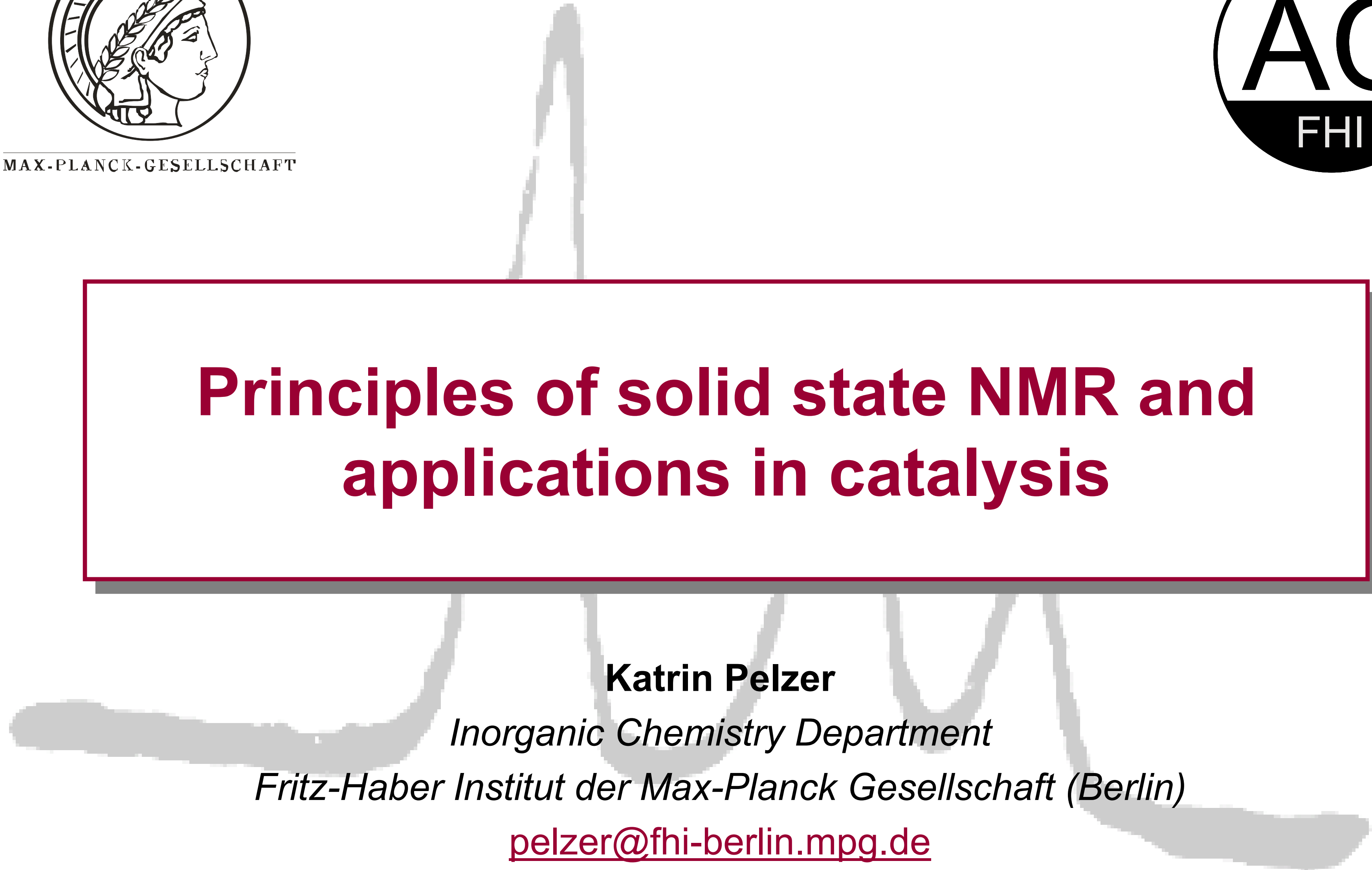

Principles of solid state NMR and applications in catalysis

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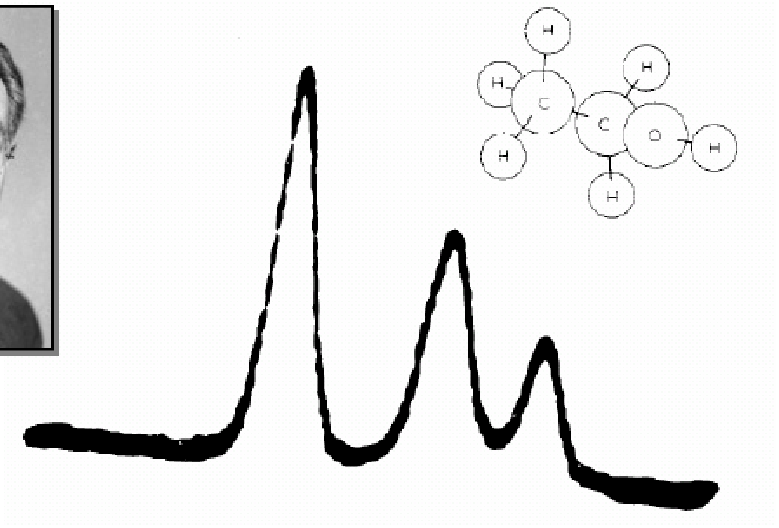
Elements of history

Isidor Isaac Rabi (1898 – 1988)

Nobel prize for physics 1944

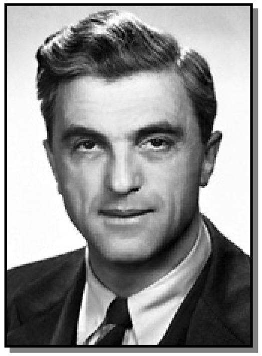
“For his resonance method for recording the magnetic properties of atomic nuclei.”

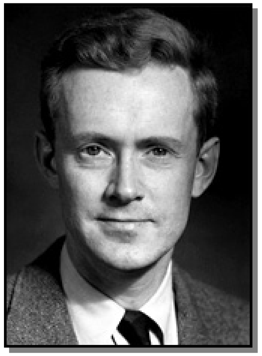


Felix Bloch (1905 – 1982) and
Edward Mills Purcell (1912 -1997)

Nobel prize for physics 1952

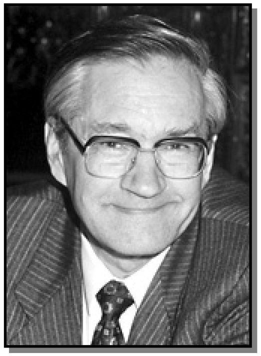
“For their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith.”

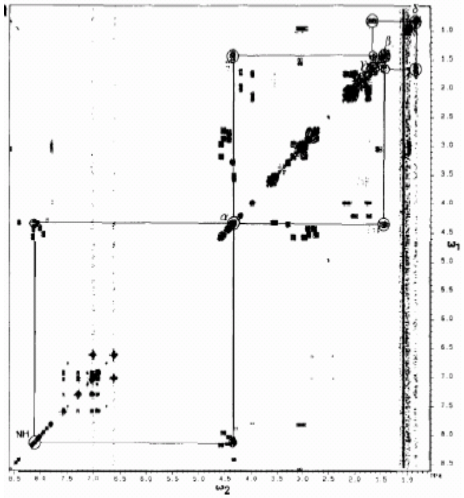




Elements of history

Richard Ernst (1933 -)

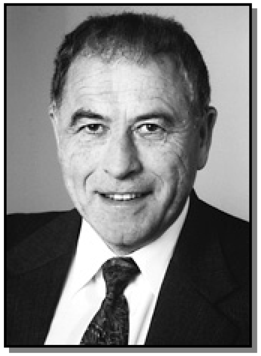


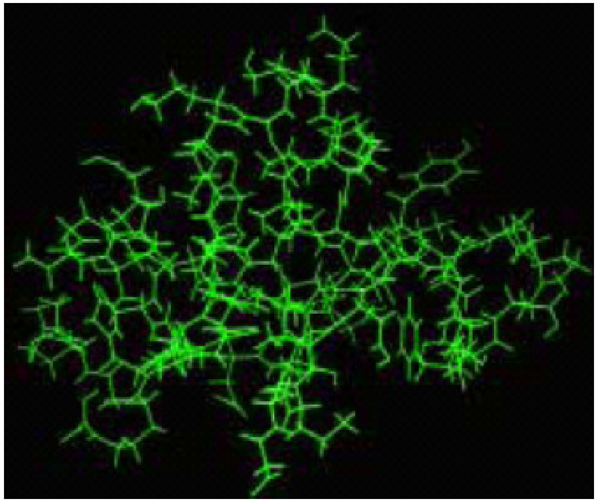


Nobel prize for chemistry 1991

“For his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy.”
(Fourier-transformation, 2D)

Kurt Wüthrich (1938 -)





Nobel prize for chemistry 2002

“For his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution“

Information available from NMR

Investigation of individual atoms and molecules

Structural and dynamic information

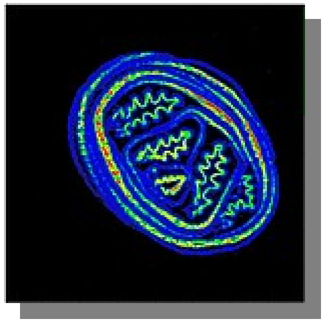
Almost any kind of phase can be investigated

- High resolution mode on homogenous solutions
- High power mode on highly relaxing nuclei which exhibit very broad lines, or on polymers

Most investigated systems:

- Solutions
- Solids (powder, crystal, polymers) using the Magic-Angle Spinning technique

Possibility of 3D imaging (medicine)



Micro-imaging

Nuclear spin and magnetic momentum

Basis of NMR spectroscopy: existence of a nuclear spin (I)

Nuclear spins depend on the nucleon compositions

- **Odd mass nuclei → fractional spins**
  ^{1}H ^{13}C ^{19}F ^{15}N ^{31}P → 1/2 ^{11}B → 3/2 ^{17}O → 5/2
- **Even mass nuclei + odd numbers of protons and neutrons → integral spins**
  ^{2}H ^{14}N → 1
- **Even mass nuclei + even numbers of protons and neutrons → zero spin**
  ^{12}C ^{16}O → 0

Non-zero spin → magnetic moments **$\mu = \gamma I h / 2\pi$**

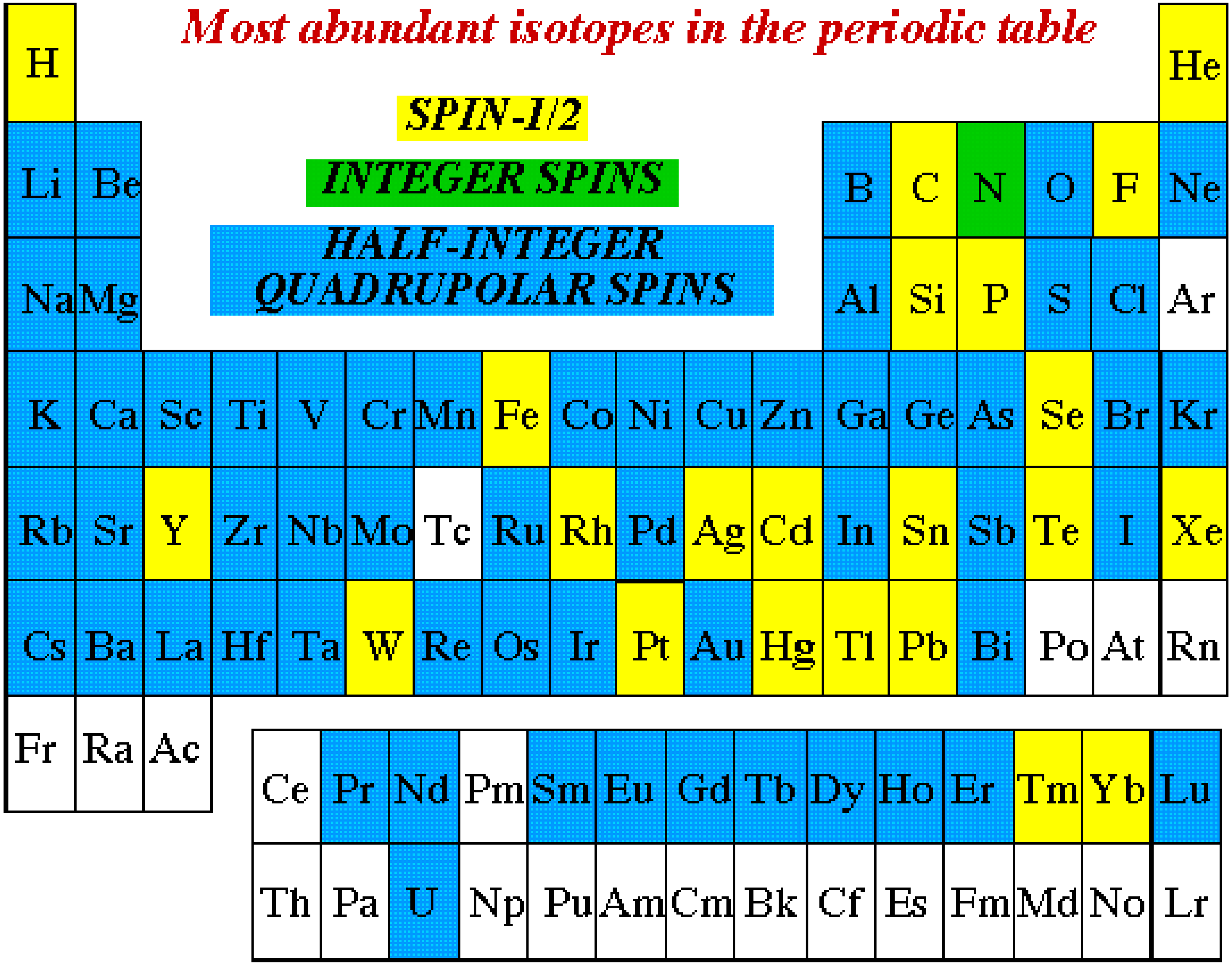
Nuclear spin and magnetic momentum

Isotope	Natural abundance (%)	Spin (I)	Magnetic moment (μ_B)*	Magnetogyric ratio (γ)†
^{1}H	**99.9844**	1/2	2.7927	26.753
^{11}B	81.1700	3/2	2.6880	8.583
^{13}C	**1.1080**	1/2	0.7022	6.728
^{17}O	**0.0370**	5/2	-1.8930	-3.628
^{19}F	100.0000	1/2	2.6273	25.179
^{29}Si	4.7000	1/2	-0.5555	-5.319
^{31}P	100.0000	1/2	1.1305	10.840

*** μ_B = $5.05078 \cdot 10^{-27}$ JT^{-1}**
† γ = 10^{7} rad T^{-1} sec^{-1}

Fundamental nuclear constant

Nuclear spin and magnetic momentum



Most abundant isotopes in the periodic table

SPIN-1/2

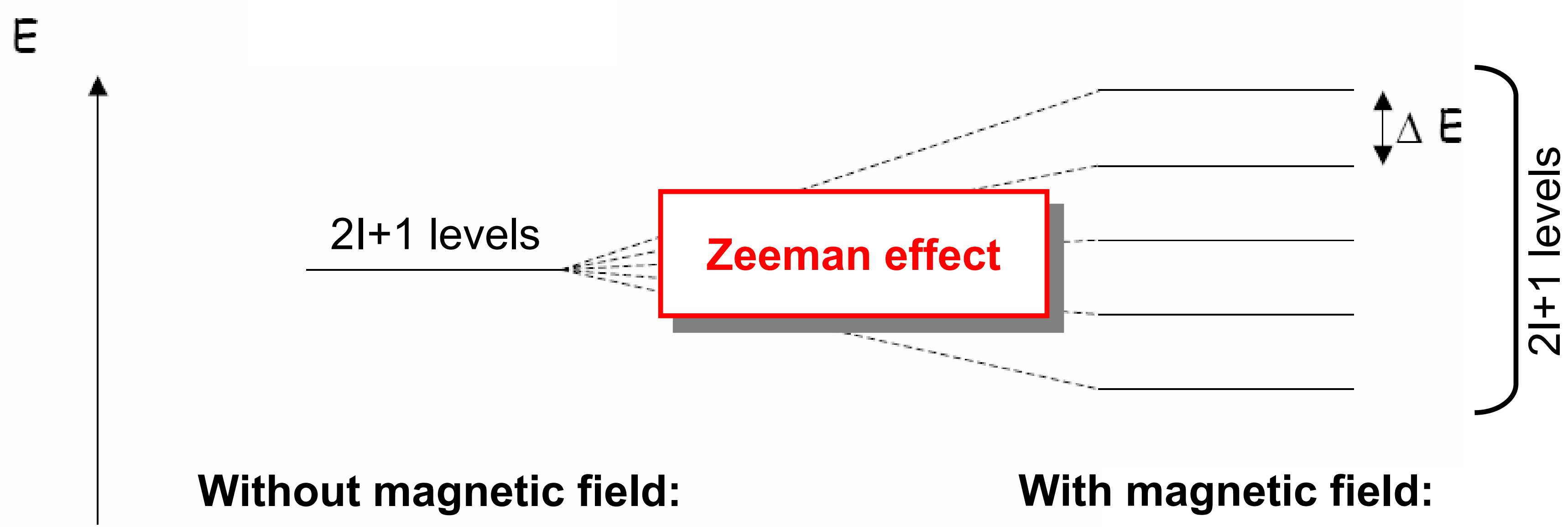
INTEGER SPINS

HALF-INTEGER QUADRUPOLAR SPINS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Influence of an external magnetic field



