Solid State NMR of Glass

Modelling NMR spectra of glass from first-principles

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Introduction

Basics of NMR: Interactions, MAS, MQMAS

NMR of disordered Materials

NMR from first-principles

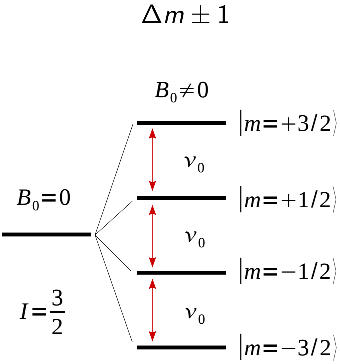
Molecular Dynamics versus NMR

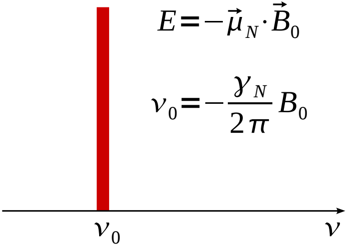
Content of the tutorial

- Basics of NMR interactions and spectra of solids
- 1D-2D NMR experiments: Static, MAS and MQMAS spectra
- NMR of disordered Materials
- Structure: Molecular Dynamics Simulations (TD)
- NMR parameters: DFT GIPAW calculations (TD)
- NMR parameters & Simulations: specific NMR software packages (fpNMR) (TD)
- ~~Principles of pulsed NMR~~
- ~~NMR Hamiltonian Art . . .~~

The Zeeman Interaction and Larmor Frequency

The NMR spectrum of an isolated nucleus . . .





$$E = -\vec{\mu}_N \cdot \vec{B}_0$$

$$\nu_0 = -\frac{\gamma_N}{2\pi} B_0$$

The Larmor frequency and its NMR spectrum.

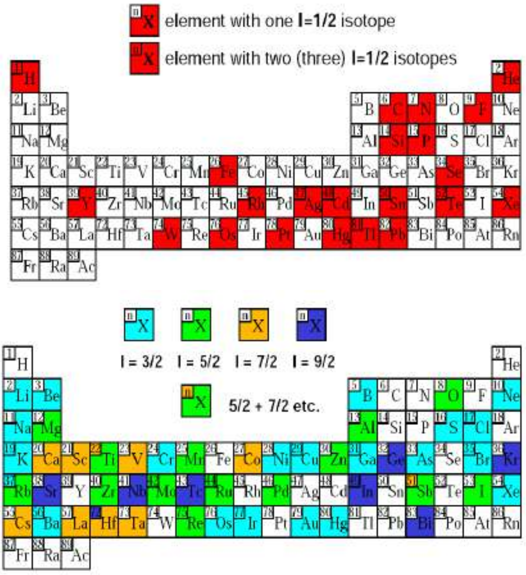
The Zeeman effect

No information on the chemical surrounding

$$(\hbar)\; H = -\hbar\gamma_N \vec{I} \cdot \vec{B}_0$$

NMR and the Periodic Table

One-half and *quadrupolar nuclei*

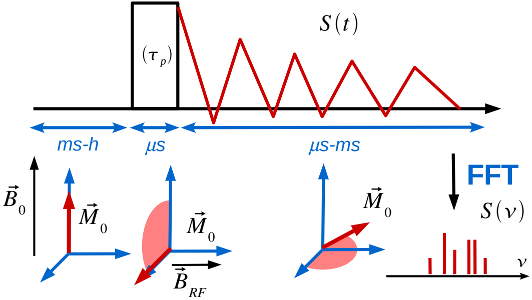


- Isotope, Nuclear Spin
- Natural Abundance
- Gyromagnetic ratio γ (rad/s/T)
  $\omega_0 = 2\pi\nu_0 = -\gamma B_0$
- Quadrupolar Moment Q (see Pyykko)

Pulsed NMR

The Basic NMR Experiment . . . One pulse !

M_0: Nuclear Magnetization at Equilibrium



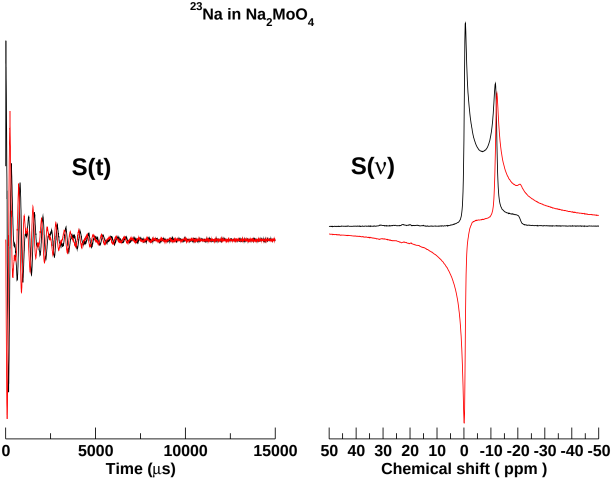
$$\begin{aligned}\vec{M}(0) &= M_0\vec{z}\\ \vec{M}(\tau_p) &= M_0\vec{x}\\ S(t) &= M_0 e^{-i\nu_0 t} e^{-\frac{t}{T_2}}\end{aligned}$$

$$S(\nu) = \int_0^\infty dt\, S(t) e^{-i2\pi\nu t} \approx \sum_{k=0}^{N-1} S(t_k) e^{-i2\pi\nu t_k} = L(\nu - \nu_0)$$

Lineshape $L(\nu)$: Gaussian, Lorentzian . . .

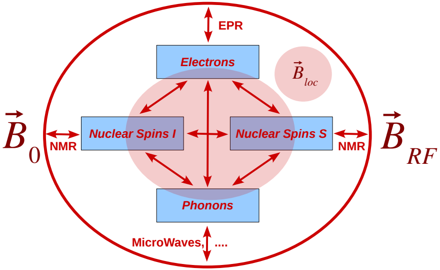
Pulsed NMR

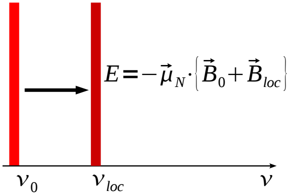
The Basic NMR Experiment: Fourier Transform



NMR Interactions for NMR spectroscopists

Effects of the *local* magnetic fields . . .





The NMR spectrum

Information on the chemical surrounding

$$(\hbar)\, H = -\hbar\gamma_N \vec{I} \cdot \left\{\vec{B}_0 + \vec{B}_{loc}\right\} = H_Z + H_{\text{inter.}}$$

$$(\hbar)\, H = H_Z + H_{CS} + H_Q + H_J + H_D + \dots$$

CS: Chemical Shift, Q: Quadrupolar, J: J couplings, D: Dipolar

NMR interactions for Quantum Chemists

The *effective* Hamiltonian

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

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

The nature of NMR interactions

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

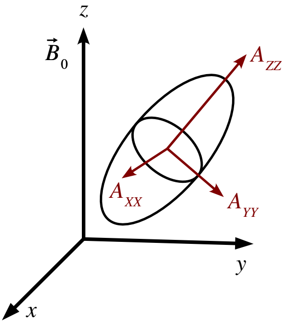
$$\vec{B}_{loc}^{(A)} = \mathbf{A}\vec{X} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \cdot \begin{pmatrix} X_x \\ X_y \\ X_z \end{pmatrix} \quad H_A = -\gamma_N \hbar \times \vec{I} \cdot \mathbf{A} \cdot \vec{X}$$

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

DFT calculations output A in its *tensorial* (matrix) form relative to a *reference frame*(x, y, z) (crystal axes).

NMR Interactions: The Principal Axes System (PAS) I

The principal values

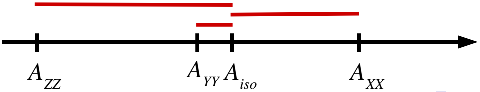


$$\mathbf{A} = \begin{pmatrix} A_{XX} & 0 & 0 \\ 0 & A_{YY} & 0 \\ 0 & 0 & A_{ZZ} \end{pmatrix}$$

Isotropic	$A_{iso} = \frac{1}{3}\mathrm{Tr}\left[\mathbf{A}\right]$
Anisotropy	$\delta_A = A_{ZZ} - A_{iso}$
Asymmetry	$\eta_A = \left(A_{XX} - A_{YY}\right)/\delta_A$
with	$0 \leq \eta_A \leq 1$

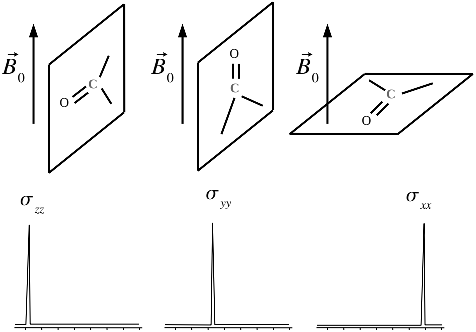
Calculations output the tensor in a *reference frame* (unit-cell definition). Its diagonalization (3D rotation) provides the principal values ($A_{\alpha,\alpha}$) and its orientation with respect to the *reference frame*.

Convention: $|A_{ZZ} - A_{iso}| \geq |A_{XX} - A_{iso}| \geq |A_{YY} - A_{iso}|$



NMR Interactions are Anisotropic ...

