High Frequency Electron Spin Resonance Spectroscopy Today and Tomorrow

CEITEC MOTES

erc

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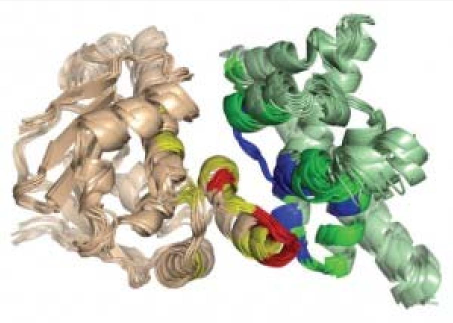
Nobel Prizes in Magnetic Resonance

Nobel Prizes Directly Related to MR

Name	Year	Category	Description
Paul C. Lauterbur	2003	Medicine	"For their discoveries concerning magnetic resonance imaging"
Sir Peter Mansfield	2003	Medicine	"For their discoveries concerning magnetic resonance imaging"
Kurt Wüthrich	2002	Chemistry	"For his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution"
Richard R. Ernst	1991	Chemistry	"For his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy"
Felix Bloch	1952	Physics	"For their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"
Edward Mills Purcell	1952	Physics	
Isidor Isaac Rabi	1944	Physics	"For his resonance method for recording the magnetic properties of atomic nuclei"



10

Nobel Prizes in Other Fields, Awarded to Individuals Who Also Contributed to the Development of MR

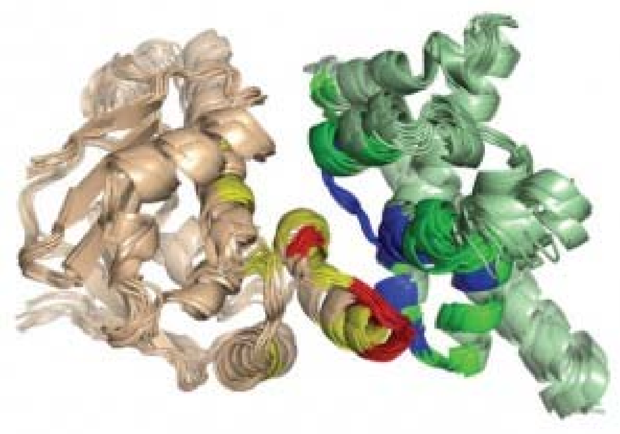
Name	Year	Category	Description
Norman F. Ramsey	1989	Physics	"For the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks"
Hans G. Dehmelt	1989	Physics	"For the development of the ion trap technique"
K. Alexander Müller	1987	Physics	"For their important break-through in the discovery of superconductivity in ceramic materials"
Nicolaas Bloembergen	1981	Physics	"For their contribution to the development of laser spectroscopy"
John H.Van Vleck	1977	Physics	"For their fundamental theoretical investigations of the electronic structure of magnetic and disordered systems"
Alfred Kastler	1966	Physics	"Optical methods for studying Hertzian resonances"

http://www.nobelprize.org/nobel_prizes

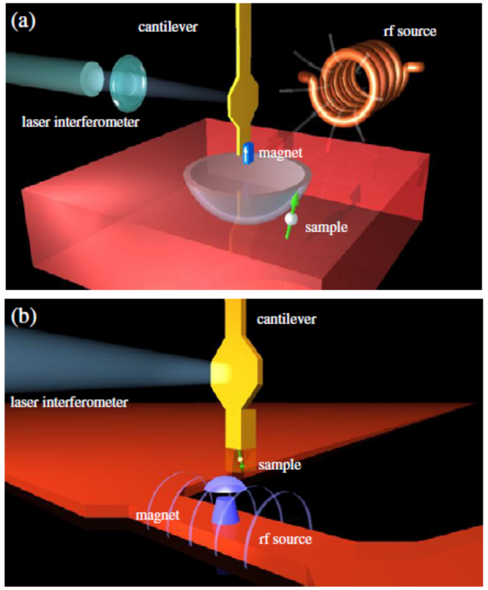
Motivation – Why is so?

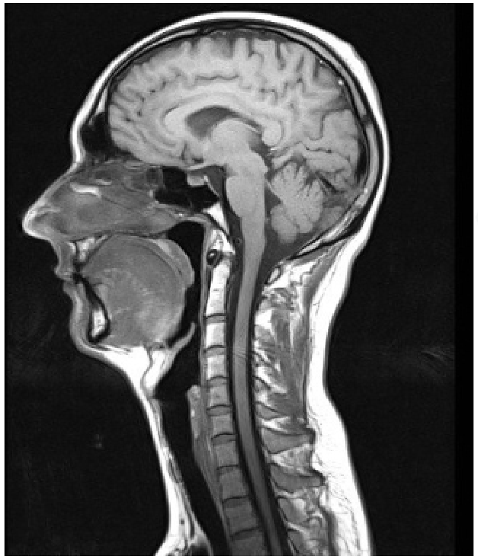
- Non invasive and not ionizing beam
- Dynamics and structure determination of biological relevant complexes (in X-ray only crystalized systems can be measured)

Determination of Structure, Function and Dynamics of Large Molecular objects



Detection of Single Spin



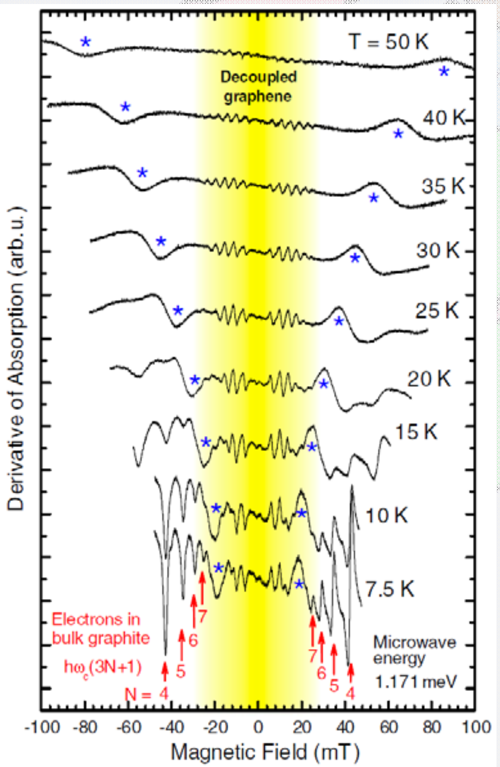


Magnetic Resonance Imaging

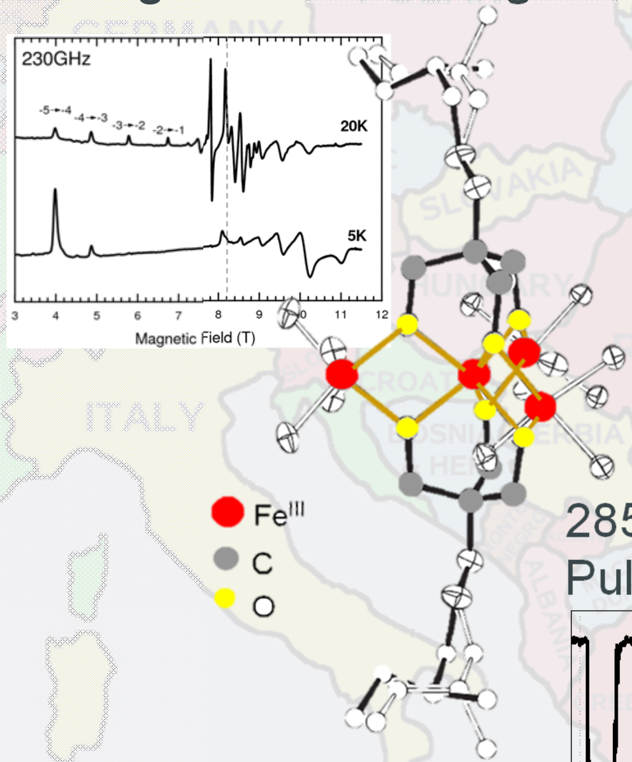
PhD topic

Development of Heterodyne High Field / High Frequency Electron Paramagnetic Resonance Spectrometer at 285 GHz

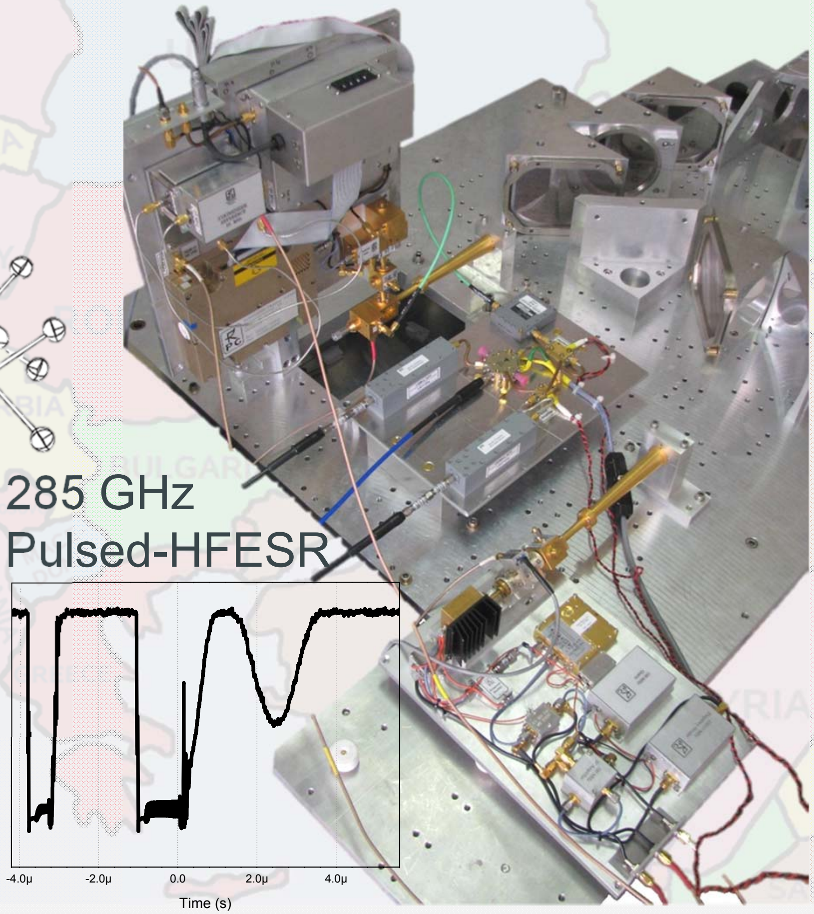
Graphene



Single Molecule Magnets



HFESR Development



- Observation of the highest electron mobility **ever demonstrated** (10^7 V cm^{-2}) in graphene!

Phys. Rev. Lett. 101, 267601 (**2008**); *Phys. Rev. Lett.* 103, 136403 (**2009**) Chem. Eur. J., 15, 6456 – 6467 (**2009**); Appl. Magn. Reson. 37, 833 (**2010**); *Phys. Rev. Lett.* 108, 017602 (**2012**); *unpublished*

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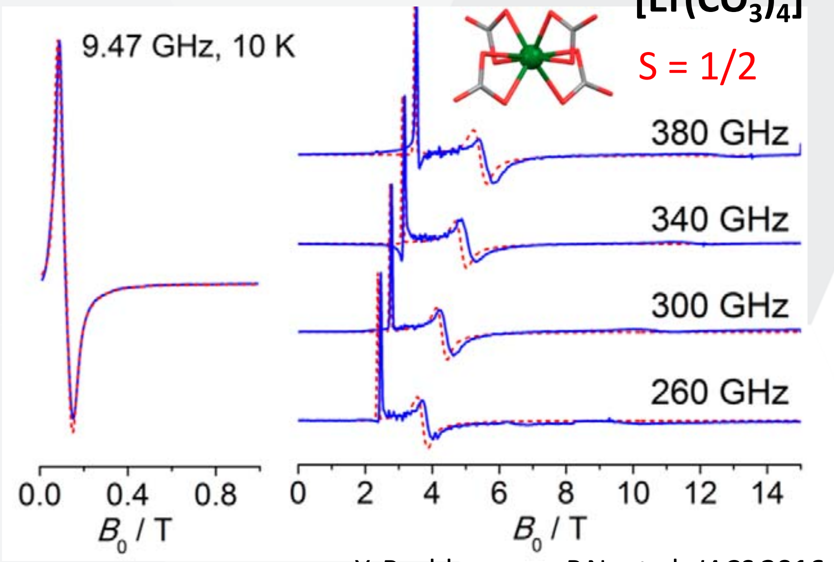
ESR

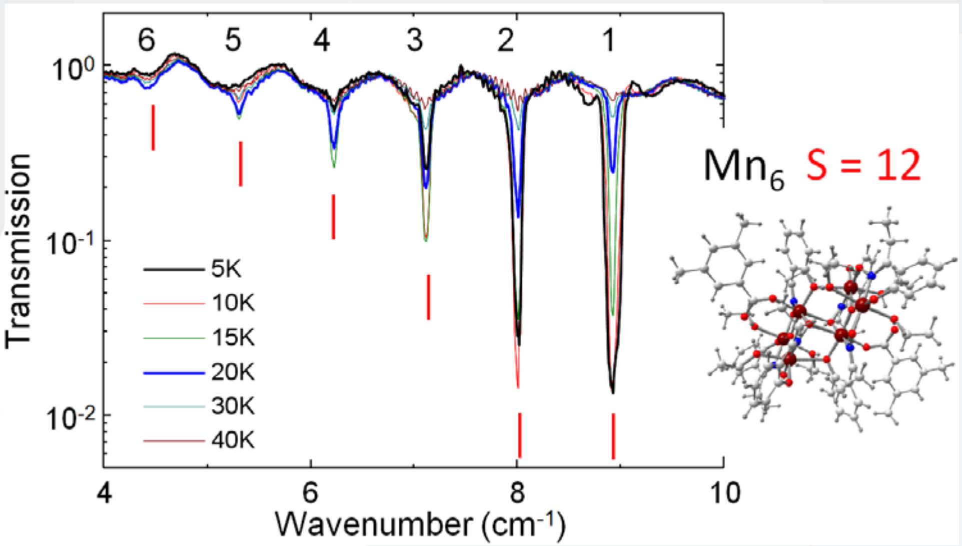
Field necessary: $H \neq 0$.



Y. Rechkemmer, P.N. et al. *JACS* **2016**

FDMR

No field necessary: $H = 0$.



Van Slageren, Carretta, Guidi et al. *PRL* **2008**; *PRB* **2010**.

HFESR:

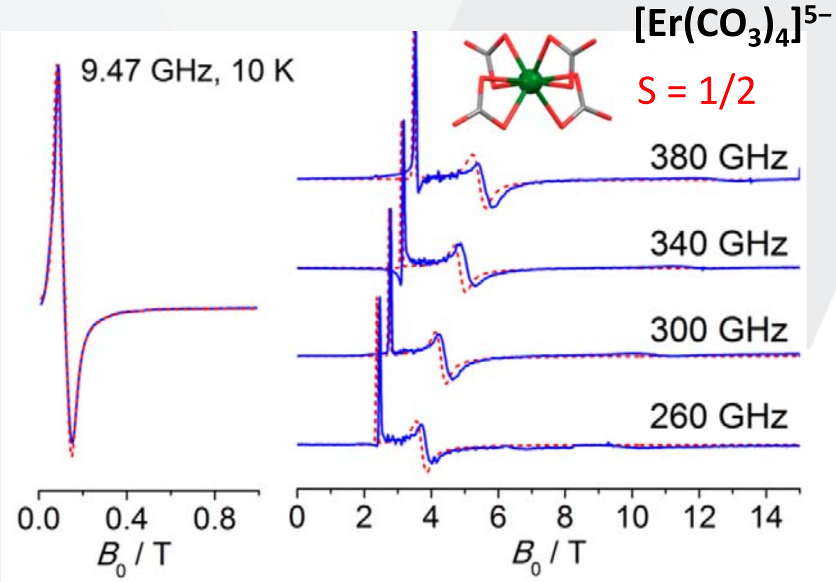
- Very powerfull tool in molecular magnetism, biology, structure determination and spin dynamics

Advantages of FDMR:

- Convenient – *spectrum is recorded as a function of energy (frequency)*
- No influence on the sample by changing high magnetic field - *no higher order field terms*
- Fast – *recording takes less than a minute*

ESR

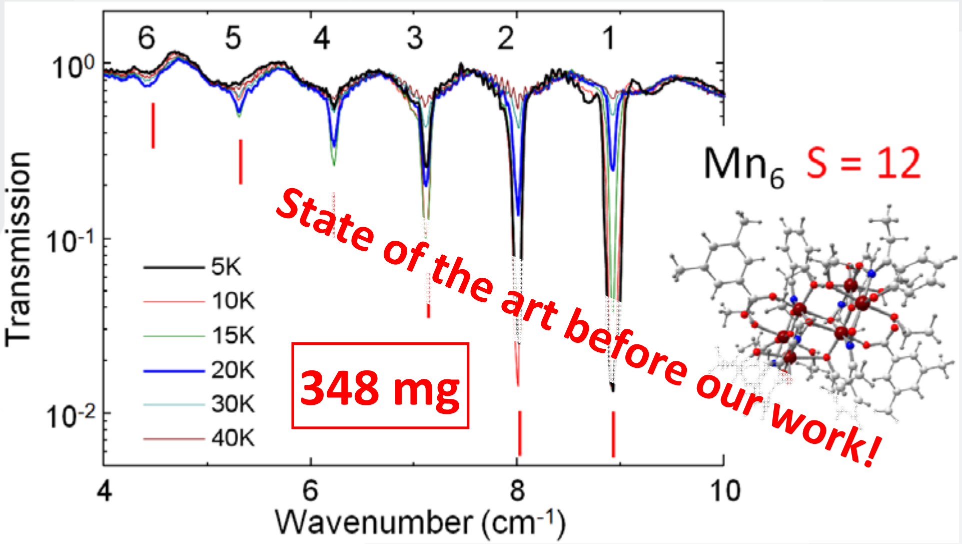
Field necessary: $H \neq 0$.



