High-Field Solid-State NMR: The Tools and Their Application in Materials Research

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Outline

- Basic NMR Introduction
- Solid-State NMR
  - NMR tools for spin 1/2
  - Case Study: melaminephosphate flame retardants
  - NMR tools for quadrupolar nuclei
- NMR tools for the future
  - NMR above 30 T (1.27 GHz)
  - Microcoil NMR
  - Polarization Enhancement Techniques
  - Mechanical Detection of Magnetic Resonance
Nijmegen Science Faculty &
Goudsmit Pavilion for NMR Research
The Concept of Spin

Goudsmit en Uhlenbeck 1925: Electrons have an intrinsic magnetic moment caused by the rotation of the electron.

Goudsmit - Pauli – Stern 1926: nuclear spin.

Zeeman effect

Goudsmit Pavilion for NMR Research
Nuclear Spin Hamiltonian

- Quantum state of the entire sample is fully described by a wave function $|\psi_{\text{full}}(t)\rangle$
  \[
  \frac{d}{dt}|\psi_{\text{full}}(t)\rangle = -i\hat{H}_{\text{full}}|\psi_{\text{full}}(t)\rangle
  \]

- Effects of rapidly moving electrons is blurred out, their "average" effect is contained in the spin Hamiltonian:
  \[
  \frac{d}{dt}|\psi_{\text{spin}}(t)\rangle = -i\hat{H}_{\text{spin}}|\psi_{\text{spin}}(t)\rangle
  \]

Study Malcolm H. Levitt
Spin Dynamics, Wiley, 2001
Nuclear Zeeman Interaction

Spin interacts with external magnetic field:

\[
\hat{H}^j_{\text{Zeeman}} = -\mu_j \cdot \vec{B} = -\gamma_j \hat{I}_j \vec{B} \quad \overset{B_0 \parallel z}{\longrightarrow} \quad \hat{H}^j_{\text{Zeeman}} = -\gamma_j \hat{I}_{j,z} B_0
\]
Transverse RF field

\[ \hat{H}_{RF}^j = \frac{1}{2} \gamma_j B_1 \{ \cos(\omega_0 t + \phi_p) \hat{I}_{j,x} + \sin(\omega_0 t + \phi_p) \hat{I}_{j,y} \} \]

nutation frequency \( \omega_{nut} = \frac{1}{2} \gamma_j B_1 \)
Precession in the Magnetic Field

Larmor precession frequency

B₀
The basic NMR experiment as viewed from the rotating frame

- The magnetization is tipped over by a rf-pulse. The precession of the magnetization in the field induces a voltage in the receiver coil.
From Free Induction Decay to Spectrum

Fourier Transform
Chemical Shift

diamagnetism

\[ \vec{B}_{j,loc} = \vec{B}_0 + \vec{B}_{j,induced} \]

\[ \vec{B}_{j,induced} = \begin{bmatrix} \delta_{j,xx} & \delta_{j,xy} & \delta_{j,xz} \\ \delta_{j,yx} & \delta_{j,yy} & \delta_{j,yz} \\ \delta_{j,zx} & \delta_{j,zy} & \delta_{j,zz} \end{bmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \]

secular approximation: \( \hat{H}_{CS}^j \equiv -\gamma_j B_0 \delta_{j,zz} (\theta) \hat{I}_{j,z} \)
Ethanol: $\text{CH}_3\text{CH}_2\text{OH}$

C–H   O–H

In isotropic liquids motionally averaged chemical shift:

$$\hat{H}^j_{\text{CS,iso}} \equiv -\gamma_j B_0 \delta^j_{\text{iso}} \hat{I}^j_{j,z}$$

$$\delta^j_{\text{iso}} = \frac{1}{3} (\delta^j_{j,xx} + \delta^j_{j,yy} + \delta^j_{j,zz})$$

Packard, Stanford 1951

Purcell: “Indeed certain branches of this work are now being pursued in chemical laboratories.”
Anisotropic Interactions

