Capturing Transient Molecular Structures with Laser Pump/X-ray Probe Time-Domain XAFS

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The goal of our ongoing research is to capture transient molecular structures involved in photochemical and photophysical processes, especially photoinduced electron and energy transfer in solar energy conversion and storage. The laser-pump, x-ray probe extended x-ray absorption fine structure (XAFS) experiments on a photodissociation intermediate of NiTPP-$(piperidine)_2$ were carried out at beamline 11-ID (BESSRC-CAT), under a special timing operation.

Figure 1. shows the schematic of the timing sequence of the experiment. The black peak is the laser pulse synchronized with the first of the six x-ray pulses in the pulse cluster (white peaks). A replica of the rf frequency of the synchrotron (352 MHz) is divided by 4 and connected to the mode-lock drive of a diode-pumped Nd-YLF laser (Lightwave), which seeds a Nd-YLF regenerative amplifier laser (Quantronix) at a 1-kHz repetition rate. The shaded profile represents the transient optical absorption obtained with the same 351-nm pump laser.

The Ni K-edge (8.333 keV) XAFS experiment was conducted. The energy of the x-rays was selected by a cryogenically cooled, fixed offset double crystal Si(220) monochromator. The x-rays were focused by a Pd toroidal mirror to a beam size of 0.5 x 1 mm^2 at the sample. A multi-element solid state Ge detector (Canberra) with a 0.25 μs shaping time was used to collect the fluorescence. The outputs from the detector amplifiers were fed to single-channel analyzers (SCA's), which were coupled to two scaler arrays, one gated with the laser pulses and the other ungated. The repetition rate of this experiment was limited by the laser at 1 kHz, which resulted in use of only 0.055% of the total flux. Therefore, the measurement took about 20 hours.

An XAFS experiment on photodissociation of the axial ligand of nickeltetraphenylporphyrin (NiTPP) in 1 mM solution was carried out. A laser pulse triggered the ejection of the axial ligand from NiTPP, creating an intermediate with a square planar coordination geometry of Ni. The x-ray superbunch, containing 6 consecutive pulses with a time span of 14.2 ns, probes the structure of this intermediate with a lifetime of 28 ns.

We have successfully captured the XAFS spectrum of the intermediate on a nanosecond time scale. The result provides for future opportunities for time-domain structural determination.

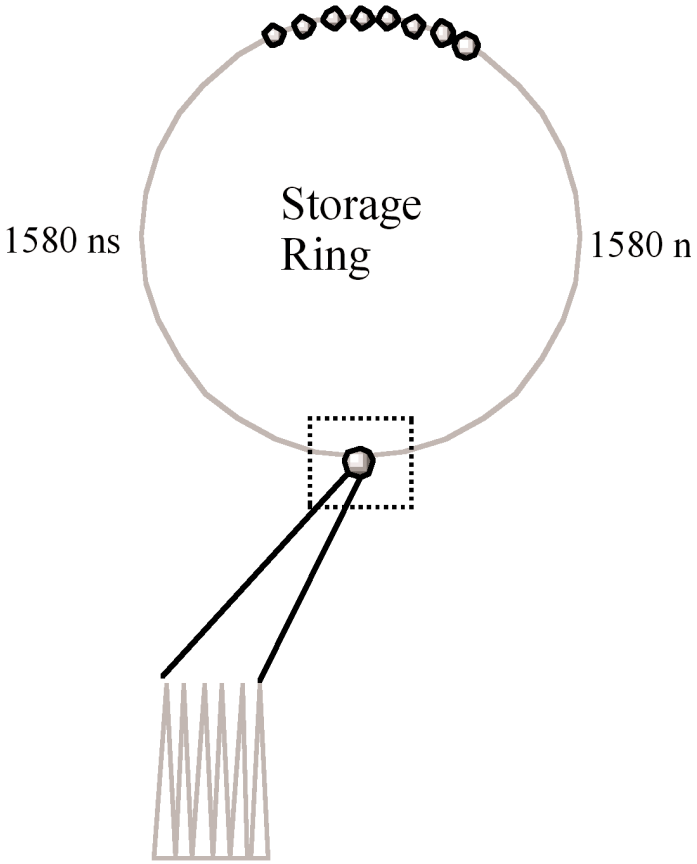

FIG. 1. Timing sequence of the pump-probe XAFS.

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