Single Molecules and Single Gold Nanoparticles: Detection and Spectroscopy

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Molecular Nano-Optics and Spins

Leiden University (Netherlands)

Strasbourg, 05 July 2016

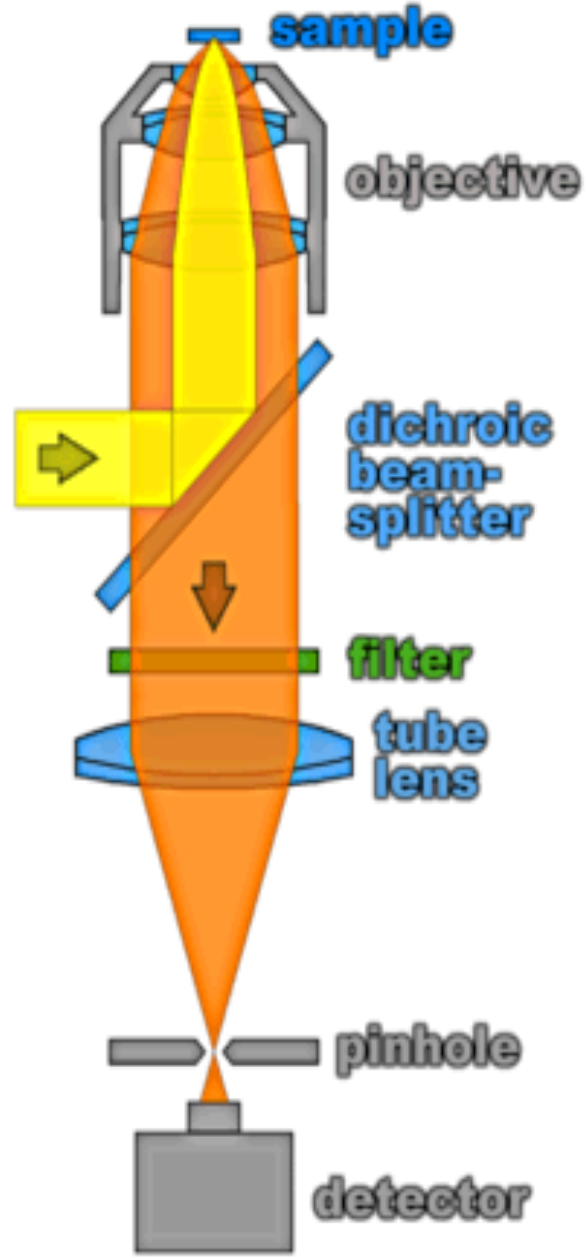
Outline

- Single molecules and gold nanoparticles
- Photothermal detection
- Sensing, luminescence, trapping and enhancement with gold nanorods
- Plasmonic creation of nanobubbles in liquids

Optical microscope

$$V_{illum.} \approx 1 \mu m^3$$

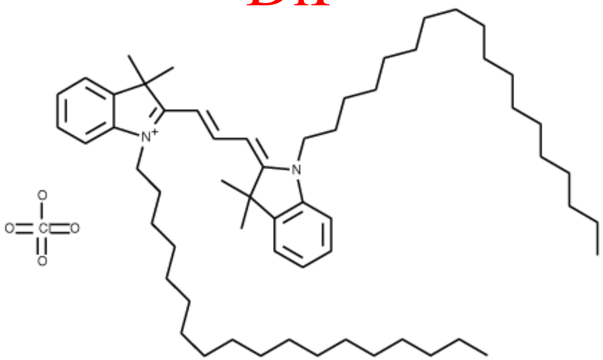
about 10^9 molecules in focal spot



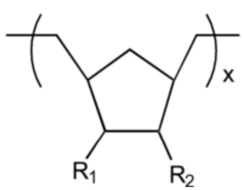
Room Temperature

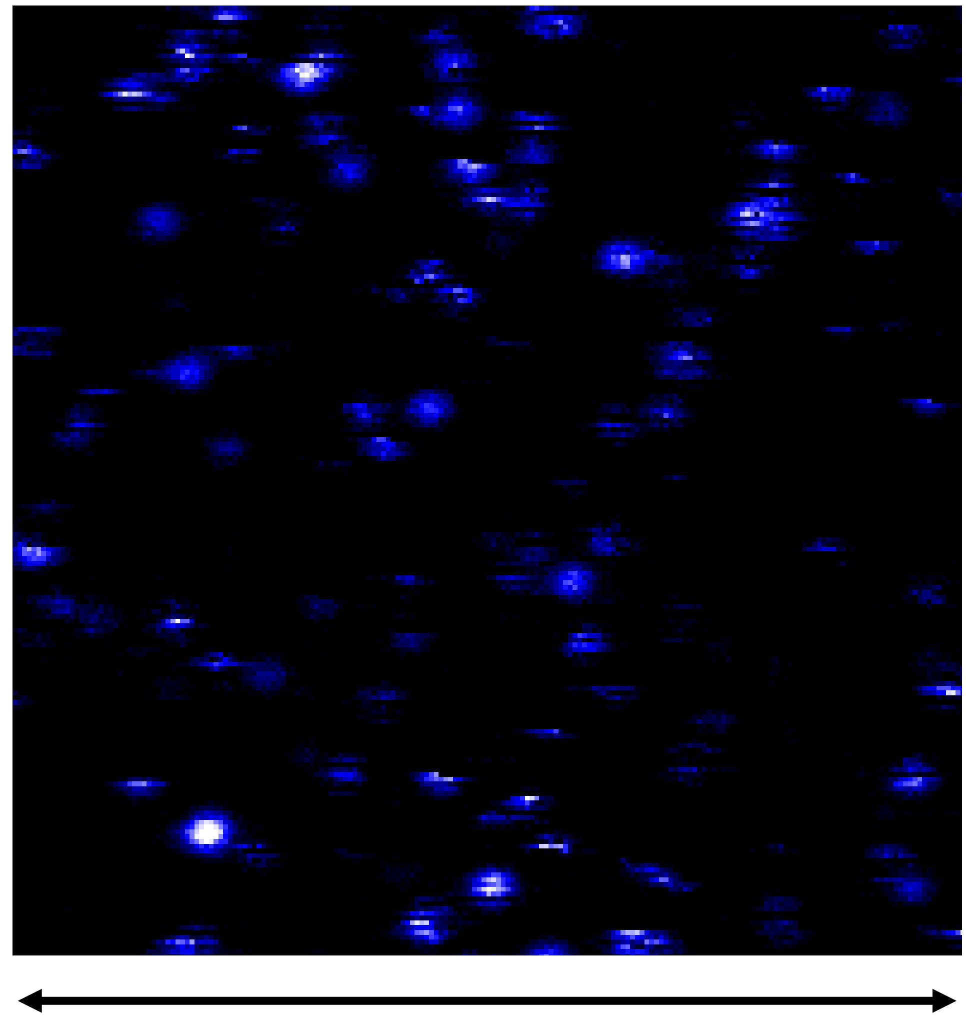
$$\frac{\sigma_{abs}(Room\ T.)}{\sigma_{abs}(Low\ T.)} \approx 10^{-6}$$

DiI



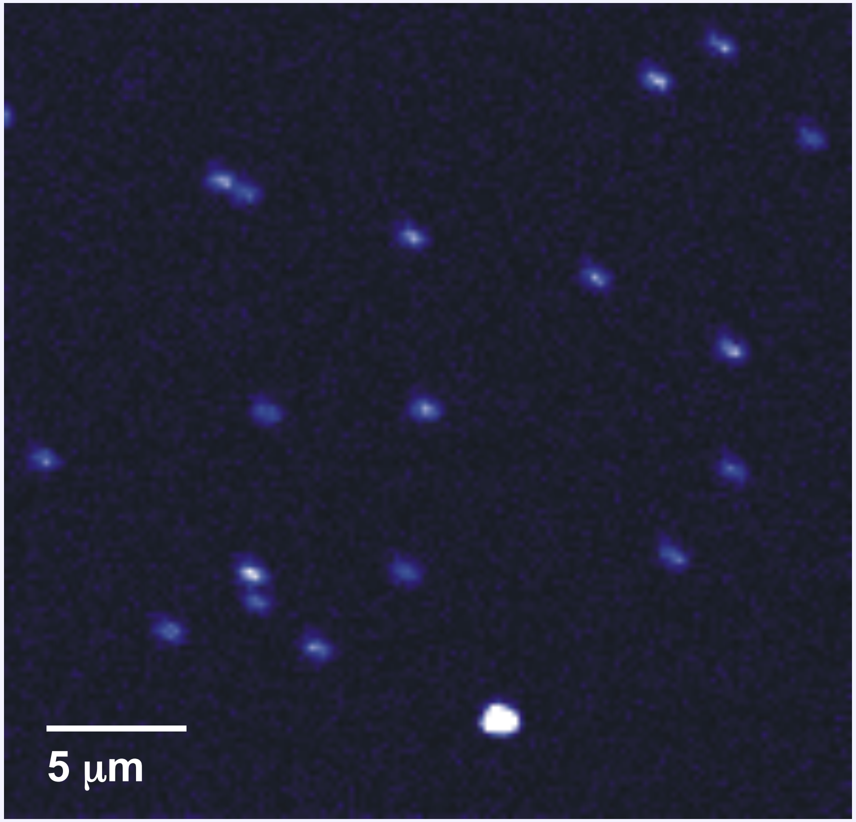
in Zeonex®





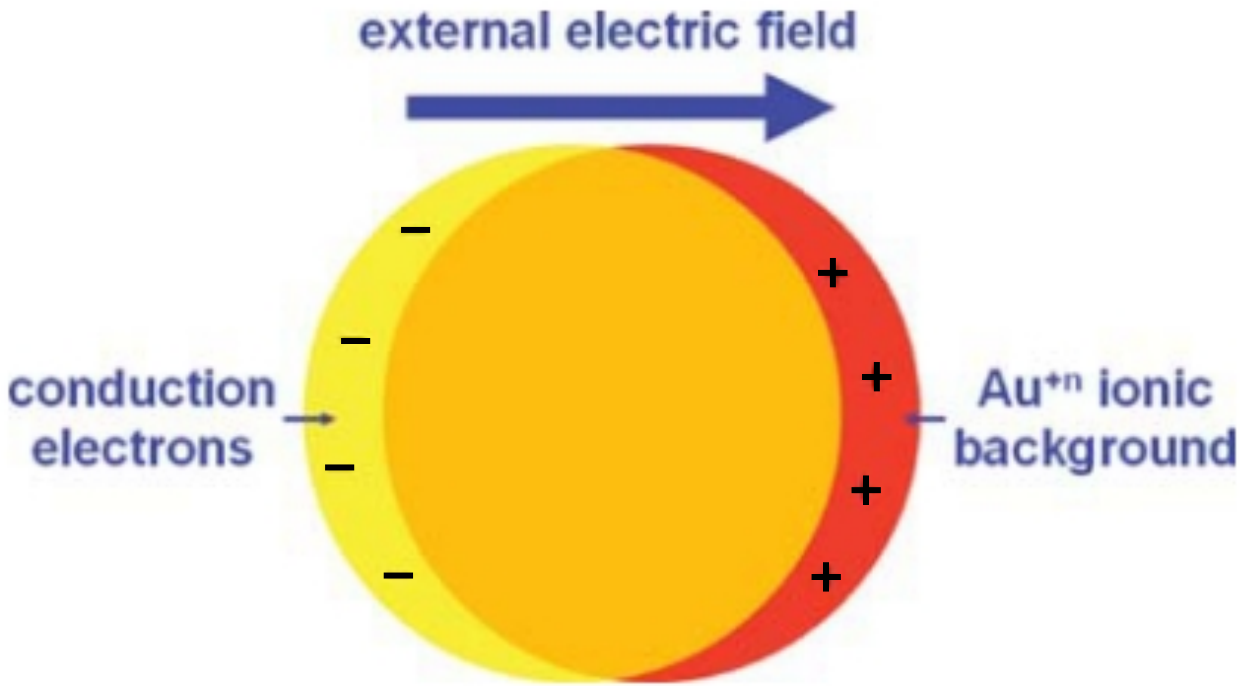
10 μm

Optical Microscopy of single gold nanoparticles

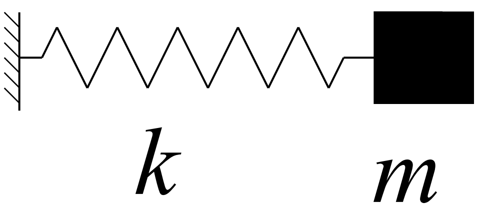


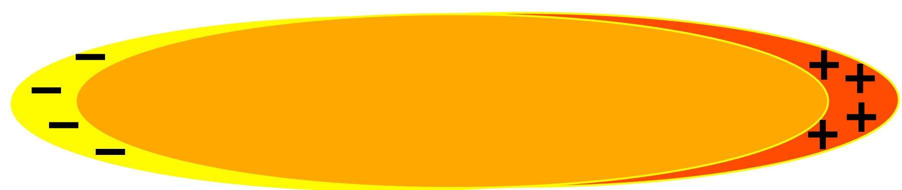
Third Harmonic, 100 nm; M. Lippitz et al., NanoLett **5** (2005) 799

Plasmons in gold nanoparticles



$$\omega = \sqrt{\frac{k}{m}}$$





Harmonic oscillator, spring constant depends on shape

Gold Nanorods

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

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

TEM images

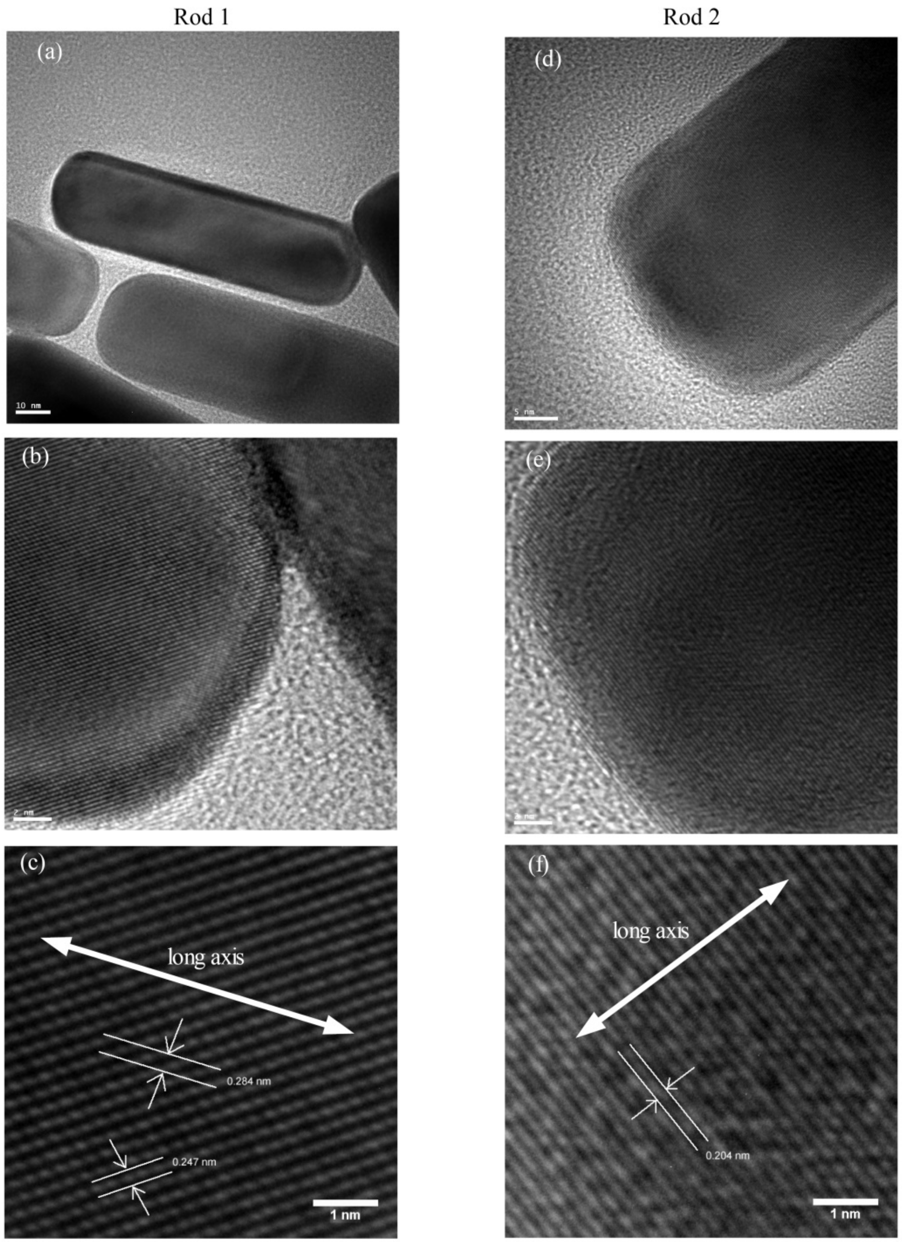
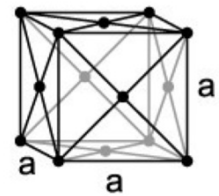
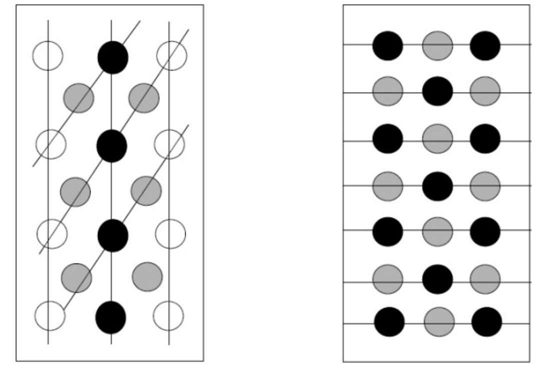
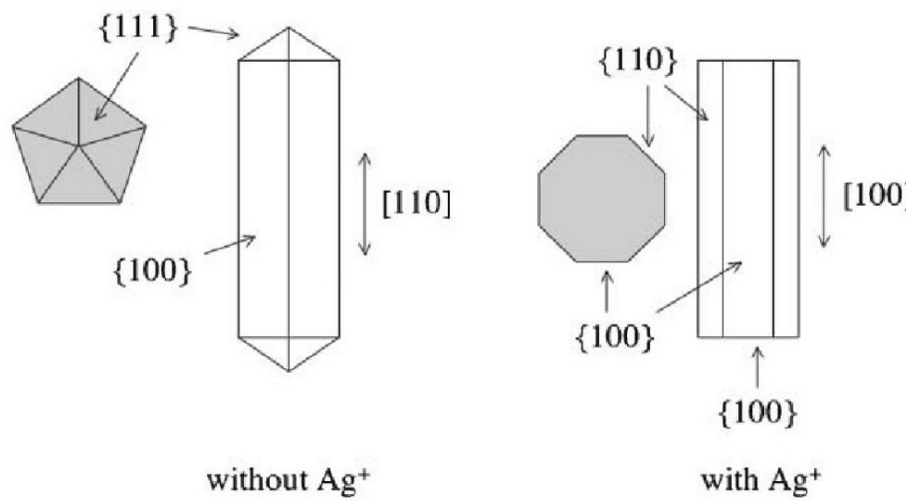


Figure 2: High resolution TEM images of two gold nanorods imaged at low (a) and (d), medium (b) and (e), and high (c) and (f) magnification (both (c) and (f) are imaged at 1.05 million times magnification). The fat arrows in (c) and (f) indicate the long particle axis. The measured lattice plane spacings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

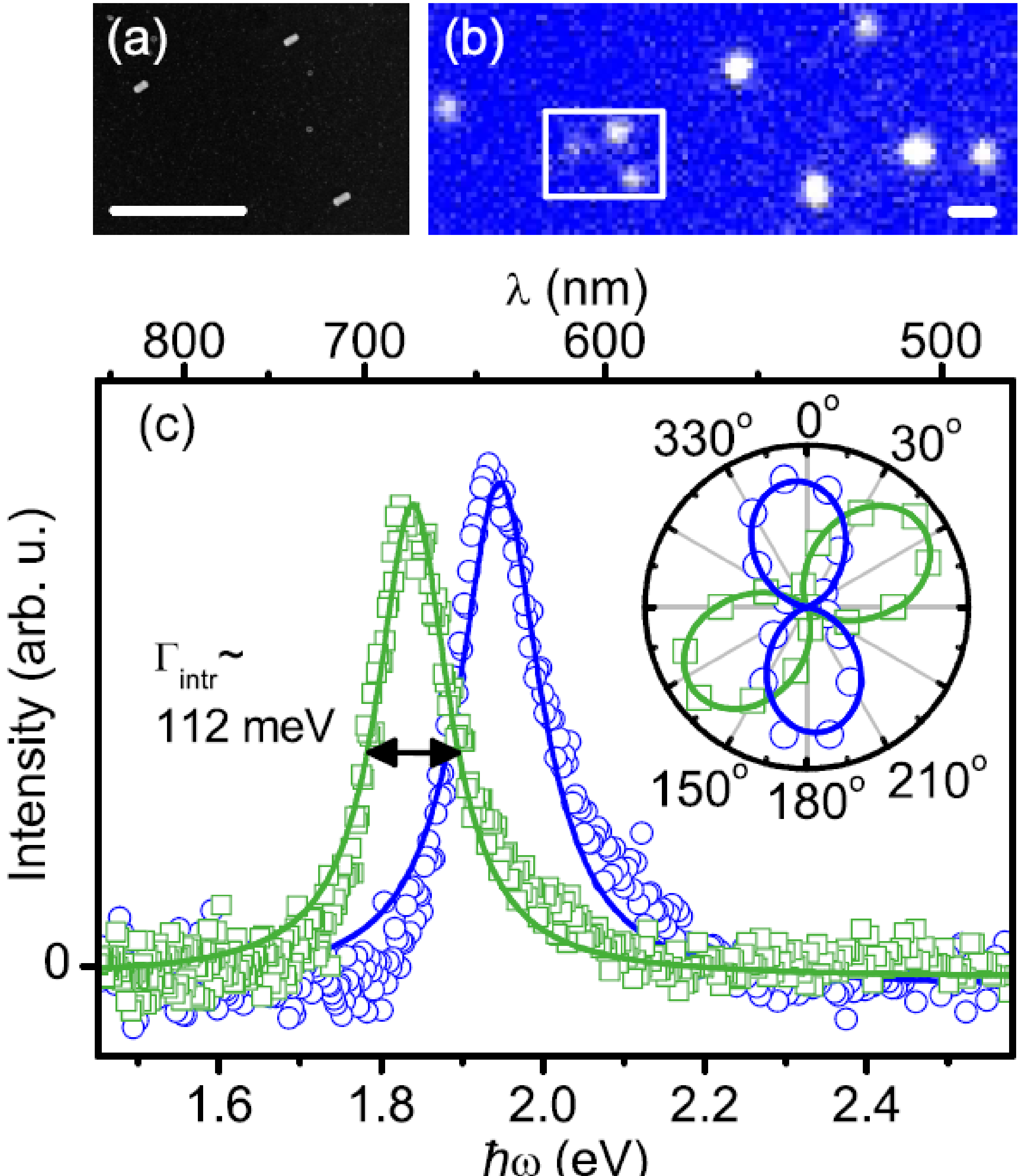




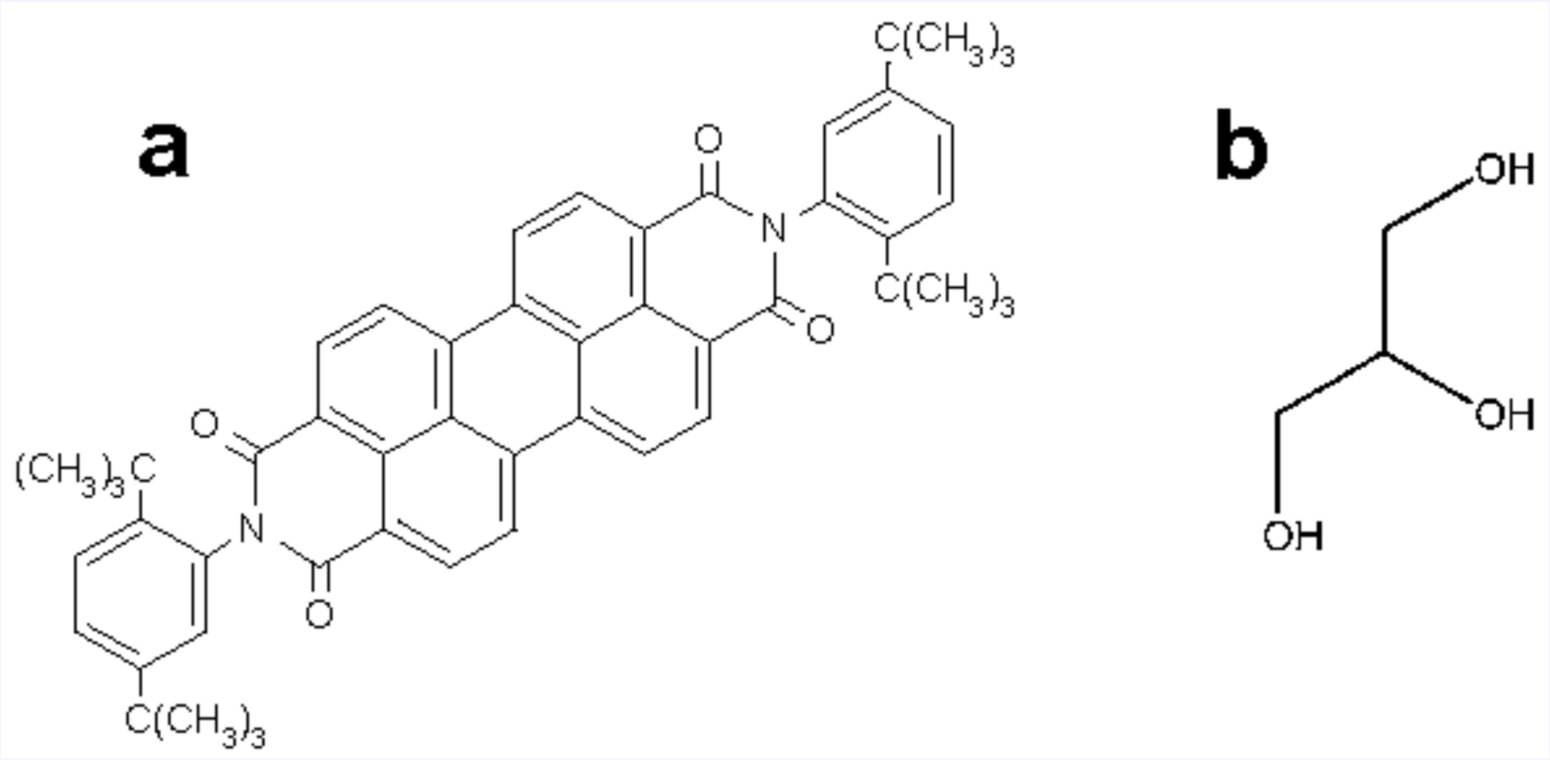


Optical scattering and SEM images

local index probe



Local probing of supercooled liquids

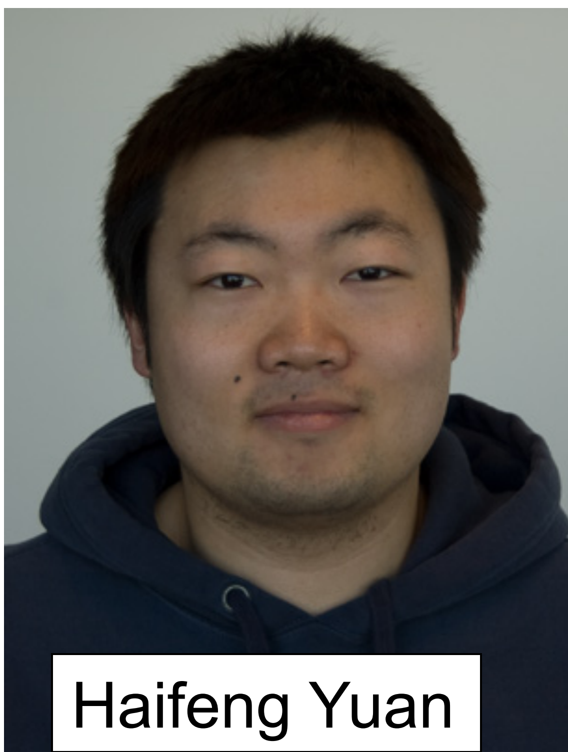


Perylene-di-imide (a) in glycerol (b)

