NMR of Solids

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Interactions of nuclear spins in a solid

E_Z = Zeeman effect
E_{RF} = RF field
E_{CS} = Chemical shift
E_J = JJ coupling
E_D = Dipolar interactions
E_Q = Quadrupolar coupling
E_{ij} = Unpaired electrons

$E_Z >> $ other interactions

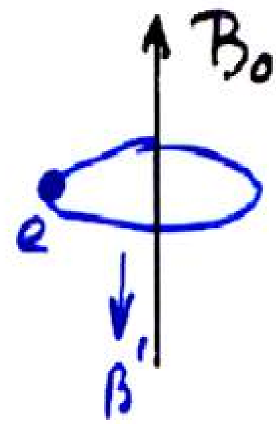
Very often some effects are masked by the others

For example $E_D >> E_J$

E_X = K (spin factor) [space factor f(θ)]

θ = angle between an axis of the system and B_0

Chemical Shift δ



$$\omega = \gamma B$$

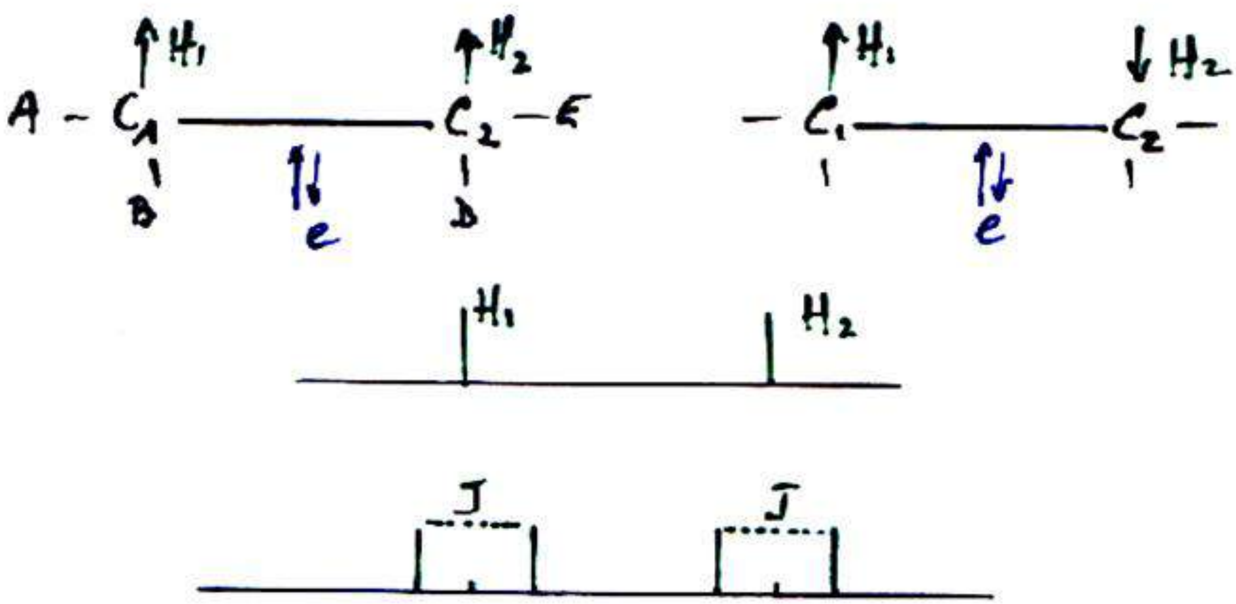
Sample: $2\pi\nu_s = \gamma B_0(1-\sigma_s)$

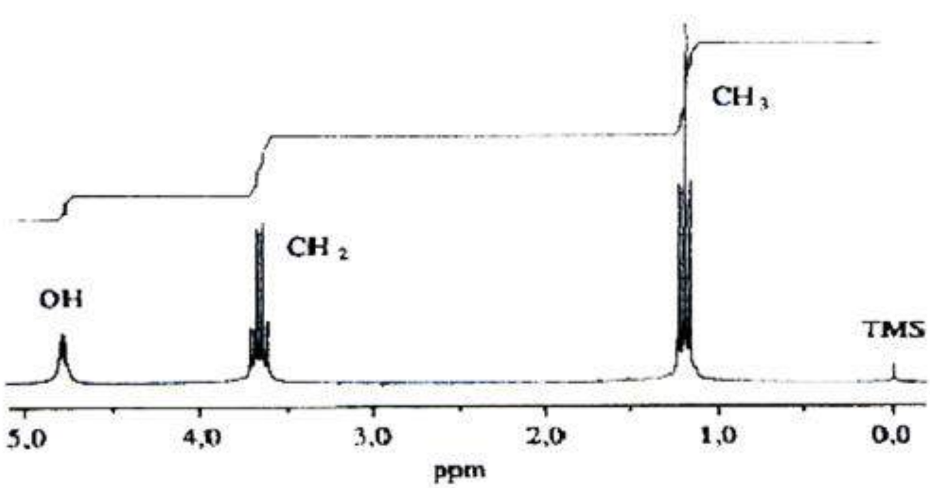
Reference: $2\pi\nu_r = \gamma B_0(1-\sigma_r)$

$$\Delta\nu = \nu_r - \nu_s = \frac{\gamma B_0}{2\pi}(\sigma_s - \sigma_r)$$

$$\delta = \frac{\gamma B_0/2\pi\,(\sigma_s - \sigma_r)}{\gamma B_0/2\pi\,(1-\sigma_r)} \sim \sigma_s - \sigma_r \quad ppm$$

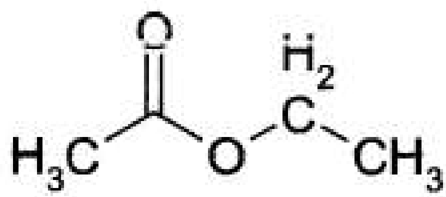
Spin-spin coupling J

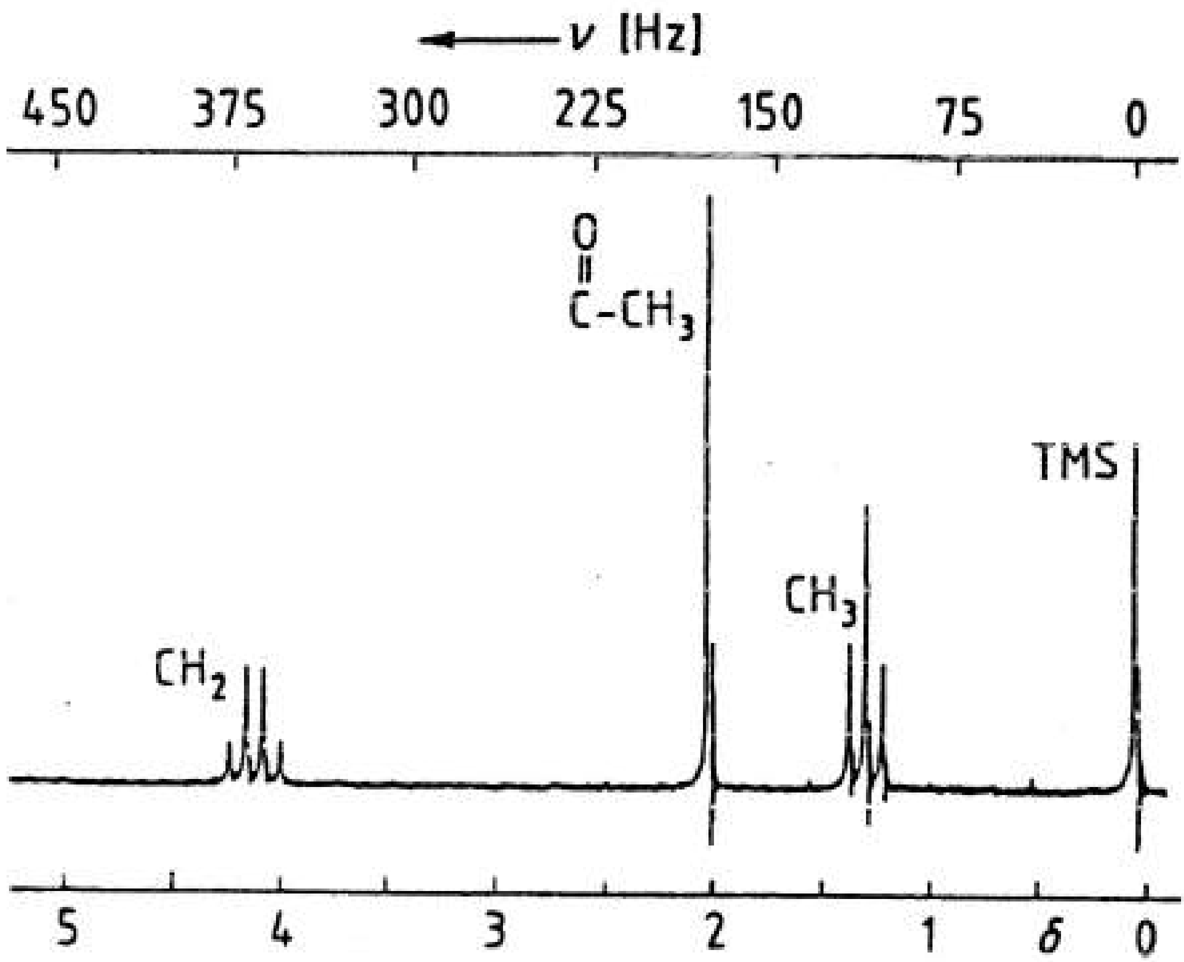




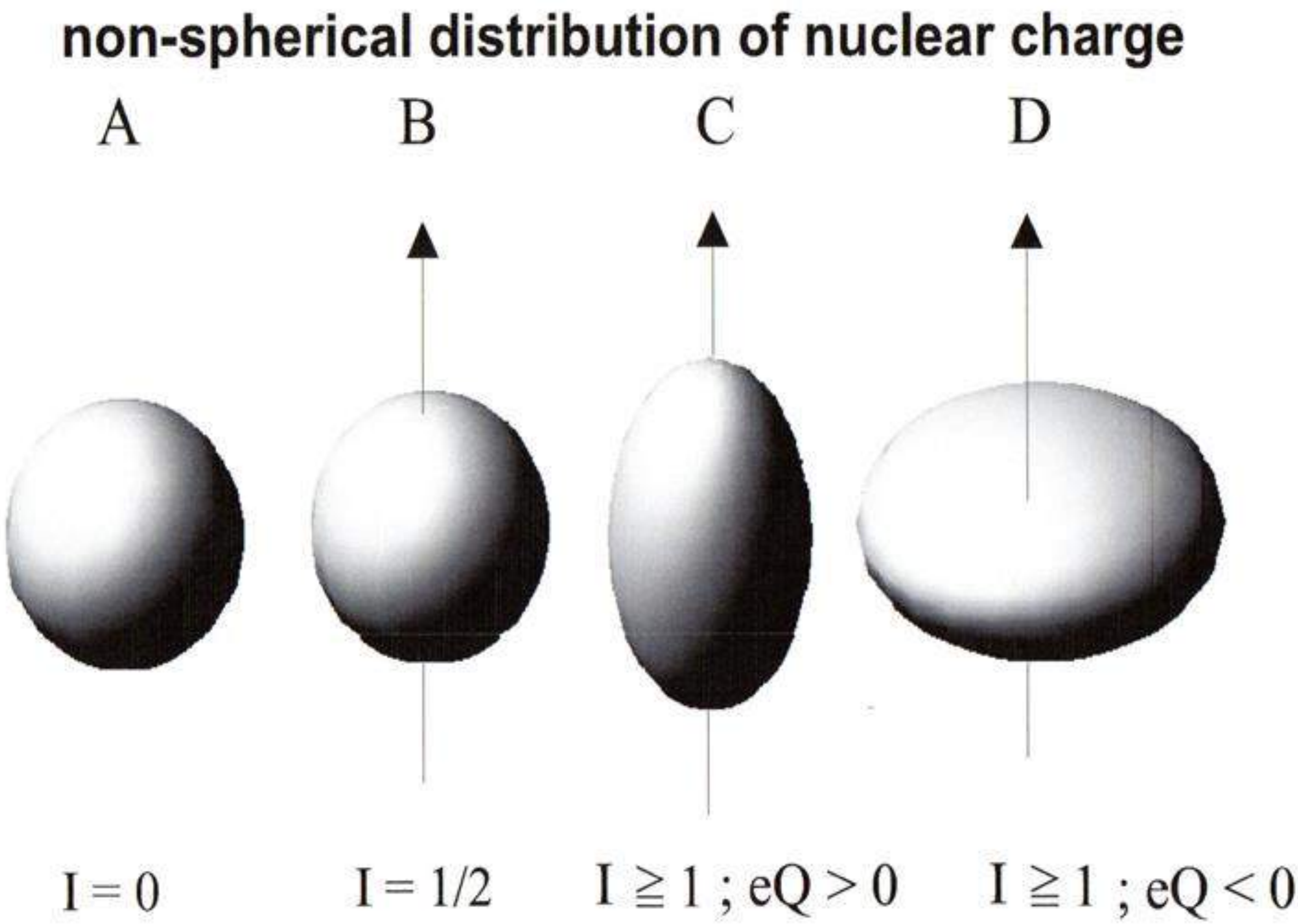
2 n I + 1

Ethyl acetate



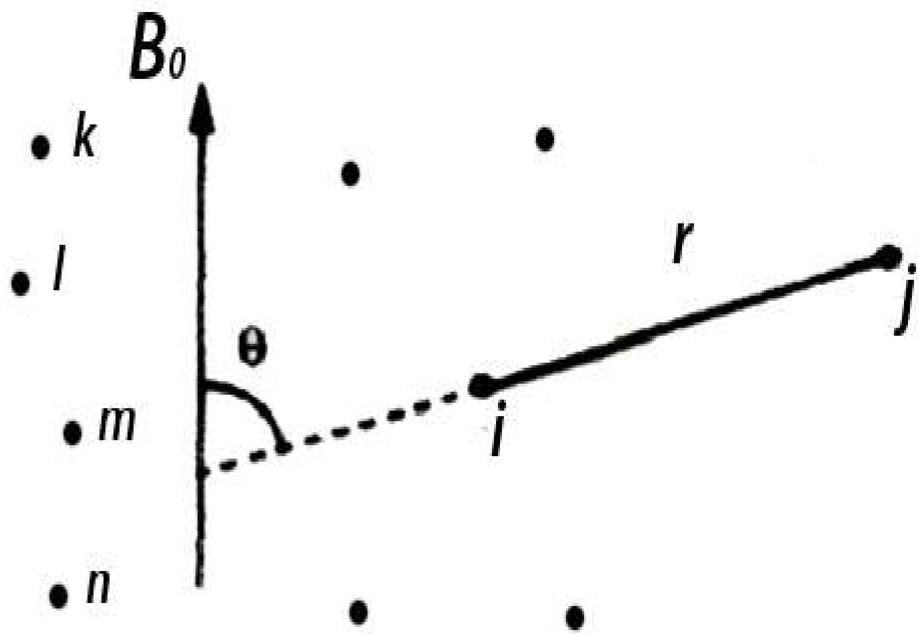


Nuclear Electric Quadrupole Moment



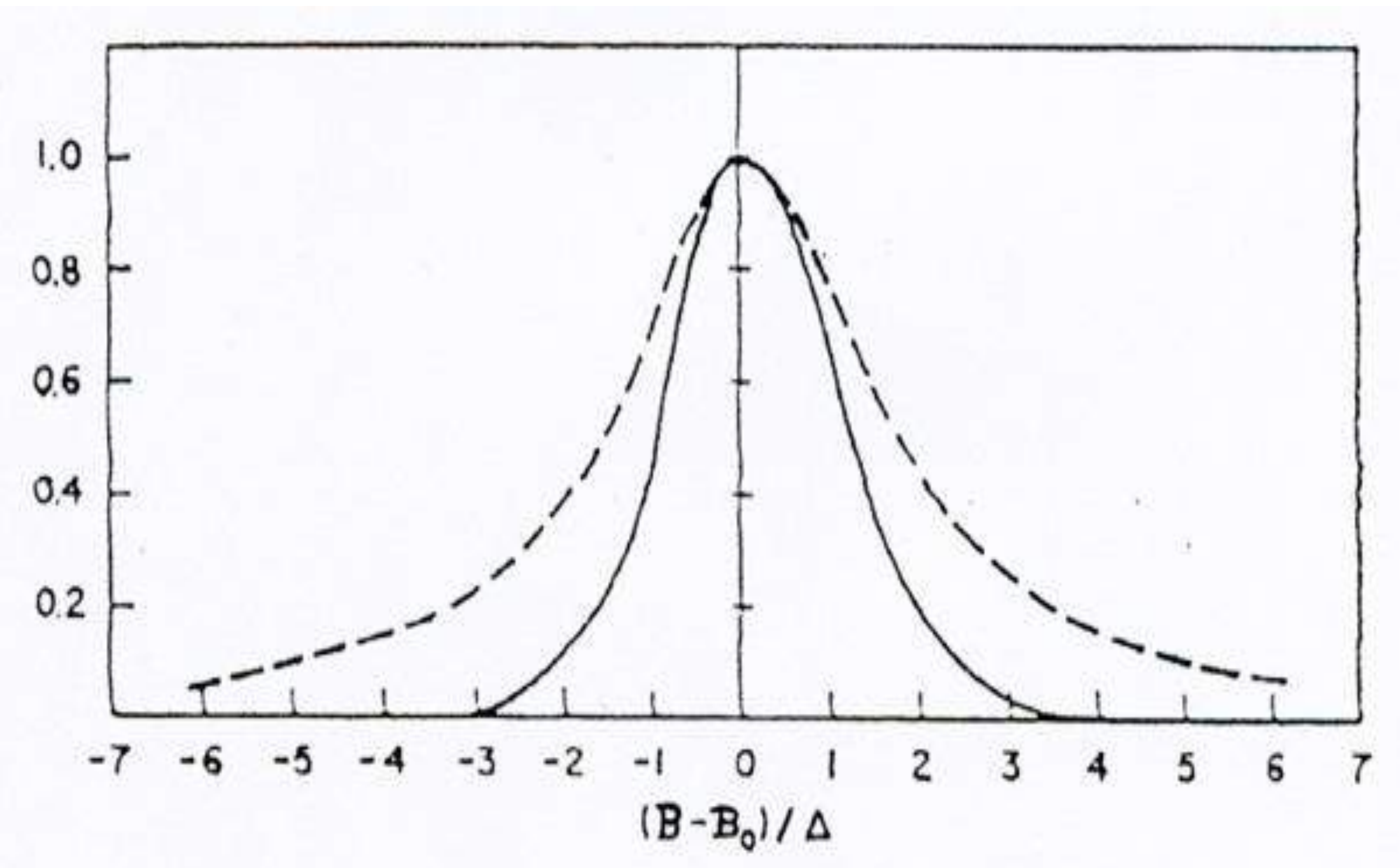
Dipolar Magnetic Interaction between nuclei

$$\text{DMI} = \text{CONSTANT} \cdot (1 - 3\cos^2\theta) \cdot r^{-3}$$



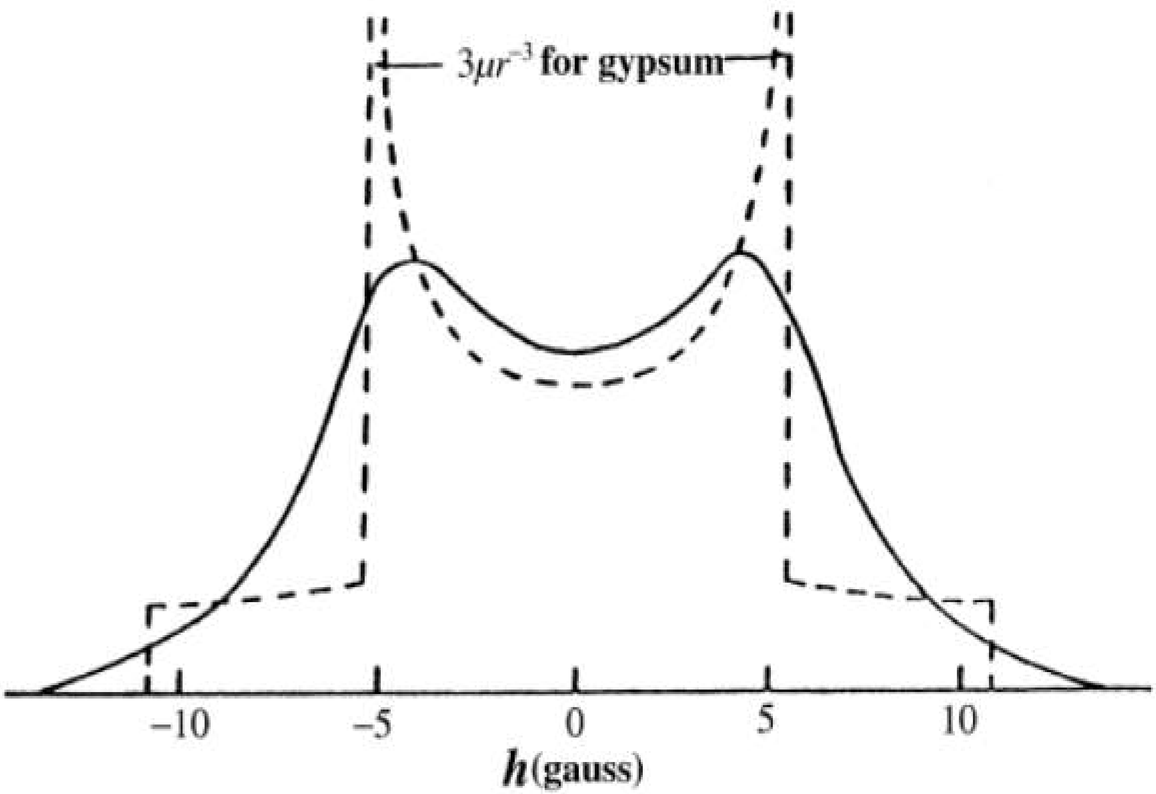
For powder samples the interactions must be summer up over all directions.

Gaussian (solid line) and lorentzian (broken lline) of curves of solids



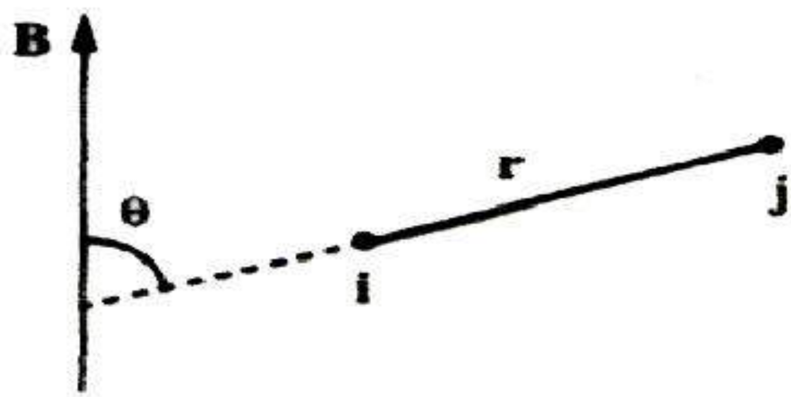
Spectrum for a two spins magnetic configurations

- - - - - theoretical; _____ real



Dipolar Magnetic Interaction between two ^{1}H nuclei

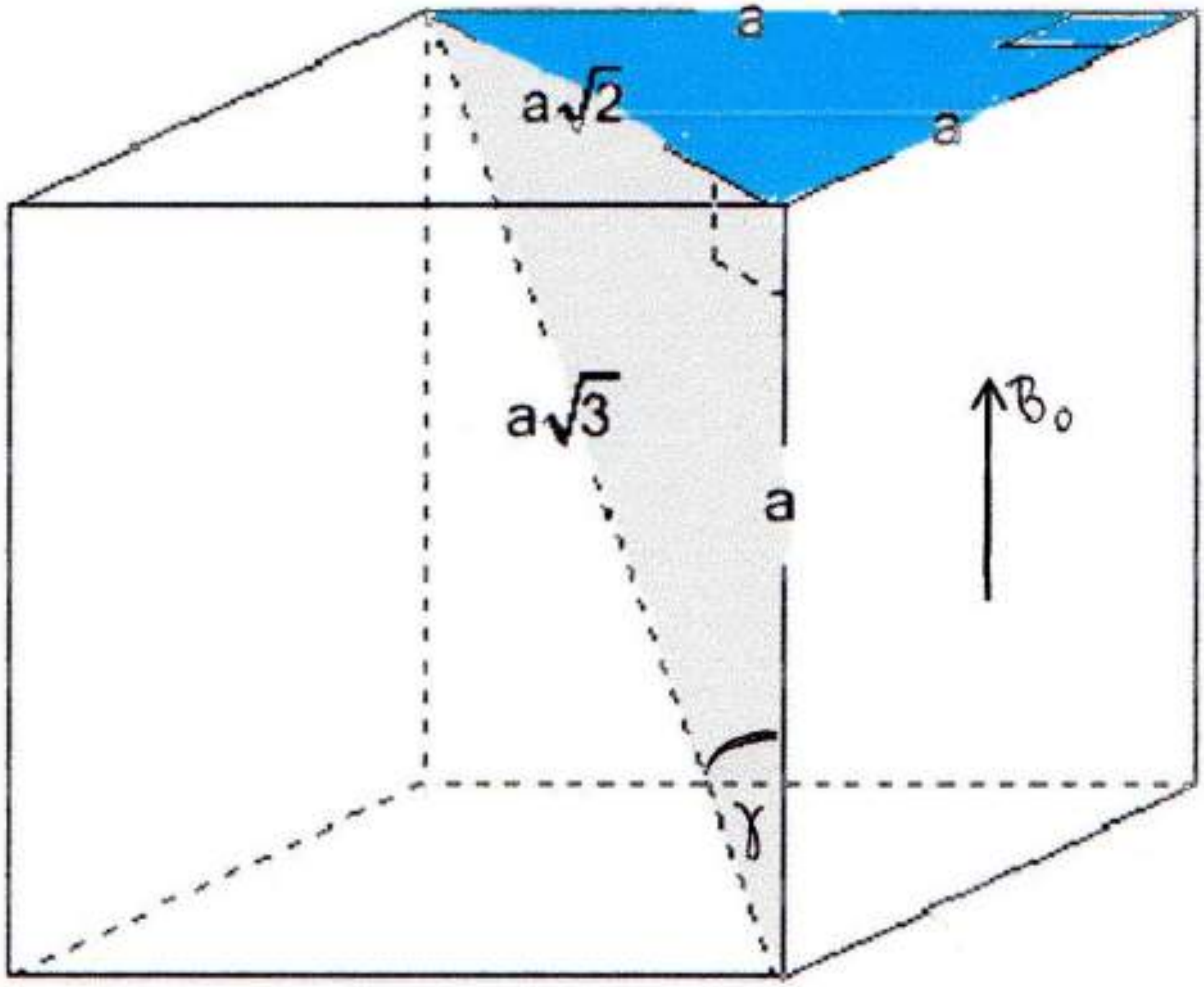
$$DMI = CONSTANT \cdot (1 - 3\cos^2\theta) \cdot r^{-3}$$



For powder samples the interactions must be summer up over all directions.

