Near-field optical imaging of single-walled carbon nanotubes

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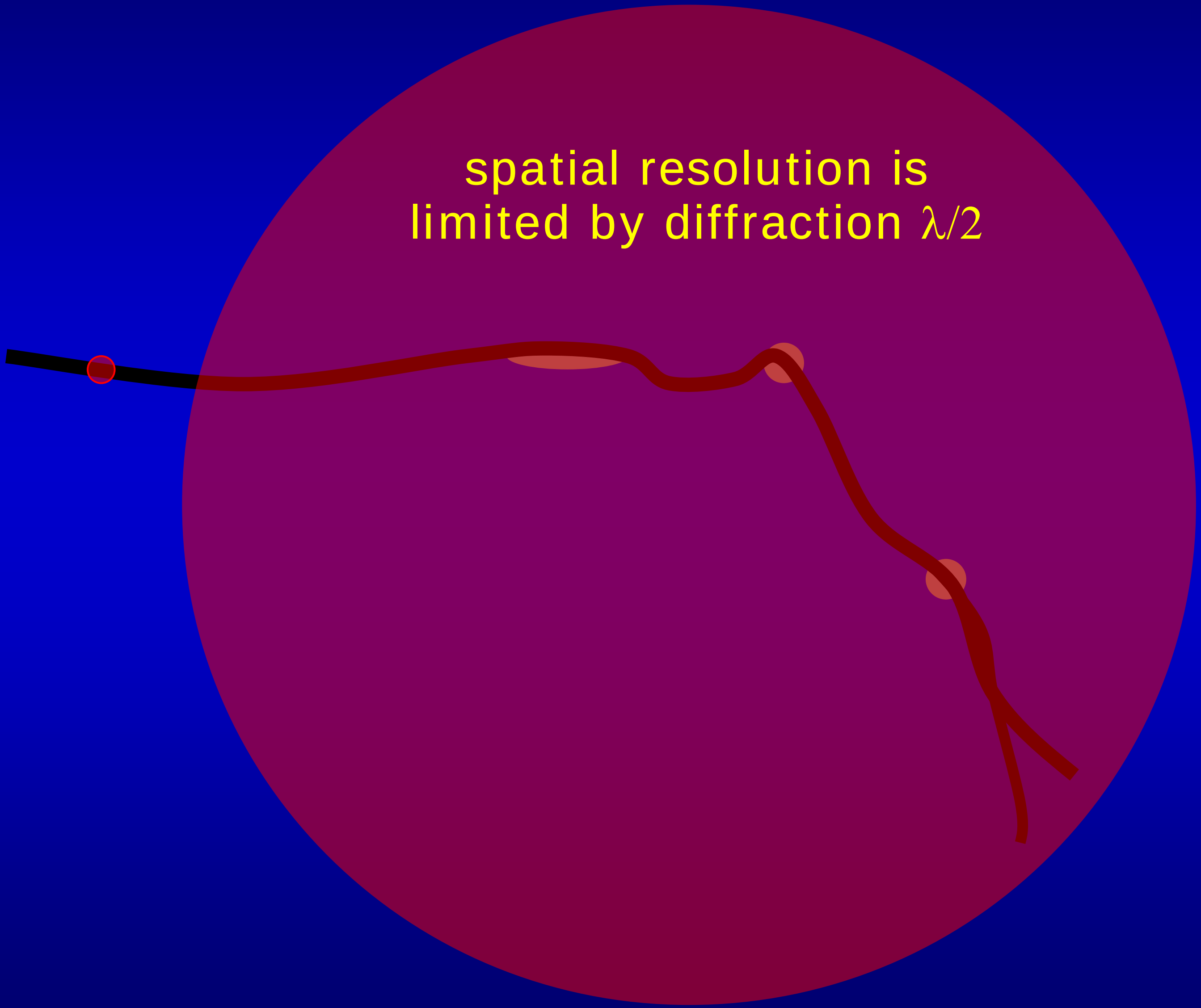
Why High Spatial Resolution Near-field Optics?

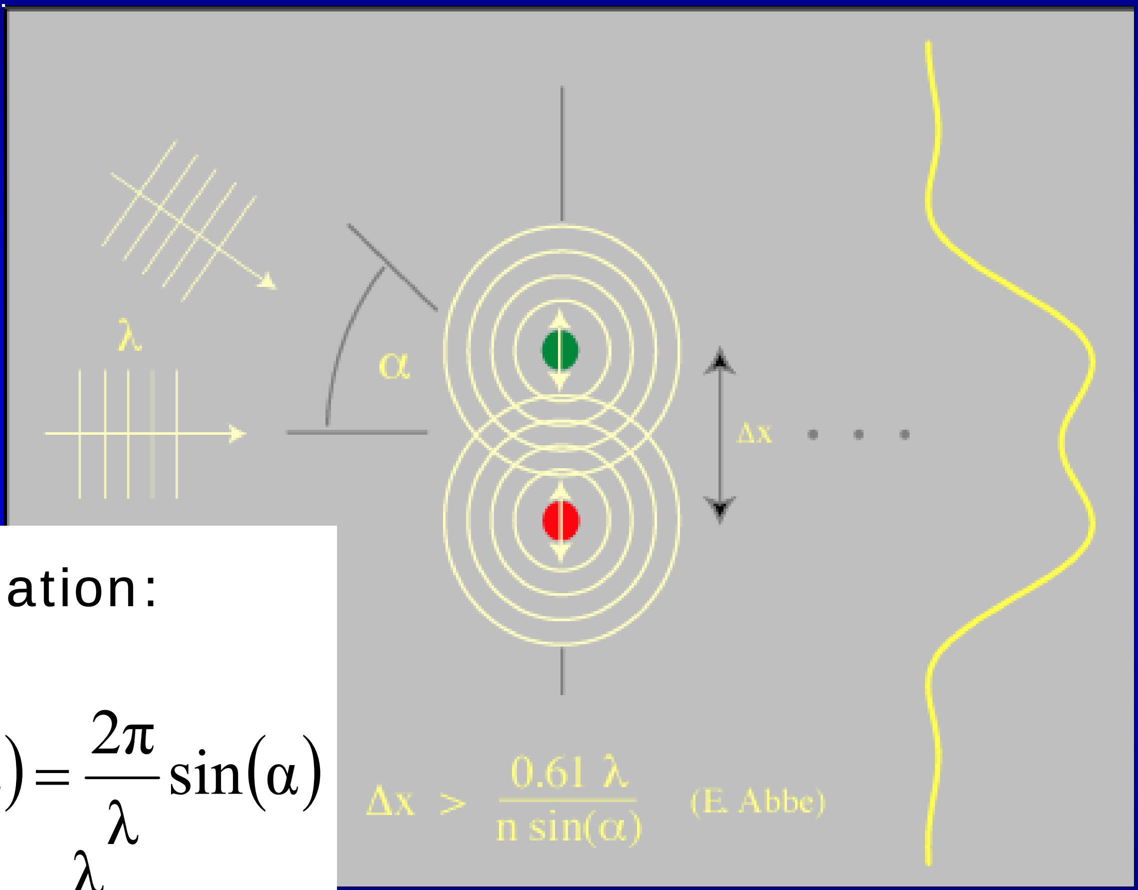
Why Near-field Optics?

Why Near-field Optics?



☹ Diffraction Limit

Abbé, Arch. Mikrosk. Anat. 9, 413 (1873)



Uncertainty relation:

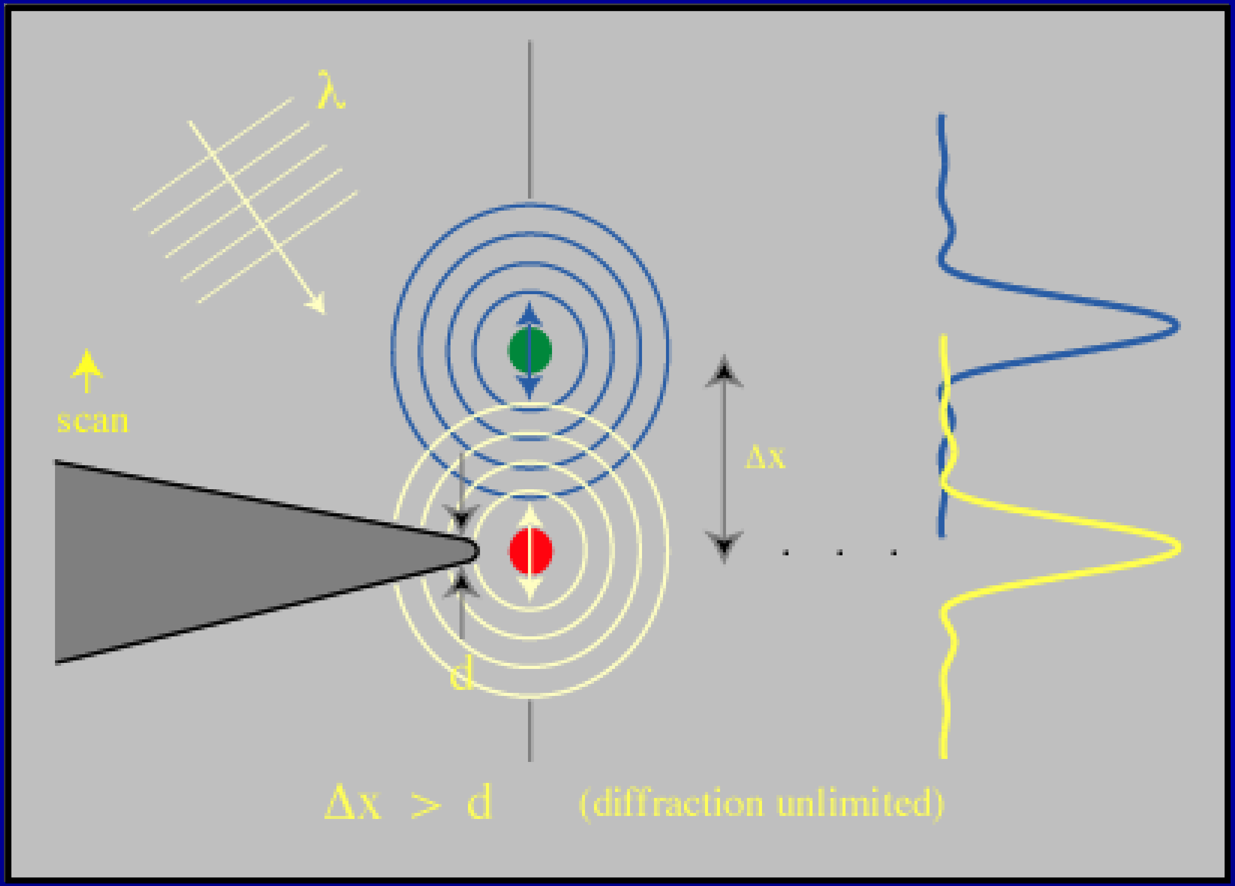
$$\Delta x \cdot \Delta k_x \geq 2\pi$$

$$\Delta k_x = |k| \cdot \sin(\alpha) = \frac{2\pi}{\lambda} \sin(\alpha)$$

$$\Delta x \geq {}^{2\pi}\!/_{\Delta k_x} = \frac{\lambda}{\sin(\alpha)}$$

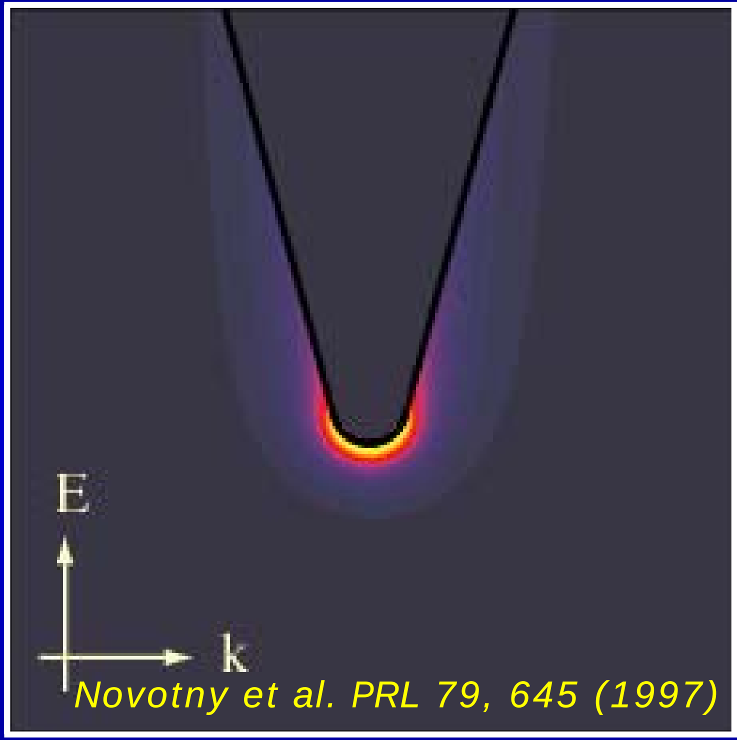
Tip-Enhanced Spectroscopy

Wessel, JOSA B 2, 1538 (1985)



Tip-Enhanced Spectroscopy

laser illuminated metal tip



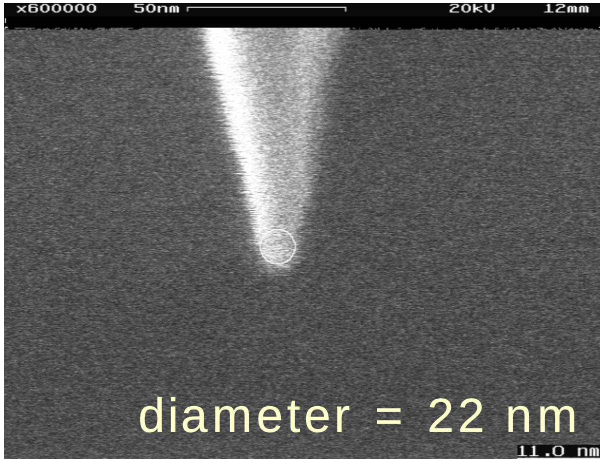
Novotny et al. PRL 79, 645 (1997)

Theory: (Giant) enhanced electric field confined to tip apex

Mechanism: Lightning rod and antenna effect, plasmon resonances

Tip-Enhanced Spectroscopy

SEM micrograph

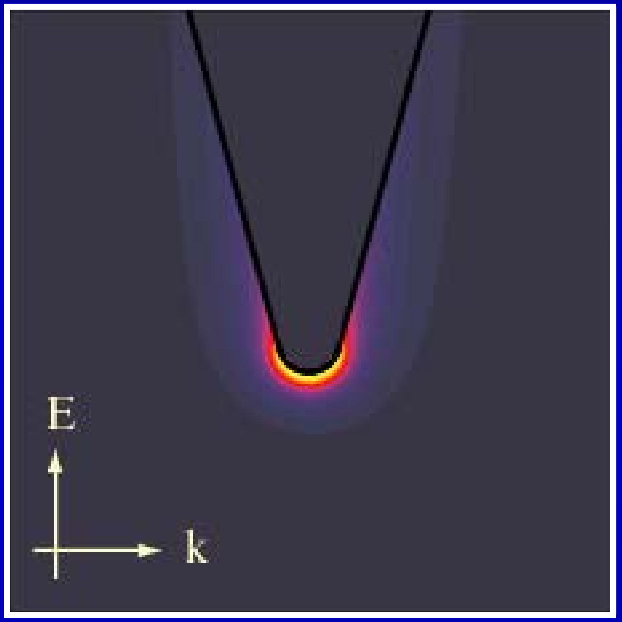


enhanced electric field confined within 20 nm ?

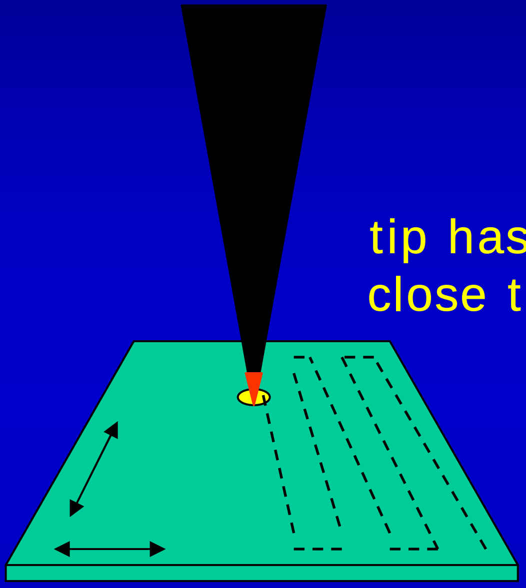
→ ………………Optical imaging with 20 nm resolution?!

→ ………………Signal enhancement !?

Tip-Enhanced Spectroscopy



enhanced electric field close to the very end of the tip

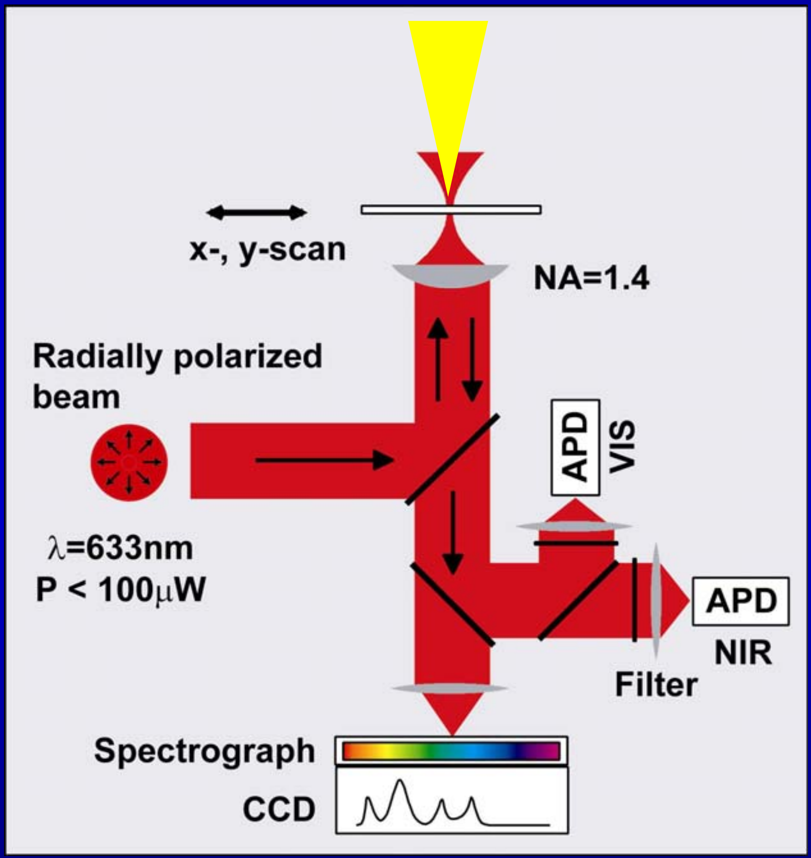


tip has to be very close to the sample

raster-scanning the sample and point-wise detection of the sample response

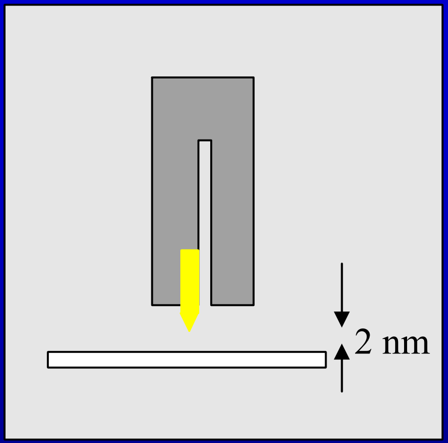
Experimental Setup

Confocal microscope + Tip-sample distance control



a sharp metal tip is held at constant height (~2nm) above the sample using a tuning-fork feedback mechanism

