Purpose of the visit

The purpose of the visit was three-fold. First, we aimed to investigate non-linear plasmonic responses of thin gold films with nano-holes, with focus on four-wave-mixing process. Second, the visit was supposed to establish exchange of experience between institutions of visiting and host scientists. Third, it was a great opportunity for professional growth, learning how to handle a high-end experimental setup not accessible at the home institution, and personal growth from communication with experienced scientists at the host institution.

Description of the work carried out during the visit

In the first part of my experiments, we optimized the experimental setup for near-field measurements. Briefly, before optimization the setup had dual wavelength excitation source of Nd:Vanadate pump laser [1064 nm, 7 ps, 76 MHz, HighQ (Hohenems, Austria) picoTRAIN] and a two ring-cavity optical parametric oscillators (OPO), [690-990 nm, APE (Berlin, Germany) Lavante]. There is possibility to combine beams from pump laser with one of the OPO's or combine beams from two OPO's for excitation of non-linear signals. There is a delay line in the arm of the one of the OPO's beam for temporal overlap of the excitation beams. Spatially beams are combined on a dichroic mirror and directed to the mirror scanning unit of the confocal microscope (Nikon Eclipse TE2000-E) and focused on the sample by a high NA objective (Nikon TIRF Plan Apochromat 100x/1.49 oil). Sample is placed on AFM/NSOM add-on for optical microscopy (Nanonics Imaging, Israel). Optical far-field signals are detected in forward- or epi-direction and near-field signals through NSOM probe using photomultiplier tubes (Hamamatsu R6357, Japan). Bandpass filters are used to isolate the signals and suppress background light.

Test experiments have shown that there is a highly efficient coupling of excitation light to the gold film through nano-holes or defects (edges of the film). When excitation powers exceed some threshold such an efficient coupling leads to heating and consequent damage of the sample and NSOM tips. Generation of *non-linear* optical responses requires high peak powers, so there was a need to minimize a fraction of excitation power contributing mostly to *linear* processes. We have addressed this issue in two ways. First, we have implemented polarization and power control of each excitation beam with the help of polarizing beam splitter cubes and half-wave plates. Such a combination allows filtering out polarization components which do not contribute to *non-linear* response, as well as control excitation power in easily controlled and smooth way. Second, we have implemented spatial filtering of excitation beams focusing them through micrometer scale pinhole. Such a spatial filter improves excitation beam mode and allows focusing with microscope objective to nearly diffraction limited focal spot. Focusing to diffraction limited focal spot requires less average power to achieve higher power densities, thus increasing ratio of non-linear to linear excitations.

Near-field collection through the NSOM fiber tip is greatly dependent on the distance between tip end and sample. In our system control of tip-to-sample distance is implemented through phase locked vertically vibrating tuning-fork cantilevers. Because the tuning-fork oscillates in a vertical direction, there is no *constant* tip-to-sample distance as the tip oscillates between the closest (strongest near-field) and the farthest (weak near-field) tip-to-sample positions. Using tuning fork oscillating vertically rather than horizontally opens up a possibility to separate near-field signals from far-field contributions with a lock-in amplifier detection, which was a next modification of the experimental setup. While implementing lock-in detection we found that there is a substantial noise in tip-to-sample feedback loop, which was attributed to mechanical noise. Despite that we could not find the exact source of mechanical noise, addition of passive vibration damping tools (air pumped optical table legs and vibration isolating sheets) reduced mechanical noise an order of magnitude.

