

Time-resolved multiple probe UV-vis transient absorption spectroscopy at 100 kHz

Contact ian.p.clark@stfc.ac.uk

IP Clark

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus,
Didcot, Oxfordshire, OX11 0QX

GM Greetham

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus,
Didcot, Oxfordshire, OX11 0QX

M Towrie

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus,
Didcot, Oxfordshire, OX11 0QX

Introduction

Transient-absorption spectroscopy whether in the UV-visible (1) or mid-infrared (2) is a powerful tool for studying transient species, enabling a wide breadth of research, from DNA photo-oxidation, (3) to catalysis, (4) (5) and protein folding. (6)

The ULTRA facility has introduced new UV-visible transient absorption capabilities. The development enables, for the first time, 100 kHz time-resolved multiple probe UV-visible transient absorption spectroscopy (TRMPS). As well as high signal to noise, the system is capable of measuring femtosecond to millisecond dynamics in a single experiment.

Method

The development uses the LIFETIME apparatus which is based on a 100 kHz dual-amplifier ytterbium laser system (Pharos and Pharos SP, Light Conversion Ltd.) (9). To maximize the UV-visible continuum, both the fundamental and second harmonic of the amplifier (Pharos SP) are used. The visible supercontinuum is generated by focusing a small fraction, 1.5 μ J, of the fundamental output (1030 nm) into a calcium fluoride plate. A UV-vis continuum is produced by focusing the second harmonic, 515 nm, 370 nJ, into the same material. The calcium fluoride must be moved in a raster pattern in the plane perpendicular to the direction of the beam to avoid an unstable continuum formed by colour-centre formation within the calcium fluoride. An appropriate short-pass filter or dye solution is placed in the probe beam before the sample to block the residual 1030 nm or 515 nm beam.

The second Pharos amplifier and its optical parametric amplifier (Light Conversion Orpheus-HP) is used to generate the pump beam. The pump-probe timing control was achieved using the combination of oscillator roundtrip timing (providing steps of 12 ns) and an optical delay line (covering the time delay span up to 12 ns) as described in detail in reference (9).

The pump and probe beams are focused into the sample and the beams overlapped. The spot sizes at sample are set to 30-40 μ m and 60-100 μ m FWHM for the probe and pump beams respectively. Typical pump pulse energies are 200-300 nJ. After the sample the probe beam is focused into a Newport 77400 spectrograph (Newport Corporation) and the spectrum detected with an OctoPlus line-scan camera (Teledyne e2v Ltd), with 2048 $10 \times 200 \mu$ m pixels. The camera can sample the spectrum of every laser shot with a NI-PXI frame-grabber, at 12-bit dynamic range.

The repetition rate of the pump pulses can be controlled by the amplifier's pulse picker and is typically set at 1 kHz, while the

G Karras

Diamond Light Source Ltd
Diamond House, Harwell Campus, Didcot, Oxfordshire, OX11 0DE

IV Sazanovich

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus,
Didcot, Oxfordshire, OX11 0QX

AE Edmeades

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus,
Didcot, Oxfordshire, OX11 0QX

probe pulse repetition rate is kept at 100 kHz. This provides the multiple probe capability, where each pump pulse has 100 probe pulses associated with it.

Results

Spectra of the continua obtained with calcium fluoride using the LIFETIME system are shown in **Error! Reference source not found.** The cut-off at 950 nm is from a short-pass filter used to block the fundamental, while the gap at ca 515 nm is from the filter used to block the second harmonic.

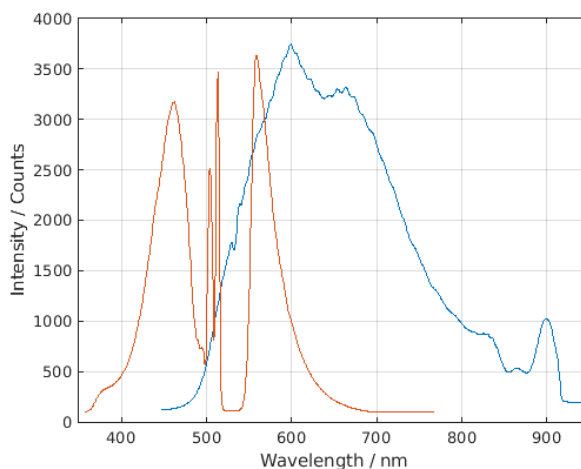


Figure 1 Spectra of continuum generated using both 515 nm driven (red) and 1030 nm driven (blue) calcium fluoride.

