

A new ultrafast transient absorption facility in the Ultrafast Spectroscopy Laboratory

K. L. Ronayne and M. Towrie

Central Laser Facility, STFC, Rutherford Appleton Laboratory, Harwell Science & Innovation Campus, Didcot, Oxon, OX11 0QX, UK

Main contact email address

k.l.ronayne@rl.ac.uk

Introduction

Visible transient absorption may be used to explore the nature and dynamics of electronic excited states and is an important complementary technique for time-resolved vibrational spectroscopy. Following on from the success of the NIR Transient Absorption apparatus^[1], silicon detectors were purchased to extend the capability of this kit into the visible.

Regenerative Amplifier

Silicon arrays from Electron Tubes Ltd, were connected to the XDAS platform as described elsewhere for InGaAs detector elements^[1]. Briefly 4 bare silicon 32 pixel arrays were coupled to the 128 channel XDAS readout card. The XDAS XCHIP analogue multiplexer acquires integrated charge in a 10 μ s time gate simultaneously from all sensor elements and digitizes this with 14 bit resolution before transfer to PC via PCI bus. Sensitivity was set to 2 pC per channel using a jumper. The XDAS was synchronised to the laser by external triggering of the nScan channel from the laser master clock and digital delay generators. The charge integration gate was set to overlap with the light signal using a Stanford DG535 digital pulse delay generator.

White Light Continuum Generation

The Ultrafast Spectroscopy Facility (USL) generates \sim 200 fs tunable radiation by commercial solid state lasers

operating at \sim 800 nm driving custom non-linear optical conversion to generate tunable pump and probe light at a repetition rate of 1 kHz. The WLC (white light continuum) was generated by focusing \sim 3 μ J of 800 nm radiation into a suitable medium. Whilst LiF₂ crystals (10 mm thickⁱ) were found to yield bright WLC, particularly towards the blue end of the spectrum, the energies required led to colour centre formation in the crystal and this in turn lead to pulse-to-pulse instabilities in the probe and reference beams. For this experiment a broadband visible probe 400-700 nm light was generated by supercontinuum generation in 2 cm of water as this gave relatively stable WLC (*vide infra*). Pump excitation light was generated by second harmonic upconversion of the 800 nm laser to 400 nm.

Spectrometer

A schematic of the spectrometer arrangement is shown in Figure 1 below. As discussed above, the white light was generated by focusing \sim 3 μ J of 800 nm radiation into a 2 cm quartz cell containing water. The 800 nm beam was attenuated from 120 μ J using an ultrafast polariser, polarisation rotator and an adjustable aperture. The polarisation was set to horizontal using an 800 nm polarisation rotator. After supercontinuum generation the 800 nm fundamental was removed using an 800 nm dichroic filter. The continuum was then collimated and split using a silvered plate to 2:3 reference and probe.

