SINS:
Synchrotron Infrared Nano Spectroscopy

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NSLS-II, BNL

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Robert Johns and Delia Milliron (UT Austin)
Elad Gross (Hebrew University of Jerusalem)
F. Toste (UC Berkeley)
Stephanie Gilbert Corder and Mengkun Liu
(Stony Brook University)
Tiger Tao (UT Austin)

ALS
SYNCHROTRON INFRARED BEAMLINES

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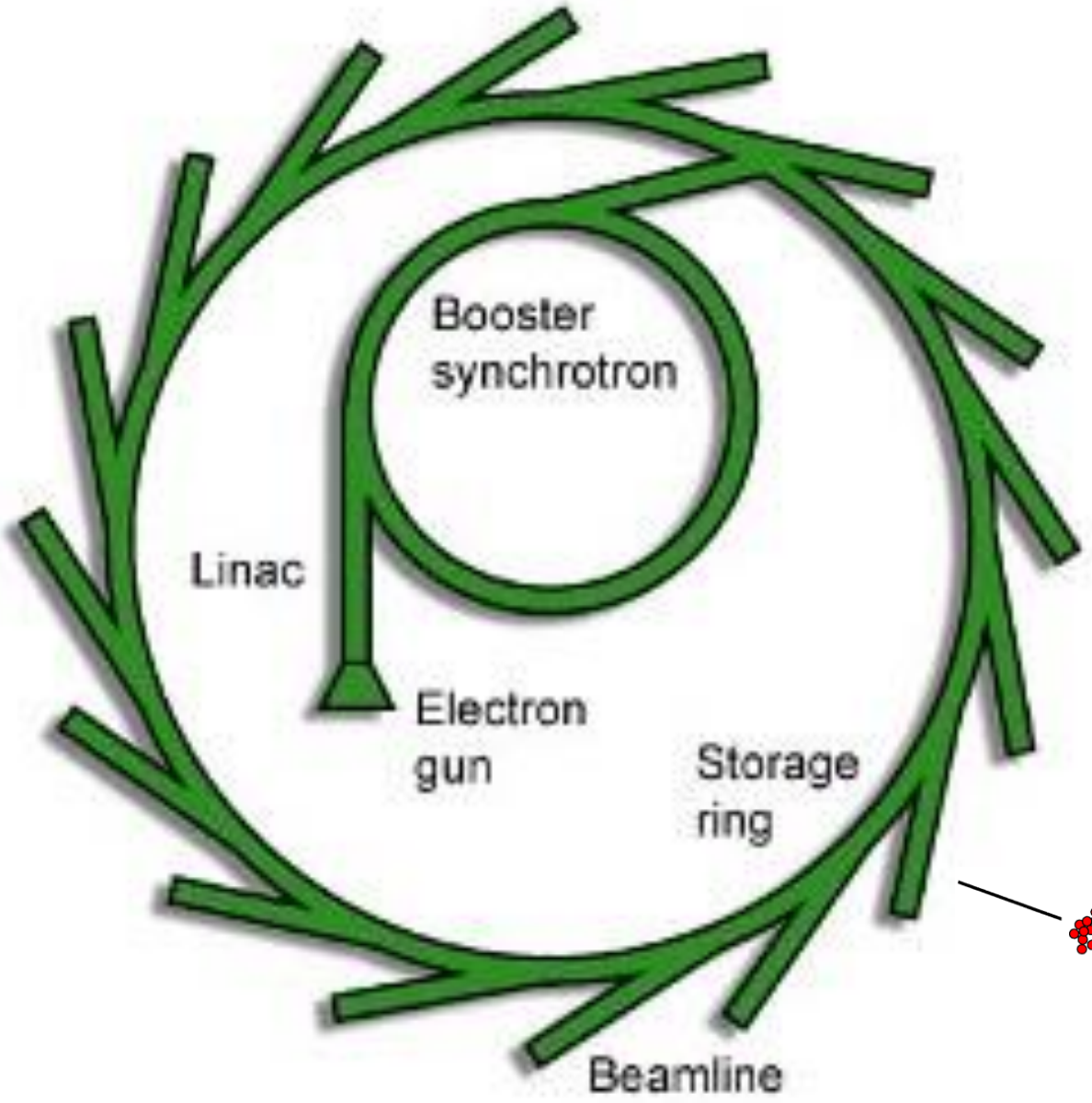
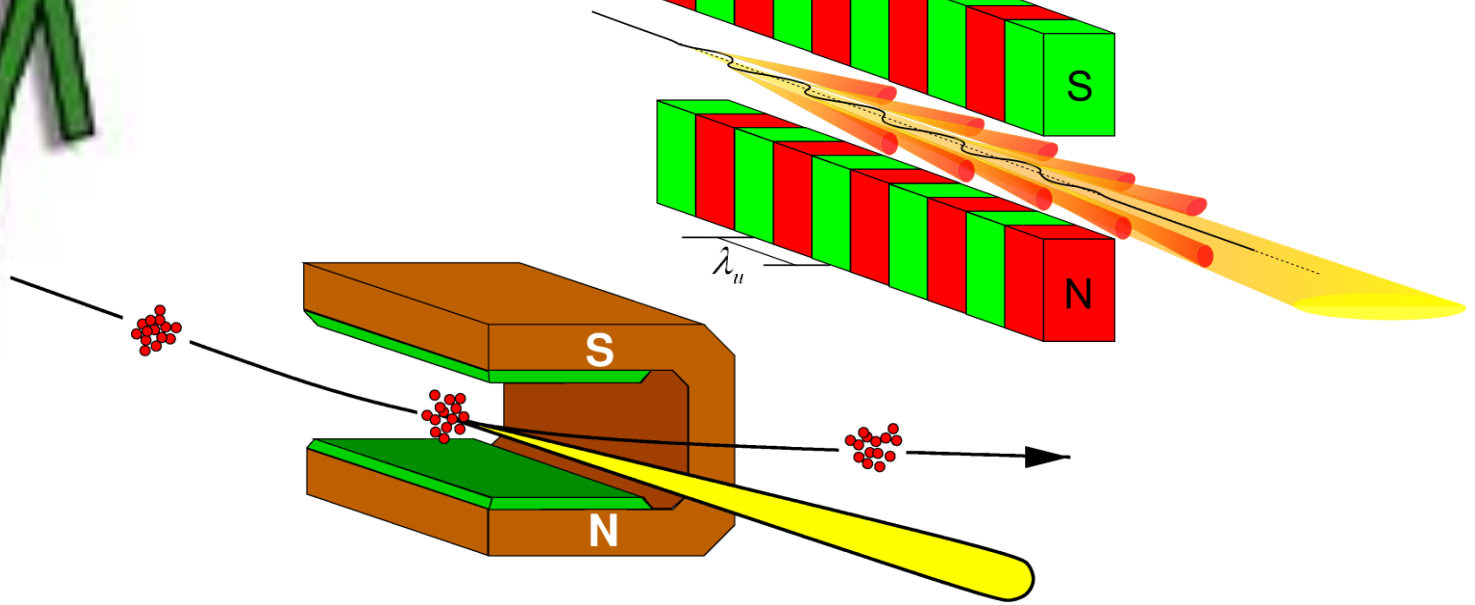
LAWRENCE BERKELEY NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

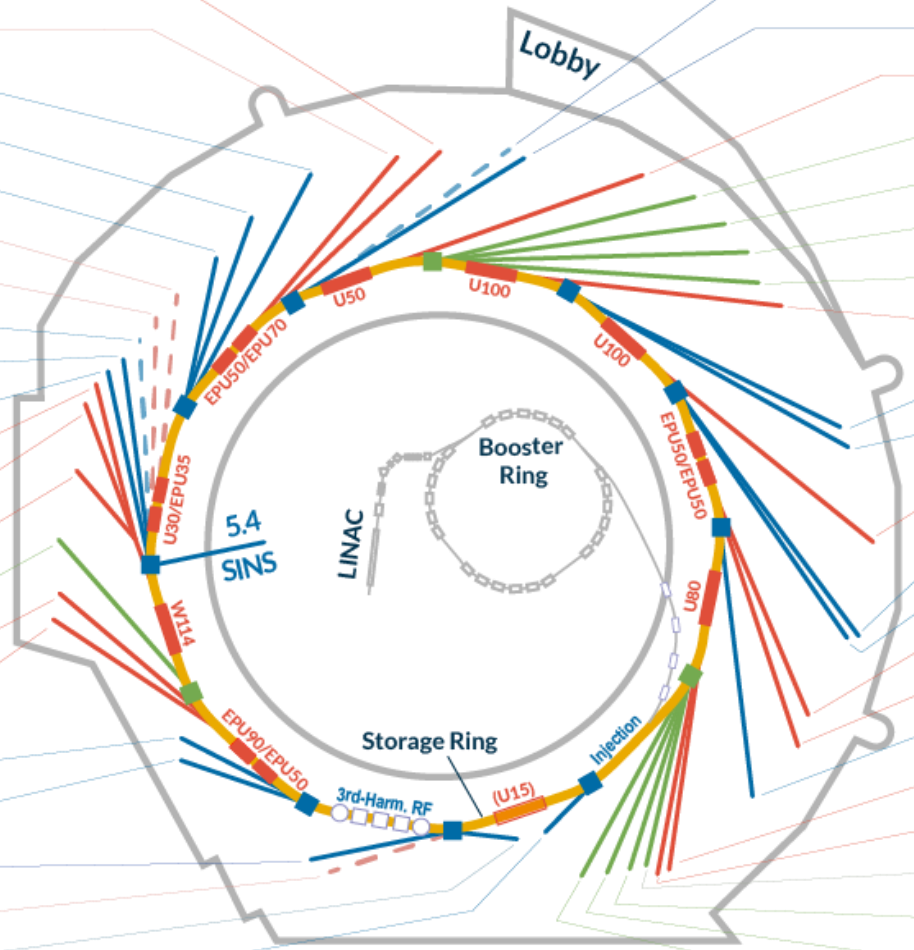
Synchrotron Light Sources





Synchrotron Light Sources

ALS Beamlines



Quantum Materials (MAESTRO) 7.0.2
Coherent Scattering and Microscopy (COSMIC) 7.0.1
Calibration, Optics Testing, Spectroscopy 6.3.2
Magnetic Spectroscopy / Materials Science 6.3.1
Full-Field Transmission Soft X-Ray Microscopy 6.1.2
Energy, Catalytic, and Chemical Science (AMBER) 6.0.1
Double-Dispersion RIXS (QERLIN) 6.0.2
Polymer STXM 5.3.2.2
STXM 5.3.2.1
Research and Development 5.3.1
Macromolecular Crystallography (BCSB) 5.0.3
Macromolecular Crystallography (BCSB) 5.0.2
Macromolecular Crystallography (BCSB) 5.0.1
Macromolecular Crystallography (MBC) 4.2.2
High-Resolution Spectroscopy (MERLIN) 4.0.3
Magnetic Spectroscopy and Scattering 4.0.2
General X-Ray Testing Station 3.3.2
X-Ray Footprinting 3.2.1
National Center for X-Ray Tomography 2.1
Macromolecular Crystallography (GEMINI) 2.0.1
IR Imaging and Tomography 2.4
IR Spectromicroscopy 1.4

7.3.1 High-Pressure In Situ Soft X-Ray Spectroscopy
7.3.3 SAXS/WAXS/GISAXS
8.0.1 Surface and Materials Science (RIXS)
8.2.1 Macromolecular Crystallography (BCSB/HHMI)
8.2.2 Macromolecular Crystallography (BCSB/HHMI)
8.3.1 Macromolecular Crystallography (TomAlberTron)
8.3.2 Tomography (micro-CT)
9.0 Chemical Transformations
9.3.1 Tender X-Ray Spectroscopy
9.3.2 Ambient-Pressure Soft X-Ray Spectroscopy
10.0.1 ARPES, SpinARPES
10.3.1 X-Ray Fluorescence Microprobe
10.3.2 Hard X-Ray Microprobe
11.0.1 PEEM3/Resonant Soft X-Ray Scattering
11.0.2 Molecular Environmental Science
11.3.2 EUV Lithography Photomask Imaging (SHARP)
12.0.1 EUV Lithography Nanopatterning (MET/MET5)
12.0.2 Coherent X-Ray Scattering
12.2.1 Small-Molecule Crystallography
12.2.2 Diffraction Under Non-Ambient Conditions
12.3.1 SIBYLS—MX and SAXS
12.3.2 Microdiffraction

