Solvatochromic shifts of a polarity probe – implicit and explicit solvent modeling

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solvent effects in absorption spectra

Absorption spectra of organic molecules in gas phase and in condensed matter (in solutions) are different → solvatochromic shifts

Two important factors contributing to the solvent effect:

-electrostatic interactions with the medium

-specific interactions (e.g. hydrogen bonding)

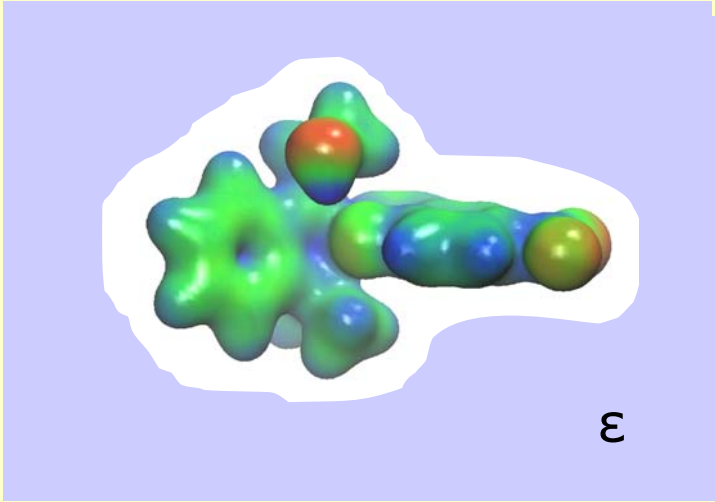
Empirical parameters describe polarity/polarizability of the solvent and its ability to form hydrogen bonds.

Kamlet-Taft parameters – derived from experimental spectra of selected molecules serving as solvatochromic probes.

Question: Are we able to reproduce the shifts in theoretical calculations?

solvent modeling: explicit vs. implicit

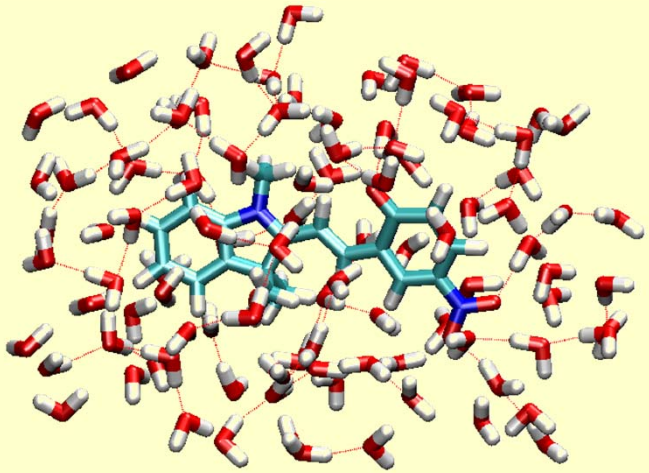
implicit solvent model (e.g. Polarizable Continuum Model):



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

solvent modeling: explicit vs. implicit

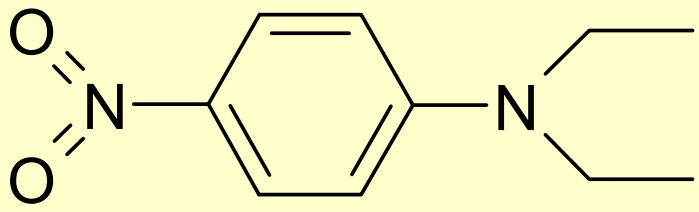
explicit solvent model:



- computationally demanding
- could describe specific interactions if appropriate method was used
- individual interactions can be traced

model system

- probe molecule: *N*,*N*-diethyl-4-nitroaniline



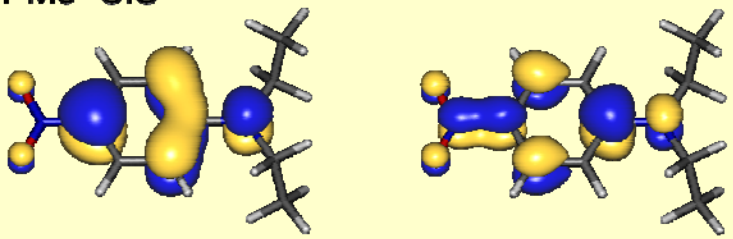
- four common molecular solvents: water, dimethylsulfoxide (DMSO), acetonitrile, acetone
- implicit solvent: variants of the PCM model
- explicit solvent: sequential MD/QM approach
- ZINDO/S, PM6-CIS and TDDFT used to compute excitation energies

