# Experiment Report (CH1746)
Photoreaction of pyridine in solution studied by picosecond x-ray diffraction

A number of time-resolved studies both in gas and in condensed phase have been dedicated to this molecule. Pyridine exhibits interesting features when excited with UV light above the first excited singlet state (S1), its fluorescence yield is dramatically reduced to the advantage of a very efficient (read very fast) structural transformation.

In our first attempts with Time Resolved X-ray Diffraction on pyridine in solution (CH1547) we discovered no laser-induced signal at high q. By contrast, the signal at low q showed a very clear temporal evolution. The goal of this experiment (CH1746) was to use pyridine as an ultrafast heat source, which dissipates all its energy stored upon laser excitation to the surrounding solvent (methanol) without itself contributing any time dependent signal. To excite pyridine we used 3rd harmonic of a 100 fs Ti:sapphire laser, 267nm, further stretched to 2ps to lower the probability of two photon absorption in the solvent. The available energy per pulse was about 45 uJ at the sample. For probing the hydrodynamics of solvent we used white beam (3% bandwidth) from the U17 undulator peaked at 18.2 keV. The experiment was run with 1kHz repetition rate. The times at which the diffraction patterns from solvent were measured spanned from 100 ps to 1µs (figure below, with zoom at high-q region). The data were averaged over 10-16 cycles, depending on the time-point.
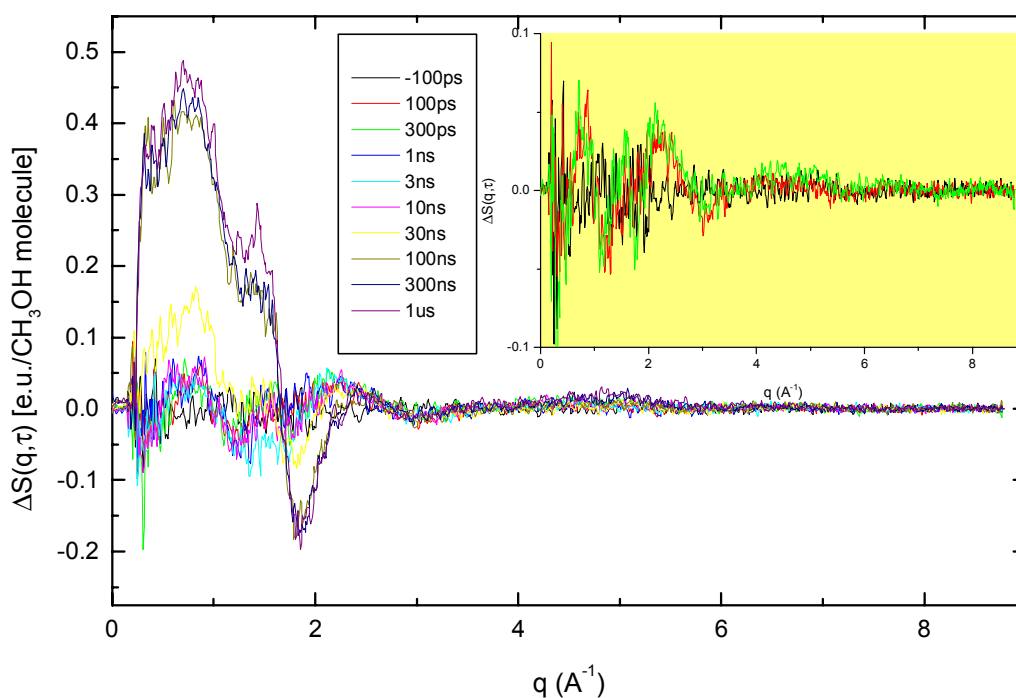

Recently developed theory and methods of simulating molecular dynamics allowed us to directly compare the simulated overheated (over pressurised) liquid, i.e. the solvent structure immediately after instantaneous inflow of heat before dissipating the excess thermal energy through sound waves, with the experimental data on sub-nanosecond timescale. After appropriate normalisation of the experimental data we found that the temperature of the solvent rises to almost 1K at 100 ps after excitation, the earliest time at which we can consider temperature uniform in the liquid. It is worth noting that the MD term has reproduced the real state of the liquid at such early time with very good accuracy (figure below).
