

## Excited-State Dynamics of Radical Ions

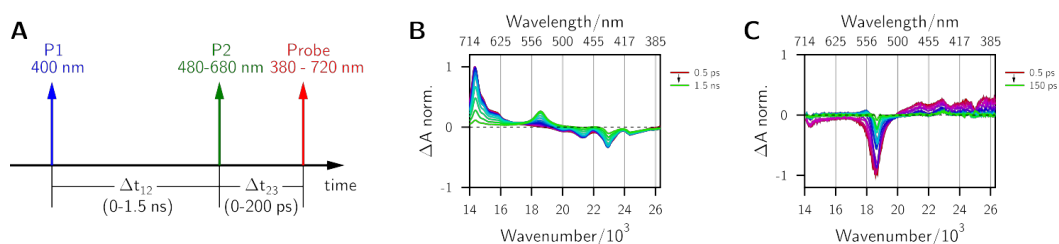
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Excited radical ions states are relevant to many important photoinduced processes, such as enzyme-catalysed reactions[1], photosynthesis[2] and indeed all electron-transfer reactions. Despite their importance in these reactions, their excited-state dynamics in solution are little studied.

In previous studies, rapid decays of the radical excited states have often been observed. These do not appear to correlate with the energy gap - for example, the roughly 2.0 eV energy gaps of the 1,4-benzoquinone radical anion and the Wurster's Blue cation were found to have lifetimes at room temperature of "at least" 63 ns[3] and roughly 200 fs[4] respectively. The short lifetimes are instead ascribed to conical intersections or photochemical reactions that can occur on very rapid timescales.[4]

As such, questions arise about the excited-state dynamics of radical ions. How prevalent are conical intersections? Do the molecular structure and the solvent have clear systematic effects? In order to answer these questions, Pump-Pump-Probe (PPP) Spectroscopy[5] (Figure A) has been used.



This is a technique where a pump first triggers a photochemical or photophysical process - an example is shown in Figure B of a transient absorption experiment in which perylene is quenched by an electron acceptor to form the perylene cation (new band at ~540 nm). Another pump pulse, tuned to the band of interest (in this case the band at 540 nm) is then used at a given delay after the first in order to achieve transient absorption measurement on the new species. In this way, anions and cations can be generated by photoinduced electron transfer and then their excited dynamics studied. An example of this PPP spectroscopy is shown above in Figure C, where the perylene cation prepared by photochemical reaction is studied.

Here, we will present results on organic radical ions studied by PPP spectroscopy. The advantages and disadvantages of the technique will be discussed, as will the excited-state dynamics of the radicals and their implications to natural and industrial processes.

[1] W. Buckel, *Angew. Chem. Int. Ed.*, 2009, **48**, 6779–6787.

[2] W. Lubitz, F. Lendzian and R. Bittl, *Acc. Chem. Res.*, **2002**, 35, 313–320.

[3] A. R. Cook, L. A. Curtiss and J. R. Miller, *J. Am. Chem. Soc.*, **1997**, 119, 5729–5734.

[4] J. Grilj, E. N. Laricheva, M. Olivucci and E. Vauthey, *Angew. Chem. Int. Ed.*, **2011**, 50, 4496–4498.

[5] S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, **2006**, 110, 7547–7553.