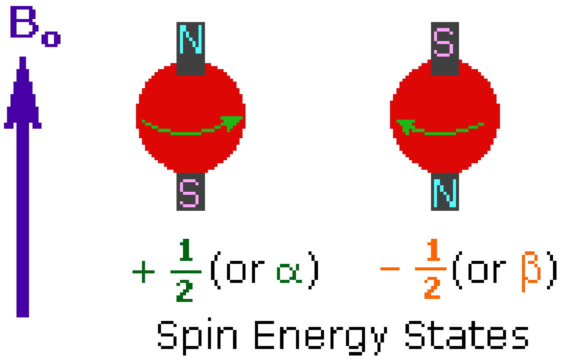
Without magnetic field:
degenerated states

With magnetic field:
energetically separated states

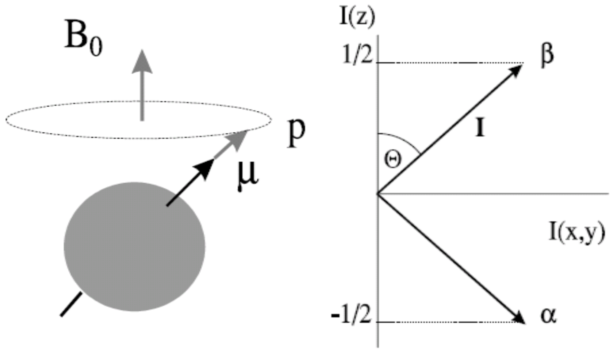
Influence of an external magnetic field

Quantum mechanic	Two Treatments	Semi-classical phys.
Dipolar operator	Spin	Vector
Spherical symmetry	No external magnetic field	Random distribution
Quantified projection (m_z)	External magnetic field (B_0)	Larmor precession (frequency: γB_0)

m_Z in $\{-I,-I+1,\ldots,+I-1,+I\}$



2I+1 authorized angles only

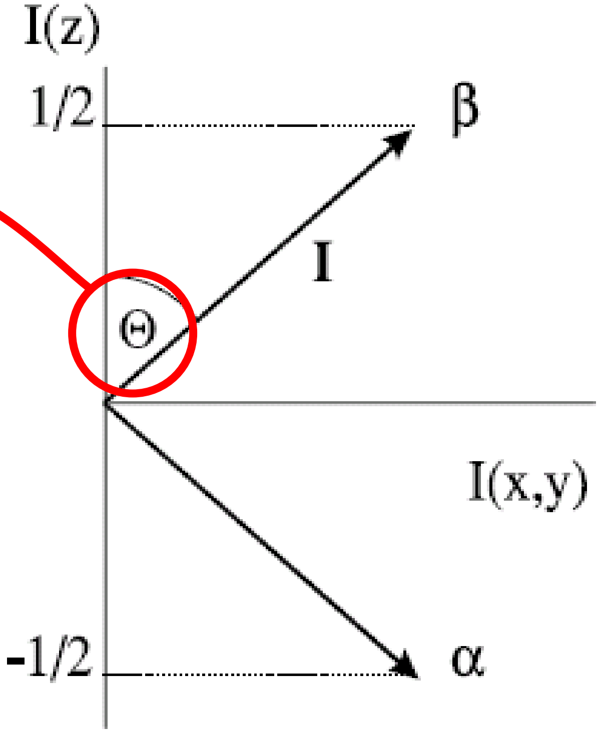


Influence of an external magnetic field

$$p_z = m_z h / 2\pi \qquad \vec{\mu} = \gamma \vec{p}$$

$$\mu_z = m_z \gamma h / 2\pi$$

$$E = -\vec{\mu}\vec{B}_0 = \mu B_0 \cos\Theta$$

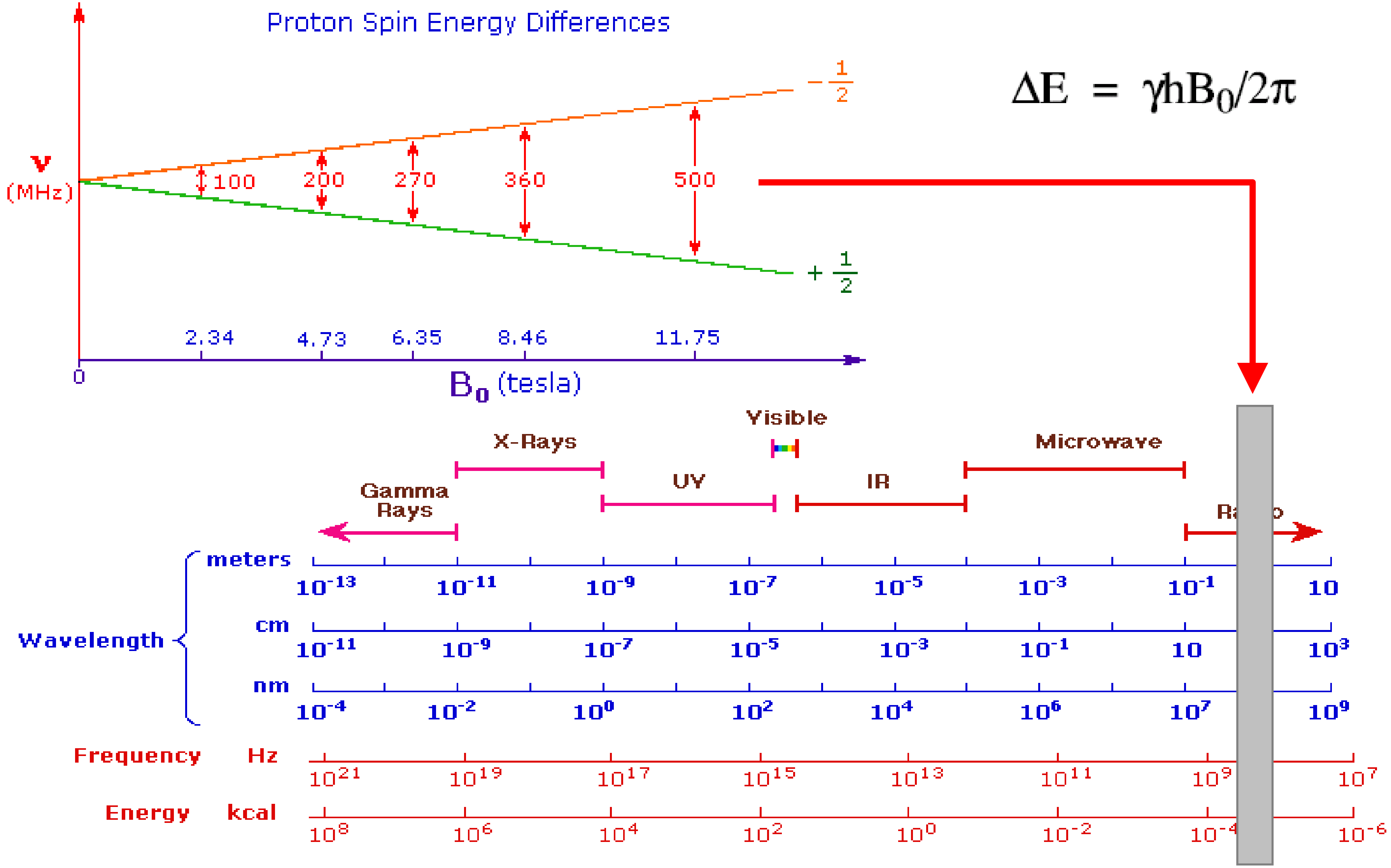


$$E = m_z \gamma h B_0 / 2\pi$$

$$\Delta E = E_{½} - E_{-½}$$

$$\boxed{\Delta E = \gamma h B_0 / 2\pi}$$

Photon absorption and emission



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

Magnetic field

Energy difference between two spin states is less than 0.1 cal/mole

Vibrational transitions (IR) 1,000 cal/mole

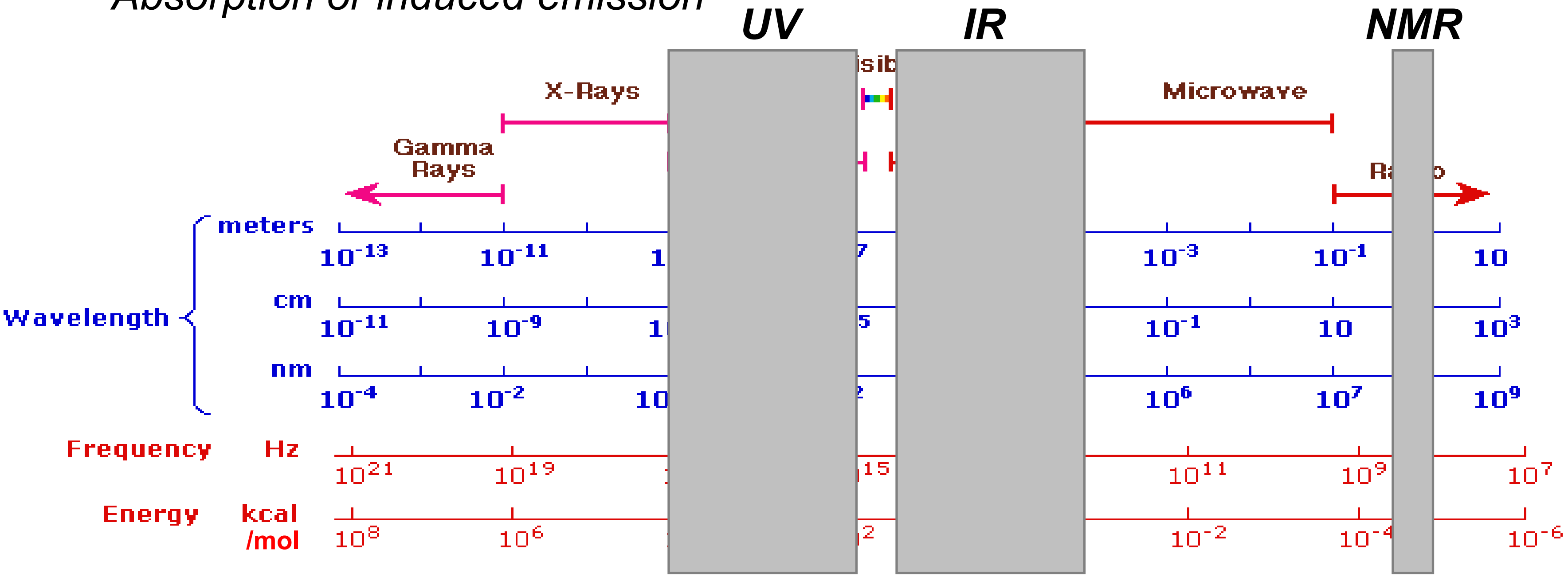
Electronic transitions (UV) 1,000,000 cal/mol

ΔE proportional to B_0 → Strong magnetic fields (1-20 T ≈ 20-900 MHz for ^{1}H)

Earth's magnetic field ≈ 10^{-4} T

Irradiation → transition between two different nuclear states (m_Z)

Absorption or induced emission



What makes NMR so interesting ?

ΔE depends on the environment of the investigated system

ΔE depends in particular on:

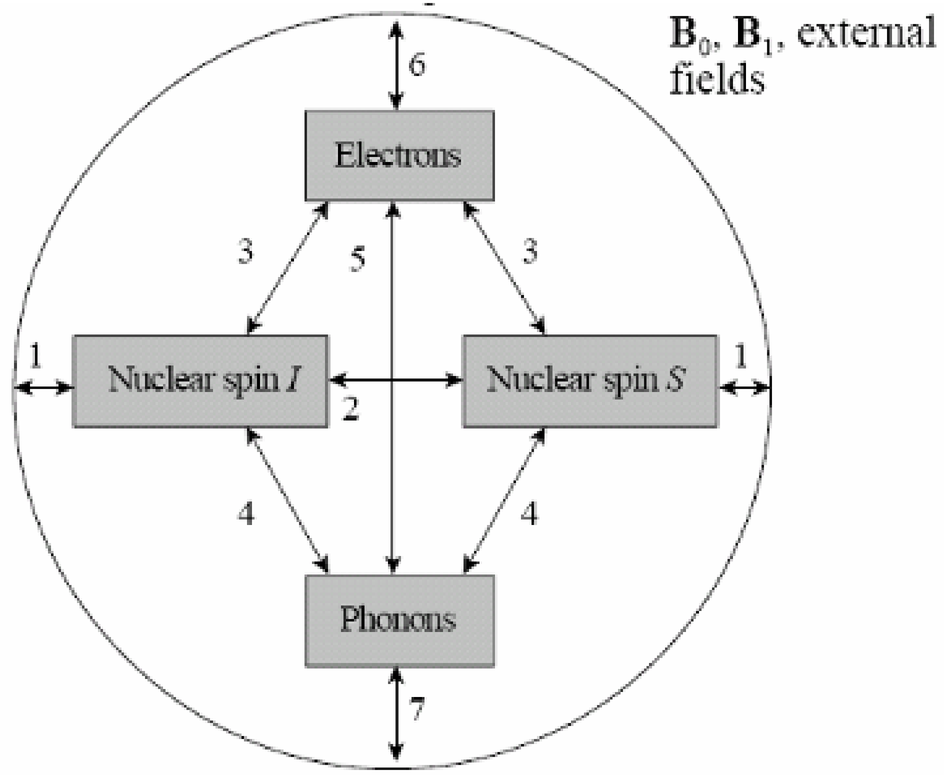
- The spatial proximity of other spins (interaction between nuclei)
- The presence of chemical bonds (shielding)

Interactions are <u>time and orientation</u> dependent

→ Strong influence of anisotropic interactions for media with no or little mobility

→ Access to the dynamic of the system

Interactions



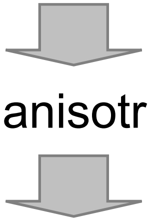
Interaction with magnetic field B_0
(Zeeman effect) [1]
$10^6 - 10^9$ Hz

Spin-spin coupling
(direct: [2], indirect: [3,4])
0 - 10^4 Hz

Dipolar interactions $3\cos^2\theta - 1$ [2]
0 - 10^5 Hz

Quadrupolar interaction if $I > ½$ [3]
0 - 10^9 Hz

Solution NMR

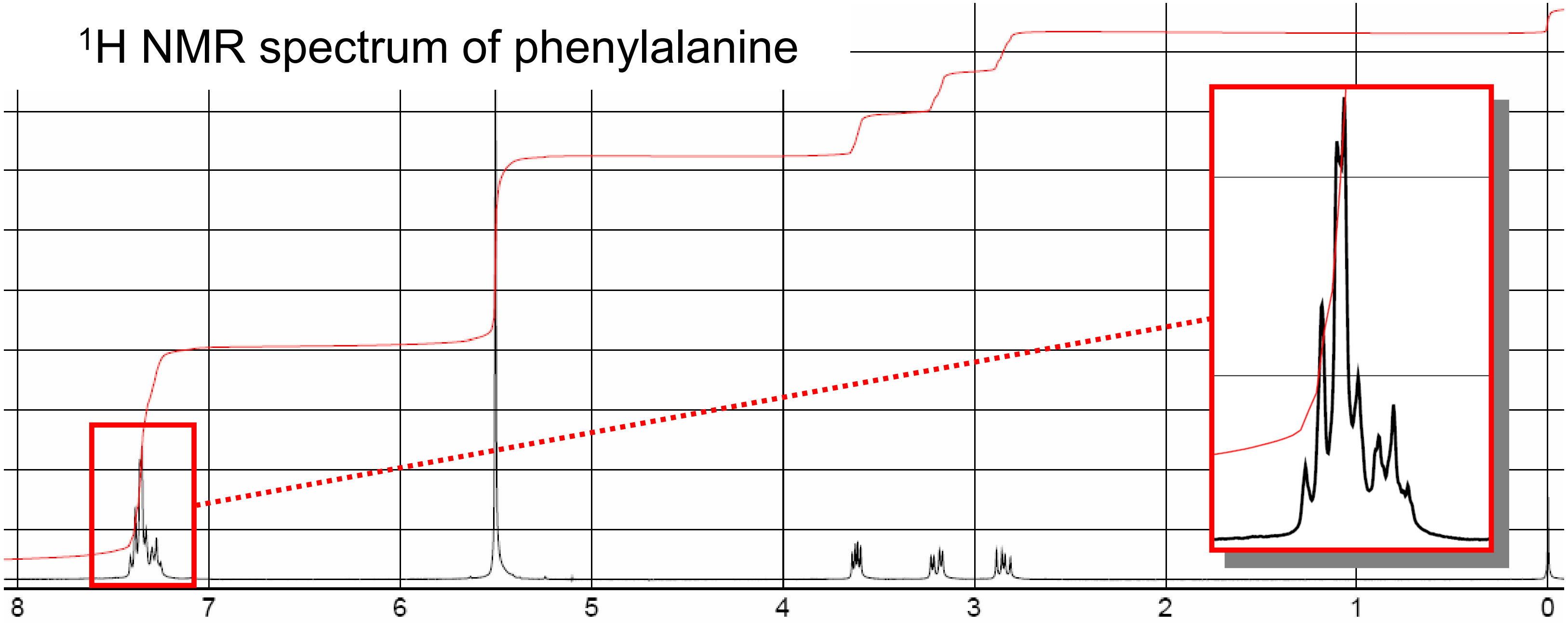


Rapid random tumbling + Brownian motion

Averaging of anisotropic interactions

Sharp transitions

^{1}H NMR spectrum of phenylalanine



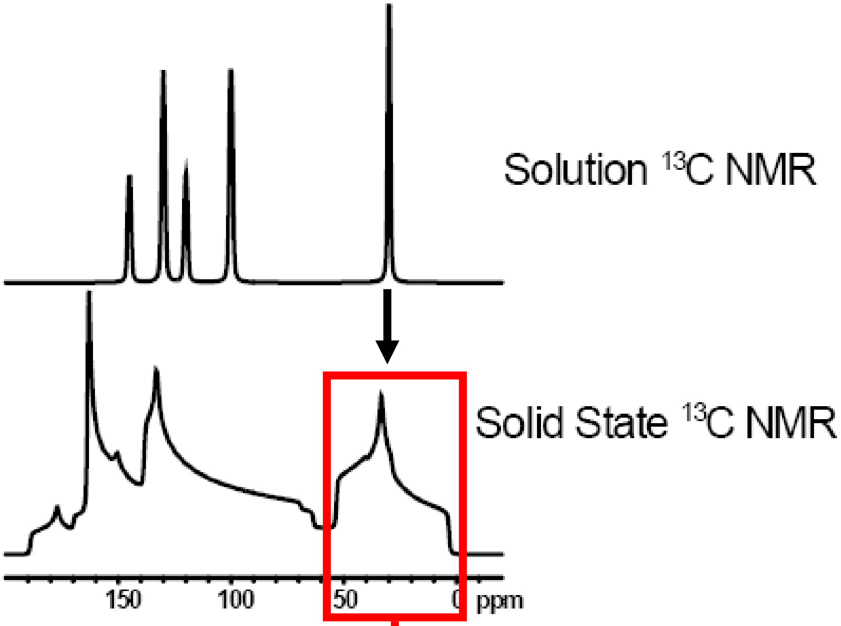
Solution NMR

Information available from 1D spectra of solutions:

- Peak intensity (depending on the nucleus, allows the quantification of each type of nucleus)
- Chemical shift (electronic environment)
- J-coupling (neighbors)
- Half-height width (mobility, chemical exchange)

Solid State NMR

Visible effect of anisotropic and orientation dependent interactions



Strong peak broadening

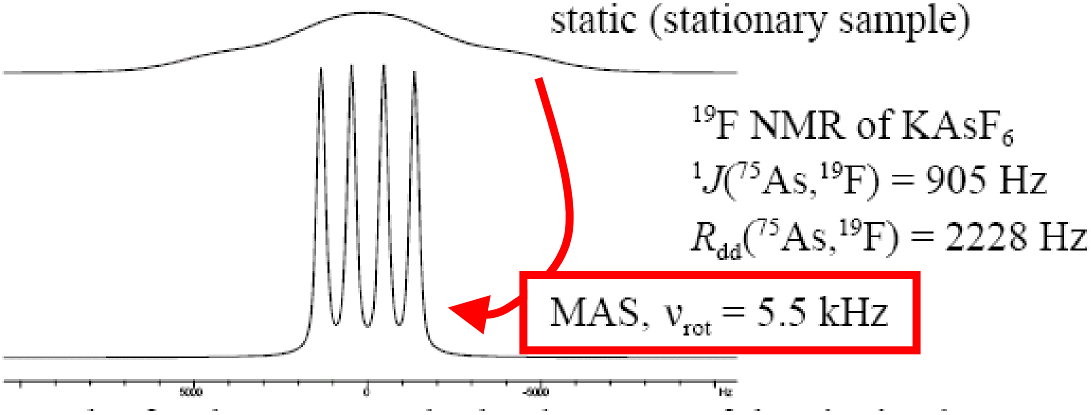
High-resolution solid NMR needs special techniques

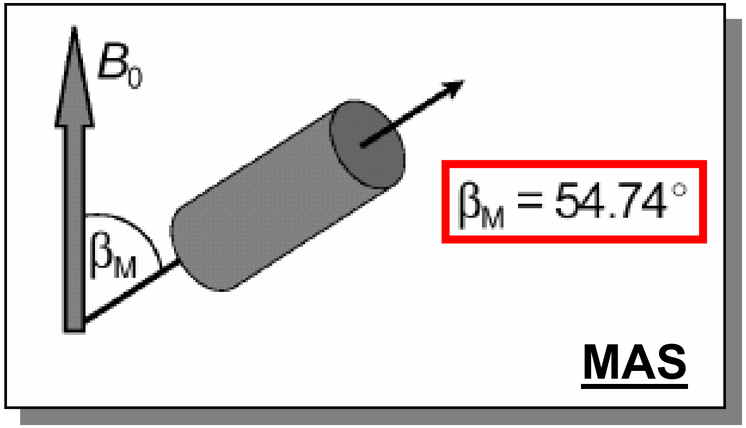
- Cross Polarization (CP)
- 2D experiments
- Enhanced probe electronics
- Magic-Angle Spinning (MAS)

Elements of history

- **First solid state NMR experiments: static ^{1}H and ^{19}F NMR**
  - Anisotropies in the local proton field → No spectral bands
  - Only ^{1}H spin-lattice relaxation time available
    → group rotations, motions in solid polymers

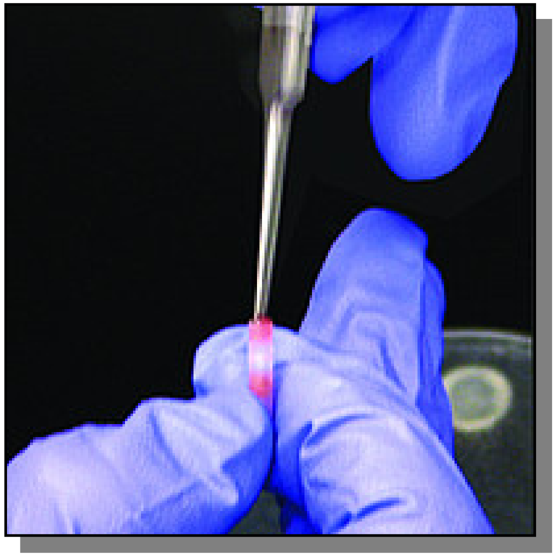
- **Introduction of artificial motions (E.R. Andrew and I.J. Lowe)**
  - Anisotropic dipolar interactions are apparently suppressed
    Condition: spinning rate (1-70 kHz) > dipolar line width ≈ kHz
  - **Magic-Angle Spinning (MAS)**





Technical aspects

http://www.bruker-biospin.com



MAS rotor

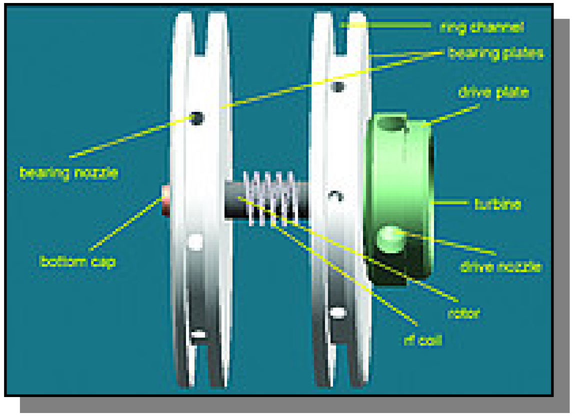
Probe

NMR spectrometer (900 MHz)

Magic-Angle Spinning (MAS)

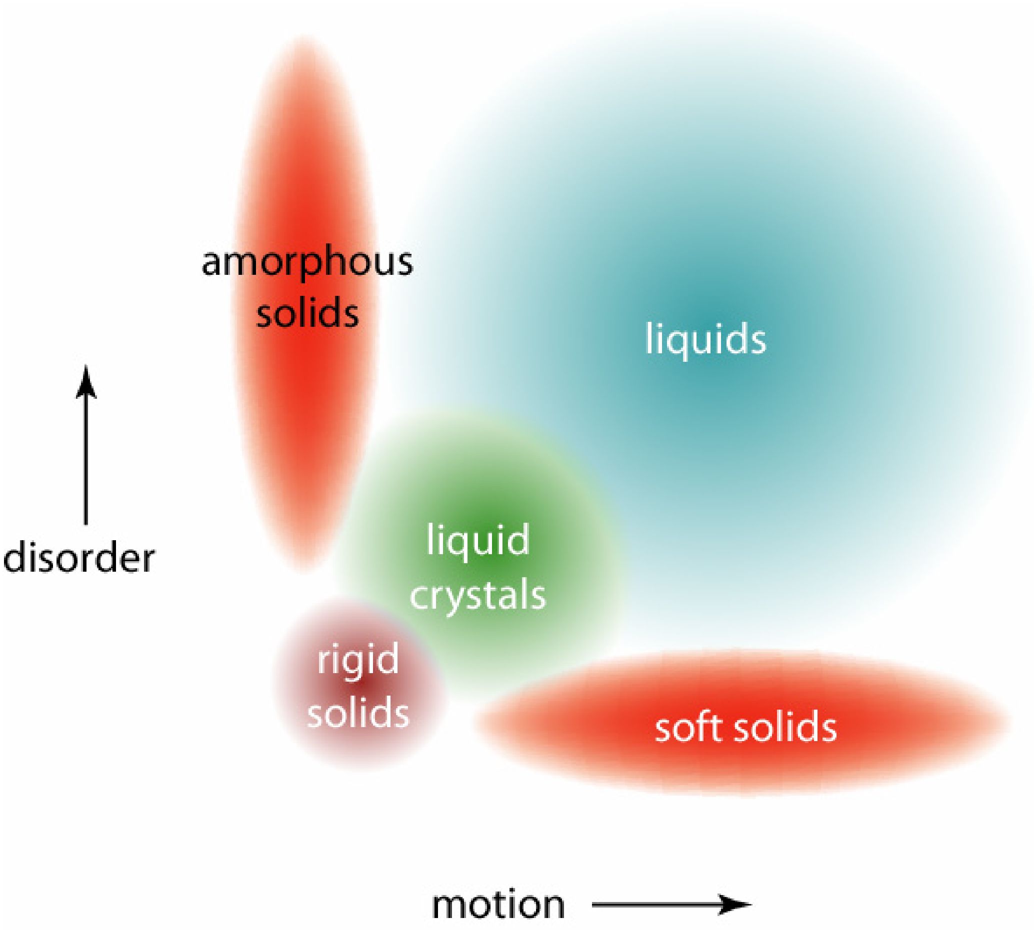
- **Physical spinning achieved via an air turbine mechanism**
  - Rotors 2.0-15.0 mm
  - Air or nitrogen gas

- **Materials**
  - ceramics e.g. zirconia, silicon nitride or polymers such as poly(methylmethacrylate) (PMMA), poly(oxymethylene) (POM)
  - Caps: e.g. Kel-F, Vespel, zirconia or boron nitride



Very High Speed MAS (70 kHz)
1.3 mm DVT MAS Probe

High-Resolution Solid-State NMR. Why?



Diffraction-based methods are most suited to “rigid solids”

Because NMR probes local environment, it is *applicable* to any system

But “inversion” to structural information may be non-trivial

High-Resolution Solid-State NMR. How?

Methods for minimizing large anisotropic interactions
→ Signal/Noise increase

Magic-angle spinning

Dilution

Occurs naturally for low natural abundance (^{13}C: 1.108%)

Dipolar interaction scale with $1/r^3$ (short range)

Condition: no heteronuclear interaction

Multiple-Pulse Sequences

Artificial motion of spin operators

Allows hetero- and homo-nuclear decoupling

Cross Polarization

Polarization transferred from abundant nuclei to rare nuclei
→ strong Signal/Noise increase

Magic-Angle Spinning (MAS)

- **Interactions are time-dependent and can then be averaged by MAS**
  → reduction of peak broadening
  - Dipolar = 0
  - chemical shift anisotropy (nuclear-electron interaction) ≠ 0
  - Quadrupolar coupling = partially averaged

- **Mimic of the orientation averaging in solution**
  → signals become much narrower
  - Access to isotropic values
    → structural determination of solid materials and compounds
  - Access to chemical shift anisotropies
    from spinning sidebands (multiples of the spinning speed)

Magic-Angle Spinning (MAS)

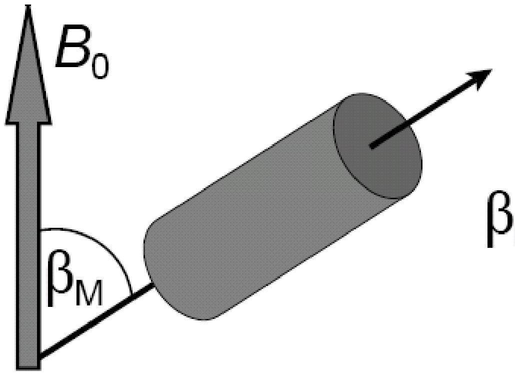
Orientation dependency of
dipolar and chemical shielding interactions:
$3\cos^2\theta-1$

$$3\cos^2\theta-1 = 0 \xrightarrow{\hspace{4cm}} \cos^2\theta = 1/3$$

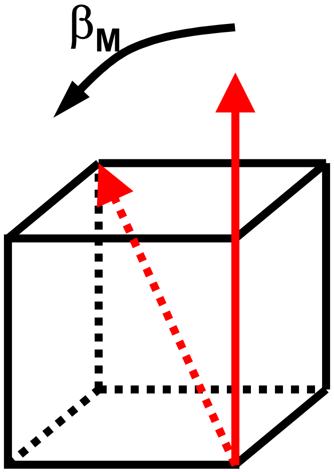
$$\theta = \cos-1(1/\sqrt{3})$$

$$\theta = \underline{54.74^\circ}$$

Magic angle



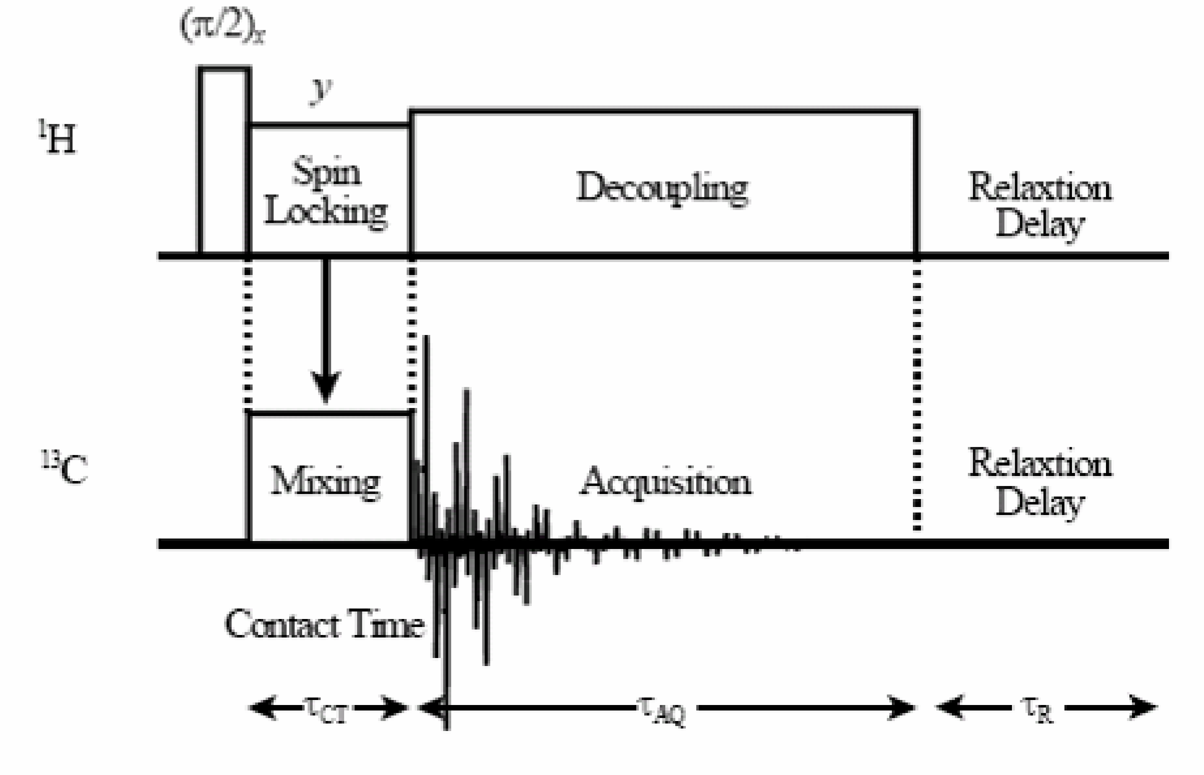
$\beta_M = 54.74^\circ$



Cross Polarization

Polarization transfer from abundant nuclei I (^1H, ^{19}F) to rare nuclei S (^{13}C)

- Useful for diluted nuclei: ^{13}C, ^{15}N (long relaxation times)
- Enhancement of S/N proportional to γ_I/γ_S
- Rapid spin-lattice relaxation

