

Spiropyran to merocyanine conversion – explicit vs. implicit solvent modeling

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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.

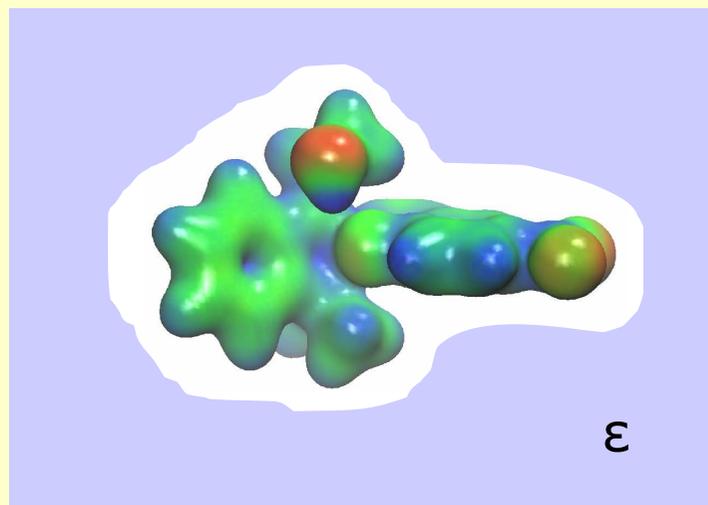
Spiropyran – merocyanine isomerization has been investigated in numerous theoretical studies using quantum-chemical methods.

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

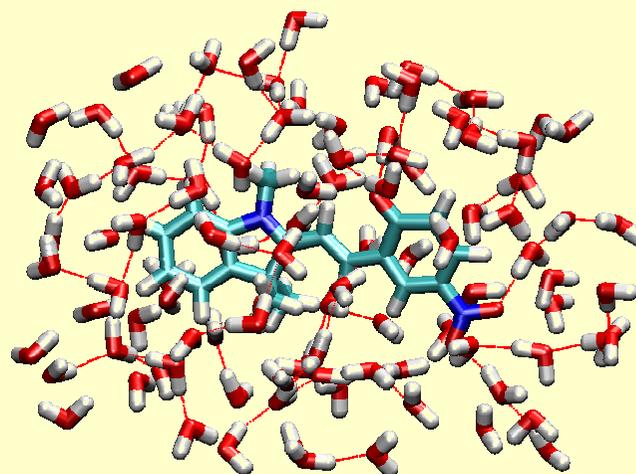
implicit solvent model (e.g. Polarizable Continuum Model):



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

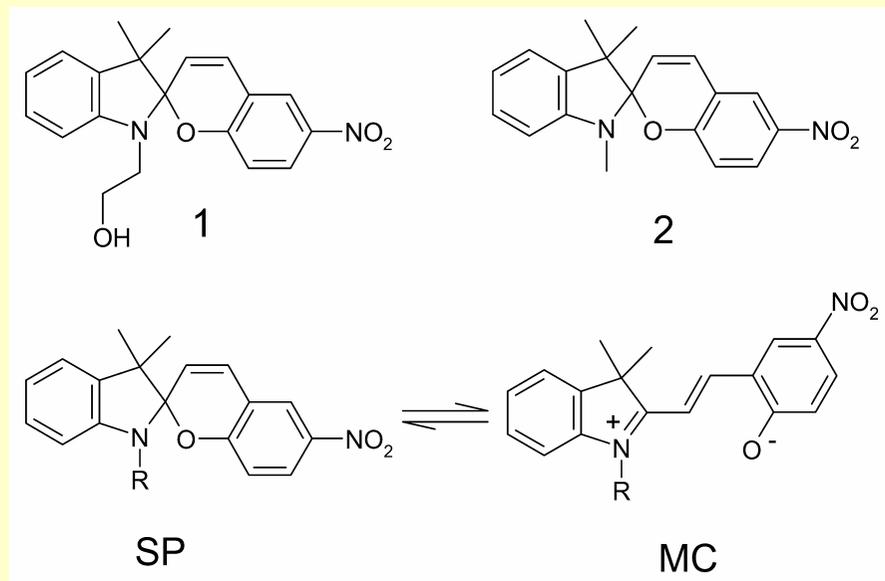
solvent modeling: explicit vs. implicit

explicit solvent model:



