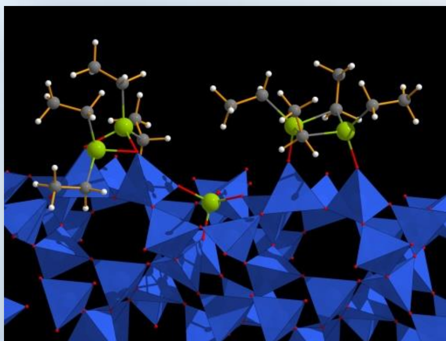
Very-High Temperature NMR of Oxide Glasses & Melts



P. Florian

CEMHTI-CNRS, Orléans, France

Ecole du GDR Verre, Fréjus, Avril 2015

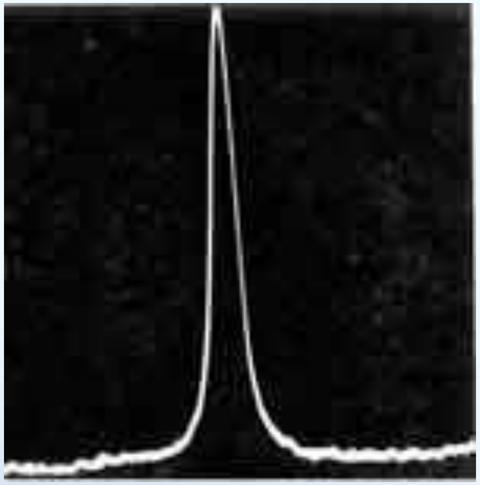
The Music of Atoms

An (Ultra) Short Introduction to NMR Spectroscopy

And in 1945 (SS)NMR was born...

Felix Bloch
1905-1983
(Stanford)

Ed Purcell
1912-1997
(Harvard)



proton NMR of paraffin wax

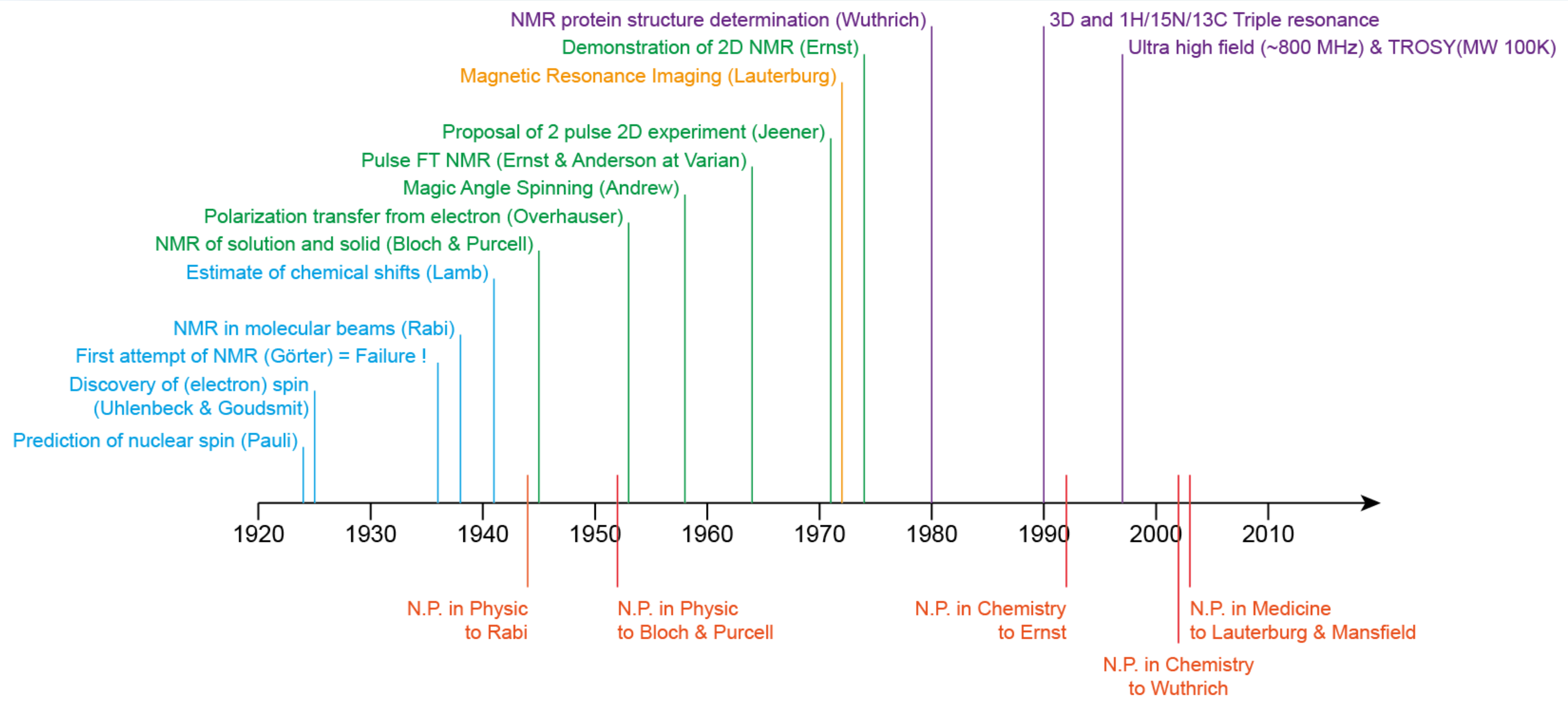
Purcell,
Phys. Rev. 1946

The Nobel Prize in Physics 1952
"for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"

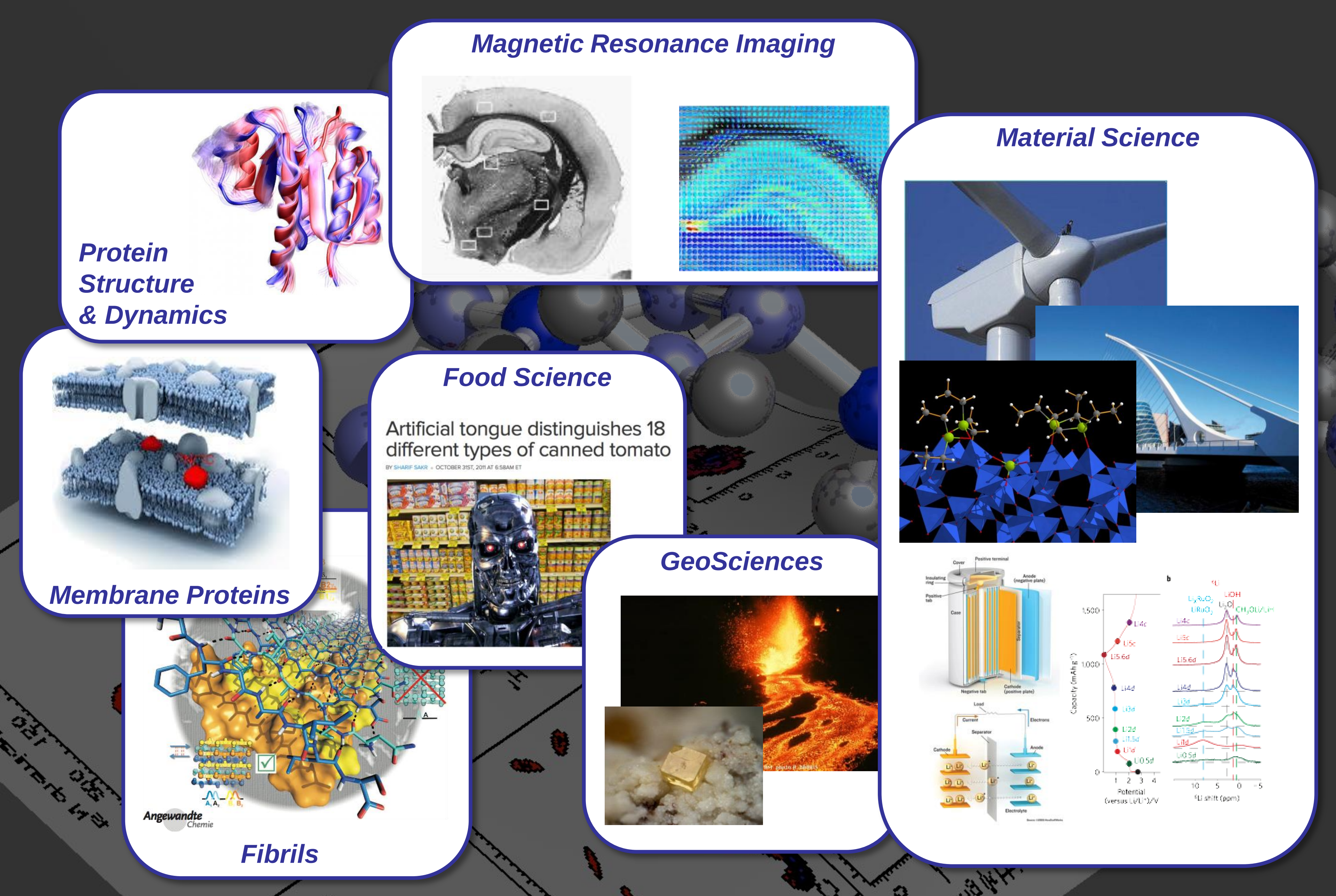
"Dr Bloch and Dr Purcell! You have opened the road to new insight into the micro-world of nuclear physics. Each atom is like a subtle and refined instrument, playing its own faint, magnetic melody, inaudible to human ears. By your methods, this music has been made perceptible, and the characteristic melody of an atom can be used as an identification signal. This is not only an achievement of high intellectual beauty - it also places an analytic method of the highest value in the hands of scientists."

from *Les Prix Nobel en 1952*, Editor Göran Liljestrand, [Nobel Foundation], Stockholm, 1953

NMR TimeLine

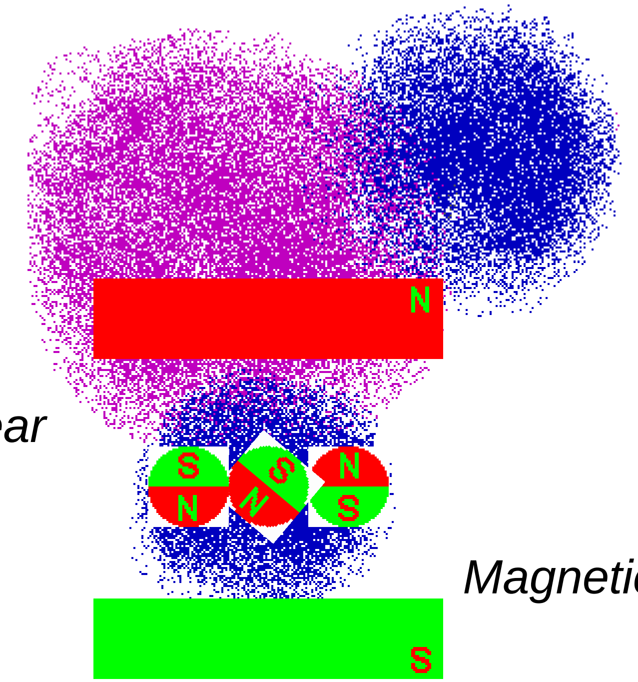


Solid-State NMR Today

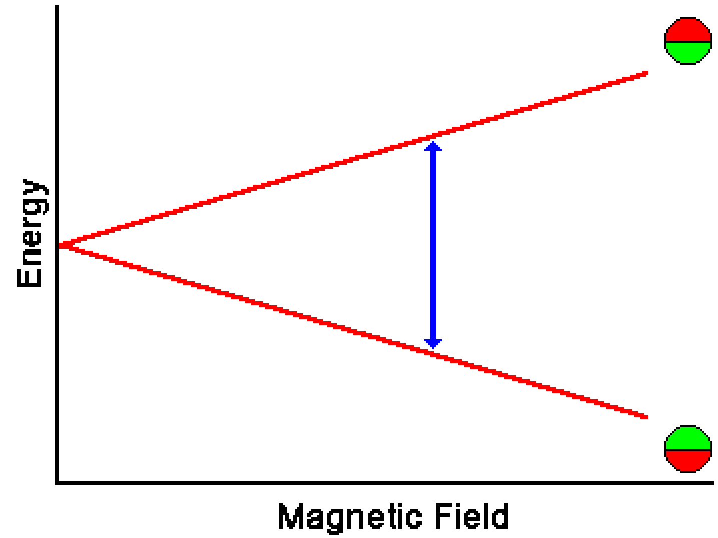


Nuclear + Magnetic + Resonance (Spectroscopy)

