BRNO UNIVERSITY OF TECHNOLOGY

Symposium iNETME:

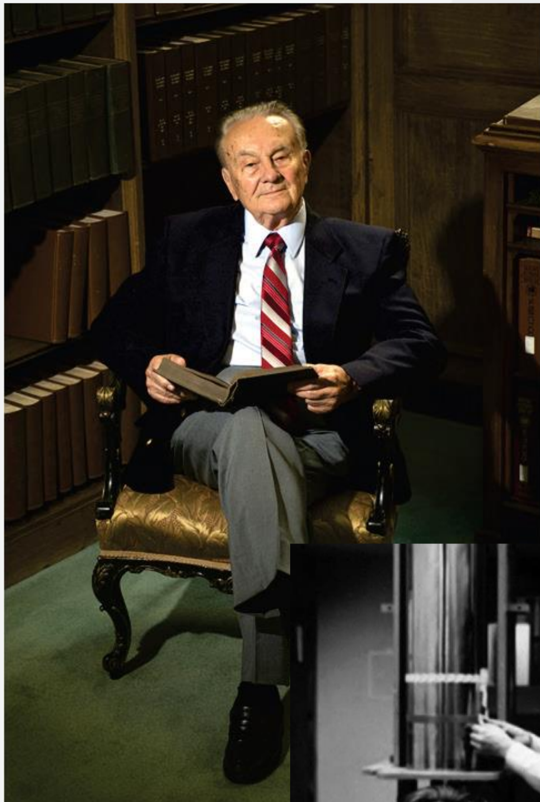
High Frequency Electron Spin Resonance Spectroscopy Today and Tomorrow

CEITEC MOTES

erc

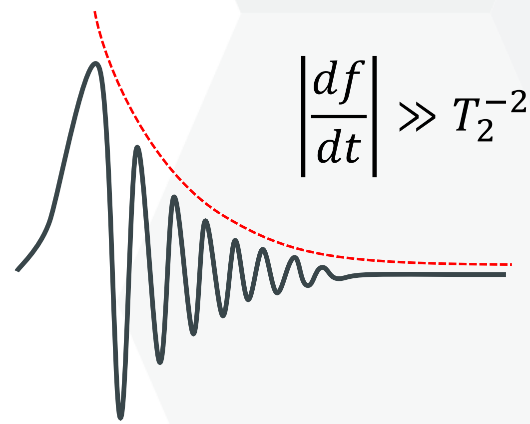
Petr NEUGEBAUER
Petr.Neugebauer@ceitec.vutbr.cz

Josef Dadok (28. 2. 1926 in Dětmarovicích)



1951 Graduated as engineer at BUT
1965 First commercial NMR instrument – TESLA Brno
In 1968 did not return from postdoctoral studies in USA

Rapid Scans



$$\left|\frac{df}{dt}\right| \gg T_2^{-2}$$

J. Dadok, R. Sprecher, *J. Magn. Reson.*, **1974**, 13(2), 243–248

Slaboproudý obzor, 72, 4 (2016) (*in Czech*)
V. Zeman (**2008**) DOI: 10.3247/SL2Nmr08.003 (*in Czech*)

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Why Brno?

- Home, parents,…
- Long history of Magnetic Resonance in Brno (TESLA Brno)

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

NMR in TESLA Brno

Our group in Stuttgart

My story in magnetic resonance development

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Grenoble (France)

QuEMolNa

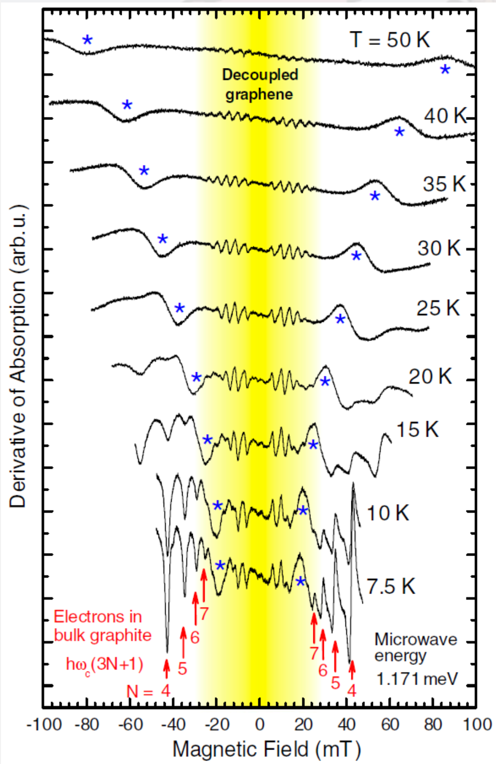
Quantum Effects in MOLecular Nanomagnets
MRTN-CT-2003-504880

1980	Born in Uherské Hradiště, Czech Republic.
2005	**Physical Engineering** at Brno University of Technology, Czech Republic.
2010	PhD. in **Physics** at Grenoble High Magnetic Field Laboratory, France.

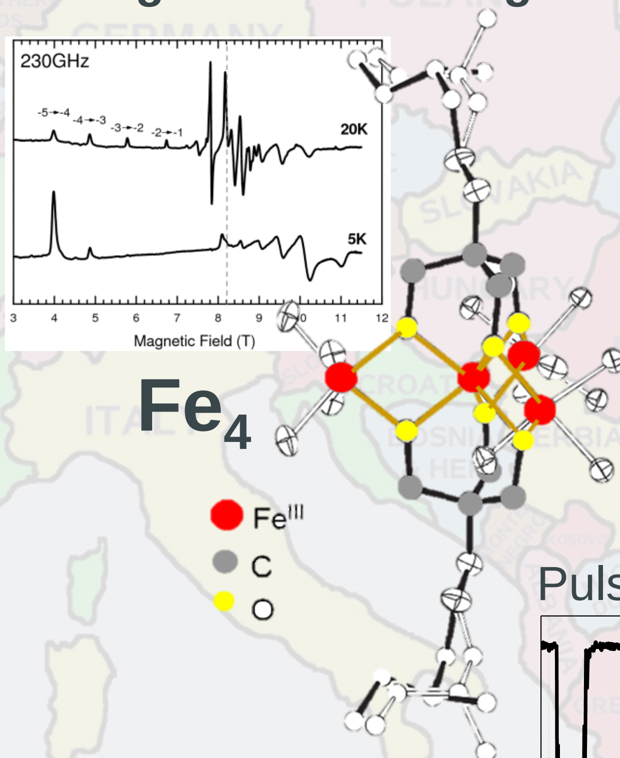
PhD topic

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

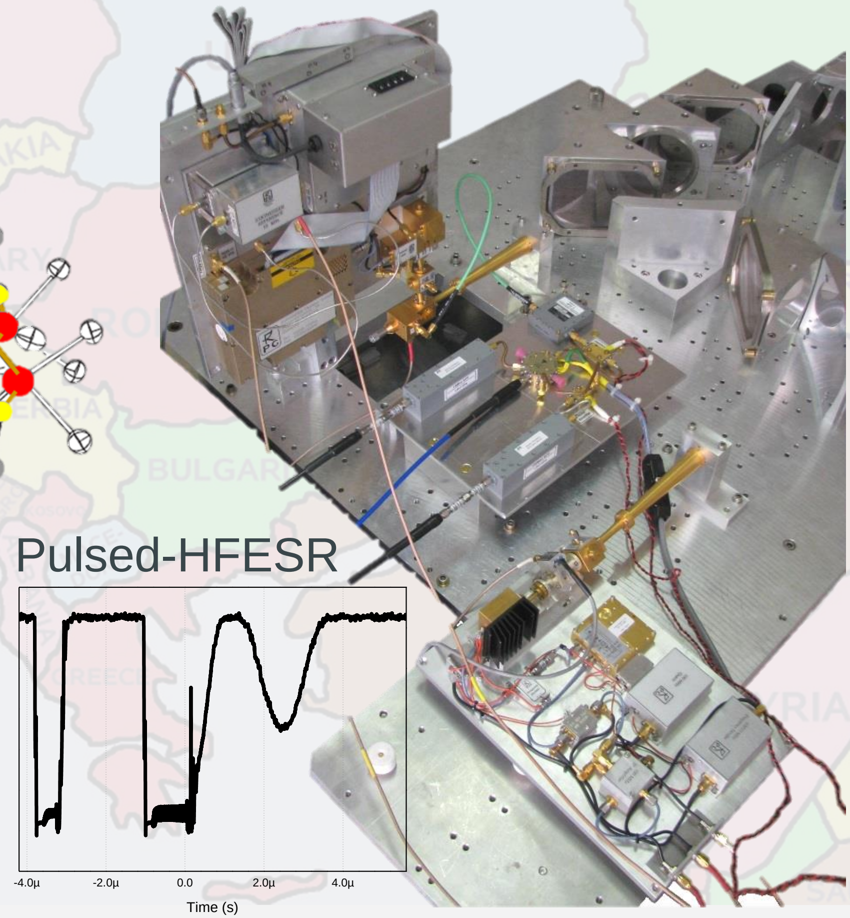
Graphene



Single Molecule Magnets



HFESR Development



Pulsed-HFESR

- 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*

Frankfurt am Main (Germany)

1980 Born in Uherské Hradiště, Czech Republic.

2005 **Physical Engineering** at Brno University of Technology, Czech Republic.

2010 PhD. in **Physics** at Grenoble High Magnetic Field Laboratory, France.

2010 – 2012 Postdoctoral fellow in **Physical-Chemistry** at the Biomolecular Magnetic Resonance Center (BMRZ) at the Goethe University Frankfurt, Germany.

1997

211 MHz / 140 GHz

Robert G. Griffin (MIT, USA)

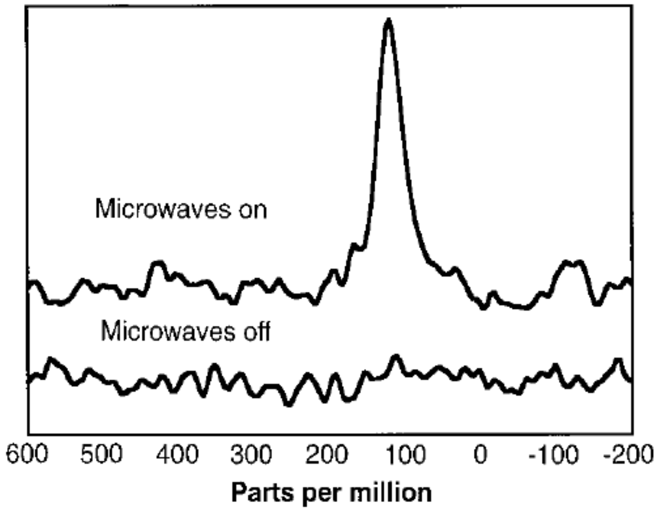


Fig. 3. DNP-CP ^{15}N solid-state MAS (3.2 kHz spin rate) spectra of ^{15}N-Ala–labeled T4 lysozyme [25 mg/ml T4 lysozyme and 40 mM 4-amino-TEMPO in 60% glycerol and 40% buffer (100 mM KCl and 30 mM potassium phosphate)] at 40 K. Microwave irradiation (139.60 GHz) was performed for 20 s with ~1 W at the sample. Sixty-four acquisitions were averaged with a 15-s recycle delay. The bottom spectrum was recorded under identical conditions with no microwave power. The magnetic field was set to maximize the positive enhancement, which is approximately 50.