... NMR spectra of a single molecule (crystal)



The NMR frequency depends on the orientation with respect to $\vec{B}_0$

$$\nu - \nu_0 = \nu_{int}(\Omega)$$

Single crystal NMR exists ... but amorphous materials ?

NMR Interactions: The Principal Axes System (PAS) II

The relative orientation of the PAS

$$\begin{aligned}\mathbf{A}_{PAS} &= A_{iso}\mathbf{1} \\ &+ \delta_A \begin{pmatrix} -\frac{1}{2}(1+\eta_A) & 0 & 0 \\ 0 & -\frac{1}{2}(1-\eta_A) & 0 \\ 0 & 0 & 1 \end{pmatrix}\end{aligned}$$

$$\begin{aligned}\mathbf{A} &= \mathbf{X}_A^{-1}\mathbf{A}_{PAS}\mathbf{X}_A \\ \mathbf{X}_A &= \mathbf{R}(\alpha_A, \beta_A, \gamma_A) \\ &= \exp(-i\alpha_A I_z) \\ &\times \exp(-i\beta_A I_y) \\ &\times \exp(-i\gamma_A I_z)\end{aligned}$$

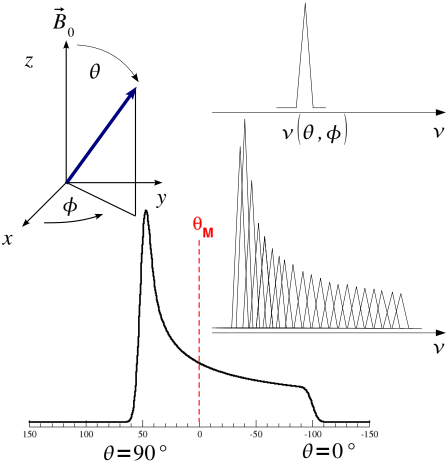
(x, y, z): reference frame axis
$(\alpha_A, \beta_A, \gamma_A)$: Euler angles

A NMR interaction is characterized by 6 parameters:
$A_{iso}, \delta_A, \eta_A, \alpha_A, \beta_A, \gamma_A$.

For a single interaction, $(\alpha_A, \beta_A, \gamma_A)$ does not affect the powder lineshape but can be determined for single crystal NMR.

NMR Interactions are Anisotropic . . .

. . . NMR spectrum (CSA) of a powder

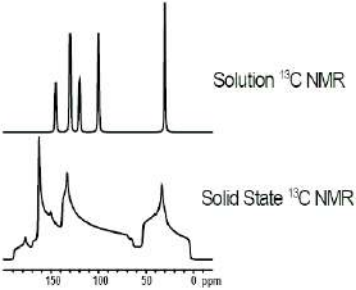


The powder average

$$S(t) = \int \sin\theta d\theta d\phi \times \exp\{-i\nu(\theta,\phi)t\}$$

NMR Interactions are Anisotropic . . .

. . . but in liquids only the isotropic part in effective



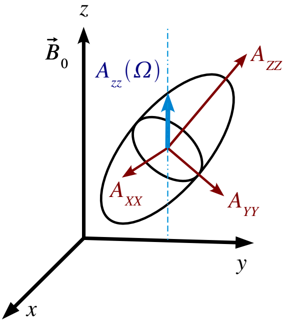
Motional averaging

- Motions affect the anisotropic lineshape.
- In the case of fast motional averaging (vs Larmor frequency), a narrow line at the isotropic frequency.
- Brownian Motion in liquid
- Motions (fluctuations) induce Relaxation

$$H(\Omega(t)) = H_{iso} + H_{ani}(\Omega(t)) \text{ with}$$
$$\overline{H_{ani}(\Omega(t))} = 0 \text{ at the Larmor time scale } (1/\nu_0)$$

The Zeeman Truncation in High Field NMR

Only the part along B_0 is *NMR active* to first order.



In case of 1-spin interaction, only A_{zz} (in the reference frame) contributes to first order to the NMR frequency.

Because $B_0 \gg B_{loc}$ (or $H_Z \gg H_{int}$), we have the *secular* approximation

$$H_{int} \approx H_{CS}^{(1)} + H_Q^{(1)} + H_Q^{(2)} + H_J^{(1)} + H_D^{(1)} \ldots$$

Typical strength of NMR interactions

- Z: 10-1000 MHz
- CS: kHz
- Q: MHz (up to second order)
- D: kHz
- J: Hz

NMR Interactions in general

An overview . . .

$$H^{(\lambda)} = C^{(\lambda)} \times R^{(\lambda)}(\Omega) \times \mathbf{T}^{(\lambda)}$$

$C^{(\lambda)}$	Constant	Obtained from DFT (σ, Q)
$R^{(\lambda)}(\Omega)$	Spatial Dependence	Manipulated through (sample) motions
$R^{(\lambda)}(\Omega) = 1$	Isotropic	Brownian motions in liquids
$\mathbf{T}^{(\lambda)}$	Spin operators	Manipulated through RF (spin rotation)
$\mathbf{T}^{(\sigma)}$	I_z	Chemical shift
$\mathbf{T}^{(Q)}$	I_z^2	First order quadrupolar interaction
$\mathbf{T}^{(Q)}$	I_z, I_z^3	Second order quadrupolar interaction
$\mathbf{T}^{(D,J)}$	$I_z S_z$	Dipolar (heteronuclear) or J interactions
$\mathbf{T}_{II}^{(D)}$	$I_z^A I_z^B$ $+\frac{1}{4}\left(I_+^A I_-^B + I_-^A I_+^B\right)$	Dipolar (homonuclear) interaction

The Shielding / Chemical Shift Tensor

NMR frequency

The *secular* contribution of the magnetic shielding is:

$$H_{CS} = \gamma \vec{I} \boldsymbol{\sigma} \vec{B}_0 \approx \gamma B_0 \sigma_{zz}(\Omega) I_z$$

$$\begin{aligned}
\sigma_{zz}(\Omega) &= \sigma_{XX} \sin^2\theta \cos^2\phi + \sigma_{YY} \sin^2\theta \sin^2\phi + \sigma_{ZZ} \cos^2\theta \\
&= \sigma_{iso} + \frac{\delta_{CS}}{2}\left((3\cos^2\theta - 1) + \eta_{CS} \sin^2\theta \cos 2\phi\right) \\
&= \sigma_{iso} + \delta_{CS} R_{20}(\Omega)
\end{aligned}$$

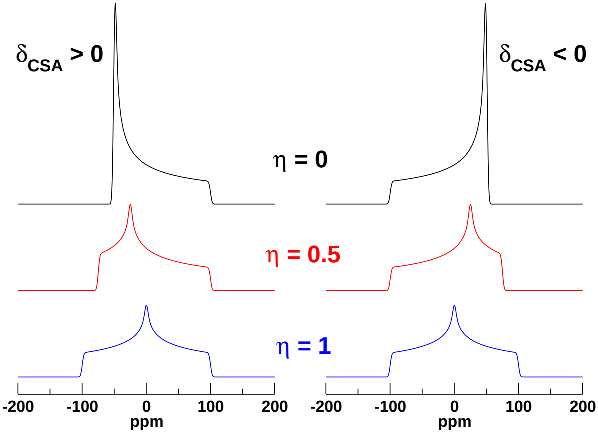
NMR measure the *chemical shift* tensor $\boldsymbol{\delta}$ (ppm):

$$\delta_{iso}^{exp}(\text{ppm}) = 10^6 \left(\frac{\nu - \nu_{ref}}{\nu_{ref}} \right)$$

ν_{ref} is a frequency reference value obtained from one tabulated reference compound, generally in liquid or in a solid (narrow peak, e.g. NaCl for ^{23}Na.

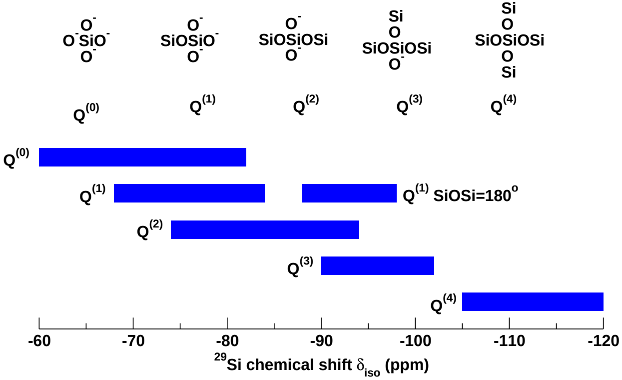
The shielding / Chemical Shift Tensor

NMR static lineshape



The magnetic shielding

Relationshield with the chemical environment



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

The quadrupolar interaction

from electric field gradient. Only for $I \geq 1$.

Because of its large strength (kHz-MHz), quadrupolar Hamiltonian are often accounted for up to second order (^{23}Na,^{17}O,^{27}Al,^{11}B...) depending on the local environment of the nucleus.

The electric field gradient **V** is a symmetric traceless ($V_{XX} + V_{YY} + V_{ZZ} = 0$) tensor.

$$C_Q = \frac{eQ}{h} V_{ZZ} \; , \eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \; , V_{iso} = 0$$

C_Q: quadrupolar couping constant, η_Q: quadrupolar asymmetry parameter.

