Spectroscopy and Microscopy of Single Molecules and Single Nanoparticles

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Molecular Nano-Optics and Spins
Leiden University (Netherlands)

Han sur Lesse, 13 December 2013

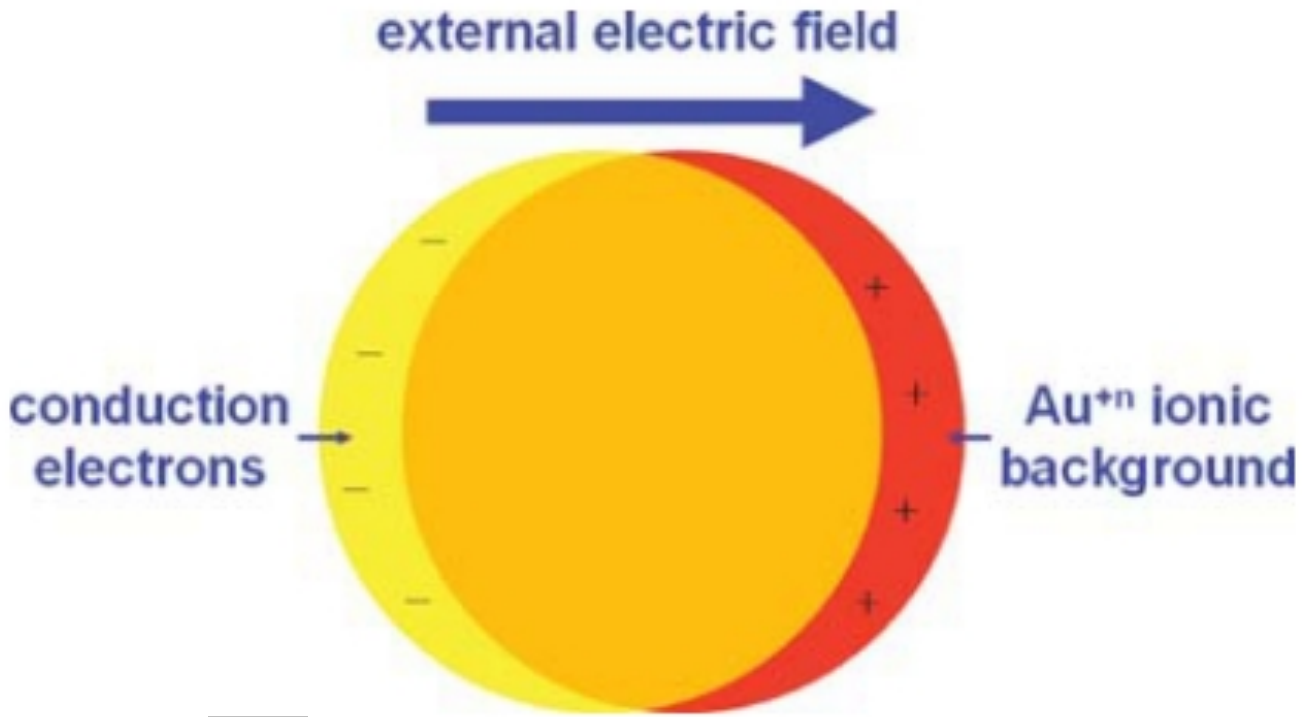
Part III

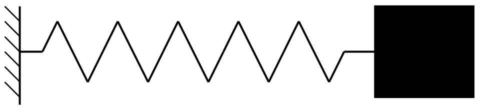
Fluorescence, scattering and absorption spectroscopy of gold nanoparticles

Outline (Part III)

- Pump-probe spectroscopy
- Gold nanorods
- Trapping
- Sensing

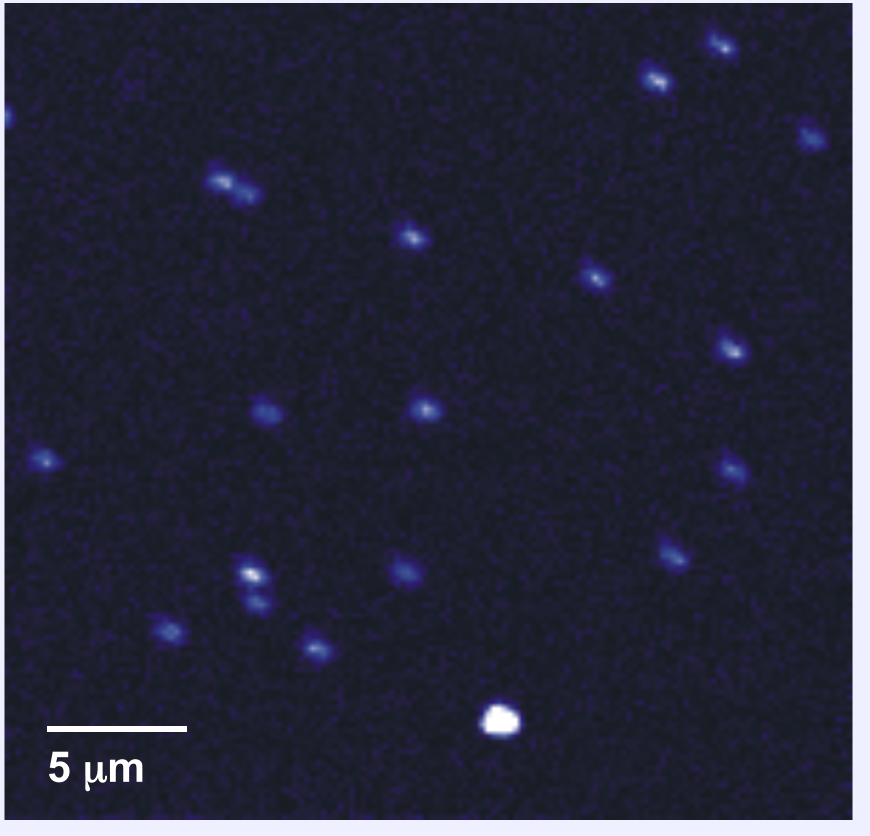
Plasmons in gold nanoparticles





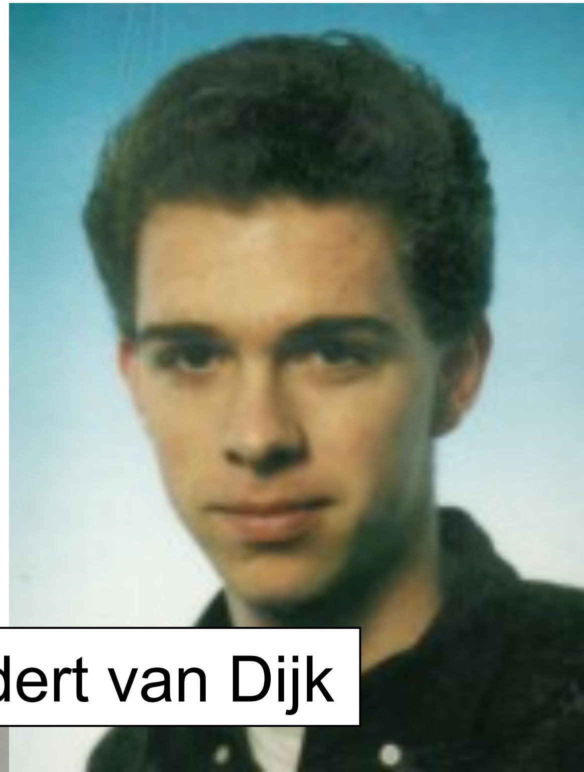
Harmonic oscillator, spring constant depends on shape and field orientation

