

Nonadiabatic Dynamics Probed via Time-Resolved X-ray Spectroscopy

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Developments in ultrafast X-ray sources offer powerful new means of probing the complex nonadiabatic dynamics in photoexcited molecules. In particular, the electronic structures associated with conical intersections are predicted to have unique spectral signatures when probed using X-ray spectroscopies[1]. Using high level *ab initio* quantum dynamics simulations, we have simulated time-resolved X-ray spectroscopy (TRXAS and TRXPS) of a number of prototypical unsaturated organic chromophores (including ethylene, allene, and butadiene). The techniques are highly sensitive to all aspects of the ensuing dynamics and can distinguish between the different nuclear dynamical pathways that result in electronic relaxation. The ability of X-ray spectroscopies to provide a clear picture of the wavepacket dynamics near conical intersections is related to transient charge localization at specific atomic sites that is driven by the nuclear dynamics. Given the ubiquity of this type of charge localization in excited state dynamics, ultrafast X-ray spectroscopies offer a unique and powerful route to the direct observation of dynamics around conical intersections.

References

[1] S. P. Neville, M. Chergui, A. Stolow, M. S. Schuurman, *Phys. Rev. Lett.*, **120**, 243001, (2018).