K. Karrai et al., APL 66, 1842 (1995)

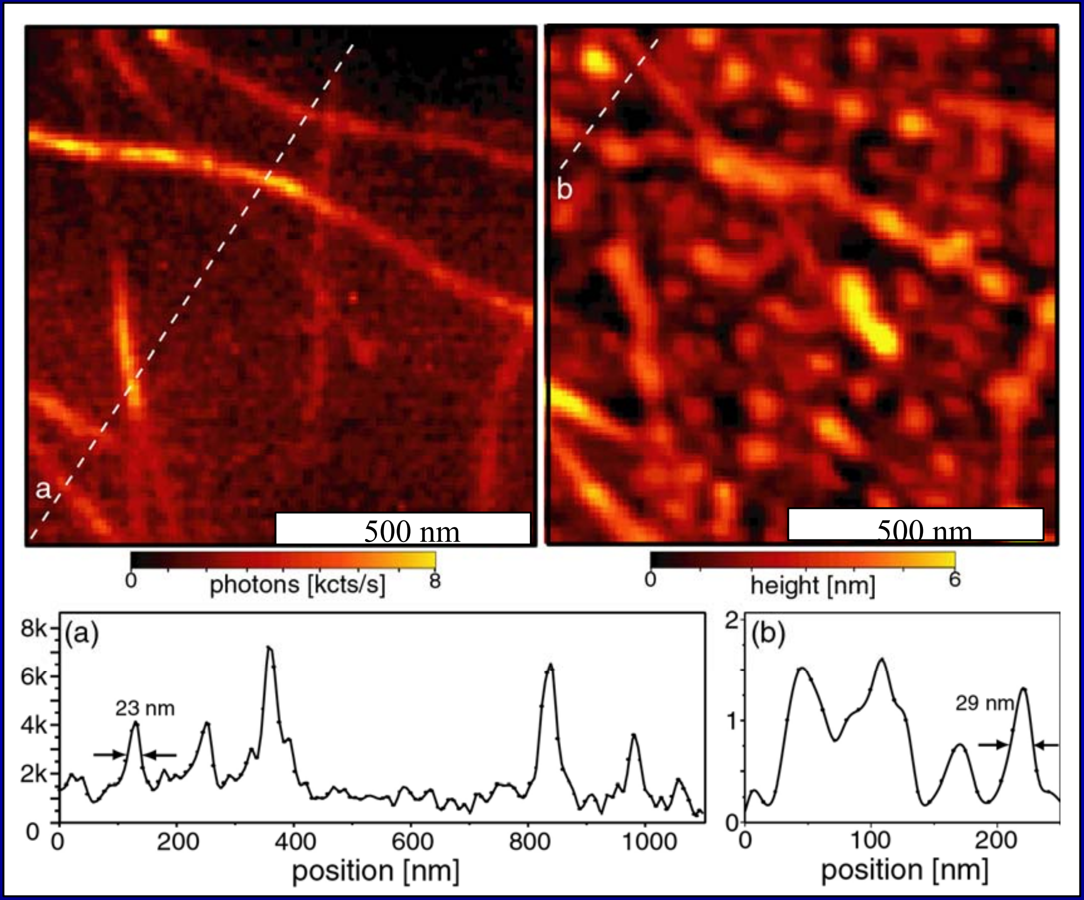


Optical Images and Spectra

Topography of the sample

Near-field Raman Imaging of SWCNTs

Raman image
(G' band)



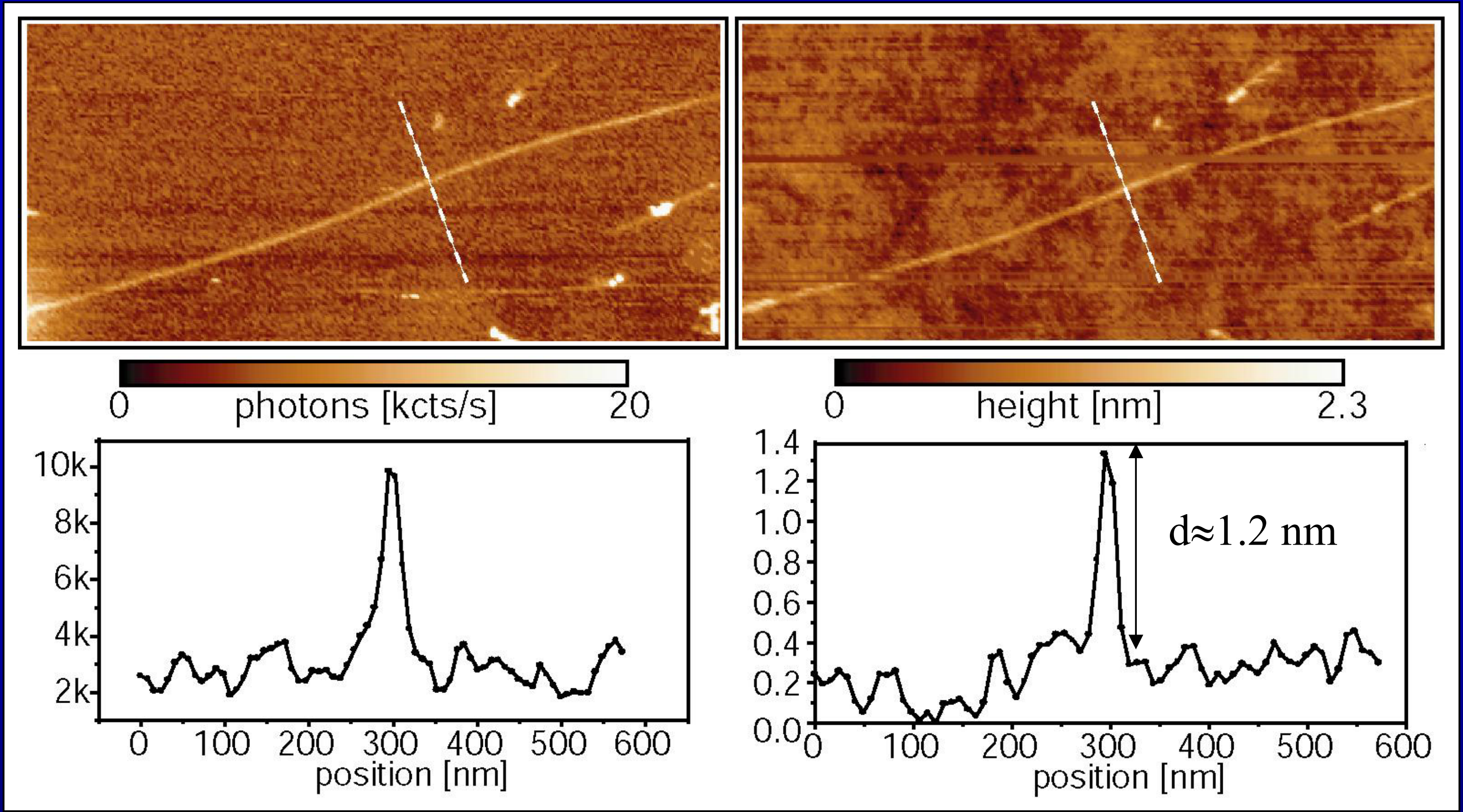
Topography

Hartschuh et al.
PRL 90, 95503 (2003)

only SWCNT detected in optical image ⟶ chemically specific
optical contrast with 25 nm resolution ⟶ enhanced field confined to tip

Near-field Raman Imaging of a SWCNT

Raman image (G band) 2 x 1 μm^2 Topography

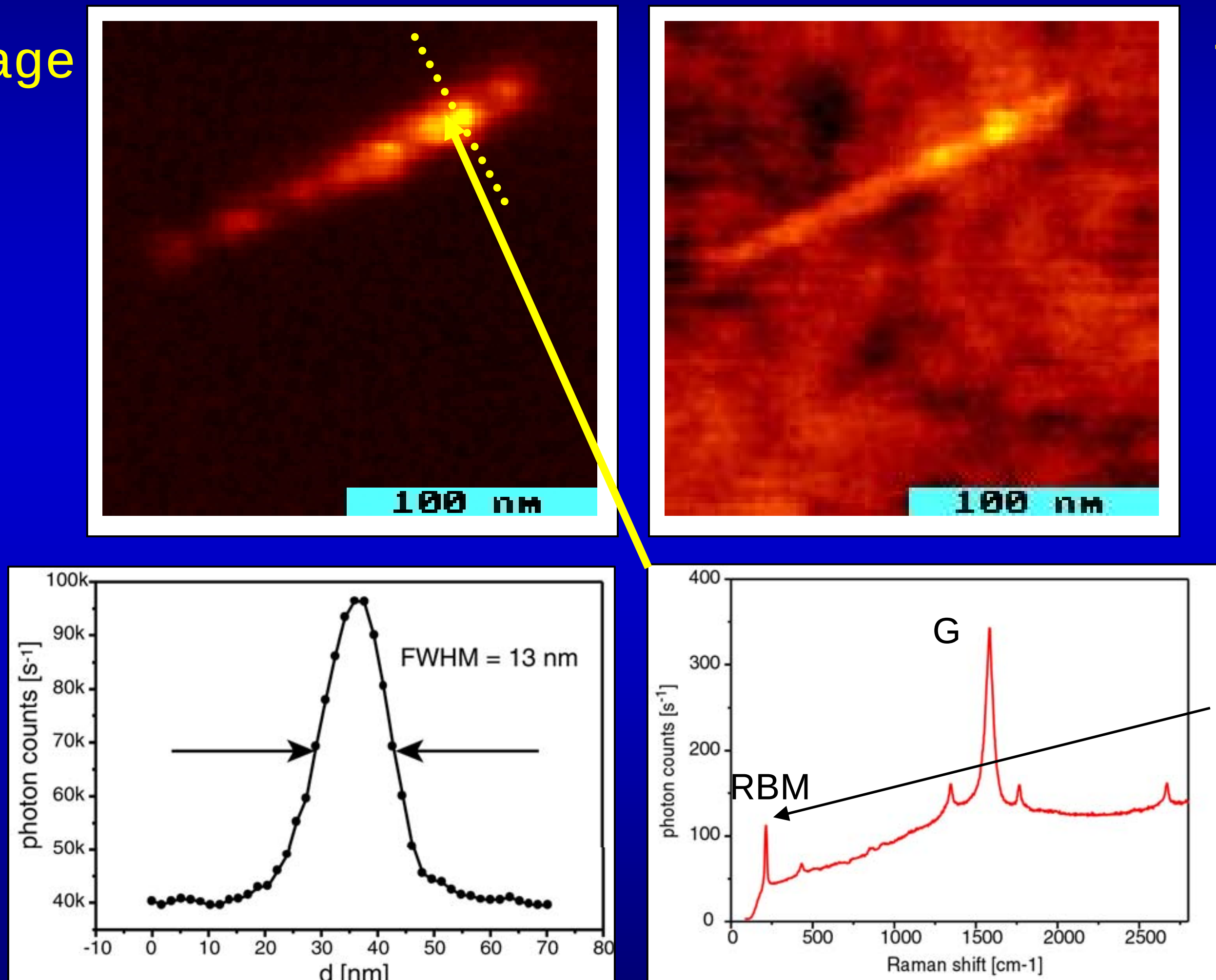


Near-field Raman Spectroscopy

Raman image (G band)