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

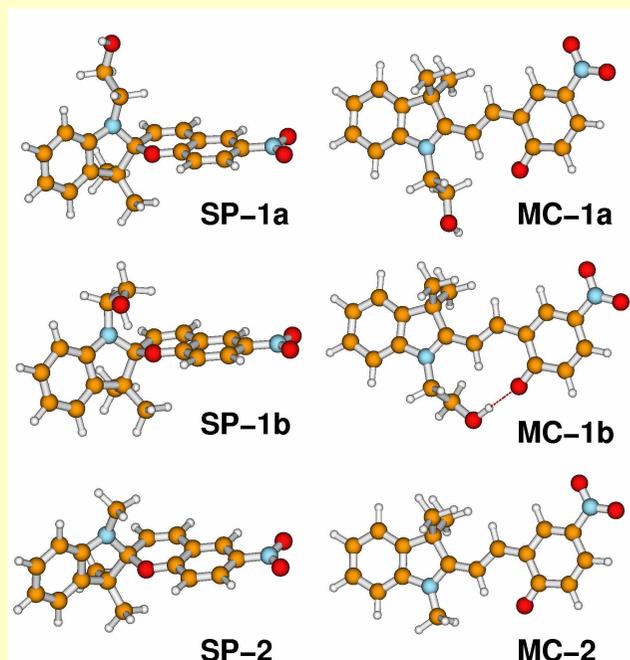
model systems



- **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 H₂O than the MC form of 2 (effect ascribed to hydrogen bonding)

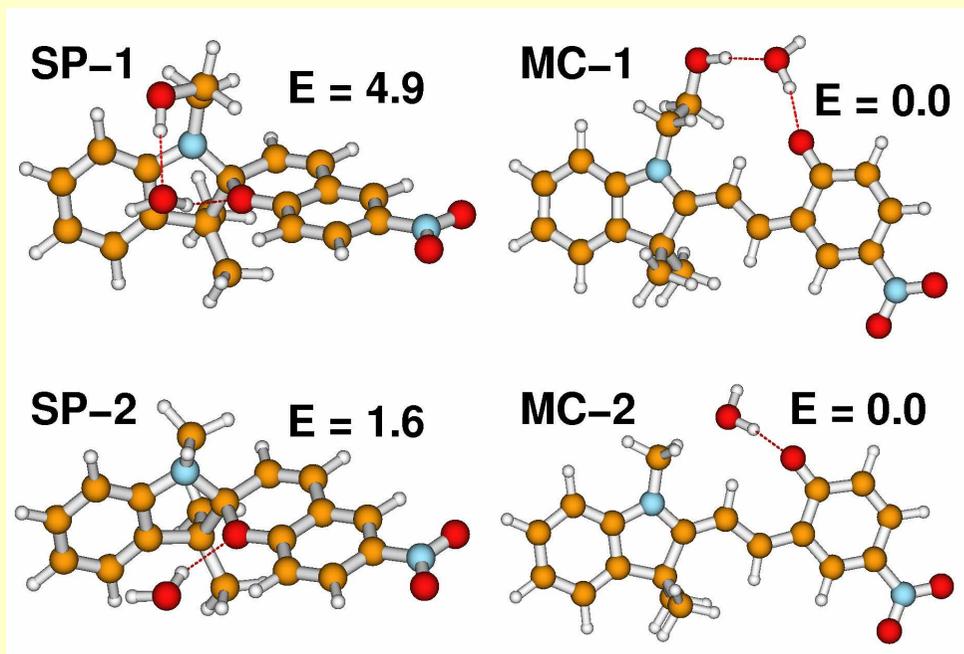
optimized structures

structure	vacuum				water (PCM)			
	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 H₂O molecule



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

- first step towards explicit solvation
- even single H₂O 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

