Experiment and Modelling in Structural NMR

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NMR of amorphous materials

[04004]

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NMR of Amorphous Materials

First-Principles Calculations combined with MD simulations

Thibault Charpentier

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Context: High Level Nuclear Waste Materials Studies

NMR: powerful probe of the glass structure *at the atomic scale*

	% (w)
$^{29}\text{SiO}_2$	45.12
$^{27}\text{Al}_2\text{O}_3$	4.87
$^{11}\text{B}_2\text{O}_3$	13.92
$^{6,7}\text{Li}_2\text{O}$	1.97
$^{23}\text{Na}_2\text{O}$	9.78
^{43}CaO	4.01
$\text{ZrO}_2, \text{ZnO}, \text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, \text{NiO}, \text{Cr}_2\text{O}_3$	
Fission Products	10.35
Actinides	0.89
Platinoides	1.54

- ▶ Chemical composition $\Leftrightarrow$ **structure** $\Leftrightarrow$ Long term behavior
- ▶ How the glass accommodates the elements present (FP) in the spent fuel ?
- ▶ Study of simplified glass compositions
- ▶ ^{29}Si ($I=1/2$) + Quadrupolar Nuclei ^{17}O ($I=5/2$) ^{23}Na ($I=3/2$) ^{11}B ($I=3/2$) ^{27}Al ($I=5/2$) ...

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Motivation: Glass Structure

Solid State NMR of disordered materials: Structure

Question:
NMR spectrum

Glass Structure & Topological and Chemical Disorder ?

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A case of study: Incorporation of MoO_3 in silicate glasses

Glass (mol%)	SiO_2	Na_2O	MoO_3
SiO_2	100		
N23S77	77.5	22.5	
NSMo	59.4	39.8	0.8
N45S55	56.9	43.1	

- ▶ Revisiting Sodium Silicate Glass structure with advanced NMR tools (2D NMR, DFT-GIPAW, MD)
- ▶ Nuclear Waste Glass context: Mo low solubility element
- ▶ How does Mo incorporate into the Glass Structure ?

Alkali (alkaline-earth) molybdate crystals can form when $\text{MoO}_3 \geq 1\% \text{ mol}$

GCA 75 (2011) 2453-2469

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^{29}Si MAS NMR

NMR peaks reflective of a Gaussian distribution of δ_{iso} ($I=1/2$)

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^{29}Si MAS NMR:
Direct access to silicon $Q^{(n)}$ speciation

^{29}Si MAS NMR: Assignment & Interpretation

Database approach: Using crystalline compounds with known structure

Tetrahedral silicon $Q^{(n)}$ units in silicates

$$\delta_{iso} = f(\bar{\theta})$$

- DFT-GIPAW: $f()$ directly derived from vitreous structures ?
- $\Rightarrow$ MD simulations

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^{17}O and ^{23}Na MAS NMR

- ▶ ^{17}O NMR parameters, nuclear spin $I = 5/2$ (^{23}Na $I = 3/2$)
 - ▶ Isotropic chemical shift δ_{iso}
 - ▶ Quadrupolar coupling constant C_Q , asymmetry η ($I > 1/2$)
- ▶ Disordered solids:
 - ⇒ NMR parameter distribution $p(\delta_{iso}, C_Q, \eta)$ needed but unknown

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MQMAS NMR: Principles

$$\begin{aligned} \nu_{(1Q=CT)} &= \delta_{iso} + a_{iso}^{(1Q)} + \underbrace{a_2(1Q) R_{20}^{(MAS)}(\Omega) + a_4(1Q) R_{40}^{(MAS)}(\Omega)}_{=0(MAS)} \\ \nu_{(3Q=TQ)} &= 3\delta_{iso} + a_{iso}^{(3Q)} + \underbrace{a_2(3Q) R_{20}^{(MAS)}(\Omega) + a_4(3Q) R_{40}^{(MAS)}(\Omega)}_{=0(MAS)} \end{aligned}$$

Refocusing of the second-order quadrupolar broadening through a coherence transfer

