Experiment and Modelling in Structural NMR

November 28th – December 2nd 2011

INSTN – CEA Saclay, France

Dominique Massiot
CEMHTI CNRS, France

Techniques of
Solid State NMR

[02002]

Organized by

Thibault Charpentier
Patrick Berthault
Constantin Meis

thibault.chapentier@cea.fr
patrick.berthault@cea.fr
constantin.meis@cea.fr

Article available at <http://www.epj-conferences.org> or <http://dx.doi.org/10.1051/epjconf/20123002002>

Techniques of solid-state NMR

Dominique Massiot
CEMHTI CNRS – TGIR-RMN-THC

Mostly focused on inorganic chemistry

- Magic Angle Spinning
- Quadrupolar nuclei
- Excitation
- MQMAS
- Homo- and hetero- nuclear correlations D and J coupling

The different perturbing interactions

^{31}P Spin 1/2 CSA

Static

Single Crystal rotation pattern

Sum of crystallite's spectra

Proton decoupling averages strong ^{31}P - ^1H dipolar interaction

^{31}P
 $I=1/2$

Unresolved
CSA + Dipolaire

Static

~~CSA + Dipolar~~

MAS

~~CSA + Dipolar~~

Resolved & Simplified

high speed MAS spinning attenuate dipolar coupling
and modulates chemical shift anisotropy

^{31}P
 $I=1/2$

Proton decoupling averages strong ^{31}P - ^1H dipolar interaction

Slow MAS ~static

D. Massiot "High Resolution Solid State NMR" in High Magnetic Fields: Applications in Condensed Matter Physics and Spectroscopy, LNP Vol 595, eds C. Berthier, L.P. Lévy, G. Martinez, Springer-Verlag, ISBN 3-540-43979-X 435-453 2002

First order $\mathcal{H}_1 \ll \mathcal{H}_z$

$$\nu_{<m,m-1>} = \nu_0 + P_2(\cos\theta) \frac{(1-2m)}{2} \nu_Q C_{\alpha,\beta} + \sum_{n=1}^2 A_n e^{-i(n\omega_r t + \phi)}$$

D. Massiot "High Resolution Solid State NMR" in High Magnetic Fields: Applications in Condensed Matter Physics and Spectroscopy, LNP Vol 595, eds C. Berthier, L.P. Lévy, G. Martinez, Springer-Verlag, ISBN 3-540-43979-X 435-453 2002

^{31}P single sited phosphate

^2H Plexiglass - static

^2H Methiodine - MAS 3.5kHz

Phosphonate (B.Bujoli – Nantes)

^{13}C $I=1/2$
1.18% ab.
100 MHz

^{17}O $I=5/2$
0.037% ab.
54 MHz

^{14}N $I=1$
99.6 % ab.
29 MHz

^{67}Zn $I=5/2$
4.11% ab.
25 MHz

Hybrid Mesoporous

B. Alonso, P. Innocenzi, L. Malfatti, F. Fayon

B. Alonso, F. Fayon, D. Massiot, H. Amenitsch, L. Malfatti, T. Kidchob, S. Costacurta, P. Innocenzi
 "Hybrid organic-inorganic mesostructured membranes: interfaces and organization at different length scales"
 J. Phys. Chem. C 114 11730-11740 2010

SUPRAMOLECULAR CHEMISTRY

A hydrophobic haven for base pairs

Hydrogen-bonded dimers of one and two base-pair nucleotides can be stabilized inside the hydrophobic pocket provided by self-assembled molecular cages. The results could bring DNA-based computing a step closer to reality.
Jim A. Thomas

NATURE CHEMISTRY | VOL 1 | APRIL 2009

G.Arrachart, C.Carcel, J.J.E.Moreau, G.Hartmeyer, B.Alonso, D.Massiot, G.Creff, J.L.Bantigniese, P.Dieudonnee, M.Wong Chi Man, G.Althoff, F.Babonneau, C.Bonhomme
J. Mater. Chem. **18** 392-399 (2008)

M.Deschamps, F.Fayon, S.Cadars, A.-L.Rollet, D.Massiot
Chem. Chem. Phys. **13** 8024 - 8030 2011

S.Cadars, G.Layrac, C.Gérardin, M.Deschamps, J.R.Yates, D.Tichit, D.Massiot
"Identification and Quantification of Defects in the Cation Ordering in Mg/Al Layered Double Hydroxides" *Chem. Mater.* **23** 2821-2831 2011

Phosphonate (B.Bujoli – Nantes)

D.Massiot, B.Alonso, F.Fayon, F.Fredoueil and B.Bujoli 'New NMR developments for structural investigation of proton bearing materials at different length scales.' *Solid State Sciences* 3 11-16 (2001)

D.Massiot, F.Fayon, M.Deschamps, S.Cadars, P.Florian, V.Montouillout, N.Pellerin, J.Hiet, A.Rakhmatullin, C.Bessada 'Detection and use of small J couplings in solid state NMR experiments.'

