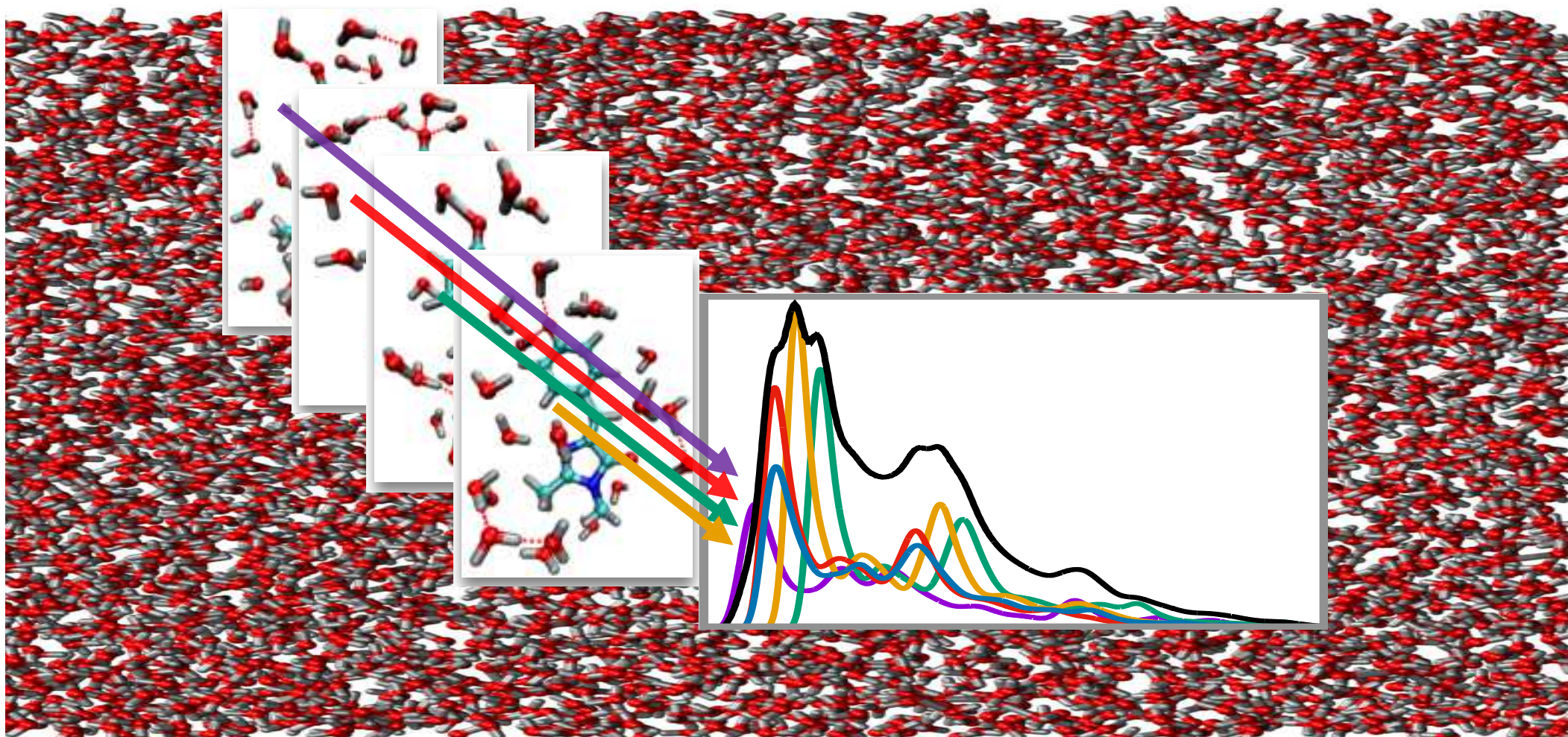


# EXCITED STATES FOR MOLECULES IN SOLUTION

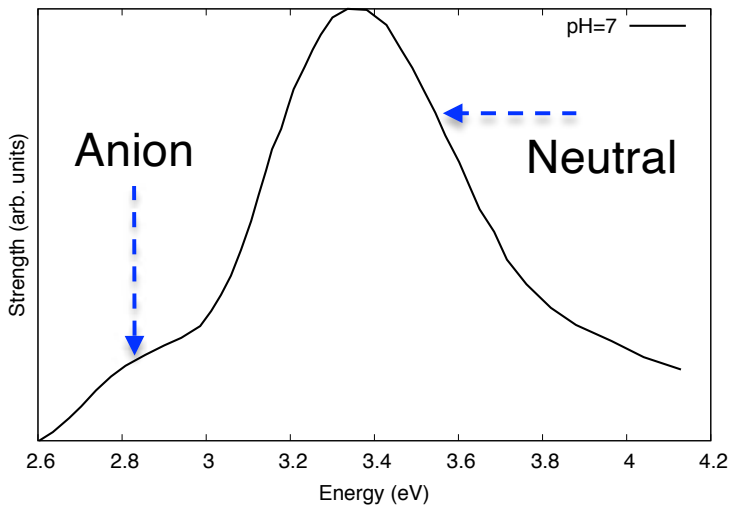
CHRISTINE M. ISBORN

UNIVERSITY OF CALIFORNIA MERCED



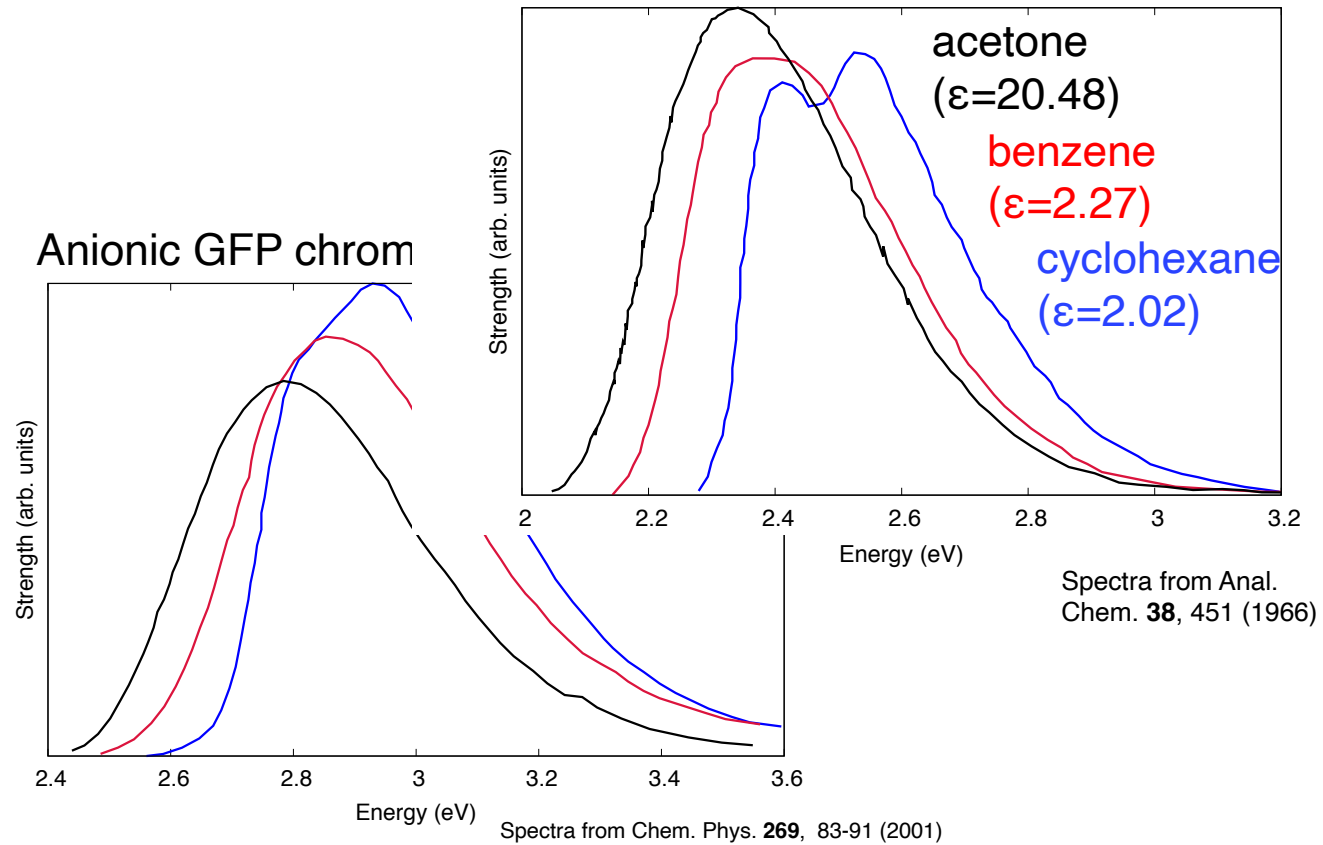
# GOAL: MODEL OPTICAL SPECTROSCOPY FOR MOLECULES IN COMPLEX, CONDENSED PHASE ENVIRONMENTS

Green fluorescent protein (GFP) chromophore in water



Spectrum from Phys. Rev. Lett. **87**, 228102 (2001)

Nile Red chromophore in different solvents



Spectra from Anal. Chem. **38**, 451 (1966)

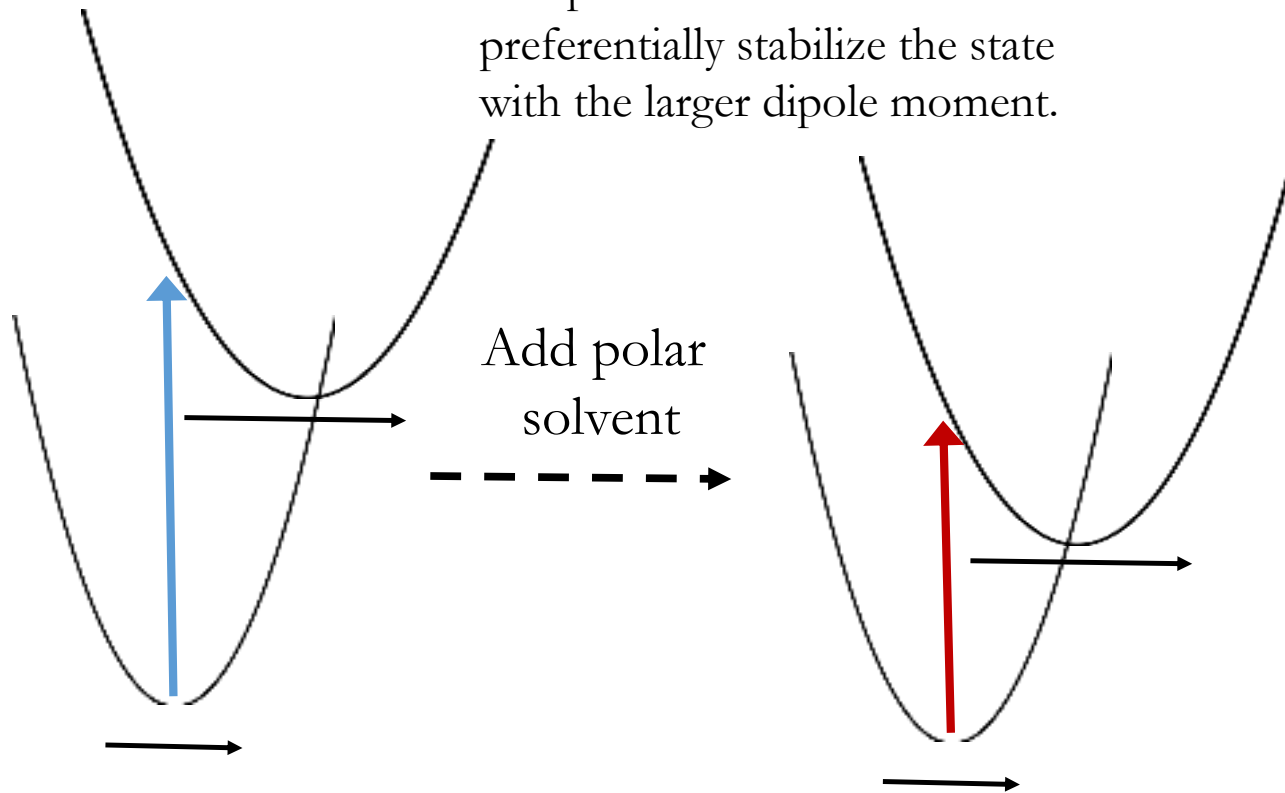
Spectra from Chem. Phys. **269**, 83-91 (2001)