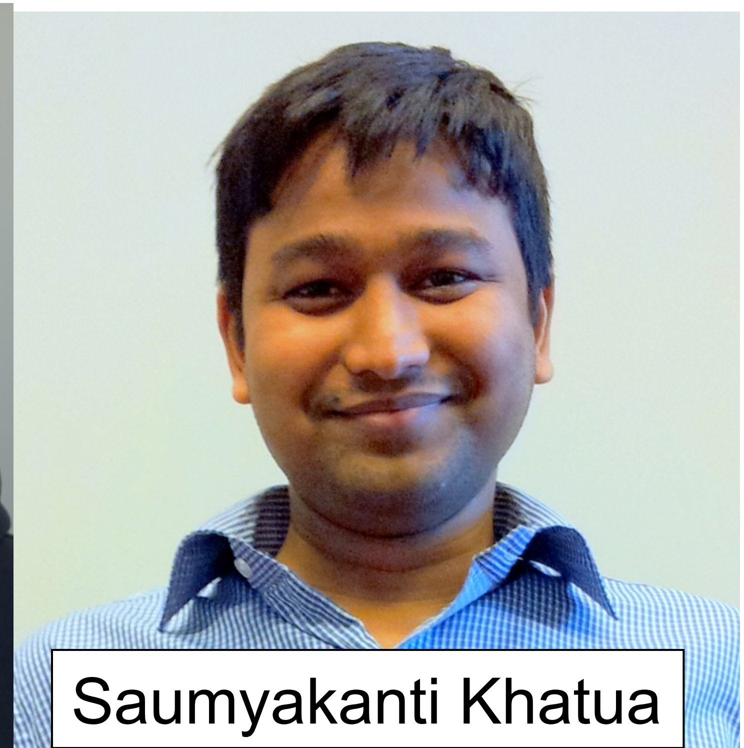
Dr. Florian Kulzer

Dr. Rob Zondervan

Dr. Ted Xia

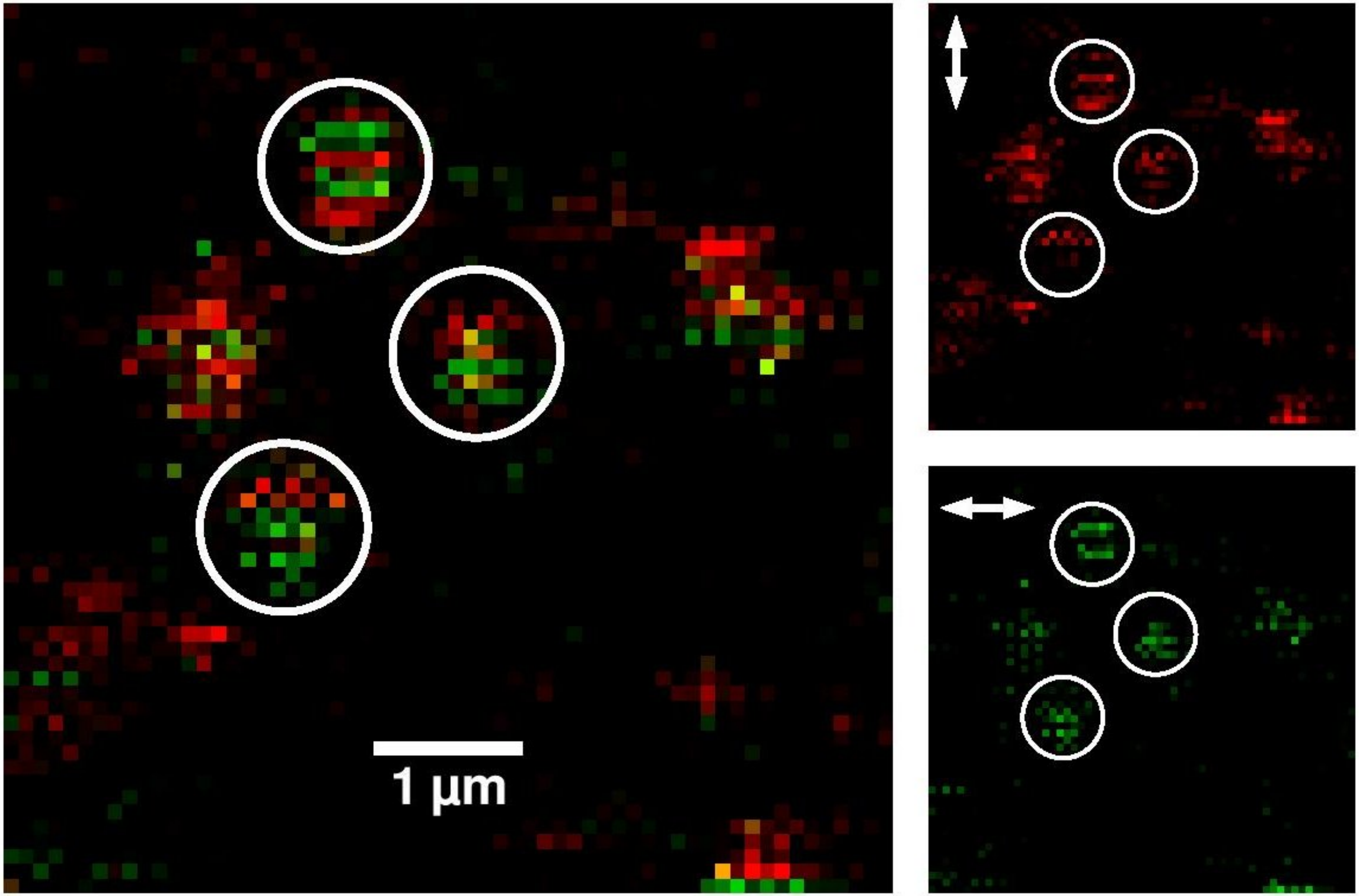


Haifeng Yuan

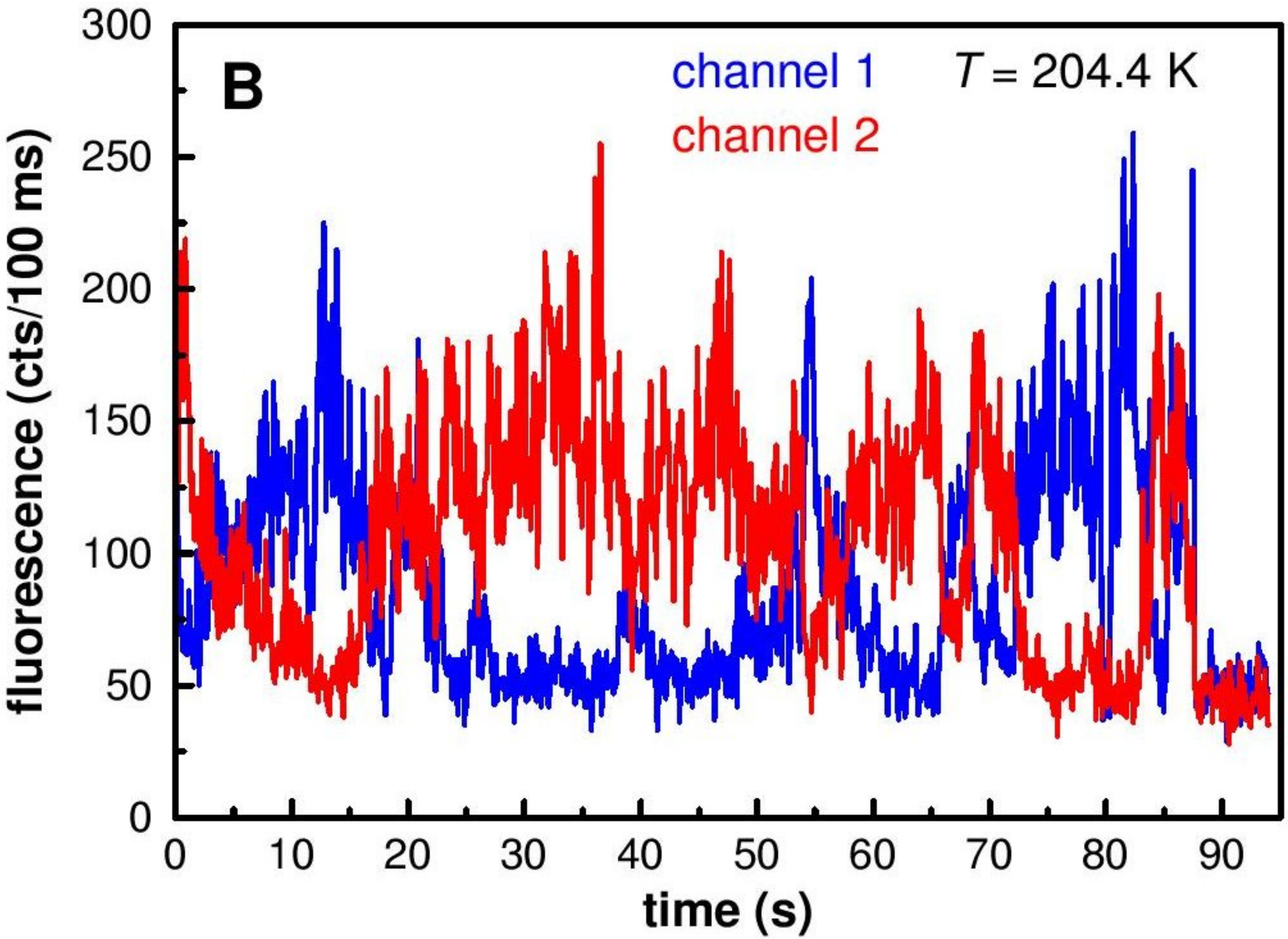


Saumyakanti Khatua

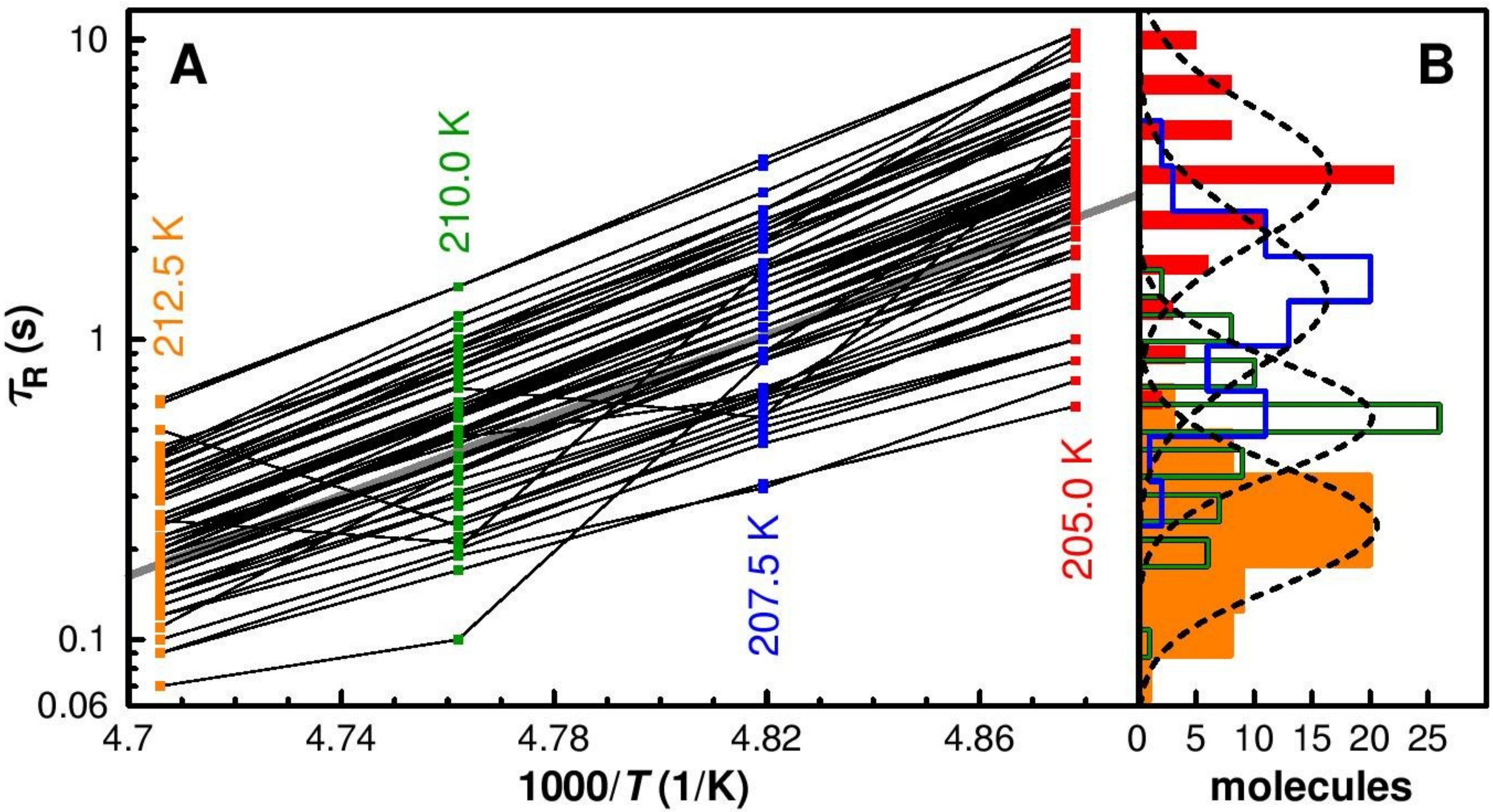
Polarized single-molecule fluorescence



Anticorrelation of polarization channels



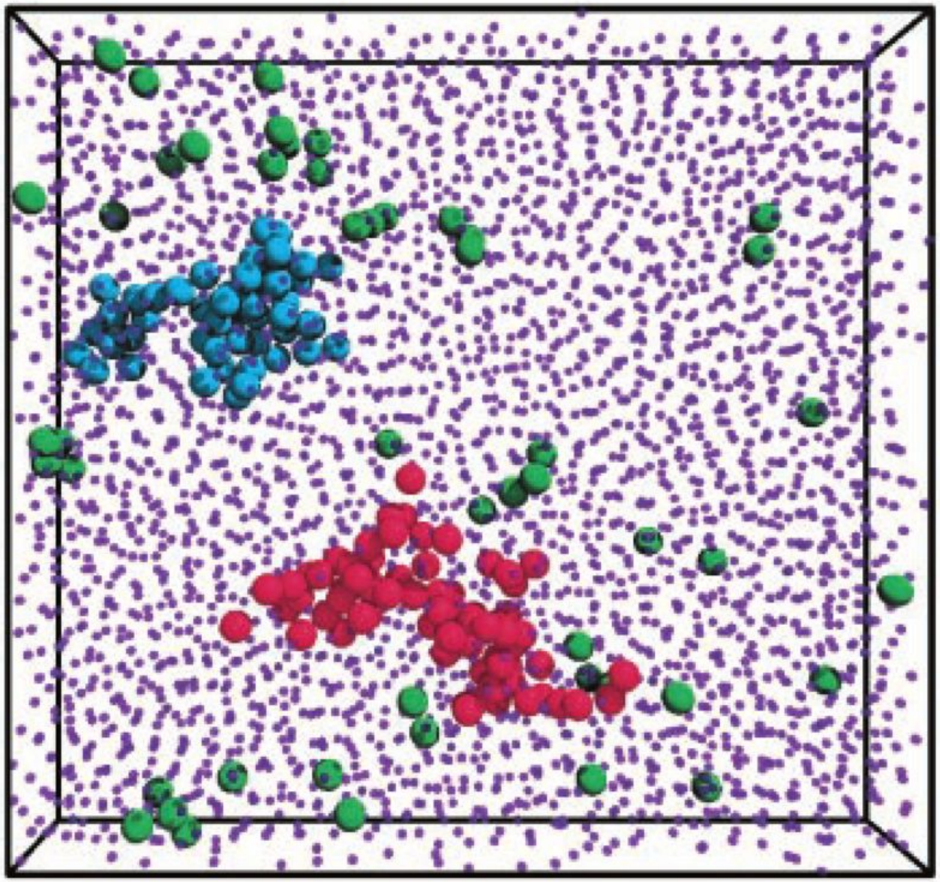
T-dep. of tumbling rates for 69 molecules



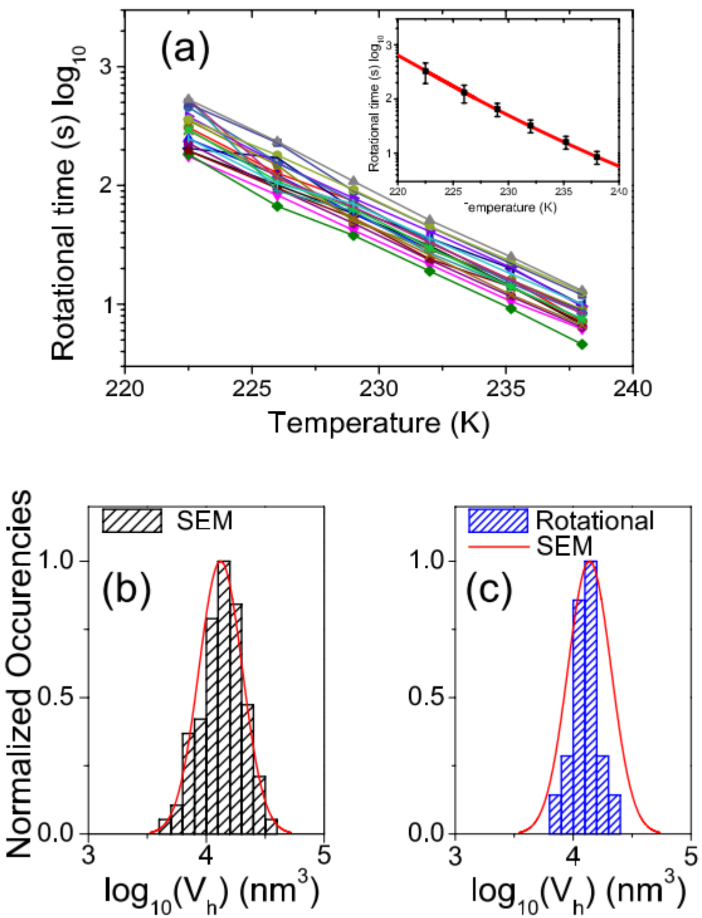
Extremely long memory of diffusion rate evidence for solid walls?

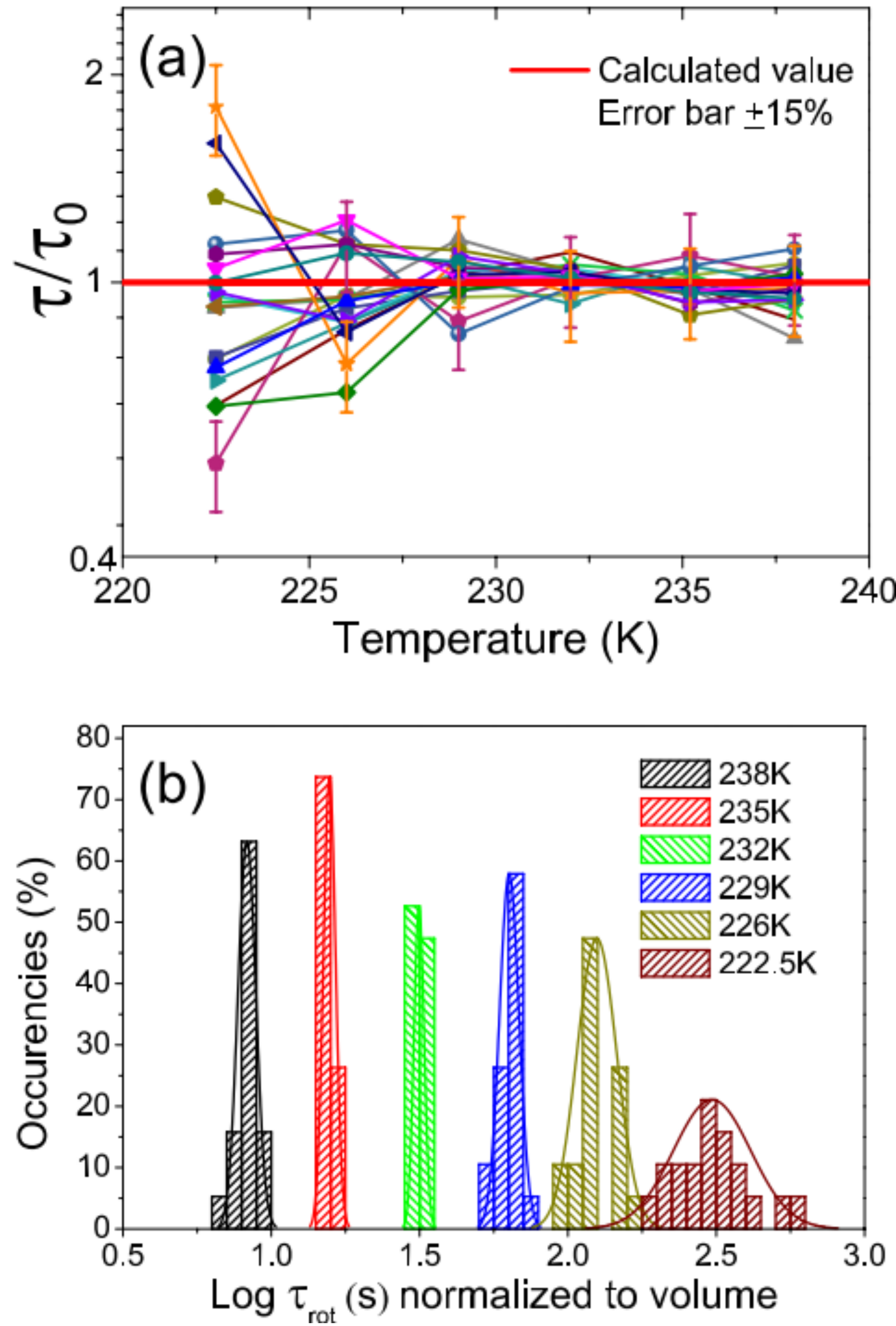
Seen already for colloidal suspensions in the glass phase:
E. R. Weeks et al., Science **287**(2000) 627

A solid matrix should be elastic : rheology

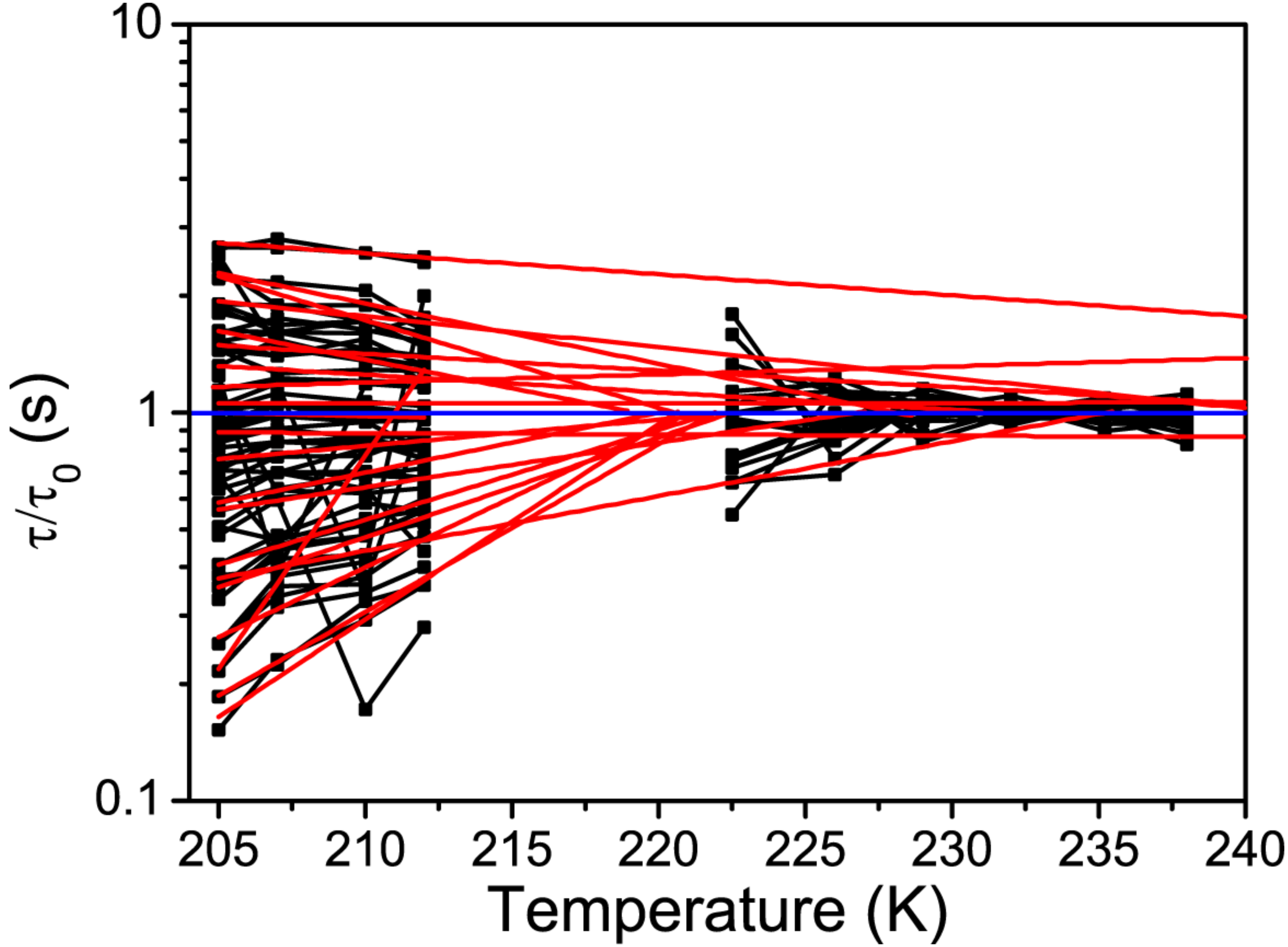


Correction for volume



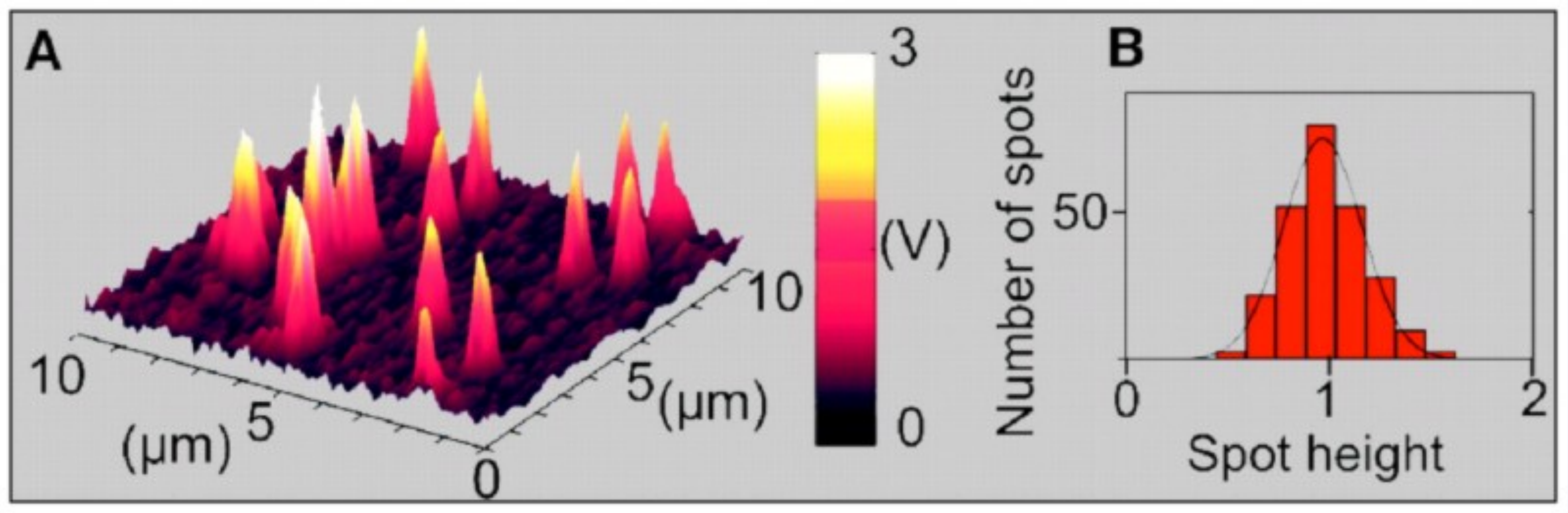


Molecules and rods on the same plot



Imaging Absorption by Photothermal Contrast

Interferometric detection of the temperature rise due to absorption



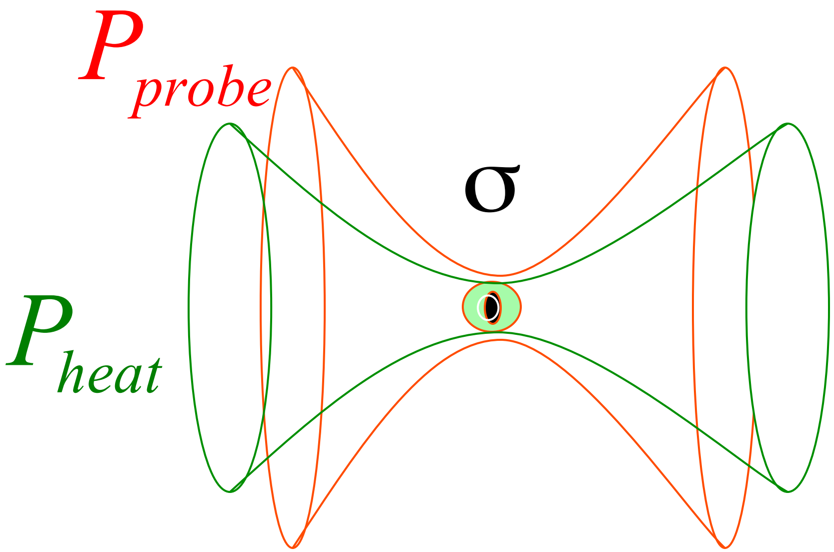
Au colloids, diameter 5 nm

from D. Boyer et al., Science **297** (2002) 1160

Dr. Alexander Gaiduk

Mustafa Yorulmaz

Signal/Noise in photothermal detection



- signal $\frac{P_{probe}}{h\nu} \cdot \frac{1}{VC_P} \frac{\partial n}{\partial T} P_{heat} \cdot \tau$