Dennis A. Hall *et al.*, *Science* 276, 930 (**1997**)

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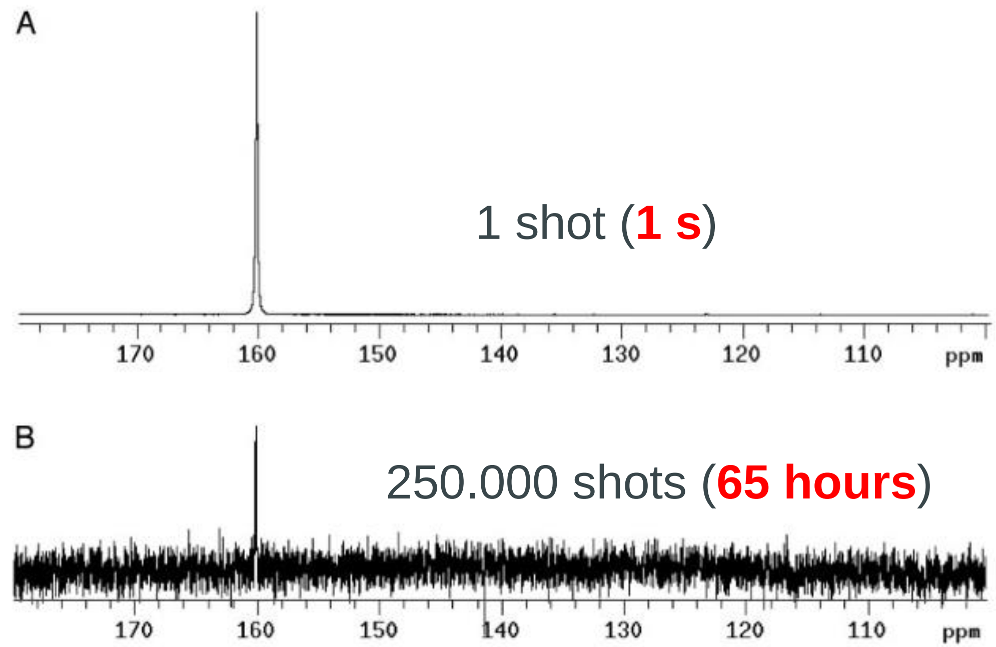
143 MHz / 94 GHz

Jan H. Ardenkjær-Larsen (Malmö, Sweden)



^{13}C spectrum of urea (natural abundance ^{13}C) hyperpolarized by the DNP-NMR method

L.H. Ardenkjaer-Larsen *et al.*, *Proc. Natl. Acad. Sci. USA* 100, 10158–10163 (**2003**)

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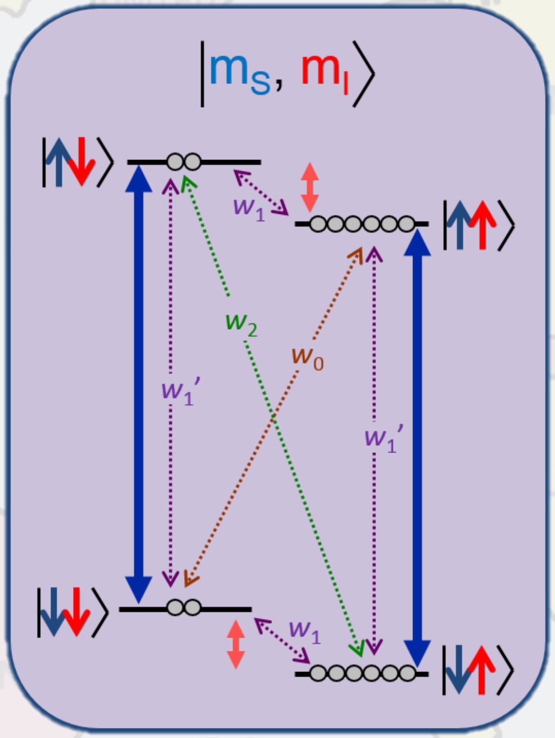
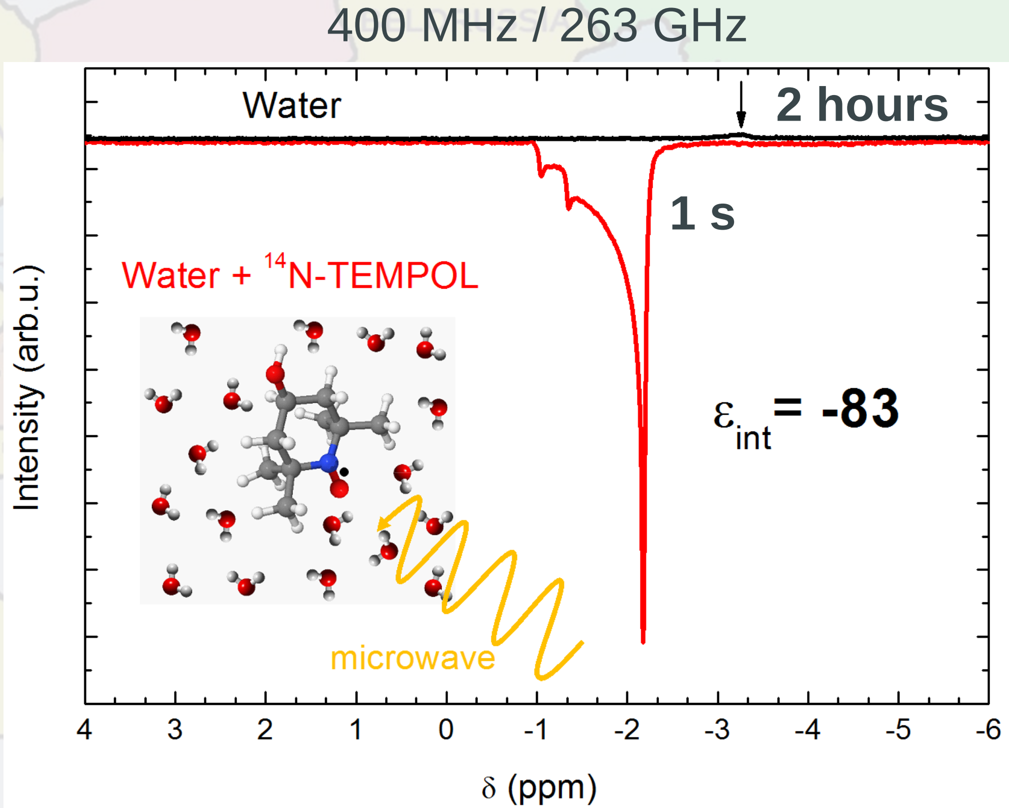
Main Focus
High field liquid 400 MHz ^{1}H-DNP





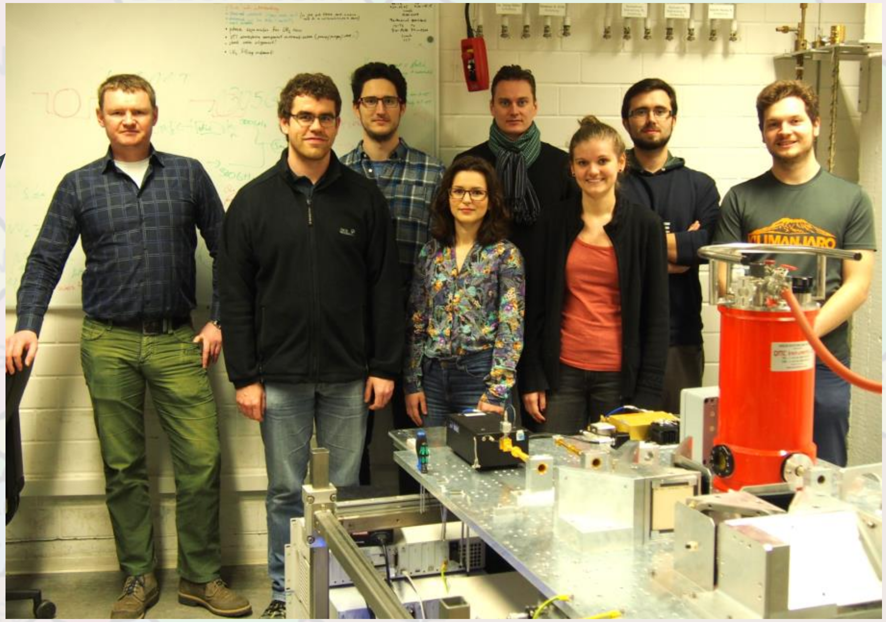
Extremely high NMR enhancement

- **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**)

Stuttgart

University of Stuttgart
Germany



2012 – 2014 Postdoctoral fellow in **Physical-Chemistry** at the University of Stuttgart, Germany.
2014 – 2017 Group leader at University of Stuttgart, Germany.
2015 Research stay at the Denver University, USA.

German Priority Program SPP1601

Baden-Württemberg Stiftung
WIR STIFTEN ZUKUNFT

U.S. NAVAL RESEARCH LABORATORY

DFG

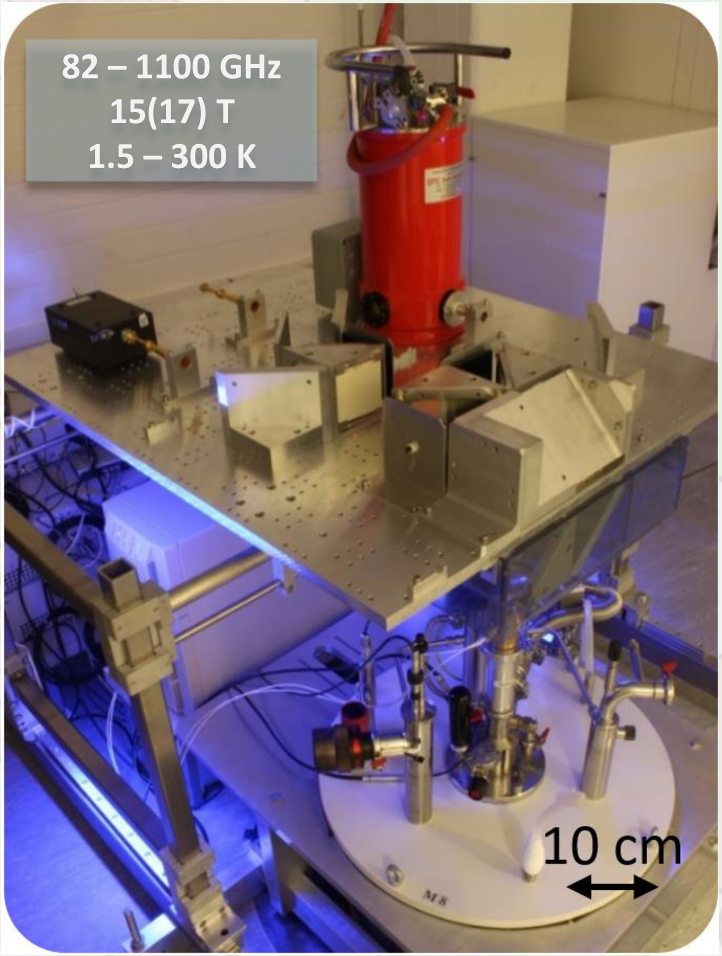
First combine ESR/FDMR spectrometer

Description of spectrometer:

[1] *Phys.Chem.Chem.Phys.*, 20, 15528 (**2018**) (already cited 20times)

Produced results (till 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**)



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**)*

Introduction to Magnetic Resonance Instrumentation

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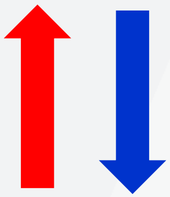
Spins

Spins (I or S)

Magnets



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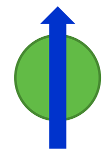
Electron Paramagnetic Resonance (EPR)
Electron Spin Resonance (ESR)



Electrons
Electronic spin S

Nuclear Magnetic Resonance (NMR)

