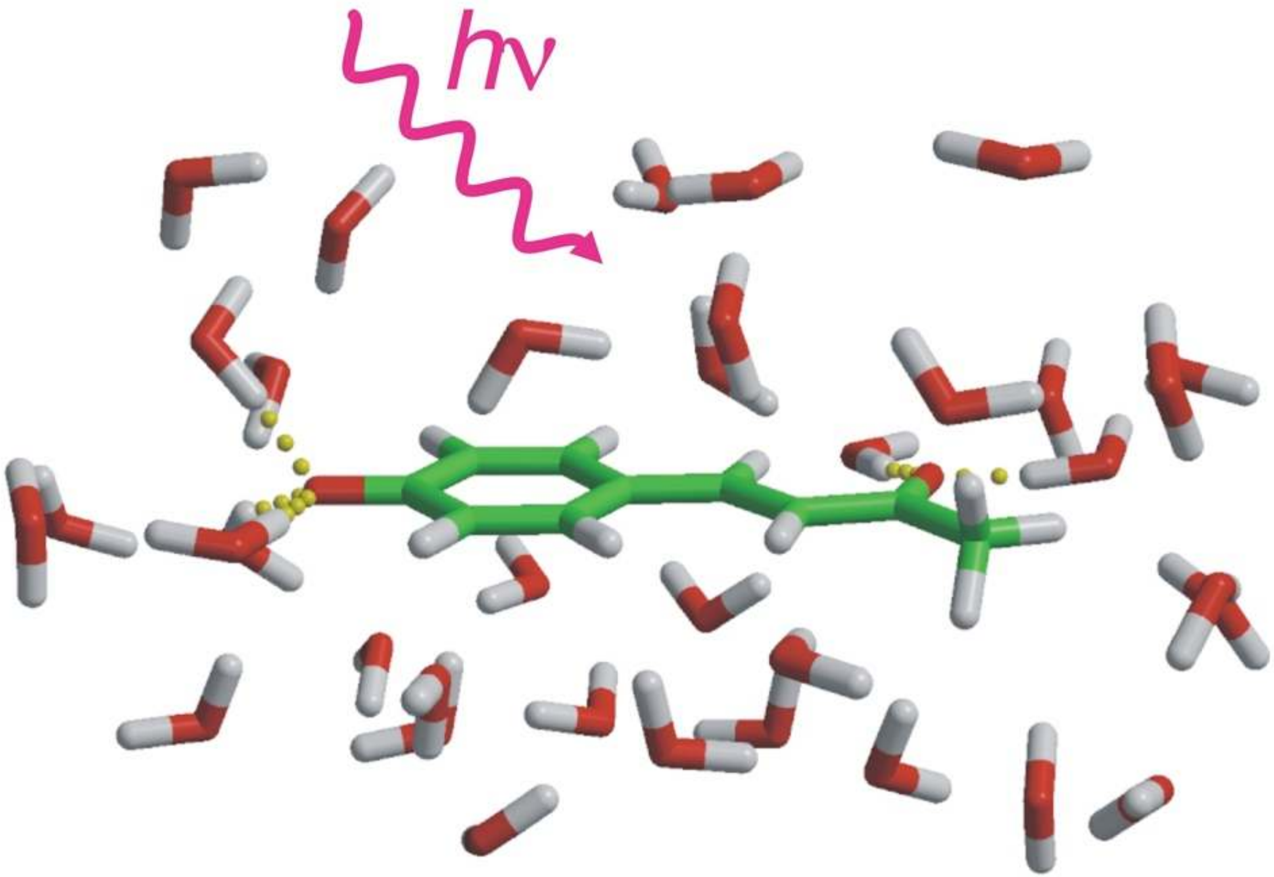
Simpler model systems

photo-isomerization in isolation and solution

lower complexity

find correlation between conformation & quantum yield

control quantum yield

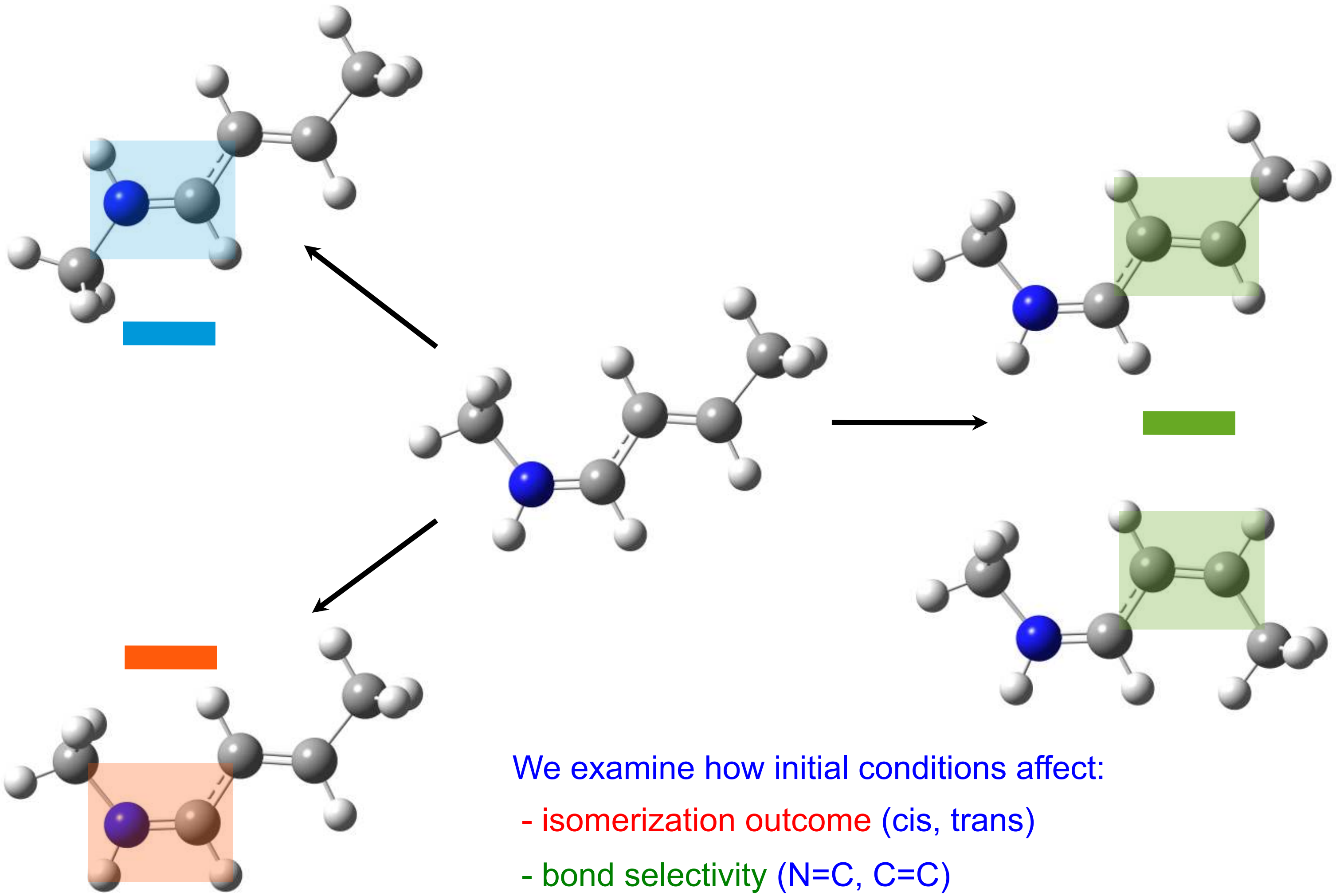


Simpler model systems

safety in numbers: many simulations

statistical analysis conformation-outcome

protonated schiff base (retinal model)



We examine how initial conditions affect:

- isomerization outcome (cis, trans)
- bond selectivity (N=C, C=C)