Pump-probe spectroscopy of single gold nanoparticles



Third Harmonic, 100 nm; M. Lippitz et al., NanoLett **5** (2005) 799

Dr. Markus Lippitz

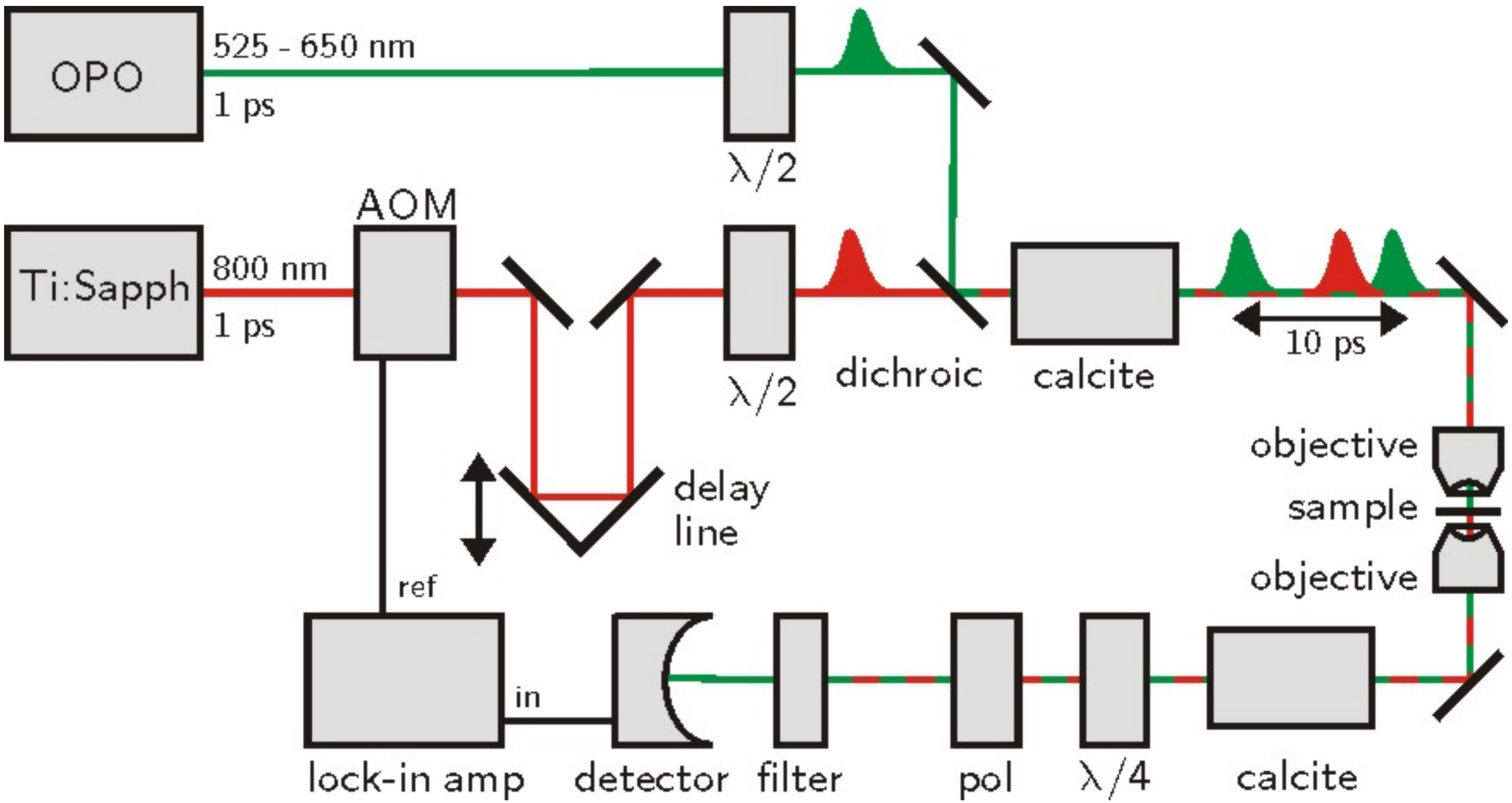


Dr. Meindert van Dijk

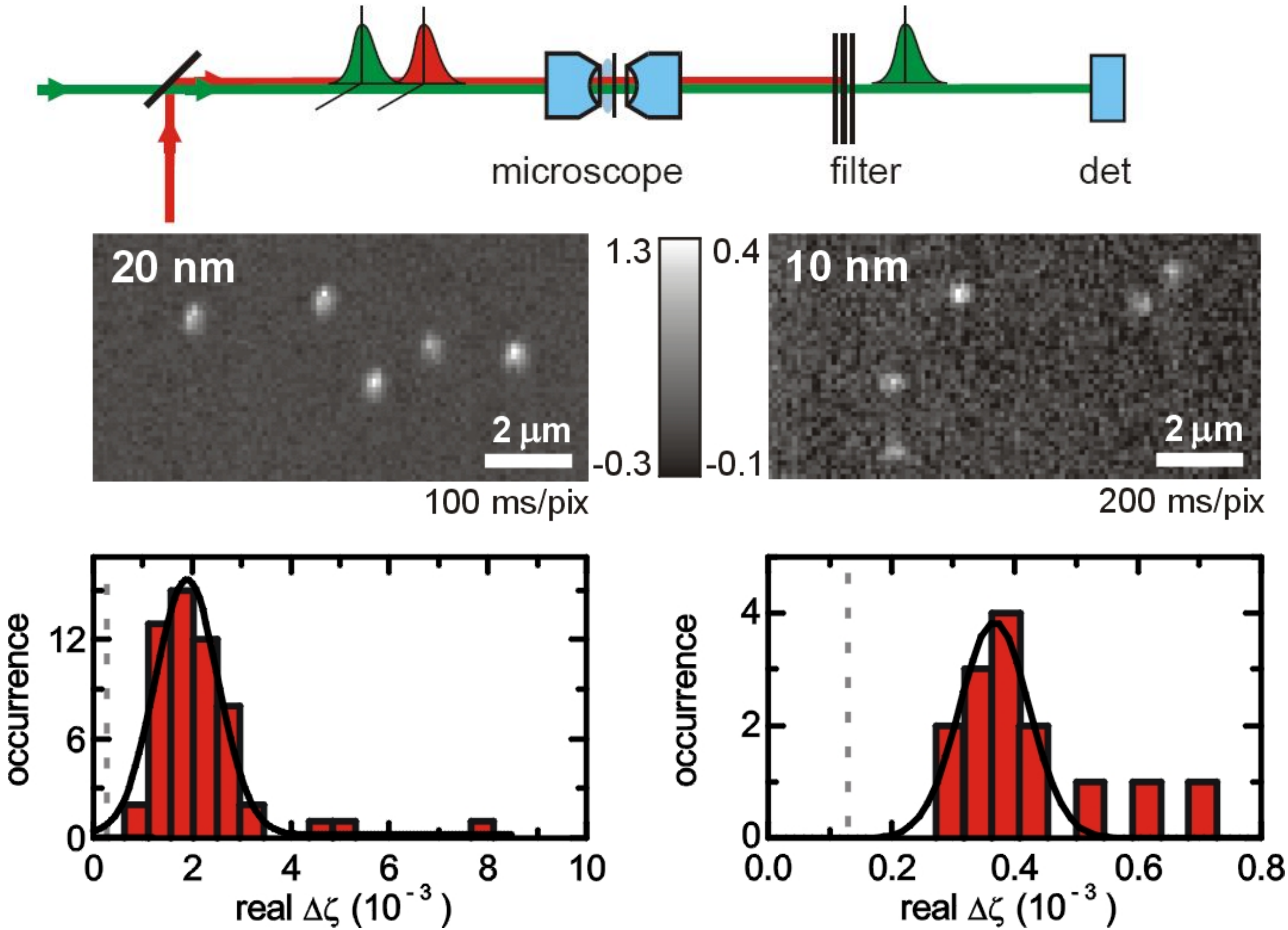
Dr. Anna Tchebotareva

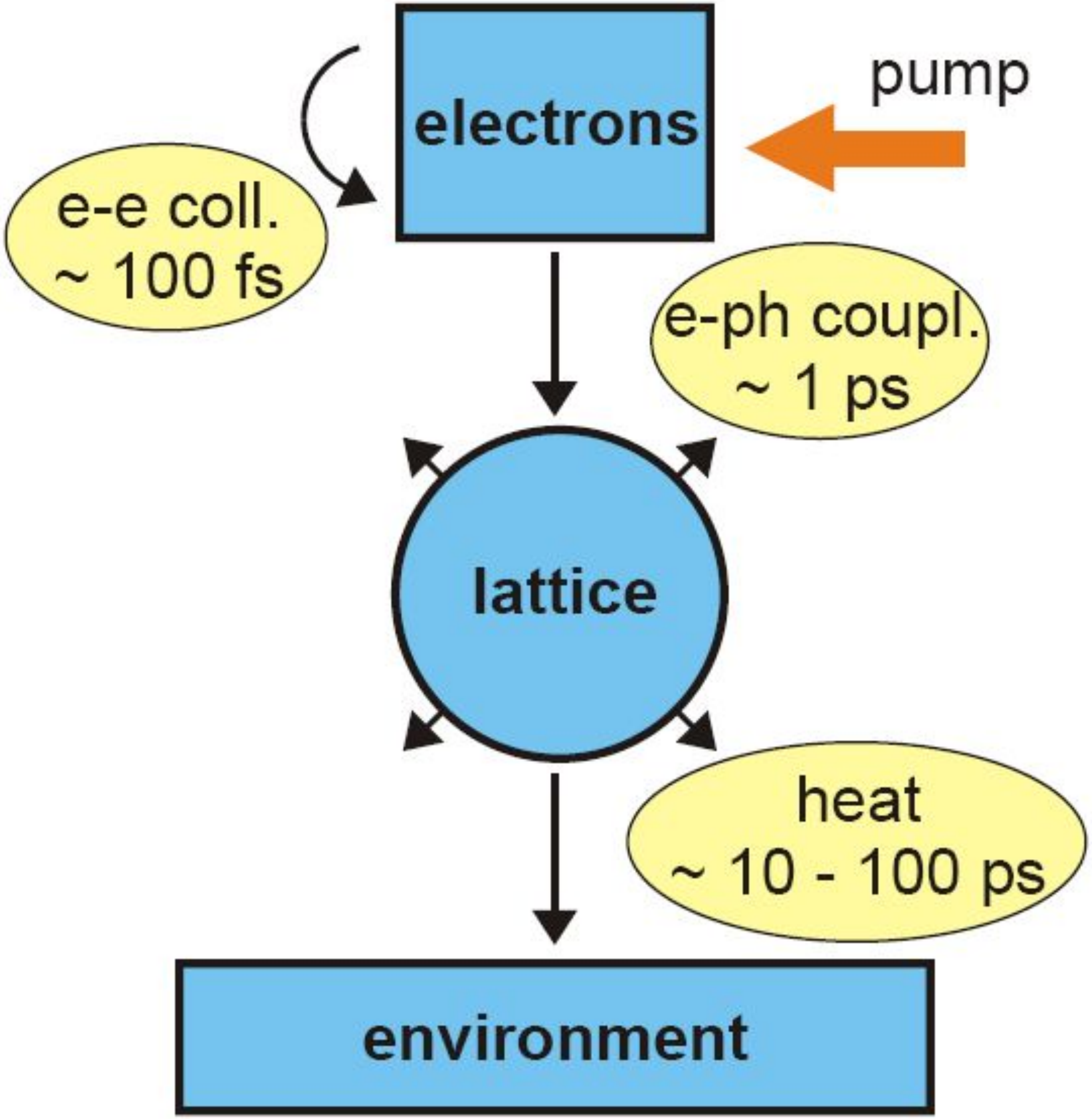
Paul Ruijgrok

Pump-probe Interferometric Microscope

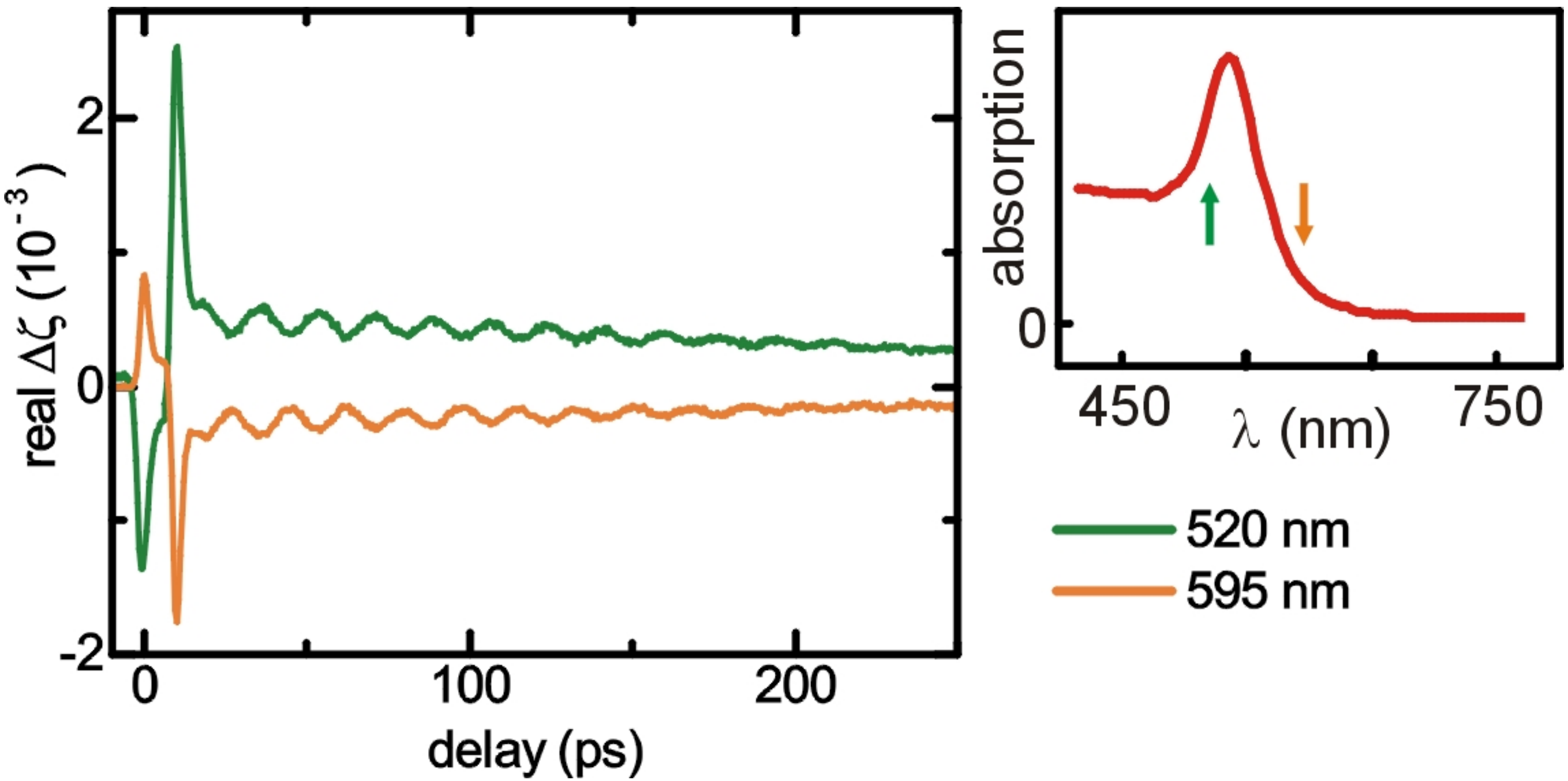


Single gold nanoparticles

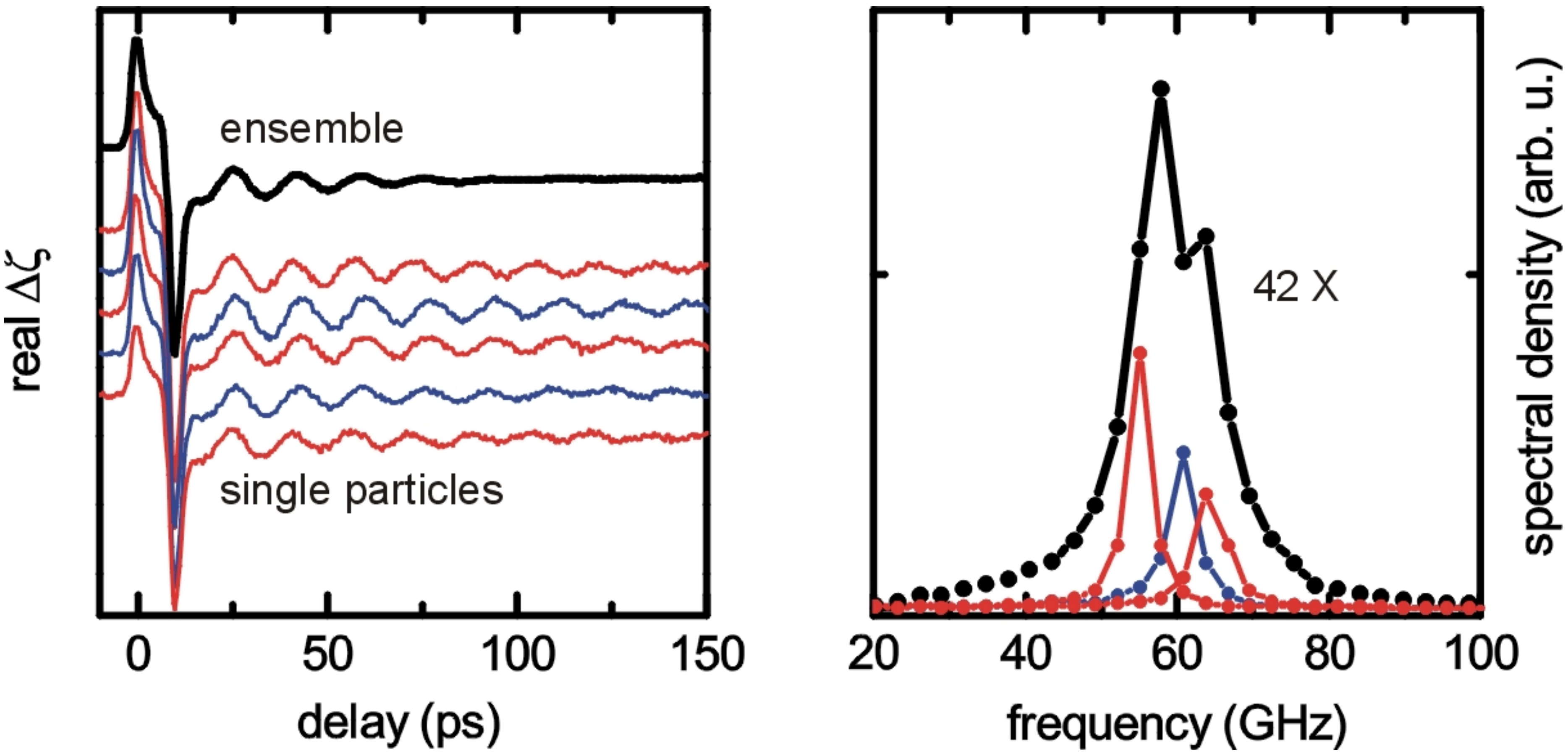


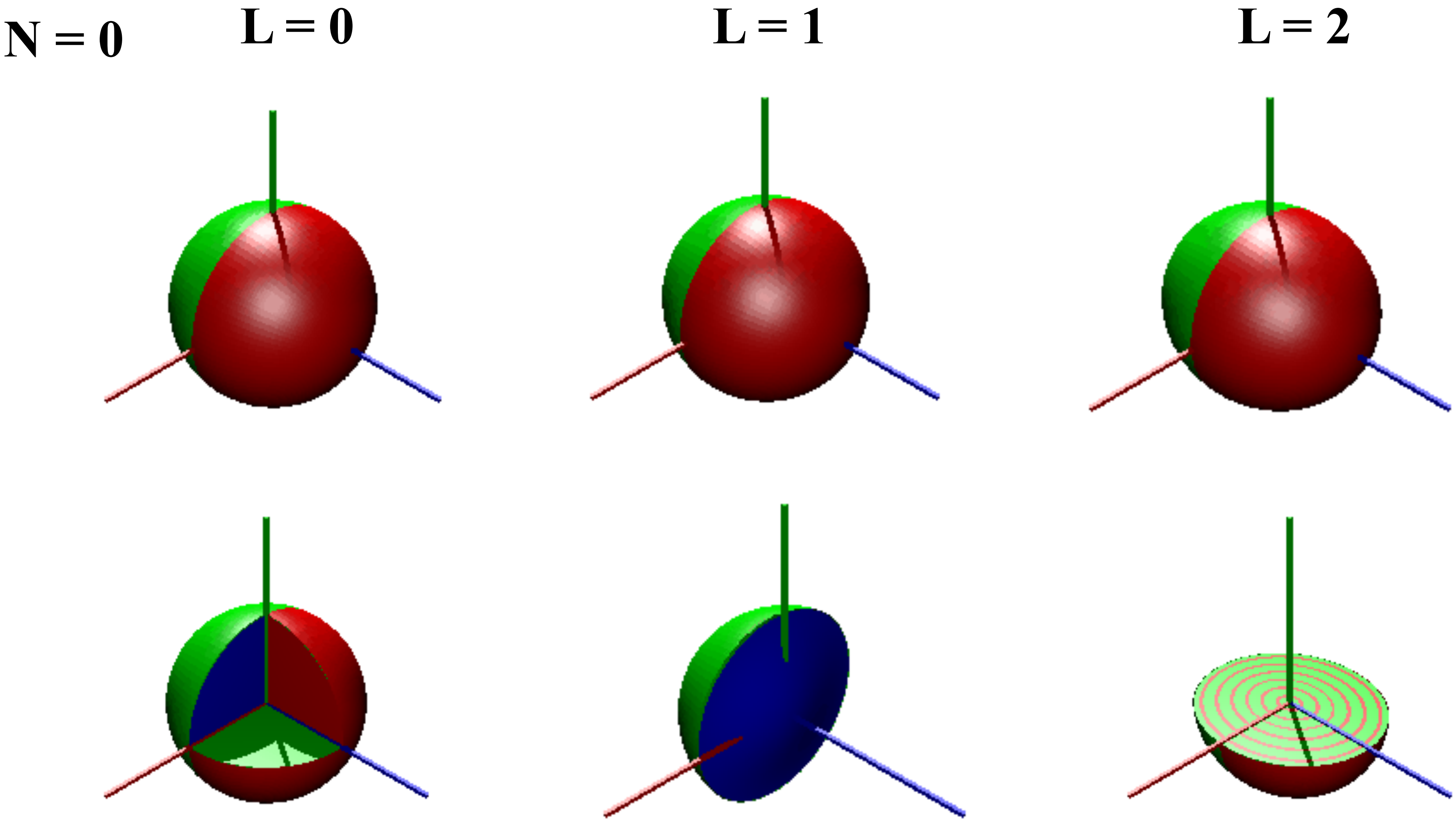

electrons
pump
e-e coll.
~ 100 fs
e-ph coupl.
~ 1 ps
lattice
heat
~ 10 - 100 ps
environment

Spectral shift of plasmon resonance



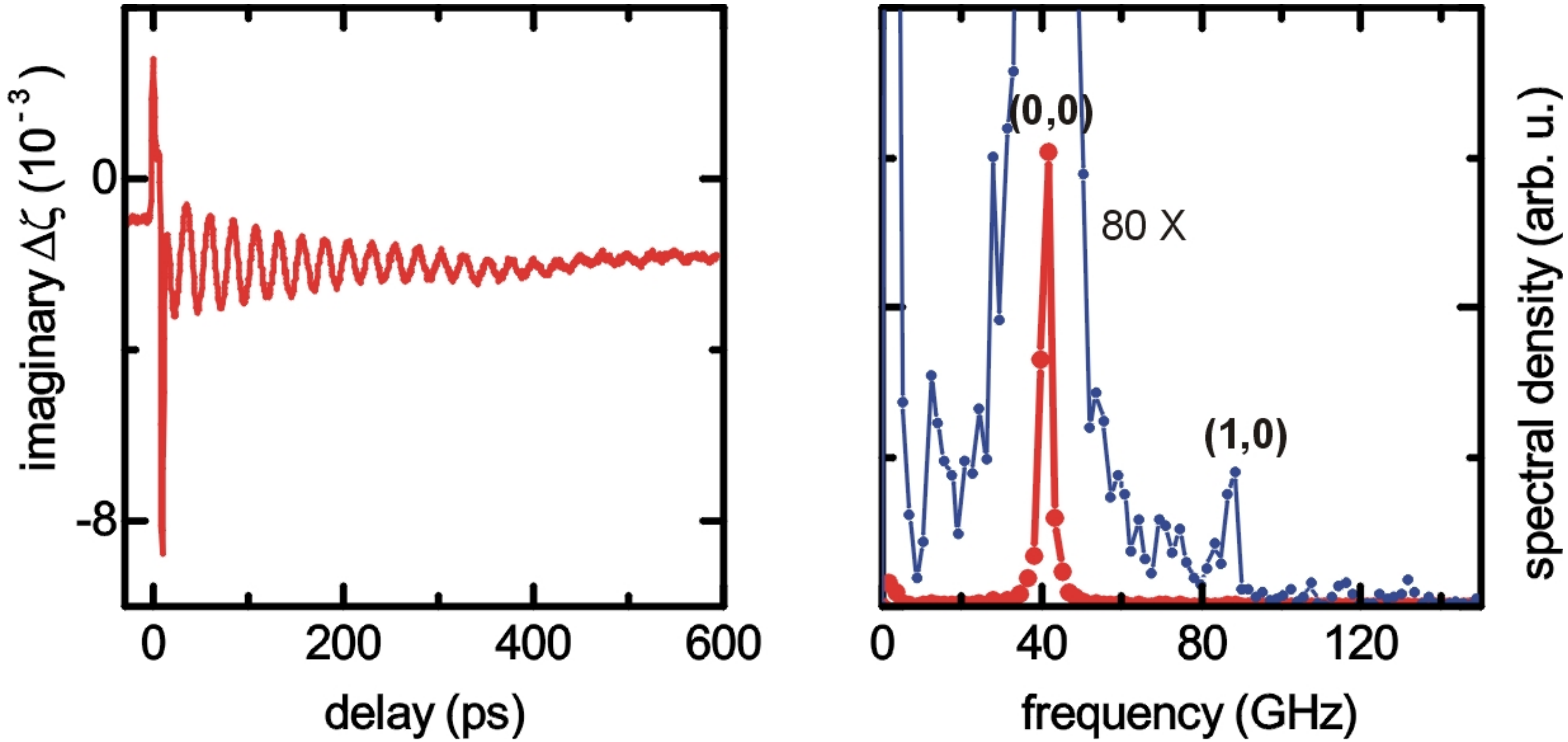
Ensemble vs. individual nanoparticles



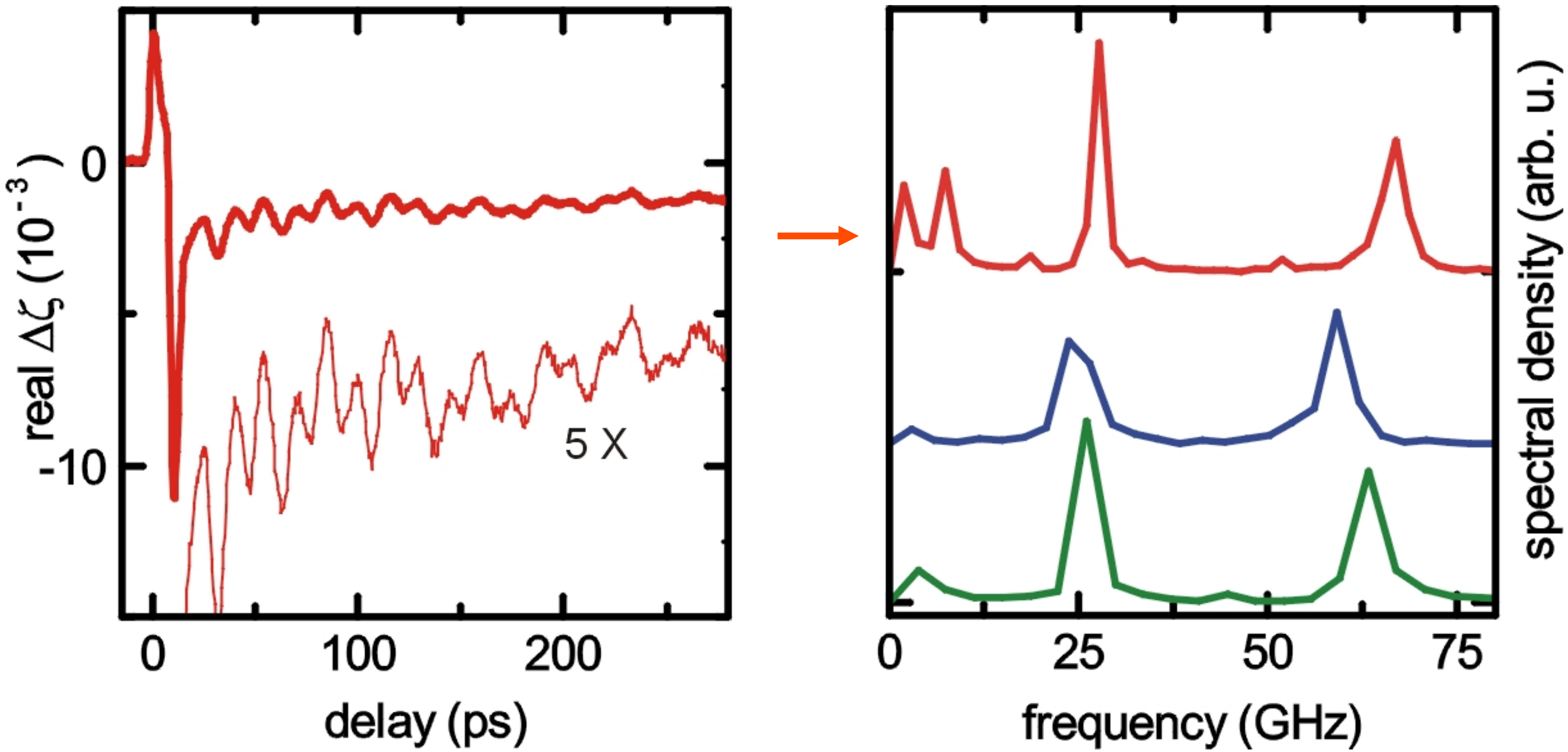


Taken from L. Saviot
http://www2.u-bourgogne.fr/REACTIVITE/manapi/saviot/index.en.html

