PROTON TRANSFER AND INTERSYSTEM CROSSING IN 2-NITROPHENOL PROBED BY GAS-PHASE TRANSIENT ABSORPTION SPECTROSCOPY

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Recent work in both experiment and ab-initio theory indicates that intersystem crossing (ISC) can occur on ultrafast timescales in certain organic compounds, offering a relaxation channel competing with internal conversion. In particular, many nitroaromatic compounds are being investigated for this behavior. 2-nitrophenol (2NP) is one such system; after UV excitation the S1 state has both strong spin-orbit coupling to neighboring triplet states allowing for fast ISC and a low barrier to excited-state intramolecular proton transfer. Recent trajectory surface hopping calculations indicate that both of these relaxation channels occur on similar sub-picosecond timescales[b]. Both transient absorption spectroscopy (TAS) in solution and time-resolved photoelectron spectroscopy (TRPES) were used to probe the dynamics but the measured time constants were not consistent between methods which makes interpretation more difficult[c].

To further elucidate the dynamics in 2NP, we perform gas-phase TAS measurements using a newly-developed broadband cavity-enhanced ultrafast transient absorption spectrometer[d]. The spectrometer has a pump wavelength of 350 nm and a tunable probe from 450 to 700 nm with a demonstrated detection limit of $\Delta\text{OD} < 1 \times 10^{-9}/\sqrt{\text{Hz}}$. This technique serves as a complement to both solution-phase TAS and TRPES and provides additional information for comparison with theory. Using molecular beam techniques we are able to vary the sample vibrational/rotational temperature or change the solvent environment with clustering to observe the effects on 2NP relaxation dynamics. In this talk, we will discuss results from 2NP under various conditions and compare to previous experiments and theory.

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[c] H. A. Ernst et al., J. Phys. Chem. A 119, 9225 (2015)

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