Solid State NMR: New Trends in Materials Science

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Sorbonne Universités

2nd Edition of the International Summer School Physical and Chemical Principles in Materials Science

PHYSICAL AND CHEMICAL PRINCIPLES IN MATERIALS SCIENCE INTERNATIONAL SUMMER SCHOOL

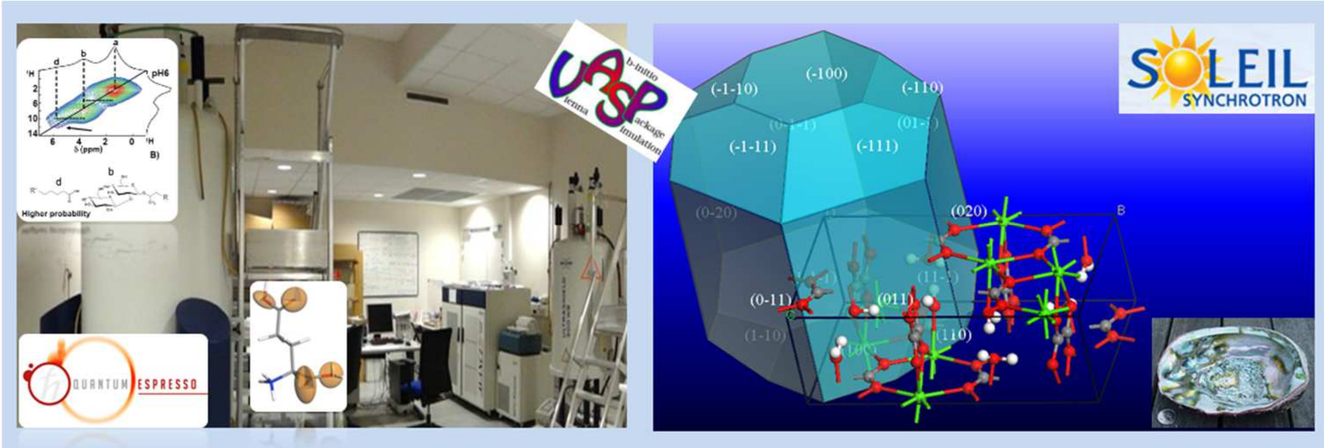
2ND PARIS • 2016

SMiLES group @ Laboratoire de Chimie de la Matière Condensée de Paris

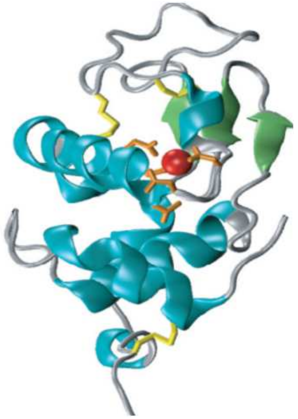
SMiLES

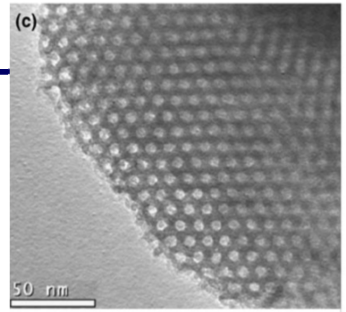
Spectroscopy, **M**odelling, **i**nterfaces for natura**L** **E**nvironment and health topic**S**.

Spectroscopic and numerical approaches for synthetic and natural materials.



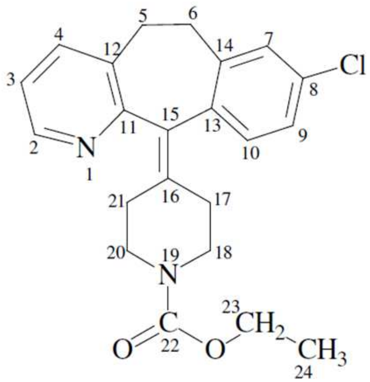
Solid state NMR in materials science

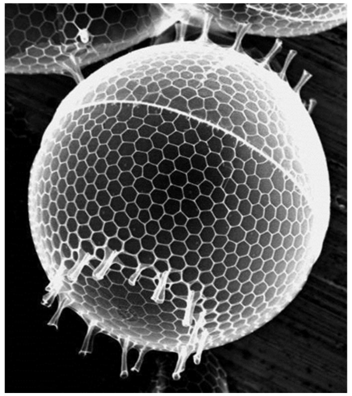




Bio-solids

Nanomaterials





Polymorphism

Hybrid materials

Biological materials

Nuclear Magnetic Resonance

The Nobel Prize in Physics 1944
Isidor Isaac Rabi

The Nobel Prize in Physics 1944

Isidor Isaac Rabi

Isidor Isaac Rabi

The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi *"for his resonance method for recording the magnetic properties of atomic nuclei"*.

→ **atomic beams**

The Nobel Prize in Physics 1952
Felix Bloch, E. M. Purcell

The Nobel Prize in Physics 1952

Felix Bloch

E. M. Purcell

Felix Bloch

Edward Mills Purcell

The Nobel Prize in Physics 1952 was awarded jointly to Felix Bloch and Edward Mills Purcell *"for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"*

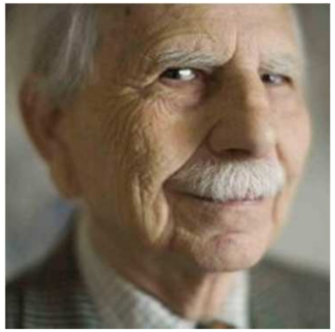
→ **condensed matter**

(high P gas, solutions, solids)

« … In this method, developed independently by two research groups headed respectively by F. Bloch and E. M. Purcell, the detection of the passage through the resonance is based on a modification *occuring at resonance* in the electromagnetic device itself that « drives » the resonant transition of interest… »

in: *Principles of Nuclear Magnetism*,

A. Abragam, 1961 (CEA, Collège de France)



A. Abragam

Purcell’s vision

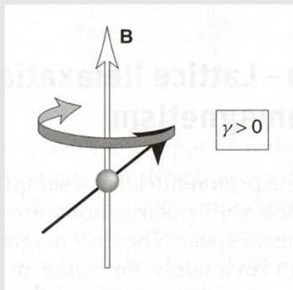
Resonance Absorption by Nuclear Magnetic Moments in a Solid

E. M. Purcell, H. C. Torrey, and R. V. Pound*
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
December 24, 1945 **(!)**

IN the well-known magnetic resonance method for the determination of nuclear magnetic moments by molecular beams,[1] transitions are induced between energy levels which correspond to different orientations of the nuclear spin in a strong, constant, applied magnetic field. We have observed the absorption of radiofrequency energy, due to such transitions, in a *solid* material (paraffin) containing protons. In this case there are two levels, the separation of which corresponds to a frequency, ν, near 30 megacycles/sec., at the magnetic field strength, H, used in our experiment, according to the relation $h\nu = 2\mu H$. Although the difference in population of the two levels is very slight at room temperature ($h\nu/kT \sim 10^{-5}$), the number of nuclei taking part is so large that a measurable effect is to be expected providing thermal equilibrium can be established. If one assumes that the only local fields of importance are caused by the moments of neighboring nuclei, one can show that the imaginary part of the magnetic permeability, at resonance, should be of the order $h\nu/kT$. The absence from this expression of the nuclear moment and the internuclear distance is explained by the fact that the influence of these factors upon absorption cross section per nucleus and density of nuclei is just cancelled by their influence on the width of the observed resonance.

A crucial question concerns the time required for the establishment of thermal equilibrium between spins and

« … There the snow lay around my doorstep – *great heaps of protons quietly precessing in the Earth’s magnetic field*. To see the world for a moment as something rich and strange is the private reward of many discovery … »



in: *Spin Dynamics*, M. H. Levitt., 2002

J. Jeener and R. Ernst : 2 dimensional (2D) Fourier Transform NMR

The unpublished Baško Polje (1971) lecture notes about two-dimensional NMR spectroscopy

J. Jeener

Faculté des Sciences (CPI-232), Campus Plaine, Université Libre de Bruxelles, B-1050 Brussels, Belgium

Abstract. — The main part of this paper is a reproduction of (previously unpublished) lecture notes, which were circulated in 1971, and which are often cited as the initiation of two-dimensional NMR spectroscopy. A brief discussion follows, about the way of handling dates and durations in time-dependent quantum mechanics, and about the use of diagrams in NMR pulse spectroscopy in the usual or the superoperator formalisms.

The Nobel Prize in Chemistry 1991
Richard R. Ernst

The Nobel Prize in Chemistry 1991

Nobel Prize Award Ceremony

Richard R. Ernst

Richard R. Ernst

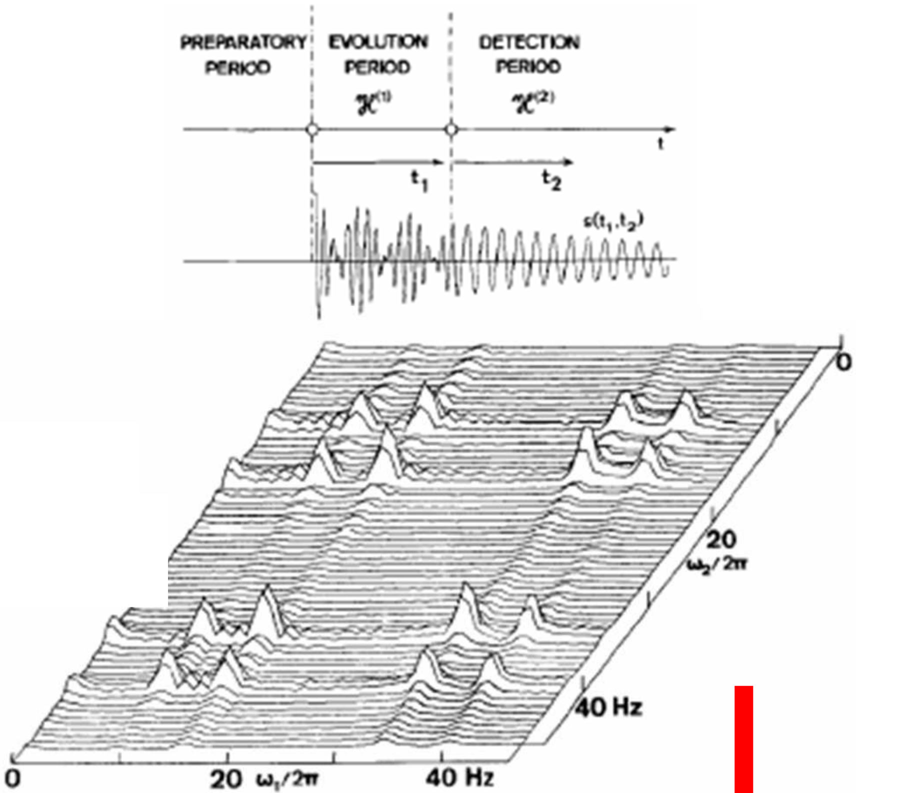
The Nobel Prize in Chemistry 1991 was awarded to Richard R. Ernst *"for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy".*

Two-dimensional spectroscopy. Application to nuclear magnetic resonance

W. P. Aue, E. Bartholdi, and R. R. Ernst

Laboratorium für physikalische Chemie, Eidgenössische Technische Hochschule, 8006 Zürich, Switzerland

(Received 13 November 1975)



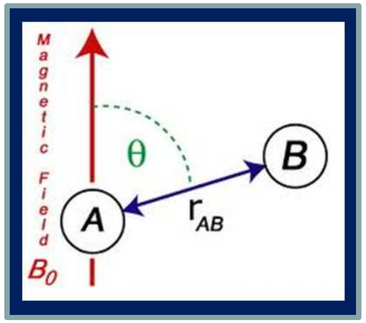
Discrete Fourier transform

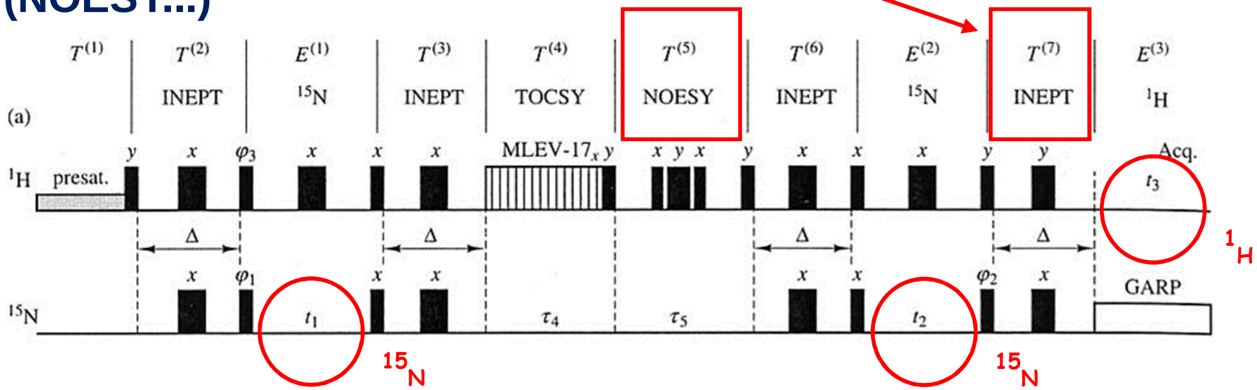
Uniform sampling

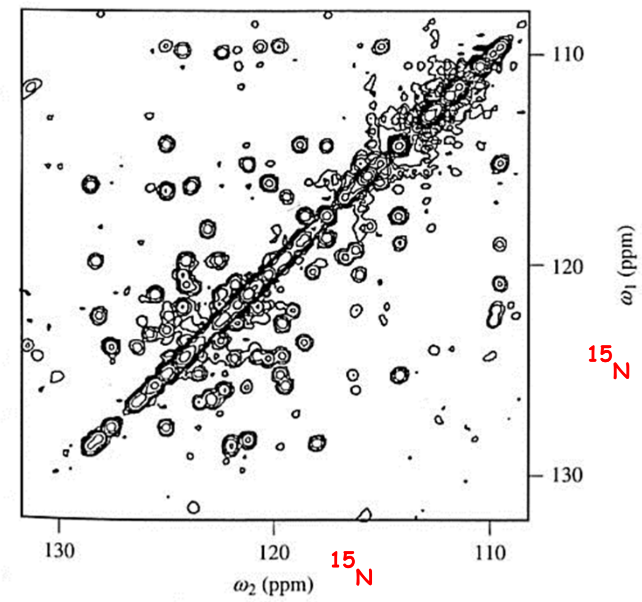
3D, 4D, … NMR

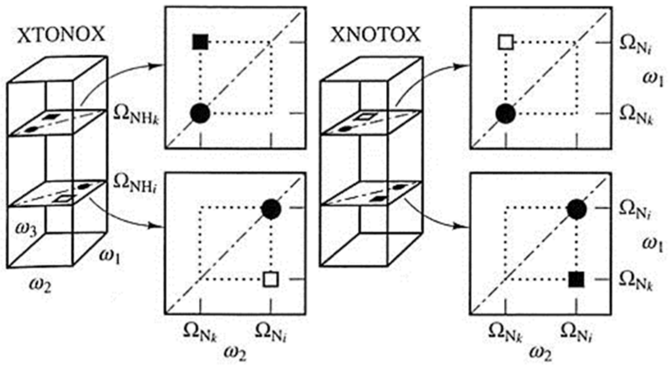
δ and J : selection, transfer, edition, correlation … (COSY, INEPT, HETCOR…)

D : relaxation … (NOESY…)







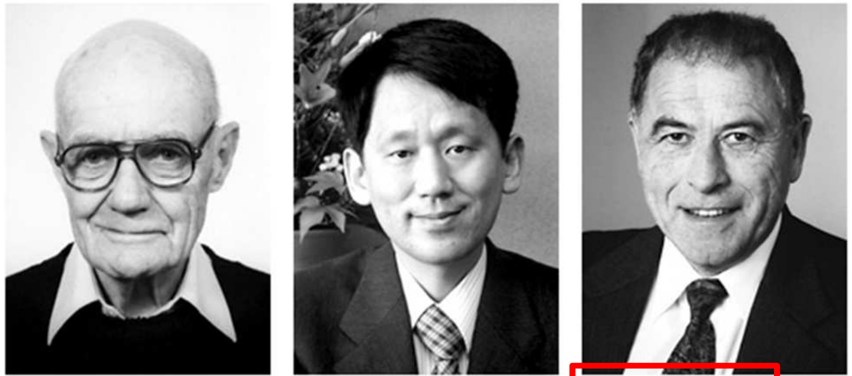


99% ^{15}N-human ubiquitin

NMR of proteins

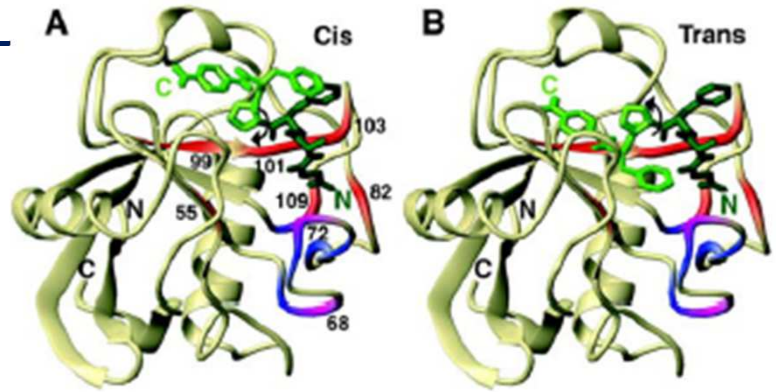
The Nobel Prize in Chemistry 2002
John B. Fenn, Koichi Tanaka, Kurt Wüthrich

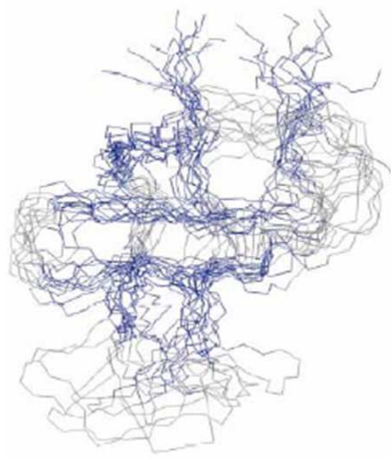
The Nobel Prize in Chemistry 2002
Nobel Prize Award Ceremony
John B. Fenn
Koichi Tanaka
Kurt Wüthrich



John B. Fenn | Koichi Tanaka | Kurt Wüthrich

The Nobel Prize in Chemistry 2002 was awarded *"for the development of methods for identification and structure analyses of biological macromolecules"* with one half jointly to John B. Fenn and Koichi Tanaka *"for their development of soft desorption ionisation methods for mass spectrometric analyses of biological macromolecules"* and the other half to Kurt Wüthrich *"for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution"*.



