RMN premiers principes appliquée à l'étude des verres de phosphates

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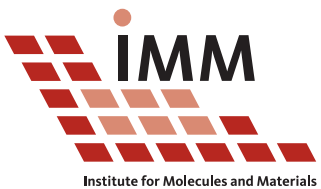
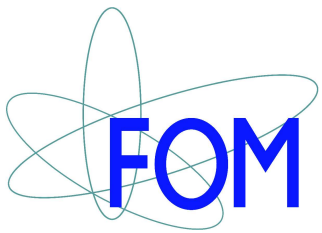
École thématique GDR-Verres
Marcoule - Mai 2011





Radboud University Nijmegen

Outline

Introduction

General context

Some elements of the methodology

NMR First Principles applied to Glass

- ✘ Motivations
- ✘ How to generate glass configurations ?
- ✘ Case study : Sodium metaphosphate glass ($NaPO_3$)
  - NMR results (spectra, correlations, . . .)
  - EFG distributions
  - Extended Czjzek Model

NMR parameters and structure

- ✘ Potential energy landscape (PEL) in glass science.
- ✘ NMR parameters revealing the PEL

General Conclusions

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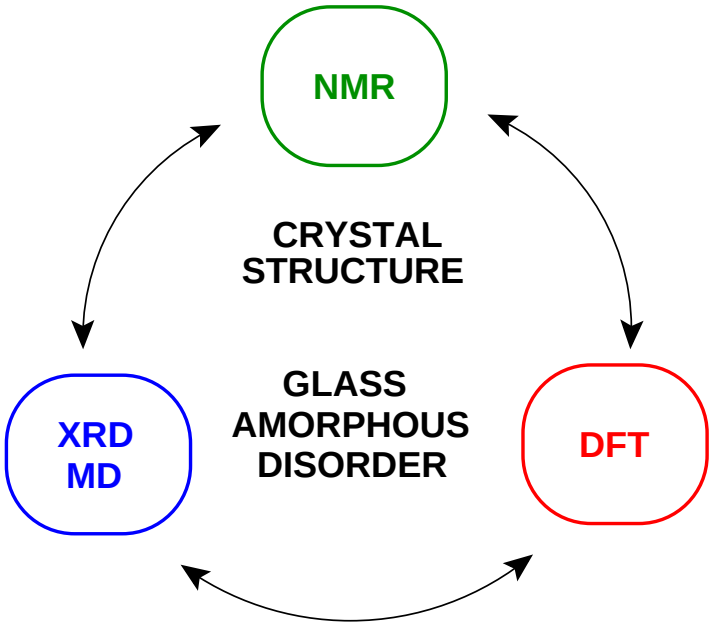

Introduction

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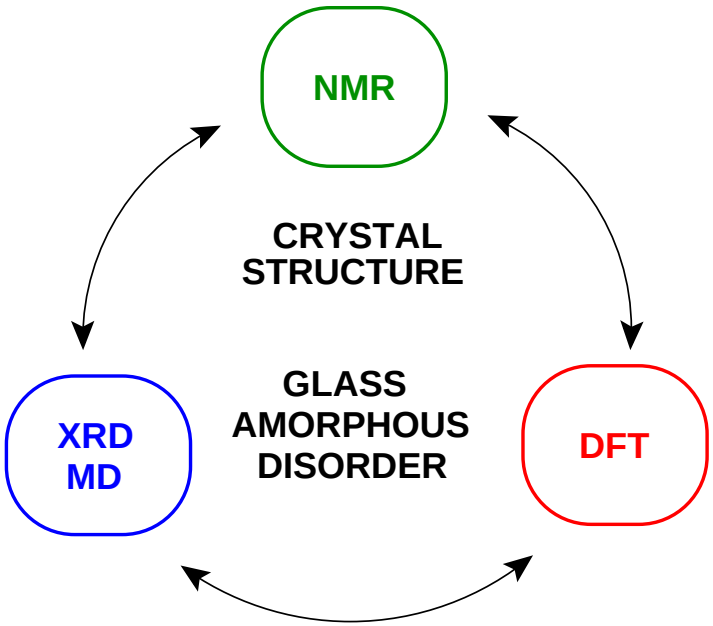
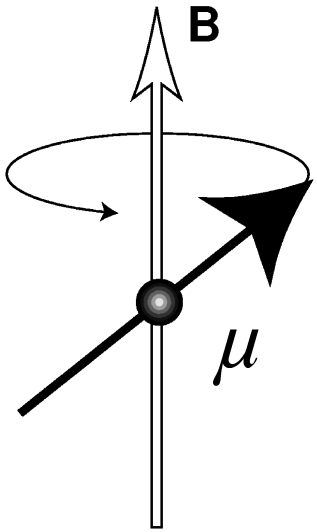


NMR :

- ✘ Better resolution → more information

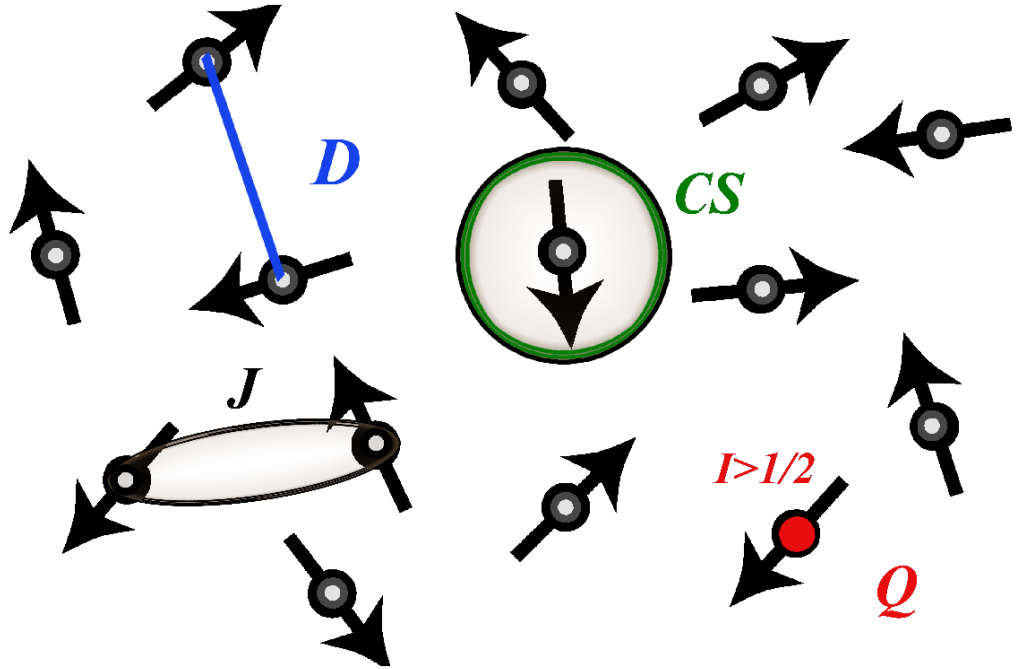
Introduction

Solid-State Nuclear Magnetic Resonance (SSNMR)



Dynamic

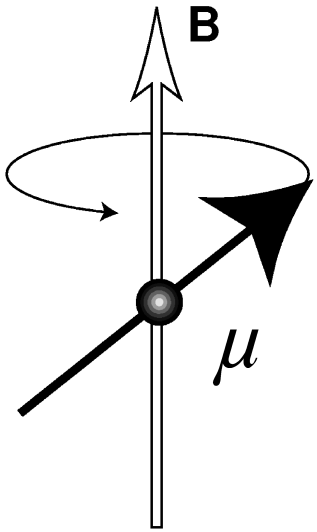
Structure



Interaction	Name	Tensor	Parameters
CS	Chemical Shift	CSA	δ_{iso}, Δ_{CS}, η_{CS}
Q	Quadrupolar	EFG	C_Q,η_Q
D	Dipolar coupling	D	r
J	Indirect spin-spin coupling	J	J_{iso}

Introduction

Solid-State Nuclear Magnetic Resonance (SSNMR)



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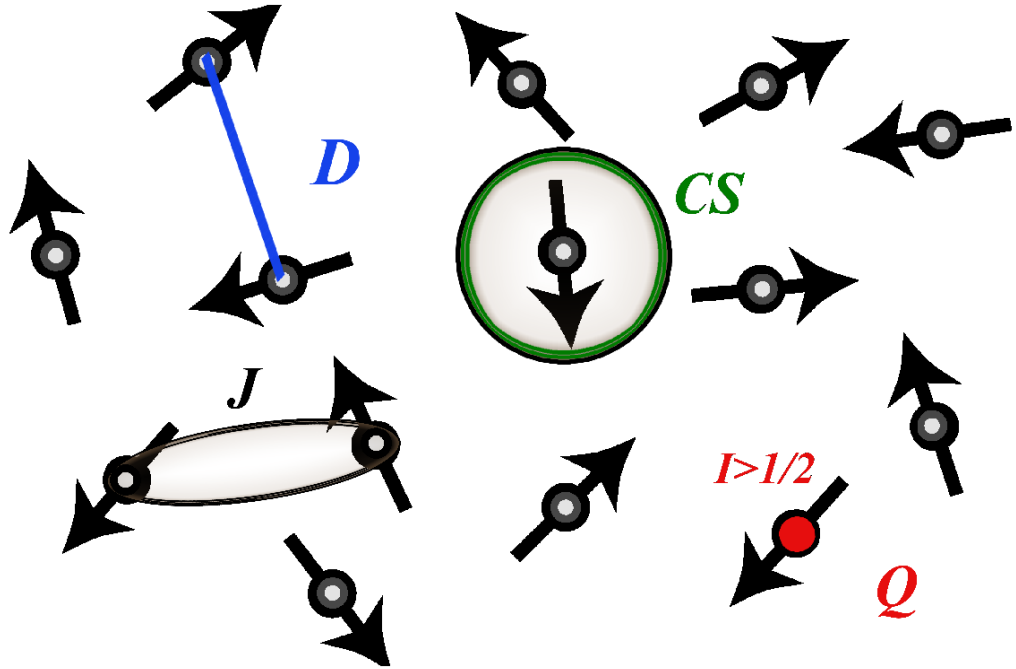

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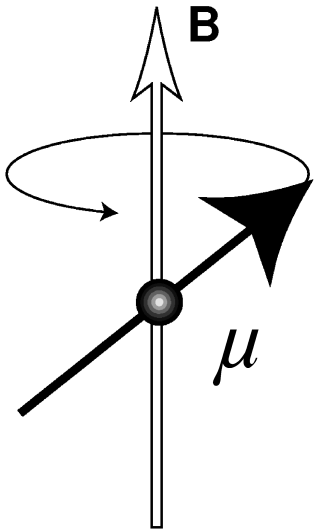

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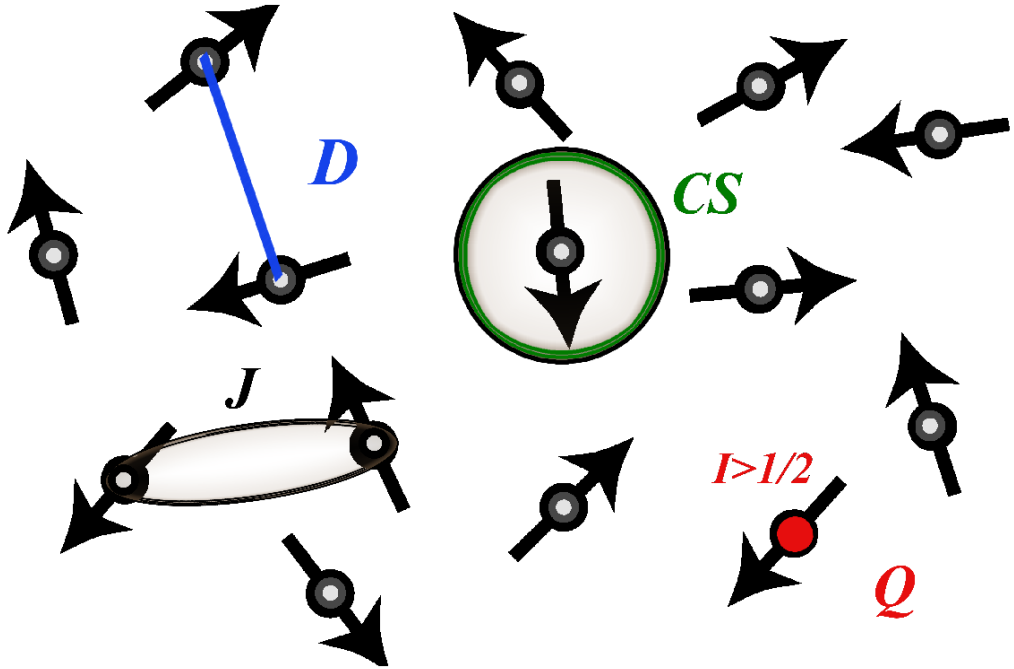

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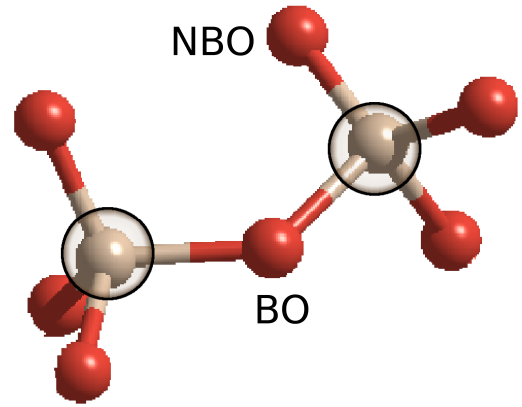
Introduction

Overview of ^{17}O



Properties

- ✘ Predominant nucleus in oxides based glasses
- ✘ Two different role in the structure (BO , NBO)
- ✘ Wide chemical shift range
- ✘ Low natural abundance (0.037%)
- ✘ Quadrupolar interaction with the surrounding EFG

Quadrupolar Interaction

- ✘ I=5/2
- ✘ Q=25.58 mb

$$EFG : \boldsymbol{V} = V_{zz} \begin{pmatrix} \frac{\eta_Q - 1}{2} & 0 & 0 \\ 0 & \frac{-\eta_Q - 1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Introduction

Elements of methodology

Experimental (NMR)

- Isotopic enrichment (^{17}O)
- High-Field (18.8 T)
- Multi-nuclei (^{23}Na, ^{31}P, ^{17}O)
- High-resolution experiments (MAS, MQMAS)

Theoretical (Modelisation)

- Electronic Struct. : DFT
- NMR parameters : DFT-PAW/GIPAW
- MD : classical, *ab-initio*
- Spectra simulation
- Used codes :
  - VASP, Quantum-ESPRESSO, PARATEC
  - DL_POLY
  - DMFIT, simpson, gen_mas, gen_MQMAS