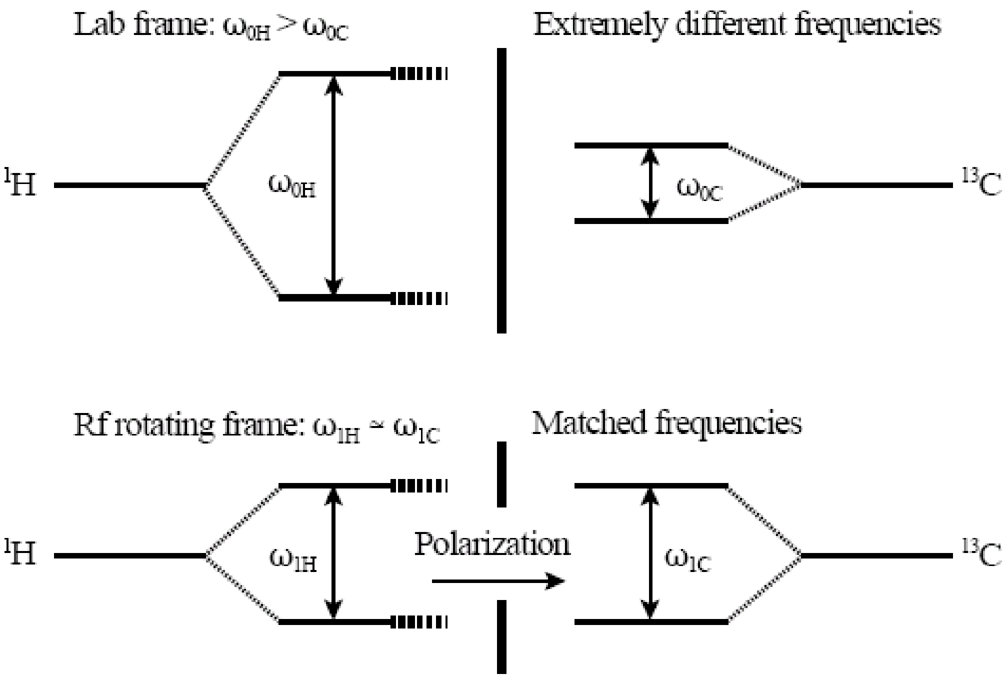


Cross Polarization

Polarization transferred from abundant nuclei to rare nuclei

<u>Key:</u> Hartmann-Hahn match

- Both nuclei are simultaneously irradiated
- Condition on Larmor frequencies: $\omega_I = \omega_S$ ($\gamma_I B_I = \gamma_S B_S$)
- Polarization transfer in the rotating frame



CP-MAS NMR. Example of ^{31}P

Experiment

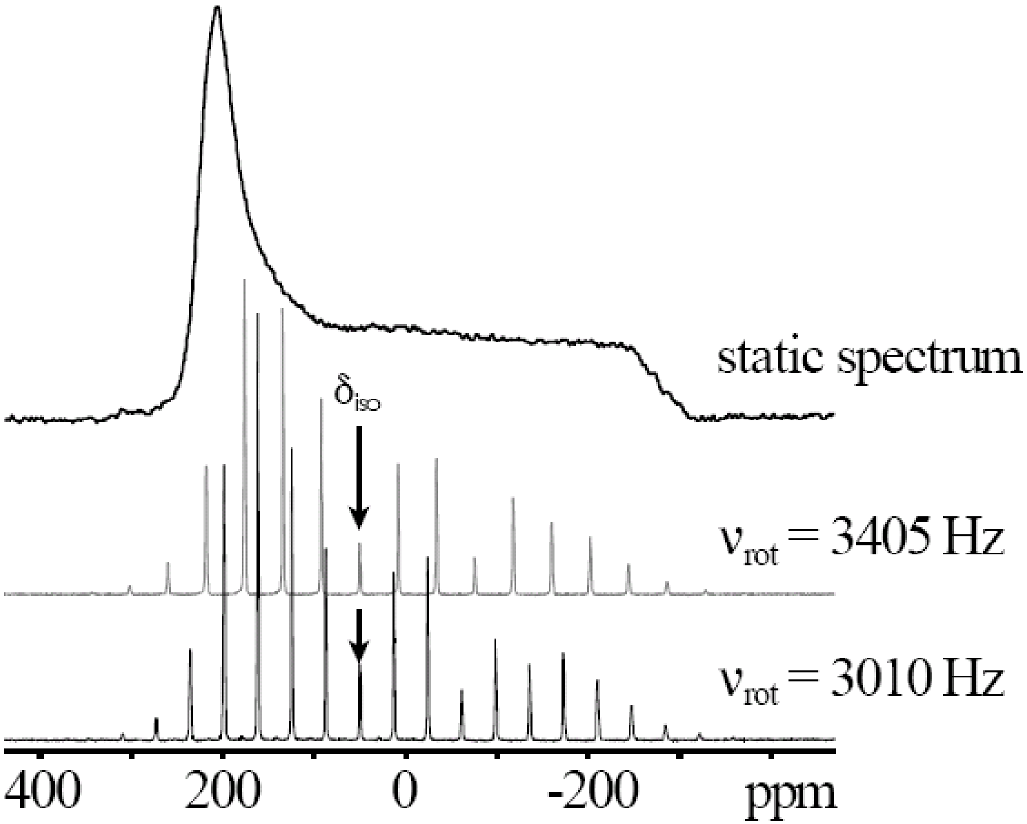
- ^{31}P at 4.7 T
- Span = 500 ppm, 40000 Hz

Isotropic central band

Remains in the same position

Rate of MAS

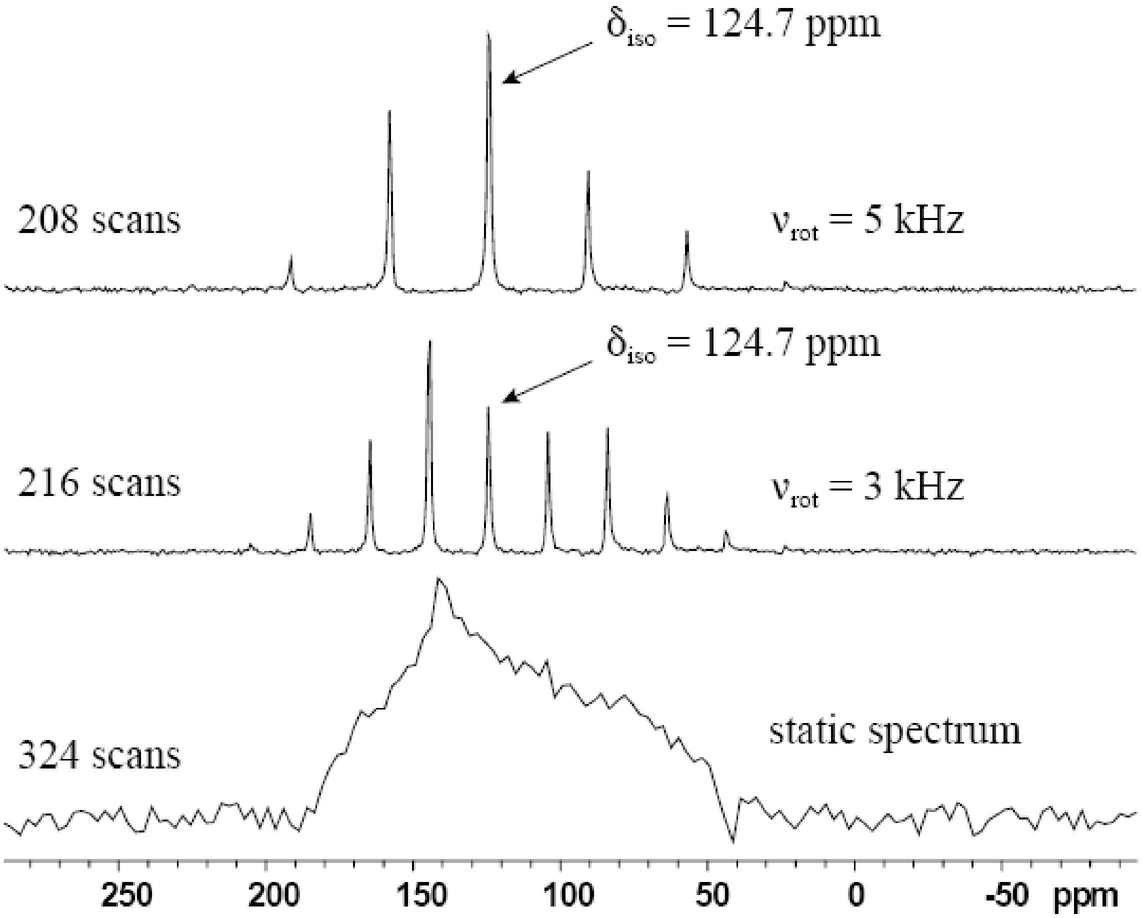
Greater than (or equal to) the magnitude of the anisotropic interaction to average it to zero (spinning side bands)



CP-MAS NMR. Example of ^{119}Sn

$Cp^*_2SnMe_2$ at 9.4 T

→ Signals under the spinning side bands
(even at MAS < anisotropic interaction)



Back on interactions in solid-state NMR

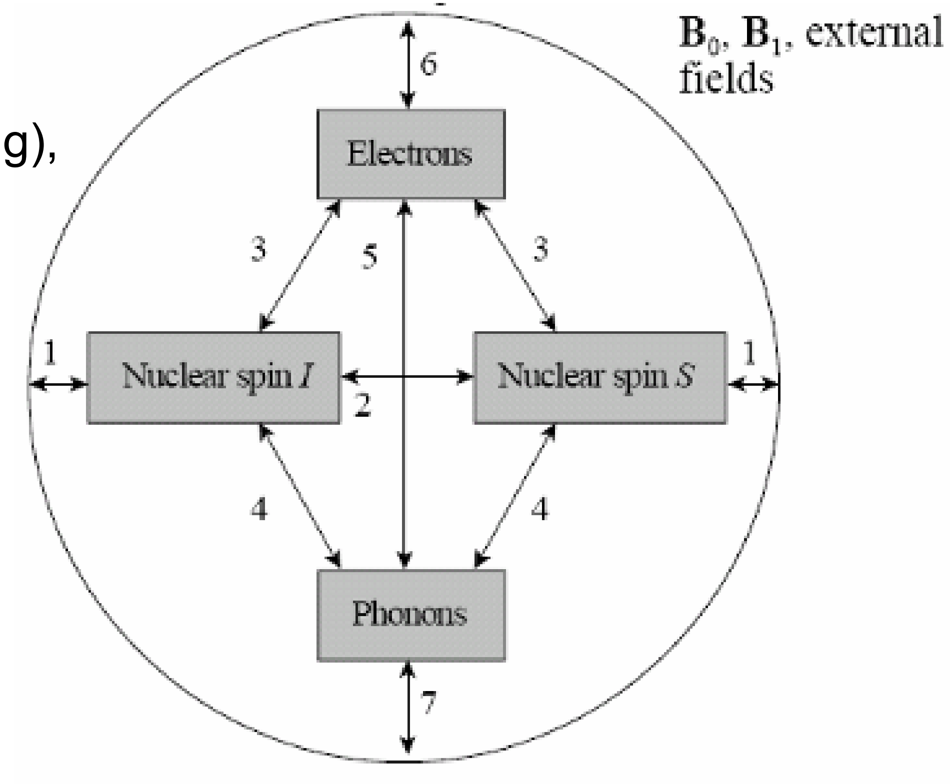
Seven ways for a nuclear spin to interact with surrounding

1. Zeeman interaction of nuclear spins
2. Direct dipolar spin interaction
3. Indirect spin-spin coupling (J-coupling), nuclear-electron spin coupling (paramagnetic), coupling of nuclear spins with molecular electric field gradients (quadrupolar interaction)
4. Direct spin-lattice interactions

3.-5. Indirect spin-lattice interaction via electrons

3.-6. Chemical shielding and polarization of nuclear spins by electrons

4.-7. Coupling of nuclear spins to sound fields



Interaction tensors

All interactions are anisotropic

→ Description by second-rank cartesian tensors (3x3 matrices)

→ Tensors describe the orientation dependencies of the interactions

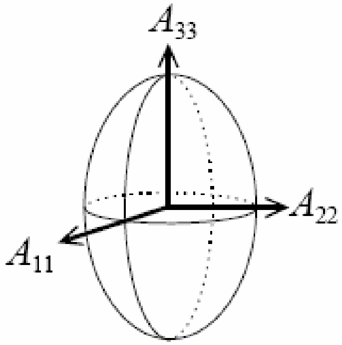
$$\mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{A}}}\cdot\mathbf{S} = [I_x,\ I_y,\ I_z]\begin{bmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{bmatrix}\begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

Interaction tensors can be diagonalized

→ 3 principal components in the Principal Axis System (PAS)

→ $A_{33} > A_{22} > A_{11}$

$$\mathcal{H}_{\mathrm{PAS}} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix}$$



Nuclear spins are also coupled to external magnetic fields B_0 and B_1 via such tensors
(B_1 = oscillating magnetic field)

$$\mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{Z}}}\cdot\mathbf{B}_0,\ \mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{Z}}}\cdot\mathbf{B}_1,$$

$$\mathbf{B}_0 = [B_{0x},\ B_{0y},\ B_{0z}] = [0, 0,\ B_0],$$

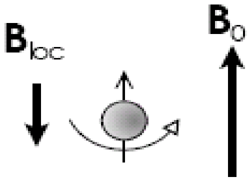
$$\mathbf{B}_1 = 2[B_{1x},\ B_{1y},\ B_{1z}]\cos\omega t$$

$$\overline{\overline{\mathbf{Z}}} = -\gamma_I\overline{\overline{\mathbf{1}}},\qquad \overline{\overline{\mathbf{1}}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Interaction tensors

$$\mathcal{H}_{CS} = \gamma \mathbf{I} \cdot \overline{\boldsymbol{\sigma}} \cdot \mathbf{B}_0$$

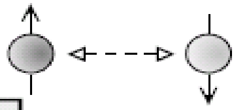
chemical shielding



$$\mathcal{H}_{DD} = \sum_{i<j} \hbar\gamma_i\gamma_j r_{ij}^{-3} \left(\mathbf{I}_i \cdot \mathbf{I}_j - \frac{3(\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right)$$

$$= \sum_{i=j} \mathbf{I}_i \cdot \overline{\overline{\mathbf{D}}} \cdot \mathbf{I}_j$$

dipolar interaction

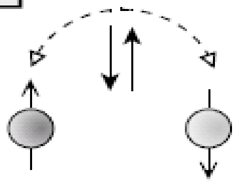


$$D_{\alpha,\beta} = \hbar\gamma_i\gamma_j r_{ij}^{-3} (\delta_{\alpha\beta} - 3e_\alpha e_\beta),$$

$\alpha,\beta = x, y, z$; e_α: α – component of unit vector along r_{ij}

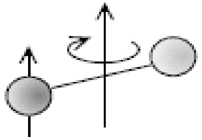
$$\mathcal{H}_J = \sum_{i \neq j} \mathbf{I}_i \cdot \mathbf{J} \cdot \mathbf{I}_j$$

indirect spin-spin (*J*) coupling



$$\mathcal{H}_{CR} = \sum_i \mathbf{I}_i \cdot \overline{\mathbf{C}}_i \cdot \mathbf{J}$$

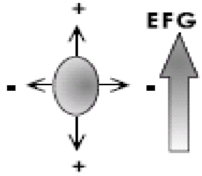
spin-rotation coupling



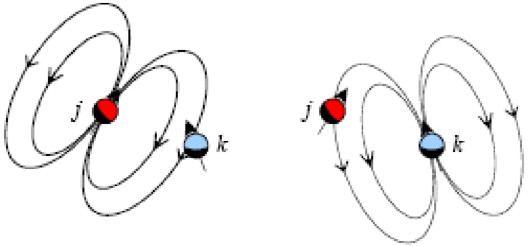
$$\mathcal{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \sum_i \mathbf{I} \cdot \overline{\mathbf{V}} \cdot \mathbf{I}$$

quadrupolar coupling

$$\overline{\overline{\mathbf{V}}} = \{V_\alpha, V_\beta\}; \; \alpha,\beta = x, y, z$$

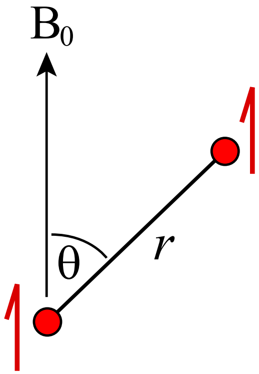


Dipolar interactions



Direct interaction between two nuclear spins. Depends on:

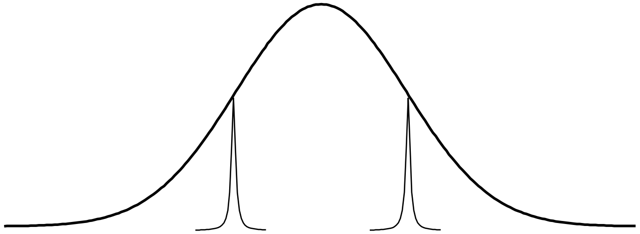
- Spin species (γ)
- Internuclear distance ($1/r^3$)
- Orientation of both interacting spins with respect to B_0 ($3\cos^2 \Theta - 1$)



Potentially contains direct information about the geometry of the system

<u>Problem:</u> Every spin is coupled to every other spin

→ Severe broadening of the spectrum (not in solution)