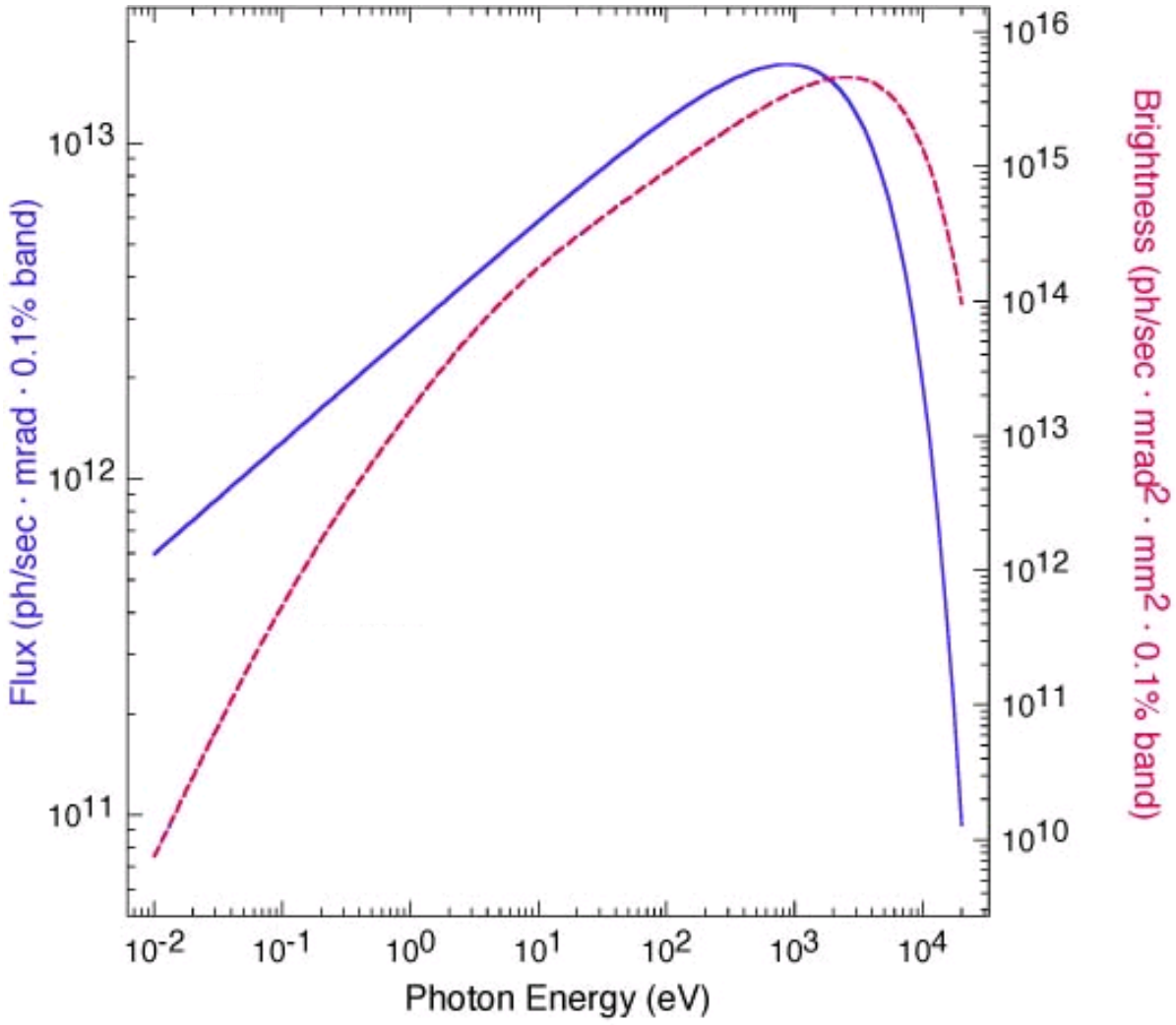
KEY — Operational — — Under Development

Insertion Device Beamlines	Bend Magnet Beamlines	Superbend Beamlines

4.2018

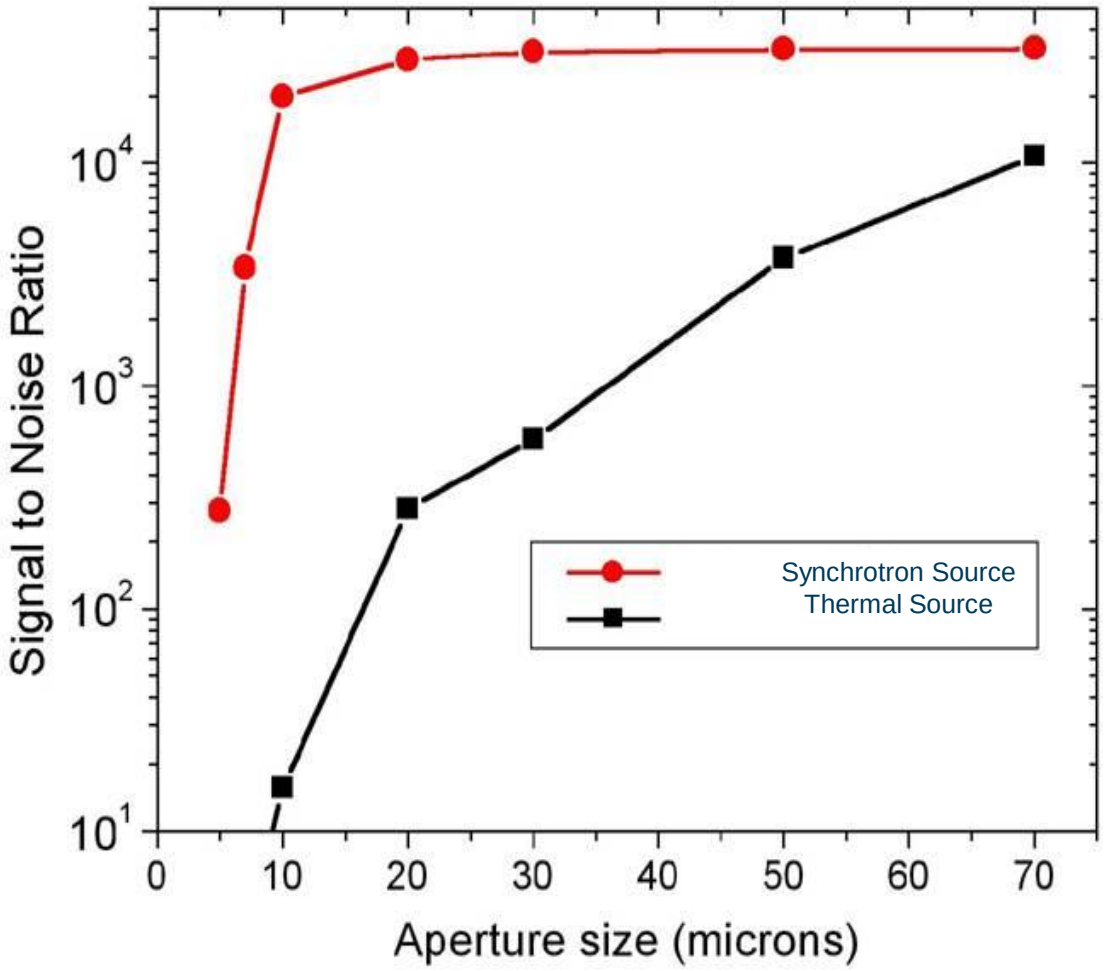
Synchrotrons make IR too!

Bend magnets: The ultimate broadband source



Why use infrared at a synchrotron?

Synchrotron IR is 1000x *brighter* than
a conventional blackbody source



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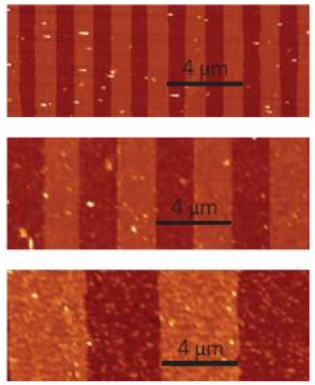
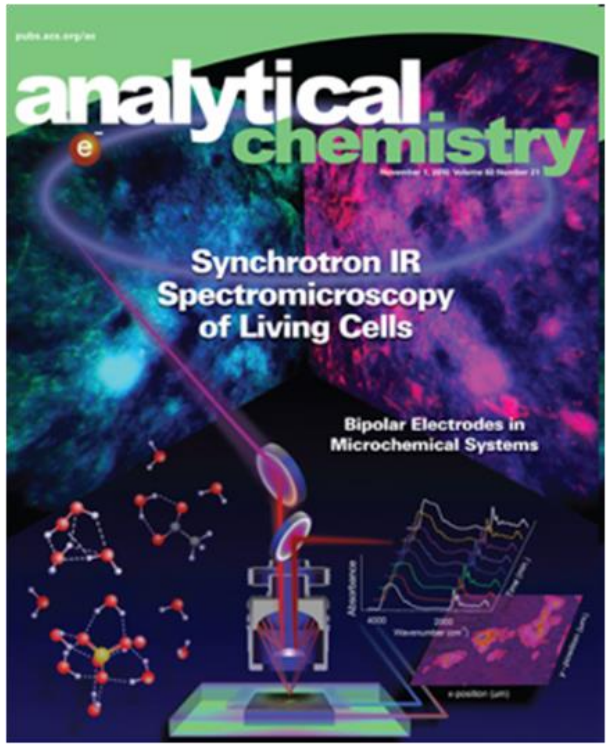
From deep oceans to outer space…



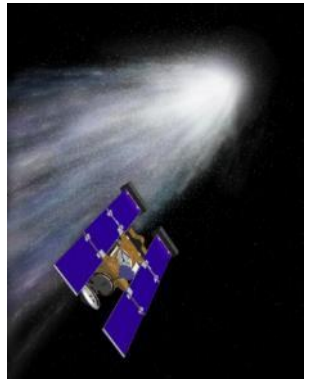
Nature Physics, 10, 743 (2014)
Nature Nanotech., 6, 630 (2011)
Nature, 471, 617 (2011)

Science, 330, 204 (2010)



Anal. Chem, 82, 8757 (2010)

Anal. Chem, 86, 521 (2014)



Science, 314, 1728 (2006)
Science 345, 786 (2014)

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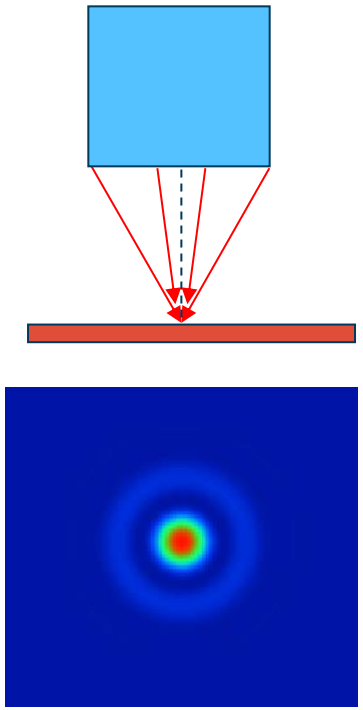
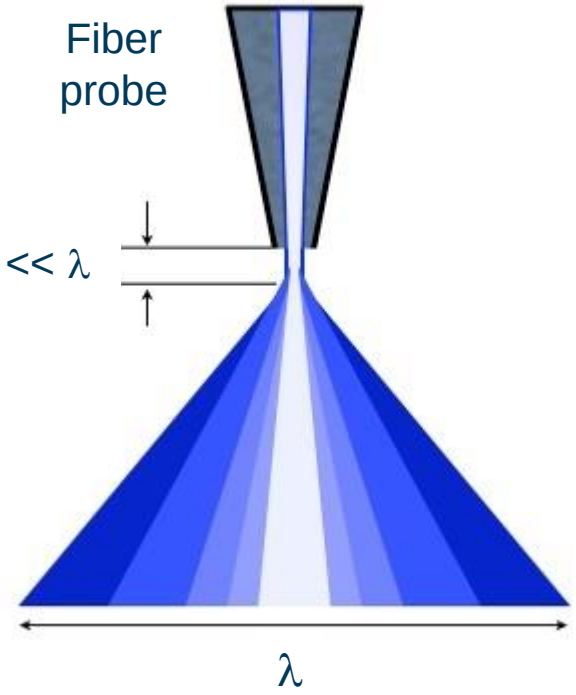
IR's wavelength problem: the diffraction limit

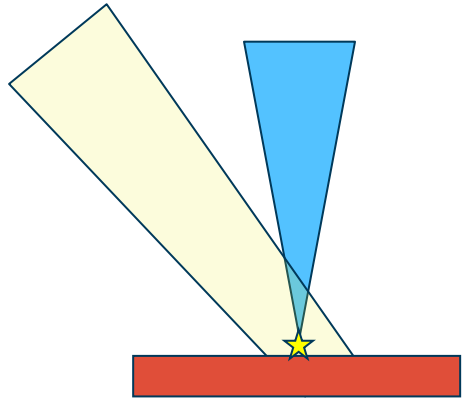
Far-field



Near-field



Apertureless



$$R = \frac{\lambda}{2\,n\sin\theta}$$

$$S \propto \left(\frac{d}{\lambda}\right)^4$$

$$R = tip\ size$$

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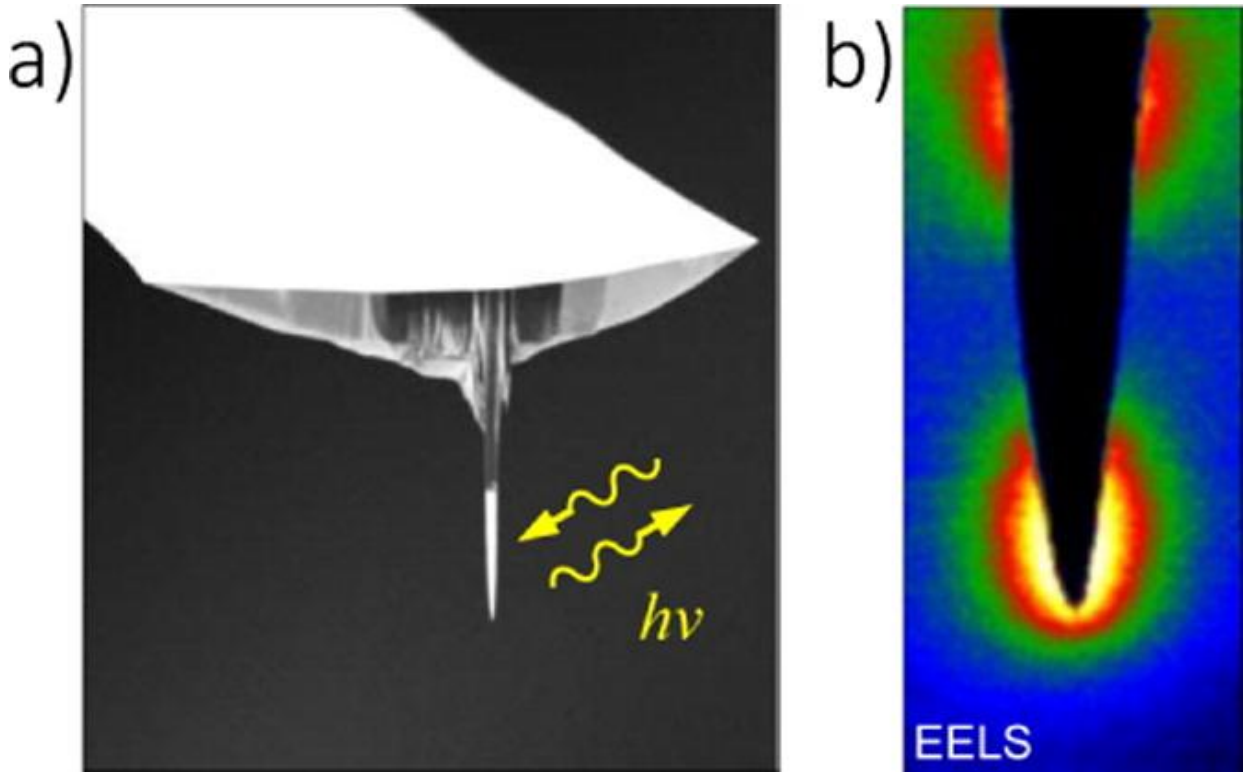
Beyond the diffraction limit

Scattering-type scanning near-field optical microscopy (s-SNOM)



