

# Dynamics and spectroscopy

## Dynamics of chemical and photochemical reactions in solution

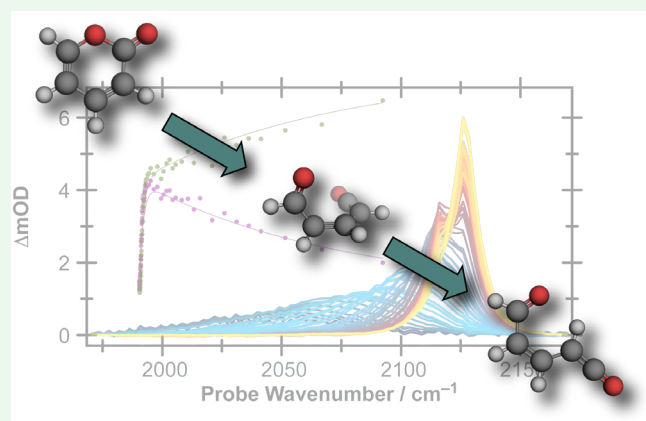
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The solvent environment plays a crucial role in many synthetic, biological, and photochemical processes, through its influence over the thermodynamic properties of the reaction. Favourable solvation of reaction intermediates can accelerate reaction rates by reducing the heights of energy barriers along reaction pathways, thereby promoting certain chemical outcomes at the expense of others.

Our research seeks to better understand this influence at the molecular level in both unimolecular and bimolecular reactions. The various relaxation and reaction pathways (including bond-breaking and bond-forming events, interaction of reactive species with the solvent, and dissipation of energy) exhibited by photoexcited molecules are probed by transient absorption spectroscopy, which allows the populations of reactants, intermediates, and products to be followed on femtosecond to picosecond timescales. By comparing the dynamics exhibited by reactions in the gas and solution phases, evidence is obtained for the influence exerted by the solvent on chemical mechanisms.

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UV laser pulses induce ring-opening in cyclic organic molecules

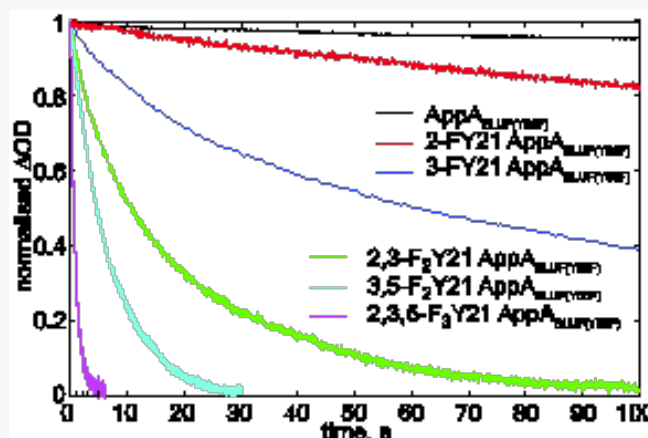
## Femtoseconds to seconds transient IR study of BLUF domain function utilizing unnatural amino acid substitution

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The BLUF (Blue Light Using Flavin) domain of the AppA photosensor was studied from femtoseconds to minutes. The key Y21 residue was probed by exchanging tyrosine for fluorotyrosines. The fast photochemical kinetics were only slightly perturbed, suggesting a weak dependence on Y21 pK<sub>a</sub> and redox potential. The recovery kinetics were, however, altered by factors of >3000, indicating a role for proton transfer in the activated complex.

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Dependence of the slow recovery kinetics for different fluorotyrosines

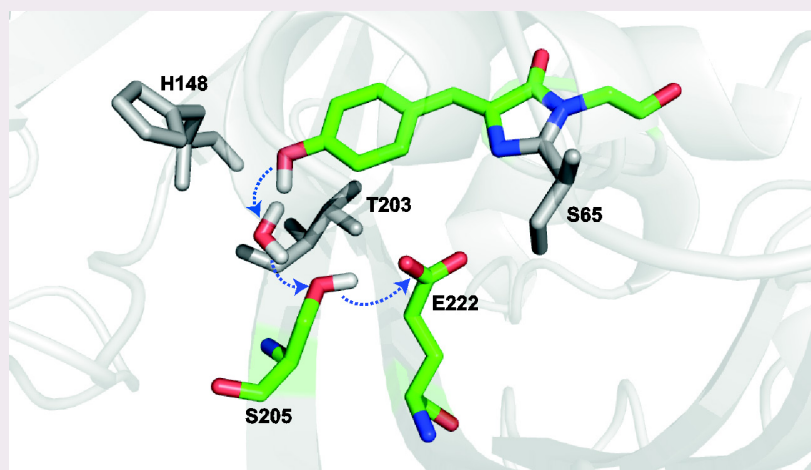
## Resolution of the complete proton relay cycle in the green fluorescent protein with femtosecond to microsecond transient infra-red

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The time-resolved multiple probe spectroscopy (TRMPS) method was used to measure the complete femtosecond to 100 nanosecond proton transfer cycle in the green fluorescent protein. Mutagenesis was used to alter the structure of the proton wire and to probe the effect on the dynamics.

