X Escuela de Síntesis de Materiales
Procesos SOL-GEL - *Miguel A. Blesa*
Workshop: Síntesis y caracterización de materiales avanzados e inteligentes
EXACTAS
Instituto de Nanosistemas INS-EByN UNSAM
INN CNEA-CONICET

NMR spectroscopic as a powerful tool for the Structural Elucidation of Sol-Gel Materials

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CeRTEV

Fundamentals of NMR

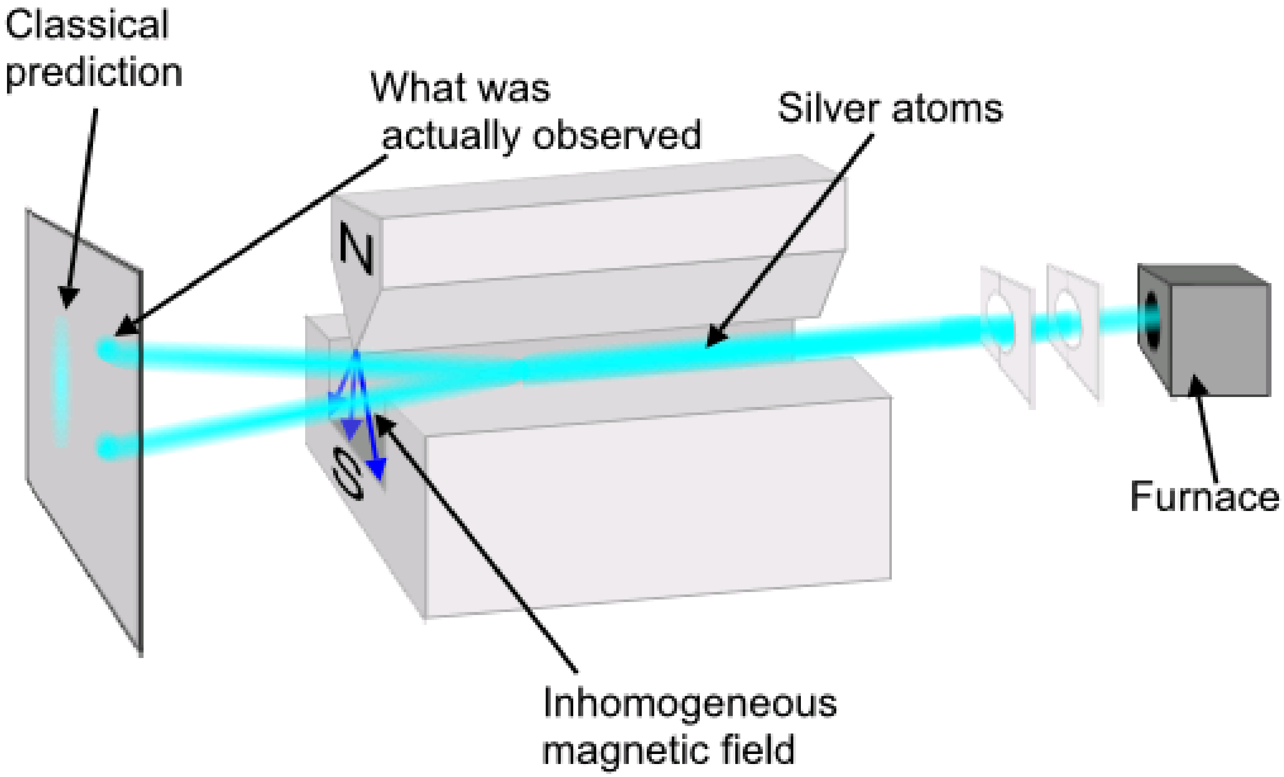
NMR = Nuclear Magnetic Resonance

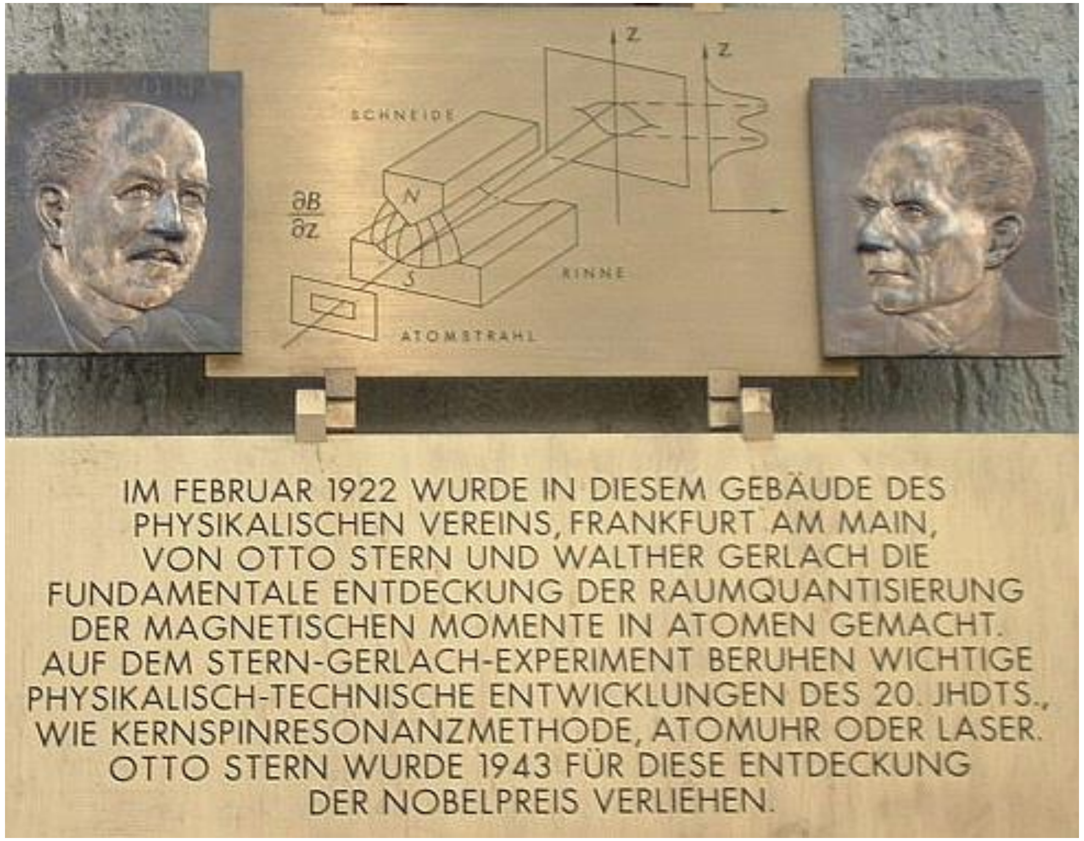
N: Property of the Atomic Nuclei in Matter

M: Magnetic Property, arising from nuclear Spin Angular Momentum

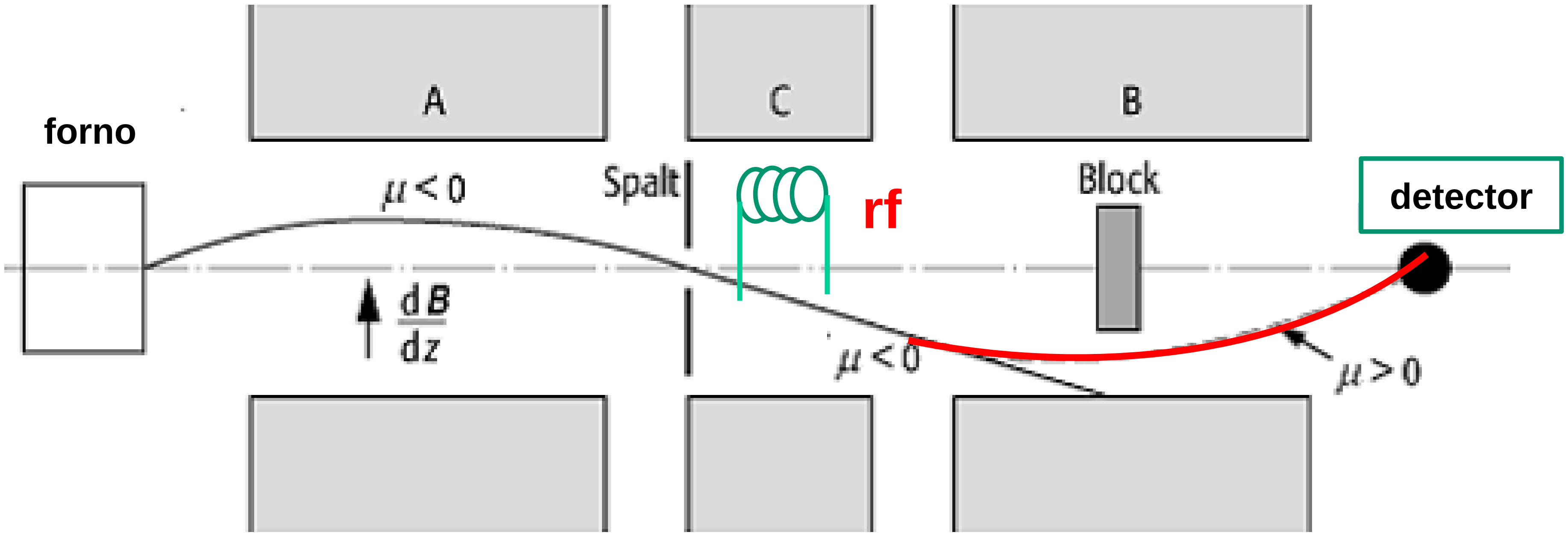
R: Interaction with electromagnetic waves spectroscopy

Stern - Gerlach experiment





Experiment of Rabi



Resonance: $\omega = \gamma B_o$

History *

1922 Stern-Gerlach Experiment
1938 Rabi- Experiment
1945/46 Purcell/Pound, Bloch: first NMR in cond. matter
1948 Bloembergen, Purcell, Pound: relaxation
1948 Pake, van-Vleck: dipolar analysis
1949 KNIGHT shift in metals
1950 Dickinson, Proctor, Yu: chemical shift
1950-s: commercial spectrometers (VARIAN)
1952 Gutowsky, Slichter spin-spin coupling
1950s Hahn, Slichter, pulsed NMR, spin echo

* Nobel laureates

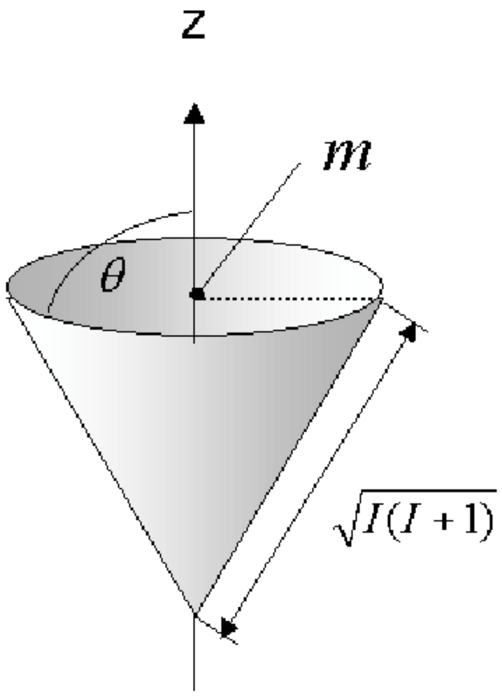
Nuclear Magnetism

Nuclear magnetic moment: $\mu = \gamma \hat{J} = \gamma \hbar \hat{I}$

I, the nuclear spin angular momentum, is subject to quantization laws, concerning both magnitude and orientationa (2I + 1)

$$\hat{\vec{I}}^2 |I, m\rangle = I(I+1)|I, m\rangle$$

$$\hat{I}_z |I, m\rangle = m|I, m\rangle$$

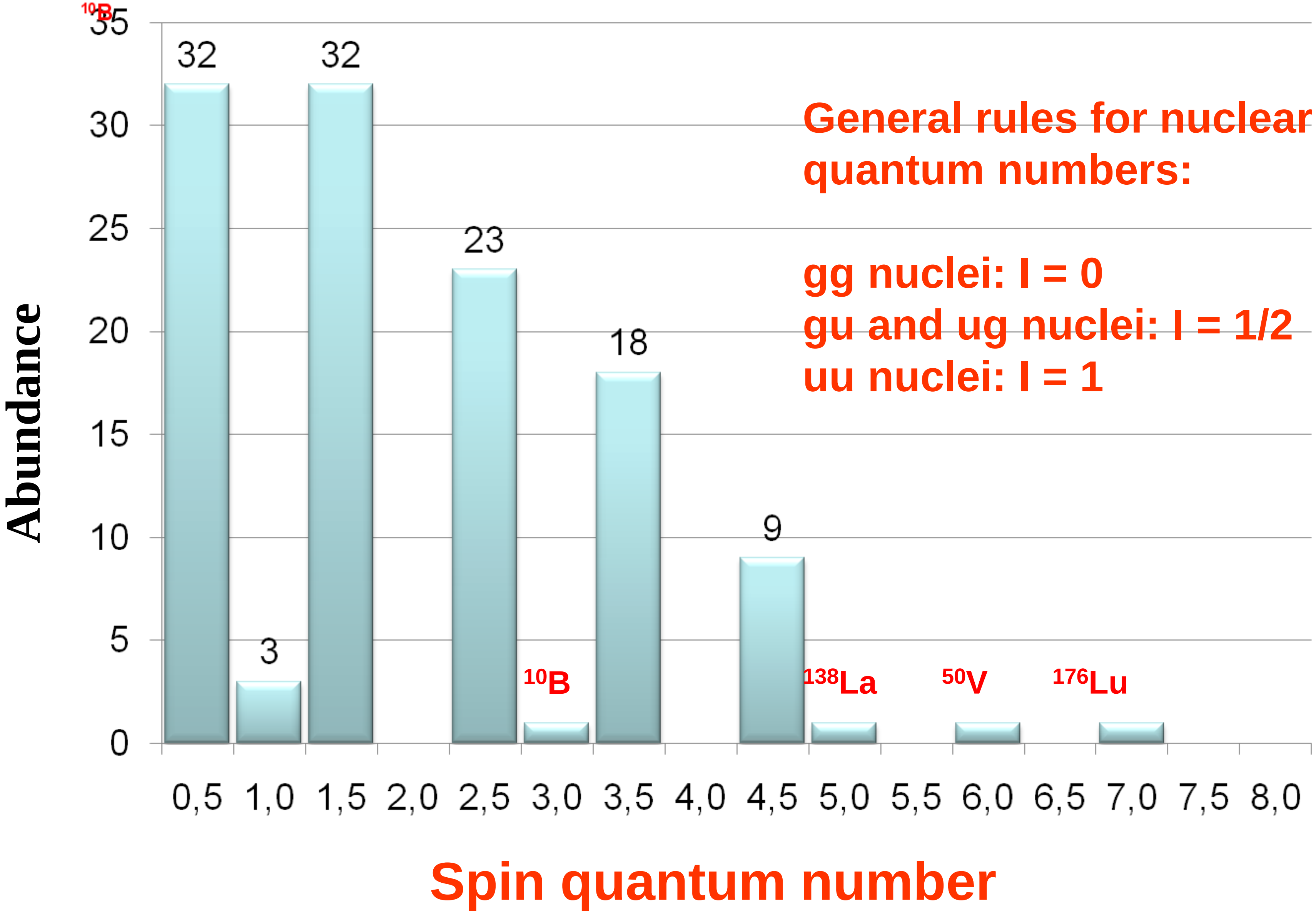


$\cos\theta = m/\sqrt{I(I+1)}$

I: spin quantum number

m: orientational quantum number
with m = -I,-I+1,…I-1,I
2I +1 orientational states

Nuclear spin quantum numbers



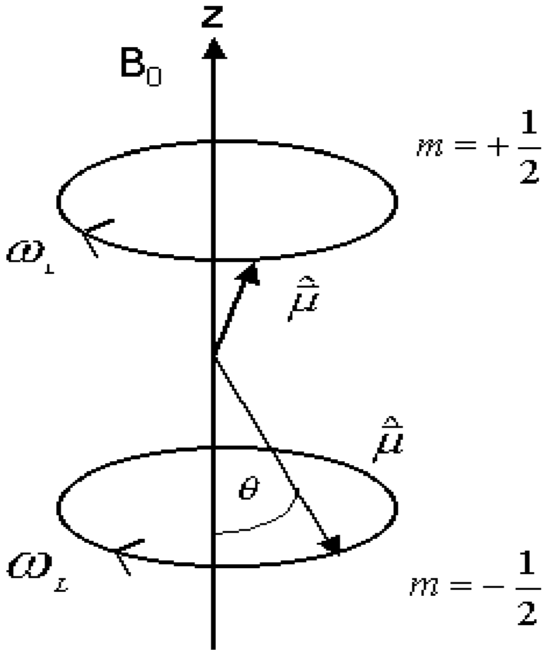
General rules for nuclear spin quantum numbers:

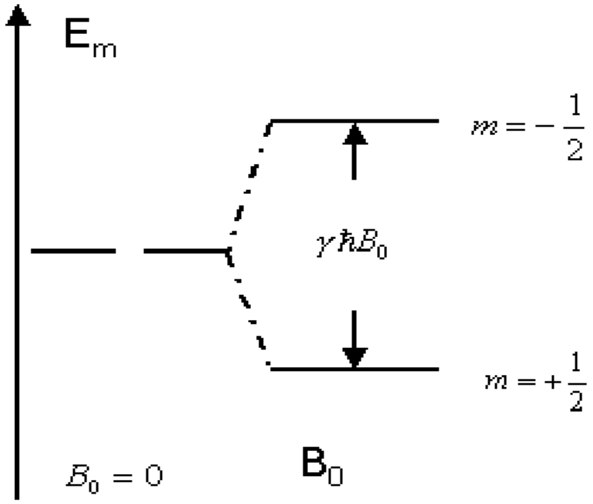
gg nuclei: I = 0
gu and ug nuclei: I = 1/2
uu nuclei: I = 1

Case spin-1/2: Two nuclear spin orientations

$E(m) = - m\gamma h B_0$ **(Zeeman-interactions)**

The two orientations have different energies, difference depends on the value of γ



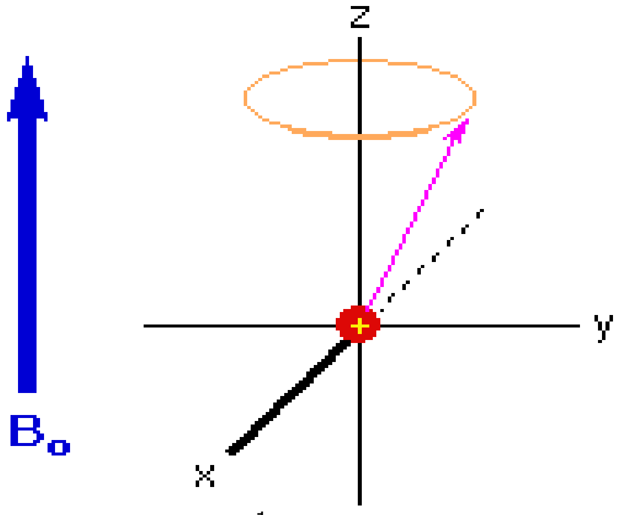


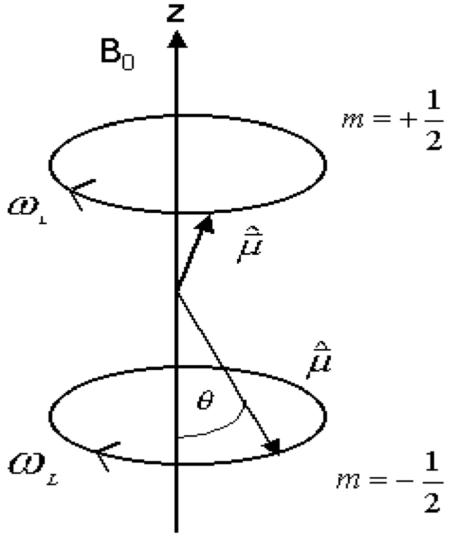
NMR is element selective!

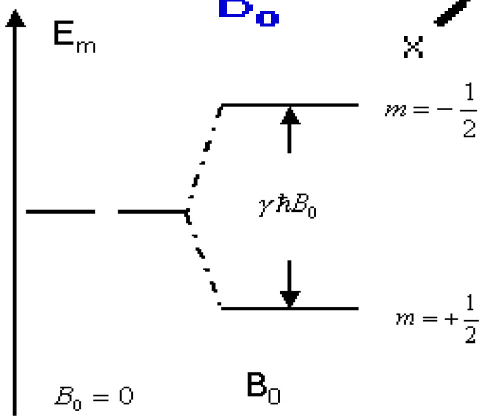
e.g. ^1H and ^{13}C at 11.7T

Precession

Precession of spins around external field (in angle, due to quantization).
Similar to gyroscope







The precession (Larmour) frequency of the nuclei is given by

$$\omega_p = \gamma B_{eff}$$

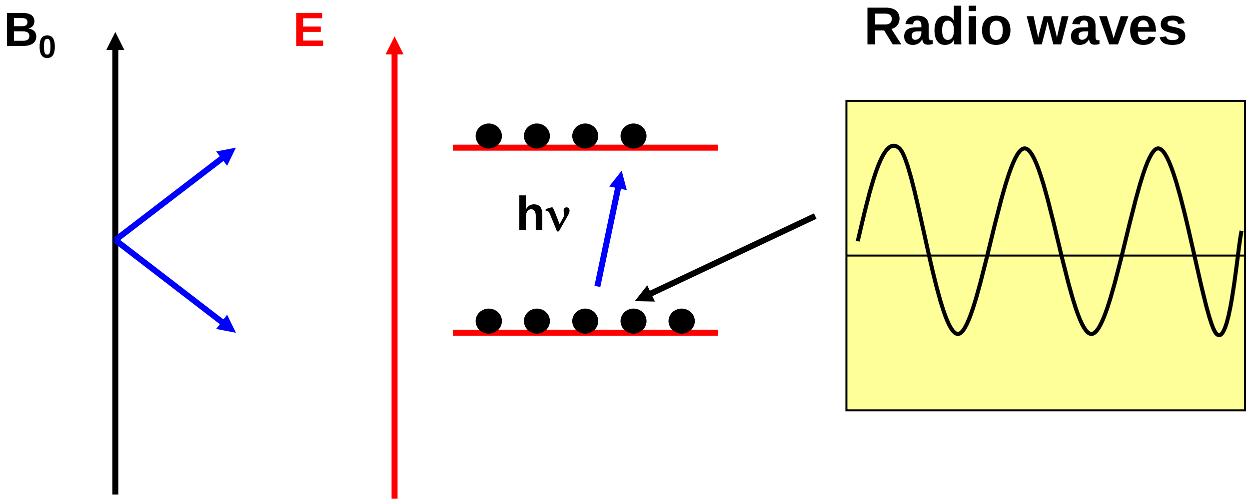
where $B_{eff} = B_0 + B_{int}$

B_{int} contains important structural and chemical information

NMR measures the precession (Larmor) frequency!

How is it done ?

