

# 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)

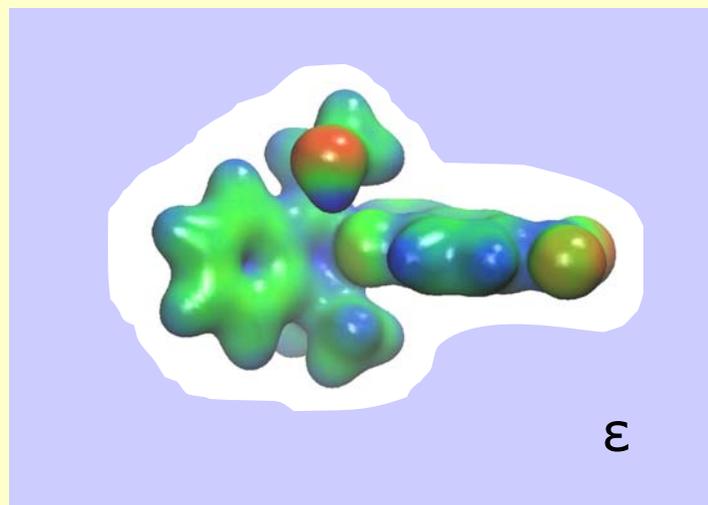
Empirical parameters describe polarity/polarizability of the solvent and its ability to form hydrogen bonds.

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

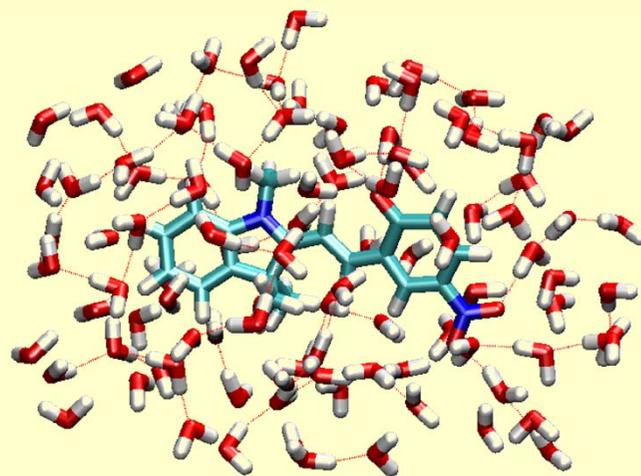
implicit solvent model (e.g. Polarizable Continuum Model):



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

# solvent modeling: explicit vs. implicit

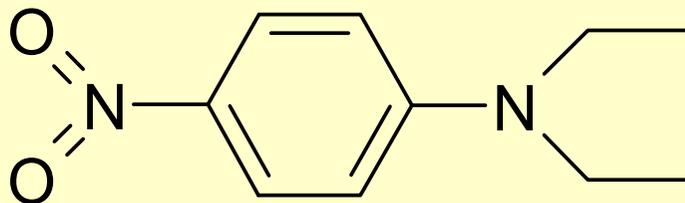
explicit solvent model:



- 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

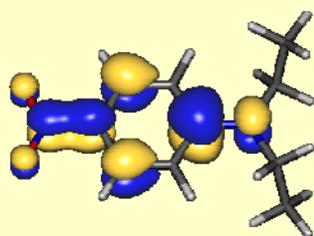
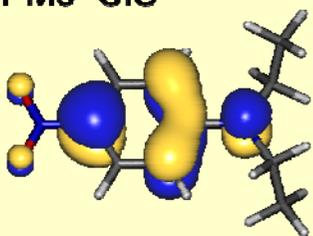


- four common molecular solvents: water, dimethylsulfoxide (DMSO), acetonitrile, acetone
- implicit solvent: variants of the PCM model
- explicit solvent: sequential MD/QM approach
- ZINDO/S, PM6-CIS and TDDFT used to compute excitation energies

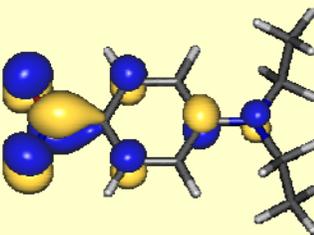
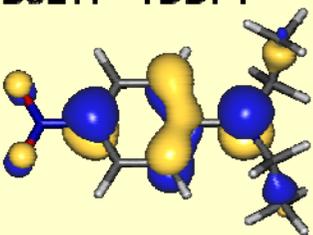
# dominant NTO pairs

vacuum

PM6-CIS

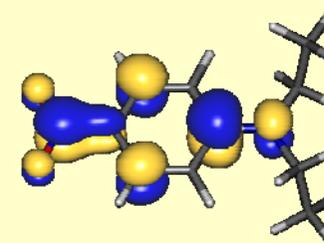
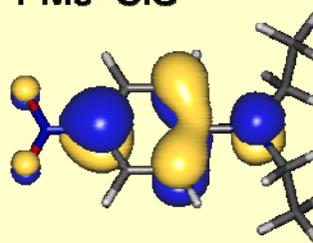