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The structure and pathway of proton motion in the GFP proton wire

## Time-resolved studies of guanine photo-oxidation by a DNA-bound Ru(II) complex in solution and crystal states

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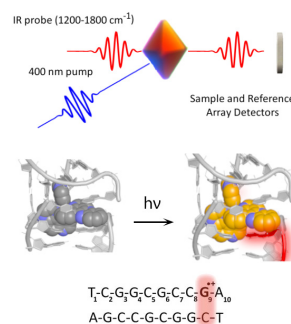
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Photo-sensitised oxidation of guanine is an important route to DNA damage, with possible applications in phototherapeutics. Such photodamage often occurs via one-electron photo-oxidation of guanine. In solution, an understanding of the process requires reliable knowledge of where and how the sensitizer is bound in DNA, a non-trivial matter due to the array of binding sites in a typical sequence. We have overcome this by performing ultrafast time-resolved infrared (TRIR) spectroscopy on photo-excited crystals of photosensitisers bound to DNA, whose structure has been determined by x-ray crystallography.

This pioneering approach has been used to determine the forward ( $1/500 \text{ ps}^{-1}$ ) and reverse ( $1/10 \text{ ns}^{-1}$ ) rate of photo-induced electron transfer for a reaction site whose molecular environment has been defined to 1.2 Å resolution.

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It also leads us to propose a specific guanine site of oxidation, and reveals similarities between the dynamics in the crystal state and the solvent medium.



Experimental overview: Visible excitation and TRIR probing of crystals of  $\Lambda$ -[Ru(TAP)<sub>2</sub>(dppz)]<sup>2+</sup> bound to {TCGGCGCCGA}<sub>2</sub> leading to identification of the site of photo-induced guanine oxidation.

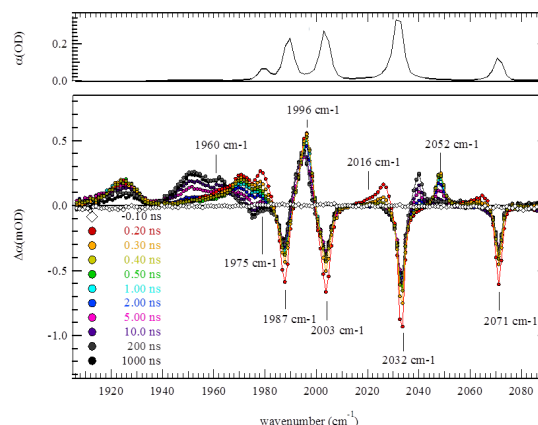
## Observing the photochemistry of [FeFe]-hydrogenase sub-site analogues from femtosecond to milliseconds

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J.A. Wright, C.J. Pickett (School of Chemistry, University of East Anglia, Norwich, UK)

G.M. Greetham, P.M. Donaldson, M. Towrie, A.W. Parker (CLF, STFC Rutherford Appleton Laboratory, Didcot, UK)

The LIFETIME spectrometer has been used to study the photochemistry and dynamics of synthetic compounds that structurally mimic the active site of [FeFe]-hydrogenase enzymes. Experiments aimed at understanding the effect of ultraviolet excitation of these species on femtosecond to picosecond timescales has shown that the dominant photochemical process is carbonyl ligand photodissociation to create a coordinatively unsaturated Fe-centre.

Here, the extended temporal range offered by the time-resolved multiple probe spectroscopy (TRMPS) methodology is exploited to extend our investigations to include the diffusive phenomena occurring on nanosecond to microsecond timescales following excitation, which could be key to hydrogen-generation by these species.



Time resolved infrared spectra of  $(\mu\text{-S}(\text{CH}_2)_3\text{S})\text{Fe}_2(\text{CO})_6$  in heptane solution, obtained using the LIFETIME spectrometer operating in TRMPS mode.