Non-adiabatic molecular dynamics

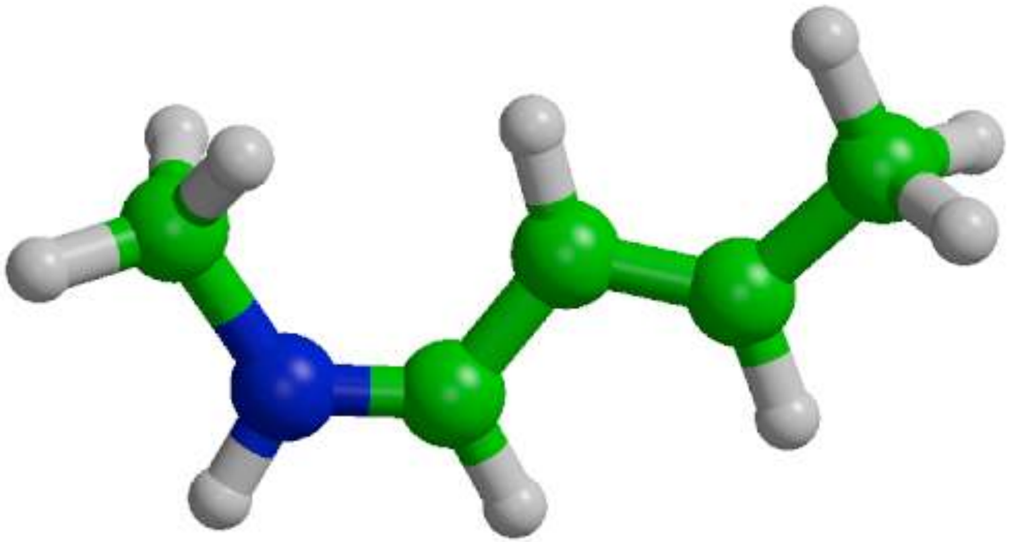
comparing diabatic hopping with fewest switches

