ETH
Eidgenössische Technische Hochschule Zürich
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Characterization of Catalysts and Surfaces with Nuclear Magnetic Resonance

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NMR Spectroscopy - An Introduction

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Outline

General Principles of NMR Spectroscopy

Interactions in NMR Spectroscopy

Information content of NMR Interactions

Characterization of (Molecular) Structure by NMR

Courses

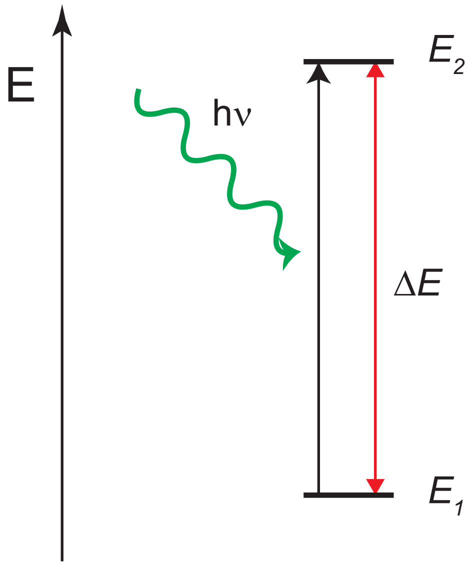
PCIV: Magnetic Resonance	B.H. Meier, M.C. Ernst, G. Jeschke	yearly
Structure Determination by NMR	M. Ebert	yearly
Advanced Magnetic Resonance	M.C. Ernst	approx. every third year

Books

M.H. Levitt: "Spin Dynamics: Basics of Nuclear Magnetic Resonance", John Wiley & Sons, 2001
J. Keeler: "Understanding NMR Spectroscopy", John Wiley & Sons, 2005.

M. Duer: "Introduction to solid-state NMR", Blackwell Science Ltd (Oxford), 2004.
K. Schmidt-Rohr, H.W. Spiess: "Multidimensional Solid-State NMR and Polymers", Academic Press, 1994.

Principles of Spectroscopy



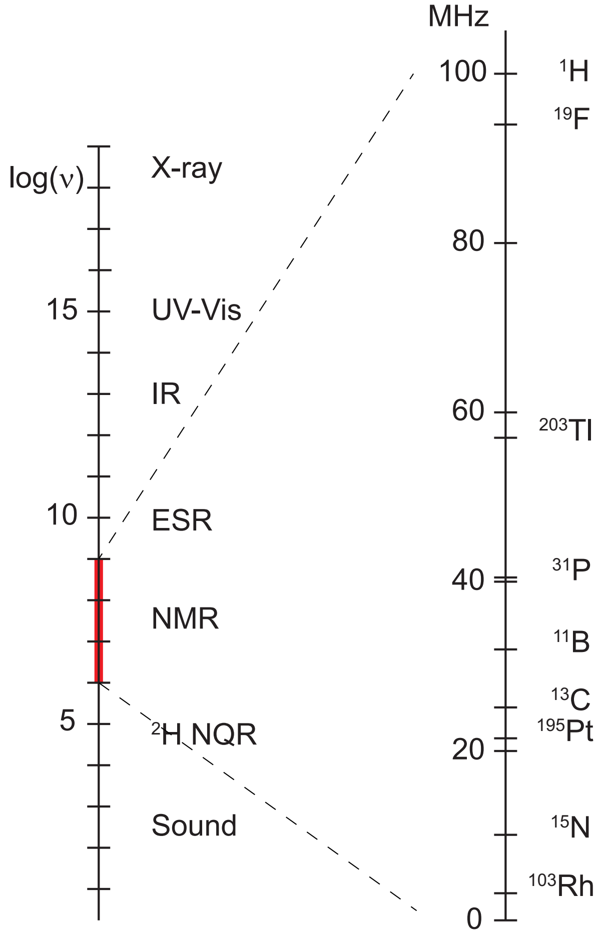
- The purpose is to obtain information about the molecular and/or atomic structure of matter

- The method is to use the interaction between EM radiation and matter

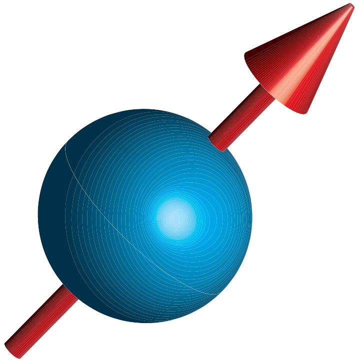
1. Absorption/Emission of Energy by the system

$$\Delta E = E_2 - E_1 = h\nu$$

2. Interaction with Electric or Magnetic part of the radiation
3. Characteristic frequency of radiation for each type of spectroscopy



The Nuclear Spin

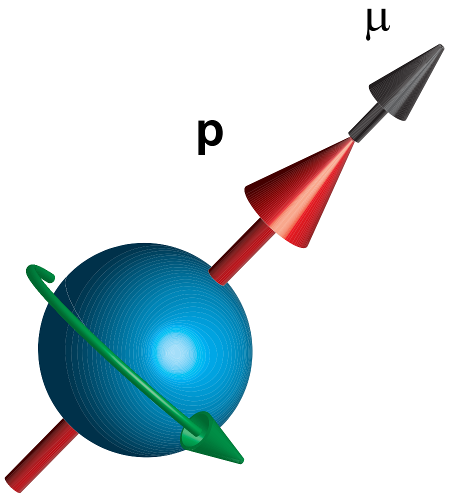


- Nuclear Property
- The inherent Angular Momentum of a Nucleus
- Purely Quantum Mechanic
- The magnitude of the Nuclear Spin is given by:

$$p = |\mathbf{p}| = \frac{h}{2\pi}\sqrt{I(I+1)}$$

- The Spin Quantum number, *I*, is a property of the nuclear species.

The Nuclear Magnetic Moment

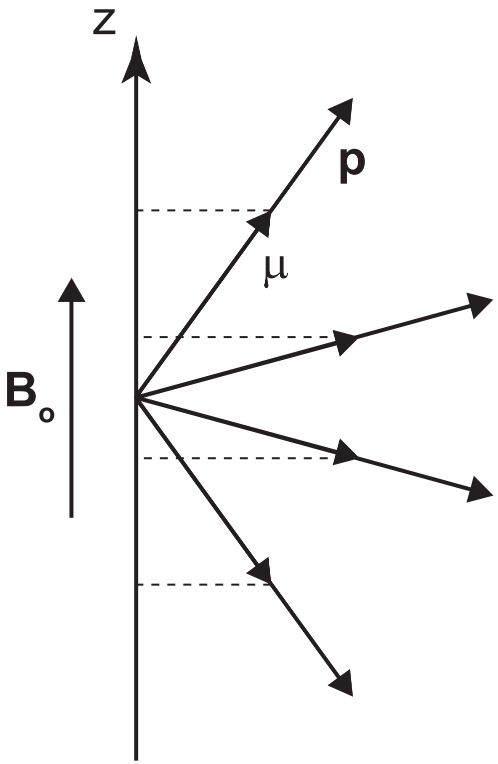


- The Nuclear Spin implies a Nuclear Magnetic Moment
- Vector parallel with the Nuclear Spin
- Proportional to the Spin with the gyromagnetic ratio, γ

$$\mu = \gamma \cdot \mathbf{p}$$

- The gyromagnetic ratio is a property of the nuclear species

Orientational Quantization States



- In a (strong) external magnetic Field the component of the nuclear spin along that field is quantized

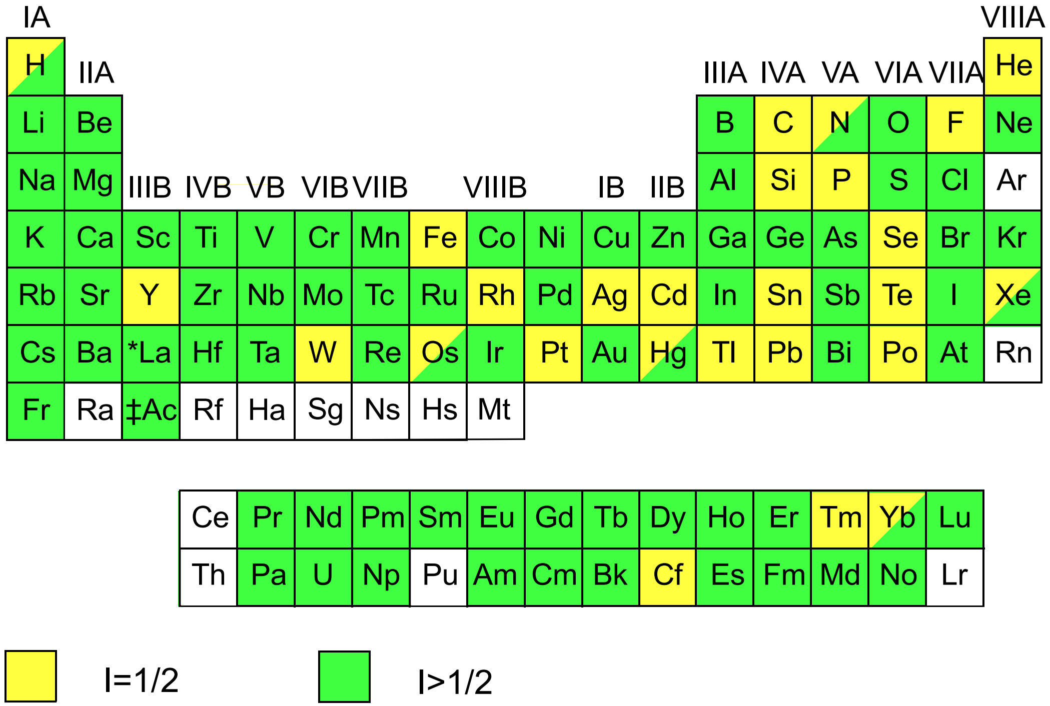
$$\begin{aligned} p_z &= (h/2\pi)I & \mu_z &= \gamma(h/2\pi)I \\ &= (h/2\pi)(I-1) & &= \gamma(h/2\pi)(I-1) \\ &= (h/2\pi)(I-2) & &= \gamma(h/2\pi)(I-2) \\ &\ldots & &\ldots \\ &= (h/2\pi)(-I) & &= \gamma(h/2\pi)(-I) \end{aligned}$$

OR

$$p_z = (h/2\pi)m \qquad \mu_z = \gamma(h/2\pi)m$$

where $m \in [-I, -I+1, -I+2, \ldots, I]$

Spin Quantum Numbers

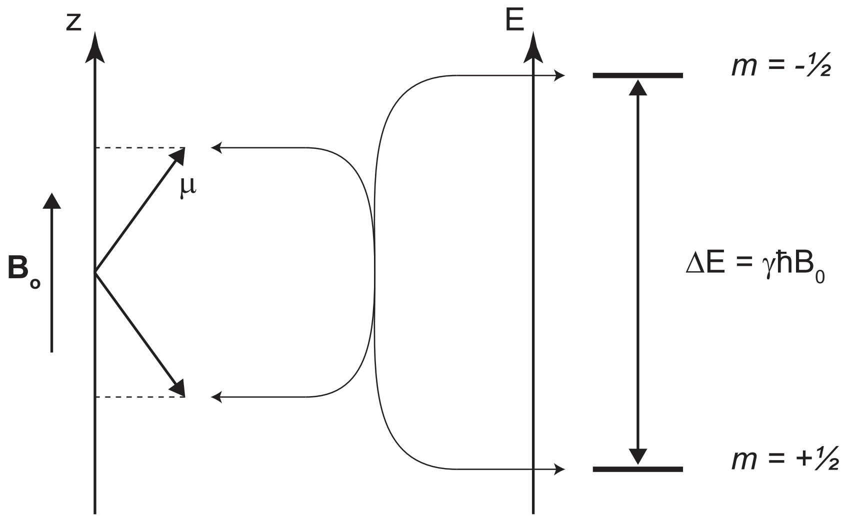


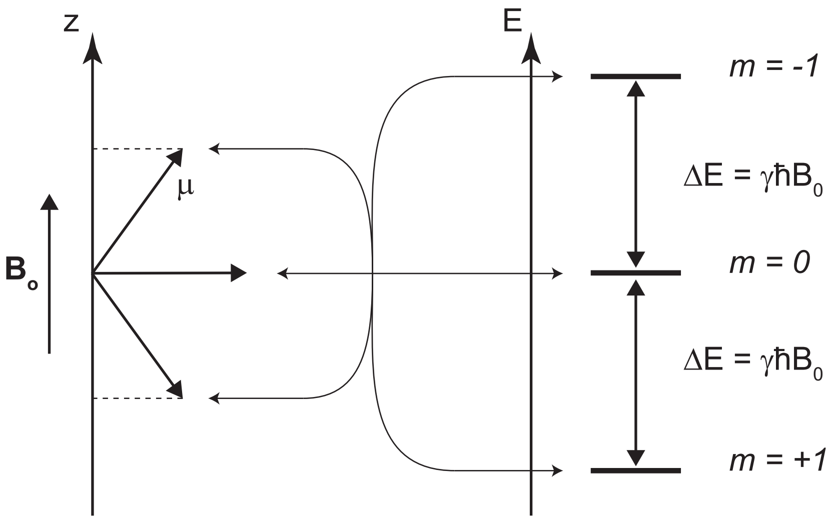
Isotope	Spin Quantum Number I	Magnetic Quantum Number m
^{12}C, ^{18}O	0	-
^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P	1/2	-1/2, +1/2
^{2}H, ^{14}N	1	-1, 0, +1
^{7}Li, ^{23}Na, ^{37}Cl, ^{87}Ru	3/2	-3/2, -1/2, 1/2, 3/2
^{17}O, ^{25}Mg, ^{27}Al	5/2	-5/2, -3/2, -1/2 1/2, 3/2, 5/2
^{45}Sc, ^{51}V, ^{59}Co	7/2	-7/2,-5/2,-3/2,-1/2, 1/2,3/2,5/2,7/2

Zeeman Interaction Energies

- A (nuclear) magnetic Moment interacts with a magnetic field with an energy

$$E_m = -m \cdot \gamma \cdot \frac{h}{2\pi} \cdot B_0$$





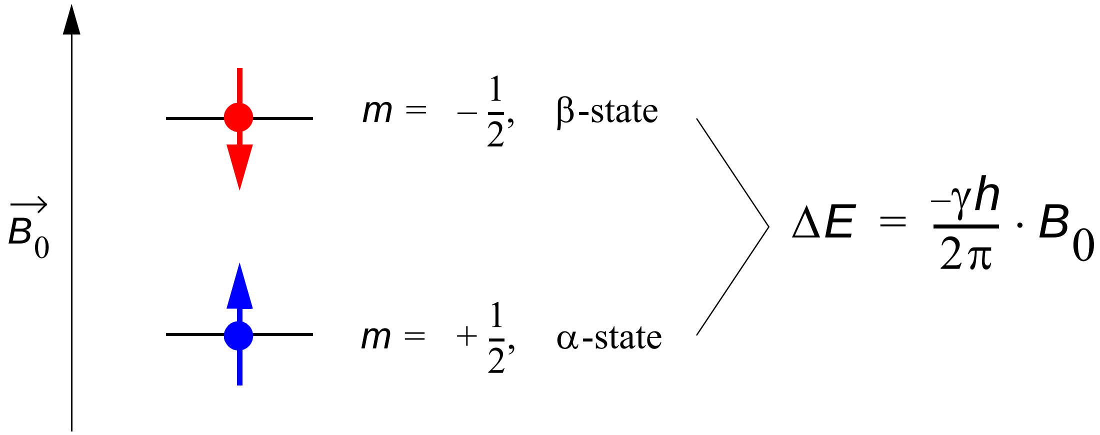
$$\Delta E = E_{m+1} - E_m = -\gamma \cdot \frac{h}{2\pi} \cdot B_0$$

Boltzmann Population

- The populations of the states is given by a Boltzmann Distribution

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E/(kT)} \approx 1 + \frac{\Delta E}{kT} \approx 1.000064$$

- Signal Strength is proportional to the *difference* between Boltzmann Populations



NMR Signal Strength

- The energy difference is usually given in frequency units

$$\nu_0 = \frac{-\gamma}{2\pi} \cdot B_0$$

Properties of some nucleotides of importance to NMR

Nucleotide	gyromagnetic ratio γ [10^7 rad T^{-1} s^{-1}]	Natural Abundance [%]	ν_0 [MHz] (B_0 = 4.7 T)
^1H	26.7519	99.985	200.0
^{13}C	6.7283	1.108	50.1
^{15}N	- 2.7126	0.370	20.2
^{19}F	25.1815	100.000	188.2
^{31}P	10.8394	100.000	81.0

More Signal

- Higher Magnetic Field (B_0)
- Higher gyromagnetic Ratio (γ)
- More Spins (e.g. higher nat. ab.)
- Lower Temperature

NMR Interactions

Zeeman Interaction	10^6-10^9 Hz
Rf Field Under experimental control for Spin rotations	10^0-10^5 Hz
Chemical Shift Interaction Reports on local electronic environment	10^2-10^4 Hz
Magnetic Dipole-Dipole Interaction Reports on the distance between two coupled spins.	10^2-10^5 Hz
Scalar J-Coupling Reports on chemical bonds between two spins.	10^0-10^2 Hz
Quadrupole Coupling Reports on the electric field gradient around the nucleus.	10^0-10^7 Hz

Sample/Structure Dependent

Only for I > 1/2

NMR Interactions

Single Spin

- Zeeman Interaction
- Rf Field
  Under experimental control for Spin rotations
- Chemical Shift Interaction
  Reports on local electronic environment
- Quadrupole Coupling
  Reports on the electric field gradient around the nucleus.

Two Spin

- Magnetic Dipole-Dipole Interaction
  Reports on the distance between two coupled spins.
- Scalar J-Coupling
  Reports on chemical bonds between two spins.

Chemical Shift

- The *exact* frequency of a nucleus depends on the *local* electronic structure

$$B_{\mathrm{eff}} = B_0 - \sigma \cdot B_0$$

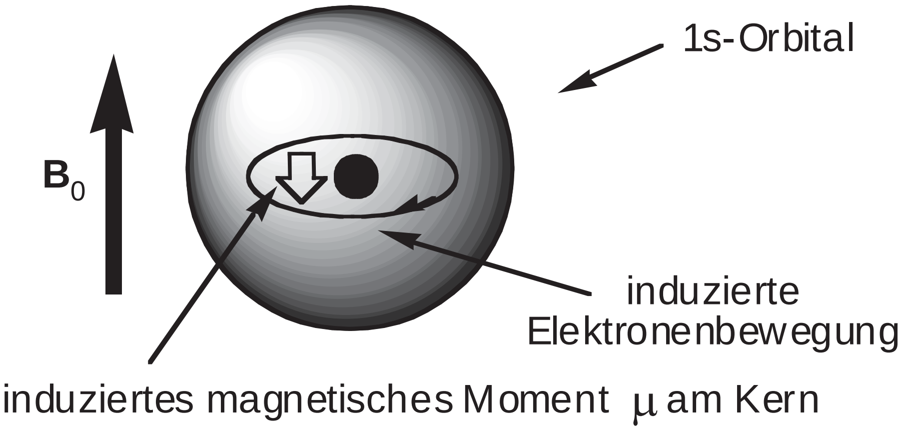
or

$$\nu_{\mathrm{eff}} = \frac{\gamma}{2\pi} \cdot B_0 \cdot (1 - \sigma)$$

- The shielding constant σ is the sum of many effects (diamagentic-, paramagentic, ringcurrent-, intermolecular-effects) and is *rather* difficult to calculate accurately.

