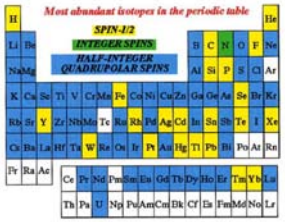

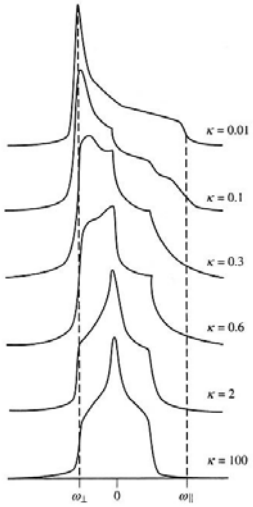

High Resolution Solid State NMR: Principles and Experimental Applications

T. Azaïs
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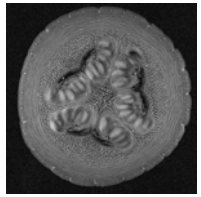
Laboratoire de Chimie de la Matière Condensée
UMR CNRS 7574 – Université P. et M. Curie, Paris

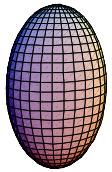
Plan and keywords

I- Spin history and NMR milestones

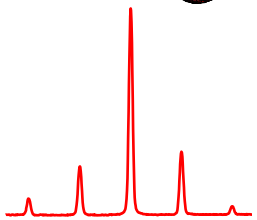


II- NMR fundamentals $\nu_0=\gamma B_0/2\pi$

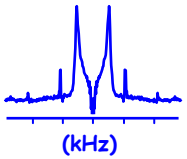
III- Specific characteristics of solid state NMR



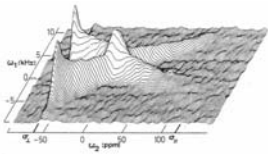
IV- High resolution solid state NMR



V- Cross polarization



VI- 2D solid state NMR experiments

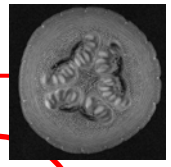


Appendix

1) Tutorials !

2) Experimental session

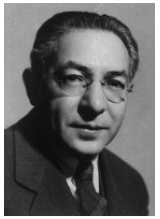
The spin: from 1925 to 2004



W. Pauli, Physics 1945

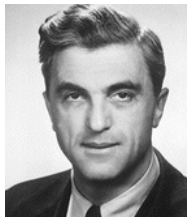
"for the discovery of the Exclusion Principle, also called the Pauli Principle"

G. Uhlenbeck, S. Goudsmit
"fathers of spin"



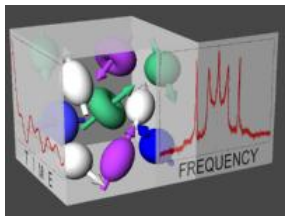
I. I. Rabi, Physics 1944

"for his resonance method for recording the magnetic properties of atomic nuclei"



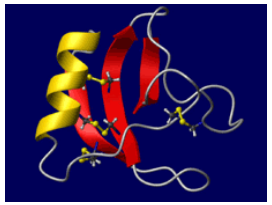
F. Bloch, E. M. Purcell, Physics 1952

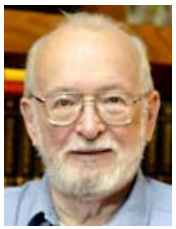
"for the development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"



K. Wüthrich, Chemistry 2002

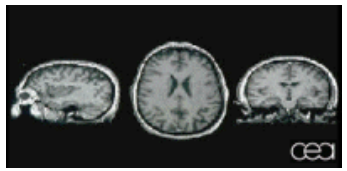
"for his development of NMR spectroscopy for determining the three dimensional structure of biological macromolecules in solution"





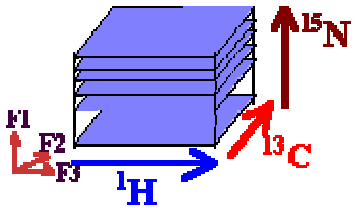
P. C. Lauterbur, P. Mansfield
Medecine 2003

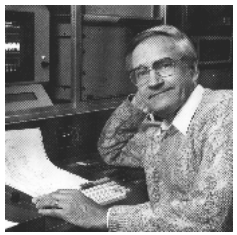
"for their discoveries concerning magnetic resonance imaging"



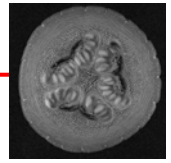
R. R. Ernst, Chemistry 1991

"for his contribution to the development of the methodology of high resolution NMR spectroscopy"

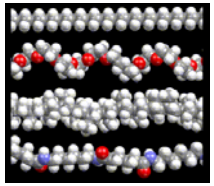


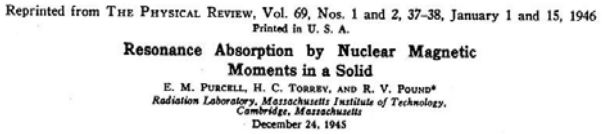


Milestones in solid state NMR



1) NMR in solid paraffin, 1946 (Purcell, Torrey, Pound)

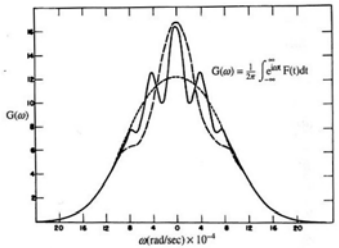




Reprinted from THE PHYSICAL REVIEW, Vol. 69, Nos. 1 and 2, 37–38, January 1 and 15, 1946
Printed in U. S. A.

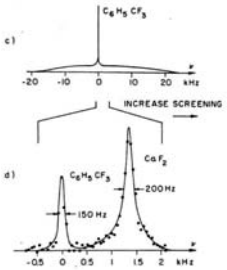
Resonance Absorption by Nuclear Magnetic Moments in a Solid

E. M. PURCELL, H. C. TORREY, AND R. V. POUND*
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
December 24, 1945

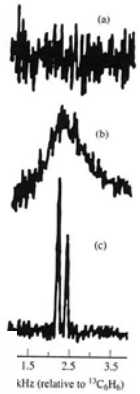


2) Magic Angle Spinning, 1959 (Andrew, Bradbury, Eades and Lowe)

3) WAHUHA sequence, 1968 (Waugh, Huber, Haeberlen)

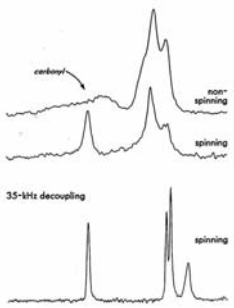


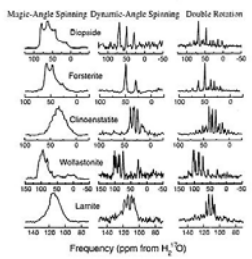
4) CP concept, 1962 (Hartmann, Hahn)



5) Direct observation of dilute spins, 1972 (Pines, Gibby, Waugh)

6) MAS returns: the CP MAS experiment, 1976 (Schaefer, Stejskal)



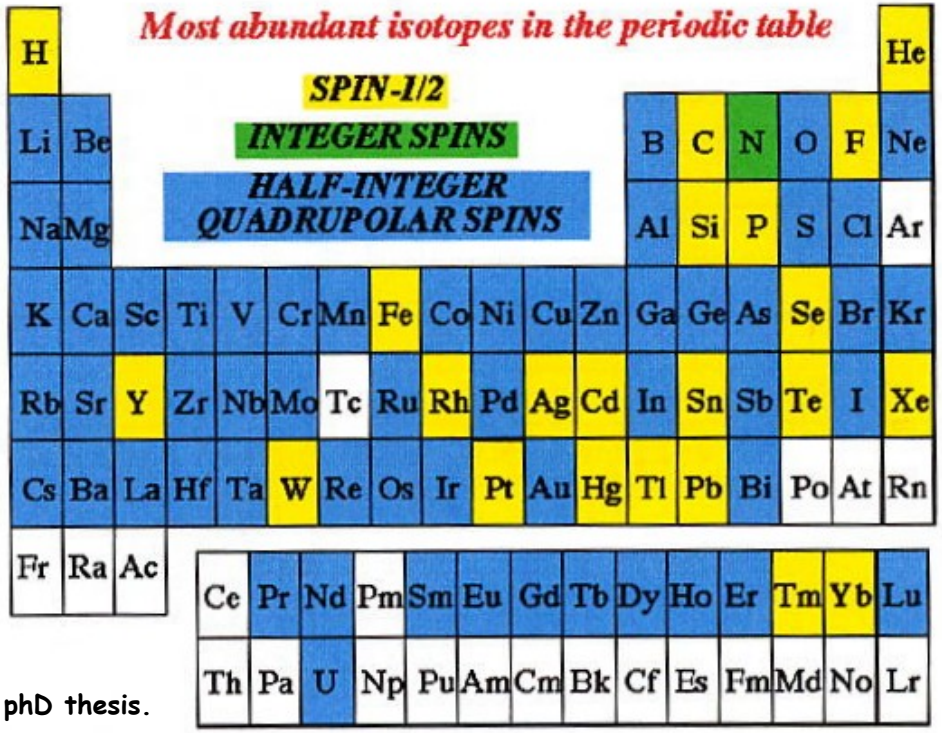


7) Line narrowing techniques for Q nuclei, 1988, 1995 (Virlet, Llor, Pines, Frydman)

The nuclear spin quantum number I

$\nu_0 = \gamma B_0 / 2\pi$

! I ≠ 0 ! ⟶ NMR...



Ziarelli, phD thesis.

spin

electron 1/2

neutron 1/2

proton I=1/2

photon 1

intrinsic angular momentum

$I = n/2$

n: integer

identity card:

isotope ^{13}C

spin I (m_I)

natural abundance (%)

gyromagnetic ratio (rad s^{-1} T^{-1})

receptivity:

$$D^P = \frac{|\gamma_X|^3 \ (\%X) \ (I_X+1)I_X}{\gamma_{1H}^3 \ (\%^1H) \ (I_{1H}+1)I_{1H}}$$

^{13}C: I = ½ (1.1%)

^{12}C: I = 0 (98.9%)

$D^P(^1H) = 1$

$D^P(^{13}C) = 0.00017...$!

Nuclear spins and... fields

$\nu_0 = \gamma B_0 / 2\pi$

$\hat{\mu} = \gamma \hat{I}$

magnetic moment

spin angular momentum

gyromagnetic ratio

$E = - \mu \cdot B$

B_0 (~10T)

$\Delta m_I = \pm 1$

$m_I = -1/2$

$\Delta E = \gamma h B_0 / 2\pi$

$m_I = +1/2$

$\nu_0 = \gamma B_0 / 2\pi$

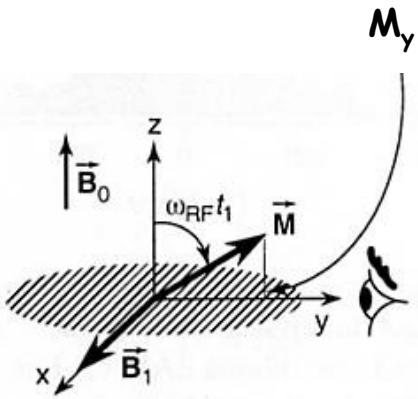
Larmor frequency !

Boltzmann equation

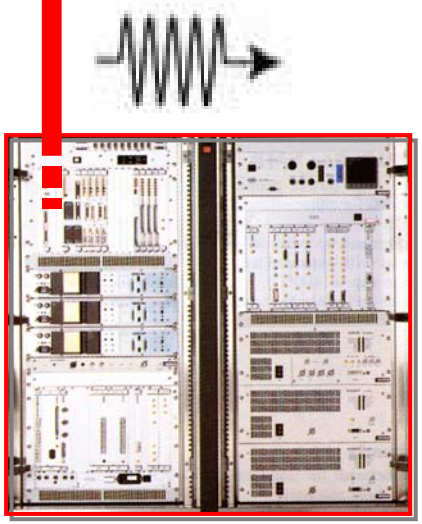
Curie law

$$M = \frac{N \gamma^2 h^2 B_0 I(I+1)}{12 \pi^2 kT}$$

M



Man, Encyclopedia of analytical chemistry, 2000, 12228.



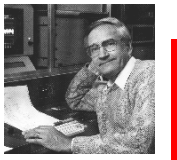
B_1(RF) at resonance !

order of magnitude: very small...
what about sensitivity in NMR ?

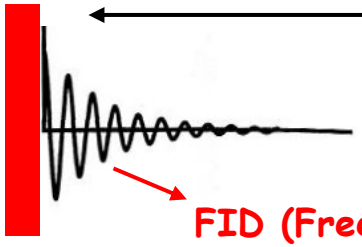
Fourier transform NMR

$\nu_0=\gamma B_0/2\pi$

the basic idea:

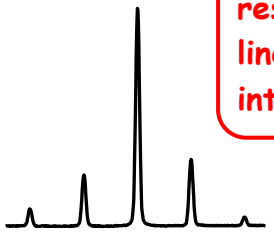


N times !



wait ~ 5 T_1

FT



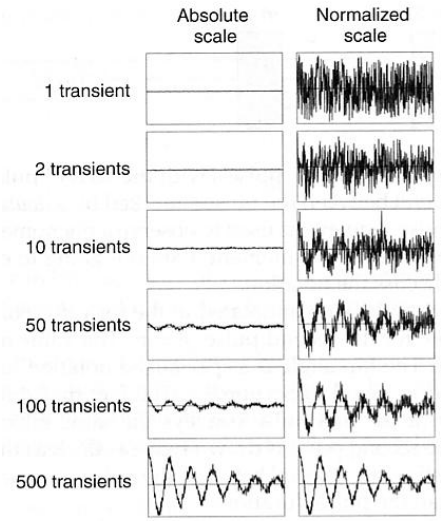
resonance shift
linewidth
intensity

RF pulse (B_1)

FID (Free Induction Decay)
(time domain !)

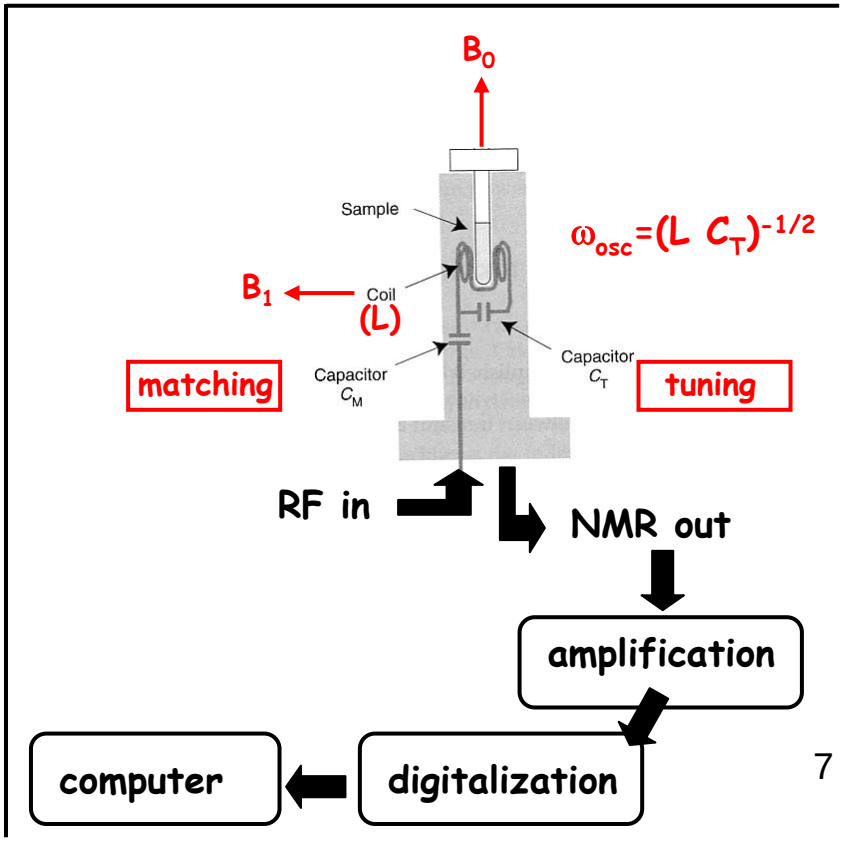
spectrum
(frequency domain !)

back to equilibrium !



Signal/Noise ~ $\sqrt{N}$

Levitt, Spin dynamics, 2002.

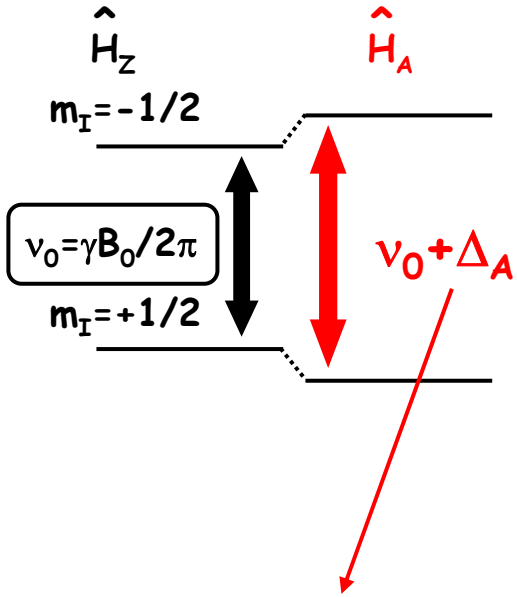


A word of quantum mechanics...

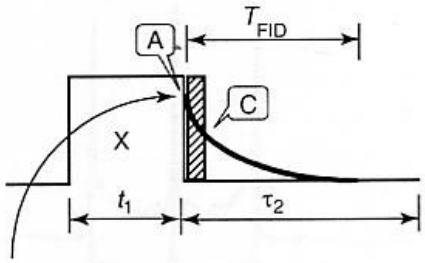
$\nu_0 = \gamma B_0 / 2\pi$

going into quantum mechanics: $\hat{H}_Z = -\gamma B_0 I_z$

$\hat{H}_{RF} = -\gamma B_1 (\cos\omega_{RF} t) I_x$



A: interaction between the nucleus and the surrounding species (nuclei, e^-) !

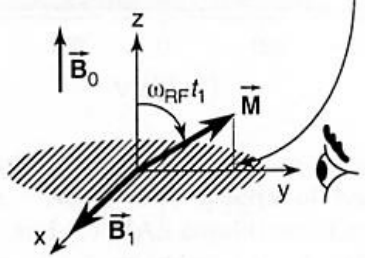


$\langle I_y(t_1)\rangle = \mathrm{Tr}[\rho(t_1) I_y]$

$\propto$ Area of the absorption line

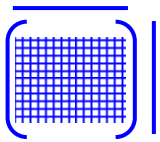
$\langle I_y(t_1)\rangle = \mathrm{Tr}[\rho(t_1) I_y]$

$\propto$ Area of the absorption line



10^{18} spins: density matrix

$$\rho_{ml} = \sum_q p^{(q)} c_m^{(q)} c_l^{(q)*} = \overline{c_m c_l^*}.$$

$\rho(t) =$ 

$$\frac{\partial}{\partial t}\rho(t) = -\frac{i}{\hbar}[H(t), \rho(t)]$$

Liouville-von Neumann equation

$$\langle A \rangle = \sum_{l,m=-j}^{j} \rho_{ml} A_{lm} = \mathrm{Tr}(\rho)(A).$$

observable

ex: I_y

Man, Encyclopedia of analytical chemistry, 2000, 12228.

Interactions in Nuclear Magnetic Resonance

INT: internal

EXT: external

Path 2

direct dipole-dipole

(dipolar)

(INT)

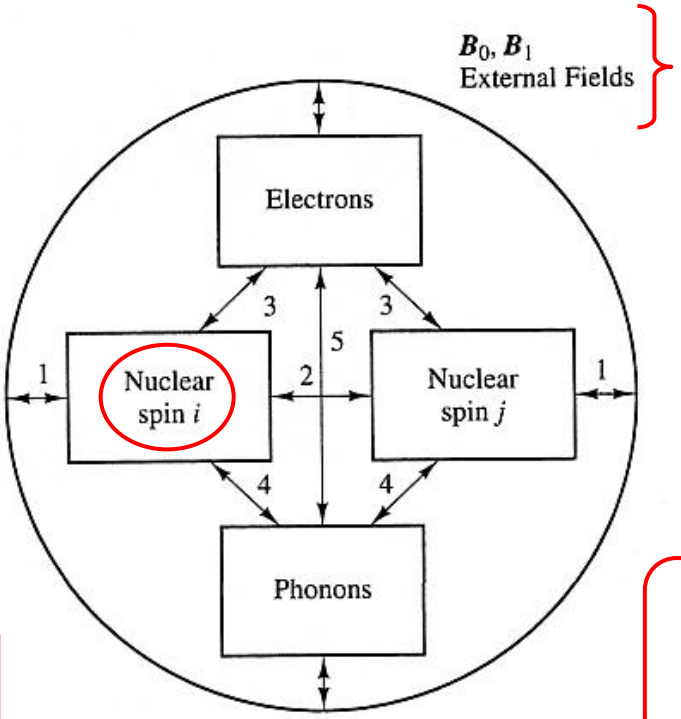
Path 3

electron-nucleus

(chemical shift, quadrupolar, J, Knight shift)

(INT)

spies for structural data !



