

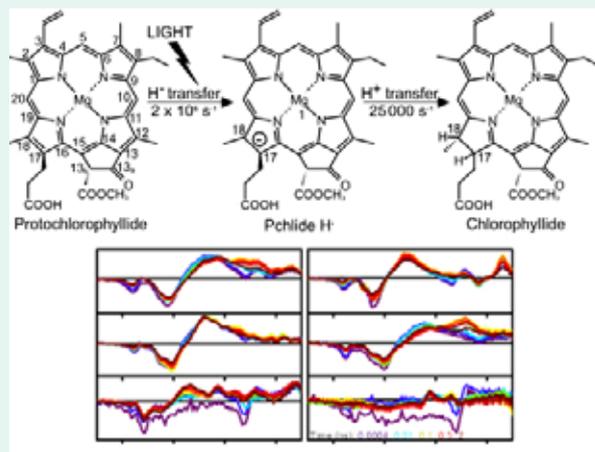
# Dynamics and spectroscopy

## Vibrational Fingerprinting of Protochlorophyllide Analogues and Implications for the Photochemical Synthesis of Chlorophyll

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A key regulatory step in the chlorophyll biosynthetic pathway is the reduction by the light-driven enzyme protochlorophyllide oxidoreductase (POR) of the C17-C18 double bond of protochlorophyllide (Pchlde) to form chlorophyllide (Chlide). In these experiments we have synthesized a number of Pchlde analogues that contain alterations at key mechanistic positions and used time resolved infra-red spectroscopy to understand how the structural changes affect the photochemical and excited-state properties of the Pchlde molecule that are so crucial for POR catalysis. The assignments we make provide direct confirmation of previous models for the involvement of specific vibrational modes in the excited state dynamics of Pchlde. More generally, these findings will now be crucial for mapping the coupling of any vibrational modes to the hydride and proton transfer chemistry in POR and for understanding the role of specific regions of the Pchlde molecule in POR catalysis.



The light-driven reduction of protochlorophyllide studied by time-resolved infra-red spectroscopy.

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## Exploring DNA with 2D-IR – spectroscopy, dynamics and ligand binding

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The link between molecular structure and function is a central tenet of biology and an important basis for understanding biological mechanisms. Rather less well-studied however is the role played by molecular motion, and in particular structural fluctuations, in determining the functional behaviour of biomolecules. This gap in our understanding is particularly acute for DNA where the fundamental process of duplex unwinding invokes a level of dynamism not necessarily found in proteins.

Ultrafast 2D-IR spectroscopy offers the potential to provide bond-level structural insight into complex molecules, combined with sub-100 fs time-resolution enabling measurement of the molecular dynamics that underpin function. Here we present an overview of two recent studies exploiting 2D-IR to investigate the vibrational relaxation of DNA and the structural impact of ligand binding to double-stranded DNA, both in the solution phase.

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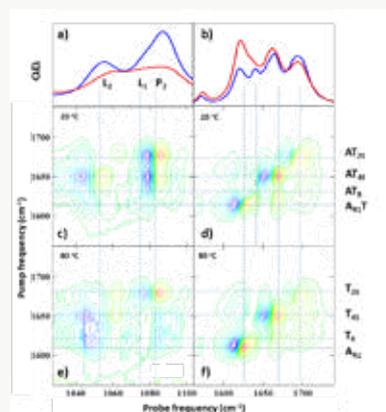


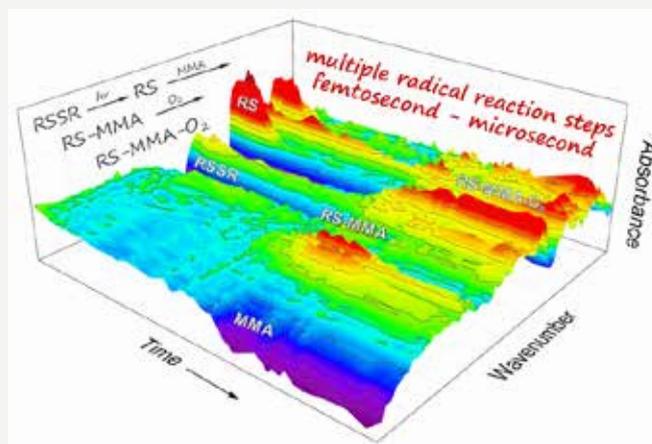
Figure: a) IR absorption spectra of AT 15-mer DNA in the backbone stretching region of the IR spectrum at 20°C (blue) and 80°C (red). b) IR absorption spectra showing vibrational modes of the bases at 20°C (blue) and 80°C (red). c-f) 2D-IR spectra showing results of one colour (d,f) and two colour (c,e) experiments at 20°C (c,d) and 80°C (e,f).

## Observation of multiple steps in radical reactions on femtosecond to microsecond timescales

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Free radical reactions in solution involve a complicated sequence of steps, which occur over a wide range of timescales. The initiation of the reactions by photochemical production of the free radicals can be complete in less than 1 picosecond, but subsequent steps require nanoseconds to microseconds to allow diffusion, encounters with co-reactants, and chemical reactions to occur. The LIFEtime facility at the CLF is well suited to observe these reactions because characteristic bands in the transient infra-red absorption spectra distinguish the intermediates involved in each reaction step, and measurements can be made over 9 orders of magnitude of time. We have studied the first steps in an example of the synthetically useful thiol-ene class of reactions in which a thyl radical is generated by ultraviolet photolysis of a disulfide compound and adds to an alkene. The LIFEtime measurements successfully resolve the first three steps in the reaction sequence.



