

Optimizing the Temperature Recovery Rate in Temperature-Jump IR Spectroscopy

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Introduction

Time-resolved spectroscopies, in a pump – probe mode, are used to study a wide variety of processes. The flexibility of ULTRA¹ allows a range of pump methods (electronic or vibrational excitation) and various spectroscopic probes (absorption or nonlinear spectroscopies) to measure molecular dynamics. Femtosecond to nanosecond pulses and novel probing techniques², allow the study of processes over femtosecond to millisecond timescales.

Recently, a new laser source and experiment have been developed to add temperature-jump (T-jump) to the ULTRA facility's capabilities³. Laser-based T-jumps rapidly increase the temperature of a sample, allowing the study of important processes in nature.

Biomolecules often rely on site-specific activity, as they interact with targeted molecules. An important part of site-specificity is controlled by large scale structure and dynamics of biomolecules. T-jump experiments at ULTRA are designed to trigger dynamic processes, such as protein⁴ and DNA⁵ unfolding, but can also be applied to molecular dynamics in other systems.

ULTRA's T-jump approach can be operated at variable pump repetition-rate (up to 1 kHz), achieving > 10 K T-jumps in solutions, in one nanosecond. A key aspect of the experiment is controlling the duration of the elevated temperature, allowing sample changes to occur on microsecond to millisecond timescales. While high repetition-rate pumping increases the signal-to-noise of experimental data, it can compromise the ability of the approach to monitor slow molecular changes. Here we demonstrate how the effect of path-length and window material can help tailor the experiment to the dynamic timescale of interest.

Experimental

A PPLN-based nanosecond optical parametric oscillator (OPO) is pumped by a Nd:YAG laser, generating 80 μJ pulses at up to 1 kHz. This OPO can be wavelength tuned with poling-period of the PPLN crystal and temperature. Here it is tuned to be absorbed by the O-D stretching frequency ($\sim 2700\text{ cm}^{-1}$) of a D_2O solution. This pump energy is deposited into the solvent, by focusing to $\sim 200\text{ }\mu\text{m}$ diameter in a $6\text{ }\mu\text{m}$ path-length cell, leading to > 10 K temperature increases. The T-jump magnitude can be confirmed by both modelling and FTIR calibration^{3,6}.

IR absorption spectrum changes were monitored from nanosecond to millisecond timescales, using the 10 kHz broadband mid-IR output from an optical parametric amplifier, pumped by the 800 nm output of ULTRA B.

Spectra in fig. 1 show the IR response of trifluoro-acetic acid (TFA) in D_2O , following the T-jump. The sharp absorption change at $\sim 1670\text{ cm}^{-1}$ is attributed to the frequency shift of the C=O vibrational mode, caused by the T-jump. The broad background is associated with the solvent's T-jump signal and etalon effects (see later). TFA is a good test sample for monitoring T-jumps, as it is a small molecule, strongly coupled

to the H-bonding network of the solvent, so responds effectively instantaneously ($\ll 1\text{ ns}$) to the temperature change.

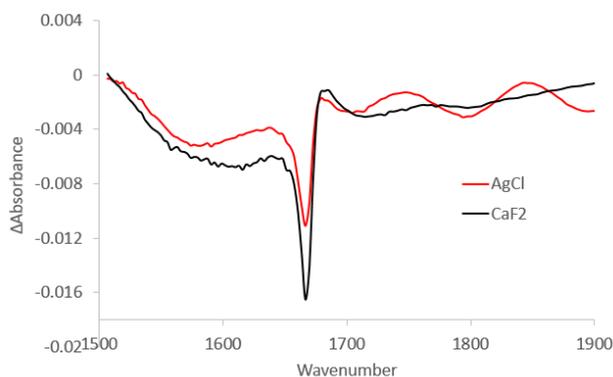


Figure 1. Normalised IR difference spectra of TFA in solution, immediately following the T-jump pulse. Two window materials, AgCl and CaF_2 are shown for comparison.

Kinetics of the T-jump (fig. 2), acquired in the pump – multiple probe mode², show an immediate change in the TFA IR absorption, followed by a recovery, as the temperature returns to the initial temperature.