Nucleus (protons and neutrons)
Nuclear spin I

Subatomic particles (electrons, protons, neutrons)

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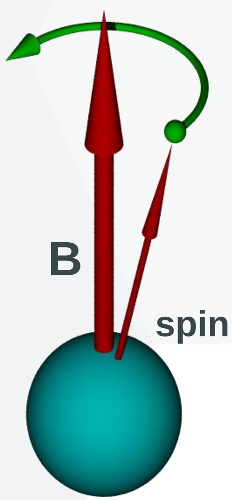
NMR vs. EPR

Larmor precession (named after Joseph Larmor) is the *precession of the magnetic moments* of electrons, muons, and all leptons with magnetic moments, which are quantum effects of particle spin, atomic nuclei, and atoms *about an external magnetic field*.

http://en.wikipedia.org/wiki/Larmor_precession



Larmor frequency (negative charge):

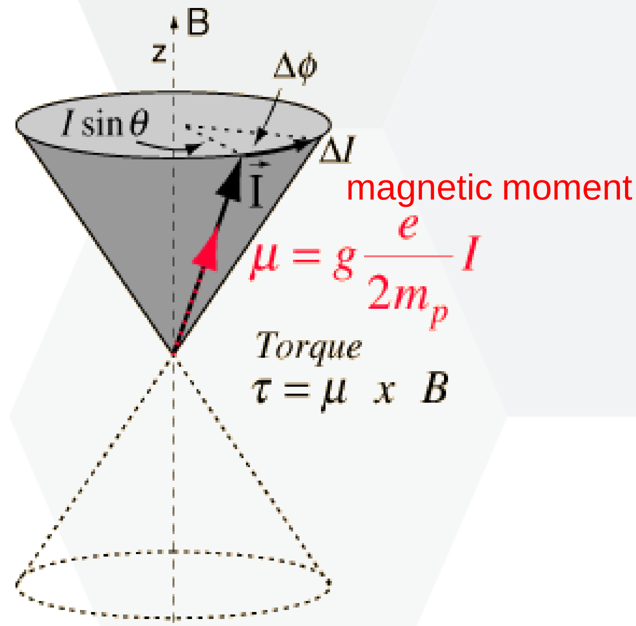
$$\omega = -\gamma B$$

Gyromagnetic ratio:

$$\gamma = \frac{eg}{2m}$$

Electron: $\left|\frac{\gamma_e}{2\pi}\right| \approx 28024 \frac{\text{MHz}}{\text{T}}$

Nucleus (proton, H^1): $\left|\frac{\gamma_n}{2\pi}\right| \approx 42 \frac{\text{MHz}}{\text{T}}$



Mass m: $m_{electron} \approx m_{proton}/2000$
$m_{proton} \approx m_{neutron}$

g-factor: $g_e < g_n$

NMR in MHz (Radio Frequency)
EPR in GHz (Microwaves)

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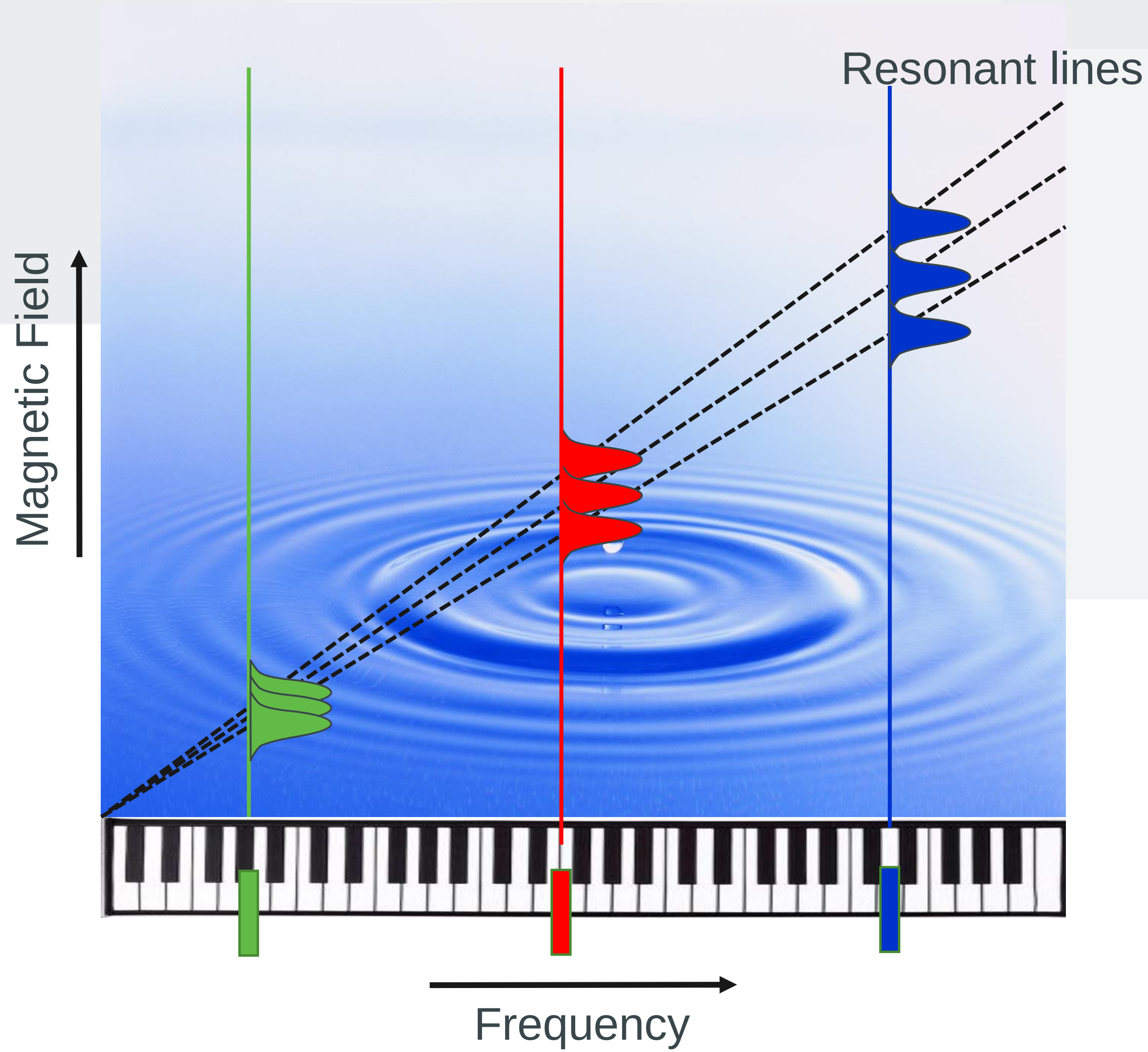
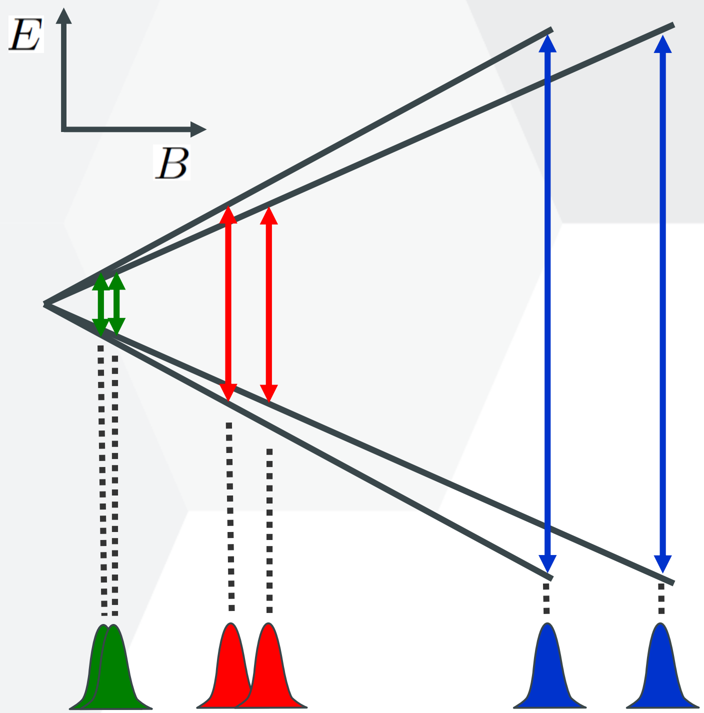
How to play?

Continuous wave

Constant irradiation
Varying magnetic field



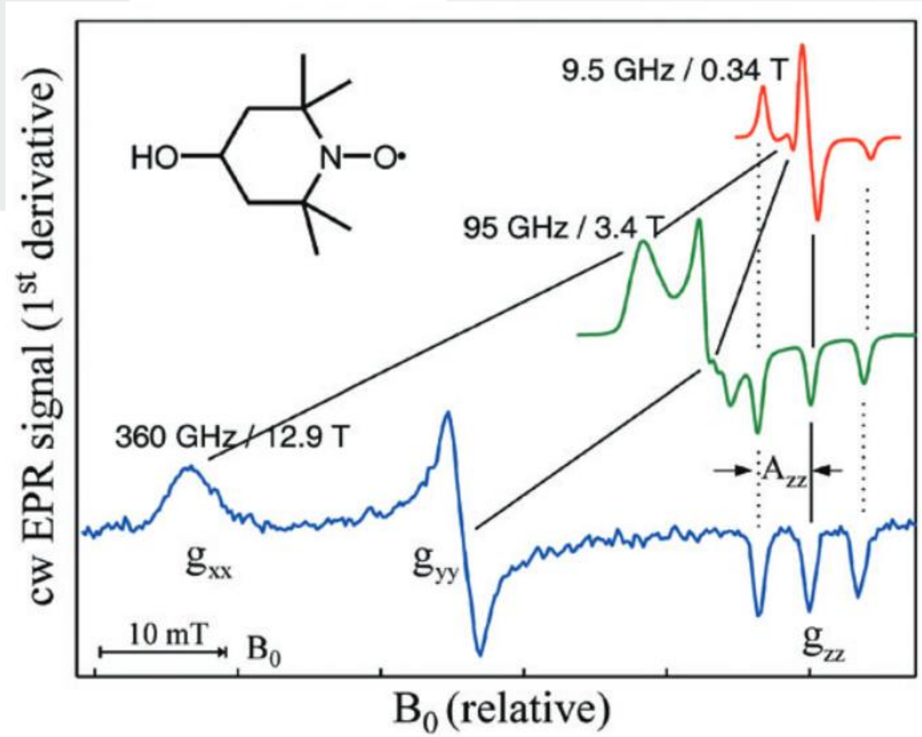
Why to go high? – Resolution / Sensitivity



