Computational Predictions of Photochemical Reaction Pathways
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The goal of this project was to develop a computational method to make predictions on the photochemical reactivity of organic molecules. Computational prediction of photochemical reactivity allows for the evaluation of the photochemical fate of organic pollutants, particularly in aquatic ecosystems where they will be exposed to ultraviolet radiation from the sun. These predictions will provide insight on whether this radiation will cause the breakdown of these compounds, and what products will be formed during their degradation. One major benefit of a computational model for making these predictions is that computational testing will become faster and cheaper as processor speeds increase, enabling the continued evaluation of new chemicals even as their numbers increase at an accelerating rate.

The first property of an organic molecule that is evaluated with this model is its ultraviolet-visible (UV-Vis) absorption spectrum. When a photon of light passes through a molecule, there is a chance that it can absorb this light. The percent chance of this absorption taking place is logarithmically related to the absorbance of the molecule, which is plotted as a function of the energy of the absorbed photon to create a UV-Vis spectrum. A molecule will only be photochemically reactive if it absorbs a photon, particularly an energetic one in the UV or low-wavelength visible region.

Quantum mechanical calculations determine the probability of a photon being absorbed at a given energy by calculating the difference in energy between electronic states. A molecule is in its electronic ground state prior to absorbing the photon, and after excitation enters an excited state. Almost all organic molecules in the ground state have a net spin of zero, which means they are in a singlet state, denoted $S_0$. The excited state, due to conservation laws in quantum mechanics, will also be a singlet state, denoted $S_1$ if it is the first excited state. The difference in energy between the two states is the energy of the photon that is absorbed. Simulated spectra are generated for this model by calculating this energy difference in a solvent of rapidly moving water molecules, which slightly perturb the difference in energy between the two states, thus creating a range of probabilities of energies that are plotted as individual Gaussian peaks and summed together. Summed together, the peaks produce a complete UV-Vis absorption spectrum.

The second component of this model developed thus far predicts the triplet quantum yield of an excited molecule. The triplet quantum yield is the percent chance the molecule will undergo a “spin-flip” and enter a triplet electronic state, denoted $T_1$, from the $S_1$ state, instead of simply returning directly to the $S_0$ state. This is calculated by first calculating the potential energy surfaces (PES) of the $S_1$, $T_1$ and $S_0$ states. The minimum energy intersections between these surfaces are calculated using specific quantum mechanical calculations, and transition state theory and the Landau-Zener model are used to calculate the relative rates of each transition, which in turn are used to calculate the quantum yield. The quantum yield indicates whether the predominant state available to undergo photochemical reaction is the $S_1$ or $T_1$ state, as well as the relative lifetimes of these excited states.

Faculty Mentor: Soren Eustis
Funded by the Hughes Family Summer Research Fellowship