université PARIS-SACLAY

ÉCOLE DOCTORALE
INTERFACES
Approches Interdisciplinaires : Fondements, Applications et Innovation

nanosciences & innovation
nimbe

UNION POUR LA SCIENCE ET LA TECHNOLOGIE VERRIÈRES

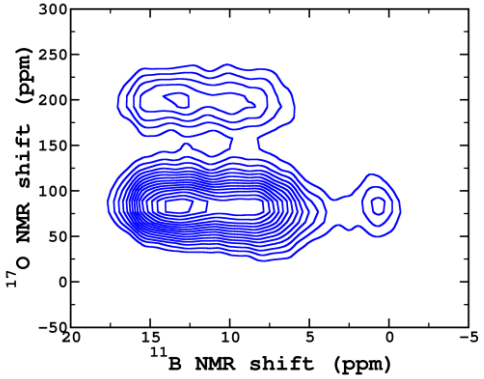
DE LA RECHERCHE À L'INDUSTRIE

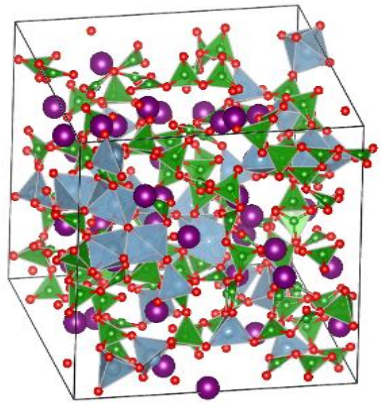
cea

Development of a new approach for the structural modeling of glasses combining atomistic modeling and NMR: Application to lanthanum aluminoborate

Prix de thèse USTV 2019
Journées USTV
Rennes 2021

www.cea.fr





E. CHESNEAU

SUPERVISORS: T. CHARPENTIER, D. CAURANT

INTRODUCTION

What is glass ?

"Glass is an amorphous material exhibiting a glass transition phenomenon"

J. Zarzycki, *Les verres et l'état vitreux*, 1982

Œnochoé, Italia, VIth century B.C

Glass is an old material …

XVIth century B,C : first man made glass

… and very widespread nowadays

Table glass (Duralex®)

Dishes Pyrex®

Window glass (float process)

➔ **Low added value**

Glass Duralex®, restaurant 1, CEA Saclay, XXIst century after J.C

dishes Pyrex

INTRODUCTION

Glass has a growing attraction

modern architecture

Saint Gobain research, Aubervilliers

Glass is also a technological material

R7T7 glass

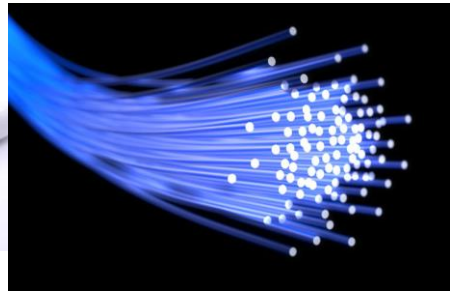
optical fiber

biocompatible glass

Gorilla glass ®

Vitrification of nuclear waste

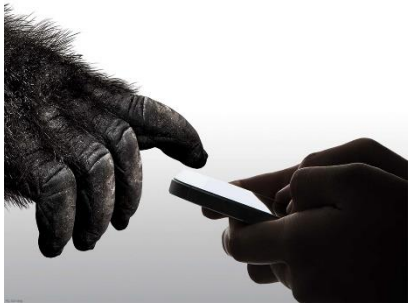
Toothpaste containing biocompatible glass



