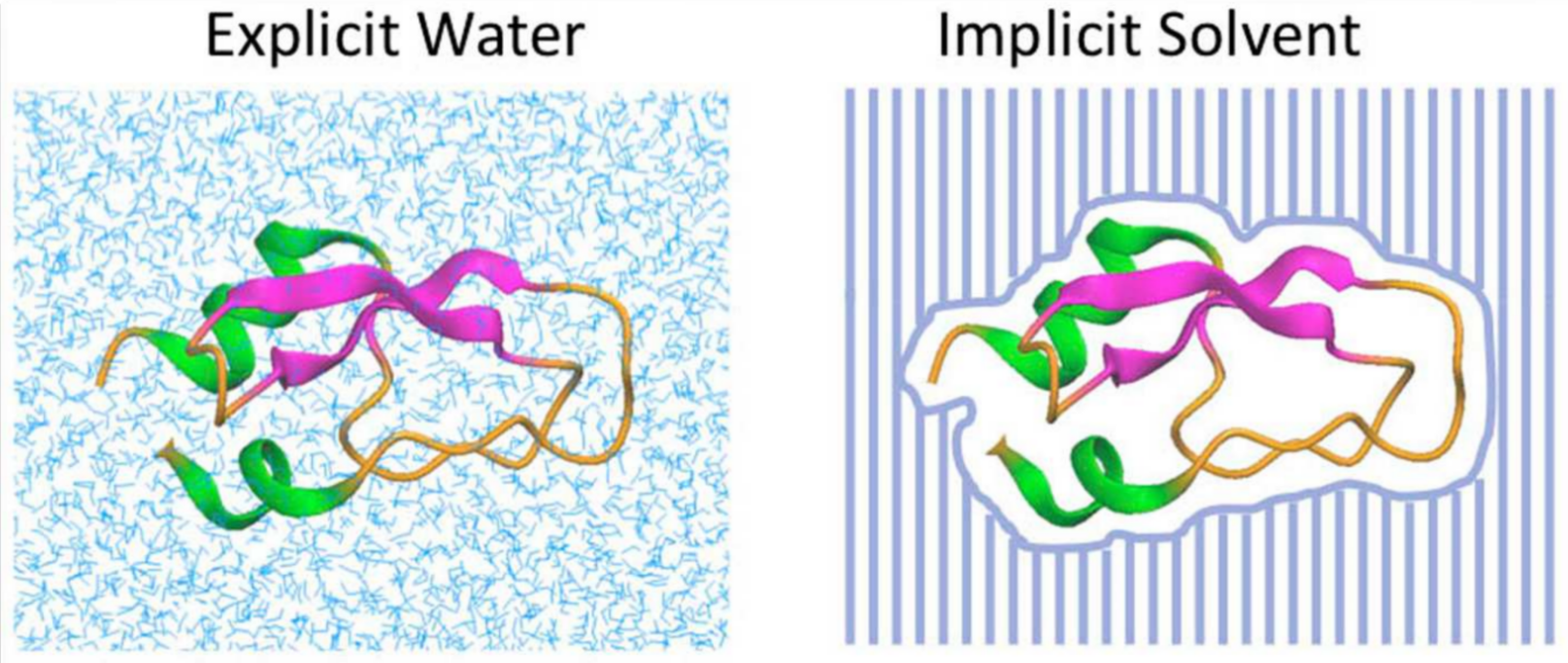
Lesson 08: Implicit Solvations: PCM and COSMO, SMD

Modeling Systems in Solution

- so far, all the calculations we've one have been doing is in vacuum
- while gas phase predictions are appropriate for many purposes, there are also a variety of systems and environments where they fail to reproduce the chemistry adequately.
- a substantial part of interesting chemical processes occur in solution.