Y. Rechkemmer, P.N. et al. *JACS* **2016**

FDMR

No field necessary: $H = 0$.



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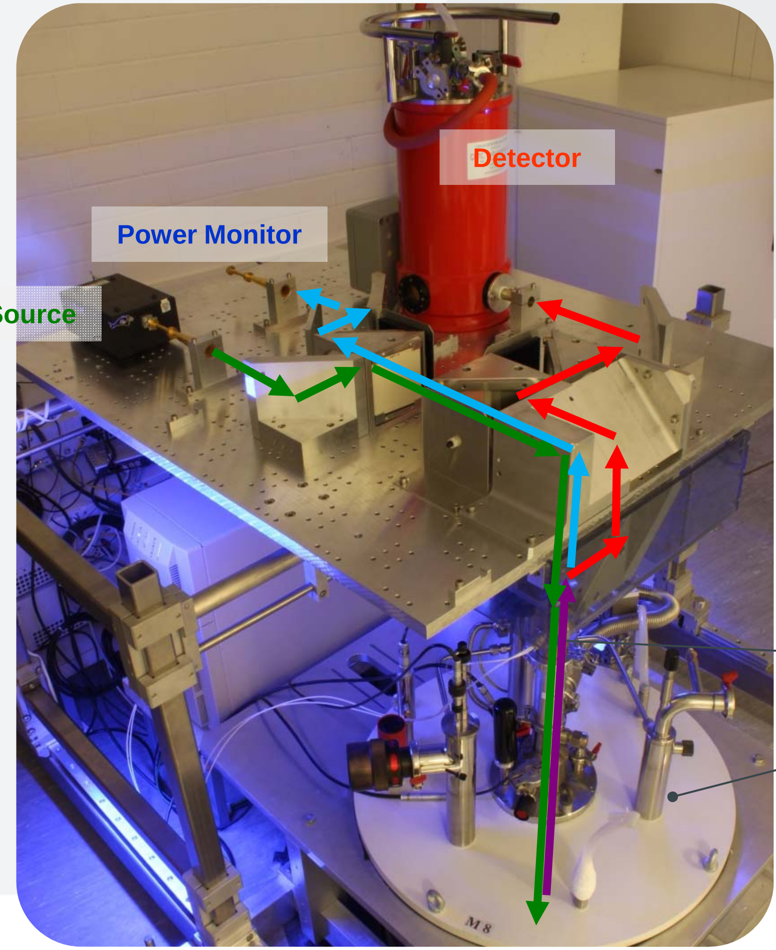
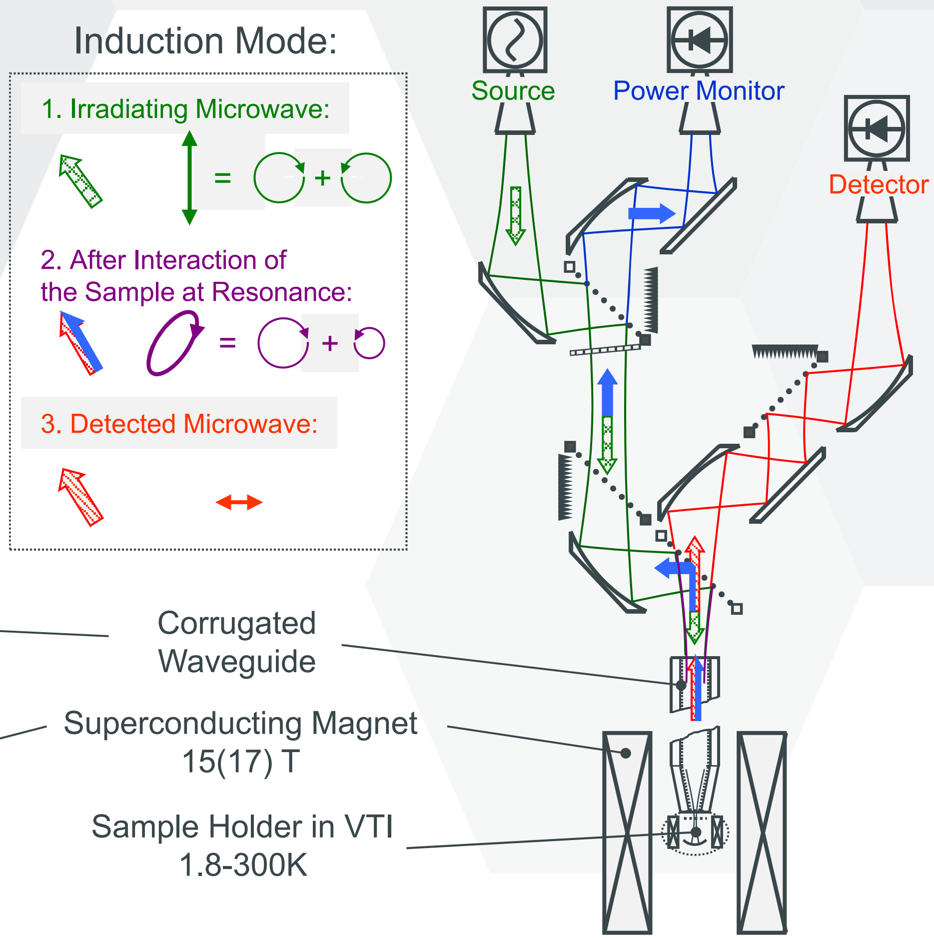
Combine HFEPR and FDMR

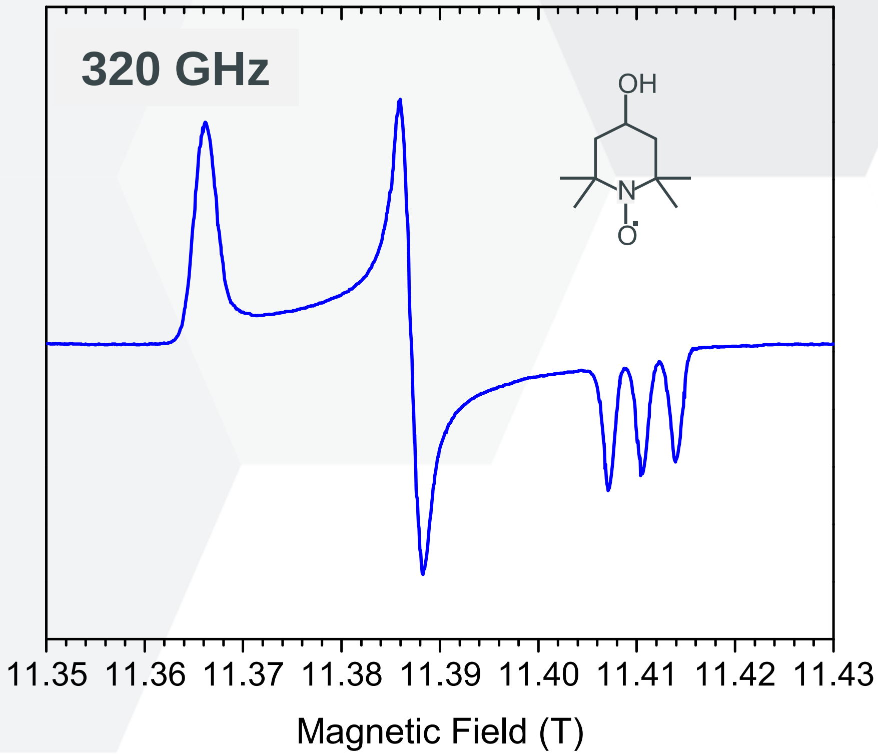




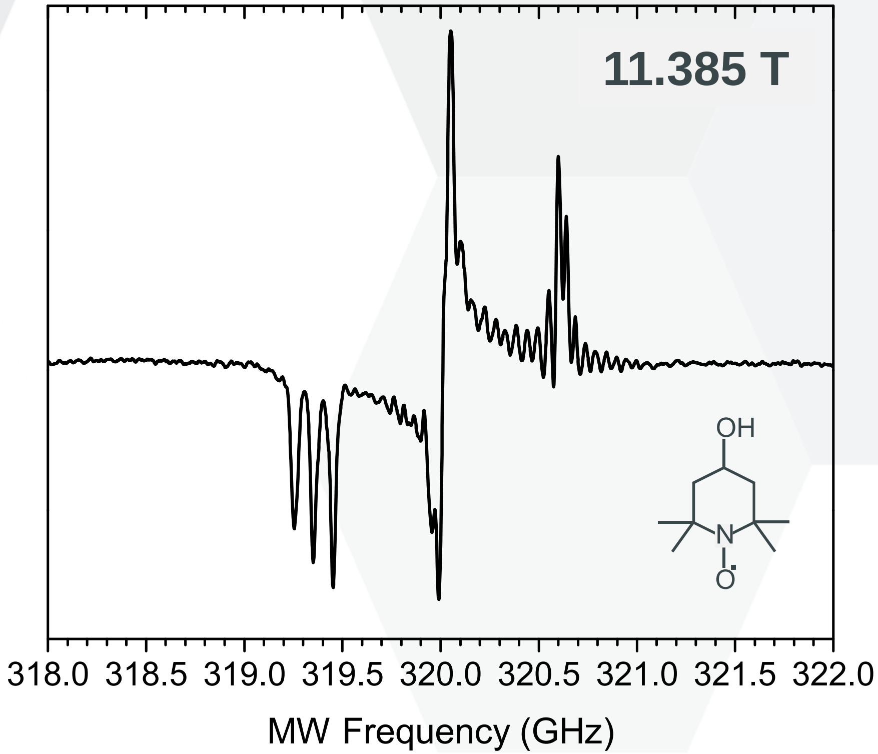
Phys.Chem.Chem.Phys., 20, 15528 (**2018**)

