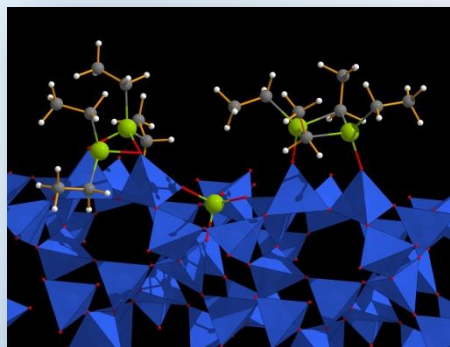


Solid-State NMR applied to Glasses: an Introduction



P. Florian

CEMHTI-CNRS, Orléans, France



Ecole du GdR Verre, Cargèse 2017



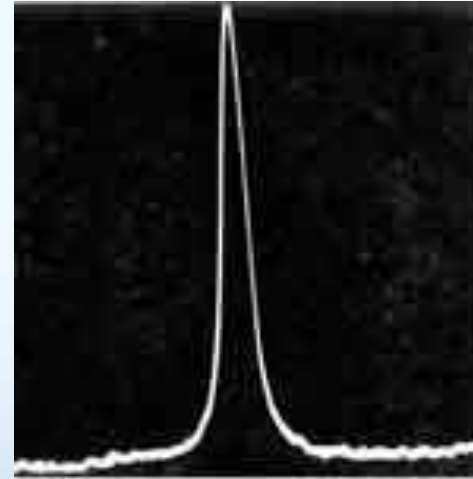
And in 1945 (SS)NMR was born...



Felix Bloch
1905-1983
(Stanford)



Ed Purcell
1912-1997
(Harvard)



proton NMR of
paraffin wax

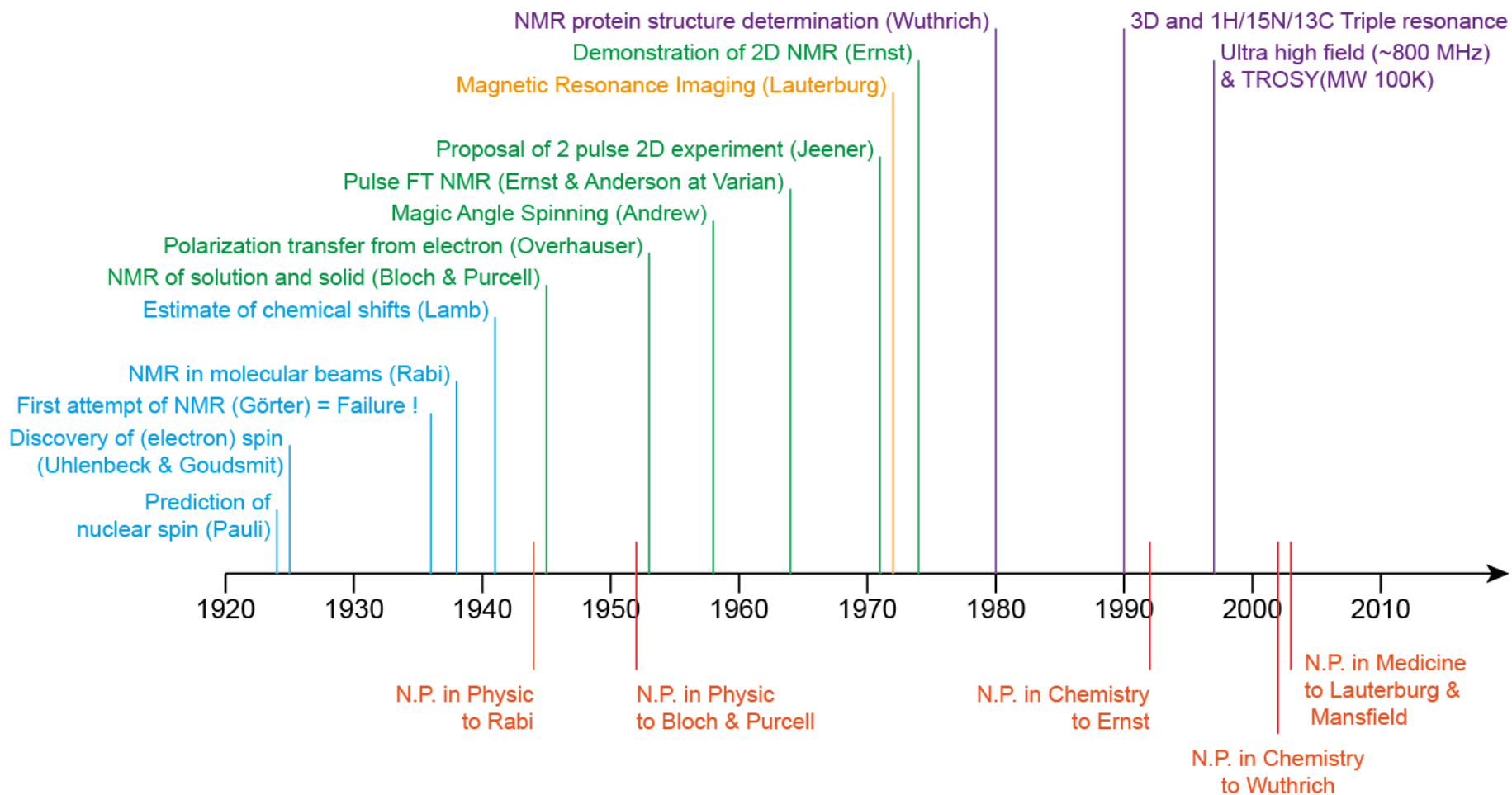
*Purcell,
Phys. Rev. 1946*

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."

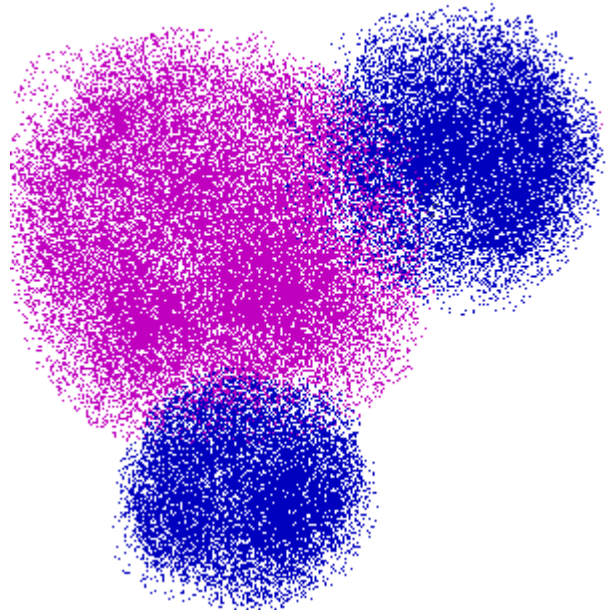
NMR TimeLine



The Music of Atoms

**An (Ultra) Short Introduction to NMR
Spectroscopy**

Nuclear + Magnetic + Resonance (Spectroscopy)



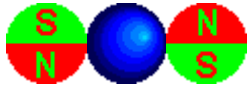
Nuclear + Magnetic + Resonance (Spectroscopy)

Nuclear

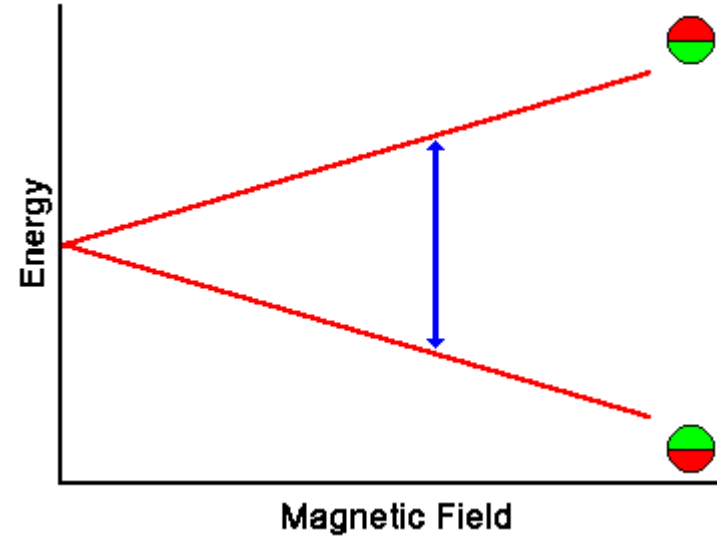


Nuclear + Magnetic + Resonance (Spectroscopy)

Nuclear

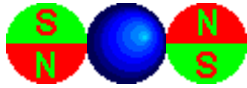


Magnetic



Nuclear + Magnetic + Resonance (Spectroscopy)

