Experimental report for CH1229.

The photo-physics of iodine in solution: determination of the recombination processes by diffuse X-ray scattering.

The aim of the experiment was to determine time-resolved Q-spectra of excited states of iodine in CCl4 and CH2Cl2. The iodine molecules were excited to the B-state by a 150 fs laser pulse at 515 nm and the dissociated molecules were probed by a delayed 150 ps x-ray pulse. The scattered x-rays were detected on a MARCCD detector centered on the incoming beam. The laser/x-ray pulse sequence was repeated at the frequency of the x-ray chopper, 896.6 Hz, and the scattering accumulated on the CCD. Now, the difference between" *laser on*" minus "*laser off*" patterns is a measure of the change in (average) electron density of the molecule and its environment (solvation cage). The experiments were done with pink-beam from the in-vacuum undulator U17, which was opened up 10 mm gap in order to produce a single-line of x-rays at 19.0 keV. The bandwidth of the pink beam is 2.5% and the intensity 450 times greater than a conventional monochromatic beam. In figure 1 we show three Q-spectra corresponding to delays at 100 ps, 10 ns and 1 µs. These spectra are fully reproducible and provide very detailed information. On the 100 ps curve for example, the high-Q region 4.7 – 8.7 Å^{-1} probes the change in the atomic/molecular structure of iodine. The oscillation period and amplitude can be interpreted by having 2% of the excited molecules in the X-state, 9% are in the elongated A/A'-state and 14% of the molecules dissociate into atoms. In the Q-range 2.0-4.7 Å^{-1}, it is the change in the size of the first solvation cage that dominates. There are two contributions: the expansion of the cage due to the stretched A/A' state and the collapse in switching from a molecular- to an atomic-cage. The modeling of these effects have been done in collaboration with Savo Bratos group in Paris by using molecular dynamics simulations. The fitting of the many time-points taken during the experiment is still in progress, but the initial results are very encouraging: the MD theory can essentially explain all the oscillations (period and amplitude).

Maybe the most striking finding in this experiment is the "explosion" at low Q at 1 µs. We assign this to thermal expansion of CCl4: as the molecules relax and the atoms recombine, their excess energy from the laser excitation is transferred to the solvent, which begins to expand. At 1 µs, the expansion is over and the solvent has reached thermal equilibrium at 2.3 K above the initial temperature.

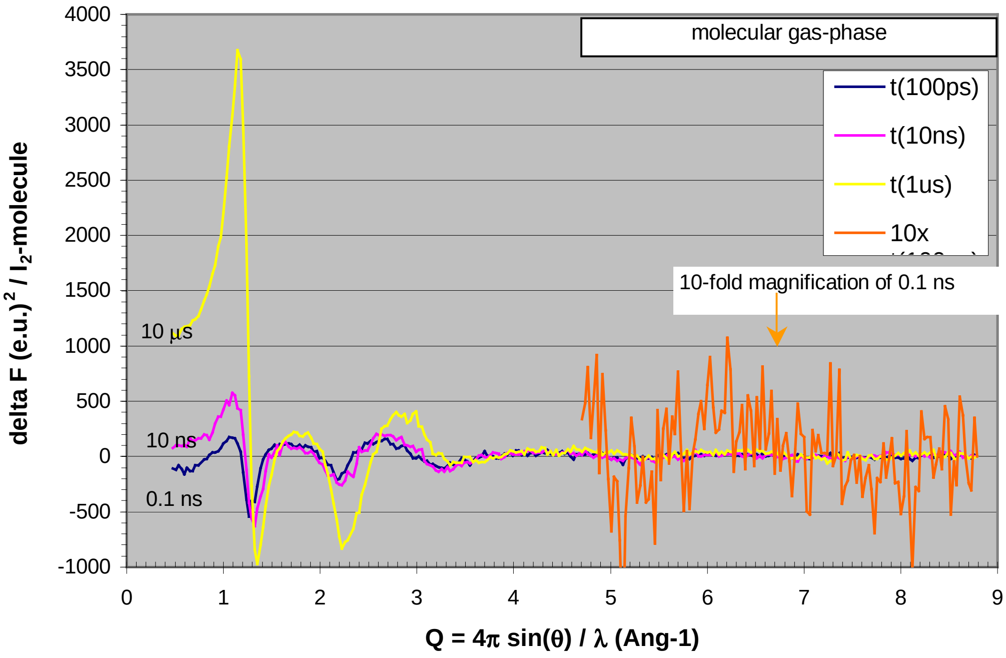

Figure 1: Difference spectra between *laser on* minus *laser off* of iodine in CCl$_4$