Nanoscale characterization with scattering-type scanning near-field infrared microscopy

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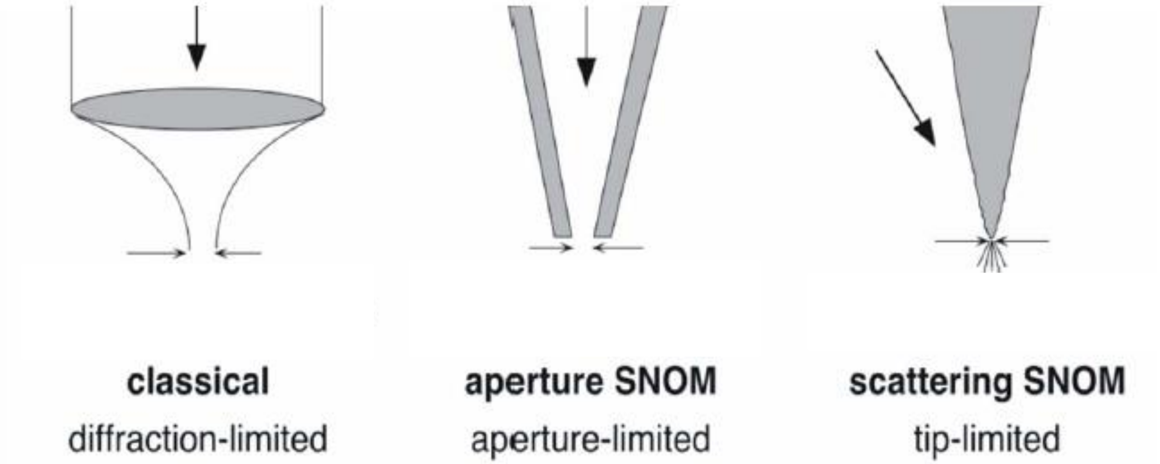
Supervisors: Katalin Kamarás, Áron Pekker

Outline

- Motivation, why do we need near fields?
- Principles of s-SNOM technique
- Measurements on carbon nanotubes and hybrid systems

Spatial resolution in classical microscopy and in near-field techniques



Airy-spot

$$\lambda \approx 10\mu m \rightarrow \Delta x = \frac{0.61\lambda}{n \cdot sin(\theta)} \approx 5\mu m$$

-metal-coated optical fiber

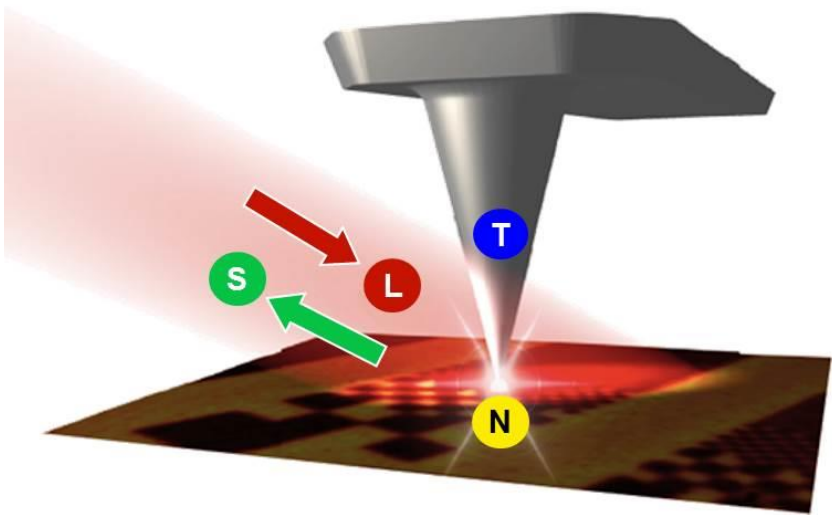
$d < \frac{\lambda}{2}$ - T drops down dramatically

e.g. $\lambda \approx 10\mu m \quad d = 100nm$

Transmission: 10^{-25}

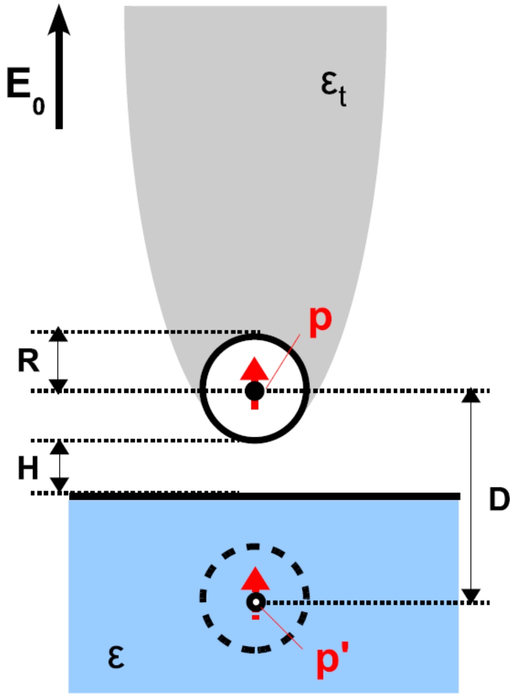
Resolution: $\Delta x > \frac{\lambda}{10} \approx 1 - 2\ \mu m$

s-SNOM principles



- Metal-coated AFM tip
- Evanescent EM field at a apex of the tip
- Very close to the sample
- Near field polarizes the sample
- Interaction results scattered EM waves

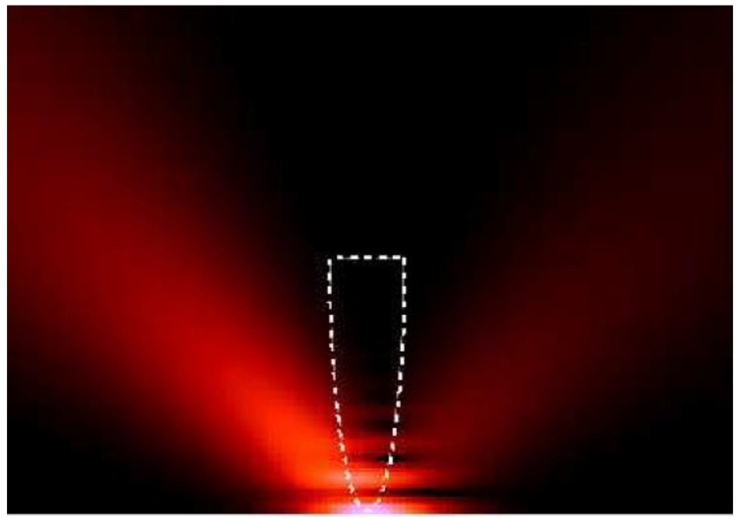
$$E_s = \sigma E_0 \quad \sigma = s \cdot e^{i\varphi}$$



- $\lambda_0 \gg$ characteristic sizes of the tip
- Electrostatic problem at each timestep
- Incoming light is polarized parallel to the tip axis
- $p = \alpha \cdot E_0$- induced dipole moment in the tip
- Mirror dipole in the sample: $p' = \beta p \; \rightarrow \beta = \frac{\epsilon - 1}{\epsilon + 1}$

Only a small part of the detected light originates from the near-field interaction

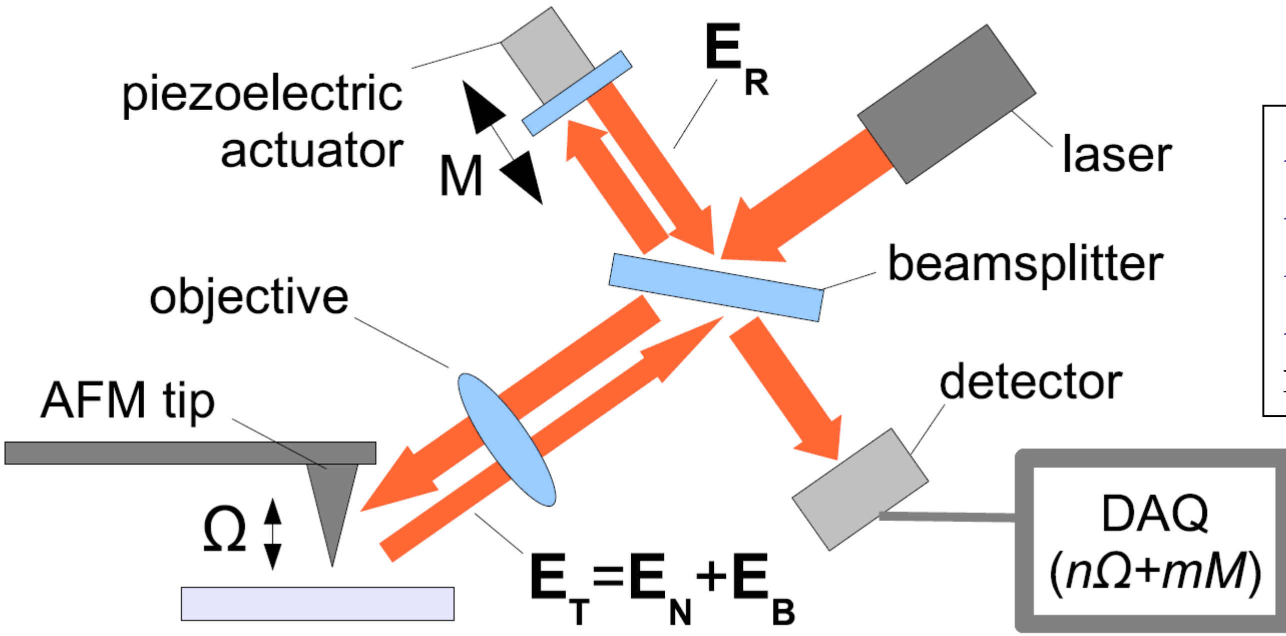
- Airy spot is few microns, near-field volume is few of 10 nm-s
- Background: direct scattering from tip shaft, reflection, scattering from surface roughness
- Incoming + reflected beam → interference → standing waves



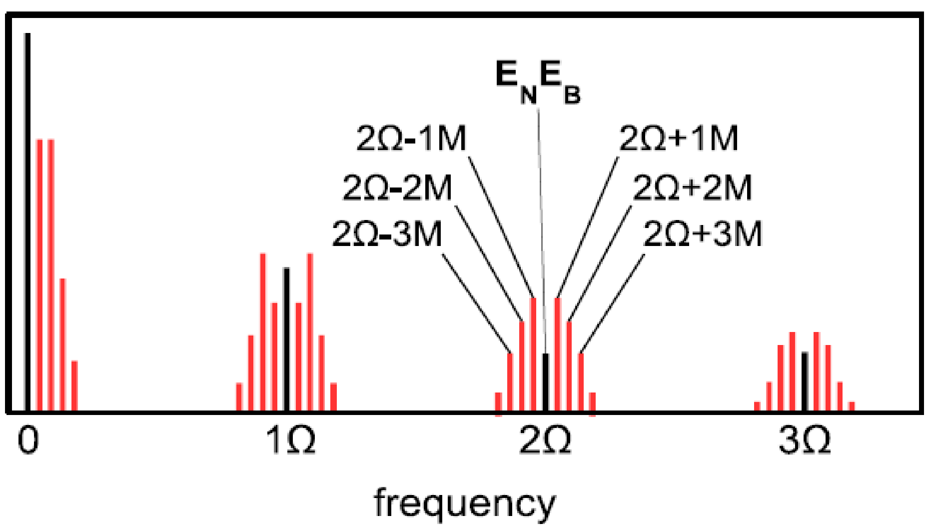
<u>Solution</u>: AFM works in tapping mode at Ω frequency + demodulation @ $n\Omega$

$I = (E_B + E_N)^2 \Rightarrow E_B^2 + E_N^2 + 2E_N E_B$ ← still contains E_B

$A_M \approx 0.21\lambda_0$



E_T – total field
E_N – near-field signal
E_B – background scattering
E_R – phase-modulated reference beam

