Using Computational Methods To Predict UV-VIS Spectra of Small Natural Organic Molecules

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Understanding the absorption spectra of a molecule is essential to predicting the rate of sunlight driven chemical transformations. However, most research either focuses only on the qualitative study of absorption spectra or utilizes a semi-empirical method to calculate these values. To quantitatively model the absorption spectra, an experiment was conducted using computer software to calculate excitation energies and oscillator strengths, the likelihood of transition, of small organic molecules from first principles (ab initio). Two approaches were selected to model the photon absorption: Molecular Dynamics–Time Dependent Density Functional Theory (MD-TDDFT) using GAMESS software and Multi Configurational Self Consistent Field (MCSCF) using DALTON software.

In MD-TDDFT, an aniline molecule equilibrated in the presence of 150 water molecules at room temperature using aug-cc-pVDZ basis set. Water molecules were placed empirically using packmol software to ensure an acceptable initial guess. To make the calculation manageable, each water molecule was treated as effective fragment (EF), whose properties had been calculated beforehand in ab initio fashion. After a one picosecond of molecular relaxation in water, multiple snapshots of aniline and water molecules were taken every ten femtoseconds. Each structural snapshot of aniline and water then became the input geometry for an excitation energy and oscillator strength calculation using TDDFT with CAMB3LYP functional. According to another previous studies in the literature, the proper equilibration time and snapshot interval will vary for each system. Due to a massive amount of data involved in MD-TDDFT, input preparation and output data analysis were carried out using python scripts written or modified by myself. First plotEnergyMD.py plotted the total Hamiltonian energy of each snapshot vs. simulated time to determine if the system has reached an energetic equilibrium. fincut1.py, written initially by Nathan Ricke '14, was used to generate input files for TDDFT calculation. 3dExtract.py was written to extract geometry and visualize aniline and water in three dimension using Jmol software. Lastly, postMDDataPull.py extracted excitation energies and oscillator strengths out of all calculations. A statistical model for molecular dynamics is still needed to process extracted excitation energies and oscillator strengths.

In MCSCF, the calculation was carried out with guess orbitals from a DFT energy calculation using aug-cc-pVDZ basis set. The implicit water model was implemented in MCSCF calculation using Polarizable Continuum Model (PCM). However, the study using DALTON has been arduous and delayed due to the stringent syntax and the incompleteness of the program.

The computed quantities would then be compared with data from experimental absorption spectra to evaluate the accuracy of the two methods. In a collaborative work with Peter Cohen ‘17, the underlying modified Gaussian functions of absorption spectra were decomposed and integrated to calculate experimental oscillator strength at a certain excitation energy. The selected method would be applied to triclosan and other water contaminants to assist in the prediction of pollutant degradation rates in natural waters.