We have started investigations of non-linear optical responses with plane thin (50 nm) gold-films without nano-holes. Non-linear signals were excited with pump laser (1064 nm) and OPO (817 nm) beams tightly focused close to gold-air interface. Four-wave mixing far-field 3D images were recorded both in epi- and forward directions, showing almost diffraction limited response in z-direction (FWHM ~1 µm). Near-field maps at gold-air interface at excitation frequencies showed typical 3D plasmon interference fringes, as was shown by Bouhelier *et al.* (Surface plasmon interference excited by tightly focused laser beams. *Optics letters* **32**, 2535–2537 (2007)). In contrast, near-field maps at the frequency of four-wave mixing showed Gaussian shaped response (FWHM z ~1 µm, x,y ~0.8 µm) with no evidence of interference fringes. The fact that we did not observe any patterns in four-wave mixing near-field maps might be due to low amplitude of possible signal intensity variations compared to noise level. Nevertheless, the broad response in x,y direction might be due to non-linear interaction taking place in larger area than we would expect from diffraction limited excitation volume (~0.3 µm), indicating that four-wave mixing excitation takes place not only through direct far-field excitation but also has contributions from plasmonic interactions.

Next we measured the optical responses from nano-holes in thin gold films. In general, there were four types of near-field measurements: (i) excitation maps - NSOM tip is positioned in the middle of the nano-hole while excitation beam is scanned in xy; (ii) emission maps – nano-hole is positioned in the middle of excitation beam while NSOM tip is scanned in xy; (iii) degenerate emission-excitation maps – tip is positioned in the middle of the excitation beam while sample is scanned in xy. All these measurements indicate enhanced excitation in-coupling through the holes in all nano-hole size and density groups probed. However, the localization of the near-fields is dependent on the frequency probed, nano-hole sizes and densities. While there are clear differences in near-field localization at excitation and four-wave mixing frequencies, respectively, the most prominent of which is the much higher localization of the near-field at the four-wave mixing frequency in the holes compared to near-fields at the excitation frequencies, further investigations with larger sample number are needed to conclude any systematic relationships between localization differences and nano-hole size/densities.

Description of the main results obtained

We have observed local interactions between nano-holes at four-wave mixing frequencies (Figure 1). When laser hits the hole, near-field intensity at four-wave mixing frequency in adjacent holes is increased. This data rises the question about the source of such an intensity increase: whether the enhanced in coupling of excitation beams in the hole creates more intense plasmonic wave at excitation frequencies, which induces four-wave mixing in adjacent holes, or there is a re-coupling of four-wave mixing from the excited hole to the adjacent holes. Experiments with excitation beams separated in space are required to investigate this question further.