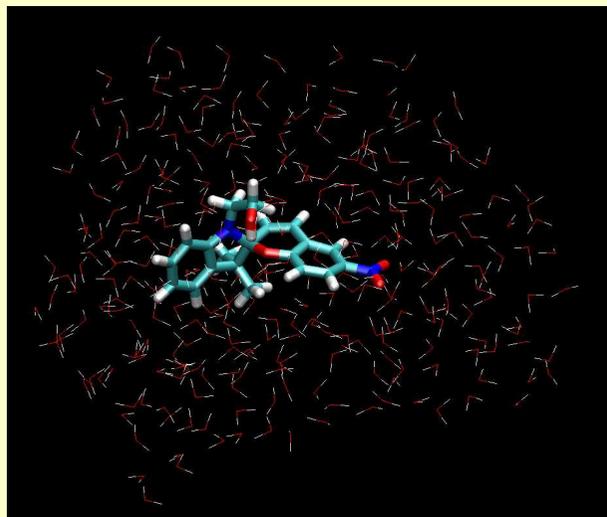
Calculations on *Zeus* cluster: GPU nodes equipped with two NVIDIA Tesla M2050 GPUs

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

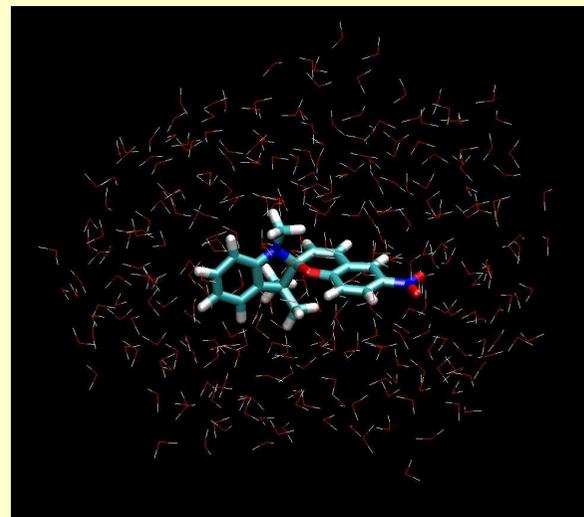
- NVT simulations for single dye molecule treated at the B3LYP/6-31+G* level soaked in 300 TIP3P water molecules.
- about 90 s walltime per MD step → 25 hours needed to calculate 1 ps of the trajectory
- simulations length about 10 – 15 ps