Optical fiber

Thanks to a wide range of accessible properties

due to the low stoichiometric constrain induced by the amorphous character

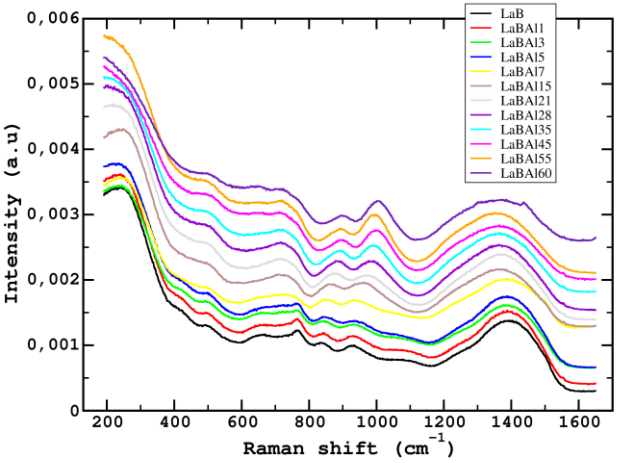


Gorilla® glass, Corning®

TOOLS : EXPERIMENTAL

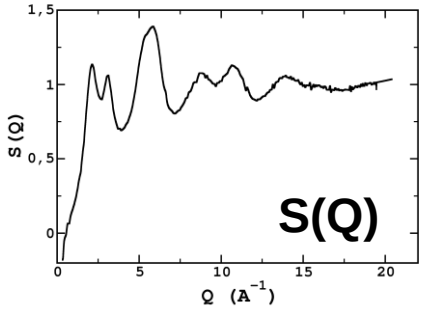
Raman spectroscopy

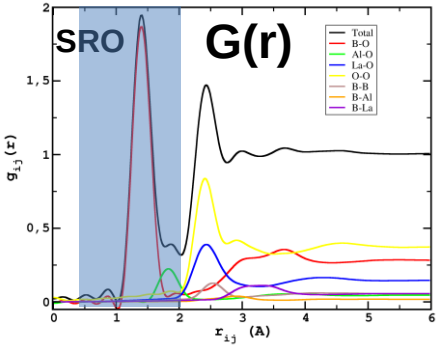
Horiba Raman spectrometer



Neutron scattering

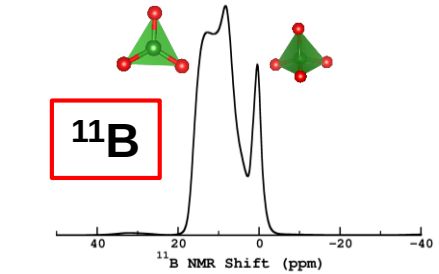
LLB, CEA Saclay

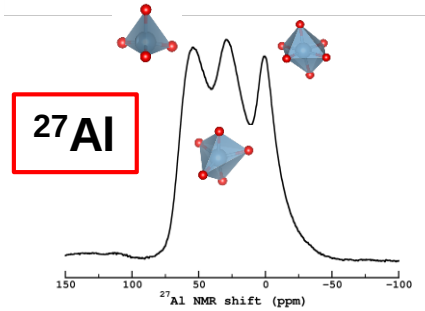




NMR

Bruker 11.7T, LSDRM, CEA Saclay

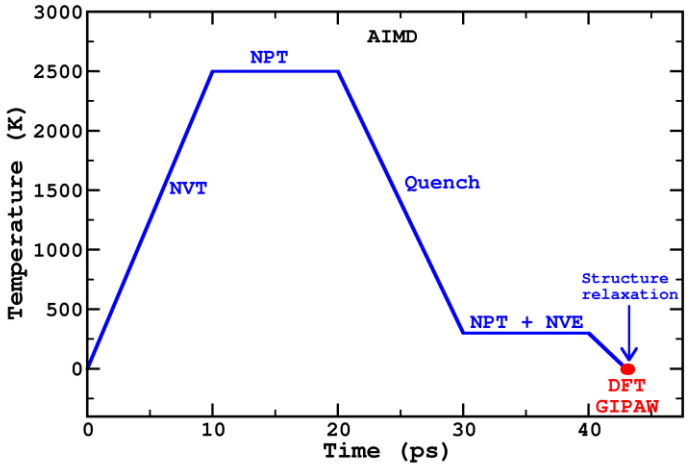




Classical and ab-initio Molecular Dynamics

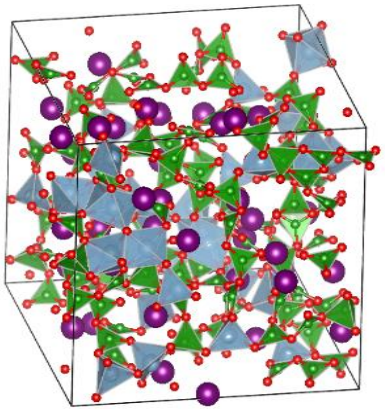
DL_POLY 4

~ K.ms^{-1}

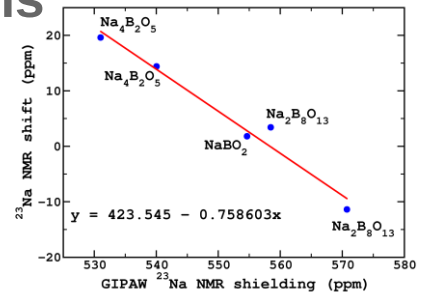


~ K.ps^{-1}

GIPAW calculations



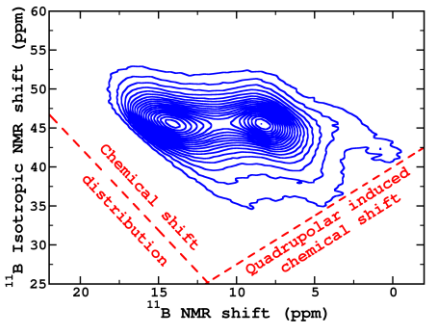
Pickard et al, Phys. Rev. B, 2001



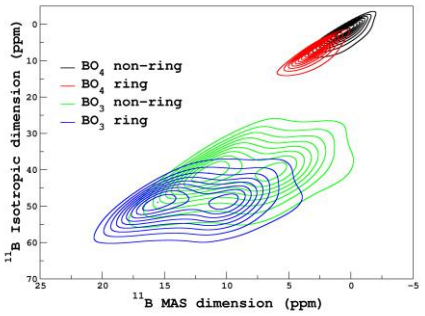
GIPAW

b-initio VASP ackage imulation ienna

Expérimental

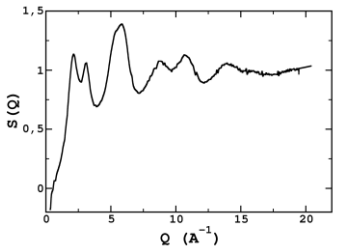


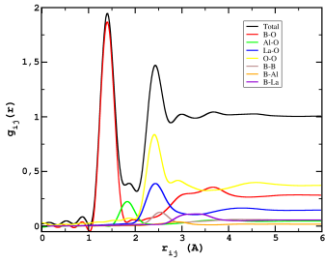
GIPAW

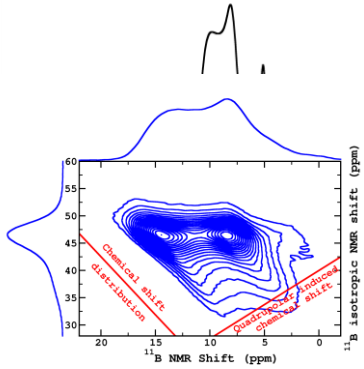


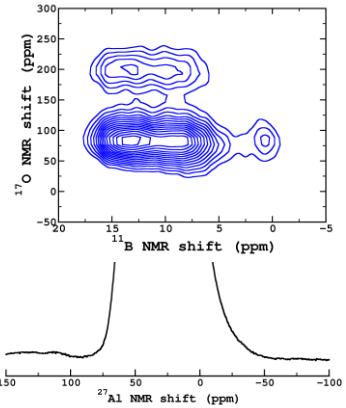
OBJECTIVE

- To create models probing more configurations
  - To characterize new conformations (more realistic)









distances

IRO

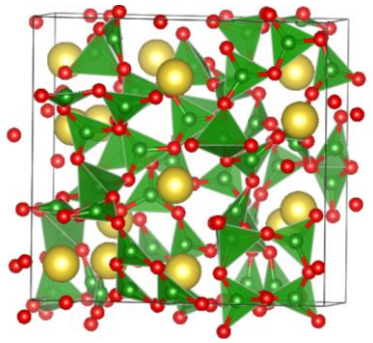
(CN + connectivity)

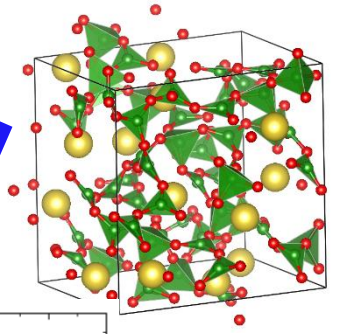
RMC

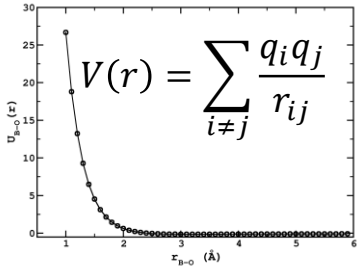
MD Box

stability

NMR Driven RMC Models



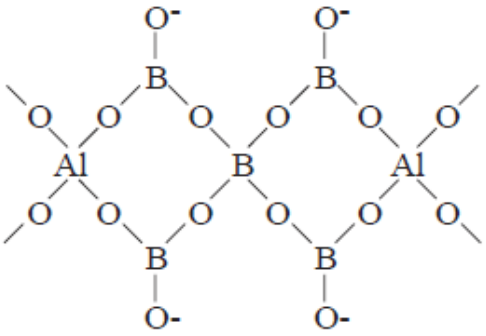




- Simulated Annealing Approach
  - Effective Temperature controlling balance between constraints and energetic terms (MD)