## Outline

- Solvatochromic shifts, excited state solvation
- Solvation models
  - Polarizable continuum (implicit solvent)
  - Point charges (QM/MM, explicit solvent)
  - QM solvent (explicit solvent)
- Methods for simulating linear absorption/emission spectra for condensed phase/solvated systems

## SOLVATOCHROMIC SHIFTS

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

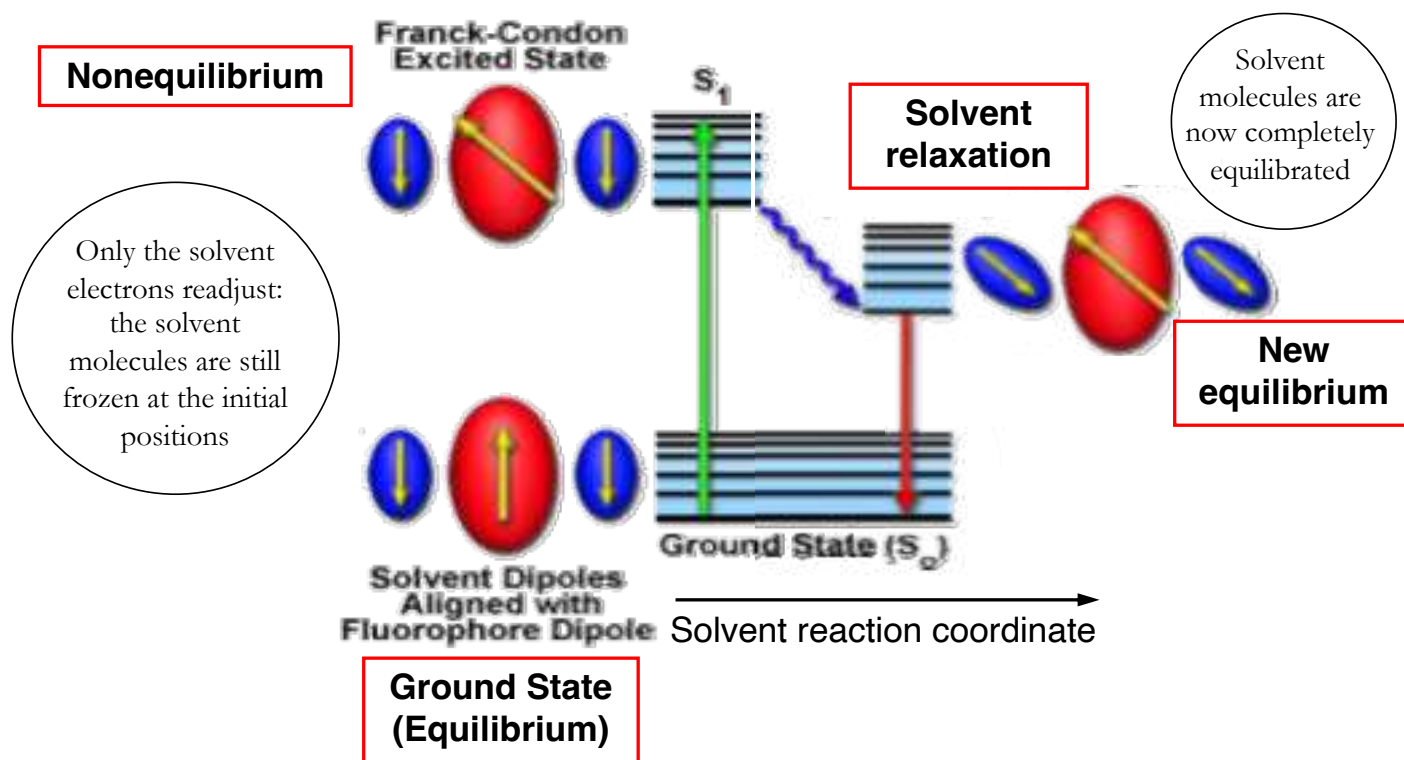


If the excited state has the larger dipole moment, this will lead to a smaller excitation energy, red-shifting the absorption

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

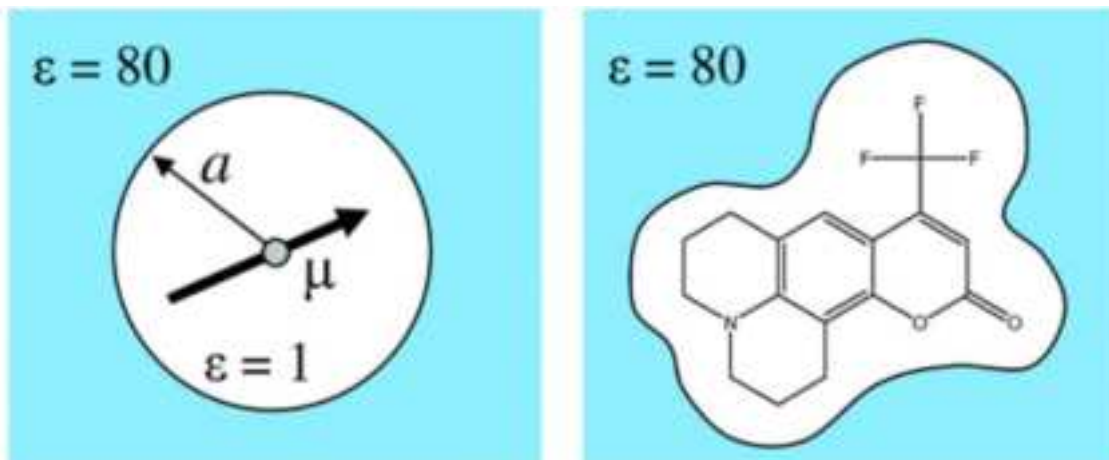


For vertical excitation energies (femtoseconds), we want non-equilibrium solvation (electronic motion of solvent)

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

# SOLVATION MODELS

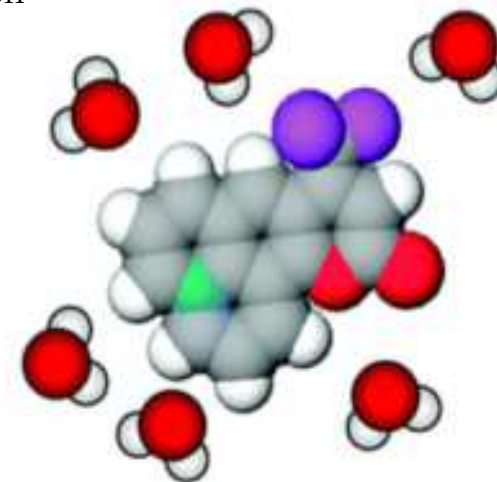
## 1) Polarizable continuum model (implicit solvent)



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

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



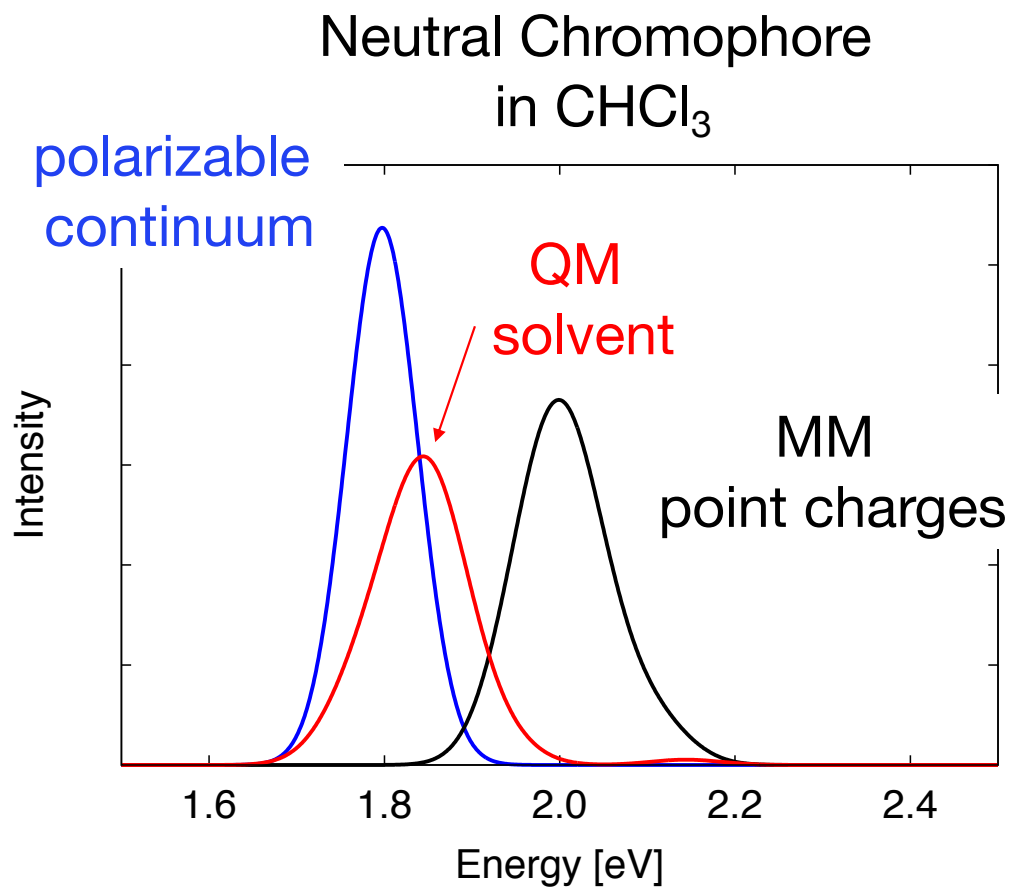
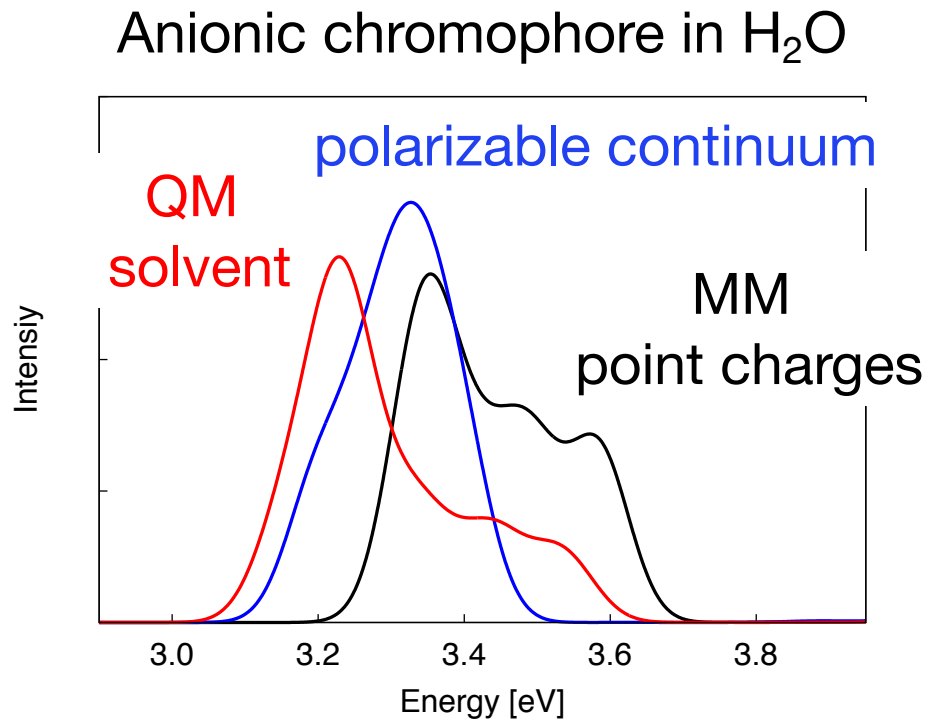
## 2) Molecular Mechanical (point charge) solvent