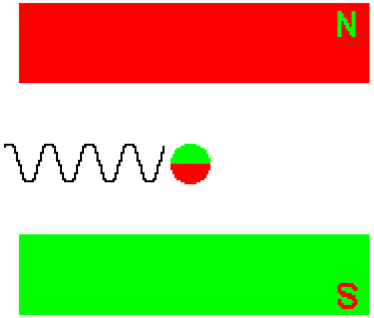
Nuclear



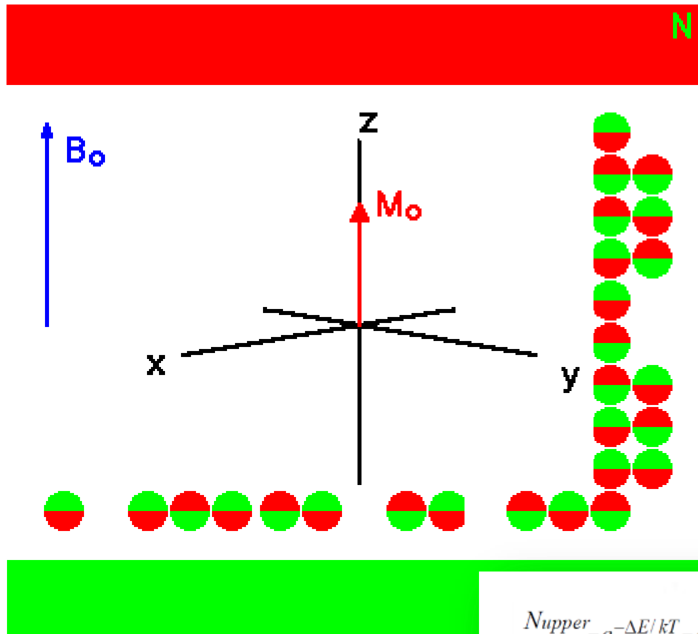
Magnetic

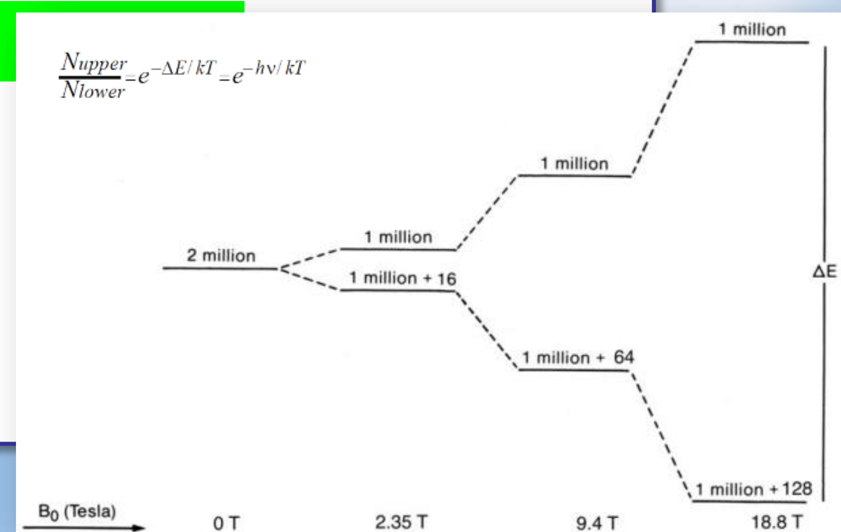


Resonance

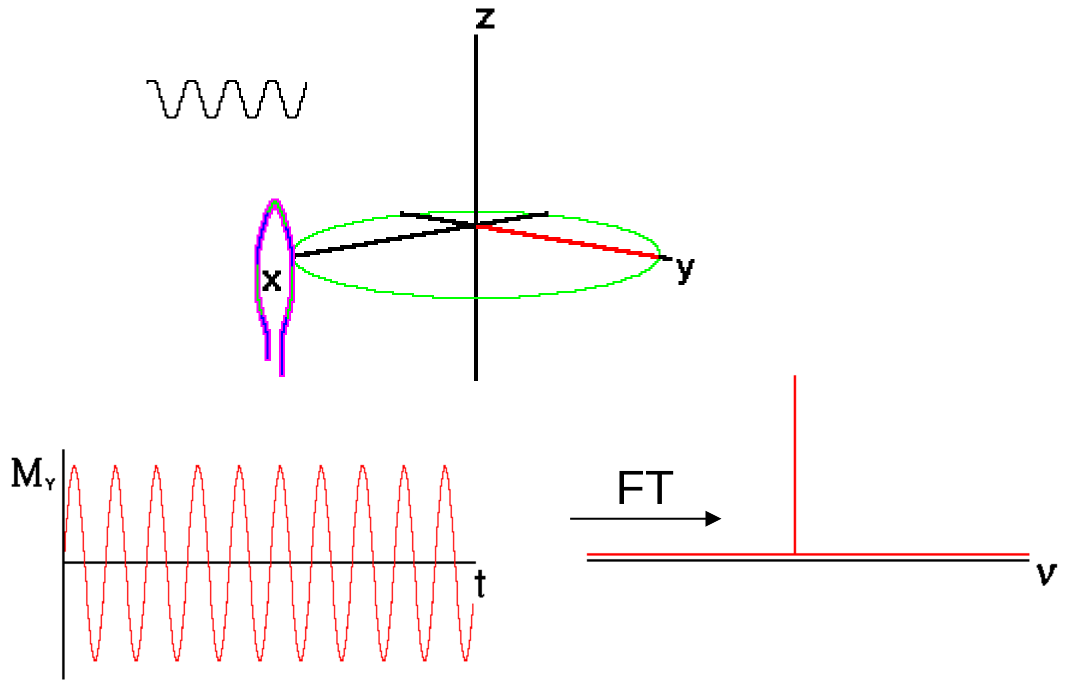


The Magnetization

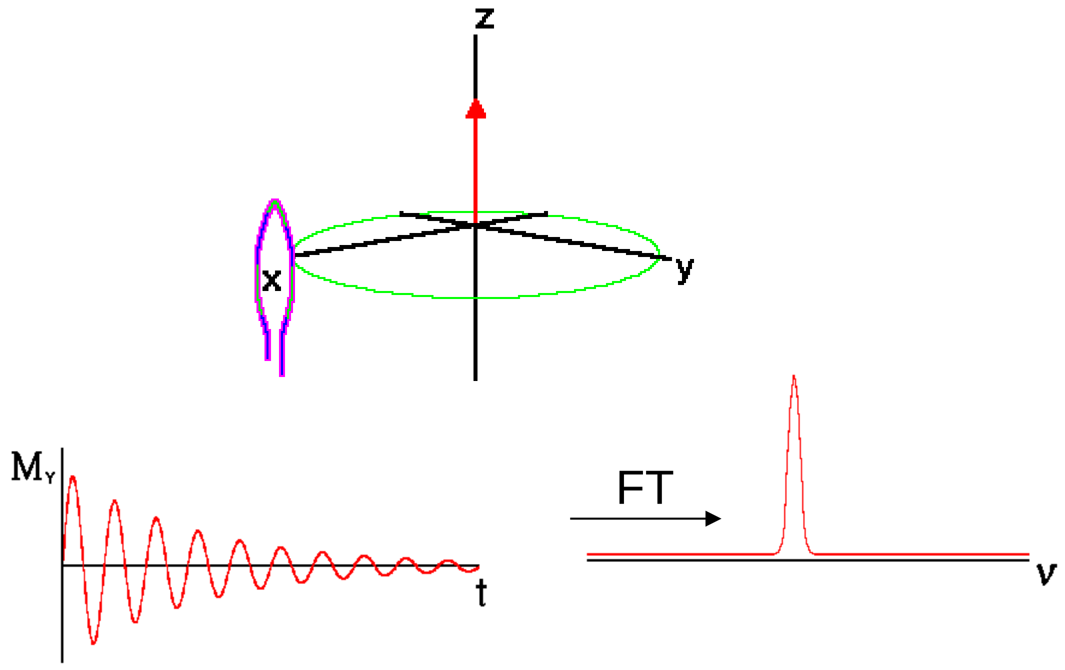




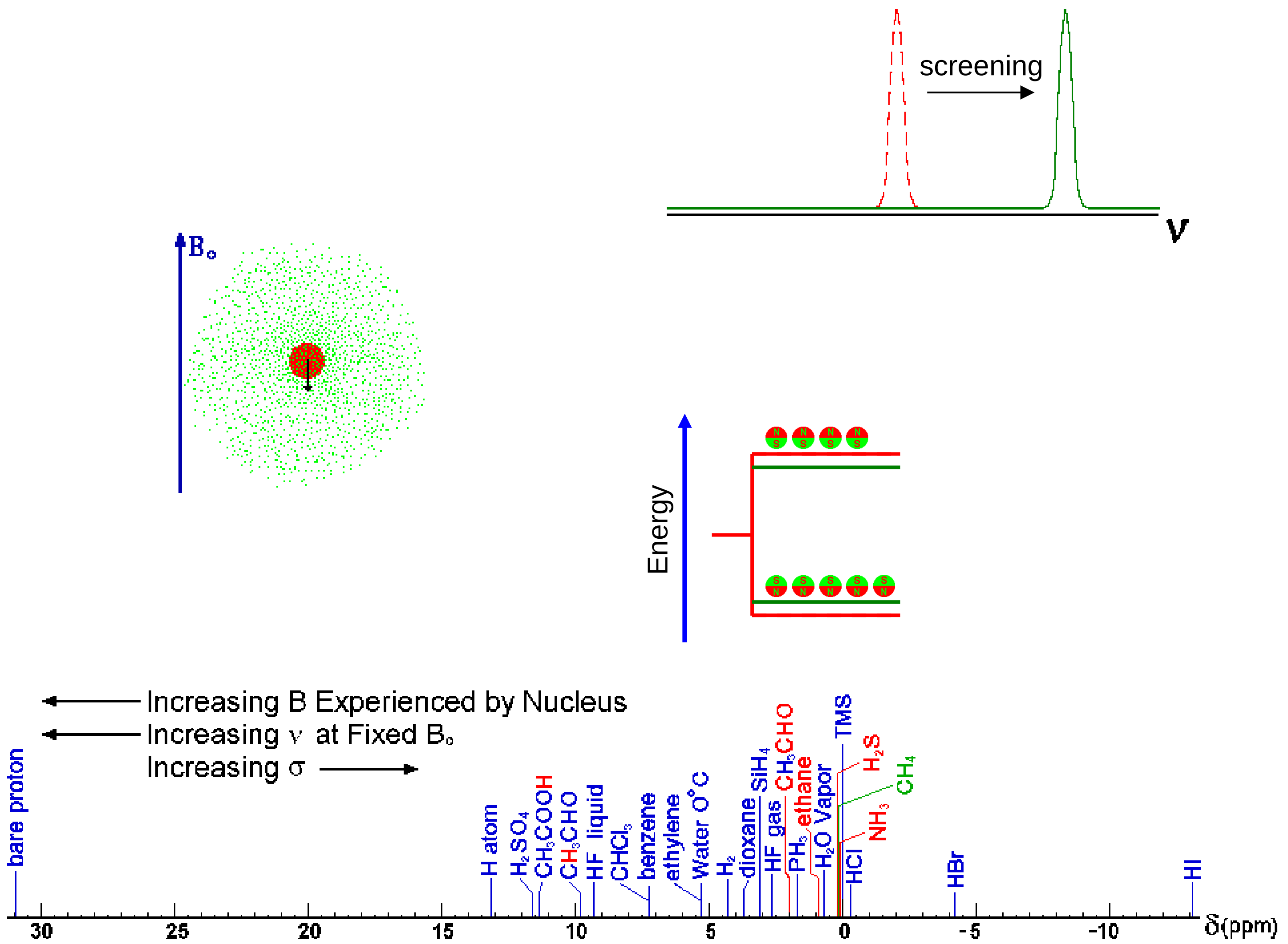
Pulse, Free Induction Decay and spectral domain



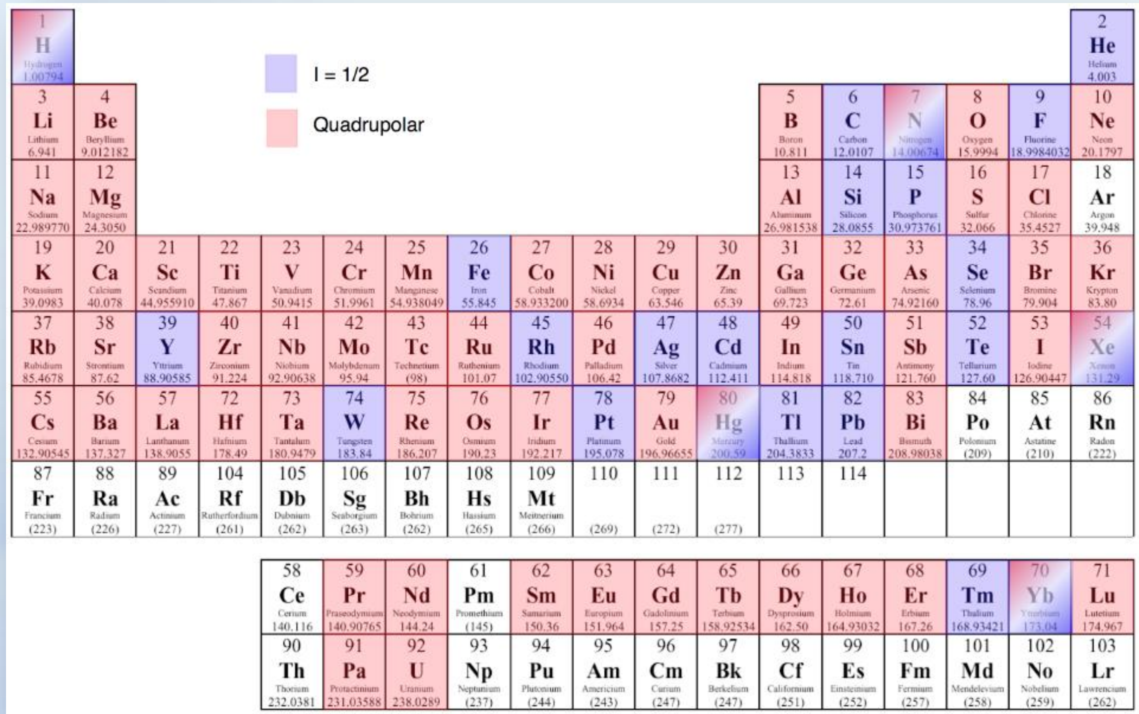
And do not forget to relax...



The chemical shift interaction



Possibilities & Opportunities



- **Observability**
  - **Abundance**
  - **Gyromagnetic ratio**
  - **Quadrupolar momentum**
  - **Paramagnetism**

Numerous possibly sensitive nuclei but few easily observed

The most usually observed are *«light»* nuclei

- **I=1/2 : ^{1}H, ^{13}C, ^{29}Si, ^{31}P**
- **I=3/2 : ^{23}Na, ^{11}B, ^{7}Li**
- **I=5/2 : ^{27}Al, ^{17}O**

Challenge: Anisotropic Interactions

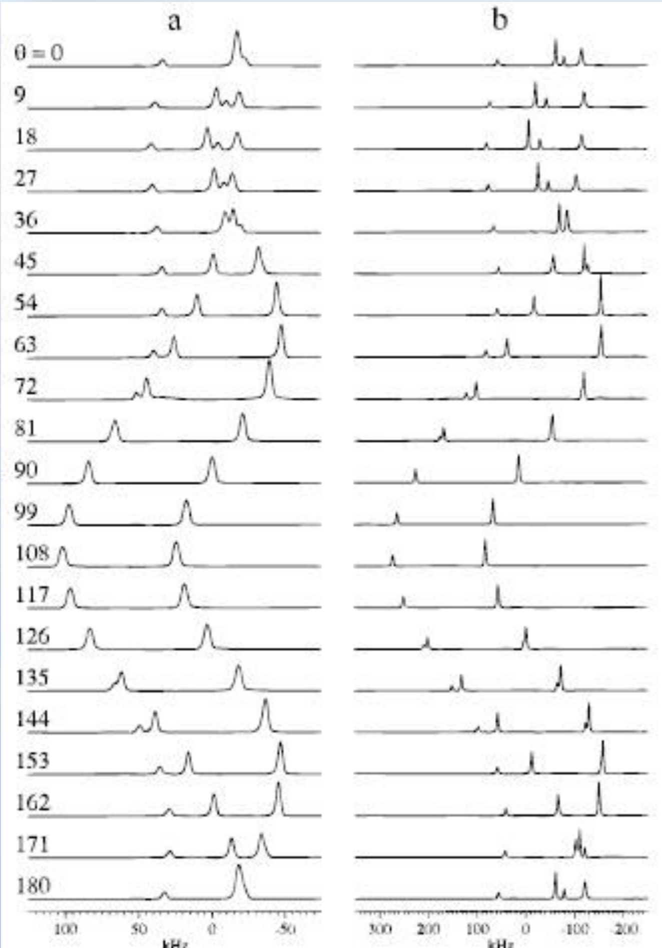
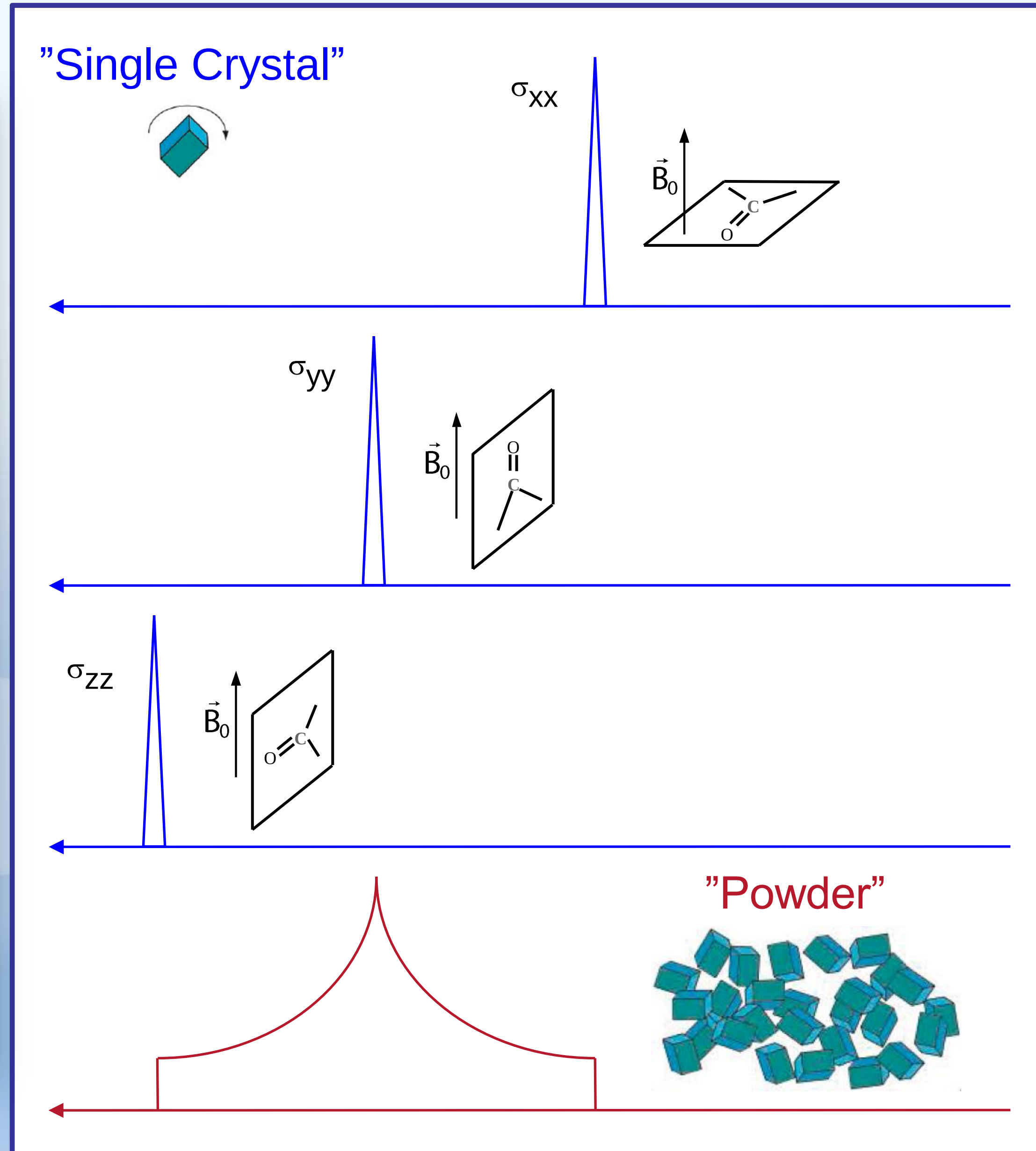
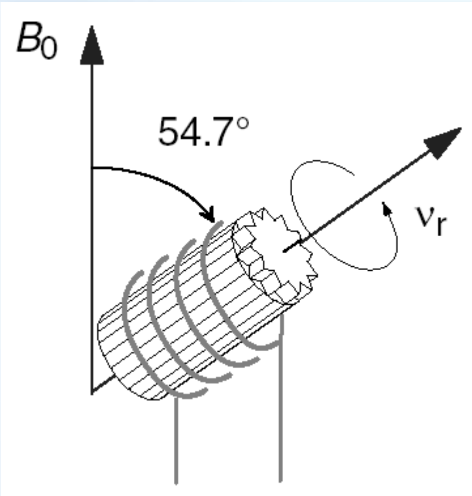
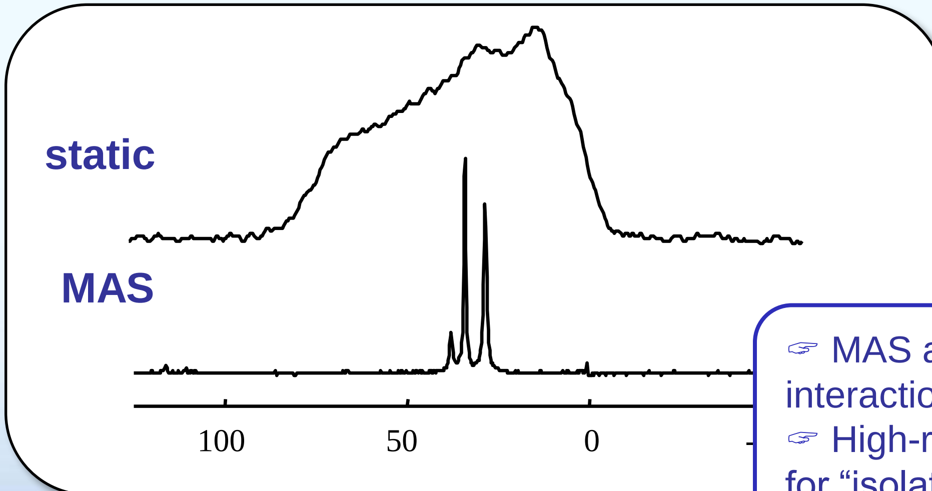


Figure 1. ^{71}Ga (a) and ^{69}Ga (b) single-crystal NMR spectra showing the region of the central transitions for the twin β-Ga_2O_3 crystal. Both sets of spectra are recorded for rotation about the $-x^T$ axis.



It's a Kind of Magic…

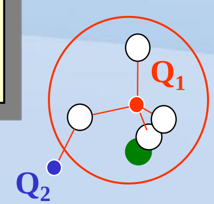


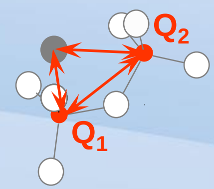


☞ MAS averages anisotropic interactions (to 1st order)
☞ High-resolution spectrum for "isolated" spin ½ nuclei

Isotropic Chemical Shift

~~*CSA*~~

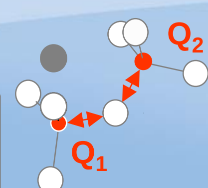


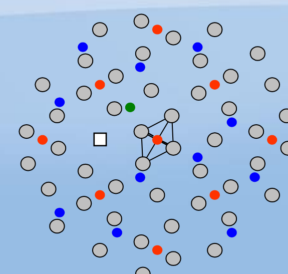


~~*Dipolar couplings*~~

Isotropic *J*-couplings

~~*J-anisotropy*~~



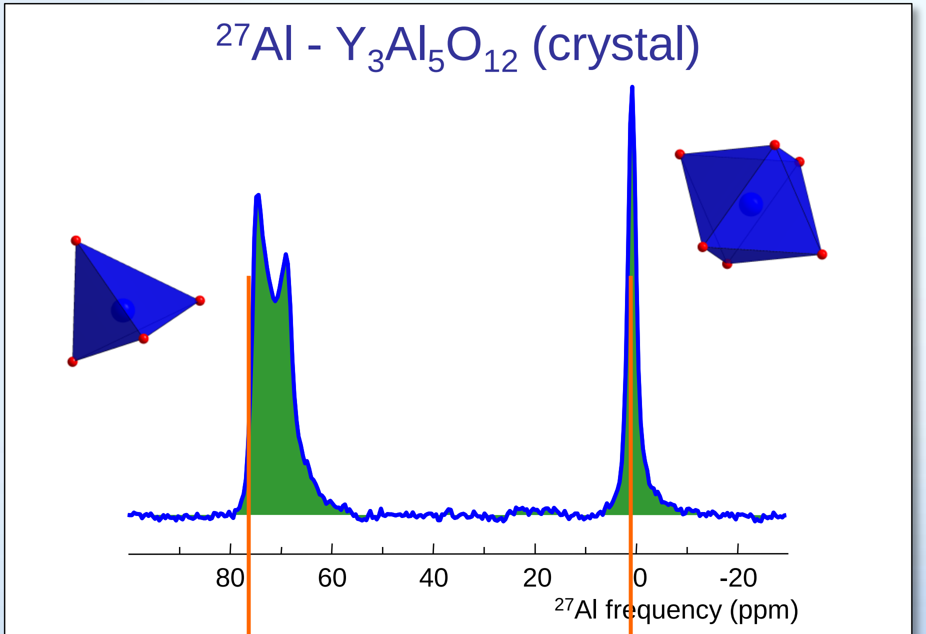


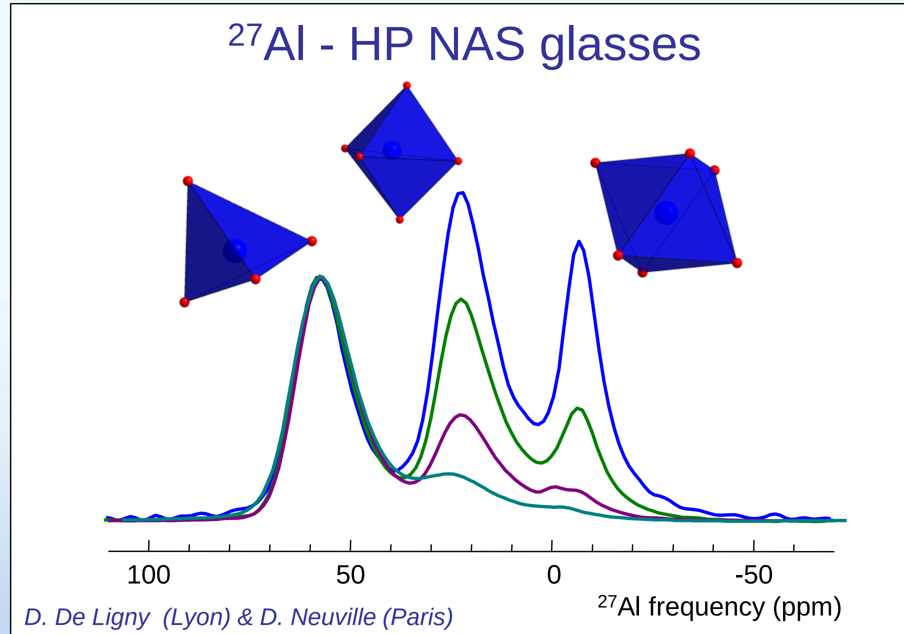
I > ½

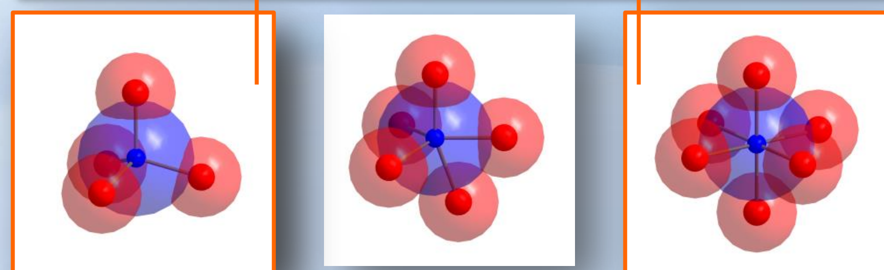
~~*1st order Quadrupolar interaction*~~

2nd order Quadrupolar interaction

(^{27}Al) Nuclear Magnetic Resonance







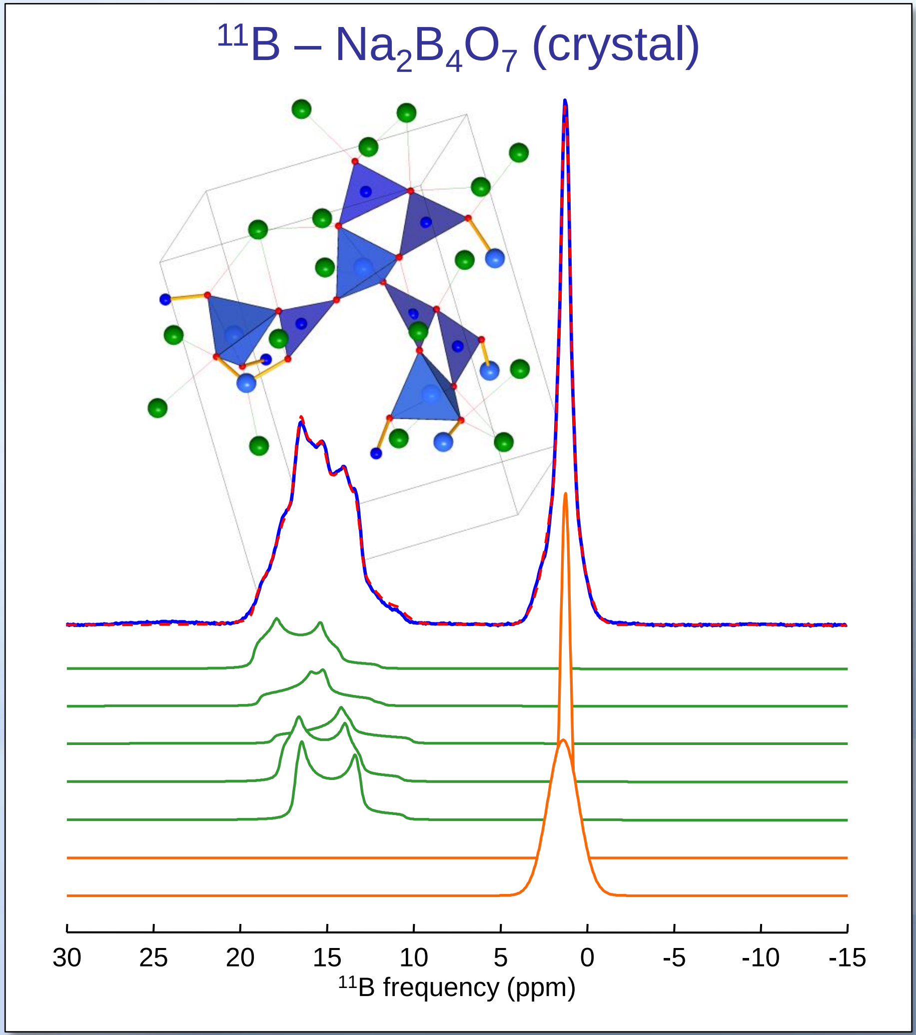
Position
(*chemical shift*, magnetic shielding):