DMI = 0 if $\cos\theta = 1/\sqrt{3}$

θ = 54° 44’

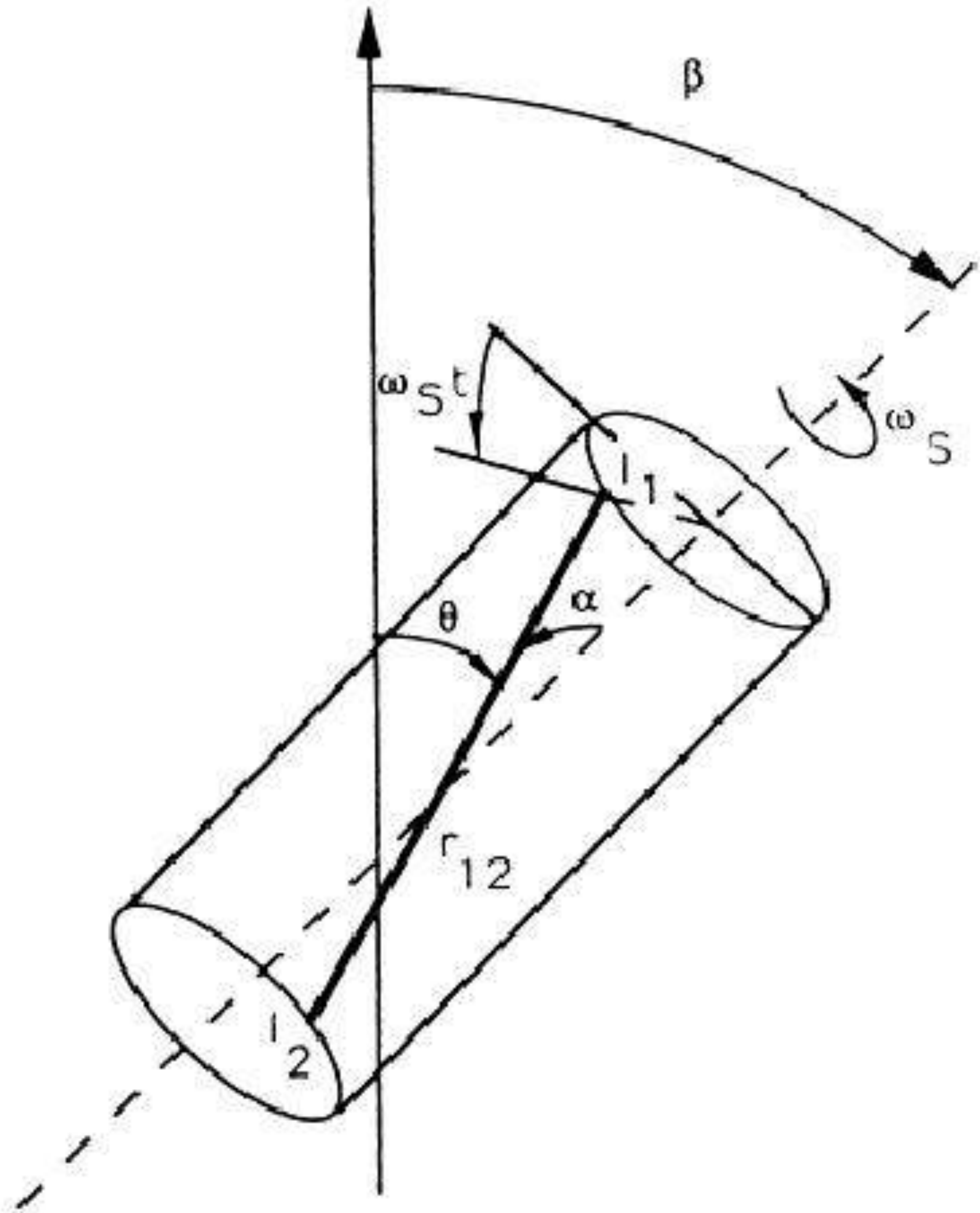


$$a^2+(a\sqrt{3})^2=(a\sqrt{2})^2+2a.(a\sqrt{3})\cos\gamma$$

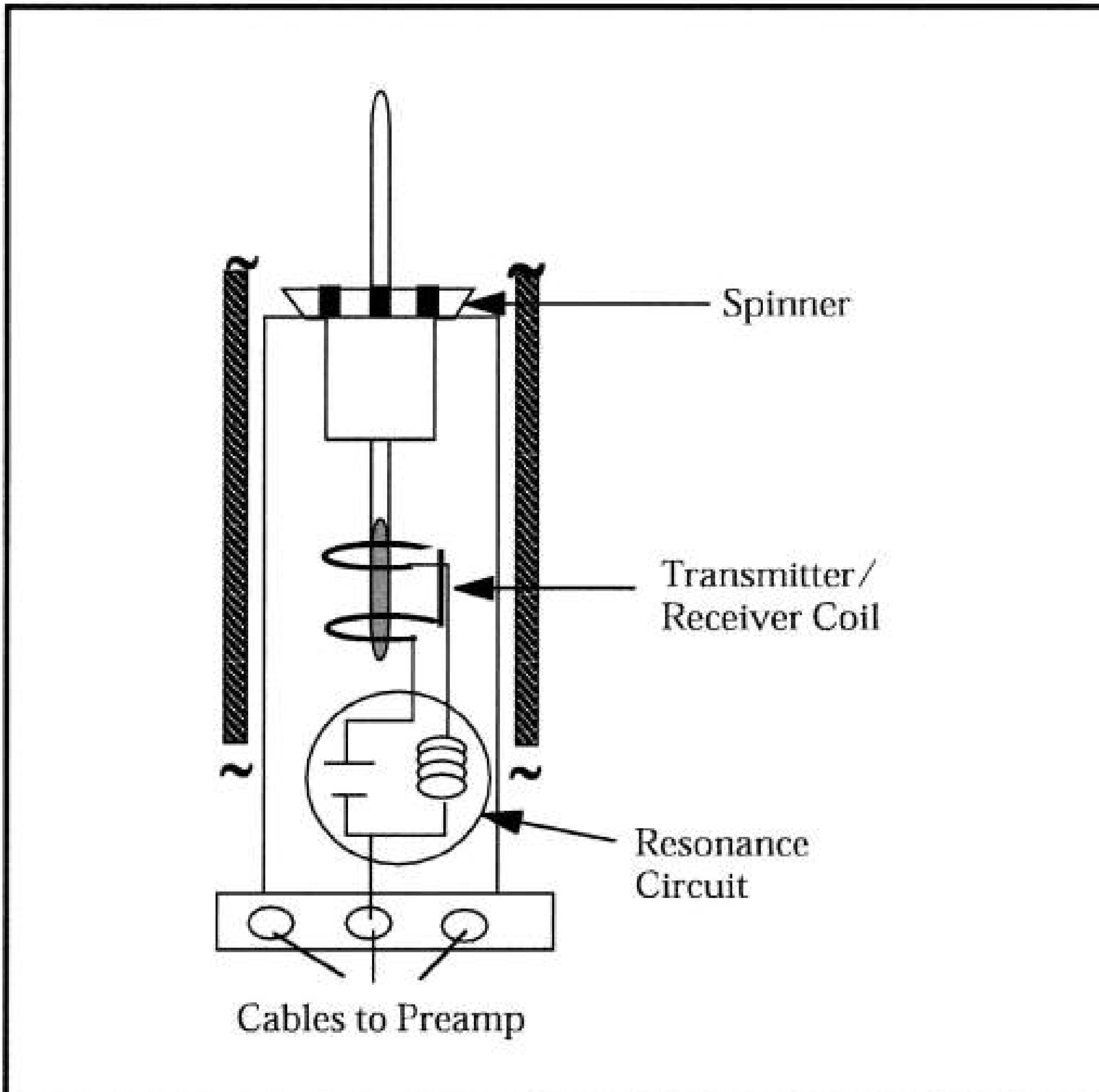
$$\cos\gamma=1/\sqrt{3}$$

$$\gamma\ =54°44'$$

Magic angle spinning (MAS)

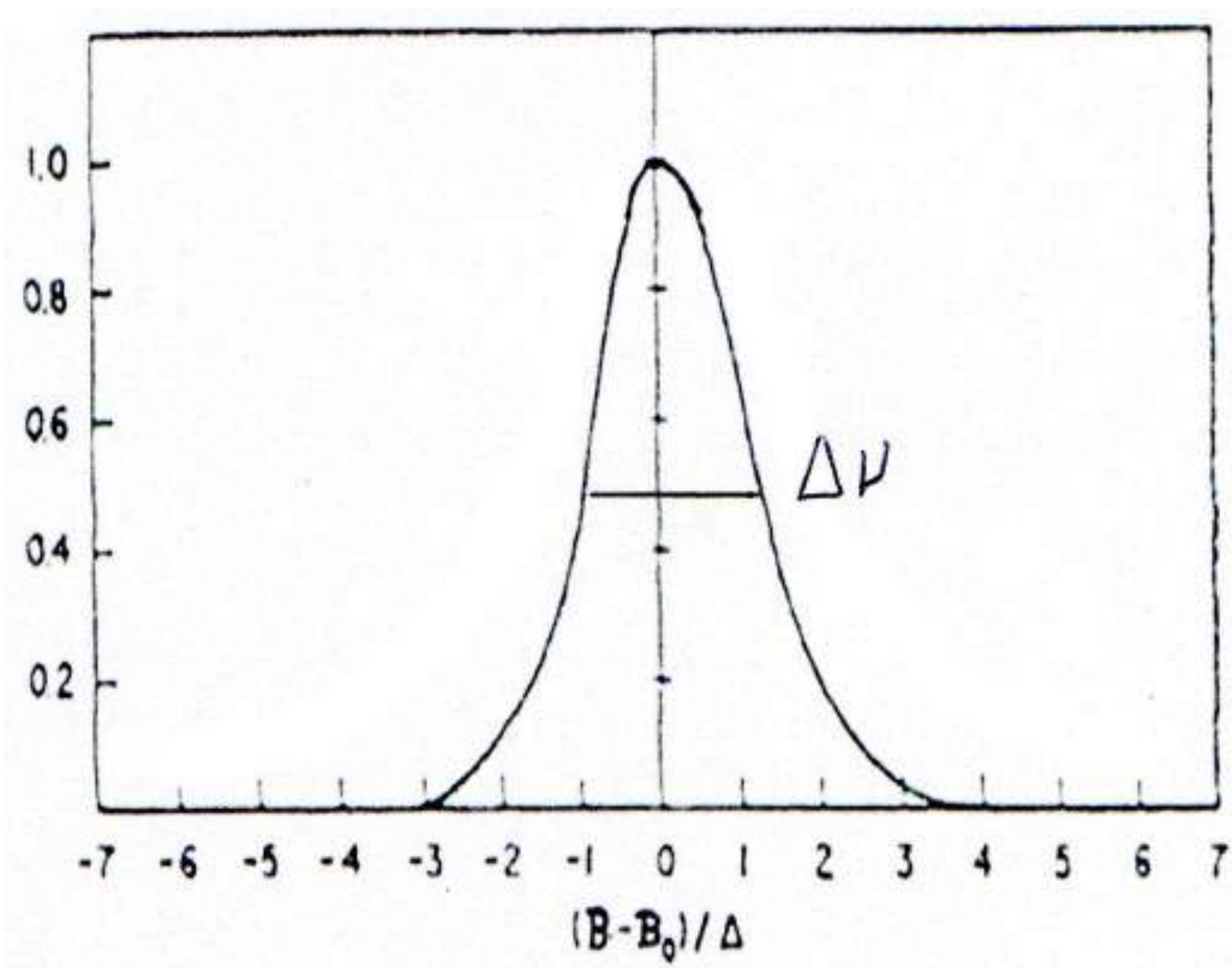


SPINNER

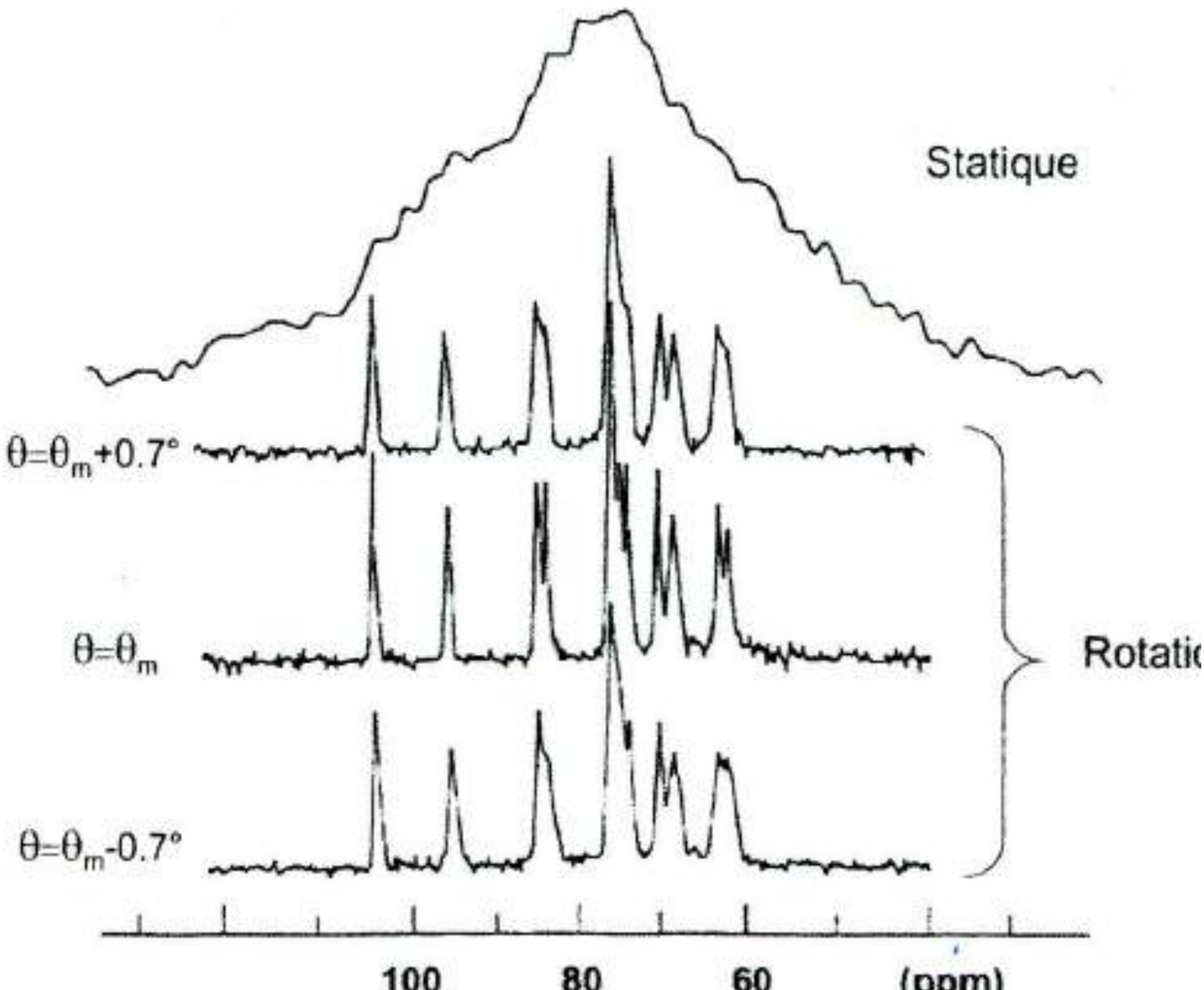


Spinner
Transmitter / Receiver Coil
Resonance Circuit
Cables to Preamp

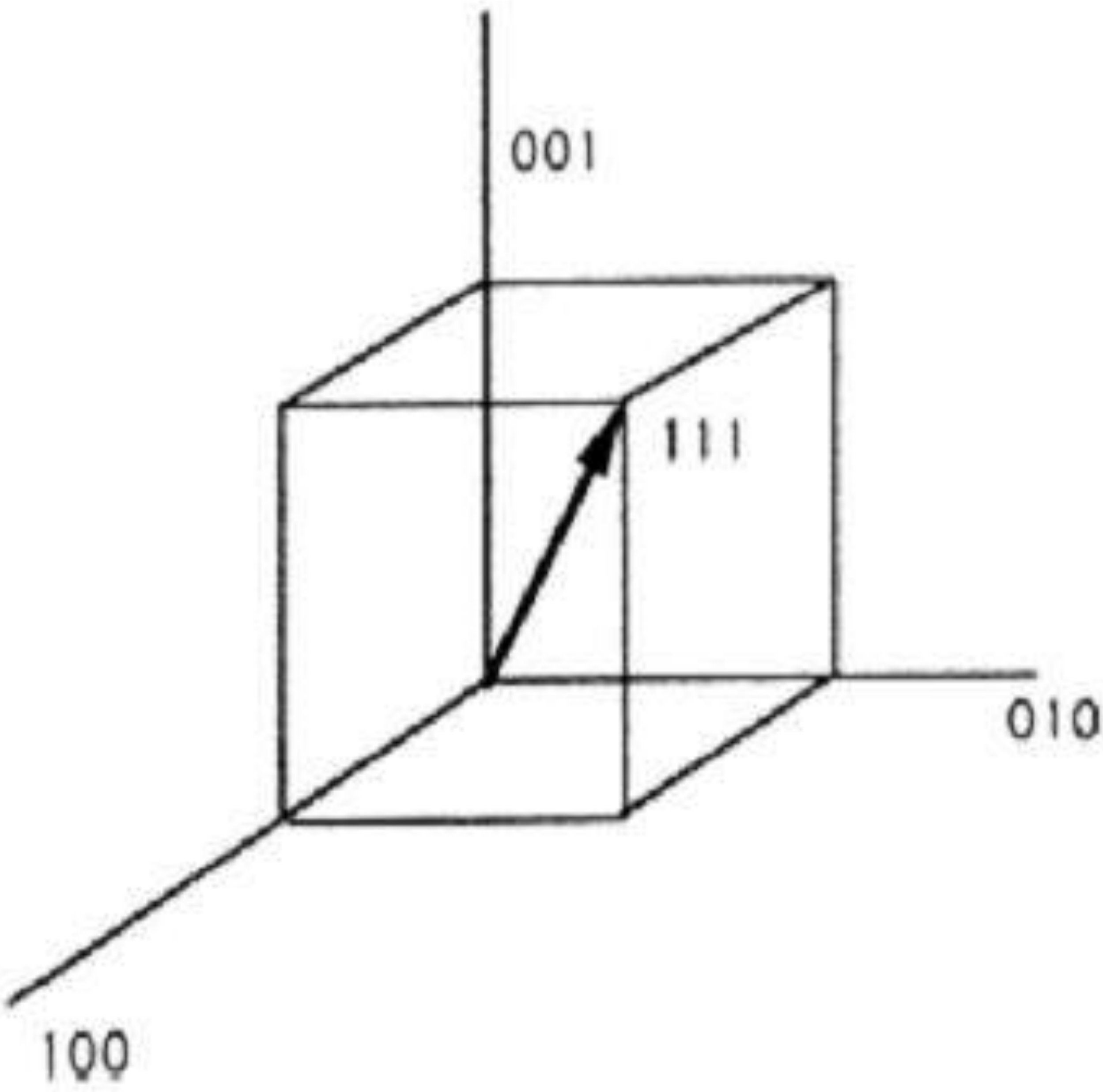
To obtain a HR spectrum, the rotation of the sample, ν_r, must be faster than the line width, $\Delta\nu$, without rotation.



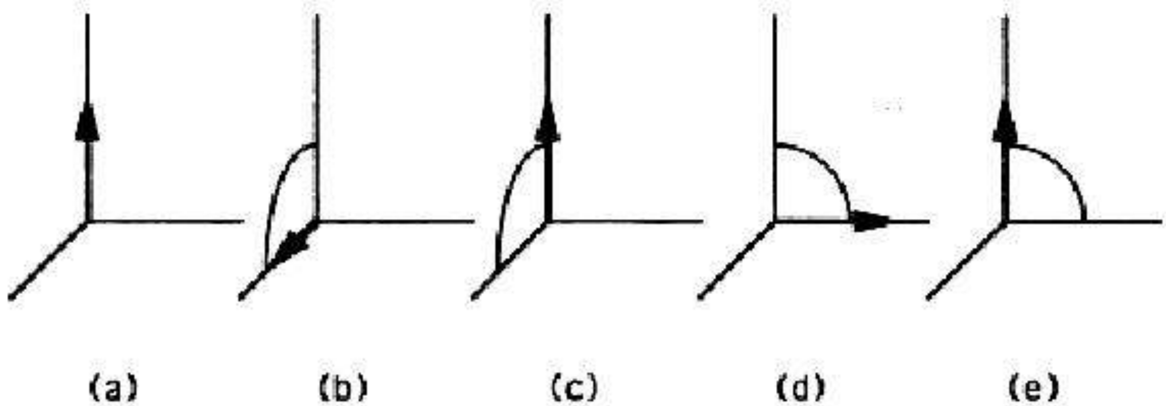
Accuracy of the angle

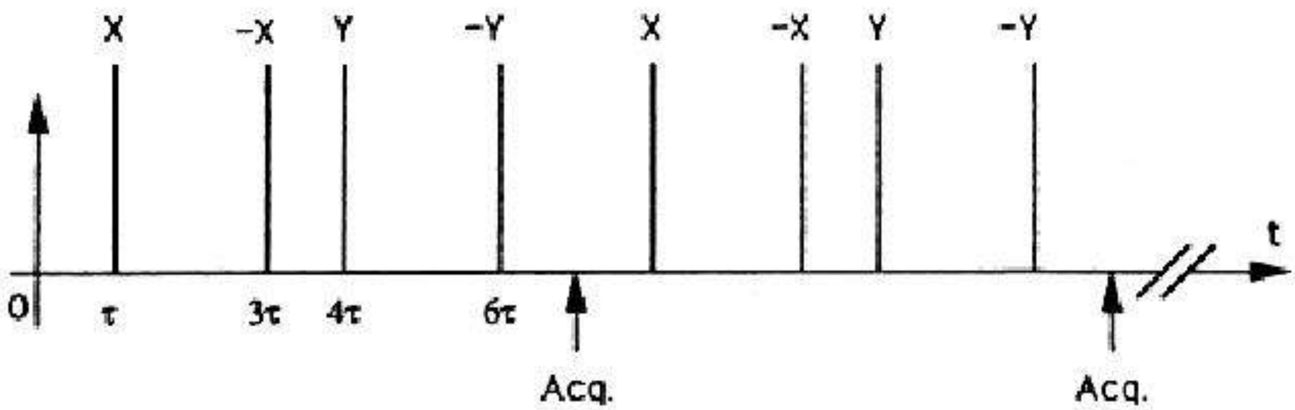


The angle between the diagonal of the cube and the side is = the magic angle



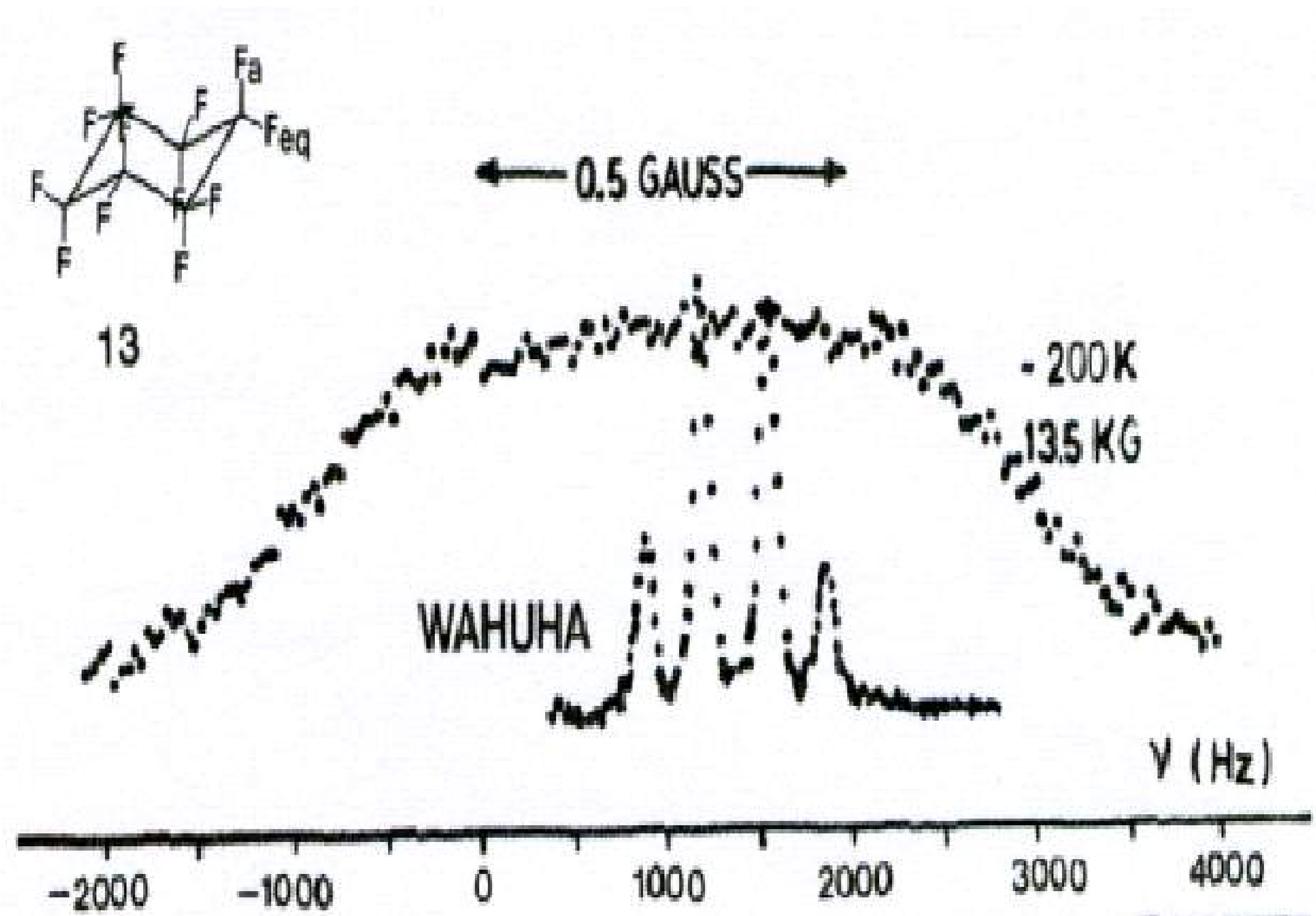
Pulse sequences





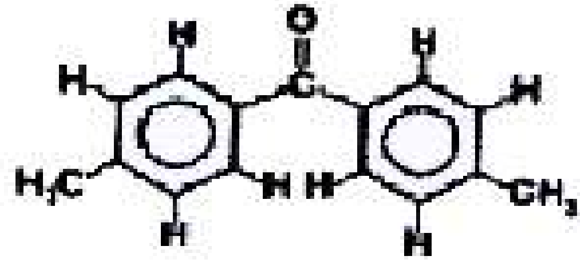
Examples

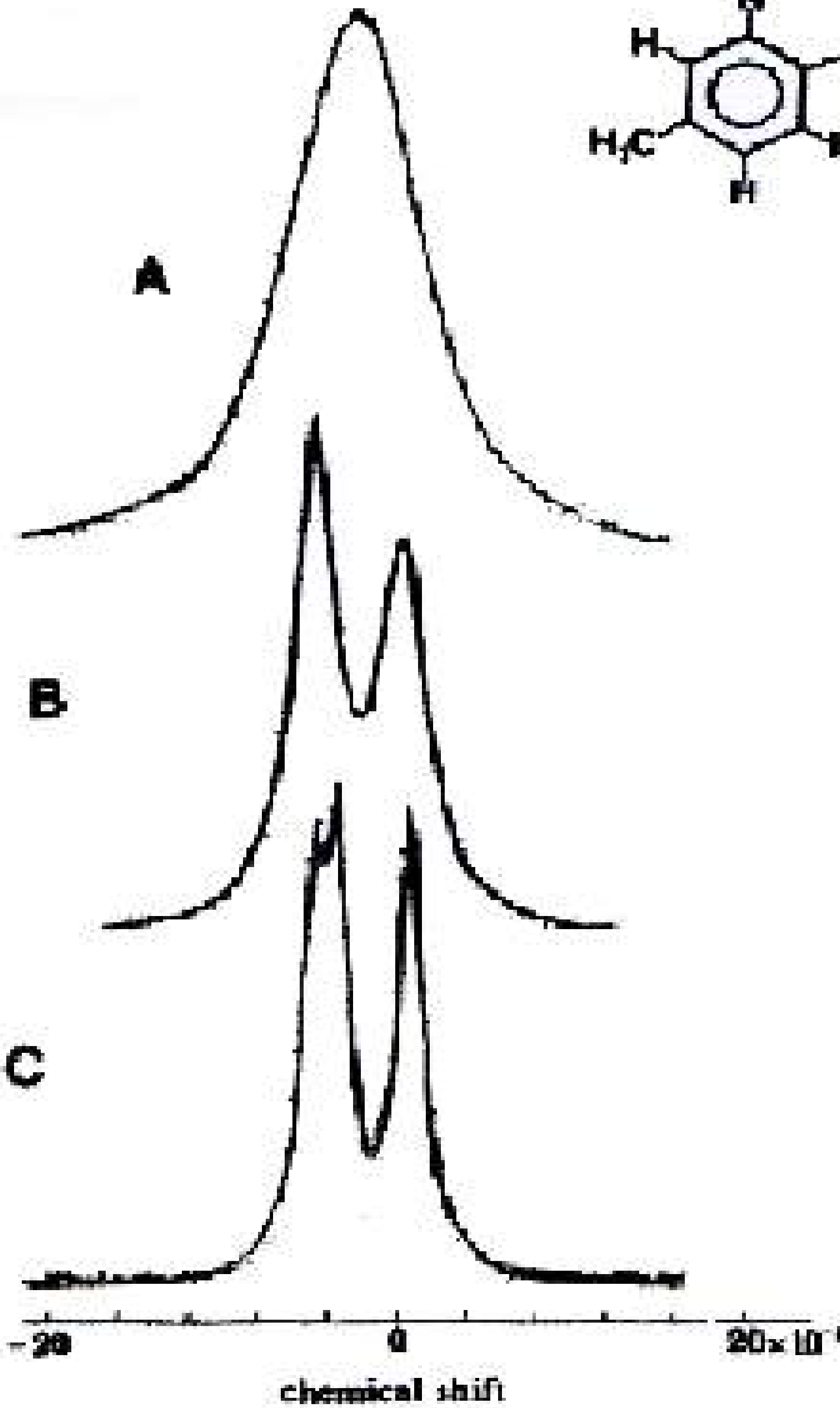
^{19}F NMR. Application of the Wahuha sequence to perfluorocyclohexane C_6F_{12} at 200 K



