Spiropyran to merocyanine conversion – explicit vs. implicit solvent modeling

Andrzej Eilmes

Faculty of Chemistry, Jagiellonian University, Kraków

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spiropyran to merocyanine conversion

Spiropyran derivatives are known as photochromic compounds (potentially applicable in optical recording, photoswitching devices, etc.).

Colorless spiropyran (SP) derivative isomerizes to colored merocyanine (MC) form upon UV light irradiation.

SP form has lower energy, therefore MC converts to SP in thermally activated process.

Solvents may change relative stabilities of both forms, e.g. in aqueous solution spiropyran form is less stable than the MC structure.

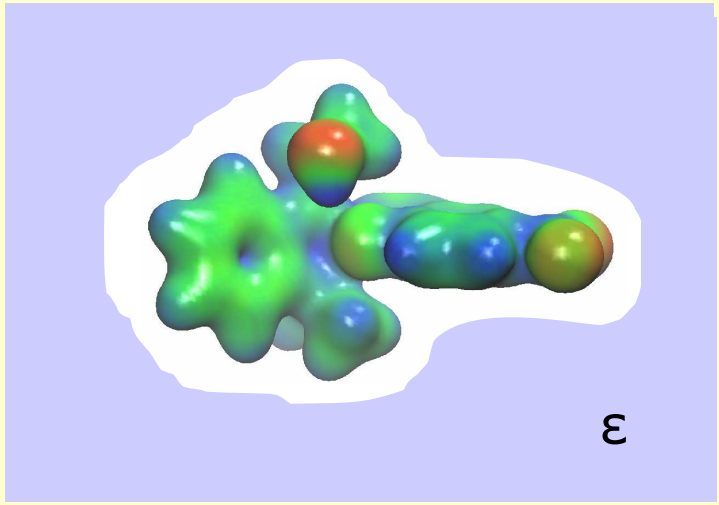
Spiropyran – merocyanine isomerization has been investigated in numerous theoretical studies using quantum-chemical methods.

In most cases implicit solvent was used to account for solvent effects.

Question: are predictions of different solvent models comparable?

solvent modeling: explicit vs. implicit

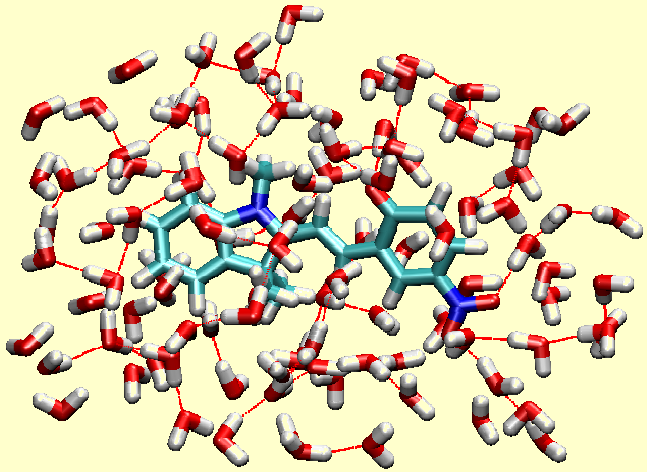
implicit solvent model (e.g. Polarizable Continuum Model):



- cheap
- accounts mainly for electrostatics
- specific interactions are usually not reproduced
- no insight into individual interactions

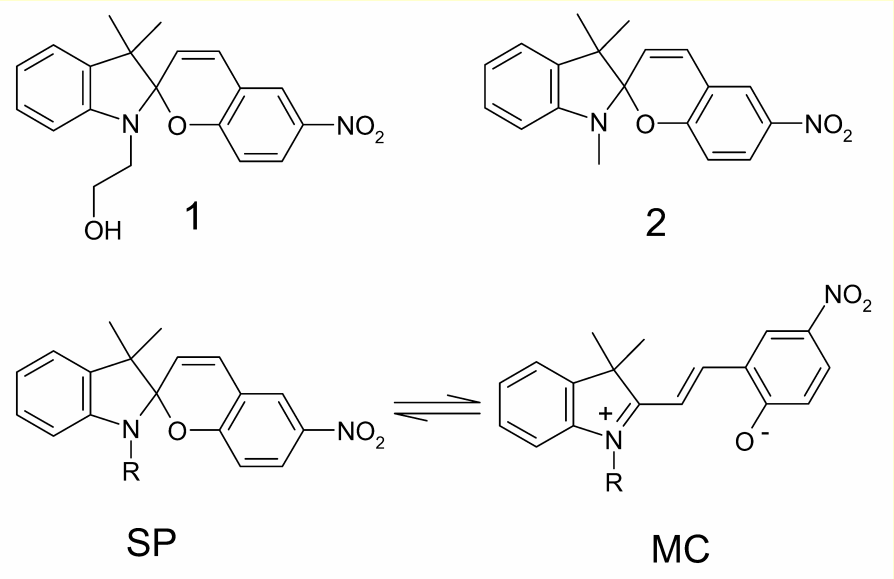
solvent modeling: explicit vs. implicit

explicit solvent model:



- computationally demanding
- could describe specific interactions if appropriate method is used
- one can trace individual interactions

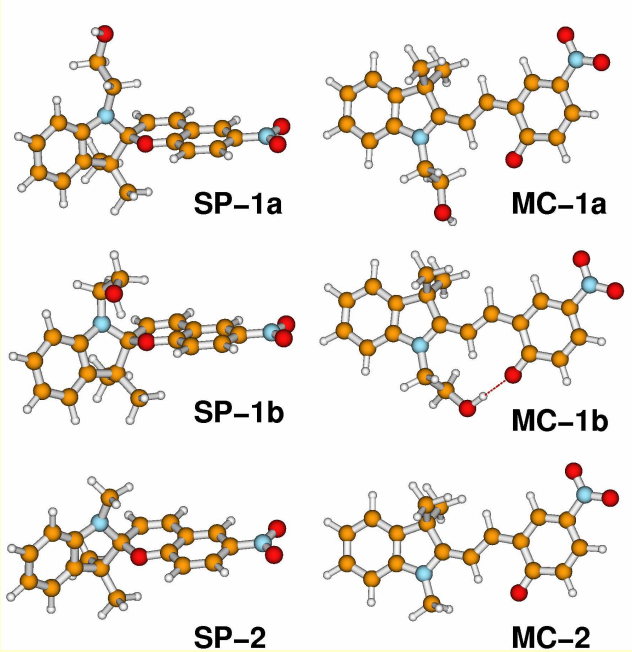
model systems



- **dye 2**: typical SP derivative studied in numerous experimental and computational works
- **dye 1**: recently investigated experimentally (suggested for colorimetric temperature indication), its MC form is more stable in H_2O than the MC form of 2 (effect ascribed to hydrogen bonding)

