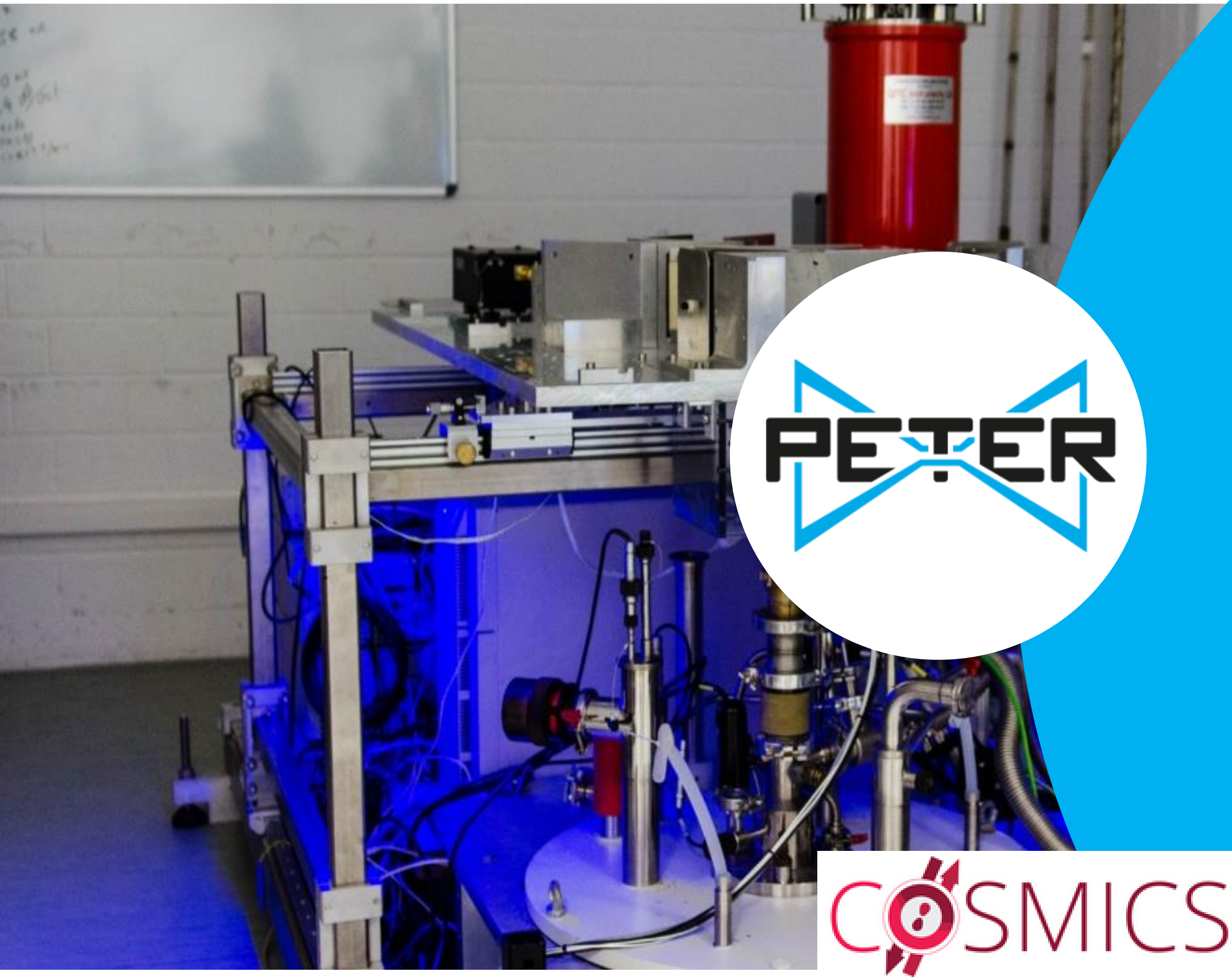
Universität Stuttgart
Institut für Physikalische Chemie



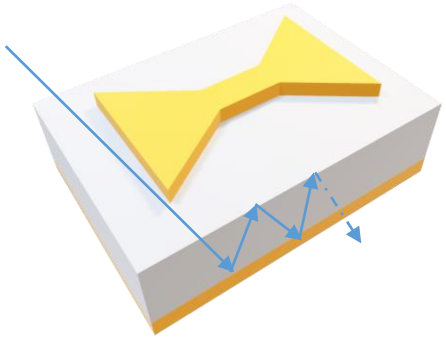
High Frequency EPR: New Tools for Investigating Thin Layers of Molecular Magnets

Lorenzo Tesi
University of Stuttgart
Joris van Slageren Group

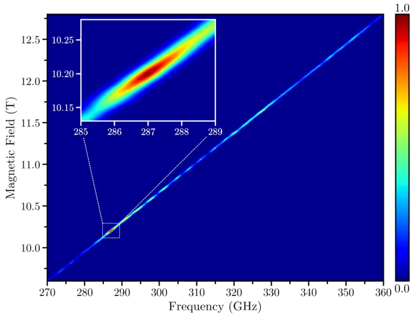
COSMICS Workshop
Magnetic Molecules on Surface
9/3/2021

Index

Introduction to the PETER project



Design of Plasmonic Metasurface Resonators

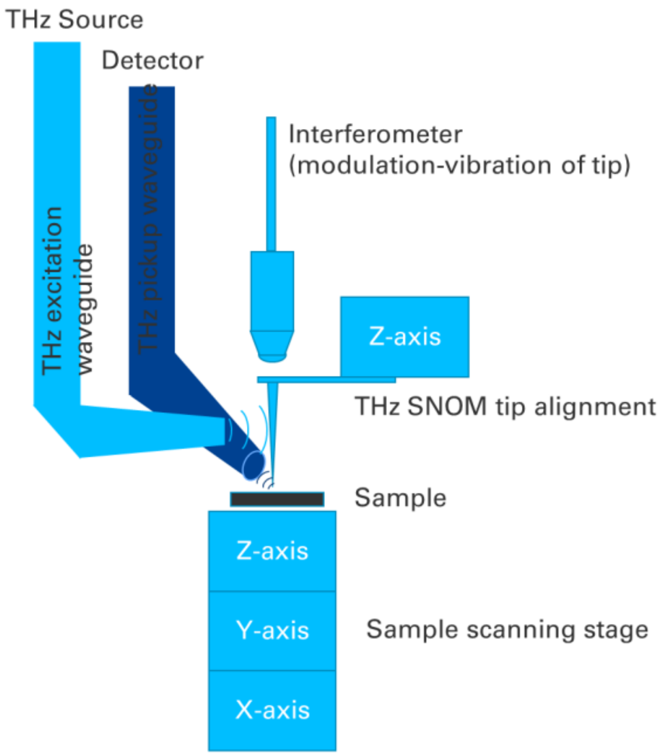


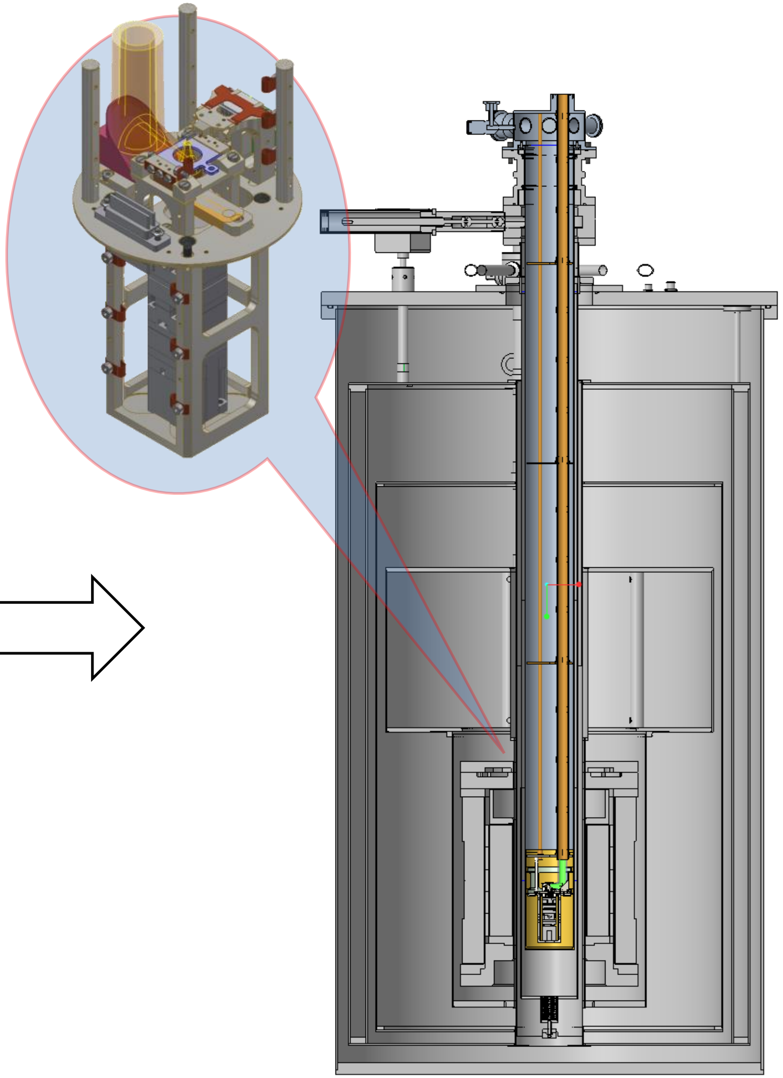
High Frequency Electron Paramagnetic Resonance Measurements

Introduction to Plasmon Enhanced THz Electron Paramagnetic Resonance

General aim

- **Combine advantages** of High-Frequency Electron Paramagnetic Resonance (HFEPR) with Scanning Probe Microscopy.
- Achieve a working prototype.





Coordinator
Tomáš Šikola

Joris van Slageren

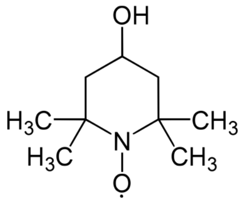
Richard Wylde

Rainer Hillenbrand

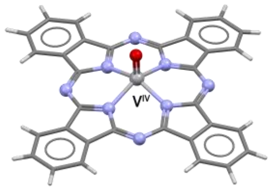
Introduction to Plasmon Enhanced THz Electron Paramagnetic Resonance

Why THz Electron Paramagnetic Resonance?

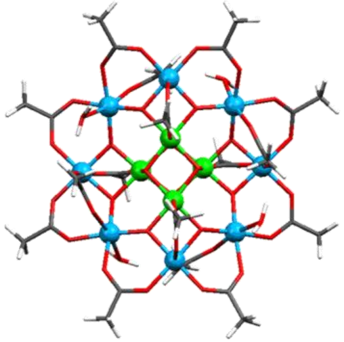
- EPR interrogates paramagnetic centers in chemistry, biology, materials science and physics.



TEMPOL

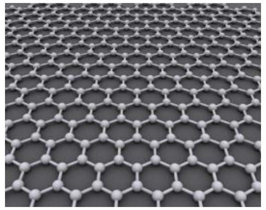


VO(Pc)

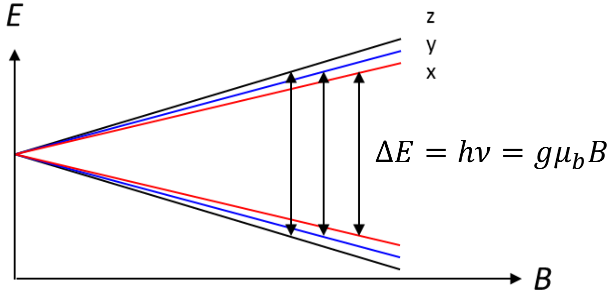


Mn12ac

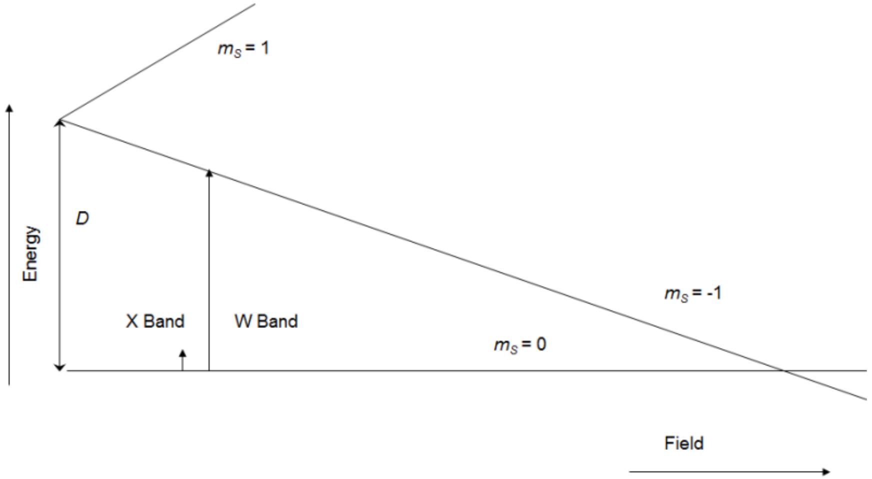
Protein

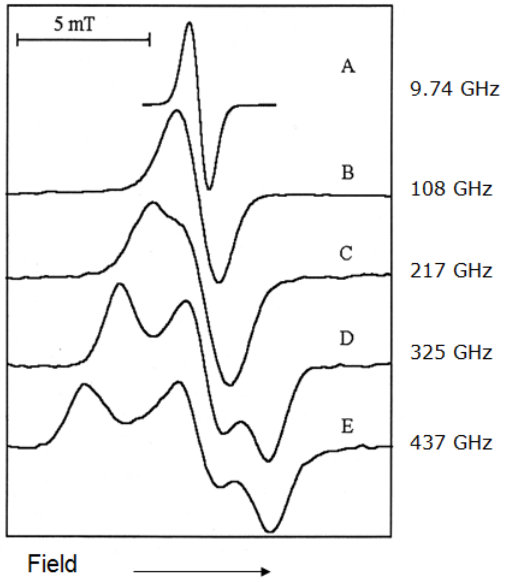


Graphene



- Reasons for going to higher frequencies in EPR:
  - Easy access to large energy splittings
  - Improve g-value resolution $\hat{\mathcal{H}} = D\hat{S}_z^2 + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + \mu_B \mathbf{B} \cdot \underline{\underline{g}} \cdot \hat{\mathbf{S}}$

