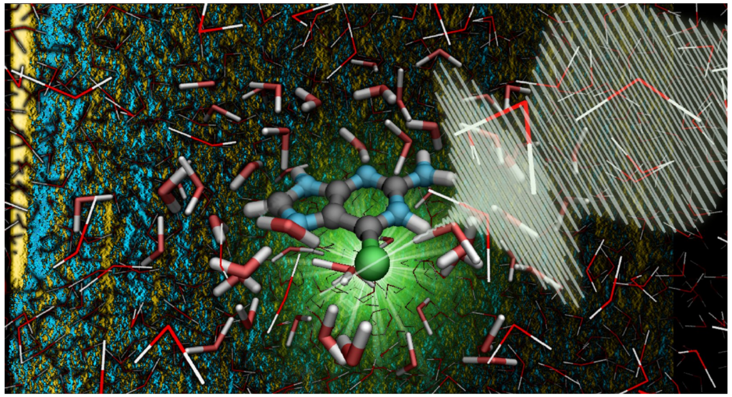
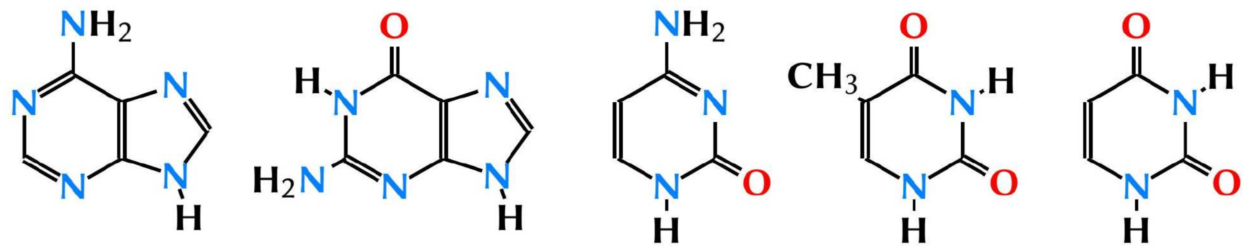
Disentangling the Photophysics of 6-selenoguanine in Water



