

Application of Ultra to 2D-IR

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Introduction

The Ultra facility^[1] will begin its first operations through 2009. Development of the system through 2008-9 has focused on the building and testing of experimental stations with UV-vis and IR experimental facilities. The UV-vis station provides time-resolved UV-vis absorption^[2] and femtosecond stimulated Raman (FSRS) spectroscopies^[3]. The IR station will be the focus of early experiments in Ultra, with 2D-IR given a priority by the sponsors of the STFC and BBSRC funded grant. An overview of Ultra's application to 2D-IR experiments is given here.

Ultrafast 2-dimensional IR spectroscopy (2D-IR) is finding increasing use in chemistry and biology as the technique is being developed worldwide^[4,5]. 2D-IR investigates the inter- or intra-molecular coupling of vibrational energy. Application of picosecond and femtosecond IR laser pulses to 2D-IR allows one to observe ultrafast dynamics of vibrational energy transfer through a molecular system as well as generating structural information and measuring how strongly one vibration is coupled to another.

The "double resonance"^[6] 2D-IR method used in Ultra, uses a narrowband (ps) pump pulse to excite specific vibrational modes in the sample, then probes the changes in the wider IR spectrum with a broadband (fs) IR pulse. Ultra's dual fs/ps IR output is well suited to this technique, allowing one to pump and probe completely independent spectral regions. The pump wavelength is scanned through the spectral regions of interest, generating 1D probe spectra of absorption changes at each position (see fig. 1) which are combined together to form a 2D map of the vibrational perturbations at each pump wavelengths (see fig. 2).

The availability of Ultra's multiple beam combinations enables transient 2D-IR (T-2D-IR), measurement of vibrational coupling dynamics in excited state species. In T-2D-IR a fs, ps or ns duration photoexcitation pump pulse (UV - IR) initiates some chemical reaction. Subsequent measurement of the 2D-IR spectrum provides information on the system's vibrational coupling as the photo-excited process occurs.

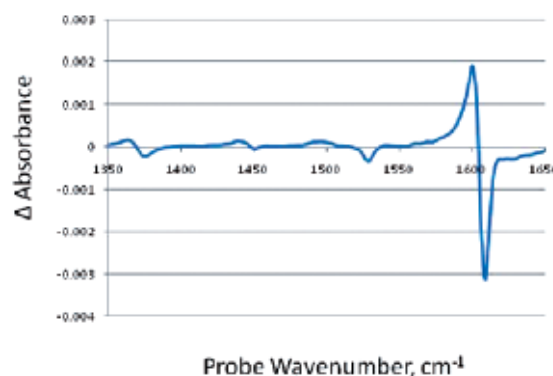


Figure 1. Difference absorption spectrum of DMABN in deuterated acetonitrile, with IR pump – IR probe time delay of 3 ps. Pump wavenumber 1610 cm^{-1} . Acquisition of many of these spectra with different pump energies generate the 2D-IR spectrum, as shown in fig. 2.

Experimental

The Ultra laser system has been described in a previous report^[2], so only a summary is given here. A custom dual output titanium sapphire laser (Alpha 10000, Thales Laser) provides synchronized 50 fs and 2 ps, 800 nm, 1mJ pulses at 10 kHz repetition rate. For 2D-IR experiments, these outputs drive two computer-controlled optical parametric amplifiers (OPAs, Light Conversion) with difference frequency generation to provide tunable 50 fs (IR probe) and 2 ps (IR pump) pulses. For a T-2D-IR experiment, the initial photoexcitation pump pulse is generated by a third tunable OPA output.

The pump pulses (IR and UV/vis) travel along computer-controlled delay lines (Newport) which provide variable time delays of up to 4 ns between each pulse arriving at the sample.

The pump and probe beams are overlapped spatially in the sample cells with typical beam sizes of 50 μm (probe) and 100 μm (pump). The sample solutions are sandwiched between two CaF₂ windows, with variable thickness spacers to define the sample path length. The sample cell (Harrick) can be attached to flow apparatus to replenish sample degraded by the pump