4.4’-dimethylbenzophenol

A: MREV-8; B: MREV-8 + MAS; C: BR24 + MAS

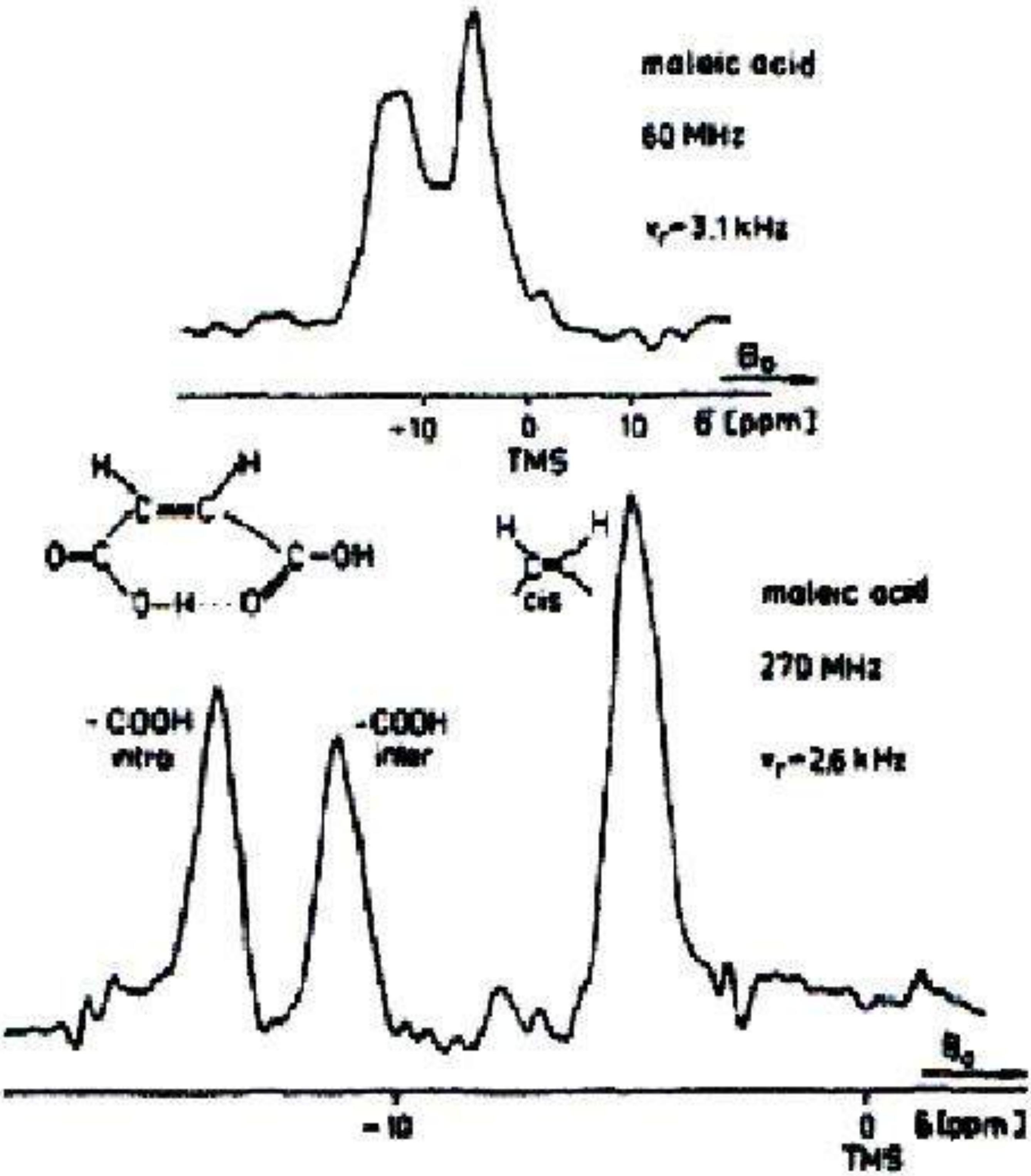




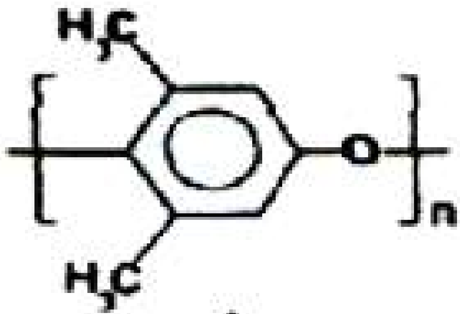
Maleic acid at 60 and 270 MHz

Influence of hydrogen bond

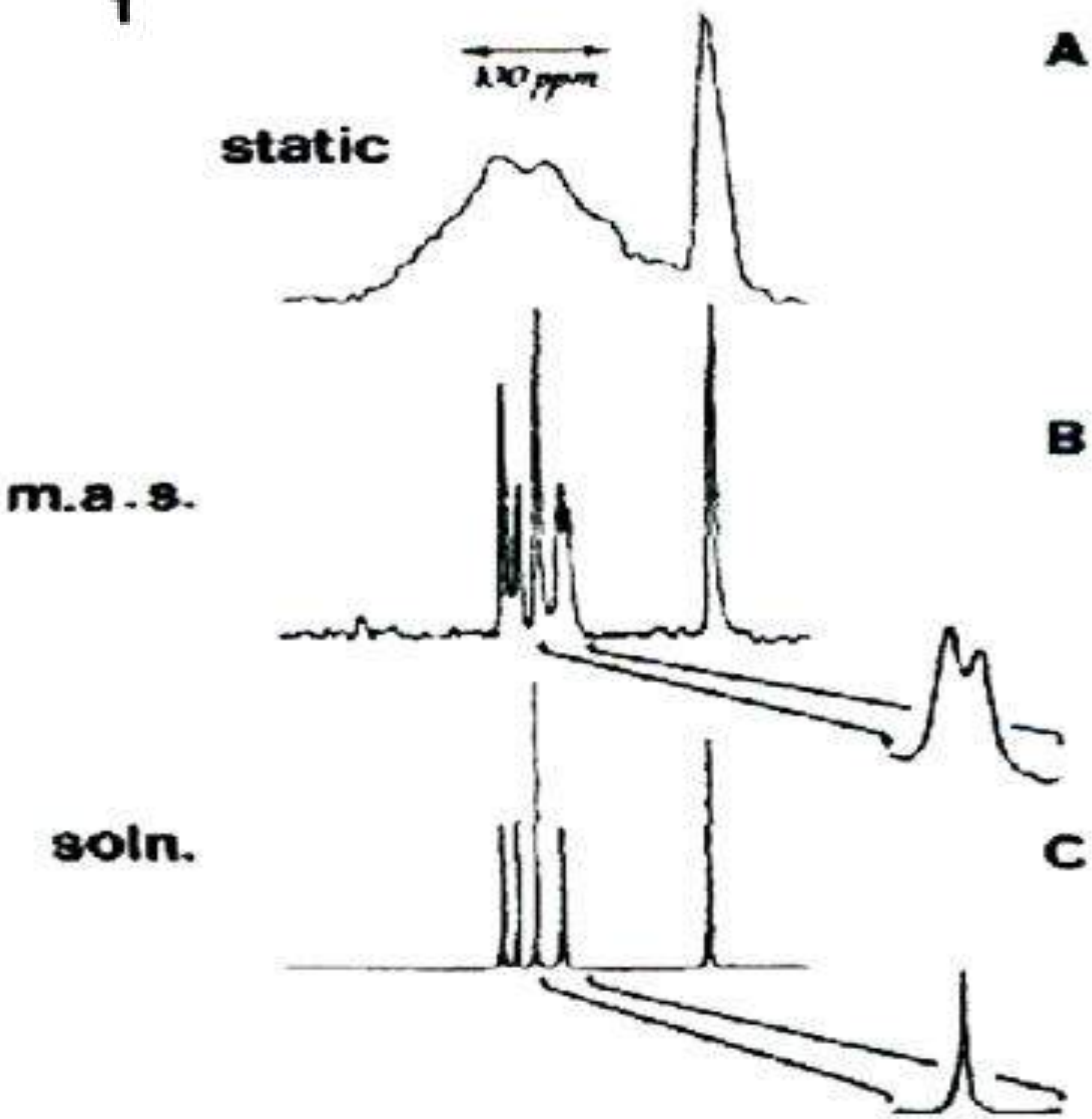
$HO_2CHC{=}CHCO_2H$



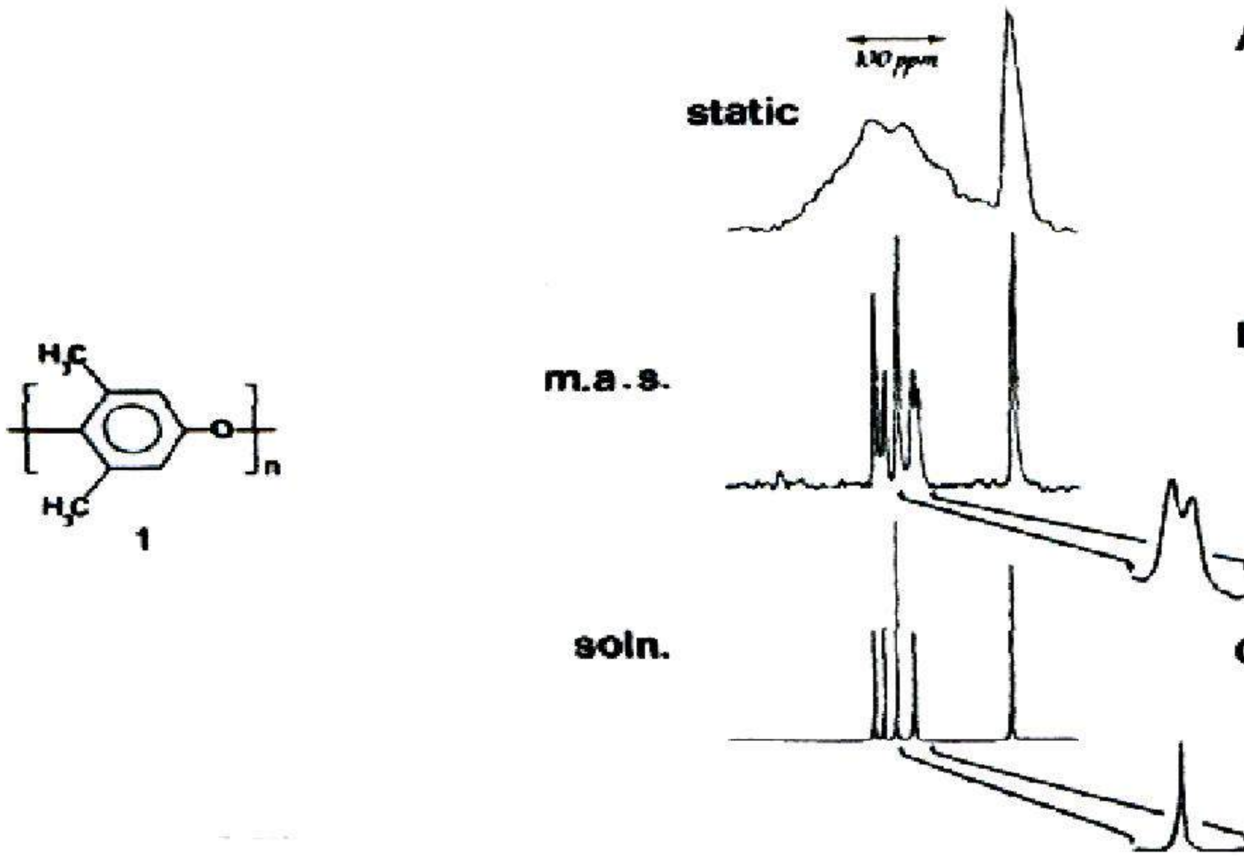
Poly phenylene oxide

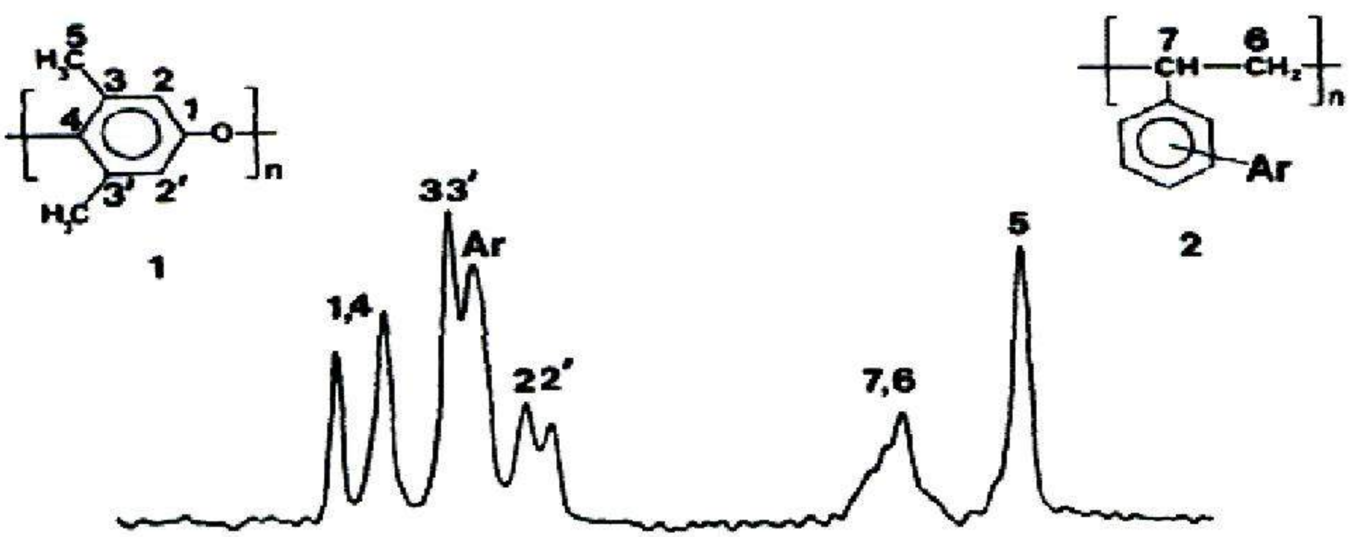


1

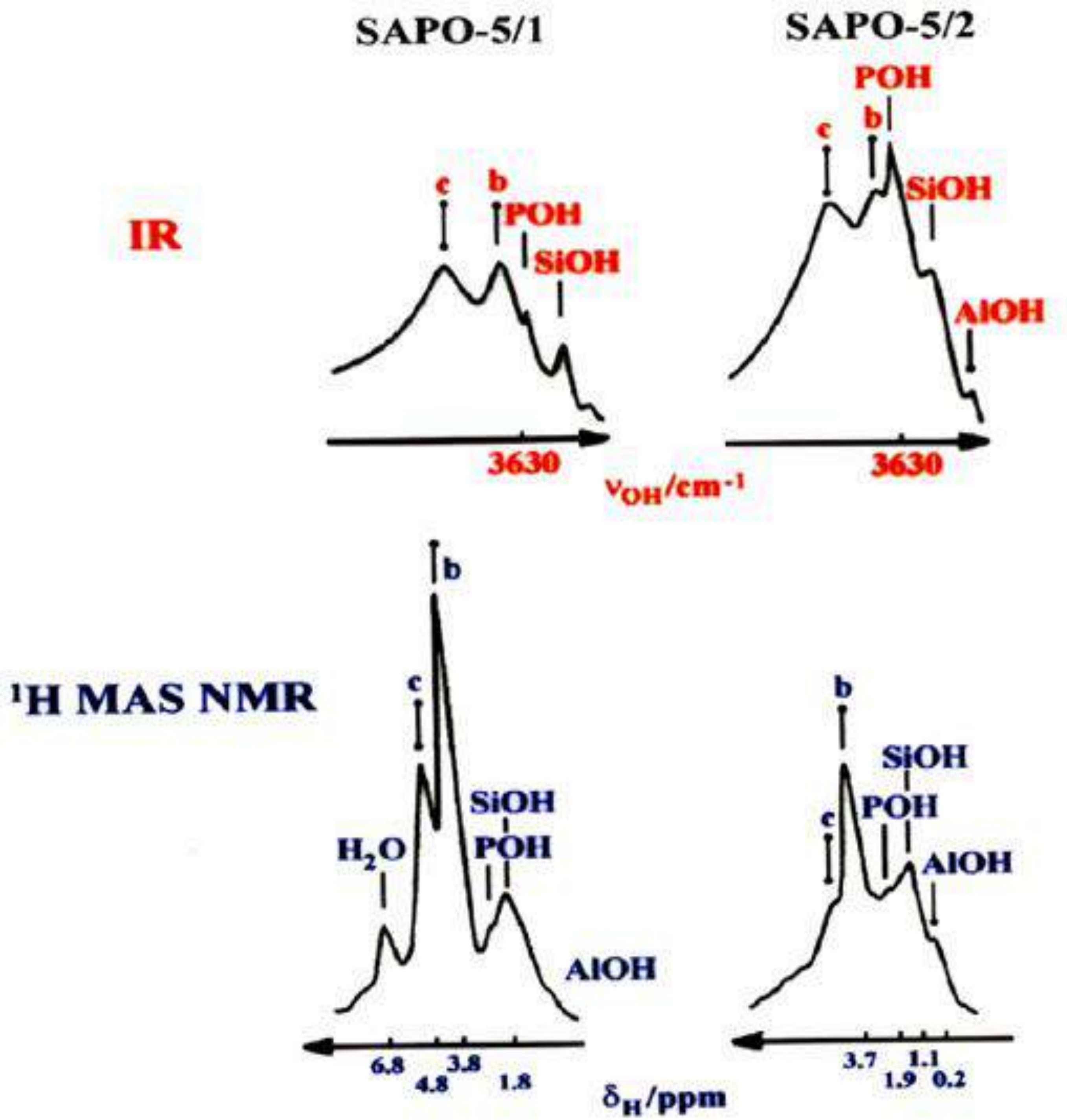


Poly phenylene oxide and blend with polystyrene

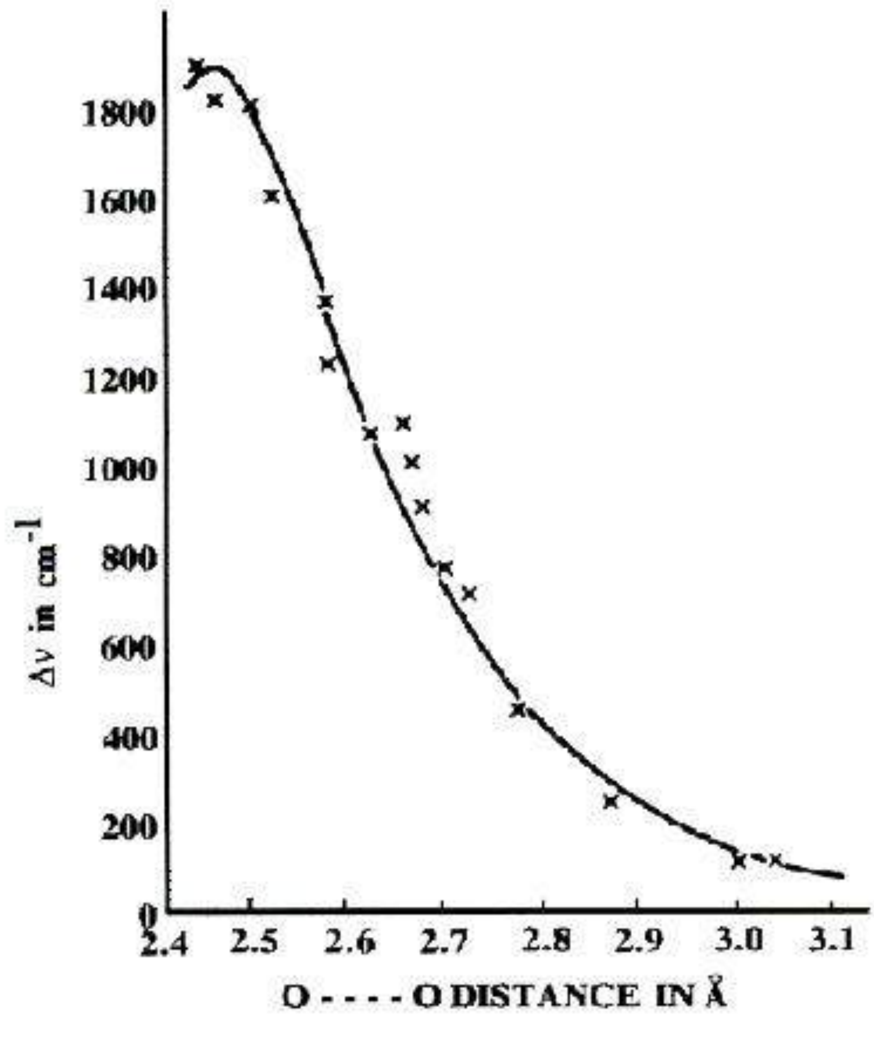




OH groups in zeolites
Hydrogen bonds: δ (OH) and ν (OH)



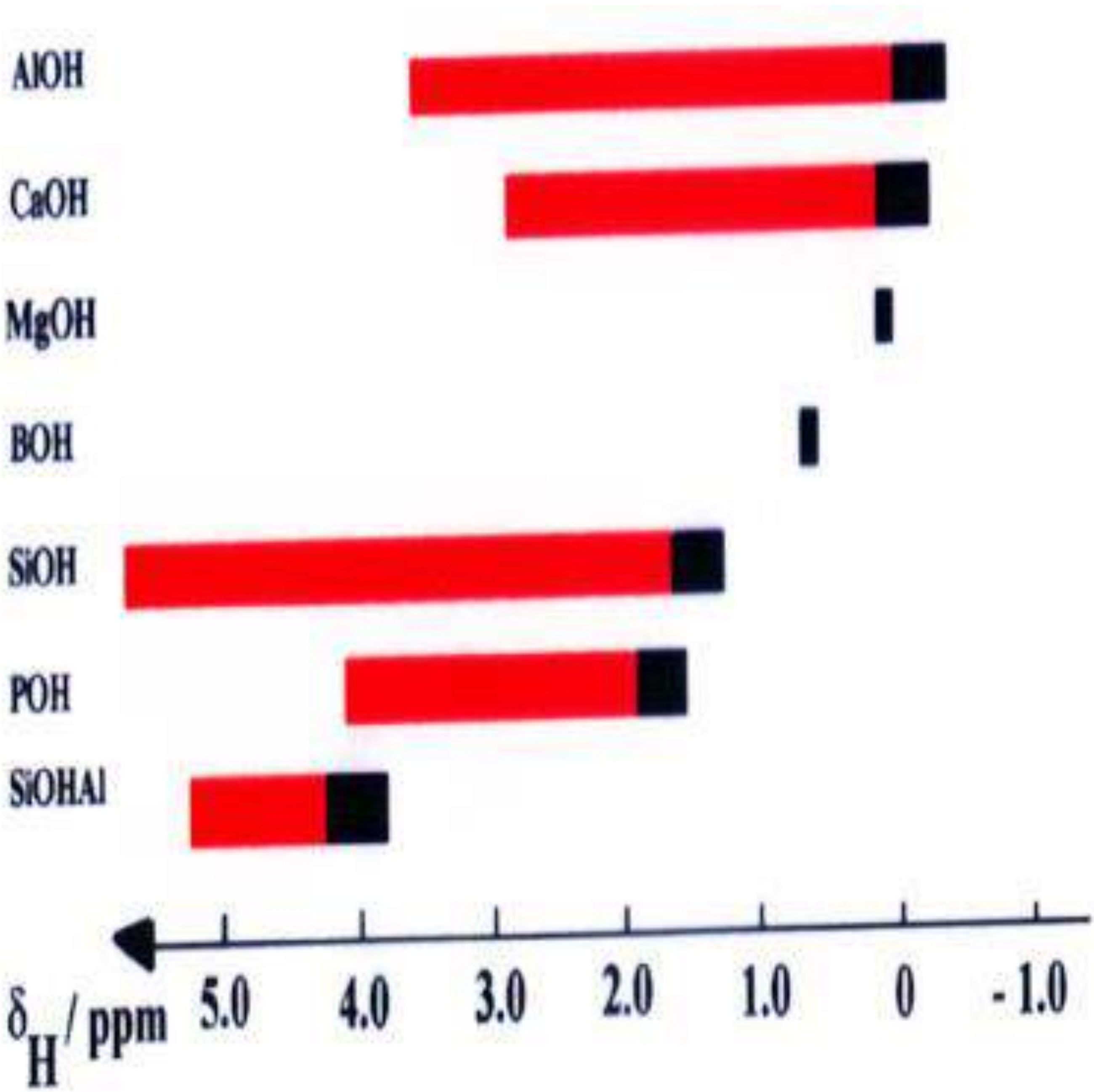
IR: $\Delta\nu$ in cm^{-1} against hydrogen bond