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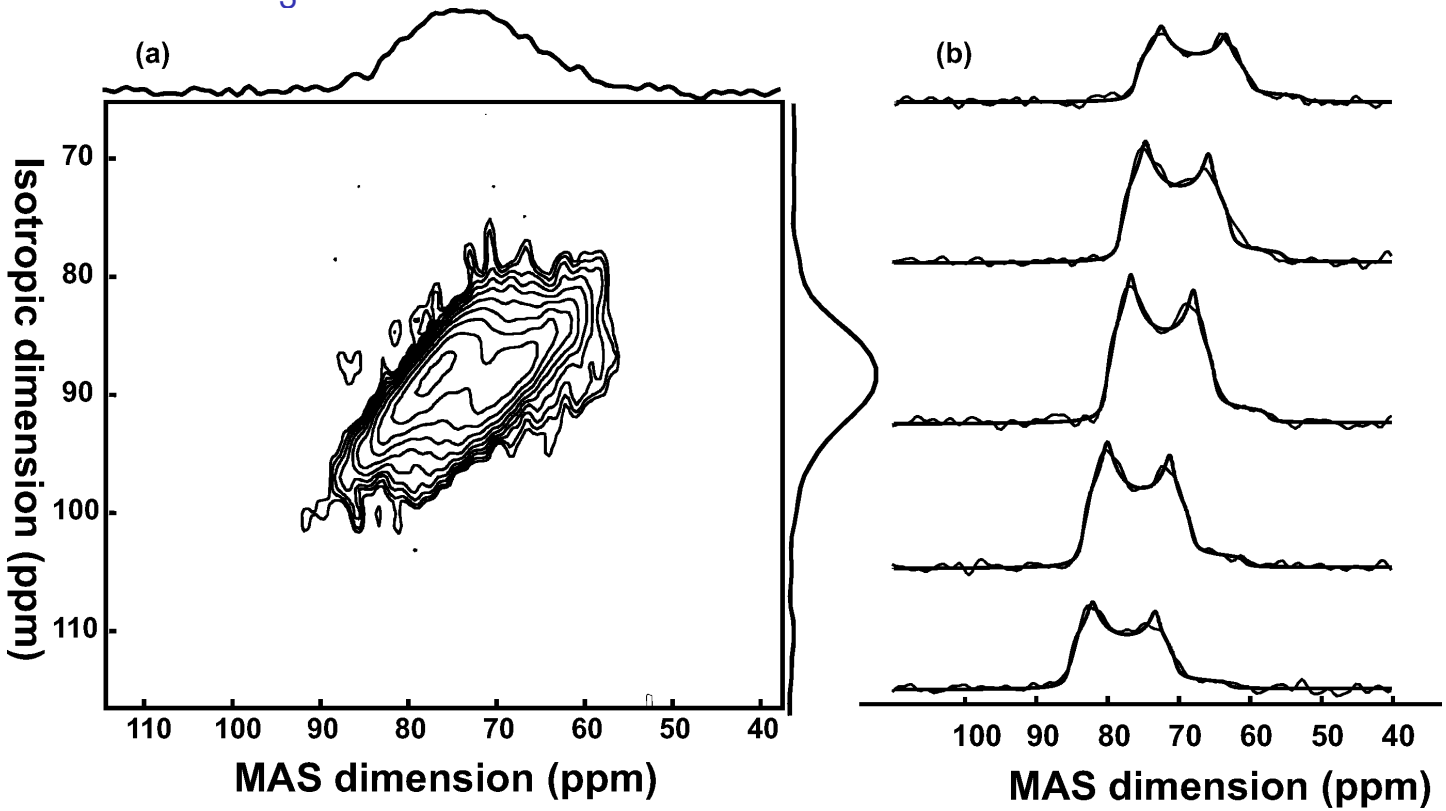
Sodium metaphosphate glass

3QMAS at 18.8T of $NaPO_3$



Non-bridging oxygens

- ✘ small distribution $(C_Q, \eta_Q) \rightarrow$ local order
- ✘ large distribution $\delta_{iso} \rightarrow$ long distance disorder

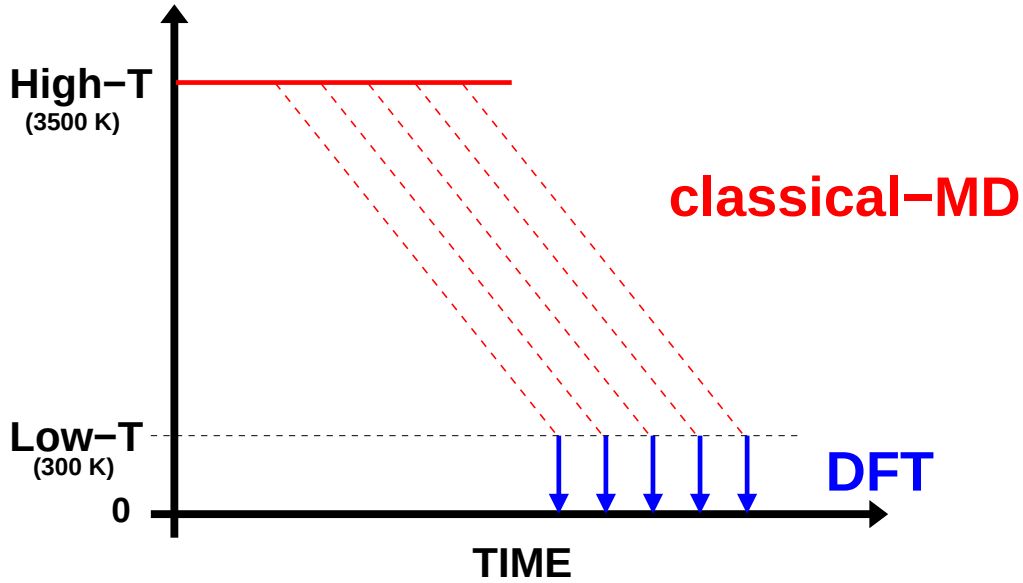
F. Vasconcelos et al., Inorg. Chem., **47** 7327 (2008)

How to generate glass configurations ?

For NMR First-Principles

What do we need ?

- ✘ Accurate structures ☺
- ✘ Good statistics ($\sim$ 1000 sites)
- ✘ Small boxes ($\sim$ 100 atoms)



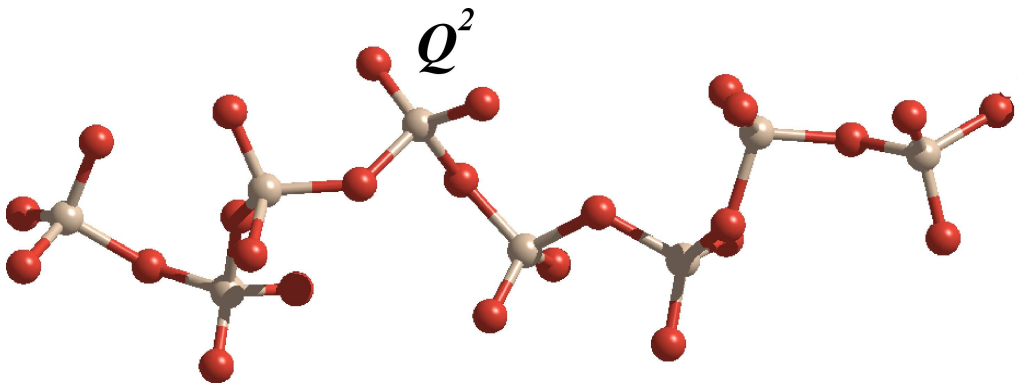
Which methods ?

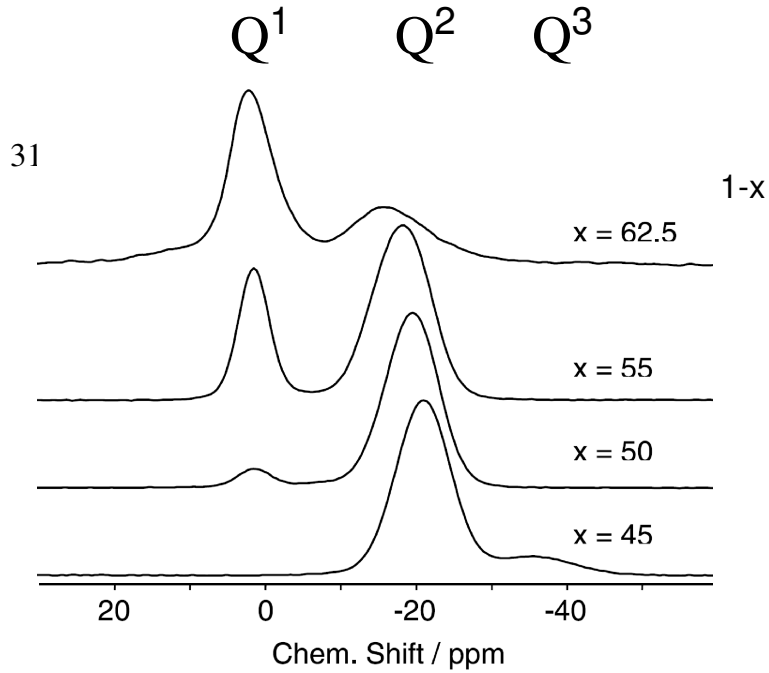
Molecular Dynamics (MD) :

- ✘ "*Ab-initio*" MD : accurate, time consuming, few configurations
- ✘ Classical MD : fast, many configurations, empirical Force-Fields
- ✘ Combined approach : classical and first-principles
- ✘ DL_POLY+ VASP (PARATEC : DFT-PAW/GIPAW)

$NaPO_3$ (metaphosphate)

Structural constraints



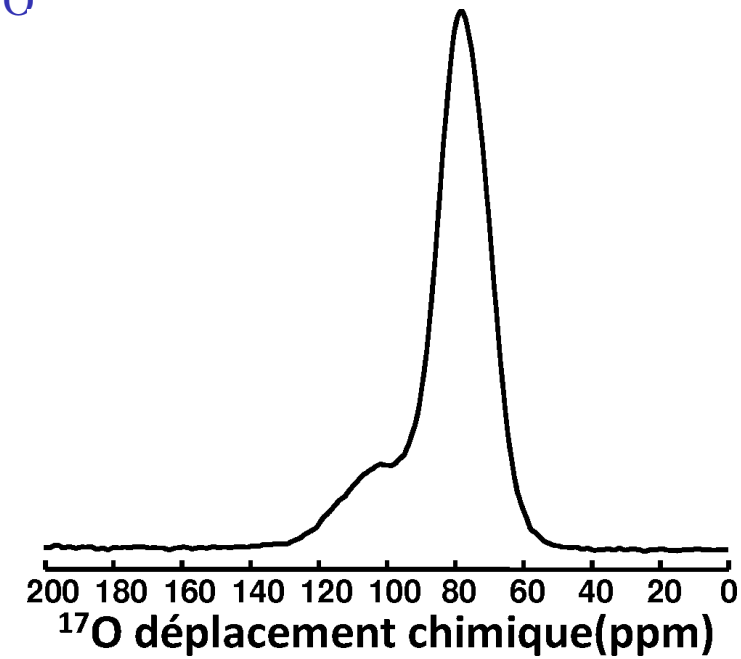


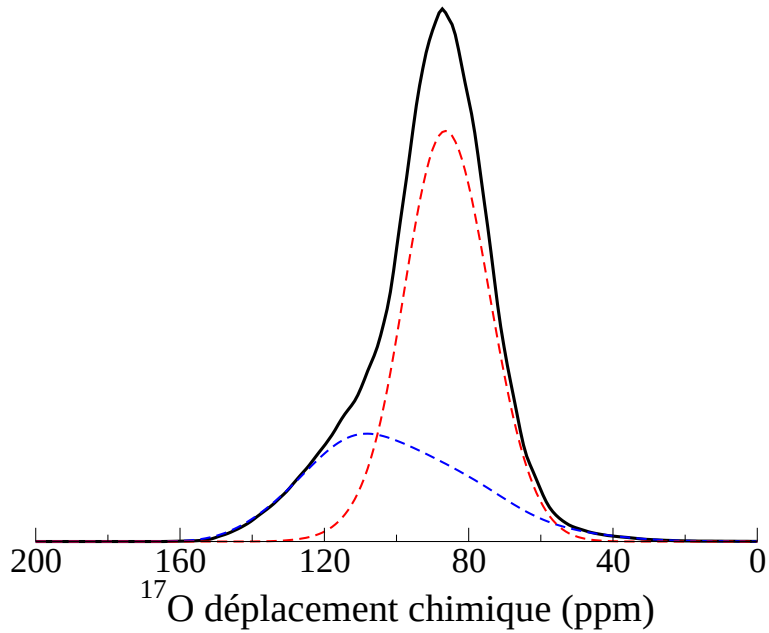
atomic pair	**MD ref [1]** d (Å)	**Neutron ref [2]** d (Å)	**our model** d (Å)
Na−Na	3.1	3.07	3.35
Na−O	2.31	2.33	2.35
O−O	2.51	2.52	2.55
P−P	3.18	2.93	2.95
P−NBO	1.50	1.48	1.45
P−BO	1.59	1.61	1.65
Q^1	25%	0%	3.5%
Q^2	50%	∼100%	93%
Q^3	25%	0%	3.5%

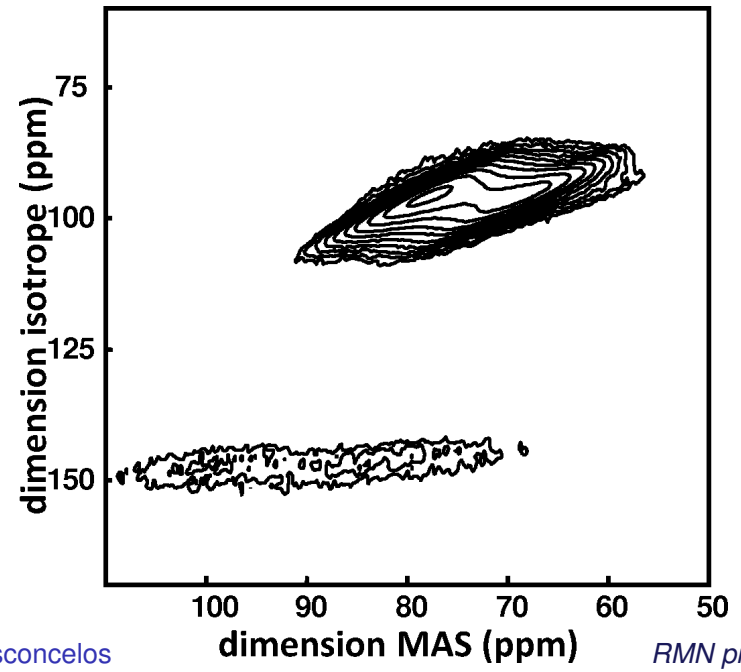
[1] Speghini et al. PCCP **1** p173 (1999)
[2] Pickup et al. J. Phys. Condens. Matter **19** p415116 (2007)

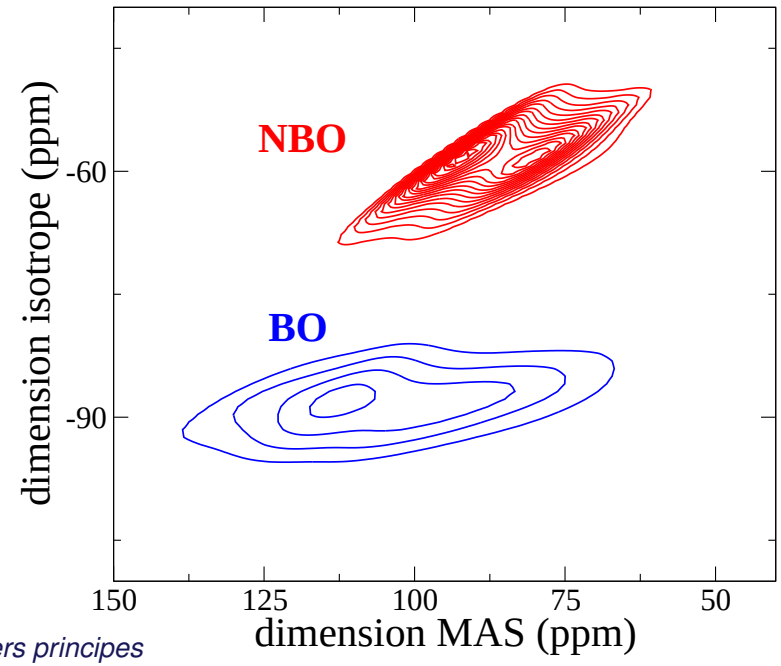
NMR/DFT-GIPAW results on MD configurations