The quadrupolar interaction

To first order. Only for $I \geq 1$.

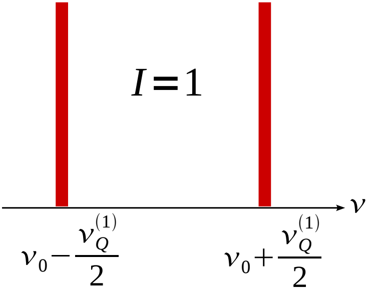
The firt-order secular quadrupolar Hamiltonian is

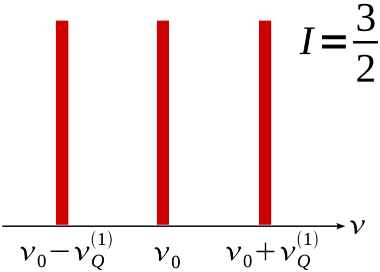
$$H_Q^{(1)} = \frac{C_Q}{6I(2I-1)} \times R_{20}\left(\Omega\right) \times \mathbf{T}_{20}\ ,\ \mathbf{T}_{20} = \sqrt{\frac{1}{6}}\left(3I_z^2 - I(I+1)\right)$$

This I_z^2 yields the NMR frequency as

$$\nu_{m,m-1} - \nu_0 = \frac{1-2m}{2}\nu_Q R_{20}\left(\Omega\right) = \nu_Q^{(1)}\left(\Omega\right)$$

The *central* transition $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ is not affected by $H_Q^{(1)}$.





The quadrupolar interaction

To second order.

The second-order secular quadrupolar Hamiltonian is (more complex)

$$
\begin{aligned}
H_Q^{(2)} &= \frac{1}{\omega_0}\left(\frac{C_Q}{6I(2I-1)}\right)^2 \times \sum_{l=0,2,4} \mathbf{A}^l R_{l0}(\Omega) \\
R_{l0}(\Omega) &= \sum_{k=l}^{-l} B_l^k(\eta) D_{l0}^k(\Omega) \quad , D_{l0}^k : \text{Wigner rotation matrix elements}
\end{aligned}
$$

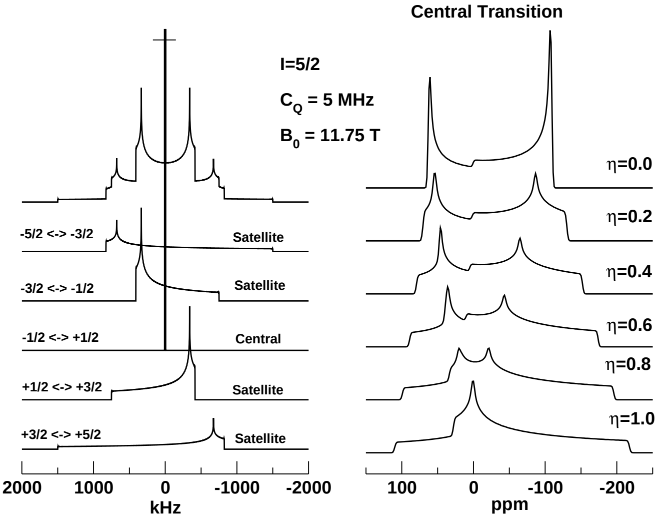
$\mathbf{A}^l = f(I_z^3, I_z)$ and *isotropic shift* (SOQS) $\delta_Q^{(2)} = A^0 B_0^0(\eta)$

The NMR frequency of the *central transition* can be written as

$$
\nu_{-1/2,+1/2}(\Omega) - \nu_0 = a_0 + a_2 R_{20}(\Omega) + a_4 R_{40}(\Omega)
$$

The quadrupolar interaction

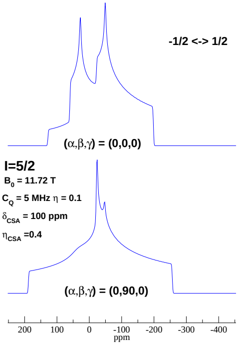
from electric field gradient

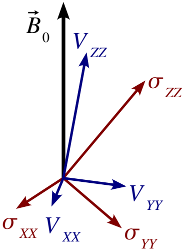


Quadrupolar + CSA NMR spectrum

Interplay of interactions

NMR lineshapes are also sensitive to the relative orientation of the CSA PAS with respect to the EFG (quadrupolar) PAS.





$$\mathbf{X}_{\sigma,c} = \mathbf{R}(\alpha_{\sigma,c}, \beta_{\sigma,c}, \gamma_{\sigma,c})$$

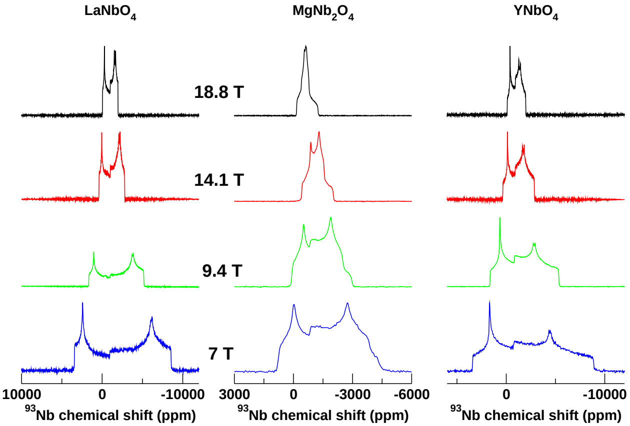
$$\mathbf{X}_{Q,c} = \mathbf{R}(\alpha_{Q,c}, \beta_{Q,c}, \gamma_{Q,c})$$

The relative orientation reads

$$\begin{aligned} \mathbf{X}_{\sigma,Q} &= \mathbf{X}_{\sigma,c} \times \mathbf{X}_{Q,c}^{-1} \\ &= \mathbf{R}(\alpha_{\sigma,Q}, \beta_{\sigma,Q}, \gamma_{\sigma,Q}) \end{aligned}$$

Quadrupolar + CSA NMR spectrum

Interplay of interactions



J.V. Hanna et al. Chem. Eur. J. 16 (2010) 3222

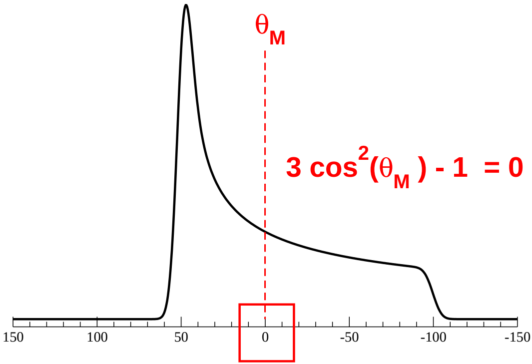
Multiple magnetic fields acquisition required to determine *accurately* both tensors (8 parameters !).

High Resolution NMR

Why Magic Angle Sample Spinning ?

$$R_{20}(\Omega) \propto 3\cos^2\theta - 1$$

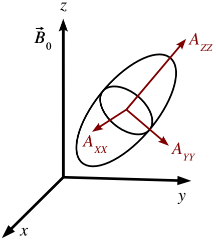
Method: Reduce all orientation to an *effective magic angle* orientation !

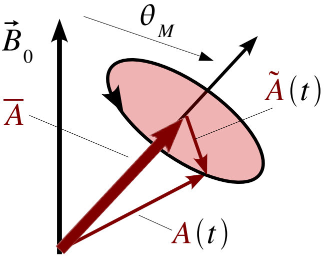


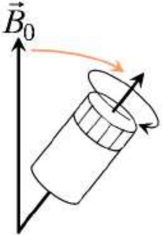
High Resolution NMR

Magic Angle Sample Spinning: a *coherent* averaging approach

$$\mathbf{A}\left(\Omega(t)\right) = A_{iso}\mathbf{1} + \overline{\mathbf{A}}(\theta_M) + \widetilde{\mathbf{A}}(t)$$







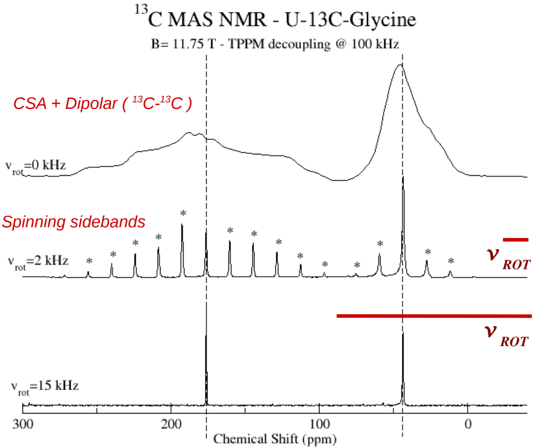
Magic Angle: $\overline{A}(\theta_M) = \overline{A} = 0$

(Fast) Spinning $\overline{\widetilde{A}(t)} = 0$

Effective $\mathbf{A}$ reduces (to first order) to $A_{iso}\mathbf{1}$.