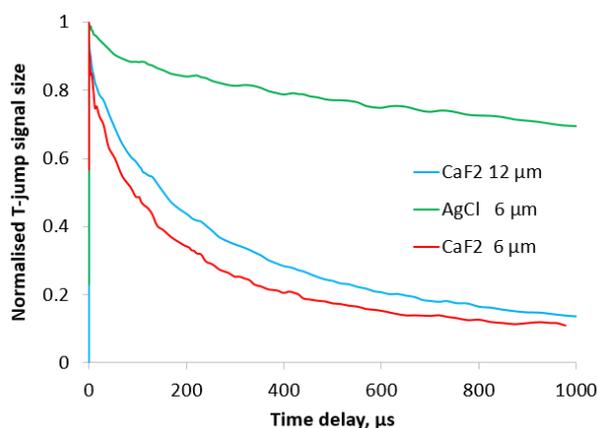


Figure 2. Kinetics of TFA T-jump signal change for different cell windows and sample path-lengths.

Results

While the TFA signal grows in magnitude on the timescale of the pump laser pulse ($\sim 1\text{ ns}$), an important aspect of the T-jump capability, is how long the raised temperature lasts, and so how long one can follow kinetics of a temperature induced-change. Here we have studied the effect of sample path-length and window material on the temperature recovery, aiming to slow the process by insulating the cells and increasing the volume of the sample.

The thermal conductivity of the CaF₂ windows (9.71 Wm⁻¹K⁻¹) typically used in time-resolved IR spectroscopy is high, compared to water (0.592 Wm⁻¹K⁻¹), so it is to be expected that the heat is lost in the direction of the windows. AgCl has a much lower thermal conductivity (1.15 Wm⁻¹K⁻¹) than CaF₂, so is expected to significantly slow this heat loss. Indeed, fig. 2, shows the extended lifetimes of T-jump signals, from < 100µs decay in CaF₂ cells to several milliseconds in comparable AgCl cells. However, one can see from fig. 1, that there is a lower T-jump signal and a significant oscillation across the spectrum when using AgCl. This is attributed to the higher refractive index of the AgCl (2.0), compared to water (1.3) and CaF₂ (1.4). The water and CaF₂ indexes are lower and comparable, minimizing the reflections at each surface. With AgCl, reflections at each surface reduce the pump power and generate an interfering etalon-like effect on the light passing through, leading to the spectral modulation we observe. This and other issues of the AgCl material, its softness and reactivity, mean it is unfortunately not well suited to use in these cells.

Figure 2 highlights the slower temperature recovery in thicker cells, when comparing 6 and 12 µm path-lengths. This is attributed to the fact that, following pumping, more of the heat is stored away from the windows in a thicker cell. Therefore, it must pass from the bulk to the surface, where the window's higher thermal conductivity accelerates the heat loss. Modelling suggests that the temperature recovery is proportional to the square of the path-length³. However, while increasing the path-length has the effect of slowing temperature recovery, the heated initial sample volume is larger. This means that the heat is diluted, and so the T-jump magnitude is reduced.

Summary

We have briefly described our recently developed T-jump apparatus and our work to control temperature recovery time following the T-jump. While fast recovery times are good for cycling the experiments at high repetition-rate, many large biomolecules of interest have dynamics timescales of 100's of microseconds and beyond. Therefore, we show how one might optimize experiments for different samples.

When considering the cell path-length, we observe an increase in temperature hold time with increasing thickness. In these experiments, a 6 to 24 µm path-length variation can increase the temperature decay time from < 50 µs to near 1 ms. While the thicker cells can access a wider range of kinetics, they unfortunately have lower T-jump magnitude. An additional consideration of a longer T-jump recovery, is that the experimental repetition rate has to be decreased, reducing signal-to-noise.

We show that insulating the sample, using low thermal conductivity windows, has the effect of slowing temperature recovery. Over an order of magnitude increase in T-jump lifetime was observed for AgCl windows in place of the usual CaF₂. While this is an exciting demonstration, the AgCl material is not well suited to these experiments, due to its high refractive index, softness and reactivity.

Acknowledgements

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