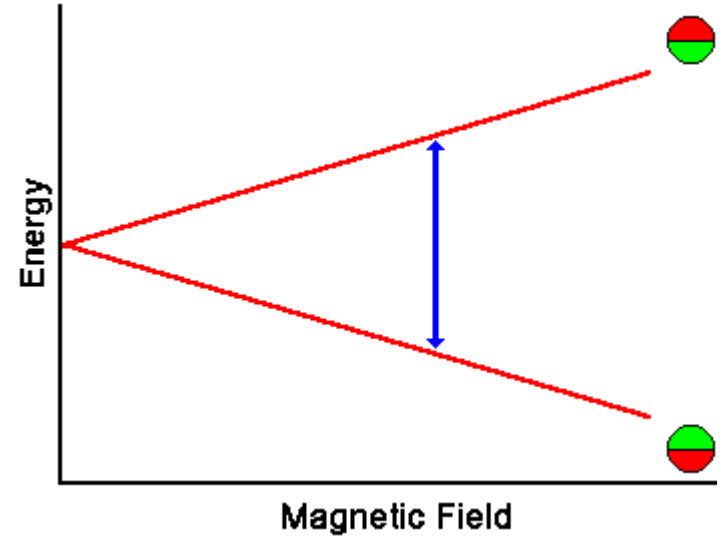
Nuclear



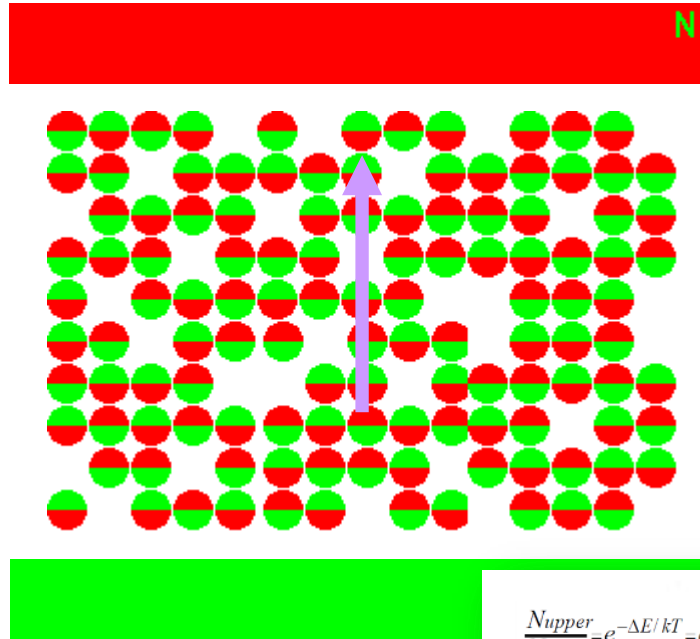
Magnetic



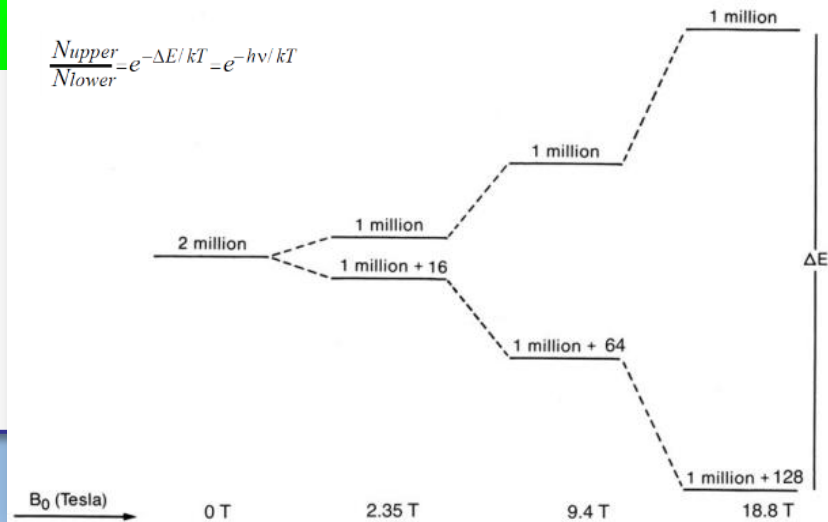
Resonance



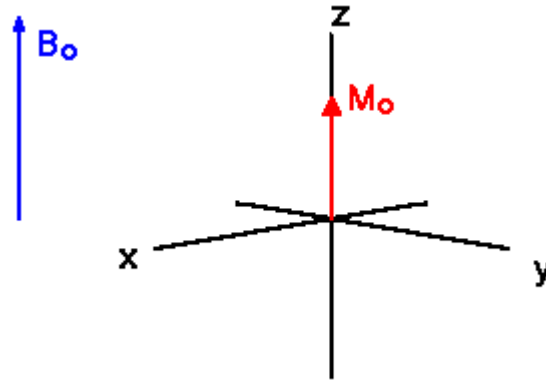
The Magnetization



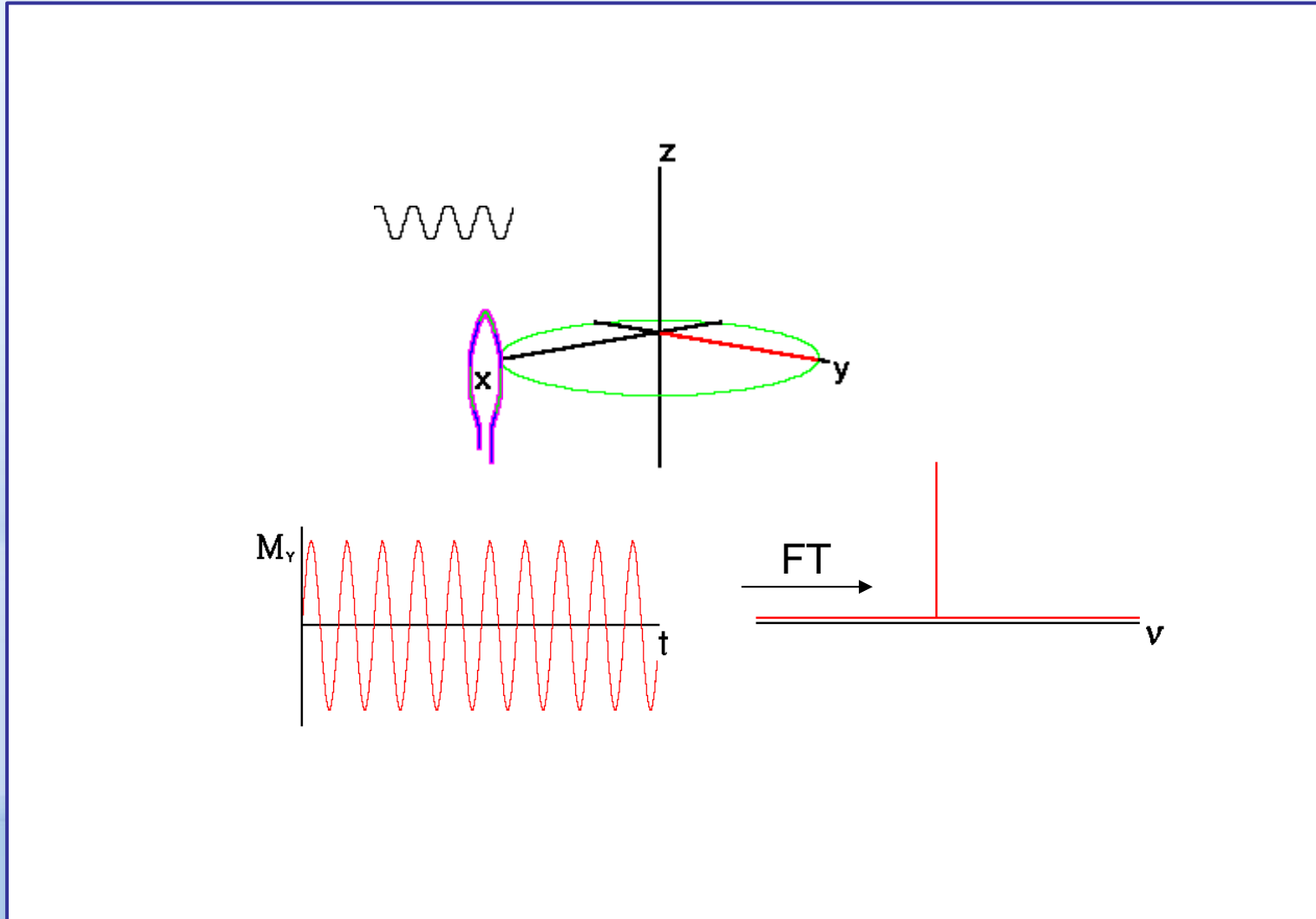
$$\frac{N_{upper}}{N_{lower}} = e^{-\Delta E/kT} = e^{-h\nu/kT}$$



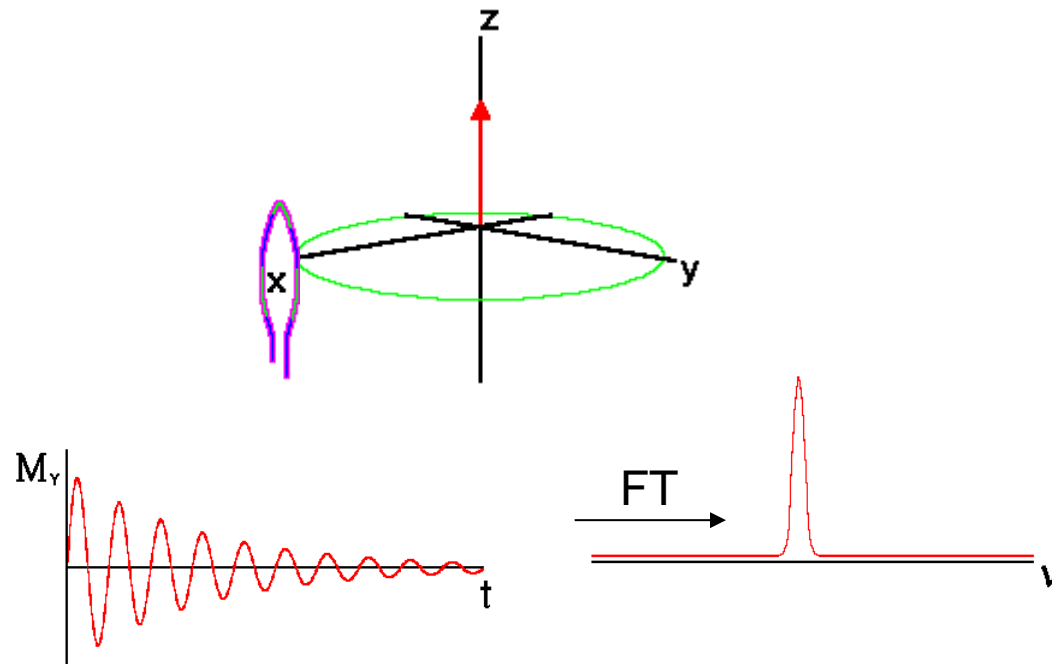
The Magnetization



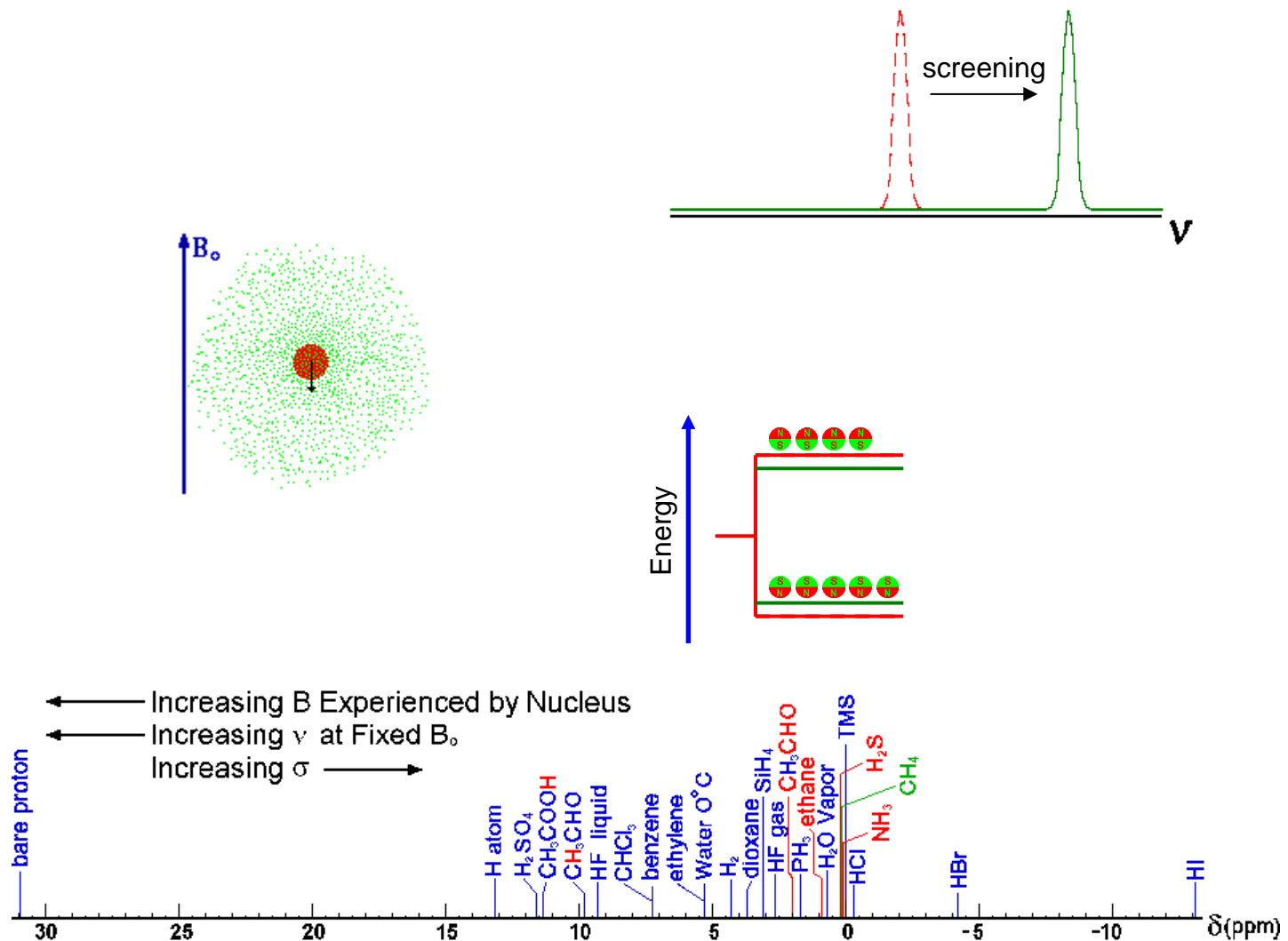
Pulse, Free Induction Decay and spectral domain



And do not forget to relax...