Path 1

(EXT)

creation and manipulation of quantum states !

Paths 4, 5

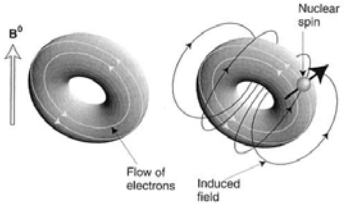
relaxation

back to equilibrium !

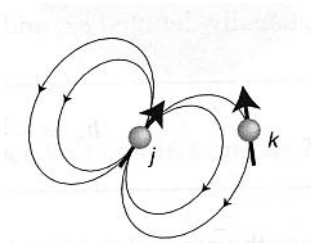
$$H = \underbrace{H_{ext}}_{(H_0 + H_{RF})} + \underbrace{H_{int}}_{(H_D + H_{CS} + H_Q \ldots)}$$

Mehring, High resolution NMR in solids, 1983, 8.

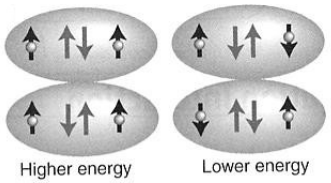
Relevant interactions for chemists



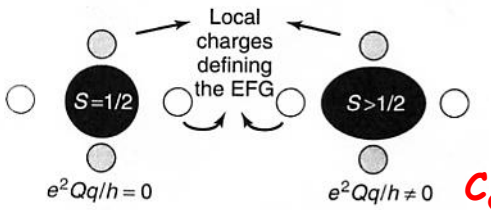
chemical shift: δ



dipolar coupling: D



indirect coupling: J



$C_Q \neq 0$

quadrupolar interaction ($I > \frac{1}{2}$)

Levitt, Spin dynamics, 2002.
Frydman, Encyclopedia of NMR, supp. Vol., 263.

mathematical treatment

$$\hat{\mathcal{H}}_{\text{int}} = \hbar \hat{\boldsymbol{I}} \cdot \boldsymbol{A} \cdot \hat{\boldsymbol{X}} = \hbar(\hat{I}_x \quad \hat{I}_y \quad \hat{I}_z) \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} \hat{X}_x \\ \hat{X}_y \\ \hat{X}_z \end{pmatrix}$$

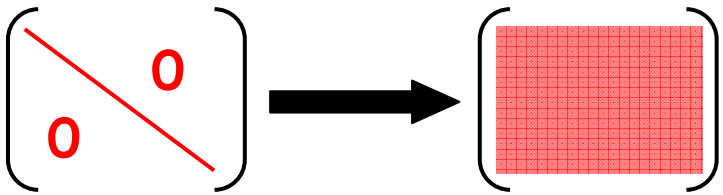
(CS, D, Q...)

nuclear spin operator

the interaction : a rank 2 (symmetrical) tensor

another nuclear spin operator or B_0...

anisotropy : why ?

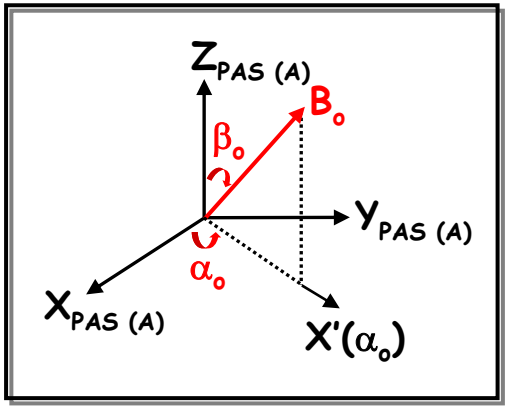


diagonal in the PAS !

LAB !

Principal Axes System (PAS) – Principal values A_{ii} -Ellipsoid representation

for any interaction A (CS, D, Q...)

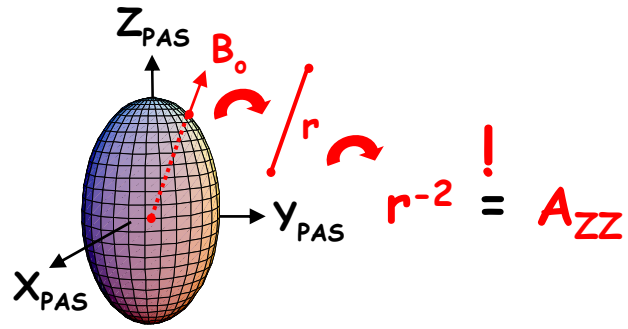


$$\begin{pmatrix} A_{11} & & 0 \\ & A_{22} & \\ 0 & & A_{33} \end{pmatrix}$$

... at the nucleus level ! ...

$$\begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix}_{LAB} = \begin{pmatrix} \\ f(\alpha_0,\ \beta_0) \\ \\ \end{pmatrix}_{LAB}$$

in « first order »...for the correction of energy levels

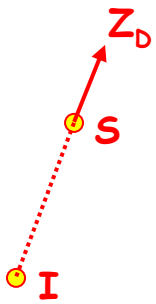


analytical equation: $A_{11}X^2+A_{22}Y^2+A_{33}Z^2 = 1$

semi-axes: $(A_{ii})^{-1/2}$

an important constant: the trace TrA = ΣA_{ii} or A_{iso} = 1/3 TrA

ex: traceless tensors: D, Q



$$[D]_{PAS} \propto D \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

dipolar constant

Interactions in solution state NMR

... a degenerate case: all interactions are averaged to their *isotropic* values...

Remember !

$Tr(CS) \neq 0$

$Tr(J) \neq 0$!

$Tr(D) = Tr(Q) = 0$

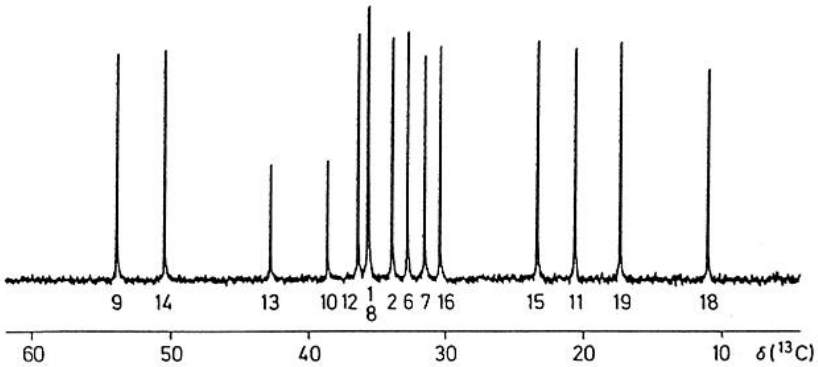
CS: « position of lines », fingerprint for given species

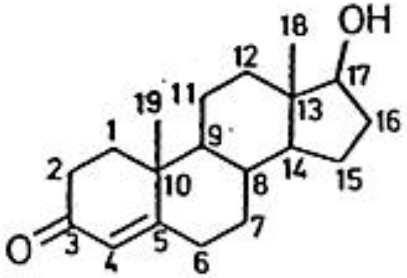
J coupling: «multiplets», connections

(note that D and Q influence relaxation processes...)

! high resolution NMR !

$^{13}C-\{^{1}H\}$: a steroid



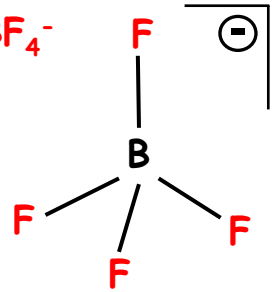


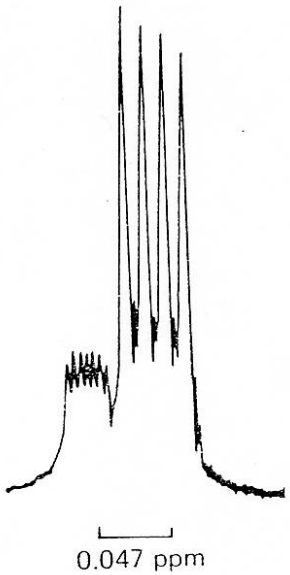
J coupling and multiplets

suppose a S spin J coupled to n spins I...

(2nI + 1) lines are expected !

ex: ^{19}F spectrum of BF_4^-

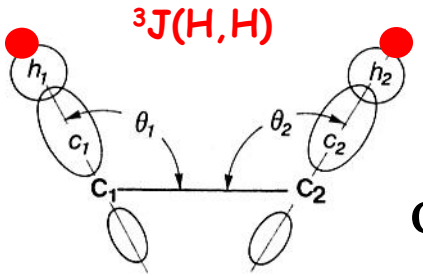


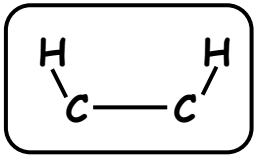


^{10}B (I=3): 7 lines (nat. ab. 20%)

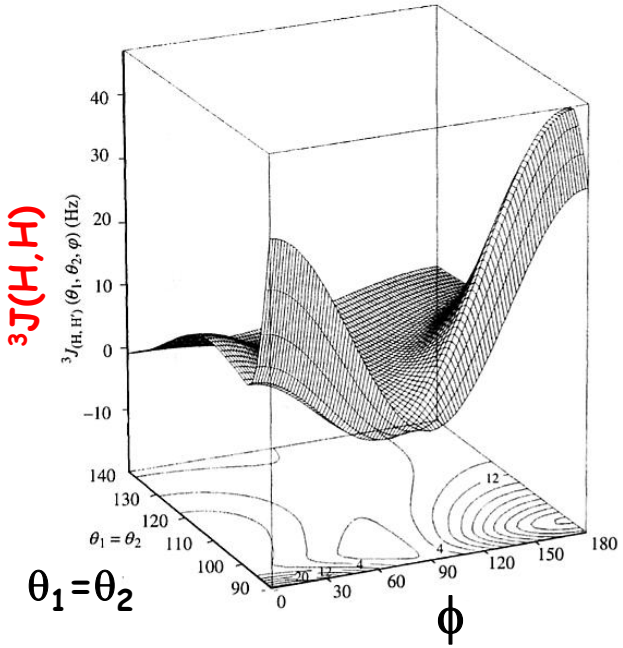
^{11}B (I=3/2) : 4 lines (nat. ab. 80%)

a tool of structural investigation



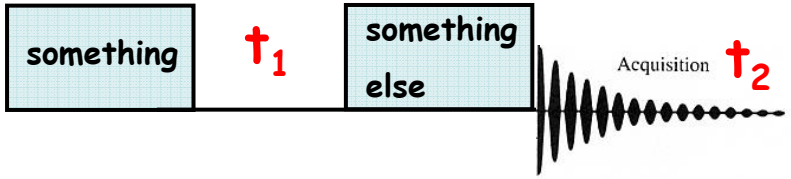


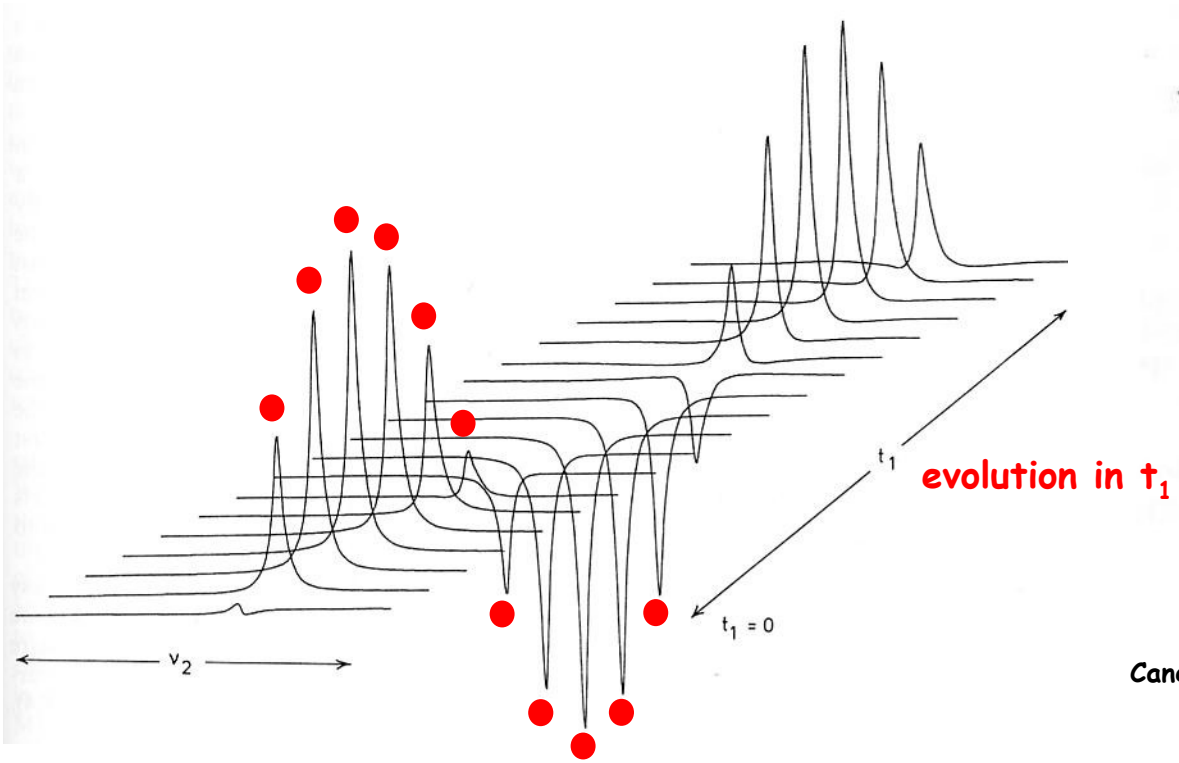
ϕ: dihedral angle



Barfield et al., J. Am. Chem. Soc., 1992, 114, 1574.

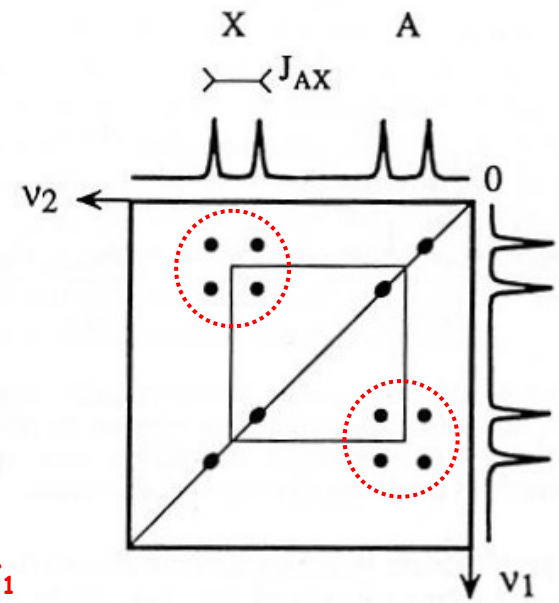
Combining dimensions





Derome, Modern NMR techniques for chemistry research, 1991.

A–X system

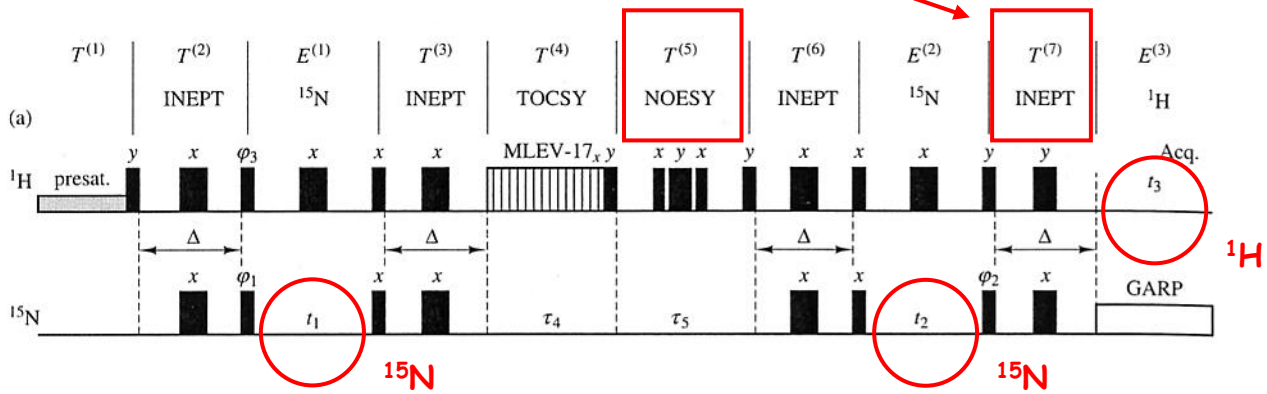


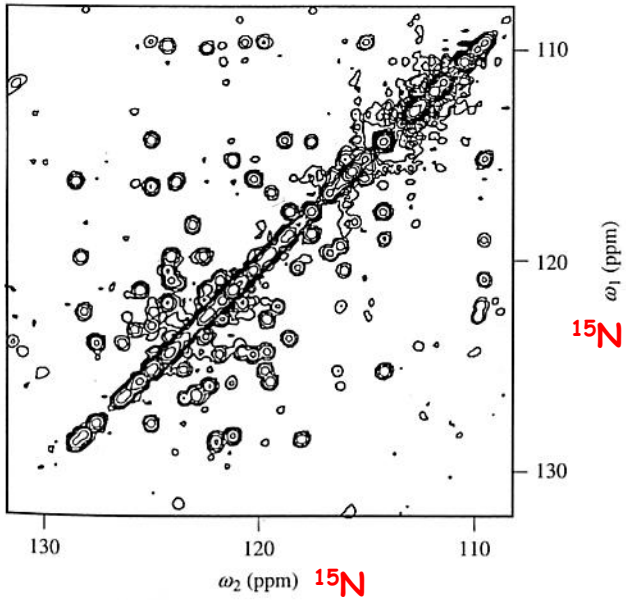
Canet, La RMN: concepts et méthodes, 1991.

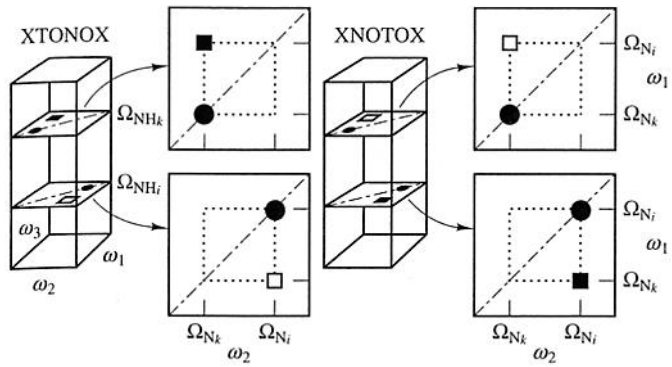
Multidimensional solution state NMR

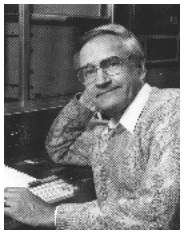
CS and J: selection, transfer, edition, correlation...(COSY, INEPT, HETCOR...)

D: relaxation... (NOESY...)







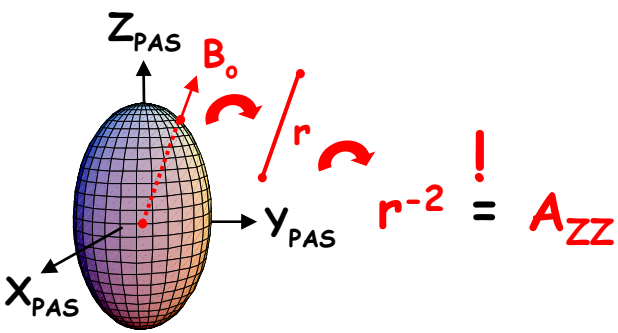


99% ^{15}N-labeled human ubiquitin

Ernst, Encyclopedia of NMR, 1996, 3130.

