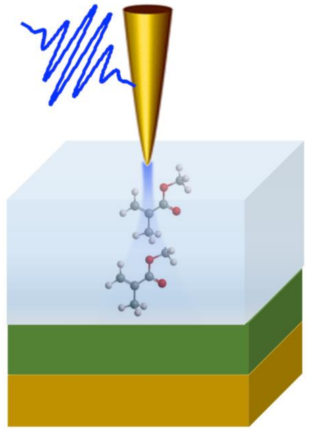
Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Nationales Metrologieinstitut

Nearfield IR Spectroscopy:

Enhancing the molecular sensitivity using **compressed sensing** and other techniques



B. Kästner, P. Hermann, A. Hornemann, G. Ulrich, A. Hoehl,
C. Elster, G. Wübbeler, F. Schmähling

IRMA BL

PTB Metrology Light Source

Funded by

EMPIR

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme

Physikalisch-Technische Bundesanstalt

Metrology:

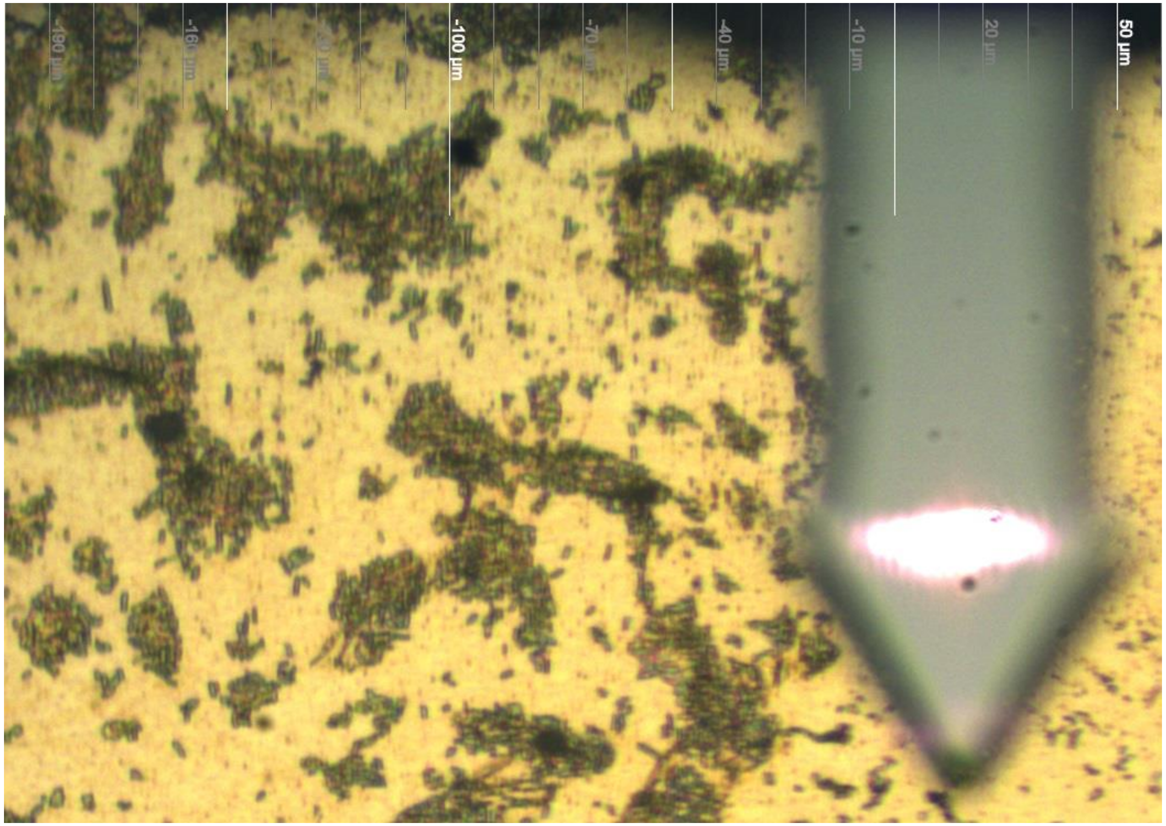
- Science and application of correct measurement
- Traceability of results to the SI through national standards
- Determination of results with verification of uncertainty

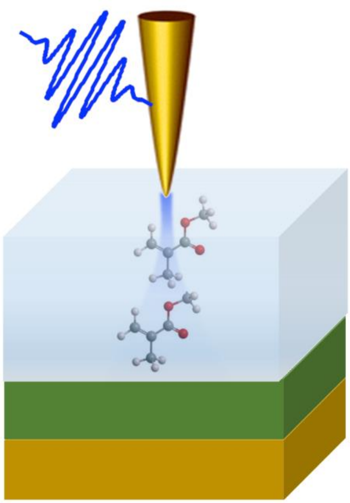
PTB:

- National Metrology Institute (NMI)
- Federal Ministry of Economics and Technology (BMWi)
- 170 Mio. € budget, plus external funding
- Approx. 1300 permanent staff and 550 non-permanent staff including 110 PhD students
- 600 scientific papers per year

Adlershofer PTB Labs

IR Spectrometry Group - Activities





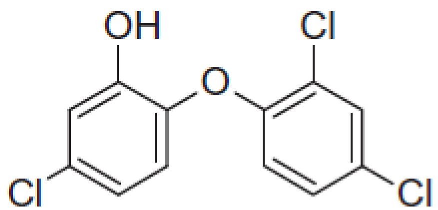
Understand interactions of drug with cell membrane

Where? Nanometer scale resolution - nearfield !

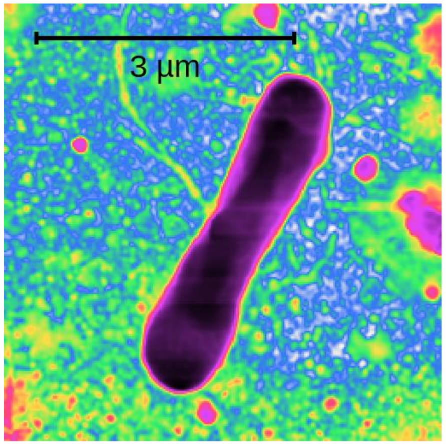
→ Metrology: quantify/localize drugs in membranes & bacterial cells

IR Spectrometry Group - Activities

Measurement requirements, example:



Antibiotic: Triclosan



Escherichia **c**oli

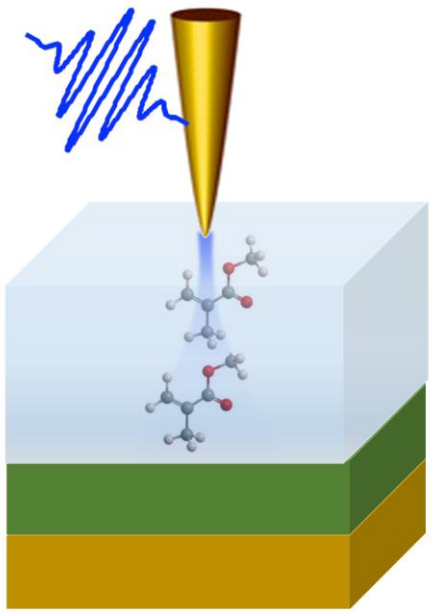
Required sensitivity: 20 molecules in 50 nm voxel

State of the art : $\Delta\varphi = 0.25°$, $t_{int} \approx 500$ s (see below, NeaSNOM 2018)

→ 500 molecules (derived from PTB measurements on triclosan)

Enhancing the sensitivity

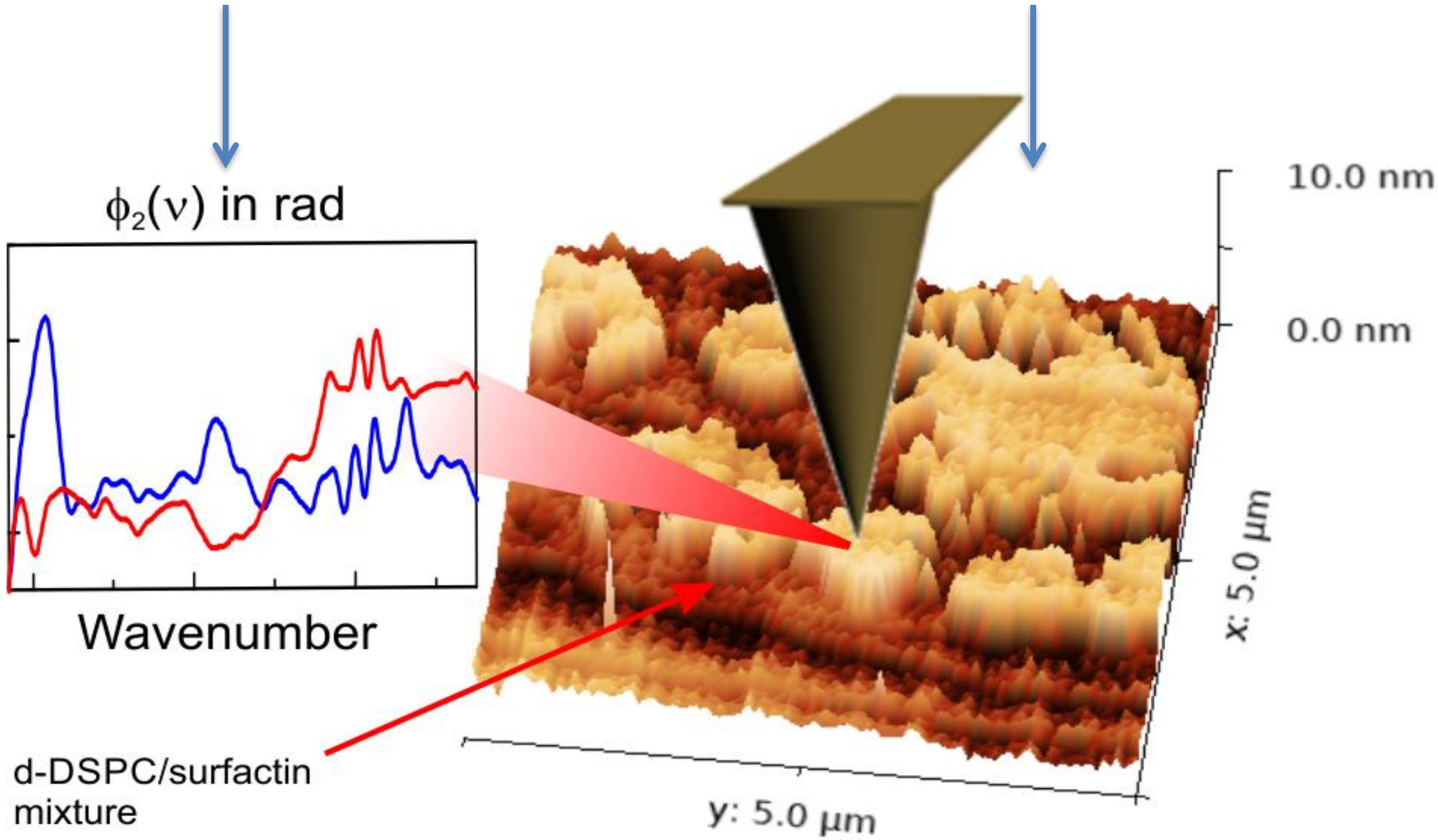
- Nearfield IR Spectroscopy using *s*-SNOM
- Compressed Sensing
- Radiation Sources and Detection
- Tailored AFM Probes
- Conclusion



