Solid-State NMR Studies of Molecular Motion

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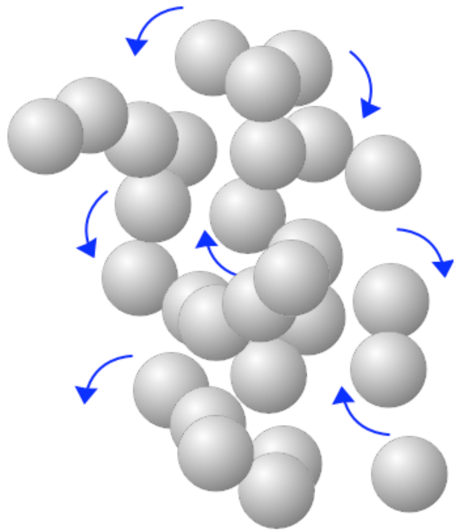
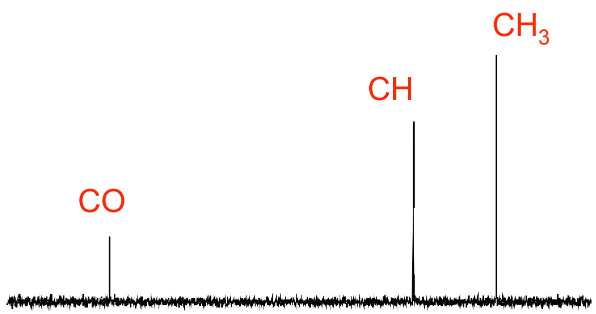
EaStCHEM

Motion in NMR

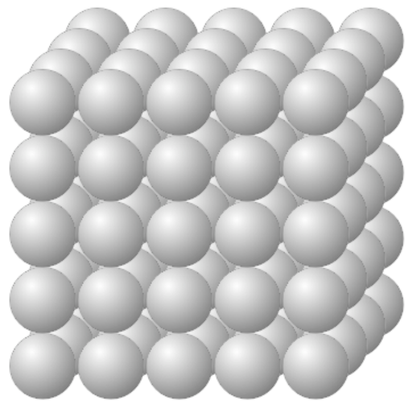
Solution





^{13}C NMR of alanine in solution

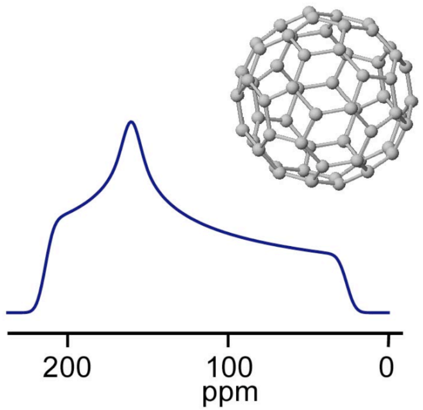
Solid



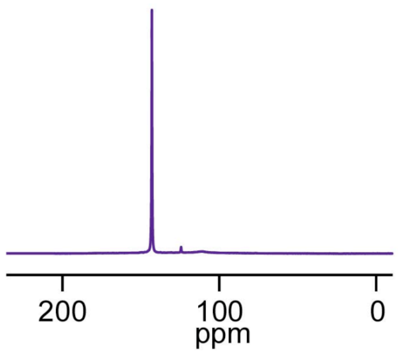
^{13}C NMR of solid alanine

Motion in NMR

fullerene - carbon-13 NMR
low temperature

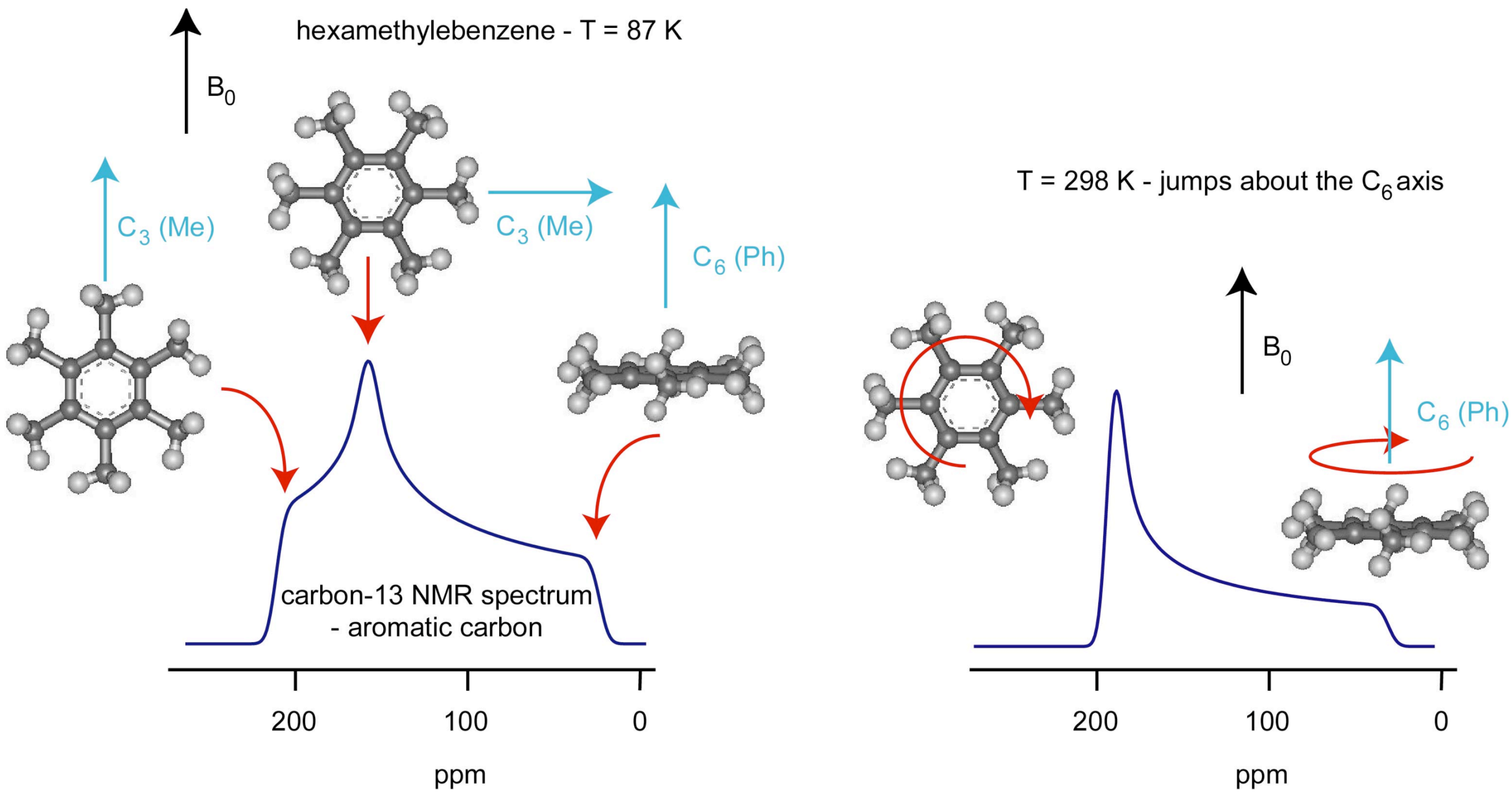


room temperature
tumbles isotropically



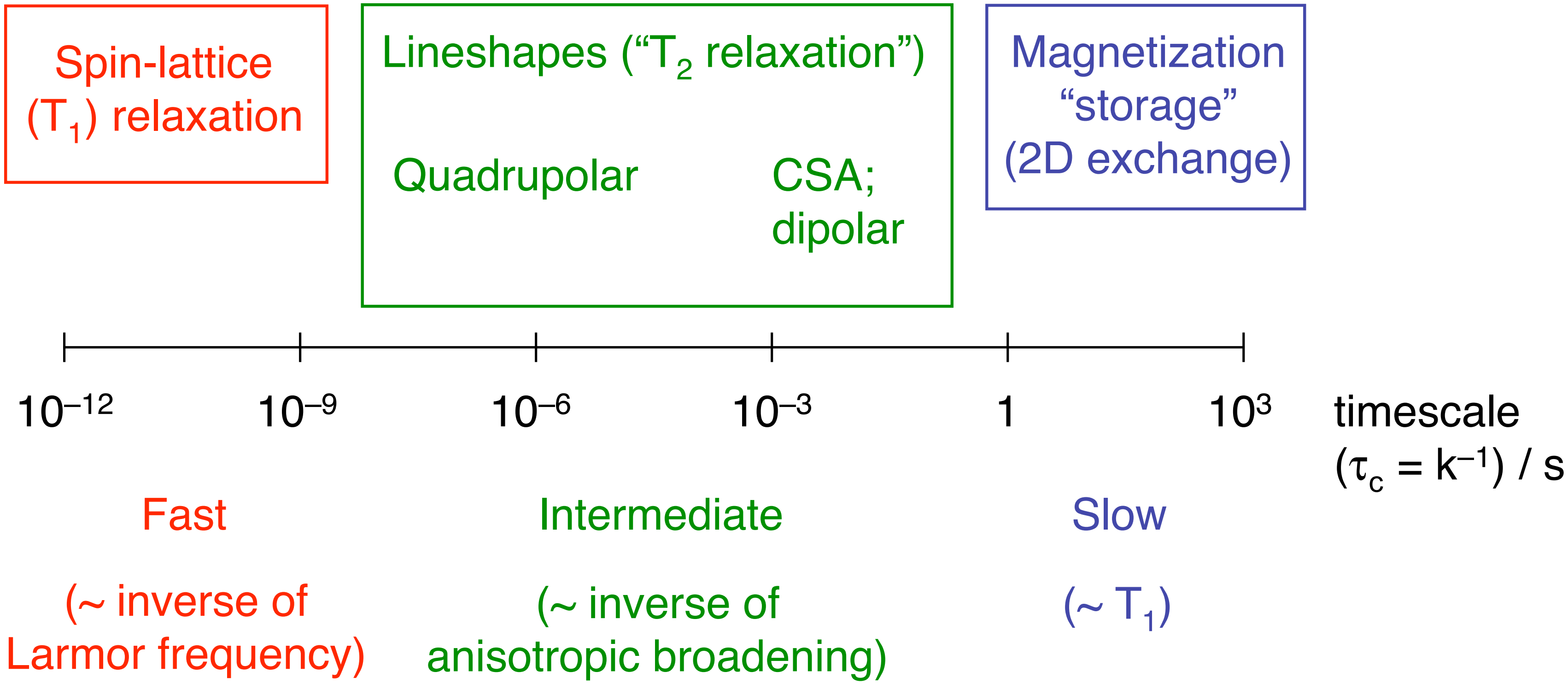
- C_{60} is a “plastic crystal”
- At low temperature lineshape broadened by CSA
- At higher temperatures molecules tumble rapidly and isotropically on their lattice sites
- A single sharp, narrow line is observed

Motion in NMR



- At low temperature CSA tensor with three principal components
- At higher temperature C_6 jump averages two components of the tensor

Timescales

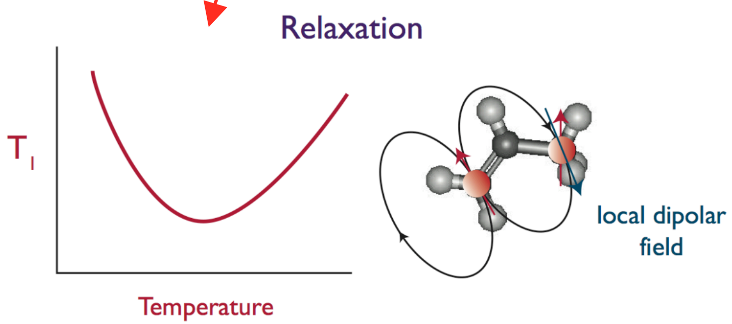


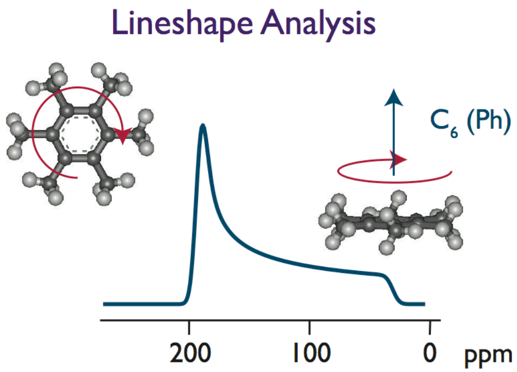
Spin-lattice
(T_1) relaxation
Lineshapes (“T_2 relaxation”)
Quadrupolar
CSA;
dipolar
Magnetization
“storage”
(2D exchange)
10^{-12}
10^{-9}
10^{-6}
10^{-3}
1
10^{3}
timescale
($\tau_c = k^{-1}$) / s
Fast
(~ inverse of
Larmor frequency)
Intermediate
(~ inverse of
anisotropic broadening)
Slow
(~ T_1)

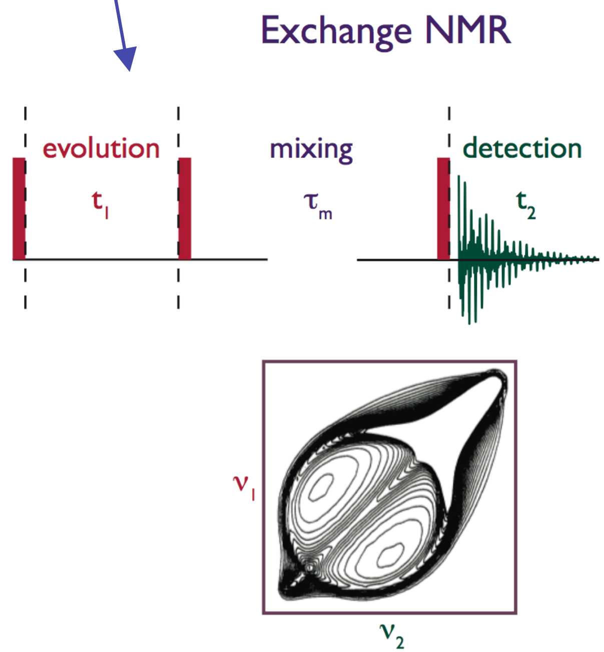
Timescales

10^{-12} — 10^{-9} — 10^{-6} — 10^{-3} — 1 — 10^{3} timescale $(\tau_c = k^{-1})$ / s

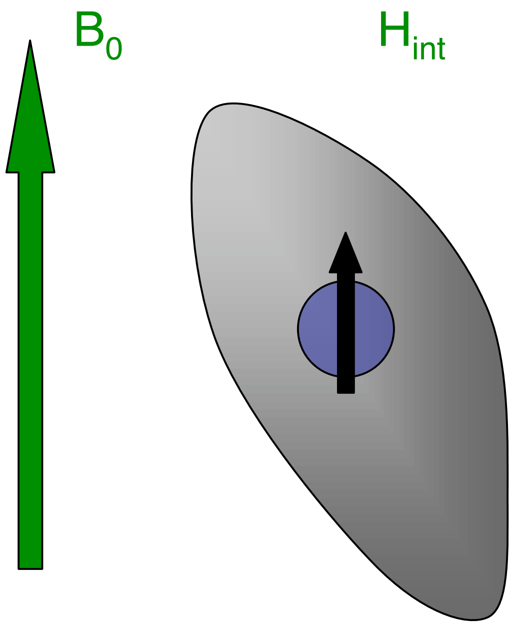
Fast — Intermediate — Slow





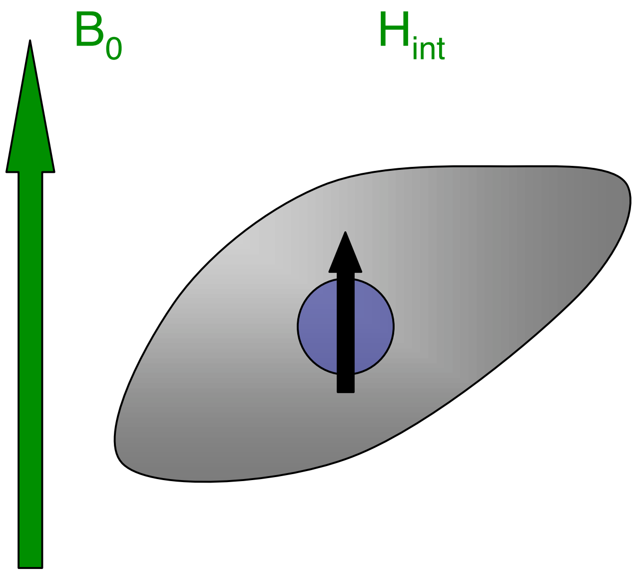


Rapidly fluctuating Hamiltonians



- Orientationally-dependent (anisotropic) interactions, H_{int}
- In liquids, rapid tumbling motion results in resonance frequency being determined only by isotropic or average value of H_{int}
- Also $\Delta m = \pm 1, \pm 2$ off-diagonal elements of H_{int} that cause $\Delta m = \pm 1, \pm 2$ transitions if motion is comparable with ω_0 or $2\omega_0$
- These random transitions give rise to the spin-lattice (T_1) relaxation and part of the spin-spin (T_2) relaxation behaviour

