ULTRA Laser Facility Applications for Chemistry, Life Sciences and Catalysis

Igor V. Sazanovich[1], Gregory M. Greetham[1], Ian P. Clark[1], Inés Lezcano-González[2,3], Andrew M. Beale[2,3], Milan Delor[4], Julia A. Weinstein[4], James P. Hall[5,6], Susan J. Quinn[7], Pavel Matousek[1], Anthony W. Parker[1], Michael Towrie[1]

[1]Central Laser Facility, STFC, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire, OX11 0QX, UK. [2]Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire, OX11 0FA, UK. [3]Chemistry Department, University College London, Gordon Street, London, WC1H 0AJ, UK. [4]Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK. [5]Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK. [6]Diamond Light Source, Harwell Campus, Oxfordshire, OX11 0QX, UK. [7]School of Chemistry, University College Dublin, Dublin 4, Ireland

Abstract: We describe ULTRA laser facility applications for chemistry, life sciences and catalysis, illustrated by vibrational control of electron transfer; photoinduced electron transfer in DNA crystals; and *operando* Kerr-gated Raman insight into catalytic hydrocarbon conversion with zeolites.

1. Introduction

The Central Laser Facility ULTRA facility is based at the Rutherford Appleton Laboratory (Oxfordshire, UK) in a unique multidisciplinary environment. The ULTRA facility is a state-of-the-art instrument designed to perform diverse ultrafast time-resolved laser spectroscopy experiments in the broad spectral range from UV to mid-IR [1,2]. Here we describe how we employed ULTRA to achieve vibrational control of light-induced charge transfer in donor–bridge–acceptor assemblies, and to define both the geometry of the reaction site and the rates of individual steps in a reversible photoinduced electron-transfer between ruthenium polypyridyl and DNA in the crystal environment. We also demonstrate how we shed a new light on the problem of zeolite deactivation by operando Kerr gated Raman monitoring of a catalytic reaction.

2. Vibrational control of electron transfer

Photoinduced electron transfer (ET) is a fundamental process enabling some of Nature's most important reactions, e.g. photosynthesis, and is instrumental for photovoltaics operation. Therefore it is highly desirable to develop the means to steer electron transfer to alter the outcome of the reaction and the overall yield.

In this work we demonstrate how we can steer the electron transfer with low-energy infrared photons by selective mid-IR excitation of the bridge in a range of Acceptor-Donor transition metal complexes linked by a acetylide bridge [3,4]. The systems studied and the schematics of the experiment are shown in Fig. 1. To initiate the electron transfer we excited the systems with the 50 fs laser pulse at 400 nm, and then a few picoseconds later, while the system is still "at the crossroads" in the non-equilibrium vibronic state, we perturb the system with narrow-band 2 ps mid-IR pulse at ca. 1900 cm^{-1}.

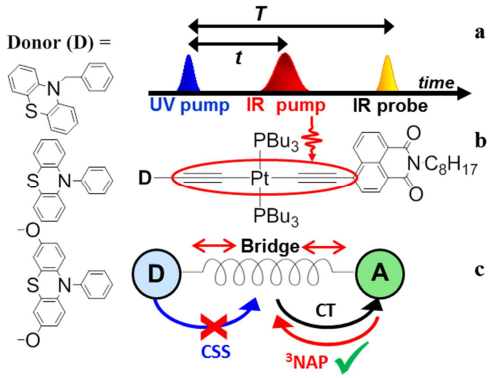

Fig. 1. The structure of the Donor-Acceptor systems studied (left and middle), the pulse sequence used in the experiments (top right), and the effect on the excited state.

We managed to suppress the formation of the distant charge-separated state; the size of the effect depends on the donor type used (Fig. 1) and can reach 100%. The excited molecules are re-directed instead towards populating intra-ligand triplet state and re-forming the ground state.

3. One-electron guanine photo-oxidation in DNA crystals

Photoinduced DNA damage is an important reaction leading to light-induced diseases (including skin cancer) but also instrumental for photodynamic therapy of cancer when photosensitiser drugs are used. The majority of the studies in this area have been done in solution, however in solution phase it is very difficult to define the precise location and orientation of the photosensitiser vs. DNA bases. Furthermore, it is impossible to achieve in solution phase the high drug concentration and molecularly crowded environment that drugs encounter in the cell.