photoisomerization of protonated Schiff base

aim a: find out if initial conditions determine outcome

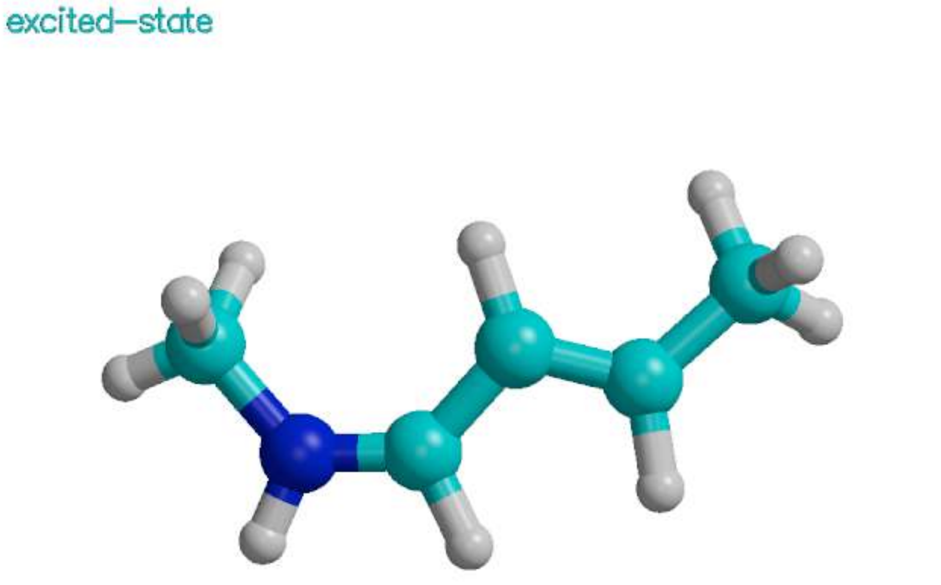
aim b: control outcome

aim c: compare hopping algorithms



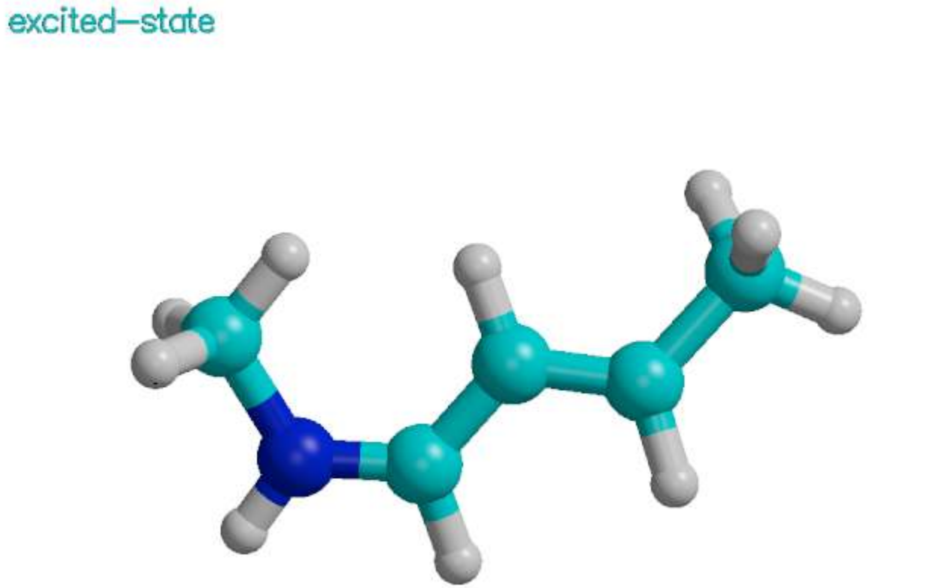
simulations

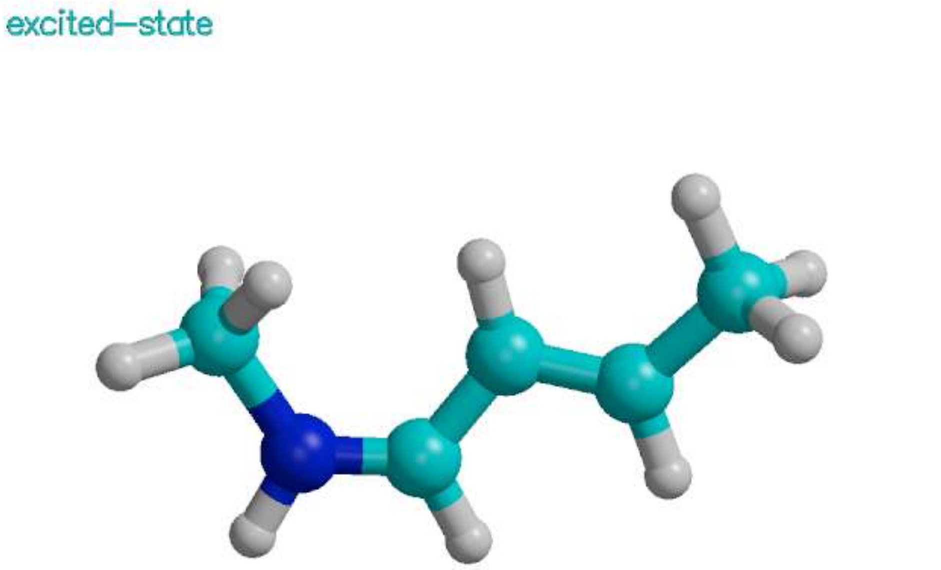
CASSCF(4,4)/6-31G*, diabatic & fewest switches surface hopping