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MQMAS NMR: the Shear Transformation

$$k = a_4(3Q)/a_4(1Q)$$

$$\nu_{(1Q=CT)} = \delta_{iso} + \underbrace{a_{iso}^{(1Q)} + a_4(1Q) R_{40}^{(MAS)}(\Omega)}_{C_{Q,\eta}}$$

$$\nu_{(ISO)} = \frac{\nu_{(3Q)} + k\nu_{(1Q)}}{1+k} = \alpha\delta_{iso} + \underbrace{a_{iso}^{(1Q,3Q)}}_{C_{Q,\eta}}$$

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MQMAS NMR with a distribution of NMR parameters

⇒ MQMAS NMR can *separate* the C_Q and δ_{iso} distributions

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^{23}Na MQMAS NMR in glasses

- Broad distribution reflective of a highly disordered environment
- What is the underlying $p(\delta_{iso}, C_Q, \eta)$? (analytical expression)
- How do we fit / process these data ?

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^{17}O MQMAS NMR in $\text{Na}_2\text{O-SiO}_2$ glasses

- Despite disorder, two lines are resolved
- BO (Si-O-Si): Quadrupolar features (covalent)
- NBO ($\text{Si-O}^- \text{Na}^+$): broader line, smaller C_Q

Data: GCA 75 (2011) 2453-2469

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The nature of NMR interactions

Second-rank tensors (i.e. matrices) define NMR interactions.

$$\vec{B}_{loc}^{(A)} = \mathbf{A} \vec{X} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \cdot \begin{pmatrix} X_x \\ X_y \\ X_z \end{pmatrix} \quad H_A = -\gamma_N \hbar \times \vec{I} \cdot \mathbf{A} \cdot \vec{X}$$

A	$\vec{X}$	Interaction	
1	$\vec{B}_0, \vec{B}_{RF}$	Zeeman interaction	
σ	$\vec{B}_0$	Magnetic Shielding	DFT
Q	$\vec{I}$	Quadrupolar interaction	DFT
D	$\vec{S}$	Dipolar interaction (spatial)	structure
J	$\vec{S}$	Indirect J couplings (through bond)	DFT

- DFT calculations output A in its *tensorial* (matrix) form relative to a *reference frame* (x, y, z) (crystal axes).
- Disorder $\Rightarrow$ Random Matrix Theory Approach

For Quadrupolar Interaction see:

G. Le Caër et al., J. Phys.: Condens. Mater. 10 (1998) 10715

G. Le Caër et al., J. Phys.: Condens. Mater. 22 (2010) 065402

NMR interactions for Quantum Chemists

The *effective* Hamiltonian

$$\begin{aligned} \mathcal{H}_S(\text{NMR}) = & -\hbar \sum_i \gamma_i \vec{I}_i (\mathbf{1} - \sigma) \vec{B}_0 + \sum_{i, |I_i| \geq 1} \vec{I}_i \mathbf{Q}_{ii} \vec{I}_i \\ & + \frac{\hbar^2}{2} \sum_i \sum_{j \neq i} \gamma_i \gamma_j \vec{I}_i (\mathbf{D}_{ij} + \mathbf{J}_{ij}) \vec{I}_j \end{aligned}$$

$\vec{B}_0$	External static magnetic field
$\vec{B}_{RF}(t)$	External radiofrequency magnetic field (NMR signal)
Internal Interactions	
$\vec{I}_i$	Nuclear spin operators $\vec{\mu}_i = \gamma_i \hbar \vec{I}_i$ (NMR)
σ	Nuclear magnetic shielding tensor (chemical shift) (DFT)
$\mathbf{D}_{ij}$	Nuclear magnetic dipolar coupling tensor (structure)
$\mathbf{J}_{ij}$	Indirect nuclear spin-spin coupling tensor (DFT)
$\mathbf{Q}_{ii}$	Nuclear quadrupolar coupling tensor ($ I_i \geq 1$) (DFT)

NMR Toolbox: Dipolar (spatial) correlations

Heteronuclear Multiple Quantum Correlation (HMQC)

$$\frac{\hbar^2}{2} \sum_i \sum_{j \neq i} \gamma_i \gamma_j \vec{I}_i (\mathbf{D}_{ij} + \mathbf{J}_{ij}) \vec{I}_j$$

NMR of **neighboring** nuclear spins (Si-O⁻Na⁺)

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NMR Toolbox: Through-bond (J) correlations

Heteronuclear Multiple Quantum Correlation (HMQC)

$$\frac{\hbar^2}{2} \sum_i \sum_{j \neq i} \gamma_i \gamma_j \vec{I}_i (\mathbf{D}_{ij} + \mathbf{J}_{ij}) \vec{I}_j$$

NMR of **bonded** nuclear spins (Si-O-Si)

⇒ Structure elucidation from atomic to molecular scale length

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First-principles calculations of NMR parameters.