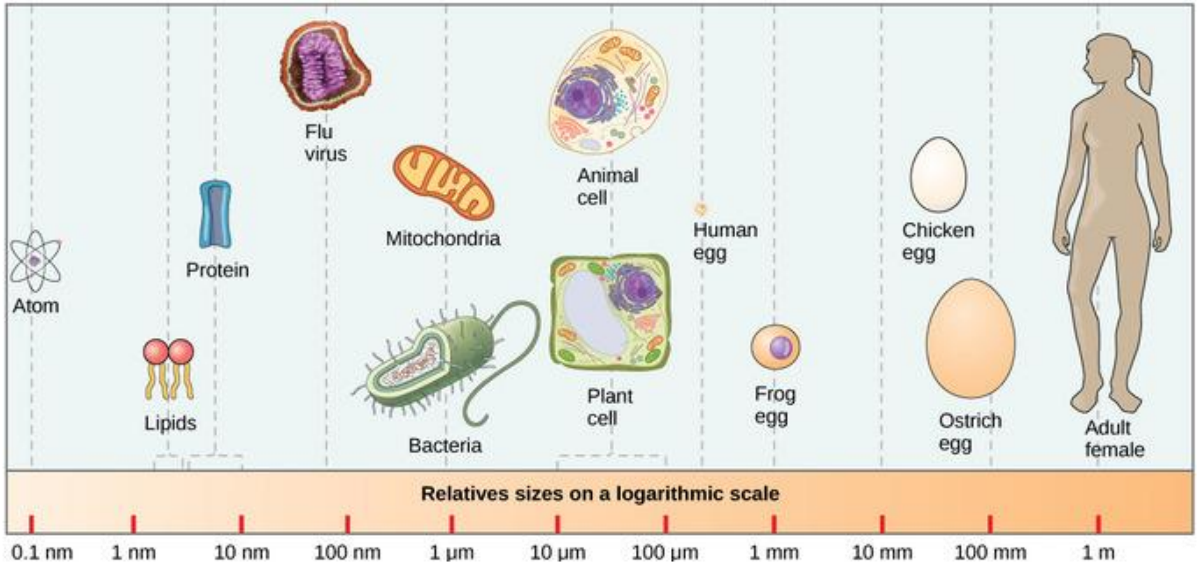




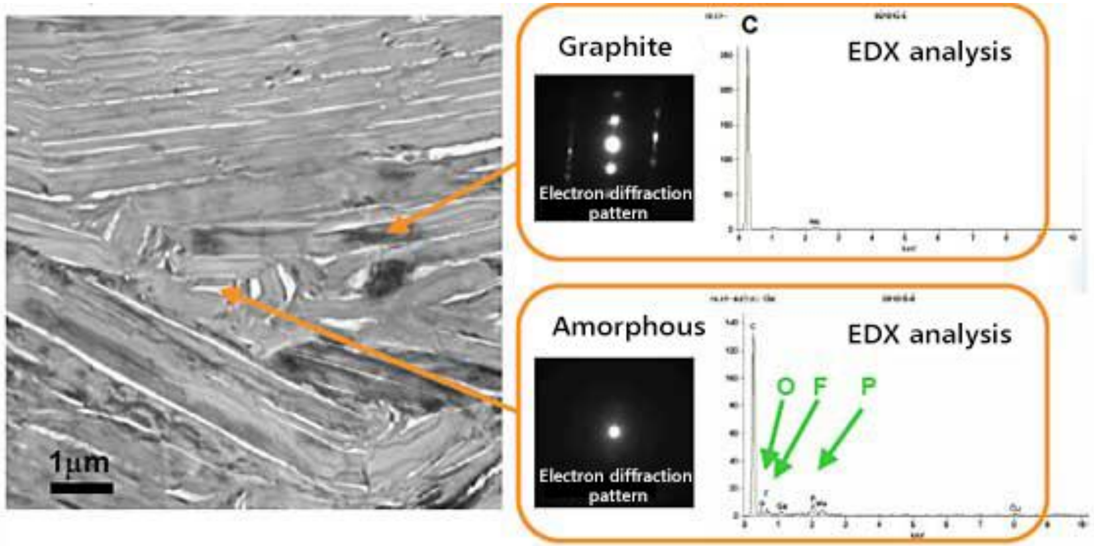
Why EPR *Microscopy*?

- In systems with structure on the microscale, **spectroscopic microscopy** allows investigation of individual components.

- Wavelength is smaller at THz than in microwave regime, allowing for investigation of smaller features.



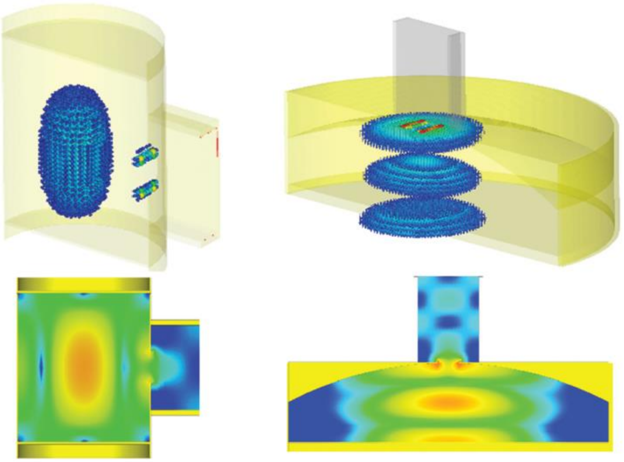
courses.lumenlearning.com



www.jfe-tec.co.jp/en/battery/case/19.html

Why Plasmon enhancement?

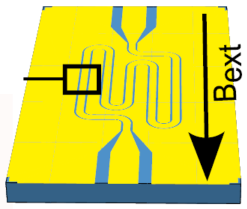
- Electron paramagnetic resonances are magnetic dipole transitions.
- Magnetic dipole transitions are much weaker than electric dipole transitions.
- Resonant structures are used to enhance the radiation magnetic field strength.



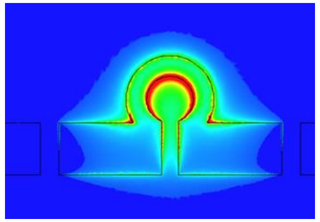
S. Lenz, et al. Chem. Comm. 2019

Why low temperatures and high magnetic fields?

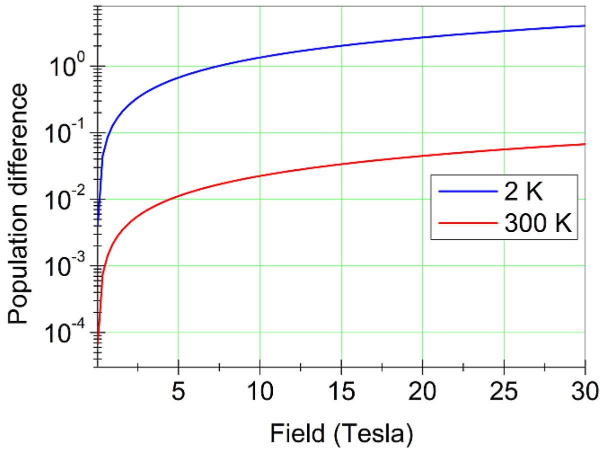
- Low temperatures increase the Boltzmann population difference.
- Magnetic field required for S=1/2 paramagnets (Zeeman splitting)

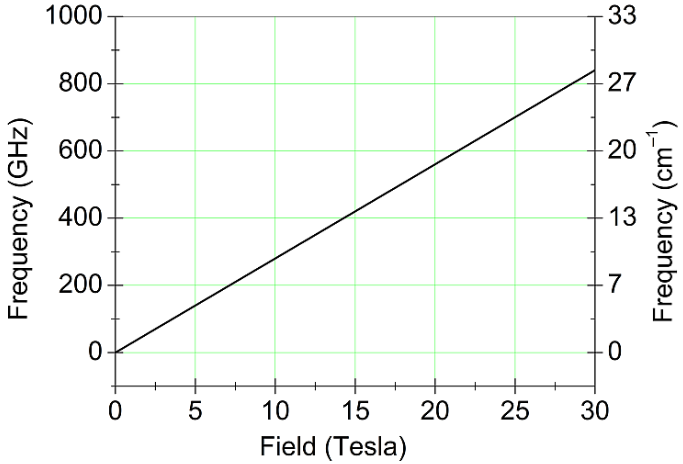


Y. Wiemann, et al. Appl. Phys. Lett. 2015



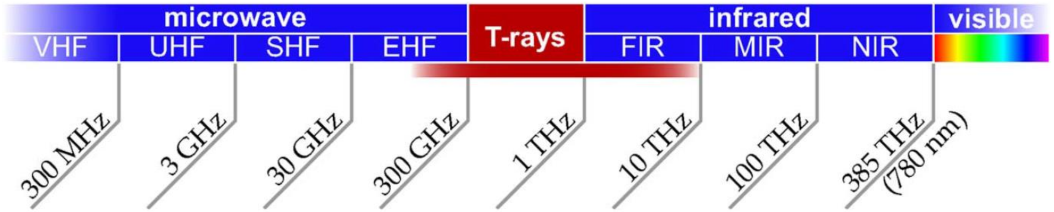
R. Narkowicz, et al. JMR 2005

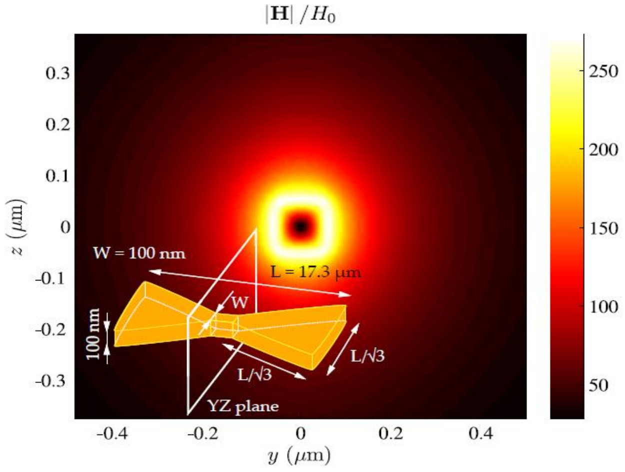


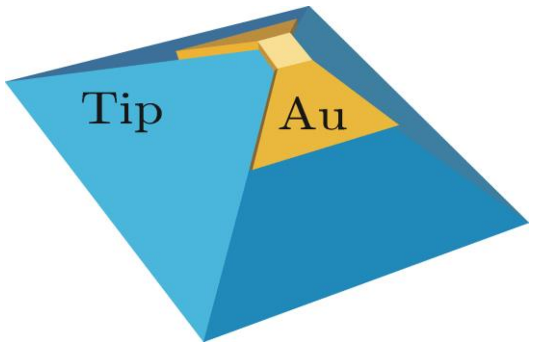


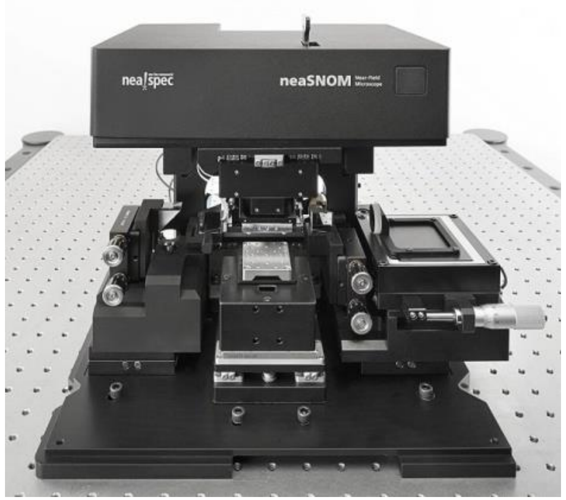
What we need for this "future and emerging technology" to work

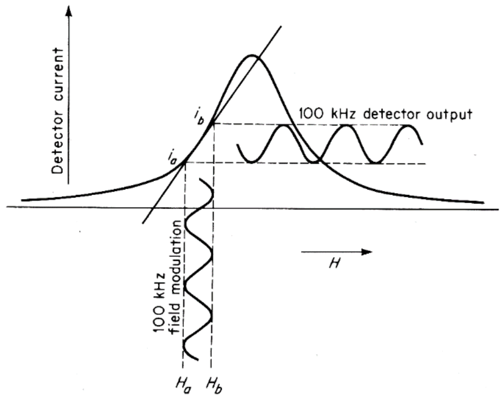
- Plasmon enhancement of THz magnetic field;
- Tip integration of plasmonic structure;
- Scanning probe unit in low-temperature/high-field environment;
- Readout of weak signal.











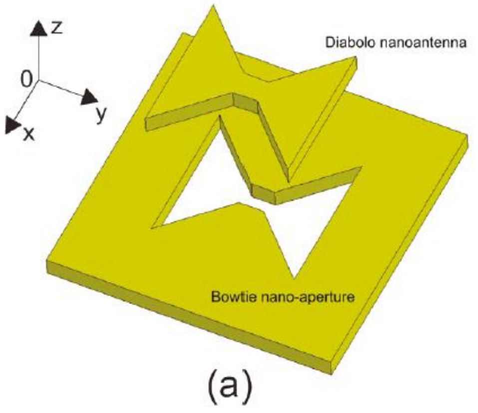
2x aims

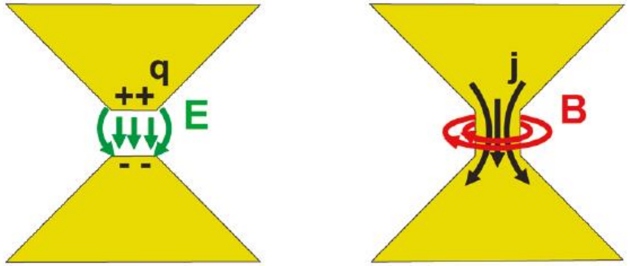
1) Proof Plasmonic enhancement of THz magnetic fields;

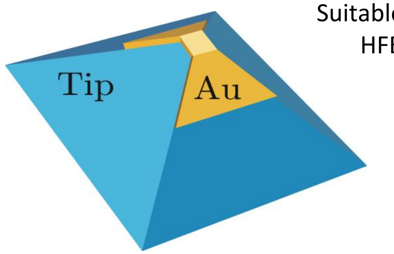
2) Realize a new type of resonator for High Frequency EPR.