High Resolution NMR

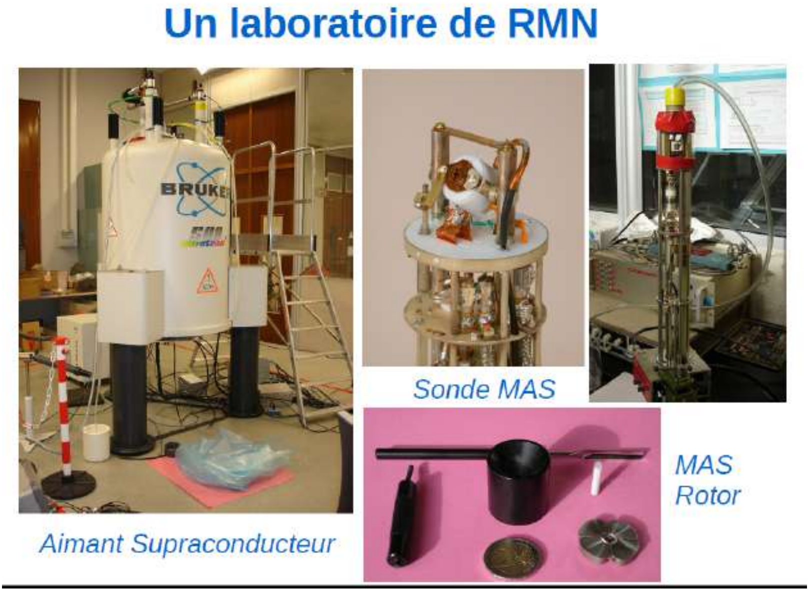
Magic Angle (Sample) Spinning for I=1/2



$$\nu_{ROT} \leq \delta_A\text{: spinning sidebands at } k \times \nu_{ROT}$$

$$\nu_{ROT} > \delta_A\text{: narrow lines}$$

(Experimental) Solid State NMR



Un laboratoire de RMN

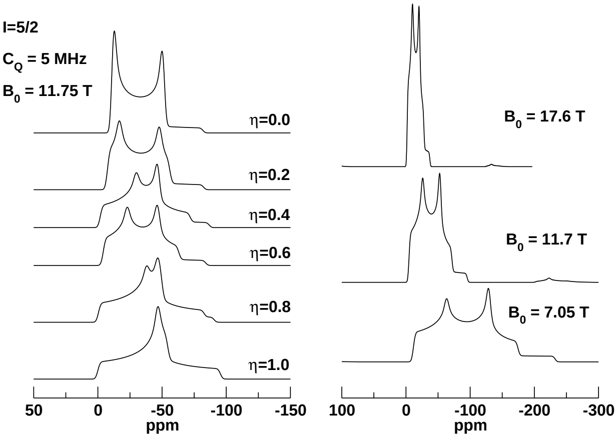
Sonde MAS

MAS Rotor

Aimant Supraconducteur

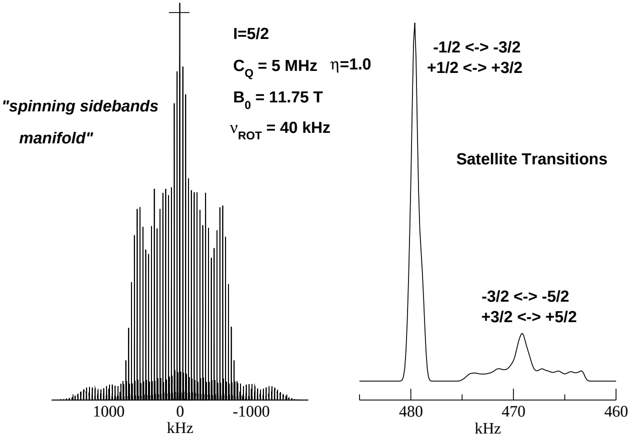
High Resolution NMR

Magic Angle Spinning for quadrupolar nuclei: The central transition



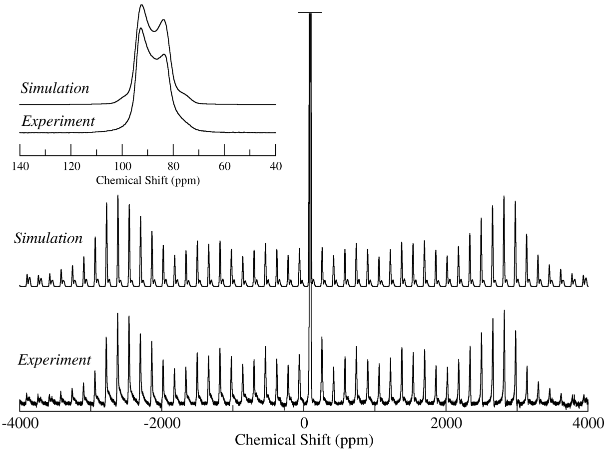
High Resolution NMR of quadruplar nuclei

Magic Angle Spinning for quadruplar nuclei: The satellite transitions



High Resolution NMR of quadruplar nuclei

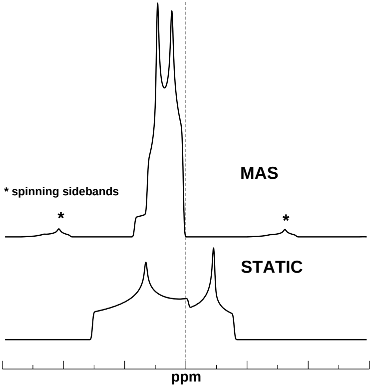
Magic Angle Spinning: one example

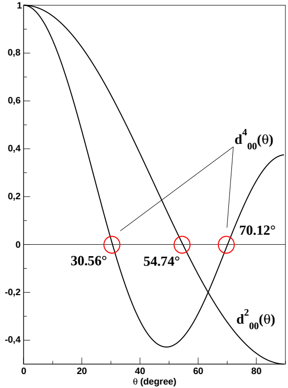


^{27}Al NMR in NaAlH$_4$

High Resolution NMR of quadrupolar nuclei

How to reduce the linewidth ?

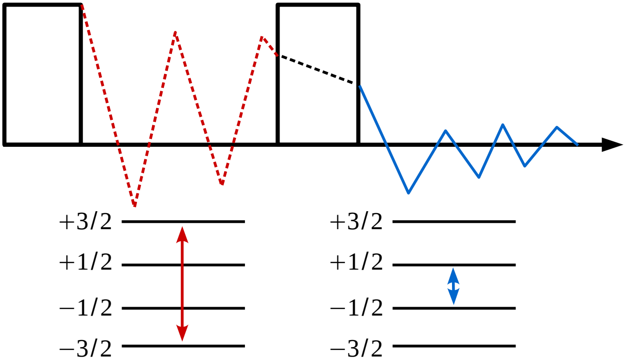




$$\begin{aligned} \text{static: } \nu_{CT} &= \nu_{iso} + a_2 R_{20}(\Omega) + a_4 R_{40}(\Omega) \\ \text{MAS: } \nu_{CT} &= \nu_{iso} + a_4 R_{40}(\Omega) \end{aligned}$$

High Resolution NMR of quadrupolar nuclei

The Multiple Quantum MAS (MQMAS) approach

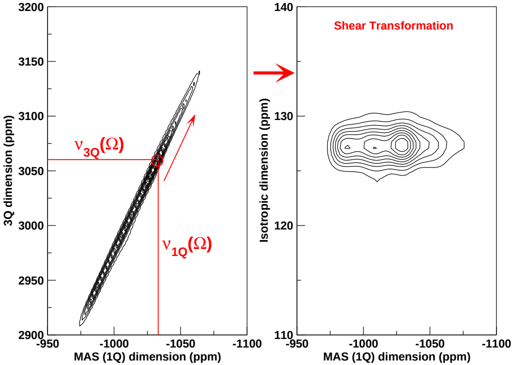


2D NMR: $S(t_1, t_2) = \exp\{-i\,\nu_{3Q}\,t_1\} \times \exp\{-i\,\nu_{1Q}\,t_2\}$

2D FFT yields a 2D spectrum $S(\nu_1, \nu_2)$

High Resolution NMR of quadrupolar nuclei

Principles of MQMAS NMR

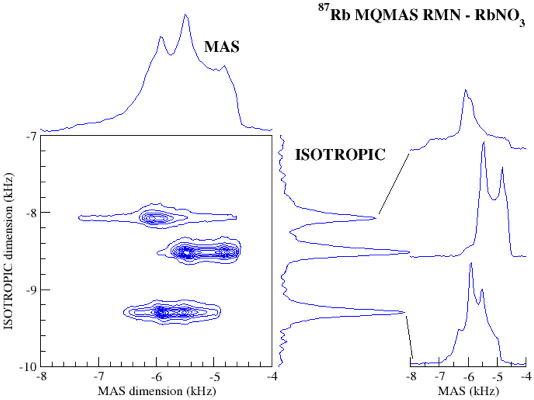


Both transitions have the same anisotropy!