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

# SOLVATION MODELS : SPECTRAL COMPARISON

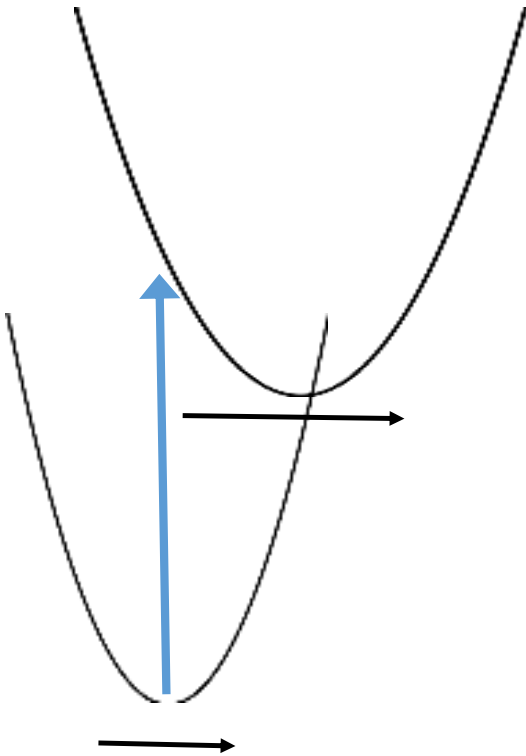
Polarization tends to shift the excitations to lower energies



## IMPLICIT 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  $\epsilon_\infty$  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.





## POLARIZABLE CONTINUUM MODEL : LINEAR RESPONSE VS STATE SPECIFIC

Excited states with PCM: Linear response or state specific?

- The molecule in its ground state in equilibrium with the solvent is excited to the  $i$ th state in the presence of solvent polarization for ground state  $\rightarrow$  Excitation energy is  $\omega_{0i}^0$
- The dynamic component of the solvent polarization rearranges to equilibrate with the excited state charge density of the solute, changing the excitation energy.

**Linear response** is computed from the transition density  $P_{0i}^T$

$$\omega_{0i}^{LR} = \omega_{0i}^0 + \langle i^0 | \hat{V} | 0 \rangle \langle 0 | \hat{Q} | i^0 \rangle$$

$\hat{V}$  is the molecular electrostatic potential operator

**State specific** based on the difference in ground and excited state density  $P_{0i}^\Delta$

$$\omega_{0i}^{SS} = \omega_{0i}^0 + \frac{1}{2} [\langle i^0 | \hat{V} | i^0 \rangle - \langle 0 | \hat{V} | 0 \rangle] [\langle i^0 | \hat{Q} | i^0 \rangle - \langle 0 | \hat{Q} | 0 \rangle]$$

$\hat{Q}$  is the dynamical apparent charge operator

Cammi, Corni, Mennucci, Tomasi  
J. Chem. Phys. 2005, 122, 104513,  
DOI: 10.1063/1.1867373

[Guido](#), [Jacquemin](#), [Adamo](#), and [Mennucci](#)  
J. Chem. Theory Comput., 2015, 11, 5782  
DOI: 10.1021/acs.jctc.5b00679

## POLARIZABLE CONTINUUM MODEL : LINEAR RESPONSE VS STATE SPECIFIC

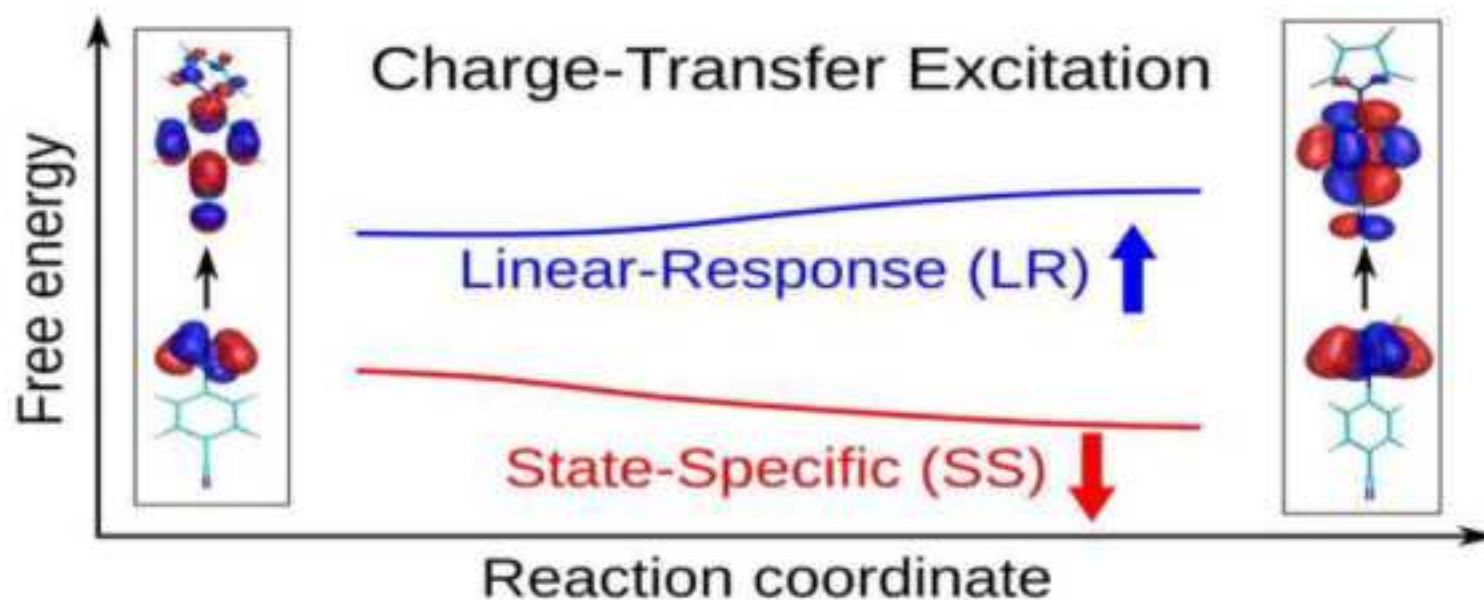
**Linear response**, based on the transition density  $\mathbf{P}_{0i}^T$

- Good for small changes in the density upon excitation
- Only non-equilibrium solvation is used

**State specific**, based on the difference in ground and excited state density  $\mathbf{P}_{0i}^\Delta$

- Good if there are large changes in the electron density (ex. charge-transfer transitions)
- Equilibrium or non-equilibrium PCM is available, based on the time scale of interest.
  - Equilibrium state specific necessary for excited state geometry optimizations.

## POLARIZABLE CONTINUUM MODEL : LINEAR RESPONSE VS STATE SPECIFIC

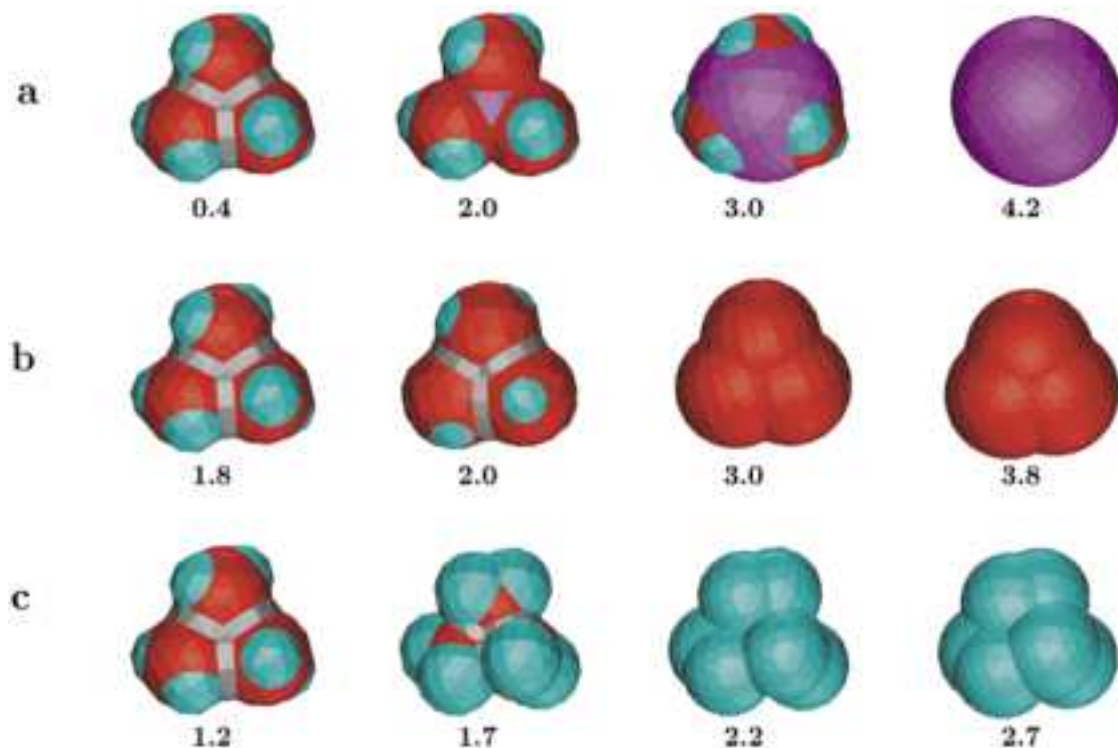


[Minezawa](#)

[Chemical Physics Letters](#) 608, 140, 2014

<https://doi.org/10.1016/j.cplett.2014.05.104>

# Polarizable Continuum Model (PCM): which shape should be used for the cavity?



Influence of the atomic radii in the cavity shape for the  $\text{Be}^{2+}$  tetrahydrate.

(a) Radius of Be is changed from 0.4 to 4.2 Å.

(b) Radius of O is changed from 1.8 to 3.8 Å.

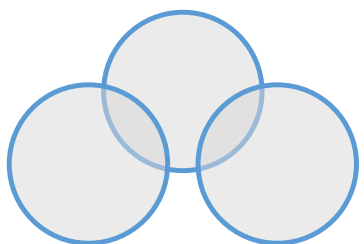
(c) Radius of H is changed from 1.2 to 2.7 Å.

(Surface contributions from Be are displayed in magenta, O in red, and H in blue, non atomic ones are in gray.)