B3LYP-TDDFT

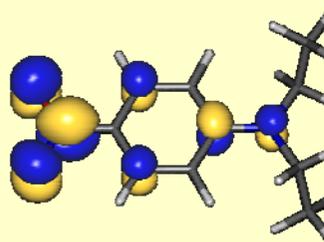
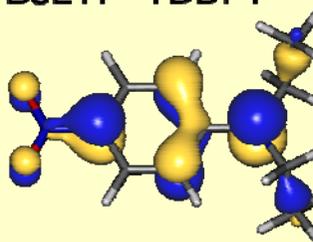


PCM water

PM6-CIS



B3LYP-TDDFT



## implicit solvation

	water	DMSO	acetonitrile	acetone
$\epsilon_{\text{static}}, \epsilon_{\infty}$	78.4, 1.78	46.8, 2.01	35.7, 1.81	20.5, 1.85
<b>exp.</b>	<b>430.5</b>	<b>411.5</b>	<b>397.9</b>	<b>396.5</b>
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

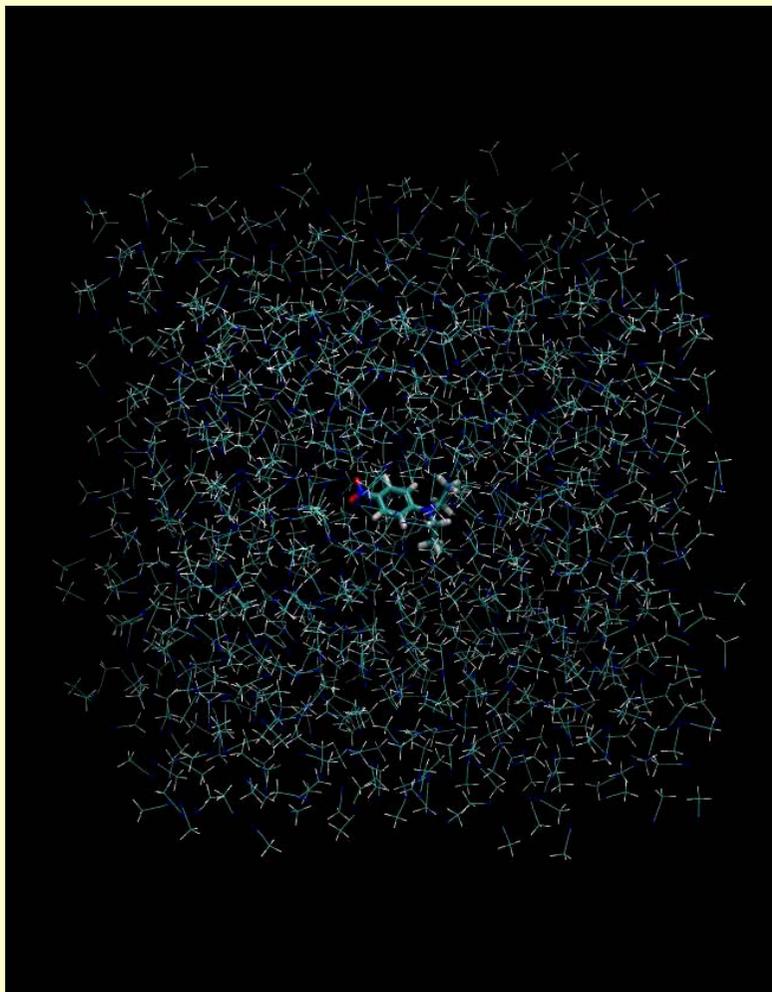
- neither model gives satisfactory reproduction of experimental results
- usually very small differences between solvents and wrong relative shift DMSO vs. water
- models with SMD atomic radii or solvent accessible surface predict significantly larger shift for water
- problem with electrostatics?
-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