Advantages

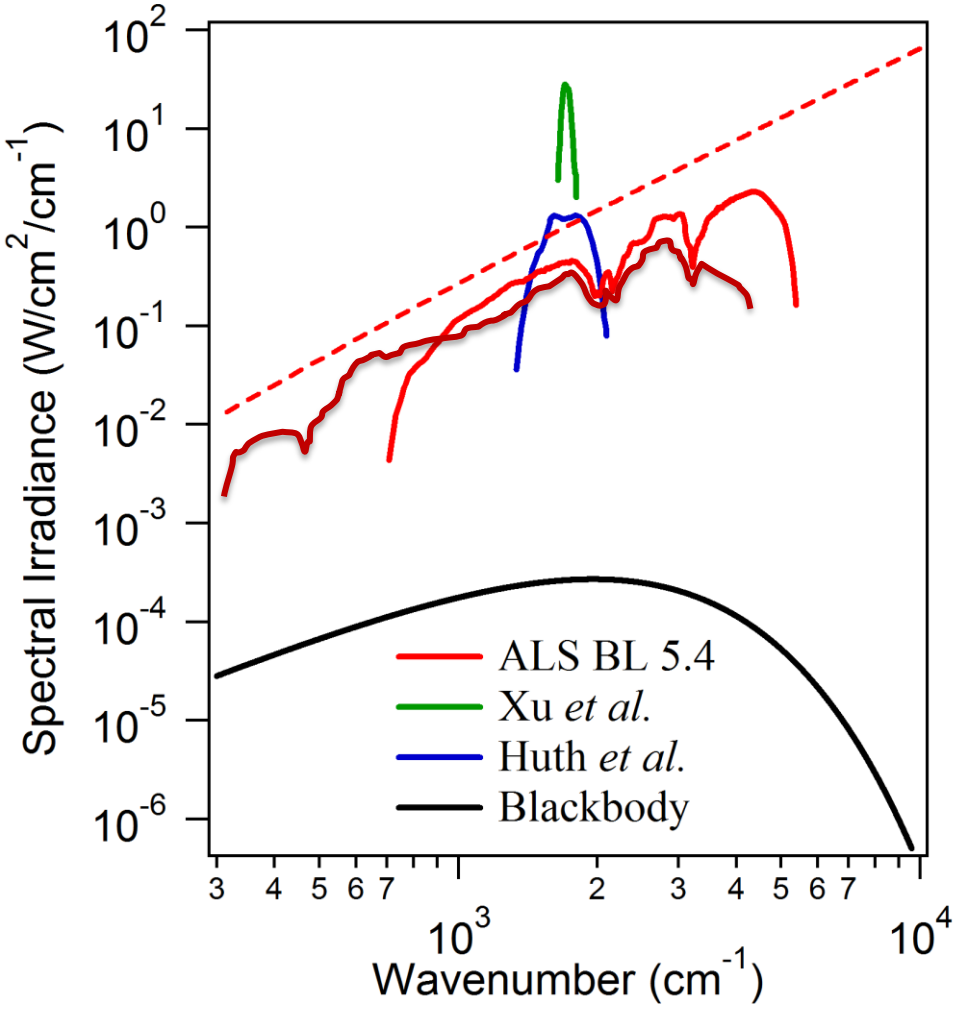
- Nanometer spatial resolution
- Wavelength independent
- Soft and hard matter
- Amplitude and phase of optical field

Muller, Pollard & Raschke, *J. Phys. Chem. Lett.*, 6 1275 (2015)
Huth, et al., *Nano Lett.* 13 1065 (2013)

Broadband sources for IR s-SNOM

Broadband sources
- More efficient spectral collection
- Improved spectral accuracy

Synchrotron IR
- Ultra-broadband
- High spectral irradiance
- Spatially coherent
- Good spectral stability



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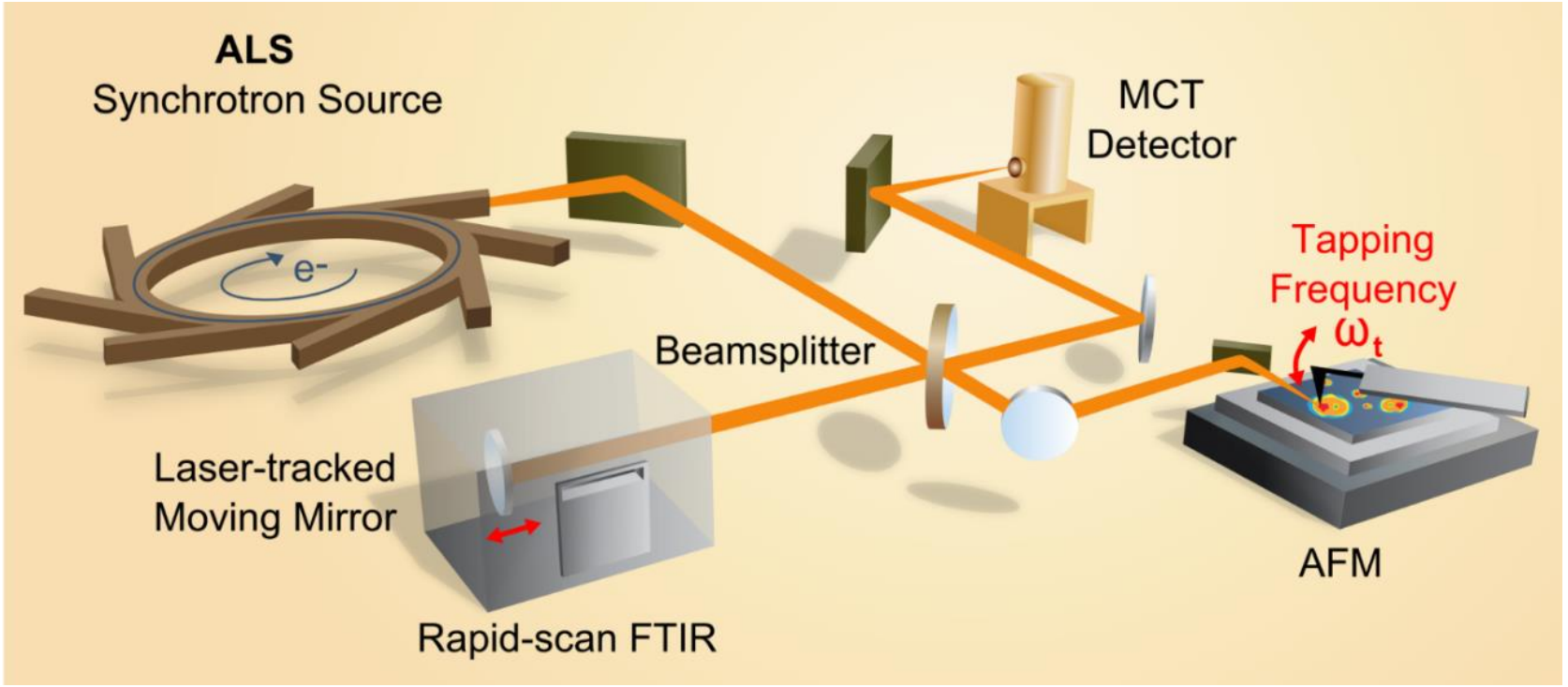
SINS: Synchrotron Infrared Nano Spectroscopy

Bechtel, Muller, Olmon, Martin, Raschke, *PNAS*, 111, 7191 (2014)



Synchrotron IR
- Ultra-broadband 330 – 5,000 cm^{-1} so far
- High spectral irradiance
- Spatially coherent
- Good spectral stability

Key Components
- Bruker Innova AFM
- Zurich Instruments lock-in amplifier
- Thermo-Scientific Nicolet 6700 FTIR bench

Or Neaspec system

- Kolmar MCT (100 um) or Cu:Ge
- Floating table & feedback system

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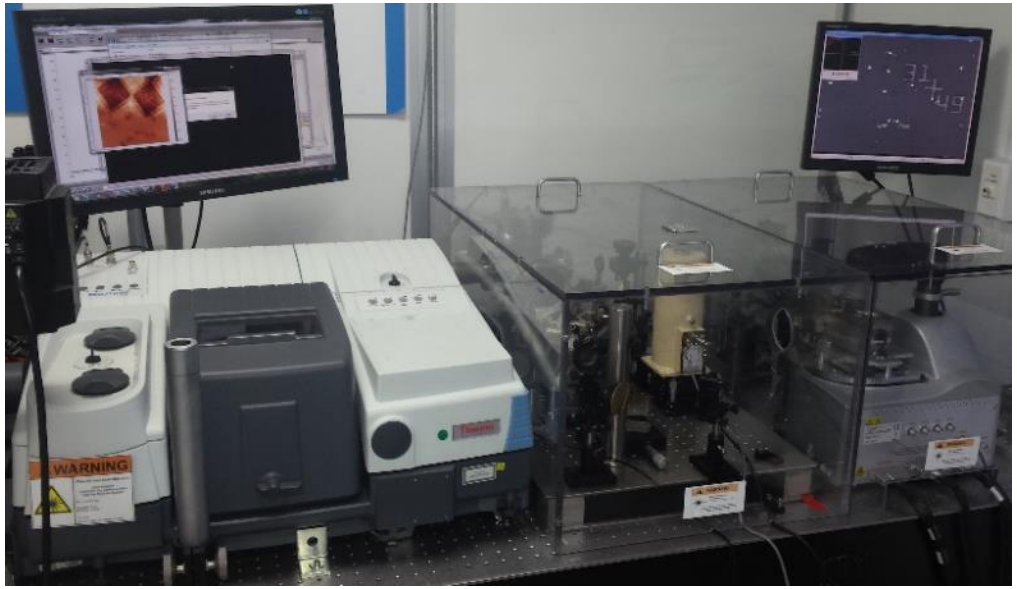
Open for Users! Free to use!

Beamline 5.4



Beamline 2.4

see the nanoworld
neaspec

Applications

- Catalysis
- Nanoparticles
- Plasmons / Polaritons
- Biominerals
- Proteins
- Biofilms

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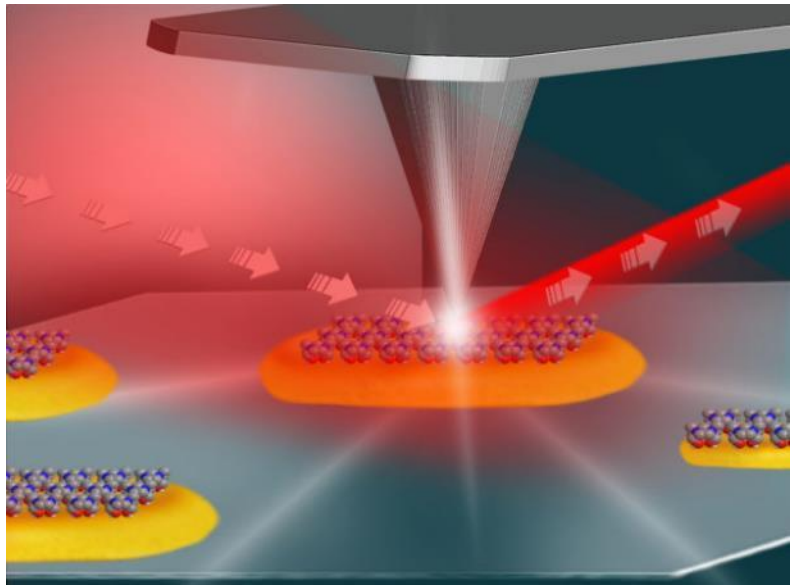
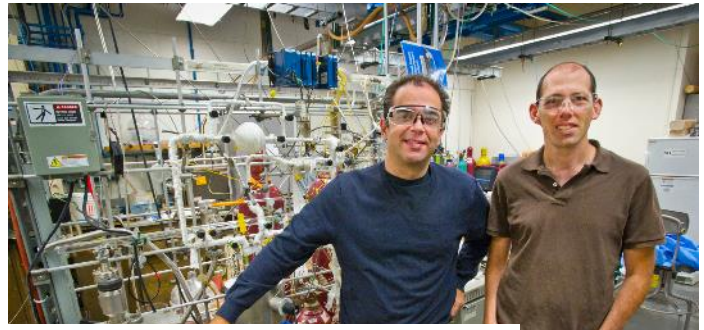
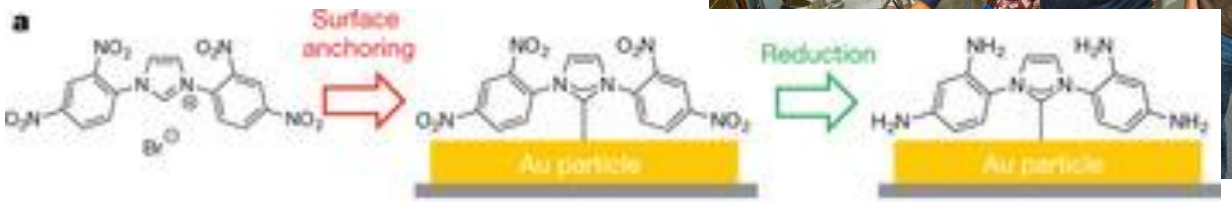
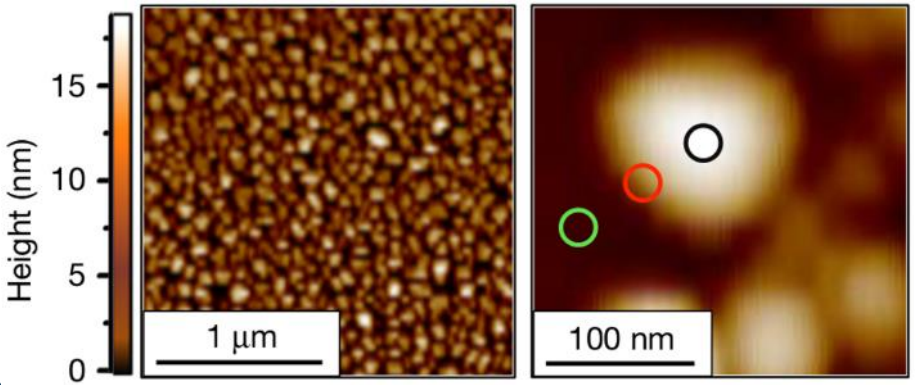
Mapping Catalytic Reactions on Single Nano-Particles