By application of electromagnetic pulse which provides a magnetic field B_1 component fluctuating with frequency $\omega_o \sim \omega_p$



Resonance absorption occurs if $\omega_o \sim \omega_p$

For B_0 in the range 1-20T, ω_0 ~ MHz (radiofrequency)

Macroscopic Sample

In a sample spins are distributed among the different energy levels (Boltzmann-distribution)

⇩

Macroscopic magnetization along B_0

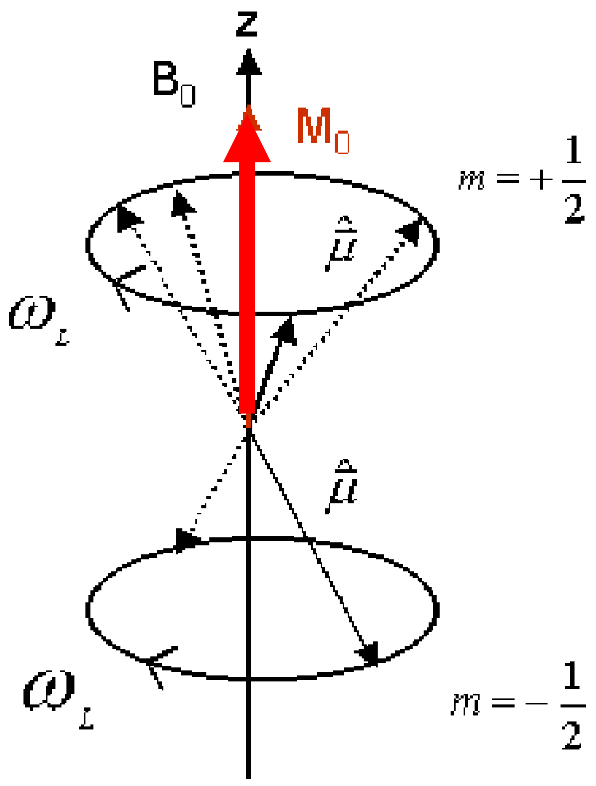
No net magnetization in x- or y-direction

⇩

Curie Law

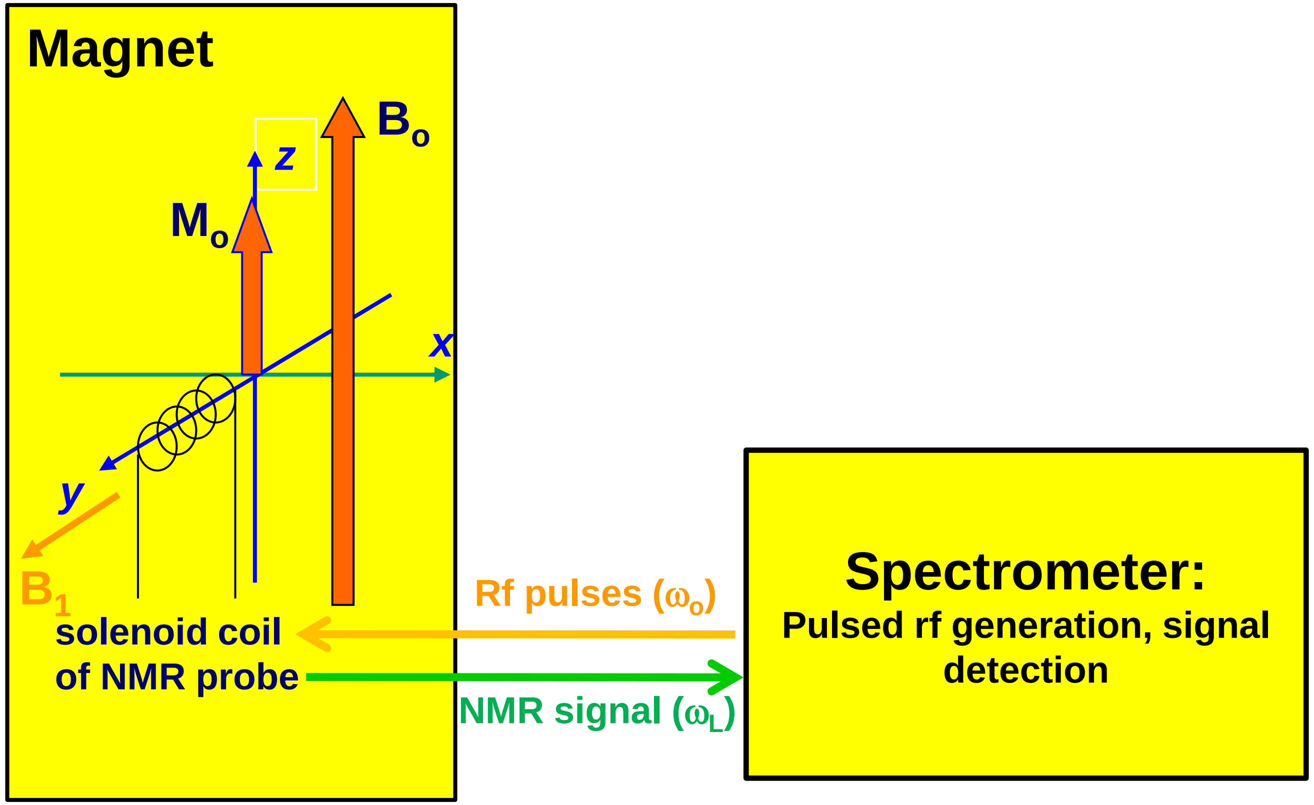
$$M_z = M_o = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT} B_o$$

NMR is quantitative!



M_z -> V_{osc} -> induction

Schematic Experimental Set-up

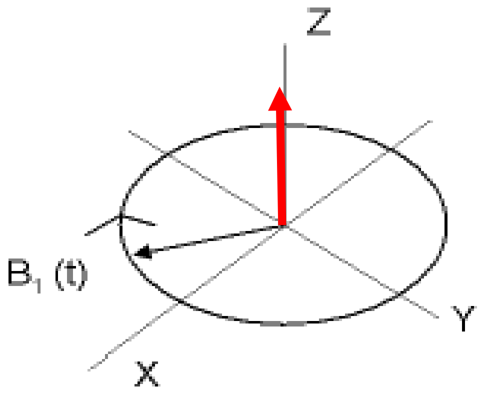


The Rotating Frame

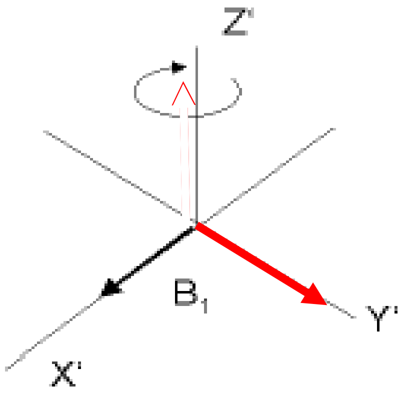
In contrast to the B_0 field, the B_1 field changes direction in time with the frequency ω_0

To simplify the description of the magnetization‘s time dependence a rotating frame is introduced

Laboratory frame



Rotating frame



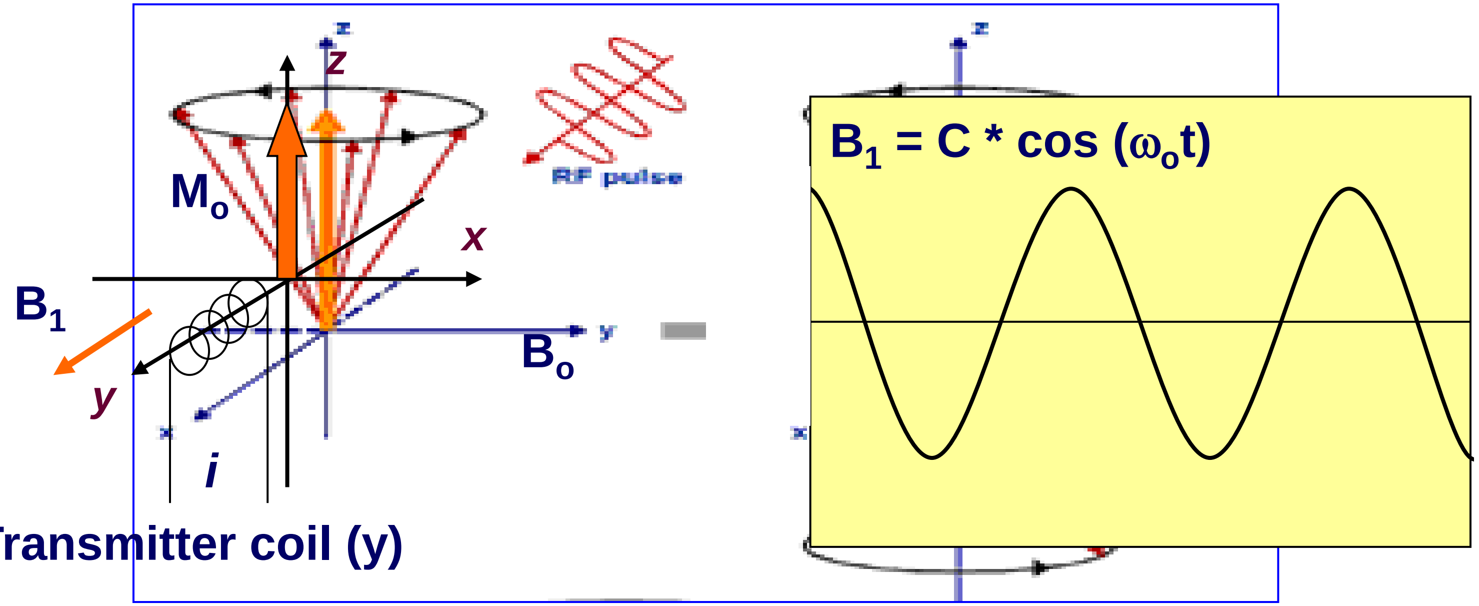
Rotating frame rotates with frequency ω_0 of B_1

90° pulse: rotates the z-magnetization into the x-y-plane
180° pulse: flips the z-magnetization into the –z-direction

Measuring NMR spectra

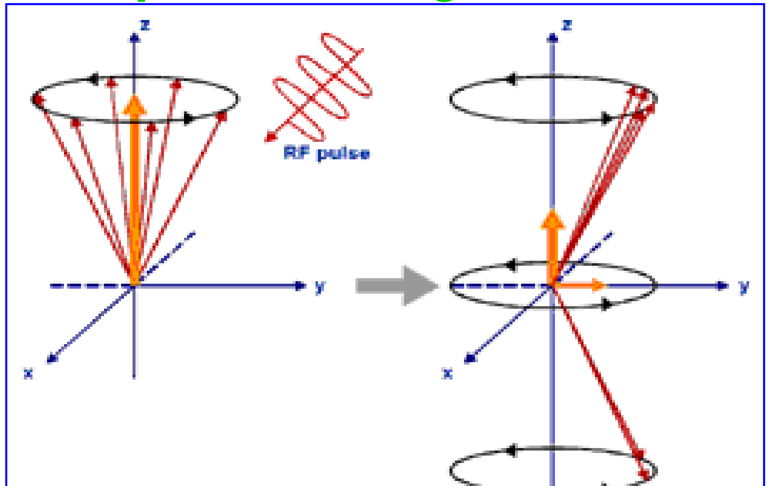
= Detection of Larmor frequencies present in the sample

1. B_1 field is irradiated for a short time t_p along the x,y direction
2. If $\gamma B_1 t_p = \pi/2$ then M_z is flipped by 90 degrees (90° pulse)
3. After the pulse, precession of M induces voltage in the coil.
4. This voltage, oscillating with ω_p, is the NMR signal



The Basic NMR Experiment

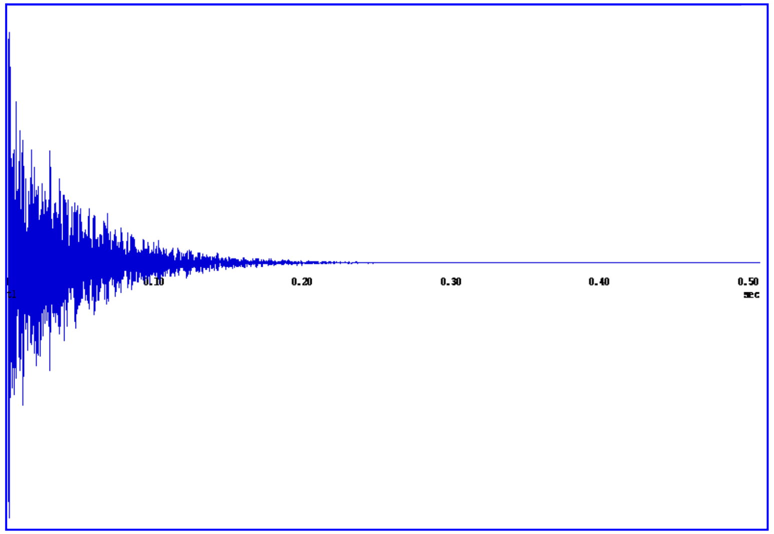
90° pulse -> magnetization flip



(taken from Siemens MR Tutorium)

Signal-detection

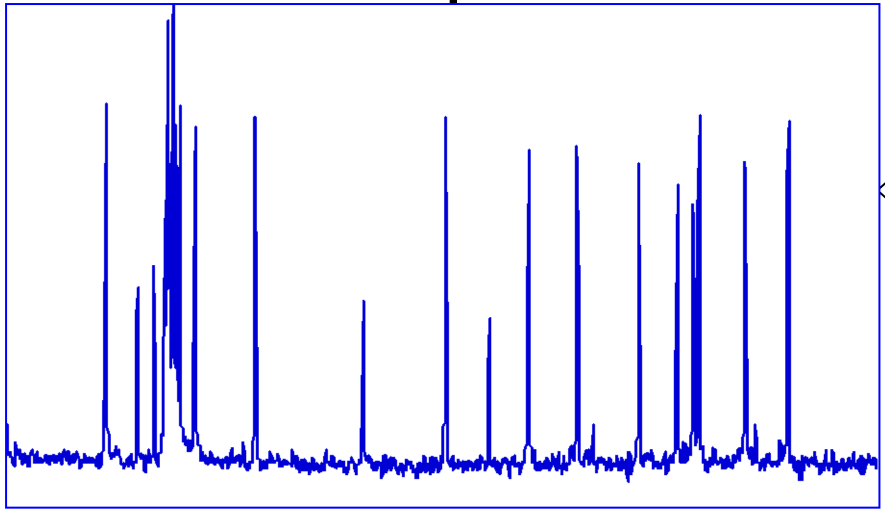
Free Induction Decay



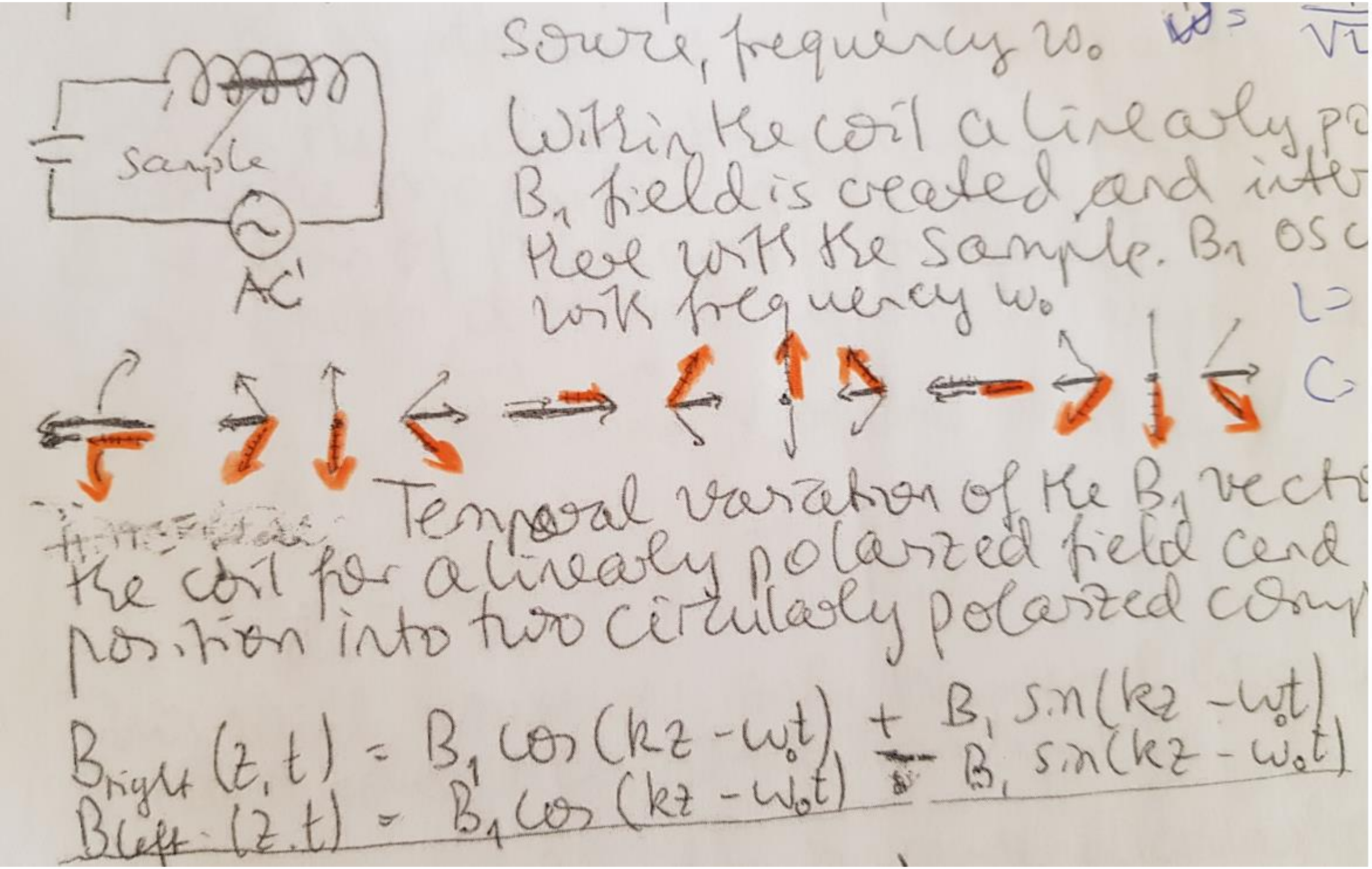
Fourier-Transformation

$$F(\omega) = \int_{-\infty}^{\infty} f(t) * e^{-i\omega t} dt$$

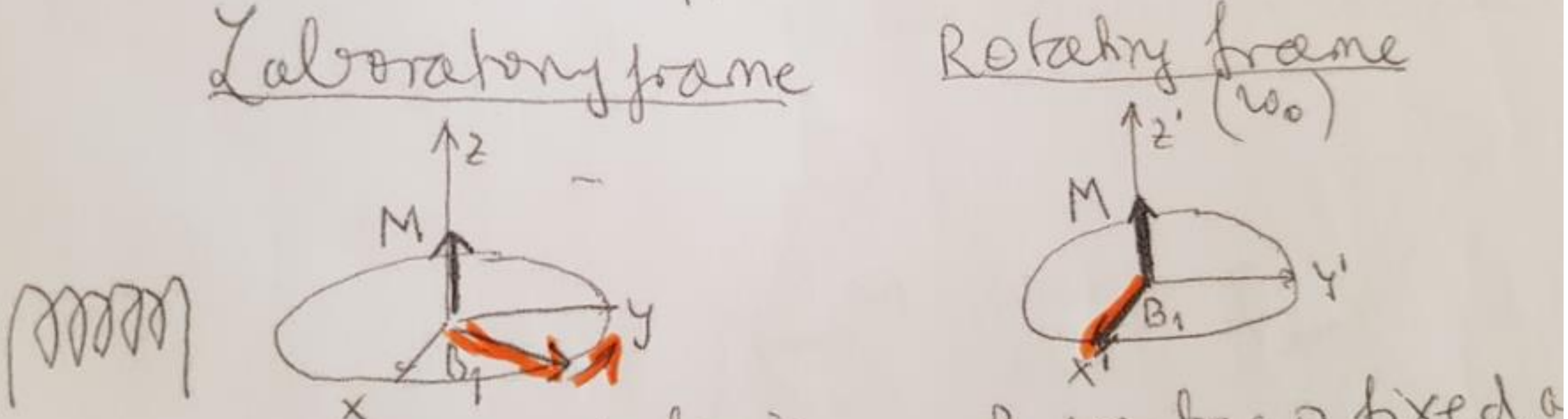
NMR-Spectrum



How does it work?



The effect of the B_1 field upon the magnetization is conveniently described in a rotating coordinate system, which moves with the frequency of the applied radio waves, i.e. ω_0.

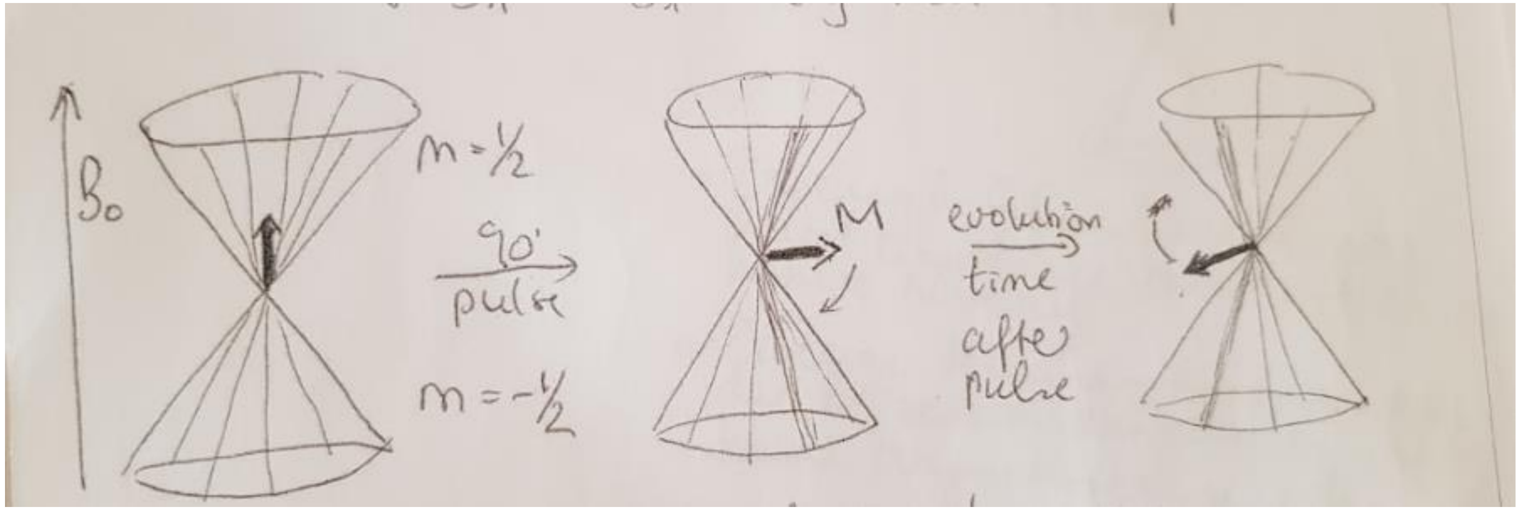


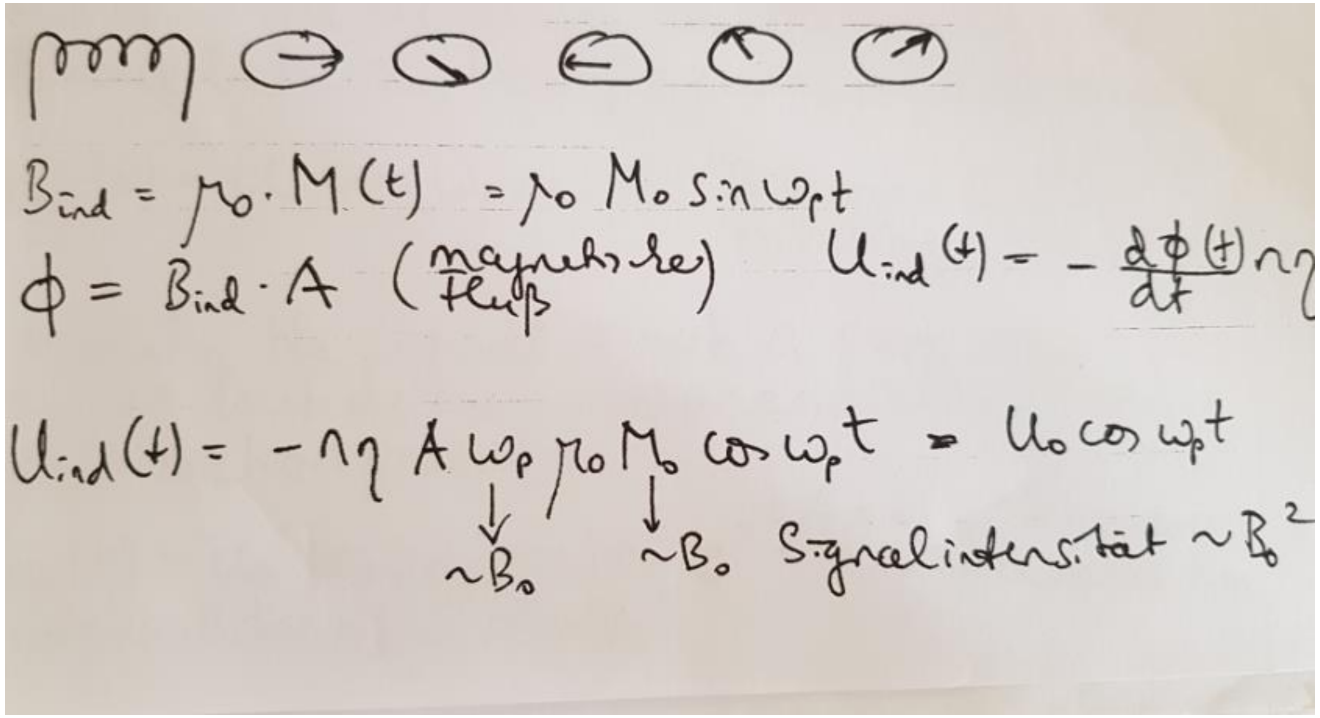
B_1 vector rotates in the xy plane ⊥ z

B_1 vector is fixed a aligned along x' axi

Both in the laboratory frame and in the rota frame the magnetization is along z, i.e. the direction of the magnetic field B_0. The B_1 ve ... the magnetizatio