Gauge Including Projector Augmented Wave **GIPAW**

C.J. Pickard & F. Mauri, PRB 2001

- ▶ DFT using GGA (PBE) or LDA
- ▶ Plane Wave Expansion ($e^{-ik \cdot r}$)
- ▶ Pseudopotential approximation of (frozen) core electrons
- ▶ Outputs NMR interactions in crystallographic axes frame.
 - ▶ Chemical shift (δ_{iso} , CSA)
 - ▶ Quadrupolar Interaction, EFG (C_Q, η)

- ▶ **Accuracy:** GIPAW outperforms all previous approaches
- ▶ No more need to construct clusters as in MO approaches
- ▶ Periodic Boundary conditions (solids)
- ▶ codes: CASTEP, Quantum Espresso, PARATEC

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Combining MD simulations with DFT NMR calculations

MD + DFT GIPAW

GIPAW: C.J. Pickard, F. Mauri PRB

2001; GIPAW+MD: J. Phys. Chem B

108 (2004)

amorphous silica

GIPAW: periodic solids:
no clusters approx.

J. Phys. Chem. C 113 (2009)

- ▶ MD simulations can (now) be compared to NMR experiments
- ▶ Effect of structural and chemical disorder on NMR
- ▶ NMR / structure (bond angle, distance, ...) relationships

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Molecular Dynamics Simulations & DFT Calculations

Glass ^(c)	Size	Composition	Cell side (Å) ^(a)	DFT vol. (Å ³) ^(b)
N23S77	300	Na ₄₆ Si ₇₇ O ₁₇₇	16.096	3887.0
N45S55	300	Na ₉₀ Si ₅₅ O ₁₅₅	15.832	3745.5

(a) (Cubic) cell side for the classical MD simulations, (b) After DFT geometry optimization +4.5%, (c) 5 models

- ▶ MD interaction potentials: $U_{ij}(r)$, $U_{ijk}(r)$...
Rigid ions q_i , Shell Model (O^{2-})
- ▶ DFT Structure relaxation & GIPAW (*frozen structure 0K*):
Plane-wave pseudopotential DFT (PBE GGA)¹ (vol+4.5%)
- ▶ NMR simulations & Analysis: fpNMR²

For the different interaction potentials, Radial pair distribution functions $\Rightarrow g_{ij}(r)$ (interatomic distances) in agreement with literature results

No differences from distances restraints ... but what about NMR ?

1. CASTEP, Quantum Espresso, 2. Phys. Chem. Chem. Phys. **12** (2010) 6054-6066 GCA 75 (2011) 2453-2469

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Effect of the force field: rigid ions versus shell model

- ▶ Silicate network is better reproduced with Shell model (& ^{17}O NMR)
- ▶ Oxygen polarization is mandatory for NMR-MD

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(MD) Analysis of NMR parameter distribution

MD-GIPAW results

- Introduction of a correlated (3D) NMR parameter distribution:

$$p(C_Q, \eta, \delta_{iso}) = G(C_Q - \bar{C}_Q) \times G(\eta - f_\eta(C_Q)) \times G(\delta_{iso} - f_\delta(C_Q))$$
- Linear correlations: $\bar{x}(C_Q) = f_x(C_Q) = a_x C_Q + b_x$ ($x = \delta_{iso}, \eta$)
- 8 adjustable parameters: $\bar{C}_Q, \sigma_{C_Q}, a_\eta, b_\eta, \sigma_{C_\eta}, a_{\delta_{iso}}, b_{\delta_{iso}}, \sigma_{C_{\delta_{iso}}}$
 $\Rightarrow$ 2D NMR needed !