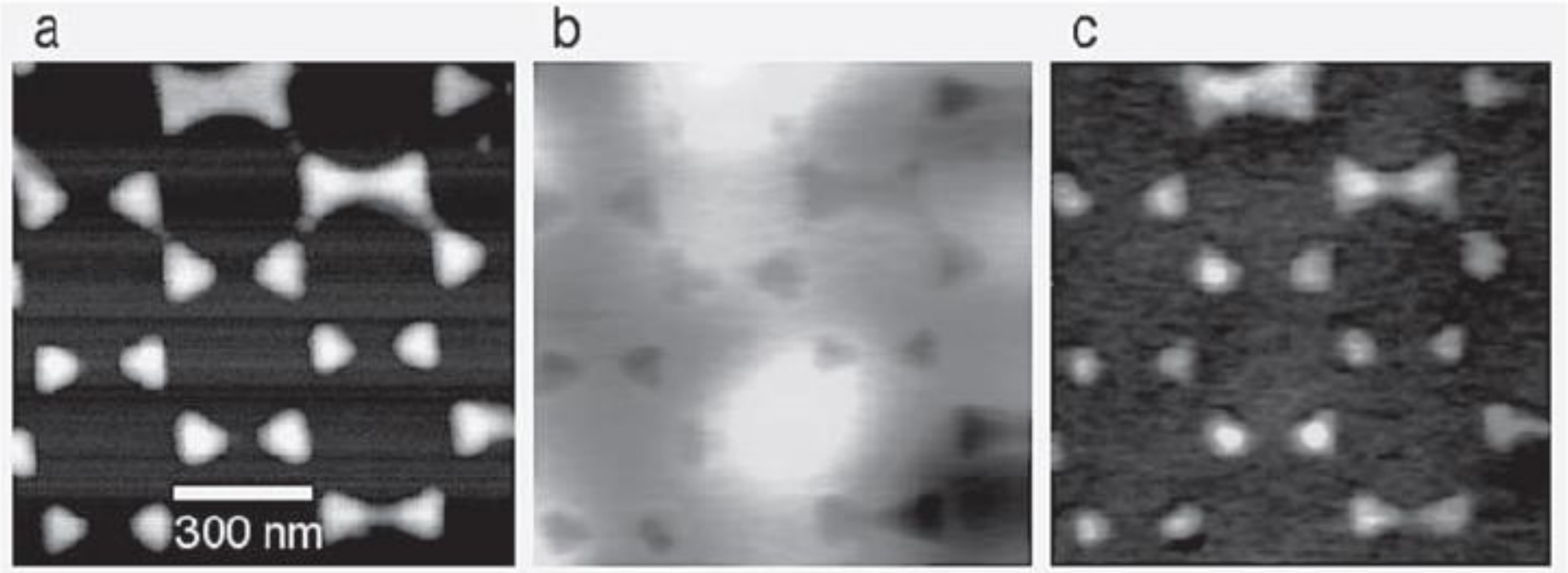


$$s_n = \sqrt{|C_{n\Omega+M}|^2 + |C_{n\Omega+2M}|^2}$$

$$\varphi_n = \arctan \frac{|C_{n\Omega+M}|}{|C_{n\Omega+2M}|}$$

N. Ocelic, A.Huber, R. Hillenbrand, Appl. Phys. Lett. **89**, 101124 (2006).

Demodulation at higher harmonics

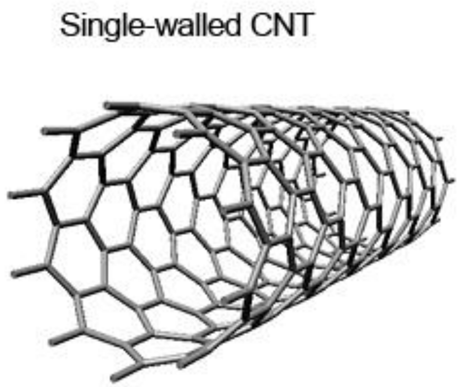


AFM topography
(20 nm high Au islands)

O1 (strong background scattering)

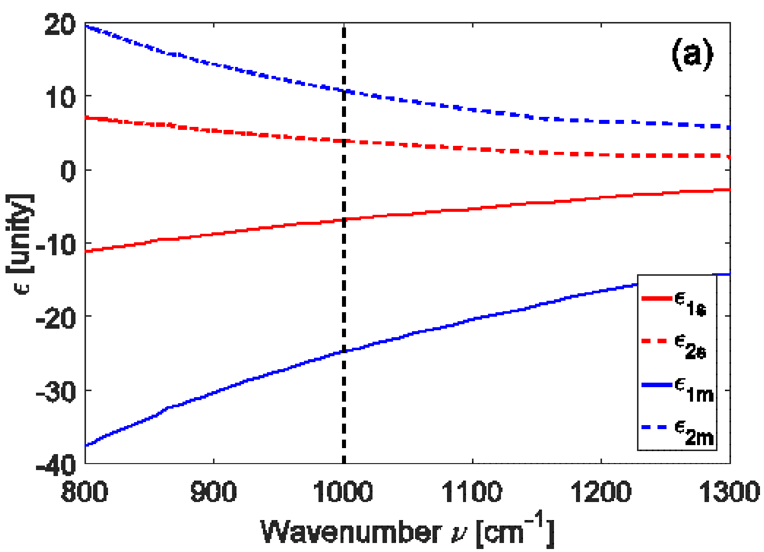
O3 (clear near-field)

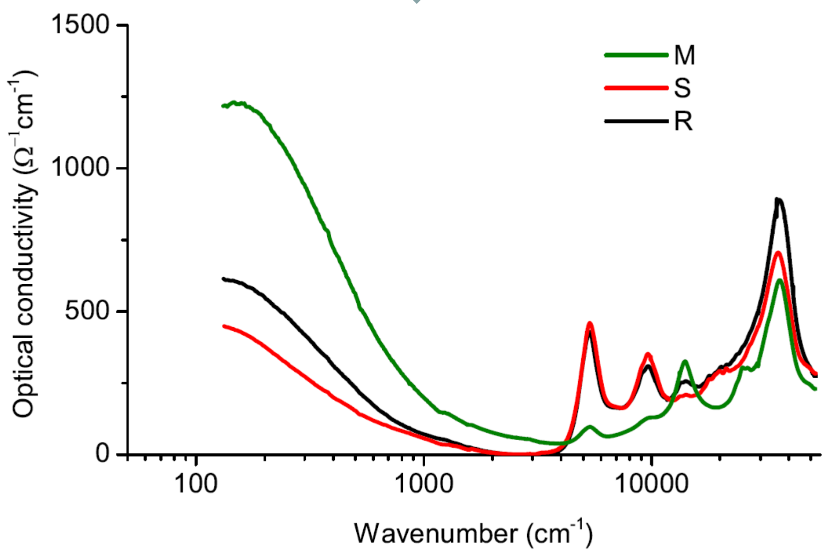
Study on single-walled carbon nanotubes



Properties are defined by their structure
- Semiconducting
- Metallic

Selective production is important
- Qualify these methods
- Different optical properties

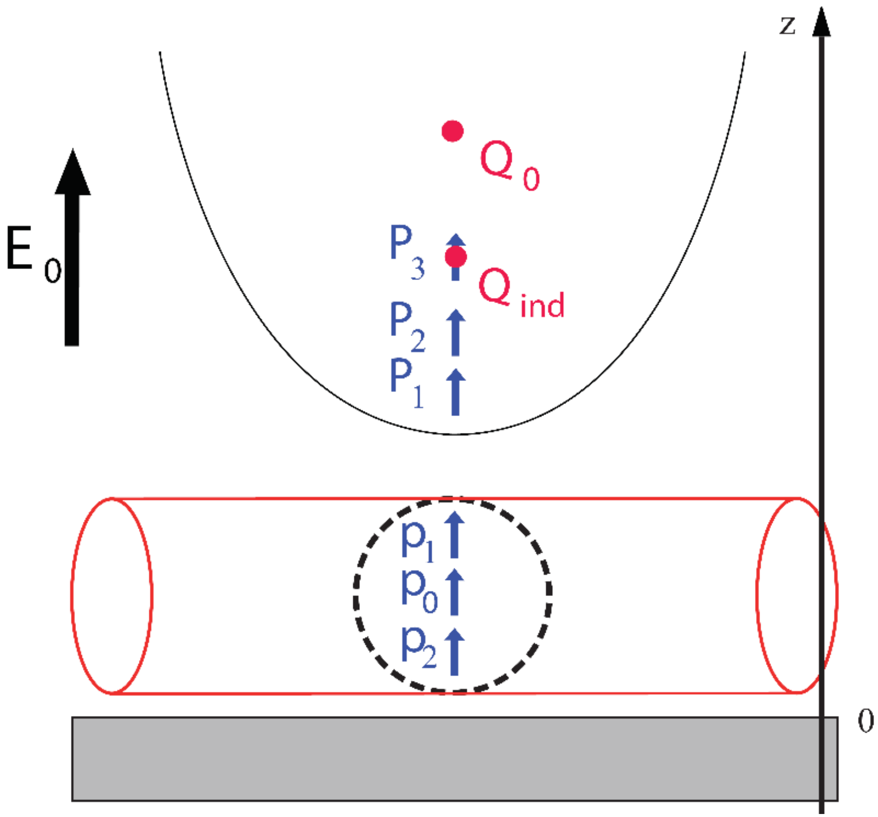




H. M. Tóháti, Á. Pekker, B. Á. Pataki, Zs. Szekrényes, and K. Kamarás, Eur. Phys. J. B **87**, 126–1–6 (2014).

Analytical model

Analytical calculations based on extended finite dipole model (EFDM)



- Substrate-particle-tip system
- Approximated with numerous charges generated by the incident E field
- p_0, p_1, p_2 describe electric field of the nanoparticle
- $p = \alpha_z \cdot E_{loc}$
- Nanotubes are cylinder-like objects
- Approximated with a prolate ellipsoid
- The following expression was used:

$$\alpha_z = \frac{\epsilon - 1}{1 + N_z(\epsilon + 1)}$$

$\epsilon = \epsilon_1 + i \cdot \epsilon_2$ - complex dielectric function

N_z– depolarization factor

$$p_{eff} \propto \sigma$$

$$p_{eff} = -2Q_0 L - Q_{ind} L + P_1 + P_2 + P_3 + p_0 + p_1 + p_2$$

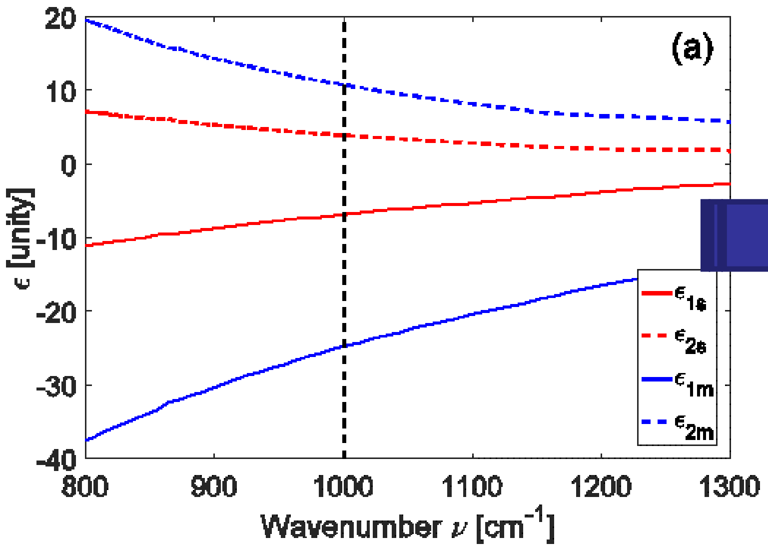
Simulating the tapping mode: $z = (H + A(1 - \cos(\Omega t)) \rightarrow$ demodulation$\rightarrow \sigma_n = s_n e^{i\varphi_n}$

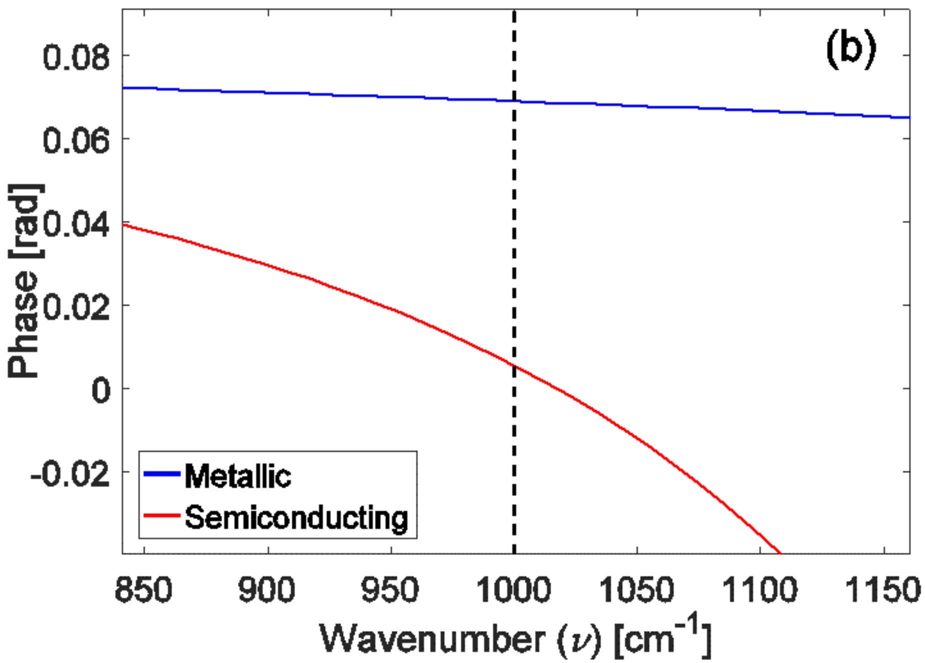
A. Cvitkovic, Ph.D. thesis, Technische Universit¨at München (2009). J.Venermo and A. Sihvola, J. Electrostat. **63**, 101–117 (2005).