INTRODUCTION : SYSTEM

- **The structure of Lanthanum Aluminoborate glasses has been scarcely studied** [1][2][3]
  - Comparing glass structure with metaborate crystal one (B-O-B chains)
  - How is Al_2O_3 inserted in the structure?
  - $\%BO_4$ is decreasing with the addition of Al_2O_3 (NMR)
  - BO_4 substituted by AlO_4 in the structure
  - Al in superstructural units (Raman)

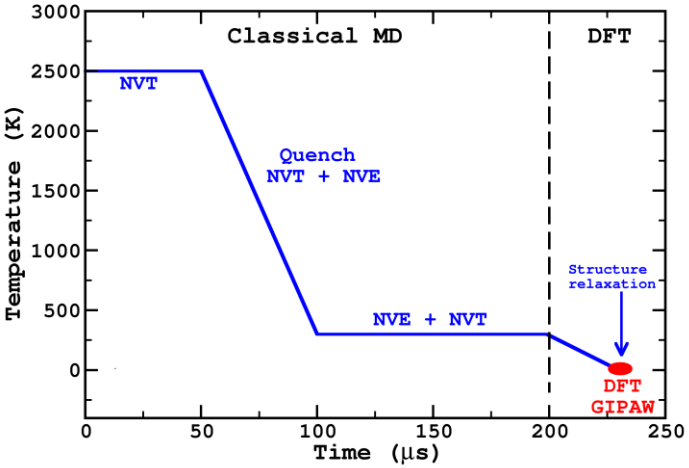


- **In this study, we focus on $(25La_2O_3\text{-}75B_2O_3)+15Al_2O_3$**
  - To determine $\%BO_x$, $\%AlO_x$, %NBO (NMR)
  - To study the connectivity between BO_x and AlO_x units (NMR)
  - To obtain information on superstructural units using a new method combining neutron, NMR and MD simulation

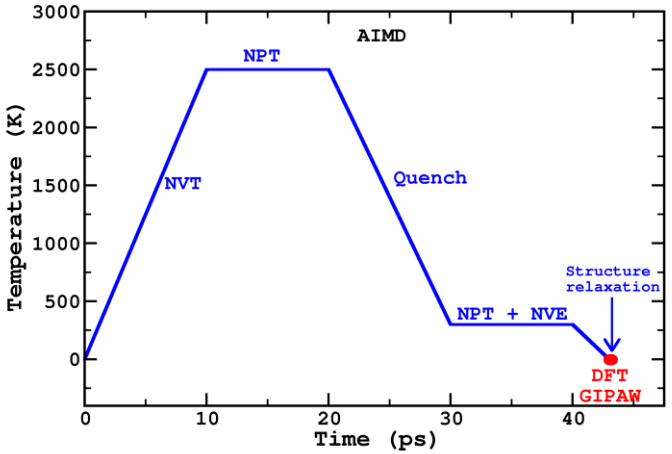
[1] :Brow et al , Journal of the American Ceramic Society, 1997
[2] : Chakraborty et al, Journal of the American Ceramic Society, 1985
[3] Pytalev et al, Journal of Alloys and compounds, 2015

MOLECULAR DYNAMICS

- **Classic Molecular Dynamics (CMD)**
  - Empirical potentials
  - Melt quench method
    (HT-Quench-300K)
  - DL-POLY 4



- **Ab-initio Molecular Dynamic (aiMD)**
  - Start : CMD structure @ 300K
  - Melt quench method
  - CP2K
- **Geometry optimization (cp2k)**
- **DFT-GIPAW : VASP**