NMR ^{17}O







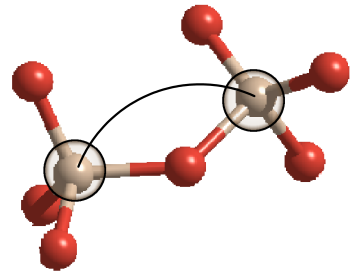


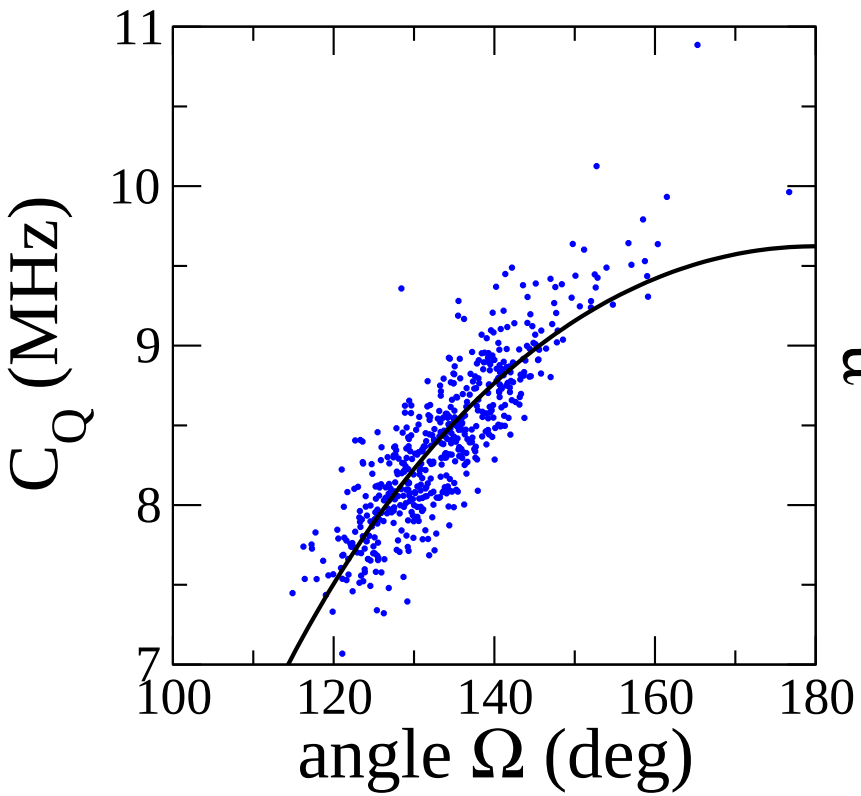
DFT-GIPAW results on MD configurations

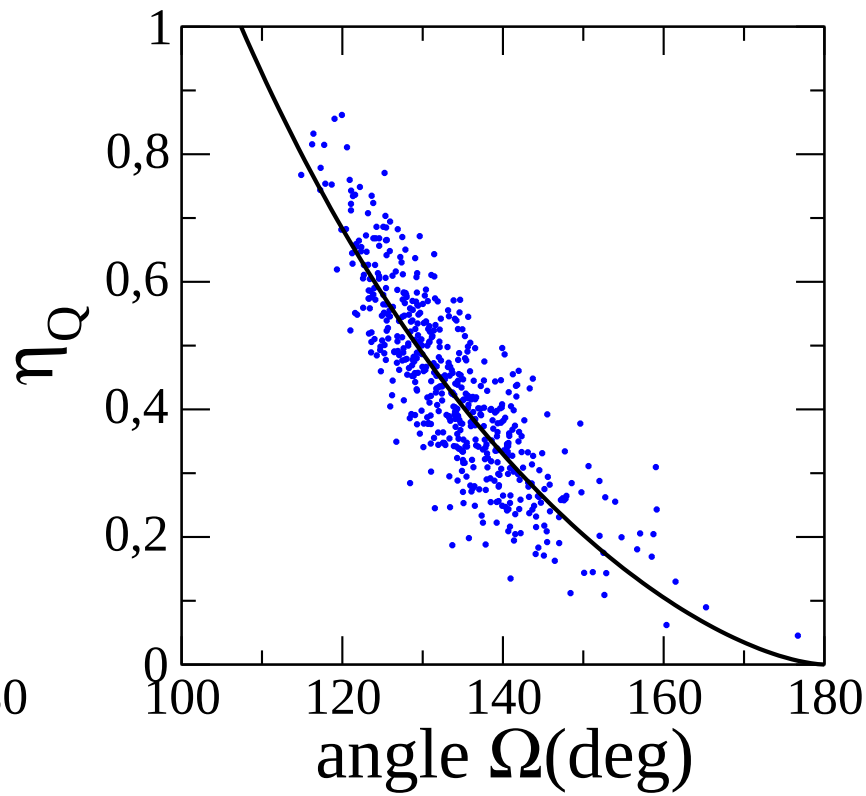
Clark-Grandinetti correlation ^{17}O

$$C_Q(\Omega) = a\left(\frac{1}{2} + \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\alpha}$$

$$\eta_Q(\Omega) = b\left(\frac{1}{2} - \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\beta}$$

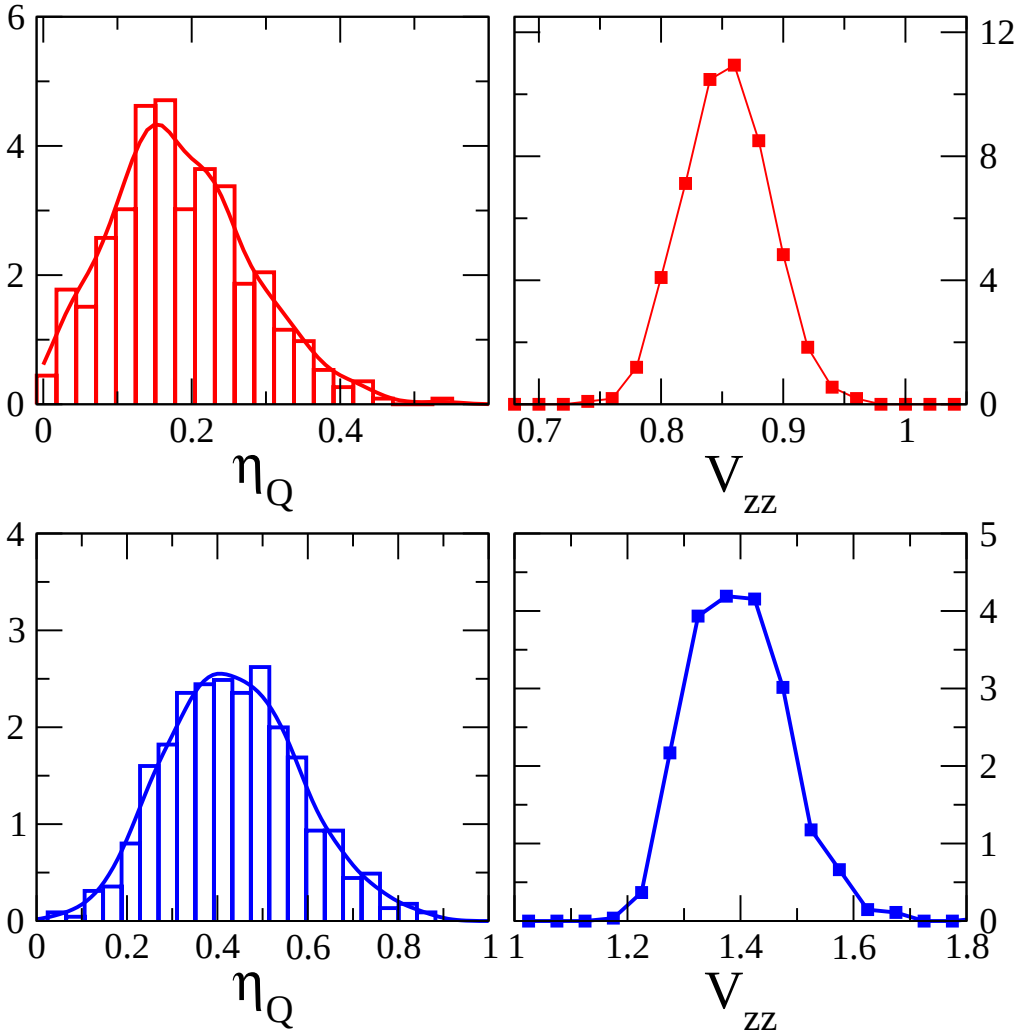






Quadrupolar parameter distributions

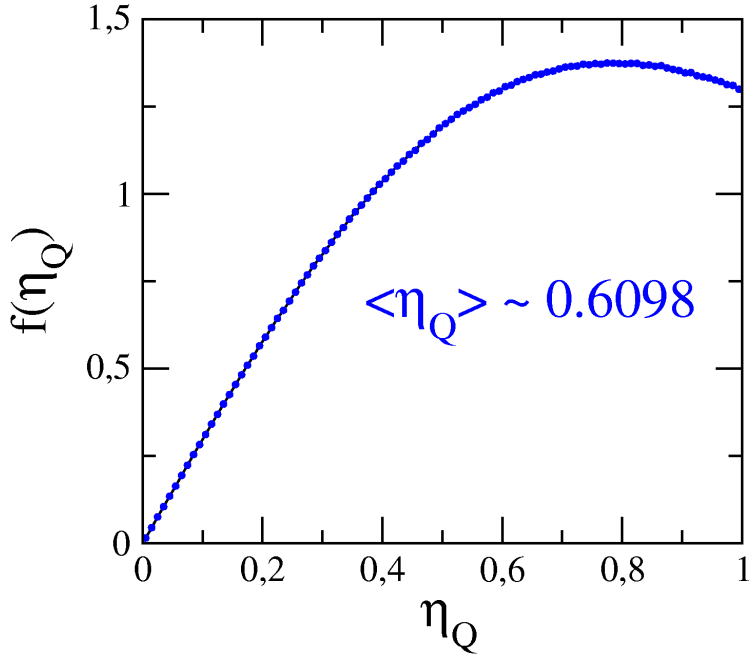
How can we use this new information ?

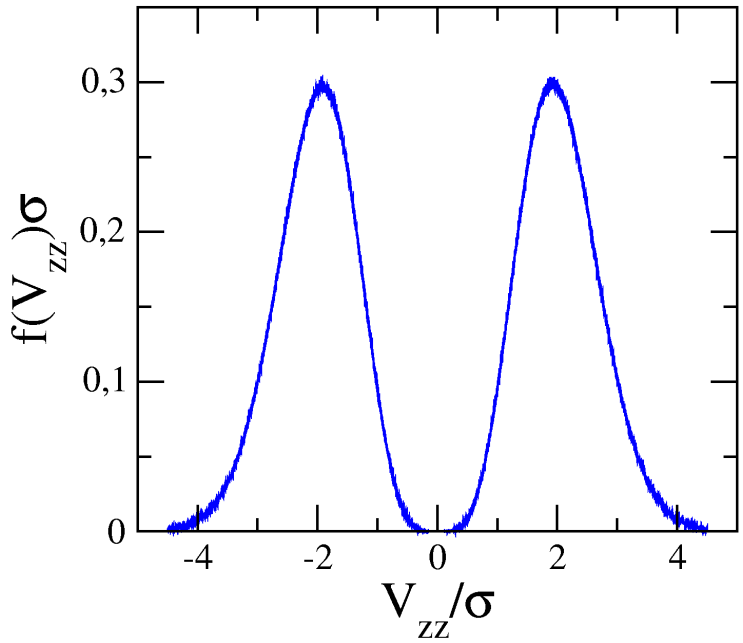


- ✘ extract experimental quadrupolar parameters see Charpentier et al. (SiO_2)
- ✘ better understand the distribution of EFG tensor

Czjzek Model

Gaussian isotropic Model for EFG distribution





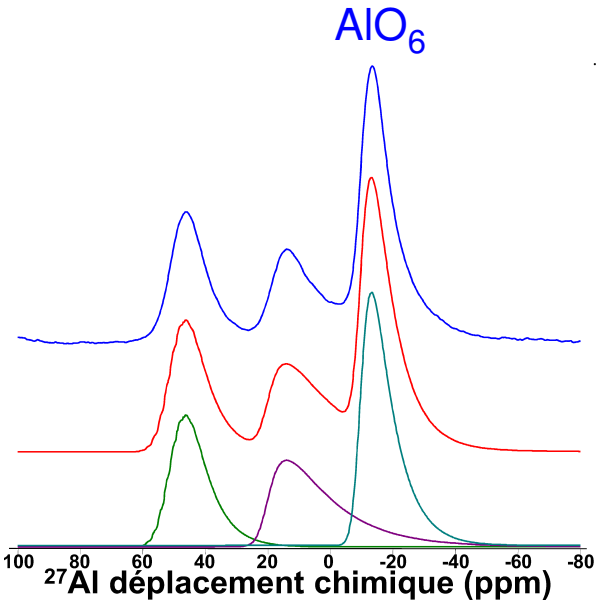
Analytical formulation

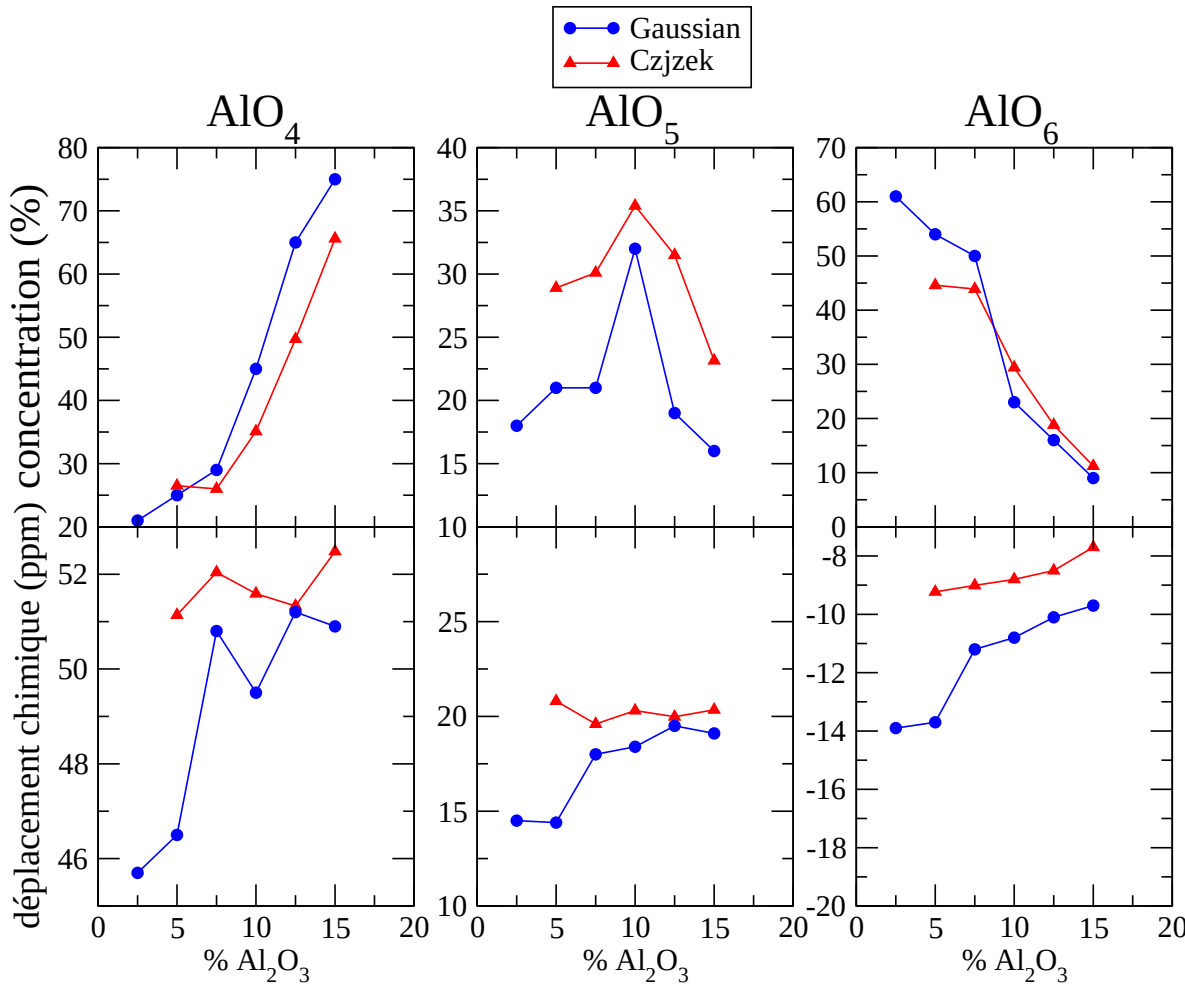
$$P(V_{zz},\eta_Q) = \frac{1}{\sqrt{2\pi}\sigma^5} V_{zz}^4 \eta_Q \left(1 - \frac{\eta_Q^2}{9}\right) \exp\left[-\frac{V_{zz}^2(1+\eta_Q^2/3)}{2\sigma^5}\right] \text{[1]}$$

[1] Czjzek et al. Phys. Rev. B **23** p2513 (1981)
[2] G. Le Caër et R. A. Brand J. Phys. Condens. Matter **10** p 10715 (1998)

Czjzek Model

Example : Application to ^{27}Al in potassium aluminophosphate glass ($50(K_2O)x(Al_2O_3)(50\text{-}x)(P_2O_5)$)