Back to solid state NMR... the case of a single crystal

remember:

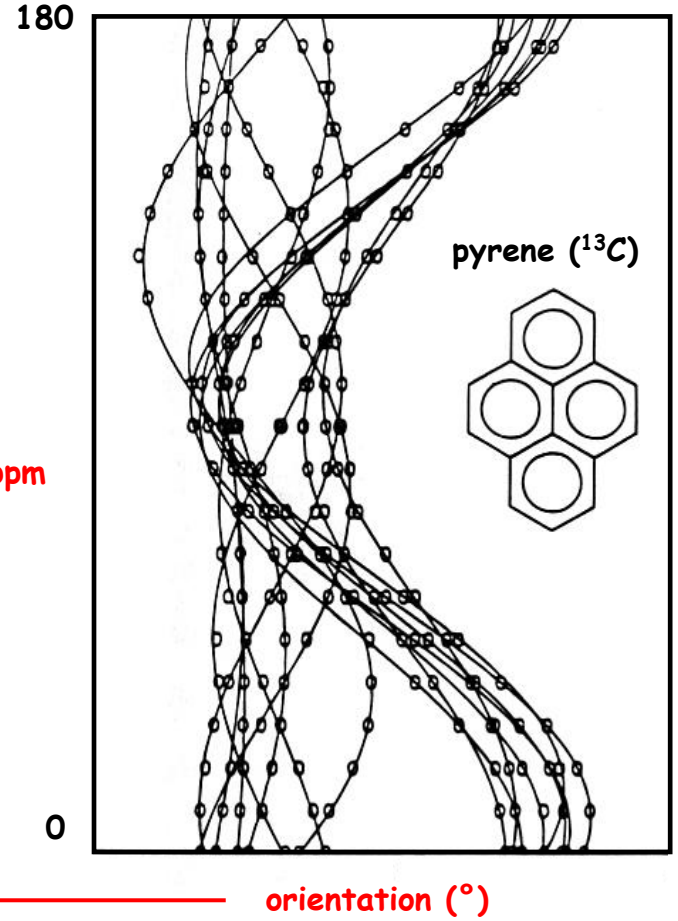


$$r^{-2} = A_{ZZ} = (A_{11}\ \mathrm{Cos}^2\alpha_0 \mathrm{Sin}^2\beta_0 + A_{22}\ \mathrm{Sin}^2\alpha_0 \mathrm{Sin}^2\beta_0 + A_{33}\ \mathrm{Cos}^2\beta_0)$$

... as α_0 and β_0 vary, the value of A_{ZZ} changes...

ex: here $A \equiv \delta$ (the chemical shift, in ppm)

δ_{ZZ}: shift of a particular crystallite oriented by (α_0, β_0) from B_0



extracted data

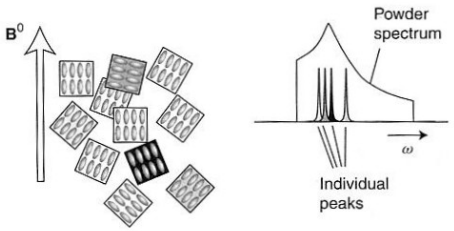
- principal values δ_{ii}
- absolute orientation of the principal axes

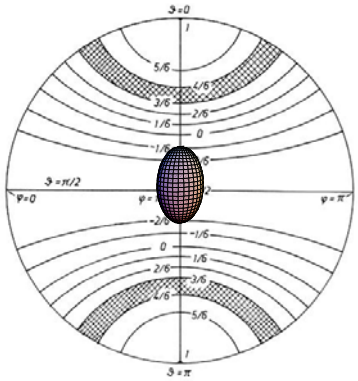
... a high resolution technique in a sense...

BUT: a very demanding technique !

Carter et al., J. Am. Chem. Soc., 1987, 109, 2639.

Only powders available !





... how to construct a CSA lineshape ?

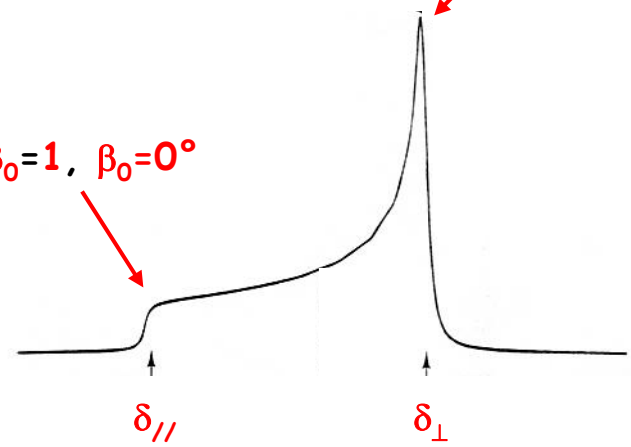
suppose $\delta_{11}=\delta_{22}=\delta_{\perp}$ and $\delta_{33}=\delta_{//}$

$$r^{-2} = \delta_{ZZ} = (\delta_{\perp}\ \mathrm{Sin}^2\beta_0 + \delta_{//}\ \mathrm{Cos}^2\beta_0)$$

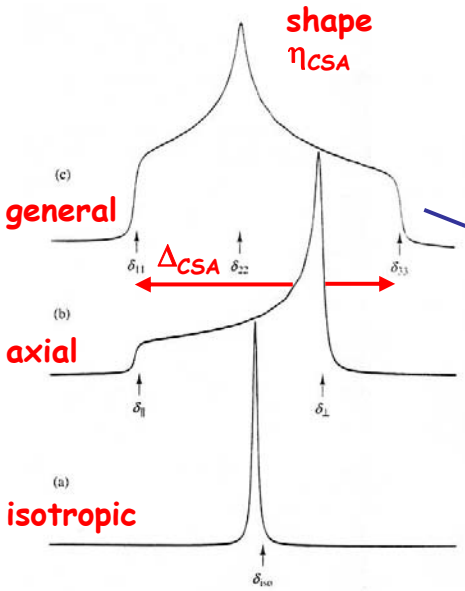
remember: ellipsoid of revolution !

$\mathrm{Cos}^2\beta_0=0$, $\beta_0=90°$

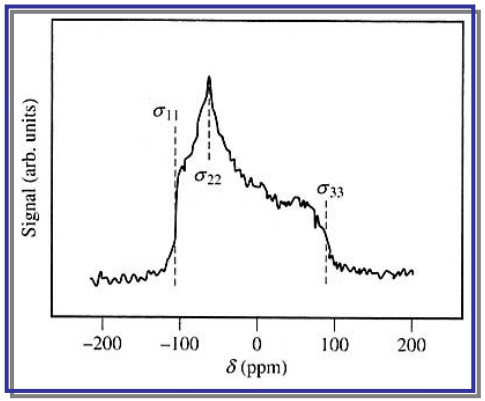
$\mathrm{Cos}^2\beta_0=1$, $\beta_0=0°$



Levitt, Spin dynamics, 2002.
Haeberlen, High resolution NMR in solids, selective averaging, 1976.



^{19}F in fluoranil, $C_6F_4O_2$

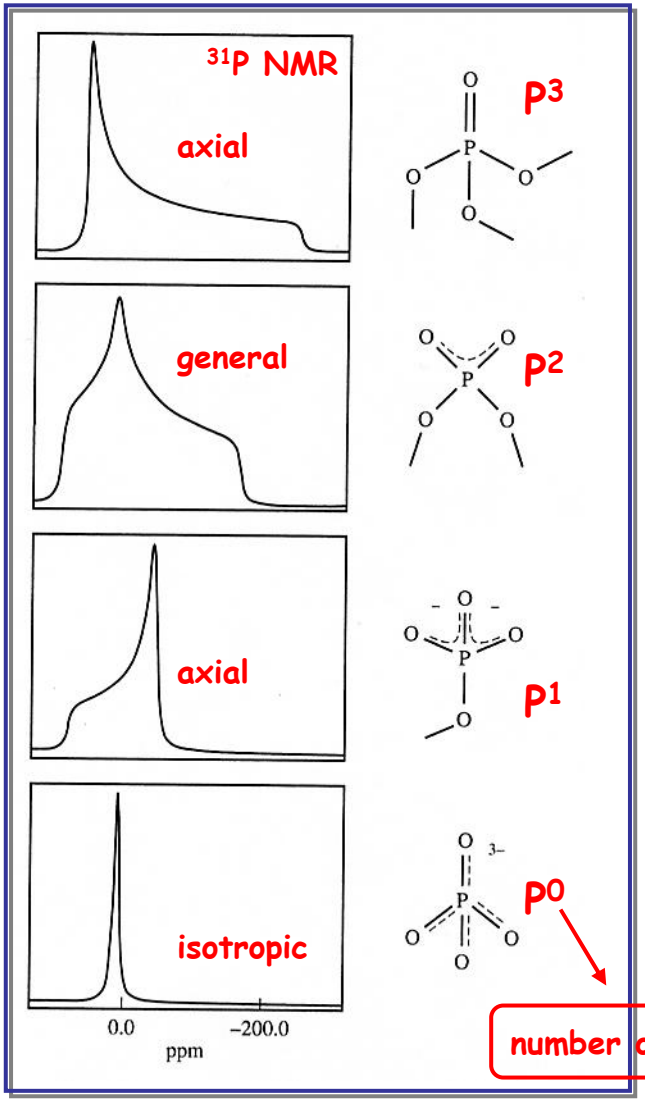


the shape: elliptic integral

$$K(m)=\int_0^{\pi/2} d\varphi\ (1-m\ \sin^2\varphi)^{-1/2}$$

Mehring et al., J. Chem. Phys., 1971, 59, 746.

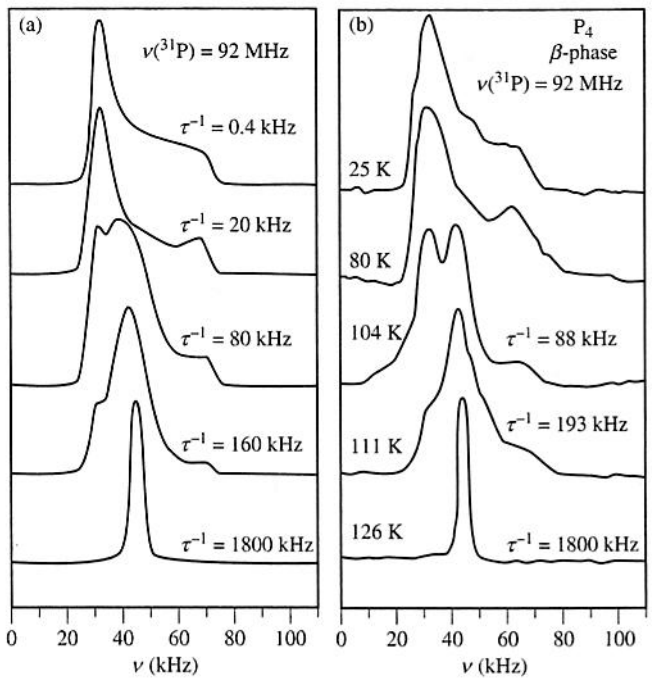
Towards the investigation of local symmetry and molecular motions...



number of P-O-P bridges

key: think at the ellipsoid !

Eckert, Prog. Nucl. Magn. Reson., 1992, 24, 159.



simulation experiment

random jumping tetrahedron (jump rate τ^{-1}) approach for: white phosphorus (β phase)

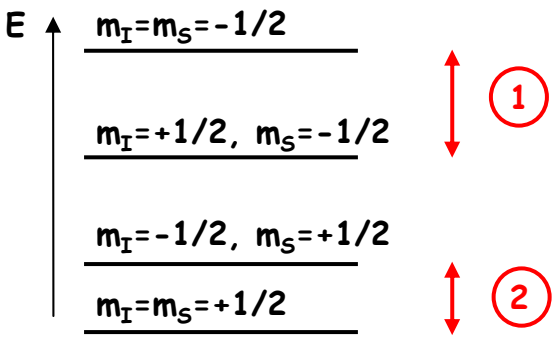
- the role of motion !
- $\tau^{-1} >> \Delta_A$ for averaging !

...time domain NMR...

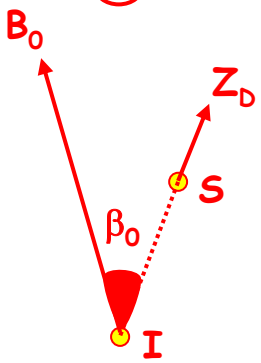
Spiess et al., Chem. Phys., 1974, 6, 226.

Dipolar interaction: the key interaction for distance measurements

consider a spin pair I-S: two I transitions ($\Delta m_I = \pm 1$)...



$$\nu_{(1,2)} = \nu_I \pm D/2\,(1-3\cos^2\beta_0)$$



remember...

$r^{-2} = A_{ZZ} =$

$(A_{11}\ \cos^2\alpha_0 \sin^2\beta_0 +$

$A_{22}\ \sin^2\alpha_0 \sin^2\beta_0 +$

$A_{33}\ \cos^2\beta_0)$

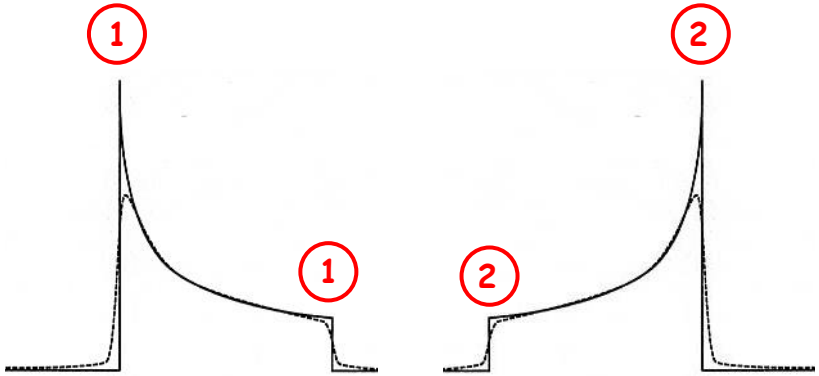
if $A_{11}=A_{22}=1$, $A_{33}=-2$, one finds...

$(1-3\cos^2\beta_0)$!

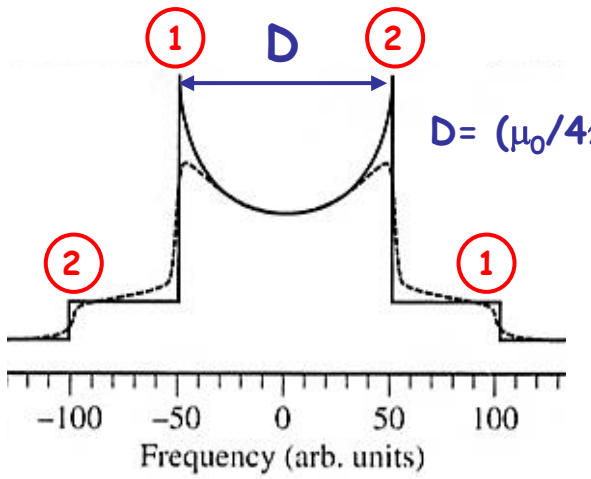
mathematical treatments for CSA and D: identical !

... how to construct a dipolar lineshape ?

no calculation: take an axial pattern and duplicate it !



then, center both lines... that's it !

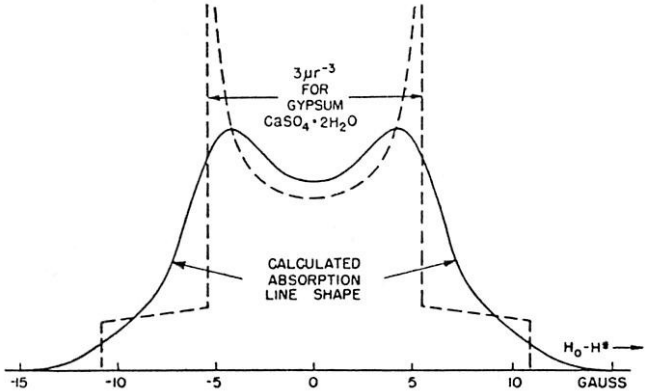


$D = (\mu_0/4\pi)\,(h/4\pi^2)\,\gamma_I\gamma_S/r_{IS}^3$

$D \sim 1/r_{IS}^3$

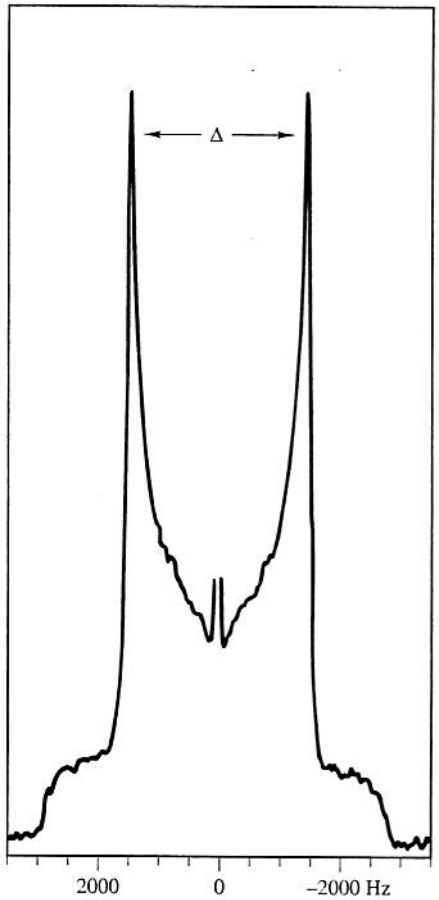
Examples of Pake doublets

Gypsum



Pake, J. Chem. Phys., 1948, 16, 327.

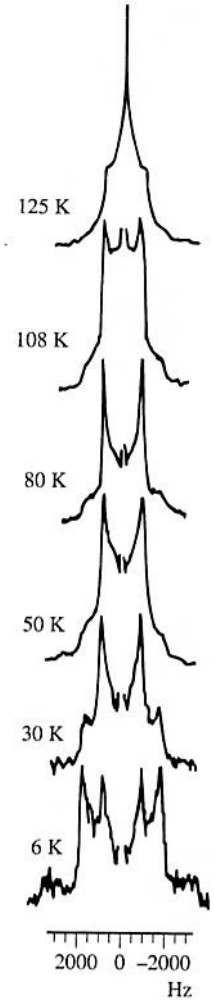
r_{HH} = 1.58 Å



^{13}C-^{13}C acetic acid at T=80K

Engelsberg et al., J. Magn. Reson., 1990, 88, 393.

dipolar interaction and motion



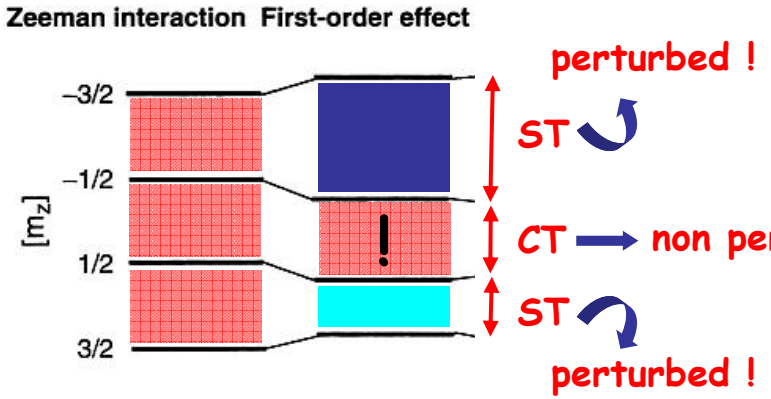
benzene (1,2-$^{13}C_2$) chemisorbed on Pt/η-Al_2O_3

Engelsberg et al., J. Phys. Chem., 1994, 98, 2397.

Quadrupolar interaction: first-order effects

remember: I > ½ (^{27}Al, ^{23}Na, ^{17}O...)

ex: I=3/2



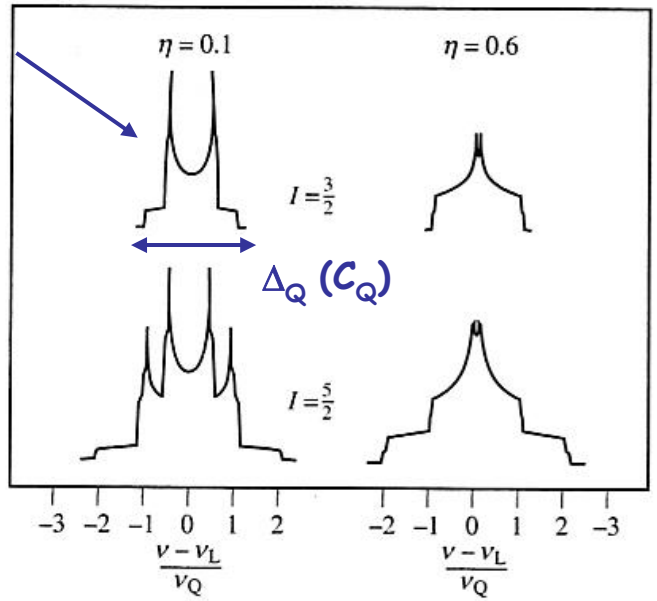
multitransitions system !

CT: central transition

ST: satellite transition

shape η_Q

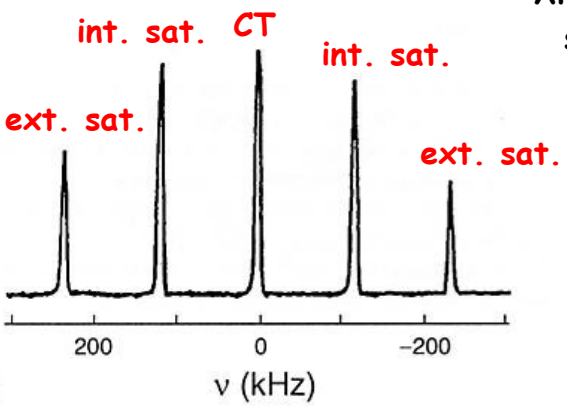
$C_Q = e^2qQ/h$



Freude et al., NMR Basic Princ. Prog., 1993, 29, 25.

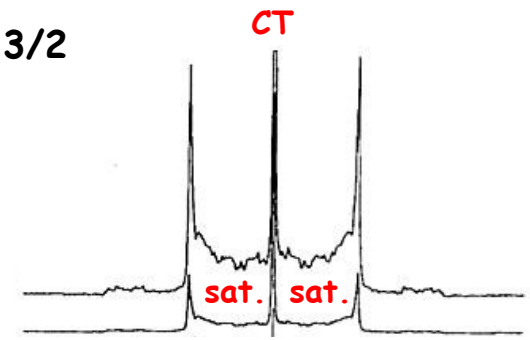
without calculation (!), find the mathematical form of the first-order quadrupolar shift...

