

## Excited-state dynamics of organic radical ions: a long story

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Over the past years, the excited-state properties of organic radical ions have been attracting considerable attention in a broad range of area, including astrochemistry and multiphoton redox catalysis. On our side, we were initially interested in determining their possible involvement in highly exergonic photo-induced electron transfer reactions. We will show that excited radical ions are generally extremely short lived,<sup>1-3</sup> which complicates their detection and the exploitation of their high reactivity.

However, a few radical anions have been found to have a relatively long excited-state lifetime. We have been trying to understand the origin of these differences and recently obtained encouraging results pointing structural flexibility as an important parameter.

Finally, excited organic radical ions are being increasingly used in photoredox catalysis, for example using the consecutive photo-induced electron transfer (conPET) approach. We will show that this conPET mechanism, as originally proposed,<sup>4</sup> is highly inefficient to due fundamental aspects of electron-transfer reactions. Possible ways to circumvent these limitations will be discussed.

- 1) J.-C. Gomy, E. Vauthey, *J. Phys. Chem. A* **1997**, *101*, 8575-8580.
- 2) J. Grilj, E. N. Laricheva, M. Olivucci, E. Vauthey, *Angew. Chem. Int. Ed.* **2011**, *50*, 4496-4498.
- 3) J. S. Beckwith, A. Aster, E. Vauthey, *Phys. Chem. Chem. Phys.* **2022**, *24*, 568-577.
- 4) I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725-728.