Laser pump, x-ray probe, time-domain XAFS study of transient molecular structures

Lin X. Chen*, David J. Gosztola*, Guy Jennings†, and Wighard J. H. Jäger*
**Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 USA*
†*BESSRC-CAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 USA*

Introduction

The goal of our ongoing research is to capture transient molecular structures involved in photochemical and photophysical processes, especially photoinduced electron and energy transfer, which are important for solar energy conversion and storage. Knowing the nuclear coordinates of reaction intermediates is important for fundamental understanding of reaction mechanisms and molecular reactivities. In addition, the structural parameters also serve as references for theoretical calculation.

Methods and Materials

During past years, we developed a laser pump, x-ray probe, and time-domain x-ray absorption fine structure (XAFS) facility at BESSRC-CAT (11-ID-D). The general description of the experiment is demonstrated in Figure 1.

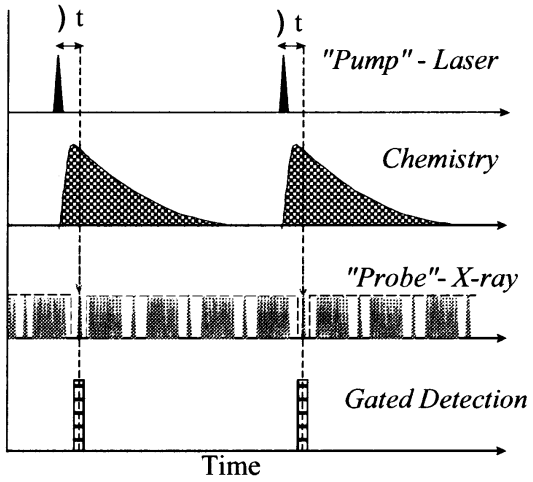

Figure 1: Time sequence of the experiment.

A photochemical process is triggered with a laser “pump” pulse followed by an x-ray “probe” pulse(s). Transient molecular intermediates are created by the laser pulse and their structures are probed by x-ray pulse(s) when their optimal population is reached. Thus, the structural information on the transient state can be obtained. At present, an x-ray shutter is not yet implemented. The multi-element x-ray detector is gated for the x-ray pulse(s) that overlaps with the laser in time and space. The layout of the experimental facility is shown in Figure 2. One of the key obstacles of the experiment is incompatibility between the repetition rates of the laser and the x-ray. To convert a high fraction of the molecules to the transient state, a reasonably high pulse energy of the laser is required, which limits the repetition rate of the laser to a few kilohertz, whereas the repetition rate of x-ray pulses are on an order of 10 MHz. This implies that only less than 1/1000 of the total x-ray photons can be used to probe the transient molecular structure. The other key issue is gating those x-ray pulses that only overlap with the laser pulses. In our setup, the detector gating requires over 1 μs separation on each side of the x-ray pulse that overlaps with the laser. Therefore, the special operating mode (SOM) of Advanced Photon Source is necessary for the operation.

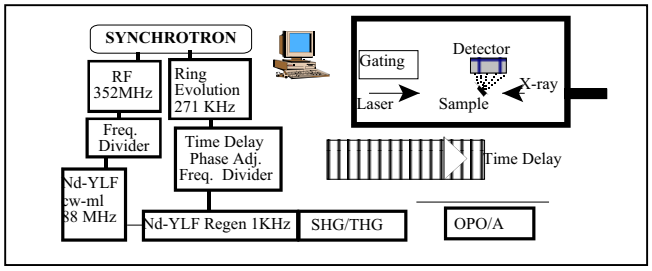

Figure 2: Synchronization and time-domain XAS setup.

Results

During the SOM operation (6 + 8 x 7) September 21–29, 1999, we successfully obtained an initial x-ray absorption near-edge structure (XANES) at the Ni K-edge for a sample of 2 mM Ni in piperdine solution with a nine-element Ge detector gating with the sextet at 1 KHz, providing a 14 ns time resolution. Preliminary XANES spectra proved the feasibility of the experiment where the x-ray flux is reduced by a factor of 1,500 at the wiggler beamline. The gated XANES spectrum synchronized with the laser at 1 KHz is shown in Figure 3.

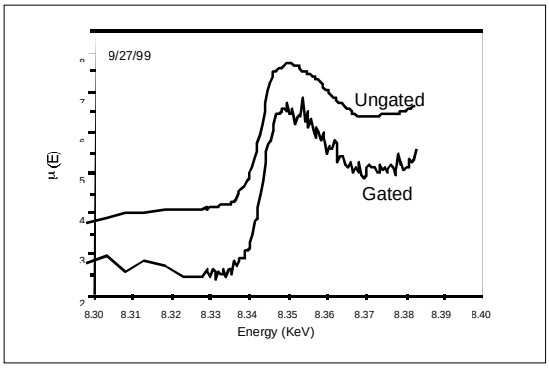

Figure 3: Preliminary XANES obtained at Ni K-edge for $NiTPP(piperdine)_2$ with and with out grating of the detector. The ungated spectrum is the sum of three scans and the gated is the sum of nine scans collected within one hour.

Acknowledgments

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