I = 5/2



^{27}Al in α-Al_2O_3 single crystal

I = 3/2



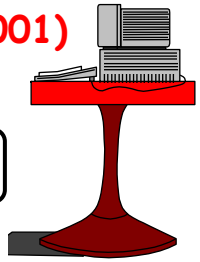
^{23}Na in $NaNO_3$ powder

Man, Encyclopedia of analytical chemistry, 2000, 12229.

Tensorial parameters: *ab initio* calculations

Pickard, Mauri (2001)
Profetta

PARATEC program



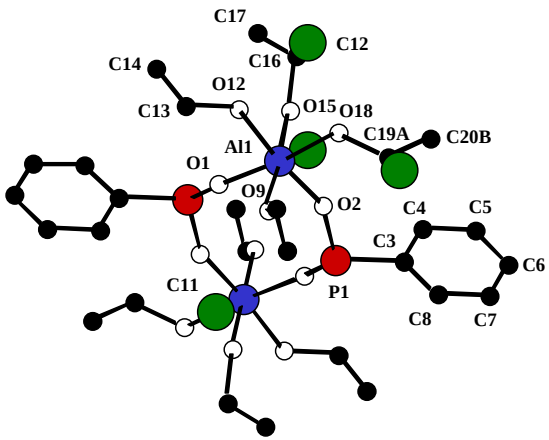
periodic systems

all-electron hamiltonians

evaluation of $j^{(1)}(r')$ using pseudopotentials

$$B_{in}^{(1)}(r) = 1/c \int d^3r'\ j^{(1)}(r') \times \frac{r-r'}{|r-r'|^3}$$

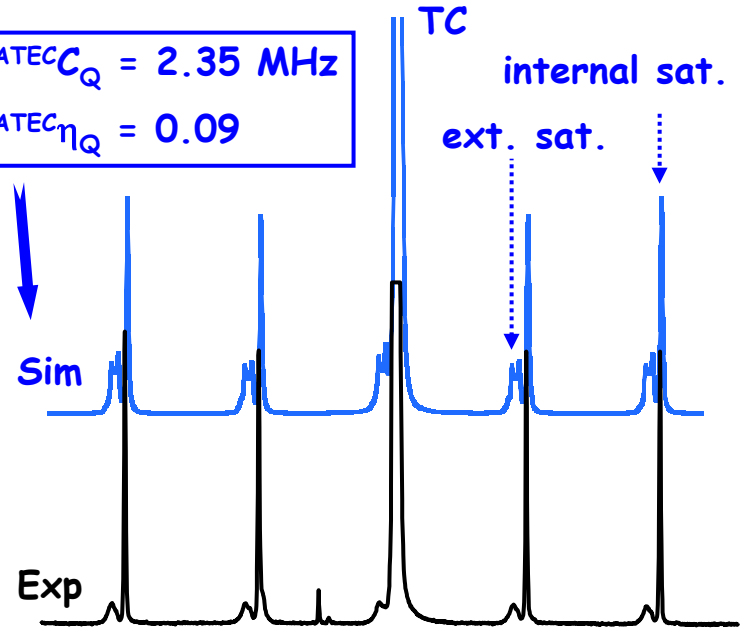
$$B_{in}^{(1)}(r) = -[\sigma](r)\ B$$



see Christel and Thierry !

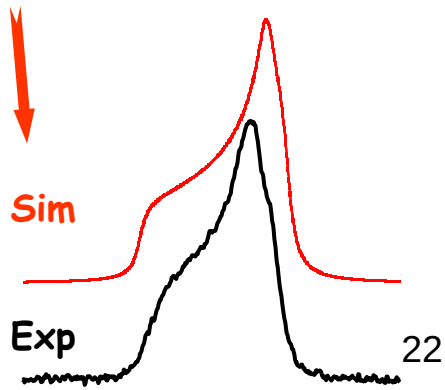
$^{PARATEC}C_Q$ = 2.35 MHz

$^{PARATEC}\eta_Q$ = 0.09



$^{PARATEC}\delta_{iso.}$ = 12.6 ppm

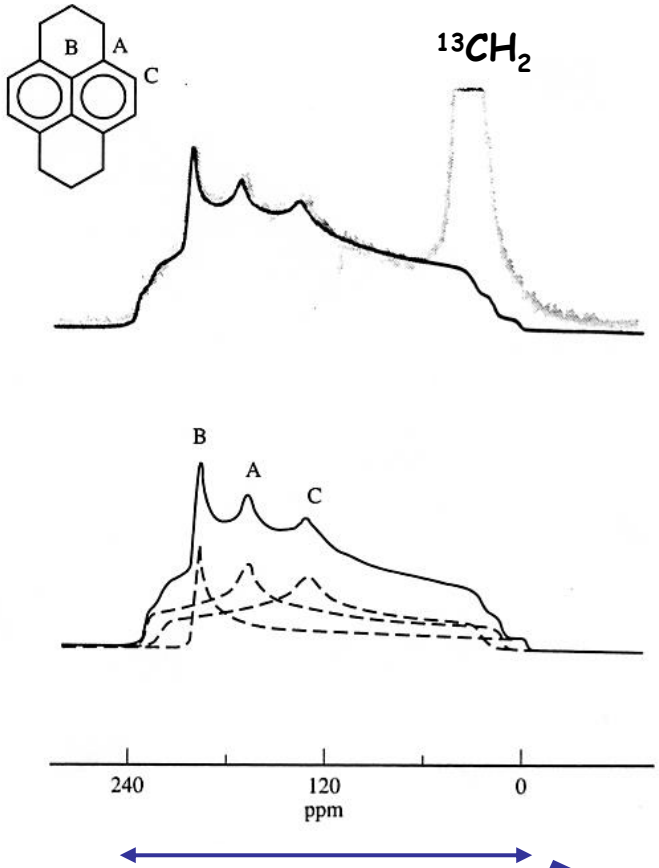
$^{PARATEC}\eta_{CSA}$ = 0.24; CSA = 60.6 ppm



Solid state NMR of powders: the lack of resolution !

let us take an example...

^{13}C: 1,2,3,6,7,8-hexahydropyrene

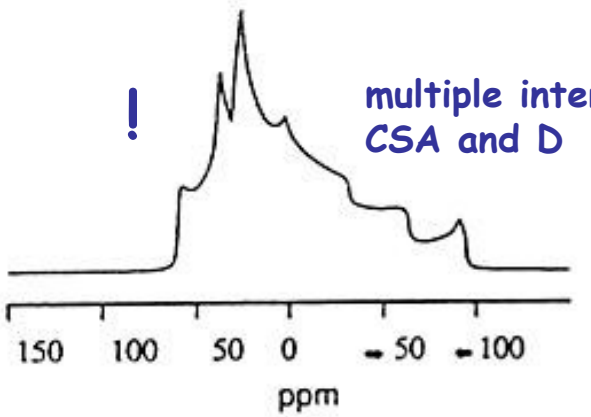


Sethi et al., Prep. Am. Chem. Soc., 1987, 32, 155.

all crystallographically equivalent nuclei contribute to one and the same powder pattern !

moreover, all interactions participate !

- CSA: it depends ! (see CH_2 vs A,B,C) ..... $\propto B_0$
- D: up to ~ 30 kHz ! ..... B_0 ind.
- Q: up to ~ several MHz ! { B_0 ind. (1st) / $1/B_0$ (2nd) }
- J: up to ~ 100s Hz ..... B_0 ind.

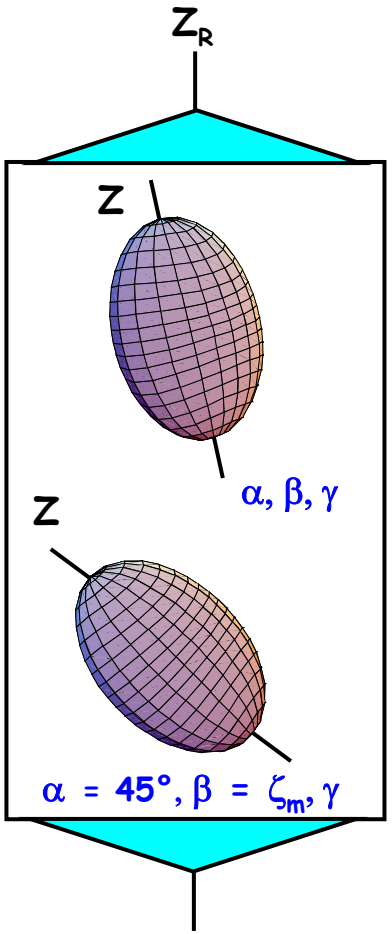


multiple interactions: here CSA and D

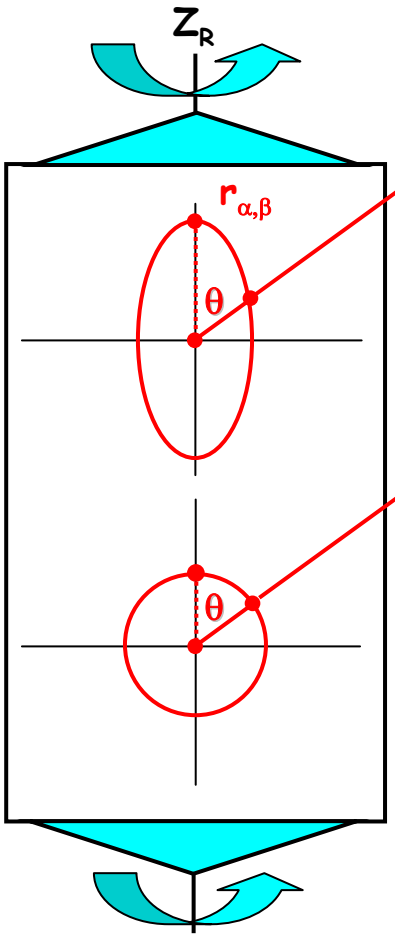
the whole ^{13}C chemical shift range !

Towards high resolution: the MAS experiment ! ($I = \frac{1}{2}$)

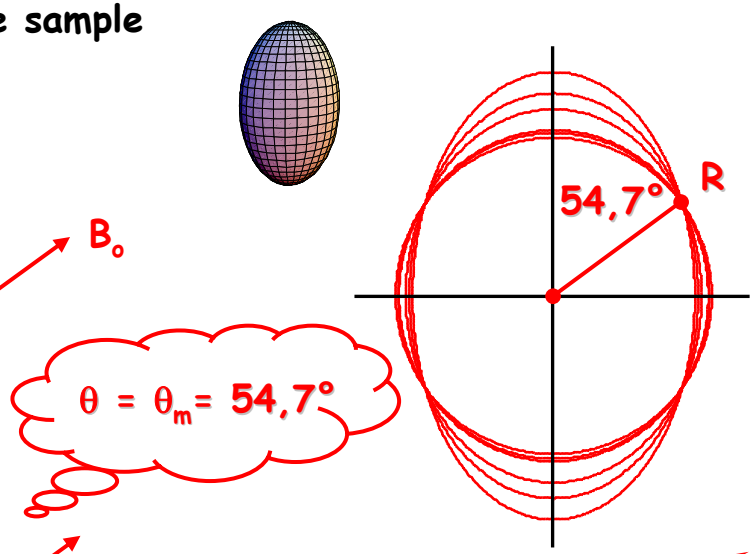
the key idea: a **macroscopic (!)** reorientation of the sample



static



MAS



R is **independant** of α,β,γ !

and $R^{-2} = \delta_{iso}$!

LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications.

Nuclear Magnetic Resonance Spectra from a Crystal rotated at High Speed

E. R. Andrew
A. Bradbury
R. G. Eades

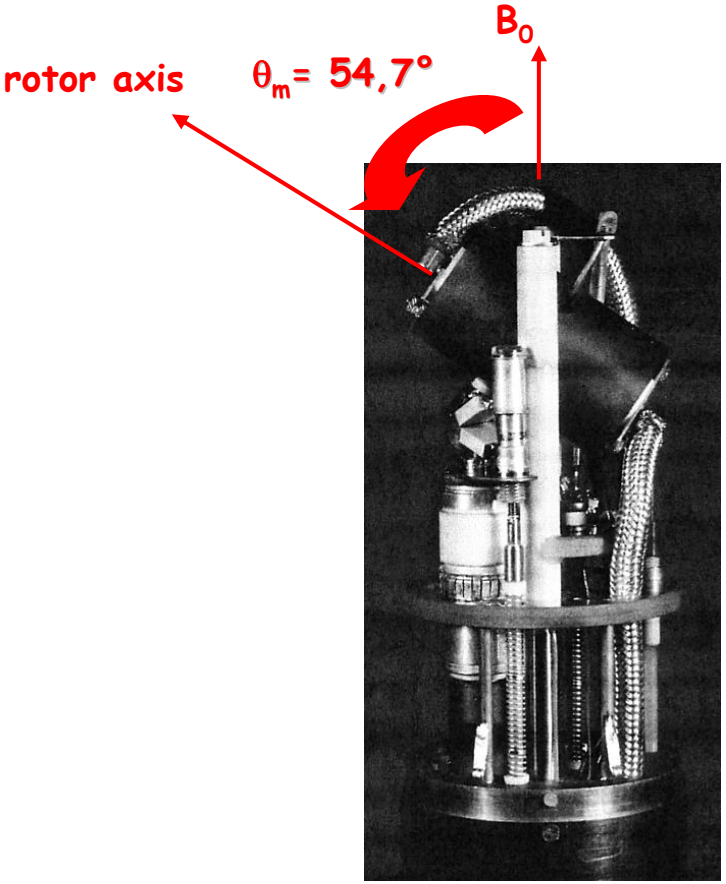
Physics Department,
University College of North Wales,
Bangor,
Caernarvonshire.
Oct. 8.

[1] Gutowsky, H. S., and Pake, G. E., *J. Chem. Phys.*, 18, 162 (1950).
[2] Pake, G. E., *Solid State Phys.*, 2, 1 (1956).
[3] Andrew, E. R., and Newing, R. A., *Proc. Phys. Soc.* (in the press).
[4] Van Vleck, J. H., *Phys. Rev.*, 74, 1168 (1948).

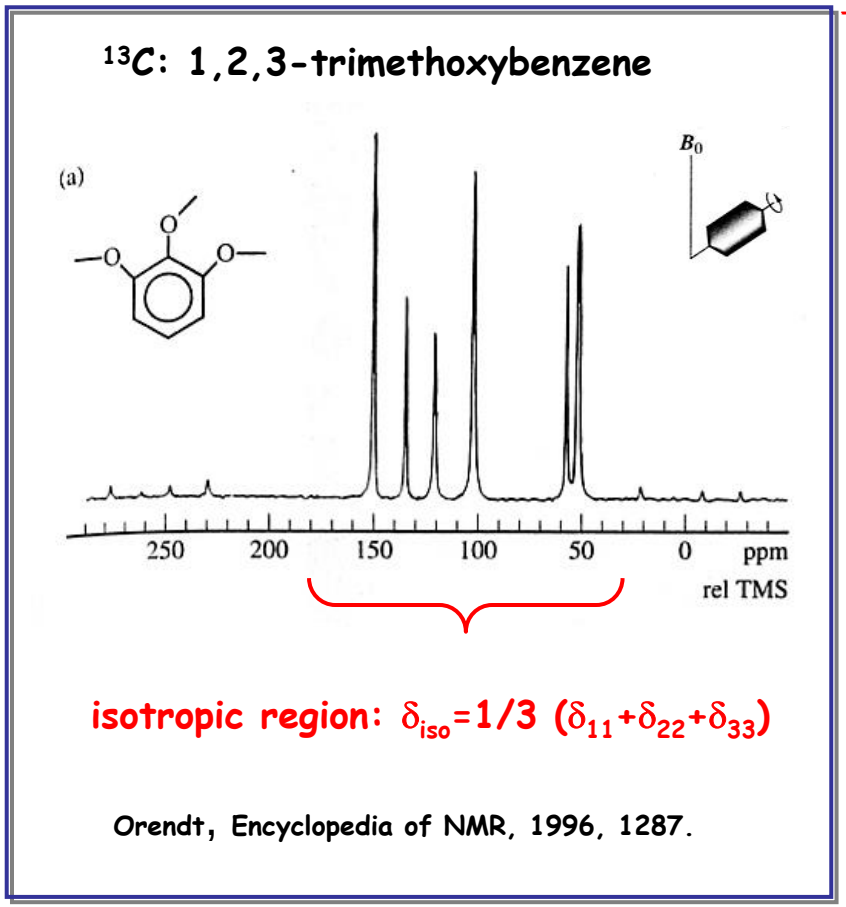
FREE INDUCTION DECAYS OF ROTATING SOLIDS*

I. J. Lowe†
Department of Physics,
Washington University, St. Louis, Missouri
(Received February 9, 1959)

MAS with «infinite» frequency



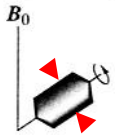
Doty, Encyclopedia of NMR, 1996, 4477.



ϕ: 7mm ⟶ up to 6 kHz

ϕ: 4mm ⟶ up to 15 kHz

ϕ: 2.5mm ⟶ up to 35 kHz



ϕ

«infinite» MAS frequency:

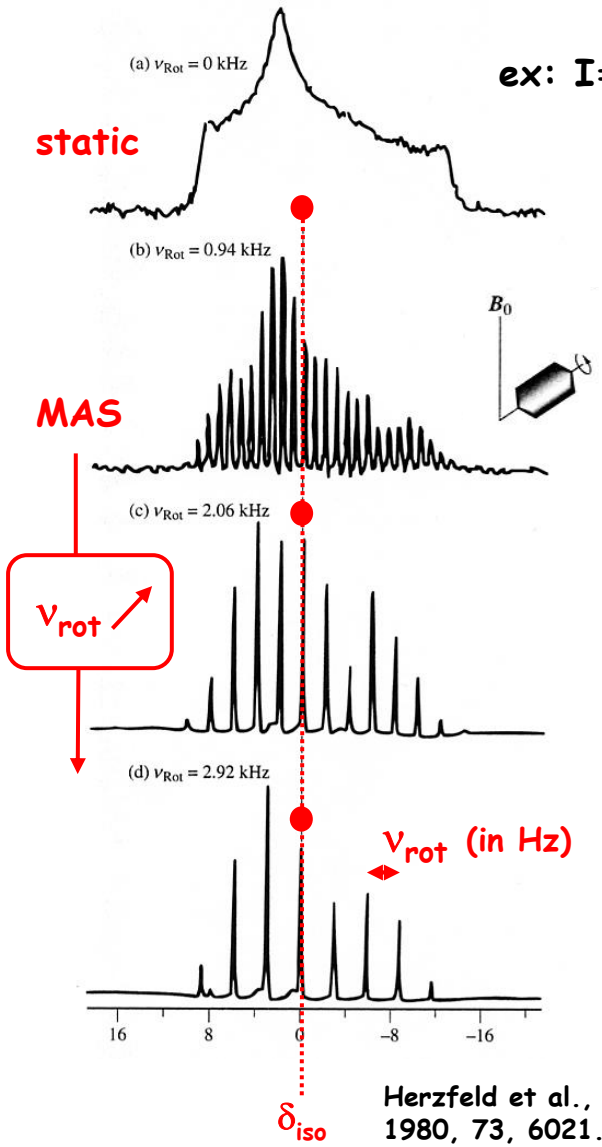
$\nu_{rot} > \Delta_A$ (A= CSA, D, Q...)

question: is it really possible ?...

When $\nu_{rot} \sim \Delta_A$ or $\nu_{rot} << \Delta_A$?

^{31}P: dipalmitoylphosphatidylcholine

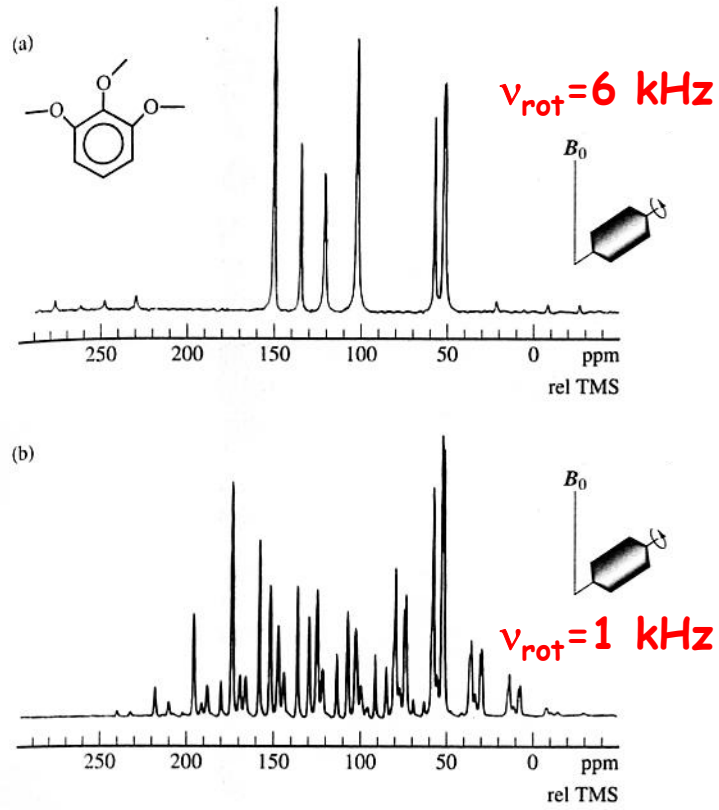
ex: I=1/2, A=CSA



Herzfeld et al., J. Chem. Phys., 1980, 73, 6021.