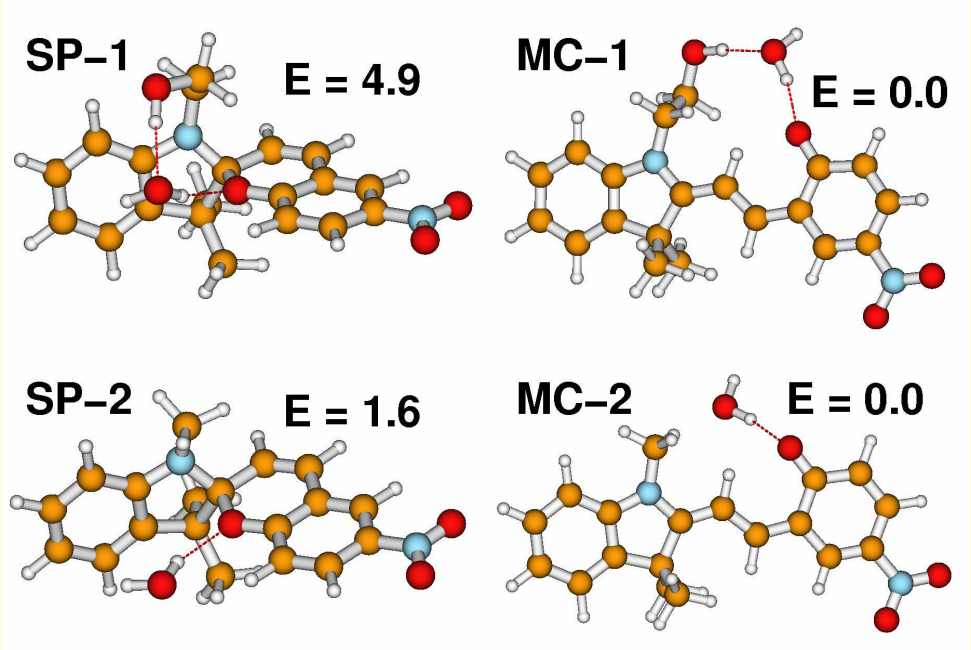
optimized structures

	vaccum				water (PCM)			
structure	6-31G	6-31G*	6-31+G*	6-31++G**	6-31G	6-31G*	6-31+G*	6-31++G**
MC-1a					2.3	1.2	0.0	0.0
MC-1b	0.3	3.2	0.9	0.8	0.0	0.0	0.2	0.4
SP-1a	2.1	1.3	0.3	0.2	6.1	2.0	4.7	4.9
SP-1b	0.0	0.0	0.0	0.0	5.0	1.6	5.3	5.6
MC-2	2.3	5.1	2.8	2.5	0.0	0.0	0.0	0.0
SP-2	0.0	0.0	0.0	0.0	4.8	1.5	5.3	5.6



- B3LYP calculations in vacuum and PCM water
- possible intramolecular hydrogen bond in molecule 1
- energies stabilize at the 6-31+G* level
- MC forms of both molecules in water are about 5 kcal/mol more stable than SP isomers

interactions with single H_2O molecule



structures optimized at the B3LYP/6-31+G* level in vacuum

- first step towards explicit solvation
- even single H_2O molecule reverts relative energies of SP/MC forms
- MC isomer more stable
- effect significantly larger for molecule 1

GP GPU BOMD simulations

Speed of time-consuming BOMD simulations may be greatly increased using GPU acceleration

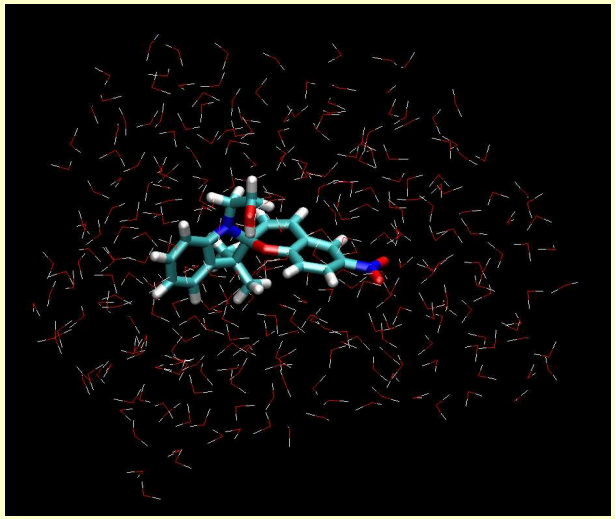
Calculations on *Zeus* cluster: GPU nodes equipped with two NVIDIA Tesla M2050 GPUs

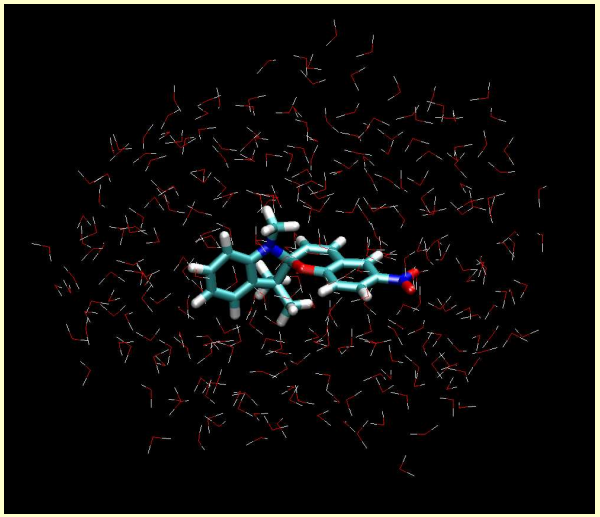
TeraChem v. 1.5 software (PetaChem, LLC, http://www.petachem.com)

- NVT simulations for single dye molecule treated at the B3LYP/6-31+G* level soaked in 300 TIP3P water molecules.
- about 90 s walltime per MD step $\rightarrow$ 25 hours needed to calculate 1 ps of the trajectory
- simulations length about 10 – 15 ps