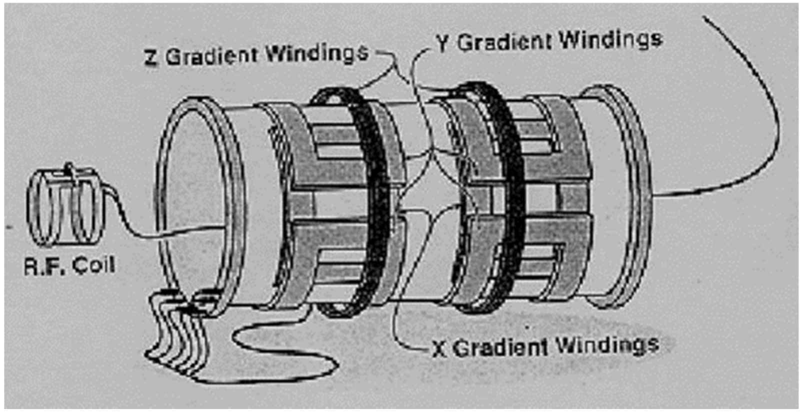


F. Castellani, B. van Rossum, A. Diehl, M. Schubert, K. Rehbein, H. Oschkinat, *Nature*, **420**, 98 (2002)

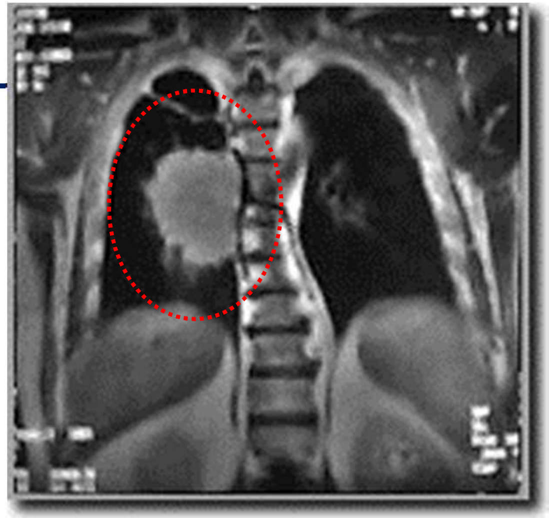
extension to solid state NMR of proteins

Magnetic Resonance Imaging (MRI)

adding field gradients



http://irfu.cea.fr/en/Phocea/



MRI

The Nobel Prize in Physiology or Medicine 2003
Paul C. Lauterbur, Sir Peter Mansfield

The Nobel Prize in Physiology or Medicine 2003

Nobel Prize Award Ceremony

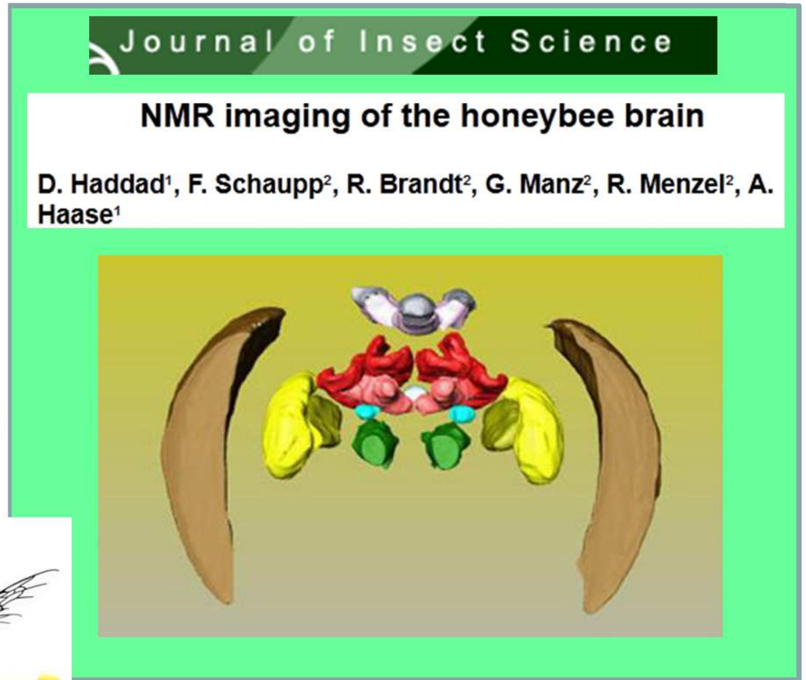
Paul C. Lauterbur

Sir Peter Mansfield

Paul C. Lauterbur

Sir Peter Mansfield

The Nobel Prize in Physiology or Medicine 2003 was awarded jointly to Paul C. Lauterbur and Sir Peter Mansfield *"for their discoveries concerning magnetic resonance imaging"*

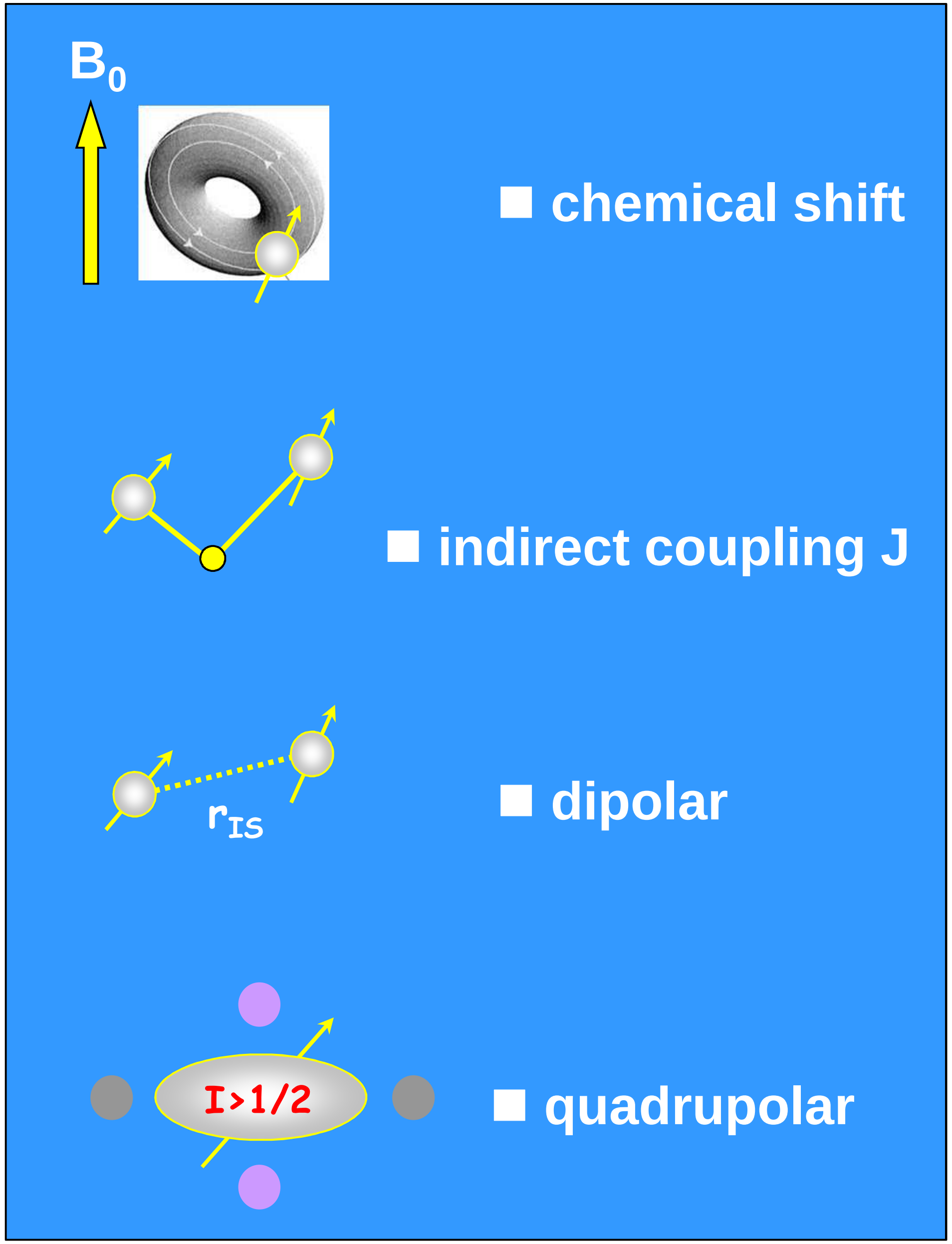


Journal of Insect Science

NMR imaging of the honeybee brain

D. Haddad[1], F. Schaupp[2], R. Brandt[2], G. Manz[2], R. Menzel[2], A. Haase[1]

NMR interactions: structural spies

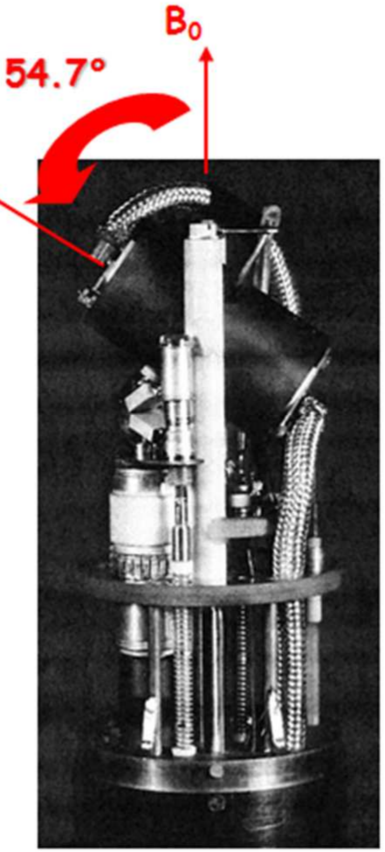


Key questions:

* Solution *vs* Solid State NMR?

* Intrinsic resolution when studying powdered samples?

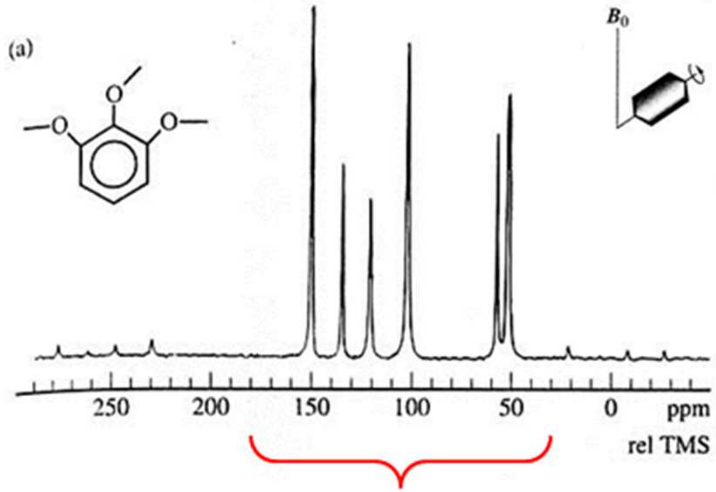
Magic Angle Spinning (MAS) – "reorientation" of sample → DYNAMICS !



Spinning Spins
A Tribute to Raymond Andrew

Doty, Encyclopedia of NMR, 1996, 4477.

^{13}C: 1,2,3-trimethoxybenzene



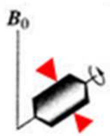
isotropic region: $\delta_{iso} = 1/3\ (\delta_{11} + \delta_{22} + \delta_{33})$

Orendt, Encyclopedia of NMR, 1996, 1287.

ϕ: 7mm ⟶ up to 6 kHz

ϕ: 4mm ⟶ up to 15 kHz

ϕ: 2.5mm ⟶ up to 35 kHz



ϕ

«infinite» MAS frequency:

$\nu_{rot} > \Delta_A$ (A= CSA, D, Q...)

question: is it really possible ?...

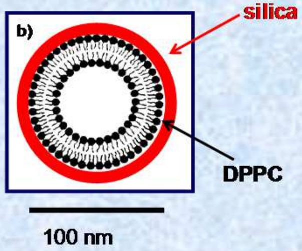
ϕ: 1 mm ⟶ up to 100 kHz

Outline

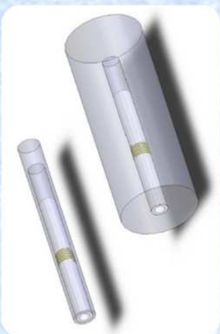
- Hybrid materials: *bio-inspired* materials as a first example

- *Ab initio* calculations of NMR parameters

- Liposils as nano-cargos for drug delivery

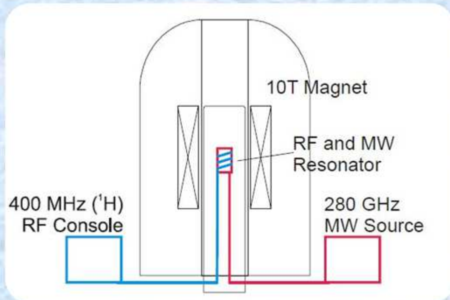


- **Sensitivity** issues:



* applications of DNP MAS to synthetic and natural biological materials

* applications of Magic Angle Coil Spinning (MACS)



Hybrid materials and solid state NMR: a review

Progress in Nuclear Magnetic Resonance Spectroscopy

Volume 77, February 2014, Pages 1–48

Recent NMR developments applied to organic–inorganic materials

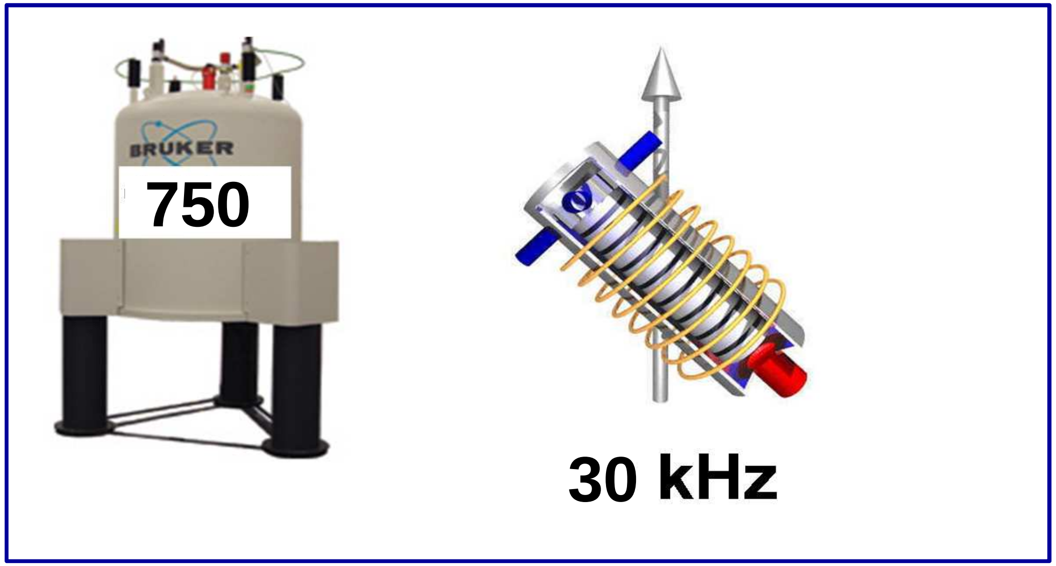
Christian Bonhomme[a], Christel Gervais[a], Danielle Laurencin[b]