Design of the Plasmonic Metasurface Resonator

Plasmonic antenna for magnetic field focusing

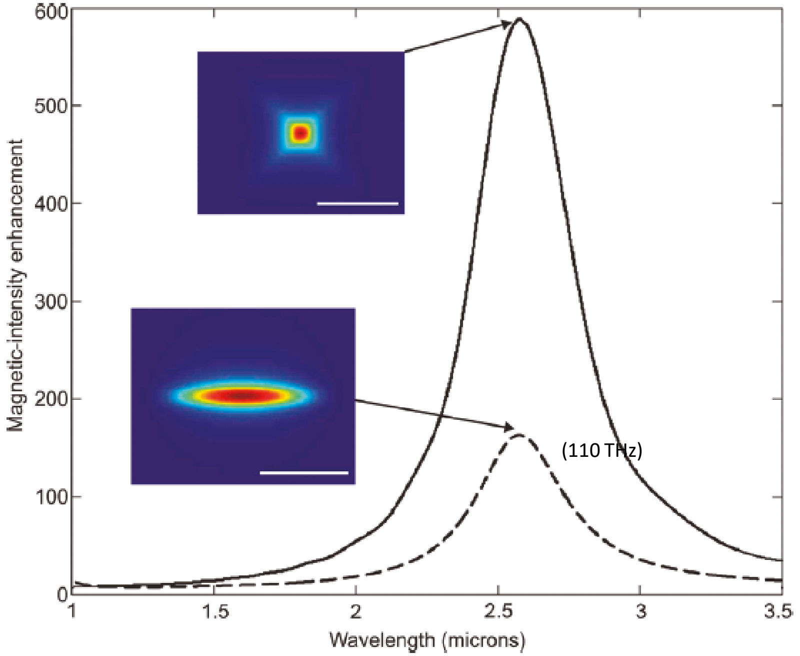


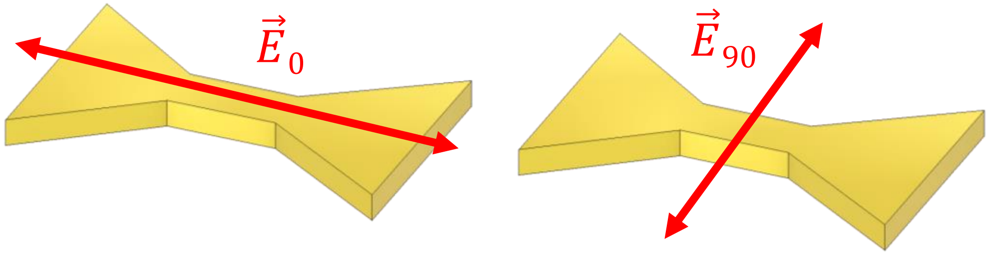




Suitable as a tip for HFEPR-SPM

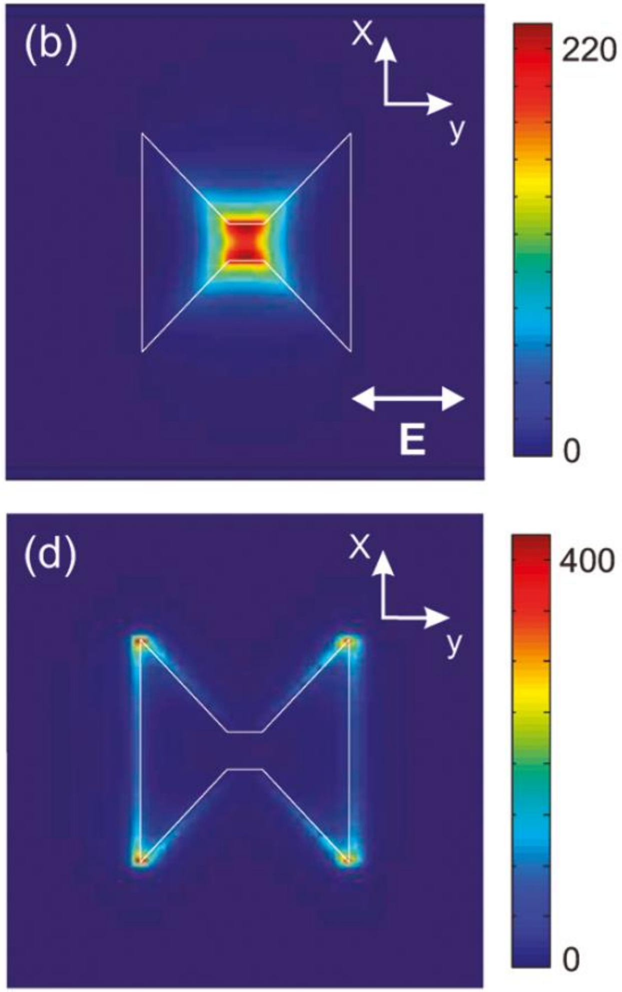
- D = 310 nm and G = T = 20 nm (diabolo antenna)
- 455 nm long gold nanowire of 20 nm large square cross section





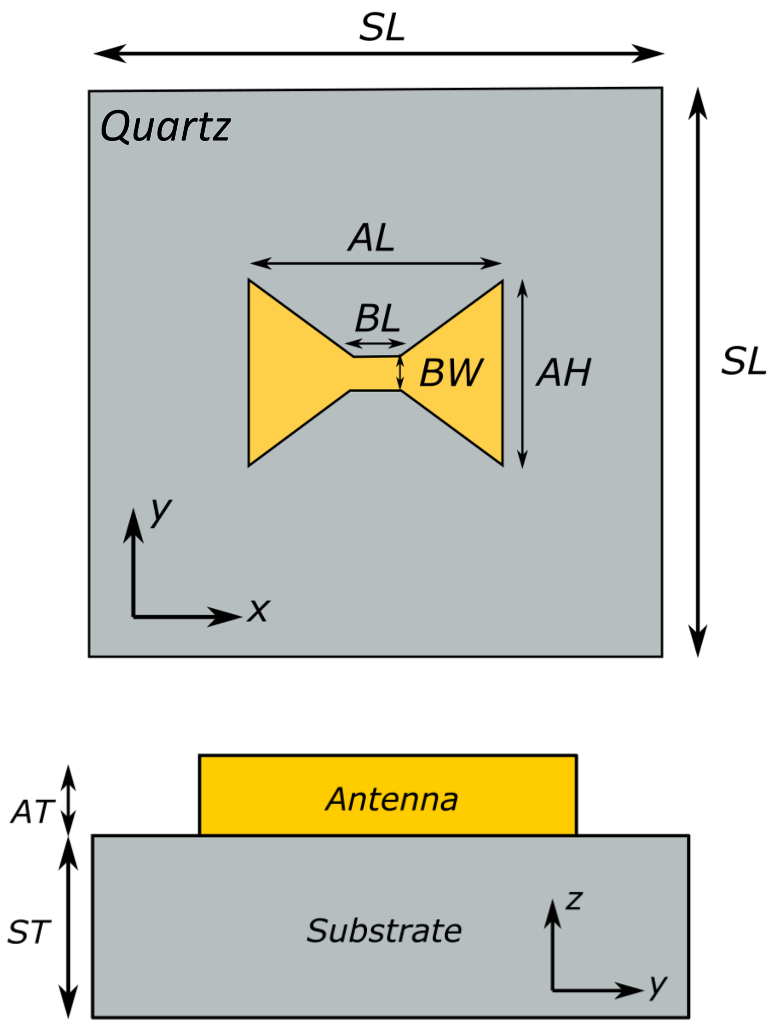
ACTIVE

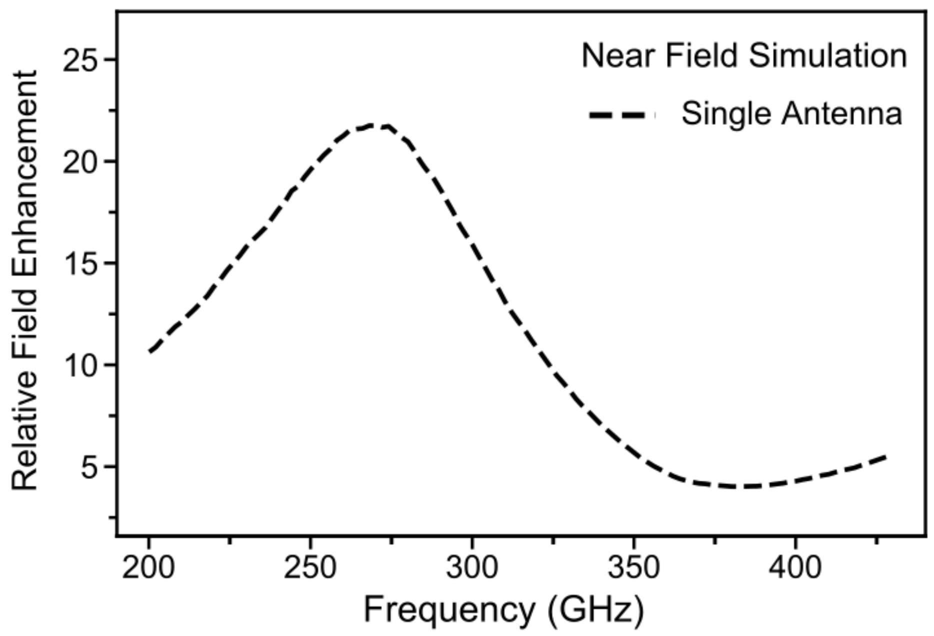
NON-ACTIVE



T. Grosjean, et al. Nano Letters 2011

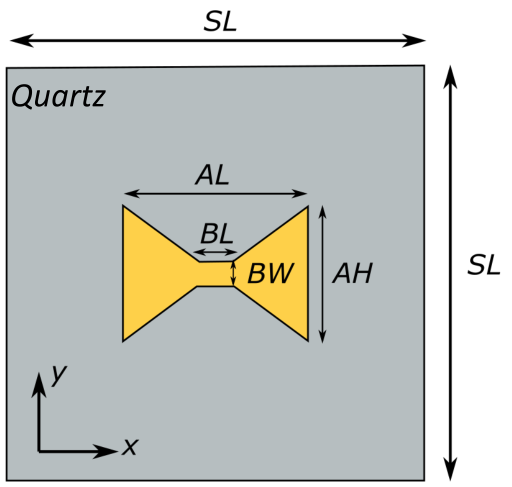
Design of a THz-field enhancement plasmonic metamaterial by numerical simulations in CST Studio

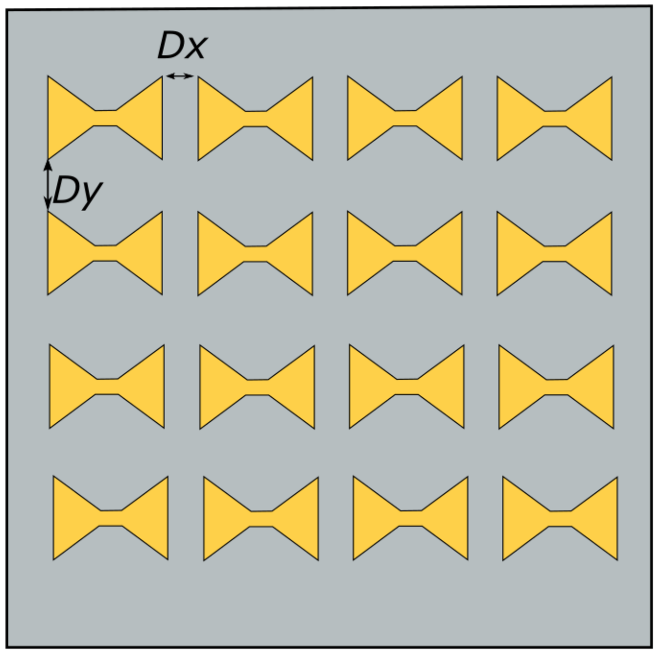


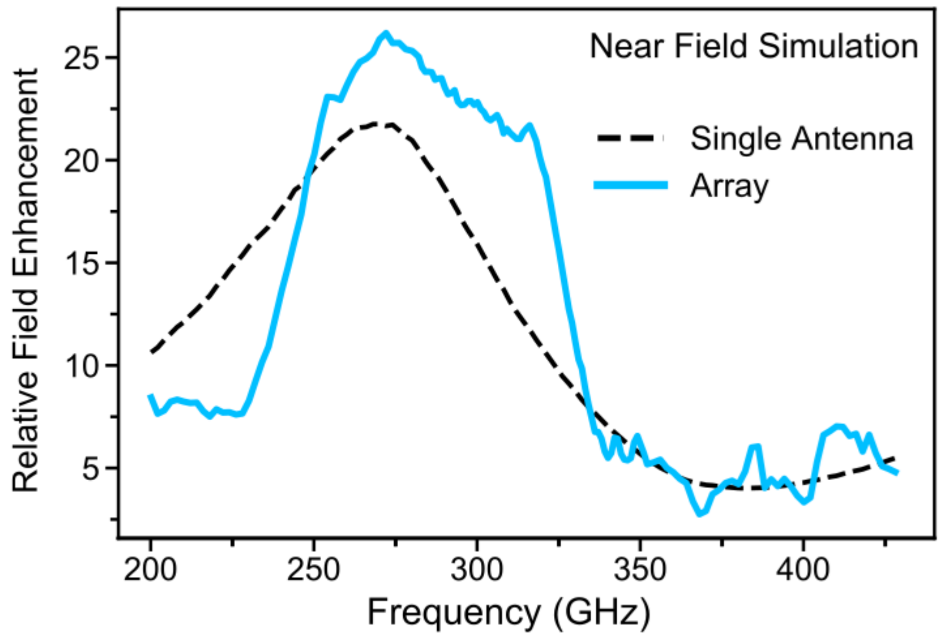


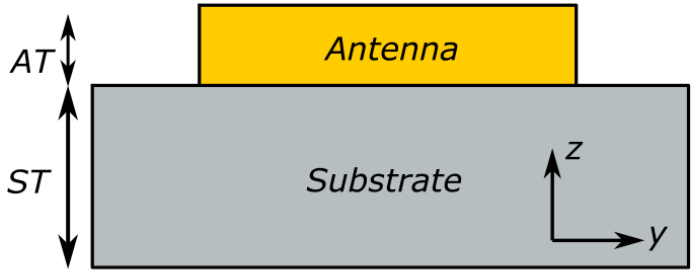
Design of the Plasmonic Metasurface Resonator

