Glass Structure and First-Principles NMR

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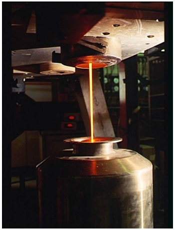
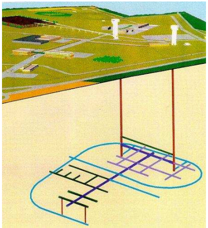
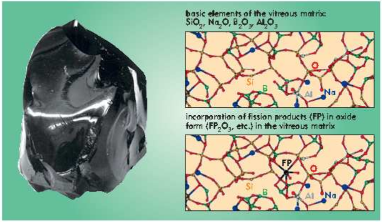
CEA / IRAMIS / SIS2M / LSDRM

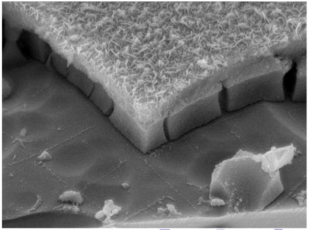
CECAM Tutorial - September 2009

Glass: a Nuclear Waste Storage Material

Long term behavior studies: structure and alteration





R7T7 & SON68 Glasses

A complex borosilicate glass comprising more than 30 oxides

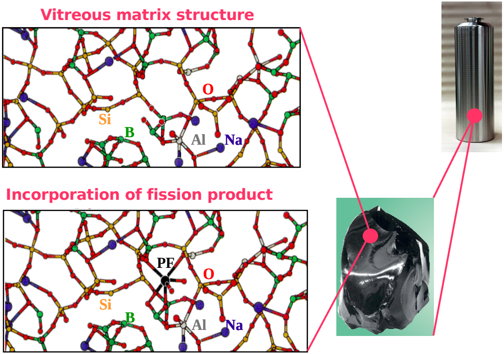
oxide	% (w)
$^{29}SiO_2$	45.12
$^{27}Al_2O_3$	4.87
$^{11}B_2O_3$	13.92
$^{6,7}Li_2O$	1.97
$^{23}Na_2O$	9.78
^{43}CaO	4.01
ZrO_2	0.99
ZnO	2.48
Fe_2O_3	2.89
P_2O_5	0.28
NiO	0.41
Cr_2O_3	0.50
Fission Products	10.35
Actinides	0.89
Platinoides	1.54

For Solid State NMR studies:
Simplified Composition
3-8 oxides
NMR Probes

^{11}B ^{27}Al ^{29}Si ^{23}Na ^{43}Ca $^{6,7}Li$ ^{17}O

NMR Structural studies

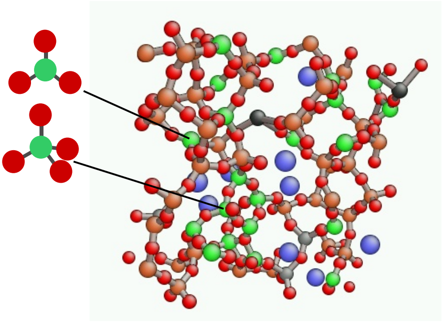
Probing the glass structure at the atomic scale



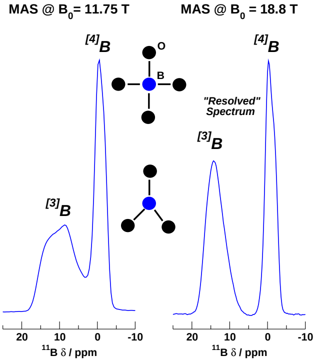
- Glass accommodates the elements present in the spent fuel
- FP atoms are an integral part of the glass

Solid State Nuclear Magnetic Resonance Spectroscopy

Boron speciation in borosilicate glass



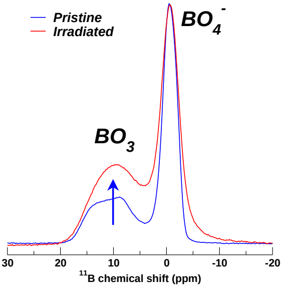
Identifying the structural units of the glass network

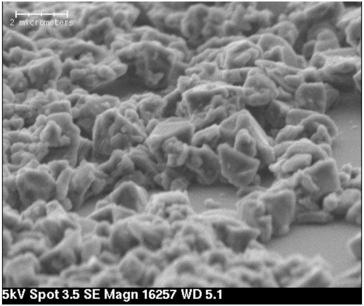


High Field MAS NMR:
Boron speciation resolved

Solid State Nuclear Magnetic Resonance Spectroscopy

Heavy Ion Damage: amorphisation of amorphous material ?