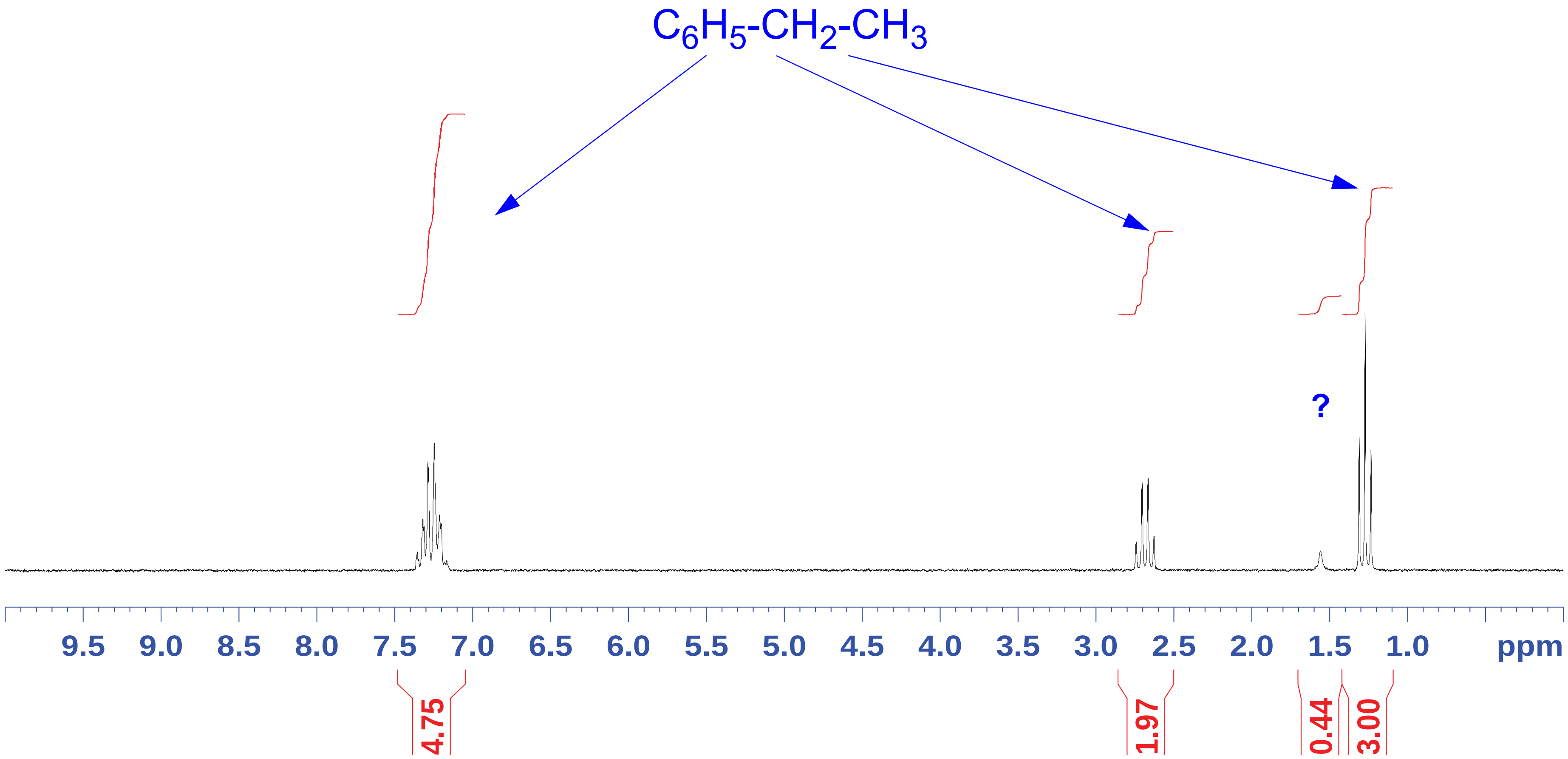
- The chemical shift modifies the magnetic field on a part per million scale (ppm).

  (e.g. when ν_0=400 MHz, then 1 ppm= 400 MHz x 10^{-6}= 400 Hz)



Chemical Shift

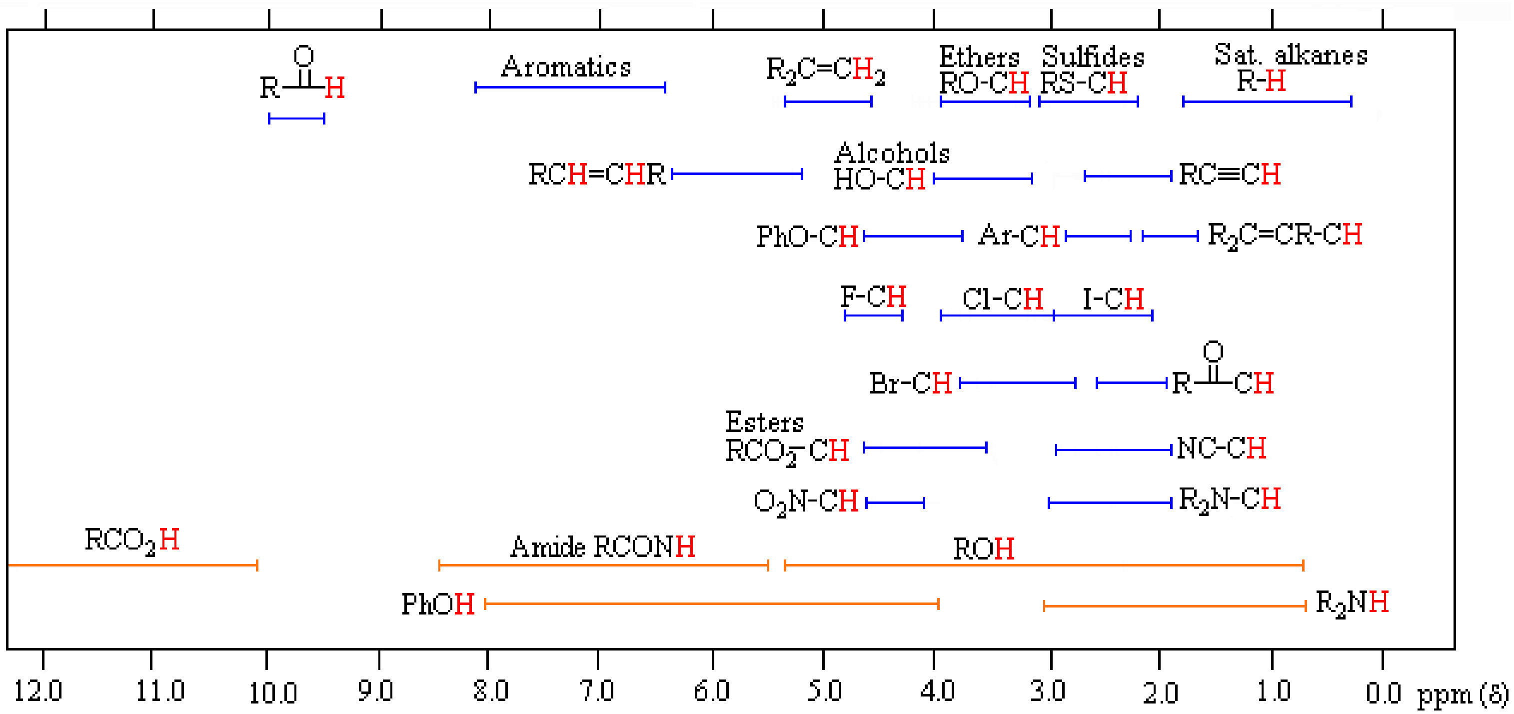
- The Integral of a signal is proportional to the number of nuclei.
- Some effects distort value of an integral more or less severely.
- The chemical shift of a given nucleus depends on the (chemical) environment of that nucleus.
- Lots of empirical knowledge about the value of the chemical shift in a given environment.



C_6H_5-CH_2-CH_3

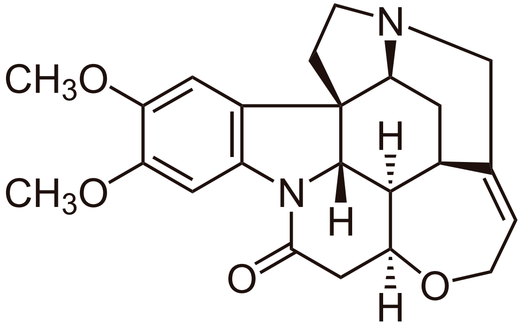
Chemical Shift

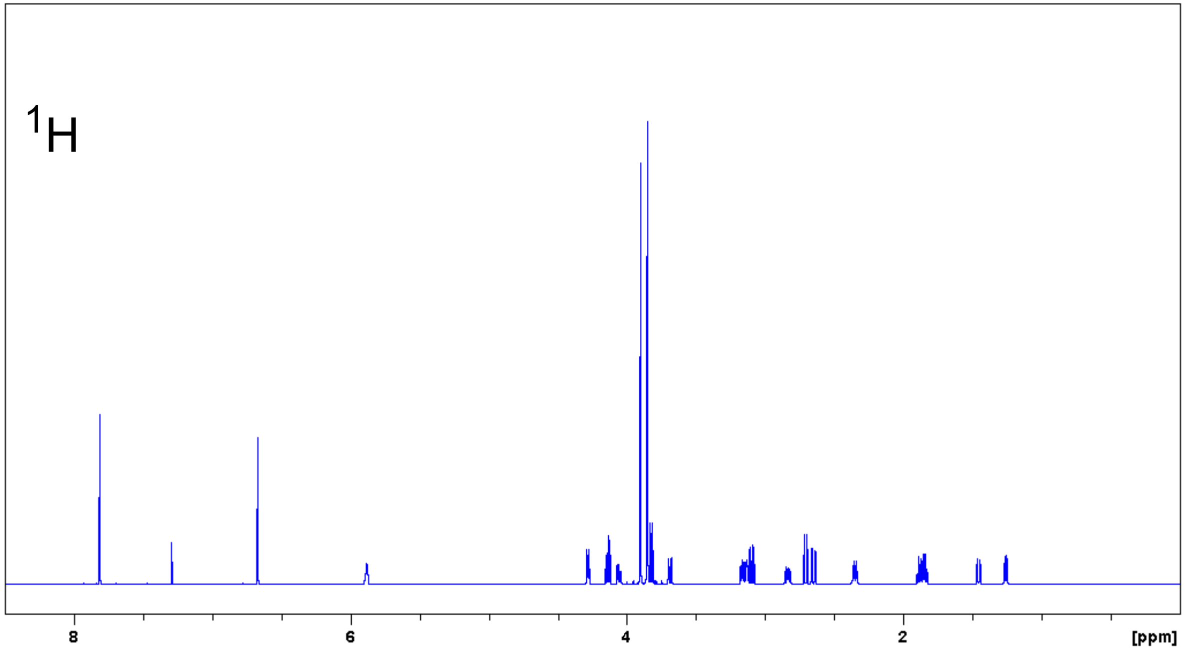
- The chemical shift of a given nucleus depends on the (chemical) environment of that nucleus.
- Lots of empirical knowledge about the value of the chemical shift in a given environment.
- The chemical shift (in ppm) is a relative scale to a reference coumpound (usually TMS for ^{1}H and ^{13}C).

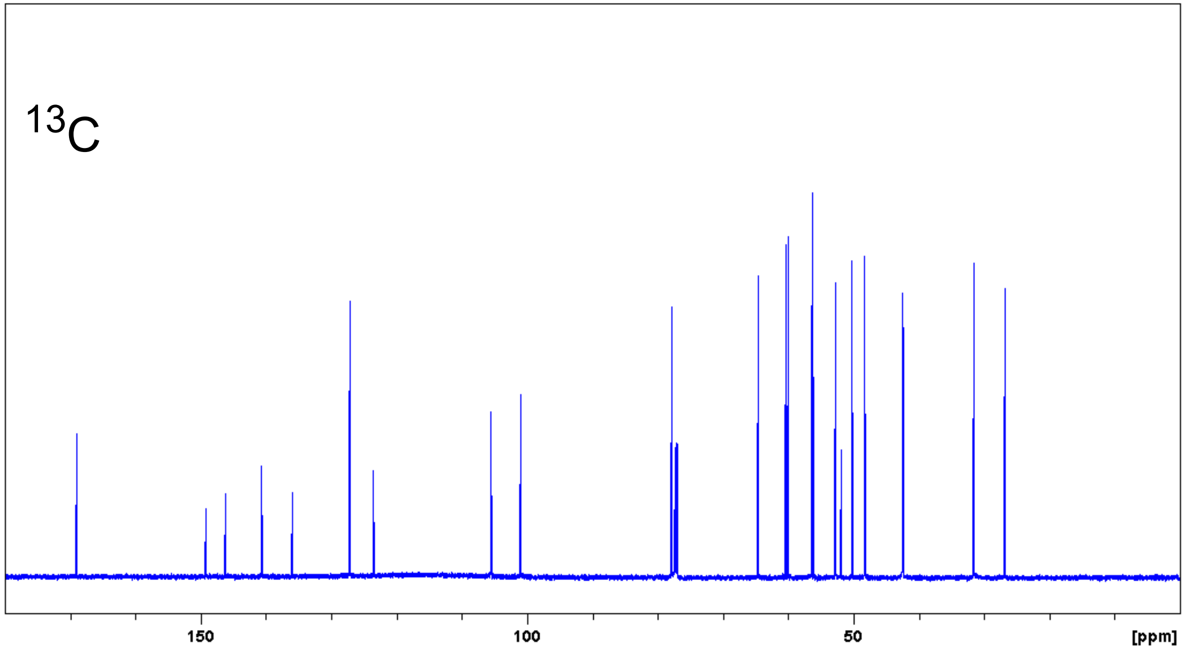


Structure Determination

- Brucine ($C_{23}H_{26}N_2O_4$)







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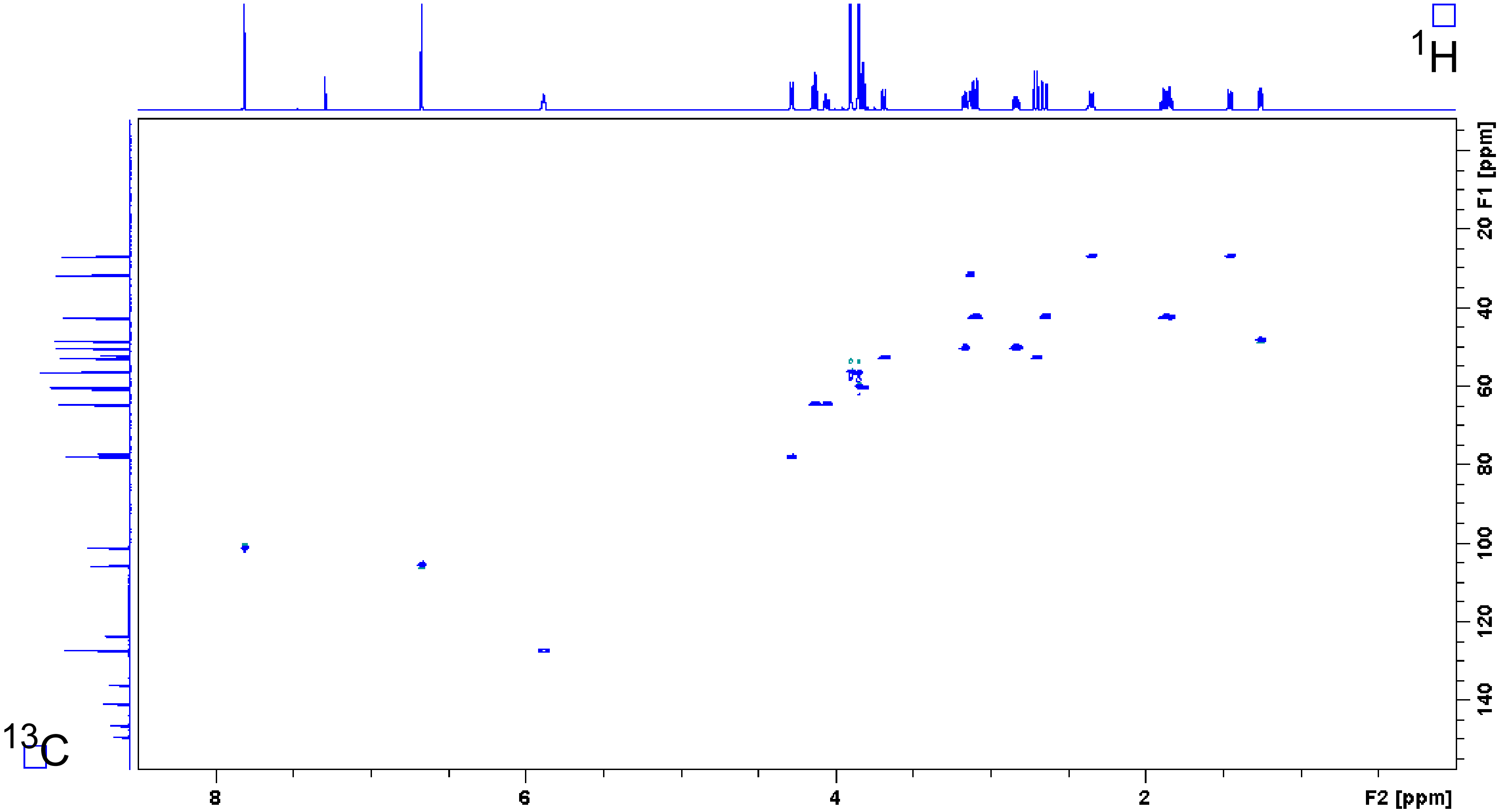

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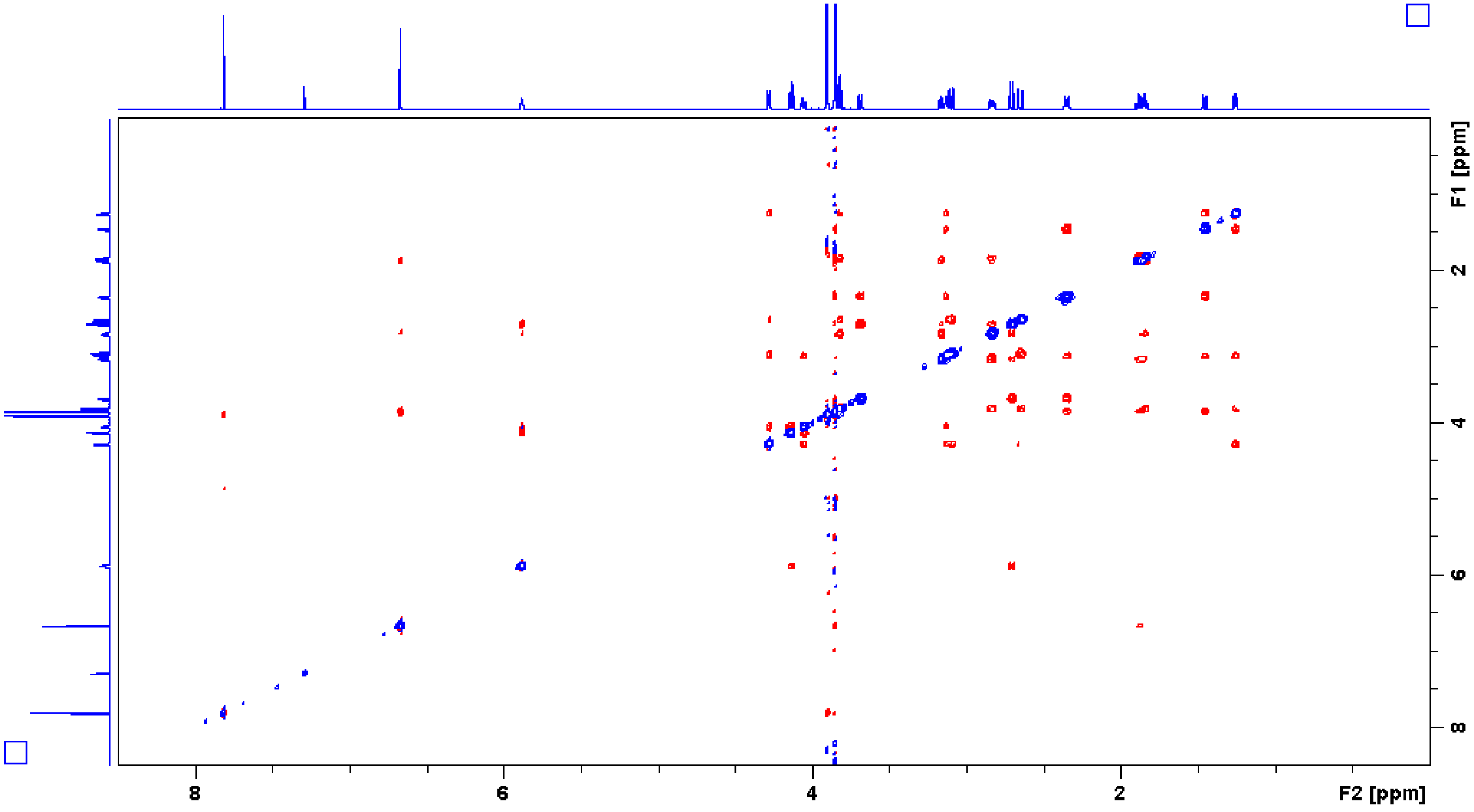
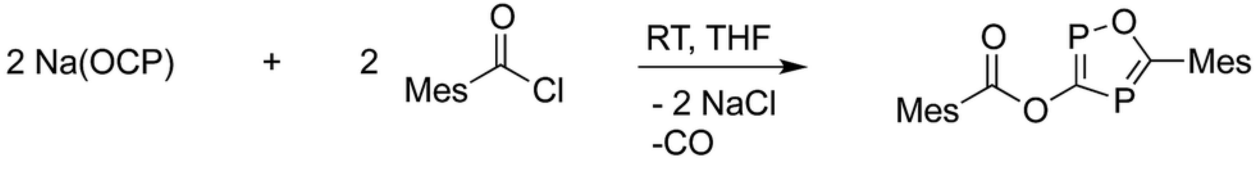