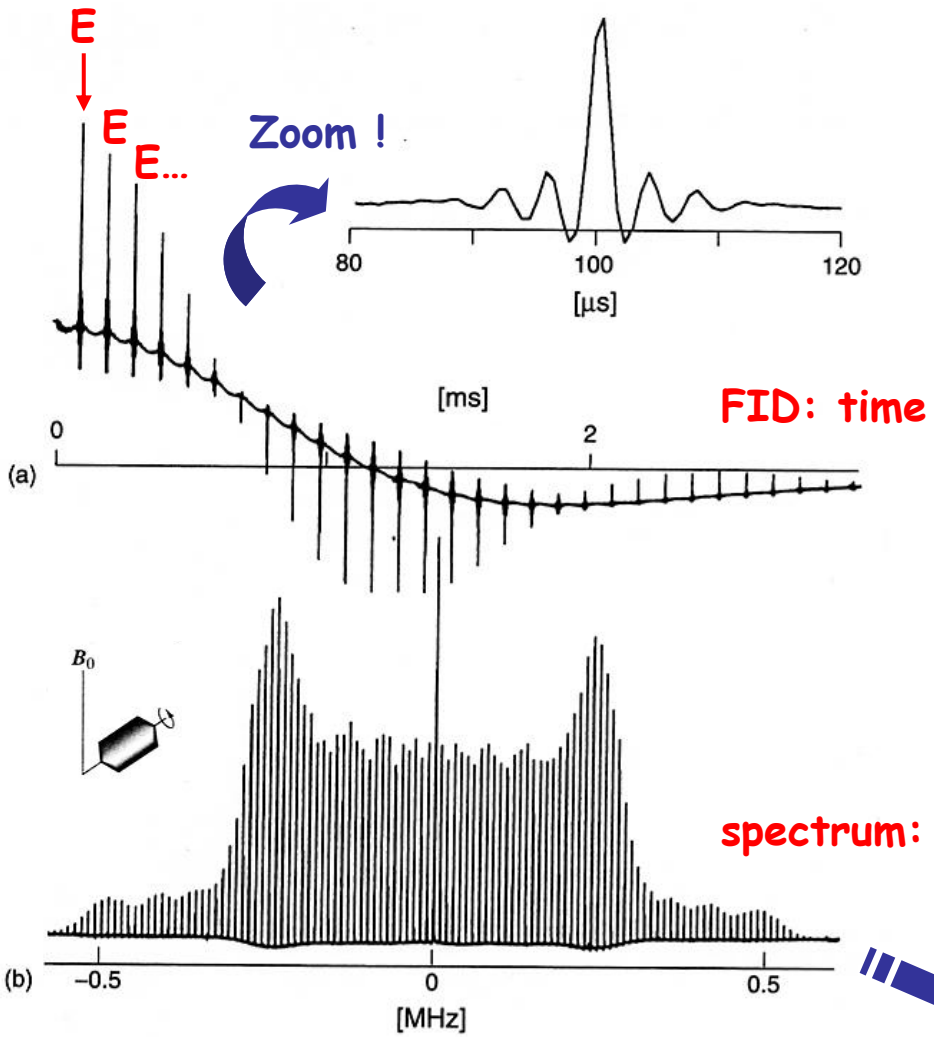
explosion of the spectrum in spinning sidebands !

note: SSB are «thin» lines for CSA



Orendt, Encyclopedia of NMR, 1996, 1287.

MAS in the time domain – Rotational echoes (E)



^{23}Na (I=3/2) in $NaNO_2$ – ν_{rot} = 10 KHz

to set the magic angle...

$K^{81}Br$ (I=3/2)

$K^{127}I$ (I=5/2)

and maximize the number of echoes in the time domain (1 scan !)...

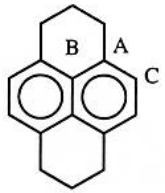
(but is it crucial ?...)

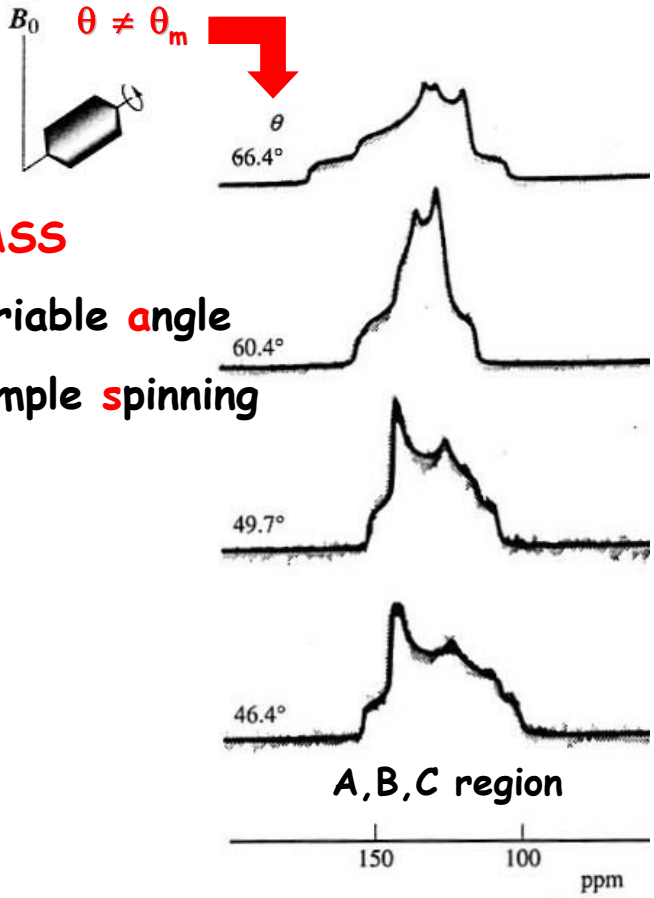
a huge number of SSB : why ?!

Gan, Encyclopedia of NMR, supp. Vol., 135.

«Off-MAS» experiments

^{13}C: 1,2,3,6,7,8-hexahydropyrene





VASS

variable angle

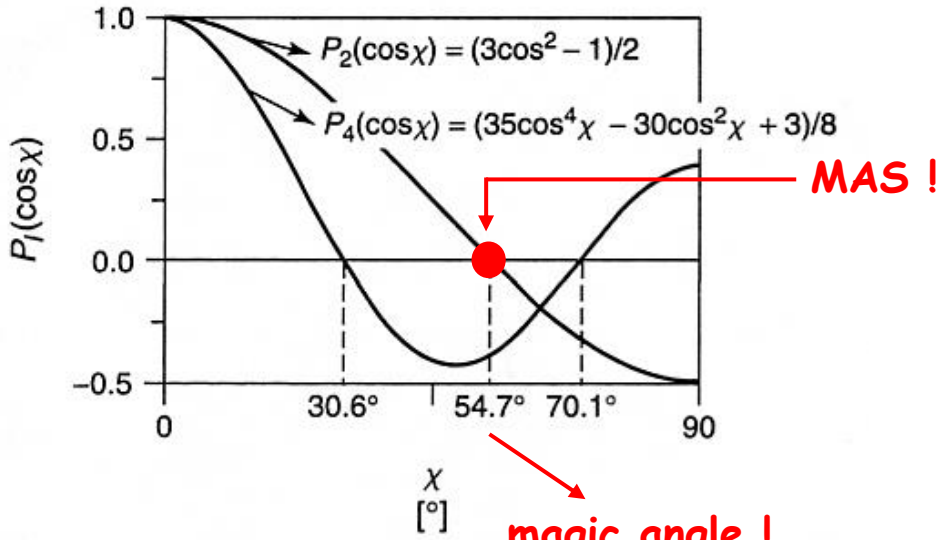
sample spinning

Sethi et al., Prep. Am. Chem. Soc., 1987, 32, 155.

fast rotation at θ: scaling factor of Δ_A

$$\Delta_A P_2(\cos\theta) = \Delta_A \tfrac{1}{2} (3\cos^2\theta - 1)$$

Legendre polynomial !



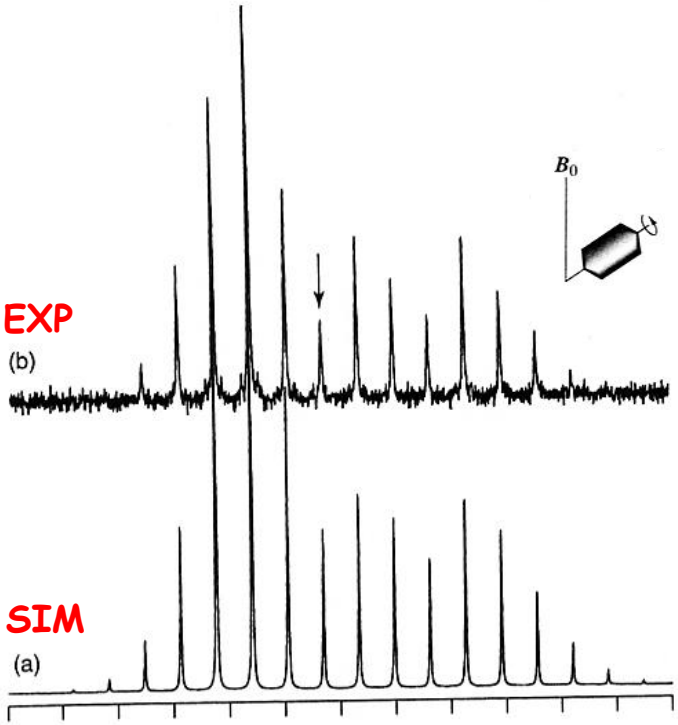
magic angle !

$\theta = \theta_m = 54{,}7°$

More information from the SSB...

ex: CS interaction I = 1/2

^{119}Sn MAS in: tin sulfate

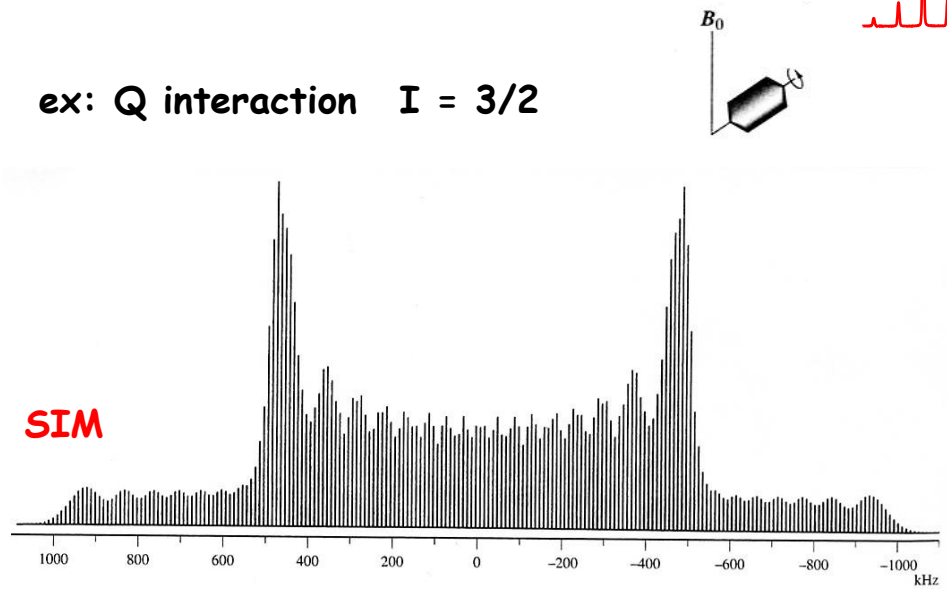


extracted data:

δ_{iso}, η_{CSA}, Δ_{CSA}

Harris et al., Encyclopedia of NMR, supp. Vol., 145.

ex: Q interaction I = 3/2



extracted data:

δ_{iso}, η_Q, C_Q

Jakobsen, Encyclopedia of NMR, 1996, 2374.

SIMulation programs:

DM2003 by Massiot

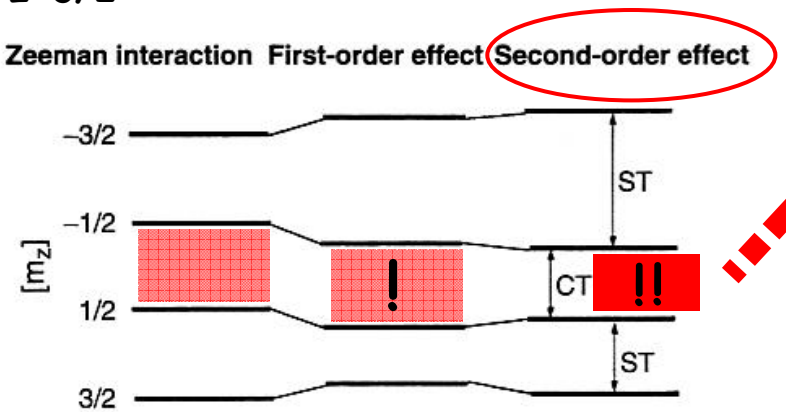
SIMPSON by Bak et al.

WEB !

Quadrupolar nuclei: when C_Q becomes huge !

consider C_Q: 3 to 15 MHz...

I=3/2



$$w^{(2)\text{static}}_{-1/2,1/2} = -\frac{1}{6w_L}\left[\frac{3e^2qQ}{2I(2I-1)\hbar}\right]^2\left\{I(I+1)-\frac{3}{4}\right\}$$
$$\times\{A(\alpha,\eta)\cos^4\beta + B(\alpha,\eta)\cos^2\beta + C(\alpha,\eta)\}$$

$$A(\alpha,\eta) = -\tfrac{27}{8} + \tfrac{9}{4}\eta\cos 2\alpha - \tfrac{3}{8}(\eta\cos 2\alpha)^2$$
$$B(\alpha,\eta) = \tfrac{30}{8} - \tfrac{1}{2}\eta^2 - 2\eta\cos 2\alpha + \tfrac{3}{4}(\eta\cos 2\alpha)^2$$
$$C(\alpha,\eta) = -\tfrac{3}{8} + \tfrac{1}{3}\eta^2 - \tfrac{1}{4}\eta\cos 2\alpha - \tfrac{3}{8}(\eta\cos 2\alpha)^2$$

Man, Encyclopedia of analytical chemistry, 2000, 12229.

as $H_Q \sim H_{Zeeman}$: energy levels are corrected up to second-order in perturbation !

⬇

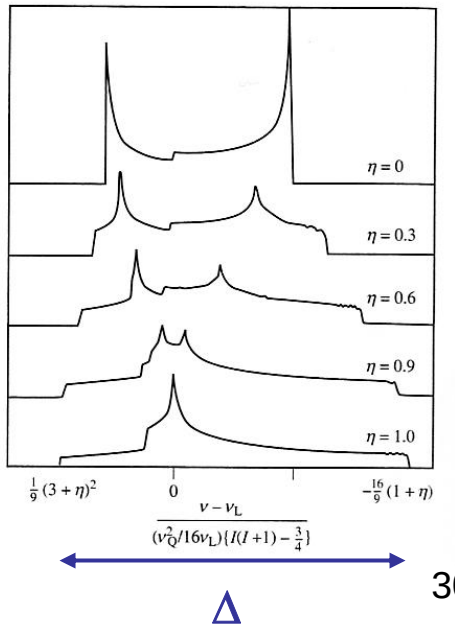
all transitions (ST and CT) are now perturbed

but what is the mathematical treatment...?

shape: η_Q

$\Delta \sim C_Q^2/\nu_L$

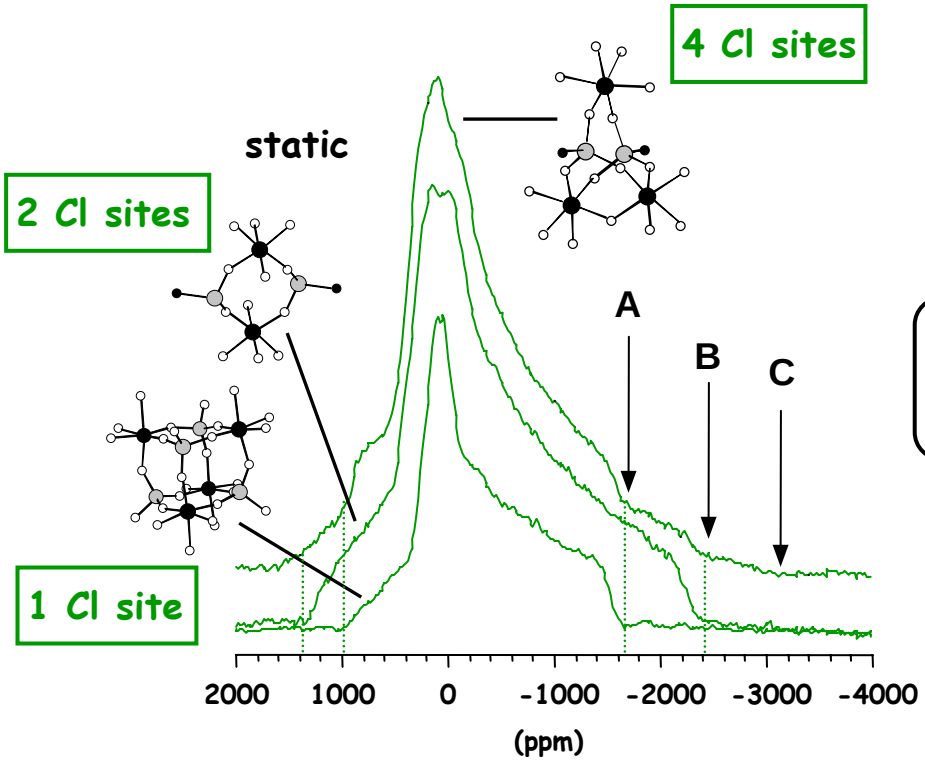
idea: increase B_0 !

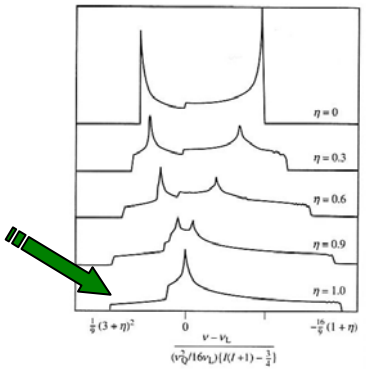


Freude et al., NMR Basic Princ. Prog., 1993, 29, 27.

An exotic nucleus: ^{35}Cl

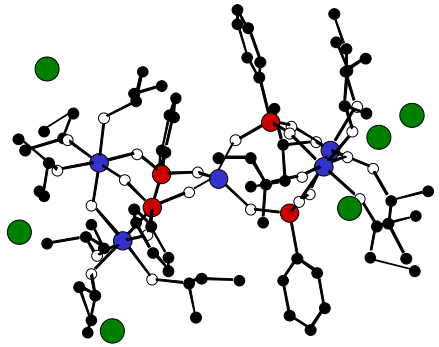
^{35}Cl: I=3/2

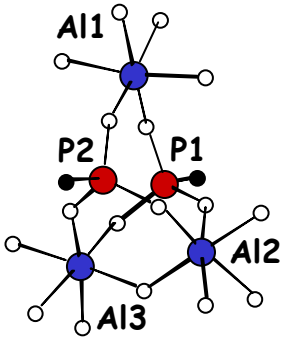




$\eta_Q \sim 1$

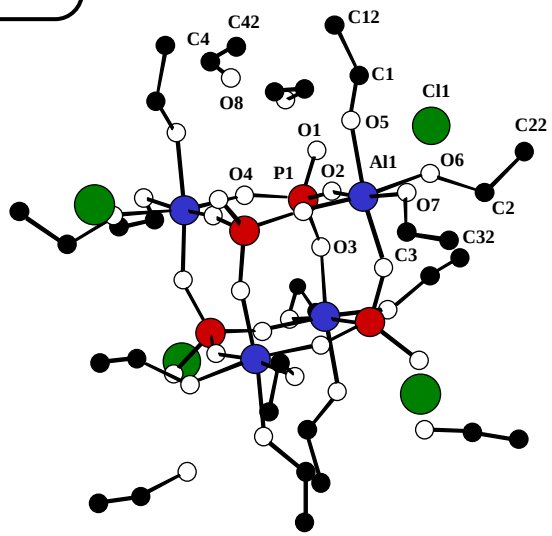
$C_Q \sim 6\text{-}8$ MHz

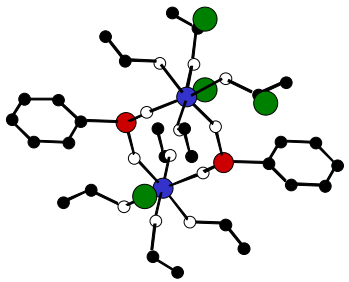




Al-O-P clusters

Cl^- as counter ions

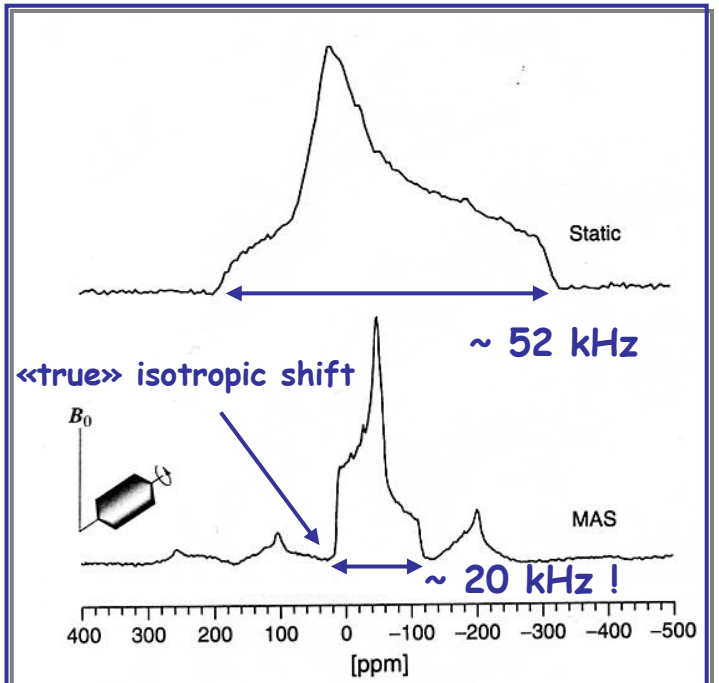




Azaïs et al., Solid State NMR, 2003, 23, 14.

