

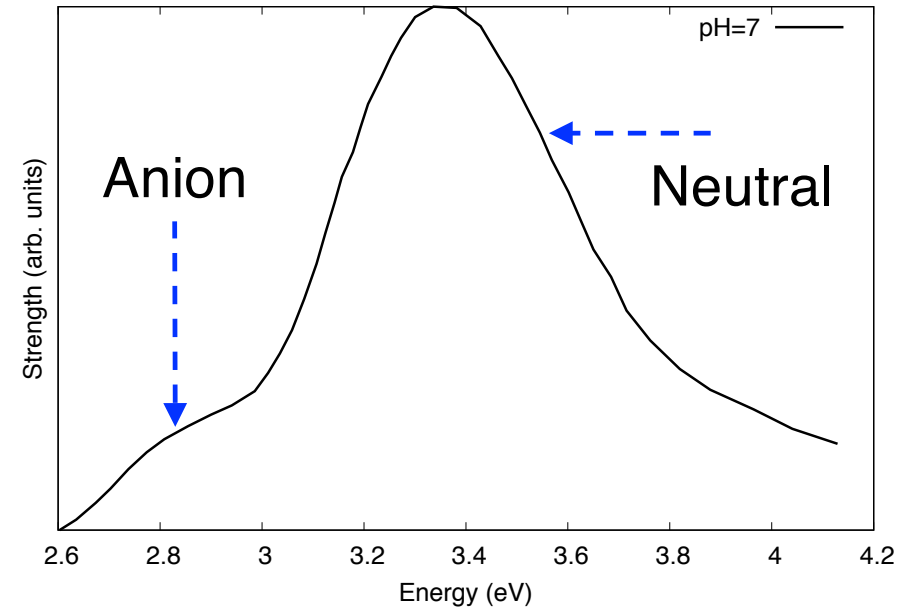
EXCITED STATES FOR MOLECULES IN SOLUTION