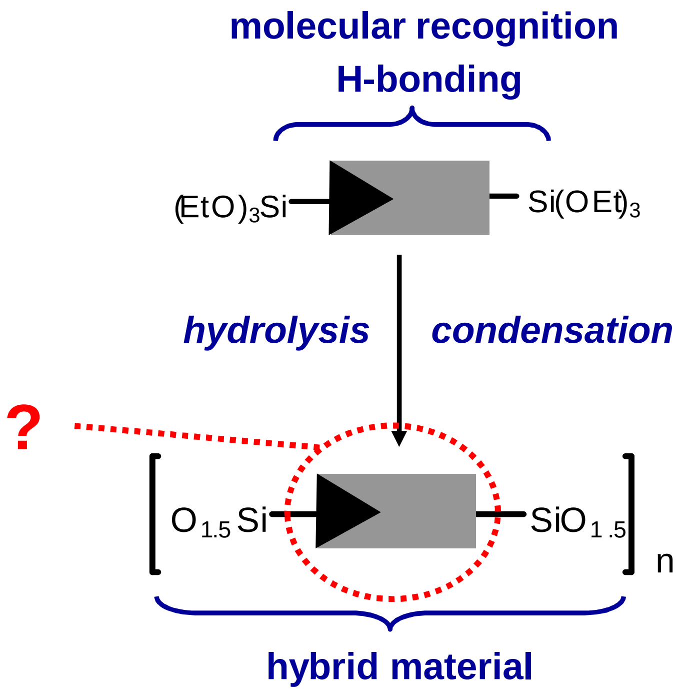
Contents

NMR methods
sensitivity issues

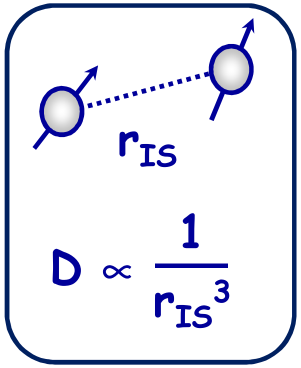
applications to
hybrids and related materials

Hybrid interfaces: a first example



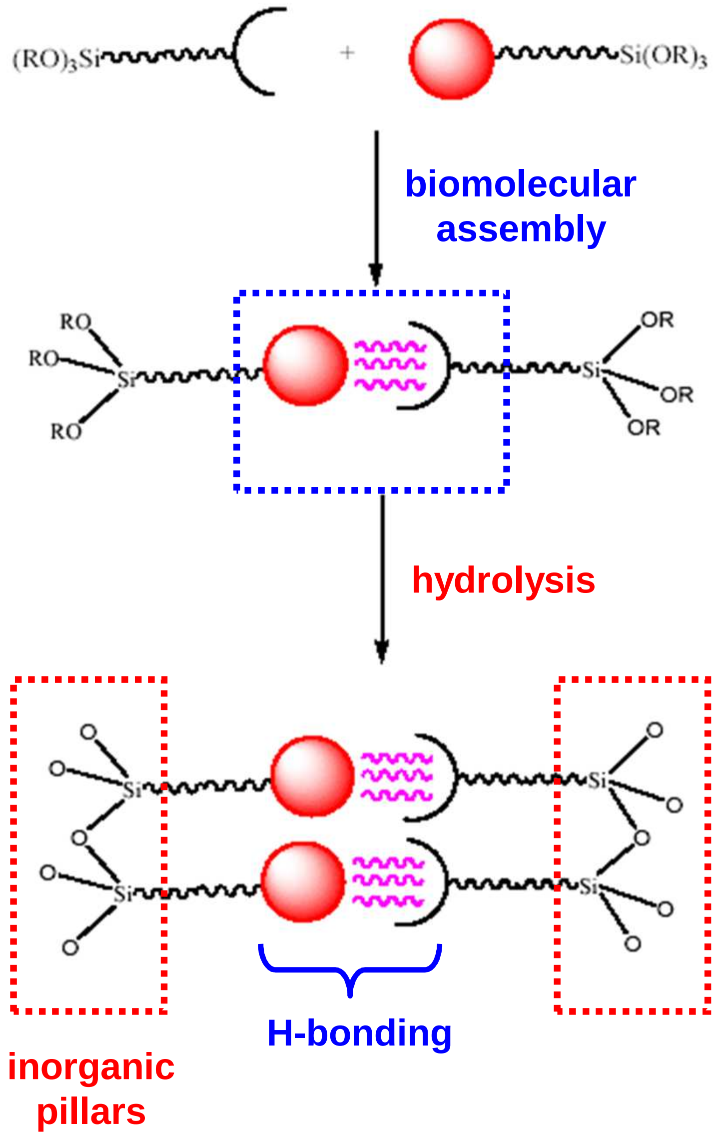


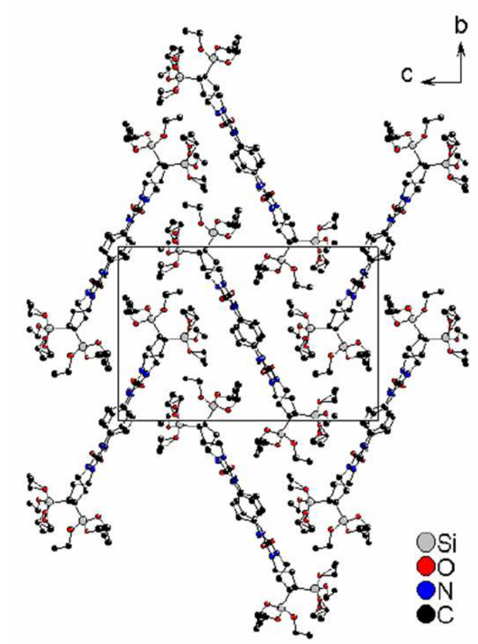
Coll.: B. Alonso & colleagues from CEMHTI, Orléans, France



- ^1H-^1H dipolar interaction
- ureidopyrimidinone models
- bio-inspired materials

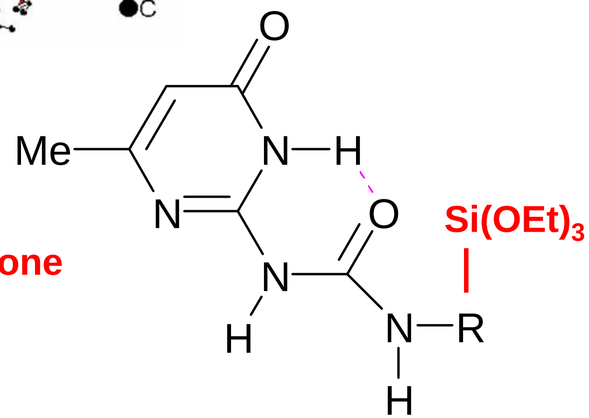
Ureidopyrimidinone based systems





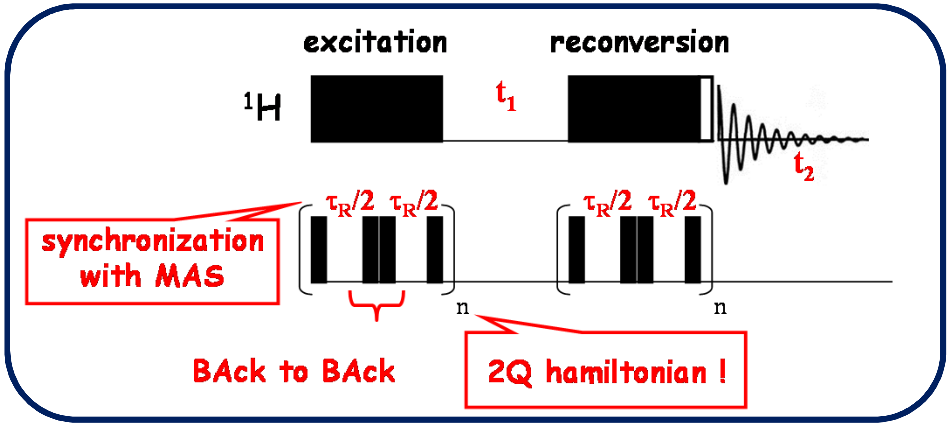
MONOCLINIC
***P* 21/n**
a = 9.0372 Å
b = 15.5020 Å
c = 23.3873 Å
β = 92.837 °

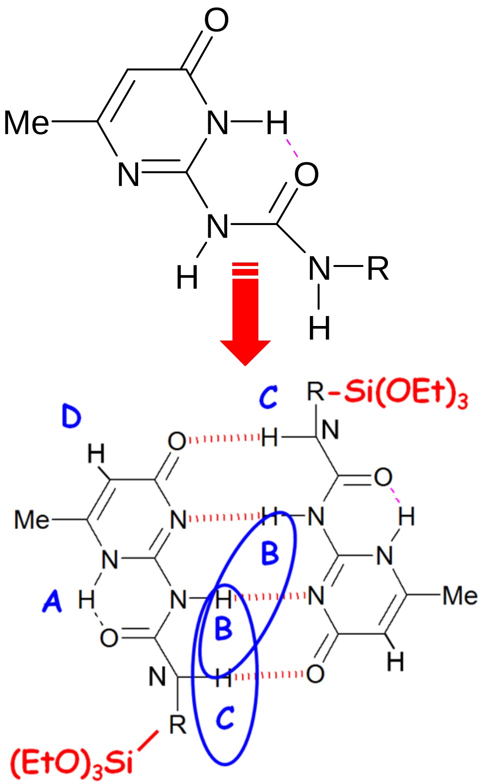
XRD of precursors

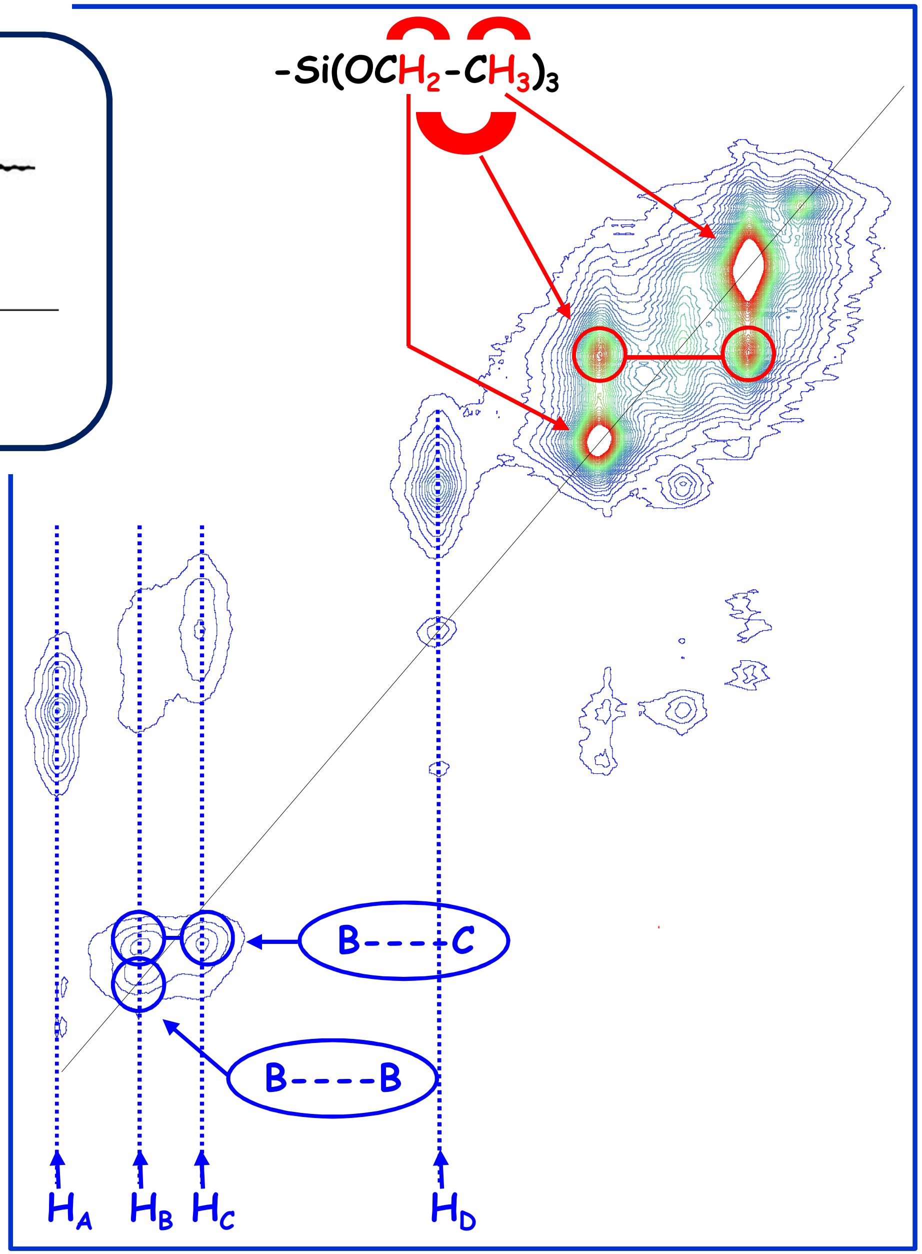


ureidopyrimidinone derivatives

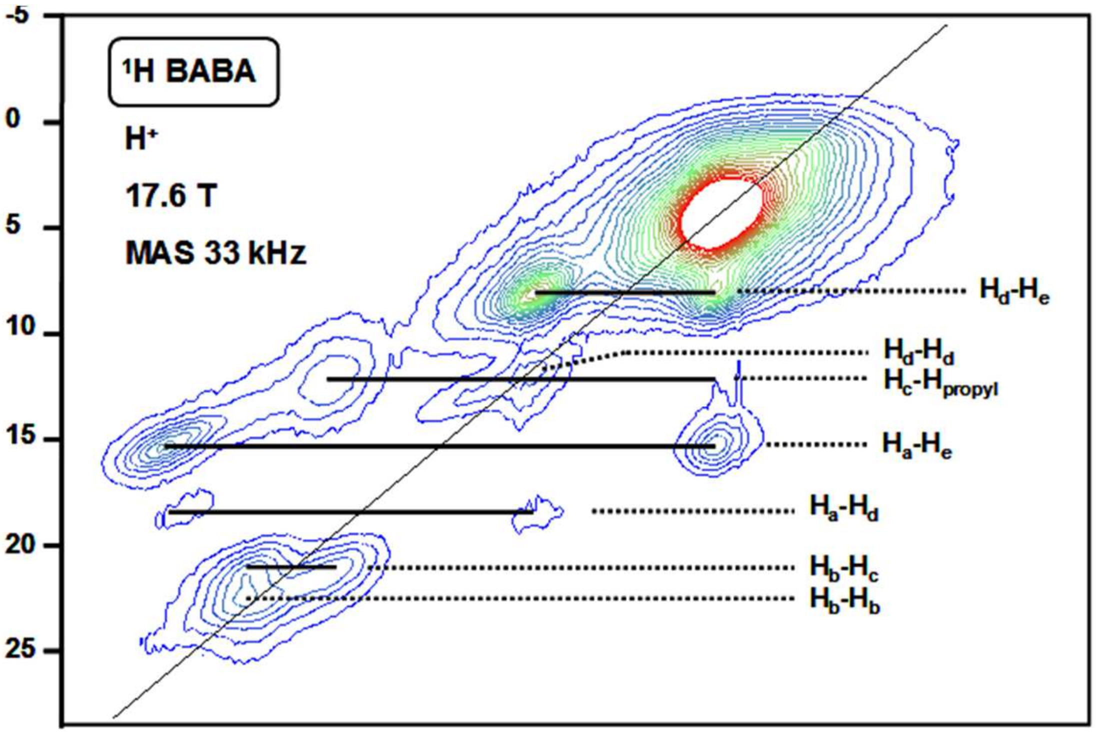
Fast MAS ^1H-^1H BABA: ureidopyrimidinone based systems