The chemical shift interaction



Possibilities & Opportunities

1 H Hydrogen 1.00794																	2 He Helium 4.003														
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797								
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050																	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948								
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80														
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29														
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)														
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)																				
																		58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
																		90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

$I = 1/2$
 Quadrupolar

❖ Observability

- ❖ Abundance
- ❖ Gyromagnetic ratio
- ❖ Quadrupolar momentum
- ❖ Paramagnetism

Numerous possibly sensitive nuclei but few easily observed

The most usually observed are «light» nuclei

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

Interactions in the Solid State

Challenge : Strong Interactions



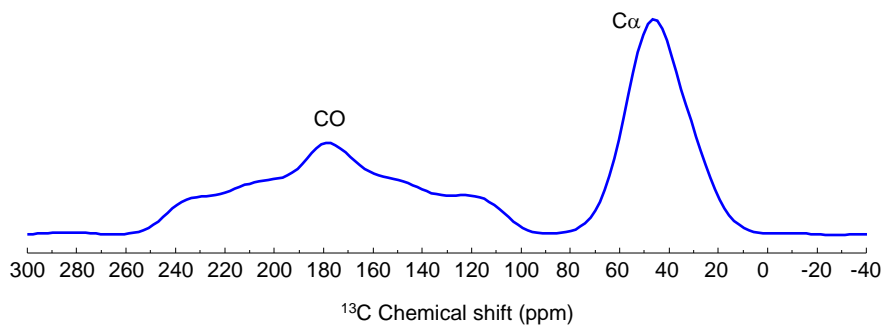
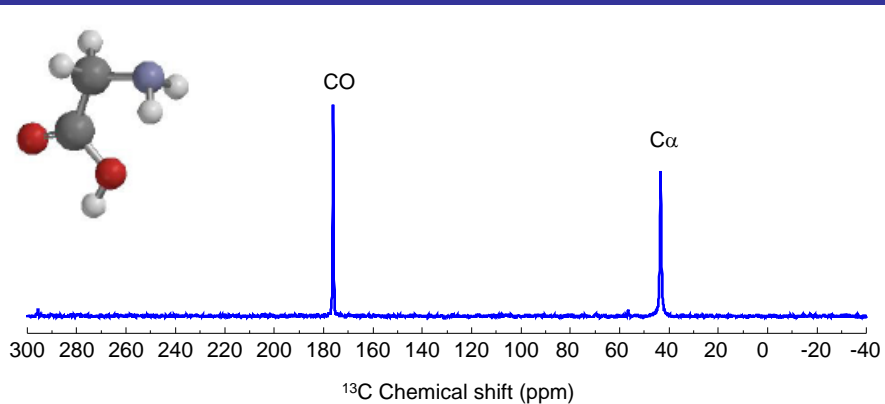
Liquid:
Weak interactions
J-couplings
(up to 150 Hz)



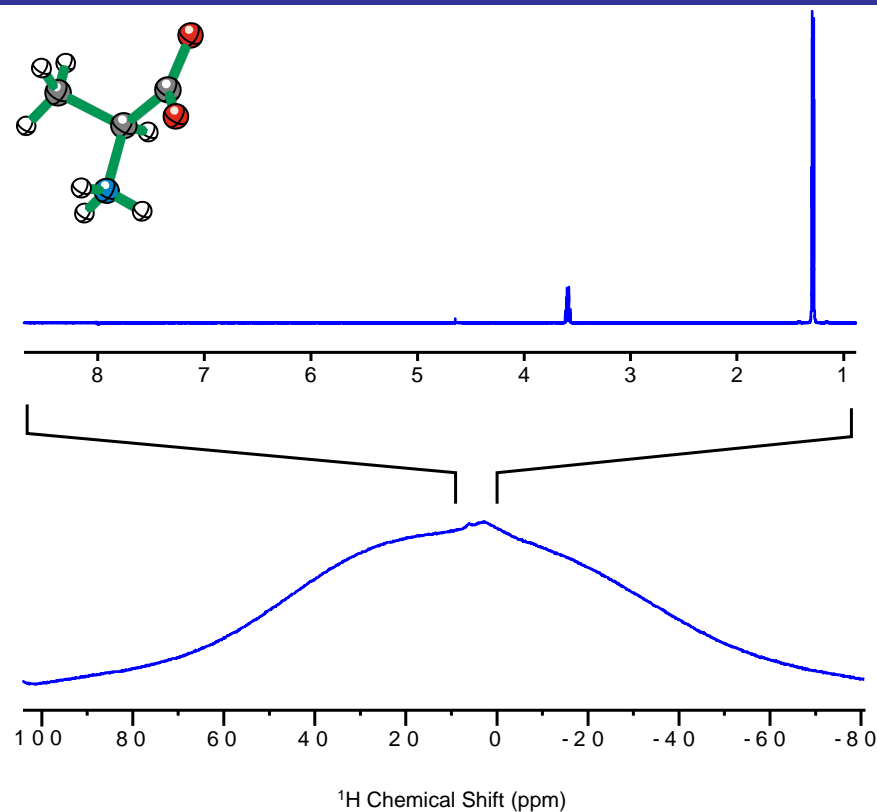
Solid:
Strong interactions
Dipolar couplings
(up to 50 kHz)
Quadrupolar couplings
(up to MHz)

Challenge : Strong Interactions

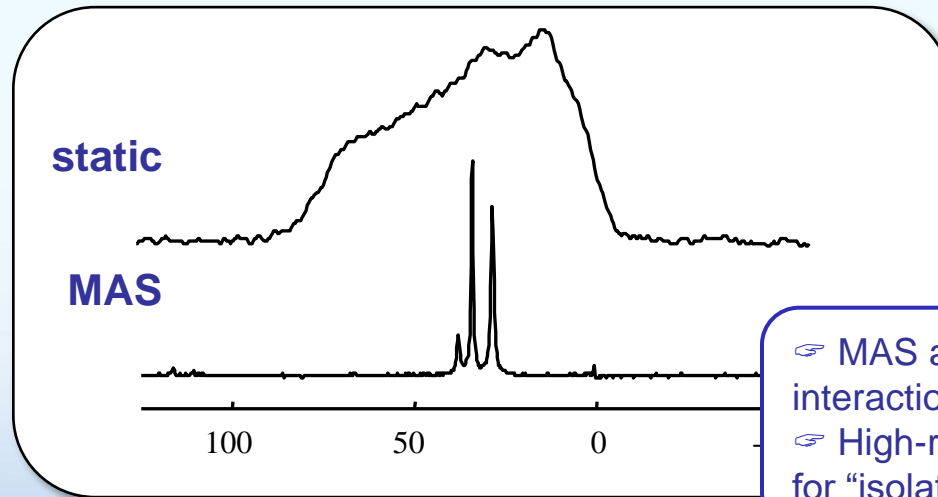
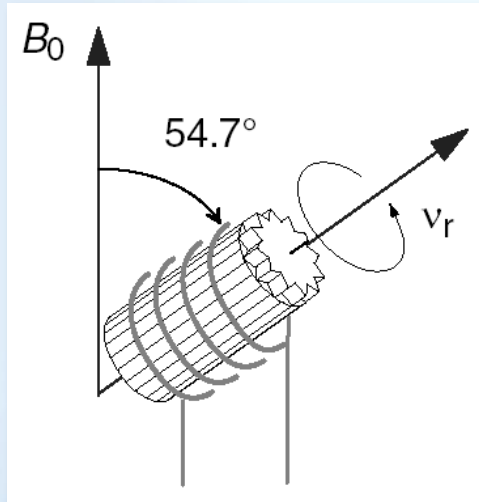
^{13}C NMR of Glycine



^1H NMR of L-alanine



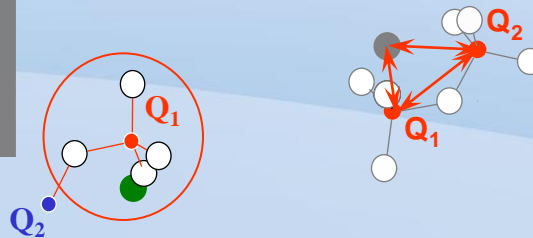
It's a Kind of Magic...



- ☞ MAS averages anisotropic interactions (to 1st order)
- ☞ High-resolution spectrum for "isolated" spin 1/2 nuclei

Isotropic Chemical Shift

~~CSA~~



~~Dipolar couplings~~

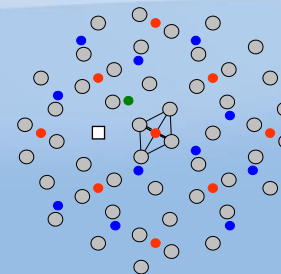
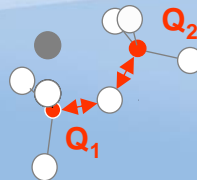
$I > 1/2$

~~1st order Quadrupolar interaction~~

2nd order Quadrupolar interaction

Isotropic J-couplings

~~J-anisotropy~~



Magic Angle Spinning



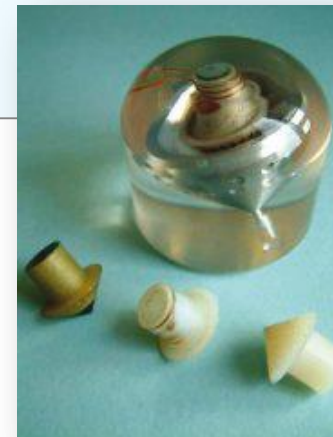
Spinning Spins A Tribute to Raymond Andrew

Today we salute
A great man of repute
We bring greetings from near and afar,
With boundless delight
We applaud his insight
Into the workings of NMR.

With magical skill
He could select at will
The weak from the strong interaction,
Revealing to all
Those shifts large and small
That yield such key information.