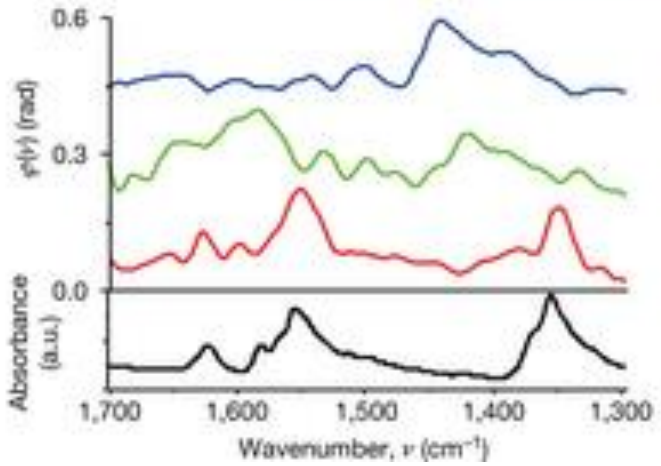
Wu, Wolf, Levartovsky, Bechtel, Martin, Toste & Gross, *Nature* **541**, 511–515 (2017)

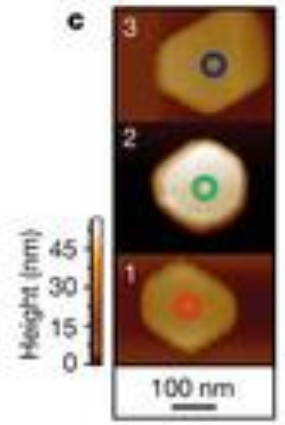








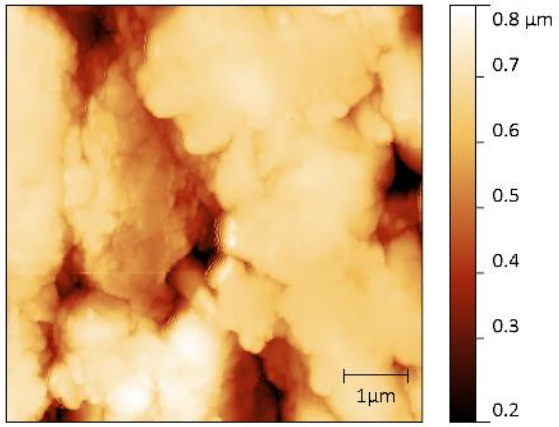


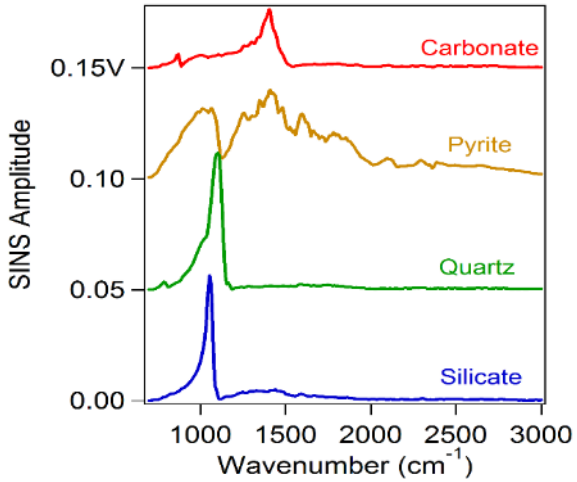


NO_2-functionalized imidazolium salt

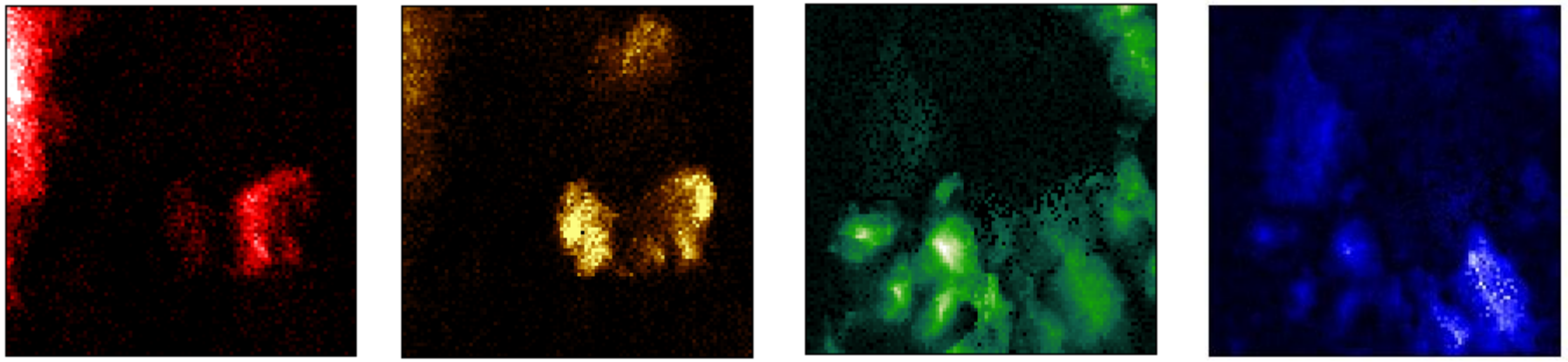
Shale: Hyperspectral Imaging

Topography





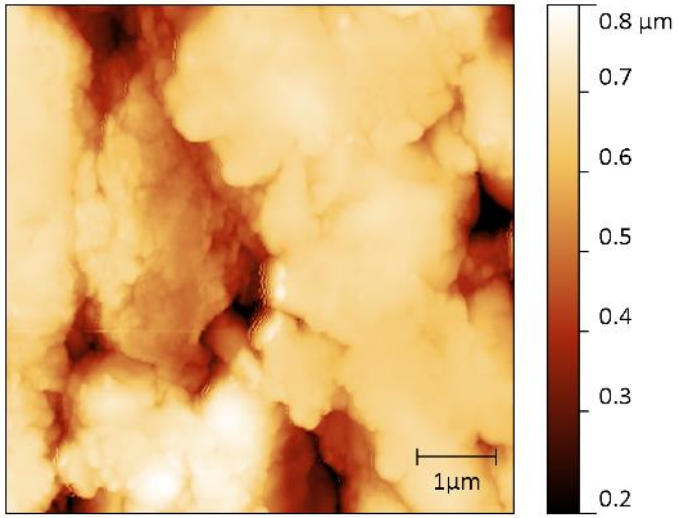
1450 cm^{-1} 1300 cm^{-1} 1140 cm^{-1} 1040 cm^{-1}

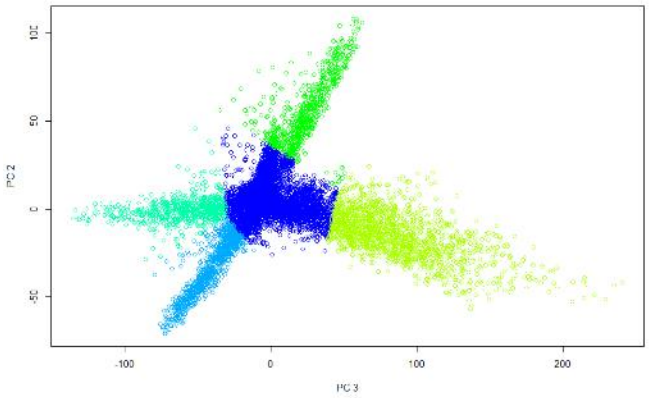


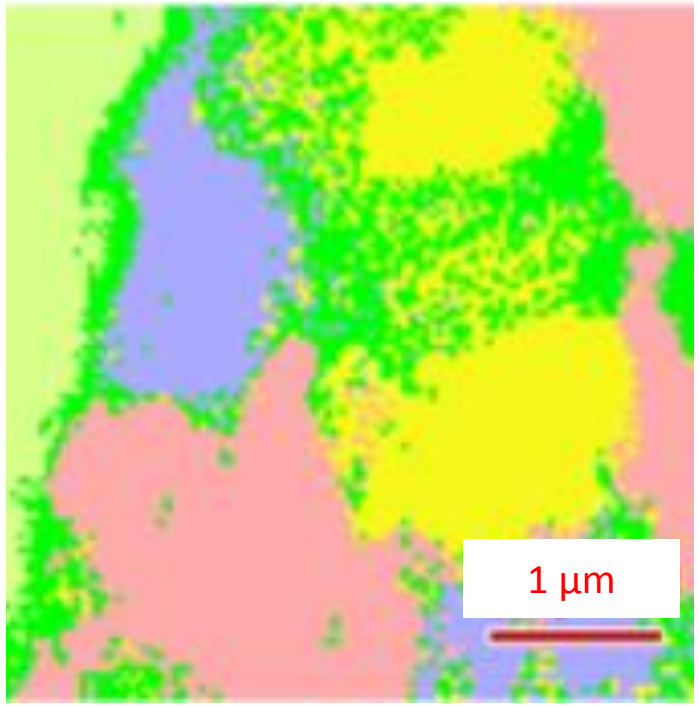
Z. Hao, H. A. Bechtel, T. Kneafsey, B. Gilbert, P. Nico,
Scientific Reports **8**, 2552 (2018).

Shale: Hyperspectral Imaging

Topography





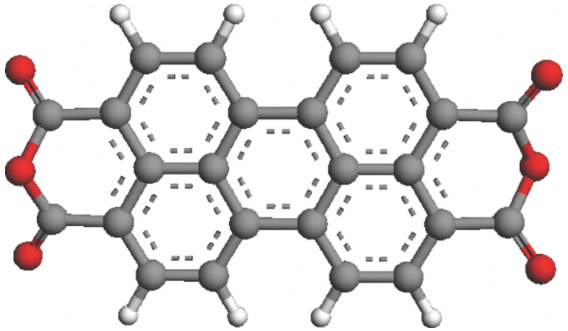


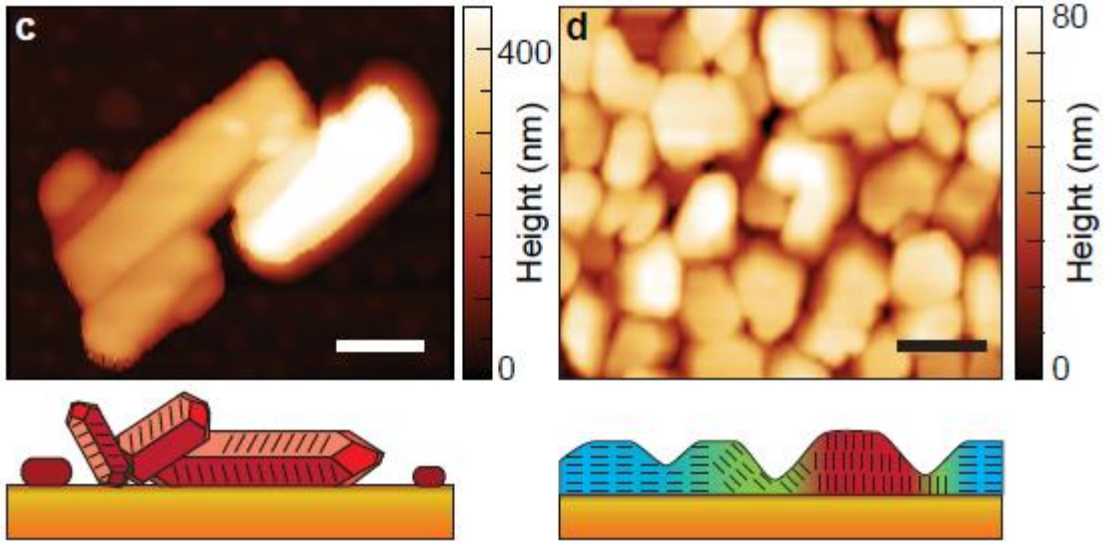
Quartz Clay Carbonate
Pyrite Organic-rich

Z. Hao, H. A. Bechtel, T. Kneafsey, B. Gilbert, P. Nico,
Scientific Reports **8**, 2552 (2018).

Domain Orientation in Molecular Materials

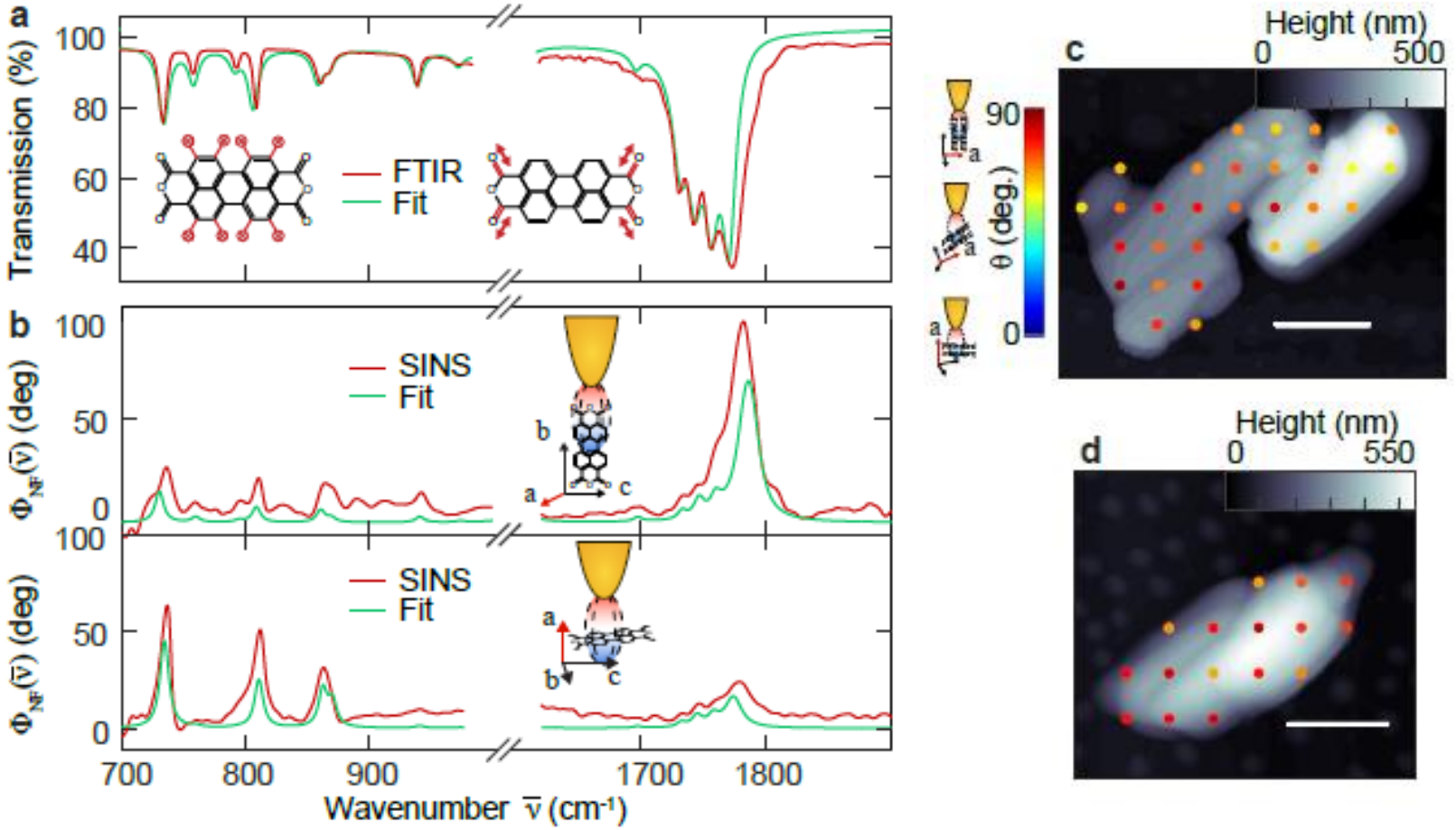
Perylene tetracarboxylic dianhydride
(PTCDA)