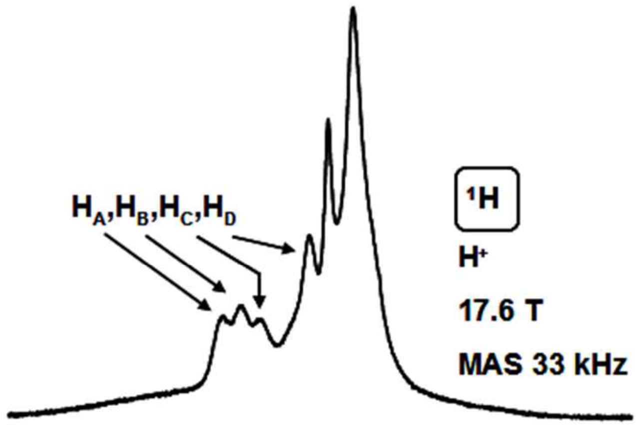


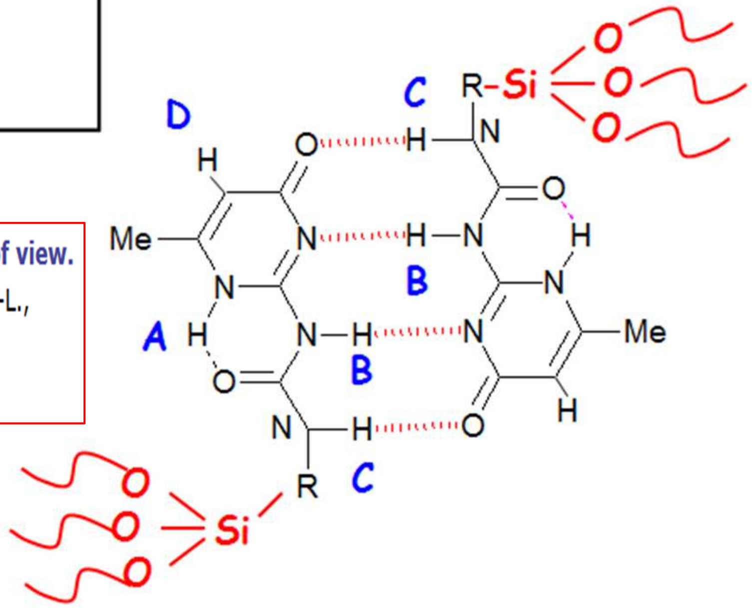


Application to hybrid silica



hydrolysis-condensation



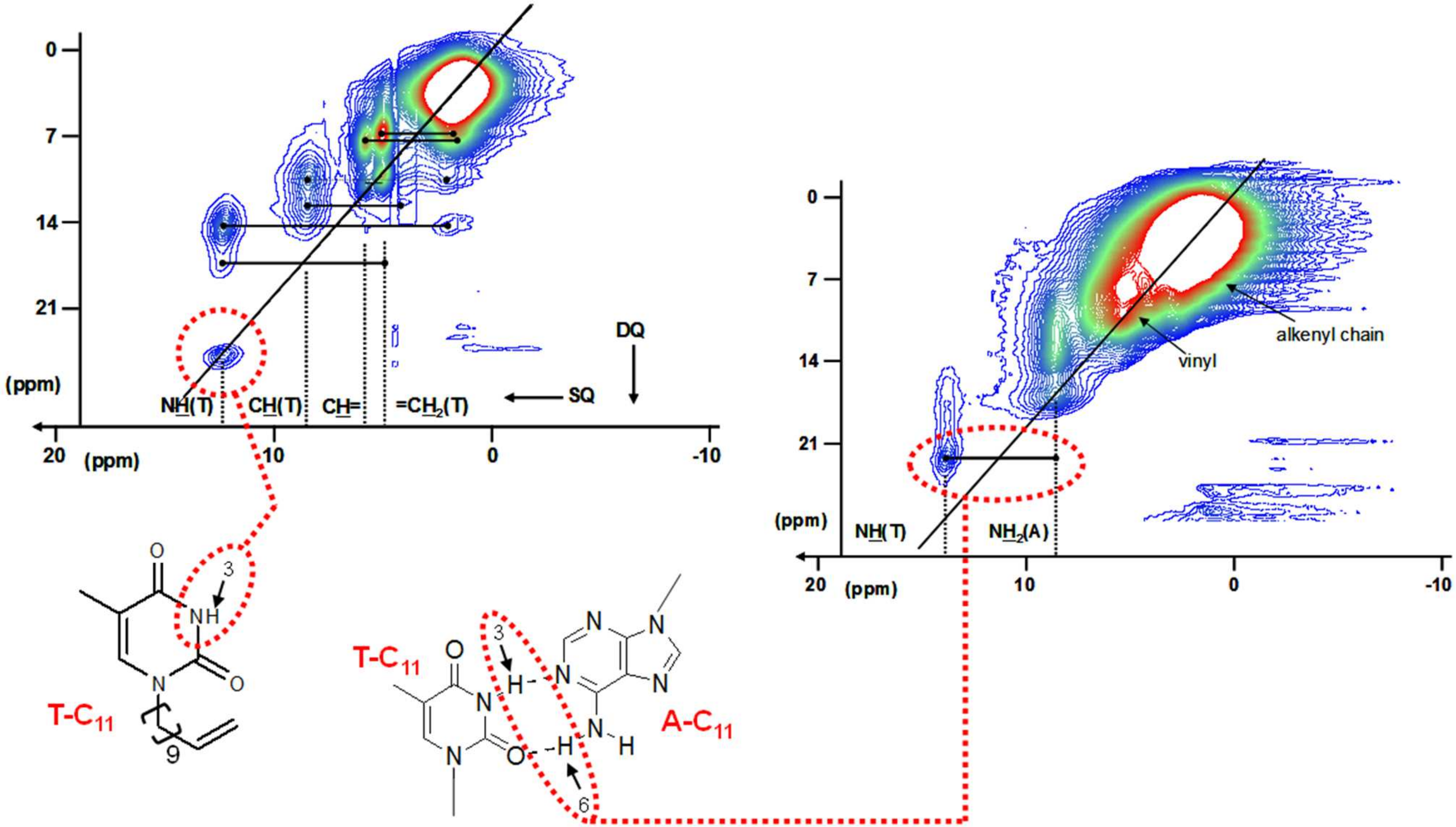


Organosilicas based on purine–pyrimidine base pair assemblies: a solid state NMR point of view.

Arrachart G., Carcel C., Moreau J. J. E., Hartmeyer G., Alonso B., Massiot D., Creff G., Bantignies J.-L., Dieudonne P., Wong Chi Man M., Althoff G., Babonneau F., Bonhomme C.

J. Mater. Chem., Vol. 18, 2008, pp. 392-399.

Towards bio-inspired materials: Adenine (A) and Thymine (T) derivatives



Nanostructuring of hybrid silicas through self-recognition process.

Arrachart G., Creff G., Wadepohl H., Blanc C., Bonhomme C., Babonneau F., Alonso B., Bantignies J.-L., Carcel C., Moreau J., Dieudonné P., Sauvajol J.-L., Massiot D., Wong Chi Man M.

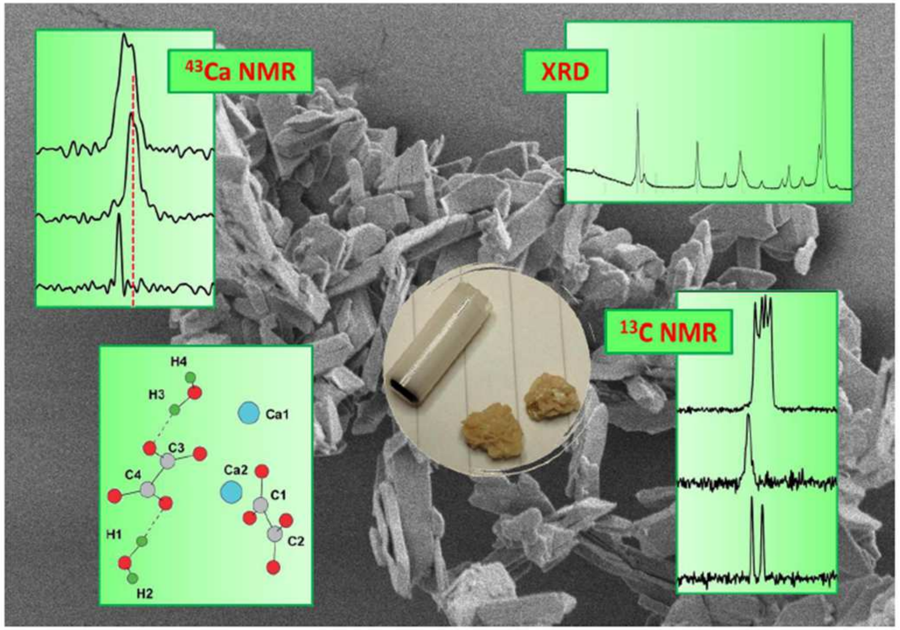
Chemistry-a European Journal, Vol. 15, 2009, pp. 5002-5005.

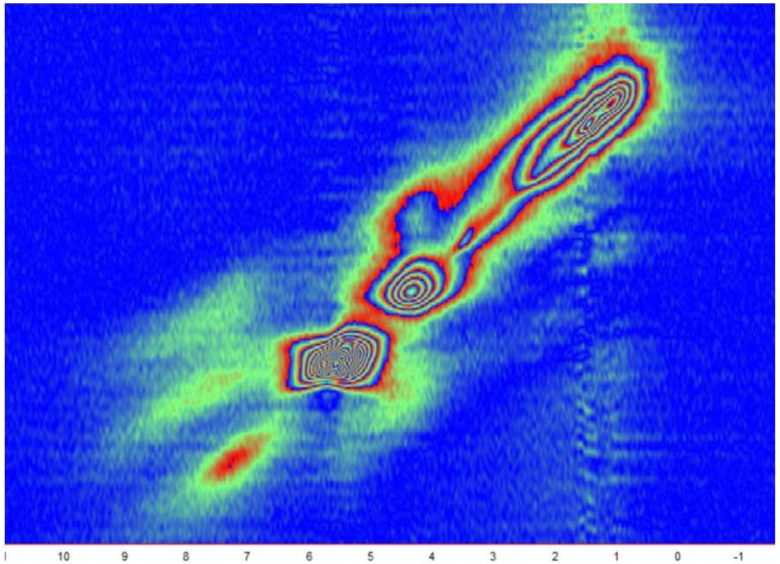
Extension to ultra-fast MAS (1mm JEOL probe – 850 MHz Warwick)

- very high field (850 MHz)
- ^{1}H-^{1}H DQ MAS at 80 kHz
- more adapted pulse sequences

from the french side …

IR RMN THC
TRÈS GRANDES INFRASTRUCTURES DE RECHERCHE
Résonance Magnétique Nucléaire, Très Hauts Champs
FR3050 CNRS





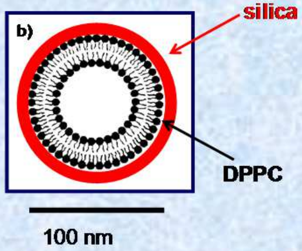
Coll.: D. Iuga, J. V. Hanna & M. E. Smith, Warwick & Lancaster, UK

Outline

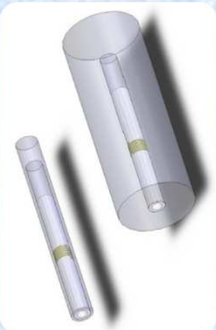
- **Hybrid materials: *bio-inspired* materials as a first example**

- ***Ab initio* calculations of NMR parameters**

- **Liposils as nano-cargos for drug delivery**

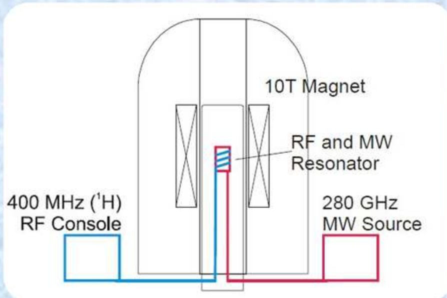


- **Sensitivity issues:**



*** applications of DNP MAS to synthetic and natural biological materials**

*** applications of Magic Angle Coil Spinning (MACS)**



First principles calculations: the GIPAW approach

Pickard, Mauri, *Phys. Rev. B* (2001)

GIPAW

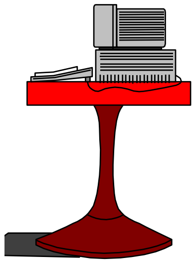
DFT
periodic systems
all-electron hamiltonians
evaluation of j(1)(r') using pseudopotentials

$$B_{in}^{(1)}(r) = 1/c \int d^3r' \; j^{(1)}(r') \times \frac{r-r'}{|r-r'|^3}$$

CSA

! J !

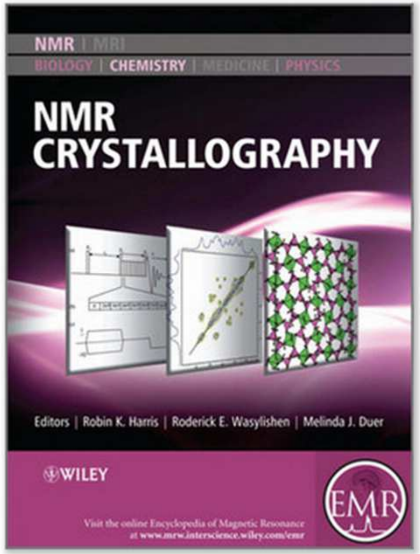
EFG

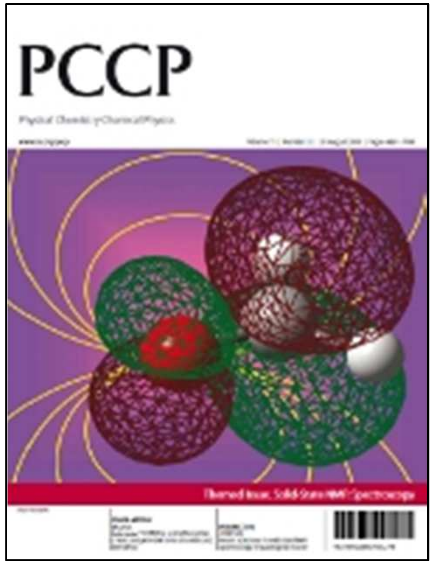


IDRIS

- assignment
- dynamics
- amorphous samples

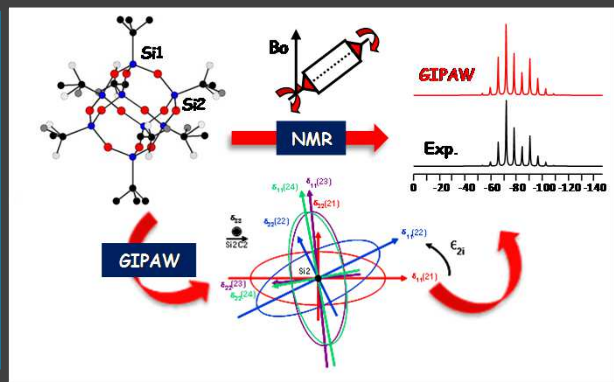
Coll.: C. Gervais, LCMCP, Paris.





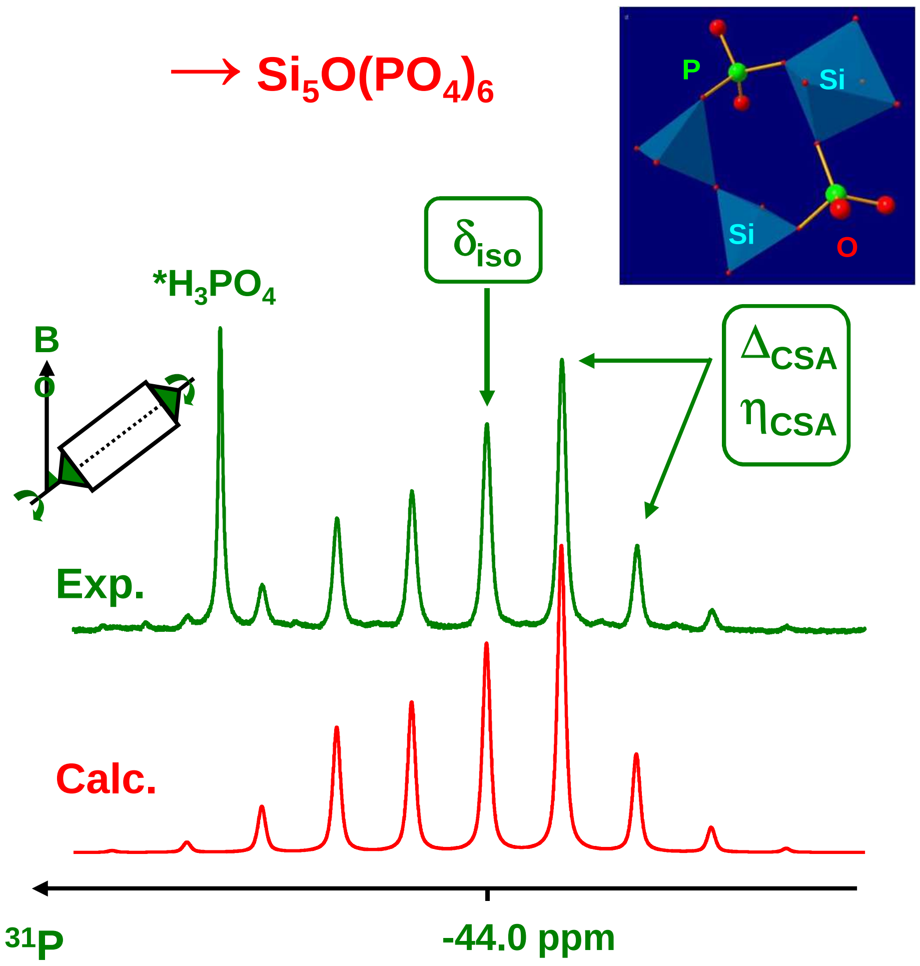
1- T. Charpentier, *Solid State NMR*, 40, 1, 2011.

