Structural Studies of Simplified Nuclear Wastes Glasses

Solid State NMR Methodologies for Probing Glass Structure

Thibault Charpentier

CEA / IRAMIS / SIS2M
Laboratory of Structure and Dynamics by Magnetic Resonance

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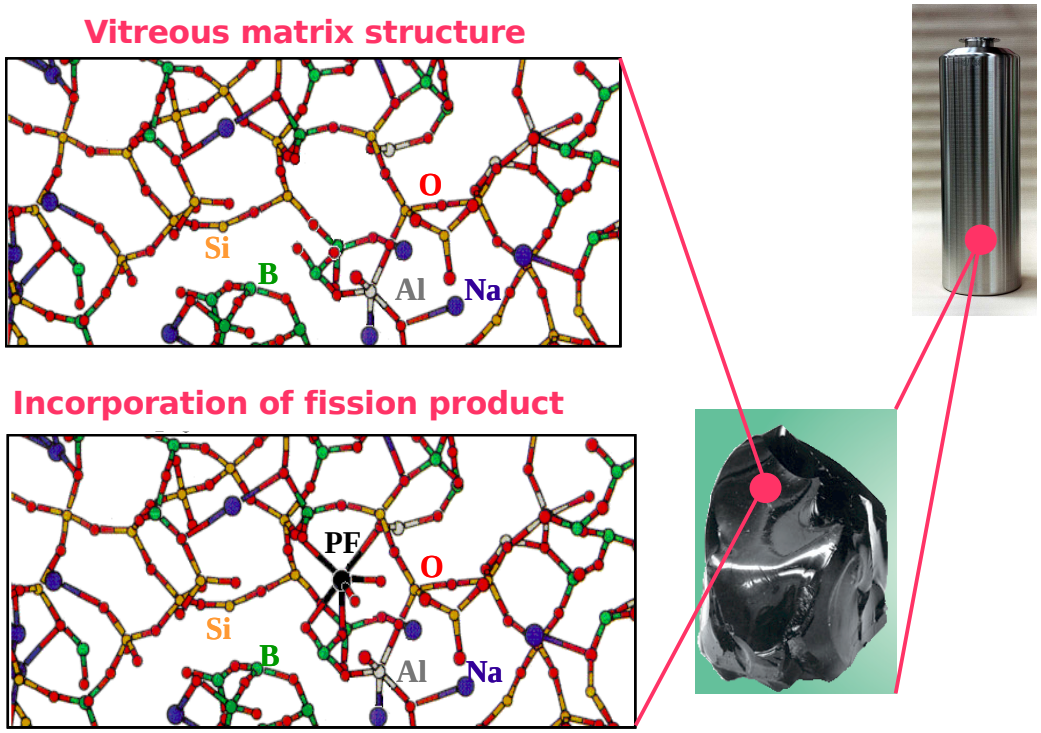
Solid State NMR Spectroscopy / Nuclear Waste Materials

Probing glass structure at the atomic scale — Long term behavior studies



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

R7T7 & SON68 Glasses

A complex borosilicate glass comprising more than 30 oxides

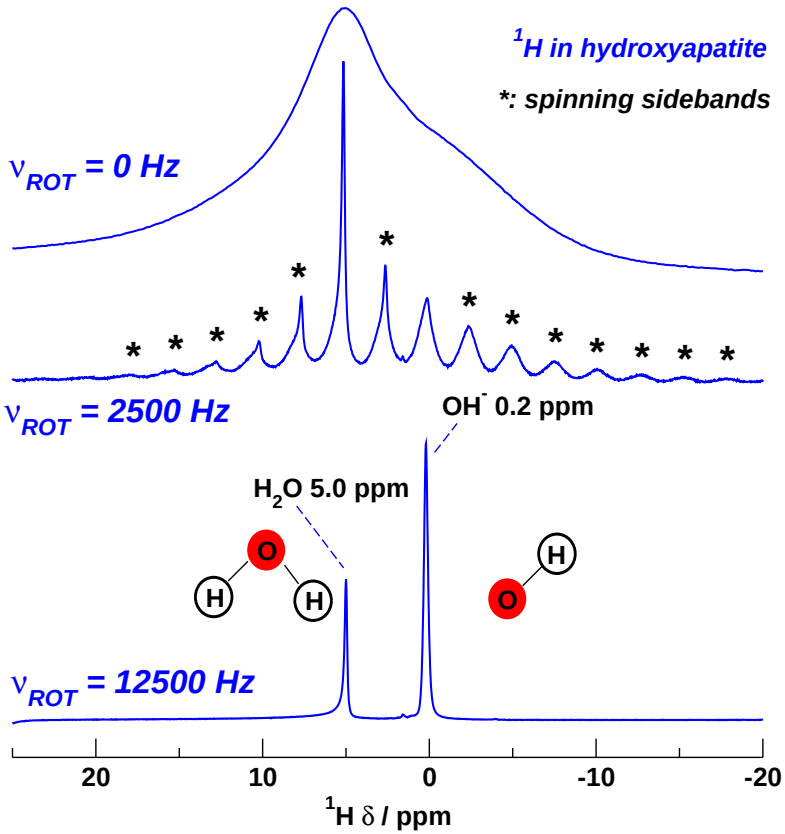
oxide	% (w)
$^{29}SiO_2$	45.12
$^{27}Al_2O_3$	4.87
$^{11}B_2O_3$	13.92
$^{6,7}Li_2O$	1.97
$^{23}Na_2O$	9.78
^{43}CaO	4.01
ZrO_2	0.99
ZnO	2.48
Fe_2O_3	2.89
P_2O_5	0.28
NiO	0.41
Cr_2O_3	0.50
Fission Products	10.35
Actinides	0.89
Platinoides	1.54

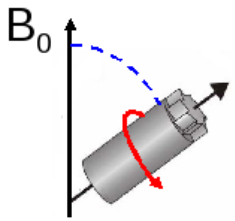
For Solid State NMR studies:
Simplified Compositions
3-8 oxides
NMR Probes

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

Solid State Nuclear Magnetic Resonance Spectroscopy

High Resolution: Magic Angle (Sample) Spinning

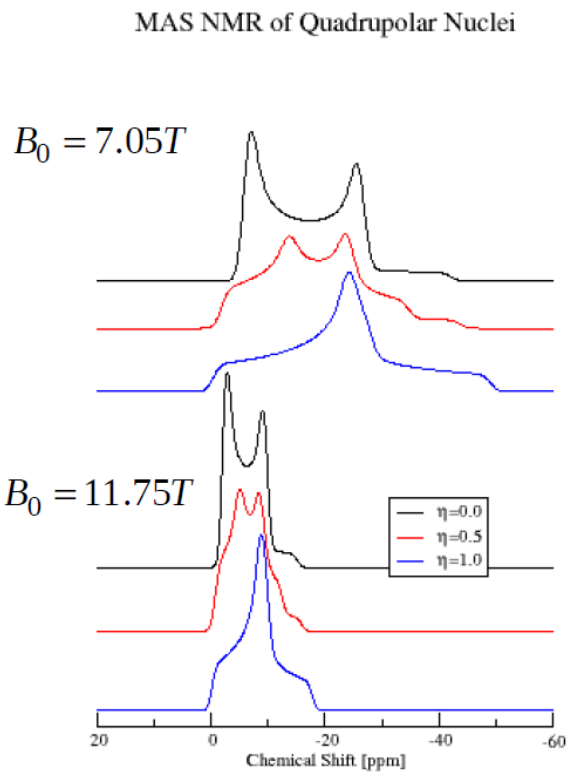


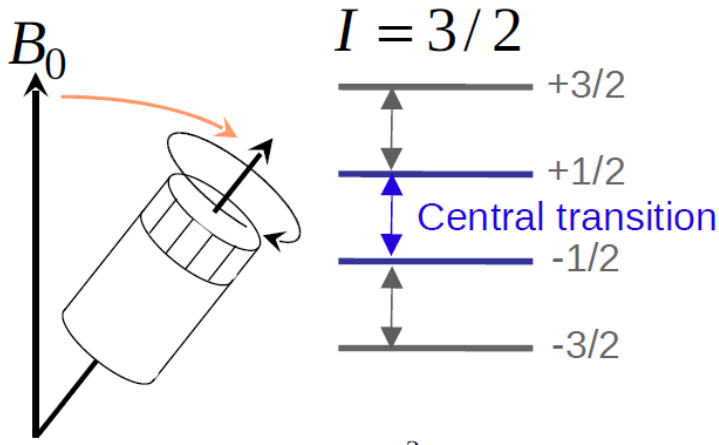


RMN MAS
(magic angle spinning)

High Resolution: NMR spectra with *narrow* lines.

MAS NMR of Quadrupolar Nuclei (I>1/2)





$$\text{chemical shift} = \delta_{iso} + \alpha \frac{P_Q^2}{\nu_0^2}:$$

δ_{iso} : isotropic chemical shift

$$\nu_0 = -\gamma B_0, \quad P_Q = C_Q \sqrt{1 + \eta^2/3}$$

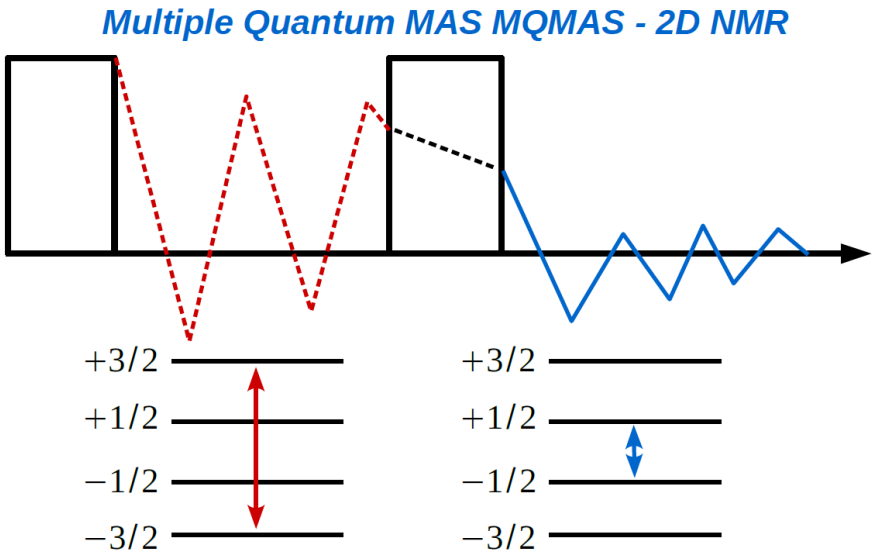
C_Q : quadrupolar coupling constant

η : quadrupolar asymmetry parameter

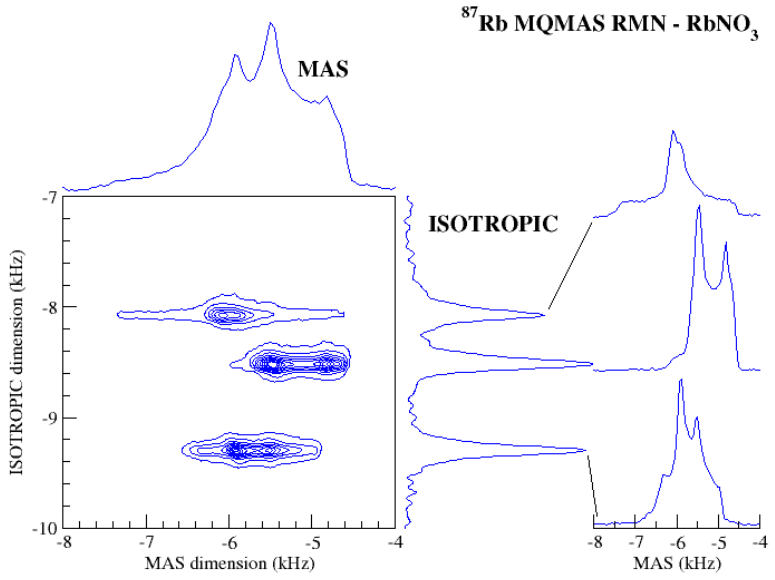
$$\text{For glasses (two fields)}: \delta_{1/2} = \langle \delta_{iso} \rangle + \frac{1}{\nu_0^2} \langle P_Q^2 \rangle$$

High Resolution NMR of Quadrupolar Nuclei

2D MQMAS spectroscopy

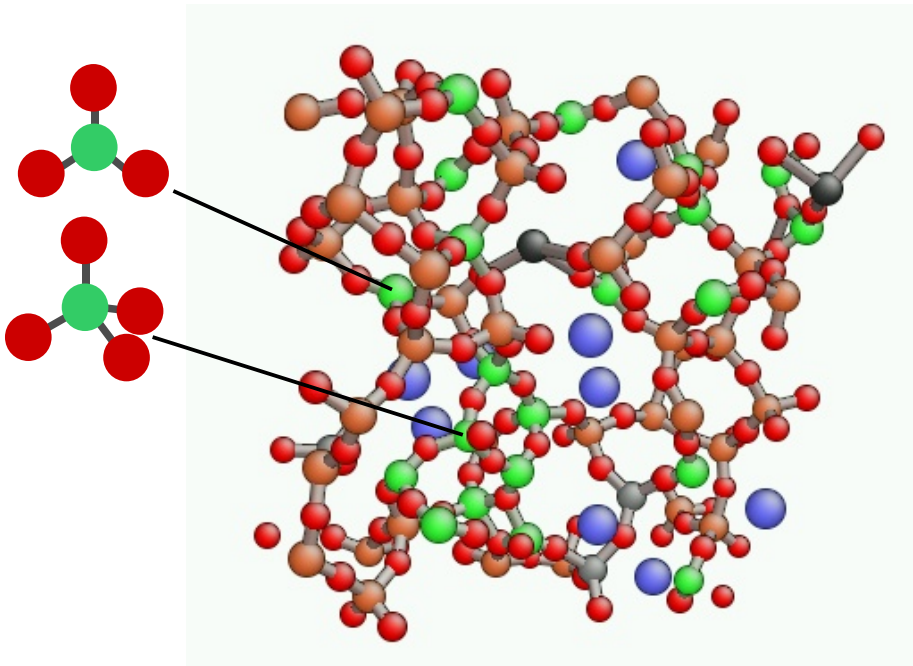


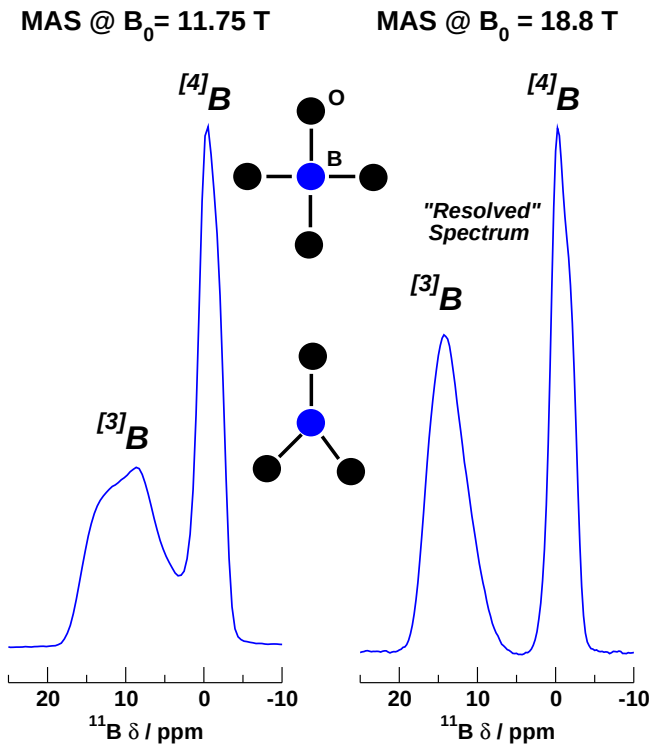
Indirection detection of a multiple quantum transition