Topography image

height: 0 - 1.9 nm



RBM at 199 cm^{-1}
diam = 1.2 nm
structure
(n,m)≈(14,2)

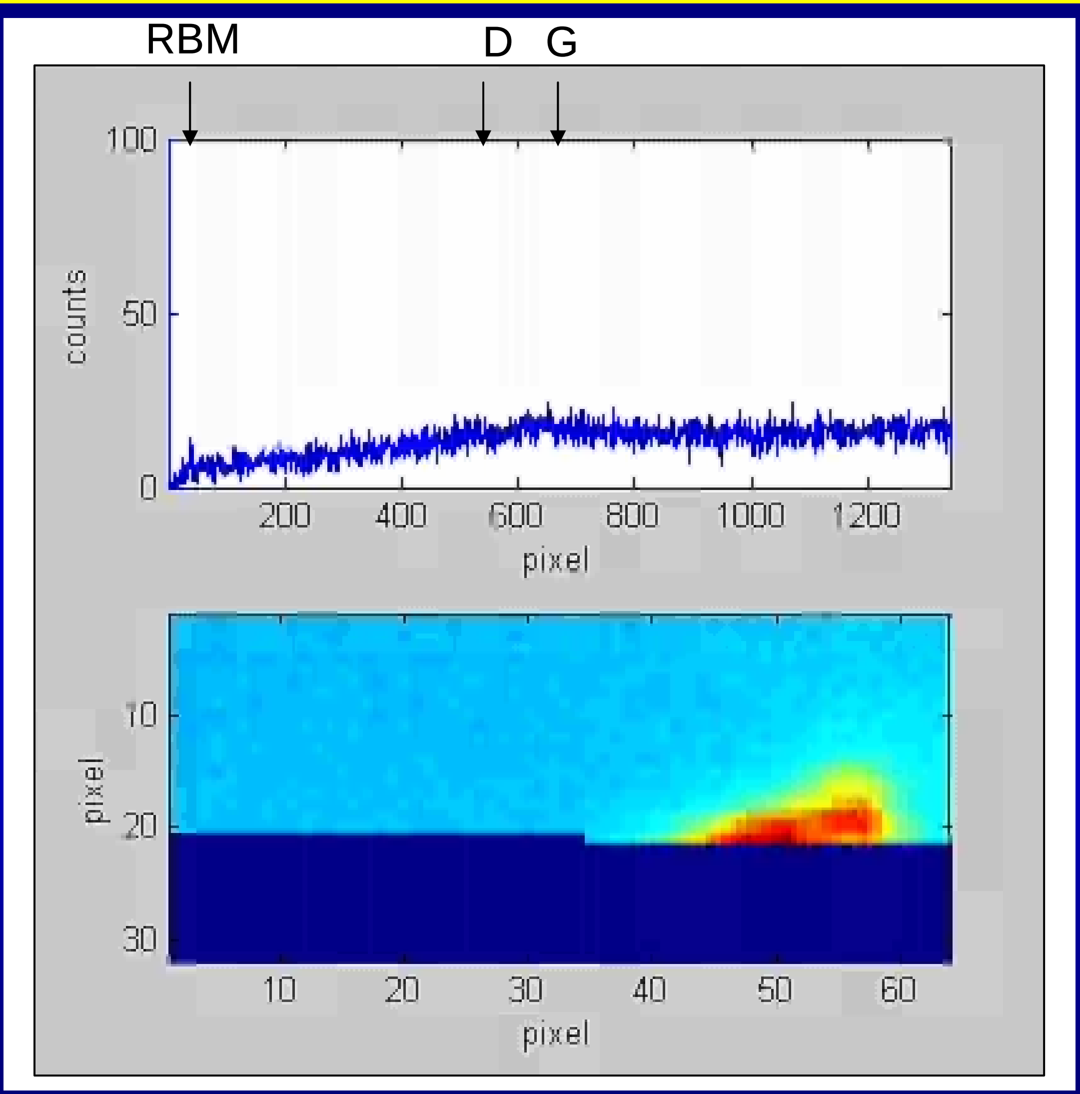
metallic SWCNT

Hartschuh et al. Int. J. Nanosc. 3, 371 (2004) *Anderson et al. JACS 127, 2533 (2005)*

Experiment

Exp. parameters:

~3 nm steps between spectra
exposure time per spectrum = 100 ms

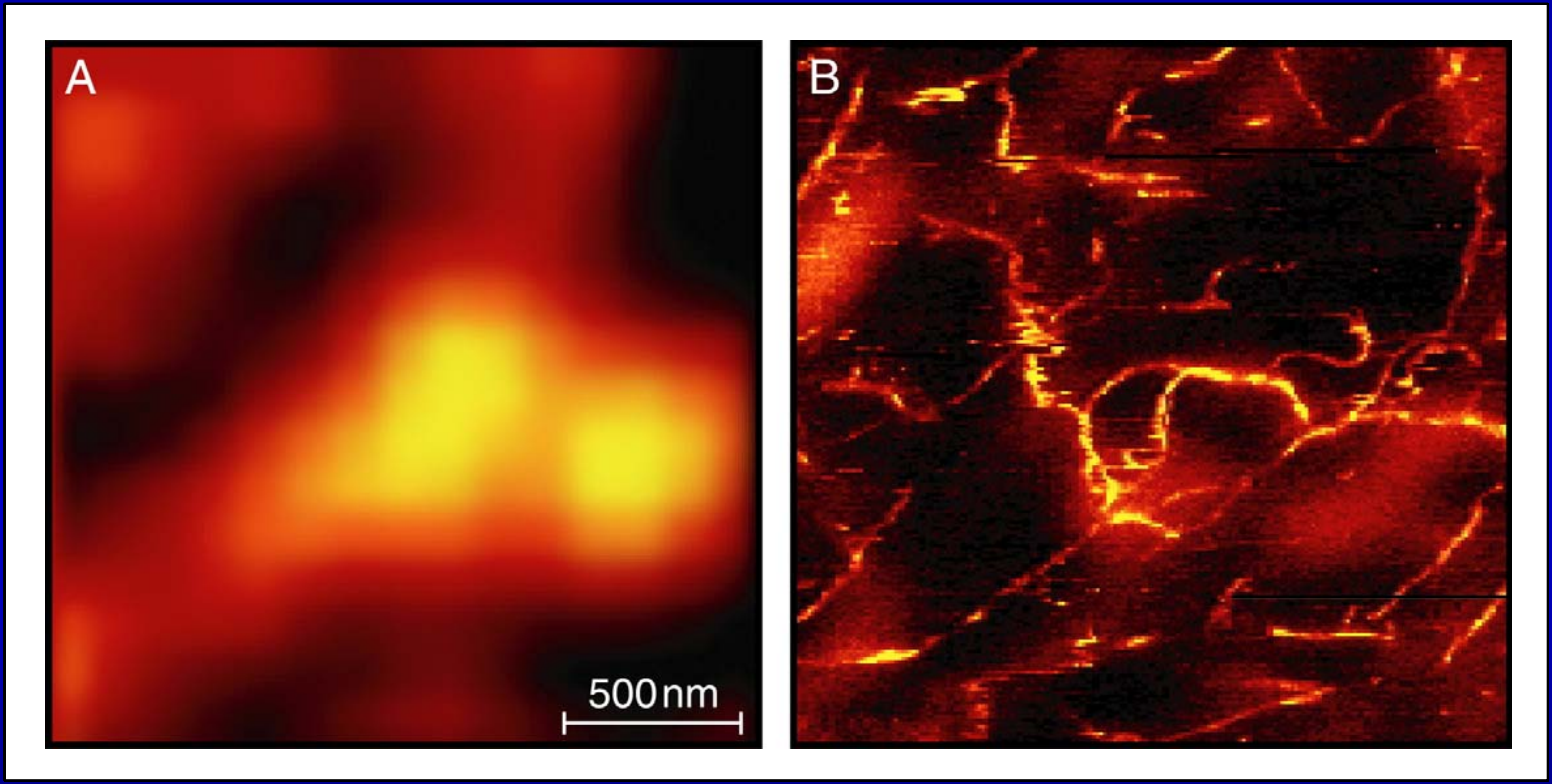


intensity of the RBM

100 nm

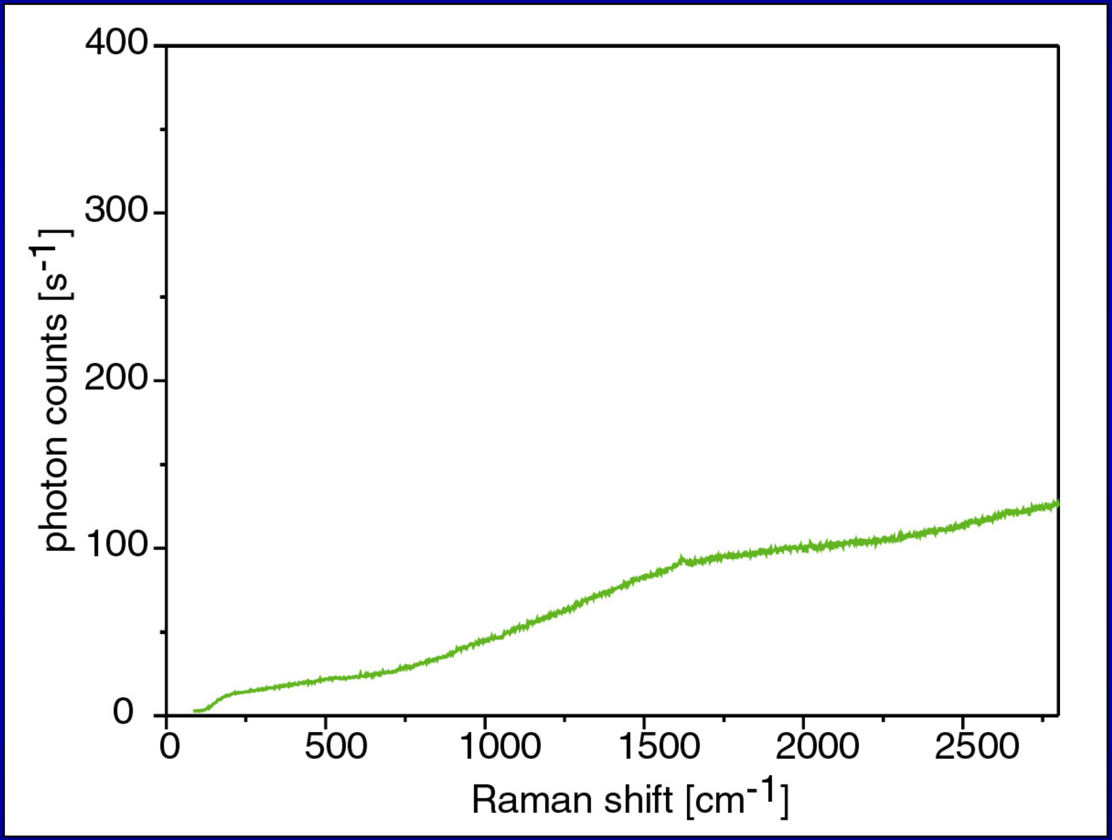
Resolution enhancement

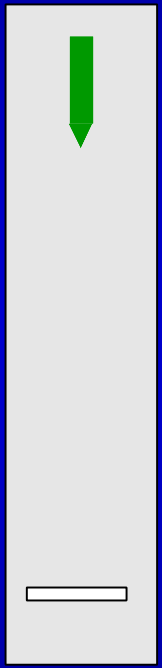
Farfield Near-field



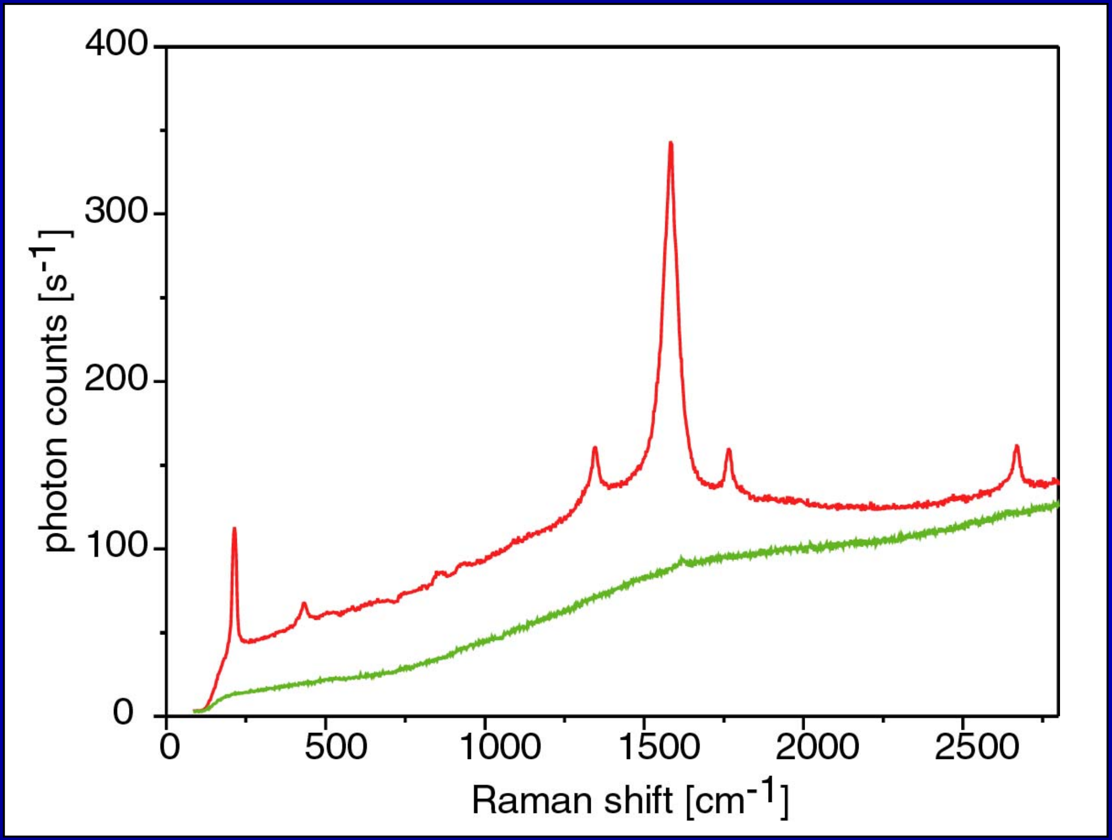
no tip same area with tip

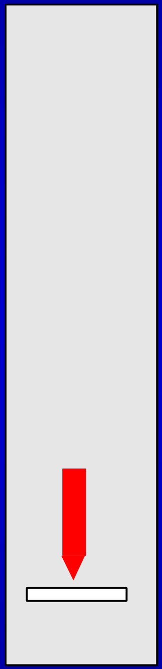
Signal Enhancement





Signal Enhancement



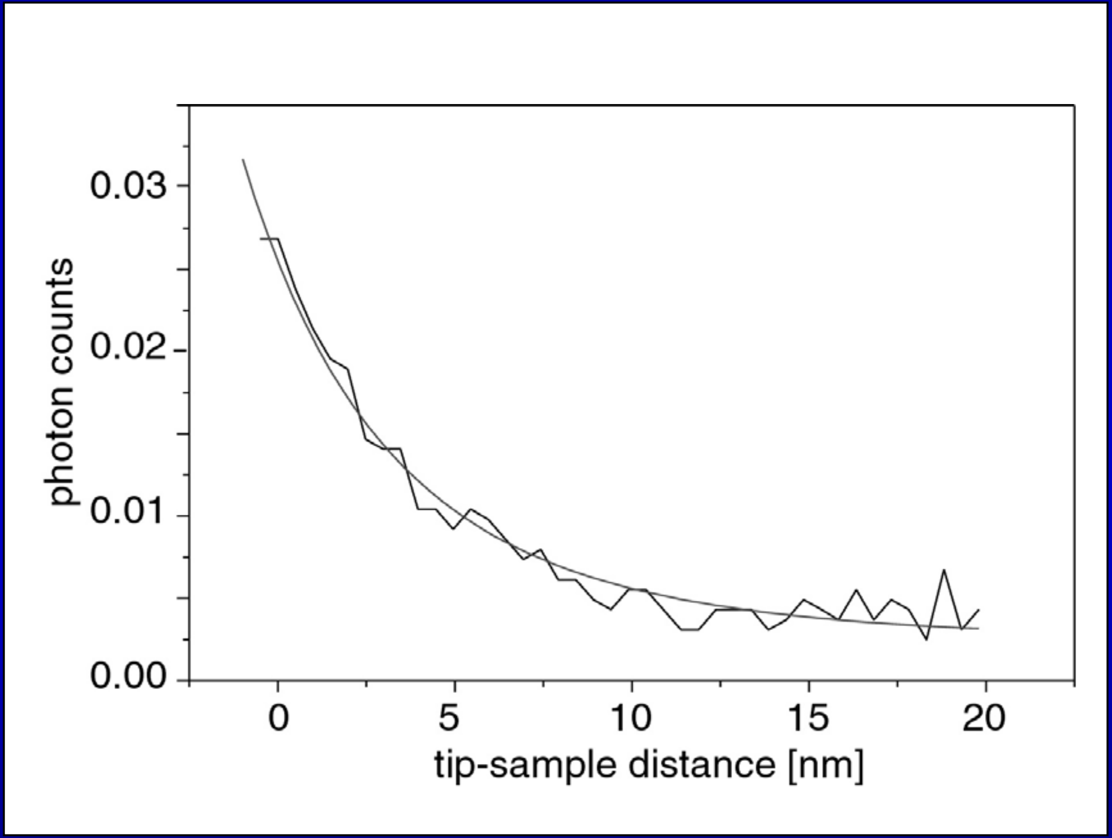


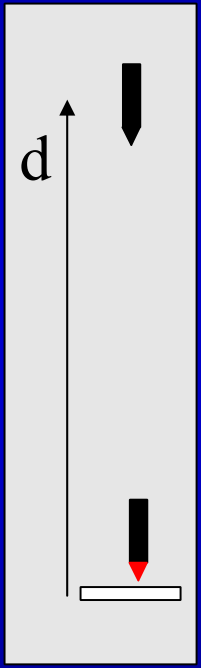
tip-enhanced signal > signal * 2500

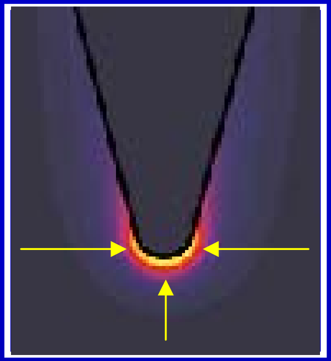
Hartschuh et al. Phil. Trans. R. Soc. Lond A, 362 (2004)