Signal Detection by electromagnetic induction



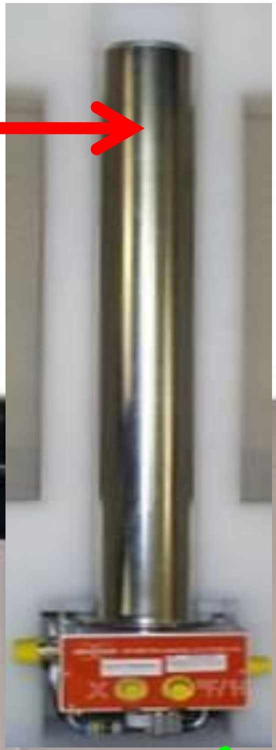


NMR Spectrometer

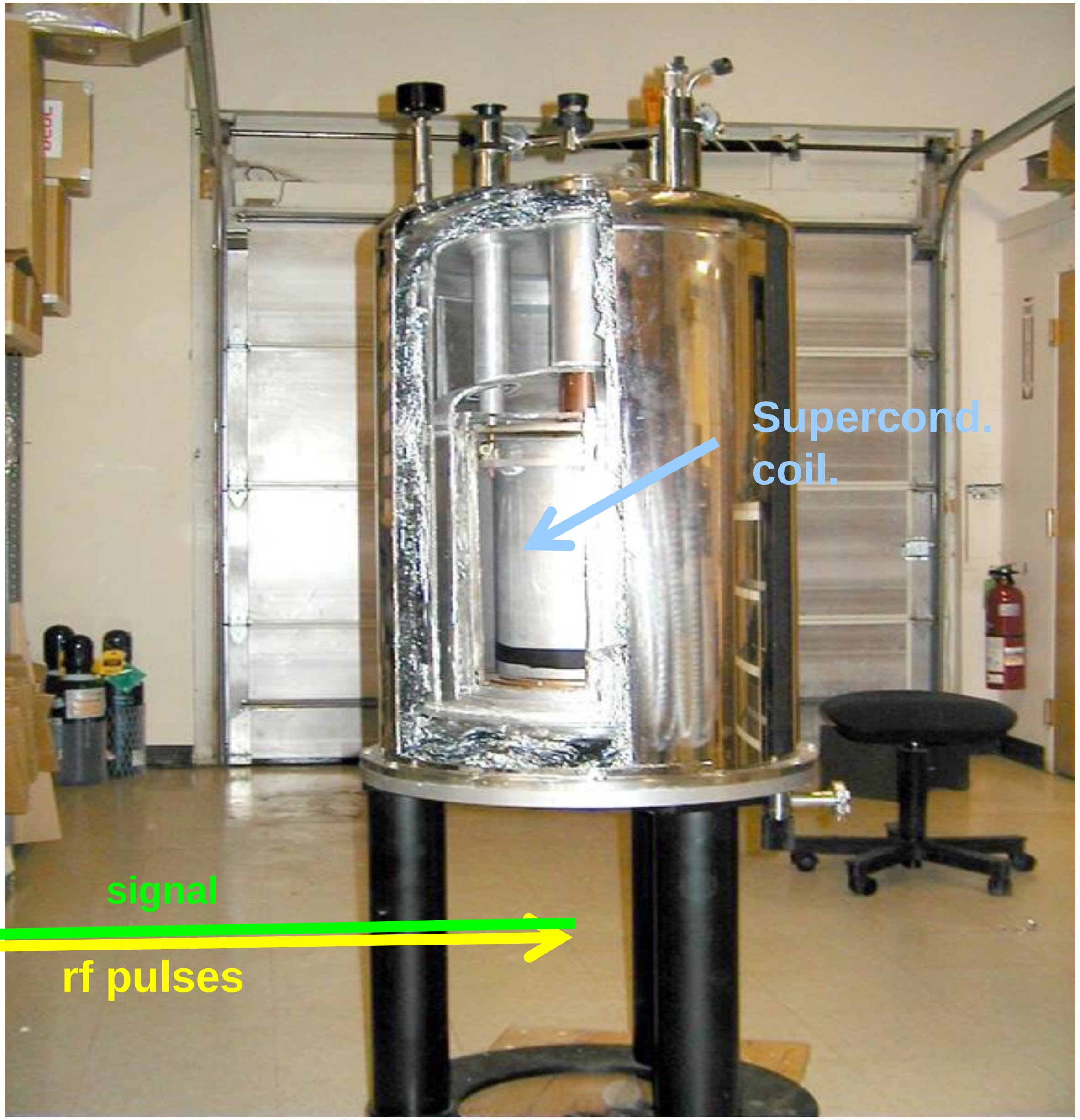
Magnet

Probe

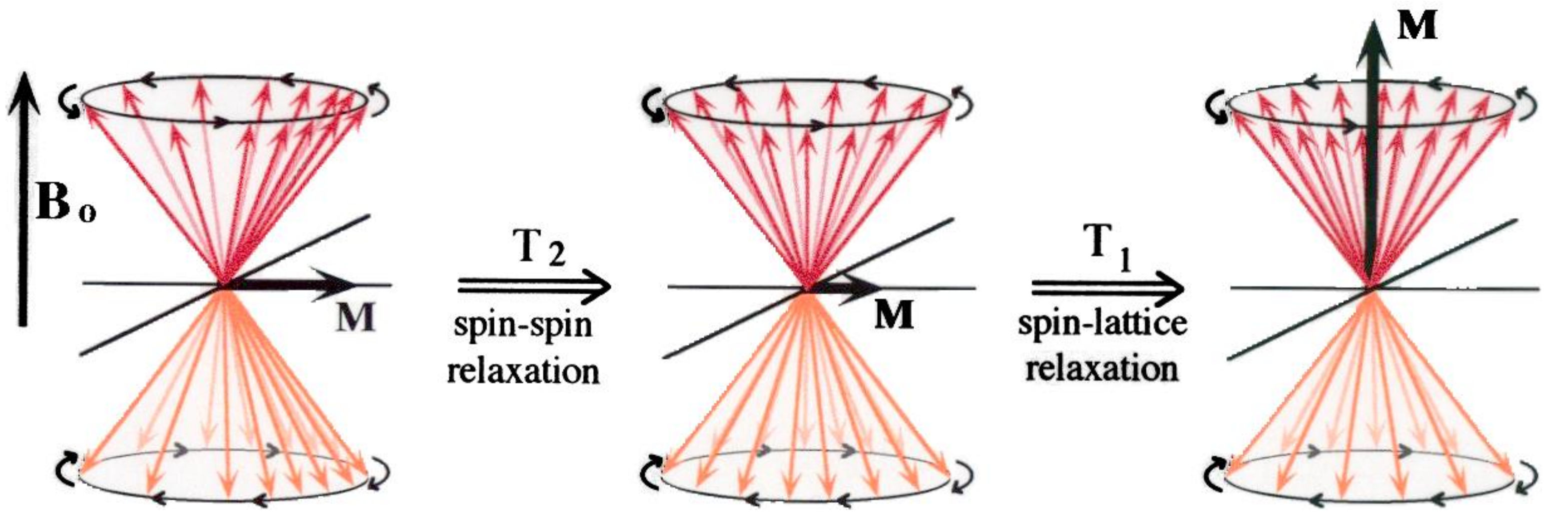
Sample in coil



Console:
signal excitation and detection



Relaxation Processes



Transverse relaxation (T_2): dephasing of spins in the x-y plane (distribution of precession frequencies, spin-spin interactions)

Longitudinal relaxation (T_1): build-up of z-magnetization (return to equilibrium, energy exchange with surroundings (lattice)

Three main distinct interactions

- magnetic shielding
- electric quadrupole coupling
- magnetic dipole coupling

In the solid state:

anisotropy: $\omega_p \sim 3\cos^2\theta - 1$

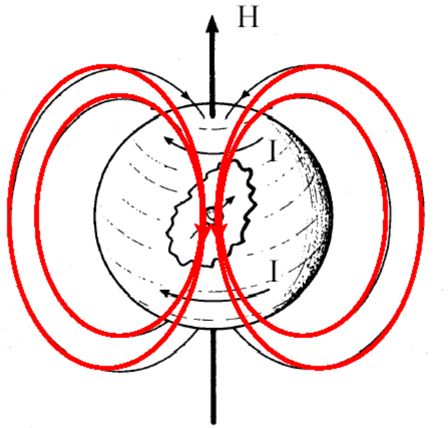
Magnetic Shielding

Resonance frequency (bare nucleus): $\omega_0 = \gamma B_0$

Effective magnetic field at nucleus: $B_{eff} = B_0(1-\sigma)$

Resonance frequency (real sample) $\omega_L = \gamma B_0(1-\sigma)$

Chemical shift $\delta \equiv \dfrac{\omega_L^x - \omega_L^{ref}}{\omega_L^{ref}}$



Effective magnetic field arises from shielding or deshielding of the external magnetic field by electrons

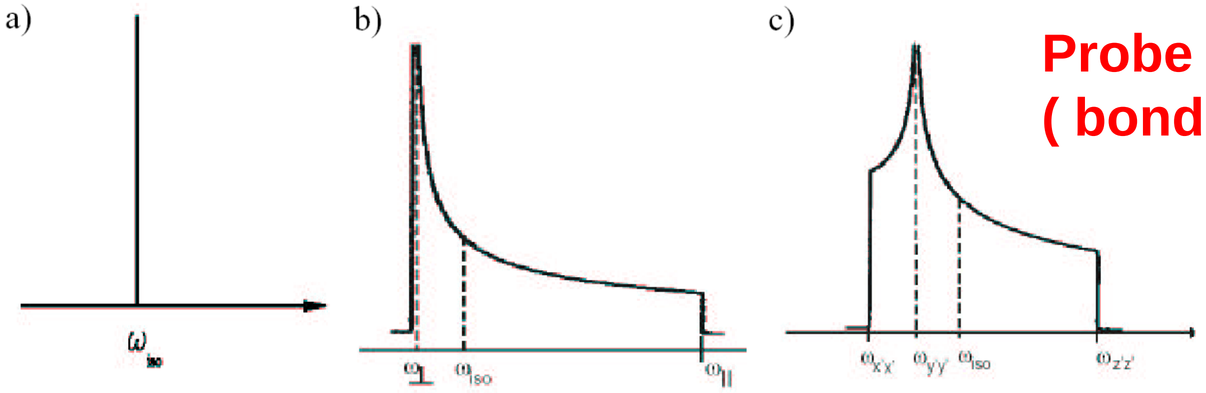
Probe for electronic environment (structure and bonding)

Chemical Shielding Anisotropy

Solid state : chemical shielding is anisotropic:
➔ tensorial description

$$\omega_L = \omega_0 \left[1 - \sigma_{iso} - \frac{1}{3}(\sigma_{z'z'} - \sigma_{x'x'})(3\cos^2\theta - 1) \right]$$

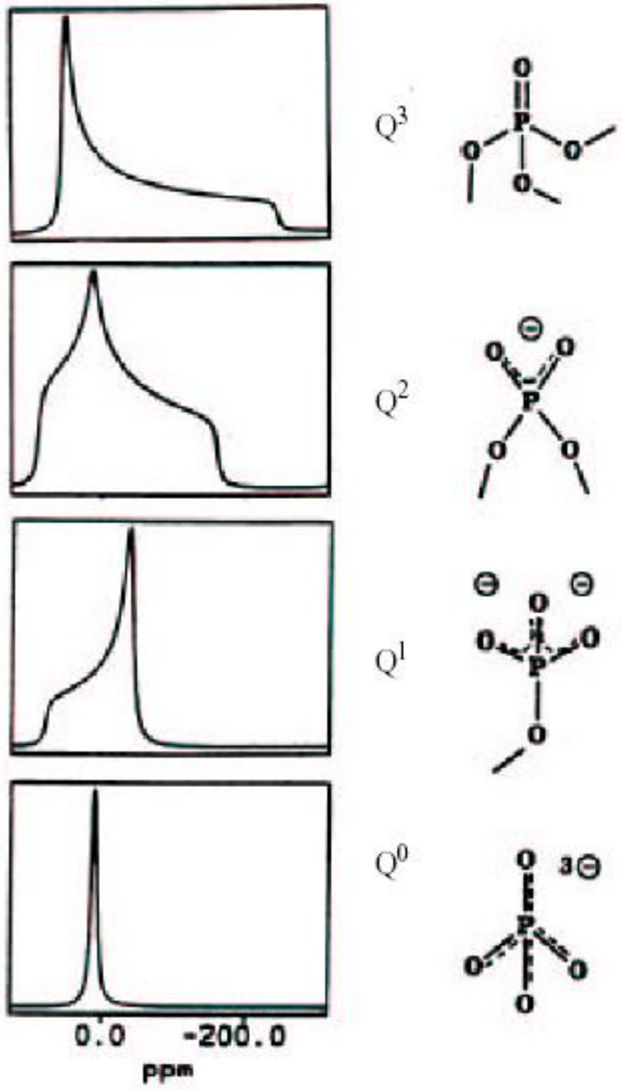
powdered sample **Distribution of orientations**

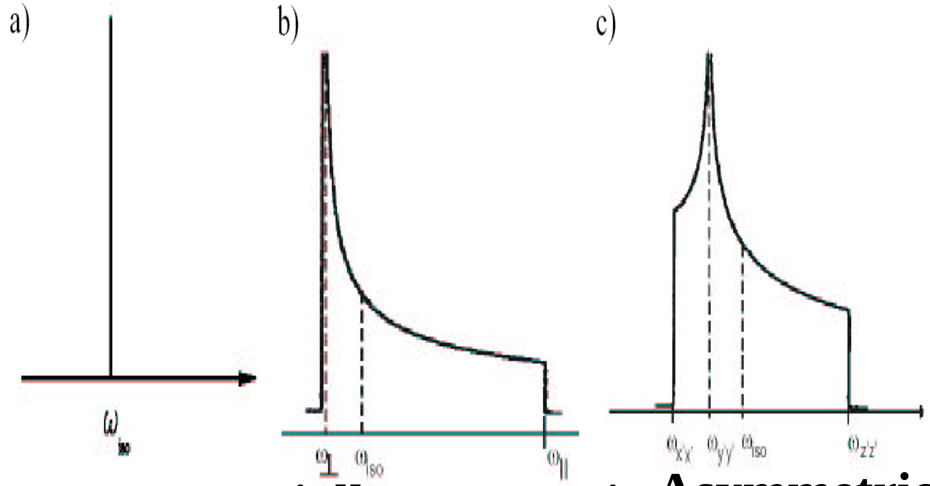


Probe for local symmetry
(bonding geometry)

cubic **Axially symmetric** **Asymmetric**

Example : ^{31}P NMR of Phosphates



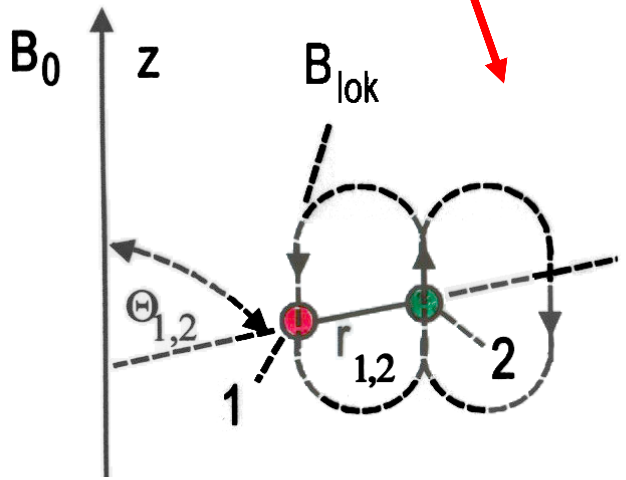


cubic Axially symmetric Asymmetric

Magnetic dipolar interactions

Magnetic moments of nearby nuclear spins affect the local magnetic field and thus the resonance frequency. „Through-space“ interaction

$$\hat{H}_{DIP}\ (ij) = -\frac{\mu_0}{4\pi}\gamma_i\gamma_j\hbar^2\, r_{ij}^{-3}\left[\hat{A}+\hat{B}+\hat{C}+\hat{D}+\hat{E}+\hat{F}\right]$$



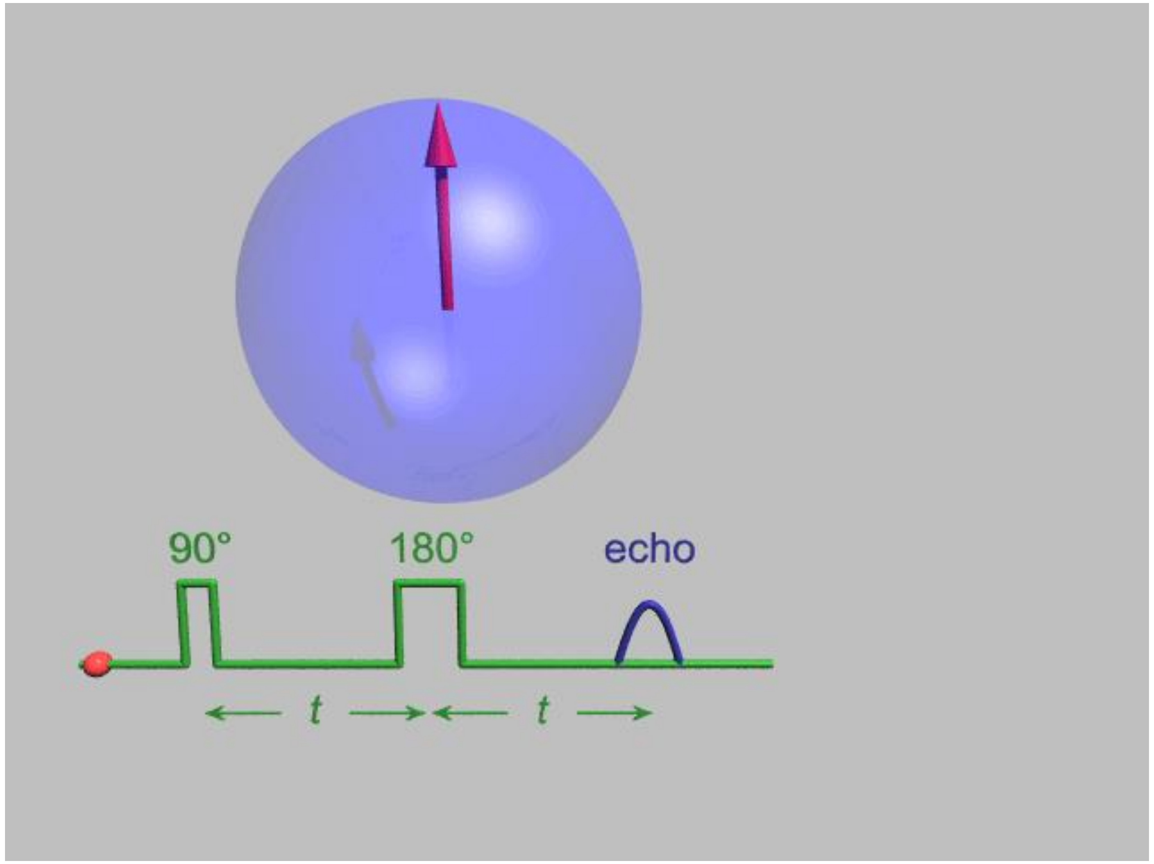
Probe of internuclear distance
NMR is locally selective!
Specially useful for systems with only short range order

$\hat{A} \sim \hat{I}_{z1}\hat{I}_{z2}$ $\quad\quad$ $\hat{I}_z S_z$

$B \sim \hat{I}^{+}_{1}\hat{I}^{-}_{2} + I^{-}_{1}I^{+}_{2}$

homo $\quad\quad$ **hetero**

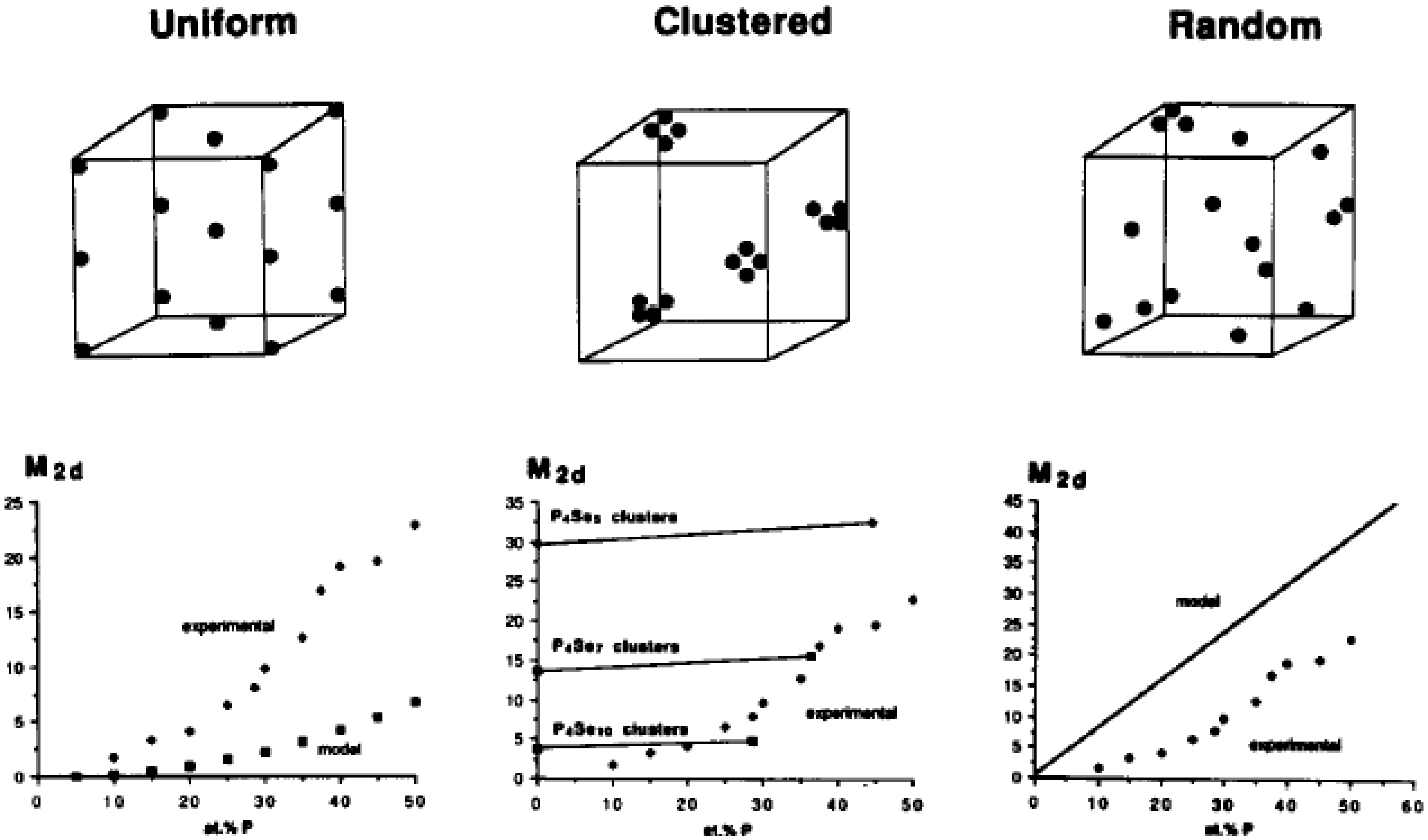
Selective measurement by spin-echo decay