Analytical calculations

Complex dielectric function of SWCNTs from Kramers-Kronig analysis

Third harmonic phase of d=4 nm bundles

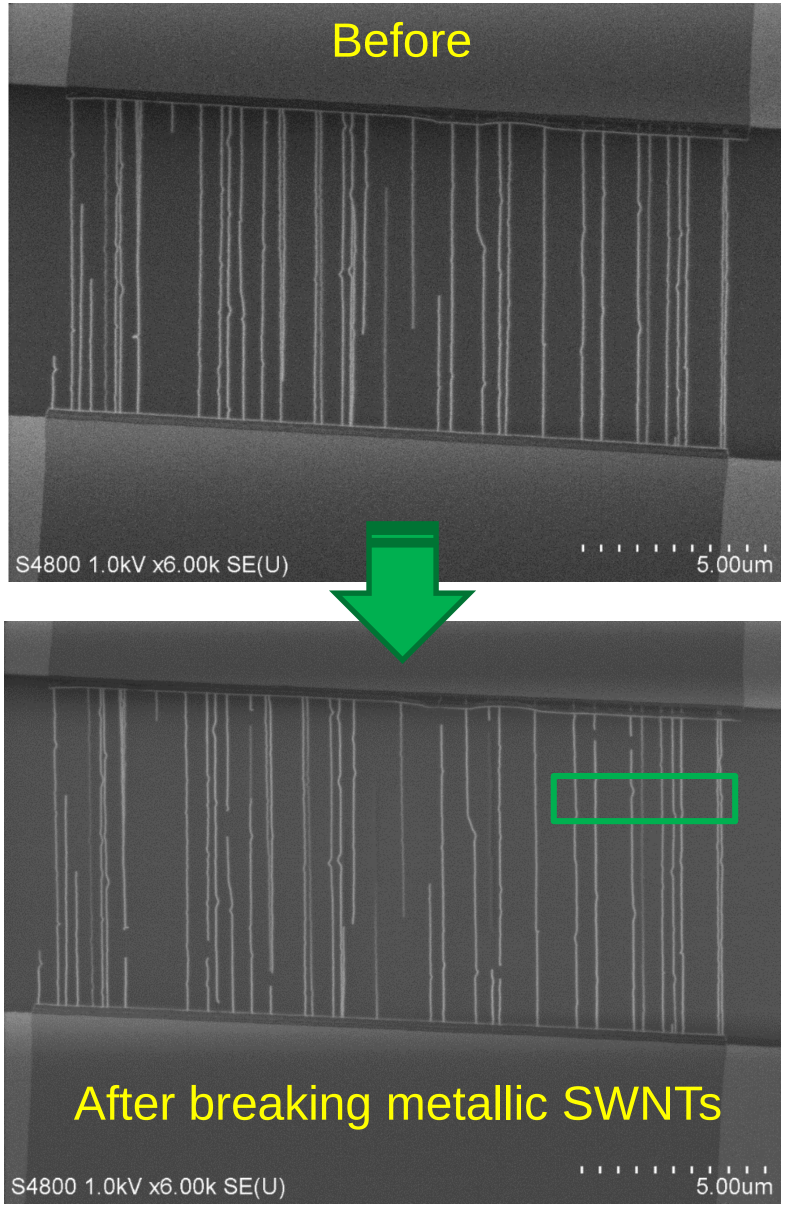




Phase data are normalized to the Si substrate

G. Németh, D. Datz, HM Tóháti, Á. Pekker, K. Kamarás, physica status solidi (b) 253 (12), 2413-2416 (2016)

Aligned SWCNT samples



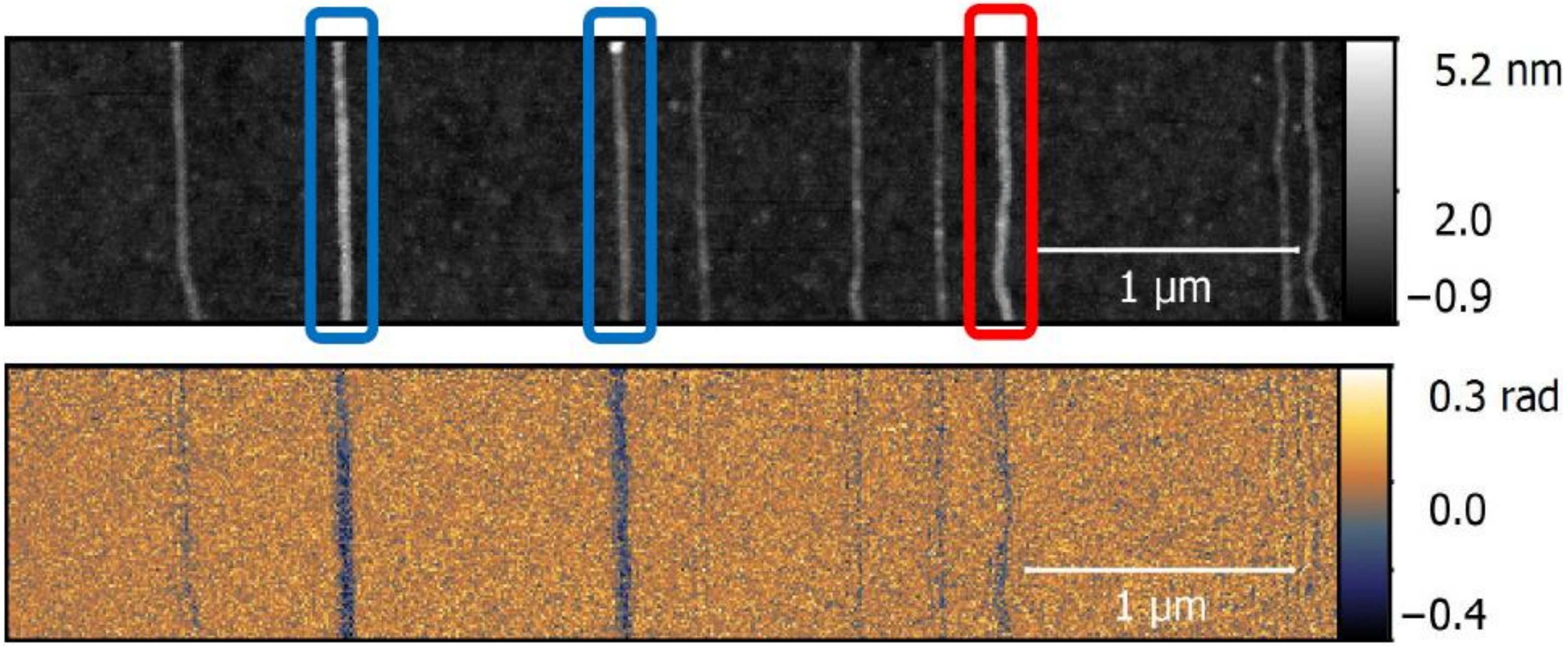
- CNT array for transistor fabrication

- Samples from University of Tokyo
- Group of Prof. Shigeo Maruyama
- Horizontally aligned nanotubes grown by CVD
- Transferred onto Si/SiO_2 substrate
- Gold contacts
- Metallic nanotubes were destroyed
    - Electrical breakdown technique

K. Otsuka, T. Inoue, S. Chiashi, and S. Maruyama, Nanoscale 6, 8831 (2014).
P. G. Collins, M. S. Arnold, P. Avouris, Science 292, 706-709 (2001).

Results on individual nanotubes

AFM topography

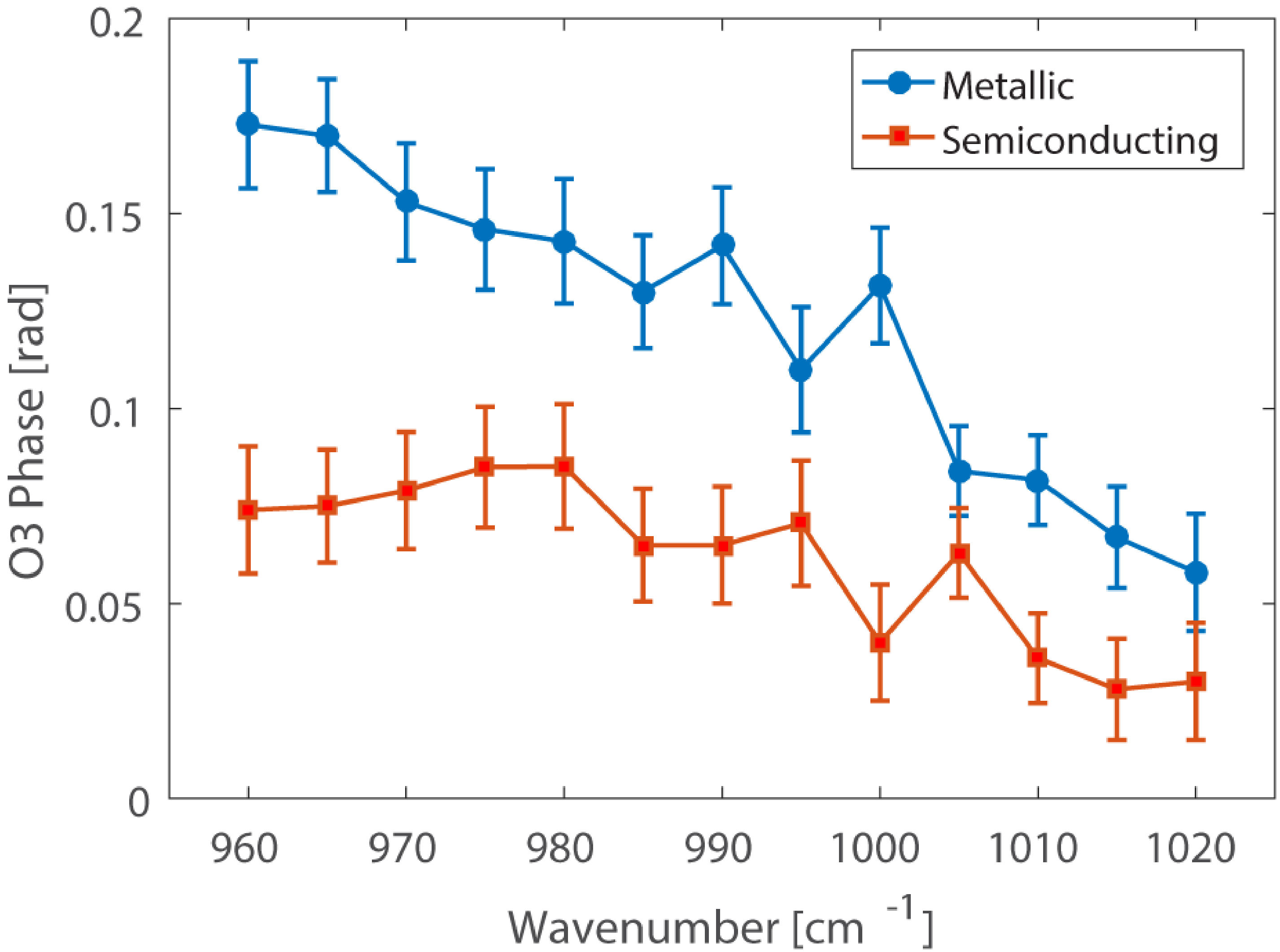


O3 demodulated near-field phase map

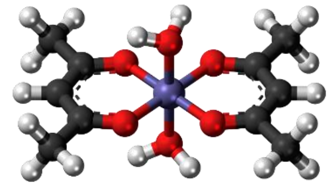
- Diameter of the metallic tubes:
  - $d_1 \approx 3\ nm$ and $d_2 \approx 1.7\ nm$
- Optical response:
  - $\varphi_{O3} \approx 0.168\ [rad]$ and $\varphi_{O3} \approx 0.132\ [rad]$

