

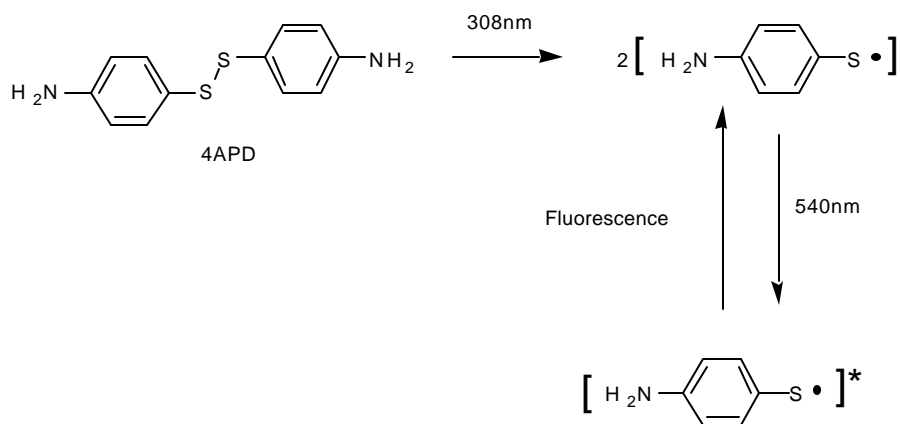
Two Laser Experiments using *p*-Aminophenylthiyl Radicals as Probes for Supramolecular Systems

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The *p*-aminophenylthiyl radicals are readily created by photo cleavage of the 4APD molecule.

These radicals have been studied extensively due to the significant changes observed in their spectral properties when placed in solvents of varying polarities (Morine G.H, Kuntz R.R, *Chem. Phys Lett.* (1979) 67, 552). The basis of the project is the observation that the fluorescence of the



excited radical can be almost entirely quenched in the presence of solvents capable of hydrogen bonding, such as water and alcohols. Long-term goals include developing a method for using the *p*-aminophenylthiyl radicals to probe the dynamics of proteins by attaching the radicals to cysteine residues. A model system is needed to study the cleavage of the S-S bond and the changes in spectral properties in various environments. Two laser experiments were developed in order to investigate the changes in absorbance and fluorescence of the radicals in non-polar and polar solvents. The two laser experiments thus far have been carried out in cyclohexane, a very non-polar aprotic solvent in which the radicals are known to fluoresce. The radicals are created by cleaving the S-S bond using a 308 nm excimer laser. A second pulse from an Infinity OPO laser at 540 nm is used to excite the radicals from the ground state to a D_1 excited state and the emission of the radicals is measured. We are working under the principle that the emission is proportional to the concentration of radicals. The OPO laser is fired at varying delays after the excimer laser. A decay curve is obtained by collecting the fluorescence intensity at different delays. Currently work is being carried out to determine the lifetime and the spectral properties of the *p*-aminophenylthiyl radicals in a variety of solvent systems. In addition, work is being carried out to determine the complexation dynamics of the radicals with supramolecular systems, such as cyclodextrin.