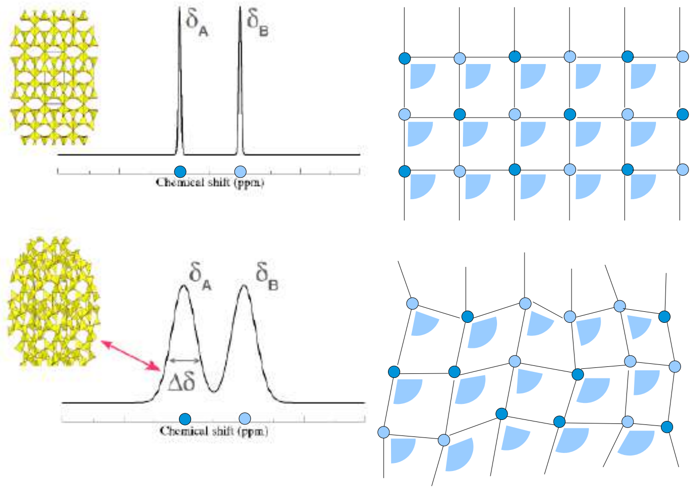
$$
\begin{aligned}
\nu_{(1Q=CT)} &= \nu_{iso}^{(1Q)} + a_4(1Q)\, R_{40}(\Omega) \\
\nu_{(3Q=TQ)} &= \nu_{iso}^{(3Q)} + a_4(3Q)\, R_{40}(\Omega)
\end{aligned}
$$

High Resolution NMR of quadrupolar nuclei

MQMAS at work in a crystalline sample



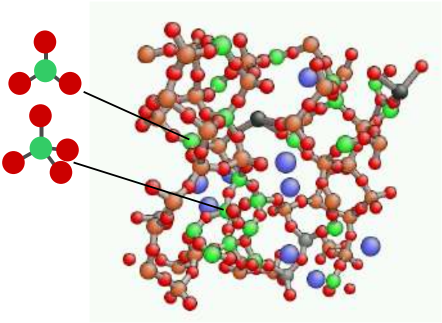
Solid State NMR of disordered materials

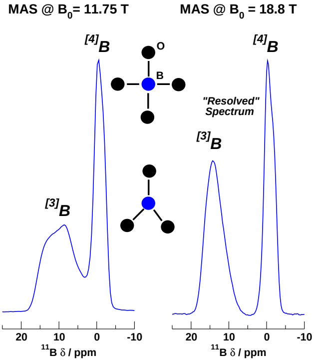


Each *site* characterized by a NMR parameter distribution.

^{11}B MAS NMR in Borosilicate Glasses

Direct access to boron speciation





Identifying the structural units forming the glass network

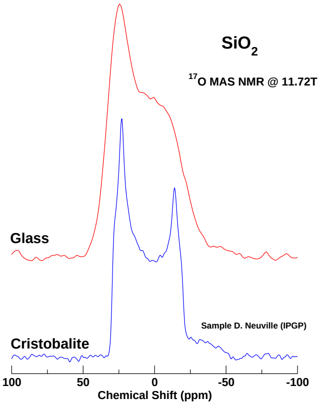
High Field MAS NMR:

Boron speciation resolved

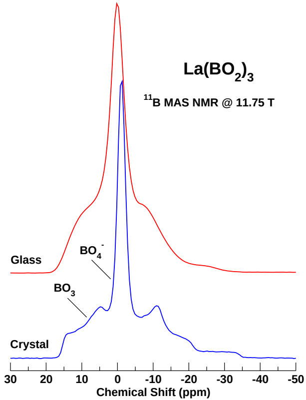
MD Picture, J.M. Delaye, CEA/DEN

Solid State NMR of disordered materials

MAS NMR: mechanisms of broadening?



Sample D. Neuville (IPGP)

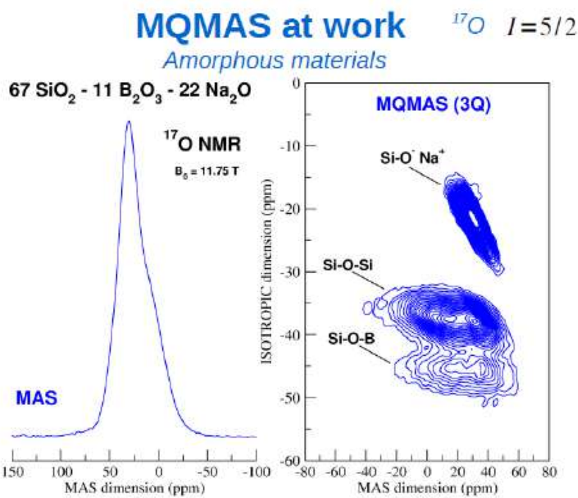


Sample. D Caurant (ENSCP)

Need of 2D NMR to elucidate the contribution of EFG and chemical shift distribution.

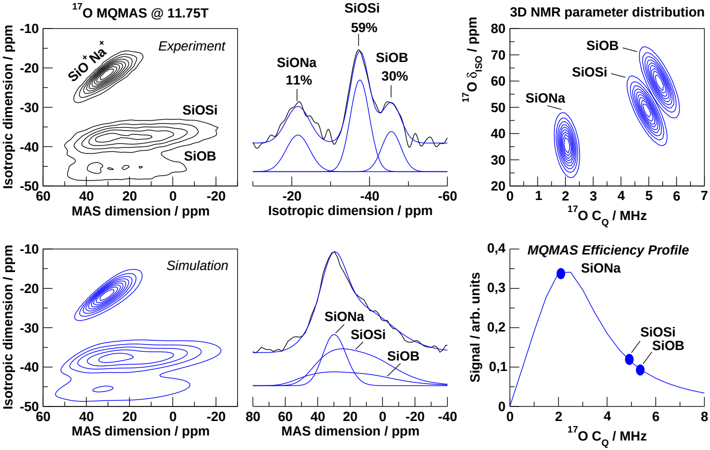
High Resolution NMR in glass

The power of oxygen-17 MQMAS NMR



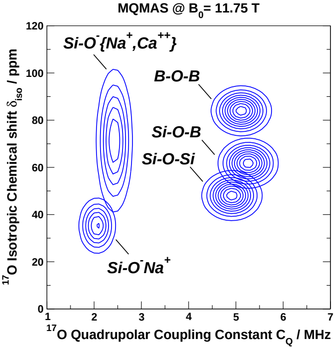
Modeling and Quantifying ^{17}O MQMAS Spectroscopy

Quantification + Spin dynamics + NMR Distribution F. Angeli, T. Charpentier et al. JNCS 2008



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

Quantifying glass topological disorder



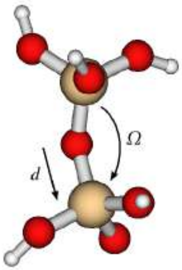
Glass Topology

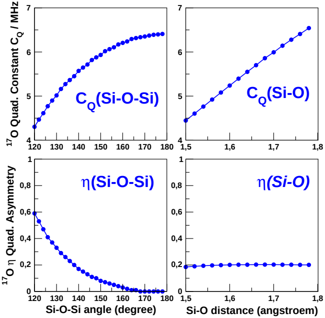
- Reconstruction of the NMR parameter distribution
- Correlating the *local disorder* to the NMR spectrum line shape ?
- $\Pi(\text{NMR}) \Rightarrow \Pi(\text{Structure})$?

Understanding NMR / Structure relationships

Quantum Mechanical calculations: the Cluster Approach

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





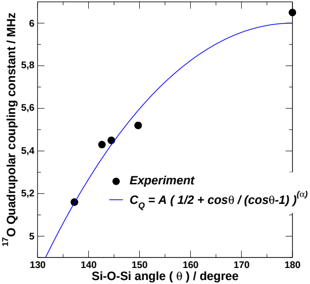
^{17}O C_Q and η_Q NMR parameters are allmost exclusively controlled by local properties: (Si-O-Si bond angle and Si-O bond length)

Understanding NMR / Structure relationships

The Phenomenological Approach: using Crystalline Reference Compounds.

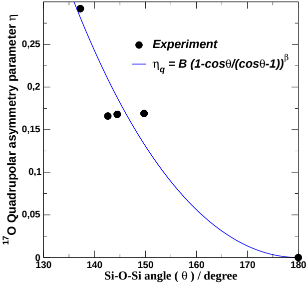
^{17}O $C_Q(\theta)$

Coesite SiO_2



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

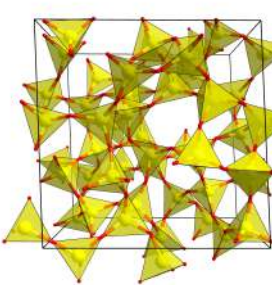
Coesite SiO_2

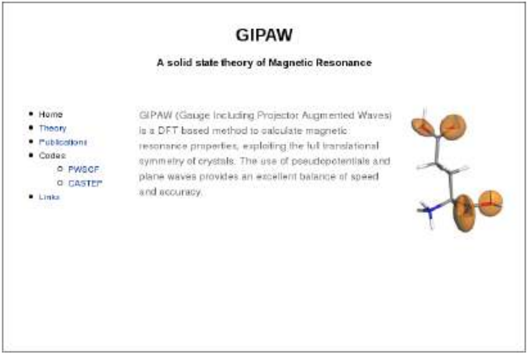


But ^{17}O NMR: very limited number of experimental data !

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.

