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## Elucidating the Interplay between Ultrafast Internal Conversion, Intersystem Crossing, and Proton Transfer for Guiding New Photochemical Reactivities

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The mechanism of newly discovered photochemical reactions of  $\beta$ -enaminones and maleimide derivatives is a topic of interest and ongoing discussion [1,2]. We have examined excited-state dynamics in these systems following femtosecond UV excitation by means of ultrafast transient absorption spectroscopy with dispersed, broadband probing, complemented by the tools of computational photochemistry.

Excited-state relaxation of the  $\beta$ -enaminones in protic and aprotic solvents has been found to be within the 500 fs range and involve a tautomerization process. A fast sub-50 fs molecular descent from the Franck-Condon region leads to a flatter portion of the  $S_1$  potential which region is defined by three degenerate potential energy surfaces forming a conical intersection and a singlet-triplet crossing.

For the substituted maleimides, the maleimide structure is modified by adding the hydroxy (-OH) functionality to introduce the possibility of excited-state intramolecular proton transfer (ESIPT). Maleimides where a proton source for ESIPT is not present were also studied. We have shown that, following UV excitation of these molecules into the weakly allowed  $\pi$  to  $\pi^*$  transition, they follow a major cascade-like ultrafast radiationless relaxation pathway via two lower-lying singlet  $\pi^*$  excited states into the ground  $S_0$  state. In addition, the hydroxy-substituted maleimide displays a minor pathway with spectral and kinetic signatures consistent with excited-state proton-transfer reaction [3]. The maleimide system lacking the hydroxyl substituent reveals an intersystem crossing channel. The dynamics in these systems is compared with excited-state dynamics of unsubstituted maleimide.

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[1] S. K. Kandappa, L. K. Valloli, S. Jockusch, J. Sivaguru, *J. Am. Chem. Soc.* **2021**, *143*, 3677.

[2] J. Parthiban, D. Garg, S. Ahuja, S. Jockusch, A. Ugrinov, J. Sivaguru, *ACS Catal.* **2024**, *14*, 8794.

[3] D. Garg, A. N. Tarnovsky, J. Sivaguru, *J. Phys. Chem. A* **2025** (accepted).

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