


Experiment title:

Investigations on the dynamics of solvent reorganisation in binary mixtures

Experiment number:
CH1648

Beamline:
ID09B

Date of experiment:

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15

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Report:

In binary liquid mixtures, the composition in the near vicinity of a solute molecule can differ from that in the bulk provided the solute interacts differently with each of the solvent components, a phenomenon called preferential solvation [1-3]. In recent years, scientific interest in preferential solvation in binary solvents, which has been motivated over decades by the challenge to establish a general mechanism of the influence of solvents on chemical reactions. In experiment No **CH-1648** we investigated the structural response function of dye systems upon photoexcitation and solvent reorganisation based on preferential solvation. The system was chosen in such a way, that a fast large amplitude motion which is initiated by optical excitation of the chromophore initiates an isomerisation process on which the solvation cavity has to react on. The mechanism of the solvation process is based on preferential solvation.

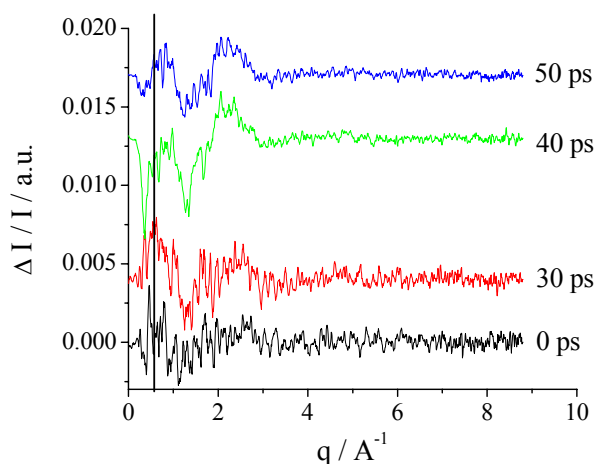


Figure 1: Time-resolved x-ray scattering of binary mixtures upon photoexcitation and photoreaction of the chromophore.

Figure 1 summarises the experimental results of this experiment. In particular at lower scattering angle DI/I signal changes are recognized.

Figure 2 summarises the preliminary data evaluation of the 30 ps time point. We think that the signal changes are a convolution of solvent signal changes going along with signal changes due to the photo-reaction of the chromophore. The data evaluation suggested that during the reaction two substates with different configurations are involved in the reaction process. However, as can be seen in Figure 2, still differences between the experimental (black) and simulated (red and blue curves) exist in particular at $q = 1.8 - 3.4 \text{ \AA}^{-1}$ which we assign to solvents reorganisation processes during the preferential solvation. Currently we are performing high level MD simulations on this process and hope that by adding the results of these simulations we will be able to fit the experimental curve to nearly 100 %.

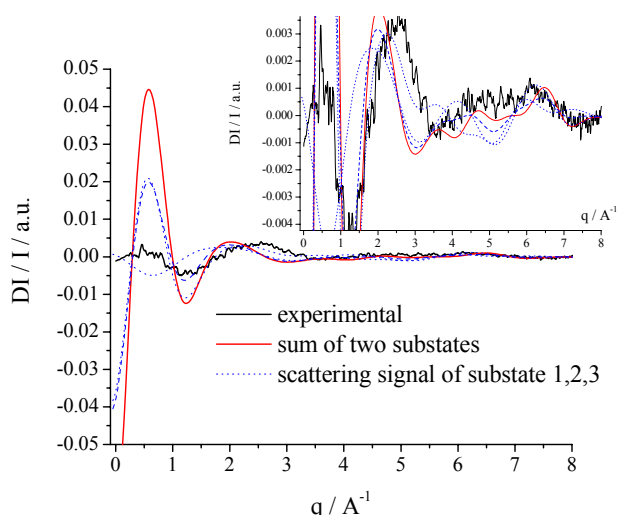


Figure 2: Refinement of several substates during the solvation process (deconvoluted signal).

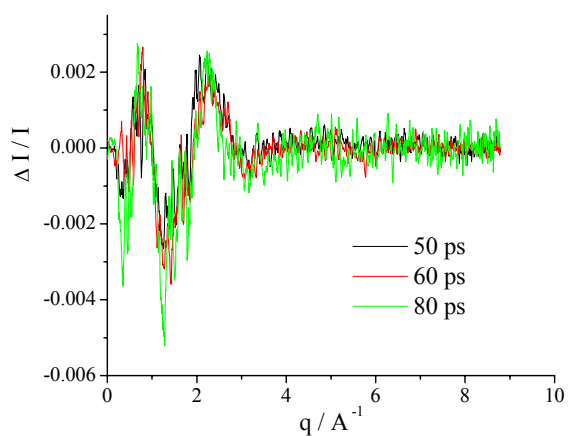


Figure 3: Time-dependence of the transient signal at later time points.

However, the most interesting and exiting result is shown in Figure 3. According to our spectroscopic experiment, the status of preferential solvation should hold about 500 ps. As can be seen in Figure 3, the structural reorganisation process of the preferential solvation seems already to be finished within the first 100 ps, which is very surprising and non-expected. We interpret this results with the fact, that in spectroscopic experiments only indirect evidence on the solvation structure can be drawn. Also here the MD simulations will help to understand the solvation behaviour. Part of the results have already been published in [3] and we further hope that we can publish the results in near future [4].

References

- [1] N. Kh. Petrov, M. N. Gulakov, M. V. Alfimov, G. Busse, B. Frederichs, S. Techert, *J. Phys. Chem.*, **107**, 6341 (2003).
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