Nearfield IR Spectroscopy: *s*-SNOM

Combination of

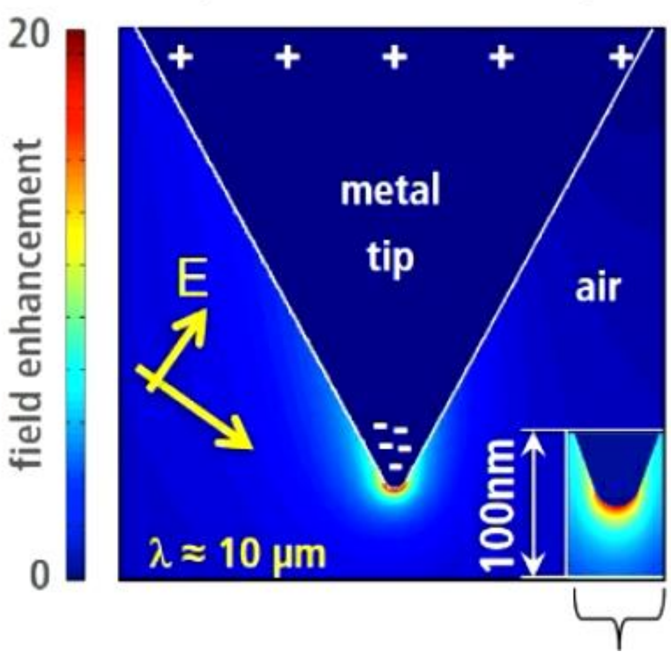
IR Spectroscopy and **A**tomic **F**orce **M**icroscopy



B. Kästner *et al*. ACS Omega 2018

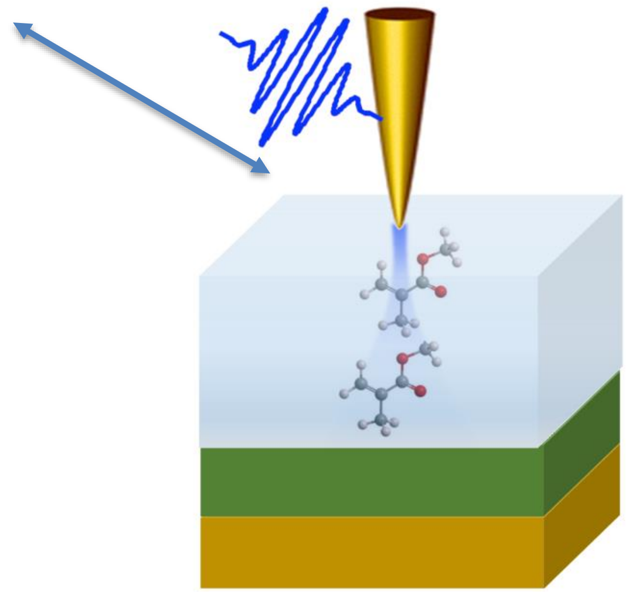
s-SNOM Principle

IR Radiation incident on metal cone (antenna)



Focus << λ

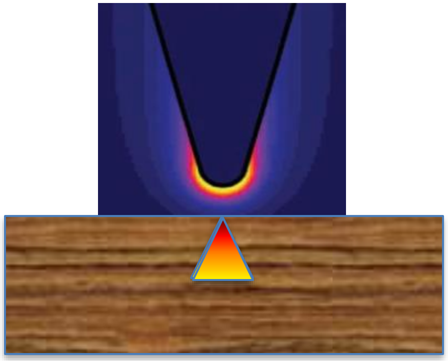
Detection of radiation scattered from antenna as **dressed dipole**



→ scattering-type **SNOM**

A. Huber et al. Nano Lett. 2008

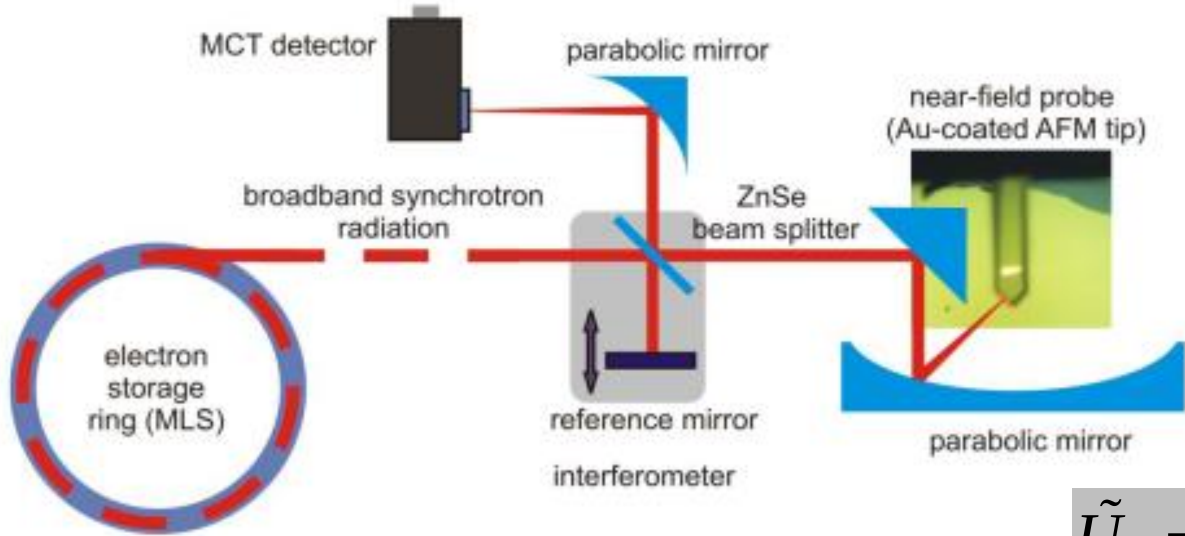
Background suppression



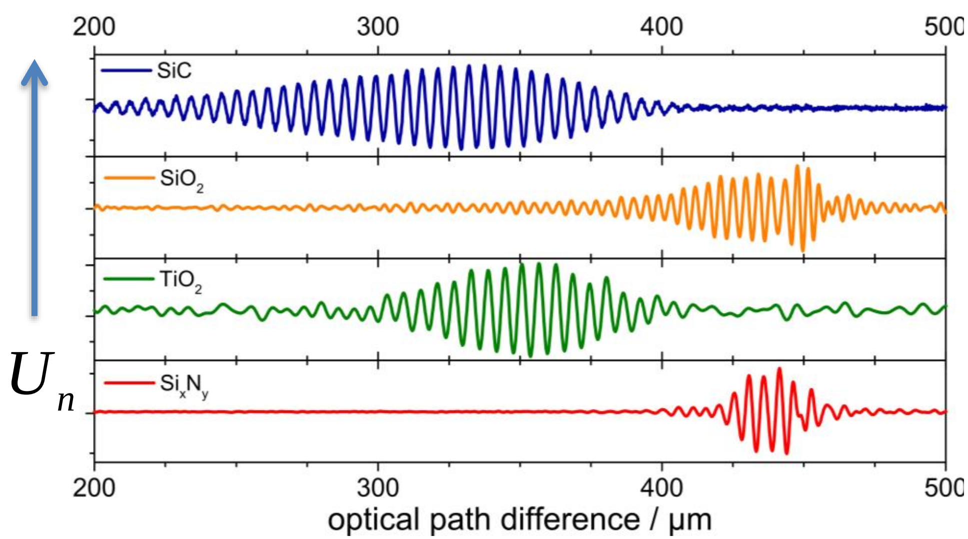
- Strong field between tip and substrate (of high refractive index)
- Field enhancement depending **exponentially on the distance**
- In tapping mode: periodic emission with **higher** harmonics
- Background suppression: **higher** harmonic demodulation

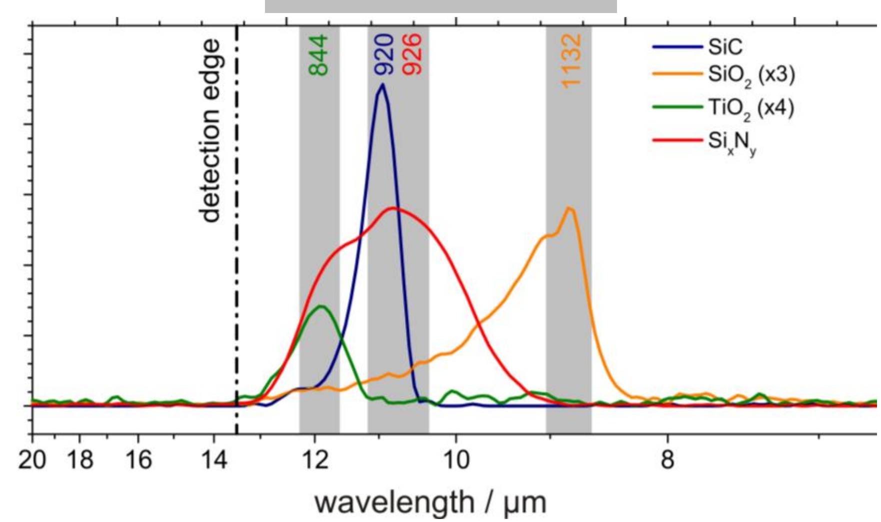
⇨ Detection voltage signal U_n

Nearfield Spectroscopy



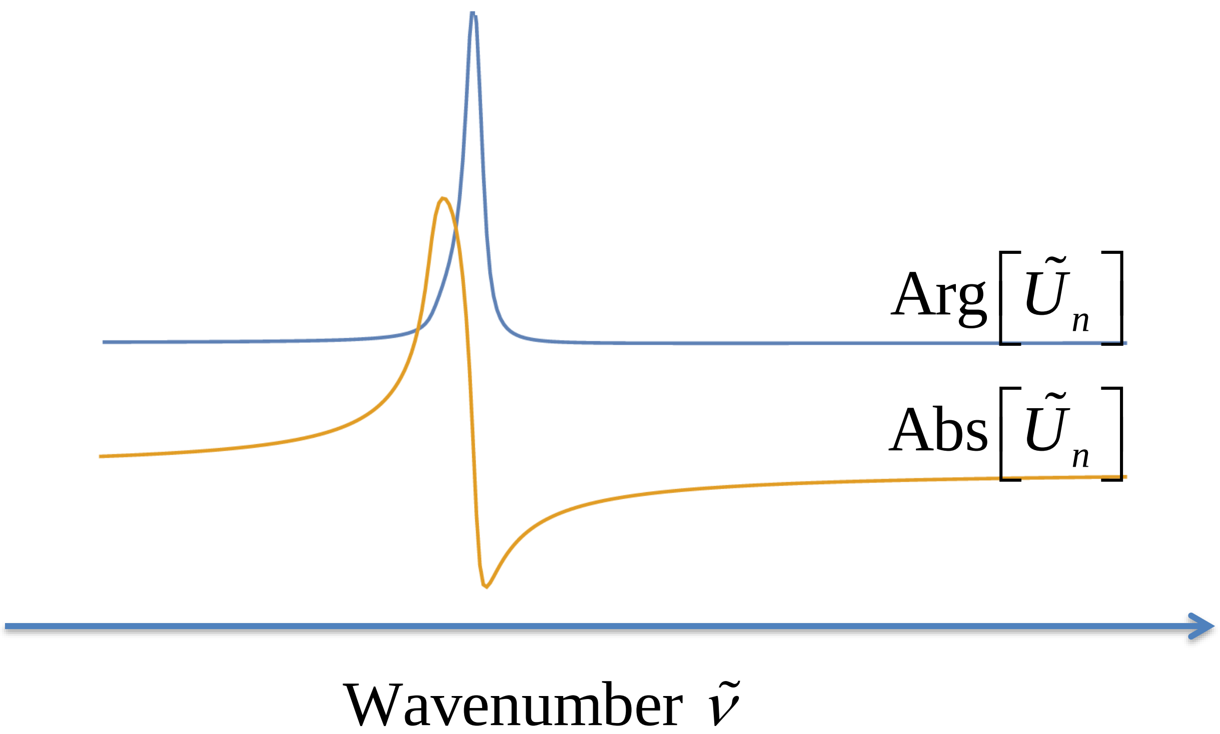
$$\tilde{U}_n = \mathrm{FT}\left[U_n\right]$$