Rapidly fluctuating Hamiltonians



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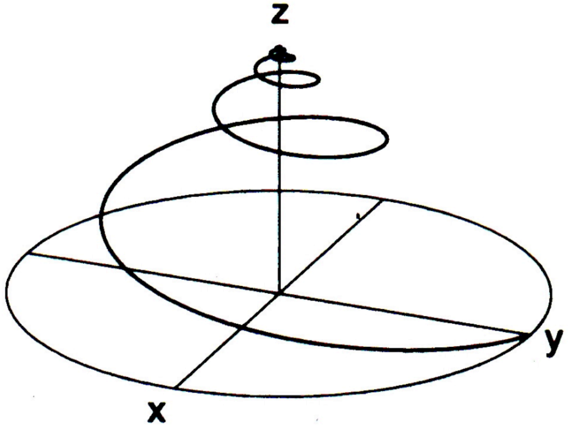
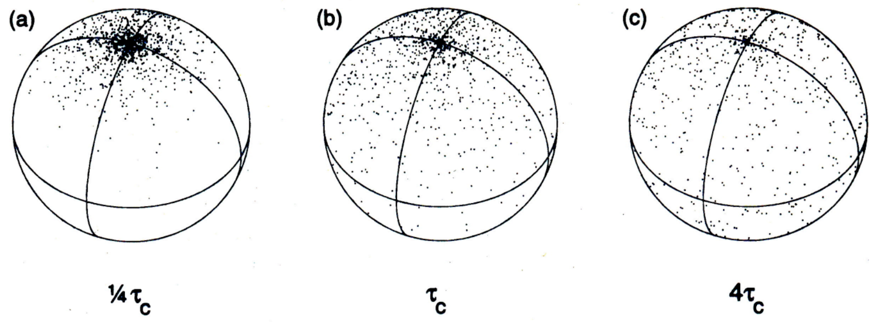
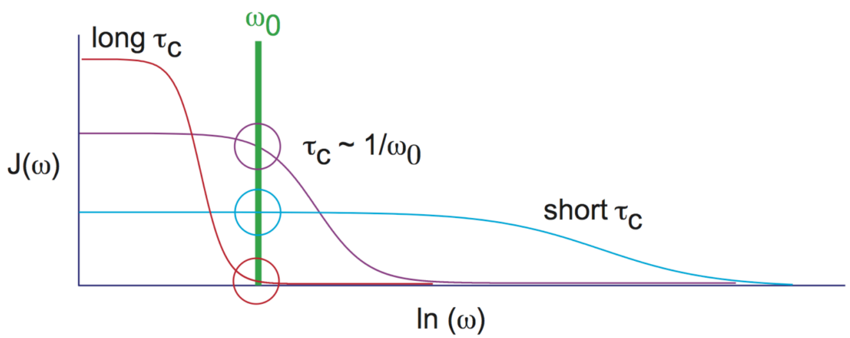
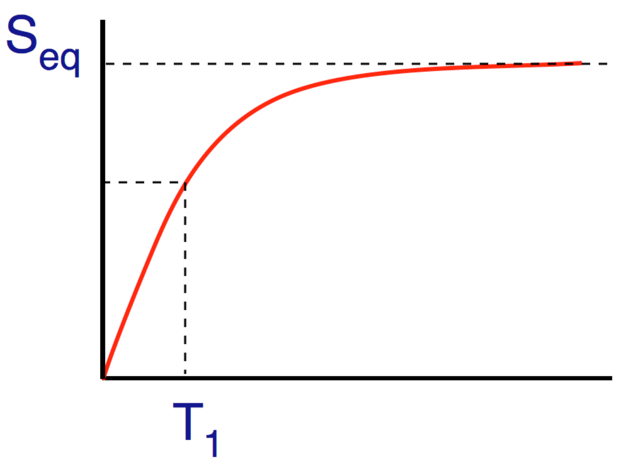
Spin-lattice (T_1) relaxation

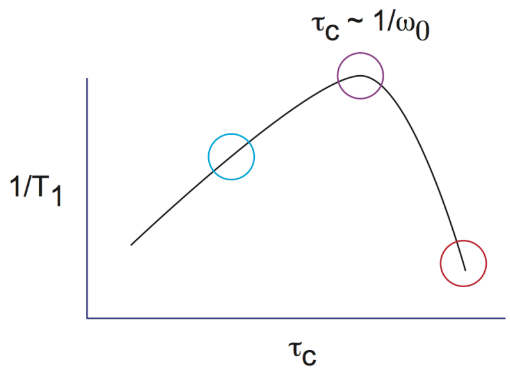




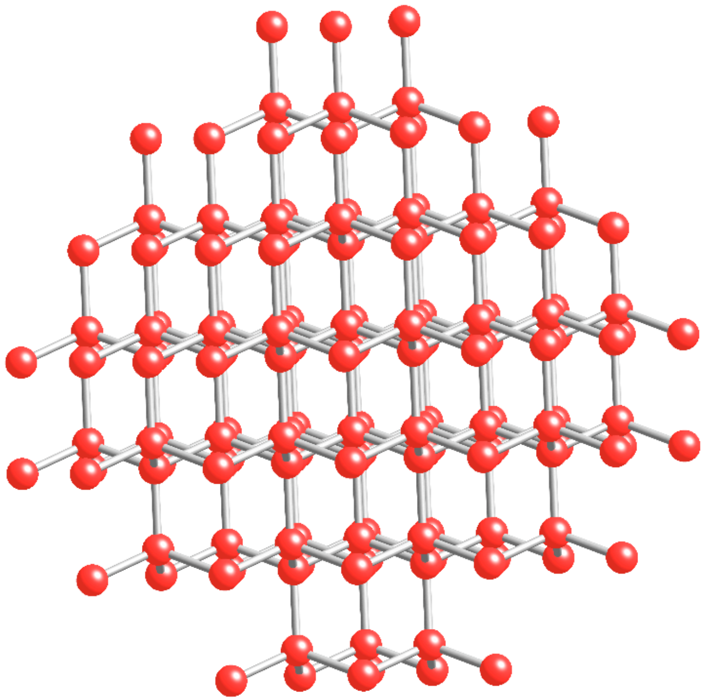




$$S(t) = S_{eq} (1 - \exp(-t/T_1))$$

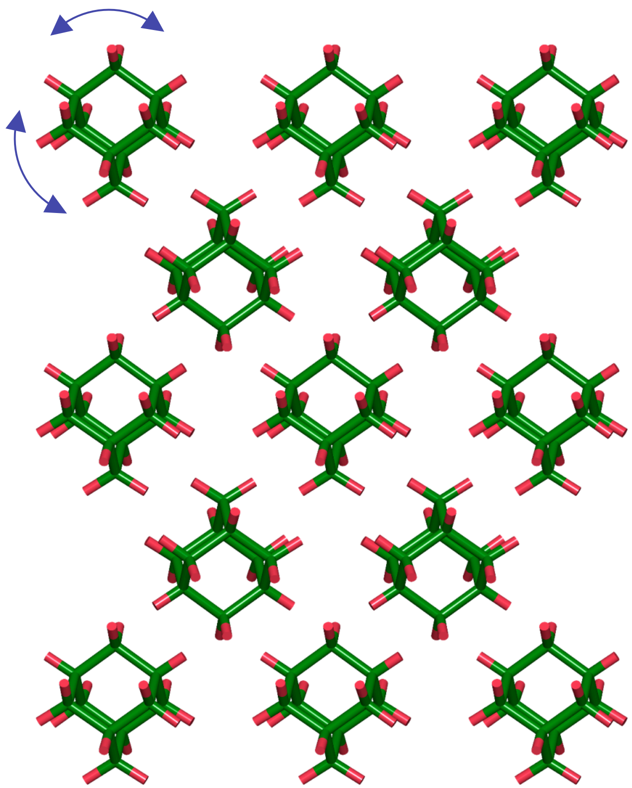


Spin-lattice (T_1) relaxation



Diamond

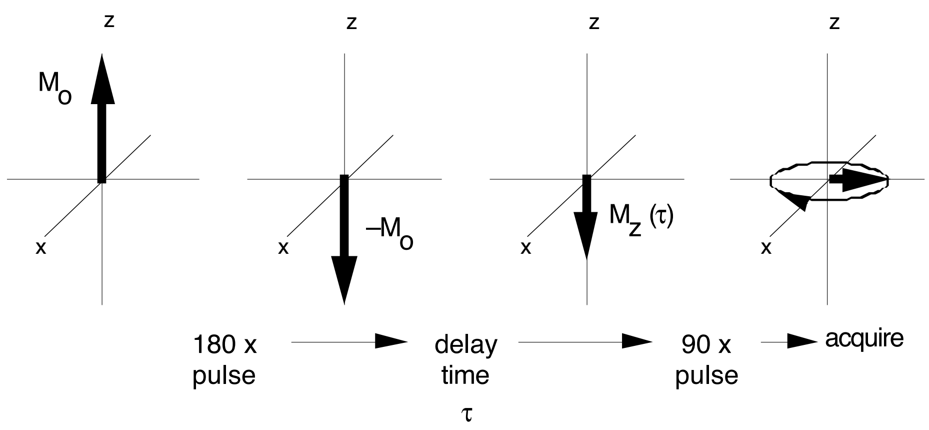
T_1 ~ 24 hours

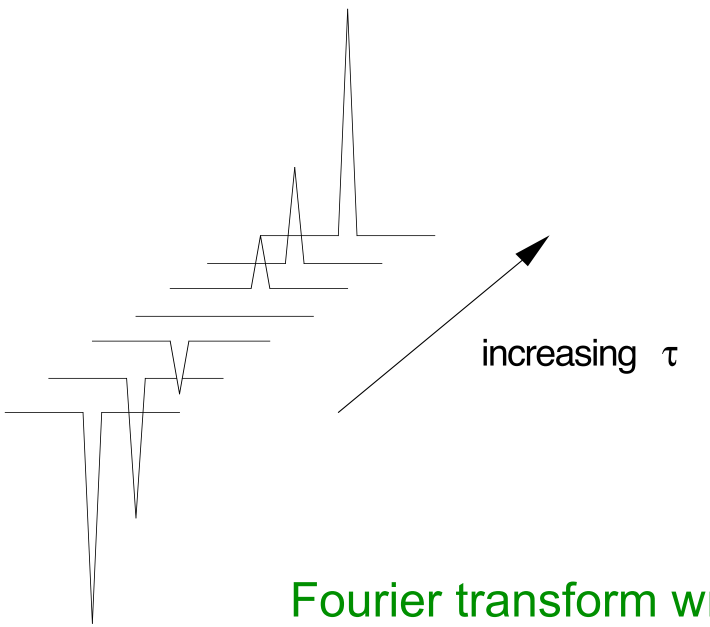


Adamantane

T_1 ~ 5 s

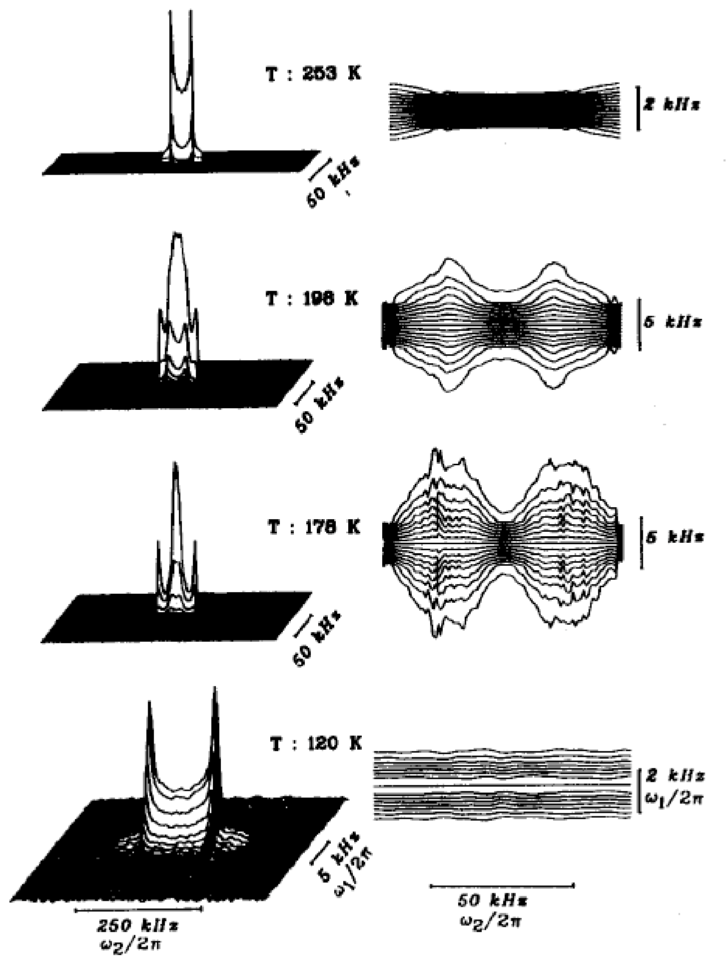
Anisotropic T_1 in ^2H NMR





Fourier transform wrt τ

spinning methyl group
in d_3-alanine

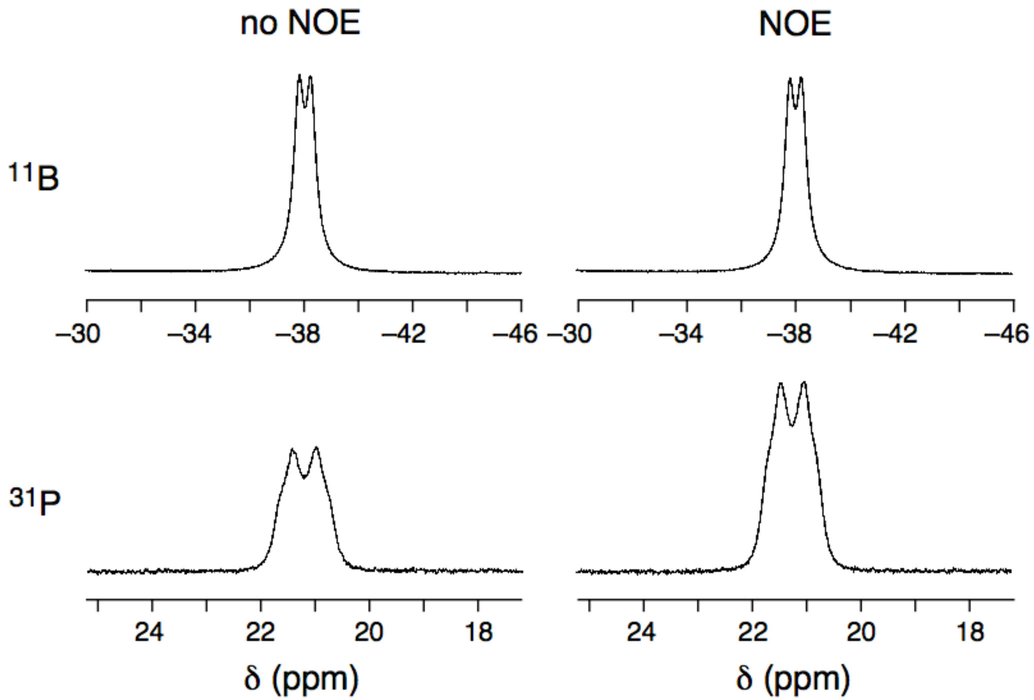


Schleicher et al., J. Chem. Phys. ***92****, 6432 (1990)*

NOE measurements

- NOE common in the liquid state for I = 1/2 nuclei
- Not usually observed for quadrupolar nuclei (efficient quadrupolar relaxation)
- Rare in solids as motion usually too slow

