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Solid-state nuclear magnetic resonance: from physics to materials

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Physics

Nuclear spin

Zeeman effect
 NMR is precise but not sensitive

Larmor frequency
 $2\pi \nu = \gamma B_0$

Excitation Radio Frequency pulse

Liquid state:
 $T_1 \approx T_2 \rightarrow$ narrow peaks

Solid state:
 $T_1 > T_2 \rightarrow$ broad peaks

Return to equilibrium

CSA

D

Zeeman quadrupolar coupling

David D. Laws, *Angewandte Chemie International Edition*, 2002, 41, 3096-3129

Mechanics

2.4 tons Floor reinforcement

Probe

Spinning rate depending on rotor size

Centrifugation

Cryogenics

Warming up

Asphyxia risk

Cryostat frozen

Liquid	Boiling point (K)	Heat of vaporization (kJ.mol ⁻¹)	Vol. for cool down (L)	Vol. in cryostat (L)	Filling frequency (days)	Cost (€L ⁻¹)
Nitrogen	77.4	5.56	1000	286	7	0.50
Helium	4.22	0.08	1000	256	90	7.00

Mathematics

Truncation

First order phasing

Zero order phasing

Comparison of types of apodization

J.-C. BELOEIL, NMR course, 1999, IUT d'Orsay, France

Nuclear Magnetic Resonance

Electronics

Put up to field: 200A!!!
 2-3 days needed
 Permanent magnet

UPS 15 kVA, 1h

Without any maintenance

Radio frequency control

Temperature unit

Stability control

Pneumatic unit

Power amplifiers (1kW)

J.-C. BELOEIL, NMR course, 1999, IUT d'Orsay, France

Informatics

Spectrometers park administration:
 3 Linux Redhat workstation 4
 4 Windows 2000
 2 Windows XP
 Processing software
 Backups

Pulse programming

```

:echorot.gul
:theta1-theta2 echo with rotary resonance
:cnst31 :frequence de rotation
:p1 :30 deg on H
:p11 :H power for hard pulse
:p110 :H power for spin lock, RF=MAS*2
:j6 :loop counter for echo
:j10 :loop counter for spin lock
#include <Avancesolids.incl>
*2p1*2
*10=1/16/cnst31*
*10=16/cnst31-p2/2*
1 ze
2 d1
3 10u p1:f1
(p1 p1):f1
0.3u
(p10 p10 p10):f1,RF=MAS*2 rotary resonance echo
d10
d10
d10
(p10 p10 p10):f1,RF=MAS*2 rotary resonance echo
wr=2 ph31
wr #0
exit
ph0= 0
ph1= 0 1 2 3
ph2= 0 0 0 1 1 1 1 2 2 2 3 3 3 3
ph10= 3 0 1 2
ph31= 0 3 2 1 2 1 0 3
    
```

Predictive computations

main program

explanations

definitions

phase cycling

Christel GERVAIS, *Journal of Magnetic Resonance*, 2007, 187, 131-140

Chemistry

¹³C SC14

³¹P IRCP

³¹P inadequate

³¹P calc.

³¹P exp.

³¹P P1 and P2

³¹P P3, P4, P1

³¹P P2, P3, P4, P1

Niki BACCILE, *Chem. Mater.*, 2007, 19, 1343-1354

Niki BACCILE, *J. Phys. Chem. C*, 2009, 113, 9644-9654

Frédérique POURPOINT, *Chem. Mater.*, 2007, 19, 6367-6369

Biology

Thalassiosira Pseudonana
 Benoit TESSON, Sylvie MASSE¹
Anal Bioanal Chem, 2008, 390, 1899-1898

Frustulins

Pleuralins

Polyamines

Silaffins

²⁹Si

¹H

³¹P

2D-NOESY ¹H-¹H

INEPT ¹H-¹³C

¹⁵N CP

¹³C

¹³C CP

Conclusions

Nuclear Magnetic Resonance is a powerful technique that interacts with many fields, for instance physics, mechanics, cryogenics, electronics, mathematics, informatics, and of course chemistry and biology. In liquid state, NMR is sometimes used as a black box, just to check if synthesis works. However, in solid state it is difficult to use it this way. Indeed, physical interactions are not averaged anymore, leading to signal broadening. Some tools can be used to narrow the signals and / or to manipulate interactions either in the laboratory frame or in the rotating frame. Solid state NMR can be used on a wide range of nucleus to quantify species, study their mobility, check proximities between different parts of the sample, either by dipolar coupling or by chemical bonding. One sometimes need to avoid physical artifacts such as dead time in order to get a correct spectrum. In this case, linear prediction and other mathematic tools can be very useful. Finally, one has also to keep in mind that the sample itself can induce difficulties, especially when studying nanoparticles where the side effects become not negligible at all.