P. Hermann *et al.,* Optics Express 2014

Scattered Signal: Interpretation



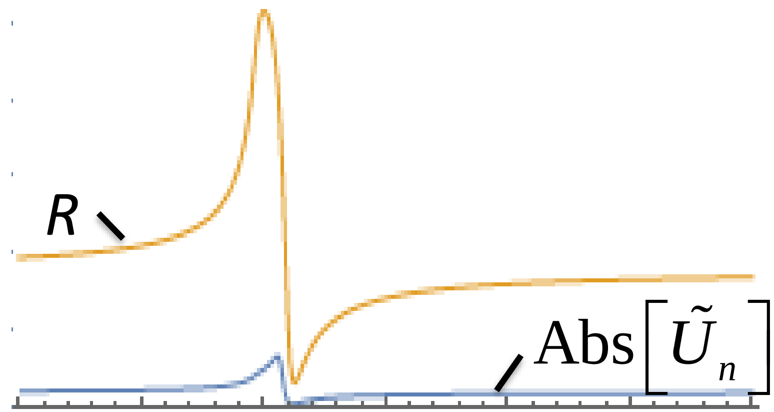
Interpretation:

$\mathrm{Arg}\left[\tilde{U}_n\right]$ →Absorption in grazing incidence, see Mastel *et al*. Appl. Phys. Lett. 2015

Scattered Signal: Interpretation

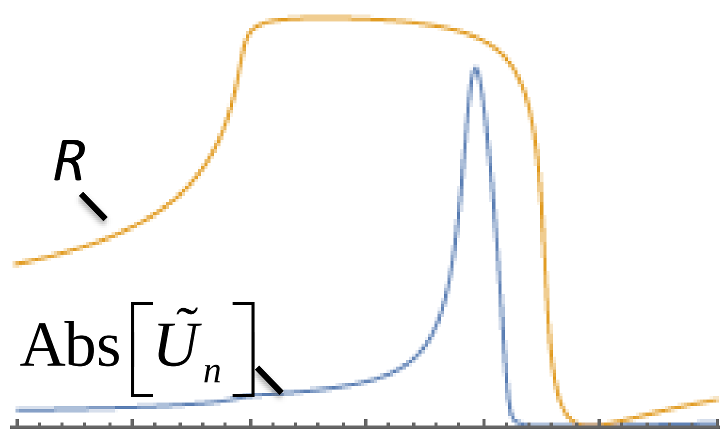
Interpretation: $\mathrm{Abs}\left[\tilde{U}_n\right]$

Reflectivity *R* for
weak oscillator (organics):



➡ Measuring Absorption and Reflectivity in one measurement

For strong oscillator (e.g. SiC):



Enhancing the sensitivity

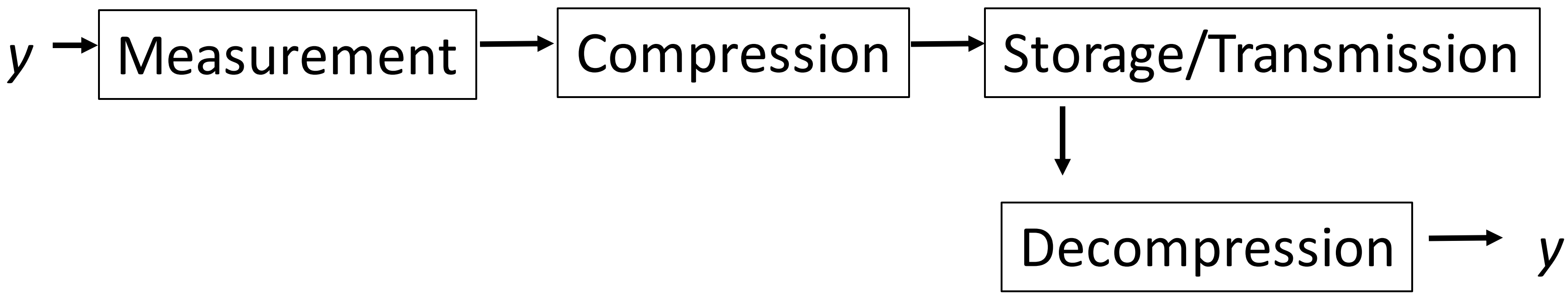
- Nearfield IR Spectroscopy using *s*-SNOM
- **Compressed sensing**
- Radiation sources and detection
- Tailored tips
- Conclusion

In collaboration with
M. Raschke

Center for Ultrafast Nano-Optics

What is Compressed Sensing

Without Compressed Sensing -> compresses only the *data*



Example: digital imaging / JPEG

- DCT of Image y
- Only largest *k* components are stored
- Decompression before viewing

What is Compressed Sensing

Compressed Sensing -> Measurement itself is compressed

y → Compressed Measurement → Storage/Transmission ↓ Reconstruction → *y*

Requirement for Reconstruction:

y must be *sparse* in a suitable basis, $\phi_1(t), \phi_2(t), \ldots$ i.e.:

$$y(t) = \sum_{i=1}^{K} z_i \, \phi_{\pi(i)}(t)$$

Principle:

m Measurements $y(t_1), \ldots, y(t_m)$ and matrix *A* (*m* x *n, n>>m*)

$$\min_z ||\mathrm{z}||_0 \text{ under } \quad y = Az$$

$$\text{with } A_{ij} = \phi_{\pi_j}(t_i), i = 1, \ldots, m, j = 1, \ldots, n$$

Compressed Sensing -Example

Application to a 2D map of SNOM spectra:

44 x 41 = 1804 spectra

How many interferometer samples:

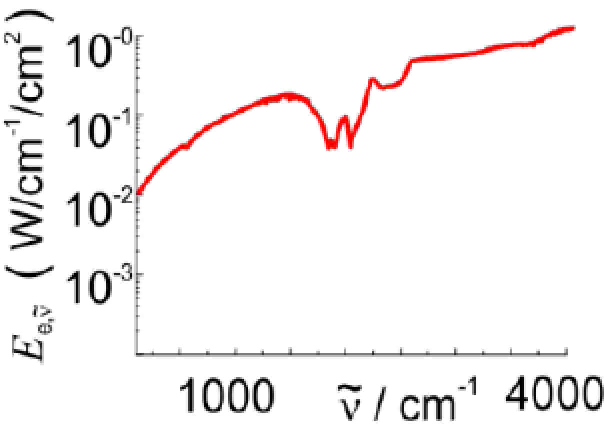
Spectral range $\tilde{\nu} \leq 3200 \text{ cm}^{-1}$

Resolution $\Delta\tilde{\nu} = 6 \text{ cm}^{-1}$

→ Sweep interferogram over

$x = 1600\ \mu\text{m}$ at 1024 samples

IR radiation provided by the electron storage ring



Datapoints: 1804 x 1024 $\approx$ 1.8 x 10^6

with typical integration time of 10 ms → more than 5 hours

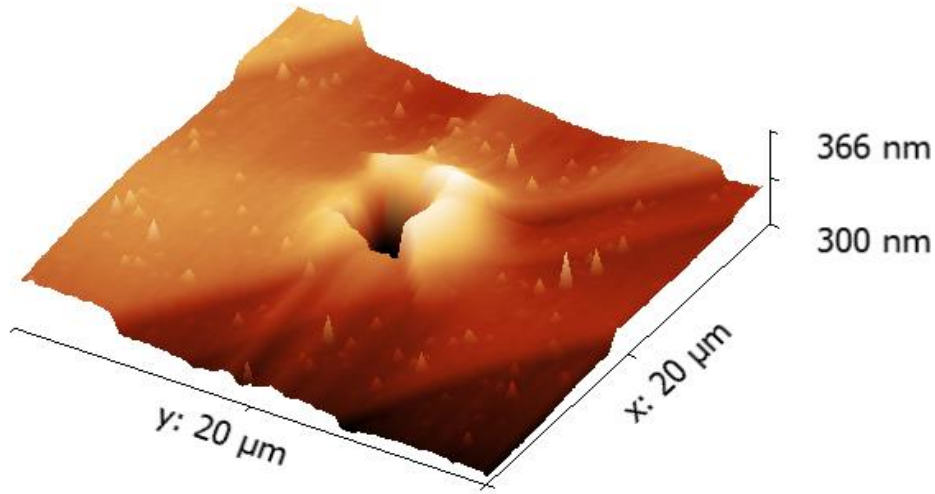
Compressed Sensing - Example

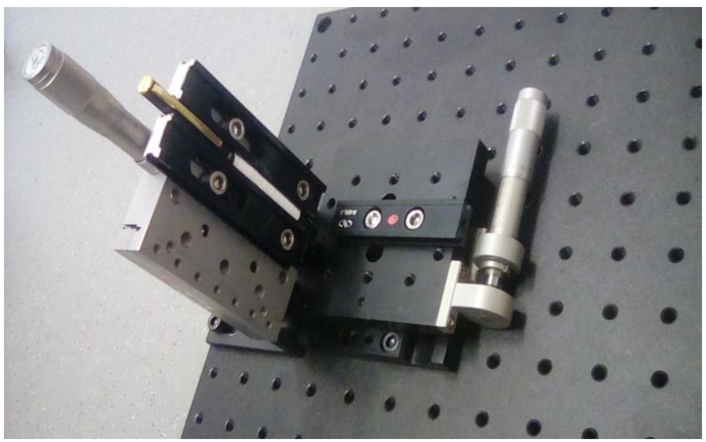
Sample:

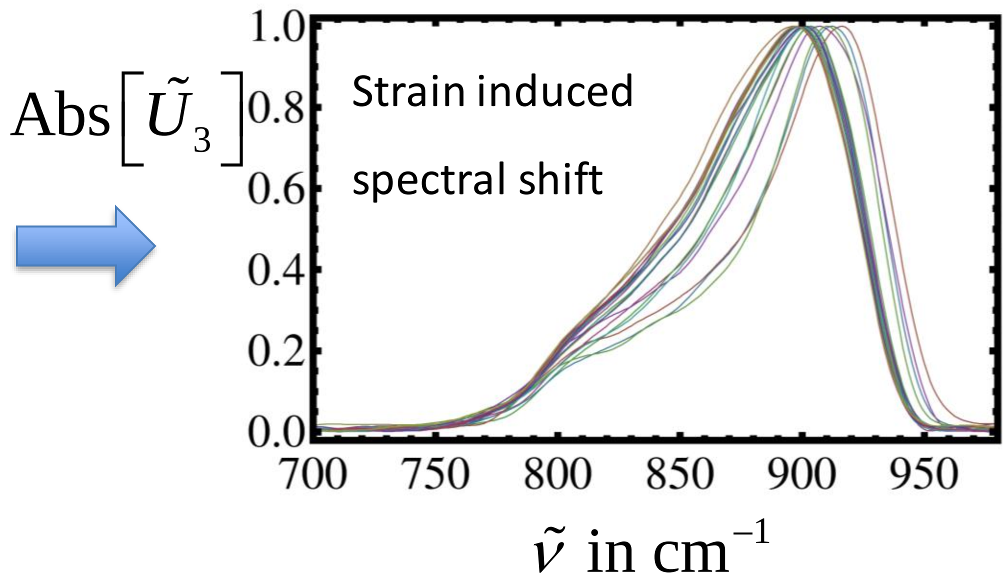
6H-SiC with Graphene

Indent to generate

2D strain:

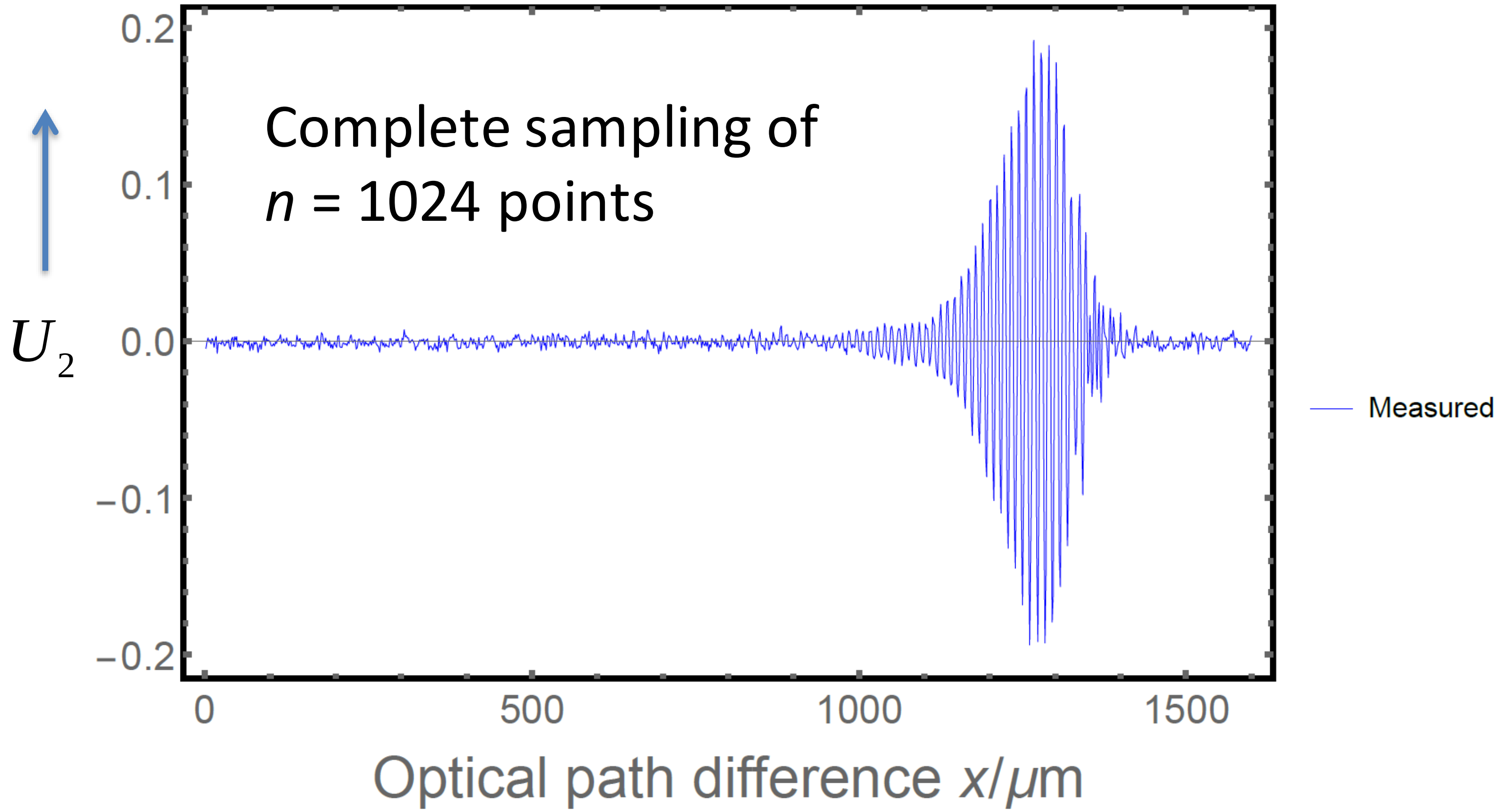






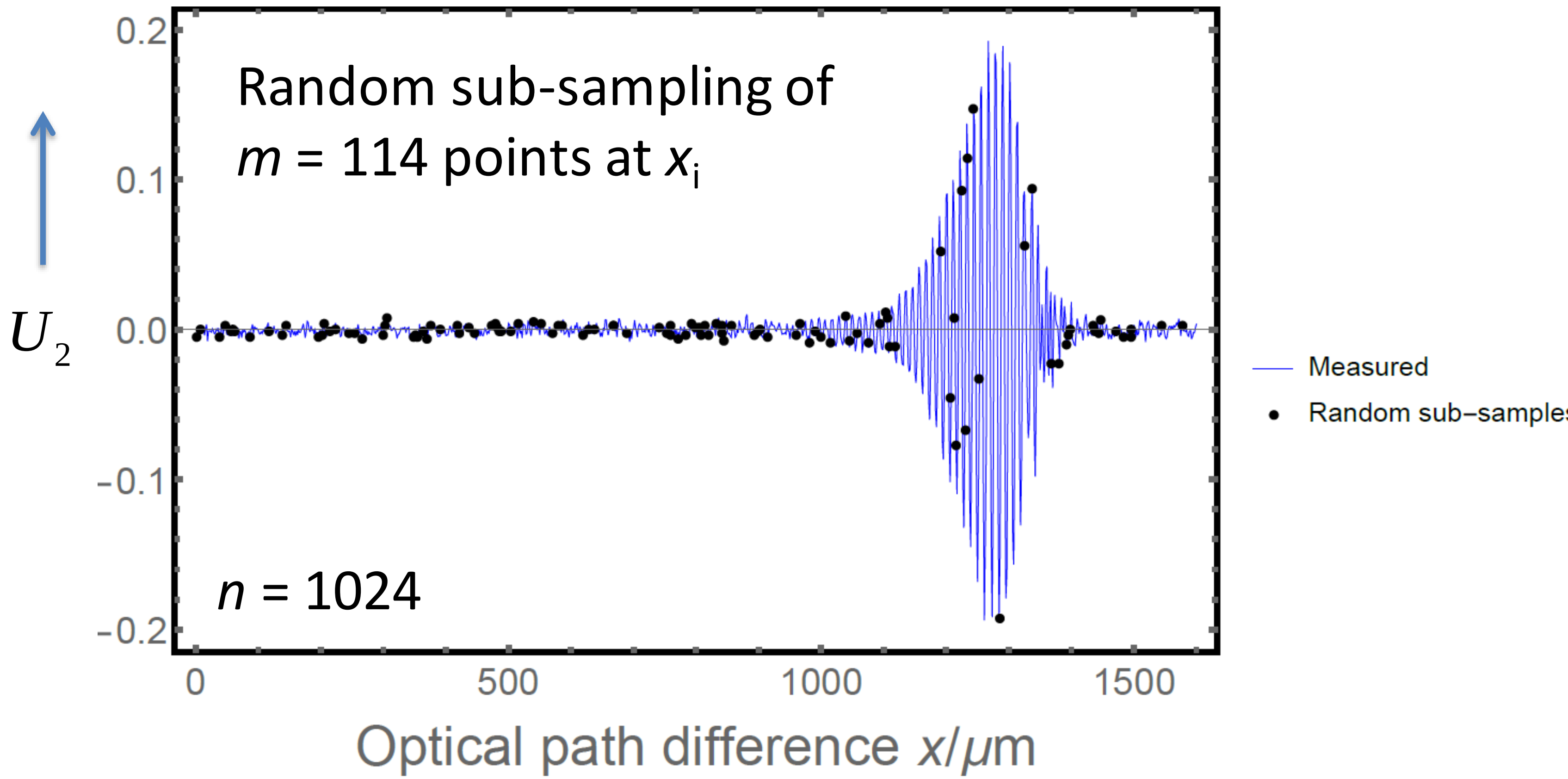
B. Kaestner, F. Schmähling, A. Hornemann, G. Ulrich,
A. Hoehl, M. Kruskopf, K. Pierz, M. B. Raschke, G. Wübbeler, C. Elster, Optics Express 2018

Compressed Sensing - Example



Simulate a compressed measurement:

Compressed Sensing - Example

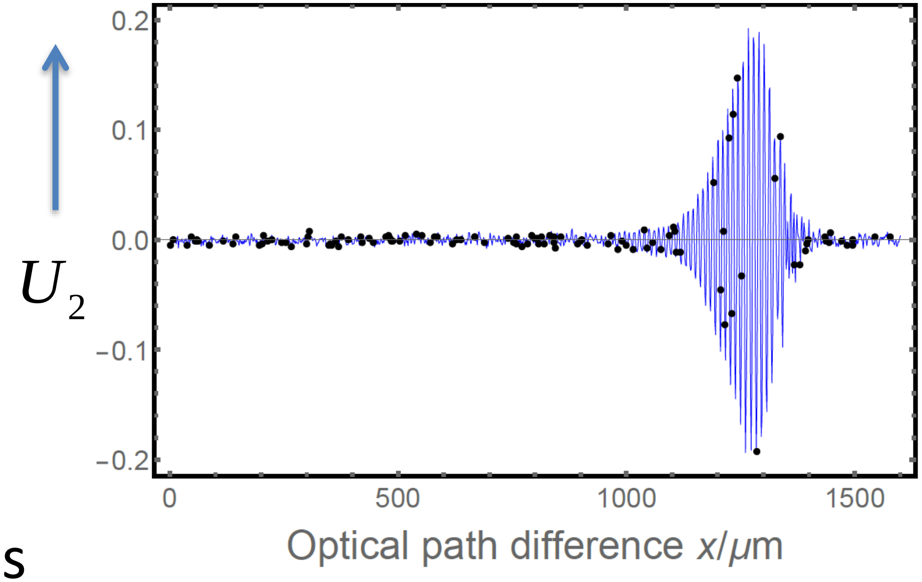


→ Only use 1/9th of measurement samples

Compressed Sensing - Example

Reconstruction of

complete interferogram:



$$y = \left(U_2(x_1), \ldots, U_2(x_m)\right)^T$$

z - the vector of weights

A - matrix $A_{ij} = \phi_j\left(x_i\right)$

Fourier basis function
(in this case)

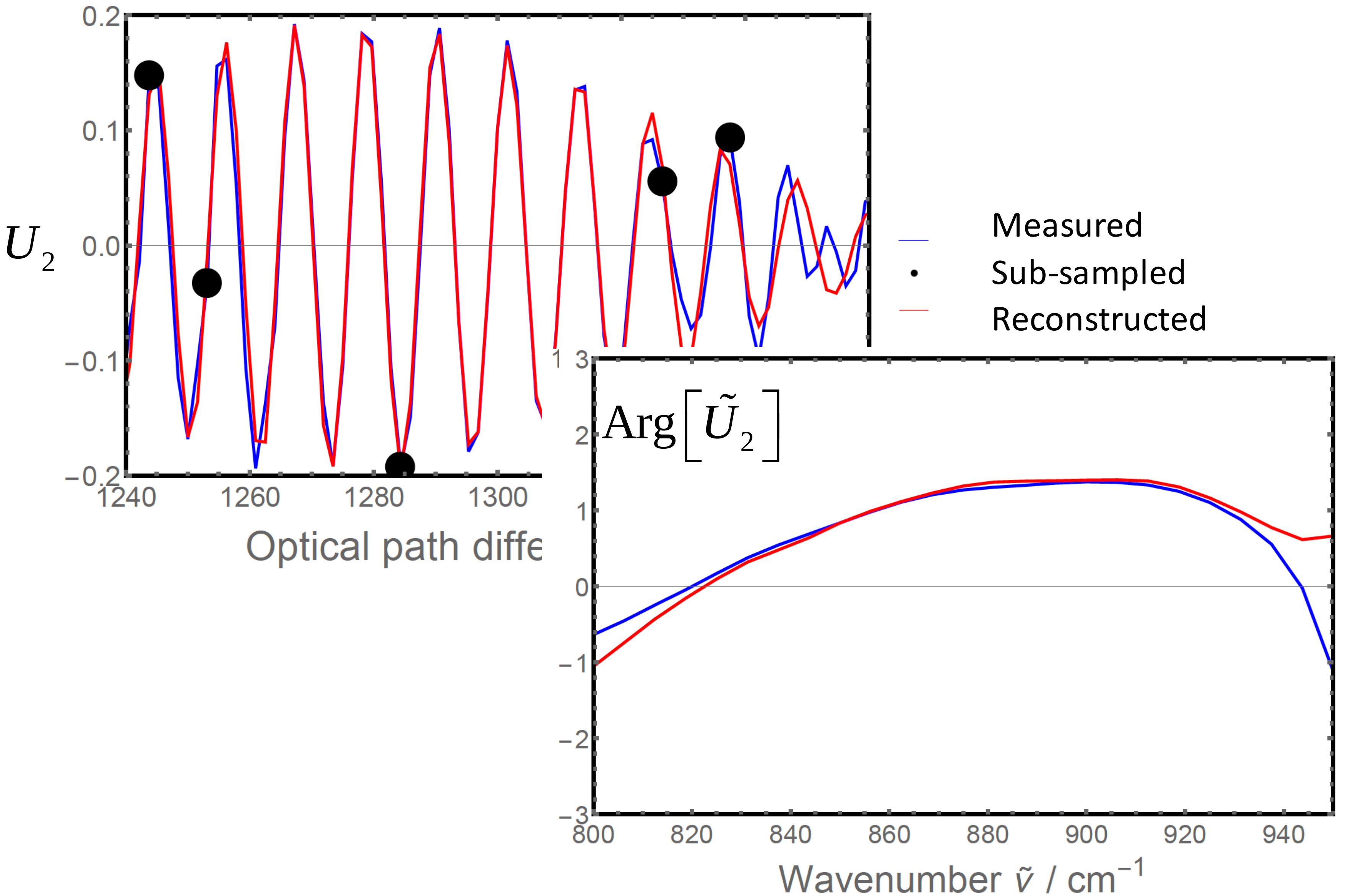
Solve optimization problem:

$$\min_z \|z\|_0$$

subject to $y = Az$

$\|z\|_0$ number of nonzero elements of z

Compressed Sensing - Example

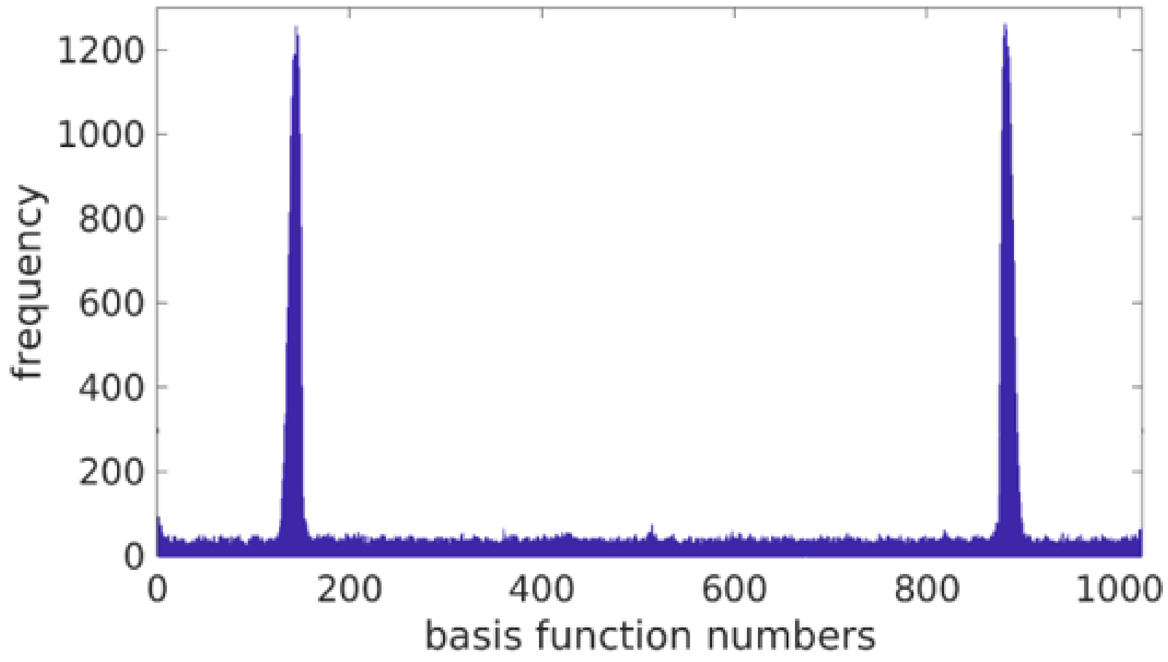


Compressed Sensing - Example

Incorporation of further prior knowledge:

1. Similar spectral components across 2D map (1804 pixel)

➢ Out of 1024 basis functions choose the 50 most frequent ones



➢ Fix this sub-set of 50 functions for the whole 2D map

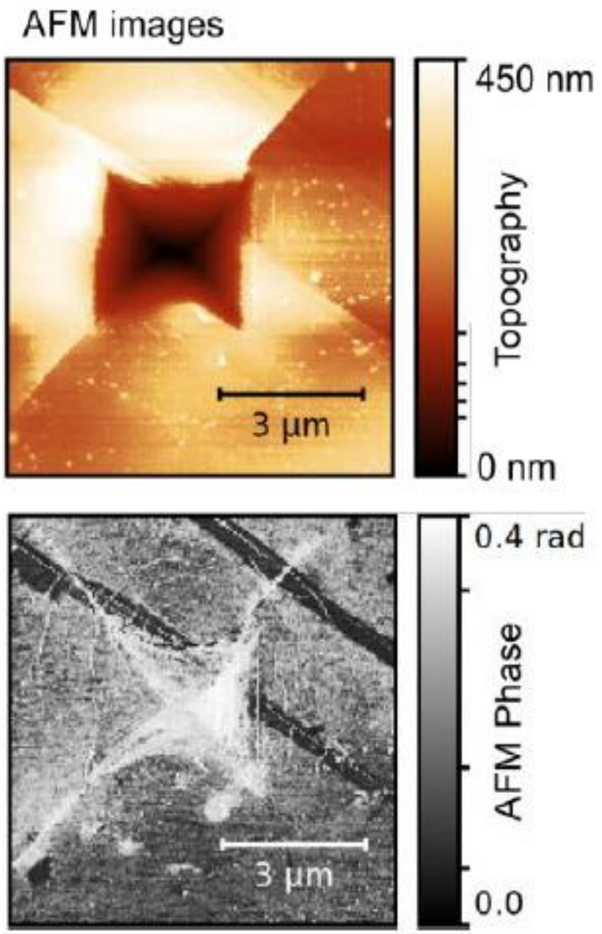
Compressed Sensing - Example

Incorporation of further prior knowledge:

2. Coefficients of basis functions vary smoothly

- The determination of the z-coefficients by fitting to fixed basis set, i.e. solve $y = Az$
- Augment by regularization functional which favours similar values for 8 neighboring pixels
- Regularization parameter determined by L-curve principle

Compressed Sensing - Example



Hypothesis: sensitivity enhancement by measuring 1/9th samples at 9 fold increased integration time

Enhancing the sensitivity

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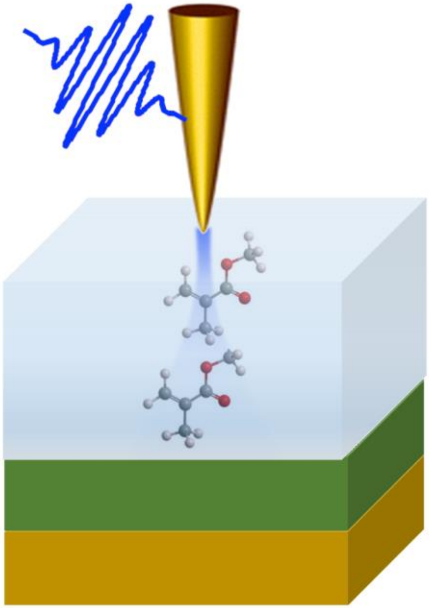
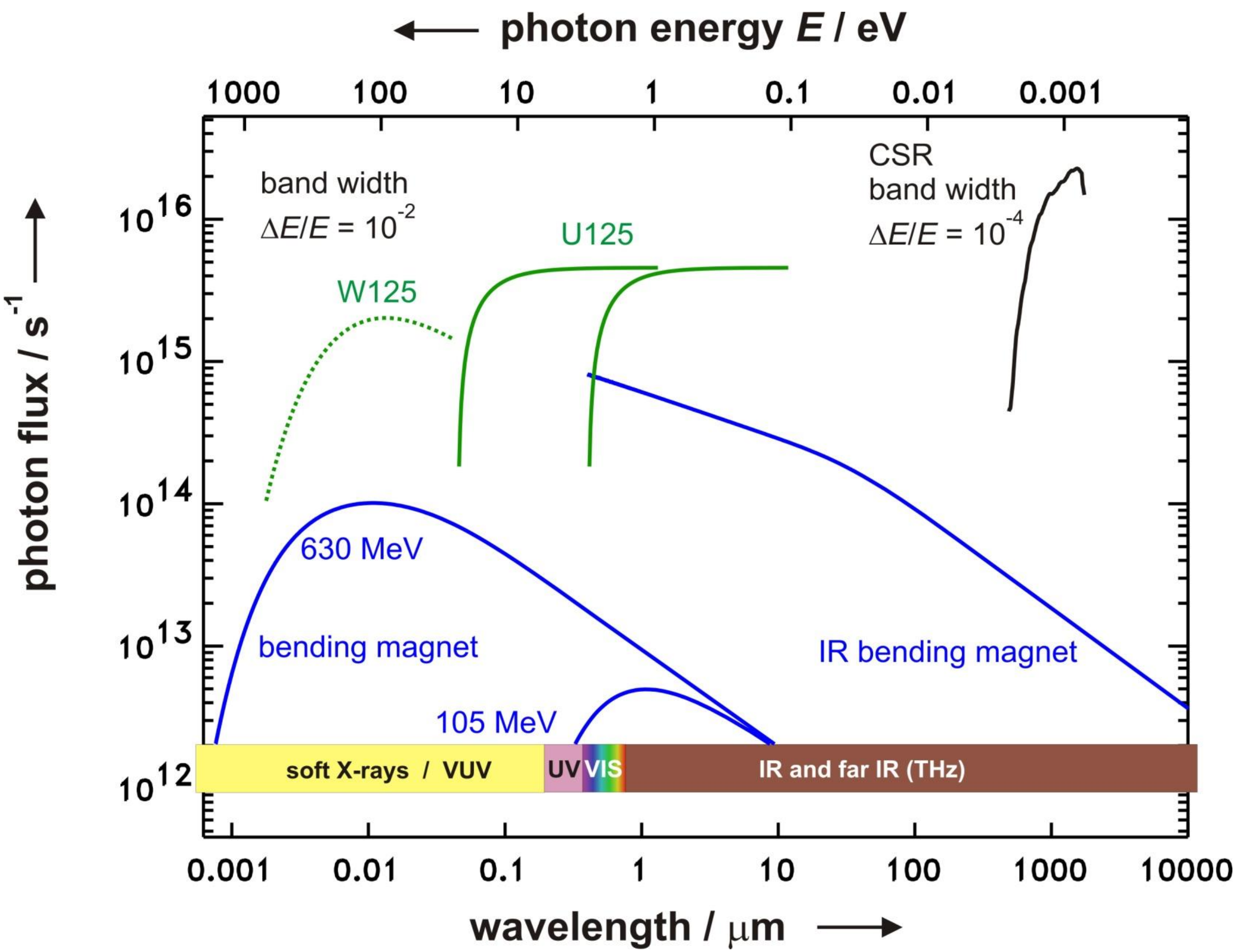
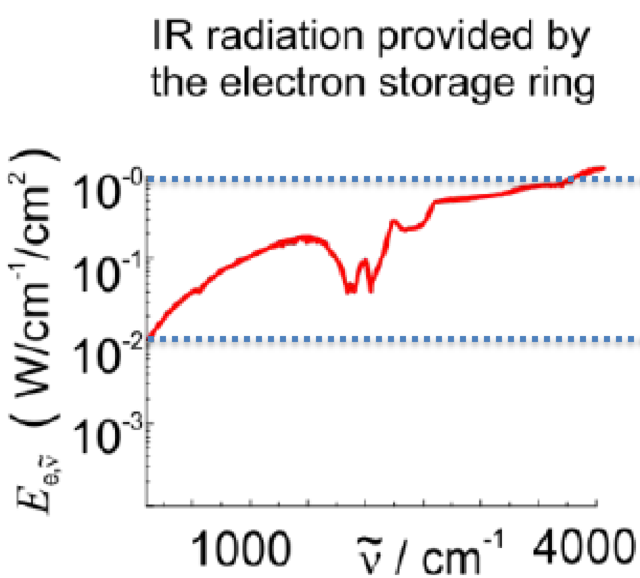