BH_3PPh_3



steady-state
NOE in $CDCl_3$

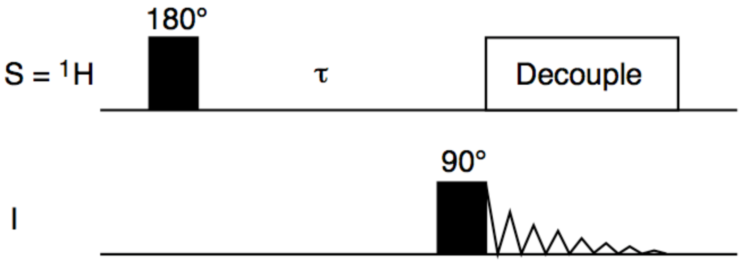
0% ^{11}B NOE

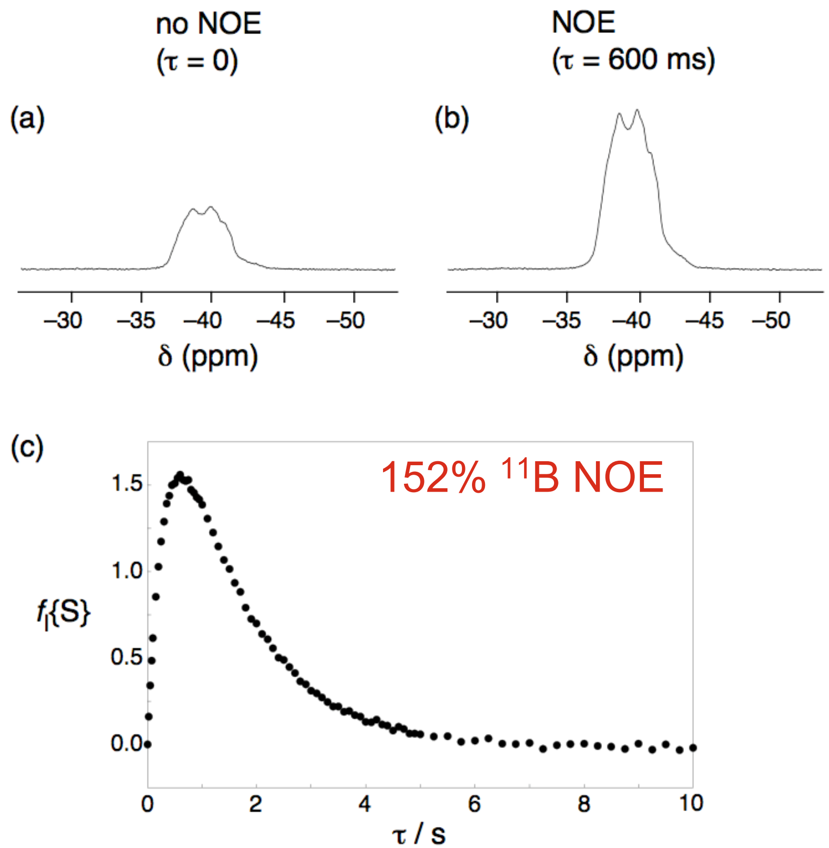
53% ^{31}P NOE

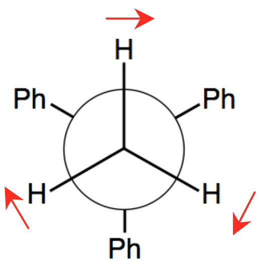
Ashbrook et al., J. Am. Chem. Soc. ***128****, 6782 (2006)*

NOE measurements

transient NOE in BH_3PPh_3 solid



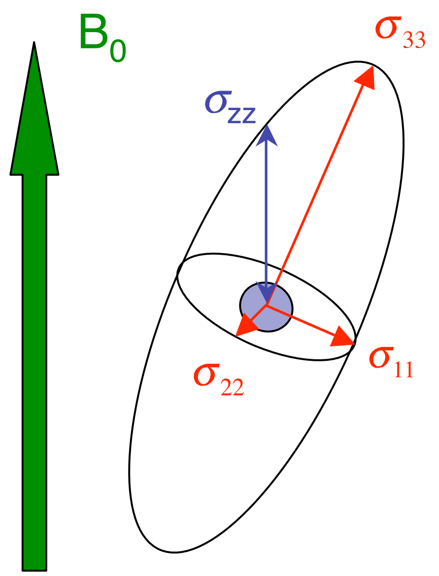




- Rapid BH_3 rotation modulates the dipolar interaction (to produce NOE) but not the quadrupolar interaction (so no rapid relaxation)

Ashbrook et al., J. Am. Chem. Soc. ***128****, 6782 (2006)*

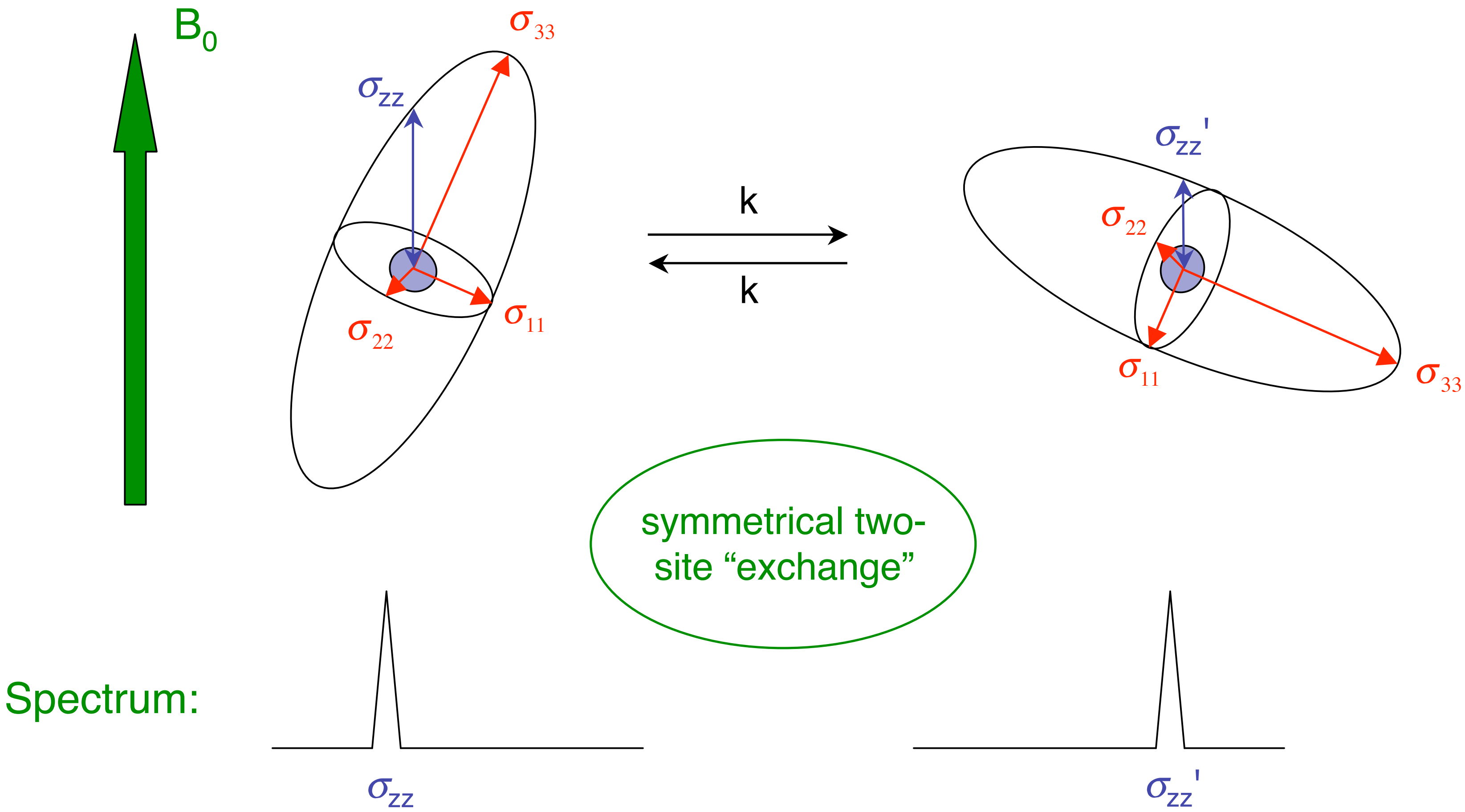
Slowly fluctuating Hamiltonians



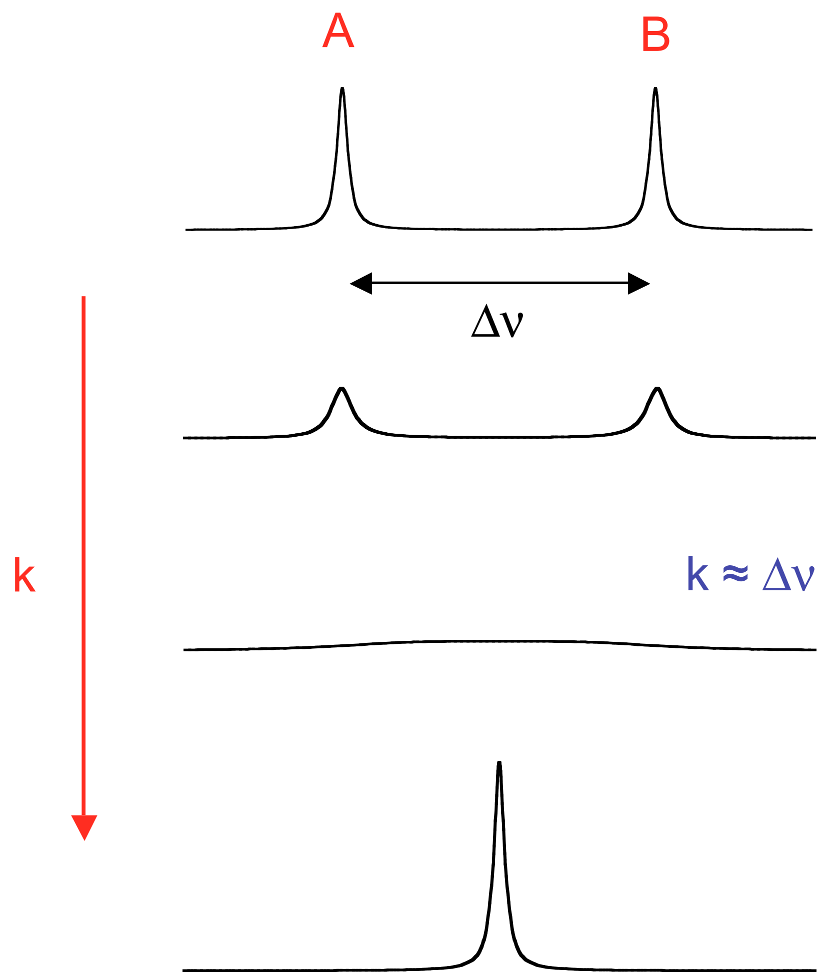
- To calculate resonance frequencies we truncate H_{int} ("make the secular approximation", "retain only the terms that commute with H_Z")
- Example: the truncated shielding can be represented by an ellipsoid or shielding tensor, $\boldsymbol{\sigma}$, that has three principal axes: $\boldsymbol{\sigma}_{11}$, $\boldsymbol{\sigma}_{22}$, and $\boldsymbol{\sigma}_{33}$
- In a solid, observed shielding is given by $\boldsymbol{\sigma}_{zz}$

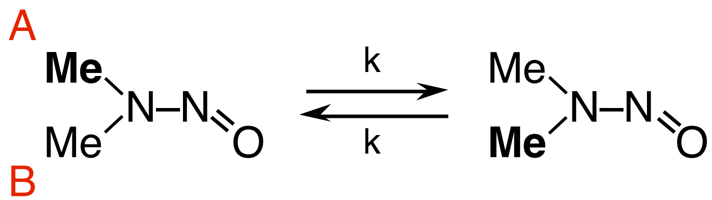
Isotropic shielding: $\sigma_{iso} = \sigma_{zz} = (1/3)\,(\sigma_{11} + \sigma_{22} + \sigma_{33})$