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## UV laser spectroscopy of mass-selected ionic liquid building blocks in the gas-phase

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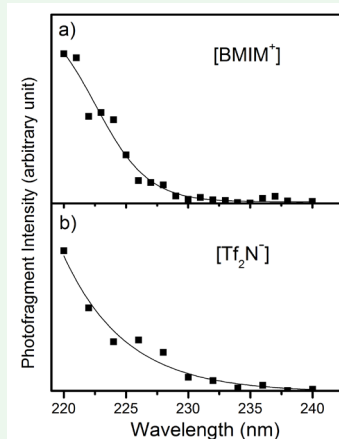
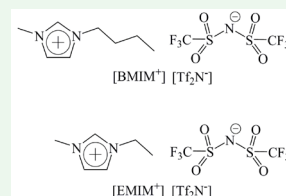
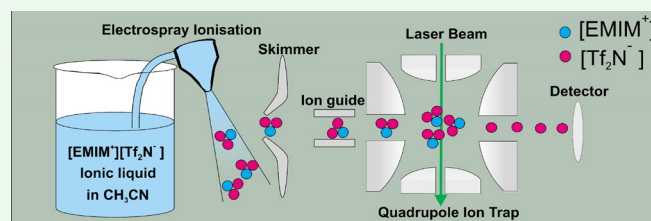
This work reports the application of laser photodissociation spectroscopy to study the electronic spectra of aggregate clusters of the components of ionic liquids in the gas-phase. These spectra have been recorded in a custom-adapted commercial mass spectrometer, which incorporates a laser interface. The ionic liquid aggregates are introduced to the gas-phase by electrospray ionization. The spectra obtained are the first UV laser action spectra of mass-selected gas-phase ionic liquid aggregates, i.e.  $[\text{BMIM}^+]_n[\text{Tf}_2\text{N}^-]_m$  and  $[\text{EMIM}^+]_n[\text{Tf}_2\text{N}^-]_m$  where  $n \neq m$  and  $n, m = 1, 2$ . Each aggregate cluster displays a spectral maximum absorption at 220 nm, the high energy limit scanned. However, the anionic and cationic aggregate photofragmentation cross-sections are notably different, indicating distinctive decay mechanisms.

Our spectra compare well to spectra of gas-phase ionic liquids obtained by other methods, indicating the utility of our technique as a facile route to obtaining gas-phase electronic spectra of isolated ionic liquids.

Top: Schematic representation of the experiment, illustrating production of ionic liquid aggregates by electrospray, and laser photodissociation spectroscopy within an ion trap.

Left: Structures of the (top)  $[\text{BMIM}^+][\text{Tf}_2\text{N}^-]$ , and (bottom)  $[\text{EMIM}^+][\text{Tf}_2\text{N}^-]$  ionic liquids.

Right: Cluster laser photofragment action spectra of a)  $[\text{BMIM}^+]$  from the  $[\text{BMIM}^+]_2[\text{Tf}_2\text{N}^-]$  cationic aggregate, and b)  $[\text{Tf}_2\text{N}^-]$  from the  $[\text{BMIM}^+]_2[\text{Tf}_2\text{N}^-]_2$  anionic aggregate.



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## Peroxy radical photolysis in the near UV

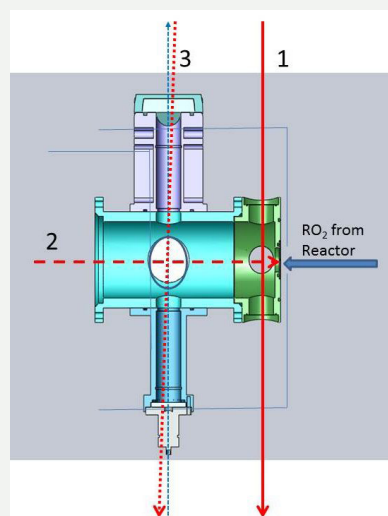
M.A. Blitz, T. Ingham (School of Chemistry, University of Leeds, UK)

The hydroxyl radical (OH) is the most important species in atmospheric chemistry as it is the primary reagent for initiating reactions. However, in pristine, forested environments (low ozone and low NO<sub>x</sub>) the predicted OH concentration can be too low by up to an order of magnitude. A potential source of this missing OH is from the photolysis of peroxy radicals, which are much less reactive than OH and are present in much higher concentrations.

To test this hypothesis, the NSL2 laser was used to photolyse peroxy radicals (RO<sub>2</sub>) in the near UV (300 – 350 nm). The peroxy radicals were flowed into a low-pressure cell, especially designed to measure the OH radical with great sensitivity via fluorescence.

OH was detected from the photolysis of peroxy radicals found in forested environments. The observed efficiency of OH generation in the near UV suggests this is a significant additional source of atmospheric OH.

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A solid model drawing of the photolysis cell. RO<sub>2</sub> radicals flow through the pinhole and are photolysed in the near UV with the NSL2 laser system using three geometries (in red), before OH is detected via the second laser (blue).