dominant NTO pairs

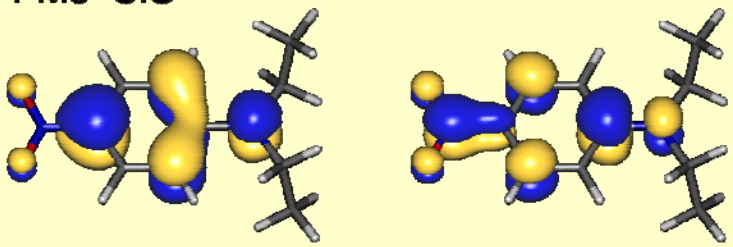
vacuum

PCM water

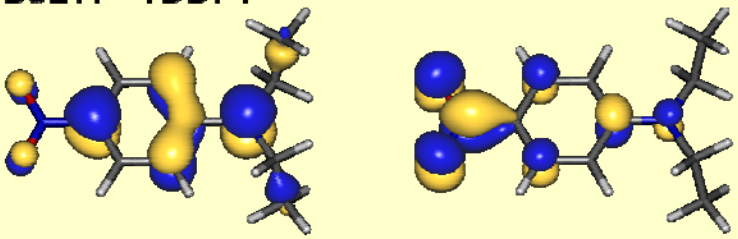
PM6–CIS



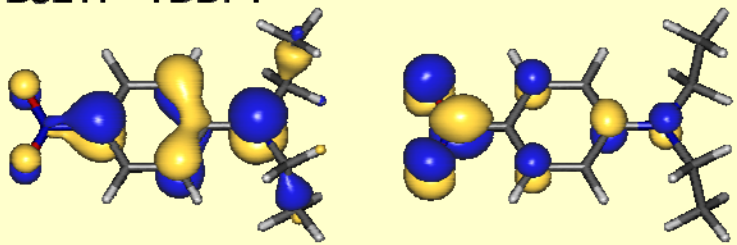
PM6–CIS



B3LYP–TDDFT



B3LYP–TDDFT



implicit solvation

ε_{static}, ε_{∞}	water 78.4, 1.78	DMSO 46.8, 2.01	acetonitrile 35.7, 1.81	acetone 20.5, 1.85
exp.	**430.5**	**411.5**	**397.9**	**396.5**
TDDFT/PCM	392.8	394.3	392.1	391.2
TDDFT/PCM(equil. solv.)	417.4	416.2	415.2	412.4
TDDFT/PCM(st. spec. solv.)	426.3	427.8	425.0	423.3
TDDFT/PCM(SAS)	365.6	357.2	358.6	357.1
TDDFT/CPCM	394.5	396.3	394.0	393.3
TDDFT/SCIPCM	378.1	377.7	377.4	376.4
TDDFT/SMD	411.4	394.8	395.2	393.2
TDDFT/SMD(st. spec. solv.)	445.8	429.3	430.6	427.4
ZINDO/PCM	502.8	513.6	501.2	499.1
PM6-CIS/PCM	430.9	436.8	431.1	431.4

implicit solvation

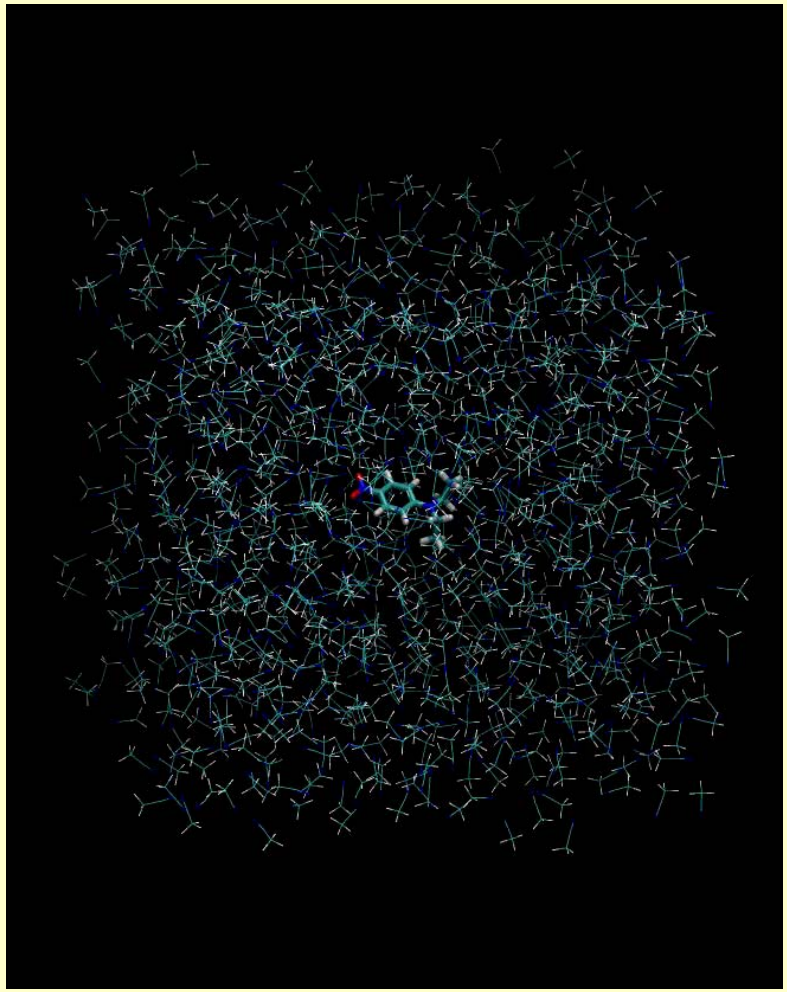
- neither model gives satisfactory reproduction of experimental results
- usually very small differences between solvents and wrong relative shift DMSO vs. water
- models with SMD atomic radii or solvent accessible surface predict significantly larger shift for water
- problem with electrostatics?
- possible hydrogen bonds?