BOMD simulations of model systems

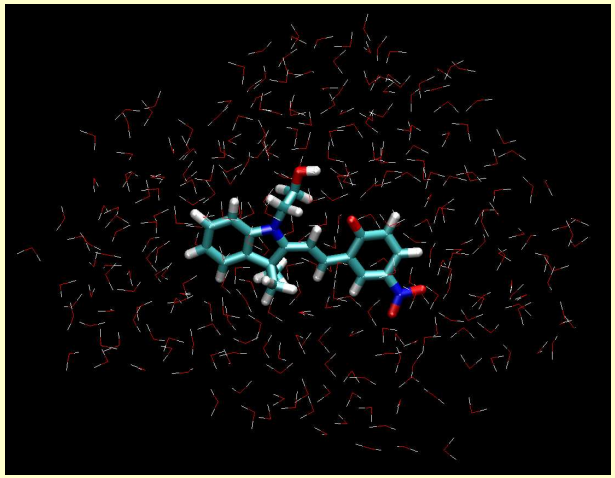
SP-1

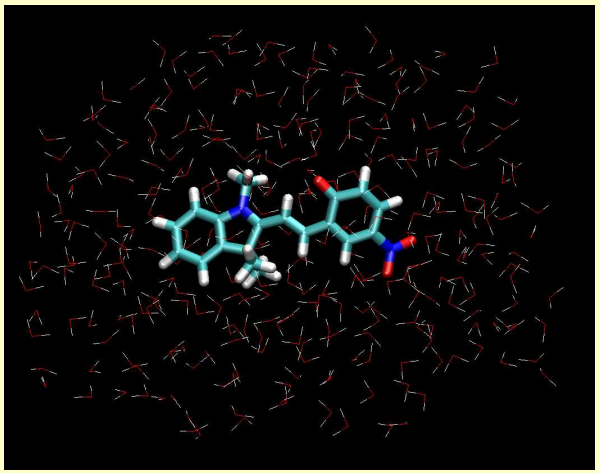




SP-2

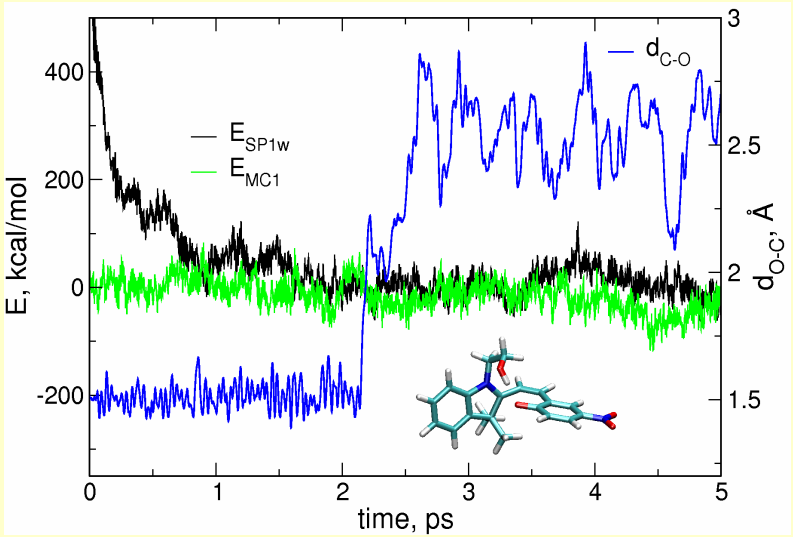
MC-1

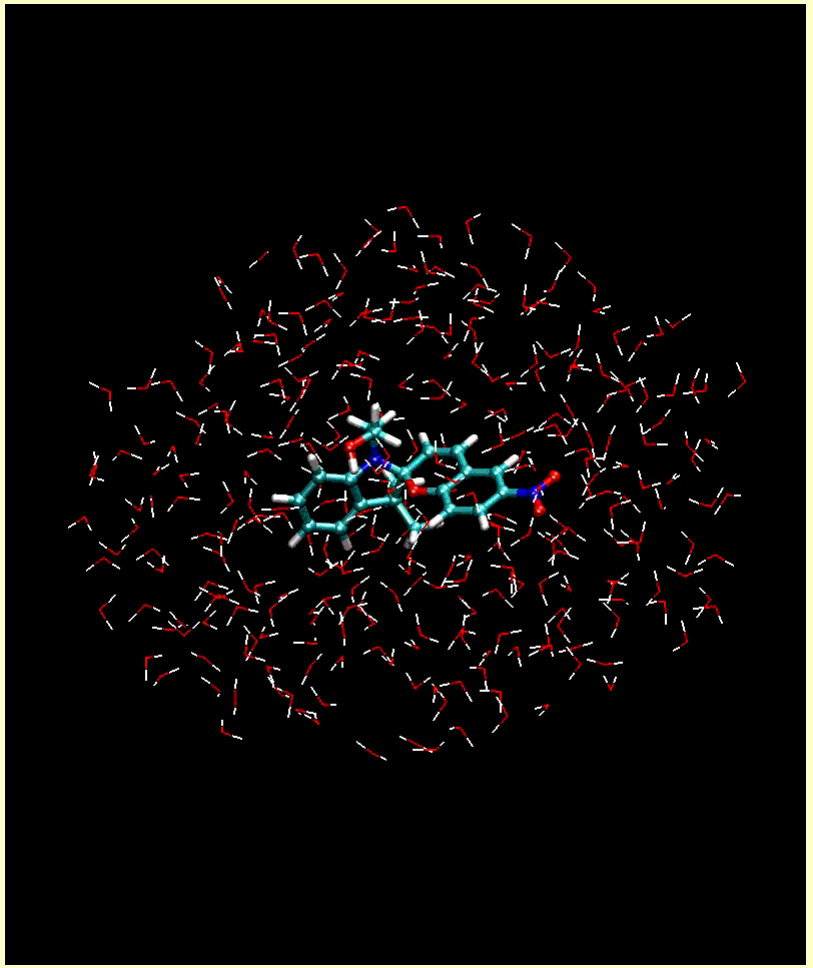




MC-2

SP → MC conversion from BOMD





- after about 2 ps of simulation for molecule 1 the C-O bond breaks
- no significant change in the energy
- effect not observed for the other molecule