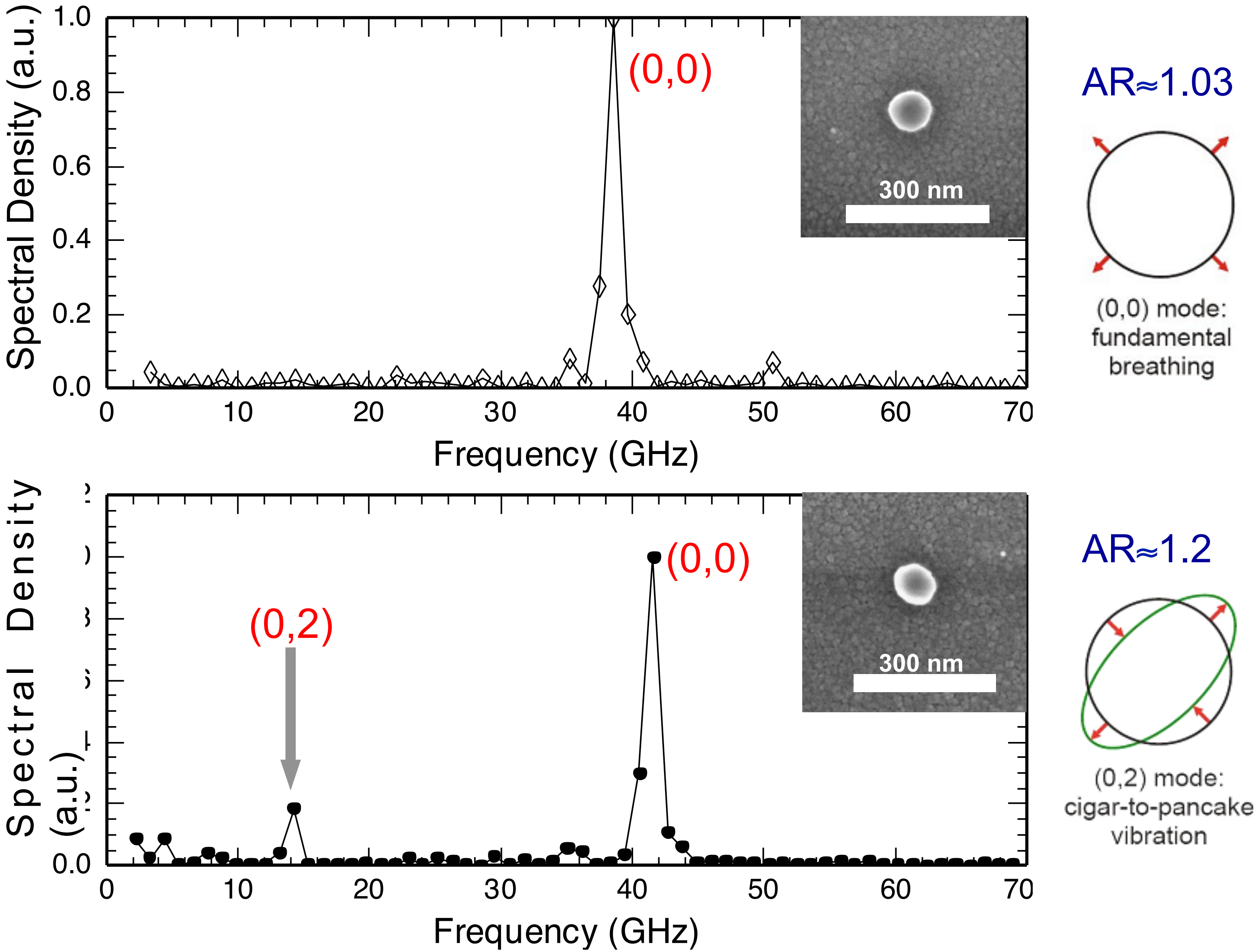
Other vibrational modes
Higher radial harmonics



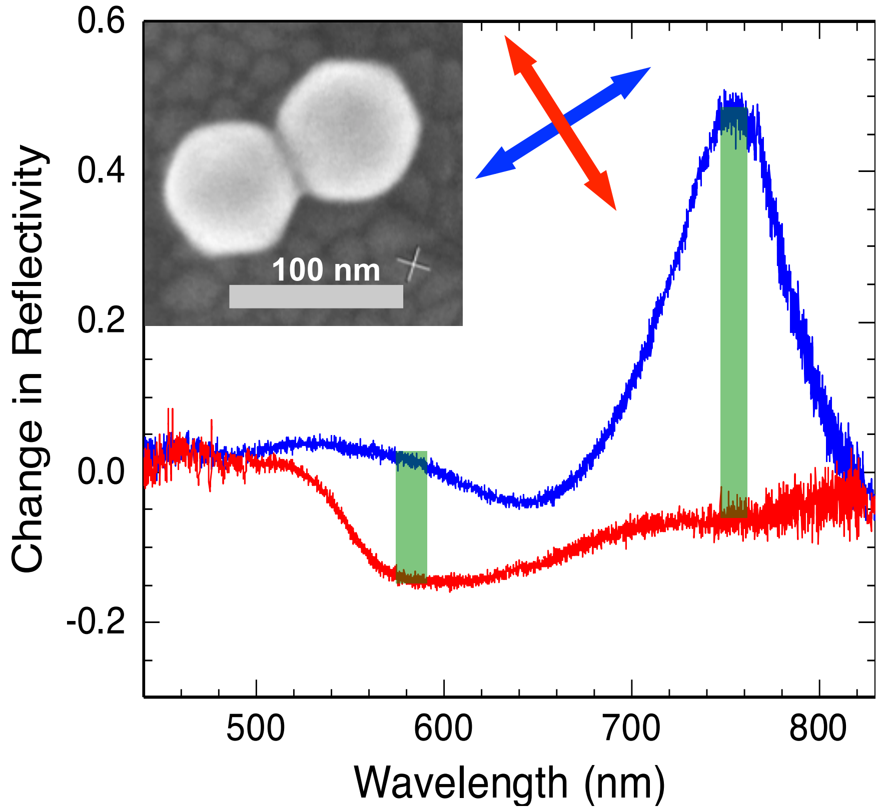
Ellipsoidal deformation mode

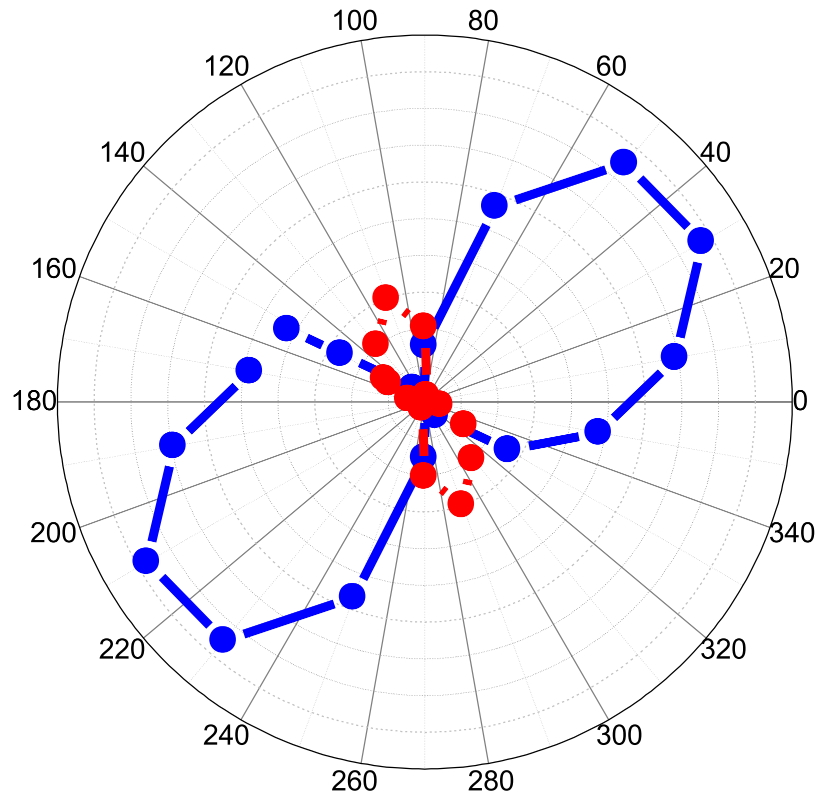


Correlation with shape

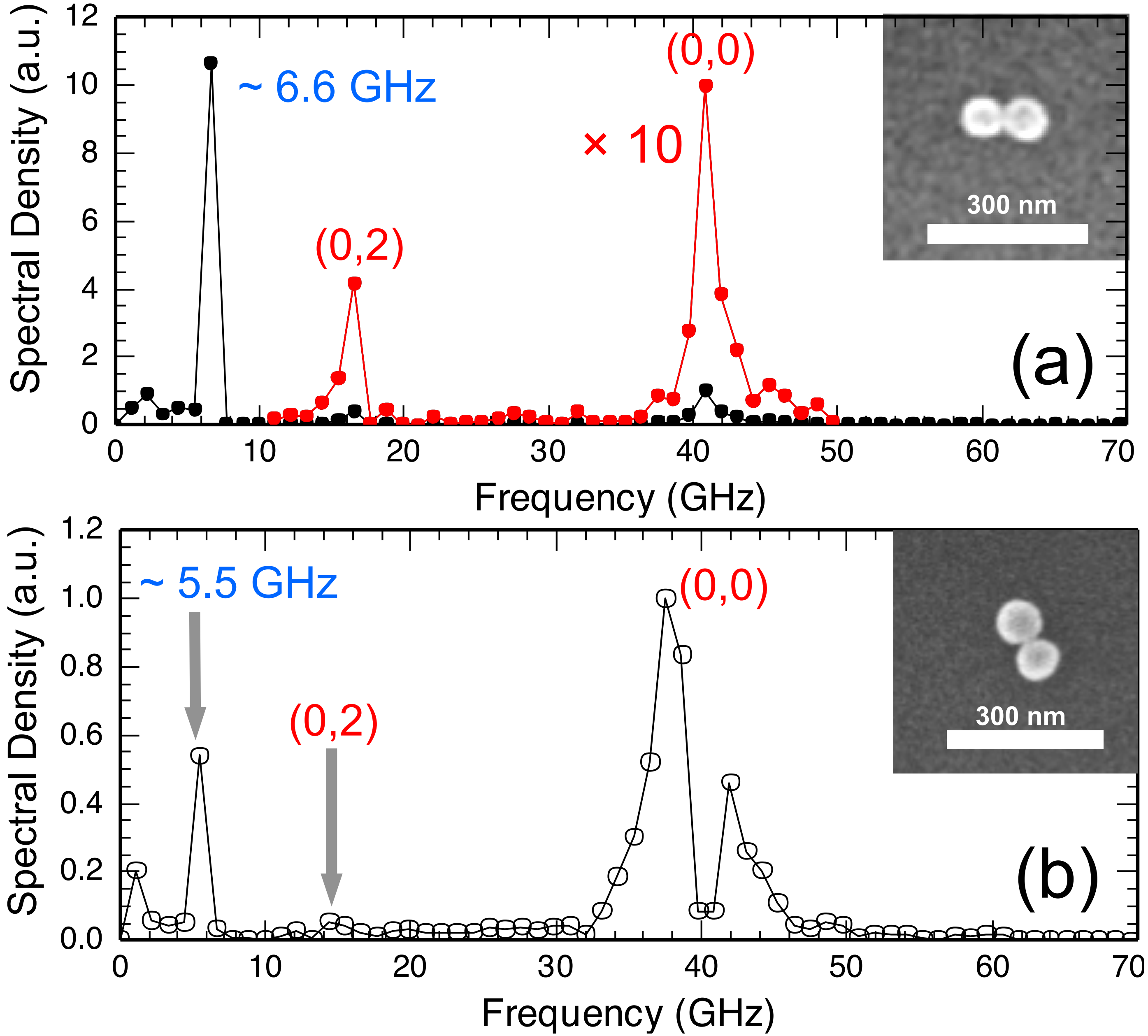


Dumbbells

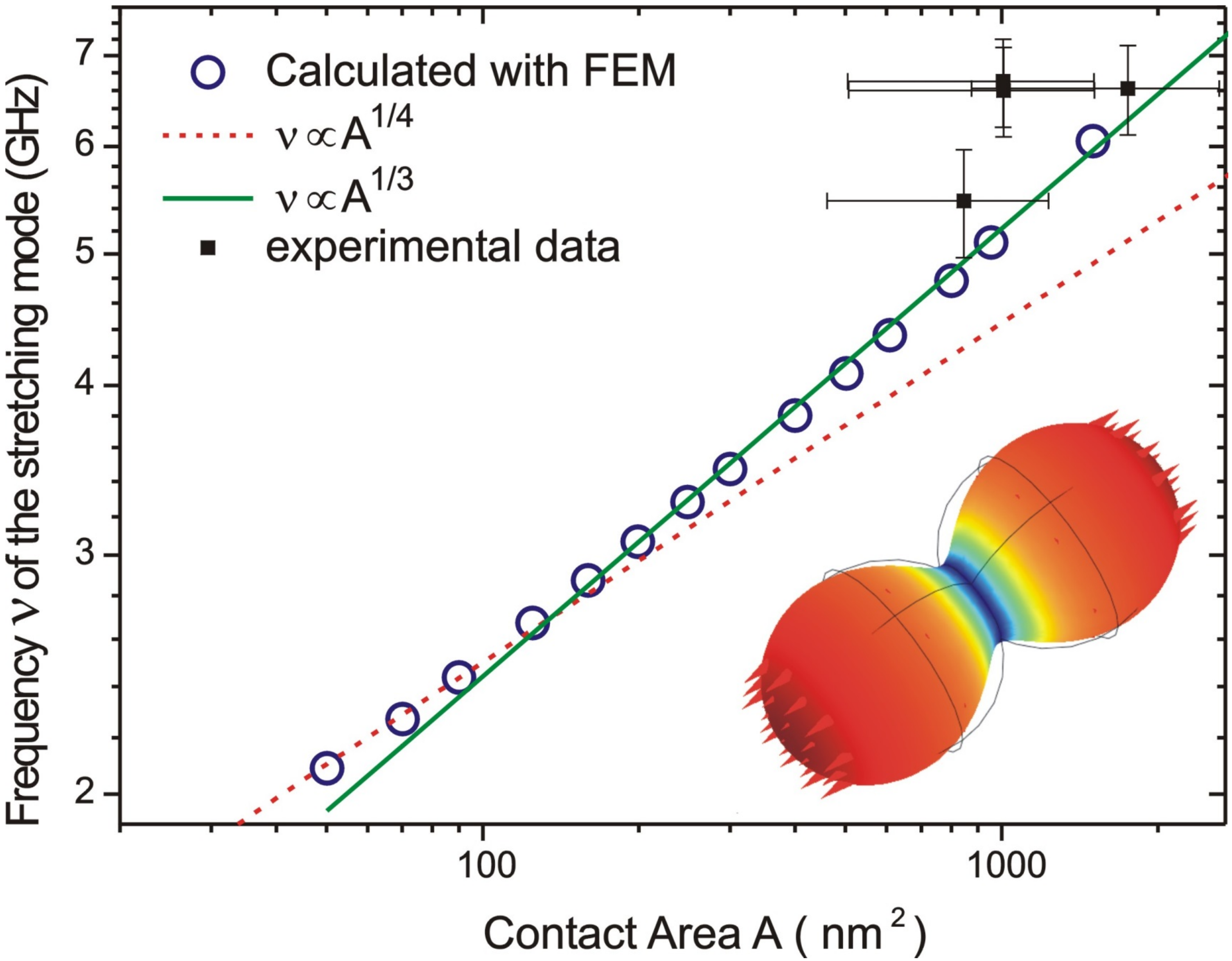

0.6
0.4
0.2
0.0
-0.2
Change in Reflectivity
100 nm
500
600
700
800
Wavelength (nm)


100
80
120
60
140
40
160
20
180
0
200
340
220
320
240
300
260
280

Acoustic spectra of dumbbells



FEM calculations of vibrations



Gold Nanorods

collab. P. Zijlstra, J. Chon, M. Gu
Swinburne U. (Melbourne, Australia)

- SEM and TEM images
- Plasmons and scattering
- Acoustic modes

Dr. Peter Zijlstra

TEM images

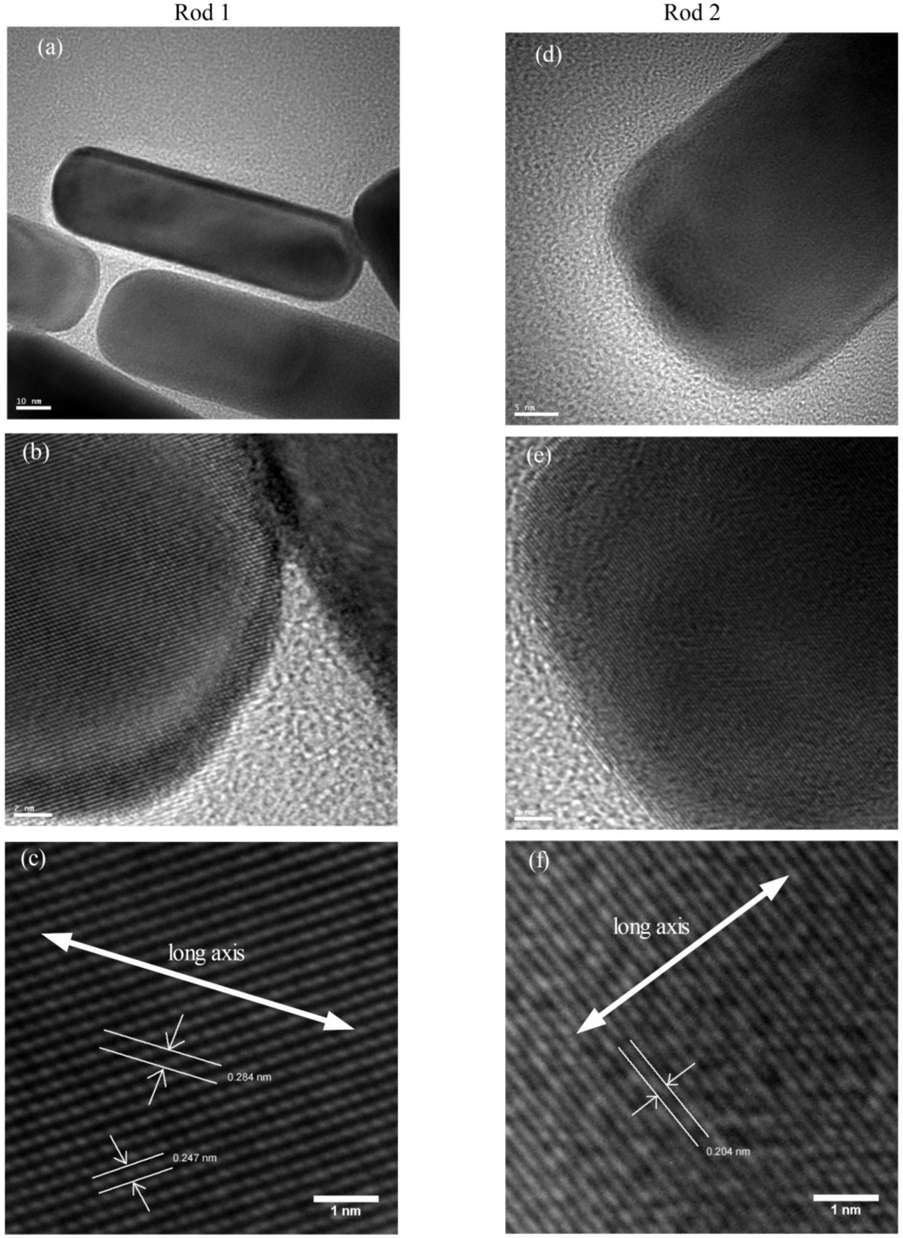
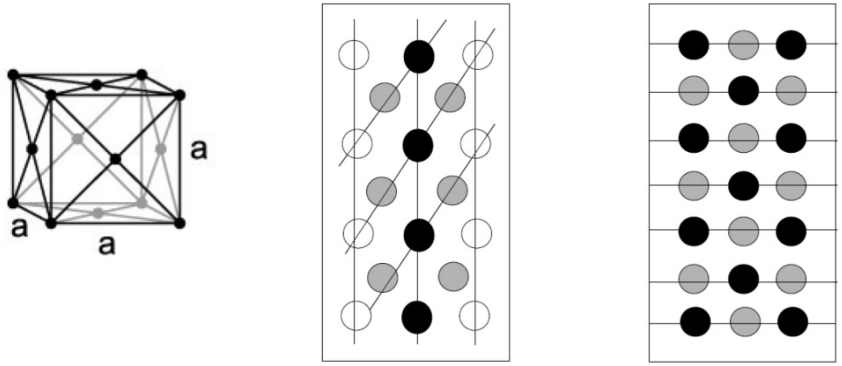
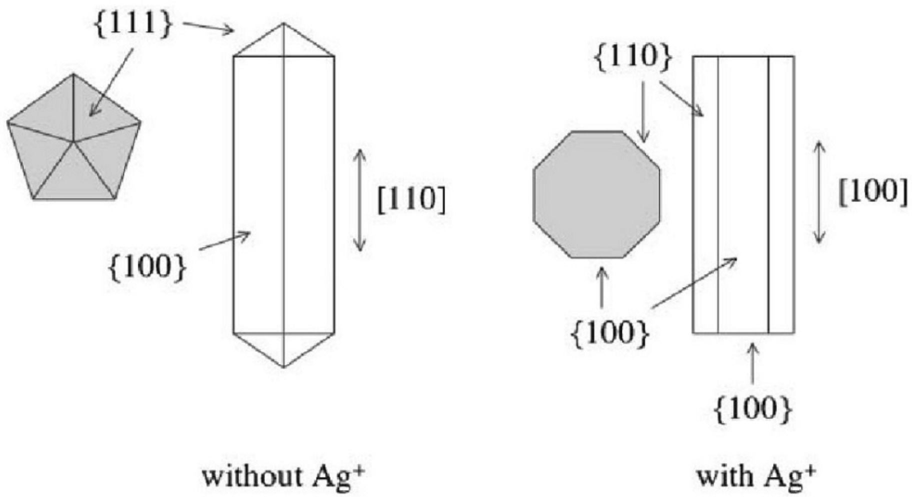
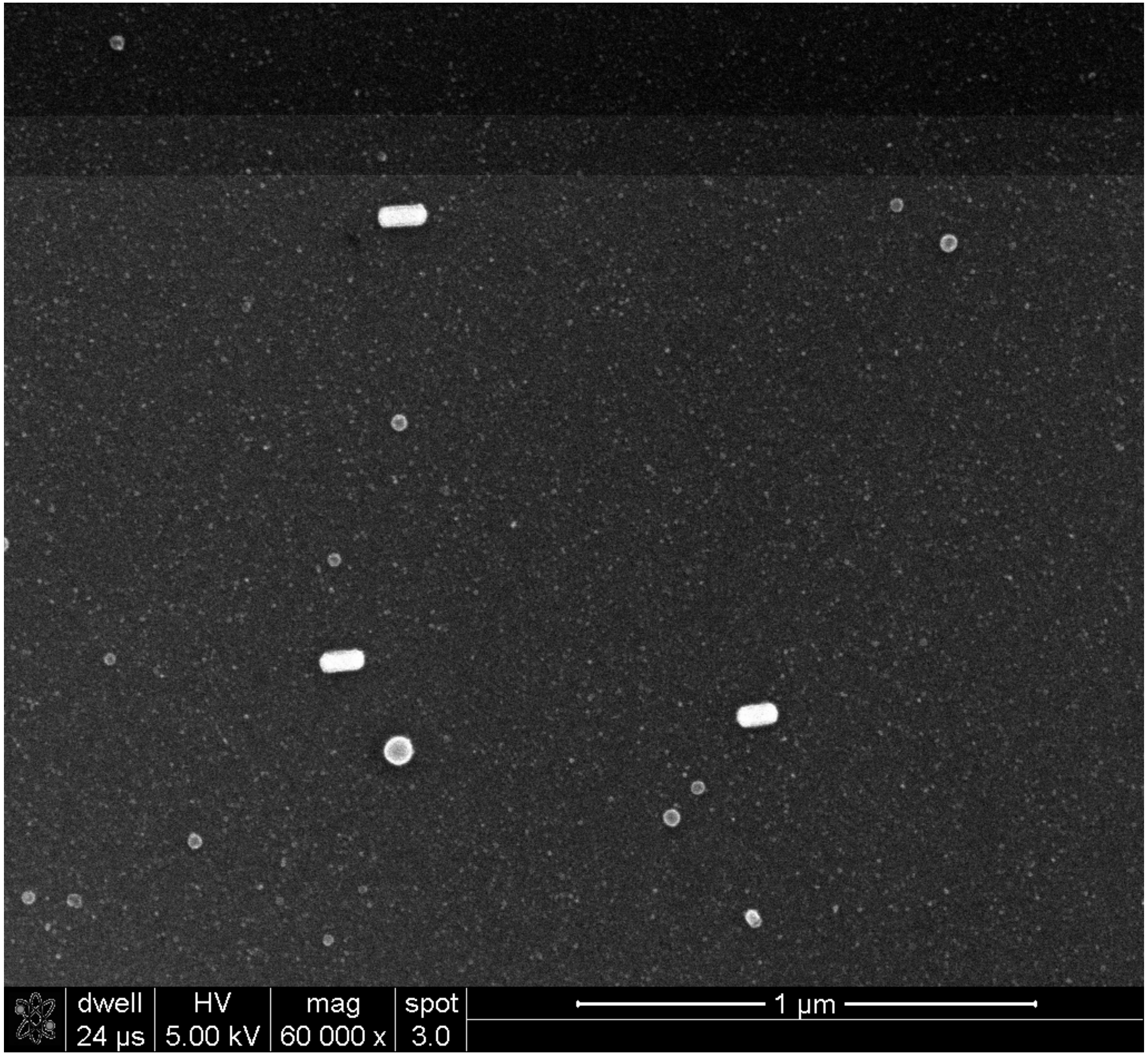