Liquid: rotational and translational motions

Single crystal

Powder Spectrum

Individual Peaks
What Information Can NMR Give

Site Identification

- **Chemical Shift**
  - Identification of structural building blocks ($^1$H, $^{13}$C).
  - Coordination of $^{27}$Al, $^{69,71}$Ga, $^{29}$Si etc).
  - Hydrogen bonding ($^1$H, $^{15}$N, $^{17}$O)
  - Majority of periodic table is accessible

- **Knight shifts, Fermi-contact shifts etc (Lecture Berthier).**
  - Li-ions in paramagnetic battery materials
Anisotropic $^{13}\text{C}$ interactions

**Identification**

**Alignment**

**Molecular motions**

Fig. 6.5 Some chemical shift anisotropy line shapes under conditions of molecular motion. Three different models of molecular motion are considered: (a) two-site hopping, chemical shift tensor principal z-axis reorientates by 109.5°; (b) two-site hopping, chemical shift tensor principal z-axis reorientates by 120° and (c) three-site hopping about a rotation axis orientated at 70.5° to the chemical shift tensor principal z-axis in each site. In all cases, the chemical shift tensor is axially symmetric and the populations of each site are equal. The $\tau^{-1}$ (s) for each case are given with the spectra.
Site Identification

$^{27}$Al NMR of oxides

- 4-fold coordinated Al: 80 - 40 ppm
- 5-fold coordinated Al: 40 - 20 ppm
- 6-fold coordinated Al: 20 - -10 ppm

$\delta_{cs}$ Tetrahedral $\text{Al-O-Si}$ in aluminosilicates

\[ \delta_{iso} = -0.50 \theta + 132 \]
Anisotropic Interactions

😊 Broad lines
😊 Structural information
😊 study dynamics
😊 Manipulation in ordinary and spin space

😢 use adequate tools

31P powder spectra

Na₃PO₄

Na₄P₂O₇

(NaPO₃)ₙ

δ [ppm]
Tool: Magic-Angle Spinning

Averaging of anisotropic interactions in ordinary coordinate space.

12000 Hz

870 Hz

static

\[ \omega/2\pi \text{ [kHz]} \]
**Direct dipole-dipole interactions**

\[
\hat{H}_{DD}^{jk} = b_{jk} \left( 3 (\hat{I}_j \cdot e_{jk})(\hat{I}_k \cdot e_{jk}) - \hat{I}_j \cdot \hat{I}_k \right)
\]

\(e_{jk}\) is the unit vector connecting spin \(j\) and \(k\)

secular approximation:

homonuclear: \(\hat{H}_{DD}^{jk}(\theta_{jk}) = b_{jk} \left( 3 \cos^2(\theta_{jk}) - 1 \right) \left( 3\hat{I}_j \hat{I}_k - \hat{I}_j \cdot \hat{I}_k \right)\)

heteronuclear: \(\hat{H}_{DD}^{jk}(\theta_{jk}) = b_{jk} \left( 3 \cos^2(\theta_{jk}) - 1 \right) \left( 2\hat{I}_j \hat{I}_k \right)\)
Anisotropic Dipolar Interaction

Pake doublet

For abundant spins MAS is only effective if spinning speed significantly exceeds the line width
What Information Can NMR Give

Intersite correlations

- *Dipolar Interactions (through space)*
  - Spatial proximity of nuclei (~1/r^3)
  - Homonuclear
  - Heteronuclear

- *J-couplings (mediated through chemical bonds)*
  - Existence of chemical bonds.

- *Hyperfine interactions (coupling to electron spin > Lecture Berthier).*
Tool: Radio Frequency Irradiation

- Heteronuclear decoupling of nuclei by CW-irradiation with resonant RF waves. Pulsed alternatives TPPI, XiX etc.

- Homonuclear decoupling by CW irradiation at the magic angle (Lee-Goldburg decoupling). Pulsed alternatives: WAHUHA, MREV-8, FSLG, Dumbo etc.