CHRISTINE M. ISBORN

UNIVERSITY OF CALIFORNIA MERCED

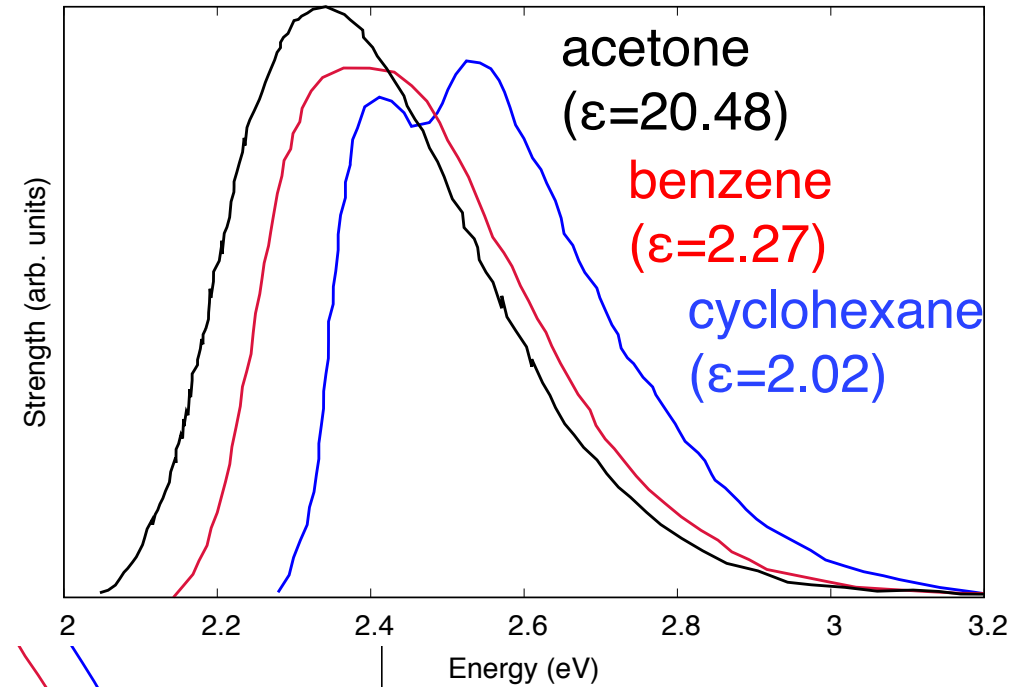
GOAL: MODEL SPECTROSCOPY FOR MOLECULES IN COMPLEX, CONDENSED PHASE ENVIRONMENTS

Green fluorescent protein (GFP) chromophore in water



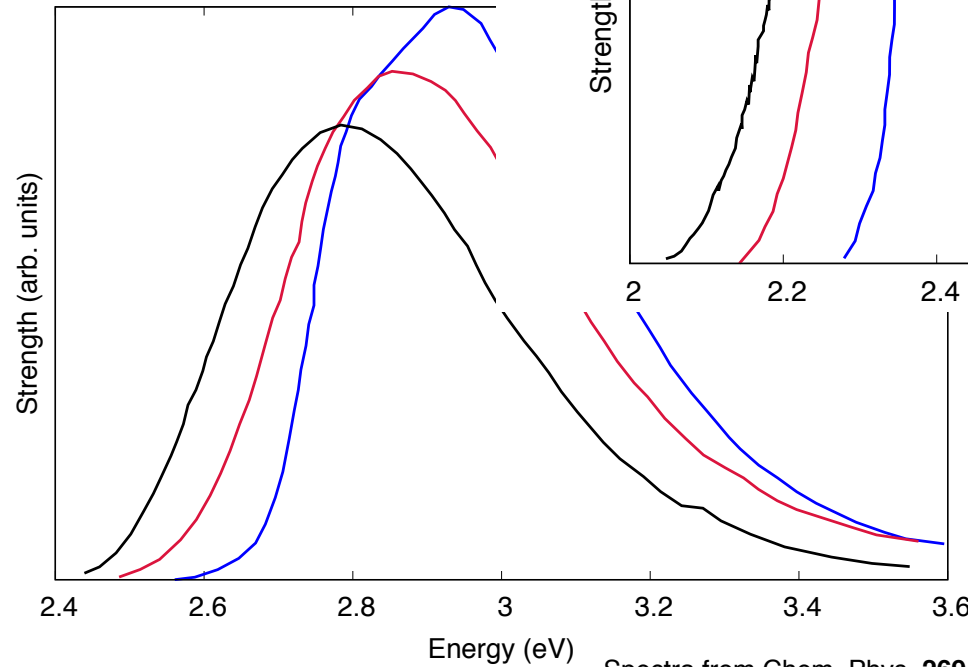
Spectrum from Phys. Rev. Lett. **87**, 228102 (2001)

Nile Red chromophore in different solvents



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

Anionic GFP chrom



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

CLICKER QUESTION:

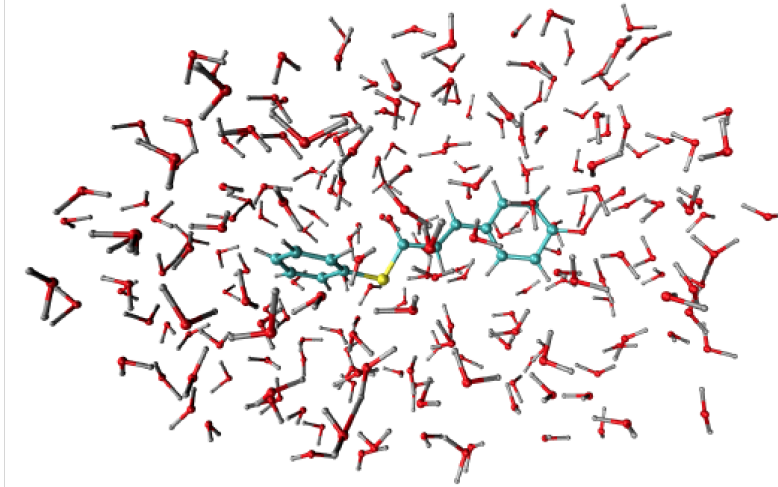
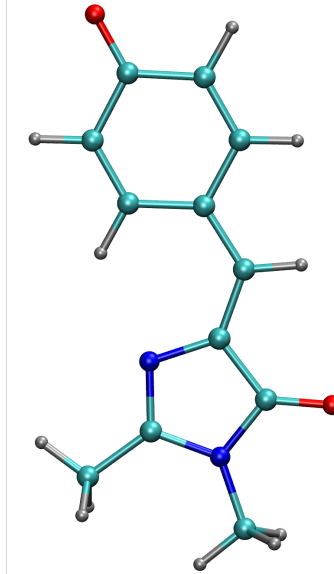
HOW WOULD YOU MODEL THE LINEAR ABSORPTION SPECTRUM FOR THIS SYSTEM?