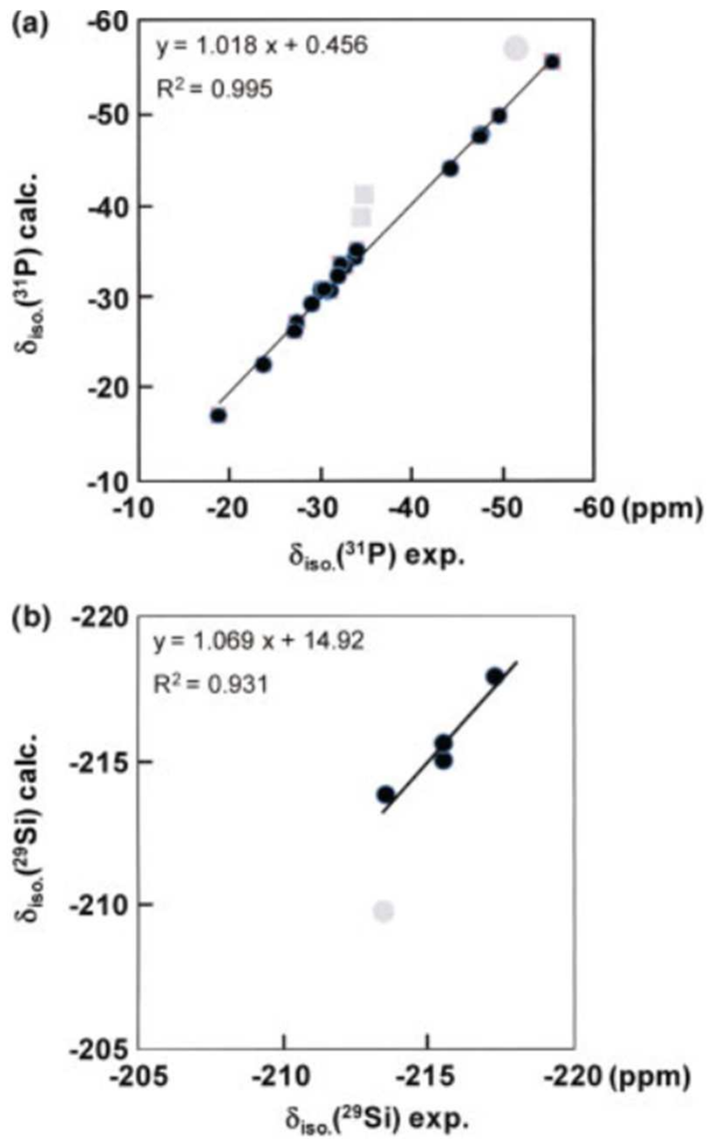
2- C. Bonhomme, C. Gervais, F. Babonneau *et al.*, *Chemical Reviews*, 112, 5733, 2012.



Validation of GIPAW: the example of ^{31}P

→ $Si_5O(PO_4)_6$





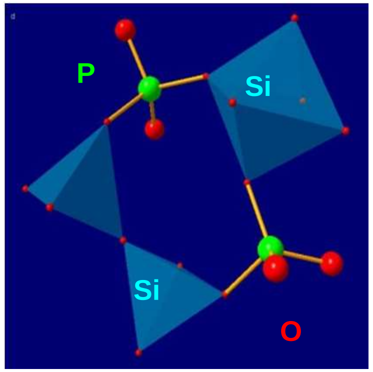
New perspectives in the PAW/GIPAW approach: $J_{P\text{-}O\text{-}Si}$ coupling constants, antisymmetric parts of shift tensors and NQR predictions (pages S86–S102)

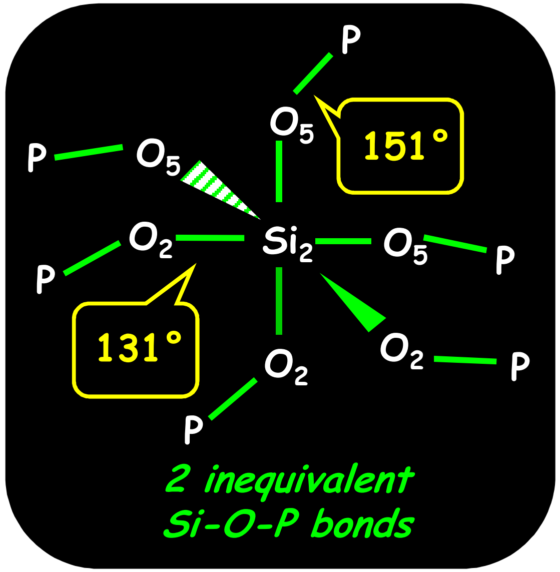
Christian Bonhomme, Christel Gervais, Cristina Coelho, Frédérique Pourpoint, Thierry Azaïs, Laure Bonhomme-Coury, Florence Babonneau, Guy Jacob, Maude Ferrari, Daniel Canet, Jonathan R. Yates, Chris J. Pickard, Siân A. Joyce, Francesco Mauri and Dominique Massiot

Article first published online: 29 JUN 2010 | DOI: 10.1002/mrc.2635

First principles calculations of *J* coupling constants: $Si_5O(PO_4)_6$

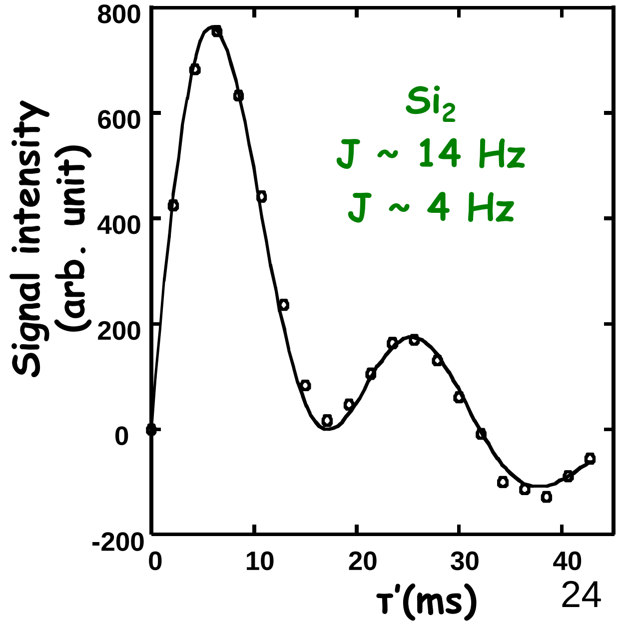
→ $Si_5O(PO_4)_6$





INEPT MAS data: J ~ [4 Hz – 15 Hz]

		$^2J_{P\text{-}O\text{-}Si}$ (Hz)	
Phase	Sites	exp	calc
$Si_5O(PO_4)_6$	Si(1)-O(3)-P	15 ± 2	-17,08
	Si(2)-O(2)-P	14 & 4 ± 2	-16,22
	Si(2)-O(5)-P		-1,17
	Si(3)-O(4)-P	12 ± 2	-14,18



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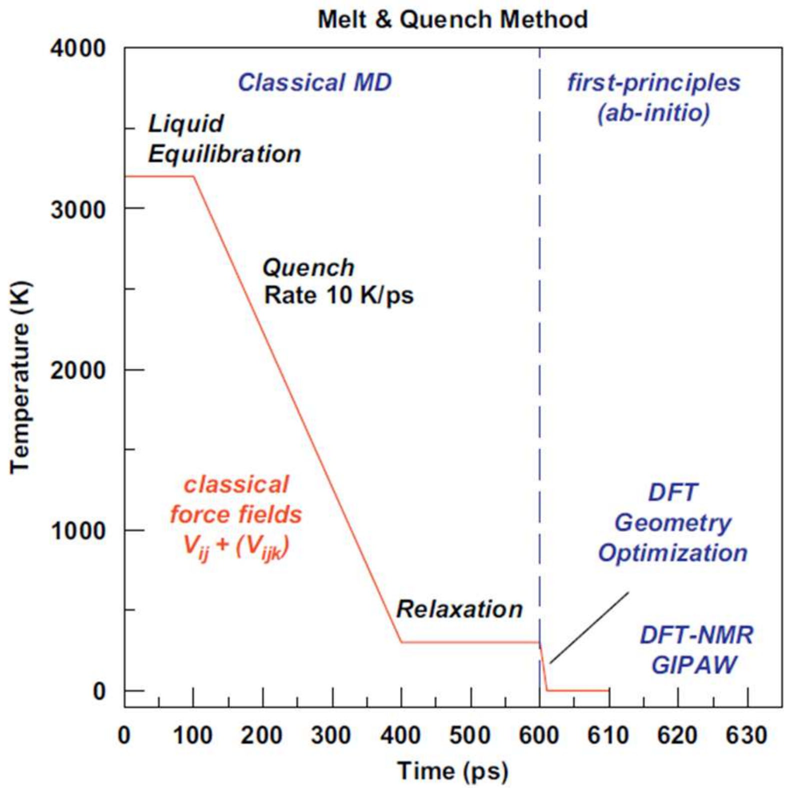
More references: applications of GIPAW to glasses

■ **a pioneering work by T. Charpentier (CEA, Saclay, France): MD, DFT, GIPAW**

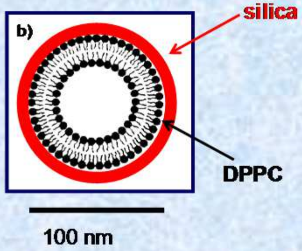


T. Charpentier, *Solid State NMR*, 40, 1, 2011.

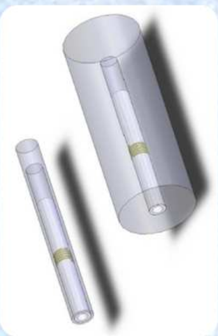
■ **MD–GIPAW methodology for NMR glass studies**

Outline

- Hybrid materials: *bio-inspired* materials as a first example
- *Ab initio* calculations of NMR parameters
- **Liposils as nano-cargos for drug delivery**

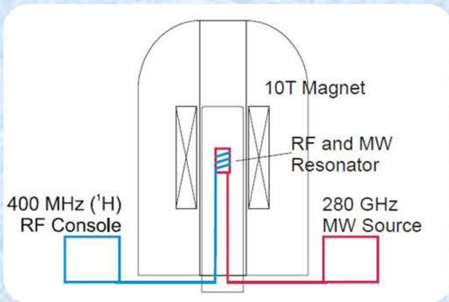


- Sensitivity issues:



* applications of DNP MAS to synthetic and natural biological materials

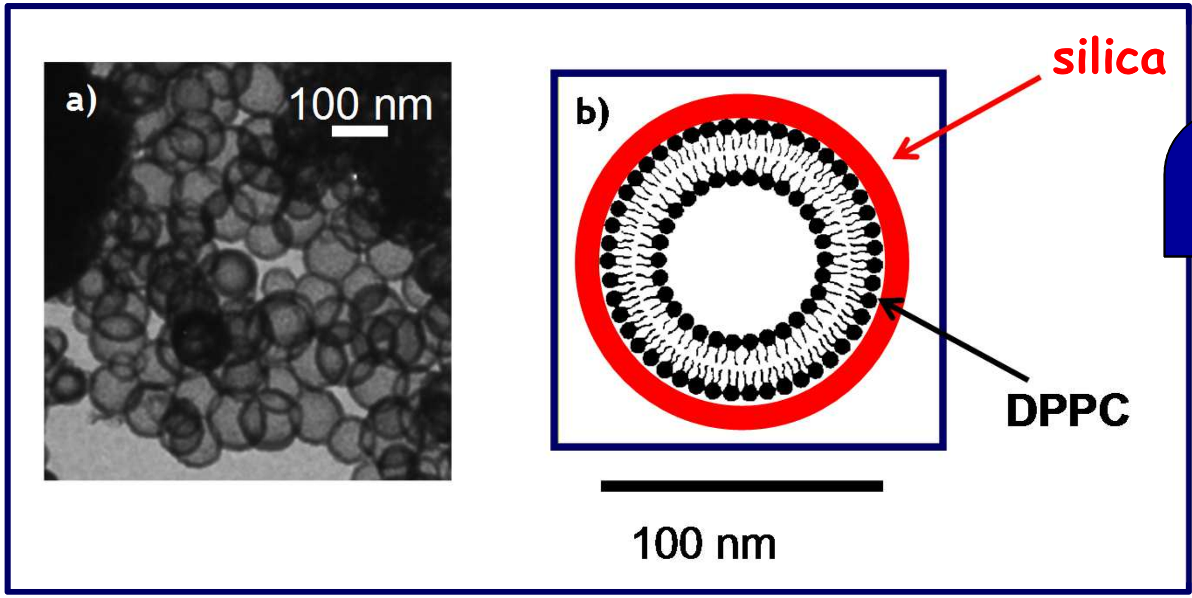
* applications of Magic Angle Coil Spinning (MACS)



A combined approach: silica based nano-cargos

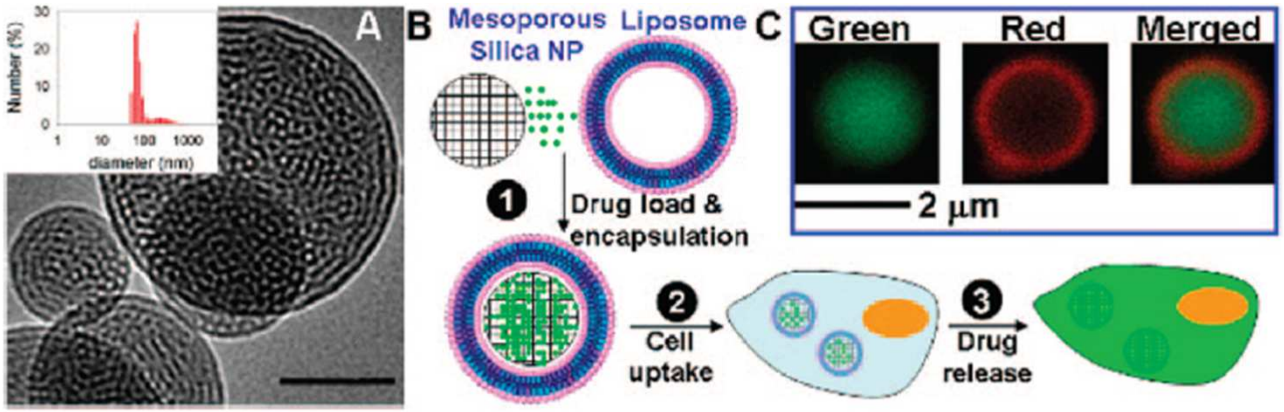
Coll.: T. Azaïs, LCMCP, Paris.

L-α-dipalmitoylphosphatidycholine



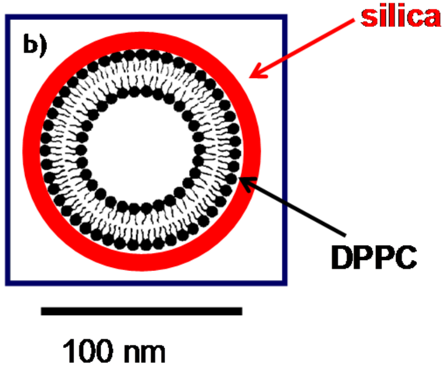
- **Liposomes (DPPC) and silica**
- **Drug delivery systems**

see also: J. Brinker *et al. (proto-cell concept, JACS, 2009)*

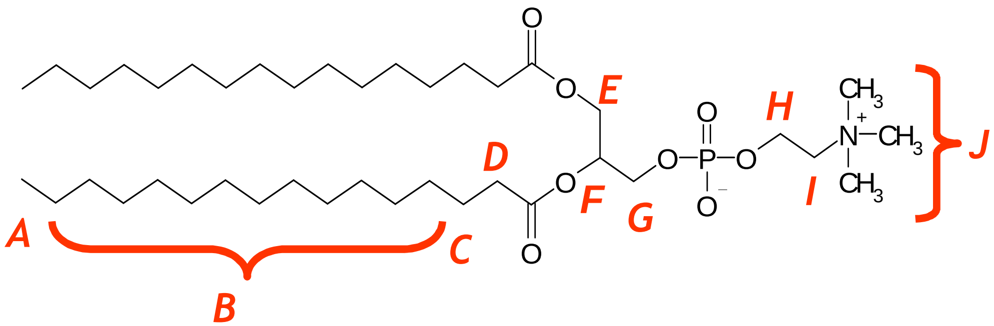


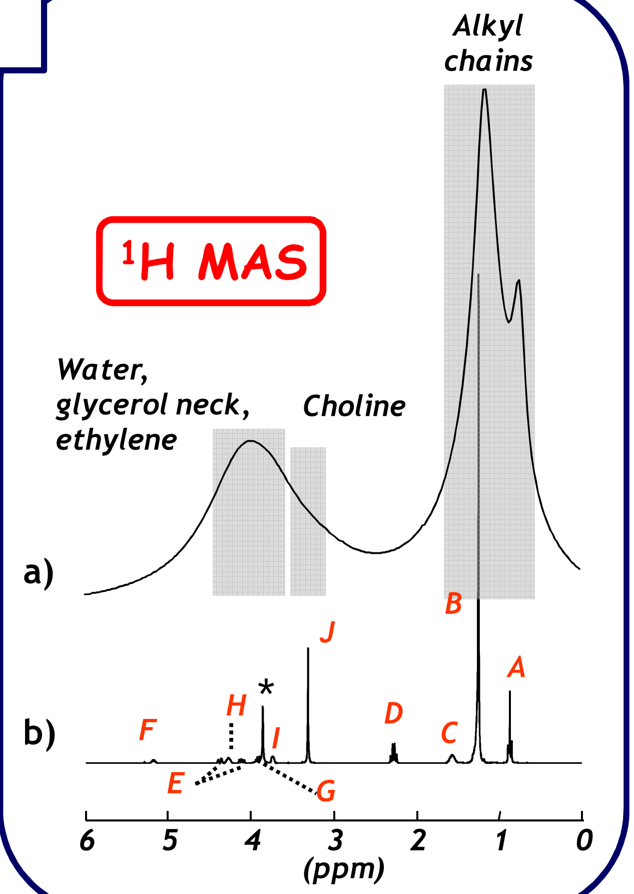
Liposils (*Lipo*somes and *sil*ica)

- a realistic model for hydroxylated amorphous silica
- a realistic model for silica/DPPC interactions
- full NMR *ab initio* calculations
- selection of adequate configurations !