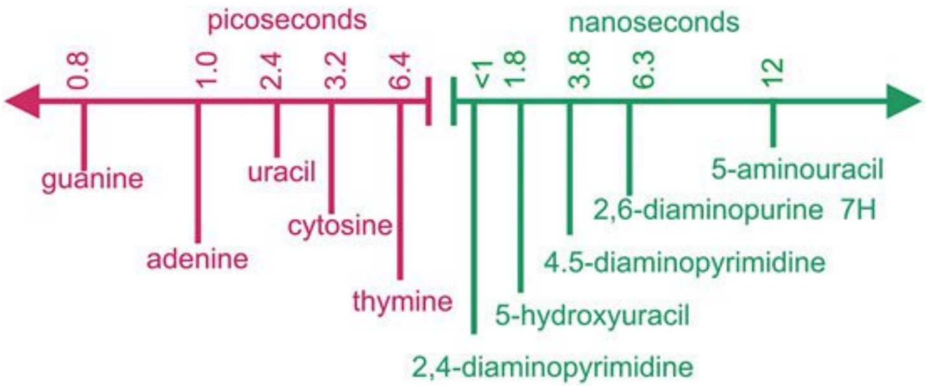
Danillo Valverde

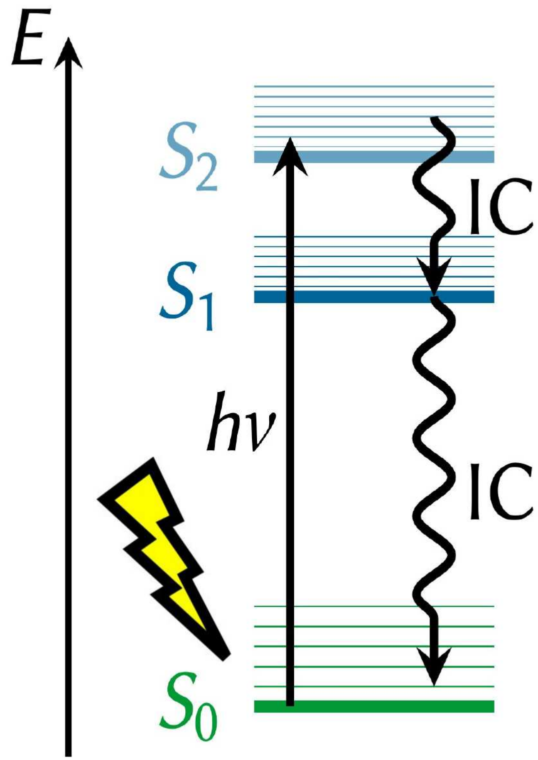
17th April 2024

DNA/RNA Canonical Nucleobases



Adenine Guanine Cytosine Thymine Uracil



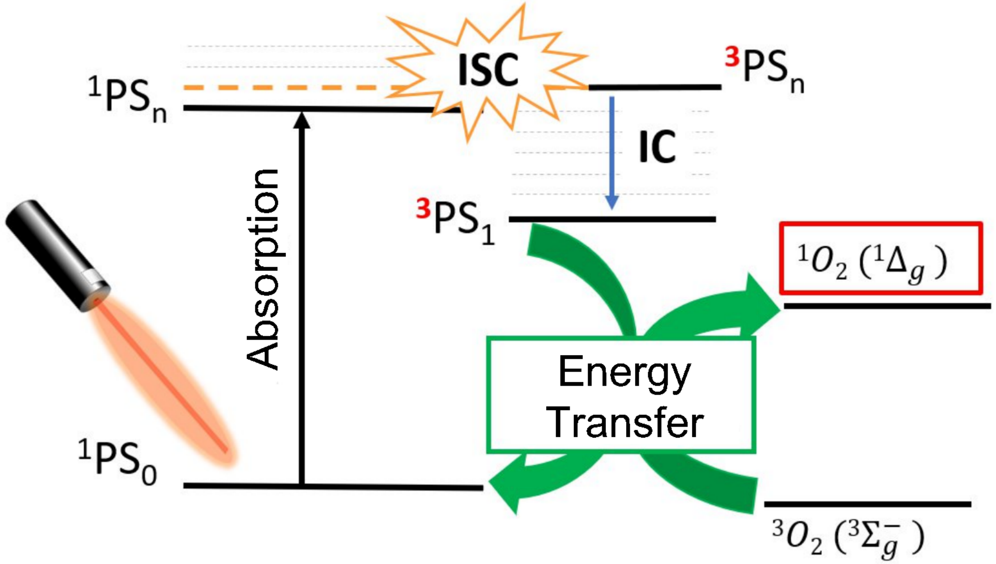


Conical Intersections are the keys to explain the nonradiative decay

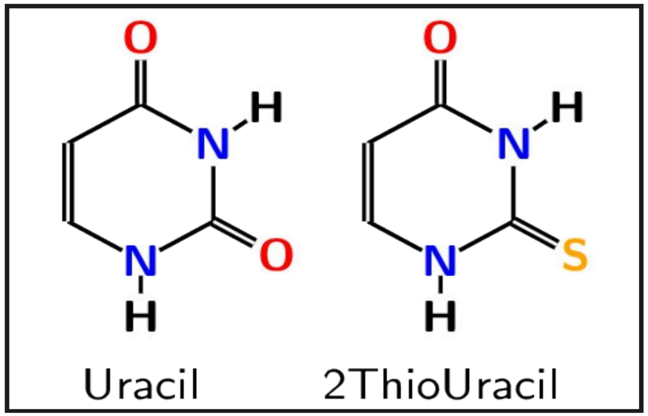
Barbatti, M., Borin., A. C., Ullrich, S. (2014). Photoinduced processes in nucleic acids. In Photoinduced phenomena in nucleic acids I (pp. 1-32). Springer, Cham.

Modified Canonical Nucleobases

- Fluorescent markers;
- Increase of the genetic biodiversity
- New base-pairing schemes
- Suppression of the internal conversion and enhacement of the triplet state yield;
- **Photodynamics therapy**



Thiobases



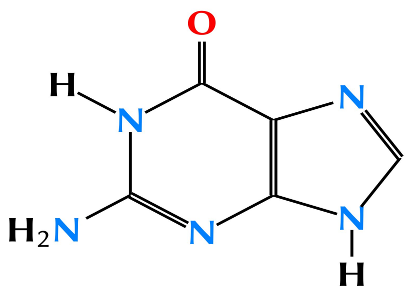
Ashwood, B. et. al. Molecules 22, 379 (2017)

Motivation

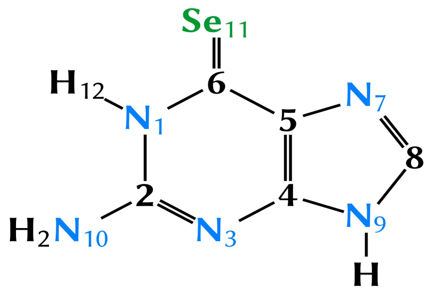
JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
Cite This: J. Am. Chem. Soc. 2018, 140, 11214–11218
pubs.acs.org/JACS

Heavy-Atom-Substituted Nucleobases in Photodynamic Applications: Substitution of Sulfur with Selenium in 6-Thioguanine Induces a Remarkable Increase in the Rate of Triplet Decay in 6-Selenoguanine

Kieran M. Farrell,[†,§] Matthew M. Brister,[†,¶] Michael Pittelkow,[‡] Theis I. Sølling,[‡] and Carlos E. Crespo-Hernández*[,†]



Guanine



6-selenoguanine

Time constants

T1/fs	T2/ps	T3/ns
130+50	31+2	1.7+0.1

Ultrafast ISC from singlet to triplet manifold

Spectral evolution in the TAS measurement

ISC to the ground state

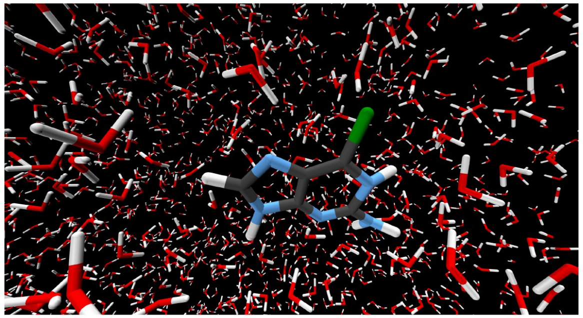
Objectives

- Description of the predominant photochemical relaxation pathways
- Simulation of the absorption and transient absorption spectra
- Inclusion of the water effects