Figure 2: High resolution TEM images of two gold nanorods imaged at low (a) and (d), medium (b) and (e), and high (c) and (f) magnification (both (c) and (f) are imaged at 1.05 million times magnification). The fat arrows in (c) and (f) indicate the long particle axis. The measured lattice plane spacings averaged over 30-50 planes are indicated in (c) and (f).

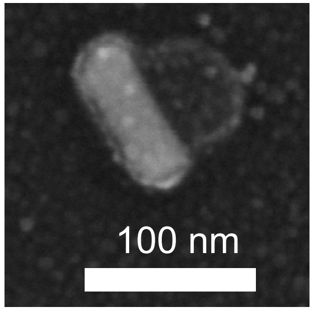




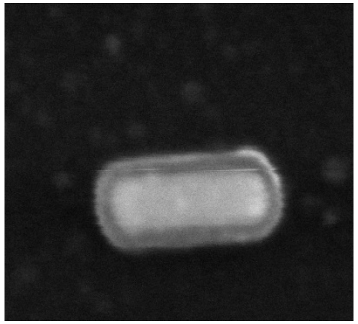
SEM images

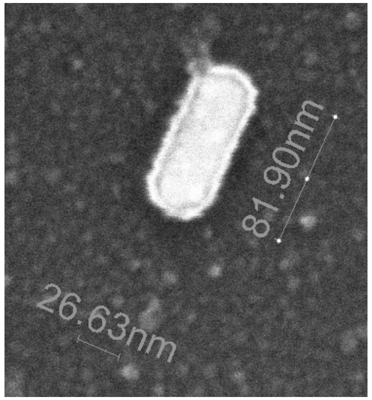


dwell
24 µs
HV
5.00 kV
mag
60 000 x
spot
3.0
1 µm



100 nm

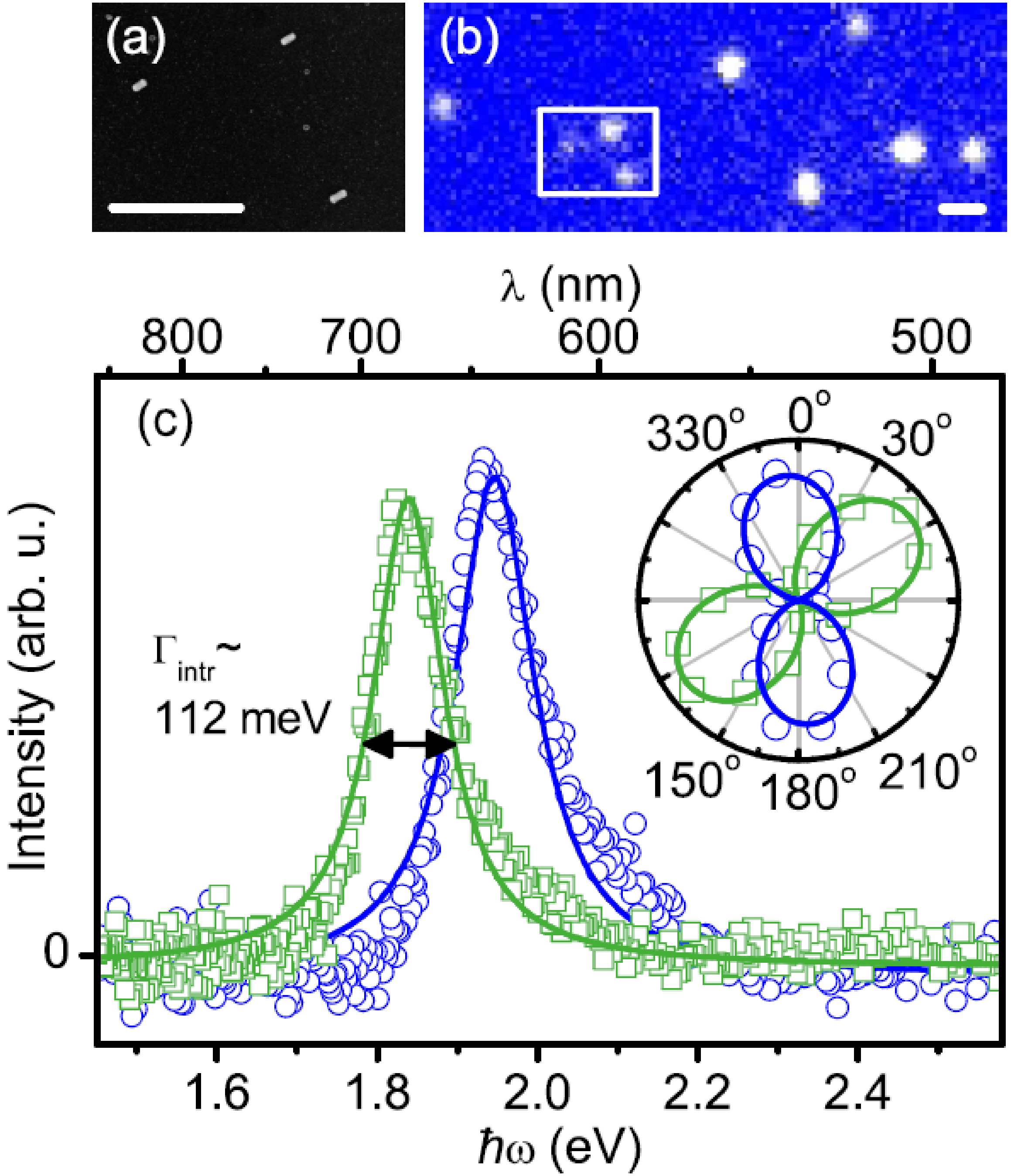




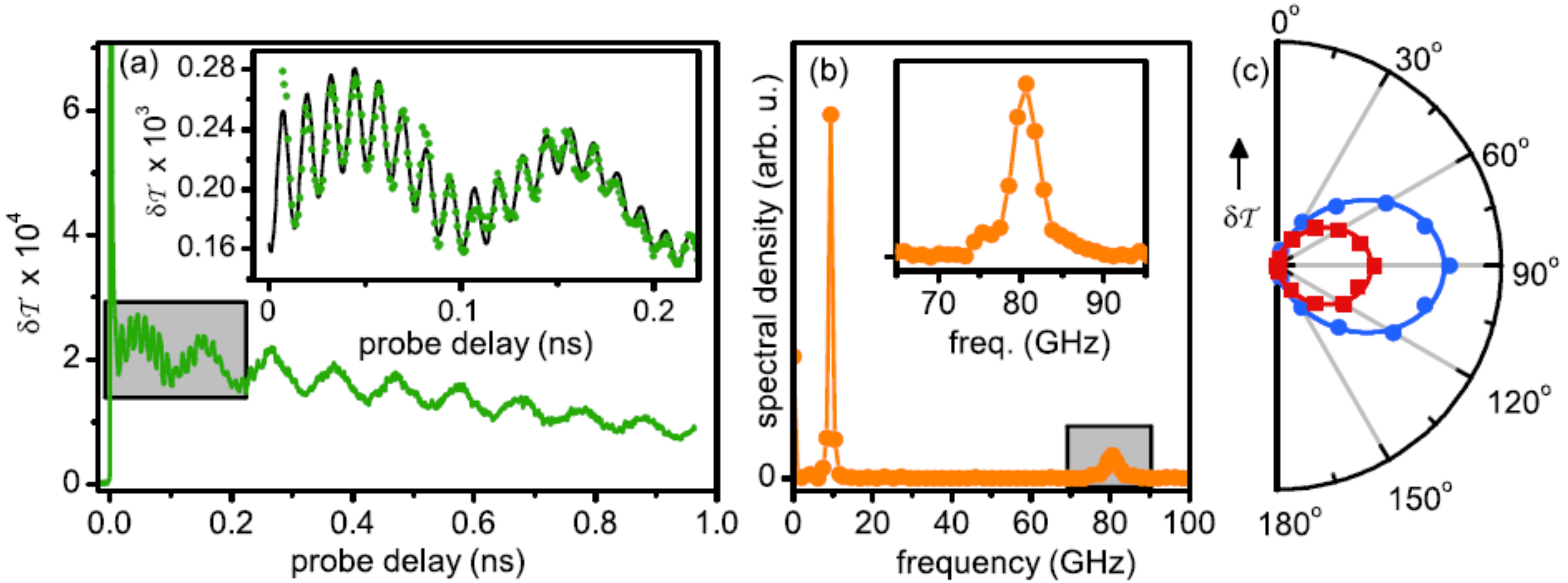
81.90nm
26.63nm

Optical scattering and SEM images

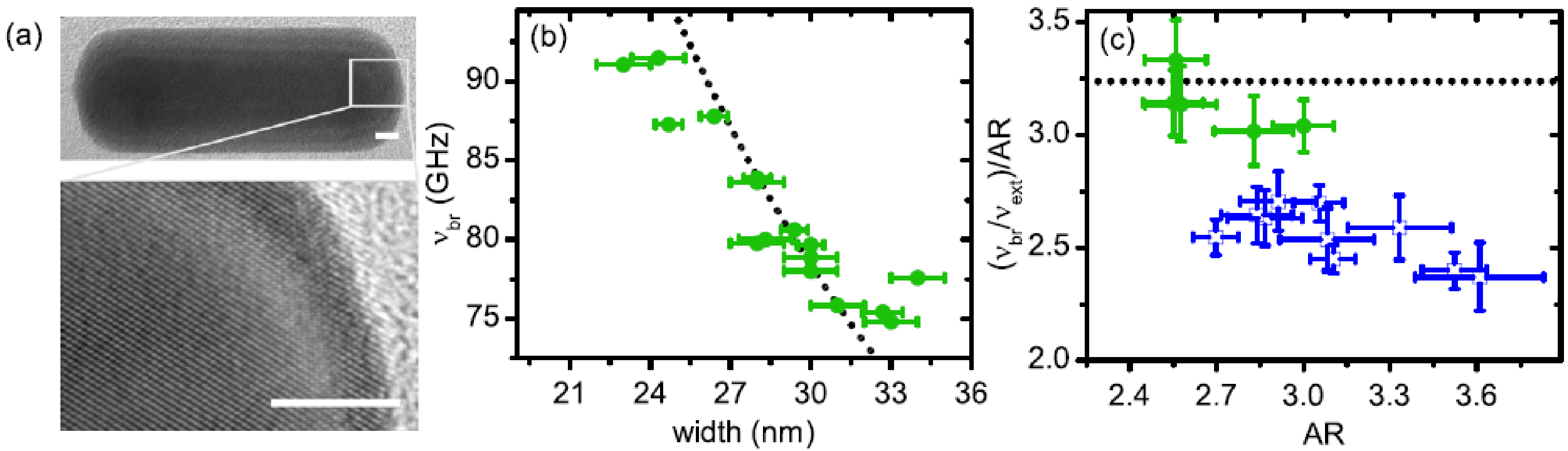
local index probe



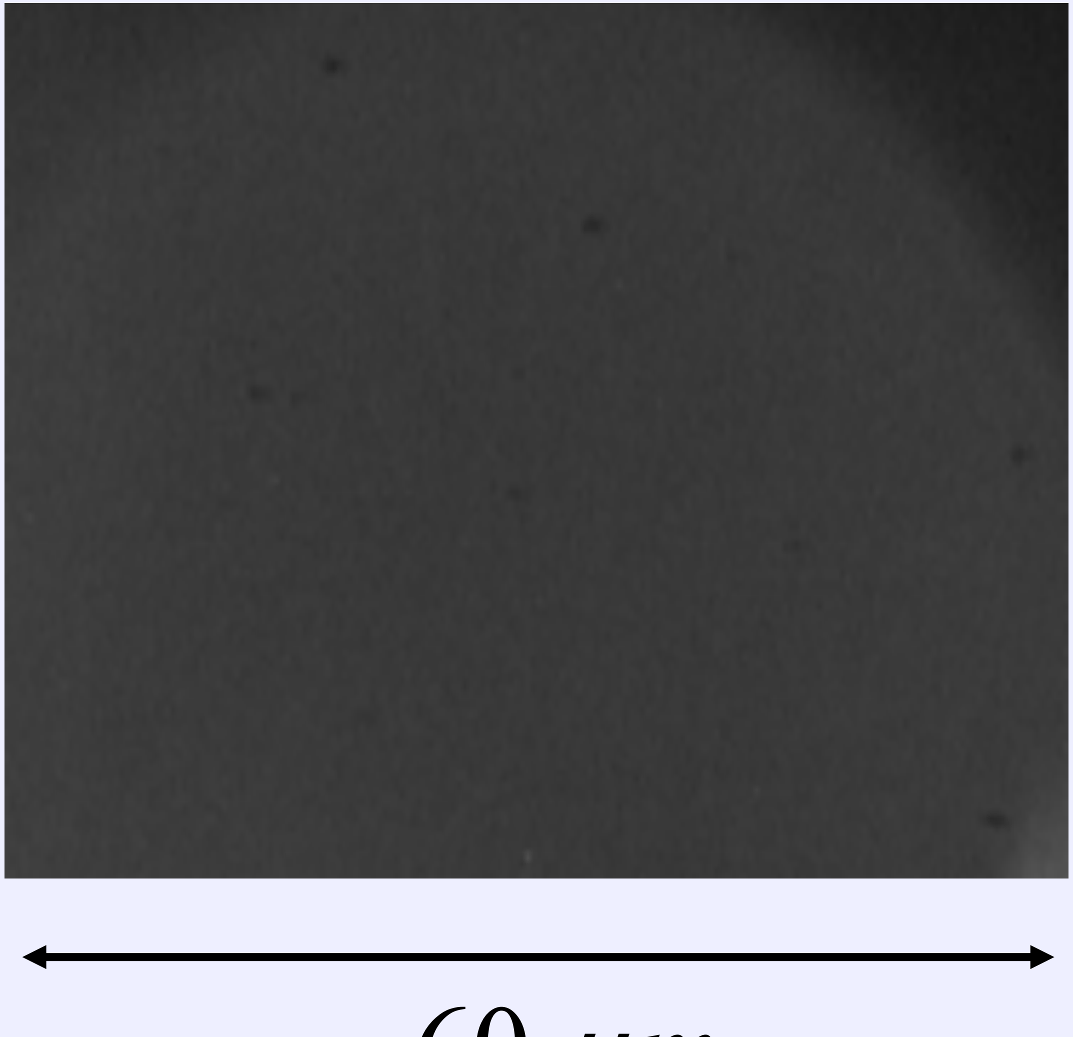
Vibrational transient with FT and angular dependence