$H_{DD} \propto R^{DD} (3 \cos^2\theta - 1)$

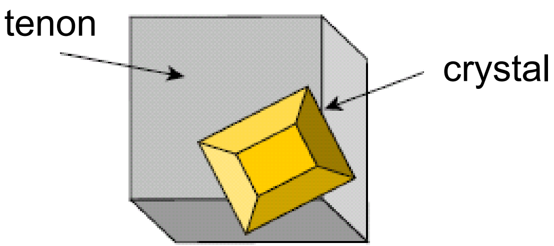
$$R_{jk}^{DD} = \frac{\mu_0}{4\pi} \frac{\gamma_j \gamma_k \hbar}{\langle r_{jk}^3 \rangle}$$

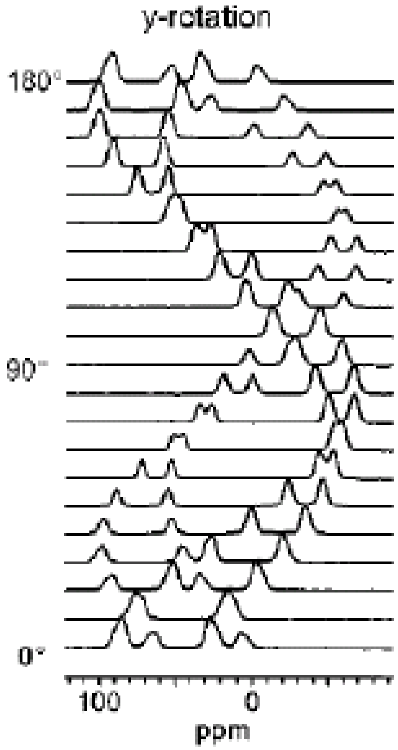
Solid state NMR on single crystals

Crystal mounted on a tenon with known orientation

- o NMR interaction tensors can then be determined with respect to the molecular frame
- o <u>In particular:</u> Anisotropic NMR chemical shielding tensors → Chemical shift anisotropy (CSA)

^{31}P NMR spectrum of tetra-methyldiphosphine sulfide





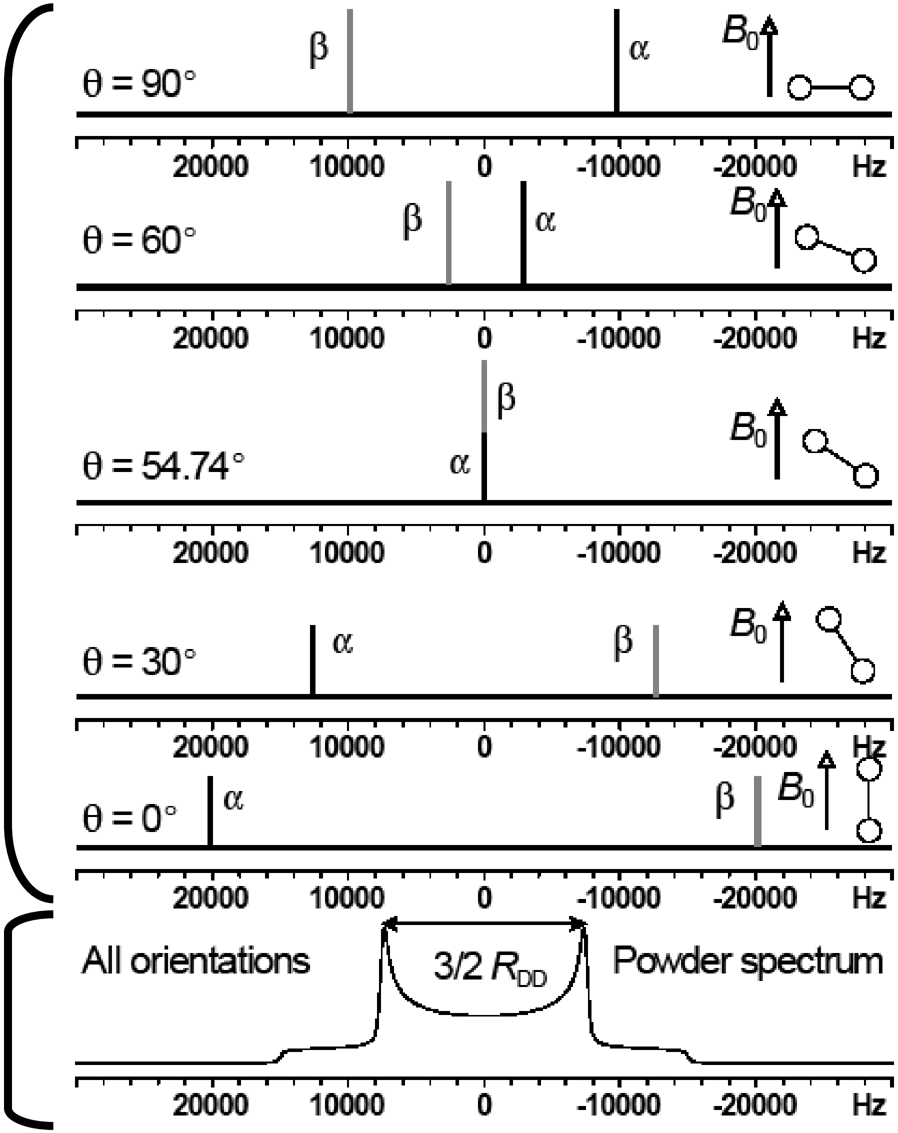
Dipolar interactions

Single crystal spectra:

One set of peaks per orientation

Powder:

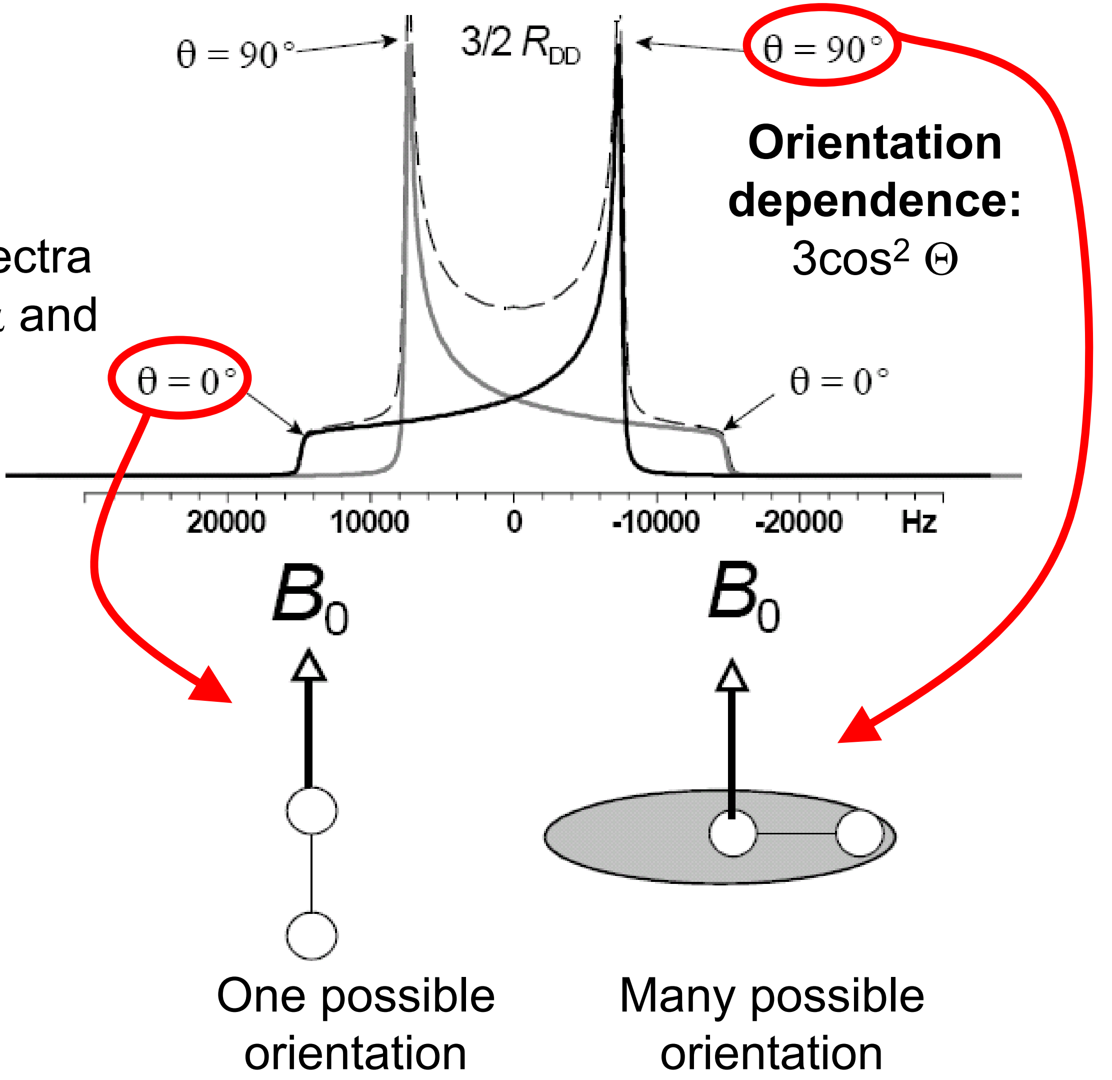
broad band



Dipolar interactions

Example: **^1H NMR spectrum of solid $CaSO_4 \cdot H_2O$**

- Peak doublet
- Superimposition of two subspectra resulting from interactions of α and β spin states



Orientation dependence:
$3\cos^2 \Theta$

Local band intensity representative of the number of possible orientations with θ fixed

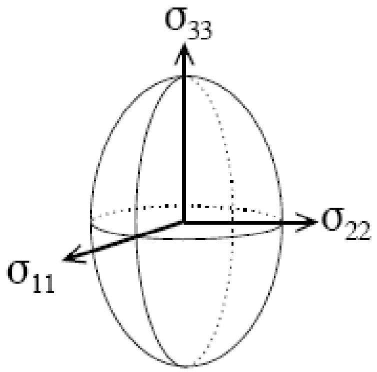
One possible orientation

Many possible orientation

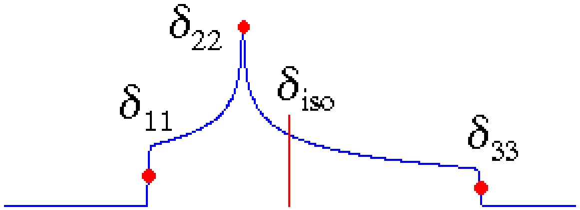
Chemical Shielding Anisotropy

Existence of an anisotropic shielding tensor σ

$$\begin{matrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{matrix} \rightarrow \begin{matrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{matrix}$$



→ Band broadening and shape



Properties:

Isotropic chemical shift $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$

Anisotropy of chemical shift $\Omega = \sigma_{33} - \sigma_{11}$

span: breadth of CSA in ppm

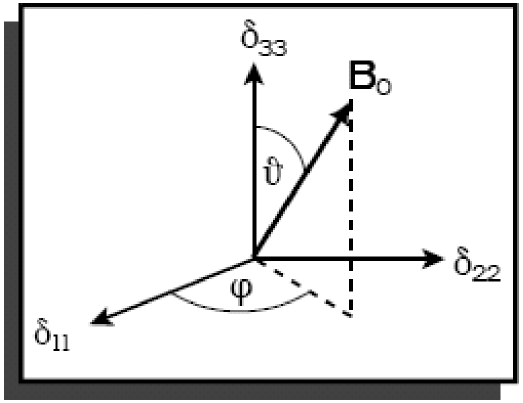
Parameter for asymmetry $\kappa = \dfrac{\sigma_{iso} - \sigma_{22}}{\Omega}$

Chemical Shielding Anisotropy

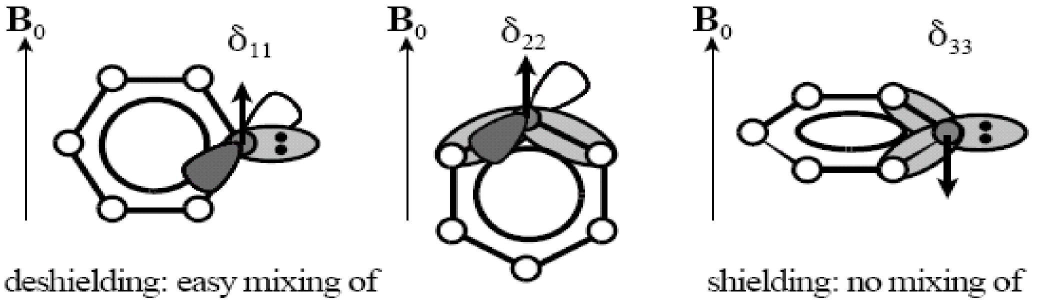
Calculation of powder patterns:

- Calculation of frequencies for a large number of orientations of interaction tensor
- Orientation dependence of the frequency:

$$\nu_{CS} = \nu_0 \left(\sigma_{11}\sin^2\theta\cos^2\varphi + \sigma_{22}\sin^2\theta\sin^2\varphi + \sigma_{33}\cos^2\theta\right)$$



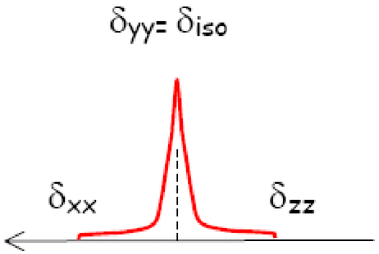
Origin of the orientation dependence of the chemical shift



deshielding: easy mixing of ground and excited states

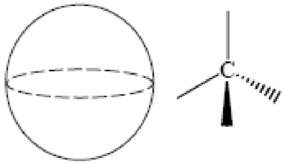
shielding: no mixing of ground and excited states

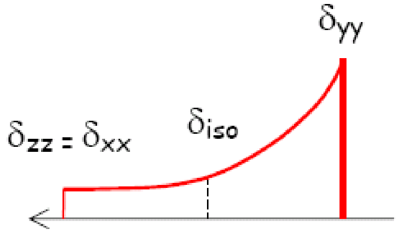
Chemical Shielding Anisotropy



Spherical symmetry

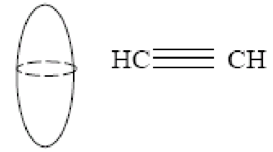
CSA = 0 et $\eta = 0$

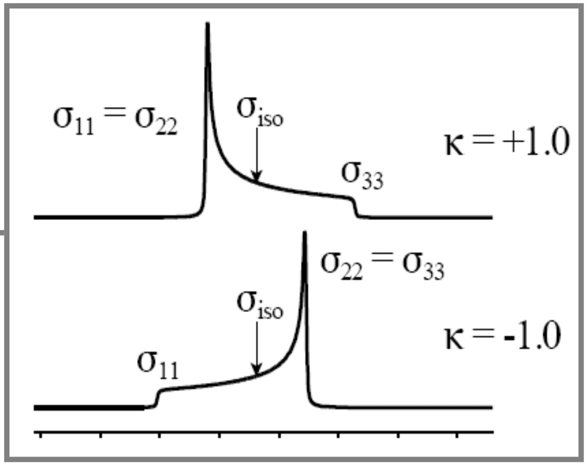


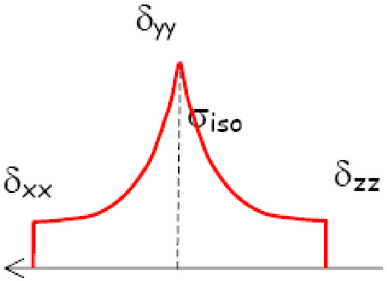


Tensor with axial symmetry

CSA $\neq 0$ et $\eta = 0$

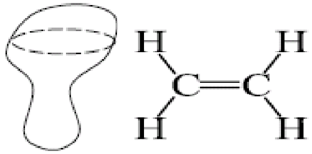


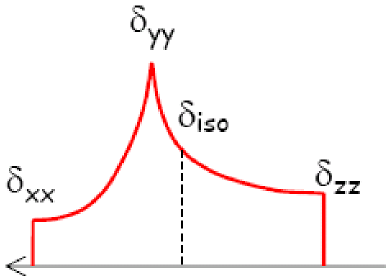




Symmetrical tensor

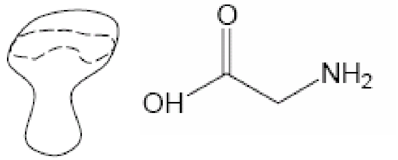
CSA $\neq 0$ et $\eta = 1$





Asymmetric Tensor

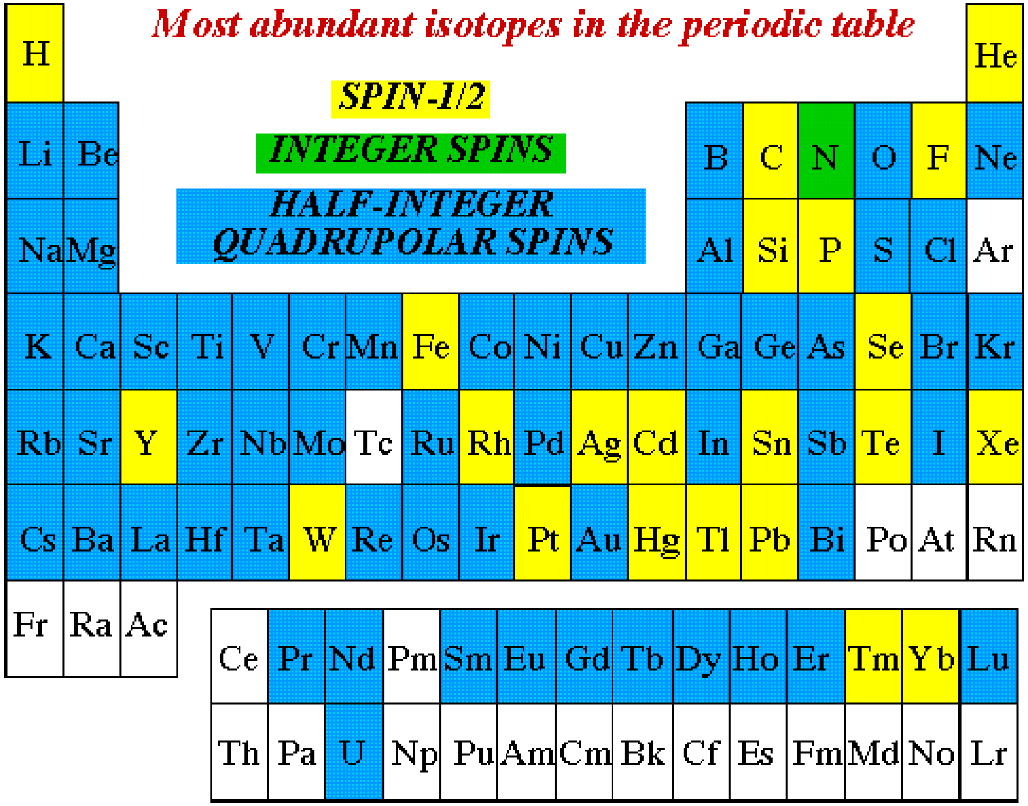
CSA $\neq 0$ et $0 < \eta < 1$



The quadrupole interaction

Quadrupolar nuclei (blue) relax rapidly due to large quadrupolar interaction

- 73% of the periodic table
- Broadening can now be exploited: Structure & dynamics