Slowly fluctuating Hamiltonians



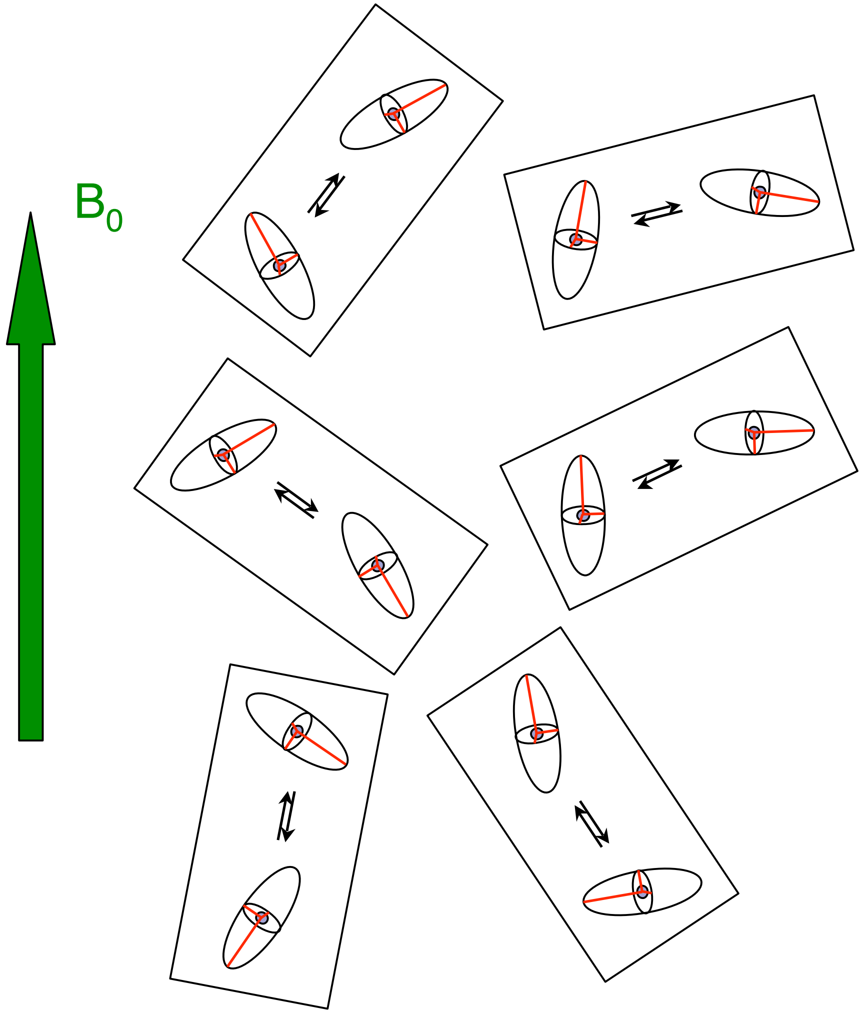
Exchange broadening





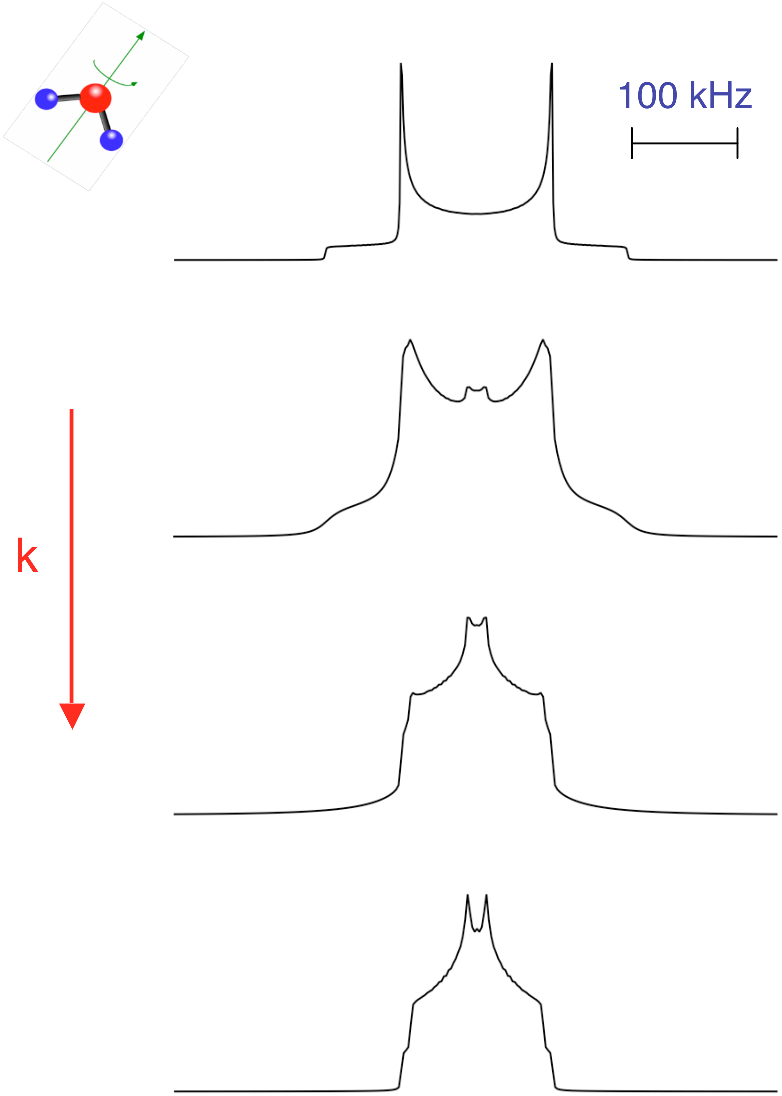
Dimethylnitrosamine –
the textbook example in
liquids NMR

Powder averaging and dynamics



- A powdered solid consists of microcrystals with a random, spherical distribution of orientations
- Therefore, exchange-broadened “pairs” must be averaged over all orientations to obtain powder spectrum

Powder averaging and dynamics



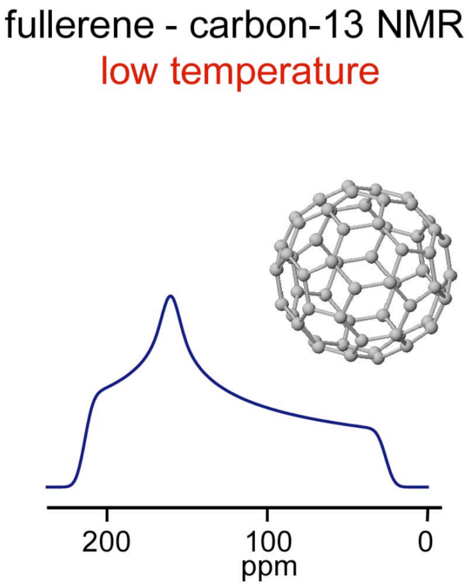
- Example: ^2H (spin I = 1) powder NMR spectrum as function of k

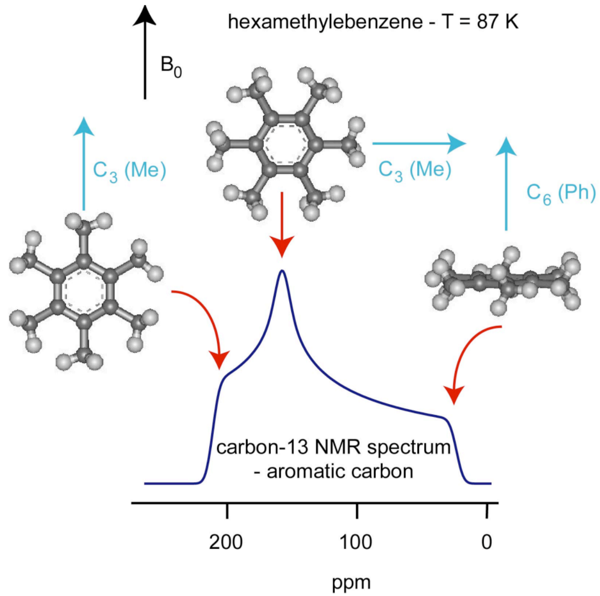
- Changes in powder lineshape and underlying linewidth (“T_2 relaxation”) are best observed using echo methods (e.g., quadrupolar echo)

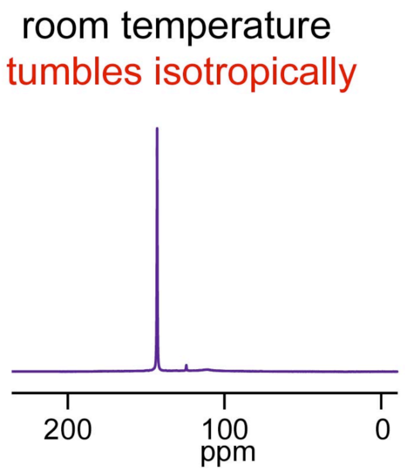
- Very powerful method of testing mechanism of reorientation and determining k

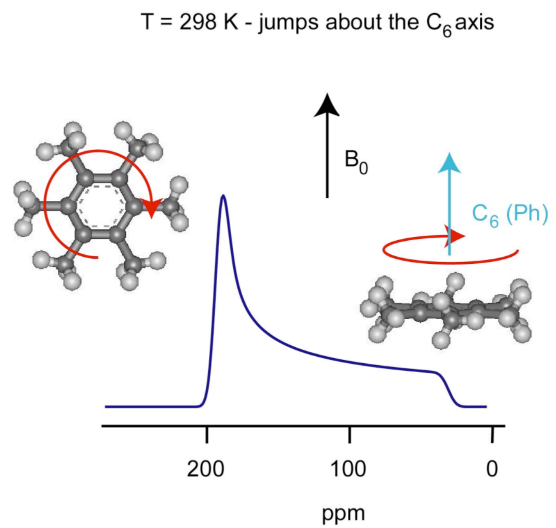
- “Exchange broadening” and “T_2 relaxation caused by slow motions” can be thought of as the same thing

Powder averaging and dynamics

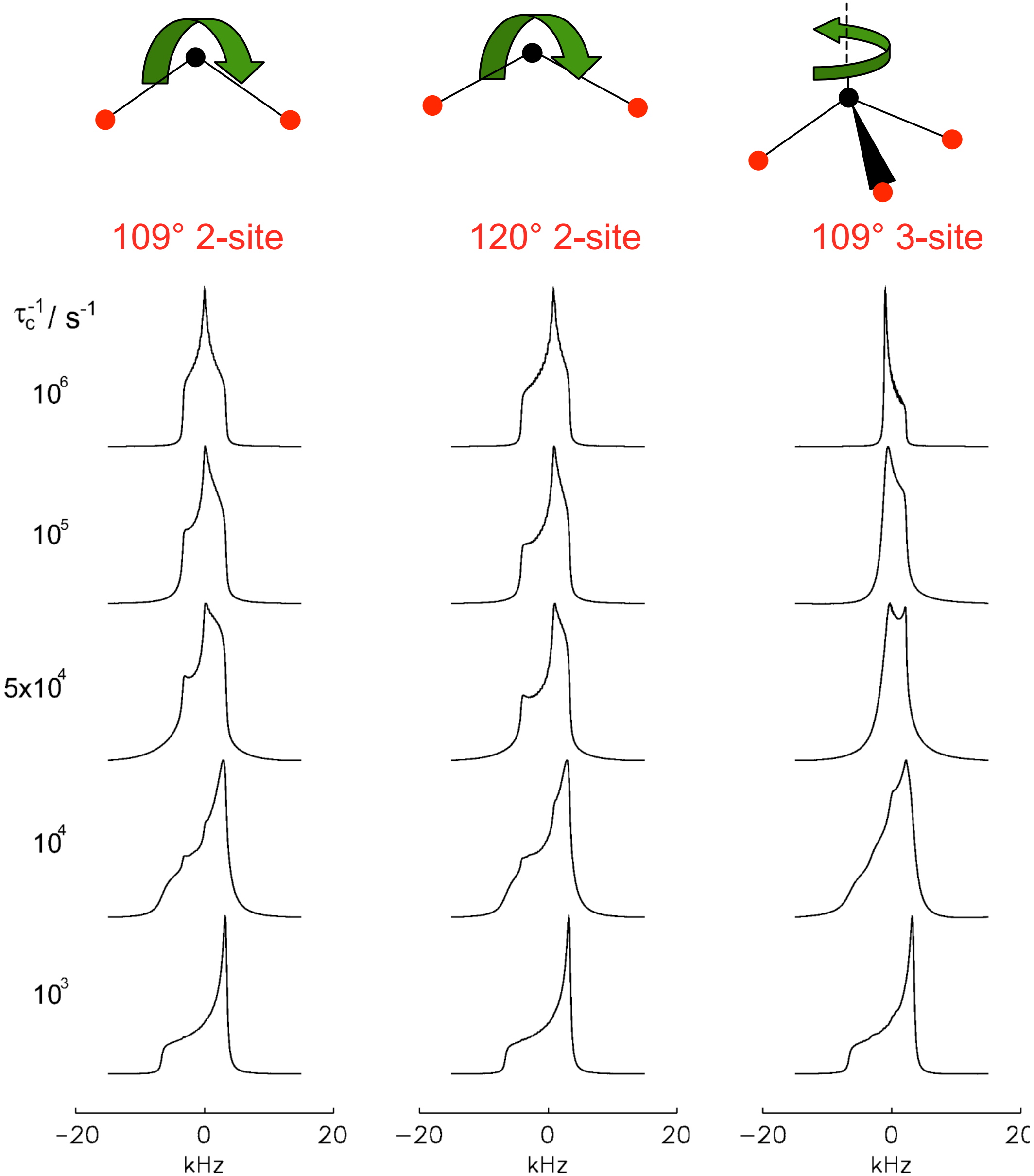






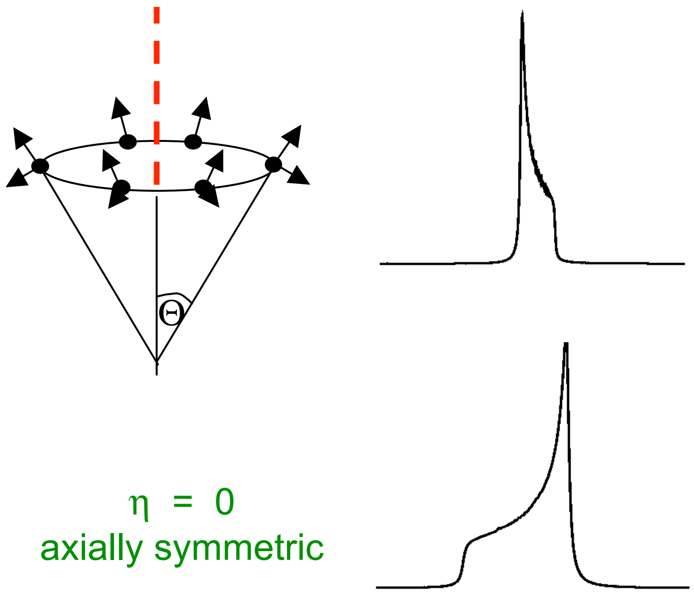


Powder averaging and dynamics

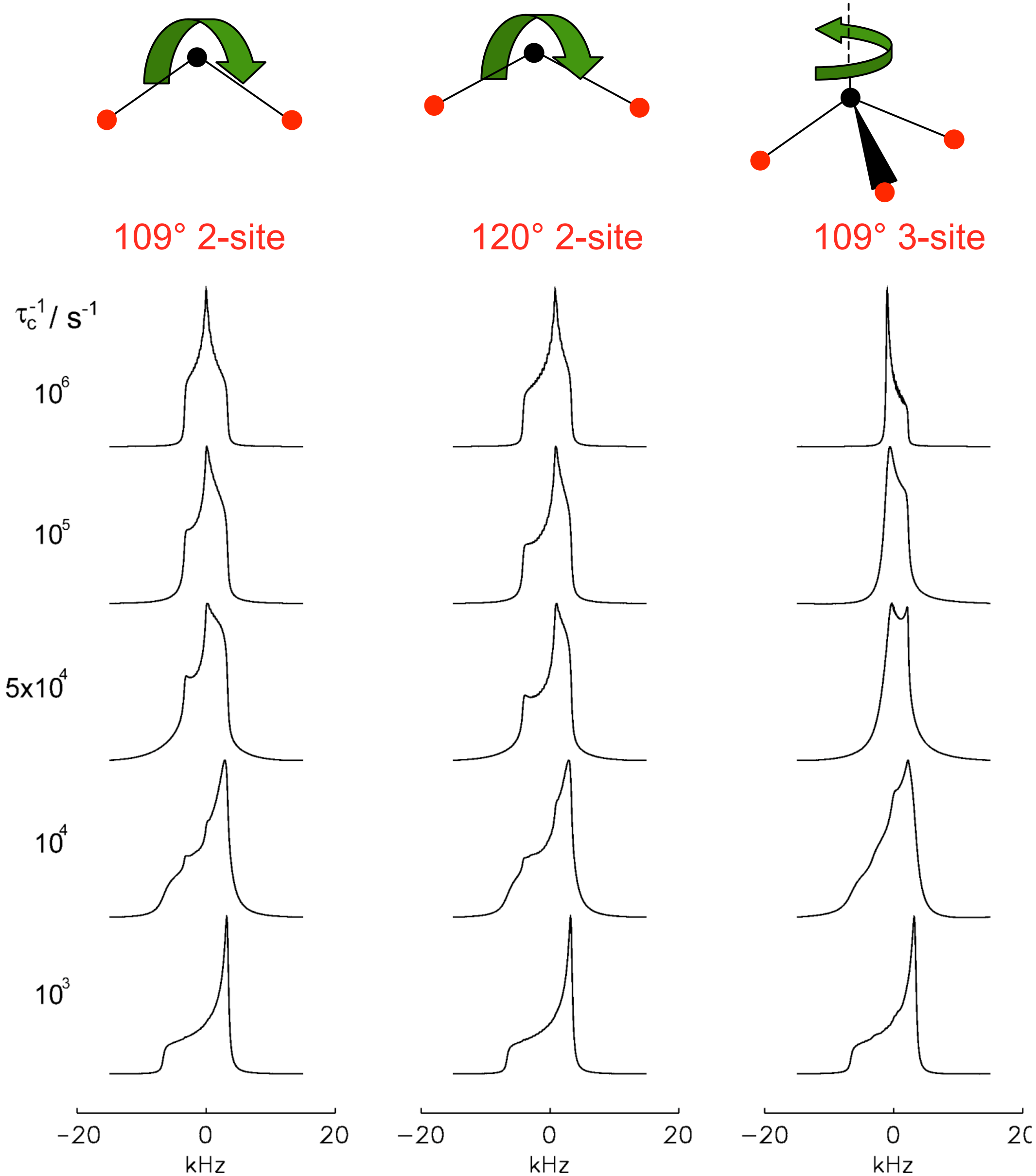


Effective CSA interaction tensor is the AVERAGE over all the sites visited during the motion