MAS and quadrupolar nuclei

theorem: MAS has an effect... but can not completely average the *second order* quadrupolar broadening !



^{87}Rb in $LiRbSO_4$

Pruski, J. Magn. Reson., 2000, 147, 286.

even at «infinite» MAS frequency !

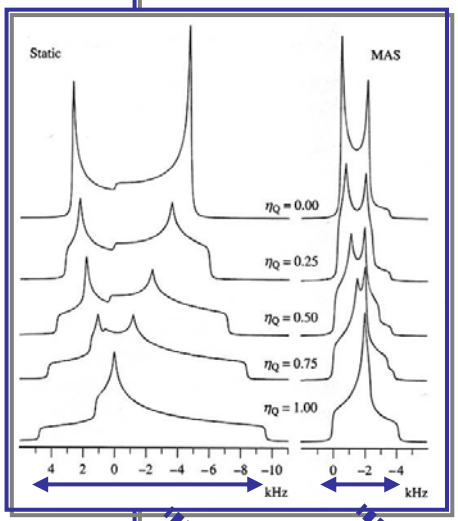
WHY ? (no calculation...)

MAS is completely efficient for:

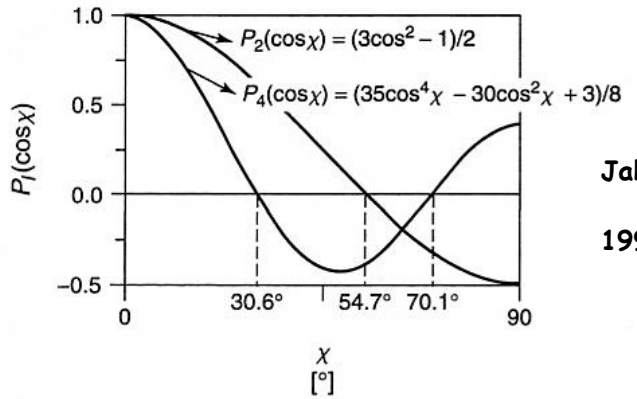
- ellipsoids
- $Cos^2(\alpha_0,\beta_0)$
- $P_2(Cos\theta)$

...but not for:

- quartics
- $Cos^4(\alpha_0,\beta_0)$, $Cos^2(\alpha_0,\beta_0)$
- $P_4(Cos\theta)$, $P_2(Cos\theta)$



Δ_{static} Δ_{MAS}



Jakobsen, Encyclopedia of NMR, 1996, 2371.

ie $P_4(Cos\theta) = P_2(Cos\theta) = 0$...NO !

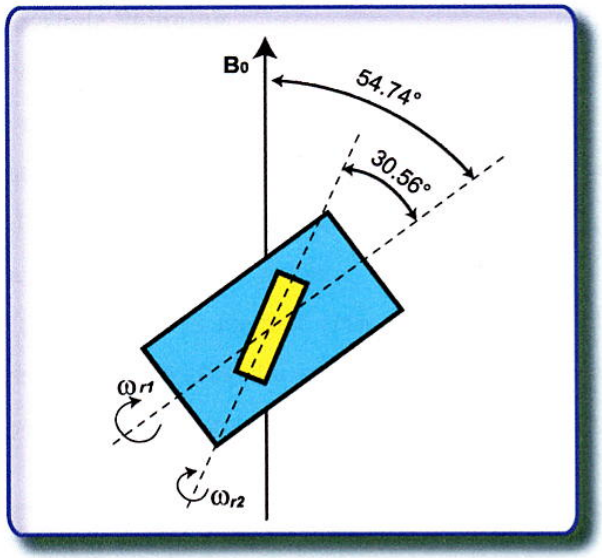
Quadrupolar nuclei and high resolution: the saga

remember MAS: one «degree of freedom» (1959)

let us invent experiments with 2 «degrees of freedom»: for instance 2 angles of reorientation !

DOR (DOuble Rotation) experiment

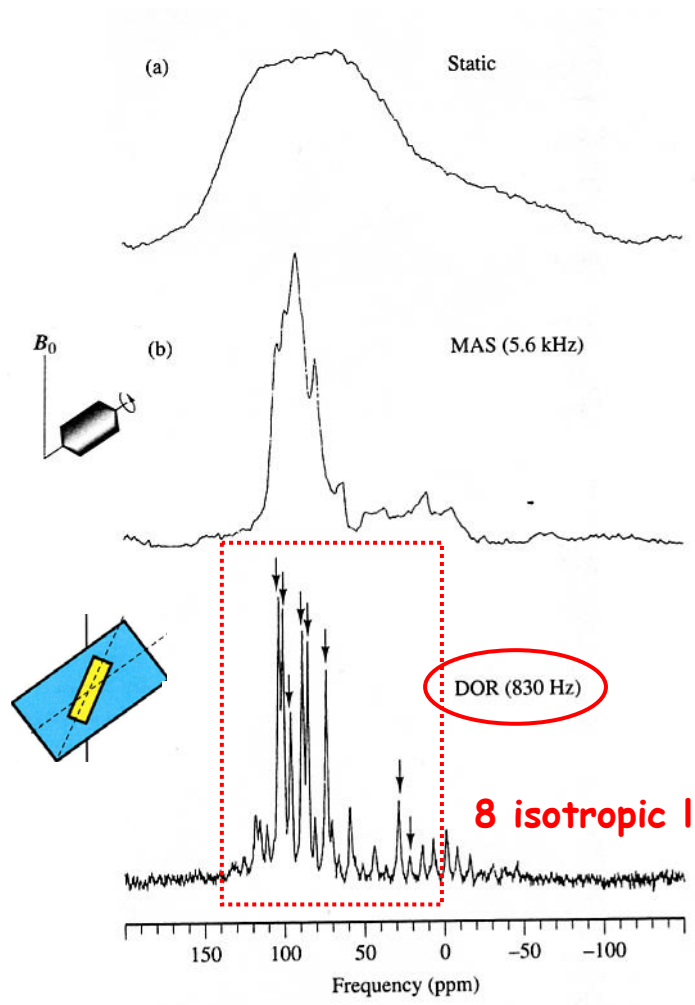
(Samoson, Pines, 1988)



Ziarelli, phD thesis.

a 1D experiment...

^{17}O (I=5/2) in $CaSiO_3$ wollastonite: 9 ^{17}O sites



8 isotropic lines !

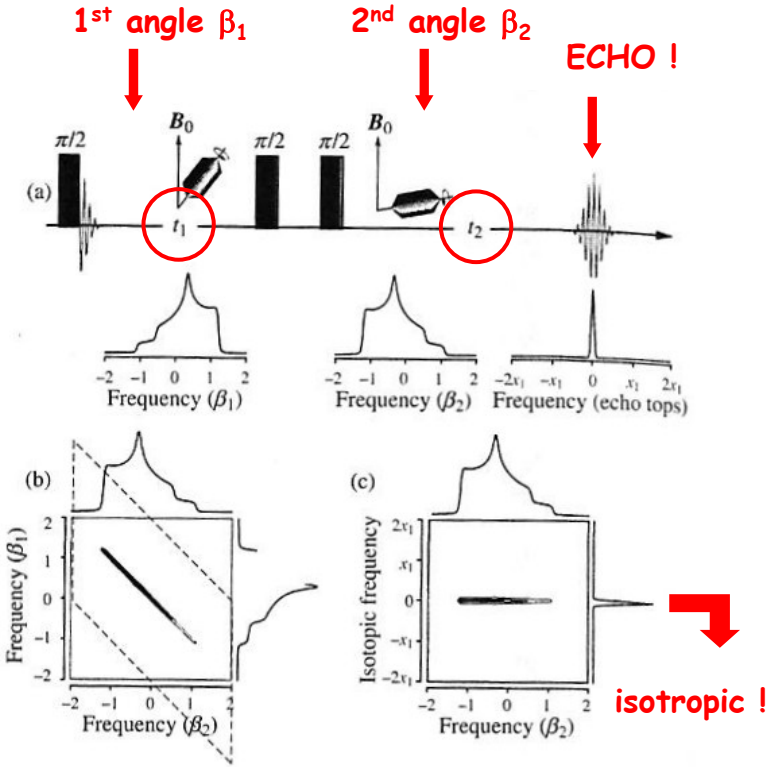
Wu, Encyclopedia of NMR, 1996, 1749.

The DAS approach

another way to introduce 2 angles of reorientation !

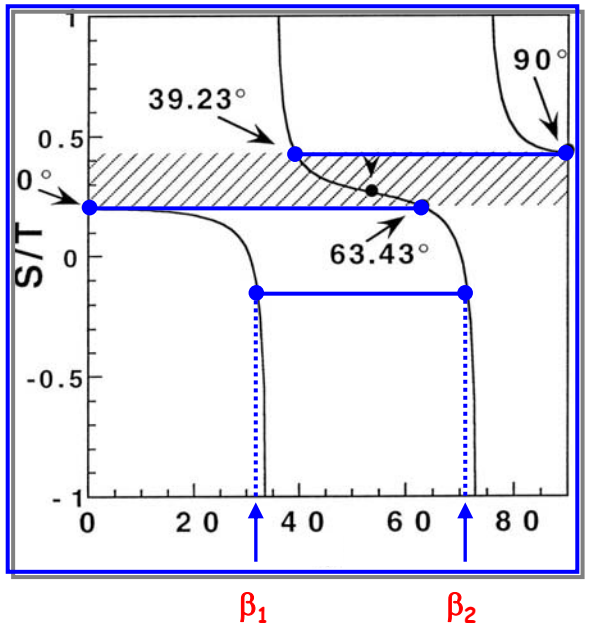
DAS (Dynamic Angle Spinning) experiment

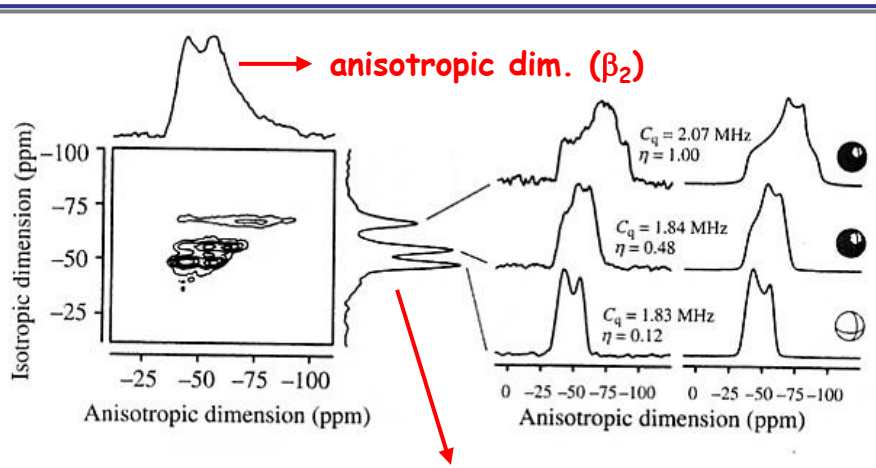
(Llor, Virlet, 1988)



Grandinetti, Encyclopedia of NMR, 1996, 1770.

DAS angle pairs





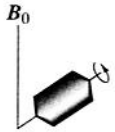
^{87}Rb in $RbNO_3$ 3 isotropic sites !

Spinning around a single axis: MQ-MAS !

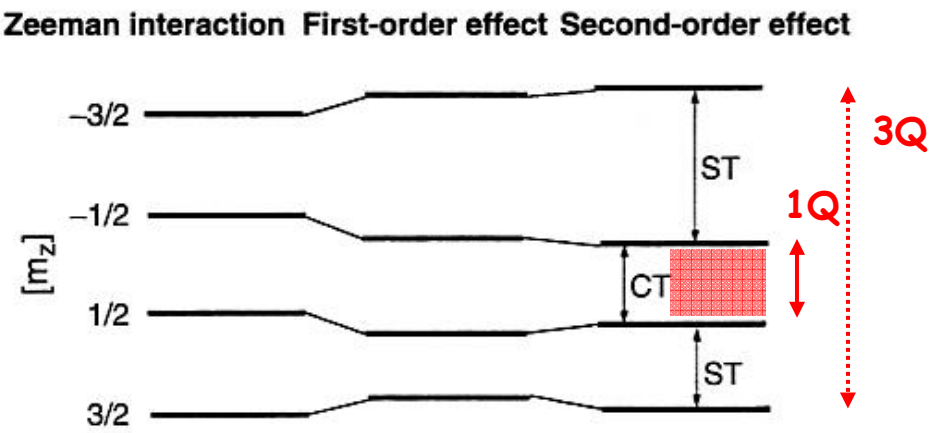
DAS and DOR: 1 transition (CT) and 2 angles...

MQ-MAS (Multiple Quantum MAS)

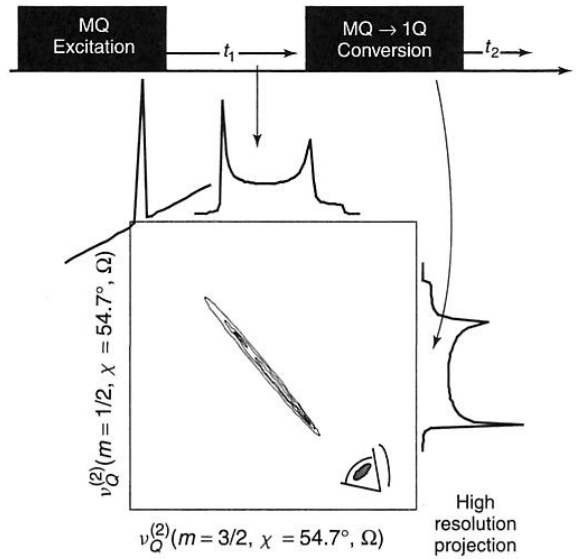
(Frydman, 1995)



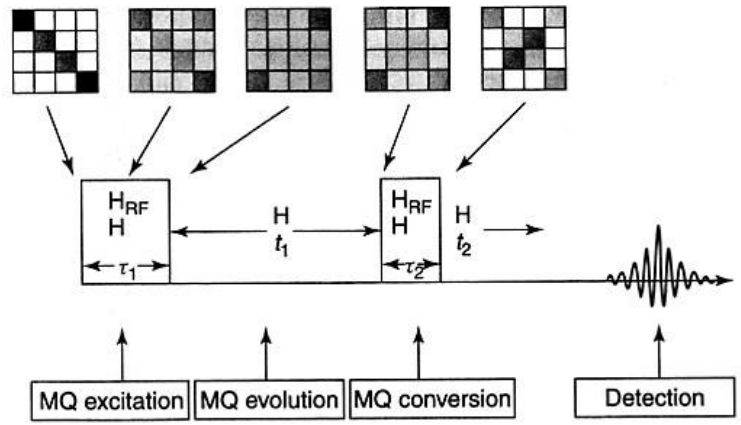
2 transitions (CT/MQ) and 1 angle (MAS) !



the key idea: to correlate 1Q and 3Q and to produce... an ECHO !



Frydman, Encyclopedia of NMR, supp. Vol., 265.

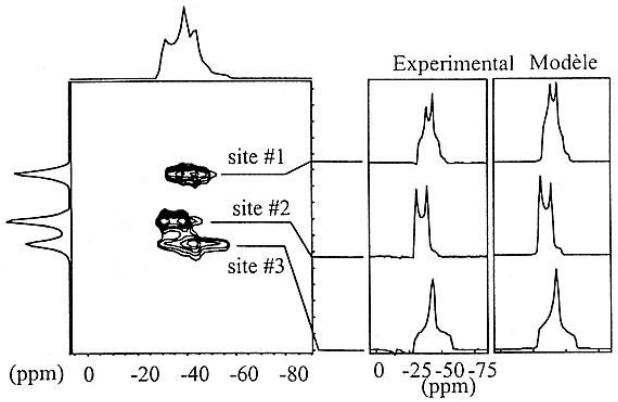


Amoureux et al., Encyclopedia of NMR, supp. Vol., 230.

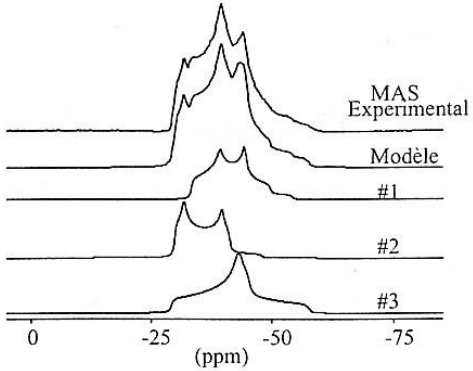
Examples of MQ-MAS spectra

DAS and DOR: very demanding techniques !

MQ-MAS: relatively easy (...)

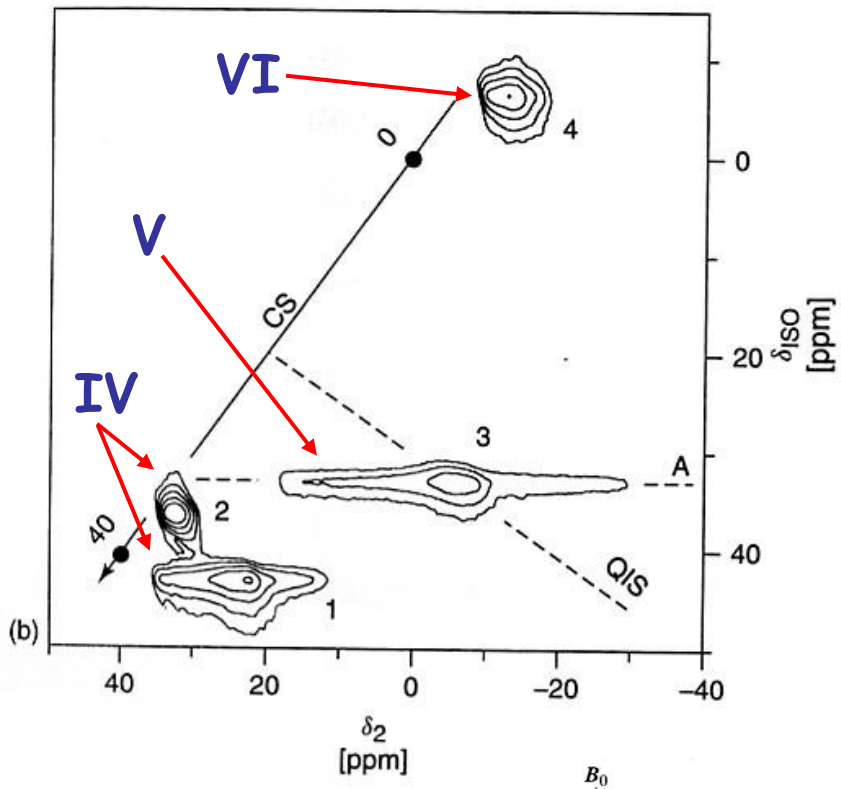


Site	MQ-MAS δ_{CS}^{ISO} (ppm)	MQ-MAS C_Q (MHz)	MQ-MAS η_Q	Baltisberger *et al.* (1992) δ_{CS}^{ISO} (ppm)	Baltisberger *et al.* (1992) C_Q (MHz)	Baltisberger *et al.* (1992) η_Q
#1	-31.3	1.79	0.55	-30.9	1.85	0.48
#2	-26.6	1.75	0.18	-26.2	1.83	0.12
#3	-28.5	1.99	0.91	-26.8	2.07	1.0



^{87}Rb in $RbNO_3$

Massiot, Ecole RMN des Houches, 1997.



