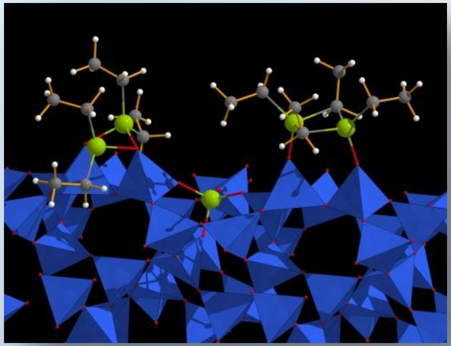
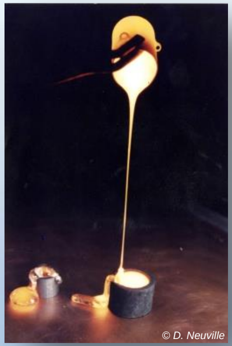
Solid-State NMR applied to Glasses: an Introduction





P. Florian

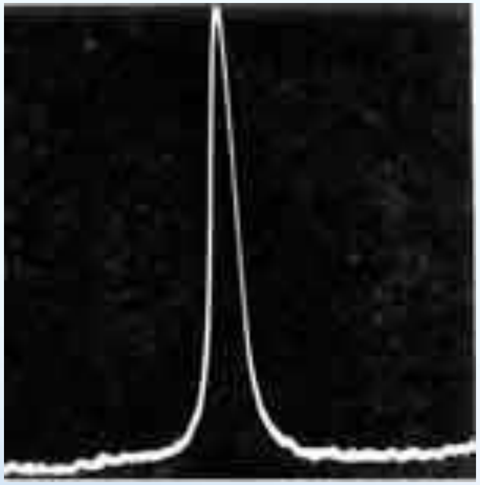
CEMHTI-CNRS, Orléans, France

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

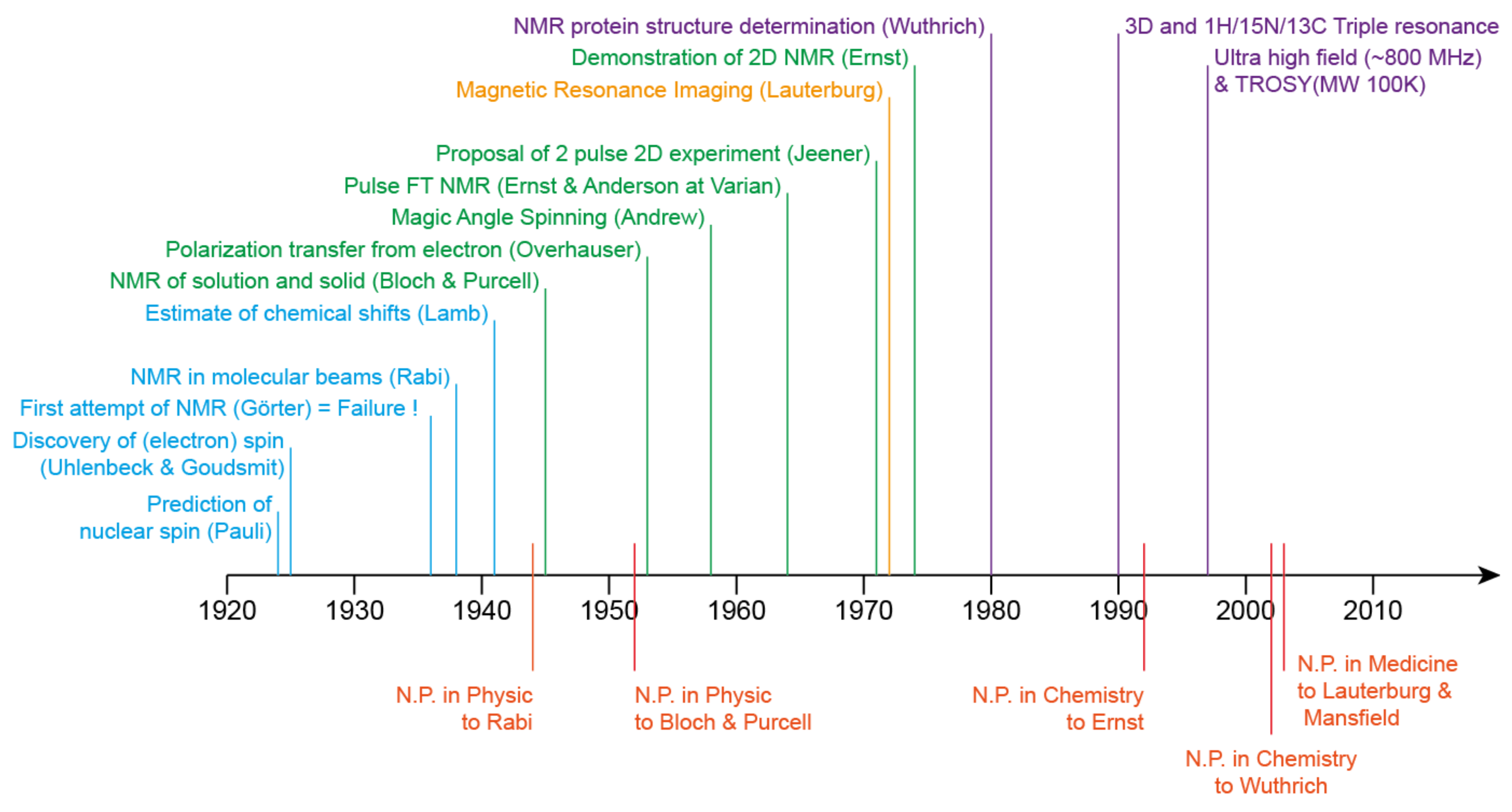
Purcell, Phys. Rev. 1946

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."

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

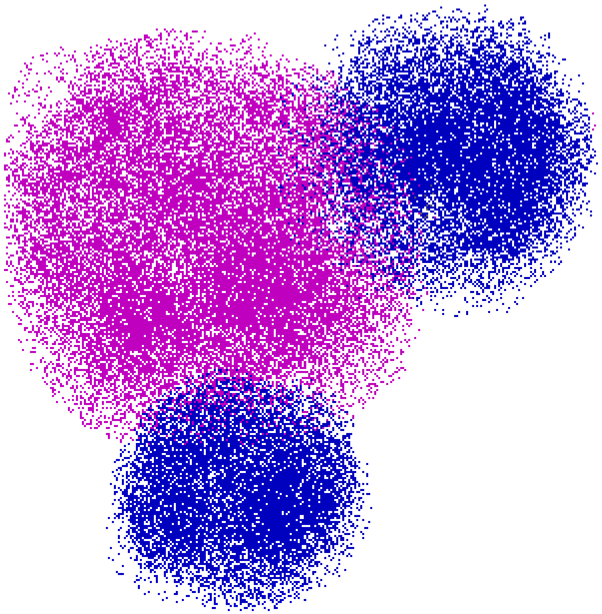
NMR TimeLine



The Music of Atoms

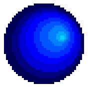
An (Ultra) Short Introduction to NMR Spectroscopy

Nuclear + Magnetic + Resonance (Spectroscopy)

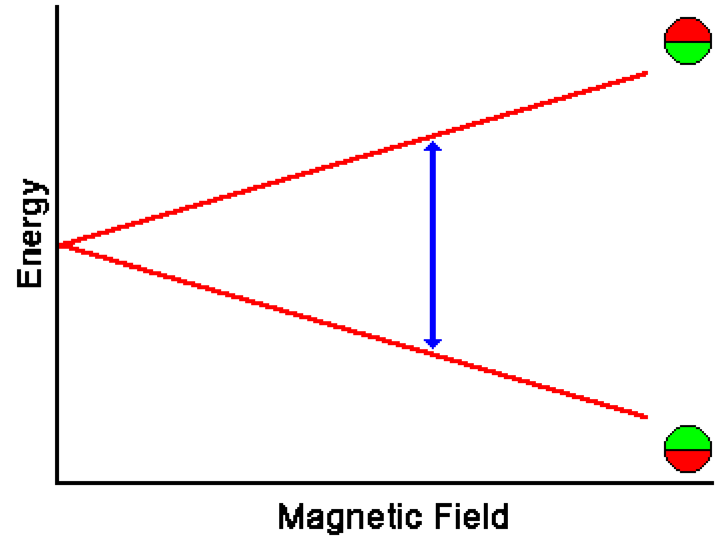


Nuclear + Magnetic + Resonance (Spectroscopy)

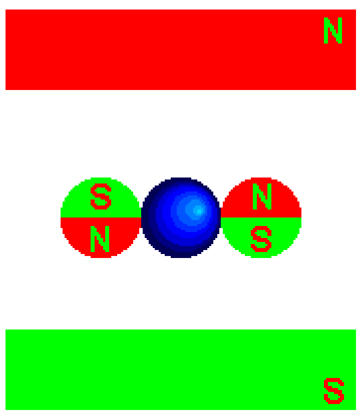
Nuclear



Nuclear + Magnetic + Resonance (Spectroscopy)

