

Ultrafast Charge Separation and Vibrational Control of Photochemical Dynamics: An insight from Time-Resolved Infrared and 2D-IR spectroscopies

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One of the major challenges in the field of photoinduced charge separation - a fundamental process which lies at the heart of reactions in natural and artificial systems powered by the energy of light – is how to control reaction pathways, and direct reactivity “at will”.

Nuclear-electronic (vibronic) coupling is of particular interest in this regard since the Born-Oppenheimer approximation is not valid on the ultrafast timescales intrinsic to photoprocesses. Perturbing vibronic coupling may thus offer a way to affect photochemical reactions.[1-2] Such perturbation can be achieved by introducing a narrow-band IR pulse after initial population of an excited state to selectively affect vibration(s) that are coupled to electron transfer processes; the overall sequence of ultrafast pulses used is {UV pump - narrowband IR pump - broadband IR probe}.

The first part of the talk will discuss the methods of time-resolved IR and 2D-IR spectroscopies.

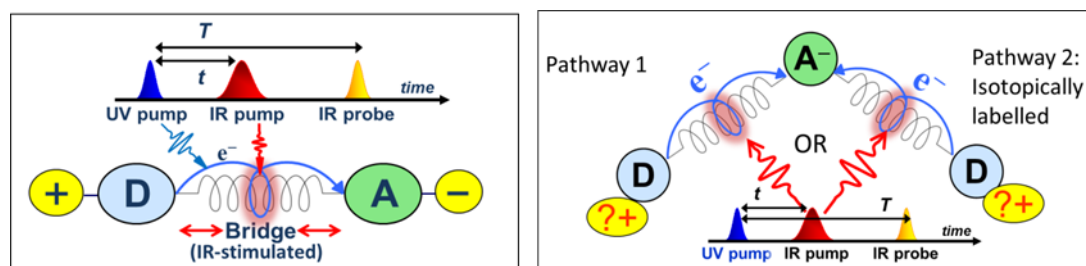


Fig 1. Modulation of electron transfer in a linear D-B-A system (Left), and in a “fork” system which has two electronically identical, but vibrationally distinct pathways.

The second part of the talk will focus on our recent work on IR-perturbation of photoinduced charge separation in transition metal Donor-Bridge-Acceptor complexes, especially those based on Pt(II) light-absorbing complexes.

In the first type of systems, D-B-A, (Fig. 1, left), selective excitation of bridge-localised vibrational modes in the excited state was shown to change the yield of the product states, up to 100%.[3-4] In the second, fork-type, system D-B-A-B-D (Fig. 1, right), which have competing electron transfer pathways differing only by ¹³C-isotopic labelling of one bridge, selective IR-excitation of either bridge affects the yield of charge-separation along both ‘arms’.[5] This effect potentially offers the means to direct electron flow along a pre-selected reaction pathway. The suggested mechanisms and potential applications of the fundamental effects observed will be discussed in the broad context of the field.

References

1. Lin, Z. et al, *J.Am.Chem.Soc.*, **2009**, 18060; 2. Yue, Y. et al, *Dalton Trans.*, **2015**, 8609.
3. Delor, M. et al, *Science*, **2014**, 346, 1492; 4. Delor, M. et al, *Nature Chem.*, **2015**, 7, 689.
5. Delor, M. et al, *Nature Chem.*, **2017**, 9, 1099.