Chemical Dynamics Applications Exploiting the Femtosecond X-Ray Beamline 5.3.1

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INTRODUCTION

Time-resolved x-ray absorption spectroscopy is a challenging new technique because of the low x-ray fluxes available in a pump-probe scheme with fs lasers. In order to achieve a reasonable degree of excitation in a given sample only amplified laser pulses with several tens of micro-Joules are useful, which have reduced repetition rates in the 1 kHz range. We have therefore assessed the feasibility of key experiments on simple condensed phase systems [1] in a setup optimized for laser-pump x-ray probe experiments at the Femtosecond X-Ray Phenomena Beamline 5.3.1 currently in commissioning phase. The described results are also used to check the utility of a recently proposed extraction undulator beamline for femtosecond-sliced x-rays.

EXPERIMENTAL SETUP AND MODEL SYSTEM

The experiments were performed at beamline 5.3.1 of the ALS-Berkeley, which is equiped with 2 amplified fs-laser systems with adjustable repetition rates between 1 and 5 kHz. The amplified laser pulses are synchronized to the single-bunch rf. The electron bunch pattern in the ALS camshaft mode consists of a multibunch train followed by an empty section filled with one single pulse (Fig. 1). With suitably fast detectors and subsequent electronics this camshaft pulse can be recorded without any multibunch contributions. It is thus well suited to be exploited in the pump-probe scheme. The sample, NaI/H_2O solution, is flown through a sapphire jet generating a flat sample surface with a thickness of d = 0.1 mm inside a He-filled sample chamber. With a frequency-tripler we have obtained the required UV laser light for this pump-probe experiment.

Iodine photogeneration in aqueous solution was chosen as a model system to advance towards condensed phase dynamics due to the following properties [1]: It exhibits strong x-ray absorption cross section changes between ground and excited states at the iodine L1-edge (5.2 keV), one-photon activation with UV light is very efficient, and we find useful time scales for time-resolved XAS ranging from the femtosecond to nanosecond regions.

LASER PUMP PROCESS AND PROBING WITH 100 ps X-RAY PULSES

A UV laser pulse excites an electron to a short-lived charge-transfer-to-solvent (CTTS) state, which escapes into the solvent within 300 fs [2]. The nascent iodine radical survives geminate recombination for several hundred picoseconds with a probability of Φ = 0.25. The optical absorption cross section ($\sigma_{opt} = 6 \times 10^{-17}$ mm^2) is large enough to allow near-complete absorption of the 0.8 mol/l I^-/H_2O solution. We have measured undesired absorption losses in a neat water jet and verified that they are due to solvent-surface reflectivity and nonlinear (2-photon) absorption of the solvent. We had routinely achieved 50 μJ of 256 nm laser light, and sometimes even above 80 μJ. Fig. 2 displays the

nonlinear absorption losses in water as a function of focal diameter. It can be seen that for foci well above 100 µm these contributions are not large. This translates to a laser intensity of 3 TW/cm^2 (for an assumed laser pulse width of 200 fs at 256 nm) for which UV experiments in aqueous solutions are not hampered by undesired laser intensity losses. We also measured nonlinear losses in water with 400 nm light, which allows somewhat higher intensities around 6 TW/cm^2 to be used.

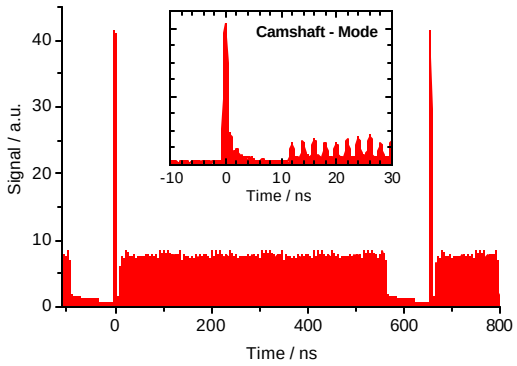

Figure 1: Oscilloscope trace from a fast photodiode recording visible light available at beamline 5.3.1 for timing and synchronization purposes.

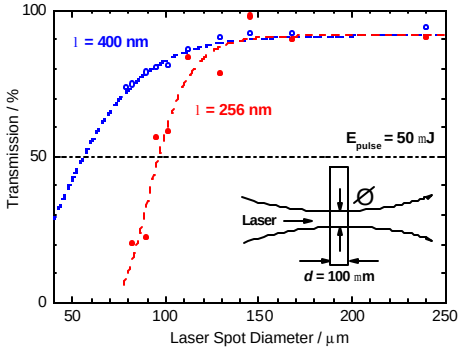

Figure 2: Nonlinear absorption losses in neat water (d = 0.1 mm) as a function laser focus (E = 50 µJ). Laser wavelengths are as indicated.

A fast large-area APD is placed behind the sample and records the ALS multibunch train. In order to single out the x-ray pulses associated with the pump laser, we have utilized two different schemes: 1.) With a gated integrator triggered to the laser source we acquire an amplified output of the integrated pulse form. 2.) Alternatively, we have employed a triggered track-and-hold-device to deliver an amplified output of the pulse height maximum of every selected single x-ray pulse. Both methods delivered similar pulse height distributions as the one displayed in Fig. 3.