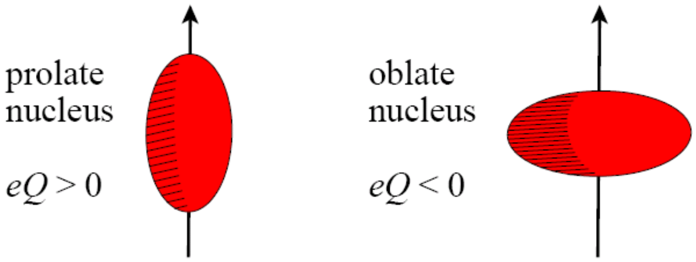
Most abundant isotopes in the periodic table

🟨 SPIN-1/2
🟩 INTEGER SPINS
🟦 HALF-INTEGER QUADRUPOLAR SPINS

H 🟨																	He 🟨
Li 🟦	Be 🟦											B 🟦	C 🟨	N 🟩	O 🟦	F 🟨	Ne 🟦
Na 🟦	Mg 🟦											Al 🟦	Si 🟨	P 🟨	S 🟦	Cl 🟦	Ar
K 🟦	Ca 🟦	Sc 🟦	Ti 🟦	V 🟦	Cr 🟦	Mn 🟦	Fe 🟨	Co 🟦	Ni 🟦	Cu 🟦	Zn 🟦	Ga 🟦	Ge 🟦	As 🟦	Se 🟨	Br 🟦	Kr 🟦
Rb 🟦	Sr 🟦	Y 🟨	Zr 🟦	Nb 🟦	Mo 🟦	Tc	Ru 🟦	Rh 🟨	Pd 🟦	Ag 🟨	Cd 🟨	In 🟦	Sn 🟨	Sb 🟦	Te 🟨	I 🟦	Xe 🟨
Cs 🟦	Ba 🟦	La 🟦	Hf 🟦	Ta 🟦	W 🟨	Re 🟦	Os 🟦	Ir 🟦	Pt 🟨	Au 🟦	Hg 🟨	Tl 🟨	Pb 🟨	Bi 🟦	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr 🟦	Nd 🟦	Pm	Sm 🟦	Eu 🟦	Gd 🟦	Tb 🟦	Dy 🟦	Ho 🟦	Er 🟦	Tm 🟨	Yb 🟨	Lu 🟦
Th	Pa	U 🟦	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The quadrupole interaction



Concerns nuclear spins with I>1/2:

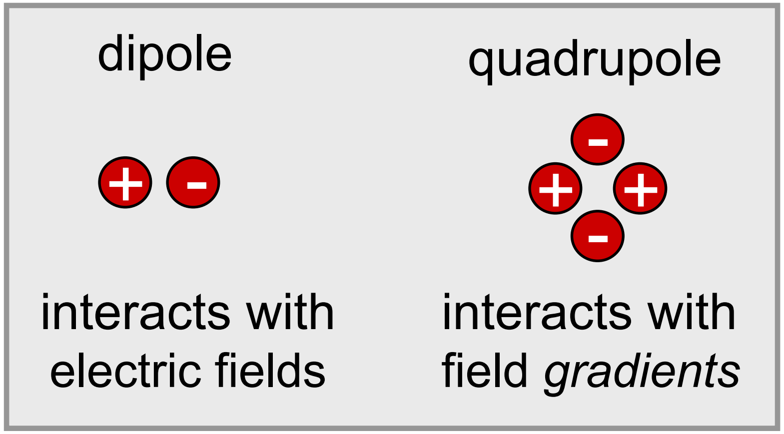
→ Intrinsic property
→ Non spherical positive charge distribution
→ Electric quadrupole moment

Electric quadrupole moment (eQ) unit:

barn = 10^{-28} m^2

Interaction with electric field gradients

(EFG, Ground state interaction)

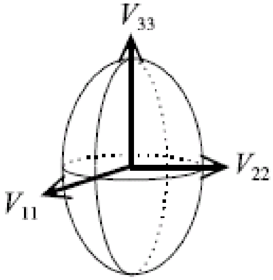


dipole	quadrupole
interacts with electric fields	interacts with field *gradients*

The quadrupole interaction

Electric field gradient at quadruolar nucleus:

Symmetric traceless tensor with $V_{11} < V_{22} < V_{33}$



$$\mathbf{V} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \qquad \mathbf{V}^{\mathrm{PAS}} = \begin{bmatrix} V_{11} & 0 & 0 \\ 0 & V_{22} & 0 \\ 0 & 0 & V_{33} \end{bmatrix}$$

Properties

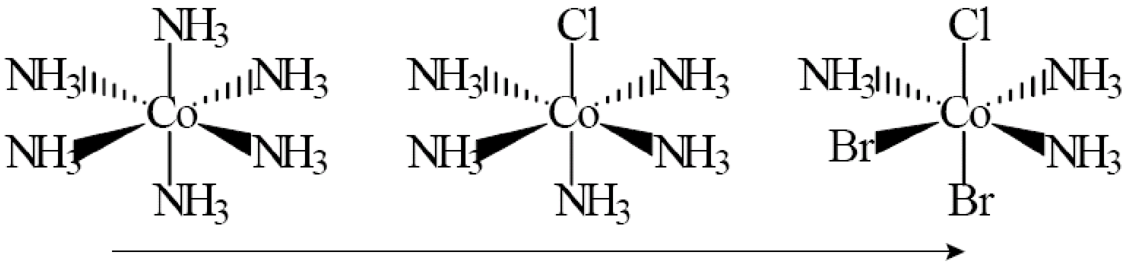
Nuclear quadrupole coupling constant:

$C_Q = eQ \bullet V_{33} / h$ (kHz, MHz)

Asymmetry parameter:

$\eta = (V_{11} - V_{22}) / V_{33}$ where $0 \leq \eta \leq 1$ (0: axially symmetric)

EFG and C_Q grow when symmetry becomes smaller

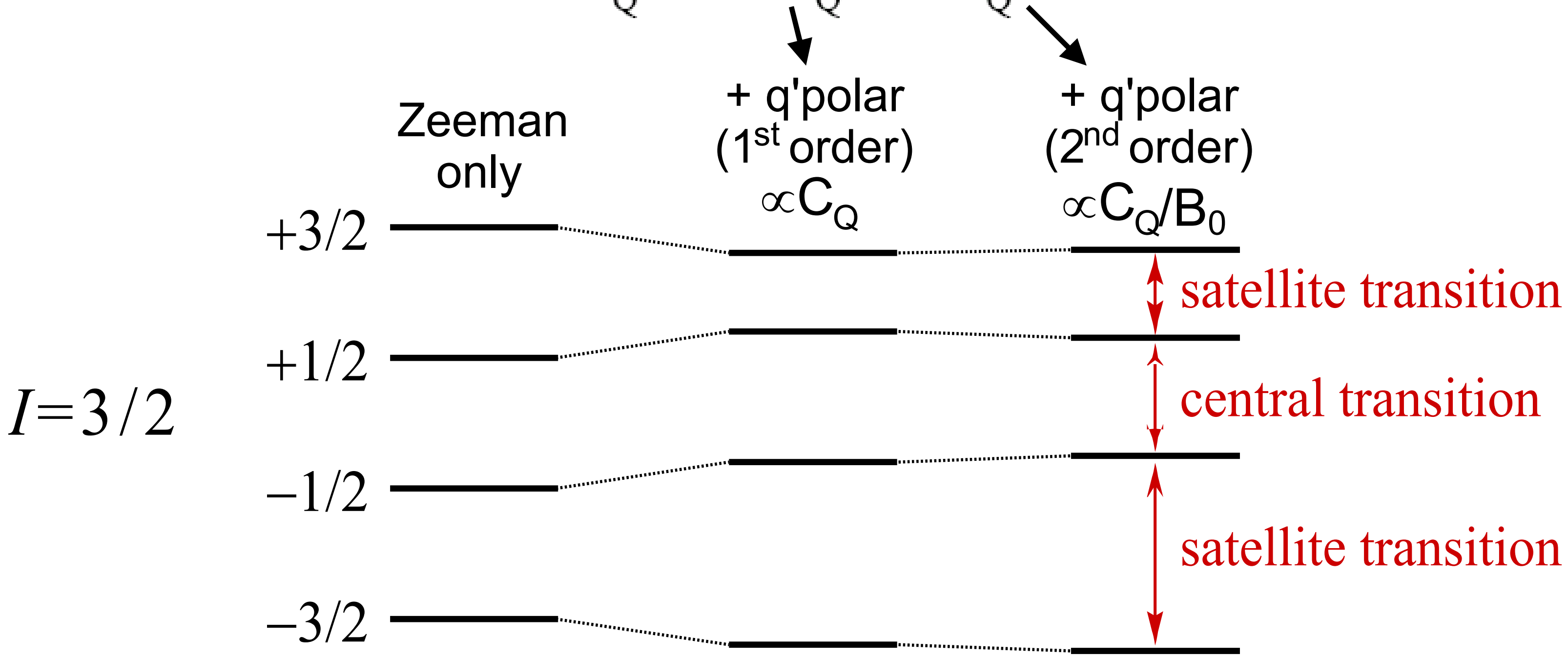


Increasing EFGs, increasing quadrupolar interaction

First and second order quadrupolar effects

May not be small compared to Zeeman interactions (10-1000 MHz)

$$\mathcal{H}_Q = \mathcal{H}_Q^{(1)} + \mathcal{H}_Q^{(2)}$$



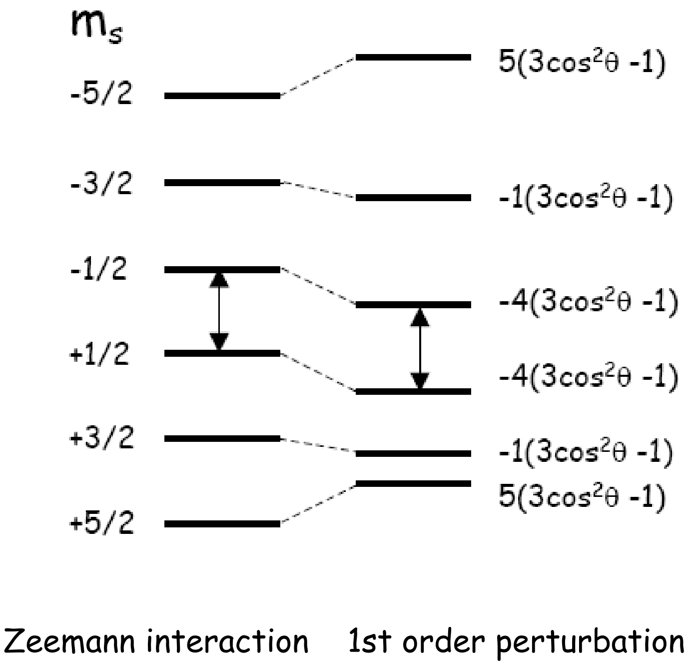
<u>To first order:</u> Central transition unaffected by the quadrupole interaction