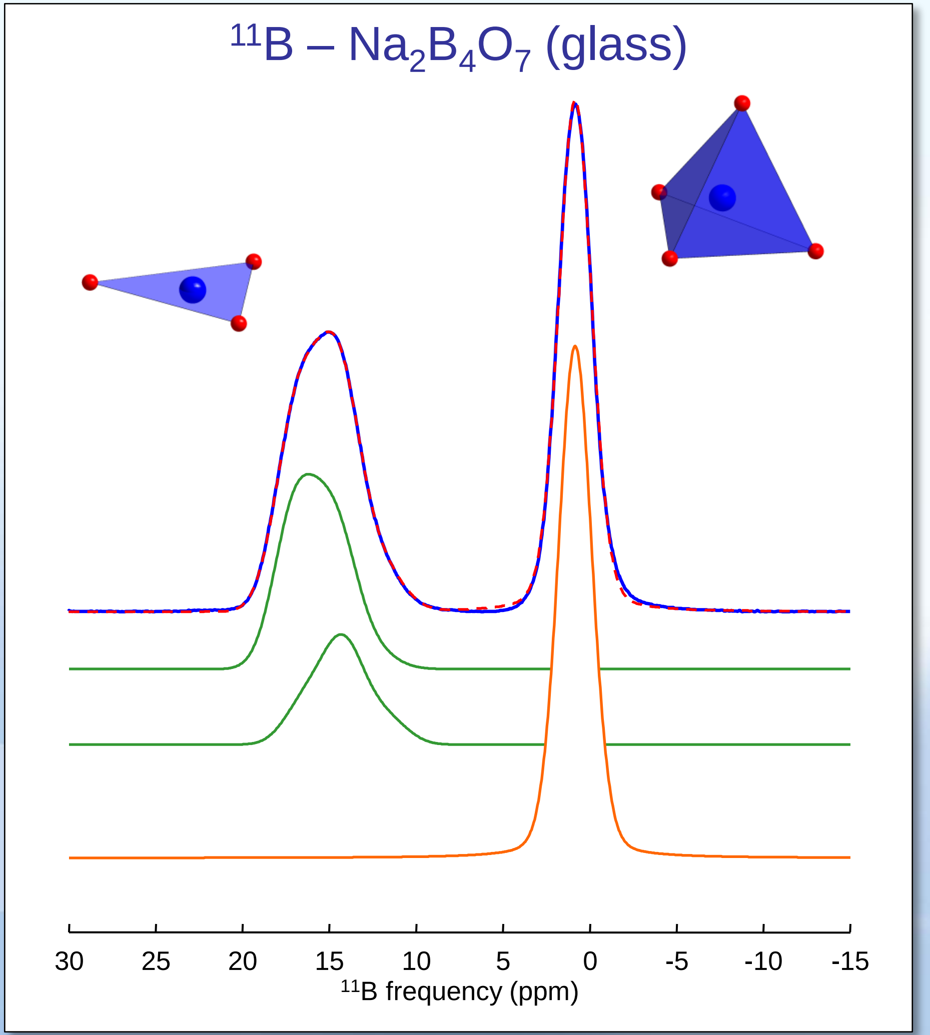
- ☞ coordination number
- ☞ 2nd coordination sphere neighbors
- ☞ local geometry

Width & shape
(*quadrupolar coupling*, EFG):

- ☞ (*p*-) orbital population unbalance
- ☞ local polyhedra distortion
- ☞ possibly long-range effect

Solid-State Nuclear Magnetic Resonance





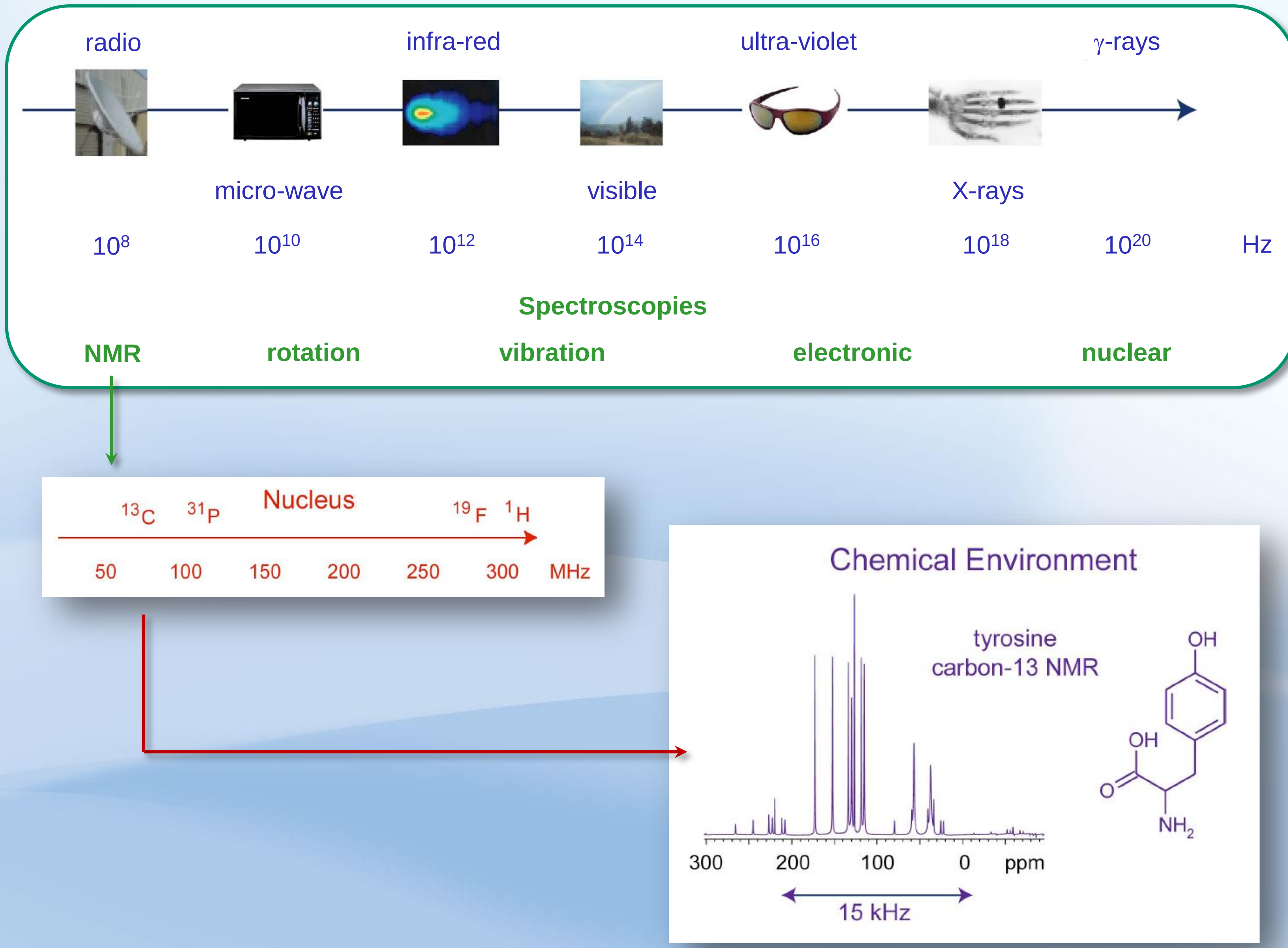
NMR is an atom-specific local probe

☞ distinguish between chemical environments

☞ quantitative

NMR & Motion…

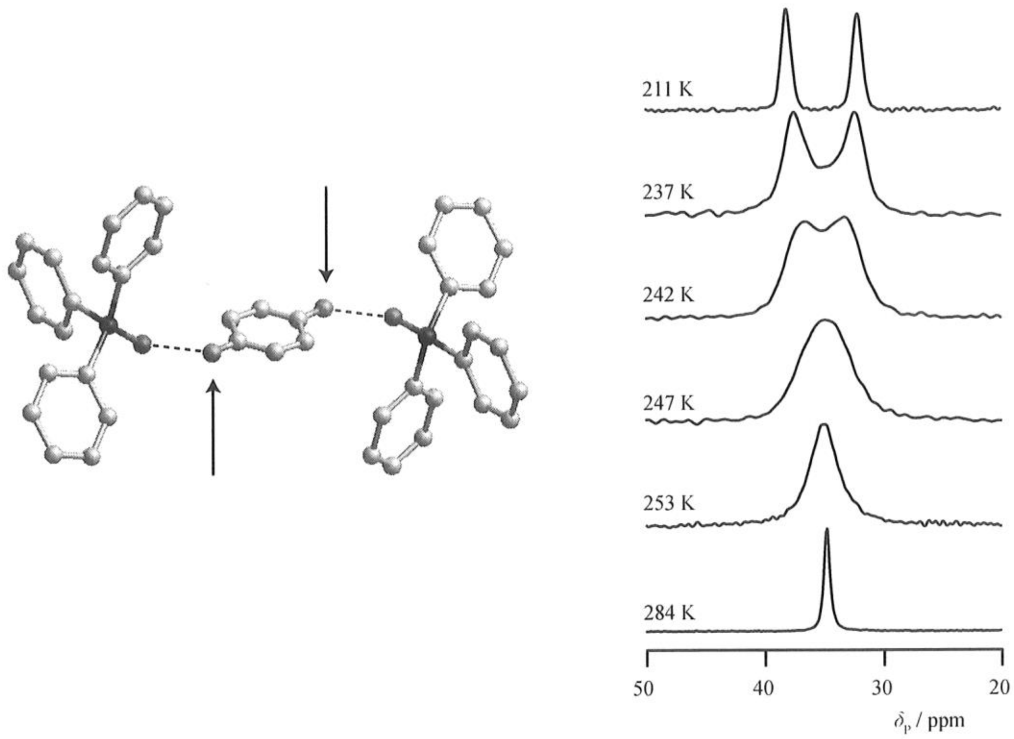
Time Scales



radio
infra-red
ultra-violet
γ-rays
micro-wave
visible
X-rays
10^8 10^{10} 10^{12} 10^{14} 10^{16} 10^{18} 10^{20} Hz
Spectroscopies
NMR
rotation
vibration
electronic
nuclear
Nucleus
^{13}C ^{31}P ^{19}F ^{1}H
50 100 150 200 250 300 MHz
Chemical Environment
tyrosine
carbon-13 NMR
OH
OH
O
NH_2
300 200 100 0 ppm
15 kHz

Effect of Dynamic « Disorder »

Effect of Mobility

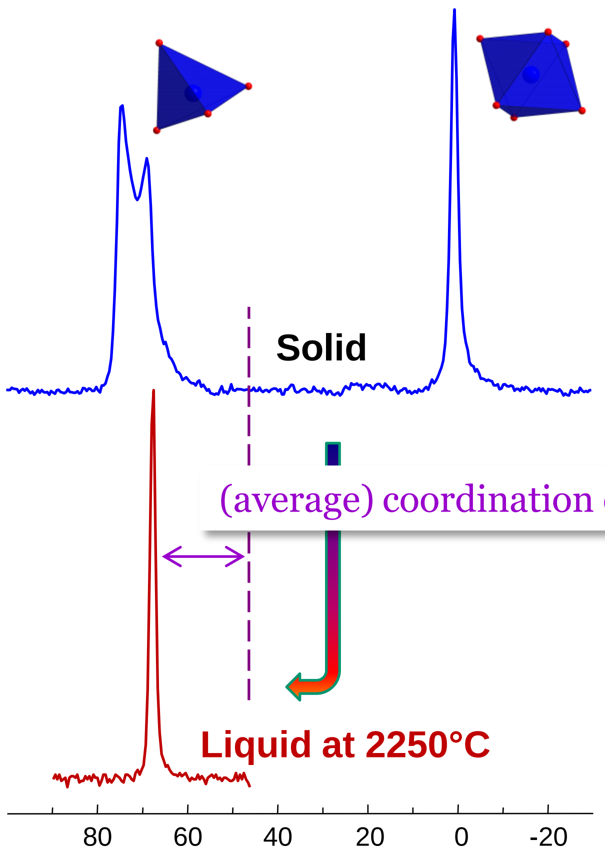


^{31}P spectra of 3:2 adduct of phenol and triphenylphosphine oxide

NMR & Melts: What Can We Learn?

"Structure" of the Melt

^{27}*Al* - $Y_3Al_5O_{12}$



High-Temperature Dynamics

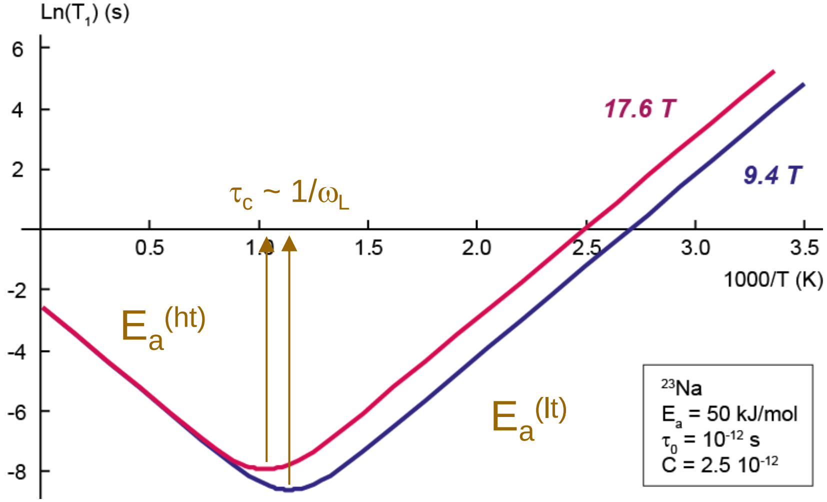
➡ "Brownian motion in a liquid or noncrystalline solid" (autocorrelation function α exp(-t/τ_c))

➡ Relaxation dominated by the fluctuation of the quadrupolar interaction

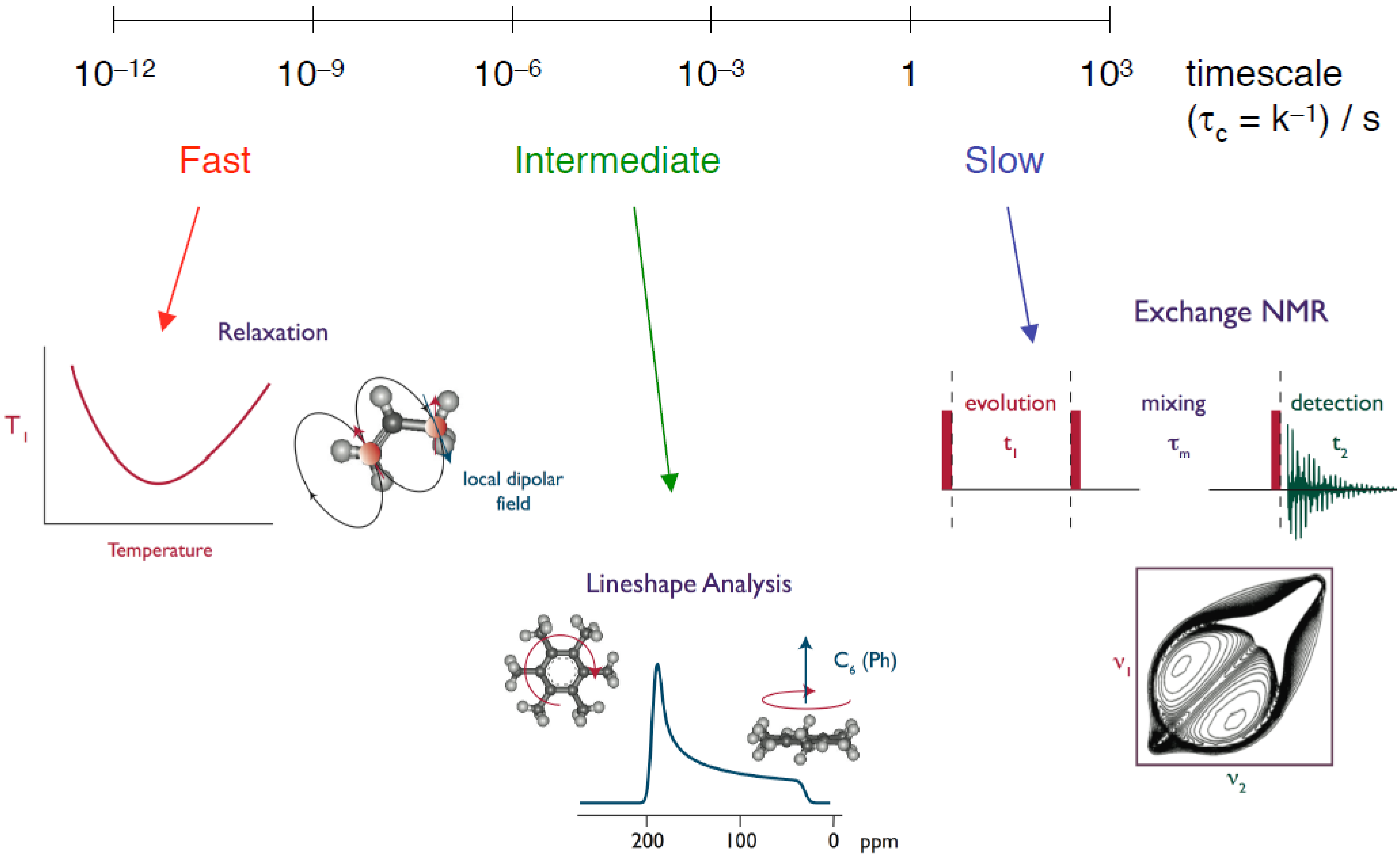
$$1/T_1 = C\left(\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{4\tau_c}{1+(2\omega\tau_c)^2}\right)$$

➡ Correlation time thermally activated

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

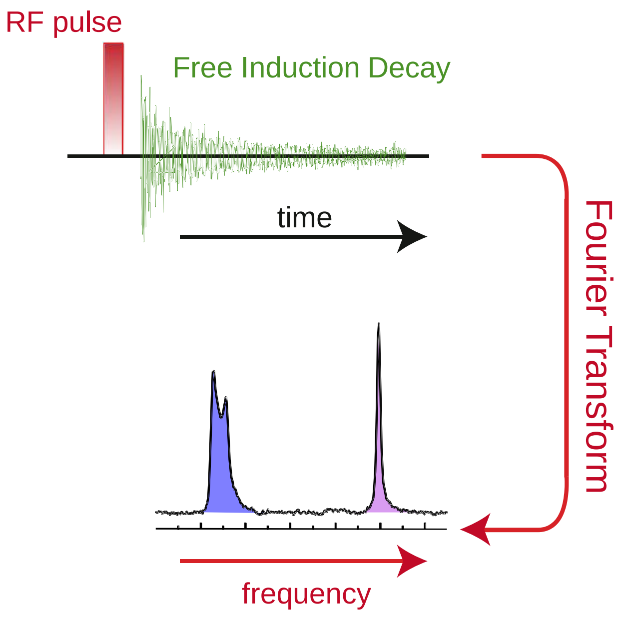


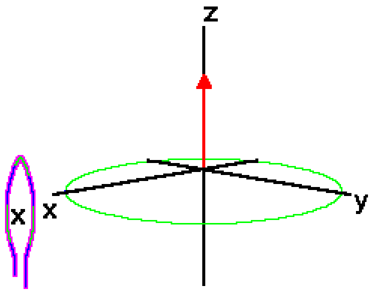
Timescales

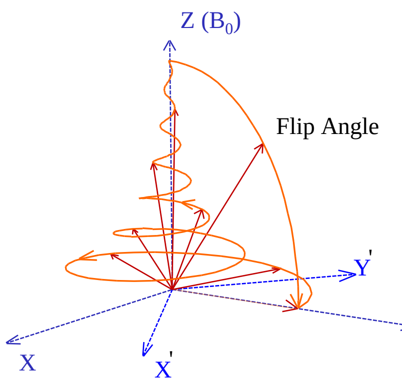


10^{-12}
10^{-9}
10^{-6}
10^{-3}
1
10^{3}
timescale
$(\tau_c = k^{-1})$ / s
Fast
Intermediate
Slow
Relaxation
T_1
Temperature
local dipolar field
Exchange NMR
evolution
t_1
mixing
τ_m
detection
t_2
ν_1
ν_2
Lineshape Analysis
C_6 (Ph)
200
100
0
ppm

Relaxation







Two types of relaxation process:

- **Spin-lattice relaxation**. Involves exchange of energy with the lattice and requires transitions between Zeeman levels.
- **Spin-spin relaxation**. Involves loss of the x,y-components of the magnetization. Does not require energy to be exchanged with the surroundings and does not necessarily result in changes in the populations in the nuclear spin energy levels.

