Time-Resolved Multiple-Probe Spectroscopy on ULTRA-LIFEtime

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Introduction

The BBSRC and STFC funded ULTRA-LIFEtime system[1] has been commissioned for time-resolved multiple-probe spectroscopy (TRMPS) experiments[2]. The new 100 kHz ultrafast laser based on a custom dual Yb:KGW system (Pharos, Light Conversion, see fig. 1) provides new capability in TRMPS experiments.

Figure 1. Dual Yb:KGW laser system and OPAs.

Ultrafast molecular rearrangements are often followed by slow changes in the wider environment, as subsequent diffusion of molecules and energy through solution and macromolecules occur. The TRMPS capability of the new ULTRA-LIFEtime system will address light activated protein dynamics, which naturally occur over several orders of magnitude in time[4-10].

The TRMPS method uses a pump pulse at arbitrary repetition rate to excite a sample, followed by an optically synchronised train of 100 kHz pulses. The first pulse in the probe pulse train can measure ultrafast changes in a sample (< 200 fs), while the subsequent pulses follow the changes (at 10 µs intervals) over longer timescales. Time delay of the probe pulse train can be varied by traditional optical delay along a translation stage (fs - ns) or by seeding the probe and pump amplifiers with different pulses from the oscillator seed pulse train (ns - µs). Thus, photo-initiated changes in a sample can be tracked continuously across femtoseconds to seconds timescales. Compared to our previous TRMPS system[3] the new system has an arbitrary pump pulse rate (0 – 50 kHz) defined by an electro-optic pulse picker, compared to previous fixed 1 kHz rate, and the probe has a higher 100 kHz rate, compared to 10 kHz previously. This allows more flexible experiments providing 10x more data per experiment acquisition.

In this report we discuss comparison of ytterbium (Yb) and titanium sapphire (Ti:S) based ultrafast amplifiers and describe TRMPS measurements made over > 10 orders of magnitude in timescale, with an experimental time response of < 200 fs.

Ytterbium vs. Titanium Sapphire

To our knowledge, the present system is the first application of Yb-baser ultrafast laser technology to time-resolved IR (TRIR) spectroscopy. Time-resolved spectroscopy has long been dominated by Ti:S systems. However, Yb-based systems are now seeing dramatic advances as their better efficiency is suited to high average power applications. Significant uptake in the laser machining industry has supported the development to more advanced scientific applications, from high power (kW level average power) optical parametric chirped pulse amplification pump lasers[11] to the time-resolved spectroscopy applications discussed here.

Although these Yb lasers generally have longer pulses (< 180 compared to < 30 fs in Ti:S), their pumping of optical parametric amplifiers (OPA) provides widely tunable output across UV to mid-IR with < 150 fs (< 7 fs using non-collinear OPAs) appropriate for many TRIR experiments. Fig. 2 shows a Kerr effect measurement, to demonstrate the time-resolution of the system using UV pump and IR probe pulses.

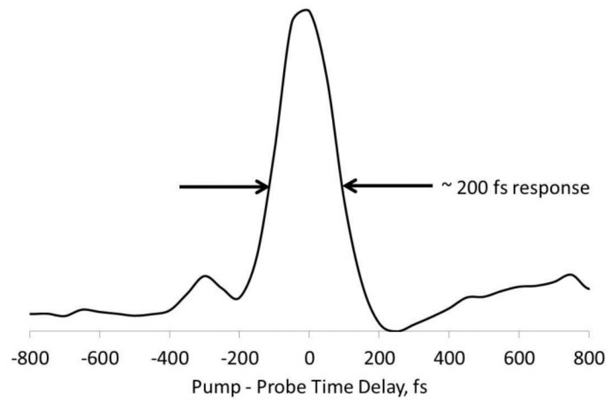

Figure 2. Cross correlation of the UV (330 nm) pump pulses with IR (5000 nm) probe pulses. 200 fs response is measured through the Kerr effect on the IR pulses induced by the UV pulses in ZnS.

The narrower bandwidth that accompanies a longer pulse does limit the spectral window for time-resolved experiments. Typical probe IR spectra from OPA outputs of the present system cover 200 cm^{-1} (compared to > 500 cm^{-1} in other Ti:S systems[12]). However, the present system generates two synchronised probe OPA outputs to double this limited range to 400 cm^{-1}. Additional advantage can be gained from this dual-OPA approach as the 400 cm^{-1} is not limited to a continuous region, so simultaneous high and low frequency probing can be more flexible.