The measured distribution for single x-ray pulses consists of the shot-noise statistics of the incident flux and all noise contributions from the avalanche process of the APD itself to the subsequent electronics. The incident x-ray flux was measured to ca. 10^4 photons at 5 keV per pulse. The pulse height distribution is then 2.2 times larger than the shot noise value, if we correct the incident flux for the transmission loss through the sample (Fig. 3). This factor did not depend on the chosen signal-processing electronics, and could therefore be attributed to additional noise within the APD and the avalanche process. Further investigations are still underway. The achieved sensitivity is remarkably good. However, more severe experimental limitations reduce our sensitivity, which are discussed in the following section.

RESULTS AND DISCUSSION

We have attempted to measure photogenerated iodine radicals via the 2s → 5p transition below the iodine L1 edge, which shows up only for I atoms and not for the reactant iodide. To ensure optimum overlap conditions we have measured the x-ray focus at sample to be 0.35 x 0.25 mm^2 (h x v). A tightly focussed laser beam deposits its energy in a small volume, which leads to evaporation of the sample on a microsecond time scale. This feature serves us as a check of the spatial overlap on the sample after using x-ray pinholes for the coarse alignment. However, the small foci required for this check (ca. 40-60 µm diameter) were not useful in the actual pump-probe experiment, since this results in a reduced laser flux for the excitation process (Fig. 2).

A number of limitations still need to be overcome to obtain an ultrafast pump-probe signal. Figure 4 illustrates the contributions to our current model experiment on iodide photolysis. The diagonal

curve displays the required number of incident x-ray photons to observe the 2s → 5p transition as a function of excited species for a 0.1 mm thick sample with 0.8 mol/l NaI/H_2O, thus including all absorbing species. With 50 µJ pulse energy we can excite 16 % of the population within a 100 µm spot with 256 nm light. Probing the 2s → 5p transition with 100 ps x-ray pulses will only measure the surviving fraction of generated I atoms ($\Phi(I^0)$), while polarization issues allow only 1/3 of the remainder to be sampled (¦ , _ in Fig. 4). Solvent absorptions (Fig. 2) could contribute to as much as a factor of 2. However, including linear absorbers (I^-) will reduce this loss somewhat.

The main contribution reducing the photoexcitation yield stems from the large probe diameter. With 0.35 x 0.25 mm^2 x-ray focus we can not obtain a significant amount of excited species with 50 µJ focussed to 100 µm (denoted overlap in Fig. 4). However, screening out the x-rays to a residual width of 100 µm with an x-ray pinhole and consequently reducing the x-ray flux by a factor of 3, will still increase the sensitivity of this experiment (eliminating the overlap loss in Fig. 4). The present status of our experimental sensitivity (yellow region in Fig. 4) is therefore suitable to measure a photoinduced change by x-ray absorption. Femtosecond x-ray pulses (e.g., from 5.3.1) could measure the initially generated population, and possibly even sample dichroic contributions. Therefore, the required number of incident x-rays on the sample can be considerably reduced (2 orders of magnitude) against the current values required for 100 ps x-ray pulses. The proposed undulator for femtosecond-sliced pulses is expected to have a reduced pulse intensity by roughly the same amount. This suggests that successful experiments with the current source will most likely succeed on the ultrashort time scales with the proposed fs-pulse extraction undulator.

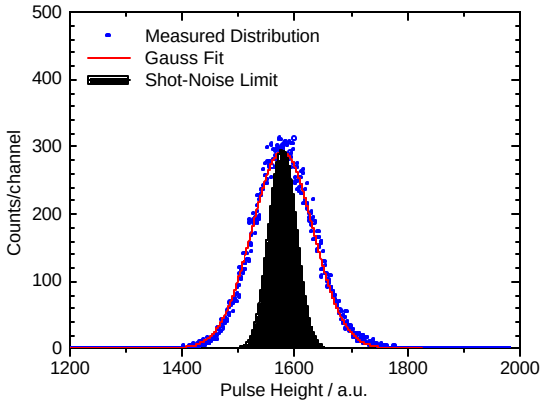

Figure 3: Pulse height distribution of recorded single camshaft pulses at 5 keV. The shot-noise contrubution is included for comparison.

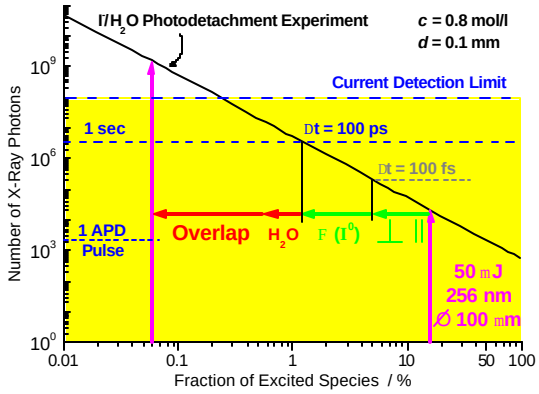

Fig. 4: Required number of incident x-ray photons to observe a pump-probe signal in the iodide photodetachment experiment for 0.8 mol/l concentration and sample thickness 0.1 mm.

REFERENCES

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