In Solids:

$$T_1 \neq T_2 \neq T_2^*$$

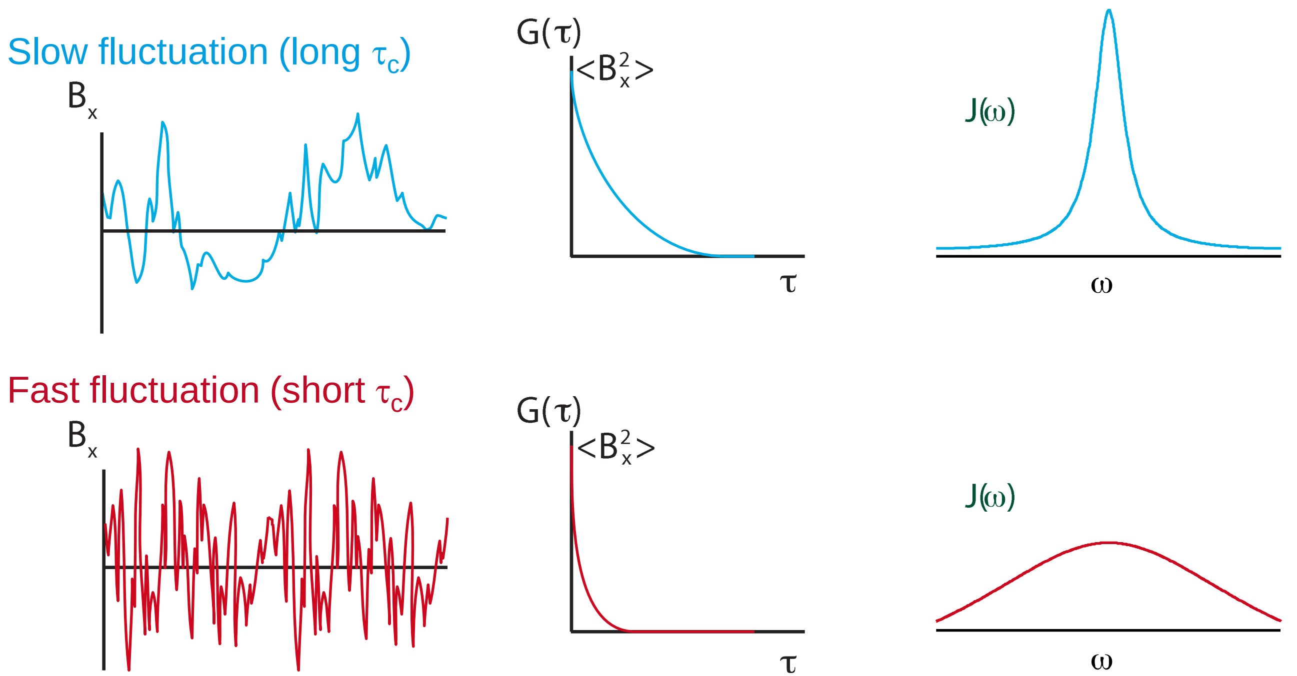
The Autocorrelation Function

→ Relaxation is caused by fluctuating local magnetic fields
→ Fluctuations at the Larmor frequency cause spin-lattice relaxation
→ Local fields which are almost static are effective for the spin-spin relaxation.

The autocorrelation function of the local field descibes how rapidly the field fluctuate

$$G(\tau) = \langle B_x(t) B_x(t+\tau) \rangle \neq 0$$

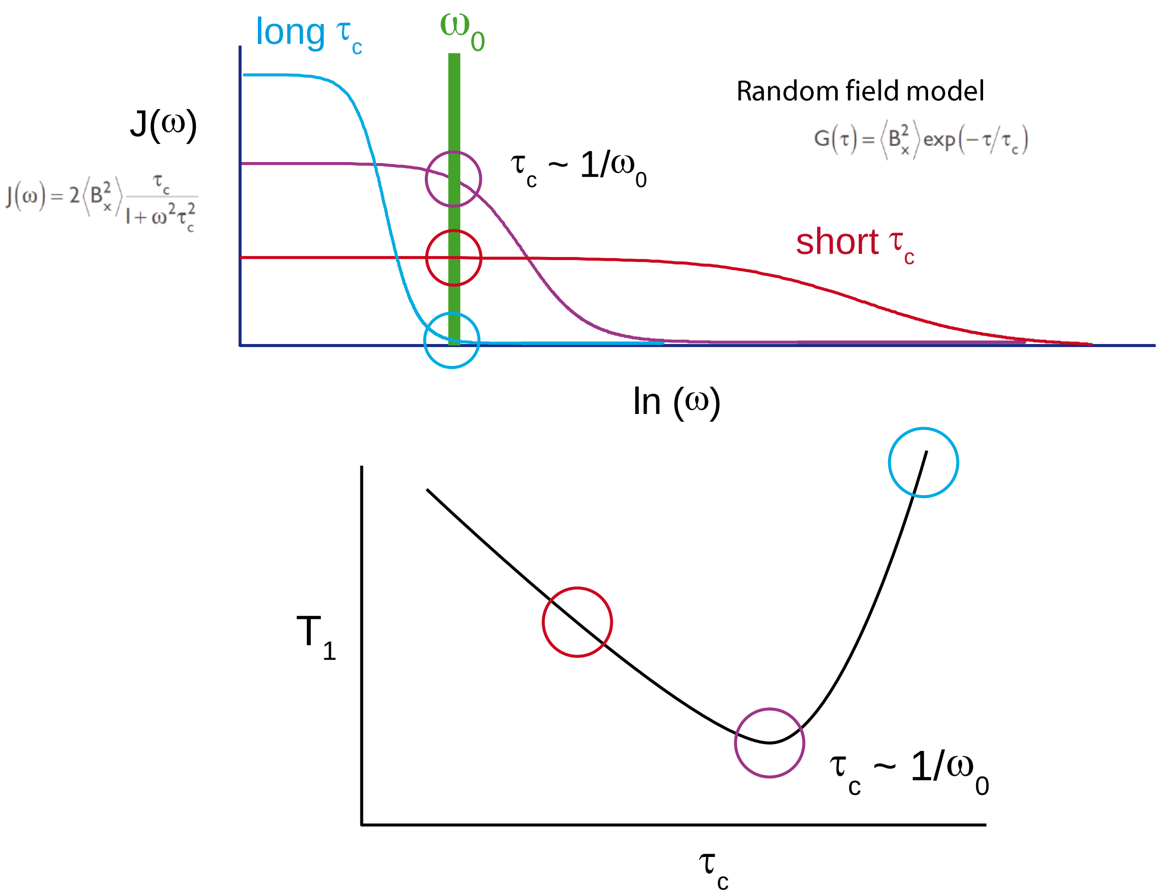
$$J(\omega) = 2\int_0^{\infty} G(\tau) \exp(-i\omega\tau) d\tau$$



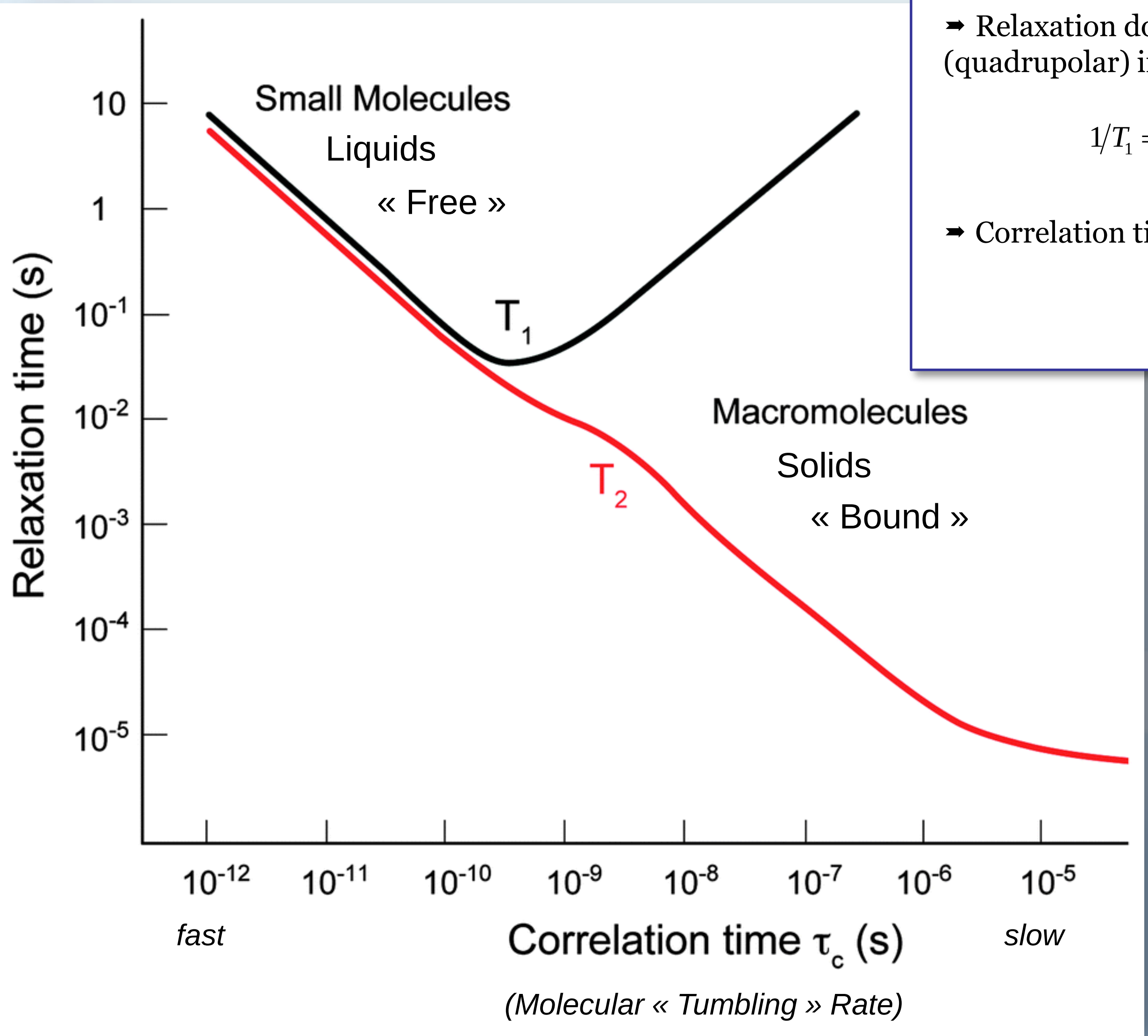
Autocorrelation Function   *Spectral Density*

The Spectral Density

→ The highest the spectral density at a given frequency, the more efficient the relaxation
→ A T_1 minimum may appear as a function of temperature



T_1 and T_2 Relationships



- "Brownian motion in a liquid or noncrystalline solid" (autocorrelation function α $\exp(-t/\tau_c)$)
- Relaxation dominated by the fluctuation of the (quadrupolar) interaction

$$1/T_1 = C\left(\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{4\tau_c}{1+(2\omega\tau_c)^2}\right)$$

- Correlation time thermally activated

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

Designs

Designs

Static (home made!)

- Stebbins, J. F.; Schneider, E.; Murdoch, J.B.; Pines, A.; Carmichael, I. S. E. “*New probe for high-temperature NMR-spectroscopy with ppm resolution*” Review of Scientific Instruments **1986** *57* 39-42
- Shimokawa, S.; Maekawa, H.; Yamada, E.; Maekawa, T.; Nakamura, Y.; Yokokawa, T. “*A high-temperature (1200°C) probe for NMR experiments and its application to silicate melts*” Chemistry Letters **1990** *4* 617-620
- Adler, S.B.; Michaels, J.N.; Reimer, J.A."*A Compact High-temperature Nuclear-Magnetic-Resonance Probe for Use in a Narrow-Bore Superconducting Magnet*" Review of Scientific Instruments **1990** *61* 3368-3371
- Kolem, H.; Kanert, O.; Schulz, H.; Guenther, B. "*Design and Operation of a Variable High-Temperature Oxygen Partial-Pressure Probe Device for Solid-State NMR*" Journal of Magnetic Resonance **1990** *87* 160-165.
- Massiot, D.; Bessada, C.; Echegut, P.; Coutures, J. P.; Taulelle, F. “*High-Temperature NMR-Study of Lithium Sodium-Sulfate*” Solid State Ionics **1990** *37* 223-229

MAS

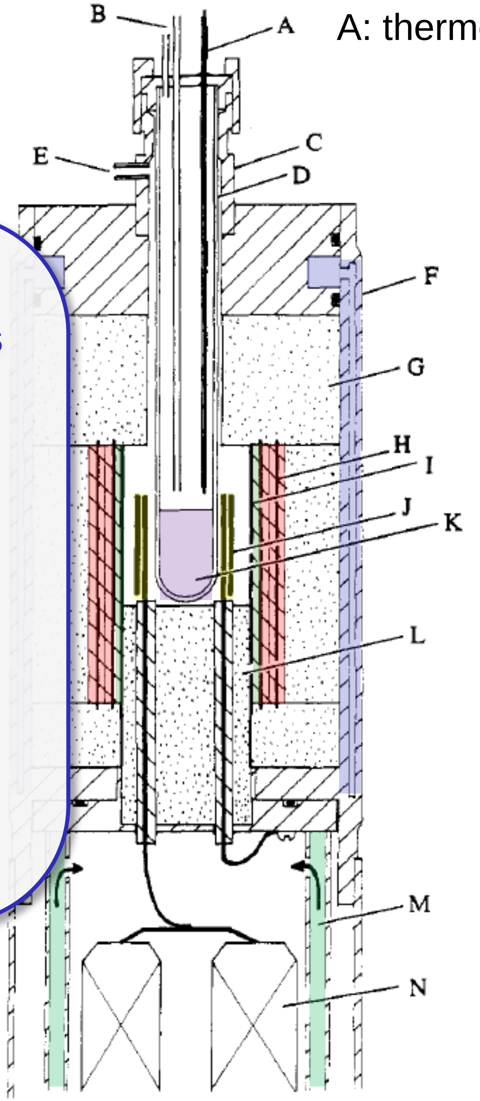
- Stebbins, J. F.; Farnan, I.; Williams, E. H.; Roux, J. “Magic Angle Spinning NMR Observation of Sodium Site Exchange in Nepheline at 500°C” Phys. Chem. Minerals **1989** *16* 763 (Doty Scientific)
- van Wüllen, L.; Schwering, G.; Naumann, E.; Jansen, M. “*MAS-NMR at very high temperatures*” Solid State Nucl. Magn. Reson. **2004** *26* 84 (Bruker)

Furnace Designs

sample gaz in/out: B

furnace gaz outlet: E

- → **Up to 1300°C**
- → **Mo Coil & heating elements**
- → **Careful design of heating elements**
- → **Coil shielded from heating elements**
- → **Reverse current (=> two experiments for each T)**
- → **Probe isolation from magnet (water cooled)**
- → **Air cooling of electronics separated from sample**



