ESRF	**Experiment title:** Vibrational symmetry breaking in laser excited nanoparticles	**Experiment number**: SI1011
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Shifts: 15	**Local contact(s)**: Dr. Maciej LORENC	*Received at ESRF:*

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Report:

The aim of the present experiment was to record lattice changes in nanoparticles, that are exposed to intense femtosecond laser pulses. The thermal effect, namely a conversion of the photon energy via the electron gas into a thermal phonon distribution is the most prominent signature of laser absoption. Is is detected by a peak shift of the fcc lattice peaks of the crystalline gold lattice [1]. Besides the pure thermal excitation, a pathway of coherent lattice motion can be opened if the excitation force acts shorter than the oscillation period. This is the case for femtosecond laser excitation and electron phonon coupling times of 2-5ps. We utilized 150 nm gold particles adsorbed on a glas surface. The ground mode with spherical symmetry is expected to have an oscillation period of 52 ps [2].
Within the present experiment we tried to resolve the oscillations of these particles and resolve the motion in relation to the orientation to the surface, ie. try to see any symmetry breaking of the vibrational motion as induced by the particle surface contact.
The temporal resolution with the setup of beamline ID09B is however nominally around 80-200ps, depending on the filling mode. Therefore we took advantage of the specific properties of the hybrid mode. It contains a part of the electron pockets filled with pulses of 2.8 ns spacing of low current opposed by one high current pulse, which is extracted with the chopper for the time resolved studies. As in hybrid mode the refill is only done twice a day, the single pulse current decays further than what would be the case in other time resolved filling modes. Consequently the pulses become shorter as the current decays. After discussion with the machine group (thanks to G. Naylor and K. Scheidt), we found the lower limit for the pulse length to be about 70ps just before refill. Together with the possibility of detecting Bragg peak changes to a high precision due to the Q resolution, the final resolution function can be as narrow as 40ps FWHM !

With this setup we measured the angular change of the (111) reflection of an ensemble of gold particles on a flat surface, while having the possibility to discern in between lattice motion perpendicular to the surface and within the surface (actually not completely in plane due to the high incidence angle) from the Debye Scherrer distribution on the CCD camera.

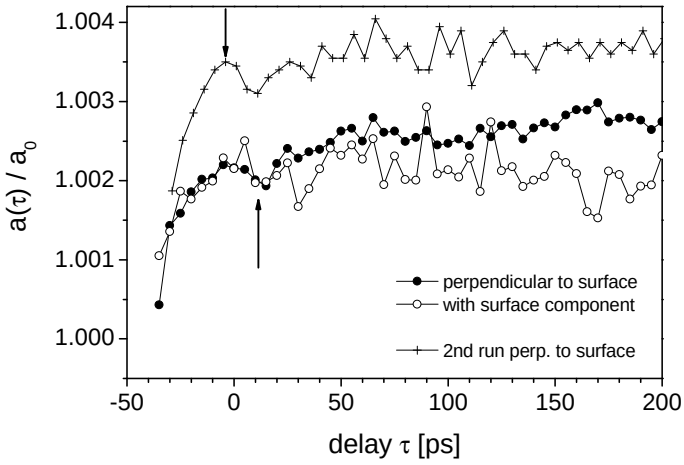

Fig. 1*: Change of the lattice parameter a of 150 nm gold particles as function of time delay τ after the femtosecond laser excitation. Around τ = -25ps both laser and x-ray pulses coincide. At this point the lattice starts to expand followed by relaxional motion. All data show a high expansion at $\tau \sim 0$ followed by a lower expansion at τ = 20ps. Due to a preferential adsoption of the particles with (111) facets, there is more scattering perpendicular to the surface and hence better accuracy of the data in this direction.*

The rise of the lattice parameter can be seen directly after lattice excitation, followed by some oscillatory motion, which is exactly the 52 ps period of the spherical vibration. This is also corroborated by the fact that the motion is in phase for both resolved directions. This vibration is damped very strongly (disappearance of the undulations after 1 period) possibly followed by a longer period motion. Here however the signal qualtiy does not allow to assign the modes to any symmetry.
It has been shown, that a sub-100ps resolution is achievable to study the vibrational eigenmodes of a coupled particle –surface ensemble. The laser excitation had to be kept to a very low power level (200 K) in order not to modify the particles irreversibly. The thresholds for particle modifications are found to lie considerably below the melting point [3] and a connection to anharmonic lattice coupling or other dissipation channels [4] can be studied.

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[2] N. del Fatti, C. Voisin, F. Chevy, F. Vallée and C. Flytzanis, J. Chem. Phys**. 110** (1999) 11484; C. Voisin, N. del Fatti, D. Christofilos and F. Vallée, J. Phys. Chem. **105** (2001) 2264 ; G. V. Hartland, J. Chem Phys. **116** (2002) 8048.

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