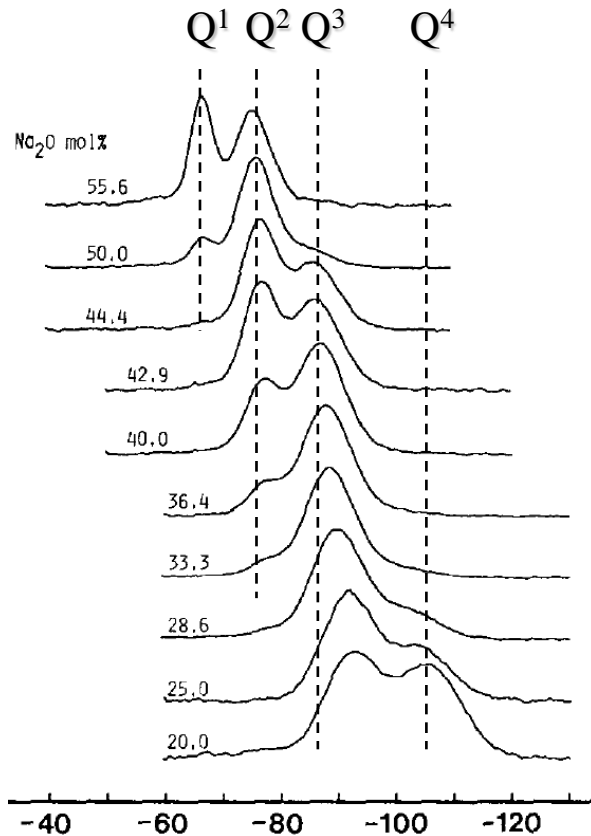
Few experiments can surpass
The versatility of MAS
In probing the secrets of nature
We ponder anew
The progress that's due
To Raymond's great genius and stature.

Vincent McBrierty, 1997

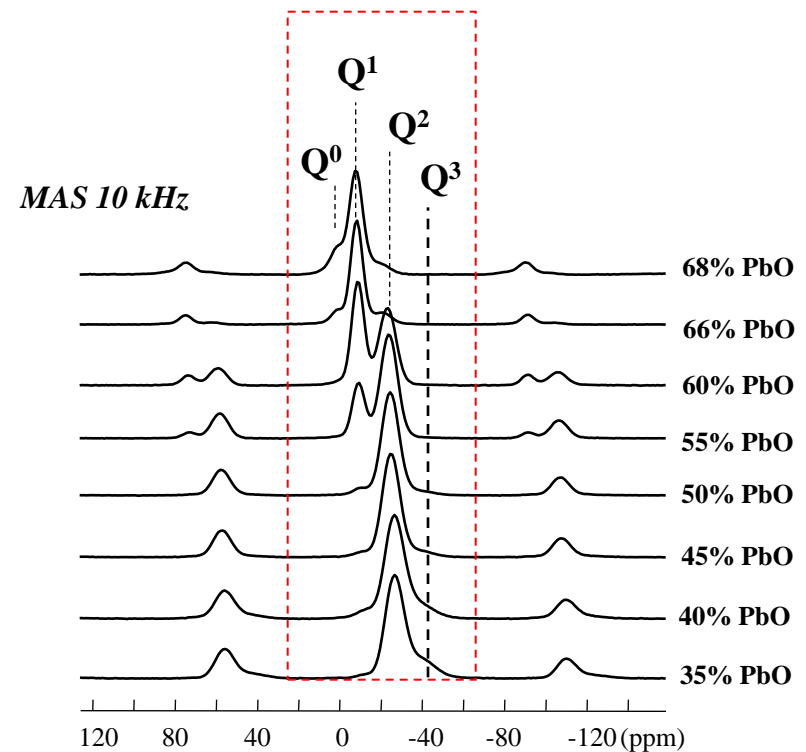


Observing Q^n Species

^{29}Si MAS NMR of $\text{Na}_2\text{O}-\text{SiO}_2$ glasses



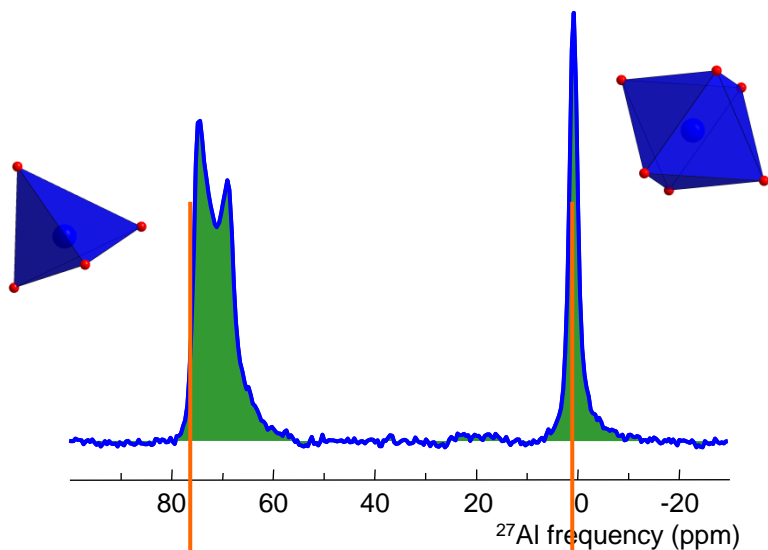
^{31}P MAS NMR of $\text{PbO}-\text{P}_2\text{O}_5$ glasses



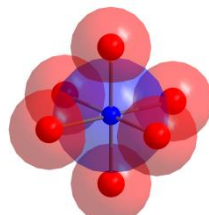
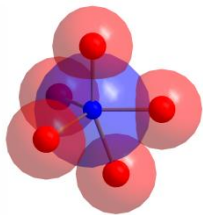
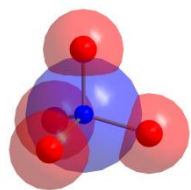
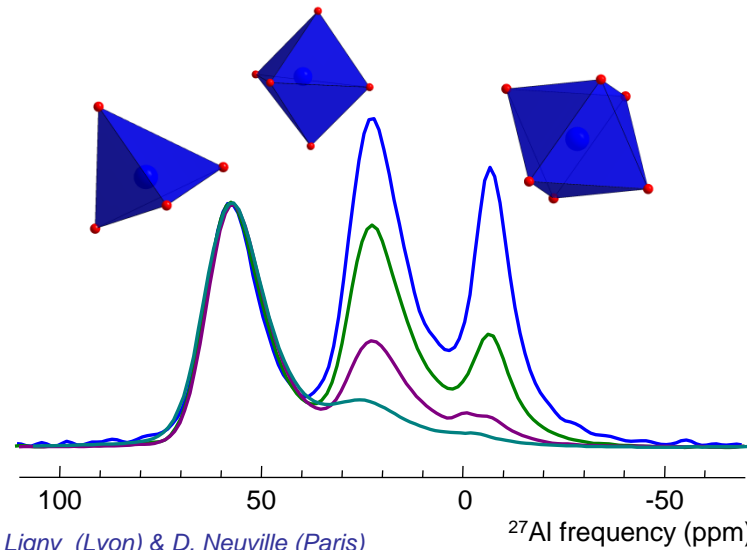
- ☞ Broad resonance lines : distribution (of ^{29}Si or ^{31}P) chemical shift due to structural disorder
- ☞ Assignment of the resonances from (^{29}Si or ^{31}P) chemical shift range in crystalline lead phases
- ☞ **Unambiguous identification & quantification of the Q^n units**

(²⁷Al) Nuclear Magnetic Resonance

²⁷Al - Y₃Al₅O₁₂ (crystal)



²⁷Al - HP NAS glasses



Position

(*chemical shift*, magnetic shielding):

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

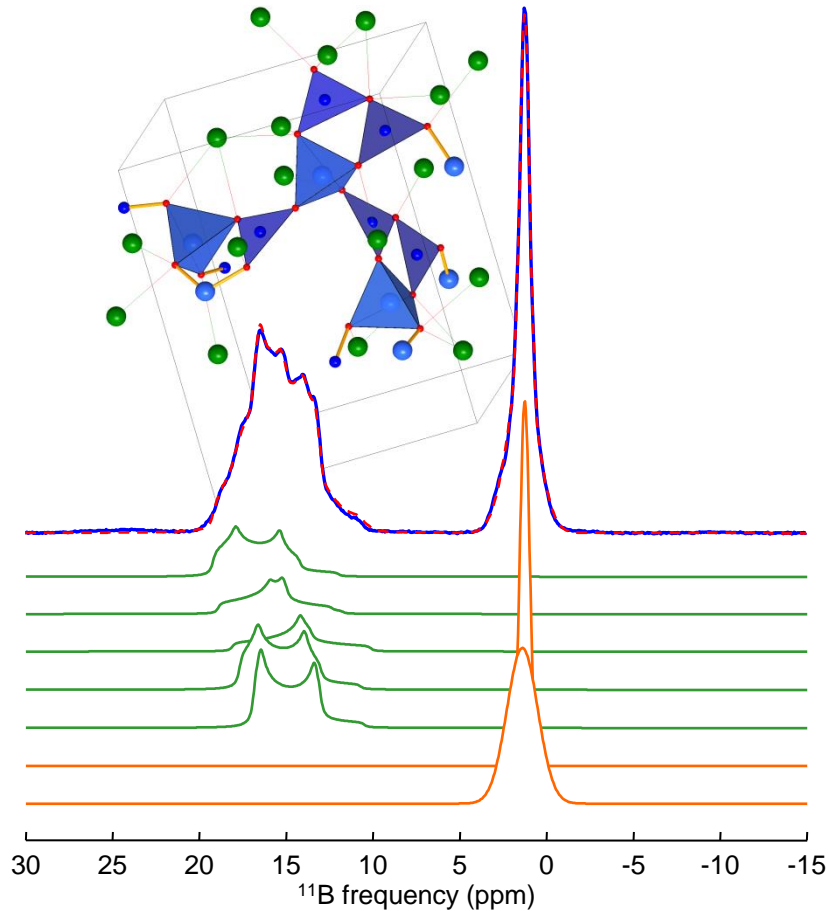
Width & shape

(*quadrupolar coupling*, EFG):