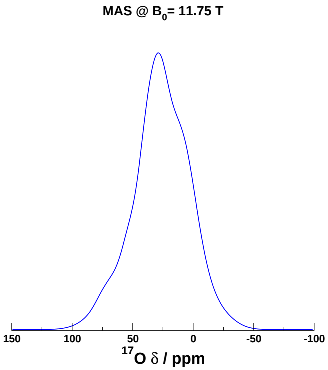




Coll. CEA/DEN/DTCD S. Peuget, J.M. Delaye

Oxygen Speciation in borosilicate glass

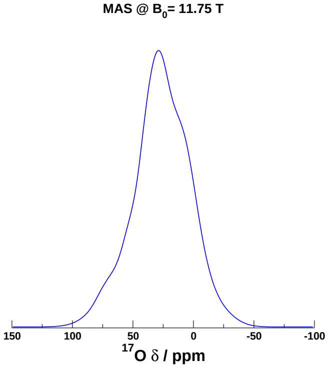
Reading the silicate network structure



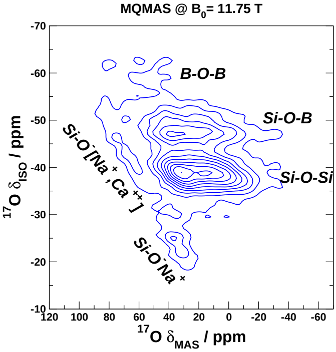
MAS *Unresolved*

Oxygen Speciation in borosilicate glass

Reading the silicate network structure



MAS *Unresolved*

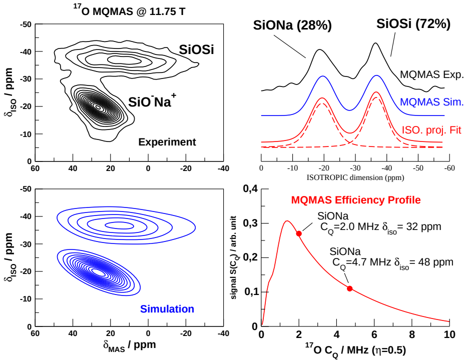


2D technique required: *MQMAS*

Modeling and Quantifying ^{17}O MQMAS Spectroscopy

Quantification & NMR Distribution

F. Angeli, T. Charpentier et al. JNCS 2008



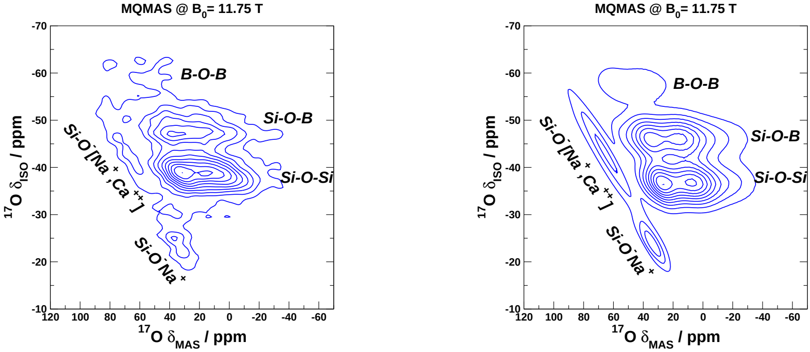
Uncorrelated model of NMR parameter distribution

$$p(C_Q, \eta, \delta_{iso}) = G(C_Q) \times G(\eta) \times G(\delta_{iso})$$

Oxygen Speciation in borosilicate glass

Reading the silicate network structure

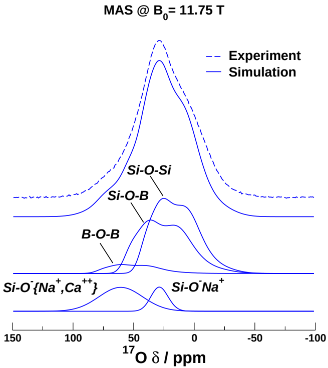
F. Angeli, T. Charpentier et al., JNCS 2008