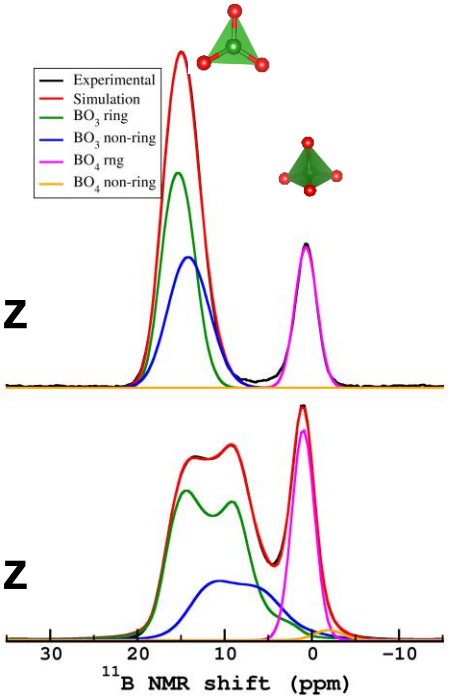


NUCLEAR MAGNETIC RESONANCE: MAS

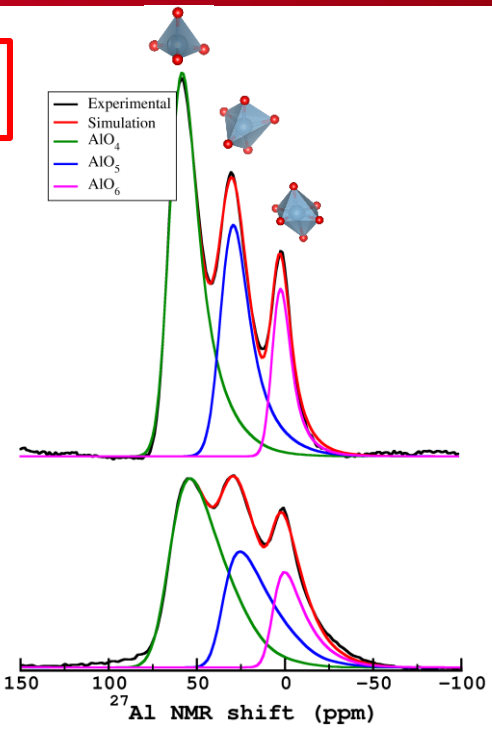
^{11}B

800MHz

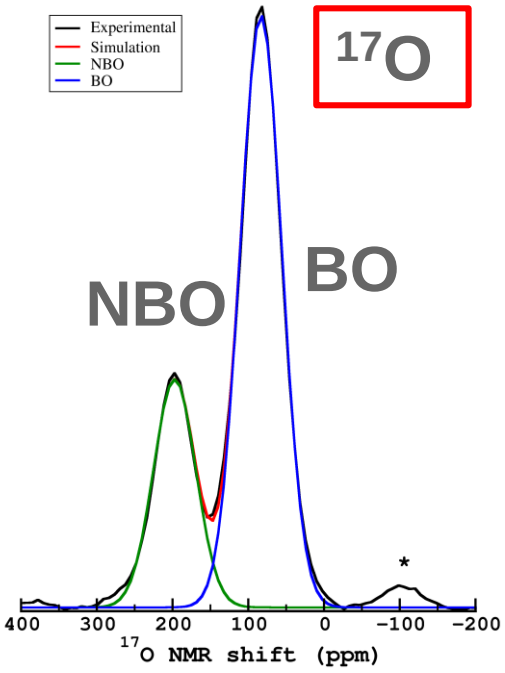
500MHz



^{27}Al



^{17}O



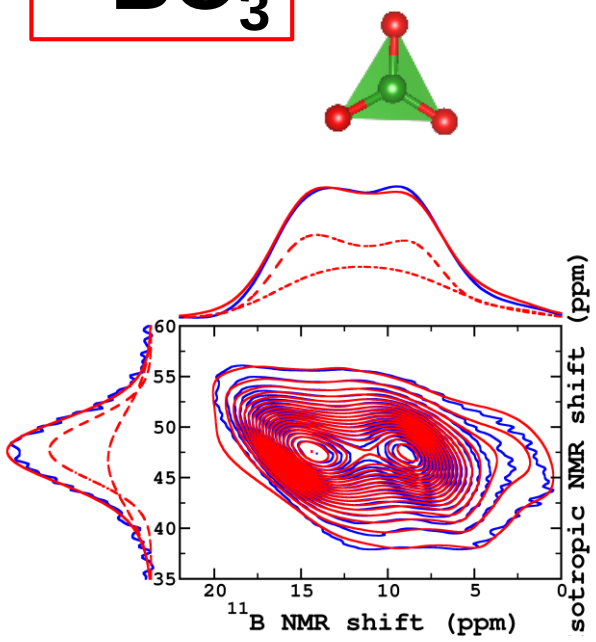
- **1D MAS spectra are quantitative :**

	%BO_3	%BO_4	%AlO_4	%AlO_5	%AlO_6	%BO	%NBO
LaBAl15	76	24	53	30	17	72	28

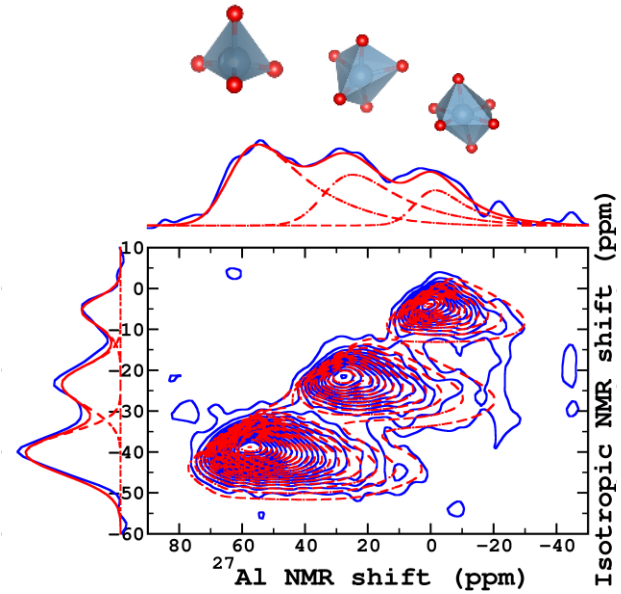
- **What about connectivity ?**

NUCLEAR MAGNETIC RESONANCE: MQMAS

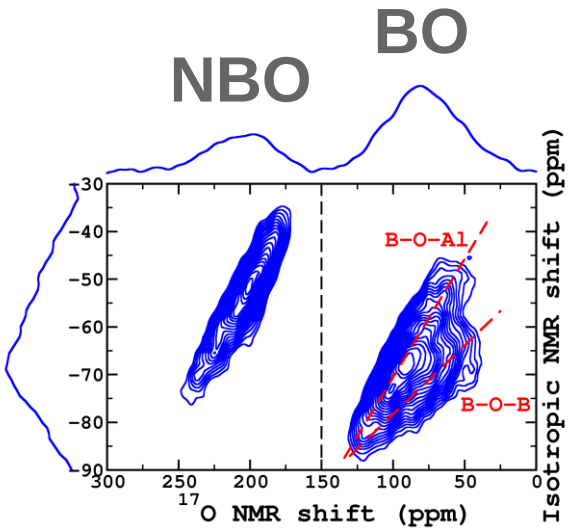
$^{11}BO_3$



^{27}Al



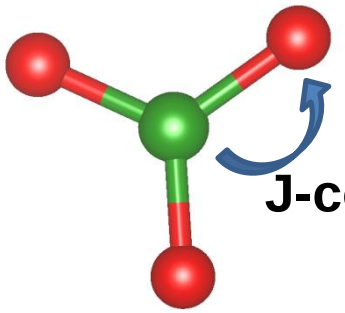
^{17}O



- ^{11}B : two BO_3 species
- ^{27}Al : only three Aluminum sites observed
- ^{17}O : one NBO site and at least two BO

ADVANCED 2D NMR: THROUGH BOND CONNECTIVITY (J-HMQC)