## explicit solvent: MD simulations

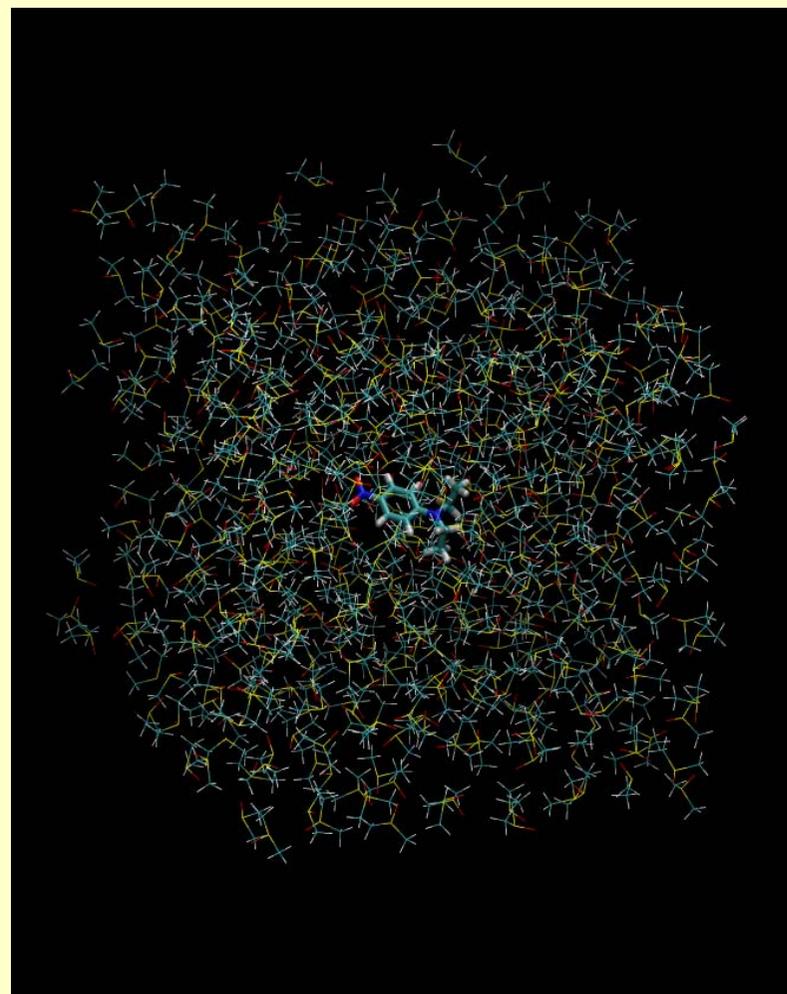
Classical Molecular Dynamics simulations (Tinker v.5)

- 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

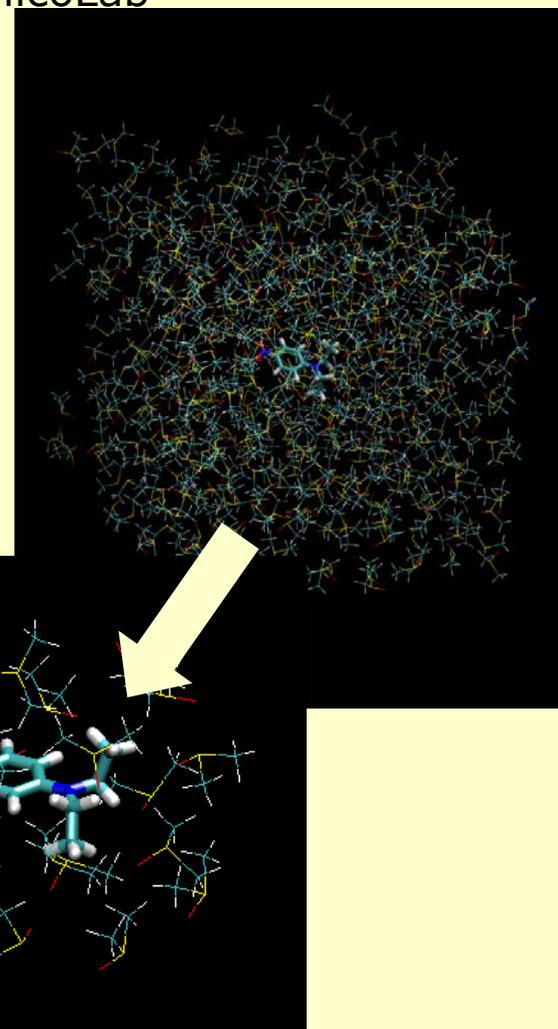
# InSilicoLab and Trajectory Sculptor

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

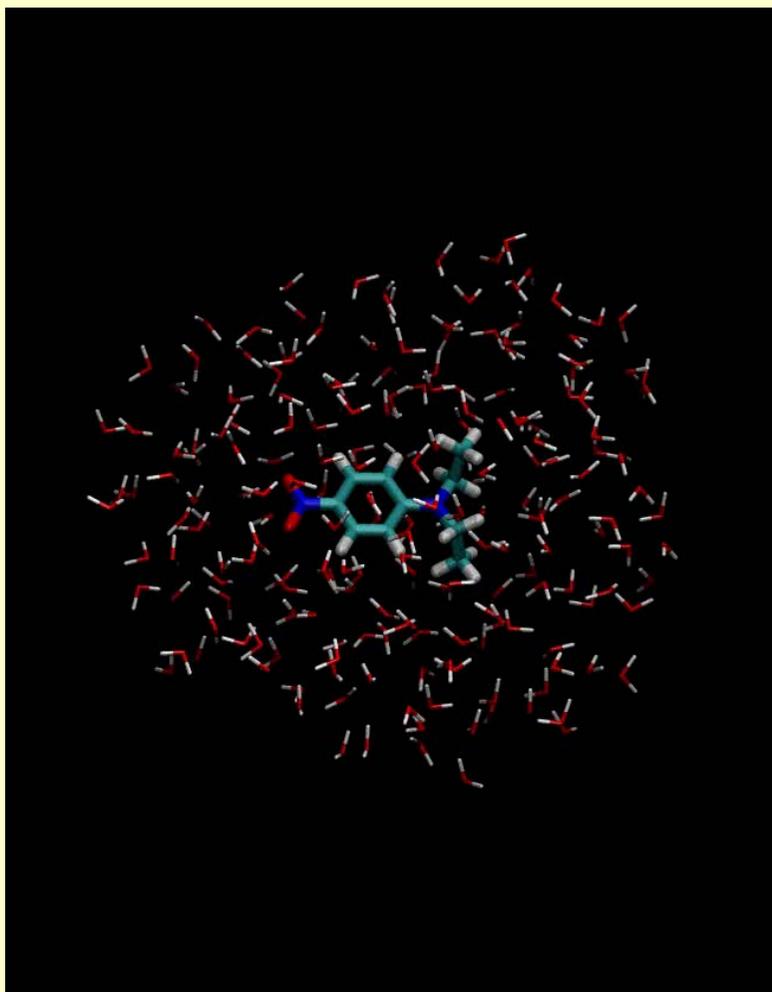
The screenshot shows the InSilicoLab Trajectory Sculptor web interface in a Mozilla Firefox browser. The page title is "InSilicoLab - Portal - Mozilla Firefox" and the URL is "https://insilicolab.grid.cyfronet.pl/". The user is logged in as "pijeimes". The interface is divided into several sections:

- Welcome Trajectory Scul...:** A section for loading a trajectory. It shows "Trajectory dms0-sztywny.xyz loaded. Found 100 frames." and buttons for "Preview frame..." and "Download frame...". There is a checkbox for "Use Periodic Boundary Conditions" and input fields for box dimensions: A = 39.1, B = 39.1, C = 39.1, with a checked option for "Equal period values".
- Define the molecules:** A section for defining solute and solvent. The solute is defined by "Atom Range" (1-28). The solvent is defined by "Atom Sequence(s)" (CSCOHHHHHH). A "Find molecules" button is present. Below it, search results show: "Found: 1 solute with molecular formula: C10H20O2H14 Preview" and "505 solvents with molecular formula: S1C20H46 Preview sample".
- Define distance metric:** A section for defining the distance metric. The solute is set to "Measure from Nearest atom" and the solvent to "Measure to Nearest atom". A checkbox "Use the same metric for each solute-solvent pair" is checked. The "Choose" section is set to "Closest molecules" with a value of 20.
- Reduce frame:** A section for reducing the frame. It shows "The reduced frame contains: 1 solute with molecular formula: C10H20O2H14" and "20 solvents (out of total 505) with molecular formula: S1C20H46". A "Reduce frame" button is present.
- Choose frames:** A section for choosing frames. The "Only first frame" radio button is selected. Other options include "List frames", "Define range" (1 to 0 step 1), and "All frames".

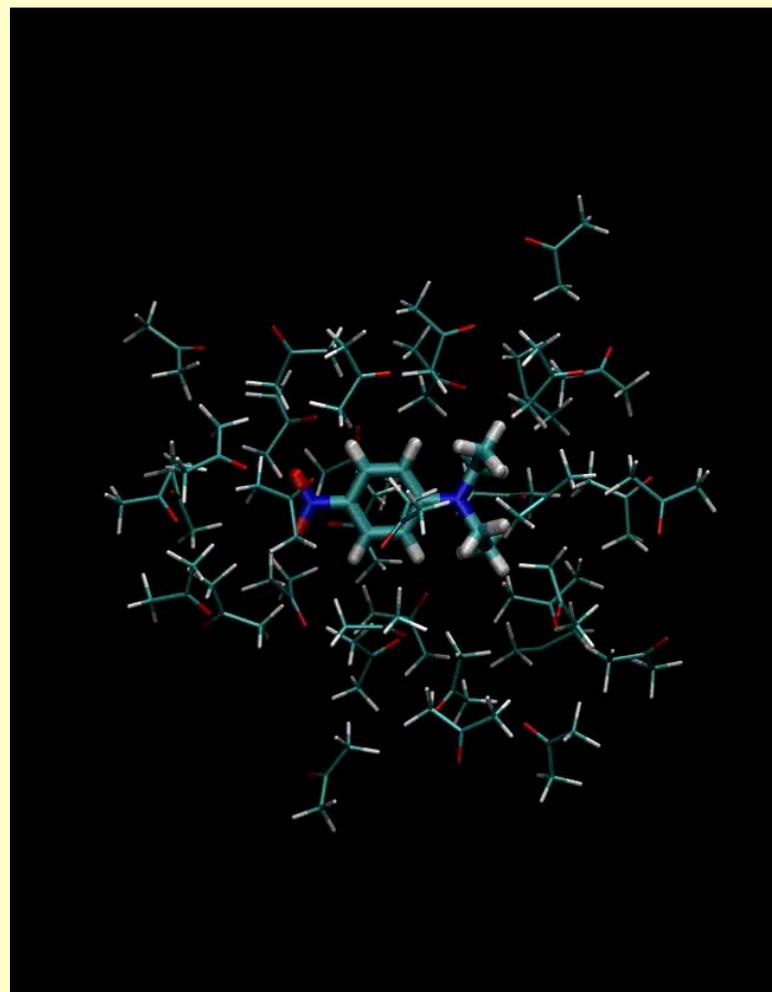
On the left side, there is a "Your Experiments" section with a menu and a list of experiments: "(no title)", "perchl1", and "perchl". Below that is an "LFC Catalogue" section with a filter by name and a message: "Cannot display LFC contents - no valid proxy". At the bottom left, there is a copyright notice: "© 2013 InSilicoLab v1.3" and a "Done" button.