GIPAW





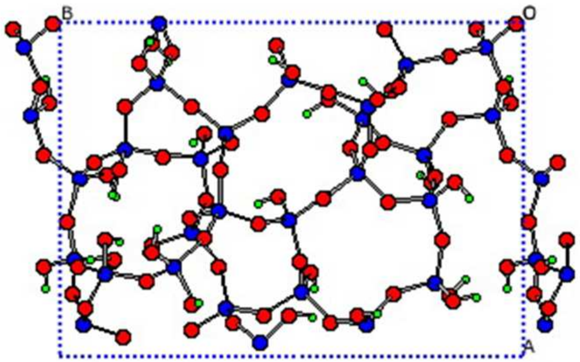
Investigation of the interface in silica-encapsulated liposomes by combining solid state NMR and first principles calculations.
Folliet, N., C. Roiland, S. Bégu, A. Aubert, T. Mineva, A. Goursot, K. Selvaraj, L. Duma, F. Tielens, F. Mauri, G. Laurent, C. Bonhomme, C. Gervais, F. Babonneau and T. Azais
Journal of the american chemical society, Vol., 133, 2011, pp. 16815-16827.

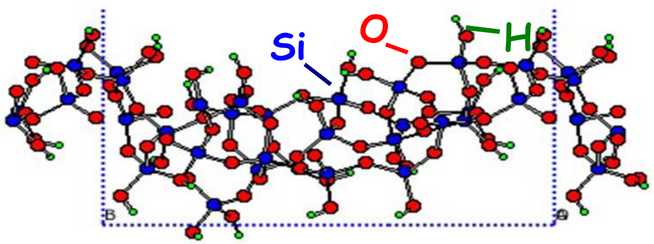
A model for hydroxylated amorphous silica

SiO_2

amorphous "slab"

(~ 13Å × 18Å × 10Å)

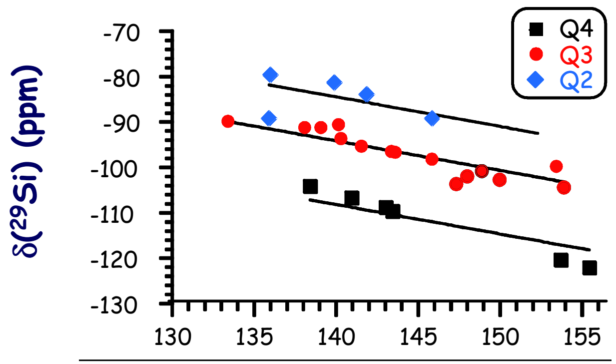




~ 6 OH/nm²

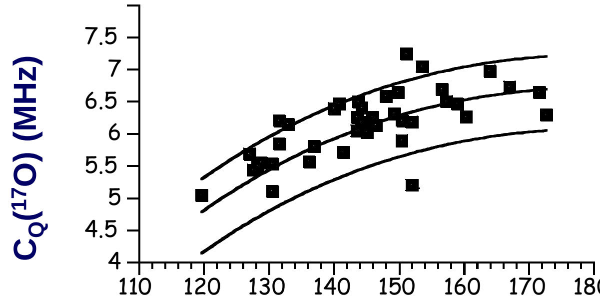
F. Tielens, C. Gervais, J.-F. Lambert *et al*., *Chem. Mater*. 20 (2008) 3336.

GIPAW



^{29}Si NMR

Si-O-Si angle (°)

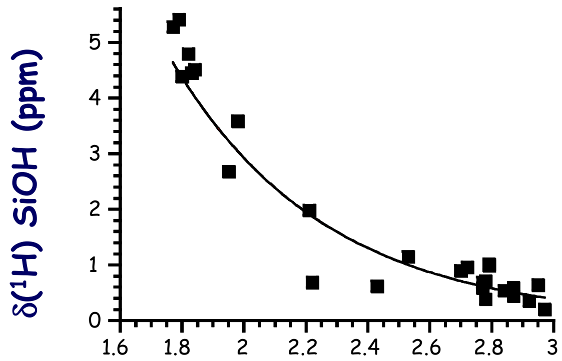


^{17}O NMR

Si-O-Si angle (°)

Clark *et al*., *Solid State NMR* 16 (2000) 55.

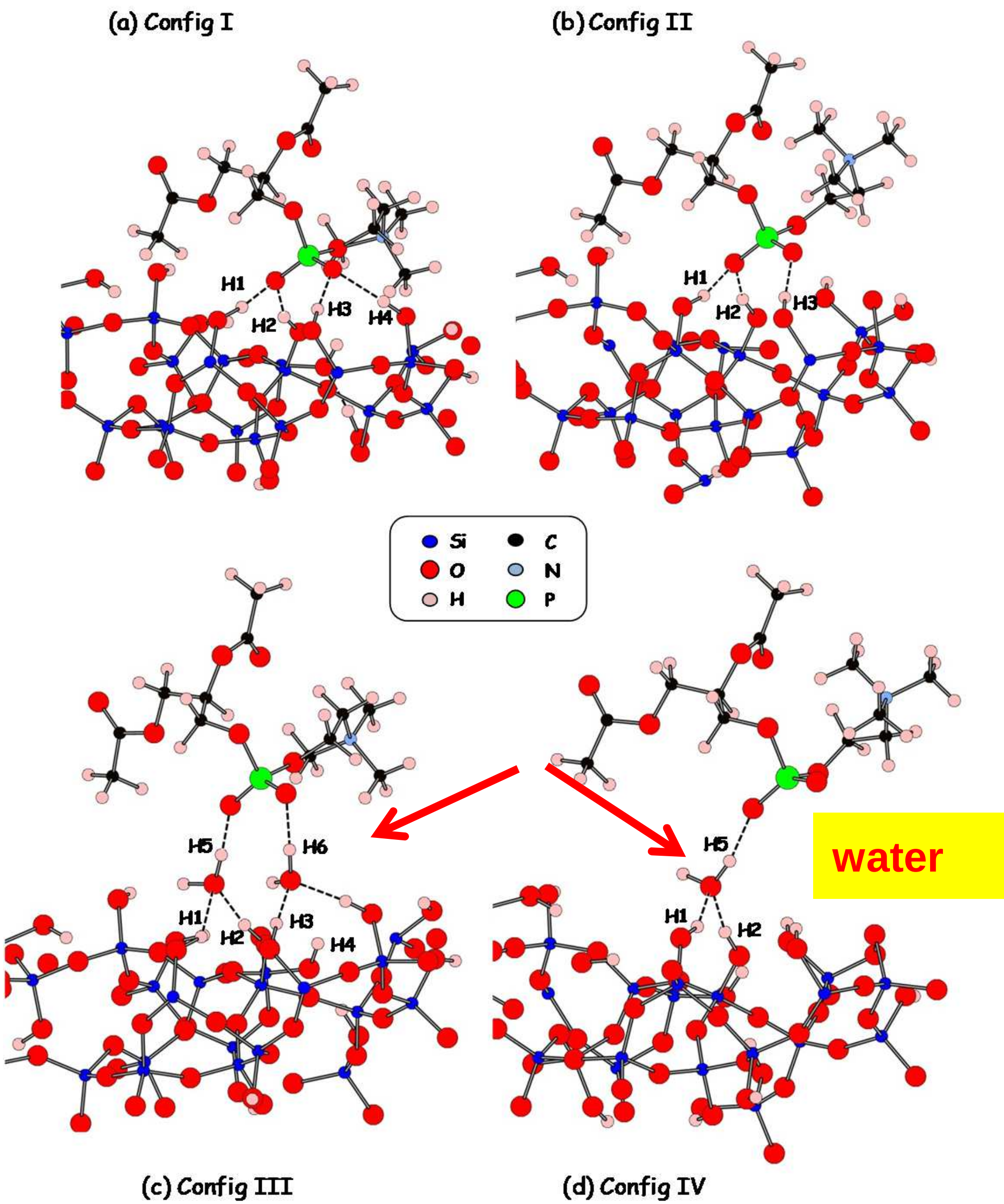
$C_Q = a\,(0.5 + \cos\alpha/(\cos\alpha - 1))^b + m(d - d^0)$



^{1}H NMR

OH ... O (Å)

The DPPC/silica interface: the role of water



decreasing number of H- bonds

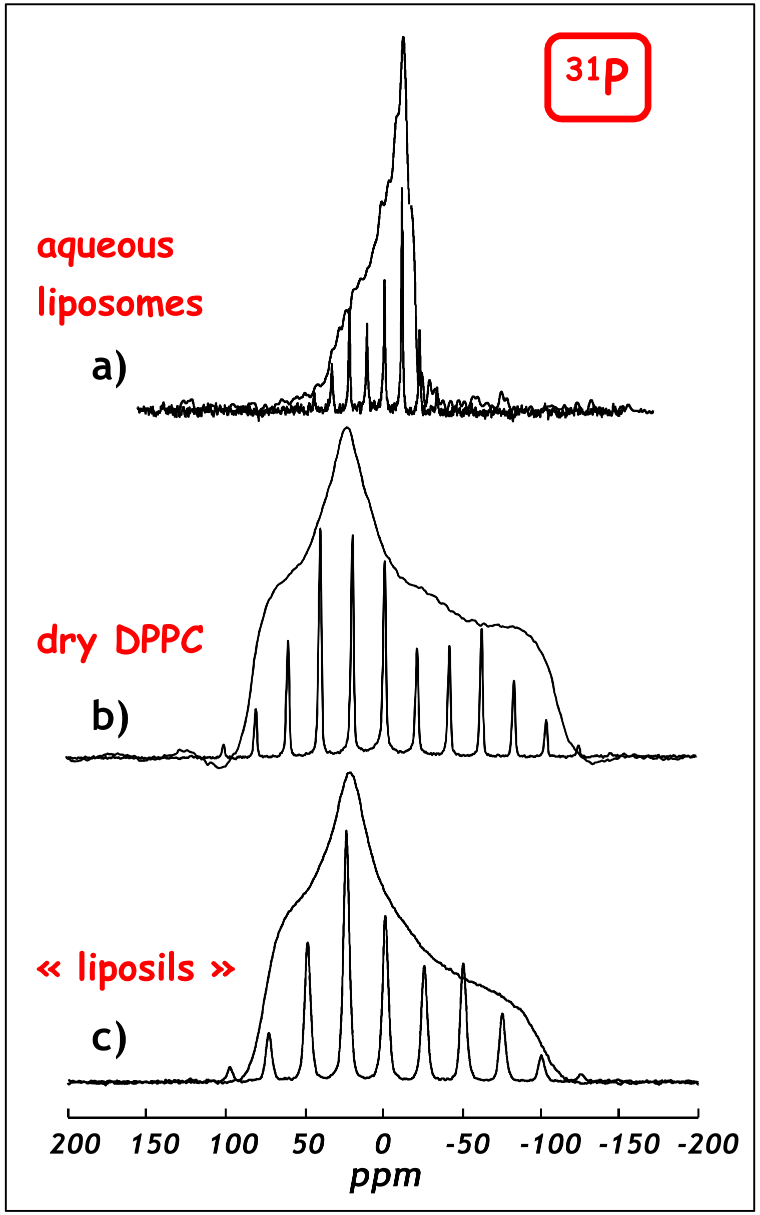
GIPAW $\delta_{iso.}(^{31}P)$

config. 1: $\delta \sim 7.0$ ppm

config. 4: $\delta \sim -0.3$ ppm

exp.: $\delta = -0.7$ ppm

Local dynamics: ^{31}P slow MAS and static NMR

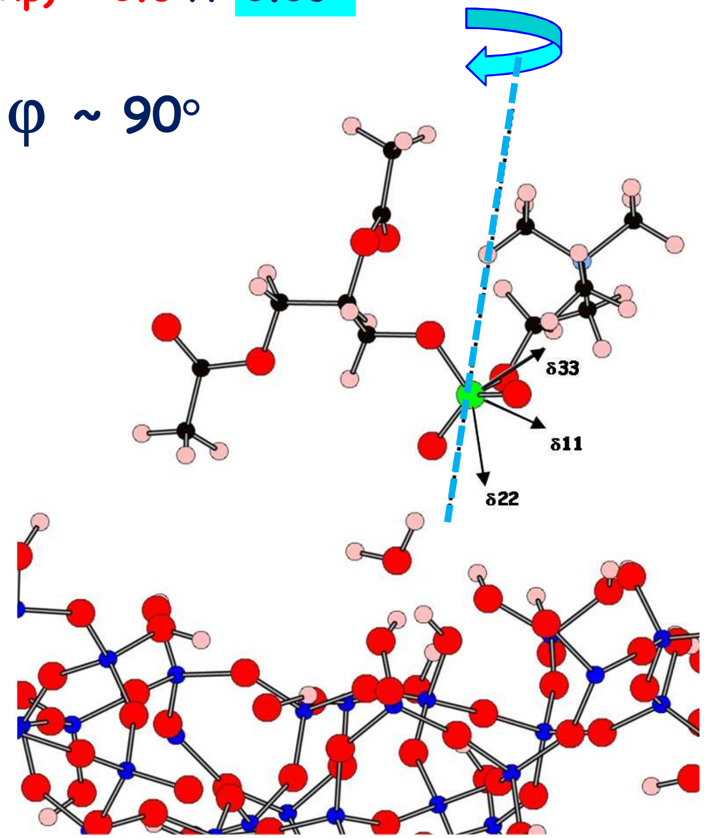


for « liposils »:

GIPAW

Δ_{CS} (exp) = - 99.5 ppm // -174.93 ppm

η_{CS} (exp) = 0.6 // 0.36



Δ_{CS} (averaged) = - 98.22 ppm

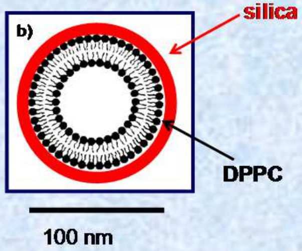
η_{CS} (averaged) = 0.63

Outline

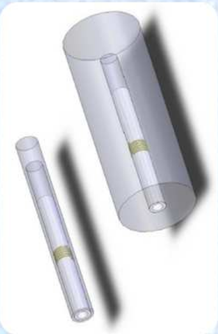
- **Hybrid materials: *bio-inspired* materials as a first example**

- ***Ab initio* calculations of NMR parameters**

- **Liposils as nano-cargos for drug delivery**

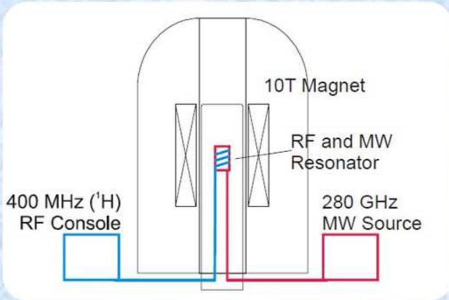


- **Sensitivity issues:**



*** applications of DNP MAS to synthetic and natural biological materials**

*** applications of Magic Angle Coil Spinning (MACS)**



Sensitivity in solid state NMR

"… the sensitivity of conventional NMR techniques is fundamentally limited by the ordinarily low spin polarization achievable in even the strongest NMR magnets…" in: B. M. Goodson, *J. Magn. Reson.* 155 (2002) 157.