Total Simulation of MQMAS spectroscopy

Oxygen Speciation in borosilicate glass

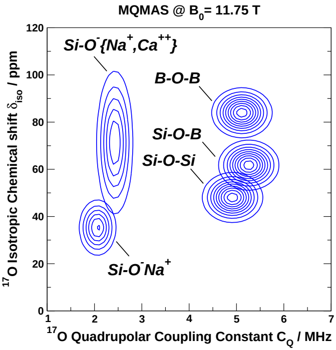
Quantifying the glass network structure



Glass Topology

- Bridging Oxygen Atoms:
  Si-O-Si, Si-O-B, B-O-B
  Glass homogeneity at nanoscale
- Non Bridging Oxygen: Si-O^-Na^+
  Glass Polymerization degree
- Non Bridging Oxygen:
  Si-$O^-(Na^+,Ca^{++})$
  Evidence of a Mixed Alkali - Alkaline Earth Effect

Quantifying glass topological disorder



Glass Topology

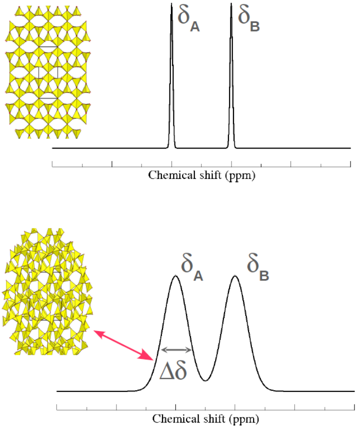
- Reconstruction of the NMR parameter distribution Π
- Correlating the *local disorder* to the NMR spectrum line shape ?
- Π(NMR) ⇒ Π(Structure) ?

NMR of disordered Materials

Modeling and Interpreting

A fundamental question:

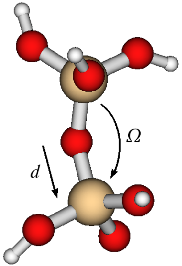
Correlating the local disorder to the NMR spectrum line shape

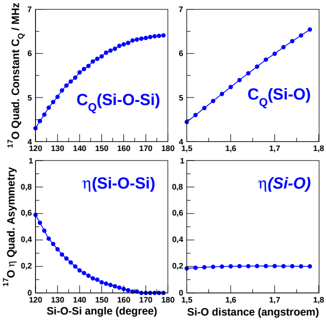


Understanding NMR / Structure relationships

Quantum Mechanical calculations: the Cluster Approach

$Si(OH)_3$-O-$Si(OH)_3$

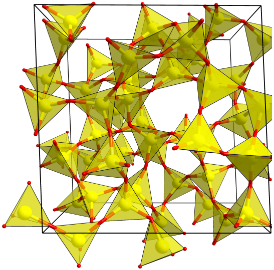


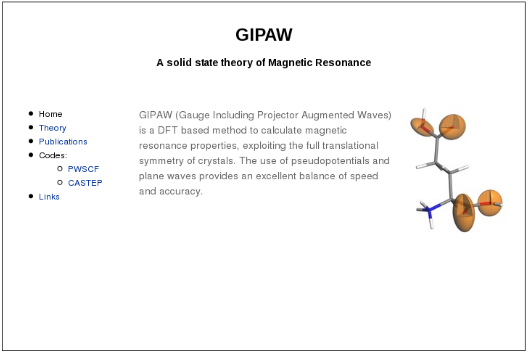


^{17}O C_Q and η_Q NMR parameters are allmost exclusively controlled by local properties: (Si-O-Si bond angle and Si-O bond length)

Combining MD simulations with fp NMR calculations

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





GIPAW

A solid state theory of Magnetic Resonance

- Home
- Theory
- Publications
- Codes:
  - PWSCF
  - CASTEP
- Links

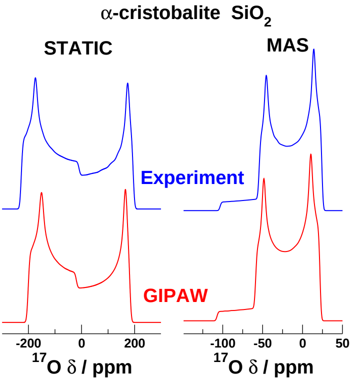
GIPAW (Gauge Including Projector Augmented Waves) is a DFT based method to calculate magnetic resonance properties, exploiting the full translational symmetry of crystals. The use of pseudopotentials and plane waves provides an excellent balance of speed and accuracy.