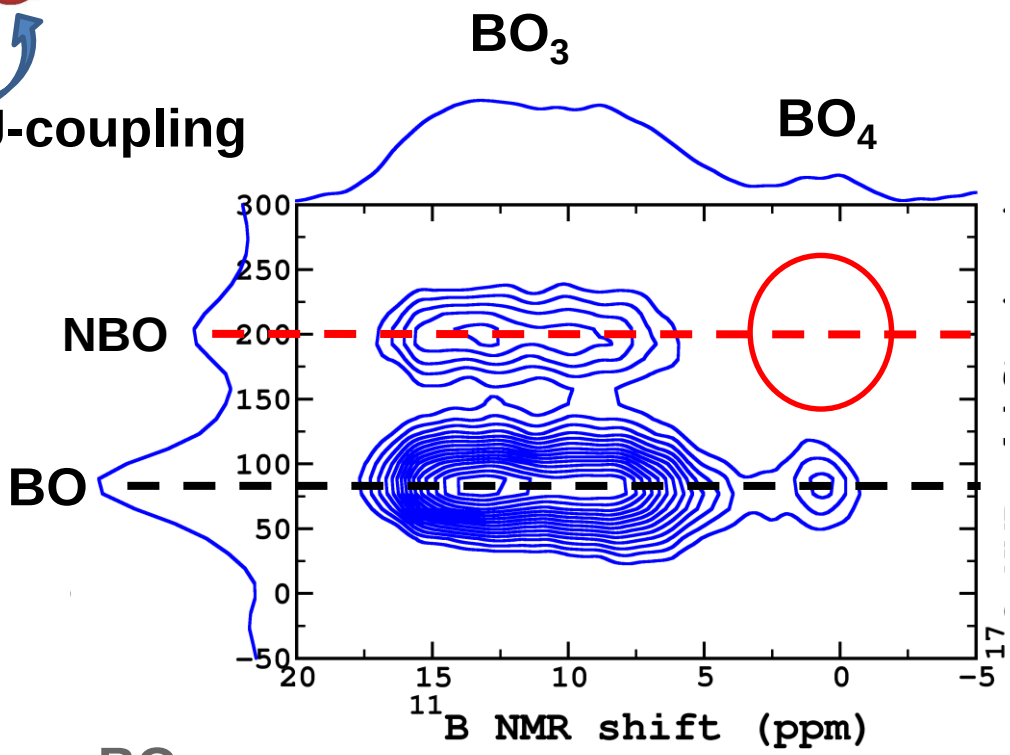
- J-HMQC $^{11}B\{^{17}O\}$

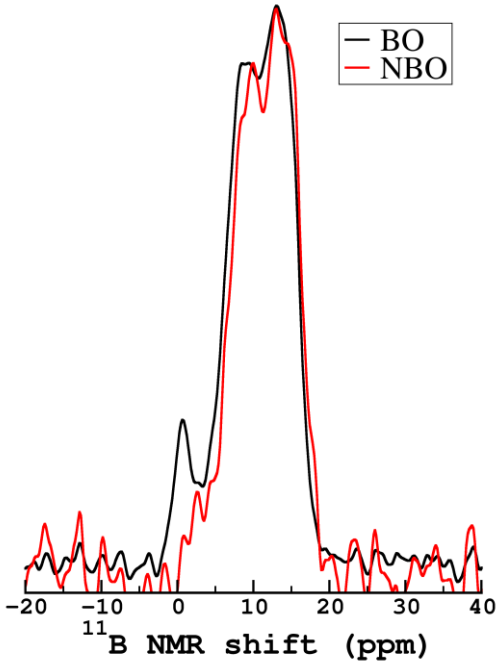


J-coupling

^{11}B

^{17}O

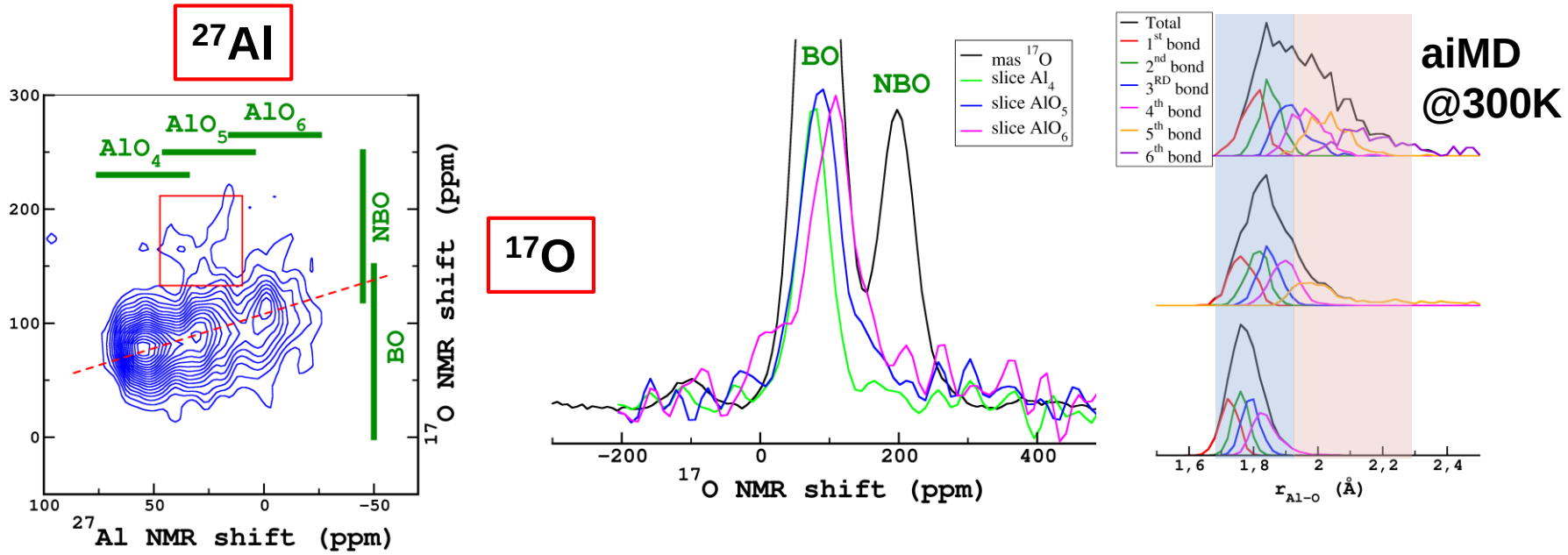




- No NBO on BO_4
- BO and NBO seem to be connected at the same BO_3
  - Only $B\emptyset_2O^-$: $n(BO_3) \sim n(NBO)$

ADVANCED 2D NMR: THROUGH BOND CONNECTIVITY (J-HMQC)

- J-HMQC $^{27}Al\{^{17}O\}$



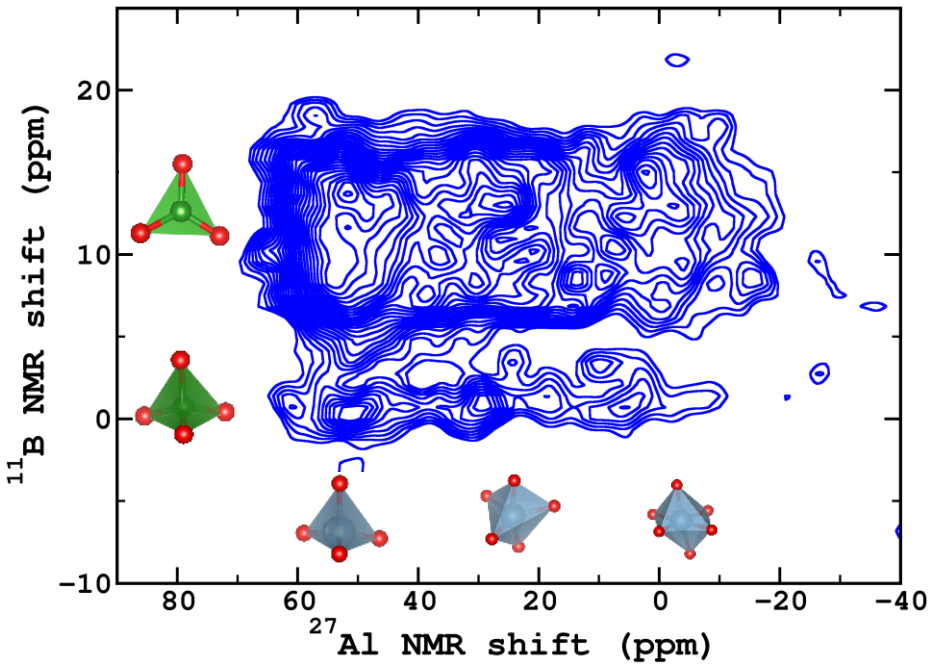
- AlO_4-BO and AlO_5-BO peaks are at similar ^{17}O NMR shift
  - Suggests that both units are former
- AlO_6-BO at higher ^{17}O NMR shift
  - Weaker bonds
- Maybe a small amount of NBO on $AlO_{5,6}$