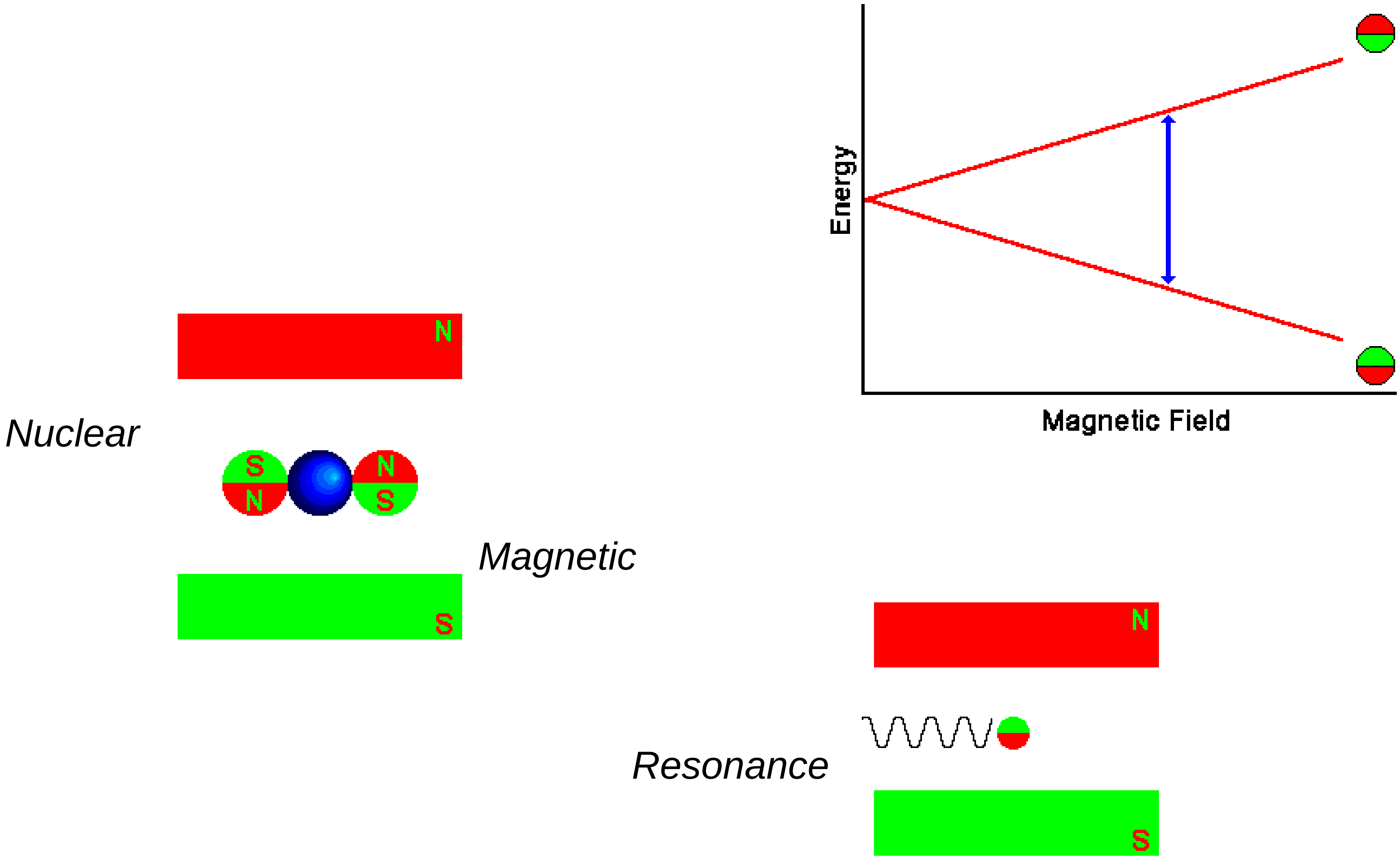


Nuclear

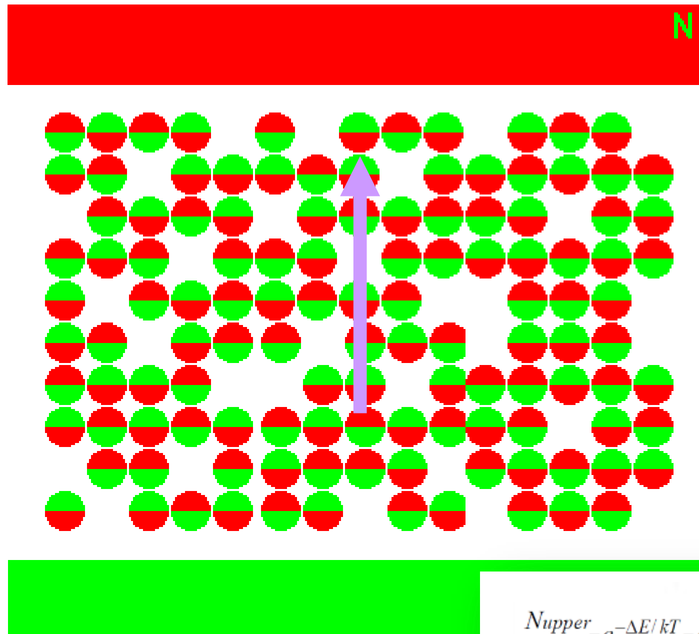


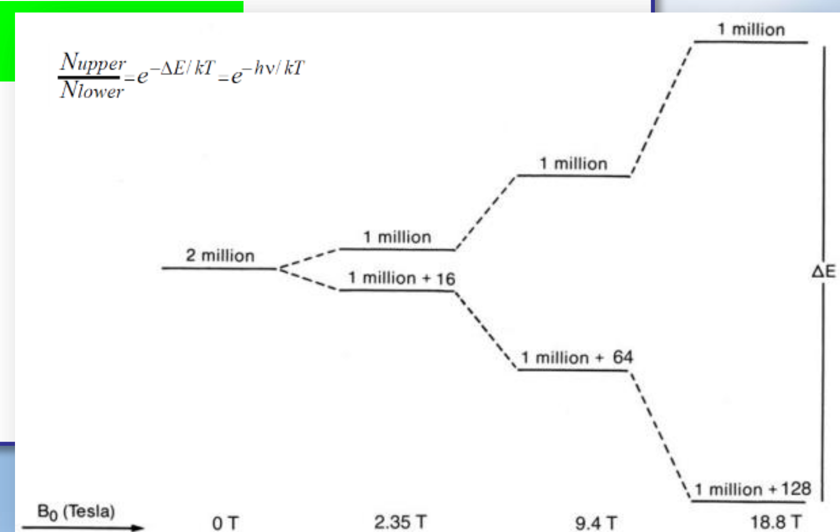
Magnetic

Nuclear + Magnetic + Resonance (Spectroscopy)

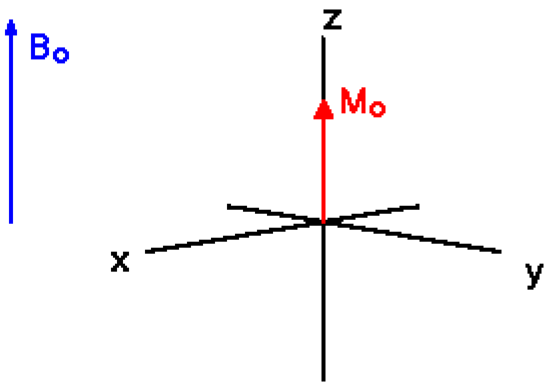


The Magnetization

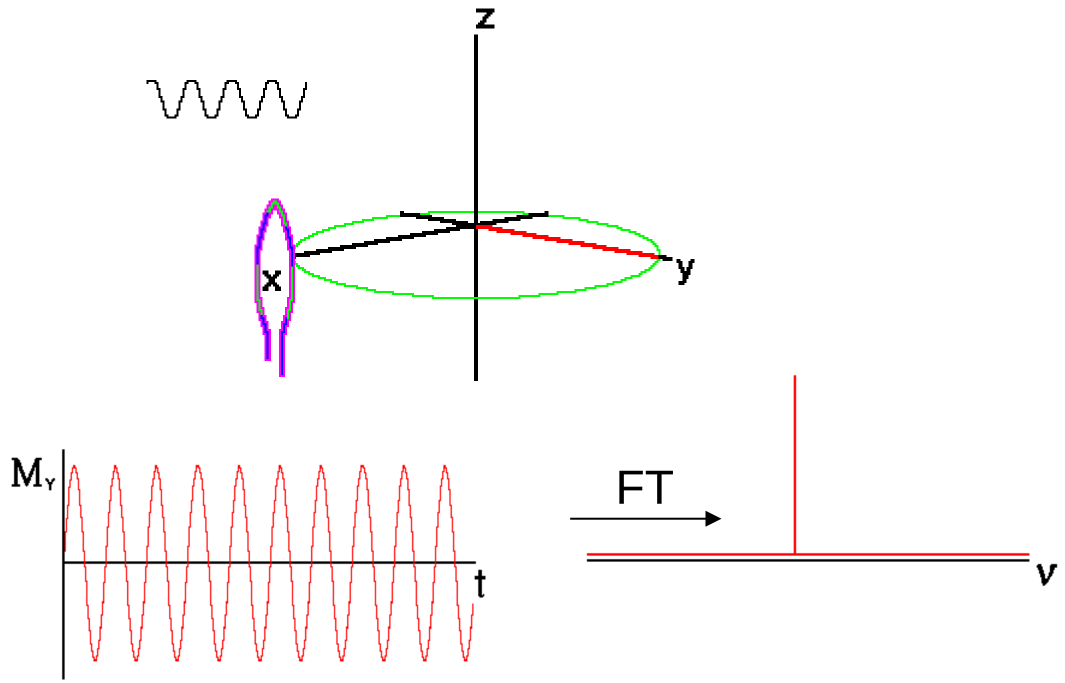




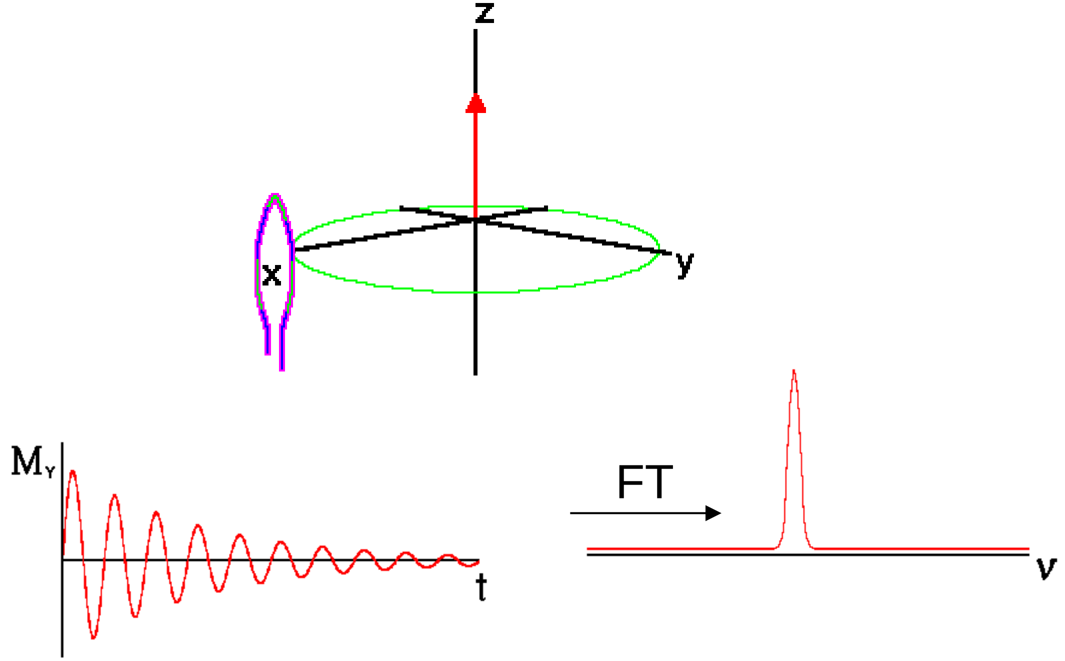
The Magnetization



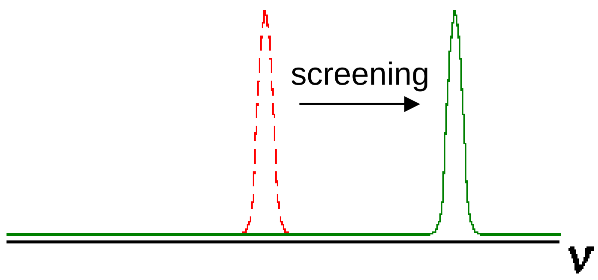
Pulse, Free Induction Decay and spectral domain