Combine HFEPR and FDMR

100 µM ^{14}N-TEMPOL in polystyrene
60 K, **1 mg**, ~10^{15} spins



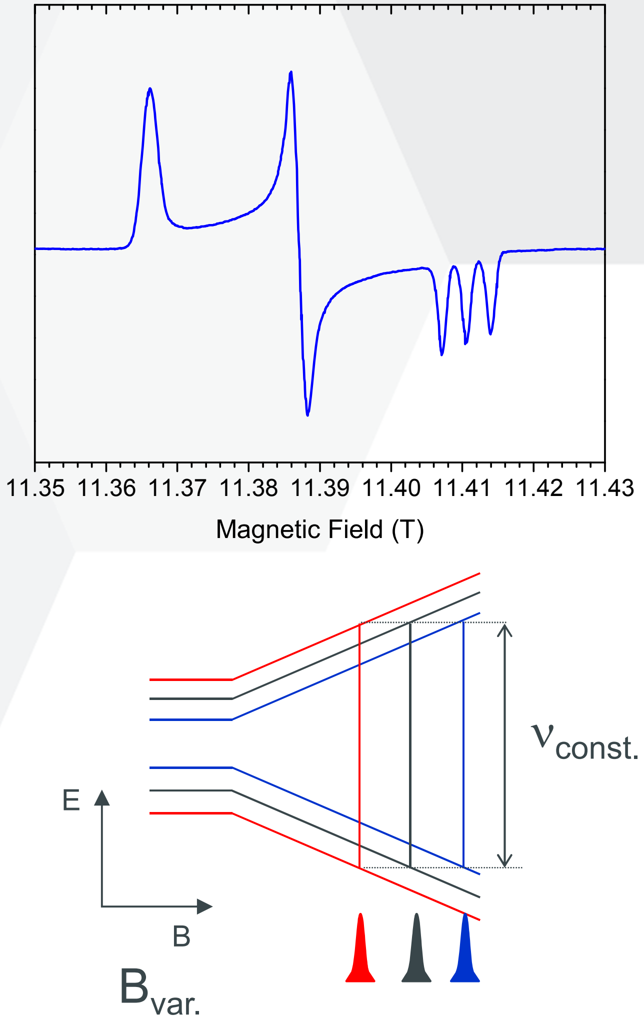
EPR



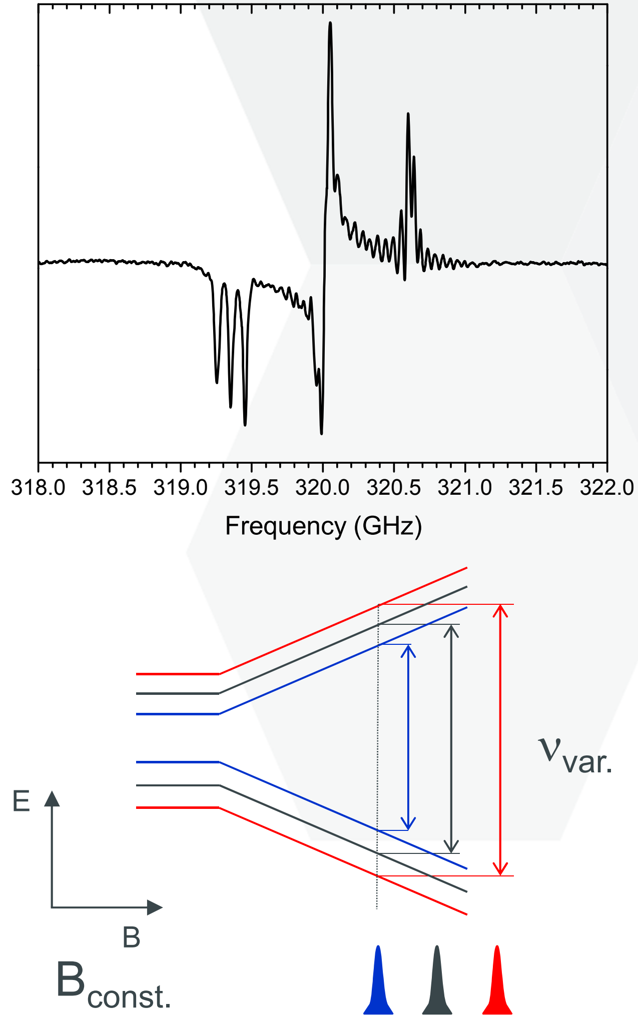
FDMR

Combine HFEPR and FDMR

EPR



FDMR



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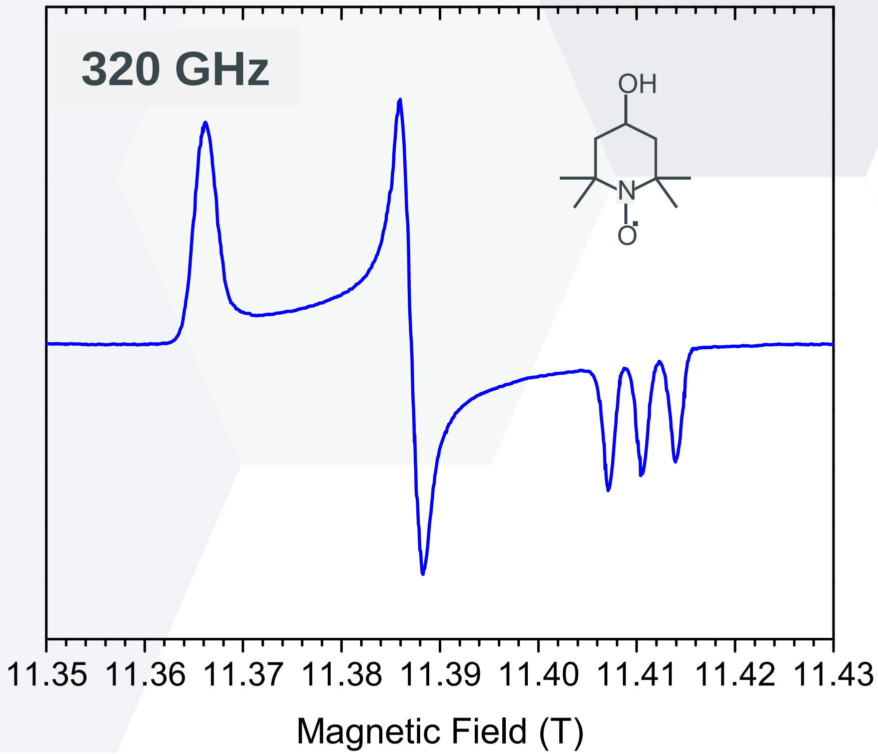
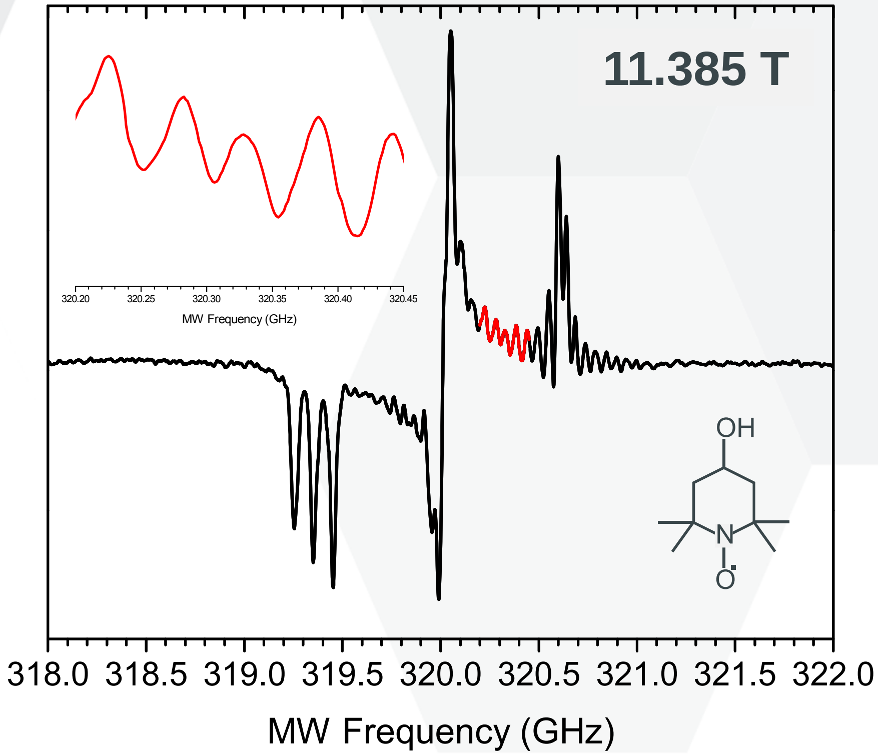


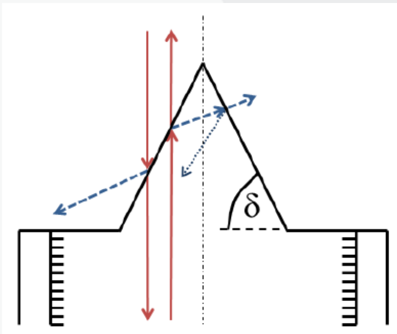
EPR



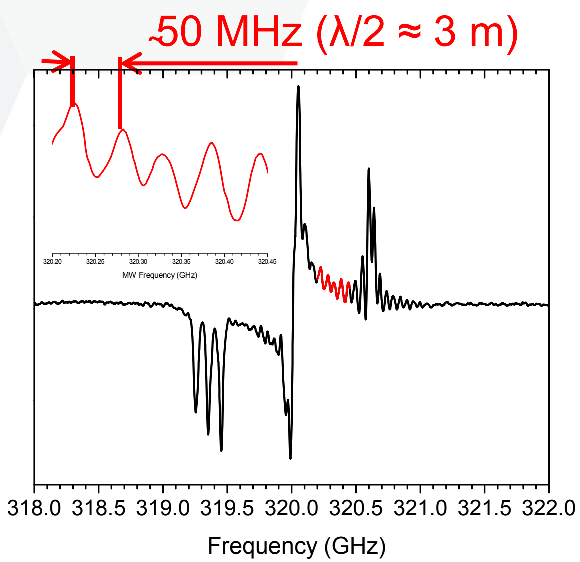
FDMR

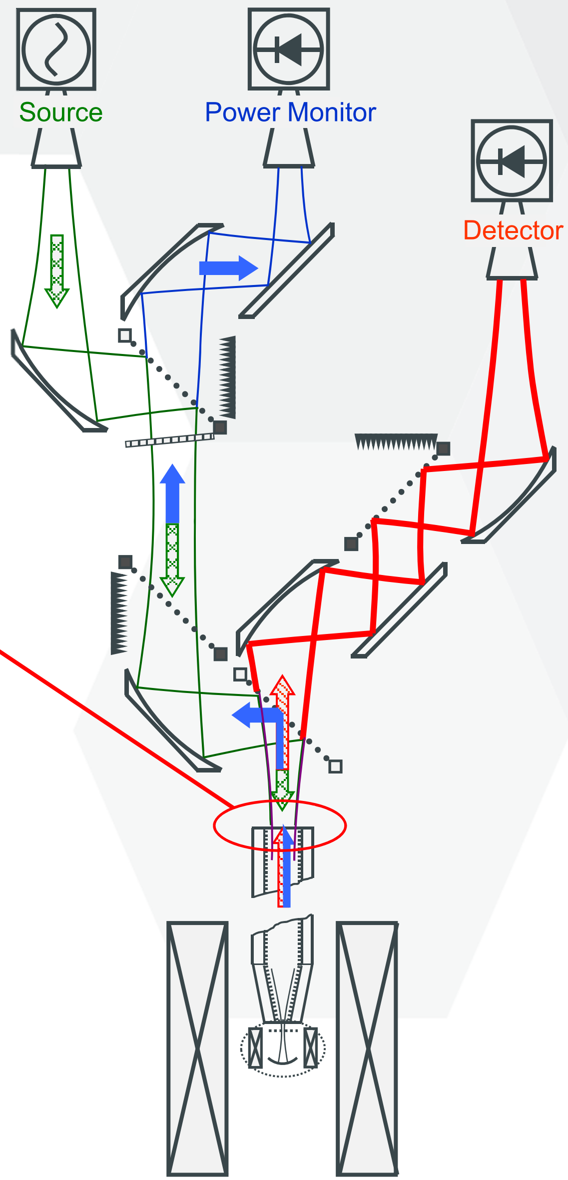
Standing Waves

- Off axial quasi-optical components
- Elimination of standing waves in a probe:



- Standing waves between sample and detector

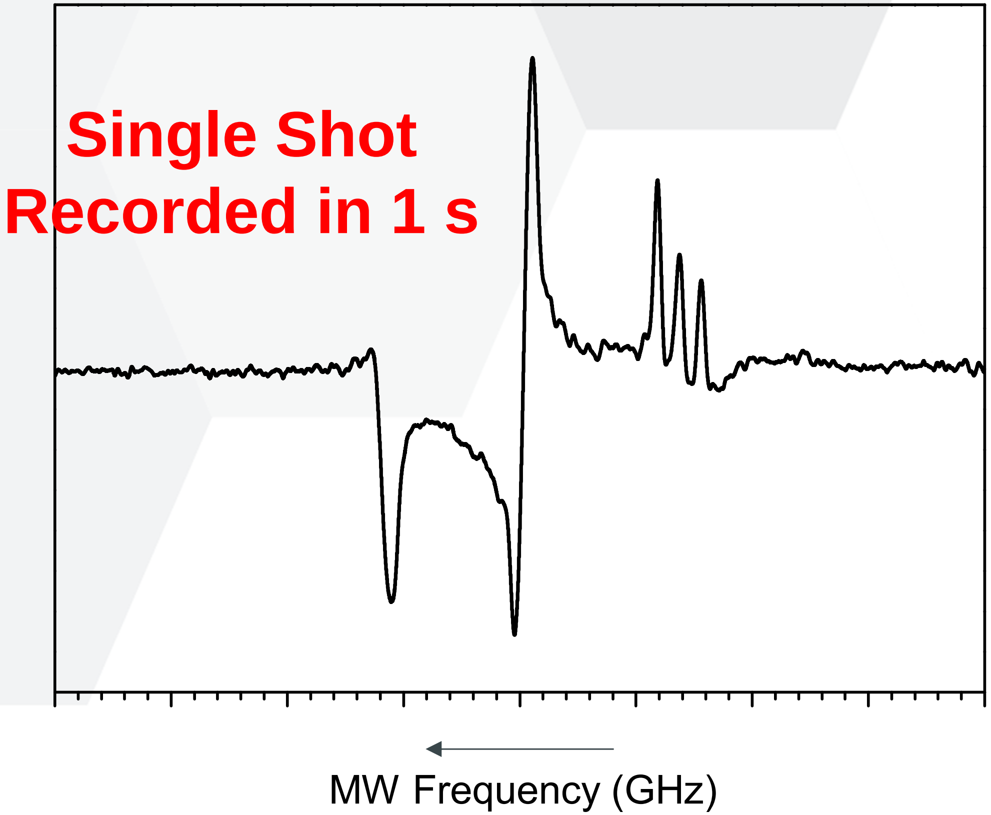


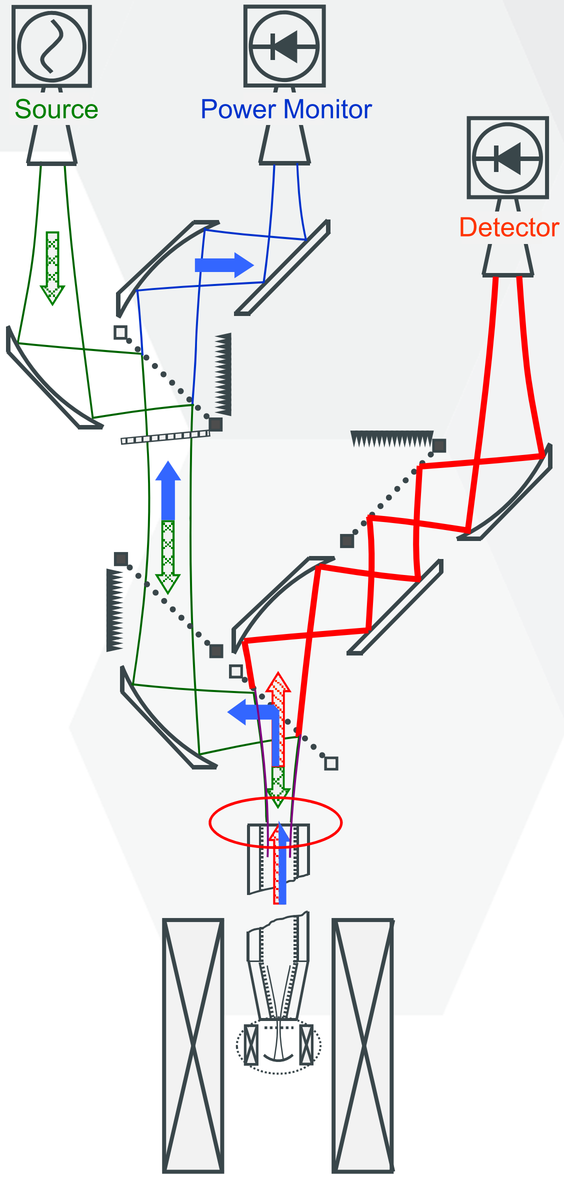


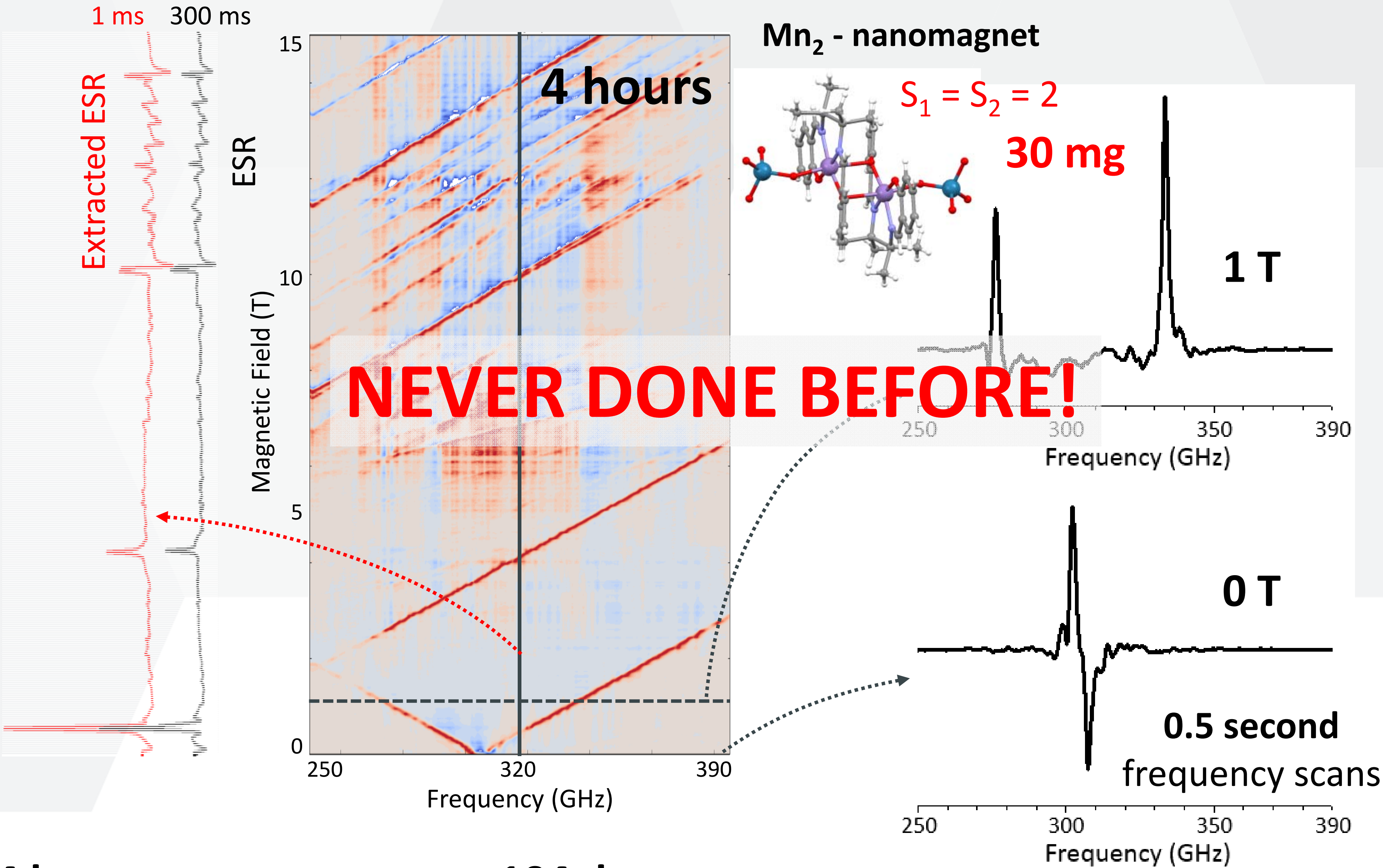
Standing Waves

Implementation of 2nd quasi optical isolator

100 µM ^{14}N-TEMPOL in polystyrene
60 K, **1 mg**, ~10^{15} spins



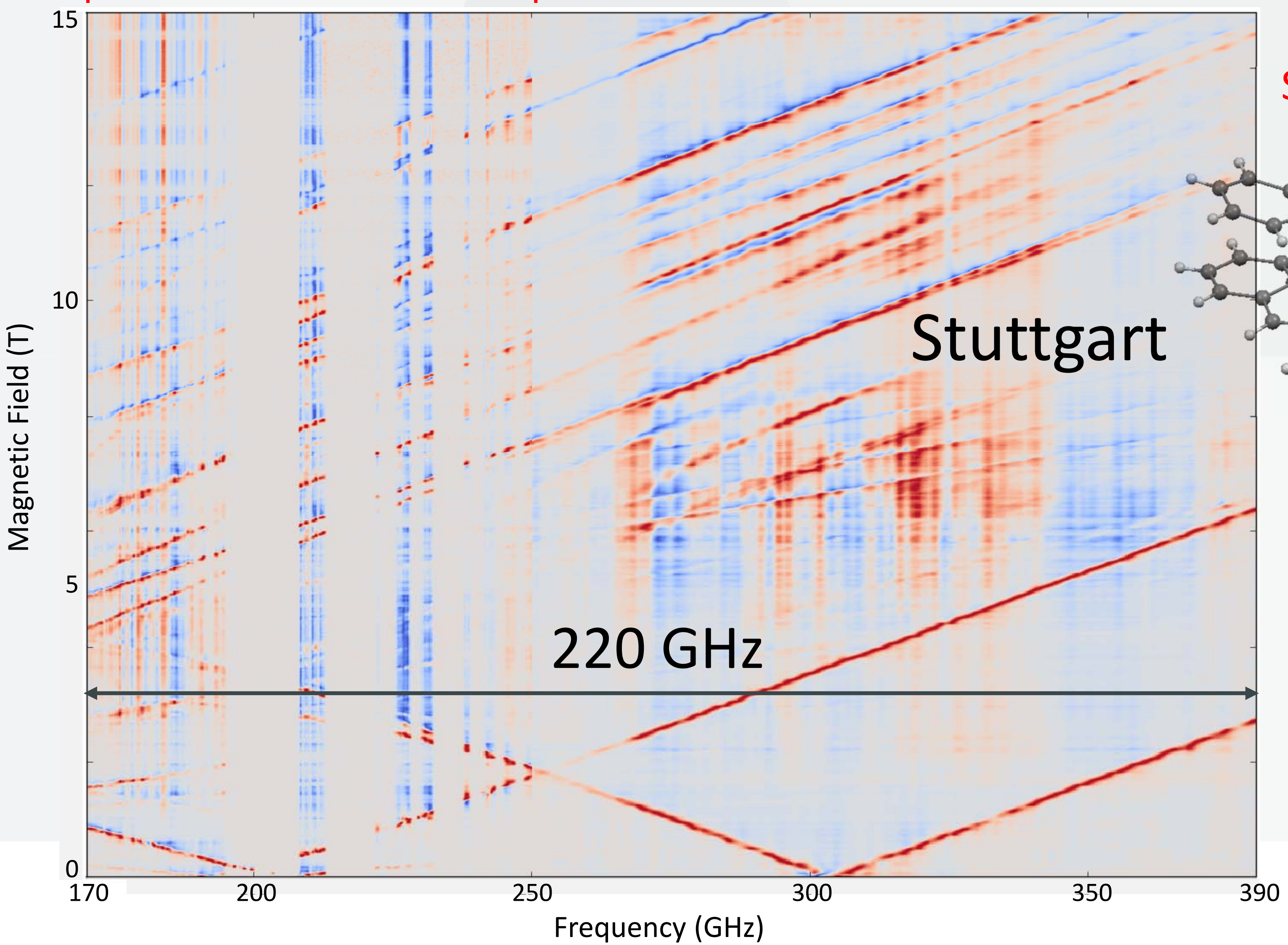




4 hours (frequency scans) vs. **104 days** (field scans - ESR)

Phys.Chem.Chem.Phys., 20, 15528 (**2018**)

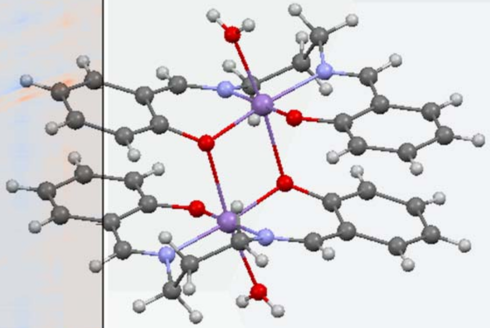
- Implementation of 170-250 GHz band and VDI synthetizer



[$Mn_2(salpn)_2(H_2O)_2$] $(ClO_4)_2$

30 mg

$S_1 = S_2 = 2$

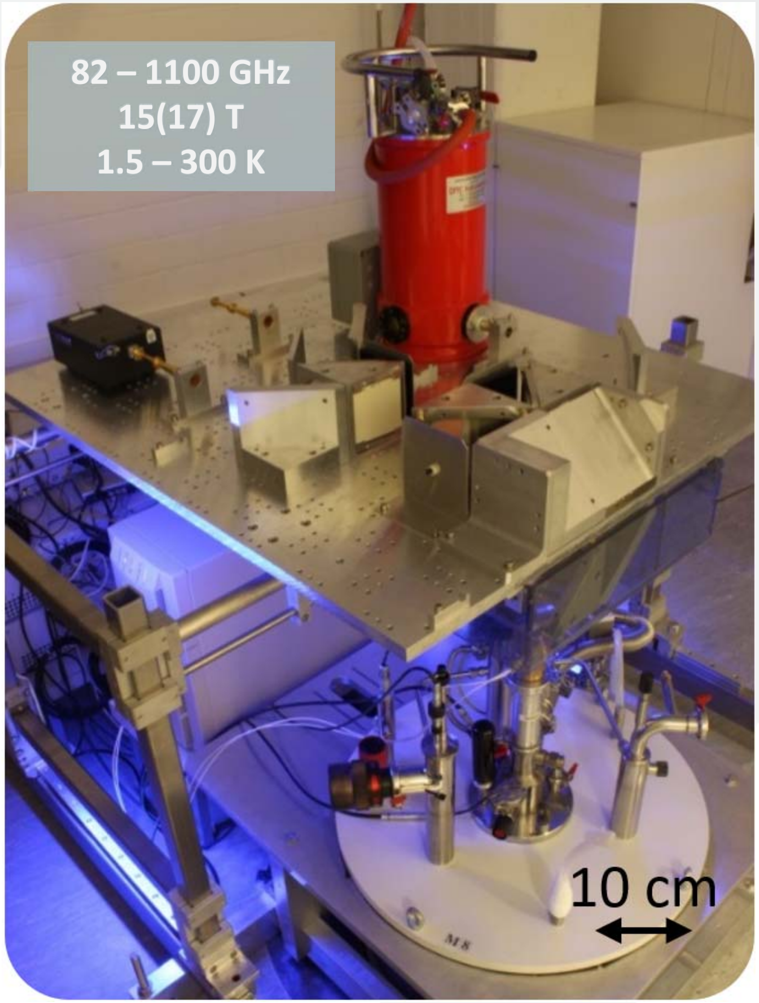


Phys.Chem.Chem.Phys., 20, 15528 (**2018**)

First combine ESR/FDMR spectrometer

- The current **worldwide state of the art** THz ESR spectrometer.

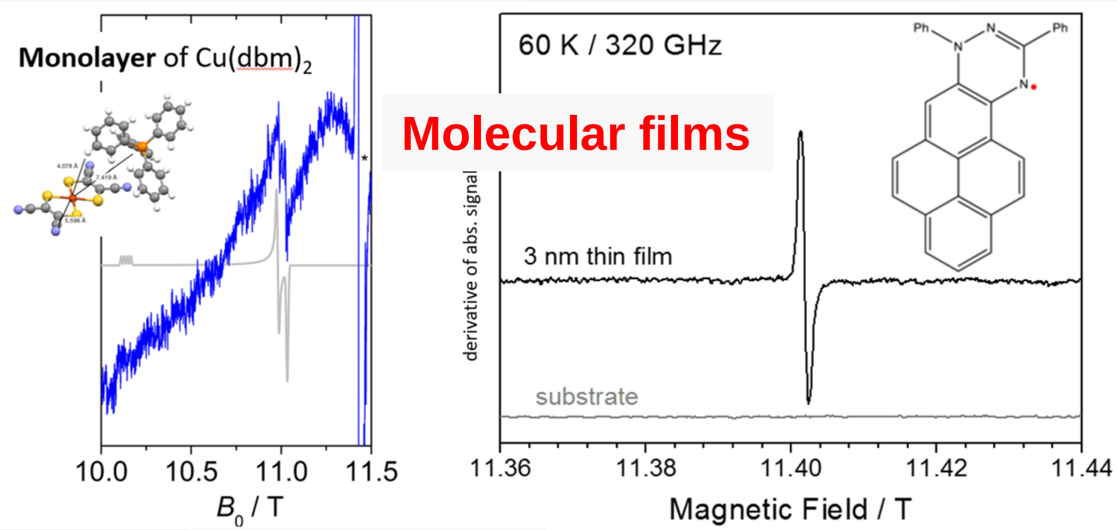
[1] *Phys.Chem.Chem.Phys.*, 20, 15528 (**2018**)
[2] *Inorg. Chem.*, 56, 402–413 (**2017**)
[3] *Inorg. Chem.*, 56, 2417–2425 (**2017**)
[4] *Phys. Rev. B*, 96, 094415 (**2017**)
[5] *Z. Anorg. Allg. Chem.* DOI: 10.1002/zaac.201700282 (**2017**)
[6] *Materials*, 10(3), 249 (**2017**)
[7] *Nat. Commun.*, 7, 10467 (**2016**)
[8] *Chemical Science*, 7,4347–4354 (**2016**)
[9] *Dalton Trans.*, 45, 12301-12307 (**2016**)
[10] *Inorg. Chem.*, 55 (12), 6186-6194 (**2016**)
[11] *Dalton Trans.*, 45, 7555-7558 (**2016**)
[12] *Dalton Trans.*, 45, 8394-8403 (**2016**)
[13] *J. Am. Chem. Soc.*, 137, 13114-13120 (**2015**)
[14] *Dalton Trans.*, 44,15014-15021 (**2015**)
[15] *J. Mater. Chem.* C, 3, 7936-7945 (**2015**)
[16] *Dalton Trans.*, 44,15014-15021 (**2015**)
[17] *J. Mater. Chem.* C, 3, 7936-7945 (**2015**)
[18] *Nat. Commun.*, 5, 5243 (**2014**)
[19] *Nat. Phys.*, 10, 233–238 (**2014**)
[20] *Chem. Eur. J.*, 20, 3475 – 3486 (**2014**)
[21] *Chem. Commun.*, 50, 15090-15093 (**2014**)
[22] *Chem. Sci.*, **5**, 3287 - 3293 (**2014**)
And others…



Used by institutions from: *Manchester (**UK**), Washington DC (**USA**), Bordeaux, Grenoble (**France**), Lisbon (**Portugal**), Valencia, Barcelona (**Spain**), Berlin, Leipzig, Stuttgart (**Germany**), Buenos Aires (**Argentina**), Brno, Olomouc (**Czech**), Vienna (**Austria**), Beijing, Xi'an (**China**), Dublin (**Ireland**), Copenhagen (**Denmark**)*

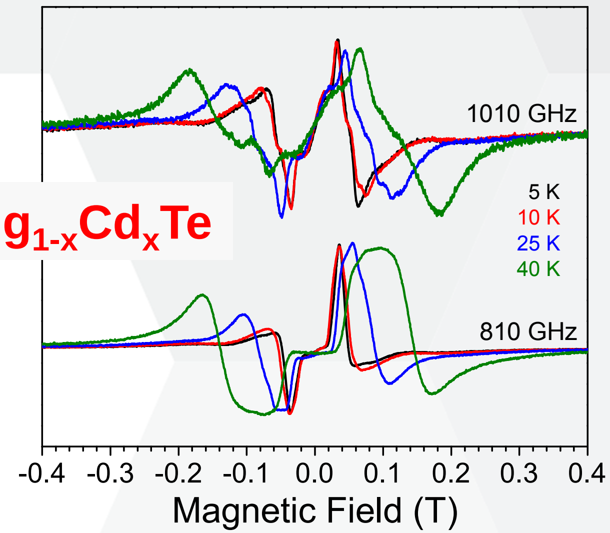
Thin Films, Modern Materials,…

Molecular films



J. Mater. Chem. C, **2018**, 6, 8028--8034

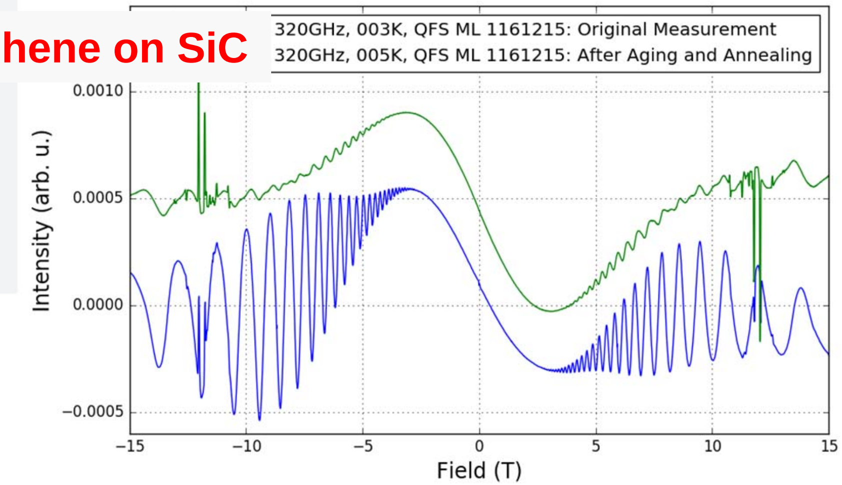
$Hg_{1-x}Cd_xTe$



Nat. Phys., 10, 233–238 (2014)

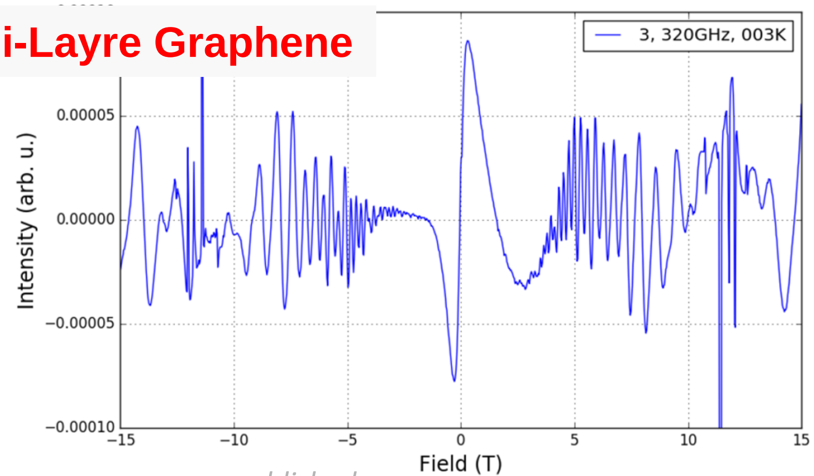
unpublished

Graphene on SiC



2D Mater. 6 035028 (**2019**)

Bi-Layre Graphene



unpublished

EU FET-Open Project

Starting date 1.1.2018

PETER - Plasmon-**E**nhanced **T**erahertz **E**lectron paramagnetic **R**esonance spectroscopy

- scanning Electron Paramagnetic Resonance (EPR) microscopy
- high-sensitivity local analysis of paramagnetic organic and inorganic species and materials
- 4 partners, 3 MilEUR

Czech Republic	BRNO UNIVERSITY OF TECHNOLOGY	**T. Šikola (project coordinator)** J. Čechal, V. Křápek
Germany	University of Stuttgart Germany	J. Van Slageren P. Neugebauer
Spain	CIC nanoGUNE nanoscience cooperative research center	R. Hillenbrand A. Nikitin
United Kingdom	TK INSTRUMENTS	R. J. Wylde K. Pike

2018 Brno
Spin and Molecular Dynamics

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BRNO UNIVERSITY OF TECHNOLOGY

Magneto-Optical and THz Spectroscopy group, established 1.1.2018 at Brno.

Why Brno?

- Home, parents,…
- Long history of Magnetic Resonance in Brno (TESLA Brno); J. Dadok.

