**Mapping the Energetic Landscape for the PNA(P)/Pyridine Chemical Actinometer System: A Full Experimental and Theoretical Quantum Dynamics Investigation**

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The chemical reaction between p-nitroanisole (PNA) and pyridine is one example of a chemical actinometer: a tool widely used by quantum and environmental chemists paramount to understanding photodegradation of micropollutants in aquatic ecosystems. An actinometer must have an accurately characterized quantum yield, a parameter that represents how much the system reacts per photon absorbed, obtained and verified through repeated analysis. With the quantum yield measurement, an actinometer can be used as a reference for pollutants that degrade in sunlight, allowing us to quantify a pollutant's light absorption and characterize its potential danger to the environment. Both the PNA/Pyridine and the PNAP/Pyridine actinometer systems were introduced and their quantum yields reported in 1982. In 2017, the actinometers were re-examined in a report that included new quantum yield measurements, 23% less than the originals. The Eustis lab believes that a more detailed understanding of the actinometers' reaction mechanisms would be a solid check of their capabilities in the lab and expand their application to environmental chemistry. This project's goal is to numerically characterize the most significant excited state pathways undergone in both the PNA and PNAP actinometer systems.

In order to properly use an actinometer as a standard, one must have an accurate measurement of the sensitizer's molar absorptivity, which tells how effectively the sensitizer absorbs a given wavelength. The Eustis lab made molar absorptivity measurements its first priority. These values were obtained by collecting absorbance spectra of PNA and PNAP at various concentrations and running a program that manipulates the Beer Lambert equation, $A = \varepsilon bc$, to calculate molar absorptivity at each wavelength from 200nm to 500nm (figure 1). The sensitizer's absorbance is important to consider when using an actinometer in a photoreactor, as the light bulbs must produce wavelengths that will be effectively absorbed by the sensitizers but not by pyridine. Since pyridine's absorbance is negligible over 280nm, the 300nm and 350nm bulbs are both sufficient in the photoreactor.

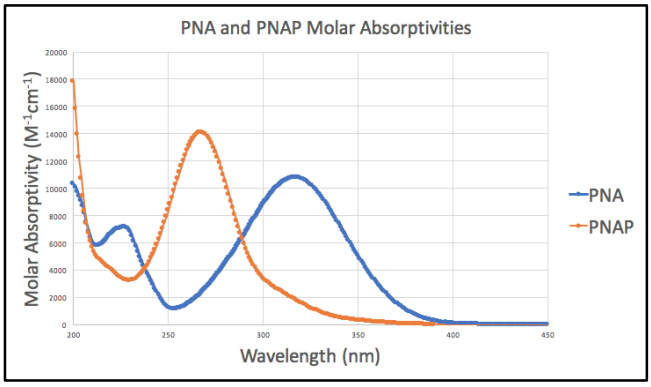


Figure 1. Data collected with UV-Vis spectroscopy and processed through MATLAB.

Fluorescence and phosphorescence spectroscopy were used to study photons emitted from excited singlet and triplet states, giving information about how the sensitizers behave upon absorbing light. Further analysis was conducted in which multiple PNA/pyridine samples were placed in a photoreactor, several containing specific quencher molecules that inhibit the stability of individual excited states. Liquid chromatography of samples taken from various time points showed that PNA/pyridine product formed more slowly in the presence of triplet quenchers, indicating that triplet excited states are likely involved in the reaction. The findings so far certainly contribute to the general understanding of both actinometer systems and will increase their utility in the lab. Particularly, the work done this summer will greatly accelerate any future work with the actinometers in the Eustis lab as calibration parameters for instrumentation such as spectrophotometers, the photoreactor, and the liquid chromatography system have been determined and refined.

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