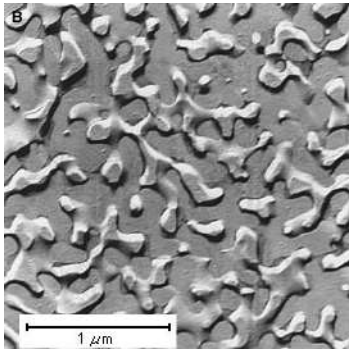
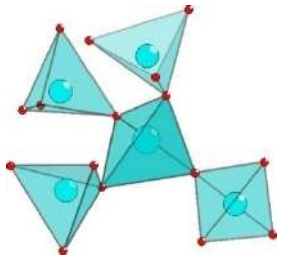
Nucléation - Cristallisation
Ordre / Désordre : point de vue de la RMN

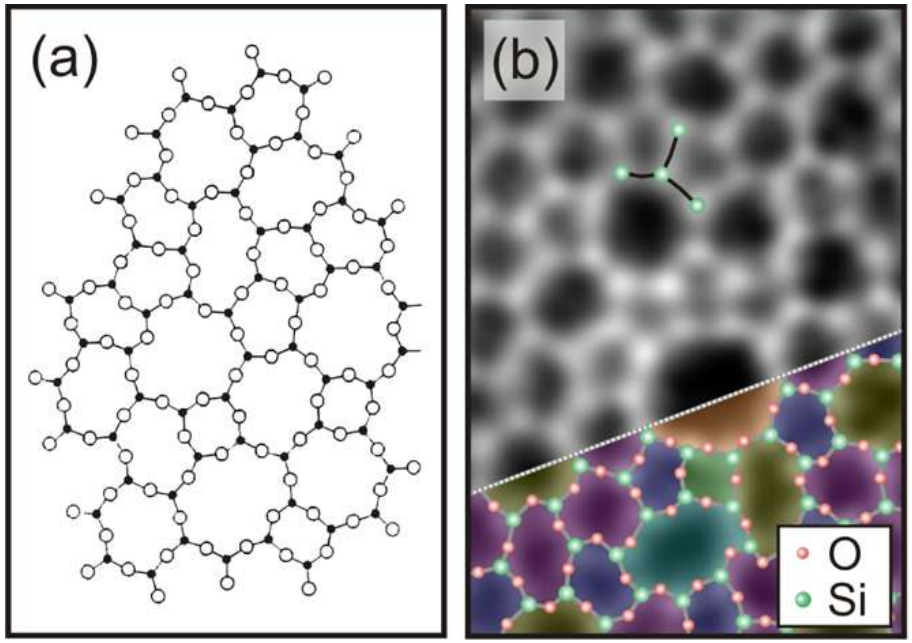
D. Massiot, Thibault Charpentier

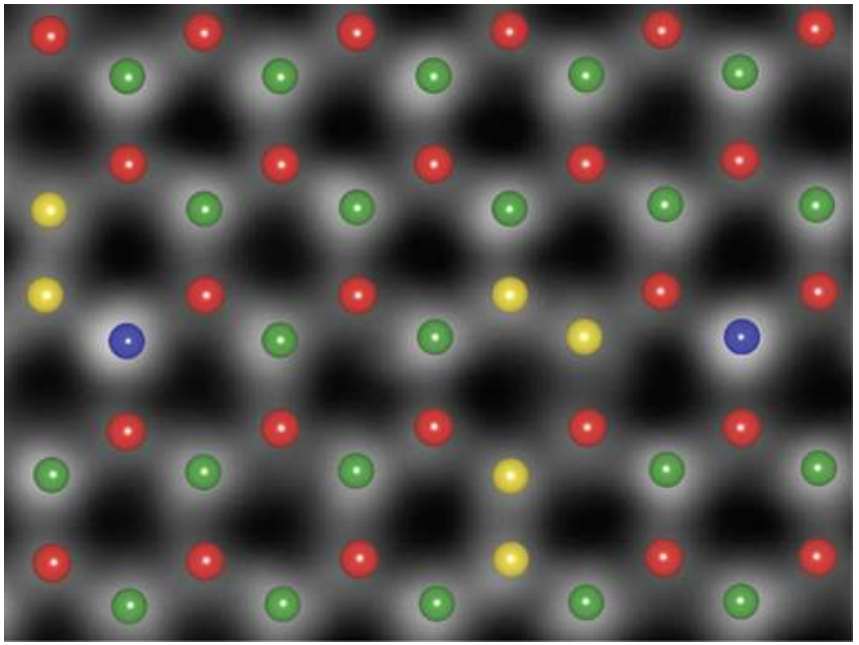
CEMHTI UPR3079 CNRS, Orléans France
CEA / IRAMIS / SIS2M / LSDRM





Geometrical & Chemical Order





THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Atomic Arrangement in Two-Dimensional Silica: From Crystalline to Vitreous Structures

Leonid Lichtenstein, Markus Heyde,* and Hans-Joachim Freund

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Direct Imaging of a Two-Dimensional Silica Glass on Graphene

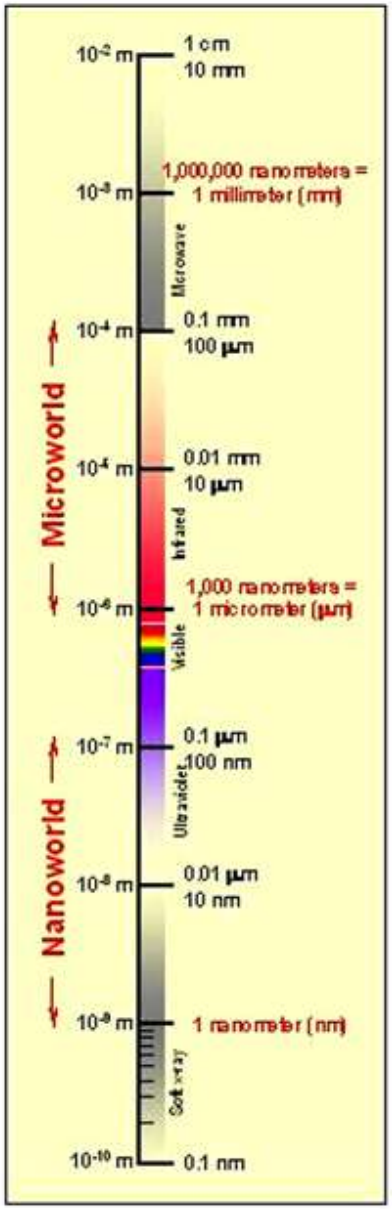
Pinshane Y. Huang,[†,■] Simon Kurasch,[‡,■] Anchal Srivastava,[§,○] Viera Skakalova,[§,∥] Jani Kotakoski,[∥,⊥] Arkady V. Krasheninnikov,[⊥,¶] Robert Hovden,[†] Qingyun Mao,[†] Jannik C. Meyer,[‡,∥] Jurgen Smet,[§] David A. Muller,[*,†,□] and Ute Kaiser[*,‡]

Vol 464|25 March 2010|doi:10.1038/nature08879
nature
nature
LETTERS

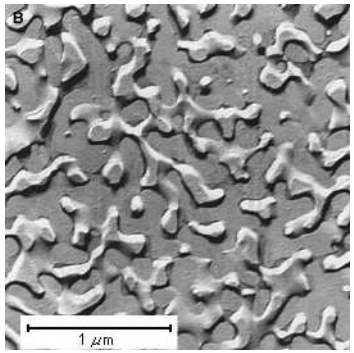
Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy

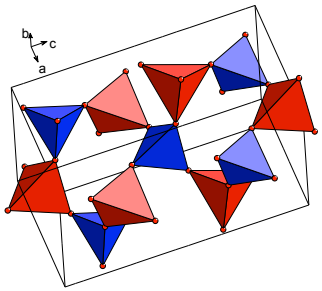
Ondrej L. Krivanek[1], Matthew F. Chisholm[2], Valeria Nicolosi[3], Timothy J. Pennycook[2,4], George J. Corbin[1], Niklas Dellby[1], Matthew F. Murfitt[1], Christopher S. Own[1], Zoltan S. Szilagyi[1], Mark P. Oxley[2,4], Sokrates T. Pantelides[2,4] & Stephen J. Pennycook[2,4]

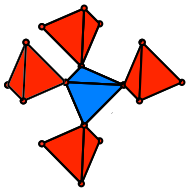
Glass structure at different scales

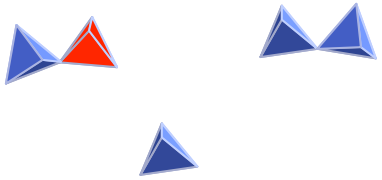


Homogeneous
Isotropic
Disordered

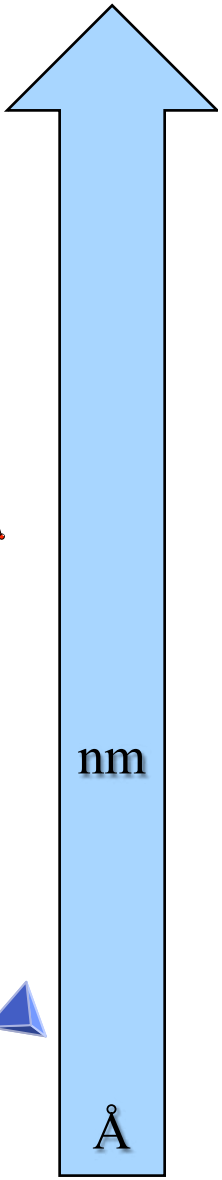




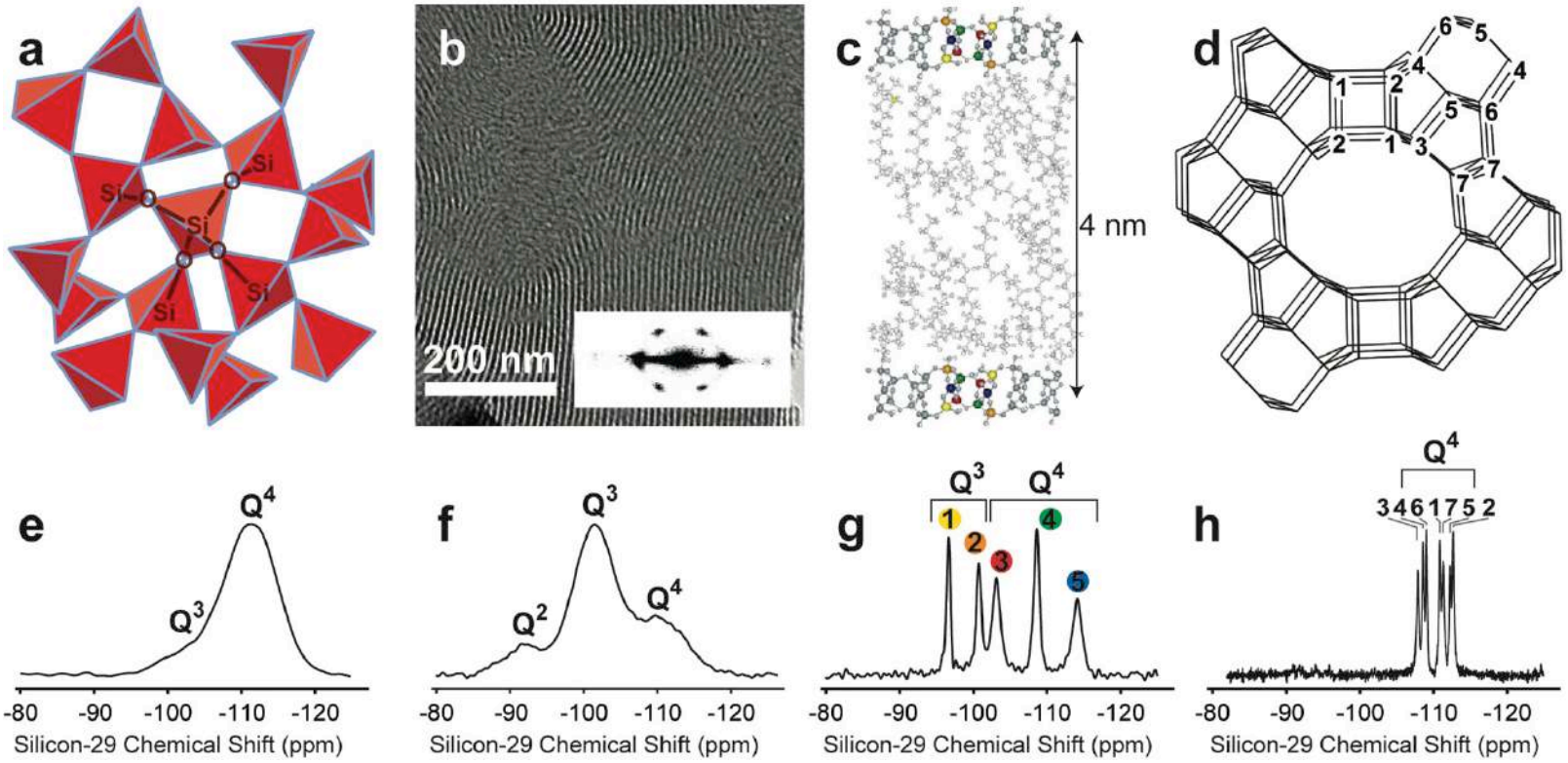




Heterogeneous
Anisotropic
Partly Ordered



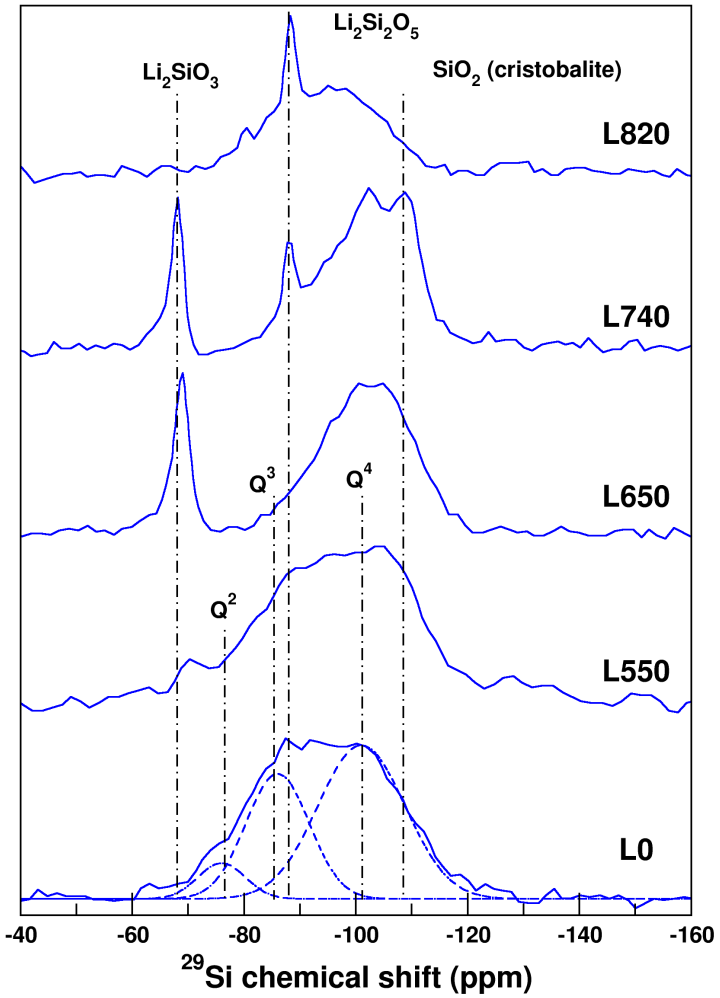
^{29}Si - Silica based materials

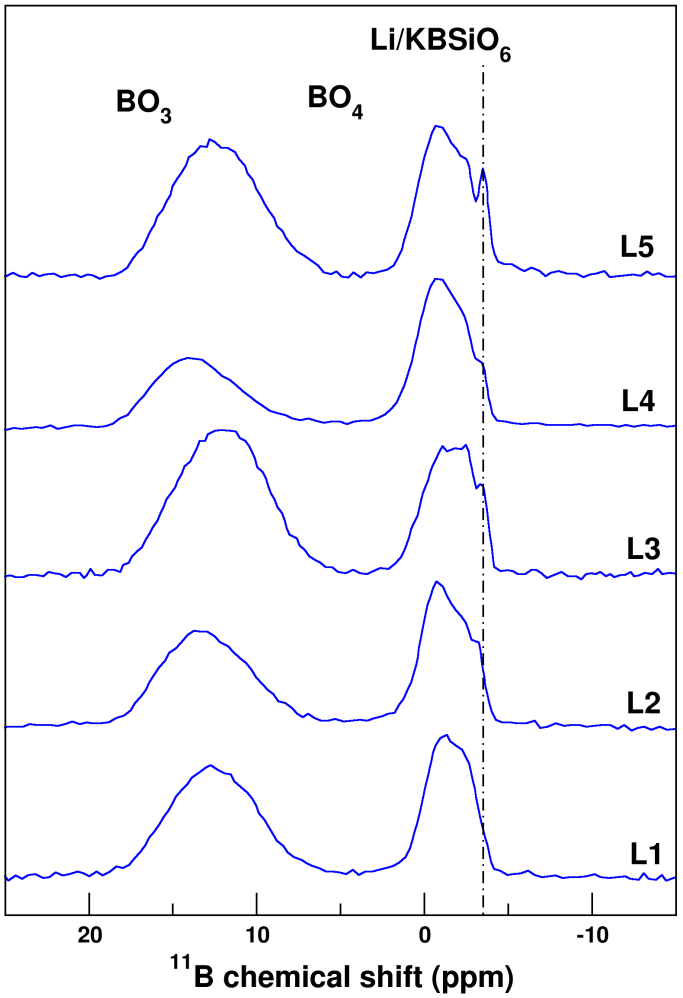


Glass | Mesoporous Silica | SiO_2-surfactant Mesophase | Zeolite

D.Massiot, F.Fayon, M.Deschamps, S.Cadars, P.Florian, V.Montouillout, N.Pellerin, J.Hiet, A.Rakhmatullin, C.Bessada *'*
Detection and use of small J couplings in solid state NMR experiments.'
Comptes Rendus de Chimie 13 117-129 ***2010***

29Si Cristallisation d'un verre



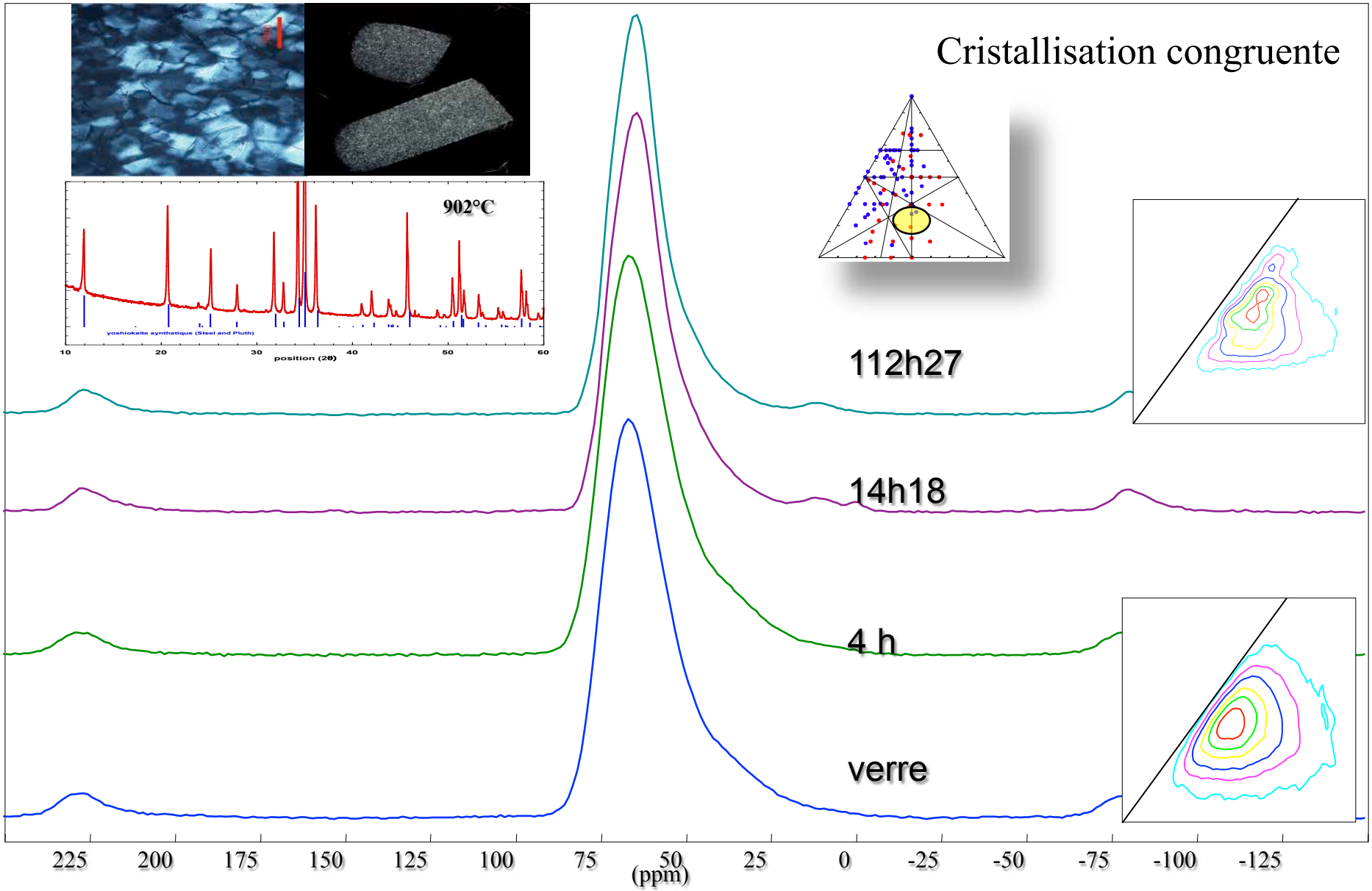


SiO_2-Li_2O

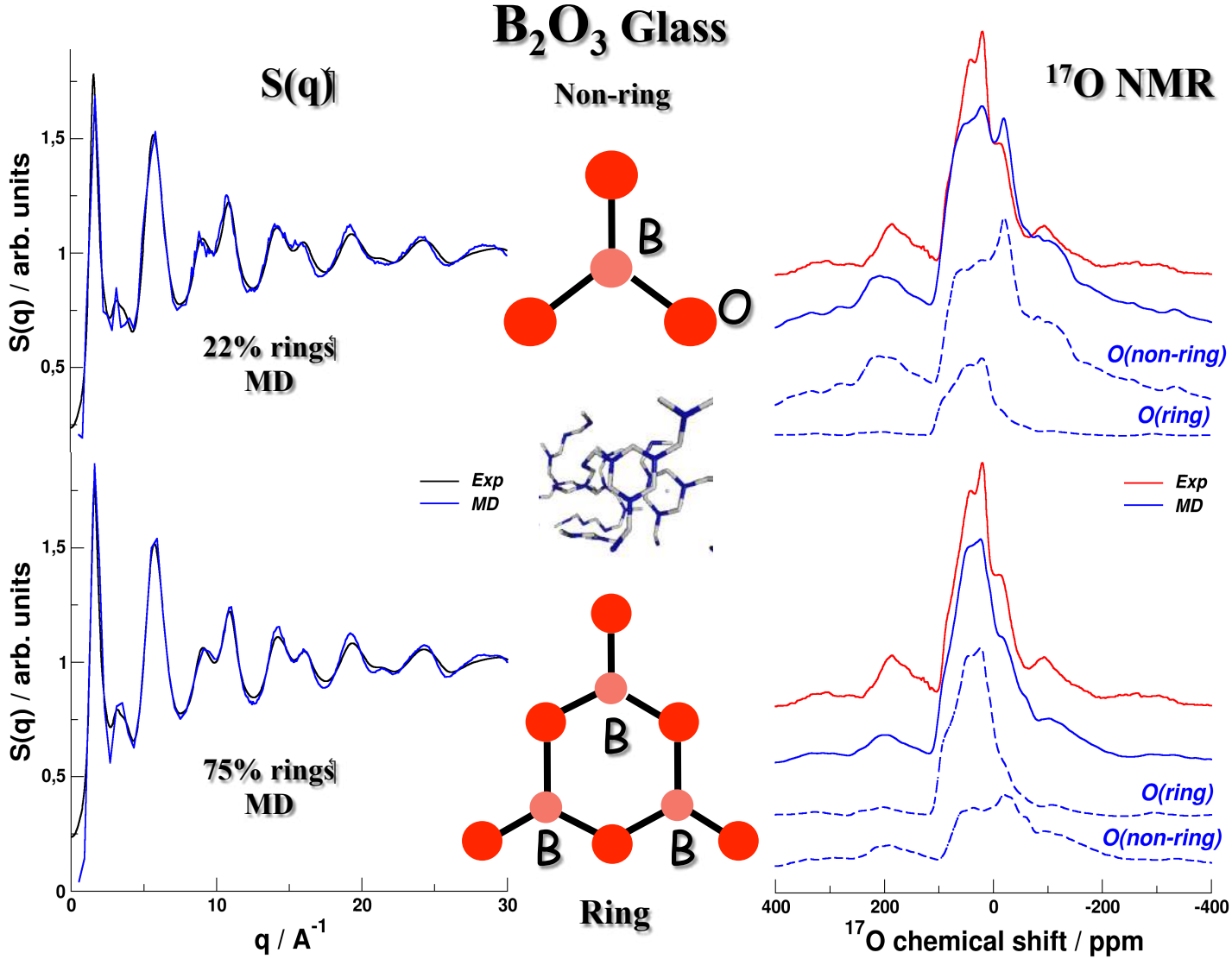
SiO_2-B_2O_3-K_2O

Ananthanarayanan, A., Kothiyal, G.P., Montagne, L., Revel, B .
Journal of Solid State Chemistry, 183(6):1416-1422 2010
Journal of Solid State Chemistry, 183(1): 120-127 2010