- Largest semiconducting tube:
  - $d \approx 2.5\ nm$
- Optical response:
  - $\varphi_{O3} \approx 0.06\ [rad]$

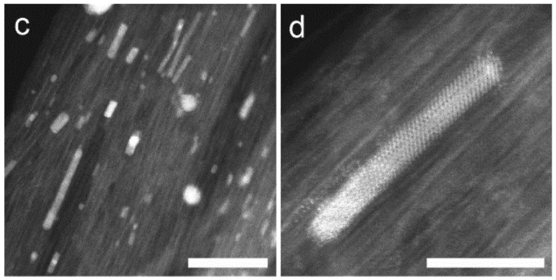
Spectral behaviour of individual tubes

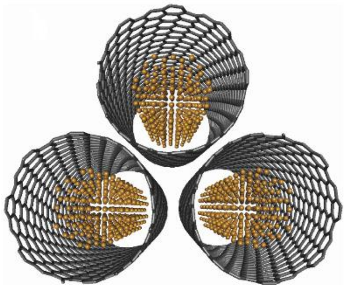


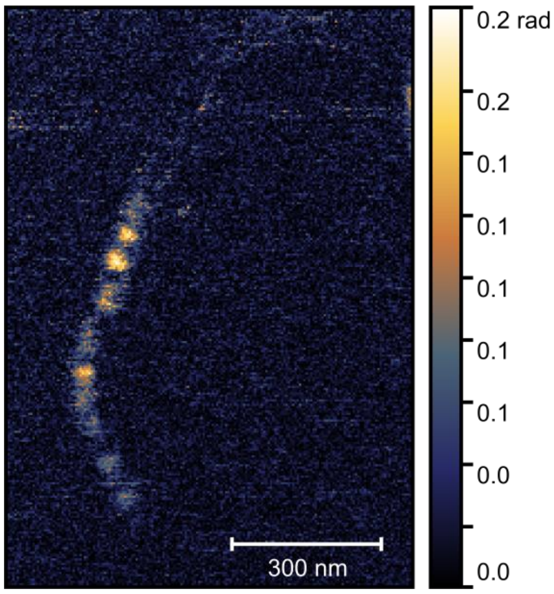
Hybrid nanotube systems



- eDip single-walled carbon nanotubes filled with Nickel(II) acetylacetonate (NiACAC)
- The molecules encapsulated inside SWCNTs can be transformed by heating in vacuum to metal clusters



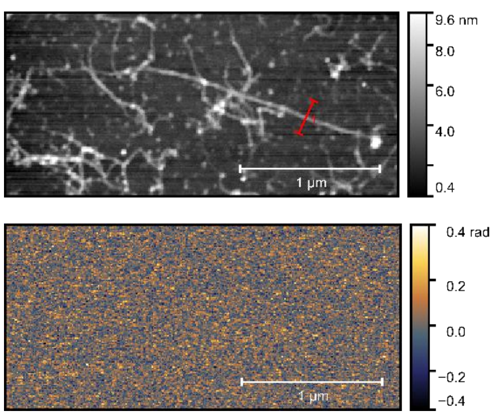


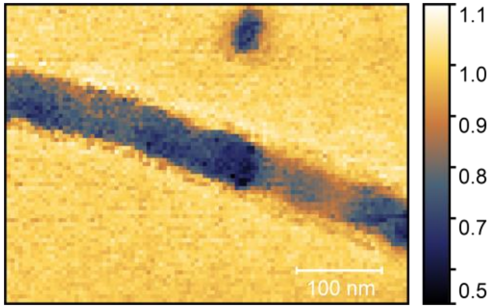


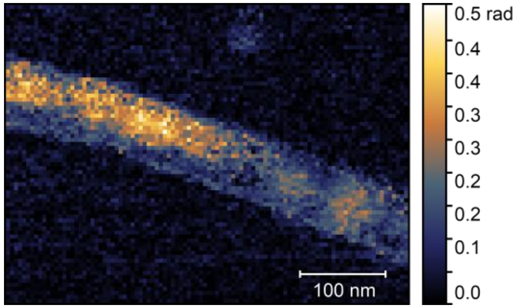
- Theoretical predictions: Ni clusters can locally influence near-field phase with their extra dipole moments

After heating

Before heating







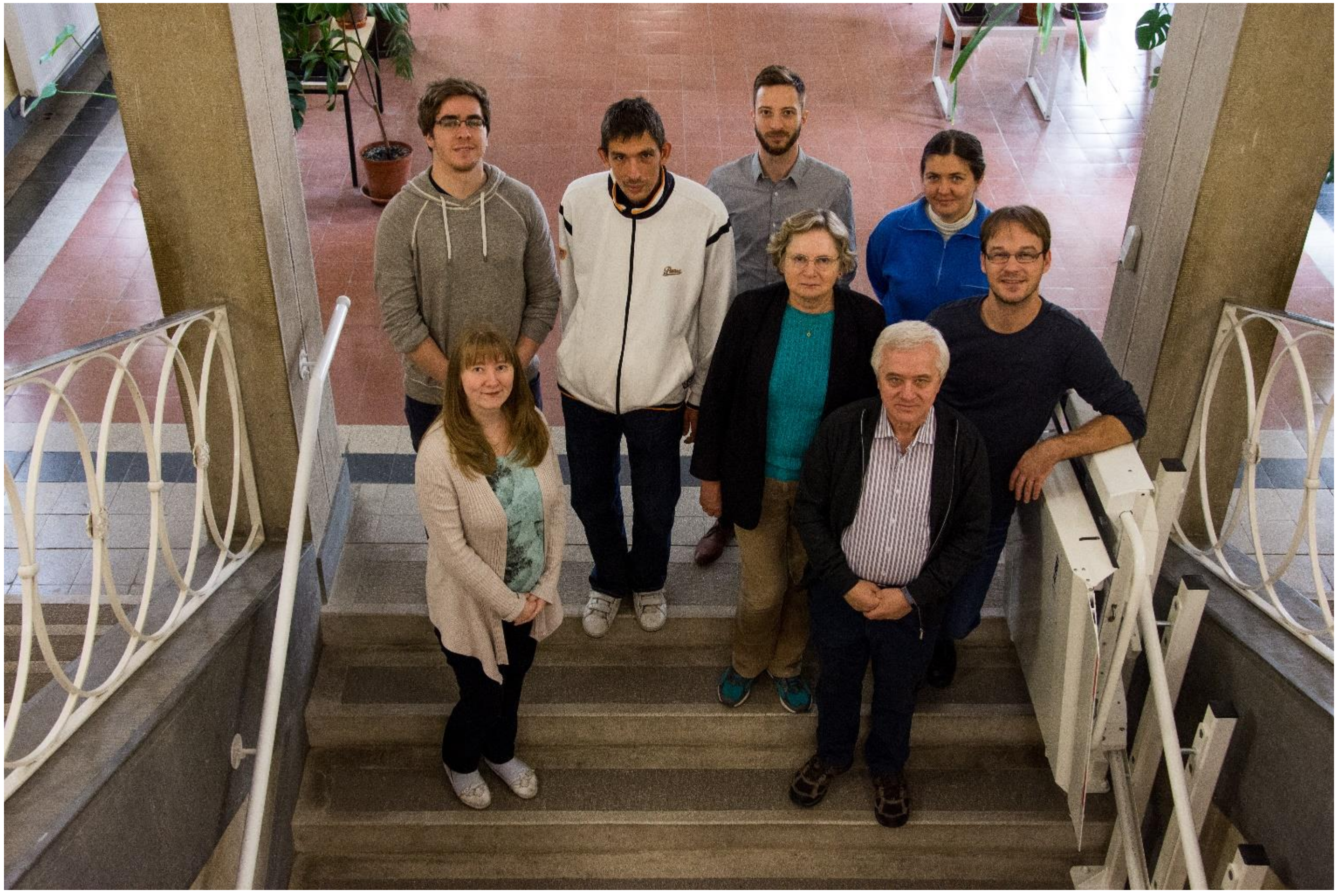
Conclusions

Spatial resolution $\approx 10-20nm$
Sensitivity level is much higher $\approx 1nm\ \rightarrow SWCNTs$

Signal from difference in polarizability → many different sources
- Collective excitations → BNNTs
- Molecular vibrations
- Charge density difference
- Material specific recognition

Huge variability and possibilities
- We are open for collaboration

Acknowledgement



BME

- Koppa Pál
- Sepsi Örs

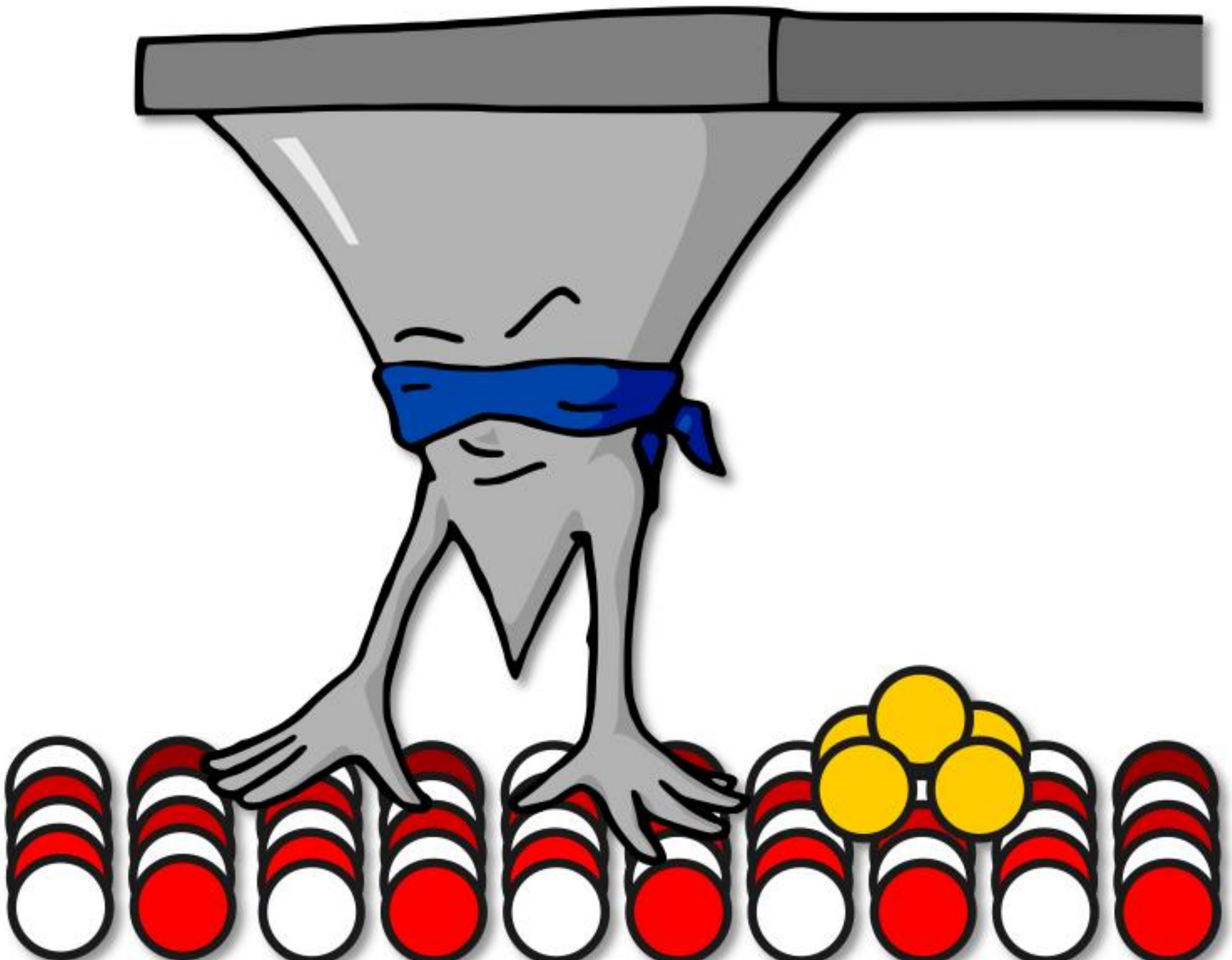
University of Tokyo

- Group of Prof. Shigeo Maruyama

University of Nottingham

- Group of Prof. Andrei N. Khlobystov

Thank you for your attention!