ADVANCED 2D NMR: THROUGH BOND CONNECTIVITY (J-HMQC)

- J-HMQC $^{27}Al\{^{11}B\}$: $J^{2}_{Al\text{-}O\text{-}B}$

^{27}Al

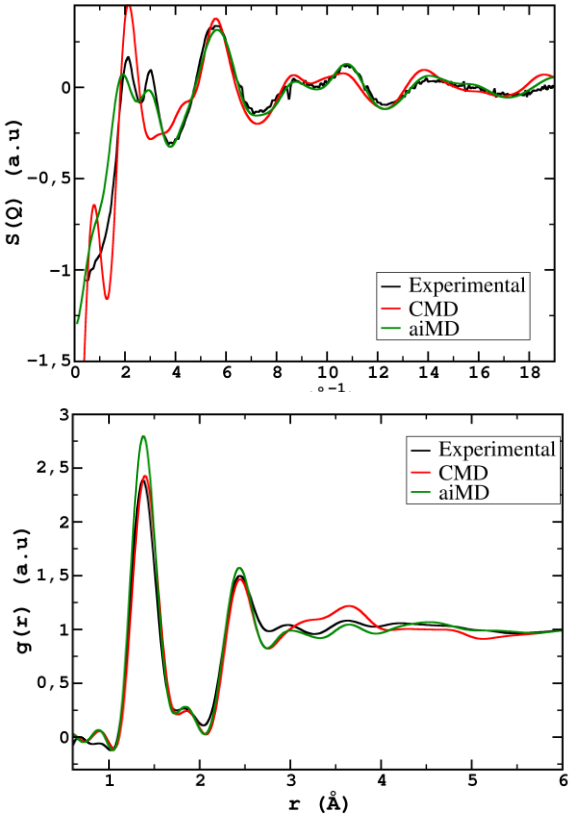
^{11}B

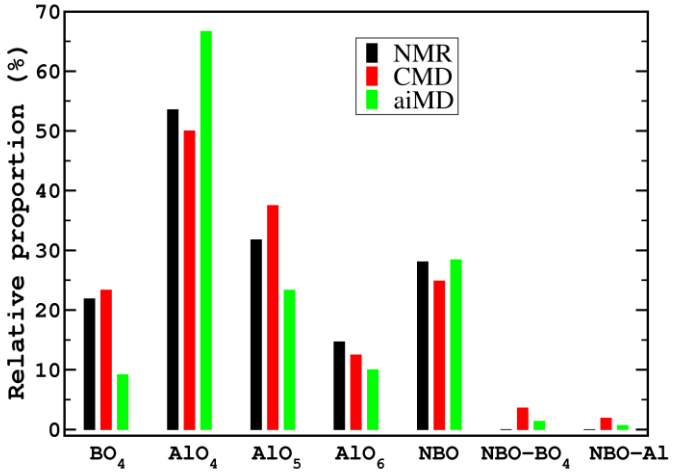


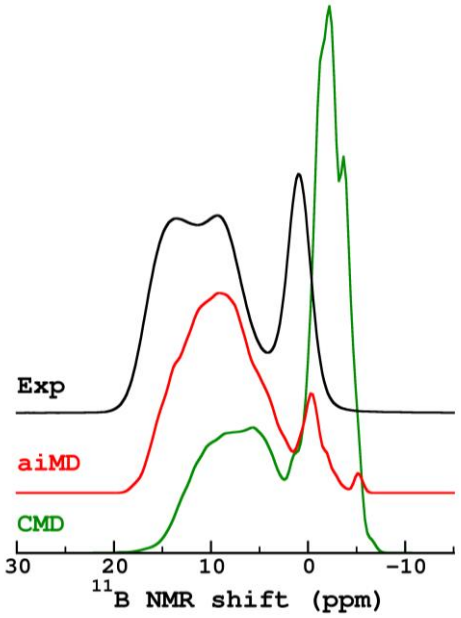
6 days…

- Presence of bonds BO_3-O-Al and BO_4-O-Al
- Slight or no difference between different AlO_x