preparation

- HP ^{129}Xe
- Dynamic Nuclear Polarization (DNP)

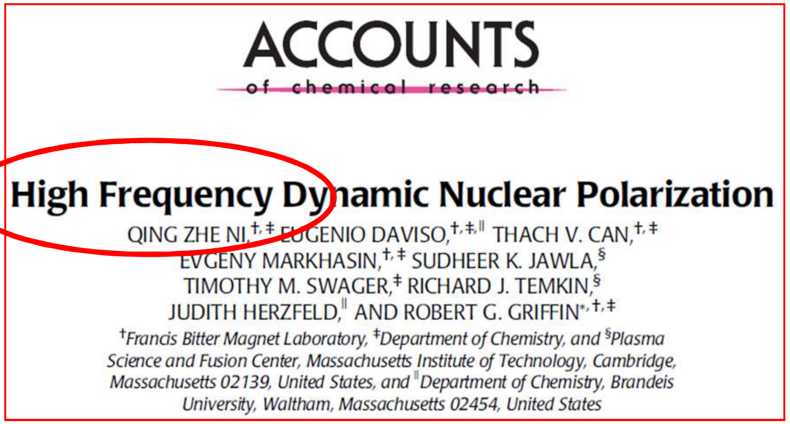
instrumentation

- ultra fast MAS
- Magic Angle Coil Spinning (MACS)

signal

- Singular Value Decomposition
- inverse harmonics
- denoising
- Non Uniform Sampling

New trends in DNP

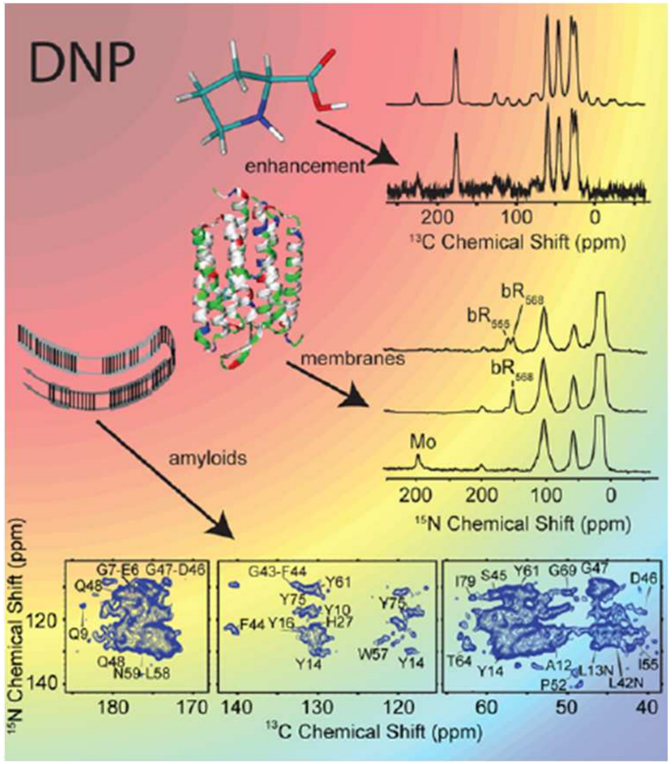

ACCOUNTS
of chemical research

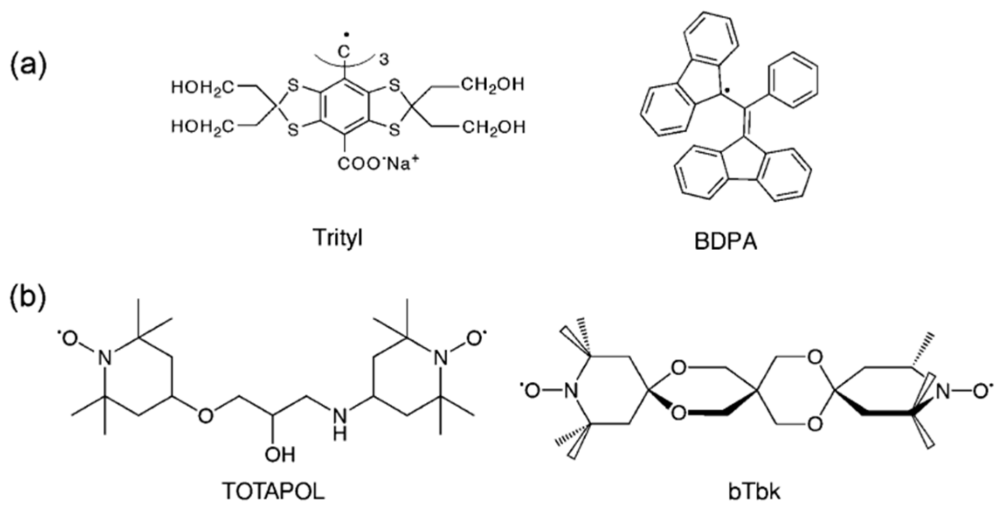
High Frequency Dynamic Nuclear Polarization

QING ZHE NI,[†,‡] EUGENIO DAVISO,[†,‡,||] THACH V. CAN,[†,‡] EVGENY MARKHASIN,[†,‡] SUDHEER K. JAWLA,[§] TIMOTHY M. SWAGER,[‡] RICHARD J. TEMKIN,[§] JUDITH HERZFELD,[||] AND ROBERT G. GRIFFIN*,[†,‡]

[†]Francis Bitter Magnet Laboratory, [‡]Department of Chemistry, and [§]Plasma Science and Fusion Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States, and [||]Department of Chemistry, Brandeis University, Waltham, Massachusetts 02454, United States

- transfer of electronic polarization to nearby nuclei **under fast MAS**, **low T**
- microwave (μW) irradiation of the spin system
- using **radicals…**

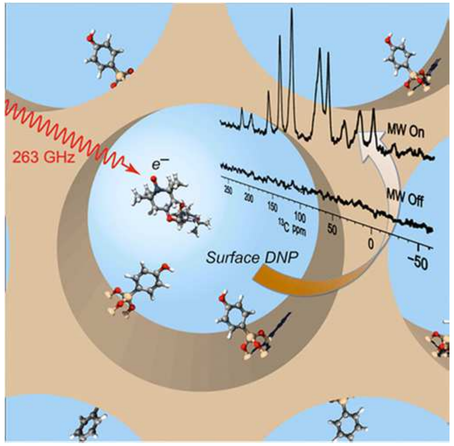




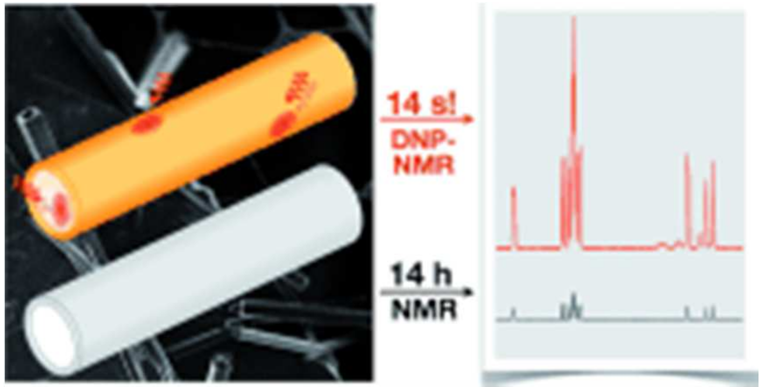
Overhauser, Schlichter, Abragam ….

R. G. Griffin: 1993 → today !

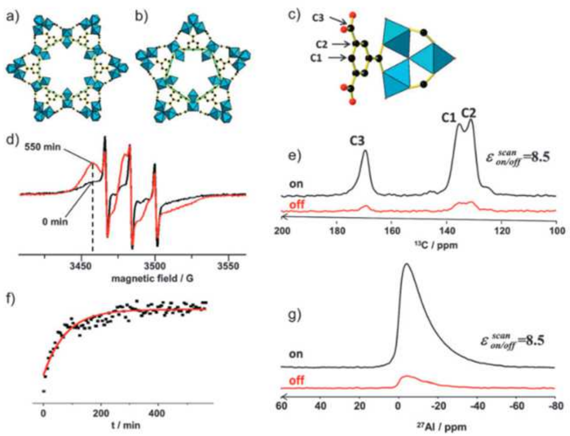
DNP in France



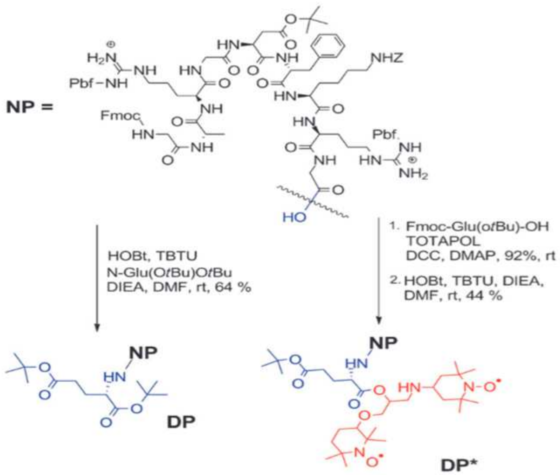
Lyon



Grenoble

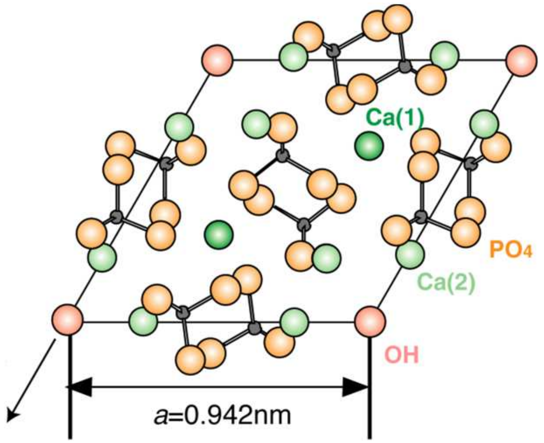


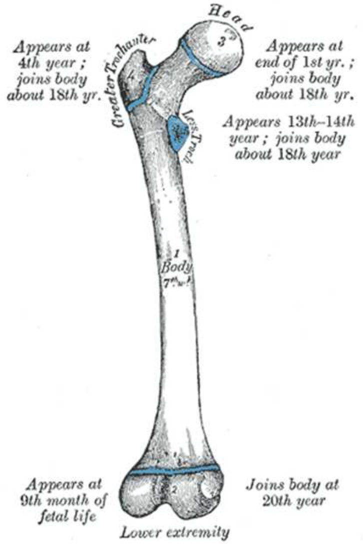
Lille



Lausanne / Paris

Substitutions in apatitic (HAp) structures





$Ca_{10} (PO_4)_6 (OH)_2$

Mg^{2+}, Zn^{2+}, Na^{+}, K^{+} ...

SO_4^{2-}, CO_3^{2-}...

CO_3^{2-}, F^{-}, Cl^{-}...

$Ca_{10} (PO_4)_6 (OH)_2$

B A

SiO_4^{4-}

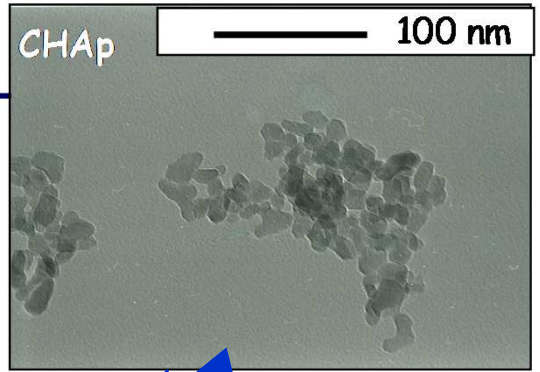
CO_3^{2-}

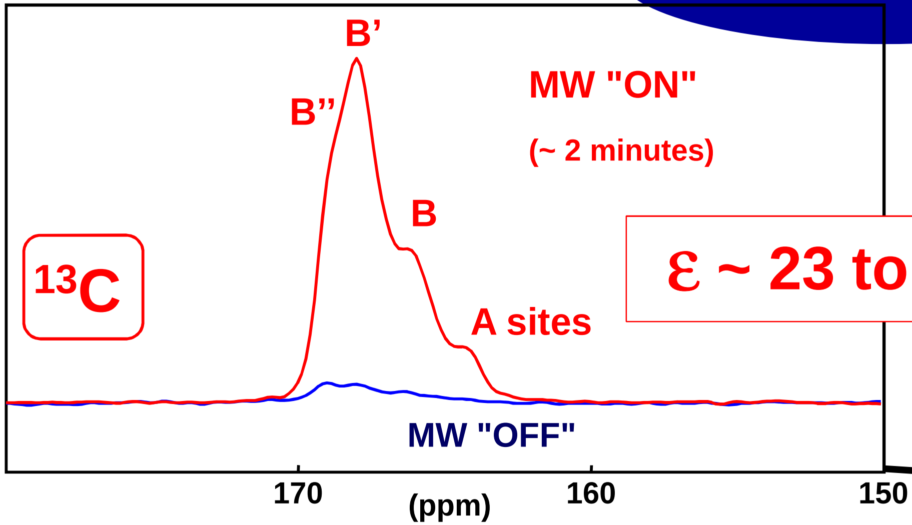
Carbonated nanosized HAp

- synthetic HAp, ~ 5 wt %

e-

$^{1}H \rightarrow {}^{13}C$

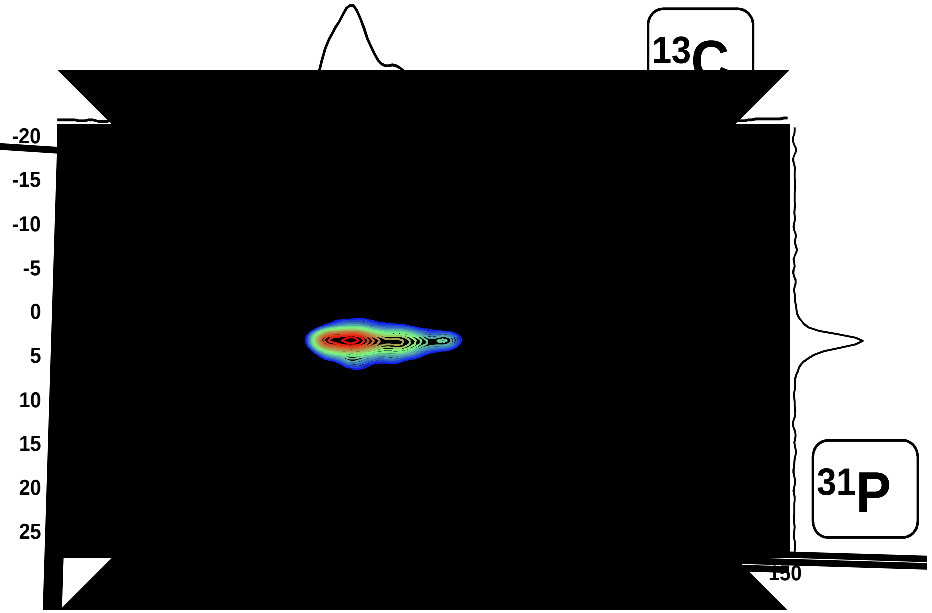




ε ~ 23 to 42

e-

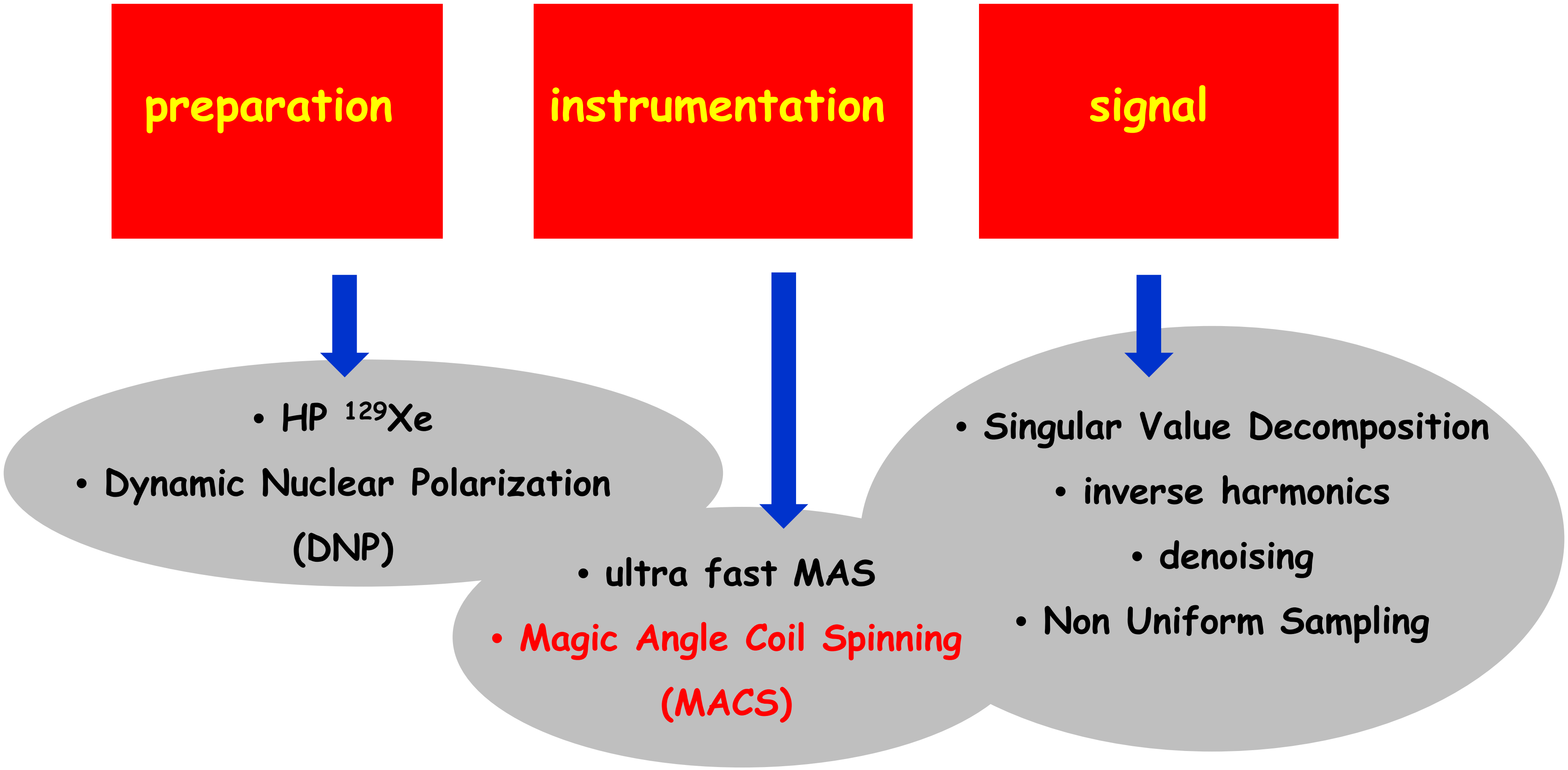
$^{1}H \rightarrow {}^{31}P \rightarrow {}^{13}C$