^{11}B MAS NMR in Borosilicate Glasses

Direct access to boron speciation





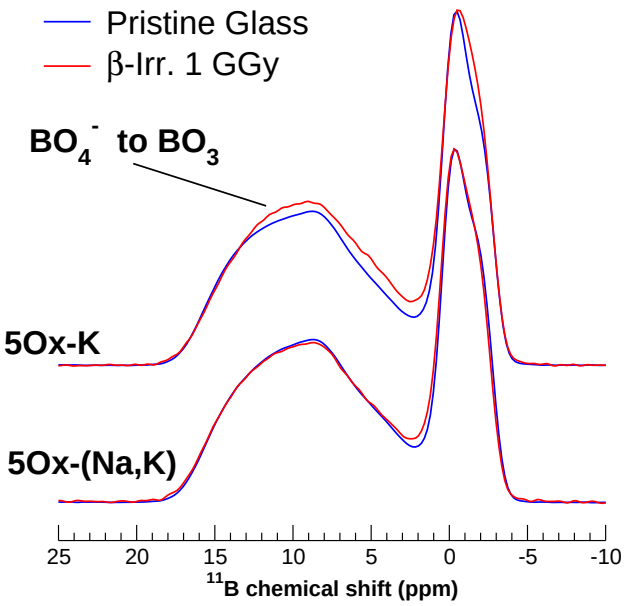
Identifying the structural units forming the glass network

High Field MAS NMR: Boron speciation resolved

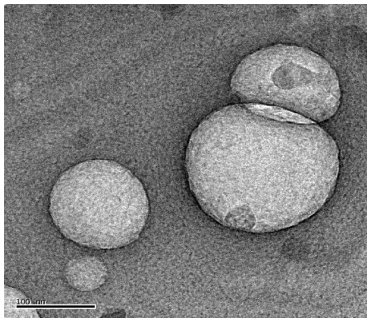
^{11}B MAS NMR at work

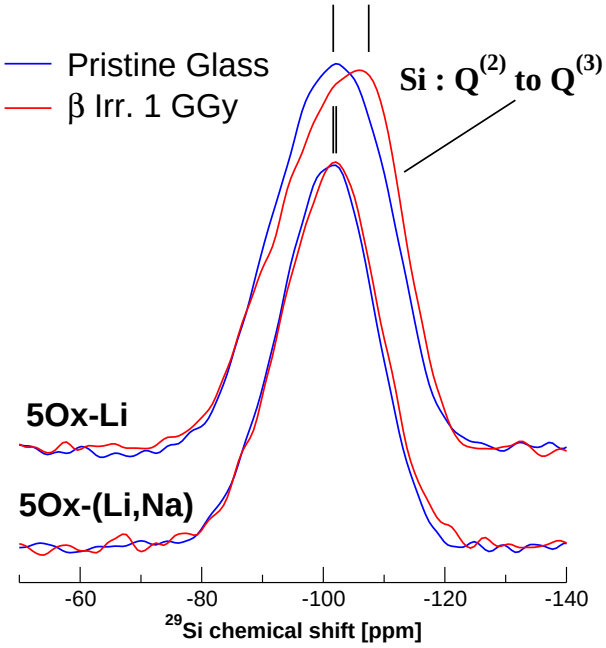
Alkali migration under β-irradiation

Mixed Alkali Effect



Oxygen Bubbles



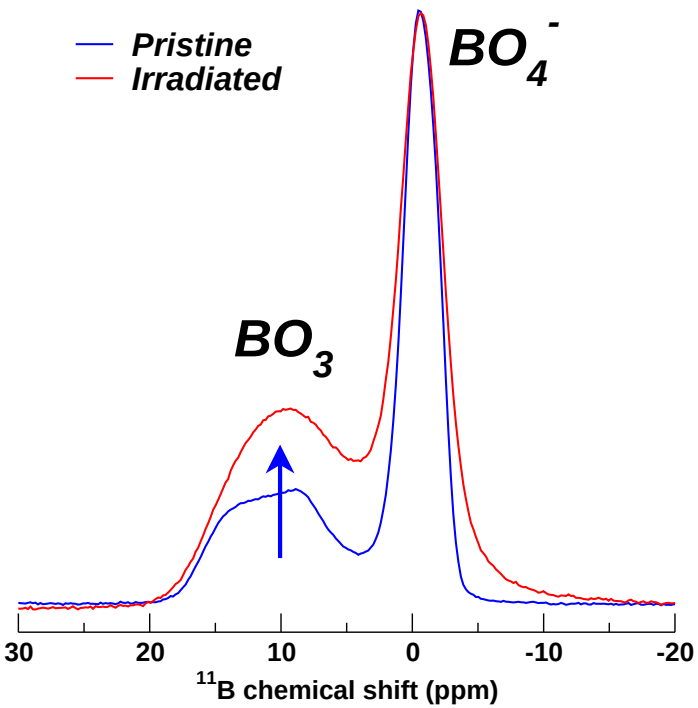


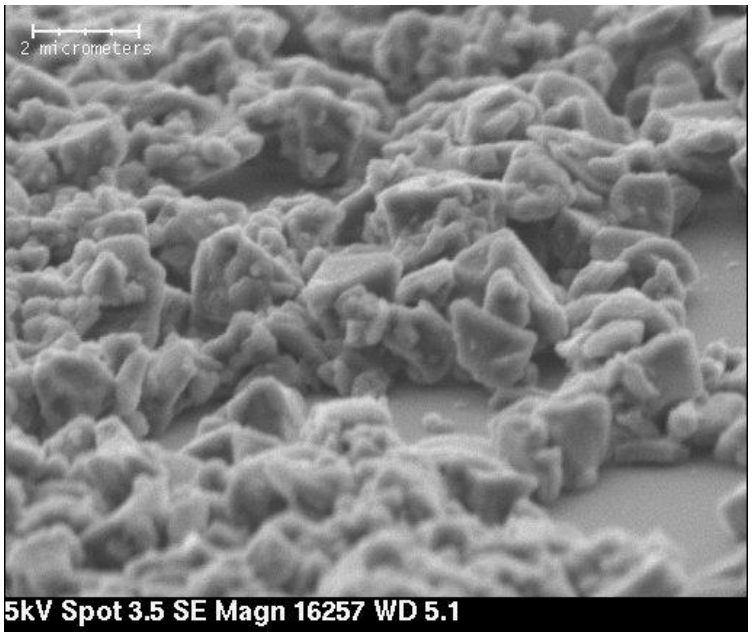
Selective Migration Mechanisms in Mixed-Alkali Borosilicate Glasses

N. Ollier et al., J. Non-Cryst. Solids 341, (2004), J. Phys. C: Condens. Matter 16 (2004), J. Appl. Physics (2006)

^{11}B MAS NMR at work

Heavy Ion Damage: amorphisation of amorphous material ?





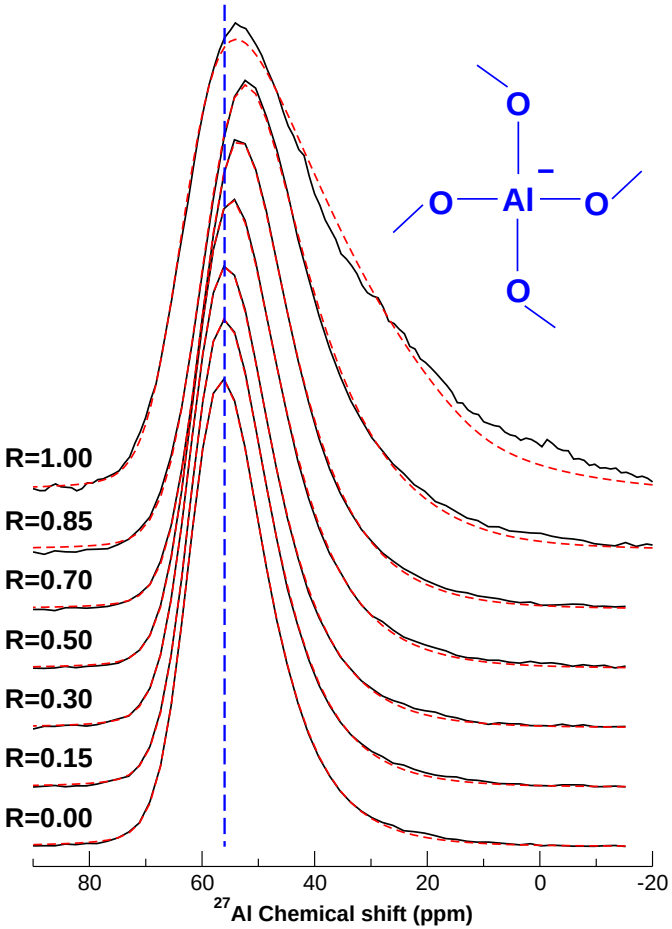
Coll. CEA/DEN/DTCD S. Peuget, J.M. Delaye

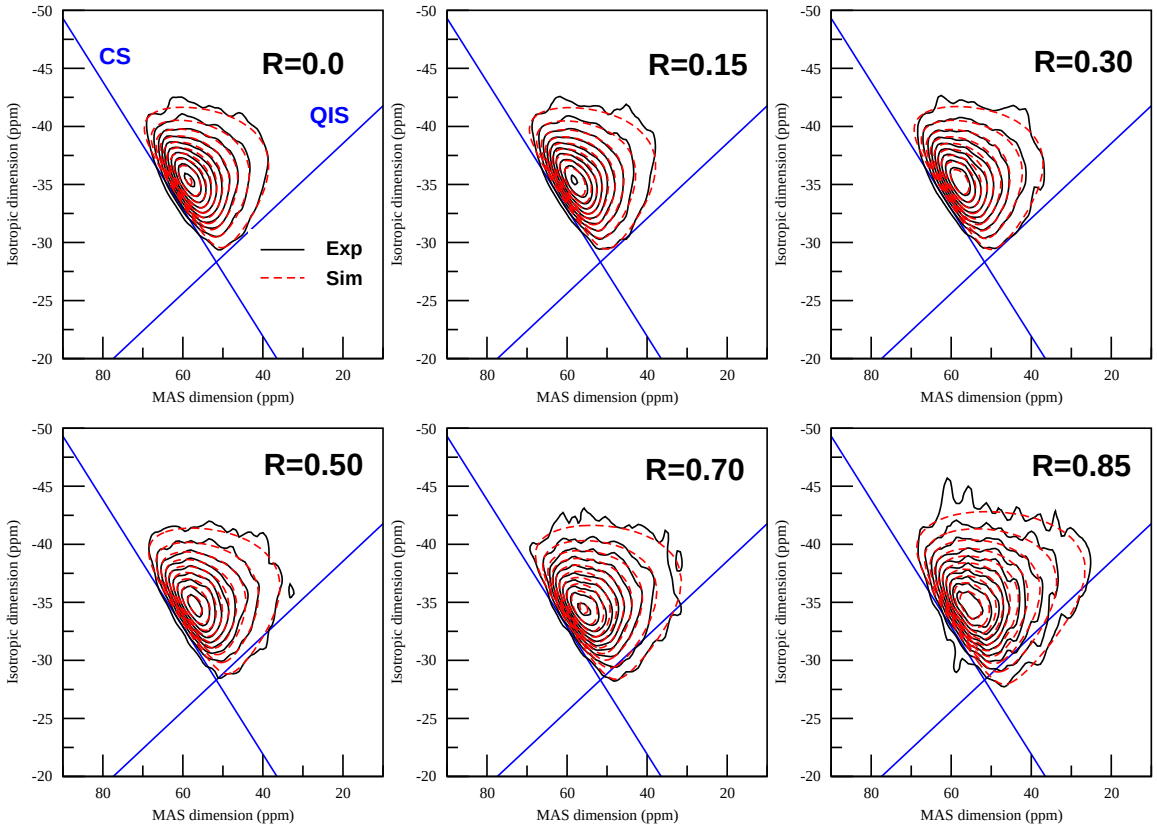
Modeling and Quantifying MQMAS Spectroscopy

Composition effects in complex glasses.

A. Quintas et al. Appl. Magn. Reson. 2007

62 SiO_2 - 9 B_2O_3 - 20 (**(1-R) Na_2O + R CaO**) - 3 Al_2O_3 - 2 ZrO_2 - 3.5 La_2O_3





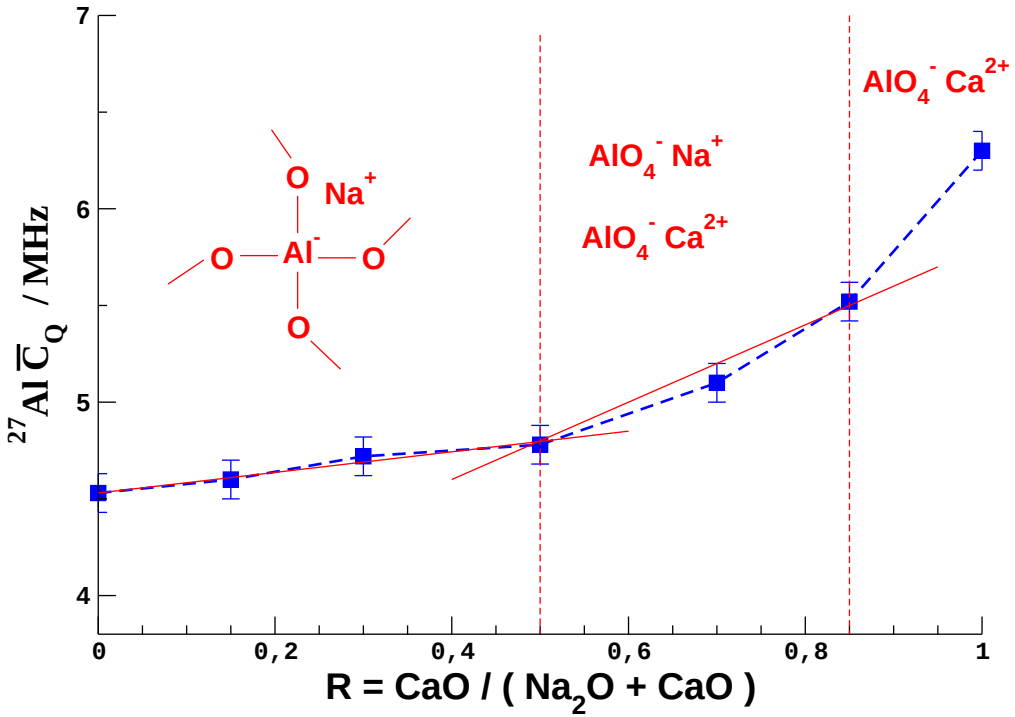
$\Rightarrow$ Getting more insights into AlO_4^- units charge compensation Mechanism

^{27}Al MAS NMR at work

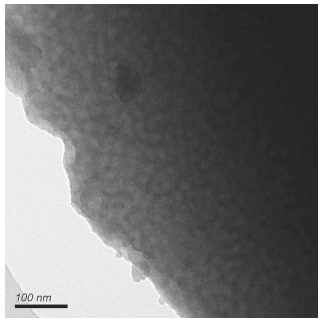
Composition effects in complex glasses - Crystallization