Design of a THz-field enhancement plasmonic metamaterial by numerical simulations in CST Studio



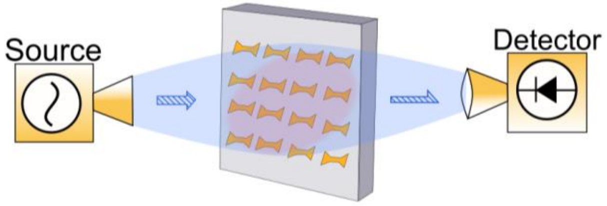




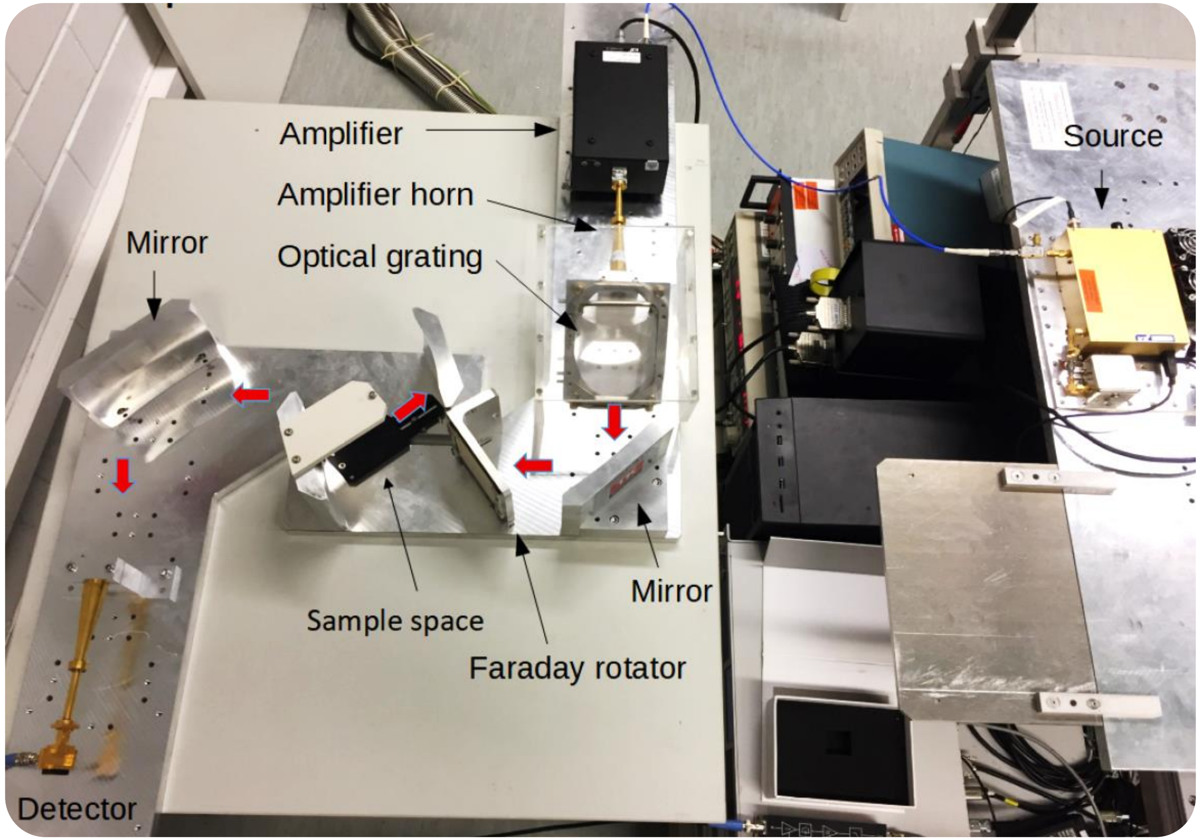


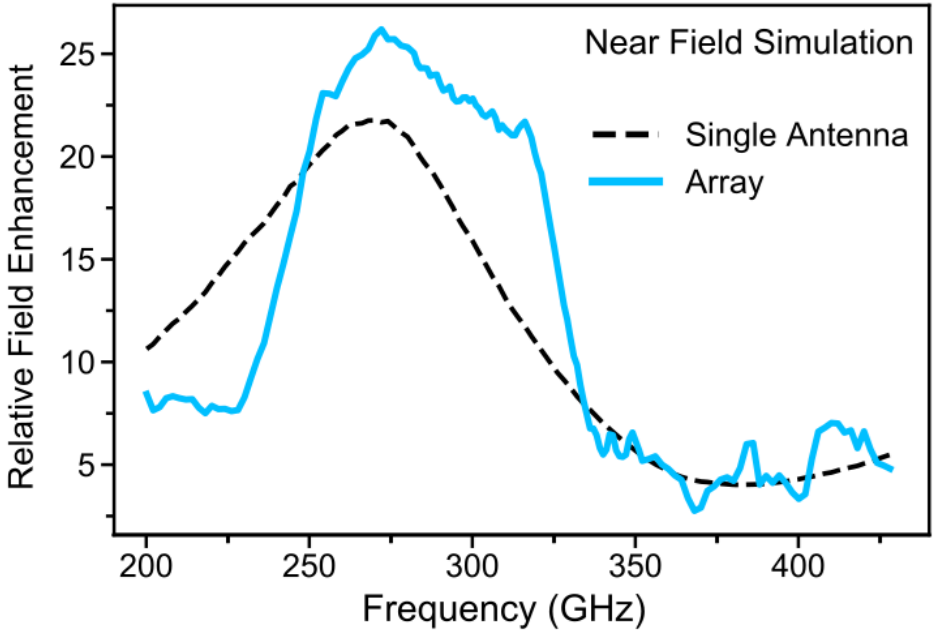
Design of the Plasmonic Metasurface Resonator

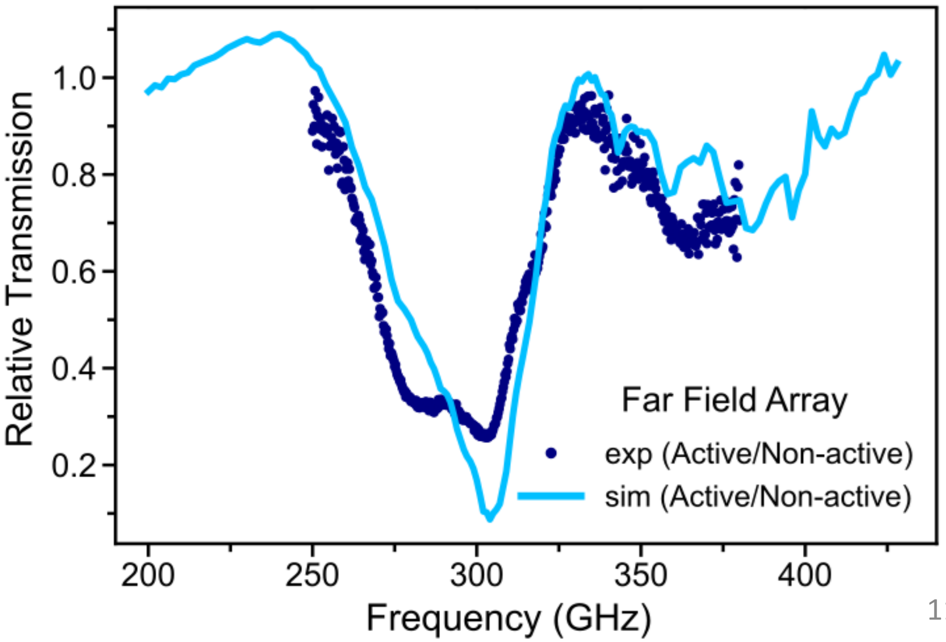
Cw-THz transmission measurements



Room Temperature from 82 GHz up to 1 THz







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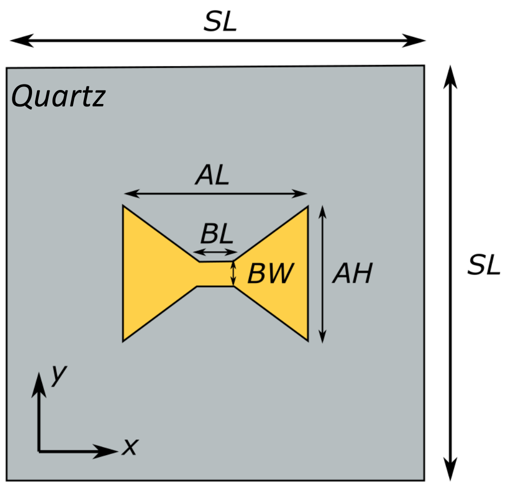
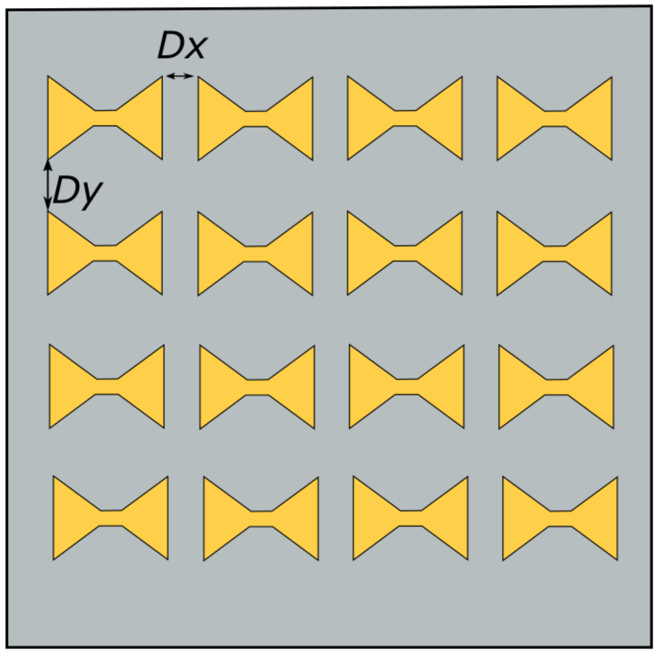
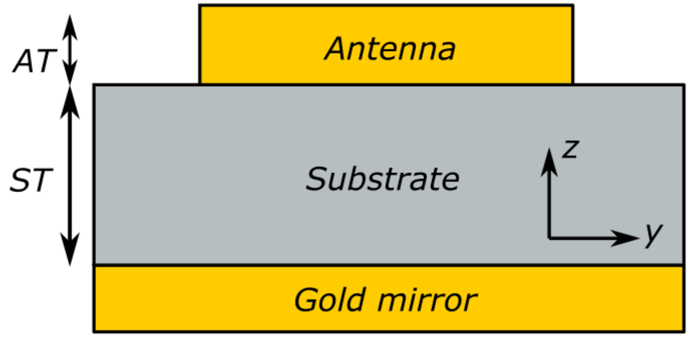
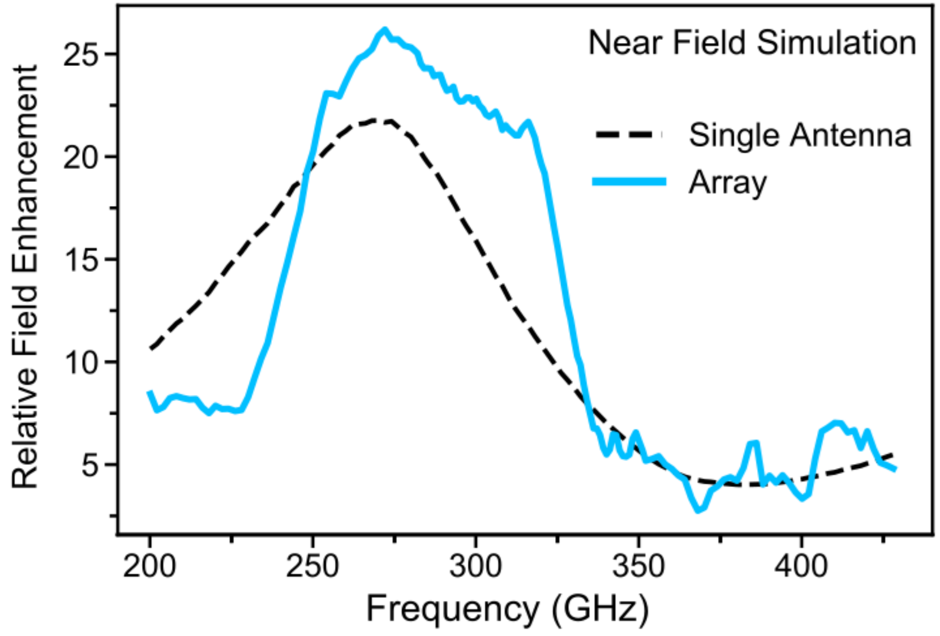
Design of the Plasmonic Metasurface Resonator