explicit solvent: MD simulations

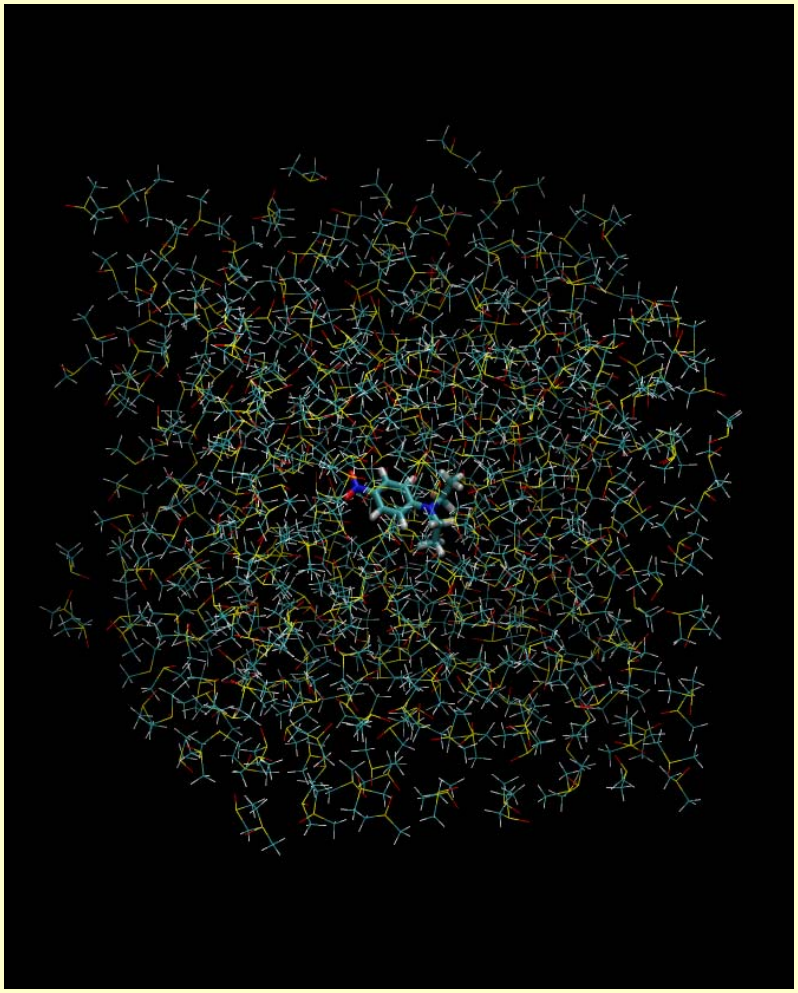
Classical Molecular Dynamics simulations (Tinker v.5)

- MM3-based force field
- frozen geometry of the probe molecule
- periodic simulation box 500 – 1500 solvent molecules
- NVT ensemble at 300 K
- short (0.2 ns) equilibration, production trajectory collected for 1 ns

Got MD trajectories, what next?