A. Quintas et al. Appl. Magn. Reson. 2007

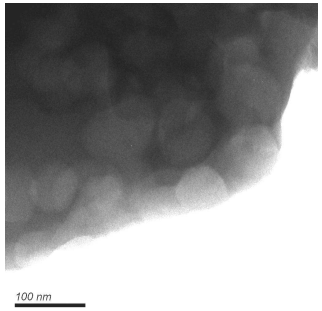
62 SiO_2 - 9 B_2O_3 - 20 (**(1-R) Na_2O + R CaO**) - 3 Al_2O_3 - 2 ZrO_2 - 3.5 La_2O_3



R=0.7



R=0.85



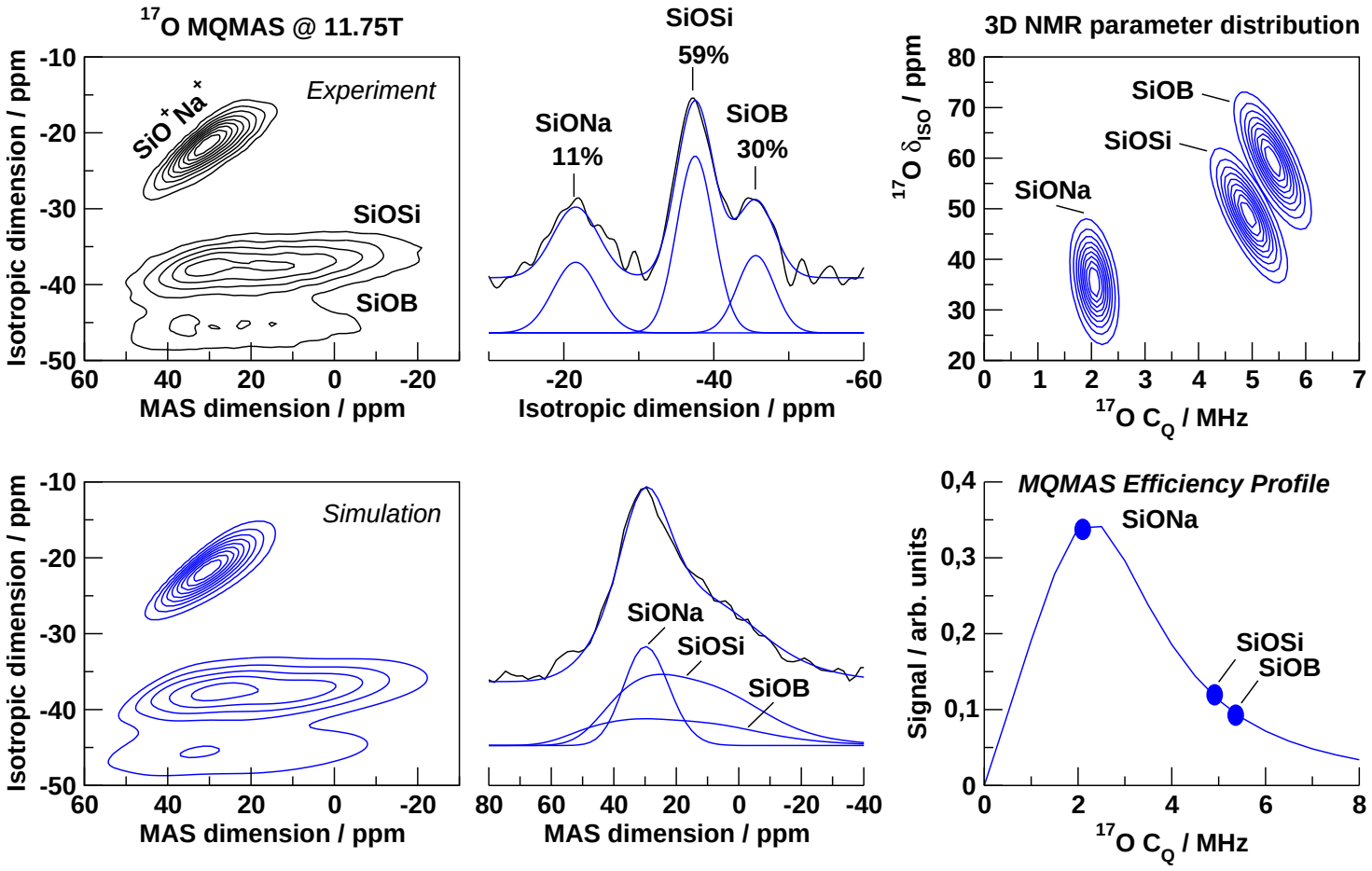
$\Rightarrow$ Na^+ preferential charge compensator of AlO_4^- .

$\Rightarrow$ Ca^{++} compensation of AlO_4^- favors crystallization tendency.

Modeling and Quantifying ^{17}O MQMAS Spectroscopy

Quantification + NMR Distribution

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



Correlated model of distribution $p(C_Q, \eta, \delta_{iso})$

Boron speciation in Soda-Lime Borosilicate Glasses.

Mixed Alkali / Alkaline Earth Effect

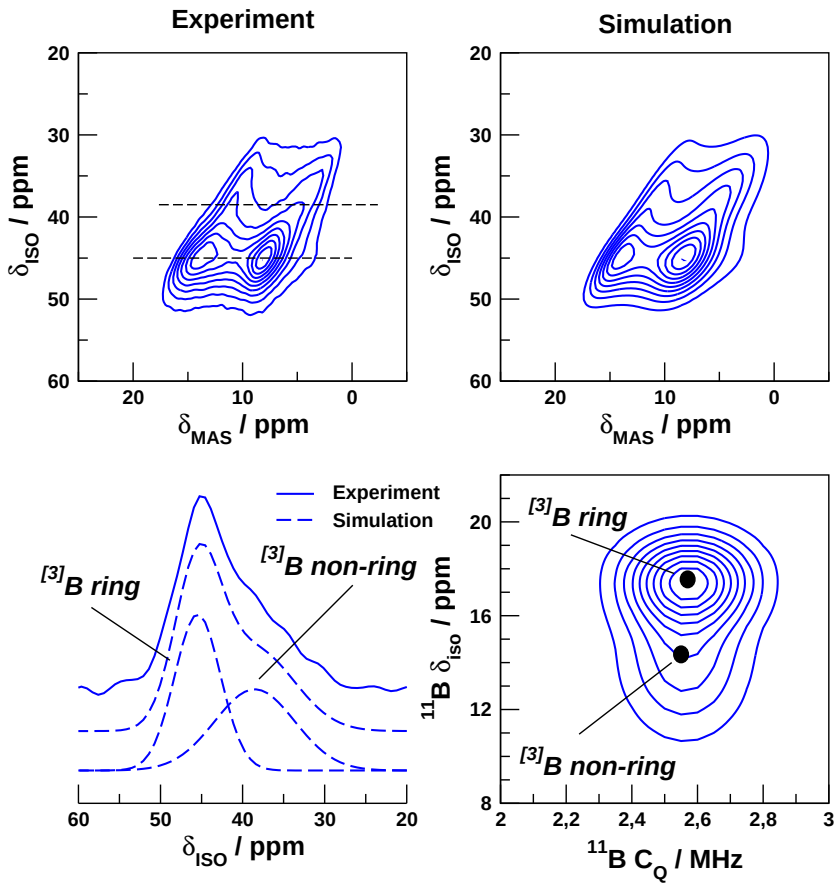
F. Angeli, T. Charpentier et al., submitted.

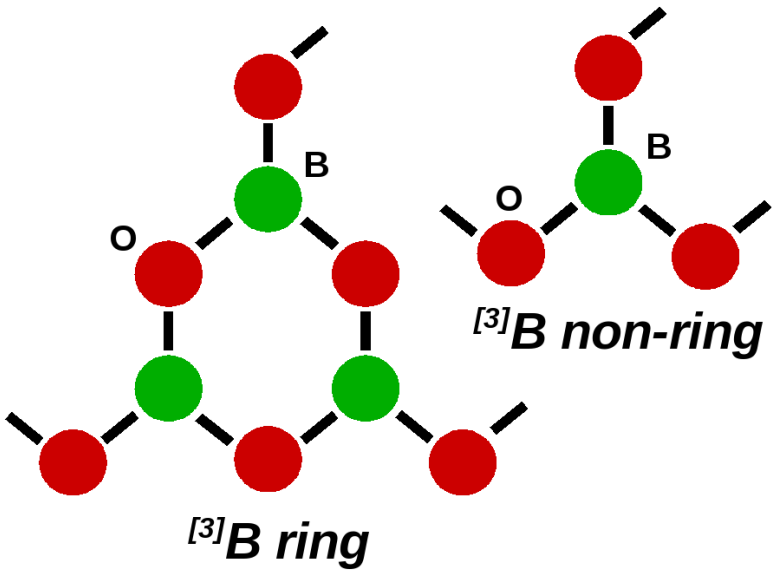
Composition	Zr series					
mol(%)	0Zr	1Zr	2Zr	4Zr	6Zr	8Zr
SiO_2	61	60	59	57	55	51
B_2O_3	17	17	18	18	17	18
Na_2O	18	18	18	18	18	19
CaO	4	4	4	4	4	4
ZrO_2	0	1	2	4	6	8

Composition	Ca series				xZr10Na series	
mol(%)	0Ca	3Ca	6Ca	9Ca	0Zr10Na	4Zr10Na
SiO_2	63	63	62	62	69	65
B_2O_3	17	16	17	17	17	18
Na_2O	18	16	13	10	10	10
CaO	0	3	6	9	4	4
ZrO_2	2	2	2	2	0	4

Boron speciation in Soda-Lime Borosilicate Glasses.

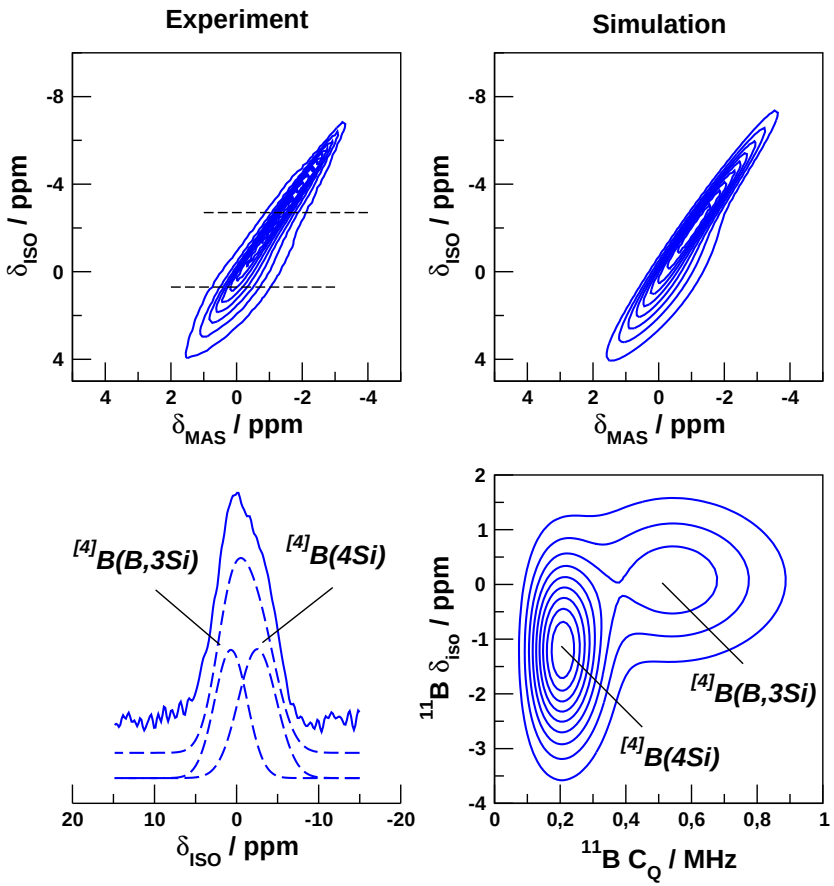
3-coordinate Boron Speciation.

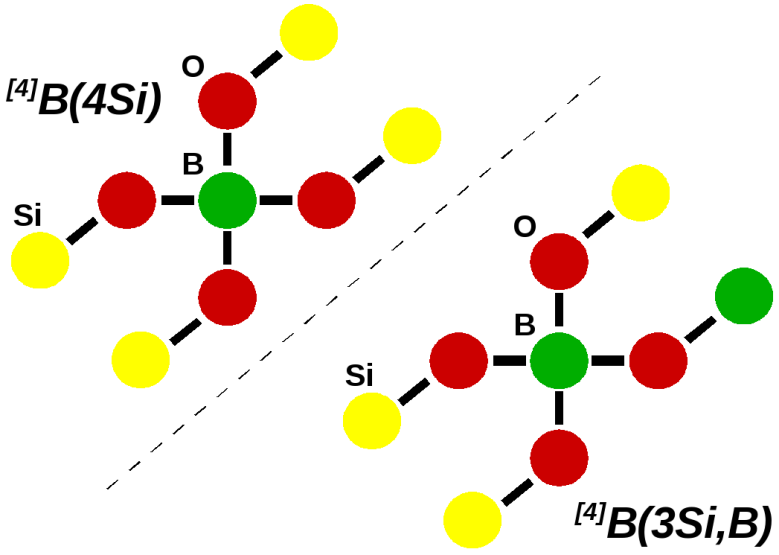




Boron speciation in Soda-Lime Borosilicate Glasses.

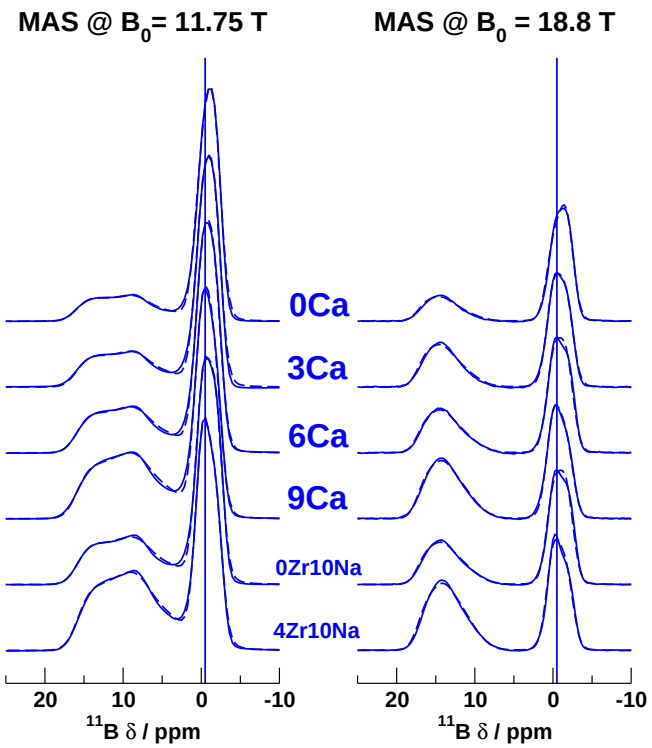
4-coordinate Boron Speciation.