Selective for homonuclear dipole coupling strengths

$$S/S_0 = \exp - (2t^2 M_2)$$

Spatial Atomic Distributions in P-Se Glasses

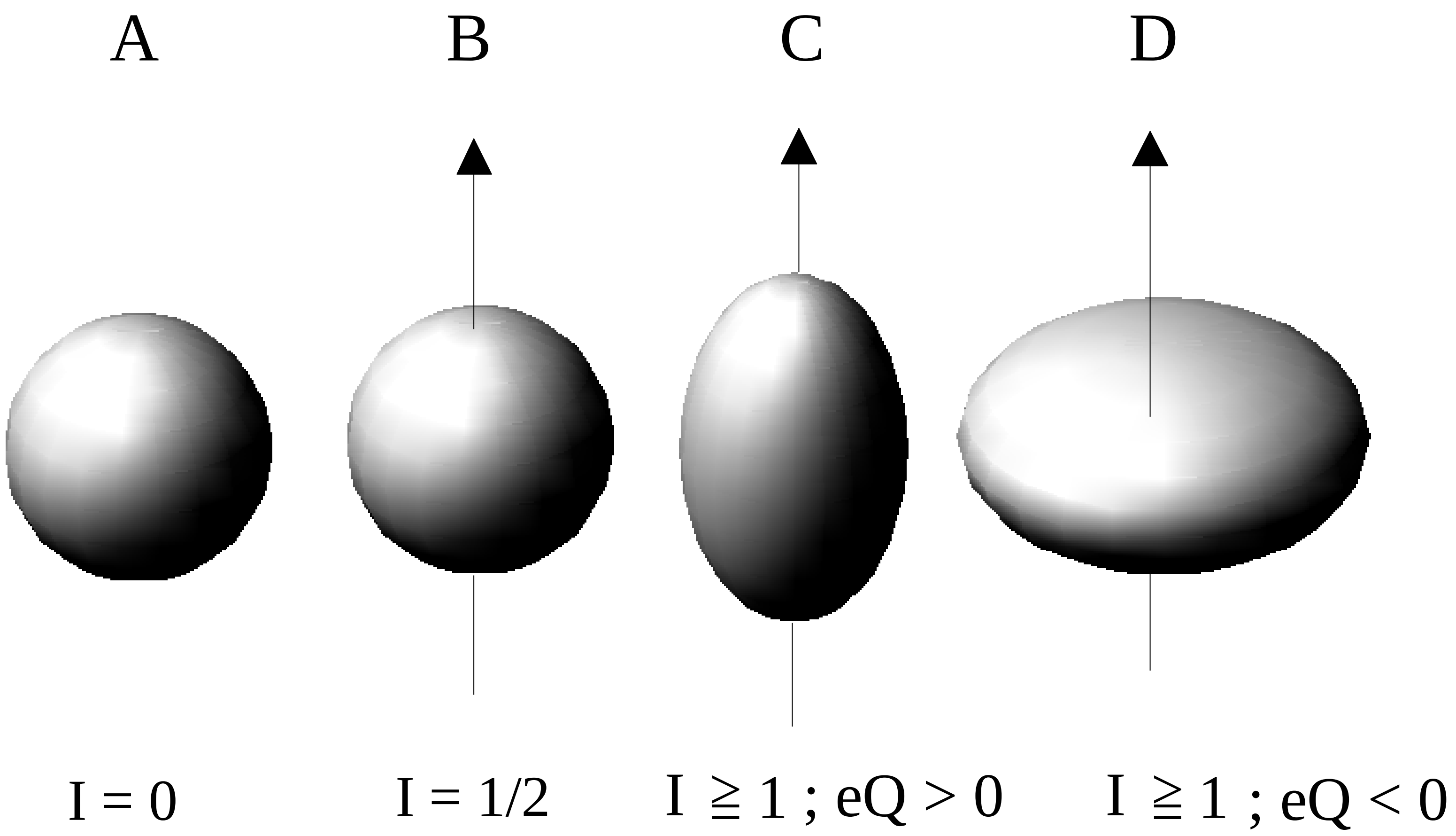


P-Se vs. P-P- bonding

D. Lathrop, H. Eckert, J. Am. Chem. Soc. 111 (1989), 3536
D. Lathrop, H. Eckert, Phys. Rev. B 43 (1991), 7279

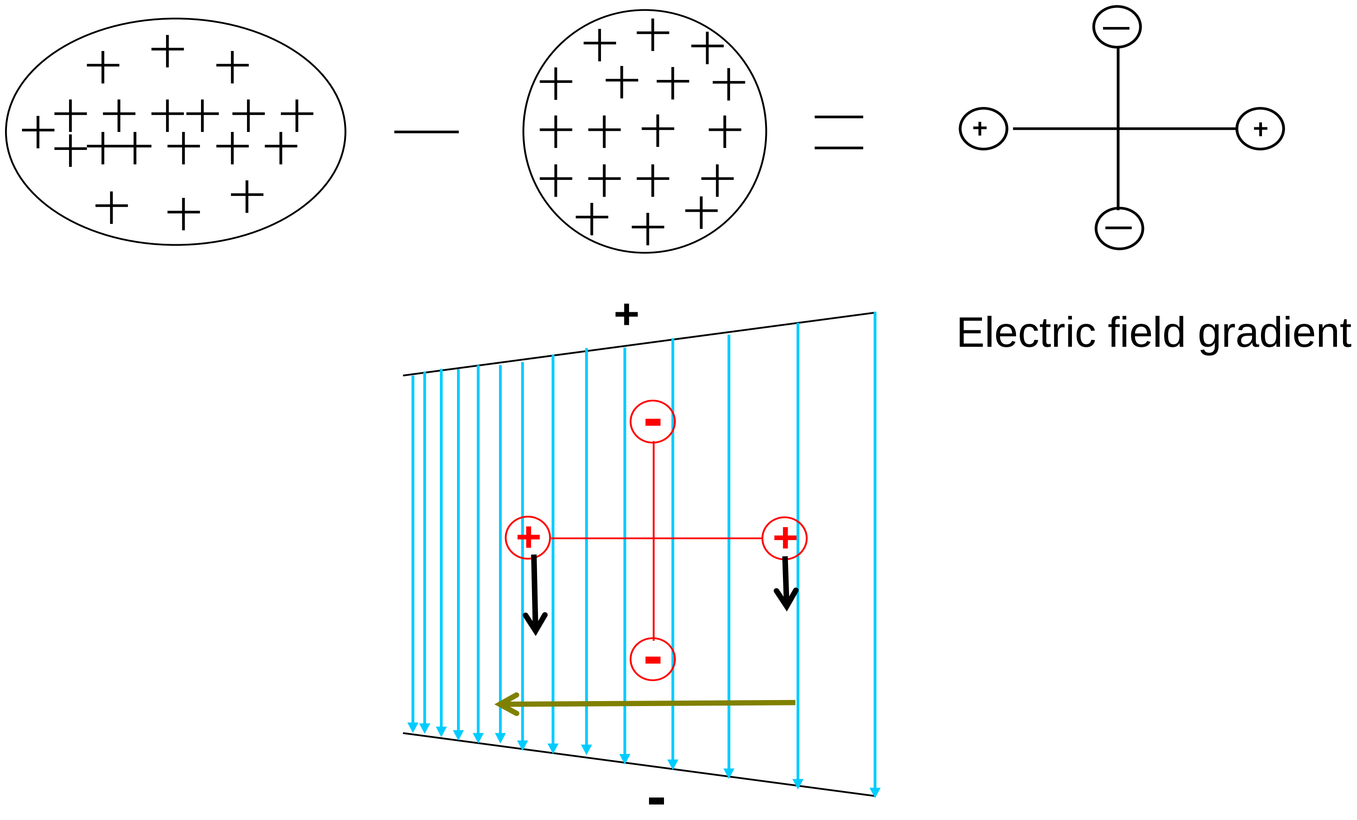
Nuclear electric quadrupole moment:

non-spherical distribution of nuclear charge



$eQ \sim 10^{-25}$ to 10^{-30} m^2

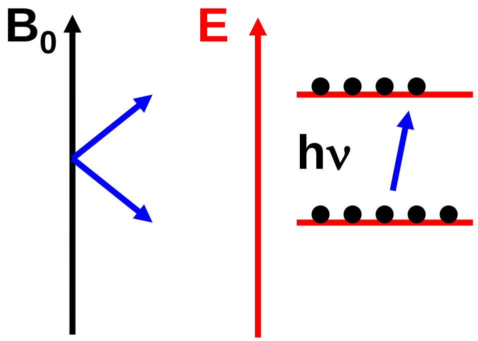
Quadrupole interaction: The physical picture



This quadrupole moment interacts with local electric field gradients created by the electronic and bonding environment of the nuclei, allowing probing of local symmetry!

Solid State NMR

- element-selective
- locally selective
- quantitative
- experimentally flexible: **Selective averaging**



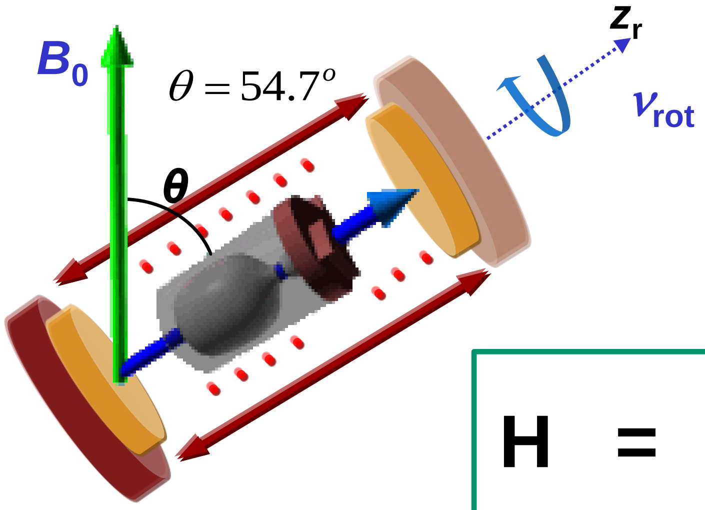
$$\Delta E = \gamma \hbar B_0$$

$$H = H_Z + H_D + H_{CS} + H_Q$$

H_D → Internucl. distances

H_{CS}, H_Q → Coordination numbers and symmetries

Magic Angle Spinning - MAS



$$H_{aniso} = A \cdot \{\overline{3\cos^2\theta - 1}\}$$

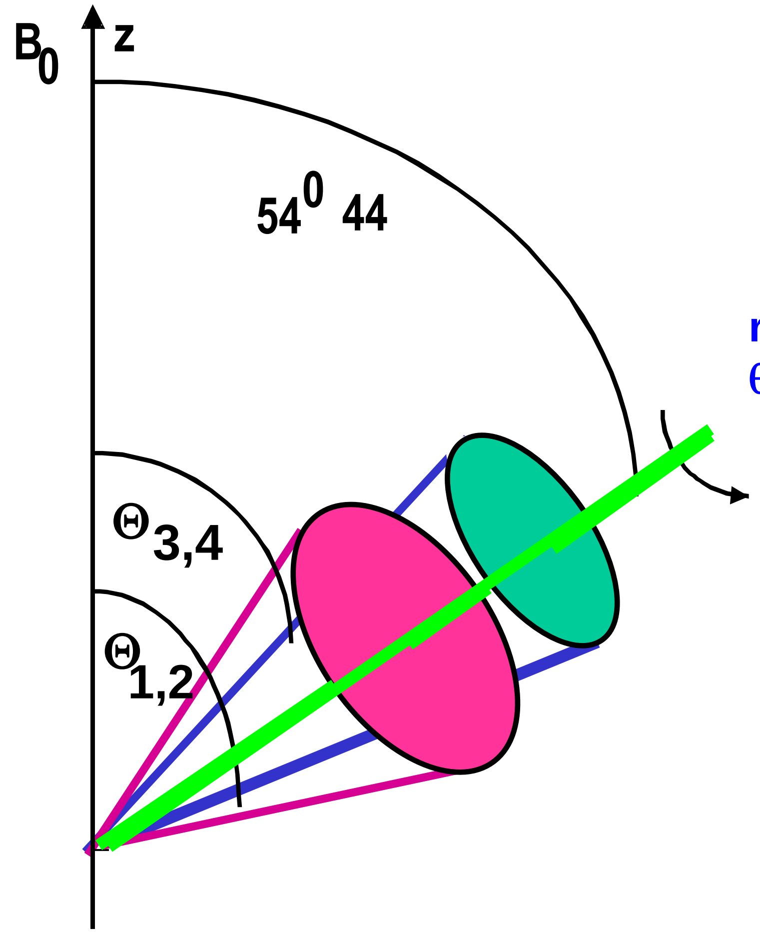
$$H = H_Z + \cancel{H_D} + \cancel{H_{CS}}_{iso} + \cancel{H_Q}_{2nd.}$$

High-resolution spectra, governed by chemical shifts
MAS is equivalent to liquid state NMR

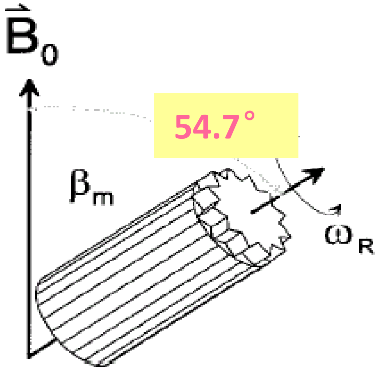
-- bonding partners
-- coordination numbers

Magic Angle Spinning

$$\mathcal{H}_{aniso} = A \cdot \{\overline{3\cos^2\theta - 1}\}$$



rotation axis
θ = 54.7°

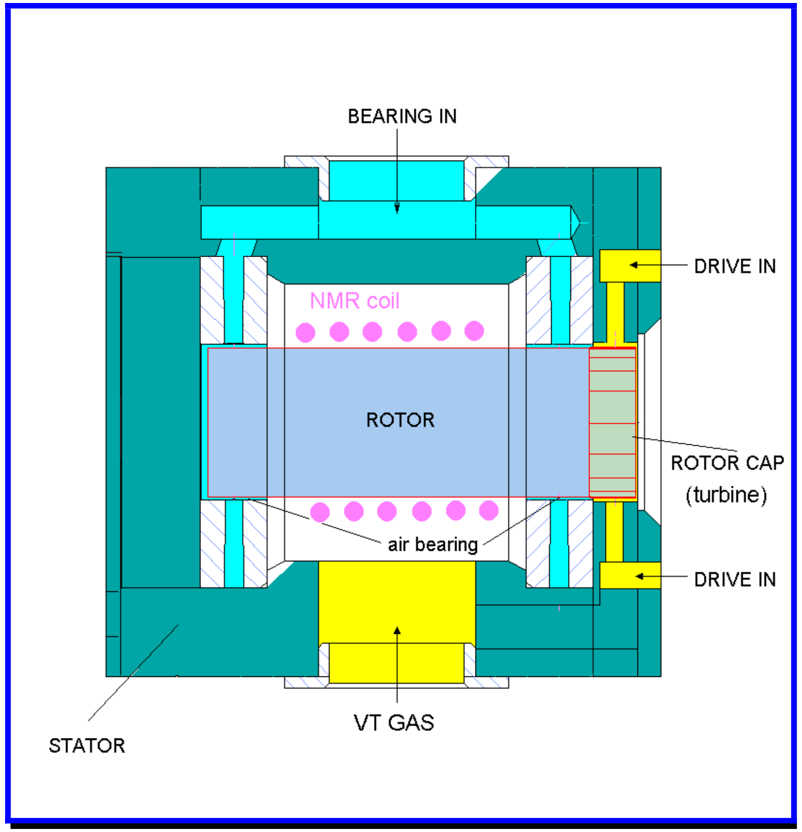


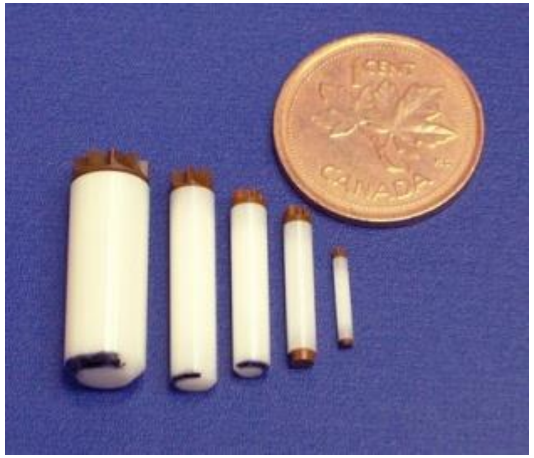
$$H = H_Z + H_D + H_J + H_{CS} + H_Q$$

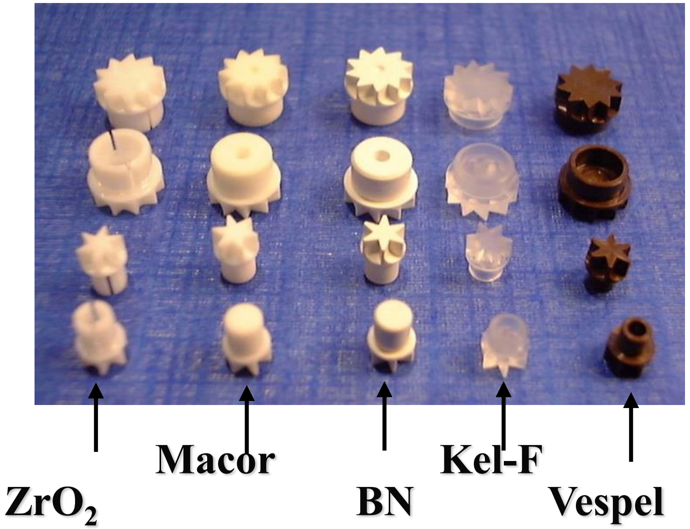
iso iso 2nd.

MAS-NMR probe

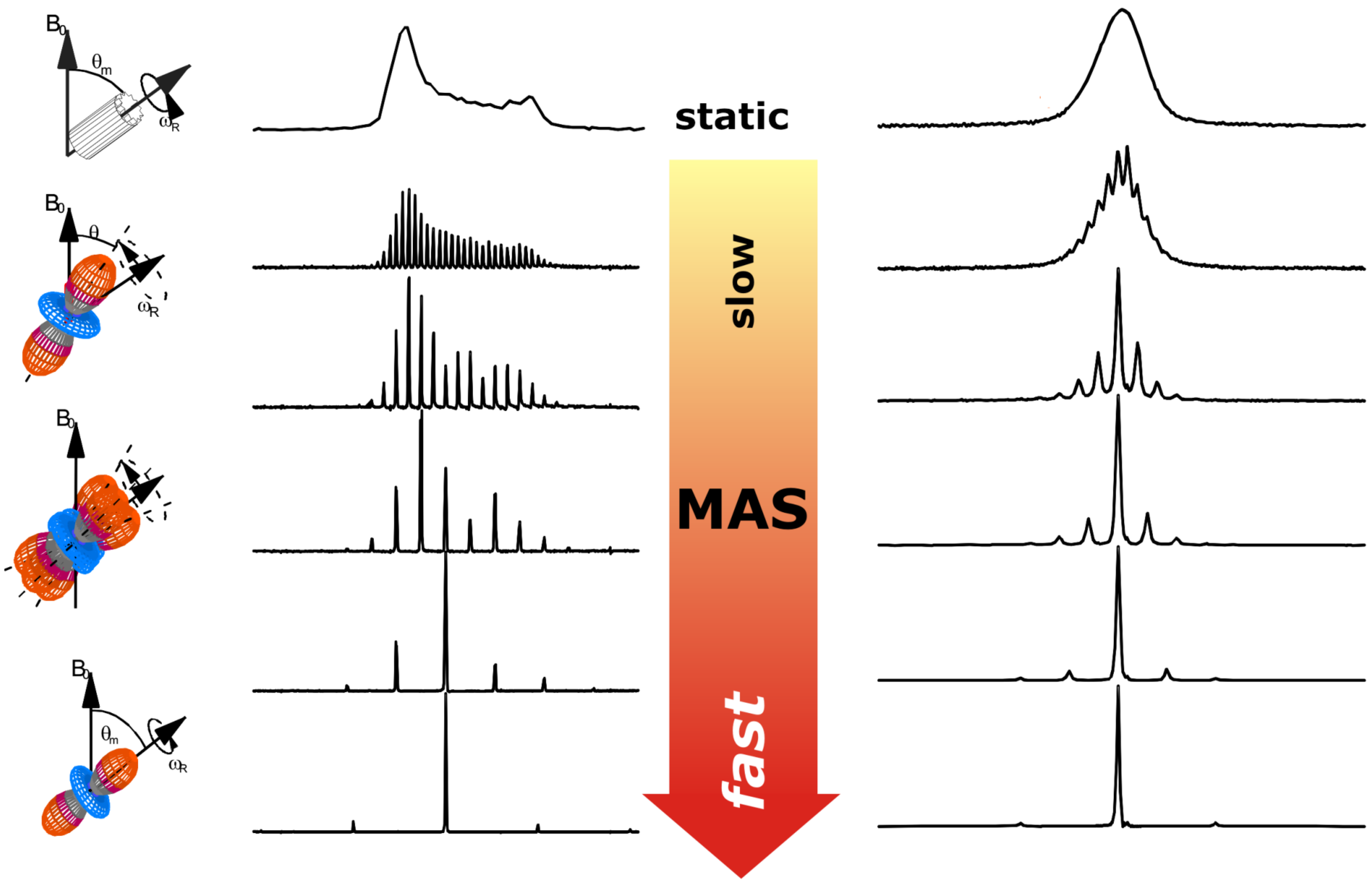
Cylinders made of crystalline zirconia
With a air driven turbine cap spin at f = 5 to >120 kHz







The effect of spinning speed



NMR spectroscopy of insensitive nuclei:

Problems with direct detection of ^{13}C, ^{15}N and others:

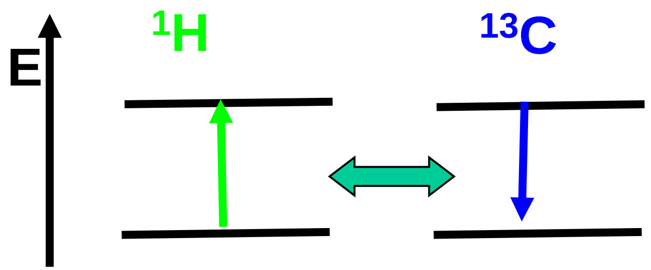
- Low natural abundance
- Small magnetic moments
- Long spin-lattice relaxation times

Basic idea of cross-polarization (CP):

exploit dipole-dipole coupling with abundant ^{1}H nuclei in the sample to transfer magnetization from ^{1}H to ^{13}C spins