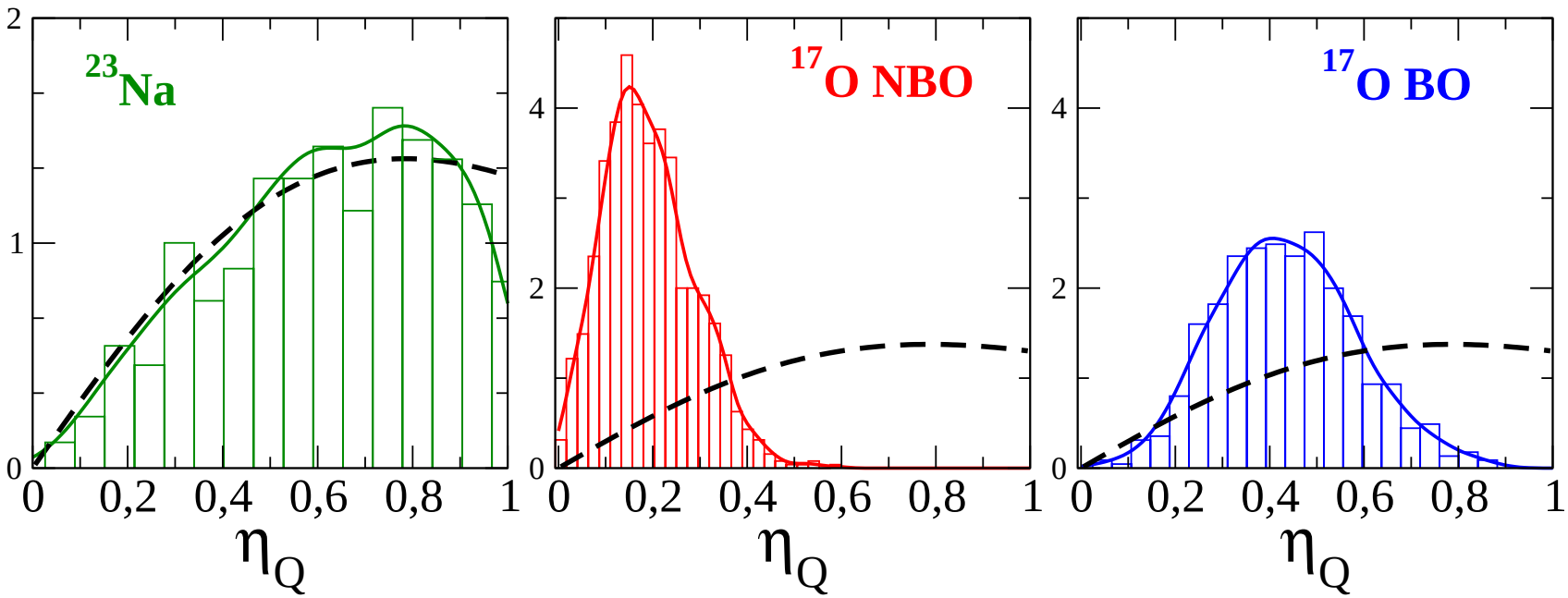


DMFIT : Magn. Reson. Chem. **40** 70-76 (2002)

Discussion about the Czjzek model

an isotropic model

- ✘ No structural information can be extracted from an isotropic distribution [1]
- ✘ In case of ^{17}O, some structural data can be deduced from lineshape analysis. [2]



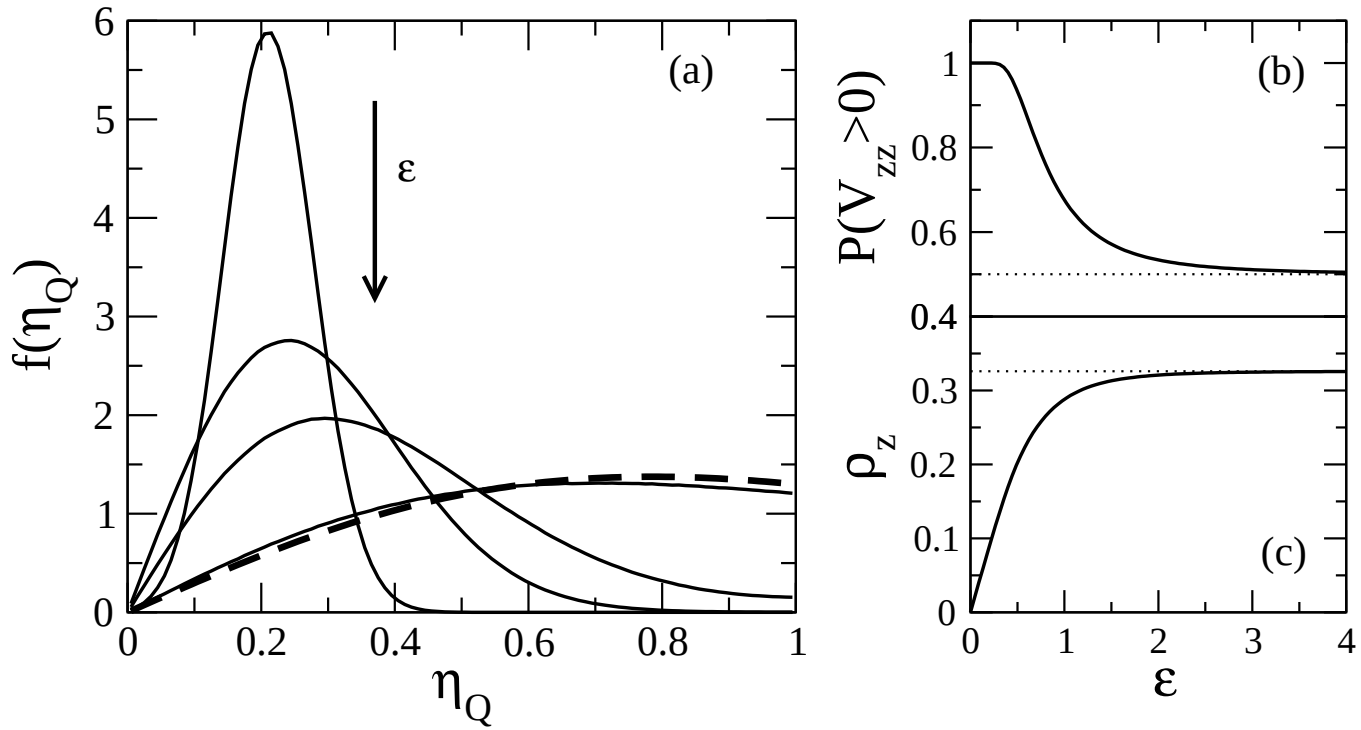
[1] G. Caër et al., J. of Phys. : Condens. Matt. **22**, 065402 (2010)
[2] F. Vasconcelos et al. (coming soon ! ! ;)

Extended Czjzek Model (Le Caër et al., 1998)

A perturbation of an anisotropic EFG tensor

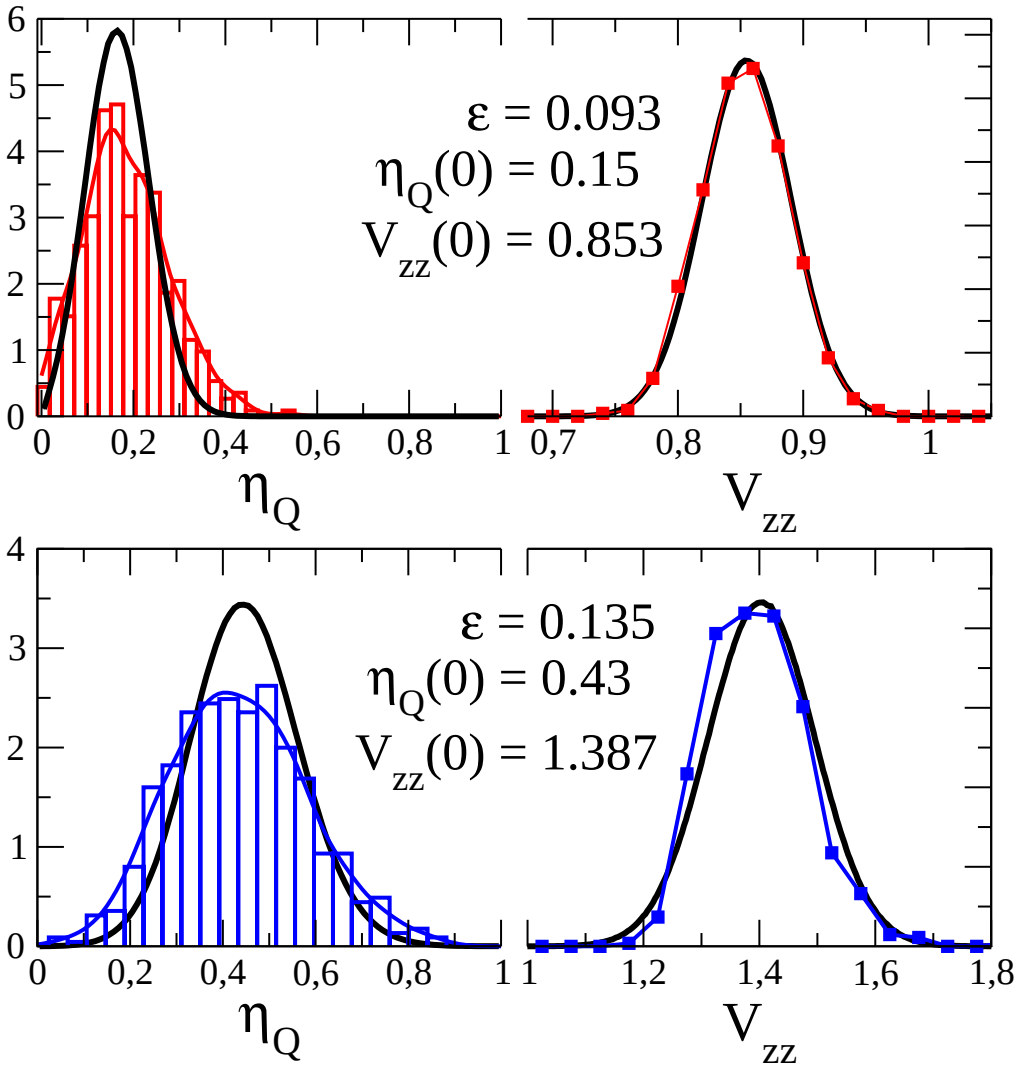
$$\mathbf{V}(\epsilon) = \mathbf{V_0} + \rho\,\mathbf{V_{Czjzek}} \qquad \epsilon = \frac{\rho||\mathbf{V_{Czjzek}}||}{||\mathbf{V_0}||}$$

- V_0 : local EFG tensor local with $V_{zz}(0)$ and $\eta(0)$ fixed
- V_{Czjzek} : Czjzek tensor (isotropic noise)



Extended Czjzek Model

Quantification of the anisotropy part



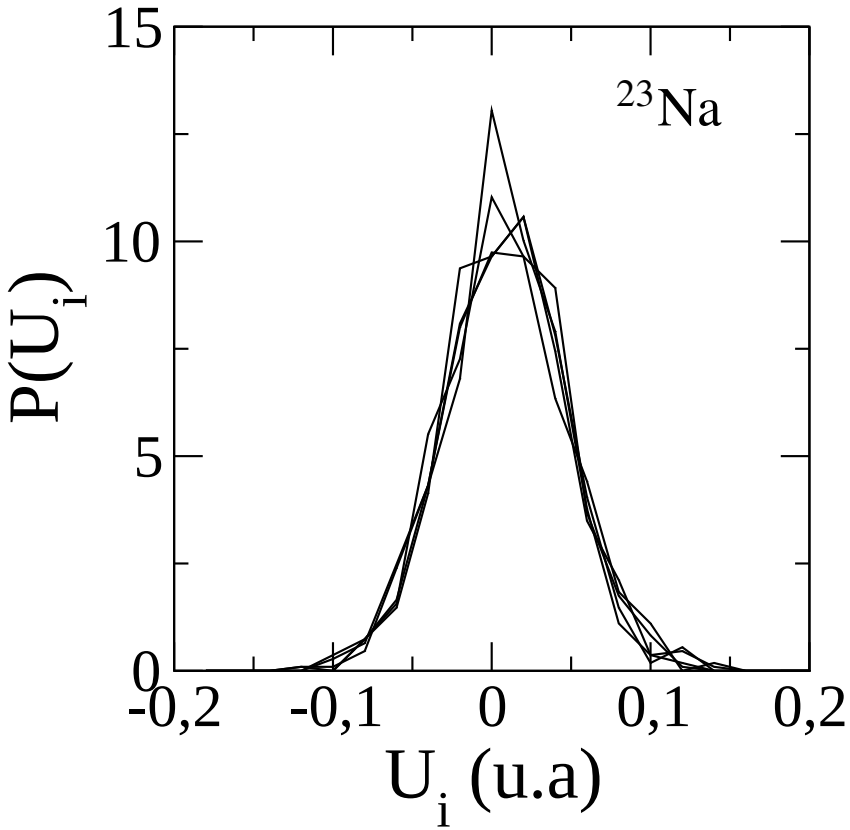
- η_Q and V_{zz} distributions accurately reproduced

Extended Czjzek Model

. . . looking for structural information

Reminder : Tensor distribution

- ✘ tensor components are distributed not the eigenvalues
- ✘ EFG tensor $\rightarrow$ 5 components ($U_i, i = 1, 5$)
- ✘ Czjzek Model $\rightarrow$ all U_i components are normally distributed



$$\boldsymbol{V} = \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{xy} & V_{yy} & V_{yz} \\ V_{xz} & V_{yz} & V_{zz} \end{pmatrix}$$

$$U_1 = V_{zz}/2$$

$$U_2 = \frac{V_{xz}}{\sqrt{3}}$$

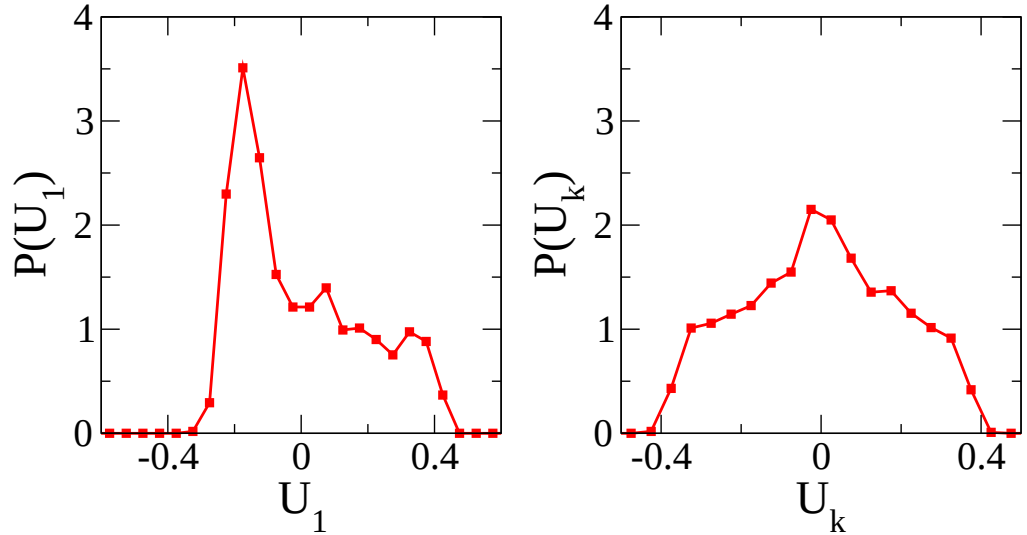
$$U_3 = \frac{V_{yz}}{\sqrt{3}}$$

$$U_4 = \frac{V_{xy}}{\sqrt{3}}$$

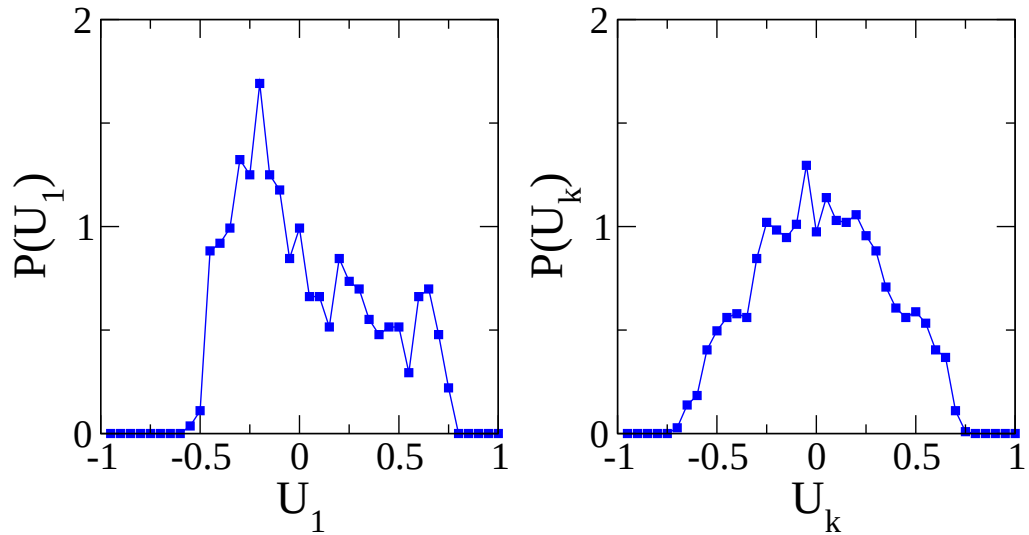
$$U_5 = \frac{(V_{xx} - V_{yy})}{2\sqrt{3}}$$