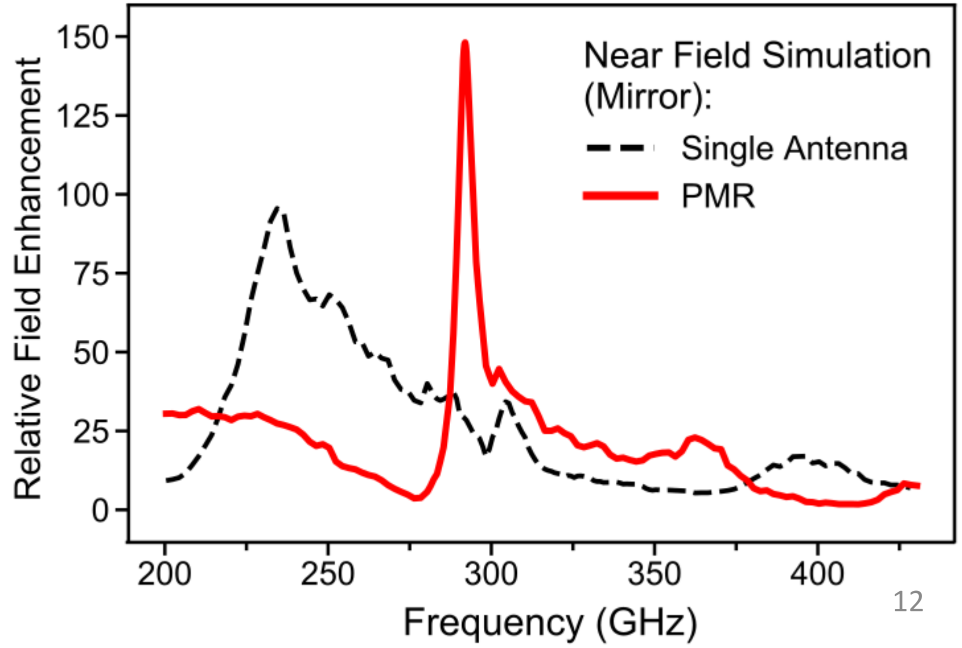
Adding a back reflector to the substrate











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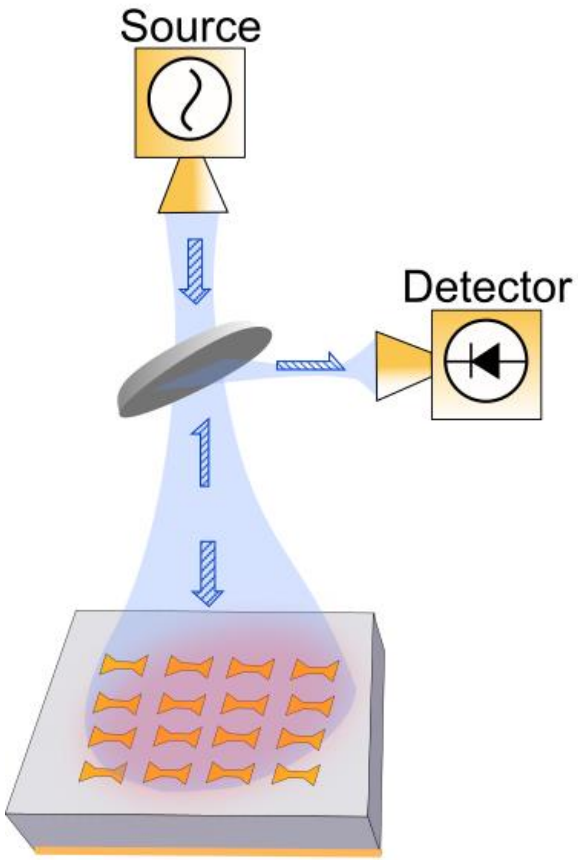
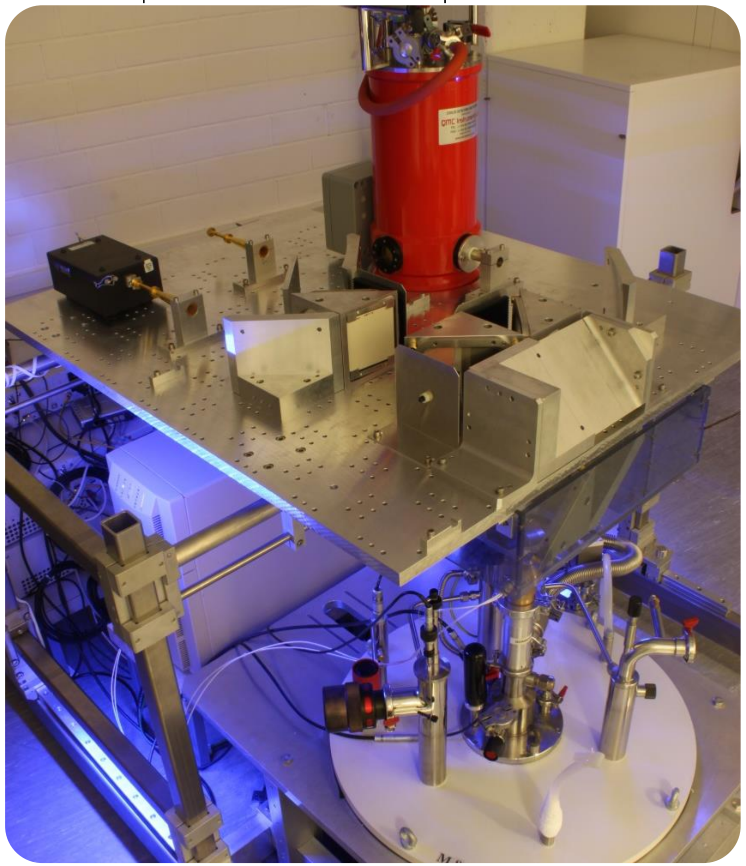
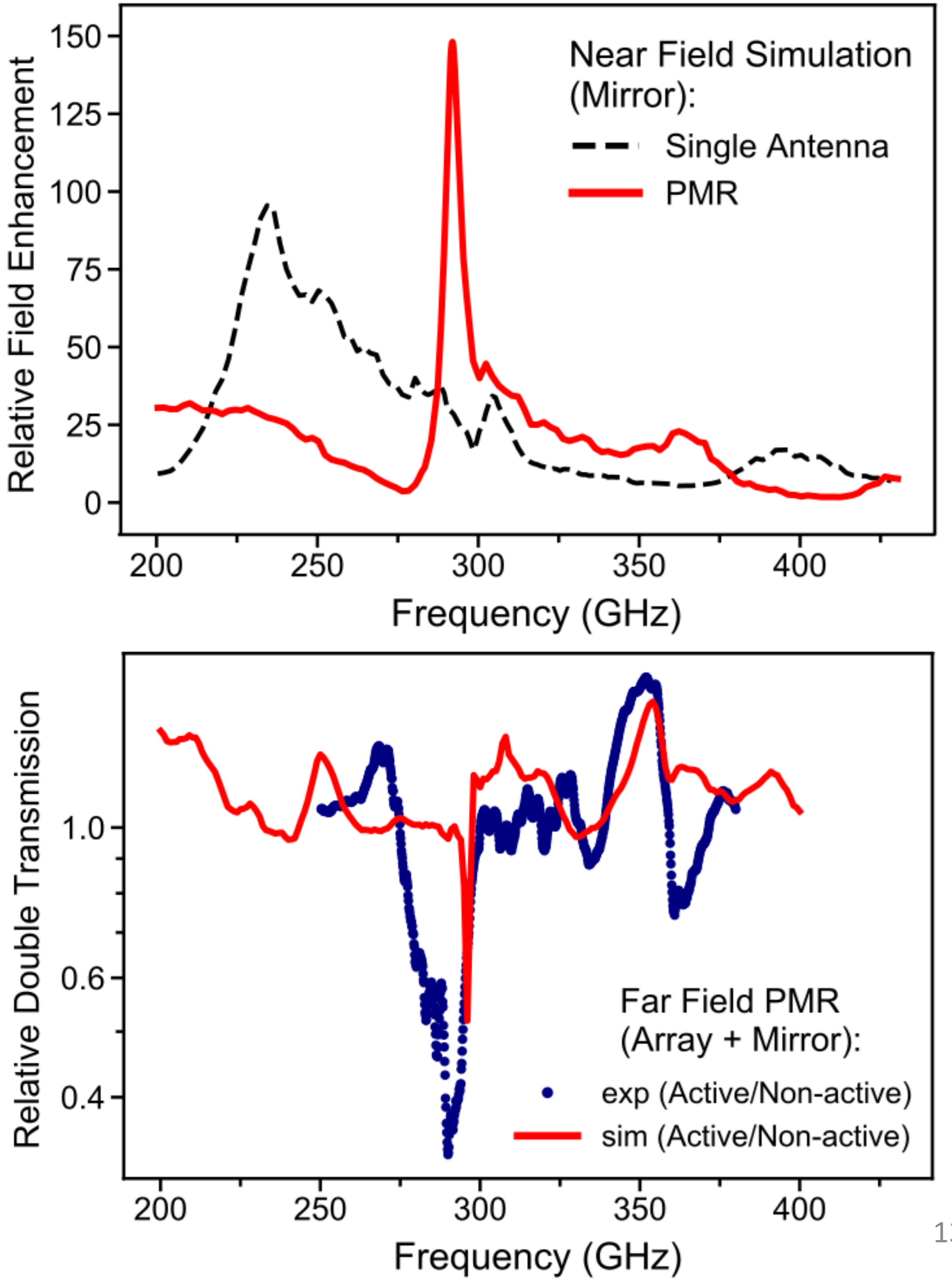
Design of the Plasmonic Metasurface Resonator

Double-THz transmission measurements



Room Temperature from 82 GHz up to 1 THz





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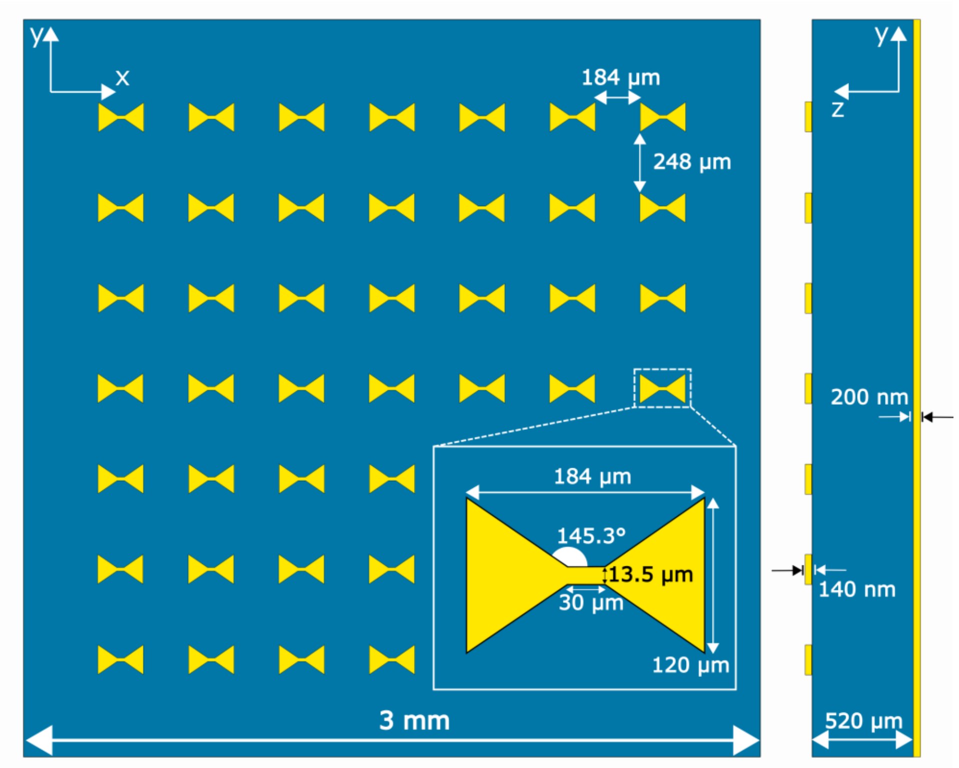
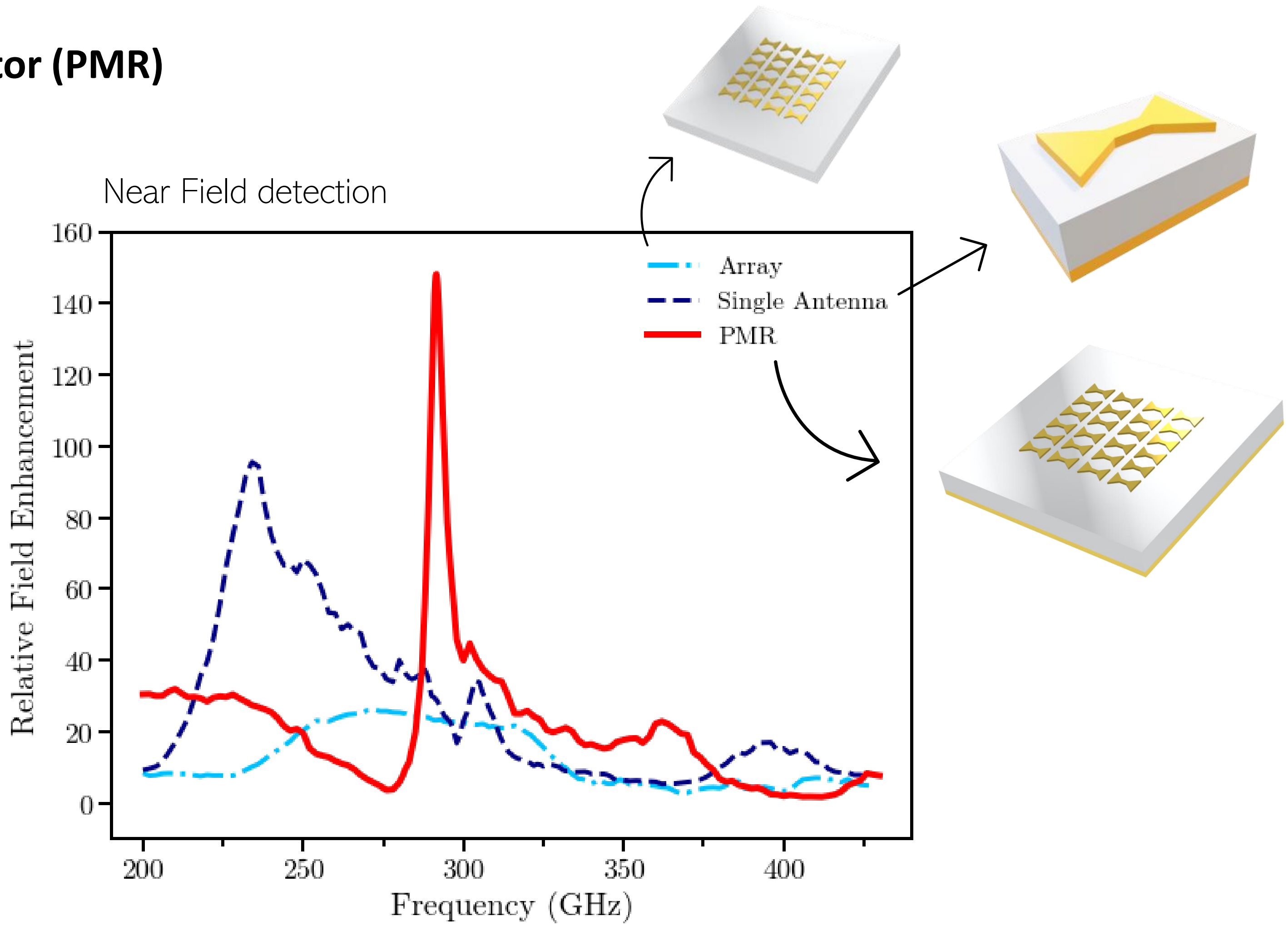
Design of the Plasmonic Metasurface Resonator