^{27}Al in $AlPO_4$-14

2 IV-fold sites
1 V-fold site
1 VI-fold site

15 kHz

Amoureux et al., Encyclopedia of NMR, supp. Vol., 235.

One of the last problems in high resolution solid state NMR: ^1H !

^1H: strongly coupled by the homonuclear dipolar interaction !

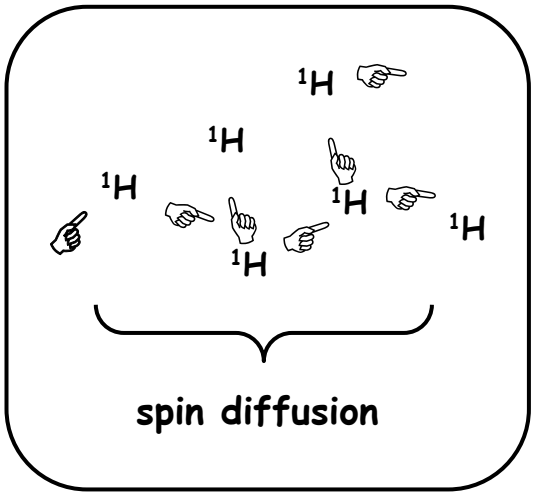
remember:

high for ^1H

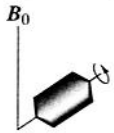
$$D_{II} \sim \gamma^2/r_{II}^3$$

up to 30 kHz...

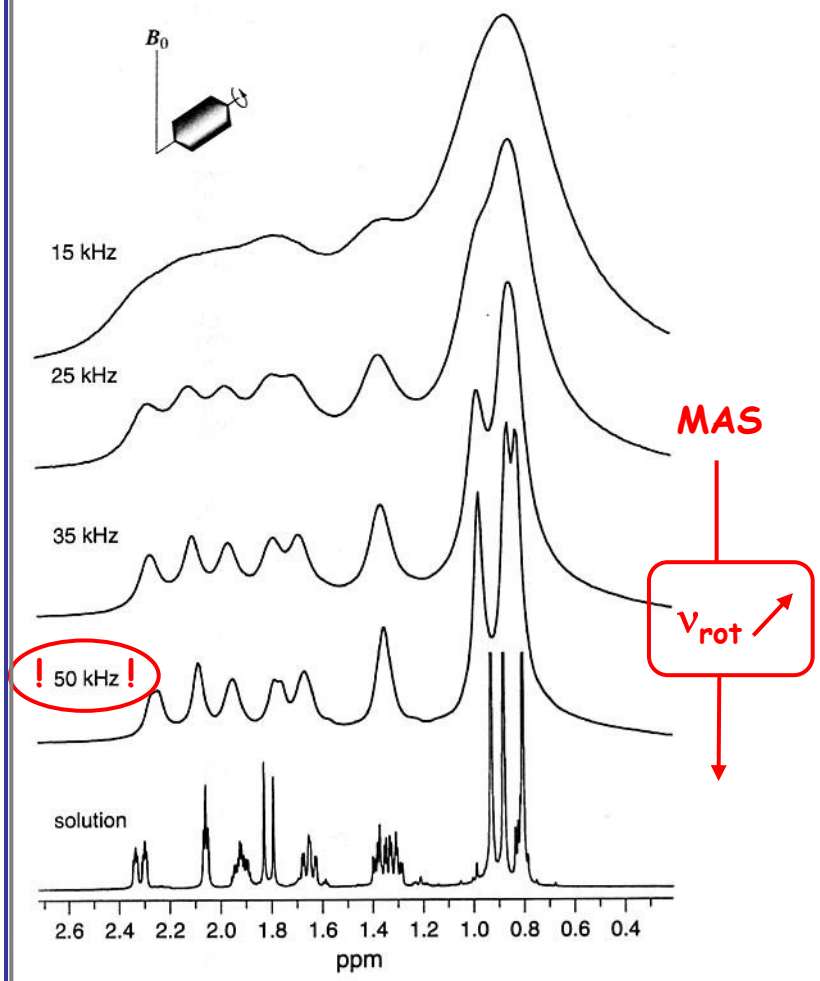
rather small



question: is the MAS reorientation efficient ?



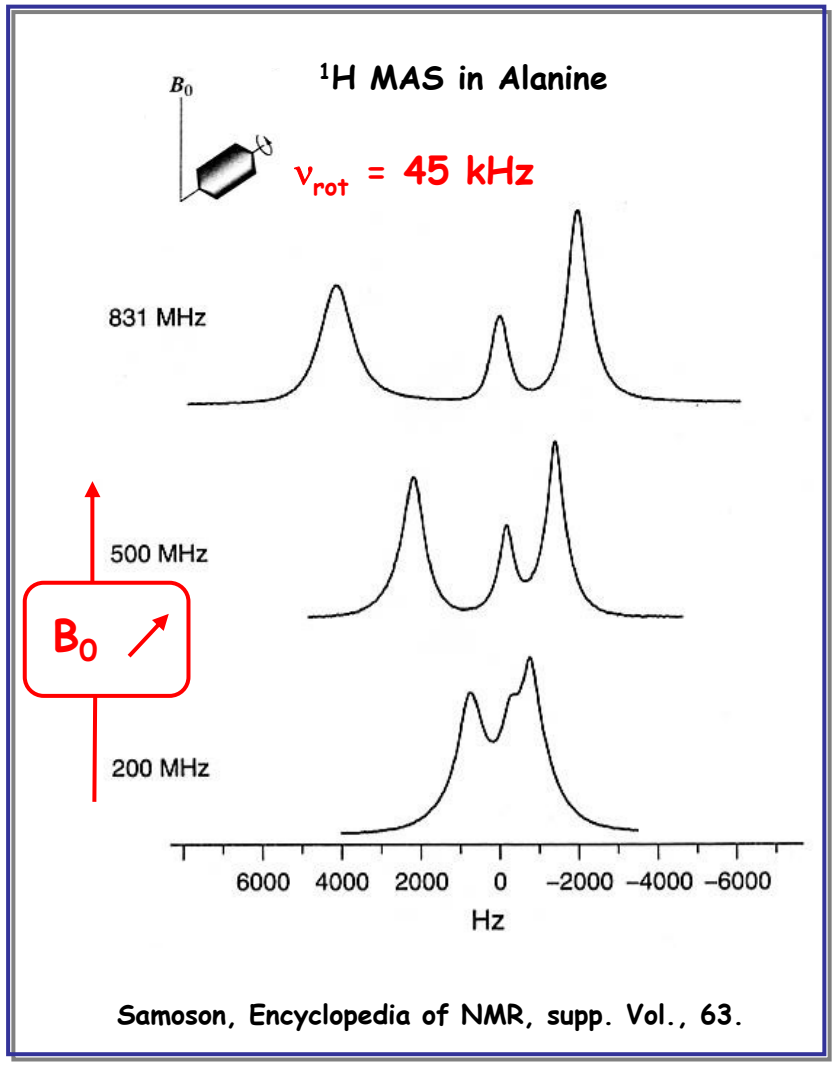
^1H MAS in Camphor (500MHz)



Samoson, Encyclopedia of NMR, supp. Vol., 63.

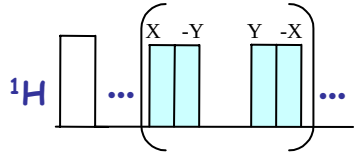
How to cure the disease ?

first idea: highest B_0 and highest ν_{rot} !

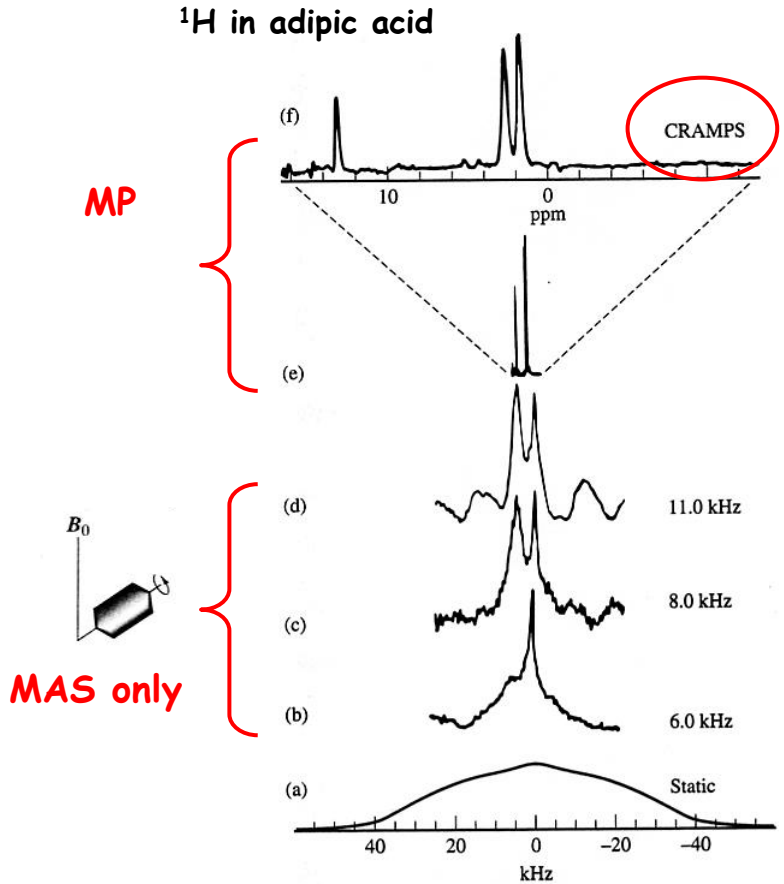


Samoson, Encyclopedia of NMR, supp. Vol., 63.

second idea: rotations in spin space !

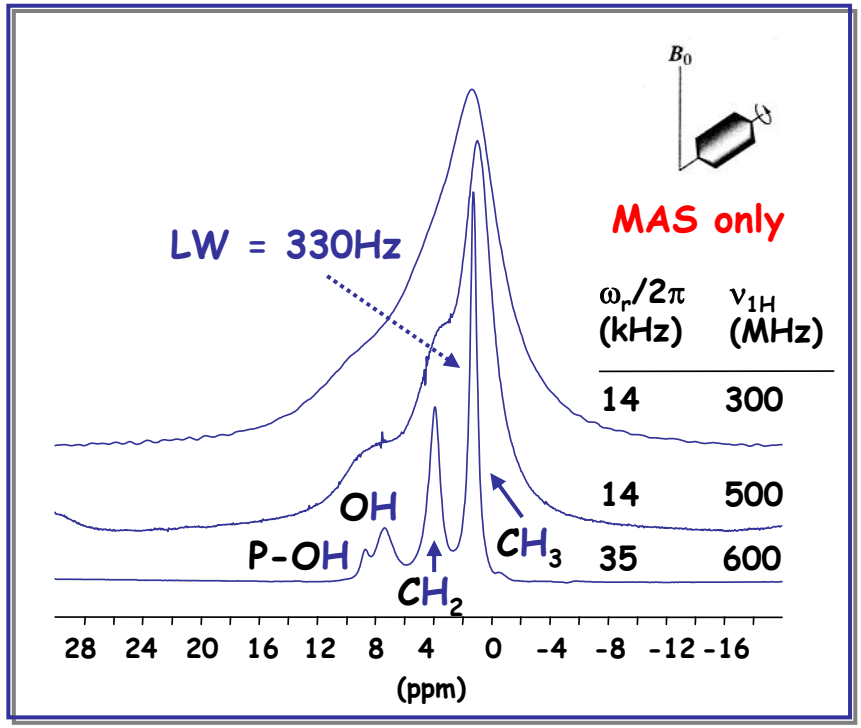


multiple pulses (MP)



Gerstein, Encyclopedia of NMR, 1996, 1502.

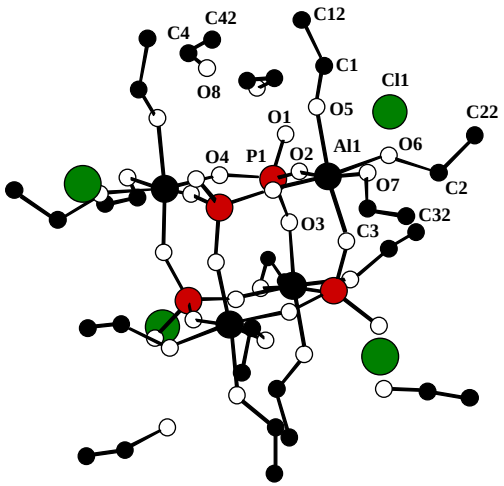
Comparison of techniques

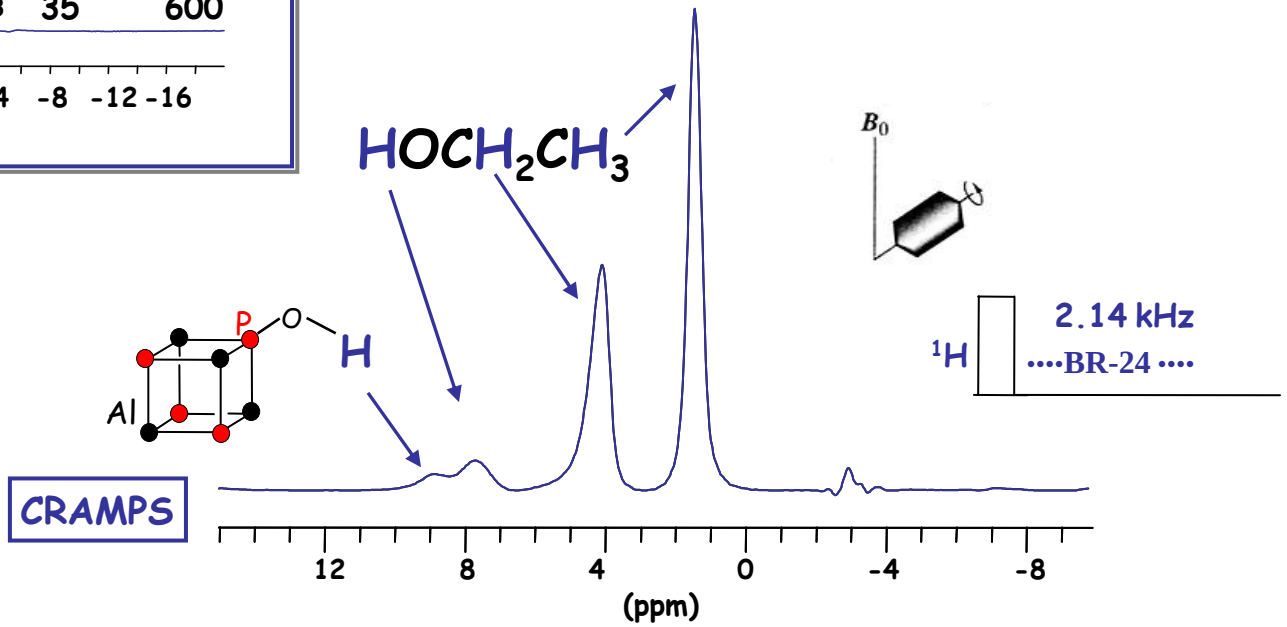


... what is the limit of resolution in ^1H solid state NMR !?

don't forget the role of molecular motion !...

CRAMPS: **C**ombined **R**otation **A**nd **M**ultiple **P**ulses **S**pectroscopy

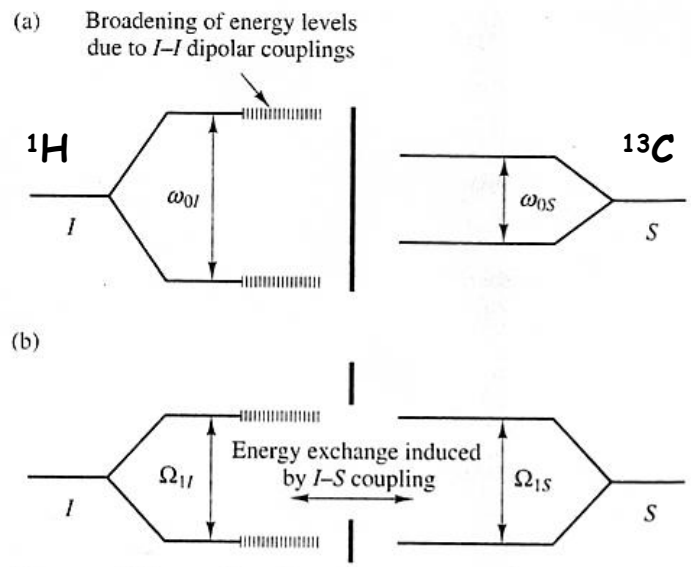




Azaïs, phD thesis.

Cross Polarization (CP): fundamentals

question: is it possible to transfer magnetization from ^{1}H to ^{13}C ?



Engelke, Encyclopedia of NMR, 1996, 1530.

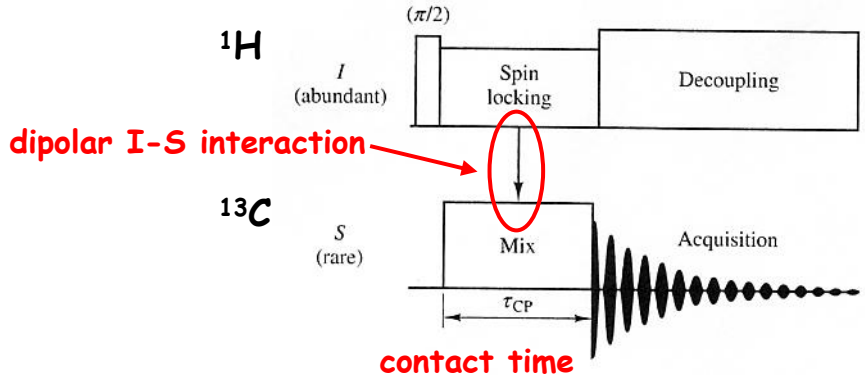
answer given by Hartmann and Hahn (1962 !):

NO in the laboratory frame but YES in the rotating frame if...

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

Hartmann-Hahn condition: B_1(RF) fields !

the most popular sequence

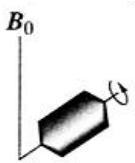


advantages !

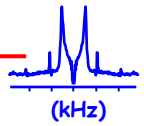
- gain: M_S $(\gamma_{1H}/|\gamma_S|)$ → 4 for ^{13}C, 10 for ^{15}N !
- τ_{CP} ~ ms !
- $T_1(^{1}H) << T_1(^{13}C)$
- ^{13}C FID decoupled from ^{1}H

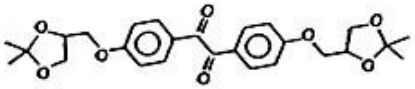
but, what about the ^{13}C CSA ?

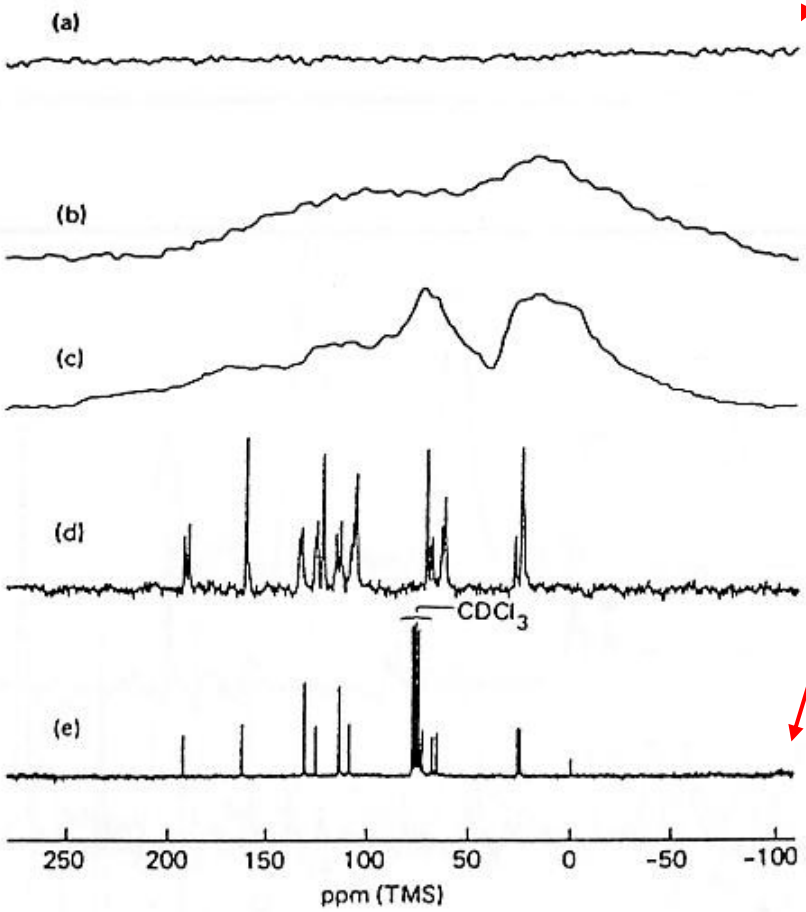
idea...