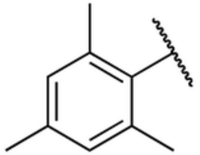
Reaction Kinetics

- ❖ The reactivity of acyl chlorides towards Na(OCP)
  Chem. Sci., 2016, **7**, 6125-6131 DOI: 10.1039/C6SC01269H



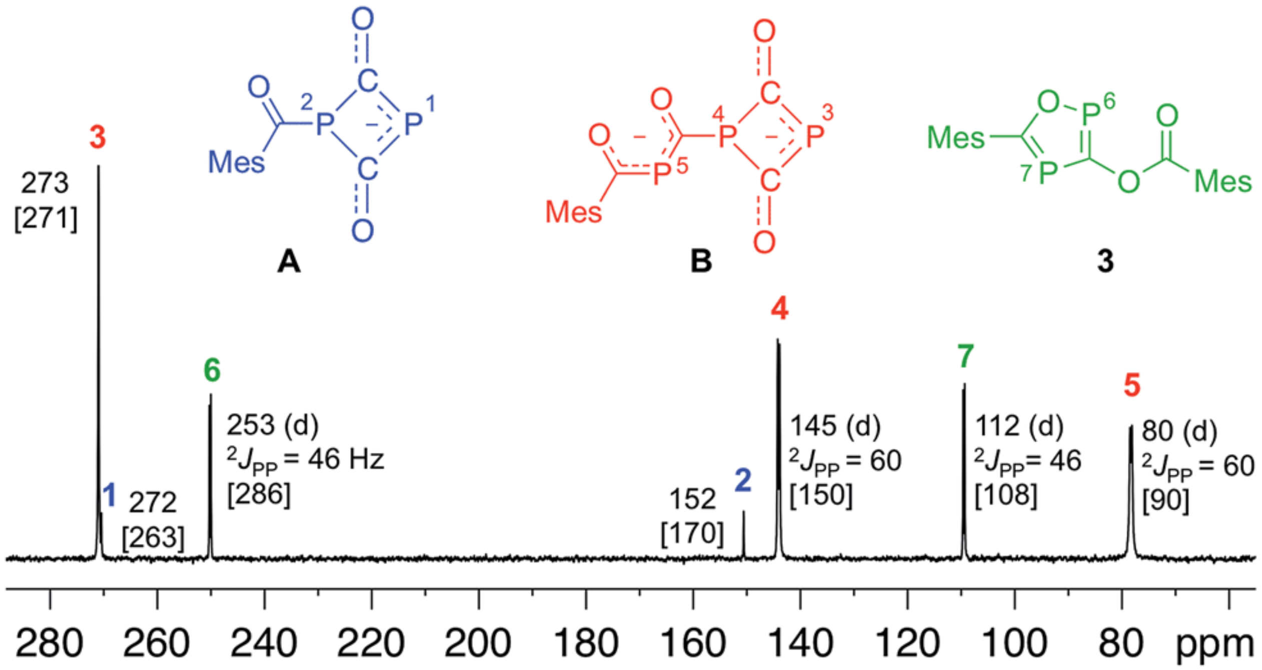
1 **2** **3**

Mes =



^{31}P

-35° C / 17 h



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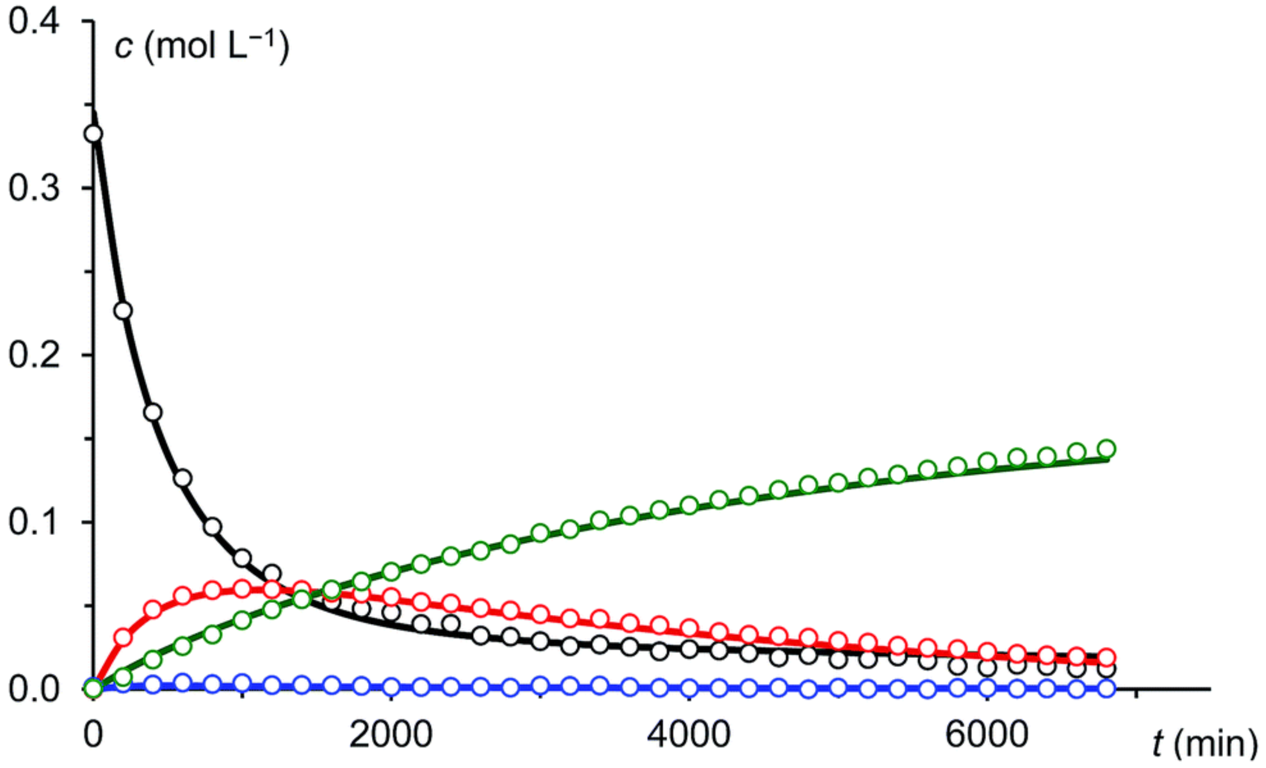

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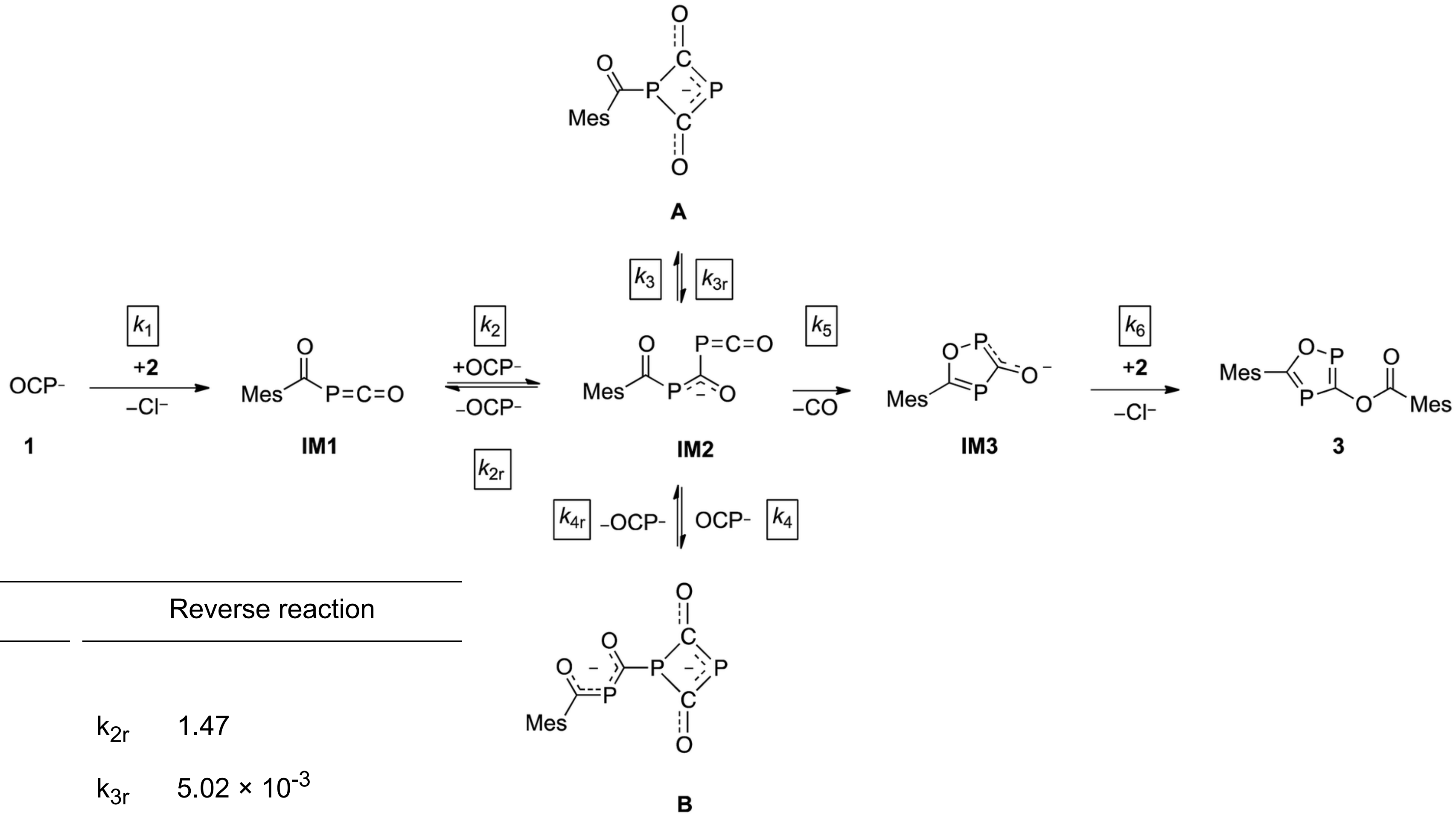


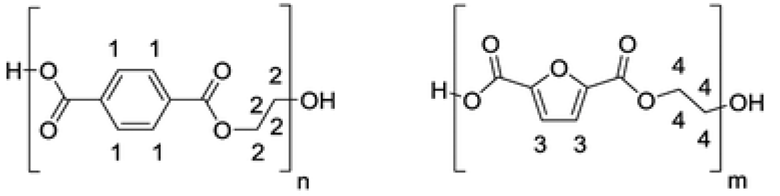
Table 1:

Forward reaction		Reverse reaction	
k_1	2.36×10^{-3}		
k_2	4.98	k_{2r}	1.47
k_3	2.08×10^{-2}	k_{3r}	5.02×10^{-3}
k_4	8.40×10^{-1}	k_{4r}	3.64×10^{-4}
k_5	8.19×10^{-2}		

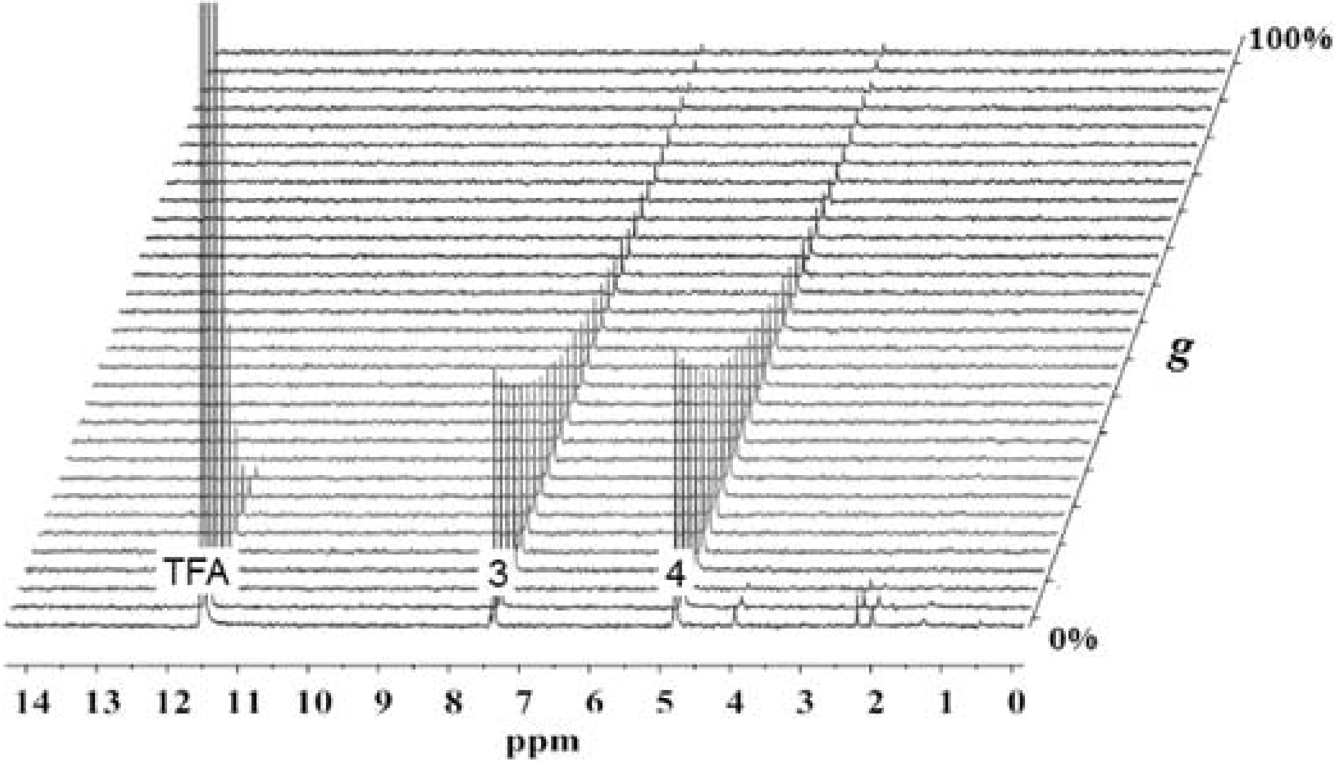
Molecular Weight Determination

- Diffusion (DOSY) 1H NMR as an Alternative Method for Molecular Weight Determination of Poly(ethylene furanoate) (PEF) Polyesters

J-G. Rosenboom et. al., *Macromol. Chem. Phys.*, 2017, **218**, 1600436 DOI: 10.1002/macp.201600436



PET PEF



$$\frac{I(g)}{I(0)} = \exp\left(-(\gamma g \delta)^2 D \left(\Delta - \frac{\delta}{3}\right)\right)$$

D : Diffusion Coefficient

g, δ, Δ : Experimental Parameters

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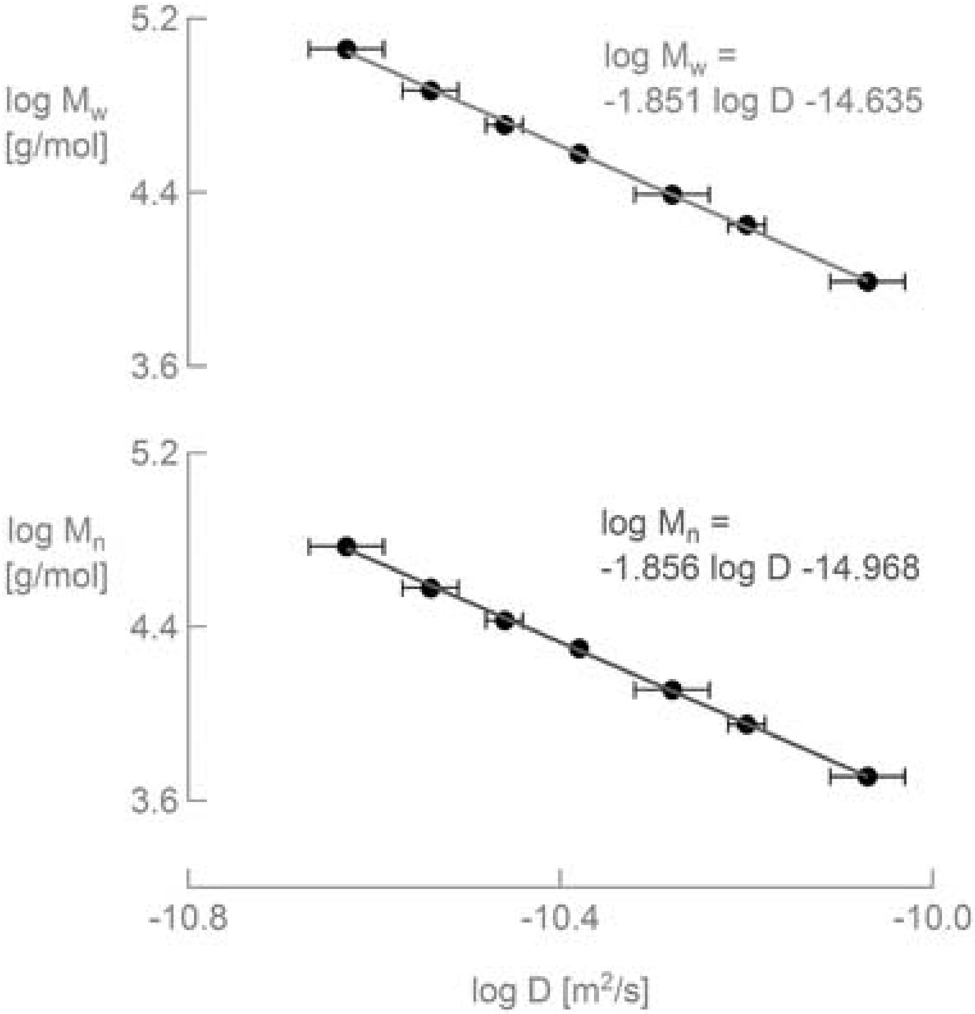