Yoshiokaite – 50.23



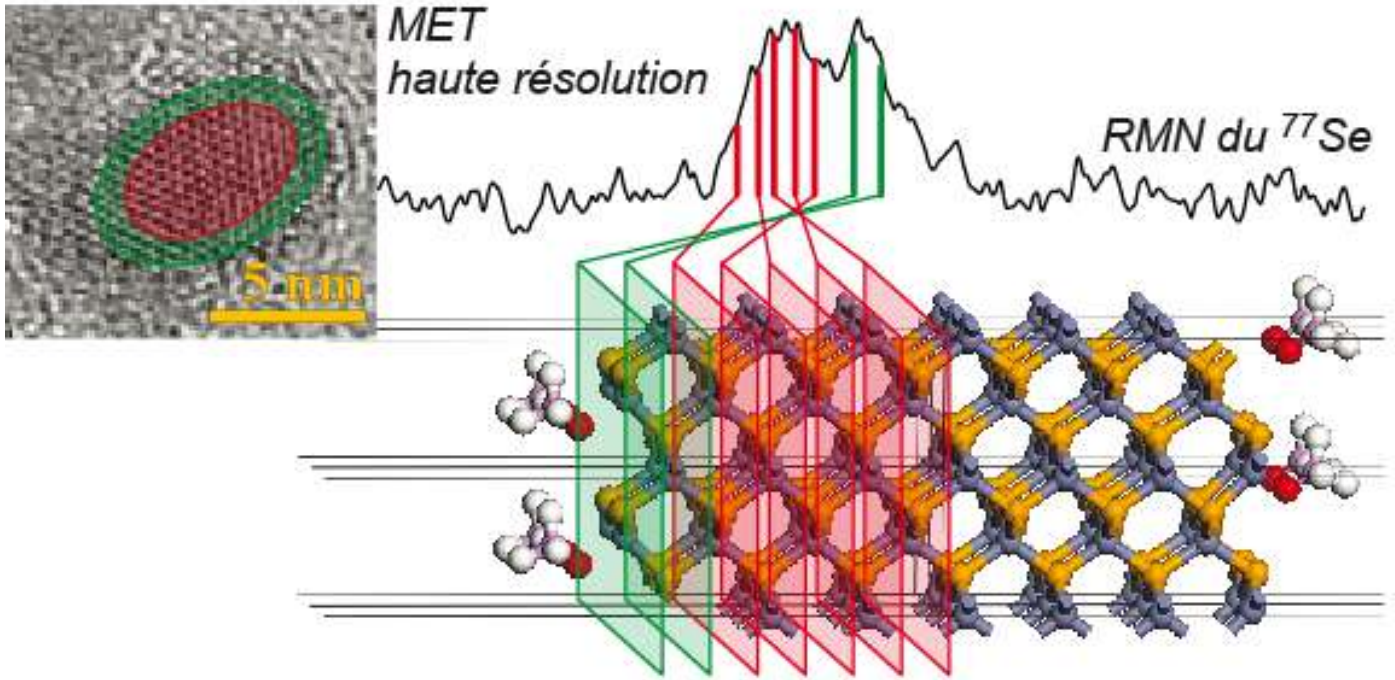
Diffusion / Model / NMR : local order



G.Ferlat, T.Charpentier, A.P.Seitsonen, A.Takada, M.Lazzeri, L.Cormier, G.Calas, F.Mauri
"*Boroxol Rings in Liquid and Vitreous B2O3 from First Principles*"
Phys. Rev. Lett. 101 065504 ***2008***

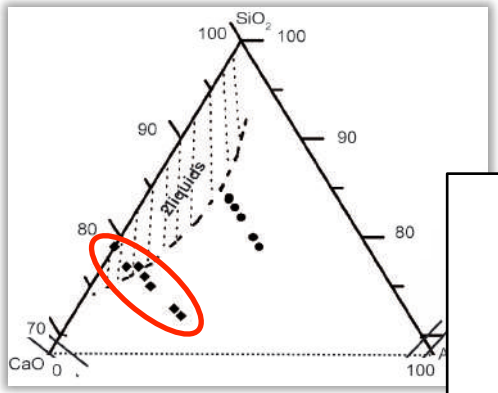
Nanoparticules ZnSe

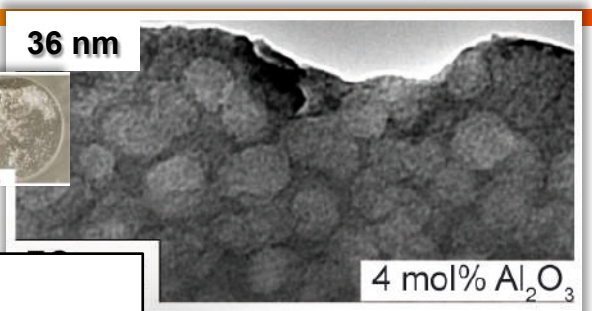
Calculs DFT de paramètres RMN
en conditions limites periodiques

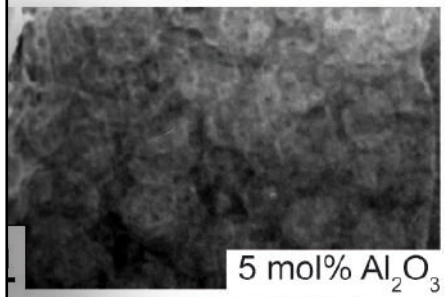


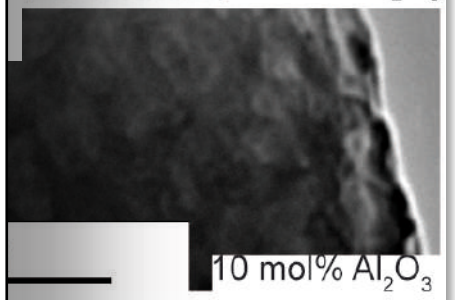
S.Cadars, J.D.Epping, S.Acharya, N.Belman, Y.Golan, B.F.Chmelka
"Positional and Electronic Order in Semiconducting ZnSe Nanoparticles"
Phys. Rev. Lett. 103 136802 2009 .

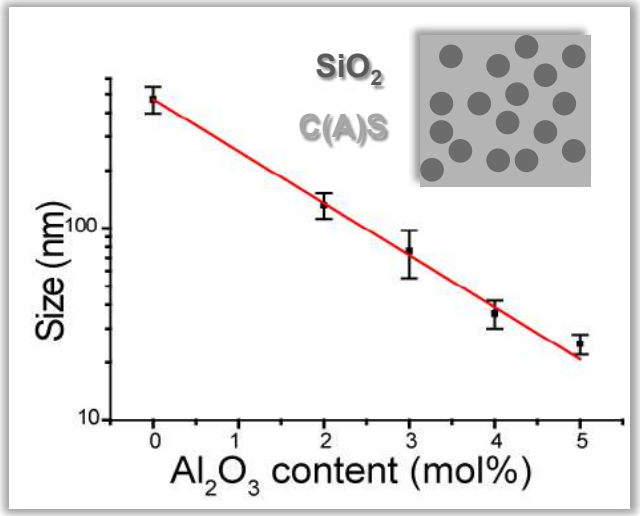
Transmission Electron Microscopy











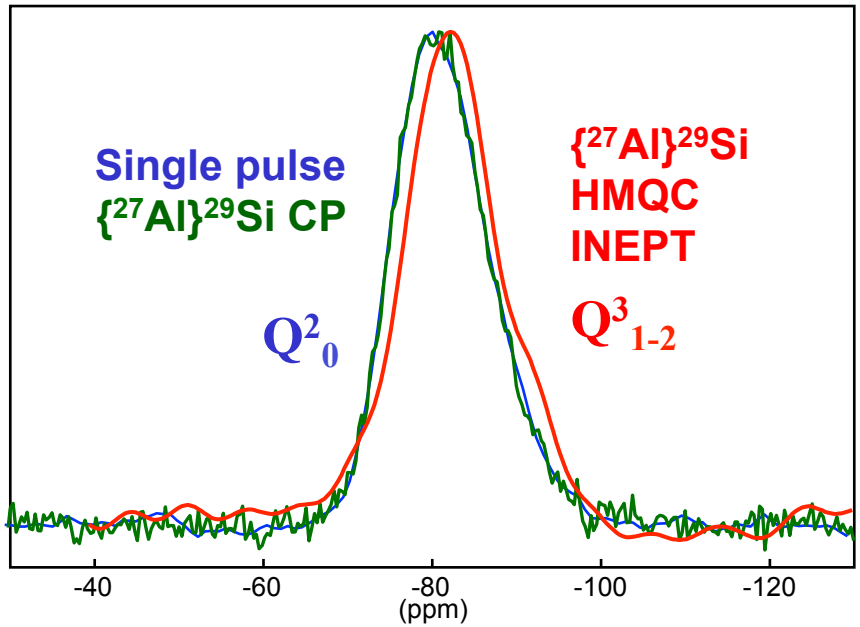
•Under 3 TEM

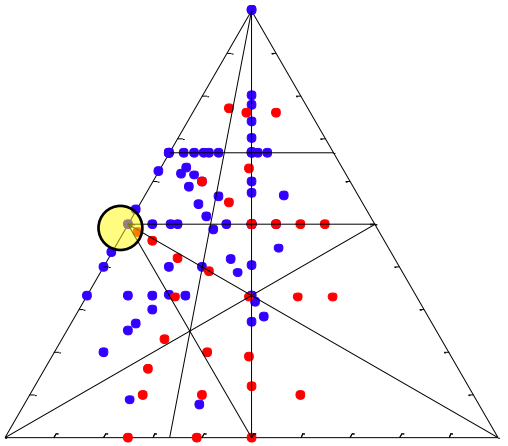
•Increasing alumina content from 0 to 12 mol% phase separation is still observed

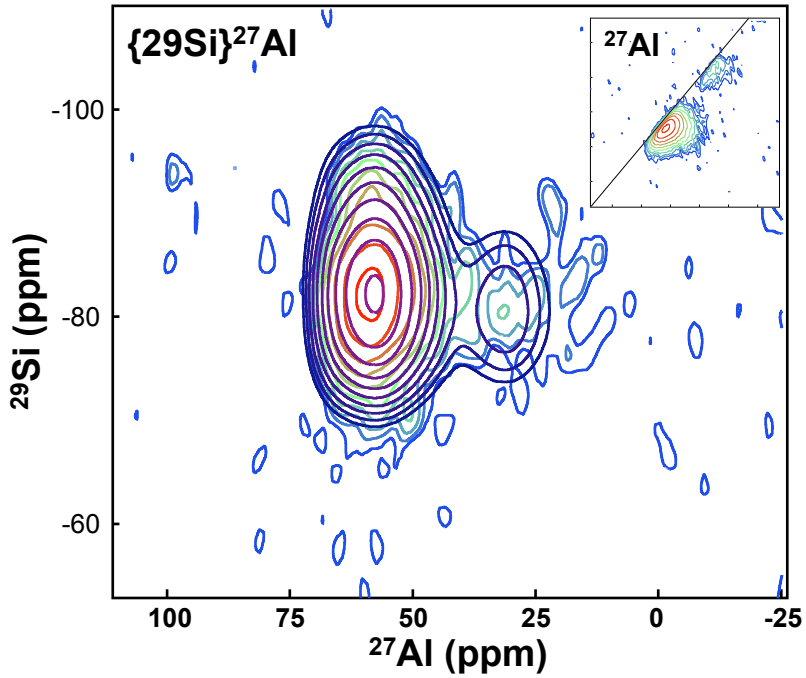
L.Martel, M.Allix, F.Millot, V.Sarou-Kanian, E.Véron, S.Ory, D.Massiot, M.Deschamps

"*Controlling the size of nanodomains in calcium aluminosilicate glasses* » *J. Phys. Chem. C* 115 18935–18945 ***2011***

{^{29}Si}^{27}Al Correlation SiO_2-CaO + εAl_2O_3

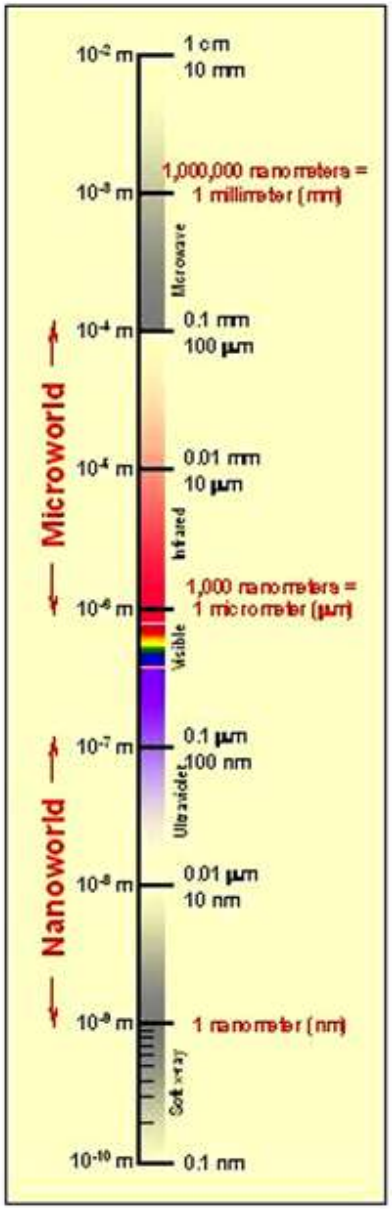




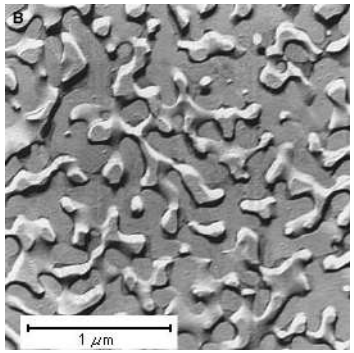


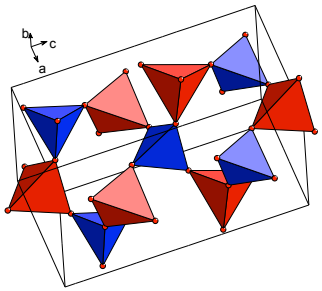
- Al is in a more polymerized environment than Si
- The glass is inhomogeneous at the nano-meter scale…
- AlO_4 & AlO_5 are bound to chemically similar SiO_4 species

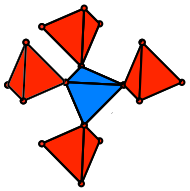
Glass structure at different scales

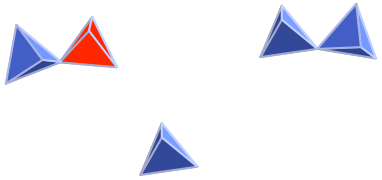


Homogeneous
Isotropic
Disordered

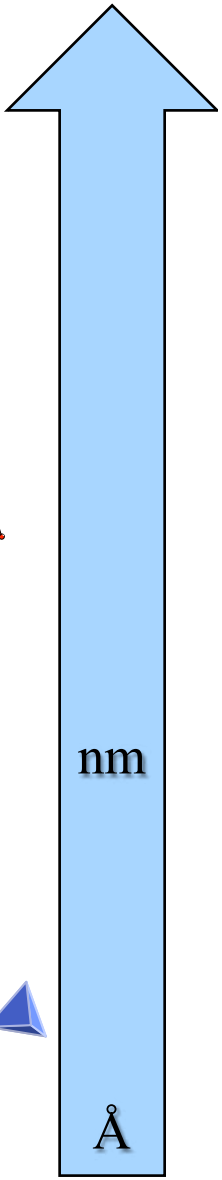






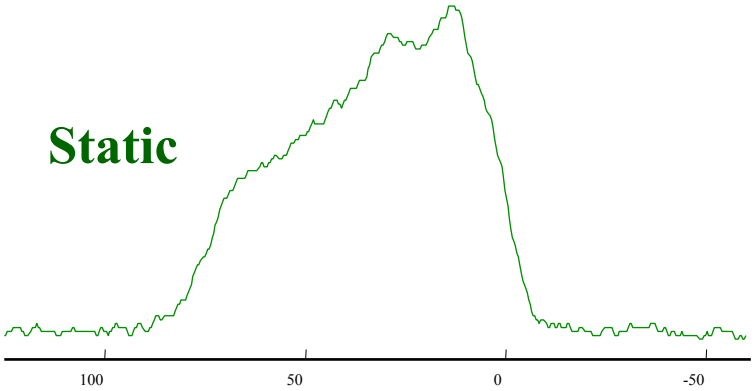


Heterogeneous
Anisotropic
Partly Ordered



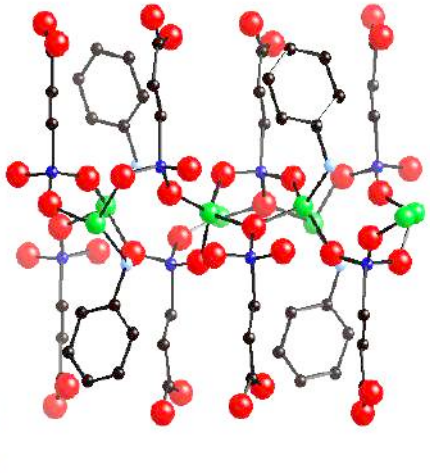
Echantillon Statique ? Trop d'information ?

^{31}P Spin 1/2 CSA

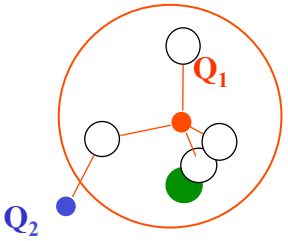


$Zn\ O_3P\ C_2H_4\ CO_2H$ - 0.5 $C_6H_5NH_2$

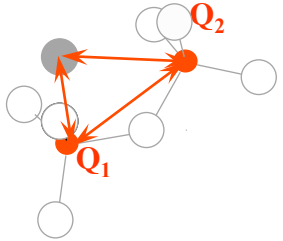
Phosphonate (B.Bujoli – Nantes)

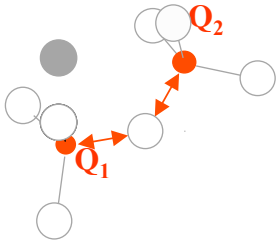


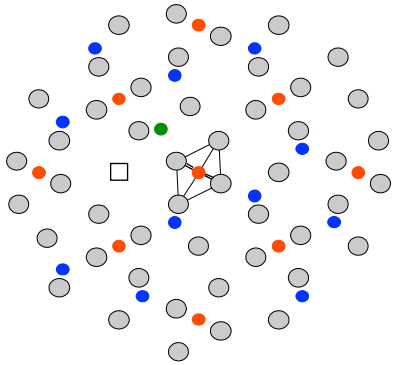
CSA



Dipolaire







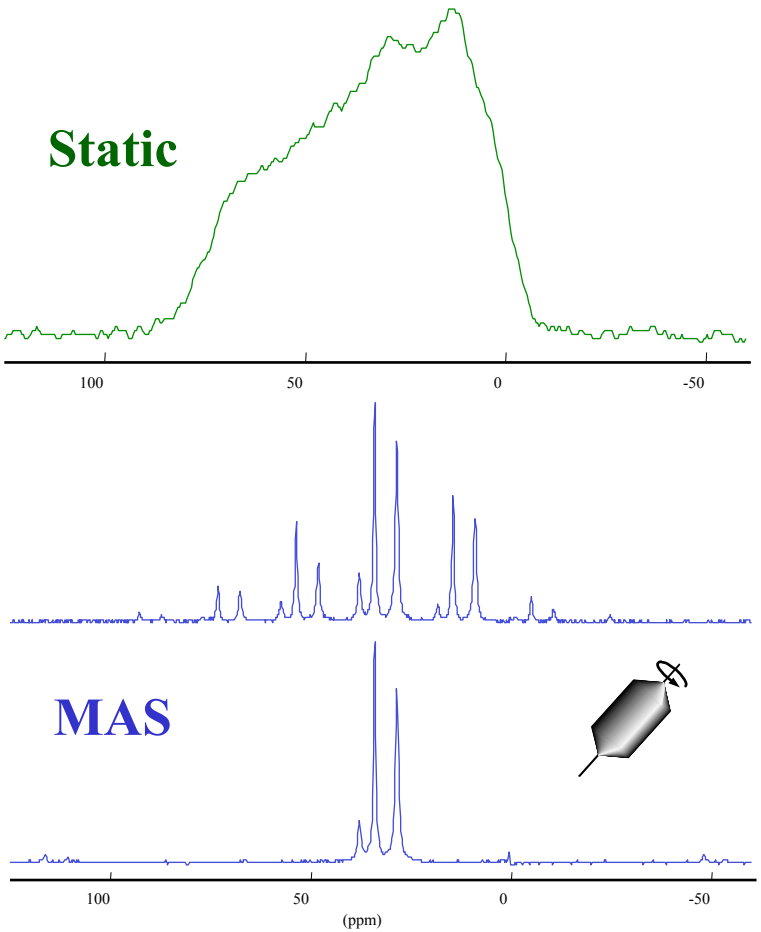
J Coupling

Quadrupolaire

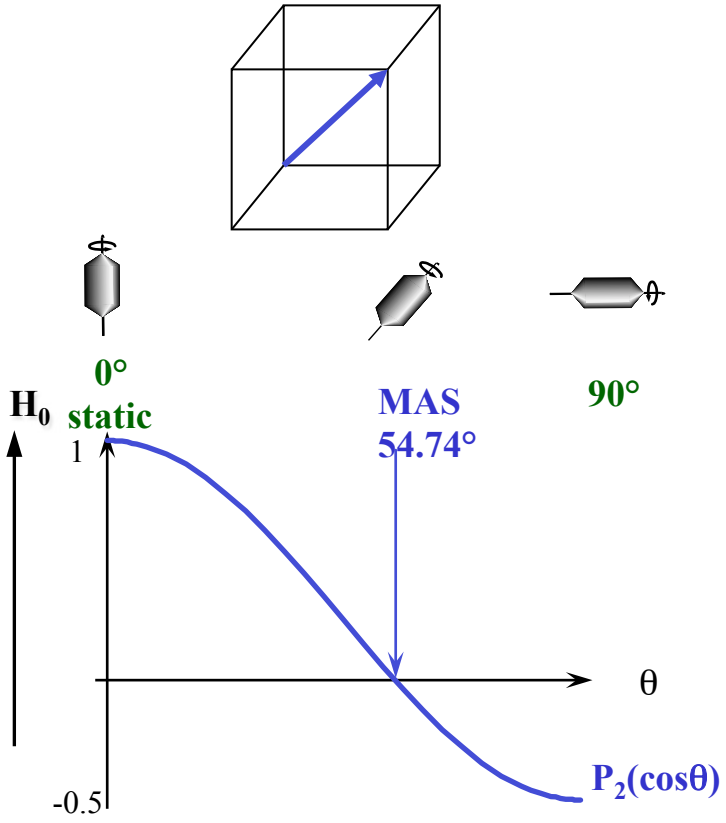
Spectre large :
toutes les interactions anisotropes