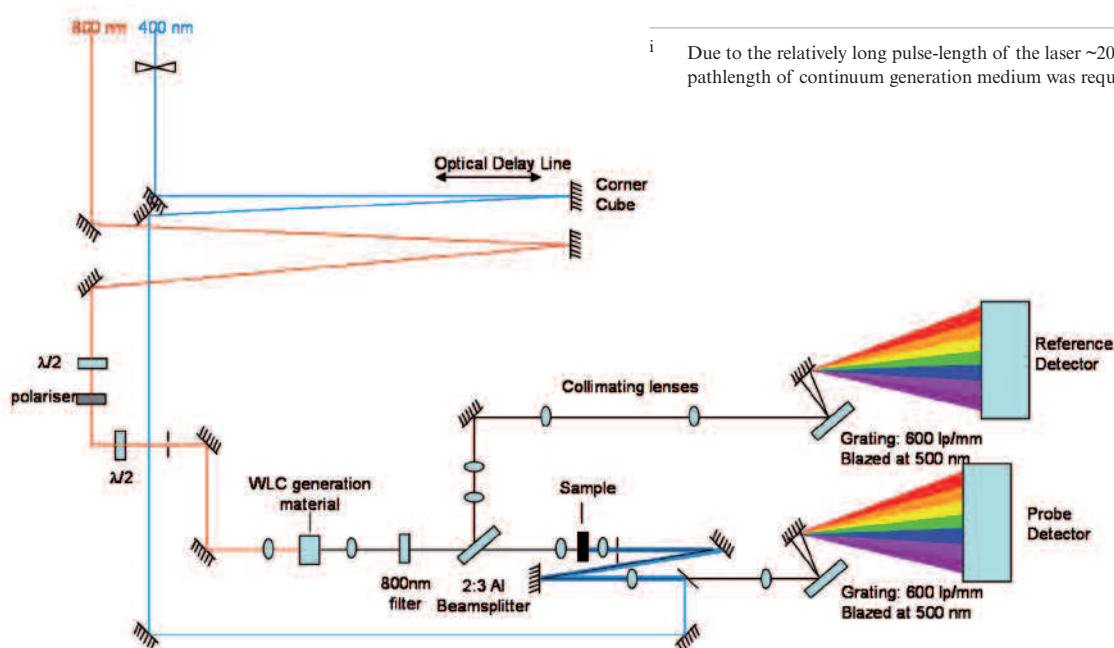


Figure 1. Schematic of spectrometer.

ⁱ Due to the relatively long pulse-length of the laser \sim 200 fs, a long pathlength of continuum generation medium was required.

The visible probe FWHM spot diameter in the sample was measured with a piezo-electric stage and a knife-edge. The reference and probe beams were re-collimated and then focused onto the reference and probe diode arrays after dispersion from a 600 l/mm 500 nm blazed diffraction grating (Thorlabs) set ~30 cm from the arrays. An averaged spectrum of the white light continuum measured on the probe and reference arms is shown in Fig. 2. The continuum ranged from the UV (~350 nm) to the red (~750 nm) but due to the filters used to remove scatter from the pump beam at 400 nm, we were unable to measure transient absorption signals below about 450 nm. The integrated pulse energy of the visible was measured to be 80 nJ using a Moletron J3-5 energy meter connected to a lock-in amplifier. The noise of the spectrometer in the 420 to 700 nm range was measured to be ± 0.0003 ΔA in 1 second.

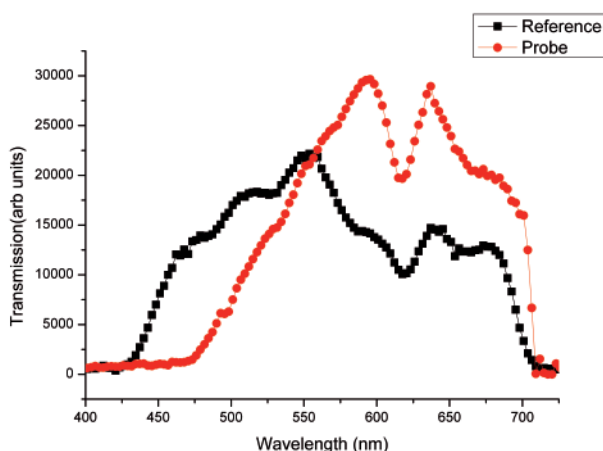


Figure 2. Probe and reference signals. The cutoff at 420 nm is due to the filters used to remove the pump wavelength at 400 nm and at 700 nm due to filters to remove residual 800 nm scatter.

Transient Absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Acetonitrile

Although present in small amounts in the earth's crust (natural abundance of ruthenium is $\sim 10^{-3}$ ppm^[2]), complexes of ruthenium have attracted a lot of attention over the past 40 or so years because of their unique properties. They tend to exhibit long-lived excited states, which can undergo inter- or intramolecular electron or energy transfer to a suitable acceptor molecule or substituent, and the visible luminescence of these complexes offers a useful handle for the monitoring of such reactions. This has led to widespread application of these systems in solar dye cells^[3,4], nanodevices^[5], artificial photosynthesis^[6,7], and solid state luminescent displays^[8]. The paradigm for ruthenium polypyridyl complexes is the ubiquitous $[\text{Ru}(\text{bpy})_3]^{2+}$ which has been extensively studied by time-resolved electronic and vibrational spectroscopic techniques.