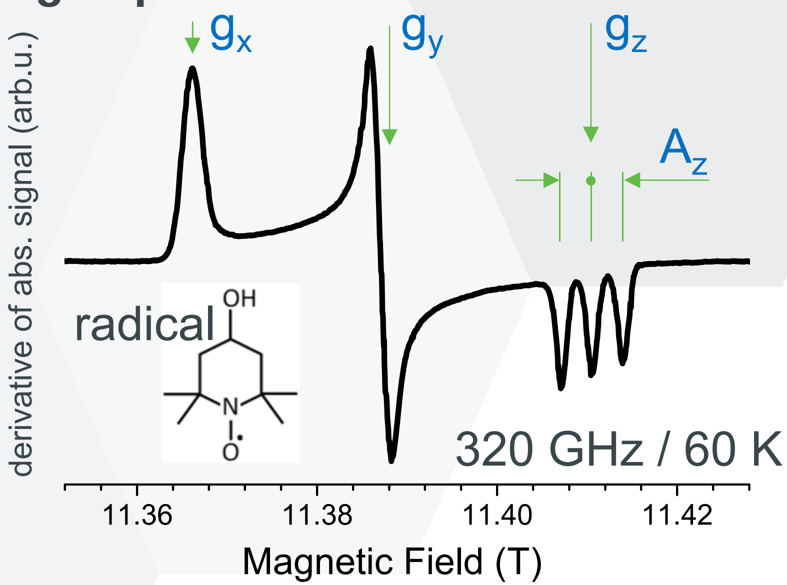
V. Zeman (**2008**) DOI: 10.3247/SL2Nmr08.003 (*in Czech*)

NMR in TESLA Brno

Our group in Stuttgart

Today's THz Electron Spin Resonance
(single frequency, field sweeps)

High spectral resolution:



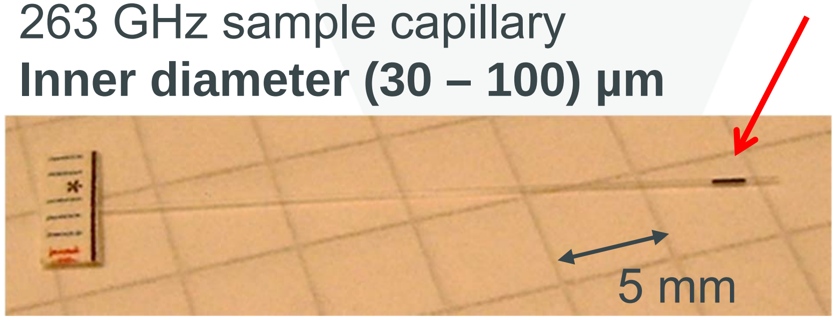
Powerful tool in:

- systems with zero field splitting
- biomolecules
- heterogeneous catalysis
- solar-cells, batteries
- … everywhere where unpaired electrons are involved

Limitations:

- resonant cavities
- restrictions on samples
- single frequency / narrow bandwidth
- high power MW sources (expensive)

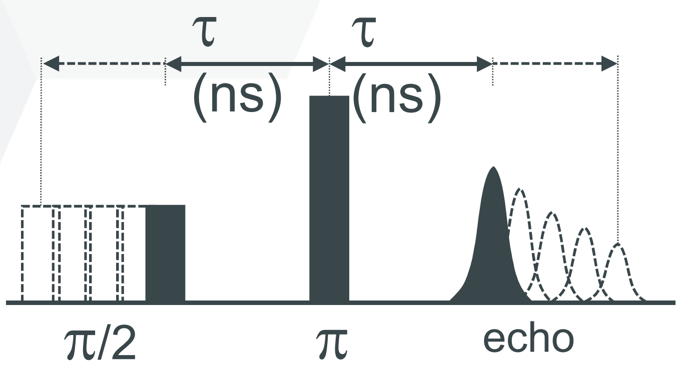
263 GHz sample capillary
Inner diameter (30 – 100) µm



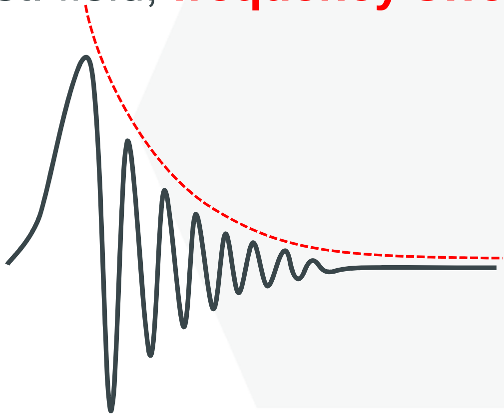
PROBLEM:

- **NO method to investigate spin dynamics** of **bulk and thin film materials at THz frequencies.**
- **NO method** to provide comprehensive information about spin dynamics in a **broad frequency range**.
- Limiting the technological progress in quantum computation and NMR signal enhancement.

TODAY
(single frequency, **field sweeps**)

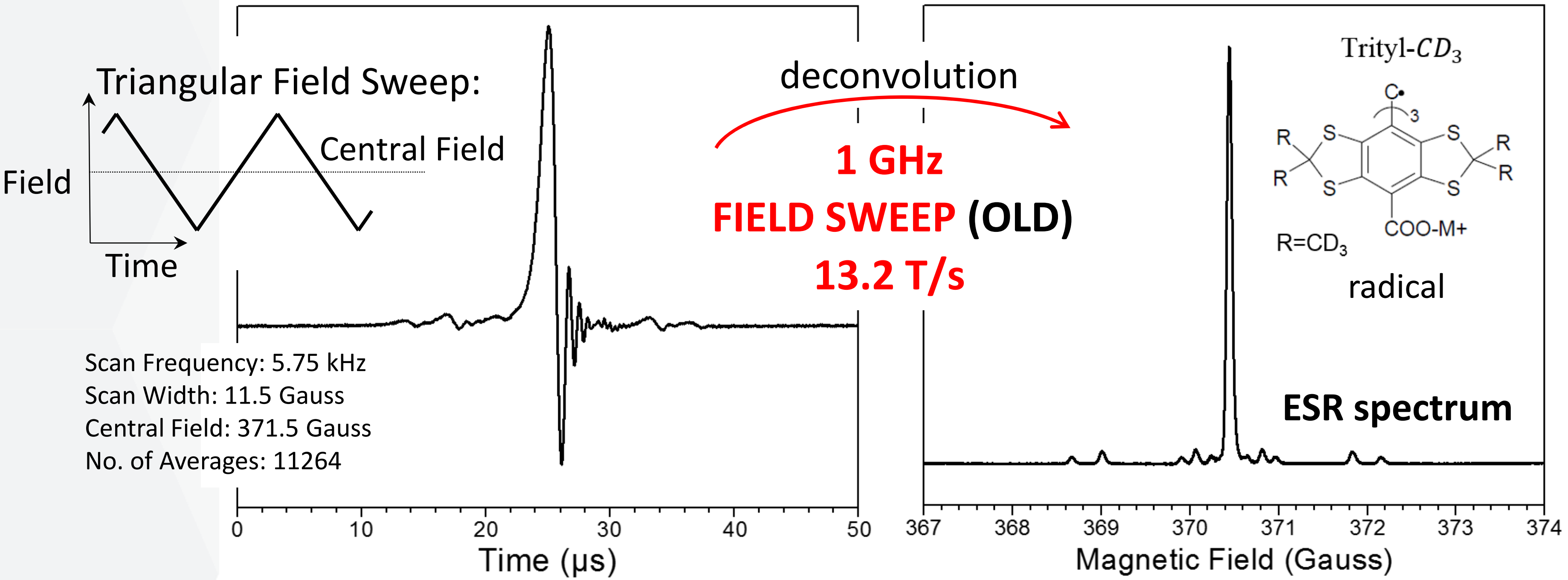


TOMORROW
(const. field, **frequency sweeps**)



Determination of electron spin dynamics.

Development of the THz-FRaScan-ESR Spectrometer



- **Access to relaxation rates** if $|\gamma|(d\nu/dt) > T_2^{-2}$
- **Rapid FREQUENCY sweeps (NEW)** above **100 THz/s (3600 T/s)**
- Access to spin **relaxation times below 10 ns (1 ns)**!
- **Multi frequency relaxation studies of large samples** – non-resonant sample holders
- Measurement of spin dynamics at user selected frequency in range of **85 GHz – 1100 GHz**

Conventional ESR Vs. THz-FRaScan-ESR

+ established method
- single frequency / narrow bandwidth
  - different setups for different frequencies
- high power MW sources
- restrictions on samples
  - limits the studies to liquid or powder samples
- ring down of the cavity
  - limits the studies to relaxations above 100 ns
- expensive
- the method approaches its limits
  - there is no more space to lower the cavity dimensions

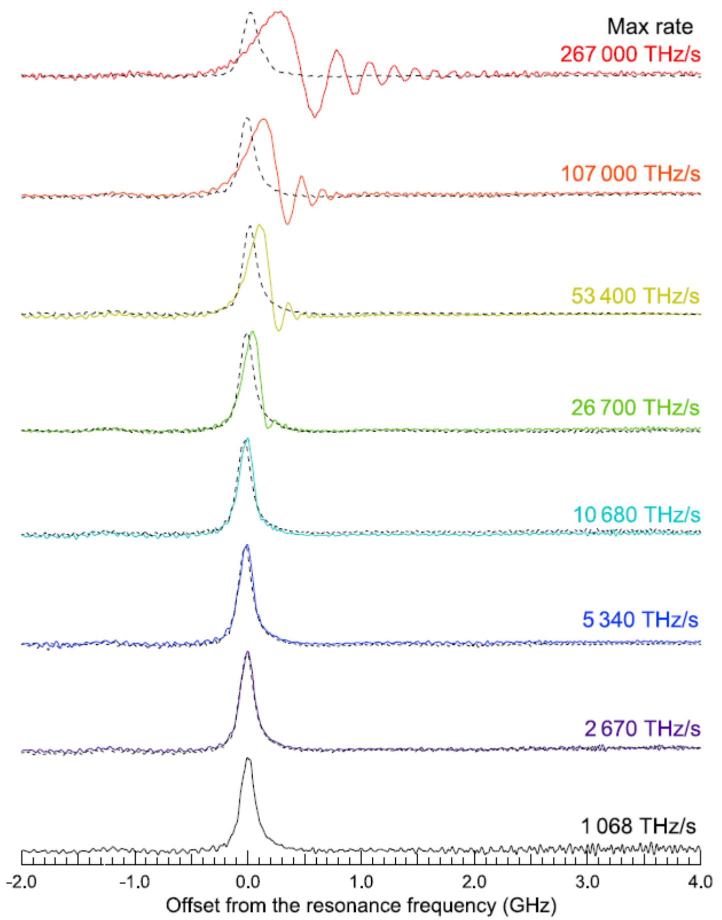
+ non-resonant cavities
+ no restrictions on samples
  - thin films, oriented crystals, powders, liquids
+ multi frequency relaxation studies in one setup
  - frequency is defined only by magnetic field
+ zero field experiments
+ operating at low MW power
+ very fast and direct measurement
  - provides significantly better S/N ratio in given time
  - higher content of information in the spectra
+ convenient
  - spectra as a function of energy (frequency)
+ opens new possibilities
+ cheap and extendable concept
+ applications in NMR magnets
+ reduction of MW heating in DNP exp.
– novel approach

Multi-frequency rapid-scan HFEPR

O. Laguta[a], M. Tuček[b], J. van Slageren[a], P. Neugebauer[b,*]

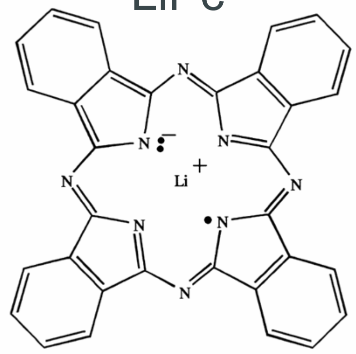
[a]*Institute for Physical Chemistry and Center for Integrated Quantum Science and Technology, Universität Stuttgart, Pfaffenwaldring 55, Stuttgart D-70569, Germany*

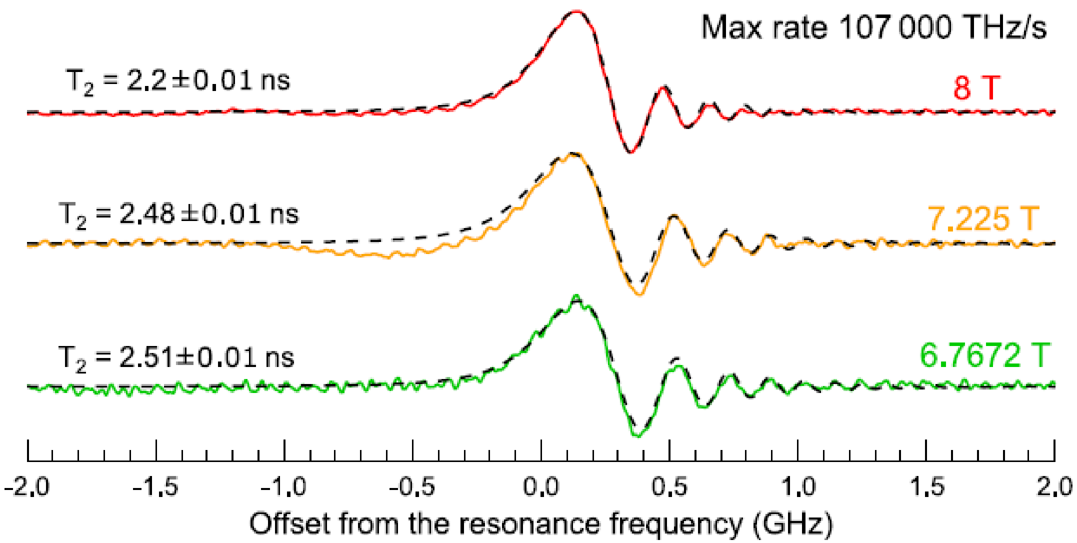
[b]*Central European Institute of Technology, Brno University of Technology, Purkyňova 656/123, Brno 61200, Czech Republic*



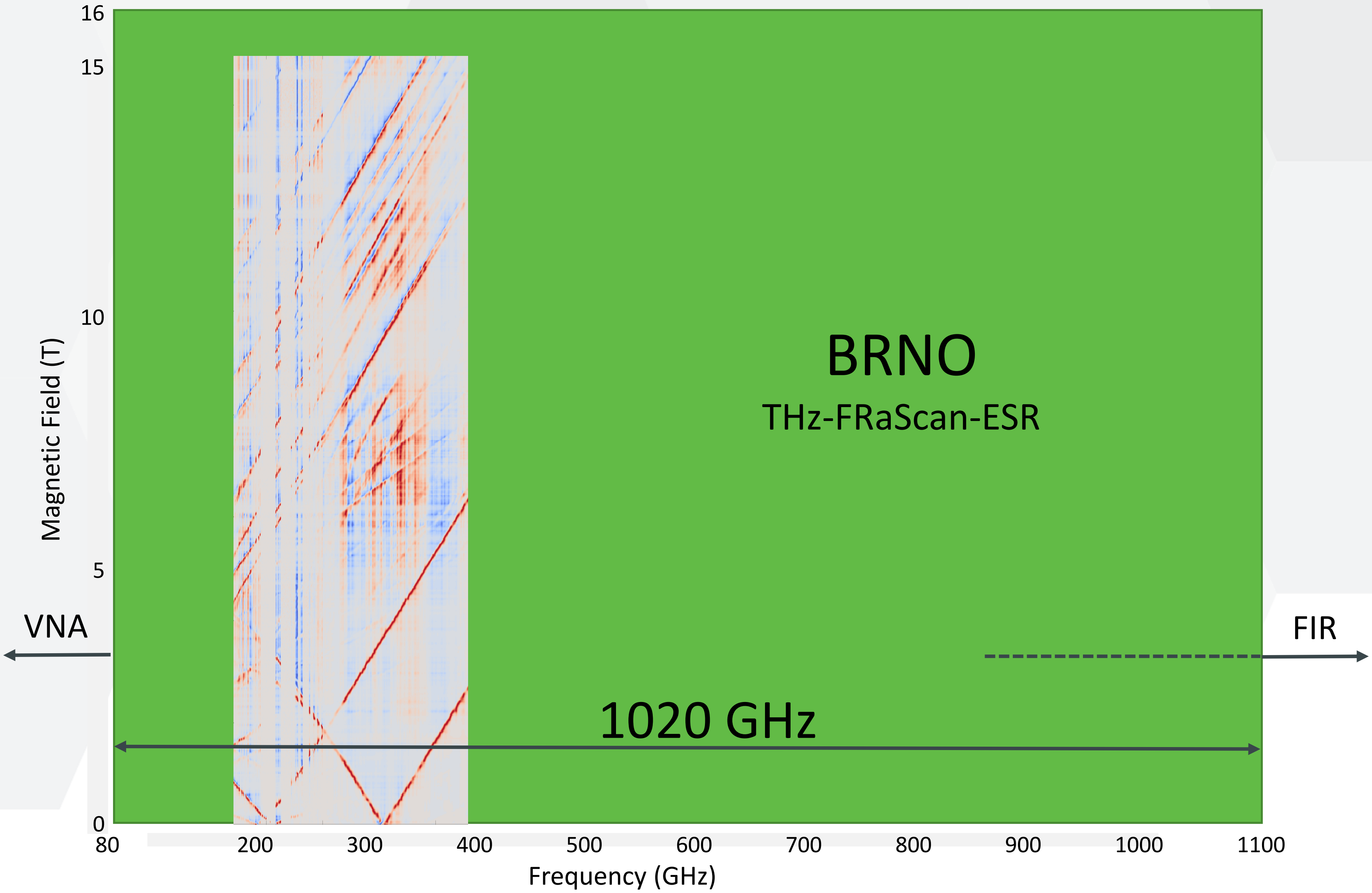
Note:
100 000 THz/s ~ **36 MT/s**!