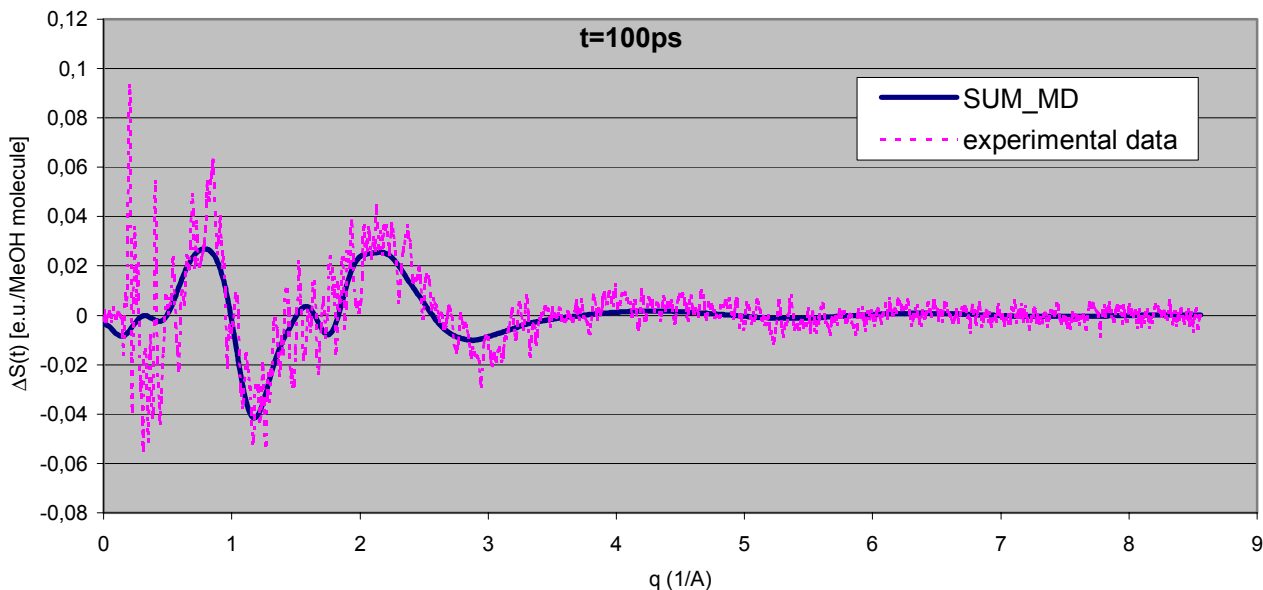
At much longer times we observe the liquid in its thermodynamic equilibrium, where the bulk has reacted to the heating by expanding, or alternatively speaking decreasing its density. It is straightforward to express the density change in terms of temperature jump through expansion coefficient (0.0011 K^{-1} for methanol). Again, we compared the measured difference map at 1μs to the one predicted by molecular dynamics. Another way of reading density change is by following the Fourier transform of the signal resolved in q at the shortest interpretable distances, where the limits are imposed by finite q-range. The value of the signal in the vicinity of 1A, if appropriately normalised, should read exactly minus density change. We found that methanol density drops by 2.5×10^{-3} g/cm^3 having absorbed all the energy released by photo-excited pyridine (60mM concentration). This amount of density decrease corresponds to heating up the methanol by almost 2.5 K. The difference between the temperature we read at 100ps (~1K) and 1μs (~2.5K) can only be explained by the fact that excited pyridine recovers its ground state over a long time. The recovery may involve intermediate isomers or a triplet state, which can trap the excited pyridine for more than 1 μs. We made preliminary fits to a possible deactivation model proposed in (1) combined with analytical expressions for density and temperature change of a liquid undergoing time dependent heating (2, 3), figures below.
