JPUR
JOURNAL OF PURDUE
UNDERGRADUATE RESEARCH

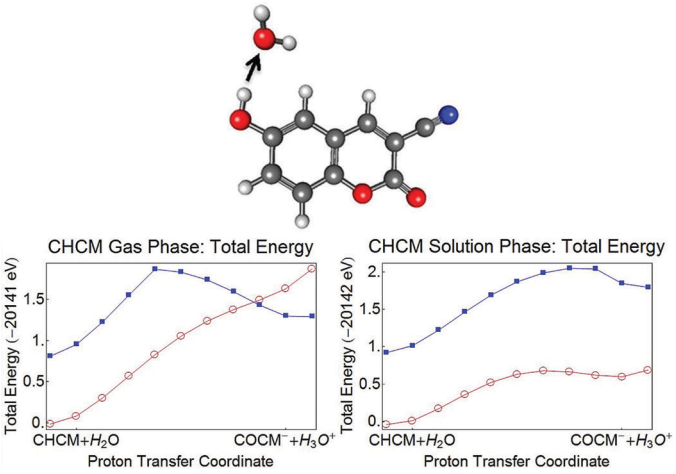
ENGINEERING/TECHNOLOGY

Ultrafast Radiationless Decay of 3-cyano-6-hydroxycoumarin Photoacid

Student researcher: SungMin Hong, Junior

Photoacids, molecules that become strong acids when electronically excited by a photon, provide a means to photocontrol the local acidity of the environment, which is used in photolithography, acid-base catalysis, and measuring drug activity. However, a search for the ideal photoacid is still ongoing. Apart from a significant decrease in pKa upon radiation, the photoacid should remain in the deprotonated state for a sufficiently long time. However, transient absorption spectra of the photoacid 3-cyano-6-hydroxycoumarin (CHCM) show that electronically excited molecules undergo rapid deexcitation by radiationless decay to the anionic ground state, which is a strong conjugate base. Electronic structure simulations can shed light on the mechanism of this undesired phenomenon. Interestingly, simulations of CHCM in the gas phase show that the bright, excited state and spectroscopically dark state cross during proton transfer to a water molecule, suggesting that the excited CHCM molecule may undergo intersystem crossing to the dark state and then undergo nonradiative relaxation to the ground state. However, in solution phase, simulations show no state crossing between the bright and dark states, eliminating a plausible route for nonradiative deexcitation in CHCM. Then we hypothesized that an elongated hydrogen vibration of a hydrogen-bonded water molecule may cause deexcitation of the anion. Indeed, preliminary calculations show a state crossing between the bright and dark states along this vibrational coordinate. This unrecognized mechanism might explain the short lifetime of the deprotonated excited state in CHCM and other related photoacids.

Research advisor Lyudmila Slipchenko says, "SungMin Hong investigated excited state proton transfer in CHCM photoacid using electronic structure calculations. He discovered an interesting alternative pathway of nonradiative relaxation of the electronically excited molecule via back-protonation. This mechanism might explain short lifetimes of excited states in CHCM and other potential photoacids."



The gas phase plot indicates state crossing between the bright (red) and dark (blue) electronic states in CHCM, whereas the solution phase plot does not show a crossing along the proton transfer pathway.

Hong, S. (2014). Ultrafast radiationless decay of 3-cyano-6-hydroxycoumarin photoacid. *Journal of Purdue Undergraduate Research, 4,* 77. http://dx.doi.org/10.5703/1288284315439