

# First microsecond time-resolved XAFS

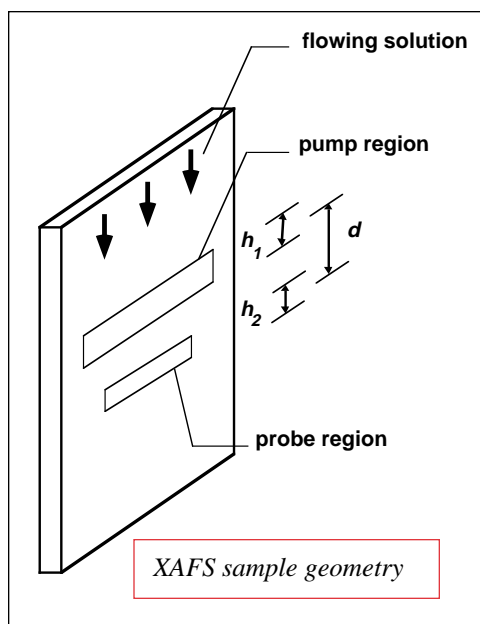
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We have recently completed the first microsecond x-ray absorption fine structure (XAFS) measurement, which is the best temporal resolution ever obtained with this technique. This experiment required both a new experimental method as well as a new method of XAFS data analysis. In collaboration with P. Livins (Western Washington Univ.) and E. A. Stern (Univ. of Washington) and A. Lewis (Cornell and Hebrew Univ.), we studied the triplet excited state of the inorganic complex  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^+$ . For the first time, a direct structural method has been used to determine the molecular structure of an electronic excited state, thereby allowing us to obtain unprecedented structural detail of a transient excited-state molecule. The 1- $\mu\text{sec}$  resolution of the technique has broad applications to chemistry and biology since many molecules display interesting photo-induced changes on such a time scale.

Our technique combines XAFS and rapid-flow laser spectroscopy. Flow spectroscopy has been used in Raman spectroscopy but never combined into an XAFS measurement. In our technique, the solution containing the molecule of interest is passed through a nozzle to form a free-standing jet, similar to that of a dye laser. The flowing sample (see figure) is excited by focussing the laser onto the jet, and the x-ray beam is subsequently directed at the jet downstream of the laser focus. The spatial separation of the laser beam and the x-ray beam  $d$  translates directly into a time delay  $t=d/v$  with the velocity of the flowing sample given by  $v$ .

To achieve microsecond time resolution, both the exciting laser beam and the probing x-ray beam

must have small spatial dimensions along the flow direction, denoted by  $h_1$  and  $h_2$ . These values are typically  $10\mu\text{m}$  in order to limit the time in which the flowing molecules reside in the beams. This condition on the x-ray beam puts a premium on maximizing the available x-ray intensity (flux/unit area). Our data was collected on the A2 station using a sagittally focussing monochromator to focus the synchrotron beam horizontally. Due to restricted space, no vertical focusing was used. Although the A2 station is relatively large, space was restricted primarily due to the installation of a high-power (25 W in the visible / 5 W in the ultraviolet)



argon ion laser inside the hutch, along with the various optical components.

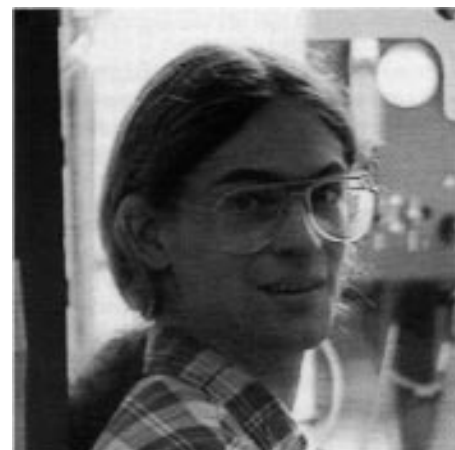
While flowing the molecules at a velocity of about 15 m/sec, or 32 miles/hour, we excited the sample with 0.75 W of laser light which excited about 18% of the illuminated  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^+$  molecules into the triplet state. By reducing the time delay to 0.8  $\mu\text{sec}$ , we easily observed the triplet state which had a 4- $\mu\text{sec}$  lifetime in our aqueous glycerol solution.

The fluorescence x-rays from the Pt  $L_{III}$  absorption edge were collected at a count rate of 2400 cps.

The analysis begins by comparing the excited state to the ground state (no laser) data. We subtracted the post-edge background using a procedure developed by the U. of Washington group. We found it beneficial to use the results of the proven computer code FEFF developed by the group of J. J. Rehr (U. of Washington) to calculate the XAFS amplitudes and phases.

From our analysis, we have been able to determine the change in three of the molecule's radial parameters upon excitation to the triplet state. This determination indicates that the molecule undergoes an overall contraction when excited. Our technique has allowed us to determine the contracted values with a precision as small as  $0.01 \text{ \AA}$  although the errors in our parameters are large, typically 20%.

By accomplishing the first  $\mu\text{sec}$  XAFS measurement, we have obtained the first XAFS data from an electronic excited state. We expect many more interesting results will emerge from this powerful technique especially in regard to biological molecules. Finally, we are developing better x-ray focusing devices such as tapered glass capillaries to improve this type of measurement.



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