BOMD simulations of model systems

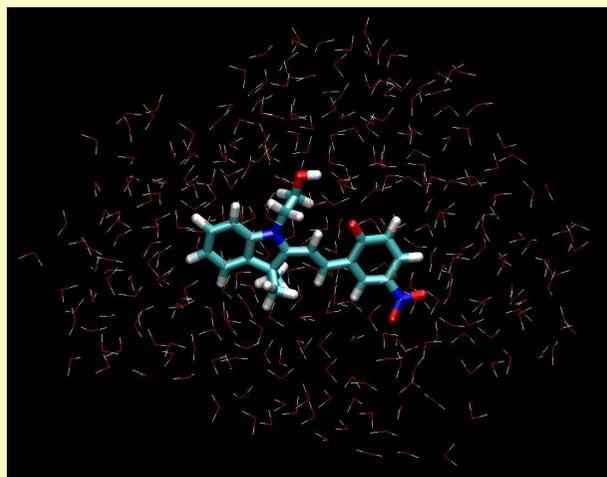
SP-1



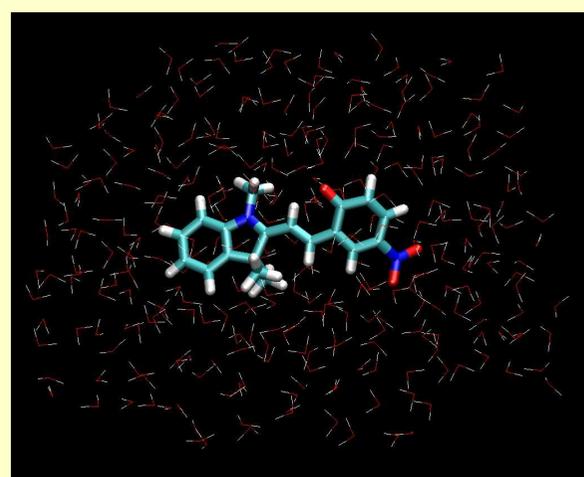
SP-2



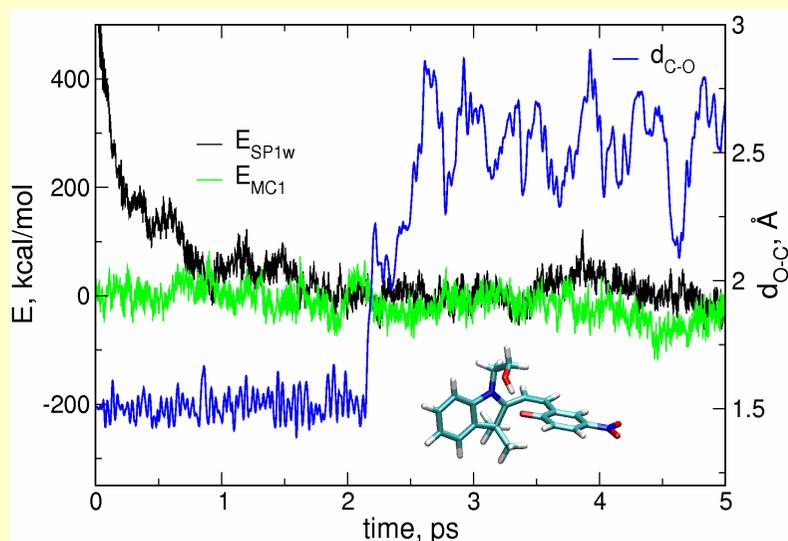
MC-1



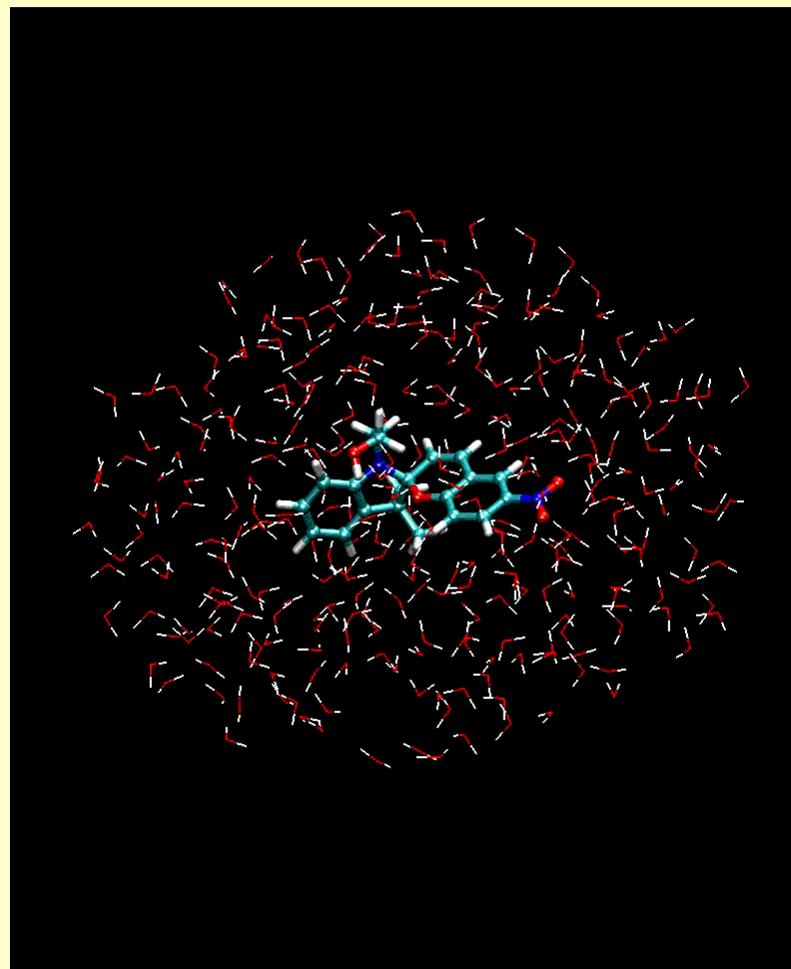
MC-2



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 H₂O 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 H₂O molecules