- Calibration Curves using PET reference samples

- Usually: Stokes-Einstein

$$r = \frac{kT}{6\pi\eta D}$$

Molecular Weight Determination

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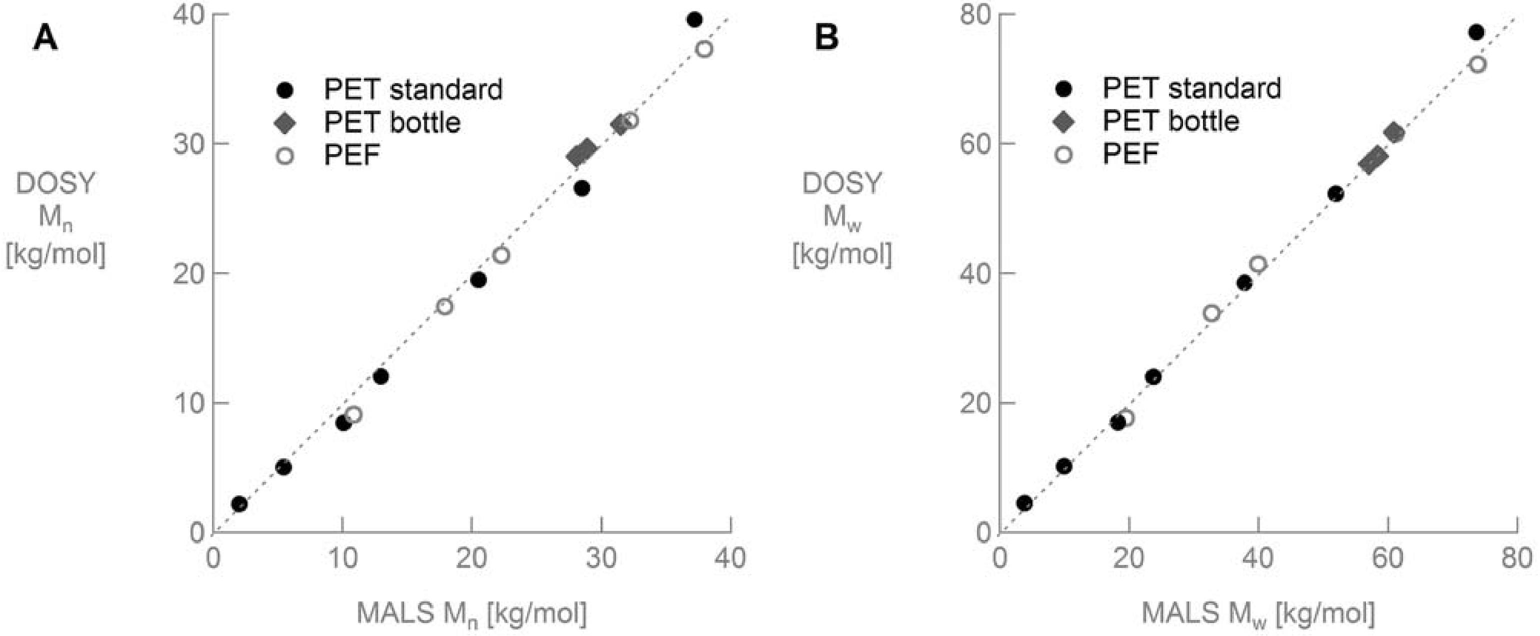
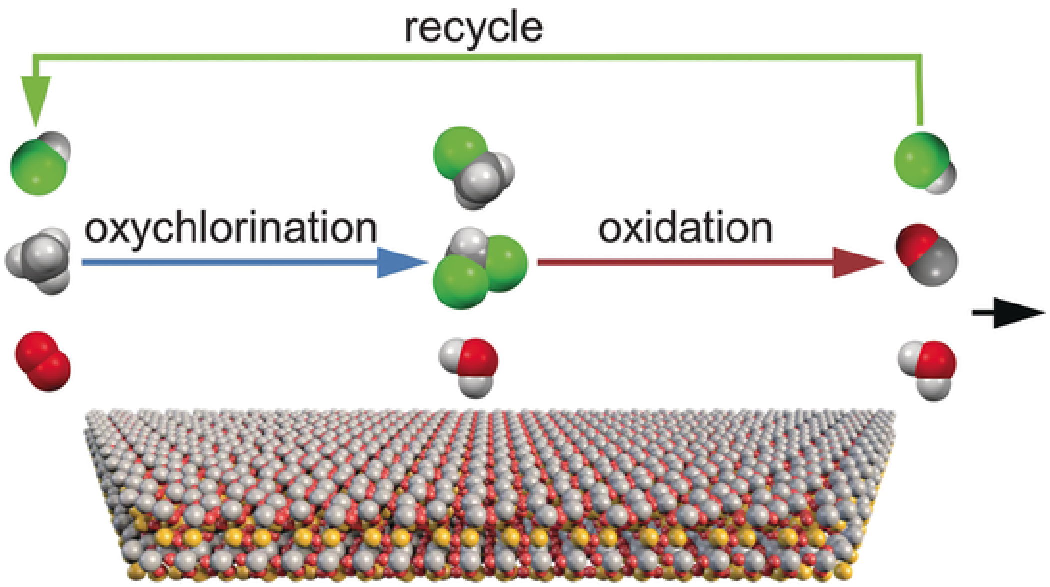


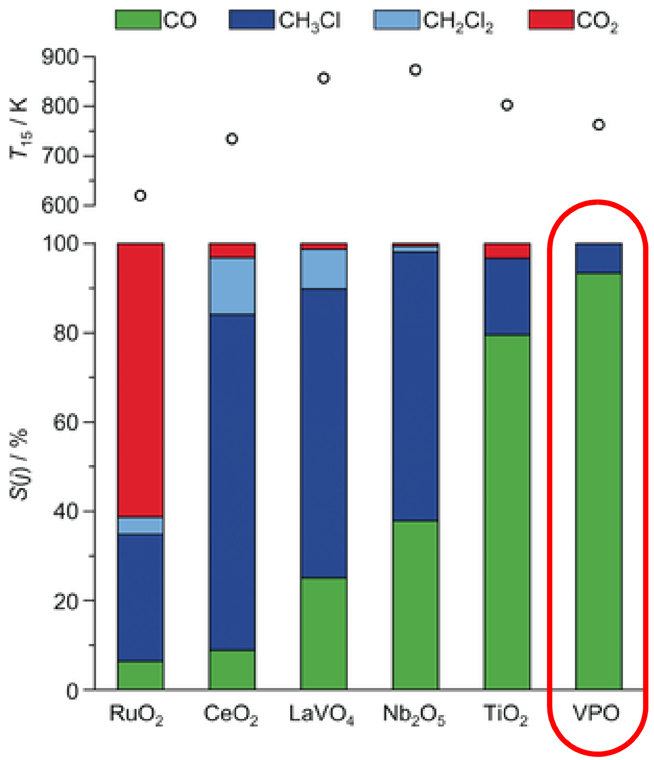
Catalyst Stability

- Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate

  V. Paunovic, et. al., *Angew. Chem. Int. Ed.* 2016, **55**, 15619. DOI: 10.1002/anie.201608165



formic acid
hydrogen
methanol
F-T



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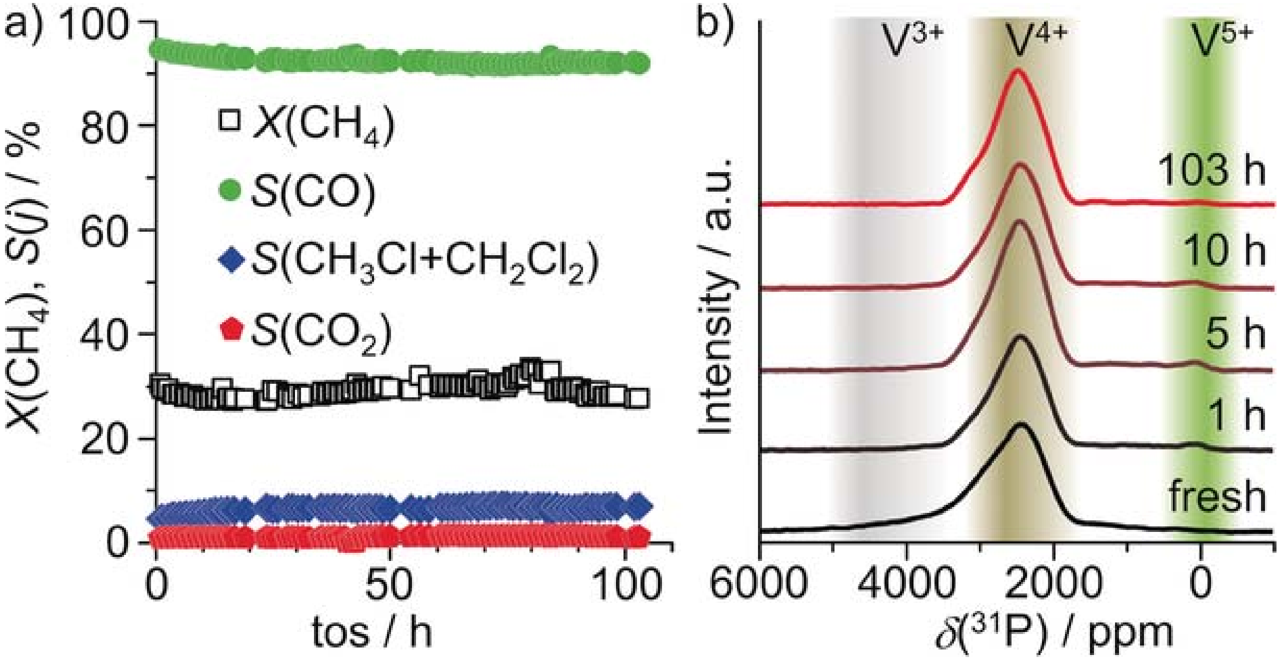


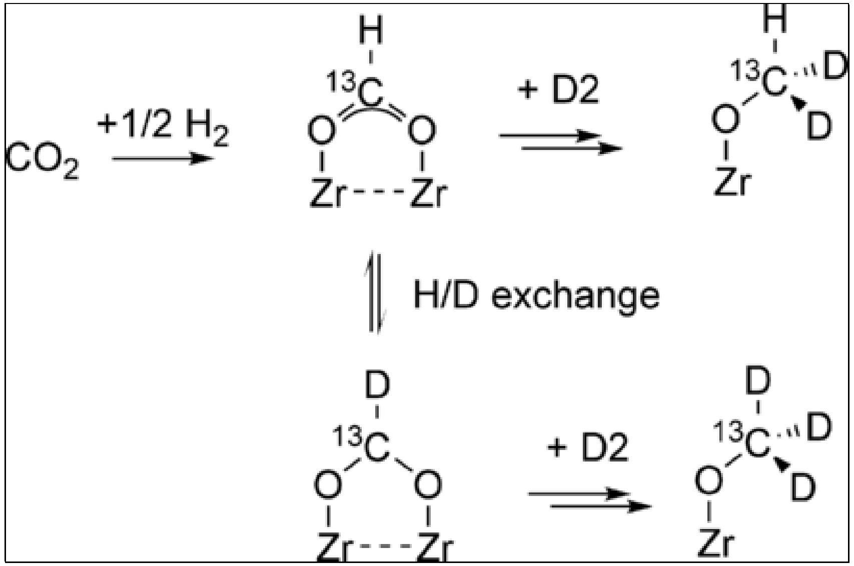
- V^{4+} and V^{3+} are paramagnetic. *Strong* shift of the (spatially close by) ^{31}P resonances through the Hyperfine interaction.

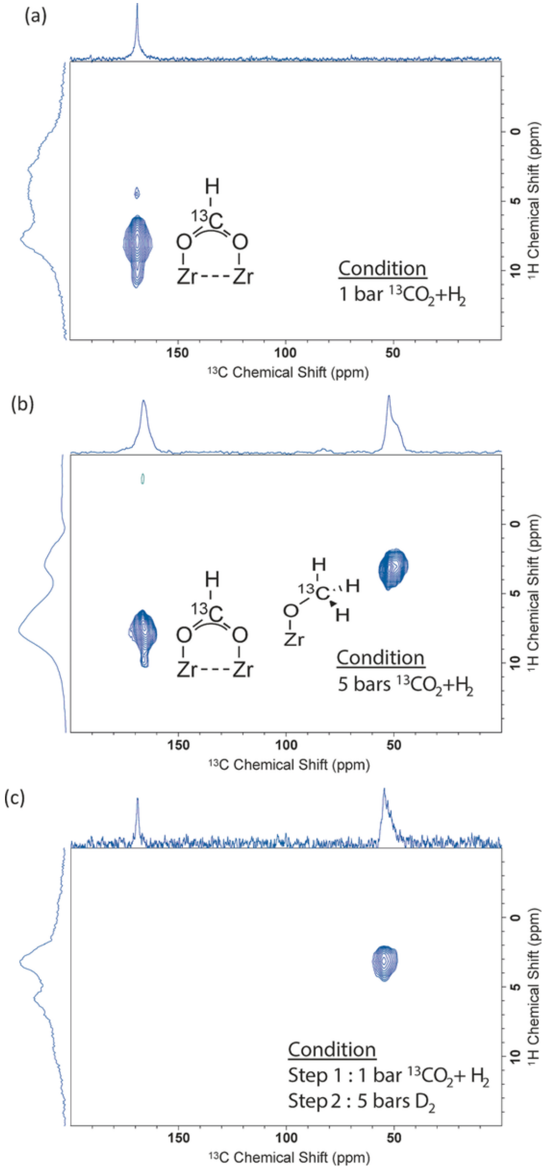
Catalyst adsorbed Species

- CO_2-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal–Support Interface

K. Larmier, et. al., *Angew. Chem. Int. Ed.* 2017, **56**, 2318.

DOI: 10.1002/anie.201610166





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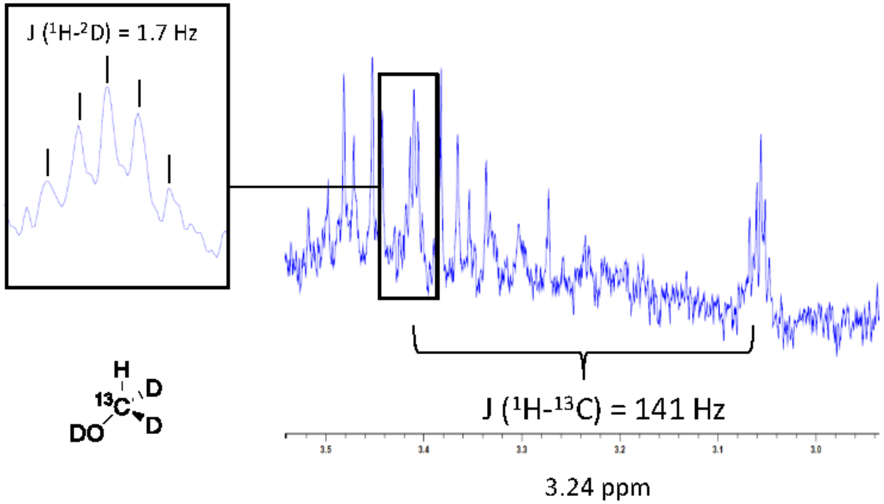


Figure S18. Liquid-state ^{1}H NMR after washing Cu/ZrO_2 with D_2O after the two steps hydrogenation of $^{13}CO_2$. A doublet of pentet centered at 3.24 ppm can be observed, related to the ^{1}H-^{13}C and ^{1}H-^{2}D J-couplings. This is consistent with a $^{13}CHD_2$ group. This signal merges into a single peak at 3.24 ppm when a ^{13}C decoupling pulse is applied. The other peaks are impurities introduced during the process. They do not change upon ^{13}C decoupling.

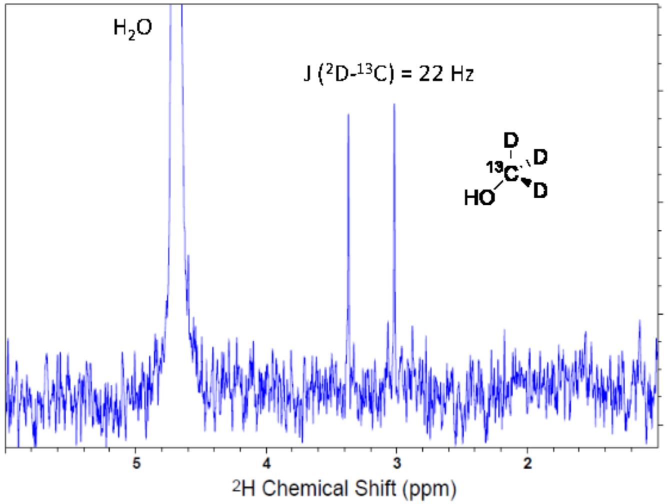
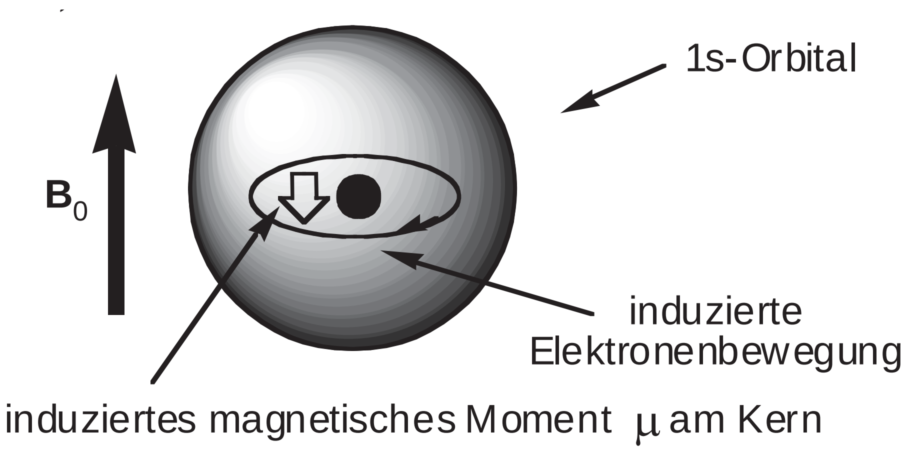
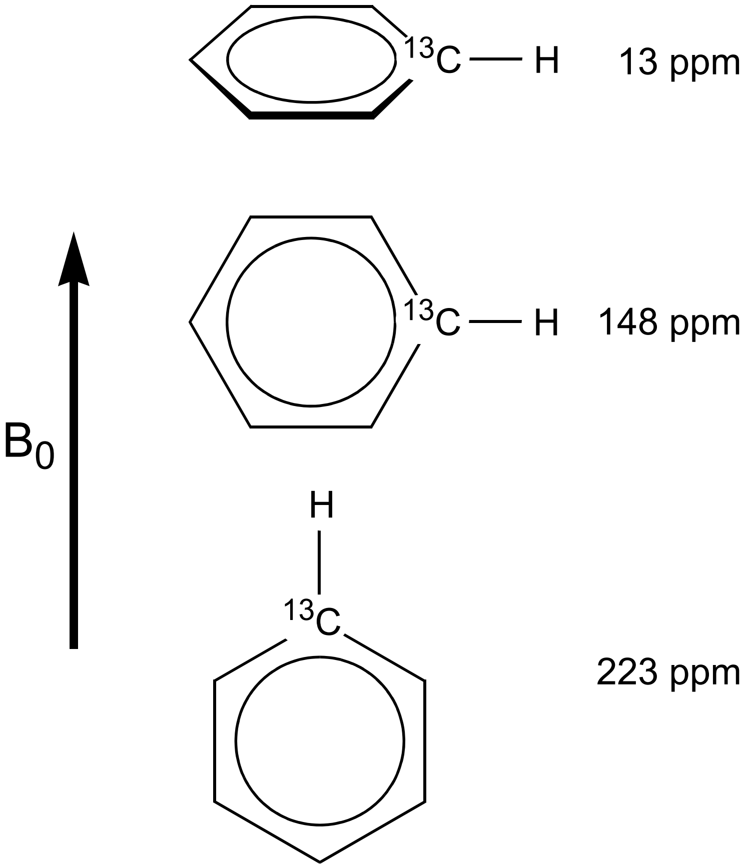


Figure S19. Liquid-state ^{2}D NMR after washing Cu/ZrO_2 with H_2O after the two steps hydrogenation of $^{13}CO_2$. A doublet centered at 3.19 ppm can be observed, related to the ^{2}D-^{13}C J-coupling. No fine structure can be distinguished (no ^{1}H decoupling was applied).