- noise $\sqrt{\frac{P_{probe} \cdot \Delta t}{h\nu}}$

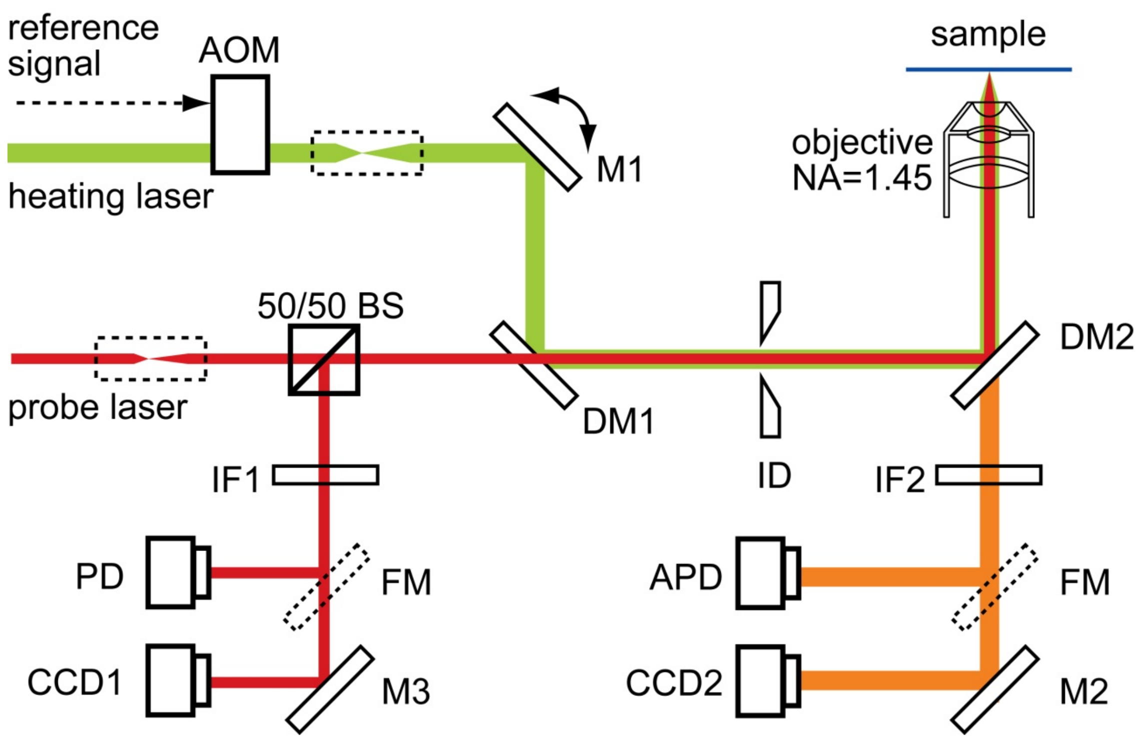
$$(SNR)_{phototh.} = \Delta n_{sat} \sqrt{\frac{P_{probe} \cdot \Delta t}{h\nu}}$$

$$\Delta n_{sat} = \frac{1}{VC_P} \frac{\partial n}{\partial T} P_{sat} \cdot \tau$$

is limited by saturation,

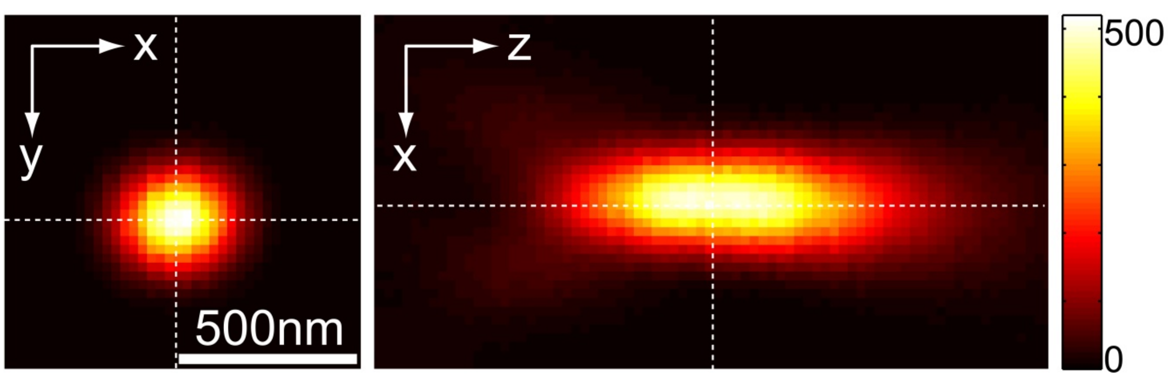
but SNR is not (in principle).

Optical setup



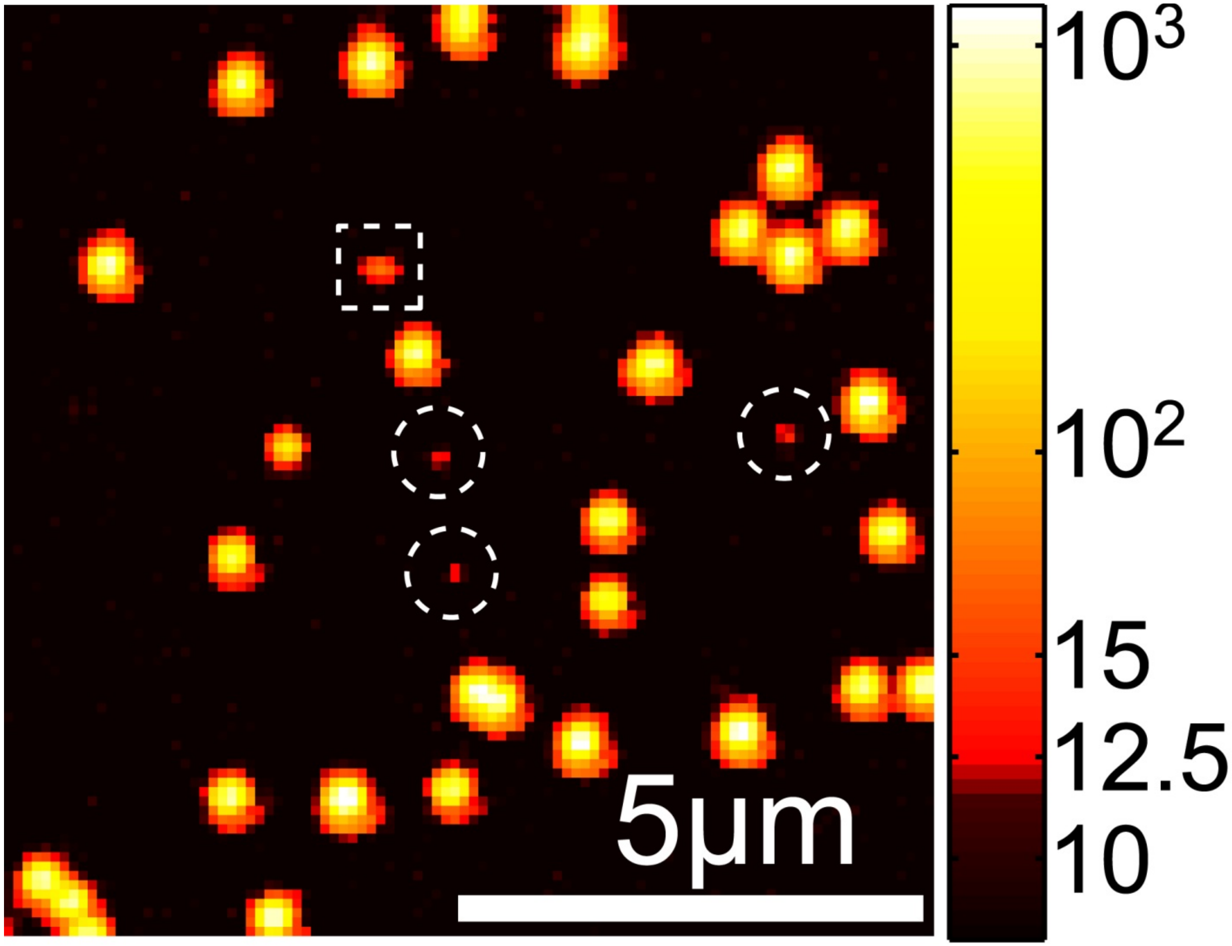
Similar to:
Berciaud et al., PRB **73** (2006) 045424

Fluorescence and photothermal



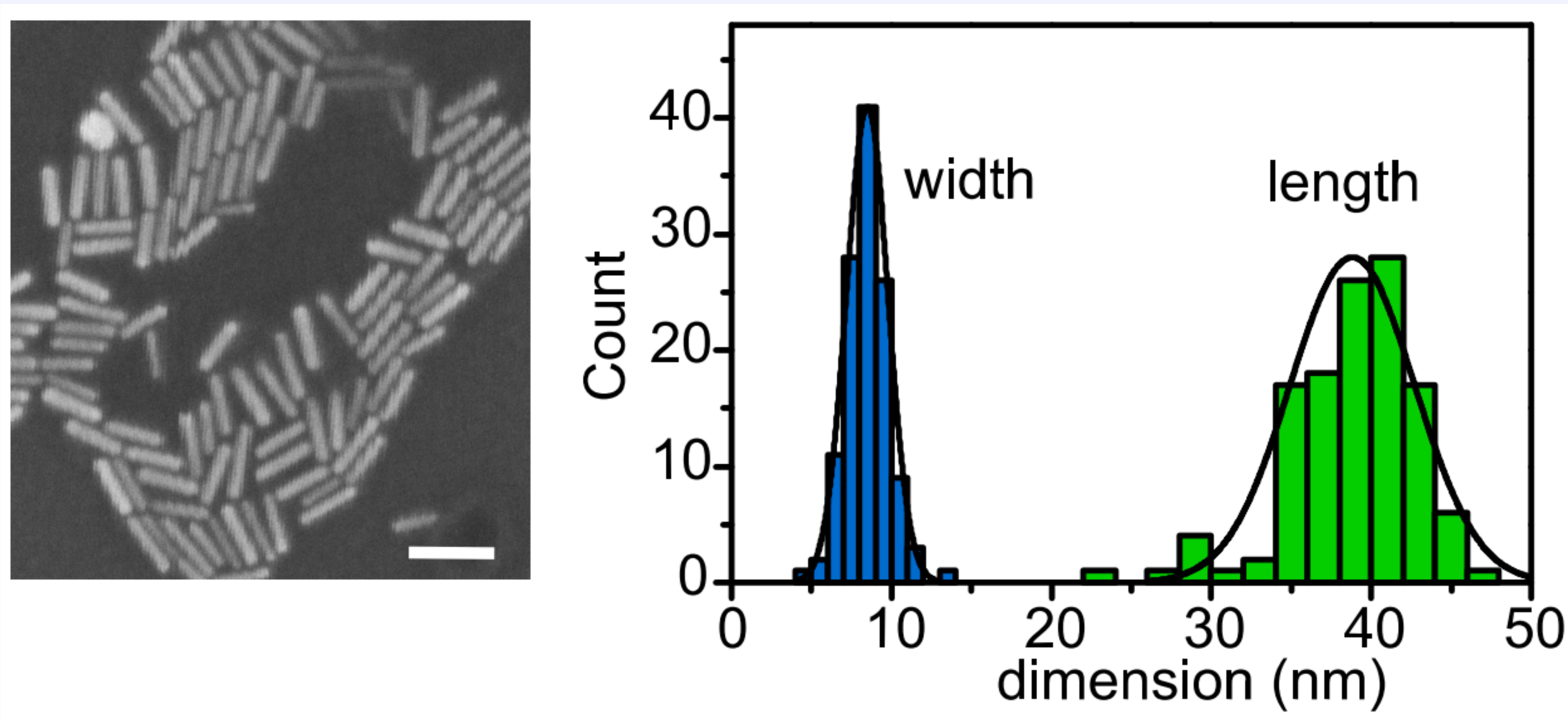
Point spread function:
about 200 nm FWHM

Simultaneous imaging of 5 nm and 20 nm Au NP's



Gaiduk et al., Chemical Science 1 (2010) 343.