Manipulation of interactions in spin space.
Combining Tools

👍 Combined Rotational and Multiple Pulse Decoupling

👍 Recoupling of dipolar interactions using radio-frequency sequences synchronized with sample spinning and matched rf-field strength.

👍 Transfer of coherence of coupled nuclei
$^1$H Spectroscopy

FSLG
12.5 kHz MAS

RF

30 kHz MAS

NH$_3^+$

CH

CH$_2$

Alanine

MAS

static

proton chemical shift (ppm)

14 12 10 8 6 4 2 0 -2 -4

100 80 60 40 20 0 -20 -40 -60 -80

Combining Tools

$^{13}$C Single Pulse Excitation

+ $^1$H CW Decoupling

+ Magic Angle Spinning

+ MAS + $^1$H LG decoupling

+ MAS + $^1$H CW decoupling
Two-dimensional NMR

\[ (\pi/2)_{\phi_1} \rightarrow t_1 \rightarrow (\pi/2)_{\phi_2} \rightarrow t_2 \rightarrow \phi_{\text{rec}}, \phi_{\text{dig}} \]

Fourier Transform \( t_2 \) and \( t_1 \)
**Case Study: Environment-Friendly Condensed Phase Flame Retardants**

Melamine Phosphates:
- MP
- (MP)$_2$ (Pyrophosphate)
- M Polyphosphate

Conversion ~200°C - 260°C
Above 260 °C decomposition

Crystal structures unknown
Polymerization process unknown
FR Mechanism unknown

A. Brinkmann, E.R.H van Eck & A.P.M. Kentgens
Magnetic Resonance in Chemistry, 2007 submitted
Site ID
with added *anisotropic* information

\[ \sigma_{11} = 46 \text{ ppm} \]
\[ \sigma_{22} = 4 \text{ ppm} \]
\[ \sigma_{33} = -51 \text{ ppm} \]

\[ \sigma_{11} = 68 \text{ ppm} \mid 64 \text{ ppm} \]
\[ \sigma_{22} = -12 \text{ ppm} \mid -8 \text{ ppm} \]
\[ \sigma_{33} = -84 \text{ ppm} \mid -91 \text{ ppm} \]

\[ \sigma_{11} = 77 \text{ ppm} \]
\[ \sigma_{22} = 14 \text{ ppm} \]
\[ \sigma_{33} = -168 \text{ ppm} \]
1D $^1$H Spectra at 18.8 T

- **MP**
- **(MP)$_2$**
- **MPpoly**

$^1$H Spectra
- **MAS**
- $\omega_r/2\pi = 49$ kHz
- $B_0 = 18.8$ T

$\omega_r/2\pi = 12$ kHz
- $B_0 = 7.1$ T
Heteronuclear Correlation $^{1}\text{H}-^{31}\text{P}$

**Diagram Description:**
- **FSLG** and **LG-CP** pulses are applied during $t_1$.
- **TPPM** pulse is applied during $\tau_{ct}$.
- **RAMP** is used during $t_2$.
- **$^{31}\text{P}$** and **$^{1}\text{H}$** are detected.

**Parameters:**
- $\omega_r/2\pi = 12$ kHz
- $\tau_{ct} = 0.1$ ms
- $\tau_{ct} = 2.5$ ms

**Equation:**
$$\tau_{ct} = 0.1 \text{ ms}$$

**Graph:**
- 2D correlation spectroscopy plots showing $\delta_1$ and $\delta_2$.
- The spectra display distinct peaks corresponding to $^{31}\text{P}$ and $^{1}\text{H}$.