Transient IR spectra observing a thiol-ene reaction over femtosecond to microsecond timescales.

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## Long-wavelength Laser-driven Ultrafast Magnetization Dynamics in Gadolinium

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We studied the ultrafast laser-driven demagnetization of ferromagnetic gadolinium in time-resolved ARPES at the Artemis facility. Femtosecond excitation at 1300nm was followed by probing with 36eV high-order harmonic pulses. The 40-fs time resolution at Artemis revealed new aspects of non-equilibrium magnetism on the femtosecond timescale. In particular, d-band exchange splitting increased within the first 100fs after laser excitation as the majority spin component moved to higher binding energy. Further investigations will help to clarify whether this new observation is the signature of a coherent excitation of the exchange coupled 4f5d spins.

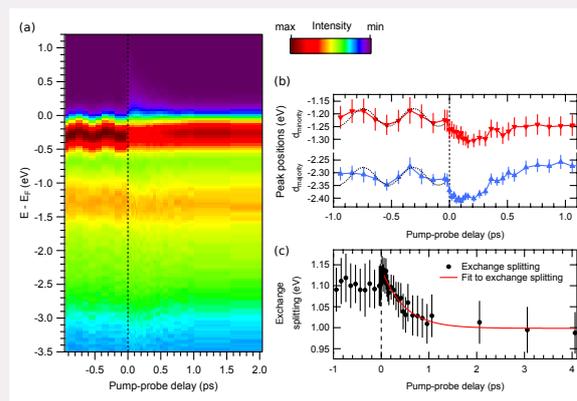


Figure 1: (a) Time-resolved photoemission spectrum. The strong feature at  $\approx 0.3\text{eV}$  binding energy is the Gd(0001) surface state. Its oscillations result from ponderomotive acceleration of photoelectrons by the laser field. (b) Binding energy dynamics of the minority-spin (red) and majority-spin (blue) bulk d bands. The difference between them is the exchange splitting, shown in (c).

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## Time resolved photoelectron imaging with an XUV high harmonic source

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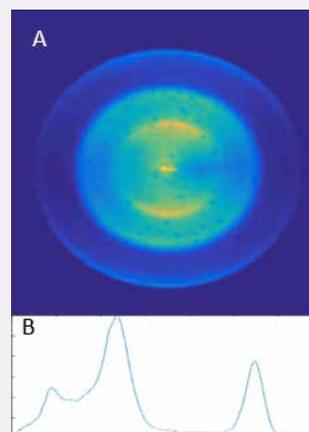
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We have performed a UV pump-VUV probe photoelectron imaging experiment on the photodissociation dynamics of CS<sub>2</sub>. The dynamics in the CS<sub>2</sub> molecule is initiated using a 70 fs 200 nm pump that populates the S<sub>2</sub> excited state of the molecule. Once in the excited state the molecule dissociates on a sub picosecond timescale leading to the formation of CS and S. The dynamics are probed by a delayed VUV probe at 15.5 eV. The probe is generated using high harmonic generation with a driving 400 nm pulse. The 15.5 eV harmonic is then separated from the other harmonic frequencies in a time preserving monochromator. The probe is then used to ionise both the excited state and remaining ground state population. Analysis of the changes in the resulting photoelectron images show features that correspond to ground state depletion and the delayed formation of the dissociation products.



Photoelectron image (A) and spectrum (B) of CS<sub>2</sub> following excitation with UV (6.2 eV) and probing with XUV (15.5 eV) light.

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## Decay dynamics of conduction band electrons on hydroxylated TiO<sub>2</sub>

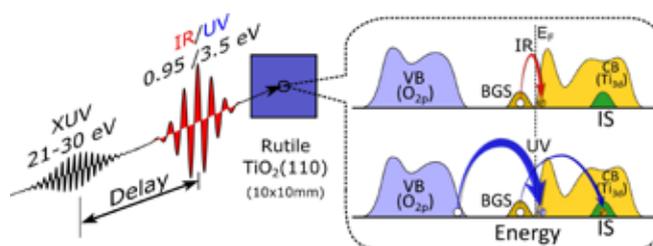
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We performed IR/UV-pump XUV probe experiments on a rutile TiO<sub>2</sub>(110) surface. The pump energies, either larger or smaller than the band gap of rutile TiO<sub>2</sub>, are chosen to distinguish the dynamics of different charge carriers. A trapping time of ~50 fs of electrons at the bottom of the conduction band is observed in the IR-pump XUV-probe measurements. In the UV-pumped measurements, the fast electron dynamics will also arise from electron trapping as it lies in a similar time scale. In addition, slow processes with lifetimes extending up to picoseconds can be understood under the scheme of trap-assisted recombination. This observation confirms the critical role of the band gap states to the annihilation of electrons and holes under low illumination conditions, which has long been proposed in photochemistry studies of TiO<sub>2</sub>.



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Schematic of the IR-/UV-pump XUV-probe experiments. The pump pulses are either 1300 nm (0.95 eV) or 350 nm (3.5 eV), which are followed by an XUV (21 and 30 eV, respectively) pulse with a controlled delay time. The IR pulse can create excitations from the BGS to the CB bottom, while UV can create excitations from the VB to CB bottom (big arrow) and from the BGS to a resonant intermediate state (IS) in the CB manifold (small arrow).