Plasmonic sensing with a single gold nanorod

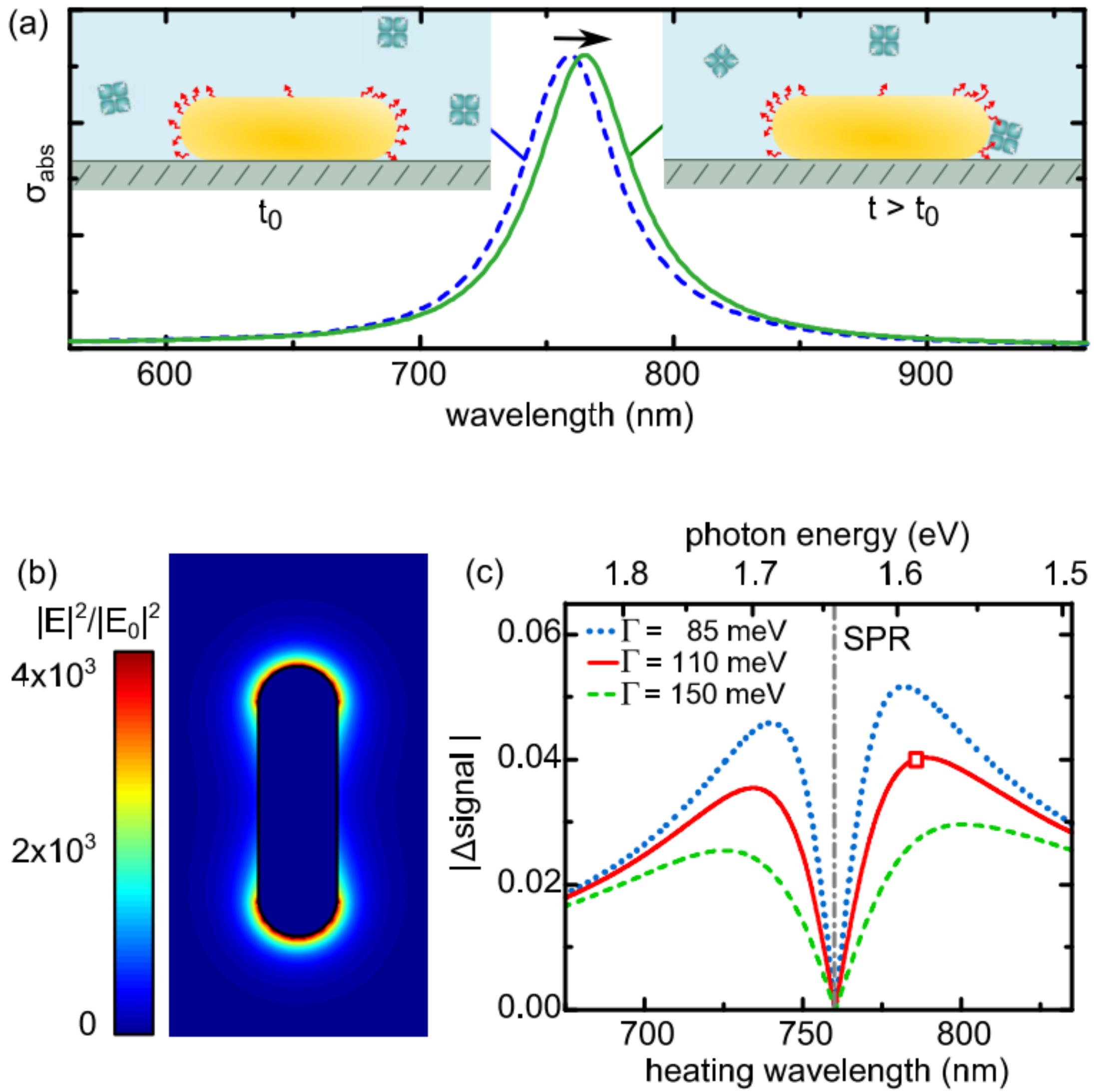


P. Zijlstra et al., Nat. Nanotechn., **7** (2012) 379

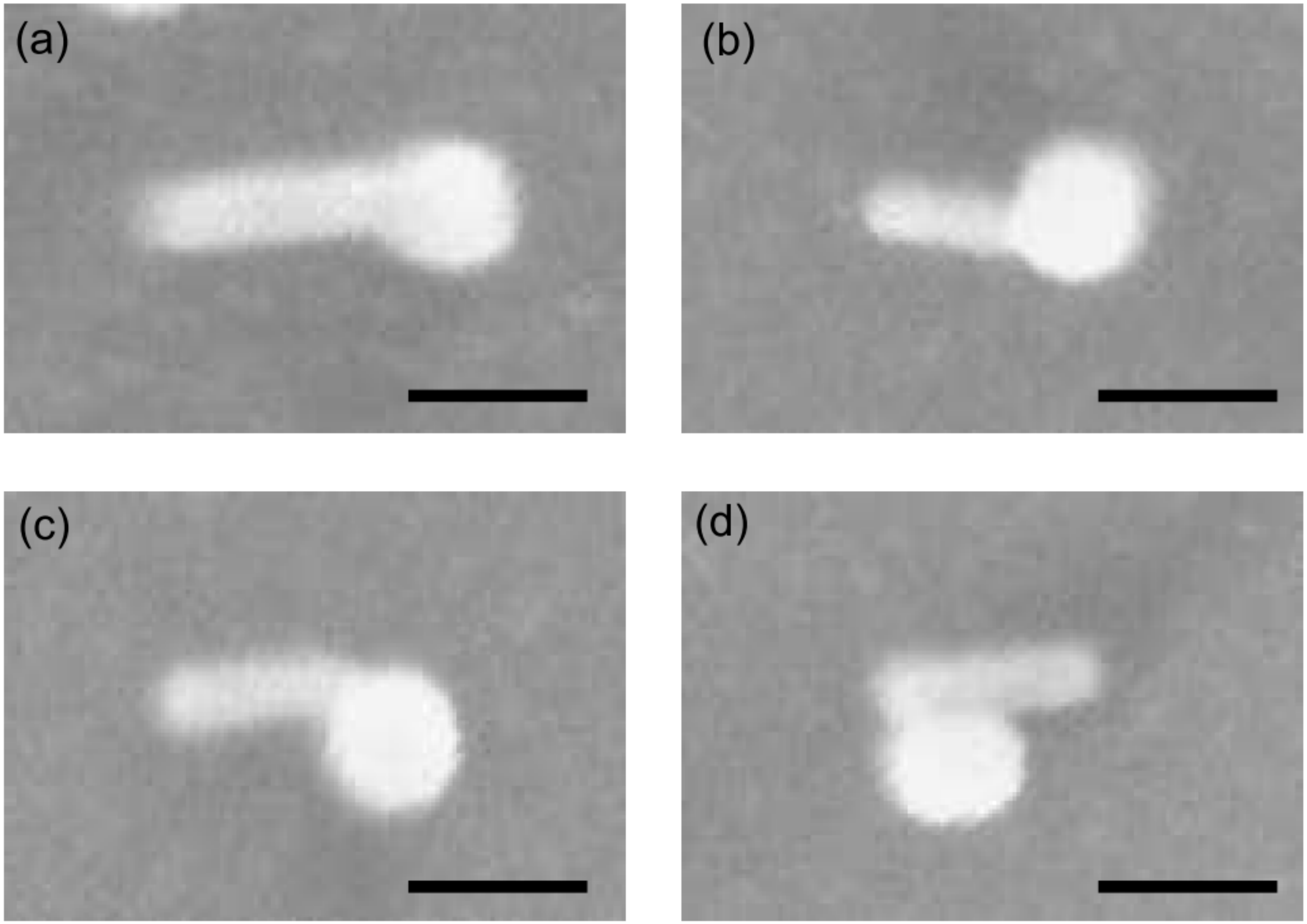
Dr Peter Zijlstra

Dr. Pedro Paulo

Principle of the sensing

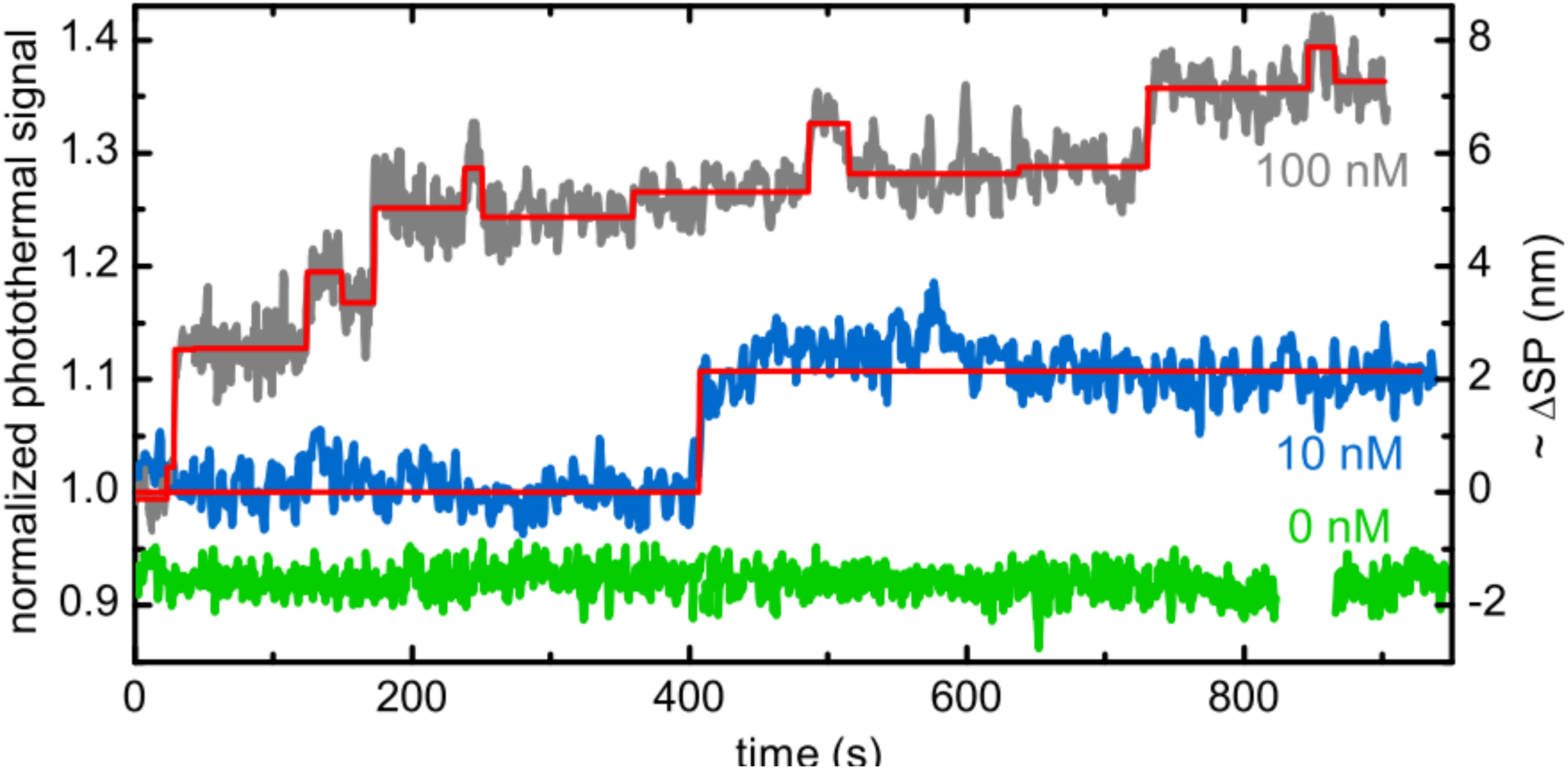


Preferential conjugation at the tips

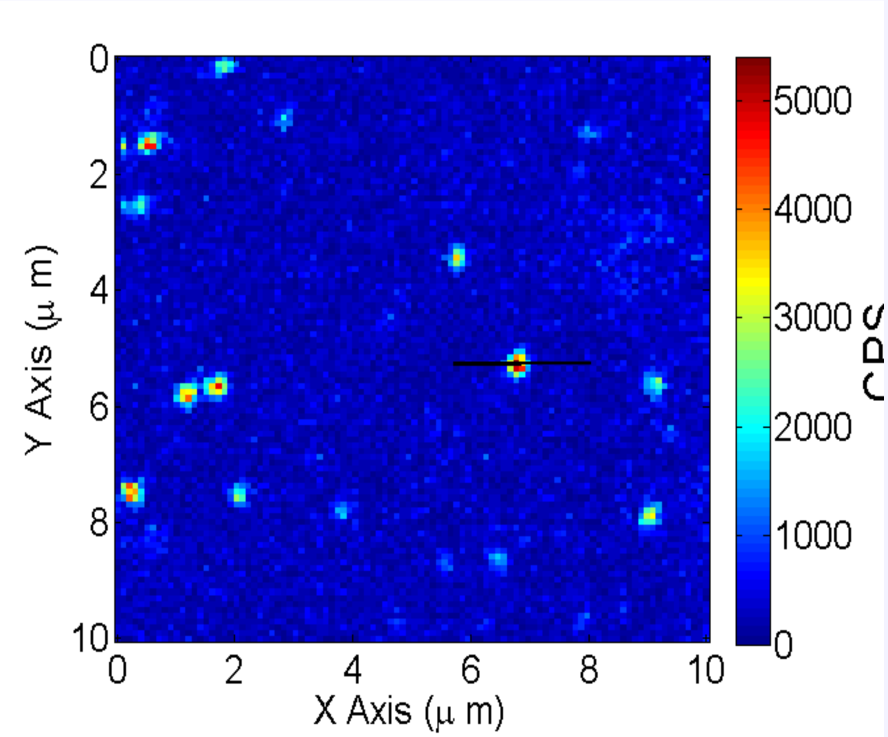


P. Zijlstra et al., Angew. Chem., **51** (2012) 8352

Binding of Streptavidin-phycoerythrin



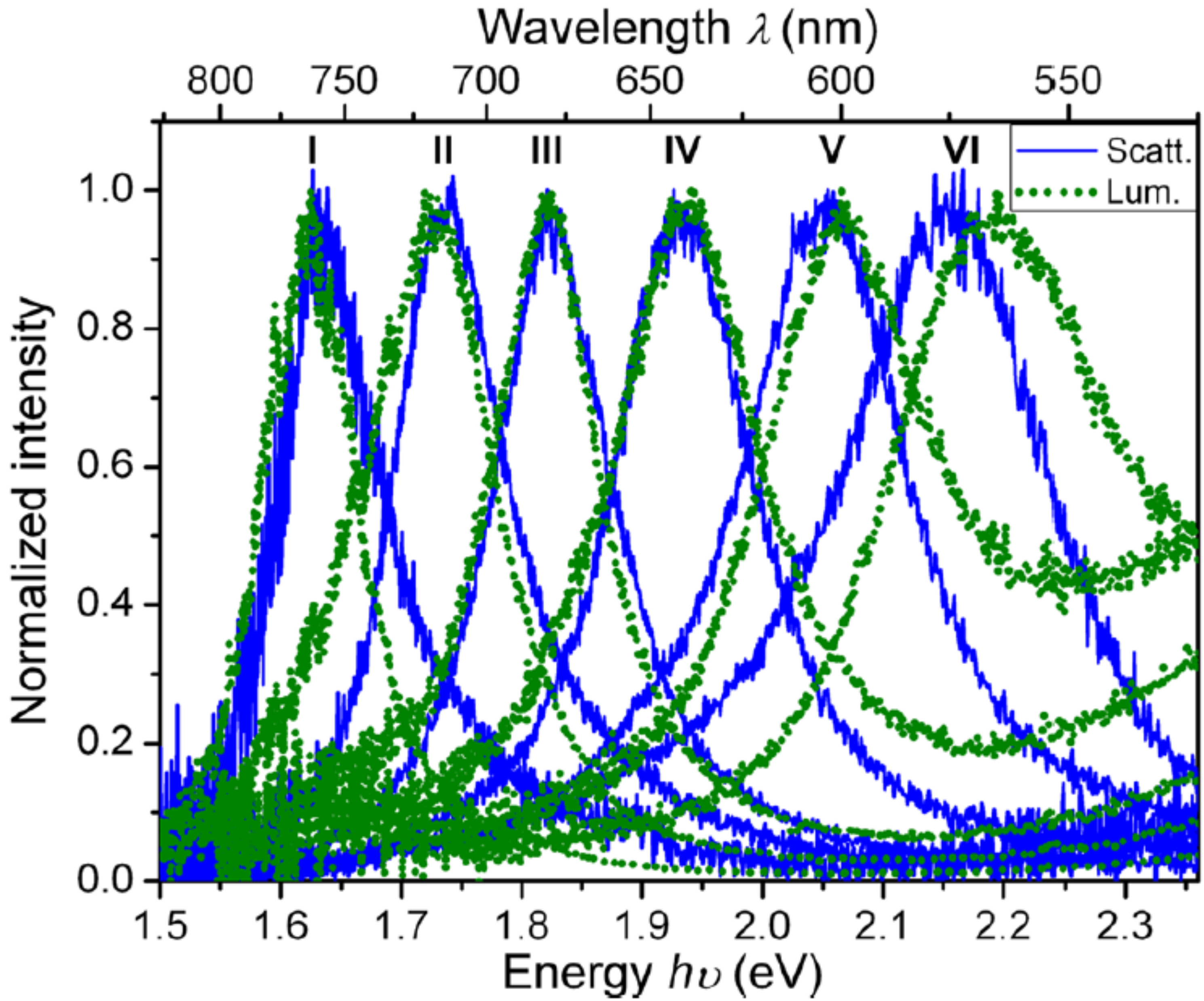
Stokes and Anti-Stokes Photoluminescence of Gold Nanoparticles



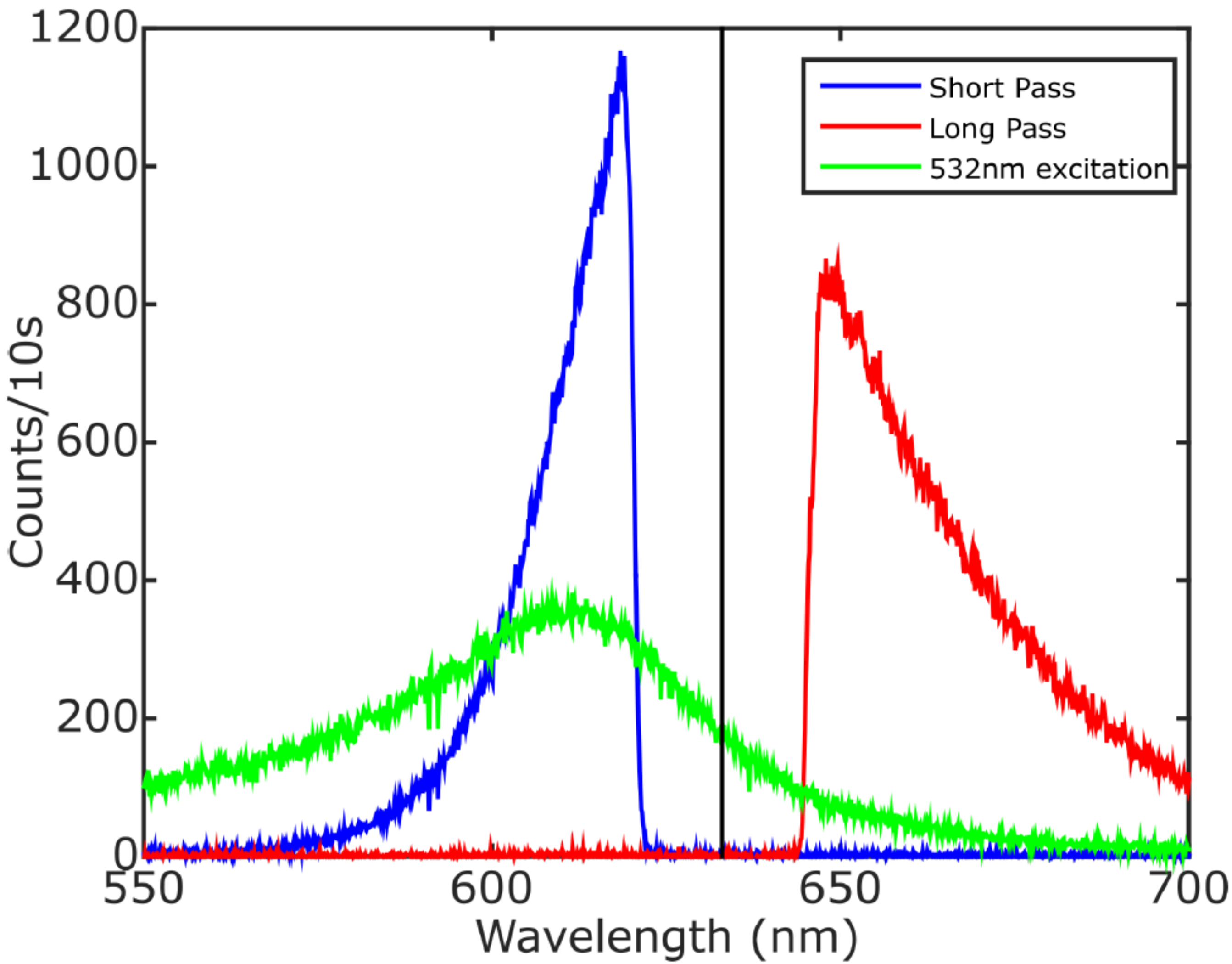
Carattino et al., in preparation

Aquiles Carattino

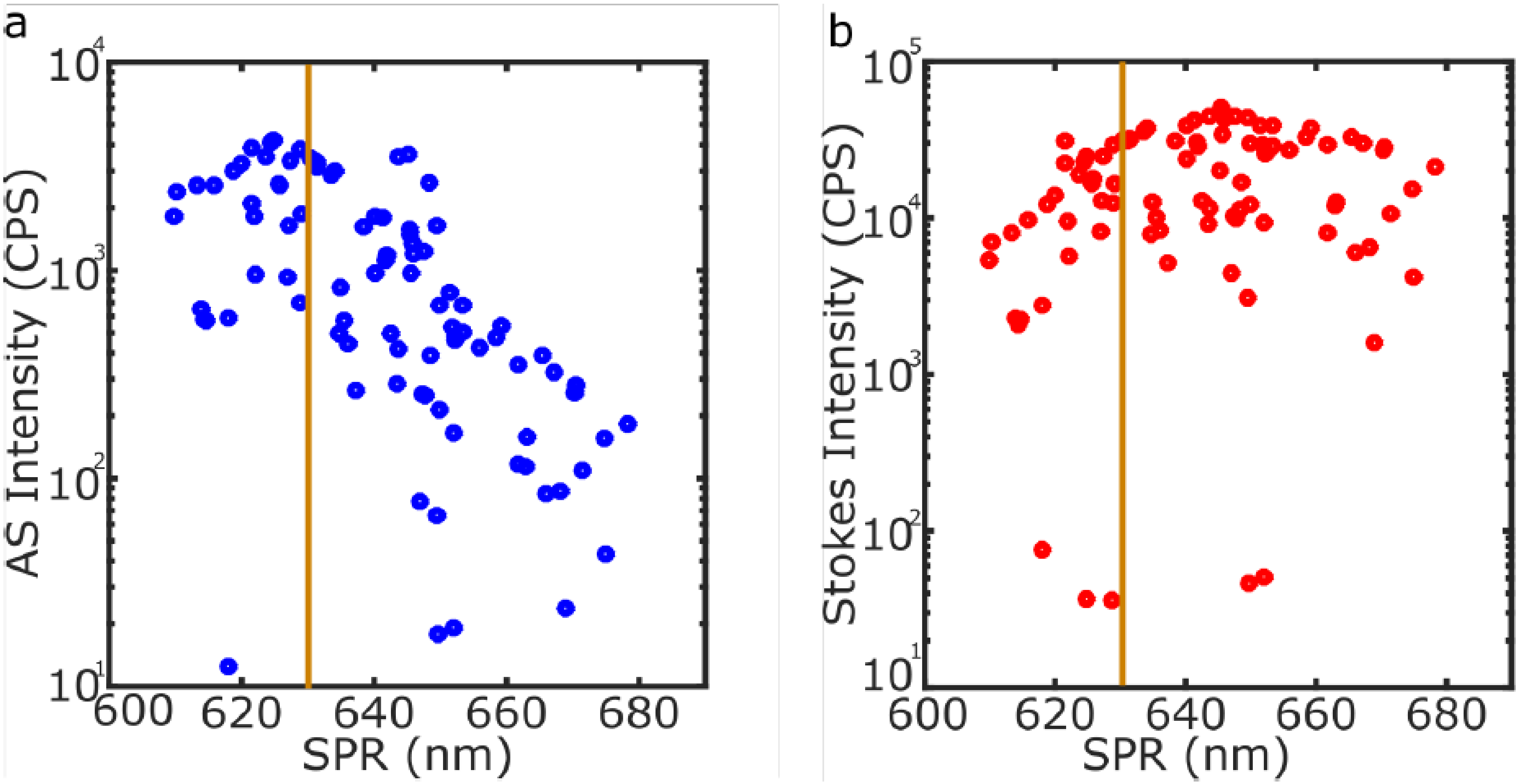
Photoluminescence and scattering spectra



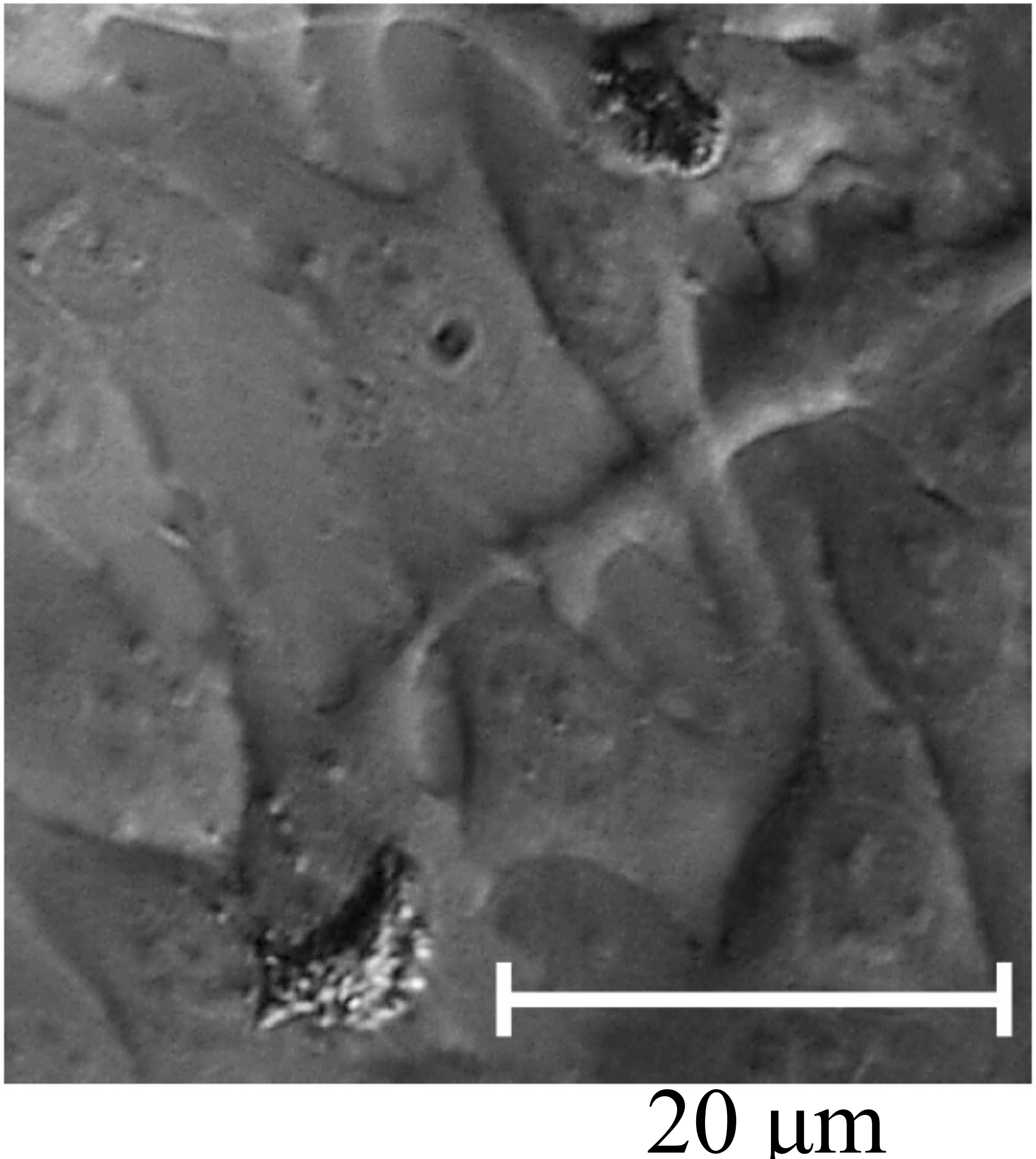
Photoluminescence spectra of a gold nanorod (60×25 nm²)



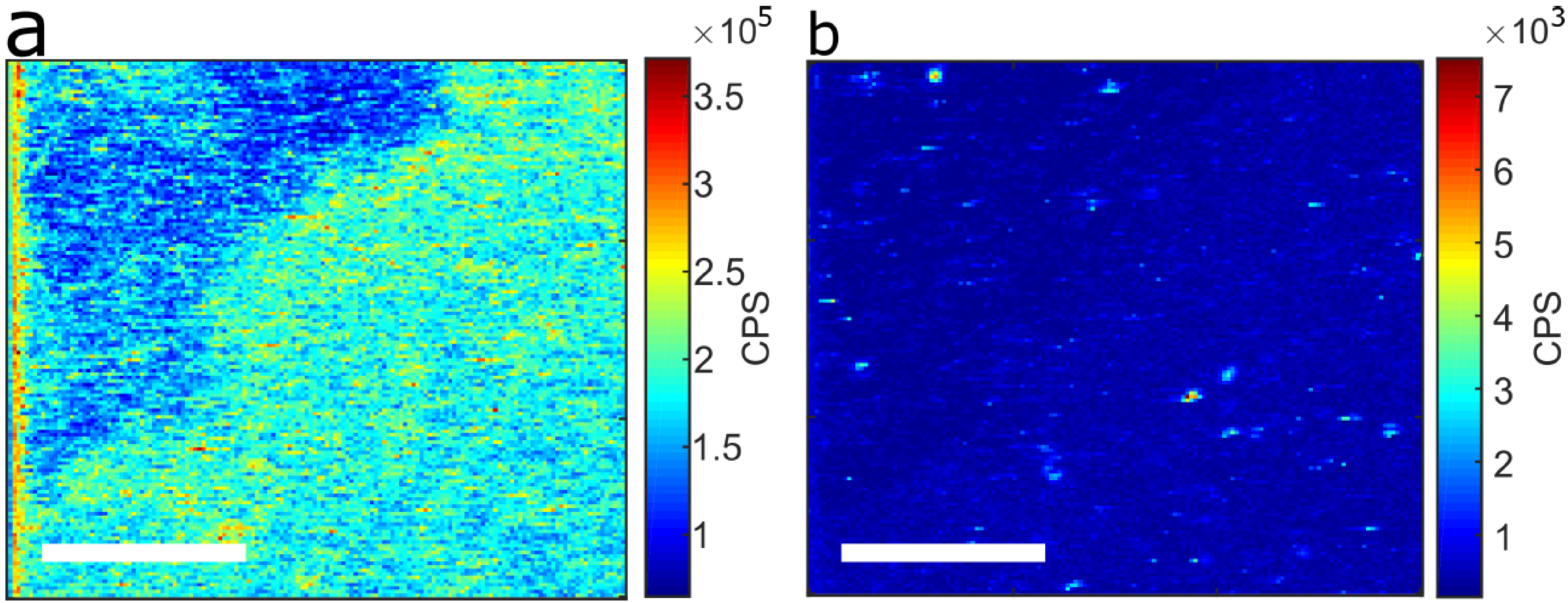
Intensities of AntiStokes and Stokes PL of single gold nanorods (60×25 nm^2)



Cells on glass slide with gold nanorods



Background reduction in anti-Stokes image

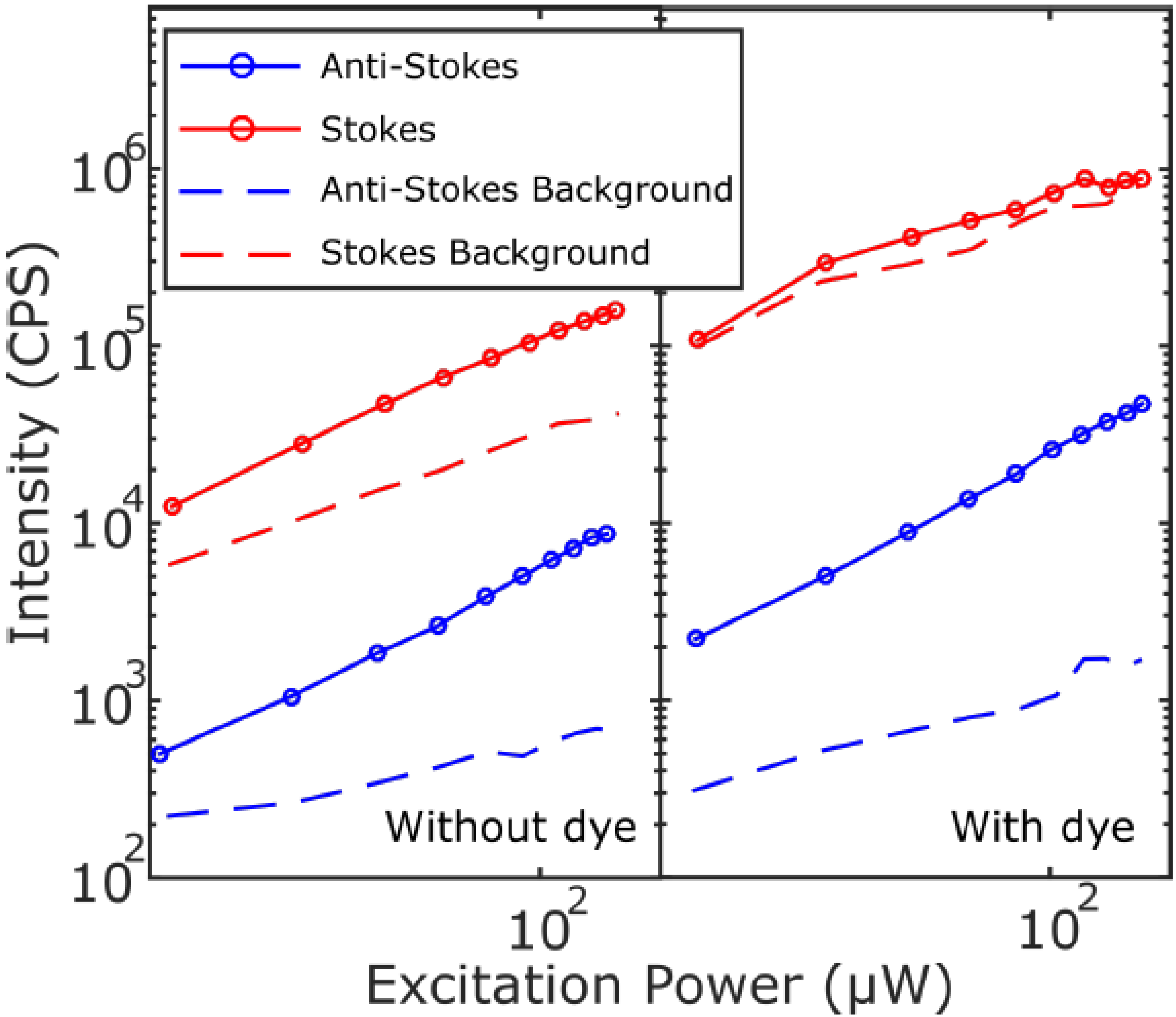


Stokes

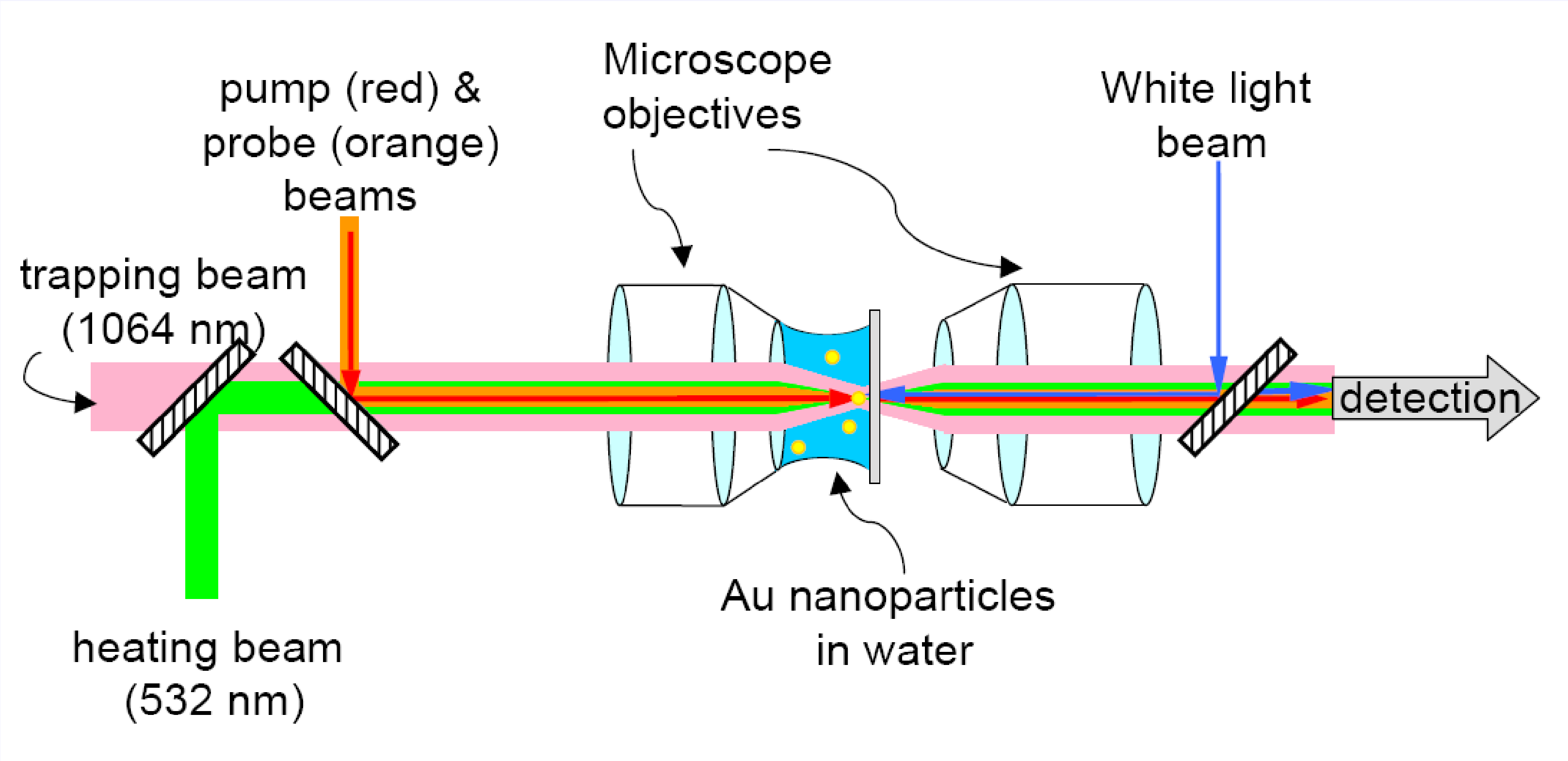
anti-Stokes

(stained cells)