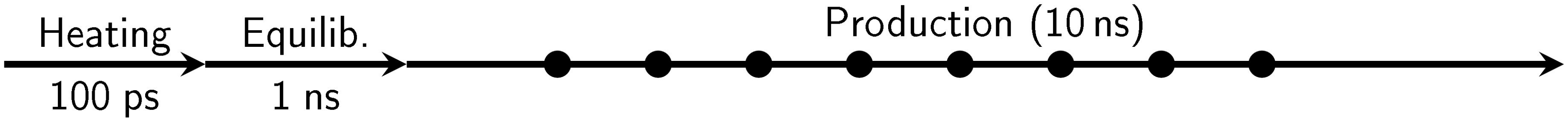
	6tGua	6SeGua
T3/ns	1420+180	1.7+0.1

Triplet state lifetime decreases 835 times

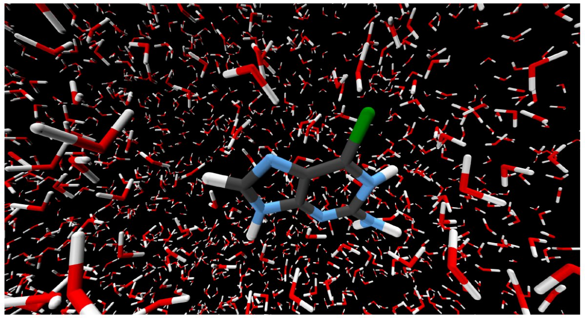
Protocol for the excited-state dynamics



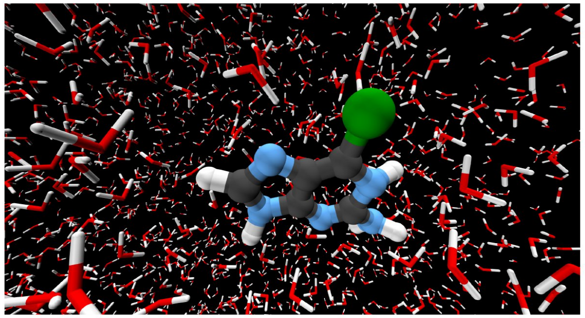
MM



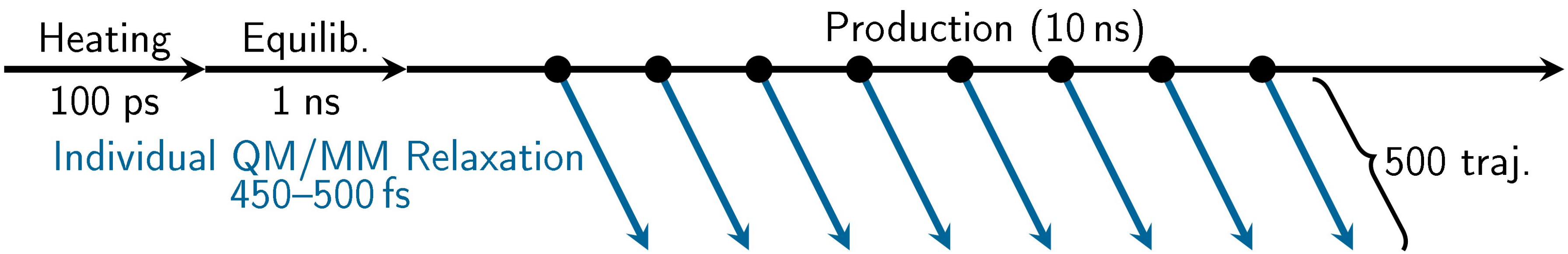
Protocol for the excited-state dynamics



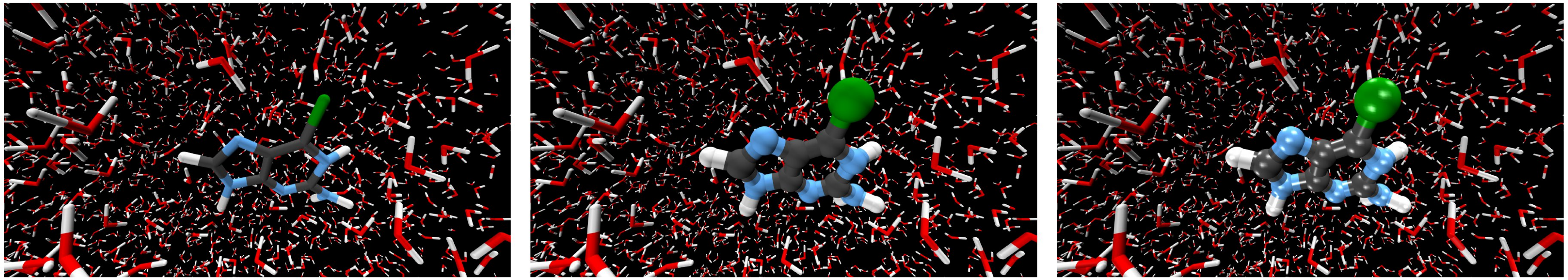
MM

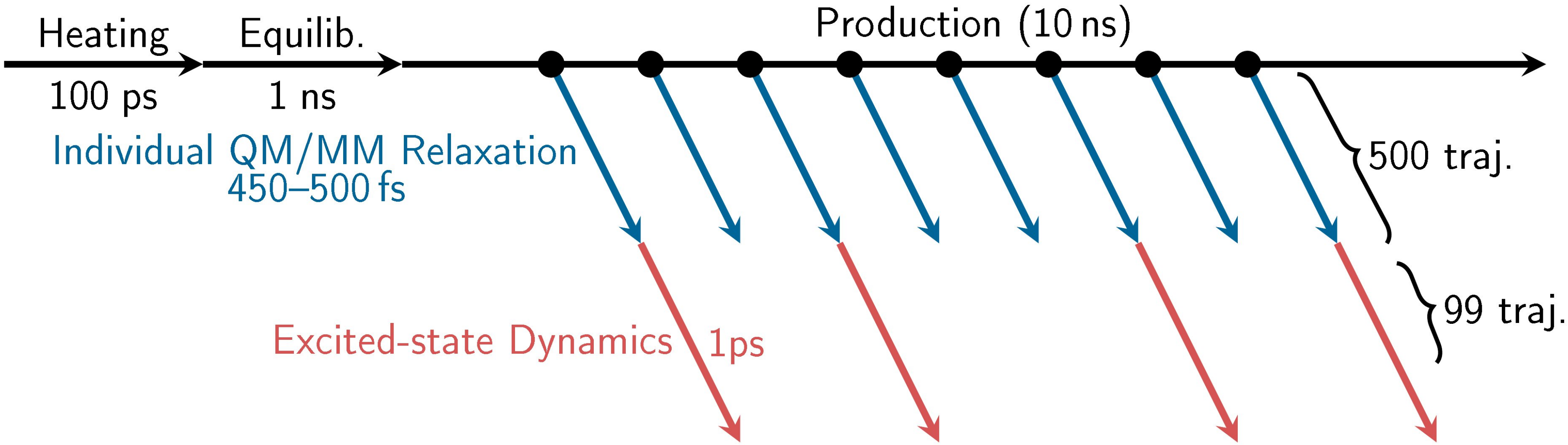


QM/MM



Protocol for the excited-state dynamics