The GIPAW method

Gauge Including Projector Augmented Wave

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

- DFT using GGA (PBE) or LDA functionals.
- Plane Waves Expansion ($e^{-i\mathbf{k}.\mathbf{r}}$)
  - 3D FFT, Parallel Code
  - Periodic Boundary Conditions
- Pseudopotential approximation of core electrons
- GI-PAW
  - PAW: Reconstruction of the wave function *at* the nucleus
  - GI: Gauge Invariance

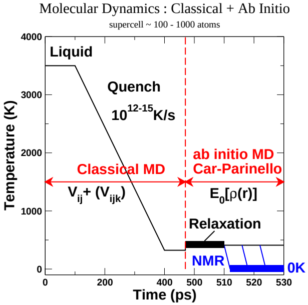


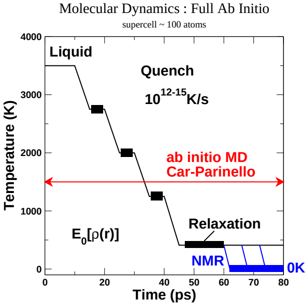
Exp.: Spearing et al. Phys. Chem. Minerals 1992.

Accuracy: GIPAW outperforms all previous approaches

Molecular Dynamics

MD-GIPAW Methodology





MD: Collaboration S. Ispas, P. Kroll, G. Ferlat, F. Mauri, J.M. Delaye

The controversy: Bond Angle Distribution in vitreous silica

Revisiting the interpretation of ^{17}O NMR data

PHYSICAL REVIEW B **70**, 064202 (2004)

Correlated structural distributions in silica glass

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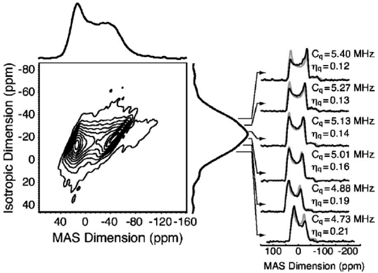
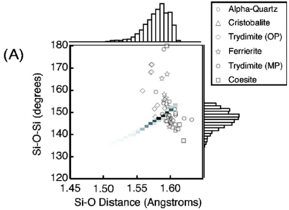
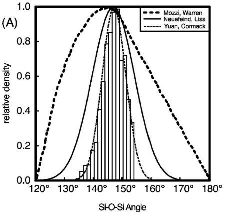
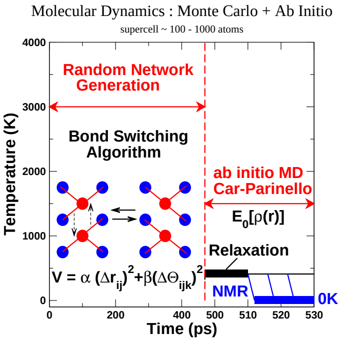