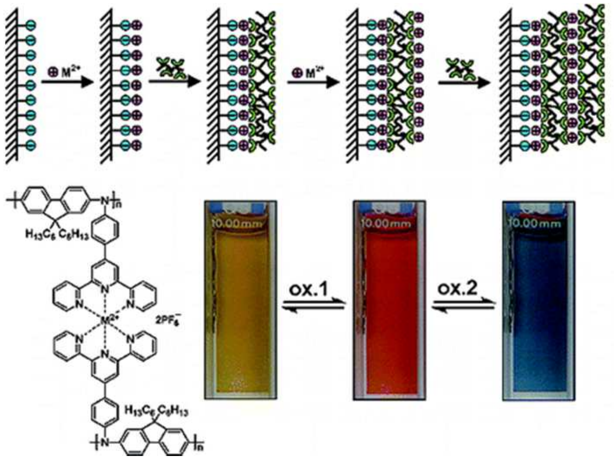
Coll.: M. Caporini, G. Bodenhausen, EPFL, Lausanne & F. Aussenac, Bruker Biospin

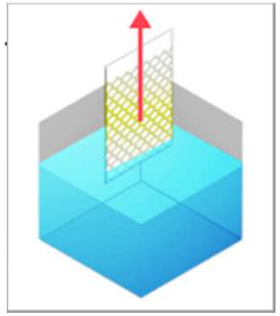
Sensitivity in solid state NMR

"… the sensitivity of conventional NMR techniques is fundamentally limited by the ordinarily low spin polarization achievable in even the strongest NMR magnets…" in: B. M. Goodson, *J. Magn. Reson.* 155 (2002) 157.

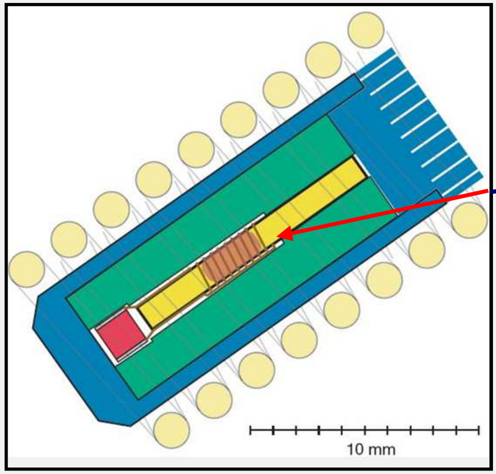


NMR of hybrid mesoporous thin films





Magic Angle Coil Spinning



rotor at θ_m

μ-coil

Static coil

D. Sakellariou *et al.*, *Nature*, 447, 2007.

Applications potentielles :

- films

S ~ 2 cm^2

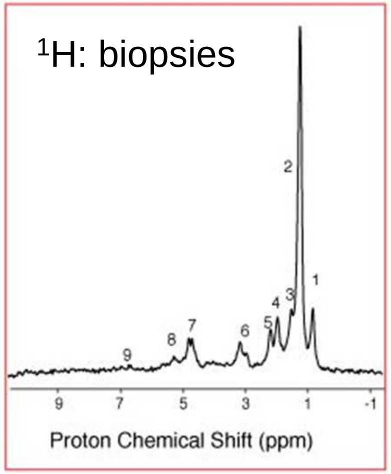
h ~ 300 nm

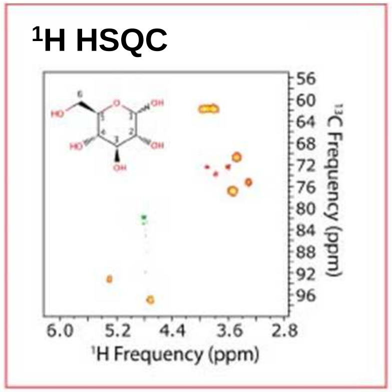
m ~ 100 μg

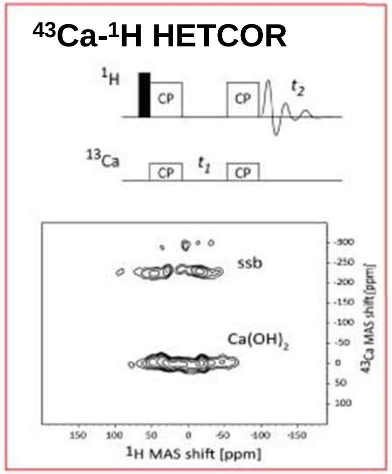
^{1}H … ^{29}Si, ^{13}C, $^{47/49}Ti$ (!) …

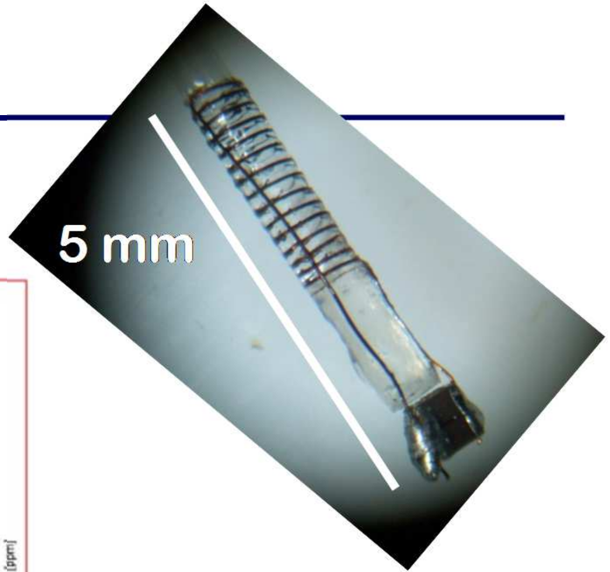
MACS experiments

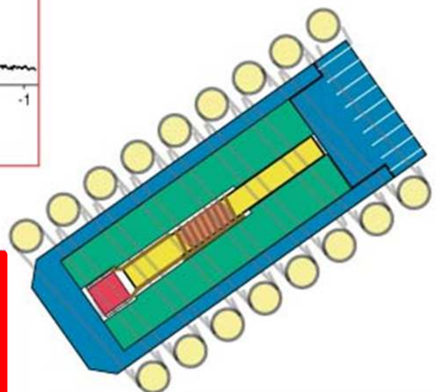
(Coll.: D. Sakellariou)

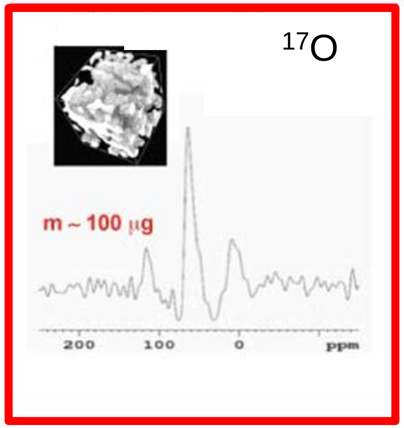


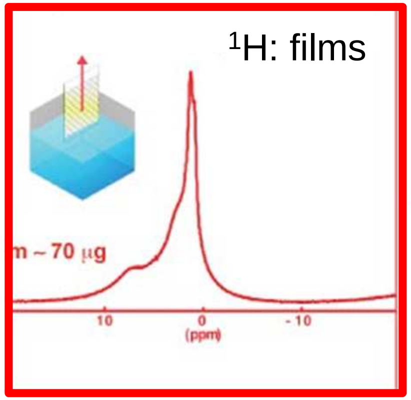


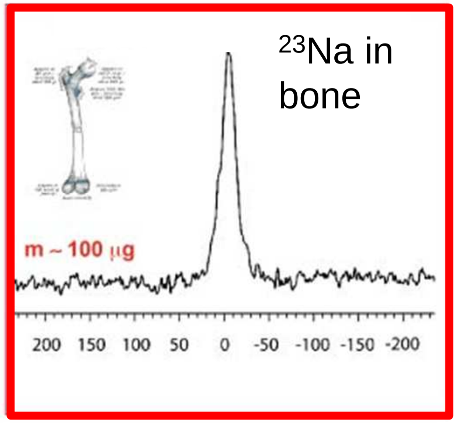












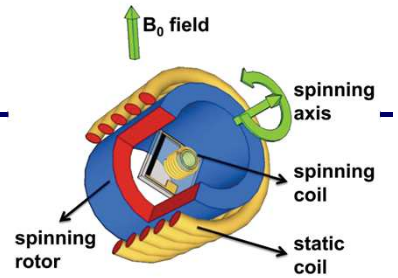
"hand made" micro-coils

100 µg

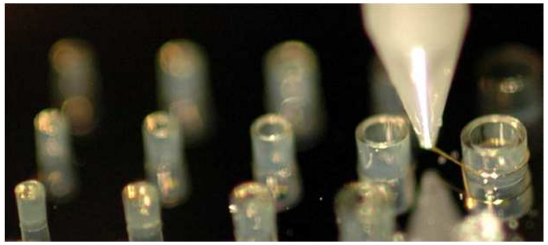
70 µg

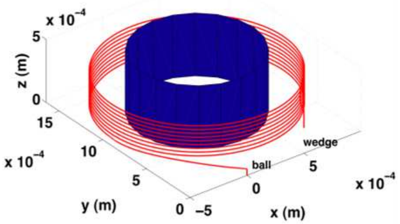
***Magn. Reson. Med.* 2010, *Chem. Commun.* 2011, *Concepts in NMR* 2011, *Chem. Sci.* 2011, *Anal. Chem.* 2012 …**

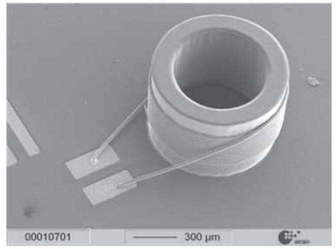
MEMS techniques applied to micro-coils



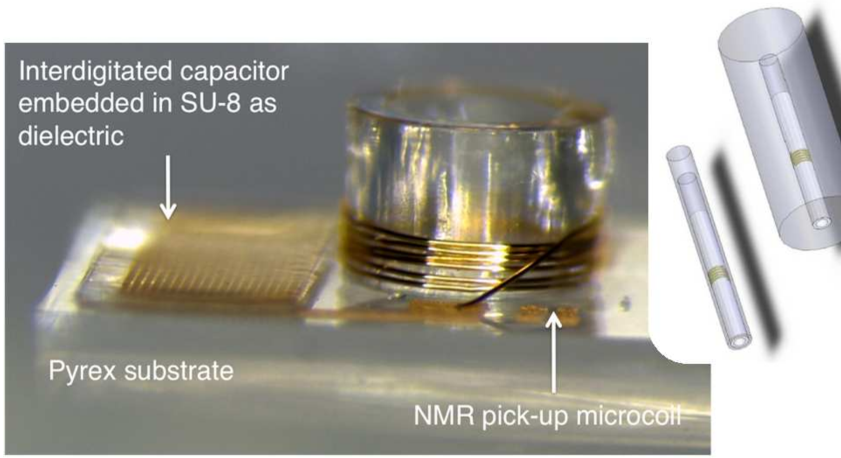
Coll. : V. Badilita, U. Wallrabe, J. G. Korvink – IMTEK, Freiburg, Germany

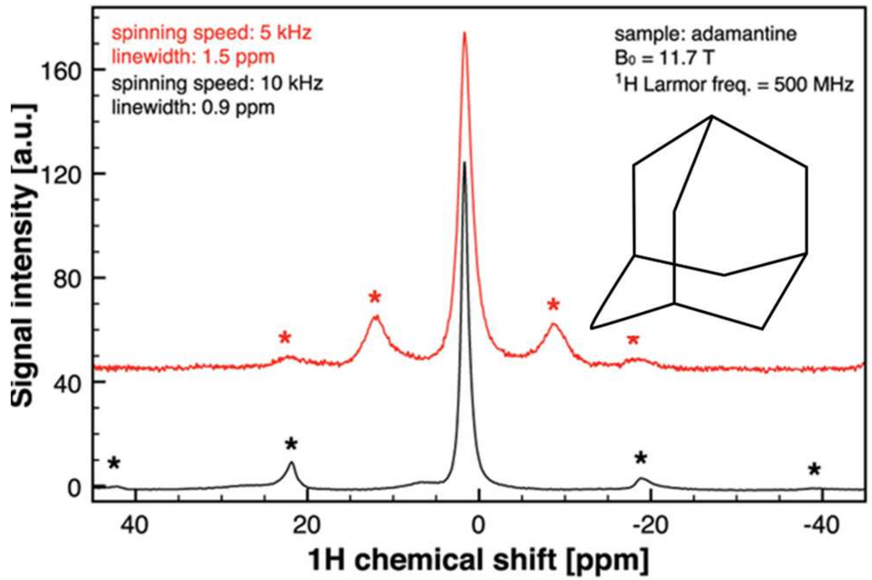






Microfabricated inserts for magic angle coil spinning (MACS) wireless NMR spectroscopy.
Badilita, V., B. Fassbender, K. Kratt, A. Wong, C. Bonhomme, D. Sakellariou, J. G. Korvink and U. Wallrabe
PloS one, Vol., 7(8), 2012, pp. e42848-e42848.





Microcoil based solid state NMR: more references in the literature

Solid State Nuclear Magnetic Resonance
Volumes 47–48, October–November 2012, Pages 1–9

Trends

review article

Microcoils and microsamples in solid-state NMR

Kazuyuki Takeda

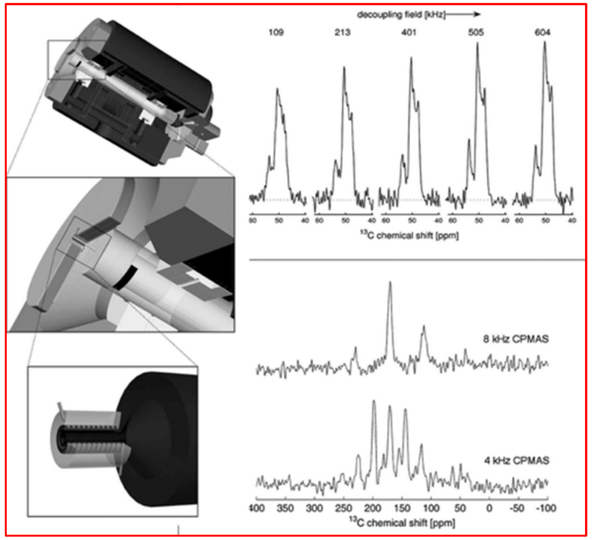
Journal of Magnetic Resonance
Volume 213, Issue 1, December 2011, Pages 192–195

Communication

disk MAS NMR

Nondestructive high-resolution solid-state NMR of rotating thin films at the magic-angle

Munehiro Inukai, Yasuto Noda, Kazuyuki Takeda



Microcoil High-Resolution Magic Angle Spinning NMR Spectroscopy

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DOI: 10.1021/ja061350+
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