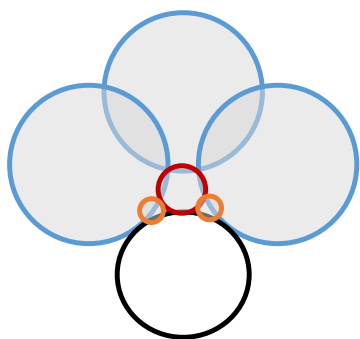
[Martínez](#), [Pappalardo](#), [Sánchez Marcos](#), [Mennucci](#), [Tomasi](#)  
*J. Phys. Chem. B*, 2002, 106 (5), pp 1118–1123  
<https://doi.org/10.1021/jp012404z>

# Polarizable Continuum Model (PCM): Choice of Cavity

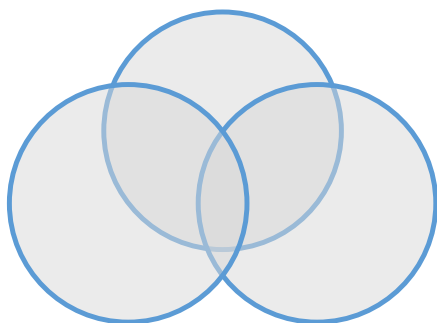
van der Waals



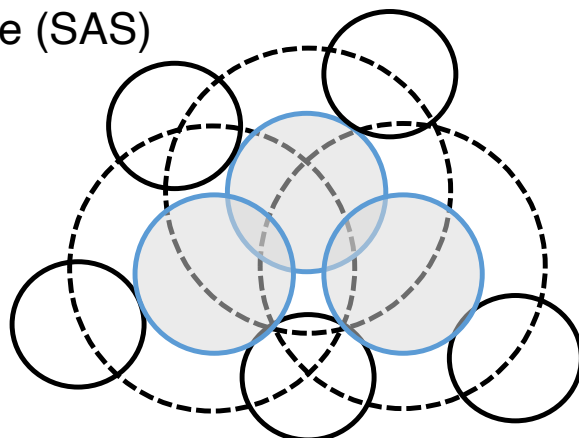
Solvent Excluded Surface (SES)



Scaled VDW

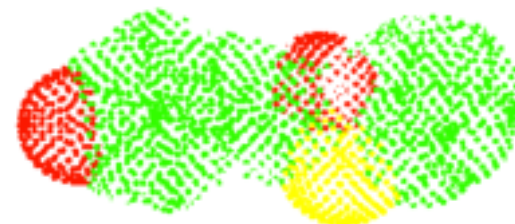


Solvent Accessible Surface (SAS)

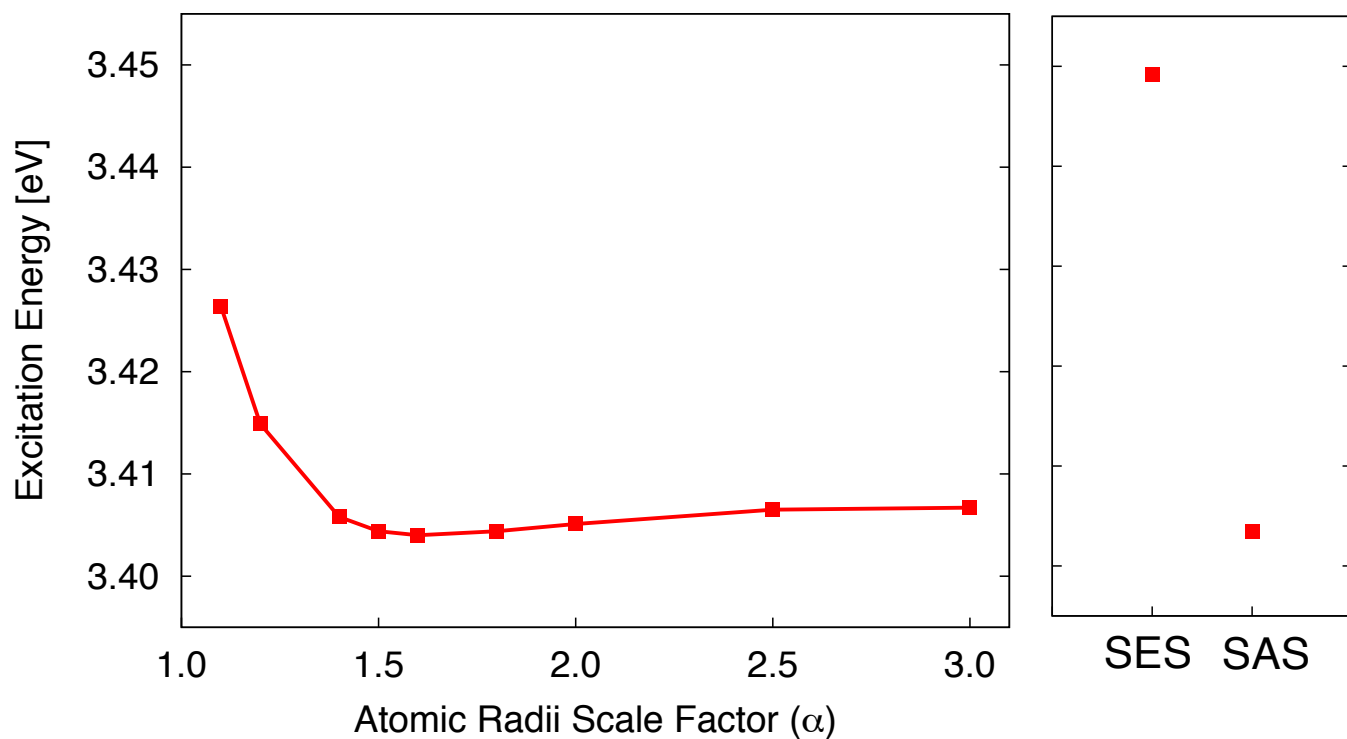


A set of radii (often parameterized to reproduce some solvation property) are often used to create the van der Waals surface (e.g. UFF or SMD radii)

The cavity surface is then divided into small tiles (tesserae). The reaction field is determined by apparent point charges assigned to each surface tesserae, adjusted until self-consistency is reached with the QM region.



# How Does the PCM Cavity Affect the TDDFT Excitation Energy?



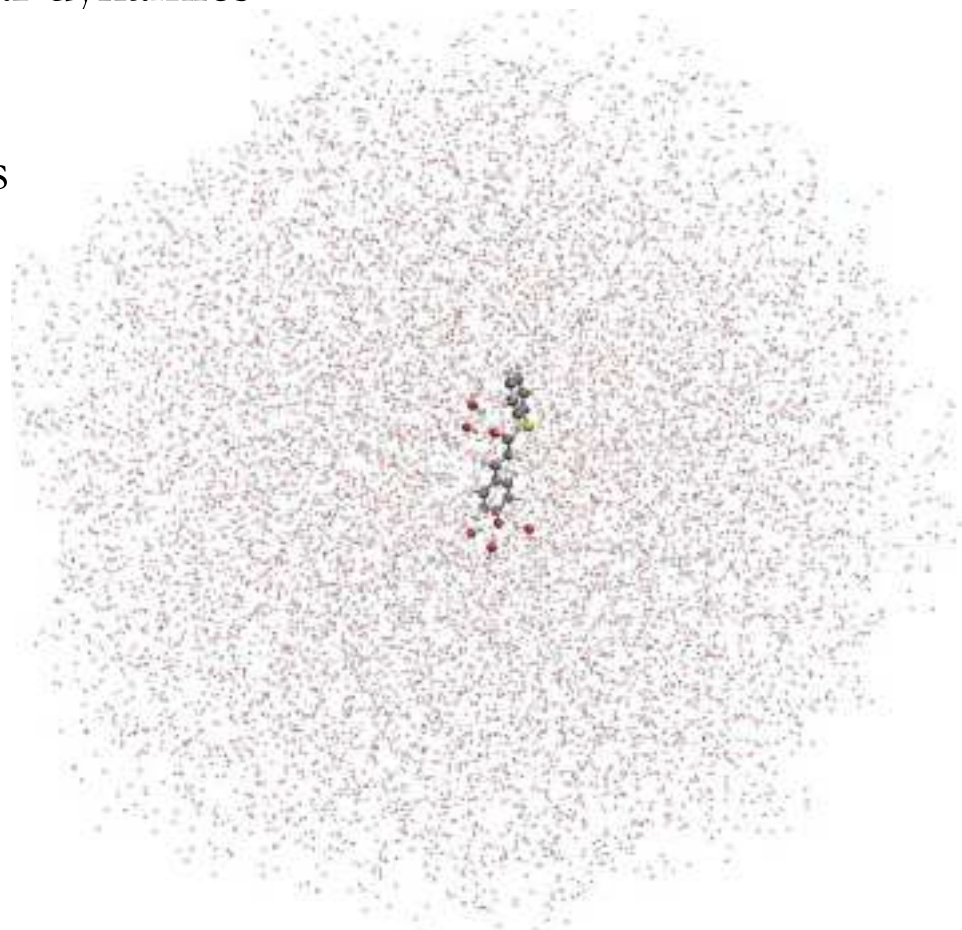
Q: For a smaller cavity, should the excitation energy increase or decrease?

A: It depends on the excited and ground state dipole moment difference

The choice of cavity can change the excitation energy by a nontrivial amount

## Molecular mechanics (MM) solvent as point charges

- Configurations often obtained from molecular dynamics
- Computationally very affordable for fixed point charges: included as one-electron terms in the QM Hamiltonian (similar to electron-nuclear attraction). Can easily add thousands of MM solvent molecules to a calculation.
- The MM fixed charges do not explicitly appear in the TDDFT equations. They polarize the ground state density and will change the orbital energies.
- Polarizable MM solvent **will** have a term in the response equations



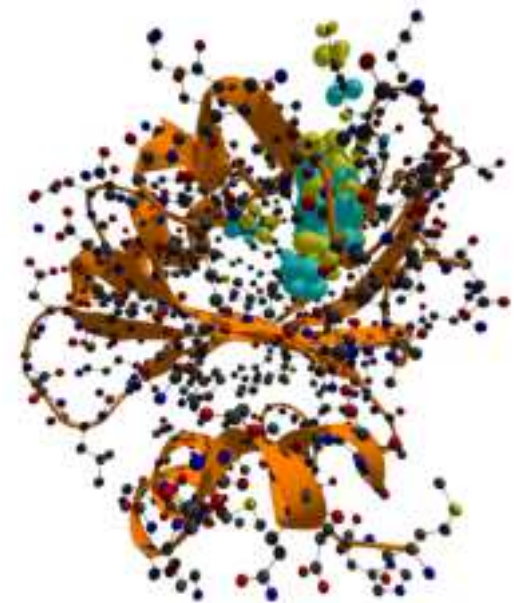
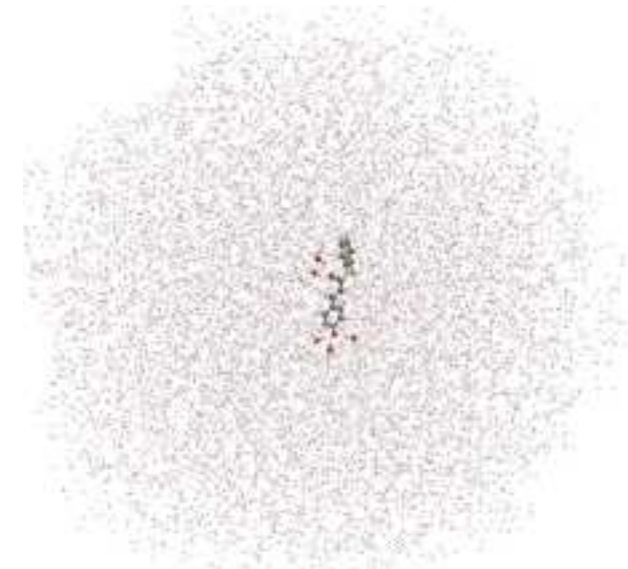
## MM solvent/environment

The most challenging part of the calculation is setting up a solvated molecular dynamics simulation.

No bonds to cut/cap with MM solvent, but you may have to deal with this in other condensed phase environments (e.g. proteins).