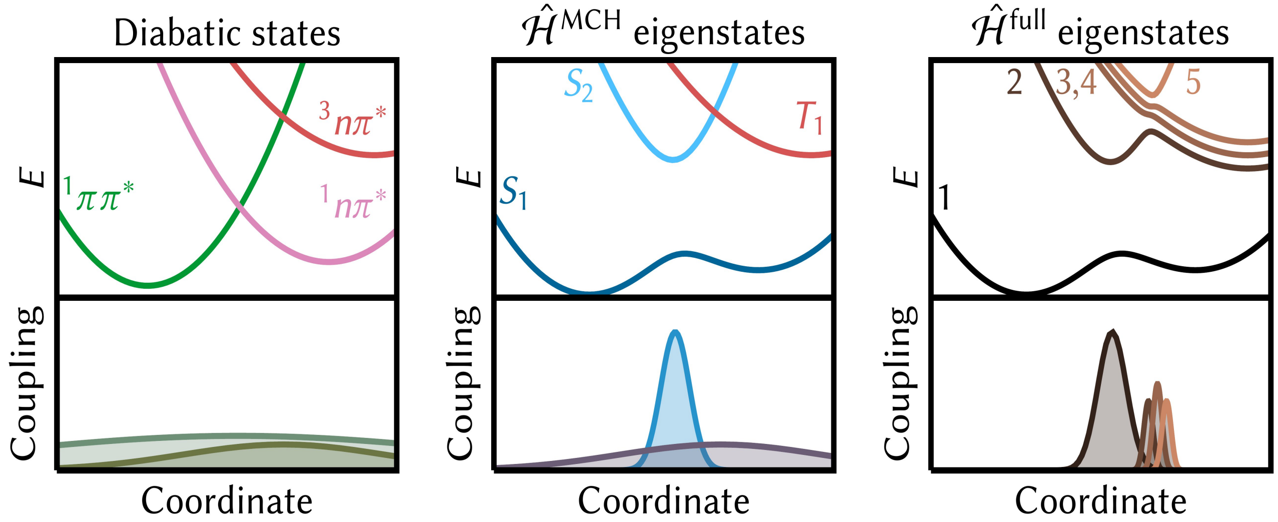




Excited-state dynamics setup

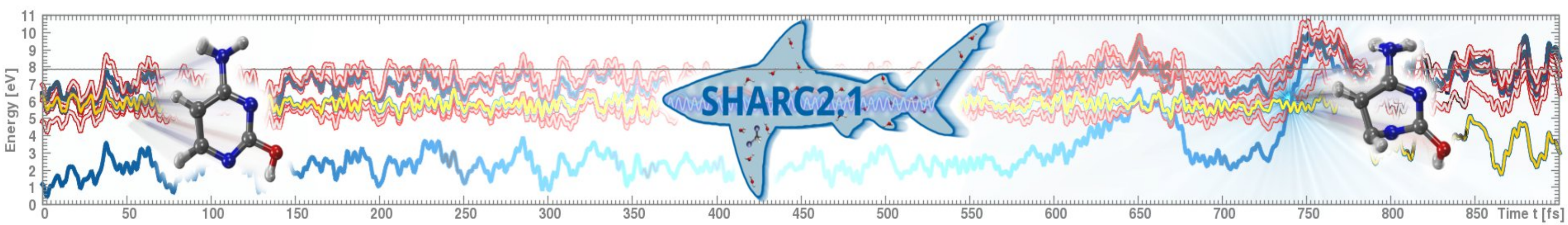
Level of theory:

- ADC(2)/def2-SVP
- 3 singlets, and 3 x 3 triplets (diagonal representation)



Dynamics Setup:

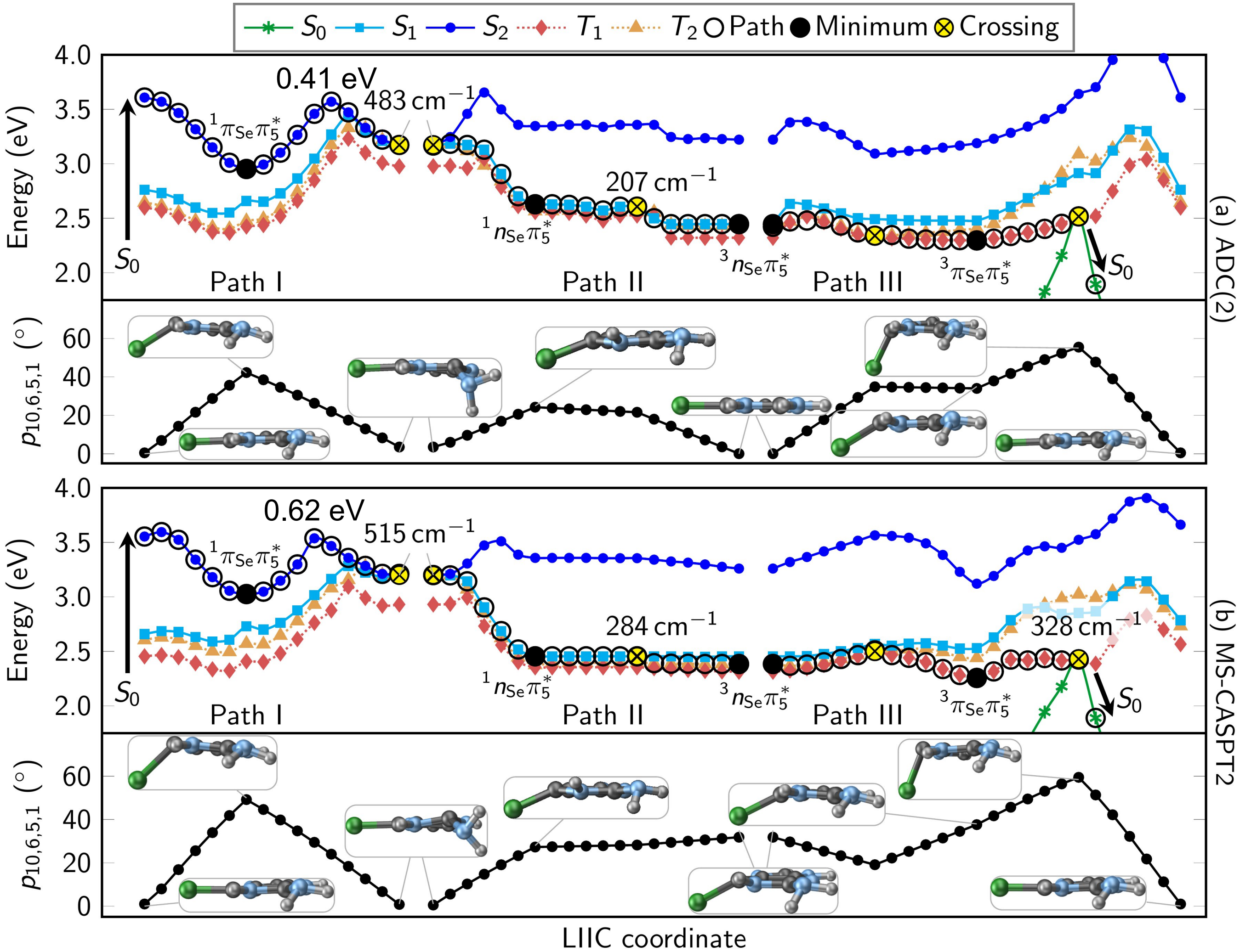
- 99 initial conditions;
- Simulation time: 1 ps
- Kinetic energy adjustment: reescaling the complete velocity vector



TURBOMOLE

Mai et. al. Wiley **8**, e1370 (2018)