Breathing and extensional frequencies dependence on aspect ratio

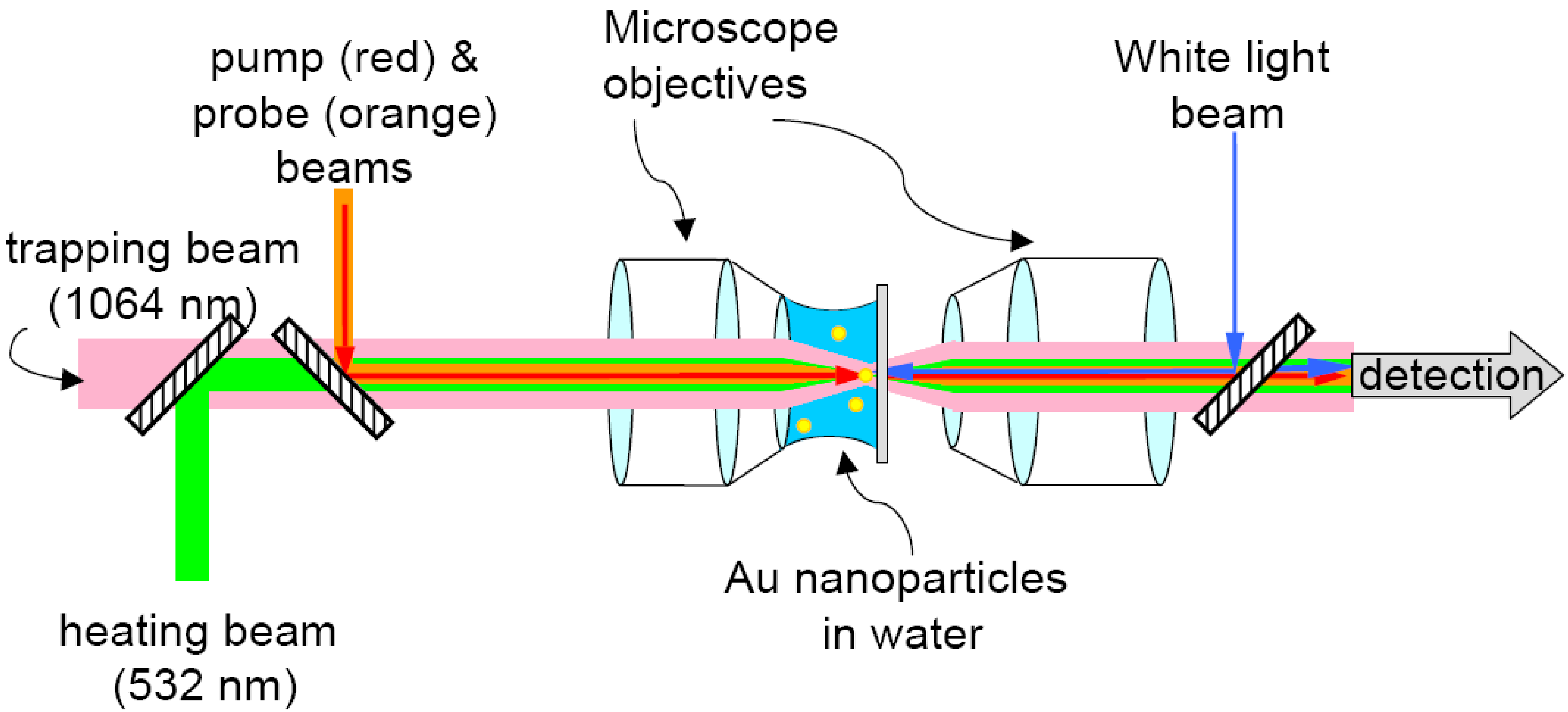


Trapping individual gold nanorods



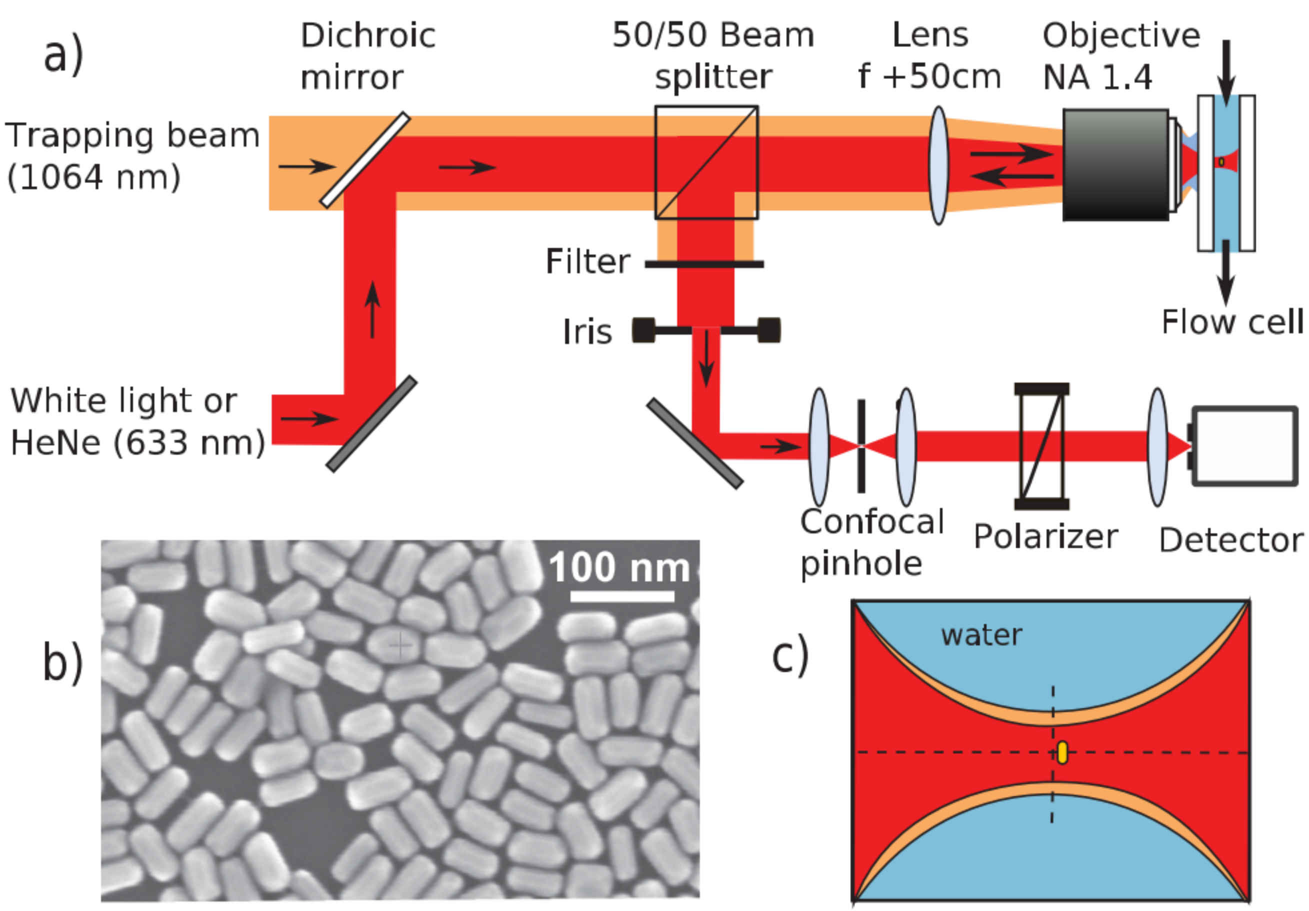
- real time

Gold nanoparticle in an optical trap

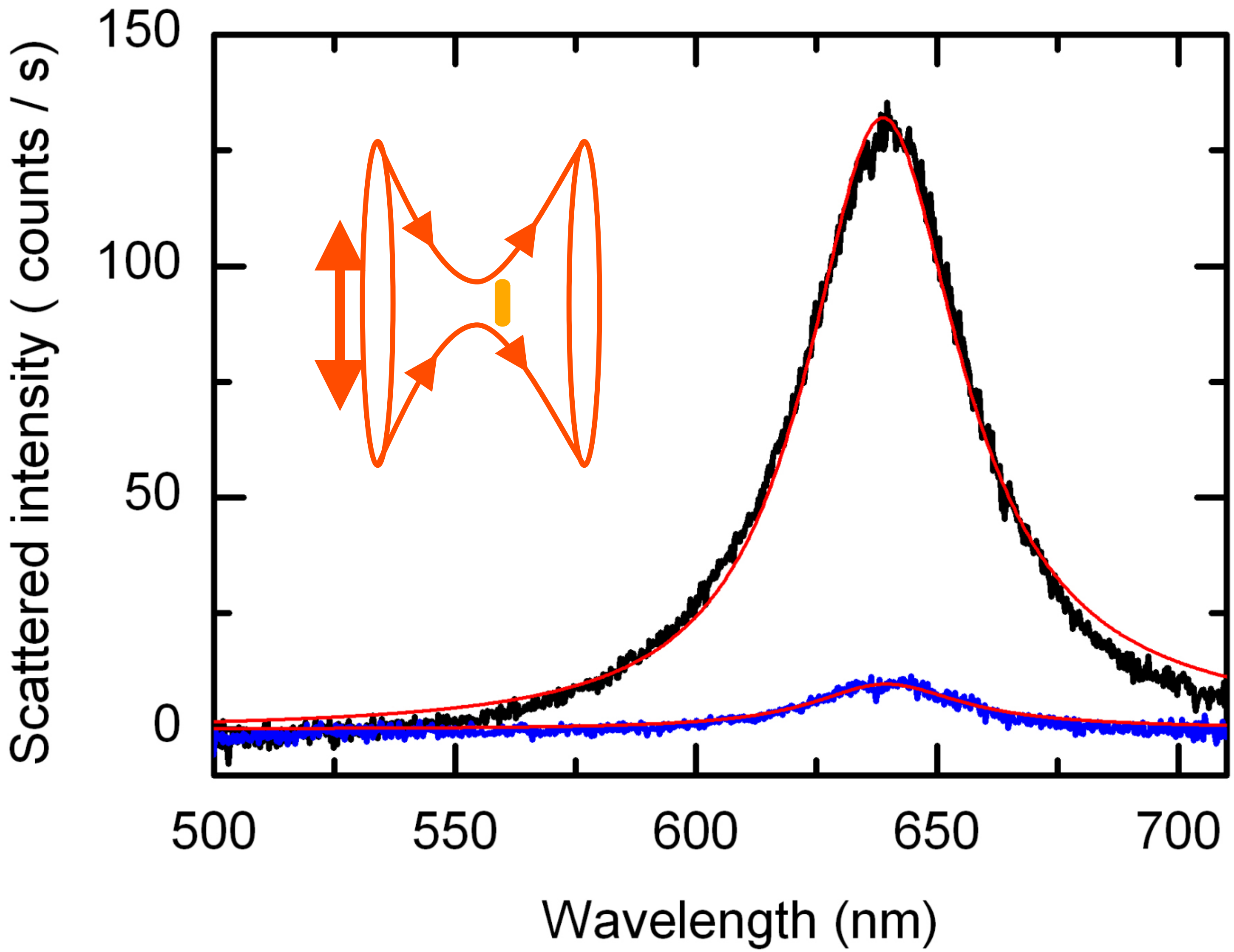


- Advantages: no perturbation by the substrate; manipulations possible

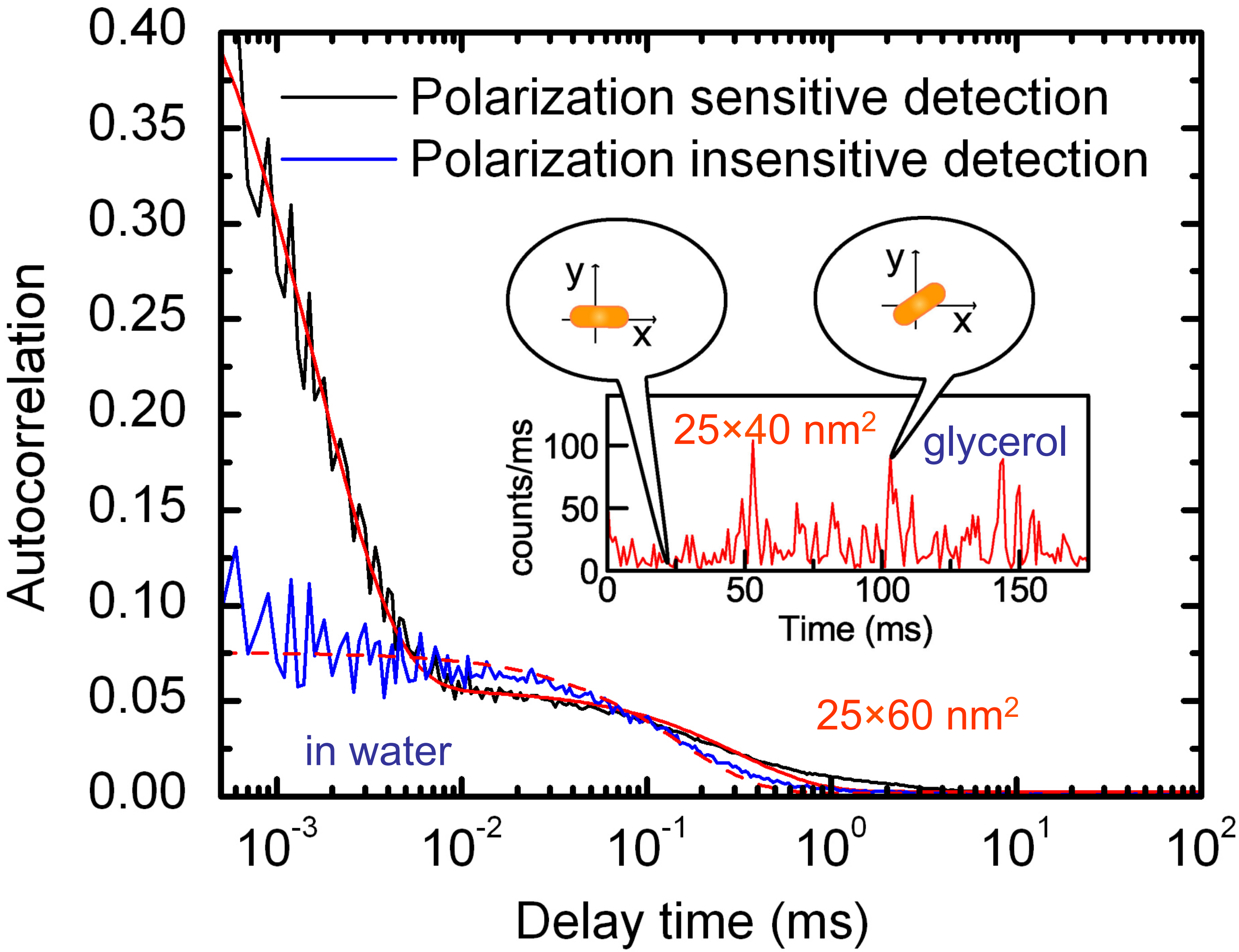
Trapping single gold nanorods



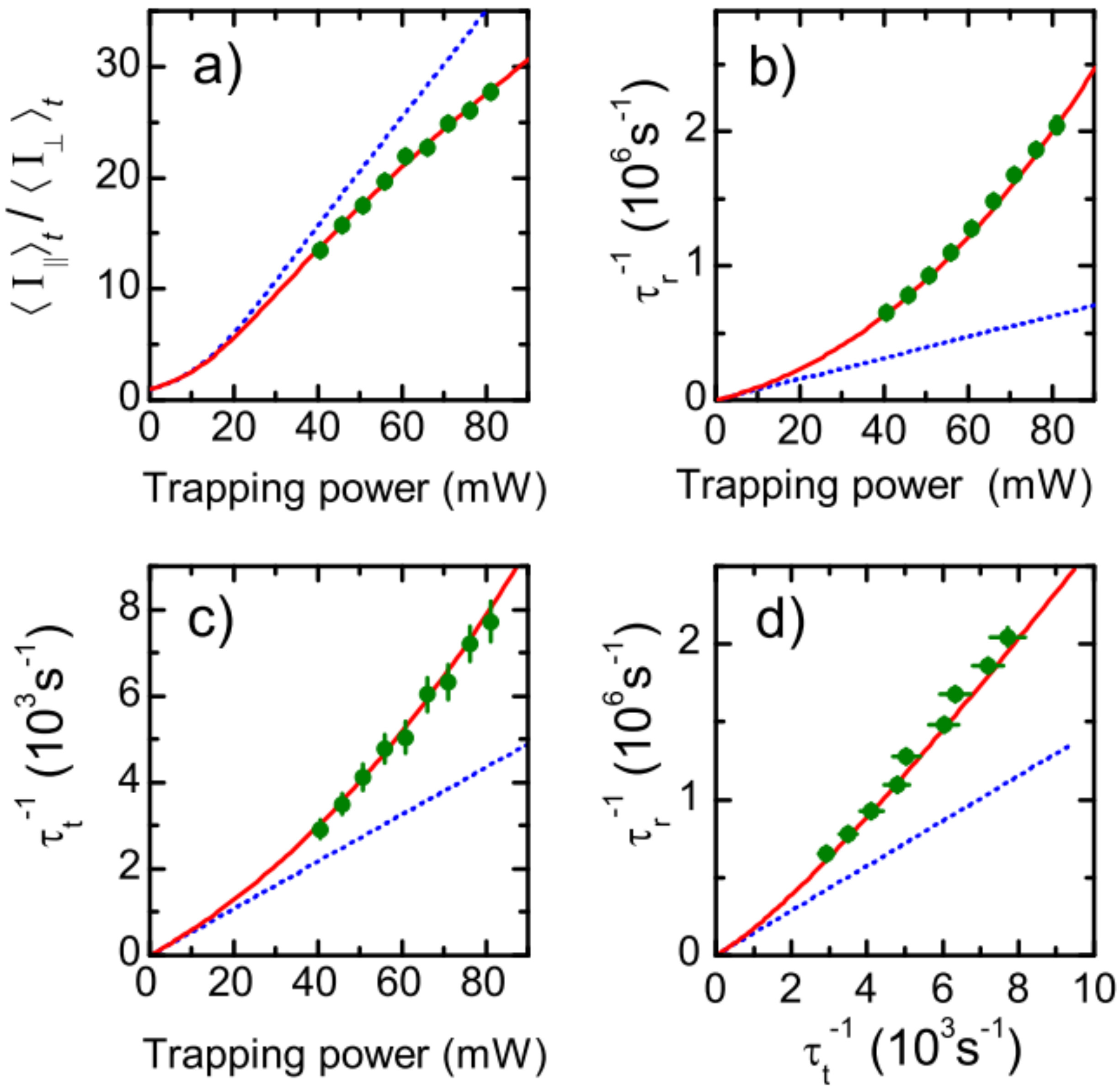
Orientation of gold nanorod along trap polarization



Fluctuations of orientation by autocorrelation



Local temperature and viscosity



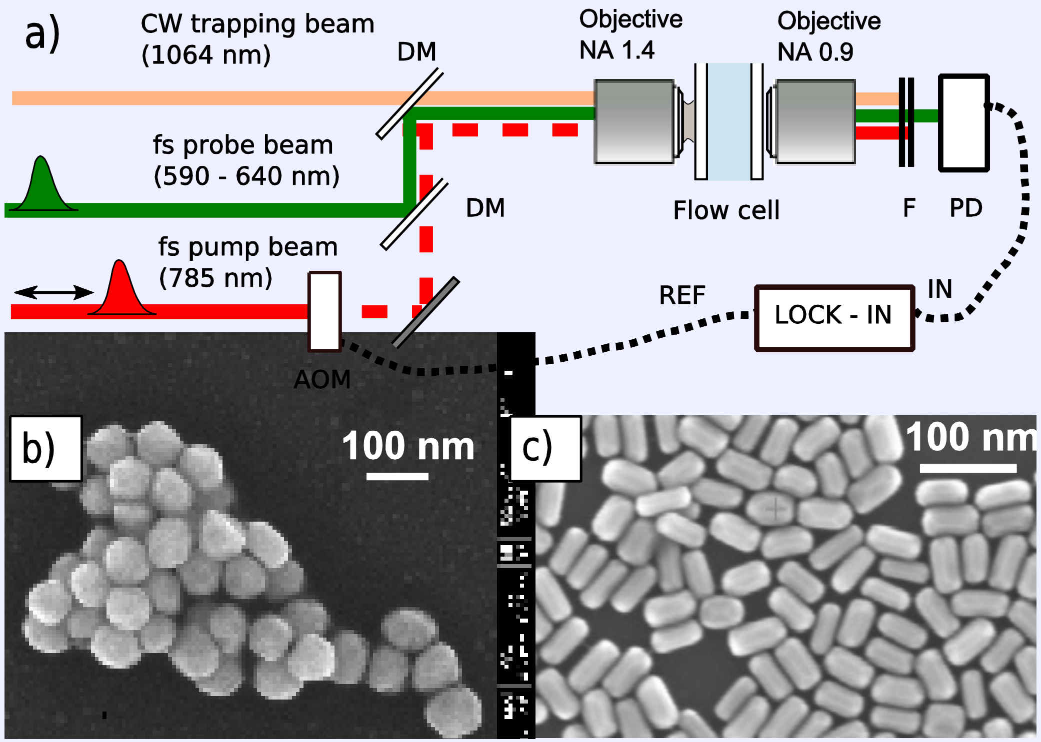
Single 60x25 nm^2 nanorod in the optical trap