Distance Dependence

Enhanced Raman scattering signal

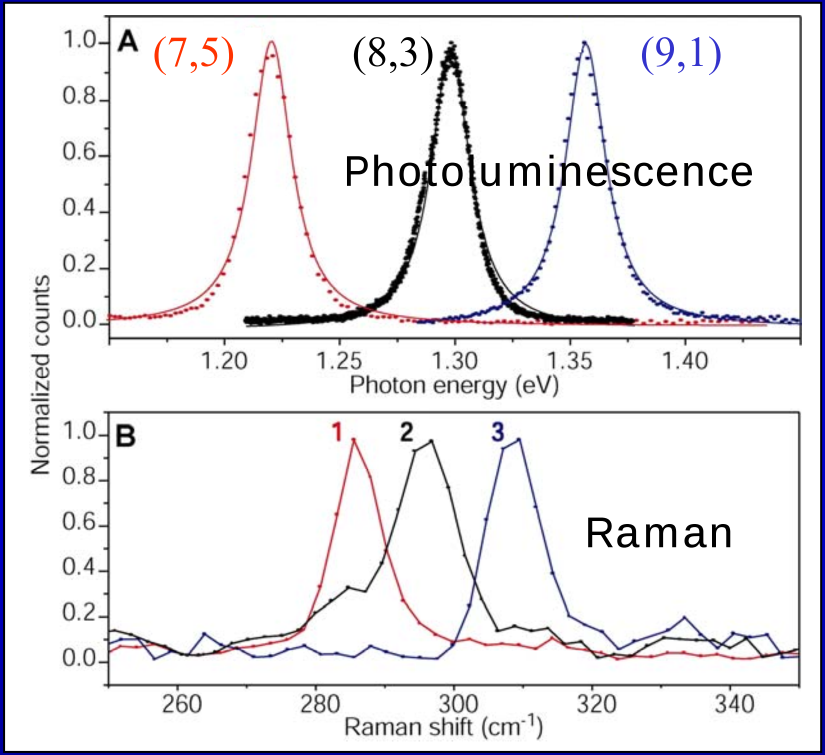


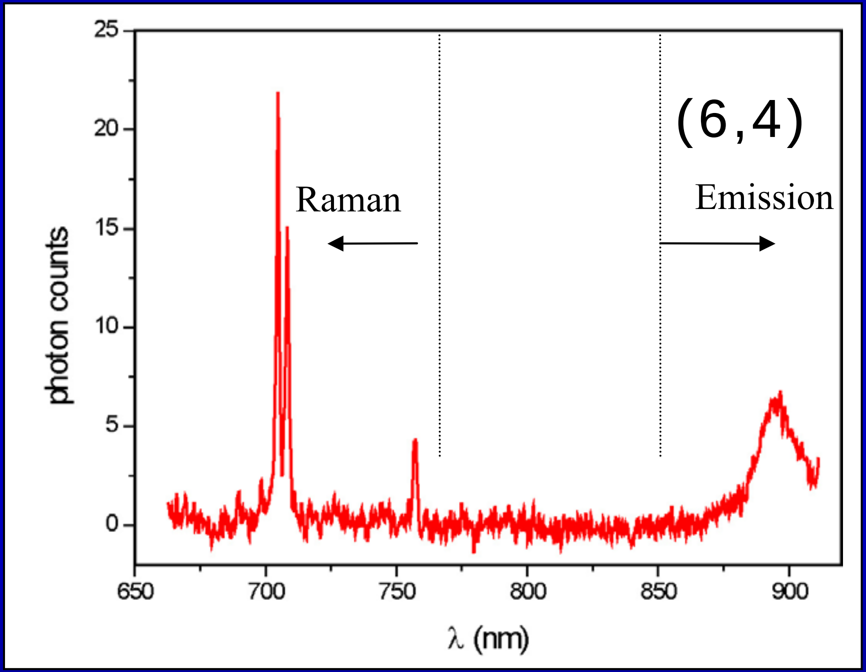




tip-enhancement is near-field effect => tip has to be close to sample

Simultaneous Raman and PL Spectroscopy

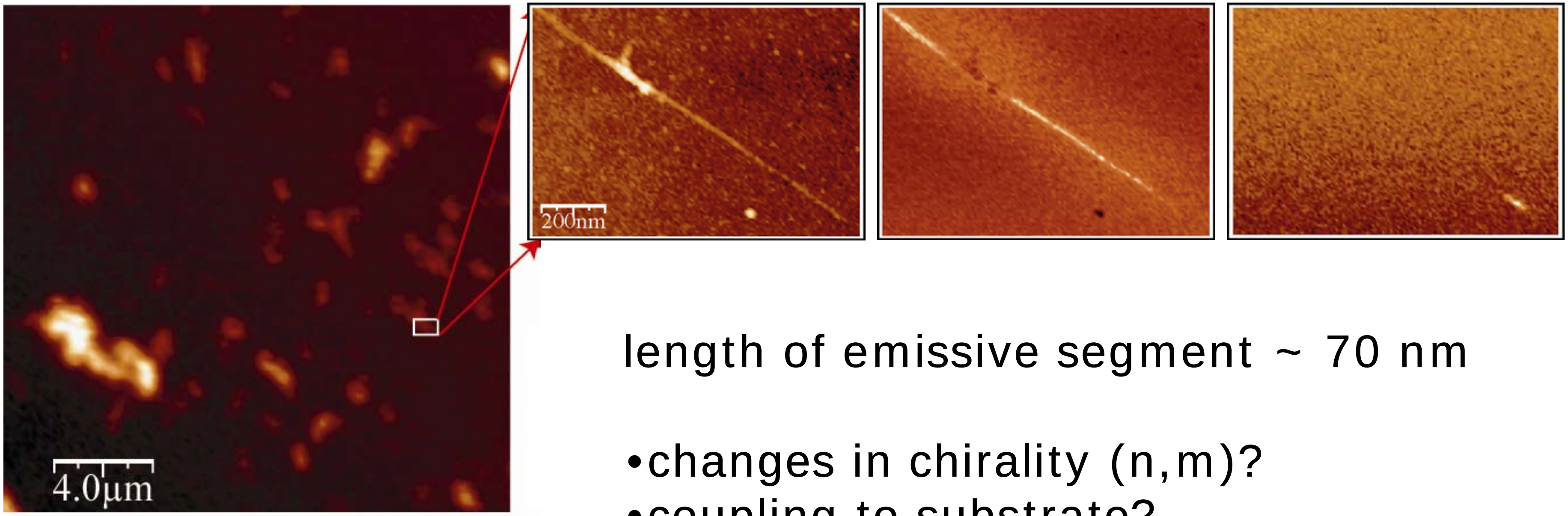




Excitation at 633 nm ⇒ Emission and Raman signals are spectrally isolated

Near-field optical imaging of SWCNTs

Farfield Photoluminescence | Topography | Raman (G-band) | Photoluminescence

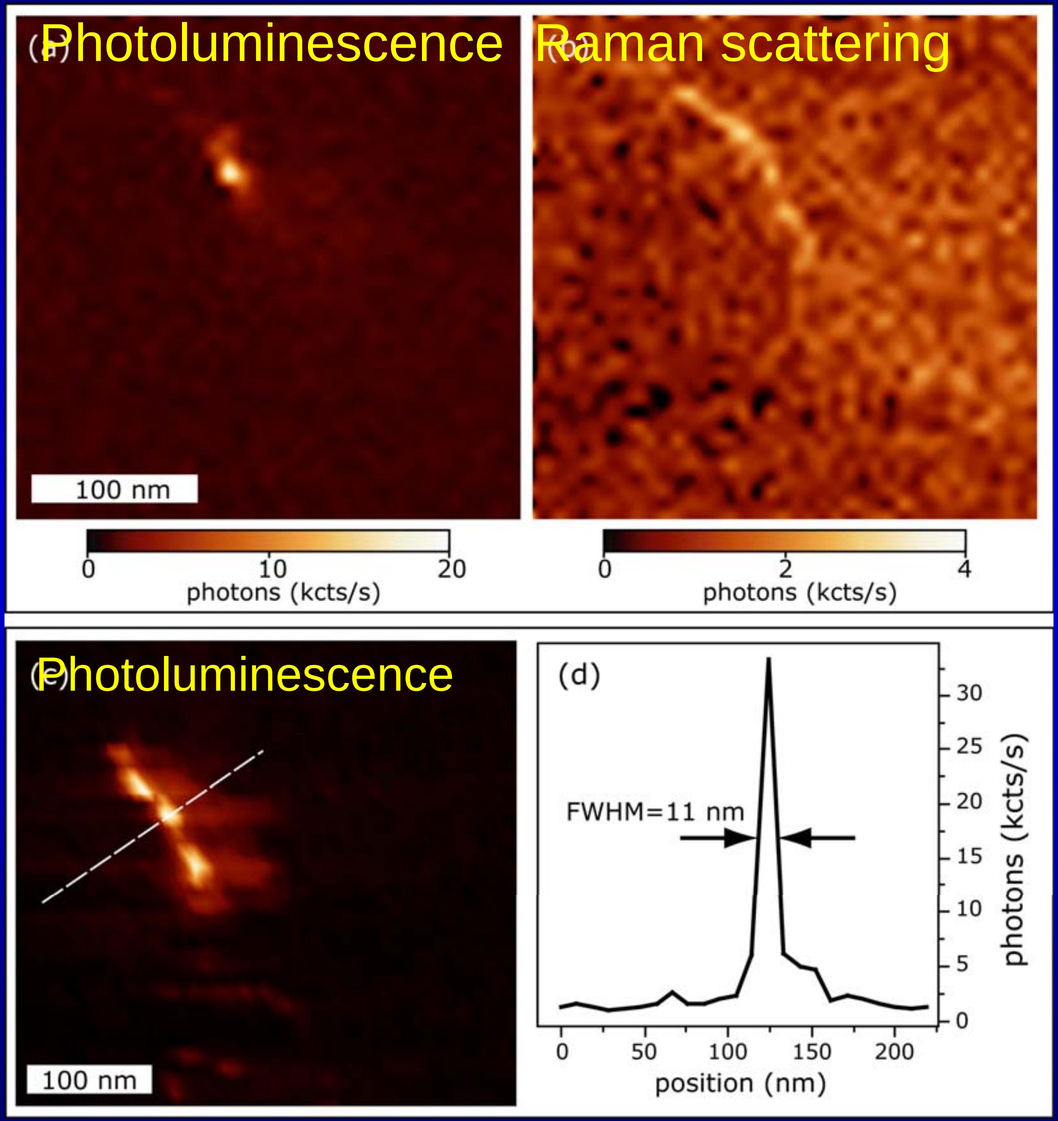


DNA-wrapped SWCNTs on mica

length of emissive segment ~ 70 nm

- changes in chirality (n,m)?
- coupling to substrate?

Localized PL-Emisssion on Glass



SWCNTs on glass

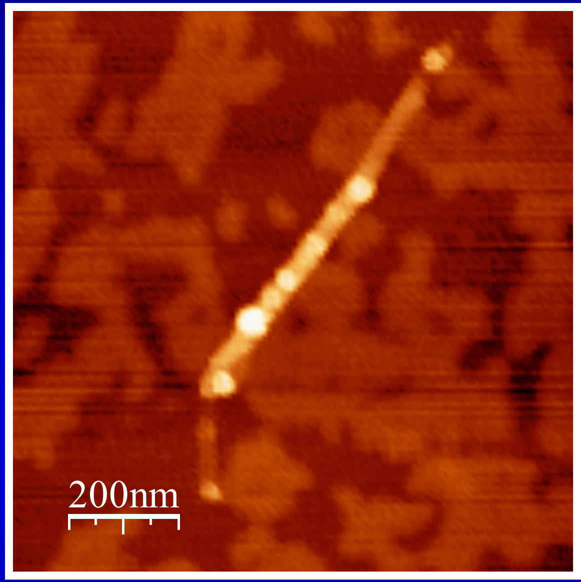
Emission spatially confined to within 10 – 20 nm

$\Rightarrow$ Localited excited states
Bound excitons?