Final design of the Plasmonic Metasurface Resonator (PMR)

Design of the PMR



Near Field detection



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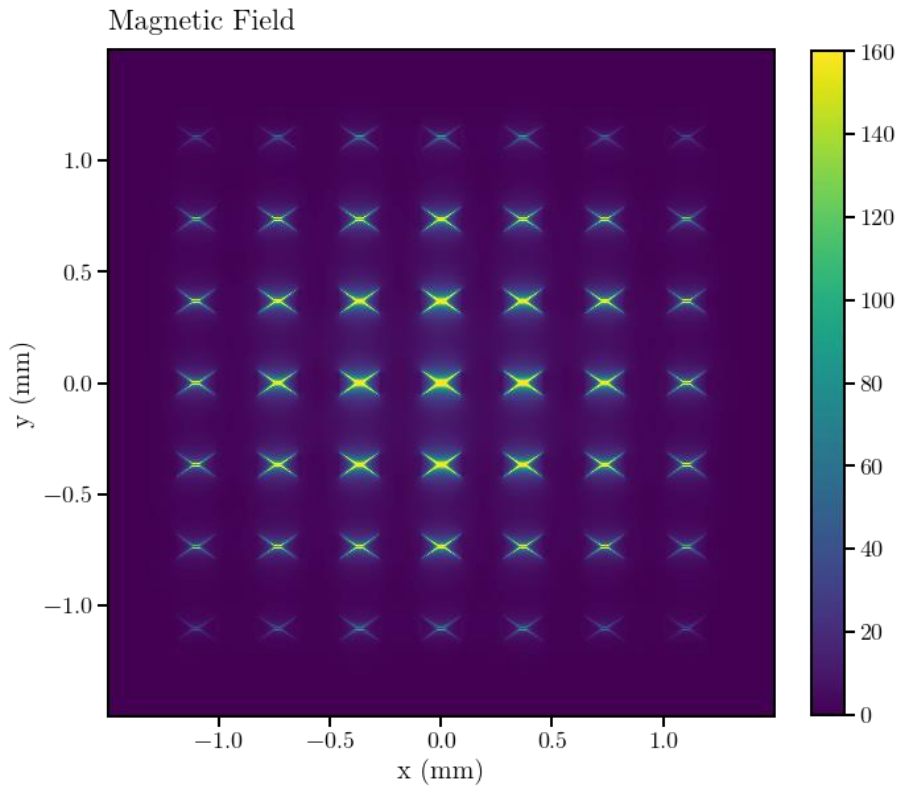
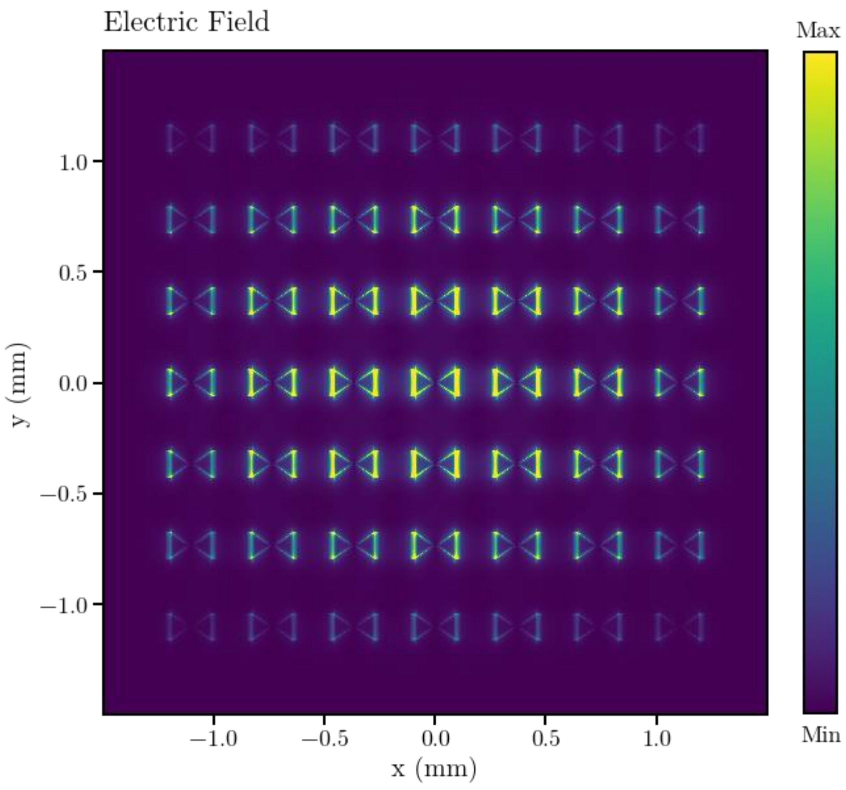
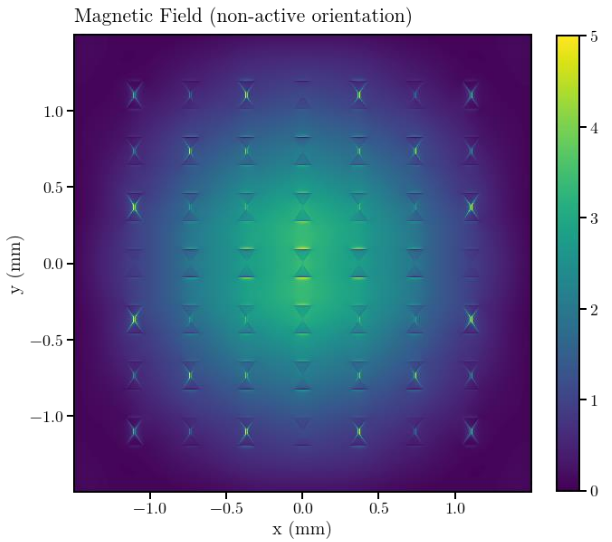
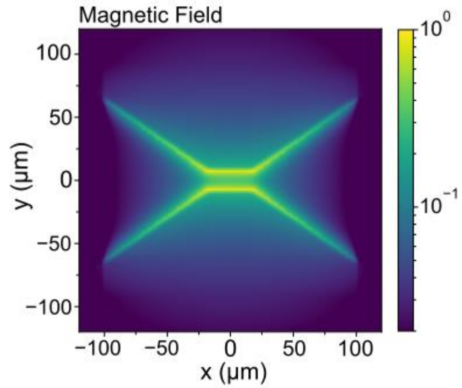
Electromagnetic Fields Map of the PMR

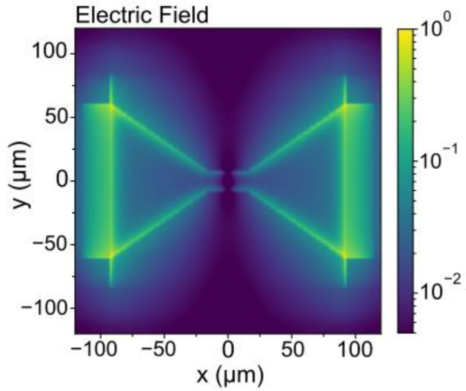
At the resonant frequency value (291.5 GHz):

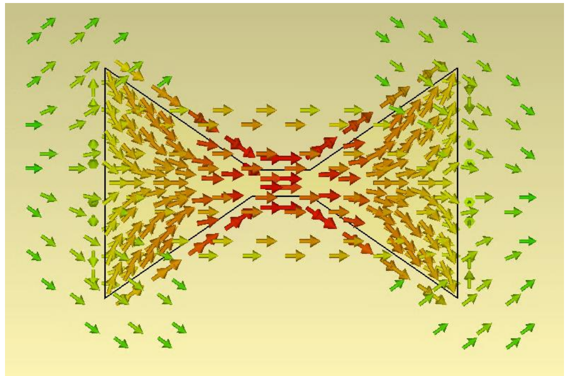


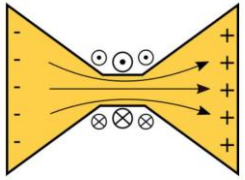












Longitudinal Dipole Mode

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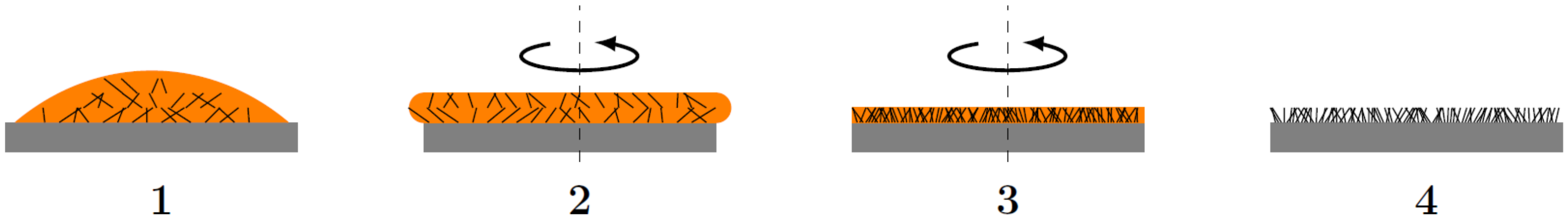
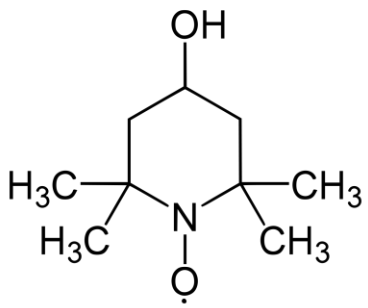
Sample preparation for High Frequency EPR measurements

Deposition of a thin film by Spin Coating





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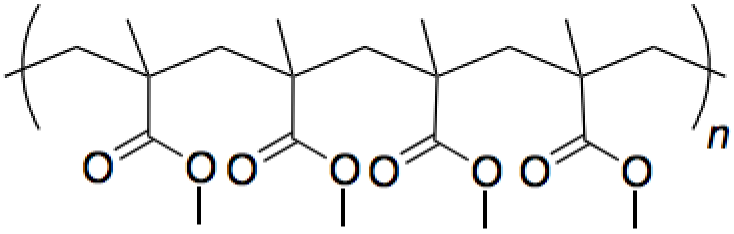
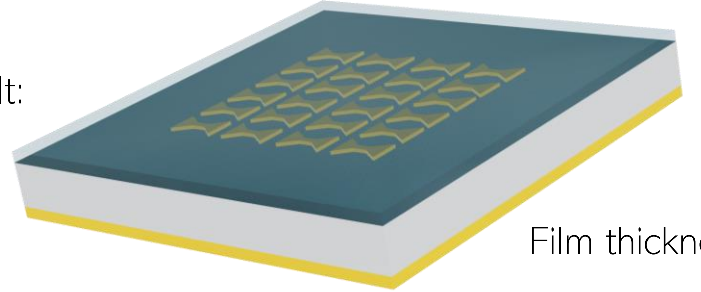


TEMPOL
(4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl)

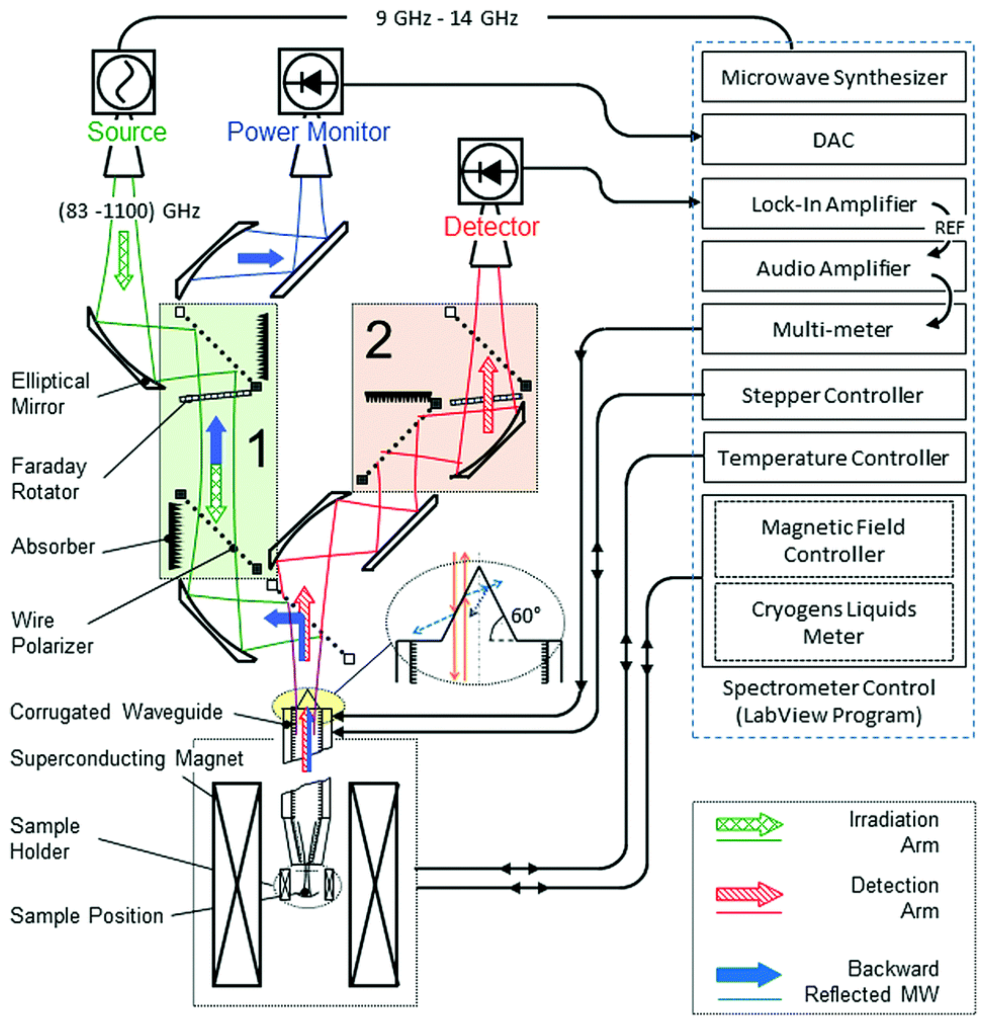
PMMA
(poly(methyl methacrylate))