Rotation à l'angle magique

^{31}P Spin 1/2 CSA



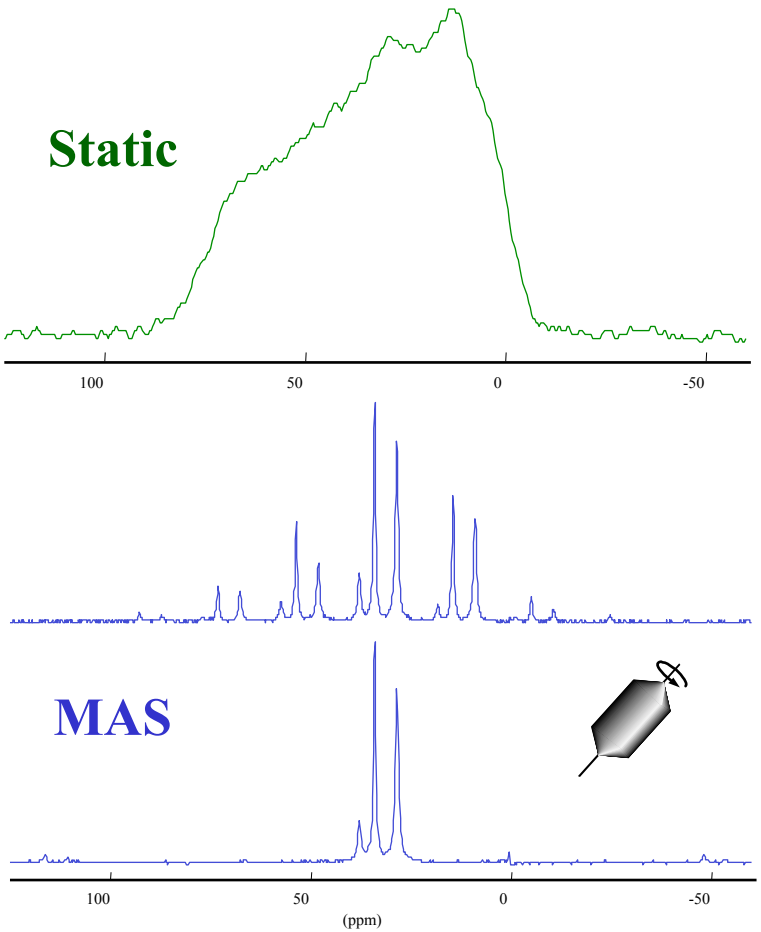
Modulation into sharp lines



Dipolar
Chem. Shift
Quad 1st and 2nd

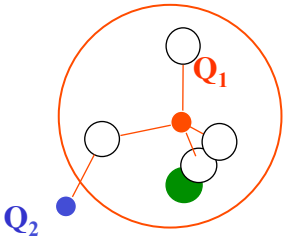
MAS : Rotation à l'angle magique

^{31}P Spin 1/2 CSA

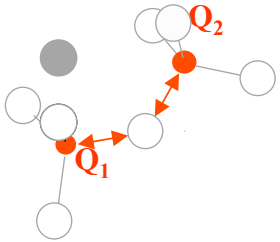


Modulation into sharp lines

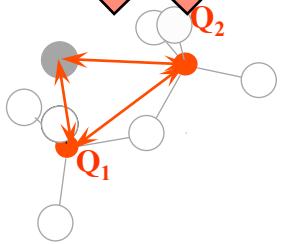
CSA

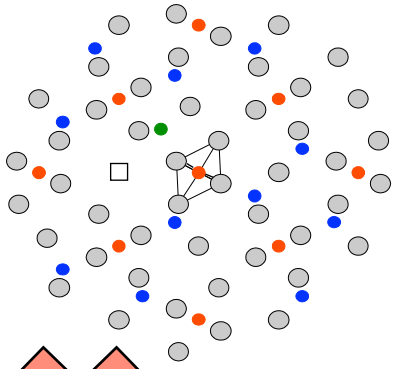


J Coupling



Dipolaire





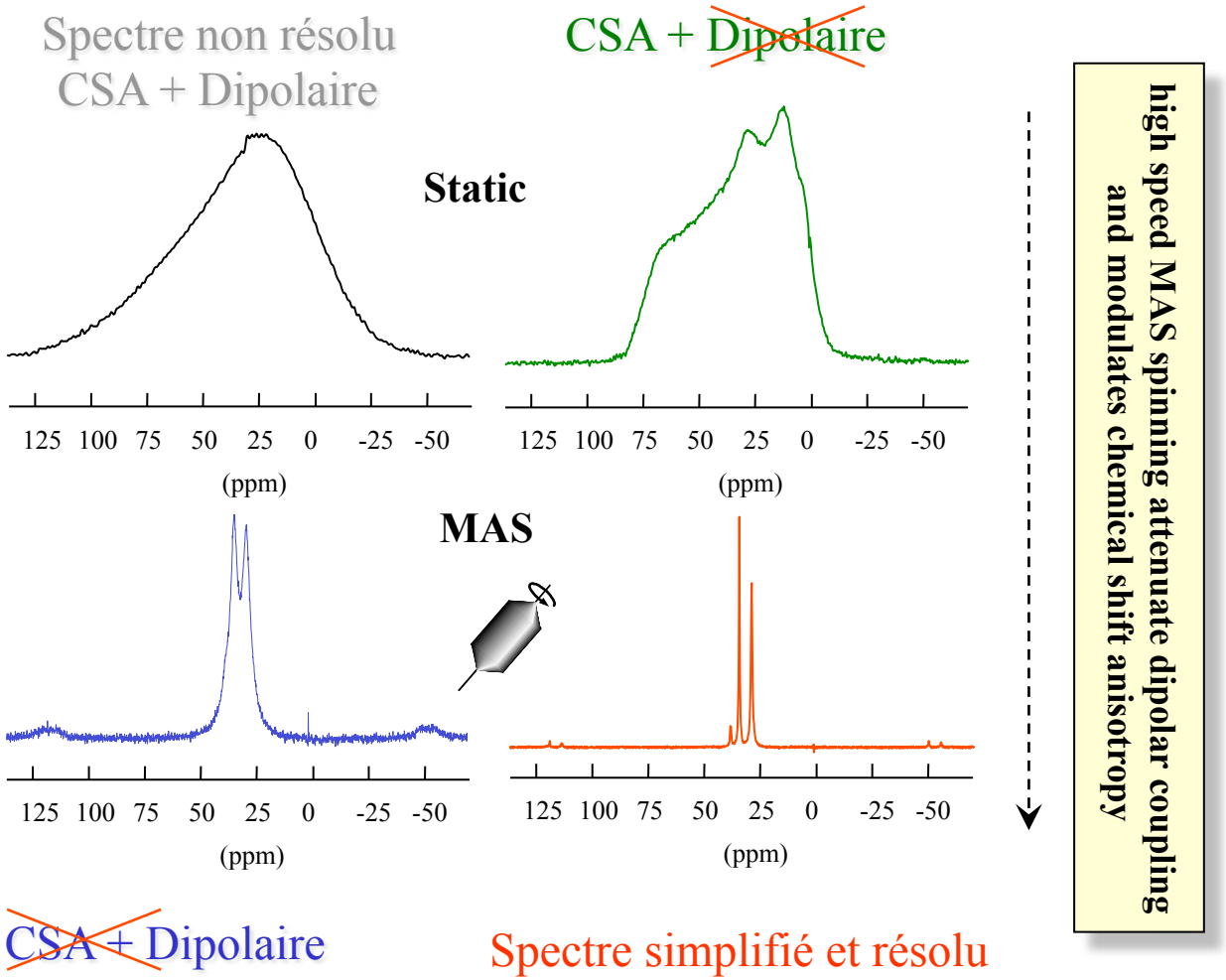
Quadrupolaire

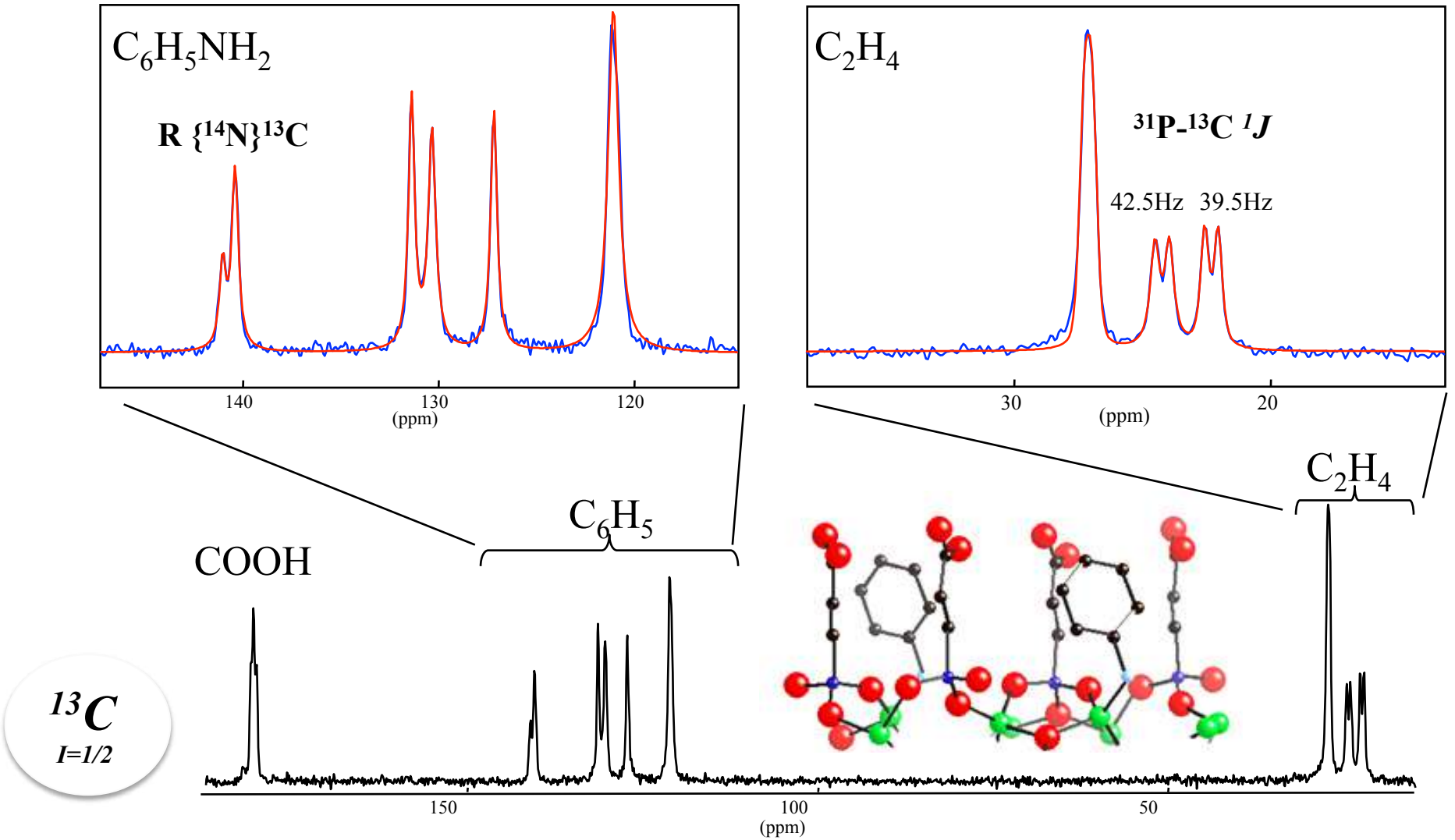
Statique → MAS haute résolution

^{31}P

$$\propto P_2\left[Cos(\theta)\right]$$

Proton decoupling averages strong ^{31}P-^{1}H dipolar interaction



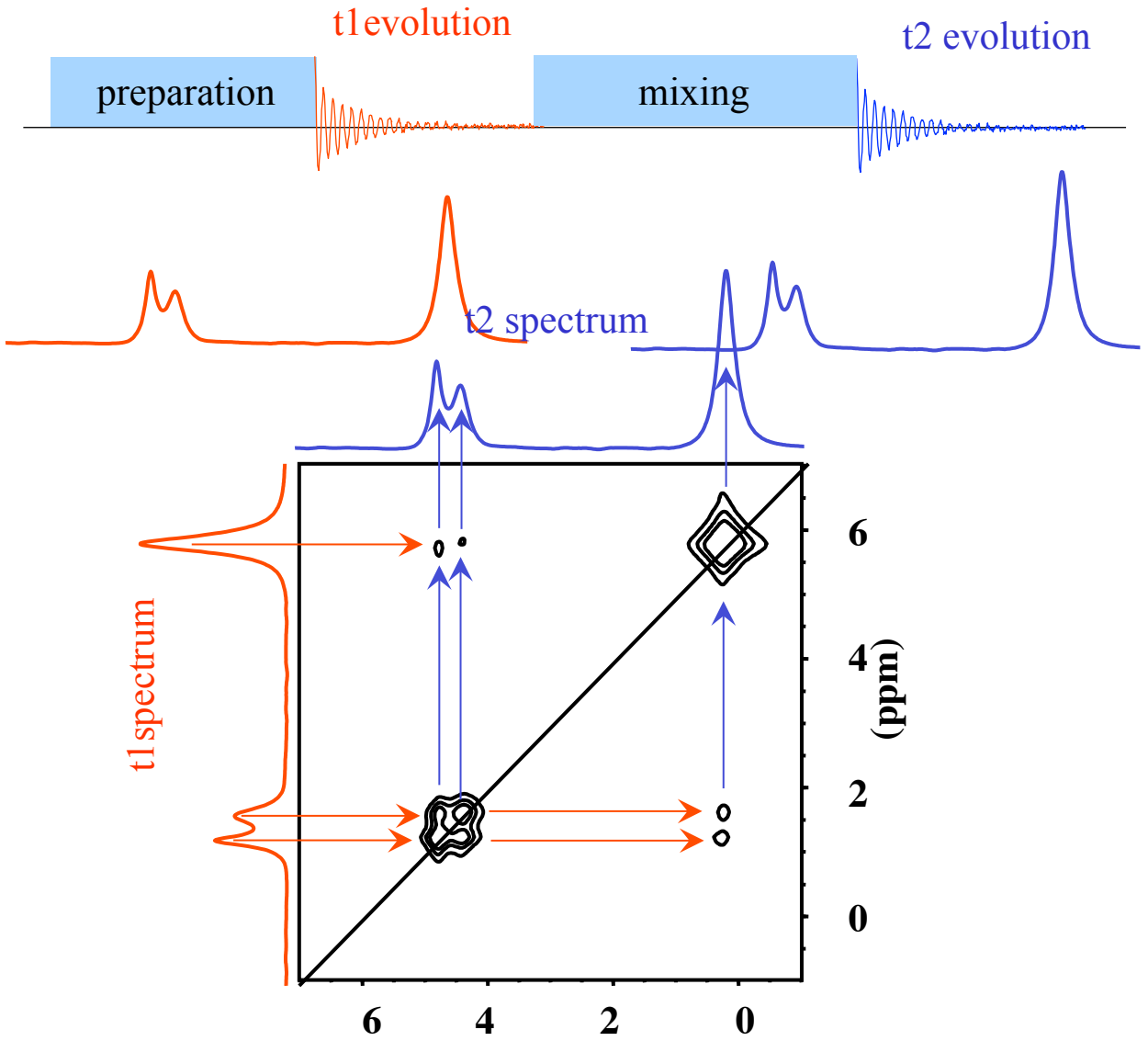


D.Massiot, F.Fayon, M.Deschamps, S.Cadars, P.Florian, V.Montouillout, N.Pellerin, J.Hiet, A.Rakhmatullin, C.Bessada

'Detection and use of small J couplings in solid state NMR experiments.'

Comptes Rendus de Chimie 13 117-129 ***2010***

Principle of a 2D homonuclear experiment

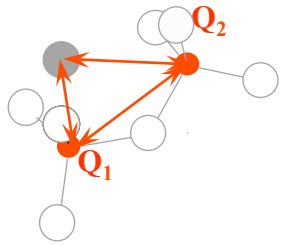


J Couplings in Solid State Materials - Glasses

Dipolar
through space

distances
(0.1 to 1, 10s 100s nm)

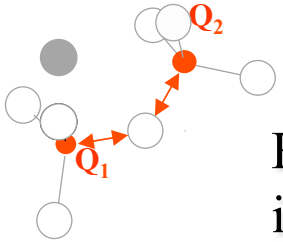
~kHz $1/r^3$



J Coupling
through bond

chemical bonding

<100s of Hz



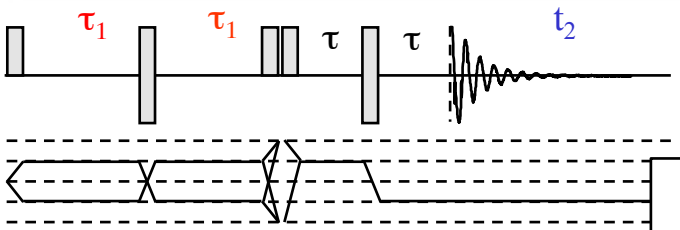
Homo- or Heteronuclear J-coupling isotropic part

➢Remaining Isotropic interactions under fast Magic Angle Spinning

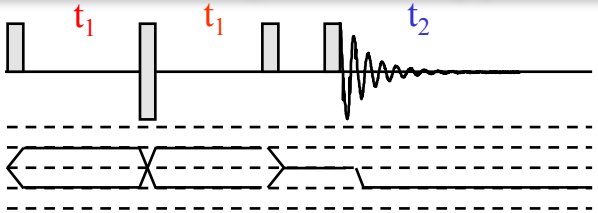
➢Can be used to generate homo- or heteronuclear correlations...

Homonuclear J-Correlation and J-Spectroscopy

refocused INADEQUATE

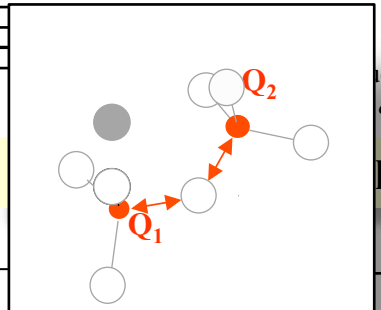


2D J-Spectroscopy

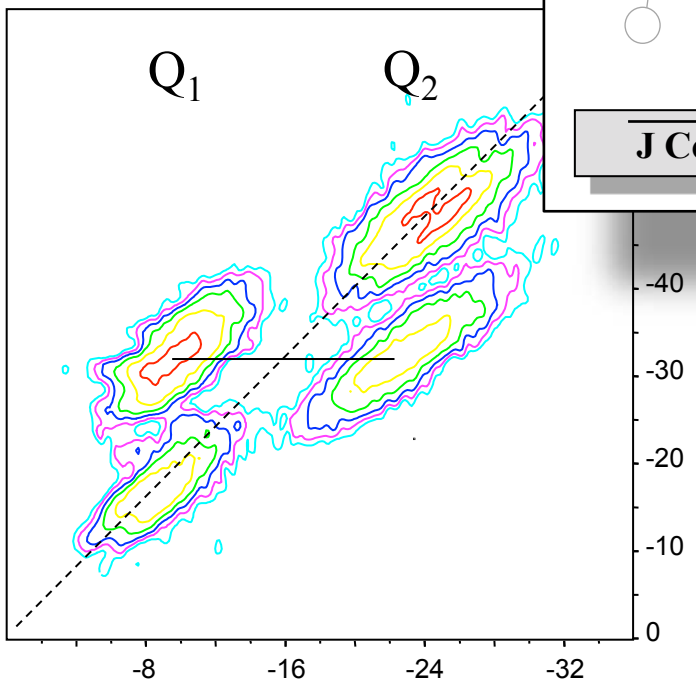


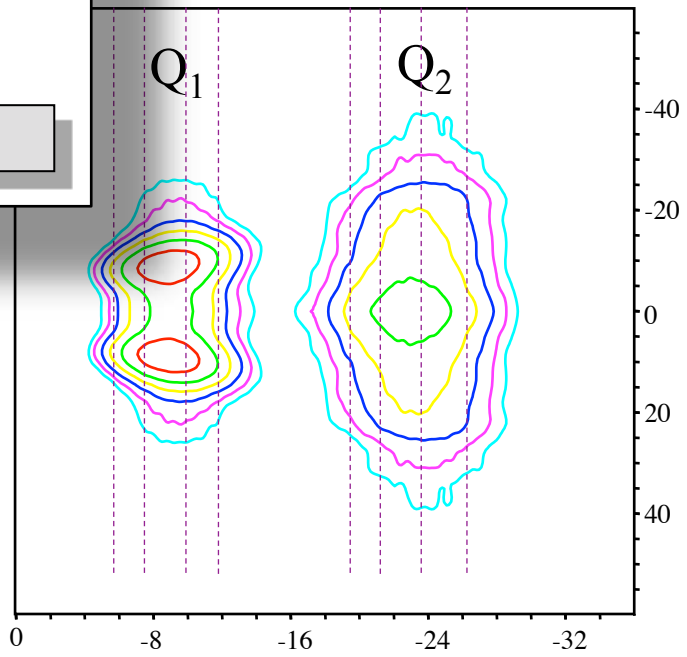
ue, J. Karhan, R.R. Ernst, *J. Chem. Phys.* **64**, 4226 (1976) ;
& Wasylishen; Emsley *et al*...

lass



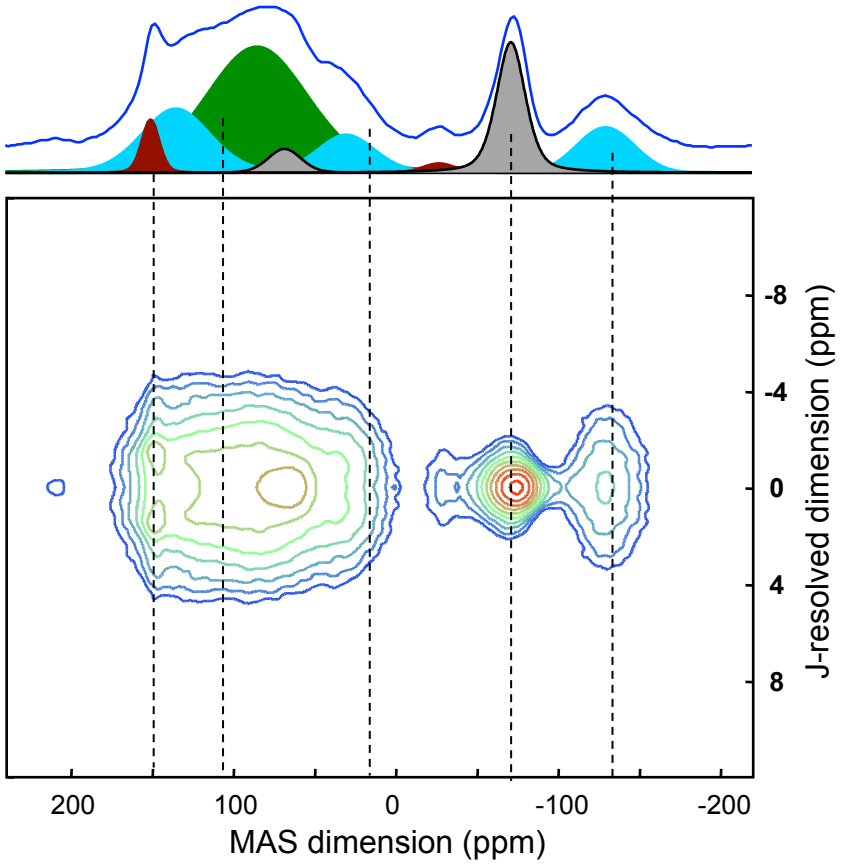
J Coupling



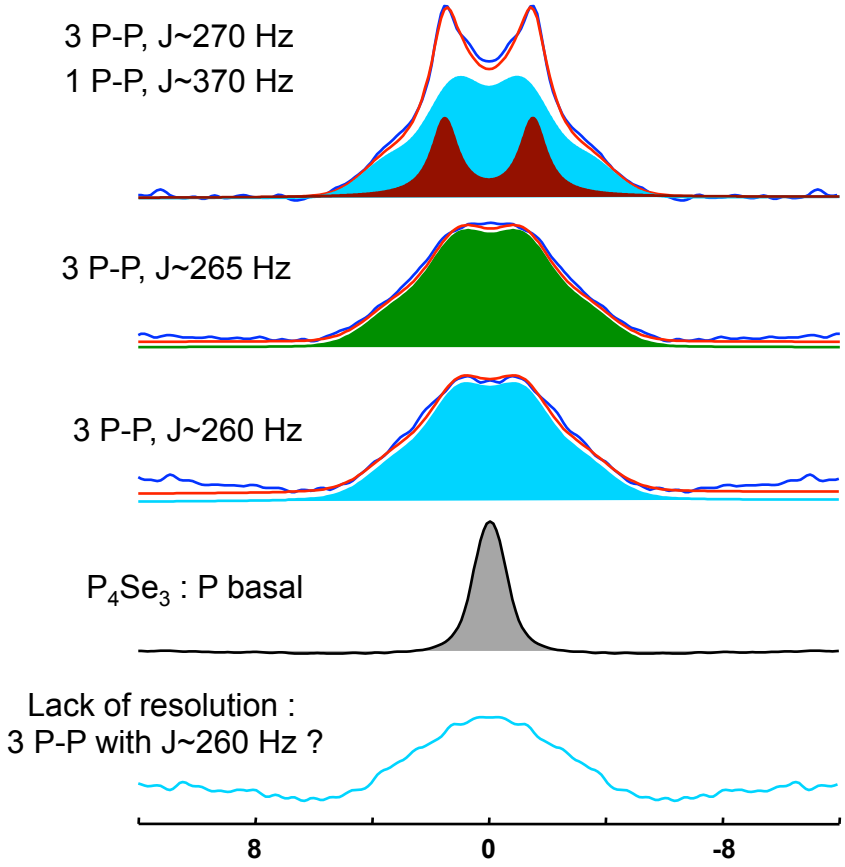


$P_{(1-x)}Se_x$ Glasses – P *rich* x>0.67

P84Se16 glass
2D J-resolved spectrum (MAS 34kHz)



Fit of Cross-sections of 2D J-resolved spectrum



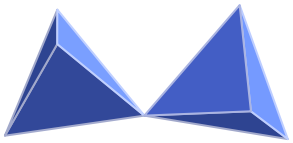
- Narrow peak at ~150 ppm with large ^1J(P-P) ~ 370 Hz : possibly —P=P— ?