Axial motion:



Powder averaging and dynamics



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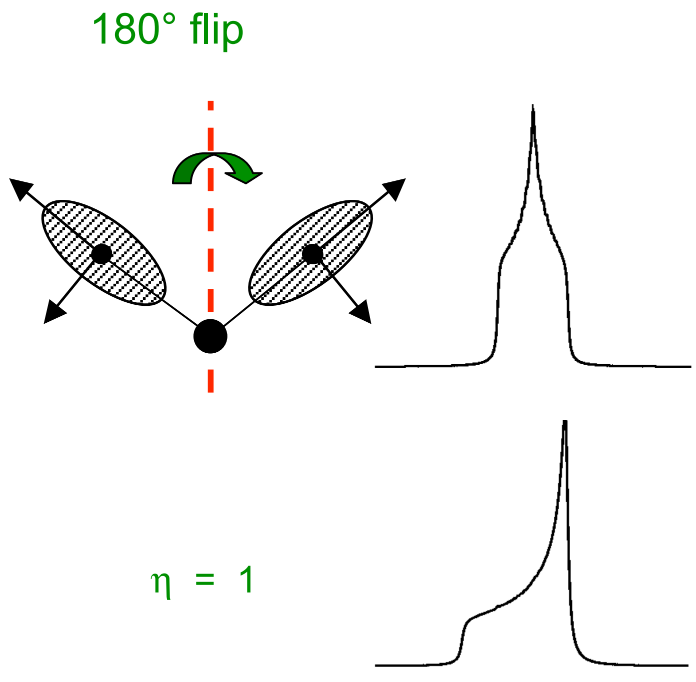
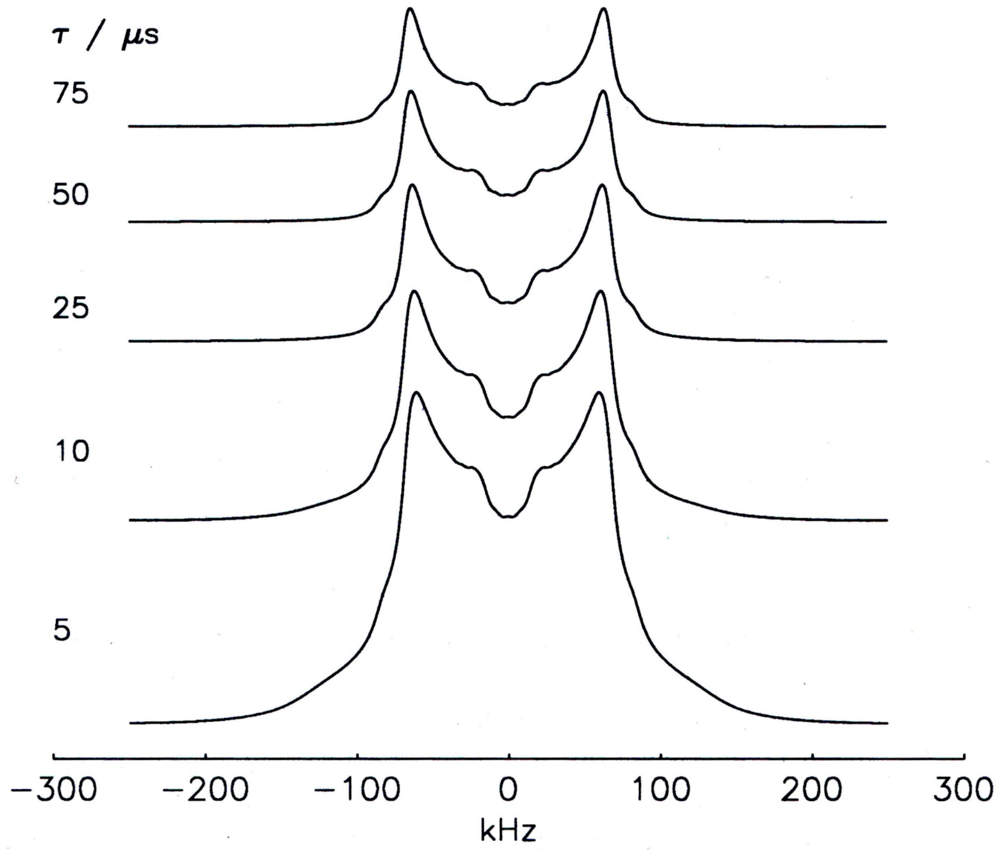


NB- Change to handout

Powder averaging and dynamics



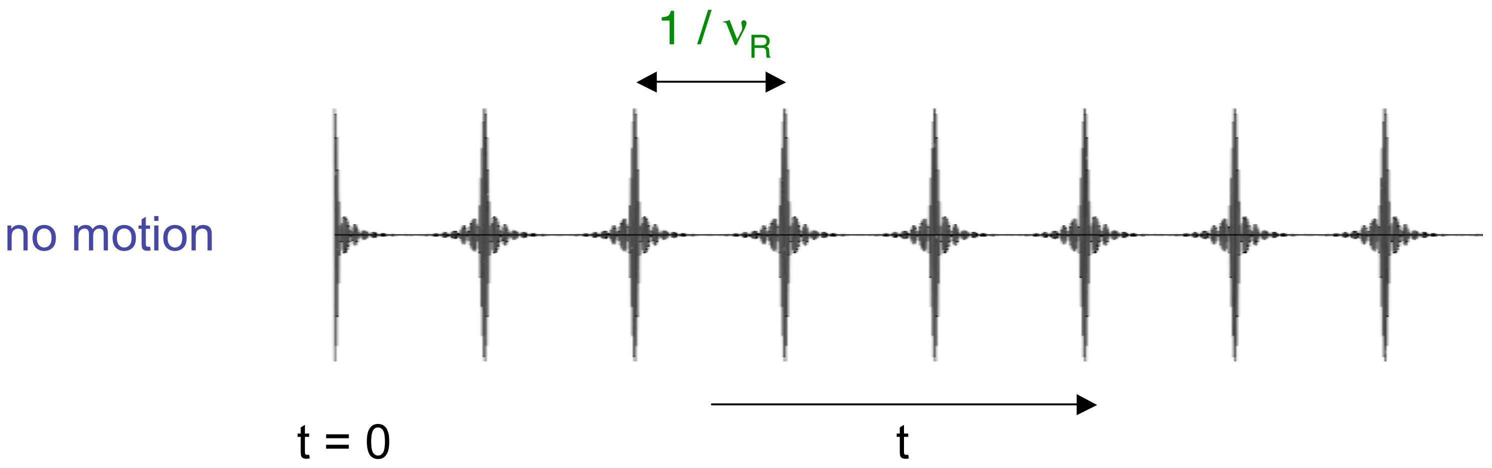
- In addition to lineshape changes with temperature motion can also be probed by lineshape changes with echo delay

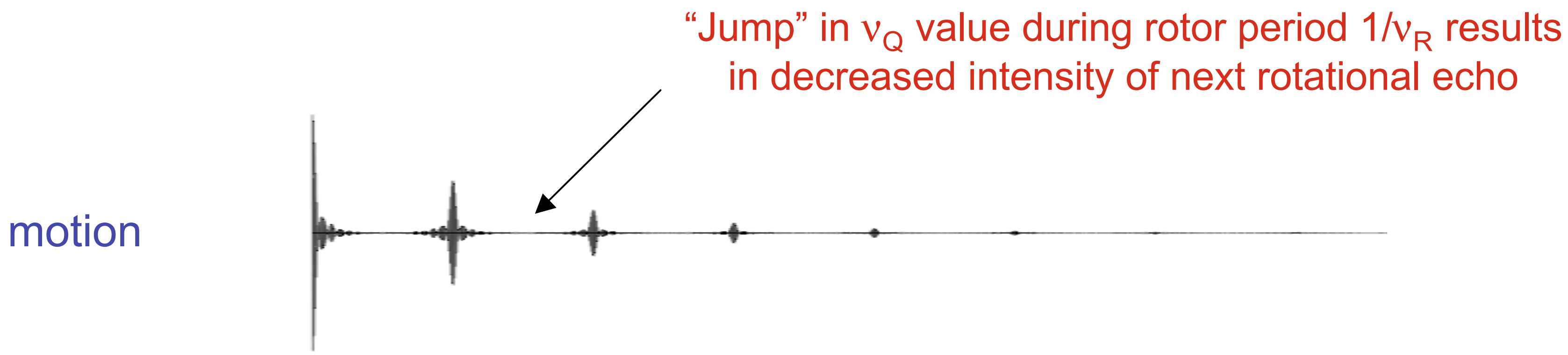
- Anisotropic "T_2" relaxation depending upon type of motion and orientation with respect to B_0

^{2}H two-site exchange with hopping angle = 120º, with $\tau_c = 10^{-5}$ s

Duer, Introduction to NMR Spectroscopy (2004)