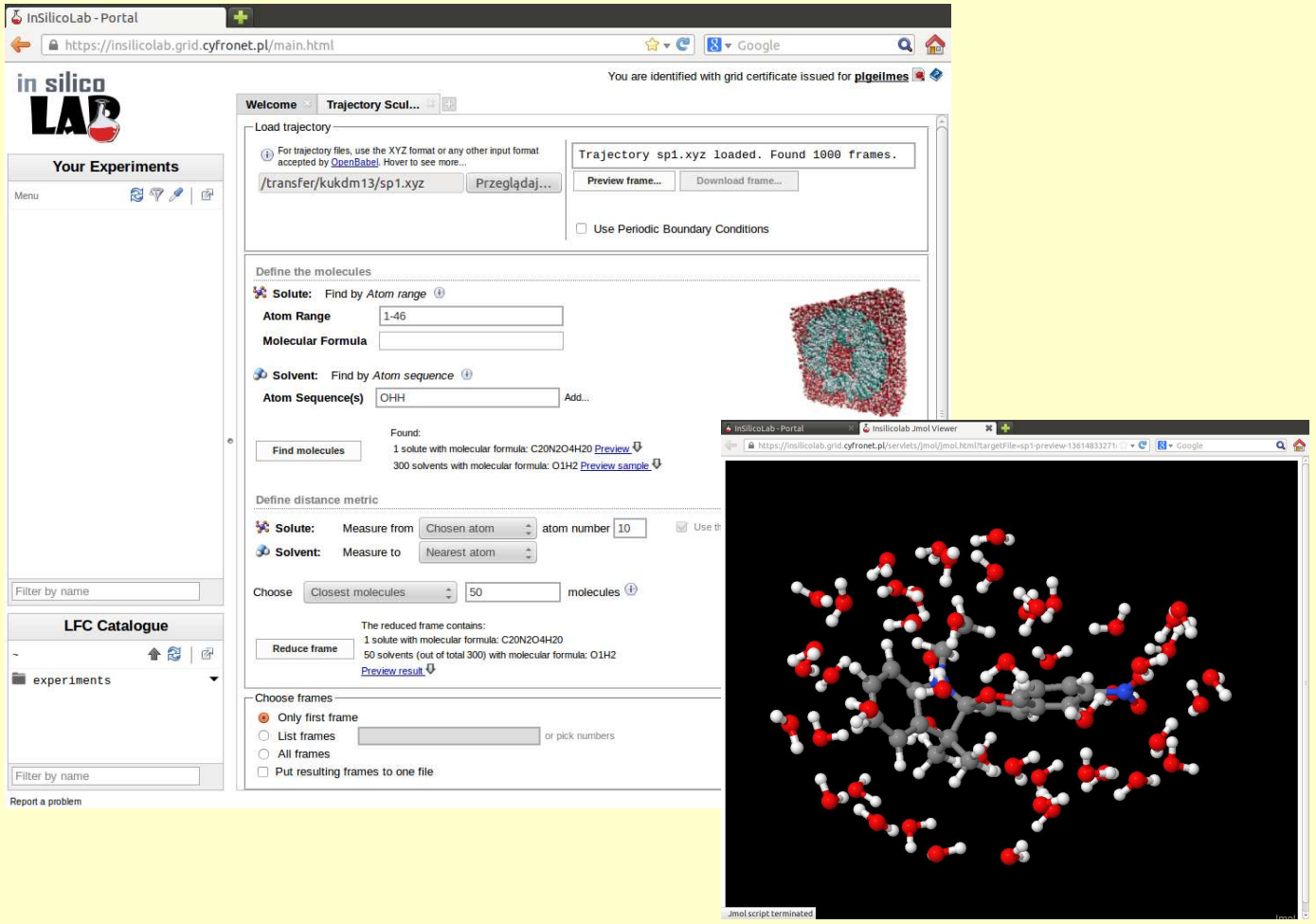
QC calculations for BOMD structures

How to get insight into the bulk solvent effect using a solute solvated in small number of solvent molecules?

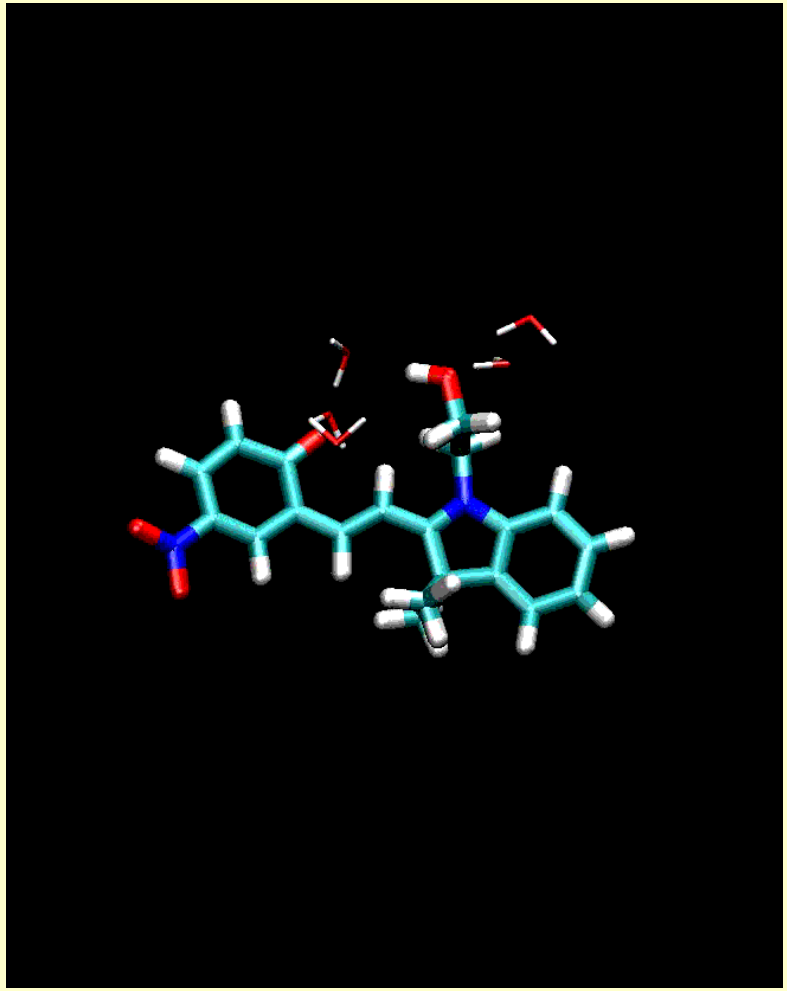
- based on BOMD trajectories series of input data prepared for QC calculations (B3LYP/6-31+G*)
- increasing number *N* of H_2O molecules ranging from *N* = 0 to *N* =100
- 100 individual structures for each molecule and *N* value used to calculate energies
- energy difference $E_{SP} - E_{MC}$ calculated for each *N* from averaged results
- for the SP-1 $\rightarrow$ MC-1 simulation absorption spectrum (averaged over 25 structures with 50 water molecules) calculated for different parts of the trajectory

selection of nearest H_2O molecules

preparation of large sets of input files from MD trajectory may be greatly facilitated by the Trajectory Scupltor tool in InSilicoLab