QY: 44.6%/42.4%

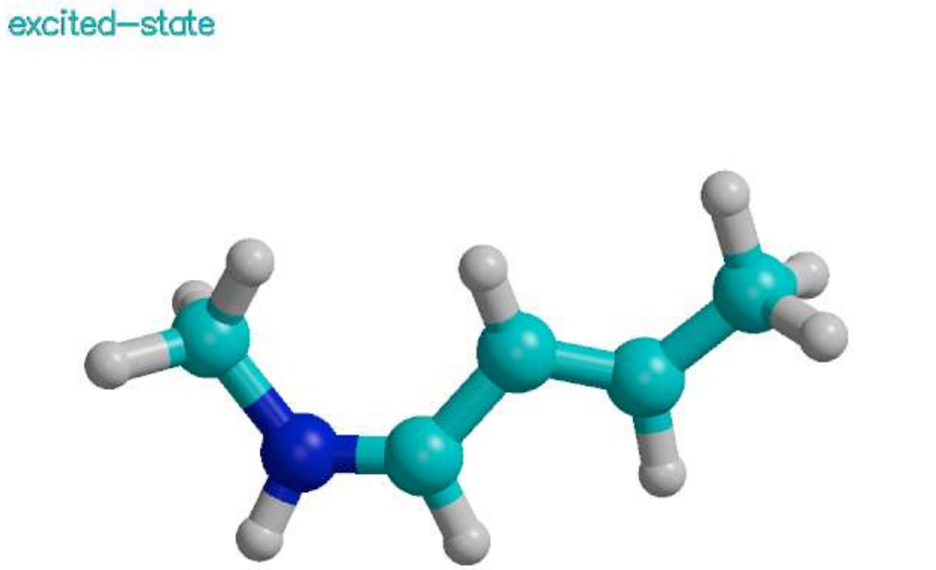
average lifetime: 115.8 fs/75.2 fs





QY: 35.5%/34.8%

average lifetime: 139.5 fs/83.7 fs



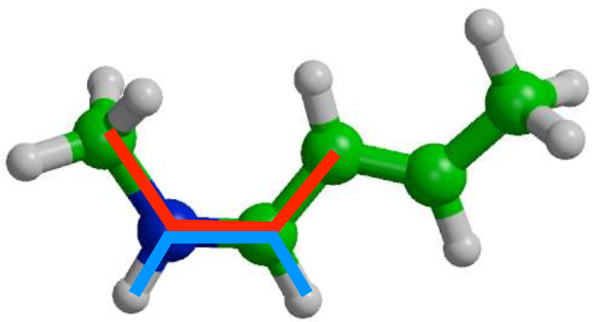
QY (both): 19.9 %/22.8%

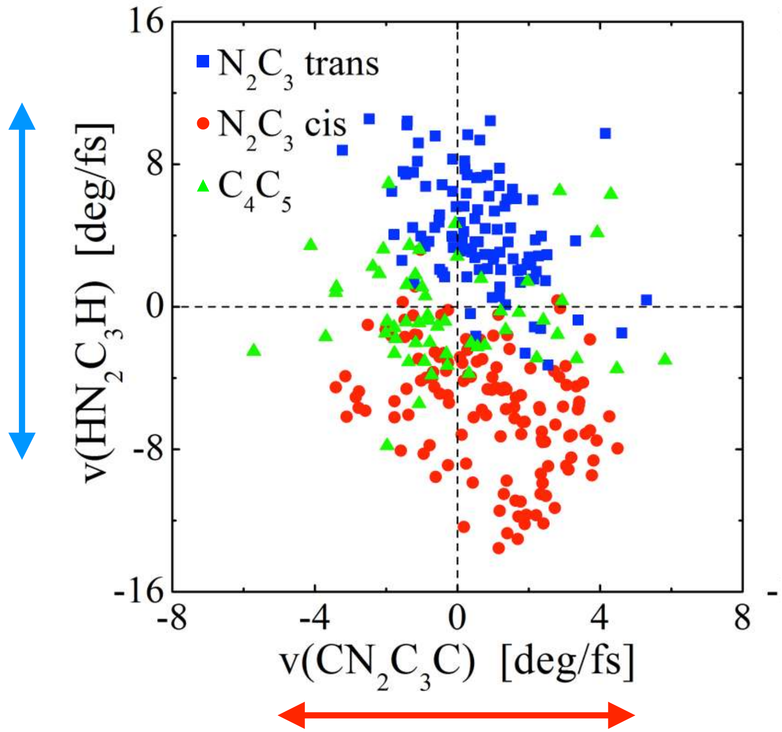
average lifetime: 60.2 fs/54.6 fs

Simpler model systems

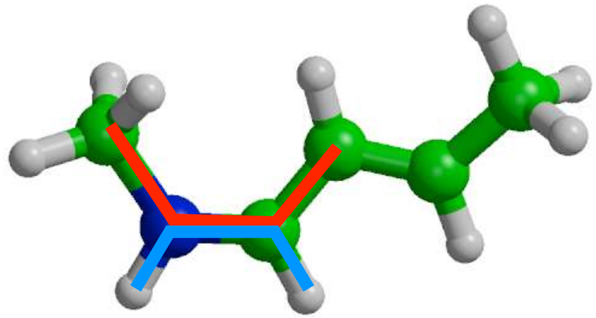
free unbiased simulations

what determines outcome: hydrogen-out-of-plane motion



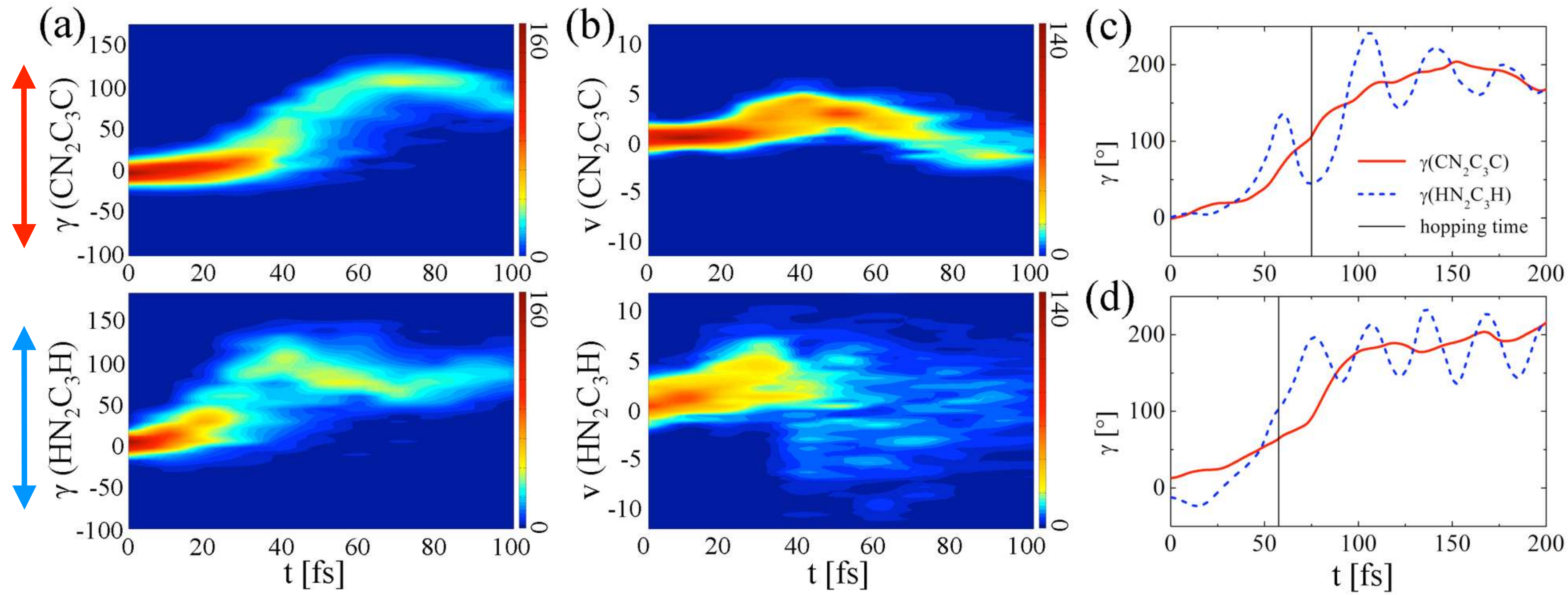


Simpler model systems



free unbiased simulations

phase between HN=CH and CN=CC

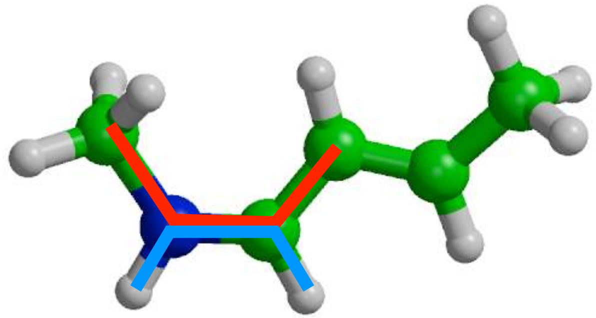


evolutionary approach: optimize for synchronicity

constrain dihedral angles from synchronous simulations

generate new ensemble

Simpler model systems



free unbiased simulations