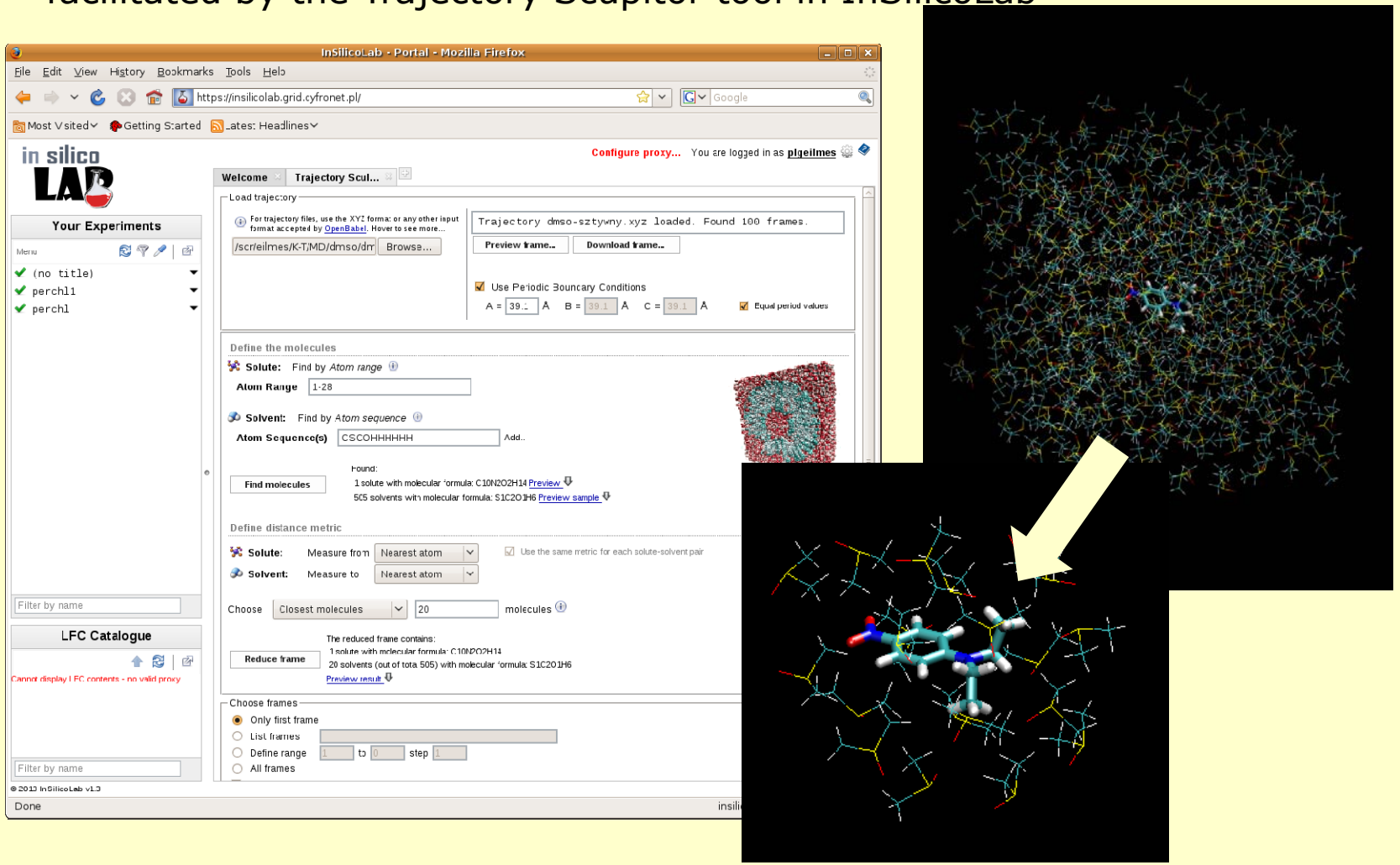
acetonitrile



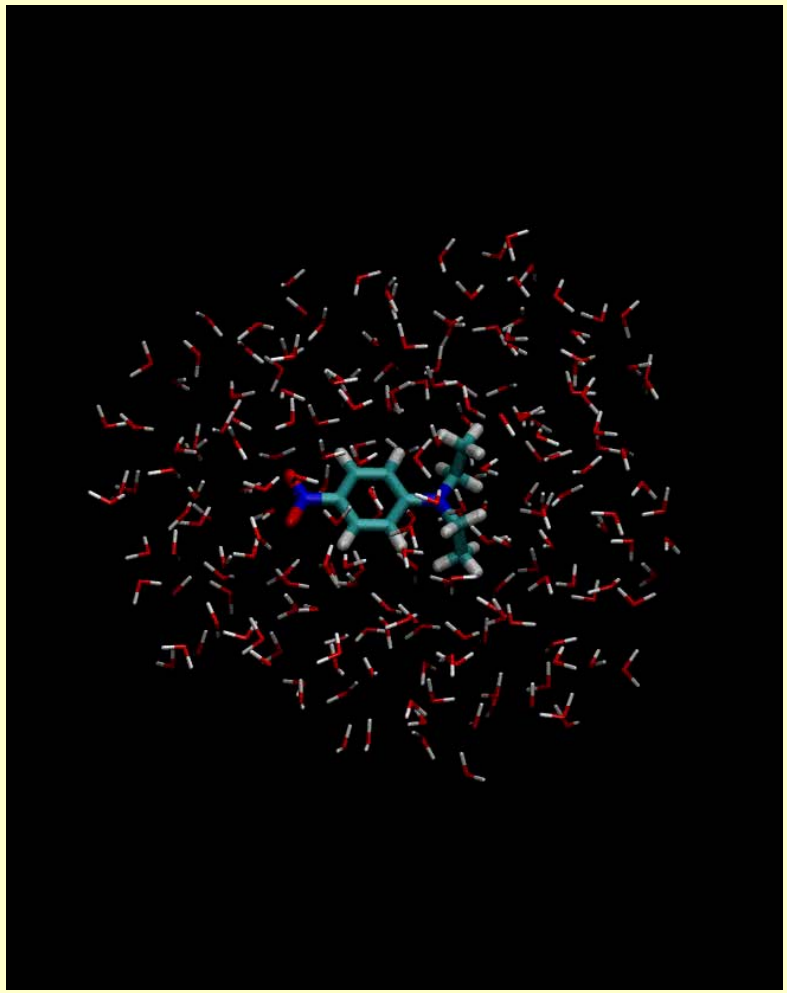
DMSO

InSilicoLab and Trajectory Sculptor

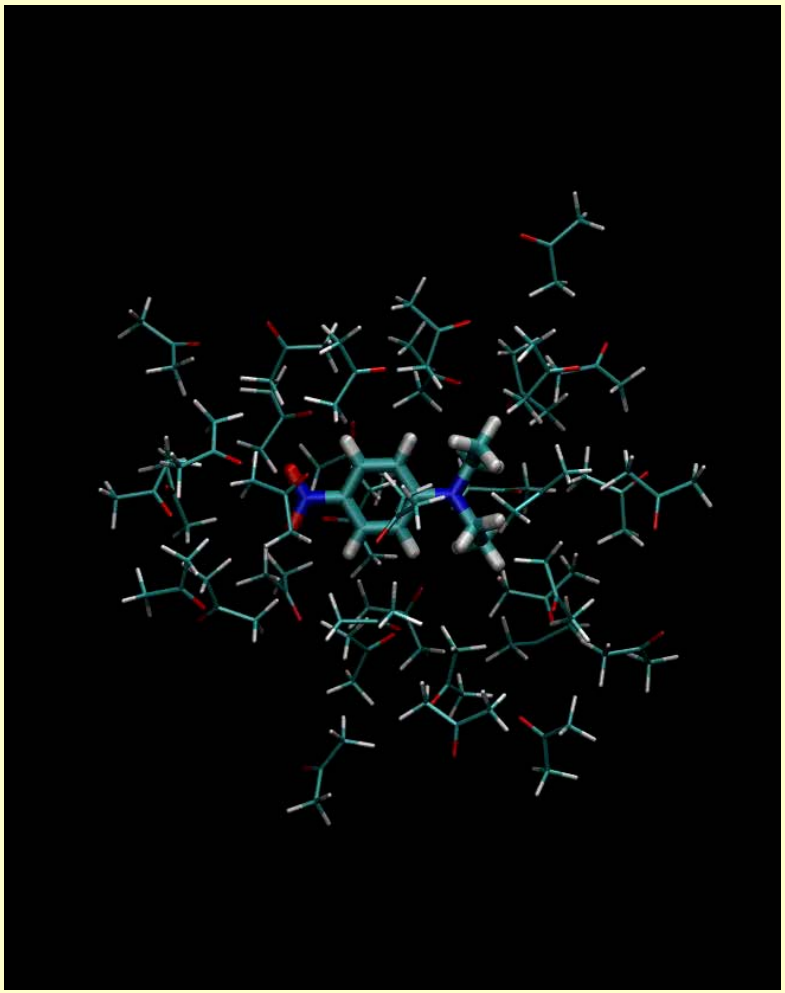
Preparation of large sets of input files from MD trajectories may be greatly facilitated by the Trajectory Scupltor tool in InSilicoLab