Be careful about:

- making sure you have a neutral MM environment (no solvent / protein fragments)
- making sure you have enough MM environment to converge the excitation energy

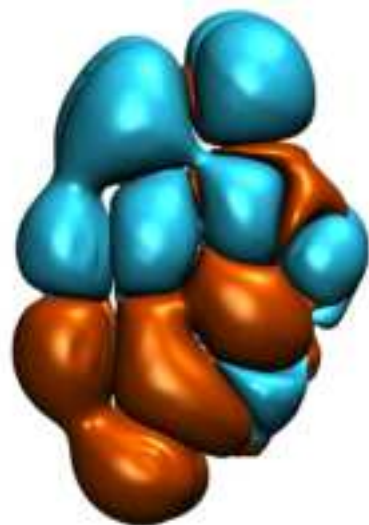




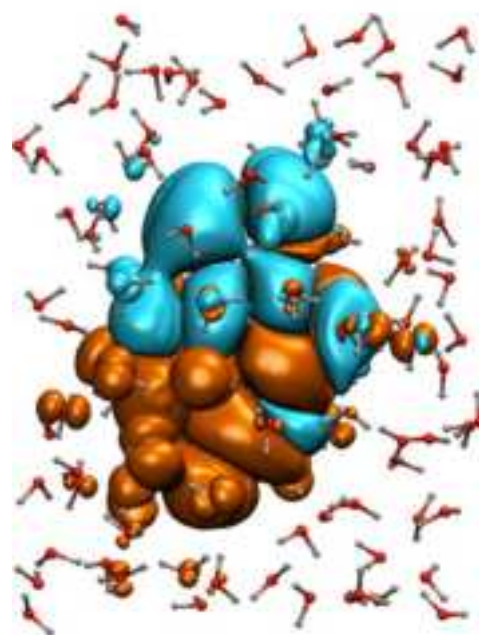
# QM solvent: charge transfer and polarization



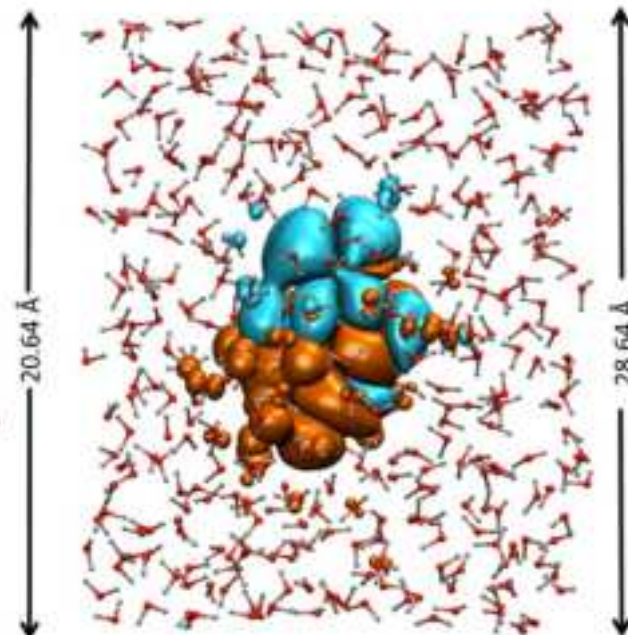
a) Alizarin structure



b) Implicit solvent



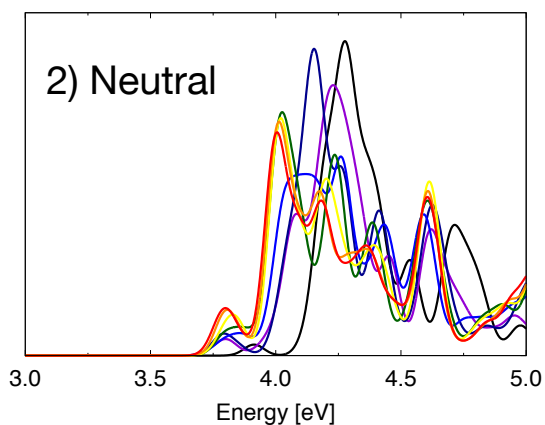
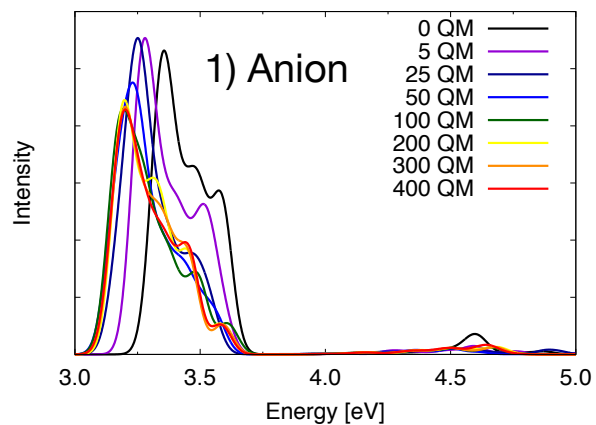
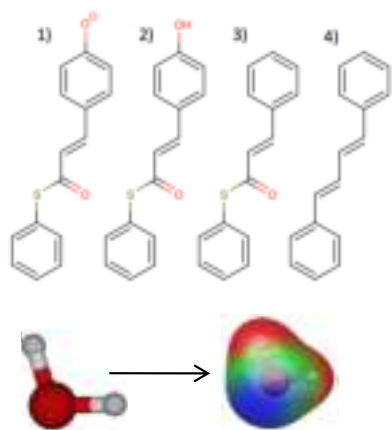
c) 6 Å water



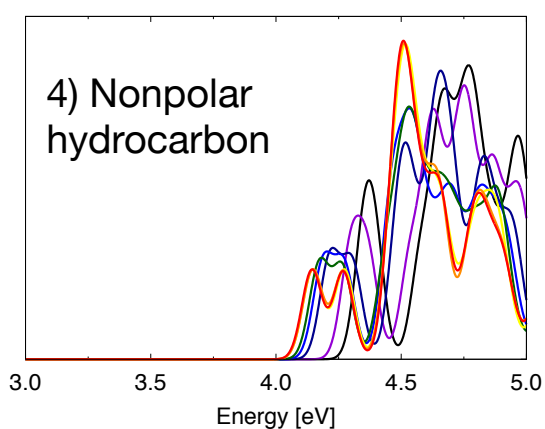
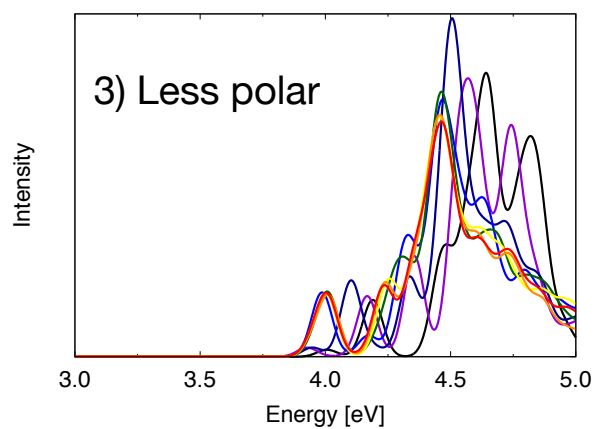
d) 10 Å water

Zuehlsdorff; Haynes; Hanke; Payne; Hine;  
*J. Chem. Theory Comput.* **2016**, 12, 1853  
DOI: 10.1021/acs.jctc.5b01014

# QM solvent – how much to include for converged excitation energies?

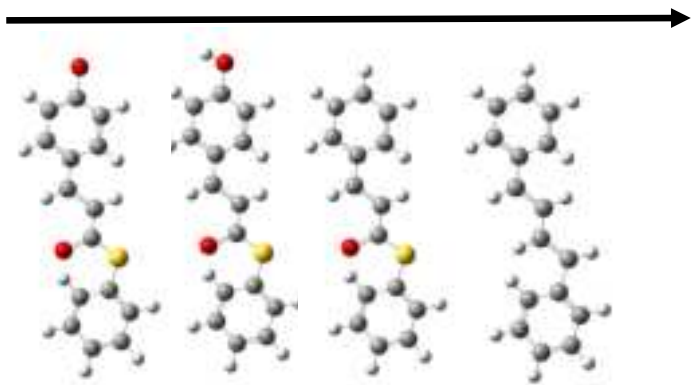


For all solutes, 100-200 QM solvent molecules are necessary to converge most spectral features

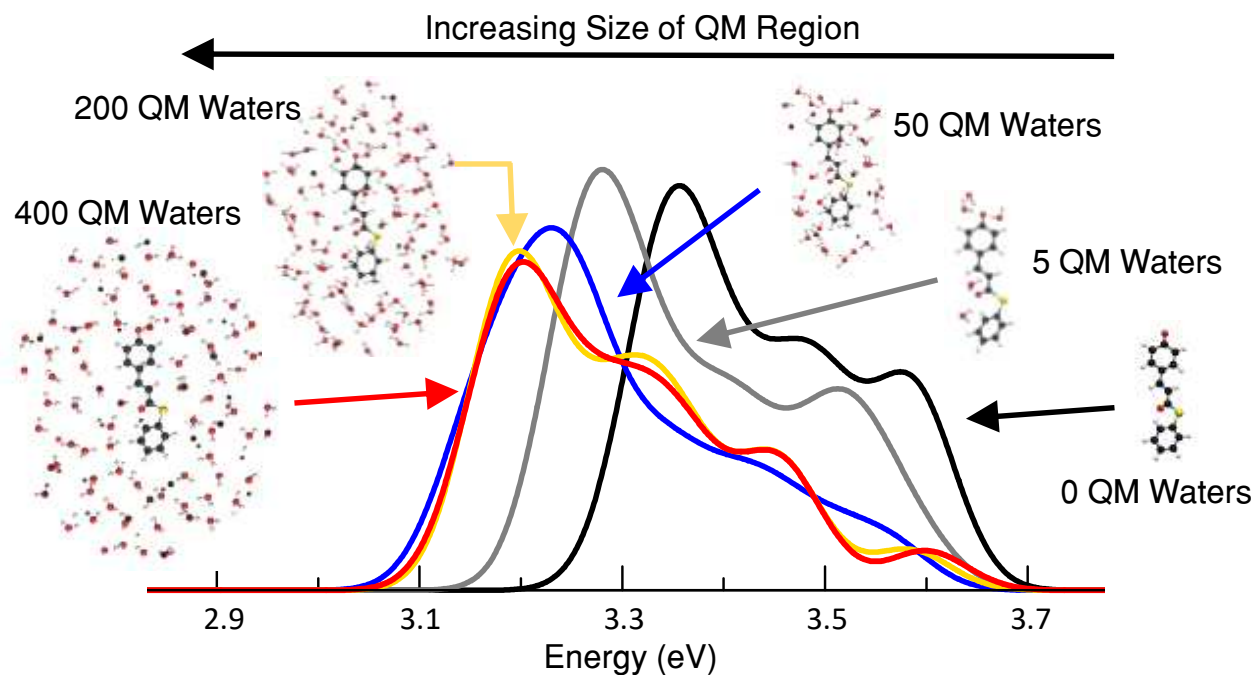


# EFFECT OF QUANTUM MECHANICAL SOLVENT

Solutes of decreasing polarity

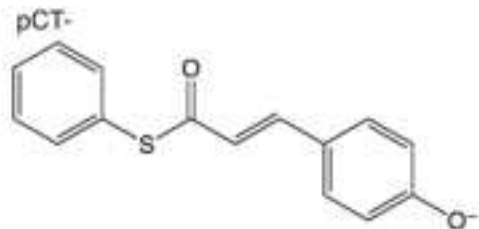


For all solutes, 100-200 QM solvent molecules are necessary to converge most spectral features

