

Understanding photoresponse of molecules based on exploring non-adiabatic decay pathways: Application to the Knowles intramolecular hydroamination using photoredox catalyst

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○Abstract (250 words)

The Photoresponse of molecules can be understood by four processes, *i.e.* internal conversion, intersystem crossing, fluorescence, and phosphorescence. In the mechanistic analysis of photoreactions based on quantum chemical calculations, it is important to obtain the conical intersection (CI) and seam of crossing (SX) regions because non-radiative decays efficiently occur via these regions. We proposed systematic search methods for CI and SX geometries and analyzed various types of photofunctional molecules based on the system. Explorations of non-radiative decay paths were effective in the mechanistic analyses of molecular fluorescence, ultrafast decay processes of molecules, and photoreactions of metal complexes where both singlet and triplet states are related.

Recently, we investigated the mechanism of Knowles's light-promoted catalytic intramolecular hydroamination [1] using systematic reaction path exploration. The obtained reaction path network includes reaction paths via transition states and non-radiative decay paths through the SX between different electronic states. It was shown that the bond formation/cleavage competes with single electron transfer (SET) between the catalyst and substrate. The energetically favorable SET path by introducing a practical computational model representing SET as non-adiabatic transitions via SXs between substrate's potential energy surfaces [2] for different charge states adjusted based on the catalyst's redox potential. Calculations showed that the reduction and proton shuttle process proceeded concertedly. Also, the relative importance of SET paths varies depending on the catalyst's redox potential, affecting the yield [3].

[1] A. J. Musacchio, L. Q. Nguyen, G. H. Beard, and R. R. Knowles, *J. Am. Chem. Soc.* **136**, 12217 (2014).

[2] M. Hatanaka and K. Morokuma, *J. Chem. Theory Comput.* **10**, 4184 (2014).

[3] Y. Harabuchi, H. Hayashi, H. Takano, T. Mita, S. Maeda, *Angew. Chem. Int. Ed. Engl.*, in press (2022).