X-band
10 GHz
λ = 30 mm

Q-band
40 GHz
λ = 8 mm

W-band
100 GHz
λ = 3 mm



K. Möbius *et. al.*, *Phys. Chem. Chem. Phys.*, 19, 7 (**2005**)

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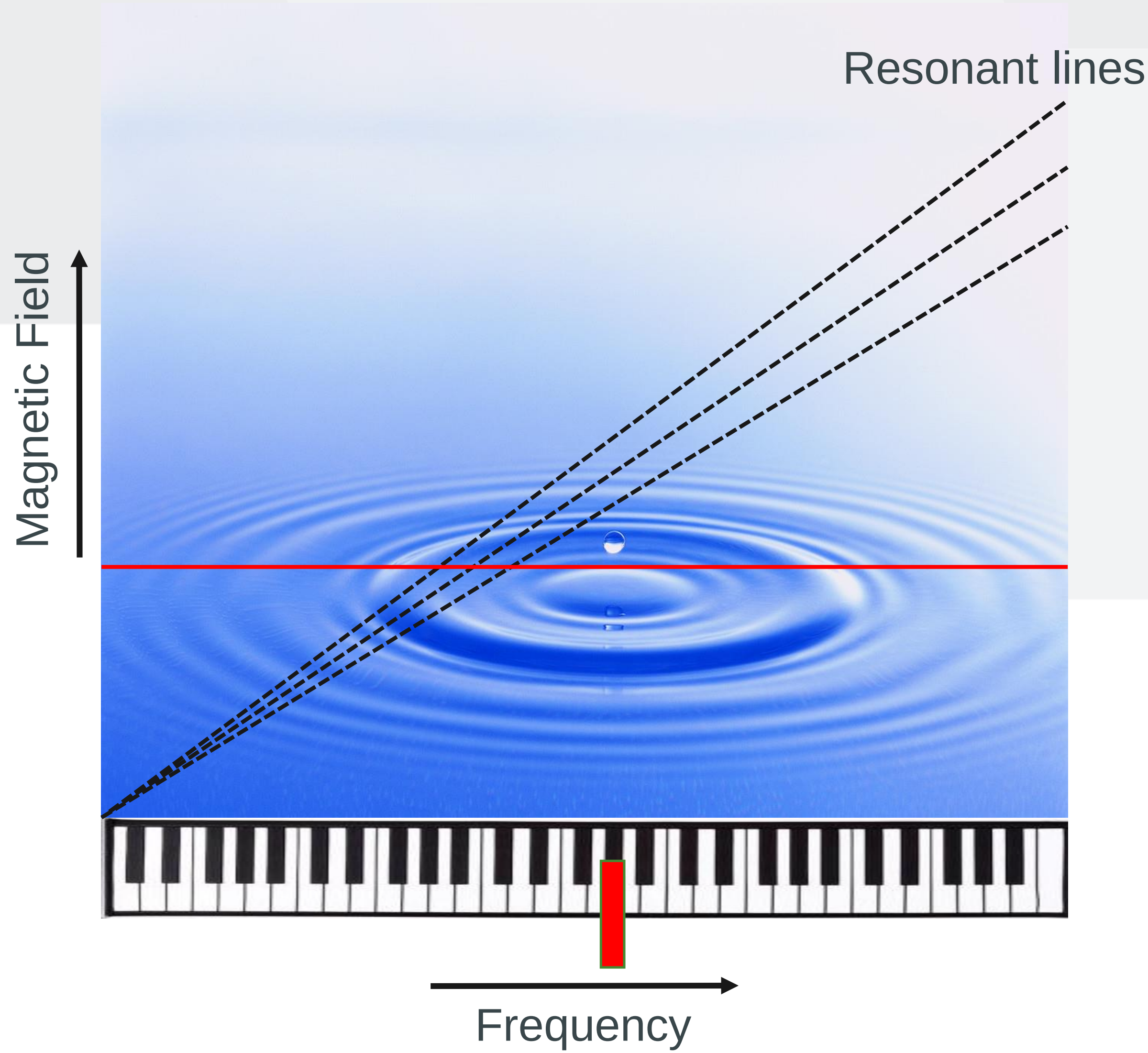
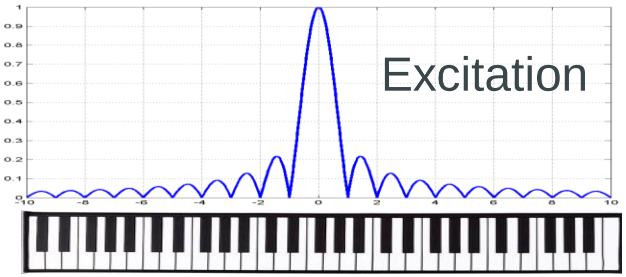
How to play?

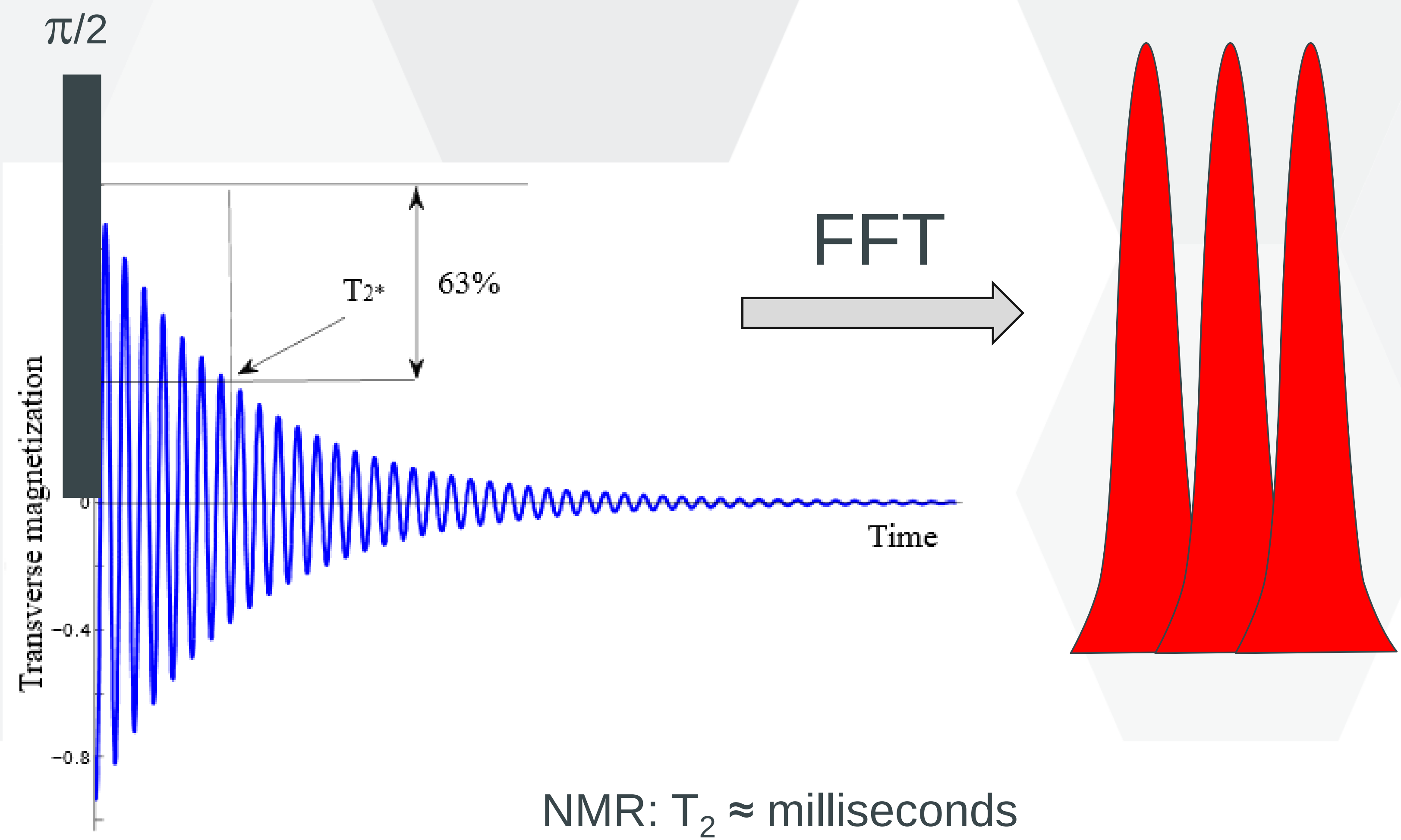


Pulsed method

Short frequency pulse
Constant magnetic field



How to play?



NMR: T_2 ≈ milliseconds

EPR: T_2 ≈ nanoseconds

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How to play?

Continuous wave

Constant irradiation
Varying magnetic field

- Spectrum
- Low Power Sources

Pulsed method

Short frequency pulse
Constant magnetic field

- Spectrum
- T1, T2 relaxations
- High Power Sources

Spectrometers Operate at Single Frequency!

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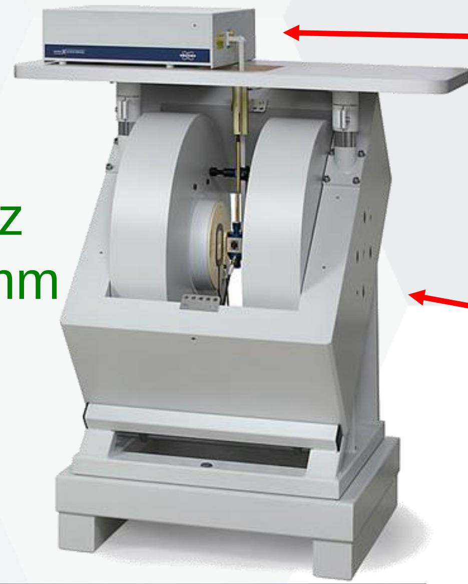
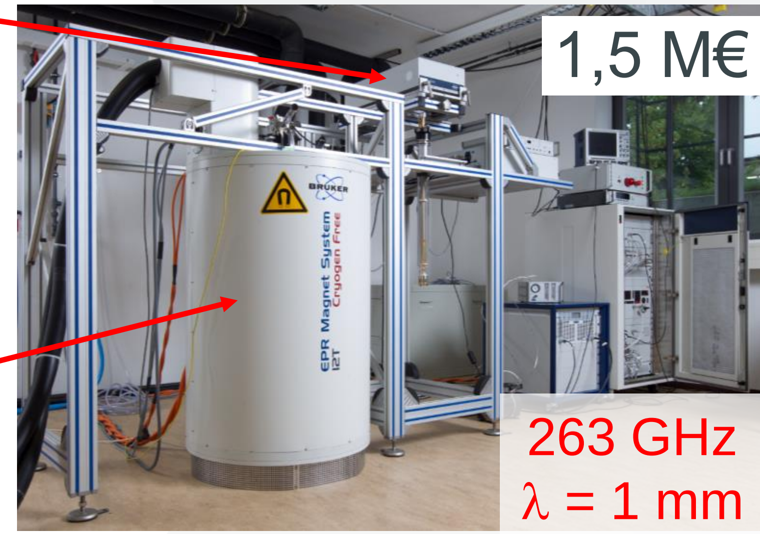
EPR Instruments