## reduced MD trajectories

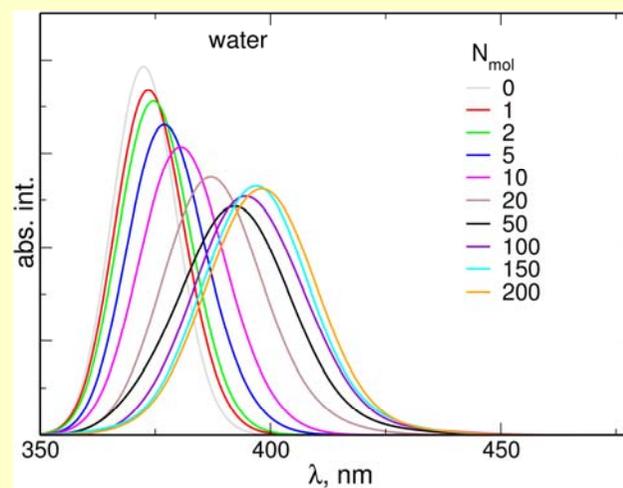
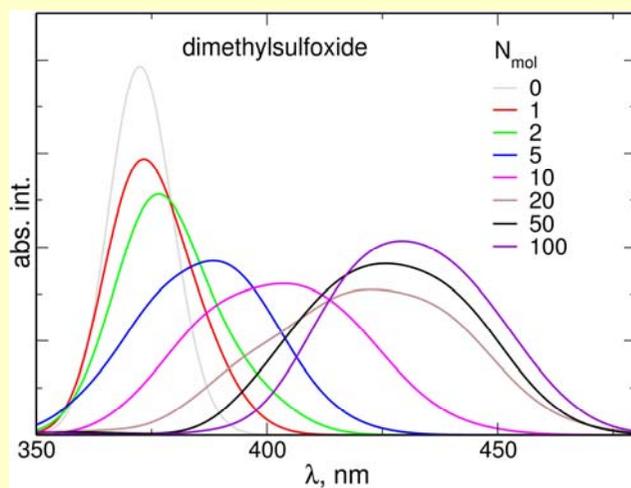
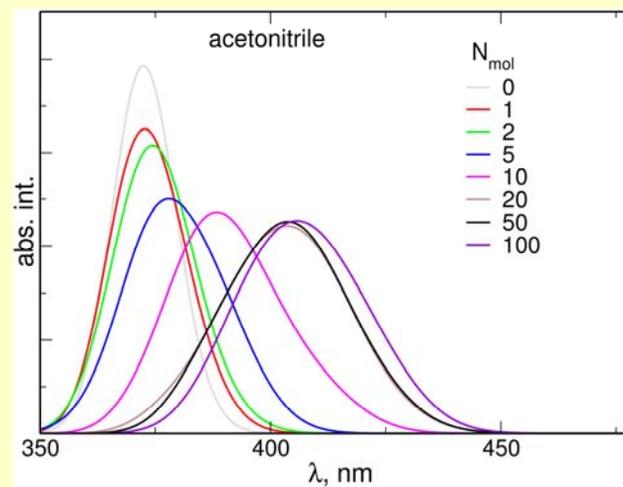
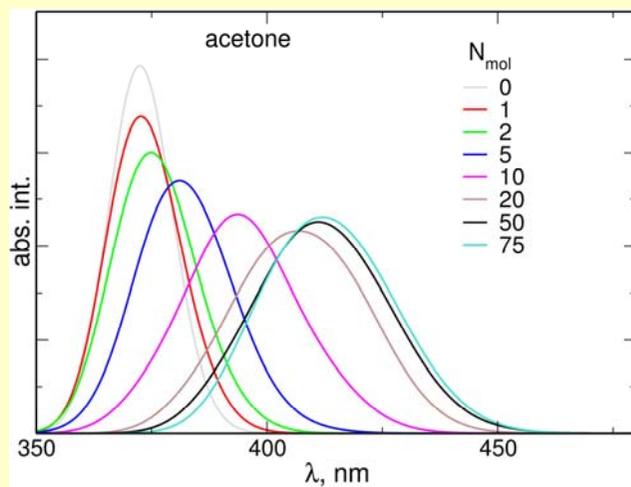