reduced MD trajectories

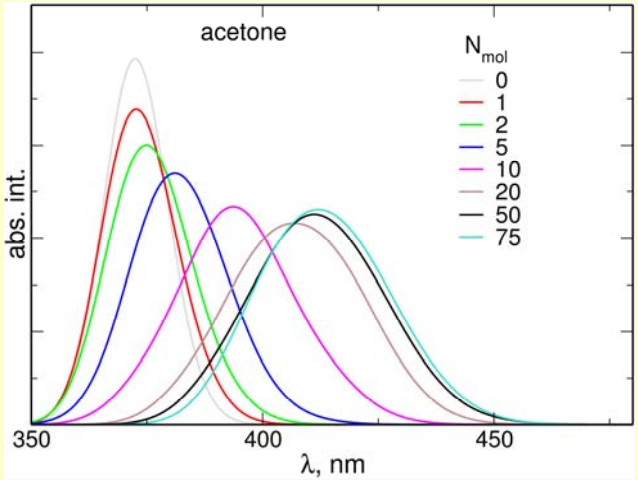


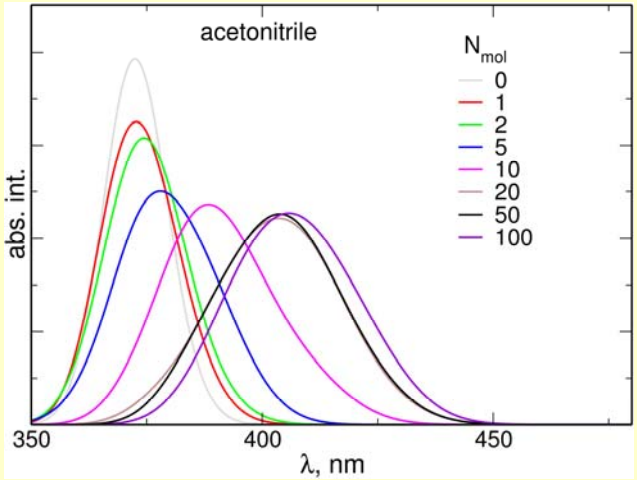
water

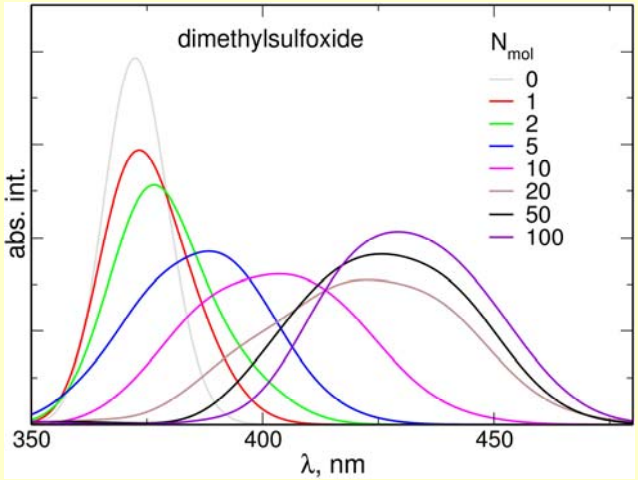


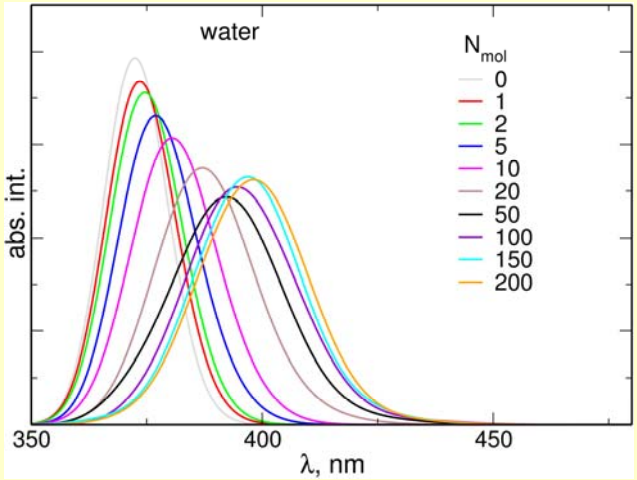
acetone

explicit solvent: simulated spectra



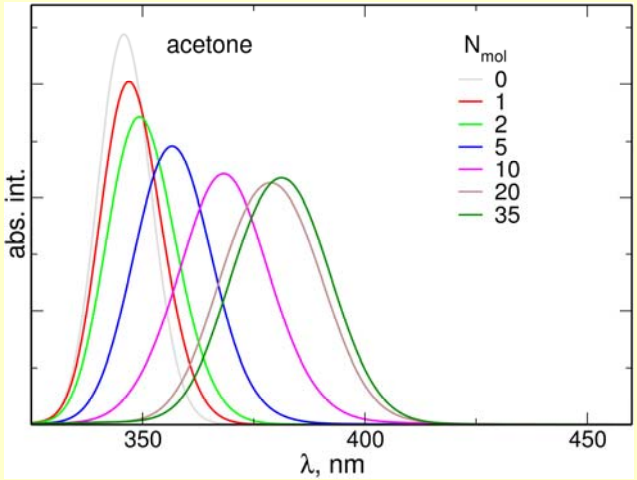