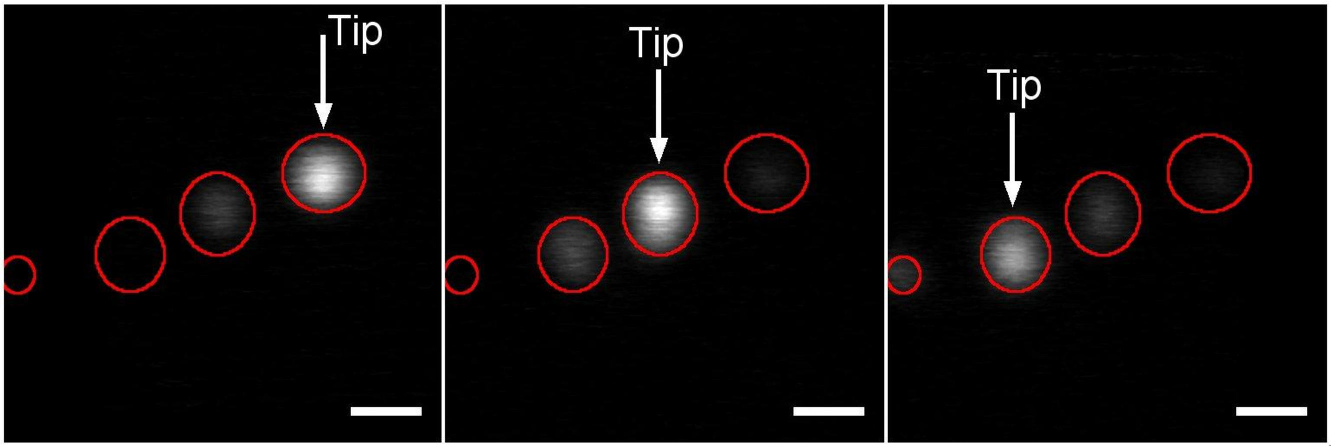

Figure 1. Plasmonic interaction between nano-holes in thin gold film. Images show excitation maps of four-wave mixing: NSOM tip is fixed in the middle of the hole highlighted with arrow while excitation beam scans the sample. Position of nano-holes is highlighted in red. It is clearly seen that when excitation beam hits the hole where the tip is intensity of detected near-field is highest, while there is almost no signal when laser scans the areas without holes. There is also an increase in near-field intensity when excitation beam hits nearest holes, showing plasmonic interaction between adjacent nano-holes. Scale bar 0.5 µm

When the distance between nano-holes becomes comparable or smaller than the size of the holes, we observe different near-field patterns for excitation and four-wave mixing fields (Figure 2). This is quite different from almost similar the near-field patterns of excitation and four-wave mixing fields in samples with lower density of nano-holes. The most prominent change occurs for near-fields at excitation frequencies – at low nano-hole densities it is localized to nano-holes, while at high densities of nano-holes it is more localized to the areas between nano-holes. Near-fields at four-wave mixing are localized to nano-holes at both high and low densities of nano-holes, which suggests that despite changing spatial distribution of excitation fields four-wave mixing excitation is mediated by nano-holes.

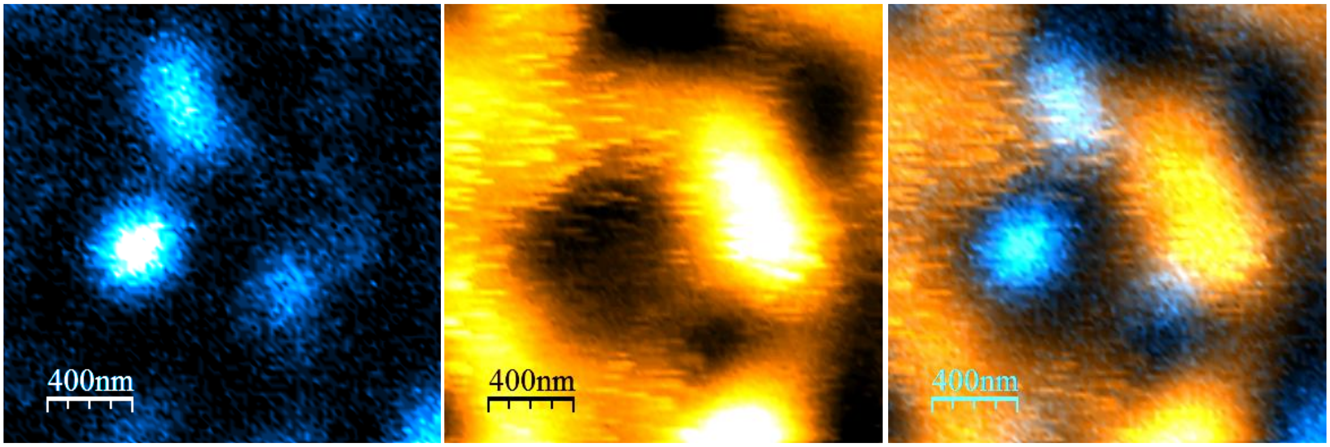

Figure 2. Distinct near-field patterns at excitation (817 nm, yellow) and four-wave mixing (663 nm, cyan) frequencies. Four-wave mixing is more localized to nano-holes, while near-fields at excitation frequency localize in areas between nano-holes.

Future collaboration with host institution (if applicable)

Short visits to host institution are planned during the summer to further optimize the experimental system and perform experiments.

Projected publications / articles resulting or to result from the grant (ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)

Measurements conducted during this visit were for proof-of-concept. We now intend to start more systematic studies on these phenomena, which hopefully will result in a manuscript for submission in the fall.

Other comments (if any)