**Institution:**
- Institute for Molecular and Materials
Heteronuclear Correlation $^{1}\text{H}-^{13}\text{C}$

$^{1}\text{H}$ Spectrum
$B_0=18.8$ T

$\omega_r/2\pi = 12$ kHz
$B_0 = 7.1$ T
Homonuclear: $^{15}\text{N}-^{15}\text{N}$ in MP

$\omega_r/2\pi = 12 \text{ kHz}$
$B_0 = 7.1 \text{ T}$
$^{15}$N-$^1$H distance measurements

Dipolar recoupling

Echo: refocus $^{15}$N chemical shift, keep $^{15}$N-$^1$H dipolar interaction
MP: Assignment

H22: 11.1 ppm
P1: -0.2 ppm
H21: 13.7 ppm
C13: 156 ppm
H17: 6.2/8.0 ppm
N7: -291.3 ppm
H18: 8.0/6.2 ppm
N10: -215.6 ppm
H19: 6.8 ppm

H23: 13.2 ppm
N8: -258.0 ppm
H16: 9.1 ppm
N6: -290.5 ppm
H15: 5.6 ppm
C12: 156 ppm
N9: -213.3 ppm
C14: 164 ppm
H20: 8.7 ppm
N11: -280.0 ppm
Hydrogen Bonding & π–π Stacking

Combined NMR and X-ray Powder Diffraction

V. Brodski, R. Peschar and H. Schenk
Univ. Of Amsterdam
Hydrogen bonding in biological molecules

N-H...O

O-H...O

Proteins and Peptides

Polysaccharides

$^{17}O$ is a quadrupolar I=5/2 nucleus
Quadrupolar Interaction

secular approximation: \( \hat{H}_Q^j(\theta) = \omega_{j,Q} \left( 3 \hat{I}_{jz}^2 - \hat{I}_j \cdot \hat{I}_j \right) \)

with \( \omega_{j,Q}(\theta) = \frac{3eQ_j}{4I_j(2I_j - 1)} V_{j,zz}(\theta) \)
First order quadrupolar interaction

$^{23}$Na (I=3/2) in NaNO$_3$
Second order quadrupolar interaction

As Coordinations in AlGaAs

\[ ^{75}\text{As NMR @ 18.8T} \]
\[ \text{Al}_{0.47}\text{Ga}_{0.53}\text{As} \]
What Information Can NMR Give

Site Identification

• Quadrupolar Interaction
  - Determination of local symmetry (distortions).
  - \(^{17}\)O NMR parameters are sensitive to H-bond formation.
  - Majority of periodic table has I>1/2
Quadrupolar Interaction:
Site Symmetry

Framework aluminosilicate glasses with varying charge-balancing cations (Li, Na, K, Rb, Cs)
Tool: Magic Angle Spinning

- Fast magic-angle spinning
- Averaged: $P_2$
- Not averaged: $P_4$

Spin-½:
- $\omega_2/2\pi = 870$ Hz
- $[^{13}\text{C}_2]$-glycine
- $^{13}\text{C}$

Spin-½:
- $\omega_2/2\pi = 12$ kHz

Use high fields!
Tools: Double Rotation (DOR)  
Dynamic Angle Spinning (DAS)

\[ \nu_{m,-m} = C_0(1,m) \cdot \nu_0 + C_2(1,m) \cdot \nu_2(\alpha, \beta) \cdot P_2(\cos(\theta)) + C_4(1,m) \cdot \nu_4(\alpha, \beta) \cdot P_4(\cos(\theta)) \]

Multiple-Quantum MAS

\[ \nu_{m,-m} = C_0(I,m) \cdot \nu_0 + C_2(I,m) \cdot \nu_2(\alpha, \beta) \cdot P_2(\cos(\theta)) + C_4(I,m) \cdot \nu_4(\alpha, \beta) \cdot P_4(\cos(\theta)) \]

Sensitivity issue (multiple-quantum excitation and conversion)

Dehydrated H-ZSM5

- High Field (14.1 T)
- Fast MAS (27 kHz)
- MQ→1Q DFS conversion

$^{27}$Al MQMAS

$\bar{\sigma}_{iso} = 55 \text{ ppm}$
$\bar{C}_{qcc} = 16.4 \text{ MHz}$
$\eta = 0.1$
rDFS $^{17}$O MAS NMR