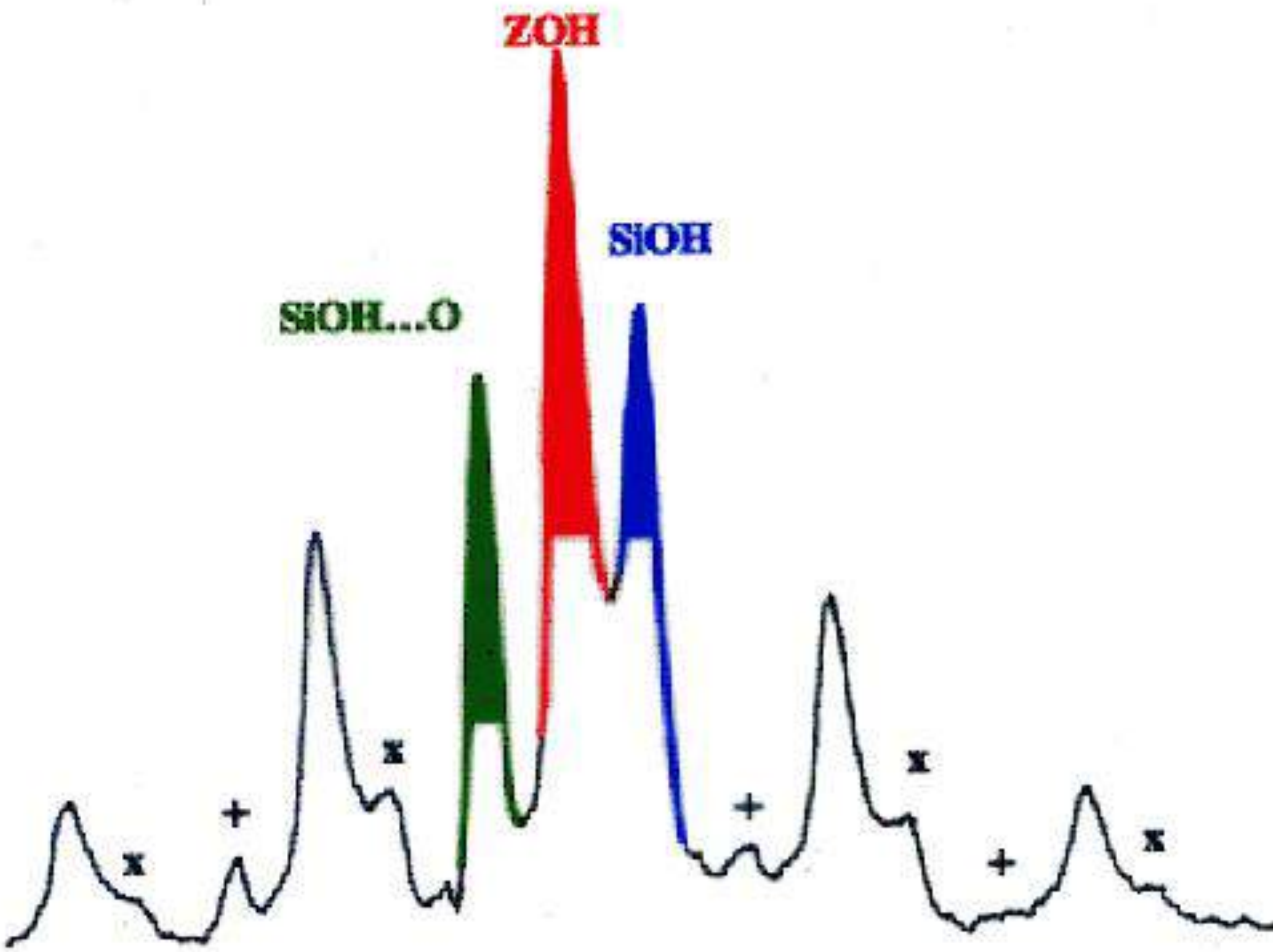
The relation between OH frequency shift and O - - - - O distance during hydrogen-bonding interaction

Influence of hydrogen bonds

Experimental chemical shift δ_H of isolated (black) and interacting (red area) groups in zeolites



Anhydrous H-mordenite



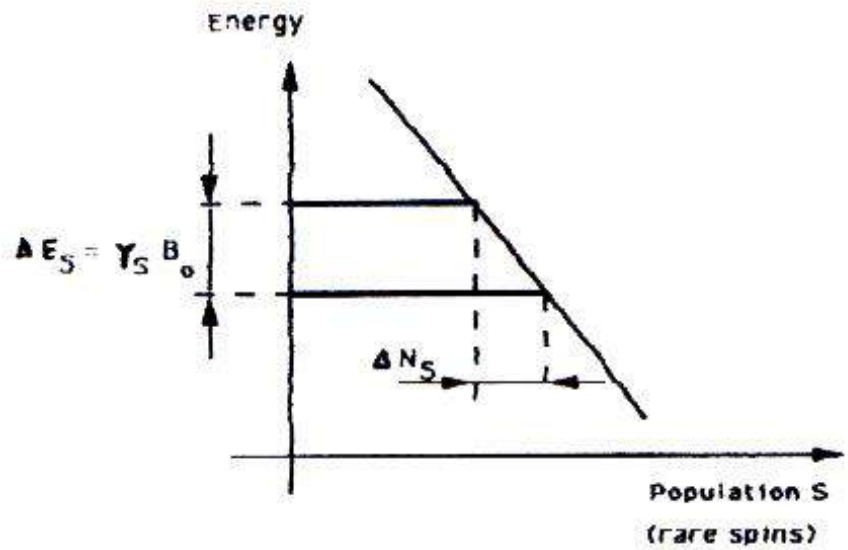
Spins with low γ

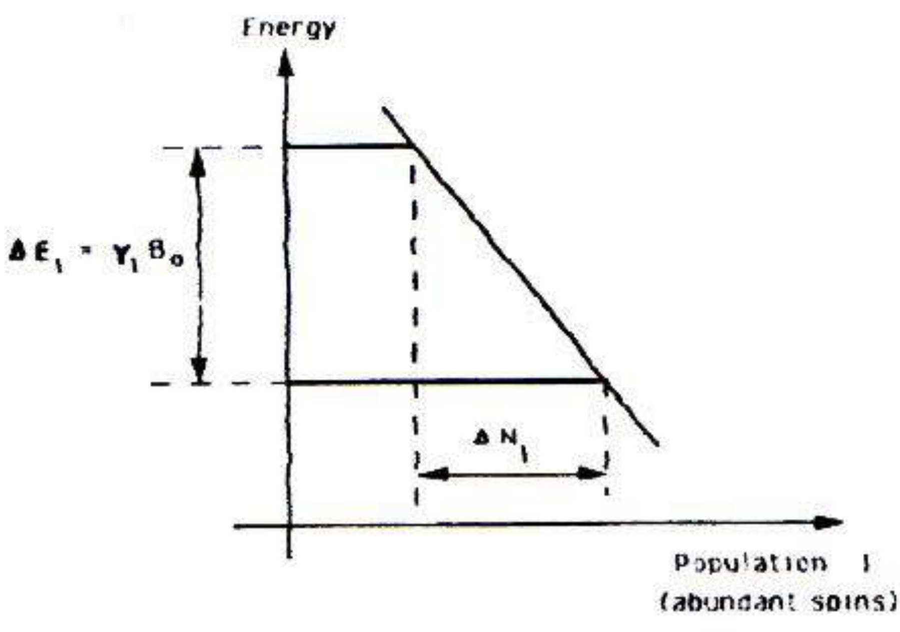
Polarization transfer from abundant spins I (high γ_I) to the low concentration spins S (low γ_S)

-:-:-:-:-:-:-

For spins ½,
magnetization : $M = (N/4k_BT)\,\gamma\hbar B_0$

Signal/ noise ratio: $\propto (I+1)\,N\gamma^{5/2}$

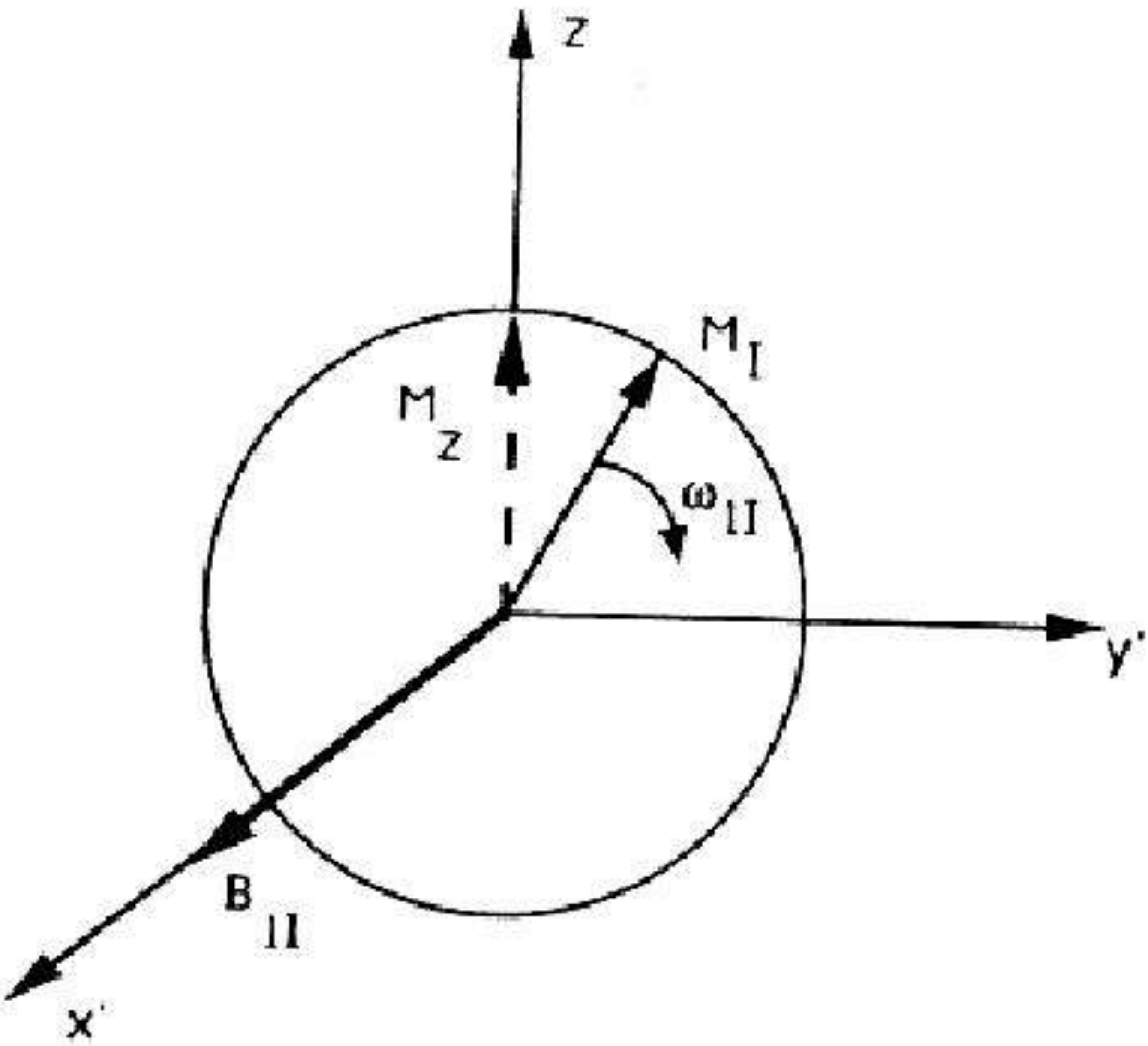


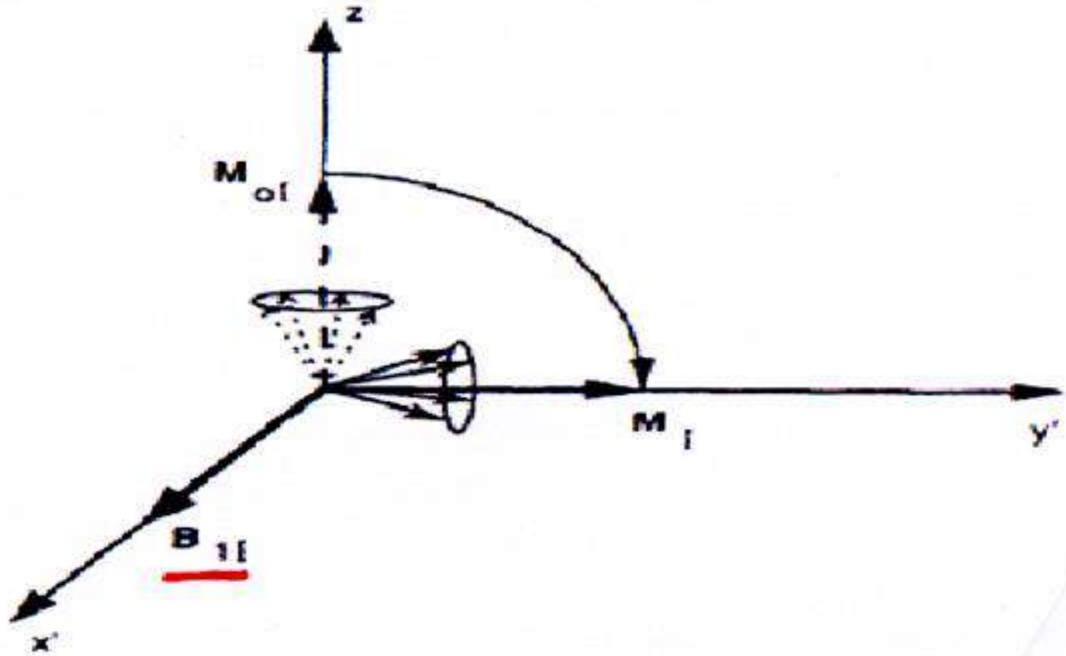


For the same B_0, ΔN_I and ΔN_S are proportional to γ_I and γ_S.

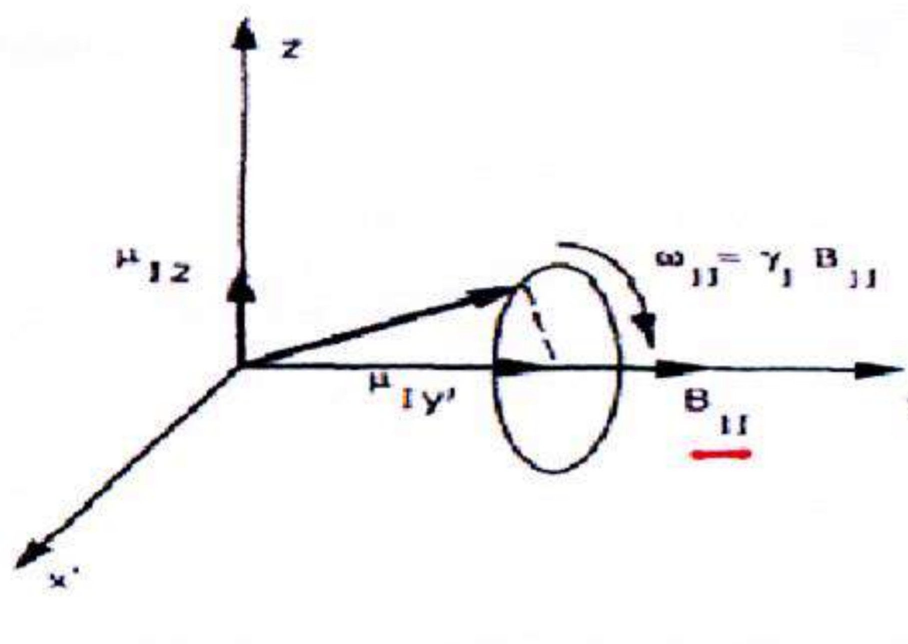
$\Delta N_I/\Delta N_S = \gamma_I/\gamma_S$

In the rotating framework
B_{1I} along x' →rotation of M_I in the plane zoy'



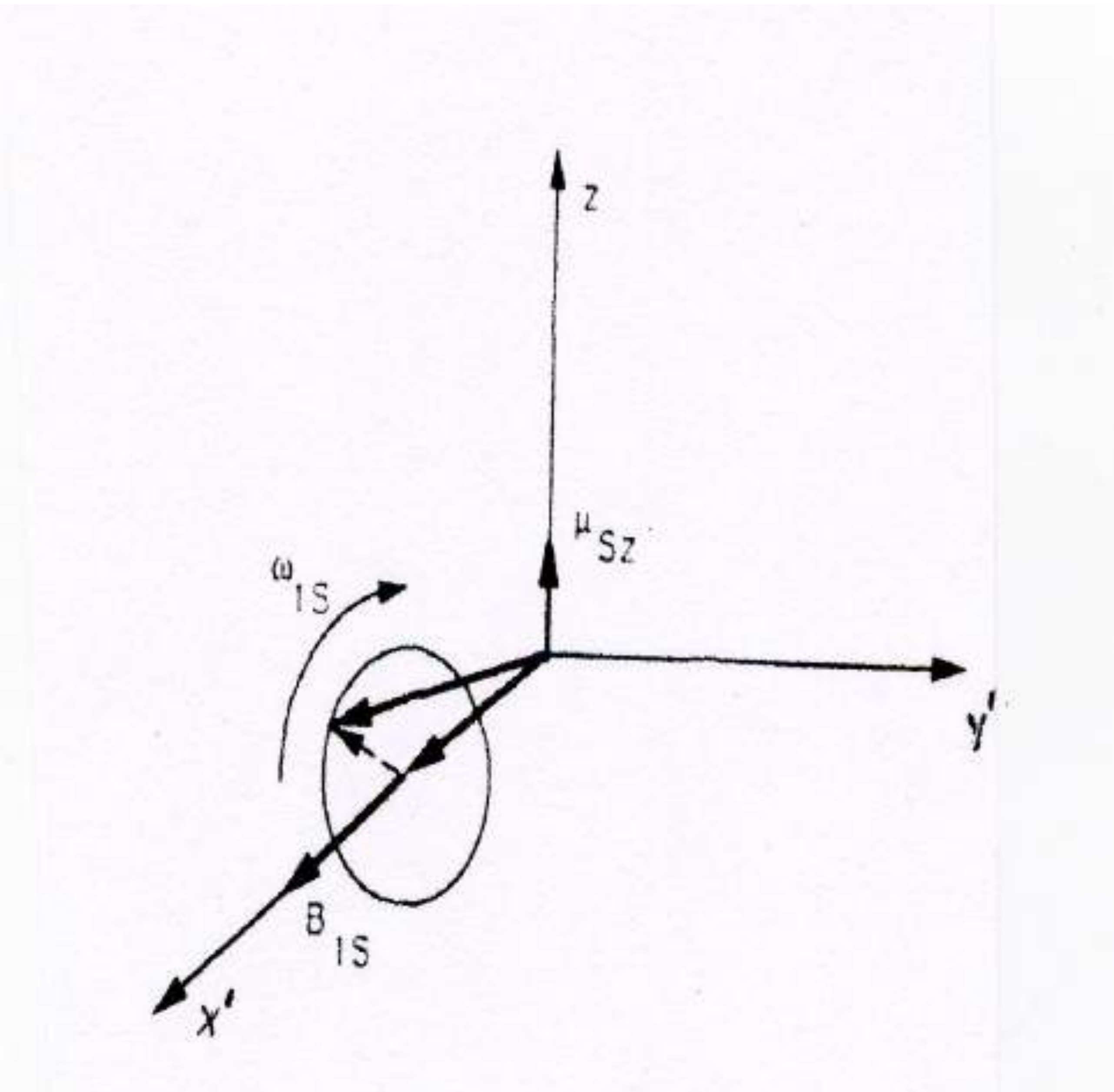


After a $\pi/2$ pulse along x' at frequency ω_{0I} the abundant spin magnetization M_I lies along y'.



Immediately after a second $\pi/2$ pulse along y' the I spins rotate around y'. The resultant magnetization M_I is "spin-locked" on the axis.

Due to another rf field $B_{1,S}$ along X', individual magnetic moment μ_S turns around X' with a frequency $\omega_{1,S}=\gamma_S B_{1,S}$



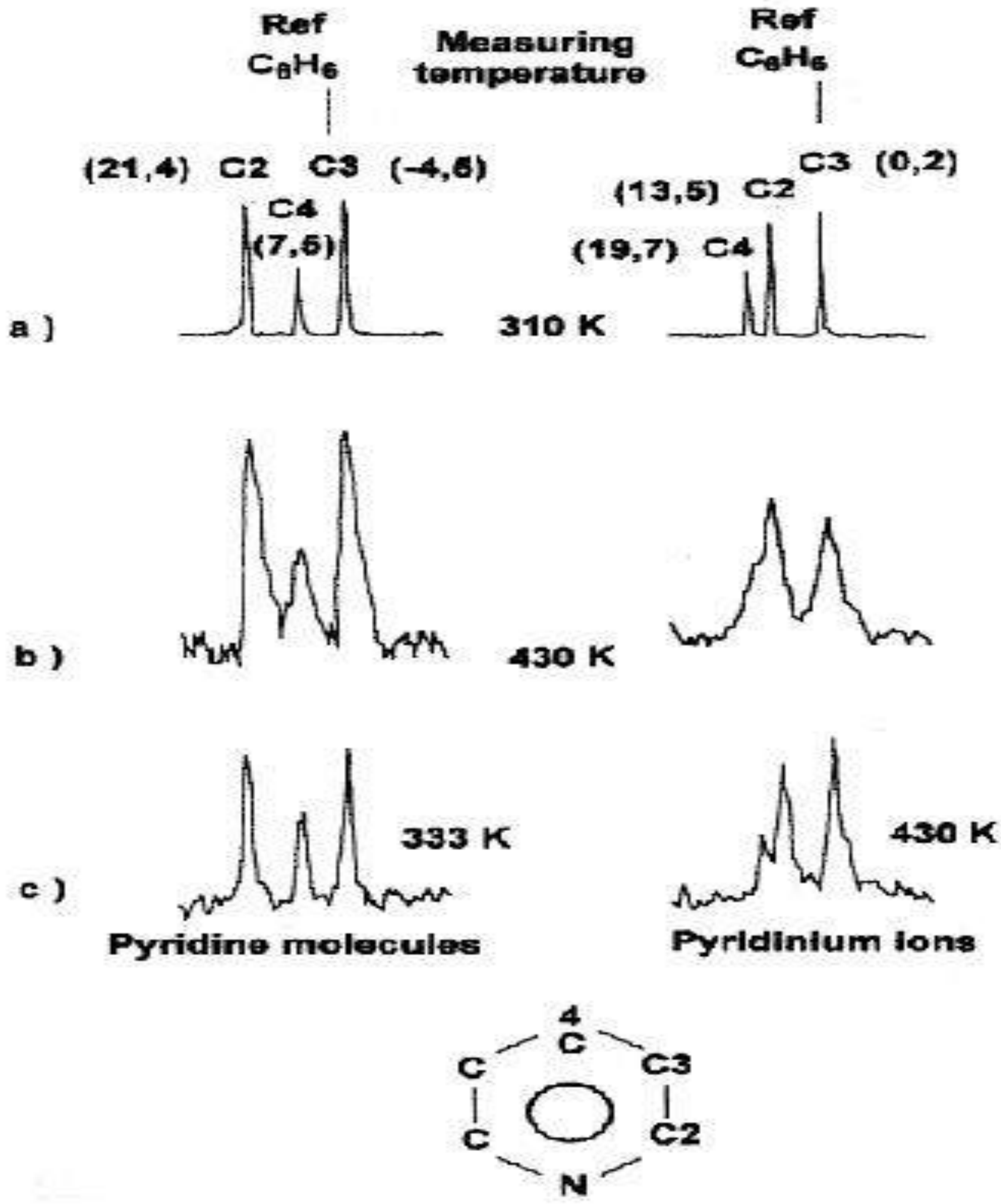
Hartmann-Hahn condition

I and S have the oscillating components which may have the same time dependence if

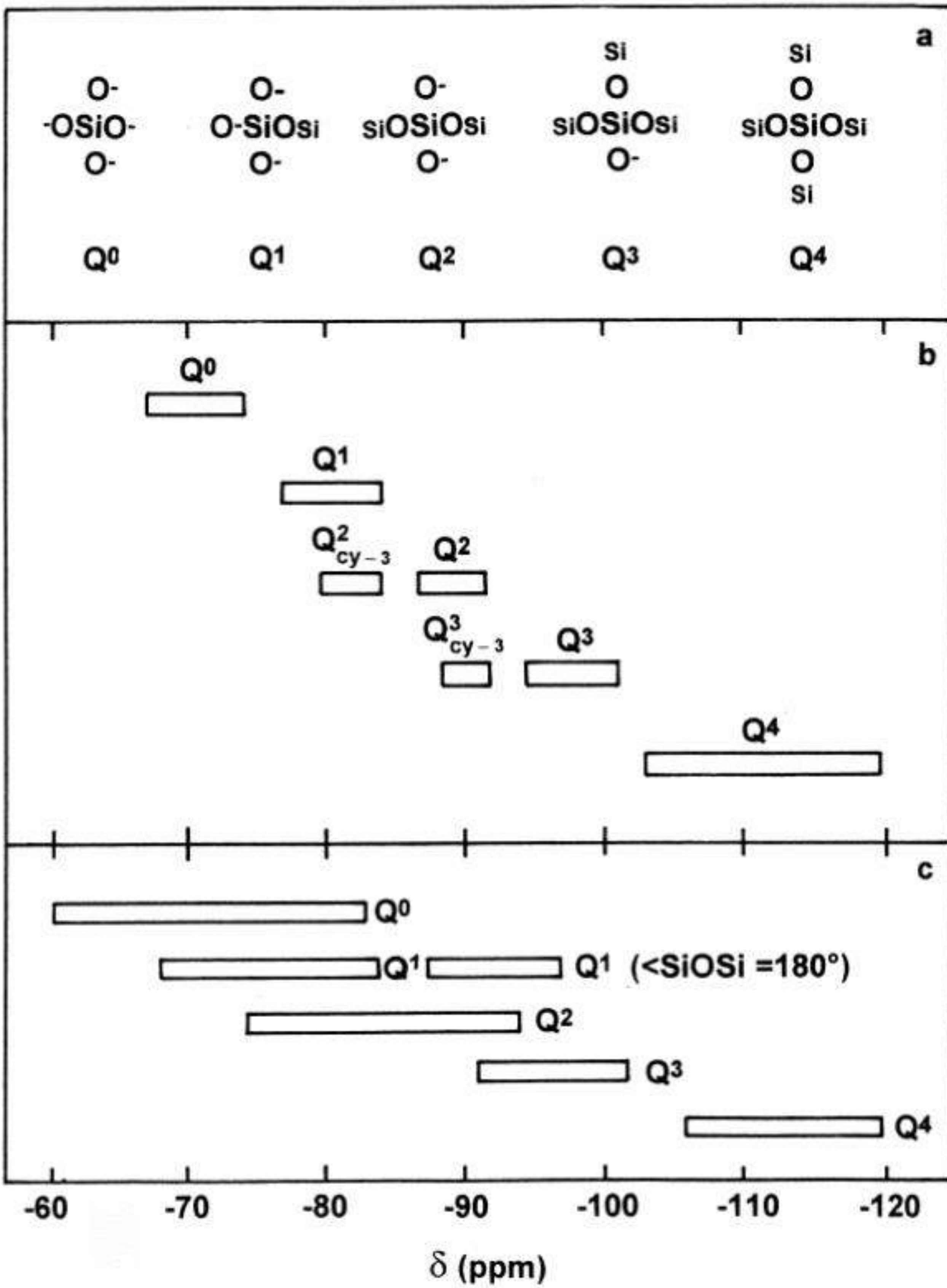
$$\omega_{1I} = \omega_{1S}$$

$$\gamma_S B_{1S} = \gamma_I B_{1I}$$

^{13}C NMR of Pyridine
a: liquid (left)and in H_2SO_4(right)
b and c:adsorbed on NaY(left) and HY(right)