Photoluminescence Signal and Background



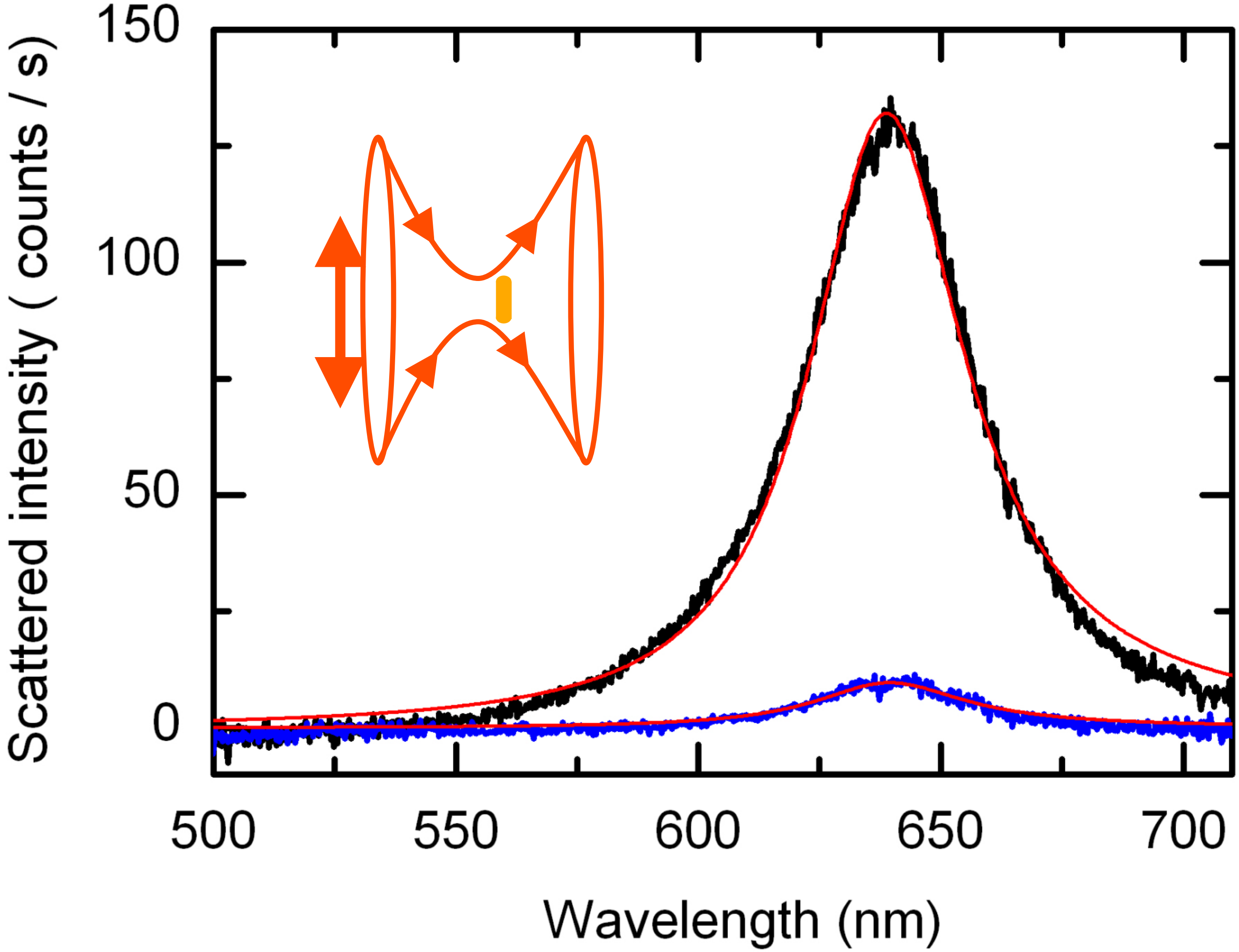
Optically trapping nanoparticles



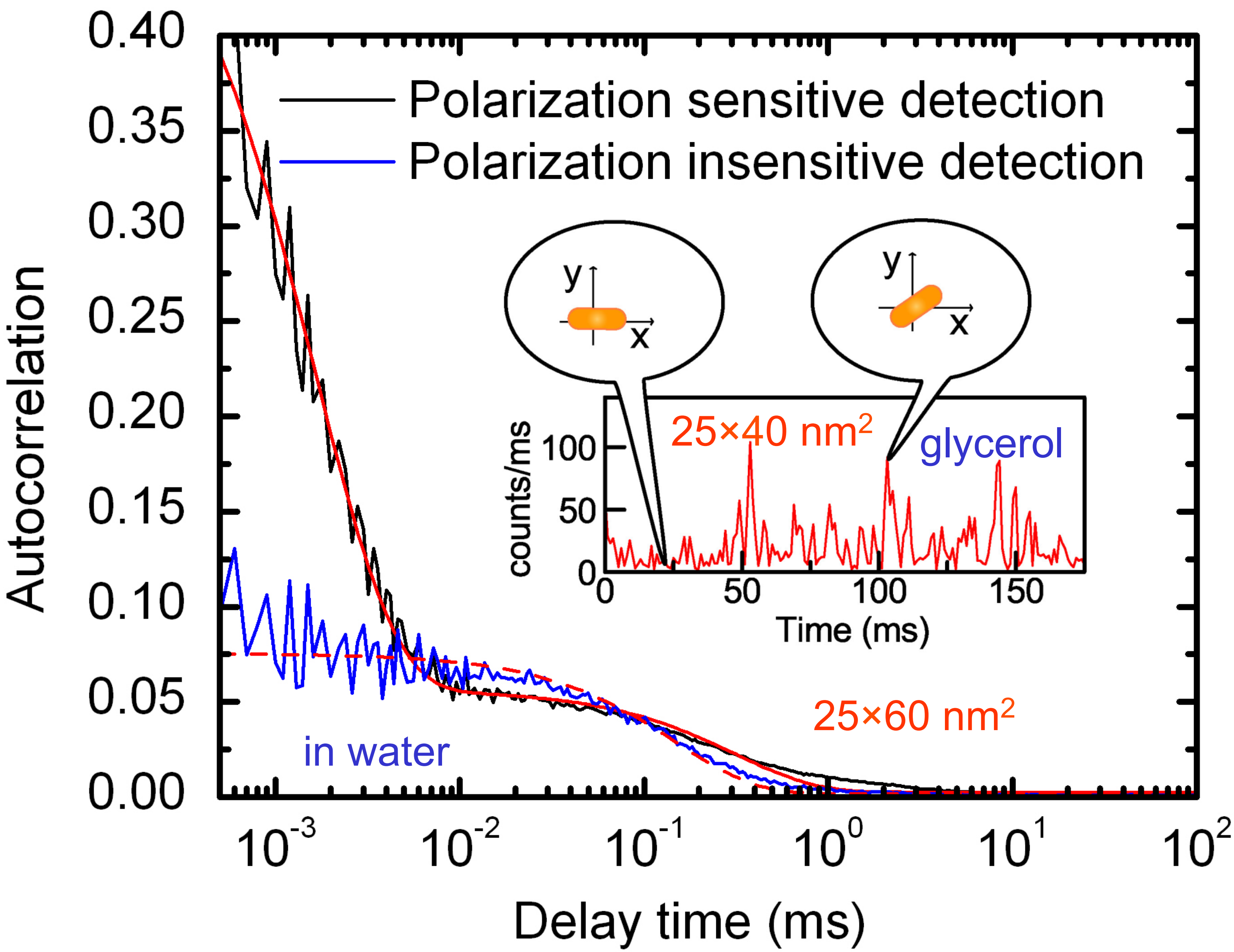
- Advantages: no perturbation by the substrate; manipulations possible

Paul Ruijgrok

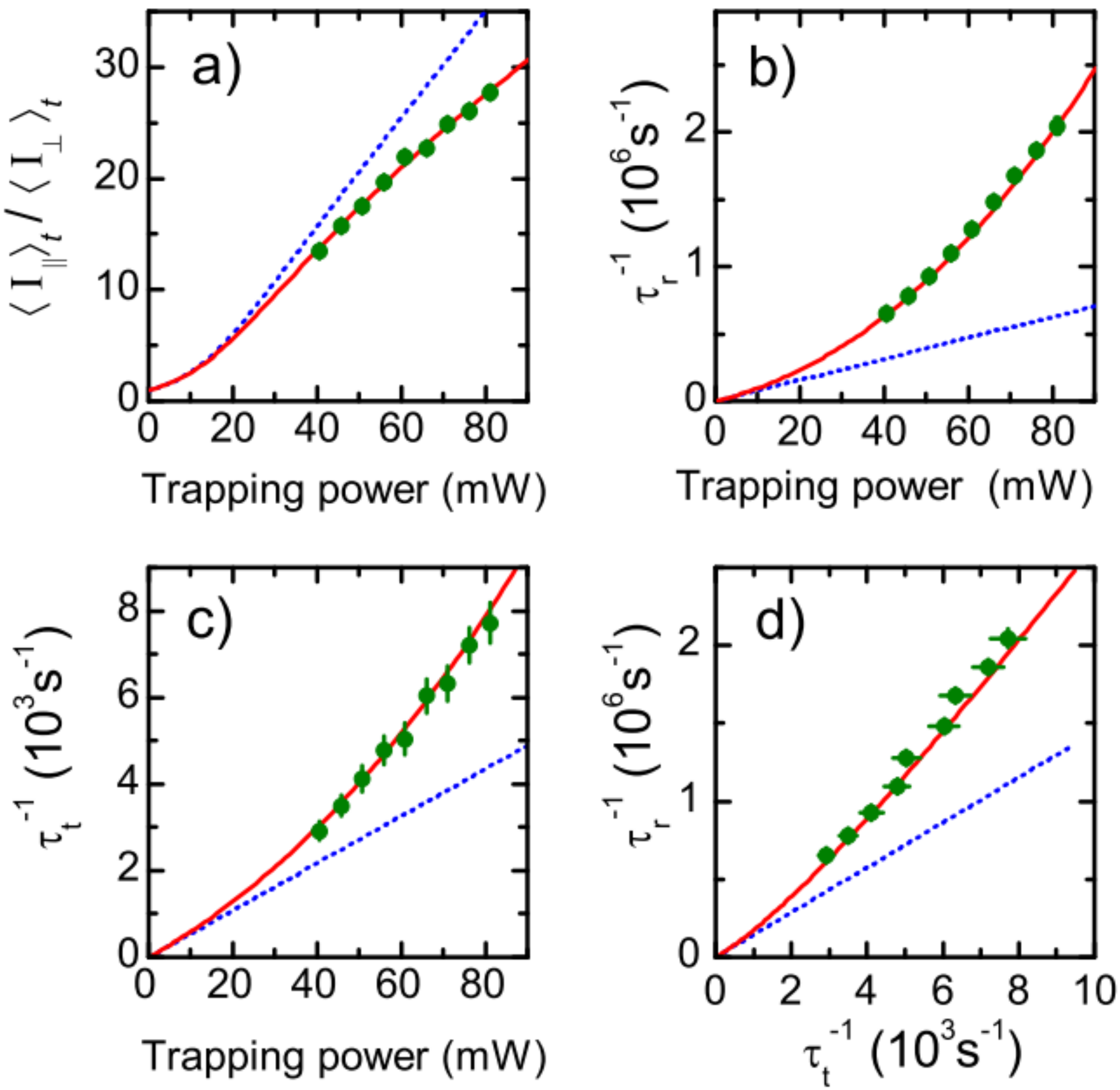
Orientation of gold nanorod along trap polarization



Fluctuations of orientation by autocorrelation



Local temperature and viscosity



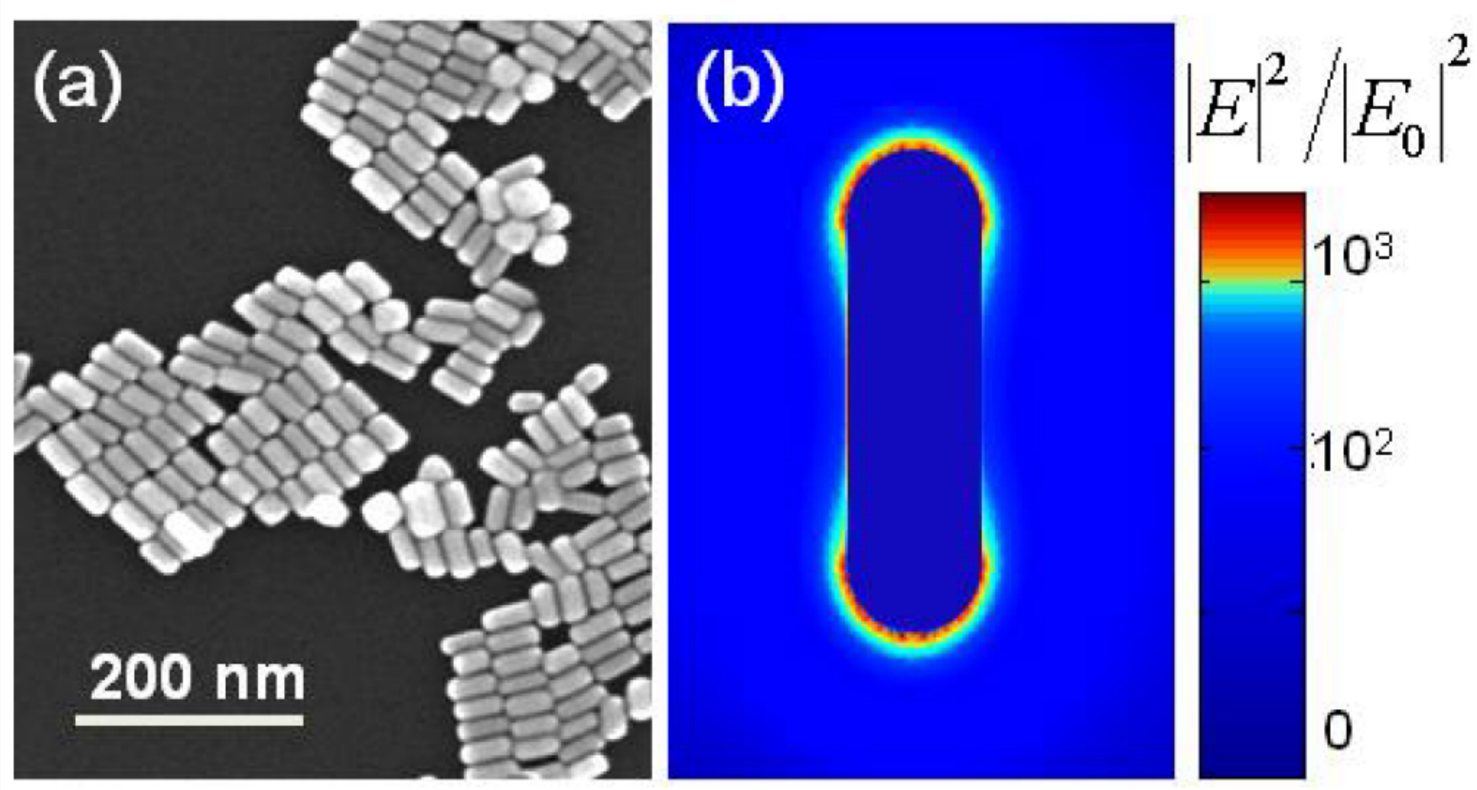
Single 60x25 nm^2 nanorod in the optical trap

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

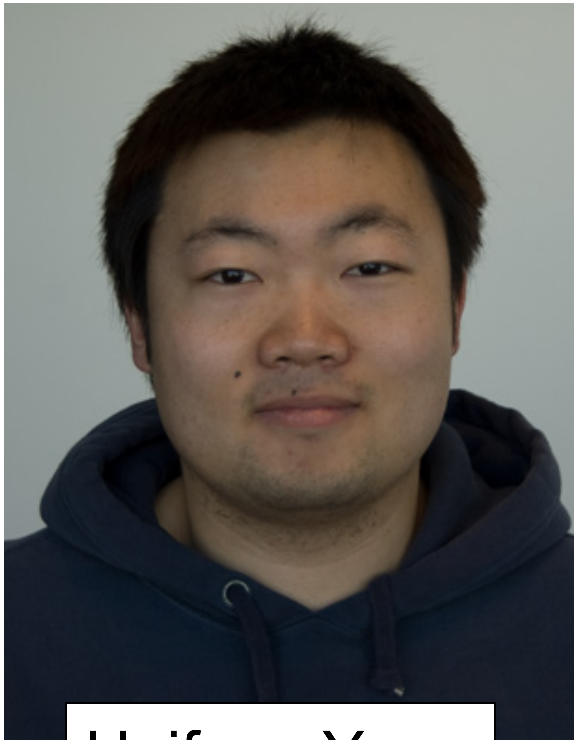
Maximum temperature change about 80 K

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

Fluorescence enhancement by a single gold nanorod

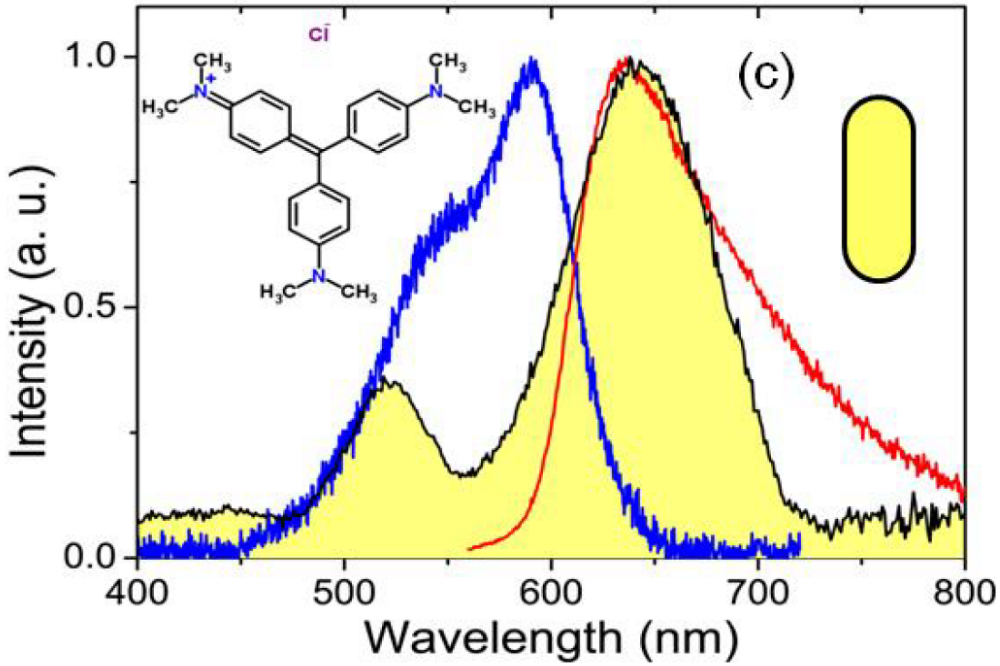


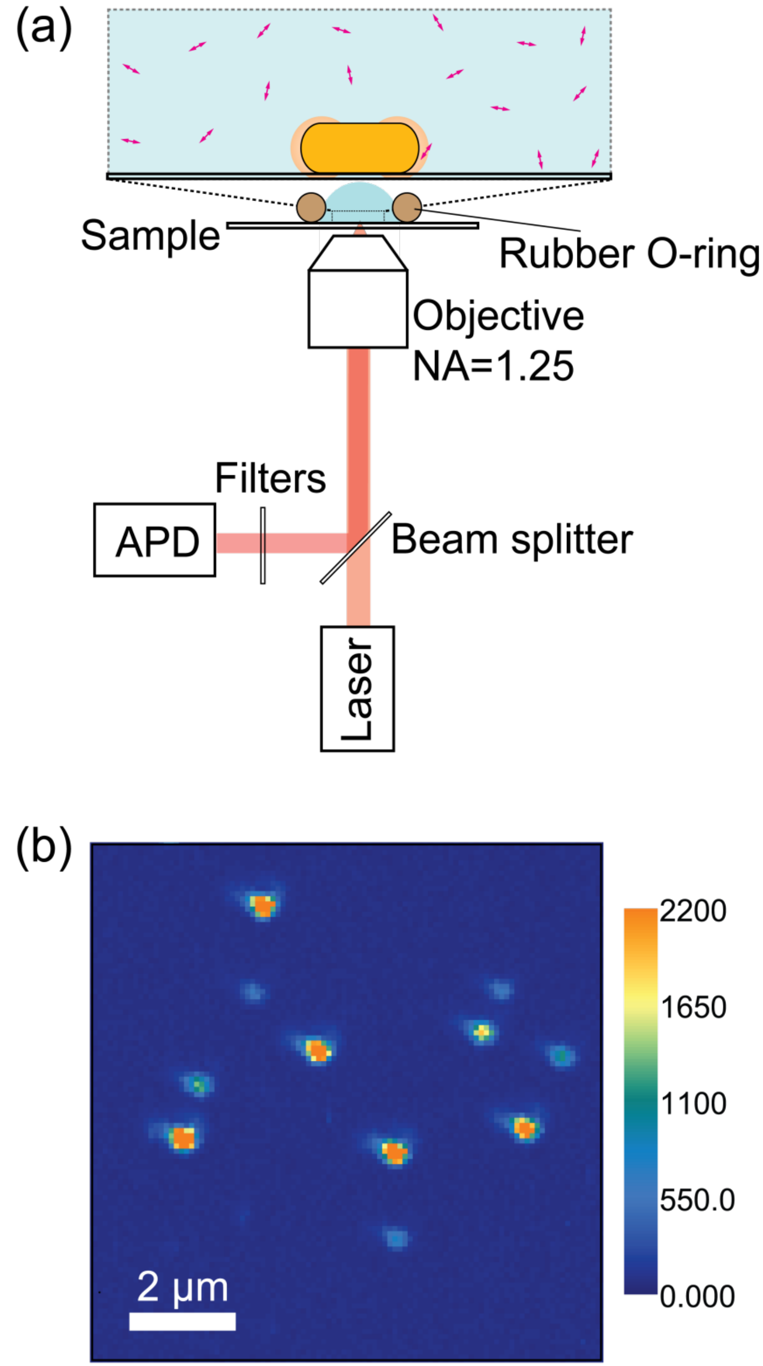
HF Yuan et al., Angew. Chem. **52** (2013) 1217
S. Khatua et al. ACS Nano **8** (2014) 4440
S. Khatua et al. PCCP DOI 10.1039/c4cp03057e