La résolution peut venir d'autre chose que du déplacement chimique

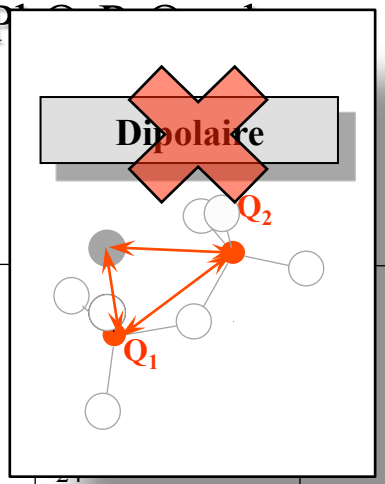
Recoupling Dipolar interaction

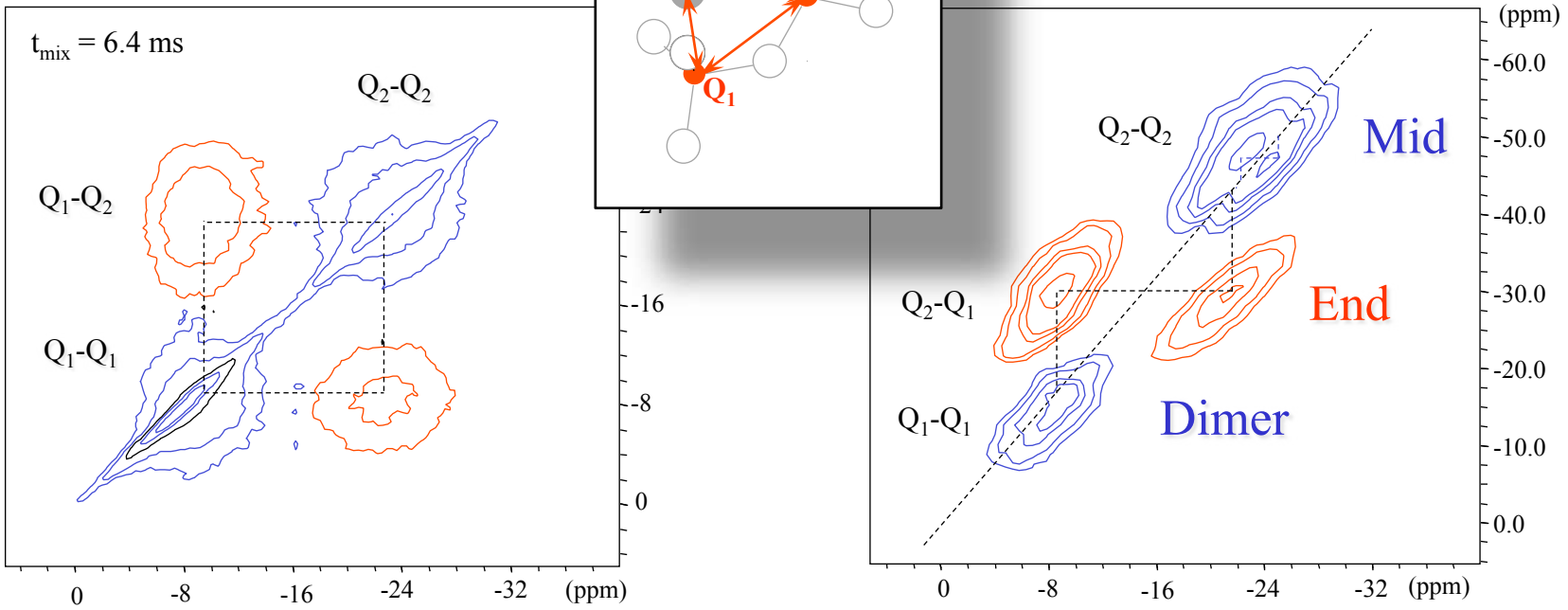
RFDR : Radio Frequency Driven Recoupling

Double Quantum selection



^{31}P NMR



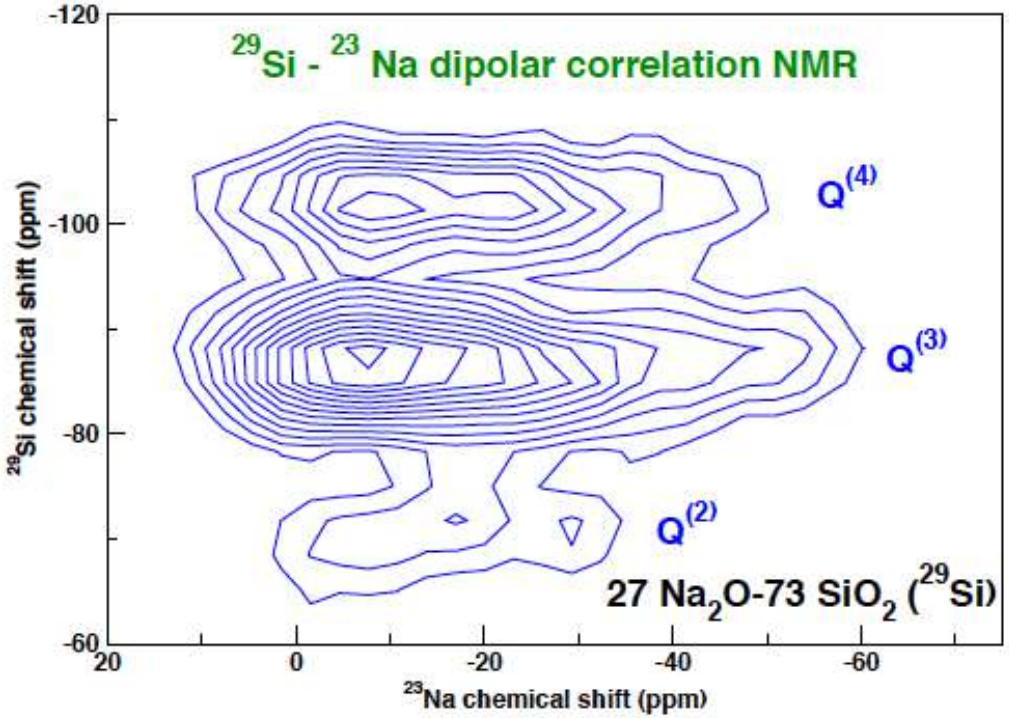


F. Fayon, C. Bessada, J.P. Coutures, D. Massiot, "High Resolution Double Quantum 31P NMR Study of intermediate Range Order in Crystalline and Glass Lead Phosphates.", Inorg. Chem., 38 pp5212-5218 (1999).

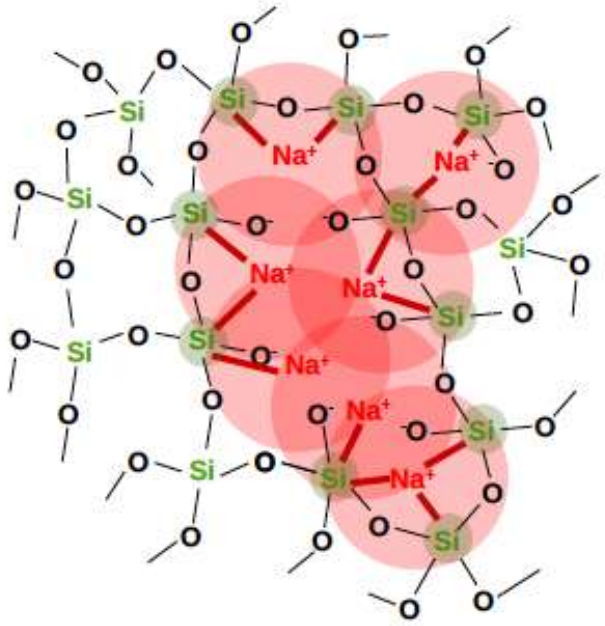
Through-bond correlation

Heteronuclear Multiple Quantum Correlation (HMQC)

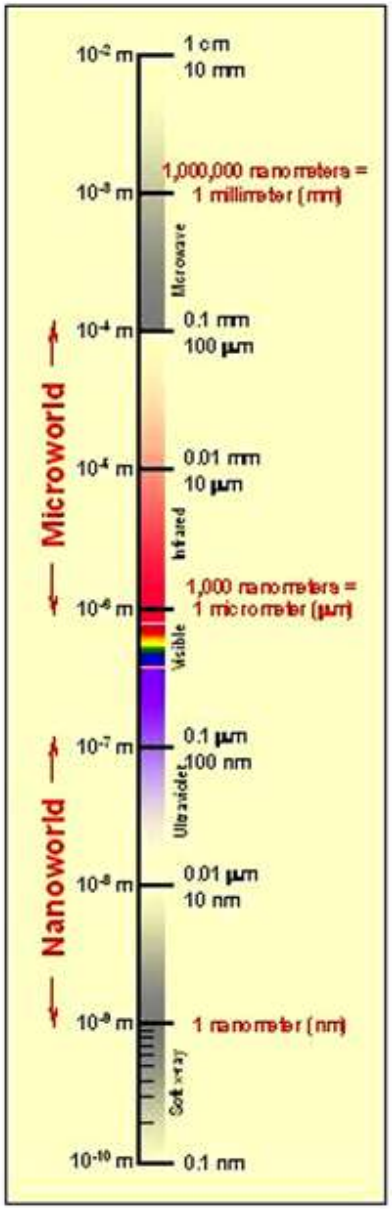
$$\frac{\hbar^2}{2}\sum_i\sum_{j\neq i}\gamma_i\gamma_j\vec{I}_i\left(\mathbf{D}_{ij}+\mathbf{J}_{ij}\right)\vec{I}_j$$



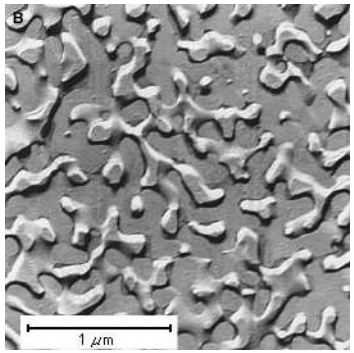
NMR of neighboring nuclear spins (Si-O$^-$ Na$^+$)

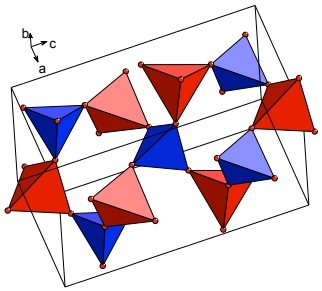


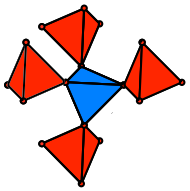
Glass structure at different scales

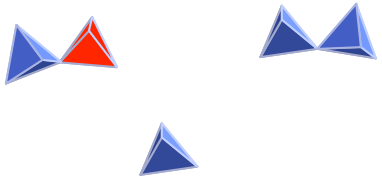


Homogeneous
Isotropic
Disordered

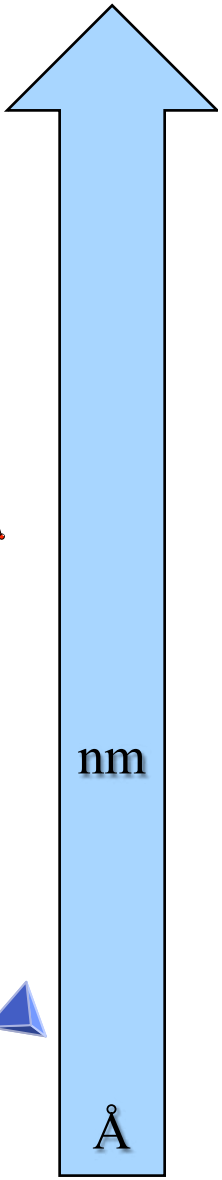




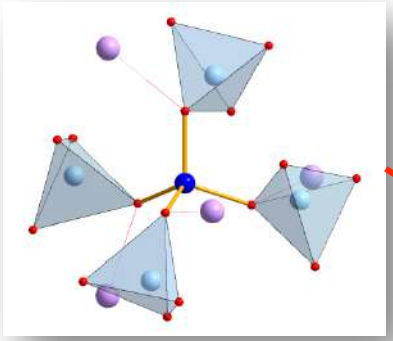




Heterogeneous
Anisotropic
Partly Ordered

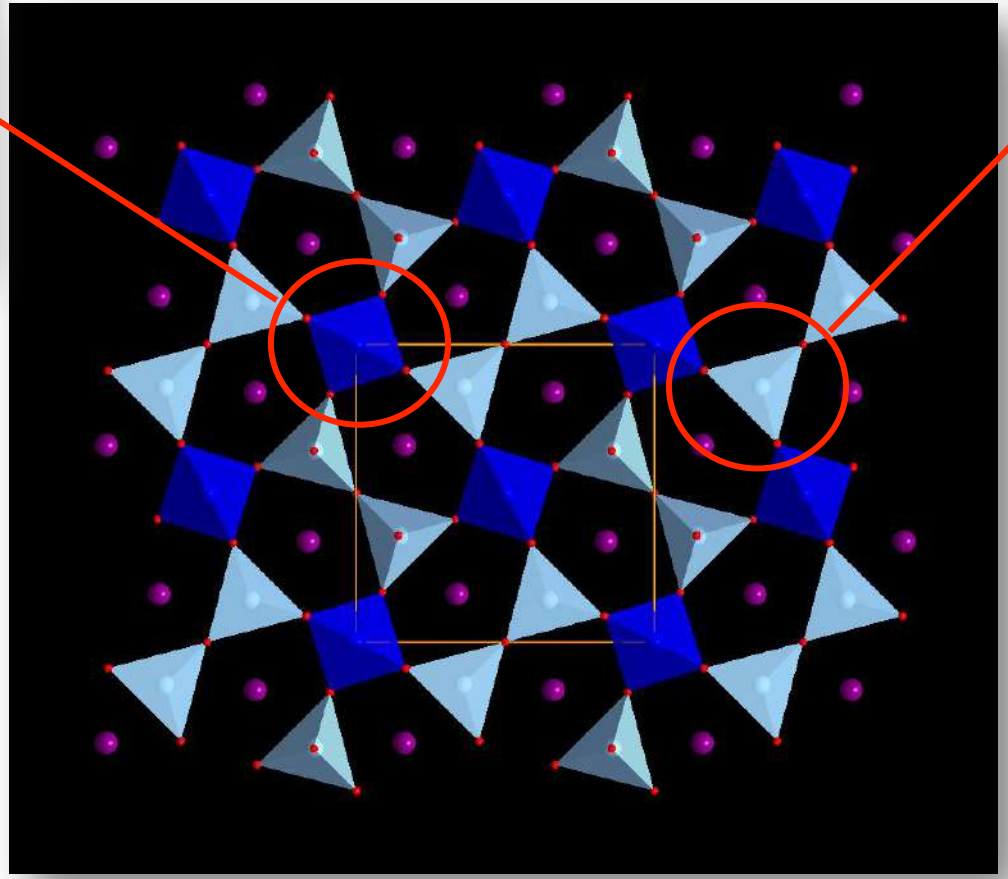


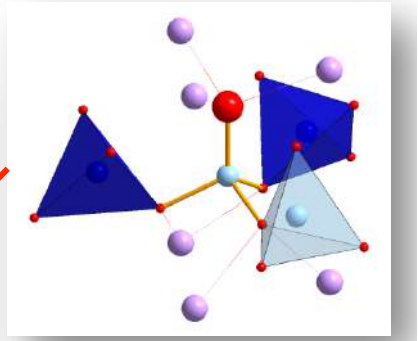
Chemical Disorder in a Structural Order



T_1 :Al only
5 configurations

$Al\text{-}Al_4$
$Al\text{-}SiAl_3$
$Al\text{-}Si_2Al_2$
$Al\text{-}Si_3Al$
$Al\text{-}Si_4$





T_2 : $(Al_{0.5},Si_{0.5})$
2 configurations

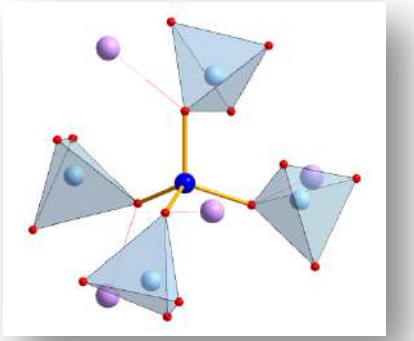
$Al\text{-}SiAl_2$ $Si\text{-}SiAl_2$
$Al\text{-}Al_3$ $Si\text{-}Al_3$

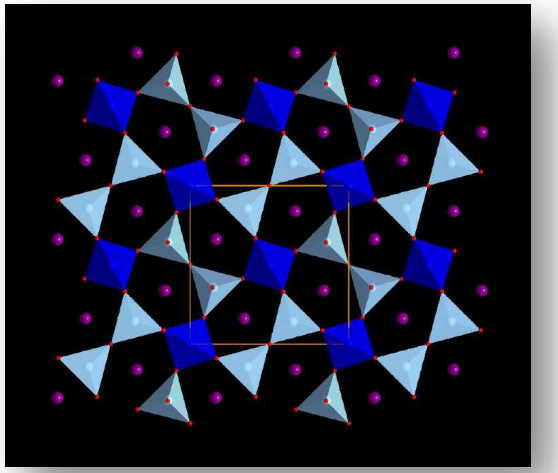
Gehlenite $Ca_2Al_2SiO_7$

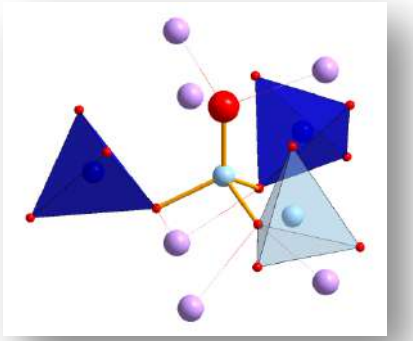
P.Florian, E.Veron, T.F.G.Green, J.R.Yates, D.Massiot Chem. Mater. 24 4068–4079 **2012**

Chemical Disorder in a Structural Order

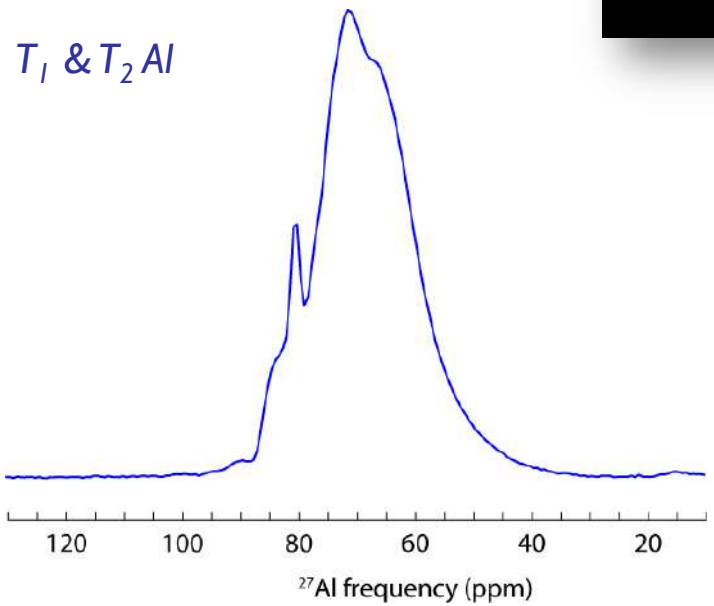
Gehlenite $Ca_2Al_2SiO_7$



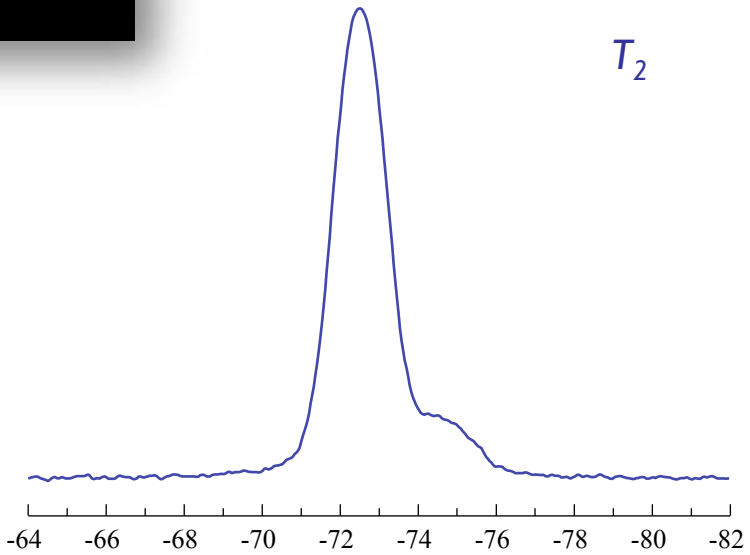




^{27}Al MAS @ 17.6T



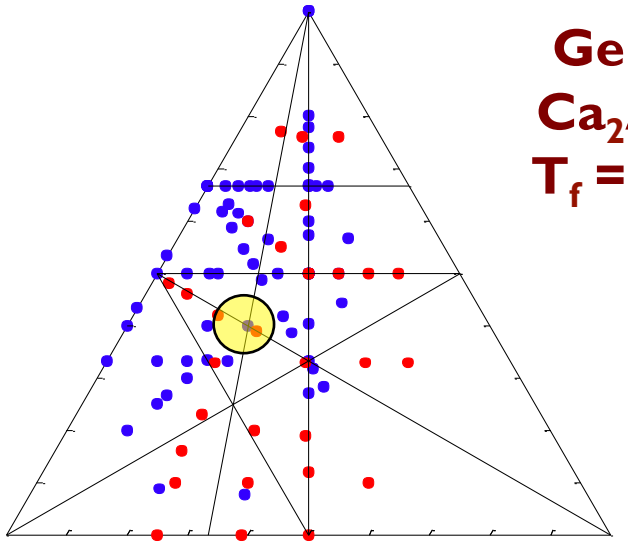
^{29}Si MAS



CHEMISTRY OF MATERIALS

P.Florian, E.Veron, T.F.G.Green, J.R.Yates, D.Massiot Chem. Mater. 24 4068–4079 **2012**