Satellite transitions are often too broad to be observed

First order quadrupolar effects

The first-order quadrupolar interaction can be averaged by MAS

$C_q \ll \nu_0$



m_s

-5/2 — $5(3\cos^2\theta - 1)$

-3/2 — $-1(3\cos^2\theta - 1)$

-1/2 — $-4(3\cos^2\theta - 1)$

+1/2 — $-4(3\cos^2\theta - 1)$

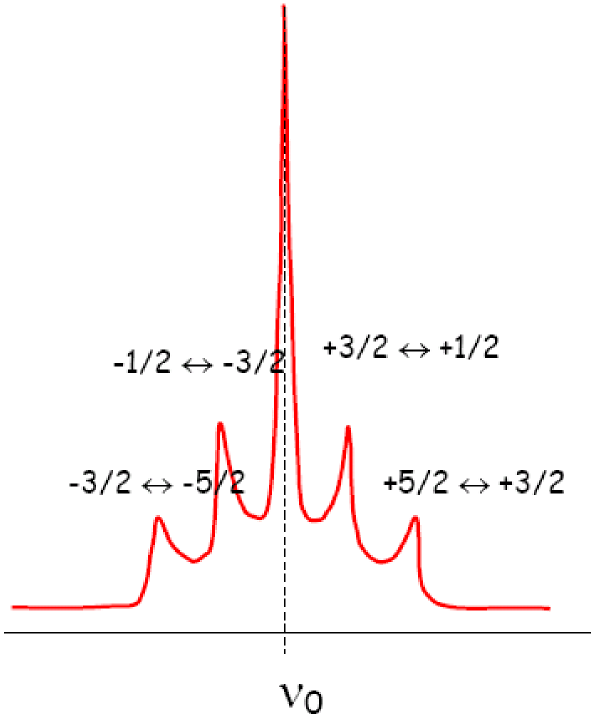
+3/2 — $-1(3\cos^2\theta - 1)$

+5/2 — $5(3\cos^2\theta - 1)$

Zeemann interaction 1st order perturbation

+1/2 ↔ -1/2

Central transition not affected



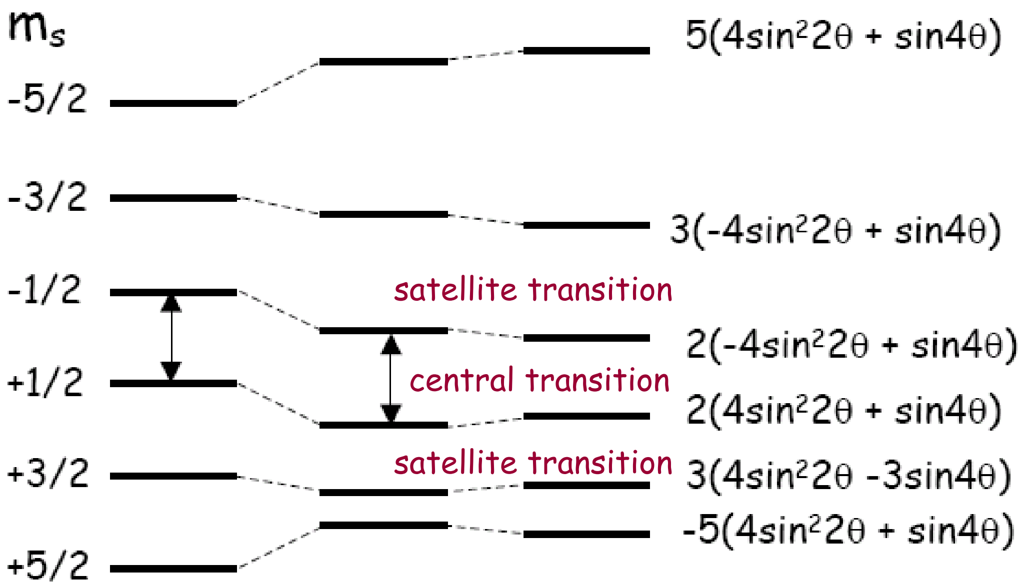
Second order quadrupolar effects

Not averaged by MAS → Calculations are necessary

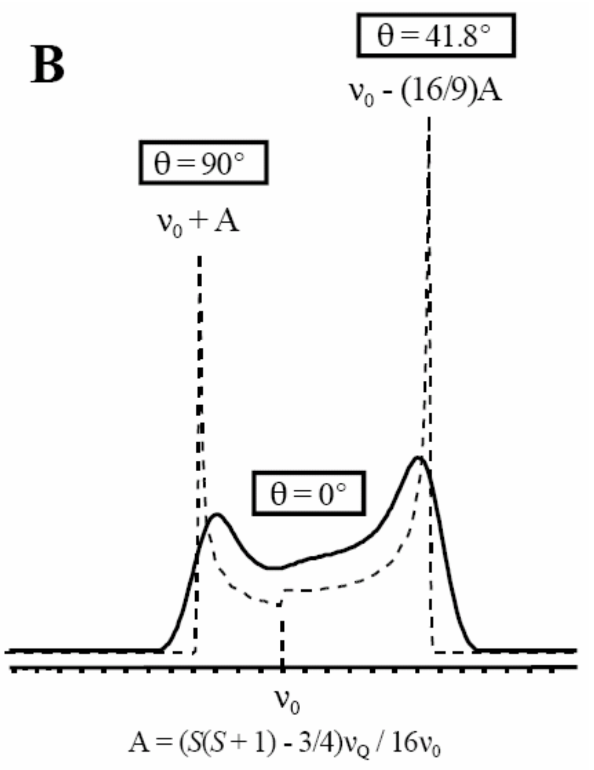
Zeemann interaction

1st order perturbation

2nd order perturbation $\propto C_q/B_0$



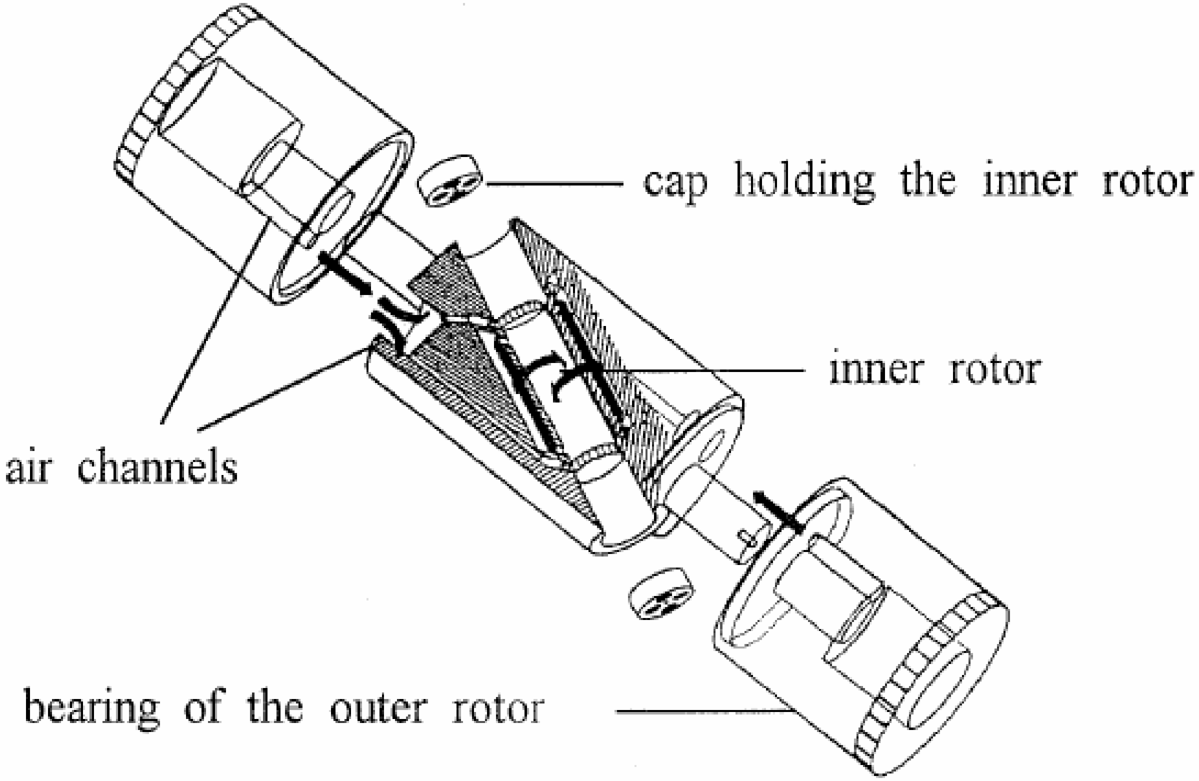
$Cq < \nu_0$



Solutions:

→ DOR (double oriented rotation)
→ DAS (dynamic angle spinning)

Technique for DOR



First and second order quadrupolar effects

Expression of the first-order quadrupolar interaction hamiltonian
(Θ and ϕ = polar angles)

$$\mathcal{H}_{Q}^{(1)} = \frac{1}{2} Q'(\theta,\varphi)\,[I_z^2 - I(I+1)/3]$$

If the EFG increases, quadrupolar interactions become larger
→ Linear combination of pure Zeeman eigenstates (second order)

$$\mathcal{H}_{Q}^{(2)} = \frac{1}{6}\omega_Q[3I_z^2 - I(I+1) + \eta(I_x^2 + I_y^2)]$$

Second-order shifts in energy when η = 0:

$$\omega_Q^{(2)} = -\frac{\omega_Q^2}{16\omega_0}\left(I(I+1) - \frac{3}{4}\right)(1 - \cos^2\theta)(9\cos^2\theta - 1)$$

Application to ^{13}C NMR

^{13}C is easily the most popular NMR nucleus for solids

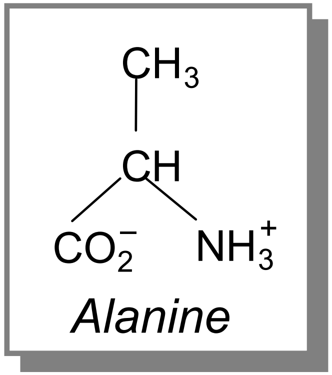
- Homonuclear coupling can be neglected
- Good chemical shift range (good for resolution)
- BUT low sensitivity

Important features of ^{13}C MAS

- ^{1}H decoupling to reduce broadening from dipolar coupling to ^{1}H (requires relatively high RF powers)
- MAS removes CSA etc.
- Cross-polarisation from ^{1}H greatly improves sensitivity

Application to ^{13}C NMR

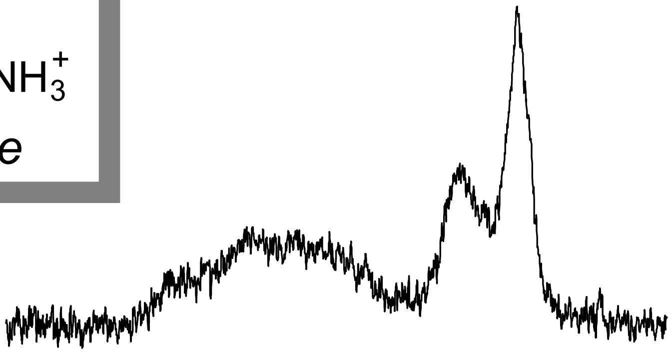
without decoupling



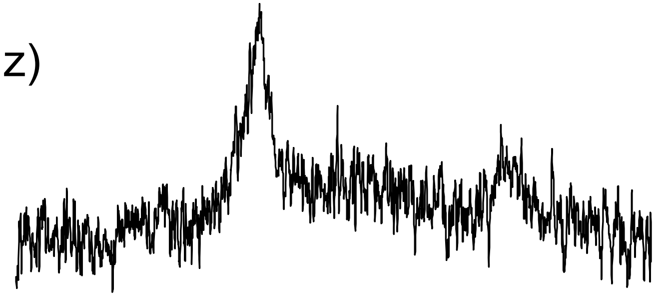
Alanine

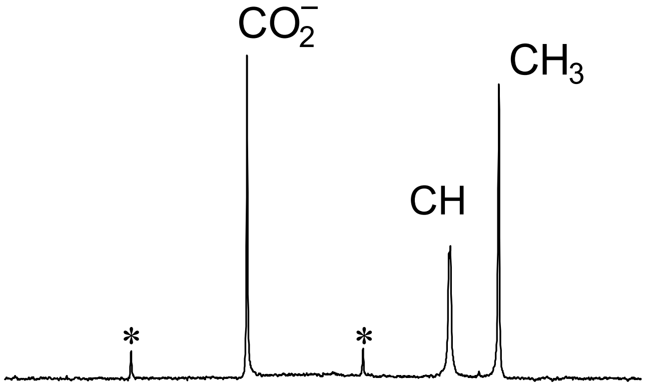
with ^{1}H decoupling

static



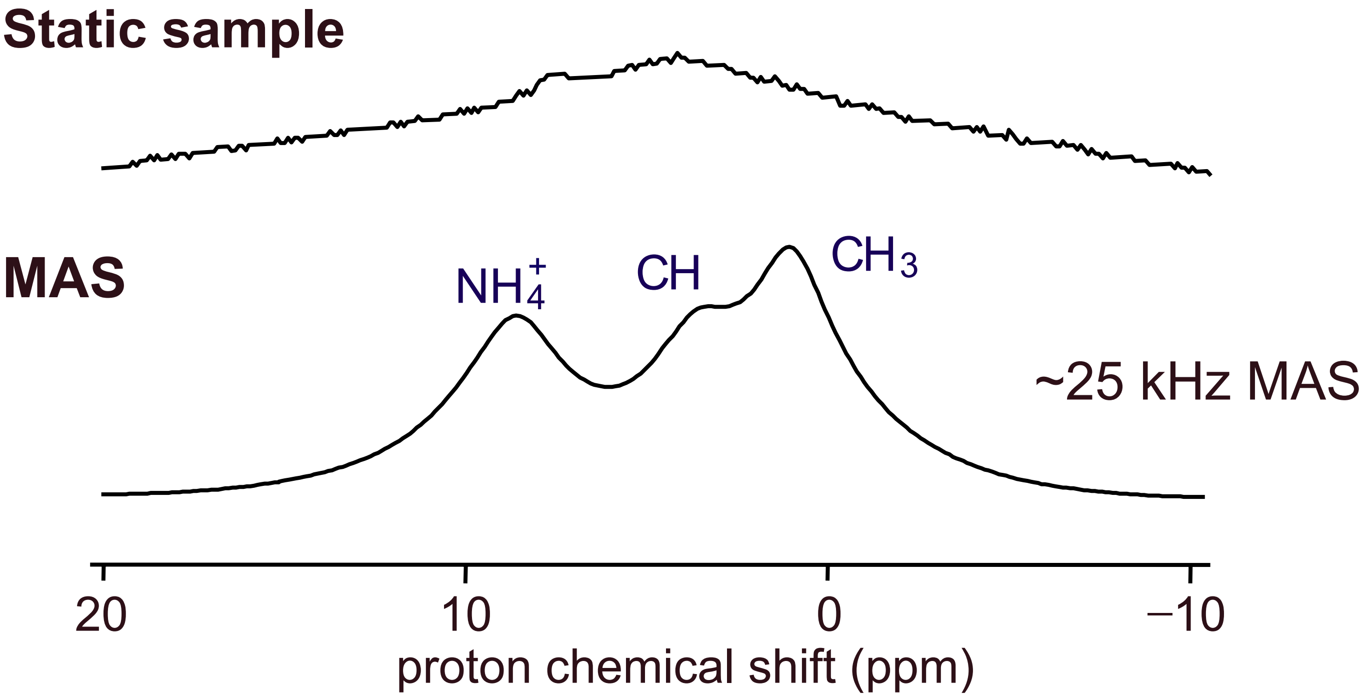
spinning (5 kHz)

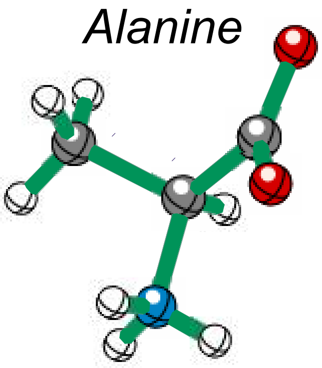




Application to ^1H NMR

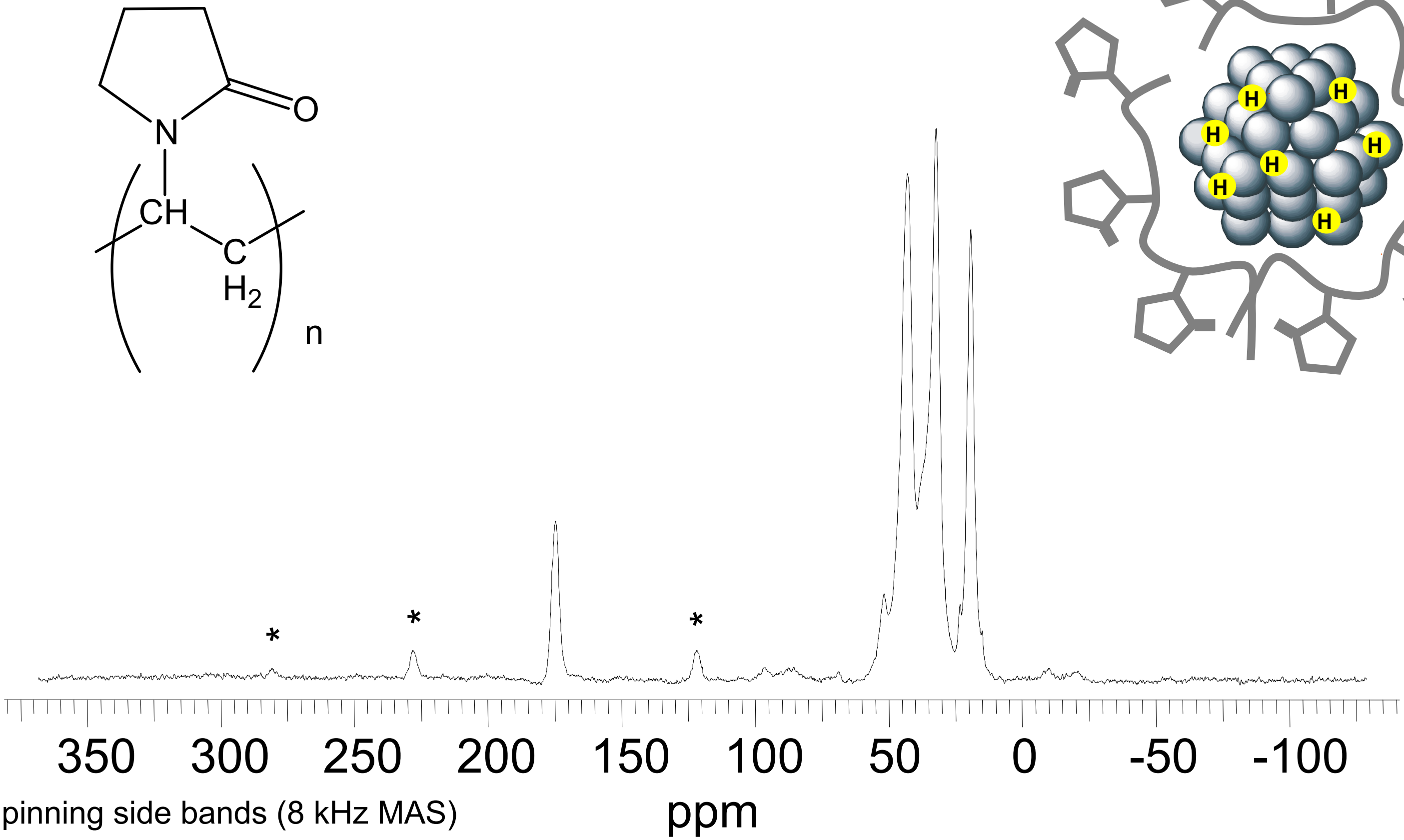
^1H NMR is difficult in organic solids due to strong dipolar couplings between protons



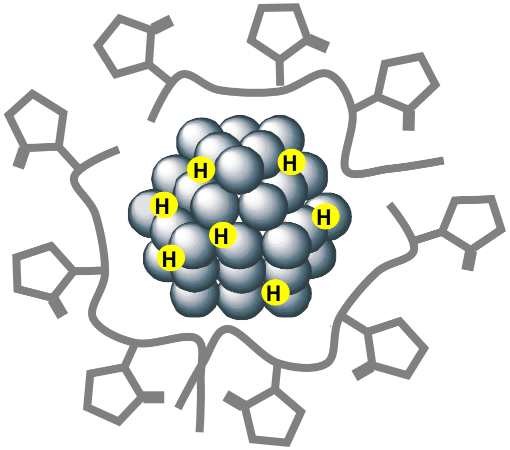


Useful resolution can be obtained, especially for H-bonded sites, with relatively fast spinning (>20 kHz) using just MAS