$^{17}$O MAS NMR

$^{17}$O challenging because of low $\gamma$ and large $C_\Omega$

$\sim 4.3$ S/N Enhancement for biologically relevant material

$^{17}$O MAS (25 kHz) @ 14.1T
1968 transients
Heteronuclear Recoupling: \( ^{17}\text{O}-^{1}\text{H} \) distance measurement

\[ r_{\text{OH}} \text{ distance } 104 \text{ pm is within 5\% of the distance determined by neutron diffraction (99 pm).} \]

O-H libration slightly averages dipolar interaction.
Heteronuclear Recoupling: $^{17}$O-$^1$H distance measurement

Heteronuclear Recoupling:

Distance measurement

$\eta_{O-H''}$ distance 161 pm

A. Brinkmann & A.P.M. Kentgens
Summary of Internal Hamiltonians

\[ \hat{H}_{\text{int}} \]

- Magnetic (all spins)
  - One-spin
    - Chemical shift
    - Spin-rotation
    - Dipole-dipole
    - J-coupling
    - Quadrupole coupling
  - Two-spin
    - Electric (spin >1/2 only)
Conclusions

- Solid state NMR is a powerful analysis technique
  - Probes microscopic interactions (1-100Å)
  - Study structure and dynamics
  - Works in crystalline, partly disordered and amorphous compounds
  - Non-destructive technique needing no special sample preparation

- Novel methodological developments will open new applications in advanced materials science
Sensitivity enhancement is driving methodological developments

Options for signal enhancement: Potential gain

- *Double* $B_0$ 3
- Cryo-cooled rf coils 3
- Population transfer in coupled or quadrupolar spin systems 2-5
- Low temperature MAS 10
- Microcoil detection 100
- Dynamic Nuclear Polarization (DNP) $10^3$
- Optical polarization (ODMR / OPMR) $10^4$
- Hyper polarized Xe, He, Kr $10^4$
- Para-Hydrogen $10^4$
- Force detection $10^3$-$10^6$
SSNMR Beyond 1 GHz

- 33 T
- 40 kA
- 20 MW
Opportunities and Problems

Opportunities
- Sensitivity ($\sim B^{7/4}$)
- Resolution ($\sim B - B^2$)
- High speed (proton) MAS
- Quadrupolar nuclei

Problems
- Intrinsic homogeneity ($\sim 10^{-3}$/cm)
- Temporal stability ($\sim 10^{-5}$)
  - power supply
  - temperature and flux changes
  - Operation time

- Ferro-shims
- High speed MAS
- Reference deconvolution
- Follow-B
Field profile of a uniformly magnetized cylinder

Field profile of a uniformly magnetized cylinder

Field profile Ferroshim

Magnet field profile before and after Ferroshim

Shifting the shim off-axis allows reduction of radial gradients

Magic Angle Spinning averages residual gradients
Field map with ferroshim

Field map \( D_2O \), after x-y optimization ferroshim

Field x-y gradient < 5 kHz (drift dominated) <25 ppm/cm
Reference Deconvolution

\[ c(t) = \left( \frac{S_{\text{ideal-ref}}(t) \times W(t)}{S_{\text{exp-ref}}(t)} \right)^{\frac{\gamma_1}{\gamma_s}} \]

\[ S_c(\omega) = \text{FT}[S_{\text{exp}}(t) \times c(t)] \]

Morris, Barjat and Horne, PNMRS 31 (1997) 197-257.
Reference Deconvolution

- Discrete field steps
- MAS: resolution is stability limited
- Fourier spectrum distorted (chirp)
- Length of FID determines resolution
**Triple-tuned MAS probe**

**2D reference channel**

\[ \text{ND}_4\text{Cl} \text{ reference signal lasts 30 - 50 msec, i.e. intrinsic homogeneity of about 0.15 ppm.} \]
Field Stability