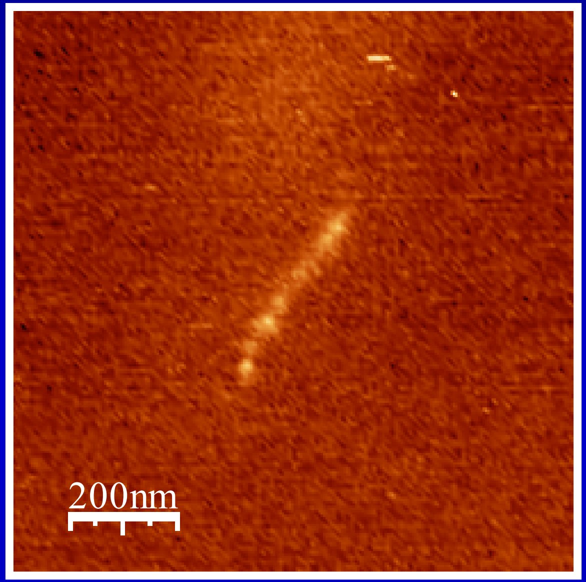
- role of defects?
- substrate?

Near-field optical imaging of SWCNTs

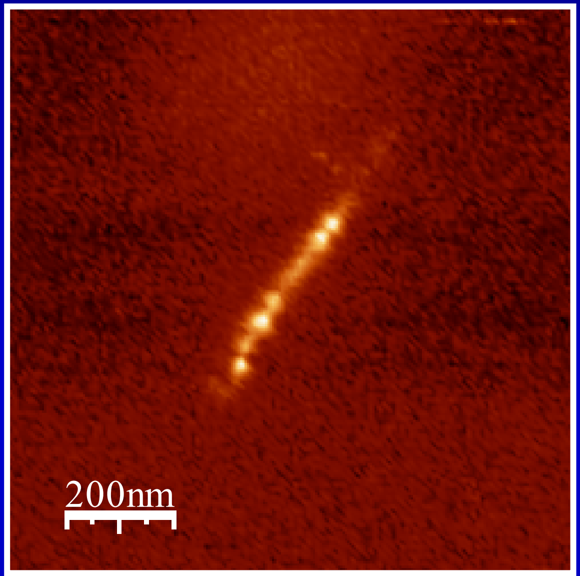
Topography



Raman (G-band)



Photoluminescence

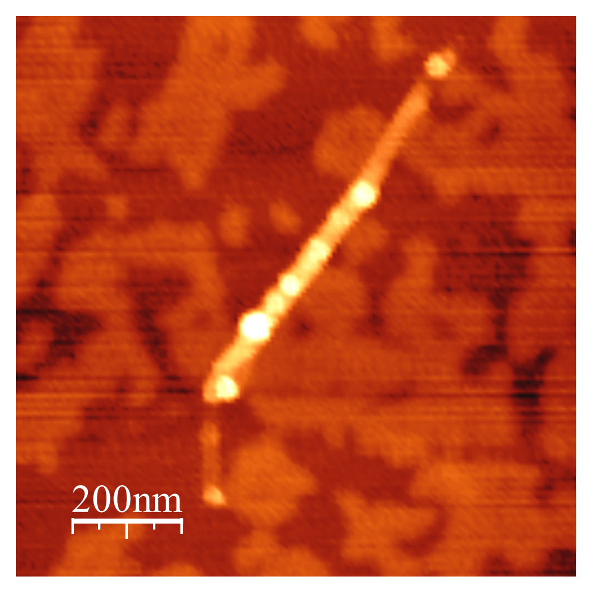


SWCNTs in SDS on mica

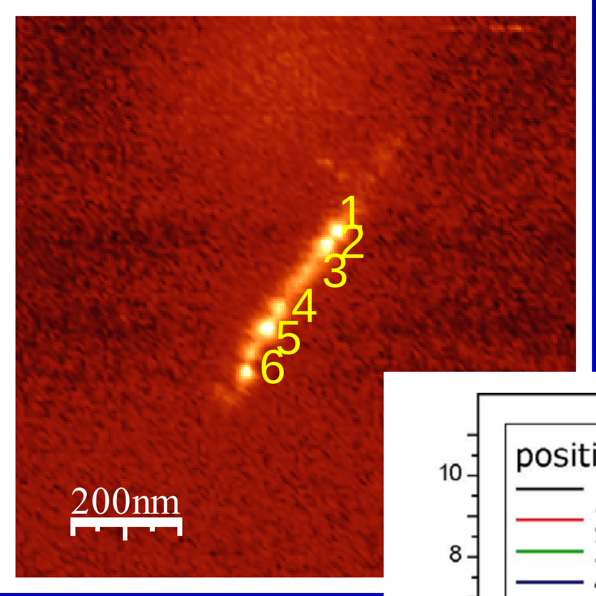
Simultaneous near-field Raman and PL imaging
⇒ PL extended along nanotube

Near-field PL-Spectroscopy

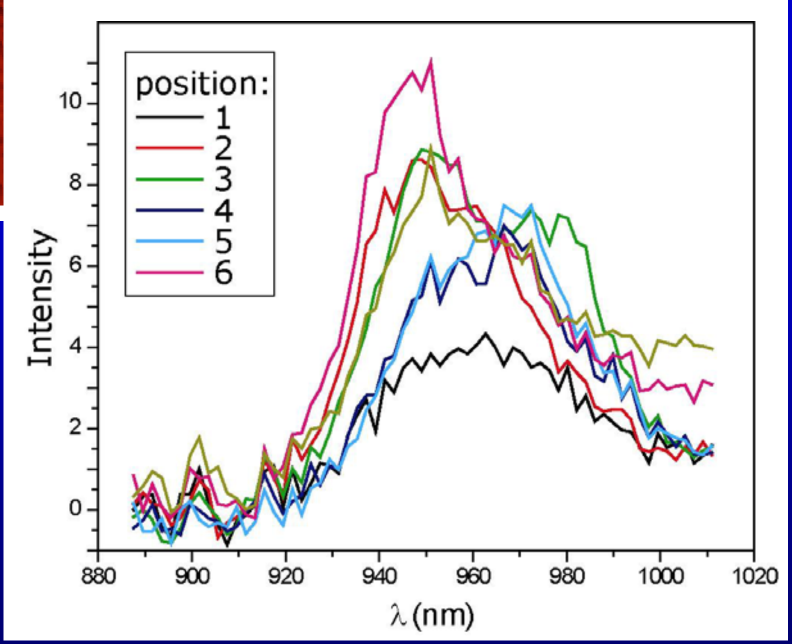
Topography



Photoluminescence



PL spectra:
30 nm steps
between spectra



⇒ Emission energy can vary on the nanoscale

A. Hartschuh et al. Nano Lett. 5, 2310 (2005)

Near-field PL-Spectroscopy

Origin of emission energy variations:

- Huge exciton binding energies E_{bind} = 400-1000 meV

  Capaz et al. cond-mat/0606474

- Electron density is confined to plane of rolled sheet.

$\Rightarrow$ Dielectric screening determined by environment.

$$E_b \propto \frac{1}{\varepsilon^{\alpha}}$$

Perebeinos et al. PRL 92, 257402 (2004)

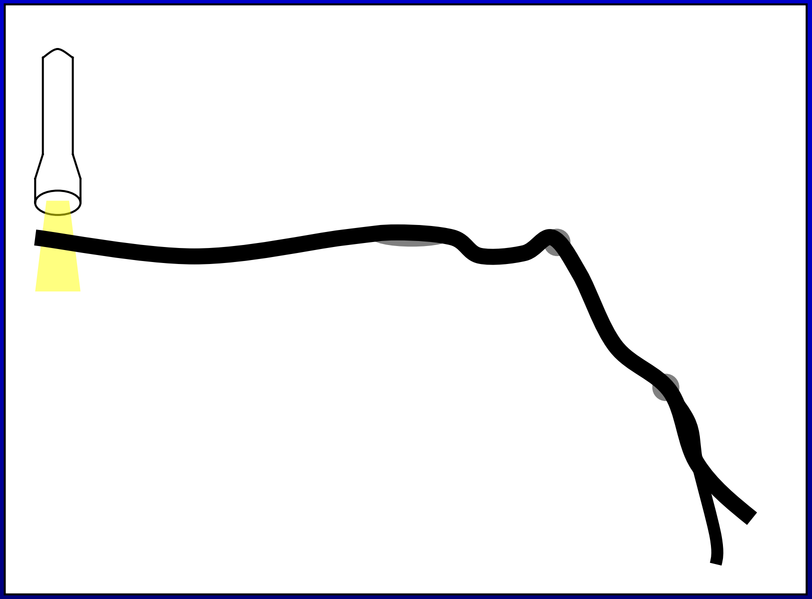
$\Rightarrow$ Emission energy sensitive to dielectric environment

$\Rightarrow$ Changes in local dielectric environment expected to modulate emission energy.

Tip-enhanced Microscopy

⇒ Spatial resolution < 15 nm
⇒ Signal amplification

⇒ Tip as nanoscale „light source“



Signal Enhancement

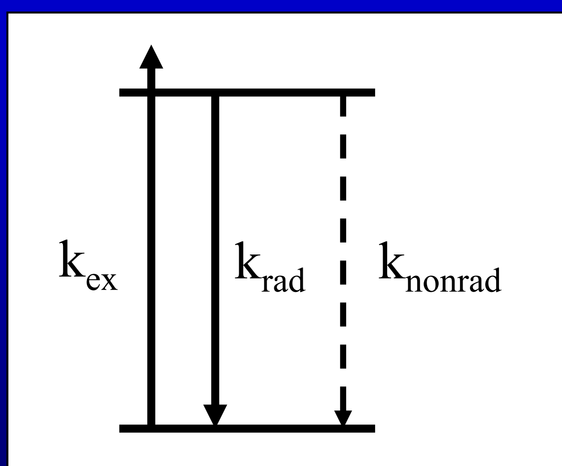
Raman scattering

Enhancement of incident field and scattered field

$S_{enhanced} \sim (E_{local} / E_0)^2 \, (E_{local} / E_0)^2 = f^4$

local field at tip

field without tip



Photoluminescene

PL depends on k_{ex}, $k_{radiative}$, $k_{non\text{-}radiative}$

- k_{ex}: enhanced excitation field
  ↗ $S_{enhanced} \sim (E_{local} / E_0)^2 = f^2$
- k_{rad}: Purcell-effect

$$Q = \frac{k_{rad}}{k_{rad} + k_{nonrad}}$$

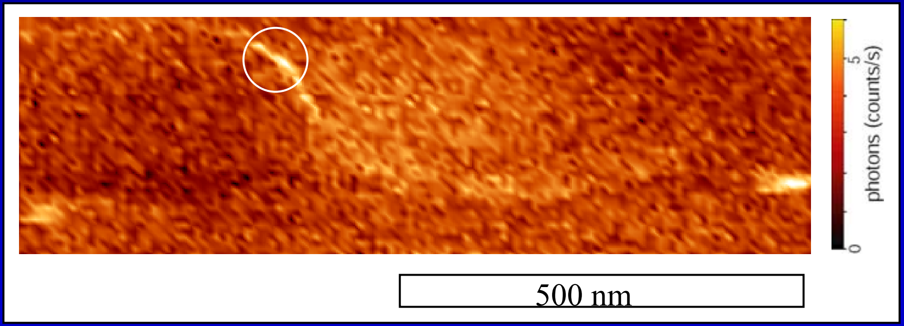
↗ Q is increased ($Q \sim 10^{-3}$)
↗ cycling rate is increased

- k_{nonrad}: energy transfer to metal
  ↘ quenching of PL

PL Enhancement depends on Q!