Extended Czjzek Model

. . . distributions of U_i components of ^{17}O in $NaPO_3$ MD model



^{17}O NBO



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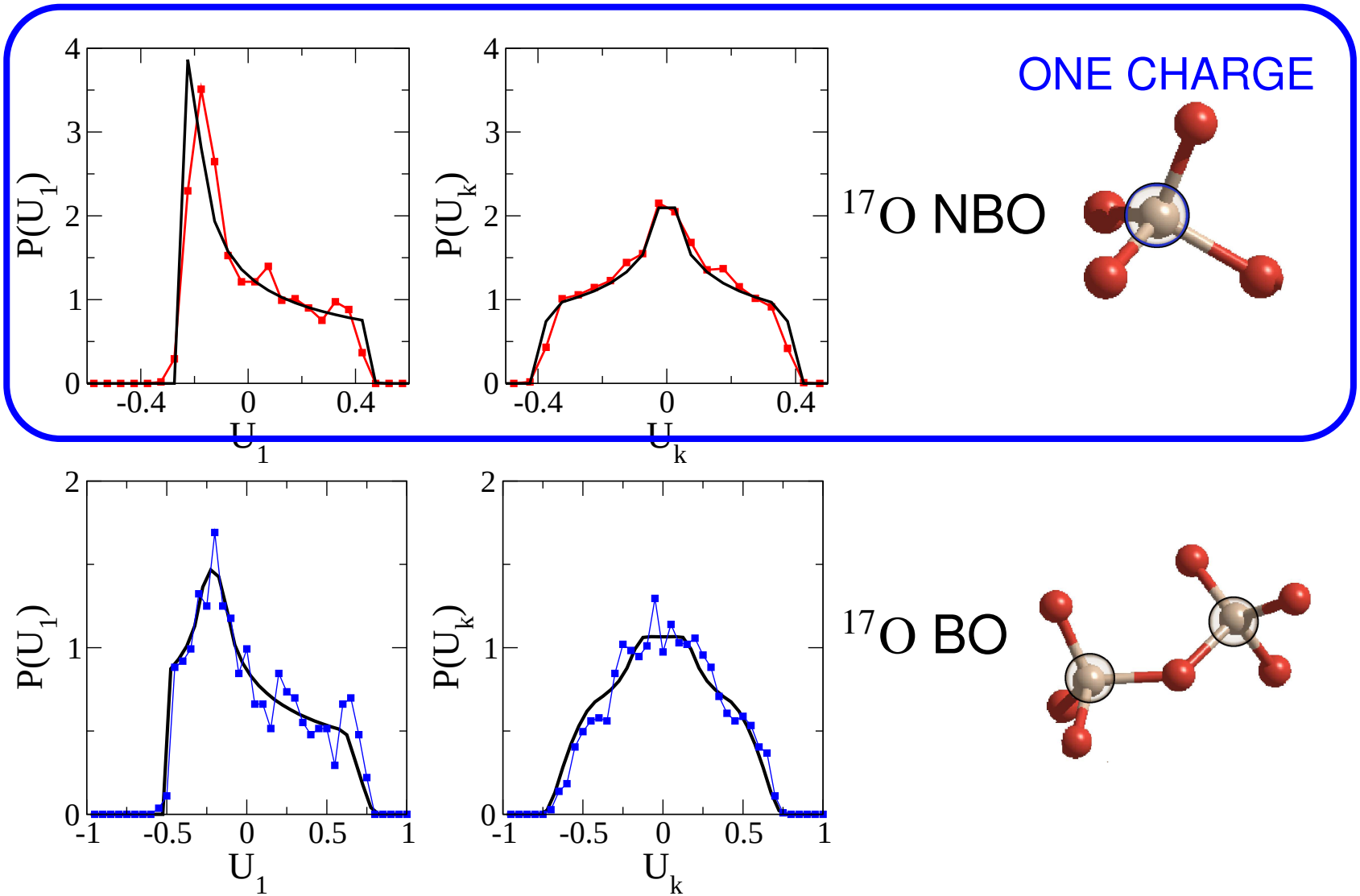

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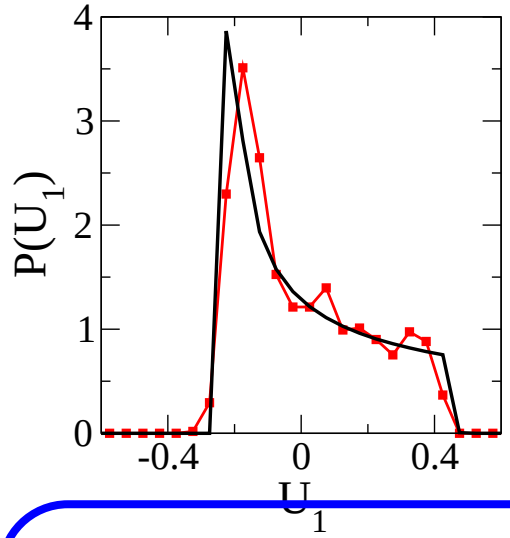

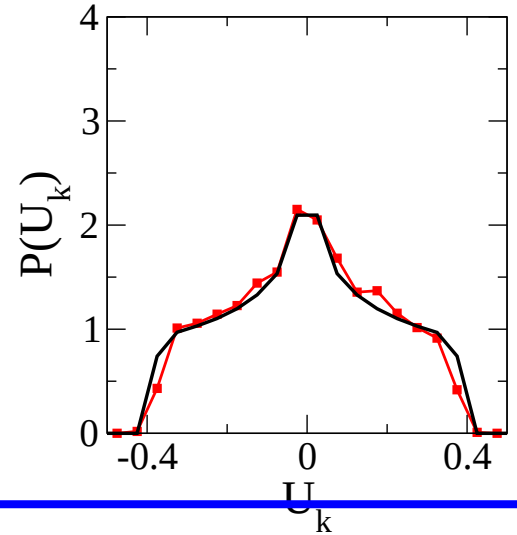

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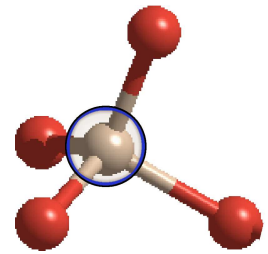
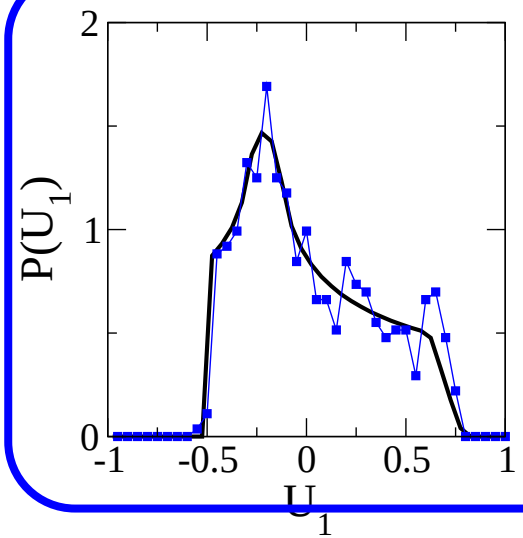
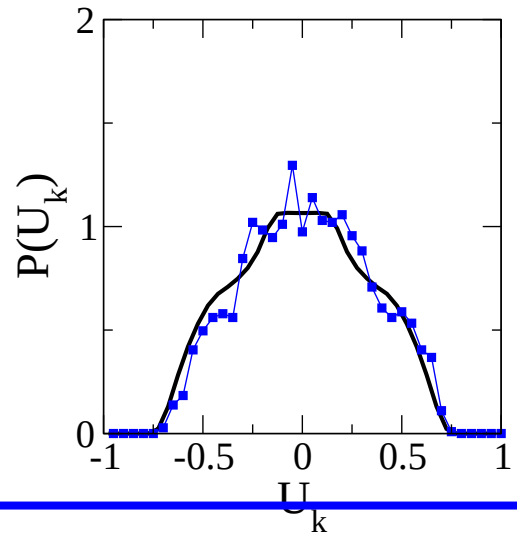


TWO CHARGES





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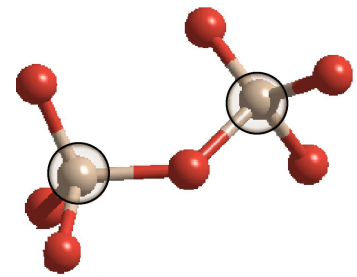

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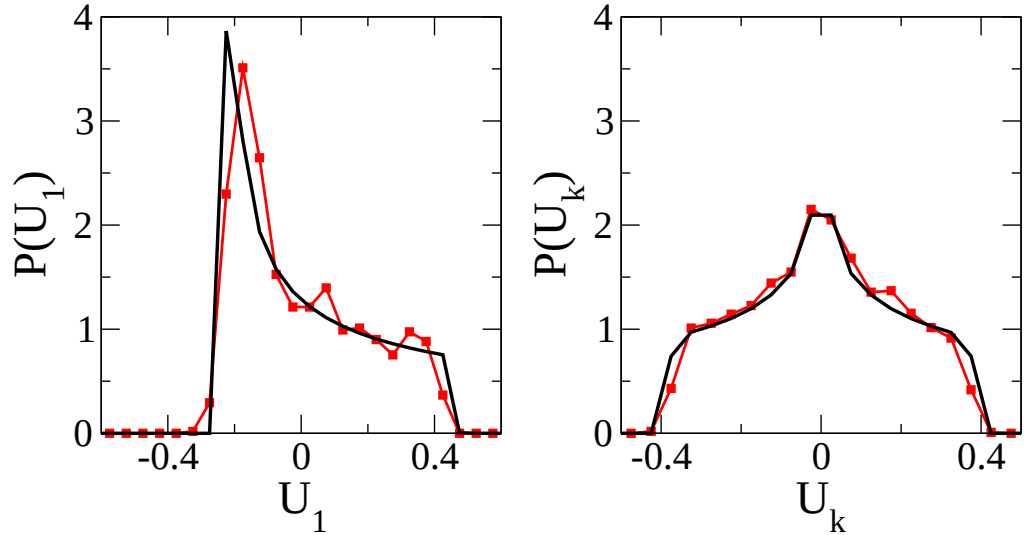
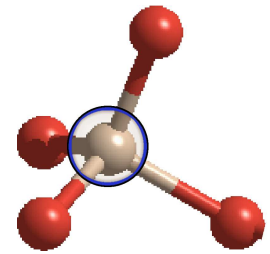
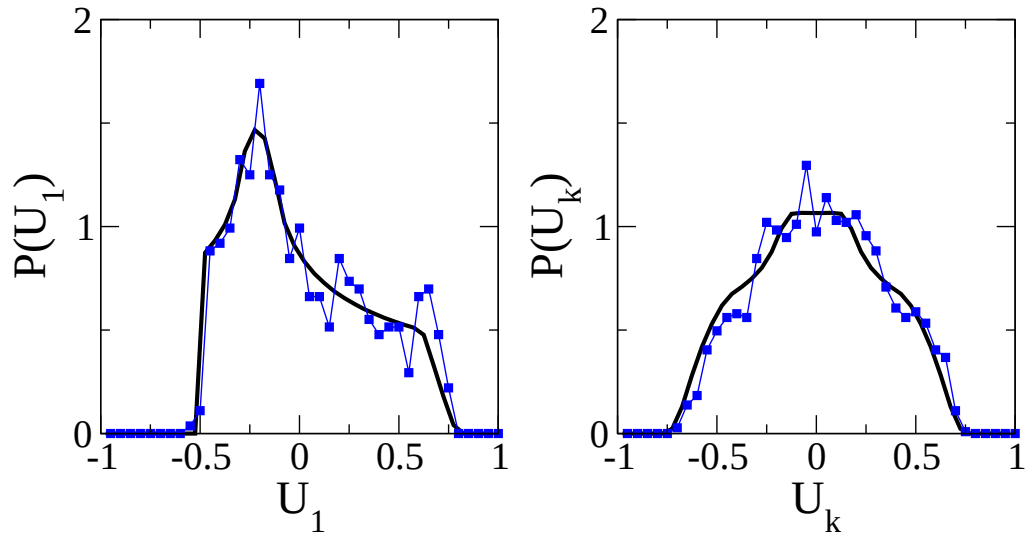
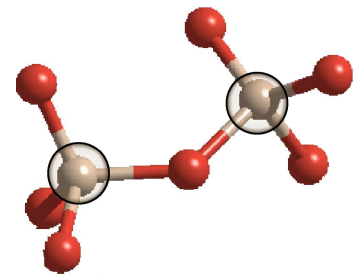


^{17}O NBO





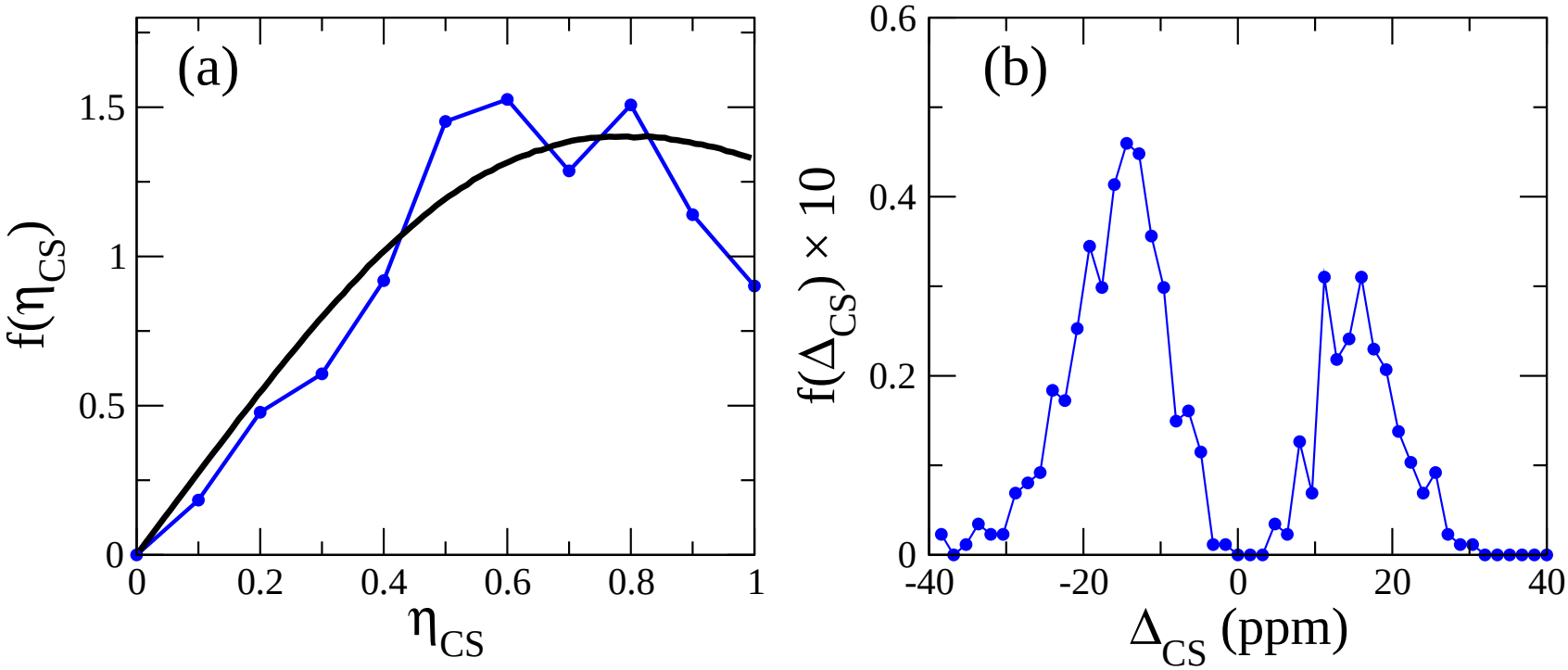
^{17}O BO



Distribution of EFG contains structural and geometric information

Perspective : CSA tensor

Distributions of CSA parameters (^{23}Na)



- Czjzek distribution on the CSA parameters of ^{23}Na
- asymetric and anistotropic CSA parameters plays the same role as the EFG parameters