Muller *et al.*, *Science Advances 2,* e1601006 (2016)

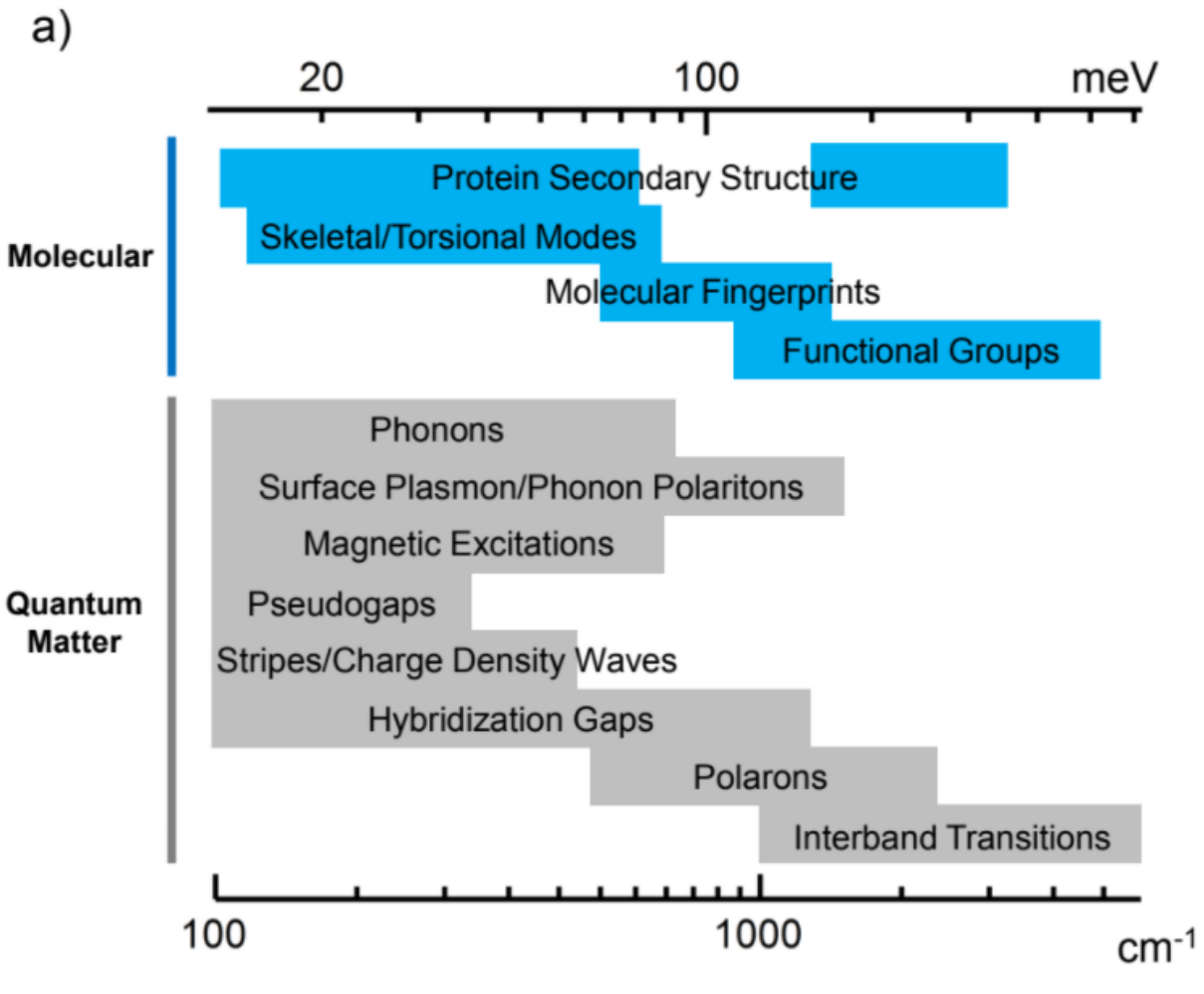
Optical Nanocrystallography

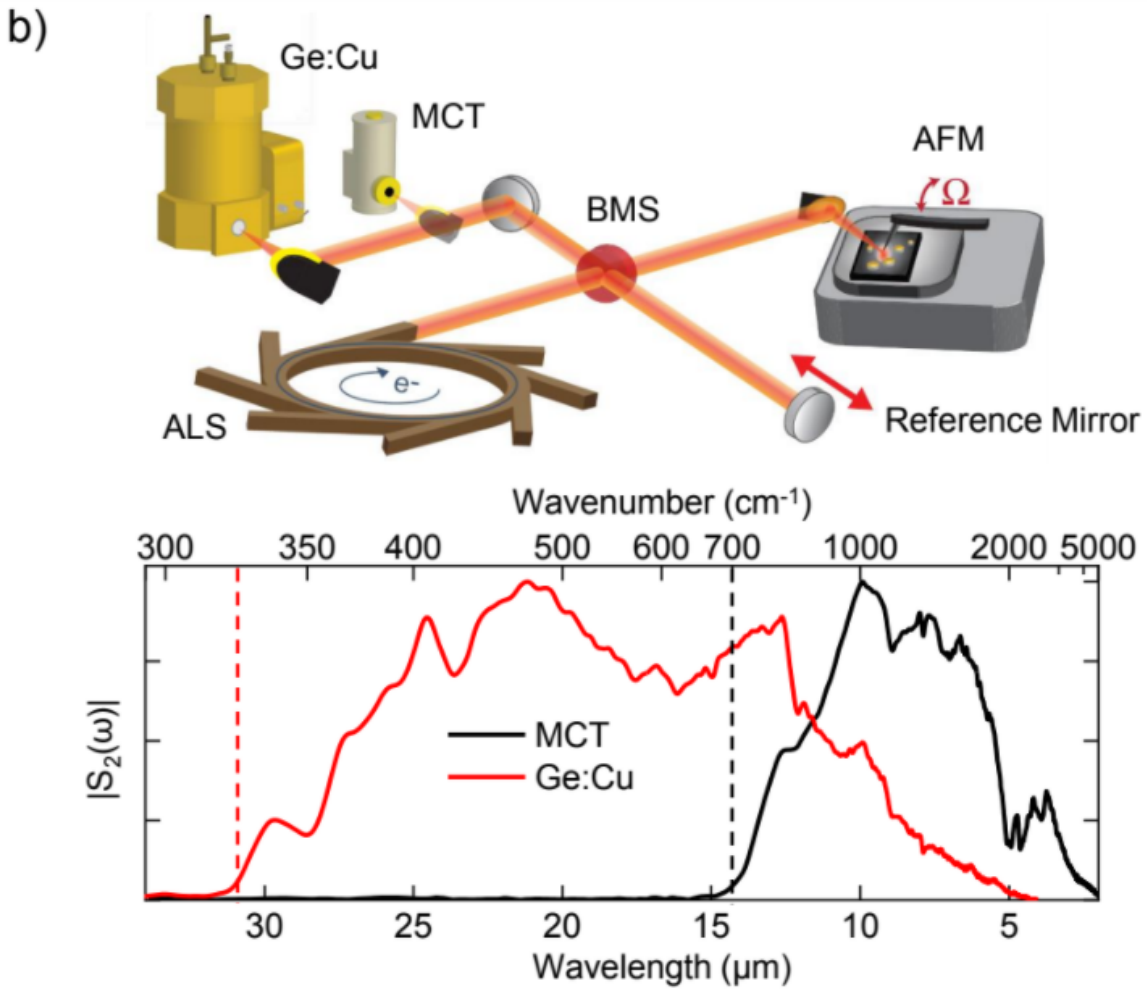


Intensity of C-H out-of-plane bend *vs.* C=O in-plane stretch → orientation

Muller *et al.*, *Science Advances 2,* e1601006 *(2016)*

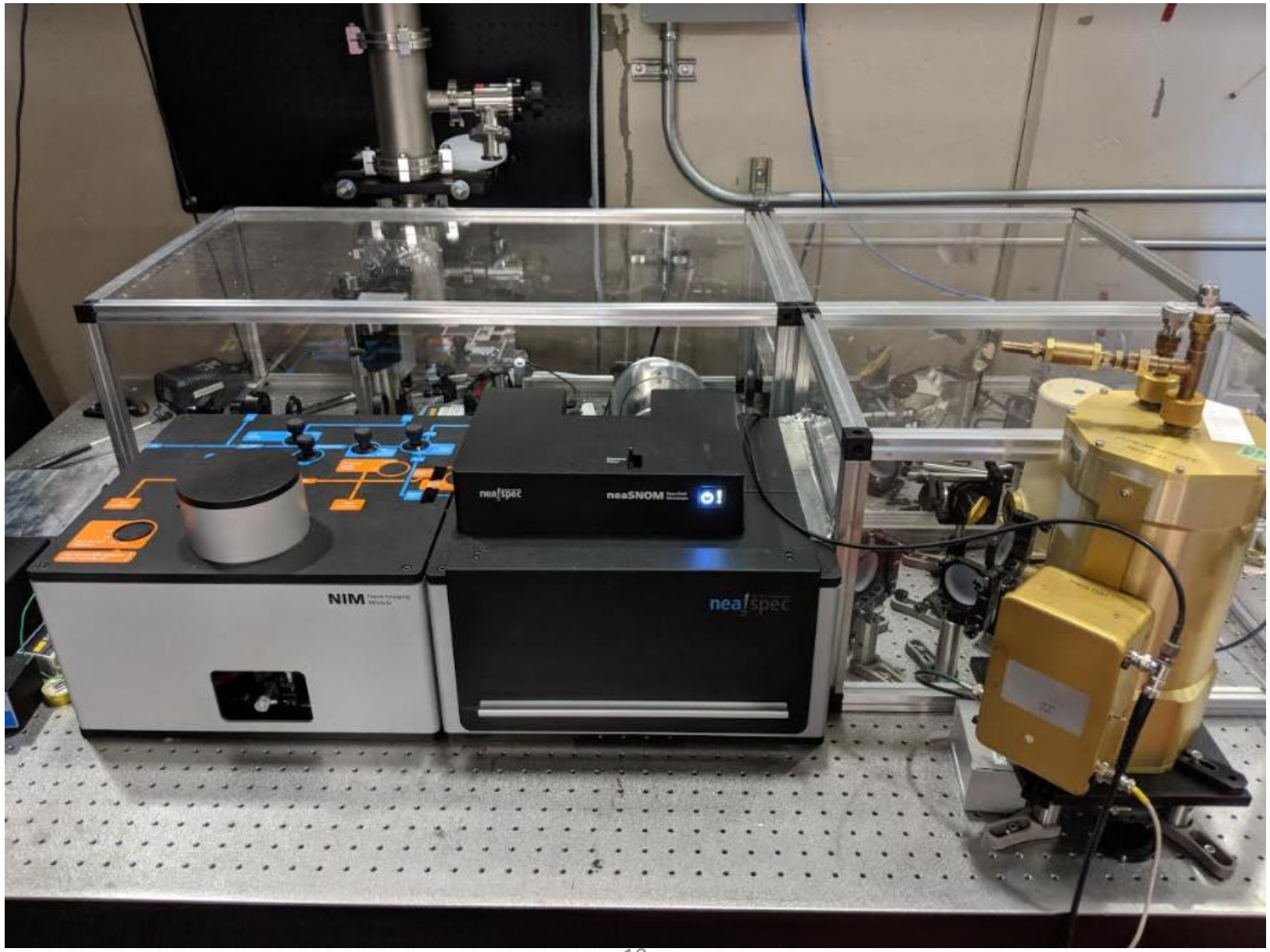
SINS in the Far-IR





Omar Khatib, Bechtel, Matin, Raschke, Carr, ACS Photonics (2018),
DOI: 10.1021/acsphotonics.8b00565