thermal ensemble

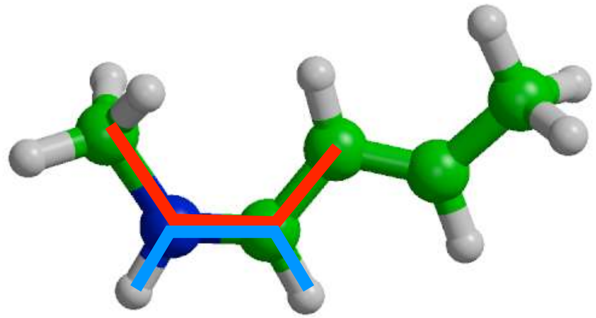
Outcome	N_2C_3 cis	N_2C_3 trans	C_4C_5
τ_{DSH} [fs]	96 ± 1	132 ± 2	51 ± 1
$N_{i,DSH}$	132	105	59
$P_{i,DSH}$ [%]	44.6	35.5	19.9
τ_{FSH} [fs]	65 ± 1	74 ± 1	46 ± 1
$N_{i,FSH}$	208	171	112
$P_{i,FSH}$ [%]	42.4	34.8	22.8

optimizing synchronicity

thermal ensemble

Therm. Ens.	γ_1 [°]	γ_2	γ_3	γ_4	P_{sync}	N_{traj}
unconstr. FSH	-	-	-	-	7.63 %	491
unconstr. DSH	-	-	-	-	1.0%	296

Simpler model systems



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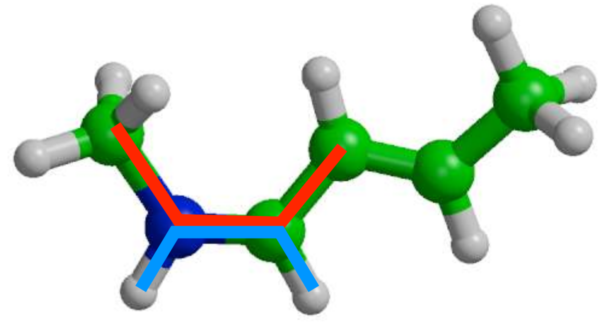
optimizing synchronicity

new ensemble with fixed dihedrals

Therm. Ens.	γ_1 [°]	γ_2	γ_3	γ_4	P_{sync}	N_{traj}
unconstr. FSH	-	-	-	-	7.63 %	491
unconstr. DSH	-	-	-	-	1.0%	296
1 FSH, γ_i - [14]	-17.5	168.6	174.1	-	6.06 %	99
2 FSH	13.0	150.0	-172.4	-	18.09 %	187
2 DSH	13.0	150.0	-172.4	-	16.24 %	193
3 FSH	-20.63	-154.4	172.9	-	14.57 %	199
3b FSH	-20.63	-154.4	172.9	11.1	14.21 %	197

Simpler model systems



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optimizing synchronicity

second generation

Outcome	N_2C_3 cis	N_2C_3 trans	C_4C_5
$P_{i,DSH}$ [%]	39.9	46.1	14.0
$P_{i,FSH}$ [%]	47.8	39.9	12.4

challenge: fixing dihedrals by chemical modification?

Acknowledgements

Computational Biomolecular Chemistry

members from the Grubmüller department

Mike Robb
IC London

Martial
Boggio-Pasqua
(Toulouse, Fr.)

funding

MAX-PLANCK-GESELLSCHAFT

SUOMEN AKATEMIA

DAAD

Université de Toulouse

Université Paul Sabatier TOULOUSE III

SFB755 Nanoscale Photonic Imaging

VolkswagenStiftung