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Modeling and Quantifying ^{17}O MQMAS Spectroscopy

- Specific model of **NMR parameter distribution**: $p(C_Q, \eta, \delta_{iso})$
- Simulation of the (full) MQMAS experiment for **quantitativeness**

JNCS 354 2008, GCA 75 2011

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Modeling and Quantifying ^{17}O MQMAS Spectroscopy

NBO calculated from ^{17}O agrees with

- ▶ with Si $Q^{(n)}$ speciation
- ▶ glass composition (NBO=Na⁺)

For Mo glass, ^{17}O corroborates formation of $[\text{MoO}_4]^{2-}$

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Variation of ^{17}O NMR parameters vs Na content

⇒ Allmost linear evolution of ^{17}O NMR parameters with Na content.
Not only NBOs are modified by Na
Both NBOs and BOs see Na.

A portion of N23S77 is shared with SiO₂. It can be attributed to $Q^{(4)}$ species.

Continuous variation of ^{17}O (BO) NMR parameters suggest an homogenous of network modifier distribution in the silicate network.

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^{17}O : relationships with structural factors

- ▶ Extraction of BAD and distances from NMR data (GCA 75 2011)

$\text{CN}_{\text{Na}}^{(a)}$	Si-O-Si	BO-Si	δ_{iso}	C_Q	η	BO-Na	BO-Na ^(b)
0	147	1.615	49.3	5.1	0.22		
1	141	1.631	53.1	4.8	0.38	2.67	2.67
2	138	1.649	60.3	4.6	0.37	2.70	2.53
3	136	1.662	66.8	4.4	0.39	2.77	2.47

(a) $r_c = 3.2 \text{ \AA}$; (b) shortest distance

- $\Rightarrow$ With Na closer to BO: Si-O-Si reduces and O-Si increases
- All observed (NMR) variations are indicative of *direct* Na-BO interactions

^{23}Na NMR

- ▶ $p(C_Q, \eta, \delta_{iso}) = GIM(C_Q, \eta) \times G(\delta_{iso})$ (Gaussian Isotropic Model)
- ▶ ^{23}Na δ_{iso} is a good probe of the **mean** Na-O distance ($g(r)$ reports the most probable $\Rightarrow$ Na-NBO):
N45S55: 2.54 Å, N23S77: 2.57 Å
- ▶ MD: both lengths, Na-BO and Na-NBO are modified by Na content

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Incorporation of MoO_3 — 59 SiO_2 - 40 Na_2O - MoO_3 glass

- ▶ ^{29}Si , ^{23}Na , and ^{17}O NMR: MoO_3 increases (dramatically) polymerization (also in borosilicate glasses)
- ▶ ^{17}O NMR reveals $[\text{MoO}_4]^{2-}$ units (only 1% mol. MoO_3 !!)

Geochim. Cosmo. Acta 75 2011

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MoO₃ in sodium silicate glasses

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Oxygen-17 MQMAS NMR: A More Complex Glass ...

60.4 SiO₂ - 15.3 B₂O₃ - 19 Na₂O - 5.2 CaO

Si/B random mixing

	Theory	¹⁷ O
Si-O-Si	34.1	35.6
Si-O-B	42.1	42.8
B-O-B	13.0	11.3
NBO	10.8	10.2

- ▶ Data in agreement with Si/B random mixing
- ▶ Evidence of Na/Ca mixing in depolymerized regions (DR)
- ▶ Ca is modifier (¹¹B NMR: BO₄⁻ → BO₃)

J. Am. Ceram. Soc 93 2010; J. Non Cryst. Solids 354 2008

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Topology of B₂O₃: closing the controversy

boroxol rings

$\Rightarrow S(q)$:
poor sensitivity to bond angles
 $\Rightarrow$ NMR:
high sensitivity to bond angles

Phys. Rev. Lett. **101** 2008

Reconstructing the Bond Angle Distribution (BAD)

Magn. Reson. Chem. **48** 2010

- ▶ Vitreous SiO₂-B₂O₃ system
- ▶ ¹¹B NMR parameter distribution of BO₃ units
- ▶ ¹¹B NMR (δ_{iso}) vs B-O-(B,Si) bond angles

Modeling and Quantifying MQMAS Spectroscopy

Composition effects in complex glasses.

A. Quintas et al. Appl. Magn. Reson. 32 (2007) 613-634

^{27}Al MQMAS NMR

AlO_4^- Charge Compensation Mechanism

The MD-GIPAW / NMR methodology