# Gas-phase photochemistry studied by time-resolved photoelectron spectroscopy with free-electron lasers

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Time-resolved photoelectron spectroscopy (TRPES) is a powerful tool to study electronic de-excitation and chemical changes during photochemical reactions. However, when using visible or ultraviolet (UV) probe pulses, the observation window is often limited to low-binding-energy excited states near the Franck-Condon region. This limitation can be overcome when probing the reaction with extreme ultraviolet (XUV) pulses produced, e.g., from a free-electron laser (FEL) or a high harmonic generation (HHG) source. This allows for the entire reaction pathway to be probed, including any structural rearrangement or dissociation occurring on the electronic ground state. I will present two examples of XUV TRPES experiments performed at the FERMI FEL that take advantage of these capabilities: an investigation of the UV-(266-nm)-induced ring-opening reaction of the prototypical heterocyclic molecule thiophenone (C4H4OS)[1], and a study of the UV-(200-nm)-induced ring-reconfiguration of the quadricyclane-norbornadiene (C7H8) photo switch[2]. I will also compare the findings to results obtained for the same molecules with other ultrafast techniques to highlight the strengths and weaknesses of each method and the power of a multi-modal probing approach[3,4]. Finally, I will present results from a time-resolved inner-shell photoelectron spectroscopy experiment studying intramolecular charge transfer by taking advantage of the site-specificity of inner-shell photoemission.

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[1] S. Pathak, L.M. Ibele, B.F.E. Curchod, D. Rolles et al. "*Tracking the ultraviolet-induced photochemistry of thiophenone during and after ultrafast ring opening*", Nature Chemistry **12**, Nat. Chem. 12, 795-800 (2020).

[2] K. Borne, J. Cooper, D. Rolles et al. "*Ultrafast electronic relaxation pathways of the molecular photoswitch quadricyclane*", Nature Chemistry **16**, 499-505 (2024).

[3] J. P. Figueira Nunes, D. Rolles, B.F.E. Curchod et al. "*Monitoring the evolution of relative product populations at early times during a photochemical reaction*", J. Am. Chem. Soc. **146**, 4134 (2024).

[4] A. Green, K. Chen, R. Boll, D. Rolles et al. "*Visualizing the three-dimensional arrangement of hydrogen atoms in organic molecules by Coulomb explosion imaging*", submitted (2025).