Spectroscopy with s-SNOM device

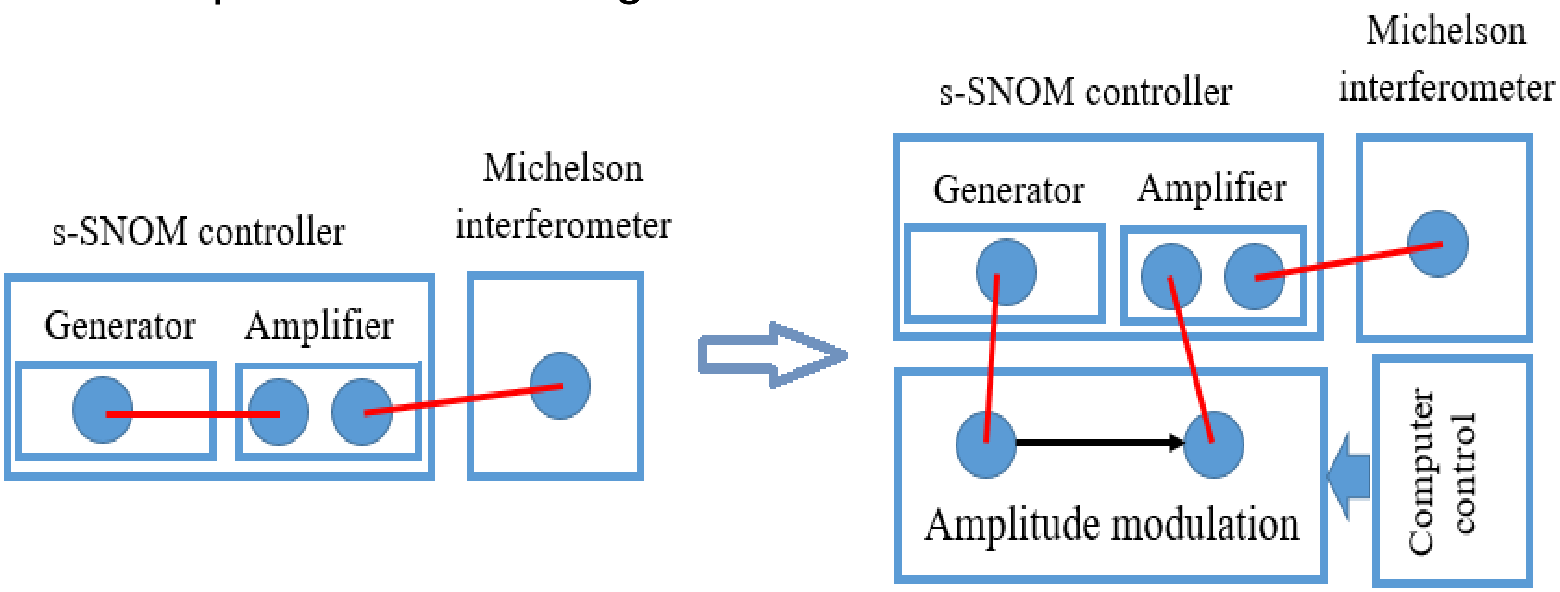
In its original setup, the s-SNOM device is a microscope

Capable of measurements on a fixed wavenumber (e.g. CNTs)

Modification for spectrum measurements

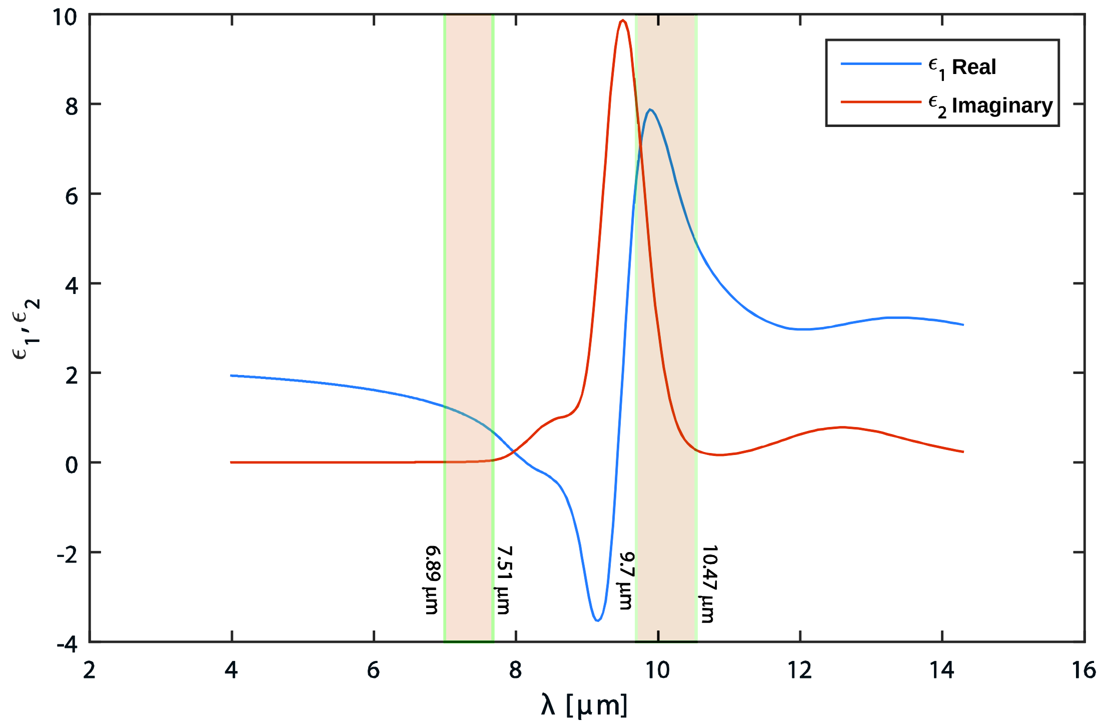
Need to set:

- wavenumber
- amplitude of vibrating mirror



Good candidates for spectroscopic measurements

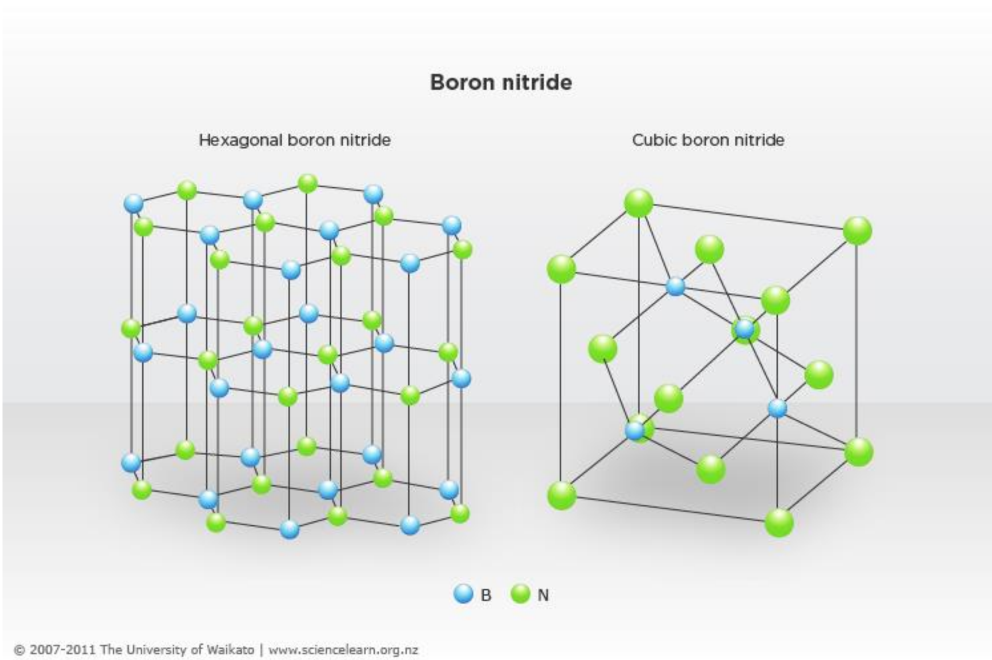
- Limited spectral range due to available lasers:
- Tunable quantum cascade lasers from 950-1050 cm^{-1} and 1320-1450 cm^{-1}.



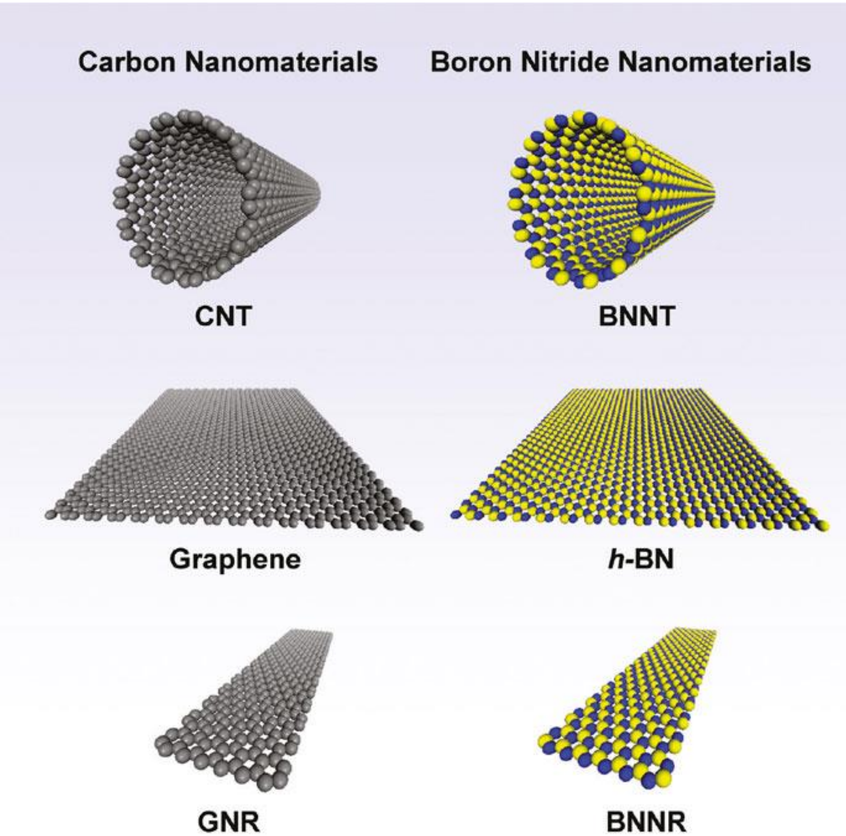
- Second laser is ideal for boron nitride.