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

D) Compute energy gap correlation function for 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

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)

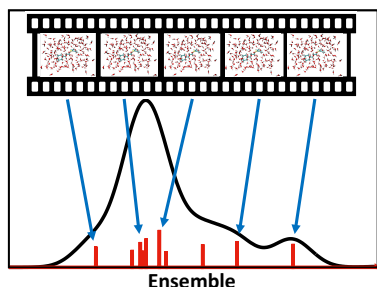
Condon approximation

Harmonic approximation of PES

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

Cumulant expansion

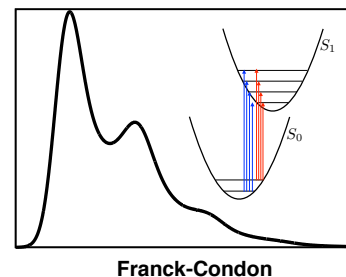
Ensemble spectrum



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

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

Franck-Condon spectrum



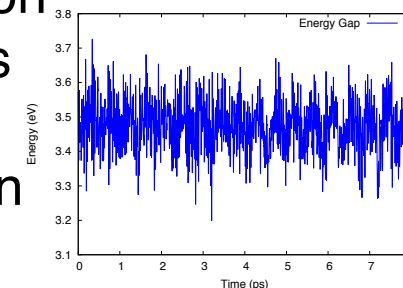
$$\chi(t) = |V_{ge}|^2 \sum_{v_e, v_g} \rho_{v_g} |\langle v_g | v_e \rangle|^2 e^{-i\Omega_{v_e, v_g} t}$$

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

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

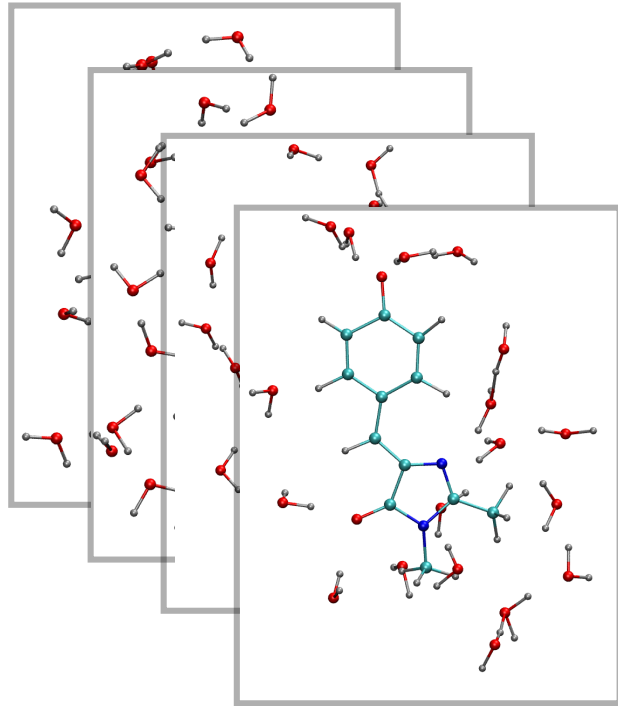
$$\sigma(\omega) = |V_{ge}|^2 \int_{-\infty}^{\infty} dt e^{i(\omega - \omega^{avg}t) - G_m(t)}$$

Requires correlation functions of the excitation energy



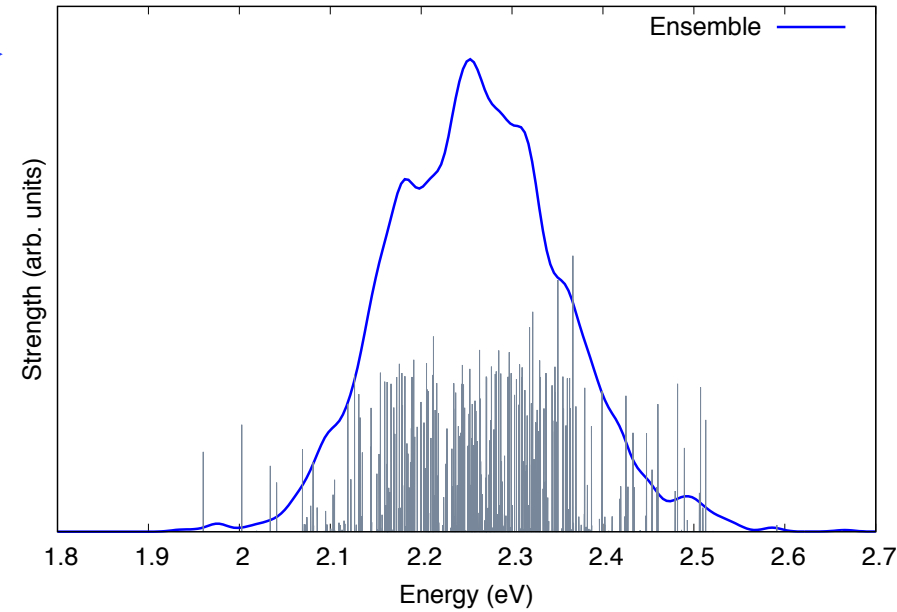
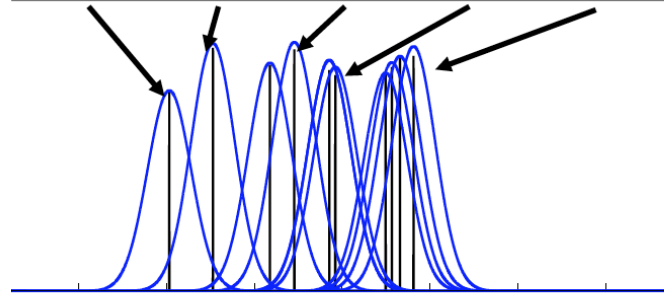
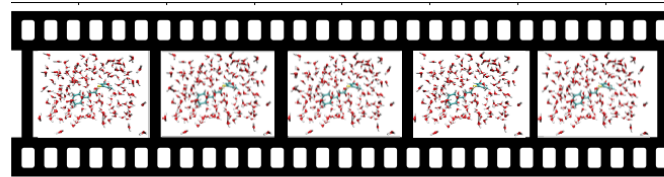
THE ENSEMBLE APPROACH

