



| | | |
|---|--|--------------------------------------|
| | Experiment title: Heat transport in a nanoscopic environment | Experiment number: SC 1177 |
| Beamline: ID09B | Date of experiment: from: 08-10-03 to: 13-02-03 | Date of report: 15-12-03 |
| Shifts: 15 | Local contact(s): Dr. M. Wulff | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Dr. A. Plech * V. Kotaidis * Dr. R. Vuilleumier | | |

Report:

The aim of the present experiment was to record the reaction of the water solvent that stabilizes metal nanoparticles, in the case, when the particles are impulsively excited by femtosecond laser radiation. It has been shown before, that diffuse scattering on liquid solutions is a very sensitive tool to study molecular photokinetics, as well as the hydrodynamics of the solvent [1]. Pressure changes are observed in iodine systems, and temperature changes (inducing volume changes) can be resolved to a fraction of a degree Kelvin.

In the present system we search for nonequilibrium reactions of the water solvent around gold and silver nanoparticles in the nanometer size range. It is known, that nanoparticles can be excited via the plasmon resonance to change the lattice temperature by several 1000 K within several picoseconds [2]. The heat is transferred to the solvent adjacent to the particles within less than a nanosecond. The high temperature at the particles liquid interface should cause a large nonequilibrium hydrodynamic reaction of the solvent.

We used the established picosecond pump-probe scheme using femtosecond pulses at 400nm and probing the reaction by x-ray scattering. The full emission spectrum of the U17 is used to record the diffuse scattering for best signal-to-noise ratio [3].

The limiting element for the quality of the experimental data is found to be the limitation of heat load on the microsecond chopper, when applying the flux available in the 16 bunch mode. The best operation condition was found, when opening the undulator gap slightly to suppress the higher orders of the undulator spectrum and reducing the vertical slit size to 0.3 mm, which narrows the spectrum, as in essence it reduces the off-axis contributions of radiation, which are red-shifted with respect to the peak intensity. The bandwidth decreased to 3 %, which is sufficient for resolving the liquid scattering from water within a Q range of 8 \AA^{-1} .

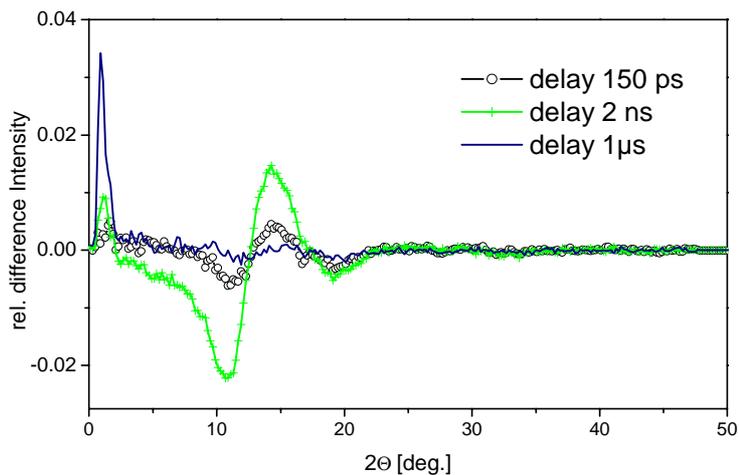


Fig. 1: Difference Scattering profiles of a water based gold nanoparticle sol after laser excitation. At about 2 ns a large pressure transient has developed, which decays towards a hydrodynamic equilibrium on the microsecond time scale.

We observe the development of large amplitude modulations in the Q resolved difference signal in between excited and nonexcited sample. These modulations are connected to the water structure and reflect the transient heating and shock wave development around the hot metal nanoparticles. The particles meanwhile are completely molten and exhibit lattice temperatures above 5000 K. After equilibration of the system, the liquid remains at an elevated temperature of 0.5 K and the particles are fragmented as indicated by the increase in small angle scattering signal below 2 degrees. Data is being analyzed in order to understand the relation in between the melting and fragmentation of the metal particles and the pressure force of the solvent surrounding the particles.

Absolute pressure and temperature calibration can be achieved via the comparison to static scattering experiments and molecular dynamics simulations [4].

Unfortunately the setup of the sample section of beamline ID09 is not ideal for resolving small angle scattering signals from the exploding nanoparticles, especially, if they surpass sizes of 5nm. The fragmentation process itself can give important information on the nature of the solvation force around the particles, a question which is not solved, regarding the short timescales involved in these experiments.

[1] M. Wulff, A. Plech, L. Eybert, R. Randler, F. Schotte and P. Anfinrud: *The realization of sub-nanosecond pump and probe experiments at the ESRF*, Faraday Discussions 122 (2003) 13.

[2] A. Plech, M. Wulff, S. Kuerbitz, K.-J. Berg, G. Berg, H. Graener, S. Grésillon, M. Kaempfe, J. Feldmann and G. von Plessen: Time-resolved X-ray diffraction on laser excited metal nanoparticles, Europhys. Lett. 61 (2003) 762.

[3] A. Plech, R. Randler, A. Geis, M. Wulff: *Diffuse scattering from liquid solutions with white beam undulator radiation for photoexcitation studies*; J. Synchrotron Radiation, 9 (2002) 287.

[4] F. Mirloup, S. Bratos, R. Vuilleumier, M. Wulff and A. Plech: Time-dependent x-ray scattering signal of laser heated liquids: a linear response theory, in: "Ultrafast Molecular Events in Chemistry and Biology" (Elsevier) 2004 in print.