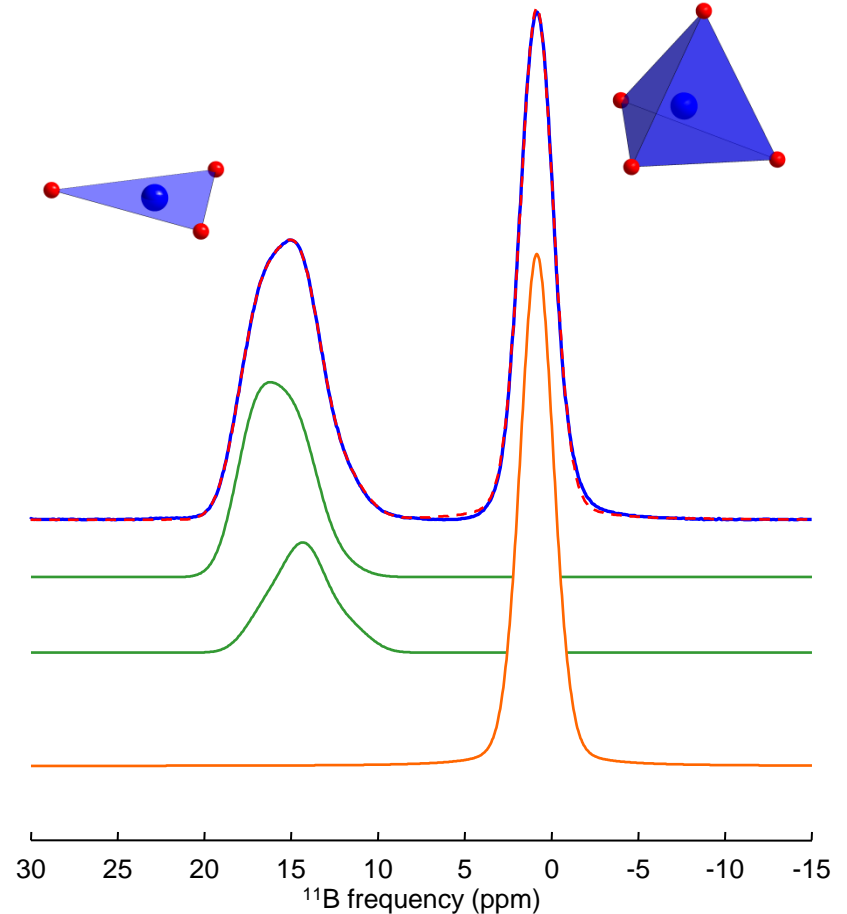
- ☞ (*p*-) orbital population unbalance
- ☞ local polyhedra distortion
- ☞ possibly long-range effect

Solid-State Nuclear Magnetic Resonance

^{11}B – $\text{Na}_2\text{B}_4\text{O}_7$ (crystal)



^{11}B – $\text{Na}_2\text{B}_4\text{O}_7$ (glass)



NMR is an atom-specific local probe

☞ distinguish between chemical environments

☞ quantitative

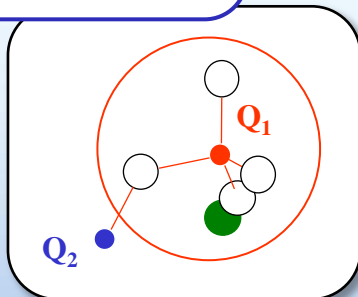
Interactions in the Solid-State

~10s of kHz

Chemical Shift Anisotropy

- ↳ Electronic shielding
- ↳ Chemical environment, coordinence & geometry

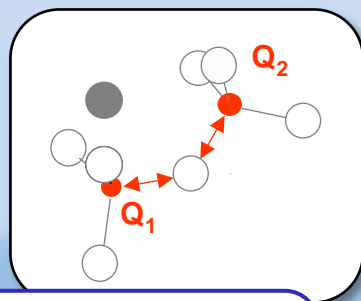
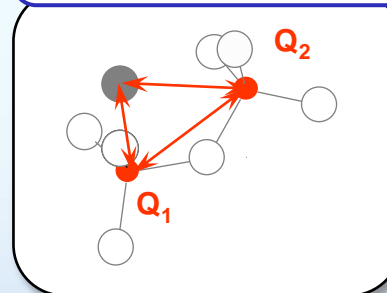
propr. B_0



Dipolar Couplings

- ↳ Neighboring spin distances

~kHz $1/r^3$



Indirect J Couplings

- ↳ Chemical bonds geometry
- ↳ Connectivity

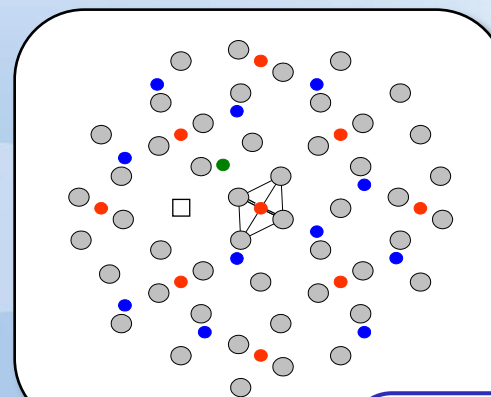
< 100s of Hz

$I > 1/2$, up to MHz

Quadrupolar Interaction

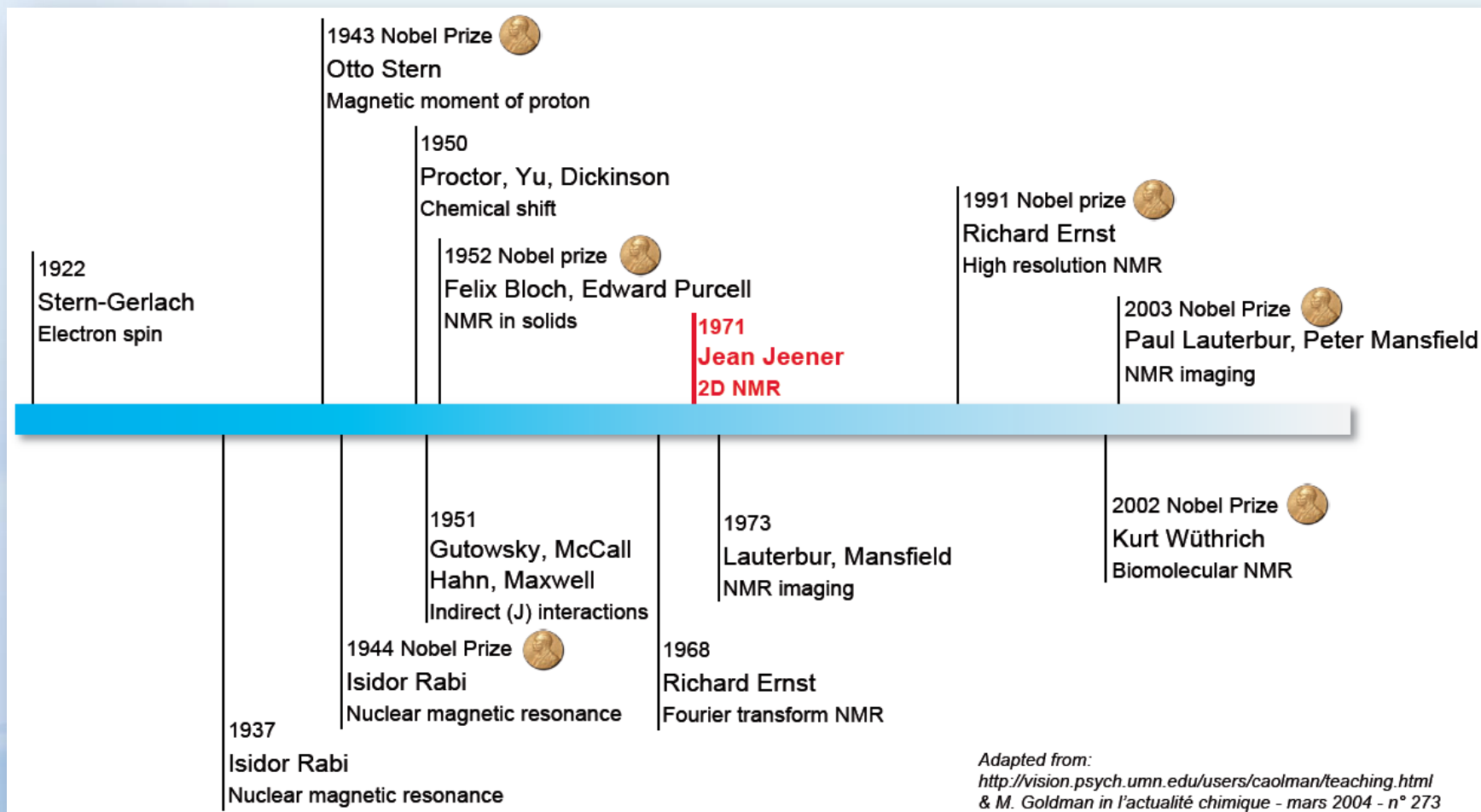
- ↳ Electric Field Gradient
- ↳ Surrounding electrons & nuclei geometry

2nd order
propr. $1/B_0$



Let's go Two-Dimensional!

NMR Timeline and Birth of 2D



Adapted from:
<http://vision.psych.umn.edu/users/caolman/teaching.html>
& M. Goldman in *l'actualité chimique* - mars 2004 - n° 273

Principle of 1D NMR

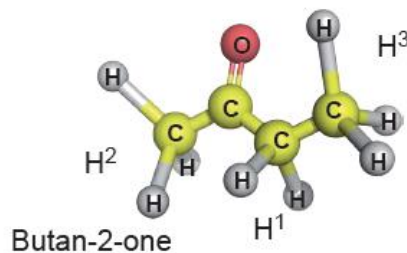
General 1D acquisition scheme :

Preparation

Mixing

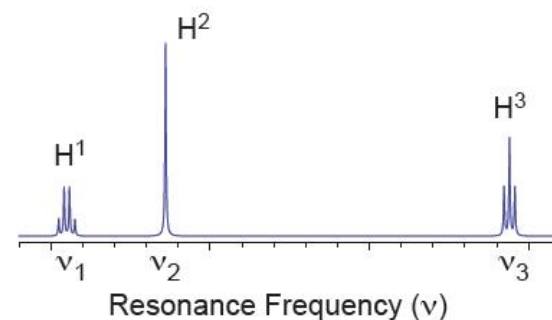
Detection

Evolution of the NMR signal during a *unique delay t*



Fourier Transform

1D NMR spectrum



The Basic Idea

General 1D acquisition scheme :

Preparation

Mixing

Detection

$\pi/2$

t

General 2D acquisition scheme :

Preparation

Evolution

Mixing

Detection

$\pi/2$

t_1

$\pi/2$

t_2

“The next fortunate event occurred in 1971 when my first graduate student, Thomas Baumann, visited the Ampere Summer School in Basko Polje, Yugoslavia, where Professor Jean Jeener proposed a simple two-pulse sequence that produces, after two-dimensional Fourier transformation, a two-dimensional (2D) spectrum. In the course of time, we recognized the importance and universality of his proposal ...”

