Implementing Time-Resolved EXAFS in a
Laser-Pump SR-Probe Experiment

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INTRODUCTION

Over the last ten years there has been a tremendous development aimed at probing in "real-time" photoinduced structural modifications for various types of systems. This has been possible thanks to the advent of pump-probe femtosecond spectroscopy. In these studies, an ultrashort optical pulse (the pump pulse) initiates a dynamical process in the system and dynamics is subsequently inspected by a delayed optical probe pulse. Both the excitation and the probing rely on an *a priori* knowledge of the spectroscopy (energy, intensity and lineshape of bands) of the system under study. Unfortunately, spectroscopic data are not easy to translate to atomic coordinates, except in a few rare cases. In addition, the spectroscopic properties of a system become less and less system-specific when the latter grows in size (e.g. biological molecules or condensed phases). On the other hand, crystallographic techniques such as x-ray or electron diffraction and x-ray spectroscopic techniques such as EXAFS (Extended X-ray Absorption Fine Structure) or XANES (X-ray Absorption Near-Edge Structure) have proven to be powerful techniques for structural determination of biomolecules and condensed matter with high spatial resolution. Diffraction techniques probe long range order in a periodic structure, while X-ray absorption techniques (EXAFS and XANES) or diffuse scattering (in liquids) probe local environments around a given atom. Inversion of the data to atomic coordinates is in addition possible. Therefore, in this project we aim at combining the direct inversion advantages of these x-ray absorption techniques and their high spatial resolution with the high temporal resolution of ultrafast pump-probe techniques [1]. This necessitates a tunable source of intense ultrashort x-ray pulses, which is provided by synchrotron radiation. In order to demonstrate the feasibility of this technique, we have decided to single out a system that has a kinetic process resolvable with the pulse duration of synchrotron x-rays (tens of picoseconds): molecular iodine in liquid solvents.

EXPERIMENT AND INITIAL RESULTS

Last November, we performed a laser-pump x-ray probe experiment at beamline 7.3.3. of the ALS, which delivers x-ray photons in the 2-12 keV region. The fs laser system of the beamline is synchronized to one single bunch in the camshaft mode, which enables laser pump x-ray probe performance at 1 kHz. The single camshaft pulse of interest is detected with a fast avalanche photodiode behind the sample and is electronically singled out via a 1 kHz triggered and gated boxcar integrator.

With this set-up we have chosen I_2 in solution as our test system. The strategy is to excite I_2 into the predissociatiove B state (Fig. 1) and monitor its stabilisation in the weakly bound A state, before the system relaxes back into $v'' = 0$ of the ground state. The L_1 5p hole (pre-edge) resonance was chosen as the probe, since we expect the 2s$\rightarrow$5p overlap conditions to change in a sensitive manner with varying internuclear separation.

Figure 1: Relevant potential energy surfaces of iodine in the condensed phase. The vertical arrow indicates the photoexcitation process, and the dotted arrows show the main relaxation pathways back to $v'' = 0$ of the ground state: 1) predissociation, 2) caging, 3) electronic relaxation and, 4) vibrational cooling.
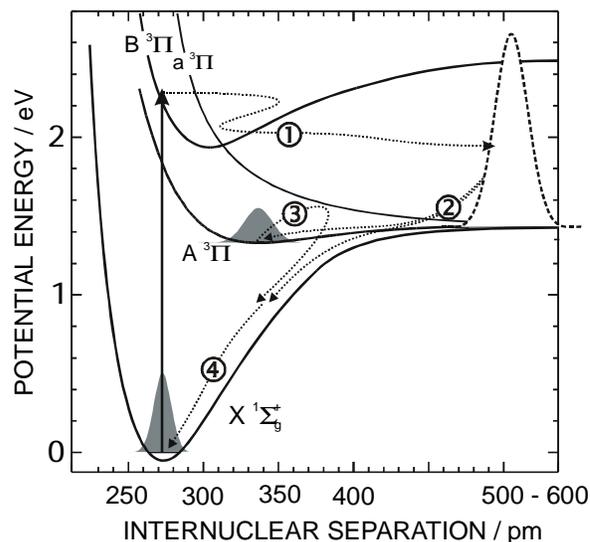
The laser system delivers pulses at the fundamental around 800 nm and the frequency-doubled output around 400 nm. The latter corresponds to an extremely weak I_2 optical absorption cross section of ca. 6×10^{-19} mm^2 in the gas phase and in non-polar solvents (2-3 orders of magnitude weaker than at the Franck-Condon maximum at 530 nm). However, in polar solvents the Franck-Condon maximum is blue shifted down to ca. 430 nm, which enhances the I_2 cross section at 400 nm by ca. 3 orders of magnitude. We have therefore used ethanol as I_2 solvent, although the time scales for relaxation back to the ground state were unknown for this system.