selection of nearest H_2O molecules



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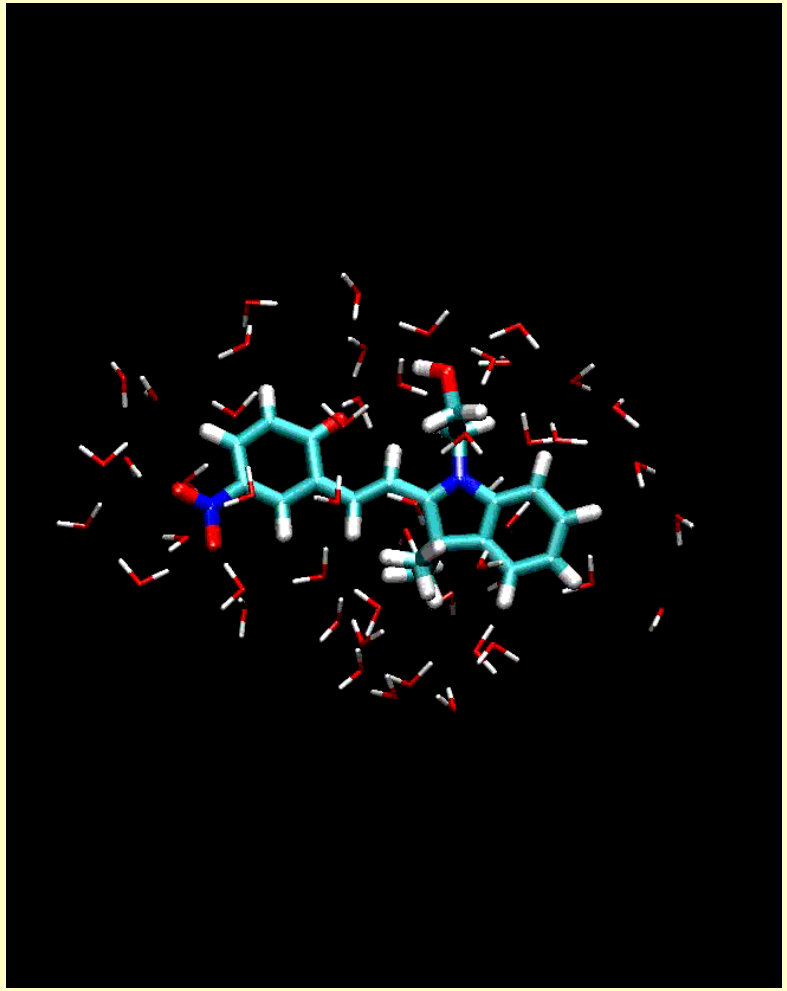

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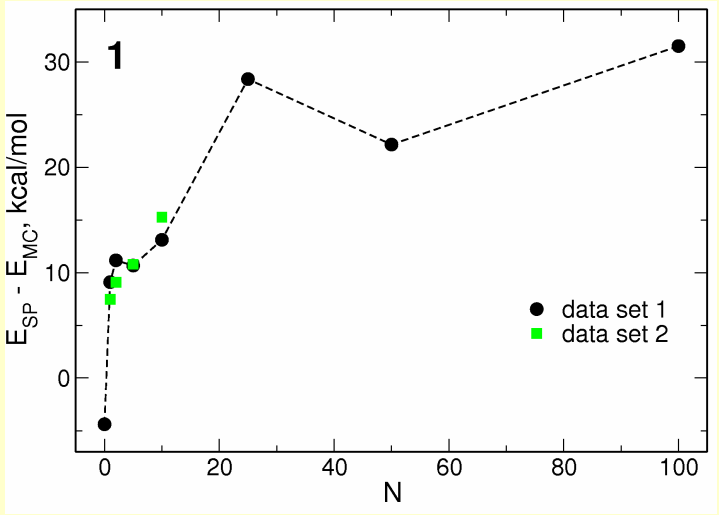
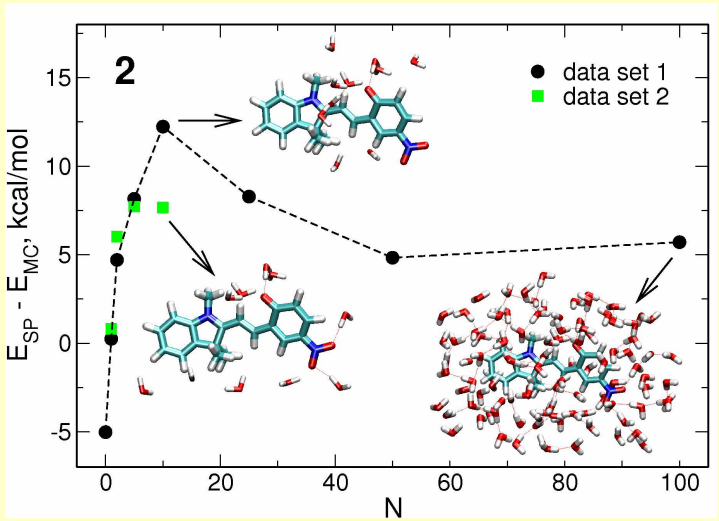
interactions with explicit water: energies