Haifeng Yuan

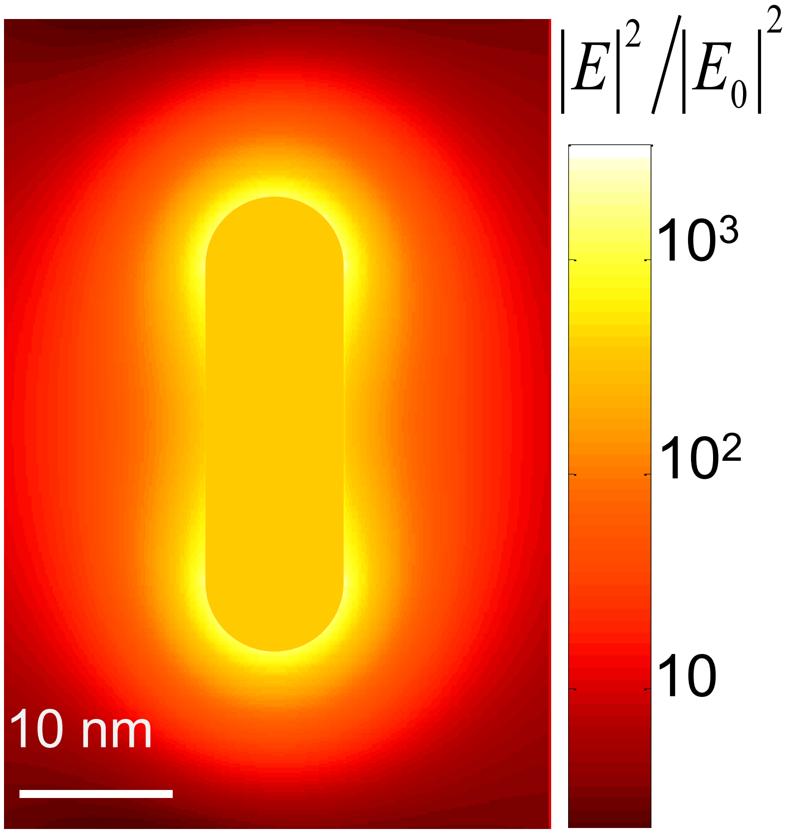

Dr Saumyakanti Khatua

Spectra and Setup

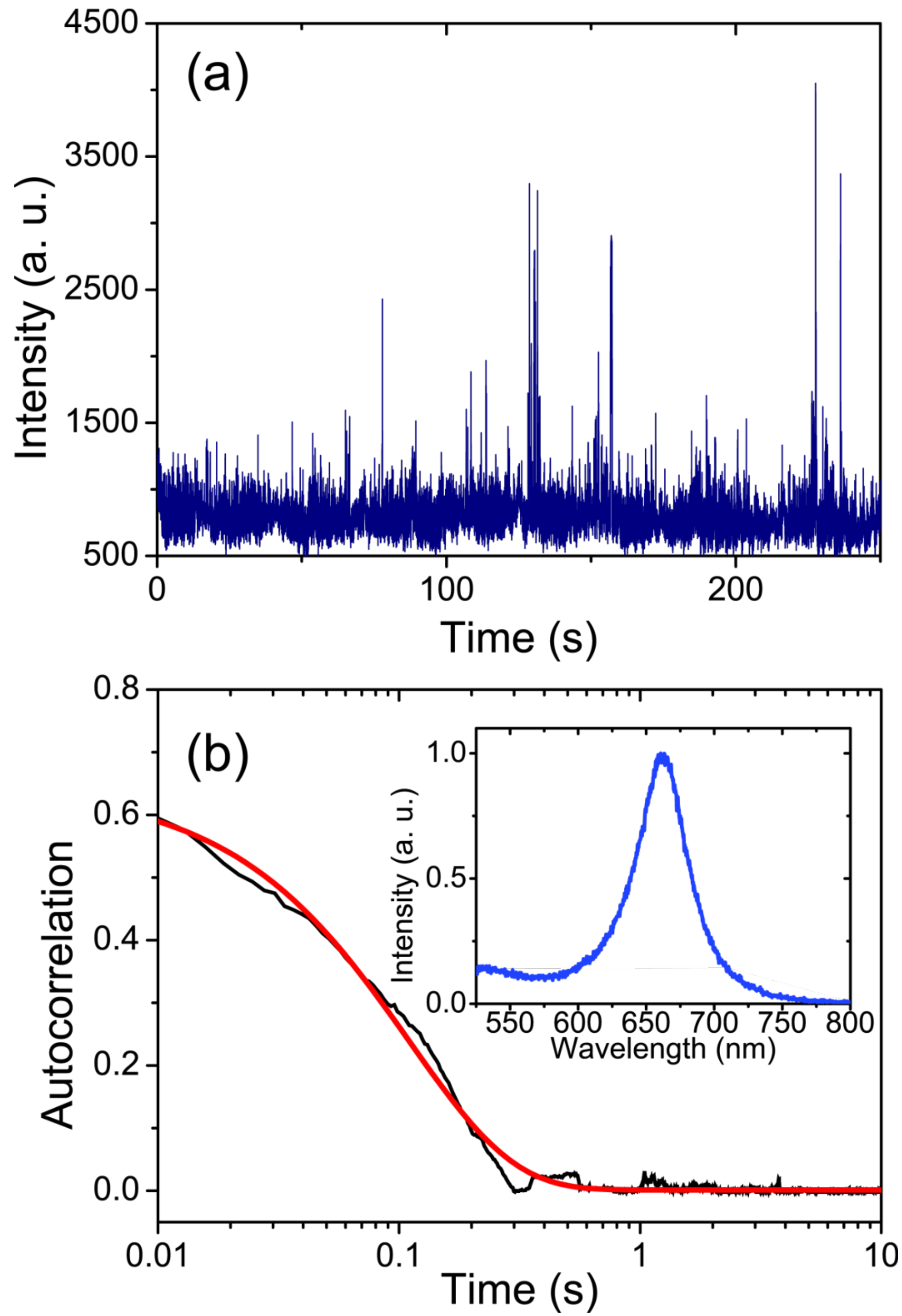




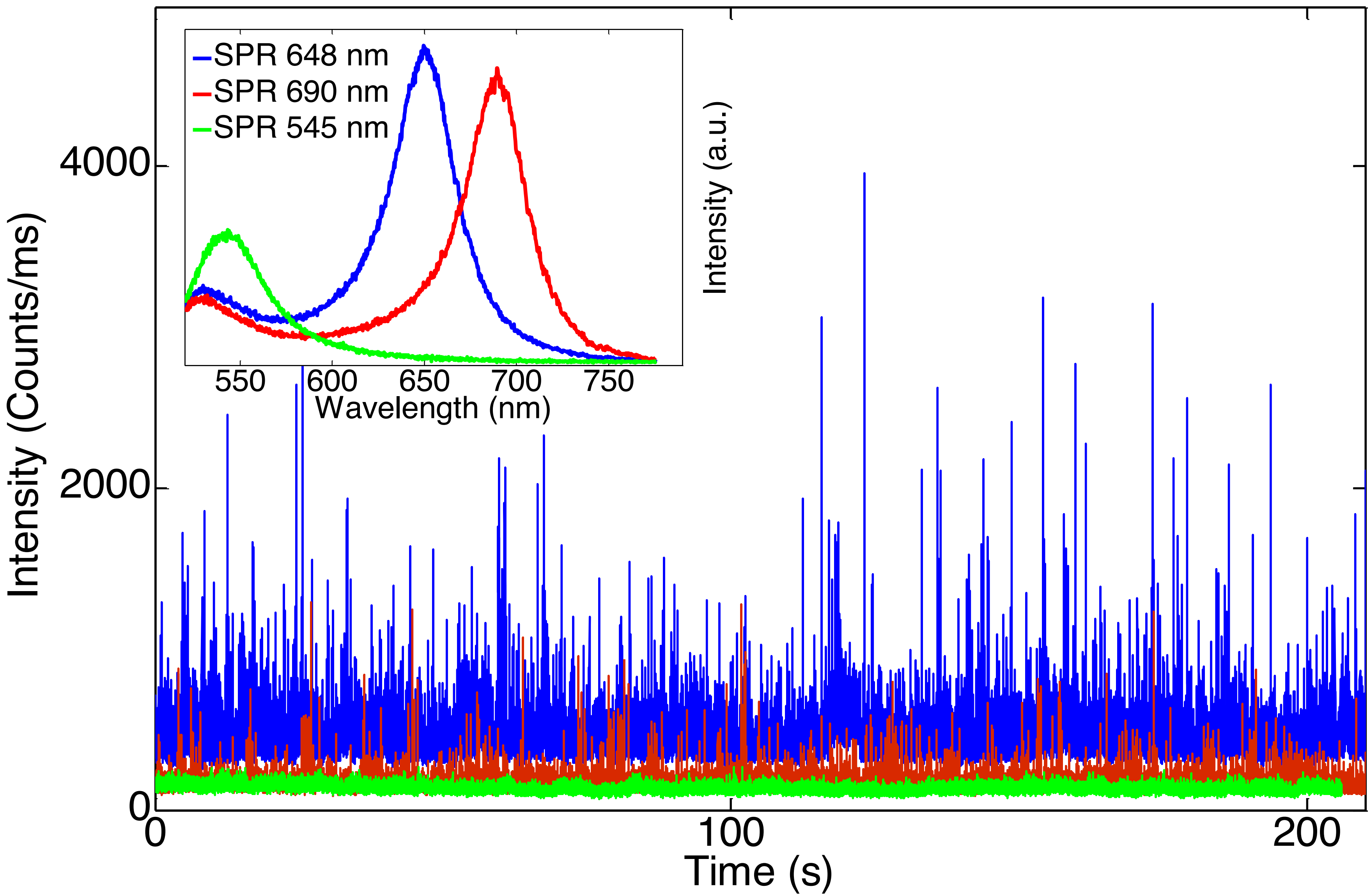
Fluorescence bursts



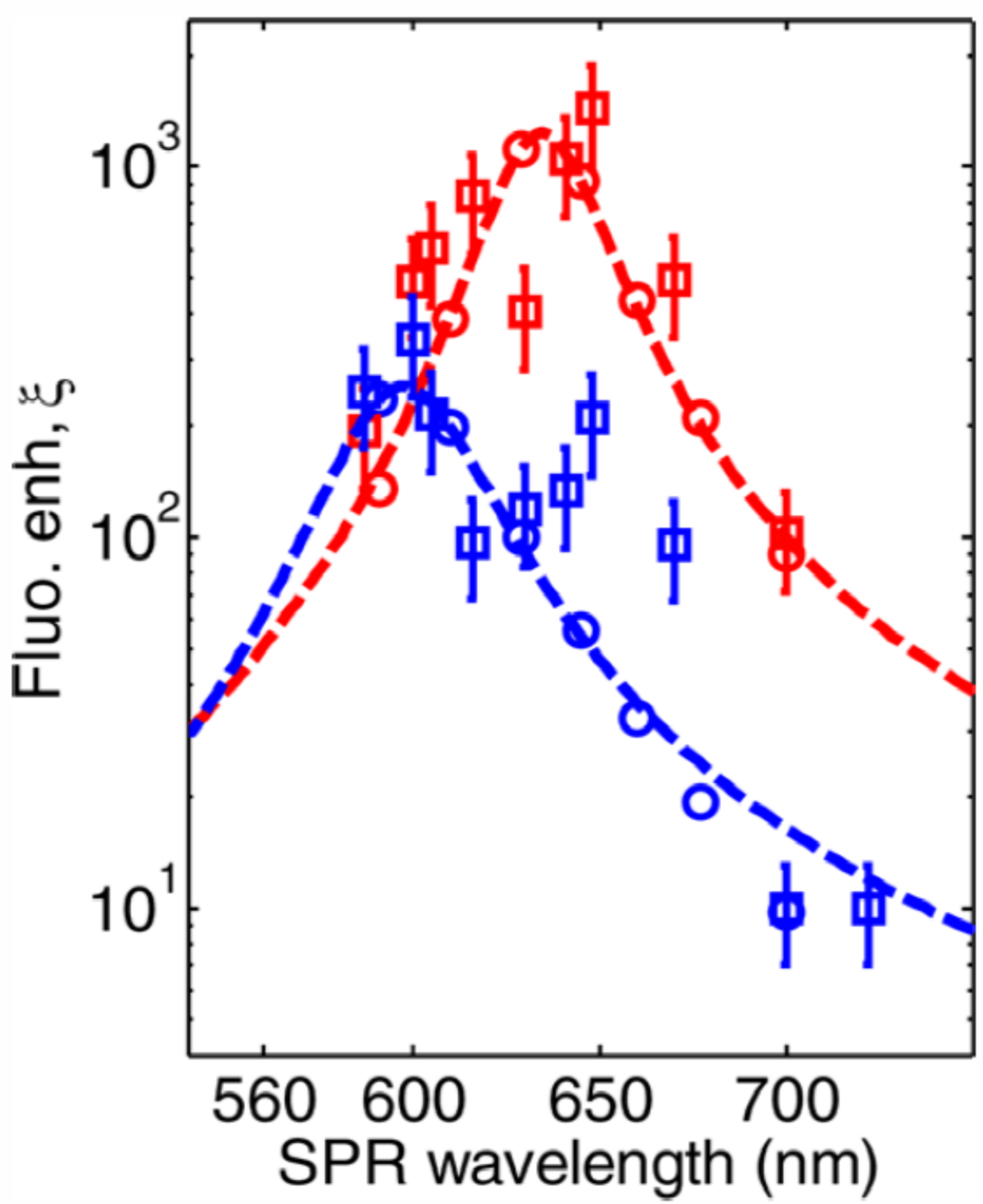
enhancement ~ 1000-fold



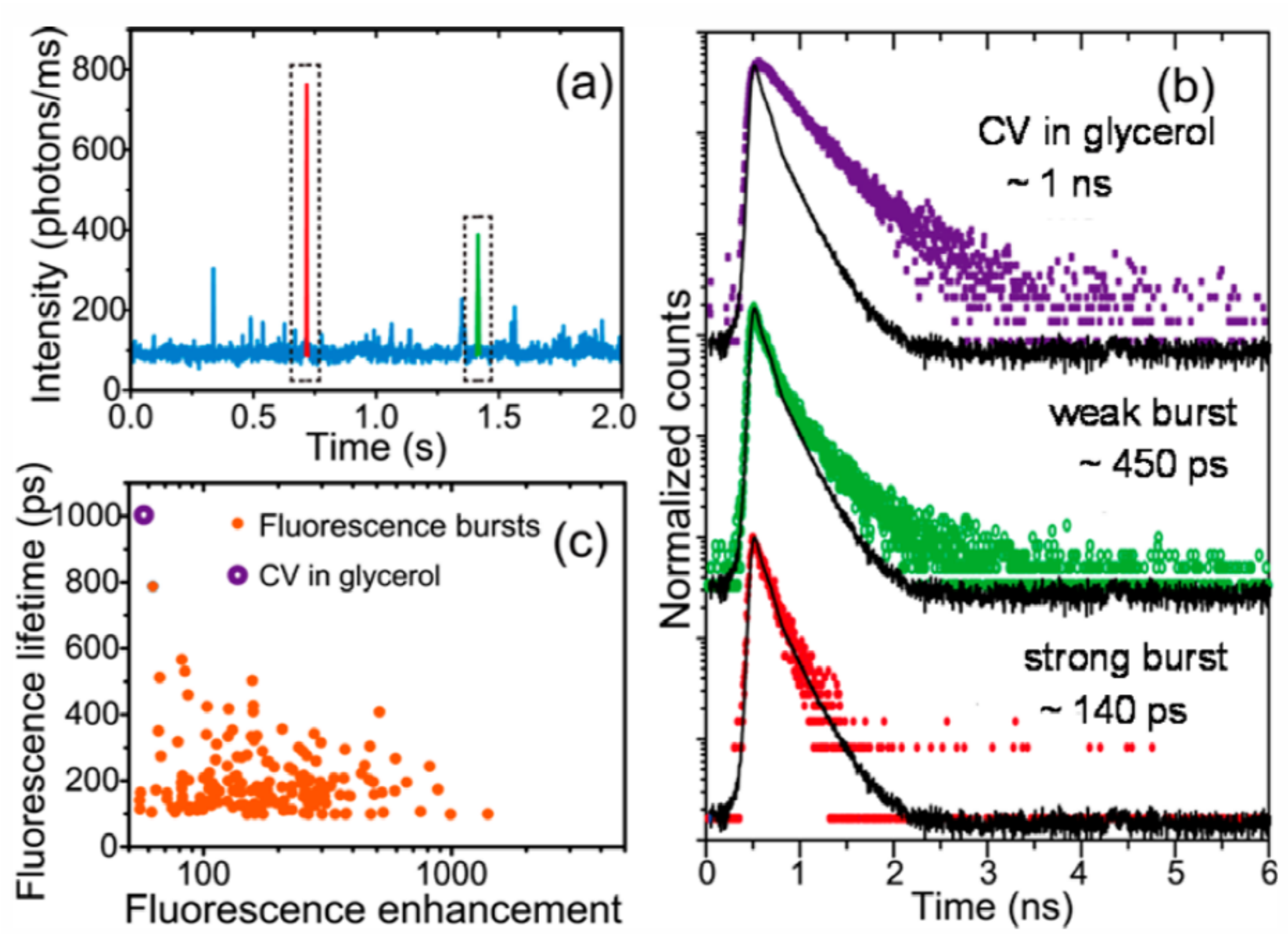
Influence of plasmon resonance



Spectral dependence of enhancement



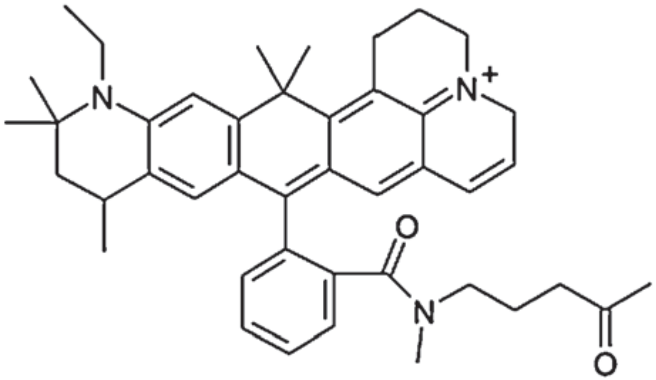
Fluorescence lifetime



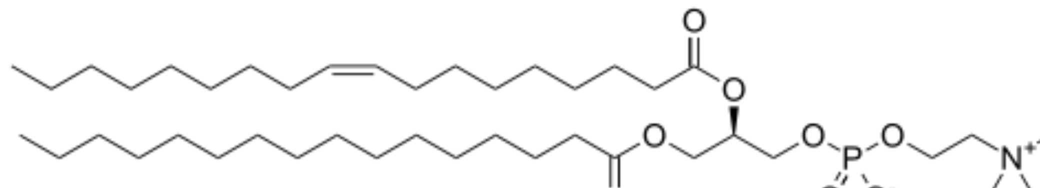
Biswajit Pradhan

Enhancement of Atto 647N

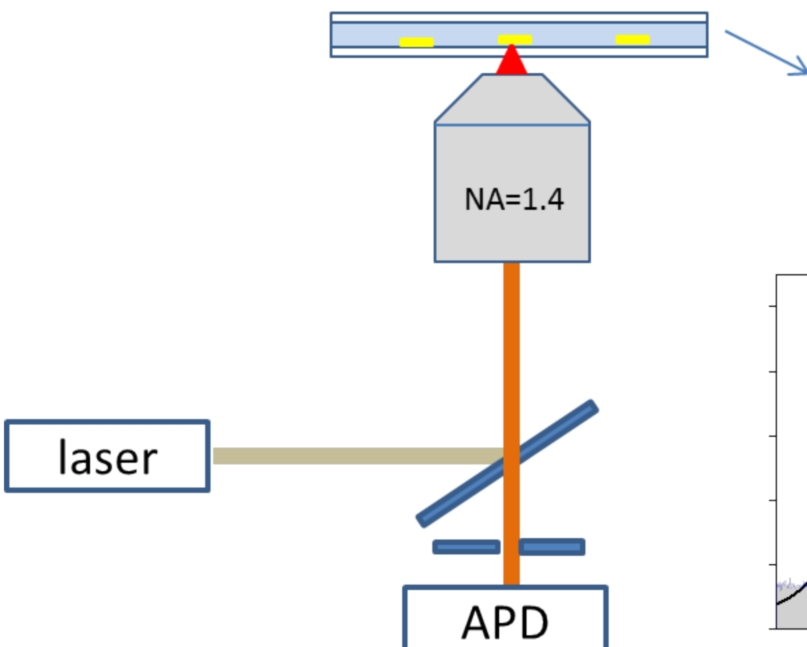
A

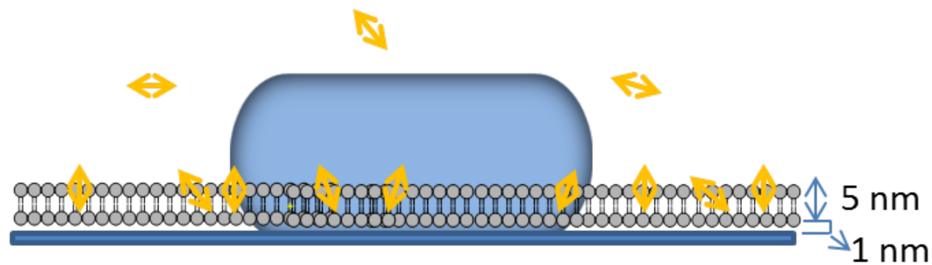


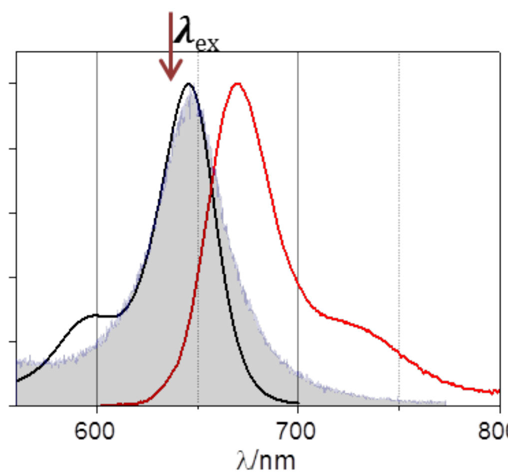
ATTO 647N

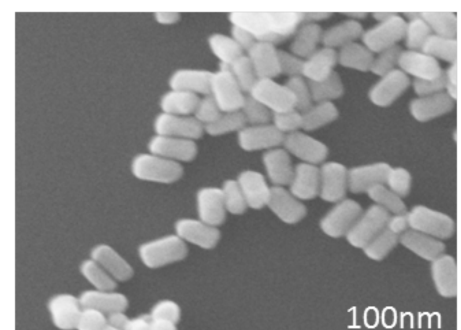


B

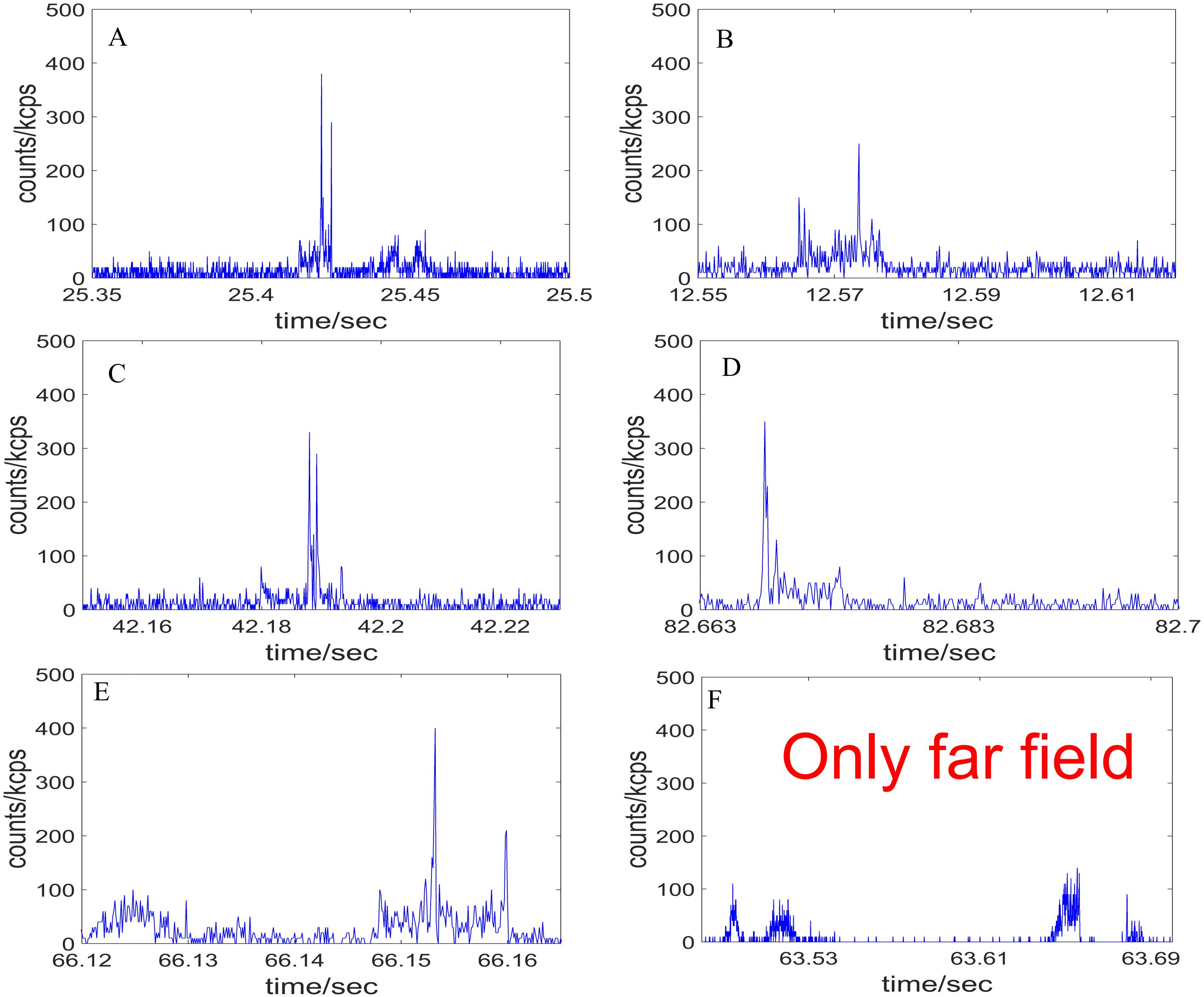




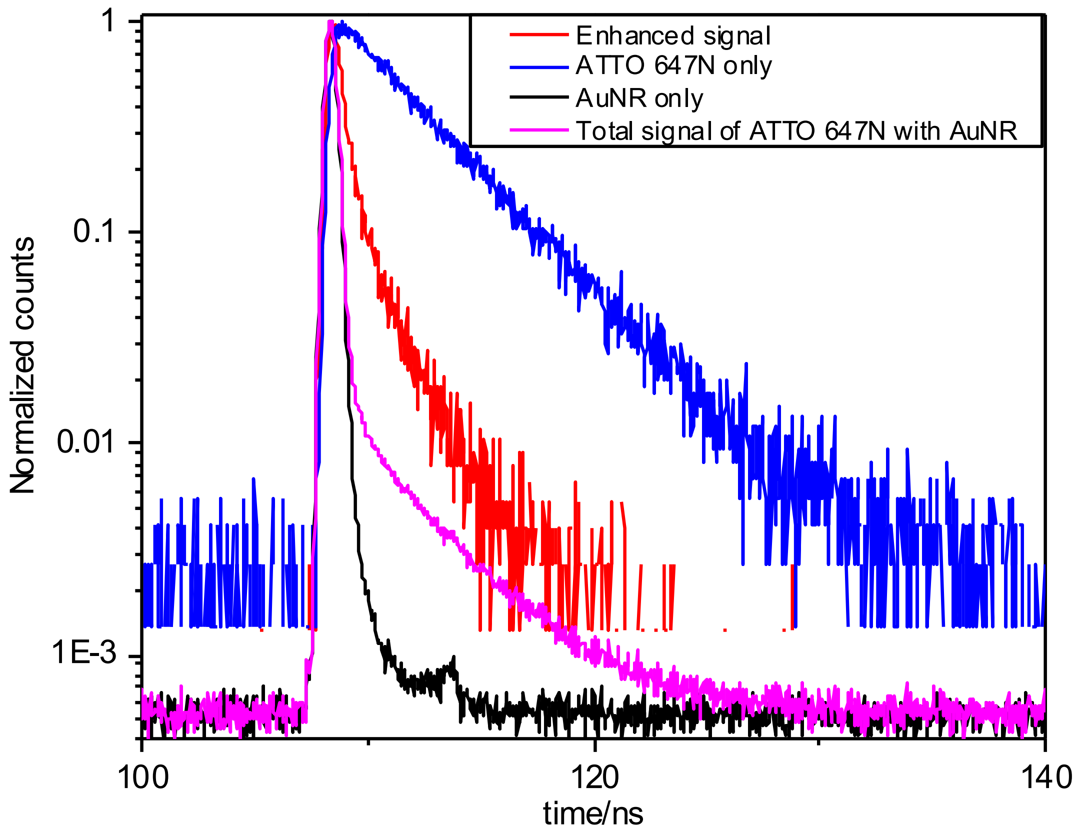




Near-field bursts in time traces



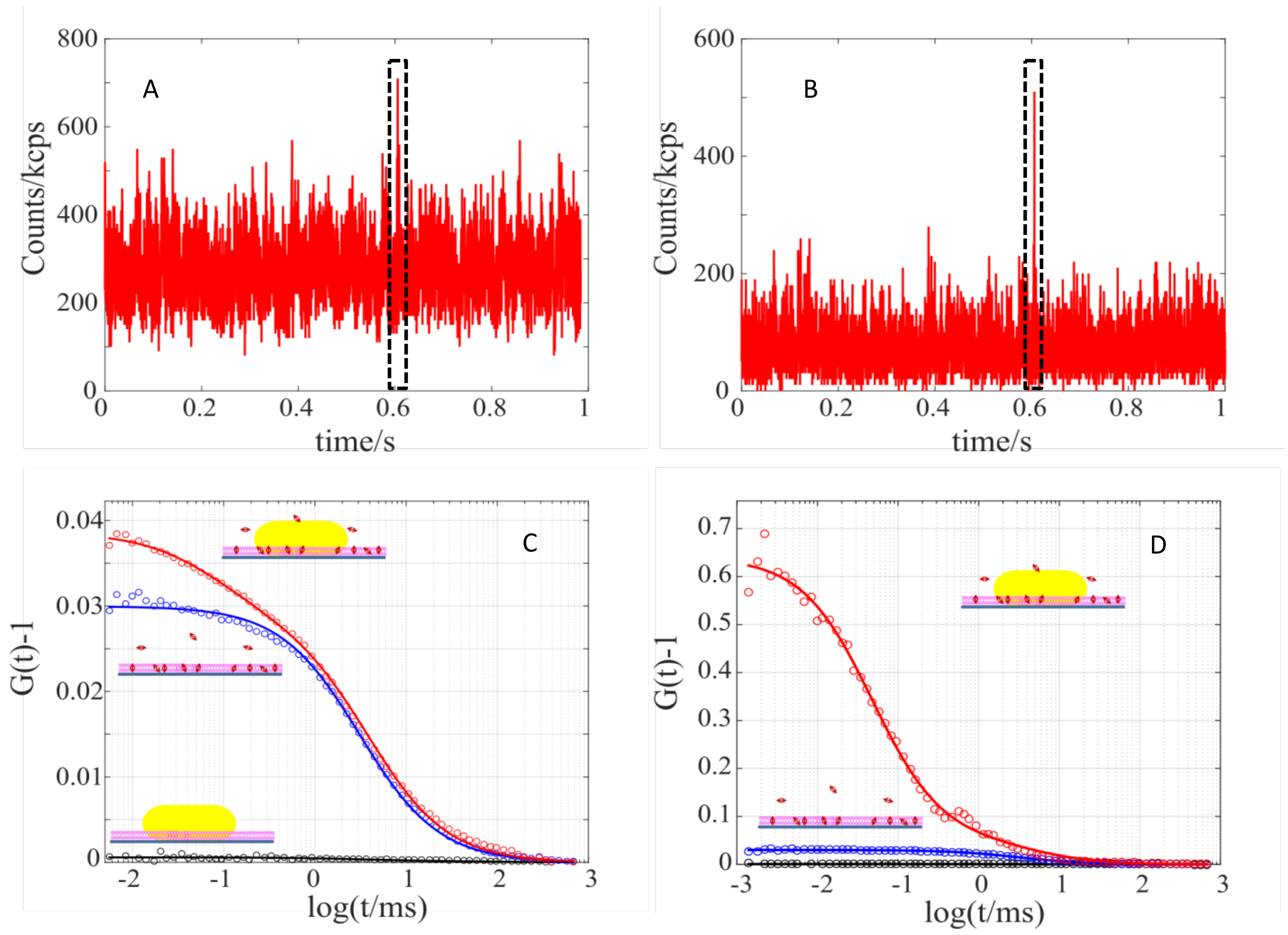
Fluorescence decays



Lifetime shortening due to antenna effect and fluorescence quenching by the metal