water



acetone

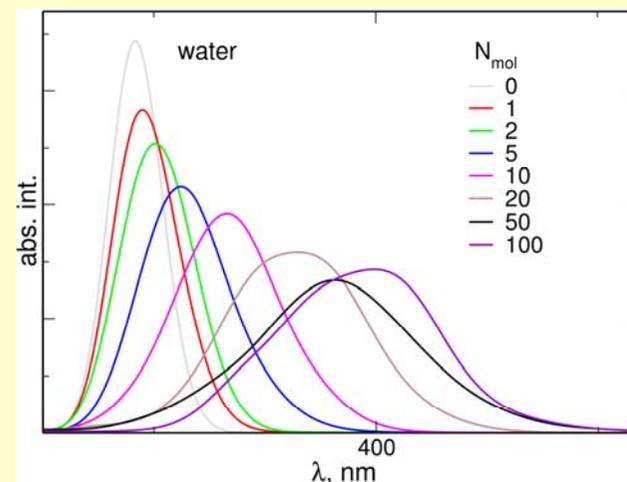
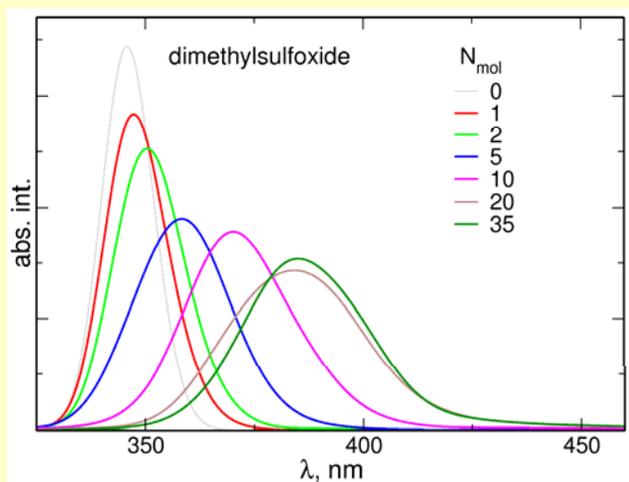
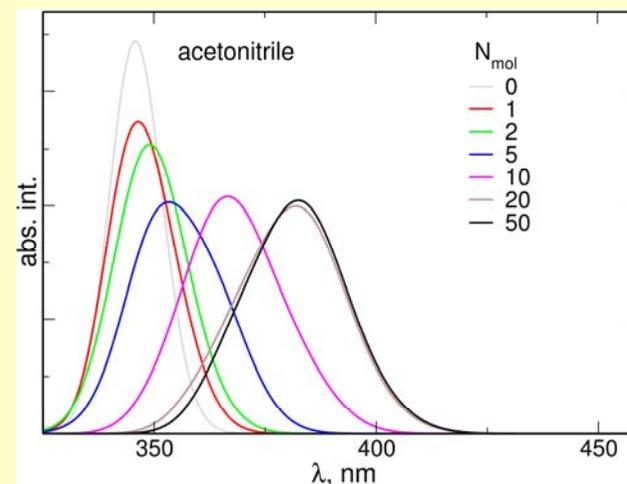
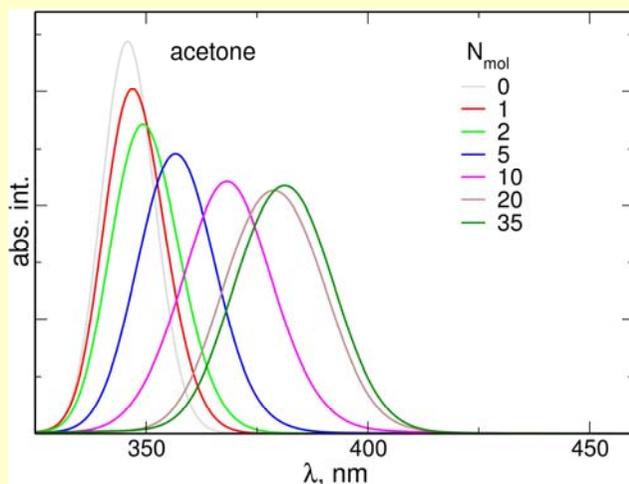
## explicit solvent: simulated spectra



ZINDO/S

KUKDM 14, Zakopane, March 13

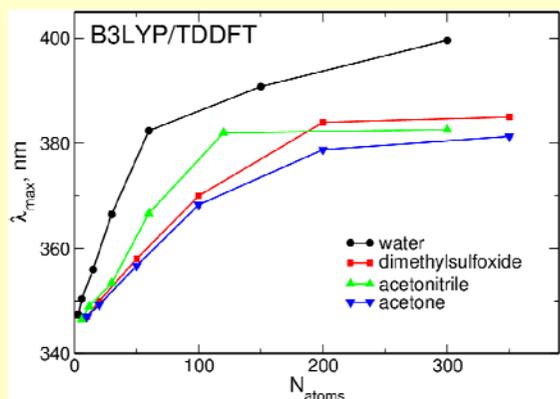
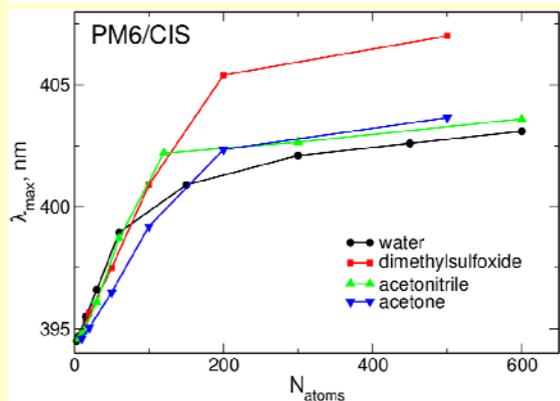
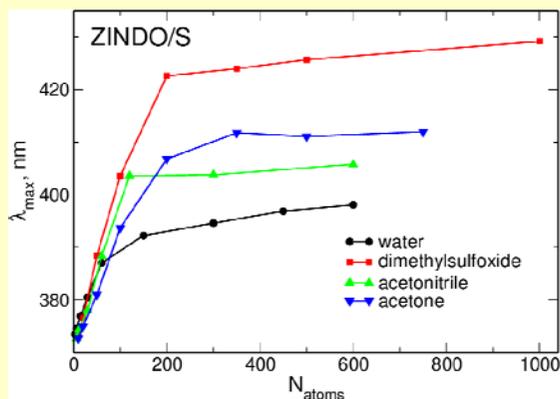
## explicit solvent: simulated spectra