## Ultrafast transient absorption spectroscopy of size-controlled colloidal nanocrystals for hydrogen generation with an inverse conical taper

F. Jäeckel (Dept of Physics, University of Liverpool, UK)

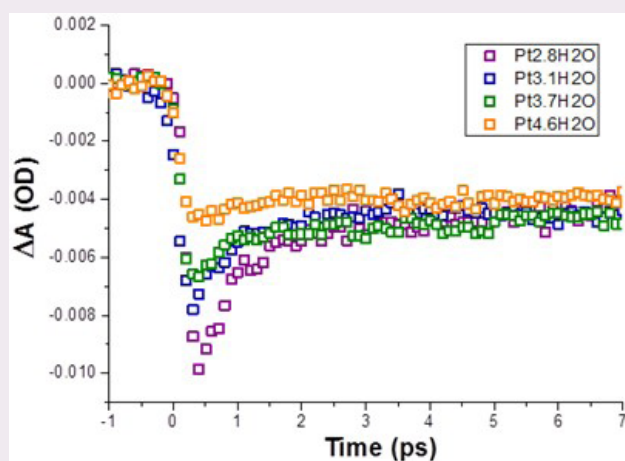
W. Li (The University of Liverpool, UK; Chemical Engineering and Applied Chemistry, Aston University, Birmingham, UK)

Solar hydrogen is currently receiving considerable attention as a potential component of a green and sustainable future energy mix. Catalyst-decorated colloidal semiconductor nanocrystals are studied as a potentially inexpensive, scalable means for photocatalytic hydrogen generation, offering wide control over their optical and electronic properties.

We have recently shown that size-controlled quantum confinement in Pt-decorated CdS nanospheres can be used to control the internal quantum efficiencies for hydrogen generation, i.e. smaller nanocrystals show higher efficiencies [1].

Here, we use ultrafast transient absorption spectroscopy to address the underlying mechanism in detail. Transient absorption traces of size-controlled Pt-decorated CdS nanospheres (see Figure) exhibit accelerated dynamics for smaller nanocrystal sizes, which is indicative of faster and thus more efficient charge separation, consistent with the observed increases in quantum efficiencies for smaller nanocrystals. This additional understanding is an important step towards the rational design of quantum confined colloidal photocatalysts.

[1] W. Li, F. Jäeckel et al. *Nanoscale* 2015, 7, 16606-16610.



Transient absorption spectroscopy of size-controlled Pt-decorated CdS SNCs, showing size-dependent charge carrier dynamics.

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## Recent developments towards time-resolved electron diffraction at York

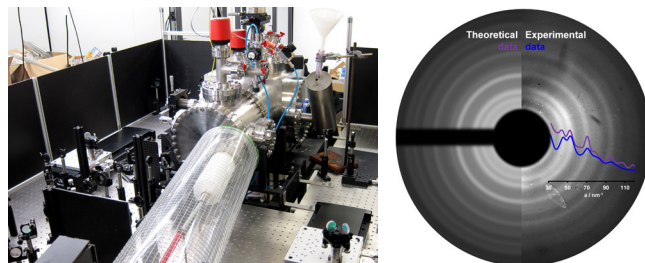
J. P. F. Nunes, M. S. Robinson, P. D. Lane, D. A. Wann (Dept of Chemistry, University of York, UK)

An apparatus has been built to allow time-resolved electron diffraction (TRED) experiments to be performed in the UK for the first time. These experiments allow for the structures of small molecules to be resolved and for their dynamics to be probed in real-time.

The Wann group TRED apparatus electron gun produces short electron bunches using the third harmonic of an 800 nm femtosecond laser focused onto a gold photocathode. This ultrafast electron beam is then used as a probe in pump-probe experiments.

Since its commissioning in 2013, the TRED apparatus at York (left-hand figure) has been used to record time-averaged electron diffraction data for both polycrystalline (right-hand figure) and gas-phase species, and preliminary time-resolved experiments showed a sub-picosecond time-resolution. The apparatus has recently been fitted with a purpose-built solenoid lens, capable of reducing the diameter of the electron beam by 30%, improving the spatial resolution of experiments.

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Left: The TRED apparatus at York. Right: Comparison between theoretical and experimental diffraction patterns and diffraction data, collected from a 20 nm-thick polycrystalline platinum sample.

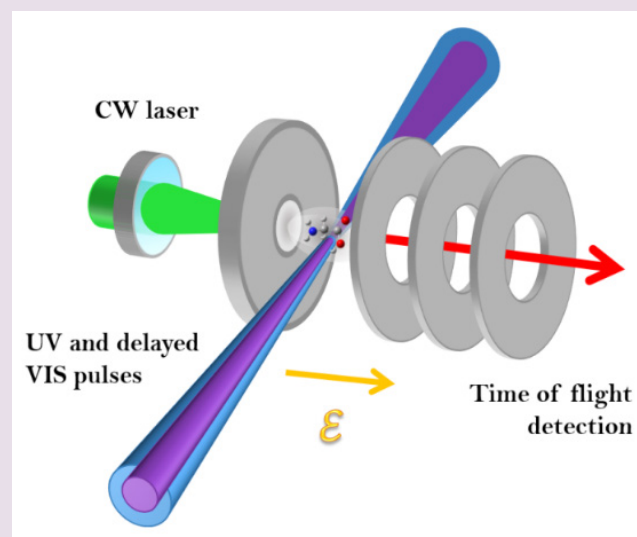
## Ultrafast non-radiative decay of neutral amino acids: phenylalanine and tryptophan

S. De Camillis, J. Miles, G. Alexander, I.D. Williams, J.B. Greenwood (Centre for Plasma Physics, Queen's University Belfast, UK)

The aromatic amino acids tryptophan, tyrosine and phenylalanine are critical building blocks of proteins. The fluorescence they produce when irradiated with mid-ultraviolet light is widely exploited to track the activity of proteins in cells. Tryptophan has the strongest fluorescence, while it is very weak in phenylalanine.