Comptes Rendus de Chimie 13 117-129 2010

F.D.Sokolov, M.G.Babashkina, F.Fayon, A.I.Rakhmatullin, D.A.Safin, T.Pape, F.E.Hahn
 "Novel Bicyclic Hexanuclear Copper(I) Aggregate. Structure and Solid State ^{31}P CPMAS NMR Spectra of $[(\text{Cu}3\text{L}3)2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ Complexes of N -(diisopropoxythiophosphinyl)- N' -phenylthiourea (HL)"
 J. Organomet. Chem. 694 167-172 2009

A multi level system of transitions

$2I+1$ energy levels, $2I$ single quantum transitions

1^{st} order quadrupolar interaction

$$H_Q^{(1)} = C_Q \sqrt{\frac{1}{6}} A_{20}^Q [3I_z^2 - I(I+1)]$$

2^{nd} order quadrupolar interaction

$$H_Q^{(2)} = \frac{C_Q^2}{2\omega_0} \left[A_{2-1}^Q A_{21}^Q \{4I(I+1) - 8I_z^2 - 1\} + A_{2-2}^Q A_{22}^Q \{2I(I+1) - 2I_z^2 - 1\} \right]$$

$$H_{\text{Zeeman}} \gg H_Q$$

$$v_{<m,m-1>} = v_0 + \frac{1}{2}(1-2m)v_Q \left(\frac{3\cos^2\beta - 1}{2} - \frac{\eta}{2}\sin^2\beta \cos 2\alpha \right)$$

E. Sclan, C. Magnenet, D. Massiot and C. Sanchez 'Surface and bulk characterisation of titanium oxo clusters and nanosized titania particles through ^{17}O solid state NMR.' *J. Mater. Chem.* **9** 2467-2474 (1999)

Second order Quadrupolar interaction

- ⇒ Second order effect implies a **shift of the line (isotropic shift)** plus a shape.
- ⇒ **All transitions** exhibit second order effects
- ⇒ Second order quadrupolar effects are scaled by the principal field.
- ⇒ Usually **only central transition** $\langle -1/2, 1/2 \rangle$ can be seen for powdered samples.

$$\nu_{\langle m, m-1 \rangle} = \nu_0 + \nu_{\langle m, m-1 \rangle}^{\text{iso}(2)} + \nu_{\langle m, m-1 \rangle}^{(2)}(\alpha, \beta, \gamma)$$

$$\nu_{\langle m, m-1 \rangle}^{\text{iso}(2)} = -\frac{I(I+1) - 3 - 9m(m-1)}{30} \frac{\nu_Q^2}{\nu_0} \sqrt{1 + \frac{\eta^2}{3}}$$

First order $H_1 \ll H_z$

$$\nu_{<m,m-1>} = \nu_0 + P_2(\cos\theta) \frac{(1-2m)}{2} \nu_Q C_{\alpha,\beta} + \sum_{n=1}^2 A_n e^{-i(n\omega_r t + \phi)}$$

Second order $H_1 < H_z$

$$\nu_{<m,m-1>} = \nu_0 + \sum_{l=0,2,4} C_{m,l}^1 B_l^{(2)} P_l(\cos\theta) + \sum_{n=1}^4 A_n^{(2)} e^{-i(n\omega_r t + \phi)}$$

Spin 5/2 - quadrupolar

Static

MAS

DOR

²⁷Al CaAl₂O₄ 6 sites

Adapted from Kentgens et al. *Solid State NMR*, 3 315 (1994)

To extract quantitative data from the simulation of multisited systems the excitation regime must be known.

➤ A linear regime of excitation (independent of ν_Q) is only possible for small pulse angles (Freude, Man...).

$$\alpha < \pi/2(2I+1)$$

$$\alpha < \pi/8 \text{ for } I=3/2$$

$$\alpha < \pi/12 \text{ for } I=5/2$$

Central
Transition
 $I=3/2$
(null offset)

$\nu_Q \ll \nu_1$ non selective regime (liquid like) sine behavior of the whole system of transitions.

Solid Quadrupolar Echo $\pi/2_{(x)} - \tau - \pi/2_{(y)} - \text{acqu}$

$\nu_Q \sim \nu_1$ intermediate regime, non pure sine behavior, excitation of multiple quanta.

multiquanta excitation $\theta_1 - \tau - \theta_2 - \text{acqu}$

$\nu_Q \gg \nu_1$ selective regime, the central transition can be approximated as an isolated fictitious spin 1/2 with a nutation frequency of $(I+1/2)\nu_1$.