A: thermocouple

F: brass water jacket

G: ceramic fiber insulation

H: heating elements

I: refractory metal rf shield

J: coil

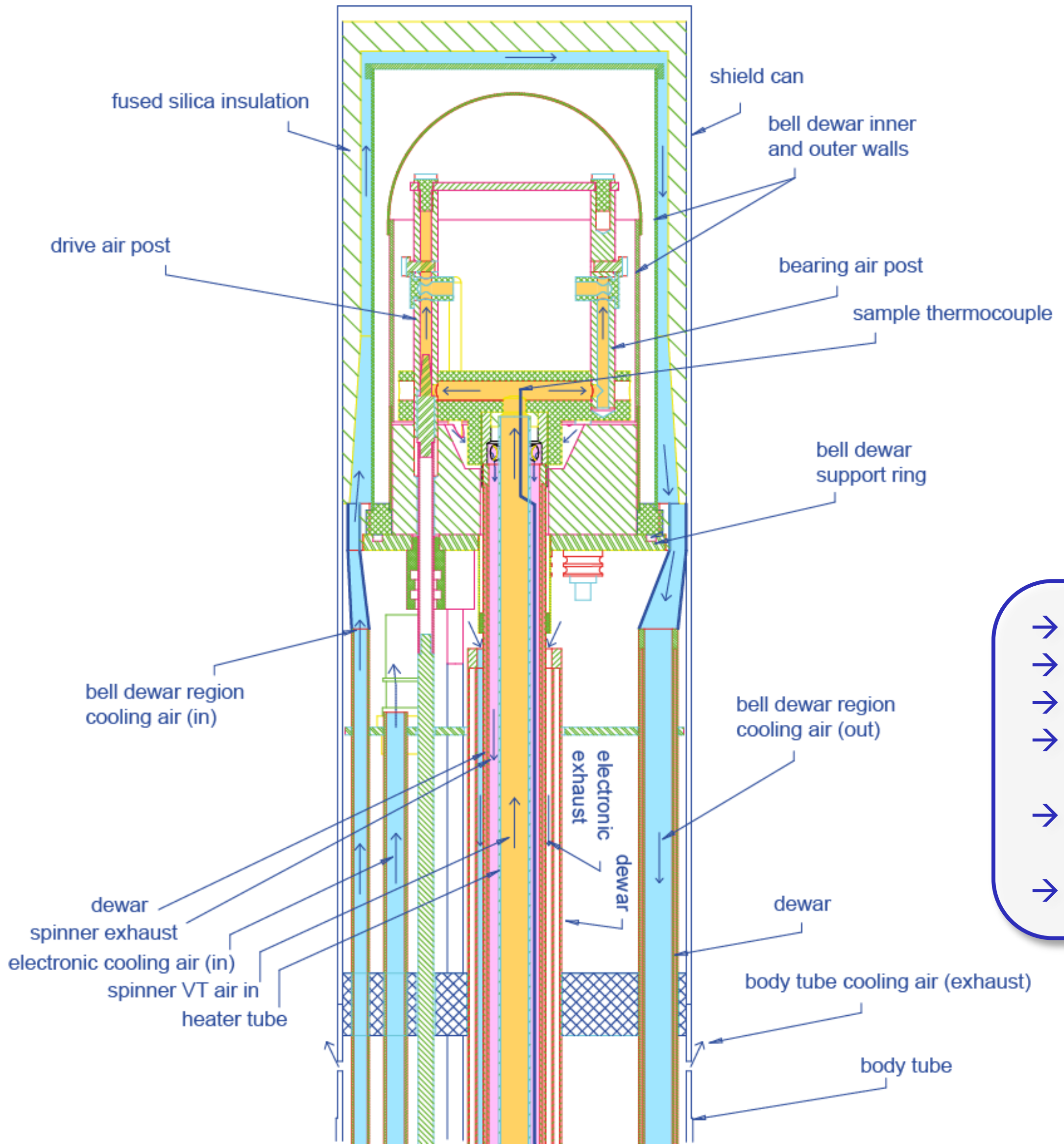
K: sample

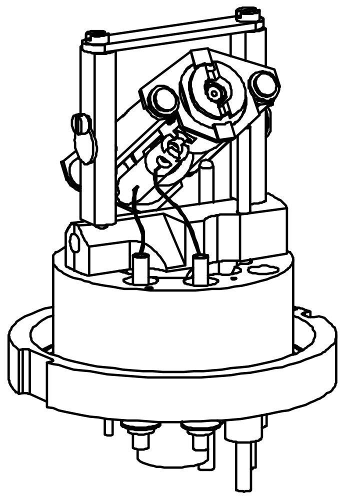
M: cooling air tube

N: tuning capacitors

Stebbins, Chem. Rev. **1991** *91* 1353-1373

HT MAS by Doty: Probe Design

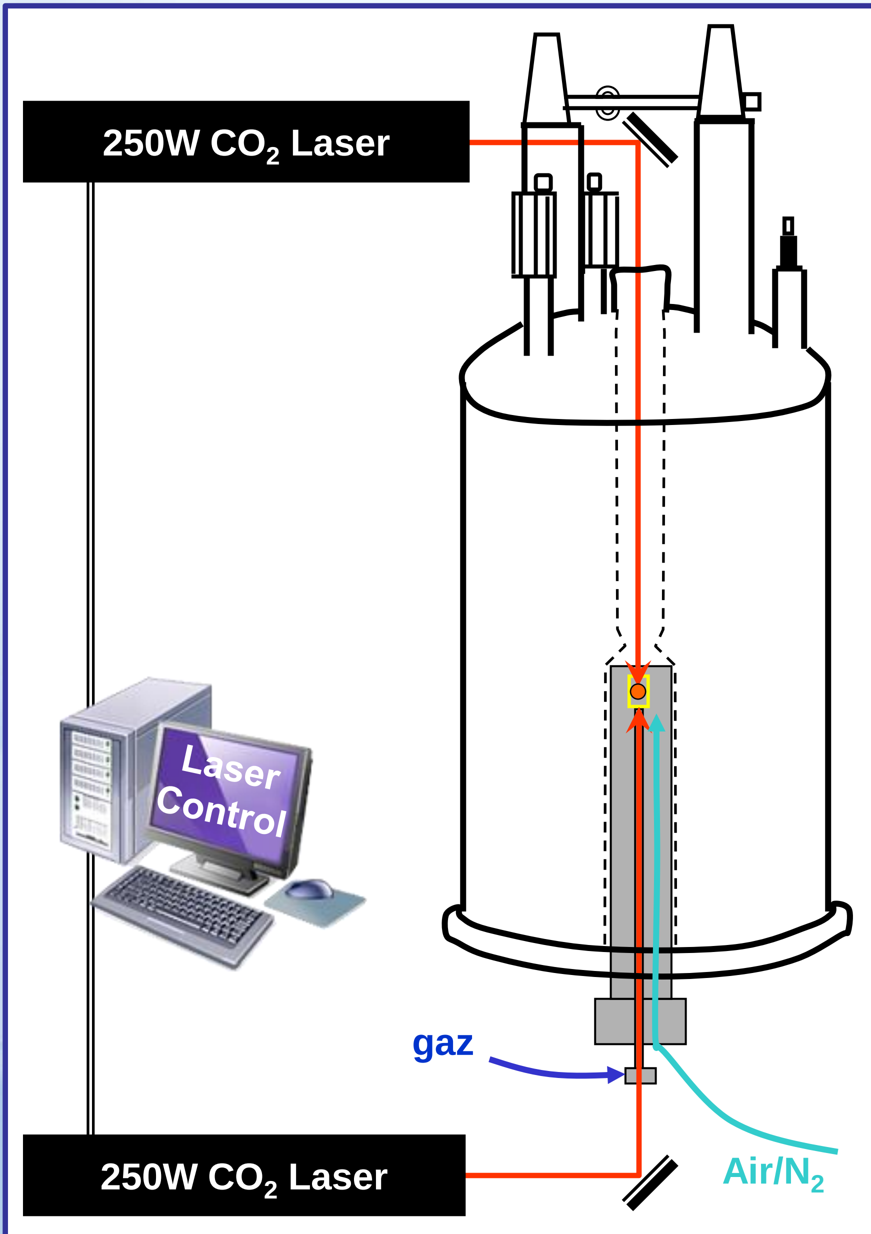


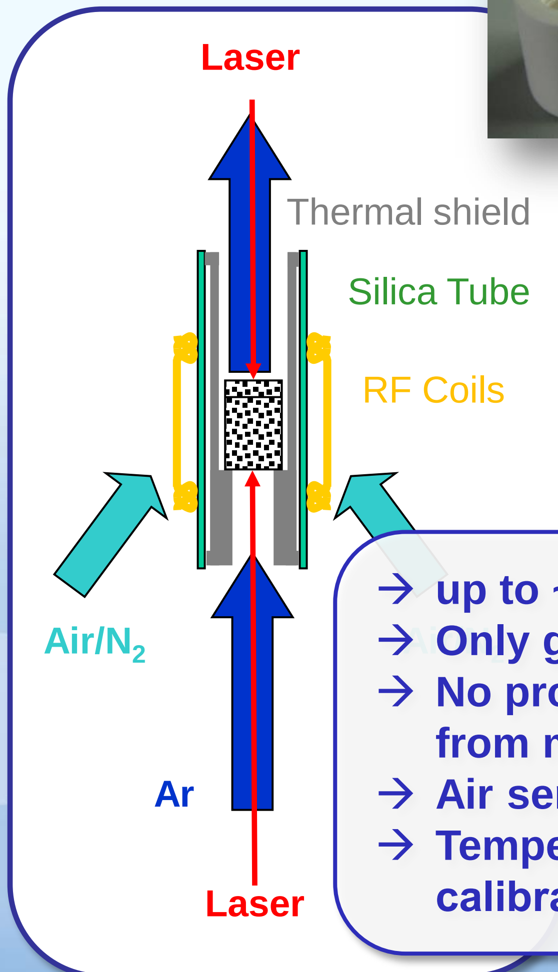


- → Simple, safe operation up to 700°C
- → Spinning up to 6 kHz (5 kHz above 700°C)
- → Double-balanced, multi-X, high-efficiency RF
- → Ultra-low (<1%) thermal gradients silicon-nitride stator, rotor and turbine
- → 45 kHz ^{1}H decoupling at 600°C, 500 MHz (double-tuned available up to 500 MHz)
- → Efficient heat exchanger for maximum safety

DOTY SCIENTIFIC

Laser UHT Probe: the Crucible Design

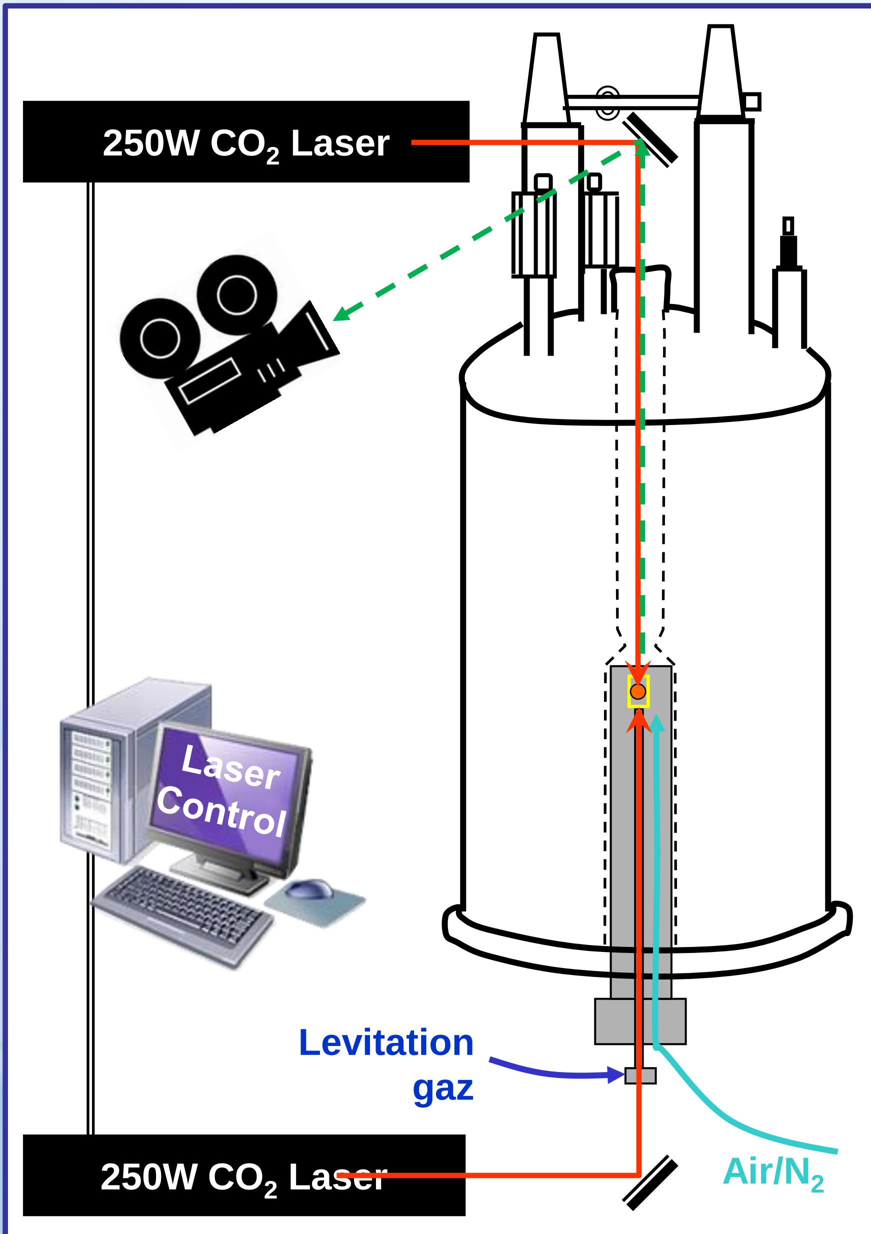


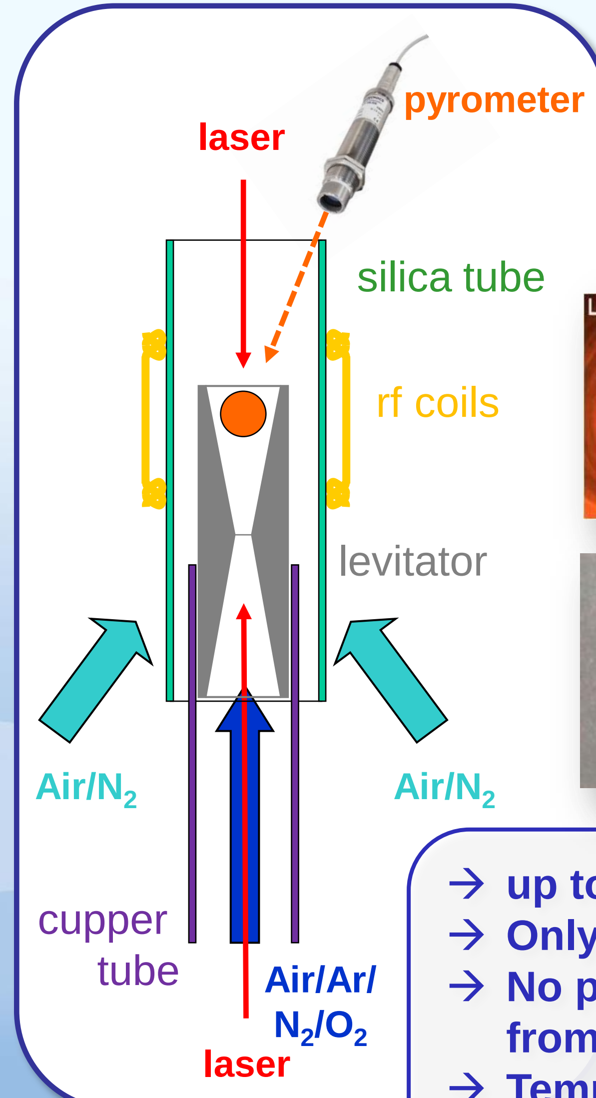


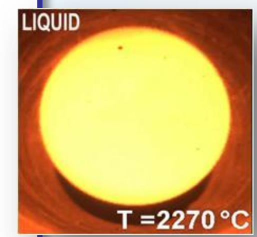
- → up to ~1300°C
- → Only gas cooled
- → No probe isolation from magnet
- → Air sensitive samples
- → Temperature calibration…

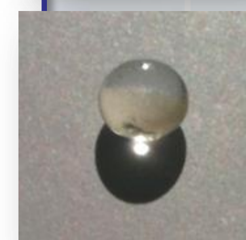
Massiot et al., Solid State Ion. **1990** *37* 223-229
Bonafous et al., J. Chim. Phys. **1995** 92 1867-1870
Lacassagne et al., J. Phys. Chem. B **2002** 106 1862-

Laser UHT Probe: the Levitation Design…





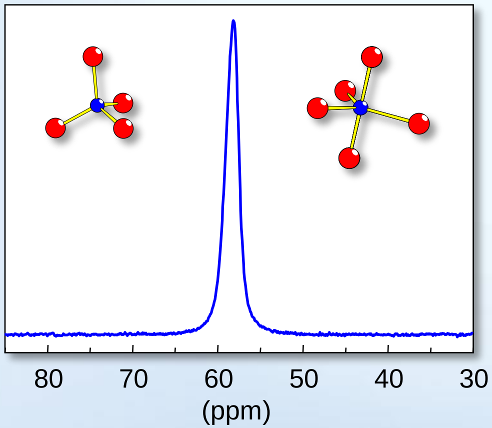


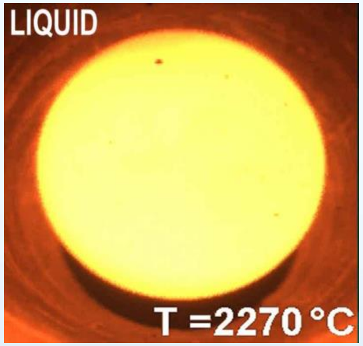


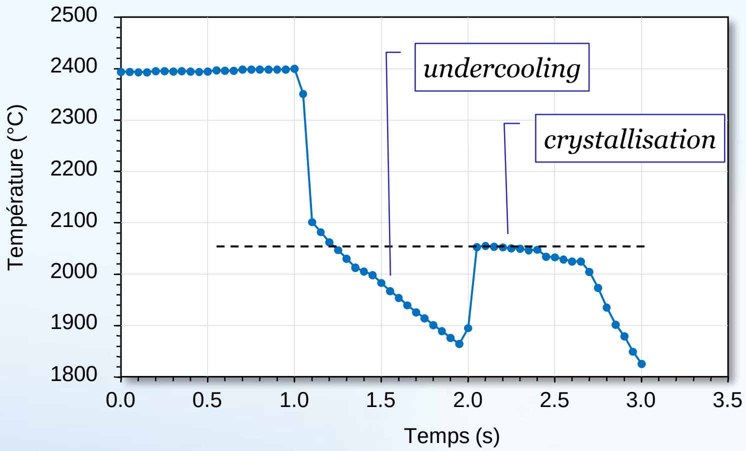
- → up to ~2500°C
- → Only gas cooled
- → No probe isolation from magnet
- → Temperature calibration…

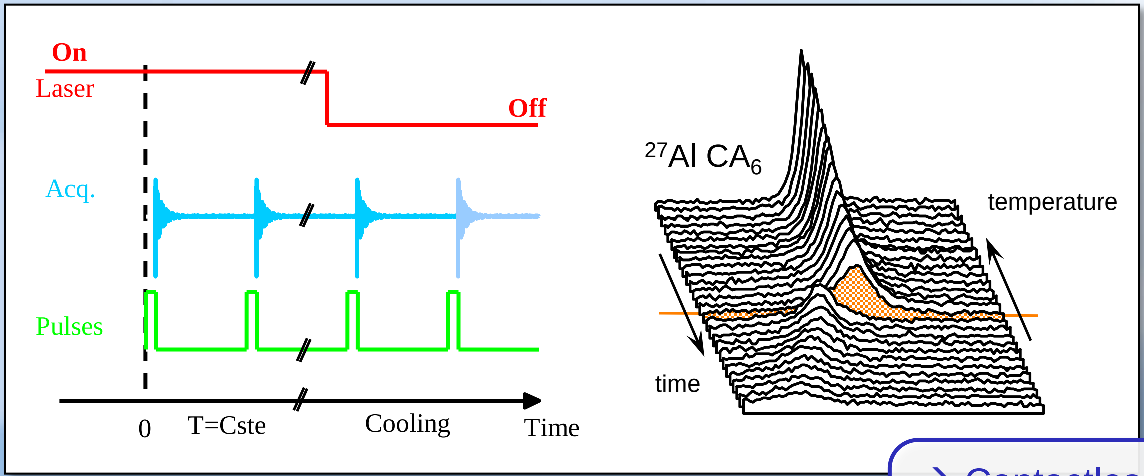
Cooling down Melts

66mg Al_2O_3 at 2320°C





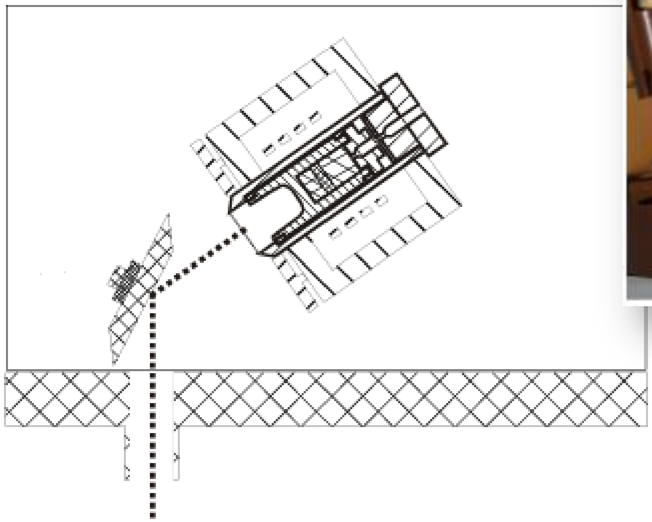


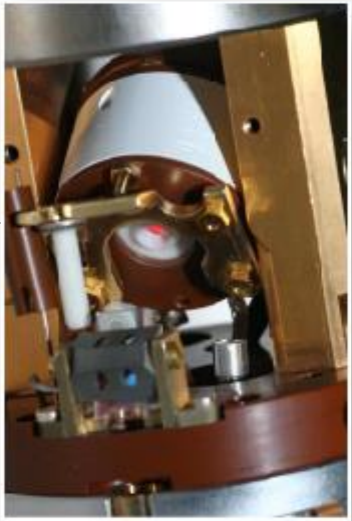


- → Contactless technology
- → Up to 2500°C
- → Time resolved experiments

Florian et al., Solid State Nuc. Magn. Reson. ***5*** *233 (1995)*
Ansel et al., Phys. Rev. Let. ***78*** *464 (1997)*

HT MAS by Bruker: Probe Design





→ Simple, safe operation up to 700°C
→ Spinning up to 5 kHz
→ Gas-cooled probe
→ Regular 7mm rf specifications