Low Frequency | **High Frequency**

10 GHz
λ = 30 mm

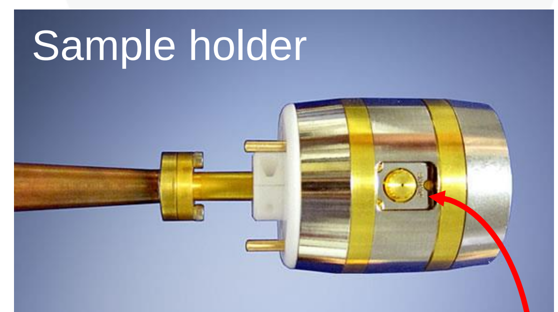


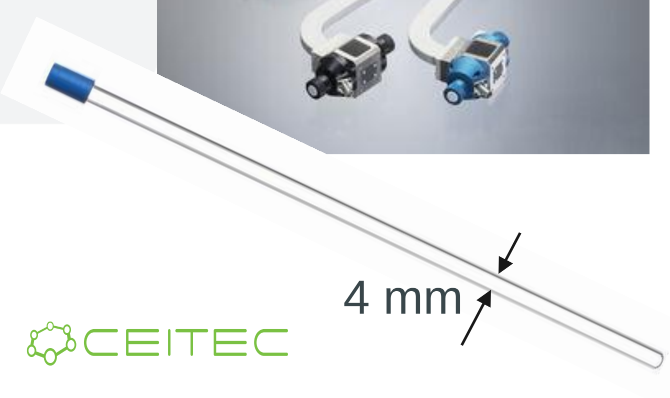
Microwave source



Magnet
Resistive
Superconductive

Cavity
Size ≈ $\lambda/2$





Sample tube
Size << $\lambda/2$

Measurement time
Minutes-Day

Inner diameter (30 – 100) µm

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NMR Instruments

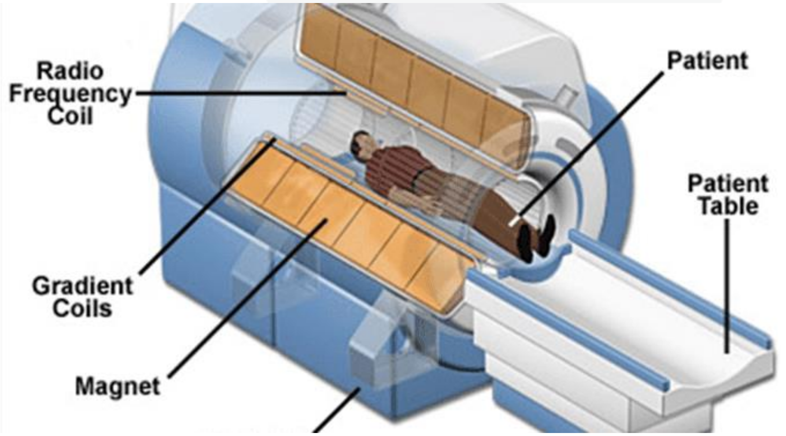
High Frequency NMR

Brno, Czech Republic

Measurement time: Minutes-Days

Clinical NMR (Magnetic Resonance Imaging, MRI)

Measurement time: ~ 30min



1997

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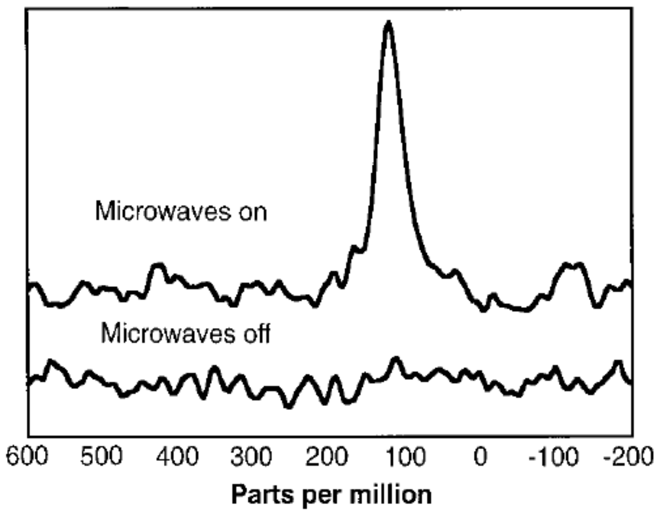

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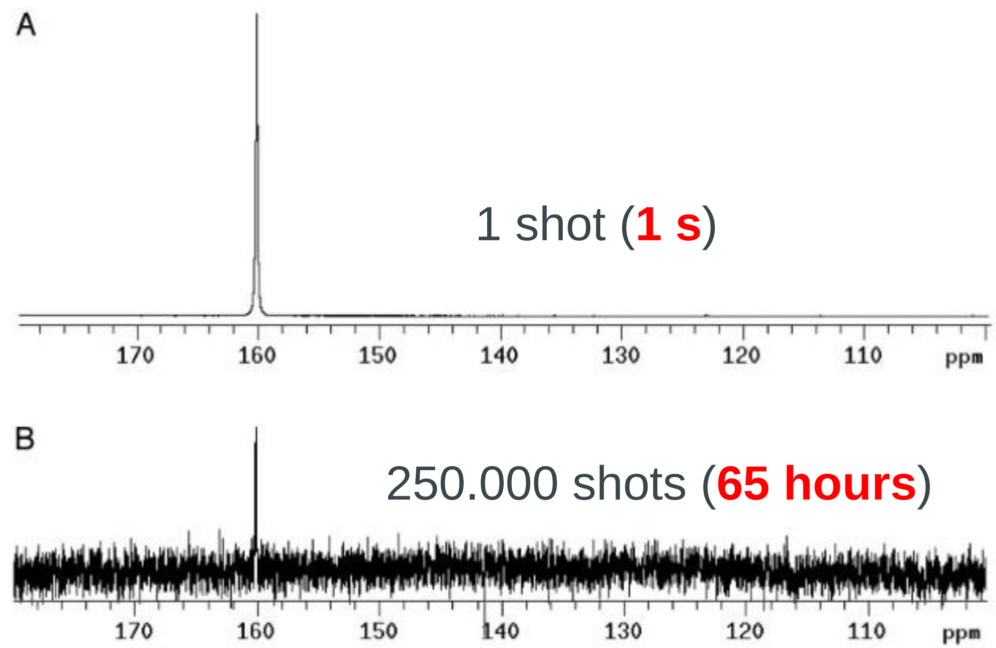

^{13}C spectrum of urea (natural abundance ^{13}C) hyperpolarized by the DNP-NMR method

L.H. Ardenkjaer-Larsen *et al.*,
Proc. Natl. Acad. Sci. USA 100, 10158–10163 (**2003**)

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THz-FRaScan-ESR

European Research Council

Action Number 714850

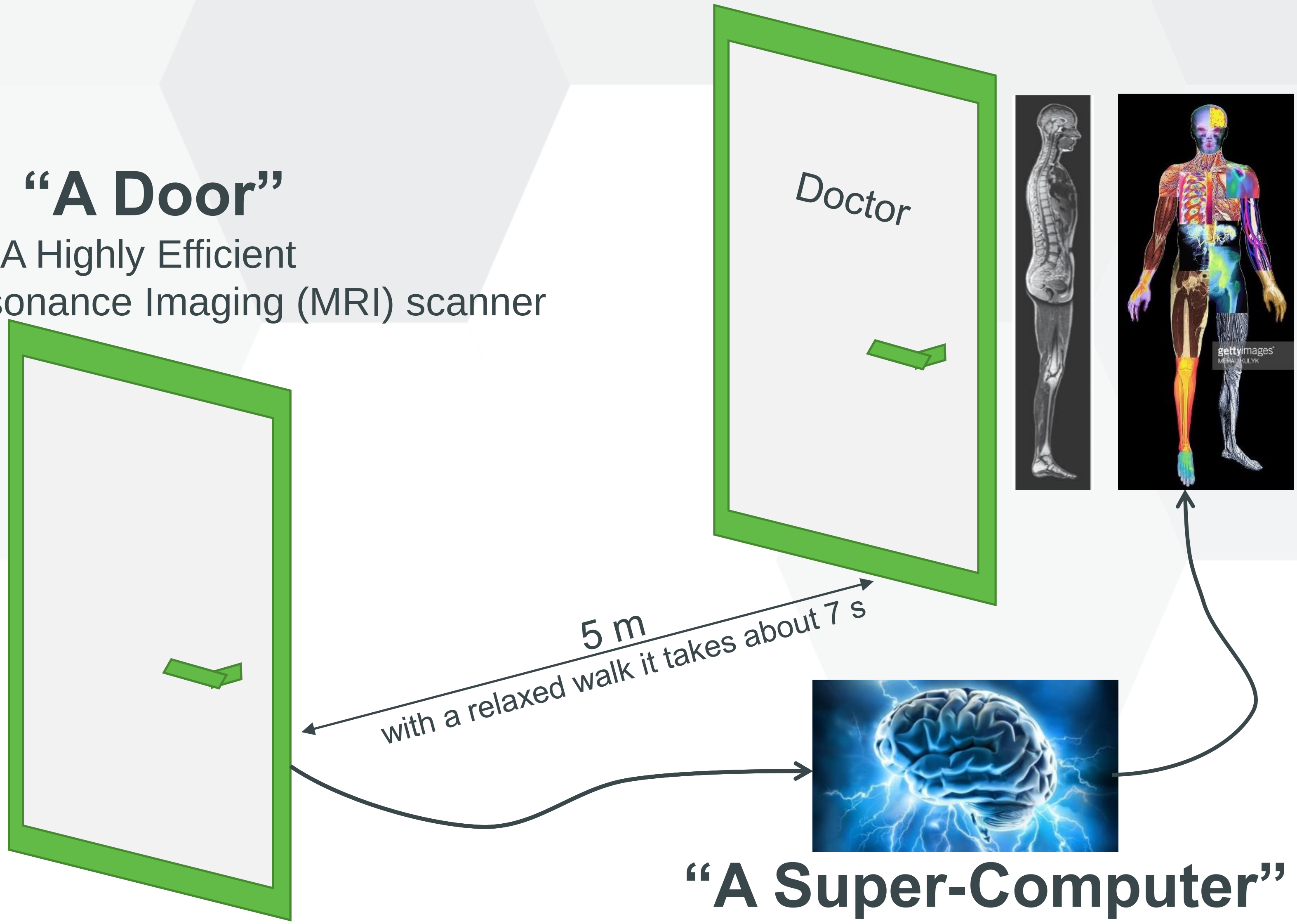
2 Millions EUR to build an unique prototype of EPR spectrometer

Starting date 1.1.2018
End date 31.12.2022

My Long Term Vision

“A Door”

A Highly Efficient
Magnetic Resonance Imaging (MRI) scanner



“A Super-Computer”

A Quantum-Computer

My Long Term Vision

1 **“A Tool” - THz-FRaScan-ESR**

3 **“A Door”**

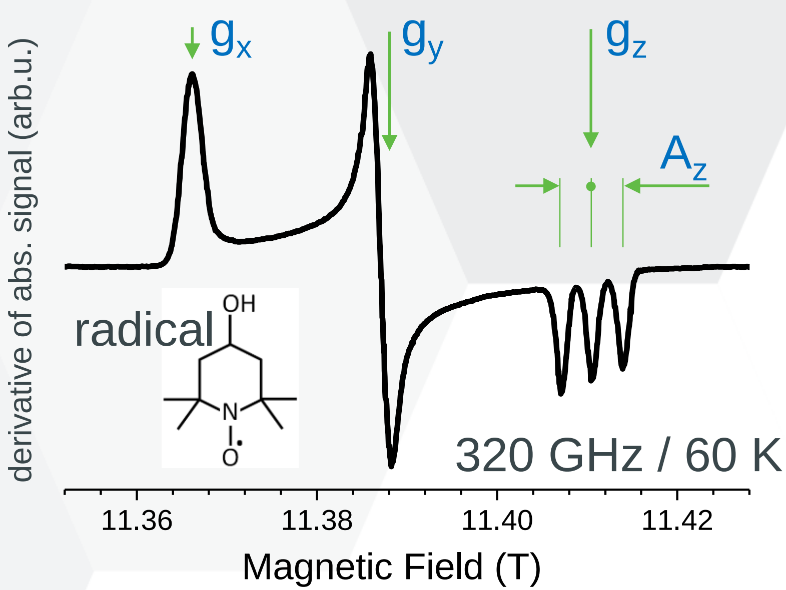
A Highly Efficient
Magnetic Resonance Imaging (MRI) scanner

2 **“A Super-Computer”**

A Quantum-Computer

Current state of HFEPR

High spectral resolution:



Powerful tool in:

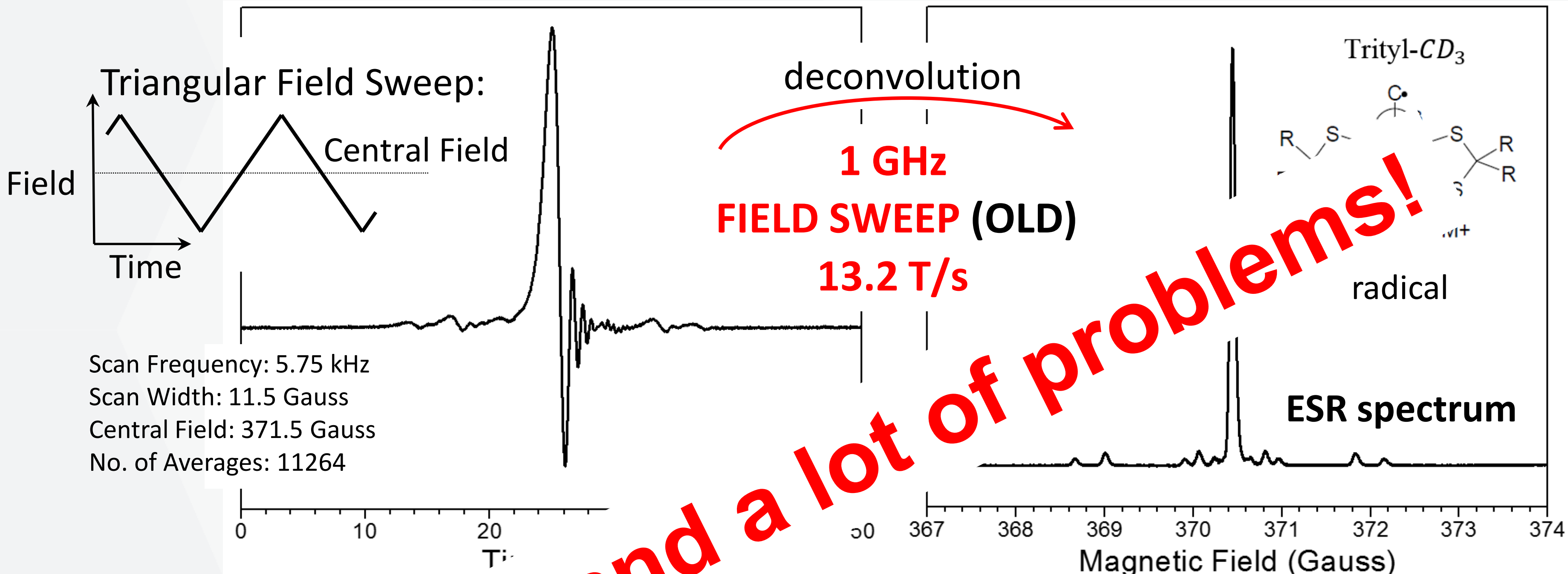
- systems in molecular magnetism
- biomolecules
- heterogeneous catalysis
- solar-cells, batteries
- … everywhere where unpaired electrons are involved

Limitations:

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

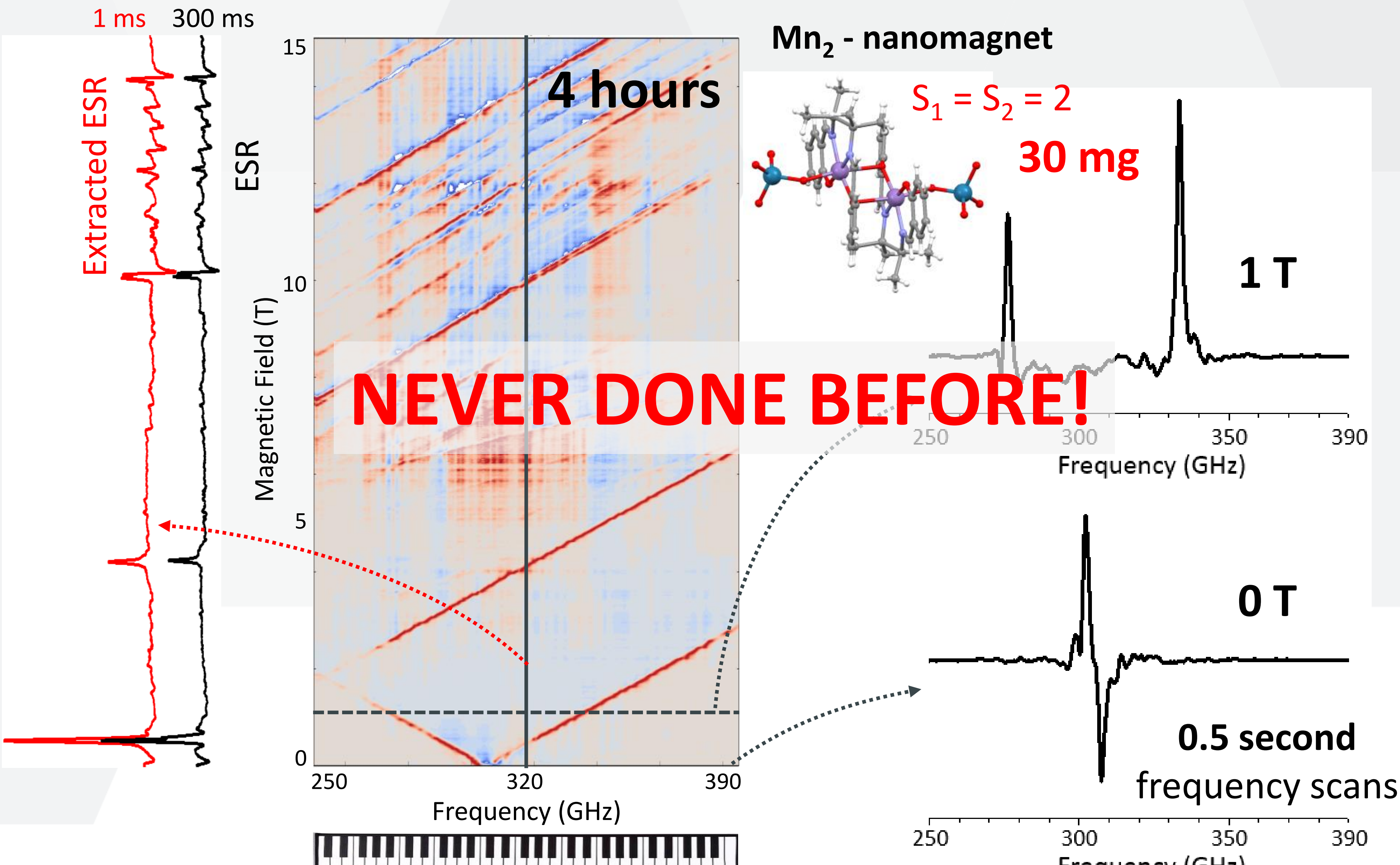
263 GHz (λ ~ 1 mm) sample capillary
Inner diameter (30 – 100) μm

Rapid Scan



Low field and a lot of problems!

- **Access** [illegible] **rates** if $|\gamma|(dv/dt) > T_2^{-2}$
- **Rapid FR**[illegible]**ENCY 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



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

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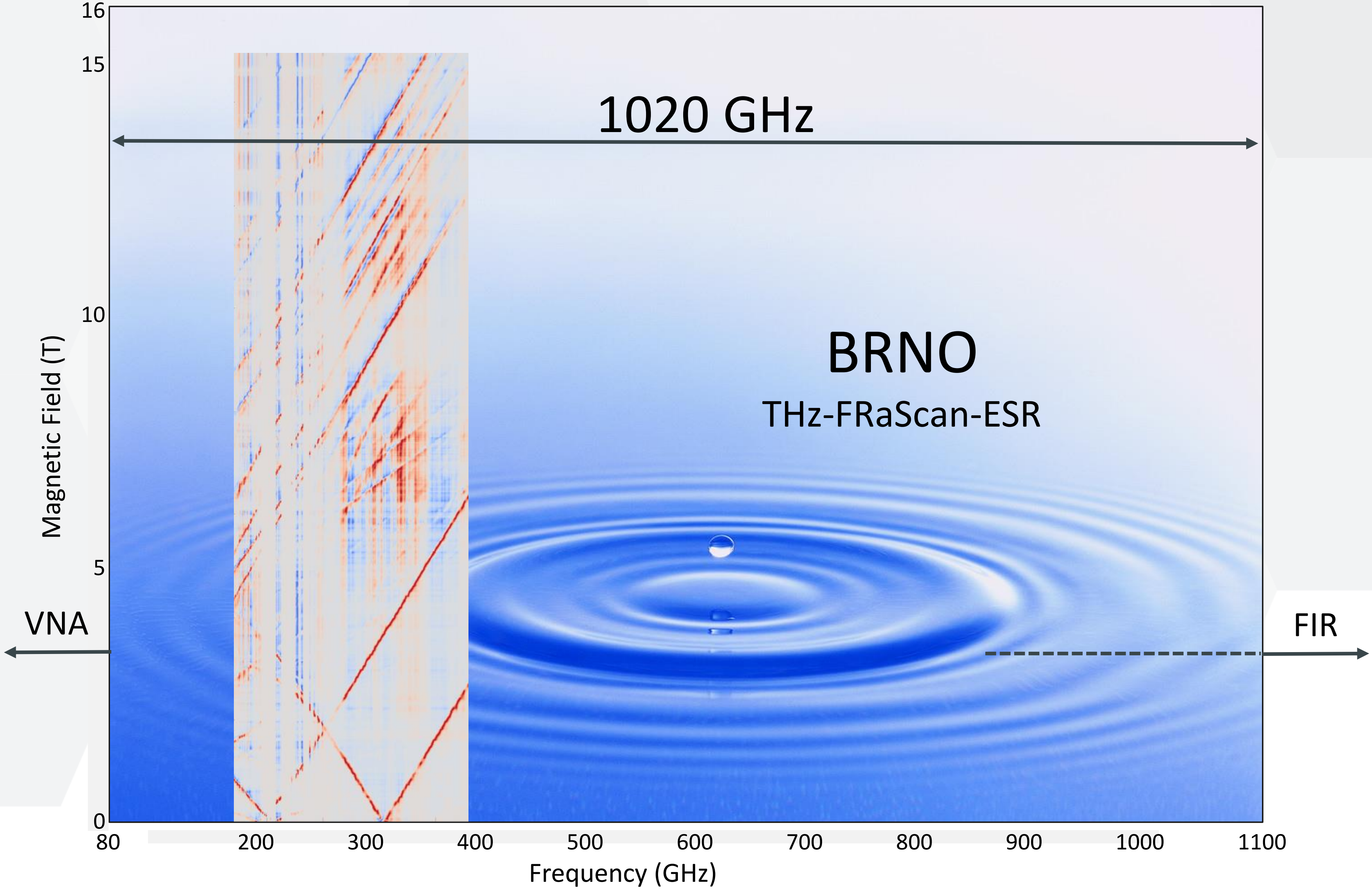
Phys.Chem.Chem.Phys., 20, 15528 (**2018**)



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

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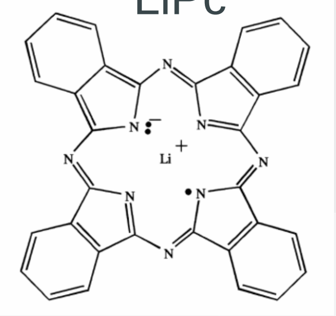
Frequency Rapid Scan

- Multi-Frequency relaxation studies
  - Frequency is defined by applied magnetic field
- Access to extremely fast relaxation times

LiPc



Low Irradiation Power – GREAT!!!

Multi-frequency relaxation studies – AWSOME!!!