ALS Beamline 2.4



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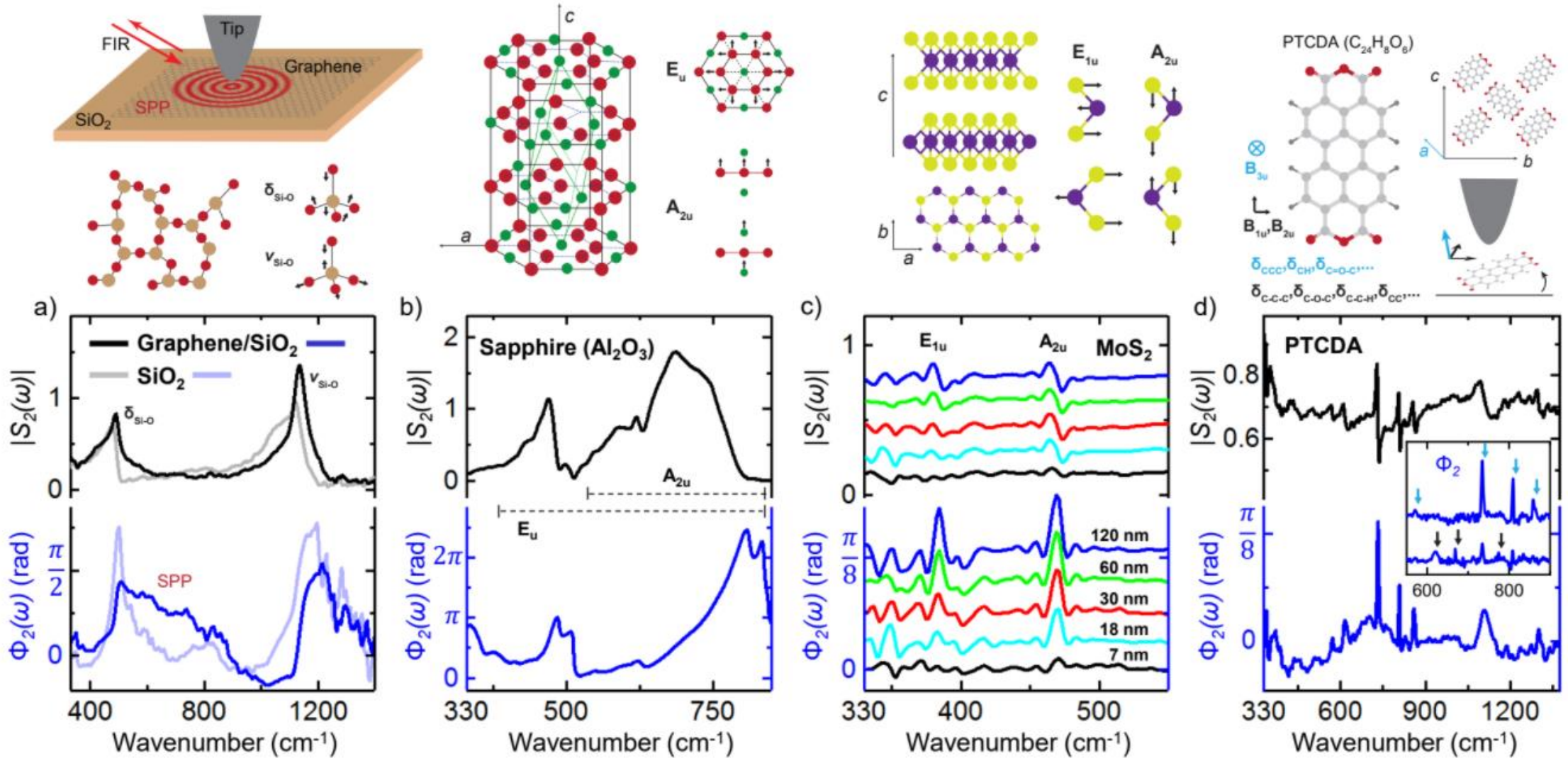
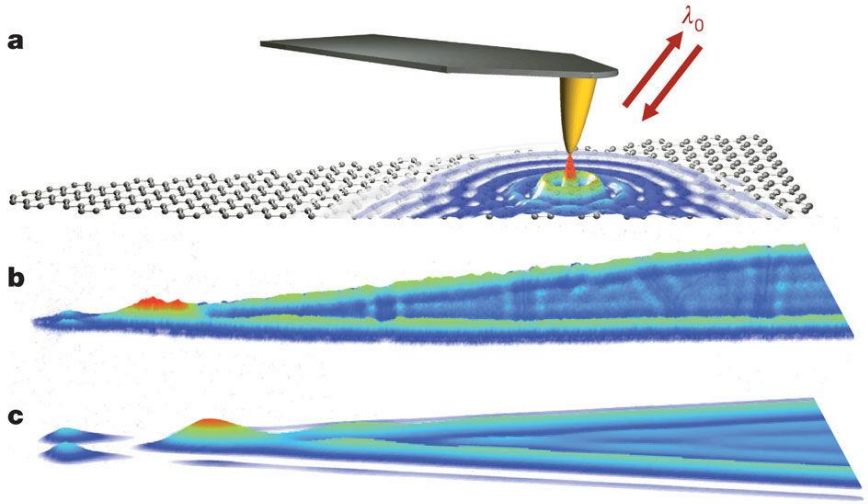
SINS in the Far-IR

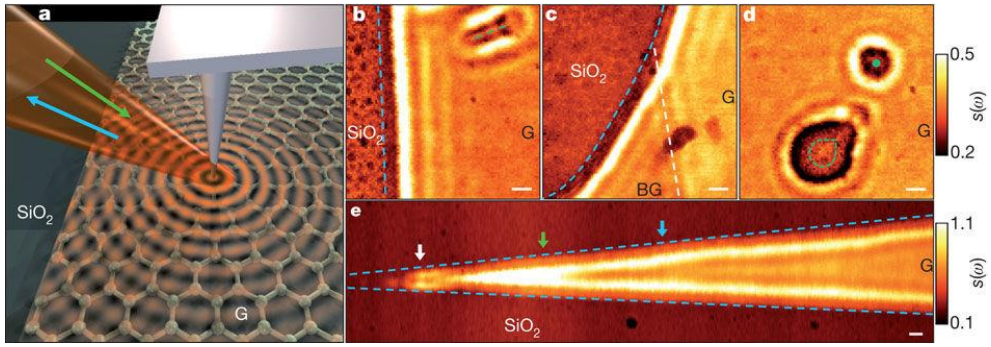
Omar Khatib, Bechtel, Matin, Raschke, Carr, ACS Photonics (2018), DOI: 10.1021/acsphotonics.8b00565



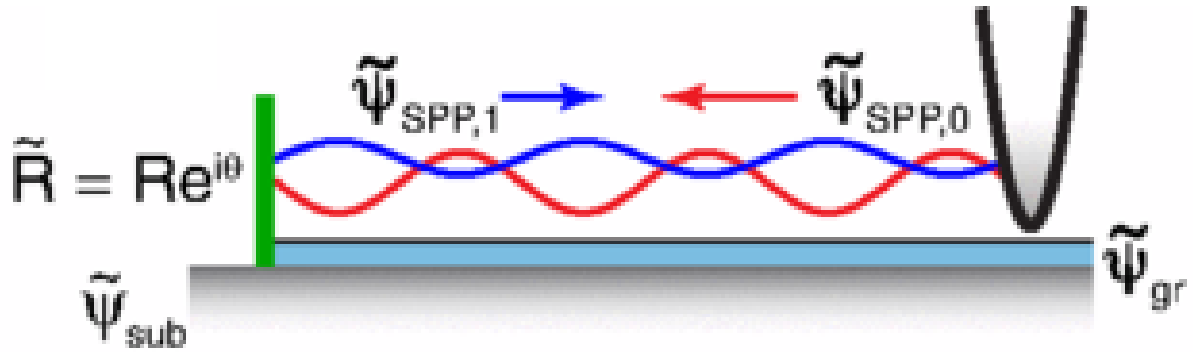
Polariton Interferometry



Chen *et al. Nature* 487, 77–81 (2012)



Fei *et al. Nature* 487, 82-85 (2012)



Gerber *et al. Phys. Rev. Lett.* 113, 055502 (2014).

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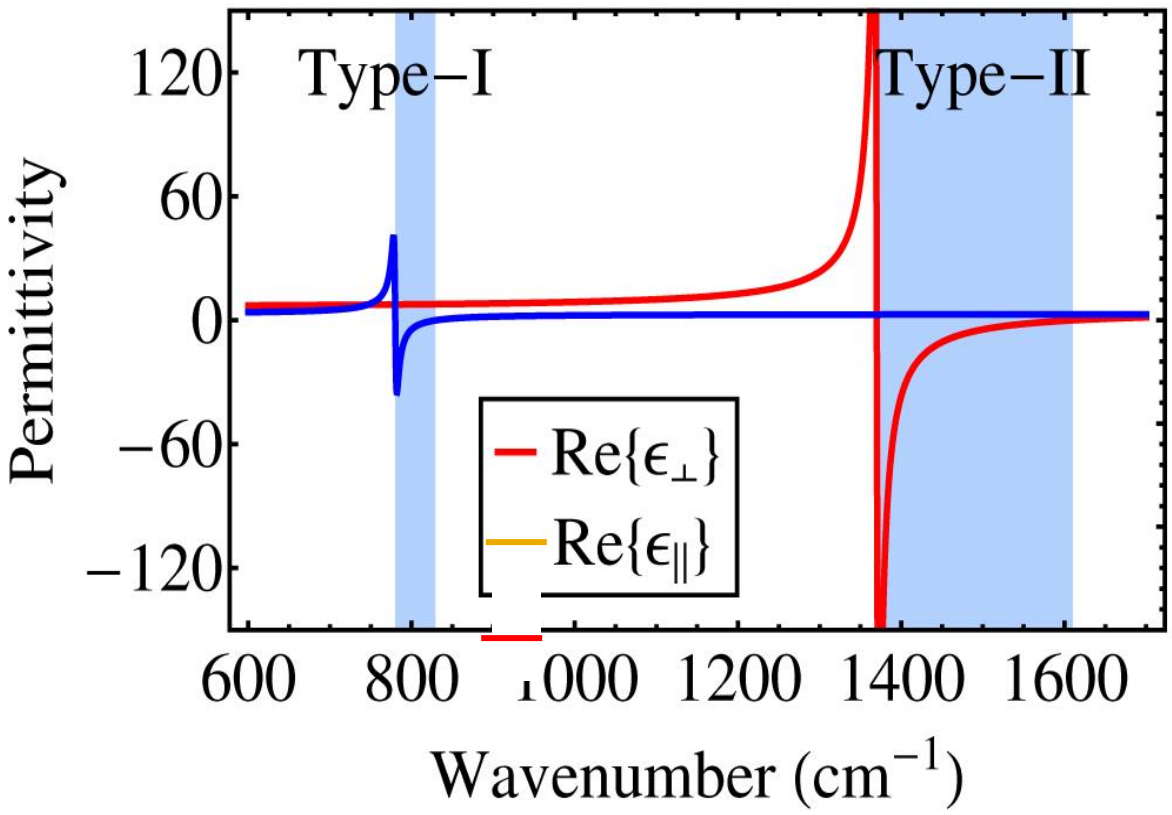
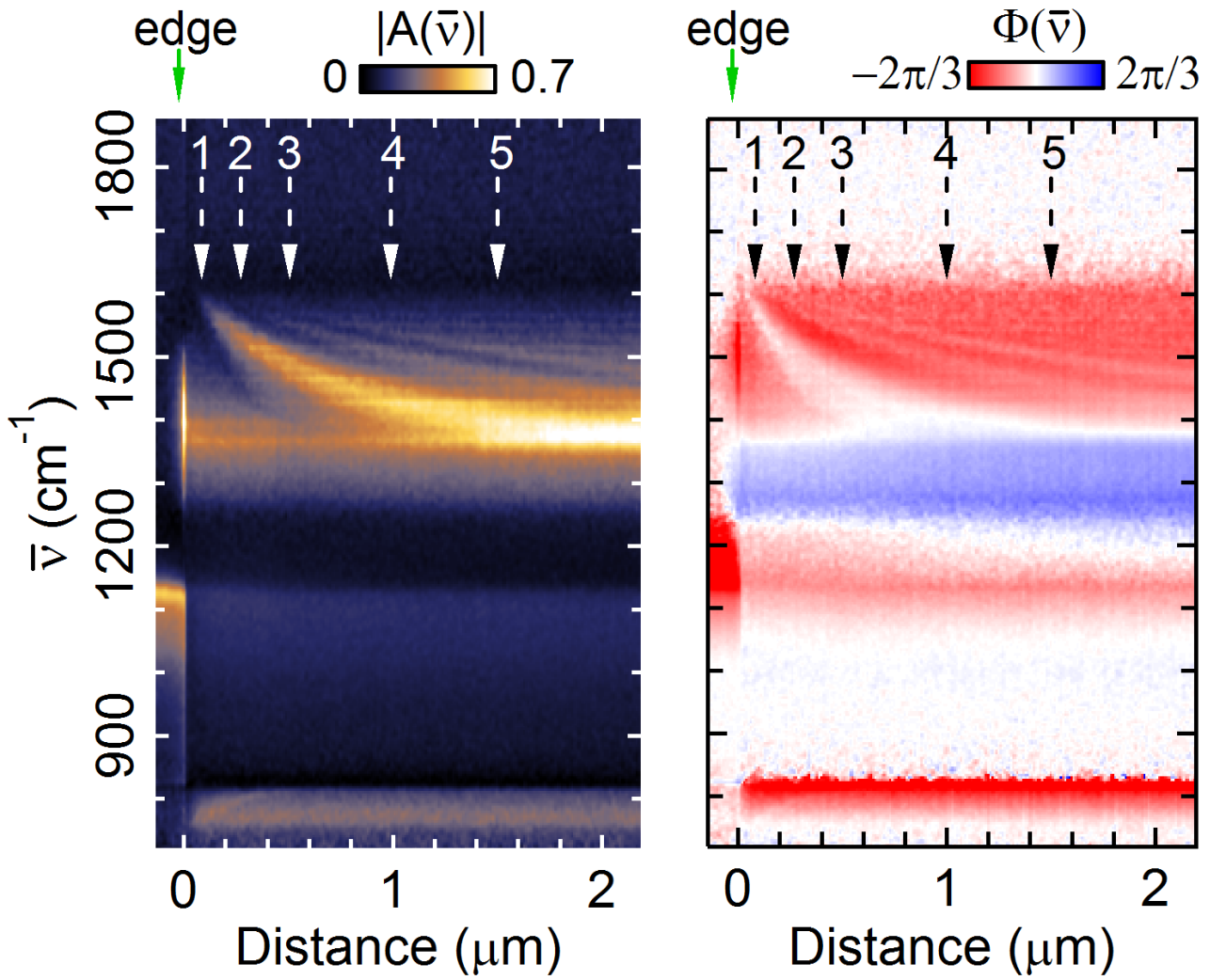
The Phonons of Boron Nitride



Caldwell *et al. Nat. Commun.* 5, 5221 (2014)

Phonon Polaritons in Boron Nitride

Shi, Bechtel, Berweger, Sun, Zeng, Jin, Chang, Martin, Raschke, Wang, *ACS Photonics*, 2, 790 (2015).