Hahn-Echo - $\pi/2 - \tau - \pi - \text{acqu}$

Central Transition - Hahn (whole) Echo

^{71}Ga ($I=3/2$) in $\beta\text{-Ga}_2\text{O}_3$

- Signal is acquired from $-\infty$ to $+\infty$ (beginning null, ending null).
- Gain of up to $2^{1/2}$ in signal to noise (negative and positive time of the echo).
- Time shift is retrieved from first order phase (shift in time).
- Imaginary part (odd) is null. Phasing can be carried out automatically or by adjusting the imaginary part to null (phase 0 and phase 1).
- Magnitude spectrum is not distorted

Usefull for very wide spectra when the loss in intensity (due to τ) is minimum with short lasting FIDs

D.Massiot, I.Farnan, N.Gautier, D.Trumeau, A.Trokiner, J.P.Coutures

"A ^{71}Ga and ^{69}Ga study of $\beta\text{-Ga}_2\text{O}_3$: resolution of four fold and six fold coordinated Ga sites in static conditions." *Solid State NMR* 4 241-248 1995

First order $H_1 \ll H_z$

$$\nu_{<m,m-l>} = \nu_0 + P_2(\cos\theta) \frac{(1-2m)}{2} \nu_Q C_{\alpha,\beta} + \sum_{n=1}^2 A_n e^{-i(n\omega_r t + \phi)}$$

Second order $H_1 < H_z$

$$\nu_{<m,m-l>} = \nu_0 + \sum_{l=0,2,4} C_{m,l}^1 B_l^{(2)} P_l(\cos\theta) + \sum_{n=1}^4 A_n^{(2)} e^{-i(n\omega_r t + \phi)}$$

¹⁷O DAS in SiO₂ crystalline Coesite

P.Grandinetti & al. *J. Phys Chem Soc* 1995

L. Frydman & al. *ENC 1995, Boston, J. Am. Chem Soc* 1995, 117, 5367

$$\Omega_p = - \sum_{l=0,2,4} C_l^p A_l(\theta, \varphi) P_l(\cos\beta)$$

- technically challenging
- hop time is long (~30ms) diluted spin systems (Zwanziger ¹¹B)
- Valid for large couplings CT as a fictitious spin 1/2 (Baltisberger, Grandinetti)
- ¹⁷O, ⁸⁷Rb, ¹¹B (diluted), ⁷¹Ga
- easy to implement, lots of different excitation (nutation, RIACT, amp. modulation, freq. sweep...)
- suitable for abundant nuclei (²⁷Al)
- Intermediate couplings : needs high rf powers ?
- ²⁷Al, ²³Na, ¹⁷O, ⁸⁷Rb, ¹¹B, ⁷¹Ga
- accurate MAS angle (1/100°) and spinning rate
- suitable for abundant nuclei (²⁷Al)
- Intermediate to large couplings
- ²⁷Al, ²³Na, ¹⁷O, ⁴⁵Sc, ⁹³Nb

Different spreading of the spectrum & scaling of δ_{iso} CS/2nd Order Quad. shift

Site	MQ-MAS			Baltisberger <i>et al.</i> (1992)		
	δ_{iso}^{CS} (ppm)	C_Q (MHz)	η_Q	δ_{iso}^{CS} (ppm)	C_Q (MHz)	η_Q
#1	-31.3	1.79	0.55	-30.9	1.85	0.48
#2	-26.6	1.75	0.18	-26.2	1.83	0.12
#3	-28.5	1.99	0.91	-26.8	2.07	1.0

D.Massiot, B.Touzo, D.Trumeau, J.P.Coutures, J.Virlet, P.Florian, P.J.Grandinetti
 "Two-dimensional Magic-Angle Spinning Isotropic Reconstruction Sequences for Quadrupolar Nuclei."
 Solid State NMR 6 73-83 1996

Isotropic Part of Interaction

- small but remain when spinning fast @ MAS
- need long T₂' to develop
- Pulse sequence (liquid like) are simple and involve few rf powers
- Usually ignored in most inorganic solids

Anisotropic Interaction

- larger but need to be reintroduced
- suffer limitation with spinning rate or spin lock possibilities – T_{1ρ} for quadrupoles
- Pulse sequence may be complex and often involve large rf powers
- Hard to transpose to quadrupoles

¿ Applicability to amorphous or disordered systems ?

¿ Applicability to spin system involving quadrupoles ?