Synchrotron radiation

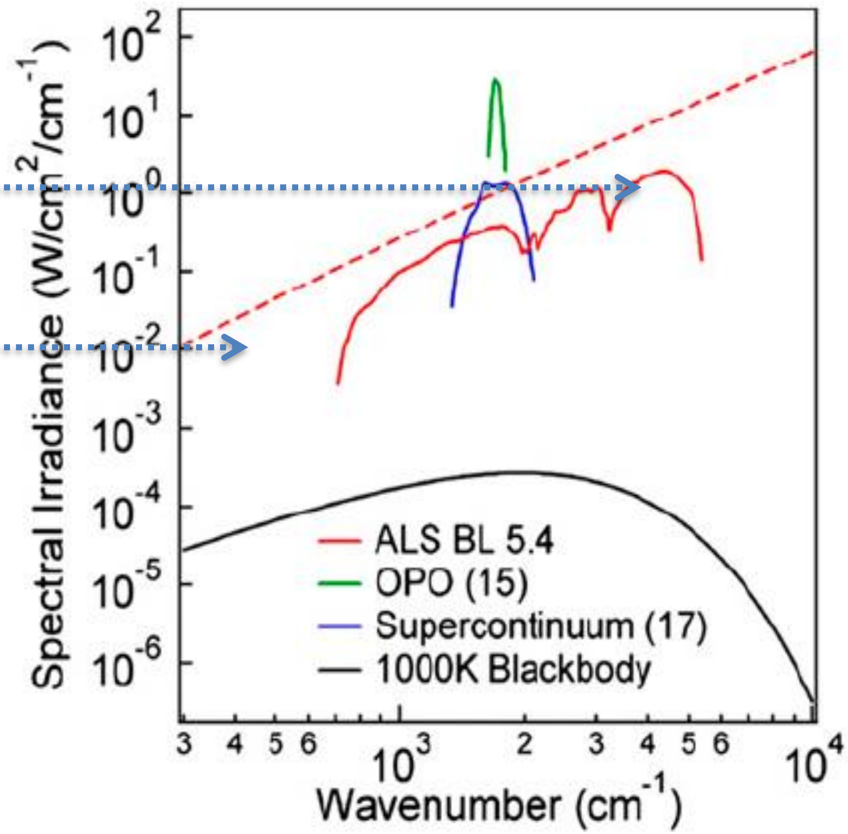
Advantage of synchrotron radiation: ultra-broadband spectrum



Metrology **L**ight **S**ource,
Berlin-Adlershof

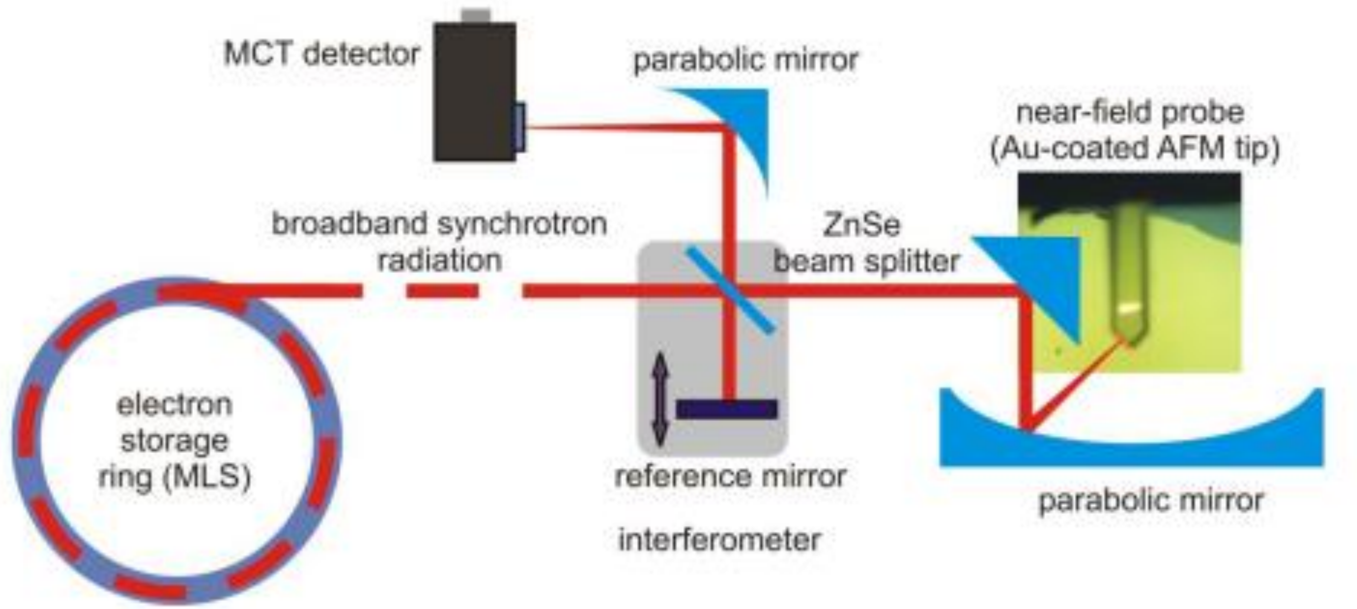


For comparison:
Bechtel et al, PNAS 2014



Pulsed at 500 MHz, 30 ps

Detection

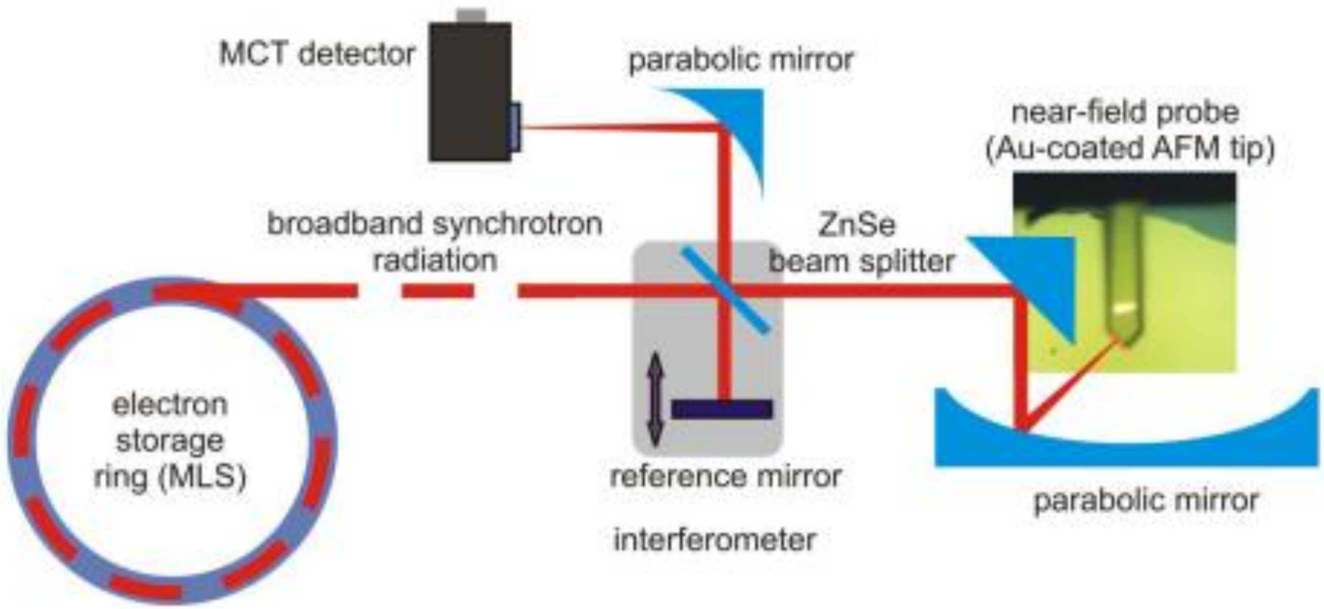


Requirements: scattered nearfield from tip VERY WEAK!

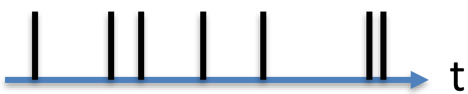
Judge by NEP:

Signal power for SNR = 1 for ½ sec integration time

Detection



Ultimate limit: shot noise of optical radiation



$$\frac{\left\langle \Delta p^2 \right\rangle}{\Delta f} = 2h\frac{c}{\lambda}P$$

$$\approx 10^{-12}\ \mathrm{W}/\sqrt{\mathrm{Hz}}$$

For monochromnatic light of λ = 10 μm
Average power P = 200 μW x ¼ (due to beamsplitter)

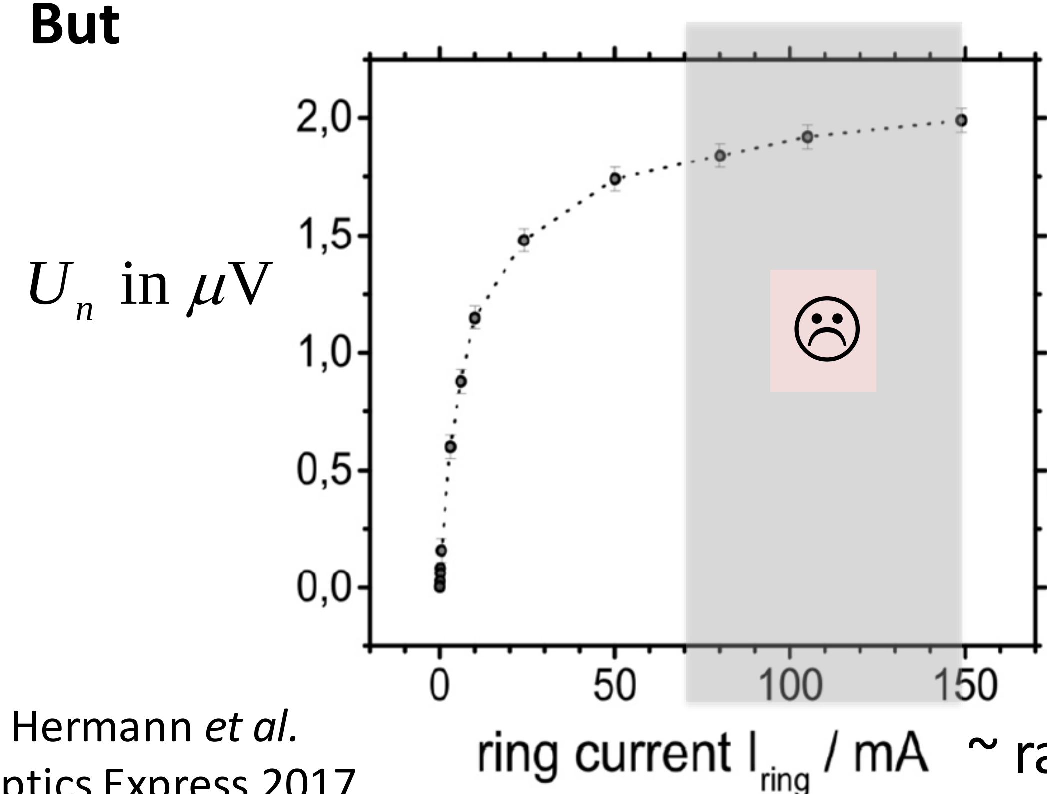
Detection

Best experience with

Mercury Cadmium Telluride photoconductive detectors

Manufacturer specifies $\mathrm{NEP} = 10^{-12}\ \mathrm{W}/\sqrt{\mathrm{Hz}}$ ☺