Richard Ernst, Nobel Prize in Chemistry, 1991

The Basic Idea

General 2D acquisition scheme :

Preparation

Evolution

Mixing

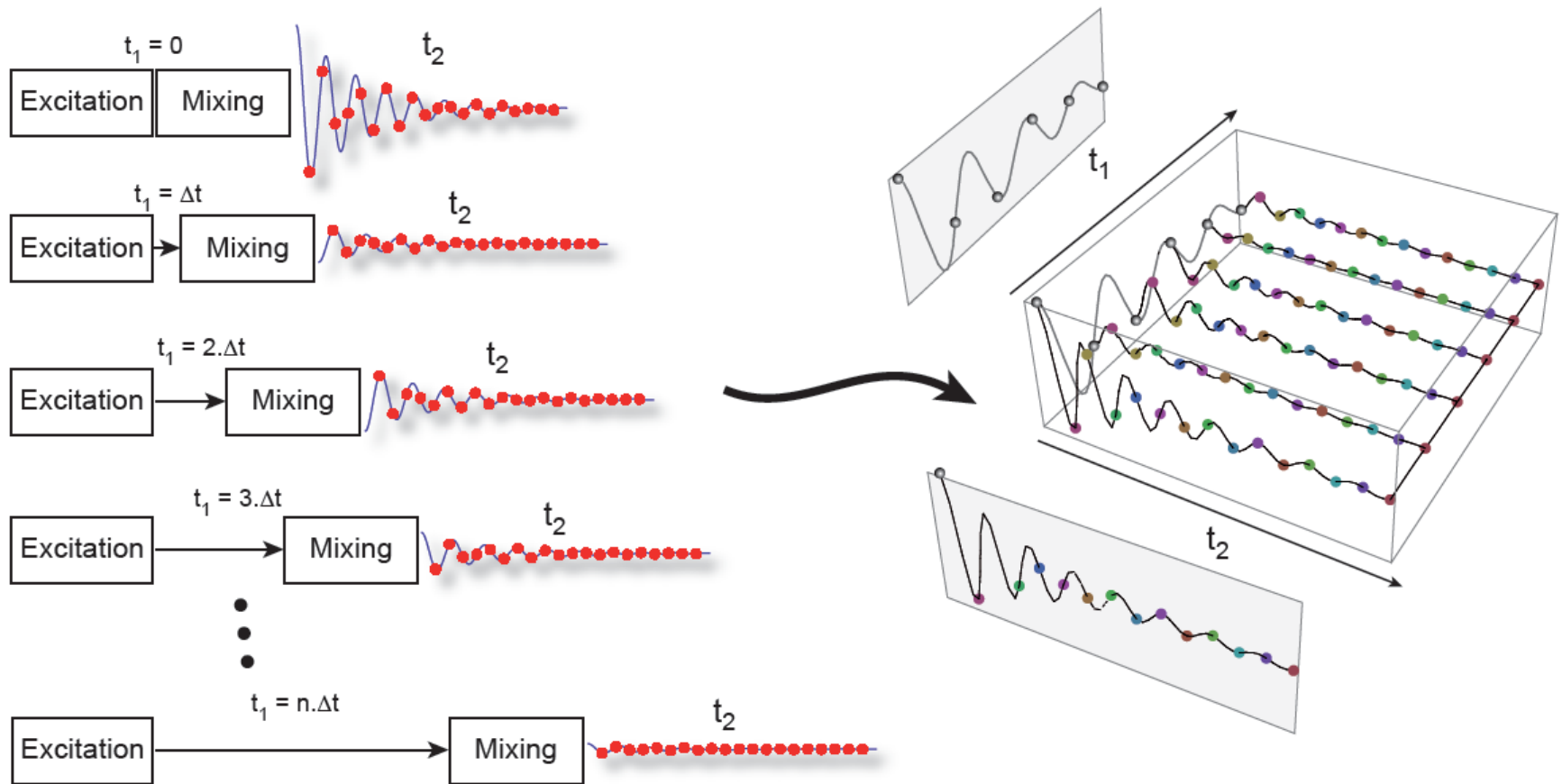
Detection

- **Preparation** : nuclear spins are put in a non equilibrium state (polarization ...)
- **Evolution** : spins evolve according to their resonance frequency as well as all the spin interactions that are active on the prepared spin state.
- **Mixing** : polarization is “exchanged” between spins. Magnetization transfers can be driven by scalar couplings (chemical bonds), dipolar couplings (spatial proximities), chemical exchange, relaxation process ...
- **Detection.**

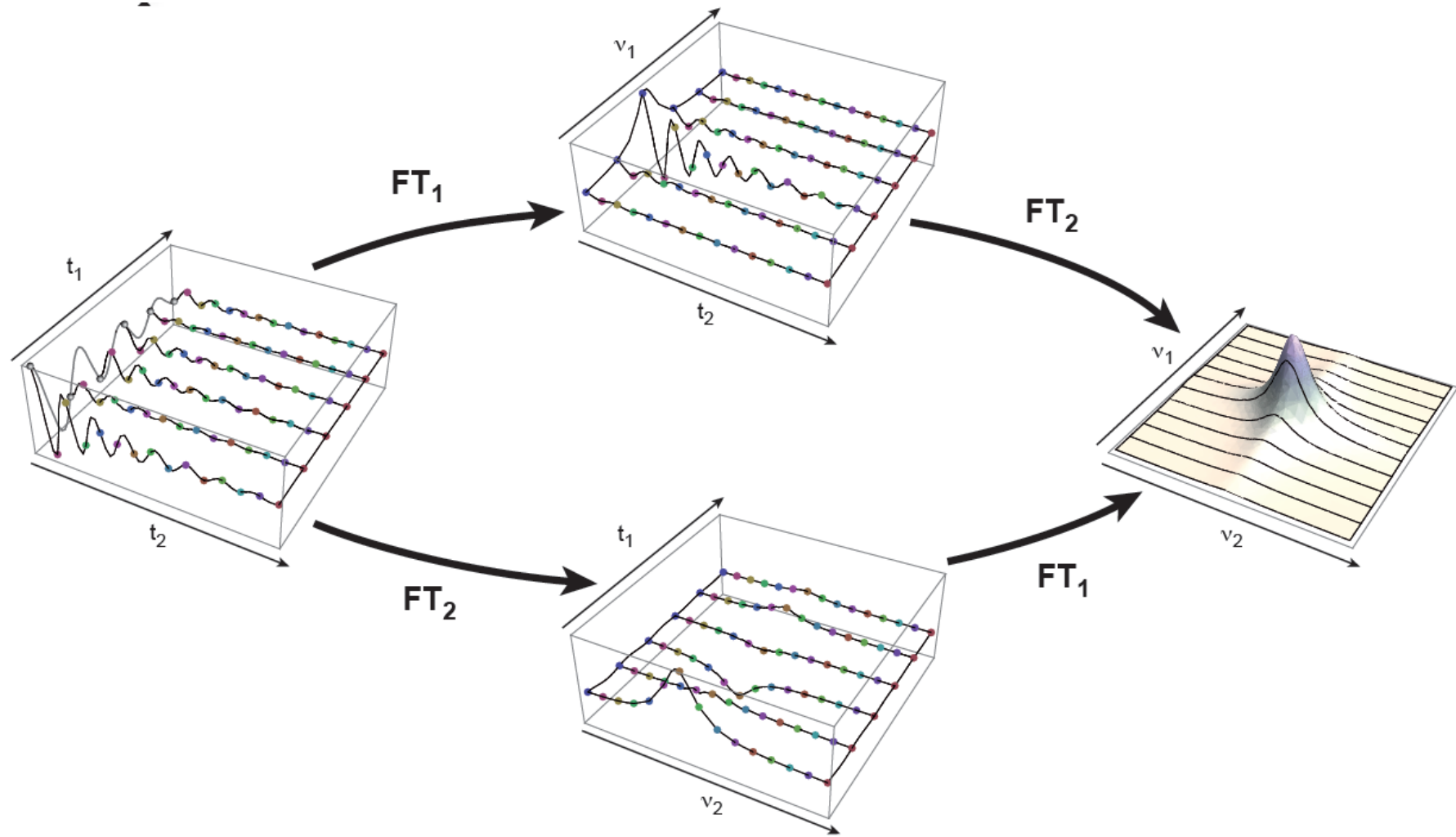
t_2



Two-Dimensional NMR

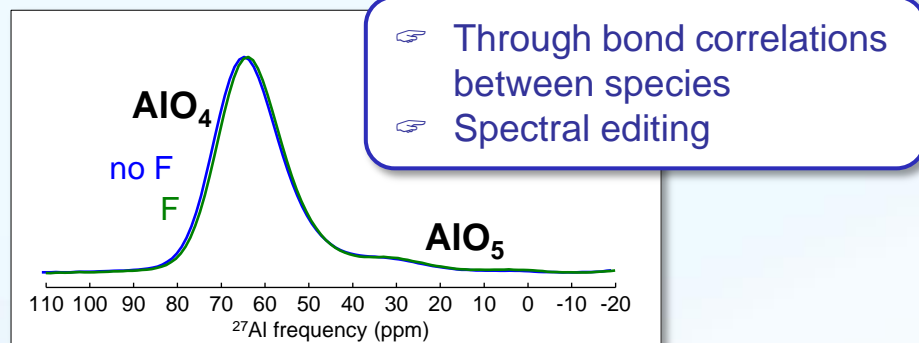
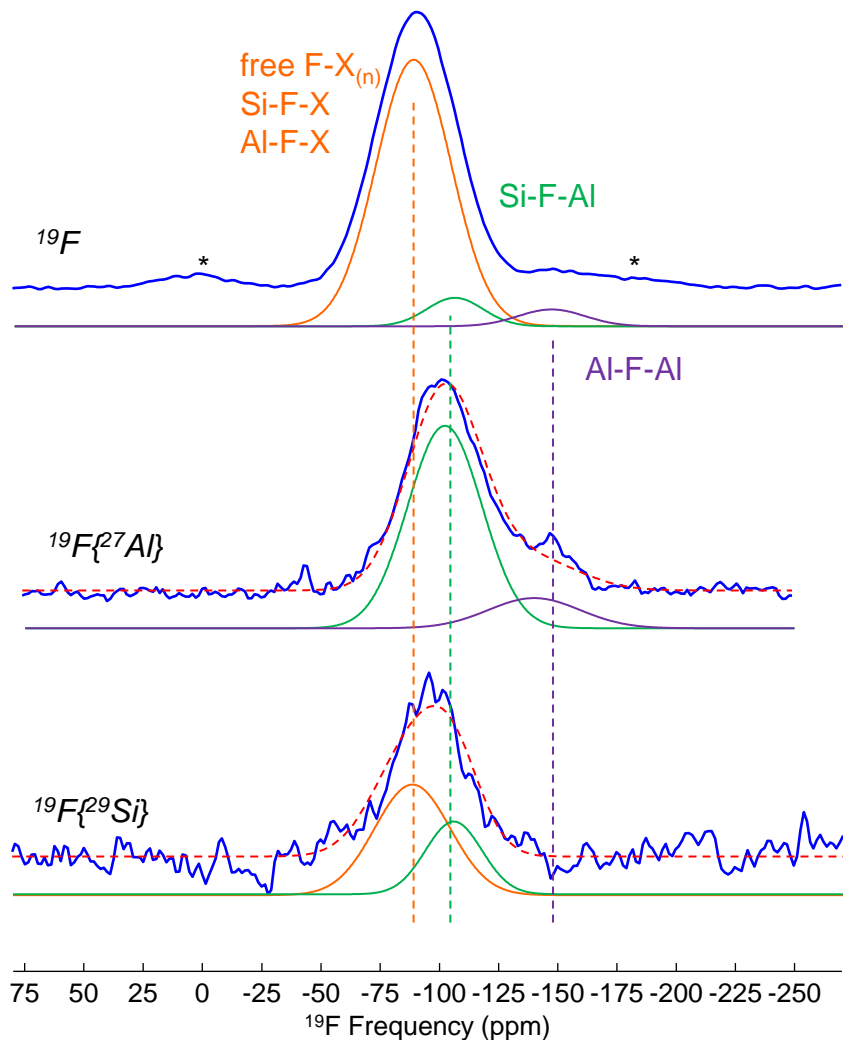