COMPARISON BETWEEN MD / EXP



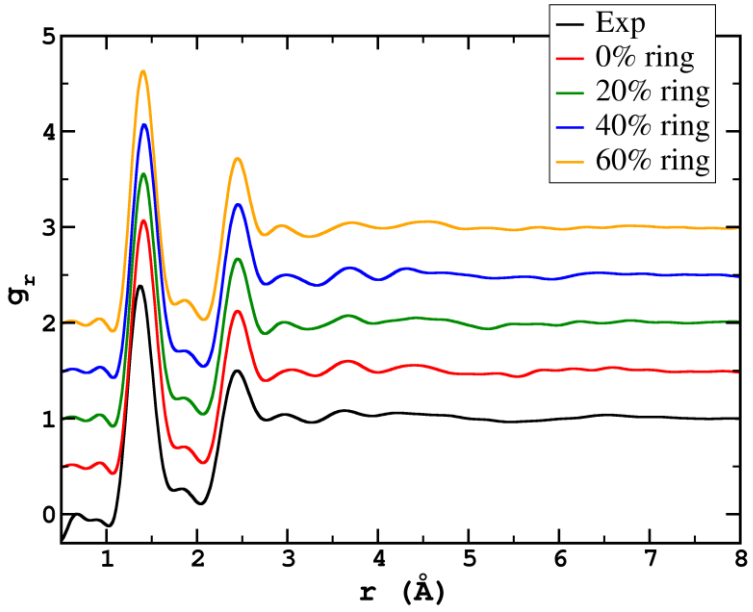


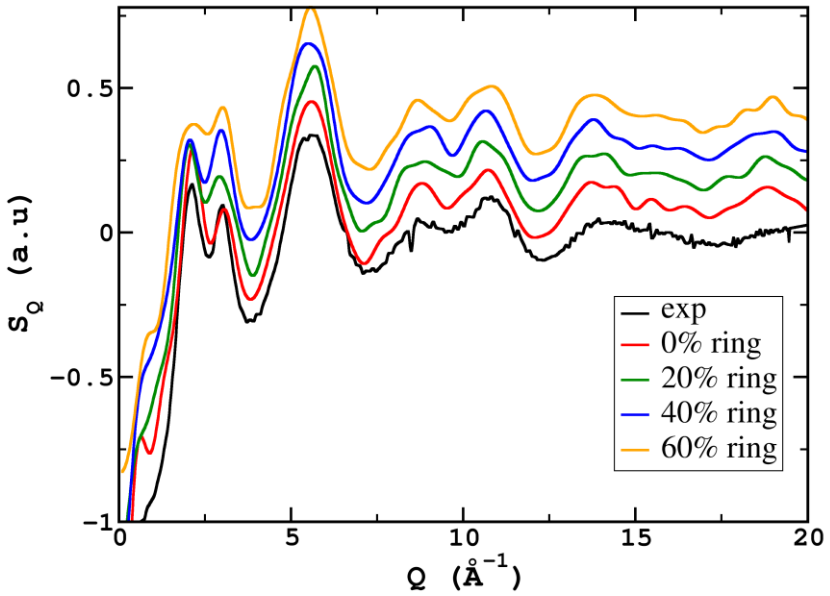


- aiMD reproduces the S(Q) but not the NMR CN
- Proportions of different species are not perfectly reproduced
  - Is it possible to improve it thanks to RMC ?

HYBRID REVERSE MONTE CARLO

- Constraints on $\%BO_4$, $\%AlO_x$ and localization of NBO
- Neutron data from (DFT) optimized RMC structures

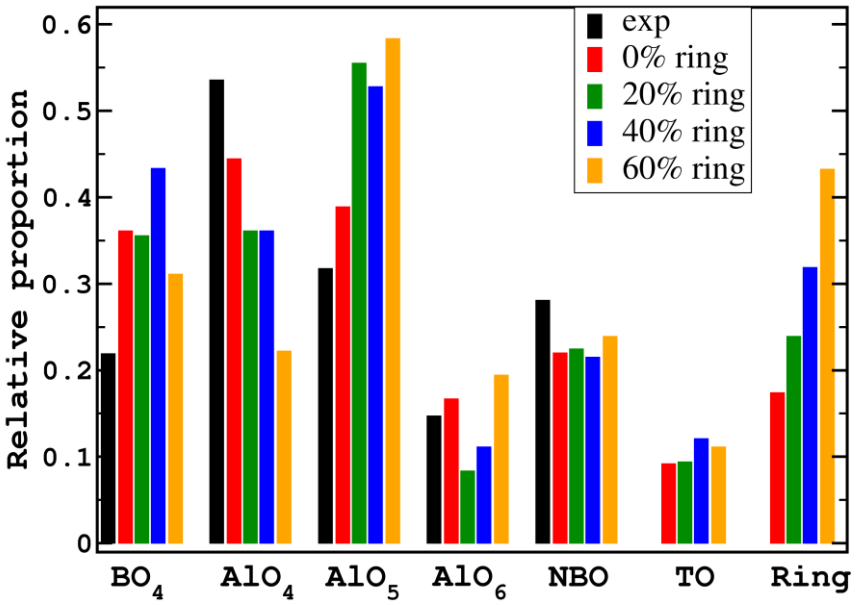


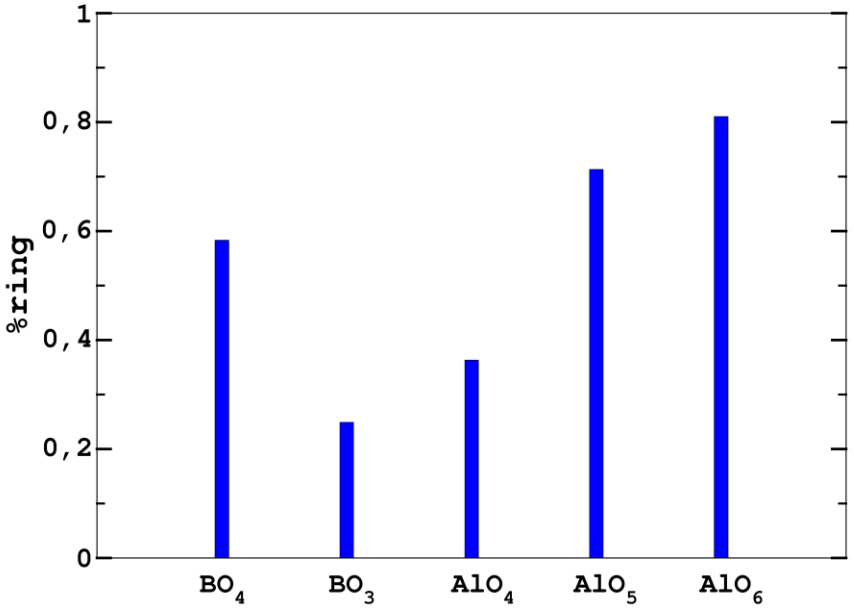


- Very good agreement after geometry optimization
  - Neutrons are not enough discriminative
  - CN and NMR agreement ?

HYBRID REVERSE MONTE CARLO

- Data extracted from optimized RMC structures

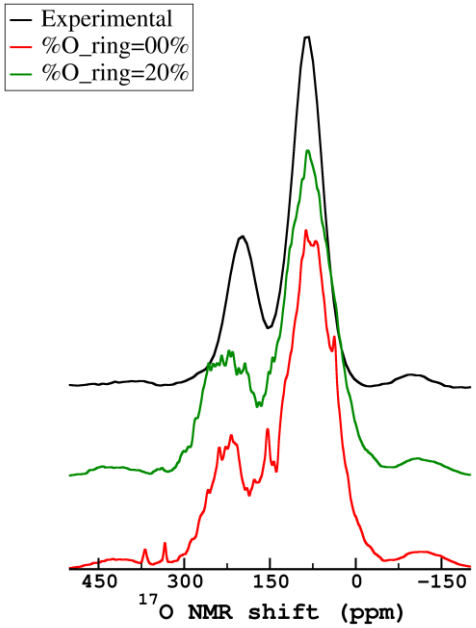


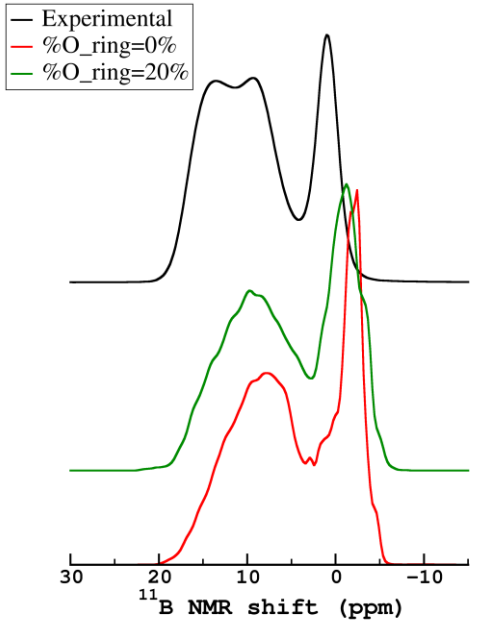


- DFT Optimization decreases the agreement with experimental data
- Overestimation of AlO_5 and BO_4
- TO ≈ 10%, rings always existing (>20% O)