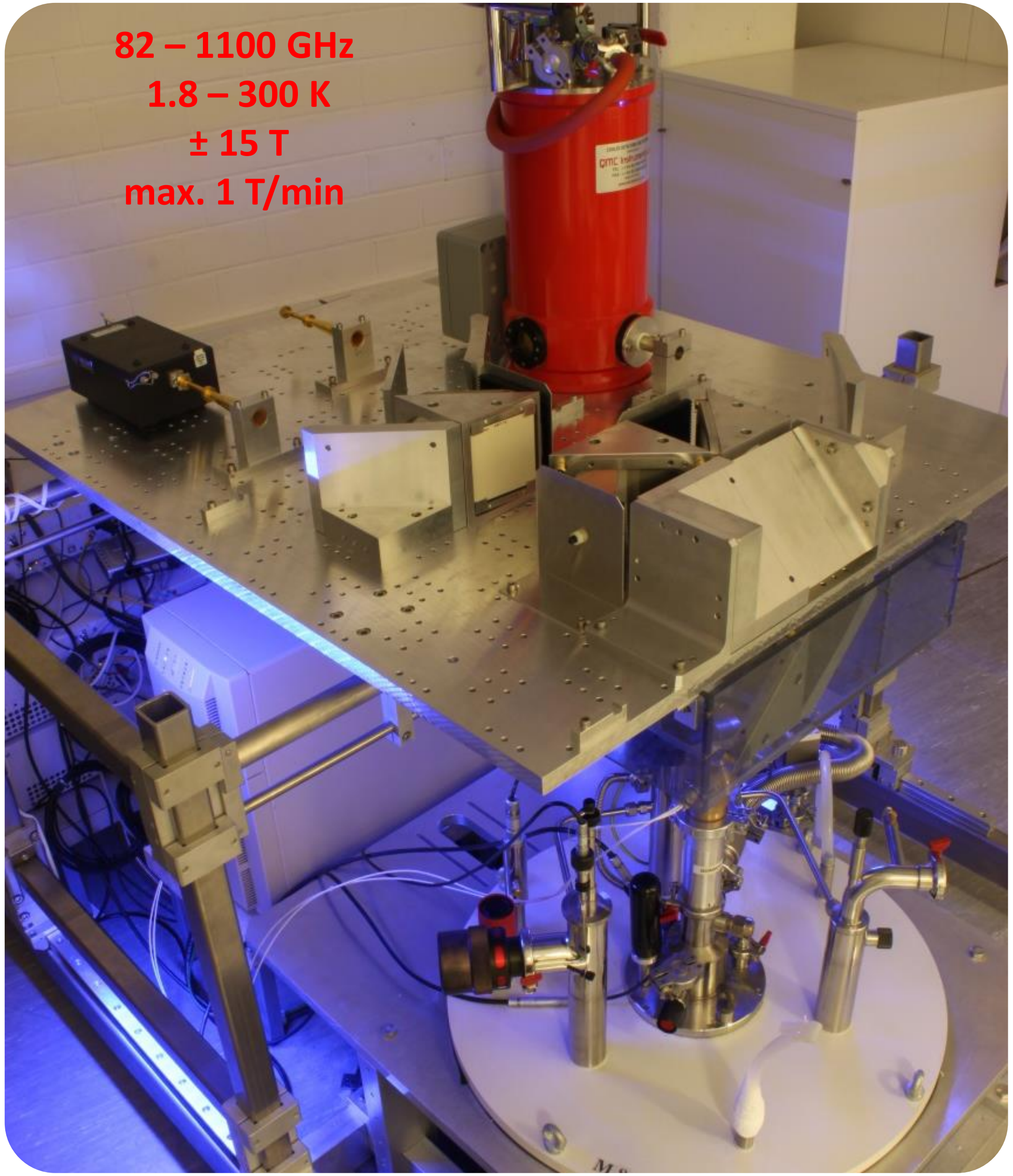
The result:



Film thickness 330 ± 10 nm

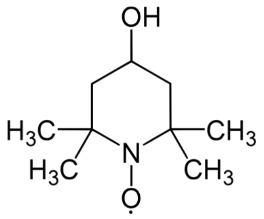
High Frequency EPR: an overview of the instrument

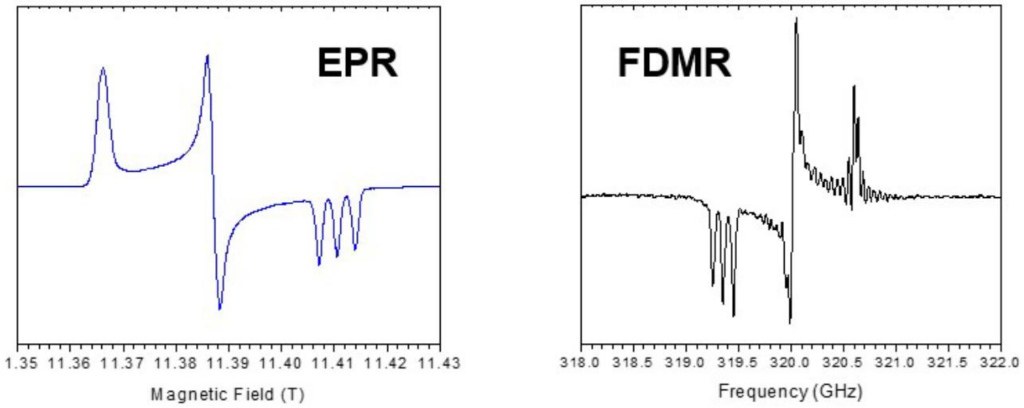


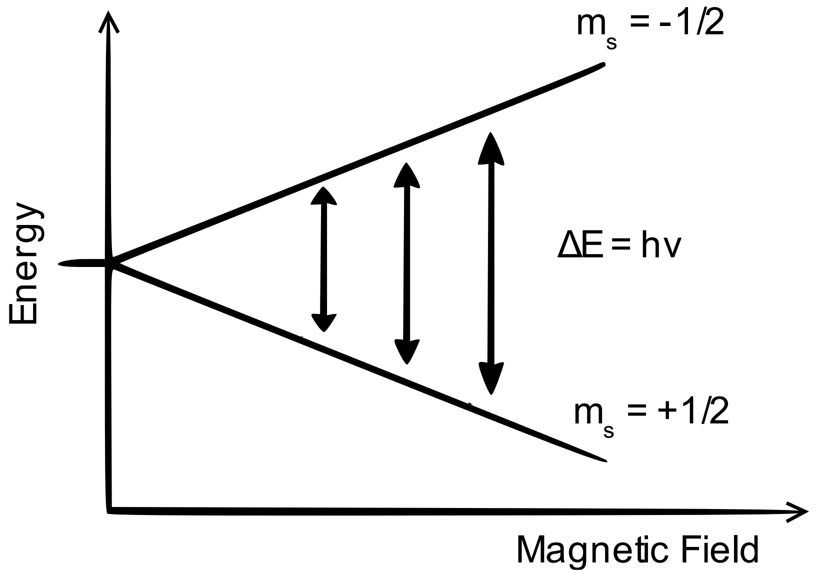


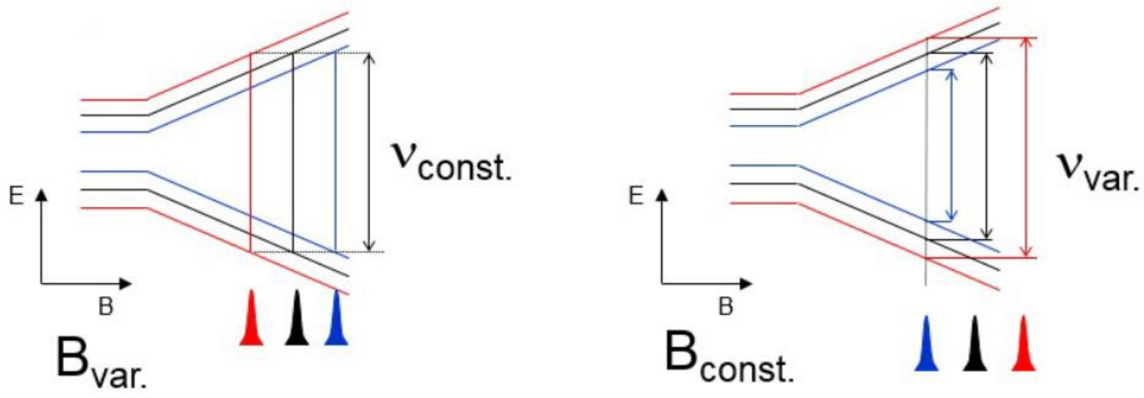
P. Neugebauer, et al. PCCP, 2018

High Frequency EPR measurements





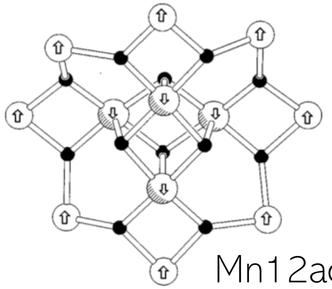




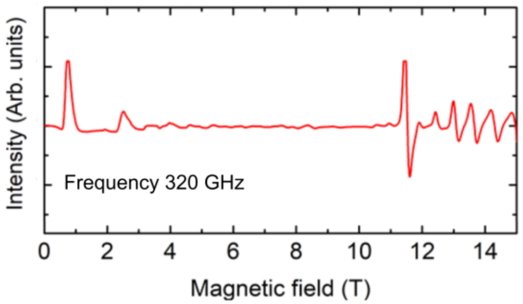
Open to the possibility of measuring Field-Frequency Magnetic Resonance Maps

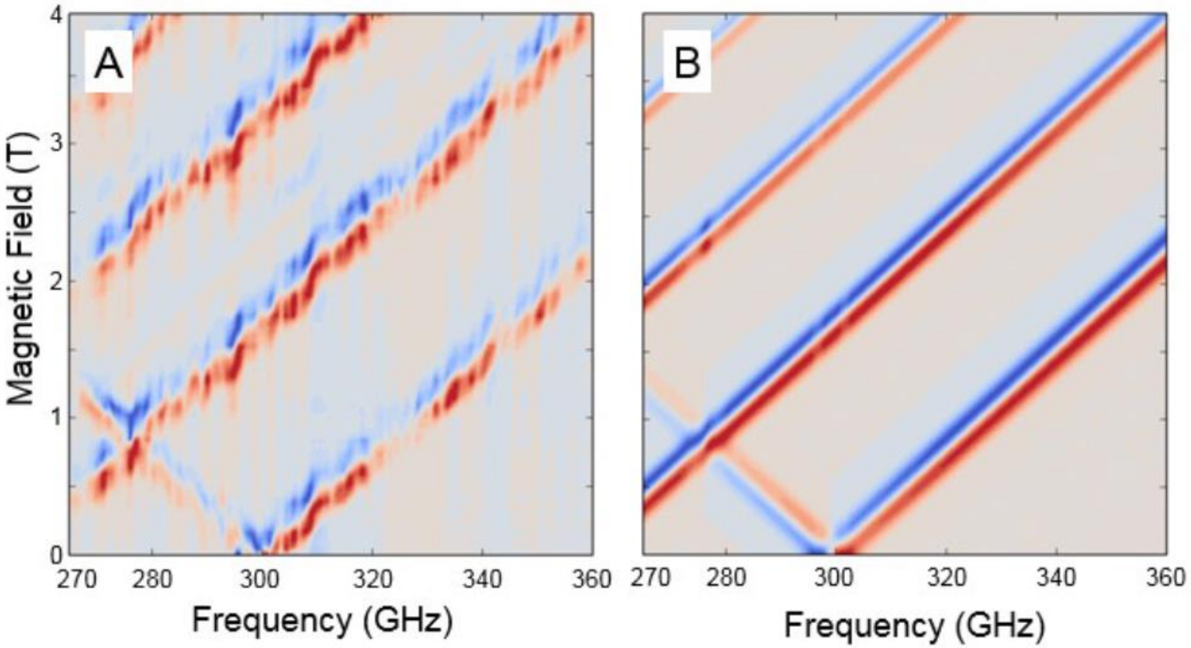
P. Neugebauer, et al. PCCP, 2018

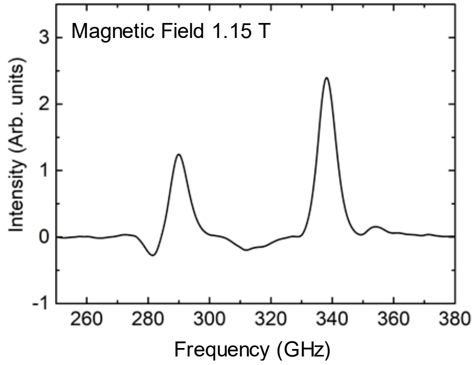
Example of Field-Frequency Magnetic Resonance Map