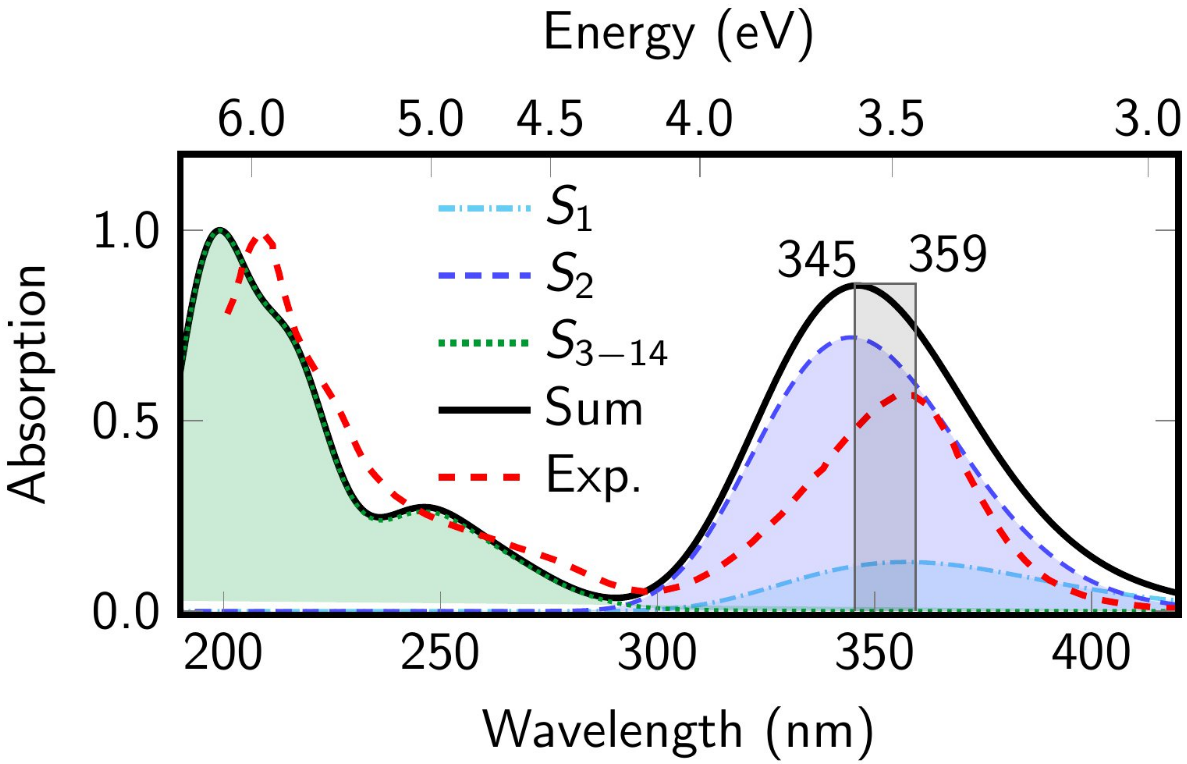
LIIC scan



Two likely photochemical events

- $S_2 \rightarrow T_2 \rightarrow T_1$
- $S_2 \rightarrow S_1 \rightarrow T_2 \rightarrow T_1$

Eletronic absorption spectrum

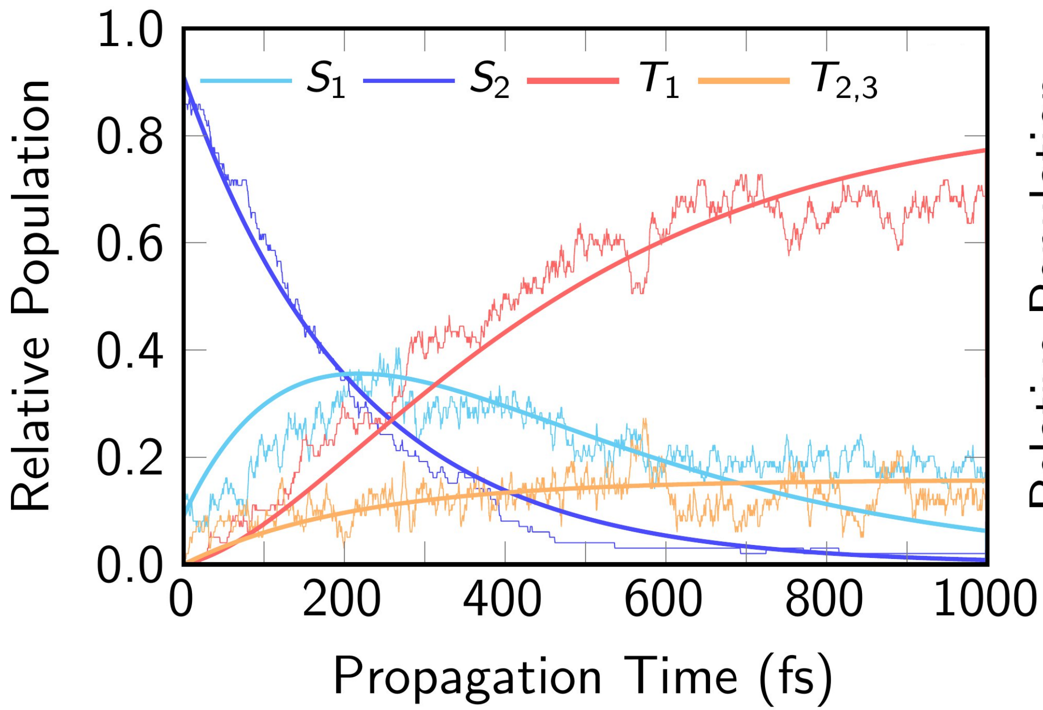


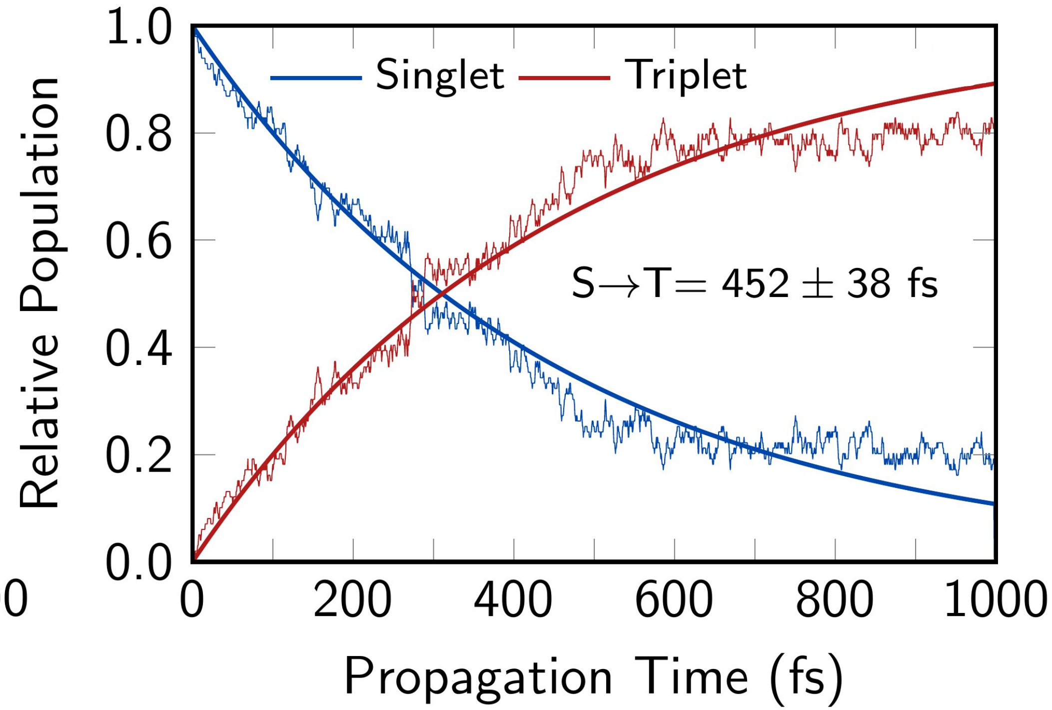
- Experimental peaks: 357 and 209 nm
- Theoretical peaks: 345 and 199 nm