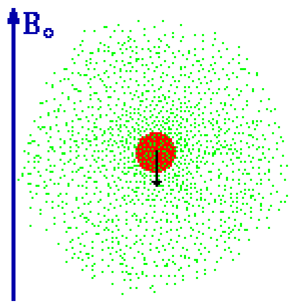


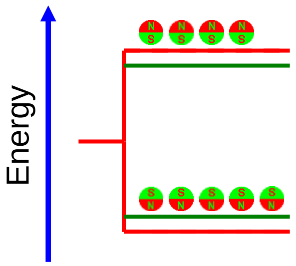
And do not forget to relax…

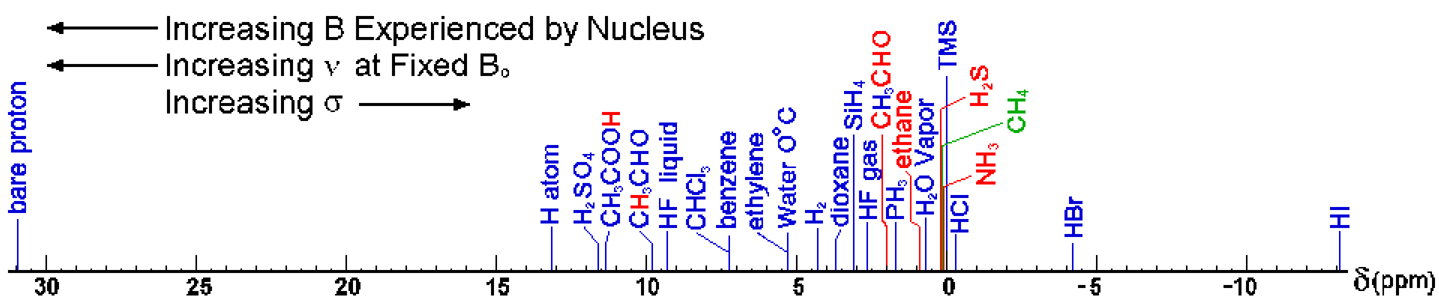


The chemical shift interaction

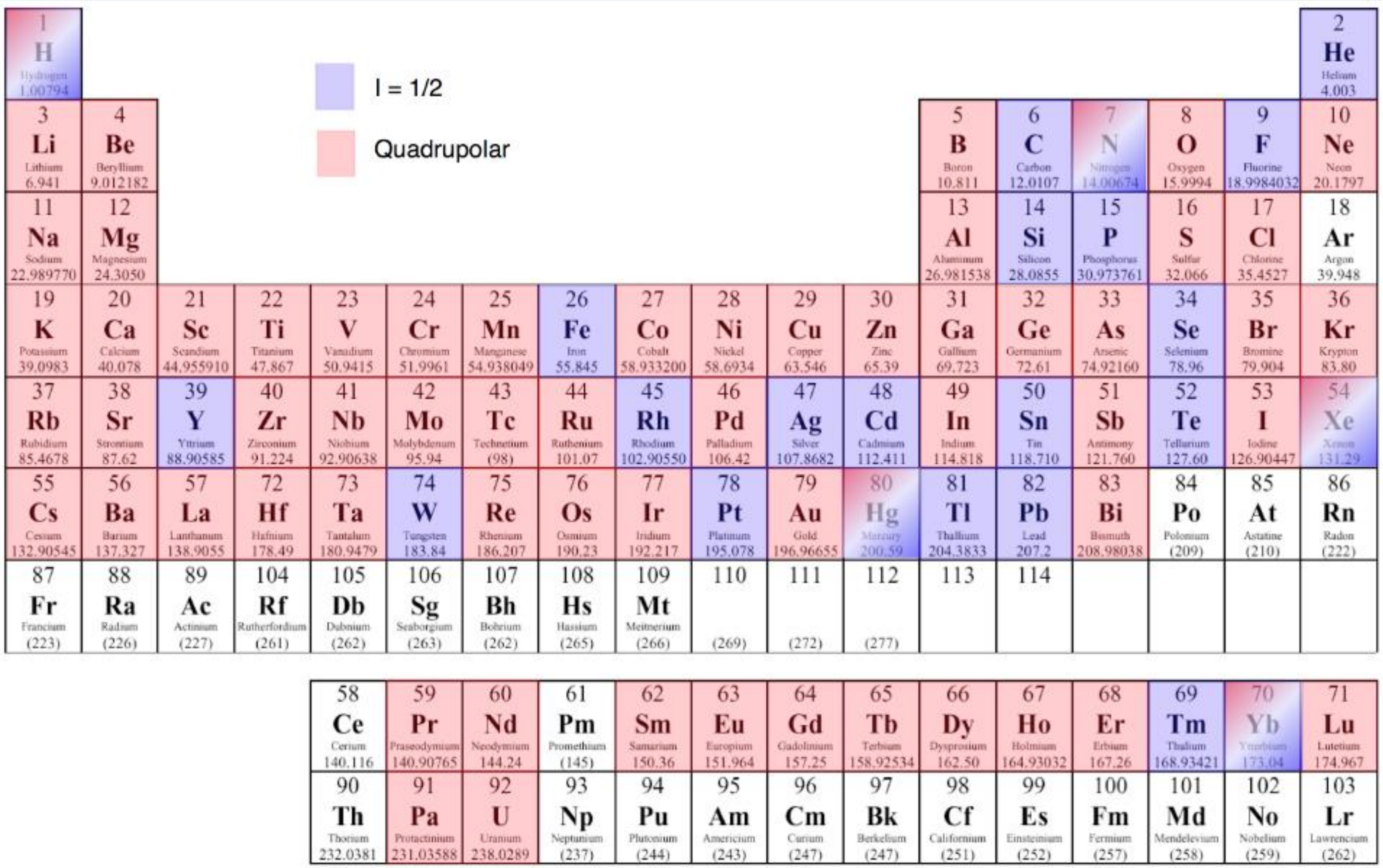








Possibilities & Opportunities



- **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**

Interactions in the Solid State

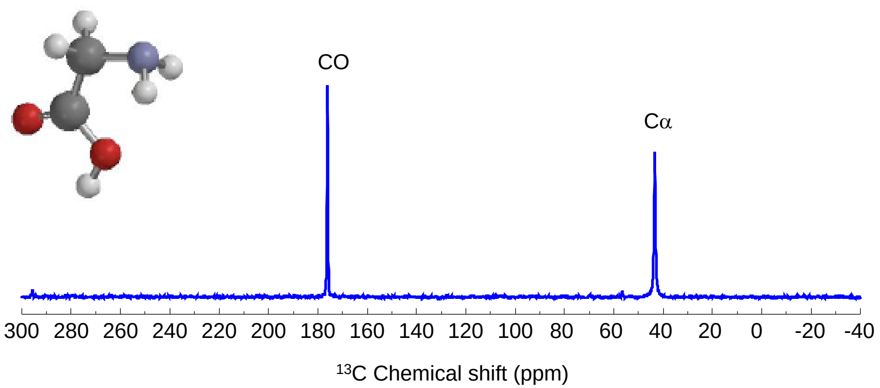
Challenge : Strong Interactions

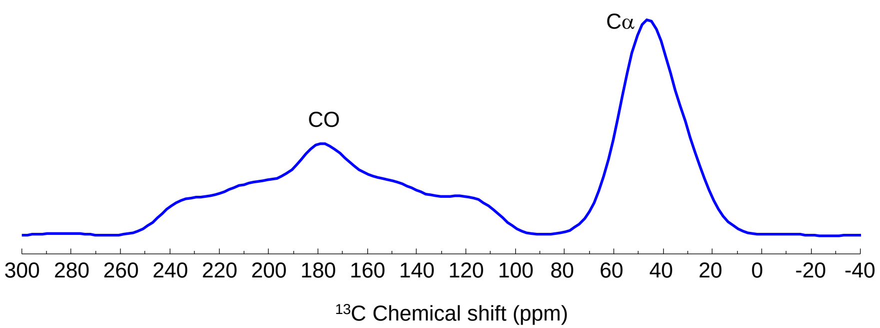
Liquid:
Weak interactions
J-couplings
(up to 150 Hz)

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

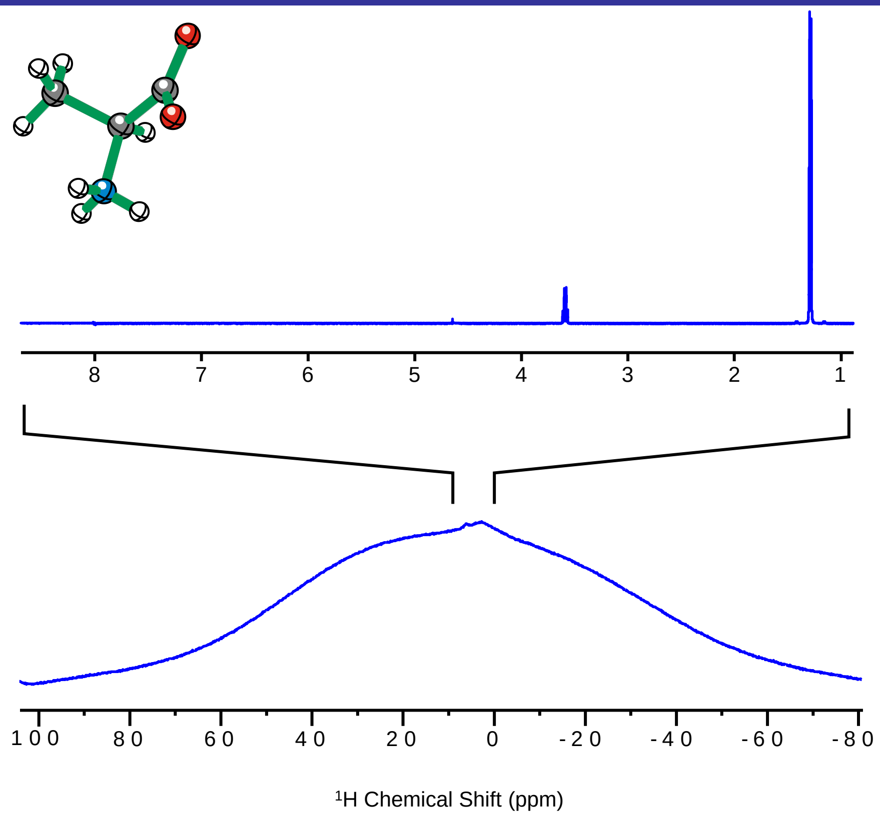
Challenge : Strong Interactions

^{13}C NMR of Glycine

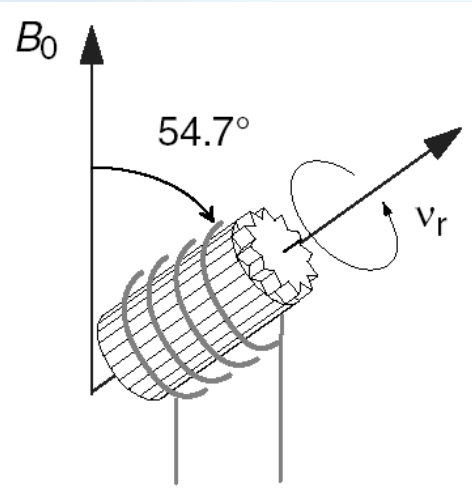


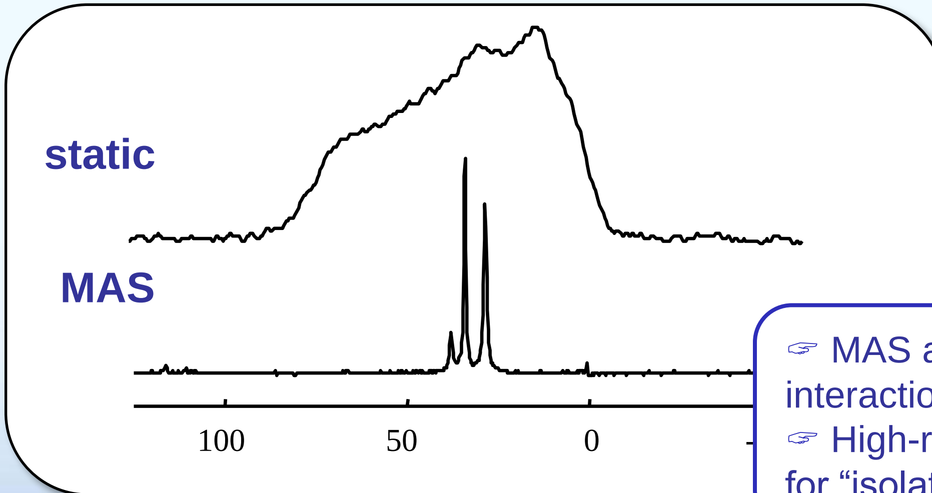


^{1}H NMR of L-alanine



It's a Kind of Magic…

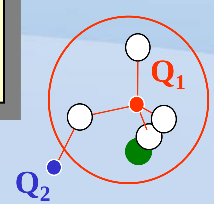


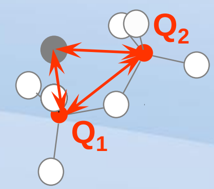


☞ MAS averages anisotropic interactions (to 1st order)
☞ High-resolution spectrum for "isolated" spin ½ nuclei

Isotropic Chemical Shift

CSA

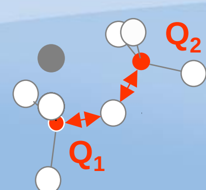


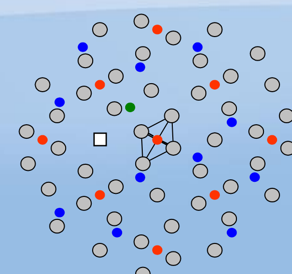


Dipolar couplings

Isotropic *J*-couplings

***J*-anisotropy**





I > ½

1st order Quadrupolar interaction

2nd order Quadrupolar interaction

Magic Angle Spinning

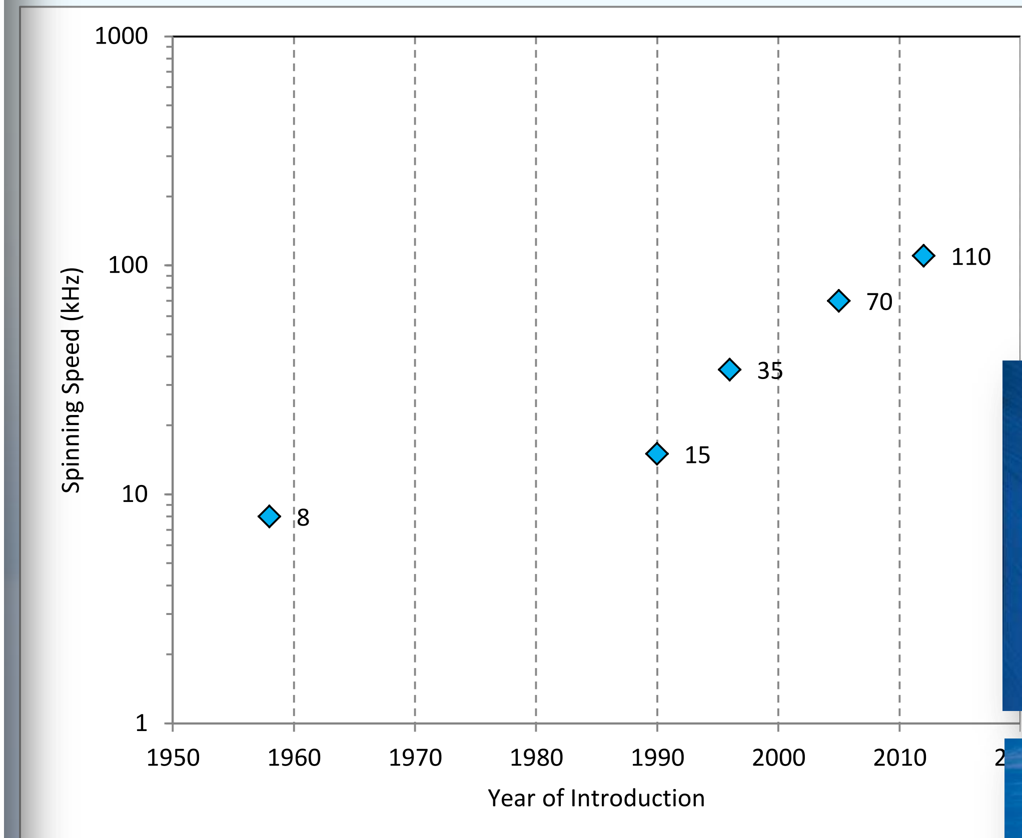
Spinning Spins
A Tribute to Raymond Andrew

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.