Chemical Shift in solids

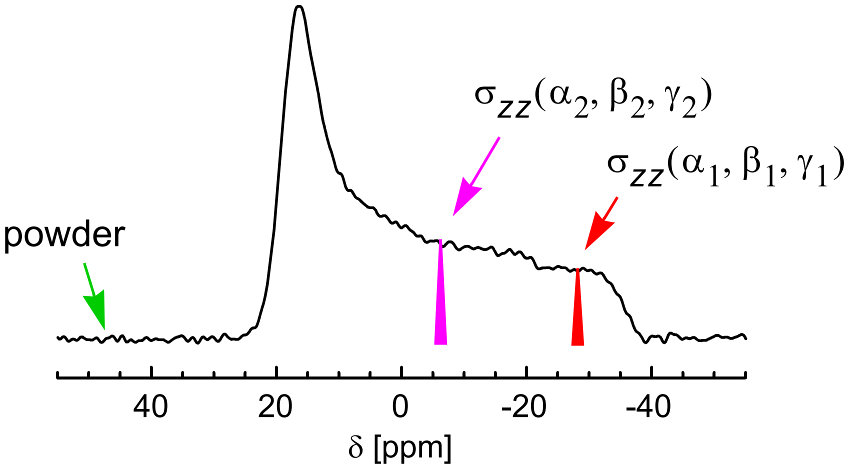
- No Brownian Motion but “static” molecules
- The Chemical Shift is dependent on the orientation wrt the Magnetic Field (Rank 2 Tensor)

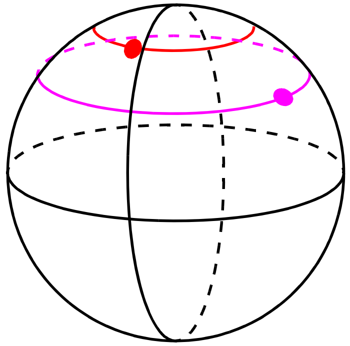




Chemical Shift in solids

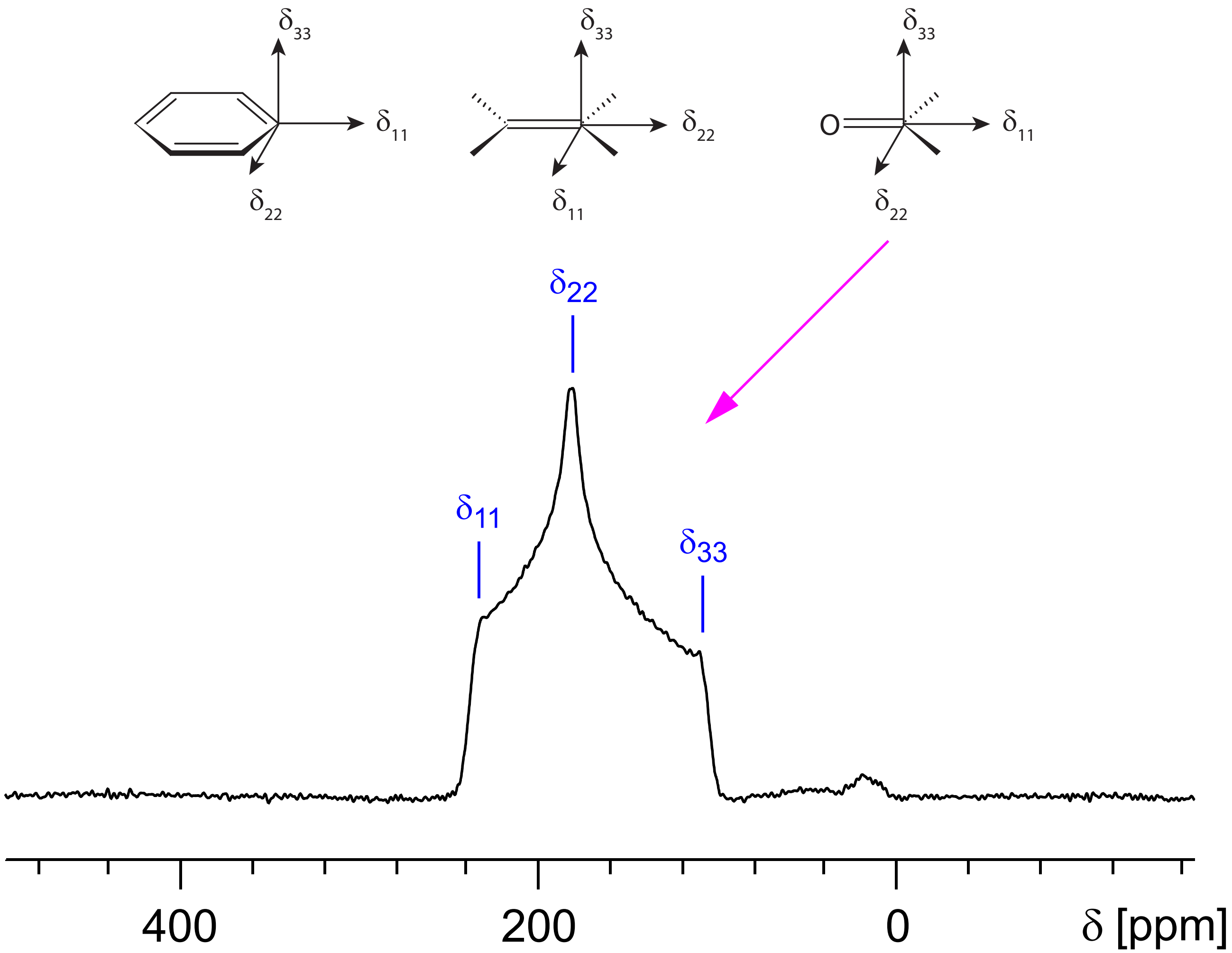
- Orientation dependency of the signal
- Three Euler Angles (α,β,γ) needed to orient a “molecule”.
- Not all orientations are equally prevalent in a uniform and random powder. (only one polar but many equatorial)





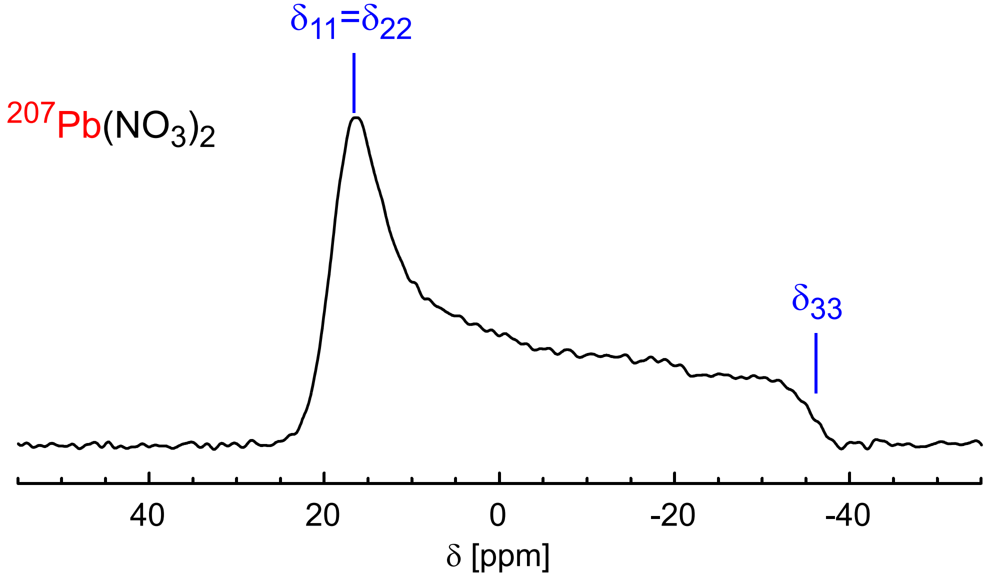
Chemical Shift in solids

- A tensor is characterized by its three principal components $(\delta_{11},\delta_{22},\delta_{33})$
- In general all three are different and easy to determine from a powder spectrum
- The principal components are connected to the molecular frame



Chemical Shift in solids

- Alternative parameterizations for the tensor characterization are common



Tensor Characterization:

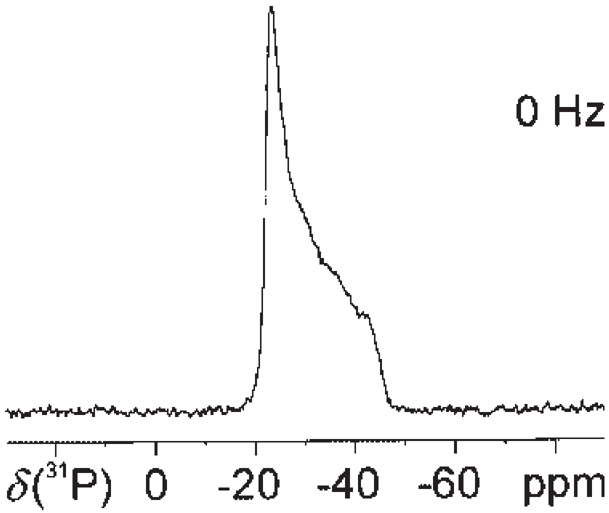
$\delta_{11}, \delta_{22}, \delta_{33}$

$$\begin{aligned} \delta_{\mathrm{iso}} &= \frac{1}{3}(\delta_{11}+\delta_{22}+\delta_{33}) \\ \text{span} &= \Omega = \delta_{11}-\delta_{33} > 0 \\ \text{skew} &= \kappa = 3(\delta_{22}-\delta_{\mathrm{iso}})/\Omega \end{aligned}$$

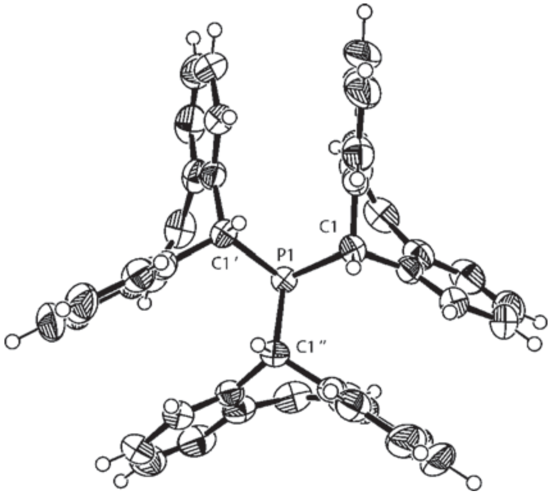
$$\begin{aligned} \delta_{\mathrm{iso}} &= \frac{1}{3}(\delta_{11}+\delta_{22}+\delta_{33}) \\ &|\delta_{zz}-\delta_{\mathrm{iso}}| \geq |\delta_{xx}-\delta_{\mathrm{iso}}| \geq |\delta_{yy}-\delta_{\mathrm{iso}}| \\ \text{anisotropy} &= \delta = \delta_{zz}-\delta_{\mathrm{iso}} \\ \text{asymmetry} &= \eta = 3(\delta_{yy}-\delta_{xx})/\delta \end{aligned}$$

Chemical Shift in solids

- When two (or more) principal values are equal, it tells us about the local symmetry around the nucleus



202 MHz ^{31}P NMR spectrum on a static sample showing the axial tensor, $\sigma_{11}=\sigma_{22}=-24.0$ and $\sigma_{33}=-43.0$ ppm



View of trop$_3$P along the threefold symmetry axis

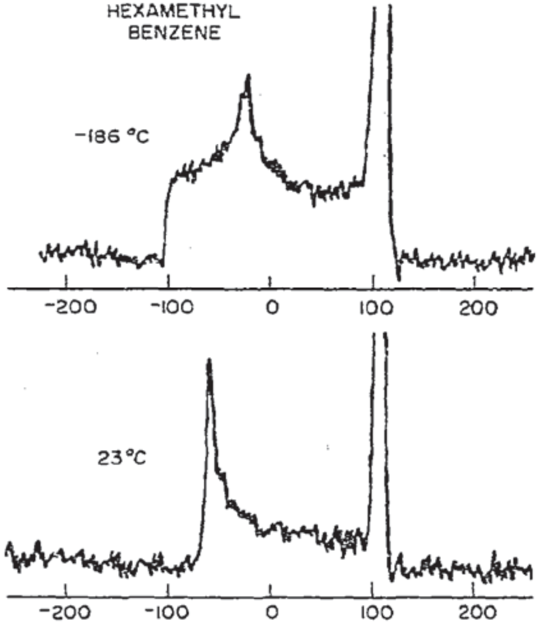
Chemical Shift in solids

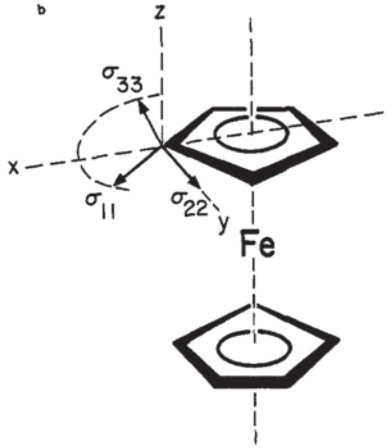
- Symmetry *might* be an effect of dynamic averaging.
  E.g. Rotor Phases lead to averaging of tensor elements

1. Hexamethylbenzene
2. Benzene
3. Permetylferrocene

^{13}C NMR of uniaxial aromatic rotors

T	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Ω	κ
Hexamethylbenzene						
87	232	154	24	137	208	0.25
296	189	189	21	133	168	1.00
Benzene						
	187	187	13	129	174	1.00
Permethylferrocene						
93	127	86	23	79	104	0.20
289	101	101	34	79	67	1.00





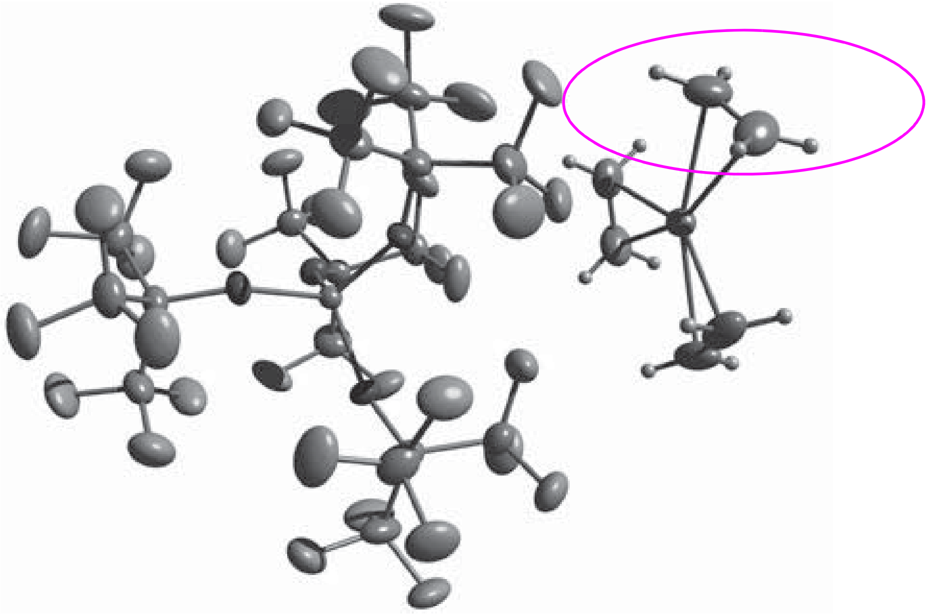
Chemical Shift in solids

- Tris-Ethene Complex of Silver Cations

^{13}C NMR of Ethene and Complexes

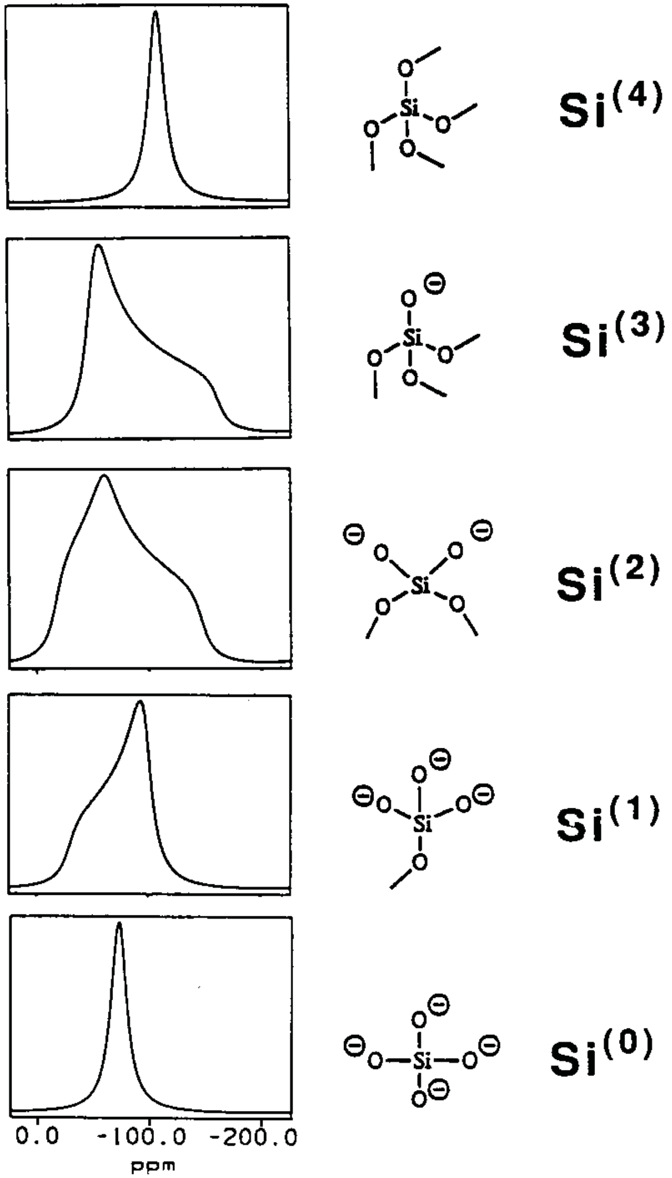
#	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Ω	κ
1	234	121	24	126	210	-0.08
2	191	72	72	112	119	-1.00
3	190	135	10	112	180	0.39
4	134	65	-11	63	145	0.05

chemical shifts of principle tensor components in ppm relative to TMS. (1) Free Ethene, (2) $[Ag(\eta^2\text{-}C_2H_4)_3][Al(OR)_4]$, (3) $[Ag(\eta^2\text{-}C_2H_4)]$ $[Al(OC(CH_3)(CF_3)_2)_4]$, (4) Zeise's Salt