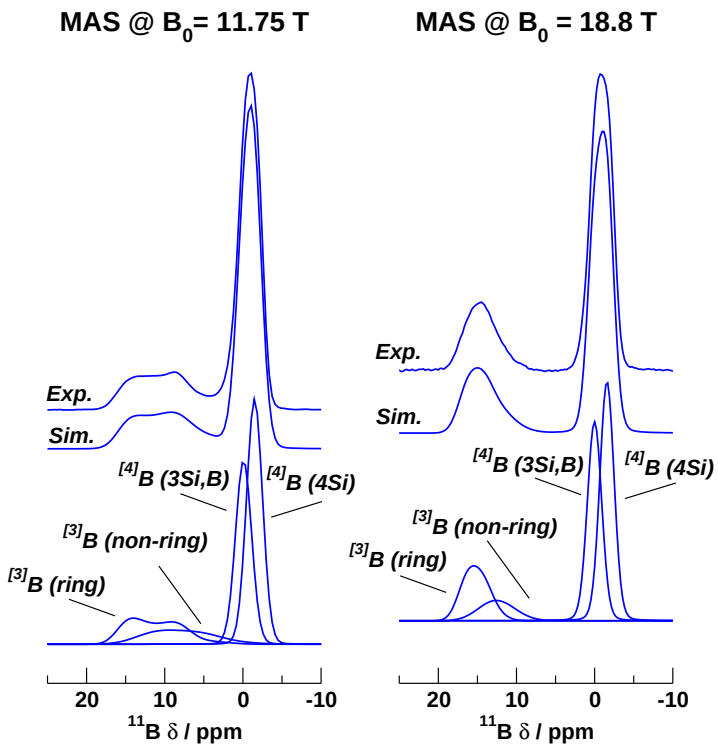




Boron speciation in Soda-Lime Borosilicate Glasses.

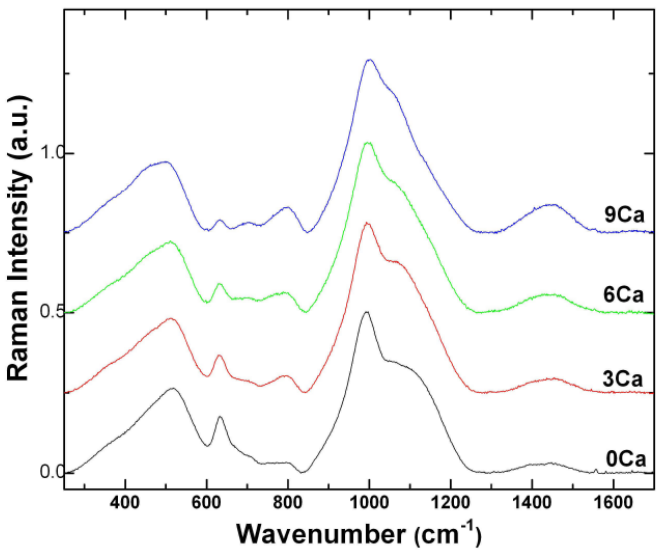
A MQMAS constrained multiple fields analysis of ^{11}B MAS NMR



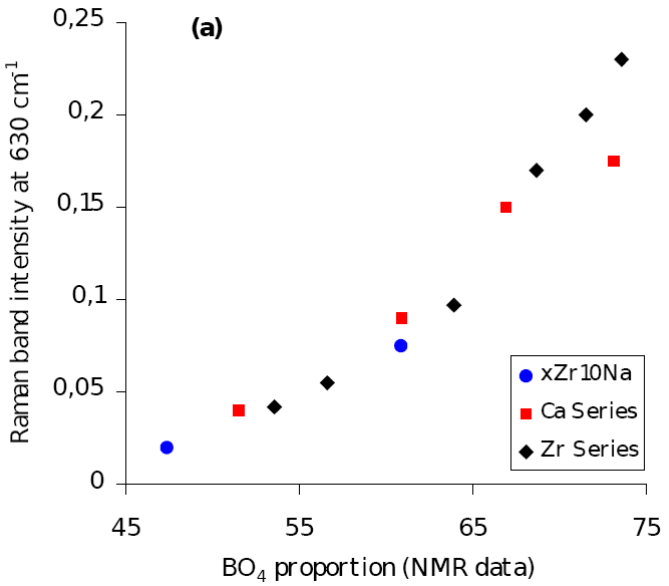


Boron speciation in Soda-Lime Borosilicate Glasses.

Tetrahedral Boron Speciation. NMR vs RAMAN spectroscopy



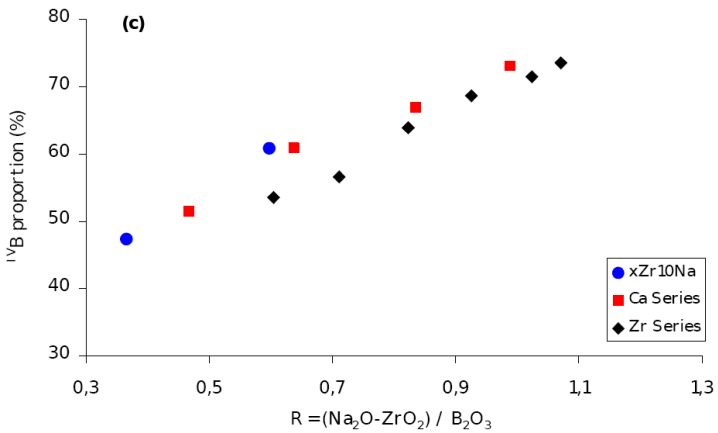
$\nu = 630\ \mathrm{cm}^{-1} \propto \mathrm{N_4}$



NMR vs RAMAN

Mixed Alkali - Alkaline Earth Effect

The Dell & Bray model for complex glass



CaO or ZrO_2 increasing

$\longrightarrow$ N_4 decreasing

$$\mathbf{BO_{3/2} + SiO_{3/2}O^- \Leftarrow BO^-_{4/2} + SiO_{4/2}}$$

$$\mathbf{{}^3B + Q^3 \Leftarrow {}^4B + Q^4}$$

Dell & Bray Model

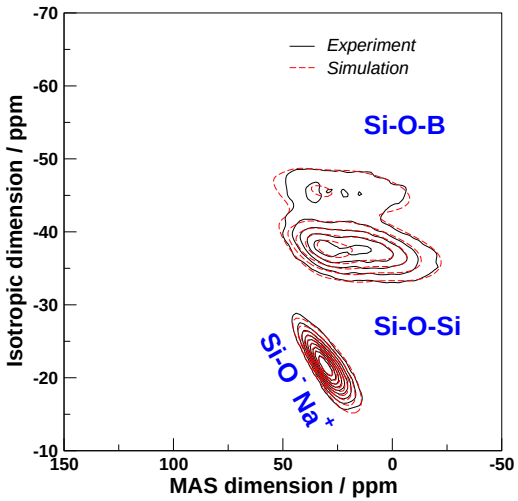
- *Structure 'reactions'*
  $K = SiO_2 \ / \ B_2O_3$
  $R = (Na_2O\text{-}ZrO_2) \ / \ B_2O_3$
- Preferential Charge compensation
  $ZrO_6^{2-} + 2\ Na^+$
- Ca^{++} Modifier (NBO) only
  $SiO^- + \{\ Ca^{++}, Na^+\ \}$
  Non random distribution

Structure of Soda-Lime Borosilicate Glasses.

The ^{17}O NMR approach

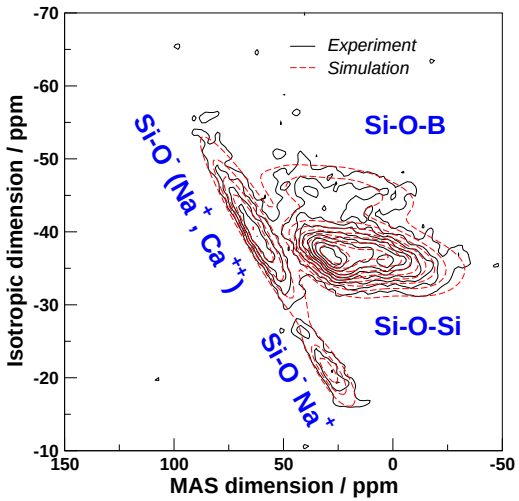
$67\ SiO_2$ - $11\ B_2O_3$

$22\ Na_2O$



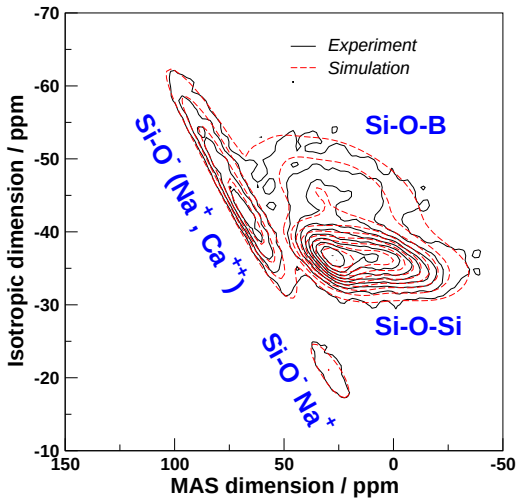
$67\ SiO_2$ - $11\ B_2O_3$

$16.5\ Na_2O + 5.5\ CaO$



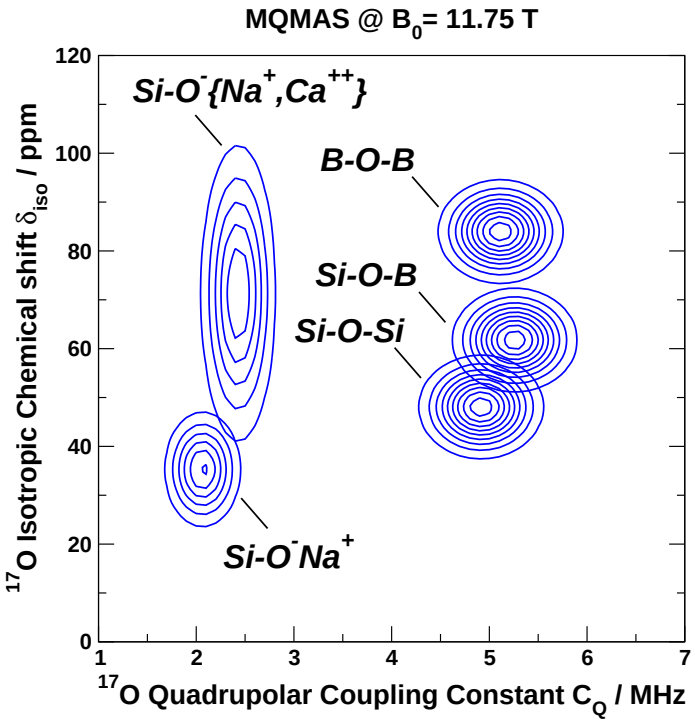
$67\ SiO_2$ - $11\ B_2O_3$

$11\ Na_2O + 11\ CaO$



$\Rightarrow$ Quantification of the Na/Ca mixing.

Quantifying glass topological disorder



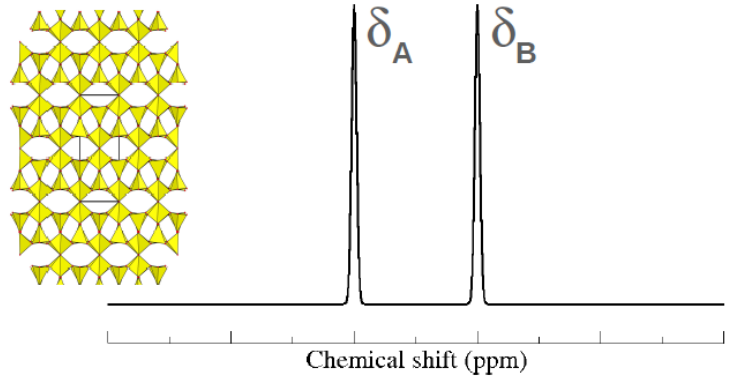
Glass Topology

- Reconstruction of the NMR parameter distribution
- Correlating the *local disorder* to the NMR spectrum line shape ?
- $\Pi(\text{NMR}) \Rightarrow \Pi(\text{Structure})$?

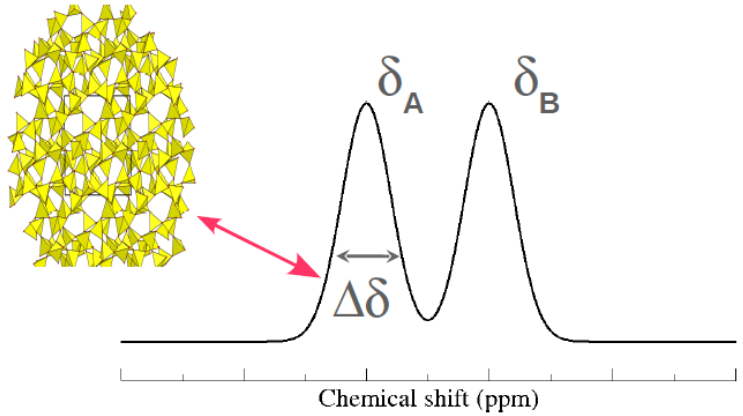
Quantifying glass topological disorder

The next step: Interpreting the NMR parameter distribution

A fundamental question:



Correlating the local disorder to the NMR spectrum line shape

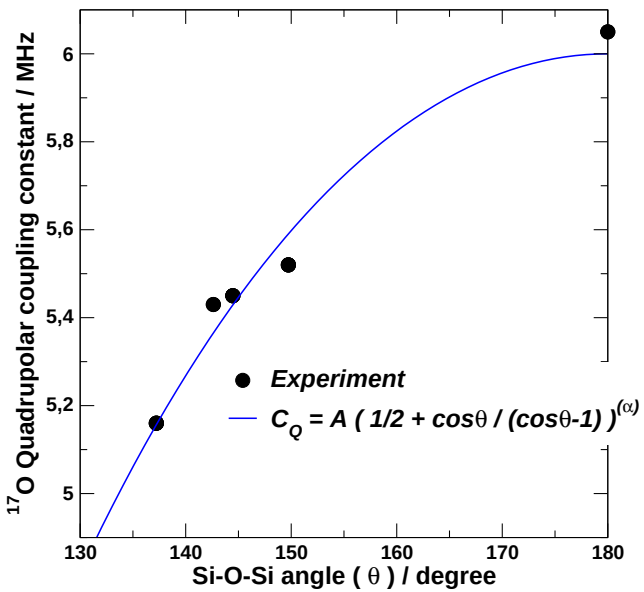


Understanding NMR / Structure relationships

The Phenomenological Approach: using Crystalline Reference Compounds.