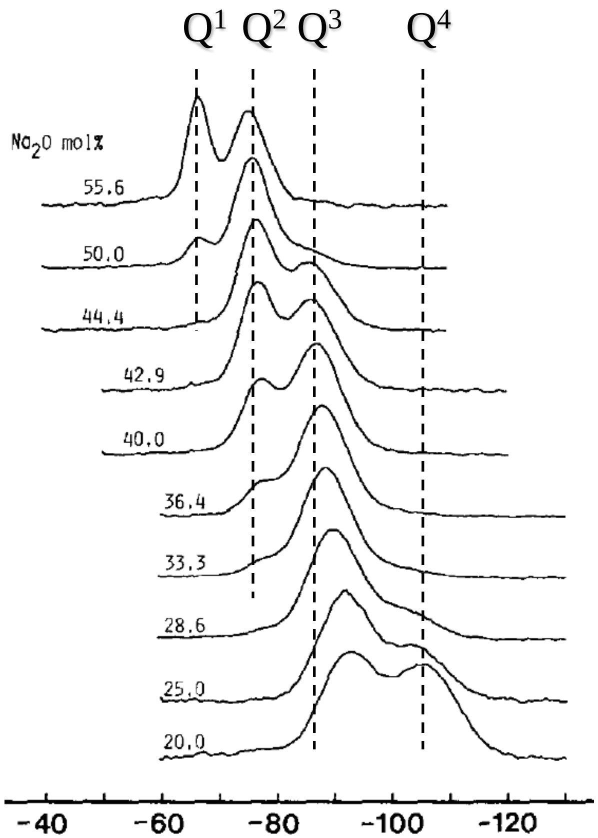
Few experiments can surpass
The versatility of MAS
In probing the secrets of nature
We ponder anew
The progress that's due
To Raymond's great genius and stature.

Vincent McBrierty, 1997



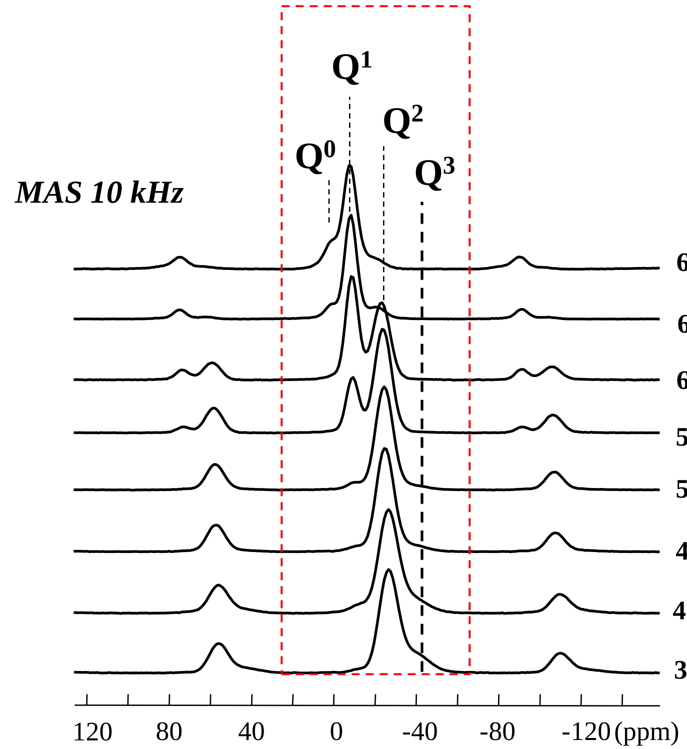
Observing Q^n Species

^{29}Si MAS NMR of Na_2O-SiO_2 glasses



H. Maekawa et al. JNCS **127** 53 (1991)

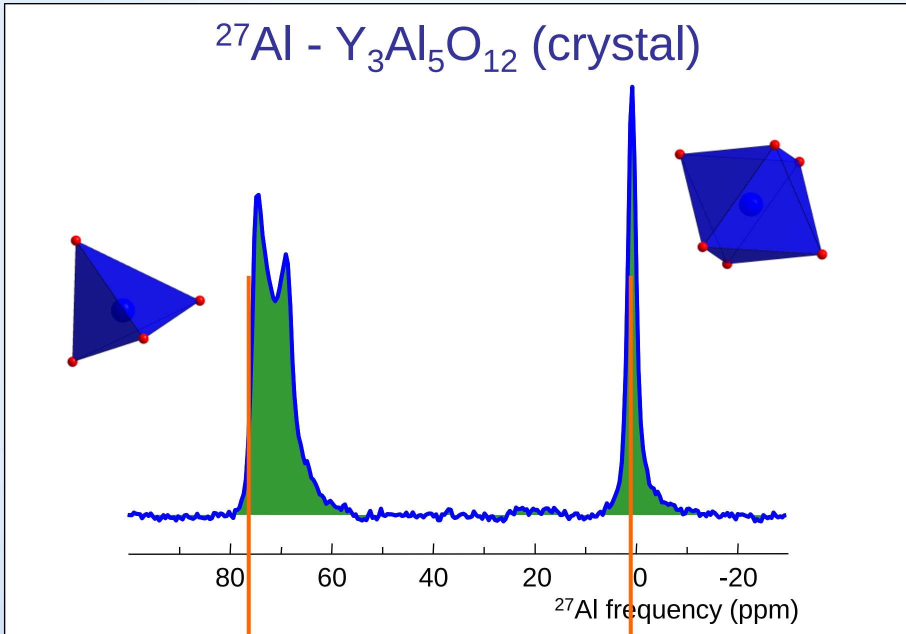
^{31}P MAS NMR of PbO-P_2O_5 glasses

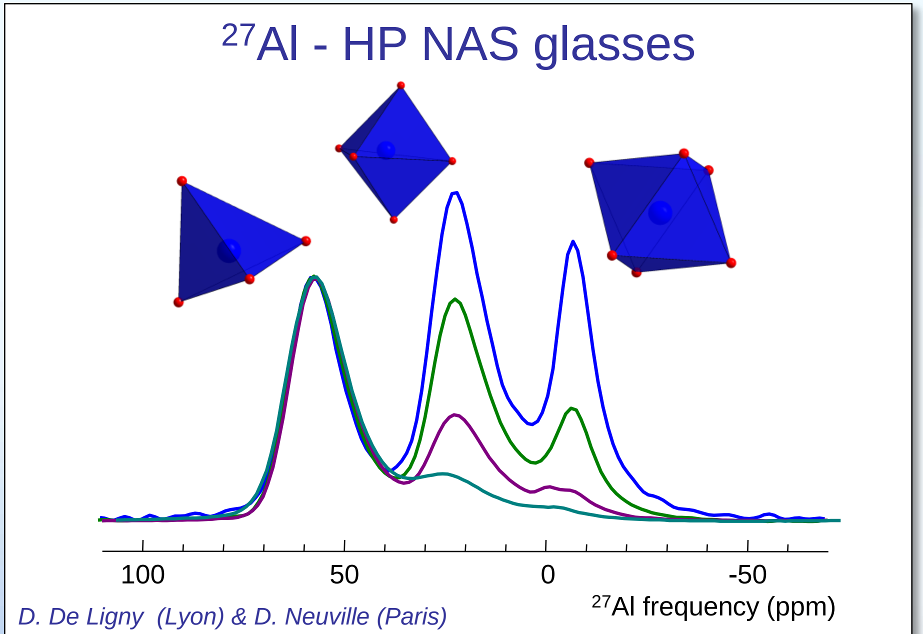


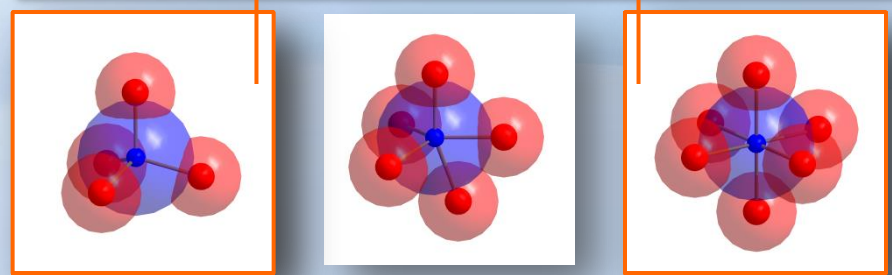
- ☞ Broad resonance lines : distribution (of ^{29}Si or ^{31}P) chemical shift due to structural disorder
- ☞ Assignment of the resonances from (^{29}Si or ^{31}P) chemical shift range in crystalline lead phases

☞ **Unambiguous identification & quantification of the Q^n units**

(^{27}Al) Nuclear Magnetic Resonance







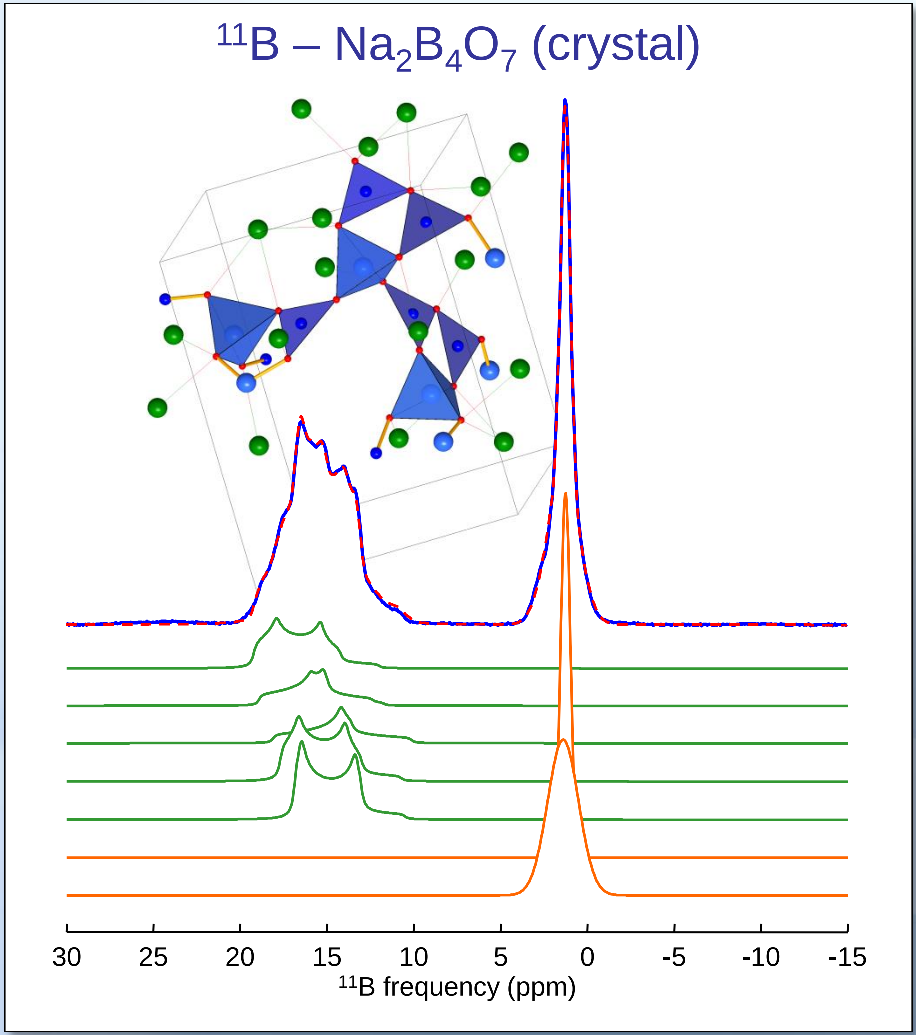
Position
(*chemical shift*, magnetic shielding):