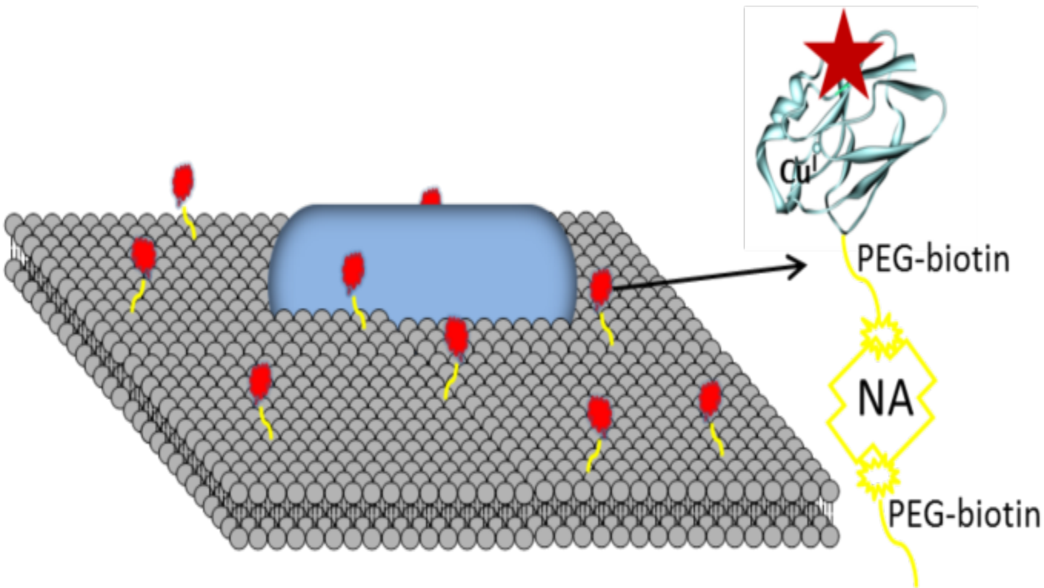
↑

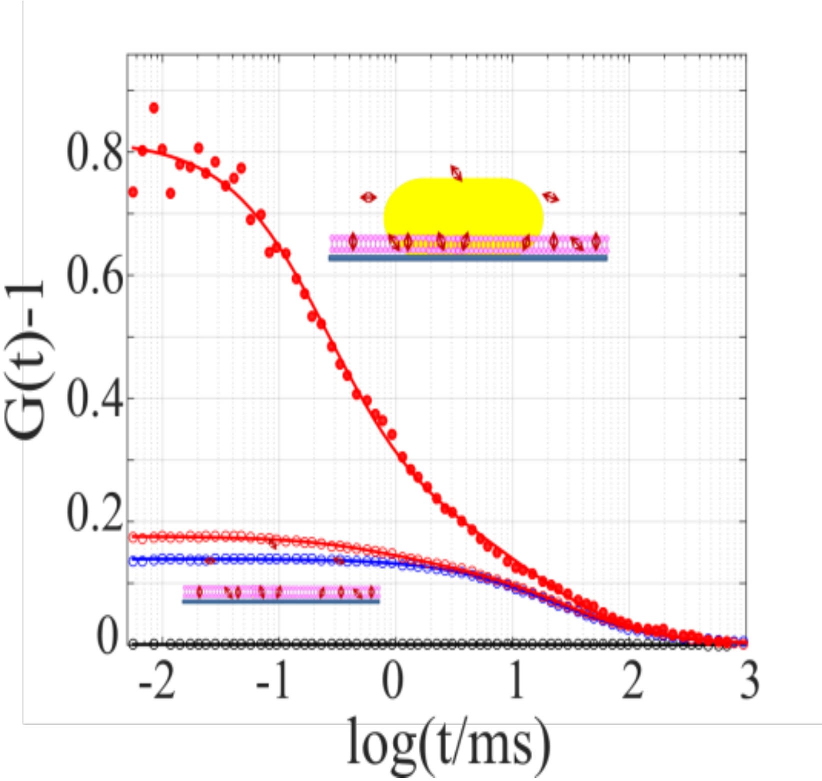
Enhanced FCS with Lifetime filtering



Ratio of diffusion times in near-field and far-field: about 60

Enhanced FCS of a labelled protein

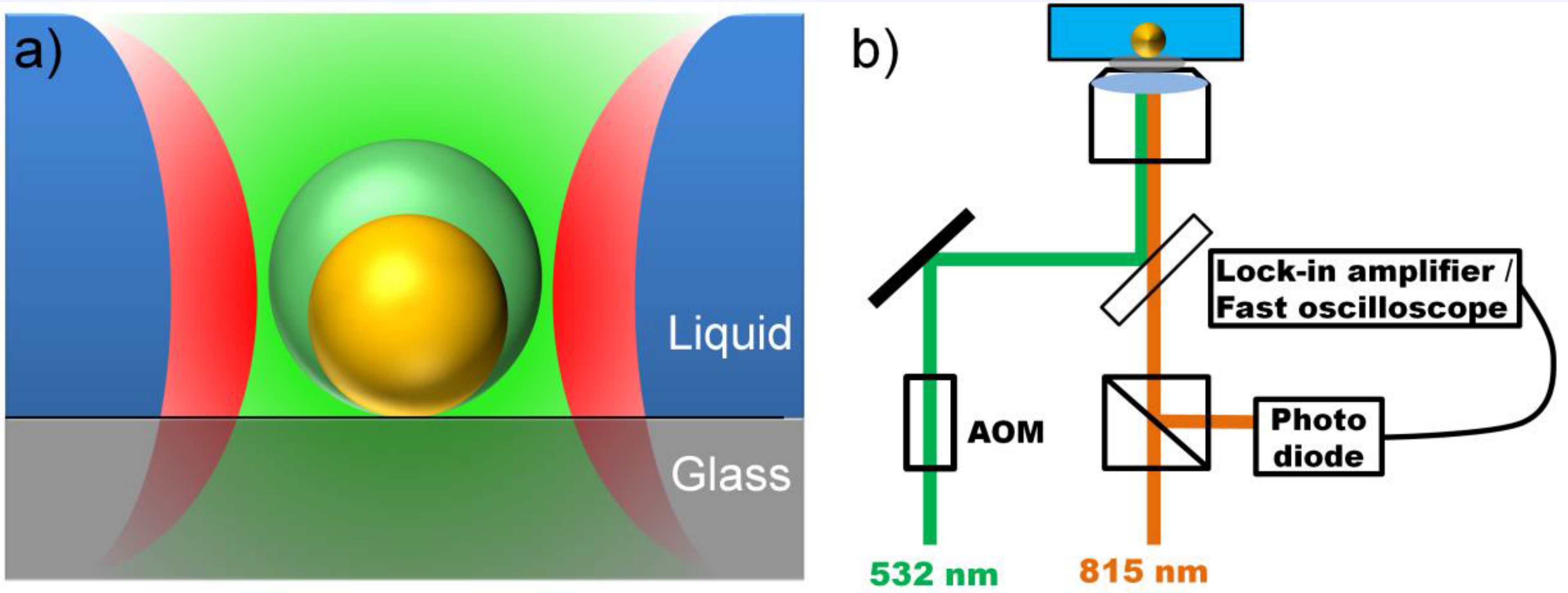




Diffusion time in bilayer longer than for the dye alone

↑

Plasmonic Nanobubbles

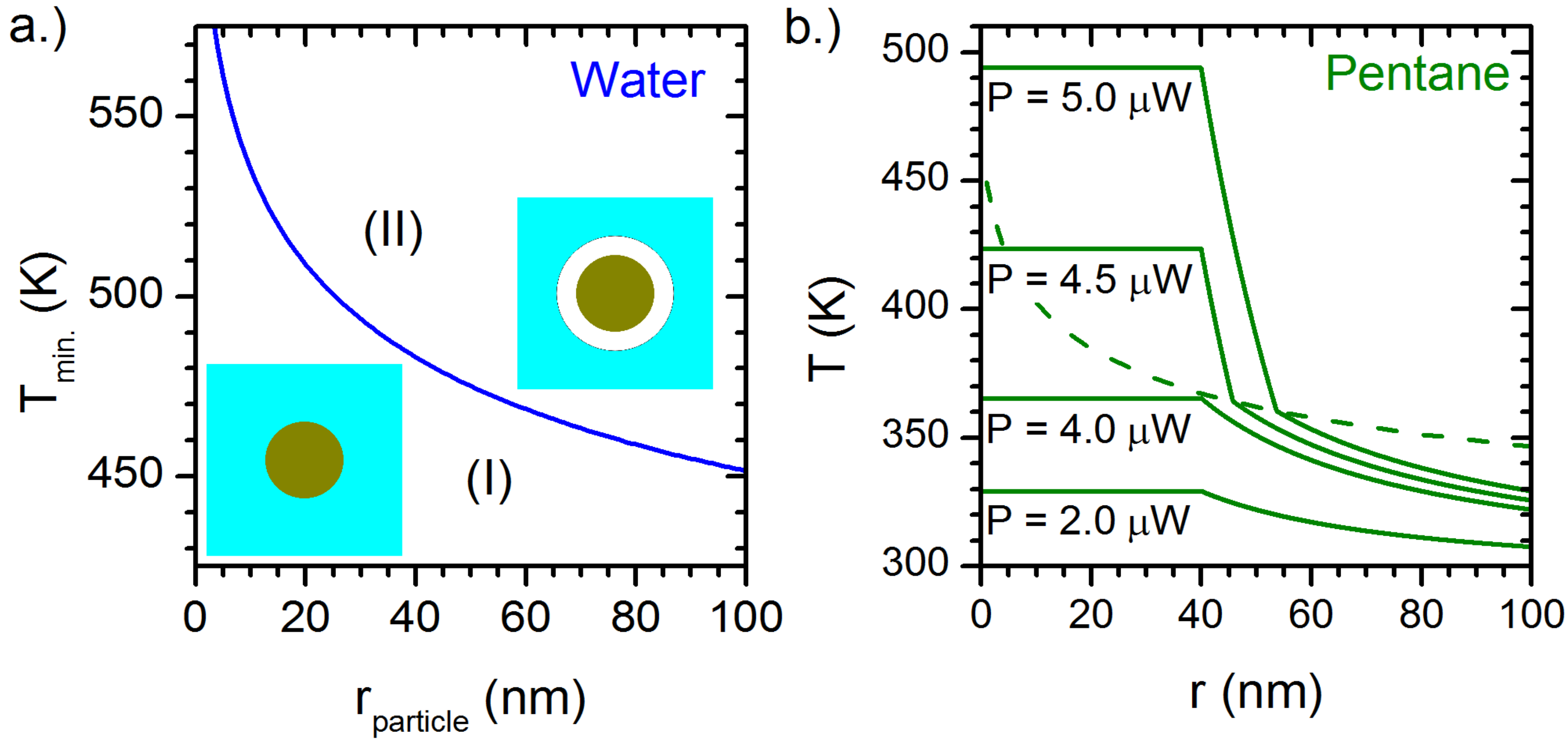


Lei Hou et al., submitted (ArXiv 1407.1221, 2014)

Lei Hou

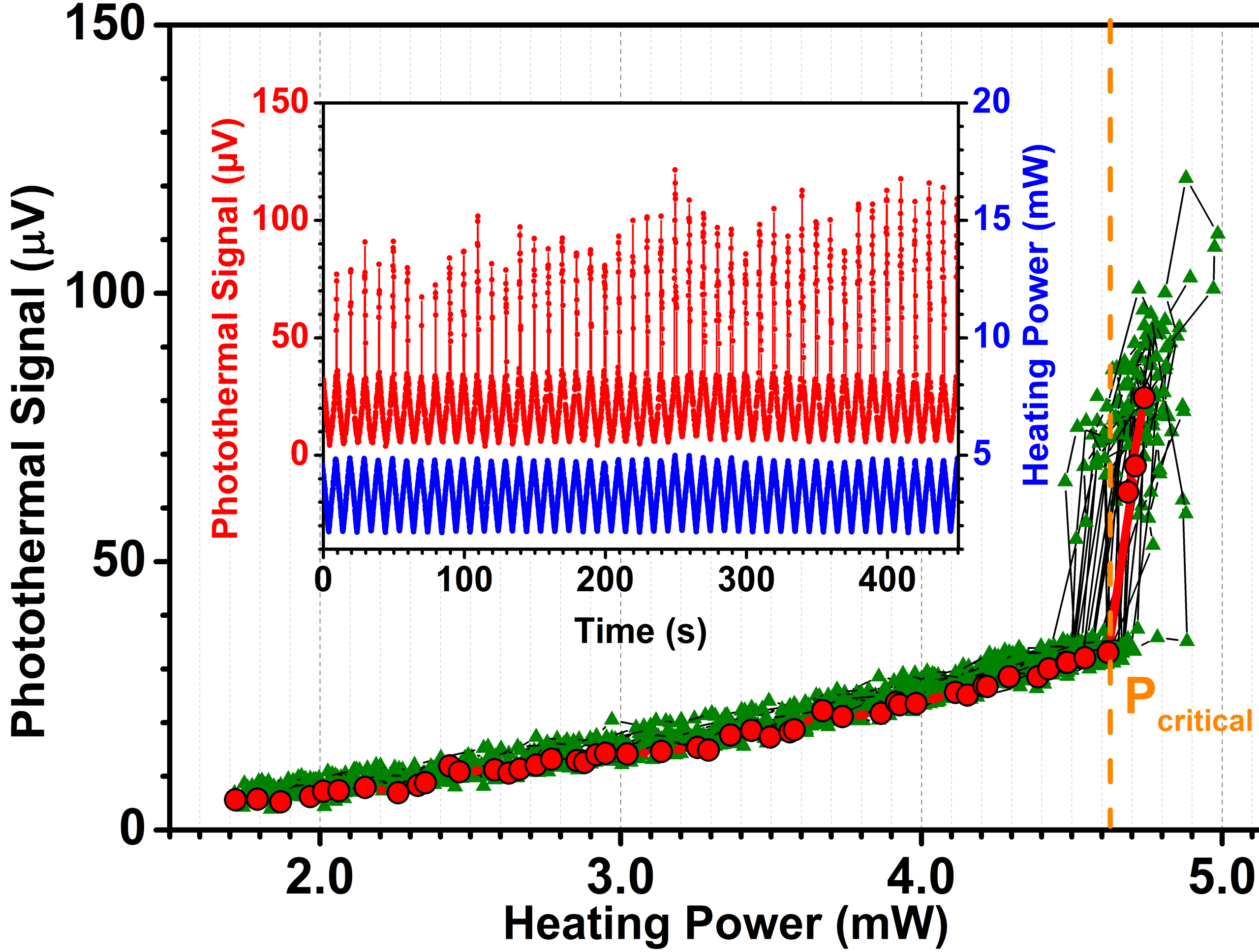
Thomas Jollans

Boiling occurs at higher temperature



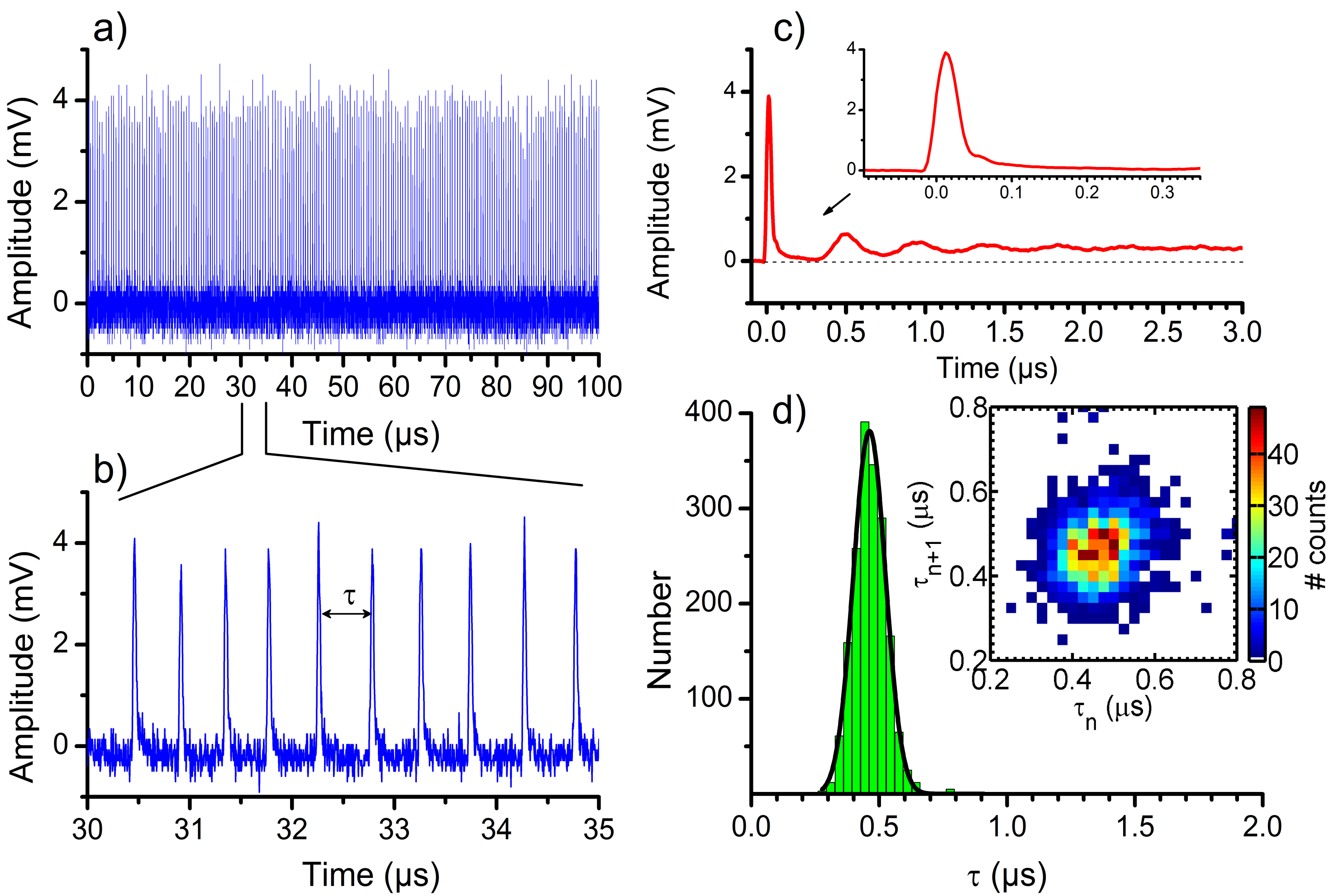
Nanobubble must overcome Laplace pressure, $p = \frac{2A}{R}$.

Threshold in water



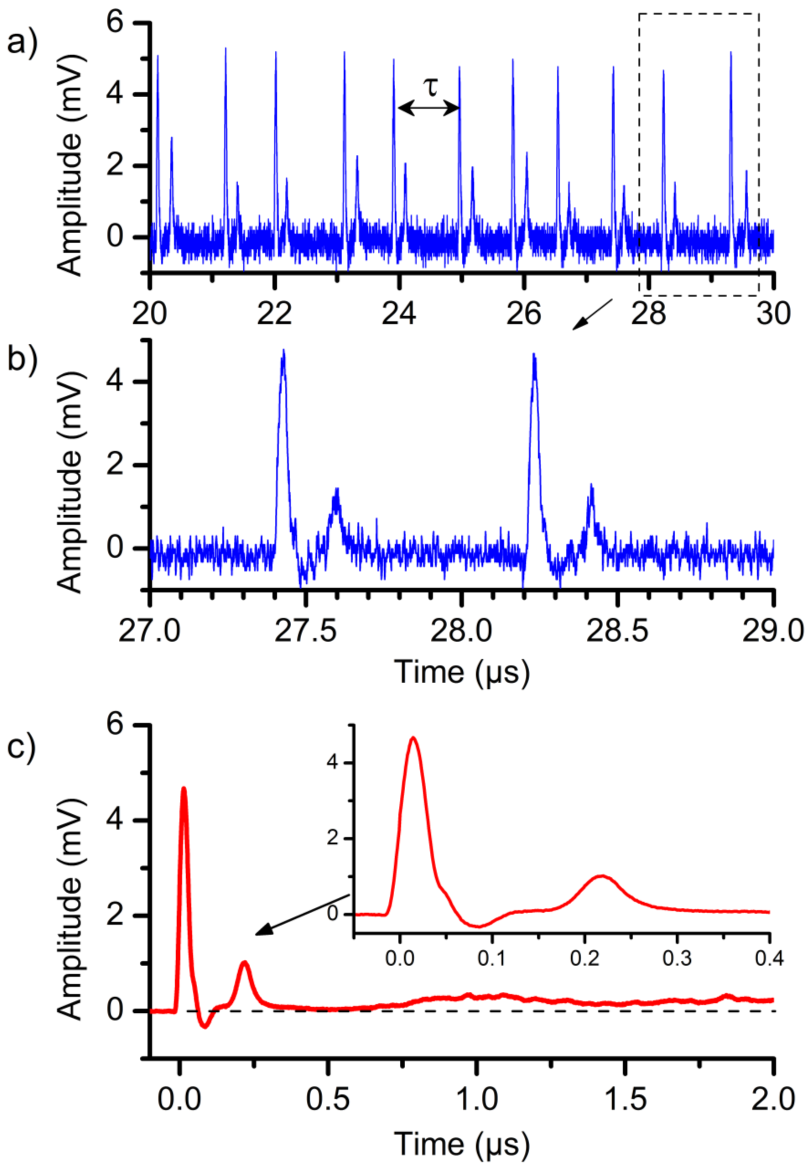
Photothermal detection of scattered probe.

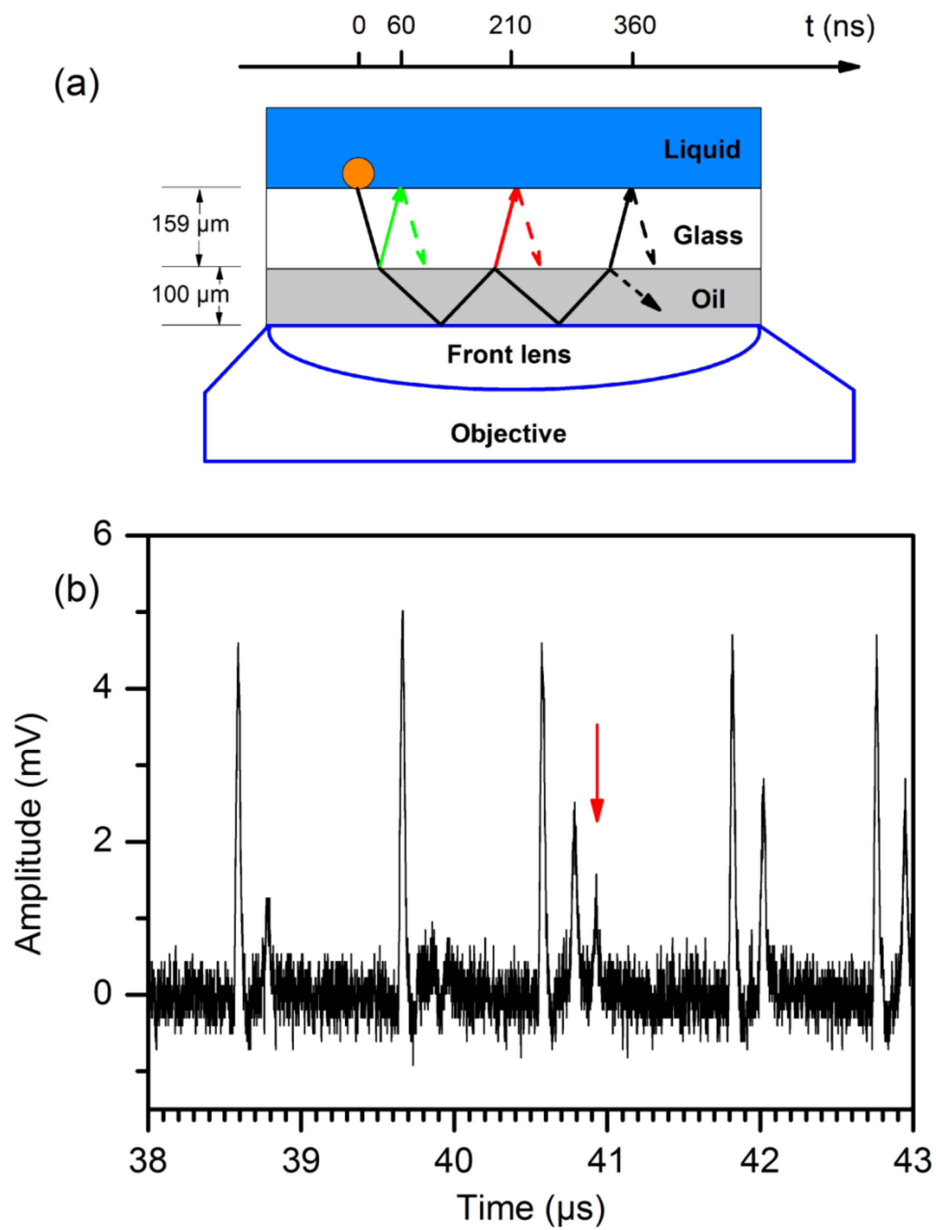
Dynamics of nanobubble in pentane



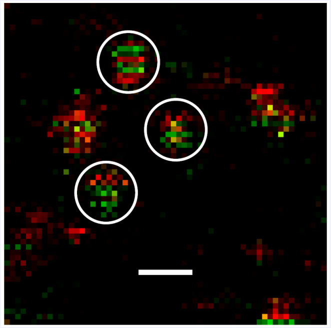
Fast explosive events (25 ns).