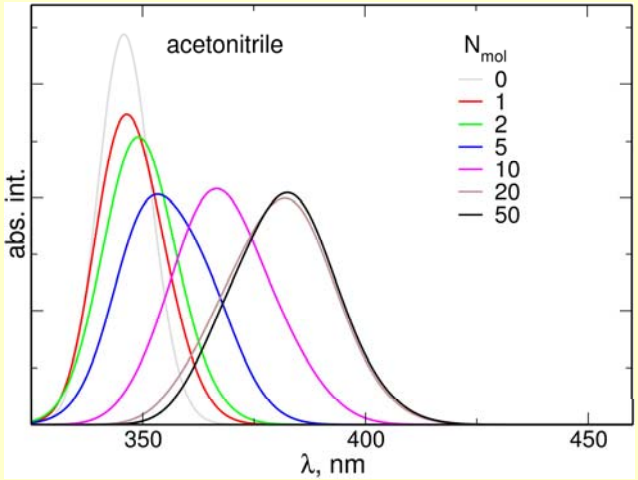


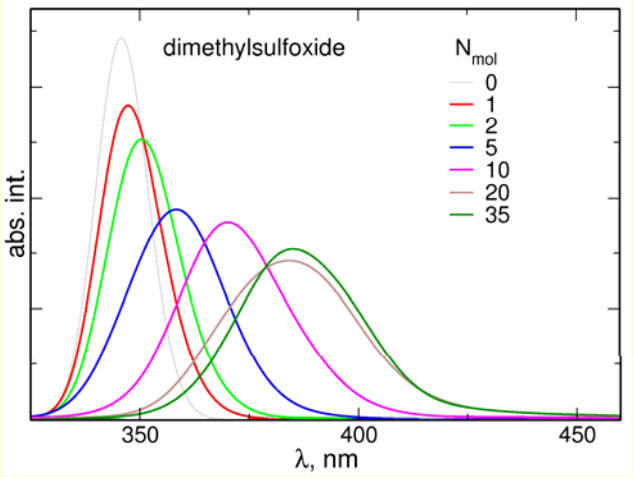


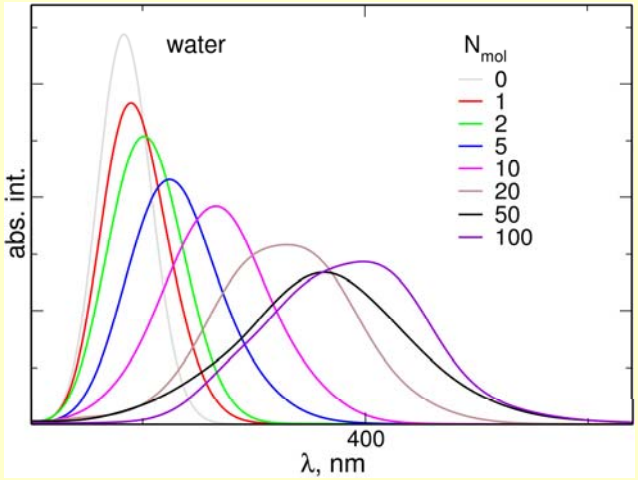
ZINDO/S

explicit solvent: simulated spectra



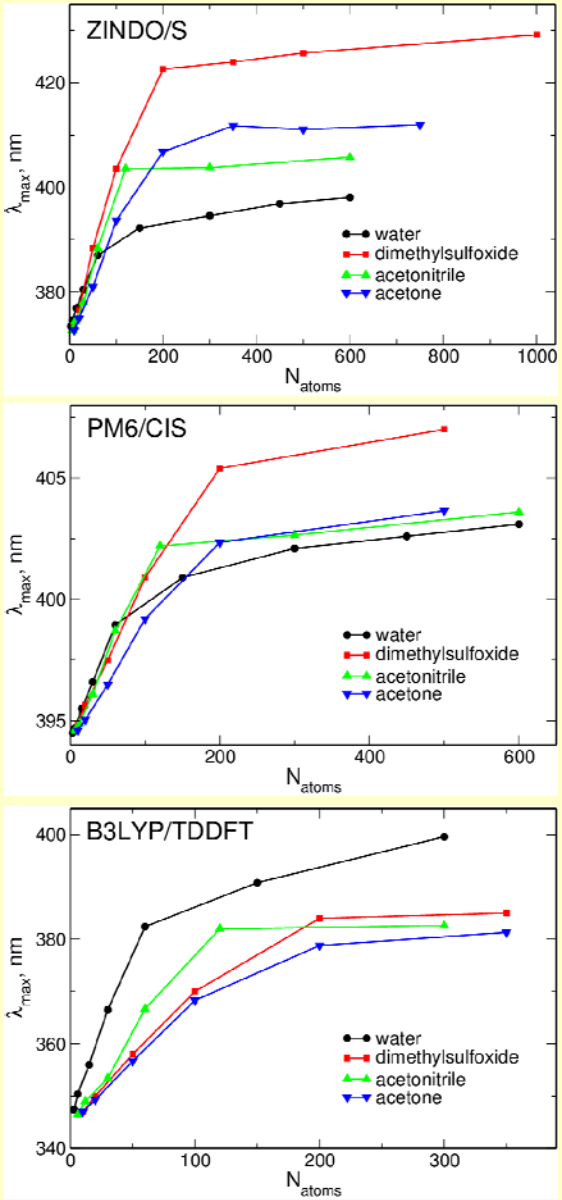






TDDFT (6-311+G* solute, 3-21G solvent)