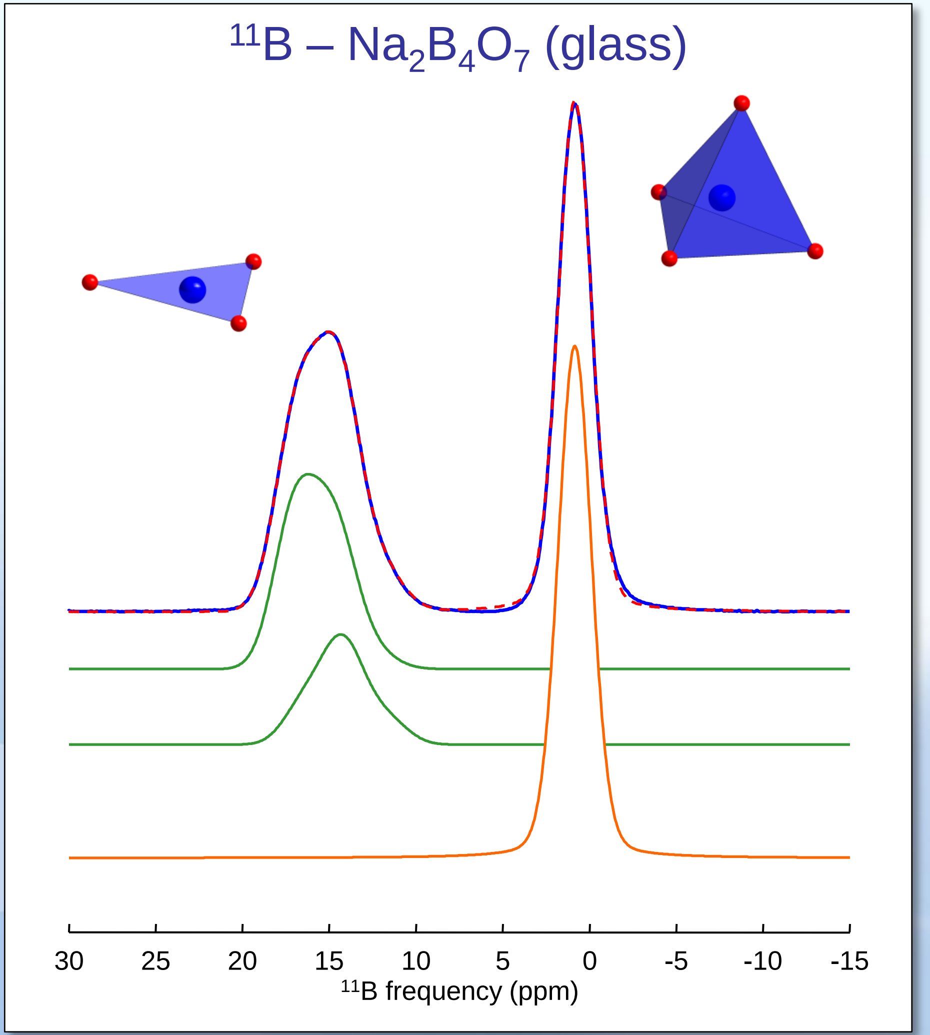
- ☞ coordination number
- ☞ 2nd coordination sphere neighbors
- ☞ local geometry

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

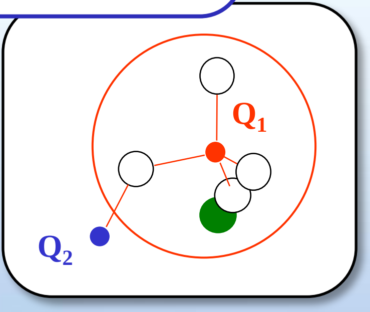
☞ quantitative

Interactions in the Solid-State

~10s of kHz

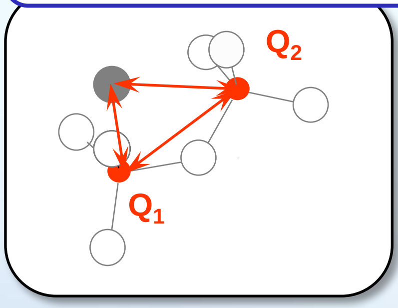
Chemical Shift Anisotropy
- ☞ Electronic shielding
- ☞ Chemical environment, coordinence & geometry

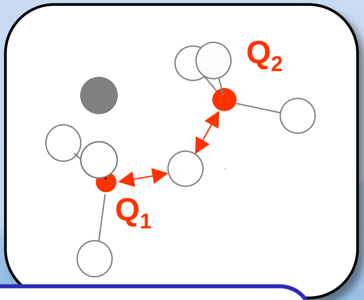
propr. B_0



~kHz $1/r^3$

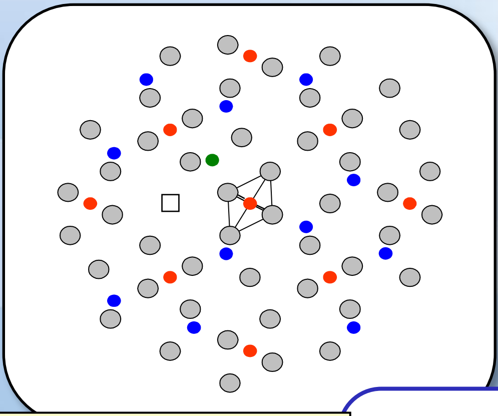
Dipolar Couplings
- ☞ Neighboring spin distances





Indirect *J* Couplings
- ☞ Chemical bonds geometry
- ☞ Connectivity

< 100s of Hz



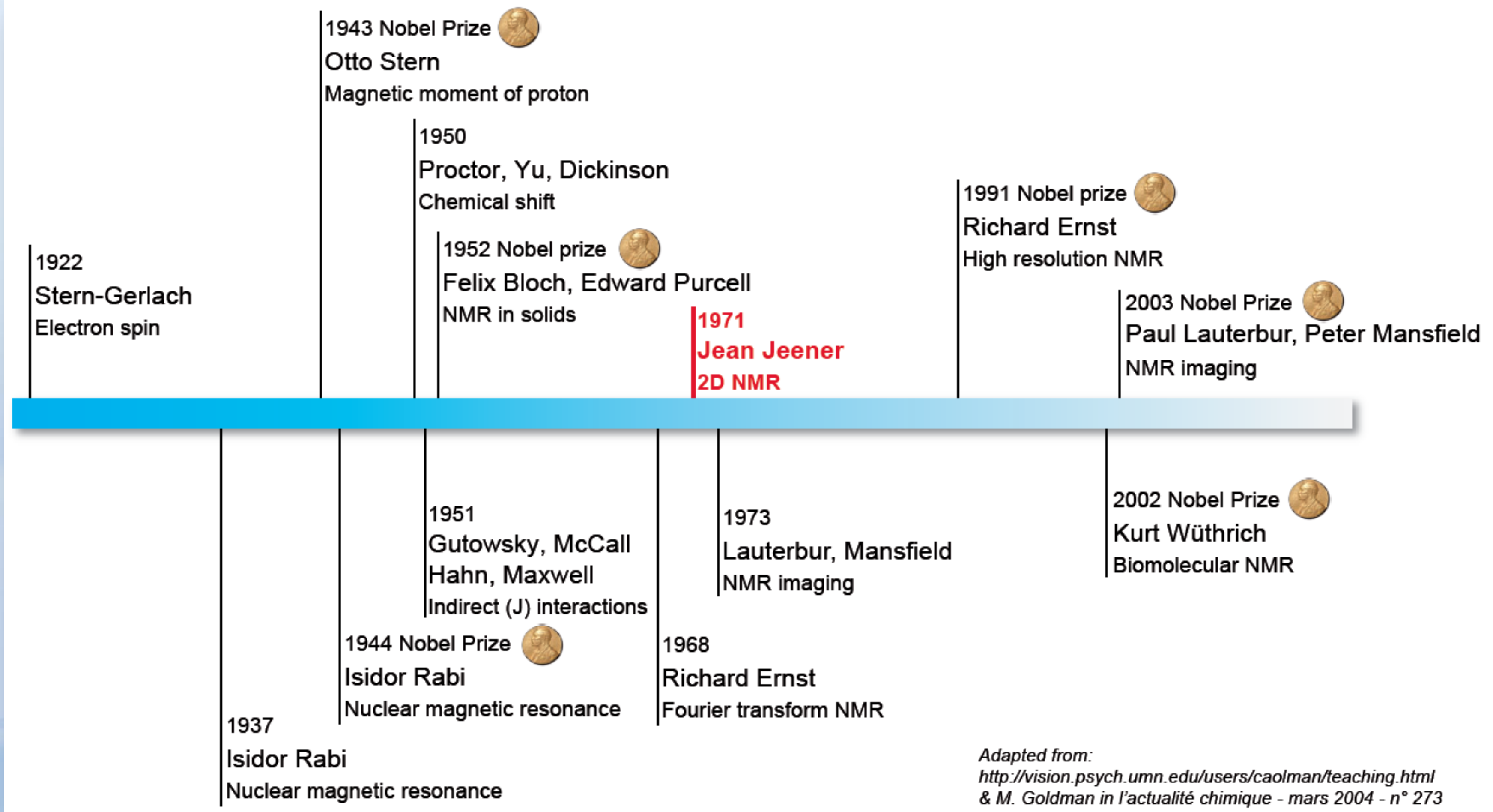
I>1/2, up to MHz

Quadrupolar Interaction
- ☞ Electric Field Gradient
- ☞ Surrounding electrons & nuclei geometry

2^{nd} order propr. $1/B_0$

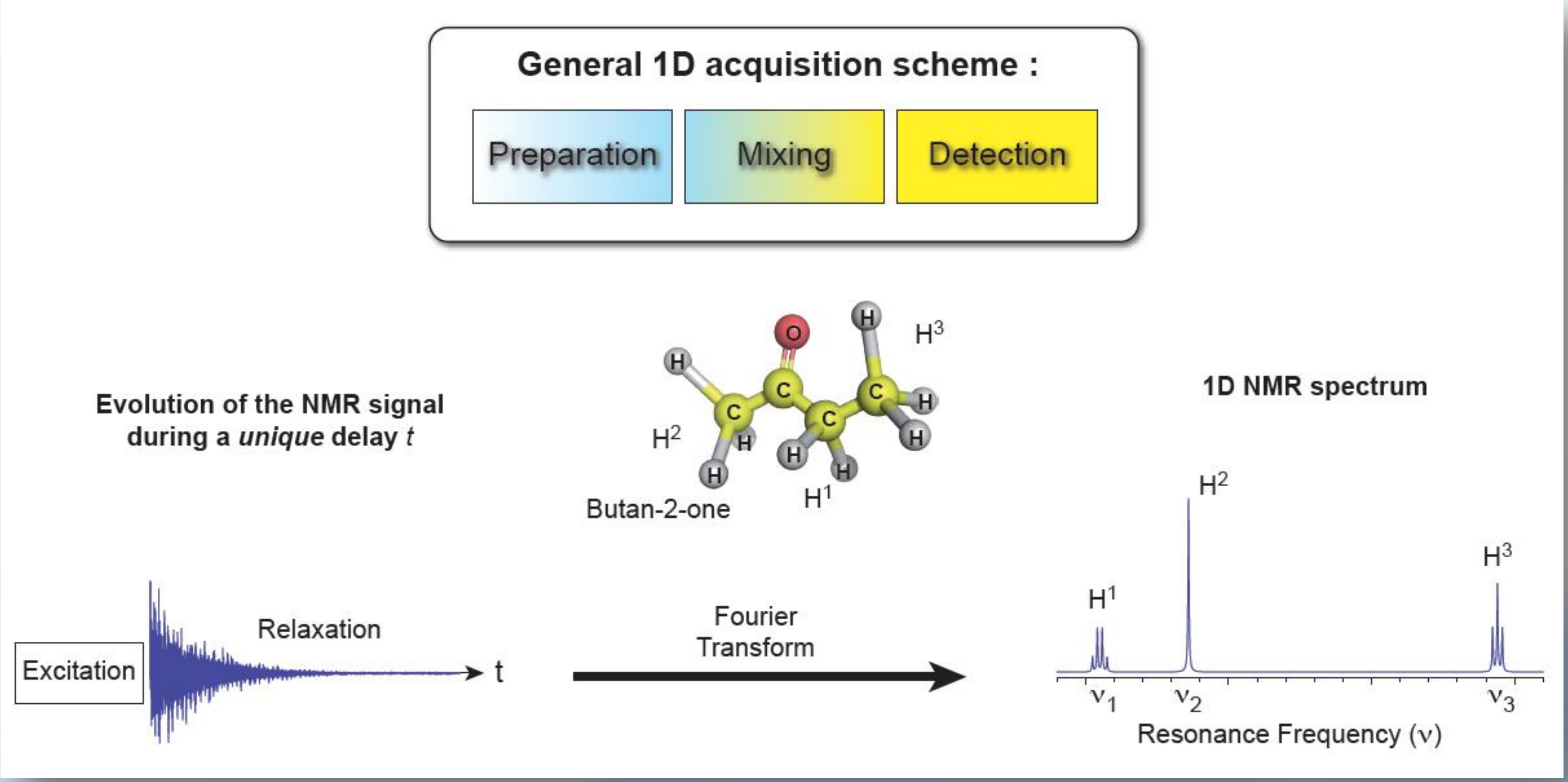
Let’s go Two-Dimensional!