Intensity ratio betweem the low- and high-energy band is not well described

Valverde et. al. JACS Au. **2**, 1699 (2022)

Temporal evolution of the adiabatic excited-state populations





- Initial population: S_2 (85%) and S_1 (15%);
- S_2 state is quickly depopulated;
- S_1 state acts as an intermediate state;

- The triplet-state population amounts more than 80% after 1 ps.
- Effective ISC time constant of 452 fs (experimental: 130±50 fs)

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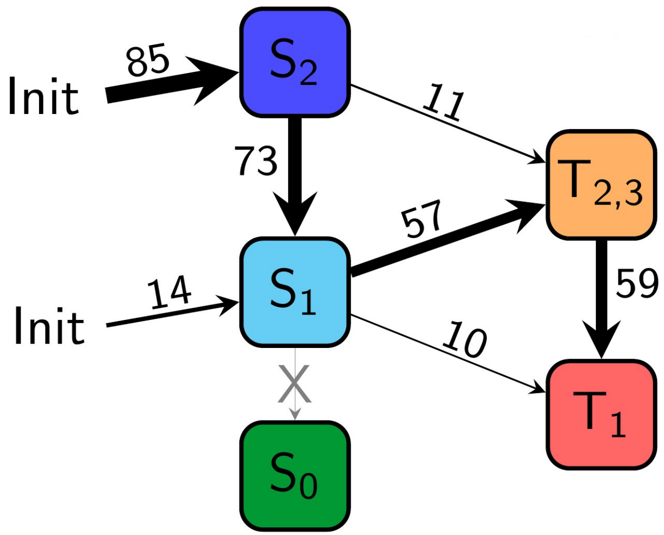
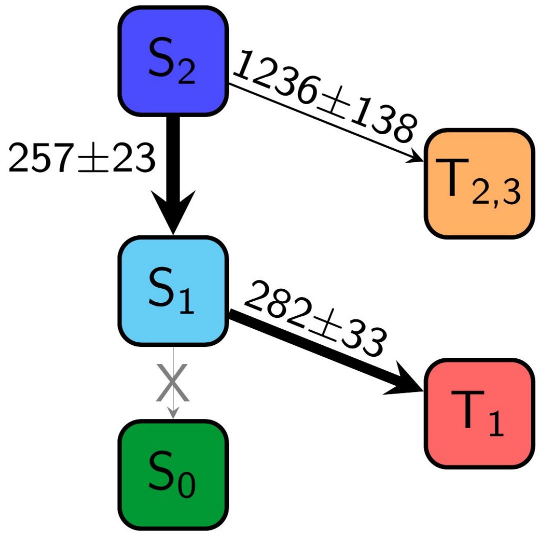
Net population transfer and time constants



- Predominant relaxation pathway: $S_2 \rightarrow S_1 \rightarrow T_2 \rightarrow T_1$
- Agreement with previous nonadiabatic dynamics in 6tGuanine
- 13% of the trajectories follow the direct $S_2 \rightarrow T_2$ path
- No deactivation to the ground state

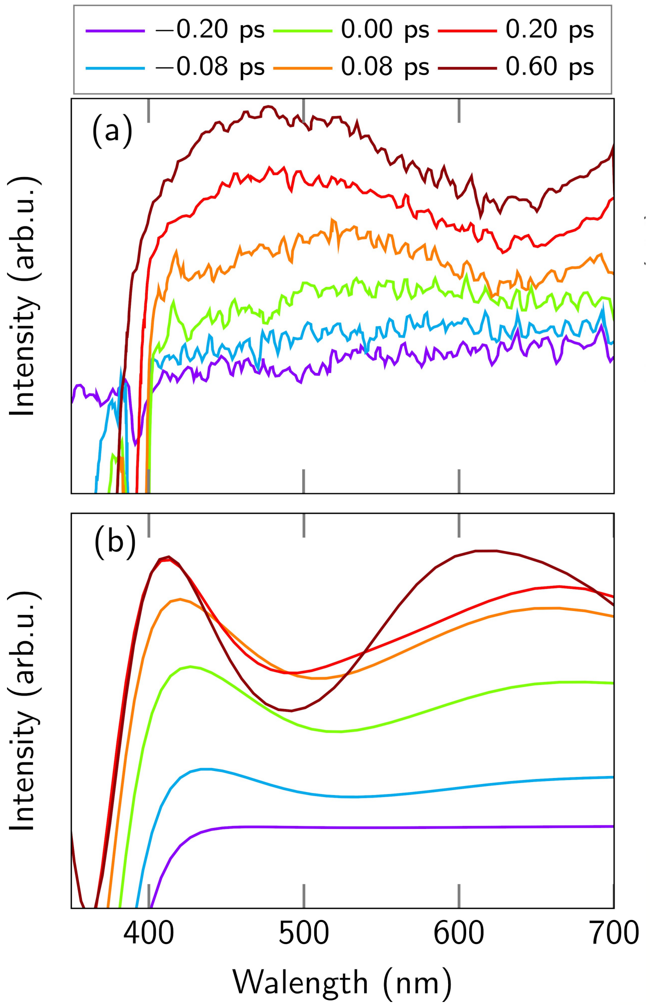
Martínez-Fernandez et. al. Chem. Sci. **5**, 1336 (2014)



- Ultrafast $S_2 \rightarrow S_1$ internal conversion
- $S_1 \rightarrow T_1$ time constant of 122 fs for 6tGuanine.
- ISC time constant of 452 fs, which agrees with previous theoretical results for 2SeUracil (540 fs)