DFT NMR Calculations

In General

The Quadrupolar Interaction (Electric Field Gradient) *Tensor* from first principles calculations :

$$\mathbf{Q}^{(k)}_{\alpha\beta} = \frac{eQ}{h}\langle\Psi_0|\frac{\delta^{(1)}\mathbf{E}_\alpha}{\delta r_\beta}|\Psi_0\rangle = \frac{eQ}{h}\mathbf{V}_{\alpha\beta}$$

$\mathbf{E}_\alpha$ Electric field, depends on the fundamental states only (easy)
The Chemical Shielding *Tensor* from first principles calculations:

$$\sigma^{(k)}_{\alpha\beta} = \frac{\delta^{(2)}E_0}{\delta\mu_{k,\alpha}B_{0,\beta}} = \frac{\delta^2\langle\Psi_0|H|\Psi_0\rangle}{\delta\mu_{k,\alpha}\delta B_{0,\beta}}.$$

Second order derivative (Response Theory)

DFT NMR Calculations

EFG from electronic density $n_0(r)$

- Kohn-Sham Orbitals / Plane wave

$$
\begin{aligned}
\phi_j(r) &= \sum_{k \in IBZ} e{-}ikr\, u_{j,k}(r) \\
u_{j,k}(r) &= \sum_{G} C_{j,k}(G)\, e{-}iGr \text{ with} G \leq G_{max} \\
n_0(r) &= \sum_{occ} |\phi_j(r)|^2
\end{aligned}
$$

- Electric Field Gradient

$$V_{\alpha,\beta}(r_N) = \int dr \frac{n_0(r)}{|r - r_N|} \left\{ \delta_{\alpha,\beta} - 3 \frac{(r_\alpha - r_{N,\alpha})(r_\beta - r_{N,\beta})}{|r - r_N|^2} \right\}$$

DFT NMR Calculations

From electronic density $n_0(r)$

Principles of a NMR shielding tensor calculation (first-order in B_O) ($\vec{r}_N$ position of the nucleus)

1. computation of the induced (quantum) current density $\vec{j}^{(1)}(\vec{r})$
2. computation of the induced magnetic field

$$\vec{B}_{in}^{(1)}(\vec{r}_N) = \frac{1}{c} \int d^3r \, j^{(1)}(\vec{r}) \times \frac{\vec{r}_N - \vec{r}}{\left|\vec{r}_N - \vec{r}\right|^3} \tag{1}$$

3. The *absolute* chemical shielding tensor σ is obtained through

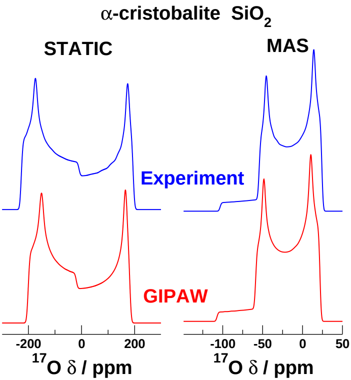
$$\vec{B}_{in}^{(1)}(\vec{r}_N) = -\sigma(\vec{r}_N)\vec{B}_0 \tag{2}$$

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
  - All-electron approach



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

Accuracy: GIPAW outperforms all previous approaches

GIPAW Calculations

Practice

- Convergence of NMR versus Plane wave cutoff, k-grid
- Outputs: magnetic shielding $\boldsymbol{\sigma}$, EFG $\mathbf{V}$ tensor
- Experimental Observable: chemical shift $\boldsymbol{\delta}$, Quadrupolar parameters C_Q, η

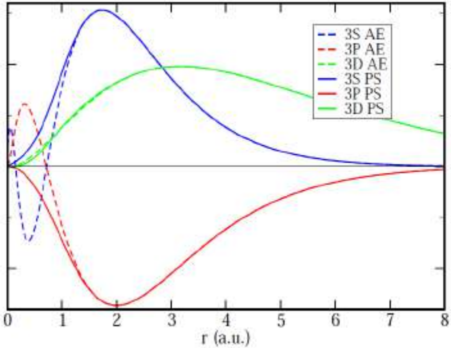
$$\begin{aligned} \delta_{iso}(calc) &= \sigma_{iso}(ref) - \sigma_{iso}(calc) \\ C_Q &= \frac{eQ}{h} V_{ZZ} \end{aligned}$$

$\sigma_{iso}(ref)$, Q from reference compound(s) with accurate experimental NMR parameters and structure.

- (DFT) Optimized structures provides better NMR predictions than X-ray structures.
- Periodic boundary conditions: GIPAW performs (much) better than cluster approximation
- Challenges: Finite Temperature (calculation at 0K), Disorder.

DFT NMR Calculations

The (art of) pseudopotential approximation



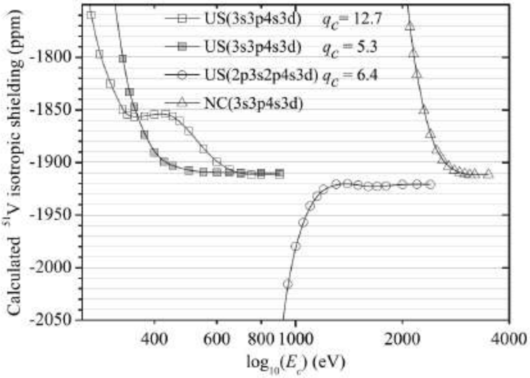
- Choice of valence (core) configuration
- choice of cutoff radii

$$\begin{array}{ccc} \text{for} & & r > r_{cut} \\ \phi_{PS}(r) & = & \phi_{AE}(r) \\ \text{for} & & r < r_{cut} \\ \phi_{PS}(r) & & \text{smooth} \end{array}$$

GIPAW Applications

Importance of the design of accurate pseudopotentials

Some elements are difficult (transition element), need of optimized pseudopotentials (ultra-soft)



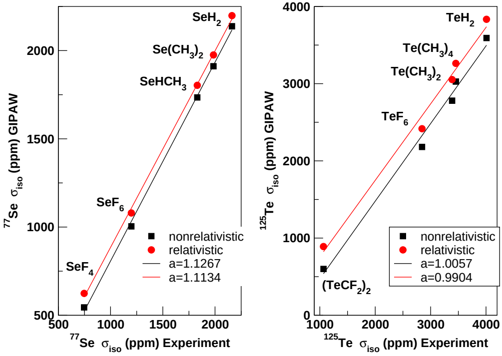
Importance of good *convergence*

L. Truflandier, M. Paris, F. Boucher, *Density functional theory investigation of 3d transition metal NMR shielding tensors in diamagnetic systems using the gauge-including projector augmented-wave method*, Phys. Rev. B. 76 (2007) 035102.,

GIPAW Applications

ZORA (Zero-Order Relativistic Approximation) Relativistic correction

Absolute magnetic shielding versus (relative) chemical shift

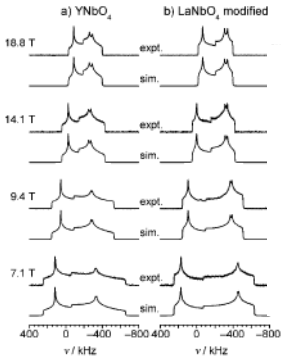


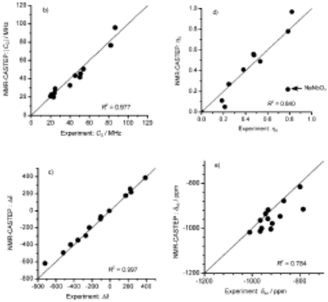
J.R. Yates, C.J. Pickard, M.C. Payne, F. Mauri, *Relativistic nuclear magnetic resonance chemical shifts of heavy nuclei with pseudopotentials and the zeroth-order regular approximation*, J. Chem. Phys. 118 (2003) 5746

GIPAW Applications

Assessment of the GIPAW method

Set of reliable NMR data are needed to assess the GIPAW method



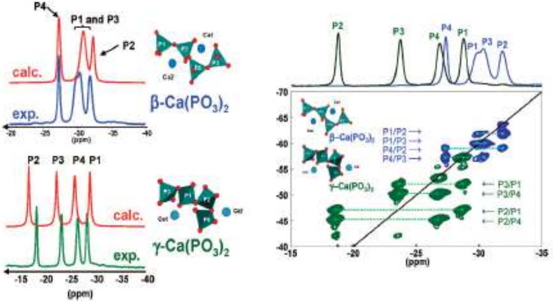


J.V. Hanna, K.J. Pike, T. Charpentier, T.F. Kemp, M.E. Smith, B.E.G. Lucier, R.W. Schurko, L.S. Cahill, *A 93Nb Solid-State NMR and Density Functional Theory Study of Four- and Six- Coordinate Niobate Systems*, Chem. Eur. J. 16 (2010) 3222-3239.

GIPAW Applications

NMR Crystallography: assign NMR peak to crystallographic sites.

Use of DFT GIPAW in support of advanced 2D NMR techniques

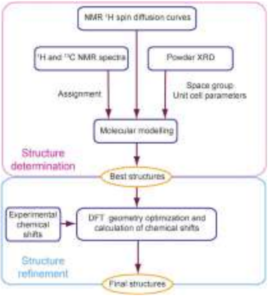


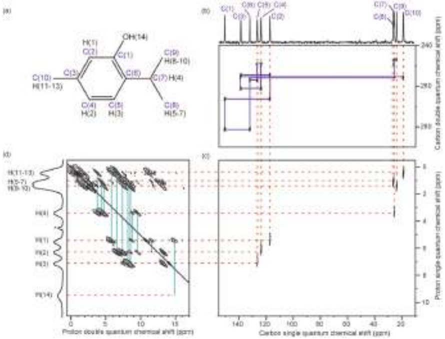
F. Pourpoint, A. Kolassiba, C. Gervais, T. Azais, L. Bonhomme-Coury, C. Bonhomme, F. Mauri, *First Principles Calculations of NMR Parameters in Biocompatible Materials Science: The Case Study of Calcium Phosphates, β- and γ-Ca(PO3)2. Combination with MAS-J Experiments*, Chemistry of Materials. 19 (2007) 6367-6369.