Signal Enhancement

Raman enhancement



Far-field Raman ~ 2000 counts/s

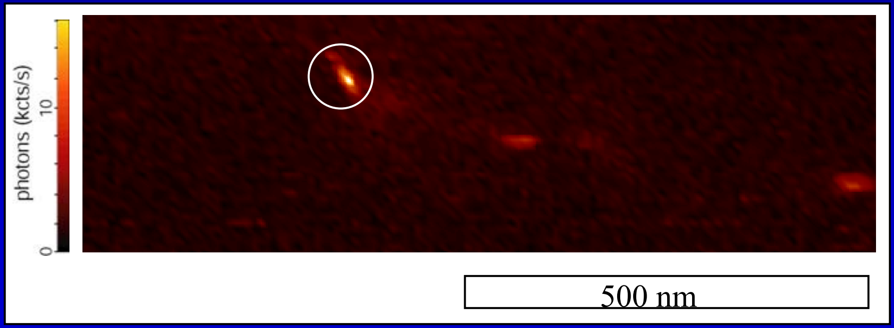
Near-field Raman ~ 4000 counts/s

Raman-enhancement ~ 6000 / 2000

= 3

$S_{enhanced} \sim f^4$

PL enhancement



No far-field PL < 200 counts/s

Near-field PL ~17000 counts/s

PL-enhancement >17000 / 200

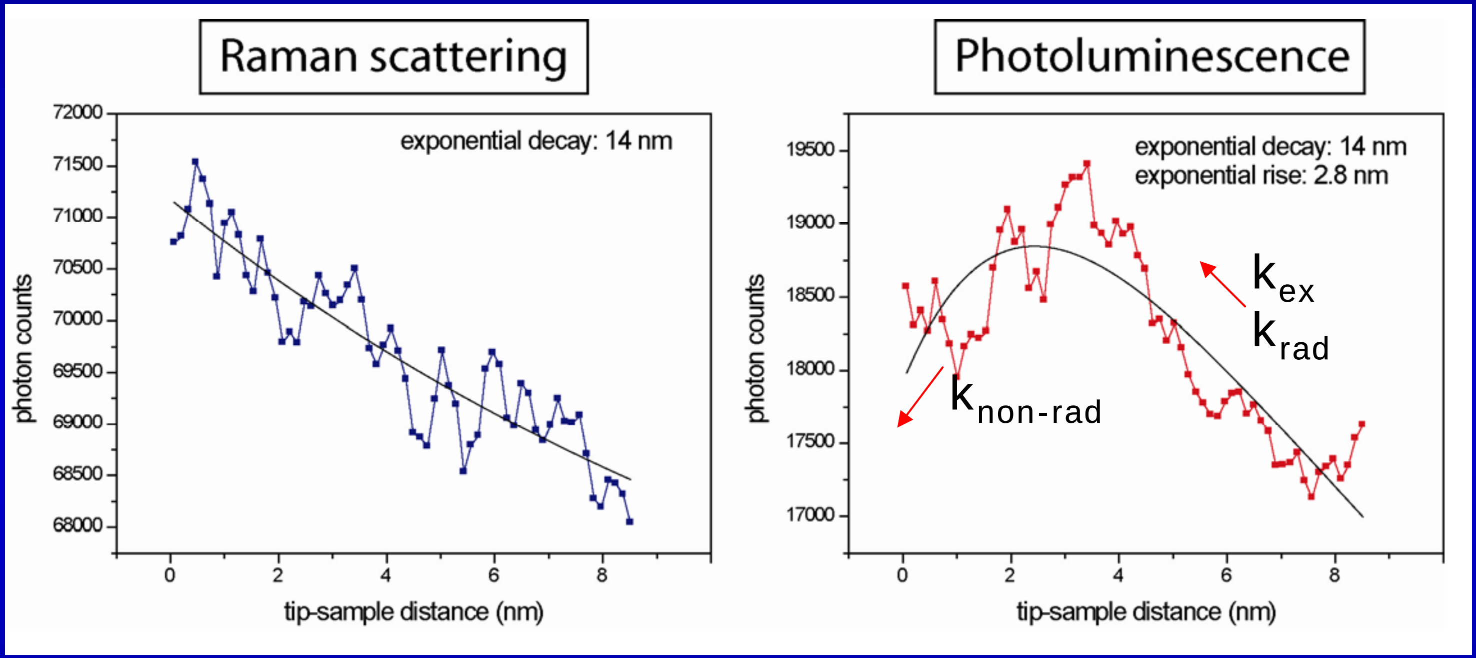
= 85

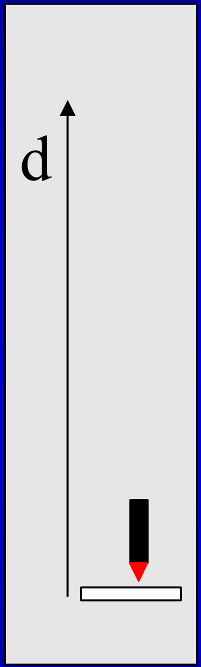
$S_{enhanced} \sim f^2$

$\Rightarrow$ PL quantum yield must be increased by tip (SEF)

Signal Enhancement

(Very first data)





⇒ PL quenching for very small distances
⇒ optimum distance for PL enhancement

Near-field Interactions

Uncertainty relation:

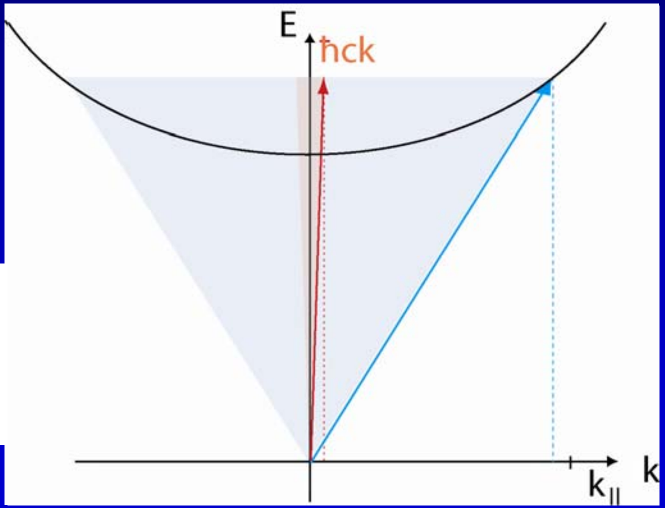
Diffraction limit for propagating waves:

$$\Delta x \cdot \Delta k_x \geq 2\pi$$

$$|k| = 2\pi/\lambda \approx 0.01\,\text{nm}^{-1}$$

Nanotubes:

$$k_{\parallel} = \frac{2d_r}{\sqrt{3}d_t} \approx 1\,\text{nm}^{-1}$$



High resolution provided by evanescent fields that have higher k-vectors:

$$\Delta k_x = 2\pi/\Delta x = 2\pi/5-10\,\text{nm} \approx 1\,\text{nm}^{-1}$$

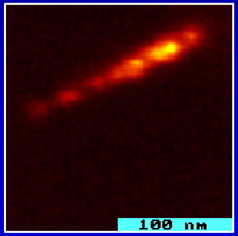
⇒ k-vectors of tip enhanced fields extend through BZ !

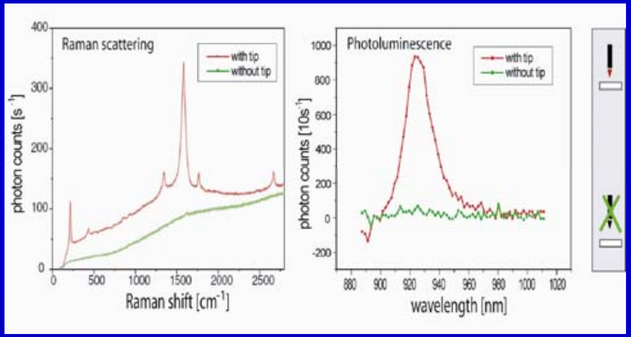
⇒ selection rules for optical transitions?

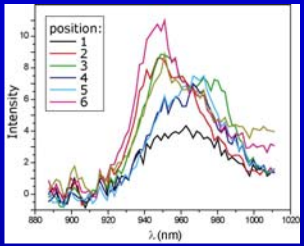
Summary

High-resolution optical microscopy of carbon nanotubes using a sharp laser-illuminated metal tip

- PL and Raman spectroscoy and imaging
- Spatial resolution < 15 nm
- Signal enhancement







Results

- Resolved RBM variations (IMJ) on the nanoscale
- Non-uniform emission energies that result from local variations of dielectric environment
- Strongly confined emission signals ⇒ bound excitons?
- PL-Quantum yield can be enhanced

Outlook

Optimize Technique

- Higher spatial resolution < 5 nm?
- Higher enhancement

Nanotubes

- Role of structural defects: Correlation between Raman and PL data
- Role of local dielectric environment…
- Enhancement of PL quantum yield

Near-field interactions

- Mechanisms for signal enhancement?
- Selection rules?

Thank you!