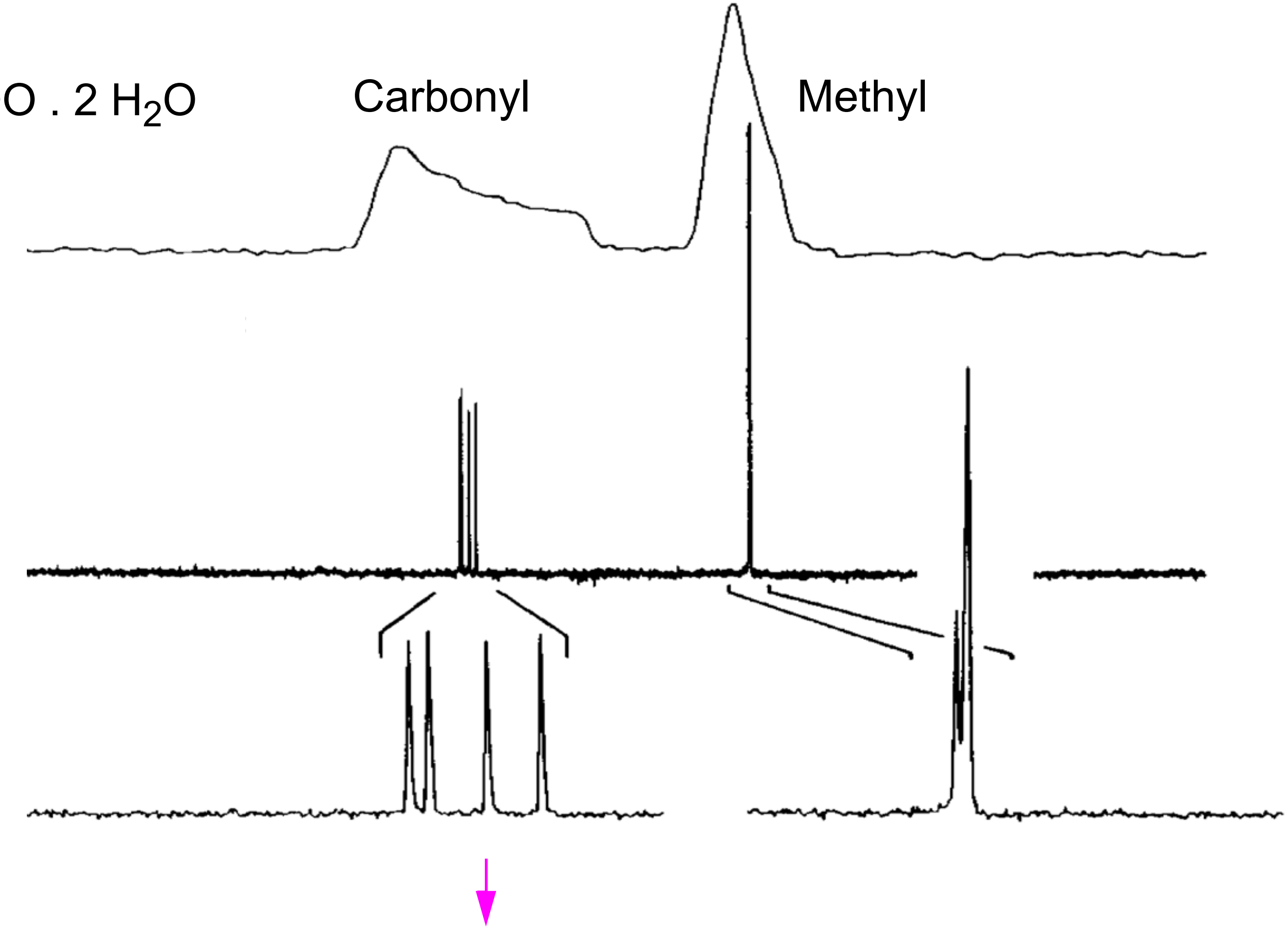
Chemical Shift in solids

- Structural Information from ^{29}Si Chemical Shifts



Powder Lineshapes

- Information vs. Resolution



Ca CH_3COO . 2 H_2O

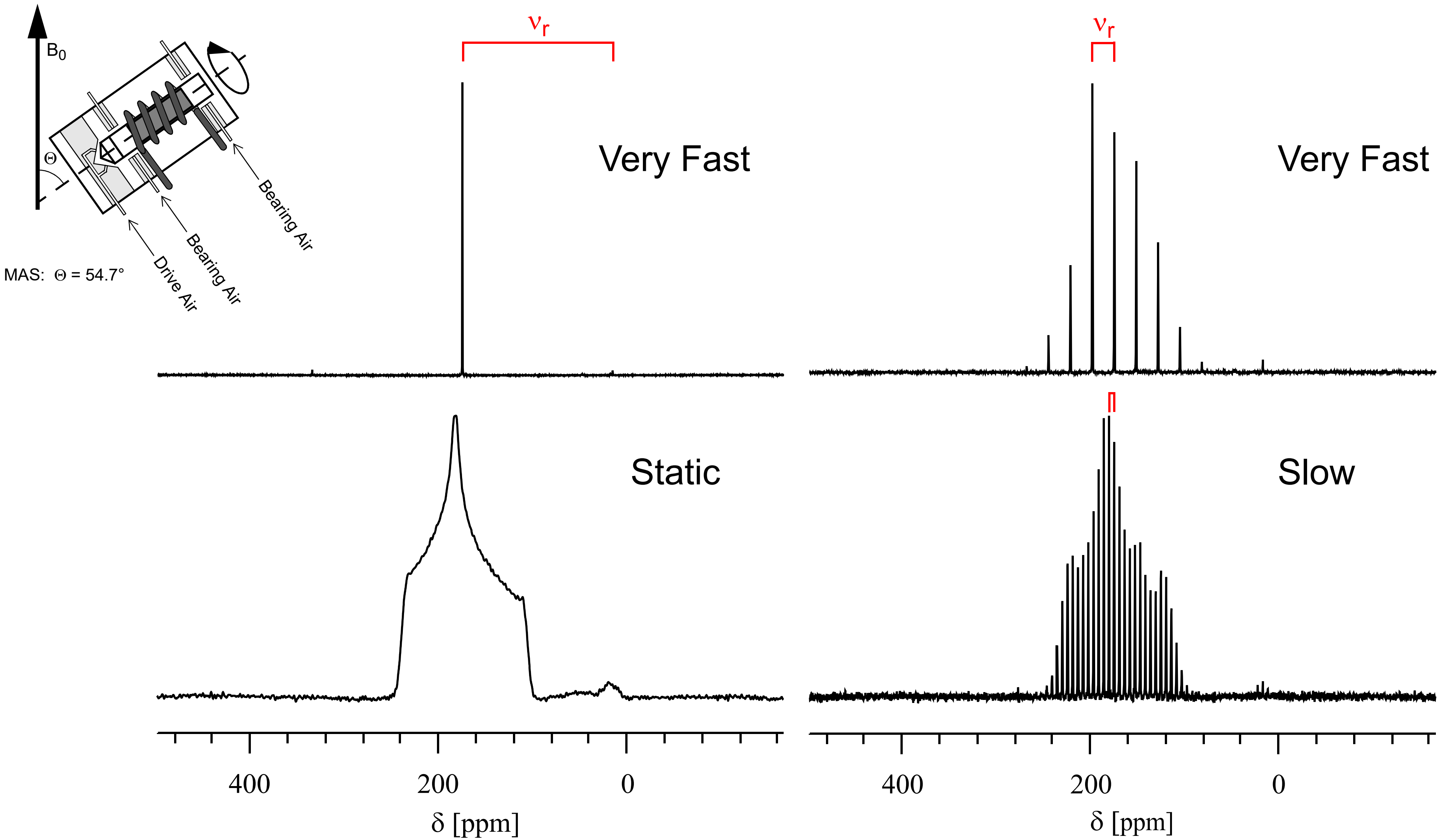
Carbonyl

Methyl

4 Inequivalent molecules

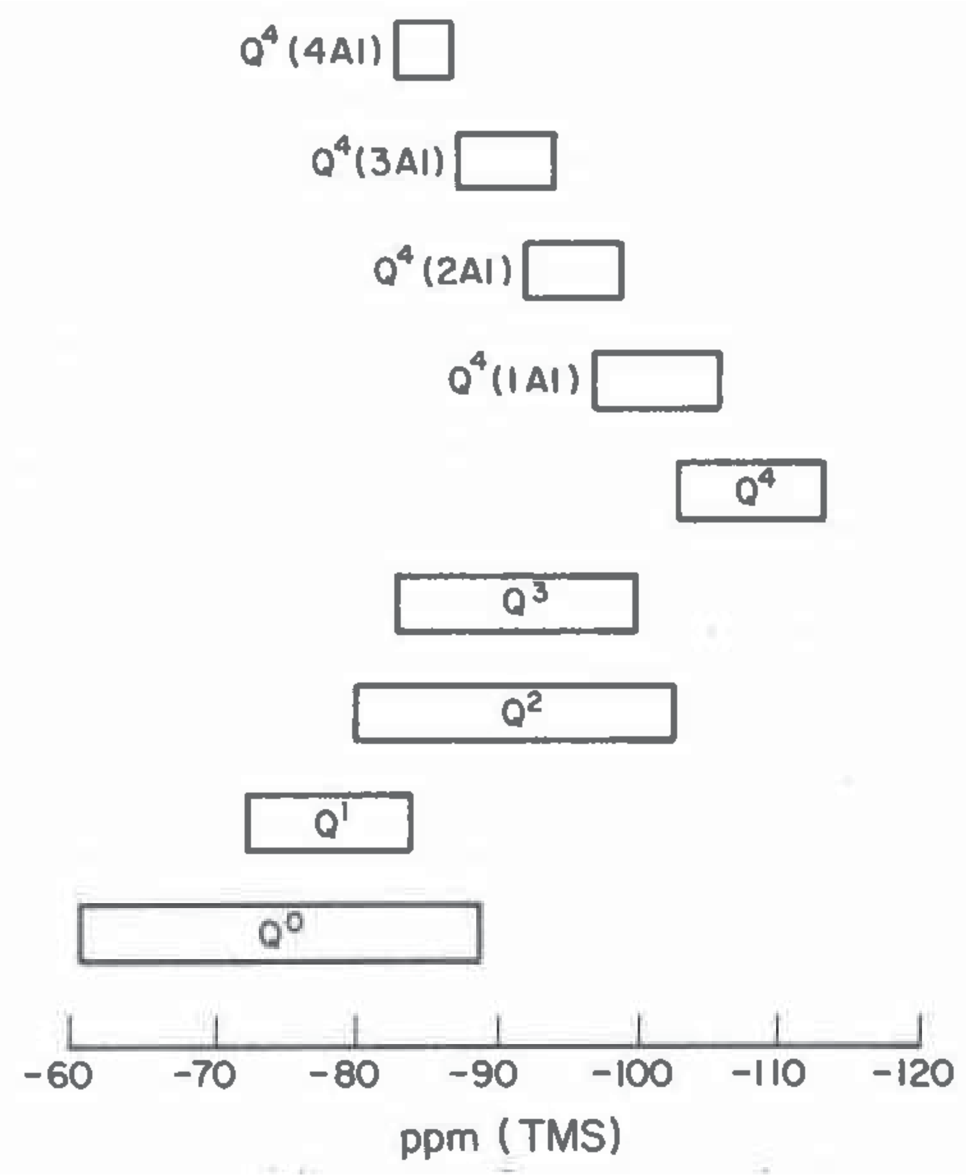
Magic Angle Spinning (MAS)

- 1-^{13}C-Alanine



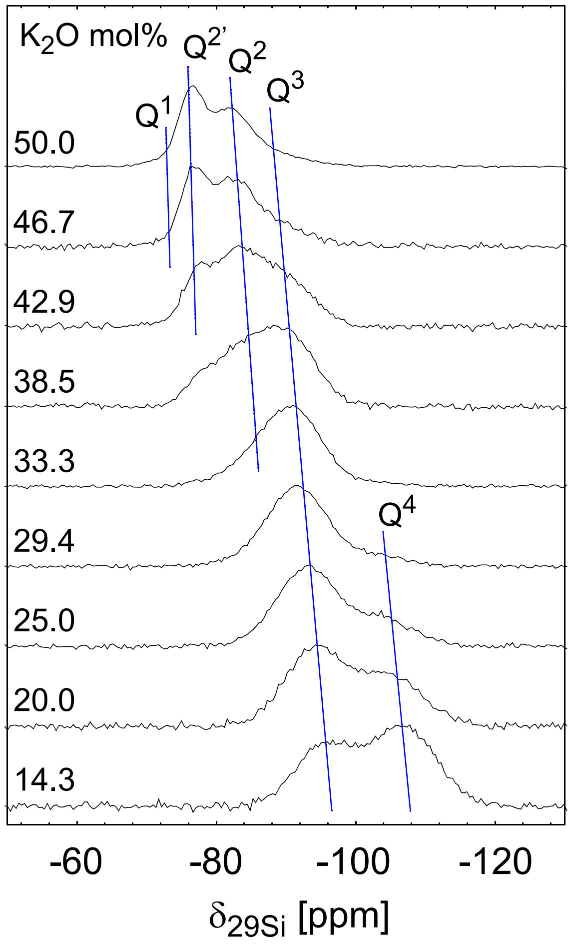
Chemical Shift in solids - MAS

- Structural Information from ^{29}Si Chemical Shifts

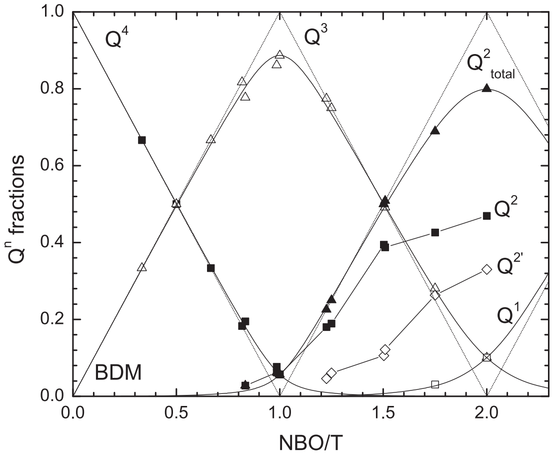


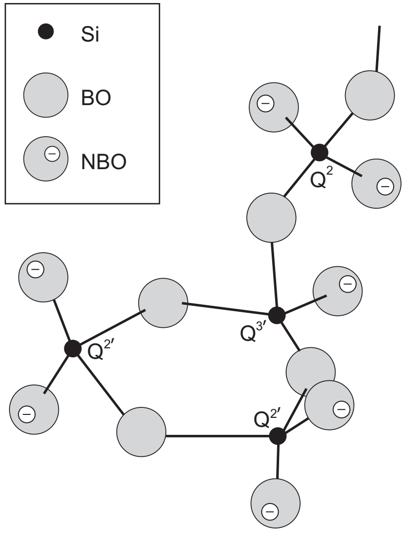
^{29}Si MAS NMR of Potassium Silicate Glasses

