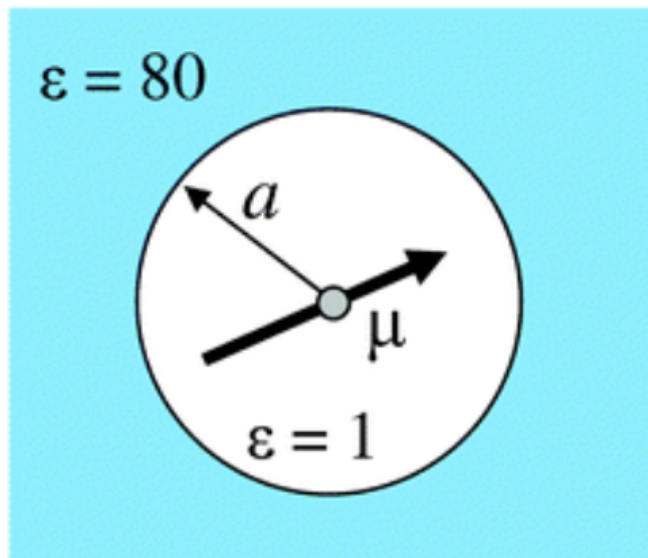
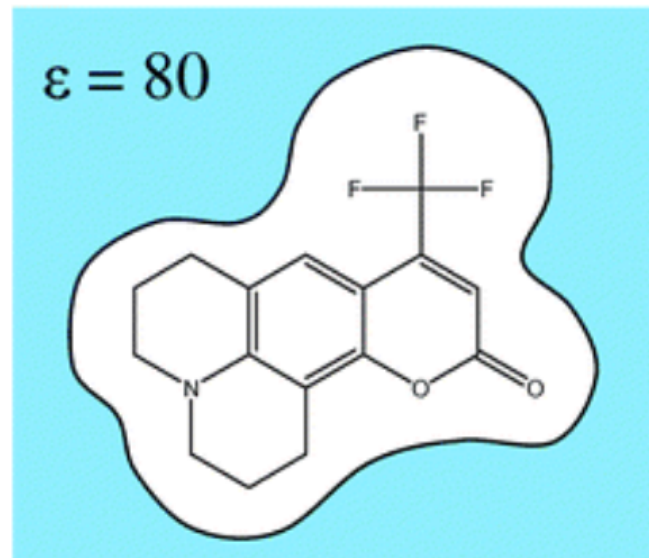


SOLVATION MODELS



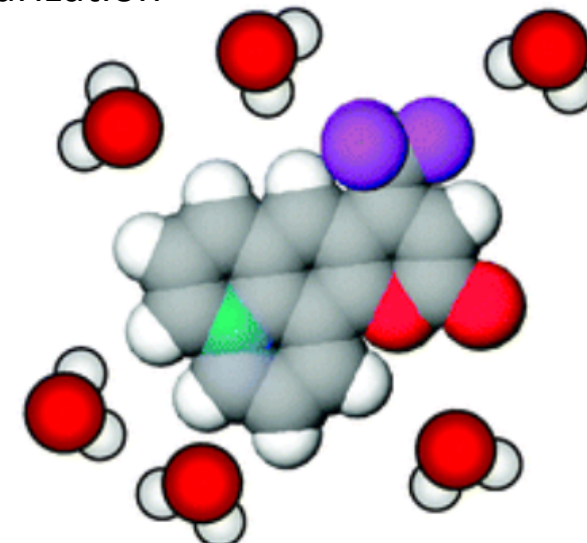
Polarizable continuum model



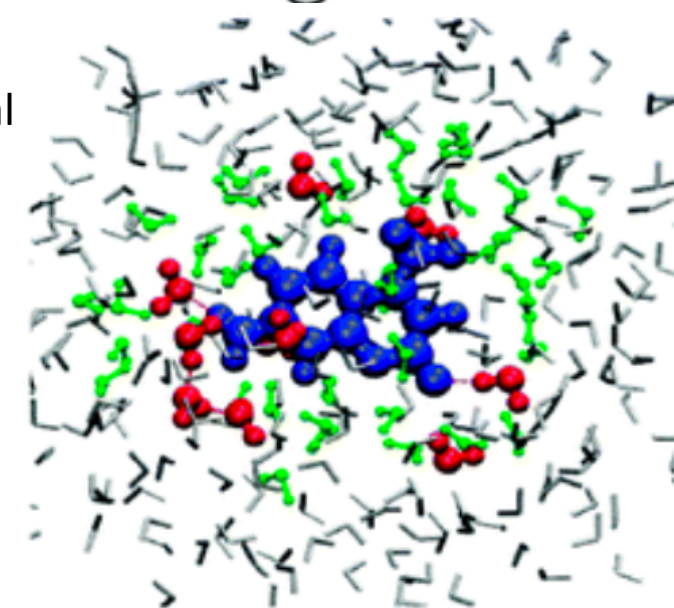
Continuum solvent:

- Spherical cavity (Debye-Onsager) vs molecular cavity
- Includes polarization response of solvent (often self-consistently)
- But is missing short-range specific solute-solvent interactions

Quantum mechanical solvent: full polarization and specific solute-solvent interactions, but missing long-range polarization



Molecular mechanical

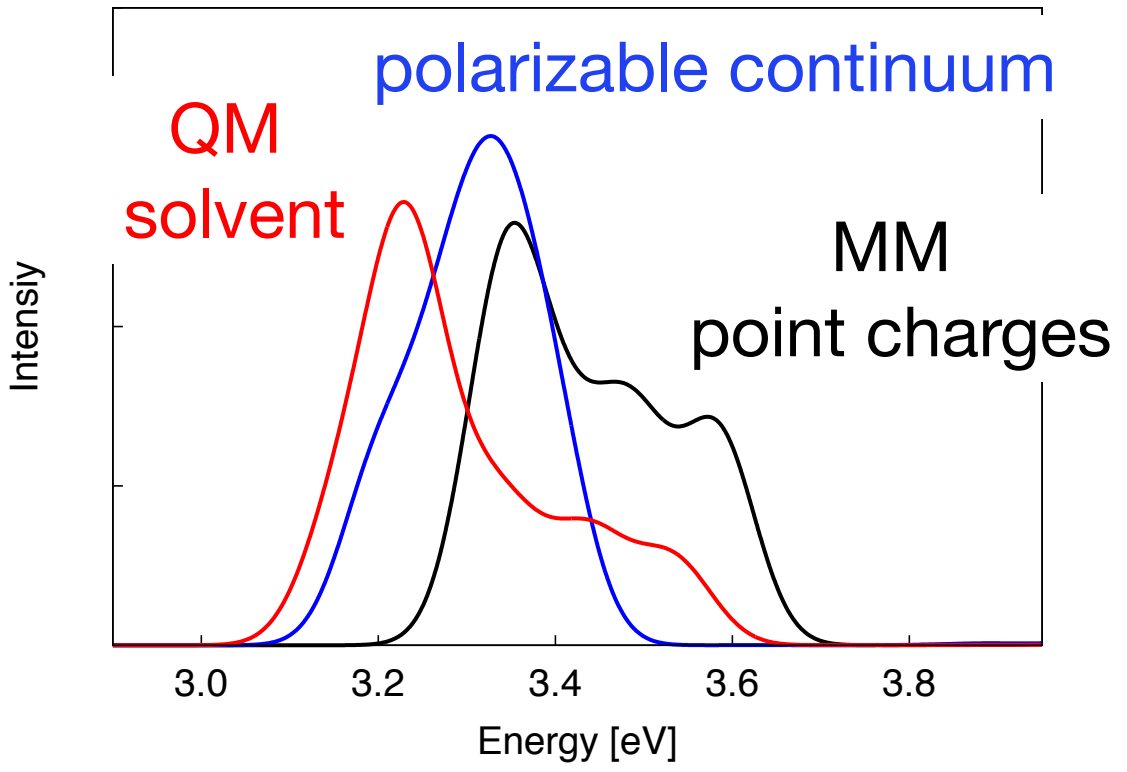


MM solvent: Point charges of solvent included
QM Hamiltonian via electrostatic embedding.
May be fixed point charges or polarizable.