In this study we have used ultraviolet and visible femtosecond laser pulses to excite these molecules and probe the ultrafast processes by which this energy is subsequently dissipated. In phenylalanine we show that there is a relaxation process lasting 300 femtoseconds, which quickly quenches the absorbed ultraviolet energy by converting it to vibrational energy before any light can be emitted. A similar but much weaker process was found in toluene, the sub-unit of phenylalanine which absorbs ultraviolet light. These results help to explain why phenylalanine fluoresces weakly compared with other molecules like tryptophan and toluene.

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Schematic representation of the experiment. Femtosecond ultraviolet and visible laser pulses were focused into the interaction chamber, where they were absorbed by the molecules to form positive ions. By analysing the masses of the ions produced for different delays between the two laser pulses, the ultrafast dynamics were observed.

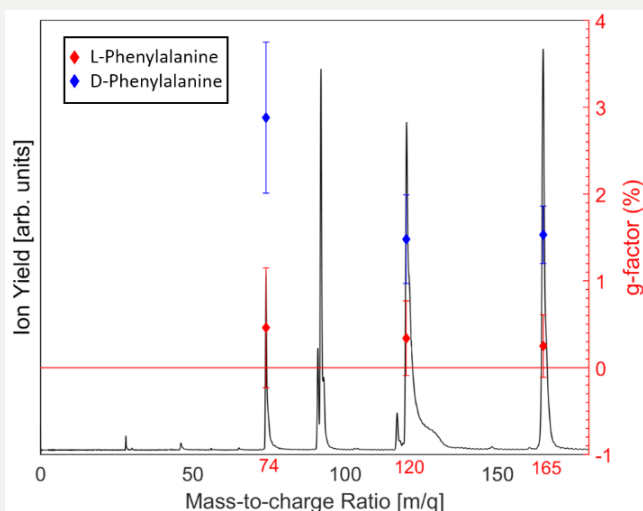
## Circular dichroism in the ion yields of amino acids

J. Miles, L. Casey, S. De Camillis, G. Alexander, I. D. Williams, J. B. Greenwood  
(Centre for Plasma Physics, Queen's University Belfast, UK)

Molecules which are non-superposable mirror images are termed chiral, with left- and right-handed versions known as enantiomers. As nature uses only one enantiomeric type for its building blocks, e.g. proteins and DNA, chirality is an integral part of biology functions. Therefore discrimination of different enantiomers is important for understanding the origins of life and efficacy of drugs in disease treatment.

In the present study, a femtosecond laser with circular polarisation has been used to discriminate between the enantiomers of the amino acid phenylalanine, by resonantly ionising the molecules and detecting relative yields of the ions produced. As this process is very efficient, it could enable different enantiomers to be detected with much higher sensitivity than is currently possible with conventional techniques.

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Mass spectra obtained from irradiating left- (blue) and right- (red) handed phenylalanine with circularly polarised femtosecond laser pulses. The difference in ion yields was used to distinguish the enantiomers.

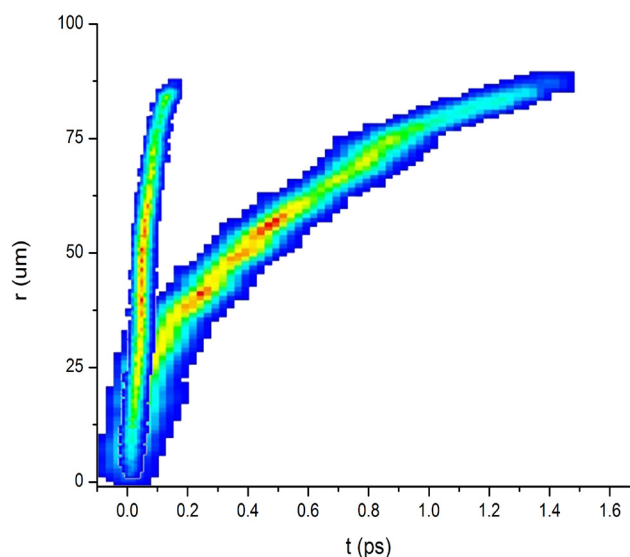
## Developing a next generation ultrafast electron microscope

C.W. Barlow Myers, P.L. Campbell, W.A. Bryan (Dept of Physics, Swansea University, UK)

We present a novel concept for a femtosecond electron microscope, capable of both diffractive and holographic imaging. Incorporated in the concept is the reduction of the three main sources of temporal broadening: geometric, space-charge, and energy broadening. Using a Nanoscale Metal Tip (NSMT) as our photoemitter, the focusing and collimation of ultrafast pulses is demonstrated with a lens located behind the emission site. This allows for an ultra-compact experimental design, reducing both broadening from path length differences and energy bandwidth effects.