Field stability 10-50 ppm on $^{13}$C

$^{13}$C MAS of alanine

Field stability 10-50 ppm on $^{13}$C
Follow B option

Use first 200 μsec of reference FID to determine field
Reset spectrometer frequencies
Use remaining part of ref-FID for deconvolution
Follow B + reference deconvolution
At 21.1 T separation of the two Sc sites is nearly achieved…
Systems with large quadrupolar interactions

$^{45}$Sc 309.5 MHz

1: $C_q=15.4$ MHz  $\eta_Q=0.61$
2: $C_q=23.4$ MHz  $\eta_Q=0.10$

Intensity ratio
exp 1:2.995
theor 1:3

64 scans
MAS 38 kHz
Fixed phase
Averaging
=> follow B
=> Ref. dec.
Important technical issues are weight, volume, discharge/recharge rates, reaction heat, safety and cost.

IEA (International Energy Agency) targets:
- at least 5-10 wt.%
- H₂ recoverable at < 80°C
- Loading/unloading at 1 atm absolute pressure.

Solid H₂ storage
- (Complex) Metal hydrides, like NaAlH₄, NaBH₄, LaNi₅H₆.

NaAlH₄ ↔ Na₃AlH₆ + 2 Al + 3 H₂
Na₃AlH₆ ↔ 3 NaH + Al + 3/2 H₂
Static $^1$H NMR on Ti-doped NaAlH$_4$

- Partly release of H$_2$ -> NaAlH$_4$ and Na$_3$AlH$_6$ are present
- Hahn-Solid-Hahn Echo to avoid spectral distortions
- Two fractions with different relaxation times $T_1$ and different line widths.
- Na$_3$AlH$_6$: Narrowing of the line shape -> proton mobility in the crystal -> fast rotating AlH$_6$ clusters

Na$_3$AlH$_6$ ↔ NaAlH$_4$ + 2 Al + 3 H$_2$
Na$_3$AlH$_6$ ↔ 3 NaH + Al + 3/2 H$_2$
$^{1}\text{H}$ and $^{27}\text{Al}$ high-speed (40 kHz) MAS of Ti-doped Alanates at 30 T

$\text{NaAlH}_4 \leftrightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2$

$\text{Na}_3\text{AlH}_6 \leftrightarrow 3\text{NaH} + \text{Al} + 3/2\text{H}_2$

M. Verkuijlen, E. van Eck, J. van Bentum, B. Dam (Free University of Amsterdam)
C. Baldé, K. de Jong (Utrecht University)
Broadband homonuclear recoupling

$^2\text{H}$

synchronize

$90^\circ$

$t_1$

$90^\circ$

$\tau_{\text{mix}}$

$synchronize$

$90^\circ$

$t_2$

$\text{[R}_6^{2}\text{]}_0$

$\text{[R}_6^{2}\text{]}_0$

$\text{[R}_6^{2}\text{]}_{120}$

$\text{[R}_6^{2}\text{]}_{120}$

$\text{[R}_6^{2}\text{]}_{240}$

$\text{[R}_6^{2}\text{]}_{240}$

$\text{[R}_6^{2}\text{]}_{240}$

$\text{SR}_6^{2}\text{-RFDR}$

$36\tau_r$

$180_{60}$

$180_{-60}$

$2\tau_r$

Andreas Brinkmann, Jorge Garibay
$^{13}\text{C}-^{13}\text{C}$ homonuclear correlation

$^{13}\text{C}$ labeled L-alanine

$\tau_{m} = 3.6 \text{ ms}$
$^{13}\text{C}-\text{H}$ heteronuclear correlation of L-alanine

CP match $\nu_1=70$ kHz; $\nu_1=30$ kHz; $\nu_r=40$ kHz
Conclusion High Field NMR

- Using a combination of hardware solutions and NMR tricks, one- and two-dimensional solid-state NMR at 30 Tesla is feasible.
- Quadrupolar systems with either very large or very small quadrupolar interactions
- High resolution proton NMR
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