

CH-1746. Determination of transient structures during photolysis of $\text{Fe}(\text{CO})_5$ in solution

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We have conducted time-resolved X-ray diffraction experiments on $\text{Fe}(\text{CO})_5$ in liquid methanol on beamline ID09B using femtosecond (fs) laser pulses and 100 picosecond (ps) x-ray pulses from the 16-bunch mode. A total of 12 shifts were allocated from December 11 to December 14, 2004. After 267 nm photo-excitation, $\text{Fe}(\text{CO})_5$ dissociates into $\text{Fe}(\text{CO})_4$ and CO. Depending on its spin state, $\text{Fe}(\text{CO})_4$ is expected to have different geometries and internuclear distances. One of the primary goal of this experiment is to determine the spin state and the molecular structure of $\text{Fe}(\text{CO})_4$ in solution and to compare the data with *gas-phase* optical spectroscopy and electron diffraction.

Before conducting the main experiment, we tested a new flow cell. In the previous set-up, a 300- μm diameter capillary, mounted on the goniometer, was used to circulate the sample. A new open-jet nozzle, composed of two flat sapphire crystals with a spacing of 300 μm , creates a very thin and naked liquid jet. The main advantage of the open-jet is that the open-jet does not give any background from the capillary material, thereby increasing the effective signal to noise. A HgI_2 in methanol sample was used in a test experiment of the new jet and the data compared with the equivalent capillary experiment. Time-resolved data were collected at several time delays. Then each diffraction image was processed. There were no outliers during 10 cycles (2-3 hours of experiment) and the jet was very stable. Moreover, the solvent response signal ratio at the 1 μs time delay was 2 times greater than in the capillary, which means that the dissociation yield and the relative signal were enhanced in the open-jet. Once the performance of the new flow system was clarified, the $\text{Fe}(\text{CO})_5$ solution was studied.

The concentration of 60 mM was chosen to maximize the photoproduct to solvent ratio while keeping inter-solute interactions negligible. Based on our experience in previous liquid experiments, we stretched the fs laser to 2 ps to avoid multi-photon absorption, and data sets at five time delays (-3ns, -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 time zero was correct. Figure 1 shows the radial difference signal. To extract the structural change from the diffraction signal, the difference signal $\delta S(q, t)$ was generated by subtracting the reference data (-3 ns) from the data at each time delay. Figure 1 shows the difference diffraction signals at each time delay.

We observe two interesting features by inspecting figure 1. First, the difference diffraction signal in the low- q range at the earliest time delay 100 ps is remarkably different from that of the latest time delay 1 μ s. This indicates that the signals in the low- q range at 100 ps cannot be due to the solvent response alone. The negative signal at 100 ps can roughly be assigned to the dissociation of $\text{Fe}(\text{CO})_5$ and the formation of a new product (for example, recombination of $\text{Fe}(\text{CO})_4$ and solvent, respectively).

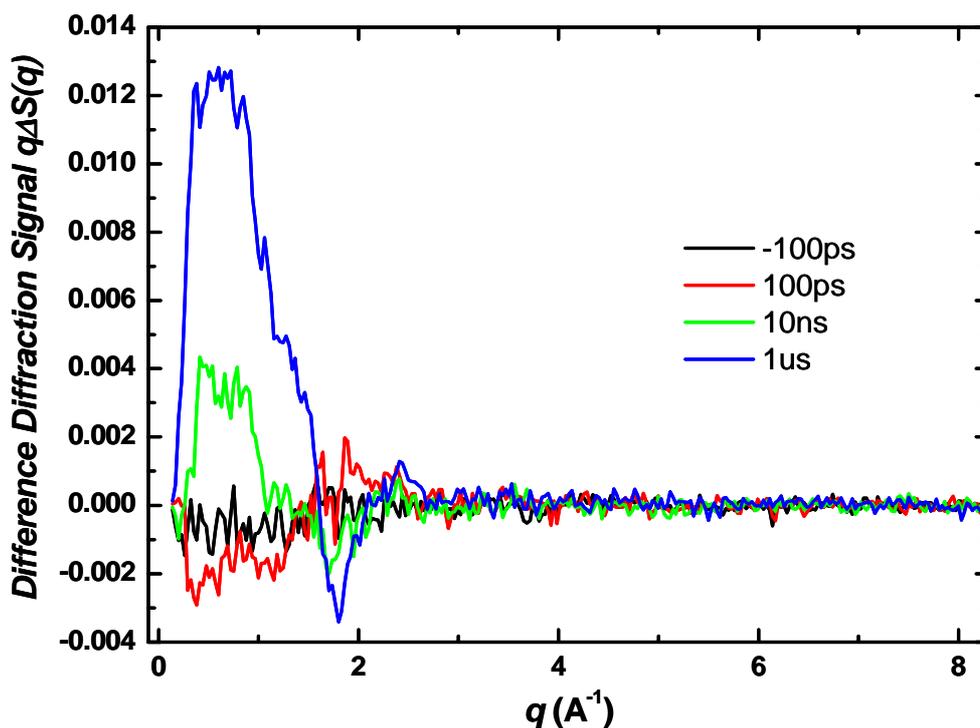


FIGURE 1 : Time resolved difference diffraction signal for $\text{Fe}(\text{CO})_5$ in MeOH

Secondly, the high-angle region at 100 ps seems to be flat. This feature indicates that the structural change of $\text{Fe}(\text{CO})_5$ is minimal or too weak to be detected with our S/N ratio. Another possibility is poor photon statistics. During the measurement, the cooling unit of the Chirped Pulse Amplifier (CPA) was out of order. So, we did not have enough time to collect more cycles and we ended up averaging only 3 cycles at each time delay. Even though the signal level is low in the high- q range, there are oscillatory features at all time delays.

Although we need to do more time-resolved diffraction measurements on $\text{Fe}(\text{CO})_5$ in solution, we can conclude the following. Using the new open-jet, we have made a first structural investigation of $\text{Fe}(\text{CO})_5$ in solution. Unlike the pyridine molecule, there is clear evidence of structural changes at low q . The signal in the high- q range can be

attributed to poor statistics. To get a clearer picture of the structural change, we need more beamtime. This will offer a good opportunity to test the sensitivity of *state of the art* time-resolved X-ray diffraction techniques in liquids.