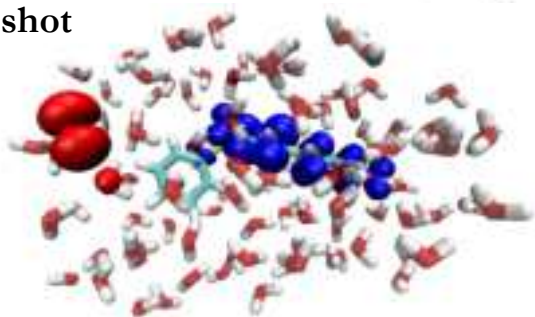


# An extreme CT problem: molecules in QM solvent

*trans*-thiophenyl-*p*-coumarate

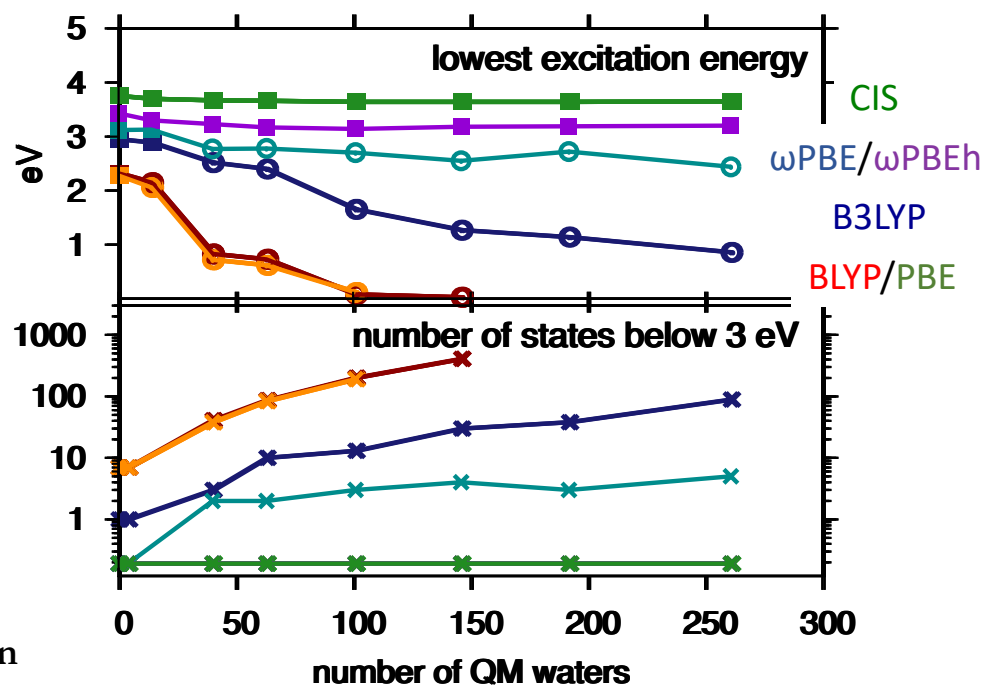


Solvated snapshot



Need Coulombic stabilization  
of electron and hole

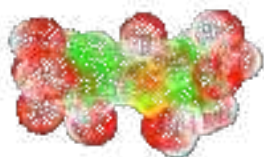
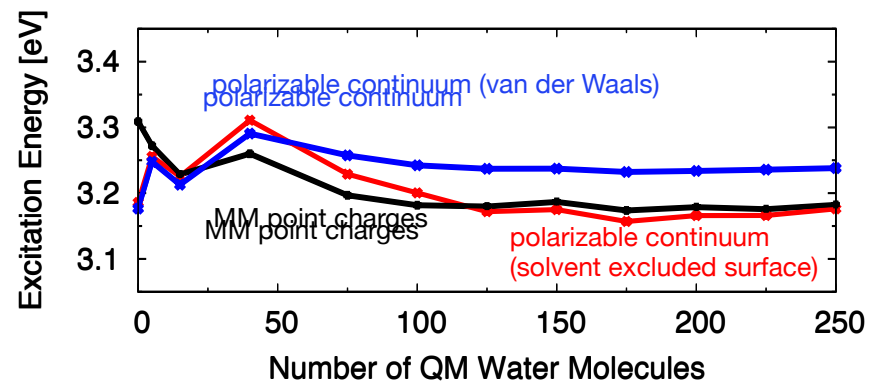
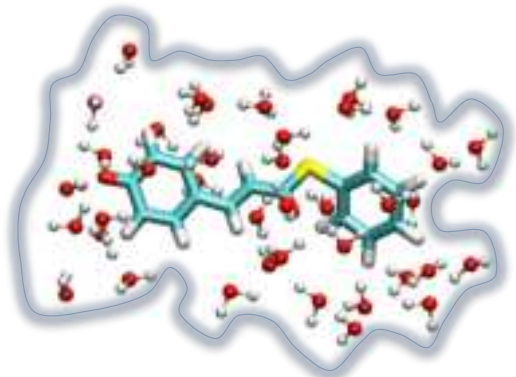
pCT- snapshot



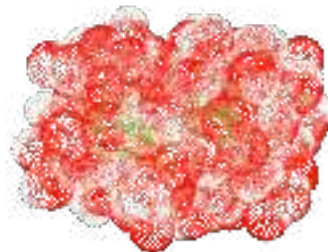
Isborn, Mar, Curchod, Tavernelli, Martinez  
J. Phys. Chem. B 2013, 117, 12189  
[dx.doi.org/10.1021/jp4058274](https://doi.org/10.1021/jp4058274)

Surrounding the QM solvent with MM solvent fixes the bandgap, further improving this CT problem.  
Long-range correction plus MM solvent around the QM solvent works well.

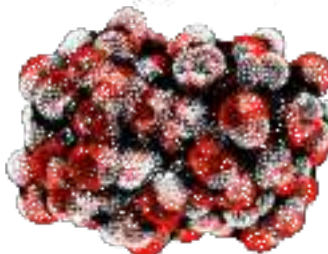
# Combine QM solvent with PCM – now which cavity?



van der Waals cavity



Solvent excluded surface cavity



## SOLUTE-SOLVENT INTERACTIONS

Mutual polarization, both short- and long-range

- ✓ QM solvent (short range, only long range if we have enough solvent)
- ✗ 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)
- ✗ Polarizable continuum model (PCM)

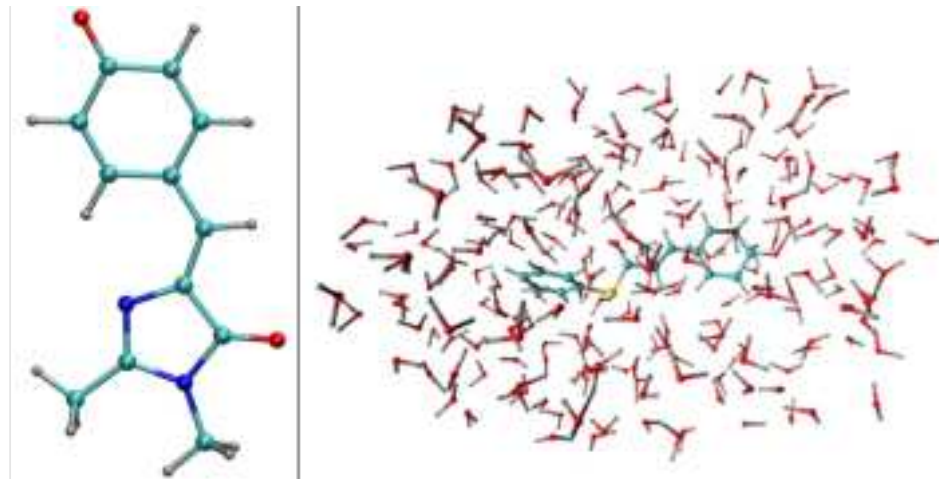
Sampling of solute-solvent configurations (usually from molecular dynamics)

- ✓ QM solvent (but can't usually run the dynamics long enough with QM solvent to fully sample)
- ✓ MM solvent
- ✗ Polarizable continuum model (PCM)

## QUESTION:

**WHICH SOLVENT MODEL WOULD YOU USE FOR THIS SYSTEM?**

- A) Polarizable continuum
- B) MM fixed point charge solvent
- C) QM solvent
- D) QM + MM
- E) QM + PCM



## ANSWER:

**DEPENDS ON YOUR COMPUTATIONAL RESOURCES  
AND WHAT YOU WANT TO MODEL**

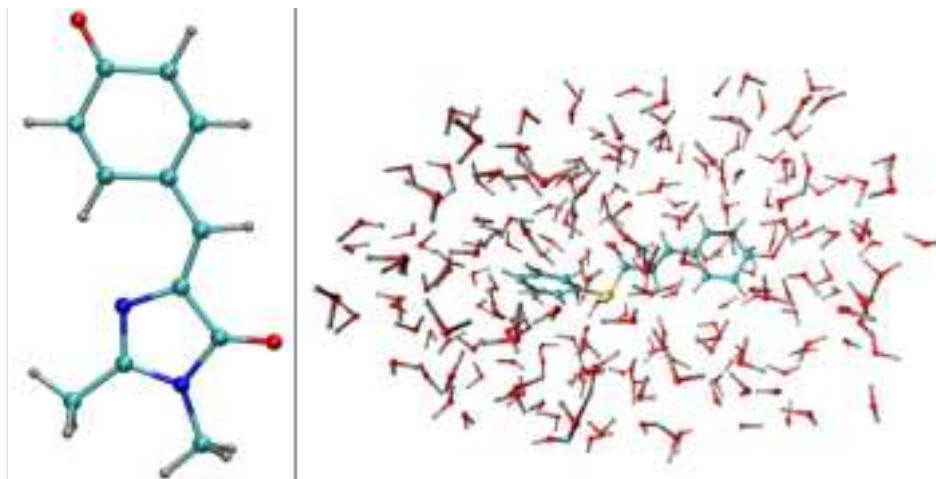
**QUESTION:**  
**HOW WOULD YOU MODEL THE LINEAR ABSORPTION SPECTRUM FOR THIS SYSTEM?**

A) Vertical excitation energy of the optimized molecule

B) Ensemble of vertical excitation energies for molecule-solvent configurations

C) Franck-Condon calculation using vibrational frequencies and harmonic potential energy surfaces, harmonic oscillator wave functions

D) Compute energy gap correlation function for input into cumulant expansion of the linear response function



Zuehlsdorff and Isborn

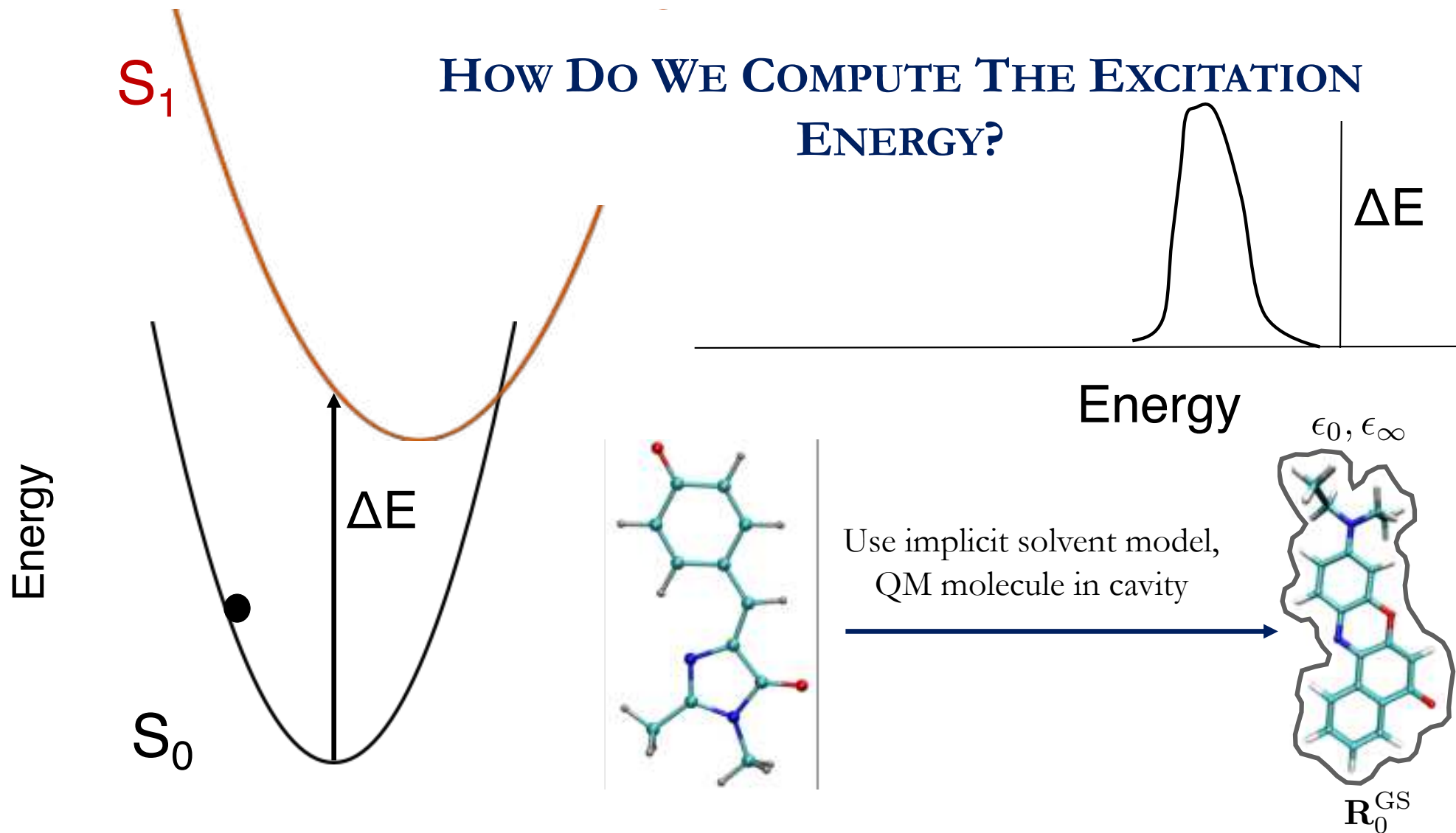
Int. J. Quantum Chem.