HYBRID REVERSE MONTE CARLO

- **Simulation of NMR spectra from optimized RMC models**

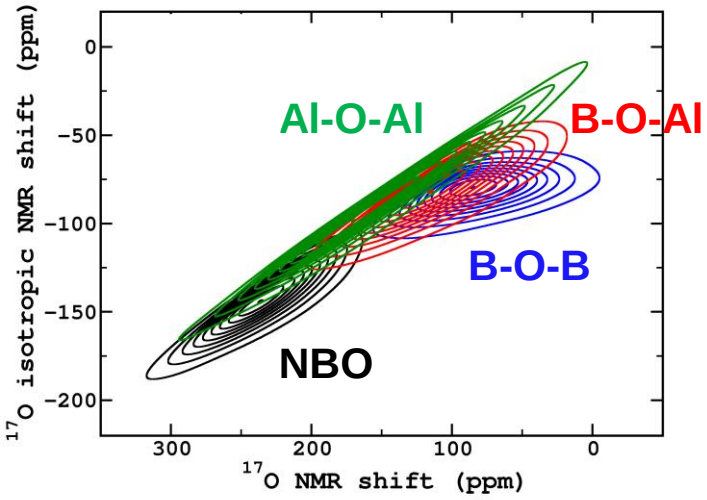


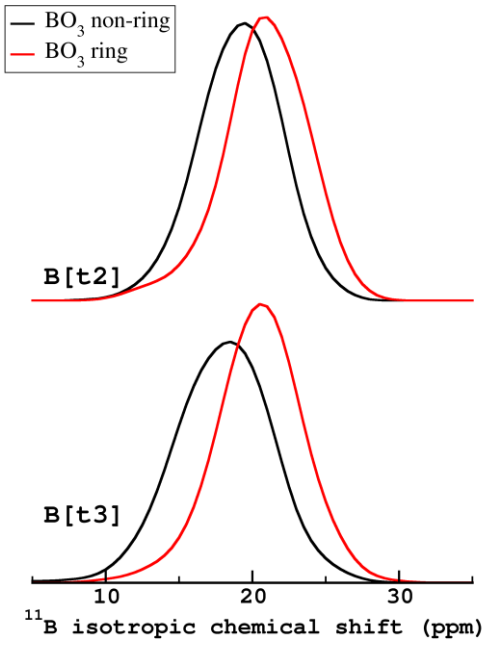


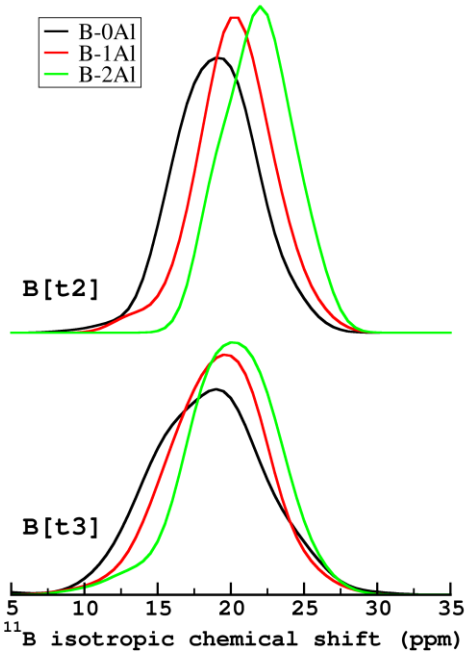
- **Oxygen-17 spectra is not sensitive to %ring**
- **Boron-11 spectra is more sensitive but experimental spectra is not well reproduced**
  - Constraints induced DFT non-stable environments

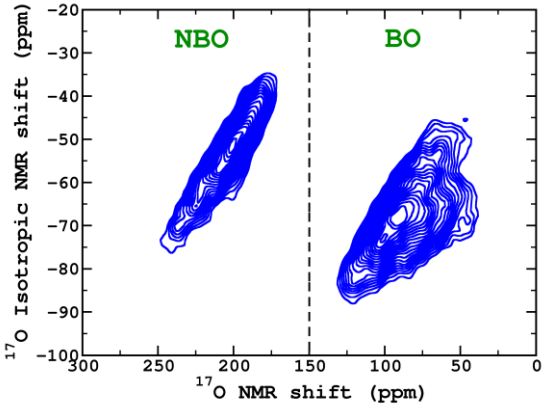
HYBRID REVERSE MONTE CARLO

DFT-GIPAW results







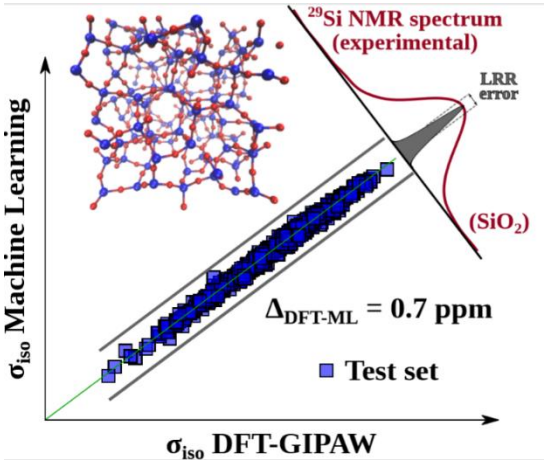


- Discrimination on ^{17}O MQMAS spectra of different BO
  - Difficulties to observe Al-O-Al
- BO_3 ring and BO_3-nAl impact the NMR shift in the same way
- Indicating that Al are in rings?

CONCLUSIONS

- **HRMC simulation give new perspectives for models generation**
- **It allows to create more realistic models with conformations that are difficult to generate by MD (small rings, …)**
- **The setting of simulations is not trivial (numerous parameters)**
- **Agreement with NMR data could be improved**
  - S(Q) agreement : **OK**
  - NMR agreement : **~ OK**

    DFT stability of some local environments must be addressed…



- **Perspectives: DIRECT consideration of NMR shifts (Machine Learning)**
  - No more constraints based on interpretation of NMR data or on advanced experiments (CN, connectivity…)
  - Flexible exploration of conformations (variable %ring)
  - Improved interpretation of experimental data (based on 3D structure)

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Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 43 38 | F. +33 (0)1 69 08 66 40

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019