GIPAW Applications

NMR Crystallography: NMR supported structure refinment

Use of NMR shifts to refine structures





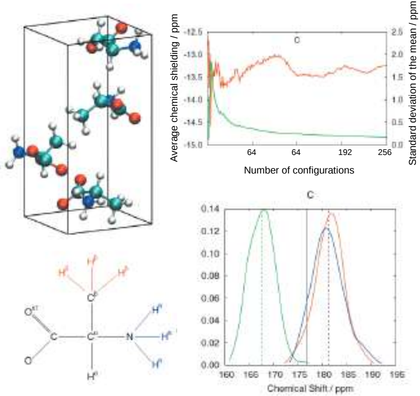
Soon in glasses ?

E. Salager, R.S. Stein, C.J. Pickard, B. Elena, L. Emsley, *Powder NMR crystallography of thymol*, Phys. Chem. Chem. Phys. 11 (2009) 2610

GIPAW Applications

Accouting for motional averaging

Use of MD trajectory and averaging to account for finite temperature (motion) effects



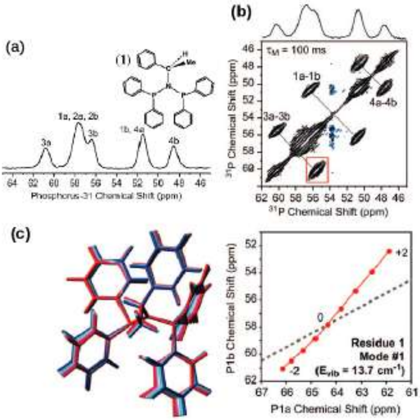
M. Robinson, P.D. Haynes, *Dynamical effects in ab initio NMR calculations: Classical force fields fitted to quantum forces*, J. Chem. Phys. 133 (2010) 084109.

Must be developped for Glasses (but coming soon. . .).

GIPAW Applications

Correlation between low-energy vibrations and disorder

Disorder correlated to vibrational properties ? A NMR answer . . .

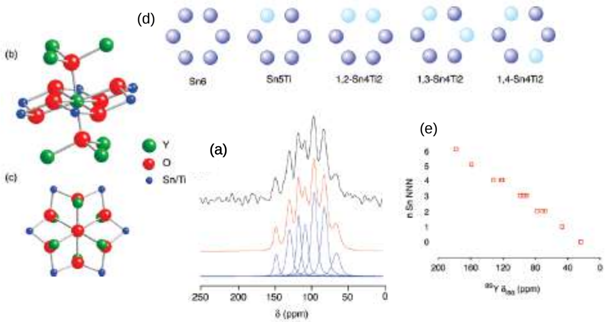


S. Cadars, A. Lesage, C.J. Pickard, P. Sautet, L. Emsley, *Characterizing Slight Structural Disorder in Solids by Combined Solid-State NMR and First Principles Calculations*, The Journal of Physical Chemistry A. 113 (2009) 902-911.

GIPAW Applications

Chemical disorder in ceramics

Sensitivity of NMR to next-nearest neighbors

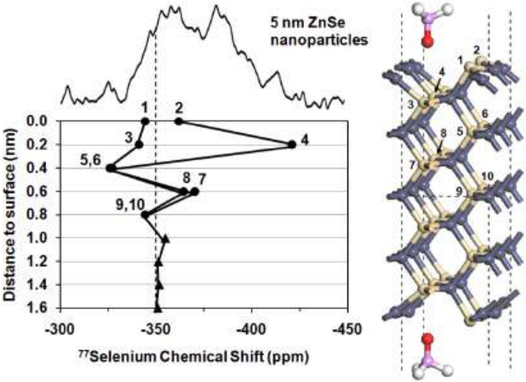


S.W. Reader, M.R. Mitchell, K.E. Johnston, C.J. Pickard, K.R. Whittle, S.E. Ashbrook, *Cation Disorder in Pyrochlore Ceramics: 89Y MAS NMR and First-Principles Calculations*, The Journal of Physical Chemistry C. 113 (2009) 18874-18883.

GIPAW Applications

Effect of surface. ZnSe Nanoparticles

Solid-state NMR: strong disorder (line broadening) despite with high degree of positional order

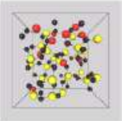


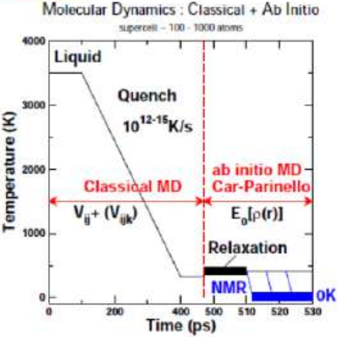
Electronic disorder spreads beyond 1 nm below the surface

S. Cadars, B.J. Smith, J.D. Epping, S. Acharya, N. Belman, Y. Golan, B.F. Chmelka, *Atomic Positional Versus Electronic Order in Semiconducting ZnSe Nanoparticles*, Phys. Rev. Lett. 103 (2009) 136802.

Combining Molecular Dynamics with NMR-GIPAW

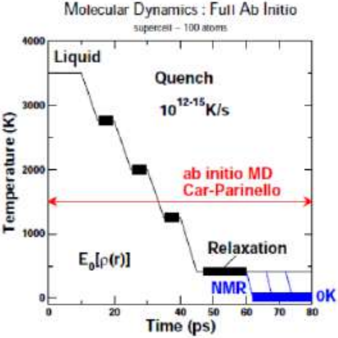
Modélisation des verres
Dynamique Moléculaire





Molecular Dynamics : Classical + Ab Initio

supercell – 100 - 1000 atoms



Molecular Dynamics : Full Ab Initio

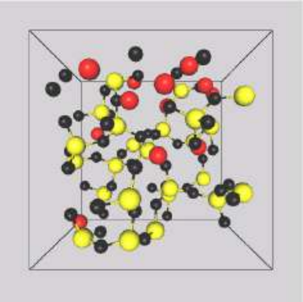
supercell – 100 atoms

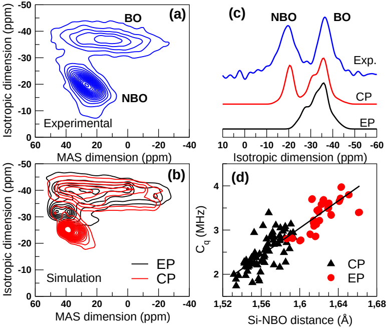
MD: Collaboration S. Ispas, P. Kroll, G. Ferlat, F. Mauri

^{17}O NMR in alkali tetrasilicate glass

Classical vs Ab Initio

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

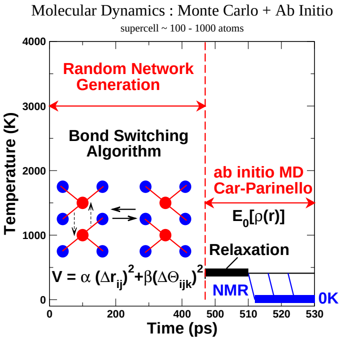




fpNMR provides complementary data (diffraction) for assessing MD models

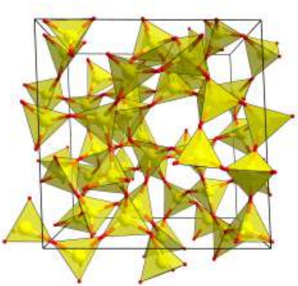
A Monte Carlo / MD Hybrid Approach

Modeling Glass Structure: Bond Switching Algorithm



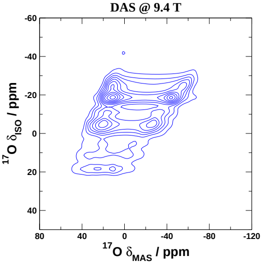
Defect Free Vitreous Silica

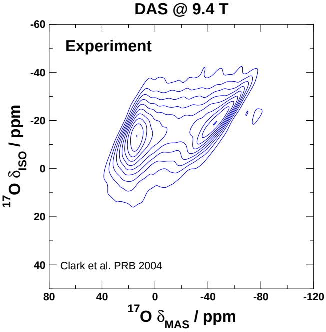
Continuous Random Network



Simulation of NMR Spectra

The simple approach

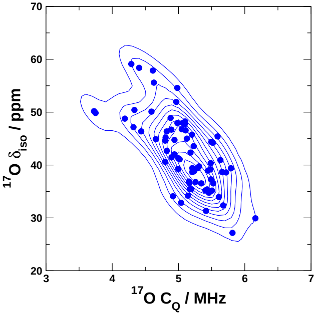




Clark et al. PRB 2004

Simulation of NMR Spectra

Kernel Density Estimate Approach



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

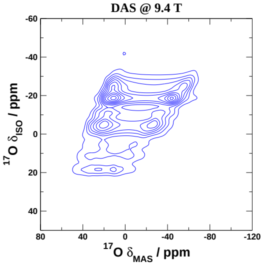
$$\text{Kernel: } p(\mathbf{x}) = \sum_i \mathcal{K}_{H_i}\left(\mathbf{x} - \mathbf{x_i}\right)$$