As can be seen the continuum spectrum stops at just above 350 nm. This is either due to the coating on the sensor, the camera's window or the sensor simply not being sensitive in this region. The gap in the 515 nm driven continuum at ca 530 nm is caused by the dye solution used to block the second harmonic.

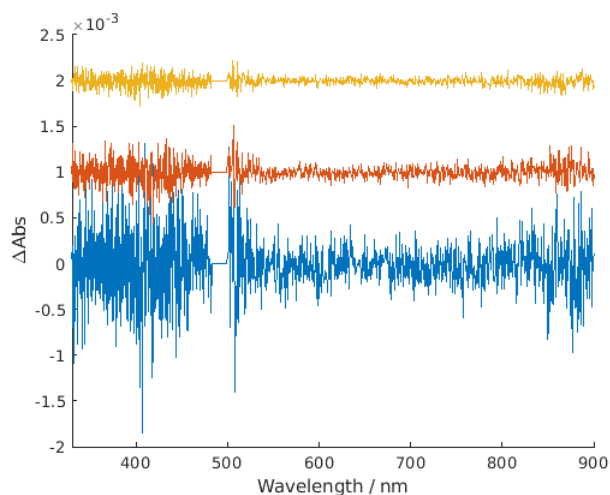


Figure 2 Offset difference spectra without sample, showing the noise level for 0.1, 1 and 3 seconds of data acquisition for the full UV-visible spectral region.

Figure 2 shows the noise across the spectral range 330-900 nm, while Table 1 shows the root mean square, RMS, for difference spectrum across the two spectral regions for 0.1, 1 and 3 seconds of data averaging, with the latter being a typical averaging time used in a single cycle of data acquisition. As would be expected the noise is greater in the < 400 nm and > 850 nm regions of the spectrum where the light intensity is reduced.

Table 1

Acquisition time	0.1 s	1 s	3 s
RMS 330-480 nm	3.8×10^{-4}	1.2×10^{-4}	6.9×10^{-5}
RMS 500-900 nm	2.5×10^{-4}	7.9×10^{-5}	4.4×10^{-5}

Transient absorption spectroscopy

Error! Reference source not found. shows an example transient absorption spectrum recorded over the full UV-visible spectral range with the new set-up. The sample is 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin ruthenium (II) carbonyl in dichloromethane.

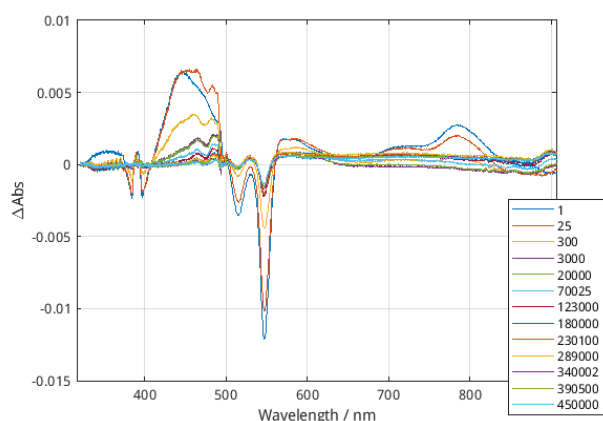


Figure 3 Unprocessed transient absorption spectra of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin ruthenium (II) carbonyl in dichloromethane at a selection of pump-probe time delays indicated in the legend (in nanoseconds). The excitation is at 390 nm with a pulse energy of 250 nJ. The notch filter used to eliminate the 390 nm pump beam obscures the spectrum in this region. Total averaging time per time-delay is 12 seconds.

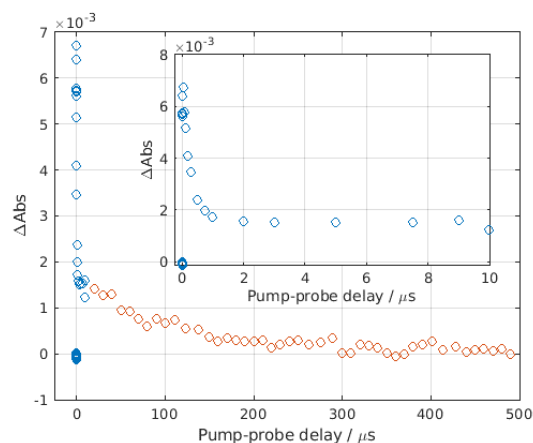


Figure 4 Kinetics of the transient observed at 460 nm for 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin ruthenium (II) carbonyl in dichloromethane. The pump-probe delays represented in blue are obtained using a combination of optical and electronic delays, while the TRMPS delays are shown in red. The inset shows a zoomed in view of the optical and electronic delays.