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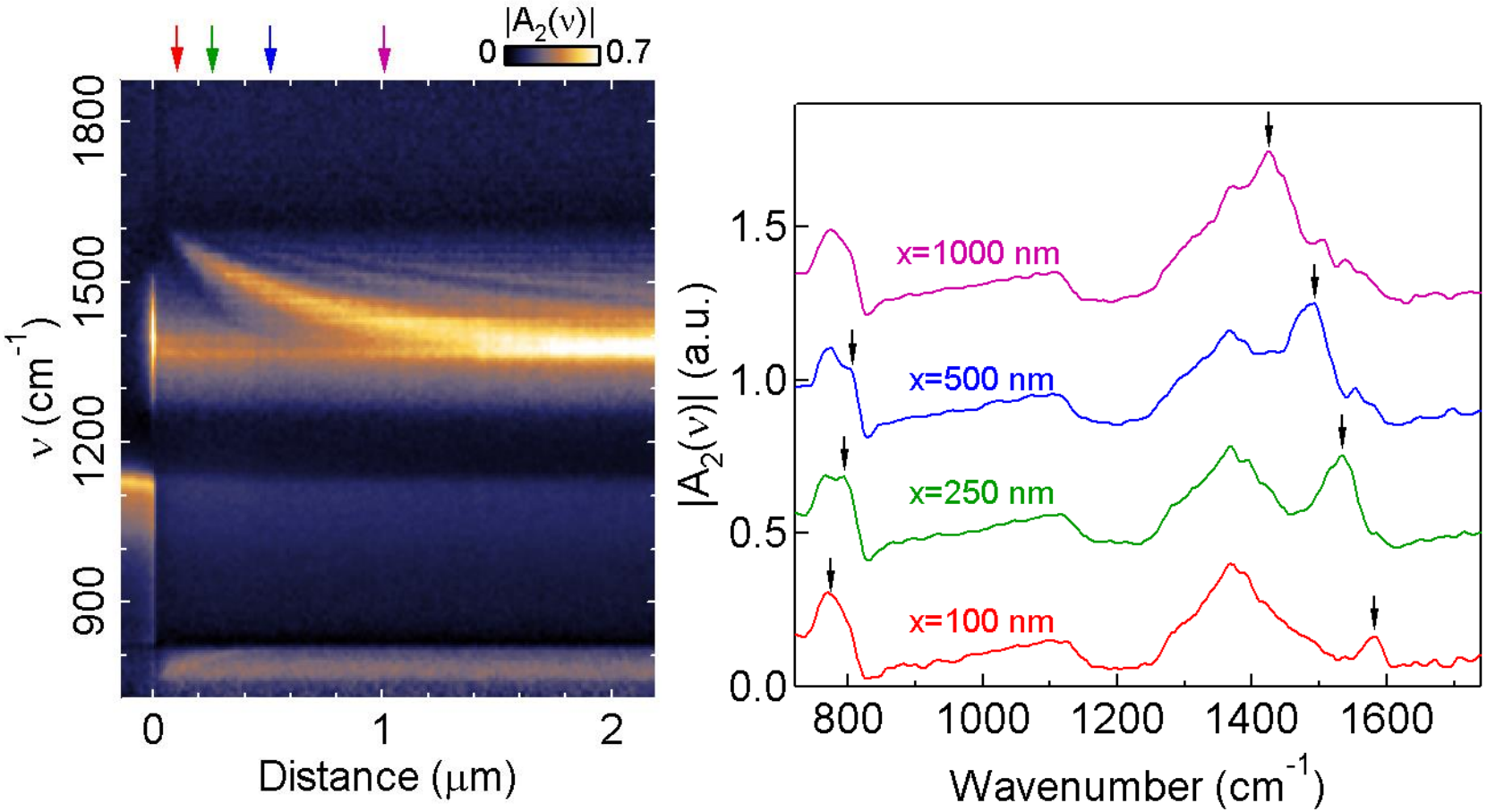
hBN Spectral Cuts

Shi, Bechtel, Berweger, Sun, Zeng, Jin, Chang, Martin, Raschke, Wang, *ACS Photonics*, 2, 790 (2015).



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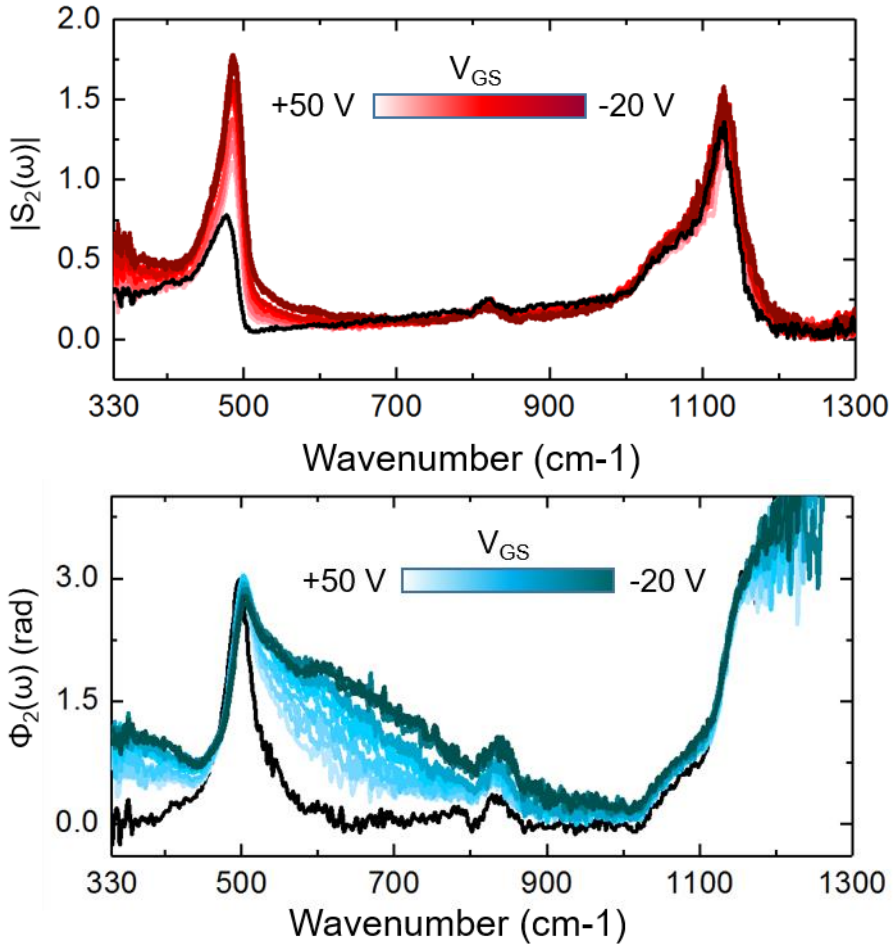
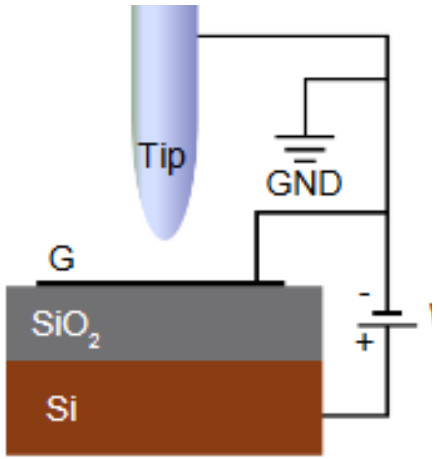
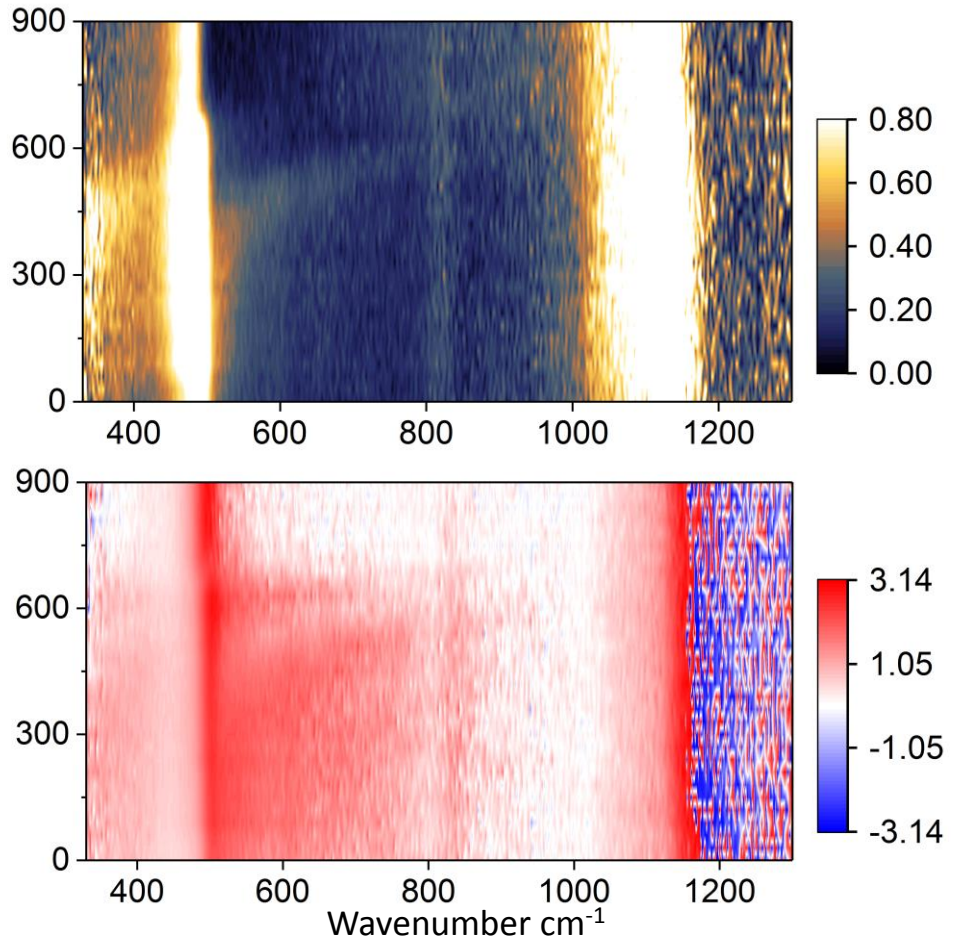
Nano-spectroscopy of graphene gated device

Far-IR surface plasmon polariton (SPP) waves



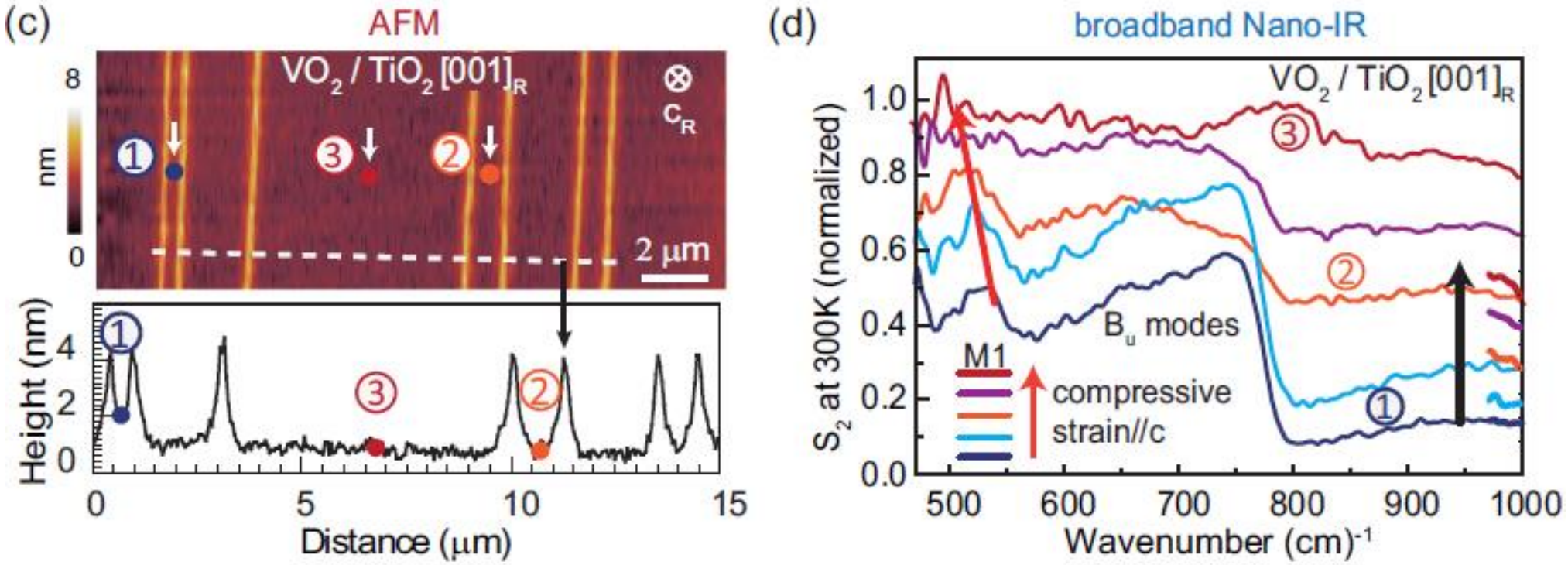




Omar Khatib, Bechtel, Matin, Raschke, Carr, ACS Photonics (2018), DOI: 10.1021/acsphotonics.8b00565

Strain-induced phase transitions in VO_2 films

Liu *et al.* *Physics Review B*, 91, 245155 (2015).