BRUKER

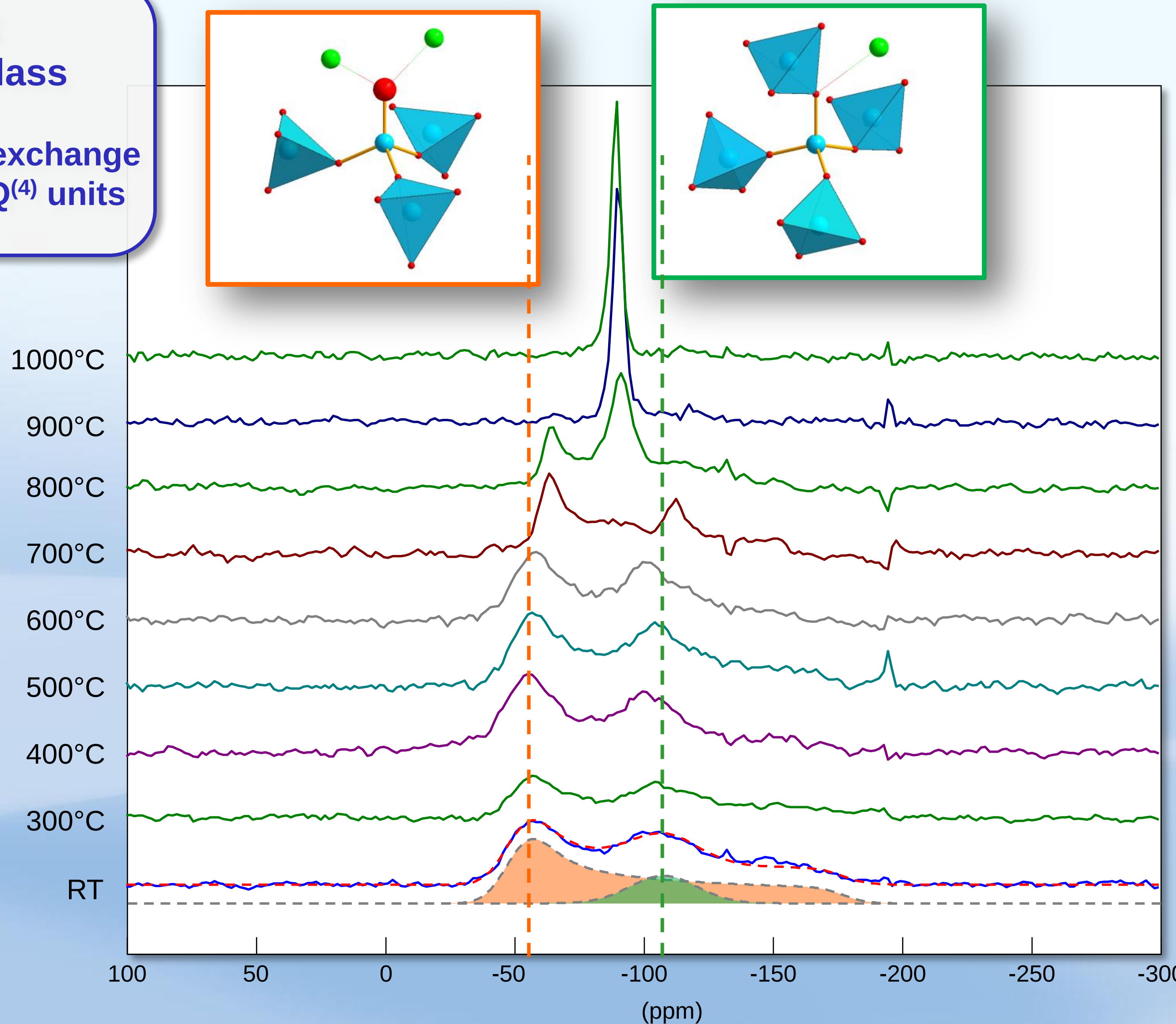
H. Ernst, D. Freude, T. Mildner, I. Wolf,
Solid State Nucl. Magn. Reson. **1996** *6* 147

NMR around T_g

The Silicate Glass Transition Dynamics

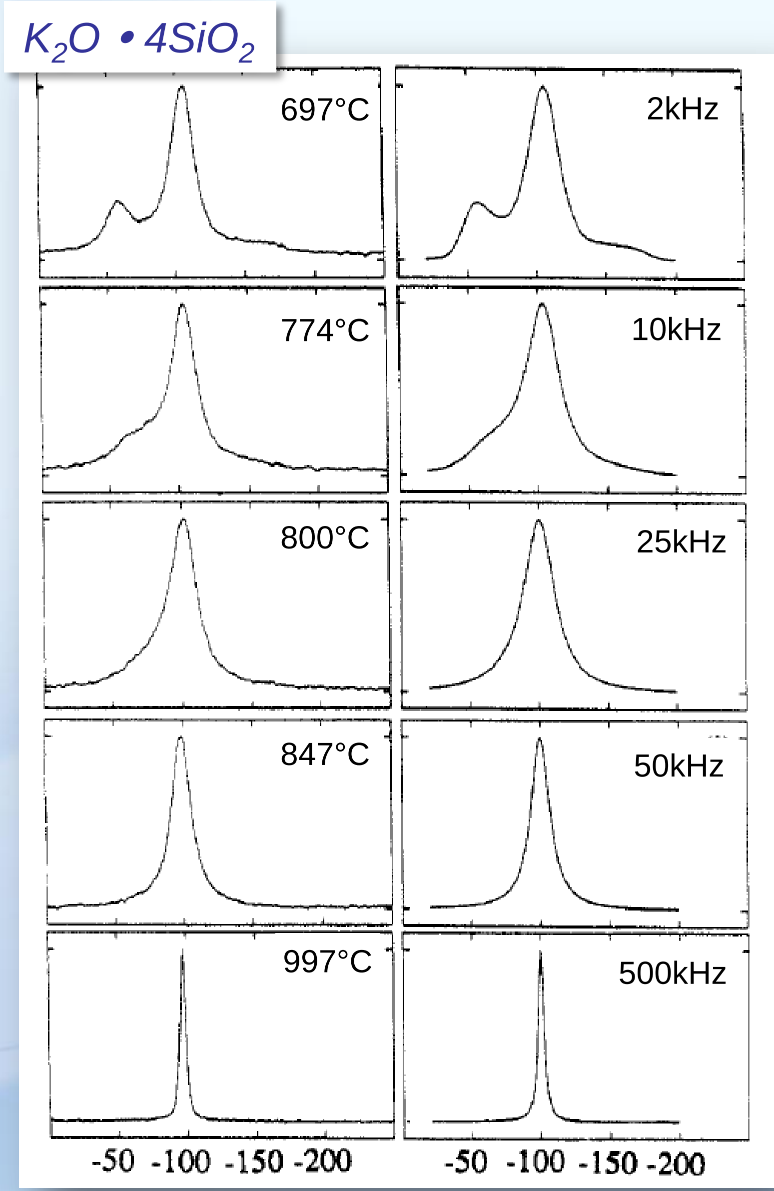
^{29}Si HT NMR
$5SiO_2 \bullet 2Na_2O$ glass

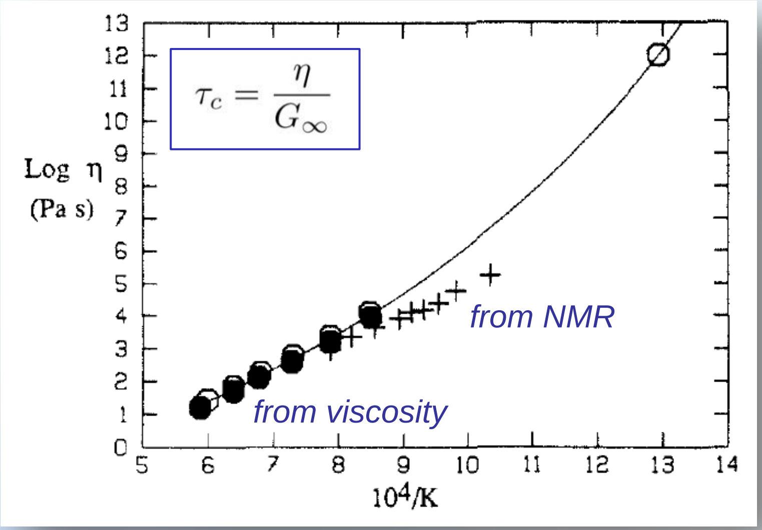
Progressive chemical exchange between the $Q^{(3)}$ and $Q^{(4)}$ units

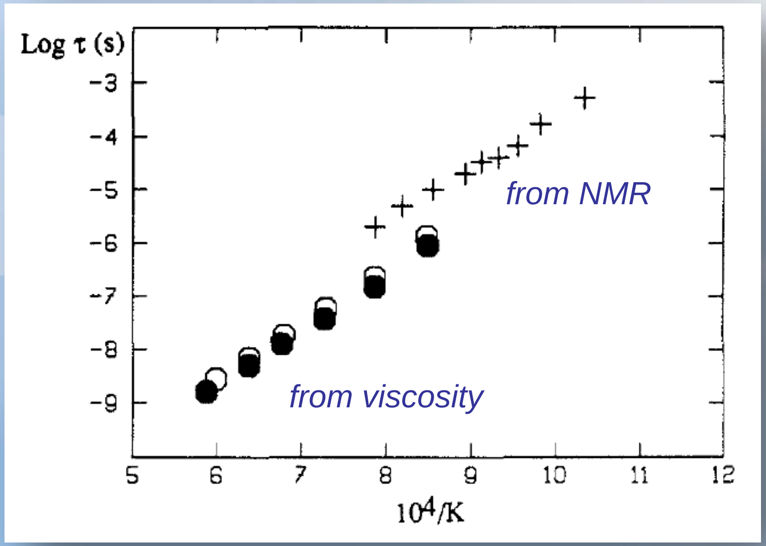


Charpentier, private comm. (2010)

The Silicate Glass Transition Dynamics





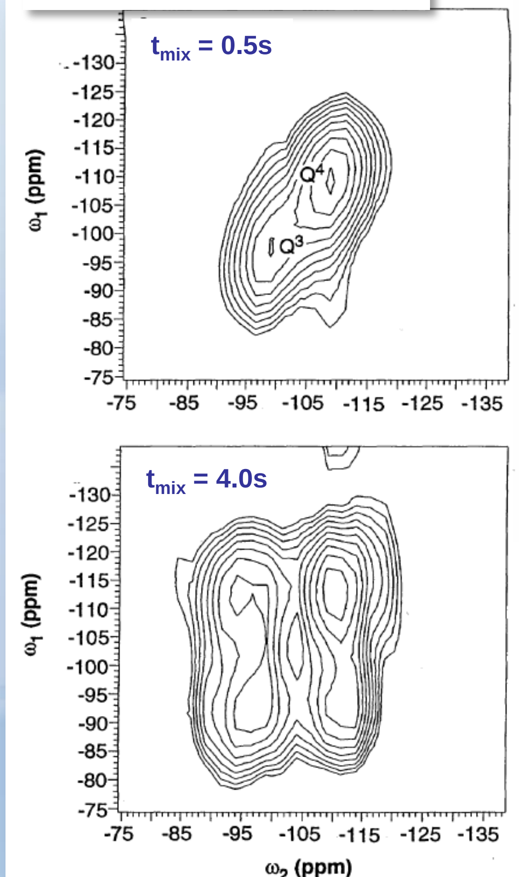


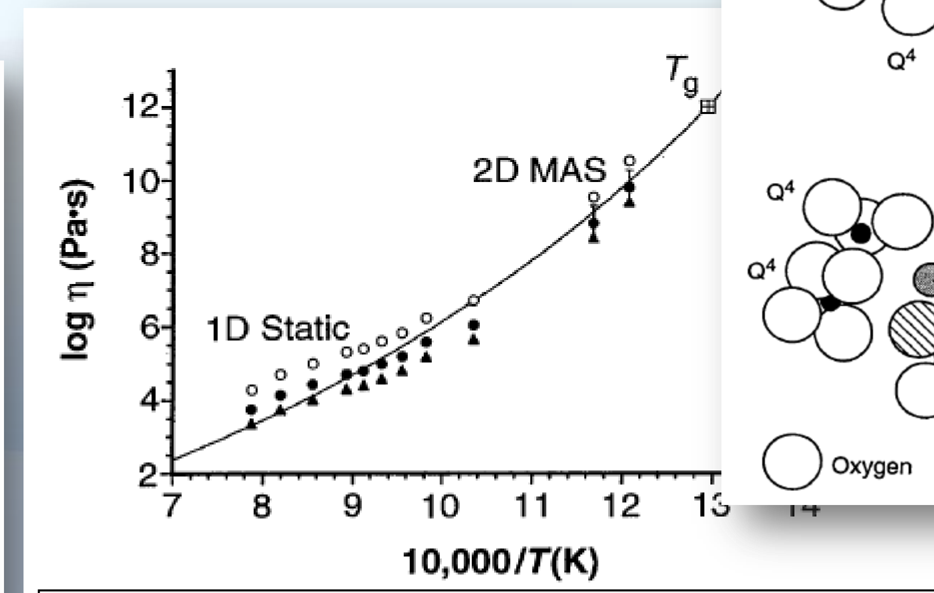
Farnan & Stebbins, J. Amer. Chem. Soc. **1990** *112* 32-38

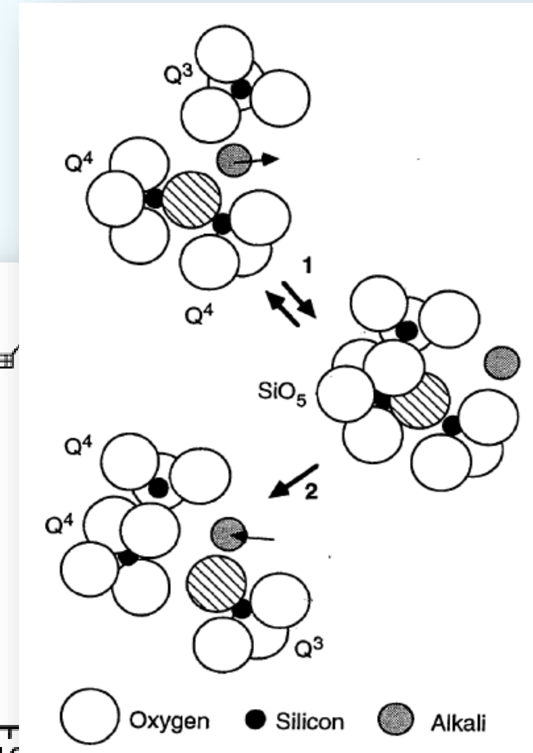
Probing Slow Motions in Silicates

Georges, Am Miner 1995 80 878-884 [^{23}Na albite]
Stebbins, J. Phys Chem Miner 1989 16 763-766 [^{23}Na nepheline]
Farnan, Science 1994 265 1206-1209 [^{29}Si silicates]

$K_2{}^{29}Si_4O_9$ T=550°C
Exchange time ~ 3 ± 2 s







Solid curve = bulk viscosity
Open circles = from Maxwell
Solid triangles = from Eyring
Solid circles = from Stokes + Einstein-Smolukowski

$$\tau_s = \eta_s / G_\infty$$

$$\eta = 2k_B T\tau / d^3$$

$$D = k_B T / 6\pi a\eta$$

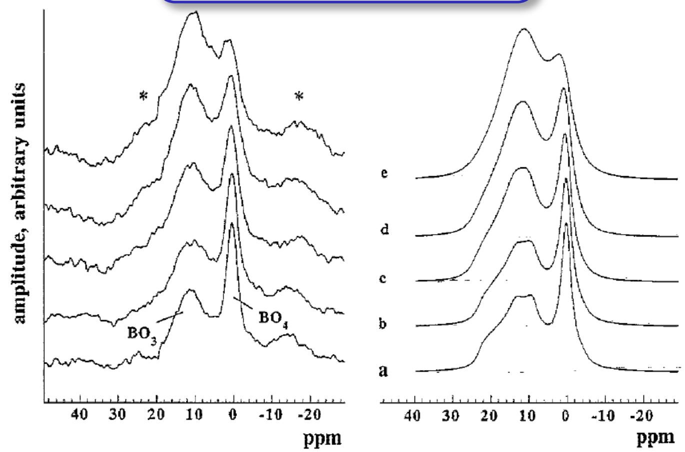
$$D = d^2 / 2\tau$$

Farnan and Stebbins, Science **1994** *265* 1206-1209

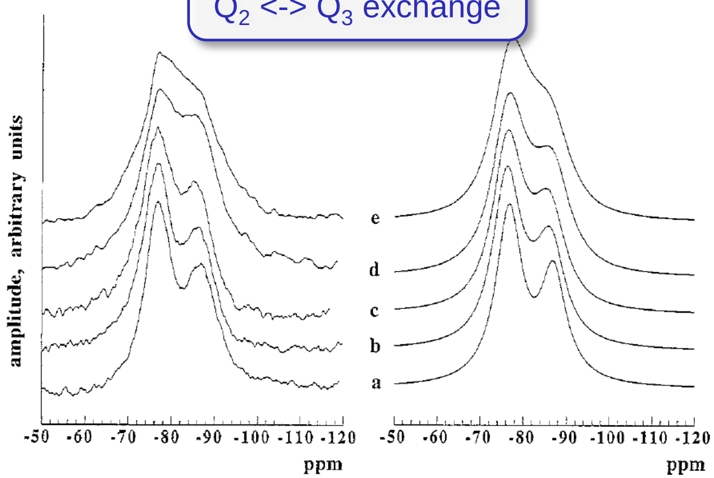
The Boro-Silicate Decoupling Case

44.5 Na_2O • 11 B_2O_3 • 44.5 SiO_2

^{11}B MAS NMR:
BO_3 <-> BO_4 exchange

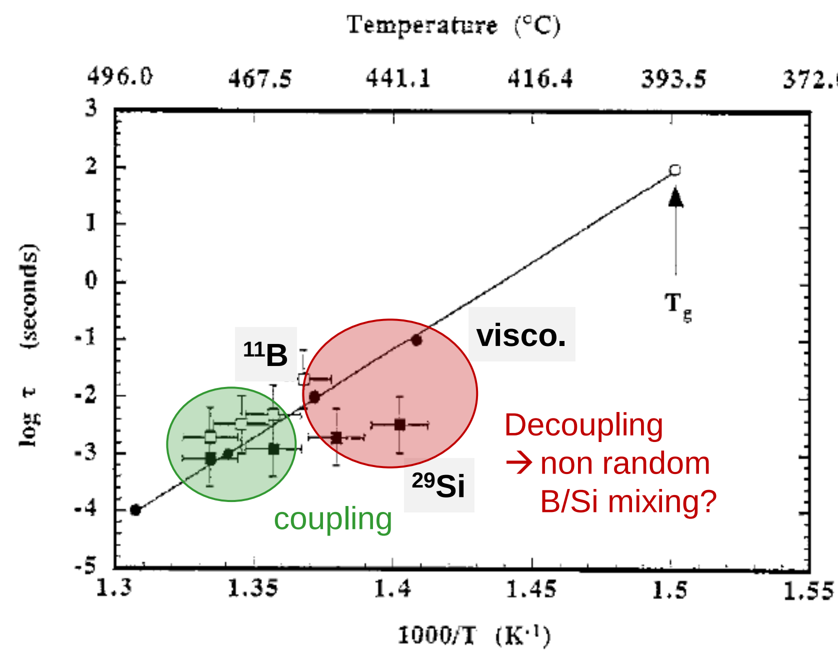


^{29}Si MAS NMR:
Q_2 <-> Q_3 exchange



Line Widths as Transverse Relaxation Time

- At high T: coupling between B-O and Si-O bond breaking, with oxygen ions moving into and out of the coordination polyhedra of B and Si with similar average rate.
- At low T: most Si-O bond breaking and site exchange is taking place at frequencies up to 50 times faster than the timescale of viscosity.

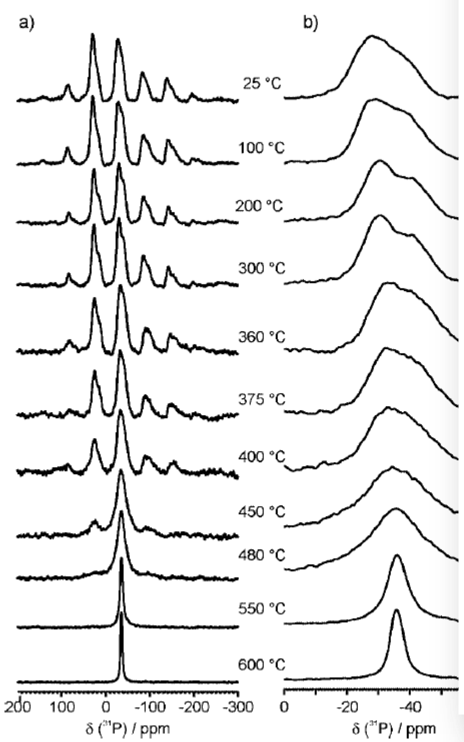


Inverse of species exchange rate data derived from ^{11}B and ^{29}Si data compared with shear relaxation times calculated from viscosity (Maxwell relation).