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

KUKDM 14, Zakopane, March 13

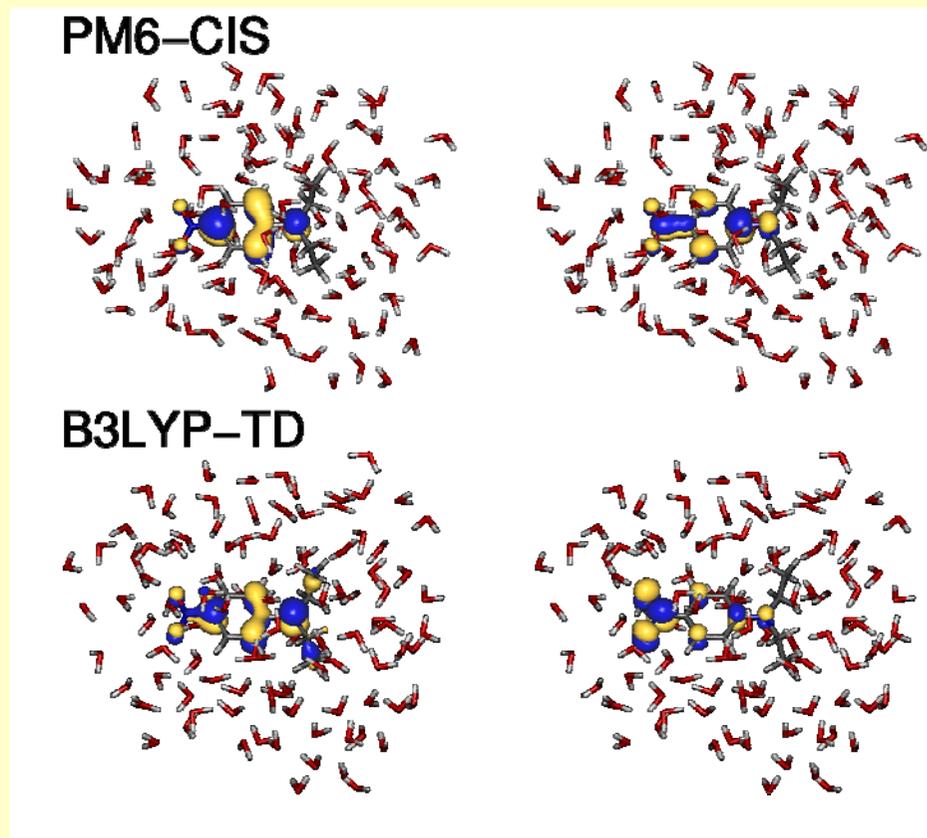
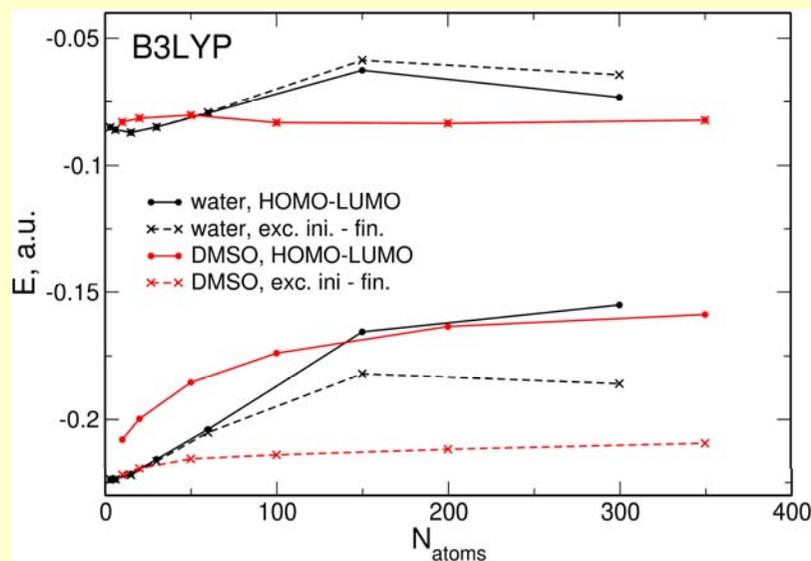
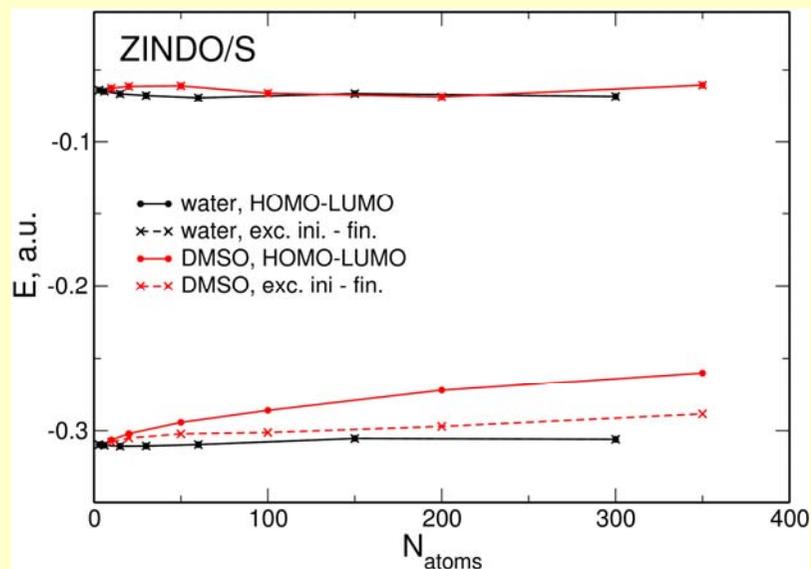
## explicit solvent: simulated spectra