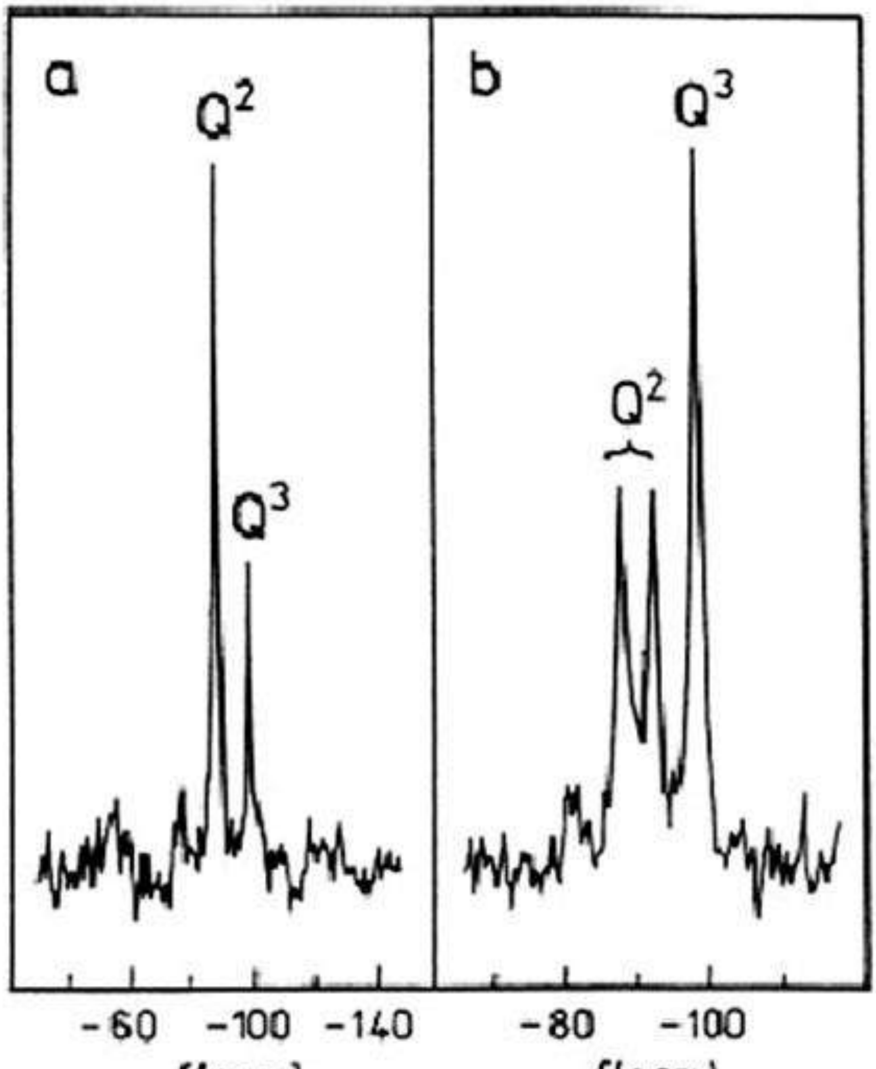


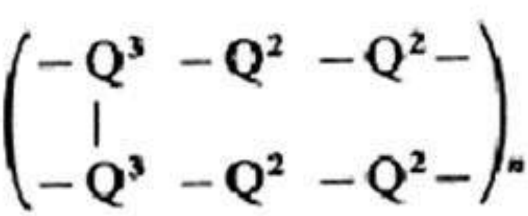
$\delta(^{29}Si)$ for silicates Q_n



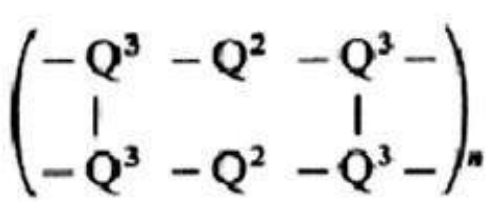
δ (Si)

Xonolite Tremolite

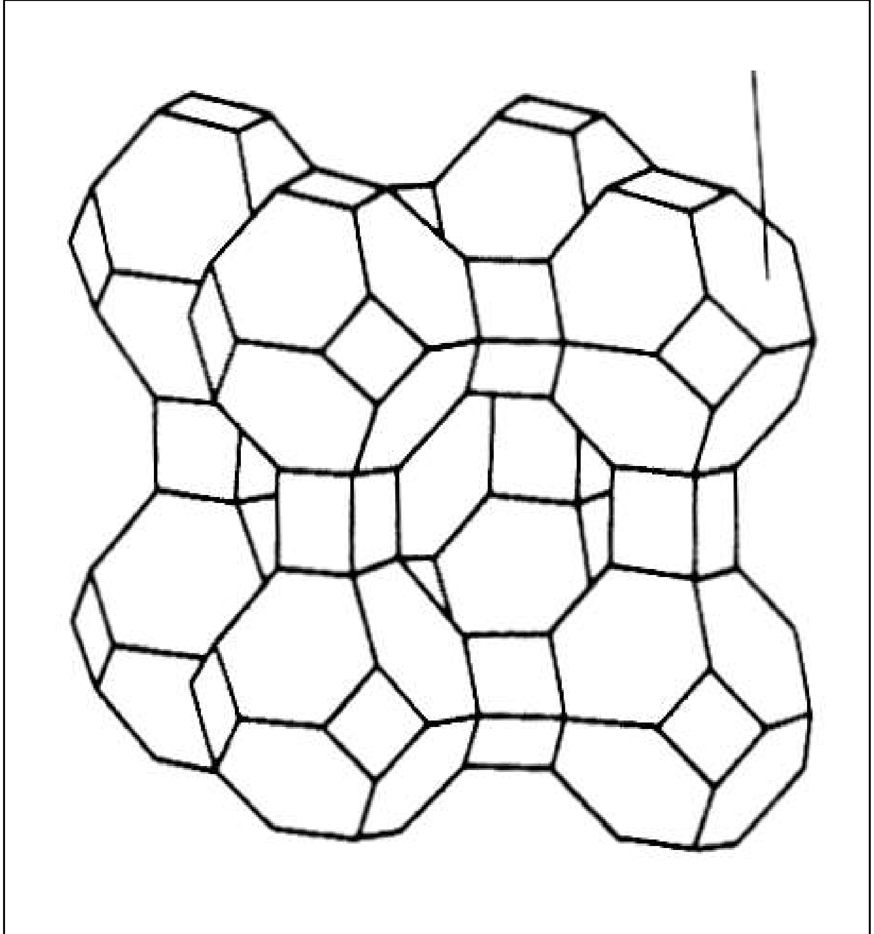




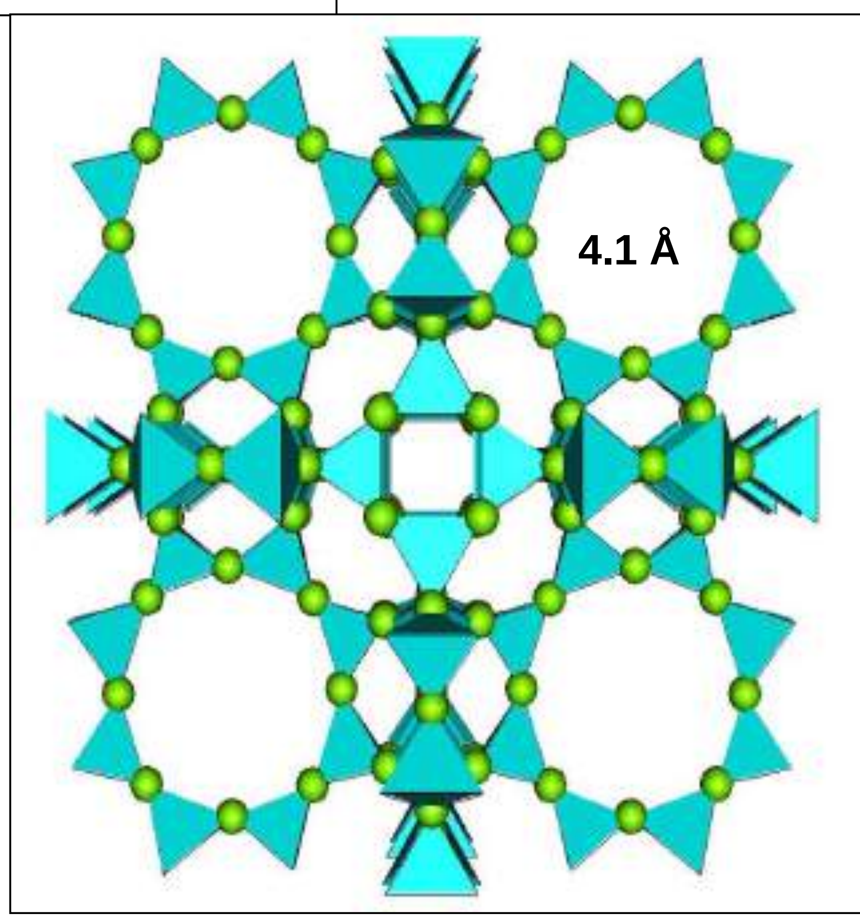
Xonolite $Ca_6Si_6O_{17}(OH)_2$

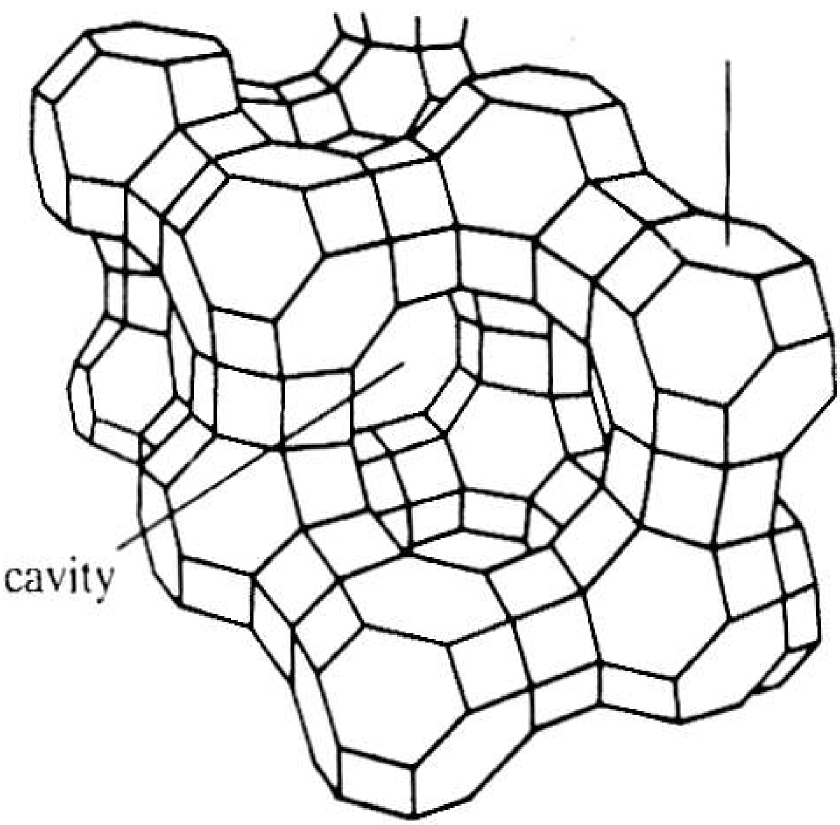


tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

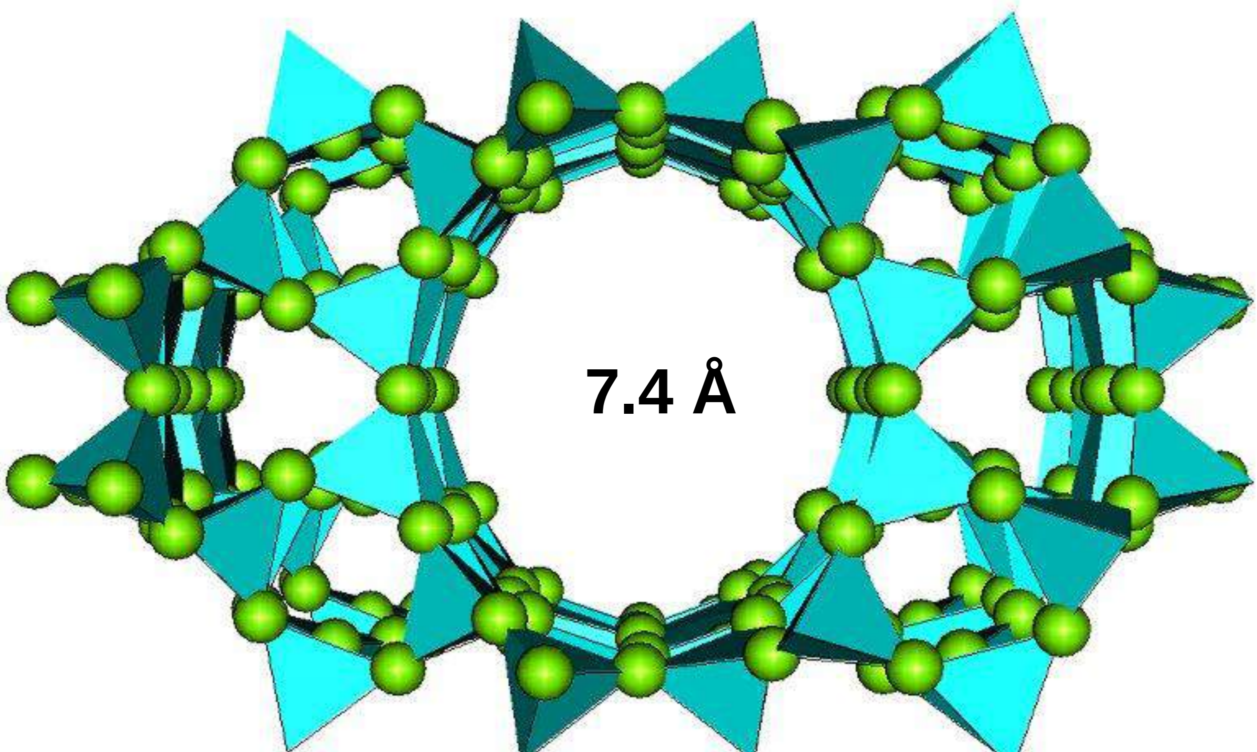


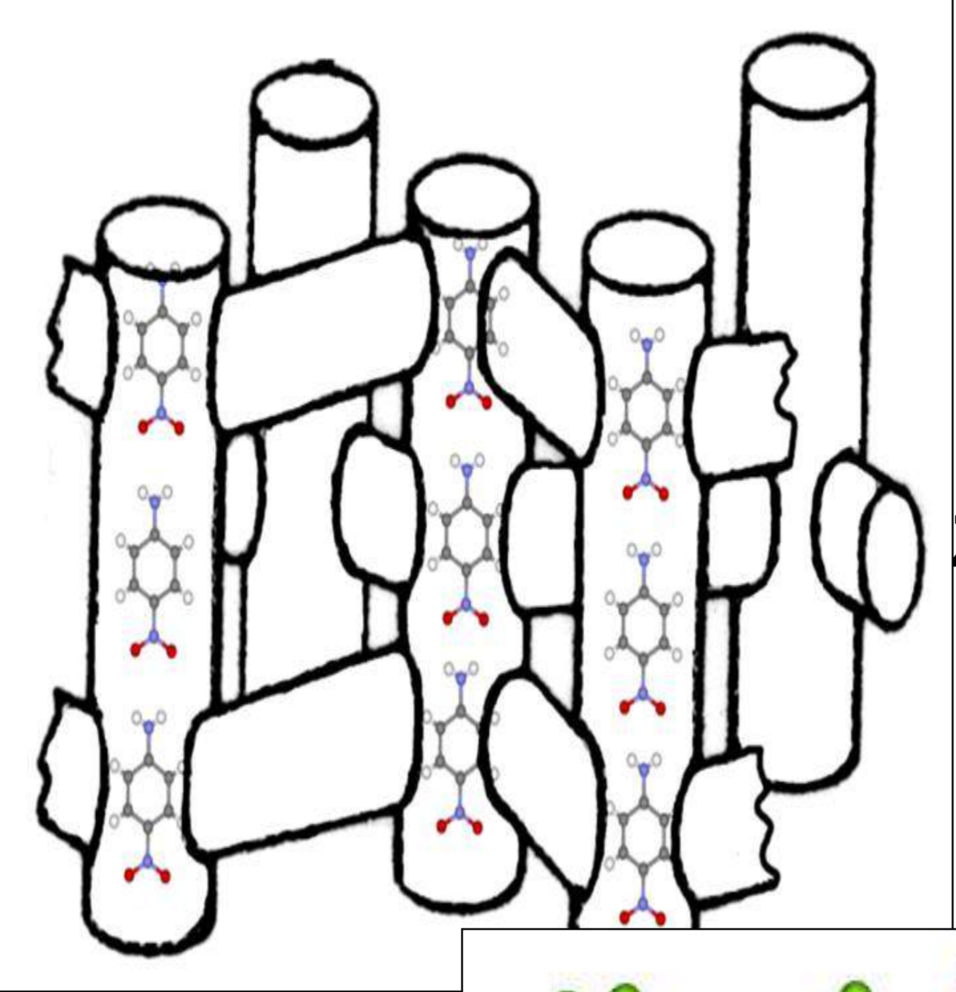
Zeolite A



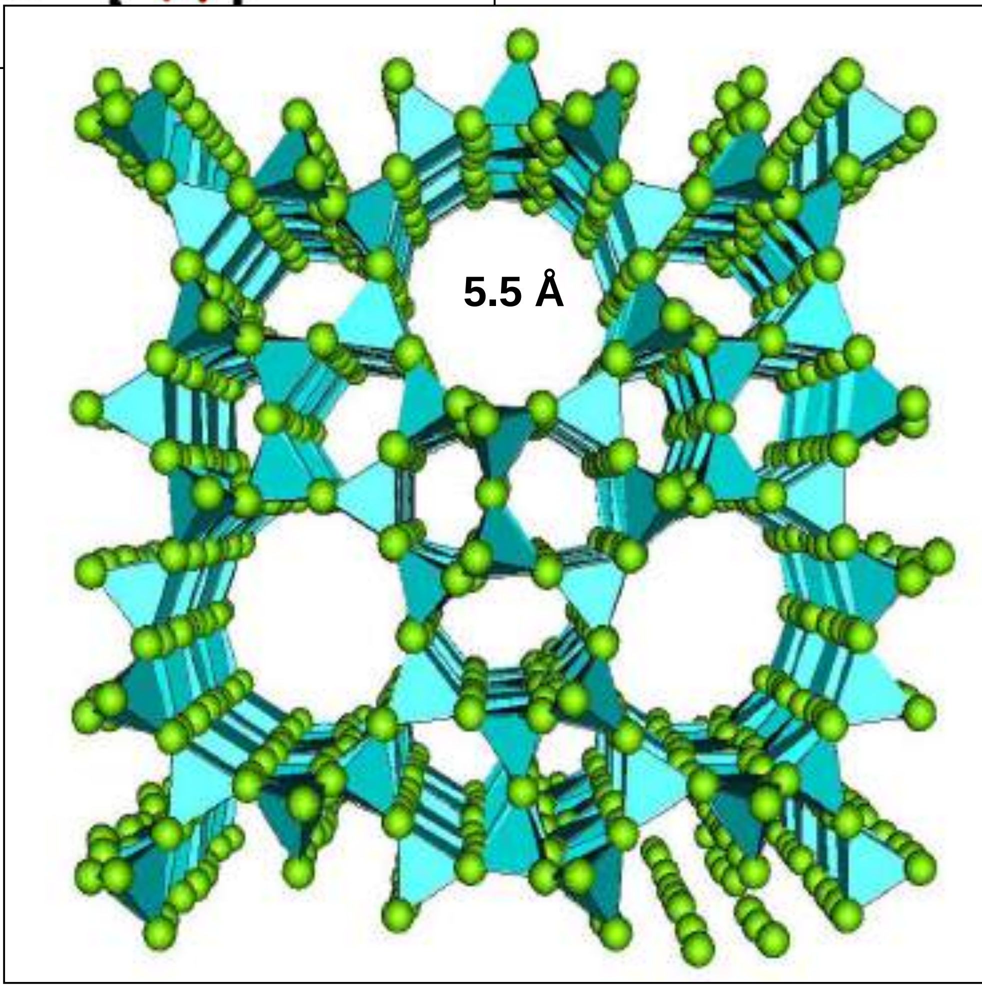


Zeolite Y
(Faujasite)

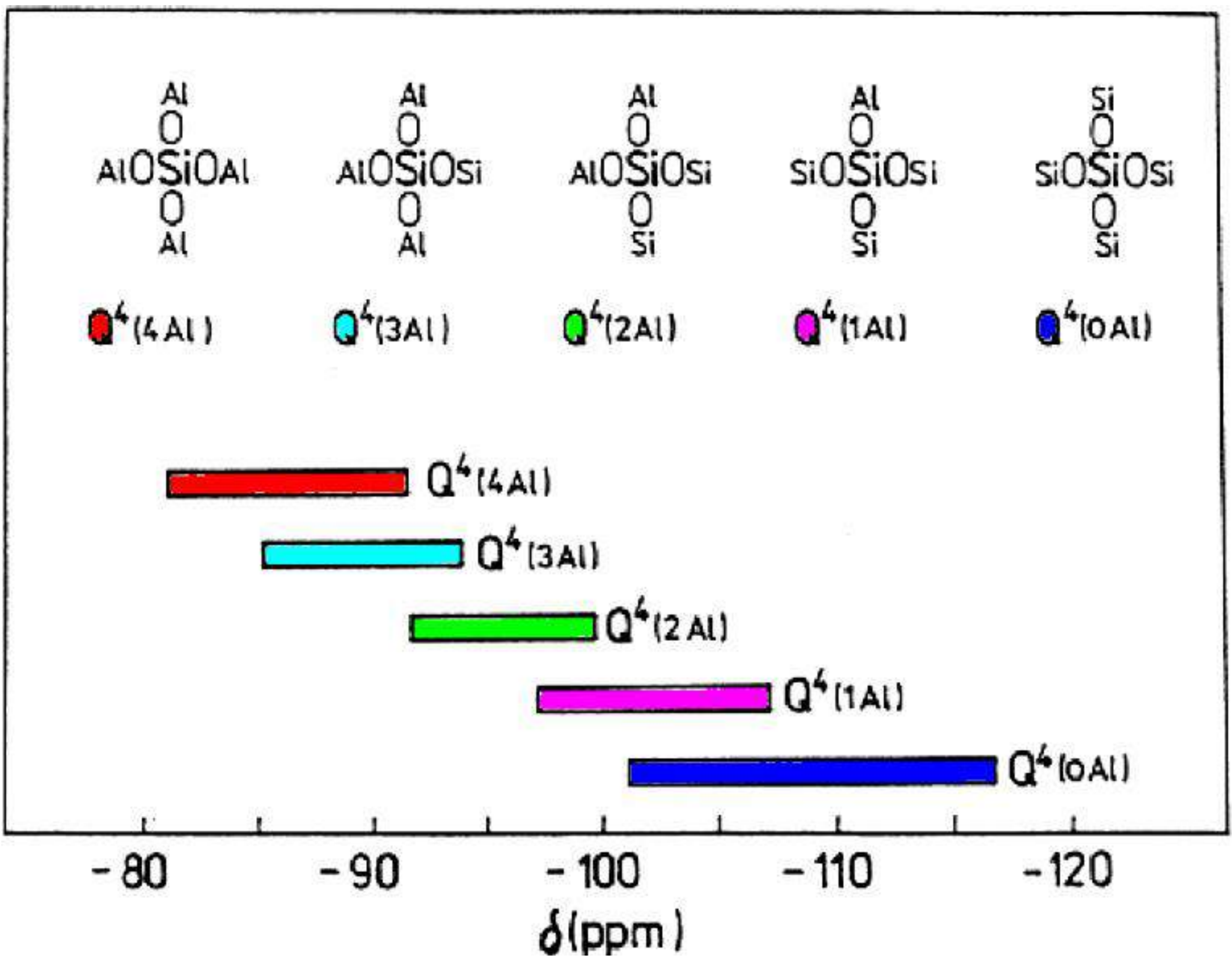


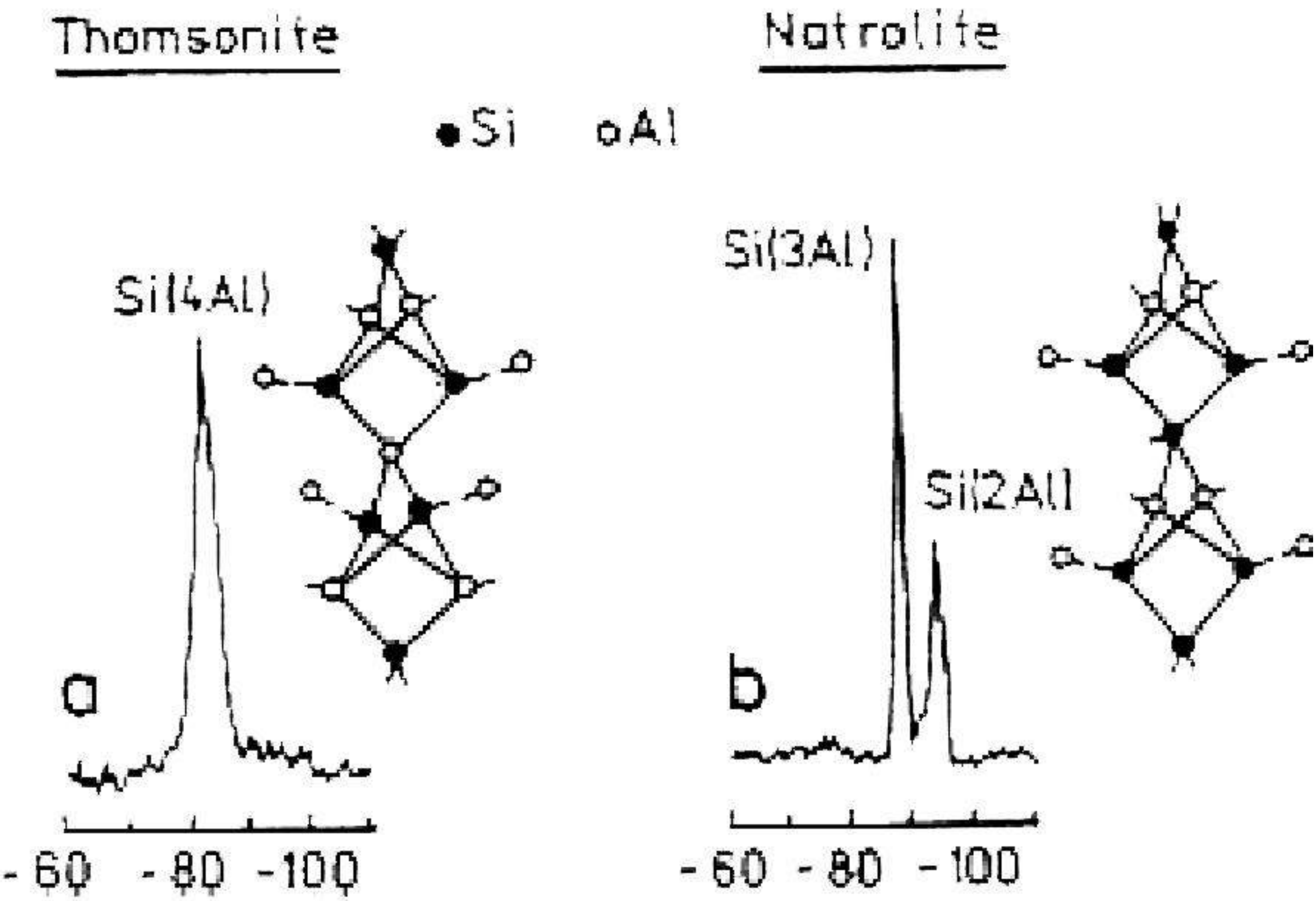


Zeolite ZSM-5



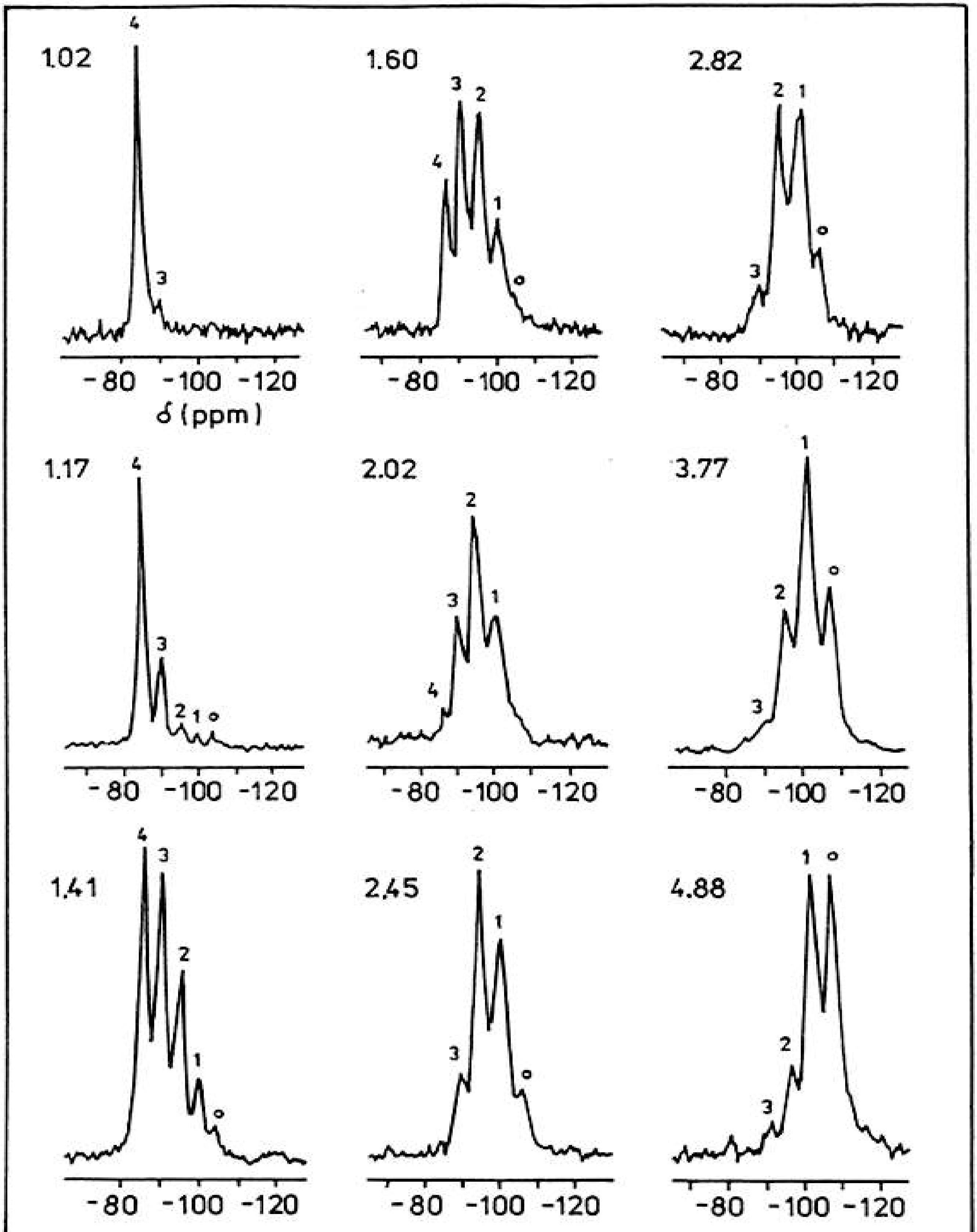
$\delta(^{29}Si)$ in units Q_4(n Al)