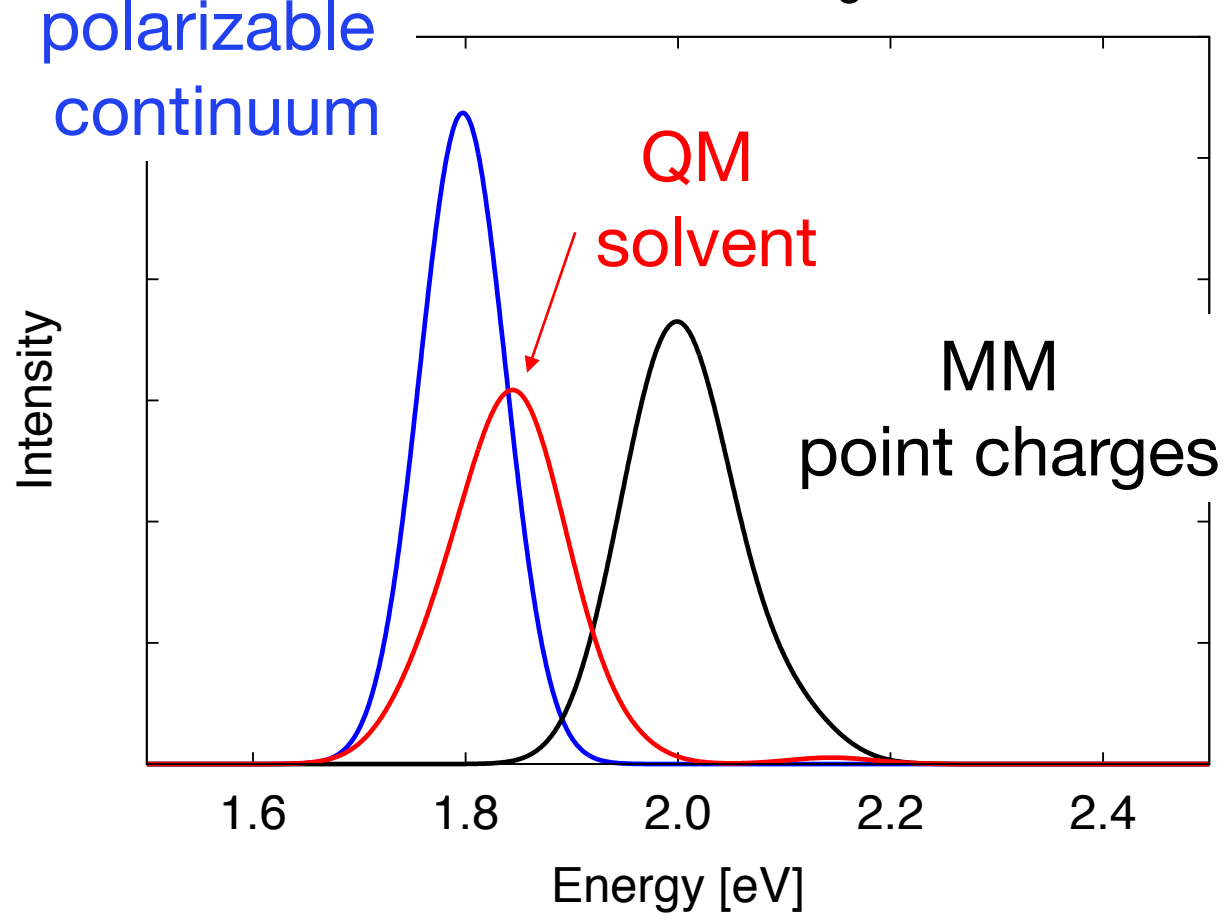
SOLVATION MODELS : SPECTRAL COMPARISON

Polarization tends to shift the excitations to lower energies

Anionic chromophore in H₂O



Neutral Chromophore in CHCl₃



SOLUTE-SOLVENT INTERACTIONS

Mutual polarization, both short- and long-range

- ✓ QM solvent (if enough is included..)
- x MM fixed point charge solvent
- ✓ Polarizable continuum model (PCM)

Specific interactions (e.g. hydrogen bonding, charge-transfer)