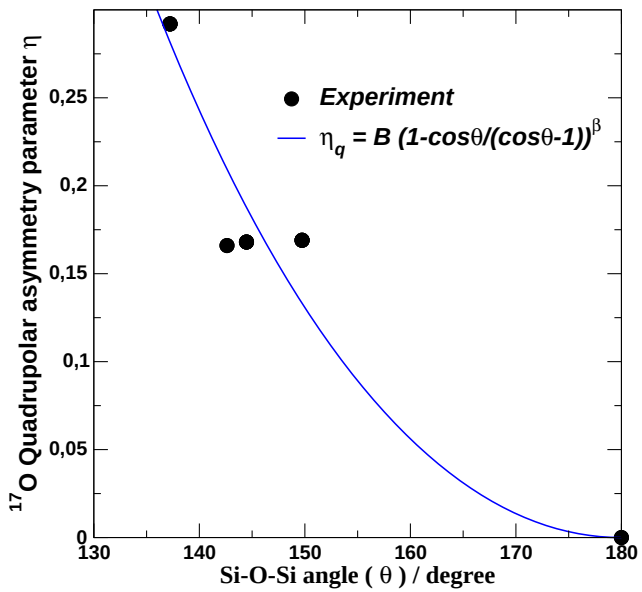
^{17}O $C_Q(\theta)$

Coesite SiO_2



^{17}O $\eta(\theta)$

Coesite SiO_2

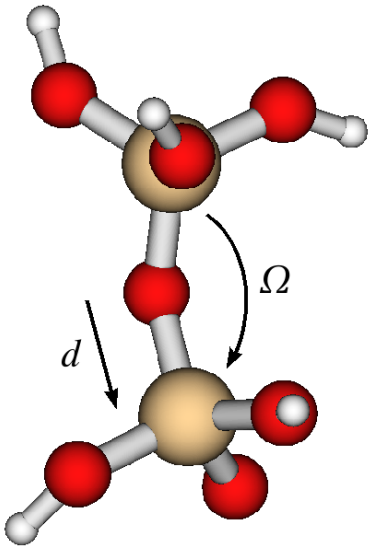


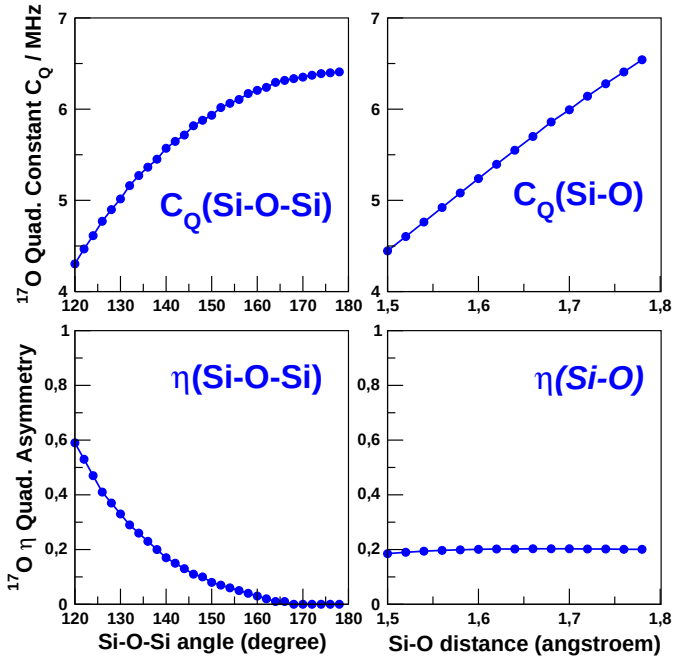
But ^{17}O NMR: very limited number of experimental data !

Understanding NMR / Structure relationships

Quantum Mechanical calculations: the Cluster Approach

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

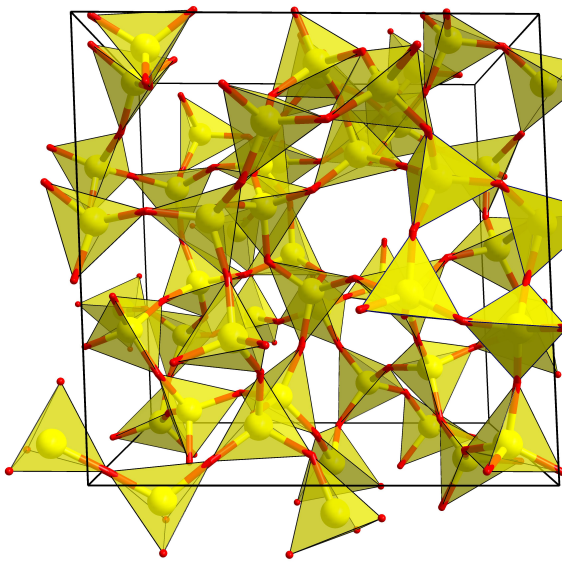


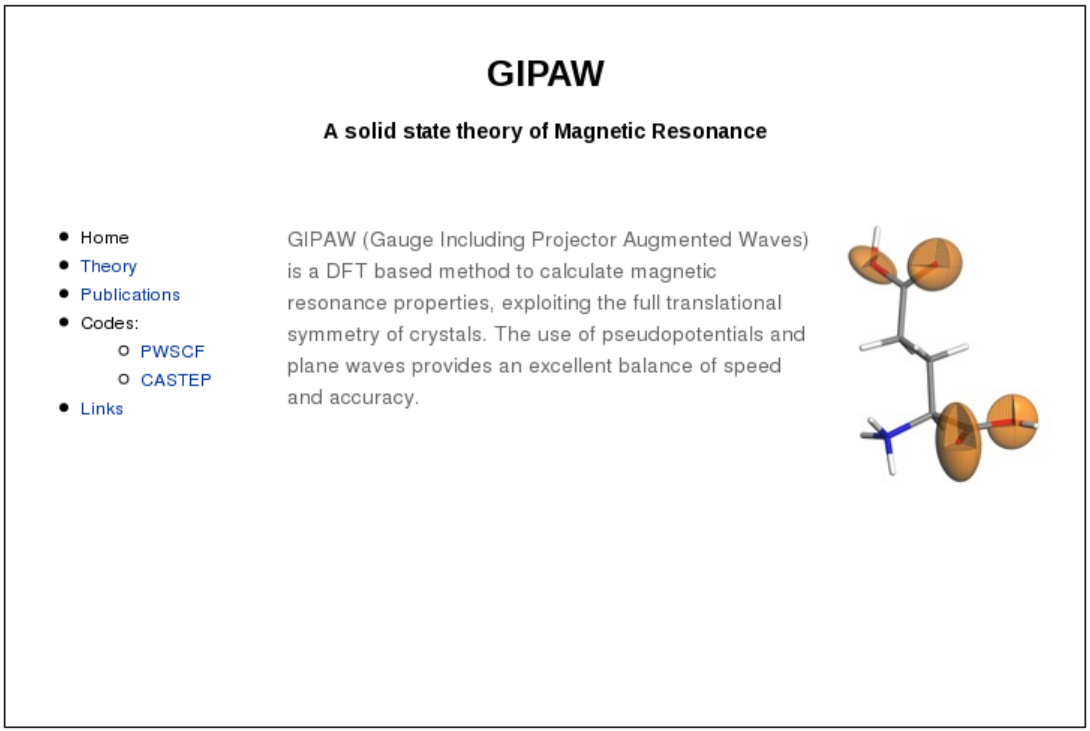


^{17}O C_Q and η_Q NMR parameters are allmost exclusively controlled by local properties: (Si-O-Si bond angle and Si-O bond length)

Combining MD simulations with fp NMR calculations

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



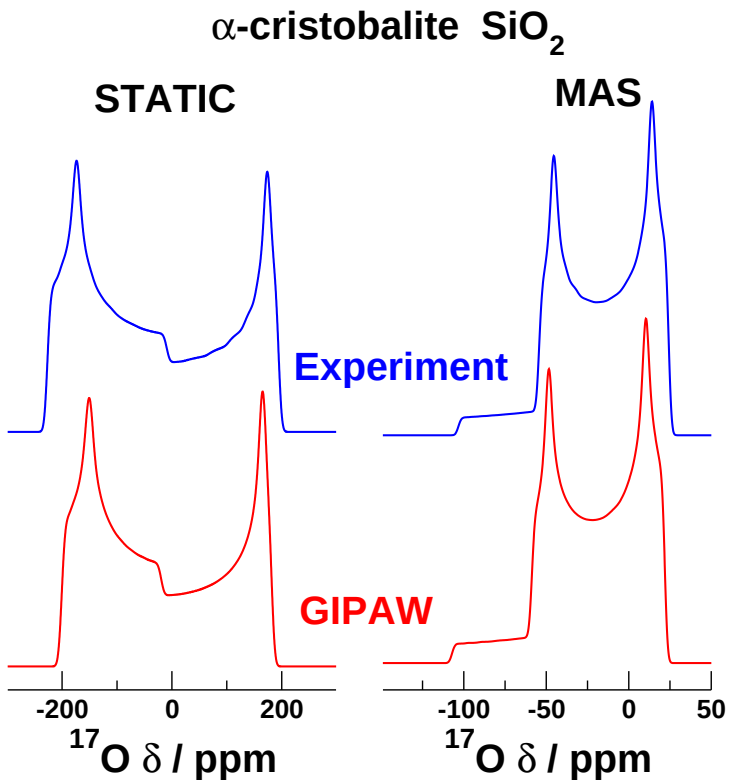


The GIPAW method

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



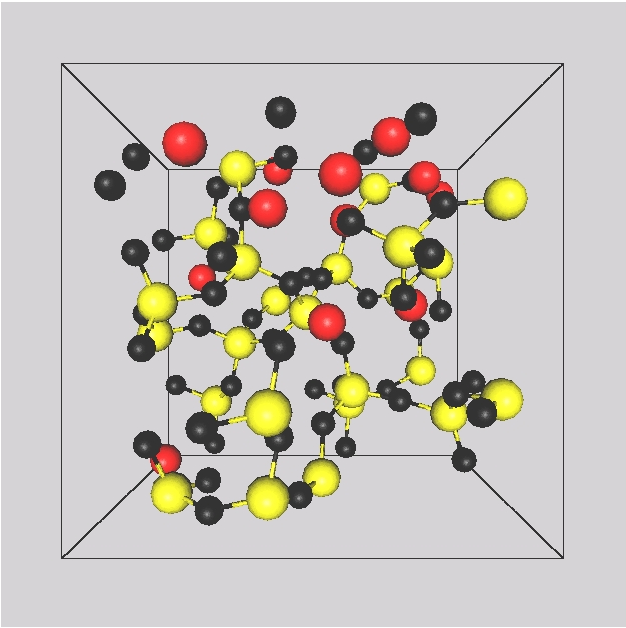
Exp.: Spearing et al. Phys. Chem. Minerals 1992.

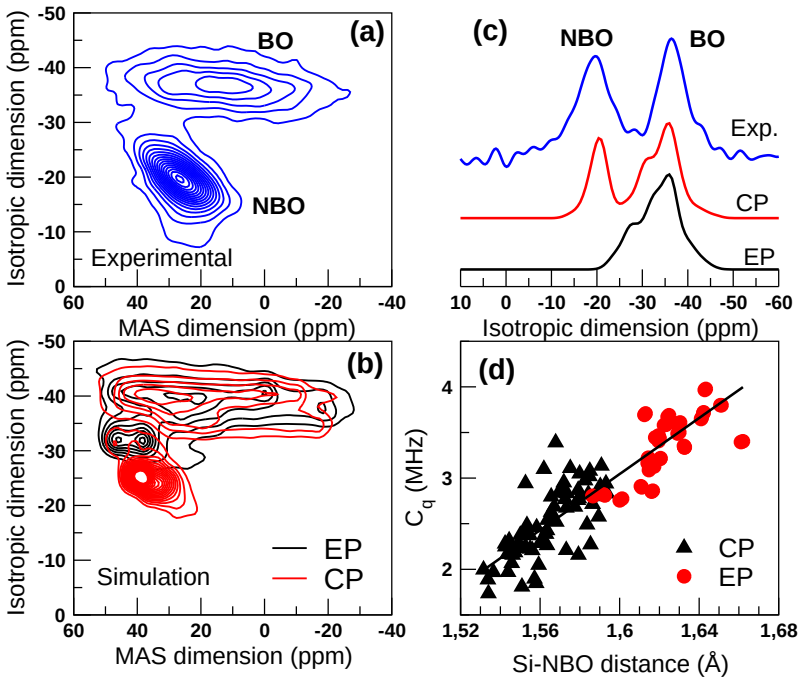
Accuracy: GIPAW outperforms all previous approaches

^{17}O NMR in alkali tetrasilicate glass

Classical vs Ab Initio

S. Ispas, T. Charpentier et al. Solid State Sci. 2009

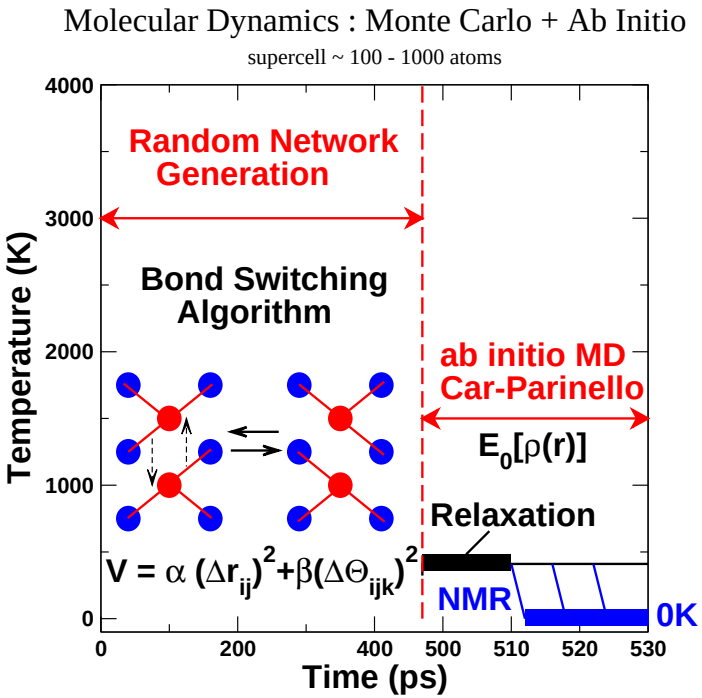




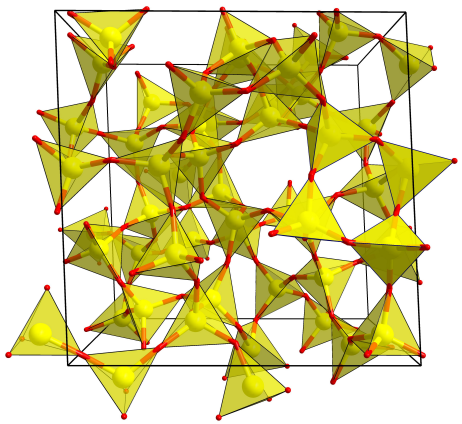
fpNMR provides complementary data (diffraction) for assessing MD models

A Monte Carlo / MD Hybrid Approach

Modeling Glass Structure: Bond Switching Algorithm



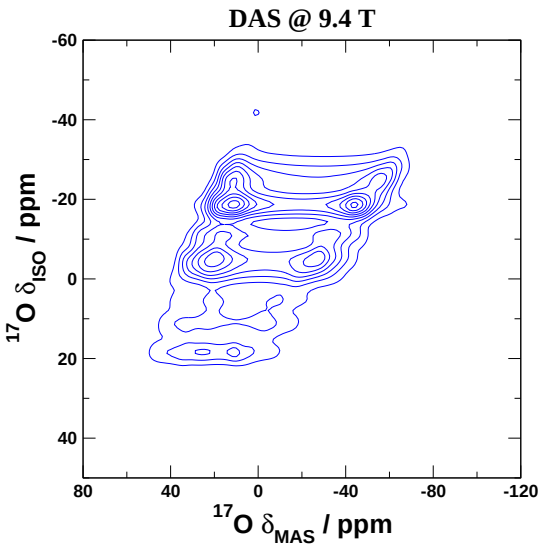
Defect Free Vitreous Silica
Continuous Random Network