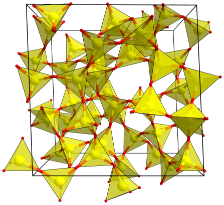
A Monte Carlo / MD Hybrid Approach

Modeling Glass Structure: Bond Switching Algorithm



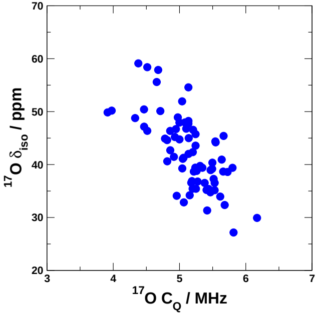
Defect Free Vitreous Silica

Continuous Random Network



Simulation of NMR Spectra

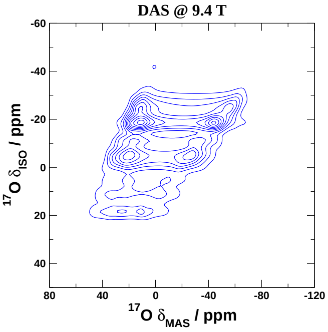
The simple approach

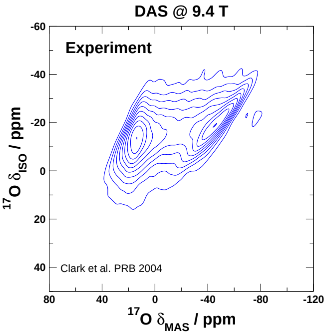


$$I(\vec{\nu}) = \sum_i I^i_{th}(\vec{\nu})$$

Simulation of NMR Spectra

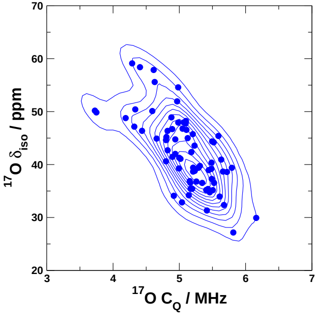
The simple approach





Simulation of NMR Spectra

Kernel Density Estimate Approach



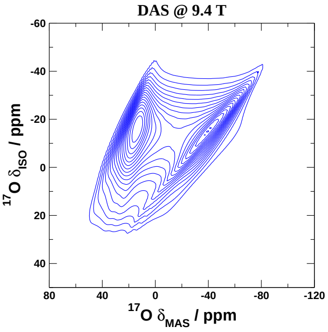
$$\{C_Q, \eta, \delta_{iso}\}_i \Rightarrow p\left(C_Q, \eta, \delta_{iso}\right)$$

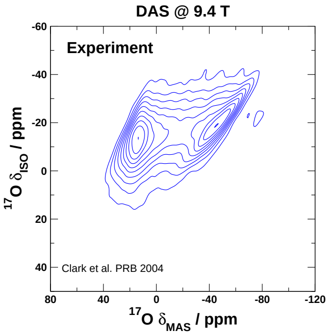
Kernel: $p(\mathbf{x}) = \sum_i \mathcal{K}_{H_i}\left(\mathbf{x} - \mathbf{x_i}\right)$

$$I\left(\vec{\nu}\right) = \int p\left(C_Q, \eta, \delta_{iso}\right) \times I_{th}\left(\vec{\nu}; C_Q, \eta, \delta_{iso}\right)$$

Simulation of NMR Spectra

Kernel Density Estimate Approach

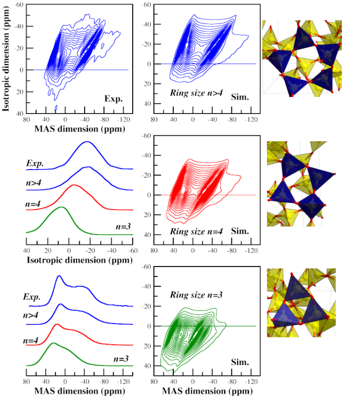




Glass Topology

The (small)-rings statistics

^{17}O NMR response of small rings



T. Charpentier, P. Kroll, F. Mauri, J. Phys. Chem C, in press.

Local structure: Ring Size	SiOSi degrees	^{17}O NMR parameters: C_Q MHz	η	δ_{iso} ppm
3	126.7 (4.1)	4.61 (0.35)	0.38 (0.15)	55.92 (7.85)
4	142.3 (10.9)	5.03 (0.39)	0.24 (0.13)	46.54 (6.42)
> 4	147.0 (12.2)	5.21 (0.41)	0.20 (0.12)	39.59 (6.55)
Experiment[a]		5.08 (0.37)	0.15 (0.04)	36.7 (4.3)