In our test run white light from the bend magnet penetrates the sample and is monochromatized by a Ge(111) crystal into an avalanche photodiode. Absorption spectra are derived by measuring the photodiode signal with and without sample (a 0.3 mm thick liquid jet in He atmosphere), and normalisation yielded spectra such as shown in Fig. 2.
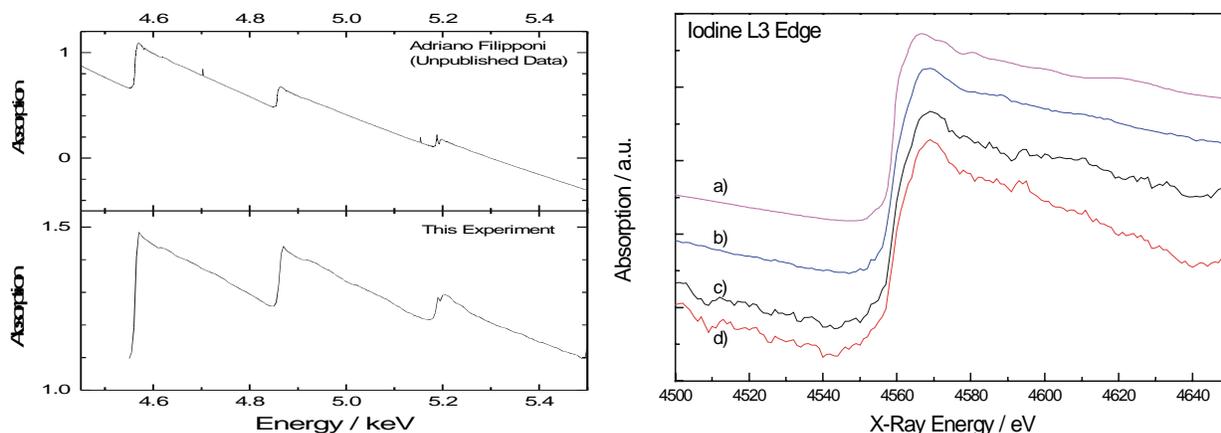

Fig. 2: Left : Static X-ray absorption spectrum of I_2/ethanol taken via a gated boxcar (15 μs gate width) and triggered with the laser repetition rate of ca. 1 kHz (bottom) compared to an EXAFS spectrum (top). Right : L3 edge of iodine, a) EXAFS from Filipponi et al., b) 10 μs gated spectrum, c) and d) 50 ns gated spectra (all at 1 kHz), c) with laser pump pulse (delay 0), d) without laser pulse (delay –550 ns.

In these experiments we employed our electronic chopping capabilities, which allows selection of a single bunch at the laser repetition rate of 1 kHz. The quality of these spectra can still be improved, but are in principle limited by the x-ray flux. Spectra b), c) and d) in Fig. 2 (right) were taken simultanously in the laser pump-SR probe experiment by running the APD signal in parallel through 3 boxcar integrators. Spectrum b) was obtained by setting the gate width to 10 μs, while both c) and d) only accepted the camshaft single pulse (via a 50 ns gate width). c) was synchronized to the laser, and the gate in d) was shifted to the single camshaft pulse 550 ns *before* the laser enters the sample. With these devices we have ample control over the experiment. In a next step, we will introduce a Lock-In amplifier referenced to an additional laser chopper at ca. 100-400 Hz, which should aid in reducing the noise.

Even though we managed to have both laser and x-ray pulse on the sample, we did not detect photo-induced changes. A possible reason is a relaxation process much faster than the x-ray pulse width. To check the latter, we have performed a one-colour laser-only pump-probe experiment to measure the relaxation time of photoexcited I_2 back to the ground state in ethanol (see Fig. 1). While our attempt to observe the stabilisation within the A state with its much larger internuclear seperation via EXAFS is feasible for nonpolar solvents due to their well known longer relaxation times (in the 100 ps to several nanosecond time scales, depending on the sovent), we had to determine the time scales for I_2/ethanol experimentally. Fig. 2 shows that the very fast recovery of ground state I_2 occurs within picoseconds, which explains our failure to observe a photoinduced absorption change. Improvements underway include a new double crystal monochromator at 7.3.3., an improved dye circulator for different I_2 solvents (e.g., hexane), and optimized data acquisition electronics.

Fig. 2: Pump probe experiment of a 0.3 mm sample I_2/ethanol (5g/l concentration) with 400 nm pump (25 μJ) and 400 nm probe (10 μJ).
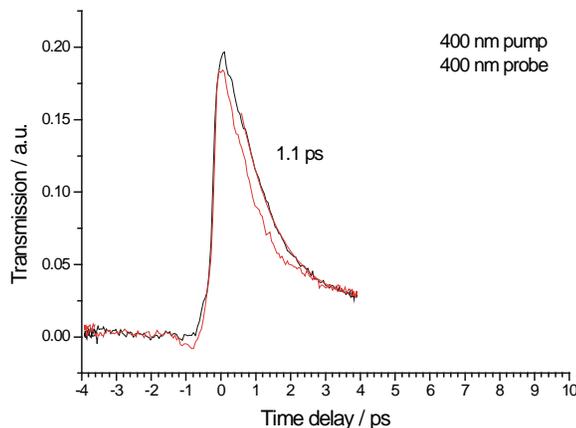
ACKNOWLEDGMENTS

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