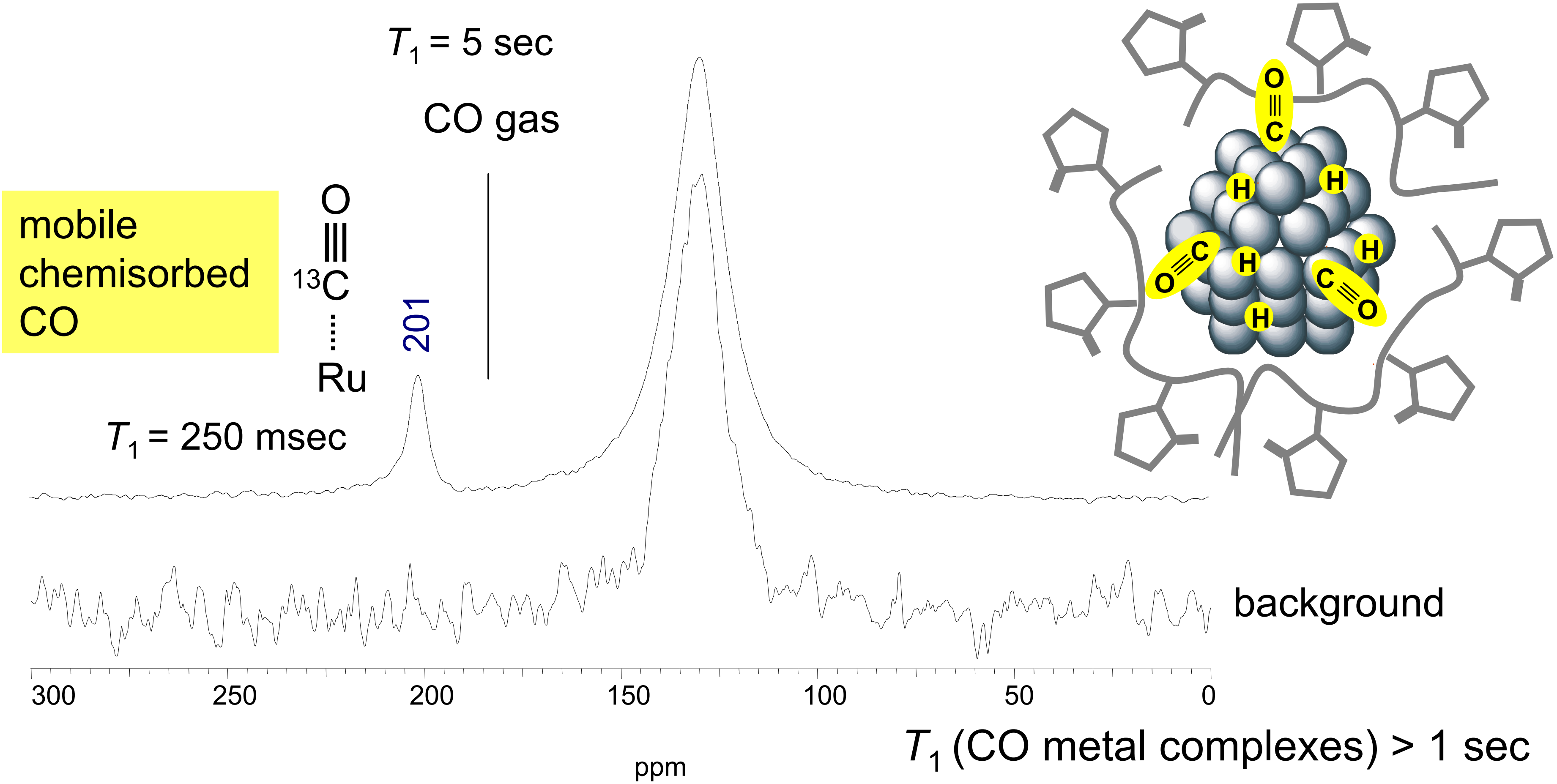
Catalyst characterization (CP MAS ^{13}C NMR)



* Spinning side bands (8 kHz MAS)



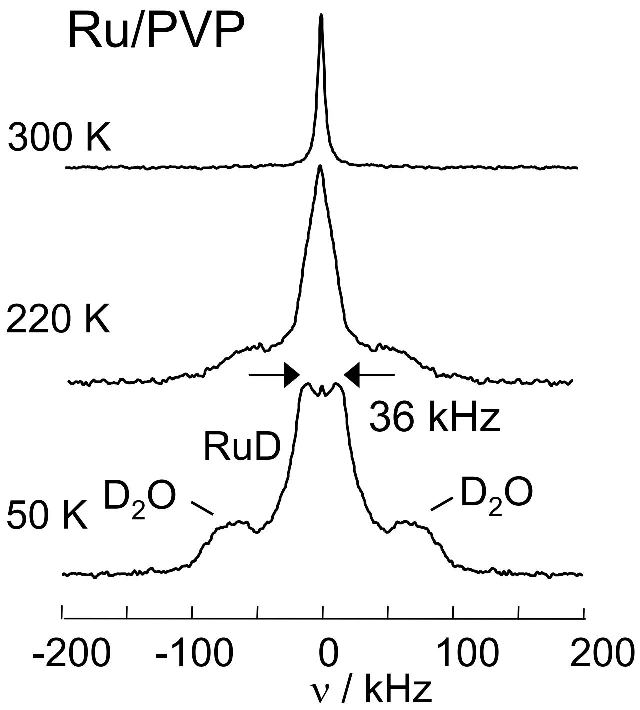
^{13}C NMR of adsorbed CO (static sample)

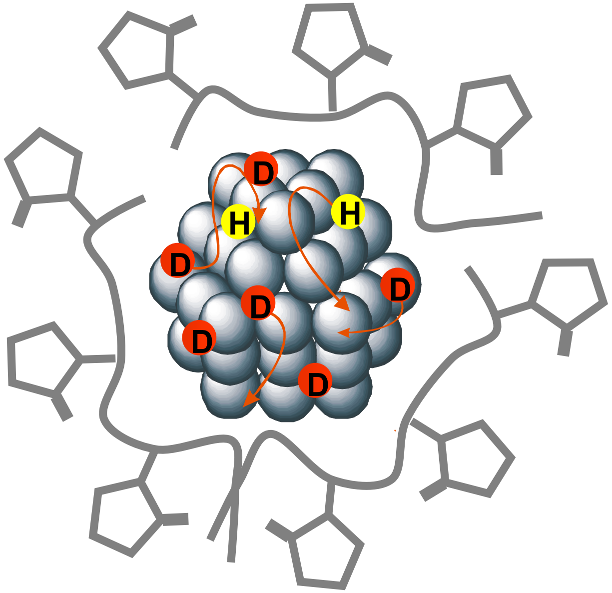


T_1 (CO metal complexes) > 1 sec

Chemical shift: 201 ppm (linear coordinated CO)
Line width: ~10 ppm (high mobiliy)
T_1 = 250 msec (CO coordinated to surface)

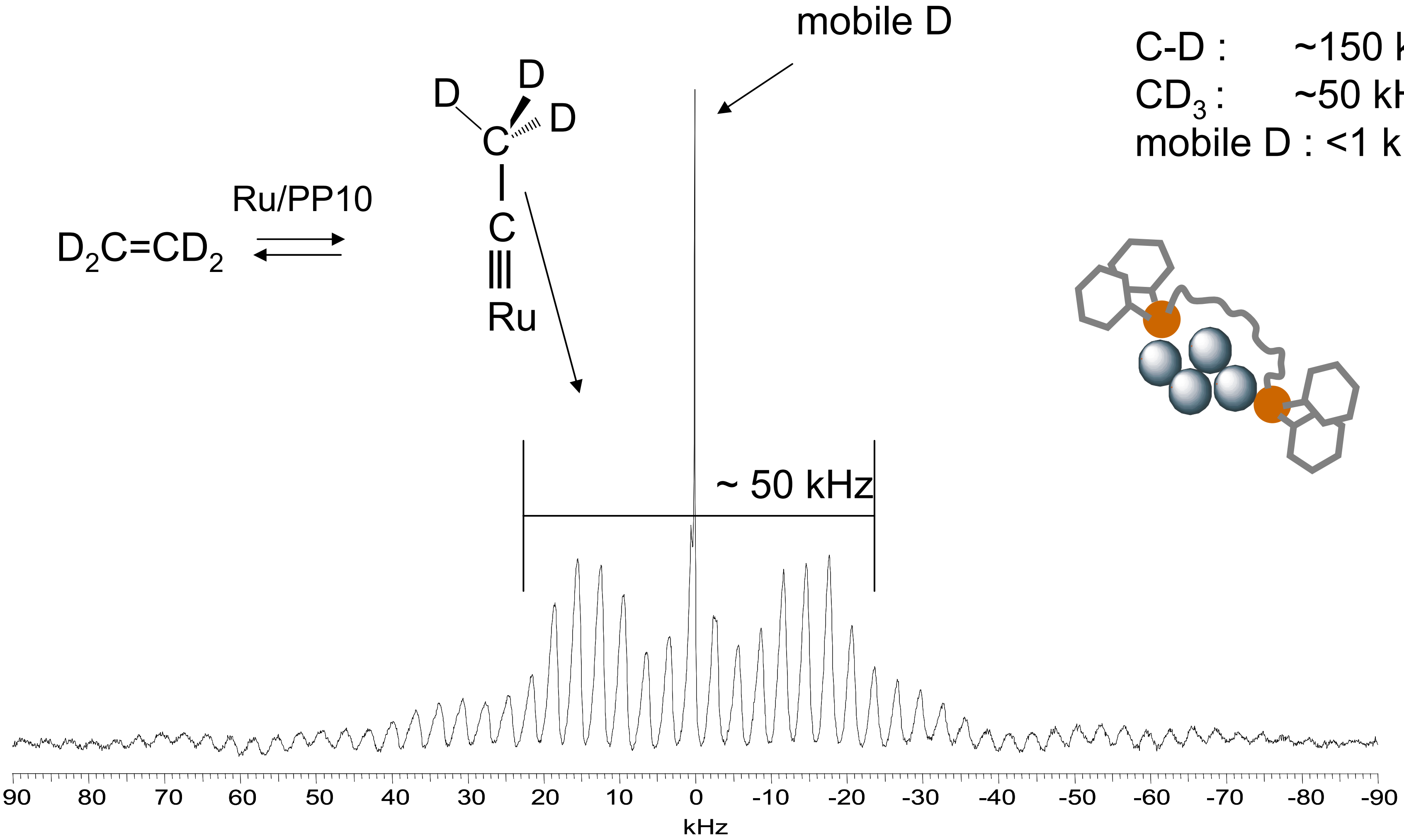
^{2}H Solid State NMR: Surface reactions





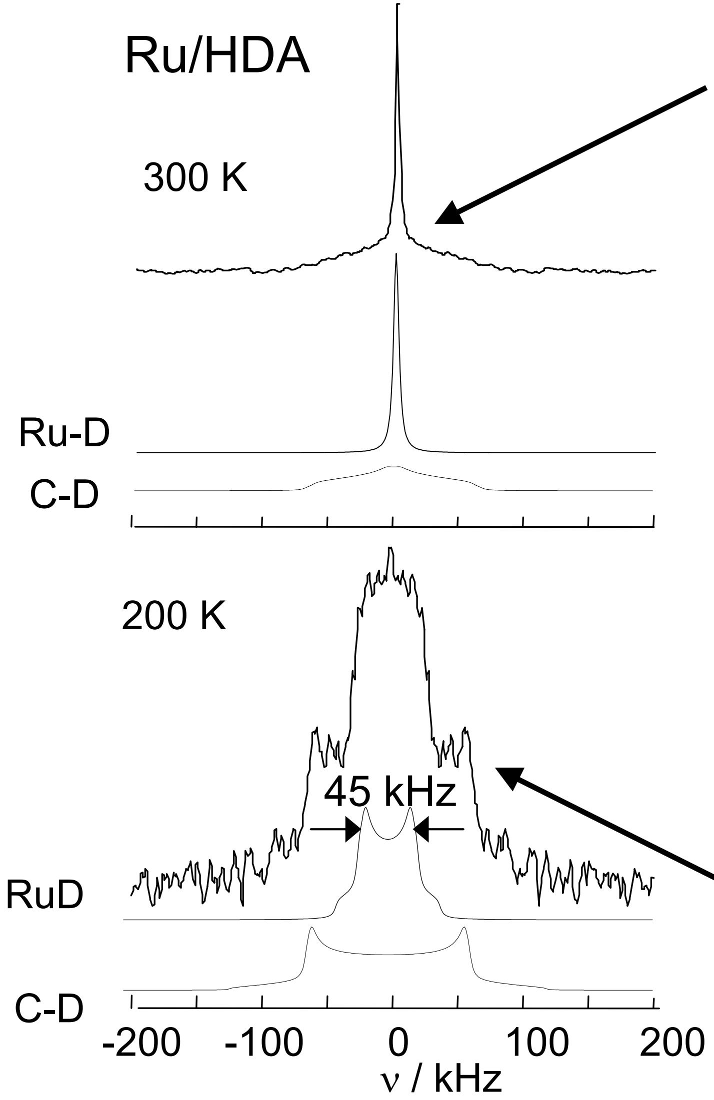
$$2\,Ru + O_2 \rightleftharpoons 2\,RuO + 2\,RuD \rightleftharpoons 4\,Ru + D_2O$$

Surface species by ^{2}H solid state NMR



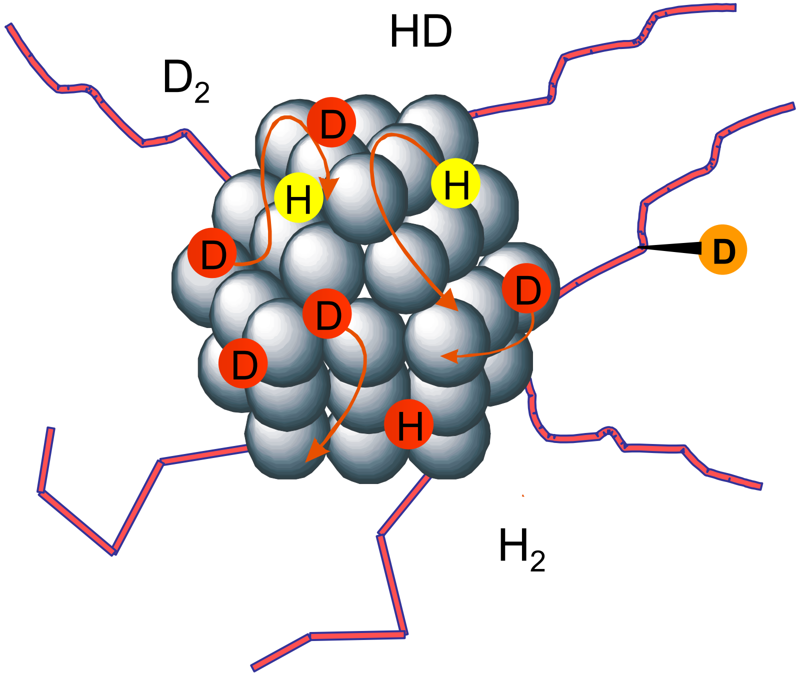
C-D : ~150 kHz
CD_3 : ~50 kHz
mobile D : <1 kHz

Application to adsorbed species



Fast isotropic diffusion of hydrogen atoms on particles

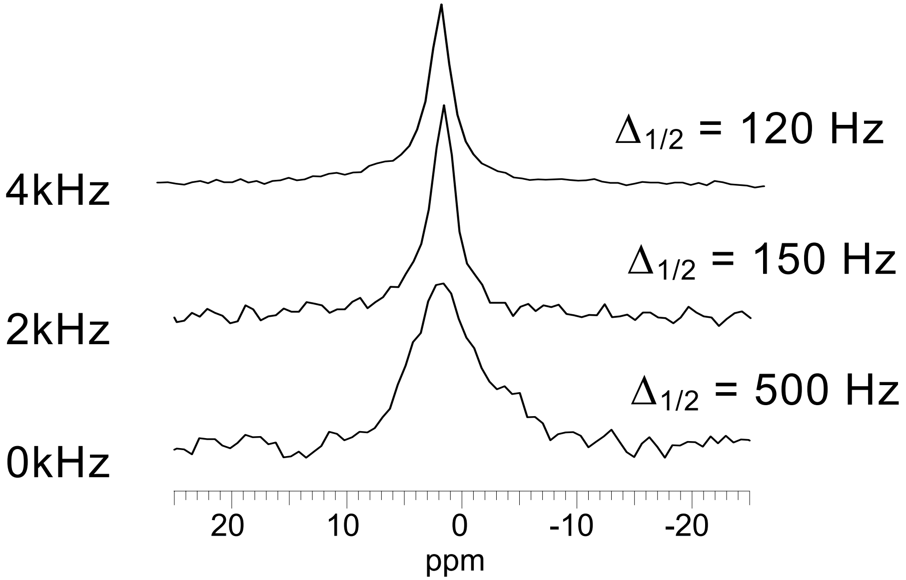
Slow diffusion of hydrogen atoms on particles



Mobility of surface species

Half-intensity widths ($\Delta_{1/2}$) at different rotation frequencies as qualitative parameter for mobility on the surface

^{2}H MAS solid state NMR spectra at various rotating frequencies of deuterated species at the surface of Ru / 0.2 eq HDA colloids after H/D exchange by bubbling

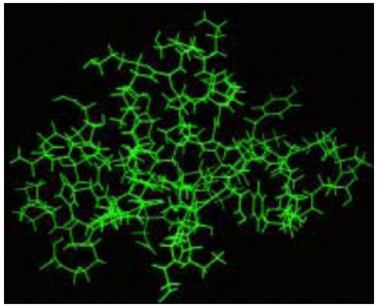


MAS rotating frequency /kHz	$\Delta_{1/2}$ HDA	$\Delta_{1/2}$ D_2 at the surface (1.59 ppm)	$\Delta_{1/2}$ free D_2
4	60	120	120
2	65	150	130
without rotation	7800	500	145

The attached HDA is less mobile than D_2 at the surface
D_2 at the surface is less mobile than free D_2

Conclusion

- **Extremely powerful and polyvalent investigation tool**
- **Technically well established for routine investigations, but new methods are still currently under development (multi-quanta transitions, …)**
- **Very weakly invasive way of investigation (study of biological systems)**



- **Multidimensional NMR for structural and dynamic characterization of large molecule (proteines)**
- **Possibility of in situ studies in heterogeneous catalsyis (structure, intermediates, concentrations,…)**