

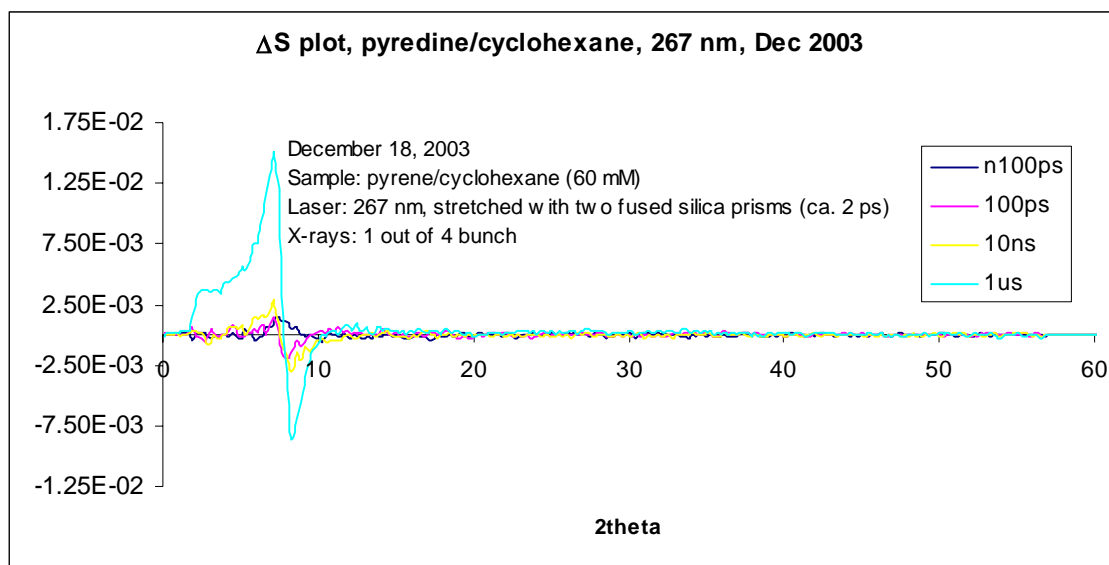
CH-1547. Time-resolved x-ray diffuse scattering of pyridine in solution

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We proposed to conduct time-resolved x-ray diffraction experiments on liquid samples of pyridine using femtosecond (fs) laser pulses at the ID09 beamline and 100 picosecond (ps) x-ray pulses in single-bunch mode and/or 16-bunch mode. The aim of this experiment was to identify the structural nature of the transient species responsible for the “channel three” nonradiative process in solution and to compare it with that in gas phase. A total of 15 shifts were allocated during December 3 to December 8, 2003.

Before we launched the pyridine experiment, the effect of two-photon process due to the intense fs laser pulse had to be characterized, and Br₂, a molecular system much simpler than pyridine, was actually used for this purpose. The sample dissolved in methanol was circulated through a capillary. In the first excitation scheme, the usual fs laser pulses out of the TOPAS OPA laser were used to excite the sample without any stretching, and time-resolved data were collected at six different laser powers. Then the magnitude of the difference signal was plotted against the laser power. The slope was larger than 2, indicating that the two- or higher- photon processes are dominating when fs laser pulses were used. In the second excitation scheme, the fs laser pulse was stretched to ca. 2 ps by passing it through two fused silica rods, and again time-resolved data sets were obtained for five different laser powers. The slope in this case was indeed 1, which means that the multi-photon process is essentially suppressed and the dynamics reflected on the diffraction signal is due to the one-photon process. Once this issue of the multi-photon process was resolved, then the pyridine solution was studied.

Cyclohexane was used as solvent and the pyridine solution was circulated through the capillary to provide a stable flow. The concentration of 60 mM was chosen to maximize the possible ratio of the photo-products while keeping the inter-solute contribution negligible. On the basis of the test experiment with Br₂ solution, the fs light was stretched to ps to avoid multi-photon processes, and data sets at five time delays (-3 ns, -100 ps, 100 ps, 10 ns, 1 μs) were collected. The data point at -3 ns serves as a reference point and one more negative time delay at -100 ps was collected to make sure that the timing setup was correct (No signal should be observed at a negative time delay). Figure 1 shows the difference diffraction signal. We made an interesting observation; the high-angle region is essentially flat. This means that the structural change within the solute molecule, that is pyridine, is absent.



The previous molecular systems studied with the time-resolved diffraction technique all involved bond-breaking of the solute molecule. In contrast, it seems that pyridine does not result in the photo-product with a dissociated bond at least after 100 ps. This is in stark contrast to the result of ultrafast electron diffraction in the gas phase. This means that pyridine absorbs the photon and converts the photon into heat without any structural change within itself, at least to our time resolution of 100 ps. Therefore, the difference signal is solely due to the change in the bulk solvent. In addition, in the figure, one can see that there are isobestic points, curve crossings which don't move with time, indicating that the difference signals are combinations of two time independent components. A thermodynamic consideration and our experience with other liquid experiments immediately lead us to the conclusion that these two components are the pressure derivative and the temperature derivative of the solvent scattering intensity. In other words, the difference signals at early time delays correspond to the pressure derivative and the signals at late time delays represent the temperature derivative. The signals between these two extreme time delays are linear superposition of the two.

This unique property of pyridine, as a heat source, can therefore be utilized not only to study the time-dependent heat expansion of the solvent, but also to extract experimental pressure and temperature derivatives of the solvent scattering intensity.