Boron nitride structures

Many different allotropes:



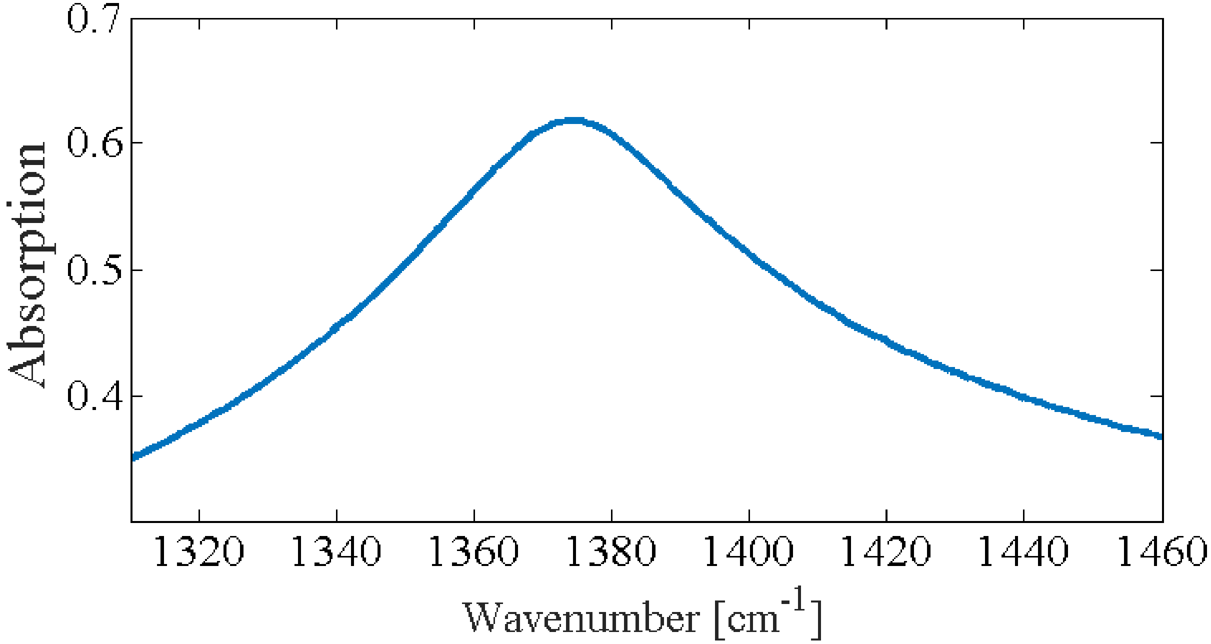
https://www.sciencelearn.org.nz/images/2208-boron-nitride



http://nanotechweb.org/cws/article/tech/46378

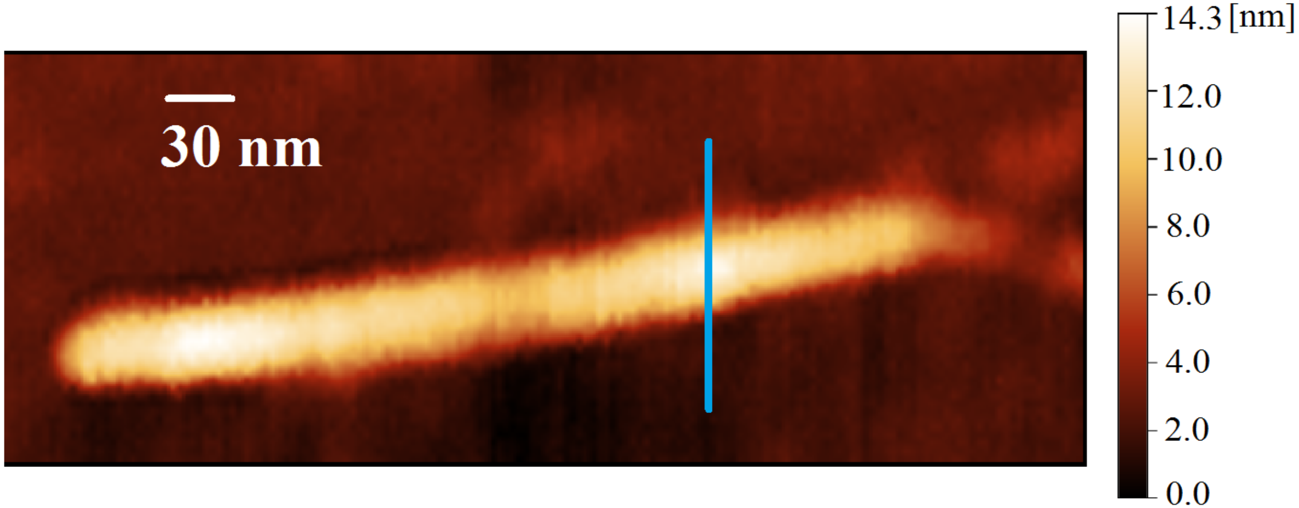
Phonon-polariton modes in BNNTs

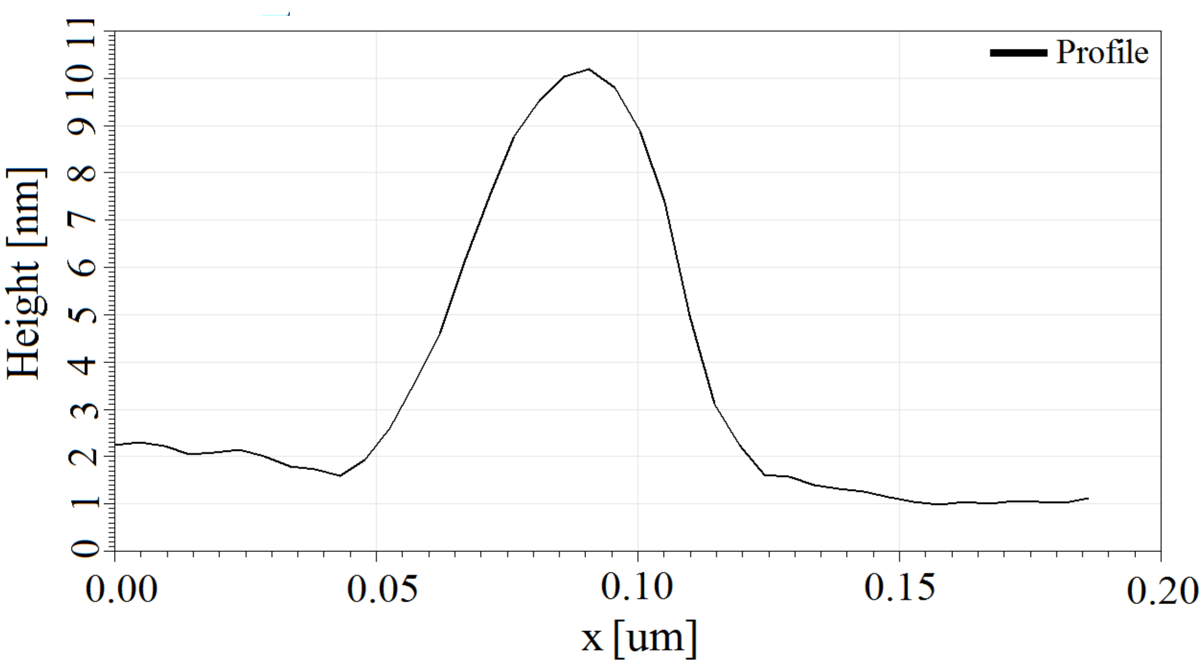
Far-field absorption peak at 1375 cm^{-1}



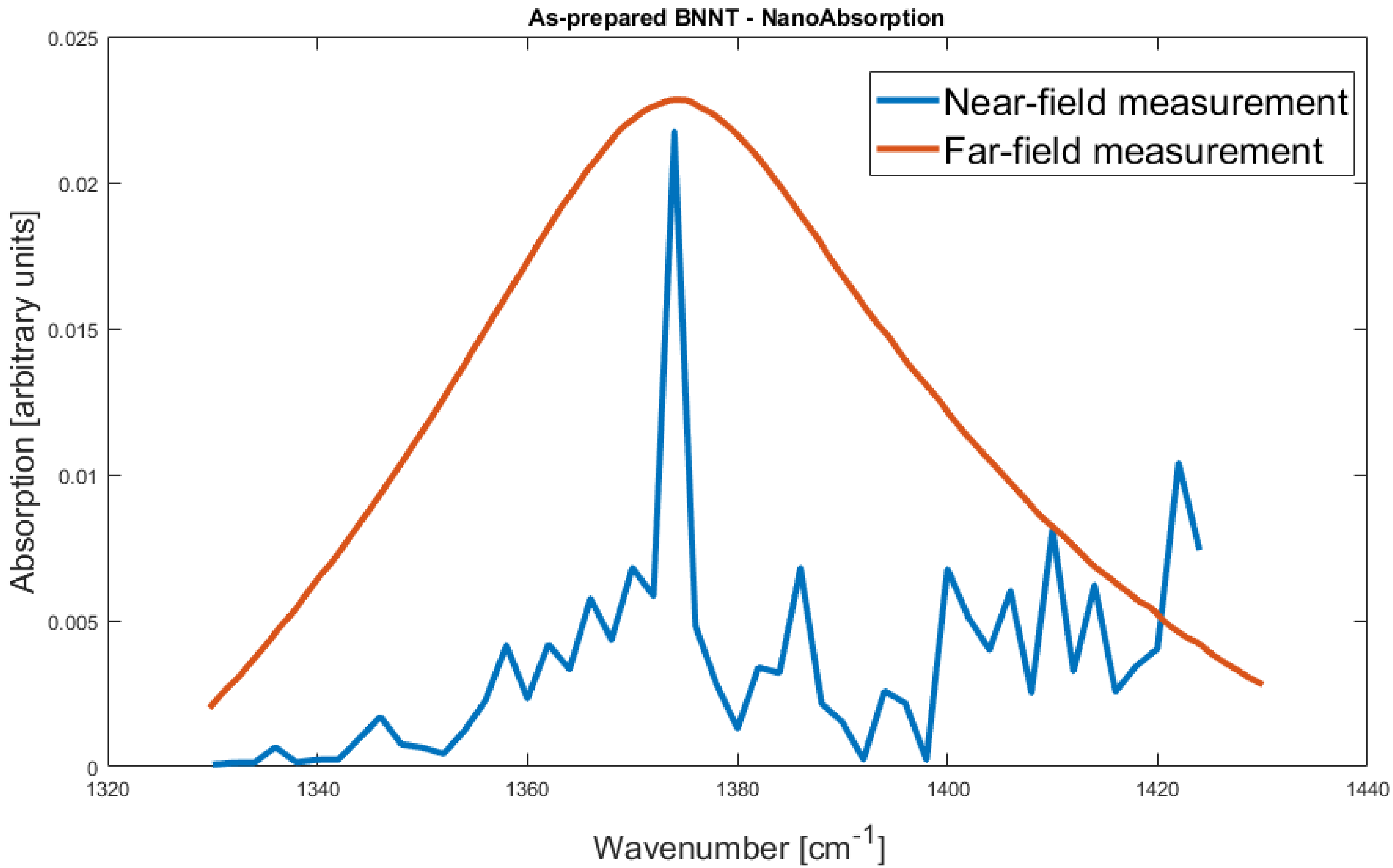
This peak corresponds to a TO mode (in-plane, longitudinal stretch).