The present Yb system has outstanding stability, with < 0.06 % S.D. shot-to-shot noise on the mid-IR OPA output. This is an order of magnitude better than many Ti:S systems achieve at the output of an OPA. Combined with the high-repetition rate, this stability means that we have been able to measure changes in IR absorbance of < 10^{-5} optical density (ΔOD) in 0.1 second.

Demonstration

To show the capability of the new TRMPS system, we performed time-resolved measurements on the photodissociation of $W(CO)_6$. The dynamics of this process have been characterised previously[3]. To summarise, excitation of $W(CO)_6$ in heptane solution leads to ultrafast photo-dissociation of the parent molecule, releasing a CO ligand which is replaced by a solvent molecule coordinating at the vacant site over < 1 ps. This newly formed $W(CO)_5$(heptane) complex then follows several 100s of picoseconds of “cooling” as excess energy is dissipated and the new heptane ligand rearranges to a preferred conformation. As the heptane is only weakly bound, water in the solution can replace this ligand. In our experiments, water is present as a trace impurity, so this exchange process occurs through slow diffusion over > 100 µs. These dramatically different timescales are easily accessed in the present TRMPS experiment. Fig. 3 shows the kinetics measured as the $W(CO)_5$(heptane) adduct is formed and subsequently exchanged to $W(CO)_5$(water).

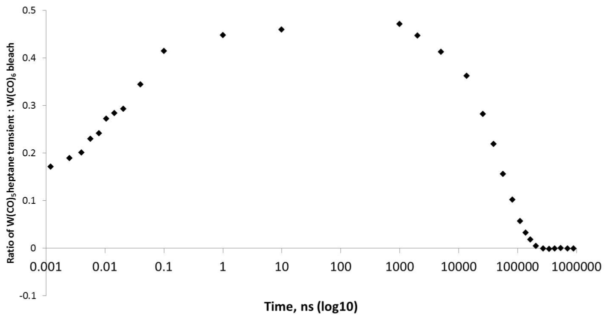

Figure 3. Kinetics of $W(CO)_6$ photo-dissociation in heptane solution. Intensity of change is shown as the ratio of $W(CO)_5$(heptane) adduct formation (1956 cm^{-1}) to $W(CO)_6$ loss (1984 cm^{-1}) on a logarithmic time-scale.

Additional TRMPS experiment have been undertaken to demonstrate high signal to noise (< 10^{-5} ΔOD in < 0.1s) and extended timescale measurements. The highest signal to noise measurements are achieved at high pump repetition rates, e.g. 50 kHz pumping / 100 kHz probing, where the experiment is cycled more often. However, to measure long timescale processes, one must have a low pump repetition rate. Ref. 2 shows measurements we performed at 3 Hz pumping rate, on a ring-opening reaction of a spiro-oxazine sample in solution out to 20 ms with ΔOD ~ 10^{-4}.

Data Acquisition

For shot-to-shot detection of IR spectra, MCT array IR detectors (IR Associates) have been integrated with spectrometers to acquire probe spectra at the full 100 kHz repetition rate (fir. 4). FPAS electronics (IR Systems Development) integrate and digitize the signals, which are then transferred to an NI-PXI PC for real-time processing into difference spectra, measuring spectral changes. “LIFEtimeNET” acquisition software is based on LabVIEW software ULTRANET, previously described in ref. 13.

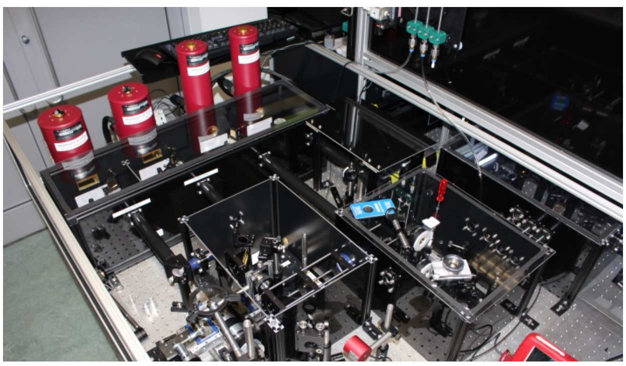

Figure 4. Time-resolved spectrometer.

Summary and Outlook

We have recently commissioned the new ULTRA LIFEtime laboratory for TRIR and IR TRMPS. Comparisons of the Yb-based laser system have been made with Ti:S systems. Despite the limitations in pulse duration and spectral bandwidth the present Yb system is a capable and highly stable source for time resolved measurements. Temporal response of < 200 fs has been recorded and kinetics out to milliseconds are demonstrated.

TRMPS measurements of light-activated protein dynamics measurements are now underway. Additional 2DIR capability being developed on the ULTRA-LIFEtime system is discussed in another article published in this annual report.

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