But



Typical measurement range

~ radiation intensity

Novel detector concept
or
Increase signal scattered from tip

P. Hermann *et al.* Optics Express 2017

Enhancing the sensitivity

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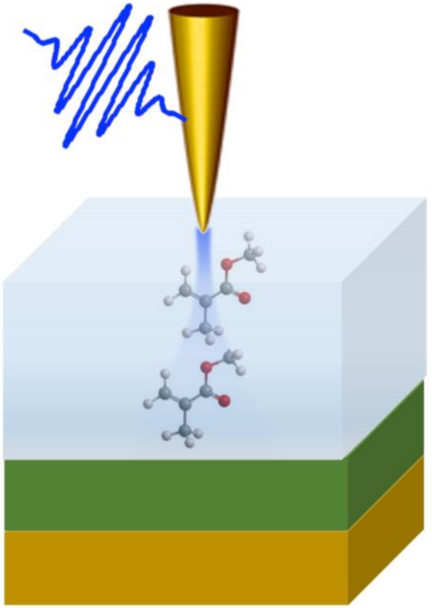
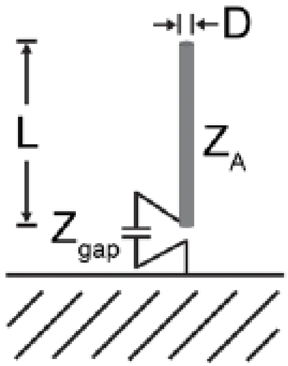


Tailored Tips

Antenna model: see Mastel *et al.* Nano Lett. 2017:

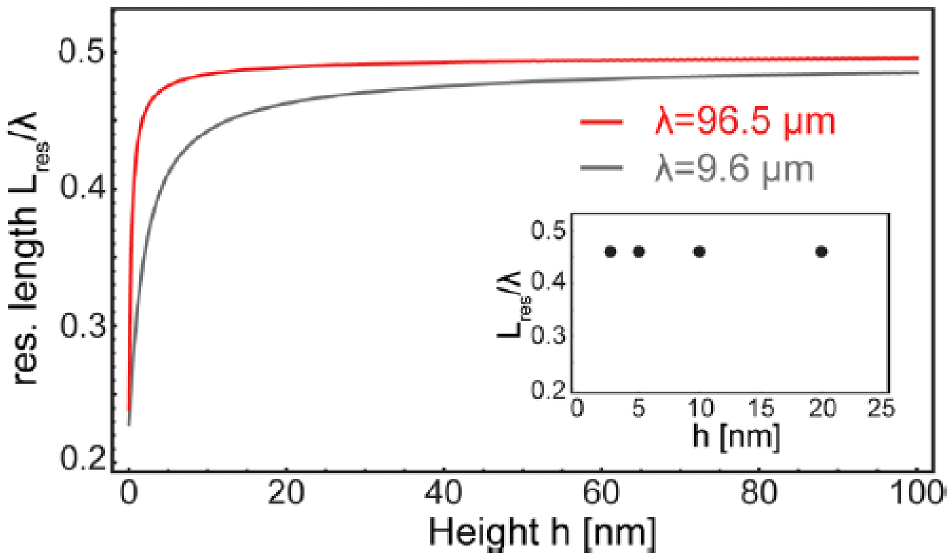


$$Z_A = R_A + iX_A$$

$$Z_{\text{gap}} = R_{\text{gap}} + iX_{\text{gap}} = -\frac{ih}{\omega\varepsilon D^2}$$

Resonance for:

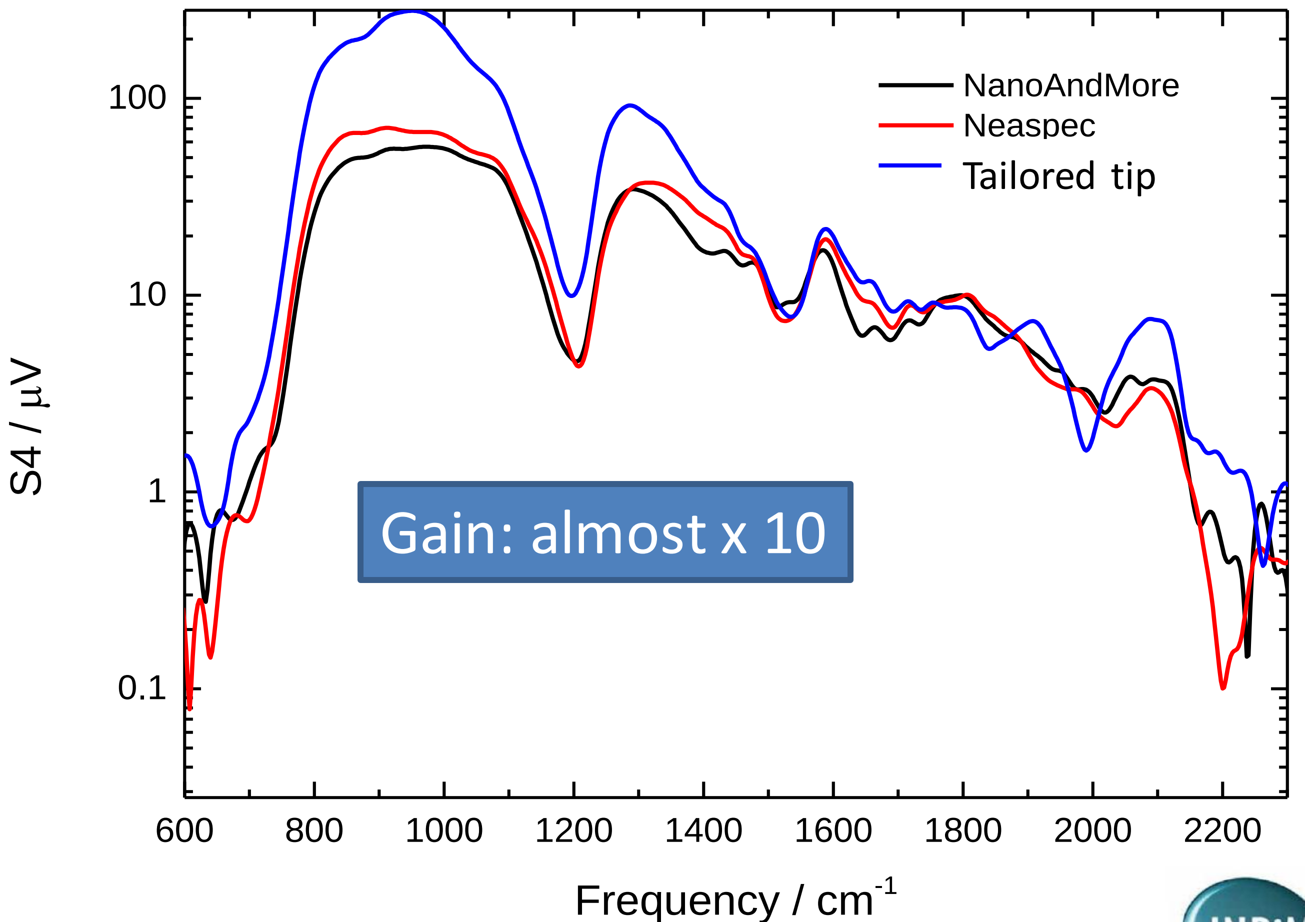
$$-X_{\text{gap}} = X_{\text{A}}$$



Choose:

≈ 4 µm long tip for resonance around λ = 10 µm

Result: Measured spectrum on Au surface



But:

alignment ciritical; need robust determination of field enhancement

ISTITUTO NAZIONALE DI RICERCA METROLOGICA

Luca Boarino, Giulia April

Field enhancement - determination

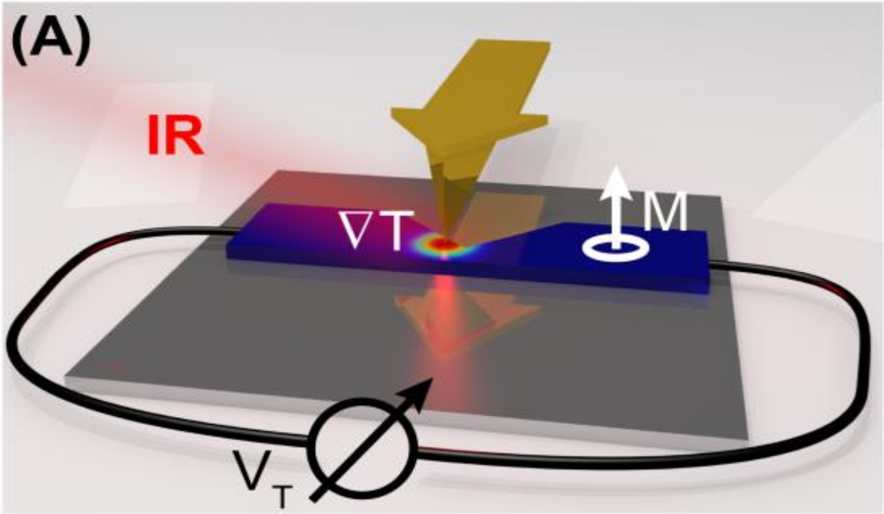
In collaboration with:
J. Wunderlich, Hitachi Cambridge Laboratory
E. Pfitzner, J. Heberle-group, FU Berlin

E. Pfitzner, X. Hu, H. W. Schumacher, A. Hoehl, D. Venkateshvaran, M. Cubukcu, J.-W. Liao, S. Auffret, J. Heberle, J. Wunderlich, and B. Kästner
arXiv1808.10767, 2018.

