

Probing Molecular Charge Transfer on Attosecond Timescales *Via* EUV and UV Spectroscopy

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Photoinduced charge transfer (CT) plays a pivotal role in numerous natural and engineered systems. Although ultrafast spectroscopy has significantly advanced in recent years, the fundamental details of the earliest moments of CT are still not fully understood. One of the key challenges lies in disentangling the intricate interplay between electronic and nuclear motions that unfolds almost instantly after optical excitation [1]. Unlocking these early-stage dynamics is essential, not only to deepen our understanding of CT in complex environments but also to drive progress optoelectronics, and molecular-scale electronics.

Ultrafast CT can be triggered using either attosecond extreme ultraviolet (EUV) pulses or few-cycle pulses in the ultraviolet (UV) range. EUV pulses induce photoionization, allowing direct observation of electron dynamics in molecular ions *via* attosecond methods. Conversely, UV excitation keeps the molecule in a neutral state and enables the exploration of the coupled evolution of electrons and nuclei. In this case, achieving femtosecond or even sub-femtosecond time resolution demands UV pulses lasting just a few optical cycles.

This work explores both of these complementary approaches. Using attosecond EUV-IR photoion spectroscopy, we track the intricate relationship between molecular structure and charge dynamics in a prototypical donor-acceptor system. Our analysis provides a coherent model to interpret the observed phenomena [2]. Rather than a smooth flow of charge from one region to another, the CT process begins with a rapid reconfiguration of electron density. This rearrangement exhibits oscillatory patterns that stem from structural changes within the molecule, highlighting the nontrivial nature of early-time charge transport.

In addition, we introduce a state-of-the-art beamline optimized for photoelectron spectroscopy, which integrates tunable UV pump pulses shorter than 3 fs and attosecond probe pulses. The ultrafast capabilities of this beamline have enabled precise investigations of electronic dynamics in selected molecular systems, which serve as benchmarks for studying phenomena such as nonadiabatic transitions, rapid internal conversion, and vibronic interactions. This level of resolution opens new windows into the ultrafast realm, allowing researchers to observe and characterize the evolution of electronic states and their coupling to nuclear motion with unprecedented clarity.

References

- [1] M Nisoli, P Decleva, F Calegari, A Palacios and F Martín, *Chem. Rev.* **117**, 10760 (2017)
- [2] F Vismarra, F Fernández-Villoria, D Mocci, *et al.*, *Nature Chem.* **16**, 2017 (2024)