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



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

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



COUPLING TO VIBRATIONAL MODES: THE FRANCK-CONDON PICTURE

- Franck-Condon 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 $|\langle \phi_{v''} | \phi_{v'} \rangle|^2$

Standard approximations:

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

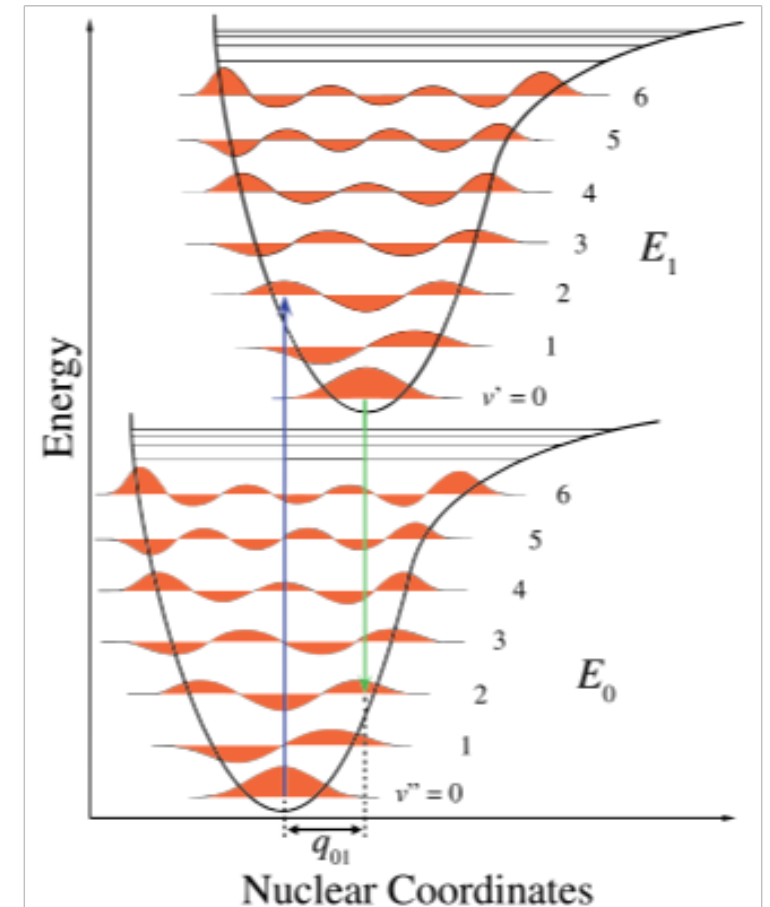
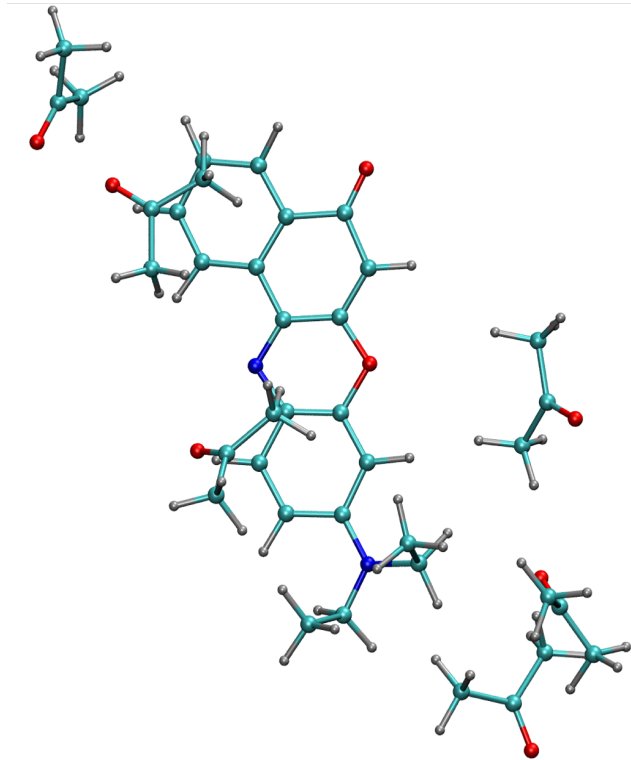


