Time-resolved X-ray Spectroscopic Measurement and Optical Cavity Manipulation of Conical Intersections

Daeheum Cho[1], Bing Gu[2], and Shaul Mukamel[2]

[1] Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 41566, South Korea [2] Department of Chemistry, University of California, Irvine, California 92697-2025, United States

Conical intersection dynamics are of central interest for understanding the function and the relaxation mechanisms of photoexcited molecules in virtually all photochemical processes. Direct real-time measurement and characterization are essential to monitor conical intersections and their paths. In this talk, various time-resolved X-ray spectroscopic techniques, such as X-ray absorption, X-ray Raman, and X-ray circular dichroism, and X-ray diffraction technique will be discussed. The techniques employ hard X-ray narrowband/broadband probe fields to probe electronic coherences at the level crossing region via X-ray chromophore. The signal carries phase information of the valence-to-core electronic coupling in the vicinity of conical intersections.

Optical cavity manipulation of conical intersections will be discussed as a platform for manipulating the excited-state dynamics of molecules via strong light−matter coupling. We employ optical absorption and two-multidimensional electronic spectroscopy simulations to investigate the effect of optical cavity coupling in the nonadiabatic dynamics of photoexcited pyrazine. We observe the emergence of a novel polaritonic conical intersection between the electronic dark state and photonic surfaces as the cavity frequency is tuned. Moreover, the absorption spectrum and excited-state dynamics could be systematically manipulated by tuning the strong light−matter interaction.