

Towards a new ultrafast time resolved near-infrared facility using custom InGaAs arrays

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Introduction

The development of novel instrumentation for ultrafast spectroscopy has been a major strength of the LSF having led to its unique resonance Raman and IR capabilities. However, it needs to be recognised that although these techniques are powerful in their own right they cannot stand alone and must be supported by complementary measurements using techniques such as time resolved fluorescence and absorption. In this way one builds a fuller picture of photochemical state dynamics. The combination of Kerr gate and time correlated single photon counting capability in the LSF provides adequate time resolved fluorescence facilities. However its visible time resolved absorption spectrometer apparatus remains rudimentary.

The Lasers for Science Facility and Engineering and Instrumentation Department have been working together to develop a new facility sensitive to the near IR (NIR) using custom InGaAs detector arrays and an innovative fast readout interface for 1D sensor arrays. The generic fast readout will be suitable for VUV to near IR detection for pump probe transient absorption measurements. CCLRC's Centre for Instrumentation (Cfi) funded development of the novel near IR InGaAs sensor array hardware. These sensors provide response from 900 – 1700 nm, although in later embodiments it would be relatively simple to replace the InGaAs with silicon to extend wavelength response down from 1000 nm to less than 300 nm. The hardware and basic readout software are developed and we report on the first tests on the detectors and on the generation of stable broadband near IR white light continuum needed for high sensitivity dispersed spectroscopy.

This new apparatus provides ultrafast pump probe capability in the near IR for studying the fast photo-dynamics of important

molecular species such as free radicals, solvated electrons and large conjugated molecules of importance in biological function, molecular electronics, chemical catalysis, polymerisation and solid state physics. An example might be new approaches to the study of the ultrafast excited state dynamics and charge transfer characteristics of long chain carotenoids, having absorption max > 1000 nm. The most well known β -carotene radical cation absorption maximum is at 1050 nm and this type of radical species can be generated via judicious photochemistry or photoionisation. Other examples include canthaxanthin (in carrots), and lycopene (red of tomatoes) both are believed to prevent cancer and the latter also to prevent heart disease, ageing and macular degeneration. The chemistry of these processes remains little understood. Other molecular systems include radical ions of multi-ring benzenoid compounds with relevance to molecular switches and light limiters. The linear InGaAs detector provides a useful non-cryogenic solution to permit these experiments and broaden the CLF applications and users.

Apparatus

InGaAs Diode arrays: The XENIX near IR (NIR) dual diode array interface was developed through Cfi funding has been described in the InGaAs Infra-red Detector Project Technical Report RAL-TR-2004-015. In brief it consists of two XENIX 256 element InGaAs arrays coupled to an XDAS interface. Wavelength response is shown in figure 2. Elements are 0.5 mm high and have a pitch of 50 μ m they are connected in pairs in order to match the 128 channel capacity of the XDAS. The XDAS XCHIP analogue multiplexer acquires integrated charge in a 10 microsecond time gate simultaneously from all sensor elements and digitizes this with 14bit resolution before transfer