Perspective : CSA

Distributions of tensor components BO and NBO (MD model)

$$A_{00} = -(1/\sqrt{3})[\sigma_{xx} + \sigma_{yy} + \sigma_{zz}]$$

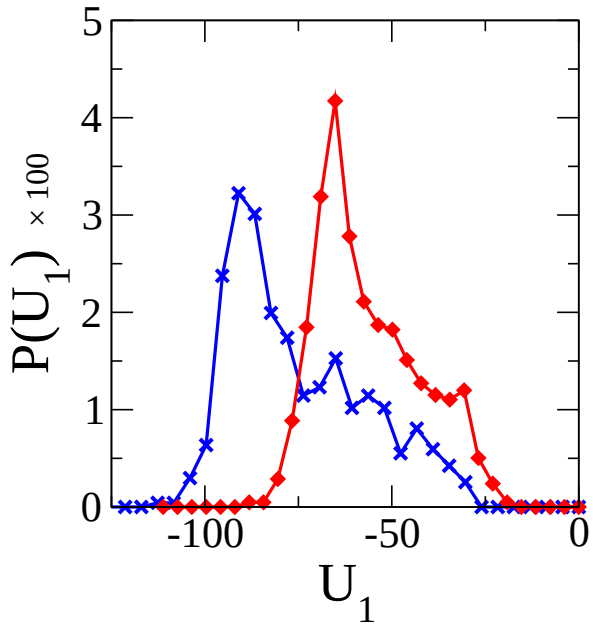
$$A_{10} = -(i/\sqrt{2})[\sigma_{xy} + \sigma_{yx}]$$

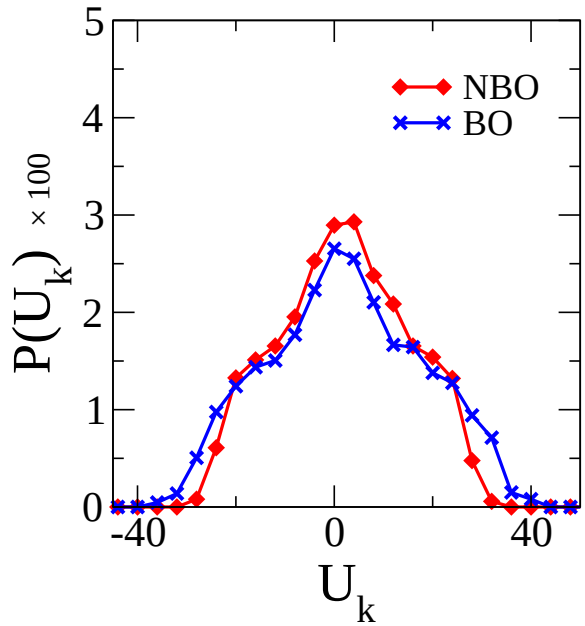
$$A_{1\pm1} = -(1/2)[\sigma_{zx} - \sigma_{xz} \pm i(\sigma_{zy} - \sigma_{yz})]$$

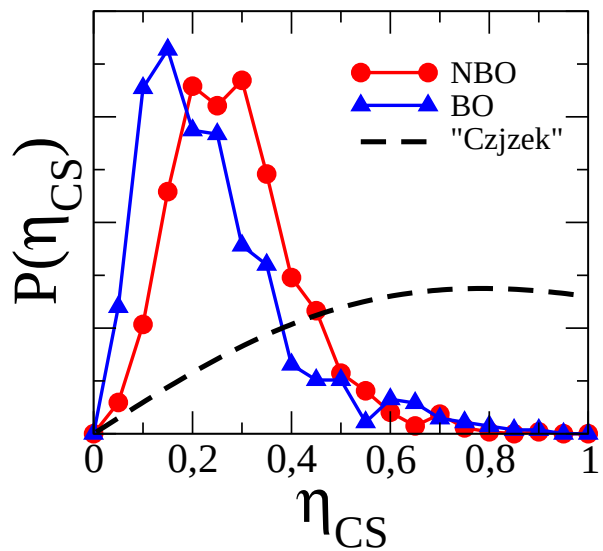
$$A_{20} = (1/\sqrt{6})[3\sigma_{zz} - (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})]$$

$$A_{2\pm1} = \mp(1/2)[\sigma_{xz} + \sigma_{zx} \pm i(\sigma_{yz} - \sigma_{zy})]$$

$$A_{2\pm2} = (1/2)[\sigma_{xx} - \sigma_{yy} \pm i(\sigma_{xy} - \sigma_{yx})]$$







Perspective : CSA

Distributions of tensor components BO and NBO (MD model)

$$A_{00} = -(1/\sqrt{3})[\sigma_{xx} + \sigma_{yy} + \sigma_{zz}]$$

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$$A_{1\pm1} = -(1/2)[\sigma_{zx} - \sigma_{xz} \pm i(\sigma_{zy} - \sigma_{yz})]$$

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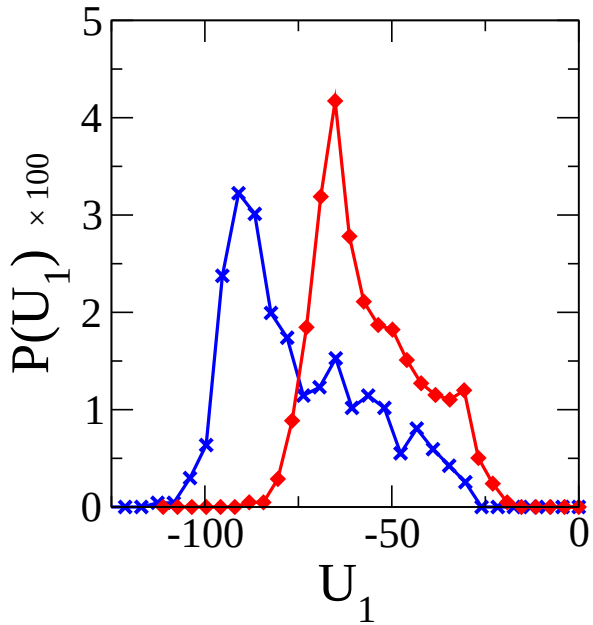
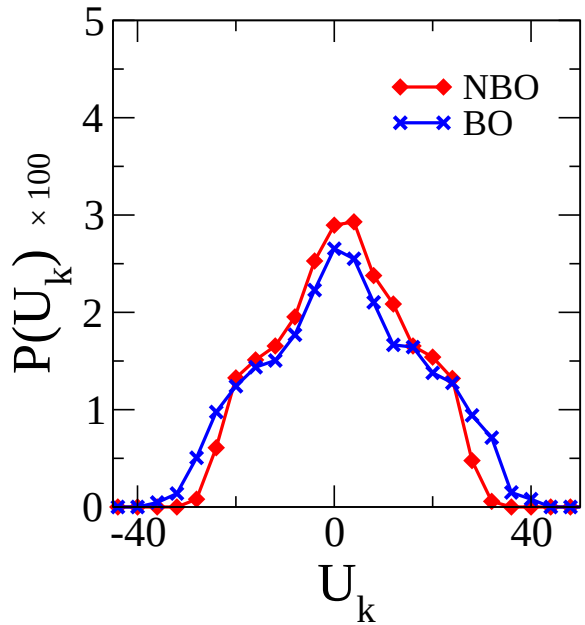
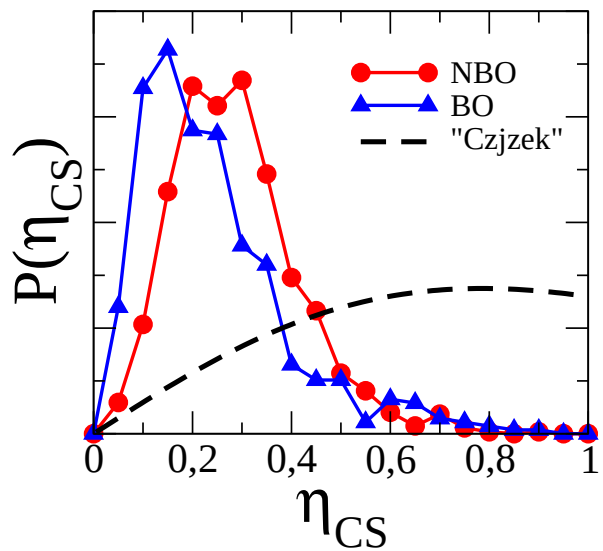
$$A_{2\pm1} = \mp(1/2)[\sigma_{xz} + \sigma_{zx} \pm i(\sigma_{yz} - \sigma_{zy})]$$

$$A_{2\pm2} = (1/2)[\sigma_{xx} - \sigma_{yy} \pm i(\sigma_{xy} - \sigma_{yx})]$$







Experimentally difficult to observe

Conclusions

. . . from the study of this glass structure

Glass structure

- ✘ MD + DFT/PAW-GIPAW are the principal tools to study glass structure
- ✘ Our structural model reproduces accurately NMR observations
- ✘ NMR parameter domains are defined for a given compound

Extended Czjzek Model

- ✘ Extended model can reproduce quadrupolar parameters distribution observed on MD model
- ✘ EFG tensor clearly presents local character

Outline

Introduction

General context

Some elements of the methodology

NMR First Principles applied to Glass

- Motivations
- How to generate glass configurations ?
- Case study : Sodium metaphosphate glass ($NaPO_3$)
  - NMR results (spectra, correlations, . . .)
  - EFG distributions
  - Extended Czjzek Model

NMR parameters and structure

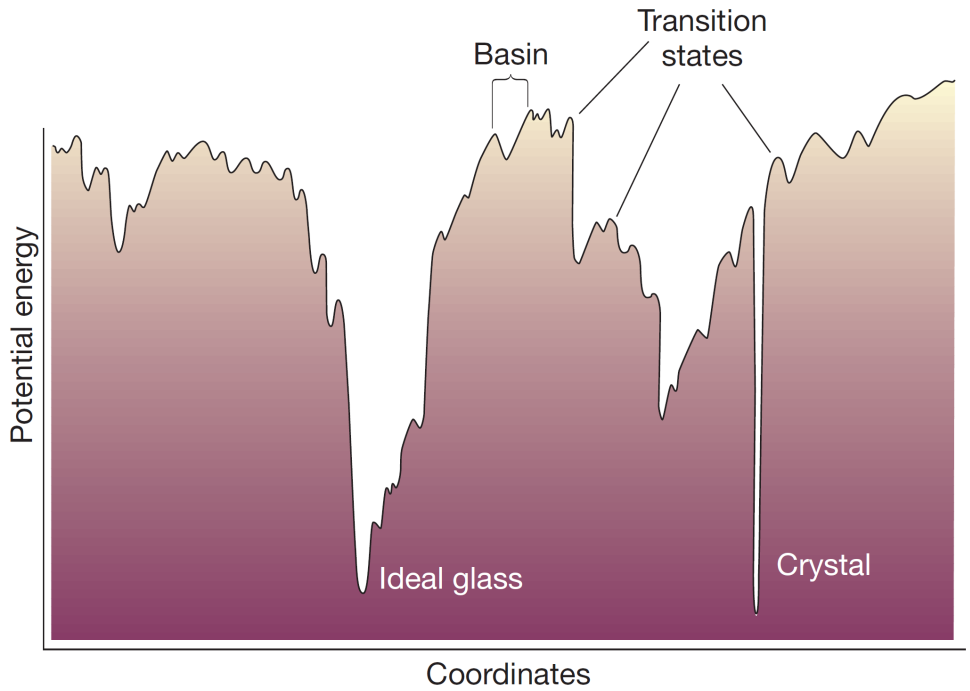
- Potential energy landscape (PEL) in glass science.
- NMR parameters revealing the PEL

General Conclusions

Potential Energy Landscape (PEL)

Concept

- Function of N-body positions $\Phi(\mathbf{R}_1, ...\mathbf{R}_N)$ [1]
- Quatilative and quantitative description of glass transitions [2,3]
- Relation between dynamics and the sampling of PEL thermodynamic and static properties

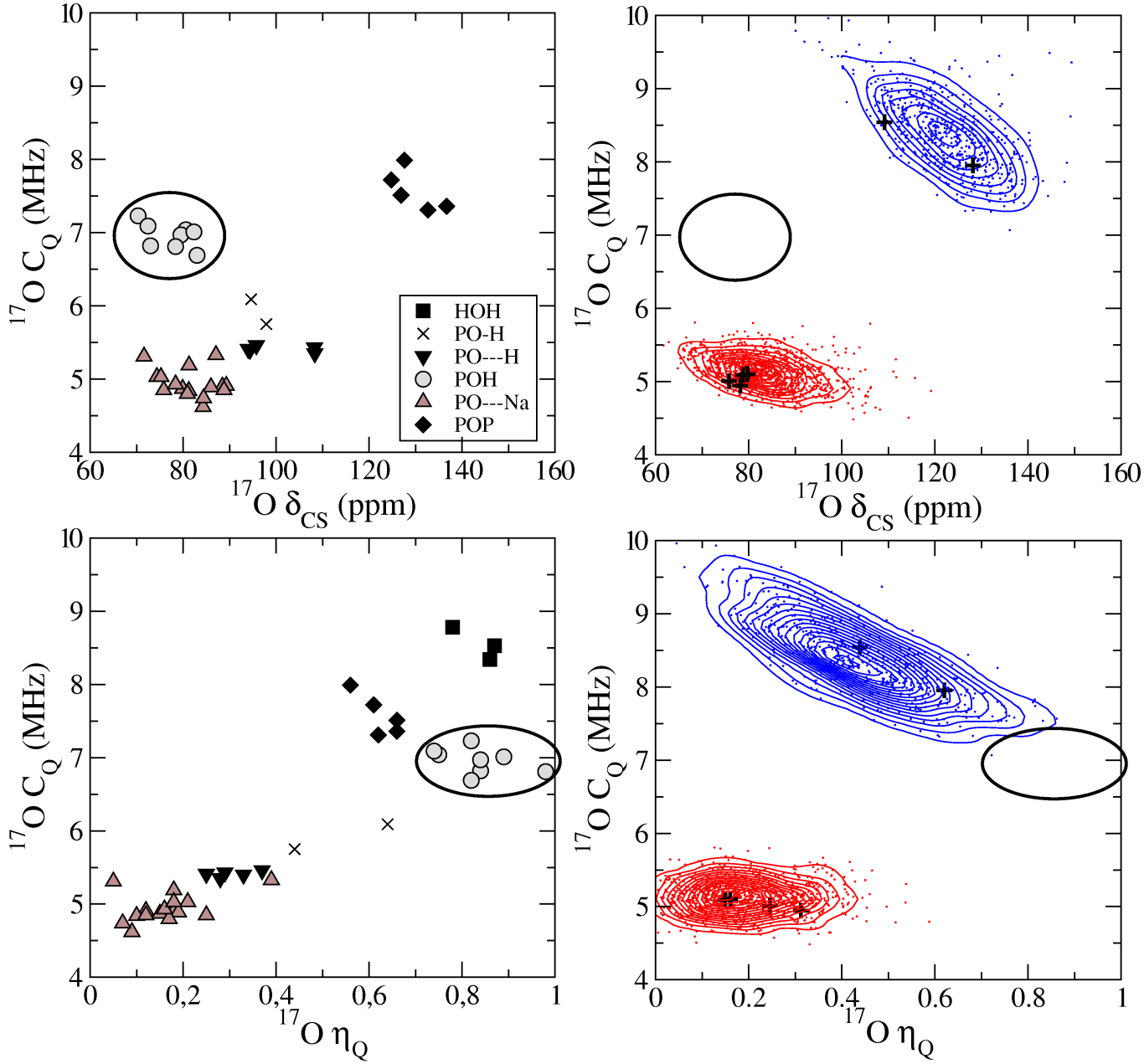


[1] M. Goldstein , J. Chem. Phys., **51**, 3728, (1969)
[3] S. Sastry, Nature, **409**, 164 (2001)
[2] P. G. Debenedetti and F. H. Stillinger, Nature, **410**, 259 (2001)

Connection between NMR parameter and PEL

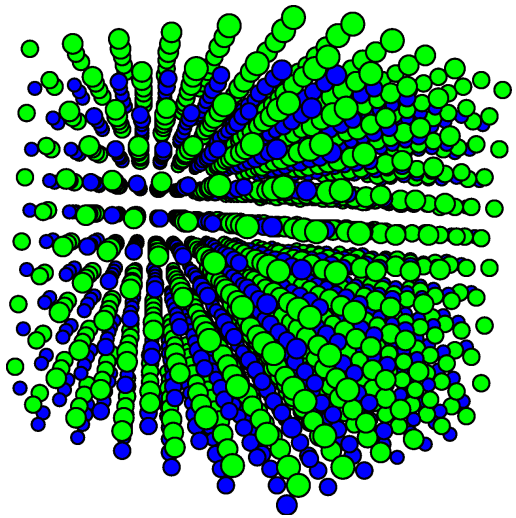
NMR	PEL
electronic structure $\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\})$	potential energy $\Phi(\{\mathbf{R}_I\})$
Chemical selectivity	fixed for a given stoichiometry and density
Structural selectivity	