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

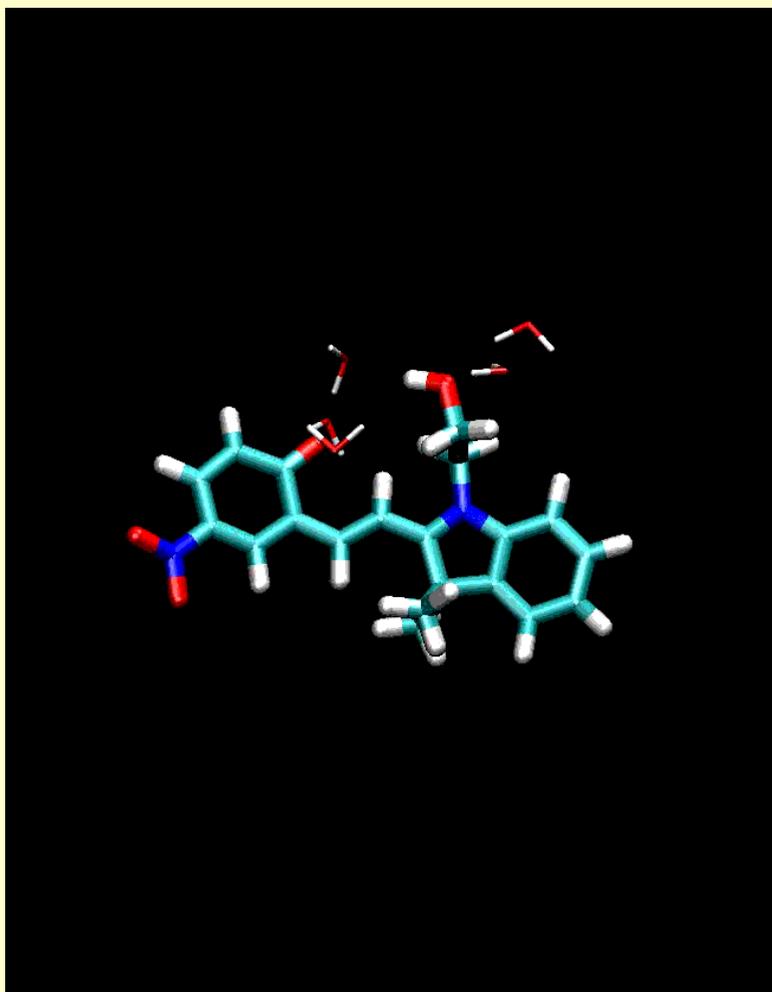
The screenshot displays the InSilicoLab Trajectory Sculptor web interface. The browser address bar shows <https://insilicolab.grid.cyfronet.pl/main.html>. The page title is "in silico LAB". The user is identified with a grid certificate issued for "plgelmes".

The main interface is titled "Trajectory Sculptor" and shows the following steps:

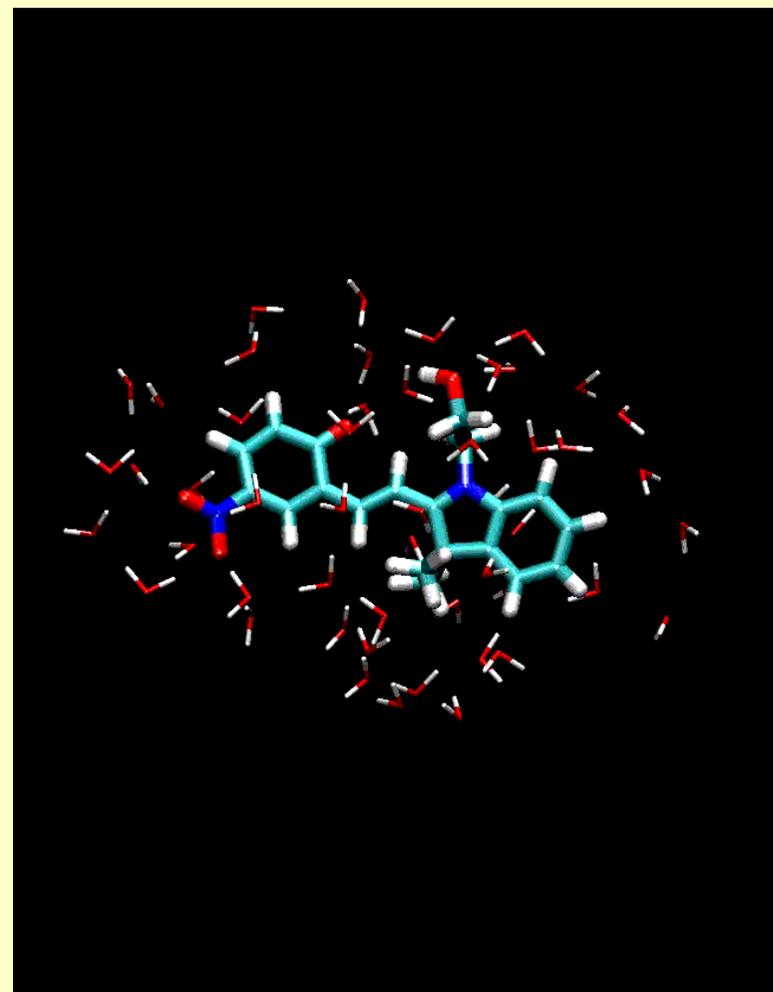
- Load trajectory:** A message states "Trajectory sp1.xyz loaded. Found 1000 frames." The file path is `/transfer/kukdm13/sp1.xyz`. There are buttons for "Przełóżaj...", "Preview frame...", and "Download frame...". A checkbox for "Use Periodic Boundary Conditions" is present.
- Define the molecules:**
 - Solute:** "Find by Atom range" with "Atom Range" set to "1-46" and "Molecular Formula" empty.
 - Solvent:** "Find by Atom sequence" with "Atom Sequence(s)" set to "OHH".
- Find molecules:** A message states "Found: 1 solute with molecular formula: C20N2O4H20" and "300 solvents with molecular formula: O1H2".
- Define distance metric:**
 - Solute:** "Measure from" "Chosen atom" "atom number" "10".
 - Solvent:** "Measure to" "Nearest atom".
- Choose:** "Closest molecules" "50" molecules.
- Reduce frame:** A message states "The reduced frame contains: 1 solute with molecular formula: C20N2O4H20" and "50 solvents (out of total 300) with molecular formula: O1H2".
- Choose frames:** "Only first frame" is selected.

On the right side, there is a 3D visualization of the molecular system, showing a complex structure of atoms (red, white, grey, blue) in a box. Below it, a larger window titled "Insilicolab Jmol Viewer" shows a detailed 3D ball-and-stick model of a molecule, likely the solute, with a black background.