Individual MWBNNT under AFM



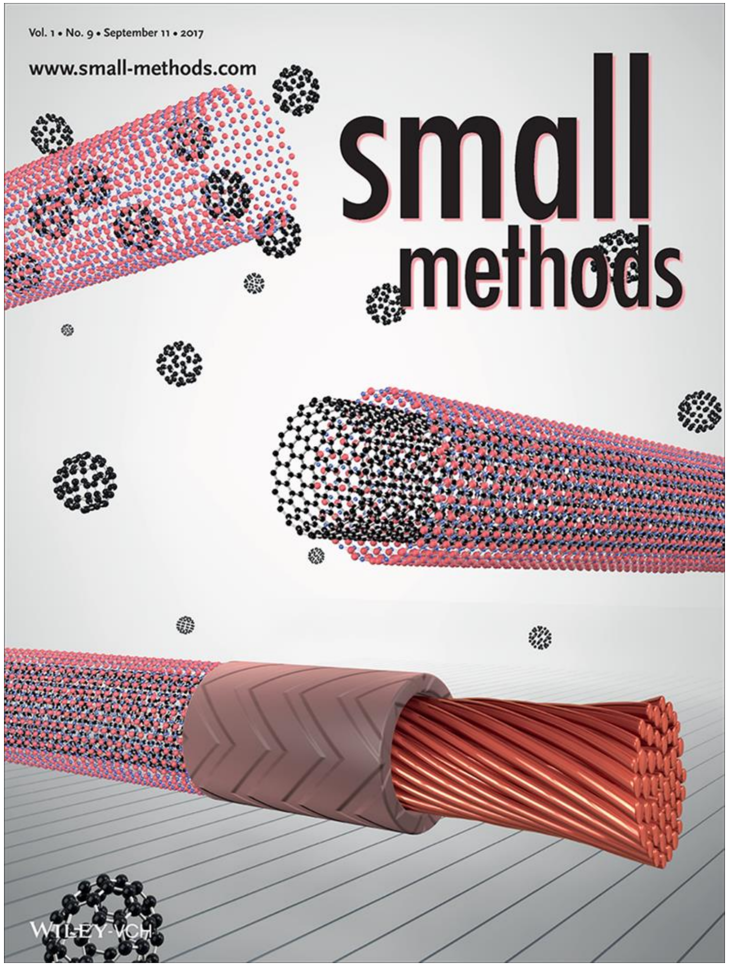


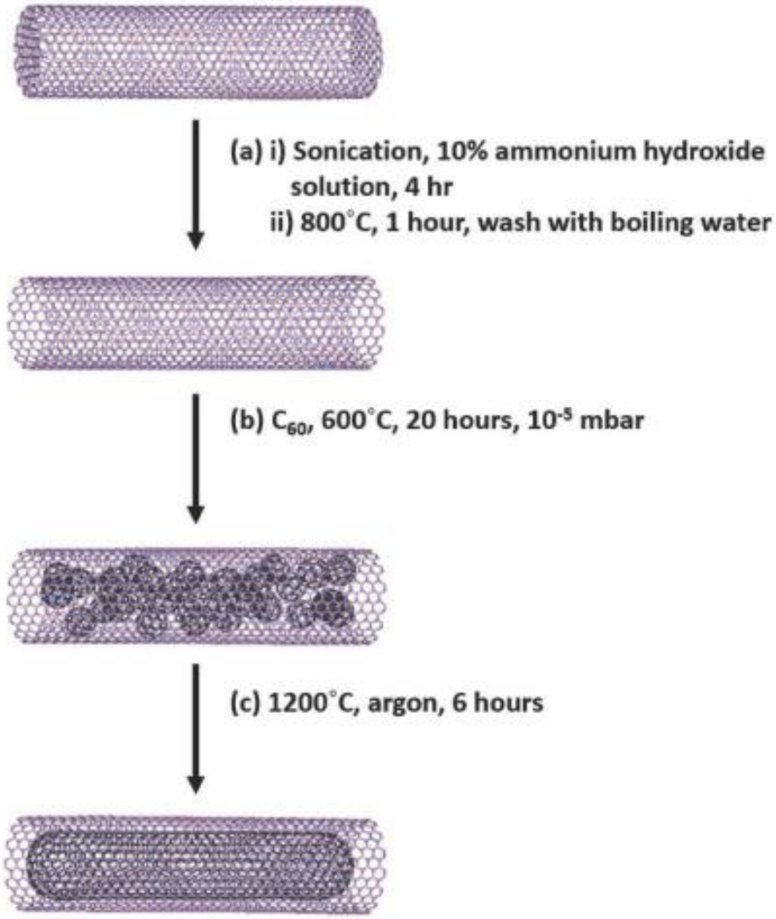
As-prepared spectrum of BNNT



Cleaning procedure

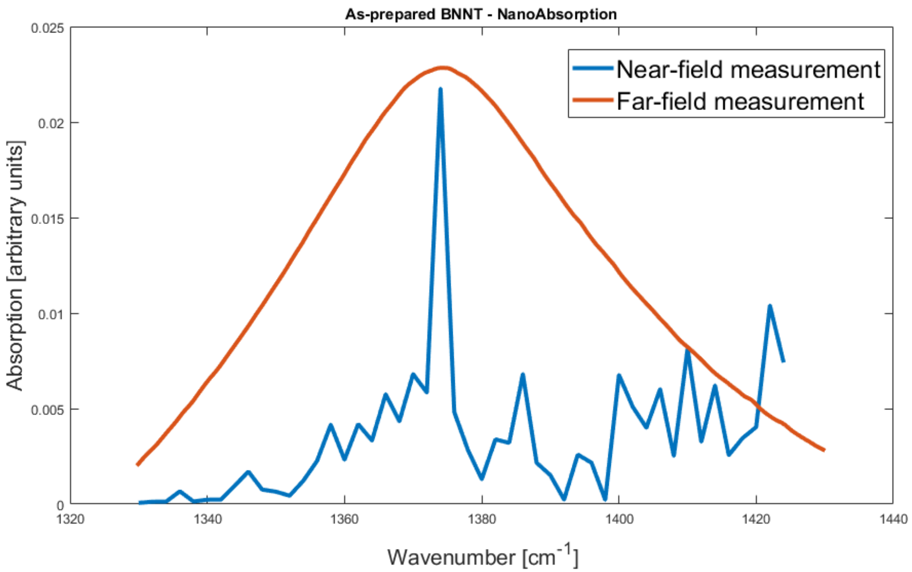
- Opening and cleaning procedure for BNNTs
- Ultimate goal: filling with molecules

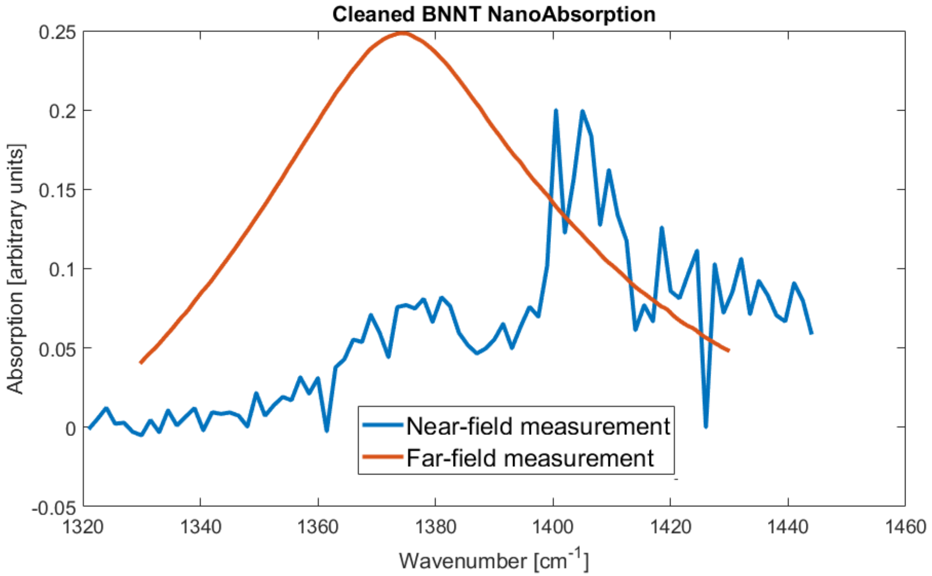




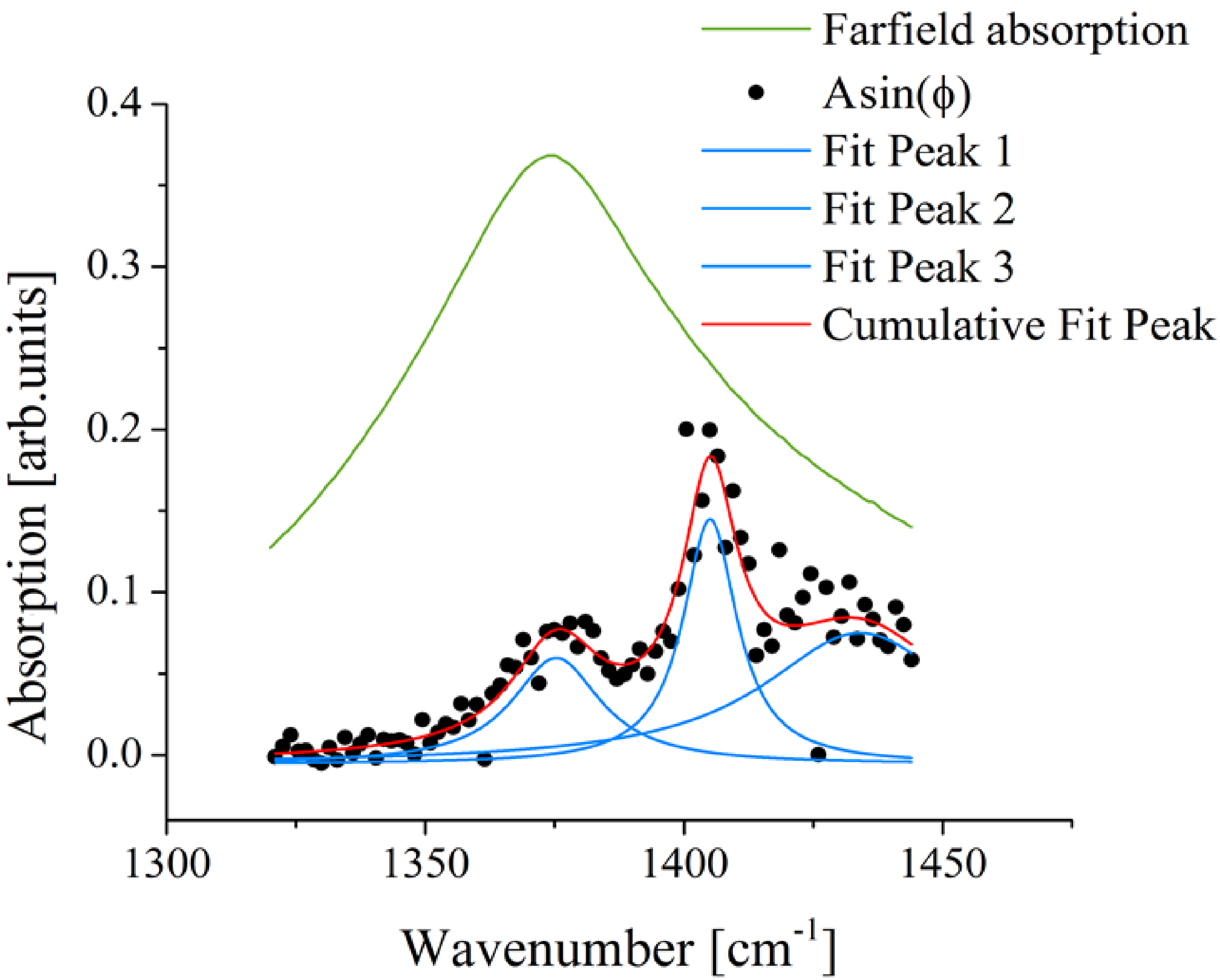
Walker, K.E., Rance, G.A., Pekker, Á., Tóháti, H.M., Fay, M.W., Lodge, R.W., Stoppiello, C.T., Kamarás, K. and Khlobystov, A.N., *Small Methods*, ***1*** (9), 1700184 (2017).