*An illustration of the influence of geometric broadening upon ultrafast electron pulses and how this may be combatted using an increased electron energy and magnetic focusing or collimation in the vicinity of the electron source. Shown are the distributions of two electron pulses overlaid on the same time-scale, comparing a pulse energy of 300 eV without magnetic focusing, with a 25 keV pulse with magnetic focusing following propagation of 7 mm. Allowing the beam to diverge (i.e. without lens) extends the temporal profile of the pulse to 1.5 ps. Catching the beam before it naturally expands is essential in reducing geometric broadening, facilitating pulses well below 100 fs.*

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## Time-resolved microscopy with femtosecond few-electron pulses

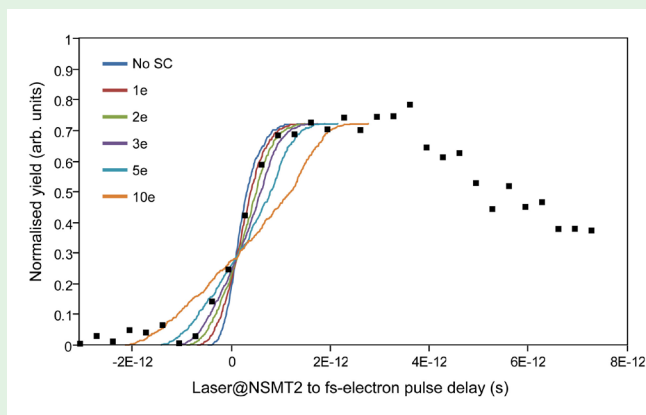
W. A. Bryan, C. W. Barlow-Myers (Dept of Physics, Swansea University, UK)  
 A. R. Bainbridge (Accelerator Science & Technology Centre, STFC Daresbury Laboratory, Cheshire, UK)

We have demonstrated a new form of electron microscopy, whereby a femtosecond laser pulse is used to generate bunches of a few electrons per shot. Keeping the number of electrons low prevents the mutual Coulomb repulsion from dominating, hence delivering as short a pulse as possible to the object being.

Here we use our femtosecond electron point-projection microscope to observe the evolution of charge at the apex of a metal tip, which comes to a point tens of nanometres across. By illuminating this nanotip with a second laser pulse, we are able to spatially and temporally image the evolution of the charge. The technique demonstrated here opens the door to time-resolved imaging of very rapid processes in conductors, dielectrics and insulators, which has significant relevance to the next generation of light-driven optically-coupled electronics.

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The graph shows a comparison between the measured temporal response of our nanoscale conducting object (black squares) with simulations of the cumulative electron density as a function of delay. The zero-delay point is identified through the use of the optical delay between the two laser pulses and confirmed by simulations. The cumulative electron flux is compared directly to the sequential image difference. No space-charge (SC) is the case whereby the geometric and bandwidth stretch of the electron pulse limit duration at the target and 1e to 10e are the predictions with full three-dimensional space charge calculations. It is clear that this observation is consistent with an electron flux of between one and three electrons per pulse on average. The best fit electron pulses in the presented experimental data have a standard deviation of approaching 100 fs, which is among the fastest ever observed.



## Ultrafast electron flux calibration for nanoscale dynamic imaging

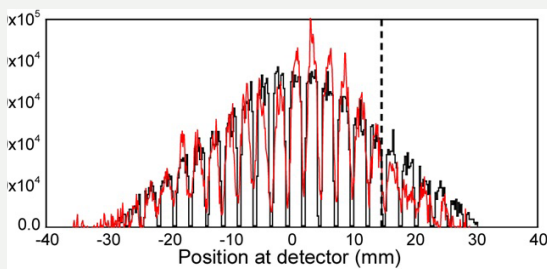
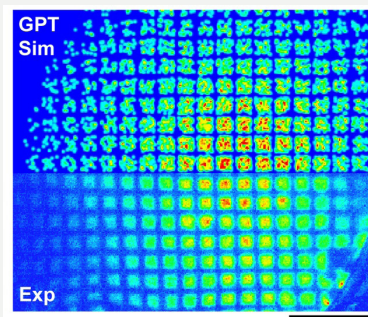
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 A. R. Bainbridge (Accelerator Technology & Science Centre, STFC Daresbury Laboratory, Cheshire, UK)

Femtosecond pulses of electrons combine the short wavelength characteristics of transmission electron microscopy with the temporal resolution afforded by pump-probe measurements on ultrafast timescales. The ideal operational mode is when each electron pulse contains, on average, less than one electron per shot. This requires highly sensitive diagnostic tools.