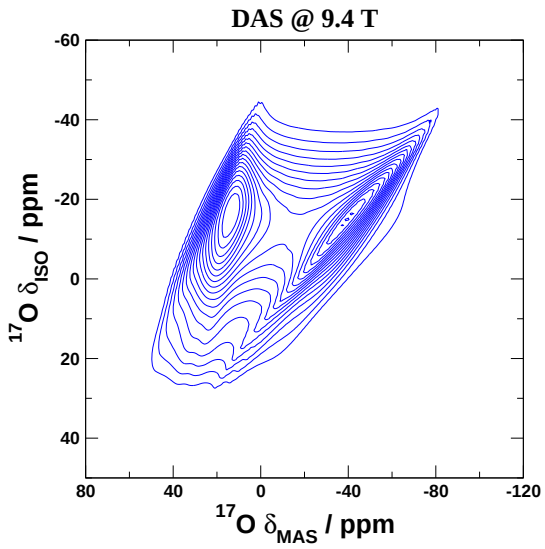
Simulation of NMR Spectra

Kernel Density Estimate Approach

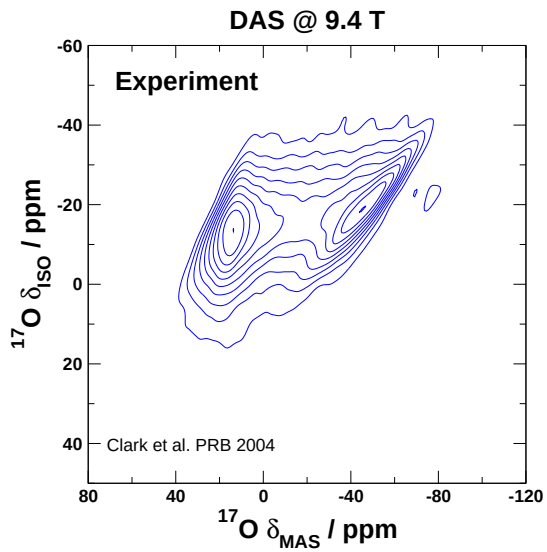
Direct Simulation



KDE simulation



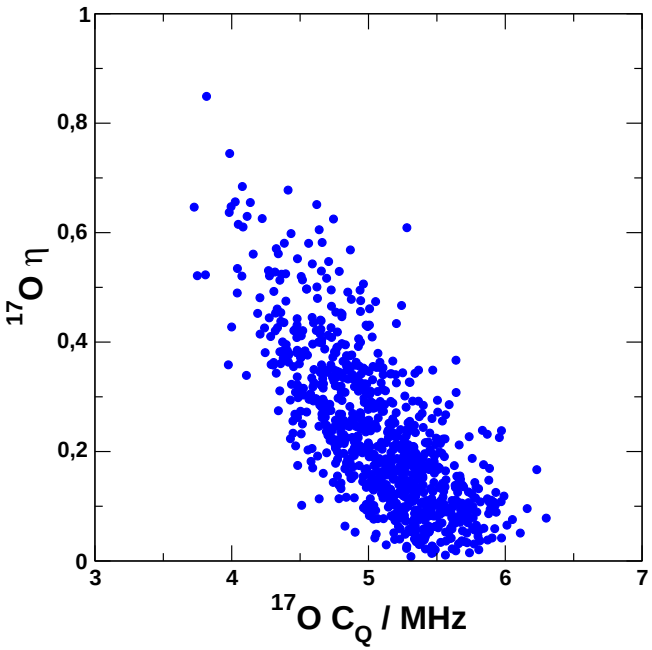
Experiment



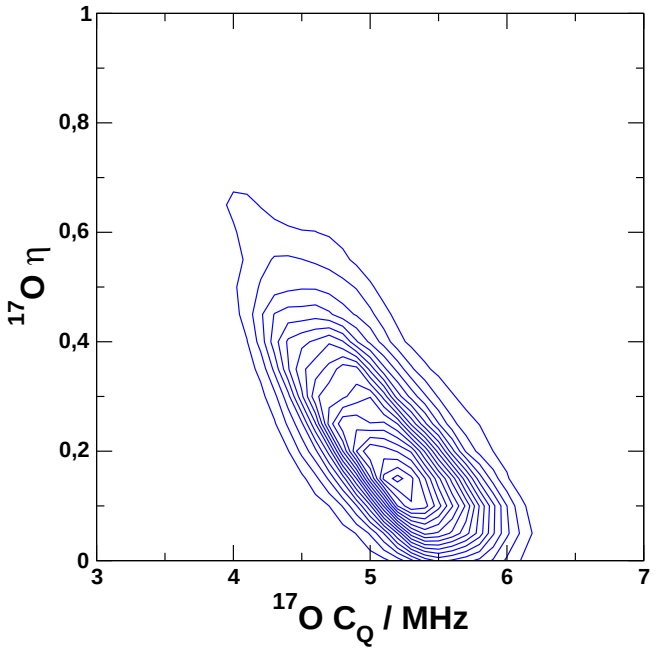
Analysis of NMR parameter distribution

Kernel Density Estimate Approach

Theoretical points



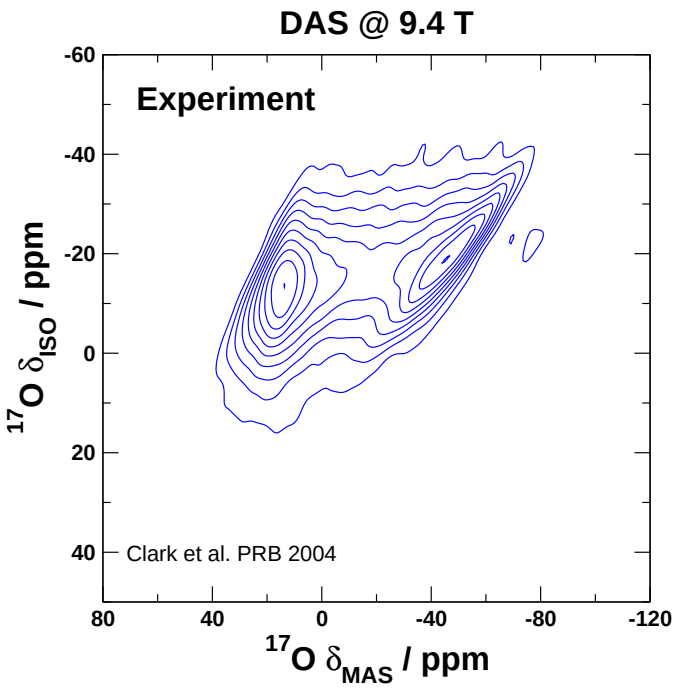
Estimated Distribution

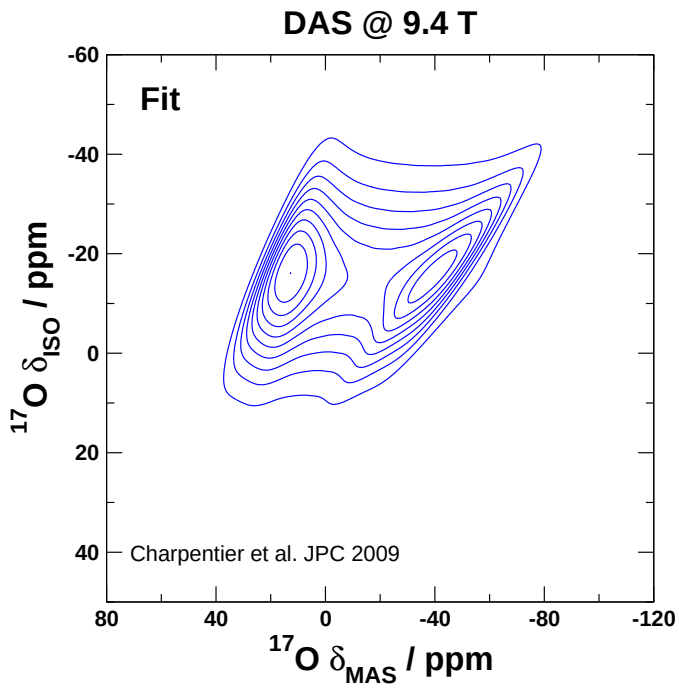


Introduction of a correlated 3D NMR parameter distribution:

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

Quantitative analysis of Experimental data





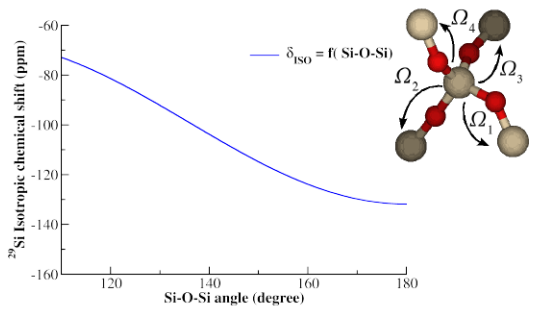
Experimental data can be well described in term of *geometrical disorder only*.

Reconstructing the Bond Angle Distribution (BAD)

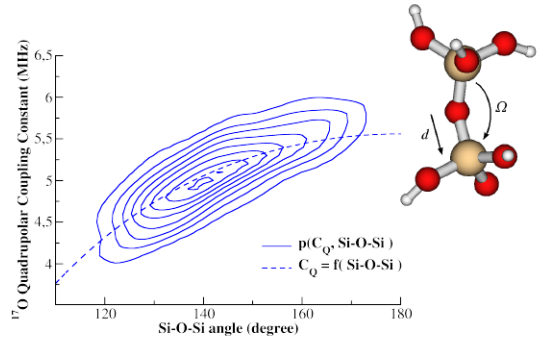
NMR / Structure relationships

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

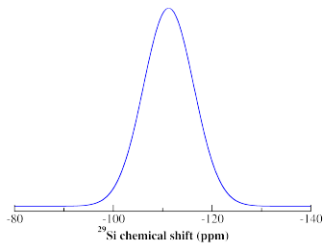
Reconstruction of the Bond Angle Distribution (SiOSi) from NMR data

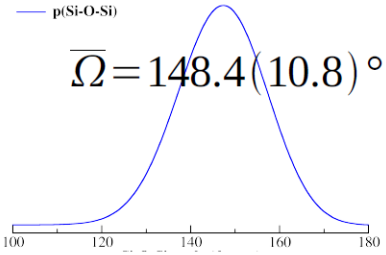


GIPAW + MD:
NMR-Structure relationships

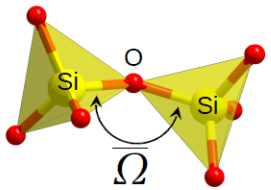


^{29}Si NMR

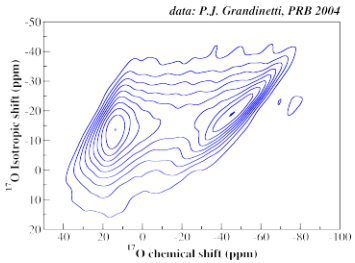


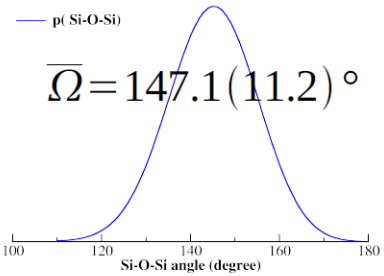


Structural Inversion



^{17}O NMR





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

Interpretation of ^{17}O Experimental data

^{17}O NMR parameter distribution

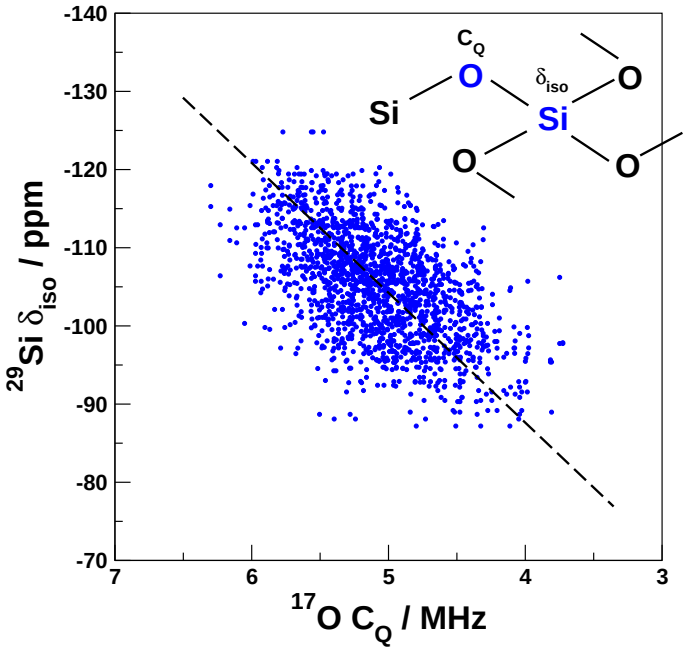
	Charpentier et al. JPC 2009		Clark et al. PRB 2004	
	Mean	Std. dev.	Mean	Std. dev.
C_q	5.07 MHz	0.453 MHz	5.08 MHz	0.372 MHz
η_q	0.157	0.095	0.150	0.0414
δ_{iso}	36.5 ppm	7.55 ppm	36.7 ppm	4.30 ppm

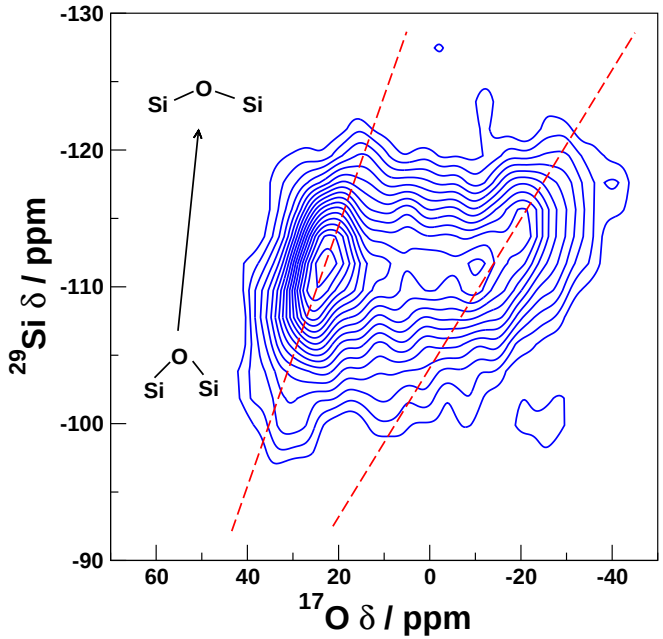
Local geometry

	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

Through Bond Correlation Spectroscopy

Perspectives: ^{29}Si-^{17}O J-HMQC experiments.





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 ...

aiNMR: Perspectives

A new powerfull tools to get more insight into NMR data

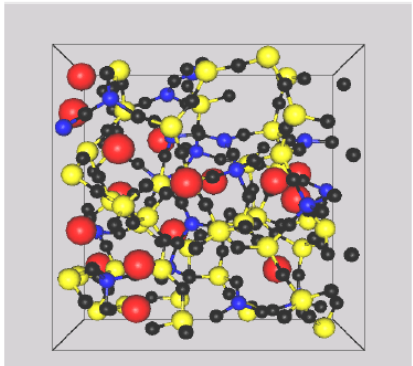
Structural studies of complex glasses (borosilicates, mixed alkali effect, Bioglass, ...)

Dynamical effects
vibration, diffusion ⇔ relaxation

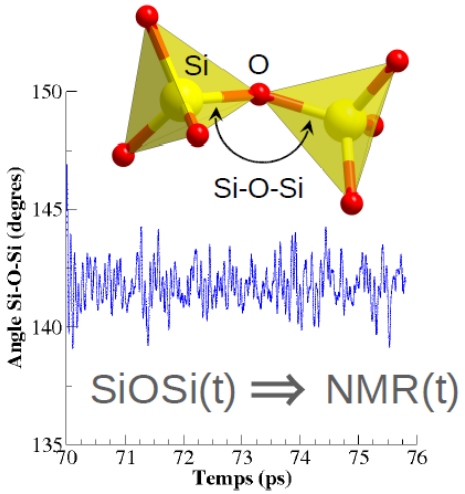
Data modelling of Glass (imitating bioNMR !)