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

Conventional ESR Vs. Freq. Rapid Scan - ESR

Conventional ESR

- \+ well 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

Freq. Rapid Scan - ESR

- \+ 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
- \+ 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)
- \+ zero field experiments
- \+ opens new possibilities
- \+ cheap and extendable concept
- – novel approach

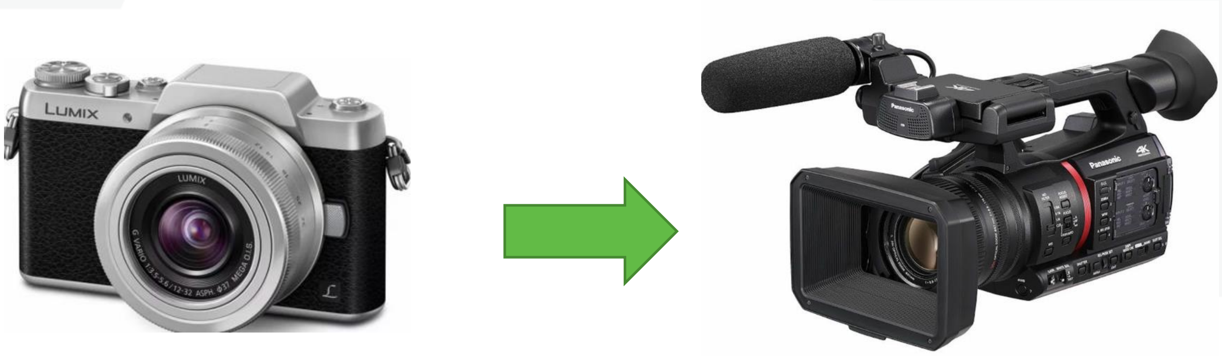
THz-FRaScan-ESR Spectrometer

- Unique concept based on ultrafast frequency sweeps
- With access to relaxation times below 10 ns (1 ns)!

Revolution in ESR Spectroscopy

+ opens new possibilities

From static picture to visualization of motion!



Conclusion

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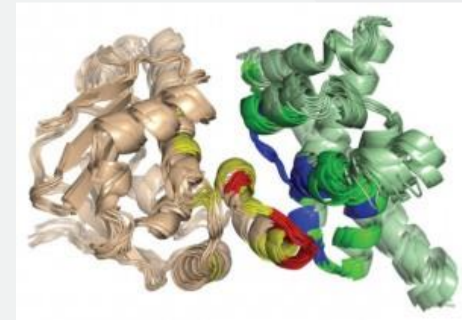
Nobel Prizes in Magnetic Resonance

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

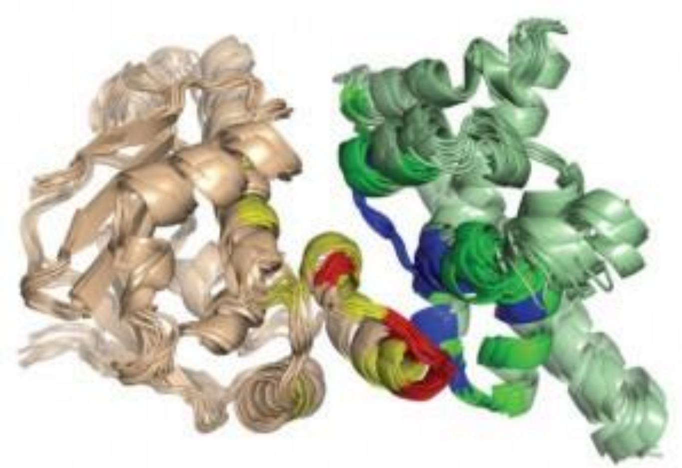
Name	Year	Category	Description
Norman F. Ramsey	1989	Physics	"For the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks"
Hans G. Dehmelt	1989	Physics	"For the development of the ion trap technique"
K. Alexander Müller	1987	Physics	"For their 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

Why is so?

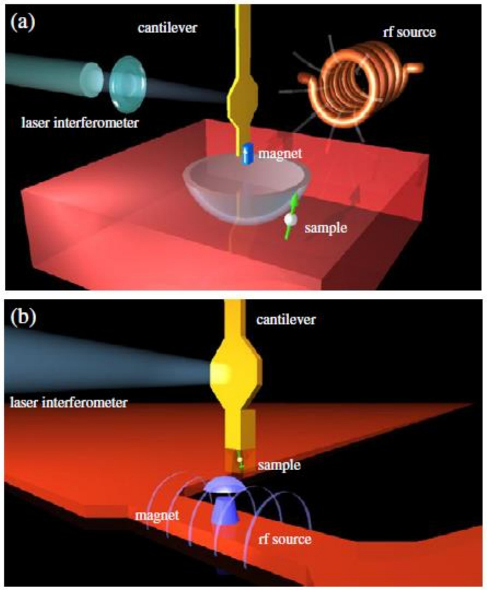
- Non invasive and not ionizing beam
- Dynamics and structure determination of biological relevant complexes (in X-ray only crystalized systems can be measured)

Determination of Structure, Function and Dynamics of Large Molecular objects



Magnetic Resonance Imaging

Detection of Single Spin



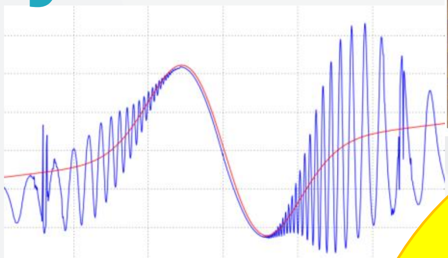
Still room for improvements!!!

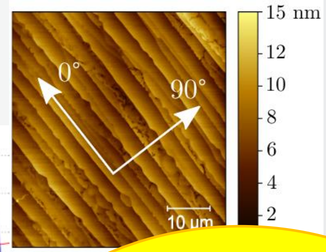
My Team

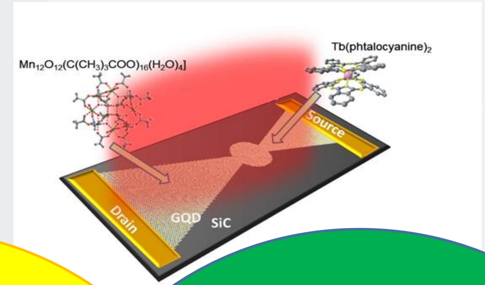
Czech, Ukrainian, Slovak, Polish, Chinese, Brazilian, Columbian, Japanese, French, India.