Acoustic echoes trigger new nanobubbles

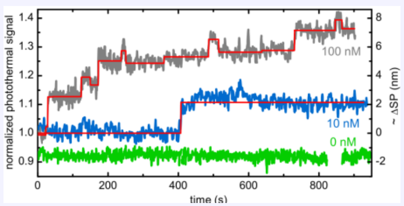




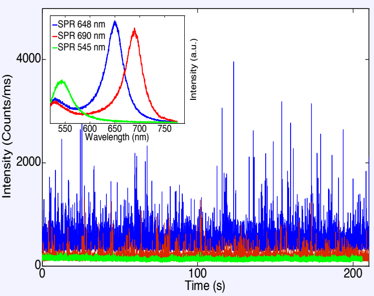
Conclusions



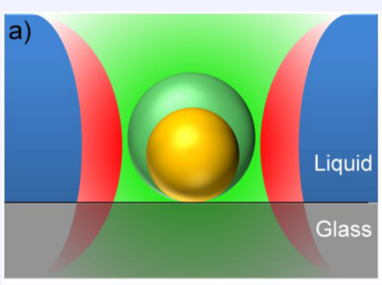
- Dynamical heterogeneity



- Plasmonic sensing with a single gold nanorod

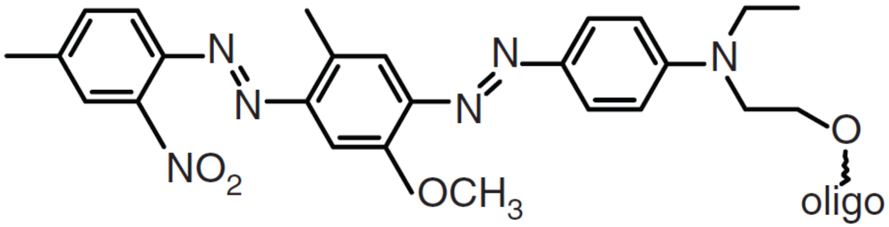


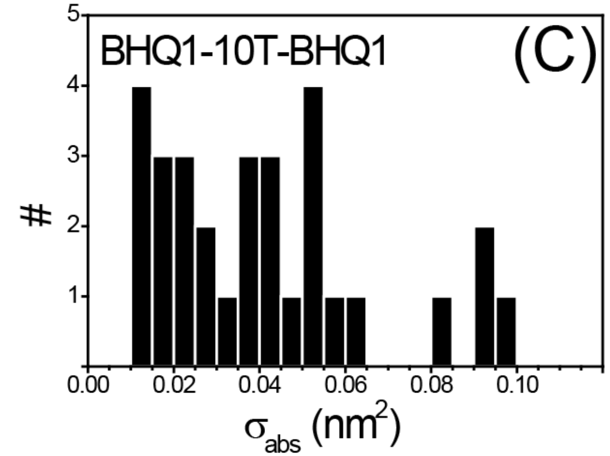
- 1000× fluorescence enhancement with spectral matching

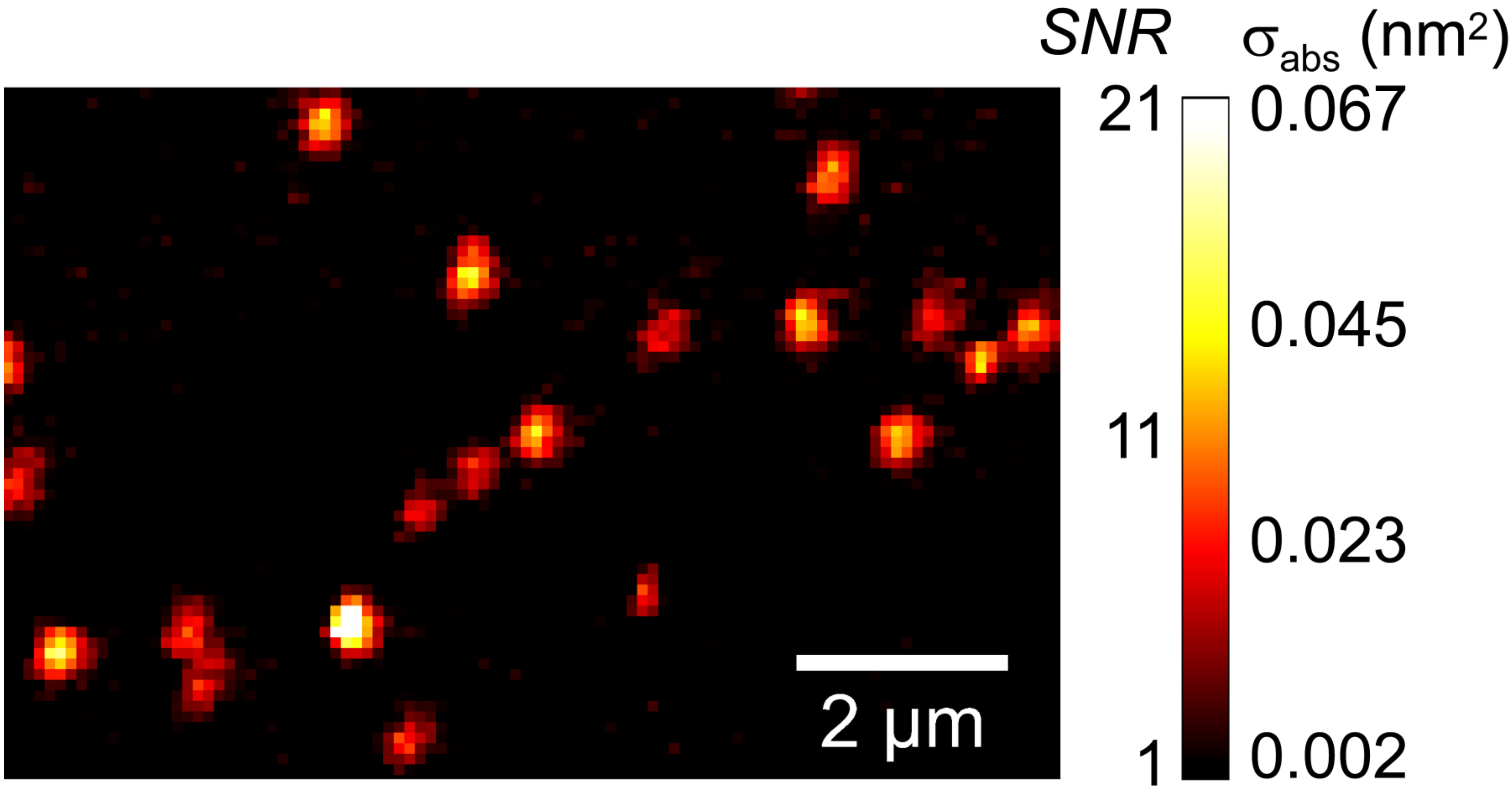


- Explosive nanobubbles upon plasmonic heating

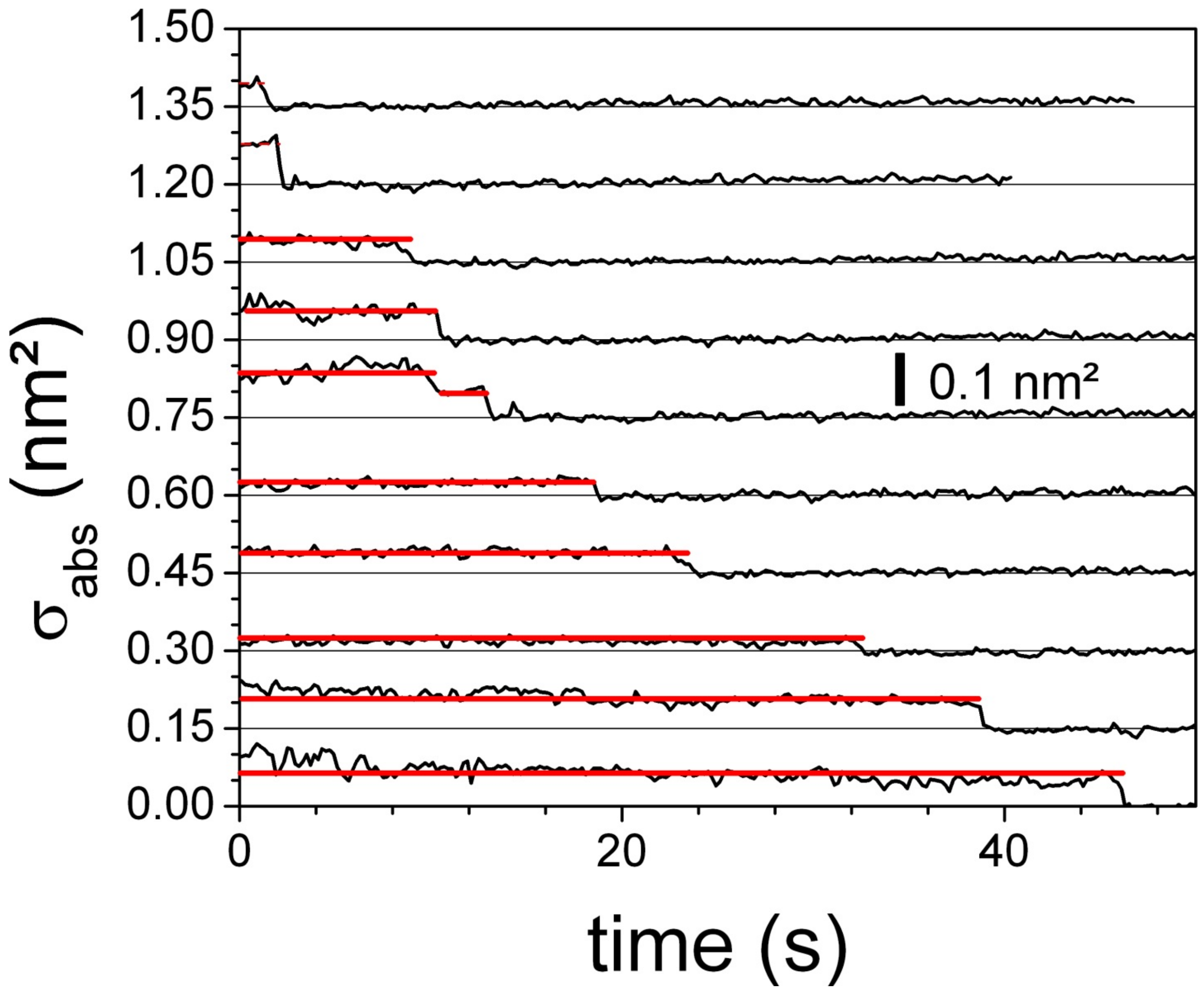
Single-molecule absorption







Single-step photobleaching

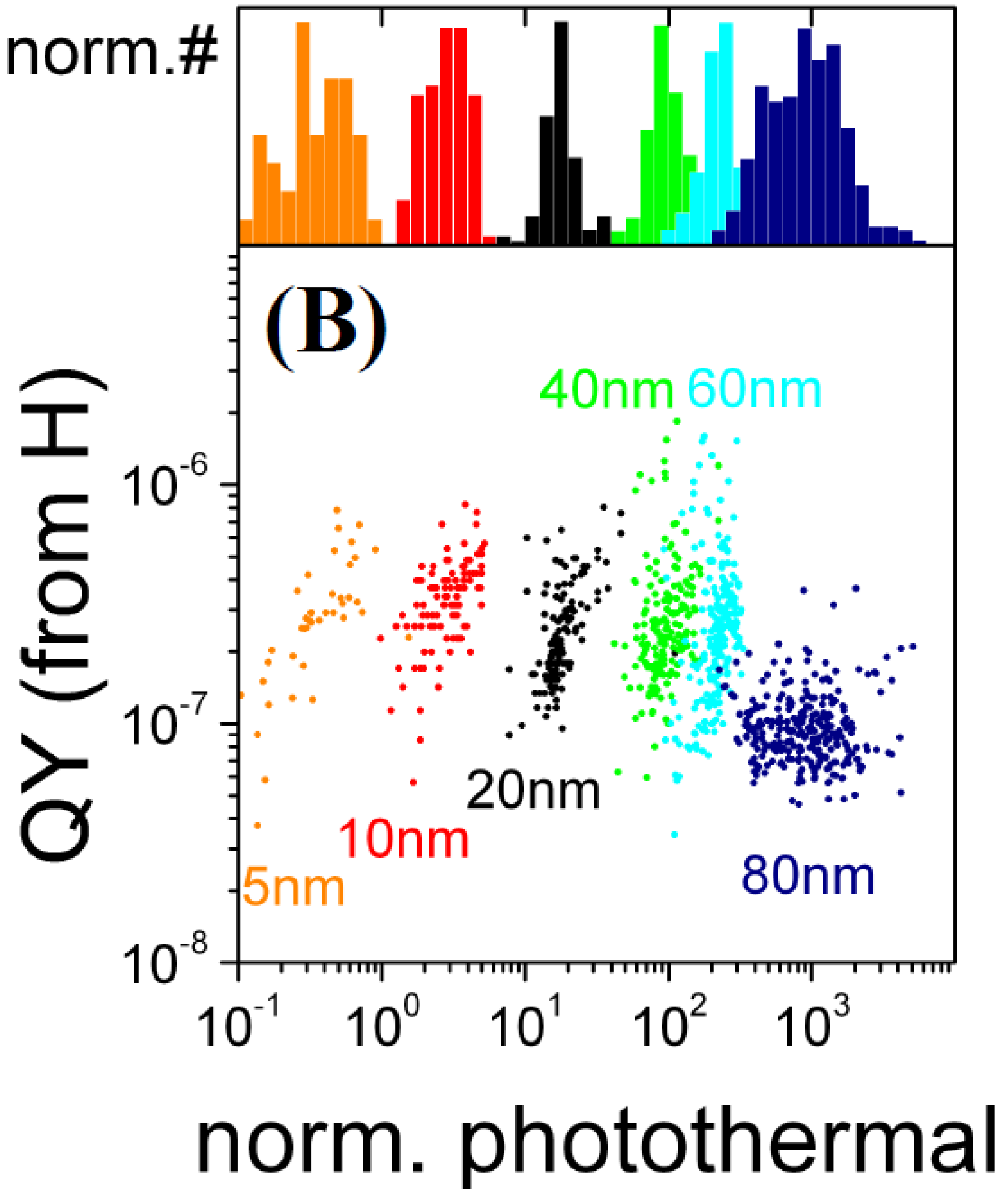


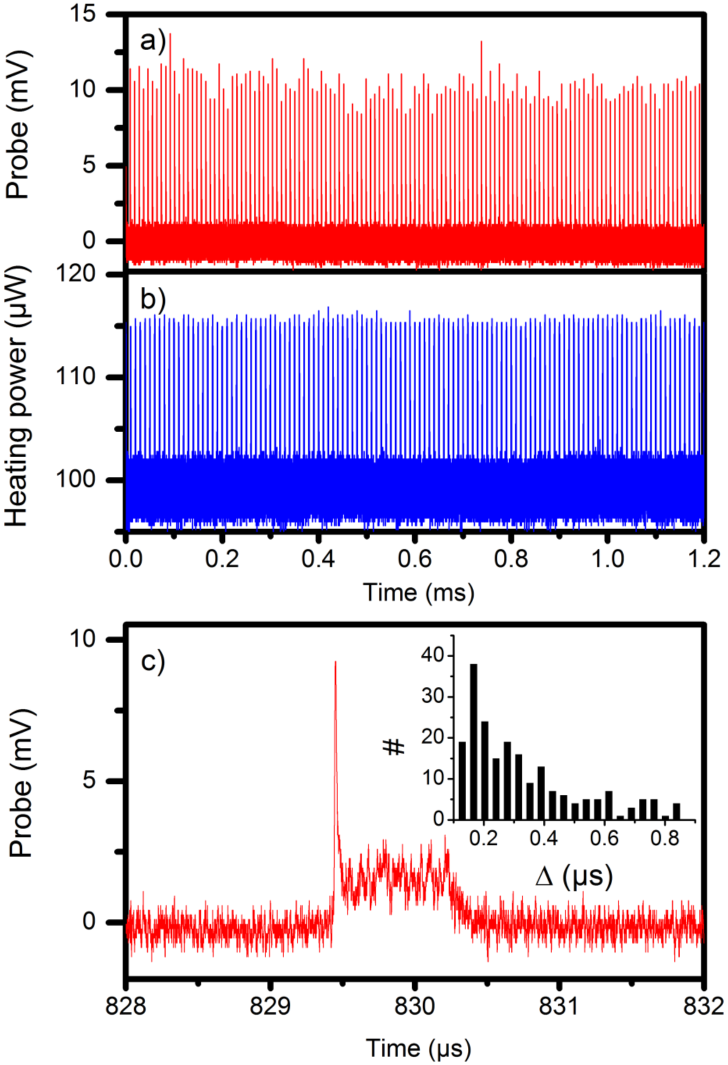
Gaiduk et al., Science 330 (2010) 353

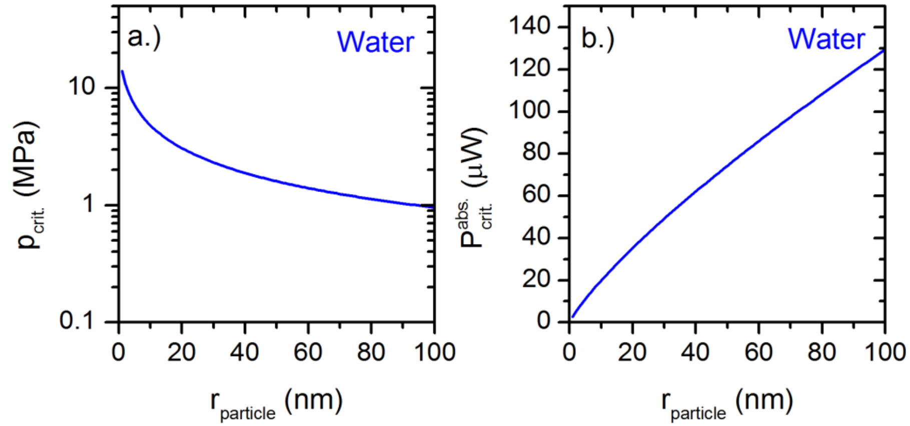
Intrinsic luminescence quantum yield

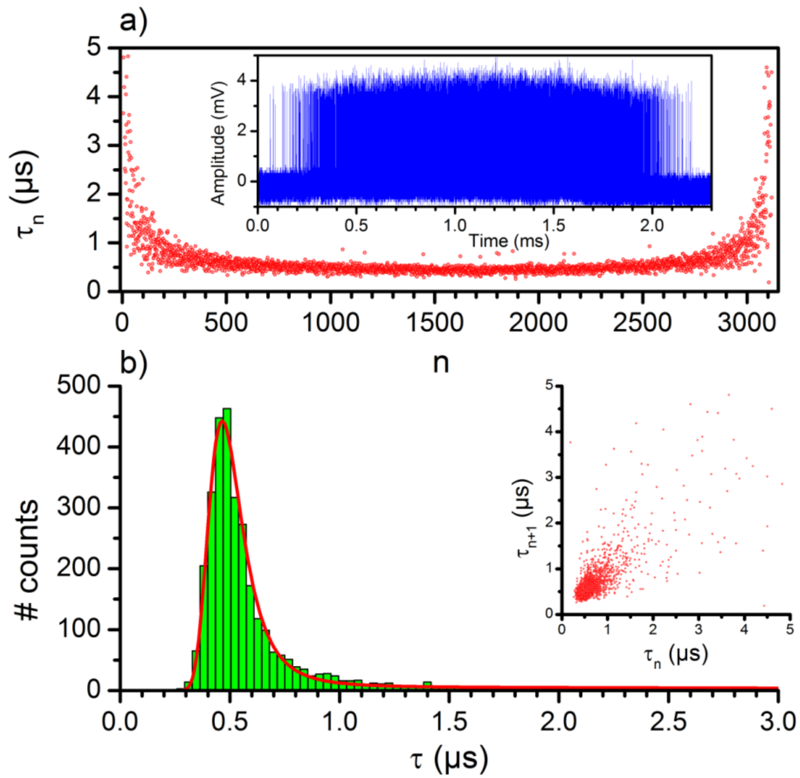
Gaiduk et al., ChemPhysChem 2011

Dulkeith et al. PRB 2004 (ensembles)

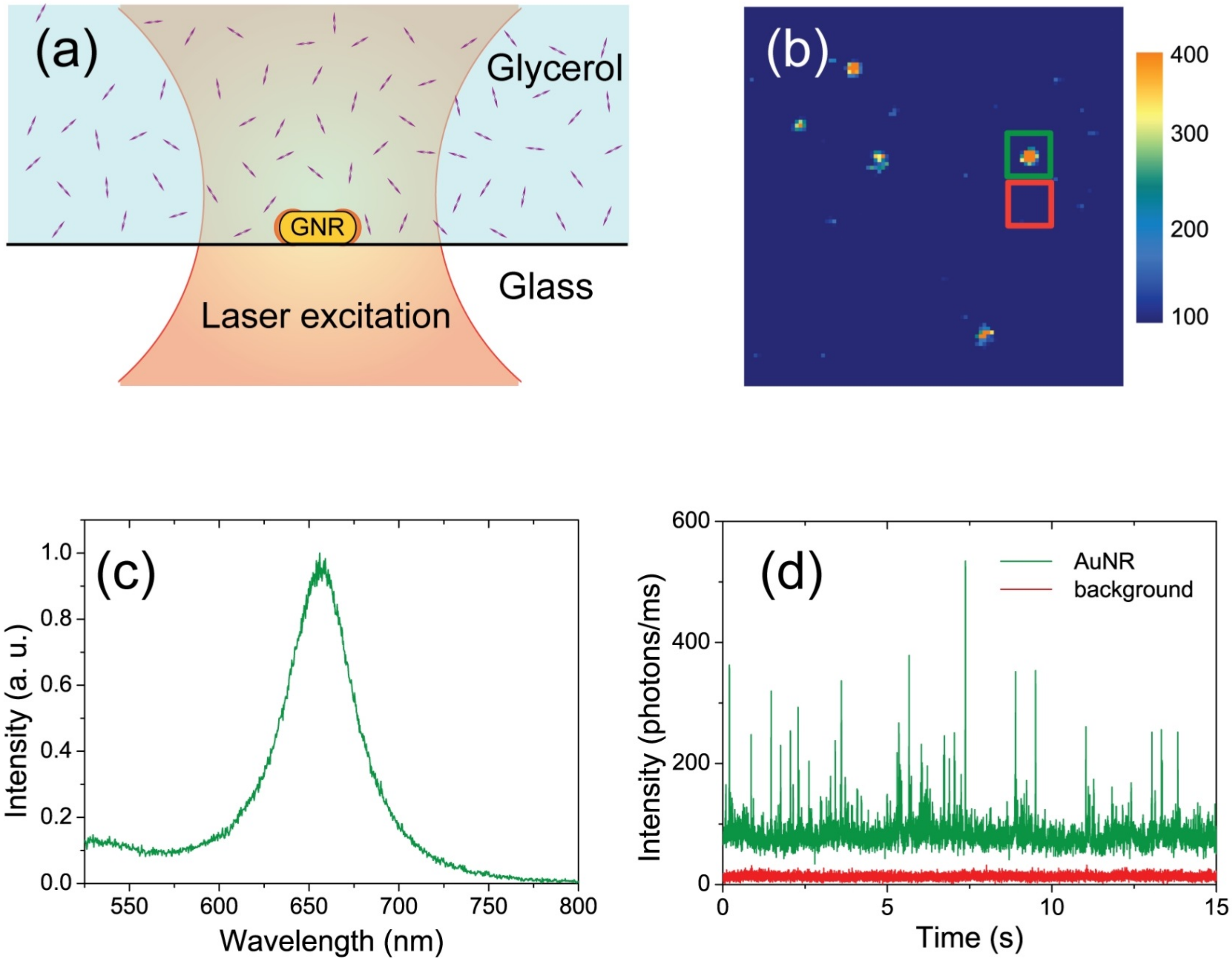



a)
Probe (mV)
b)
Heating power (µW)
Time (ms)
c)
Probe (mV)
#
Δ (µs)
Time (µs)

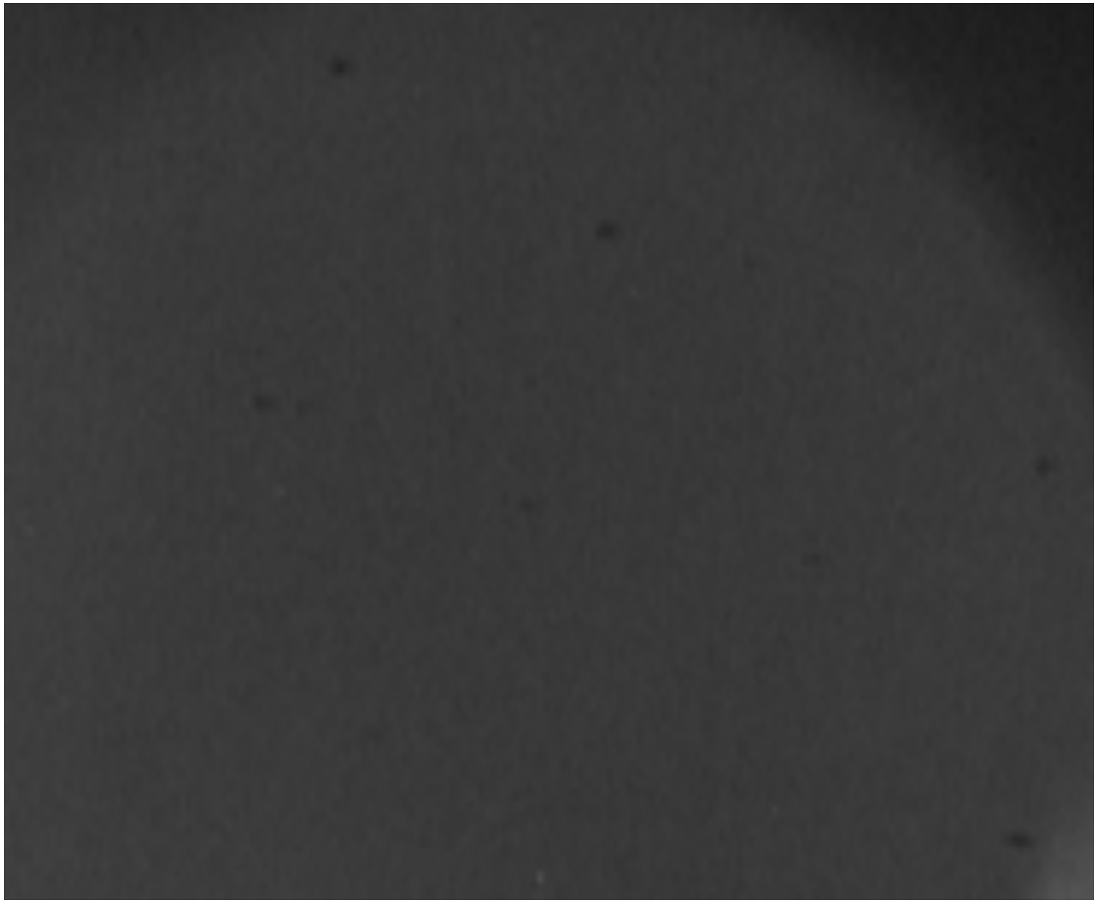

a.)
Water
$p_{crit.}$ (MPa)
$r_{particle}$ (nm)
b.)
Water
$P^{abs.}_{crit.}$ (µW)
$r_{particle}$ (nm)


a)
τ_n (µs)
Amplitude (mV)
Time (ms)
n
b)
counts
τ_{n+1} (µs)
τ_n (µs)
τ (µs)

Fluorescence bursts



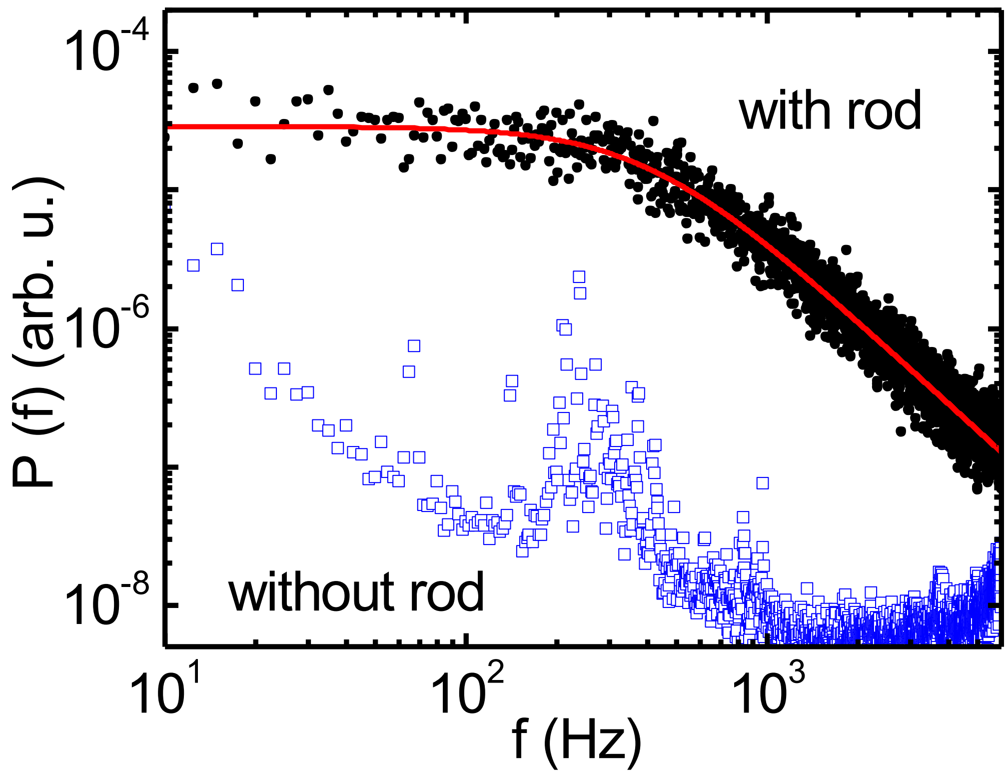
Trapping individual gold nanorods



60 μm

~ real time

Power spectrum of lateral fluctuations



Single 40x20 nm nanorod in the optical trap (P~120 mW)
Cut-off frequency ~ 400 Hz
Trap stiffness ~ 0.01 pn/nm/W

Persistent nanobubble