Mai et. al. JCTC **15**, 3730 (2019)

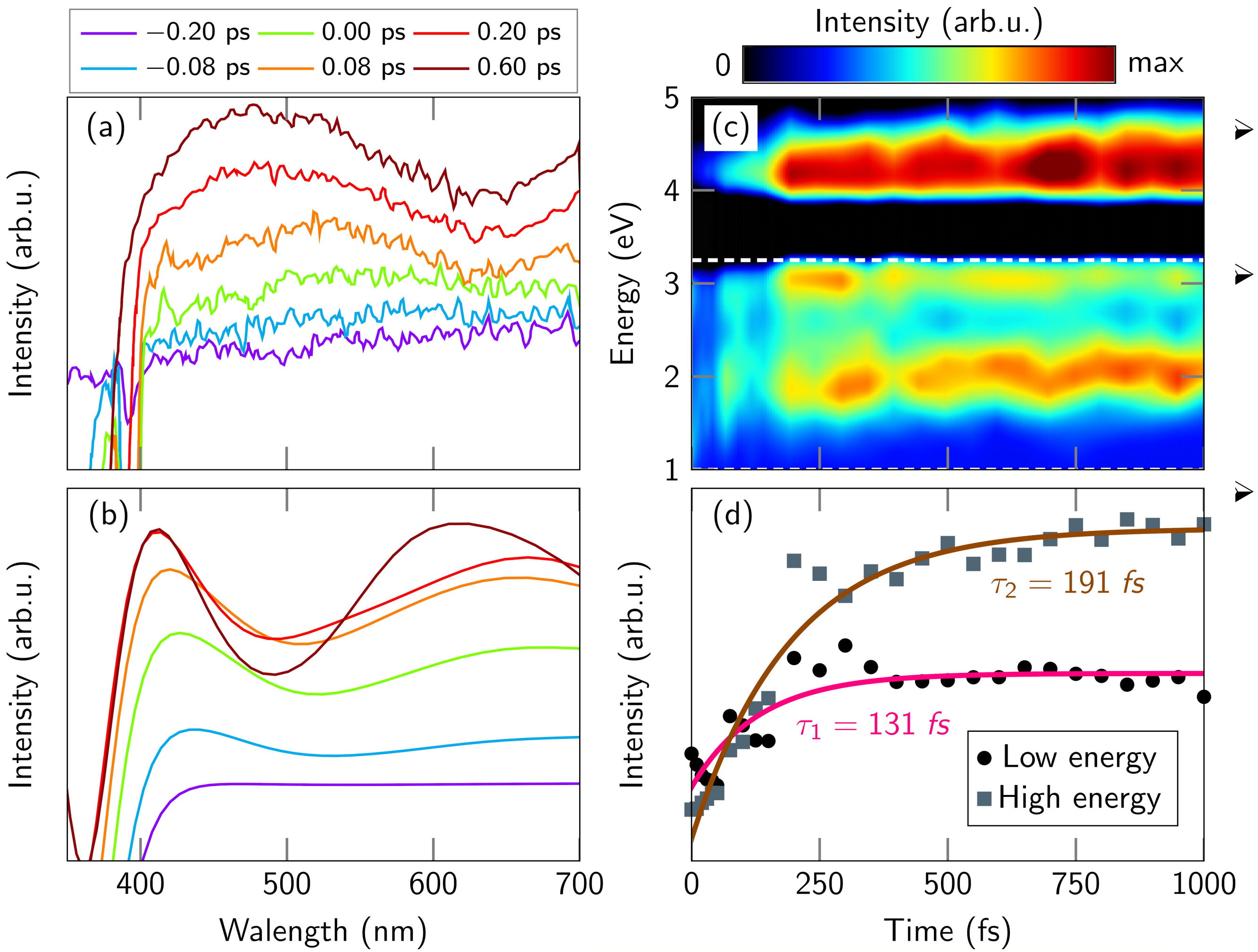
Simulation of the transient absorption spectrum



- Experimental TAS: a peak at 490 nm and a tail at 675 nm;
- Simulated TAS reproduces the experimental intensity growth over the time (bands are slighly shifted).

Valverde et. al. JACS Au. **2**, 1699 (2022)