Here we show that, using a low-flux source of secondary electrons which diffuse over our detector, we can observe

single arrival events: when scaled up to the exposure time when performing femtosecond electron microscopy, this allows us to determine the number of electrons per pulse with high fidelity. We also present the degree to which the electron trajectories through our instrument agree with numerical modelling.

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(Left top) General Particle Tracer (GPT) simulation of the propagation of a femtosecond electron pulse through a 300 mesh TEM grid placed 5 mm from our femtosecond electron source.

(Left bottom) Experimental observation of the same configuration. Scale bar is 15 mm at the detector plane. The strong agreement between experiment and simulation illustrates how we are able to quantify the propagation of our electron pulses through our instrument.

(Right) A direct comparison between the GPT model (black) and experimental measurements (red) as a slice through the data presented to the left.

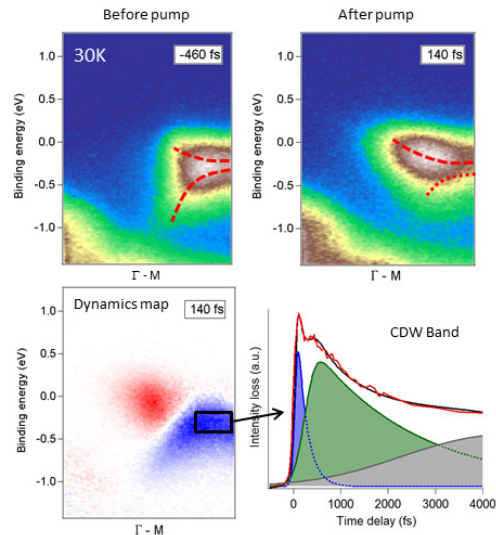
## Investigating the ultrafast recovery of the charge density wave phase in 1T-TiSe<sub>2</sub>

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 M. Wolf, R. Ernstorfer, M. Puppin, C. Nicholson (Physical Chemistry, Fritz-Haber-Institut der MPG, Berlin, Germany)

A. Magrez, H. Berger (Ecole Polytechnique Fédérale de Lausanne, Switzerland)  
 M. Hoesch (Diamond Light Source, Didcot, UK)  
 C. Cacho, E. Springate, R. Chapman (CLF, STFC Rutherford Appleton Laboratory, Didcot, UK)

In this experiment, we have used time- and angle-resolved photoemission spectroscopy to address the longstanding debate about the origin of the charge density wave (CDW) phase in 1T-TiSe<sub>2</sub>, a prototypical example of complex solid state material. We studied the recovery dynamics of both the low temperature CDW phase and its fluctuation phase at higher temperatures.

For the first time we observed a complex sequence of three different timescales in their recovery dynamics and associated them to different electronic and lattice degrees of freedoms. Furthermore, by tuning the excitation photon energy close the energy size of the CDW gap in this system, we discovered a non-trivial dependency of the amplitude of these different components. This promises deeper insights into the mechanisms of the CDW phase, the interplay of the different degrees of freedom, and emphasizes the importance of tuning the pump photon wavelength to specific energies relevant for the investigated system.



(Top) Time-resolved photoemission intensity maps of the charge density wave phase of 1T-TiSe<sub>2</sub> near the border of the Brillouin zone. (Bottom left) Difference intensity map, emphasizing the induced dynamics. (Bottom right) Transient intensity loss of the CDW band, showing the three timescales in its recovery dynamics.

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## Unveiling the role of the Mott-like electronic excitations in high-temperature superconductors by time-resolved photoemission

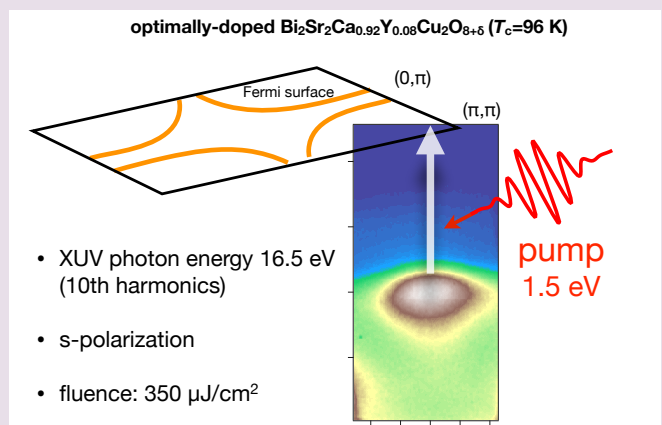
F. Cilento, A. Crepaldi (Elettra-Sincrotrone Trieste S.C.p.A., Italy)  
 S. Peli, C. Giannetti (Interdisciplinary Laboratories for Advanced Materials Physics (i-LAMP) & Università Cattolica del Sacro Cuore, Brescia, Italy)