NMR Timeline and Birth of 2D

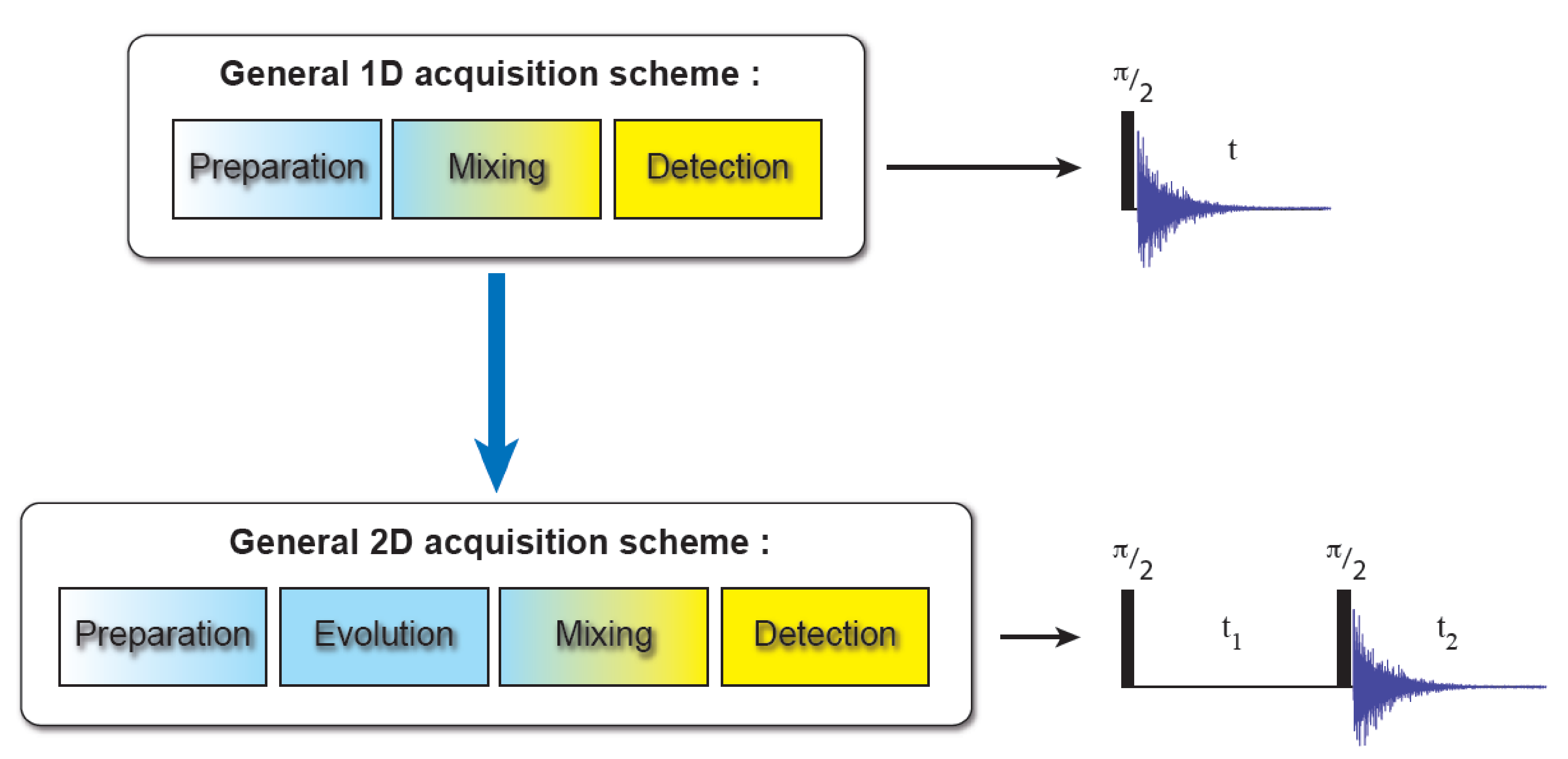


Adapted from:
http://vision.psych.umn.edu/users/caolman/teaching.html
& M. Goldman in l'actualité chimique - mars 2004 - n° 273

Principle of 1D NMR



The Basic Idea

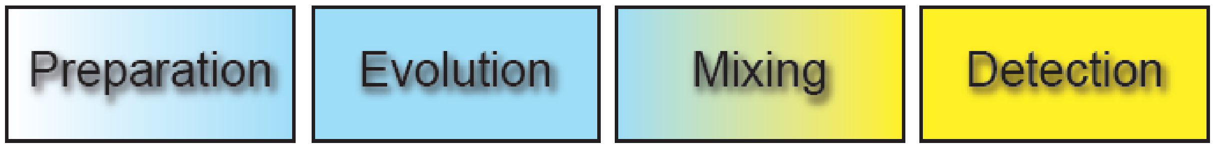


"The next fortunate event occurred in 1971 when my first graduate student, Thomas Baumann, visited the Ampere Summer School in Basko Polje, Yugoslavia, where Professor Jean Jeener proposed a simple two-pulse sequence that produces, after two-dimensional Fourier transformation, a two-dimensional (2D)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

Richard Ernst, Nobel Prize in Chemistry, 1991

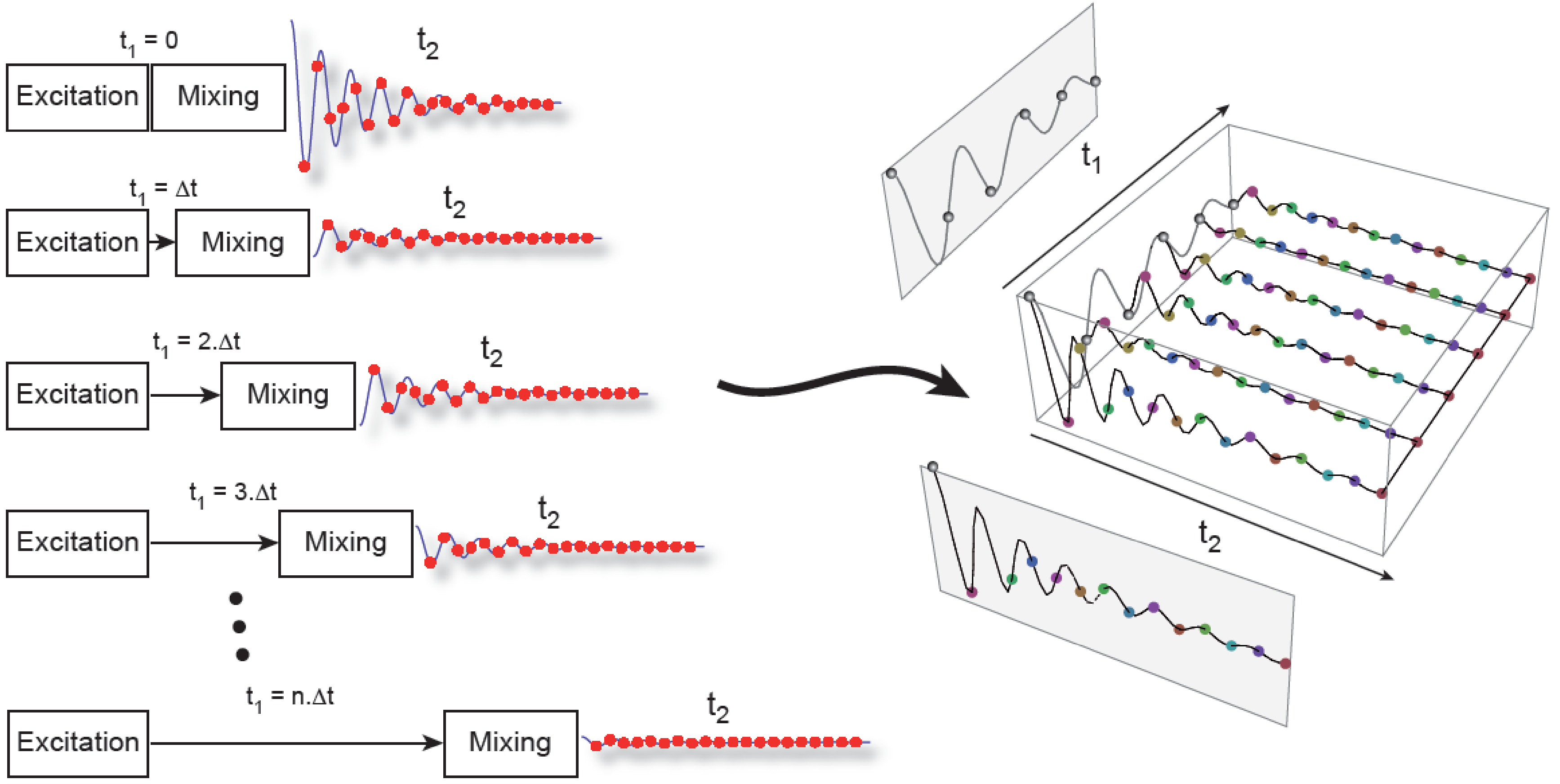
The Basic Idea

General 2D acquisition scheme :

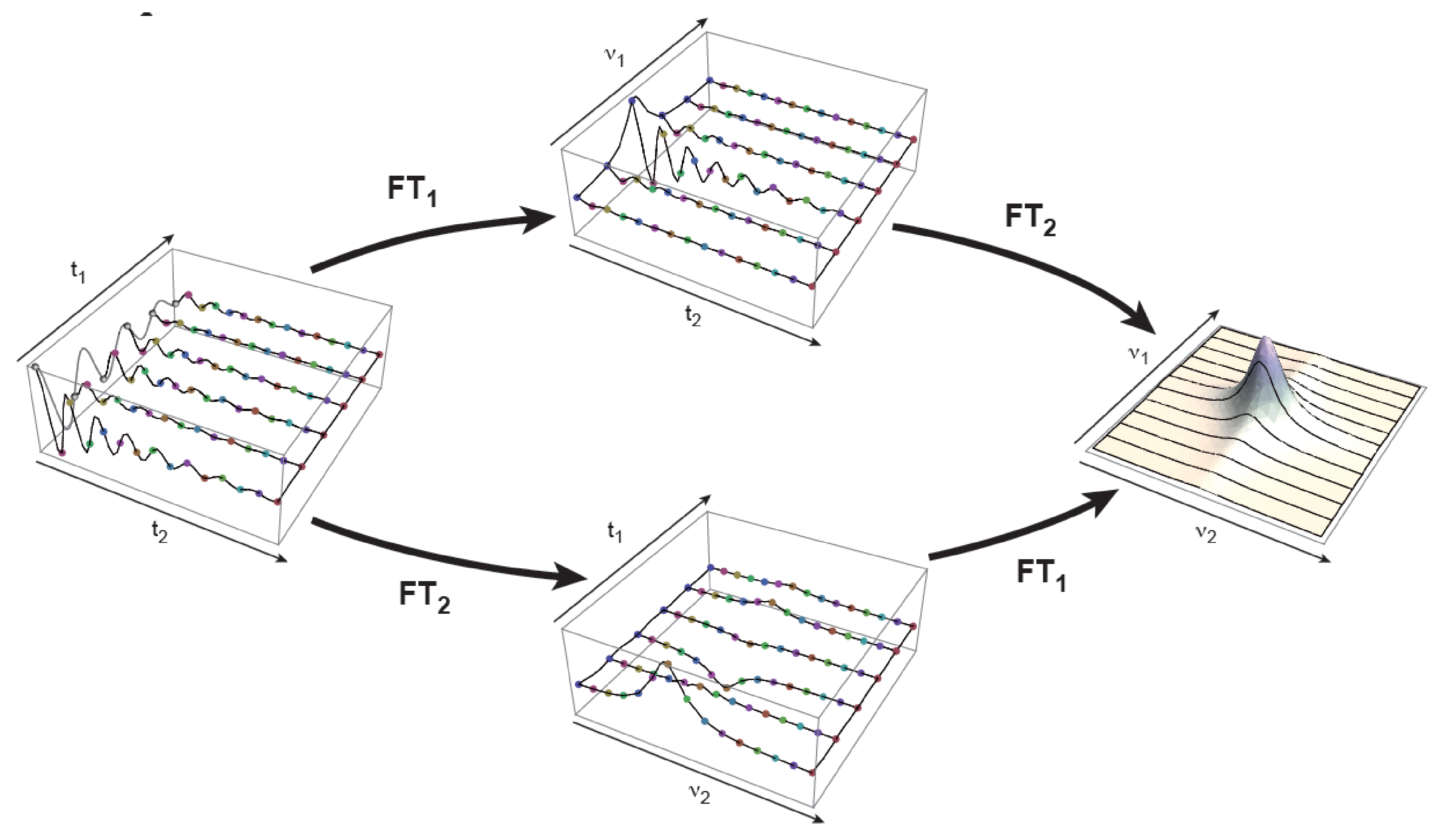


- **Preparation** : nuclear spins are put in a non equilibrium state (polarization ...)
- **Evolution** : spins evolve according to their resonance frequency as well as all the spin interactions that are active on the prepared spin state.
- **Mixing** : polarization is “exchanged” between spins. Magnetization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

