

Initiating and probing molecular modes of charge migration

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Abstract: We discuss recent theoretical progress in understanding charge migration (CM), addressing experimentally relevant questions such as: Does the manner in which CM is initiated influence how it proceeds, and does CM manifest in generic ways allowing its time-frequency characteristics to be predicted by simple rules?

Summary: Charge migration (CM) refers to the rapid movement of a positively charged hole in a molecule following localized ionization or excitation, and typically takes place on the attosecond or few-femtosecond time scale [1,2]. We present theoretical calculations that focus on questions relevant to successful CM experiments, such as which molecules best support CM, and to what extent the dynamics of CM are influenced by how it is initiated.

To address these questions, we use two strategies. First, we use time-dependent density functional theory (TDDFT) to simulate CM in halogenated hydrocarbon chains, which have been shown to support the creation of a localized hole either via strong-field or inner-shell ionization [3]. By isolating the low frequency modes we find that the double and triple-bonded molecules all support robust end-to-end CM that progresses via hopping from π bond to π bond. This occurs with a speed that is largely independent of the molecular length, but that is lower for the triple- than for the double-bonded chains. We also find that heavier halogen atoms support CM in which the hole is more localized as it moves along the molecular backbone. Second, we discuss a new way of understanding CM, using tools of non-linear dynamics to study CM in one-dimensional carbon chains [4]. In doing so, we highlight the central role of dynamical electron-electron coupling and synchronization as the engine

for CM dynamics and as an alternative to, e.g., few-orbital beating mechanisms that have previously been discussed. We also demonstrate the importance of functionalization and hybridization in synchronizing the dynamics, which would open the way for chemically controlling CM in the future. Finally, we discuss the prospect of probing CM in bromobutadiyne using high-harmonic spectroscopy calculated using TDDFT.

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References

- [1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.* **307**, 205 (1999)
- [2] F. Calegari et al., *Science* **346**, 336 (2014).
- [3] A. Folorunso *et al.*, *Phys. Rev. Lett.*, to appear (2021).
- [4] F. Mauger *et al.*, in preparation (2021).