Simulation of the transient absorption spectrum

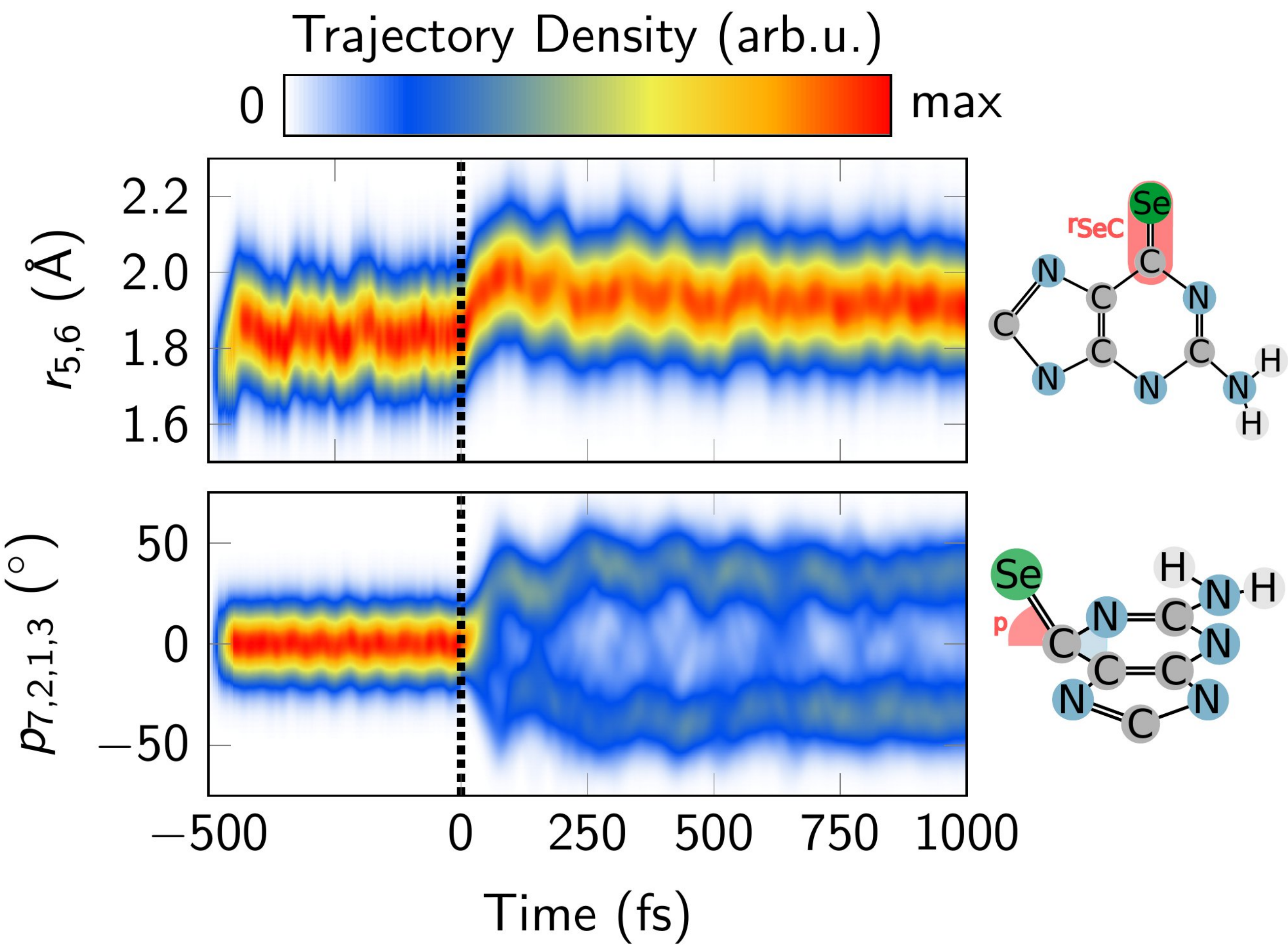


- Experimental TAS: a peak at 490 nm and a tail at 675 nm;
- Simulated TAS reproduces the experimental intensity growth over the time (bands are slighly shifted).
- τ_1 has an excellent agreement in comparison with the experimental data:

$$\langle\tau\rangle_{ISC} = 130 \pm 50 \text{ fs}$$

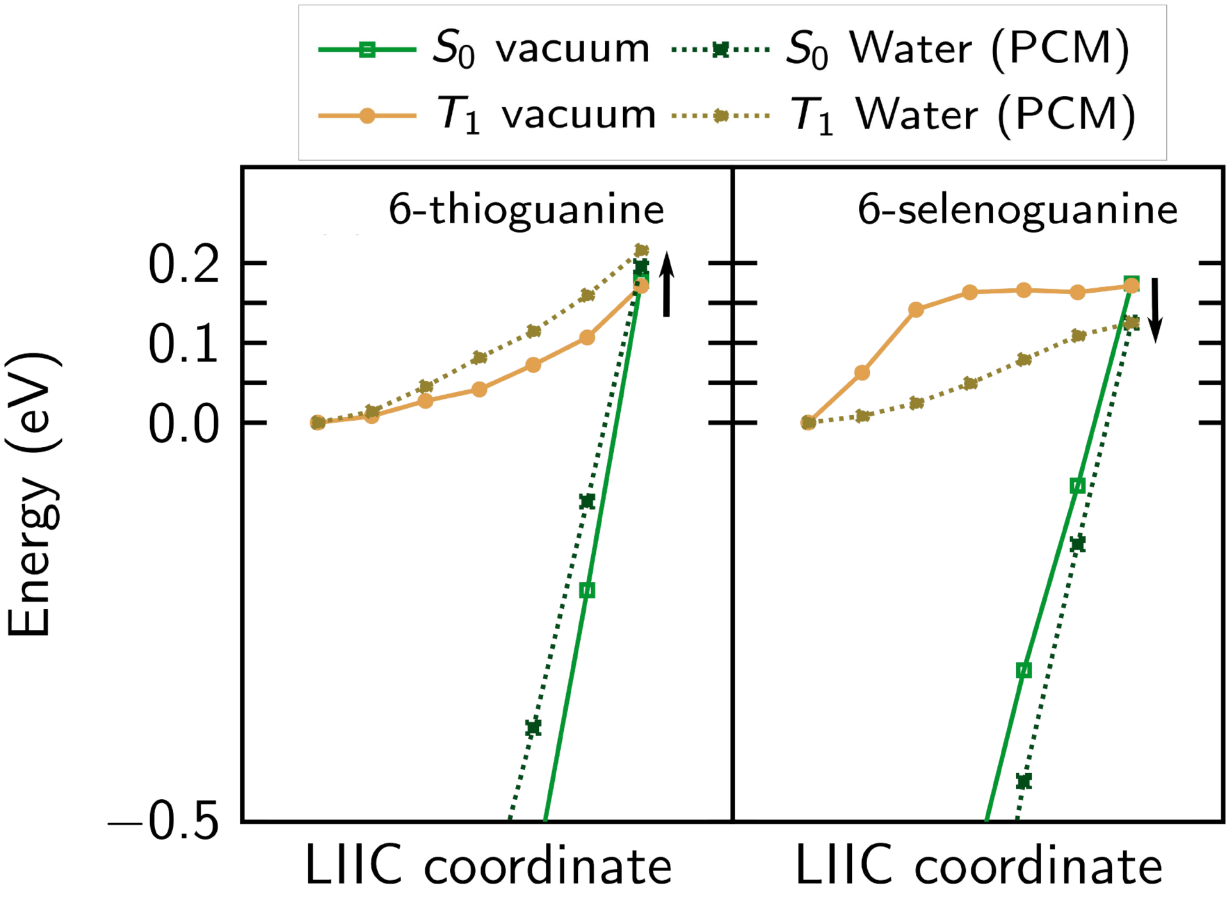
Valverde et. al. JACS Au. **2**, 1699 (2022)

Temporal evolution of keys coordinates



Valverde et. al. JACS Au. **2**, 1699 (2022)

Why the 6SeGua has a shorter triplet lifetime than the 6tGua?



Reasons

- The absence of a second minimum in the T_1 PES.
- Activation energy is smaller for 6SeGua than 6tGua in water.

Activation Energy

	Vacuum	Water
6tGua	0.17 eV	0.22 eV
6SeGua	0.17 eV	0.12 eV

MS(4,3)-CASPT2(14,12)/ANO-RCC-VDZP//MS(4,3)-CASPT2(12,10)/ANO-RCC-VDZP

Valverde et. al. JACS Au. **2**, 1699 (2022)

Conclusion

- Description of the photochemical events.
- Simulation of the same observables is mandatory.
- Explanation of why 6SeGua has a shorter triplet state lifetime.

Acknowlegments

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Thank you all for your attention!