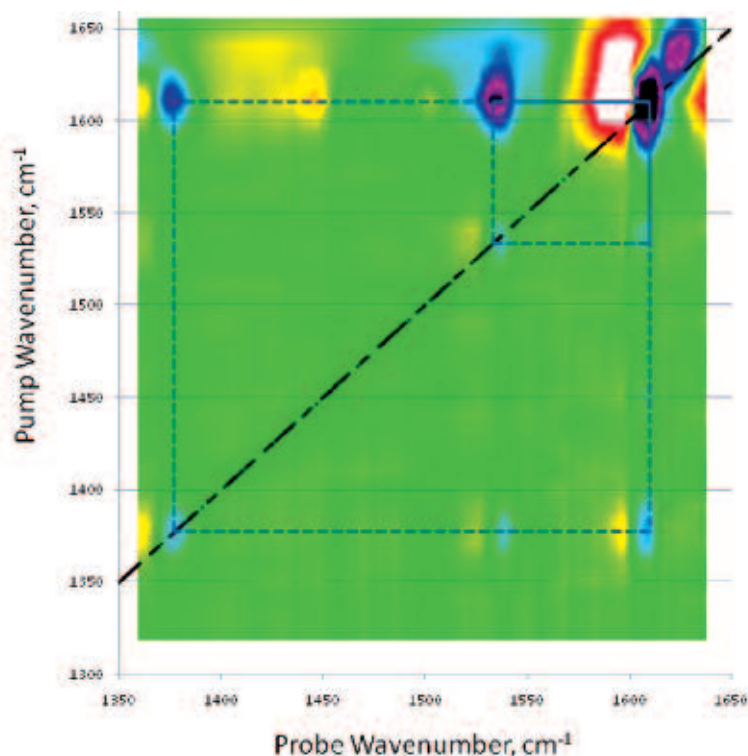


Figure 2. 2D-IR spectrum of the ground state of DMABN in deuterated acetonitrile. Negative peaks (blue/black) show decrease in absorption (i.e. band bleaches due to depletion of ground state absorptions) and positive peaks (red/white) show increase in absorption (i.e. generation of excited state absorptions). Dot-dashed line shows diagonal positions, i.e. positions where pump and probe are equivalent. Dotted squares show vibrational coupling indications with cross-peaks. The plot is zoomed in on the intensity axis (saturating some of the more intense peaks), to make some of the weaker cross peaks more visible.

pulses. Further measures to reduce photo-damage of the sample include sample rastering.

After passing through the sample the focused probe beam is collimated and directed to a 0.25 m spectrograph which images the spectrum onto a 128 channel mercury cadmium telluride (MCT) detector array (IR Associates). A second identical MCT detector and spectrometer allow advanced data acquisition possibilities, either as a reference or as a second probe to allow simultaneous measurements of two different spectral regions, increased spectral resolution or increased spectral range. We anticipate that this will be the dominant mode of Ultra as the high repetition rate allows the system sensitivity to approach the detector noise limited levels, even without referencing. This capability will be demonstrated in a forthcoming publication^[7].

The data acquisition system is described in an accompanying report^[8].

2D-IR of DMABN in deuterated acetonitrile

Demonstration experiments were carried out on a 5 mol dm⁻³ sample of DMABN (dimethyl-amino-benzonitrile) in deuterated acetonitrile, path length 50 μm . To avoid photo-damage, the sample was flowed through the cell and continuously rastered. The IR probe spectrum was tuned to the 1300-1700 cm⁻¹ region of the IR spectrum and detected by a single unreferenced detector.

The 2D-IR pump pulse ($\sim 1 \mu\text{J}$) was tuned across the 1300-1700 cm⁻¹ region of the IR spectrum, to generate a 2D-IR spectrum of the ground state. The pump beam is chopped at 5 kHz and the 2D-IR spectrum generated^[6,8] by the absorption differences between the pump on and off condition. These spectra are averaged over several seconds per pump wavelength step to obtain the final spectra shown here. If excited states are to be probed, a second pump beam is aligned into the sample and can be modulated at 2.5 kHz to obtain the 2D-IR, TRIR and T-2D-IR in a single experiment.

Fig. 1 shows a single difference spectrum of DMABN with a pump – probe time delay of 3 ps and pump wavelength at 1610 cm⁻¹. The depletion of the ground vibrational state and formation of vibrationally excited state populations, due to the IR pumping, produce the positive and negative peaks, respectively. The 2D-IR spectrum of fig. 2 combines multiple pump difference spectra with pump wavenumbers from 1300-1700 cm⁻¹.

The 1D IR absorption spectrum appears along the diagonal of the spectrum as intuitively, when pumping a band at e.g. 1610 cm⁻¹, the corresponding feature at 1610 cm⁻¹ in the probe spectrum would be expected to be perturbed. However, the interest in 2D-IR arises from the features off the diagonal, where pumping of one band at e.g. 1610 cm⁻¹ has a significant effect on other vibrations e.g. 1375 cm⁻¹, through vibrational coupling. Many of these off-diagonal peaks can be observed in fig. 2.

Summary

Ultra's IR experiment station is now active with 2D-IR, T-2D-IR and TRIR capabilities. Multiple pump capabilities and data acquisition methods are available to enable these three techniques to be applied to the same sample within a single experiment.

There are key specifications of Ultra which have not been demonstrated here, but will be the subject of a forthcoming in depth technical publication^[7]. These capabilities include a very broad probe bandwidth of $\sim 500 \text{ cm}^{-1}$ ref. 1 and the independent tunability of the pump and probe wavelength combinations of $500\text{-}4000 \text{ cm}^{-1}$ and $830\text{-}4000 \text{ cm}^{-1}$, respectively.

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