Two-Dimensional NMR

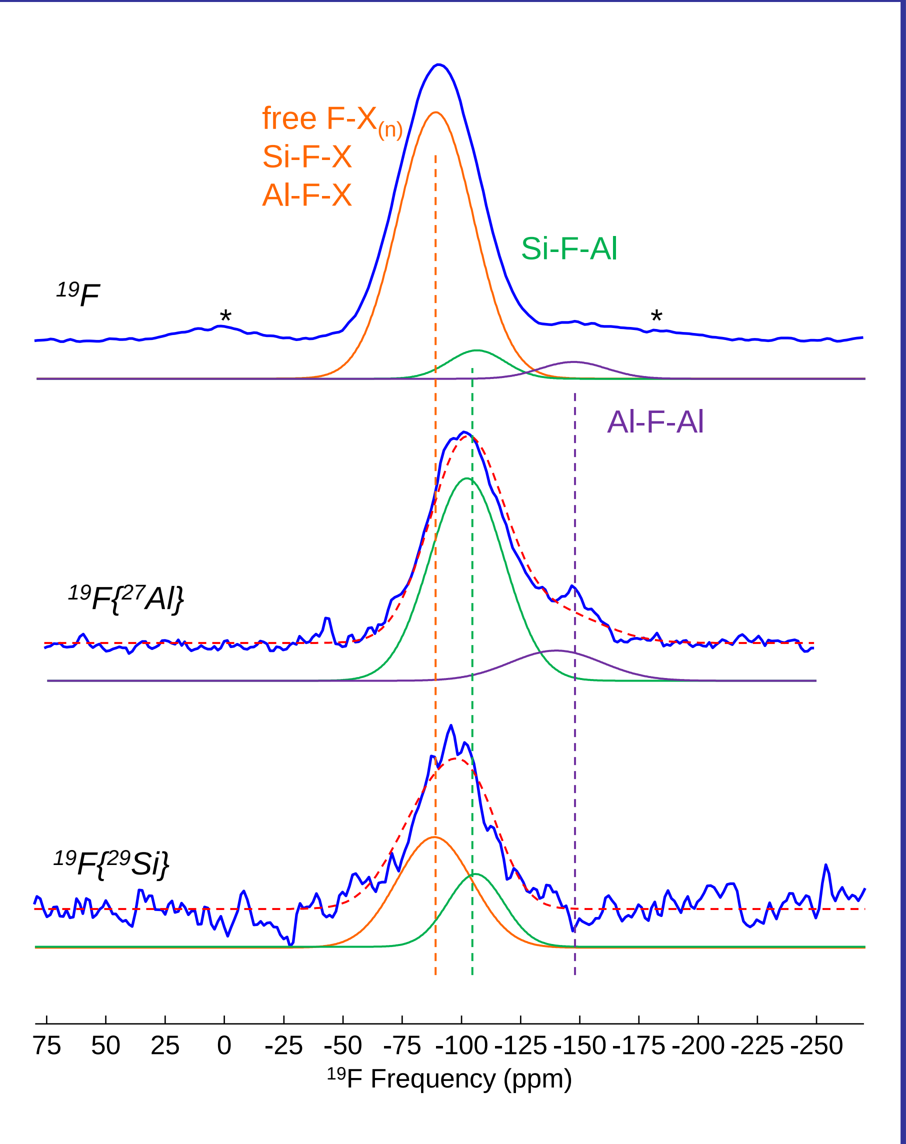


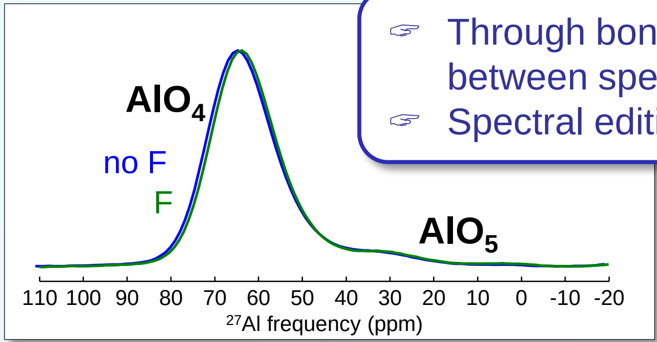
Two-Dimensional NMR



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

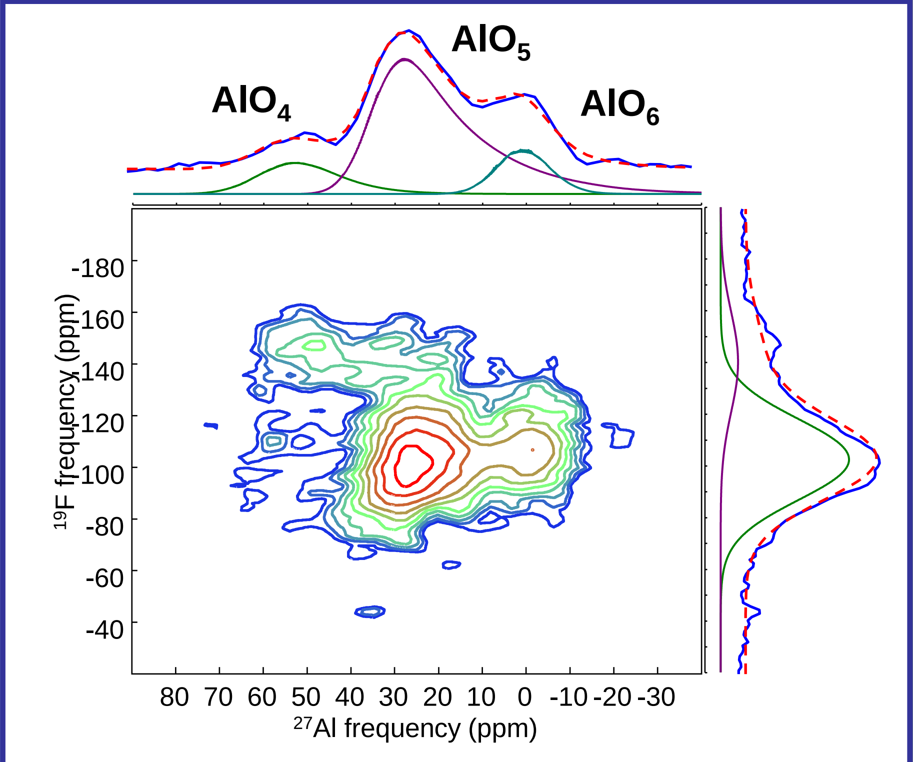
^{19}F MAS NMR Spectras



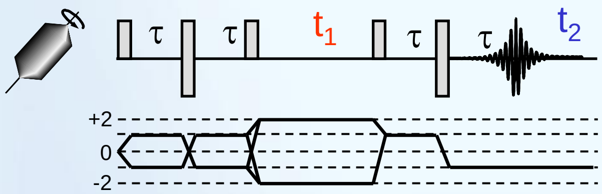


- Through bond correlations between species
- Spectral editing

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



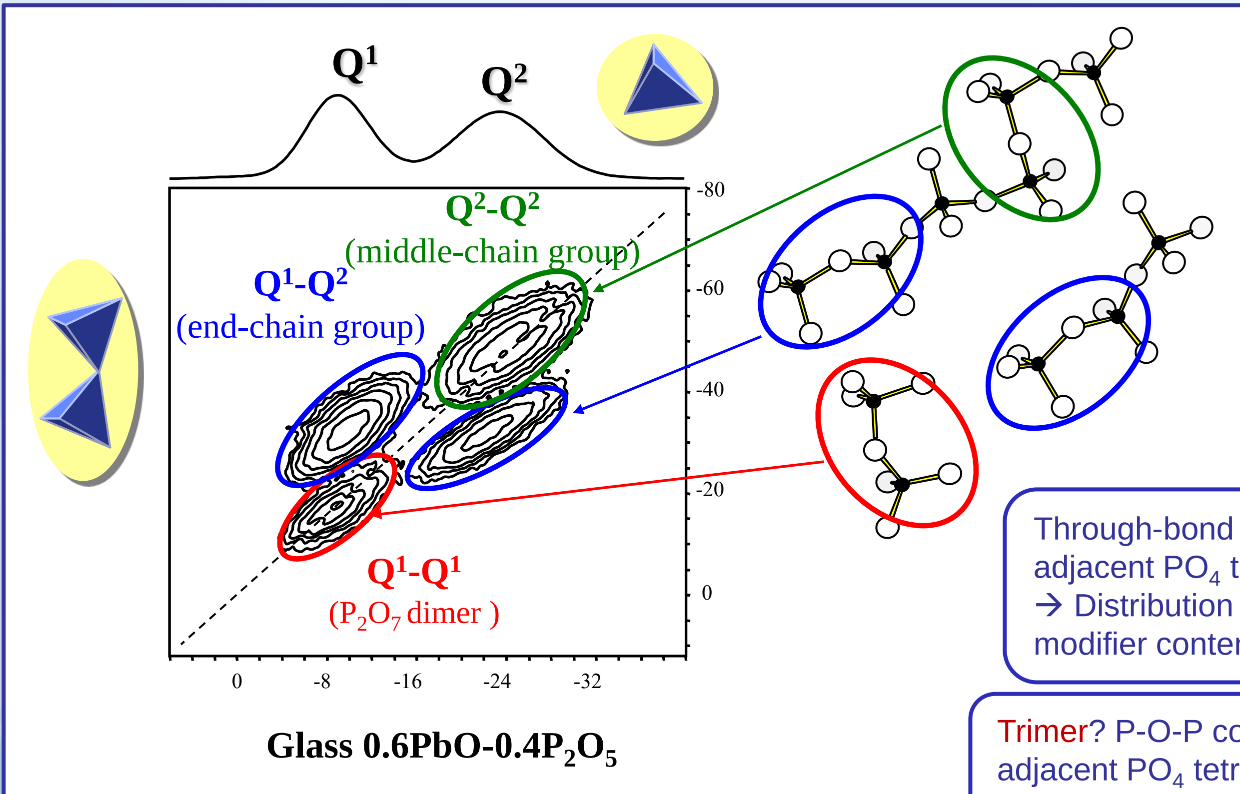
Identifying Dimers: 2Q/1Q Correlations



Refocused INADEQUATE

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

- Describes the network connectivity
- ^2J ~ 5 to 30Hz for P-O-P



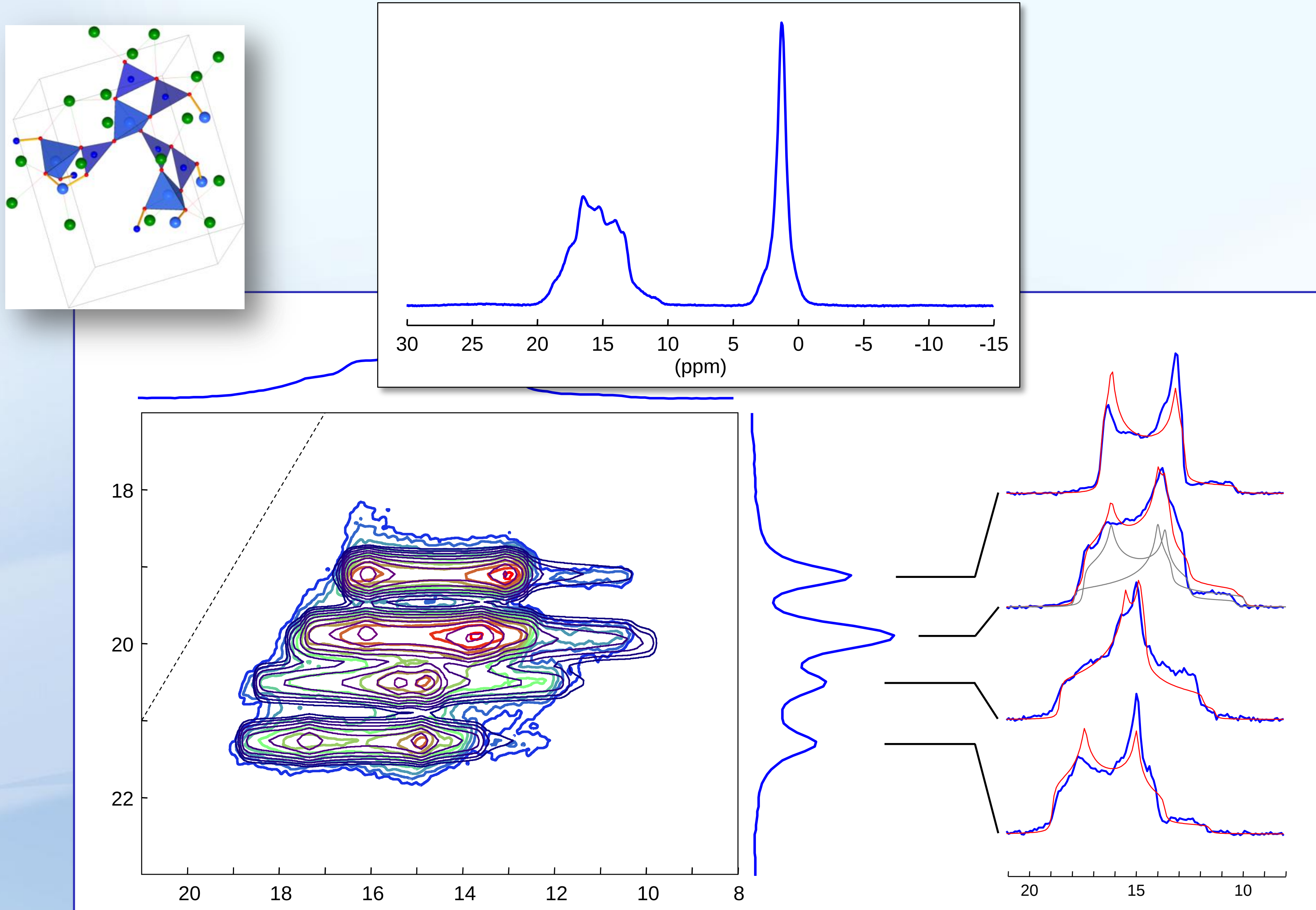