Absorption after cleaning

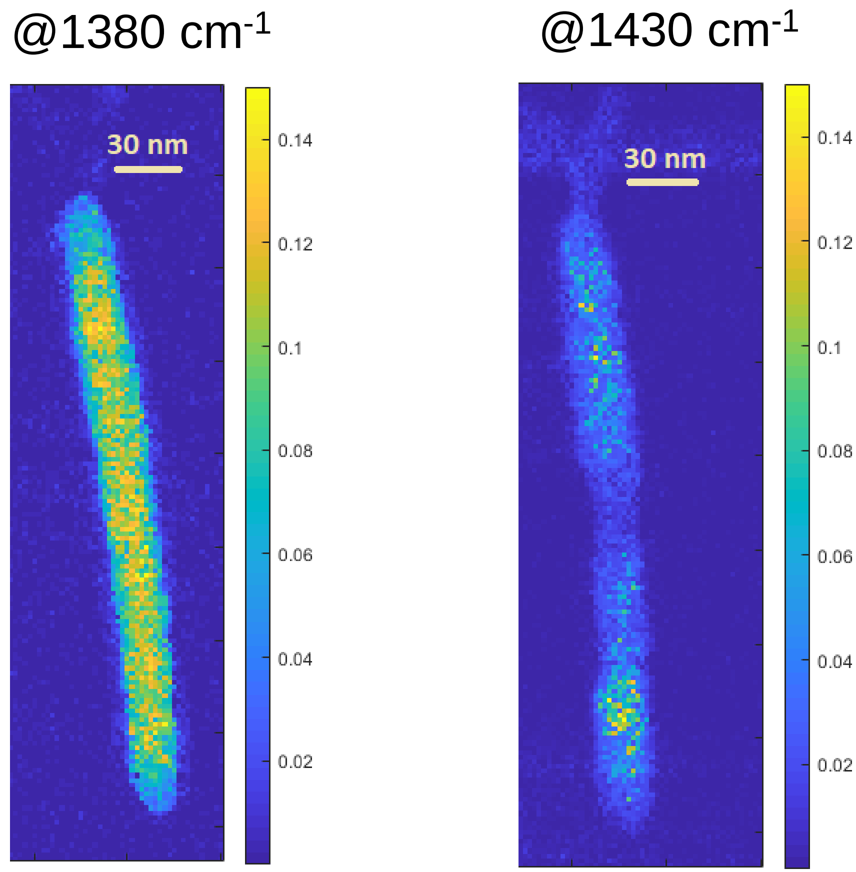




Near-field spectrum after cleaning



Mapping of impurities on a single nanotube

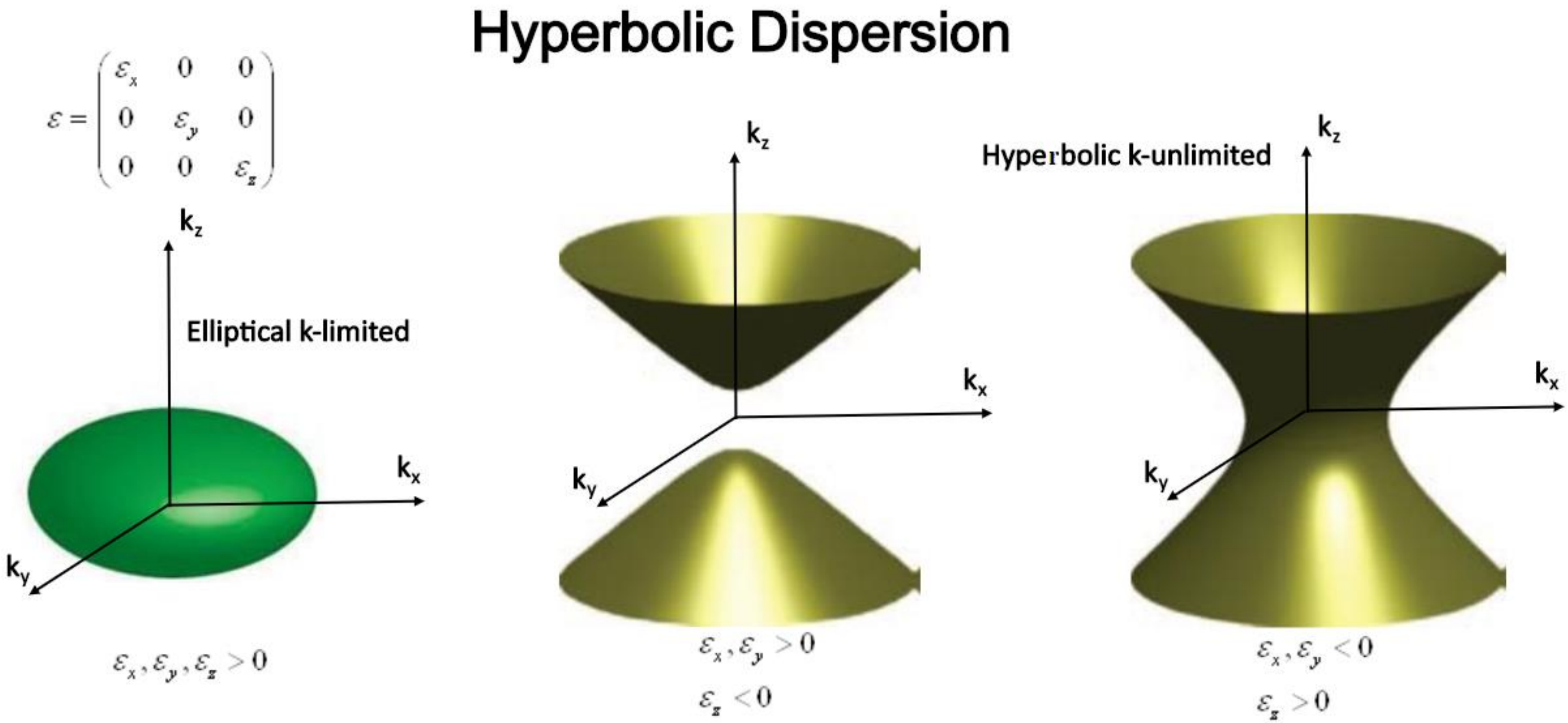


Mapping of localized phonon-polariton modes with 10 nm spatial resolution

D. Dániel, G. Németh, H. M. Tóháti, Á. Pekker and K. Kamarás, *physica status solidi (b),* 1700277 (2017).

Outlook

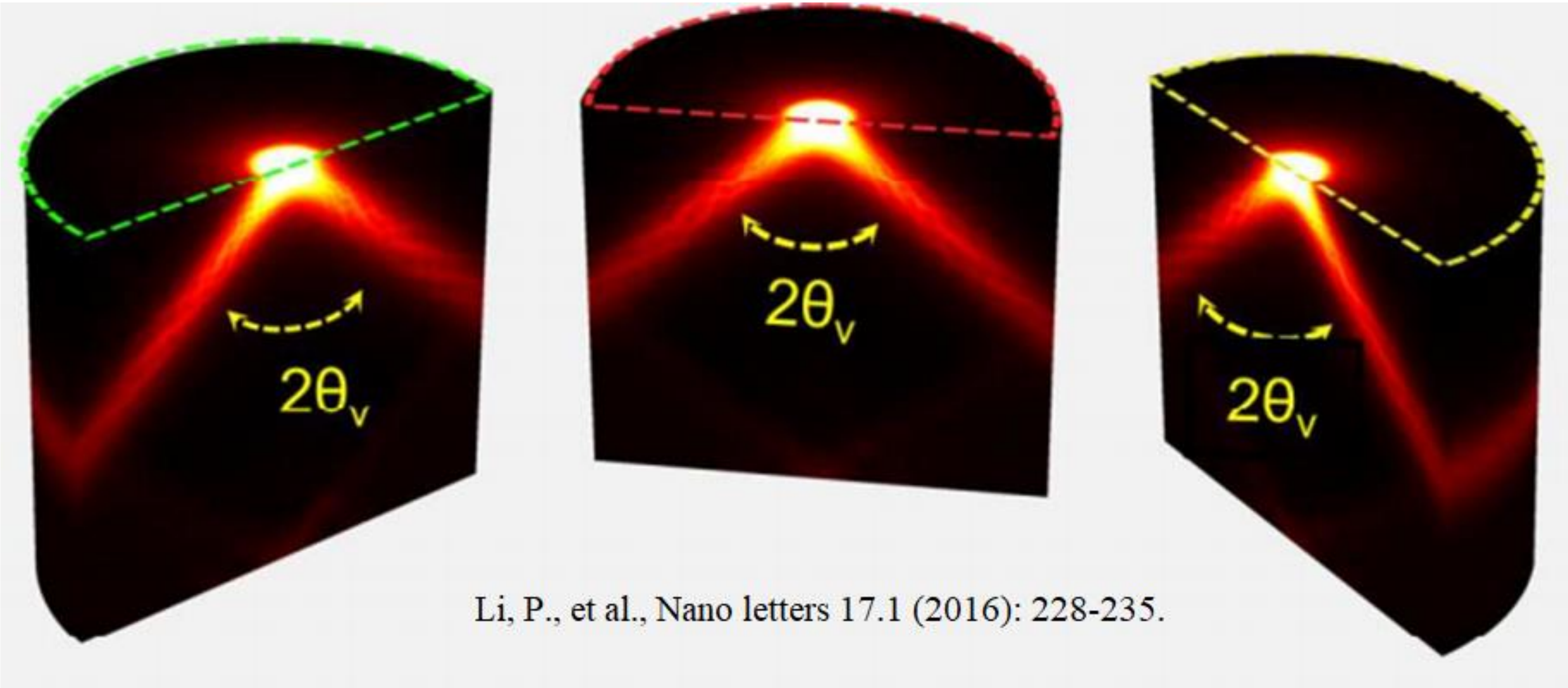
Mapping of impurities in hBN?



Jacob, Z., Alekseyev, L. V. & Narimanov, E. Optical hyperlens: far-field imaging beyond the diffraction limit. *Opt. Express* **14,** 8247–8256 (2006).
Salandrino, A. & Engheta, N. Far-field subdiffraction optical microscopy using metamaterial crystals: theory and simulations. *Phys. Rev. B* **74,** 075103 (2006).

Outlook

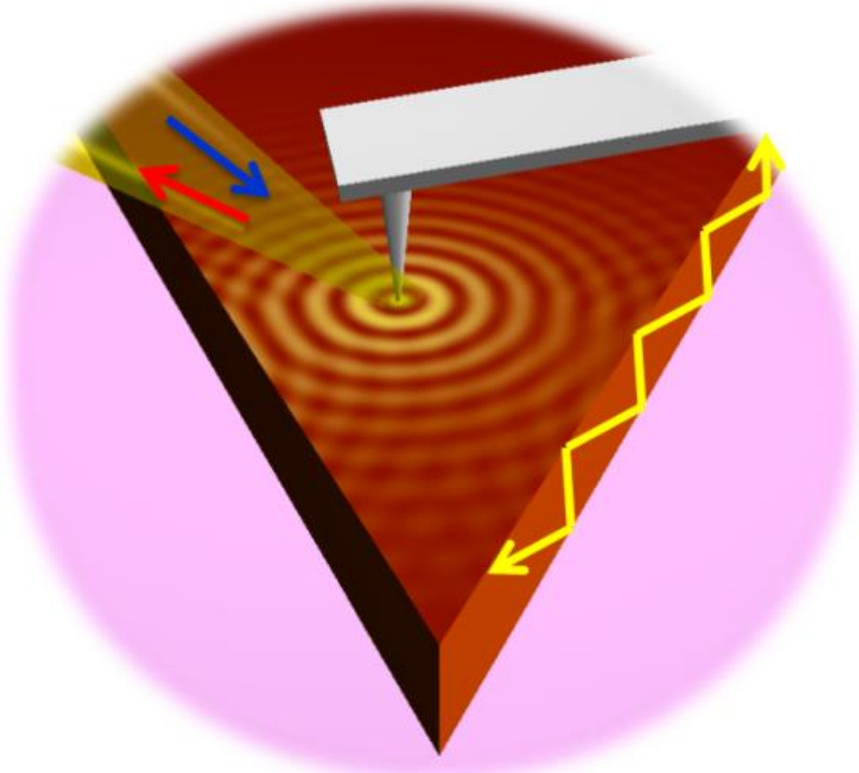
Mapping of impurities in hBN?



Li, P., et al., Nano letters 17.1 (2016): 228-235.

Outlook: hyperbolic phonon-polaritons

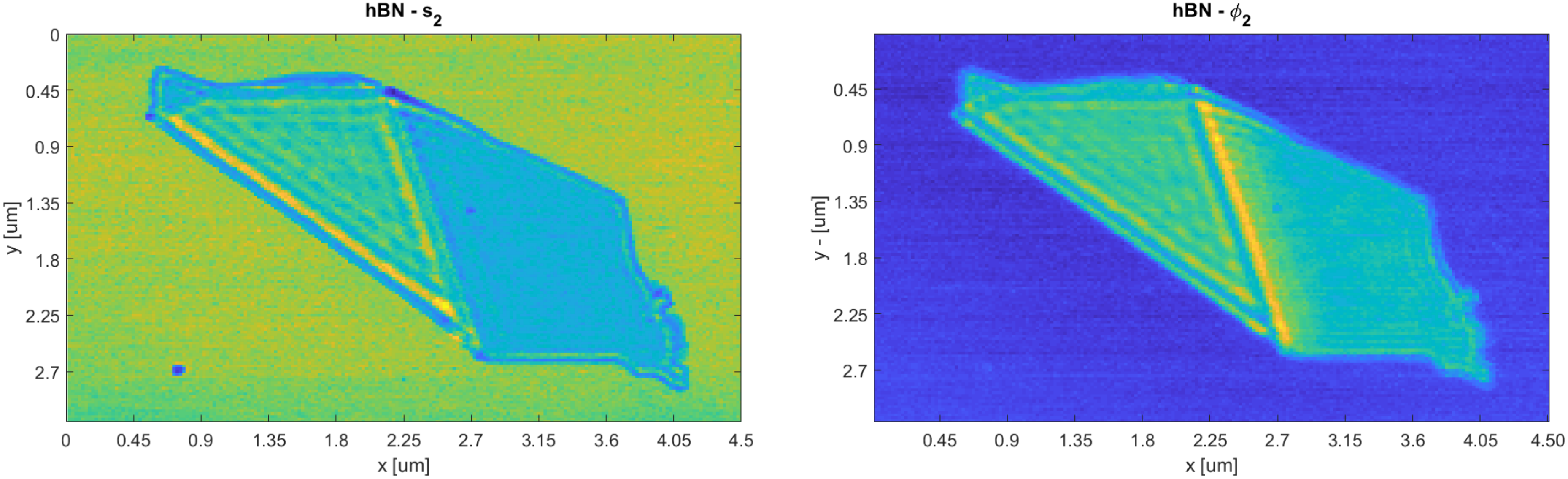
Interference patterns on edges due to reflection



S. Dai et al., *Science* **343**, 1125 (2014)

Outlook: hyperbolic phonon-polaritons

Interference patterns on edges due to reflection



D. Datz unpublished