Solvation Models

- **Implicit solvation** (sometimes termed continuum solvation) represent solvent as a continuous medium instead of individual **Explicit solvent** molecules

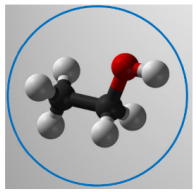


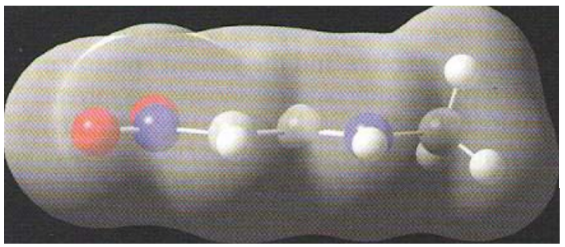
Self-Consistent Reaction Field (SCRF) methods

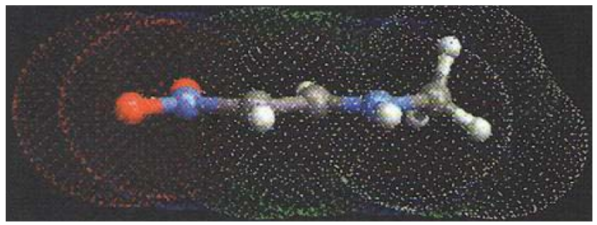
- the solvent is treated as a continuous, uniform dielectric medium characterized by its dielectric constant ε.
- the solute is typically modeled as a single molecule/complex, corresponding to a very dilute solution.
- the solute is placed inside an empty cavity within the solvent dielectric medium.
- the interaction between the solute and the solvent consists primarily of **electrostatic** interactions: the mutual polarization of the solute and the solvent.
- the charge distribution of the solute inside the cavity polarizes the dielectric continuum, which in turn polarizes the solute charge distribution.
- because of the **mutual polarization** of the solute and solvent, they are members of the family of self consistent reaction field methods.

Cavity Shapes

- single sphere. (top)
- a surface of constant electron density, also known as an isodensity surface. (middle)
- the superposition of interlocked spheres centered on the atoms in the molecule. The radii of the individual spheres are close to the van der Waals values. (bottom)







Polarizable Continuum Model (PCM)

- Cavity
  - overlapping van der Waals spheres *(for PCM and CPCM)*
  - solvent accessible surface
  - isodensity surface (IPCM, SCIPCM)
- electrostatic potential from solute and polarization of solvent must obey Poisson equation
- electrostatic interactions calculated numerically
- in Gaussian: SCRF=IEFPCM (default)

Solvation Model Based on Density (SMD)

- a universal continuum solvation model where “universal” denotes its applicability to any charged or uncharged solute in any solvent or liquid medium
- includes corrections for CDS (cavitation, dispersion and solvent structure effects) while PCM does not
- gives more accurate solvation energies compared to PCM (IEFPCM)
- in Gaussian: SCRF=SMD

Conductor-like Screening Model (COSMO)

- COnductor-like Screening MOdel
- Cavity
  - based on solvent accessible surface (SAS)
- electrostatic interactions are treated in more approximated manner
  - solvent treated as conductor not dielectric ($\varepsilon = \infty$)
- good approximation in very polar solvents
- NOTE: conductor-like PCM (C-PCM) in which the continuum is conductor-like similar to COSMO Solvation Model.
- in Gaussian: SCRF=CPCM

ACTIVITY 1: Properties in Solution

- Formaldehyde IR Spectrum in Acetonitrile (using Gaussian)
  - perform an **Optimizization** and **Freq** calculation of formaldehyde in acetonitrile and vibrational frequencies.
  - do each for Gas Phase and Solution (acetonitrile) in SCRF=IEFPCM (default in Gaussian)
    # APFD/6-311+G(2d,p) Opt Freq SCRF
    # APFD/6-311+G(2d,p) Opt Freq SCRF(Solvent=Acetonitrile)
  - complete the table:

MODE	MOTION (SYMMETRY)	VIBRATIONAL FREQ. GAS PHASE	VIBRATIONAL FREQ. SOLUTION	SHIFT (solvent effect)
1	CH_2 wag (B1)			
2	CH_2 rock (B2)			
3	CH_2 scissors (A1)			
4	C=O stretch (A1)			
5	CH asymm. stretch (A1)			
6	CH symm. stretch (B2)			

  - collect the Gas Phase and Solution Vibration Values, and the changes Δ (Shift)

ACTIVITY 2: Predicting Free Energies in Solution

- **IEFPCM vs SMD**
- solubility of Acetic Acid in Chloroform and in Water
  - perform an Optimization and Freq Calculation on Acetic Acid under chloroform and water (4 SETS OF CALCULATIONS)
    # APFD/6-311+G(2d,p) Opt Freq SCRF(IEFPCM & SMD,Solvent=Chloroform & Water)
  - NOTE: the starting structure for acetic acid should have the dihedral angles H-O-C=O and H-C-C=O equal to 0.0 (in the same plane)
  - in order to predict the free energy of solvation in each environment, optimize the geometry of acetic acid in the gas phase and in each solvent (with the second optimization starting from the gas phase-optimized structure).