”Tutorial Review: Modeling absorption spectra of molecules in solution.”

2019, 119, e25719

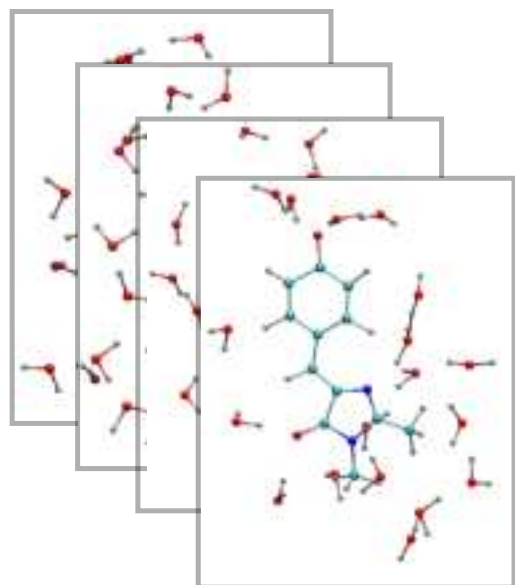


# HOW DO WE COMPUTE THE EXCITATION ENERGY?



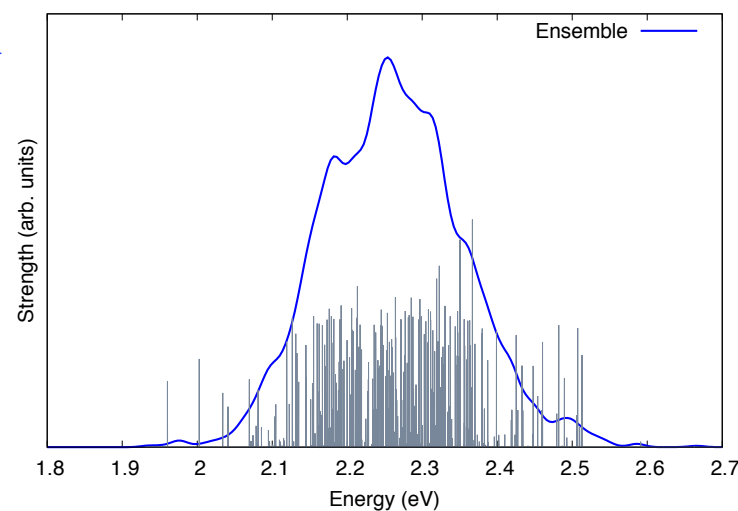
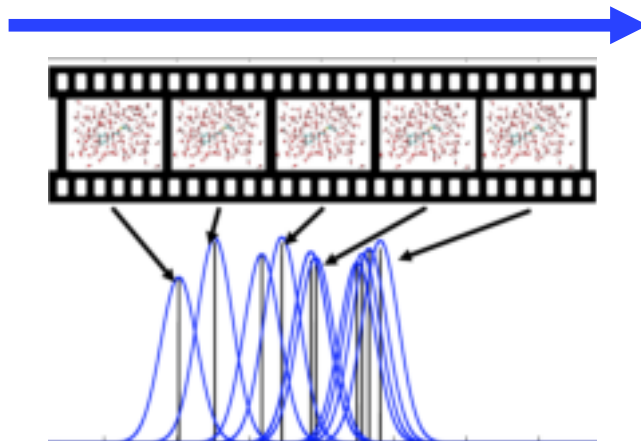
# THE ENSEMBLE APPROACH: SAMPLE FROM MOLECULAR DYNAMICS TRAJECTORY

$$\sigma(\omega) = \frac{4\pi^2\omega}{3c} \int d\mathbf{R} \rho_{\text{GS}}(\mathbf{R}, T) |\boldsymbol{\mu}_{if}(\mathbf{R})|^2 \delta(\omega - \omega_{if}(\mathbf{R})) \approx \frac{1}{N_{\text{frames}}} \frac{2\pi^2}{c} \sum_j^{N_{\text{frames}}} f_{if}(\mathbf{R}_j) \mathcal{N}(\omega_{if}(\mathbf{R}_j), \sigma^2)$$

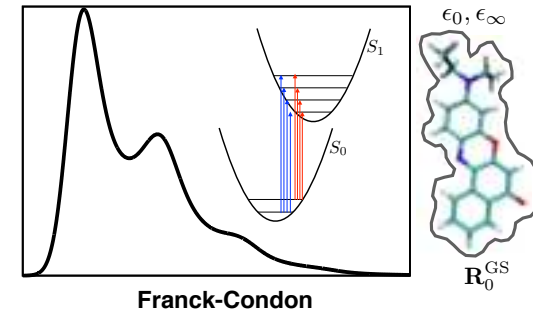


$\mathcal{O}(100) - \mathcal{O}(1000)$  Snapshots

Calculate  $f_{if}(\mathbf{R}_j), \omega_{if}(\mathbf{R}_j)$



# COUPLING TO VIBRATIONAL MODES: THE FRANCK-CONDON PICTURE



Franck-Condon

- Franck-Condon approximation: Excitations are **instantaneous** and electronic dipole moment **independent of nuclear coordinate**

- Fermi's golden rule:

$$\sigma_{\text{FC}}^{\text{vib}}(\omega) \propto |\mu_{if}|^2 \sum_{v''} \rho(v'', T) \sum_{v'} |\langle \phi_{v''} | \phi_{v'} \rangle|^2 \delta(E_{v'}^1 - E_{v''}^0 - \omega)$$

Excitation splits into several vibronic peaks with intensity given by  $|\langle \phi_{v''} | \phi_{v'} \rangle|^2$

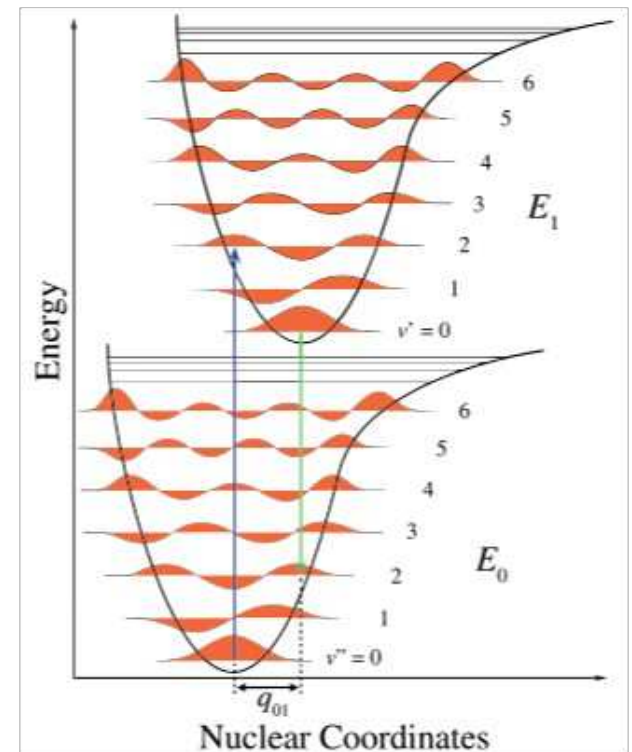


Figure from [https://en.wikipedia.org/wiki/Franck-Condon\\_principle](https://en.wikipedia.org/wiki/Franck-Condon_principle)

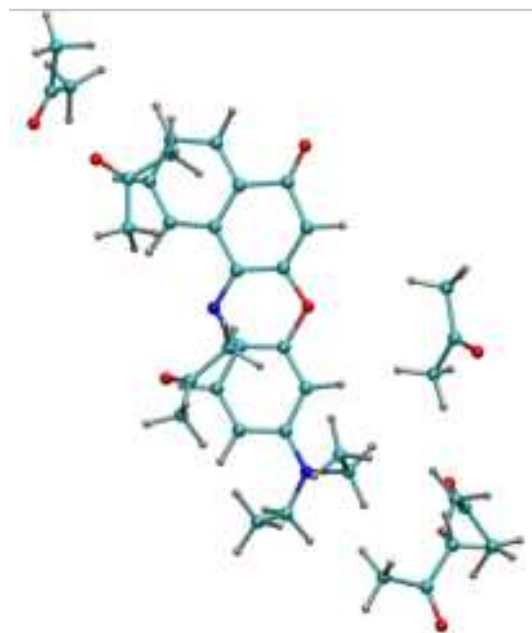
Standard approximations:

- Harmonic approximation to shape of potential
- Only ground state vibrational mode initially occupied: zero-temperature approximation

# PROBLEM WITH THE FRANCK-CONDON APPROACH: INFLUENCE OF SPECIFIC SOLUTE-SOLVENT INTERACTIONS

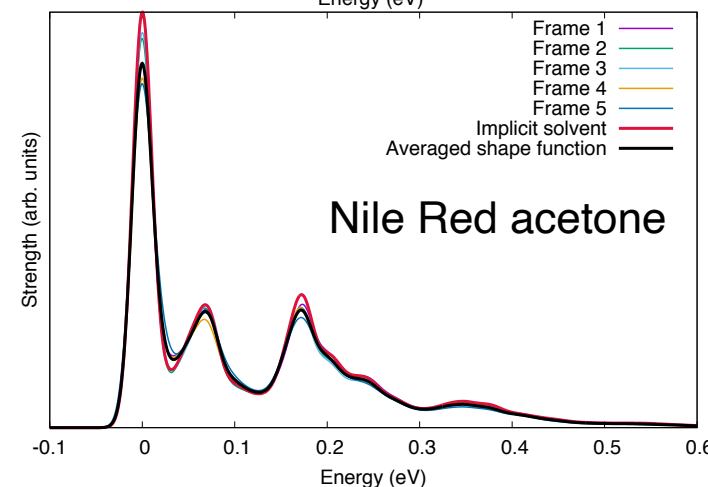
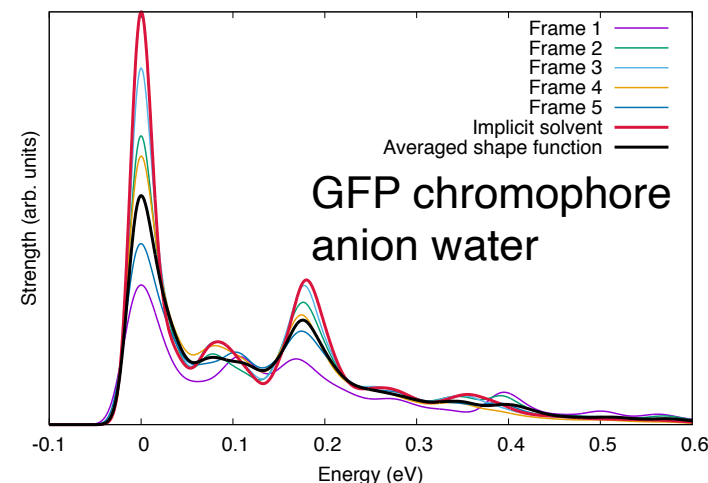
- Usually, normal modes are computed within continuum solvent
- Instead of continuum model, compute Franck-Condon spectra in frozen solvent pockets