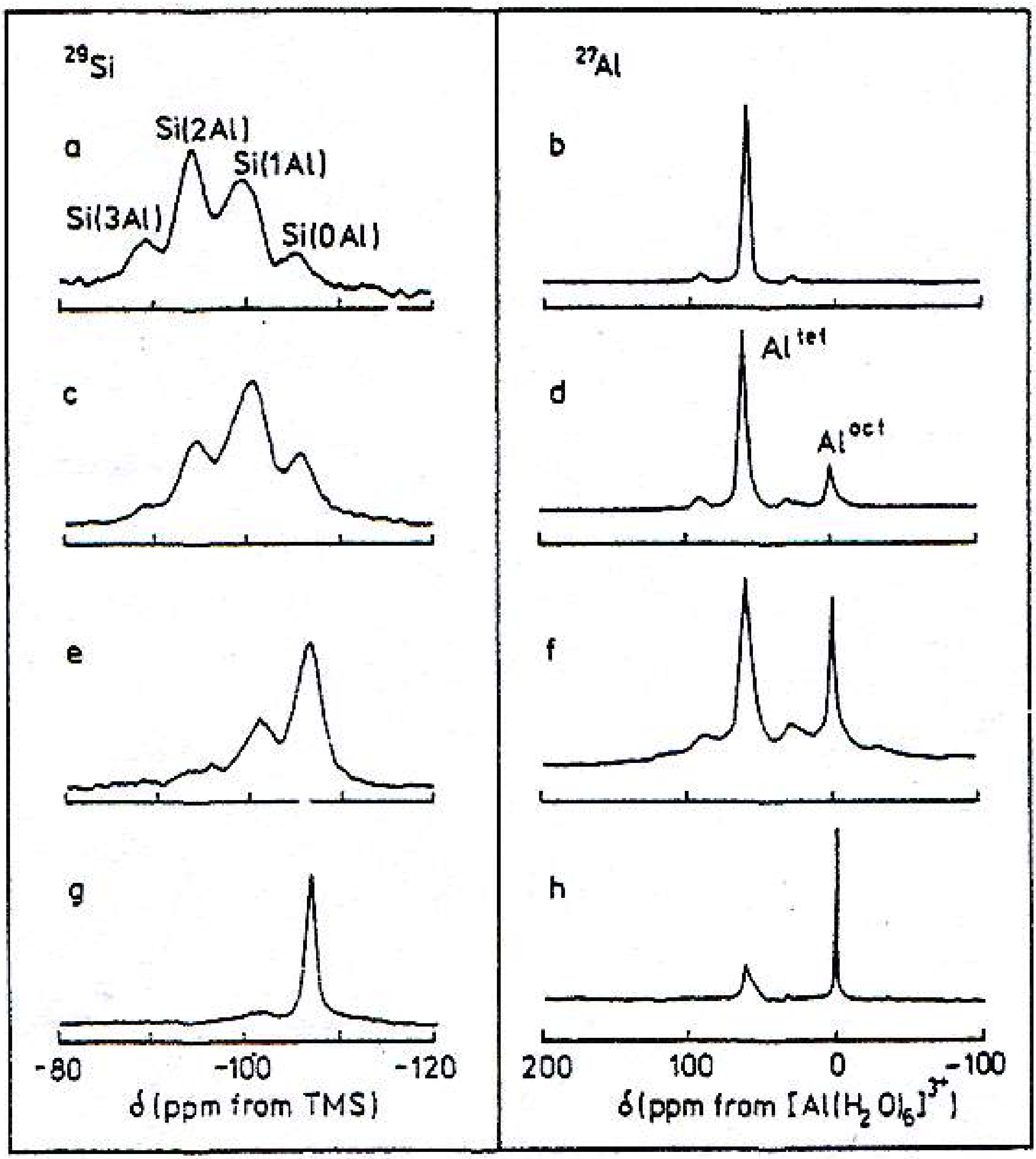


Thomsonite
Natrolite
Si
Al
Si(4Al)
Si(3Al)
Si(2Al)
a
b
-60
-80
-100
-60
-80
-100

Variation of ^{29}Si-NMR with Si/Al ratio of faujasite

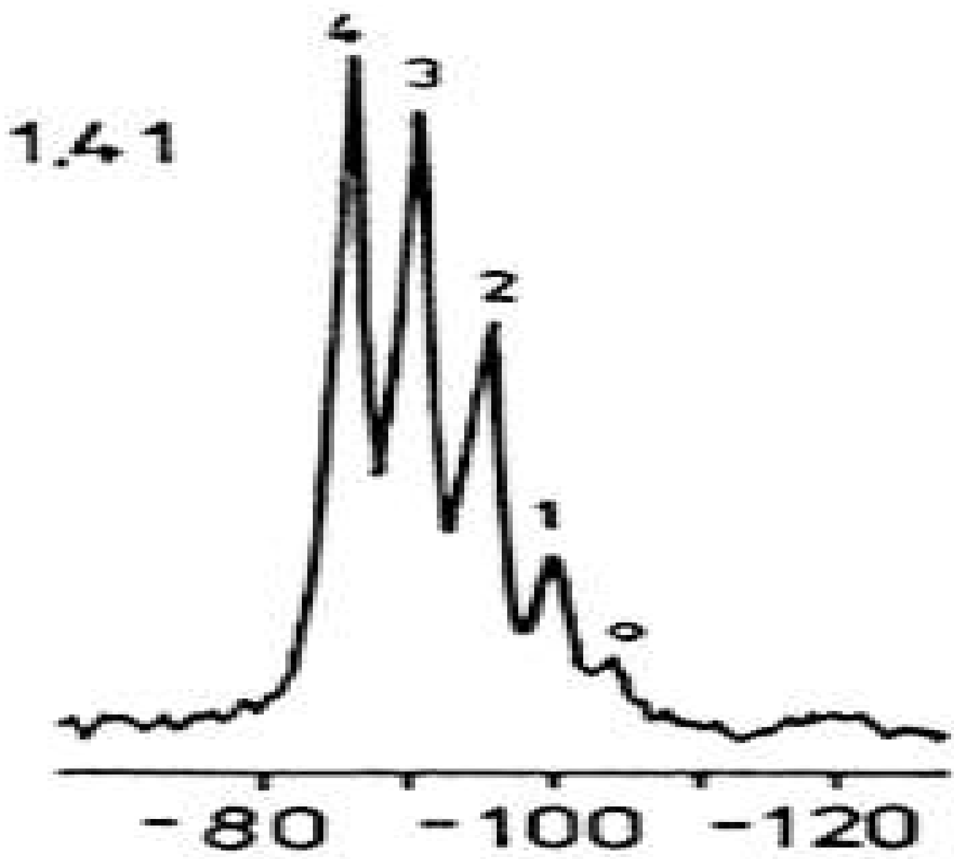


Dealumination of Y zeolite

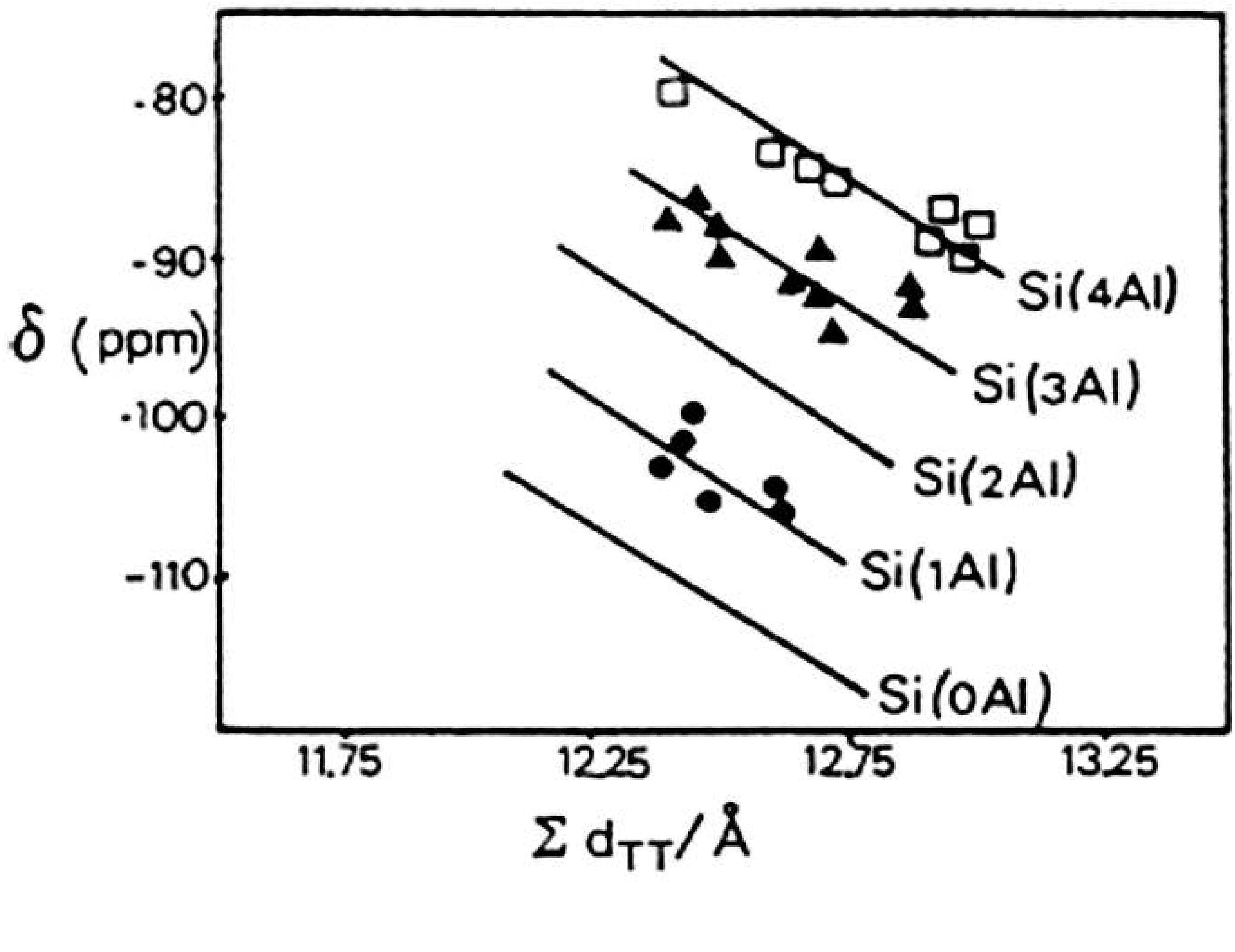


Determination of the ratio Si/Al

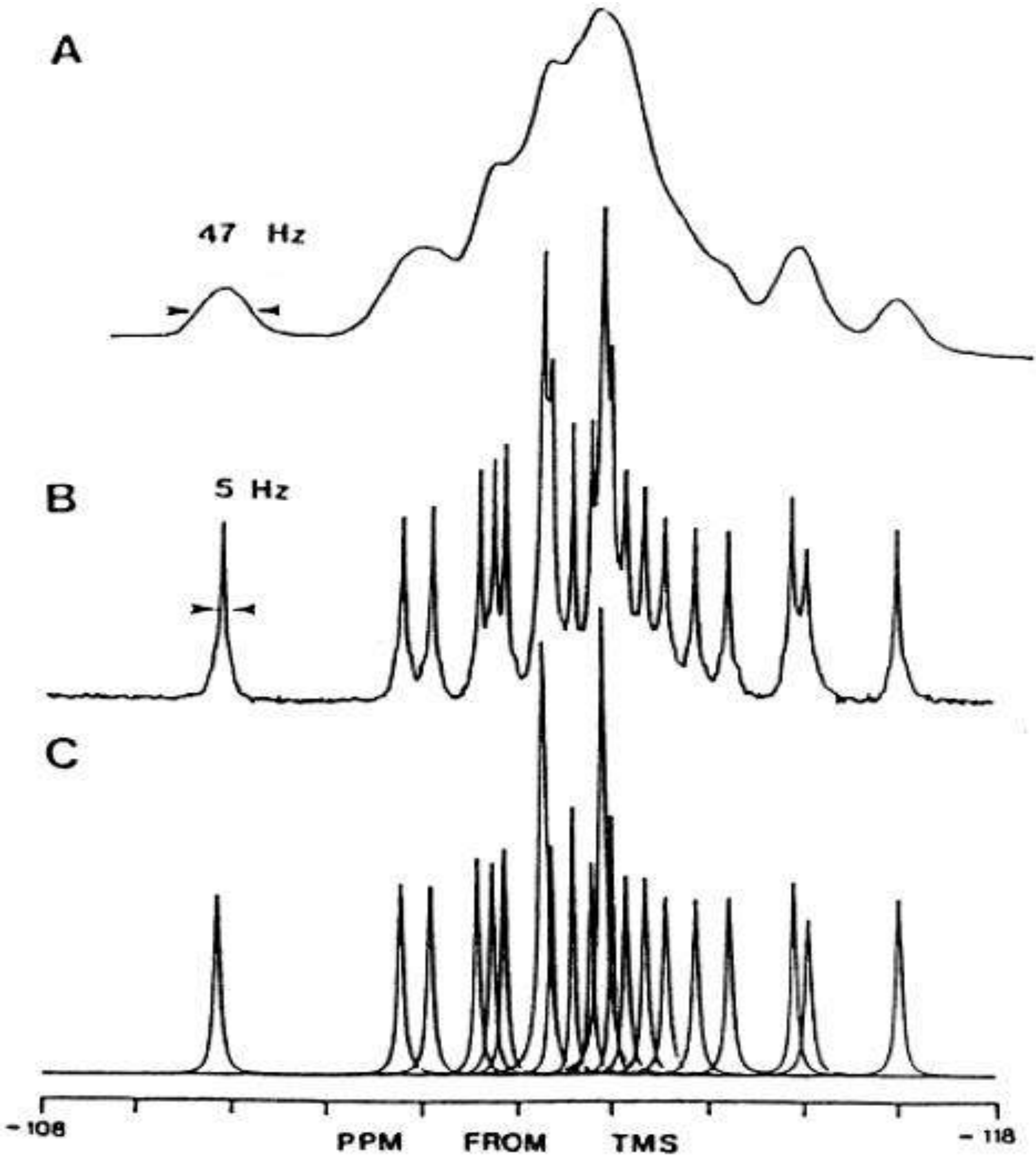
$$Si/Al = \sum_{n=0}^{4} I_{Si(nAl)} / \sum_{n=0}^{4} \frac{n}{4} I_{Si(nAl)}$$



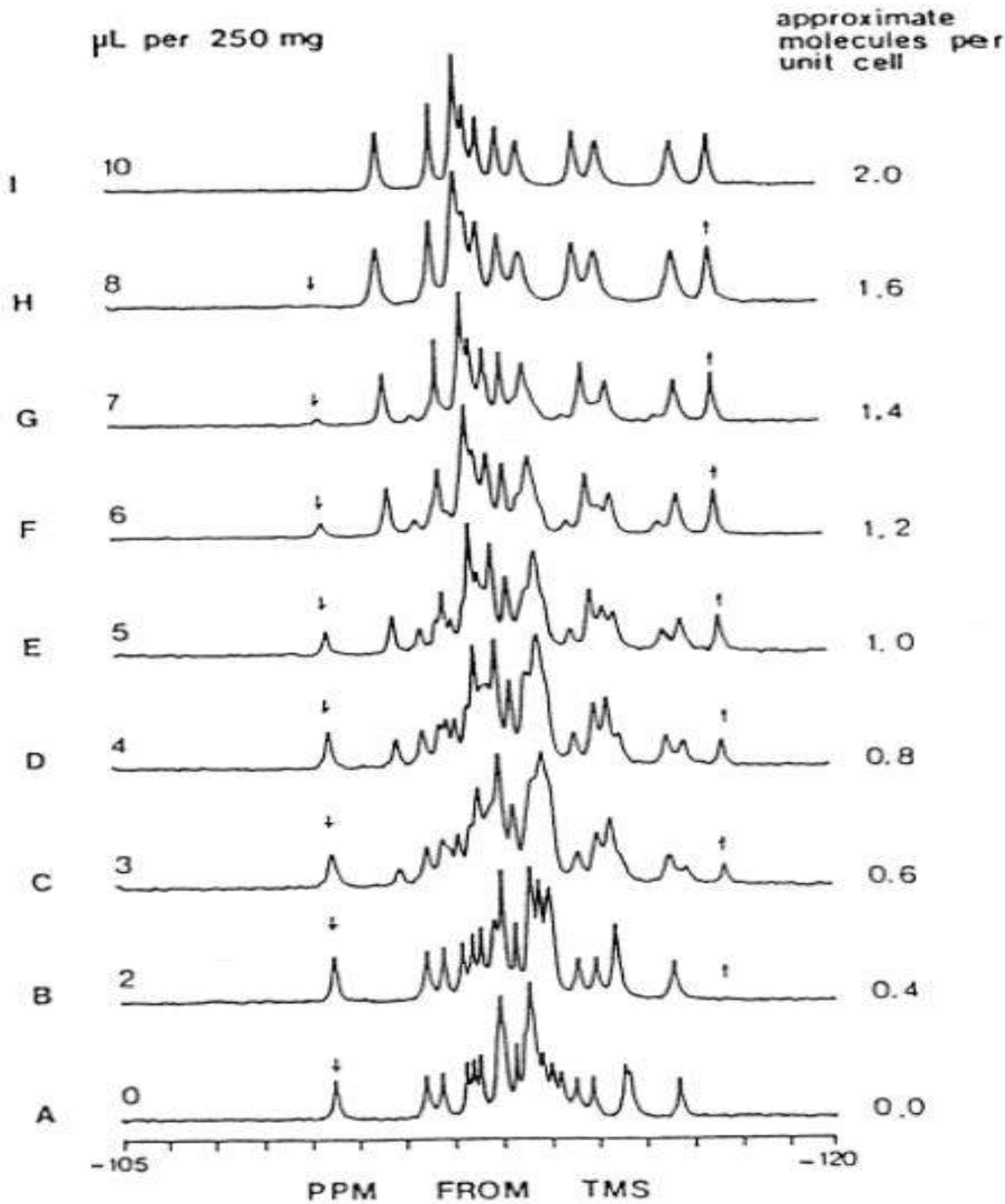
Variation of $\delta(^{29}Si)$ against distance TT



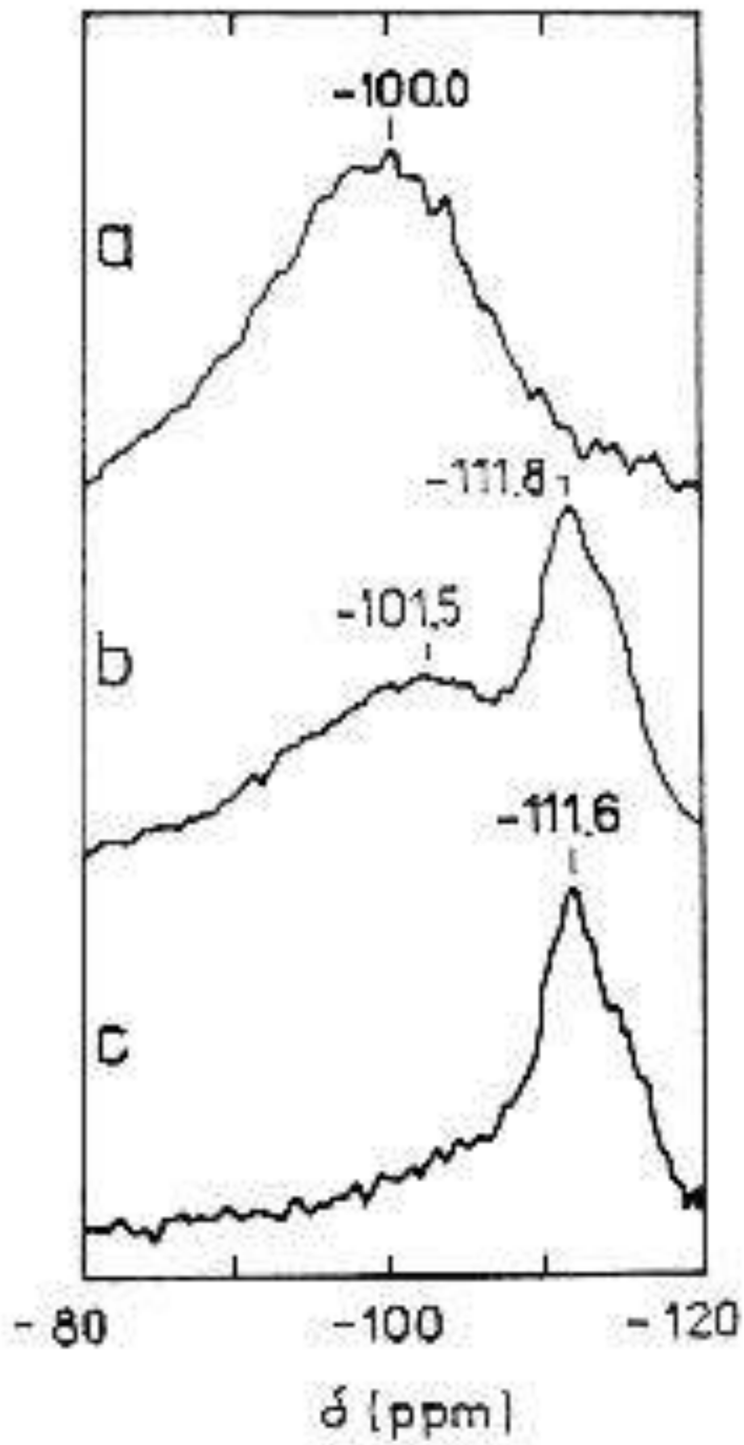
ZSM5. A: static; B: MAS; C: simulation



^{29}Si-MAS-NMR of silicalite. Influence of p-xylene concentration.Transformation of monoclinique into orthorhombique symetry

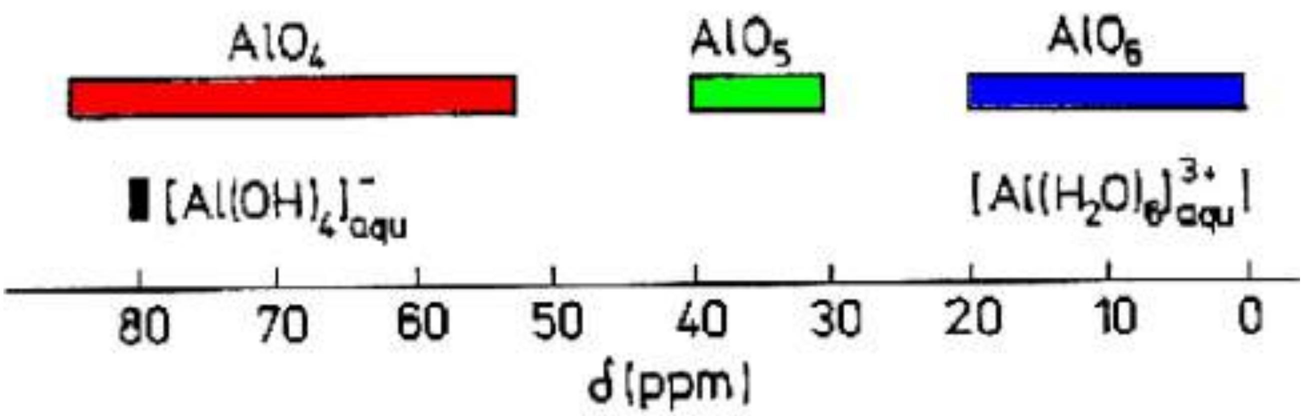


δ(^{29}Si) during the synthesis of ZSM5 crystallinity: a) 0% Si/Al=1.8 b) 45% Si/Al=5; c) 100%