Matching of energy levels required

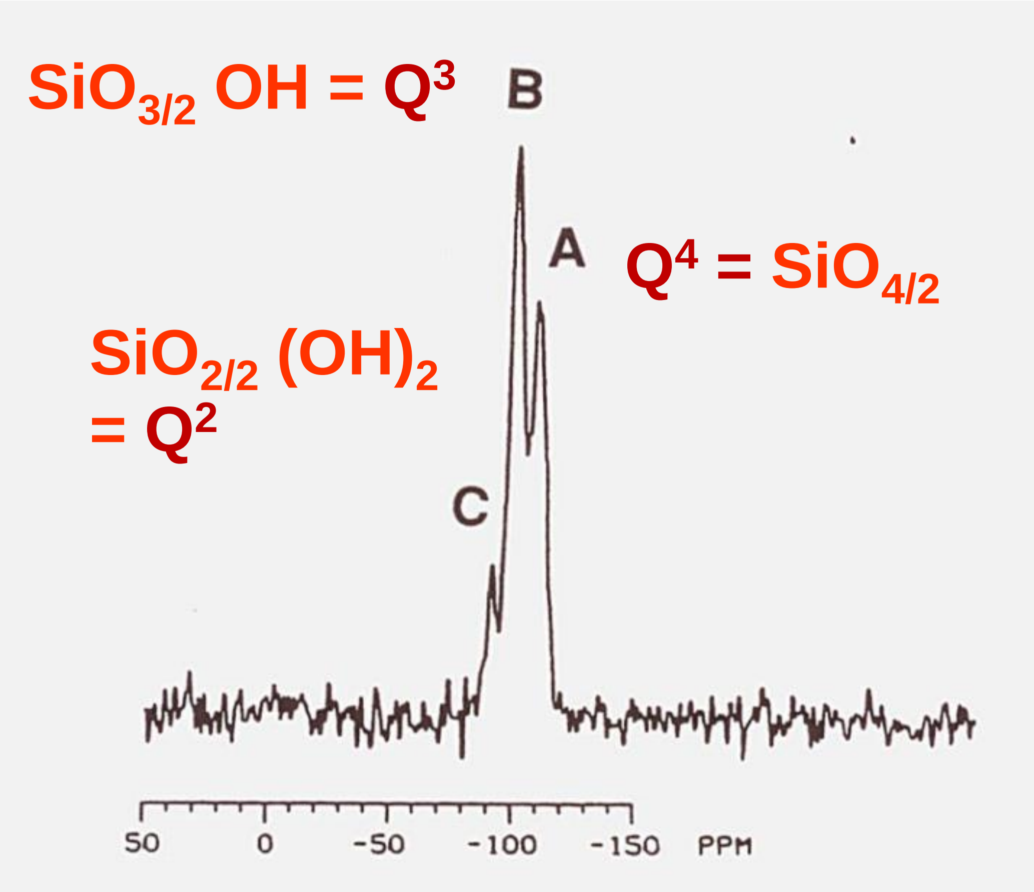
(flip-flop mechanism),
not possible in the lab frame



Applications of NMR to sol-gel materials

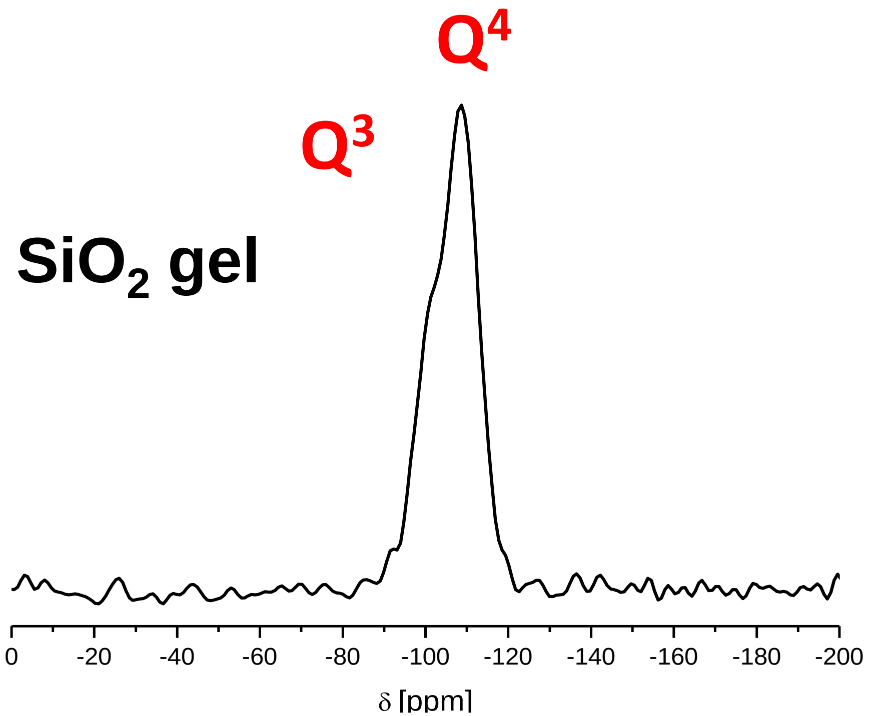
Distinction of local environments by ^{29}Si MAS NMR.

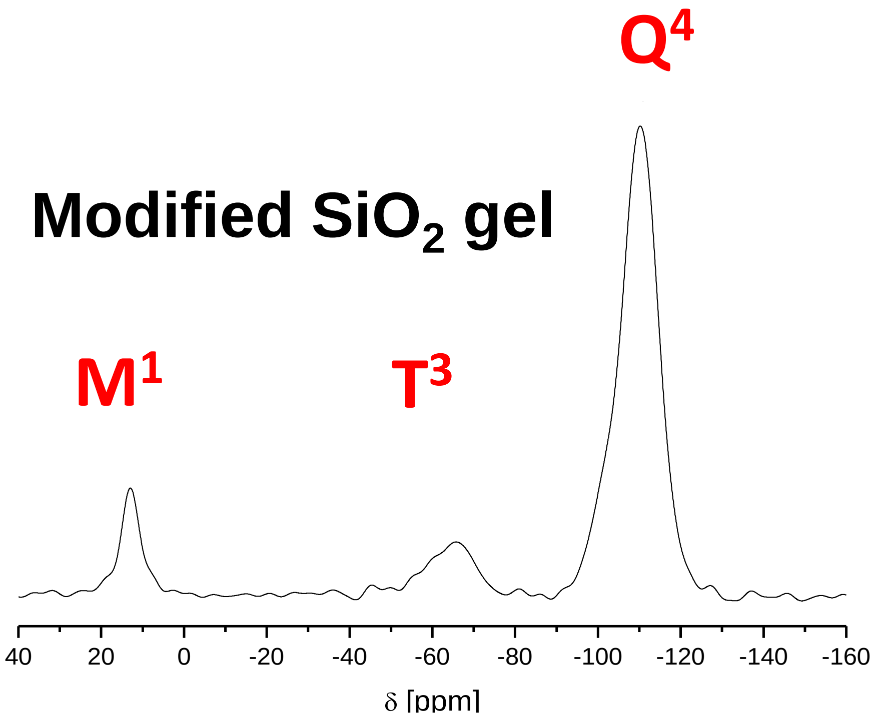
Gel-derived SiO_2

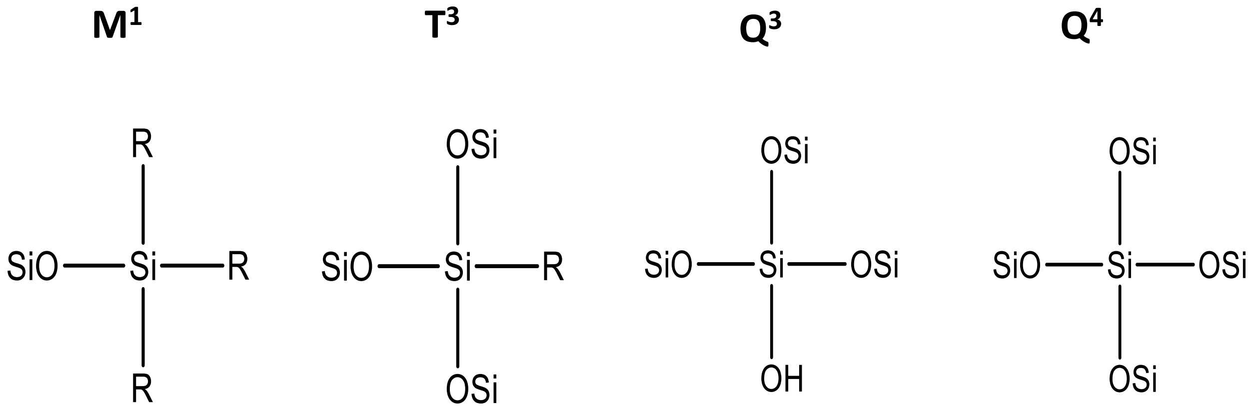


Distinction of local environments by ^{29}Si MAS NMR.

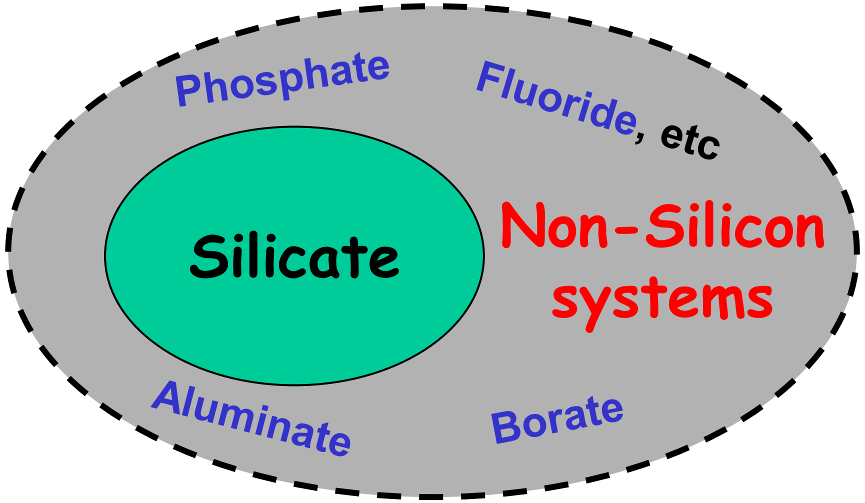
Ormosils or surface modified silica gels







Current Situation on Sol – Gel Synthesis



Aluminophosphate/Aluminoborate

- Catalyst or catalyst support
- Solid state batteries
- Laser devices, luminescent materials
- etc

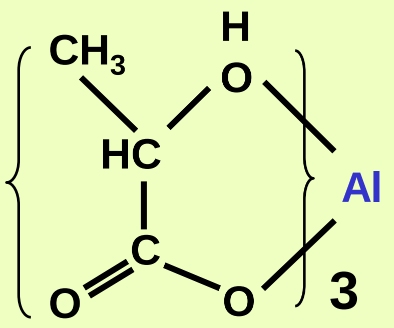
Two Main challenges (introduction of alumina into multiple-network former systems)

- Al-OR → Rapid hydrolysis → Precipitation
- Aqueous Aluminum Salt → Composition ?

Novel Sol – Gel Syntheses Based on $Al(lact)_3$

Chelating nature and pH tunable reactivity

$Al(lact)_3$

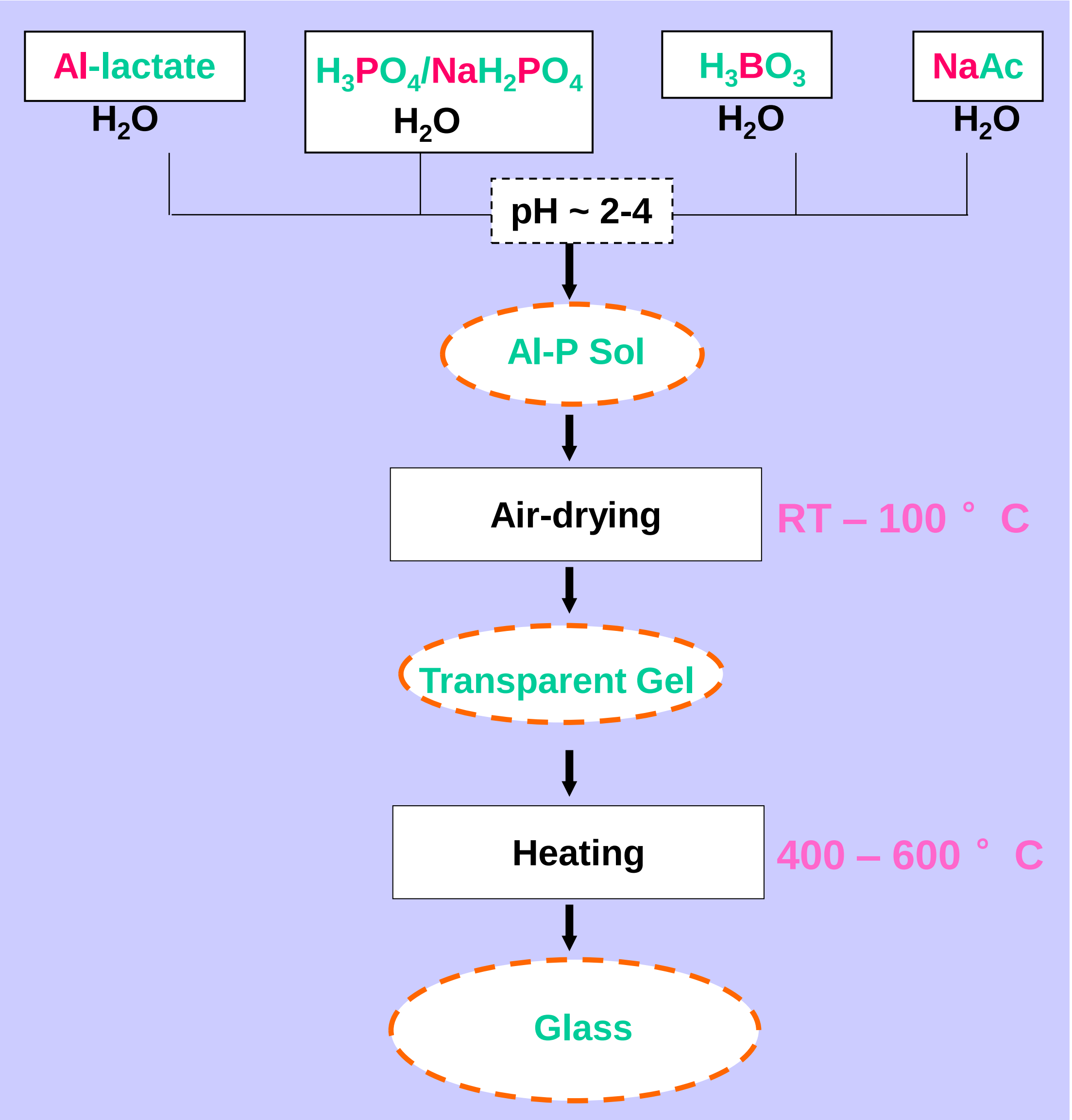


$Al_2O_3 – P_2O_5$,

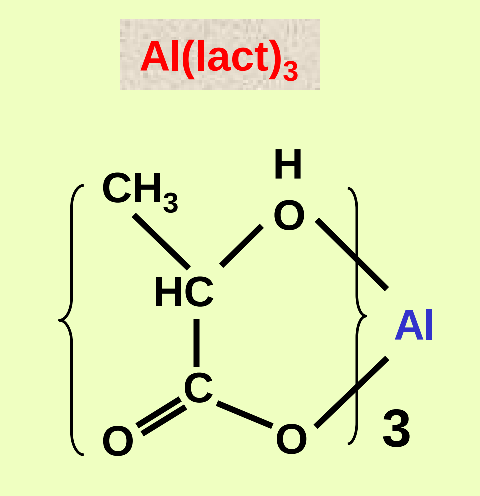
$Na_2O – Al_2O_3 – P_2O_5$,

$Na_2O – Al_2O_3 – B_2O_3$,

$(Na_2O) – Al_2O_3 – B_2O_3 – P_2O_5$,



Glassy mesoporous AlPO4 with analogue silica structure

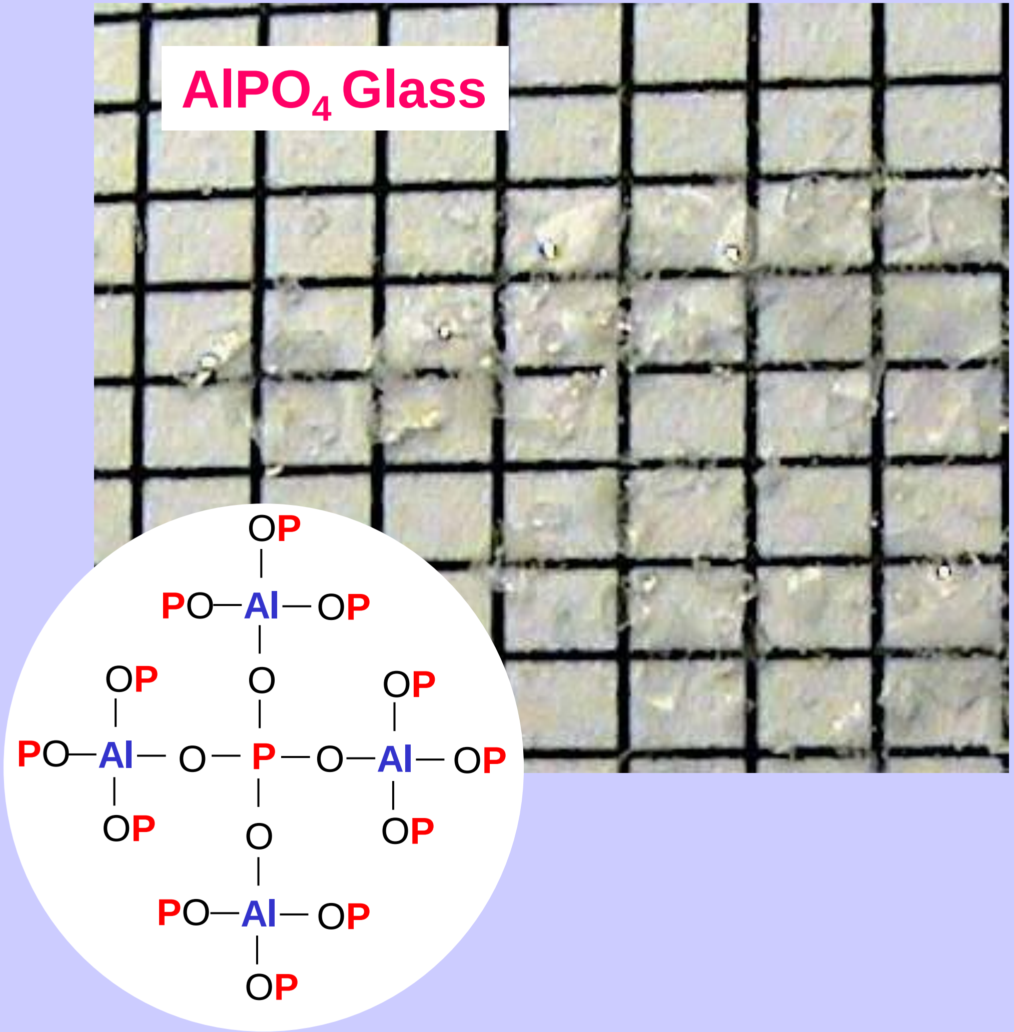


$Al_2O_3 – P_2O_5$,

$Na_2O – Al_2O_3 – P_2O_5$,

$Na_2O – Al_2O_3 – B_2O_3$,

$(Na_2O) – Al_2O_3 – B_2O_3 – P_2O_5$,



L.Zhang, H.Eckert, *J. Mater. Chem.14 (2004)1605*.

To understand the mechanism of the $Al(lact)_3$-based sol-gel

Why $Al(lact)_3$ can be widely used in these sol-gel synthesis ?

Hydrolysis —— How does the **$Al(lact)_3$** react with **water** **?**

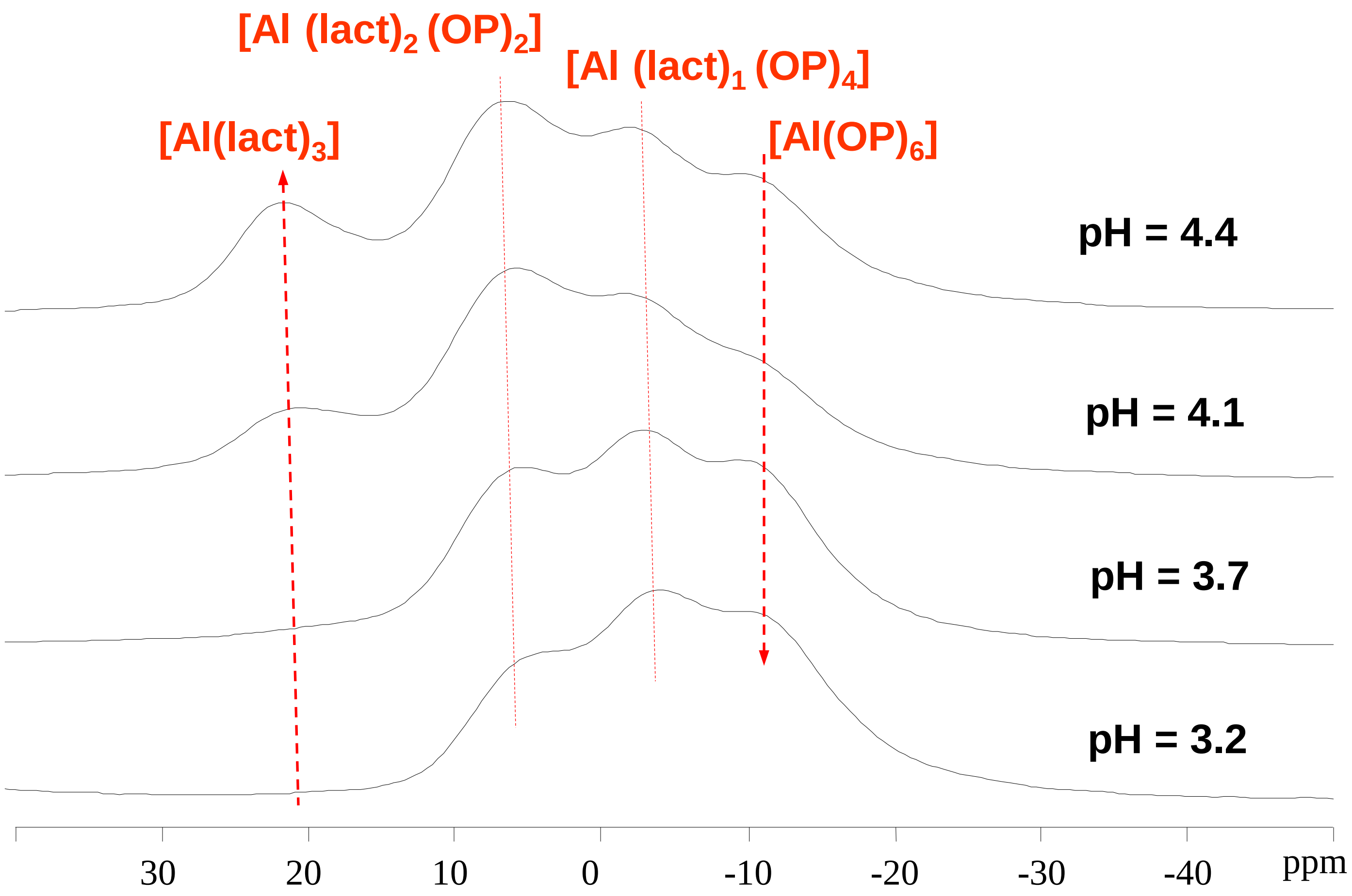
Condensation —— How does the **$Al(lact)_3$** react with **Phosphorus** (i.e. NaH_2PO_4, $NaPO_3$ or H_3PO_4) and **Boron** (H_3BO_3) precursors in aqueous solution **?**

Gel-formation —— How do the **H**ydrolysis and **C**ondensation reactions continuously proceed to form the gel with **macro-molecular** structure**?**