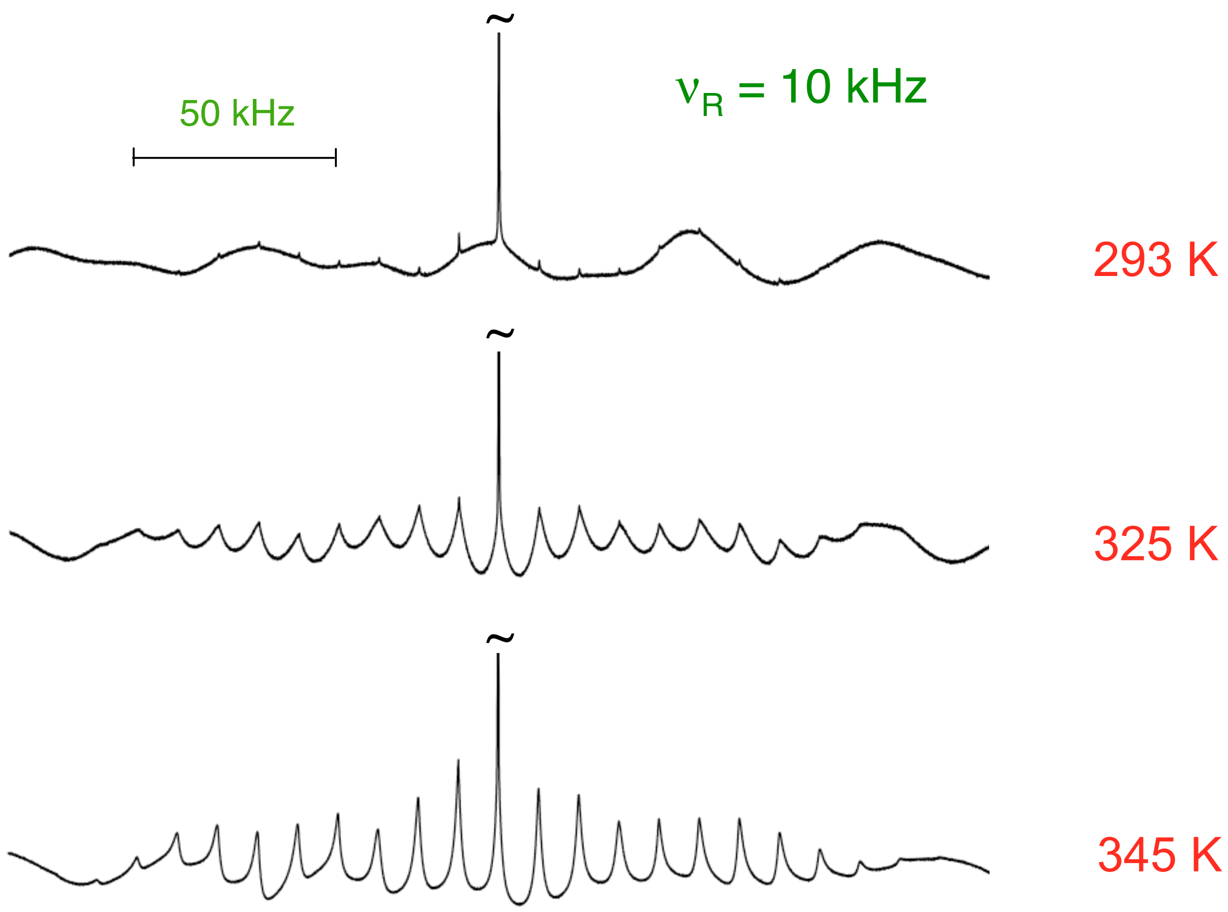
Dynamics and MAS



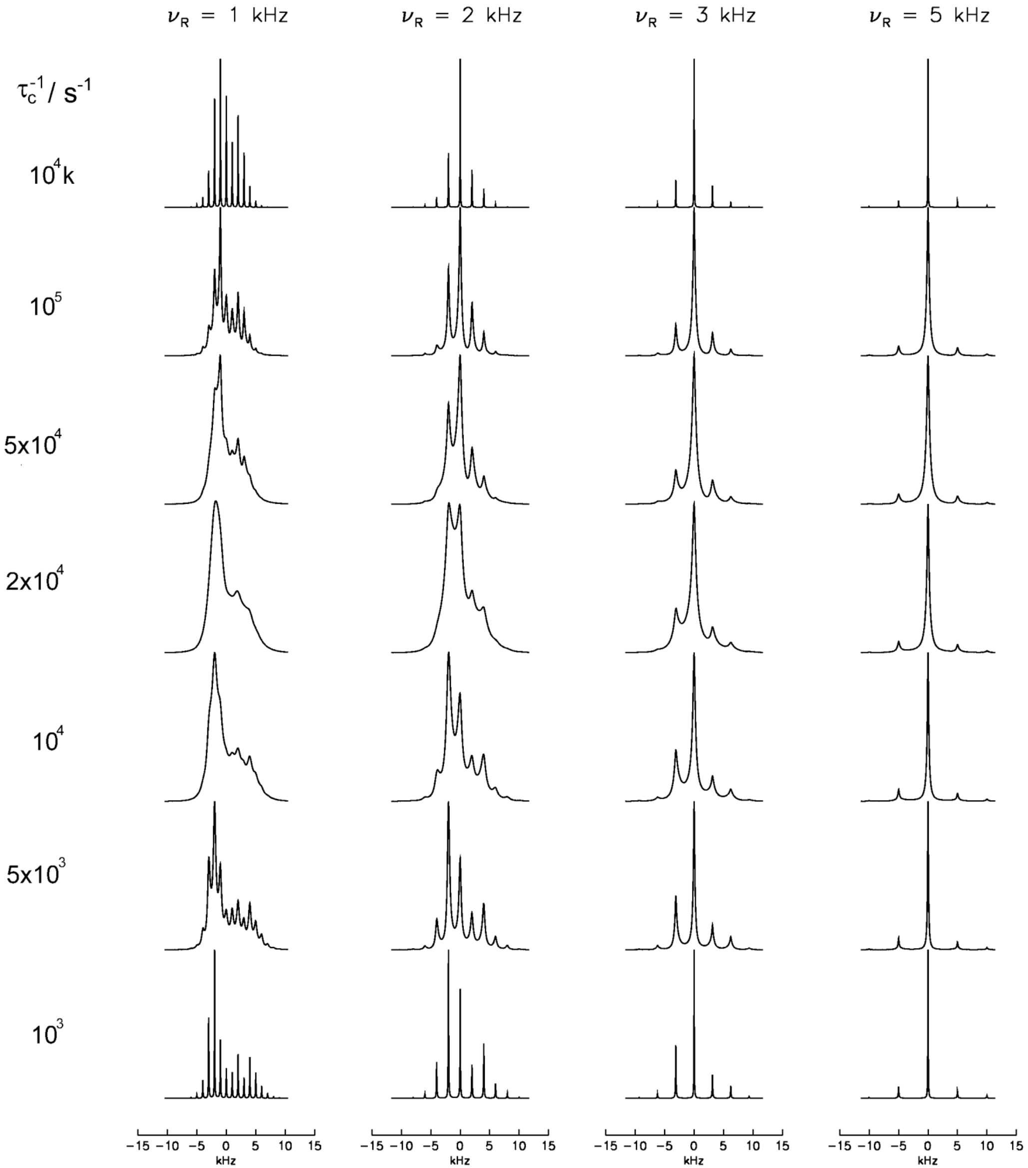


Dynamics and MAS

^2H MAS of $Na_2S_4O_6.2D_2O$



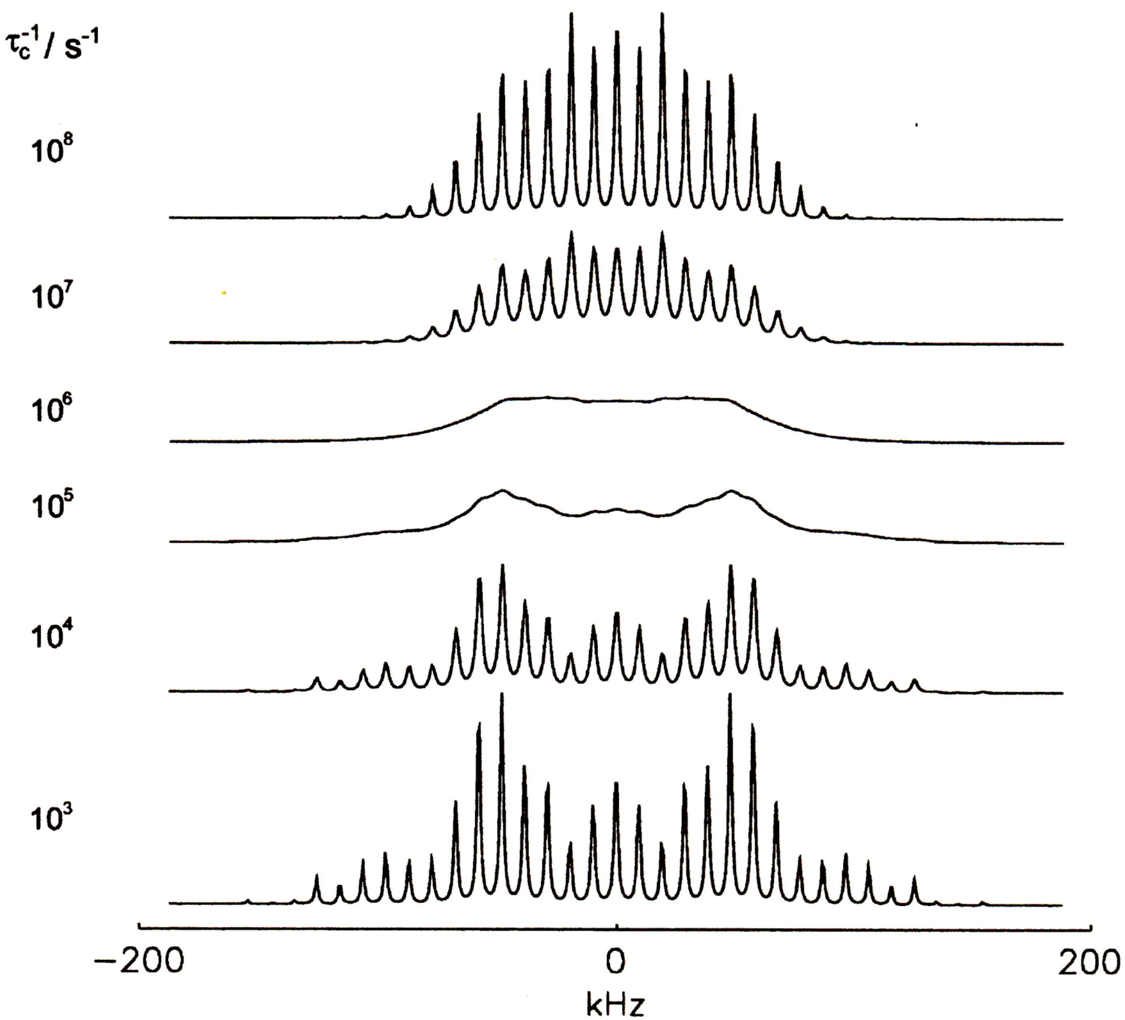
Dynamics and MAS



Typical CSA lineshapes under two-site exchange with hopping angle of 120º

Duer, Introduction to NMR Spectroscopy (2004)

Dynamics and MAS



^2H lineshapes under two-site exchange with hopping angle of 120º

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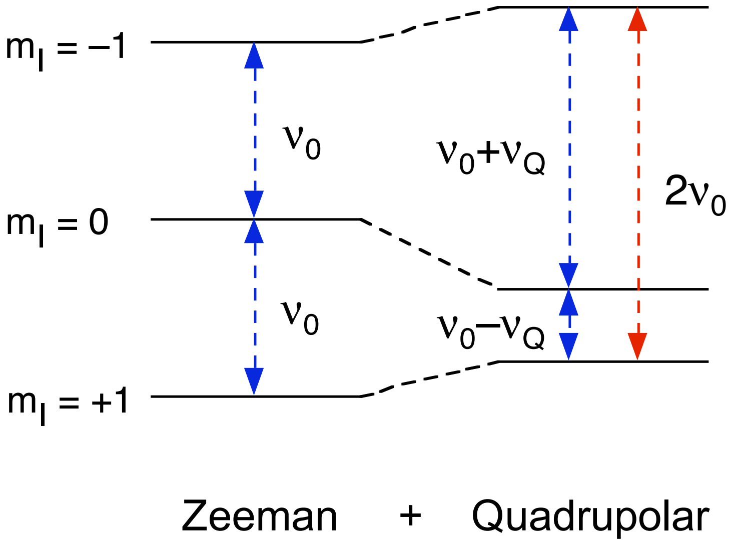
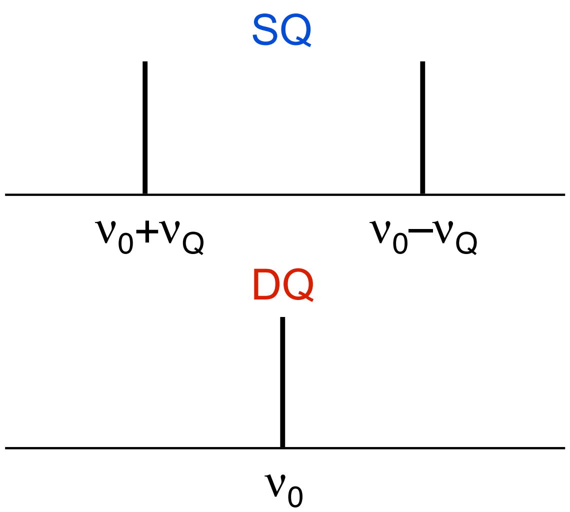
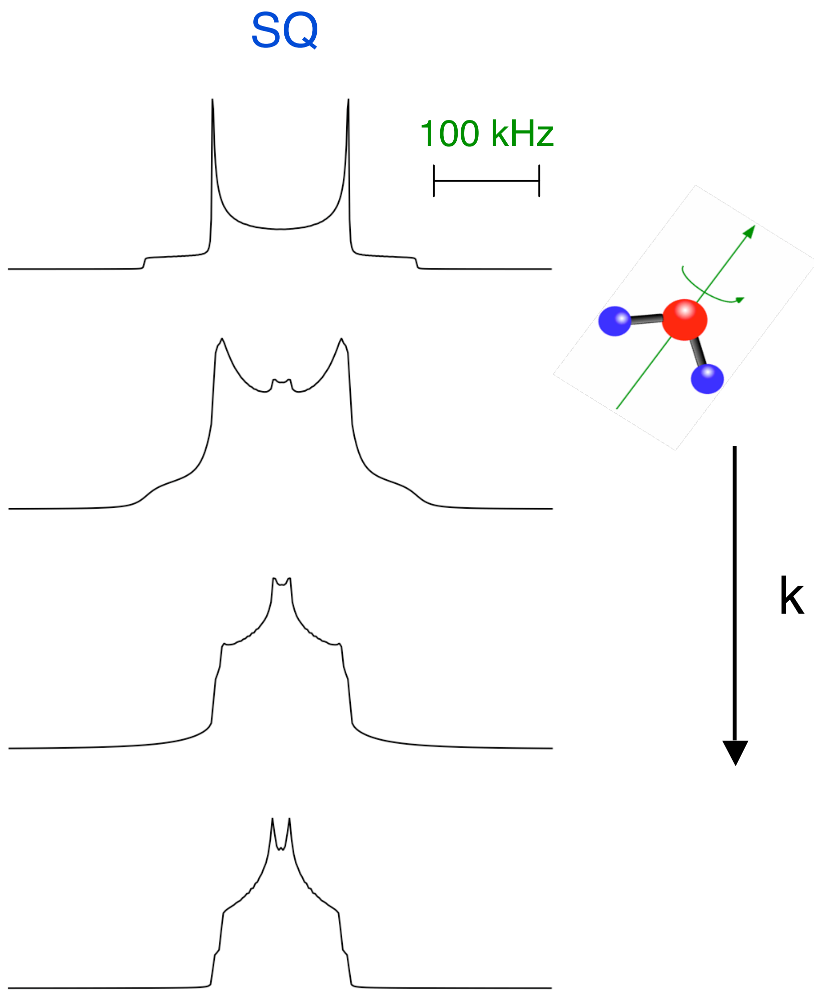
Double-quantum MAS







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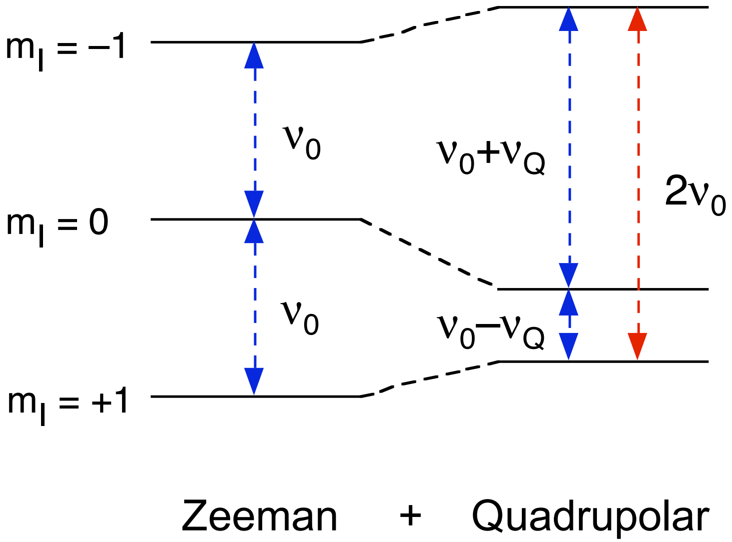
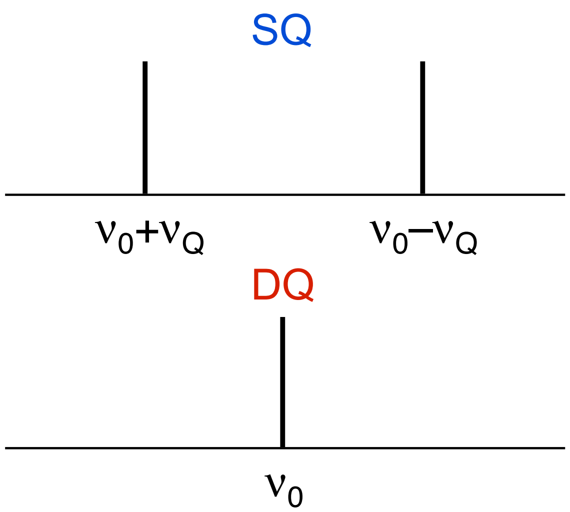
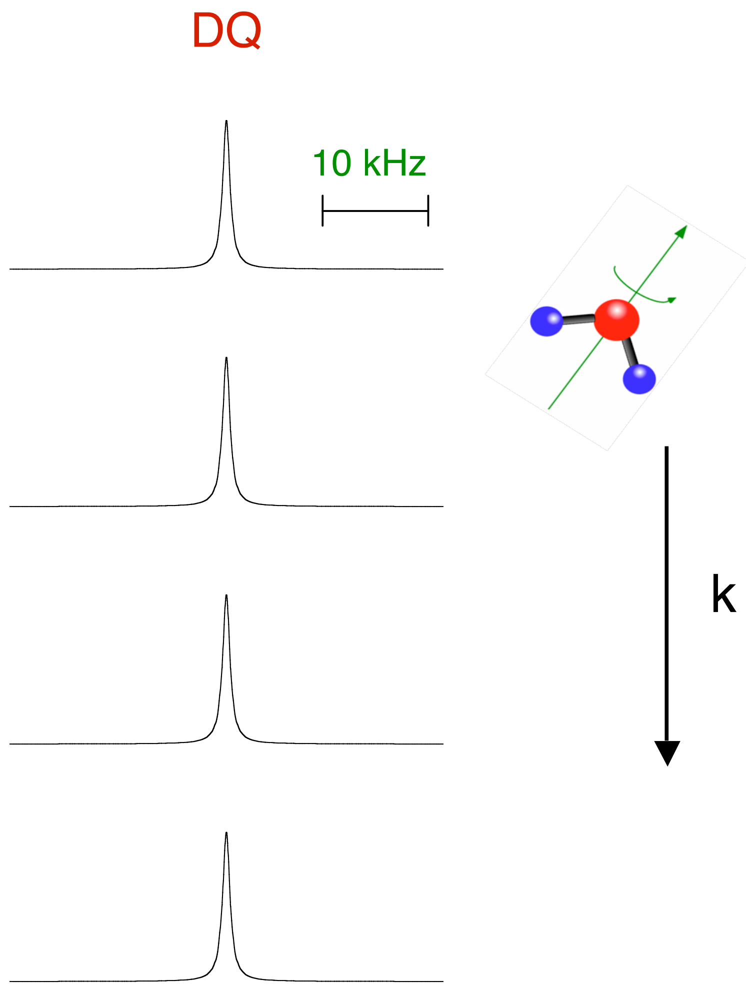
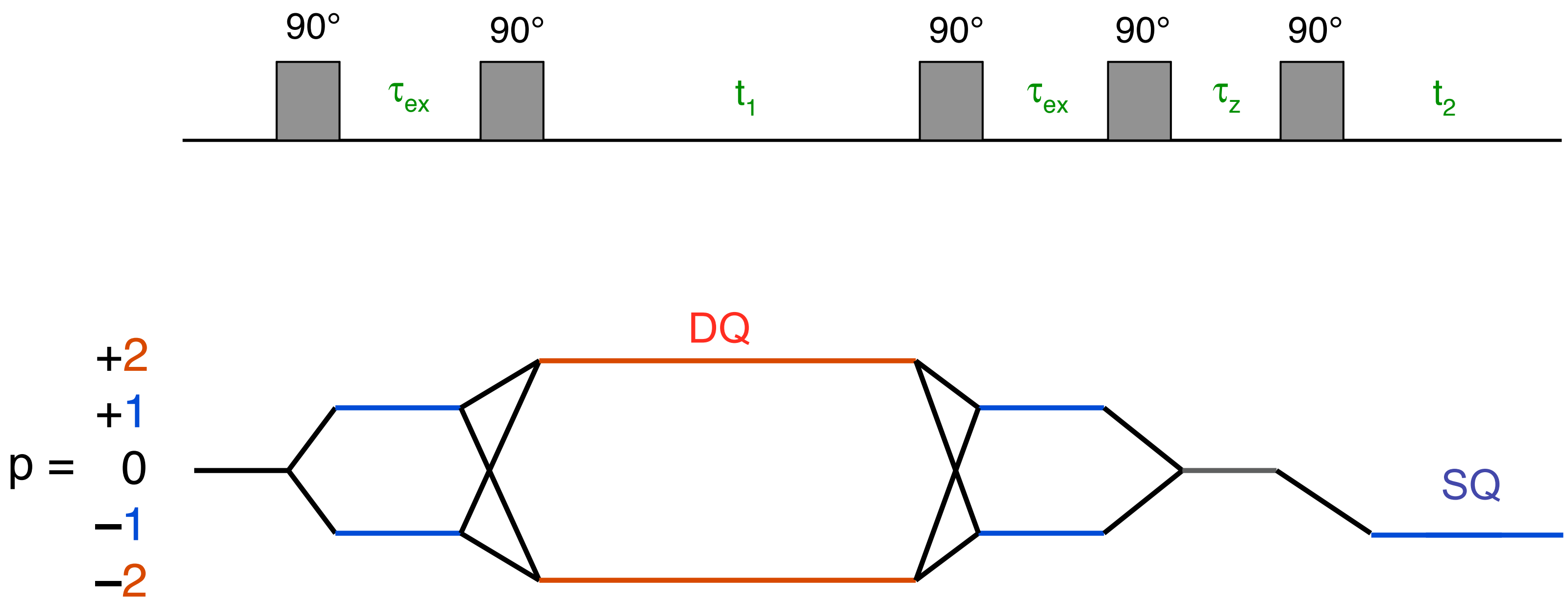