SnP_2O_7

MP_2O_7 family : model of negative thermal expansion materials

Dipolar DQ/SQ spectrum

Refocused J-INADEQUATE

Simplification of the J-mediated correlation
108 different P sites (54 pairs) P2_1 or Pc space groups

F.Fayon, I.J.King, R.K.Harris, R.B.K.Gover, J.S.O.Evans, D.Massiot

"Characterization of the room temperature structure of SnP_2O_7 by ^{31}P through-space and through-bond NMR correlations spectroscopy."
Chem. Mater. 15 2234-2239 2003

D.Massiot, F.Fayon, B.Alonso, J.Trebosc, J.P.Amoureux

Chemical bonding differences evidenced from J coupling in solid state NMR experiments involving quadrupolar nuclei.
[J. Magn. Reson. 164 165-170 \(2003\)](#)

D.Massiot, F.Fayon, B.Alonso, J.Trebosc, J.P.Amoureux
Chemical bonding differences evidenced from J coupling in solid state NMR experiments involving quadrupolar nuclei.
J. Magn. Reson. **164** 165-170 (2003)

AlPO₄ HMQC – figure 2

D.N.Shykind, J.Baum, S.B.Liu, A.Pines JMR 76 149-154 1988 – K. Saalwachter et al. 2007
 M.Deschamps, F.Fayon, J.Hiet, G.Ferru, M.Derieppe, N.Pellerin, D.Massiot
 "Spin-counting NMR experiments for the spectral editing of structural motifs in solids"
 Phys. Chem. Chem. Phys. 10 1298-1303 2008

AlPO_4 Berlinite

normalized

IS_4 "liquid" like spin system

$$J_1 = J_2 = 25.9 \text{ Hz} \text{ \& } J_3 = J_4 = 23.4 \text{ Hz}$$

(including the residual dipolar contribution due to the offset in the spinning angle)

M.Deschamps, F.Fayon, J.Hiet, G.Ferru, M.Derieppe, N.Pellerin, D.Massiot, *Physical Chemistry Chemical Physics* 10 1298-1303 2008

100% ^{29}Si Anorthite Glass

T_2'
(measured as the decay
of the sum of each
nQ pathway)

35ms

Scalar Coupling

Dipolar

16ms

Static

2ms

M.Deschamps, F.Fayon, J.Hiet, G.Ferru, M.Deriette, N.Pellerin, D.Massiot, *Physical Chemistry Chemical Physics* 10 1298-1303 2008

$(\text{PbO})_{0.61}(\text{P}_2\text{O}_5)_{0.39}$ glass

F. Fayon, I.J. King, R.K. Harris, J.S.O. Evans, D. Massiot *Comptes Rendus de Chimie* 7 351-361 (2004)
F.Fayon, C.Roiland, L.Emsley, D.Massiot, *Journal of Magnetic Resonance* 179 50-58 (2006)

TGIR-RMN

TRÈS GRANDES INFRASTRUCTURES DE RECHERCHE

[Submit a proposal >](#)

[Log into the TGIR-RMN intranet >](#)

Fédération TGE RMN Très Hauts Champs - FR3050 CNRS

connecté comme *Dominique Massiot* | [Déconnexion](#)

FR3050 CNRS
Ministère de la Recherche
CEA

Présentation

Projet Dépot/Gérer...

Users Meeting

Laboratoires

Publications...

Contact

Intranet

Admin

[Home](#)

Présentation Site CNRS

High Field NMR

Appel à projets

Spectromètre RMN 1GHZ

Inauguration le 12 Octobre 2009 (communiqué de presse du CNRS)
du premier spectromètre RMN haute résolution à 1GHz (BRUKER)
au monde installé au CRNM à Lyon. Cet instrument d'exception sera
bientôt ouvert aux utilisateurs du TGE RMN Très Hauts Champs.
contacts : Lyndon Emsley

Publications récentes

1 2 3 4 5 6 7 8 9 10 ...

C.M.Morais, V.Montouillout, M.Deschamps, D.Iuga, F.Fayon, F.A.A.Paz, J.Rocha, C.Fernandez, D.Massiot
1D to 3D NMR study of microporous aluminophosphate AlPO4-40
Magnetic Resonance in Chemistry **47** 942-947 (2009) [doi hal]

TGE : Orléans

Projet...

Appel à projets

Déposer un projet

Description de la procédure...

Suivre un projet

Remerciements

"Financial support from the TGE RMN THC FR3050 for conducting the research is gratefully acknowledged."

<http://www.tgir-rmn.org/> ou google "tgir-rmn"

RMN Solide à Hauts Champs : Orléans et Lille