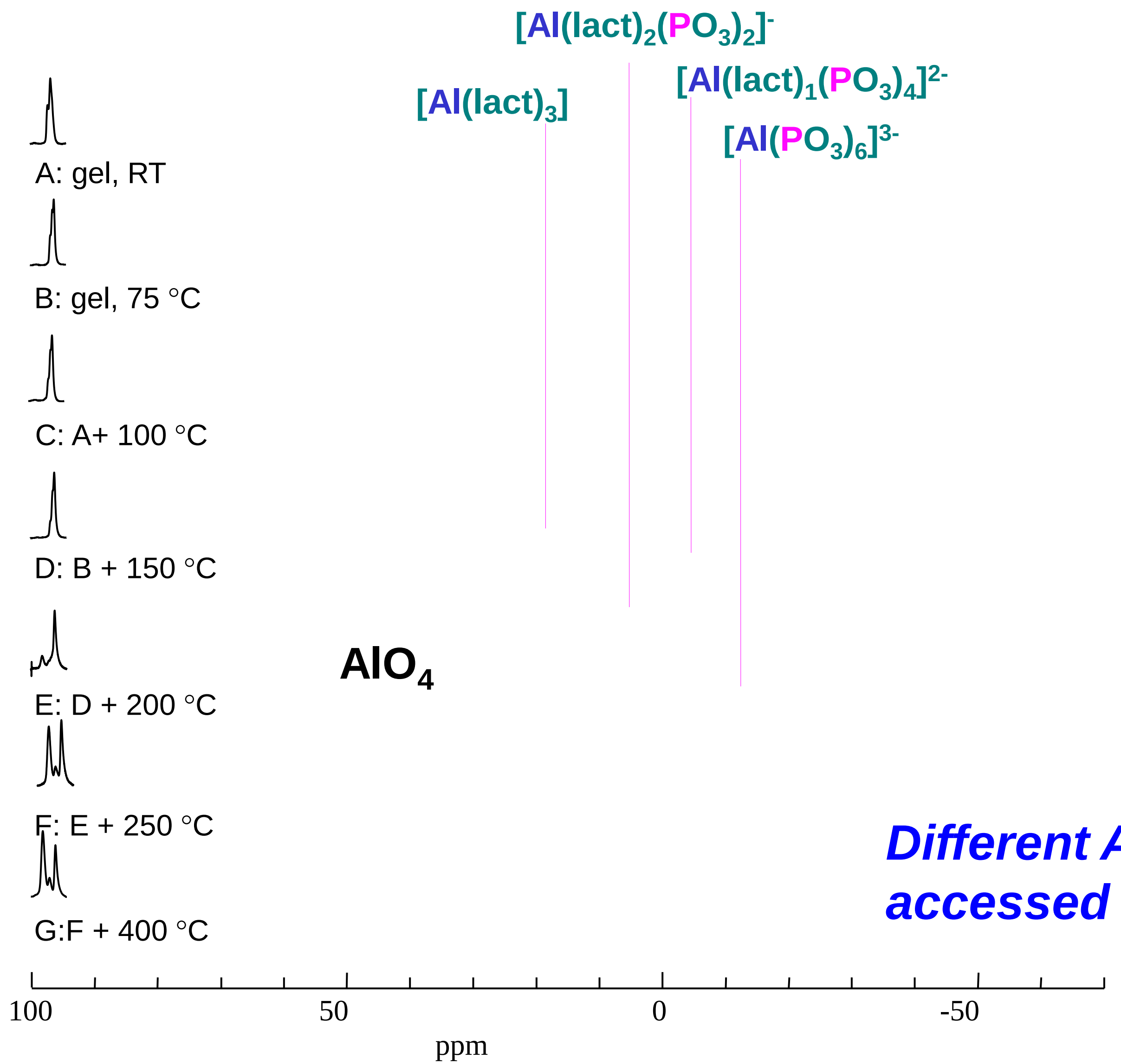
Liquid- and Solid- state **NMR**

^{27}Al MAS NMR of xerogels: pH dependence

87.5 $NaPO_3$ – 12.5Al_2O_3



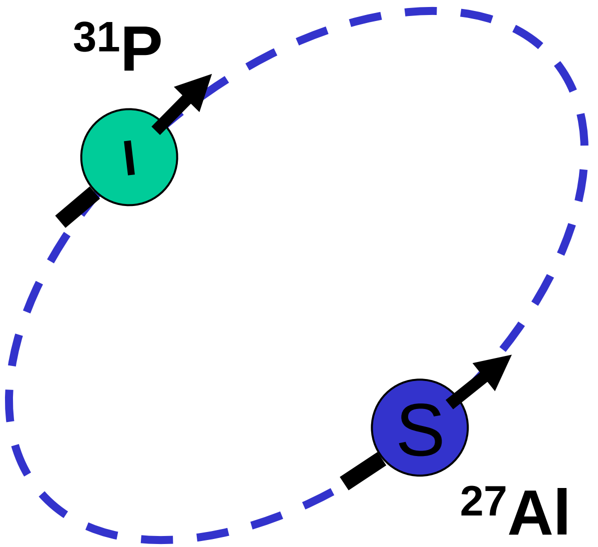
^{27}Al MAS-NMR spectra of $20Al_2O_3$-$80NaPO_3$ samples from gel → glass



Calcination of lactate ligand →

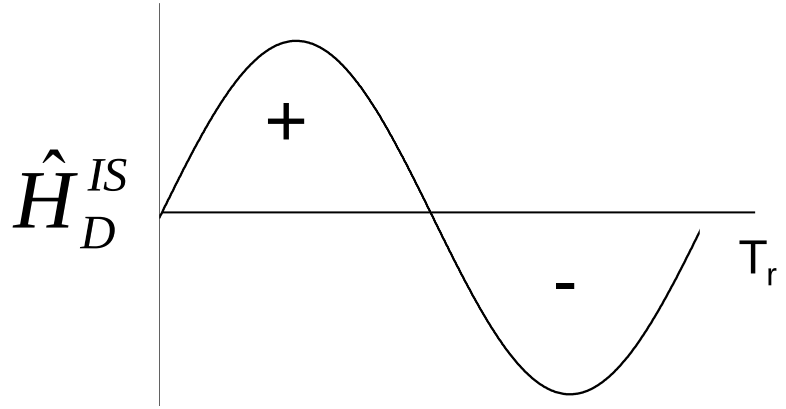
Different Al-P content compounds accessed by DQ NMR experiments!

Al-O-P Connectivity via Dipole Coupling

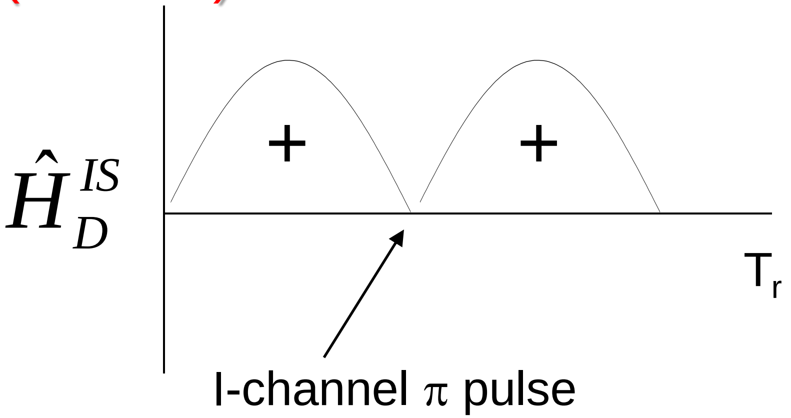


$$\hat{H}_D^{IS} = D\sin(\omega_r t)\hat{I}_z\hat{S}_z$$

Magic- Angle Spinning (MAS)

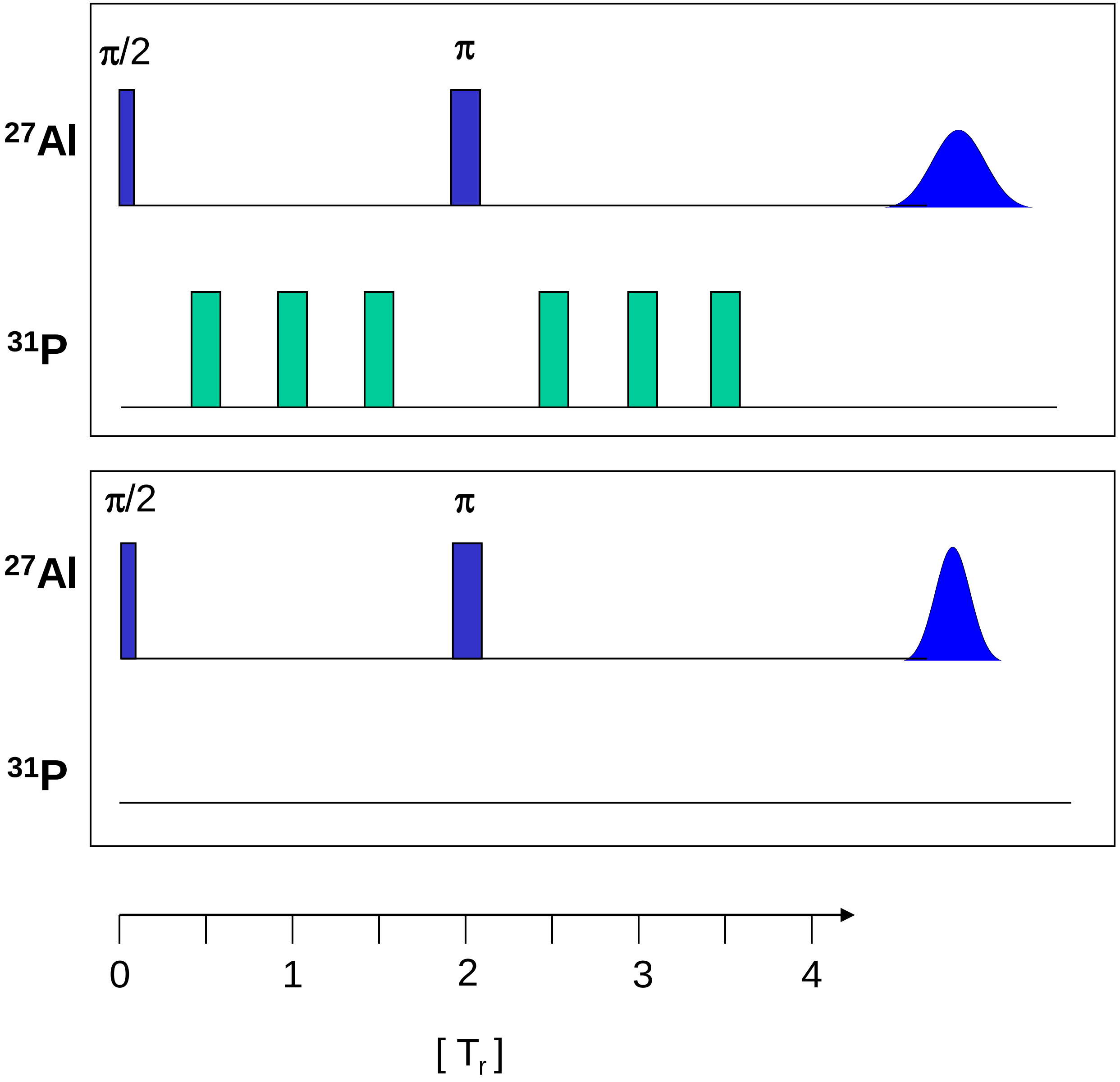


Rotational Echo Double Resonance (REDOR)



$$(\hat{I}_z \Rightarrow -\hat{I}_z)$$

REDOR pulse sequence



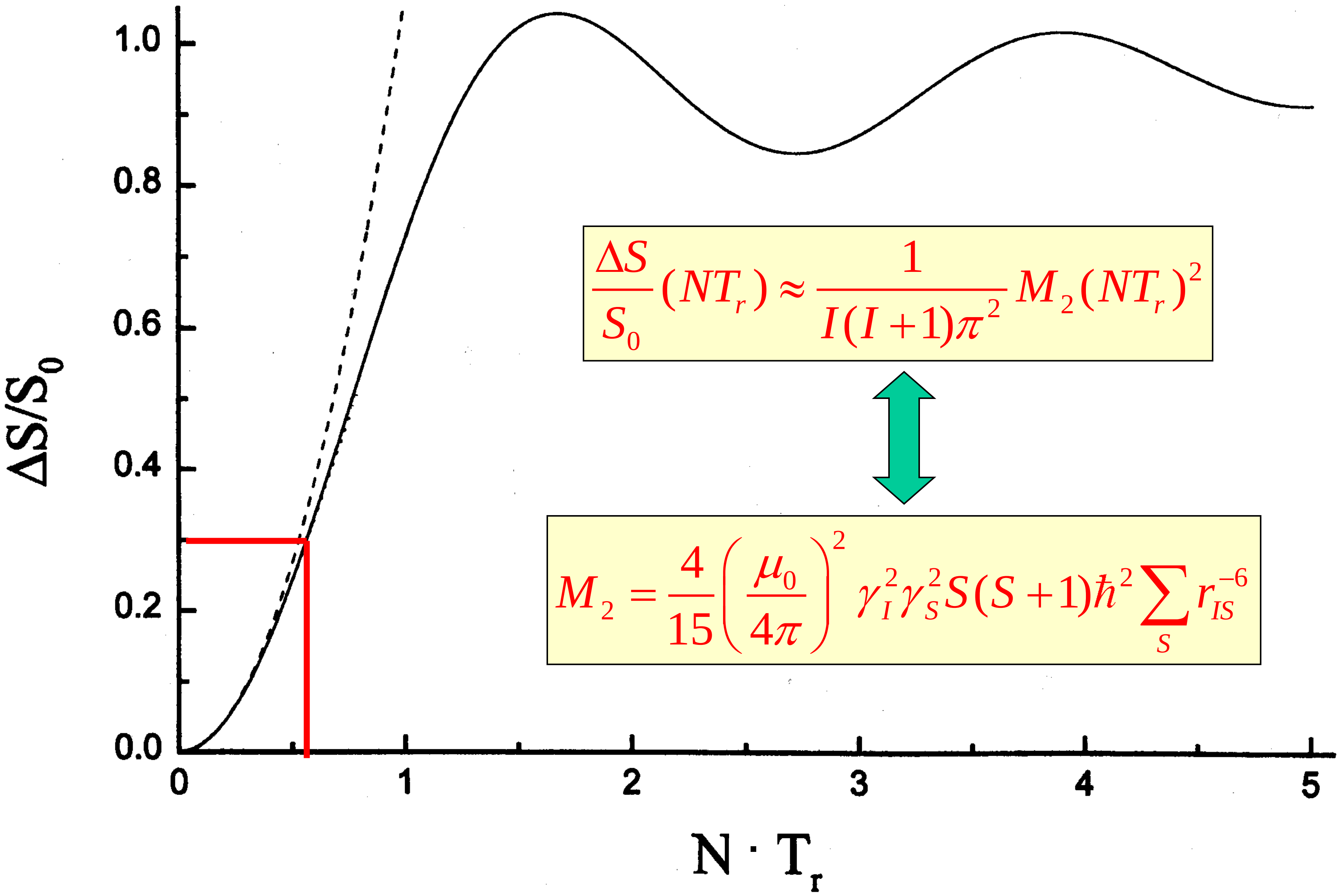
*If there is Al-P dipolar interaction there will be a decrease in Al signal intensity

$$\frac{\Delta S}{S_0}$$

depends on:

- strength of interaction (# neighbors, distance)
- dipolar evolution time $N \cdot T_r$ (N = # rotor cycles; T = period)

Analysis of REDOR Curves in Glasses

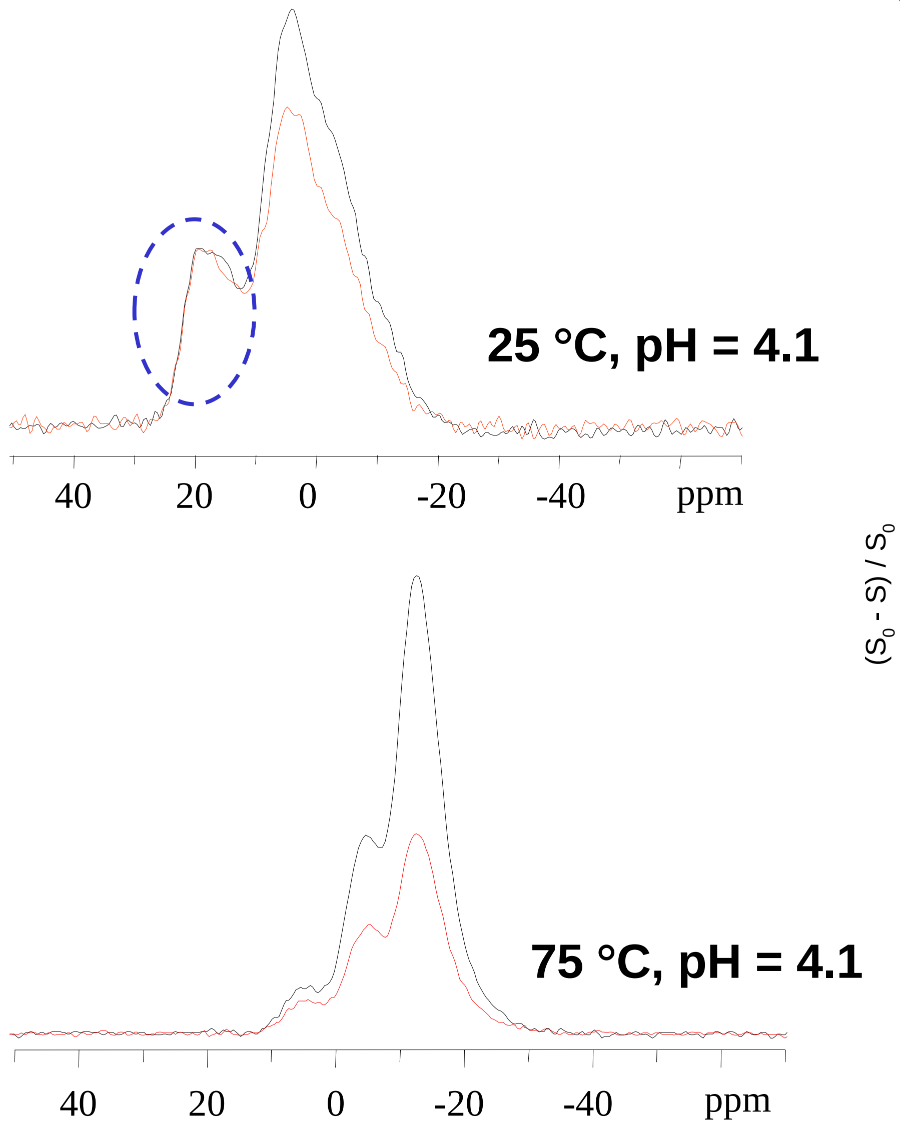


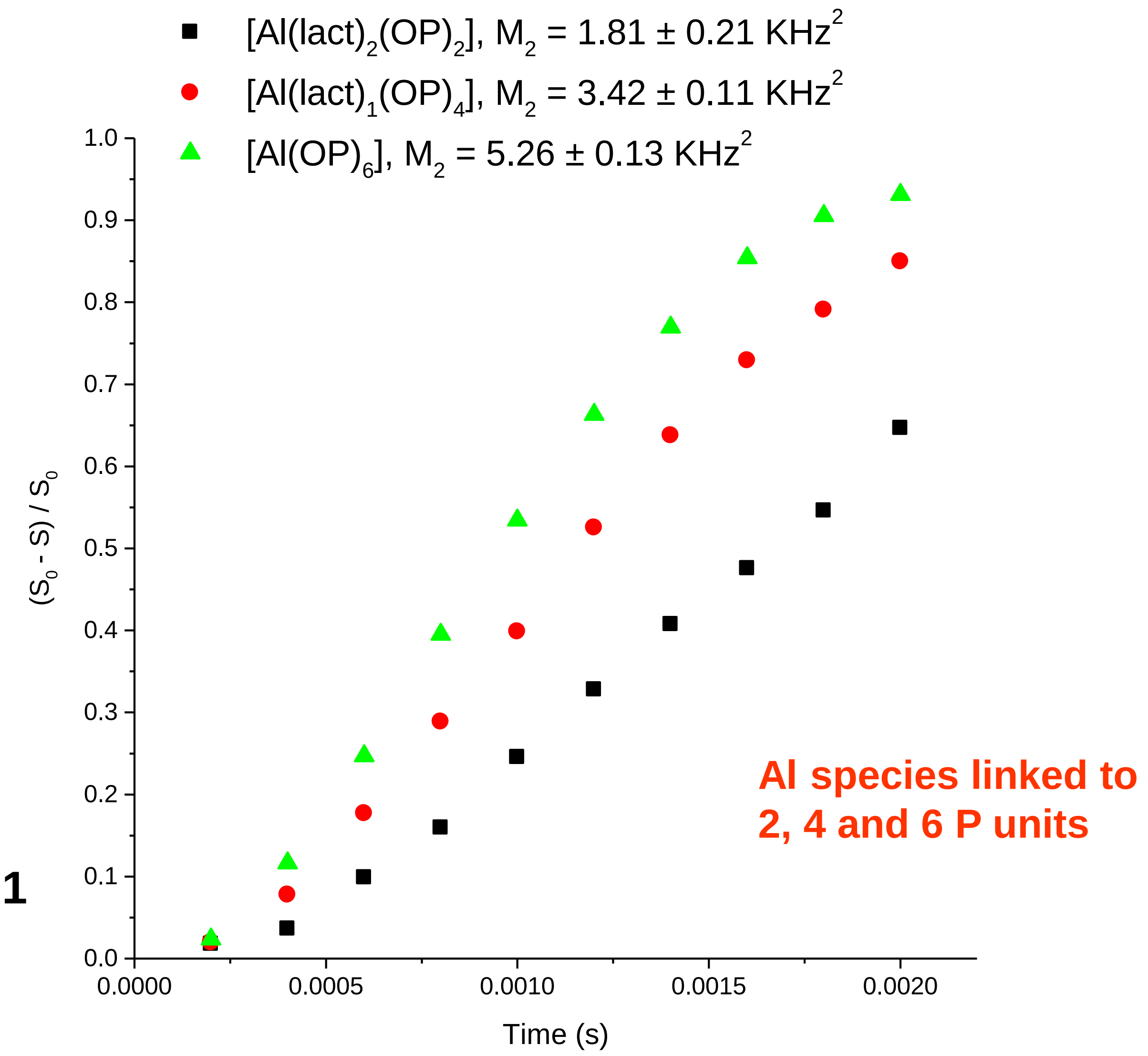
$$\frac{\Delta S}{S_0}(NT_r) \approx \frac{1}{I(I+1)\pi^2} M_2 (NT_r)^2$$

$$M_2 = \frac{4}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 S(S+1)\hbar^2 \sum_S r_{IS}^{-6}$$