Two-Dimensional NMR

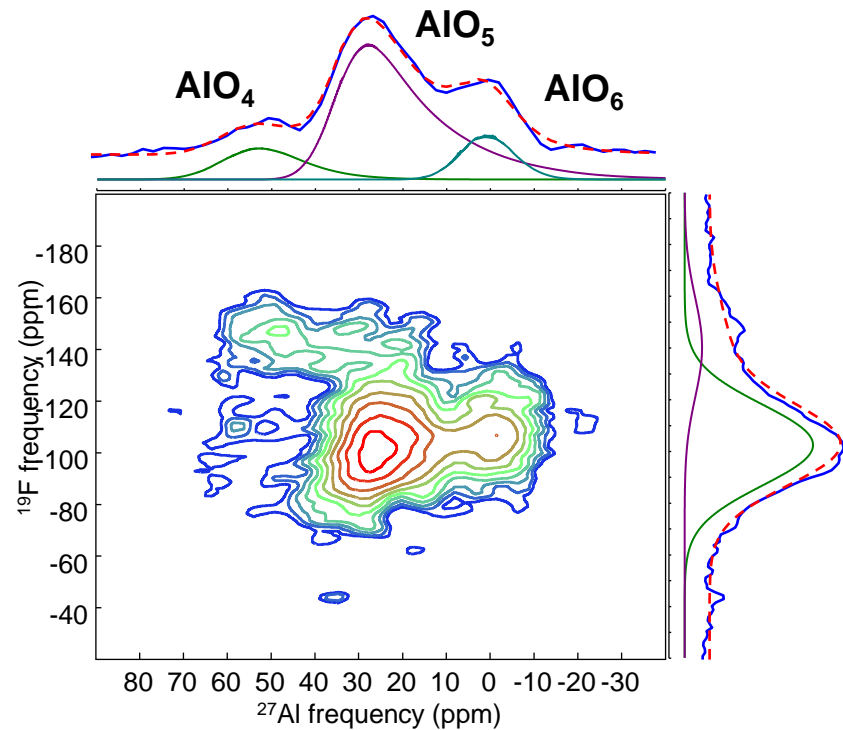


Correlating ^{19}F with ^{27}Al or ^{29}Si ...

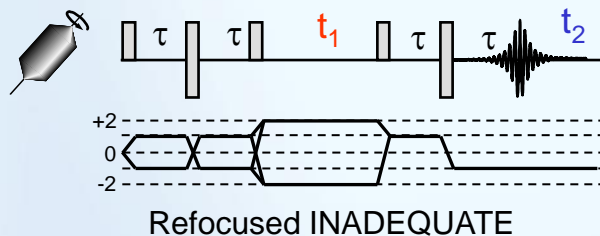
^{19}F MAS NMR Spectras



$^{27}\text{Al}\{^{19}\text{F}\}$ correlation

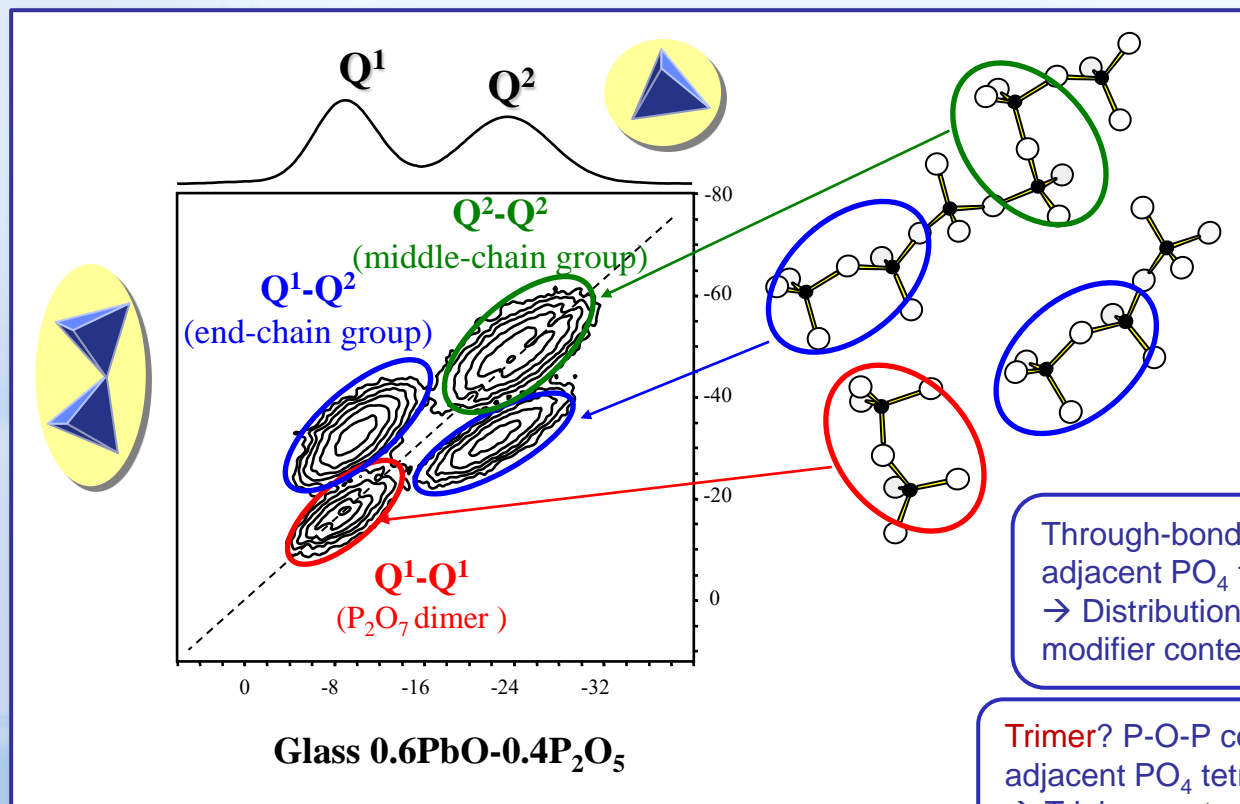


Identifying Dimers: 2Q/1Q Correlations



$^{31}\text{P-O-}^{31}\text{P}$ J Couplings (through bonds)

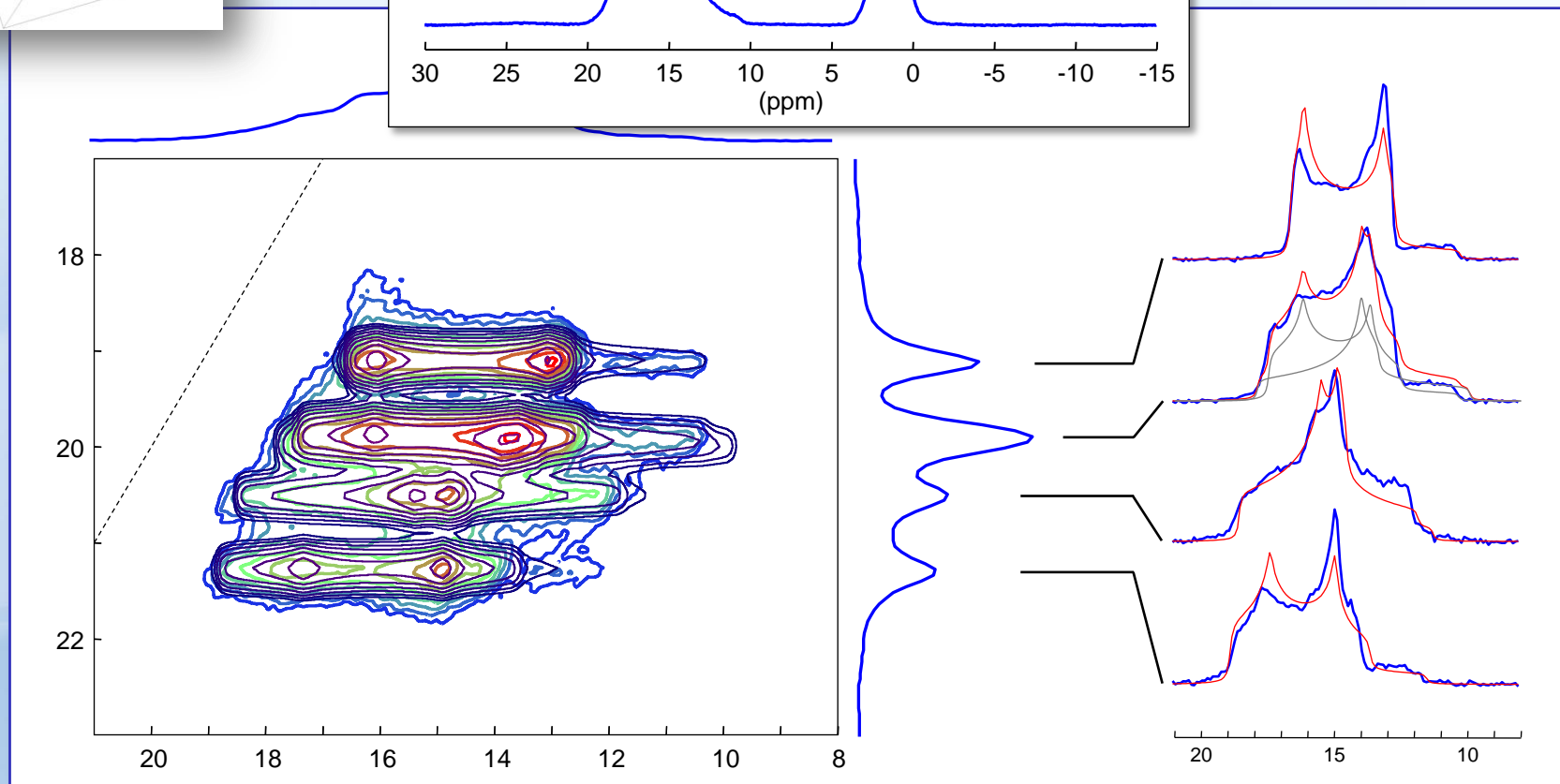
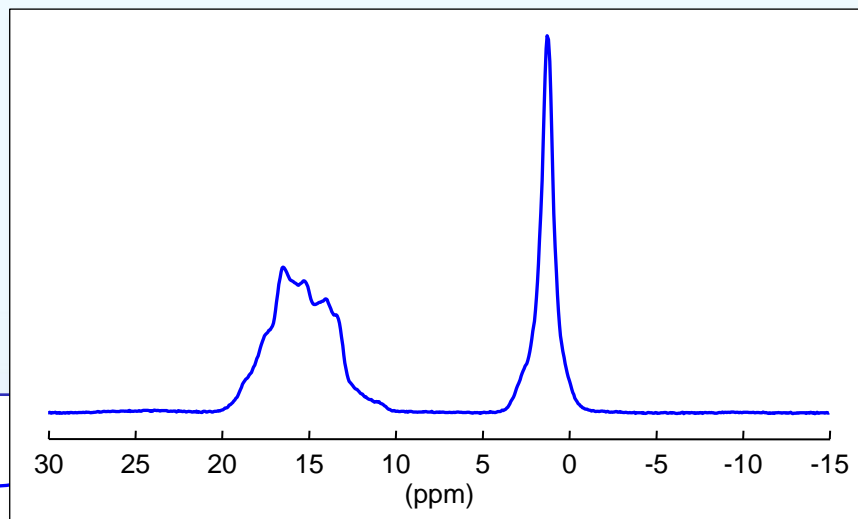
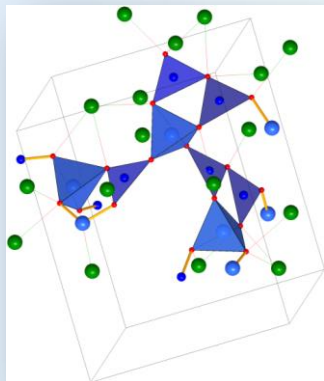
- Describes the network connectivity
- $^2J \sim 5$ to 30Hz for P-O-P