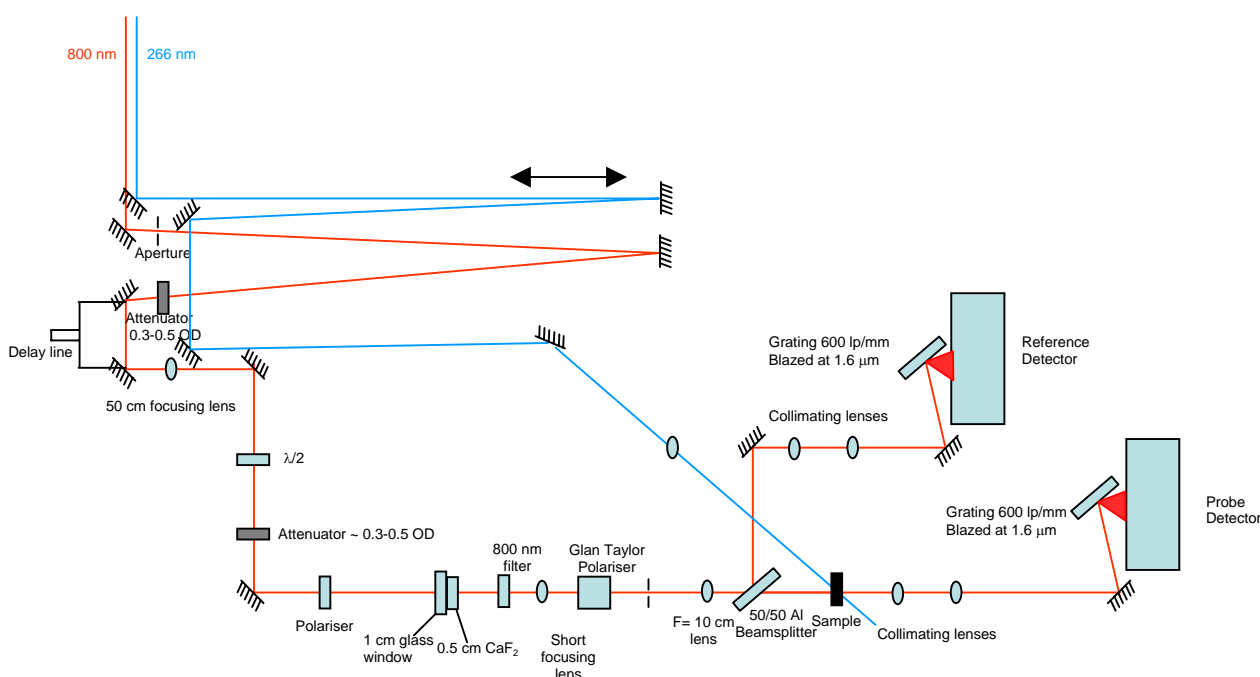


Figure 1. Schematic of Spectrometer layout.

to PC via PCI bus. Sensitivity may be set to 10 pC or 2 pC per channel using a jumper. Unless otherwise stated all measurements were made on higher dynamic range 10 pC setting.

The XDAS was synchronised to the laser via an external trigger from the titanium sapphire 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.

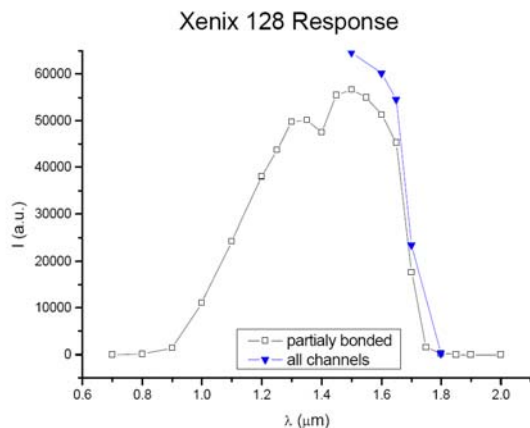


Figure 2. Measured wavelength response of the Xenix arrays.

Laser system: The Ultrafast Spectroscopy Facility (USL) generates ~150 fs tunable radiation by commercial solid state lasers operating at ~790 nm driving custom non-linear optical conversion to generate tunable pump and probe light at a repetition rate of 1 kHz. For this experiment a broadband near infrared probe 900-1700 nm light was produced by supercontinuum generation in fused silica glass and CaF₂ windows. Pump excitation light was generated by frequency upconversion to 263 nm, the third harmonic of the 790 nm laser.

Spectrometer: A schematic of the spectrometer arrangement is shown in Figure 3. The white light was generated by focusing 12 μJ of 790 nm radiation into a 1 cm thick polished fused silica glass window and 0.5 cm CaF₂ window that were slowly raster scanned to reduce the rate of photo-damage. The 790 nm beam was attenuated from 300 μJ using neutral density filters and an adjustable aperture. Polarisation was set using an 800 nm waveplate. After supercontinuum generation the 790 nm fundamental was removed using an 800 nm dichroic filter that transmitted >70% of the near IR (NIR) radiation above 900 nm. The continuum was collimated and horizontally polarised using a Glan-Taylor polariser and then passed through a 15 cm focal length lens then split using an aluminium coated plate to the ratio 1:1 on the reference and probe. The NIR probe FWHM spot diameter in the sample was measured to be ~150 microns diameter. The reference and probe beams were re-collimated