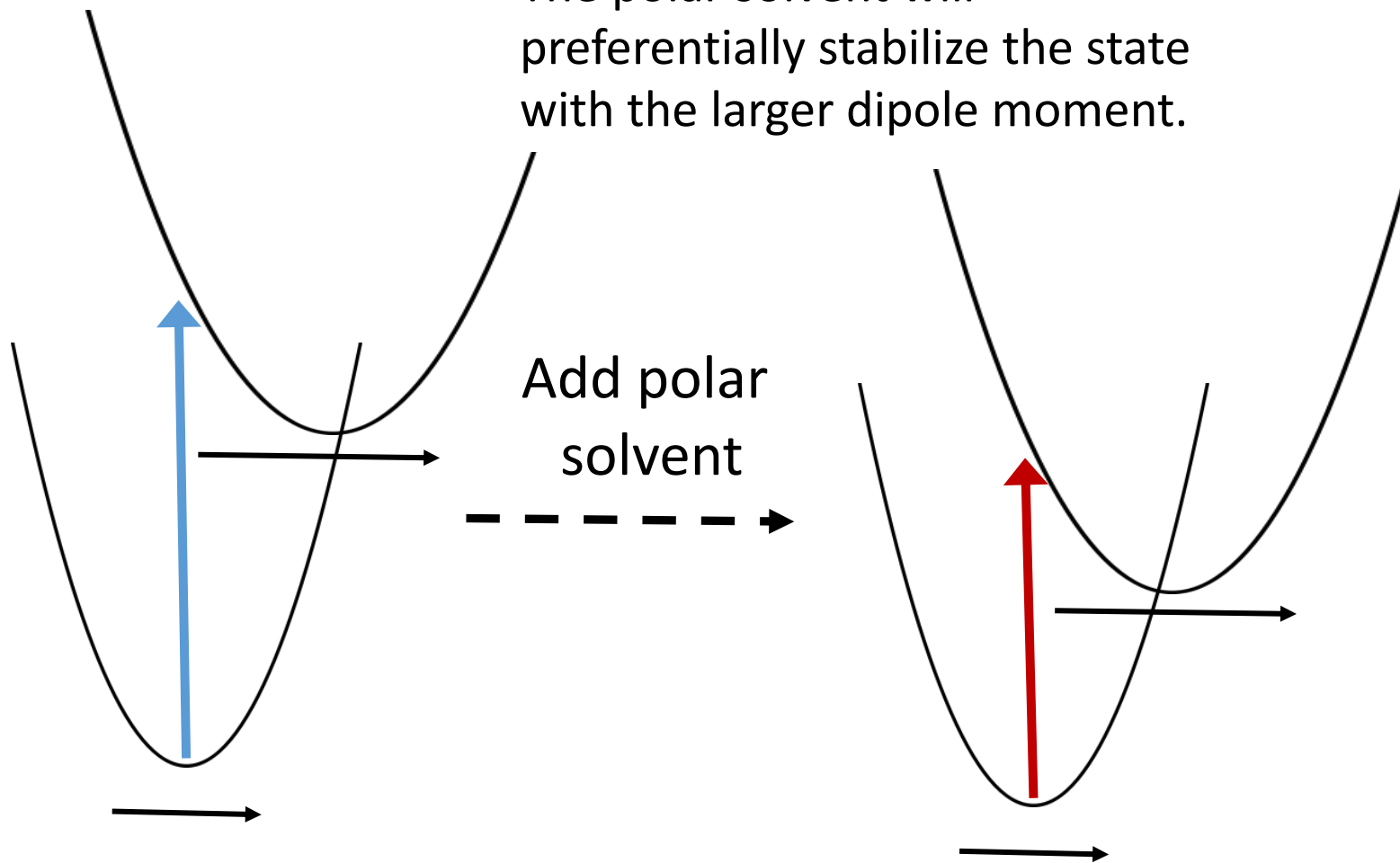
- ✓ QM solvent
- MM solvent (some measure of H-bonding, no charge-transfer)
- x Polarizable continuum model (PCM)

Sampling of configurations (usually from molecular dynamics)

- ✓ QM solvent (but can't usually run the dynamics long enough)
- ✓ MM solvent
- x Polarizable continuum model (PCM)

SOLVATOCHROMIC SHIFTS

The polar solvent will preferentially stabilize the state with the larger dipole moment.