Stebbins et al., J. Non Cryst. Solids **1998** *224* 80-85

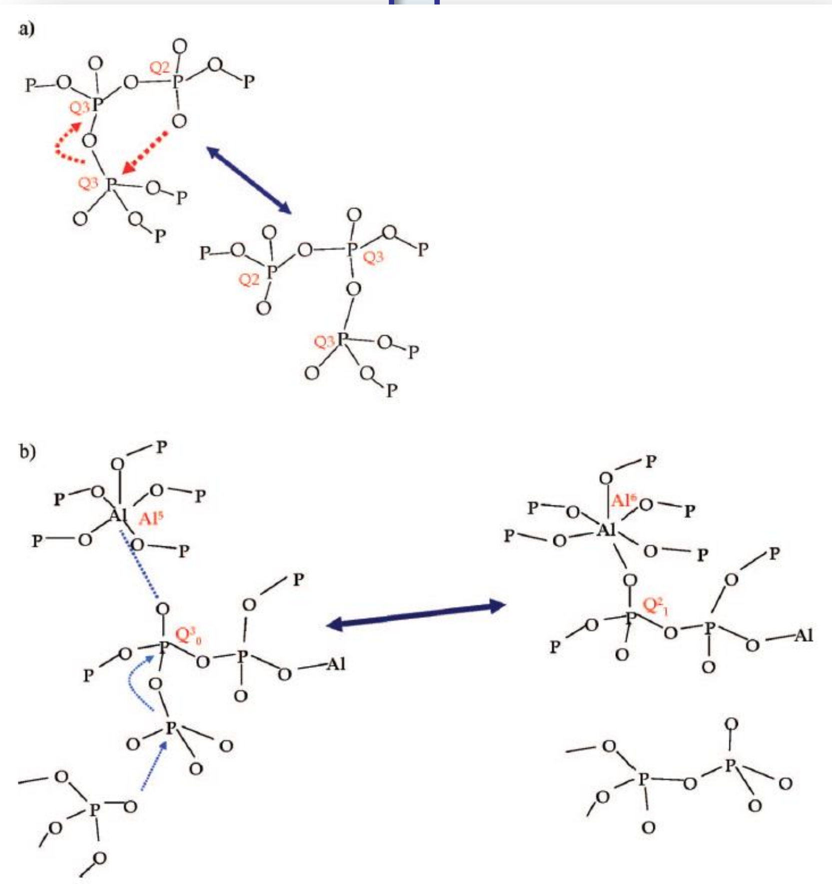
Alumino-Phosphate Glasses

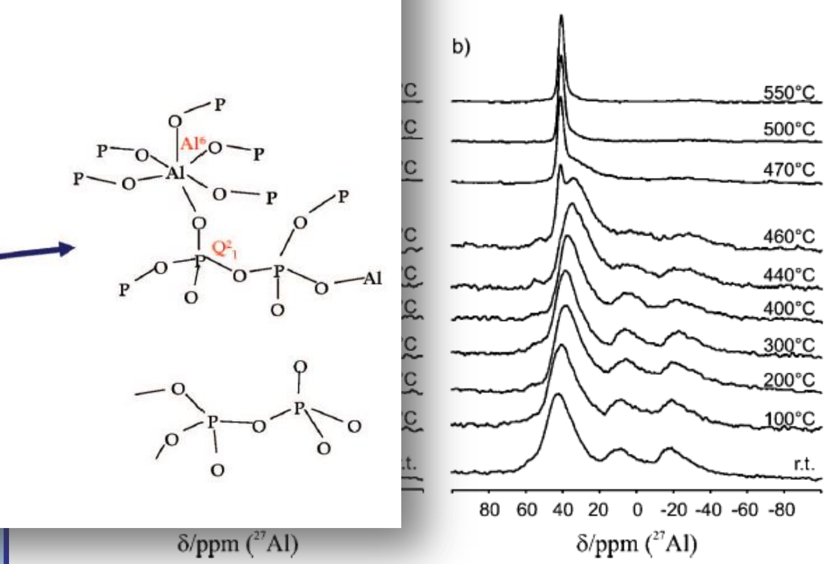
^{31}P MAS : $30K_2O \cdot xAl_2O_3 \cdot (70-x)P_2O_5$



$\nu_R = 4.50kHz, B_0 = 4.7T$

^{27}Al MAS : $50K_2O \cdot xAl_2O_3 \cdot (50-x)P_2O_5$





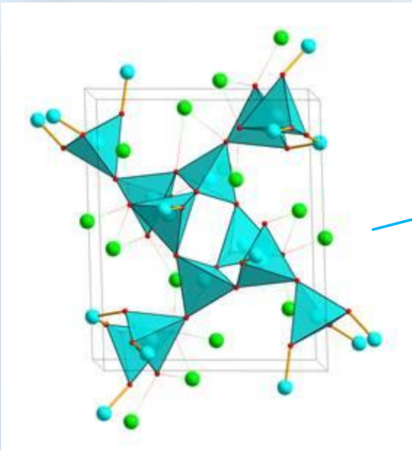
$\nu_R = 4.50kHz, B_0 = 7.0T$

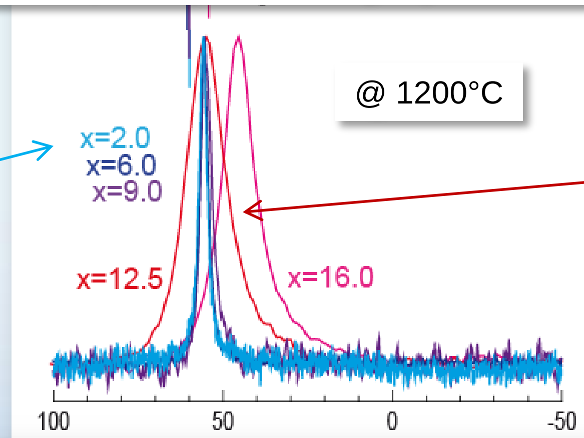
Wegner S, J Phys Chem B **2009** *113* 416-425

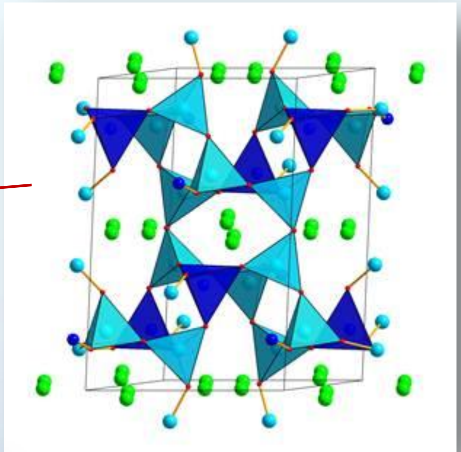
van Wullen, J Phys Chem B **2007** *111* 7529-7534

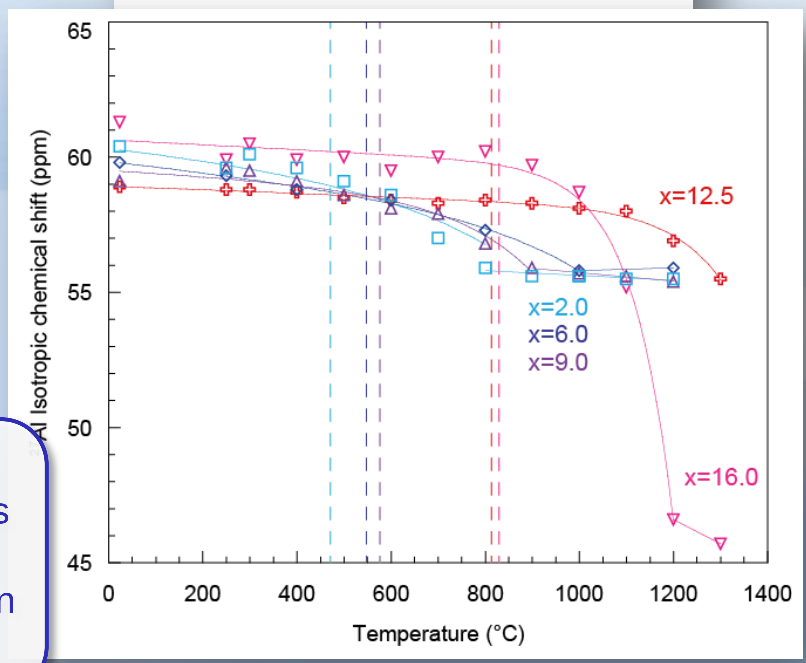
$Na_2Si_3O_7$–$NaAlSi_3O_8$: ^{27}Al NMR

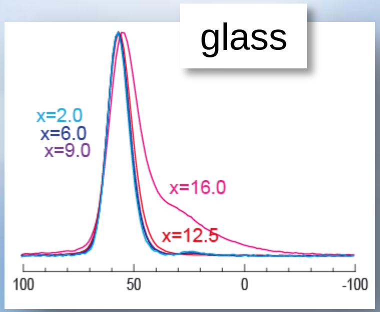
(25-x) Na_2O • x Al_2O_3 • 75 SiO_2











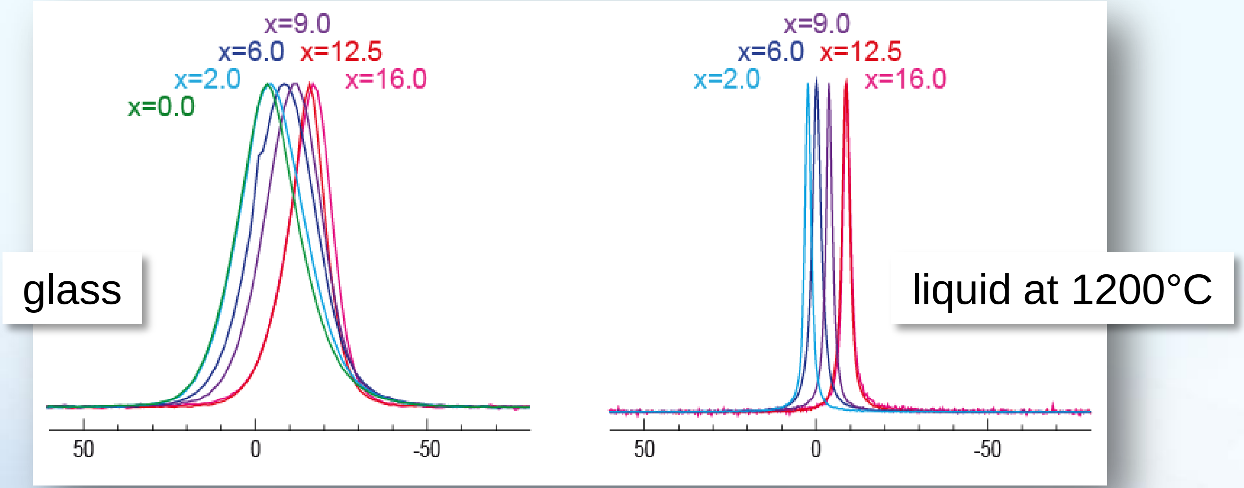
^{27}Al HT NMR

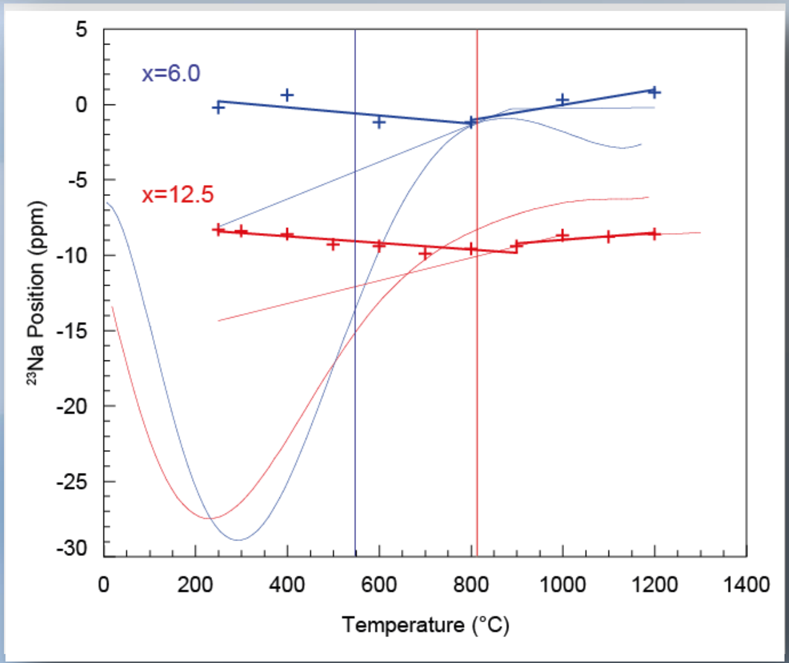
Na_2O • Al_2O_3 • SiO_2 glasses

Chemical exchange between AlO_5 and AlO_4 units

LeLosq et al., Geochim. Cosmochim. Acta **2014** *126* 495-514

²³Na Position vs Temperature





Increase of
Average d(NaO)

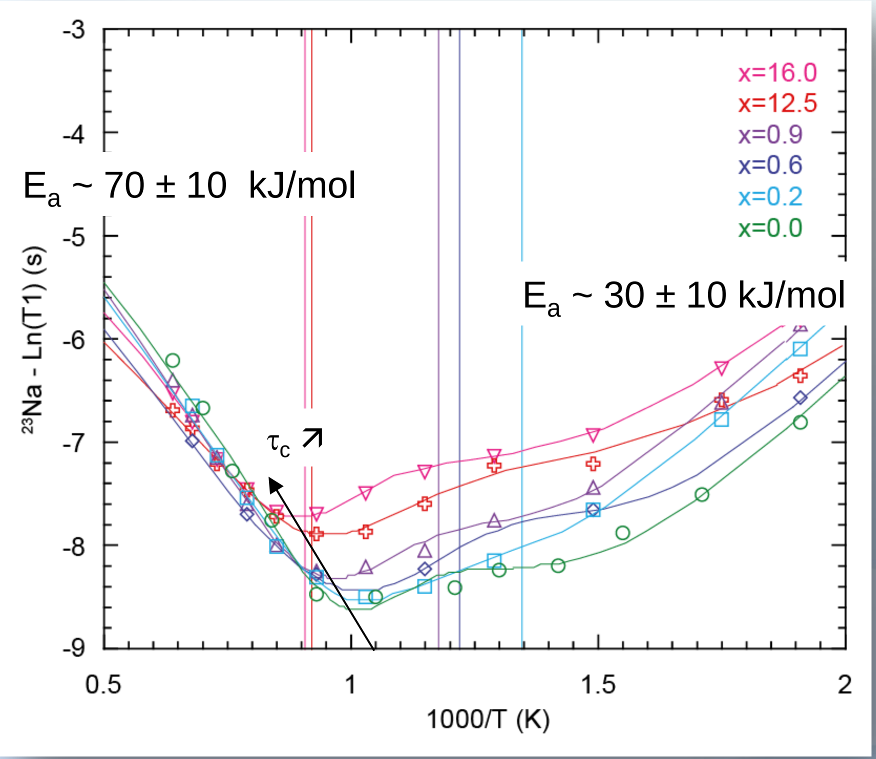
LeLosq et al., private communication

George et al., SSNMR 1997 10 9-17

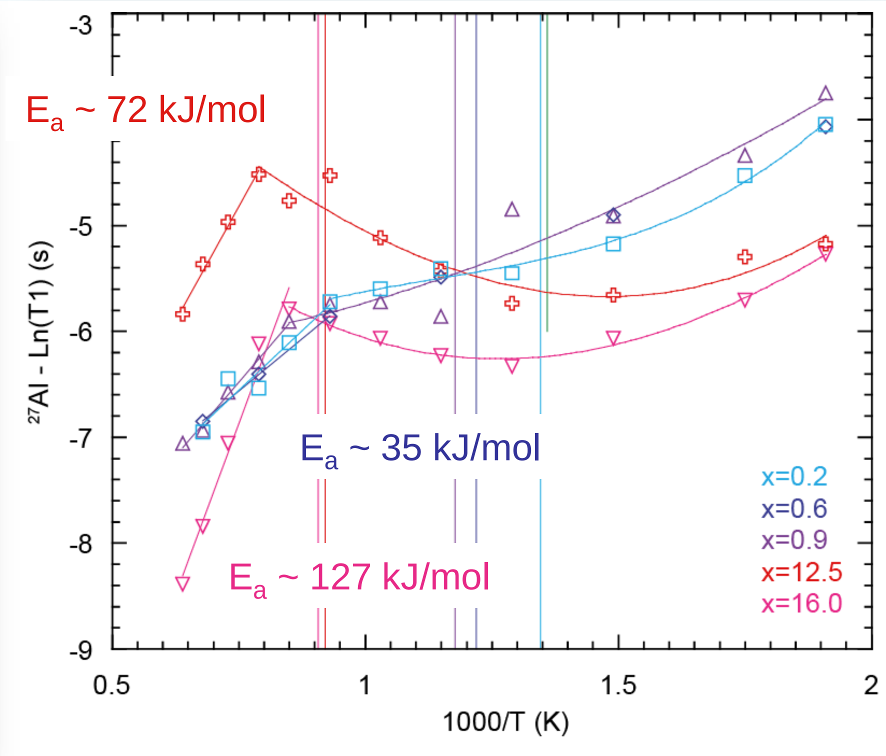
^{23}Na & ^{27}Al Relaxation Times

(25-x) Na_2O • x Al_2O_3 • 75 SiO_2

Na



Al



liquid
$E_a(^{24}Na)$ = 57 ± 12kJ/mol

« solid »
Jump diffusion

liquid
Effects of polymerisation

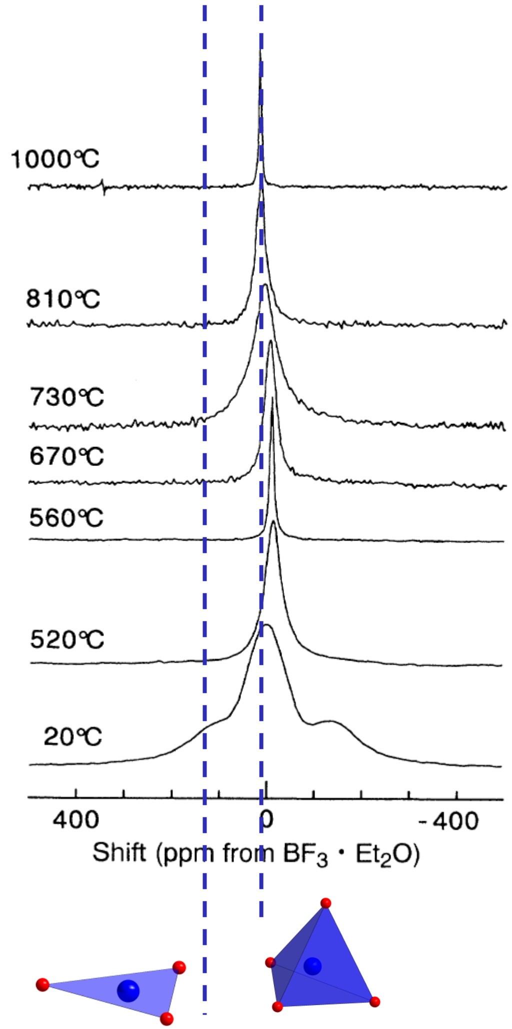
« solid »
Na diffusion

LeLosq et al., private communication

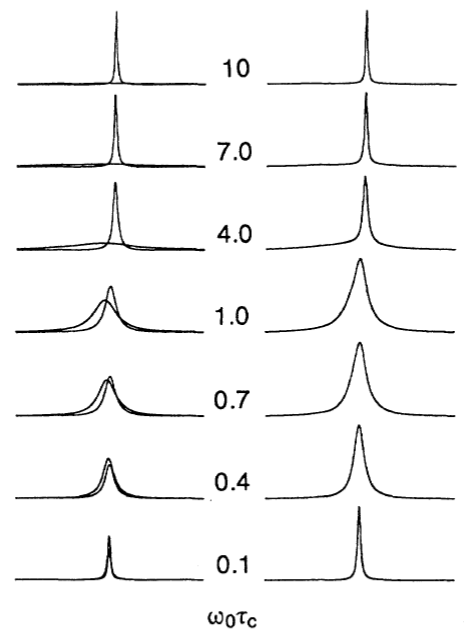
NMR in the Molten State

The Borate Liquids Dynamics

$0.33\ Na_2O \cdot 0.67\ B_2O_3$



Line Widths as Transverse Relaxation Time



Isotropic rotational diffusion

$$\langle S_x \rangle + i \langle S_y \rangle = \langle S_z \rangle^T i \exp[-i\omega_0 (t - t_0)]$$

$$\times [\tfrac{3}{5}\exp(-b_1 t) + \tfrac{2}{5}\exp(-b_2 t)]$$

$$b_1 = C(J_0 + J_1 + iQ_1)$$

$$b_2 = C(J_1 + J_2 - iQ_1 + iQ_2)$$

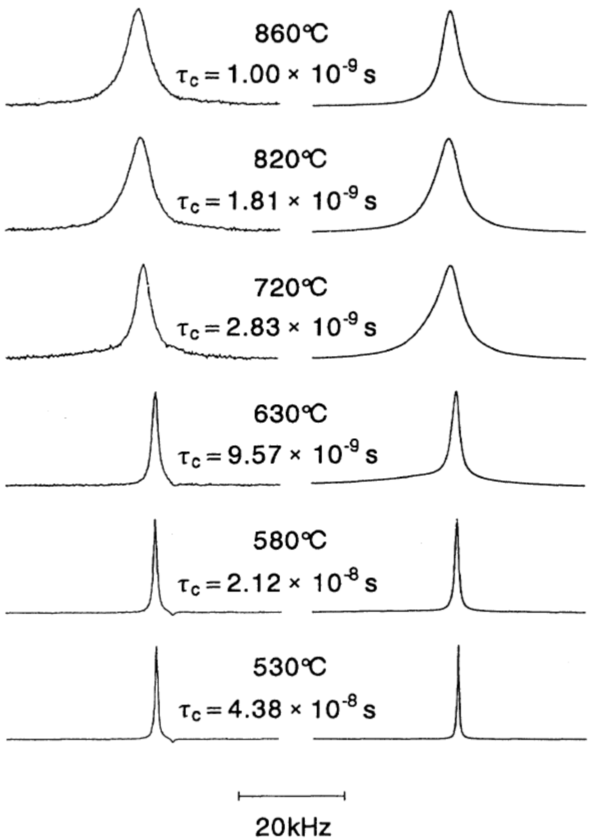
Hyperfine second-order dynamic quadrupolar shift

$$Q_n = n\omega_0 \tau_c^2 (1 + n^2 \omega_0^2 \tau_c^2)^{-1}$$

Inagaki et al., Phys. Rev. B **1993** *47* 674-680

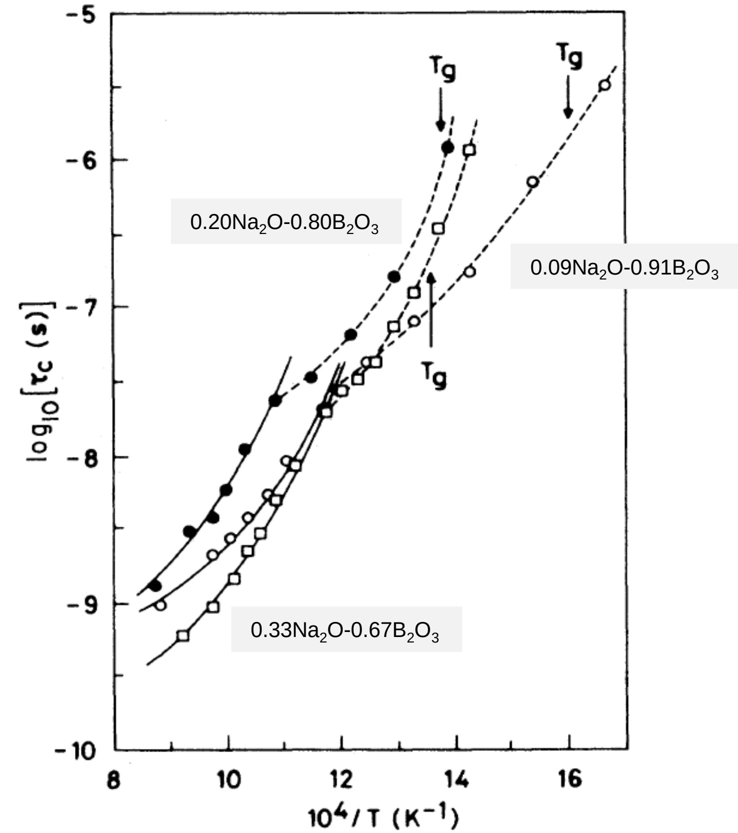
The Borate Liquid Dynamics

$0.09\ Na_2O \cdot 0.91\ B_2O_3$



Experimental (left) [11]B line shapes and calculated (right) using the parameters of the longitudinal relaxation data