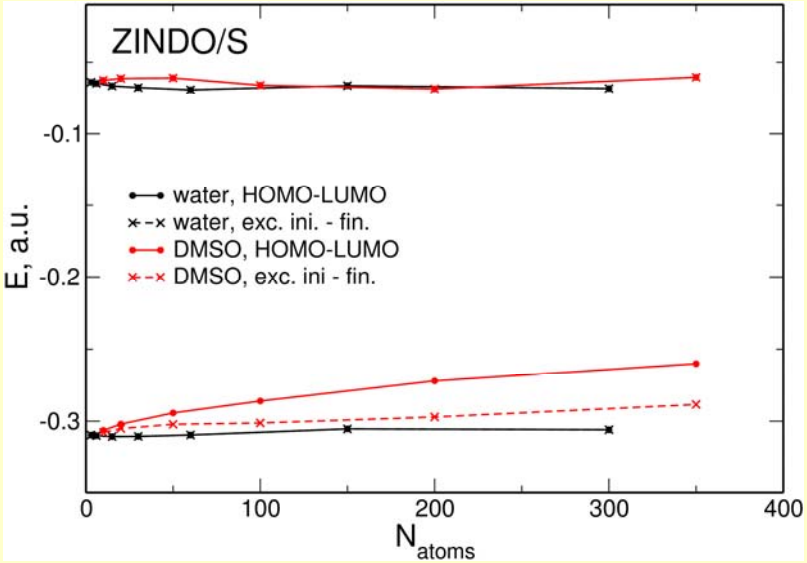
explicit solvent: simulated spectra

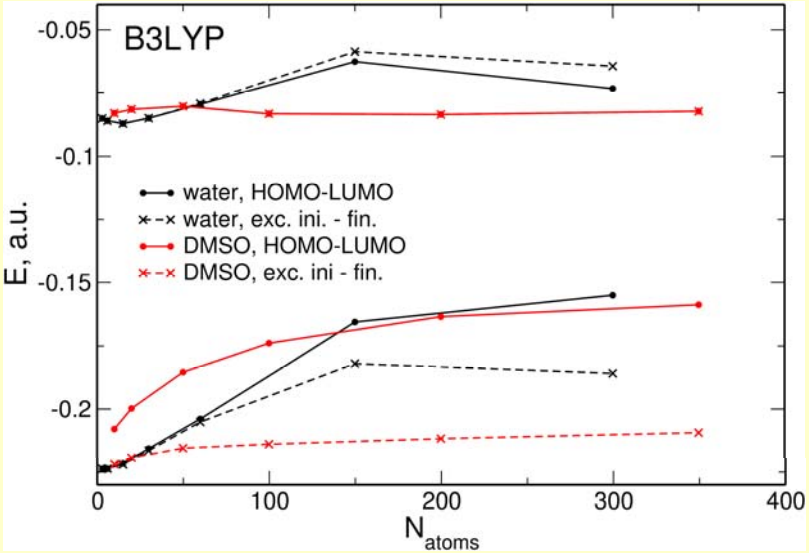


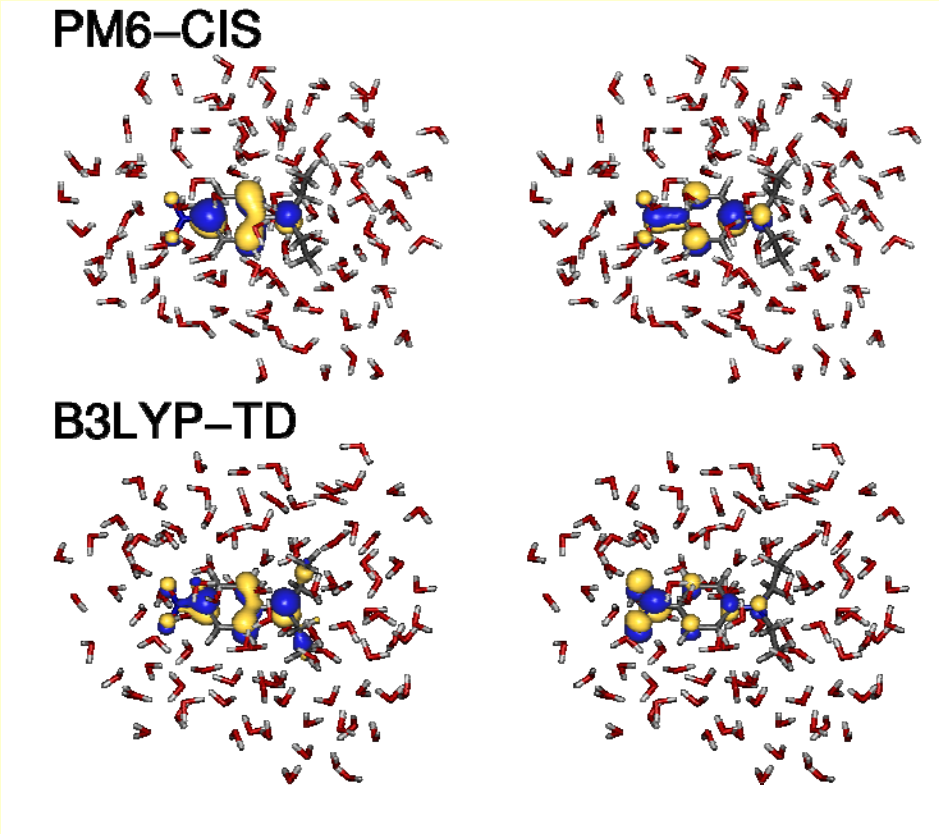
- strikingly wrong results of semiempirical approaches
- problems with water
- qualitatively correct sequence from TD-DFT (but DMSO shift too small compared to acetone and acetonitrile)

exp.	**430.5**	**411.5**	**397.9**	**396.5**

explicit solvent: orbitals

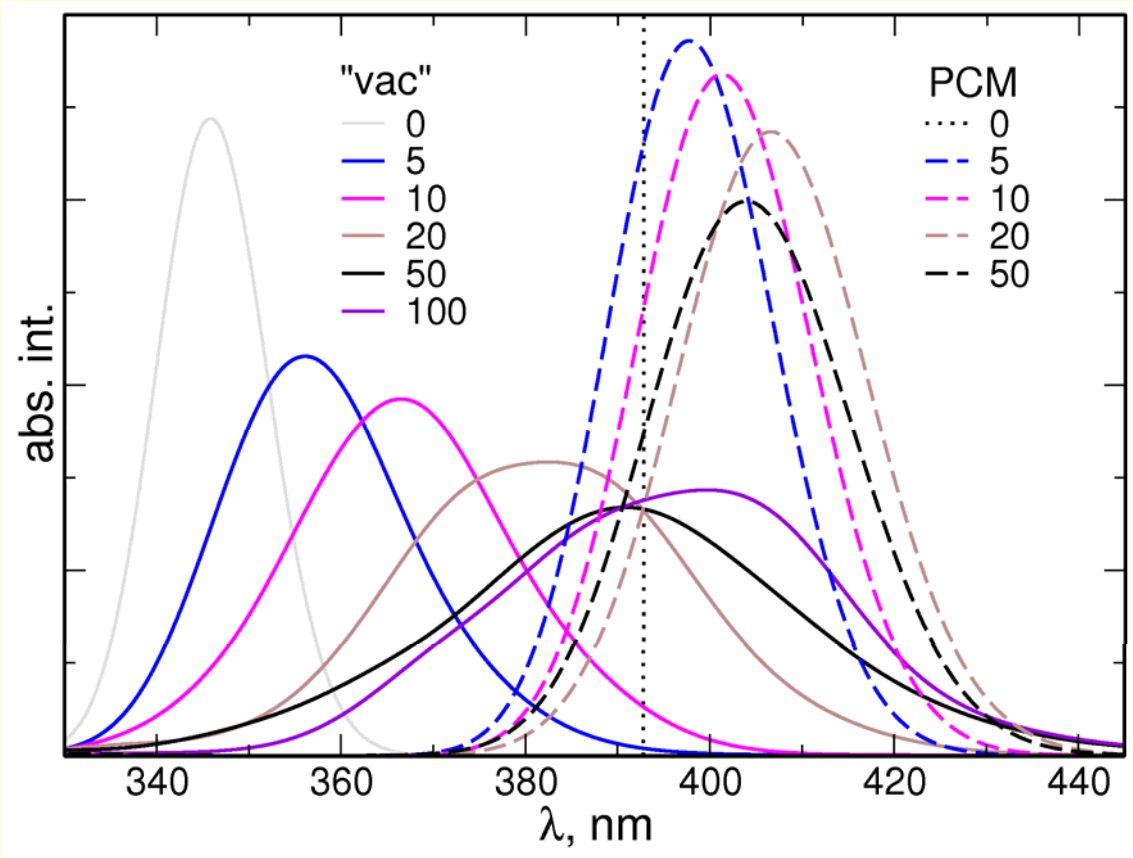






combined approach

- solute + explicit solvent molecules embedded in PCM continuous solvent



- improved convergence toward bulk solvent

conclusions

- Implicit solvent models encountered serious problems with proper description of solvatochromic shitfs of a probe molecule
- Problems related to electrostatics (atomic radii) and specific interactions
- Semiempirical approaches in explicit solvent model fail to reproduce shifts for water
- TDDFT method performs better (although not perfectly – need for better MD simulation and QC method?)
- Combined approach may improve the description of solvent effect at moderate cost, provided that the implicit method is reliable

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