LiPc





O. Laguta et al. *J. Magn. Reson.* **2018**, 296, 138


16
15
10
5
0
Magnetic Field (T)
80
200
300
400
500
600
700
800
900
1000
1100
Frequency (GHz)
BRNO
THz-FRaScan-ESR
VNA
FIR
1020 GHz


02/01/2018


13/02/2018


29/01/2018


27/02/2018

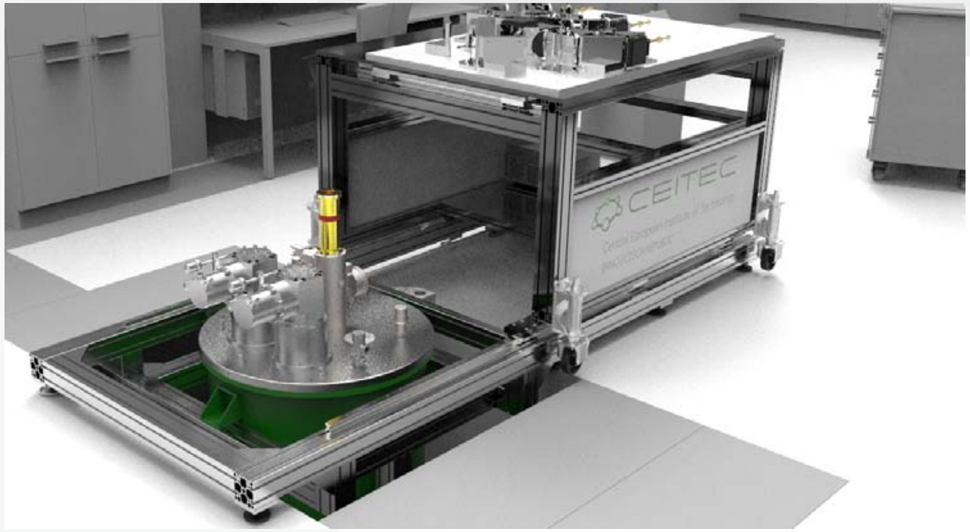
Reconstruction

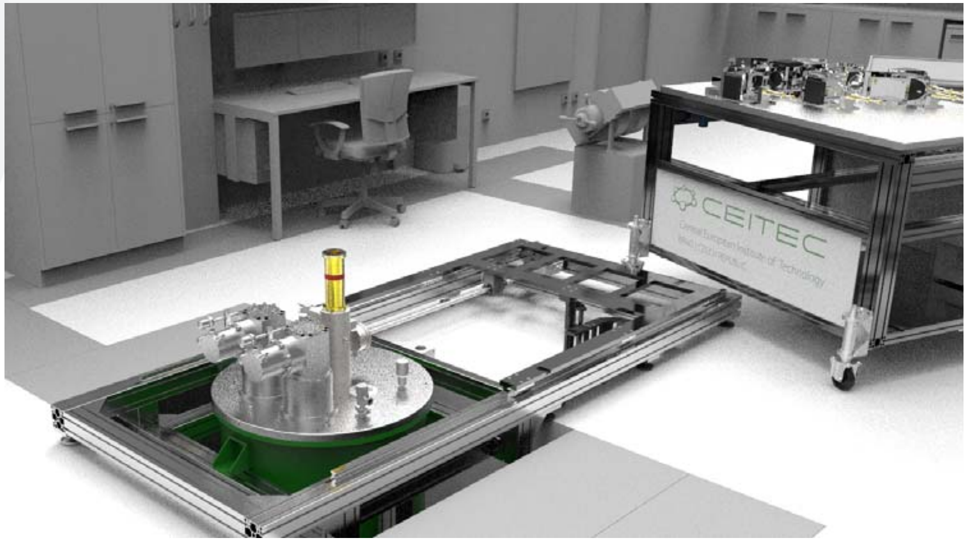
Current State

cw X-band (magnettech)

Thanks to Valentin Laguta
(Academy of Science, Prague)

THz-FRaScan-EPR





Magnetic field:
±16 Tesla (Cryogen Free)

Temperature range:
1.6 – 400 K

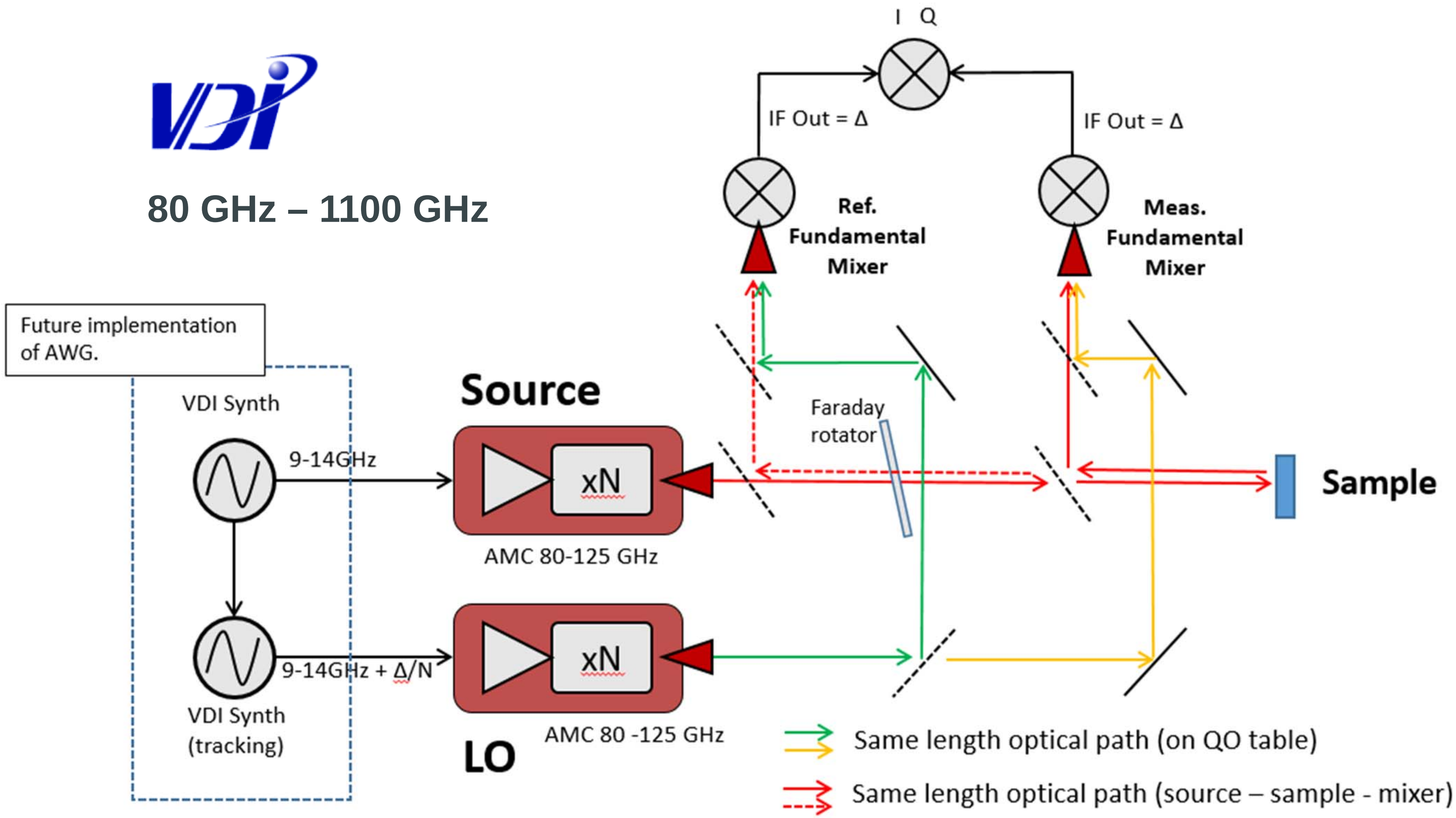
Frequency range:
80 – 1100 GHz
Heterodyne detection

