

Project title: **Unravelling enzymatic hydrogen production mechanisms with ultrafast 2D-IR spectroscopy**

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Project Description:

The hydrogenases are families of metalloenzymes that efficiently catalyse the reversible cleavage of H₂ into protons and electrons and so offer ideal prototype catalysts for sustainable energy generation involving H₂. Before we can develop technological materials based upon the hydrogenases however, a detailed understanding of the mechanism of H₂ production and usage is required. This multidisciplinary project will combine ultrafast 2D-IR spectroscopy (Hunt) with electrochemical and biochemical methods (Parkin) to understand structural changes and the role of dynamic processes in the action of these important enzymes.

2D-IR is a new ultrafast laser spectroscopy method that spreads the IR spectrum of a molecule over a second frequency axis [1]. This multidimensionality allows access to a wealth of new spectral information but the most powerful aspect of 2D-IR is the ability to determine molecular structure and changes in that structure with a time resolution of 100 fs (10⁻¹³ s). This opens up the possibility of observing reaction steps, solvent motion or H-bond vibrations that are central to the hydrogenase mechanism in real time. This is highly complementary to the insight into ultrafast electron movement in hydrogenases which can have been obtained in the Parkin group using Fourier transform large amplitude alternating current voltammetry [2].

Although synthetic models of the hydrogenases have been studied with 2D-IR [3,4], this collaboration offers the unique opportunity to compare these results with the full enzyme systems for the first time. By studying a range of site mutations and using electrochemical methods to prepare catalytic intermediates we will use 2D-IR to understand the way in which the protein scaffold interacts with the active site to influence or control the enzyme mechanism. This is a particularly important issue since biomimetic model compounds lacking the protein scaffold show very low catalytic efficiency, emphasising its importance [4], but the precise molecular function that it plays in the enzyme cycle is unknown.

The project will suit students with a background in physical or biological chemistry, molecular physics or similar with an interest in spectroscopy and an enthusiasm for multidisciplinary research.

- (1) Hunt, N. T. *Chem Soc Rev* 2009, 38, 1837.
- (2) Adamson, H.; Robinson, M.; Wright, J. J.; Flanagan, L. A.; Walton, J.; Elton, D.; Gavaghan, D. J.; Bond, A. M.; Roessler, M. M.; Parkin, A. *Journal of the American Chemical Society* 2017, 139, 10677.
- (3) Fritzsche, R.; Brady, O.; Adair, E.; Wright, J. A.; Pickett, C. J.; Hunt, N. T. *Journal of Physical Chemistry Letters* 2016, 7, 2838.
- (4) Frederix, P. W. J. M.; Adamczyk, K.; Wright, J. A.; Tuttle, T.; Ulijn, R. V.; Pickett, C. J.; Hunt, N. T. *Organometallics* 2014, 33, 5888.

Training:

All research students follow our innovative Doctoral Training in Chemistry (iDTC): cohort-based training to support the development of scientific, transferable and employability skills. All research students take the core training package which provides both a grounding in the skills required for their research, and transferable skills to enhance employability opportunities following graduation. Core training is progressive and takes place at appropriate points throughout a student's higher degree programme, with the majority of training taking place in Year 1. In conjunction with the Core training, students, in consultation with their supervisor(s), select training related to the area of their research.

The project will feature technical training in the two underpinning disciplines of ultrafast spectroscopy and metalloenzyme electrochemistry. Upon completion of the project the successful student will be able to i) produce and characterise hydrogenase enzymes in a range of catalytically-important redox states and ii) apply infrared and 2D-IR spectroscopy to understand their structure and active site dynamics. The project will therefore feature the close involvement of both supervisors in a fully multidisciplinary project.

Equality and Diversity:

The Department of Chemistry holds an Athena SWAN Gold Award and is committed to supporting equality and diversity for all staff and students. The Department strives to provide a working environment which allows all staff and students to contribute fully, to flourish, and to excel. Chemistry at York was the first academic department in the UK to receive the Athena SWAN Gold award, first attained in 2007 and then renewed in October 2010 and in April 2015. This PhD project is available to study full-time or part-time (50%).

Funding:

Value: Studentships are fully funded either by the EPSRC or a Department of Chemistry Teaching Studentship, and cover: (i) a tax-free annual stipend at the standard Research Council rate (£14,553 for 2017-18), (ii) tuition fees at the UK/EU rate.

Eligibility: EPSRC studentships are available to UK and EU students who meet the UK residency requirements. Students from EU countries who do not meet the residency requirements may still be eligible for a fees-only award. Chemistry Teaching Studentships are available to any student who is eligible to pay tuition fees at the home rate.

Further information about eligibility for Research Council UK funding can be found at the following website: <http://www.bsrc.ac.uk/documents/studentship-eligibility-pdf/>

Candidate selection process:

- Applicants should submit an application for a PhD in Chemistry by **17:00 on Wednesday 28 March 2018**
- Supervisors will interview their preferred candidates either by email, telephone, web-chat or in person
- Supervisors may nominate up to two candidates to the assessment panel
- Nominated candidates will be invited to a panel interview at the University of York in mid April (date TBC)
- The Chemistry Graduate Awards Panel will award studentships following the panel interviews
- Candidates will be notified of the outcome of the panel's decision by email

For more information contact chemgrad@york.ac.uk or see our web page: <http://www.york.ac.uk/chemistry/postgraduate/>