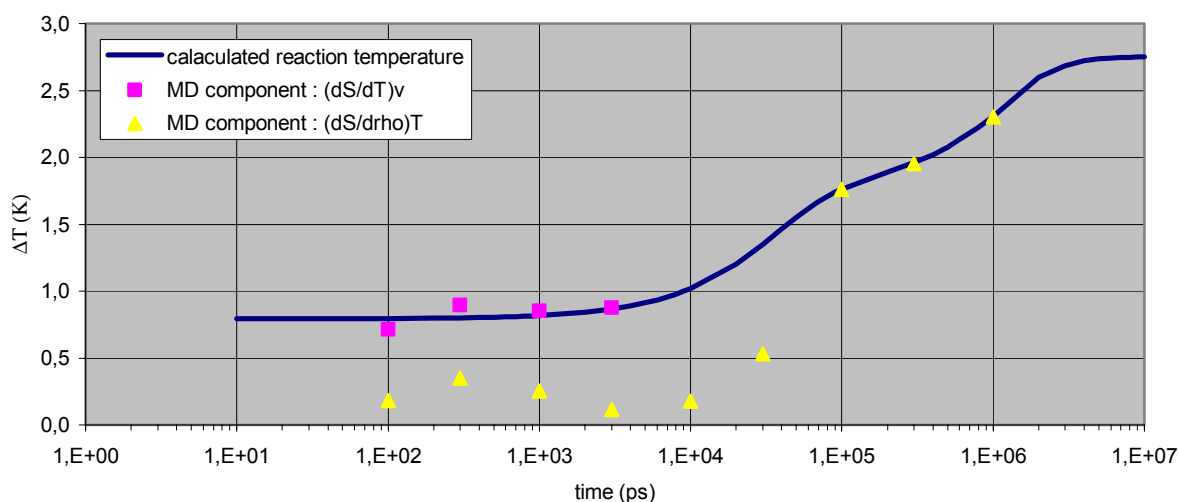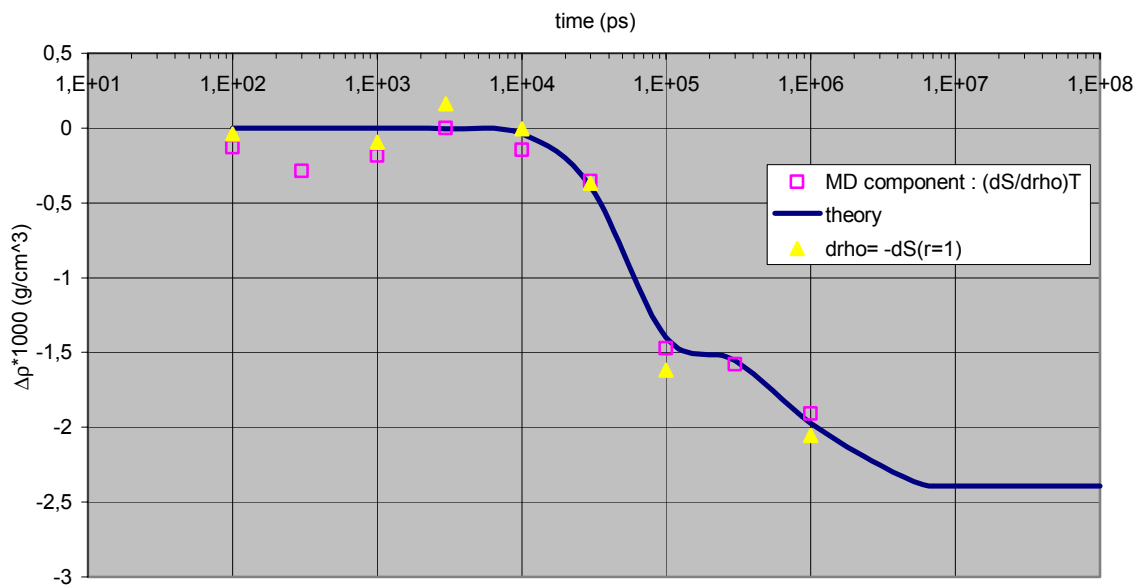
The density of points is probably not sufficient to discriminate between possible reaction pathways of photo excited pyridine, however a general trend in temperature and density dependence on time leaves a clear trail of a far richer reaction than simply ultrafast ground state recovery. We believe that by observing the hydrodynamics of the solvent, which is not only a host but also a partner in the reaction, there is a wealth of information to be learned not only about the solvent but also about the solute.

References:
(1)   M. Chachisvilis, A.H. Zewail, J.Phys.Chem.A 1999 (103) 7408
(2)   P.R. Longaker, M.M. Litvak, J.Appl.Phys. 1969 (40) 4033
(3)   F. Mirloup, Thesis, Universite Paris VI, 2004