$^{27}Al\{^{31}P\}$ REDOR of aluminophosphate xerogel

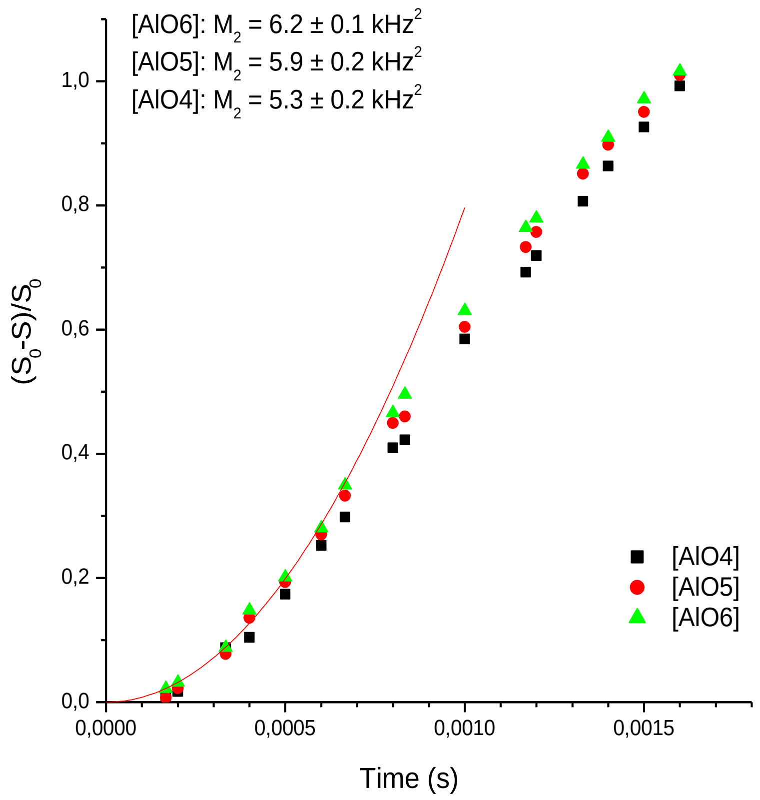
$87.5\ NaPO_3 – 12.5Al_2O_3$

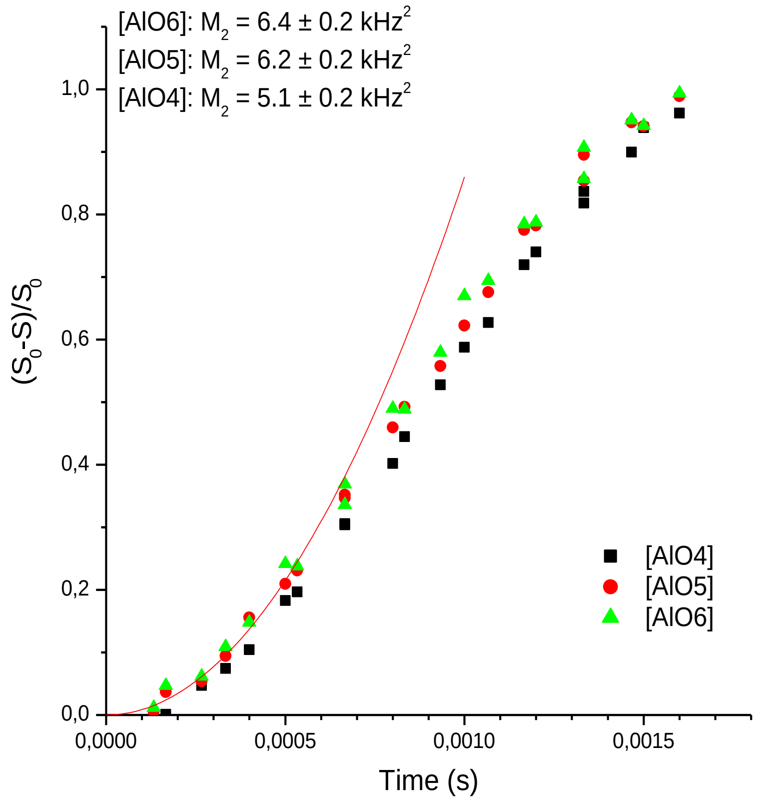




Comparison of Al-P Connectivity in gel-derived and melt-cooled glasses: $^{27}Al\{^{31}P\}$ REDOR

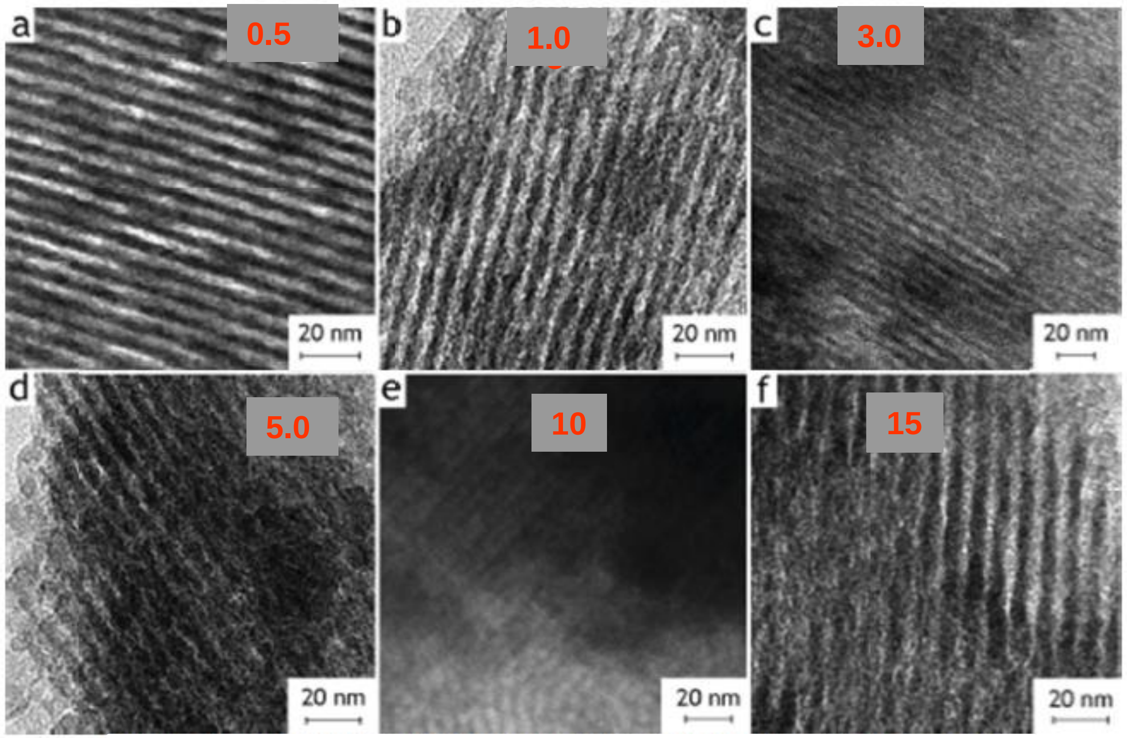
87.5 $NaPO_3$ – 12.5 Al_2O_3

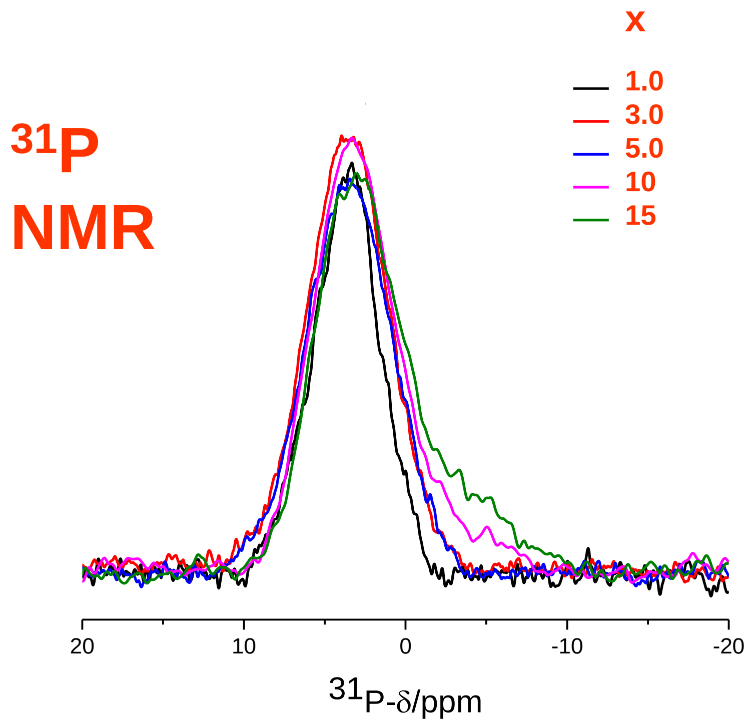




Gel –derived **melt-cooled**

Mesoporous Bioglasses
$(80-x)SiO_2 – 15CaO – 5P_2O_5 -xAl_2O_3$



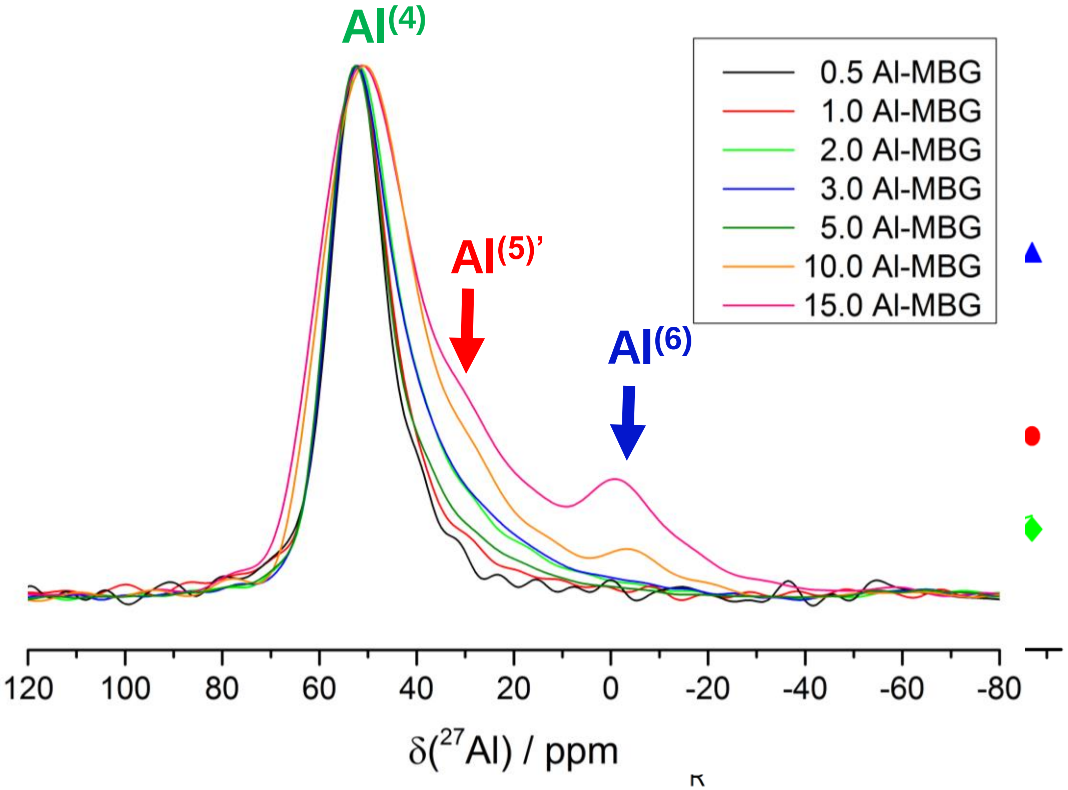


Majority of phosphate is still loosely bound orthophosphate in the studied range of Al2O3 concentrations

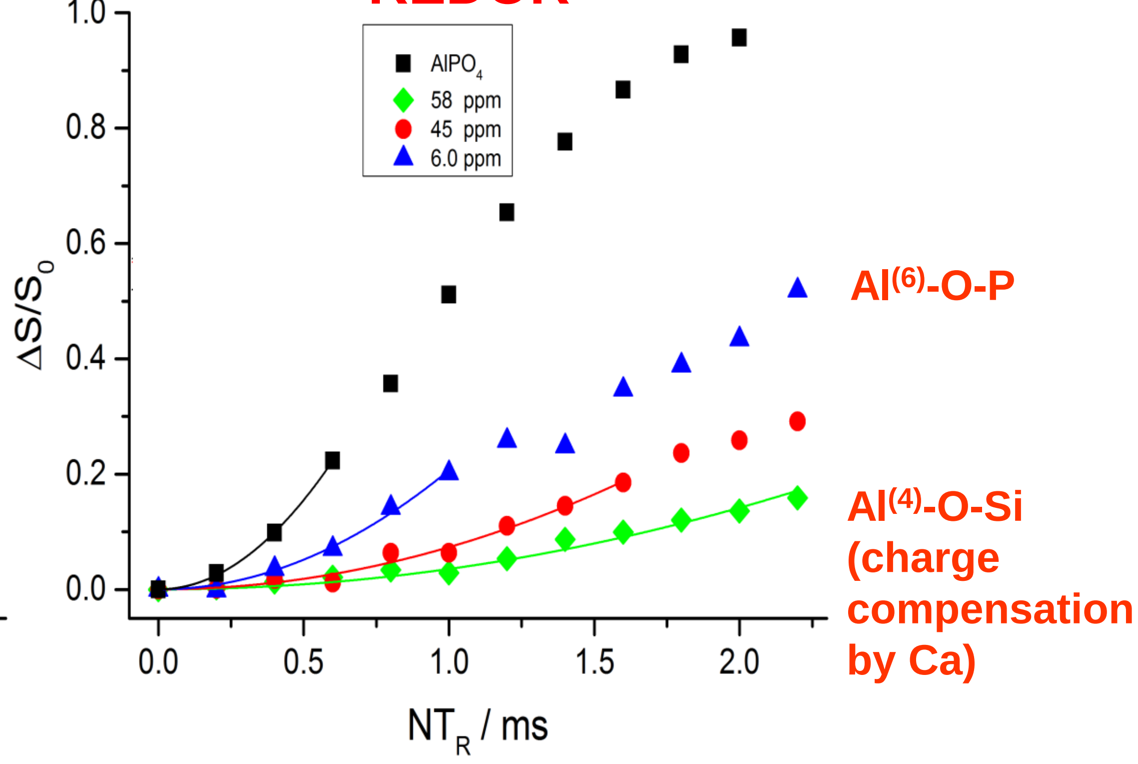
Mesoporous Bioglasses

(80-x) SiO_2 – 15 CaO - 5 P_2O_5 – x Al_2O_3

^{27}Al NMR



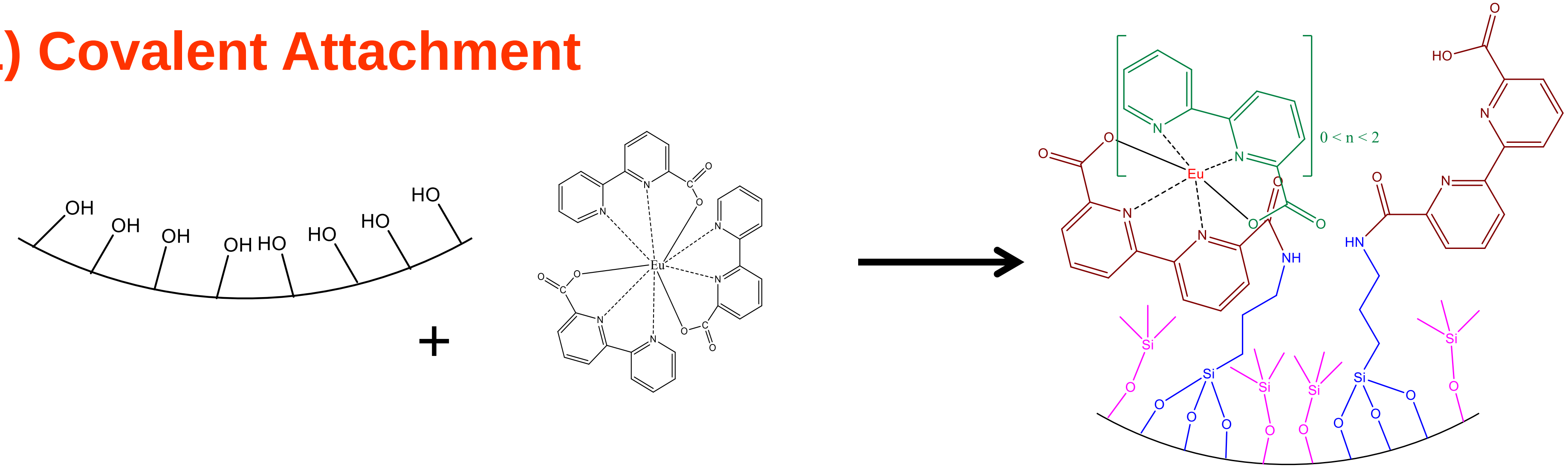
^{27}Al{^{31}P} REDOR



Strong Al/P interactions

Host-guest material based on Eu-complex immobilized in mesoporous silicate

1) Covalent Attachment



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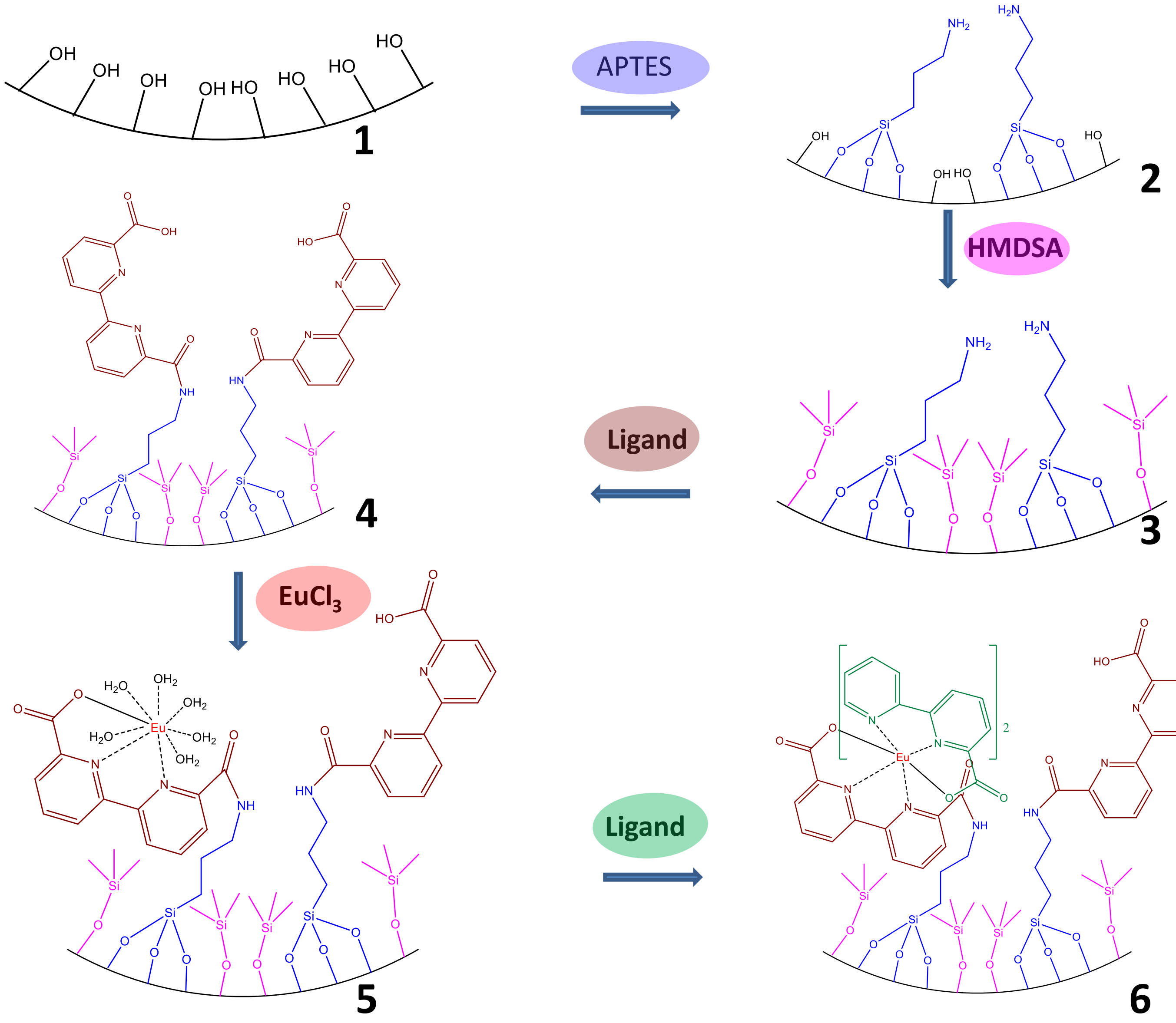
Luminescent hybrid materials based on covalent attachment of Eu(III)-tris(bipyridinedicarboxylate) in the mesoporous silica host MCM-41†

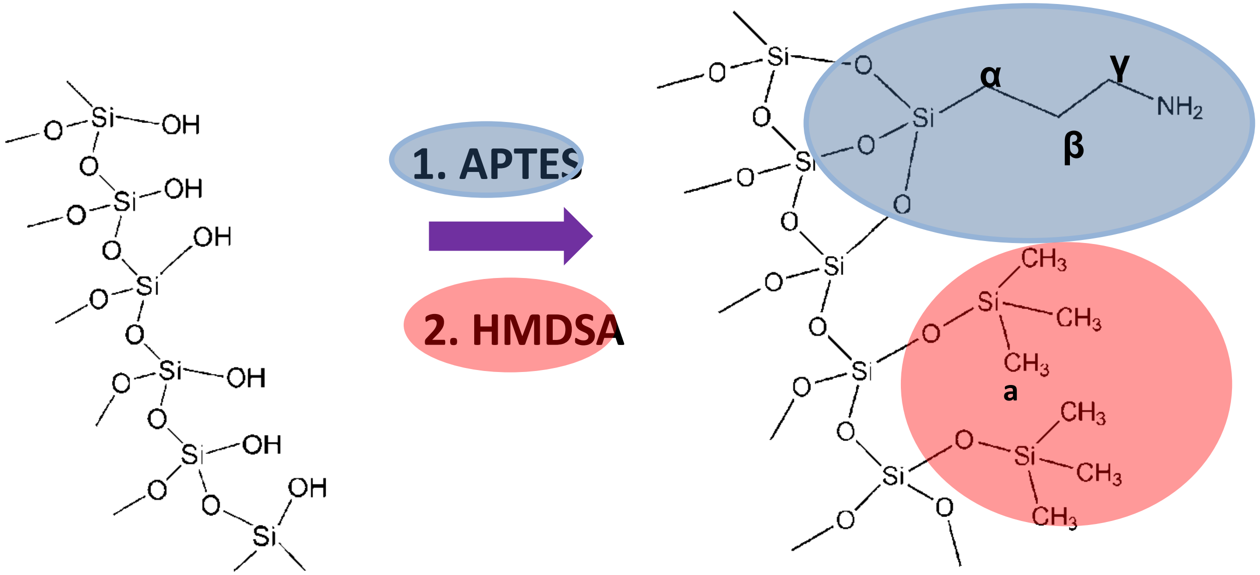
Maturi Ilibi,[a] Thiago Branquinho de Queiroz,[b] Jinjun Ren,[a] Luisa De Cola,‡[c] Andrea Simone Stucchi de Camargo*[b] and Hellmut Eckert*[a,b]

Covalent Attachment: $Eu(bipyCOO)_3$ in MCM 41

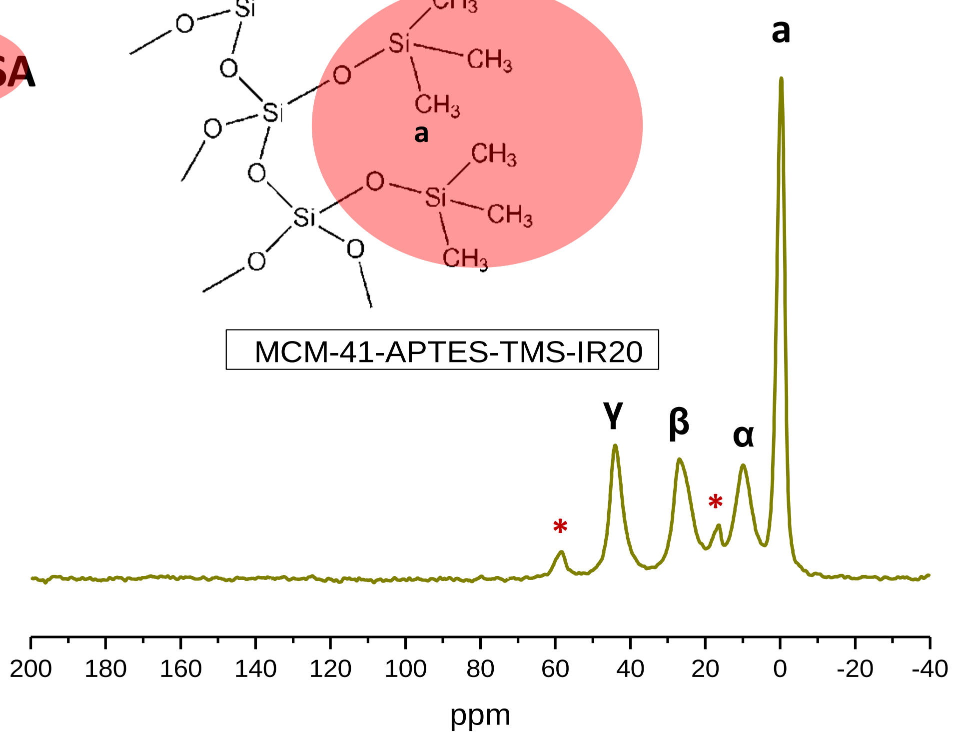


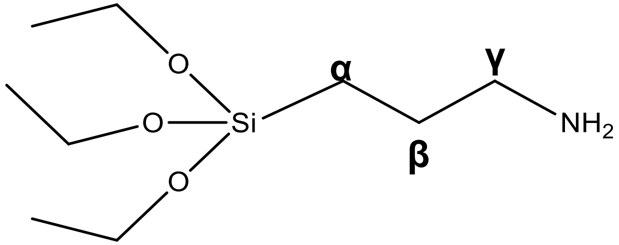
M. Ilibi, T. B. de Queiroz, J. Ren, L. de Cola, A. S. S. de Camargo, H. Eckert, Dalton Trans. 43, 8318 (2014).