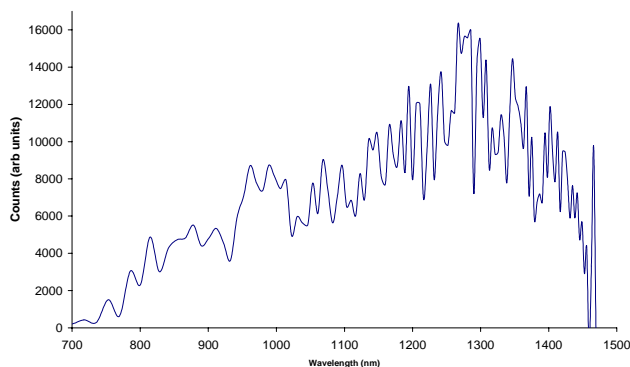


Figure 3. NIR Continuum.

and then focused onto the reference and probe diode arrays after dispersion from a 600 l/mm 1600 nm blazed diffraction grating set ~3 cm from the arrays. An averaged spectrum of the white light continuum measured on the probe and reference arms is shown in Figure 2. The resolution was measured to be 25 nm and range from 900 – 1500 nm with a dispersion of 7 nm per pixel. Shot by shot intensity variation was typically at the level of 20 % rms that, after dividing by the reference signal, was reduced to 5 % rms. The integrated full spectrum pulse energy of the NIR light was measured to be 20 nJ using a Moletron J3-05 energy meter connected to a lock-in amplifier.

It should be noted that the conventional approach to supercontinuum generation is to focus around 1 to 2 μJ of the fundamental beam tightly into a few millimetres thick sapphire plate because this generates a very stable continuum. However, we found that even at the higher (2pC) gain setting this method did not generate sufficient NIR radiation above 1300 nm and as a result considerable effort was spent in optimising optical conditions to generate moderately stable and bright supercontinuum.

Pump-Probe Transient Absorption

Using the test software spectral data were recorded shot by shot into an Excel worksheet. The test XDAS/PC interface was found to miss about 5% of shots at 1000 Hz readout therefore the pump on/off status was monitored by applying a signal to channel 0 of the probe array. Data were analysed using Excel functions. The form of calculations is shown below. The sample was photo-excited at 500 Hz to provide a pump on pump off difference measurement. The 200 microns diameter 267 nm pump beam was overlapped with the probe in the sample as shown in Figure 1.

$$\text{ratio} = \left[\frac{\text{probe}}{\text{reference}} \right]$$

$$\text{Signal} = \frac{\sum \text{Ratio}_{\text{pumpon}}}{n_{\text{pumpon}}} - \frac{\sum \text{Ratio}_{\text{pumpoff}}}{n_{\text{pumpoff}}} \times \frac{\text{Avg}_{\text{ref}}}{\text{Avg}_{\text{probe}}}$$

where ratio refers to the ratio of the single shot probe and reference spectrum; $n_{\text{pumpon/off}}$ is the number of exposures in the acquisition with pump on and off respectively. Signal is the averaged differential signal normalized to the averaged reference and probe spectra.

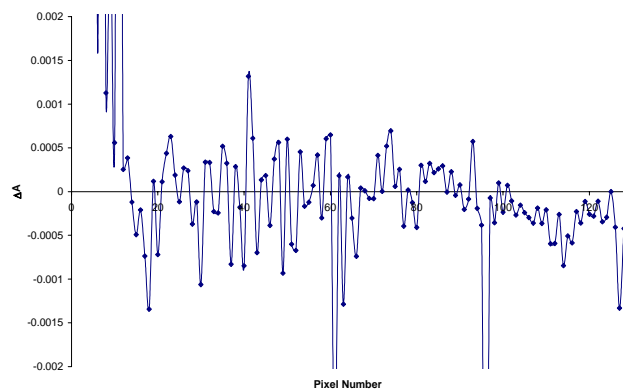


Figure 4. Change in absorption for a 2 s acquisition with no pumping.

Figure 4 shows the signal obtained after a 2 second acquisition when the sample is not excited. This represents a signal to noise of about $\pm 0.001\Delta A$ measured in 1 second (ΔA is the change in absorbance measured between pump off and pump on). This level, obtained without data discrimination, or “realtime” optimisation, represents a 5 fold improvement on the Ultrafast Lab’s current visible wavelength transient absorption apparatus that is based on silicon arrays, but remains a factor of 10 below the sensitivity of PIRATE largely due to the greater instability of the NIR continuum and lack of shot by shot signal discrimination. Figure 5 shows the corresponding averaged spectral profiles taken with the XDAS on the 10 pC capacitance setting. It can be seen that there are several bad pixels, due to broken bonds to the custom interface, particularly on the probe arm. These can be removed in the subsequent data analysis by averaging to nearest neighbor pixels with little loss in signal integrity.