Samples:
Pellets, Oriented Crystals,
Liquids, Air Sensitive

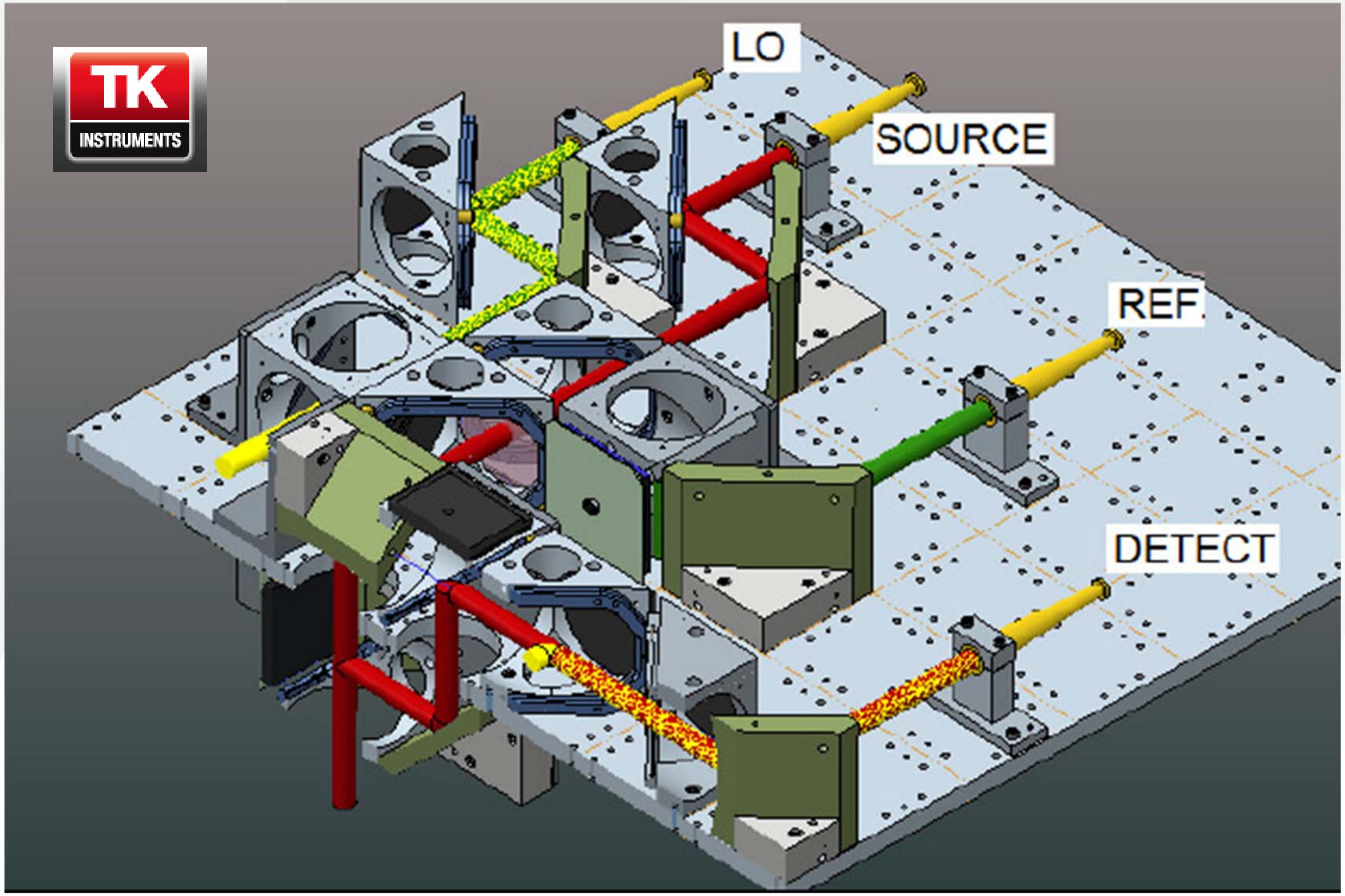
unpublished

Excitation-Detection

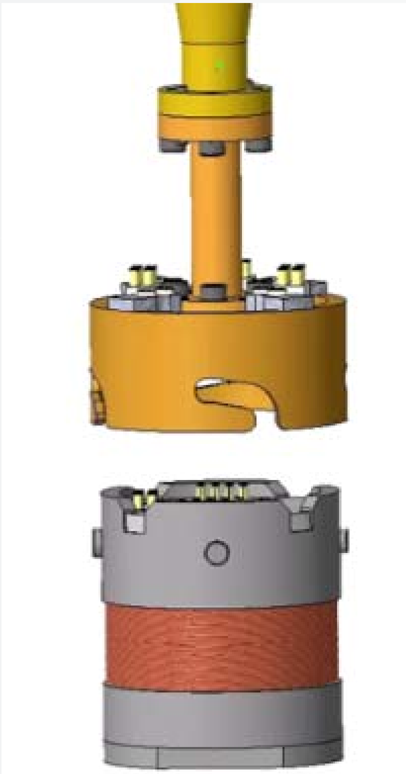
80 GHz – 1100 GHz



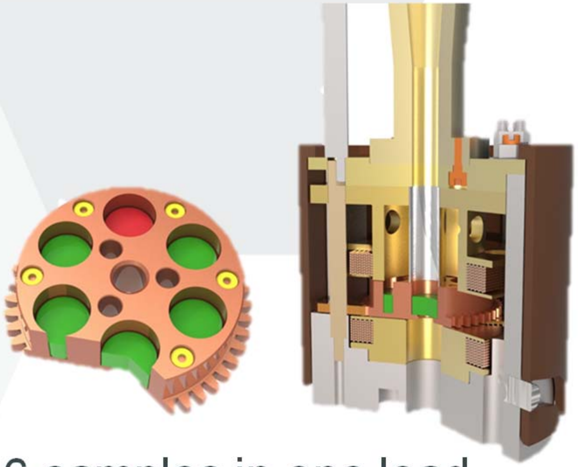
Quasi-Optics



4 Sample Holders



Carrousel sample holder

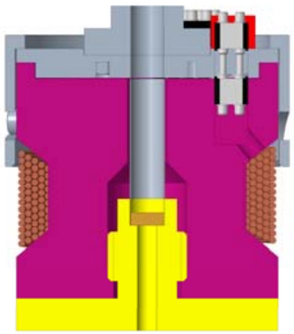


6 samples in one load

Single-crystal rotator

3D prints of prototypes

Pellets/liquid samples

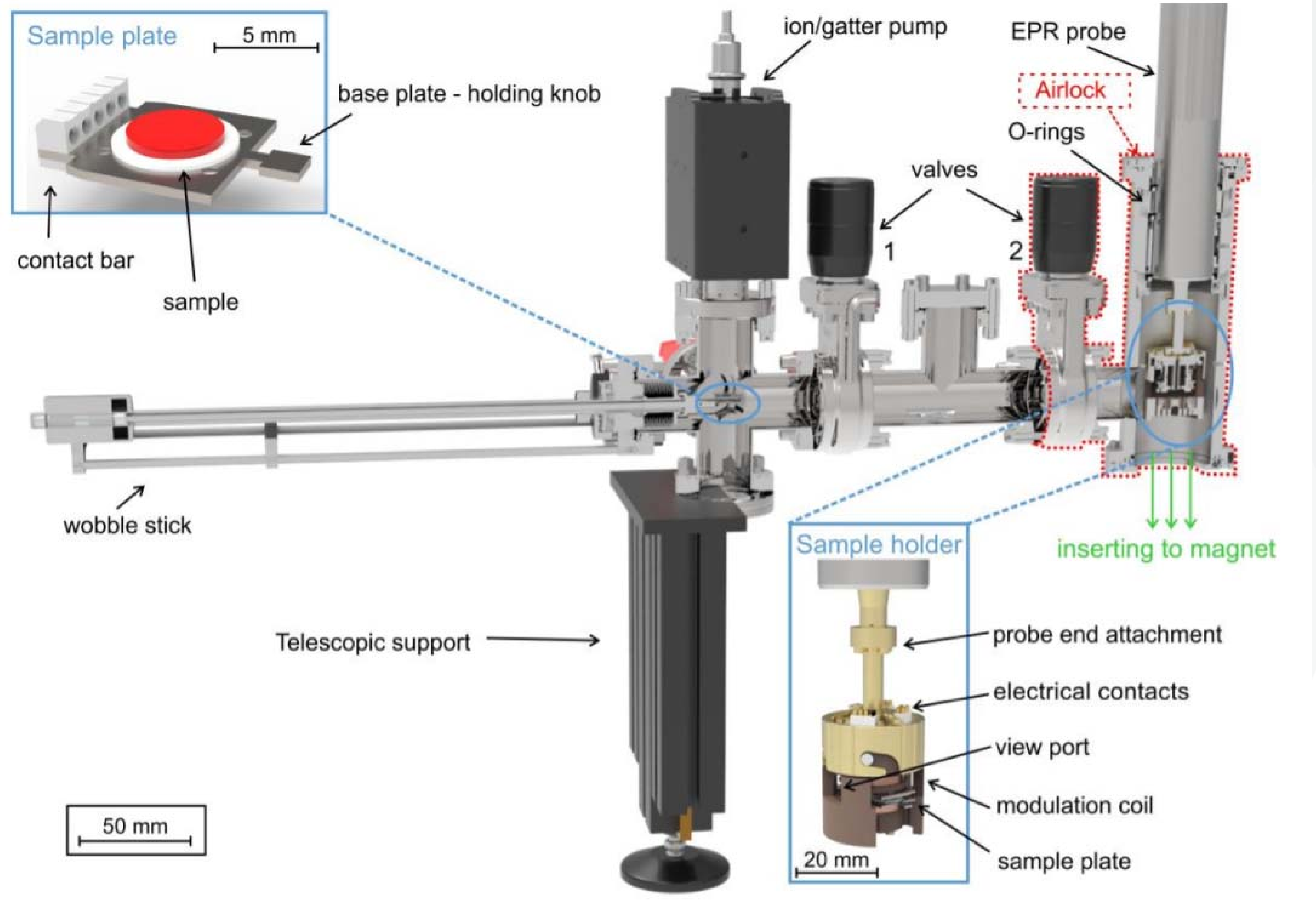


A. Sojka
unpublished

Chip-Set sample holder

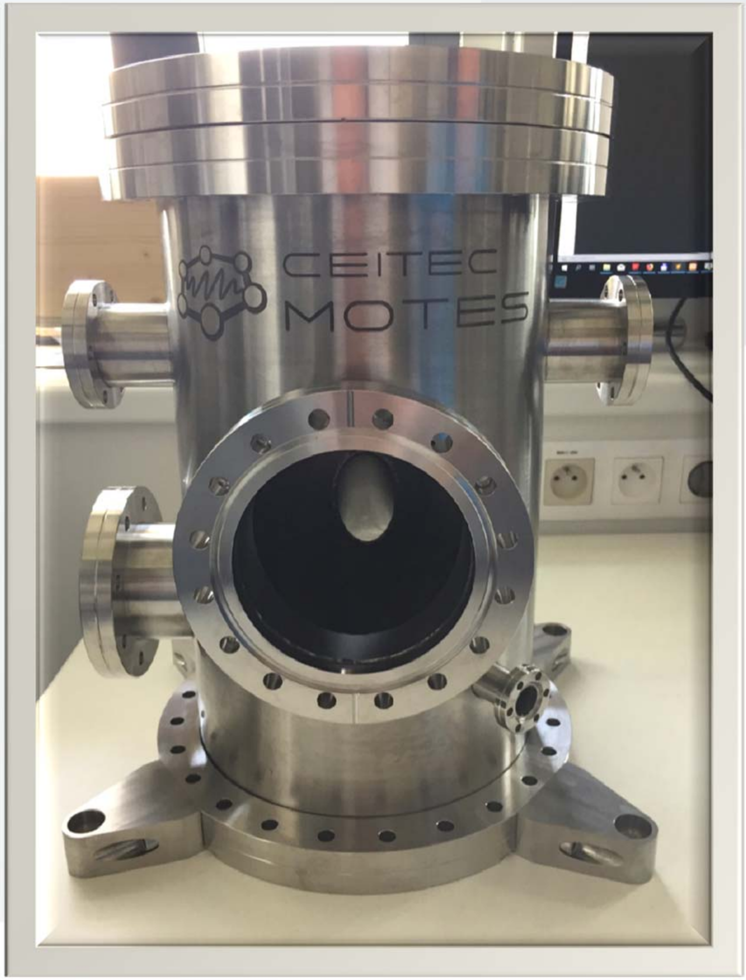
3D prints of prototypes

Sample Transfer

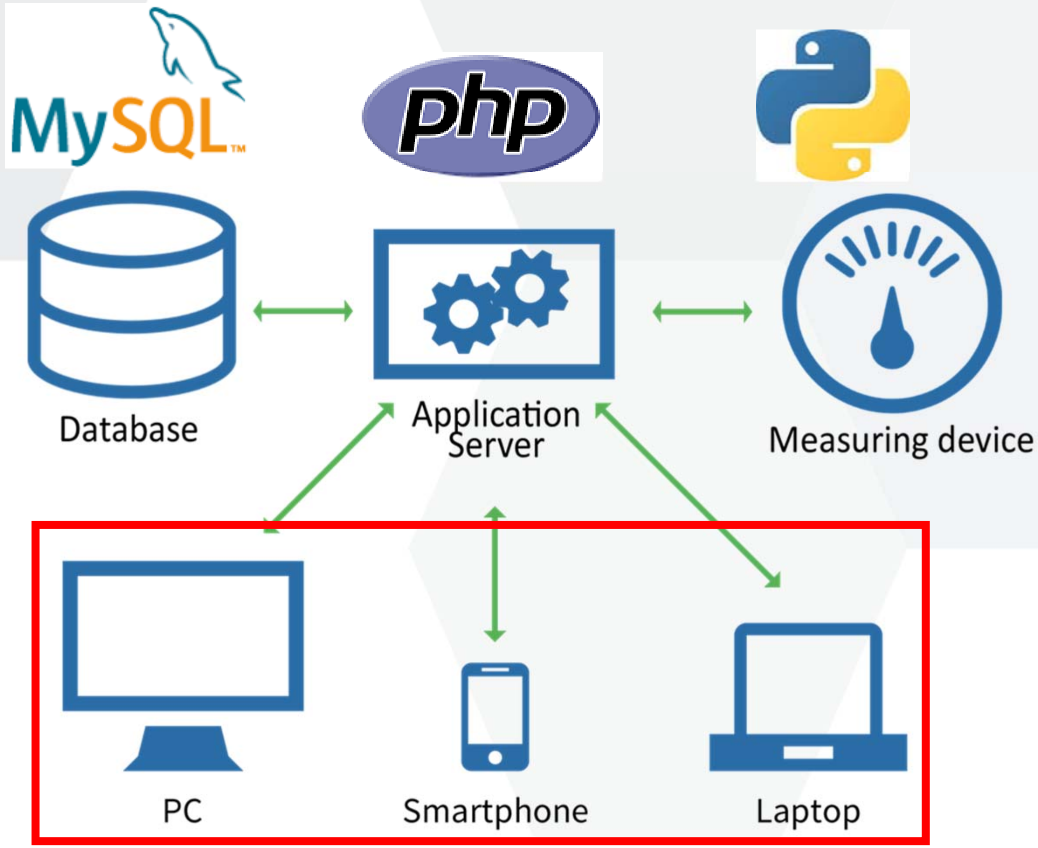


A. Sojka
unpublished

Molecular films preparation



Software



J. Hruby
unpublished

Conclusion

Our Mission

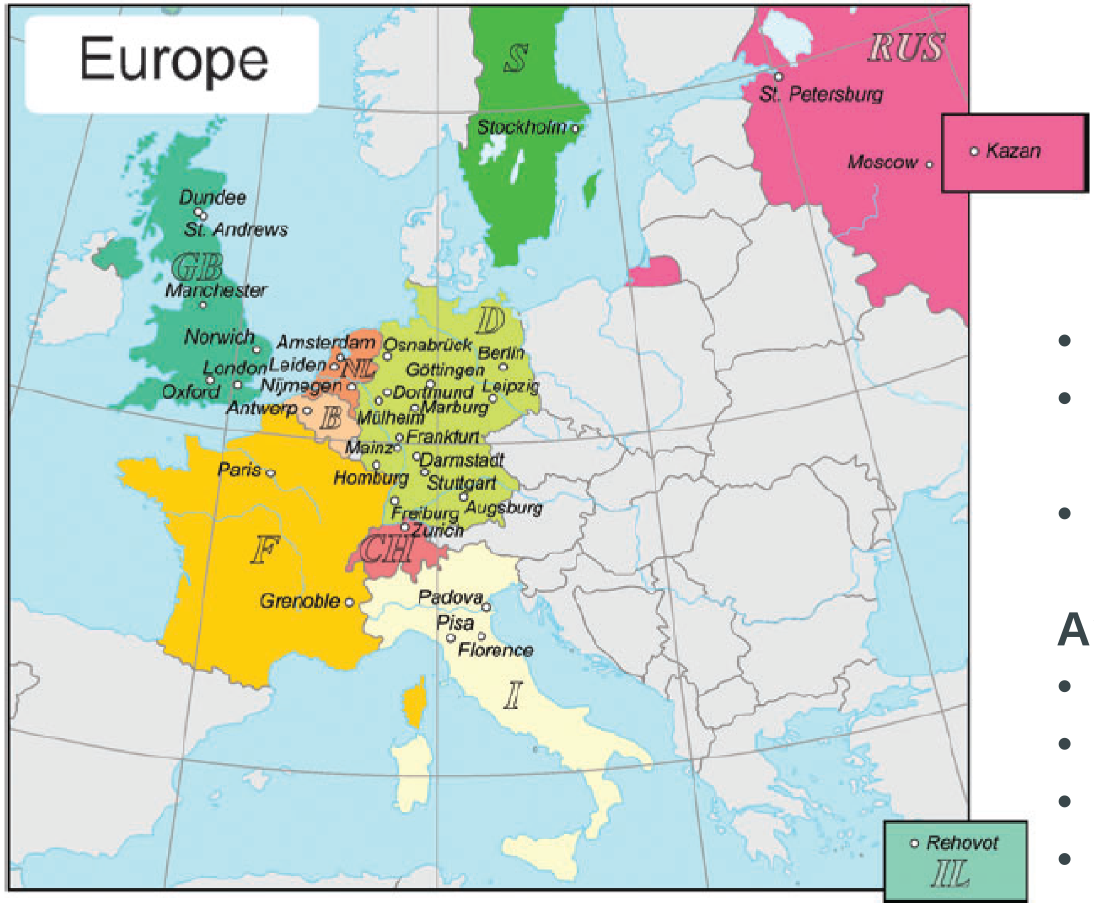


Figure 1.2 High-field EPR groups in Europe (2008).

K. Moebius

- HFEPR in central Europe
- Modern THz method development
- EPR center (user facility)

Applications

- Molecular Magnetism
- Solid State Materials
- Hybrid Materials
- …

Long Term Vision

"A Door"

A Highly Efficient
Magnetic Resonance Imaging (MRI) scanner

Doctor

5 m
with a relaxed walk it takes about 7 s

"A Super-Computer"

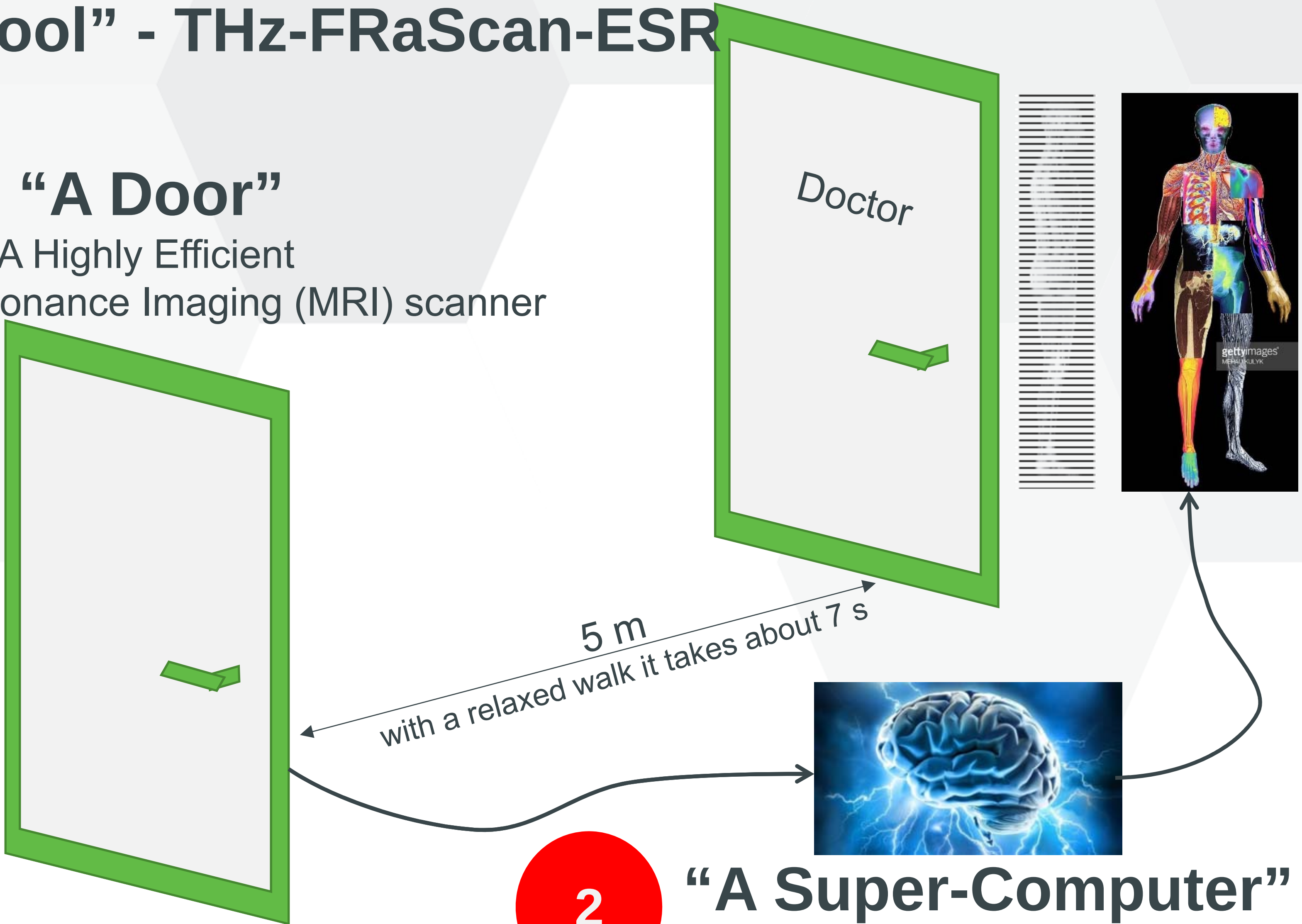
A Quantum-Computer

Long Term Vision

1 “A Tool” - THz-FRaScan-ESR

3 “A Door”

A Highly Efficient
Magnetic Resonance Imaging (MRI) scanner



2 “A Super-Computer”

A Quantum-Computer

erc

CEITEC MOTES

PETER

BRNO UNIVERSITY OF TECHNOLOGY

University of Stuttgart
Germany

GEORGETOWN UNIVERSITY

NAVAL RESEARCH LABORATORY WASHINGTON, DC

VDI

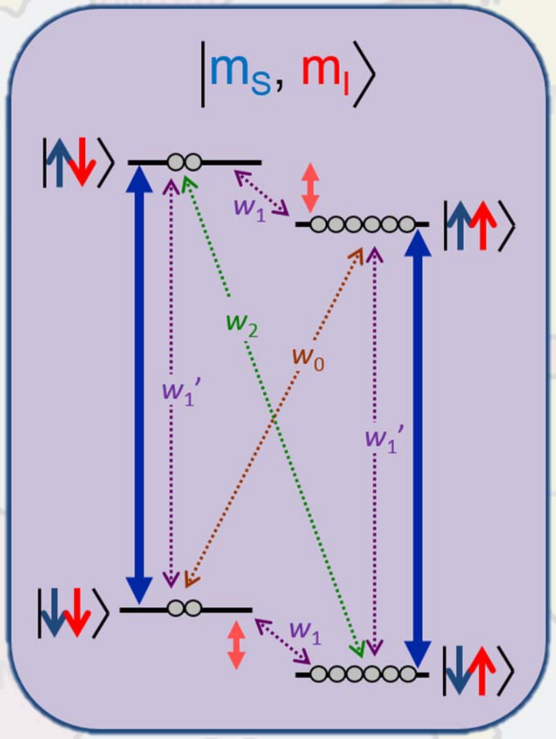
TK INSTRUMENTS

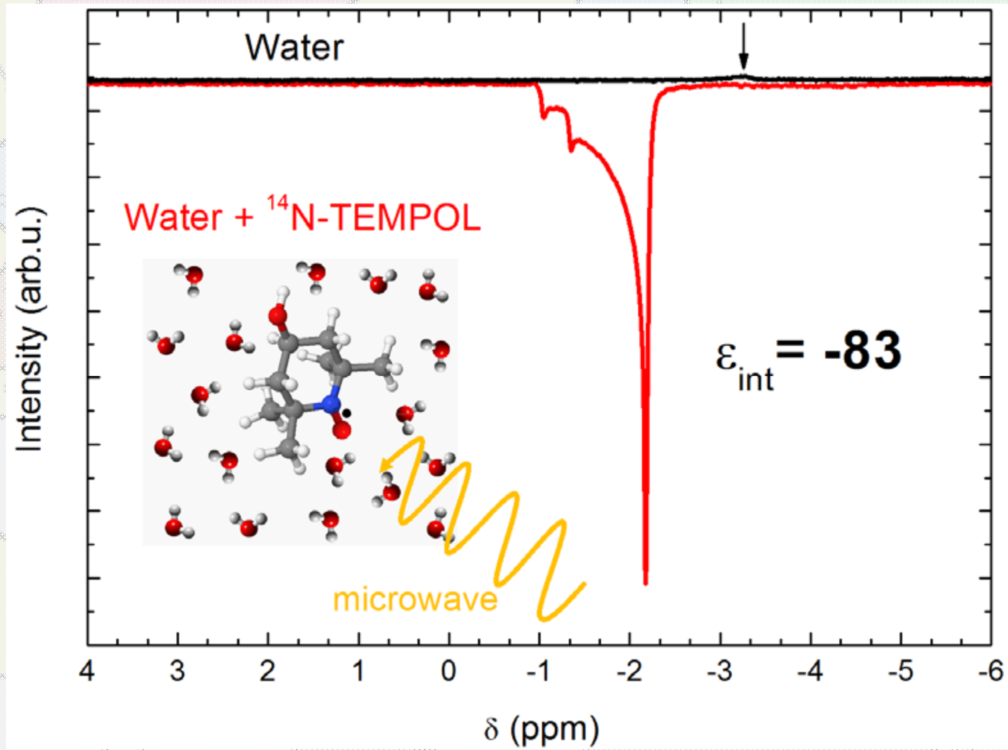
KEYSIGHT TECHNOLOGIES

DFG

Thank you for your attention!