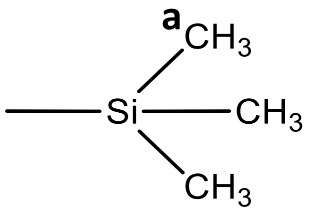
STEP 1: Surface functionalization



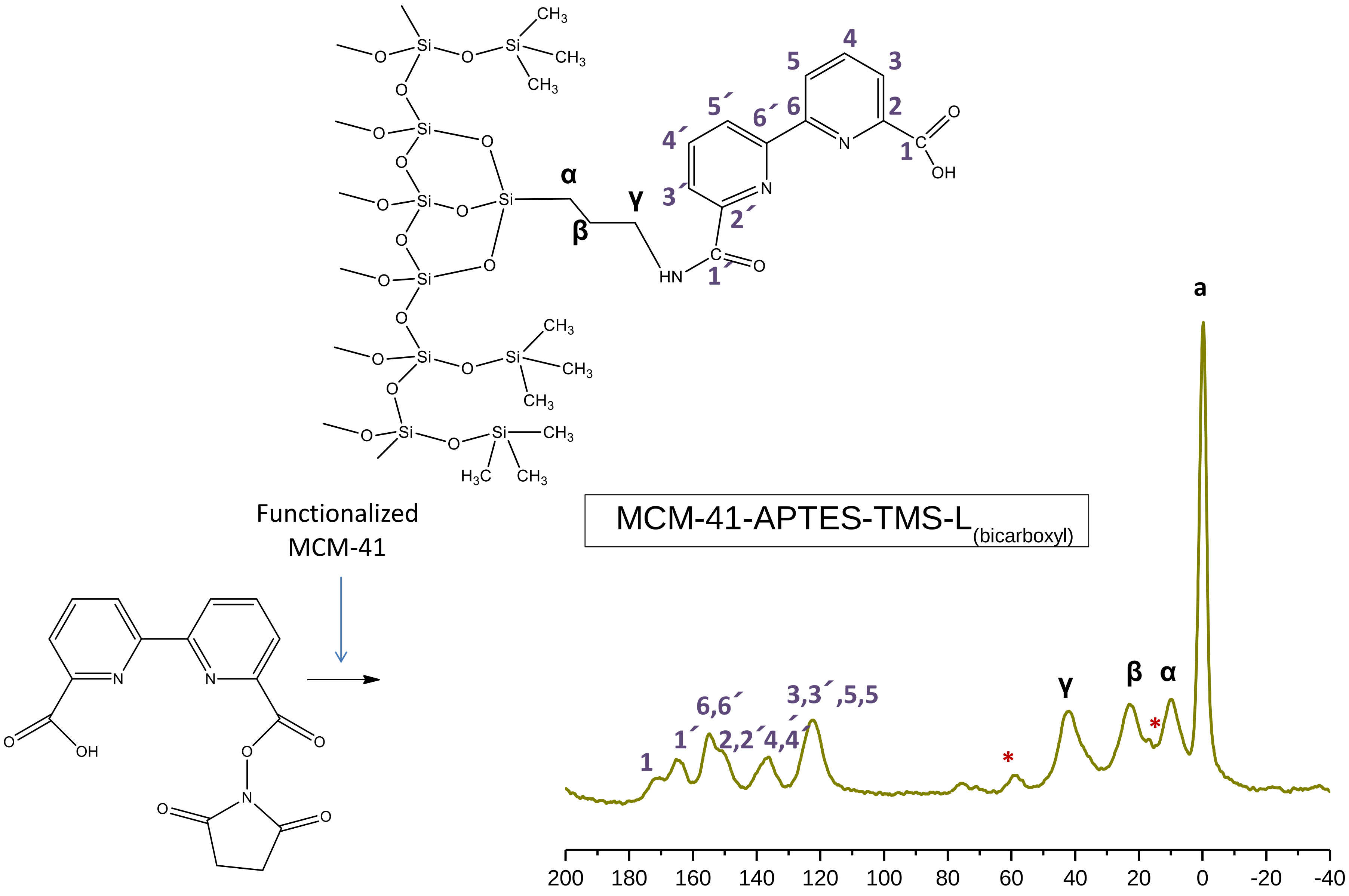
^{13}C solid state NMR





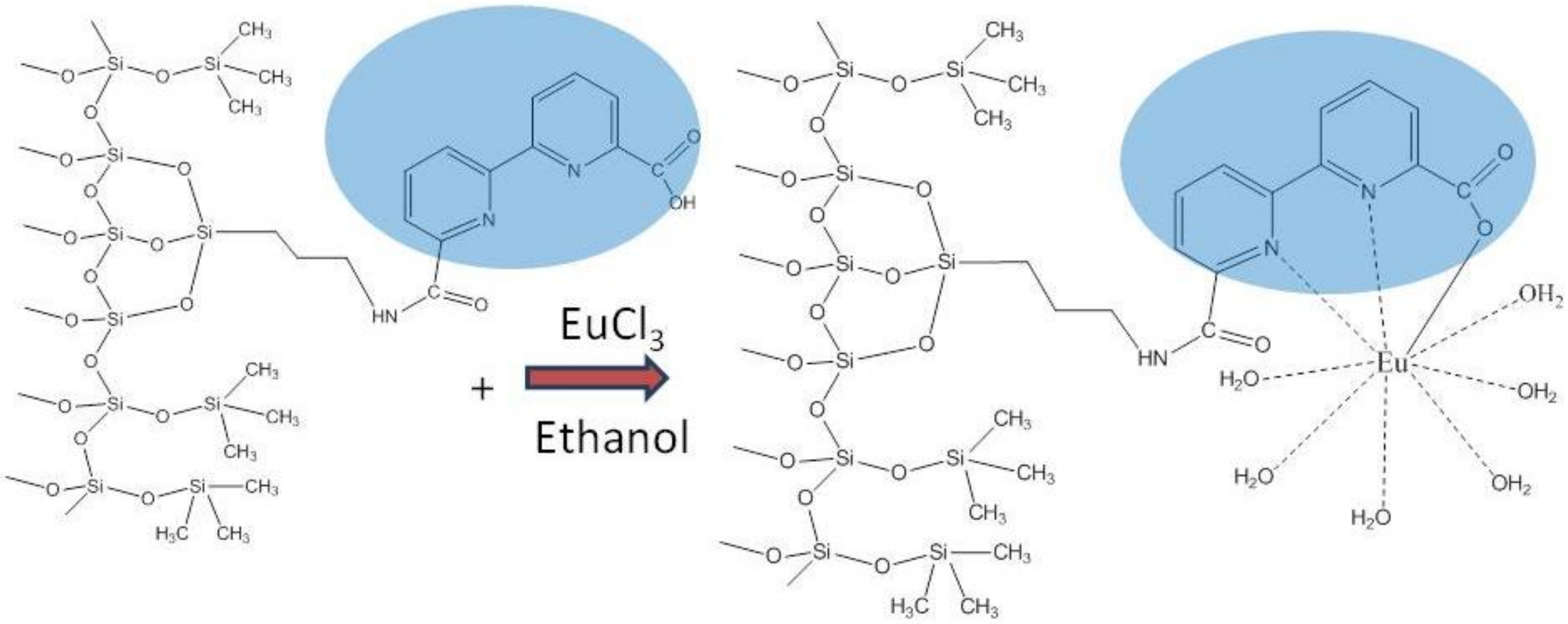


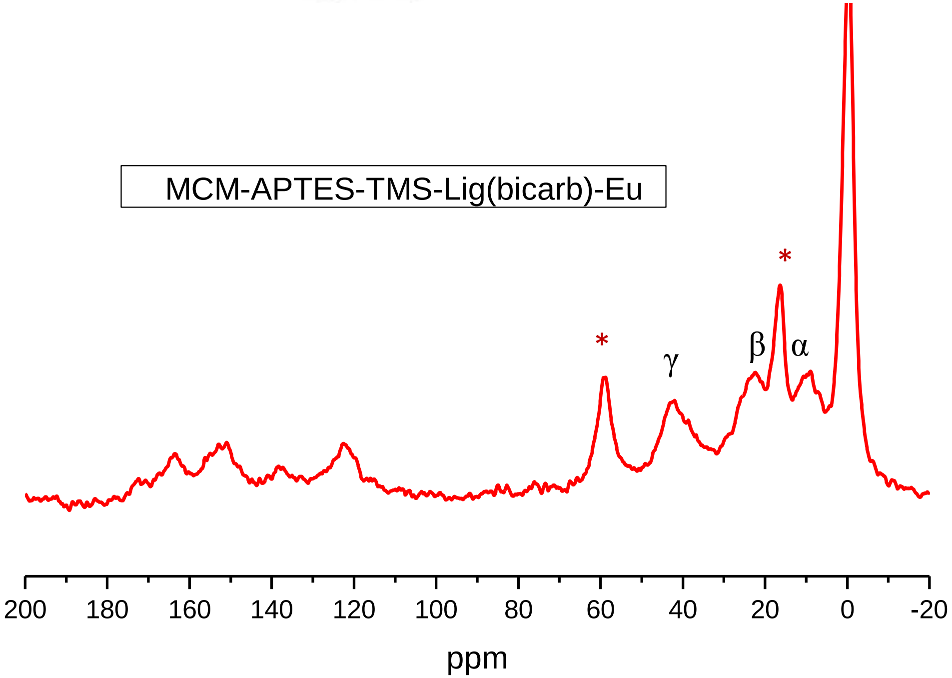
STEP 2: Ligand binding



Activated Bipyridine-Ligand

STEP 4: Metalation



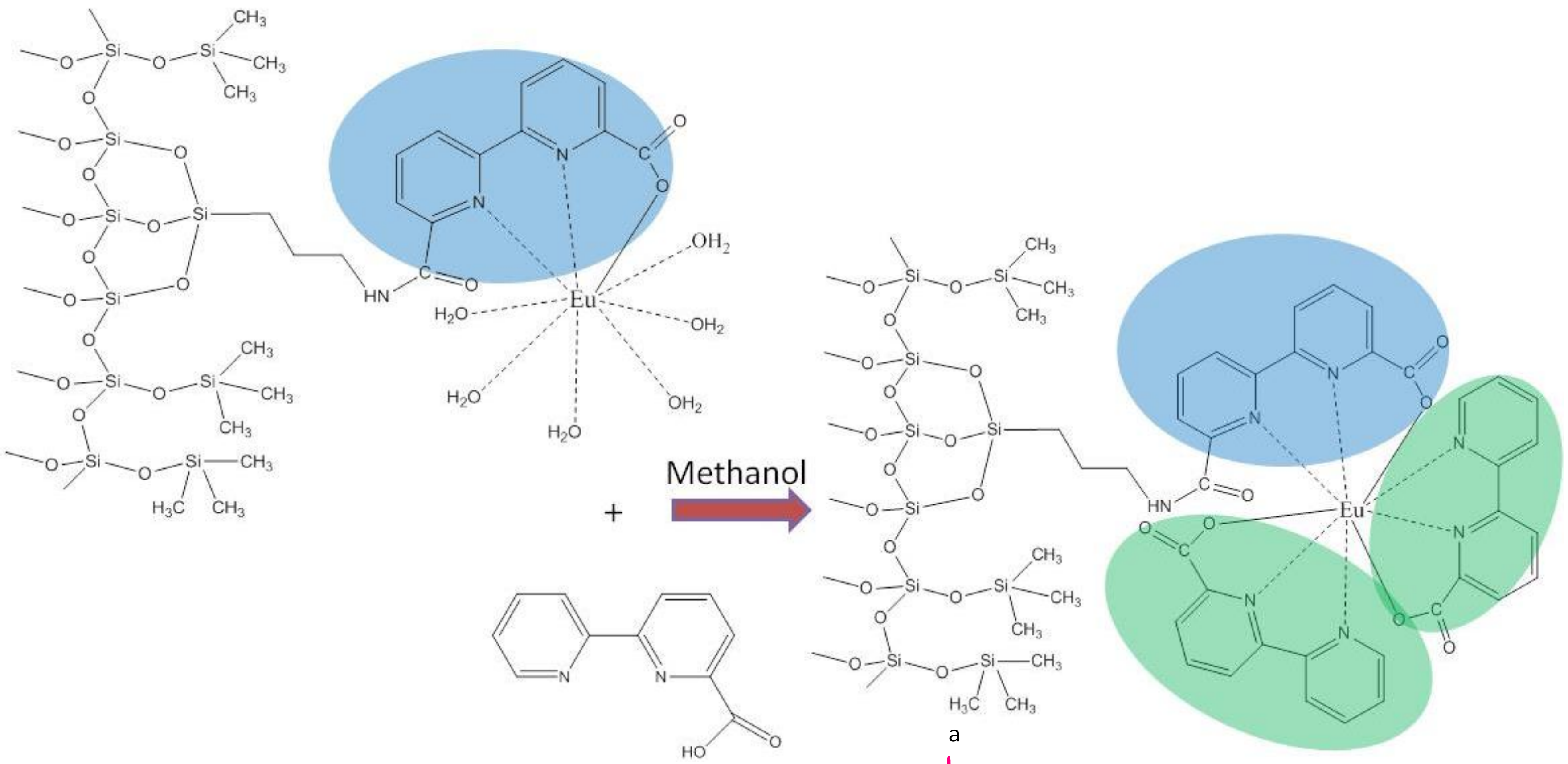


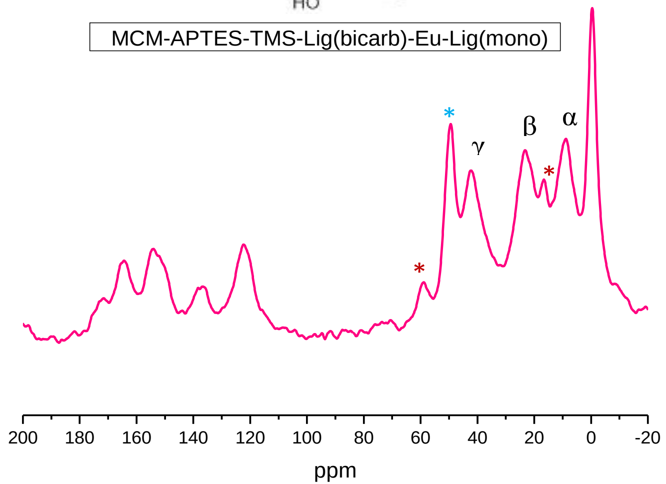
Decreasing of ligand intensity signal

⇩

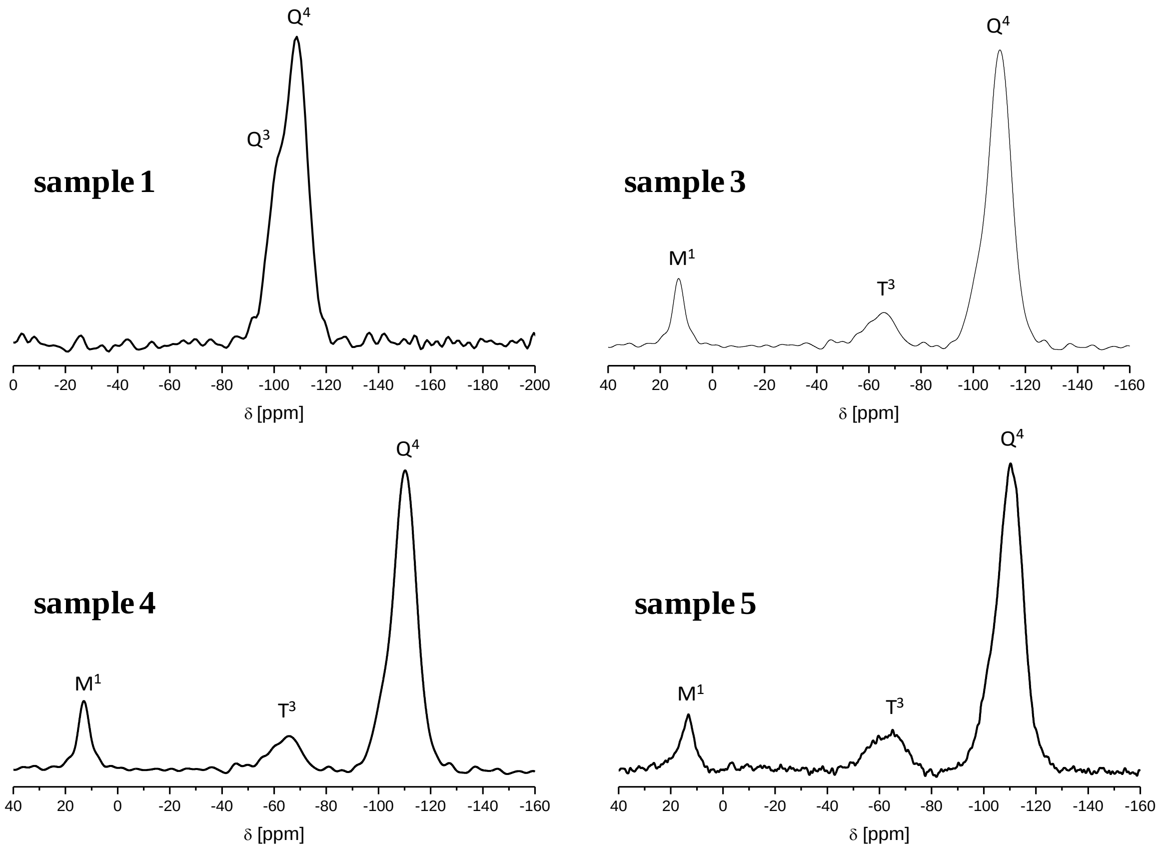
Paramagnetic effect of Eu

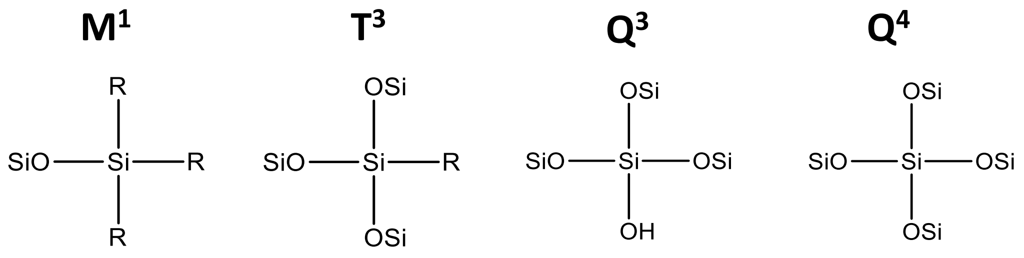
STEP 4: Completion of Eu coordination





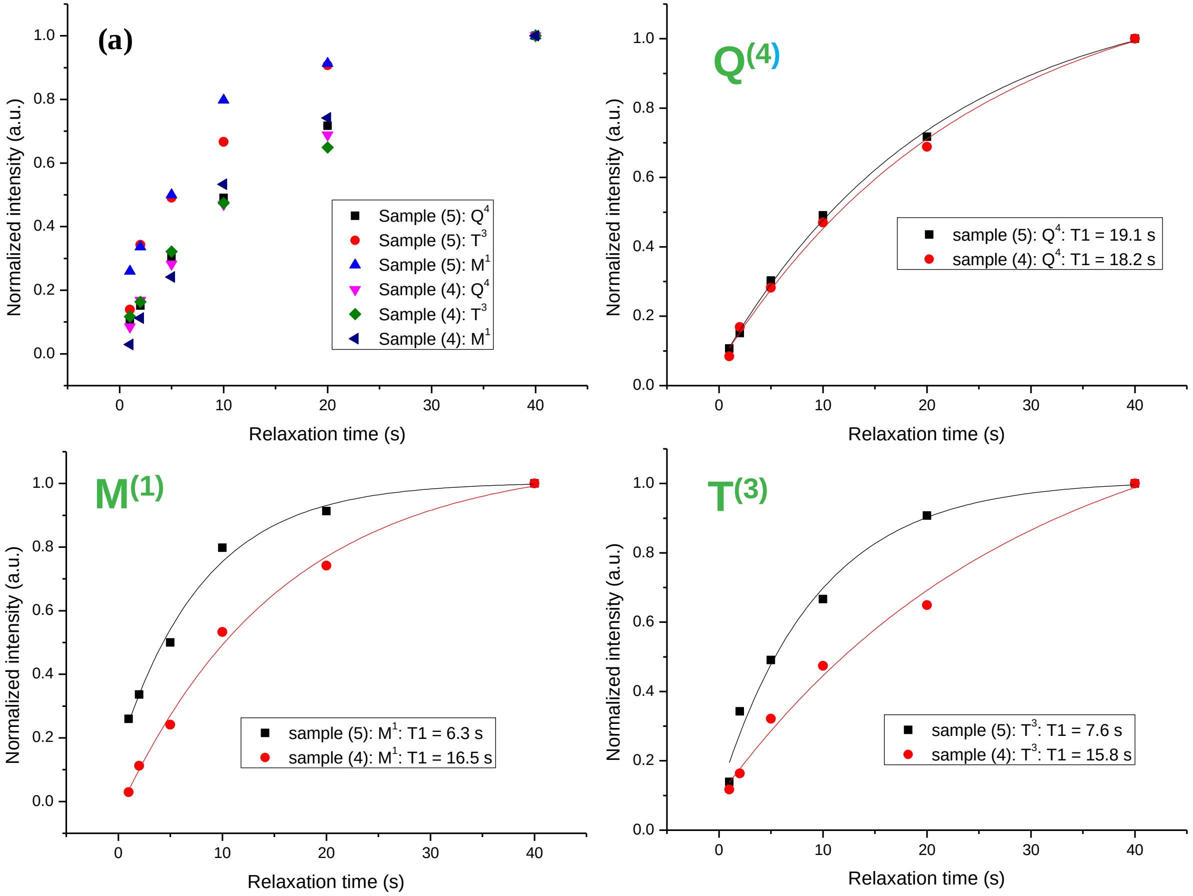
^{29}Si NMR: Quantification of the silicon species in the host





^{29}Si-T_1: paramagnetic effect of Eu(III)

Relaxation curves before and after Eu addition



M. Ilibi, T. B. de Queiroz, J. Ren, L. de Cola, A. S. S. de Camargo, H. Eckert, Dalton Trans. 43, 8318 (2014).

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- Volkswagen, Faber-Castell, Electrolux, etc
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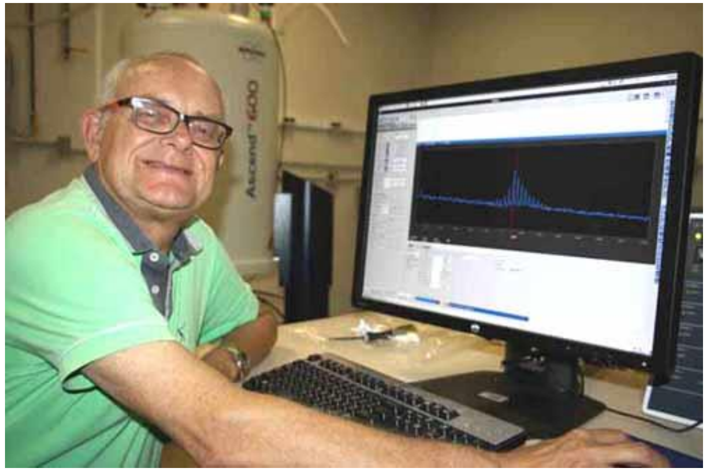
- UFSCar (f. 1968, 14.000 students)

ACKNOWLEDGMENTS



H. Eckert IFSC/USP

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Ladies specially wanted!!

Profa. Dra. Andréa S. Stucchi de Camargo

Ambassador Scientist 2020-23

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