Polarization of scattered light, rotational time, translational time as functions of trapping power

Maximum temperature change about 80 K

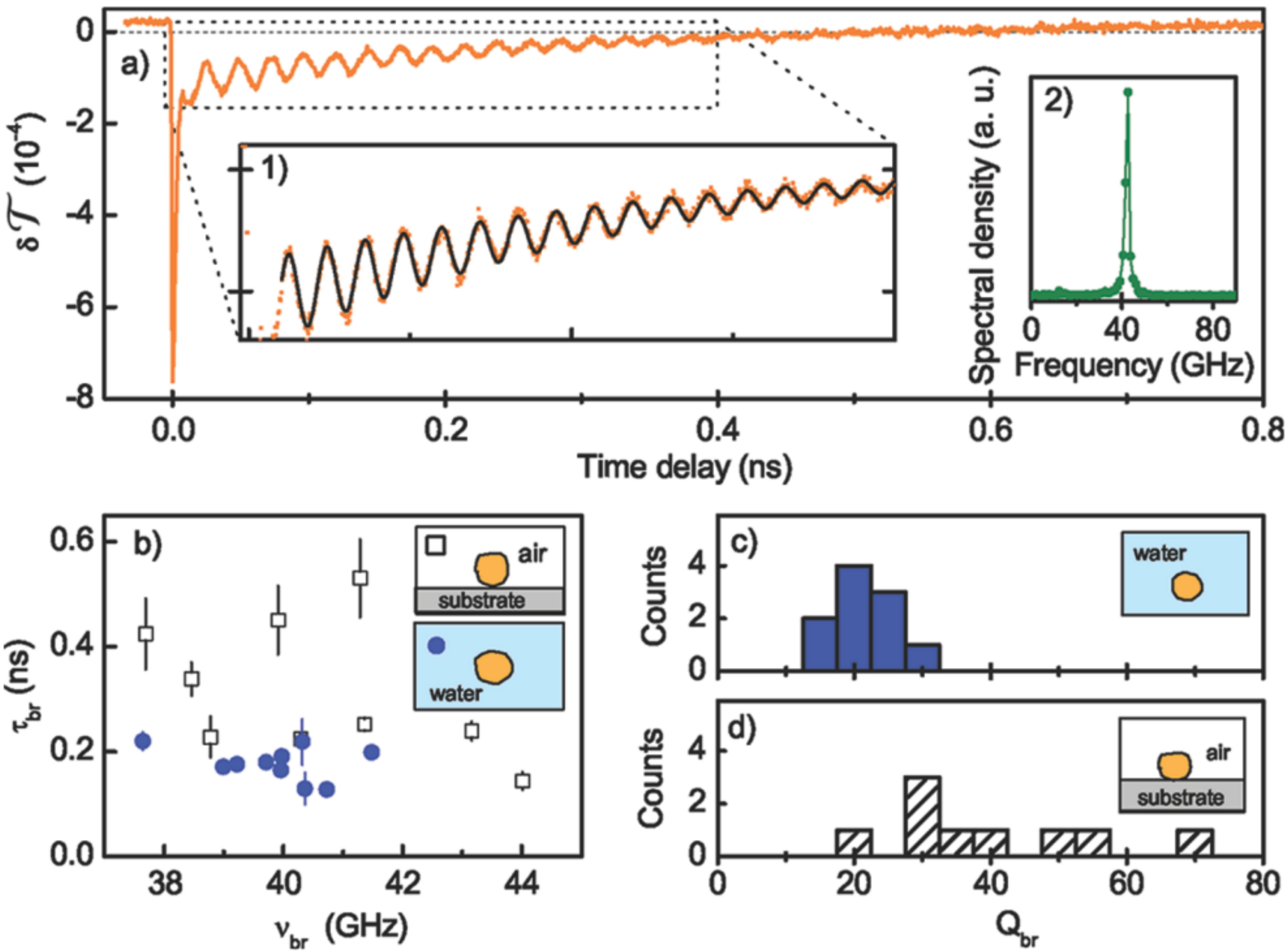
Ruijgrok et al., PRL **107** (2011) 037401

Vibrational damping in a liquid environment

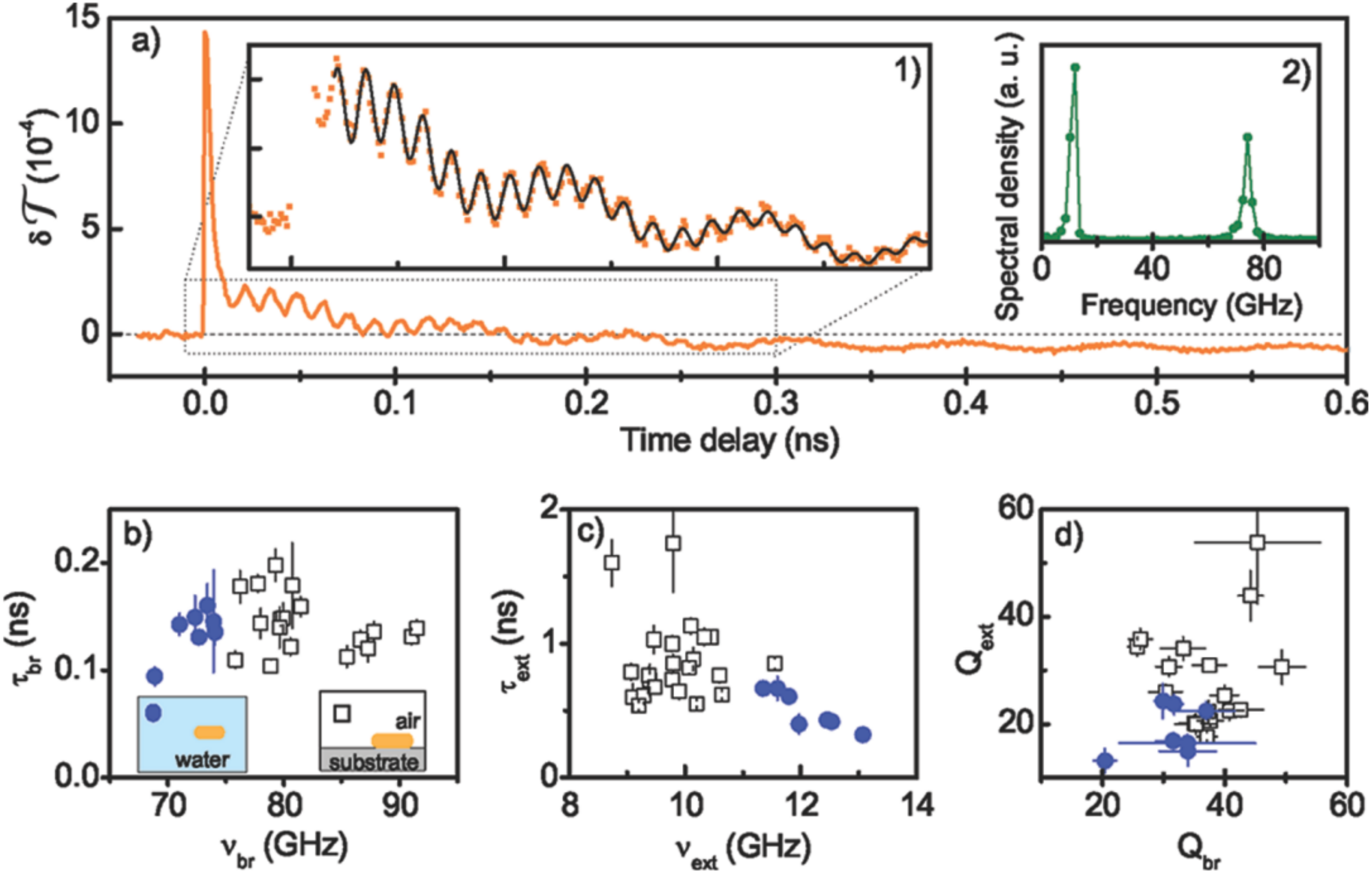


Ruijgrok et al., Nanolett. **11** (2011) 1063

Nanospheres

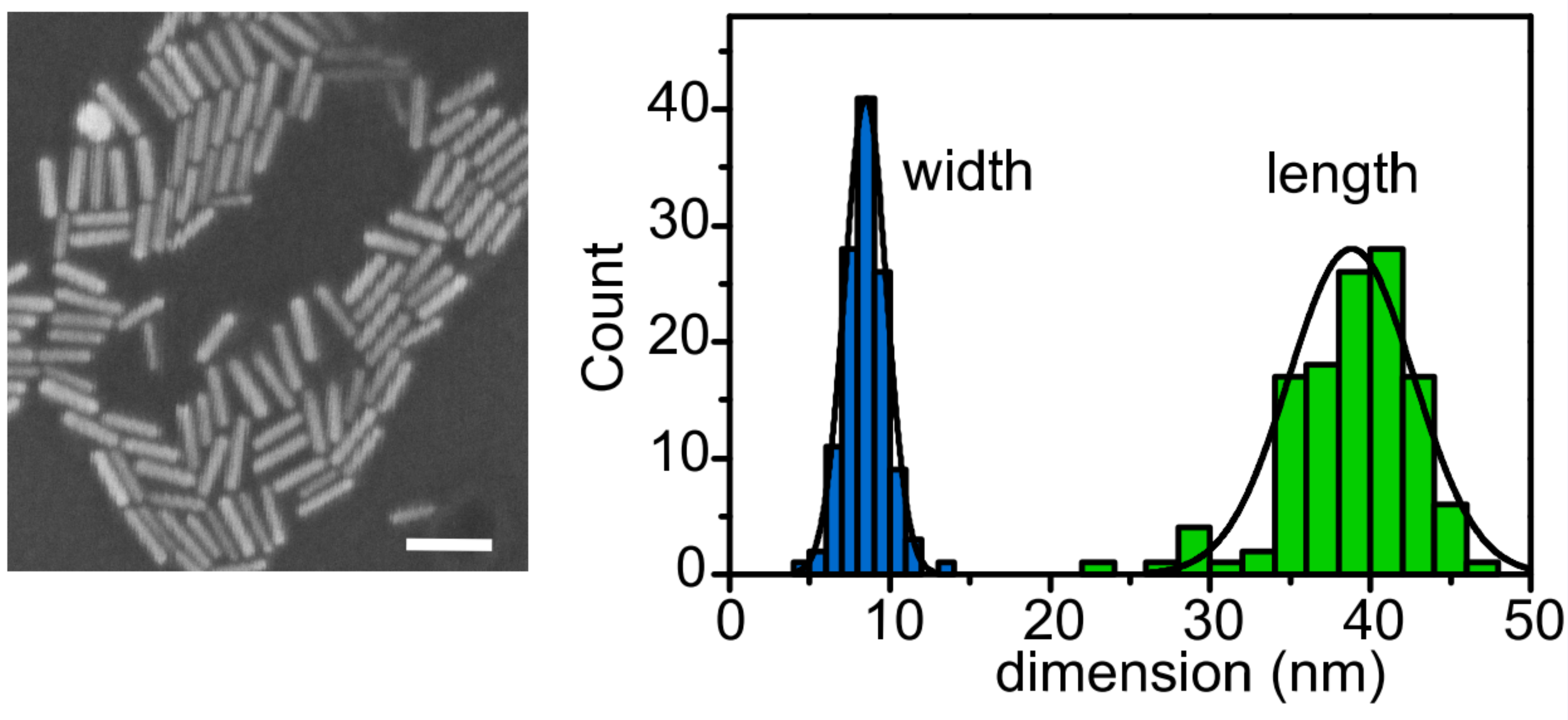


Nanorods



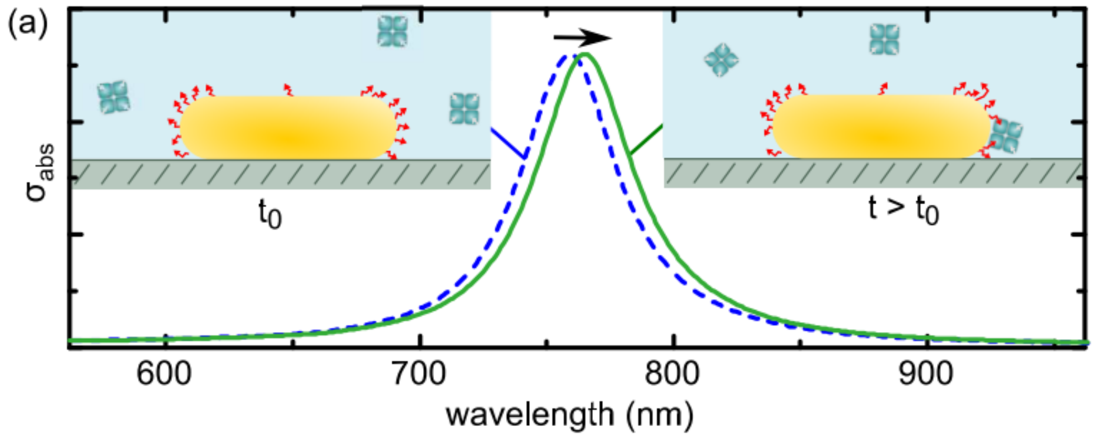
a)
1)
2)
Spectral density (a. u.)
Frequency (GHz)
0
40
80
15
10
5
0
δ𝒯 (10⁻⁴)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Time delay (ns)
b)
τbr (ns)
0.0
0.1
0.2
70
80
90
νbr (GHz)
water
air
substrate
c)
τext (ns)
0
1
2
8
10
12
14
νext (GHz)
d)
Qext
20
40
60
Qbr

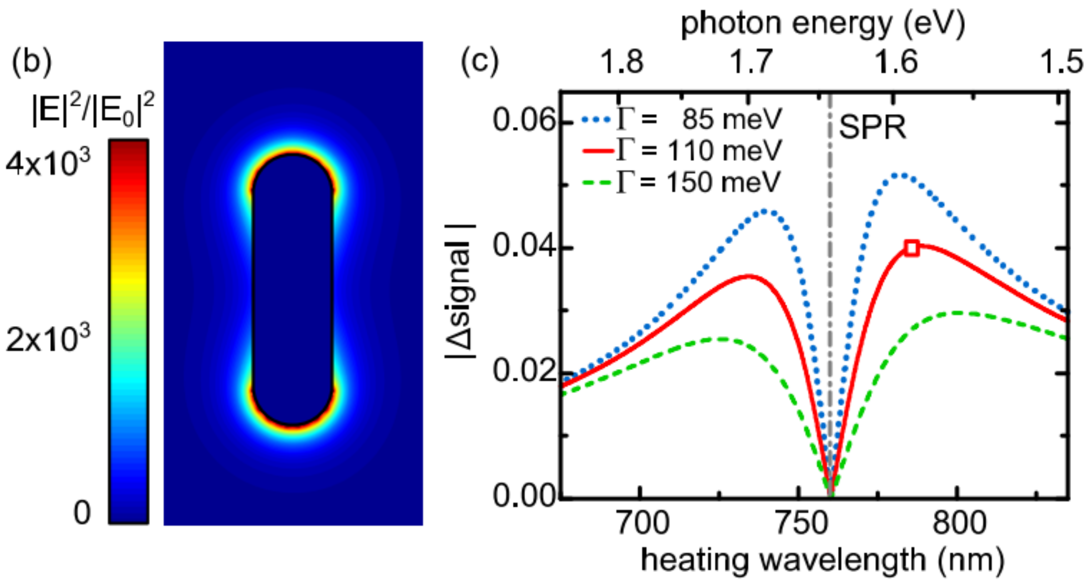
Plasmonic sensing with single gold nanorods



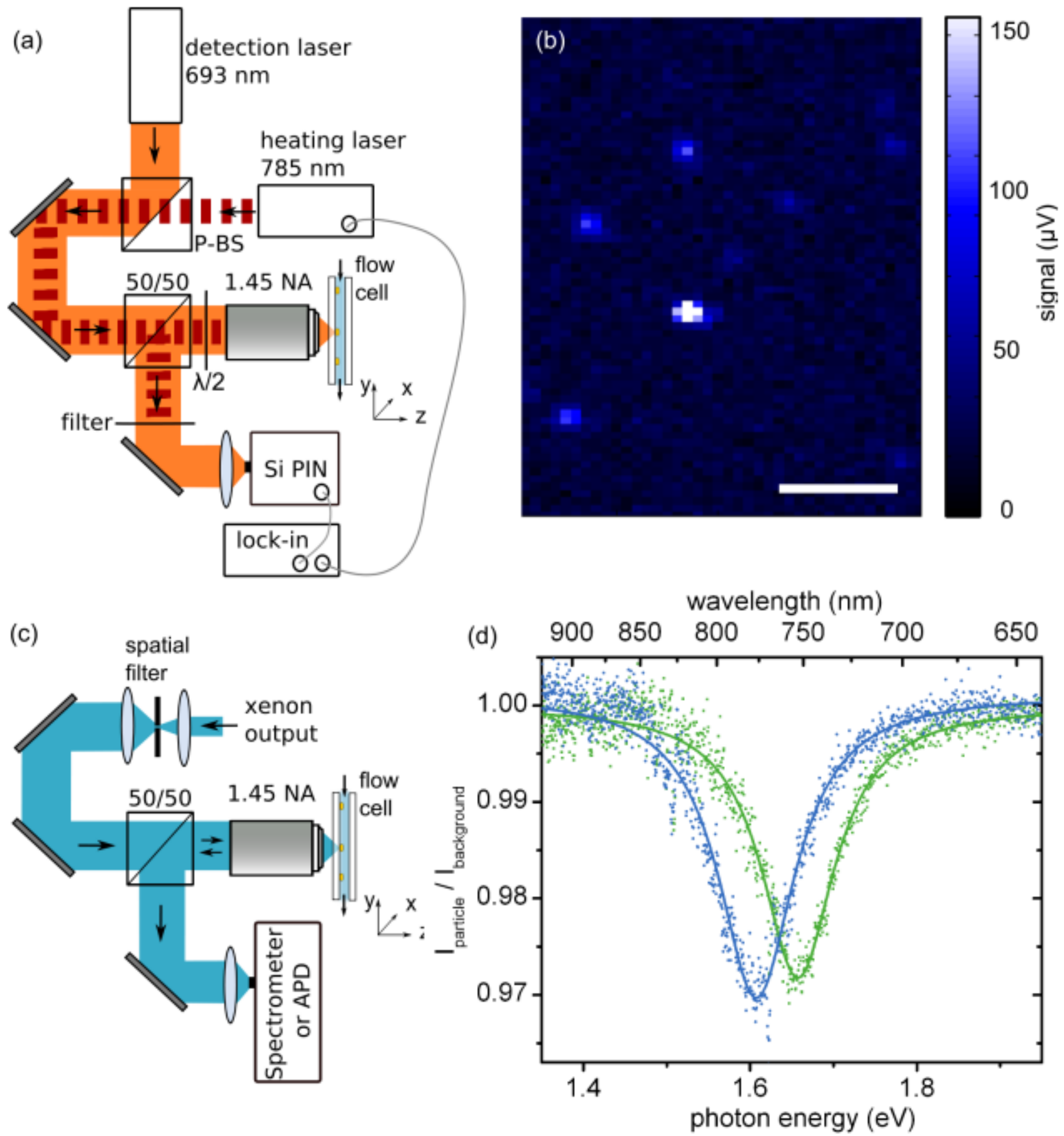
P. Zijlstra et al., Nat. Nanotechn. **7** (2012) 379