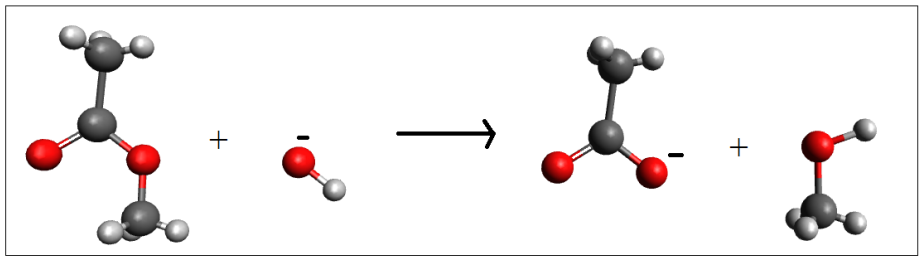
ACTIVITY 2: Predicting Free Energies in Solution (*Cont.*)

- we will compute ΔG of solvation as the difference of the predicted Gibbs free energy values in the gas phase and in solution, taken from the two frequency calculations.
- complete the entire table:

	ENVIRONMENT	ΔG^{solv} (kcal/mol) CALC.	OBS.†
	gas phase		
PCM	chloroform		-4.74
	water		-6.70
SMD	chloroform		-4.74
	water		-6.70

ACTIVITY 3: Reaction Free Energy

- **IEFPCM vs SMD vs COSMO**
- Hydrolysis of Methyl Acetate
- (base catalyzed) reaction where R=R'=CH3: methyl acetate and hydroxide ion going to acetate ion and methanol



  - perform an Optimization and Freq Calculation all species of the reaction in Gase Phase and Water (below)
    # APFD/6-311+G(2d,p) Opt Freq SCRF(IEFPCM & SMD & CPCM,Solvent=Water)

ACTIVITY 3: Reaction Free Energy, (Cont.)

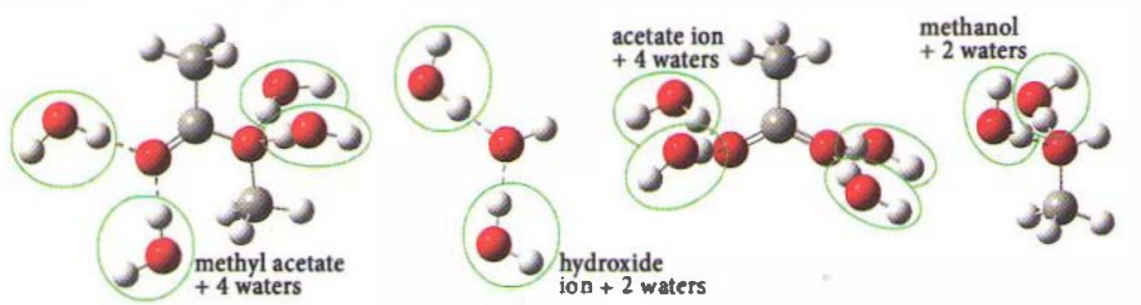
- to predict the Gibbs free energy of the reaction, you need to have free energies of the four compounds in question.
- compare it with the experimental value, complete the table:

	EXP.
ΔG (kcal/mol)	-14.4
IEF(PCM)	
SMD	
CPCM	

- NOTE: It is expected that there's a big descrepancy of the computational results vs. the experiment, most likely due to effects not included in the SCRF model. The solute-solvent interactions treated too simply by the solvation model and the non-static nature of the solvation shell. Thus the superiority of EXPLICIT SOLVATION over IMPICIT ONE is without question.

Extra Activity: (Explicit Solvation)

- **NOTE: OPTIONAL, THIS IS NOT A PART OF THE LESSON which deals with IMPLICIT SOLVATION**
- take the reaction of Activity No.3
  - explicitly add two water molecules per oxygen in the reactants and products as shown below:



  - use SCRF=SMD, Opt=CalcAll (for Gas), Opt=CalcFC (for SMD), Opt=Tight

Extra Activity: (Explicit Solvation), Cont.

- these calculations are longer
- water molecules change drastically during the course of the optimization thus be careful with your guess structures (better start with HF optimized structures)
- compare the improvement of the results in Activity 3

END