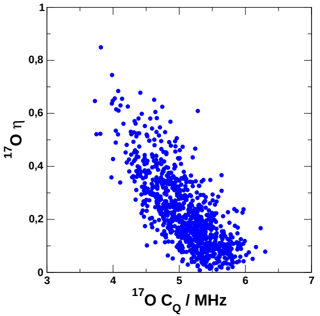
[a] Clark et al. PRB 2004

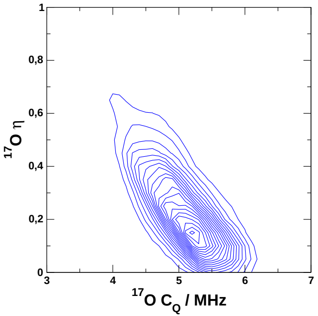
Local structure: Ring Size	SiOSi degrees	^{29}Si NMR parameters: δ_{iso} ppm	Ω_σ ppm	κ_σ
3	135.4 (12.4)	-97.97 (4.74)	31.27 (8.40)	0.10 (0.41)
4	144.0 (11.5)	-106.09 (5.52)	23.66 (8.25)	0.02 (0.40)
> 4	148.3 (12.3)	-110.31 (5.53)	17.50 (6.83)	-0.04 (0.41)
Experiment[a]		-111.2 (5.1)	n.a.	n.a.

[a] Clark et al. PRB 2004

Analysis of ^{17}O NMR parameter distribution

Kernel Density Estimate Approach

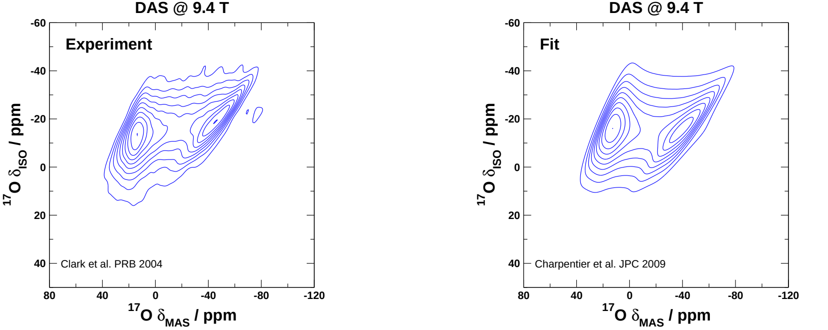




Introduction of a correlated 3D NMR parameter distribution:

$$p\left(C_Q, \eta, \delta_{iso}\right) = G(C_Q - \overline{C}_Q) \times G(\eta - f_\eta(C_Q)) \times G(\delta_{iso} - f_\delta(C_Q))$$

Quantitative Analysis of ^{17}O Experimental data



Experimental data can be well described in term of *disorder only*.

Interpretation of ^{17}O Experimental data

^{17}O NMR parameter distribution

	Charpentier et al. JPC 2009		Clark et al. PRB 2004	
	Mean	Std. dev.	Mean	Std. dev.
C_q	5.07 MHz	0.453 MHz	5.08 MHz	0.372 MHz
η_q	0.157	0.095	0.150	0.0414
δ_{iso}	36.5 ppm	7.55 ppm	36.7 ppm	4.30 ppm

Interpretation of ^{17}O Experimental data

^{17}O NMR parameter distribution

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δ_{iso}	36.5 ppm	7.55 ppm	36.7 ppm	4.30 ppm

Local geometry

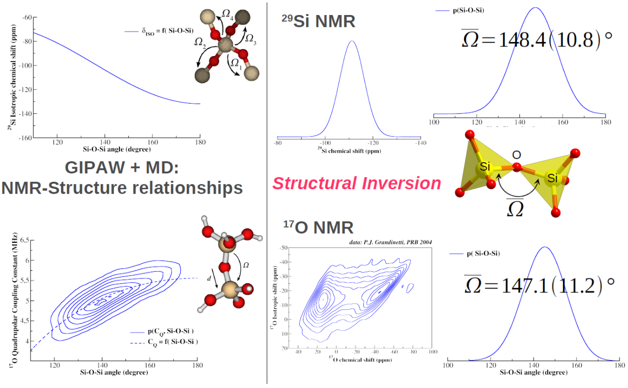
	JPC 2009		PRB 2004		Diffraction.	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
Si-O-Si	147.1°	11.17°	146.6°	3.78°	148.3°	7.5°
Si-O	1.60 Å	0.011 Å	1.58 Å	0.019 Å	1.61 Å	0.049 Å

Bond Angle Distribution (BAD)