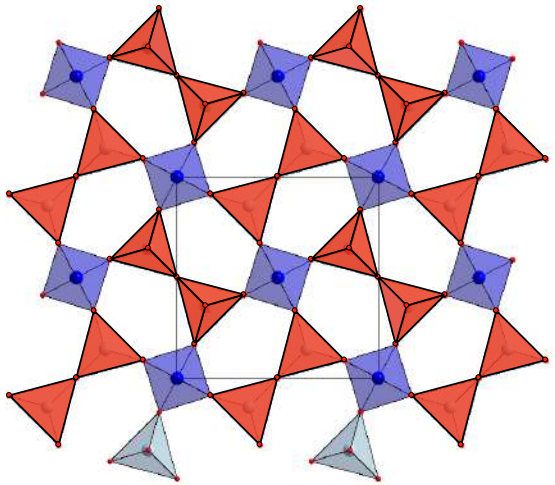
Local Order in Gehlenite from ^{29}Si



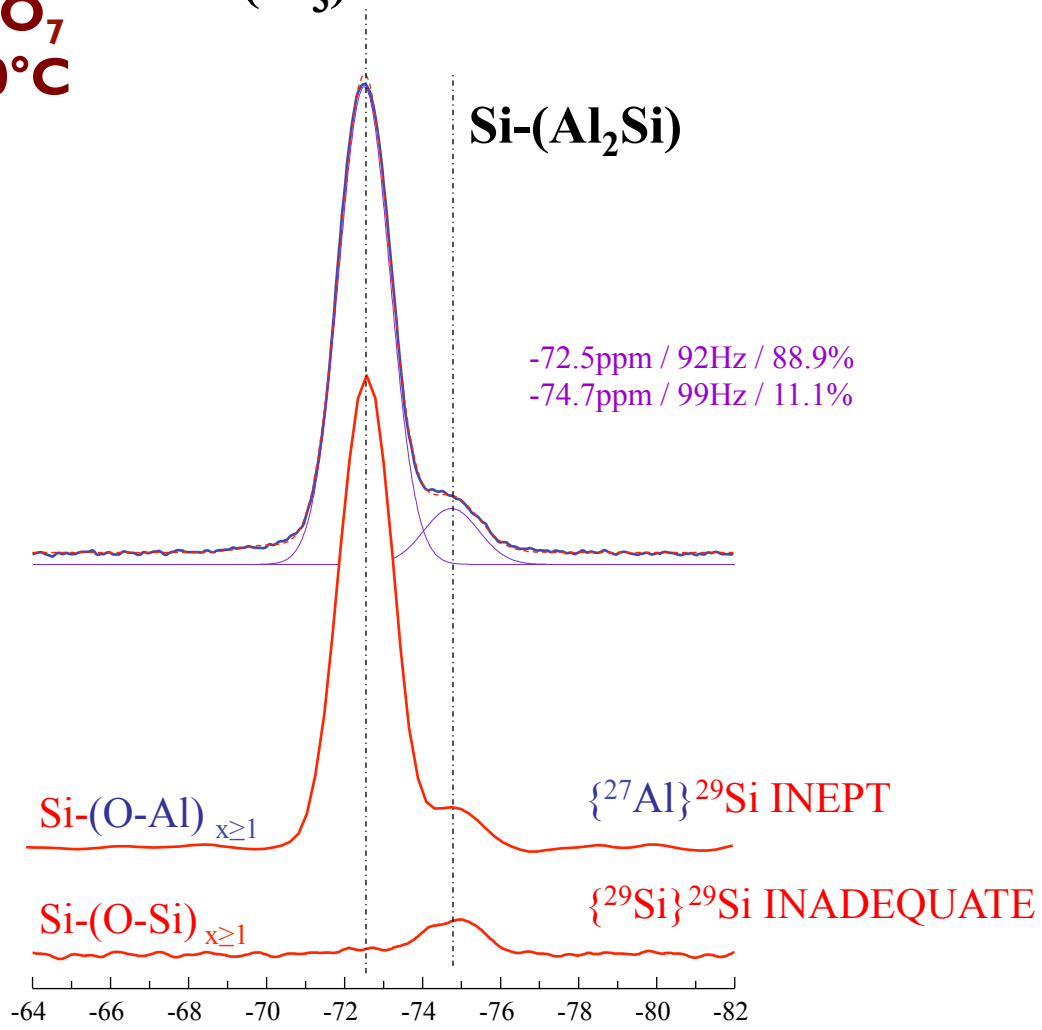
Gehlenite
$Ca_2Al_2SiO_7$
T_f = 1590°C

T1
100% Al

T2
Si 50% /Al 50%



$p(AlOAl) = p(SiOSi) = 0.11$



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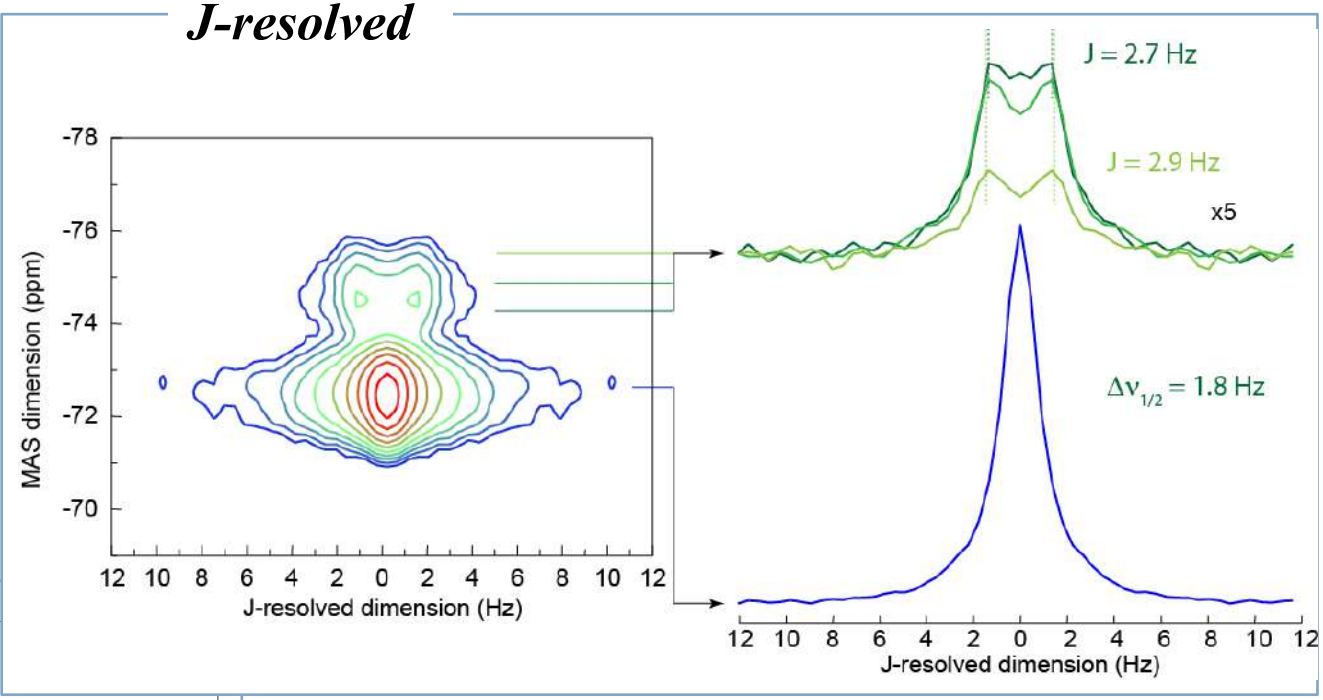
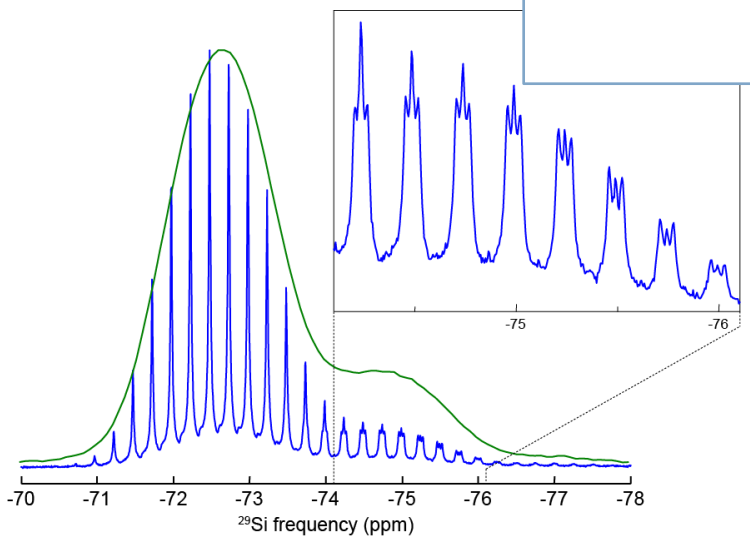
P.Florian, E.Veron, T.F.G.Green, J.R.Yates, D.Massiot Chem. Mater. 24 4068–4079 **2012**

The Si Point of view: ^2J(Si,Si) Si-O-Si

J-resolved



CPMG



Average *J*: 2.8 Hz ± 0.2 Hz
Wollastonite: Ω ~ 3.41 *J* + 127

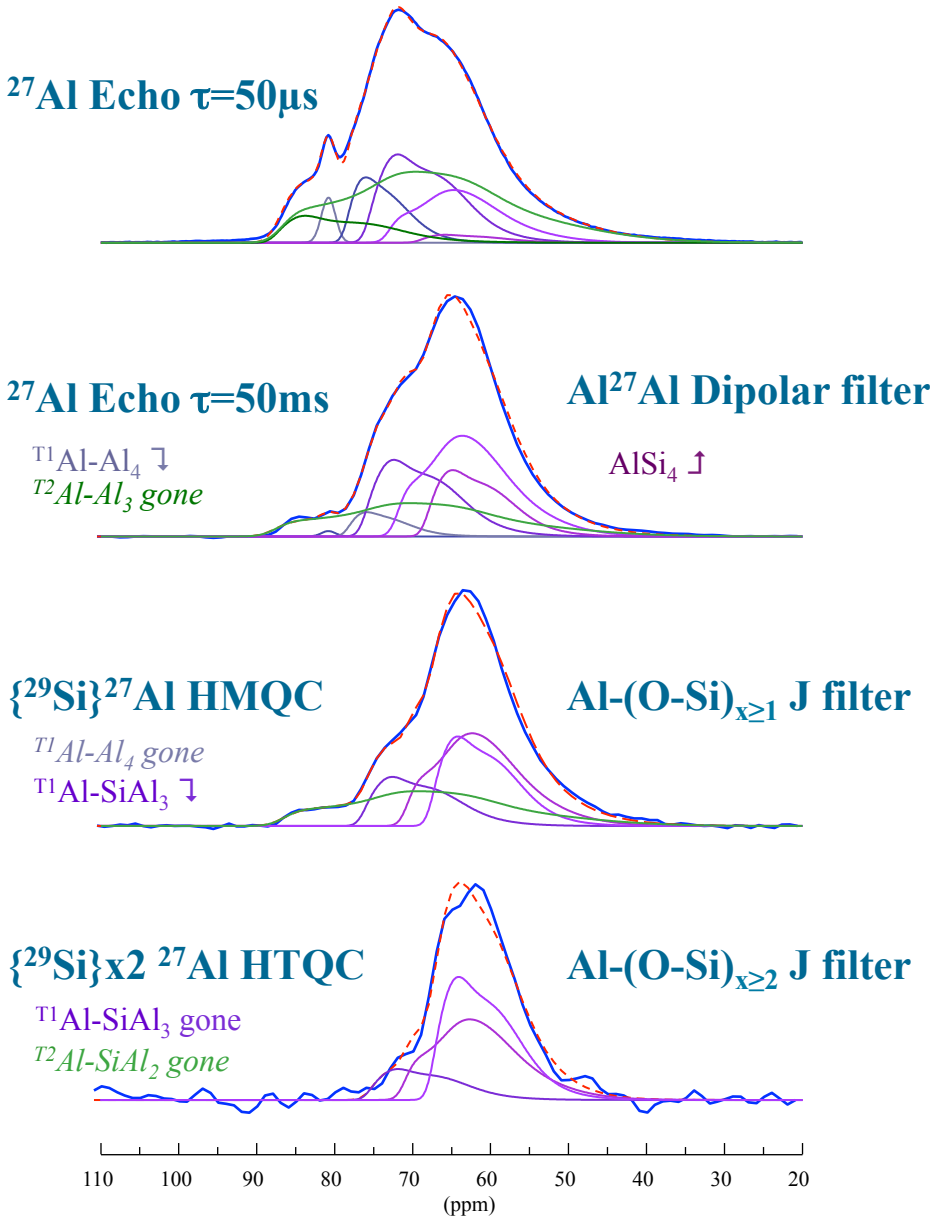
- Ω mean: ~136.5° (from ~135.7° to ~137.2°)
- Random model: Ω = 135.3° ± 1.74°

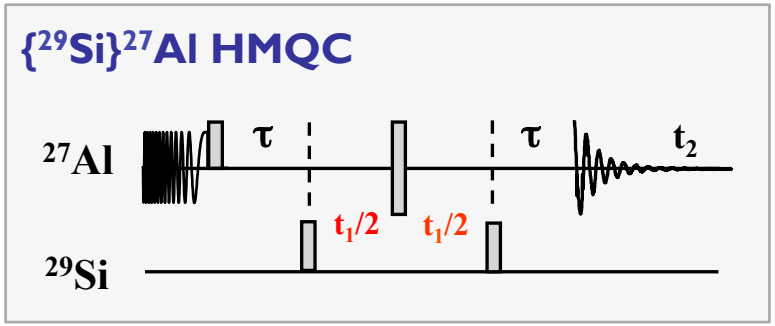
P.Florian, F.Fayon, D.Massiot
"*2J Si-O-Si scalar spin-spin coupling in the solid-state: the case of crystalline and glassy wollastonite CaSiO3*"
J. Phys. Chem. C 113 2562-2572 ***2009***

CHEMISTRY OF MATERIALS

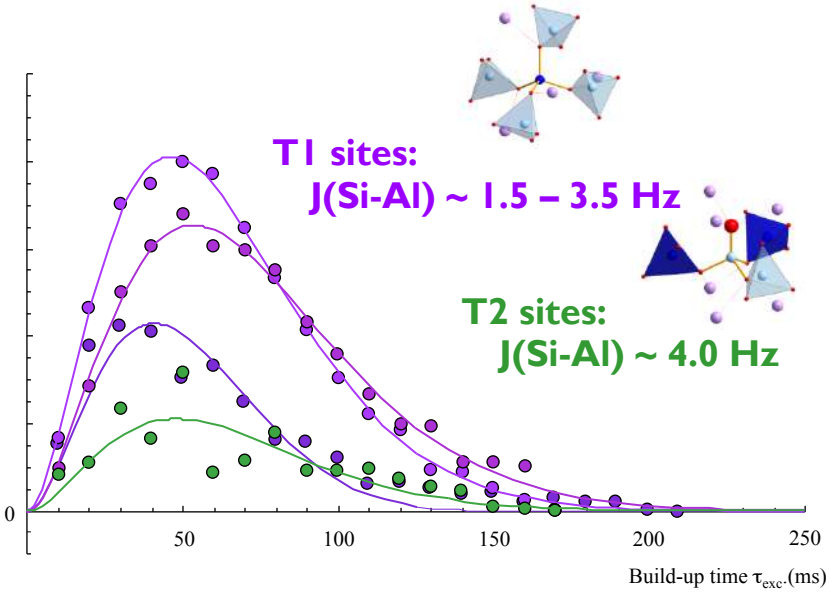
P.Florian, E.Veron, T.F.G.Green, J.R.Yates, D.Massiot Chem. Mater. 24 4068–4079 **2012**

Al spectra: how to decipher?





{^{29}Si}^{27}Al INEPT build-up
→ Bond angles from DFT

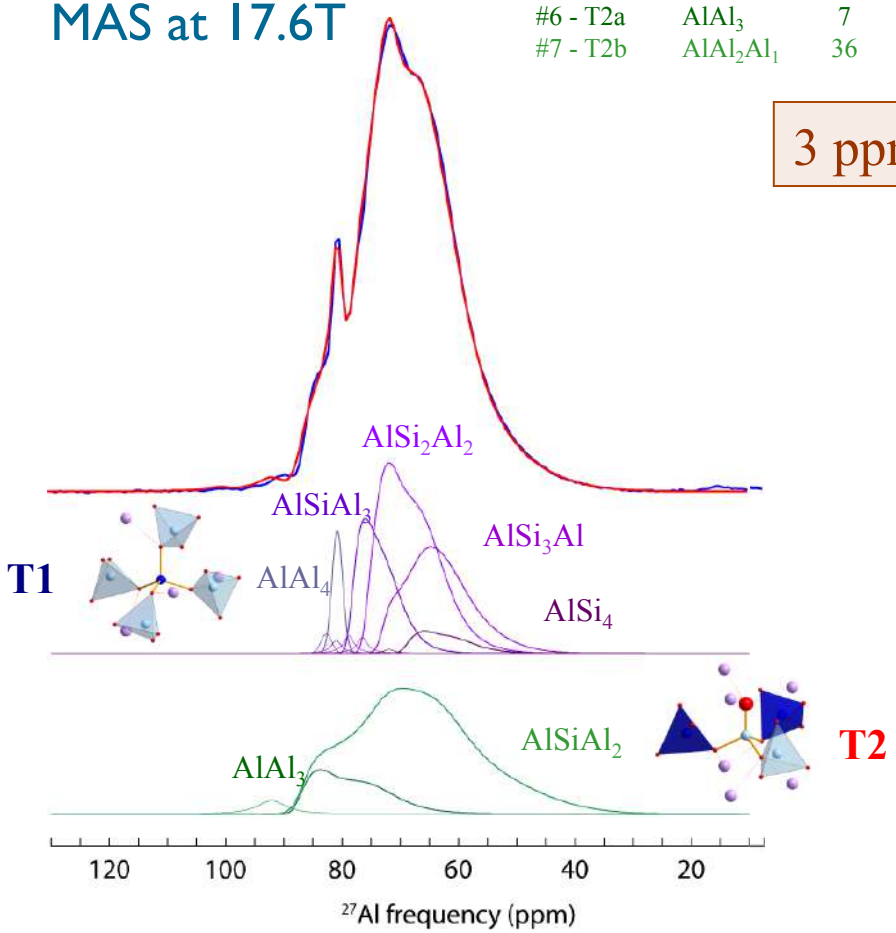


CHEMISTRY OF MATERIALS
P.Florian, E.Veron, T.F.G.Green, J.R.Yates, D.Massiot Chem. Mater. 24 4068–4079 **2012**

The ^{27}Al point of view

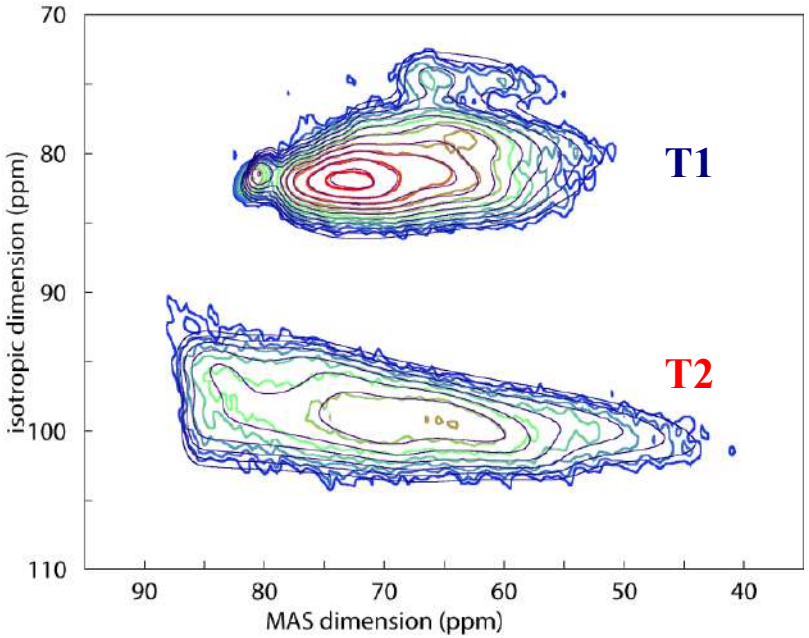
		%	δ_{iso}(ppm)	$\Delta\delta_{iso}$	C_Q(MHz)	ΔC_Q	η_Q	T_2 (ms)
#1 - T1a	$AlAl_4$	3	82.5	n/a	1.75	n/a	n/a	9 (±1)
#2 - T1b	$AlAl_3Si_1$	11	79.2	*1.50*	5.82	*2.00*	*0.3*	21 (±1)
#3 - T1c	$AlAl_2Si_2$	24	76.7	*1.50*	7.27	*2.00*	*0.3*	28 (±1)
#4 - T1d	$AlAl_2Si_3$	16	73.4	*1.50*	7.59	*2.00*	*0.6*	47 (±2)
#5 - T1e	$AlSi_4$	3	70.2	*1.50*	6.89	*2.00*	*0.3*	86 (±12)
#6 - T2a	$AlAl_3$	7	89.4	1.48	8.31	2.20	0.24	12 (±2)
#7 - T2b	$AlAl_2Al_1$	36	87.7	1.49	10.7	1.84	0.61	38 (±2)

^{27}Al quantitative MAS at 17.6T



3 ppm shift per Si/Al substitution in T1 sites

^{27}Al MQMAS at 17T



CHEMISTRY OF MATERIALS

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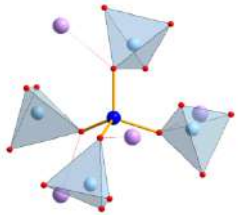
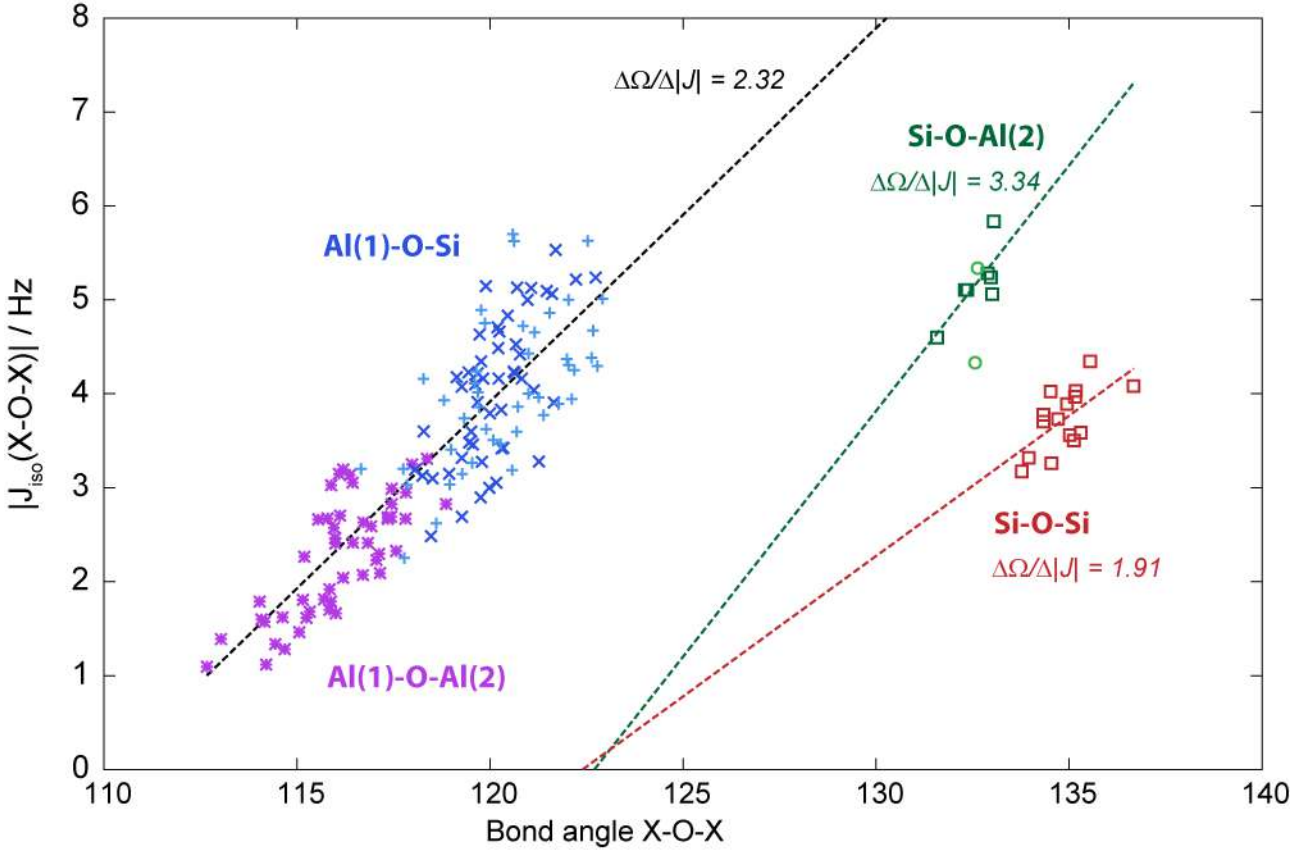
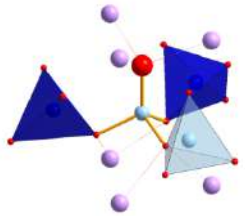
GIPAW: (Si,Al)-O-(Si,Al) *J* scalar coupling

Coll. J.Yates, Tim Green – Oxford UK



T_1 : Al-$Si_nAl_{(4-n)}$

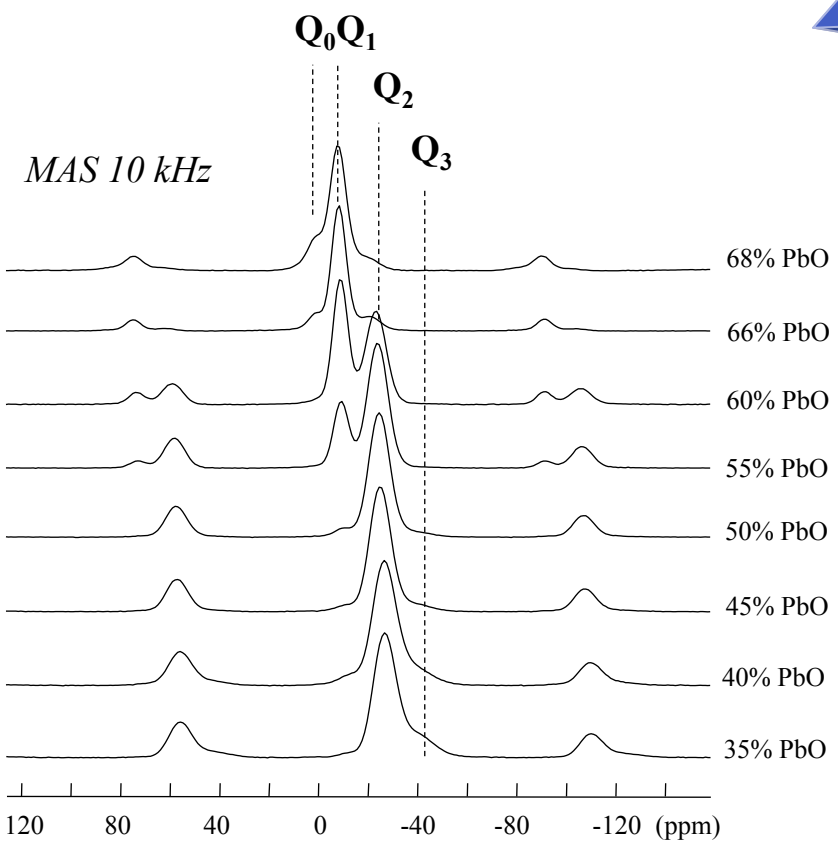




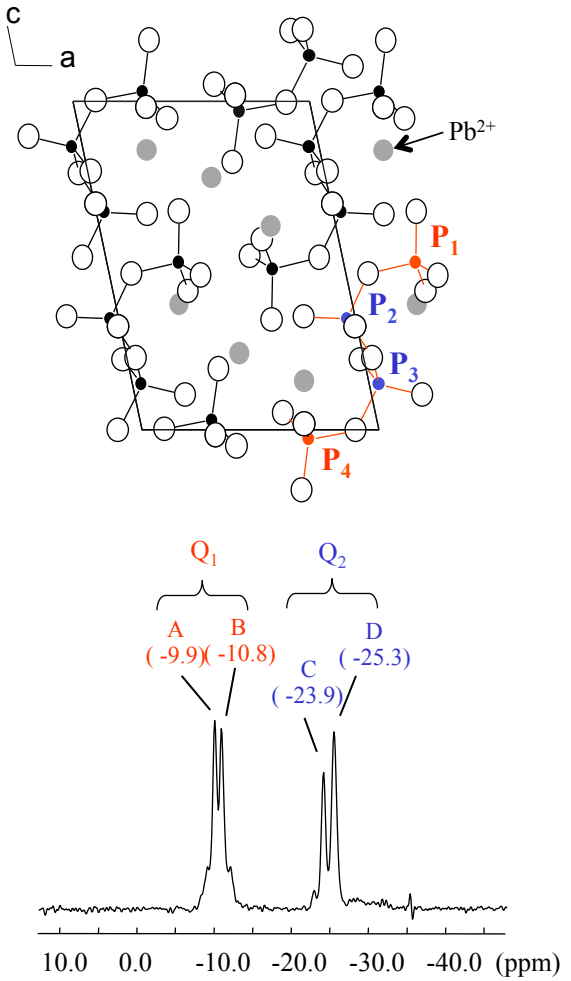
T_2 : ($Al_{0.5}$,$Si_{0.5}$)