Molecule 2

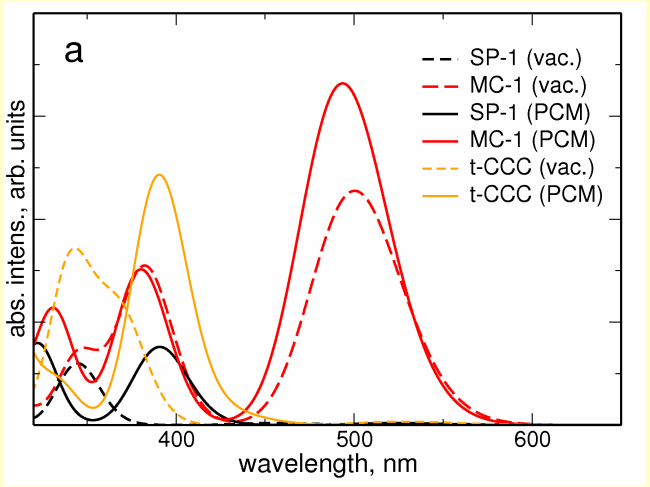
- results saturate at the PCM value
- maximum related to the structure of the solvation shell

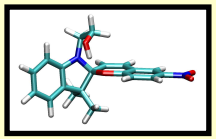
Molecule 1

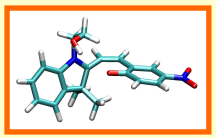
- results still not saturated for N=100 – effect of the shape of the molecule (?)
- stabilization much larger than in the PCM approach

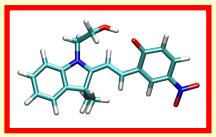
Difference may be attributed to specific interactions (hydrogen bonding), the effect probably overestimated (larger N needed)

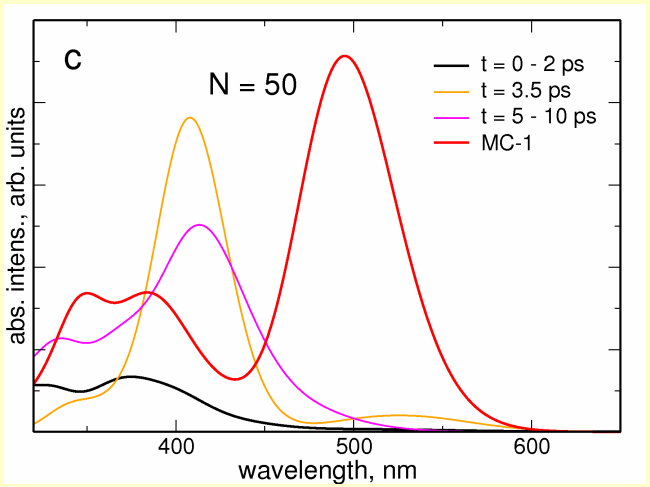
interactions with explicit water: spectra











- explicit solvent model and the PCM approach yield comparable effects in absorption spectra
- in the course of MD simulation absorption maximum shifts to lower energies indicating SP → MC conversion
- even after 10 ps absorption still differs from the MC spectrum
- molecule remains in twisted *cis-cis-cis* conformation (time too short to cross the energy barrier)

conclusions

- Only one water molecule is sufficient to stabilize the merocyanine form of the dye against the spiropyran structure
- Stabilization of the MC form larger for dye 1 (in agreement with the experiment)
- PCM and explicit water give comparable results for molecule 2; for dye 1 explicit model yields stabilzation much larger than continuous solvent – likely an effect of hydrogen bonding
- Both models produce similar effects in absorption spectra (electrostatics is dominating)
- Sequential approach may be an effective tool to study solvent effects

More information: A. Eilmes, „Spiropyran to Merocyanine Conversion – Explicit vs. Implicit Solvent Modeling", J. Phys. Chem. A, DOI: 10.1021/jp3117209

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