The setup was briefly tested on a solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ prior to the microscopy measurements discussed elsewhere^[9]. Excitation at 400 nm leads to population of the ¹MLCT (metal-to-ligand charge transfer) state followed by very rapid ISC to the triplet manifold which is populated within the time resolution of our experiment^[10] (see pink trace at 0 ps in Figure 3). The transient spectra are dominated by a strong bleach at 450 nm, corresponding to the ground state MLCT

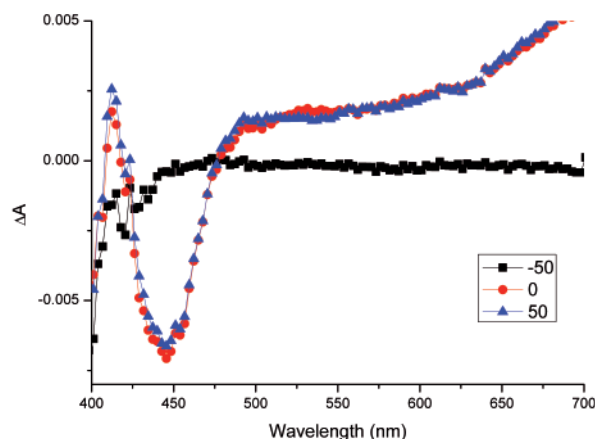


Figure 3. Transient Absorption spectra of $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ in acetonitrile solution recorded at -50, 0 and 50 ps delay after pump pulse.

absorption and the weak residual absorption above 500 nm is attributed to a combination of transitions from unreduced bipyridine ligands to the oxidised metal atom, ($\text{bpy} \rightarrow \text{Ru}^{3+}$), lower energy transitions on the reduced bipyridine and ligand-to-metal charge transfer (LMCT)^[11]. Unfortunately, due to the filters used to eliminate scatter from the 400 nm pump beam, we cannot fully observe the intense transient at 360 nm, attributed to localized transitions on the $\text{bpy}^{\cdot-}$ ligand, although the low energy shoulder of this is evidenced by the transient band at ~ 410 nm.

Summary

We have demonstrated the capability of the new transient absorption spectroscopy apparatus in the USL. Development of this apparatus using very tight focusing conditions to microscopy techniques is discussed in a separate contribution^[9].

References

1. M. Towrie, A. W. Parker, K. L. Ronayne, S. Manolopoulos, S. Martin and P. Seller, *Towards a new ultrafast time resolved near-infrared facility using custom InGaAs arrays*. CLF Annual Report 2004-2005, 235-236.
2. E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, (1984).
3. K. Kalyansundaram, *Coord. Chem. Rev.* **46**, 159 (1982).
4. Y. Tachibana, J. E. Moser, M. Grätzel, D. R. Klug, J. R. Durrant, *J. Phys. Chem.* **100**, 20056 (1996).
5. V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines: A Journey into the Nanoworld*, Wiley-VCH, Weinheim (2003).
6. a) T. J. Meyer, *Acc. Chem. Res.* **22**, 163 (1989). b) M. Grätzel, *Acc. Chem. Res.* **14**, 376 (1981).
7. M. Grätzel, *Comments Inorg. Chem.* **12**, 93 (1991).
8. J. Slinker, D. Bernards, P. L. Houtson, H. D. Abruña, S. Bernhard and G. G. Malliaras, *Chem. Commun.* 2392 (2003).
9. K. L. Ronayne, M. Towrie and A. D. Ward, *Transient Absorption Microscopy*, CLF Annual Report 2006-2007.
10. A. T. Yeh, C. V. Shank and J. K. McCusker, *Science* **289**, 935 (2000).
11. S. Wallin, J. Davidsson, J. Modin and L. Hammarström, *J. Phys. Chem.* **109**, 4697 (2005).