Figure from https://en.wikipedia.org/wiki/Franck-Condon_principle

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

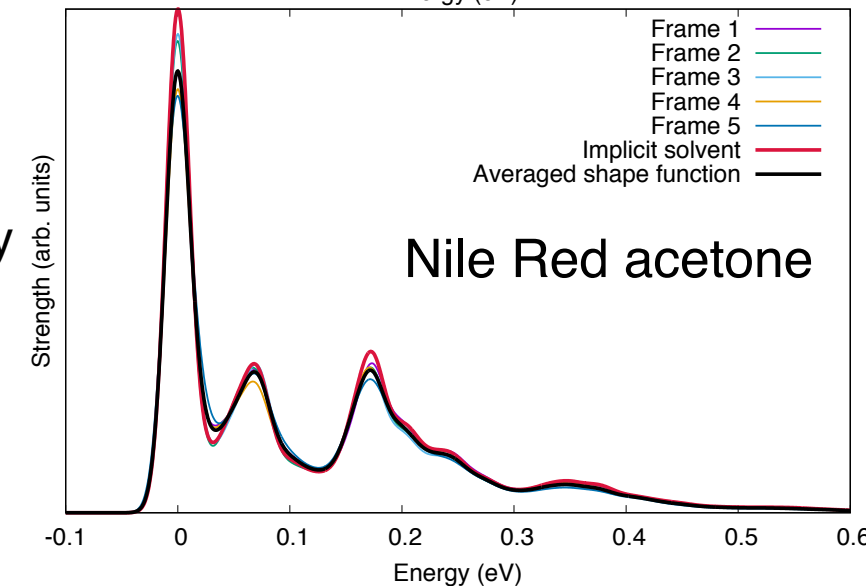
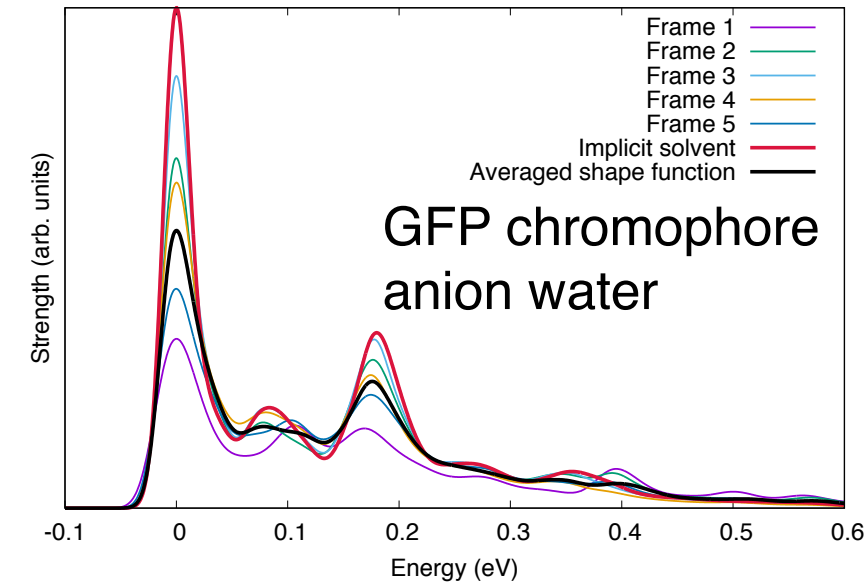
- Usually, normal modes are computed within continuum solvent
- Instead of continuum model, compute Franck-Condon spectra in frozen solvent pockets

- 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?



CUMULANT APPROACH FOR OPTICAL SPECTROSCOPY