Main Focus
High field liquid 400 MHz ^{1}H-DNP / Pulsed ESR at 180 GHz





Extremely high NMR enhancement

- **NMR enhancement by factor of >83**
- **Reduction** of NMR experimental time **by factor of 6900,** reduction **from hours to seconds!**

Phys. Chem. Chem. Phys., 15, 6049 – 6056 (**2013**); *Phys. Chem. Chem. Phys.*, 16, 18781—18787 (**2014**); *Phys. Chem. Chem. Phys.*, 17, 6618 – 6628 (**2015**)

Solid state materials

- **Molecular Nanomagnets** (qubits) – ideal candidates for quantum computations
- Relaxation studies on **oriented single crystals** – today nearly impossible
- Spin dynamics of **modern solid state materials** – graphene, topological insulators, TMDC

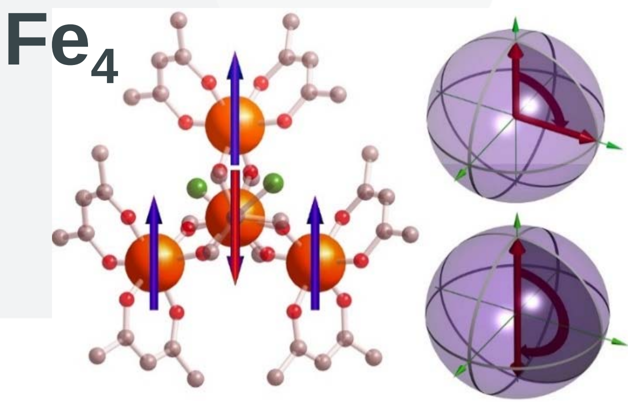
Molecular thin films

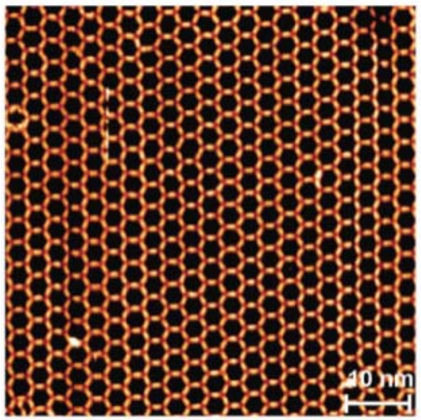
- Towards the applications
- Functionalized substrates

QUantum TEchnologies Flagship (1 billion EUR)

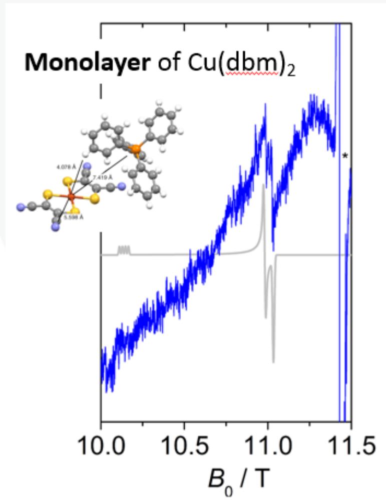
Nature 532, 426 (28 April 2016)

Molecular Nanomagnets - qubits





Molecular Framework

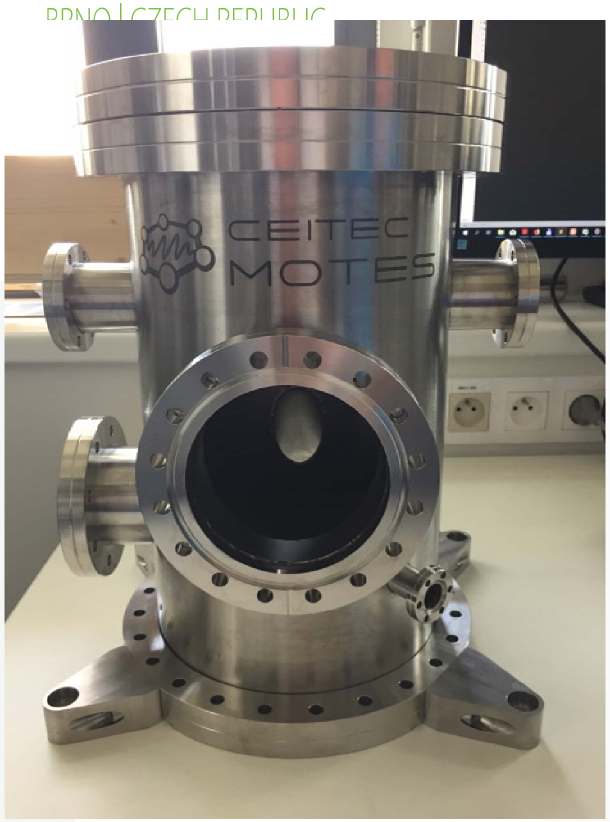


J. Mater. Chem. C, **2018**, 6, 8028--8034

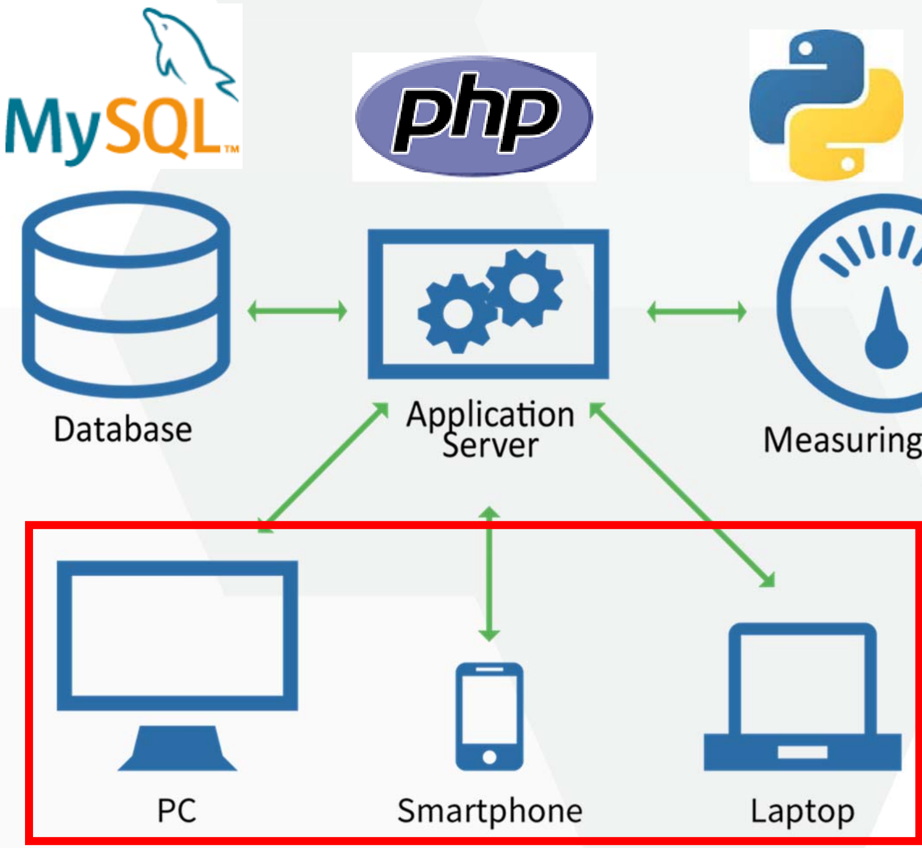
MOTeS Evaporation Chamber

CEITEC
Central European Institute of Technology
BRNO | CZECH REPUBLIC

Hardware



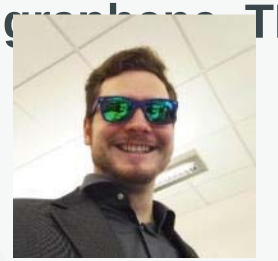
Software



- **Temperature – Thermocouple**
- **Thickness + Evaporation rate – Quartz Crystal Microbalance**
- **Pressure – Turbo Station Gauge**
- **Power Supply – Voltage, Current Control**

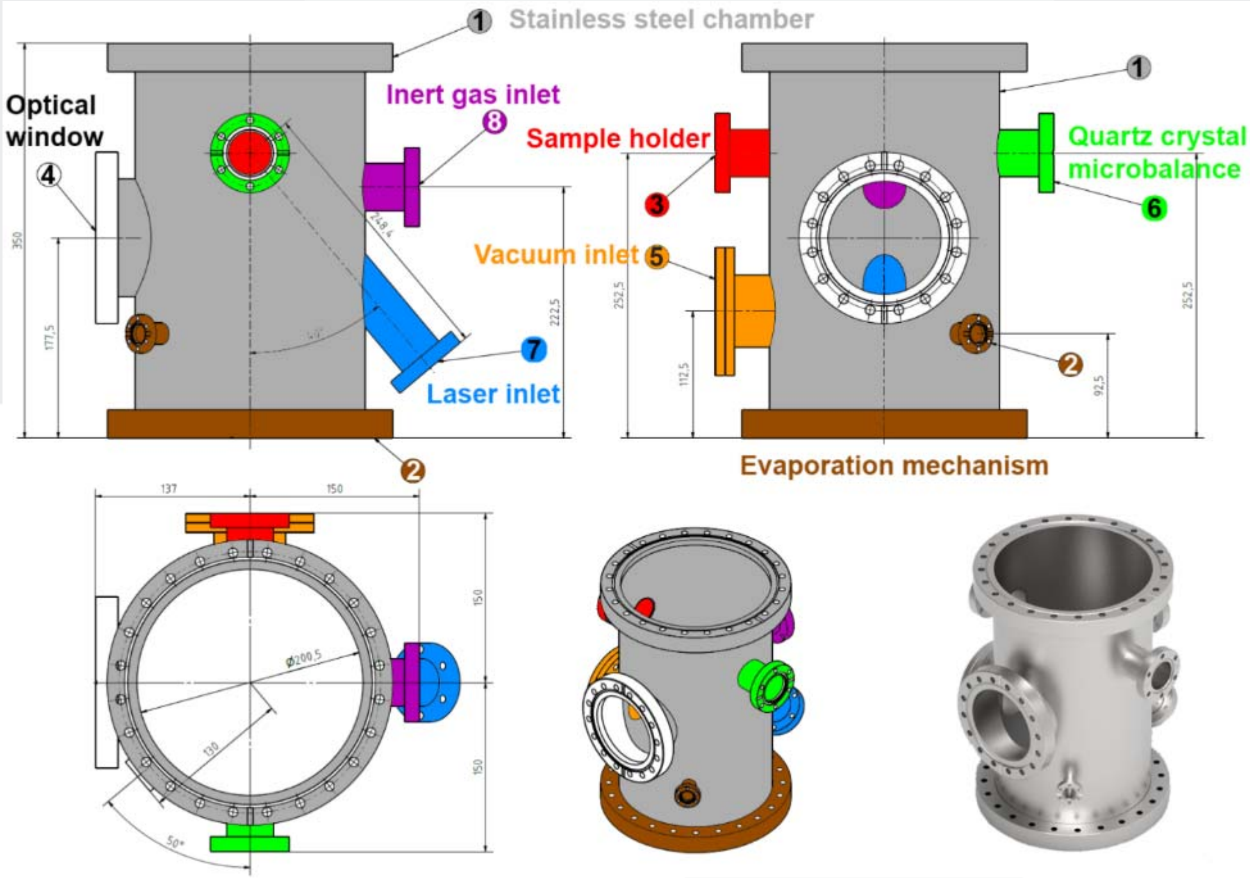
3b) Thermal evaporation

Where: MOTeS EPR lab
When: June 2019
What: Sublimable molecules
Substrate: Glass, gold, silicon, g… TMDs
Team:



Depositions

Software



- Temperature
- Thickness + evaporation rate
- Pressure

CEITEC

Multi-frequency rapid-scan HFEPR

O. Laguta[a], M. Tuček[b], J. van Slageren[a], P. Neugebauer[b,*]

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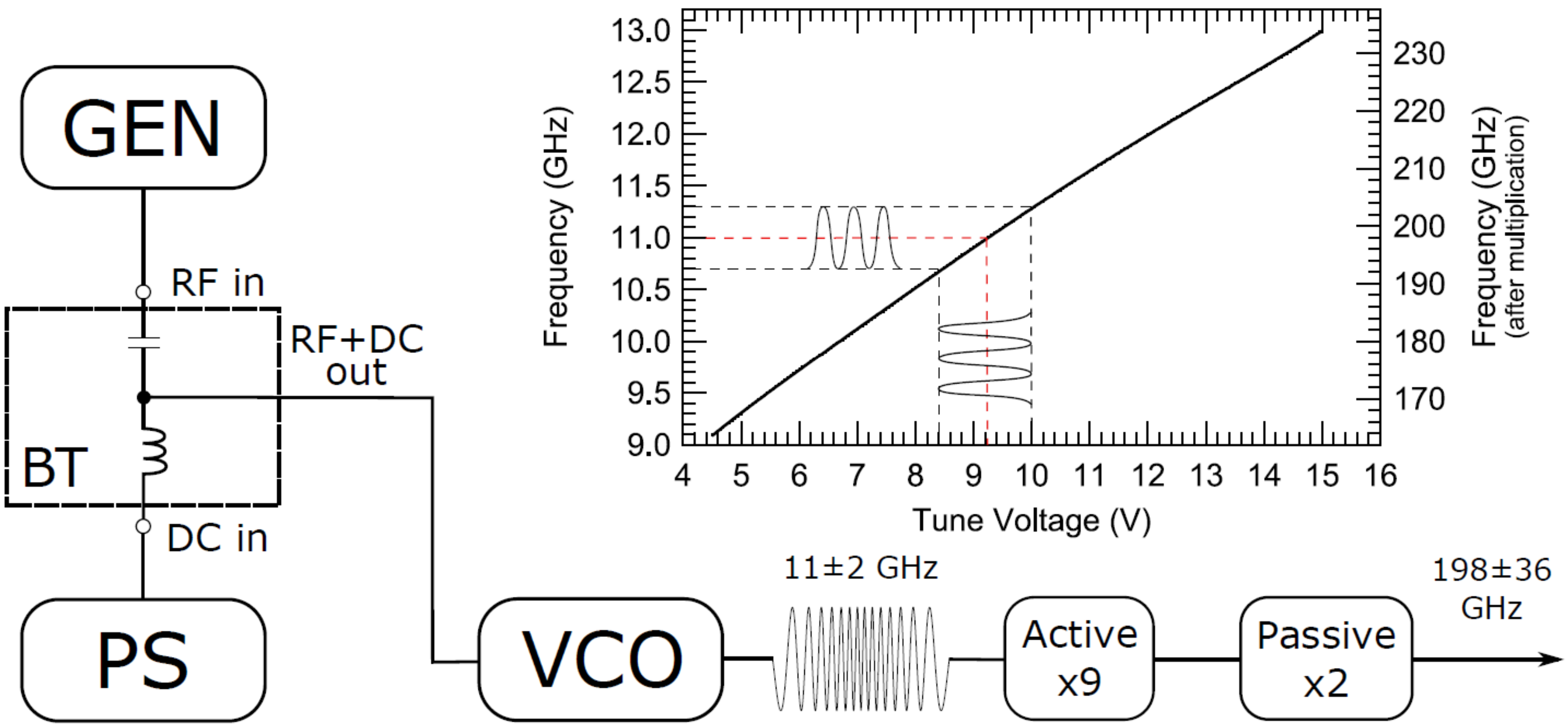

J. Magn. Reson. **2018**, 296, 138