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

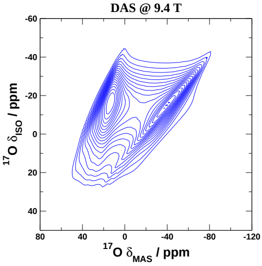
Simulation of NMR Spectra

Kernel Density Estimate Approach

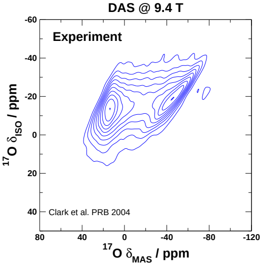
Direct Simulation



KDE simulation



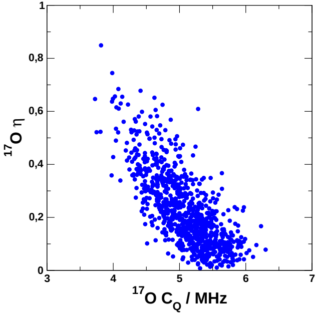
Experiment



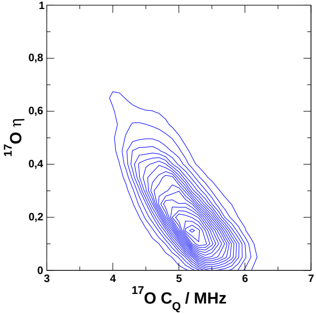
Clark et al. PRB 2004

Analysis of NMR parameter distribution

Kernel Density Estimate Approach



Theoretical points

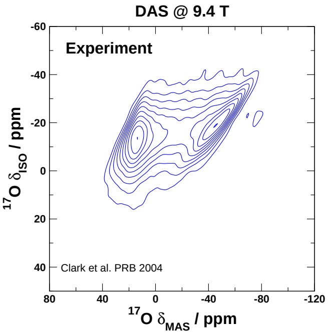


Estimated Distribution

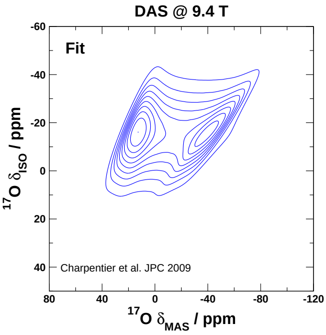
Introduction of a correlated 3D NMR parameter distribution:

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

Quantitative analysis of Experimental data



Clark et al. PRB 2004



Charpentier et al. JPC 2009

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

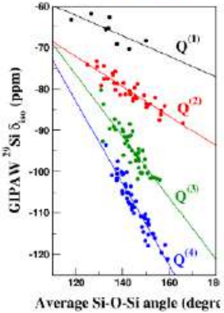
Reconstructing the Bond Angle Distribution (BAD)

NMR / Structure relationships

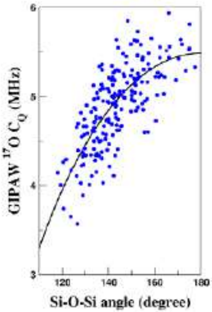
F.Angeli, O. Villain et al., Geochem. Chim. Acta 2011

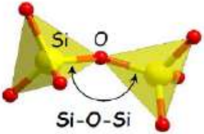
Relation structure locale - composition

$^{29}Si\ \delta_{iso}$



$^{17}O\ C_Q$





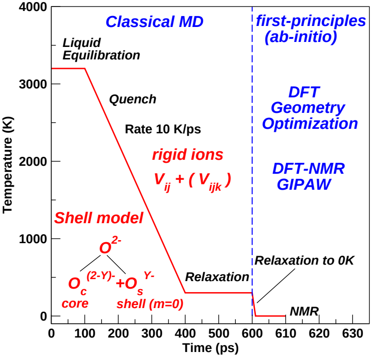
Mean Si-O-Si bond angle

	$^{29}Si\ \delta_{iso}$	$^{17}O\ C_Q$
NS1 - 43% Na_2O	133°	129°
NS3 - 23% Na_2O	142°	143°
SiO_2	146°	152°

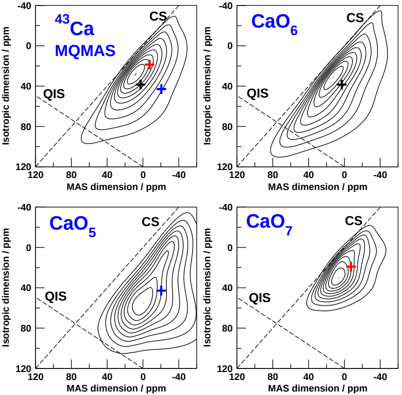
A new Tool: the first-principles (fp) NMR approach

Combining Molecular Dynamics simulations (MD) with fp NMR calculations.

Melt & Quench Method



^{43}Ca MQMAS in CaSiO$_3$ Glass



- ⇒ Including polarization effects (O^{2-}): Improved $Q^{(n)}$ description.

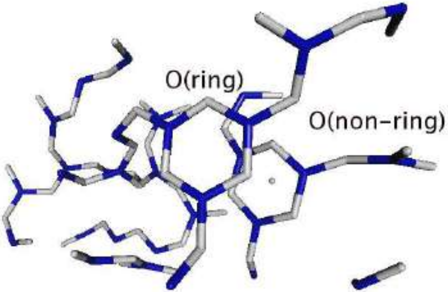
A. Tilocca, N.H. de Leeuw, A.N. Cormack , *PRB* 2006, 73, 104209.

- ⇒ The fpNMR package: Analysis of MD-GIPAW outputs

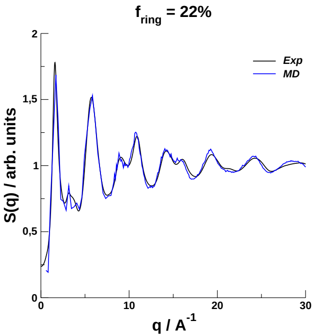
J Phys Chem B 108, 4147, 2004; *J Phys Chem C* 113, 7917, 2009; *PCCP* 12, 6054, 2010

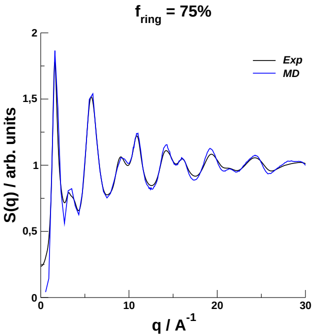
Topology of vitreous B_2O_3

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



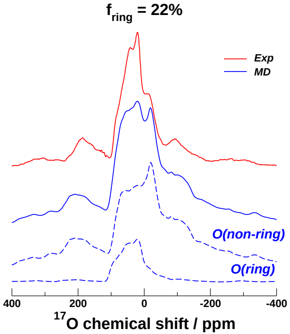
Topology of vitreous B_2O_3

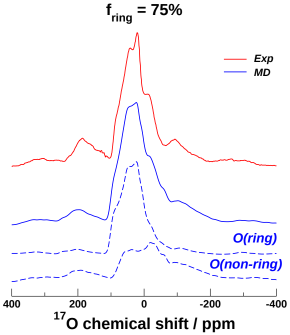




S(q): poor sensitivity to Bond Angle ?

Topology of vitreous B_2O_3



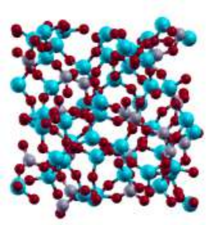


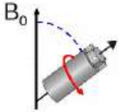
NMR: high sensitivity to Bond Angle

Molecular Dynamics versus NMR

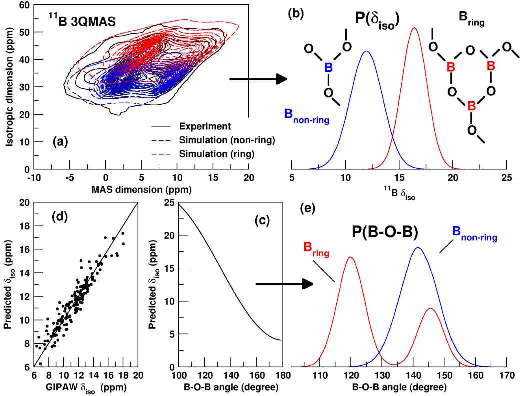
GIPAW provides an integrated approach to analyse NMR data

MD-GIPAW



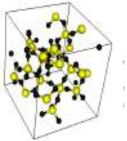


MAS NMR



Molecular Dynamics versus NMR

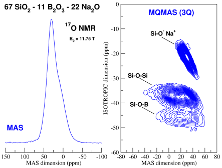
DFT Calculations



Structure

NMR Hamiltonian

NMR Simulations



DFT vs Experiments

Many 1D-2D NMR approches

STATIC, MAS, MQMAS, STMAS, DOR, DAS, MQDOR...