VO_2 phonon at ~540 cm^{-1} redshifts with increasing strain

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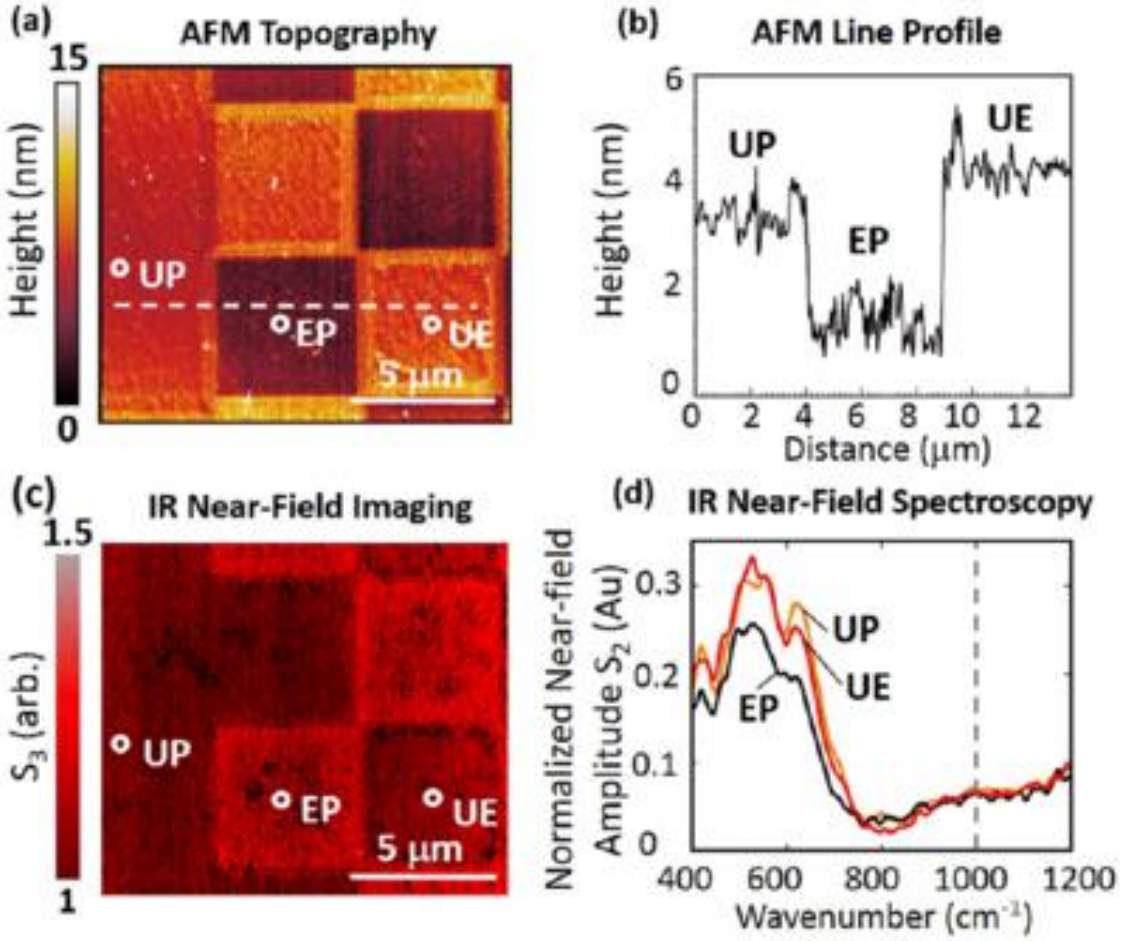
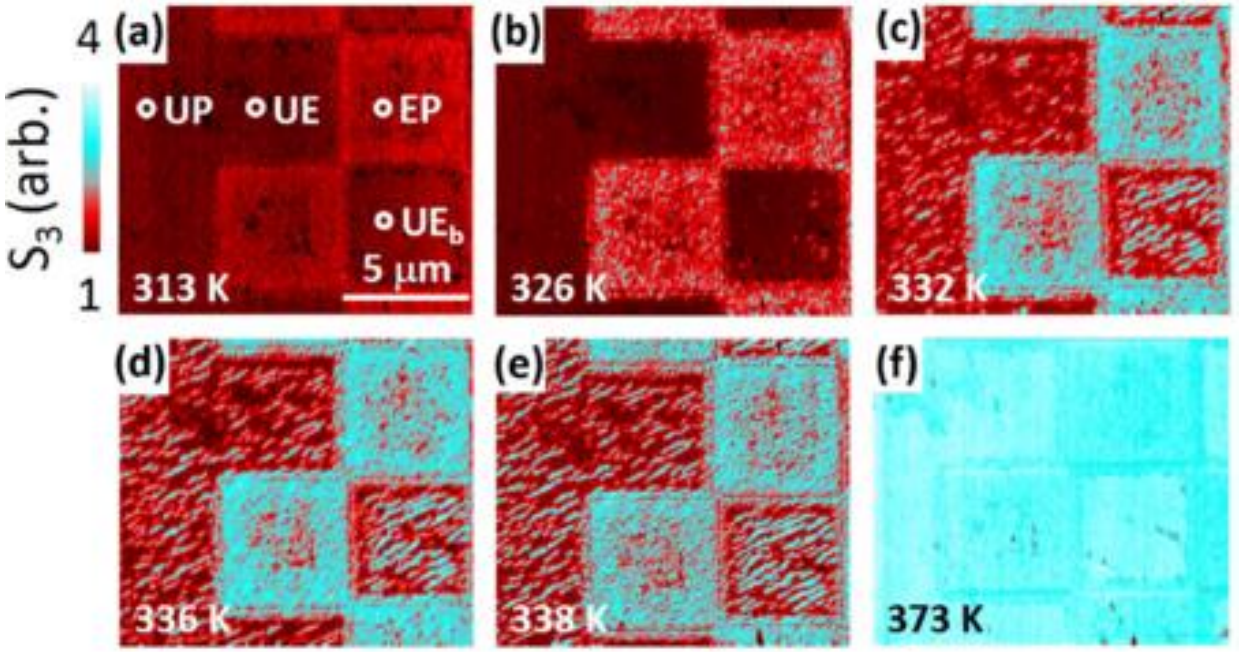
Imaging & Spectroscopy of Patterned VO_2

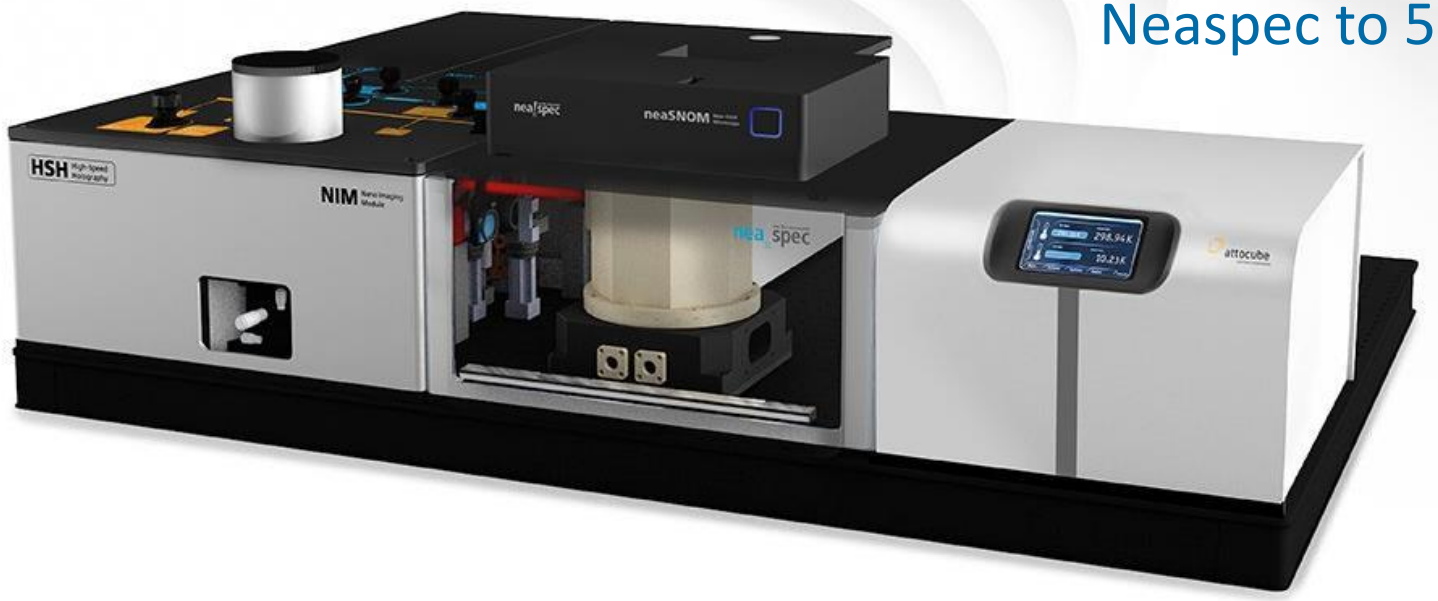
Gilbert Corder, Jiang, Chen, Kittiwatanakul, Tung, Zhu, Zhang, Bechtel, Martin, Carr, Lu, Wolf, Wen, Tao, and Mengkun Liu, Phys. Rev. B **96**, 161110(R) (2017)





(UP) unpatterned (UE) unetched-substrate patterned
(EP) etched-substrate patterned regions

Cryo SINS? UHV SINS? Matches far-IR science …



Demonstrated by
Neaspec to 5 Kelvin

Plus beautiful work by Basov Group and Eng Group

Nano Infrared is Revolutionizing synchrotron IR science

Visits from IR Beamline Scientists

Australian Synchrotron
NSLS II
LNLS (Brazil)
Max-Lab (Sweden)
Soleil (France)
Spring-8 (Japan)
Elettra (Italy)
Diamond (England)
Shanghai Synchrotron (China)
Pohang Light Source (South Korea)

SINS at other synchrotrons

MLS (Germany)
LNLS (Brazil)

Spring-8 (Japan) under development
Soleil (France) under development
Pohang (Korea) under development
NSLS II - proposed

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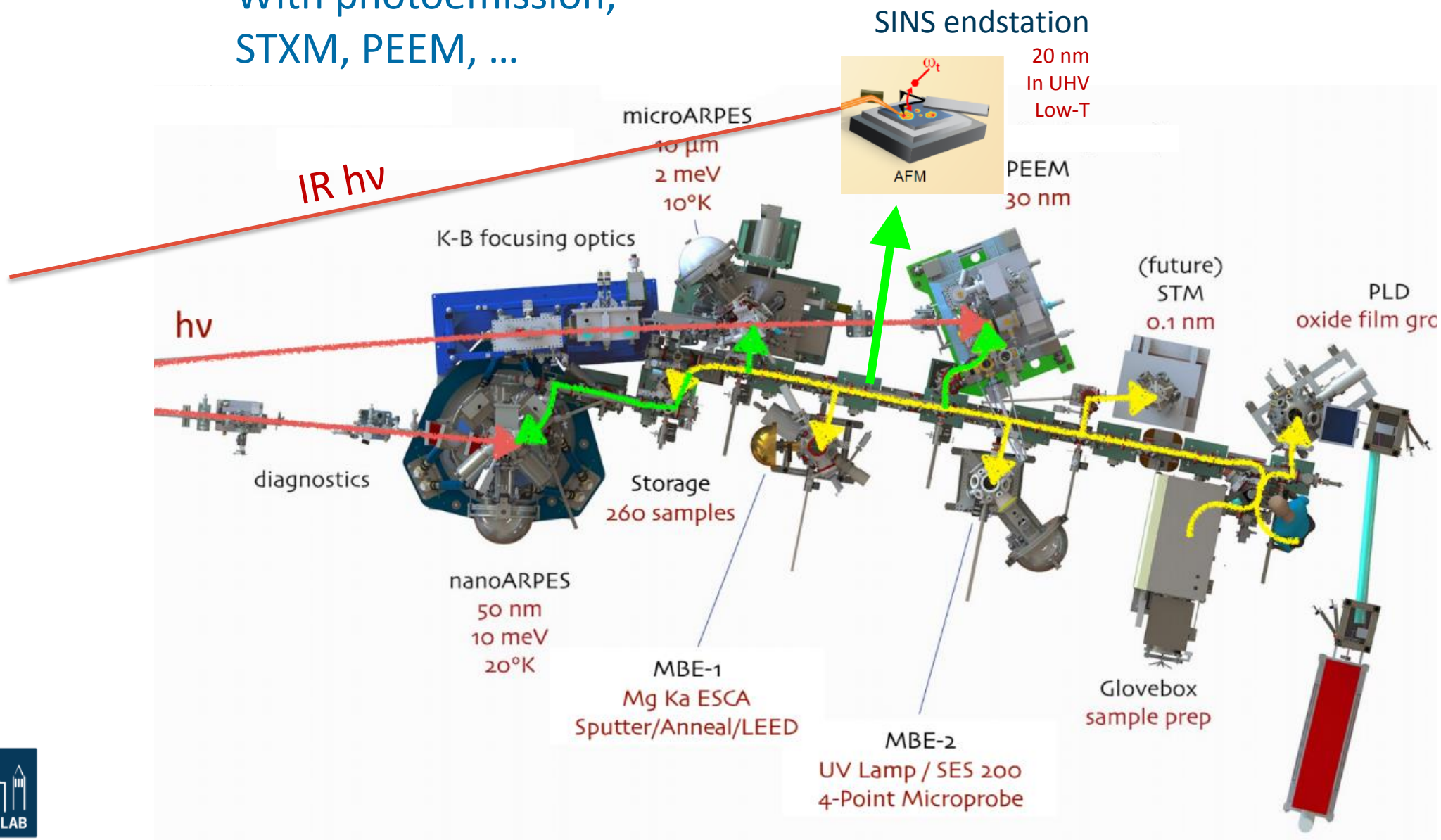
SINS as a complementary tool

With photoemission,
STXM, PEEM, …



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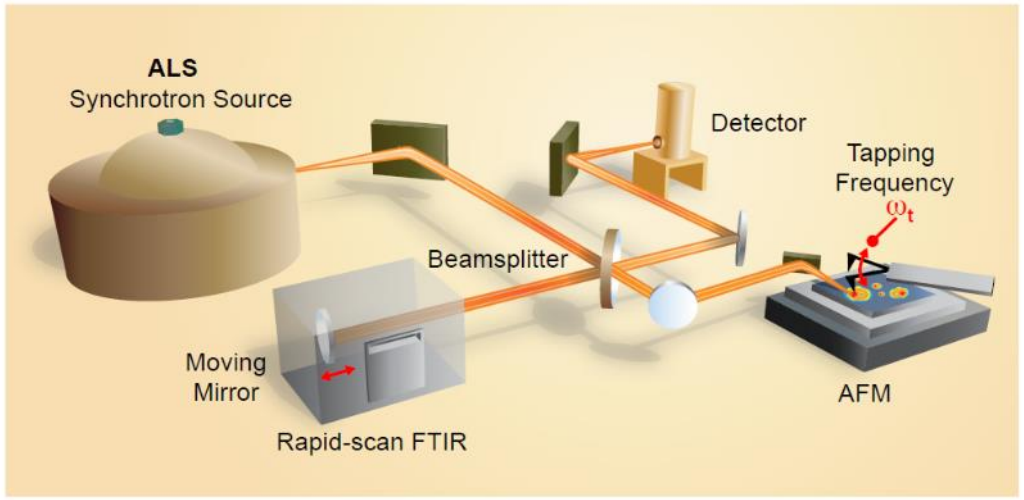
Acknowledgements



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Users & samples in this talk
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