The Effects of Hydrogen Bonding on Computed Optical Spectra and Spectral Density

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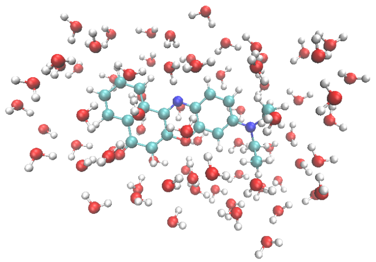
Abstract: Simulations of electronic optical spectra of molecules often must include the explicit solvent environment because the solvent affects the absorption spectrum due to polarization of chromophore electron density and direct solute-solvent interactions such as hydrogen bonding. Our main motivation for this study is to determine how including hydrogen bonded solvent molecules in our geometry optimization calculations affect the simulated electronic spectra and spectral density. In this poster, we analyze the electronic absorption spectra, spectral density, and geometry of the Nile Red chromophore in water for calculations with frozen solvent, each solvent molecule that hydrogen bonded with Nile Red individually, then with all solvent molecules that hydrogen bonded with Nile Red. Analyzing the geometries of Nile Red in water showed that changes in geometry around the nitrogen and the oxygen in the center ring of Nile Red were produced from the hydrogen bonding solvent. Including water at the central hydrogen bonding oxygen site produced the largest change in the spectra, suggesting that this may be an important factor to consider for future simulations of electronic spectra of chromophores solvated in hydrogen bonding solvents.

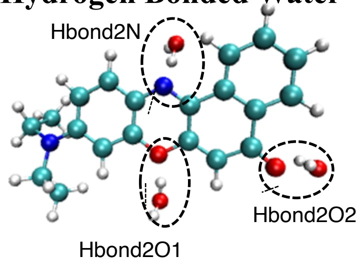
Computational Details

- Utilized Gaussian and TeraChem electronic structure programs for the geometry optimizations, frequency/normal mode computations, and excited state TDDFT calculations.
- Level of theory used was the CAM-B3LYP density functional with 6-31G basis set
- Full solvation layer of water is treated with density functional theory, but only select H-bonding water molecules are included in the geometry optimization

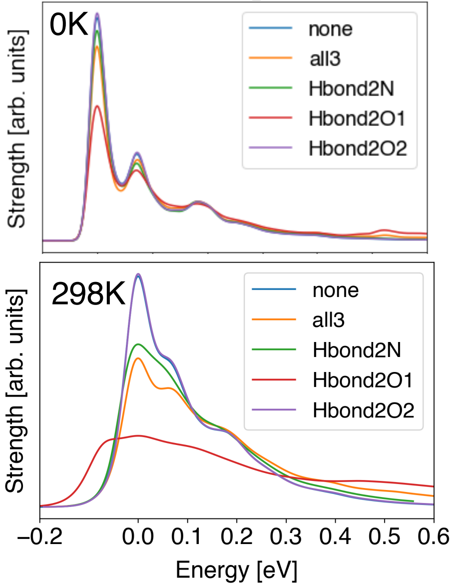
Nile Red in Water



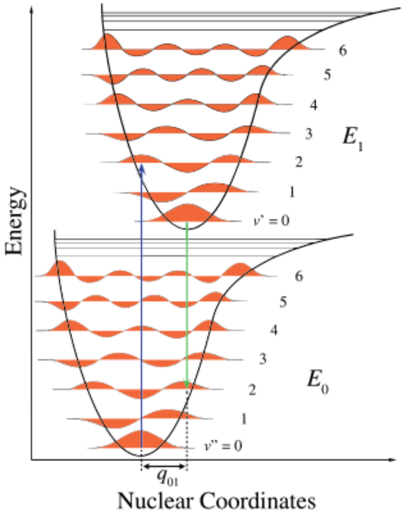
Nile Red with Hydrogen Bonded Water



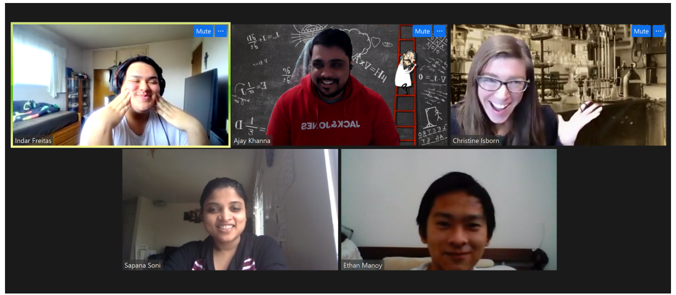
Electronic Spectra



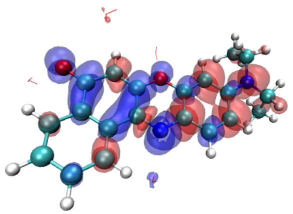
Franck-Condon principle



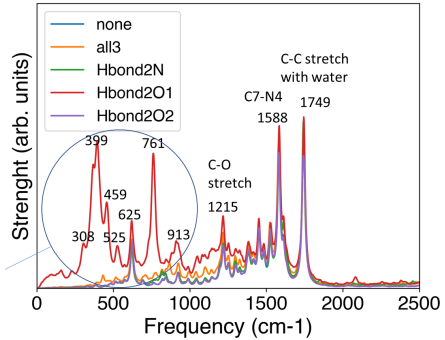
https://en.wikipedia.org



Difference of Excited State and Ground State Electron Density



Spectral Density



Conclusions and Future Work

- Including the water at O1 in the center ring causes the largest change in the spectra, whereas at O2 causes the smallest change
- Optimizing the geometry with the water at O1 makes the electronic absorption spectrum broader
- The spectral density shows changes in both low- and high-frequency modes, with low-frequency modes correlating with the motion of the water
- We plan to test how general our conclusions are by testing more snapshots and more chromophores.
- We will also compare these results to those computed with an implicit solvent model that does not account for any hydrogen bonding

References

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