To address those questions we performed the first ever ultrafast time-resolved laser spectroscopy study of photosensitised DNA oxidation in the crystal phase. We used ruthenium polypyridyl photosensitiser Λ-$[Ru(TAP)2(dppz)]^{2+}$ bound to $(TCGGCGCCGA)_2$ sequence of nucleic bases (Fig. 2), for which the structure and orientation of all counterparts in the crystal samples have been precisely established [5]. To overcome the strong scattering due to the micro crystals (up to 5 μm is size) the experiments were performed in the mid-IR while exciting samples at 400 nm.

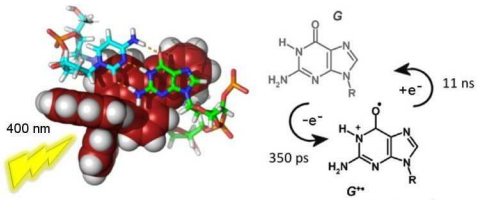

Fig. 2. The diagram of the ruthenium polypyridyl complex binding to the DNA sequence, and the forward/reverse electron transfer to guanine.

In the transient infrared data we observed formation of guanine radical cation evidenced by 1709 cm^{-1} band which decays concomitantly with the decay of the excited state signal (major feature at 1456 cm^{-1}) and ground state recovery (1275 cm^{-1} band) of Λ-$[Ru(TAP)2(dppz)]^{2+}$. The experiments revealed the individual steps in the photoinduced reversible electron transfer reaction in DNA crystals, indicating that the dynamics observed in the crystal state are similar to those in solution [6].

4. *Operando* Kerr-gated Raman monitoring of hydrocarbon conversion on zeolites

Zeolites are widely used as catalysts in the chemical industry for large-scale hydrocarbon conversion processes such as catalytic cracking, reforming or methanol-to-hydrocarbons. A major issue with these technologies is the progressive deactivation of the catalyst by the formation of carbon deposits, leading to a decline in process efficiency. To optimise catalyst performance, it is then required to understand the structure, formation mechanism and deactivating role of carbon deposits [7].

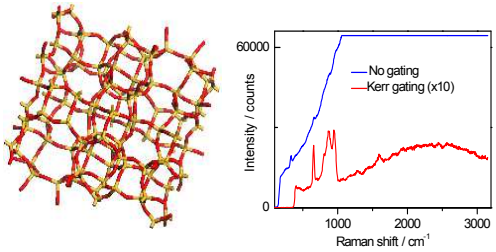

Fig. 3. ZSM-5 zeolite structure (left) and illustration of the power of Kerr gating to detect the Raman signal of Mo-ZSM-5 zeolite (right).

Raman spectroscopy is a powerful technique for characterising carbon species. However, its application to zeolite catalysts is often limited by strong sample fluorescence that dominates the Raman signal. In this work, we have followed the catalysis with Raman spectroscopy using ULTRA as a bright visible excitation source in combination with a Kerr-gated spectrometer to 'circumvent' fluorescence, in order to examine the evolution of carbon species in two relevant zeolite-based processes, i.e. methane dehydroaromatisation (MDA) and methanol-to-hydrocarbons (MTH). The results obtained have allowed us to identify the formation of graphitic carbon (Raman signatures at 1390 cm^{-1} and 1610 cm^{-1}) after the MDA reaction, as well as catalytically important carbon-containing species (aromatic/aliphatic) during the course of the MTH.

5. References

[1] G.M. Greetham, et. al., "ULTRA: A Unique Instrument for Time-Resolved Spectroscopy," Appl. Spectrosc., **64**, 1311-1319 (2010).

[2] G.M. Greetham, et. al., "A 100 kHz Time-Resolved Multiple-Probe Femtosecond to Second Infrared Absorption Spectrometer," Appl. Spectrosc., **70**, 645-653 (2016).

[3] M. Delor, et. al., "Toward control of electron transfer in donor-acceptor molecules by bond-specific infrared excitation," Science, **346**, 1492-1495 (2014).

[4] M. Delor, et. al., "On the mechanism of vibrational control of light-induced charge transfer in donor–bridge–acceptor assemblies," Nature Chem., **7**, 689-695 (2015).

[5] J. P. Hall, et al., "Structure determination of an intercalating ruthenium dipyridophenazine complex which kinks DNA by semiintercalation of a tetraazaphenanthrene ligand," Proc. Natl Acad. Sci. USA, **108**, 17610–17614 (2011).

[6] J.P. Hall, et. al., "Monitoring one-electron photo-oxidation of guanine in DNA crystals using ultrafast infrared spectroscopy," Nature Chem., **7**, 961-967 (2015).

[7] M. Guisnet, et al. "Prevention of zeolite deactivation by coking," J. Molec. Catal. A, **305**, 69-83 (2009).