Field enhancement - determination

By scanning a magnetic nanowire:

Anomalous **N**ernst **E**ffect leads to generation of V_T

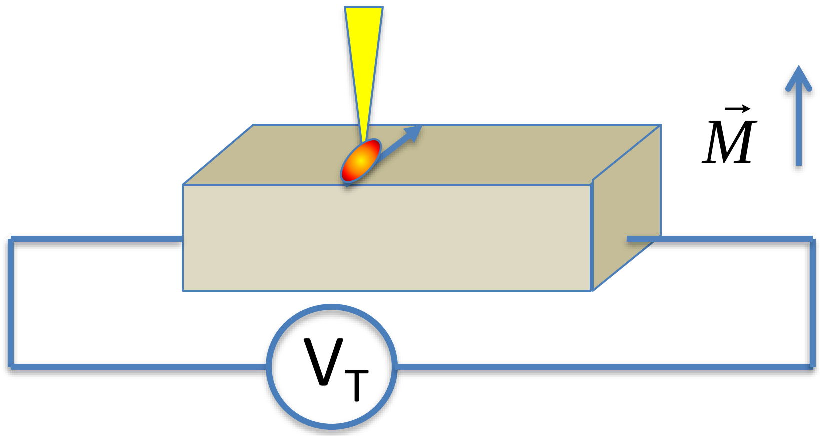


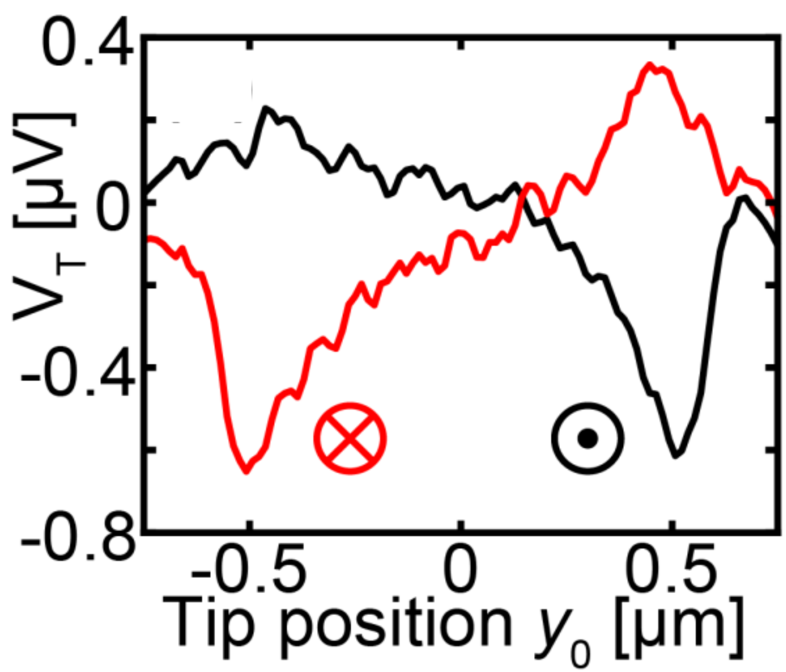
How to acess field enhancement:

- Tip heats chip surface at its position (x_0,y_0), map $V_T(x_0,y_0)$
- Relate $V_T(x_0,y_0)$ – map to temperature profile $T(x,y)$ by comparing to on-chip heaters and sensors
- Obtain power dissipation underneath tip, and corresponding field

E. Pfitzner *et al.*, arXiv1808.10767, 2018.

Field enhancement - determination





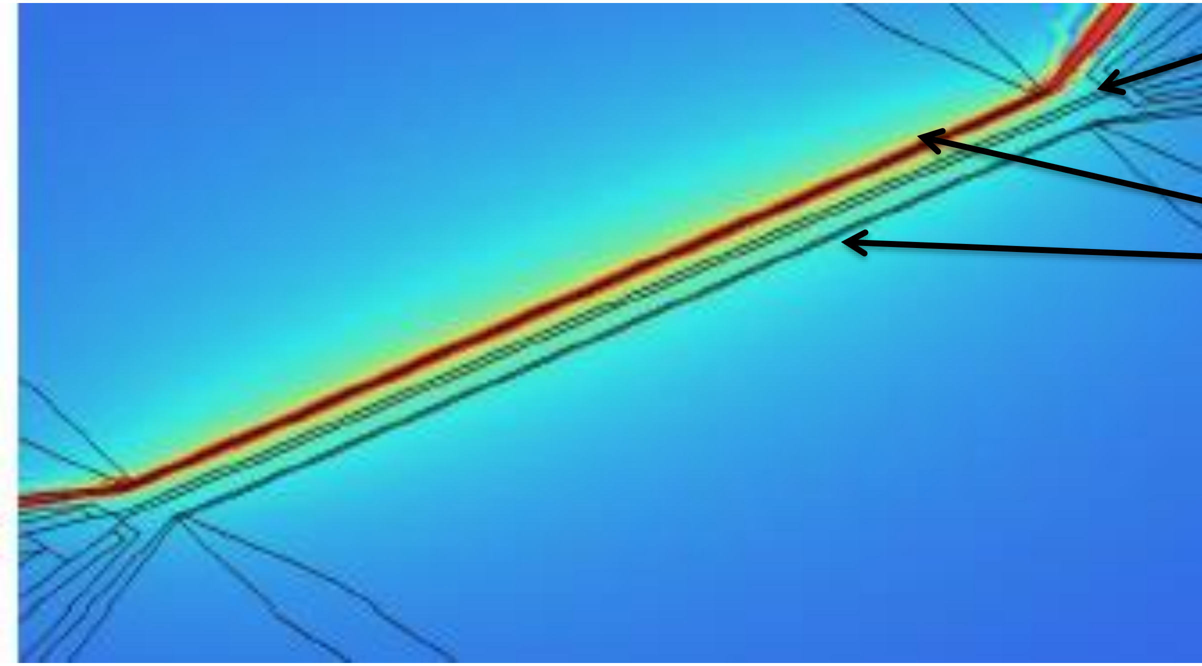
How to obtain:

$$V_T(x_0, y_0) \rightarrow T(x_0, y_0, x, y)$$

E. Pfitzner *et al.*, arXiv1808.10767, 2018.

Field enhancement - determination

Obtain $V_T\left(x_0, y_0\right) \rightarrow T\left(x_0, y_0, x, y\right)$ using external heaters:



Magnetic wire

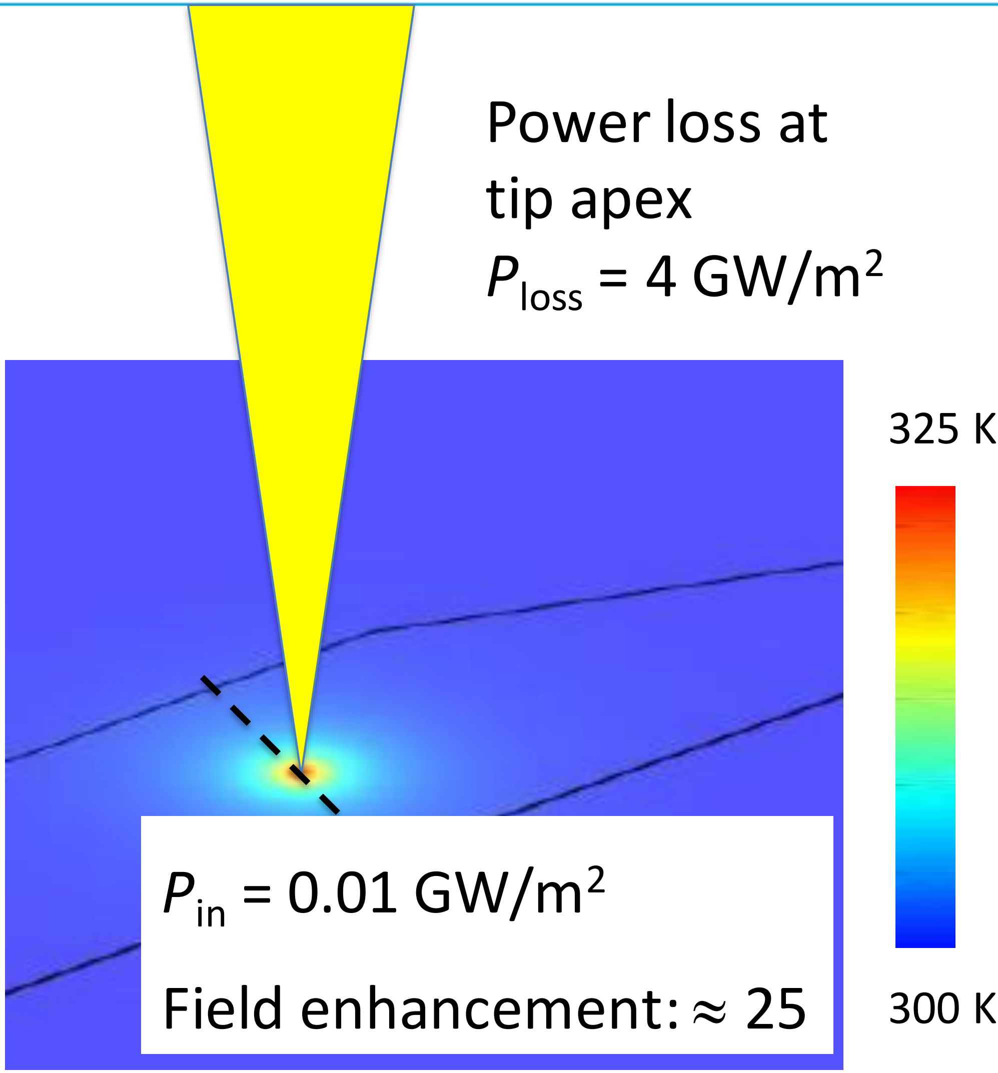
Heaters and *T*-sensors

Comsol simulations by Xiukun Xu, PTB

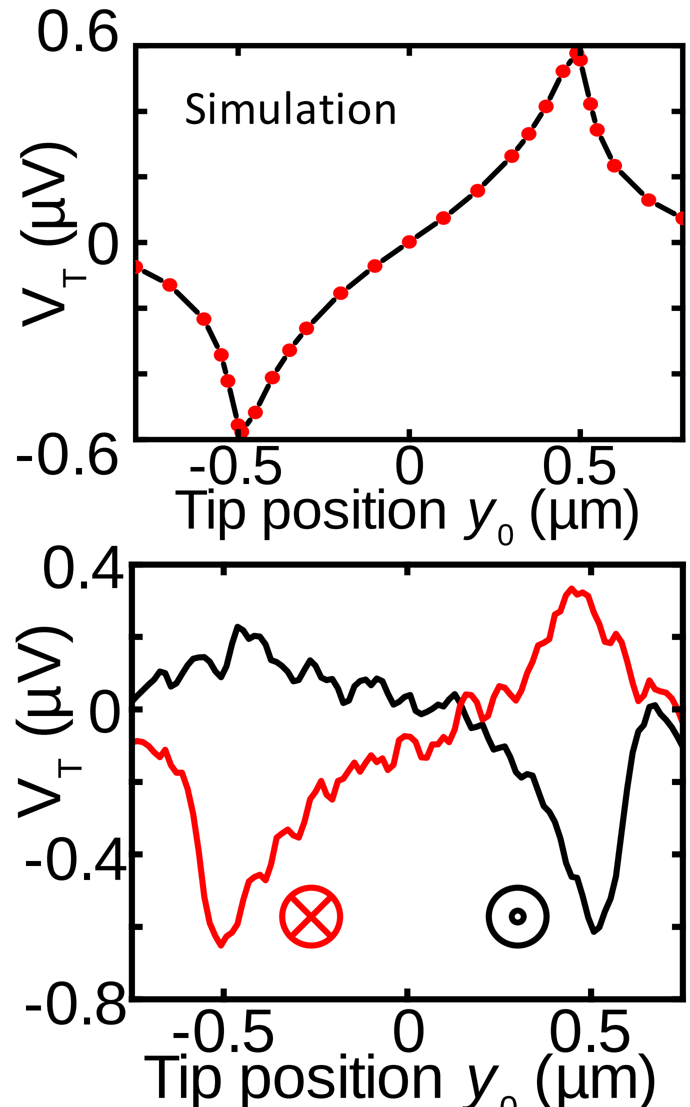
$$\left|V_{\mathrm{ANE}}\right| = \left|N_{\mathrm{ANE}}\right| \mu_0 M_S l \left\langle \frac{\partial T}{\partial y} \right\rangle$$

$$\left|N_{\mathrm{ANE}}\right| = 0.054\ \mu\mathrm{V/KT}$$

Field enhancement - determination



Comsol simulations by Xiukun Xu, PTB



E. Pfitzner *et al.*, arXiv1808.10767, 2018.

Conclusions

Standard *s*-SNOM ignores any prior knowledge.

Compressed sensing: exploit prior knowledge at measurement stage

- Spectral sparsity
- Spatial smoothness
- Future: Spectra of individual components

→Rapid hyperspectral imaging or sensitivity enhancement

Further strategies for enhancing molecular sensitivity:

- Novel detector concepts
- Tailored Nearfield-AFM tips

Acknowledgements

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HITACHI Inspire the Next

Jörg Wunderlich
Murat Cubukcu

INRiM Istituto Nazionale di Ricerca Metrologica

Luca Boarino, Giulia April

PTB

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Klaus Pierz, Mattias Kruskopf

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