«The» CP MAS experiment



^{13}C in 

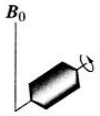


(a) solid (solution conditions)

(b) CP (low power decoupling)

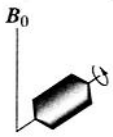
(c) CP (high power decoupling)

(d) CP MAS (high power decoupling)



(e) solution (low power decoupling)

however, be careful when ν_{rot} >>



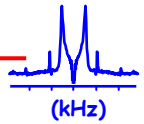
RF MAS

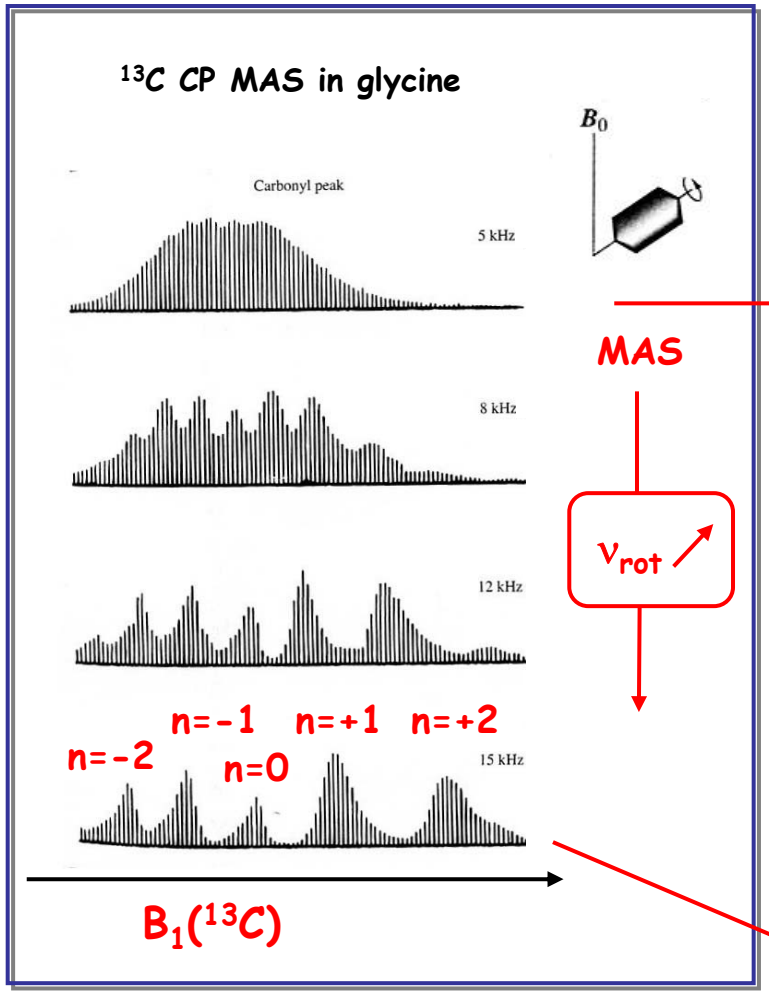
$$\Omega_{1I} = \Omega_{1S} \pm n\,\Omega_{rot}$$

with n = 1, 2,...

modified Hartmann-Hahn condition !

SSB in the Hartmann-Hahn profile

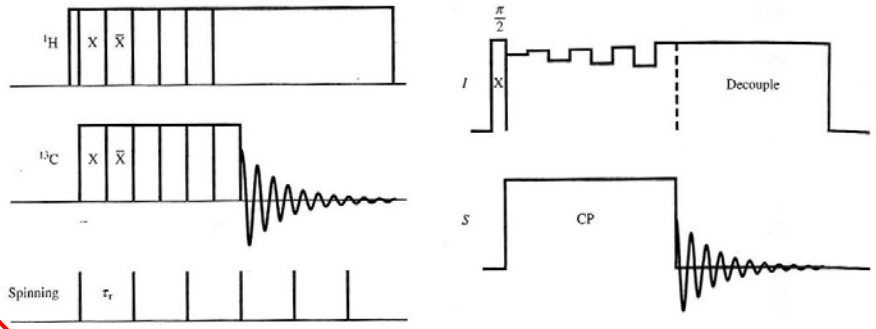




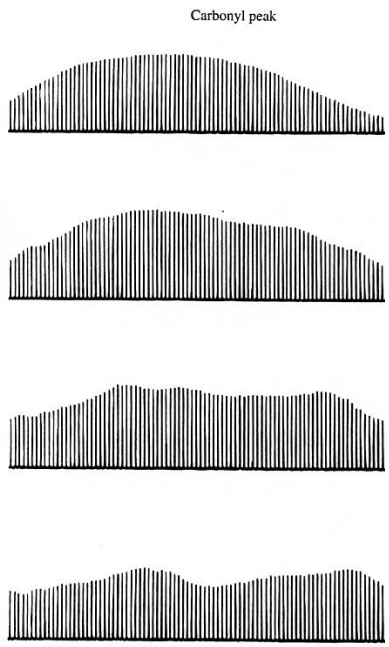
MAS

ν_{rot} ↗

solutions...



variable amplitude during the contact



Burum, Encyclopedia of NMR, 1996, 1539.

CP dynamics: distance measurements

why distances ?...

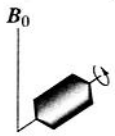
remember: $D_{IS} \sim \gamma_I \gamma_S / r_{IS}^3$

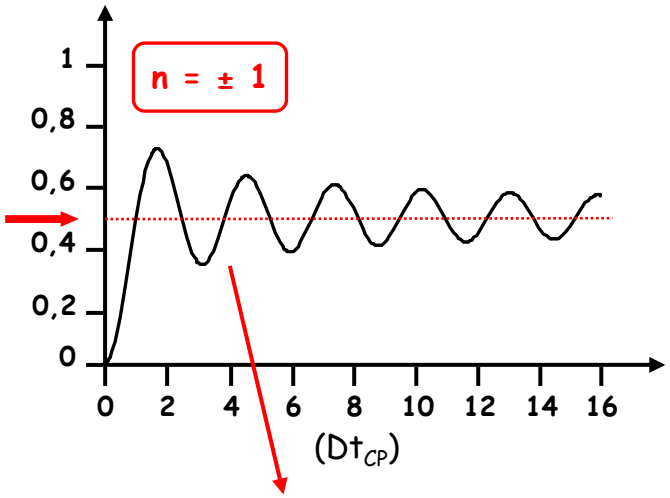
⬇

CP transfer !

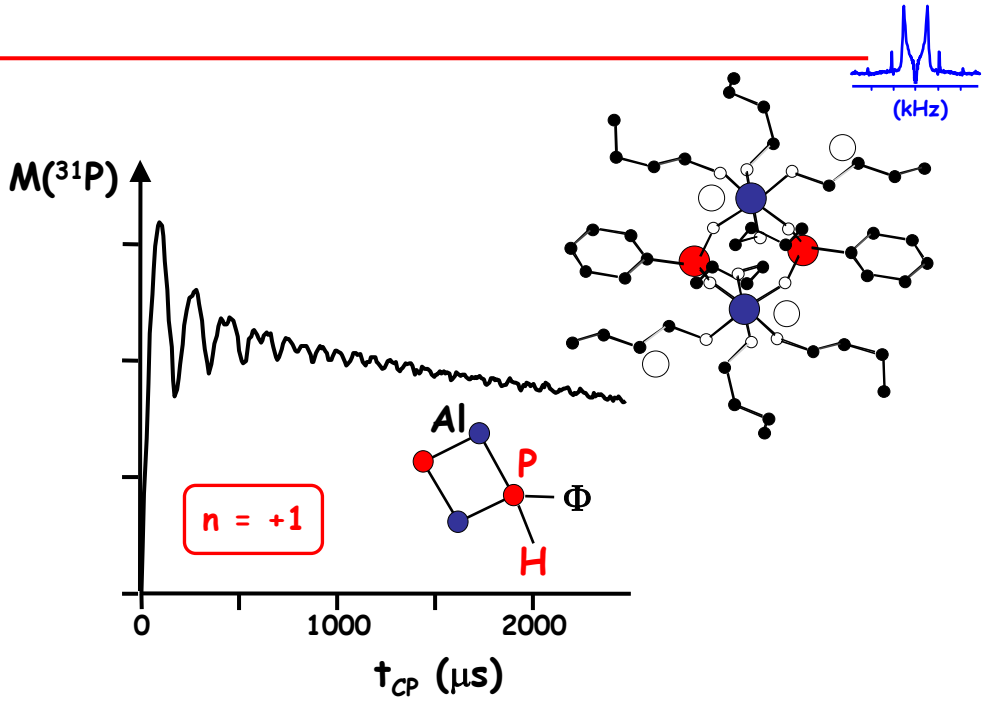
for a spin pair I-S at

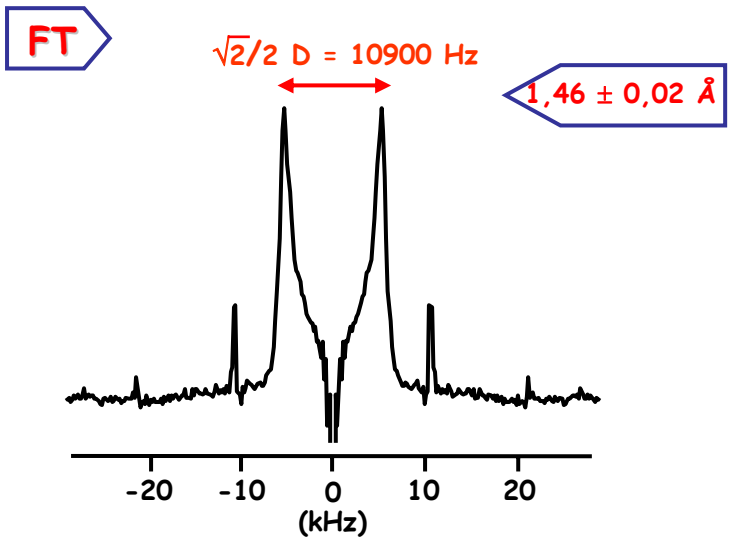
$$\Omega_{1I} = \Omega_{1S} \pm n\,\Omega_{rot}$$





the frequency of the oscillations gives D_{IS} !





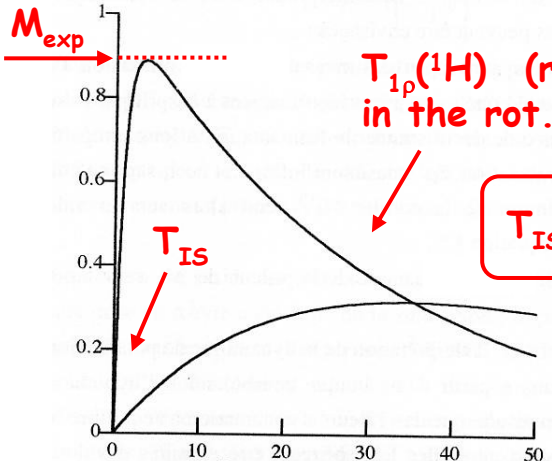
Azaïs et al., Inorg. Chem., 2002, 41, 981.

CP dynamics: quantitative approach

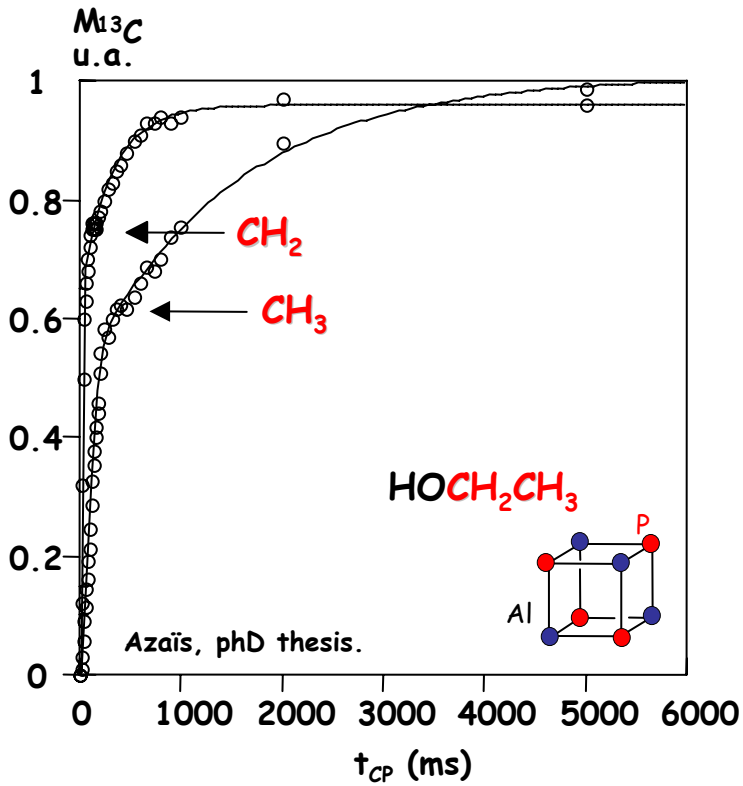
when spin pairs are not strictly isolated: more or less exponential build-up of the magnetization !

$$M_S^{CP}(t_c) = \frac{\gamma_I}{\gamma_S} M_S \frac{1}{1-\lambda}\left[\exp\left(-\frac{t_c}{T_{1\rho}^I}\right) - \exp\left(-\frac{t_c}{T_{IS}}\right)\right]$$

gain ! loss ! gain !



Camus, phD thesis.



$T_{CH}(^{13}CH2) < T_{CH}(^{13}CH) << T_{CH}(^{13}C_{quat})$

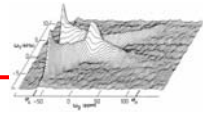
$^{13}C_{quat}$ are underestimated at short contact time !

$\lambda = T_{CH}/T_{1\rho}(^1H)$ influences M_{exp}

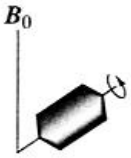
be careful with materials exhibiting several $T_{1\rho}(^1H)$!

CP: a fundamental ... but complex experiment

2D experiments: anisotropic vs isotropic data

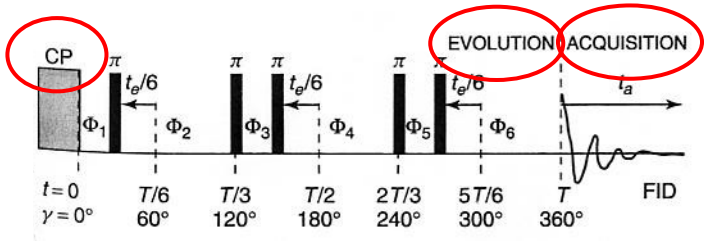


general idea: 2D correlation between the isotropic chemical shifs and a given anisotropic interaction...

if 

the interaction must be reintroduced !

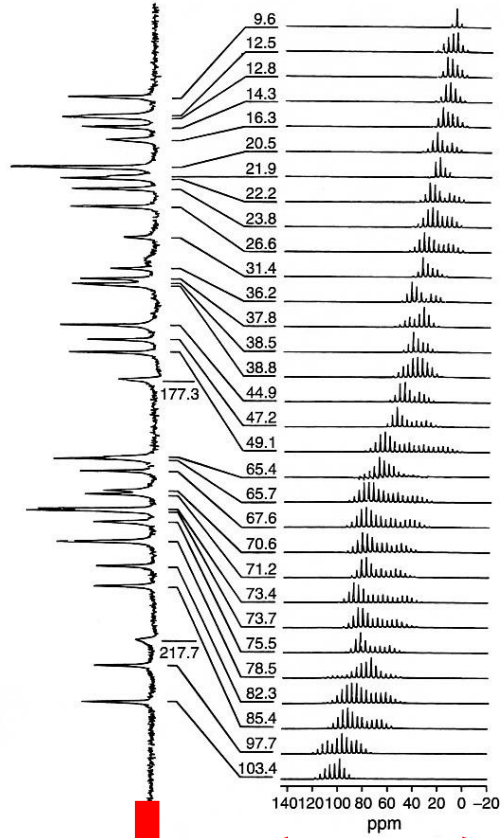
ex: δ_{iso} vs Δ_{CSA} – Magic Angle Turning expriment



sensitivity !

1st dimension

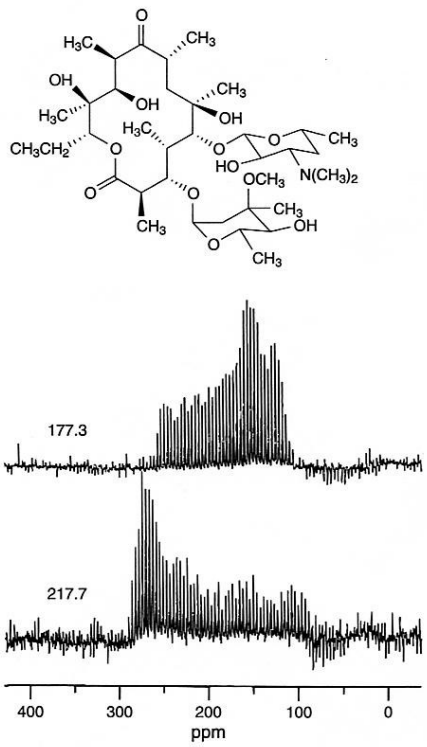
2nd dimension



isotropic dim.

CSA dim.

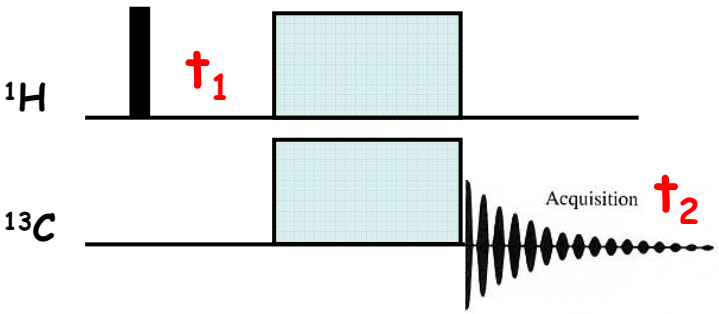
^{13}C in erythromicin A



Alderman et al., Mol. Phys., 1998, 95, 113.

2D heteronuclear correlation

general idea: ^{1}H evolves during t_1 and is transferred to ^{13}C !

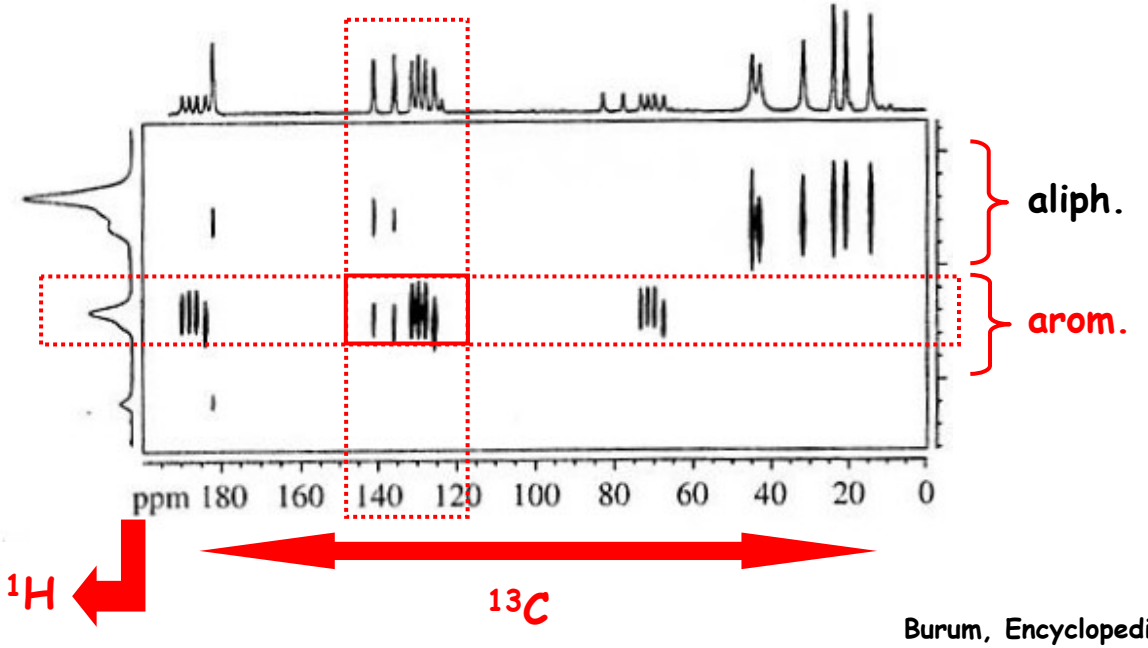


dipolar peaks of correlation

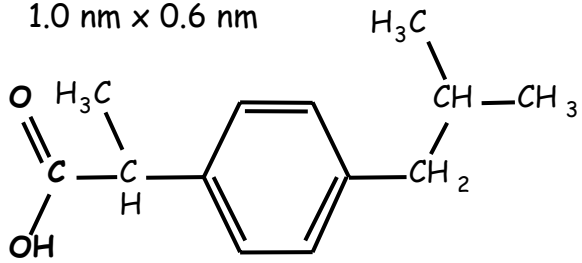
⇓

«short» distances

^{13}C-^{1}H HETCOR for ibuprofen



1.0 nm x 0.6 nm



ibuprofen

Burum, Encyclopedia of NMR, 1996, 1542.

Enjoy !

Fourier Transform Spectroscopy

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