Glass $0.6PbO-0.4P_2O_5$

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

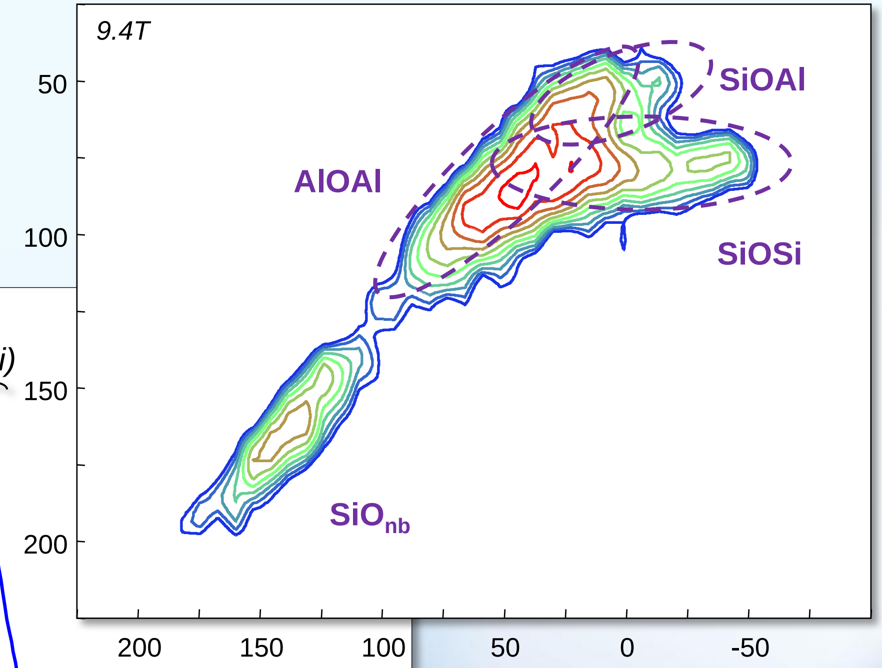
F. Fayon et al., *Chem. Commun.* 1702 (2002). F. Fayon et al., *C. R. Chimie* 7, 351 (2004).

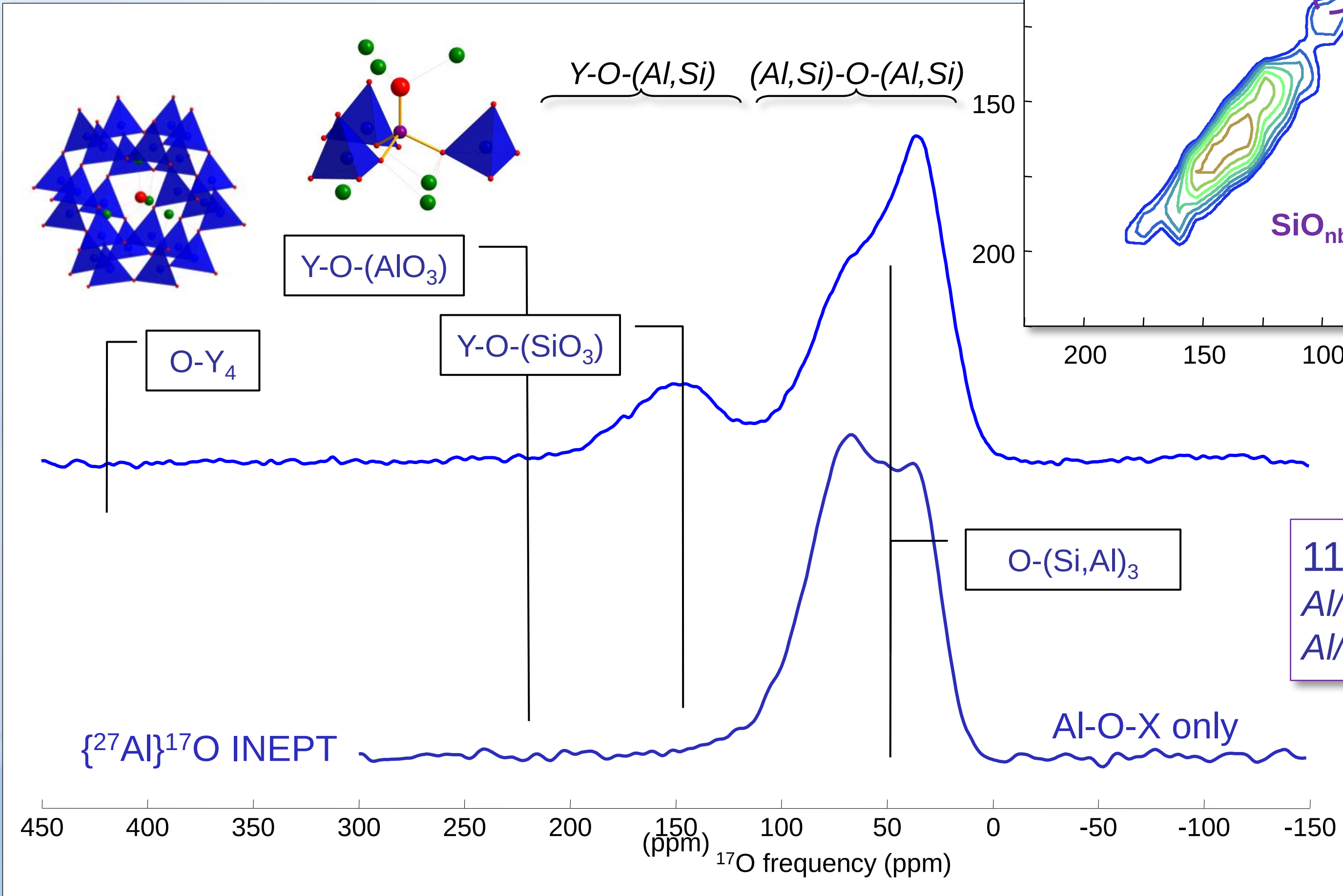
^{11}B STMAS $Na_2B_4O_7$



Deciphering Oxygen Spectra

- ☞ Unambiguous presence of Y-O-(SiO_3)
- ☞ but no obvious signs of Y-O-(AlO_3) nor OY_4





$11Y_2O_3\ 17Al_2O_3\ 72SiO_2$

Al/RE = 1.5

Al/Si = 0.24

Conclusion

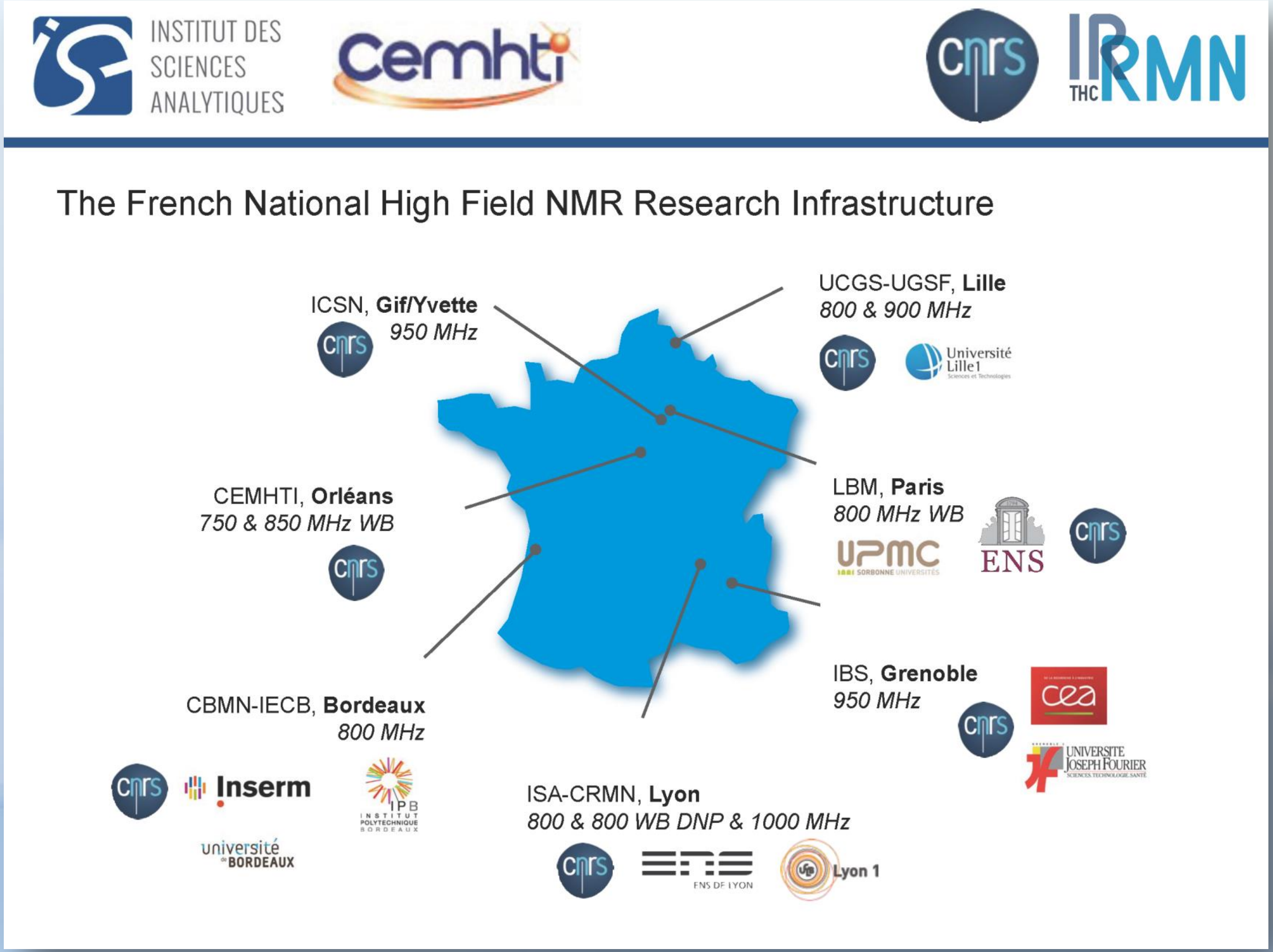
What is SSNMR Good for in Glass Science?

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



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