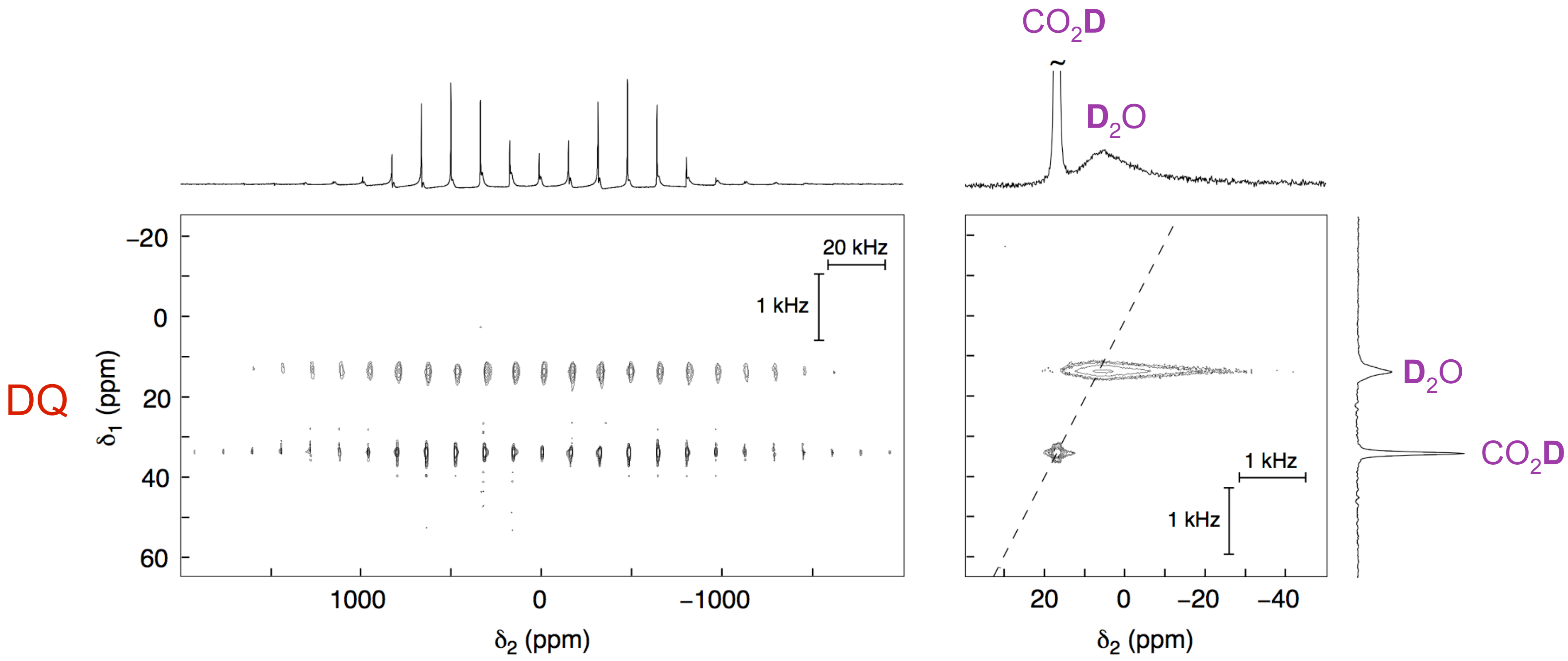
Double-quantum MAS



Cutajar et al., Chem. Phys. Lett. ***423***, *276 (2006)*

Double-quantum MAS

^2H DQMAS oxalic acid dihydrate



SQ

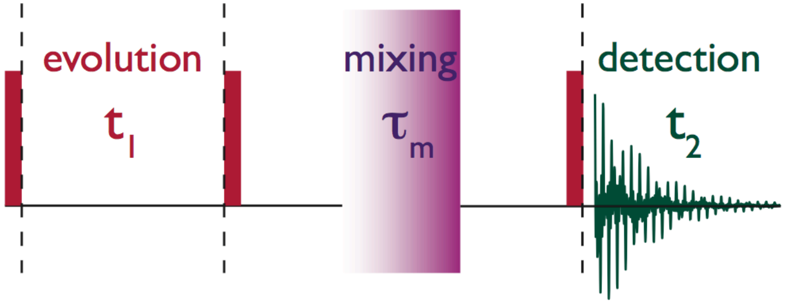
not rotor synchronized in t_2

SQ

rotor synchronized in t_2

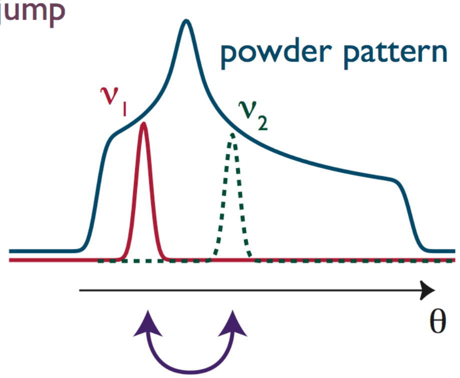
Cutajar et al., Chem. Phys. Lett. ***423****, 276 (2006)*

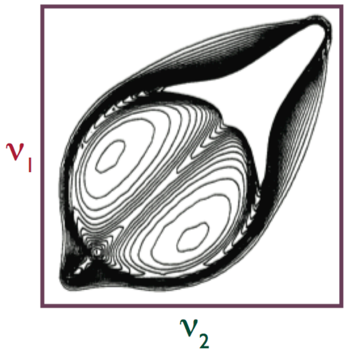
Exchange experiments



Typical two-dimensional exchange experiment

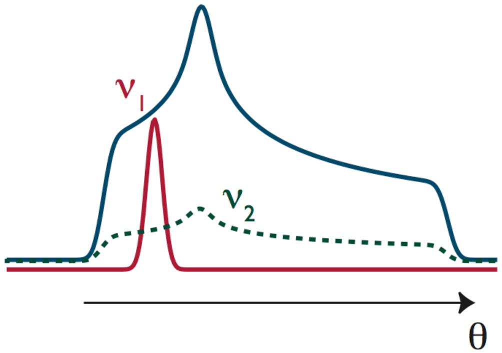
well-defined jump

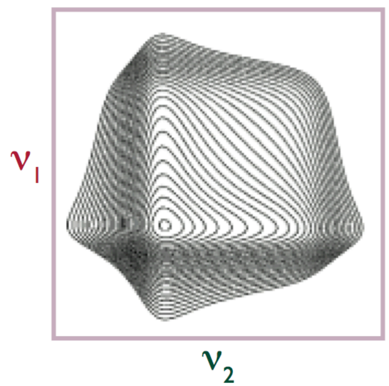




For a single site, static experiments can provide information on the type of reorientation

random jump





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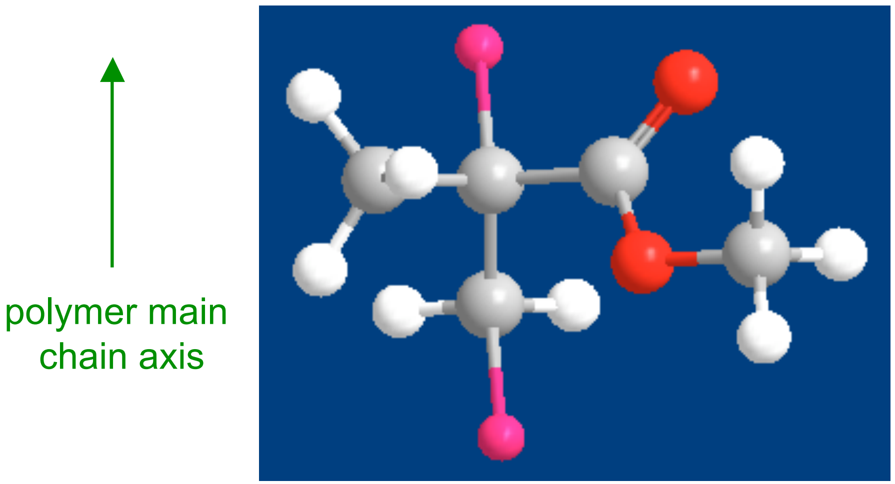
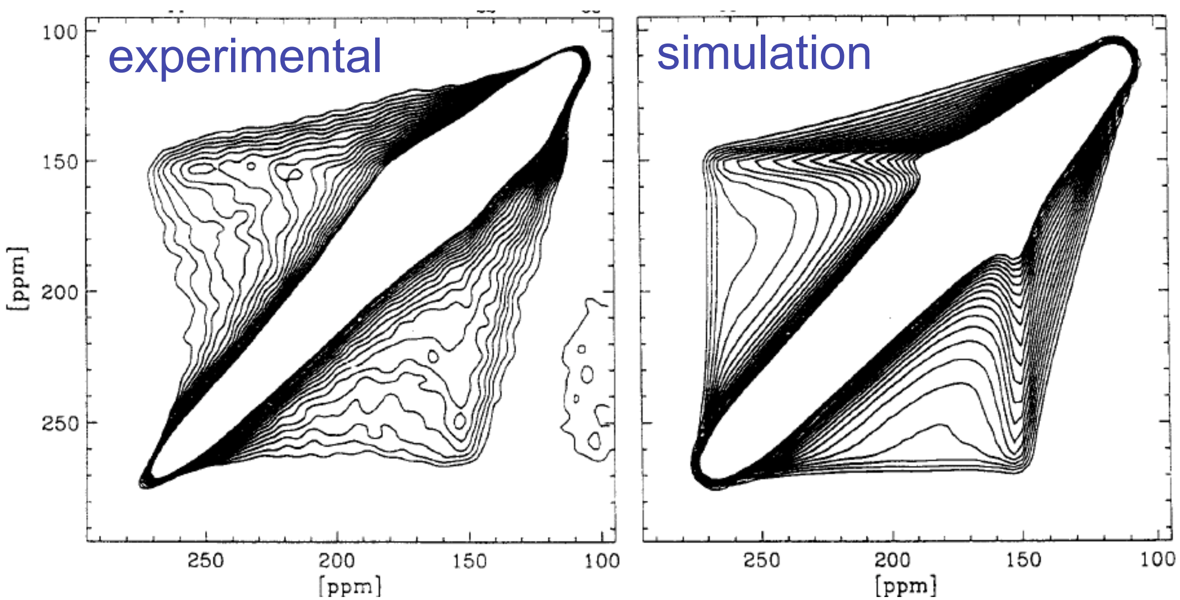


^{13}C NMR of PMMA

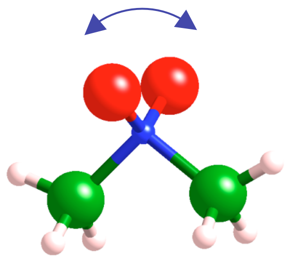
side chain flips of 180°

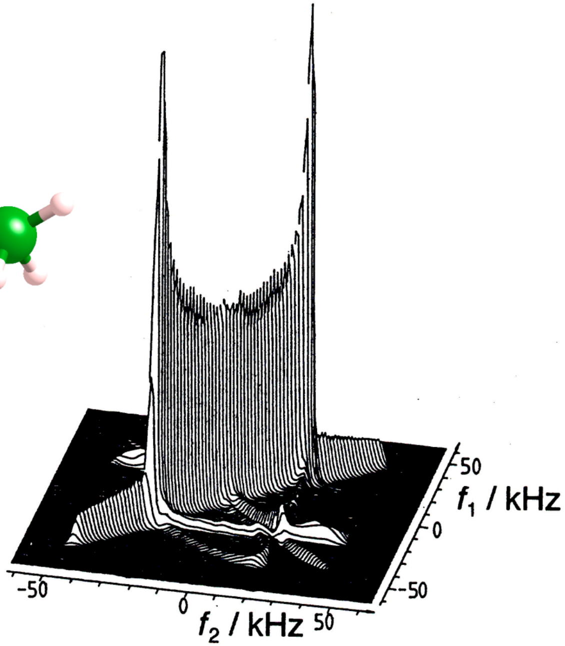


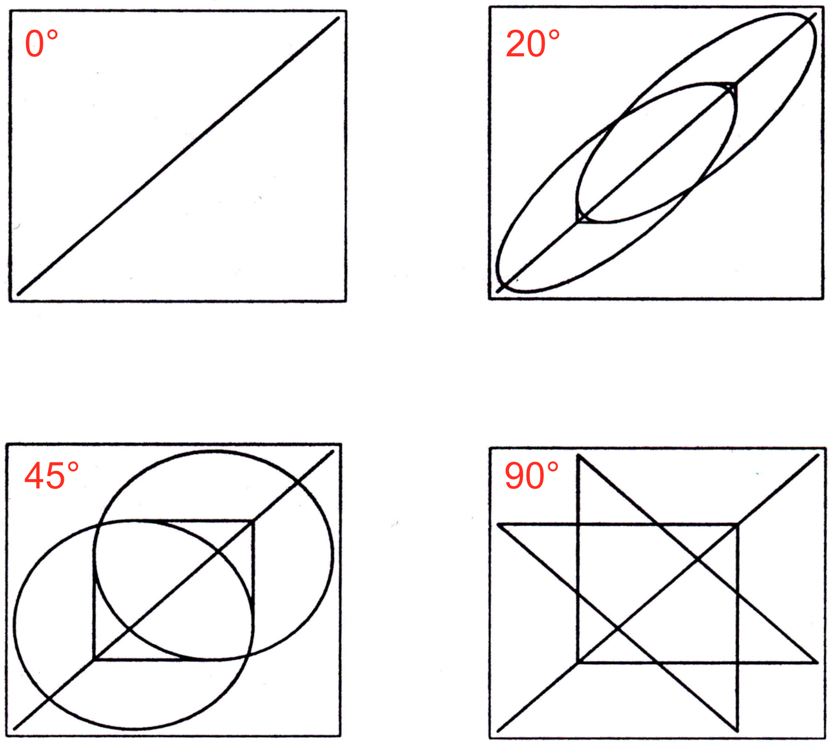
Schmidt Rohr et al.,
Macromol. ***27****, 4733 (1994)*