- 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)

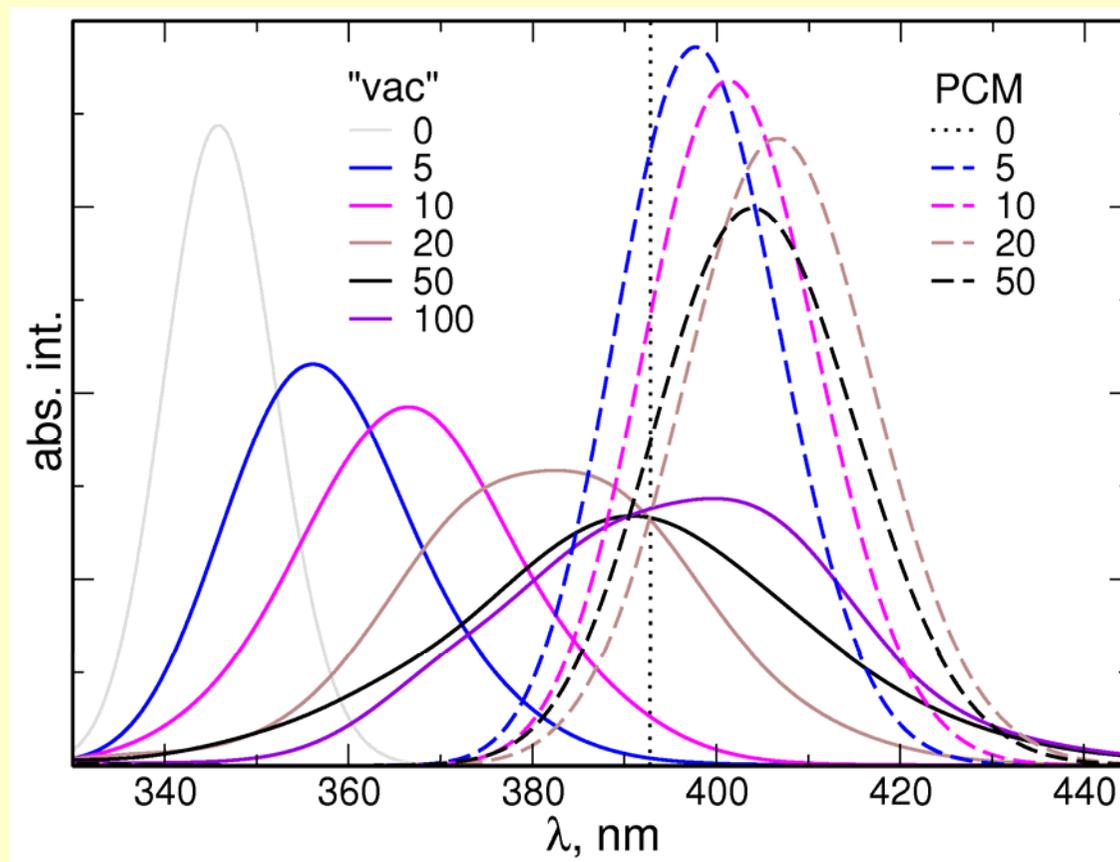
exp.	430.5	411.5	397.9	396.5
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# explicit solvent: orbitals



## 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 shifts 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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