G. Manzoni, F. Parmigian (Università degli Studi di Trieste, Italy)  
 C. Cacho, R. Chapman, E. Springate (CLF, STFC Rutherford Appleton Laboratory, Didcot, UK)  
 A. Damascelli (Dept of Physics & Astronomy, University of British Columbia, Vancouver, Canada)

The interplay between superconductivity and the high-energy electronic excitations related to the Mott physics remains one of the unsolved problems in the physics of copper oxides.

Here we perform time-resolved angle-resolved photoemission spectroscopy (trARPES) measurements, with high temporal resolution and XUV photon energy, to investigate the ultrafast dynamics of the oxygen bands in superconducting Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>0.92</sub>Y<sub>0.08</sub>Cu<sub>2</sub>O<sub>8+δ</sub> for the first time. The results unveil a non-trivial excitation pathway, which results in the long-lived trapping of holes in the oxygen O-2p<sub>π</sub> bands, probably under the form of localized polarons. The energy of the ultrafast modification of the O-2p<sub>π</sub> bands is of the order of the charge-transfer transition, which is strongly affected by the onset of superconductivity.

Our results underscore the crucial role of the photoinduced, long-lived non-thermal states in pump-probe experiments on copper oxides. This experiment also paves the way to the new era of trARPES on cuprates, in which the ultrafast electron dynamics will be mapped over the entire Brillouin zone.



Cartoon of the XUV time-resolved ARPES experiment on Bi2201. The pump excitation at 1.5 eV photon energy creates a non-thermal electronic distribution characterized by an excess of holes in the O-2p<sub>π</sub> oxygen bands and of electrons in the conduction band. Snapshots of the relaxation process are taken by XUV probe pulses ( $h\nu=16.5$  eV) that photoemit electrons at a kinetic energy  $E_{kin}=h\nu-\Phi$ , where  $\Phi$  is the work-function of the material.

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## Ultrafast free carrier dynamics in single layer MoS<sub>2</sub>

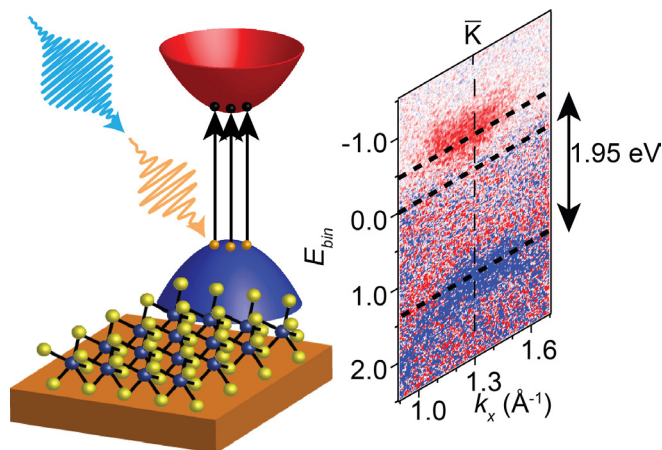
A. Grubišić Cabo, J.A. Miwa, S.S. Grønberg, J.V. Lauritsen, P. Hofmann, S. Ulstrup  
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The interplay between free carriers and bound excitons completely specifies the optical properties of semiconductors. The recently discovered class of single layer semiconducting transition metal dichalcogenides may be excellent candidates for new optoelectronic technologies, due to the presence of strongly bound excitons with remarkable properties. However, the properties of free carriers in these materials have remained unknown, because the strong exciton lines mask the free carrier signal altogether in all-optical experimental techniques.

Using time- and angle-resolved photoemission spectroscopy (trARPES) at the CLF Artemis facility for a single layer of MoS<sub>2</sub> contacted to a metal, we were able to measure the dynamics of free carriers directly for the first time. This allowed us to map out a direct band gap of 1.95 eV in single layer MoS<sub>2</sub>, and we observed that carriers are extracted by the metal contact on an ultrafast femtosecond timescale. Such ultrafast extraction by the metal contact is essential for applications that seek to exploit the properties of free carriers in MoS<sub>2</sub>, since they must be extracted before they decay via lattice vibrations or defects.

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(Left) Pump-probe experiment on single layer MoS<sub>2</sub> on Au(111). The pump pulse creates free carriers (electrons and holes) around the parabolic valence and conduction band edges of MoS<sub>2</sub>.

(Right) The excited state signal recorded with a high harmonic probe beam, revealing the photoexcited carriers and the direct band gap of single layer MoS<sub>2</sub>.