selection of nearest H₂O molecules

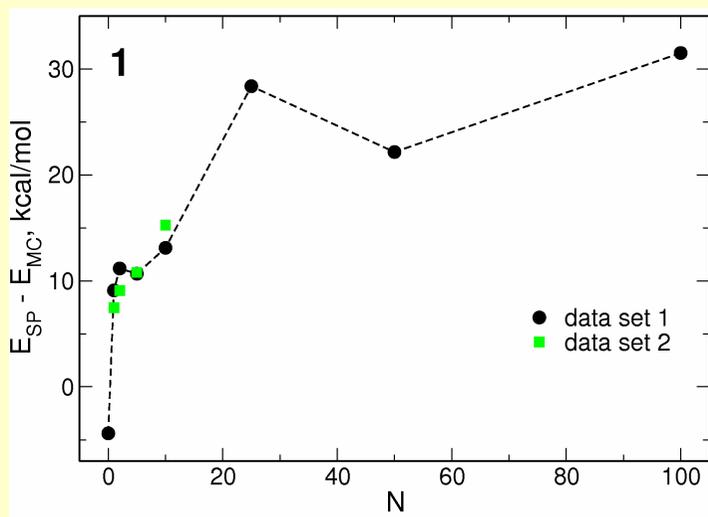


5



50

interactions with explicit water: energies

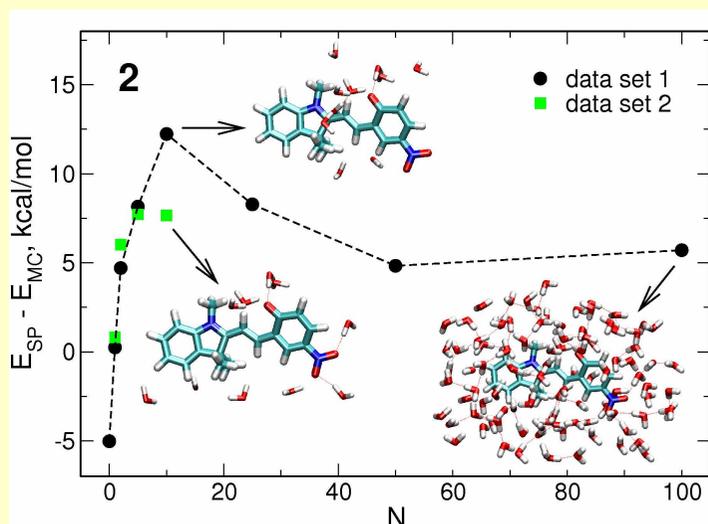


Molecule 2

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

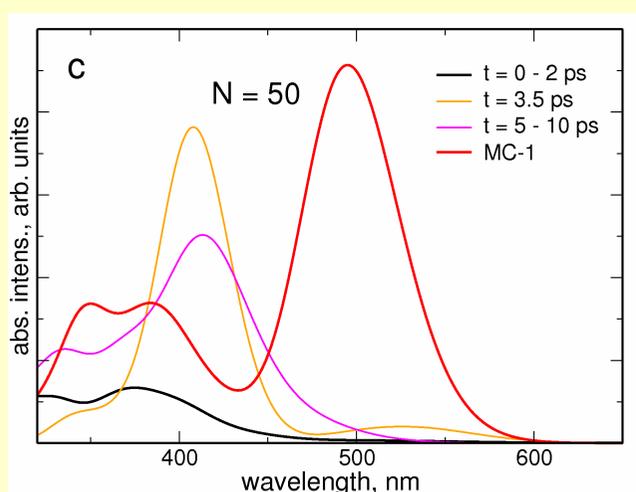
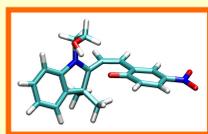
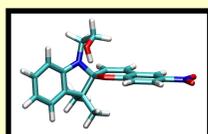
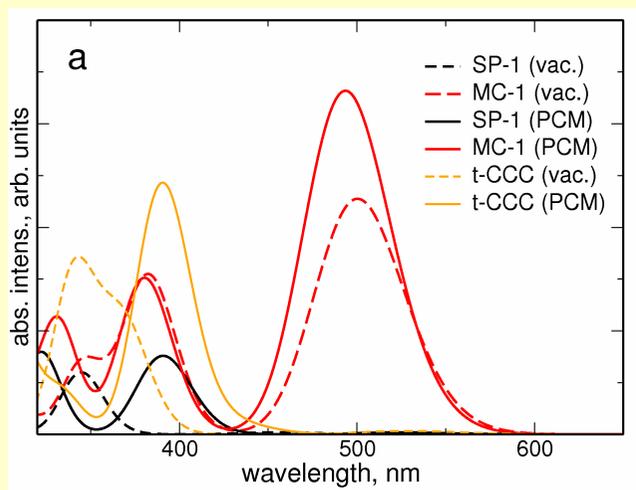
Molecule 1

- 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* 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 stabilization 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](https://doi.org/10.1021/jp3117209)

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