Molecular photofragmentation dynamics in the gas and condensed phase: similarities, differences, challenges and opportunities

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Phenols and azoles are common chromophores in the nucleobases and aromatic amino-acids that dominate the near-UV absorption spectra of many biological molecules. π\*←π excitations are responsible for these strong UV absorptions, but these molecules also possess excited states formed from σ\*←π electron promotions. These πσ\* excited states typically have much smaller absorption cross-sections, but their photochemical importance can be profound. We use photofragment translational spectroscopy (PTS) methods (and complementary *ab initio* theory) to explore πσ\*-state mediated bond fission processes following UV excitation of such heteroaromatic molecules in the gas phase, and ultrafast pump-probe studies to explore the same (and related) processes in a range of solvents. This talk will:

1. review insights gained from PTS studies of phenol and related molecules in the gas phase,
2. illustrate the extent to which such knowledge can aid interpretation of ultrafast pump-probe studies of the UV photofragmentation of similar molecules ((thio)phenols, ethers, *etc*) in solution,
3. show how such solution phase studies offer a route to exploring πσ\*-state mediated ring opening of heterocycles like furans and thiophenes.
4. outline possible related current and future research activities

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