- Separation of time-scales
- Weak solute-solvent interactions → Identical spectra to continuum model
- Strong solute-solvent interactions → Significant differences in computed spectra



Optimize chromophore geometry in frozen solvent pocket

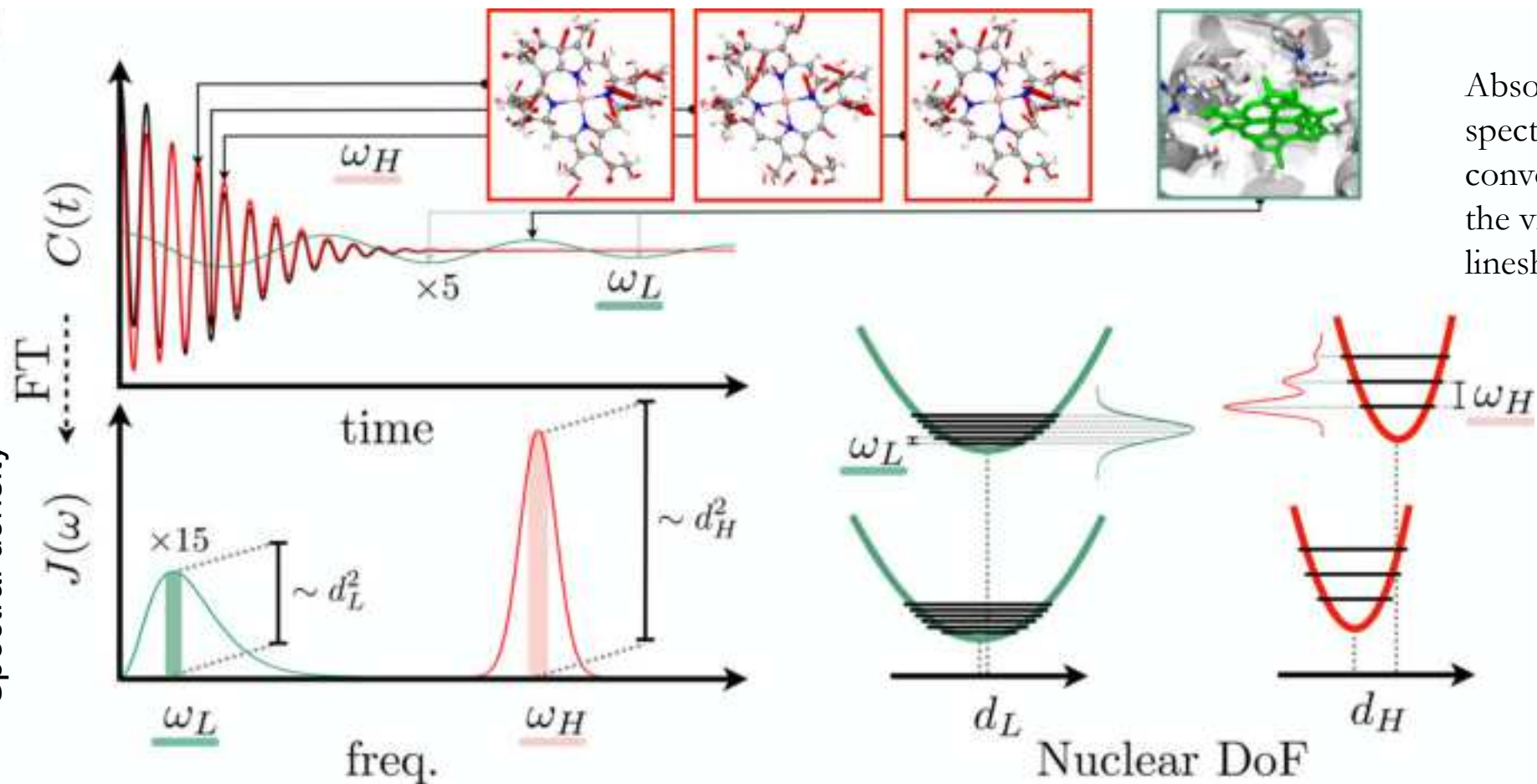
What is the correct way to include solvent effects in a Franck-Condon spectrum?



Zuehdsdorff, Isborn. *J. Chem. Phys.*, 148, 024110, 2018

# CUMULANT APPROACH FOR OPTICAL SPECTROSCOPY

Correlation function  
Spectral density



Absorption spectrum is a convolution of the vibronic lineshapes

# THE CUMULANT APPROACH

- Apply Condon approximation
- Expand time-ordered exponential of the exact response function in terms of cumulants of energy gap fluctuations:

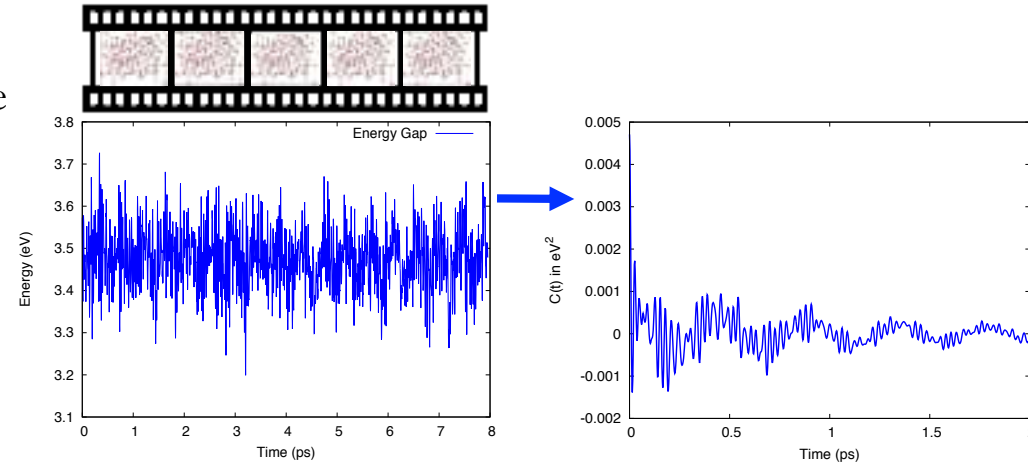
$$\chi(t) = |V_{ge}|^2 e^{-i\omega_{eg}^{av} t} \exp \left[ -g_2 [C_{\delta U}^{(2)}](t) - g_3 [C_{\delta U}^{(3)}](t) \dots \right]$$

$$C_{\delta U}^{(2)}(t) = \langle \delta U(\hat{\mathbf{q}}, t) U(\hat{\mathbf{q}}, 0) \rangle$$

$$C_{\delta U}^{(3)}(t_1, t_2) = \langle \delta U(\mathbf{q}, t_2) U(\mathbf{q}, t_1) U(\mathbf{q}, 0) \rangle$$

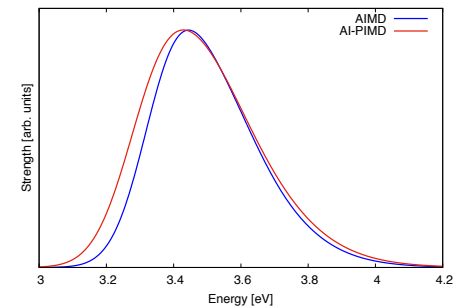
- **Basic assumptions:**

- Cumulant expansion can be truncated at finite order (true at 2nd order if fluctuations are **Gaussian**)
- Quantum correlation functions of the energy gap can be approximated by classical correlation functions and **quantum correction factors**



$$C_{\delta U}^{(2)}(\omega) \approx \frac{\beta\omega}{1 - e^{-\beta\omega}} C_{\delta U}^{(2),cl}(\omega)$$

$$g_2(t) = \frac{1}{2\pi} \int d\omega \frac{C_{\delta U}^{(2)}(\omega)}{\omega^2} [1 - e^{-i\omega t} - i\omega t]$$



# COMPUTING LINEAR ABSORPTION SPECTRA

Linear absorption spectrum

$$\sigma(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \chi(t)$$

Linear response function

$$\chi(t) = \text{Tr}[\rho(0)e^{iHt}\hat{V}(\hat{\mathbf{q}})e^{-iHt}\hat{V}(\hat{\mathbf{q}})]$$

Inhomogeneous limit :  
**Static** (nuclear coordinates are frozen)

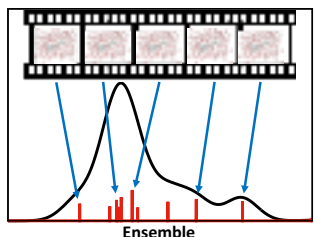
Condon approximation

Harmonic approximation of PES

$$V_{ge}(\mathbf{q}) \approx V_{ge}$$

Cumulant expansion

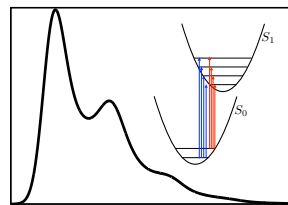
Ensemble spectrum



$$\chi(t) = \text{Tr}_n [\rho_g(\hat{\mathbf{q}}, \hat{\mathbf{p}}) |V_{ge}(\mathbf{R})|^2 e^{-iU(\hat{\mathbf{q}})t}]$$

$$\sigma(\omega) = \int d\mathbf{R} \rho_g(\mathbf{R}) |V_{ge}(\mathbf{R})|^2 \delta(\omega - U(\mathbf{R}))$$

Franck-Condon spectrum



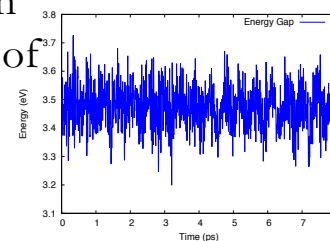
$$\chi(t) = |V_{ge}|^2 \sum_{v_e, v_g} \rho_{v_g} |\langle v_g | v_e \rangle|^2 e^{-i\Omega_{v_e, v_g} t}$$

$$\sigma(\omega) = |V_{ge}|^2 \sum_{v_e, v_g} \rho_{v_g} |\langle v_g | v_e \rangle|^2 \delta(\omega - \Omega_{v_e, v_g})$$

$$\chi(t) = |V_{ge}|^2 e^{-i\omega^{avg}t - G_m(t)}$$

$$\sigma(\omega) = |V_{ge}|^2 \int_{-\infty}^{\infty} dt e^{i(\omega - \omega^{avg}t) - G_m(t)}$$

Requires correlation functions of the excitation energy



## SUMMARY

A variety of solvation models can be combined with TDDFT calculations. Each with positives and negatives.

Continuum solvent: No sampling of solute-solvent specific interactions

Molecular mechanical solvent: very fast, some specific interactions, no polarization

QM solvent: polarization and charge transfer, but computationally expensive

Various methods exist for modeling spectra of condensed phase systems, each taking into account different physical effects.