Principle of the sensing

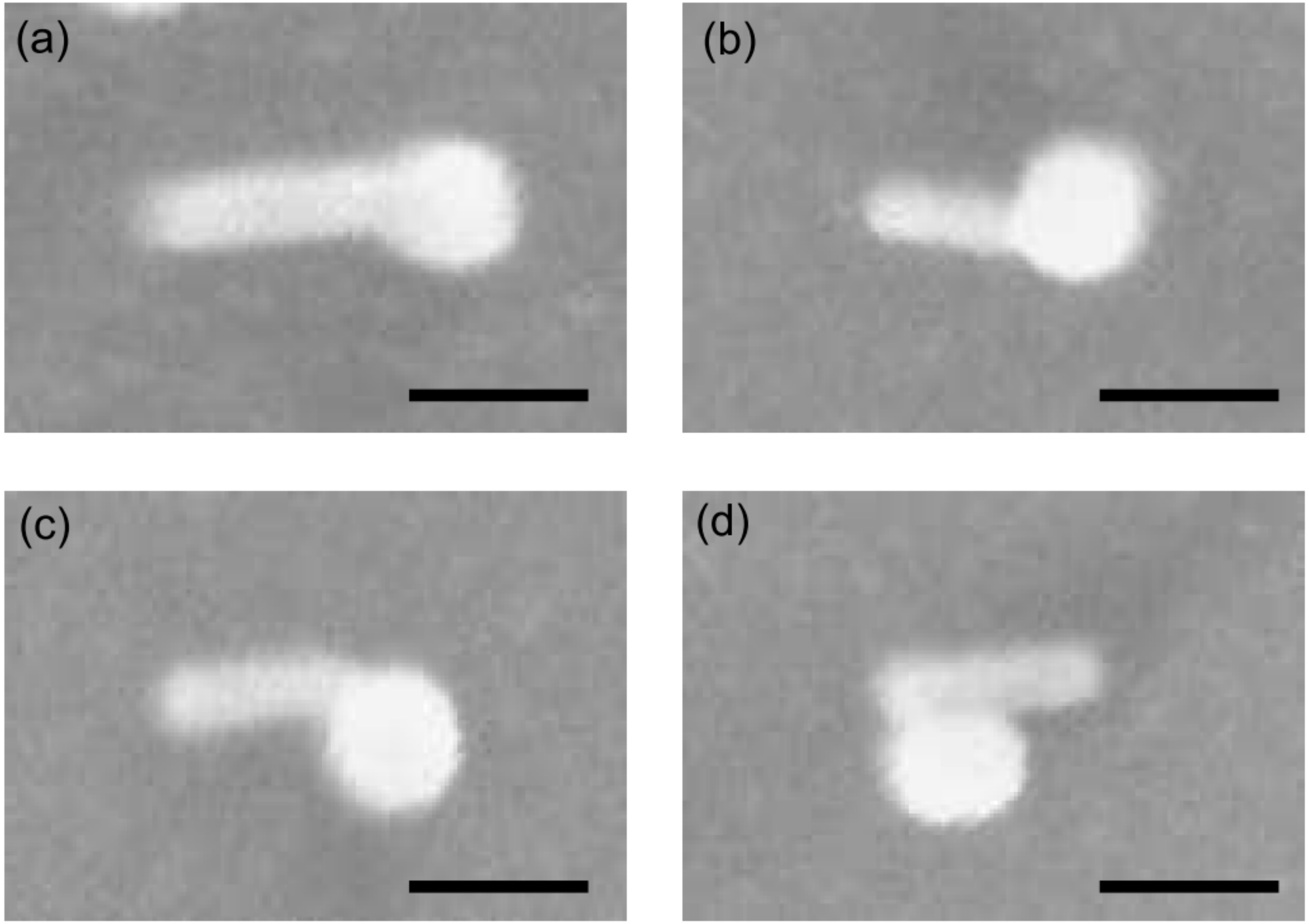




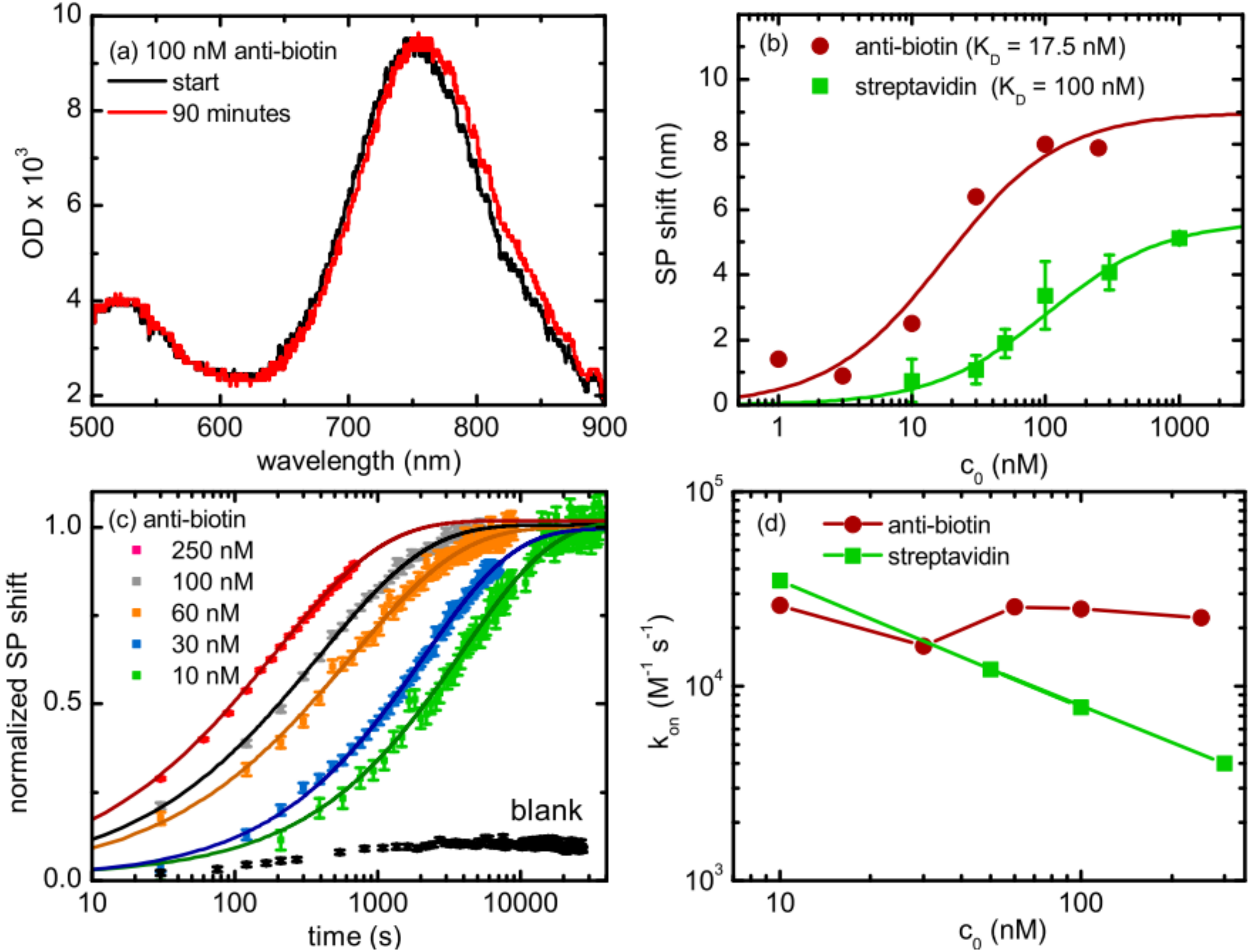
Optical setup (photothermal and scattering)



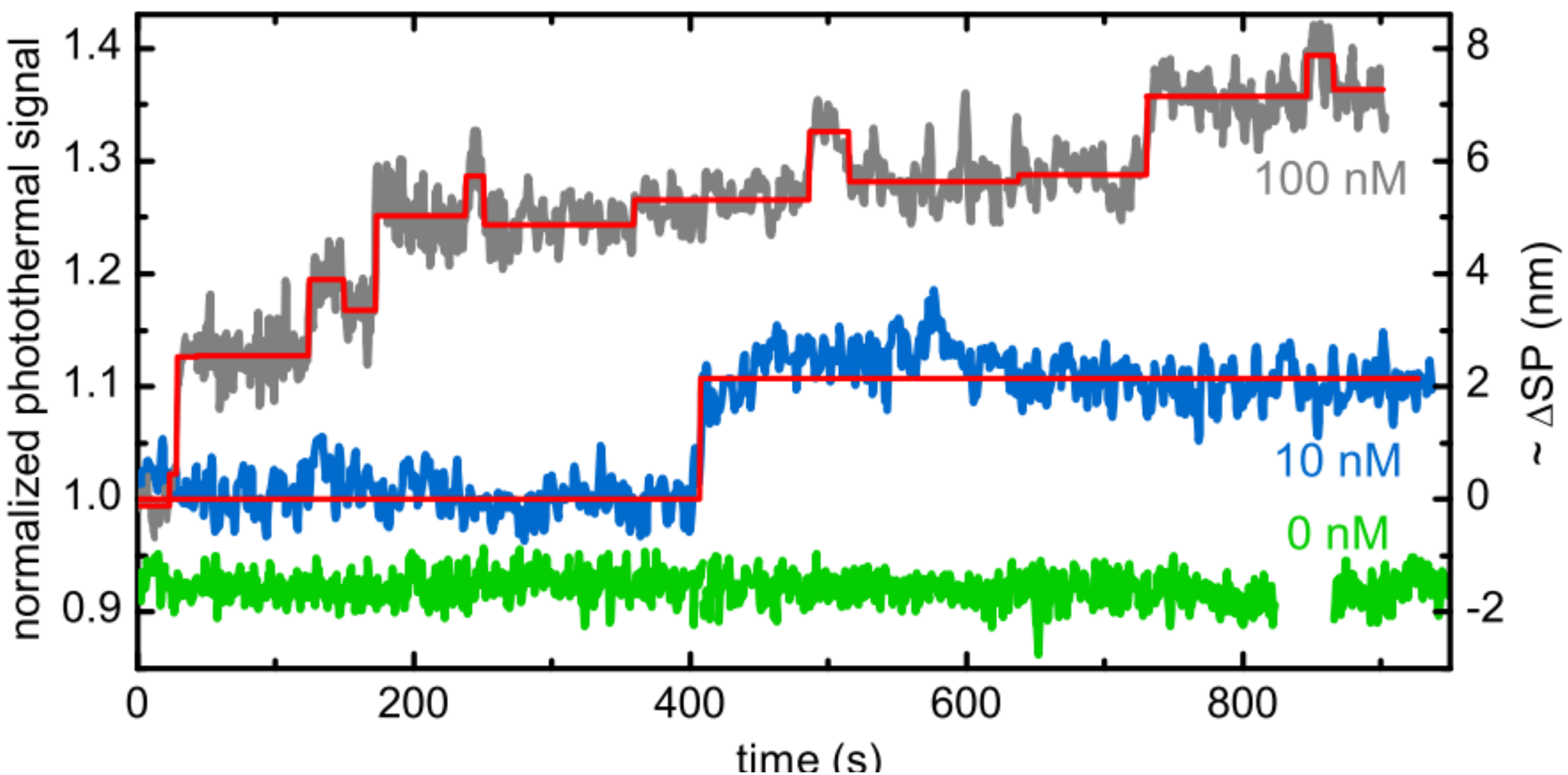
Preferential conjugation at the tips



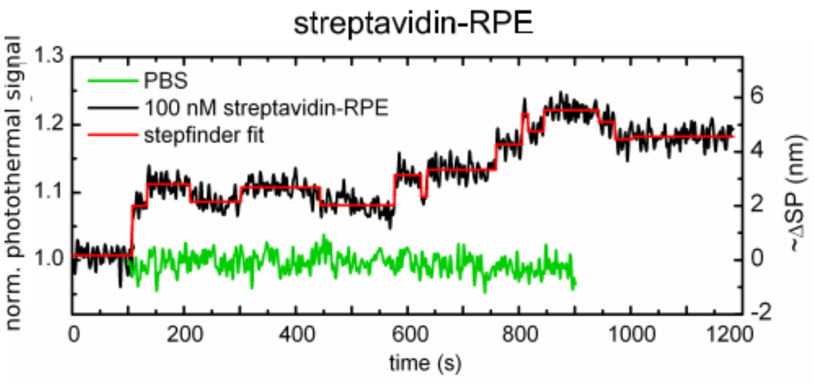
Ensemble binding experiments

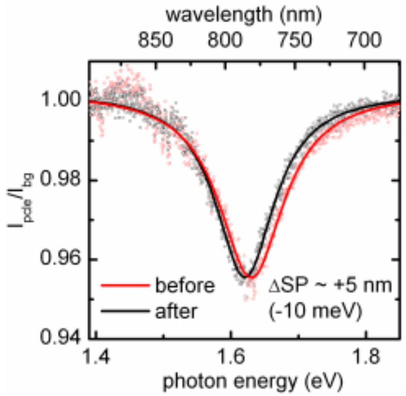


Binding of Streptavidin-phycoerythrin



Binding traces of different molecules

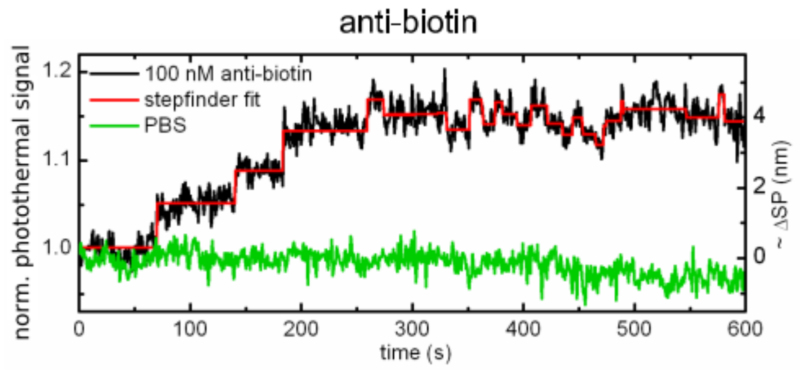


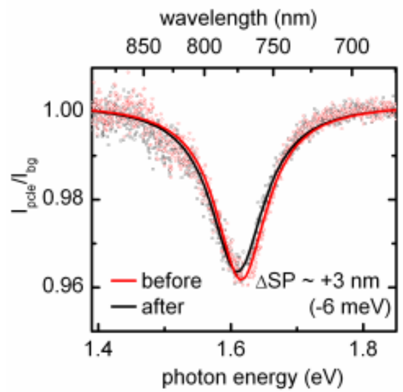


experimental parameters:

Photothermal:
Heating laser = 16 μW
Detection laser = 400 μW
integration time = 100 ms

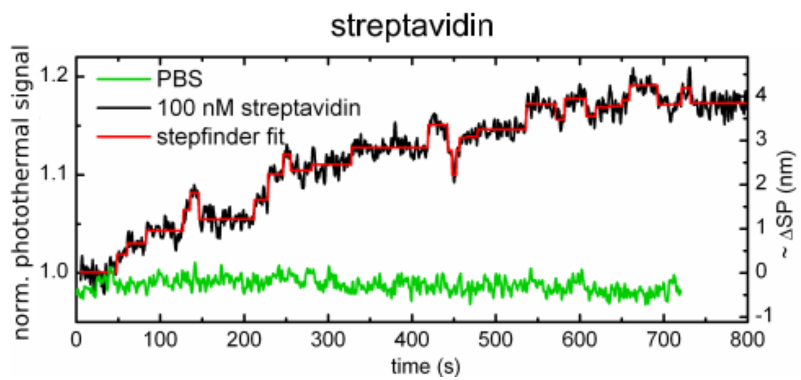
White light scattering:
Integration time = 15 s

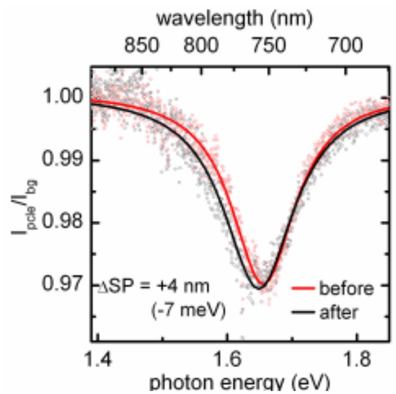




Photothermal:
Heating laser = 25 μW
Detection laser = 700 μW
Integration time = 100 ms

White light scattering:
integration time = 15 s

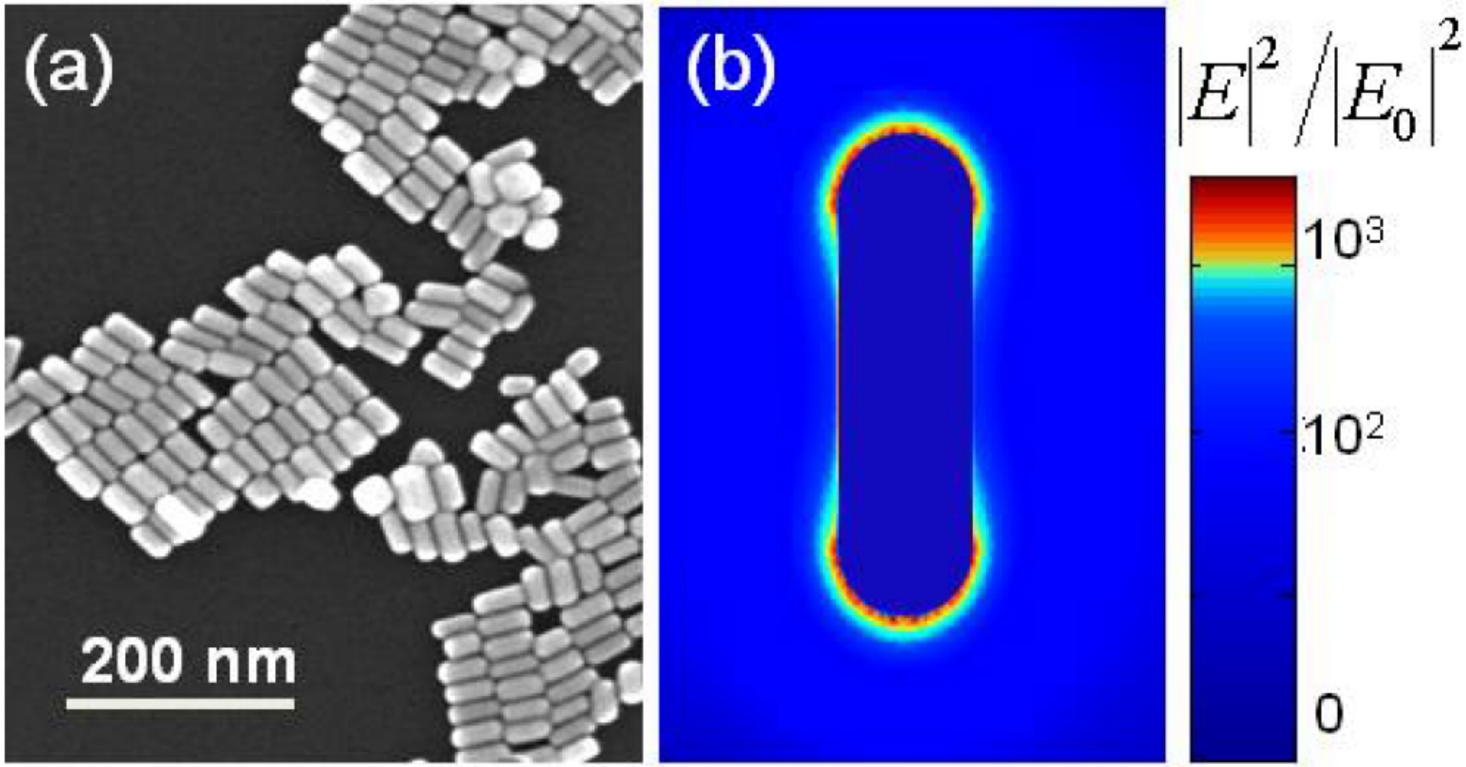




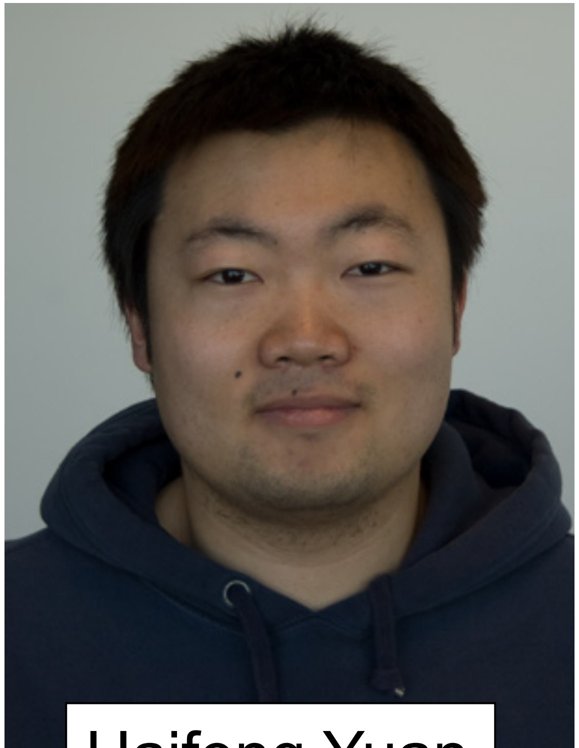
Photothermal:
Heating laser = 98 μW
Detection laser = 450 μW
integration time = 100 ms

