Time-Resolved X-Ray Absorption Spectroscopy: Photogenerated Halogen Radicals In H_2O Solution

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INTRODUCTION

The pump-probe scheme with ultrashort laser pulses is today the state-of-the-art technique to visualize structural modifications, on the atomic scale, in the sub-nanosecond time regime. Hereby structural dynamics are derived by transformation of the spectroscopic data via *a priori* known potential surfaces. In complex systems, such as biomolecules or condensed phases, this transformation becomes less precise due to the increasing number of degrees of freedom, which limits the applicability of UV-IR spectroscopic methods for elucidating structure.

Time-resolved crystallography is a young field which avoids these limitations. Hereby a laser pulse strikes the sample initiating the reaction under investigation, and a subsequent ultrashort x-ray pulse delivers a direct measure of the bond distances due to its diffraction angle. This extension of the pump-probe scheme into the x-ray region requires periodic structures to begin with, and in the experiment laser and x-ray damage during the course of an experiment limits its potential utility.

Time-resolved x-ray absorption methods are experimentally much more challenging than diffraction studies. On the other hand, they offer a variety of attractive advantages over crystallography: With EXAFS, local structural information around the selected absorbing atom can be obtained in a similar direct fashion (Fourier-transformation) than with diffraction. But now, one can work in disordered systems (no periodicity required), and, for the case of liquids, a flow geometry can refresh the sample ca. every 10-100 μs (no light-induced damage).

EXPERIMENTAL APPROACH

Therefore, we are currently working to establish time-resolved x-ray absorption techniques, such as EXAFS and XANES, and to apply this technique to complex reactions in the condensed phase. Herefore, we utilize a femtosecond laser synchronized to an x-ray beamline at a synchrotron storage ring. When interfacing a typical amplified fs-laser with a synchrotron, one has to match their very different repetition rates for the envisioned pump-probe scheme. We have accomplished this task via "electronic chopping" of the ca. 500 MHz x-ray probe source, so that only those x-ray pulses from the storage ring are recorded, that are preceeded by a laser excitation pulse with its much lower repetition rate in the 1 kHz range. This allows us to operate such experiments at any synchrotron source with a synchronized fs-laser, and we also avoid technically demanding equipment such as mechanical x-ray choppers for appropriate x-ray pulse selection [1].