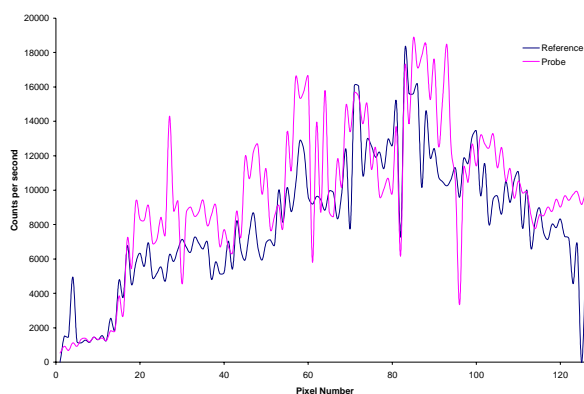


Figure 5. Probe and reference signals for the same acquisition.

Spectroscopic Measurement of Solvated Electrons

As an example of use in a pump probe experiment we measured the transient spectra of solvated electrons generated by photolysis of iodine anions in a solution of potassium iodide in acetonitrile. Point by point spectral measurements of have been reported in the literature¹⁾ and these show a broad, strong absorption in the 900 – 1500 nm spectral region allocated to the 1S to 2P electronic transition of the solvated electron.

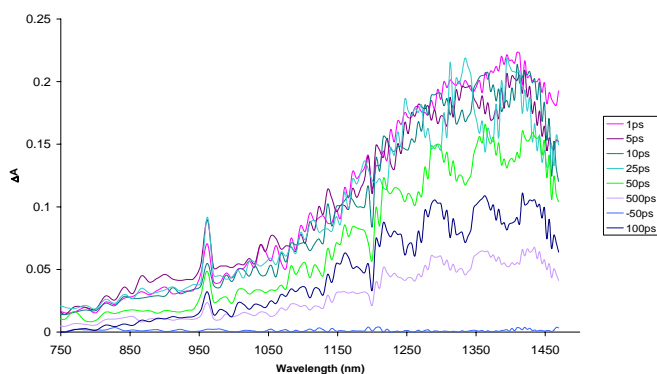


Figure 6. Time-resolved spectra of the solvated electron in CH_3CN .

Figure 6 shows the dispersed spectrum taken with 2 seconds acquisition for a number of different pump probe delays using the new NIR dispersed spectrometer. The data compares well with the single point data reported in refer interference effects that are observed when more than one waveguide filament is produced during the white light continuum generation process¹⁾. Dead pixels have been removed and replaced by averaging with nearest neighbours. There is clear systematic structure within the spectra that have yet to be diagnosed, but

are likely to stem from interference effects that are observed when more than one waveguide filament is produced during the white light continuum generation process.

Conclusion

We successfully demonstrated NIR transient absorption capability using the InGaAs arrays for pump probe time resolved spectroscopy. The signal to noise was measured to be $0.002 \Delta A$ in 1 second. The measurements were made without optimised spectral matching between the reference and probe arms and without statistical discrimination of bad data caused by large intermittent fluctuations of the probe beam. The signal to noise performance is 10 times below that of PIRATE but encouragingly is 5 times above that of the current USL visible transient absorption apparatus. We expect considerable improvements in signal to noise after the XDAS is interfaced to the PIRATE data acquisition software. We have also learned extremely valuable lessons with regard to the characterisation of the supercontinuum generated in the NIR and the capabilities and limitations of the InGaAs arrays that will impact the sensor instrument developments that form a major part of the next generation of pump probe facility, ULTRA that recently has been awarded support through joint CCLRC & BBSRC funding.

Full Commissioning as a New Facility

Internal CLF funding has been secured to complete the commissioning of the instrument. The main remaining task is to interface the XDAS units to the PIRATE data acquisition program and user interface. This work will be carried out by C.Reason (CLF Engineering Group) who has written new PIRATE code²⁾.

References

1. C. Xia, J. Peon and B. Kohler, *J. Chem. Phys.*, 117, 8855-8866 (2002).
2. C. Reason & M. Towrie, *The control and data acquisition program for the LSF PIRATE Laser*, CLF Annual Report 2004-2005, p232