δ(^{27}Al) of AlO_n

reference $[Al(H2O)_6]^{3+}$



Variation of δ^{27}Al versus Al-O-Si angle

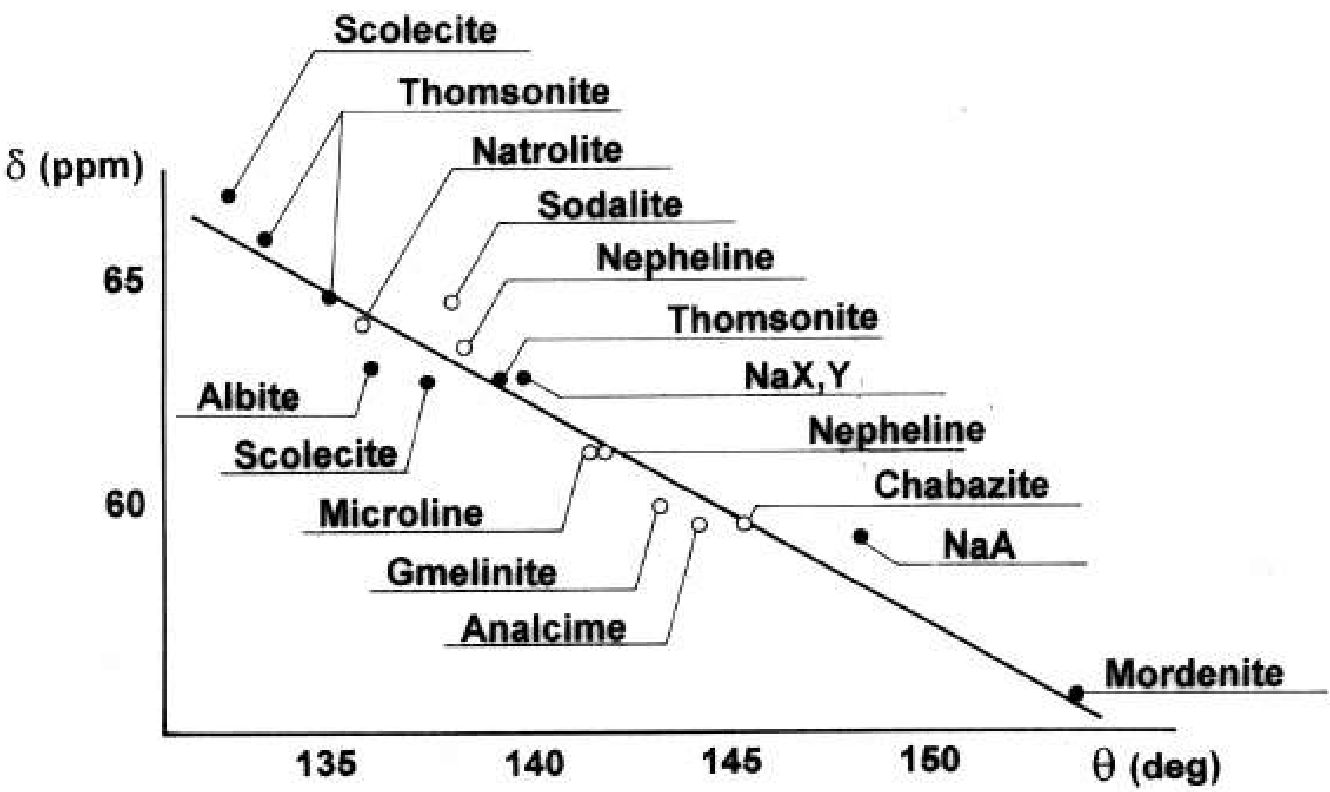
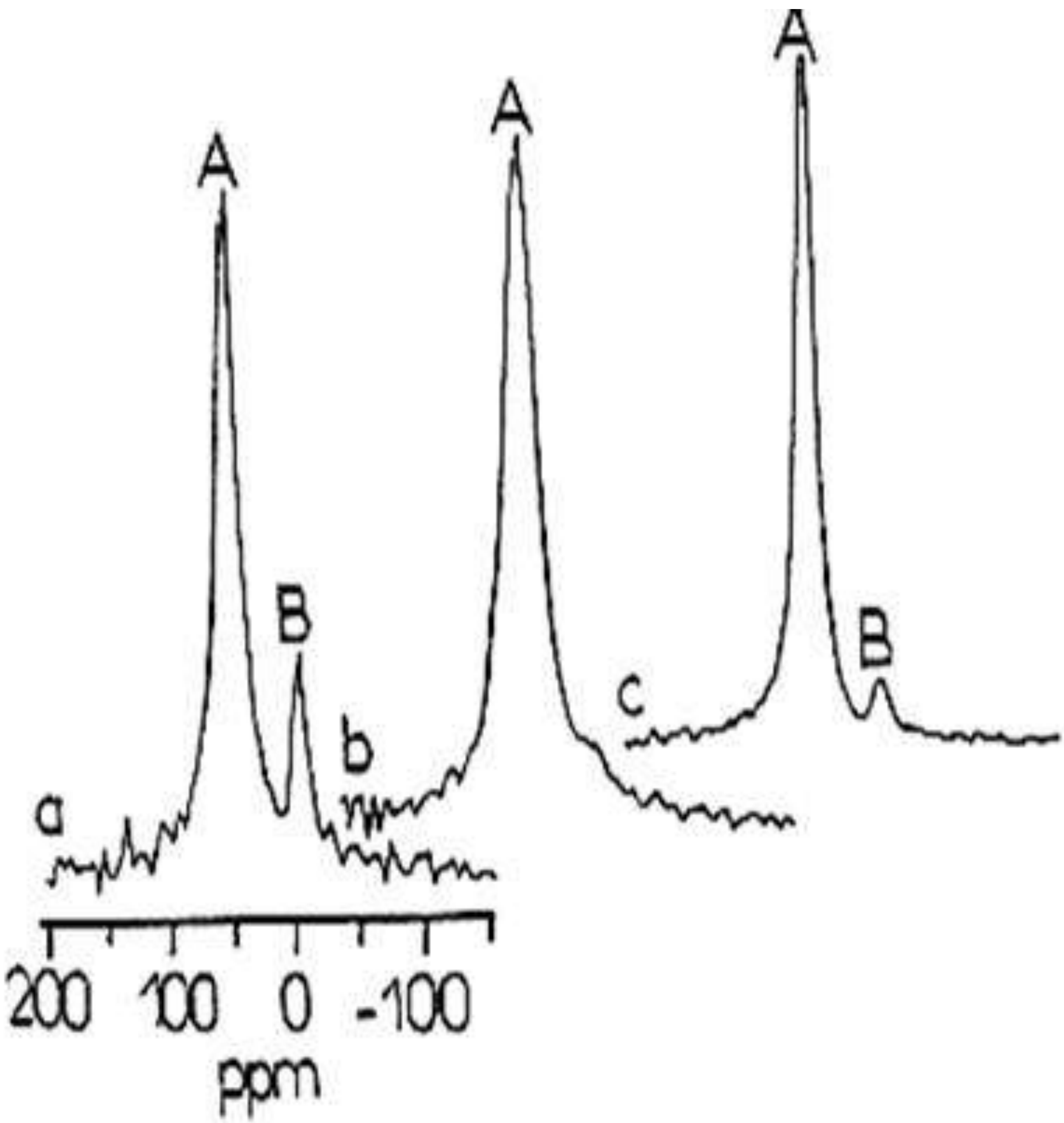


FIG. 3.36 – Variation de $\delta(^{27}Al)$ avec l'angle Al-O-Si.

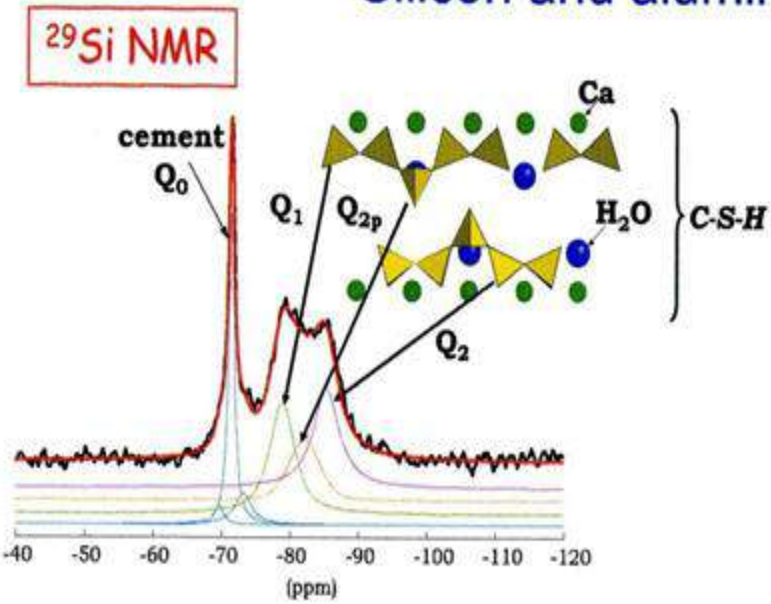
27Al NMR of HZSM5

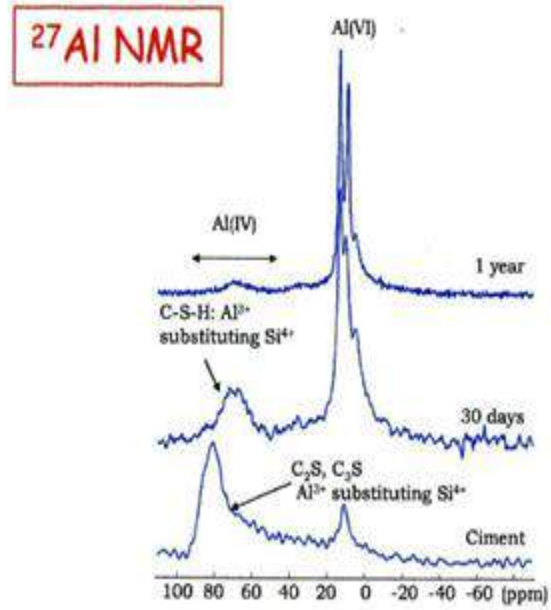
a) before cooking; b)10% coke;
c) after partial regenaration



NMR spectroscopy in cement science

Silicon and aluminum coordination





- Solid-state NMR spectroscopy is extensively utilized (^{29}Si, ^{27}Al, ^{1}H):

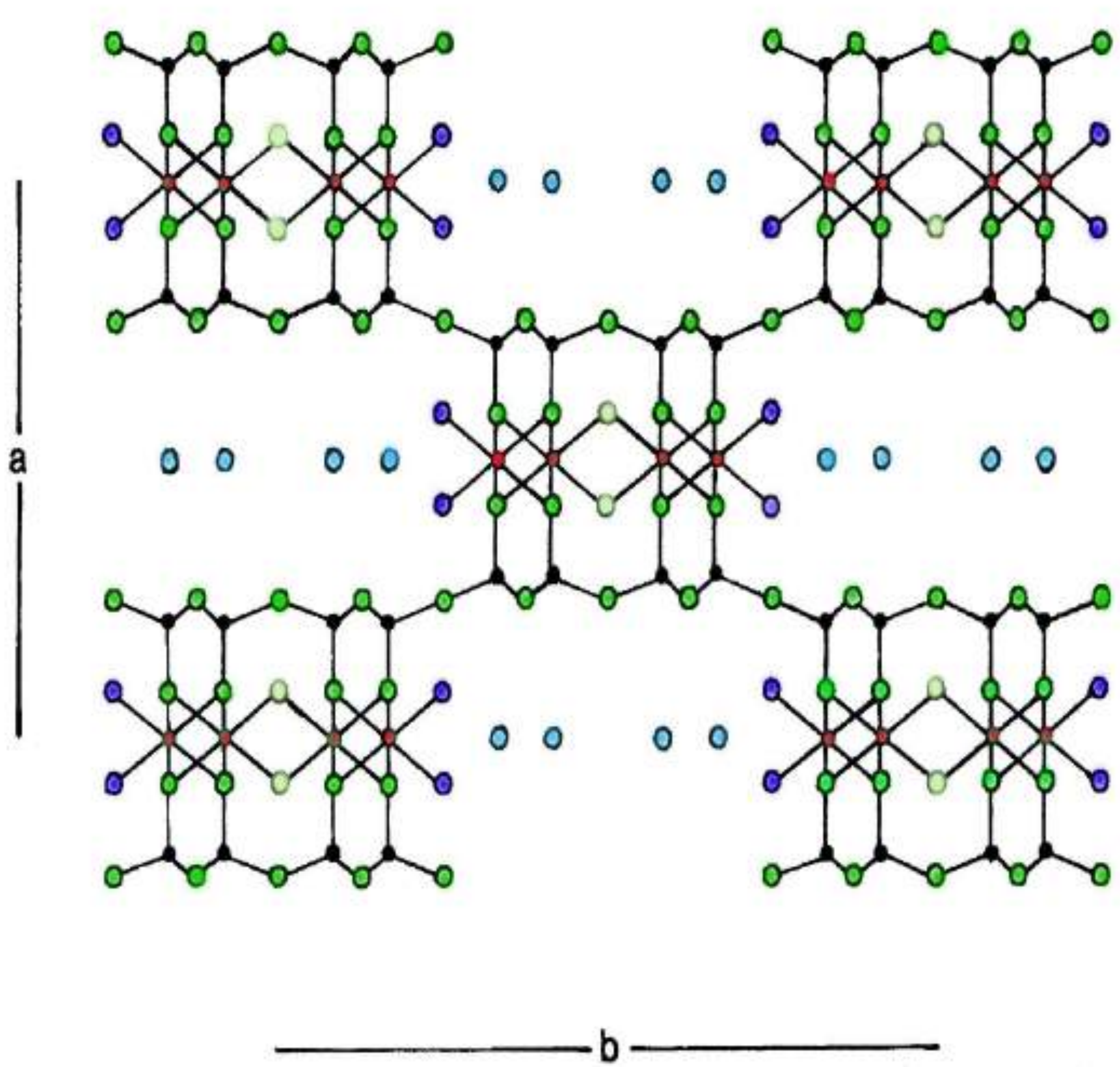
« Application of NMR spectroscopy to cement science » Gordon and Breach, 1994

« NMR spectroscopy of cement based materials » Springer 1998

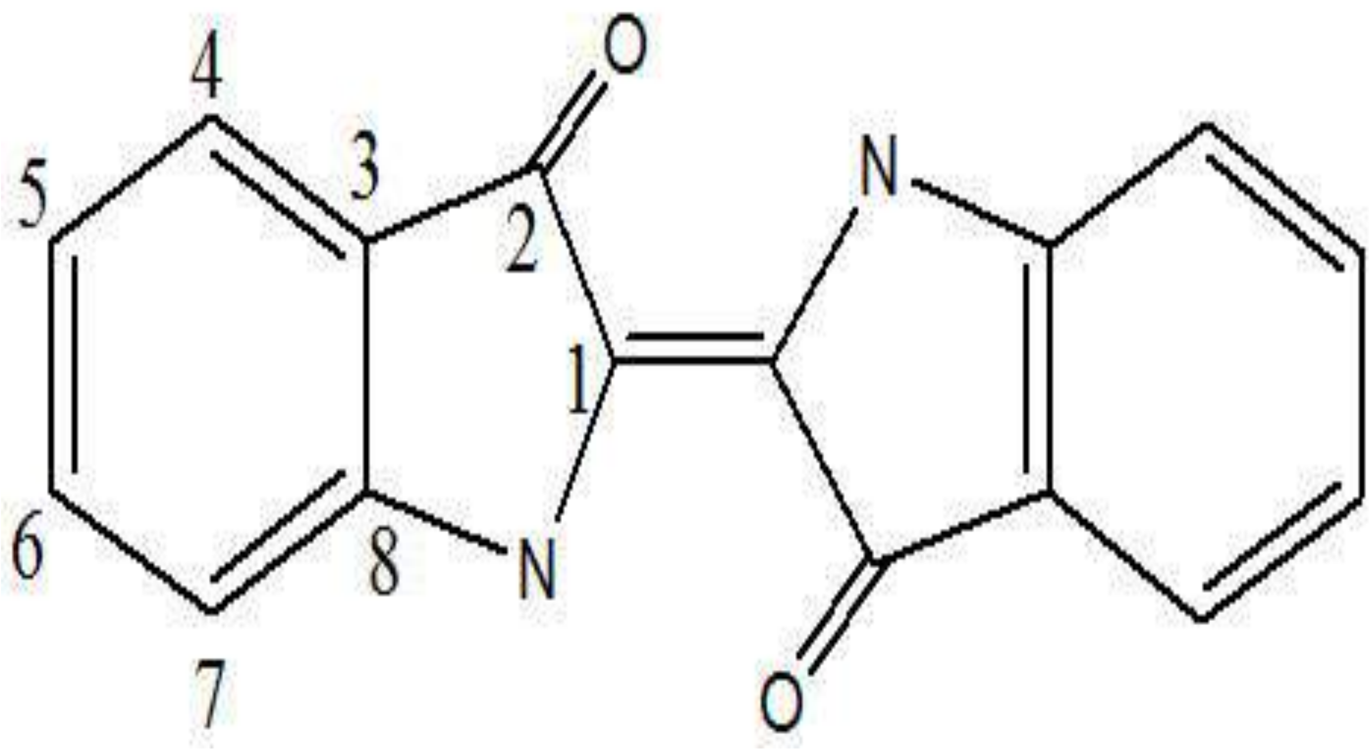
- $CaO.SiO_2.Al_2O_3.Fe_2O_3.SO_3.Na_2O.MgO.CO_2.H_2O$
- ^{43}Ca, ^{25}Mg, ^{33}S

MAYA Blue: Palygorskyte clay + indigo

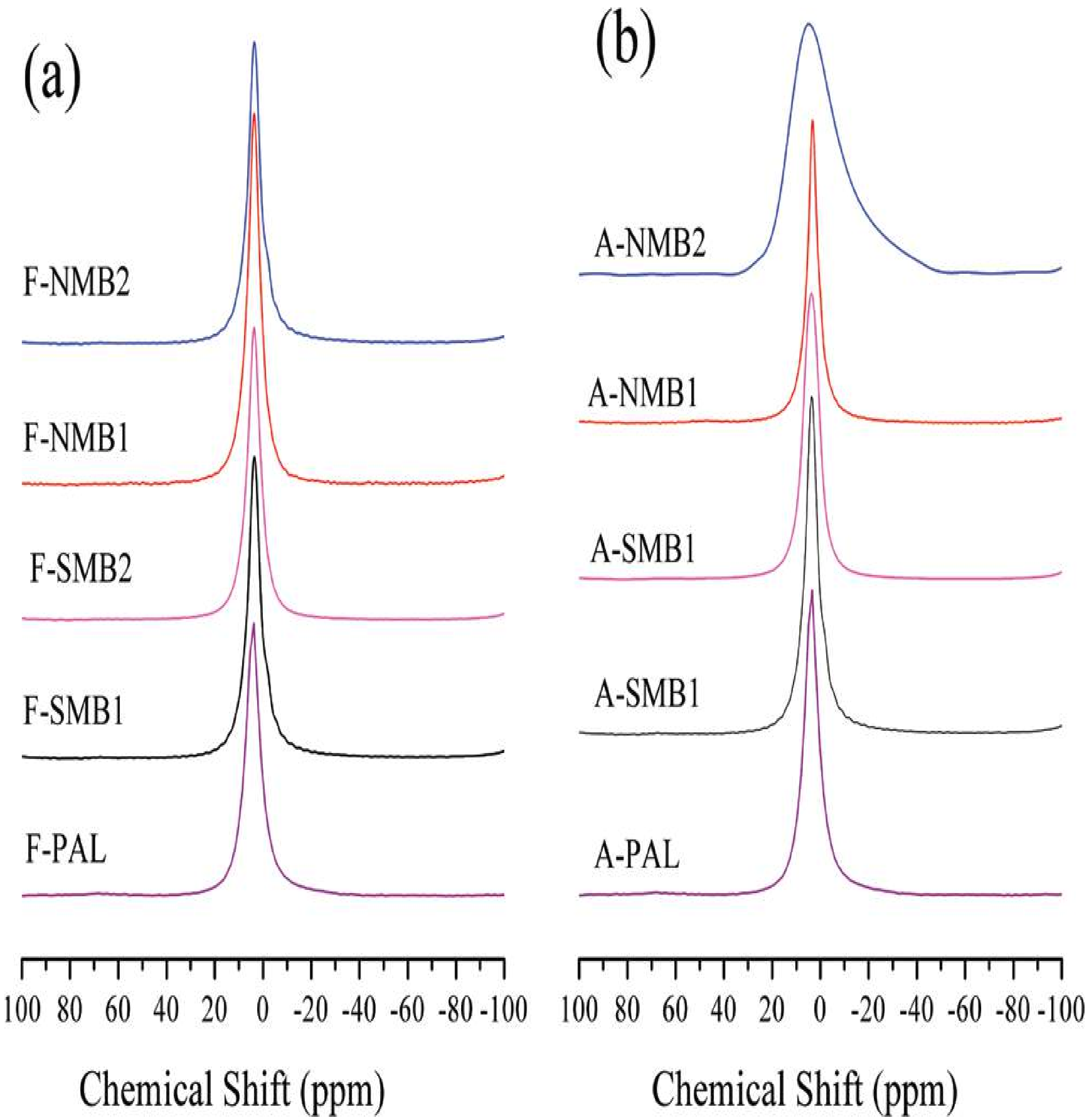
Palygorskite clay



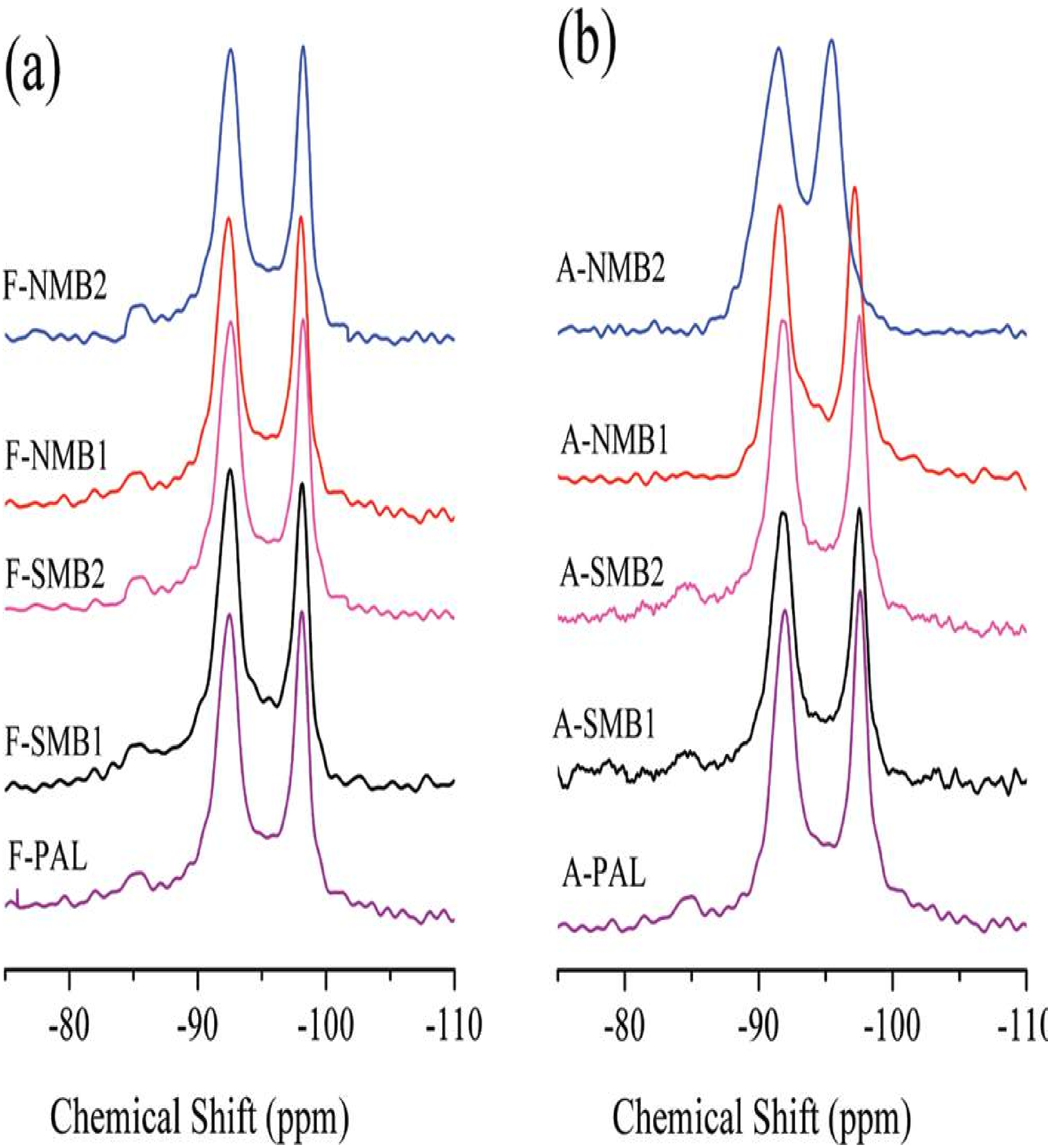
Indigo



27Al MAS NMR spectra of fresh (a) and aged (b) Maya
Blue-like pigments.



29Si MAS NMR spectra of fresh (a) and aged (b) Maya Bluelike pigments.



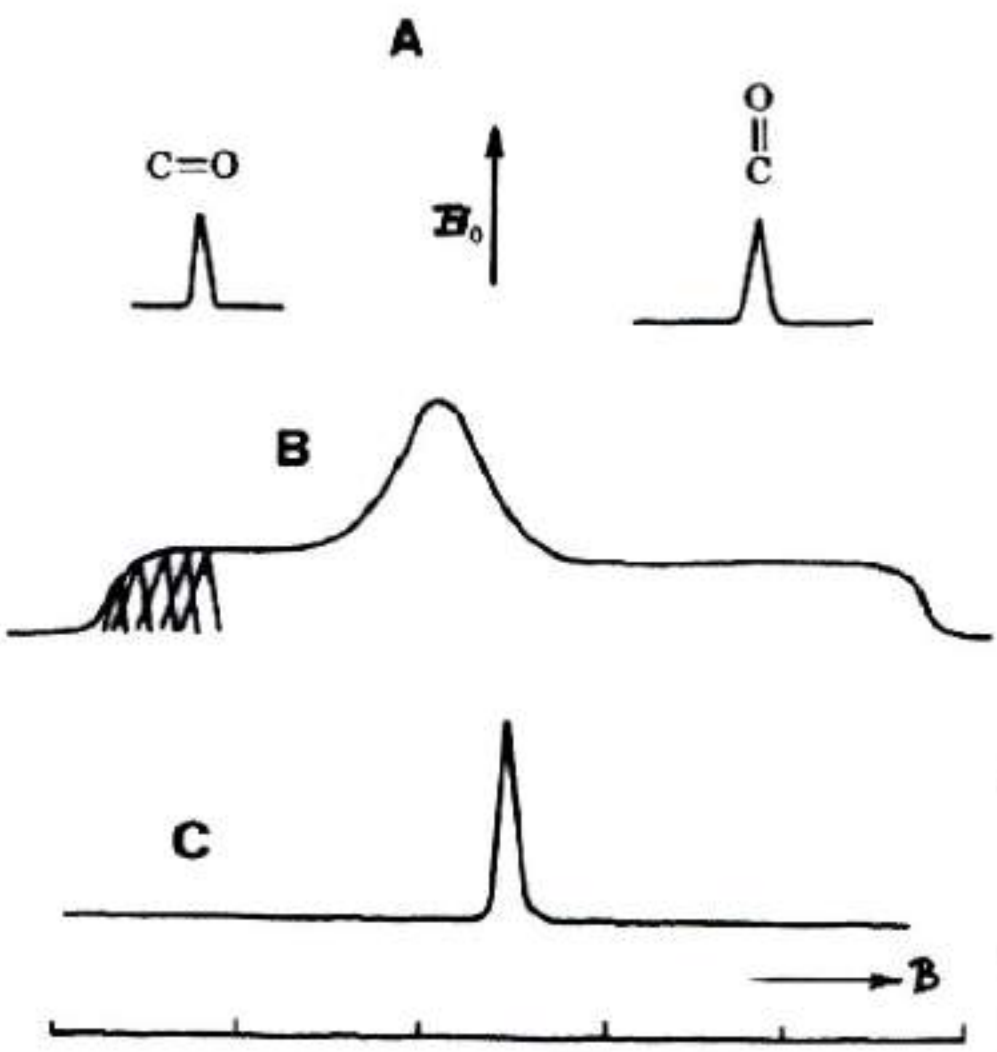
Chemical shift anisotropy

Schematic representation of the ^{13}C NMR absorption of a carbonyl functionality

A- single crystal in two different orientations/B_0

B- In a polycrystalline sample where there are contributions from the random distribution of orientations.