The sample solution (see details below) is circulated through a liquid jet with 0.3 mm thickness. Both laser and x-rays are congruently focussed onto the jet, and a fast (100 MHz bandwidth) and sensitive (quantum yield ca. unity) avalanche photodiode (APD) detects the transmitted x-ray pulse train, which allows to single out the selected camshaft pulse. Accurate synchronisation between the laser and synchrotron (jitter less than 2-3 ps) allows to maintain a constant time delay between the amplified laser pulses (repetition rate 1 kHz) and one camshaft pulse every millisecond. Data acquisition occurs by splitting the APD pulse train and feeding two boxcar averagers, one gated on the camshaft pulse associated with the laser and one gated to the preceding x-ray camshaft pulse. This way we obtain simultaneously the transmission signal of both the laser-excited and the unpumped sample. We also derive the absorption spectra by normalizing the transmitted single bunch spectra
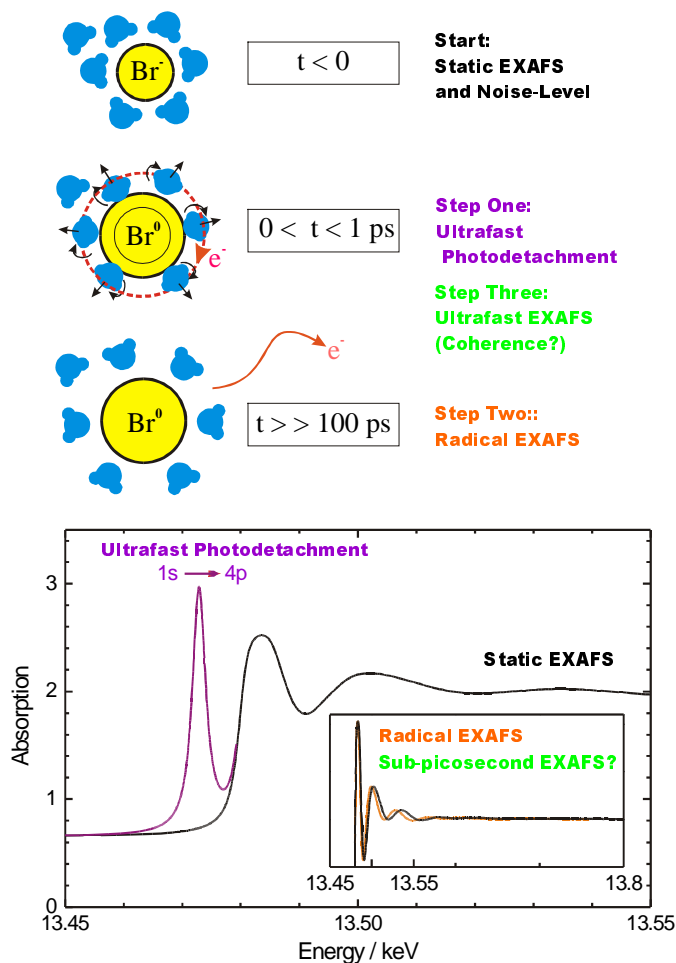
Figure 1: Scheme of the halogen ion photodetachment experiment for Br⁻ in H₂O solution. Below the expected pre-edge resonance is shown together with the static Br⁻ EXAFS. The inset zooms into the EXAFS, and a second curve is shown to illustrate the anticipated EXAFS upon laser photolysis.
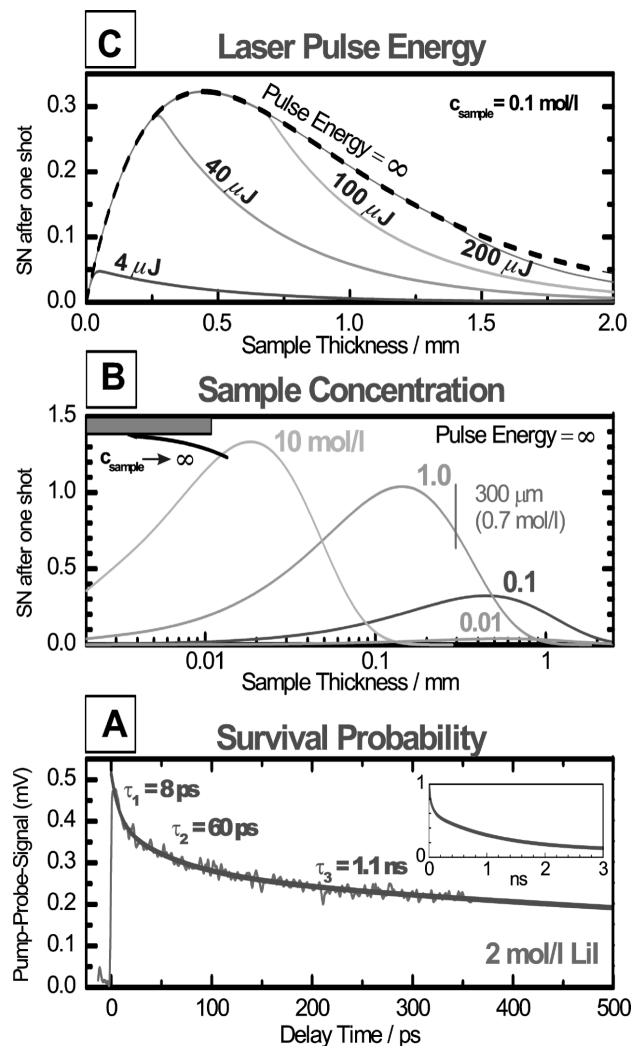
Figure 2: A) Experimental pump-probe spectrum showing the survival probability of photogenerated electrons (and thus of the nascent iodine radicals) as a function of time delay.
B) and C): Calculation of the signal-to-noise ratio (SN) for the time-resolved EXAFS study for different concentrations and laser pulse energies.

(=I_1-pumped and I_1-unpumped) with the averaged multibunch spectrum of an N_2 ion chamber upstream from the sample (=I_0), with less noise than in the transmission spectra.