- Detection and Quantification of Q^2 sites in three membered rings



Deconvolution



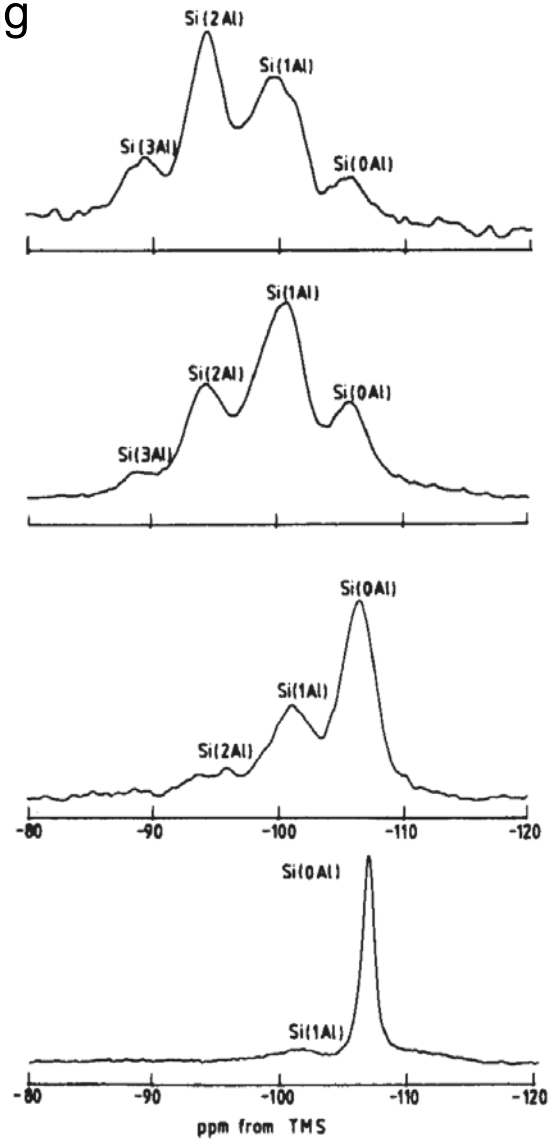


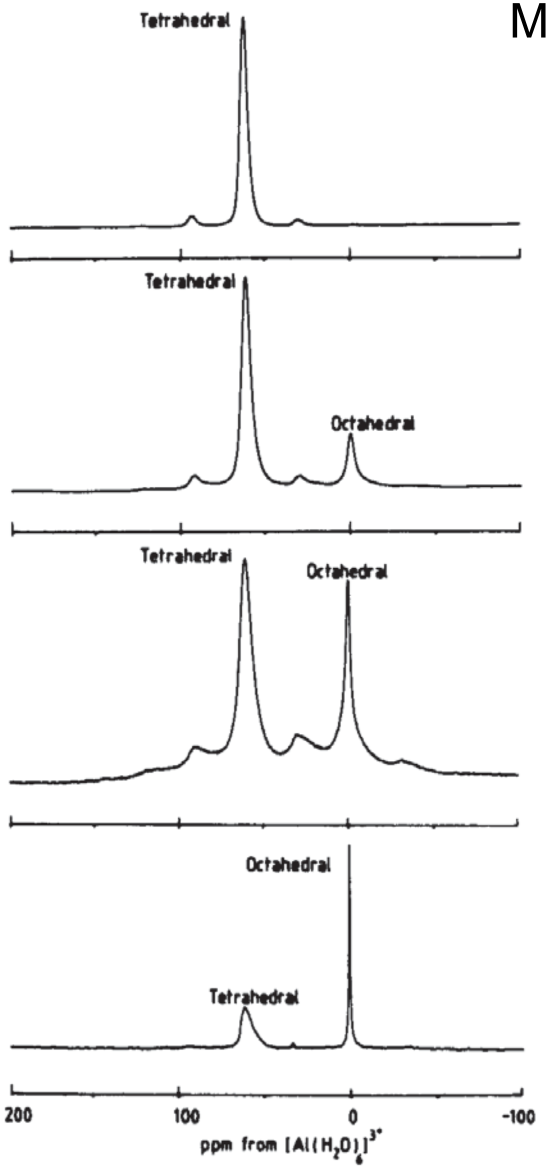
NMR Interactions - Chemical Shift

- Effect of ^{27}Al neighbours on ^{29}Si Chemical Shifts

Magic Angle Spinning
^{29}Si NMR

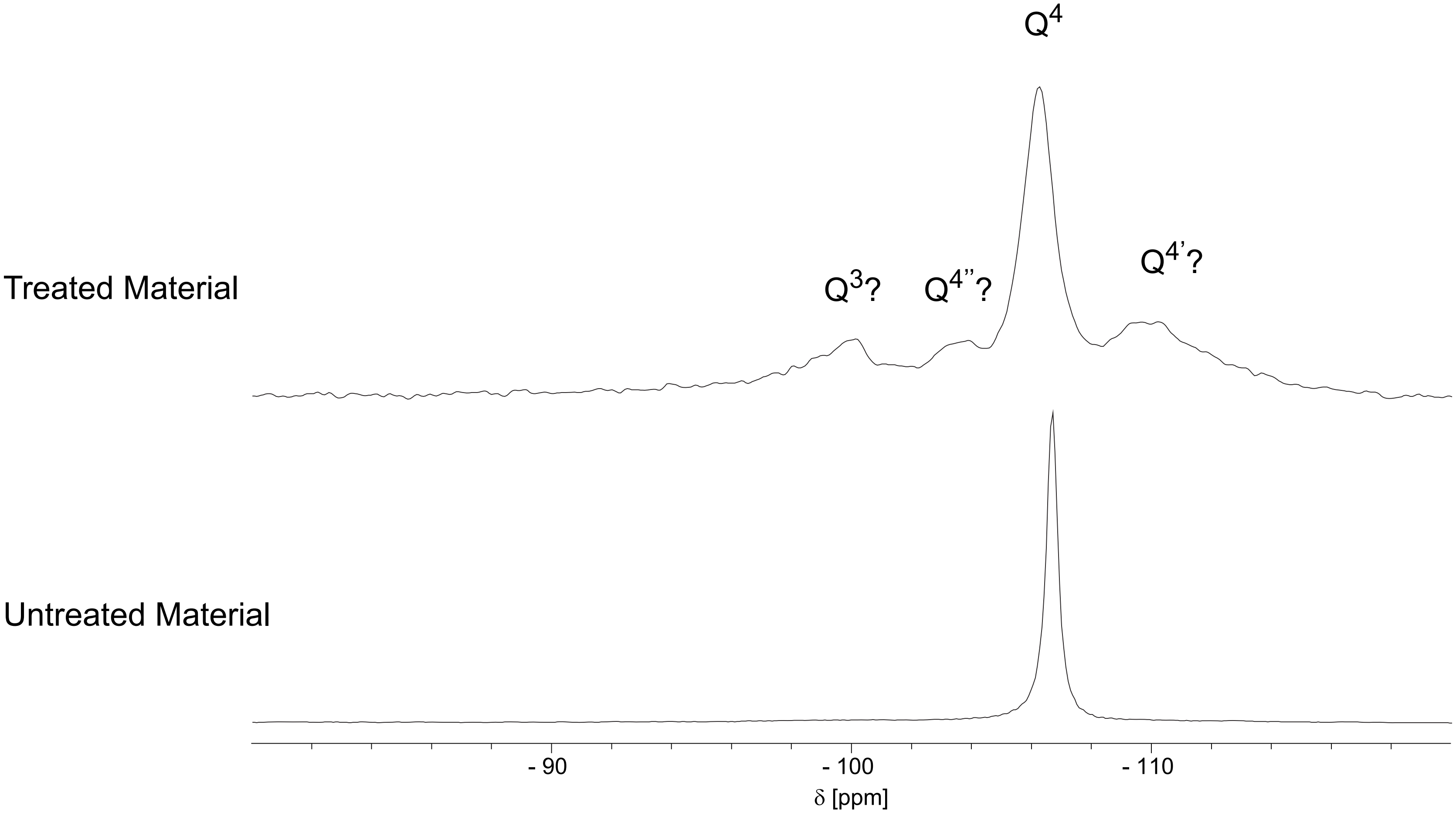
Decreasing amount of Al





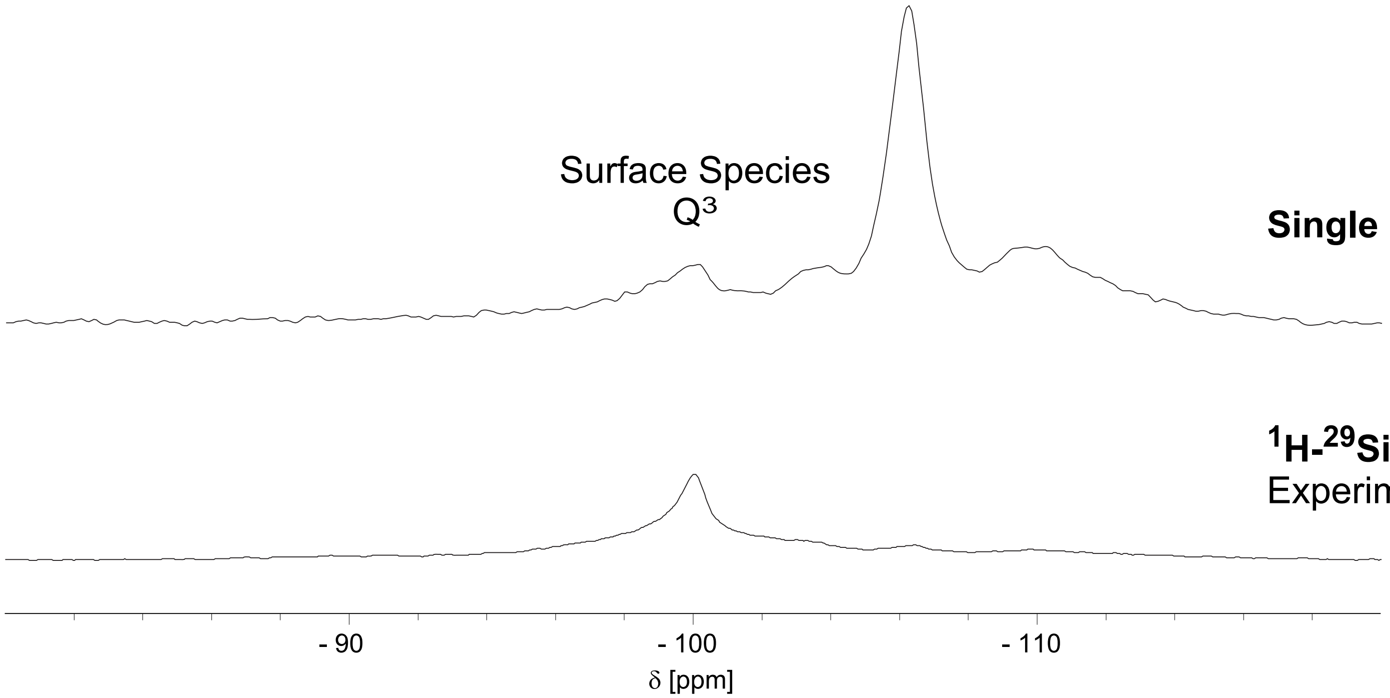
Magic Angle Spinning
^{27}Al NMR

^{29}Si MAS NMR of Treated Zeolites



^{29}Si MAS NMR of Treated Zeolites

Treated Material

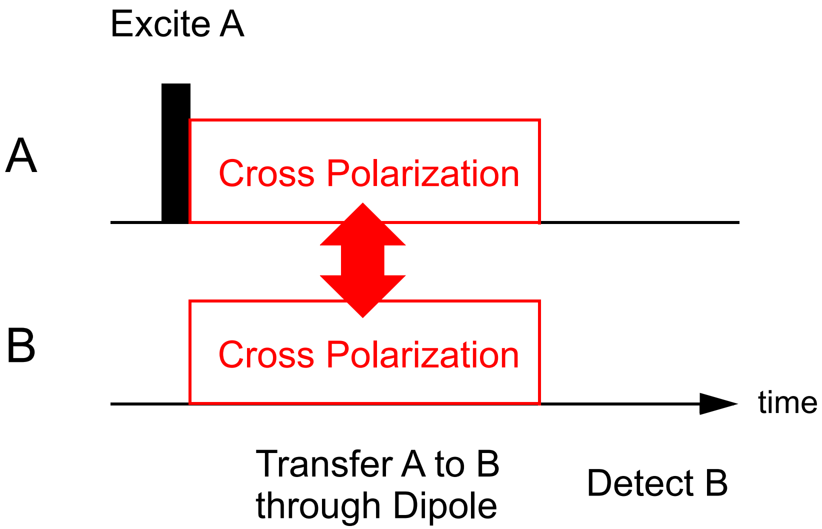


Single Pulse Experiment

^{1}H-^{29}Si Cross Polarization
Experiment

Dipole Mediated Transfer: Cross Polarization

- Transfer of Polarization from Spin A to Spin B through the dipole coupling



Excite A

A

Cross Polarization

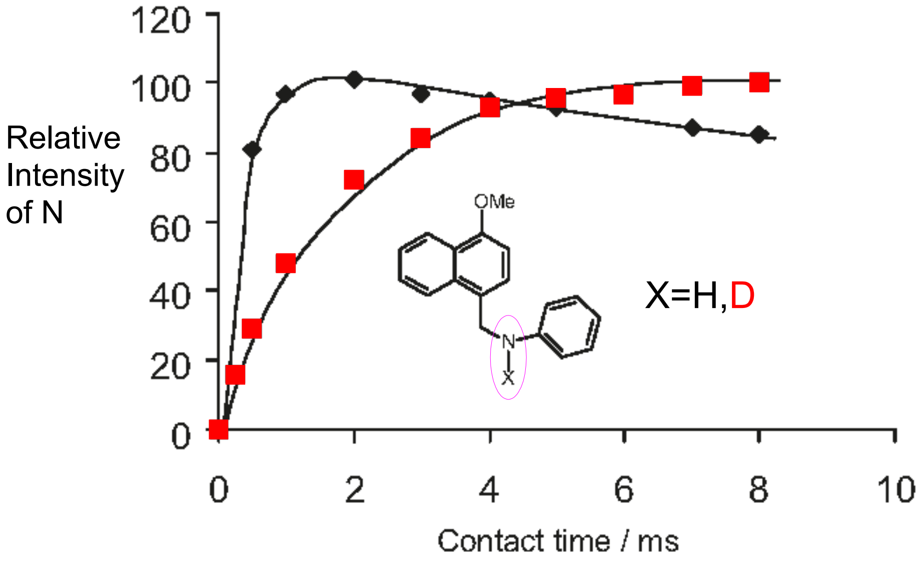
B

Cross Polarization

time

Transfer A to B
through Dipole

Detect B



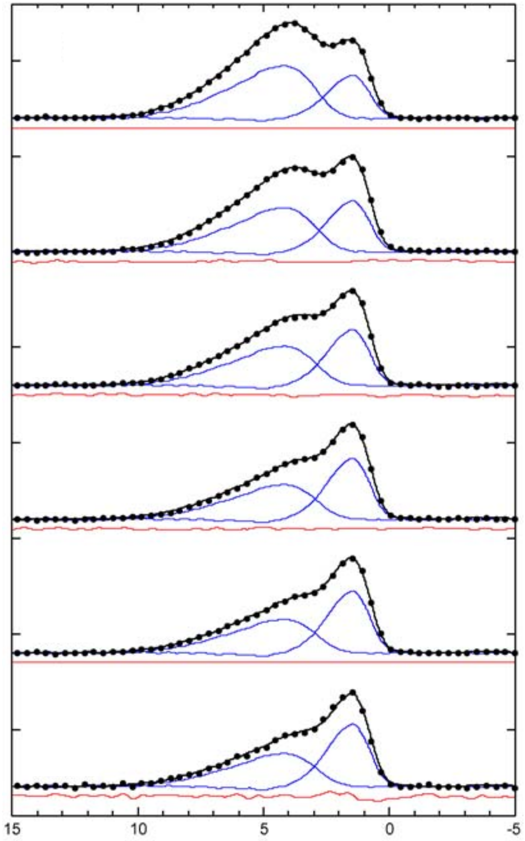
- Dipole Interaction is strongly dependent on the distance between two spins.

Dipole Mediated Transfer: Cross Polarization

- Distance based proximity filter using Cross Polarization

^{1}H Spectra acquired after polarization transfer from ^{27}Al to ^{1}H

Shorter recoupling durations selects stronger ^{27}Al-^{1}H couplings (and shorter distances)



8.0 ms

4.0 ms

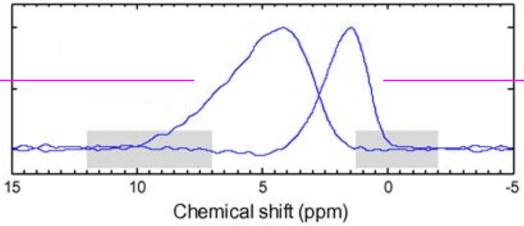
2.0 ms

1.0 ms

0.5 ms

0.25 ms

Jadeite ($NaAlSi_2O_6$)
glass with 0.62% H_2O

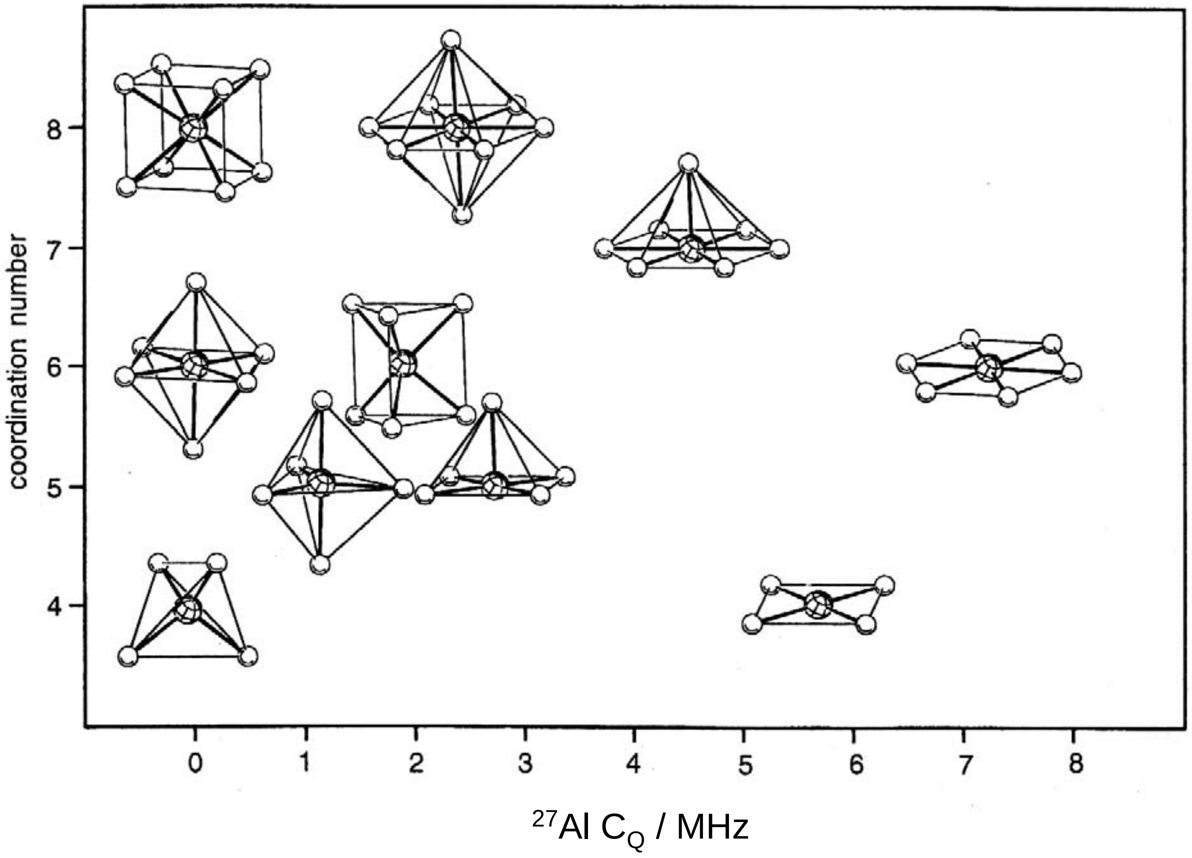


“Far from Al” (8.0 - 0.5 ms)

“Close to Al” (0.5 - 8-0 ms)

NMR Interactions - Quadrupole

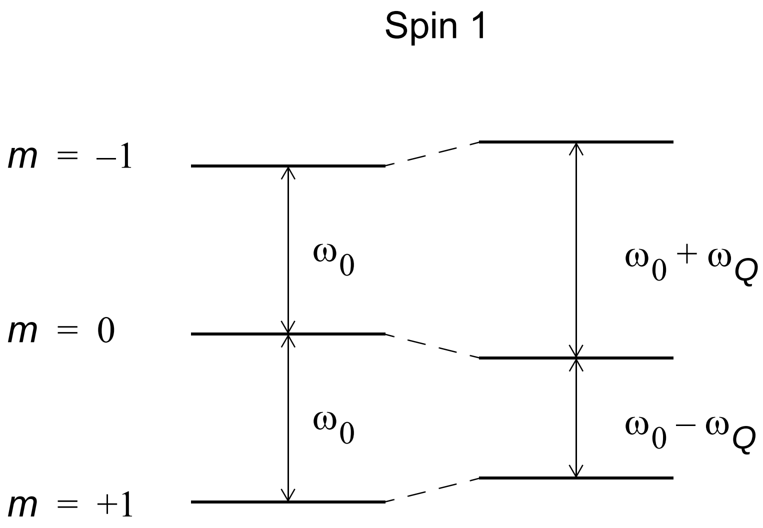
- For I>1/2, nuclei have a non-spherical charge distribution in the nucleus and this gives rise to a quadrupole moment
- The Quadrupole moment interacts with the electric field gradient
- The Quadrupole Coupling Constant, $C_Q = \frac{eQV_{zz}}{2I(2I-1)h}$ depends on the system

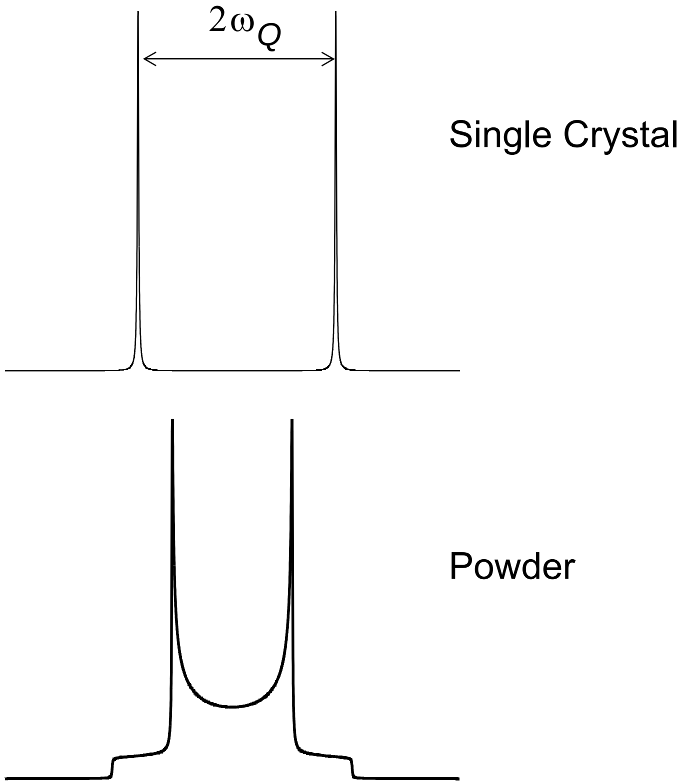


NMR Interactions - Quadrupole

- Going through the mathematics and applying the secular approximation we get a frequency caused by the quarupole interaction

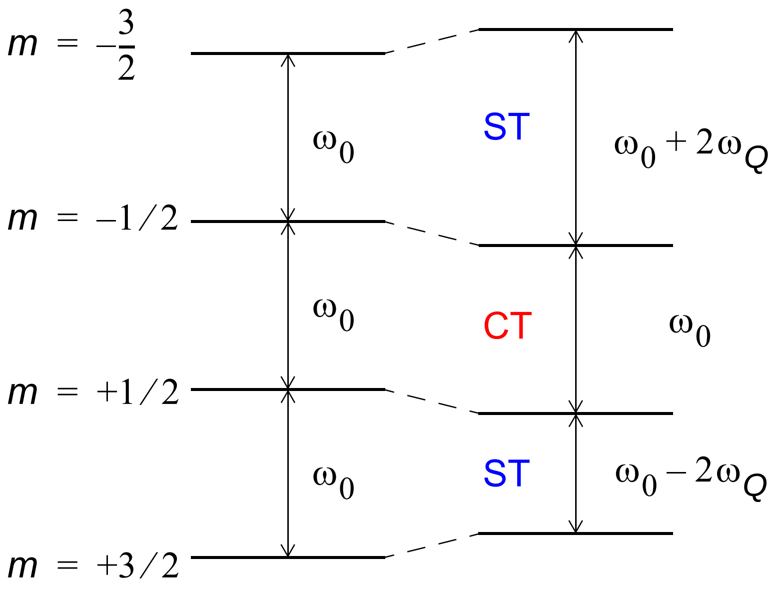
$$\omega_Q = \frac{3eQV_{zz}}{4I(2I-1)h}\frac{1}{2}(3\cos^2\theta - 1 + \eta_Q\sin^2\theta\cos 2\gamma)$$

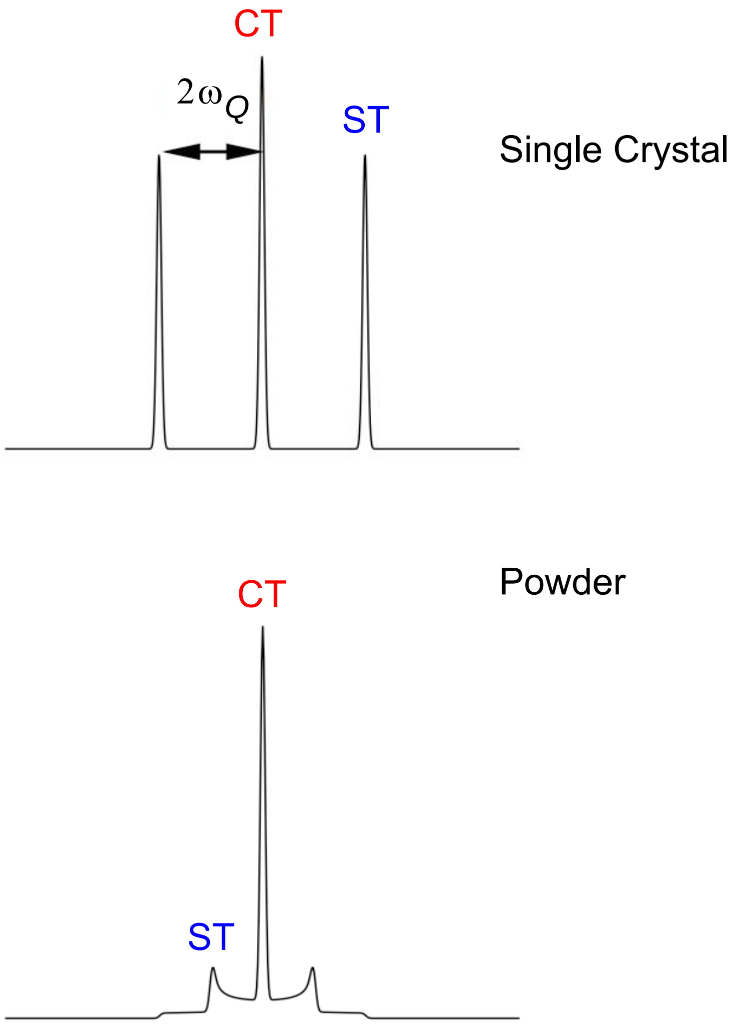




NMR Interactions - Quadrupole

Spin 3/2





The Central Transition has NO Angular Dependency

NMR Interactions - Quadrupole

- Often the Quadrupolar Interaction is big and the first order approximation is not good enough
- First Order Term

$$\omega_Q^{(1)} = \frac{3eQV_{zz}}{4I(2I-1)h}\frac{1}{2}(3\cos^2\theta - 1 + \eta_Q \sin^2\theta \cos 2\gamma)$$

- Second Order Term

$$\omega_Q^{(2)} \propto \frac{\left(\frac{3eQV_{zz}}{4I(2I-1)h}\right)^2}{\omega_0}(A + Bd_{00}^{(2)}(\theta) + Cd_{00}^{(4)}(\theta))$$

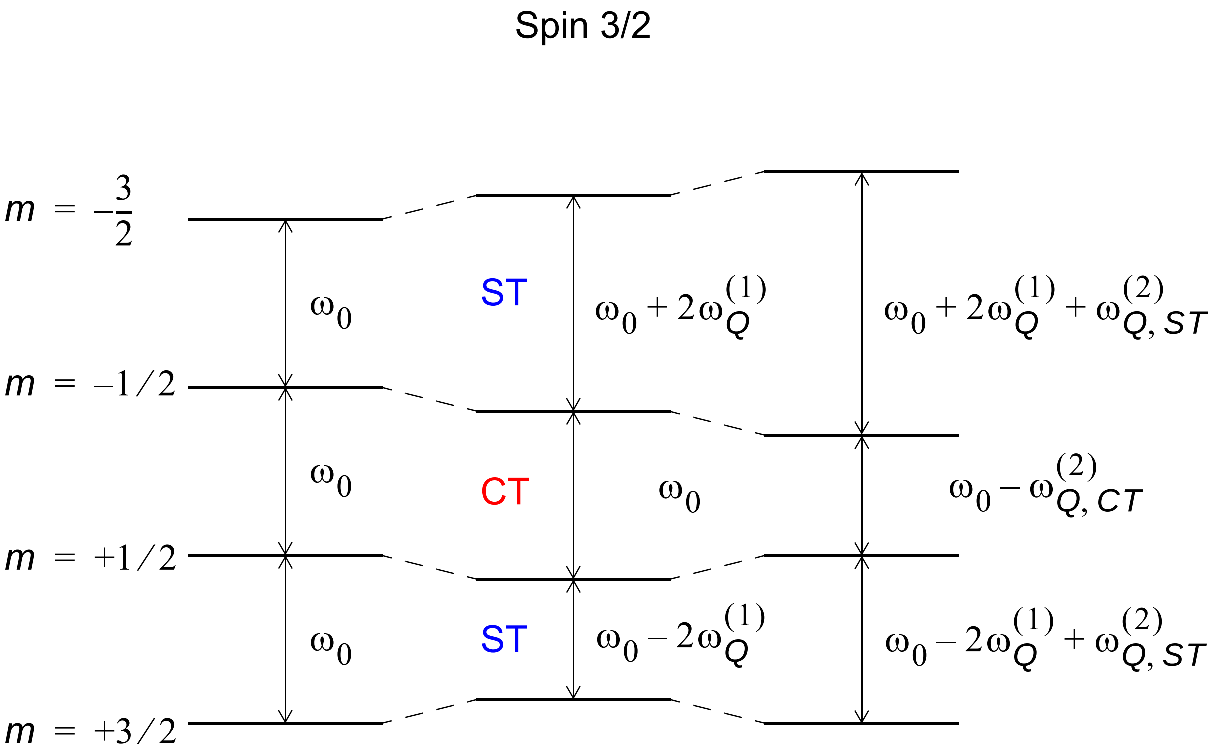
$$d_{00}^{(2)}(\theta) \propto 3\cos^2\theta - 1$$