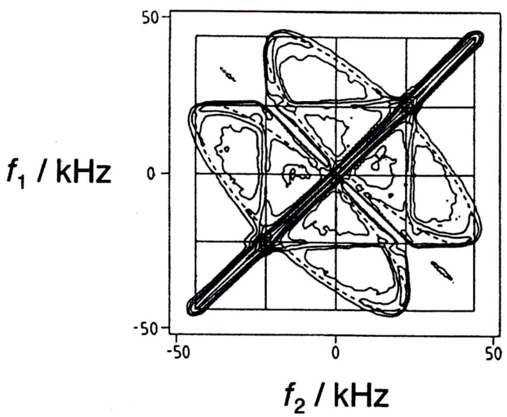
Exchange experiments

^2H exchange NMR of DMS









jumps around the C_2 axis of 106°

Spiess, NMR: Basic Principles and Progress ***15****, 55 (1978)*

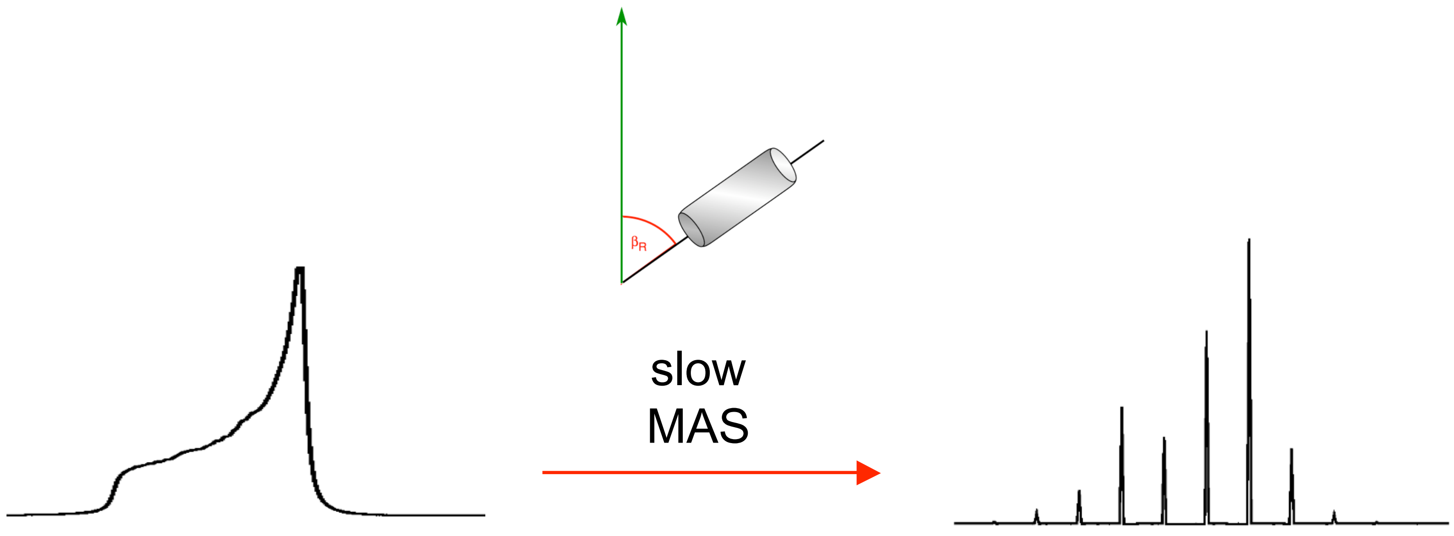
Slow MAS exchange experiments

Use MAS to improve resolution and sensitivity

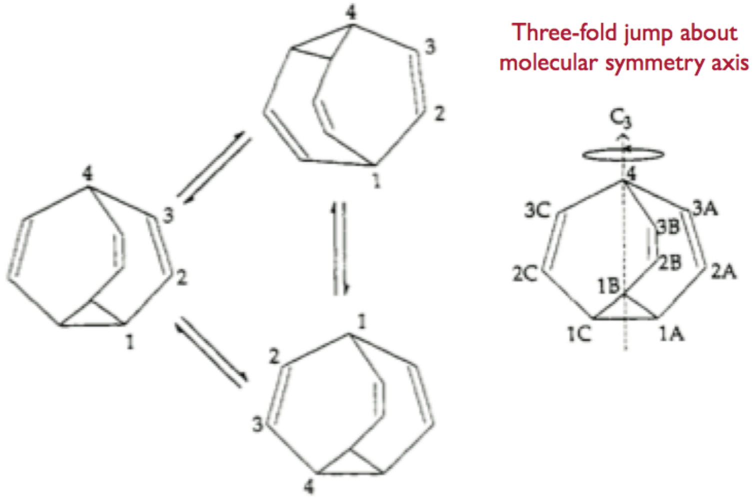
For slow MAS the interaction anisotropy is retained in spinning sidebands

Exchange peaks between different sites

Exchange peaks between sidebands of one site

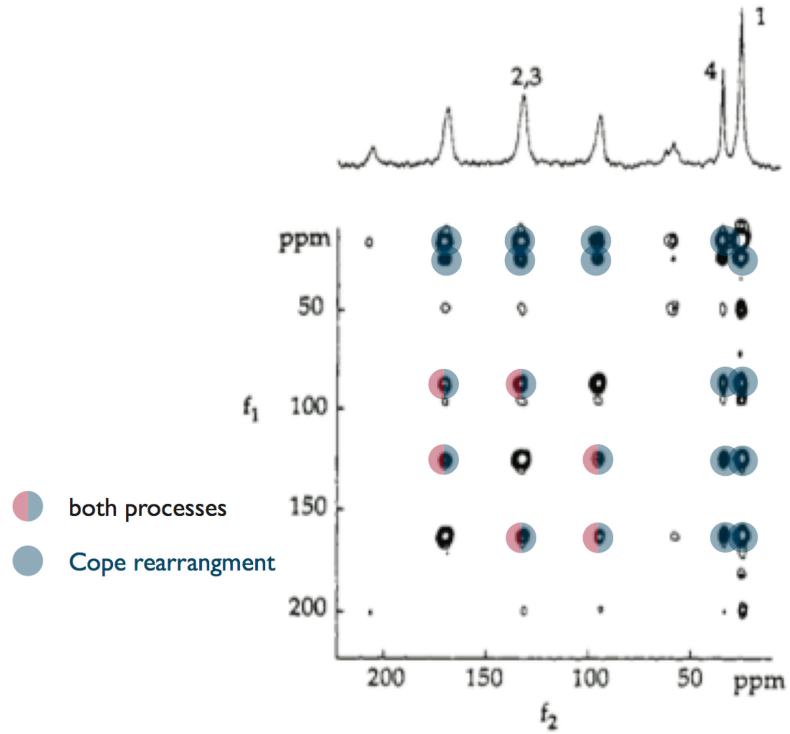


Slow MAS exchange experiments



Cope rearrangement interconverts 10!/3 tautomers
coupled with a molecular reorientation

^{13}C MAS NMR of bullvalene



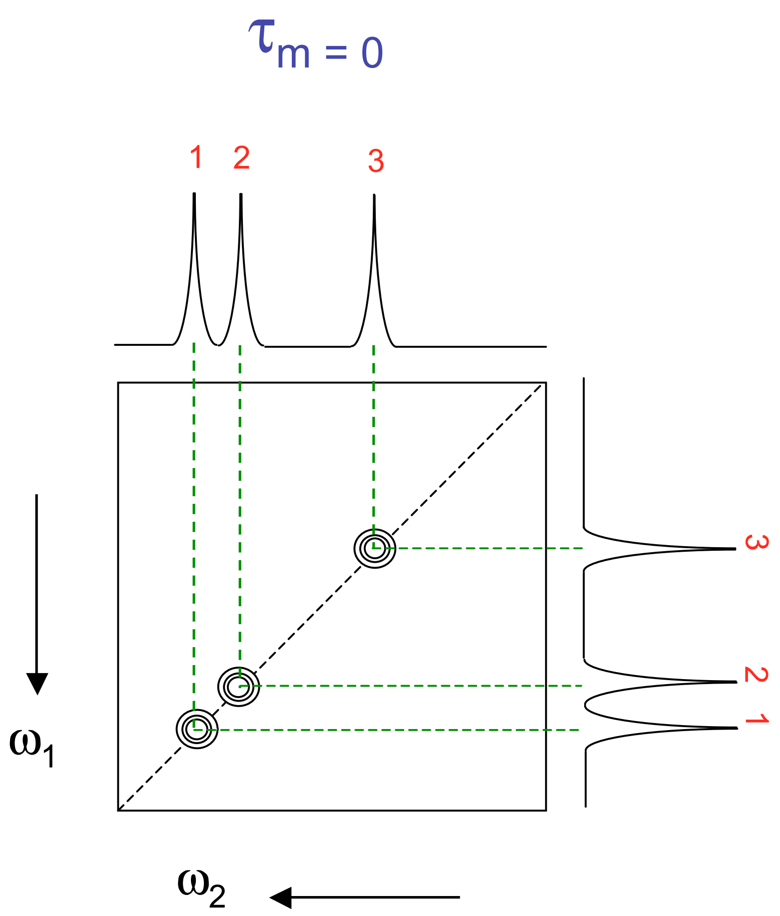
Two sets of cross peaks

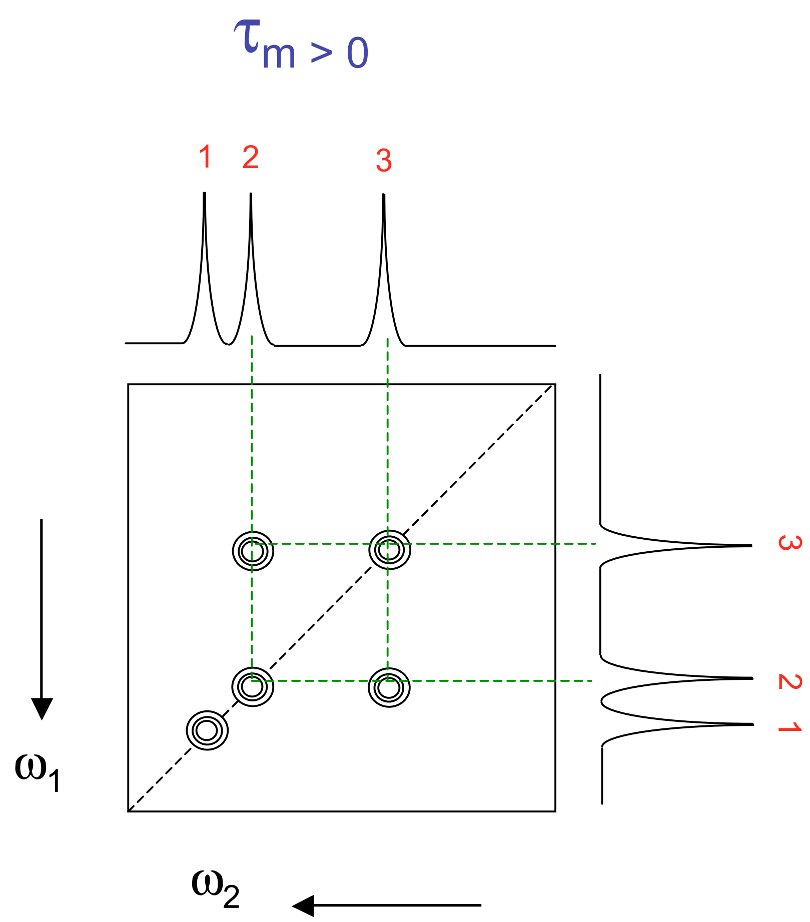
1. Sidebands of different sites
(Cope rearrangement, 15 kcal mol^{-1})
2. Sidebands of same site
(3 fold jumps, 21 kcal mol^{-1})

Titman et al. J. Am. Chem. Soc. ***114****, 3765 (1992)*

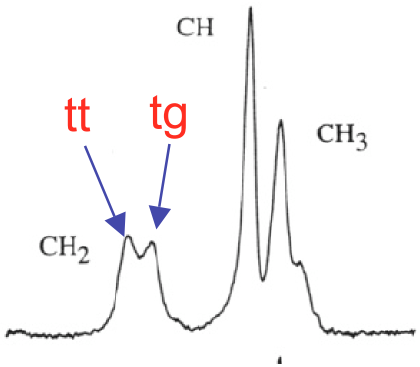
MAS exchange experiments

- Under fast MAS high resolution but no anisotropy information
- Exchange between different sites produces cross peaks





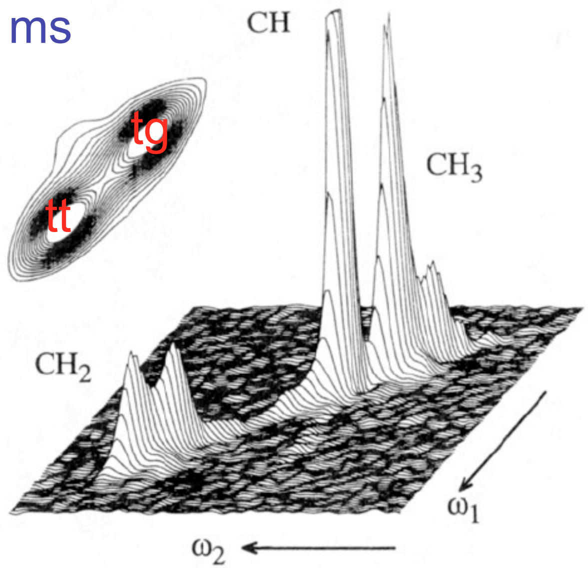
MAS exchange experiments



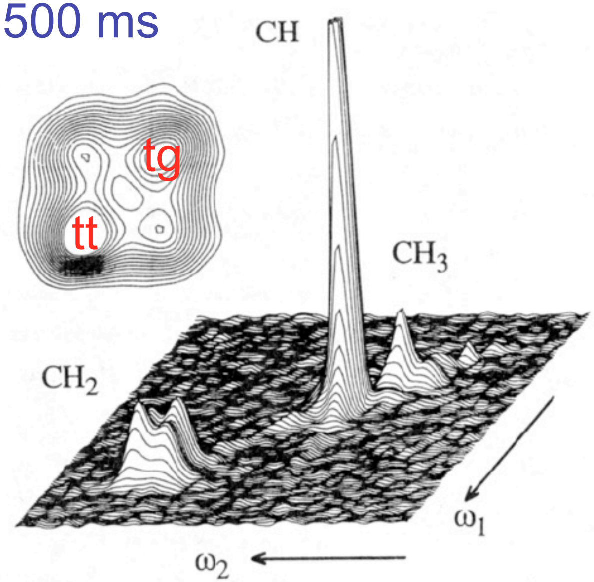
^{13}C MAS NMR atatic polypropylene

rotational motion of polymer backbone just below glass transition temperature interchanges different conformations

τ_m = 5 ms



τ_m = 500 ms



Zemke et al. Macromol. ***24****, 6874 (1991)*

Timescales

Spin-lattice (T_1) relaxation

Lineshapes ("T_2 relaxation")

Quadrupolar

CSA; dipolar

Magnetization "storage" (2D exchange)

Slow

10^{-12}	10^{-9}	10^{-6}	10^{-3}	1	10^{3}	timescale ($\tau_c = k^{-1}$) / s

Fast

(~ inverse of Larmor frequency)

Intermediate

(~ inverse of anisotropic broadening)

Slow

(~ T_1)