

CH-1645. The photoreaction of 1,3-cyclohexadiene in solution by time-resolved X-ray diffraction

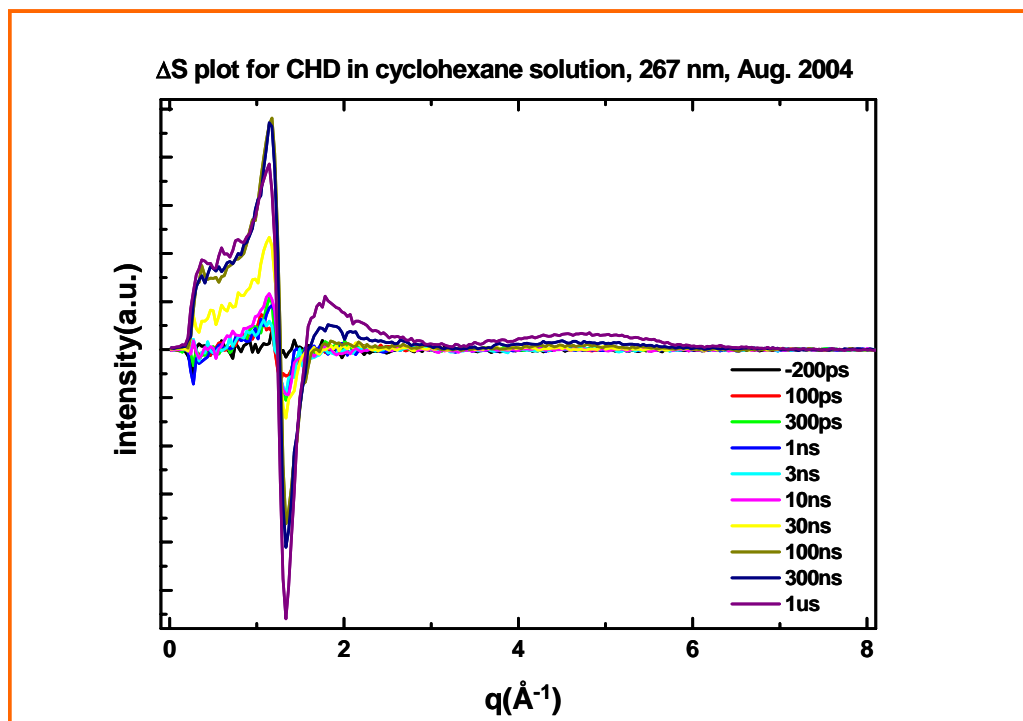
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Here we report our experimental results on the time-resolved X-ray diffraction experiments on the liquid samples of 1,3-cyclohexadiene (CHD), which were conducted at the ID09B beamline during 16-bunch mode in July and August, 2004. Total 21 shifts were allocated to this project. This project was proposed to elucidate the structural changes of the transient species in the ring-opening reaction of CHD and consecutive photo-isomerization process.

The typical pump-probe scheme was employed for time-resolved diffraction measurement where femtosecond laser pulses photoexcite samples to trigger the reaction and 100 picosecond X-ray pulses in 16-bunch mode from the synchrotron probe structural changes of a reaction. Before the measurement of diffraction data, the laser fluence should be limited to minimize multi-photon absorption. In previous attempt with pyridine solutions, we have checked the laser conditions of one-photon excitation scheme. The same excitation scheme and laser energy was used in this experiment. The 267 nm fs laser pulse, which is the tripling wavelength from a fundamental Ti:sapphire laser, was stretched to pulsewidths of ca. 2 ps by two fused silica rods. The range of energy from 45 μ J to 55 μ J at the sample was used. The sample solution (CHD in cyclohexane (60 mM)) was introduced and circulated through a quartz capillary (diameter = 300 μ m). Diffraction images in time-delay of -3 ns, -200 ps, 100 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 100 ns, 300 ns, and 1 μ s were collected. The time-delay of -3 ns was used as a control time point.

Figure 1 shows the difference signal of CHD in cyclohexane solution at various time-delays. From this, one can make interesting observations. In high q region which can reflect structural changes of the solute, the signal is very flat in early time delays. This raises two possibilities. First, it may mean that there is no nominal structural change in solute molecules in early time delays. The photo-excited CHD molecules decay to the ground state without any structural change. The energy released by the photo-excited CHD molecules heat the solvent and initiate thermal expansion. Such solvent responses are fingerprinted in low q region. The difference signal is due to the only solvent molecules. If this interpretation is correct, this finding in solution is remarkably different from that in gas phase by the electron diffraction. In gas phase, the ring-opening reaction is occurred by the excitation and related isomerization process

takes longer than few hundred picoseconds. In previous experiment of pyridine solution, we observed the similar result.



The second possibility is that the signal to noise ratio may not be good enough to extract the structural changes in solute molecules not having any heavy atoms. All solute molecules that showed a rather huge change in high q region contain heavy atoms such as Iodine. Any structural change involving this heavy atom results in a huge change in the diffraction pattern in the high q region. However, in hydrocarbons such as CHD, the structural change involves only light atoms. To resolve this small change, we need to improve the signal to noise ratio further.