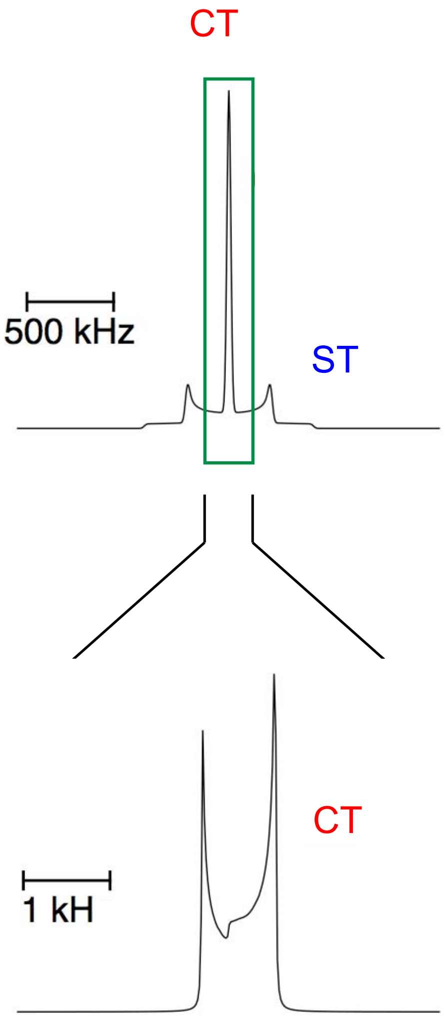
$$d_{00}^{(4)}(\theta) \propto 35\cos^4\theta - 30\cos^2\theta + 3$$

- The Second Order Term:

Scales with the inverse of the Larmor Frequency (and therefore with B_0)
Contains an orientation indenpendent term (A)
Contains a second rank term (B)
Contains a fourth rank term (C)

NMR Interactions - Quadrupole



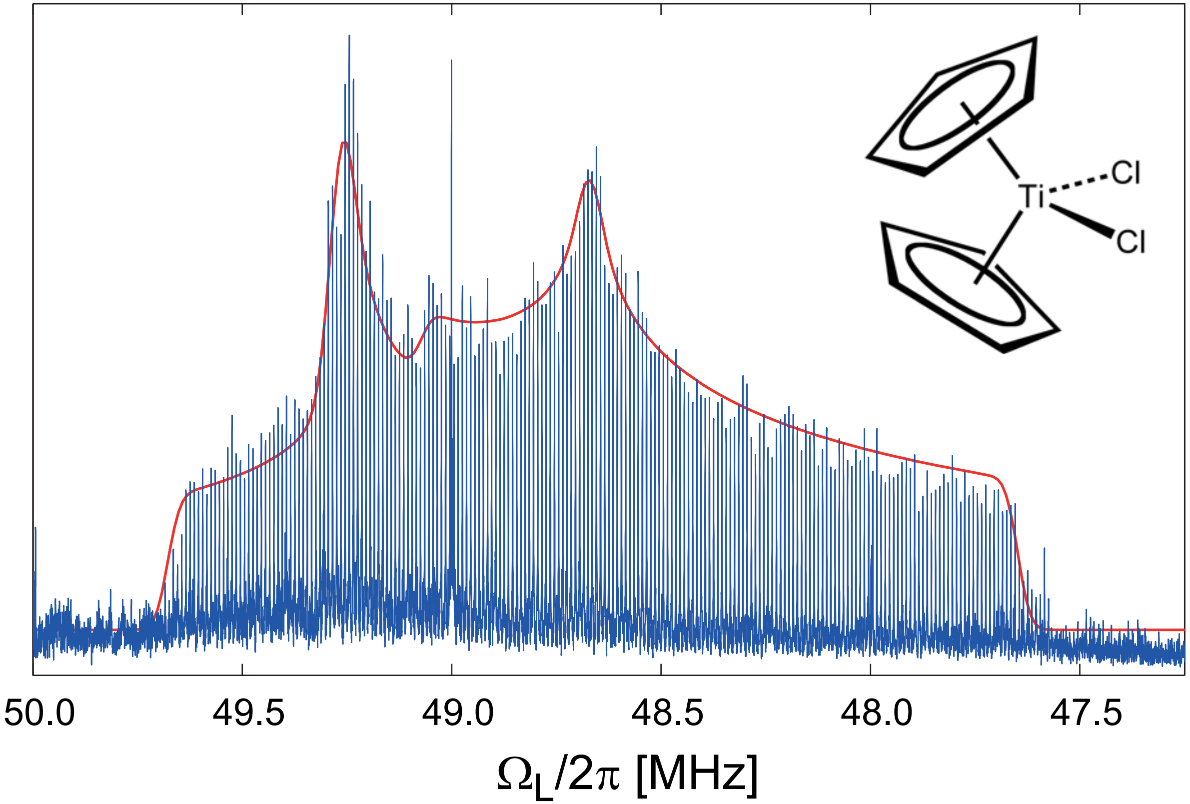


NMR Interactions - Quadrupole

Titanocene dichloride

Static powder QCPMG experiment at B_0=11.7 T (^{1}H 500 MHz)

C_Q = 22.18 (+/- 0.03) MHz
η_Q = 0.612 (+/- 0.003)



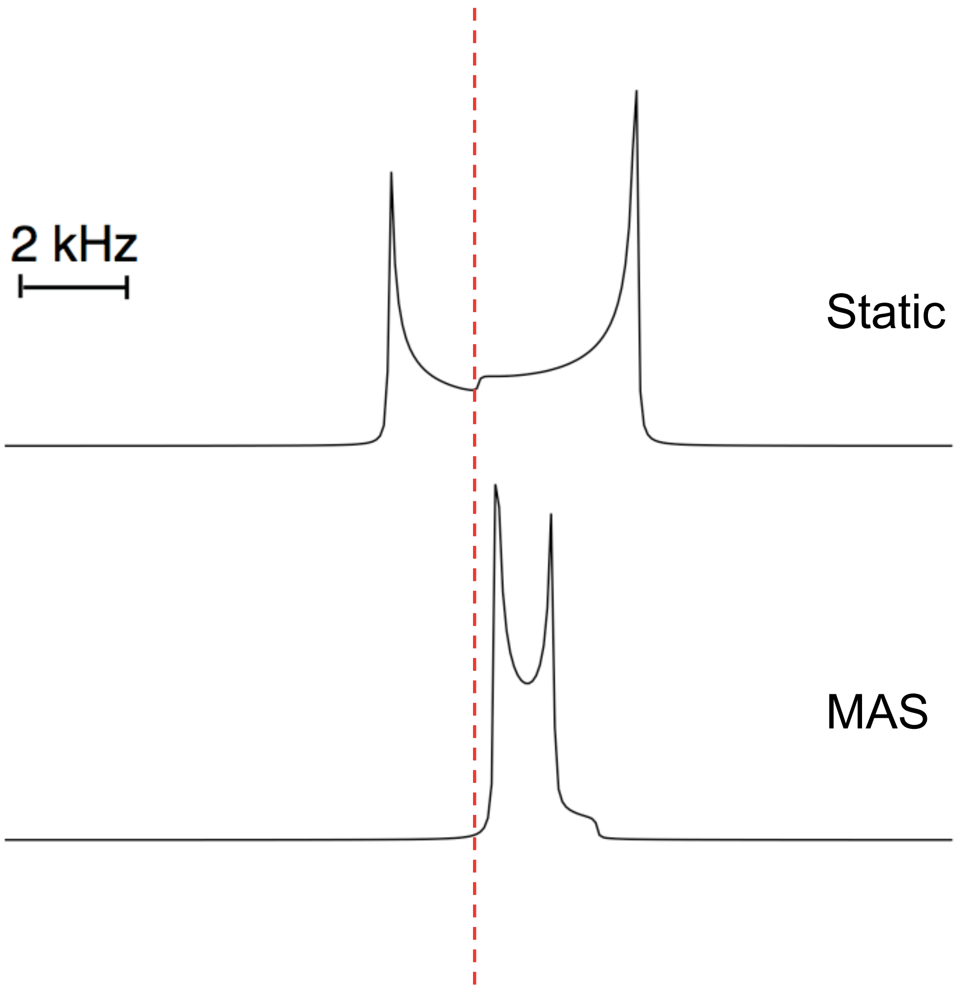
NMR Interactions - Quadrupole

- Magic Angle Spinning of Quadrupoles with second order effects

Central Transition line is narrowed

Fourth rank term (C) remains

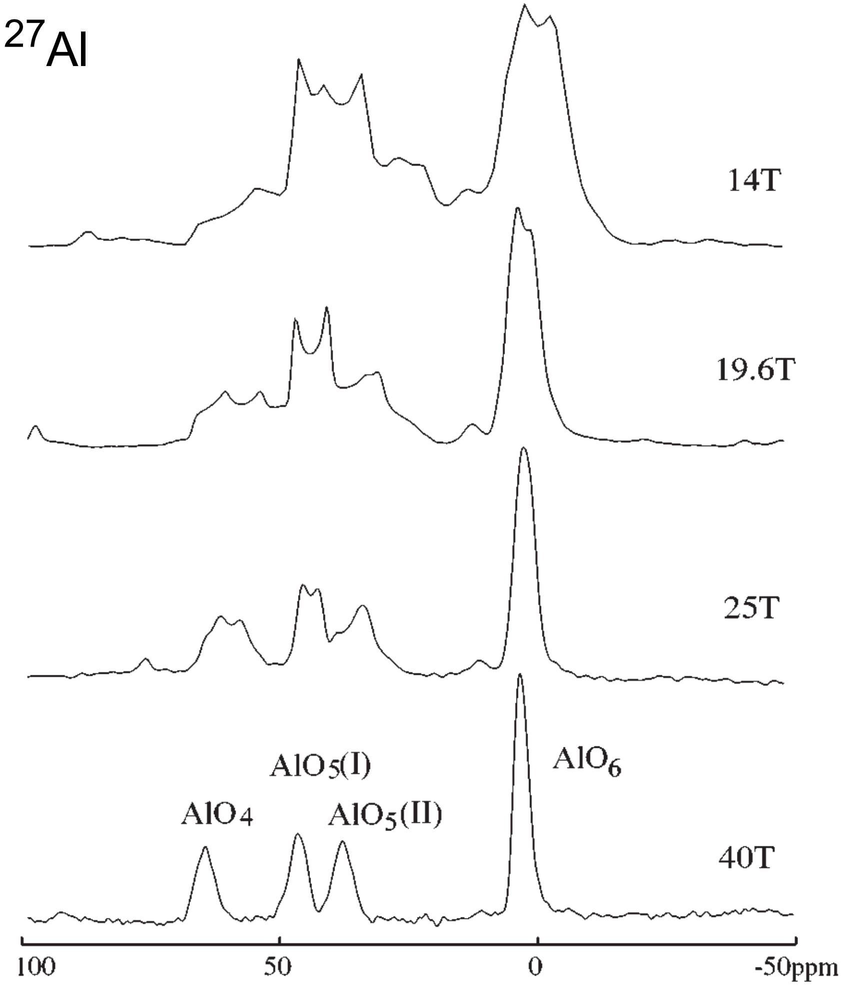
Isotropic term (A) remains



NMR Interactions - Quadrupole

- Second order Quadrupole and Magnetic Field Strength

Isotropic and fourth rank term scale with $1/\omega_0$



$9Al_2O_3.2B_2O_3$

Quadrupole Interaction: High Resolution

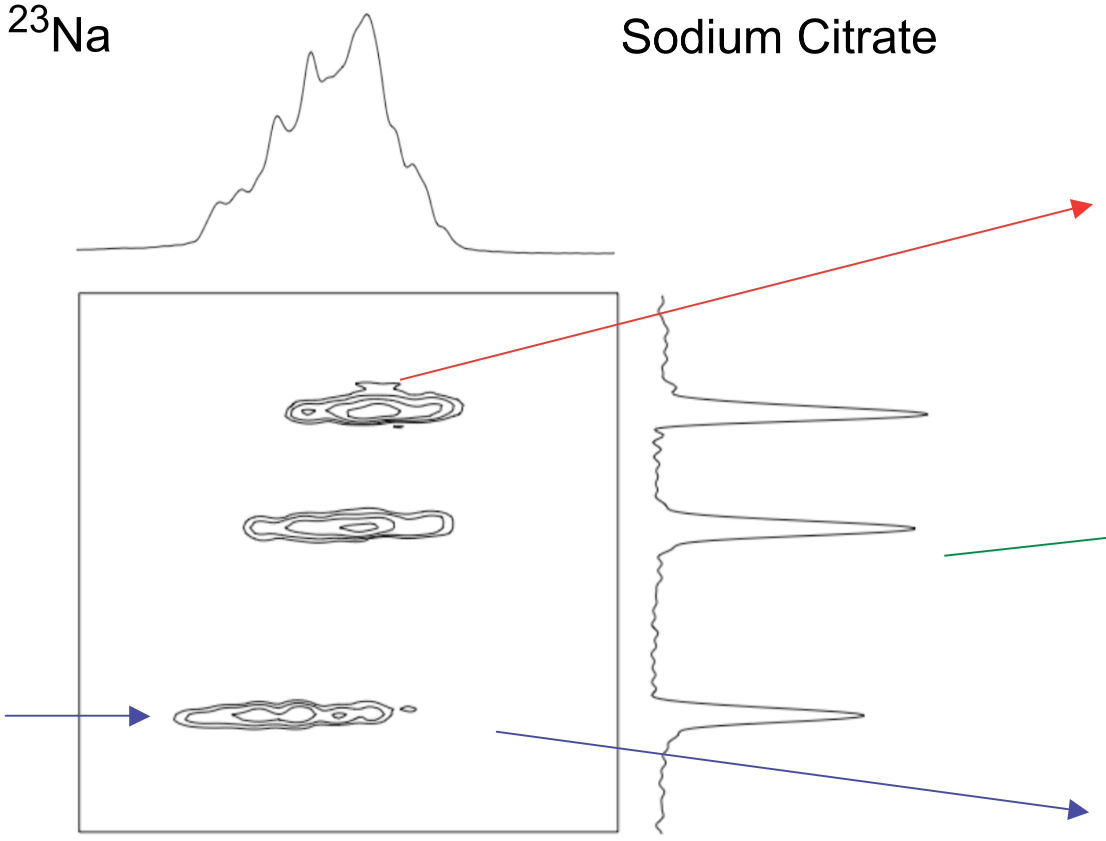
- Is it possible to get high resolution Spectra of Quadrupoles?

Well, yes:

1. Go to very high field
2. Rotate around two axes simultanously (DOR)
3. Rotate around two axes consecutively (DAS)
4. Use the different but related 2nd order shifts of the ST and CT (MQMAS and STMAS)

Quadrupole Interaction: MQMAS

- Correlation between Triple Quantum and Single Quantum Coherence in a 2D experiment



Position of centre of gravity of ridge
δ_{iso} and P_Q

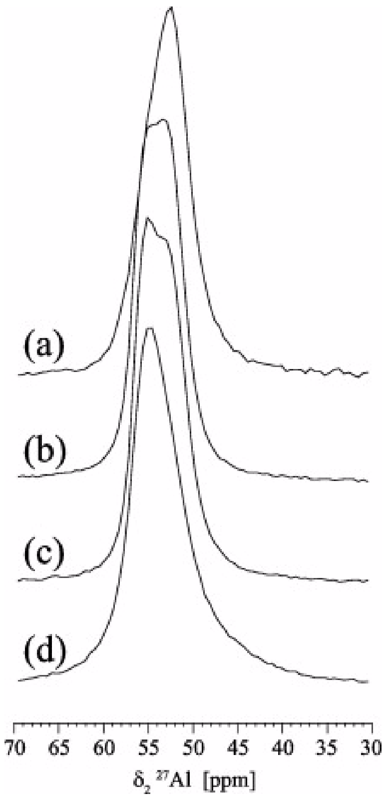
Isotropic spectrum
number of species and relative intensities

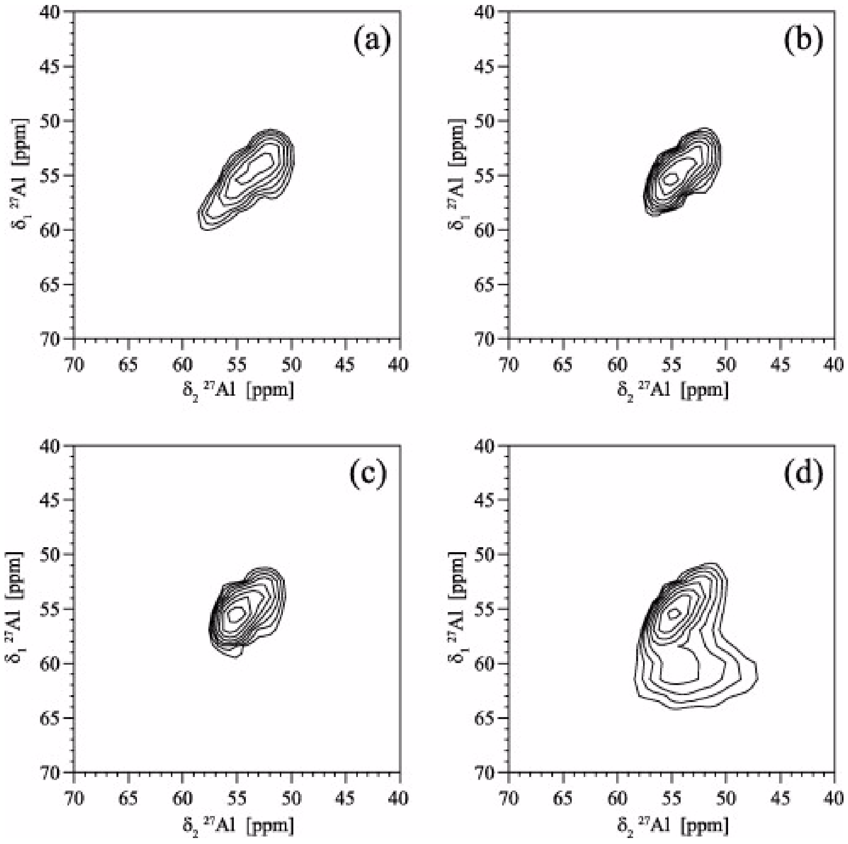
Cross-section along ridge
C_Q and η_Q

Quadrupole Interaction: MQMAS

- Direct evidence of the effect of synthesis conditions on aluminum siting in zeolite ferrierite: A 27Al MQ MAS NMR study

  Ana B. Pinar et al.,*Micro. Meso. Mater.*, 2014, **193**, 111-114. DOI: 10.1016/j.micromeso.2014.03.016

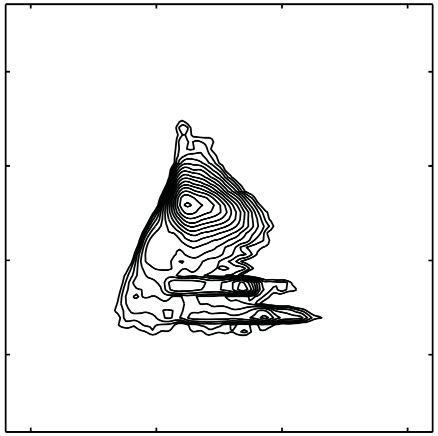


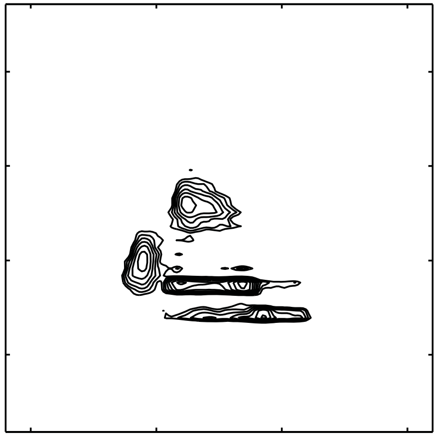


Quadrupole Interaction: MQMAS

- ^{27}Al MQMAS on differently prepared Sr/Al mixed oxides with Sr/Al = 1.25.

No Calcination





Calcination at 1000 °C

From Sr-hydroxide precursor