Figure 4 shows the kinetics of the transient peak observed at 460 nm. The figure shows both the short timescale pump-probe delays achieved using the optical delay line, or combination of electronic and optical delay and the TRMPS delays provided by the additional probe pulse.

Future improvements

The possibility of removing or replacing the window on the OctoPlus detector is being investigated. Clearly a more suitable window material which transmits UV light would be preferred. In addition, alternative filtering methods are being investigated to achieve a complete spectral coverage from 350-700 nm with the second harmonic driven continuum.

References

1. *Ultrafast transient absorption spectroscopy: principles.* Rudi Berera, Rienk van Grondelle, John T. M. Kennis. 2009, Photosynth Research, pp. 105–118. DOI 10.1007/s11120-009-9454-y.
2. *Photochemistry of transition metal carbonyls.* JJ Turner, MW George, M Poliakoff and RN Perutz. 2022, Chemical Society Reviews, pp. 5300–5329. DOI 10.1039/d1cs00826a.
3. *Adenine radical cation formation by a ligand-centered excited state of an intercalated chromium polypyridyl complex leads to enhanced DNA photo-oxidation.* FA Baptista, D Krizan, M Stitch, IV Sazanovich, IP Clark, M Towrie, C Long, L Martinez-Fernandez, R Improta, NAP Kane-Maguire, JM Kelly, and SJ Quinn. 2021, Journal of the American Chemical Society, pp. 14766–14779. DOI 10.1021/jacs.1c06658.
4. *Direct Observation of Reactive Intermediates by Time-Resolved Spectroscopy Unravels the Mechanism of a Radical-Induced 1,2-Metalate Rearrangement.* Lewis-Borrell, L. J., Sneha, M., Clark, I. P., Fasano, V., Noble, A., Aggarwal, V. K. & Orr-Ewing, A. J. 2021, Journal of the American Chemical Society, pp. 17191 - 17199. DOI 10.1021/jacs.1c07964.
5. *Direct observation of the microscopic reverse of the ubiquitous concerted metalation deprotonation step in C–H bond activation catalysis.* LA Hammarback, BJ Aucott, JTW Bray, IP Clark, M Towrie, A Robinson, IJS Fairlamb and JM Lynam. 2021, Journal of the American Chemical Society, pp. 1356–1364. DOI 10.1021/jacs.0c10409.

6. *Unraveling the mechanism of a LOV domain optogenetic sensor: A glutamine lever induces unfolding of the Ja-helix.* **JN Iuliano, J Tolentino Collado, AA Gil, PT Ravindran, A Lukacs, SY Shin, HA Woroniecka, K Adamczyk, JM Aramini, UR Edupuganti, CR Hall, GM Greetham, IV Sazanovich, IP Clark, T Daryae, JE Toettcher, JB French, KH Gardner, CL Simmerling, SR Meech and PJ T.** 2020, ACS Chemical Biology, pp. 2752-2765. DOI 10.1021/acscchembio.0c00543.
7. *2D IR spectroscopy at 100 kHz utilizing a mid-IR OPCPA laser source.* **BM Luther, KM Tracy, M Gerrity, S Brown, and AT Krummel.** 2016, Optics Express, pp. 4117-4127. DOI 10.1364/OE.24.004117.
8. *Multidimensional spectroscopy on the microscale: Development of a multimodal imaging system incorporating 2D white-light spectroscopy, broadband transient absorption, and atomic force microscopy.* **AC Jones, NM Kearns, M Bohlmann Kunz, JT Flach, and MT Zanni.** 2019, Journal of Physical Chemistry A, pp. 10824-10836. DOI 10.1021/acs.jpca.9b09099.
9. *A 100 kHz Time-Resolved Multiple-Probe Femtosecond to Second Infrared Absorption Spectrometer.* **G.M. Greetham, P.M. Donaldson, C. Nation, I.V. Sazanovich, I.P. Clark, D.J. Shaw, A.W. Parker, M. Towrie.** 2016, Applied Spectroscopy, pp. 645-653. DOI 10.1177/0003702816631302.