White light scattering:
integration time = 15 s

Fluorescence enhancement by a single gold nanorod



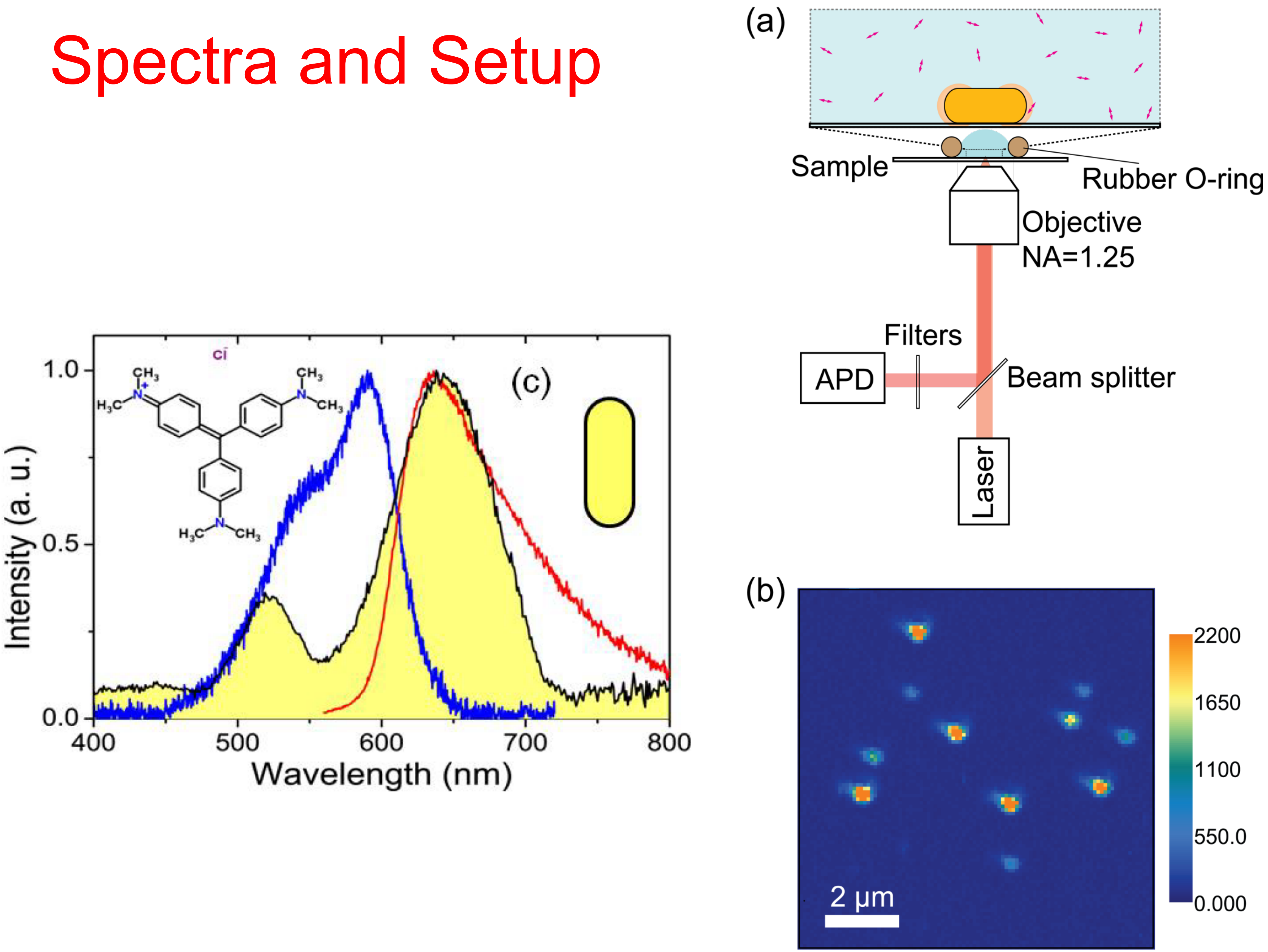
HF Yuan et al., Angew. Chem. (online 2012)



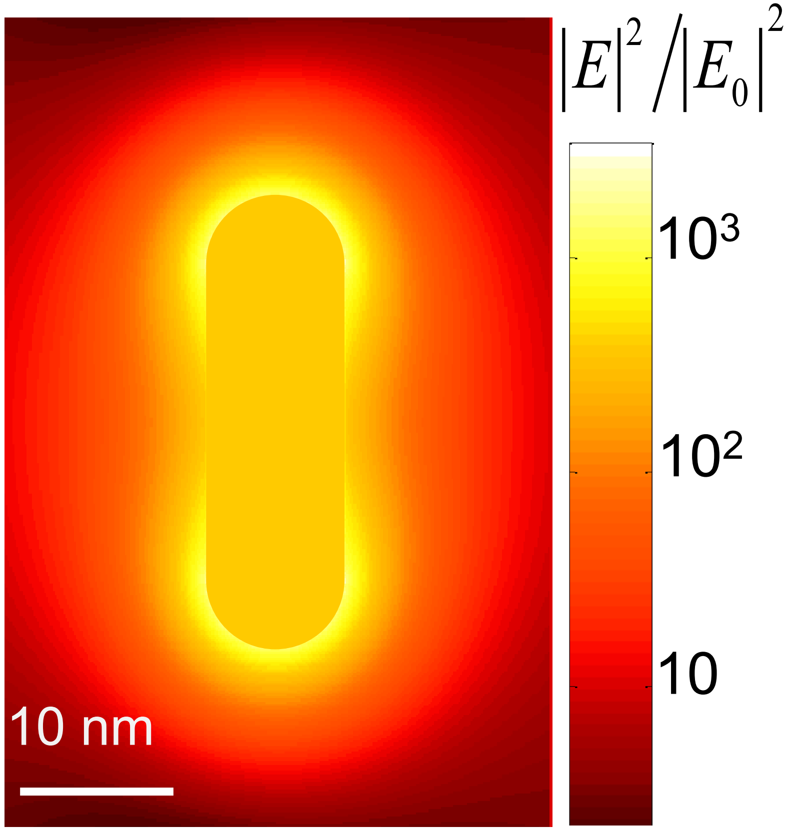
Haifeng Yuan

Dr Saumyakanti Khatua

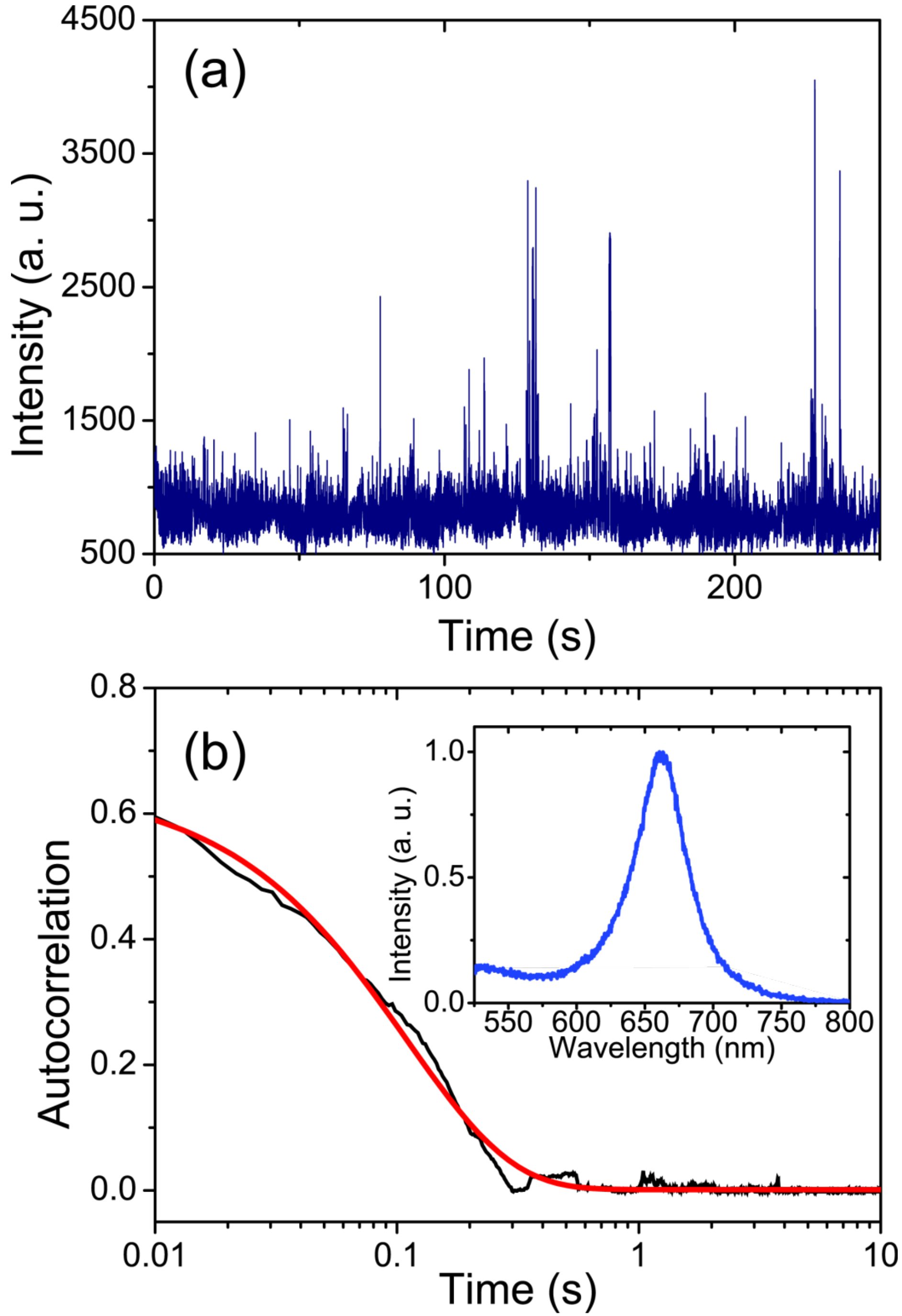
Spectra and Setup



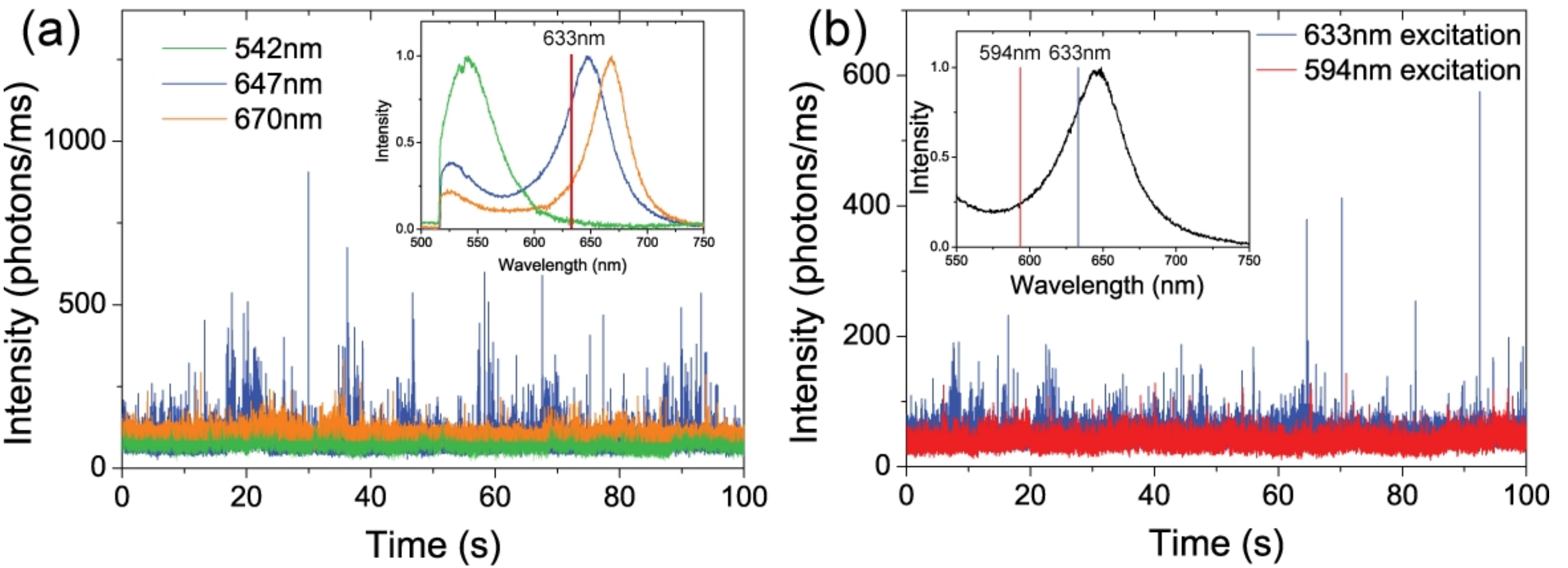
Fluorescence bursts



enhancement ~ 1000-fold



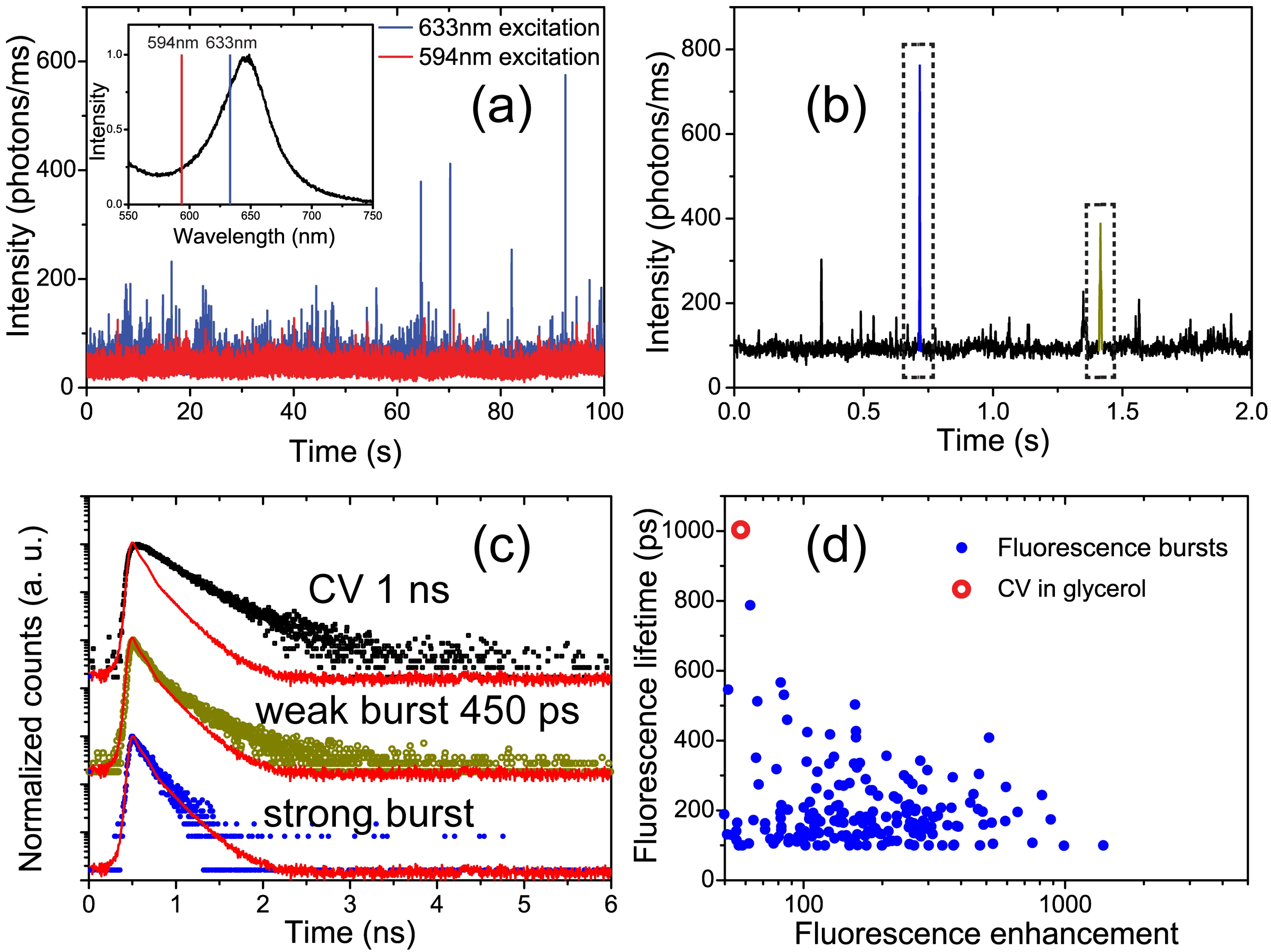
Influence of spectral overlap



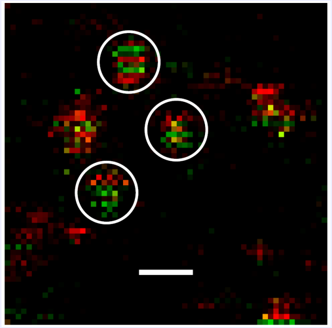
Surface plasmon resonance

Excitation wavelength

Fluorescence lifetime during bursts

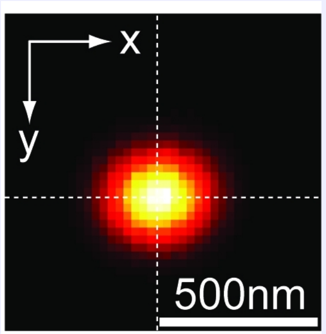


Conclusions

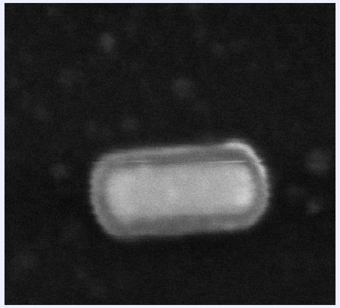


- Heterogeneity of supercooled glycerol

  Temperature cycles



- Imaging absorption by photothermal contrast



- Gold nanoparticles for probing and manipulation

Sensors and actuators for soft matter studies