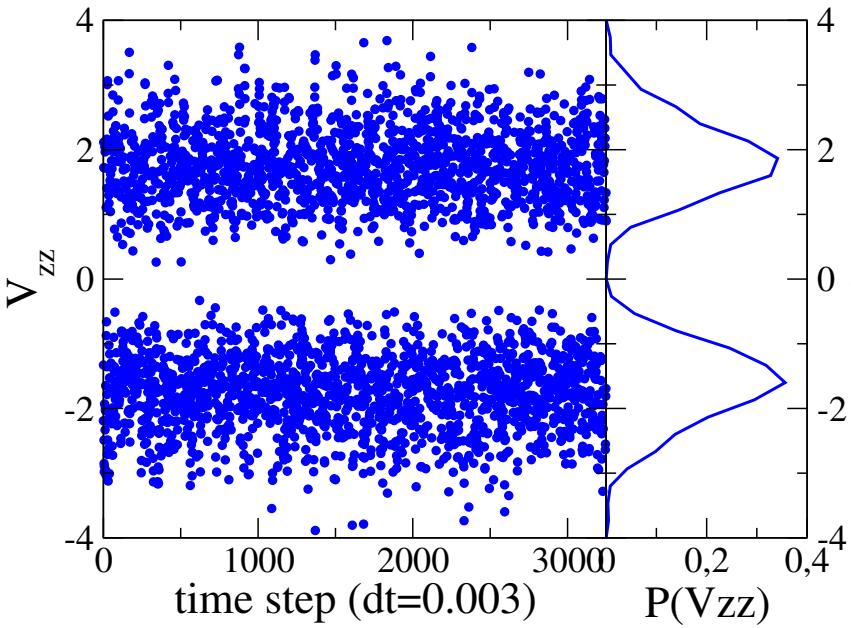
NMR parameters distribution/dispersion

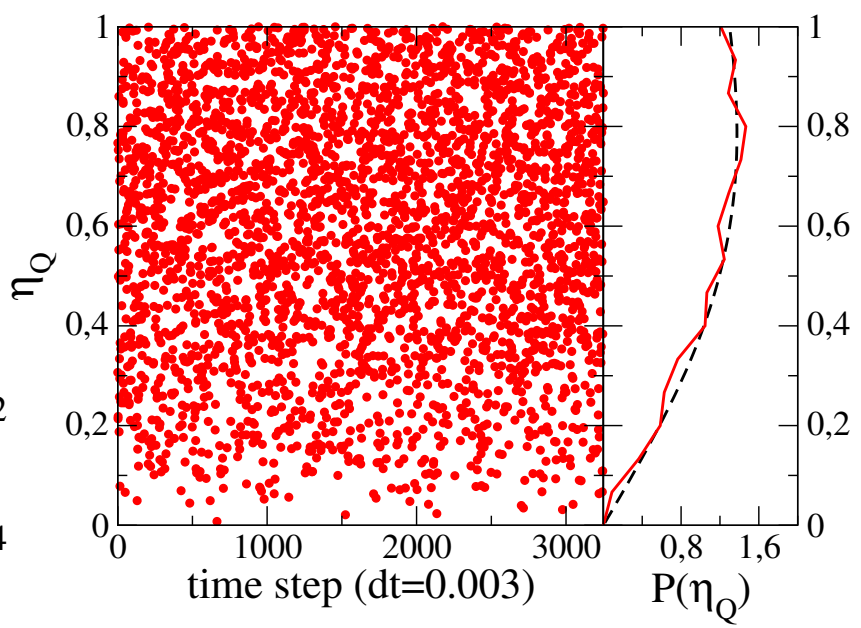


Vibrational "disorder" of EFG in NaCl-like structure

- Binary-Mixture Lennard-Jones potential
- $N = 1728$; $dt = 0.003$; $\rho = 1.58$; $qA = +1$; $qB = -1$
- NVE ensemble (berendsen scaling)
- (no electrostatic forces !)

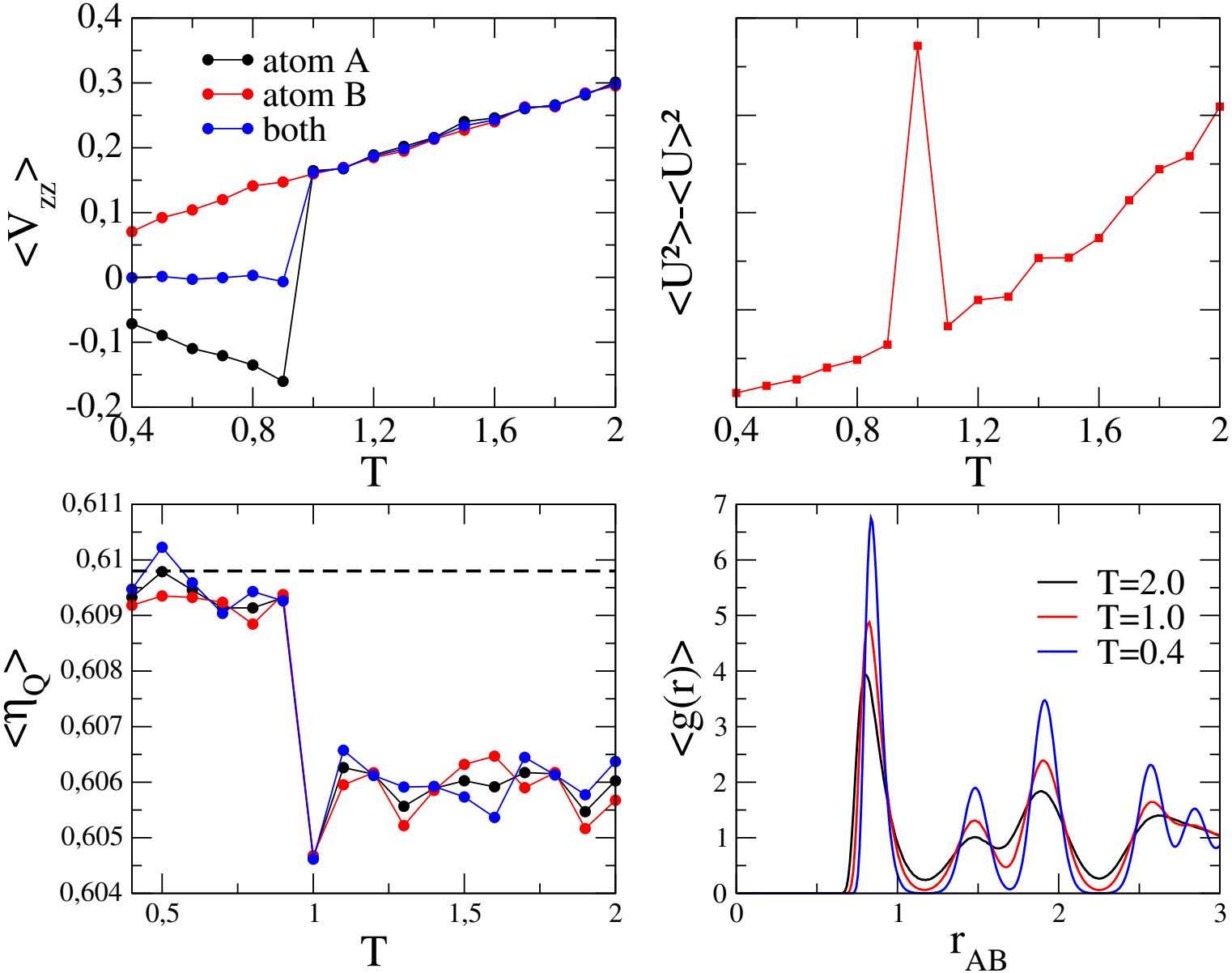






PEL/NMR representation framework

Transition Solid/Liquid



PEL/NMR representation framework

Conclusions

- ✘ Simple connection between NMR/PEL
- ✘ Structure selectivity of NMR
- ✘ The acces to the NMR param. dynamics . . .
- ✘ . . . a way to probe the dynamics of PEL

Challenging tasks

Experimental :

- ✘ get access to the distribution of the anisotropic terms (separately)
- ✘ get acces to the CSA tensors in solid state (in routine ☺)
- ✘ dynamics of NMR parameters in long-time scale (? ? ?)

Theoretical :

- ✘ following the NMR parameters during the dynamics

General Conclusions

NMR First-Principles is essential for glass structure determination

- ✘ Access to distribution (in particular η parameters)
- ✘ Extended Czjzek approach is validated for $^{17}\mathrm{O}$
- ✘ EFG tensor distribution contains structural information
- ✘ CSA tensor can be characterized by Czjzek and extended Czjzek models

NMR/PEL framework

- ✘ . . . is elegant
- ✘ . . . used in description of dynamics/structure properties of glass.
- ✘ . . . brings challenging experimental and theoretical problems.

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Chandrakala Gowda (NMR)
Ernst van Eck (NMR)
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Gilles de Wijs (ESM)

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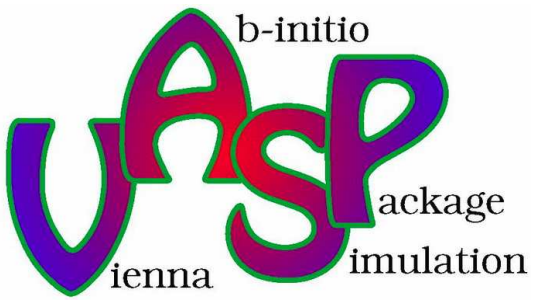
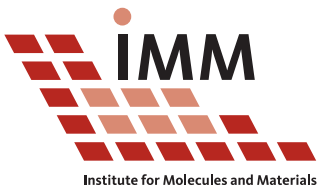
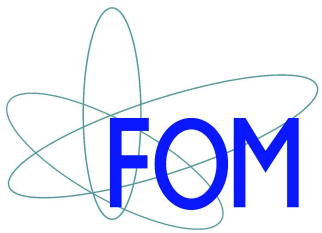
Martijn Marsman (VASP)
Francesco Mauri (PARATEC)
Thibault Charpentier (Glass+NMR)
Gérard Le Caër (Extended Czjzek)

Lille

Sylvain Cristol
Laurent Delevoye
Jean-François Paul
Lionel Montagne



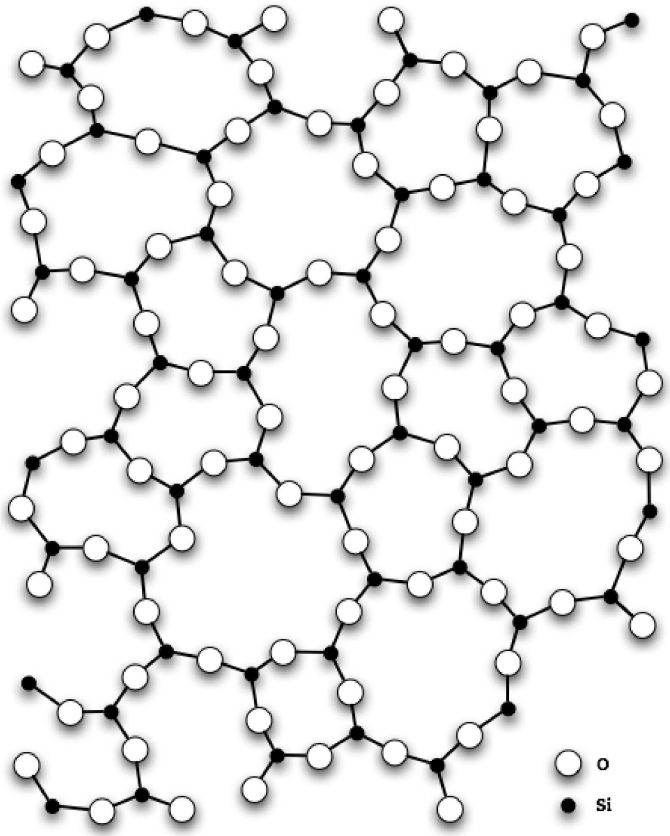




Radboud University Nijmegen

Glass structure

Experimental approach



Experimental techniques

- ✘ EXAFS $\rightarrow$ environment/short range order
- ✘ RAMAN $\rightarrow$ vibration mode (Boson's peak)
- ✘ Neutron/XRay scattering $\rightarrow$ pair distribution function $T(r)$
- ✘ ...
- ✘ Solid-State NMR $\rightarrow$ highly sensitive/ local : short, medium, (long ?) range order

Empirical Force Field

Charge of sodium

charge	Q^0	Q^1	Q^2	Q^3	Q^4
$q_{Na} = +1$	1 3.1%	9 28.1%	11 34.4%	11 34.4%	0 0.000%
$q_{Na} = +0.2$	0 0%	5 15.6%	22 68.8%	5 15.6%	0 0%
no Na	0 0%	1 3.1%	30 93.8%	1 3.1%	0 0%

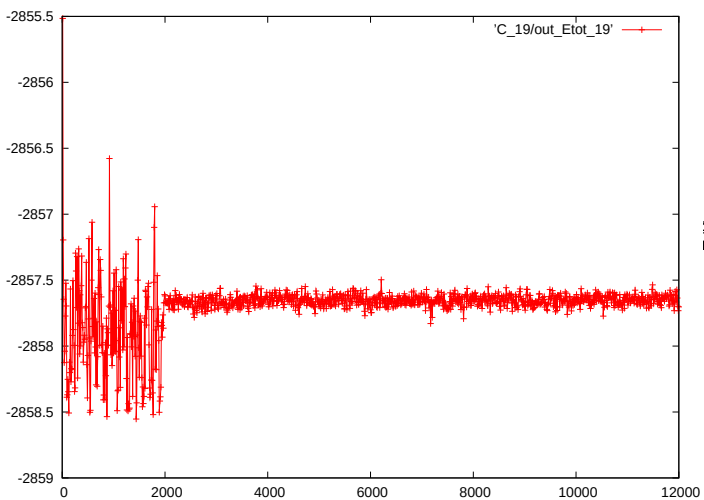
How can we avoid this « trick »

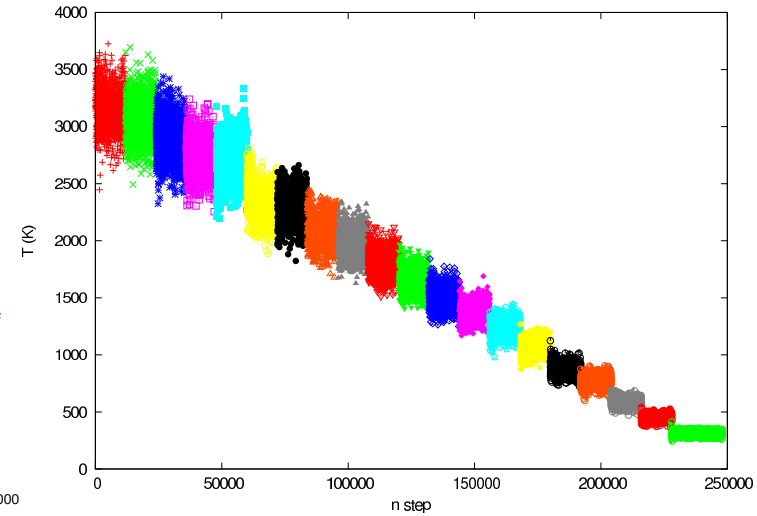
- ✘ Test finite size effect
- ✘ Test slower (or faster ?) quenching rate by 3 or 4 order magnitude