- Experimental *J*(Al-Si): T1 ~ 1.5 – 3.5 Hz, T2 ~ 4.0 Hz
- Experimental *J*(Si-Si) ~ 2.8 Hz ± 0.2 Hz
- *J* is (again) correlated to the bond-angle
- No obvious differences between *J*(^{27}Al) or *J*(^{29}Si)
- Slope close to the one obtained on clusters (3.41 for 130°-170° range)

^{31}P Solid State NMR of Crystals & Glasses

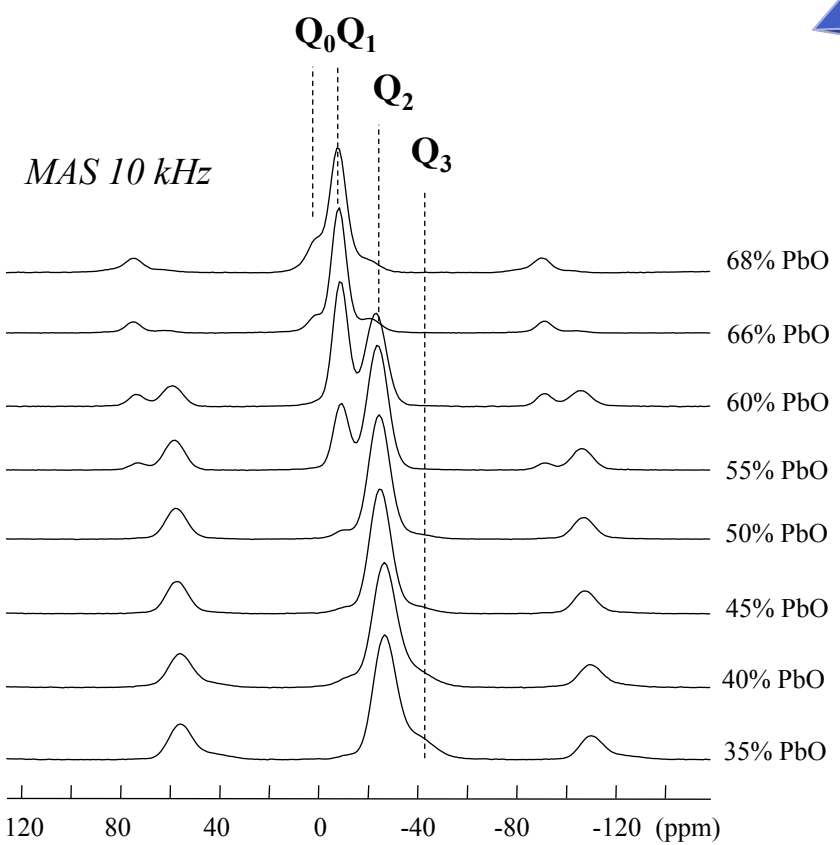


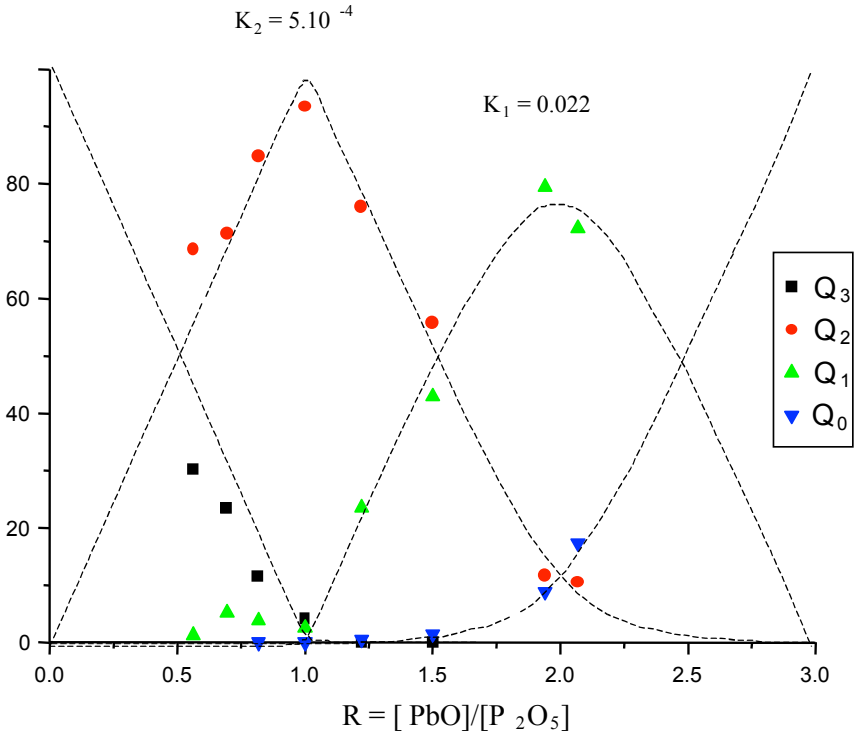
^{31}P MAS Glasses



^{31}P MAS NMR of $Pb_3P_4O_{13}$

NMR ^{31}P MAS istrope ou Statique Anisotrope





^{31}P MAS Glasses

Dissociation equilibrium

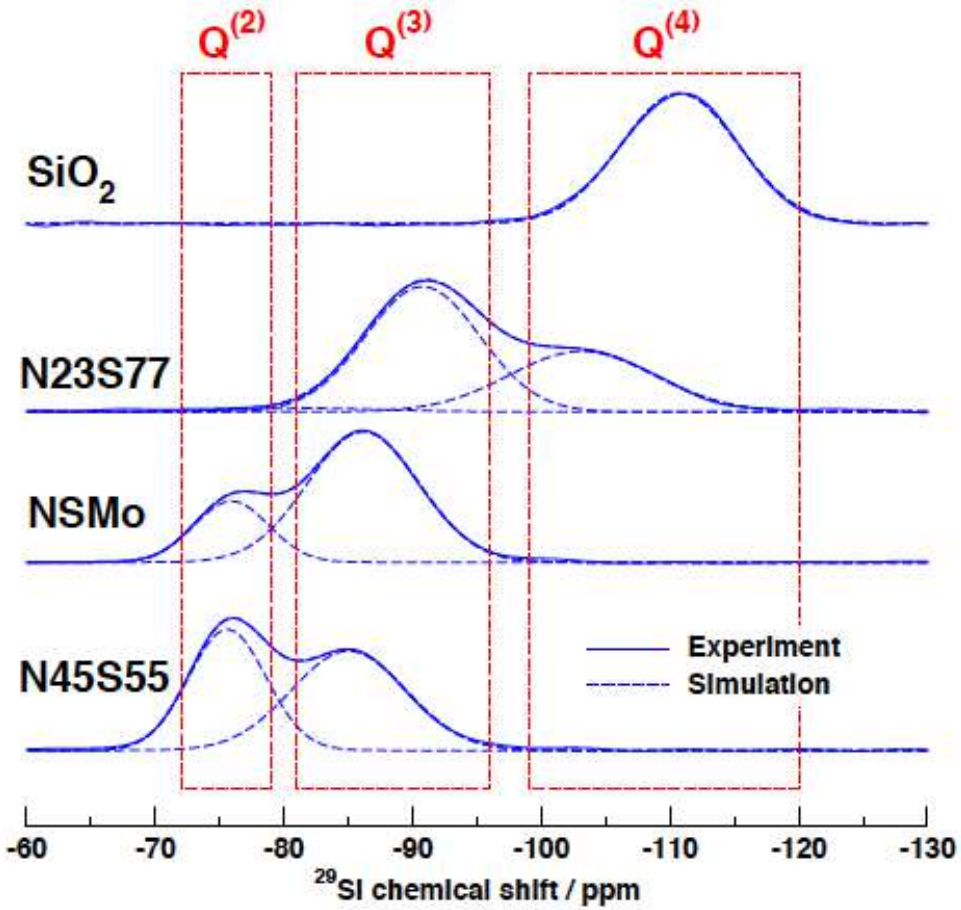
$2Q_n <-> Q_{n-1} + Q_{n+1}$

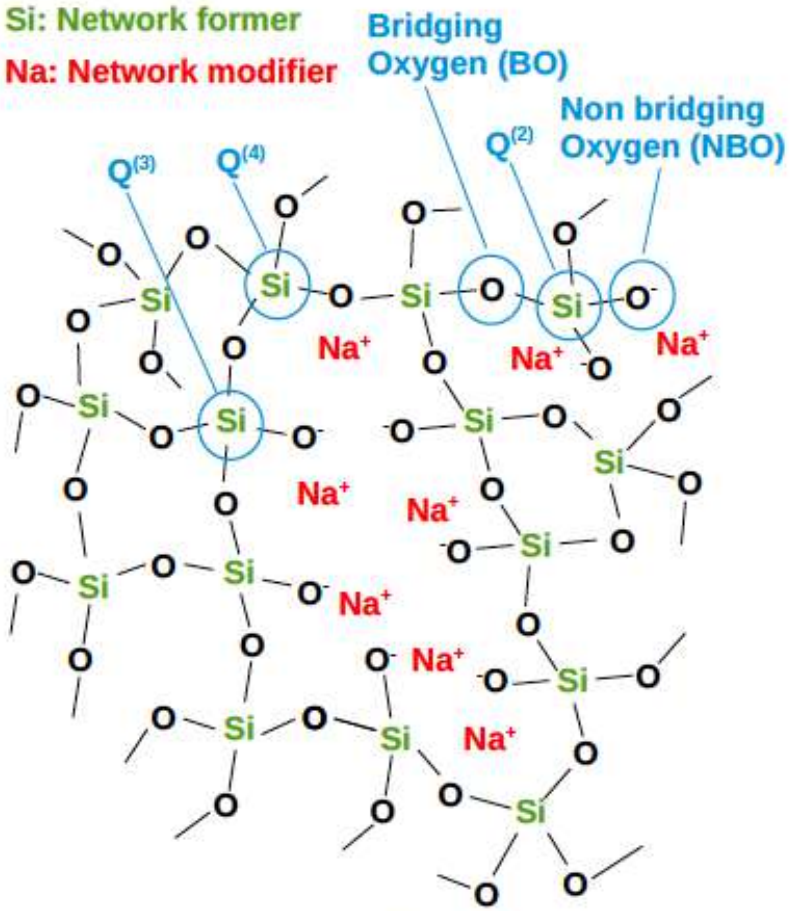
Fayon et al.

^{29}Si MAS NMR

$Q^{(n)}$: $Si(OSi)_n(O^-)_{(4-n)}$

^{29}Si MAS NMR:
Direct access to silicon $Q^{(n)}$ speciation



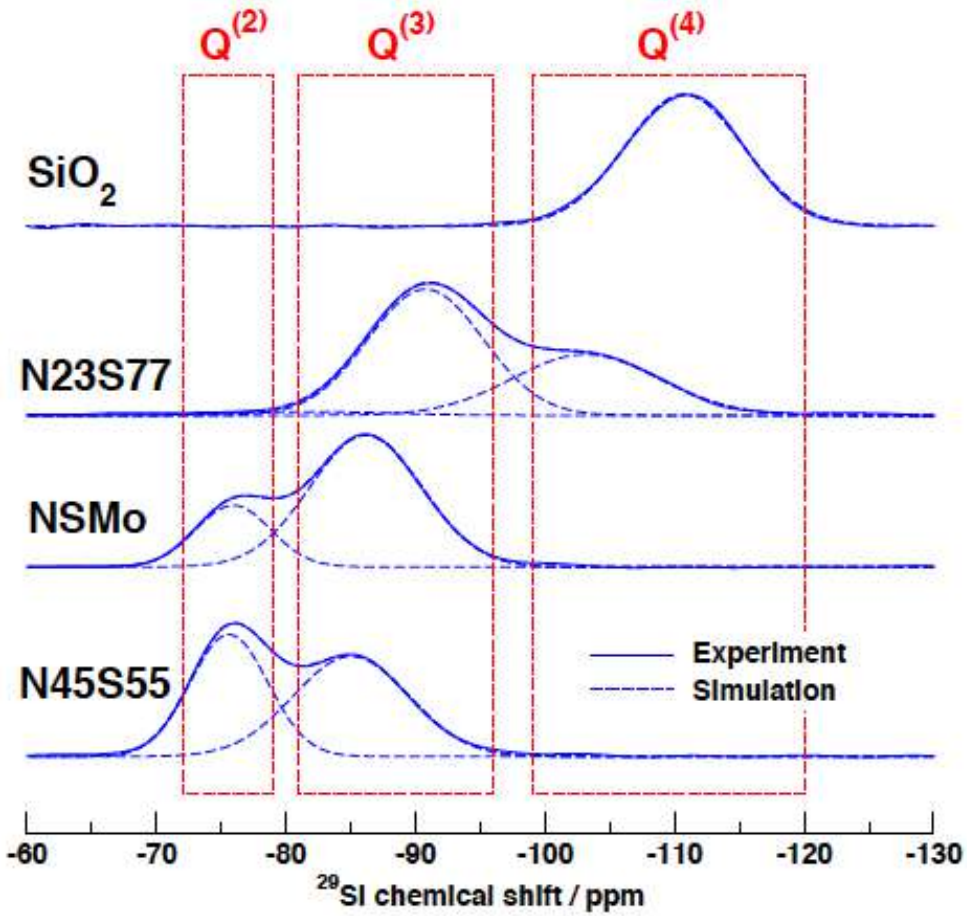


NMR peaks reflective of a Gaussian distribution of δ_{iso} (I=1/2)

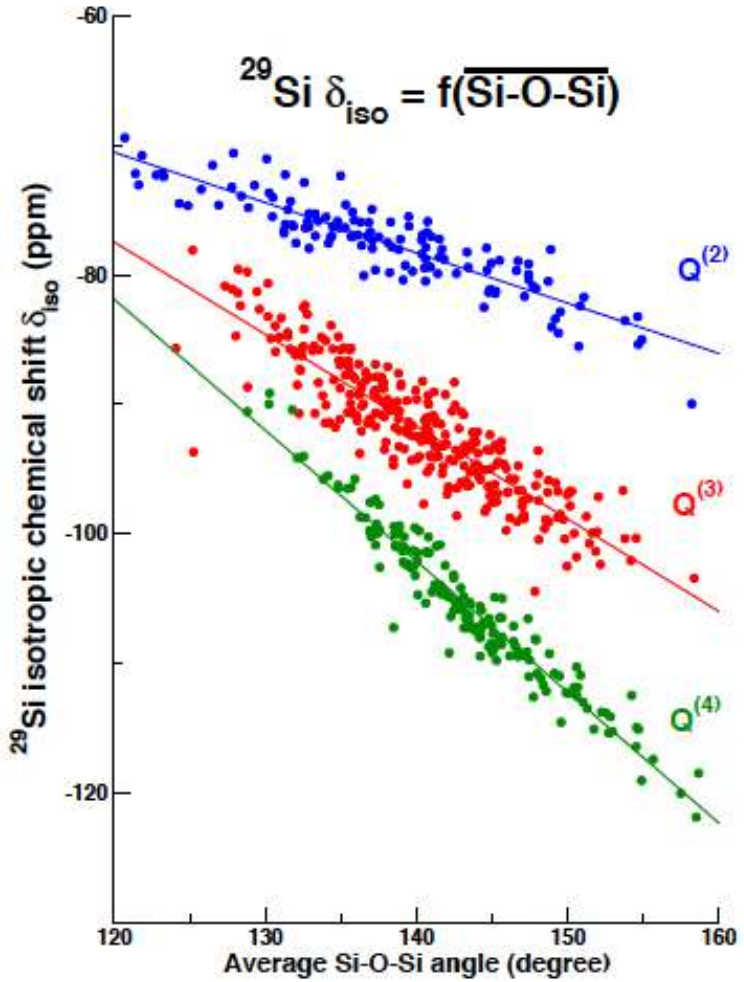
Note: $\delta_{iso} = -(\sigma_{ref} - \sigma_{iso})$

^{29}Si MAS NMR: Direct access to silicon $Q^{(n)}$ speciation

$Q^{(n)}$: $Si(OSi)_n(O^-)_{(4-n)}$



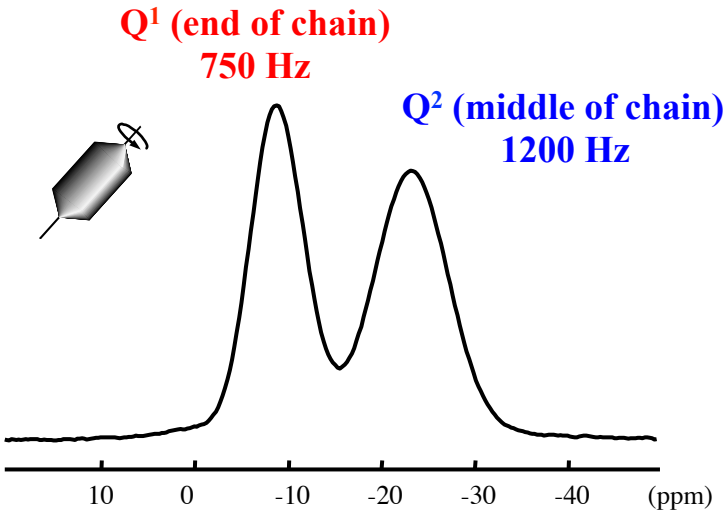
Binary Na_2O - SiO_2 glasses
NSMo: N39S60 + 1 MoO_3



The NMR response of $Q^{(n)}$ species to disorder (bond angle distribution) is different.

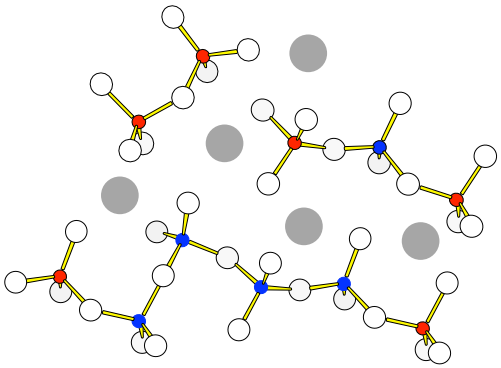
Phosphate Glasses : ^{31}P MAS NMR

$(PbO)_{0.61}(P_2O_5)_{0.39}$ verre

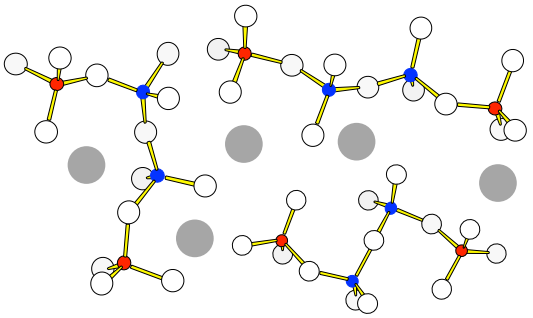


$[Q^1] = [Q^2]$

Average chain length
$N_{av.} \sim 4$



? Nature of disorder at the nanometric scale ?

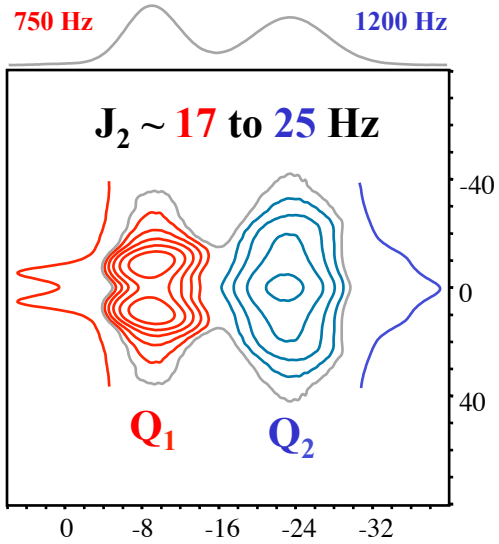


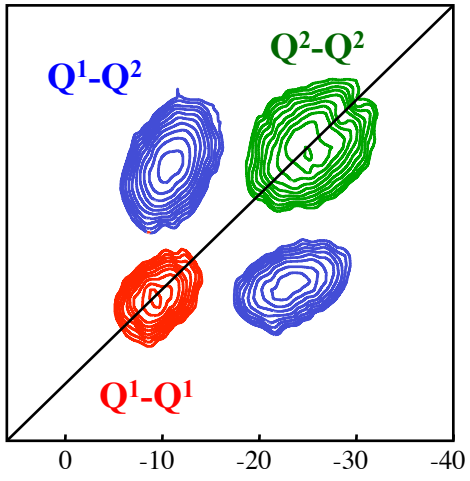
Chain length distribution?
Chemical disorder

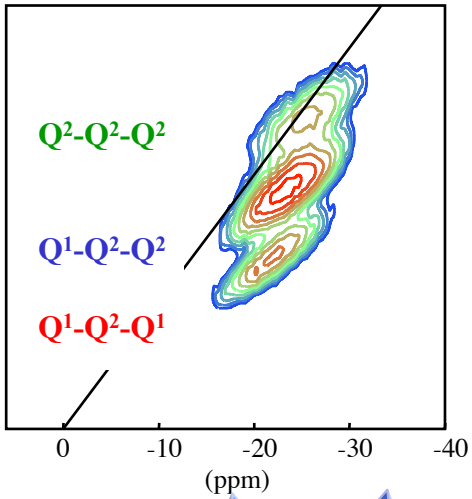
Chain geometries?
Topological or geometrical disorder

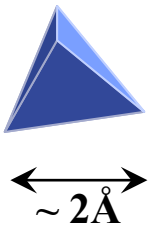
1 to 3 tetraedra – ^{31}P

$(PbO)_{0.61}(P_2O_5)_{0.39}$ glass

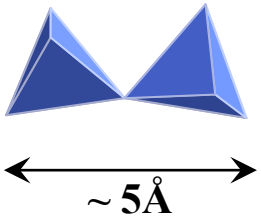




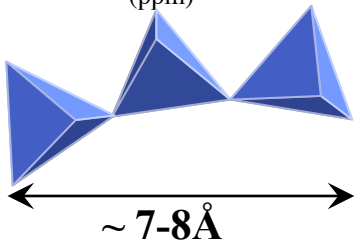




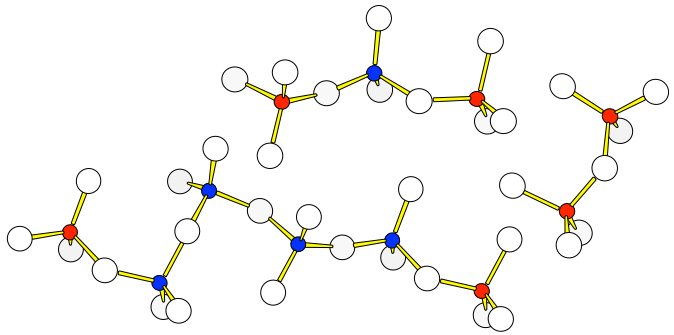
~ 2Å



~ 5Å

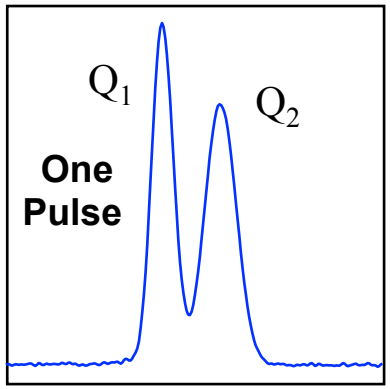


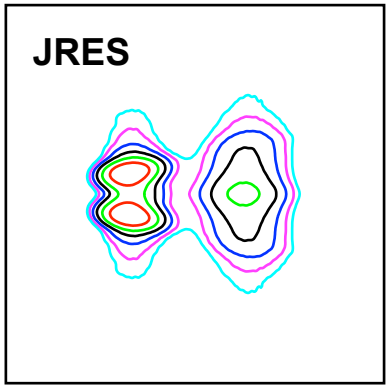
~ 7-8Å

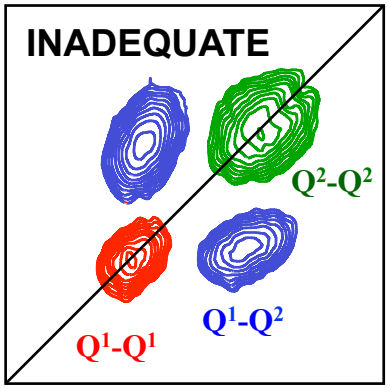


F. Fayon, I.J. King, R.K. Harris, J.S.O. Evans, D. Massiot Comptes Rendus de Chimie 7 351-361 (2004)
F.Fayon, C.Roiland, L.Emsley, D.Massiot, Journal of Magnetic Resonance 179 50-58 (2006)