Line Widths as Transverse Relaxation Time

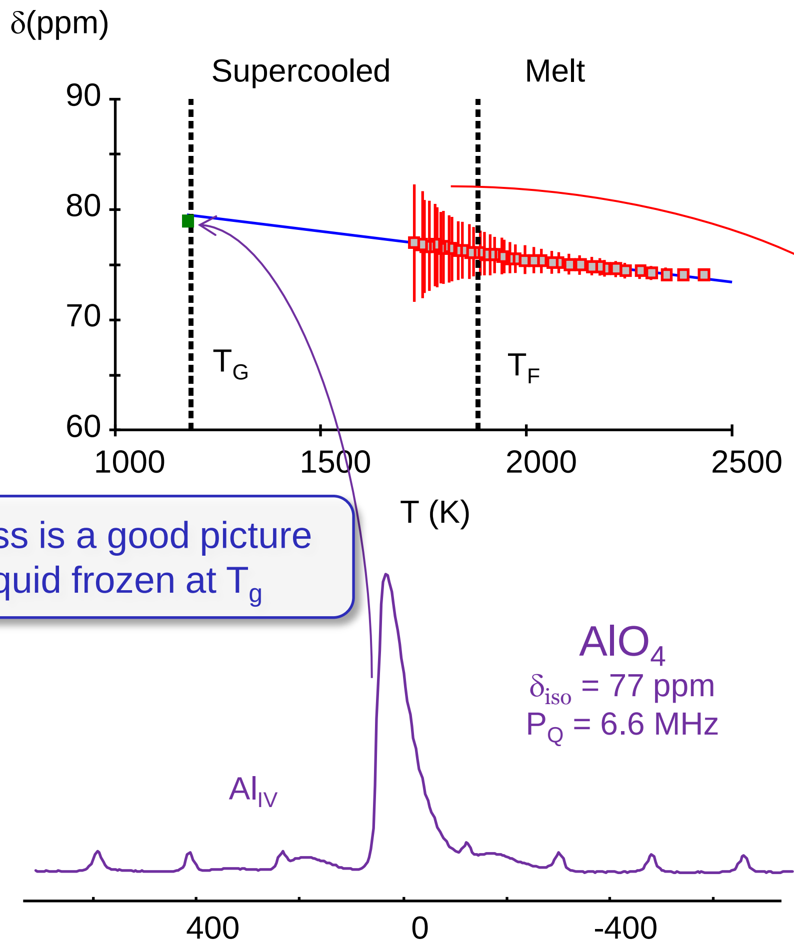


^{11}B NMR correlation times obtained from longitudinal data. The solid lines are Vogel-Tamman-Fulcher fits for the α orientational-relaxation processes (viscosity). The dashed line represents β processes (restricted BO_3 rotations).

Inagaki et al., Phys. Rev. B **1993** *47* 674-680

From Liquid to Glass: $CaAl_2O_4$

Structure



Glass is a good picture of liquid frozen at T_g

Dynamics

Extreme narrowing

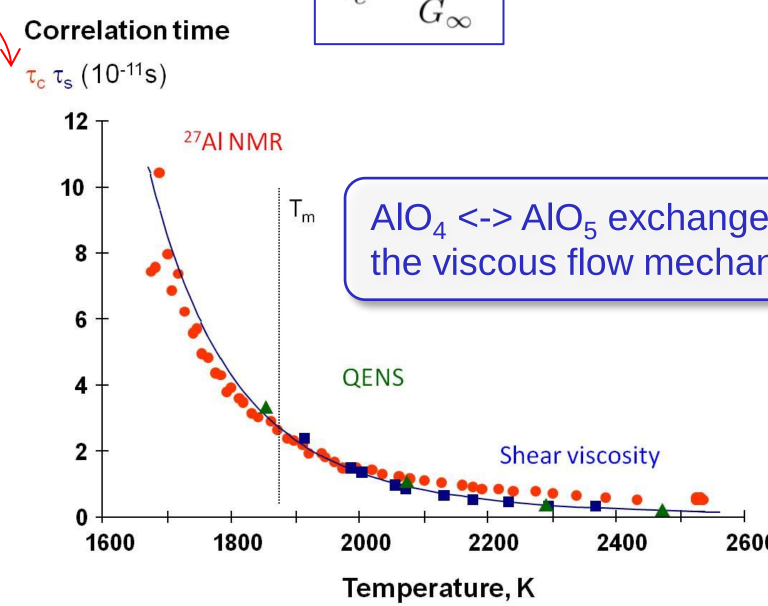
$$T_1 = \frac{1}{\pi \Delta \nu_{1/2}}$$

Quadrupolar Relaxation

$$\frac{1}{T_1} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \overline{C}^2_{Q\eta} \tau_c^2$$

Shear Viscosity

$$\tau_c = \frac{\eta}{G_\infty}$$



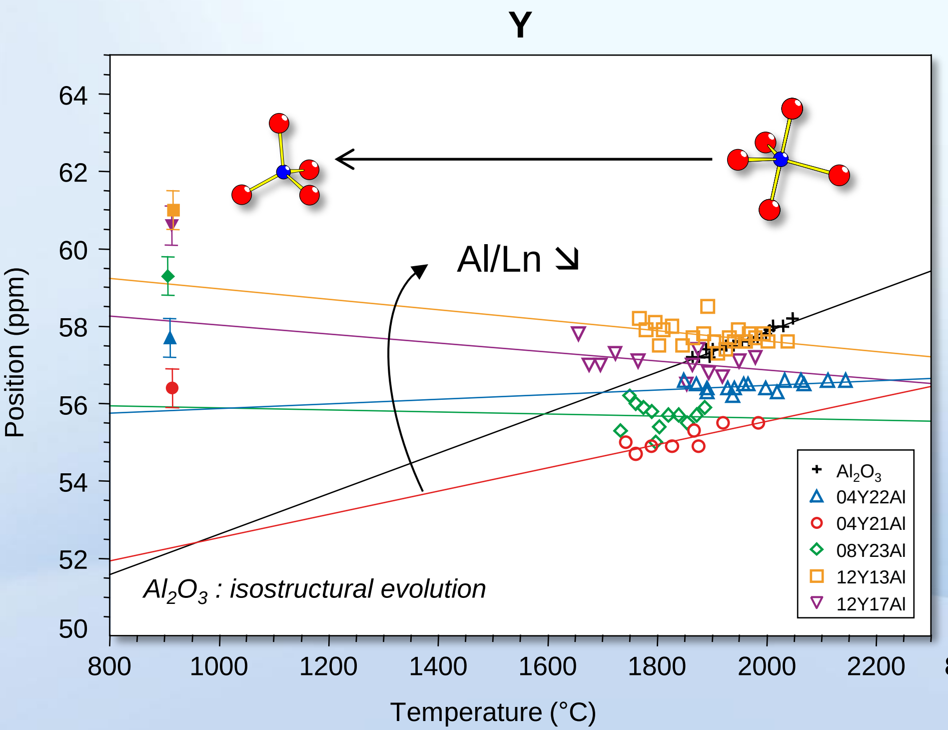
AlO_4 <-> AlO_5 exchange is the viscous flow mechanism

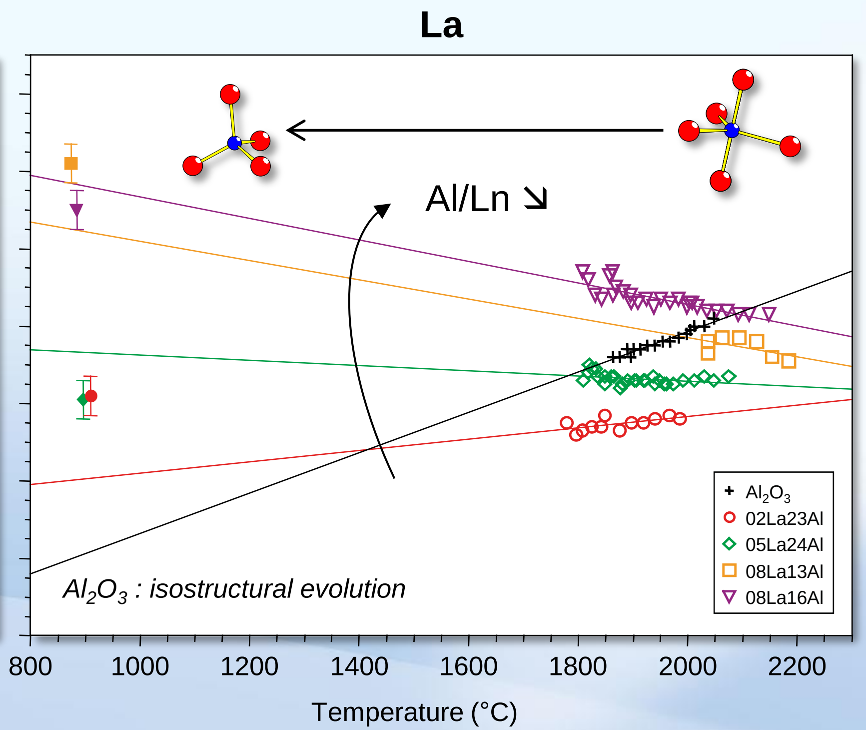
Massiot et al., J. Phys. Chem. **1995** *99* 16455-16459

Kozally et al., Phys. Status Solidi C **2011** *8* 3155-3158
Neuville et al., Rev. Miner. Geochem. **2014** *78* 779-800

Adding Silica: Effects on the Structure

Al_2O_3•SiO_2•Ln_2O_3 (SiO_2 > 50mol%)



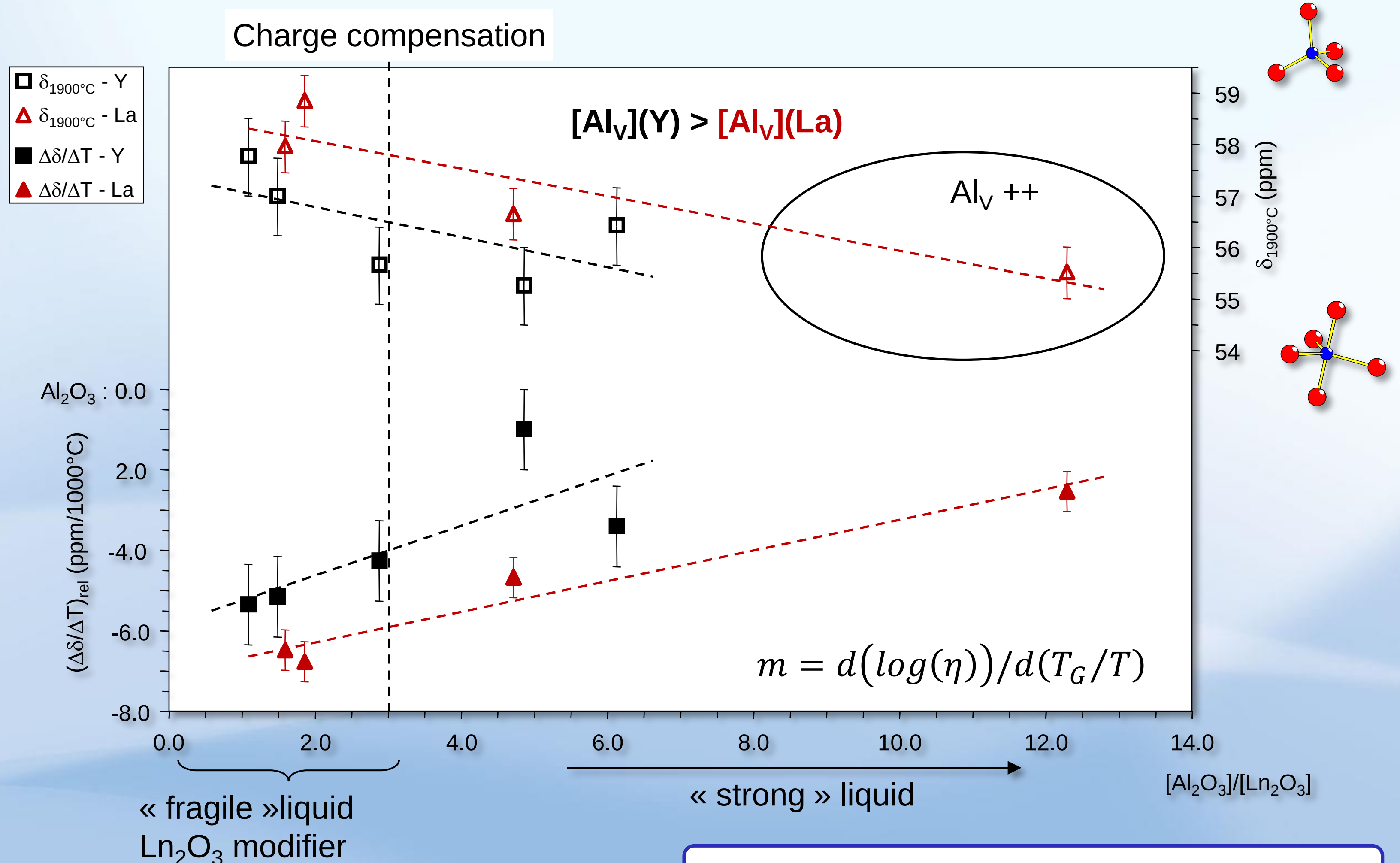


- The glass is not a linear extrapolation at T_g of the liquid
- Al^{V} favored at High temperature (what mechanism stabilizes Al^{IV} at low temperature?)
- $[Al_2O_3]/[Ln_2O_3]$ decreases → faster $Al^{V} \rightarrow Al^{IV}$ conversion with T, i.e. "fragile" liquid
- Ln does not favor Al^{V}

Florian et al., J. Phys. Chem. B. **2007** *111* 9747-9757

Structure of the Molten State

$Al_2O_3 \bullet SiO_2 \bullet Ln_2O_3$ (SiO_2 > 50mol%)



☞ Ln_2O_3 plays a modifier role and favors Al^{IV}

Florian et al., J. Phys. Chem. B. **2007** *111* 9747-9757

Adding Silica: Effects on Dynamics

NMR

$$T_1 = \frac{1}{\pi \Delta \nu_{1/2}}$$

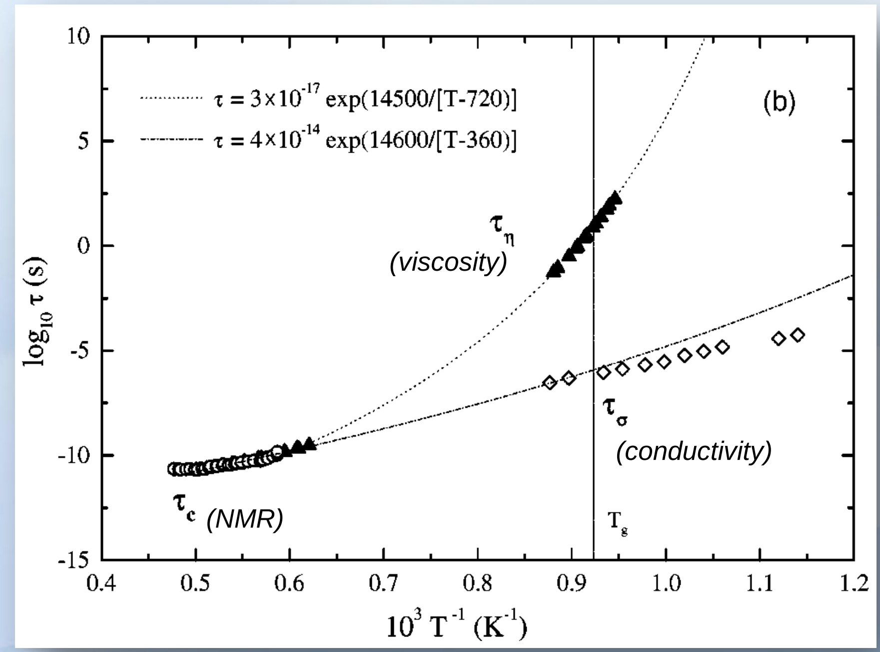
$$\frac{1}{T_1} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \overline{C}^2_{Q\eta} \tau_c^2$$

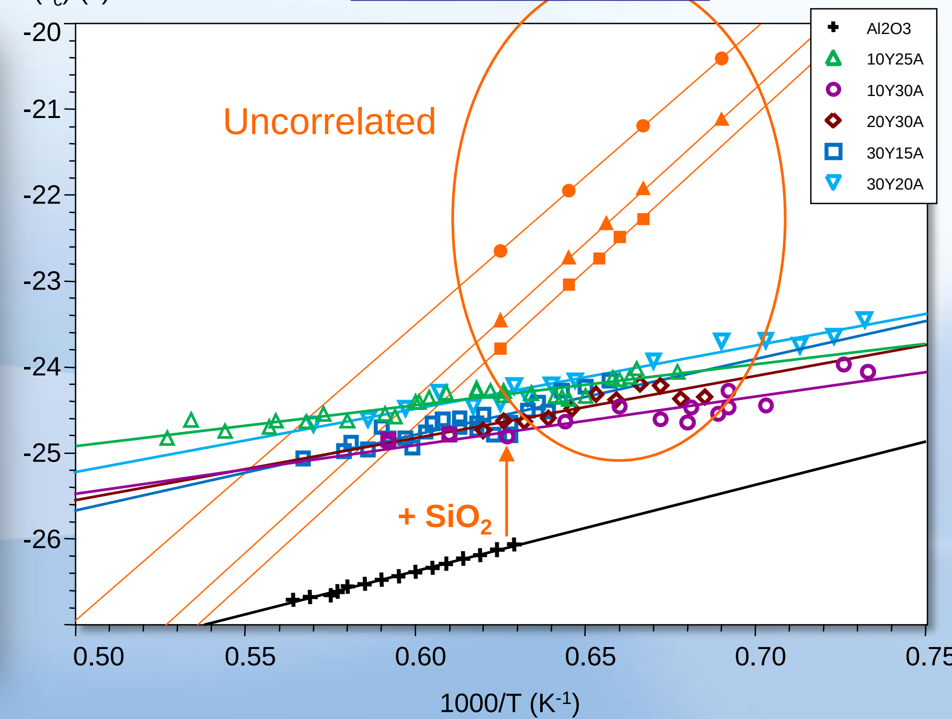
Viscosity

$$\tau_c = \frac{\eta}{G_\infty}$$

Saito *et al.*, *J. Am. Ceram. Soc.*, 2003, **86**, 711-716

Viscosity : Si- / -O
NMR : Al <-> O





CA3627, CA4412

Al_2O_3-SiO_2-Y_2O_3 (SiO_2 > 50mol%)

*Gruener et al., Phys. Rev. B **64**(2) (2001)*

*Florian et al., J. Phys. Chem. B. **111** 9747 (2007)*

Class is Over…
Do Science & Have Fun!

Aknowledgements

CEMH
Domin
Cathe
Patric
Domin
Bruno
Lauren
Anne-
Vincen
Aydar
Yannic
Philipp

rance

USA