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



Ackwnowledgement

MD-GIPAW

- A. Soleilhavoup, O. Villain, L. Truflandier (LSDRM, Post-Doc)

Nuclear Waste Glasses

- F. Angeli, P. Jollivet, S. Peuget, J.M. Delaye (CEA Valrho)
- A. Quintas, D. Caurant, O. Majérus (ENS Chimie Paris)

MD simulations

- S. Ispas (LCVN,Montpellier 2)
- G. Ferlat (IMPMC, Paris 6)
- P. Kroll (Arlington, Texas)

GIPAW

- A. Seitsonen, F. Mauri (IMPMC, Paris 6)
- J.Yates (Oxford)

J|A|C|S COMMUNICATIONS

Measurement of Long-Range Interatomic Distances by Solid-State Tritium-NMR Spectroscopy

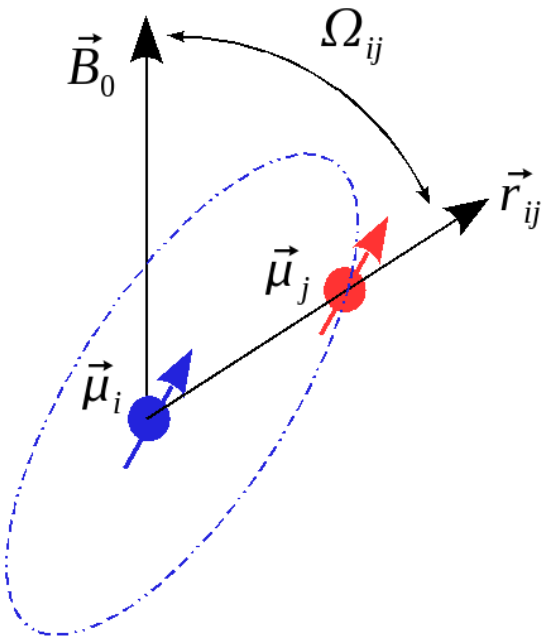
Alexander K. L. Yuen,[†] Olivier Lafon,[§] Thibault Charpentier,[*,§] Myriam Roy,[†] Francine Brunet,[§] Patrick Berthault,[§] Dimitrios Sakellariou,[§] Bruno Robert,[‡] Sylvie Rimsky,[||] Florence Pillon,[†] Jean-Christophe Cintrat,[†] and Bernard Rousseau[*,†]

CEA, iBiTecS, Service de Chimie Bioorganique et de Marquage, F-91191 Gif sur Yvette, France, CEA, iBiTecS, Service de Bioénergétique, Biologie Structurale et Mécanismes, F-91191 Gif sur Yvette, France, CEA, IRAMIS, SIS2M, Laboratoire Structure et Dynamique par Résonance Magnétique, F-91191 Gif sur Yvette, France, and LBPA, CNRS, ENS de Cachan, 61, avenue du Président Wilson, F-94235 Cachan, France

Received January 29, 2009; Revised Manuscript Received October 19, 2009; E-mail: thibault.charpentier@cea.fr; bernard.rousseau@cea.fr

Principles of NMR distance Measurements

The Dipolar Magnetic Interaction



$$H_{Dip}^{(ij)} = C_{ij} \times R(\Omega_{ij}) \times T^{ij}$$

$$C_{ij} \propto \gamma_i \gamma_j / r_{ij}^3$$

$R(\Omega_{ij})$: *Spatial component*

T^{ij} : *Spin component*

State of the Art

- ^{13}C, ^{15}N: low γ
  - $\Rightarrow$ Low Sensitivity, High Resolution
  - $\Rightarrow$ Max distance $5 - 6$Å
- ^{1}H: High γ,
  - $\Rightarrow$ High Sensitivity
  - $\Rightarrow$ Poor Resolution, Multiple couplings
  - $\Rightarrow$ ^{1}H / ^{2}H dilution required

Introducing a new nucleus in High Resolution Solid State NMR

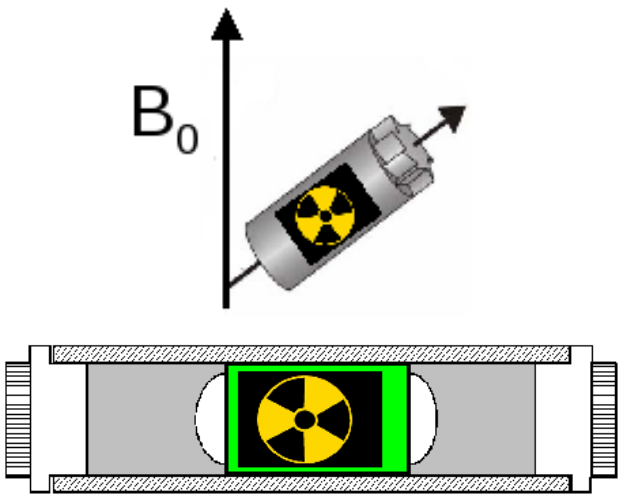
^{3}H: the highest gyromagnetic ratio (γ)

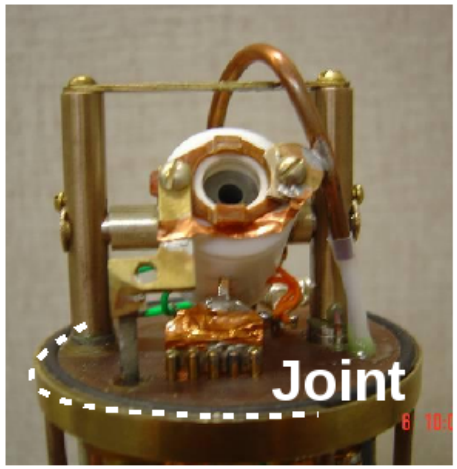
- High sensitivity and no (probe) backgroung
- Very low ^{3}H/^{1}H dilution
  - Well isolated spin pair
  - High resolution
- Higher ^{3}H-^{3}H (or ^{3}H-X) dipolar interaction
  $\Rightarrow$ Longer distances can be measured

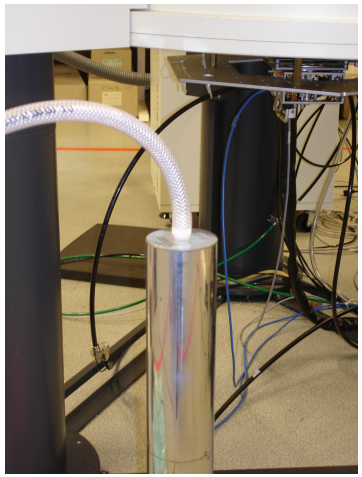
Estimated highest distance $d_{TT} \approx 15$Å

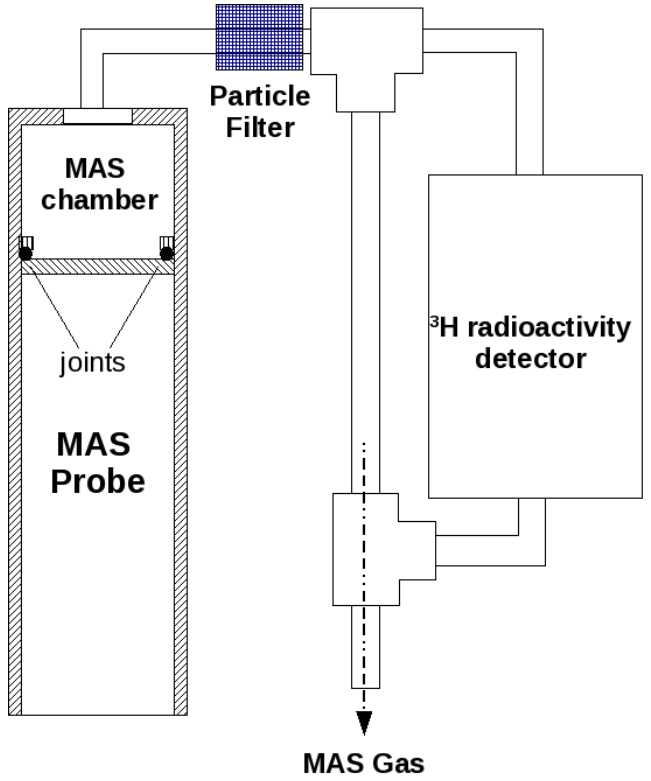
Spinning a radioactive powder sample

Probe Sealings and Exhaust gas containment system

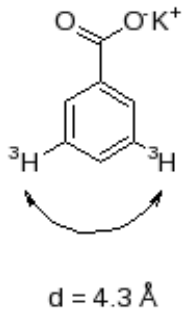


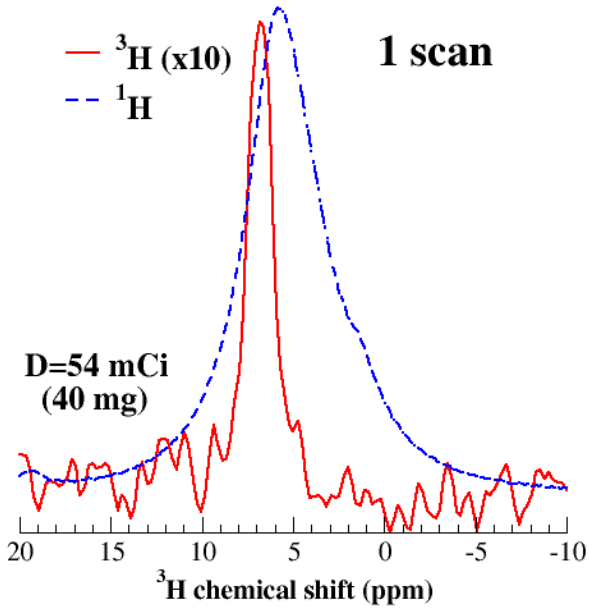




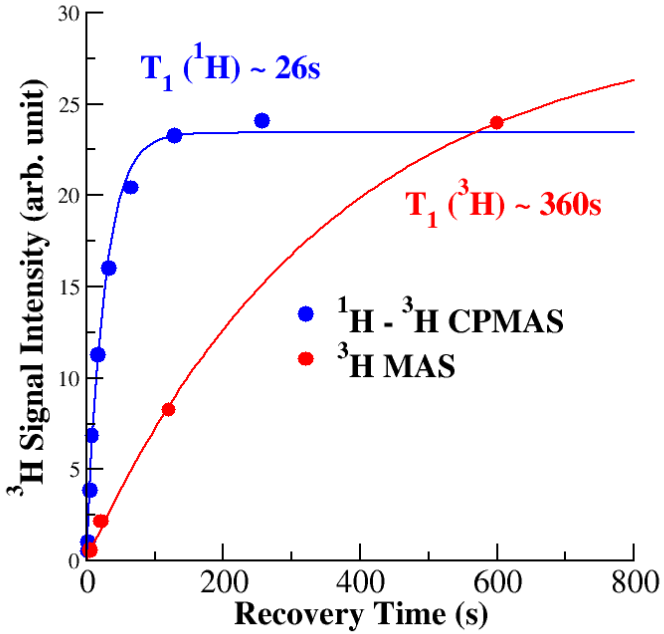


3H MAS NMR at work





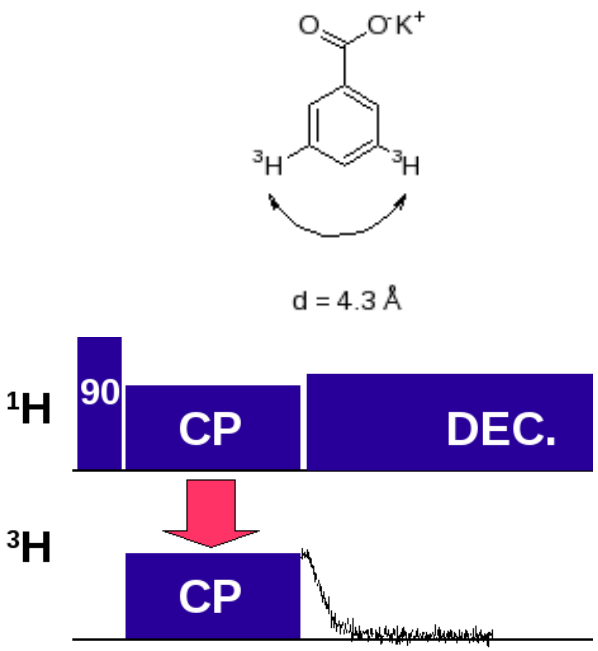
$\approx 10^{18}$ spins in one scan.

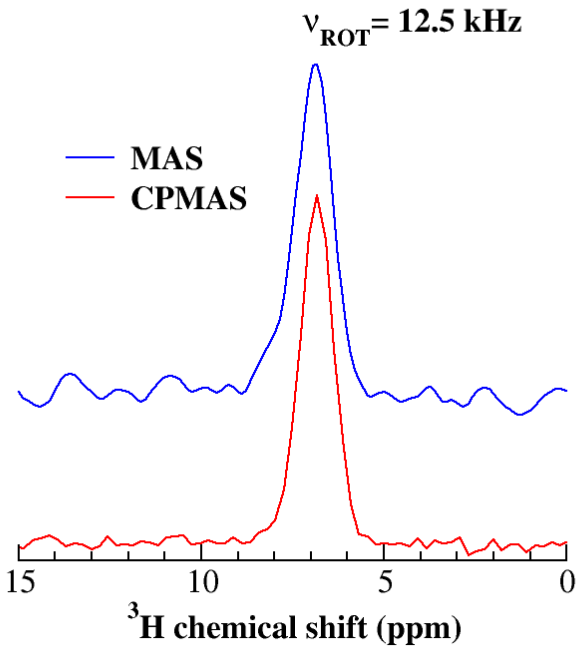


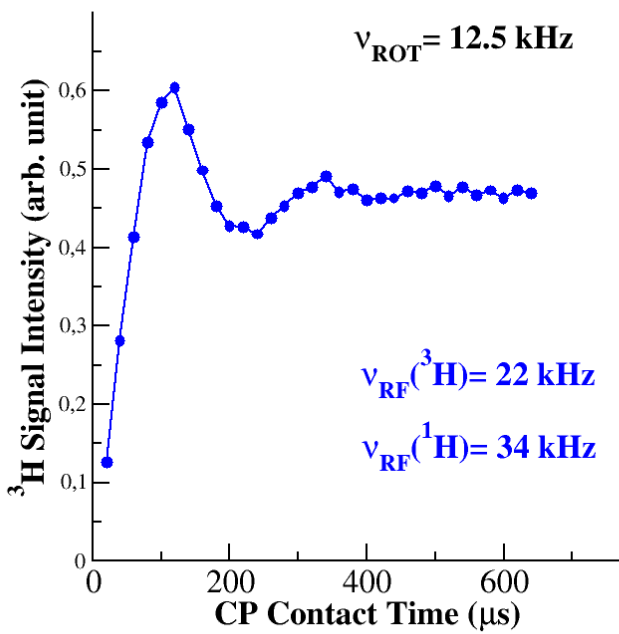
^{3}H: (very) long T_1 !

3H CPMAS NMR at work

Taking advantage of ^{3}H / ^{1}H dilution ...