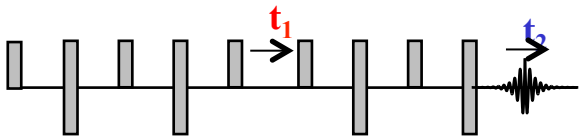
Phosphate Glass structure ^{31}P MAS



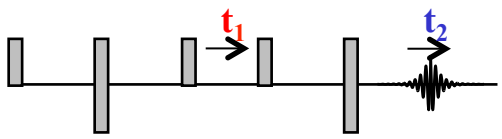


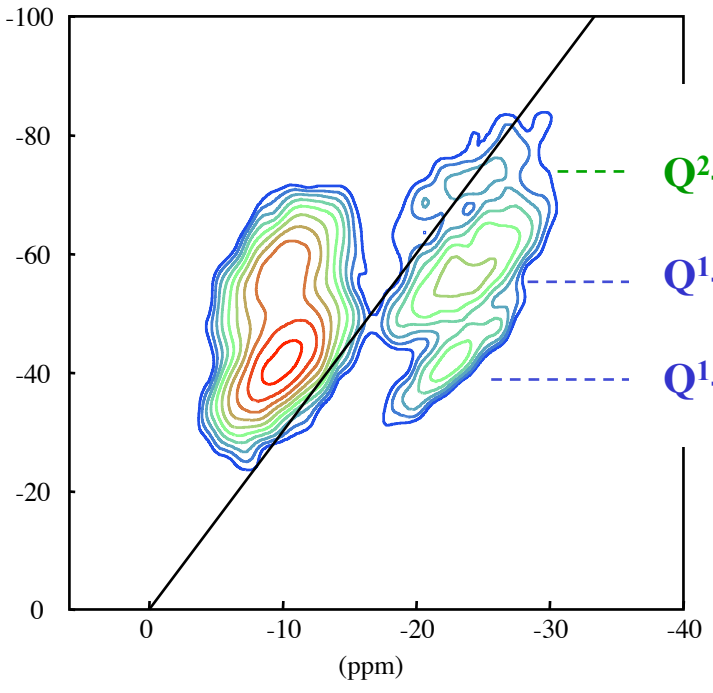


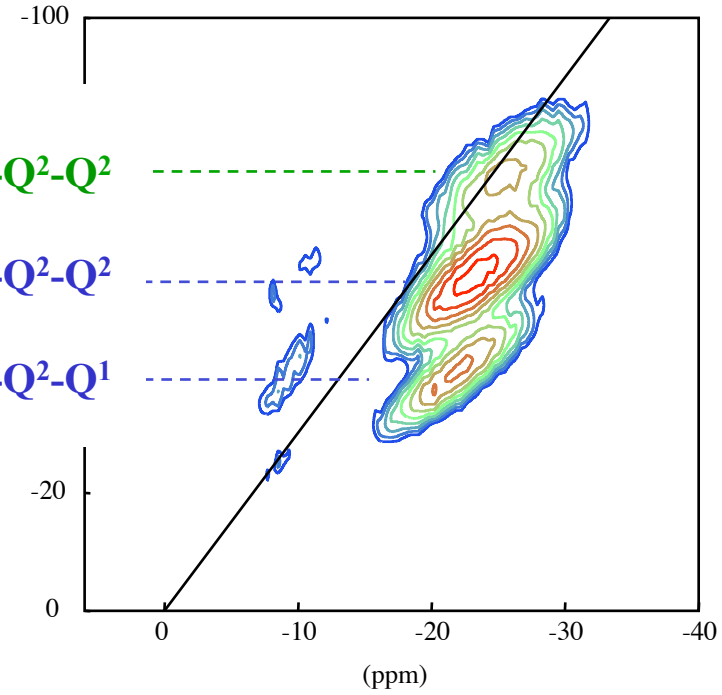
Double INADEQUATE



3Q INADEQUATE







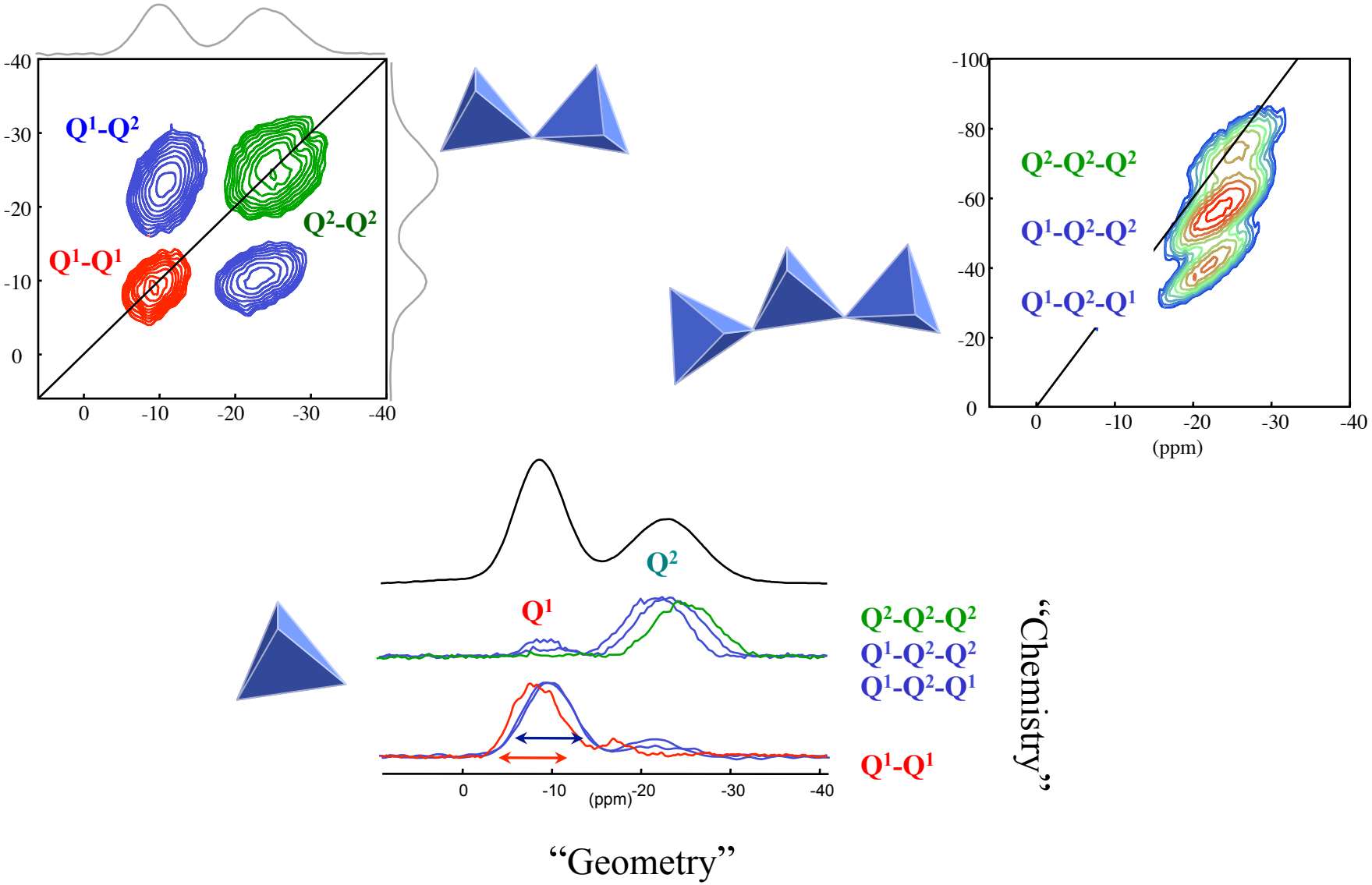
Q^2-Q^2-Q^2

Q^1-Q^2-Q^2

Q^1-Q^2-Q^1

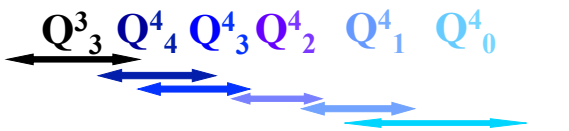
$(PbO)_{0.61}(P_2O_5)_{0.39}$ glass

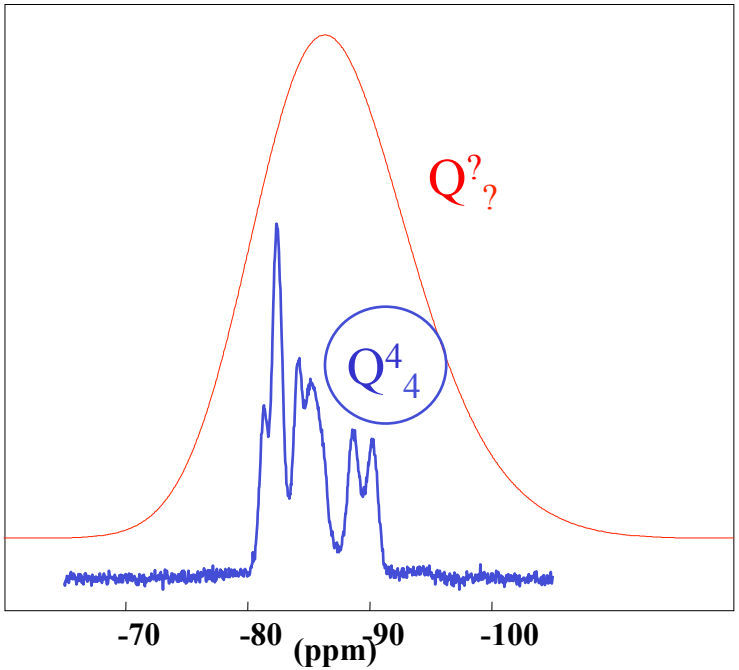
Chemical and Geometrical Order



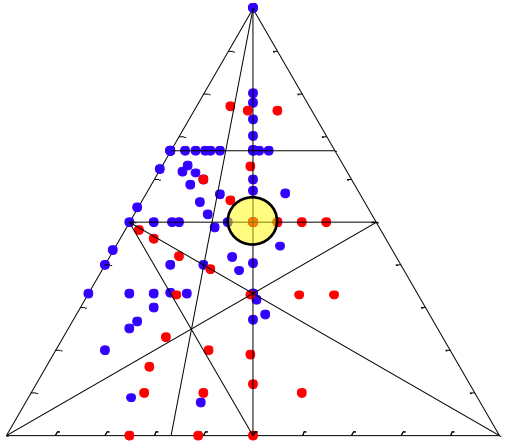
F.Fayon, C.Roiland, L.Emsley, D.Massiot, Journal of Magnetic Resonance 179 50-58 (2006)

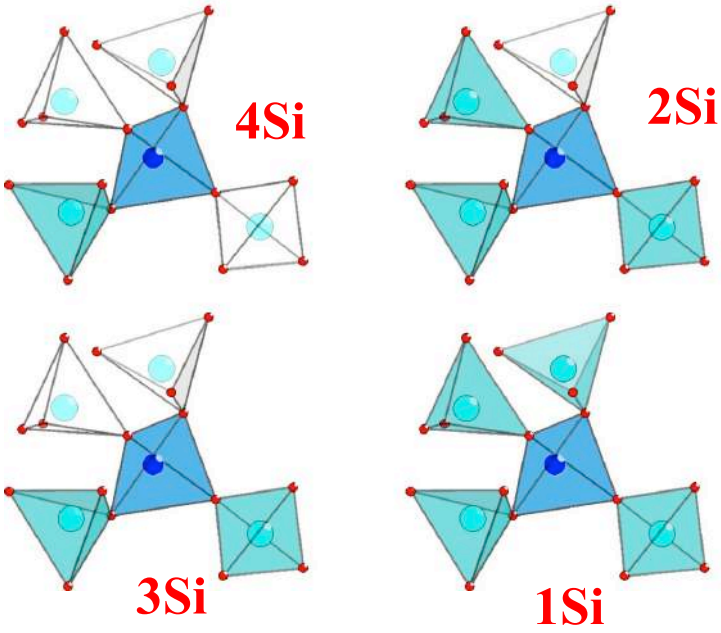
{^{27}Al} ^{29}Si(O-^{29}Si)$_{n?}$ Spin Counting





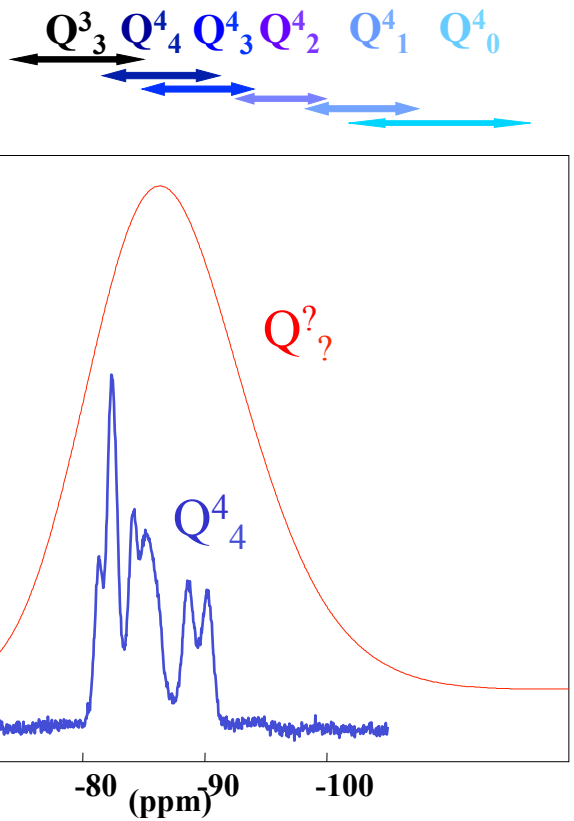
RMN ^{29}Si
Anorthite
Crystalline & Glass



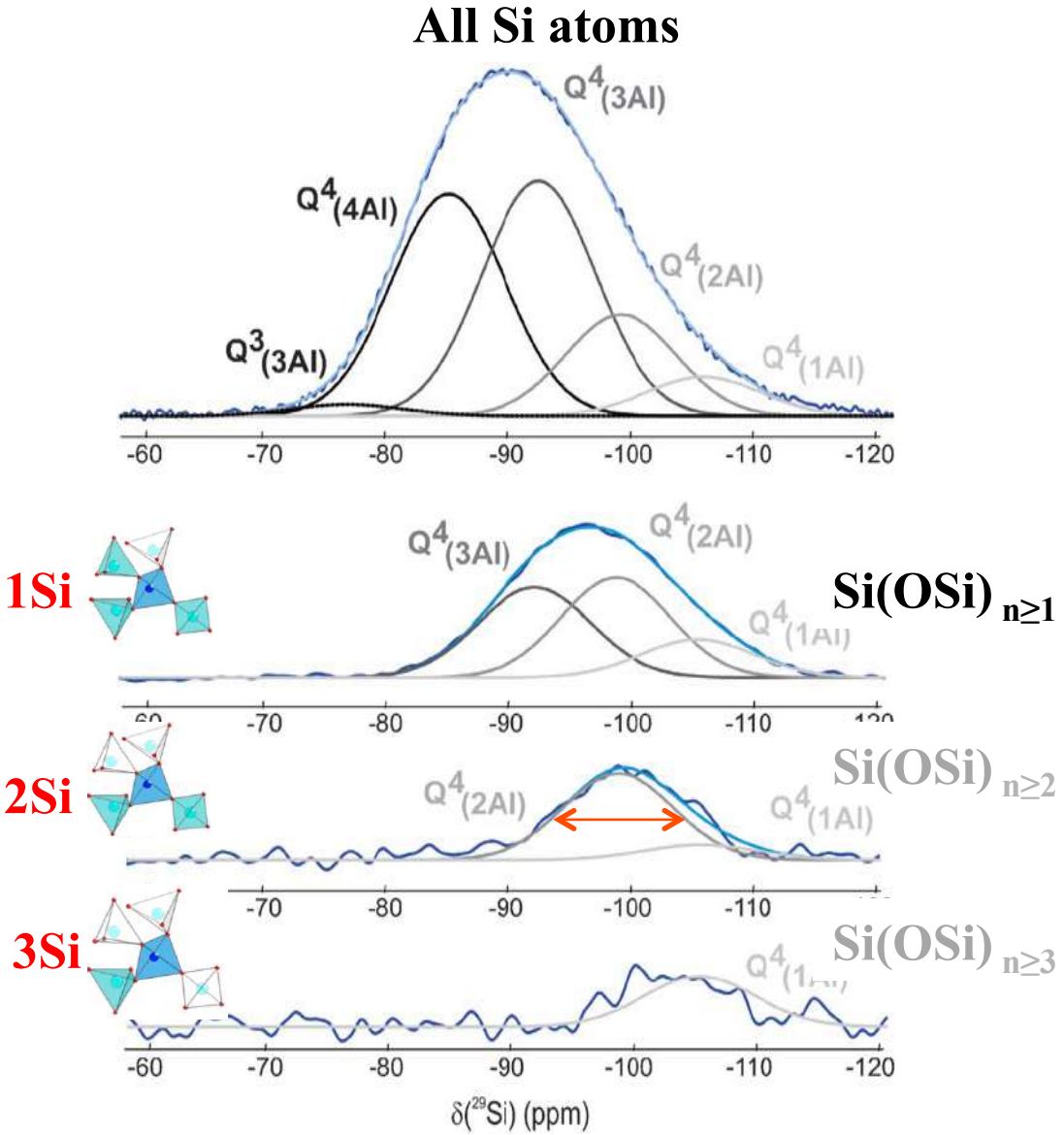


J.Hiet, M.Deschamps, N.Pellerin, F.Fayon, D.Massiot
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys.* 11 6935–6940 ***2009***

{^{27}Al} ^{29}Si(O-^{29}Si)$_{n?}$ Spin Counting

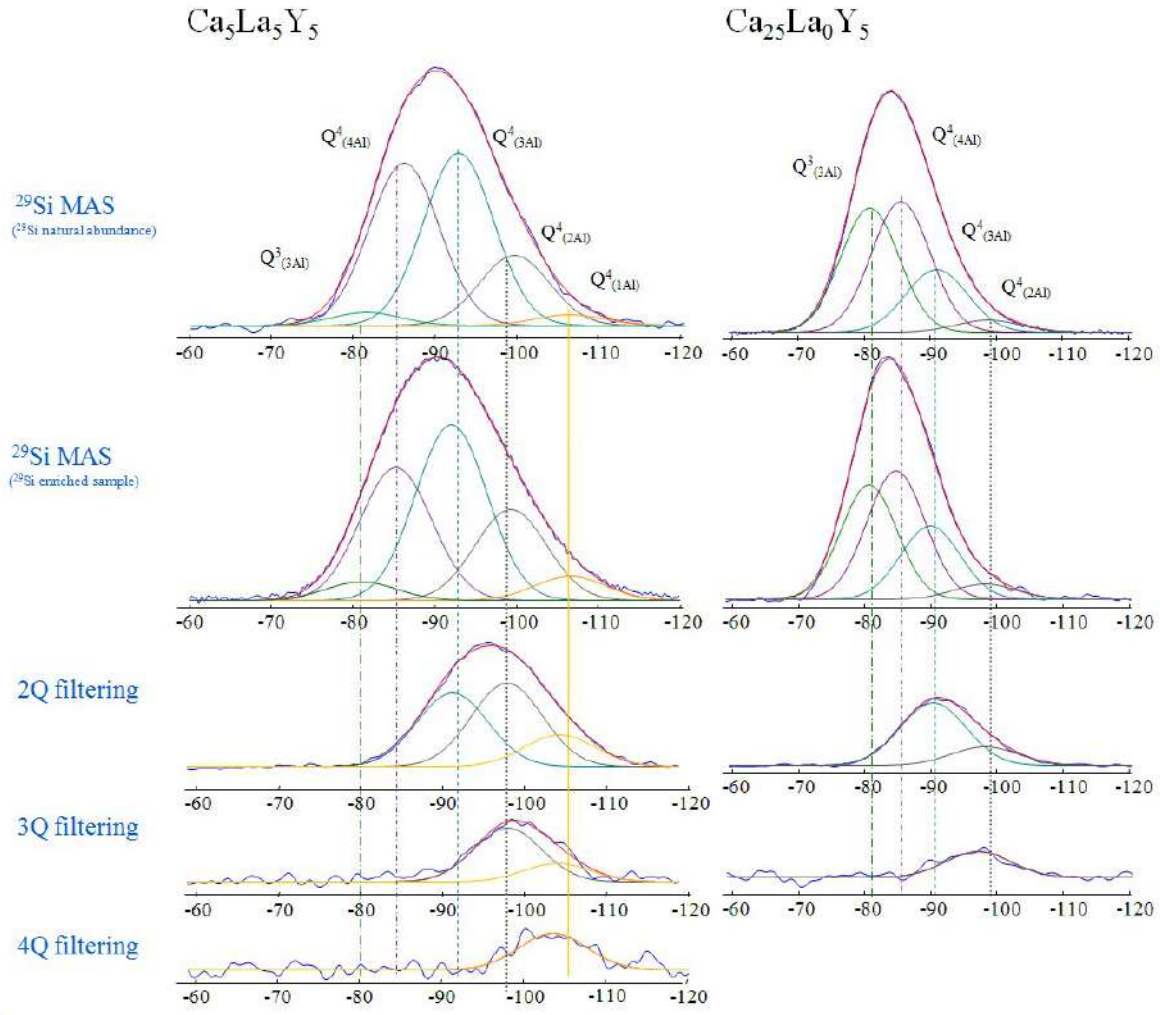


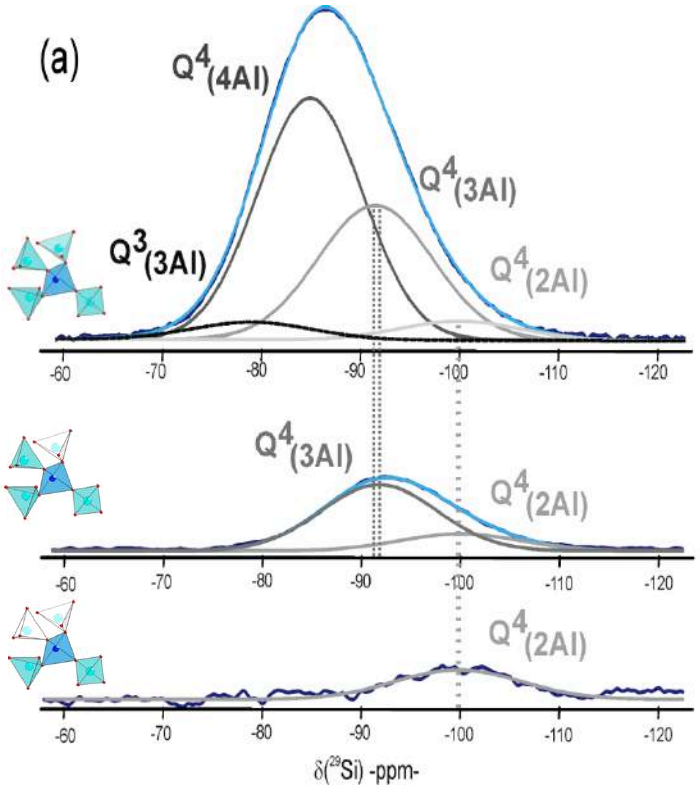
NMR^{29}Si
Anorthite
Crystalline & Glass



J.Hiet, M.Deschamps, N.Pellerin, F.Fayon, D.Massiot
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys.* 11 6935–6940 ***2009***