$NaPO_3$

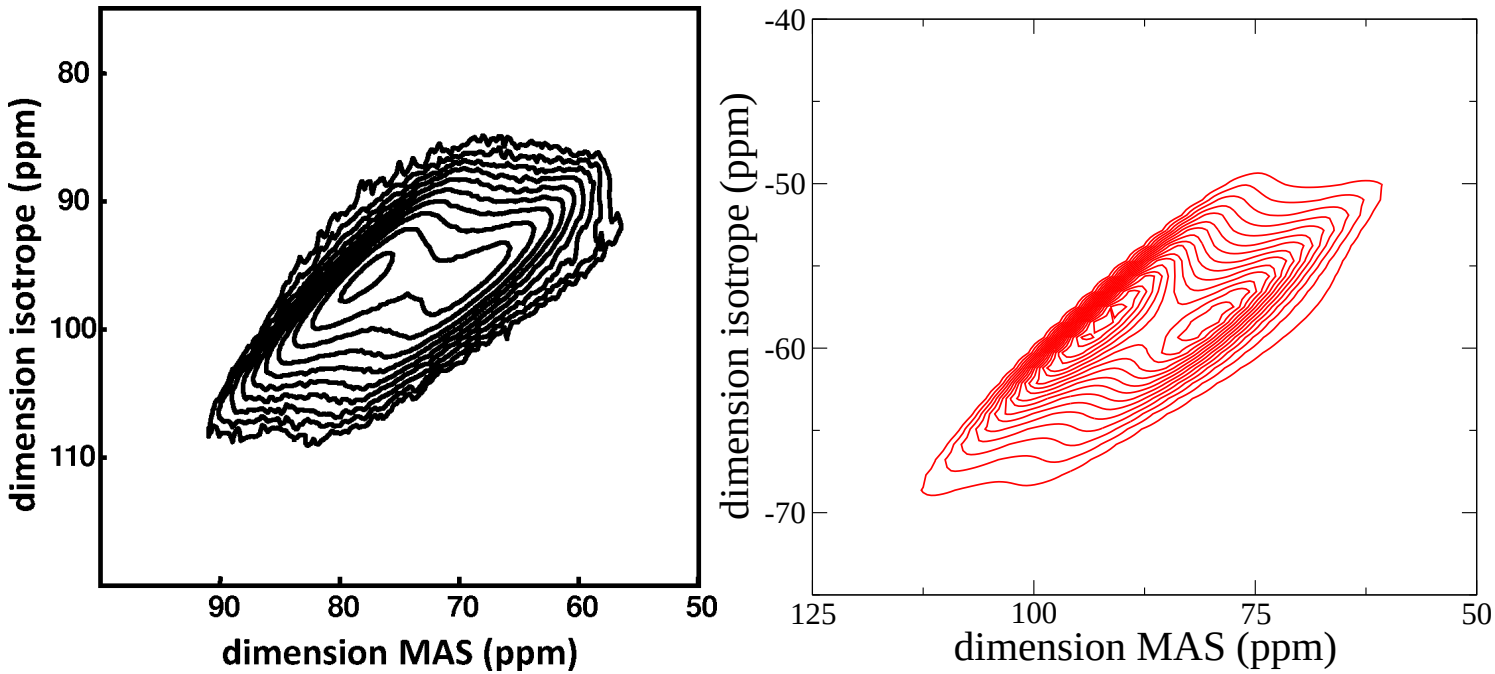
Calculation details

- 160 atoms : 32Na-32P-96O, density $\sim$ 2.53 g/ml
- quench 3500K -> 300K (rate 4×10^{12} K/s)
- BKS empirical potential
- NVE, equilibrated during 2 ps at each T
- 15 configurations.



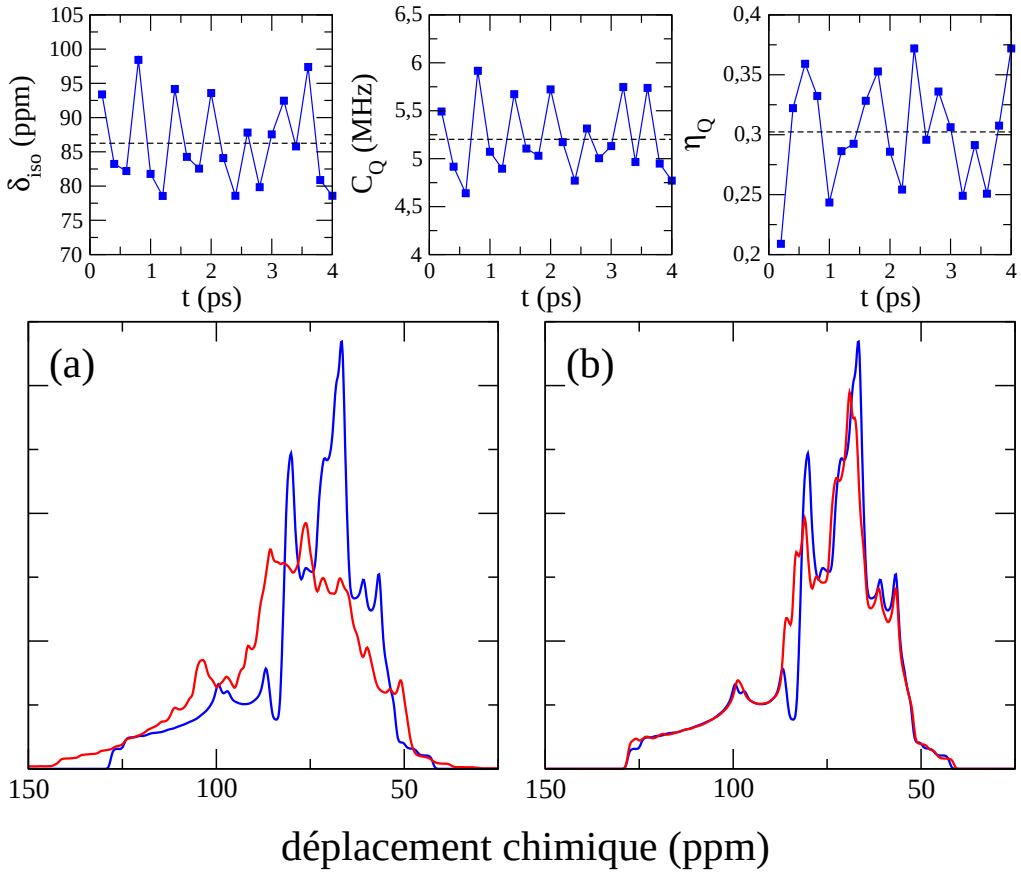


$NaPO_3$ MD ^{17}O 3QMAS zoom



FIG

Chapitre 3



	δ_{iso} (ppm)		C_Q (MHz)		η_Q	
sites	moyenne	écart-type	moyenne	écart-type	moyenne	écart-type
O1	86.3	6.3	5.20	0.37	0.30	0.04
O2	95.5	8.4	5.30	0.52	0.15	0.03
O3	133.7	5.4	7.82	0.28	0.67	0.08
O4	133.8	2.9	7.74	0.20	0.67	0.06
O5	91.9	5.3	5.13	0.28	0.15	0.03
O6	81.9	5.0	5.27	0.28	0.26	0.04

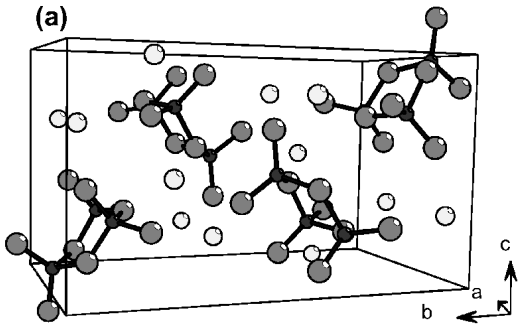
FIG

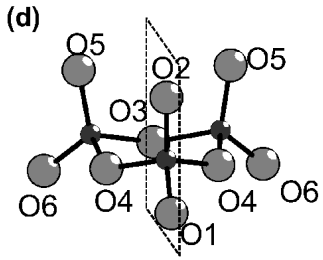
Chapitre 3

	NVE à 400K			optimisé à 0K		
sites	δ_{iso} (ppm)	C_Q (MHz)	η_Q	δ_{iso} (ppm)	C_Q (MHz)	η_Q
O1	86.3	5.20	0.30	79.2	5.04	0.30
O2	95.5	5.30	0.15	86.9	5.10	0.05
O3	133.7	7.82	0.67	126.4	7.90	0.61
O4	133.9	7.74	0.67	129.3	7.65	0.67
O5	91.9	5.13	0.15	85.2	4.95	0.09
O6	81.9	5.27	0.26	75.6	5.10	0.26

Anhydrous Sodium Phosphates

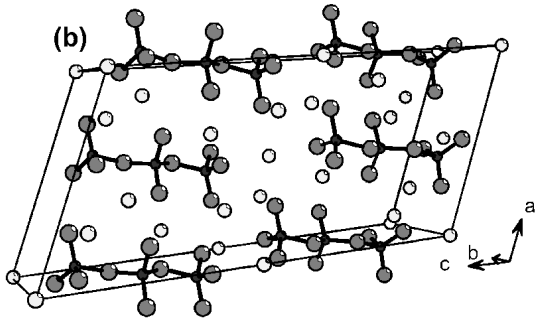
$Na_3P_3O_9$

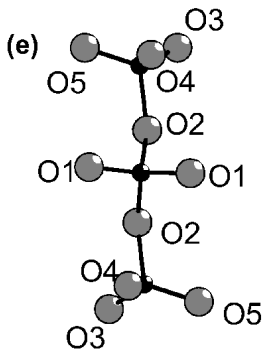




P m c n - orthorhombic
a = 7.928(2) Å
b = 13.214(3) Å
c = 7.708(2) Å
V = 807.49(34) Å^3

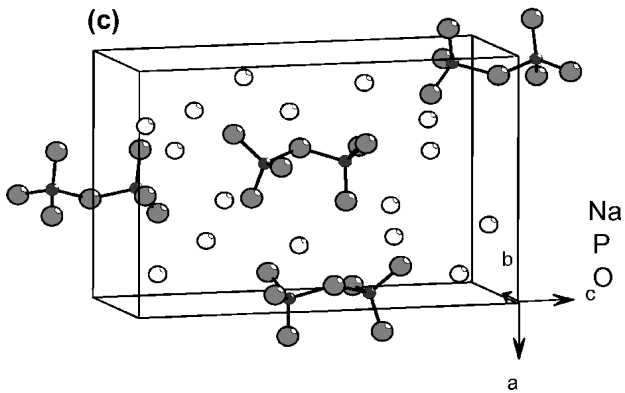
$Na_5P_3O_{10}$

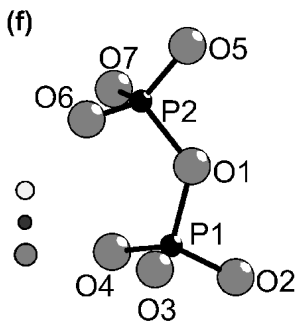




C 1 2/c 1 monoclinic
a = 9.61(3) Å
b = 5.34(2) Å
c = 19.73(5) Å
β = 112.0(5)°
V = 938.77Å^3

$Na_4P_2O_7$





P 2_1 2_1 2_1 orthorhombic
a = 9.367(5) Å
b = 5.390(2) Å
c = 13.480(8) Å
V = 680.58Å^3

F. Vasconcelos et al., Inorg. Chem., **47** 7327 (2008)

$Na_3P_3O_9$: assisted assignment

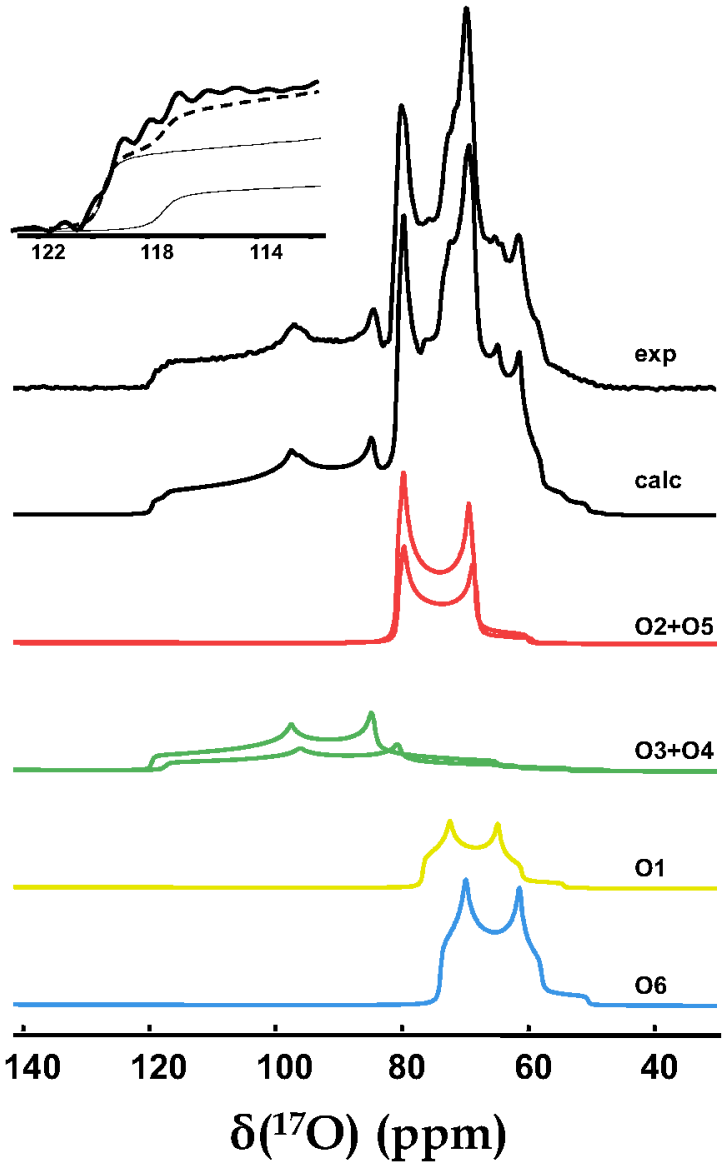
DFT-GIPAW+MQMAS

MQMAS

Type	C_Q (MHz)	η_Q	δ_{iso} (ppm)
NBO	4.5	0.3	75.5
NBO	4.3	0.4	77.5
NBO	4.3	0.1	84.0
BO	∼7.0	∼0.6	∼120

DFT-GIPAW

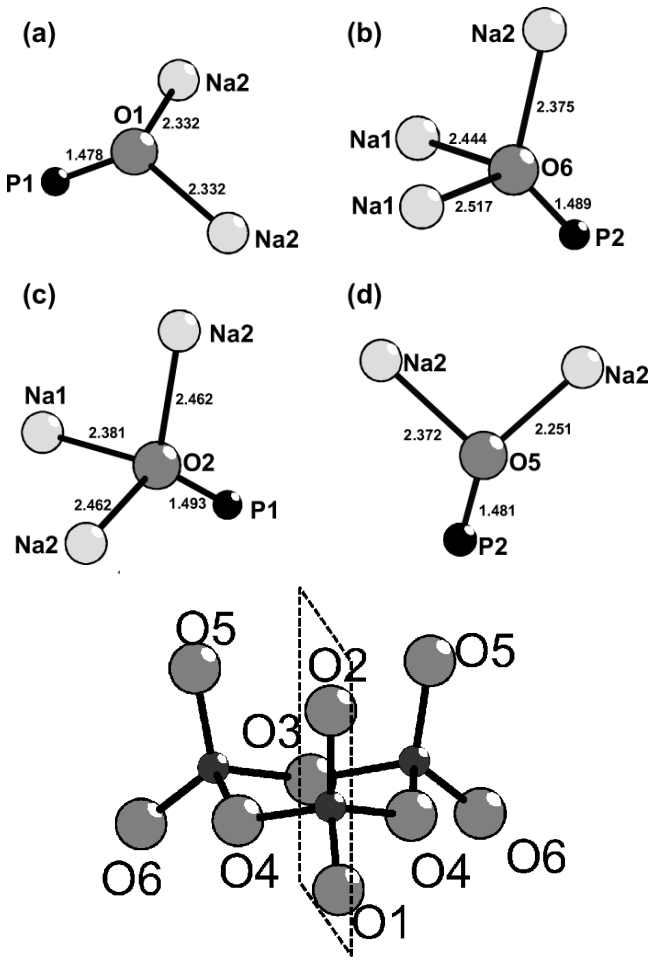
sites O	Type	C_Q (MHz)	η_Q	δ_{iso} calc (ppm)
O1	NBO	4.65	0.31	78.2
O2	NBO	4.74	0.07	84.4
O3	BO	7.72	0.61	124.8
O4	BO	7.51	0.66	126.9
O5	NBO	4.62	0.09	84.3
O6	NBO	4.78	0.26	75.5



F. Vasconcelos et al., Inorg. Chem., **47** 7327 (2008)

Discussion

Correlation Structure/NMR



Observations

- No correlation of NBO δ_{iso} with local environment
- C_Q First coordination sphere
- η_Q axial/equatorial positions, covalent

Site O	Type	C_Q (MHz)	η_Q	δ_{iso} calc (ppm)
O1	NBO	4.65	0.31	78.2
O2	NBO	4.74	0.07	84.4
O5	NBO	4.62	0.09	84.3
O6	NBO	4.78	0.26	75.5