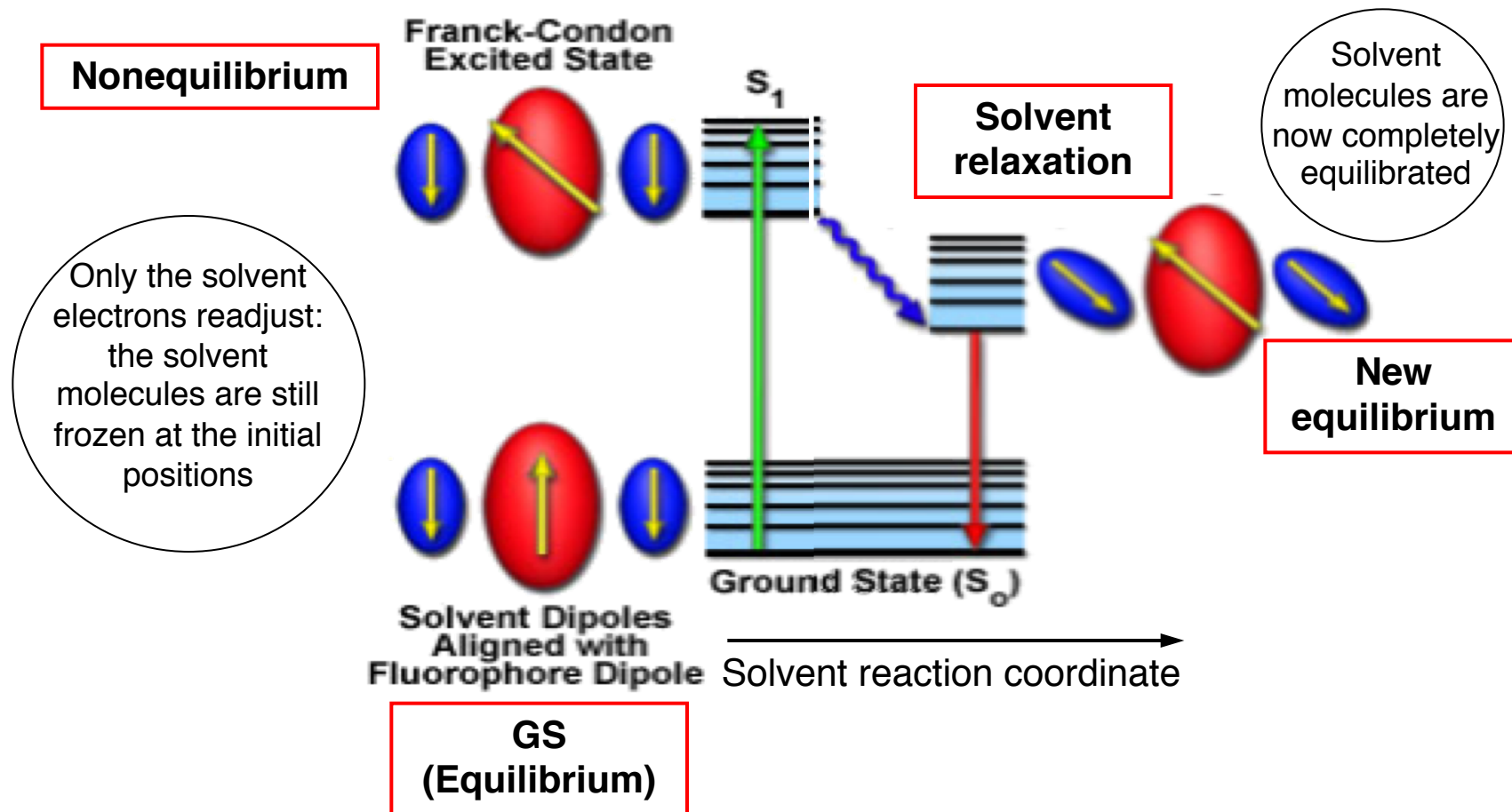


If the excited state has the larger dipole moment, this will lead to a smaller excitation energy, red-shifting the absorption

If the ground state has the larger dipole moment, this will lead to a larger excitation energy, blue-shifting the absorption

The degree of shift often can be correlated with the polarization and polarity of the solvent (related to the dielectric constants)

SOLVATION IN THE EXCITED STATE



For vertical excitation energies (femtoseconds), we want non-equilibrium solvation (electronic motion of solvent)

For excited state geometries, we want equilibrium solvation (nuclear motion of solvent). Takes into account picoseconds that solvent molecules need to rearrange.

SOLVENT DIELECTRIC CONSTANTS

For vertical excitation energies, we only consider the fast degrees of freedom of the solvent (electron movement), in which we consider only the ϵ_∞ optical dielectric constant of the solvent (For water, $\epsilon_0 = 78$, $\epsilon_\infty = 1.8$).

In continuum calculations, these are sometimes referred to as 'non-equilibrium' calculations, since the solvent is not allowed to 'equilibrate' its position around the QM region.