Mn12ac

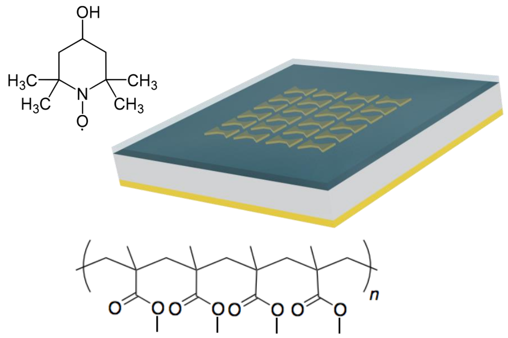




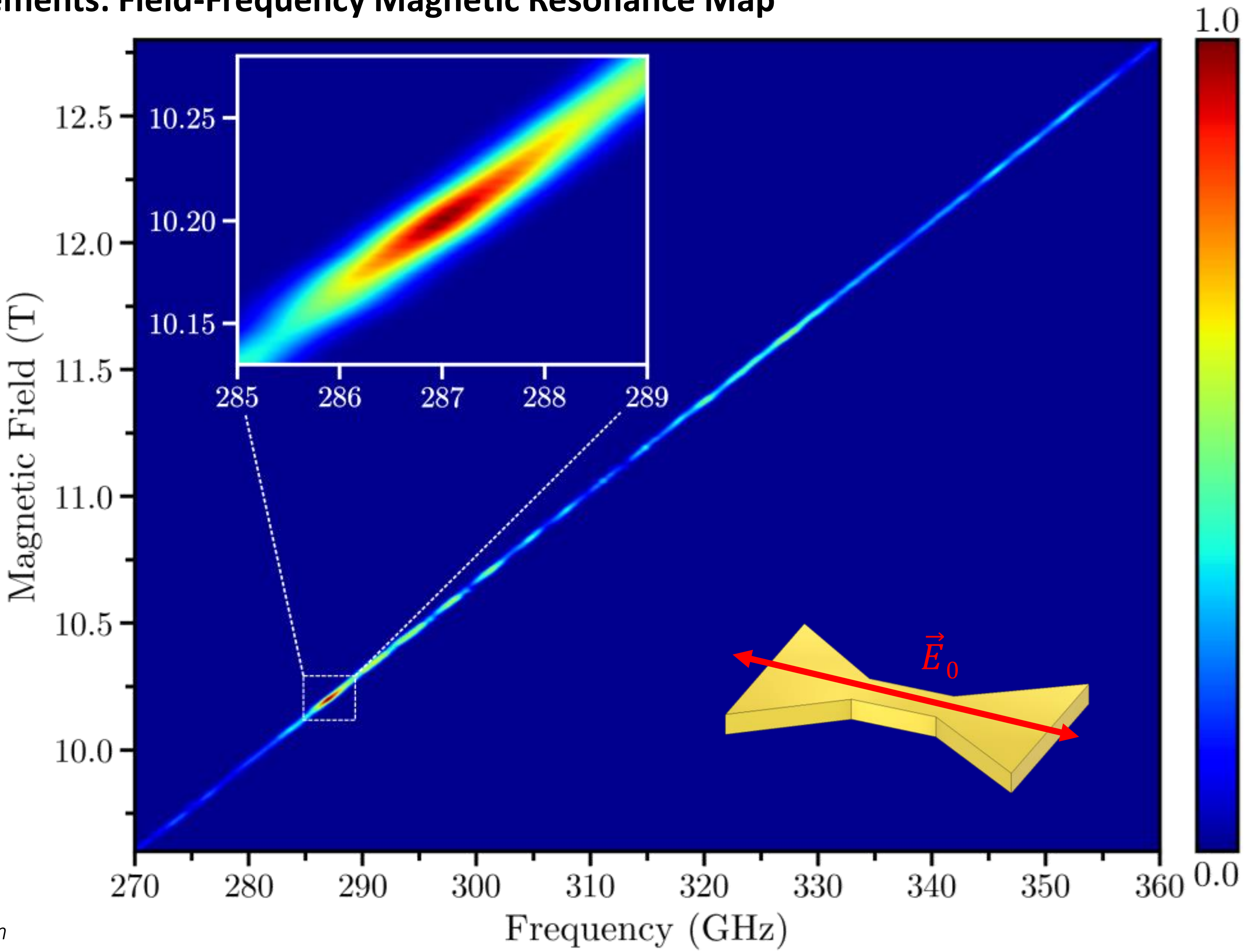


P. Neugebauer, et al. PCCP, 2018

High Field EPR measurements: Field-Frequency Magnetic Resonance Map

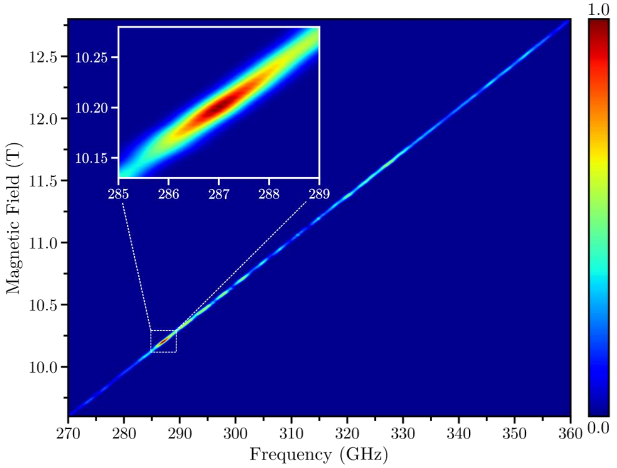


- Remove of the Standing wave
- Fit with derivative of Gaussian type linewidth
- Integration of the fit
- Plot ⟶



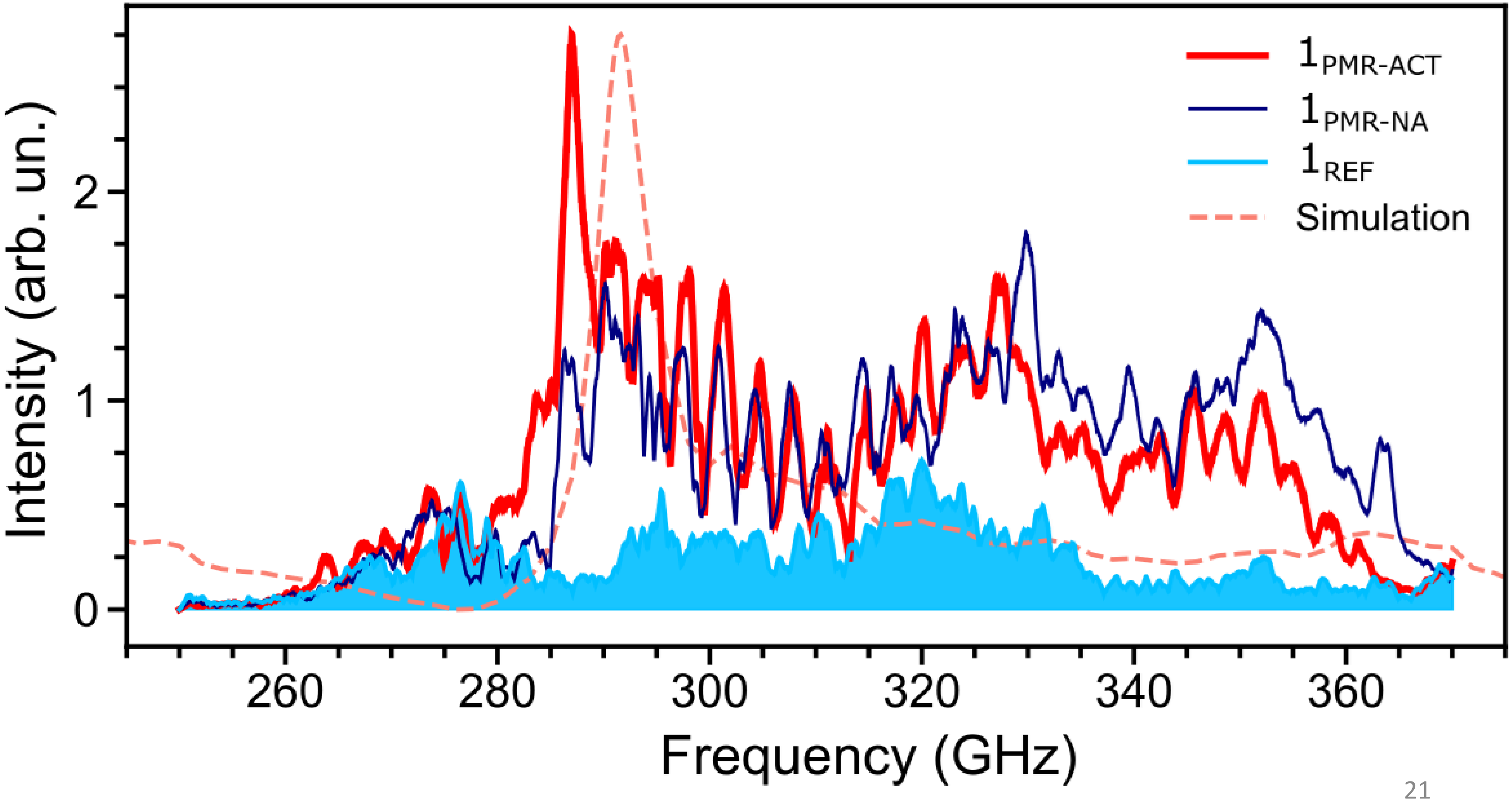
L. Tesi, et al. Manuscript in preparation

High Field EPR measurements: diagonal cut of the FFMR map



The EPR signal enhancement estimated from numerical simulations is a factor 280

The EPR signal enhancement extracted is a factor 30 →



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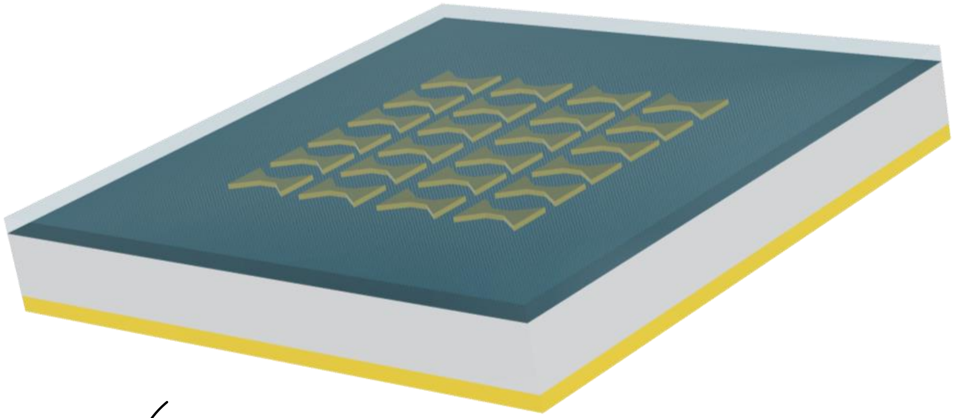
PMR for High Frequency EPR measurements

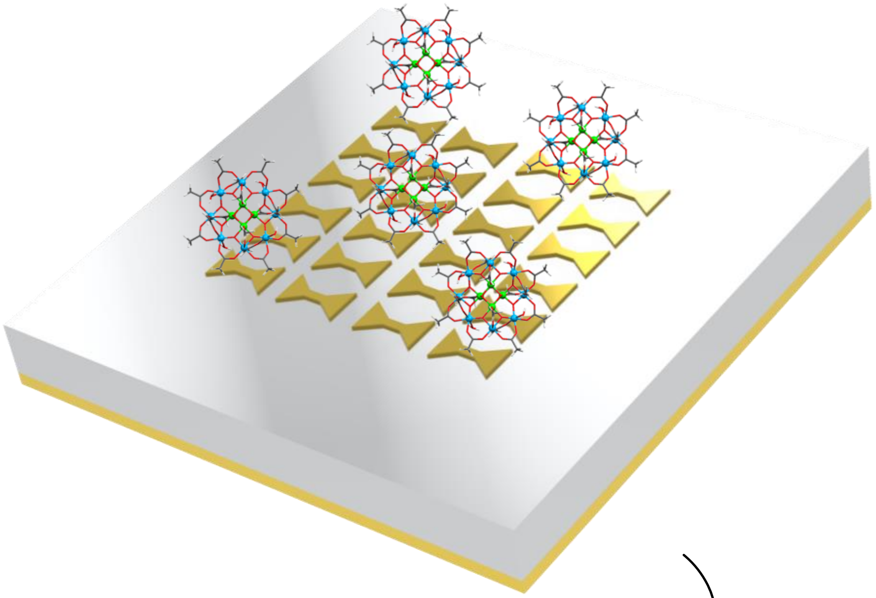
The EPR signal enhancement extracted is a factor 30 for a thin layer



- Improve the signal for thin layer samples;
- Improve the signal for micro-crystal samples

The EPR signal enhancement predicted from the simulations when depositing the molecules directly on the antennas is 7500

10^{10} spins/G·Hz$^{1/2}$ at 10 K ⟶ 10^{6} spins/G·Hz$^{1/2}$ at 10 K



- Measurement of self-assembled monolayer;
- Integration of molecules on surface for spintronic applications

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BRNO UNIVERSITY OF TECHNOLOGY

Adam Benes

BRNO UNIVERSITY OF TECHNOLOGY

Martin Hrton

HORIZON 2020

…and you for the attention!

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- **Prof. Tobias Kampfrath** (Terahertz Physics Group, Fritz Haber Institute, Berlin)
- **Dr. Sergei Zvyagin** (Dresden High Magnetic Field Laboratory, HZDR Dresden)
- **Dr. Alexander Schnegg** (Department Spins in Energy Conversion and Quantum Information Science, Helmholtz Zentrum (HZB), Berlin)
- **Dr. Magnus Jonsson** (Organic Photonics and Nano-Optics group, Linköping University)
- **Dr. Alexander A. Govyadinov** (Neaspec GmbH, Munich)

ORGANIZERS

Rainer Hillenbrand and Monika Goikoetxea (Nanooptics Research Group, CIC NanoGUNE)

Plasmon Enhanced Terahertz Electron Paramagnetic Resonance
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