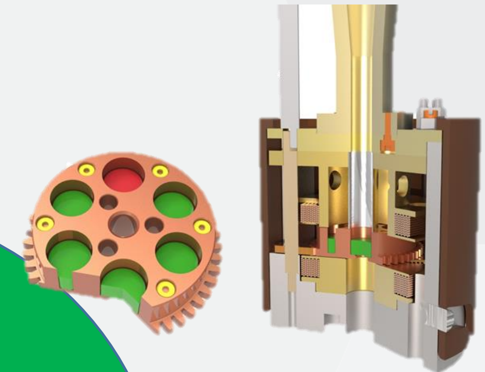
10 nationalities

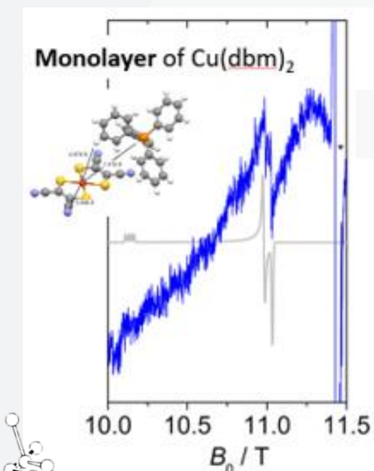
My Team

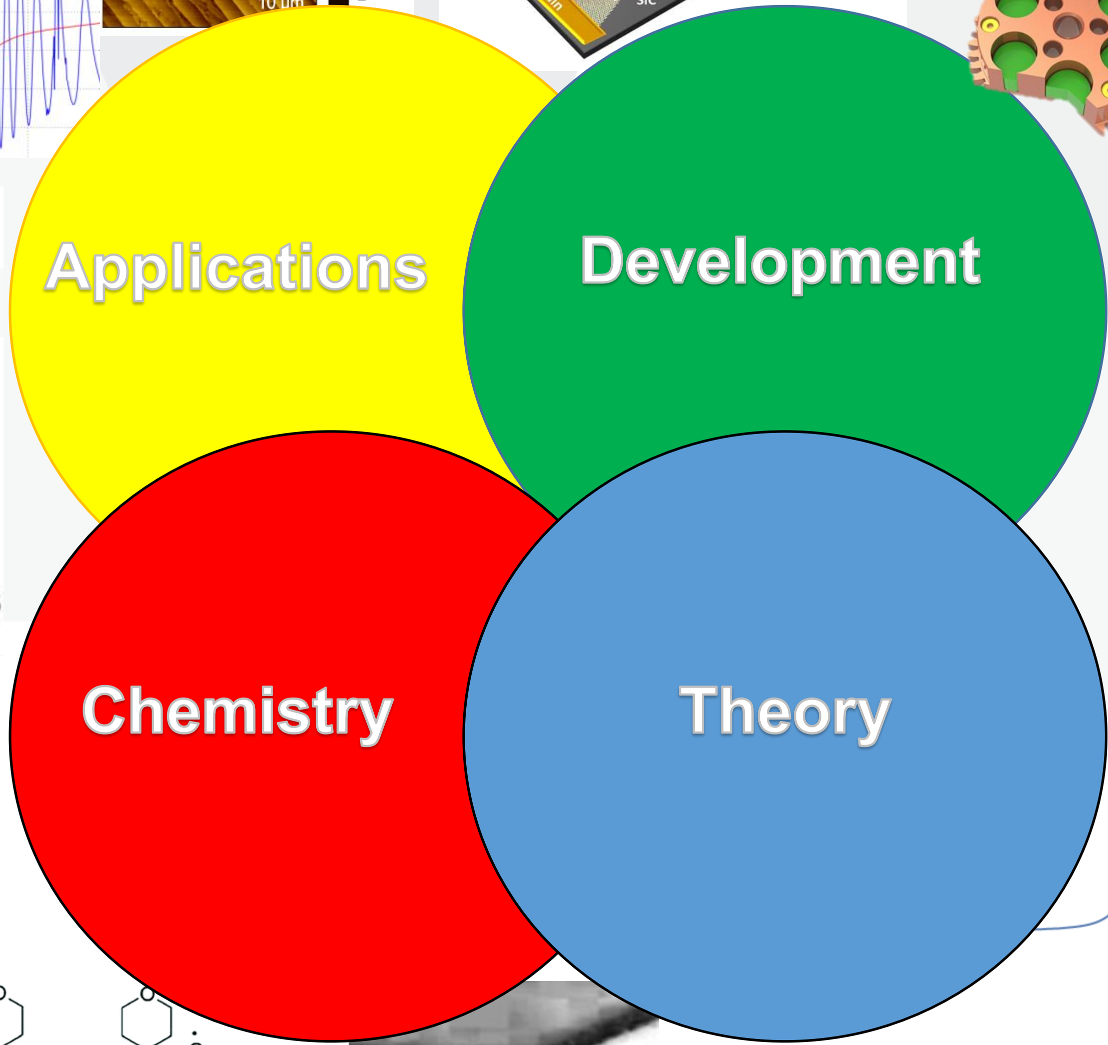


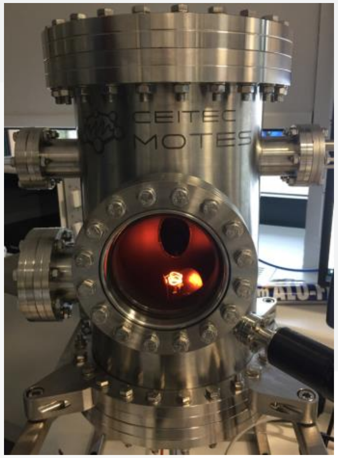


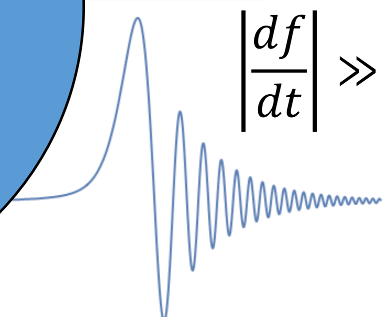




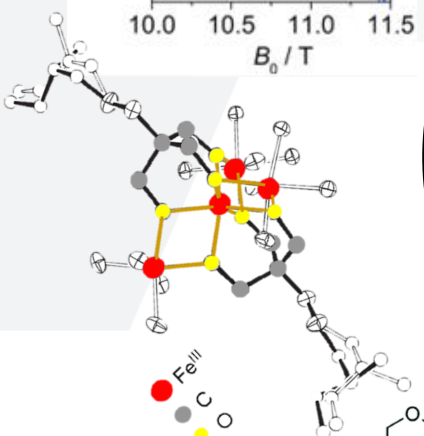


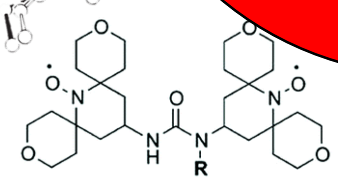




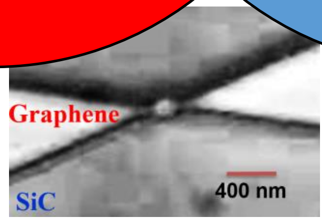


$$\left|\frac{df}{dt}\right| \gg T_2^{-2}$$





R = $(CH_2CH_2O)_4Me$, **AMUPol**



$$\sigma_{xx}(B) = \sigma_0 \frac{1}{1 + (\omega_c \tau)^2} = \sigma_0 \frac{1}{1 + (\mu B)^2}$$

CEITEC

Our Mission

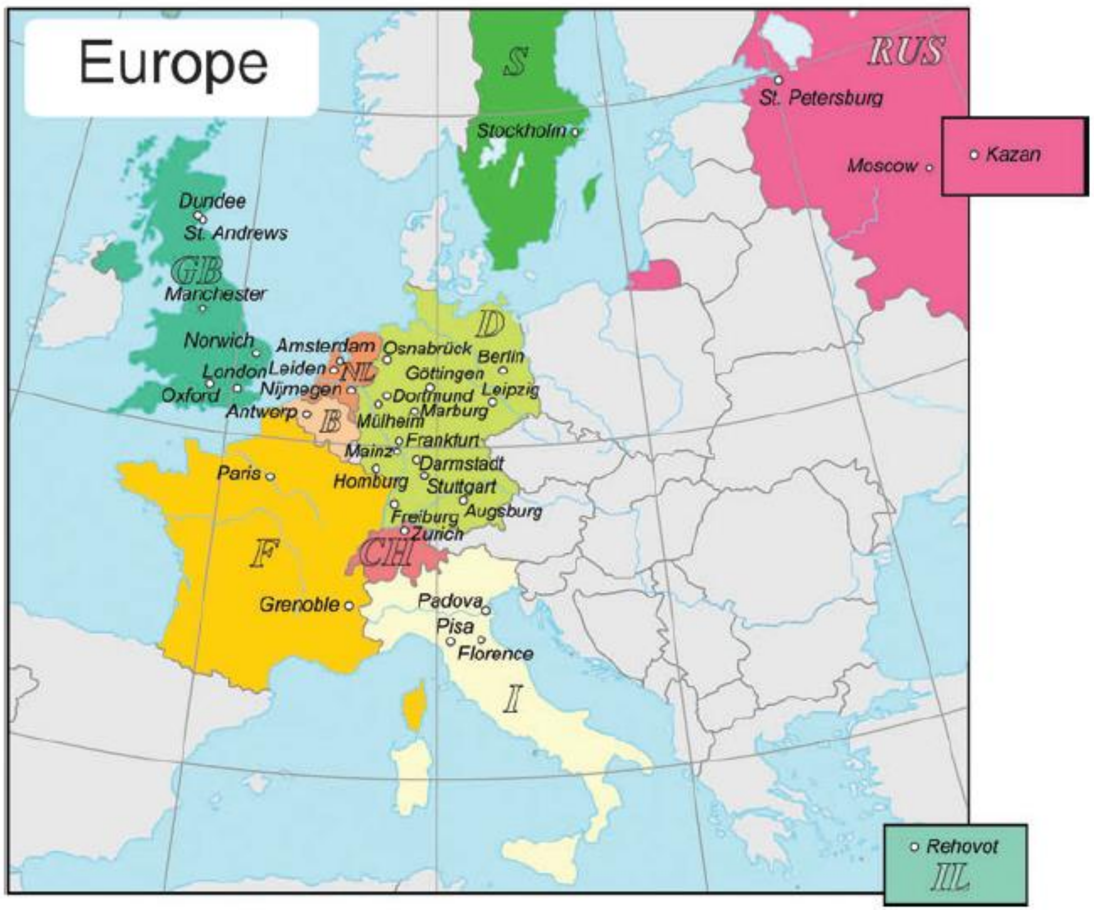


Figure 1.2 High-field EPR groups in Europe (2008).

K. Moebius

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

Applications

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

CEITEC

CEITEC MOTES

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

Thank you for your attention!

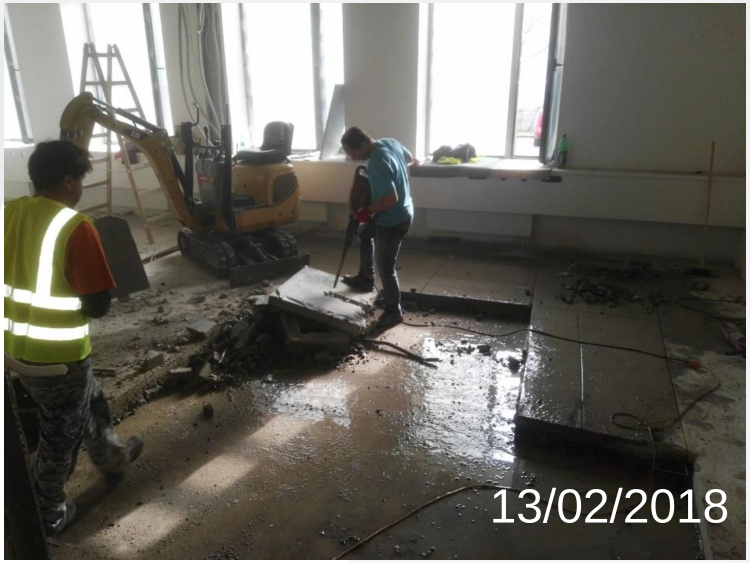
CEITEC

CEITEC MOTES

120 1899–2019 VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

Our Beginnings in Brno

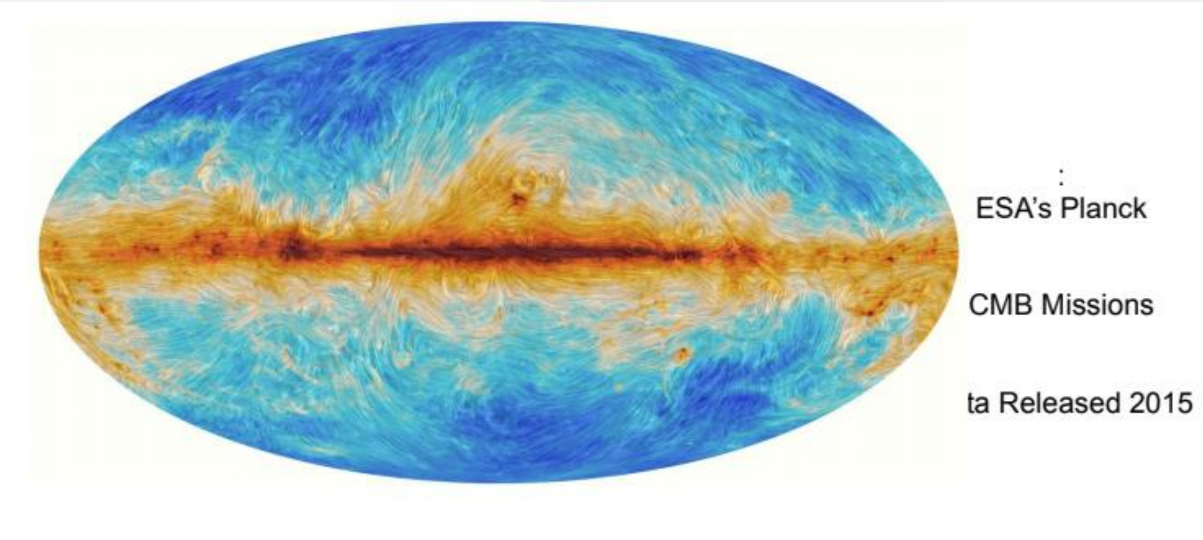
Reconstruction



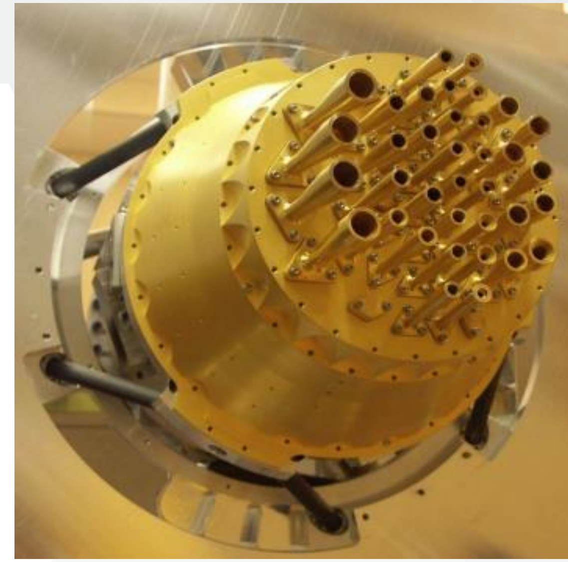
CEITEC

Reconstruction

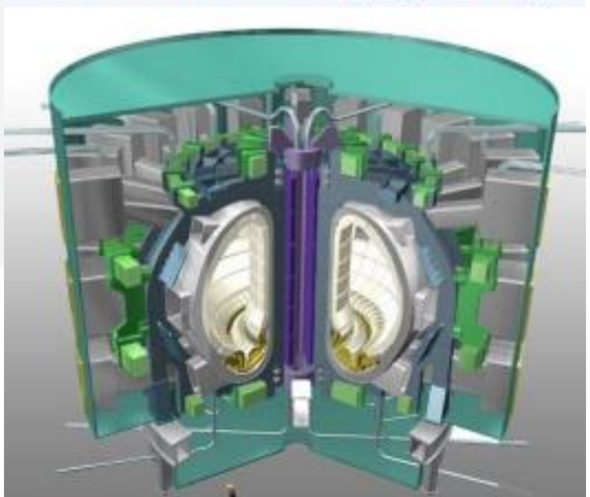
Technology we use



Magnetic field lines traced by dust emission at 353 GHz



Fusion Plasma (e.g. ITER)



ALMA Chajnantor Site (5000m)

TK INSTRUMENTS

VDI


EFEPR
8th School
of the European
Federation of EPR groups
on Advanced EPR
18–25/11/2019
CZECH REPUBLIC, Brno
Hotel Skalský dvůr, Vysočina Region
8th
BRNO
EFEPR
SCHOOL