T. Charpentier et al., J. Phys. Chem. C 2009

NMR / Structure relationships

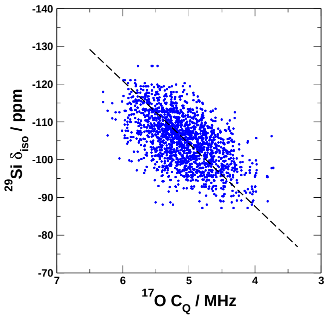
Reconstruction of the Bond Angle Distribution (SiOSi) from NMR data

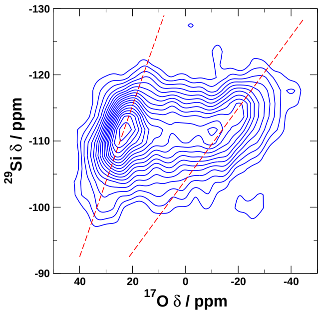


T. Charpentier, P. Kroll, F. Mauri, J. Phys. Chem C, in press.

Advanced NMR: Through Bond Correlation Spectroscopy

^{29}Si-^{17}O J-HMQC experiments. GIPAW J Calc. coll. J. Yates Oxford



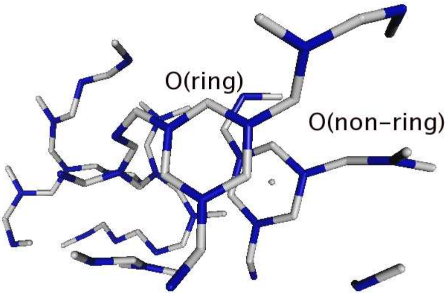


2D NMR enables the observation of spin pair ^{29}Si-^{17}O through the chemical bond (or through the space)

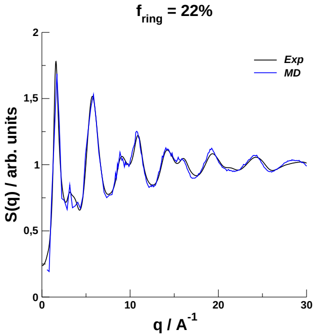
$\Rightarrow$ Observation of Bond Angle $\theta_i - \theta_{i+1}$ correlation . . .

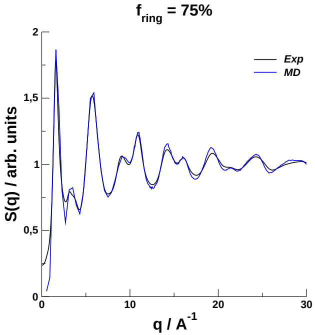
Topology of vitreous B_2O_3

G. Ferlat, T. Charpentier et al., PRL 2008



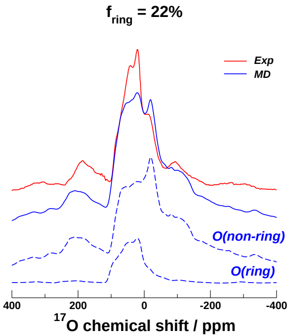
Topology of vitreous B_2O_3

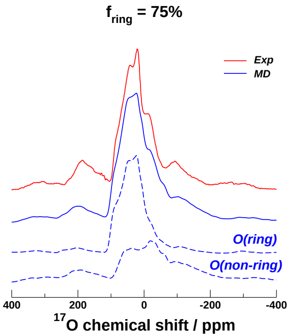




S(q): poor sensitivity to Bond Angle ?

Topology of vitreous B_2O_3





NMR: high sensitivity to Bond Angle

aiNMR: Perspectives

A new powerfull tools to get more insight into NMR data

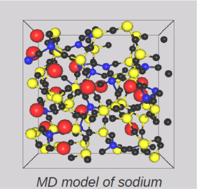
Structural studies of complex glasses (borosilicates, mixed alkali effect, Bioglass, ...)

Dynamical effects
vibration, diffusion ⇔ relaxation

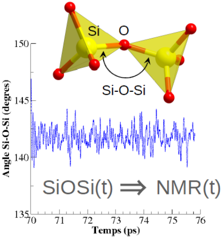
Data modelling of Glass (imitating bioNMR !)

Combining NMR constraints (from 1D, 2D, 3D) with diffraction and other spectroscopy (RAMAN, ...) to refine Glass structure models

NMR Driven Reverse Monte Carlo



MD model of sodium borosilicate glass



Acknowledgement

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