(Y/La) Complex Glasses



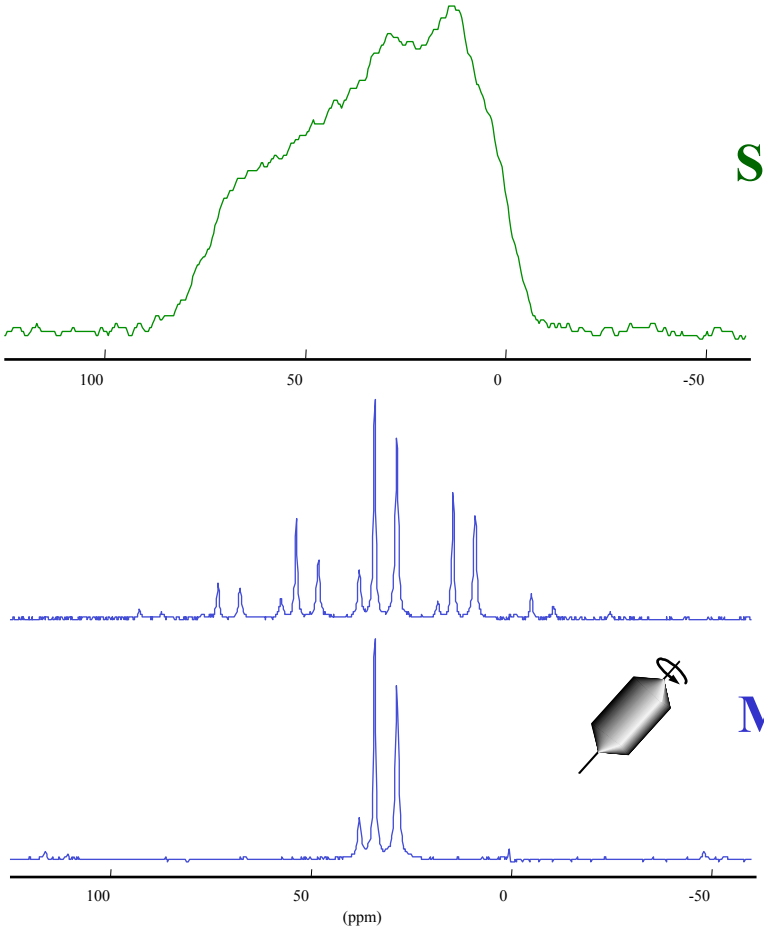


Anorthite Glass
$Si_2Al_2O_8Ca$

J.Hiet, M.Deschamps, N.Pellerin, F.Fayon, D.Massiot
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys.* 11 6935–6940 ***2009***

MAS : Rotation à l'angle magique

^{31}P Spin 1/2 CSA

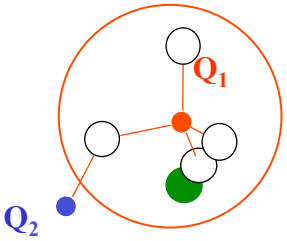


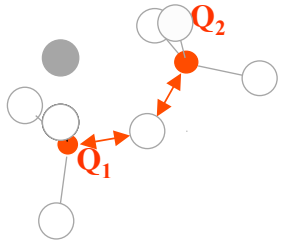
Static

MAS

Modulation into sharp lines

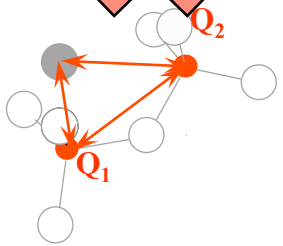
CSA

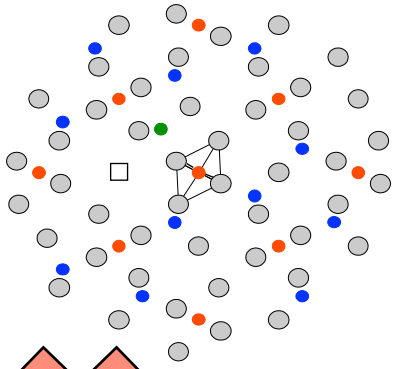




J Coupling

Dipolaire



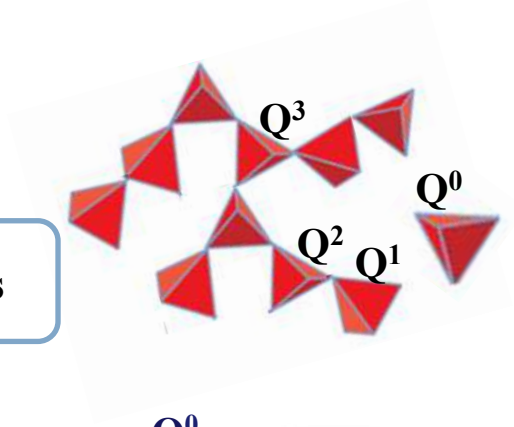


Quadrupolaire

Structure of $CaO-SiO_2-P_2O_5$ Bioglasses

Silicate (phosphate) network: Q^n units

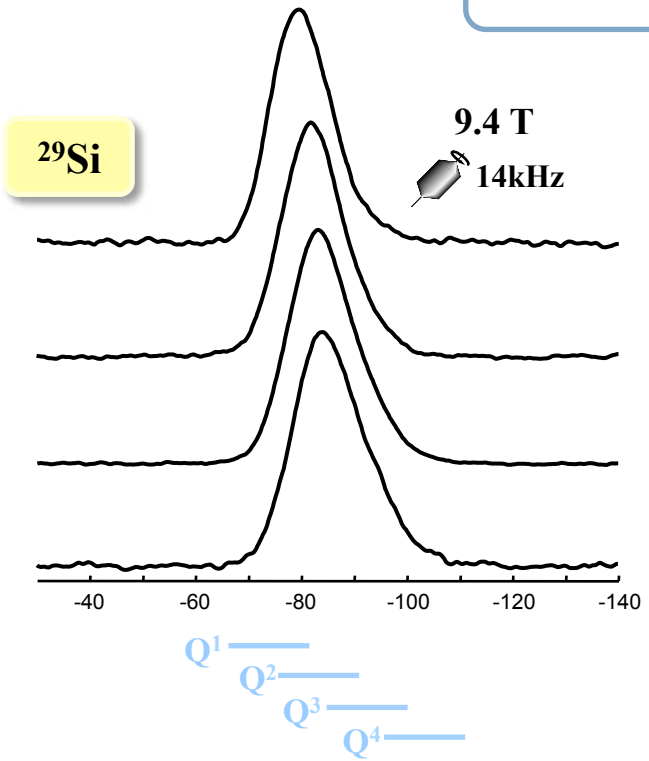
(SiO_4, PO_4 tetrahedra with n bridging oxygen atoms)

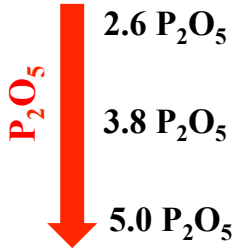


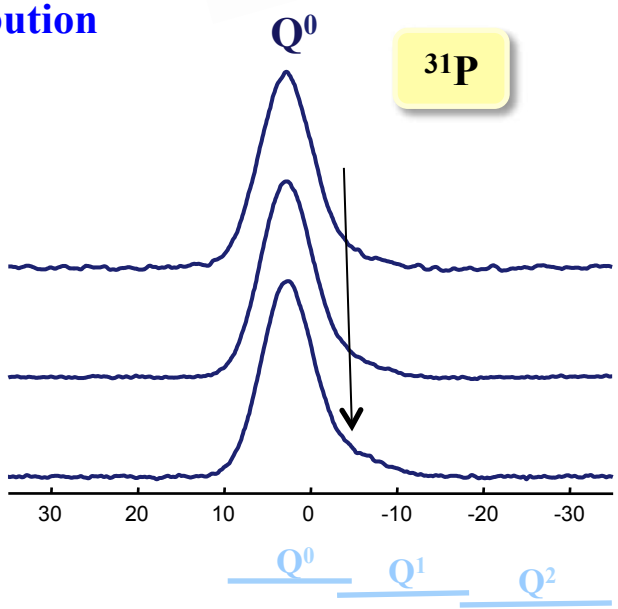
1D MAS spectra of $CaO-SiO_2-P_2O_5$ glasses

Broad chemical shift distribution (disordered materials)

Ca/Si = 1.11







Lack of resolution: Q^n units quantification ?

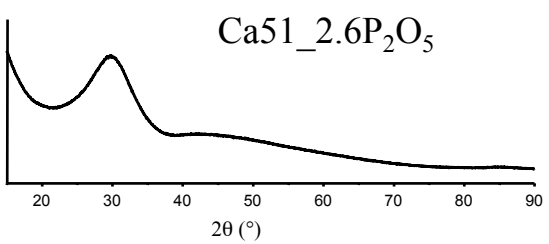
Mainly orthophosphate units (Q^0 : PO_4^{3-}) and ?

F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 2013

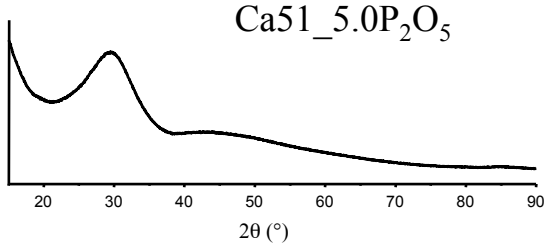
Probing phosphate clustering : TEM - XRD

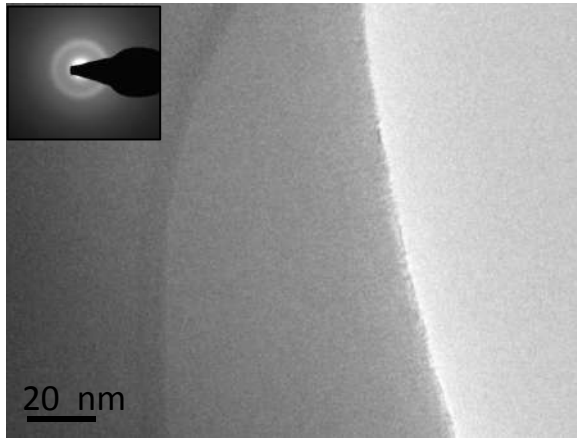
Chemical contrast in TEM – XRD of amorphous materials **: Z contrast**

Ca phosphate vs Ca silicate : very weak Z-contrast

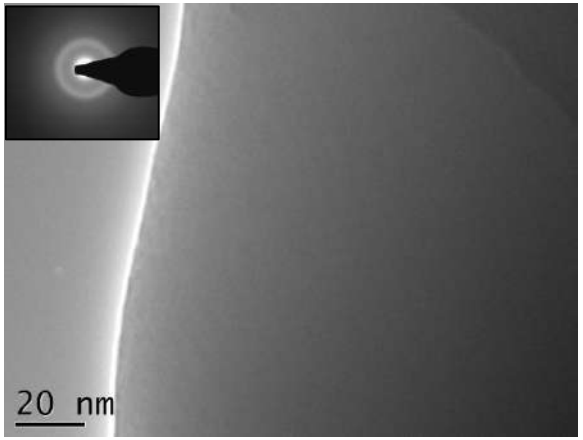


XRD





TEM



Homogeneous ?? or CaP clustering ??

HR-TEM : modification of the glass sample under the beam

Solid-state NMR

F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 2013

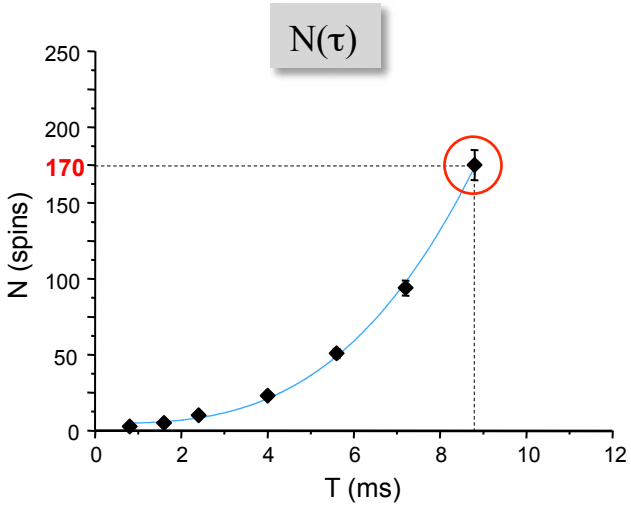
Spin Counting: $Ca_4P_2O_9$

Statistical model (A. Pines *et al.*)

- Excitation efficiency of all coherence orders are equal
  - ➡ *All dipolar couplings are the same*
  - ➡ *Differential relaxation of MQC is ignored*

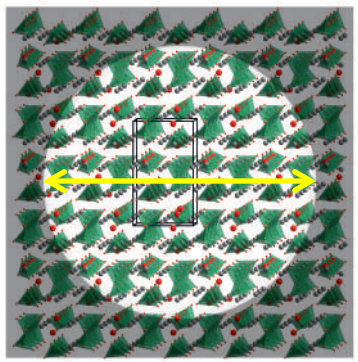
- Time dependant system size N(τ) with binomial distribution of MQC intensities

$$\frac{2N!}{(N+n)!\,(N-n)!} \approx \exp\left(-\frac{n^2}{N(\tau)}\right)$$

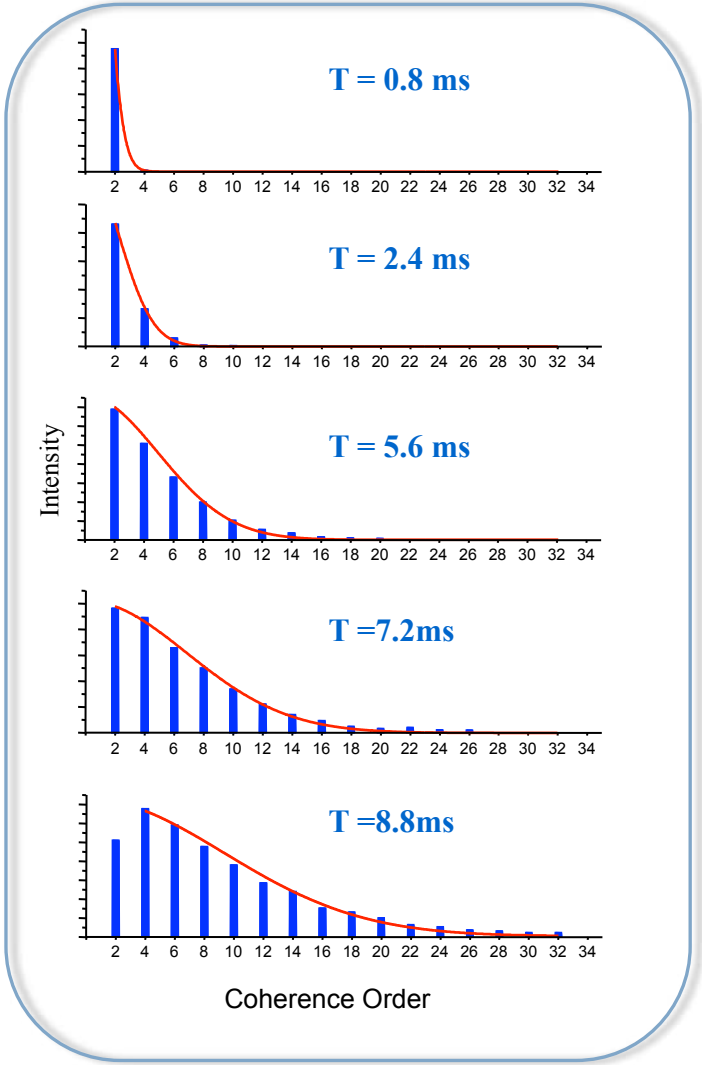


Measurement of the system size limited by transverse relaxation

170 P atoms
(21 unit cells – 17 nm^3)

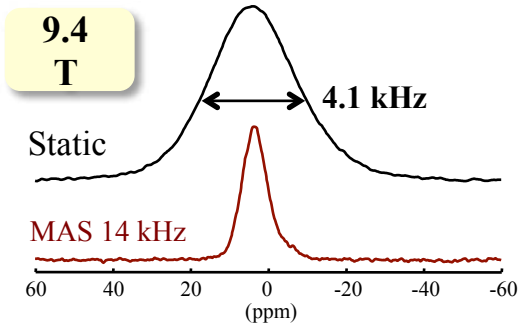


Ø ≈ 3.2 nm

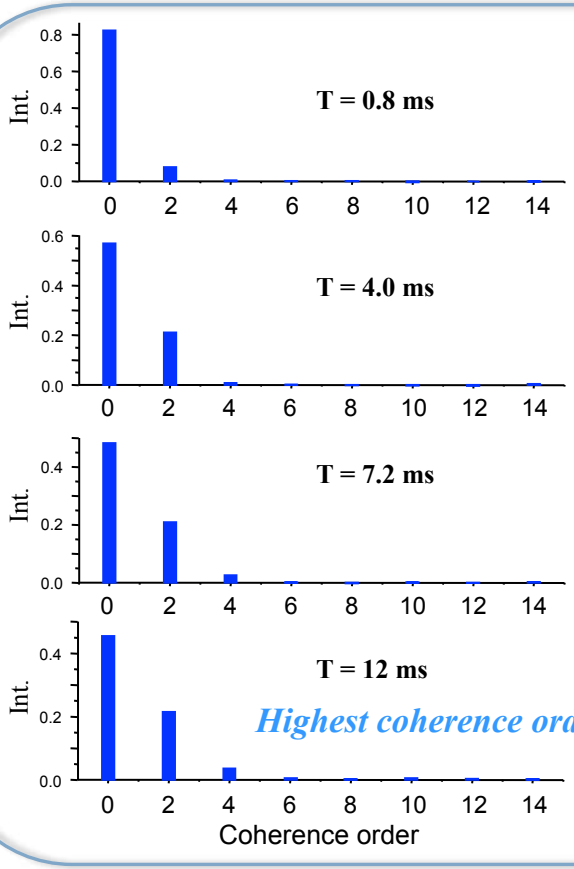


F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 2013

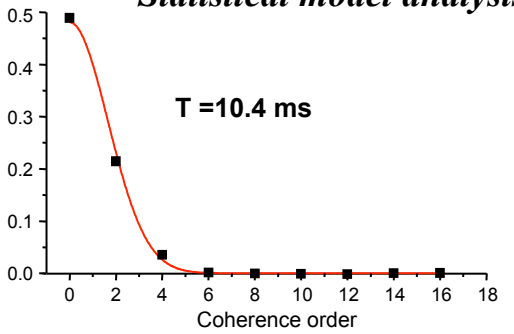
46.1CaO-52.3SiO_2– 2.6P_2O_5 Glass



- Ditribution of δ_{ISO} : 7.5 ppm (1.2 kHz)
- ^{31}P CSA: ≈14 ppm (2.3 kHz)

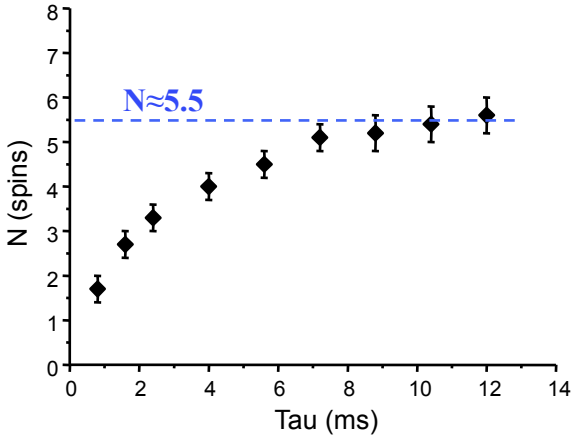


Statistical model analysis



Nicely fitted with a single Gaussian function

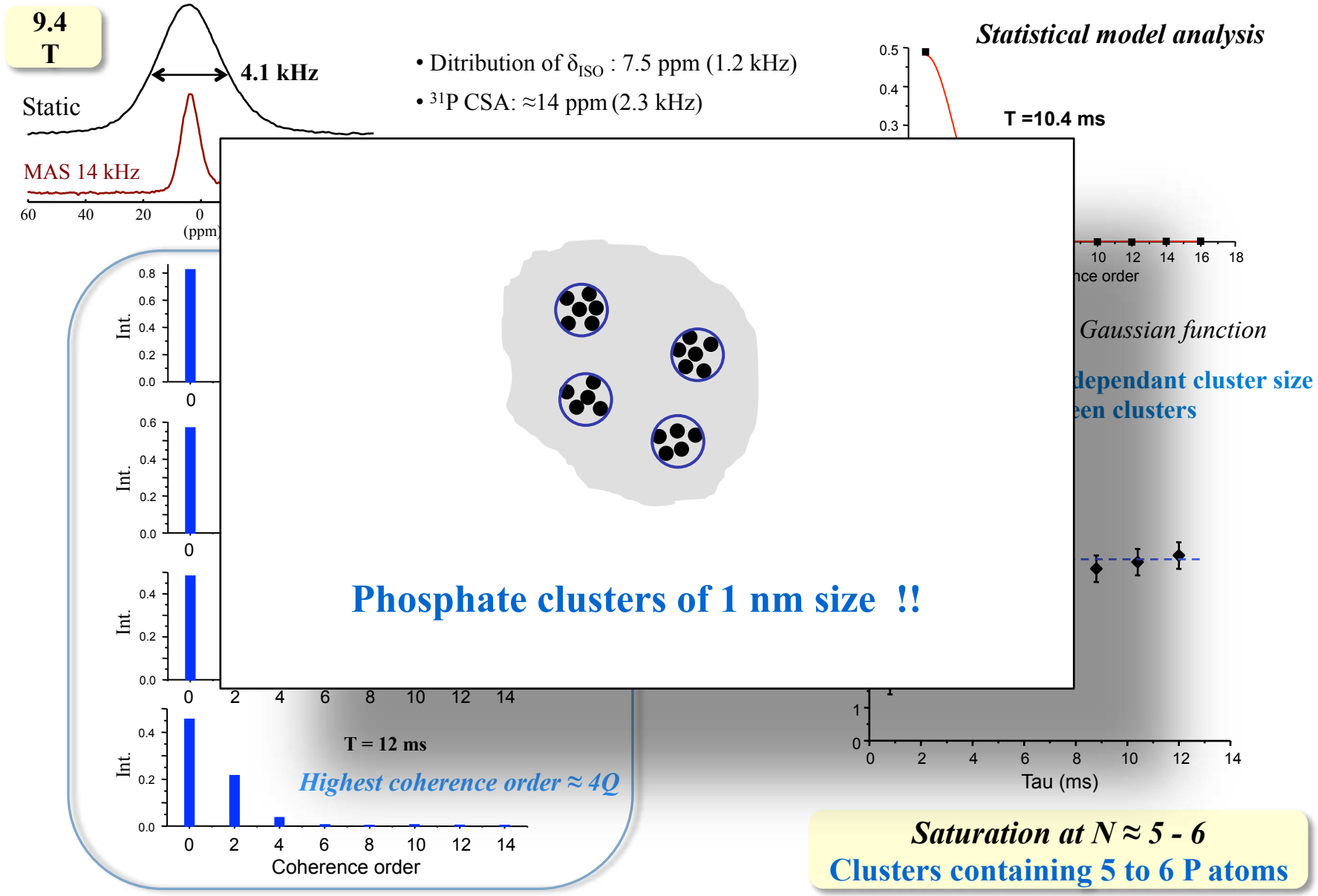
- **'Well-defined' time-dependant cluster size**
- **No interaction between clusters**



Saturation at N ≈ 5 - 6
Clusters containing 5 to 6 P atoms

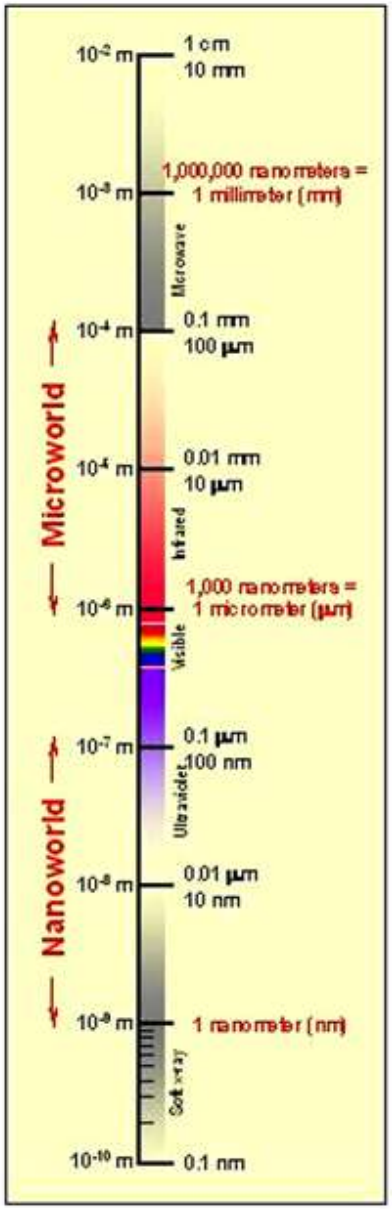
F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 2013

46.1CaO-52.3SiO_2– 2.6P_2O_5 Glass

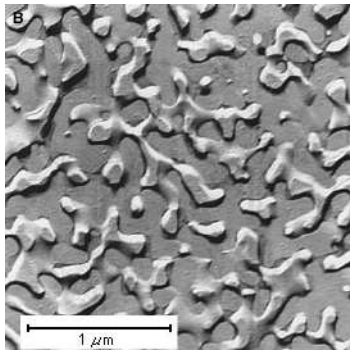


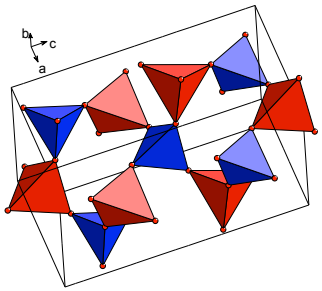
F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 2013

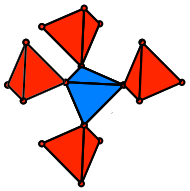
Glass structure at different scales

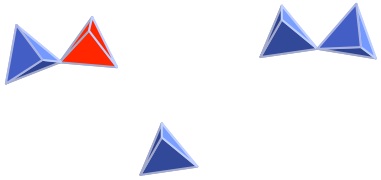


Homogeneous
Isotropic
Disordered









Heterogeneous
Anisotropic
Locally Ordered

nm

Å

Merci de votre attention

Avez vous des questions ???

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