Swiss Photochemistry Symposium 2022 June 17, 2022

Towards IR-control of Ultrafast Charge Transfer in Donor-Bridge-Acceptor Complexes

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One of the fascinating challenges in photochemistry 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 photo-processes. 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 the initial population of an excited state to selectively affect vibration(s) that are coupled to electron transfer processes. To achieve this, we use a 3-pulse sequence {UV_{pump}-“narrow”IR_{pump}-IR_{probe}}, thereafter called “IR-control”.

Our work on “IR-control“ of electron transfer explores Pt(II) complexes as chromophores and/or bridges in the Donor-Bridge-Acceptor (DBA) systems. If the excited state relaxation occurs *via* a branching excited state, it becomes possible for a selective excitation of bridge vibrations to drastically change the yield of the product states, of up to 100%.[3,4] Further, rather intriguingly, we disocovered that the mechanism of IR-control might be different in a linear system (Fig 1, left) and a „molecular fork“ system (Fig 1, right).

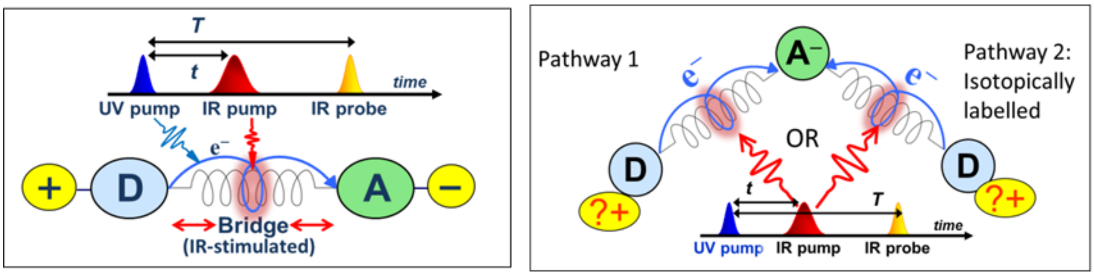

Fig 1. Modulation of electron transfer in a linear D-B-A system (Left), and in a “fork” system.

We now seek to understand the mechanism of the effect, what are the roles of high- and low-frequency modes? How does strong- vs. weak coupling regimes affect the outcome of IR-control?
To answer these questions, the dynamics of several new series of DBA-systems has been characterised by ultrafast transient absorption, time-resolved IR, 2DIR, and fluorescence upconversion[6] spectroscopies, and the IR-control studies undertaken. The results of these studies will be discussed.

Overall,“IR-control” potentially offers the means to direct charge flow along a selected reaction pathway, thus changing the outcome of light-driven reactions.

We thank the EPSRC (research grants and funding for the Lord Porter Laser Laboratory at Sheffield), the STFC, the Newton Foundation, the UK XFEL hub, and the CSC for support.

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