Initial studies performed at ESRF-Grenoble and at beamline 7.3.3 of the ALS-Berkeley have established our detection scheme [2]. Experiments are generally operated in "stroboscopic mode", i.e., every probe x-ray pulse is accompanied by a laser pump-pulse. In addition, lock-in detection, with the lock-in amplifier referenced to the frequency of an additional laser chopper in the pump-beam path, is used to reduce the noise-level of the signal.

MODEL SYSTEM AND CURRENT RESULTS

We are currently focussing on a simple chemical test system in the liquid phase: Cl⁻, Br⁻ and I⁻ in solution (e.g., in water). In this system, the negative halogen ion (=X⁻) attracts the surrounding H₂O in the first solvation shell. The EXAFS is quite pronounced due to the large coordination number of oxygen atoms surrounding the ion (e.g., see Fig. 1 for Br⁻). A laser pulse will initiate the following reaction

$$X^- + h\nu \rightarrow X_{neutral} + e_{sol} \quad (X = I, Br, Cl)$$
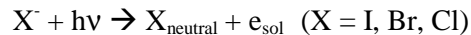
thus photodetaching the electron from the ion generating a nascent radical and a solvated electron. This ultrafast process will affect the environment, i.e., the caging H_2O molecules will rearrange around the X atom. A change in the X-O bond distance can thus be observed in the EXAFS region of the selected x-ray absorption edge.

The photodetachment process of I^-/H_2O will be detected at 5.2 keV (iodine L1 edge); for the other halogen ions we will exploit the K edge at 2.5 keV for Cl^-, and at 13.5 keV for Br^- (see Fig. 1). For L edge detection of iodine only light-weighted solvent atoms are allowed (e.g., H_2O), and one has to work in He atmosphere. The ultrafast removal of the electron from I^- will free a 5p hole for I. This valence state is easily detectable in the XANES region due to its huge absorption cross section, which even exceeds the edge absorption itself. Figure 1 illustrates this for the similar case of bromine: The 1s $\rightarrow$ 4p transition of Br is illustrated in the Lorentzian-shaped curve right below the absorption edge. On the same scale shown is the static EXAFS spectrum of Br^-/H_2O, which we recorded at BM29 of the ESRF last July 1999. The EXAFS is clearly pronounced. A similar effect can be expected for I^- according to our previous XAS measurements on I_2/ethanol at 7.3.3 from Nov. 98, where we observed this strong resonance right below the L1 edge [4]. After a long pump-probe delay (e.g., > 100 ps) we should monitor the EXAFS of the photogenerated neutral radicals.

While the response of the cage molecules occurs on an ultrafast time scale (and thus remain currently undetectable), the lifetimes of both the solvated electron and the radical are mainly diffusion-limited, once geminate recombination has terminated. In an optical pump probe experiment, the lifetimes (limited by geminate recombination) of the solvated electron following UV-photolysis of I^-/H_2O have been determined to 8, and 60 ps, respectively [3]. We observe the same dynamics in the Lausanne laboratory, together with the fact, that ca. 50 % of the population survive geminate recombination (Fig. 2 A). The latter 50 % recombine via diffusion of the I radicals and the electrons on a nanosecond to microsecond time scale, depending on concentration. With 2 mol/l, which approaches the solubility limit, we measure a non-geminate recombination lifetime of 1.1 ns. We have modeled the expected signal-to-noise ratio (SN) for observing the pre-edge resonance of iodine in H_2O under realistic pump and probe conditions. Fig. 2 B and C display a collection of results depending on the experimental parameters sample concentration and laser pump energy. For realistic experimental conditions we yield an optimal SN for ca. 0.7 mol/l concentration and 200 µJ laser pulse energy focussed to ca. 150 µm, which indicates a required data accumulation time of a few hundred ms per data point.

With this scheme we can study dynamical processes on the sub-nanosecond time scale, and we are currently only limited by the ALS x-ray pulse width of ca. 50 ps. Nevertheless, this test system will serve to assess the feasibility of ultrafast dynamic experiments, once ultrafast x-ray techniques (streak camera or fs-x-rays) become available.

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