Through-bond P-O-P connectivities between **two** adjacent PO_4 tetrahedra
 → Distribution of chain length in glasses with high modifier content

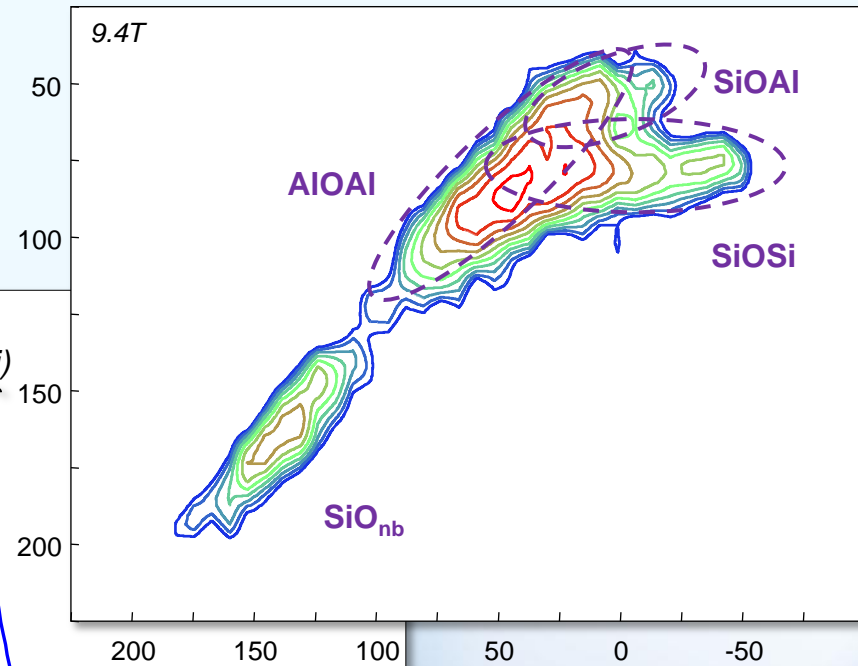
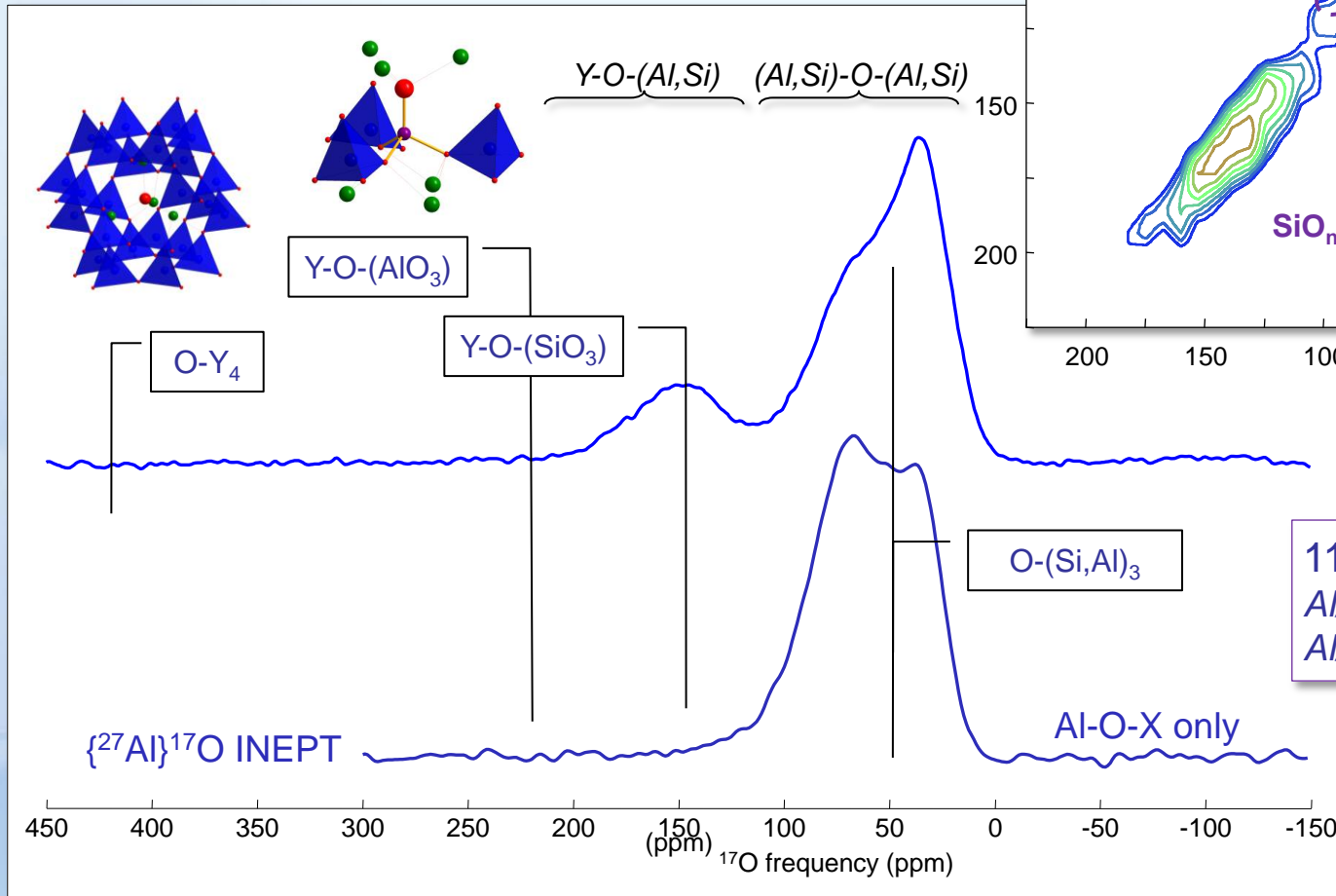
Trimer? P-O-P connectivities between **three** adjacent PO_4 tetrahedra
 → Triple quantum correlation spectra

^{11}B STMAS $\text{Na}_2\text{B}_4\text{O}_7$



Deciphering Oxygen Spectra

- Unambiguous presence of Y-O-(SiO₃)
- but no obvious signs of Y-O-(AlO₃) nor OY₄



11Y₂O₃ 17Al₂O₃ 72SiO₂
 Al/RE = 1.5
 Al/Si = 0.24

Conclusion

What is SSNMR Good for in Glass Science?

Access to topological and chemical disorder:

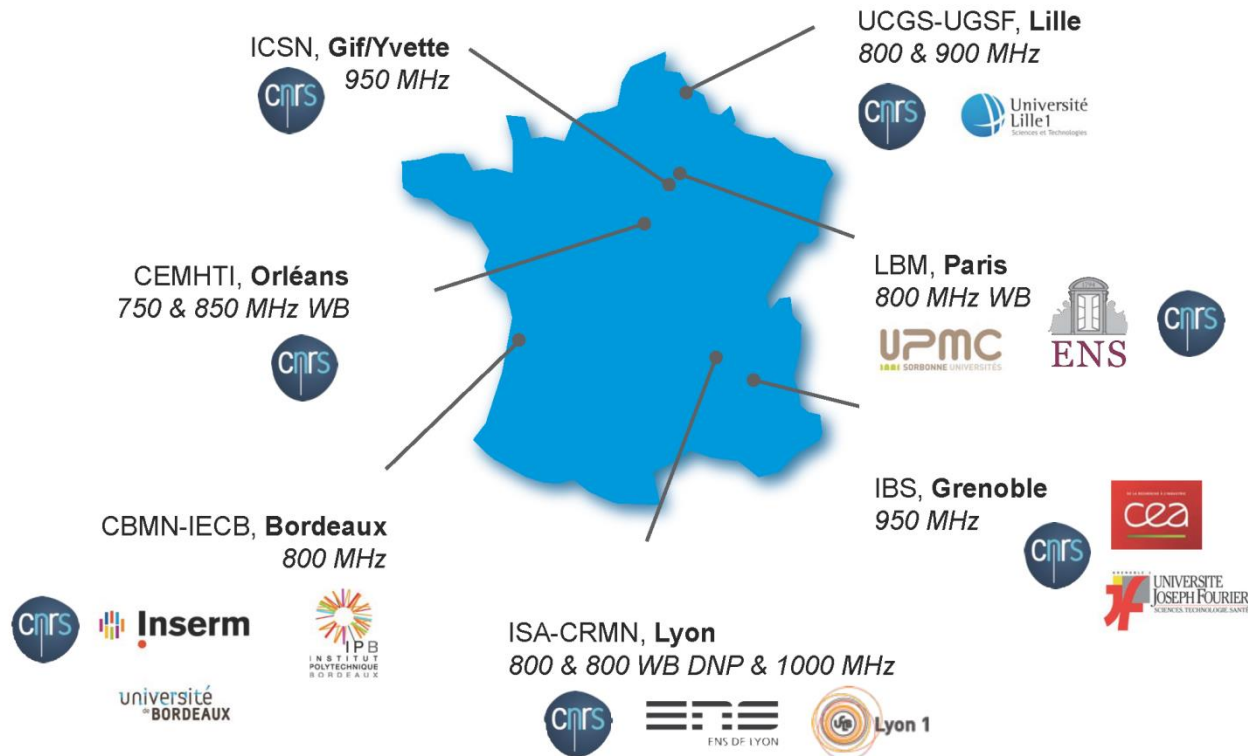
- description of the local environments (nature of 1st and second neighbors),
- quantification of their abundance,
- describes the network connectivity,
- quantification of topological disorder (bond & distance distributions)

and also: validate MD models, access to various timescales of motions through in-situ high-temperature NMR, etc...

l'Infrastructure de Recherche RMN THC



The French National High Field NMR Research Infrastructure



Class is Over...
Do Science & Have Fun!

Aknowledgments

- F. Fayon, CEMHTI (Orléans, France)
Curso RMN de Estado Sólido, Rio de Janeiro 2007
- G. Pintacuda, CRMN (Lyon, France)
Curso RMN de Estado Sólido, Rio de Janeiro 2007
- T. Charpentier, CEA (Saclay, France)
2^e école du GERM, Cargèse 2013
- P. J. Grandinetti, The Ohio State University (Columbus, USA)
2^e école du GERM, Cargèse 2013
- N. Giraud, Université Paris Sud (Paris, France)
2^e école du GERM, Cargèse 2013
- J. Titmann, University of Nottingham (GB)
<http://www.solidstatenmr.org.uk/lectures.html>
- Apperley, Harris & Hodgkinson,
« Solid-State NMR – Basic Principles & Practice », Momentum Press, New York 2012