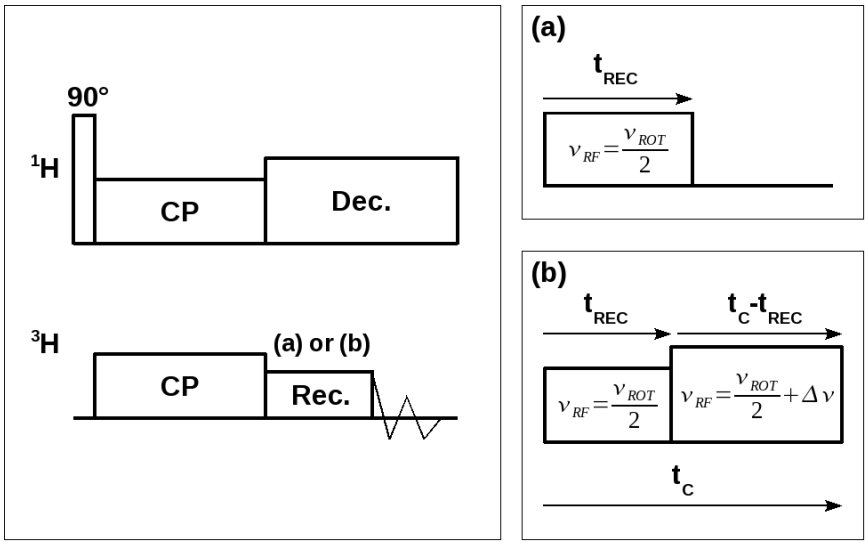






3H-3H distance Measurement

Choice of the pulse sequence



HORROR, Nielsen et al., J. Chem. Phys. 101, 1994

(b) Novel implementation Constant Time HORROR

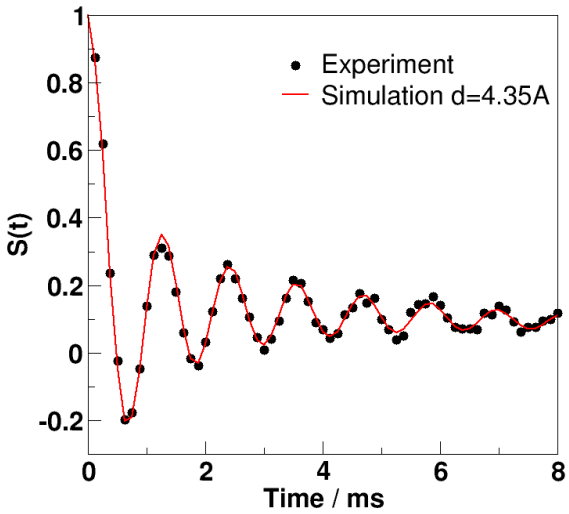
Why HORROR?

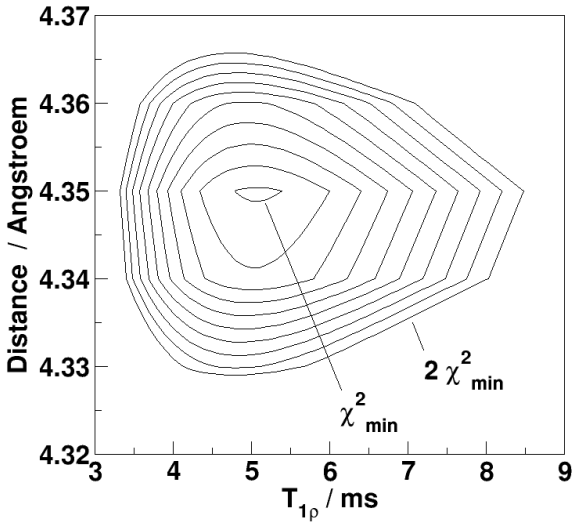
Aim: recoupling the weak ^{3}H-^{3}H dipolar interactions while decoupling the strong ^{3}H-^{1}H interactions.

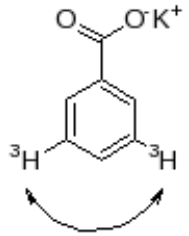
- High ^{1}H RF field for efficient ^{3}H-^{1}H decoupling.
- Low ^{3}H RF field to avoid ^{3}H-^{1}H CP match

3H-3H distance Measurement

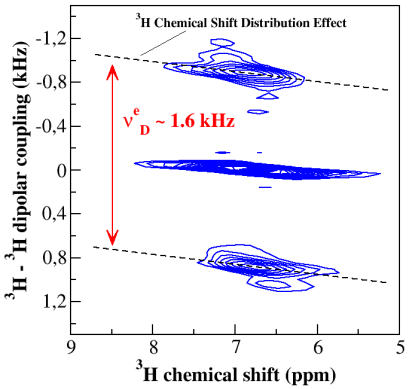
The first result !







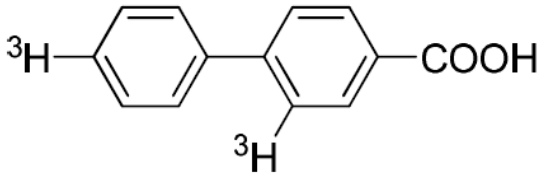
d = 4.3 Å



$$S(t) = \left\{ A \int d\Delta\, g(\Delta)\, S(t; d_{TT}, \Delta) + B \right\} \exp\left(-t/T_{1\rho}\right)$$

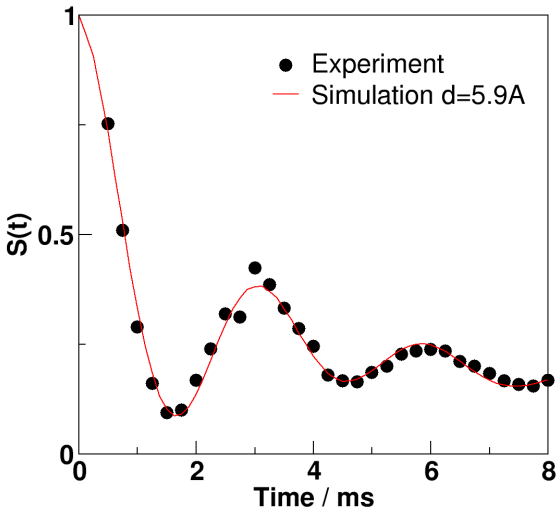
3H-3H distance Measurement . . .

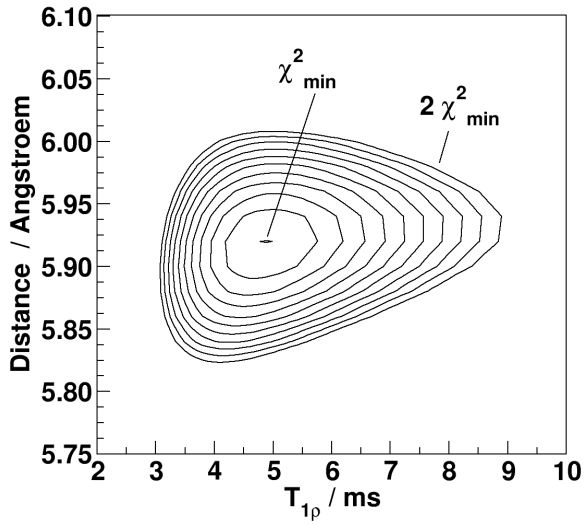
. . . at work



2,4'-Ditritiobiphenyl-4-carboxylic acid

6Å

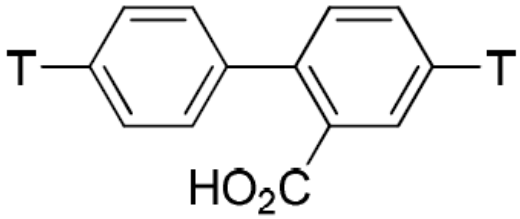




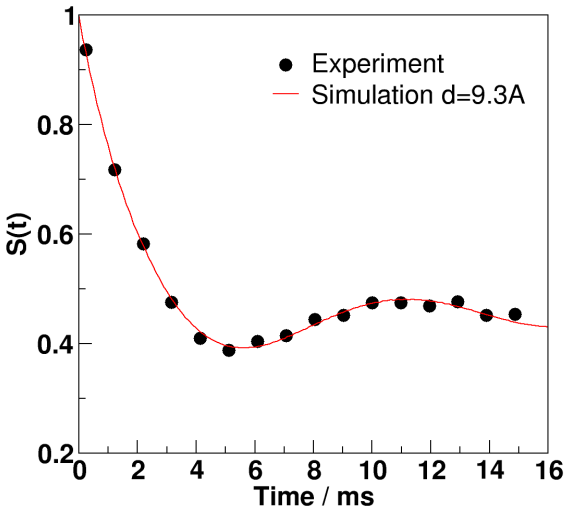
3H-3H distance Measurement . . .

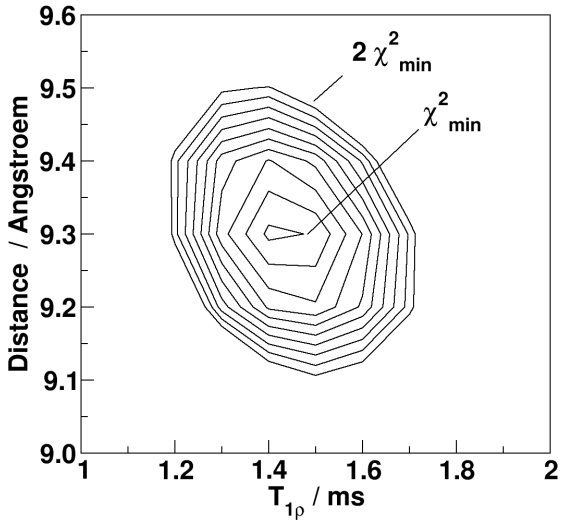
. . . at work

4,4'-Ditritiobiphenyl-2-carboxylic acid



9.4 Å

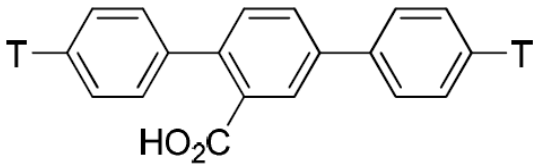




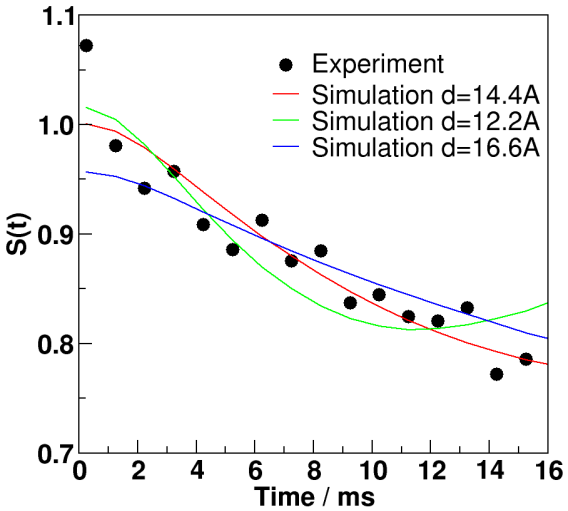
3H-3H distance Measurement . . .

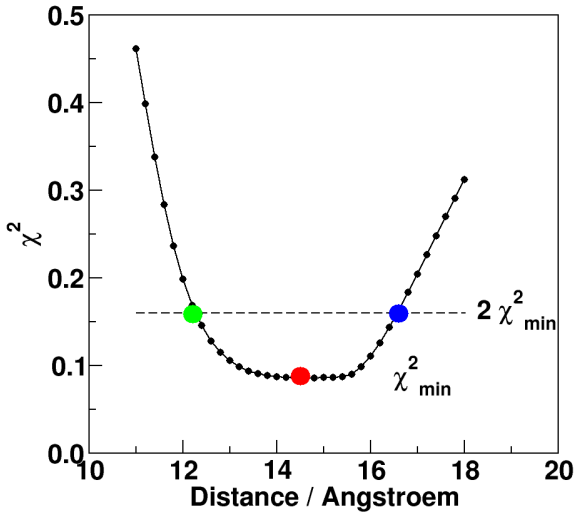
HORROR: Constant Time Approach

4',4''-Ditritio-2,5-diphenylbenzoic acid



13.8Å





$$S(t) = A \int d\Delta\, g(\Delta)\, S(t; d_{TT}, \Delta) + B$$

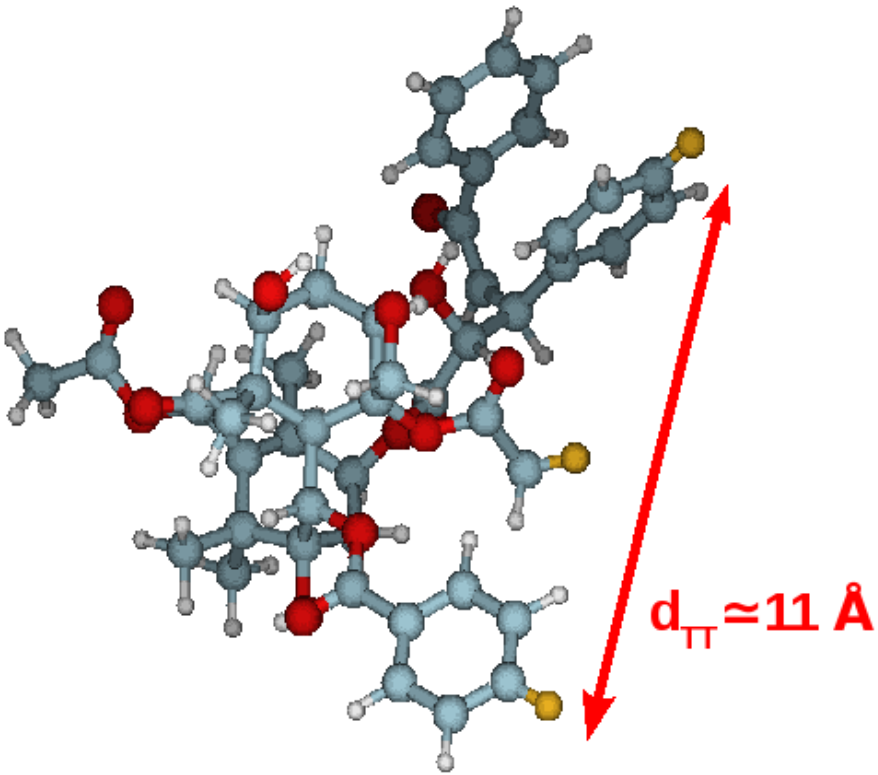
3H MAS NMR

Perspectives . . .

- ^{3}H (^{1}H) Chemical Shift Anistropy
- ^{3}H-X (^{31}P, ^{13}C) distance (and geometry) measurements
- Multidimensional ^{3}H-^{1}H-X spectroscopy

Need for long distance measurements.

Taxol - Tubulin interaction

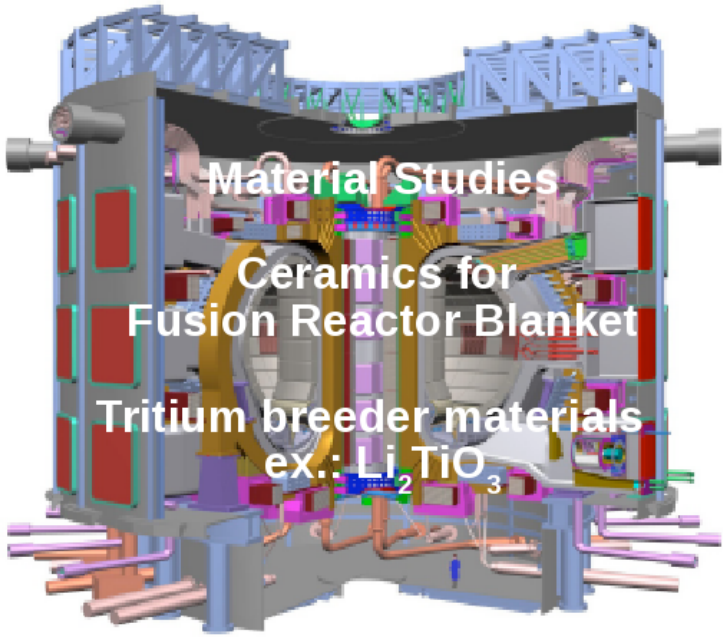


Taxol

Tubulin

Perspectives

Materials studies



$^{6}Li + n \rightarrow \alpha + T + 4.8\ MeV$