C- In solution



Chemical shift anisotropy

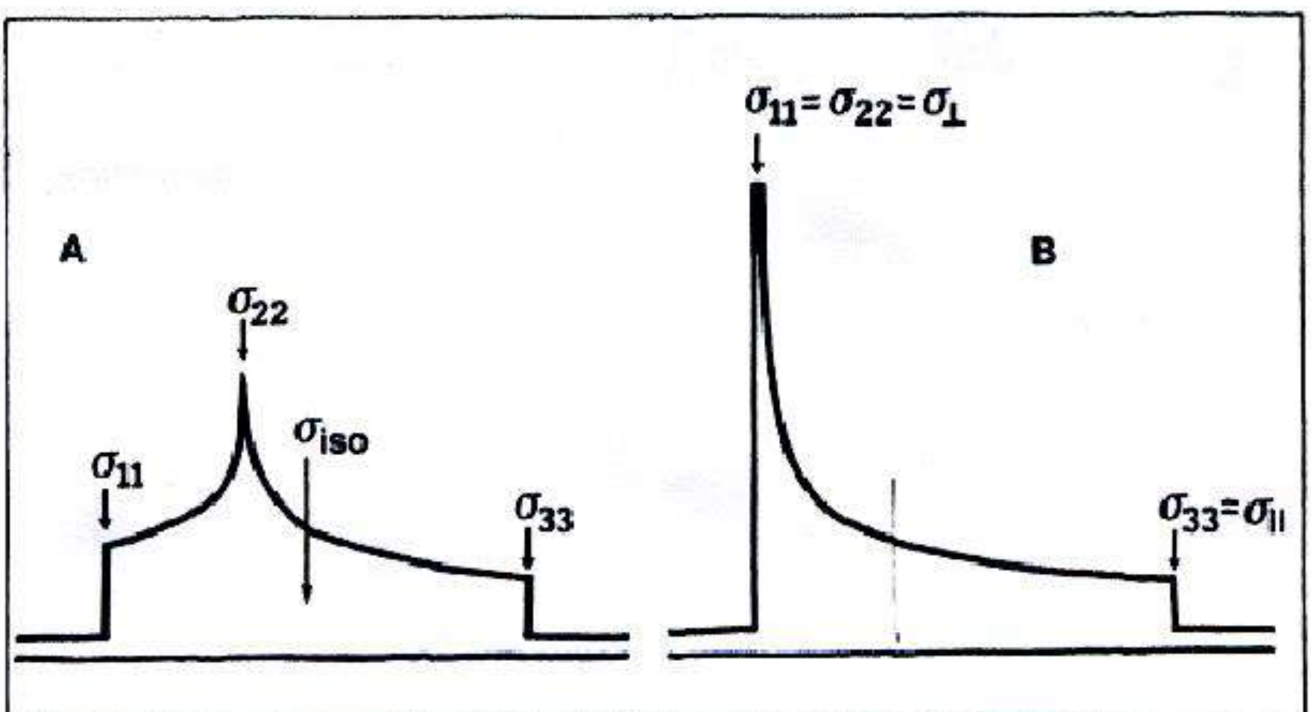
MAS removes all solid-state interactions. Multi-pulse sequence does not remove the chemical shift anisotropy.

Asymmetric shift anisotropy

$$\sigma_{iso} = \sigma_{11} + \sigma_{22} + \sigma_{33}$$

Axially shift anisotropy

$$\sigma_{11} = \sigma_{22} = \sigma_{\perp} \quad \sigma_{33} = \sigma_{\parallel}$$



13C spectra of polycrystalline compounds containing carbonyl groups. Low-field: CO; high field: CH3

31

32

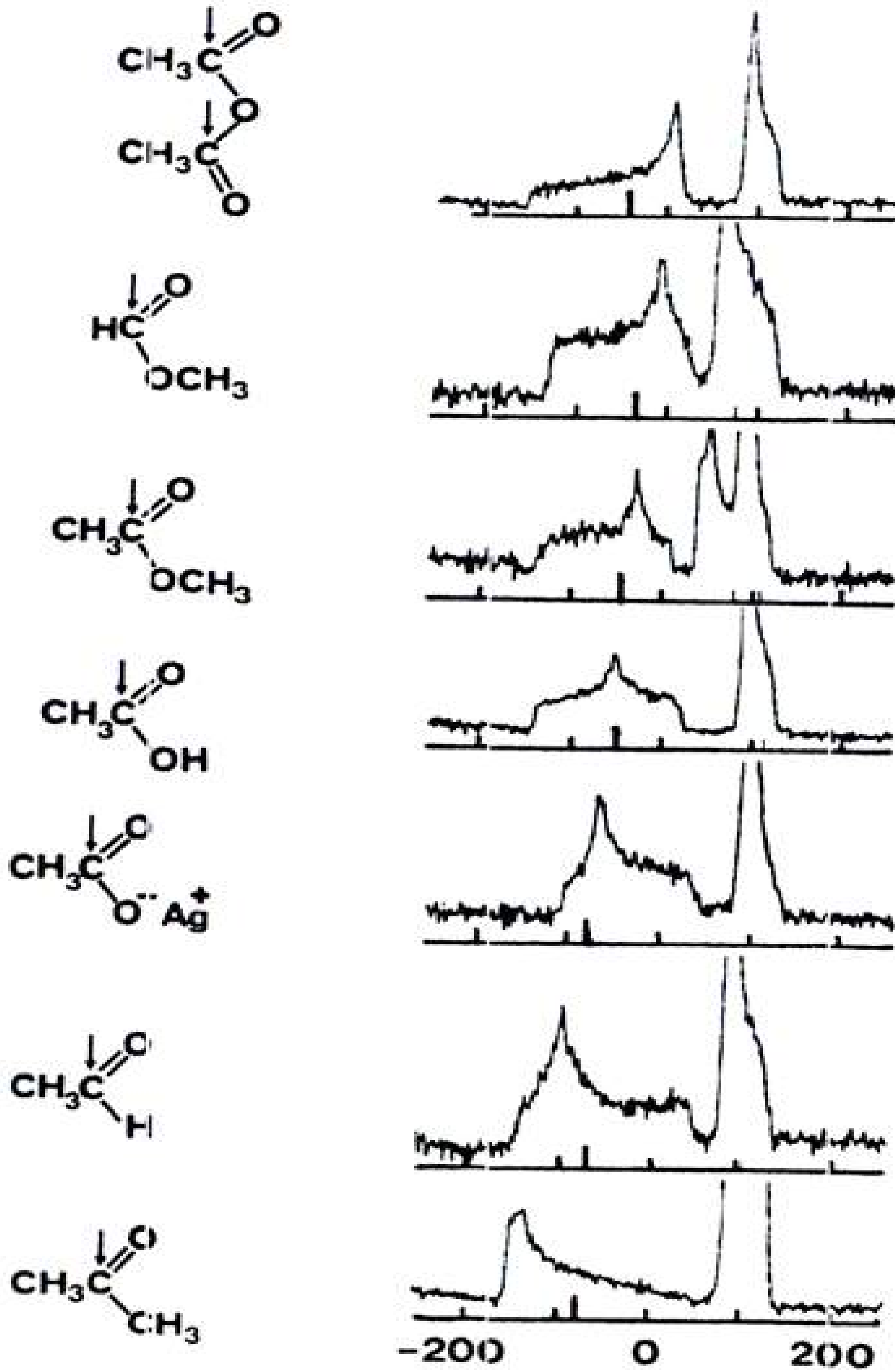
33

34

35

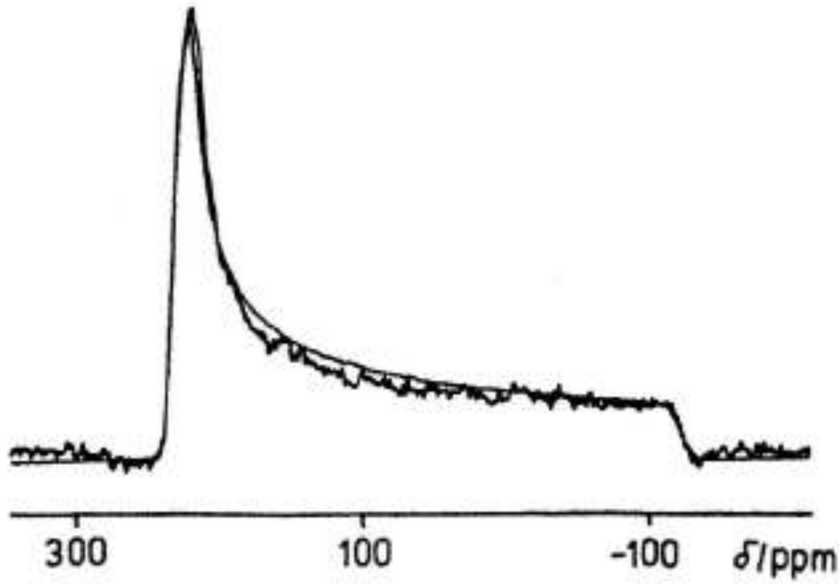
36

37

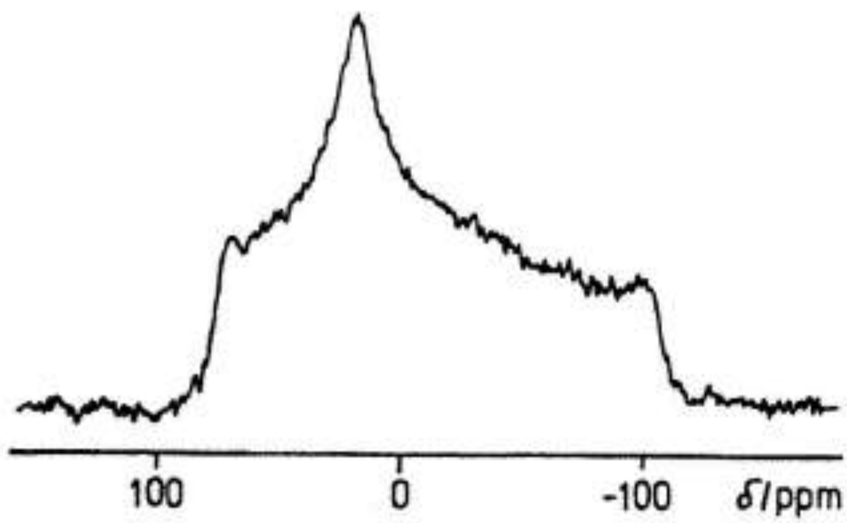


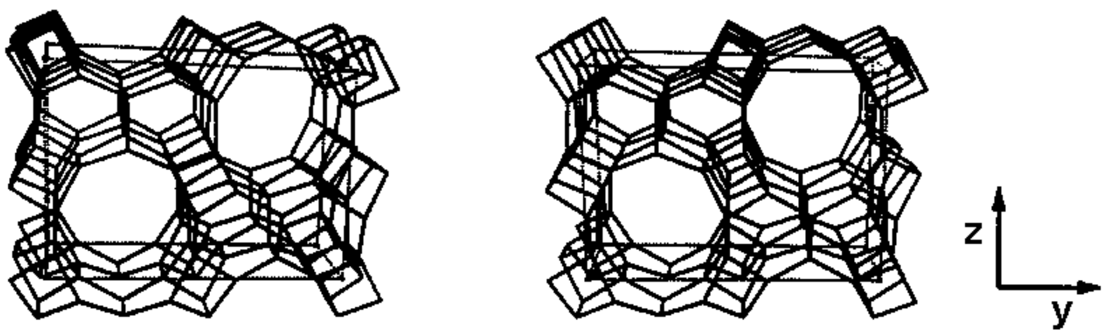
^{31}P NMR

P_4O_6

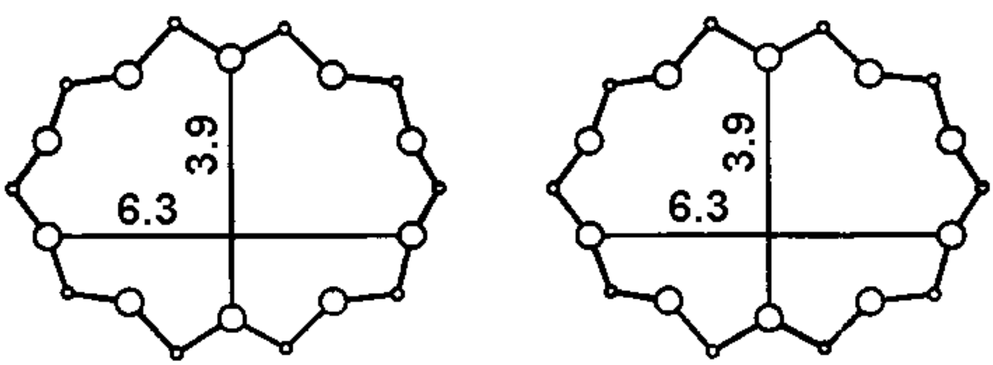


$Ba(Et)_2PO_4$



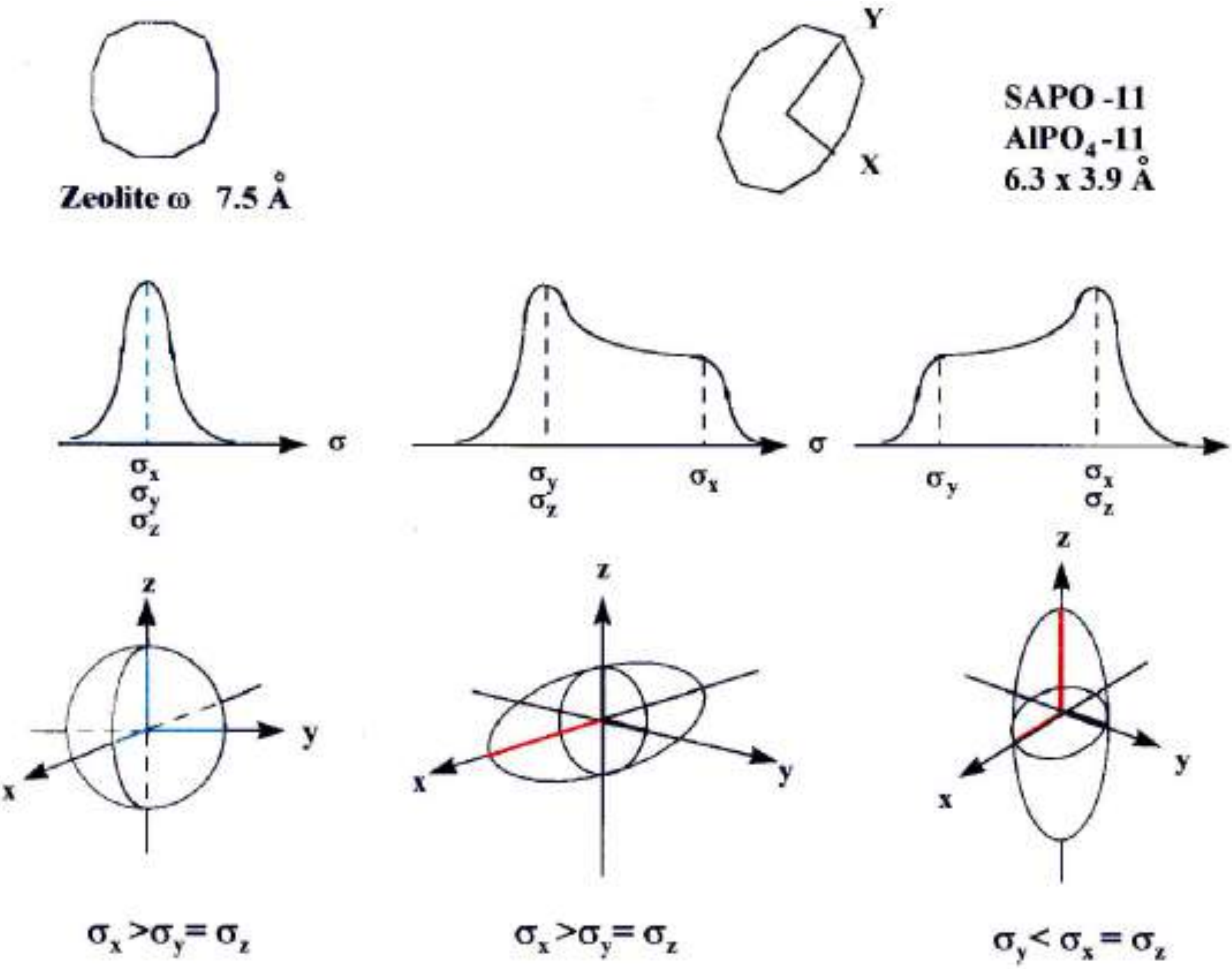


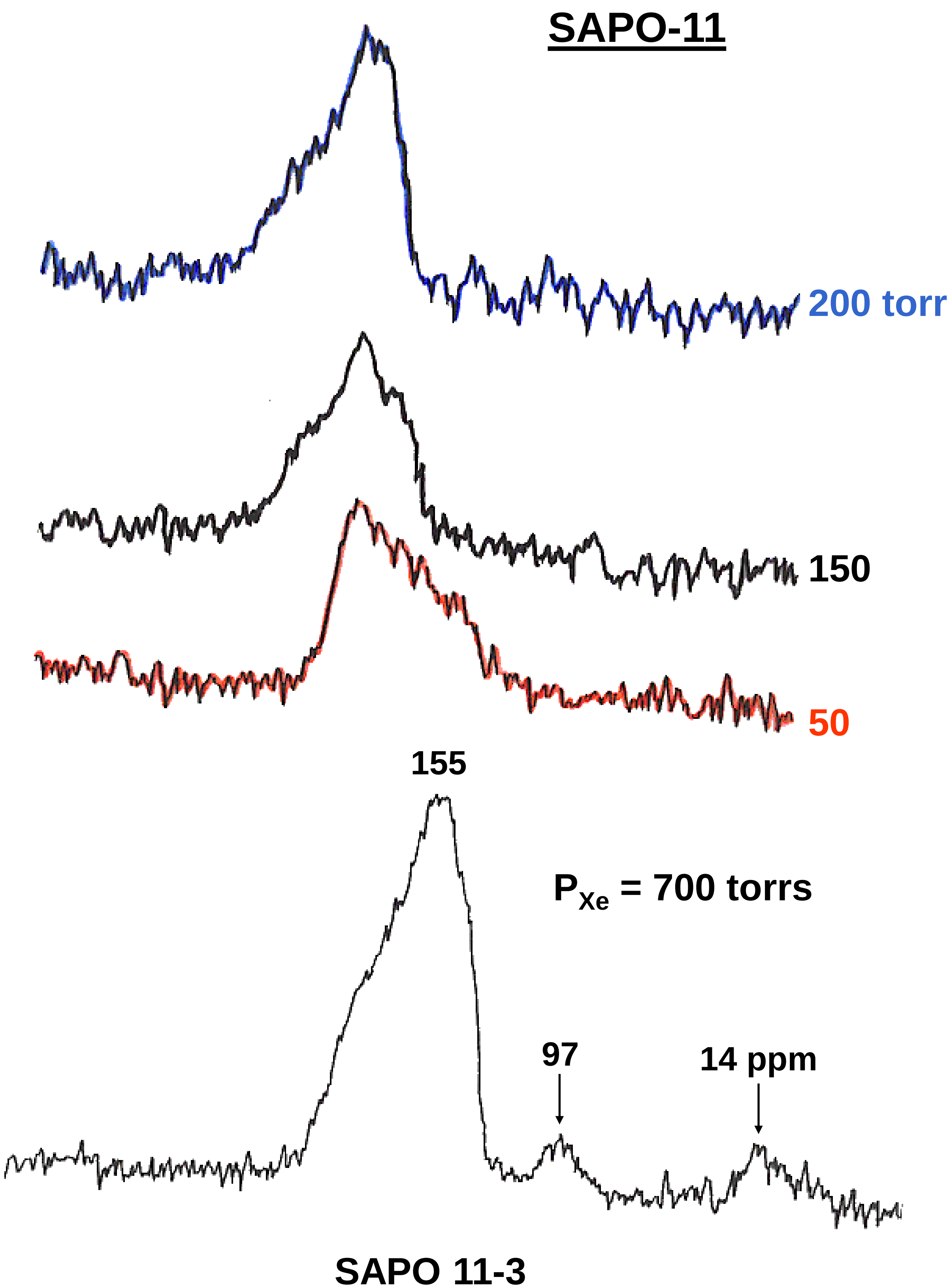
Framework viewed along [100]



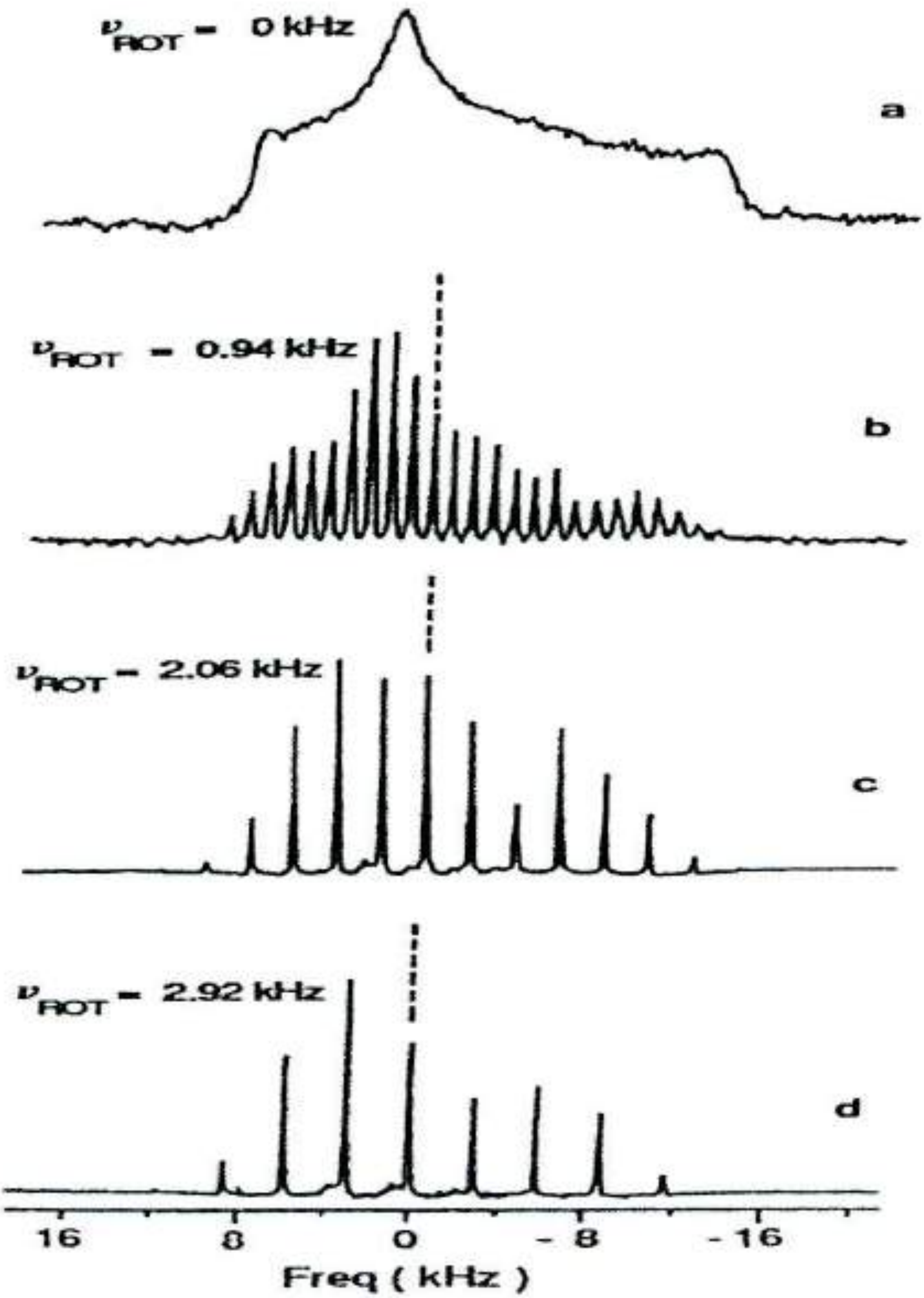
10-ring viewed along [100]

Anisotropy of chemical shift

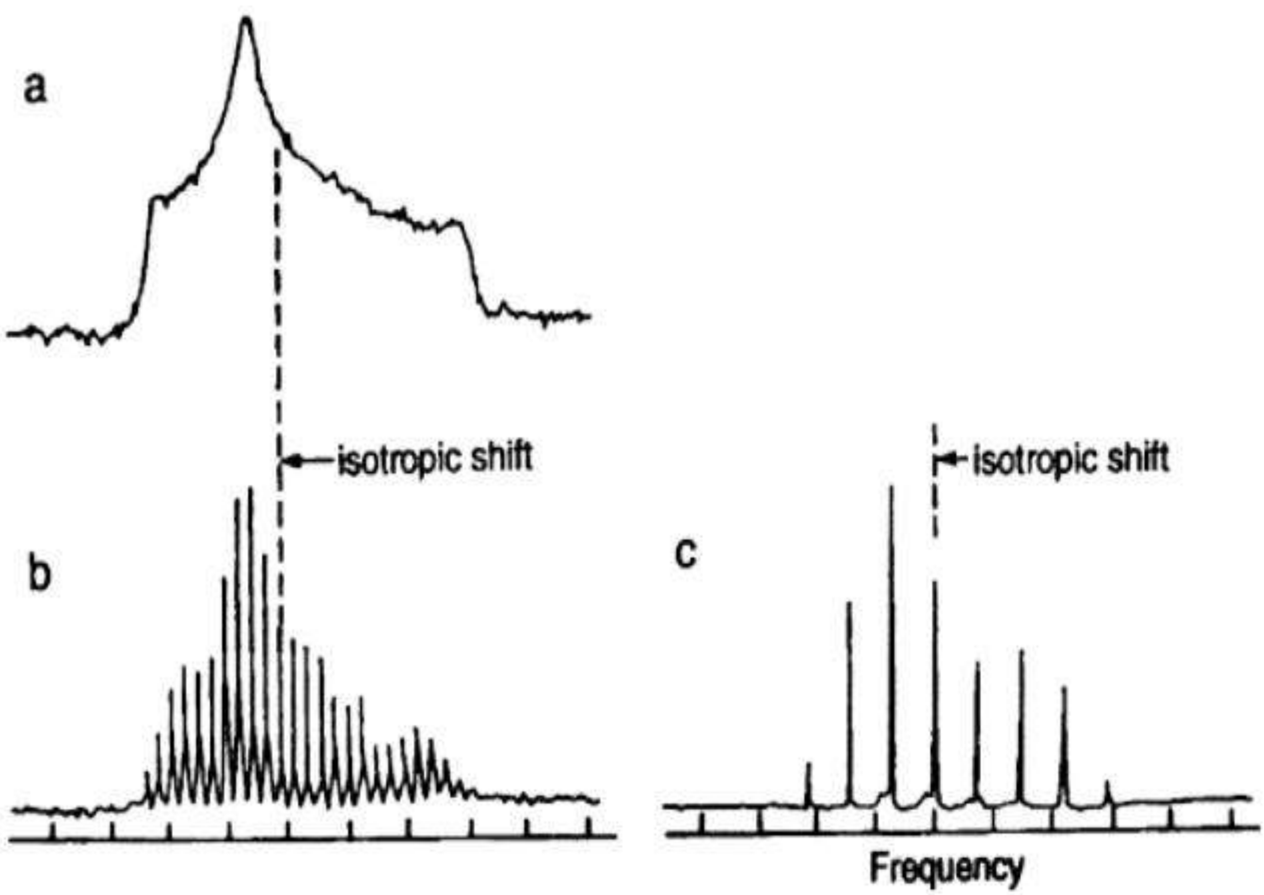



SAPO-11
200 torr
150
50
155
P_{Xe} = 700 torrs
97
14 ppm
SAPO 11-3

Influence of the rotation on the sidebands



a) Static; b) low spinning; c) fast spinning side bands



End of the second part