Nuclear Magnetic Resonance (NMR)

–

Some Basics and Comparison with BDS

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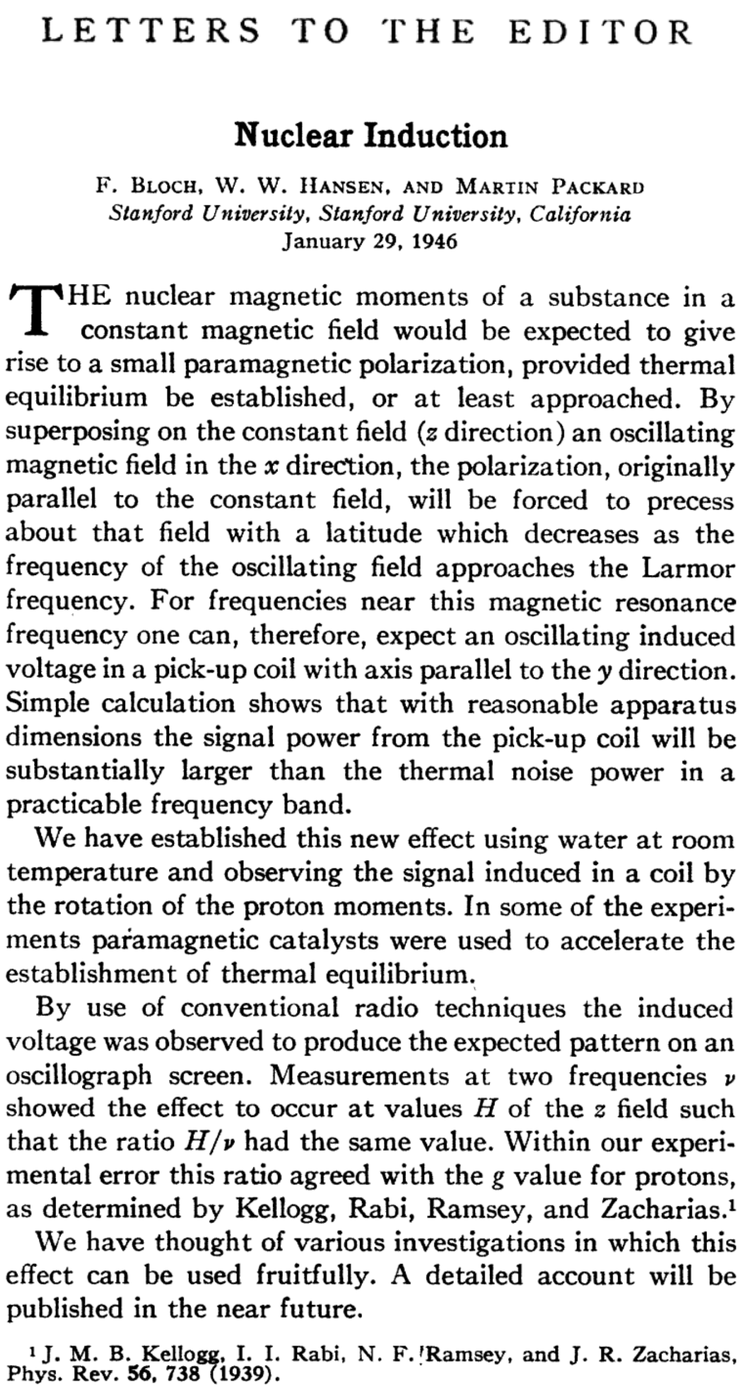
Outline

- **Brief Introduction to NMR Spectroscopy**
  - Interactions of Spins with External Fields
  - Interactions of Spins with Internal Fields
- **NMR Studies of Molecular Dynamics**
  - Spin-Lattice Relaxation
  - 1D and 2D NMR Spectra
  - Stimulated Echoes

Less than half a page, but worth half a Nobel Prize



LETTERS TO THE EDITOR

Nuclear Induction

F. Bloch, W. W. Hansen, and Martin Packard
Stanford University, Stanford University, California
January 29, 1946

THE nuclear magnetic moments of a substance in a constant magnetic field would be expected to give rise to a small paramagnetic polarization, provided thermal equilibrium be established, or at least approached. By superposing on the constant field (z direction) an oscillating magnetic field in the x direction, the polarization, originally parallel to the constant field, will be forced to precess about that field with a latitude which decreases as the frequency of the oscillating field approaches the Larmor frequency. For frequencies near this magnetic resonance frequency one can, therefore, expect an oscillating induced voltage in a pick-up coil with axis parallel to the y direction. Simple calculation shows that with reasonable apparatus dimensions the signal power from the pick-up coil will be substantially larger than the thermal noise power in a practicable frequency band.

We have established this new effect using water at room temperature and observing the signal induced in a coil by the rotation of the proton moments. In some of the experiments paramagnetic catalysts were used to accelerate the establishment of thermal equilibrium.

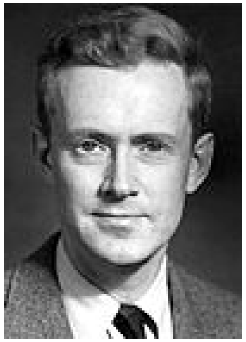
By use of conventional radio techniques the induced voltage was observed to produce the expected pattern on an oscillograph screen. Measurements at two frequencies ν showed the effect to occur at values H of the z field such that the ratio H/ν had the same value. Within our experimental error this ratio agreed with the g value for protons, as determined by Kellogg, Rabi, Ramsey, and Zacharias.[1]

We have thought of various investigations in which this effect can be used fruitfully. A detailed account will be published in the near future.

[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. 56, 738 (1939).

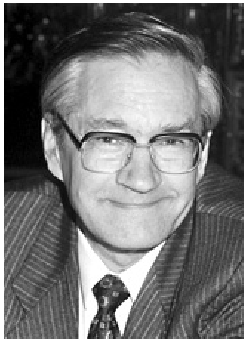
Phys. Rev. 69, 127 (1946)

Nobel Laureates in NMR Spectroscopy

Bloch & Purcell (Physics 1952)

… for their development of new methods for nuclear magnetic precision measurements

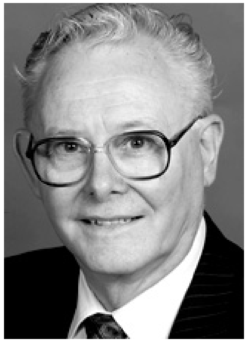


Ernst (Chemistry 1991)

… for his contributions to the development of the methodology of high-resolution NMR spectroscopy

Wüthrich (Chemistry 2002)

… for his development of NMR spectroscopy for determining the 3D structure of biological macromolecules in solution




Lauterbur & Mansfield (Medicine 2003)

… for their discoveries concerning magnetic resonance imaging

Some Basics Means: Many Topics *not* Covered

Chemical Solution NMR

Stuff with Fancy Acronyms
Spectral Editing, …

MQ-MAS Experiments

Magic Angle Spinning
Multiple-Quantum NMR, …

This tutorial focuses on correlation functions and molecular dynamics

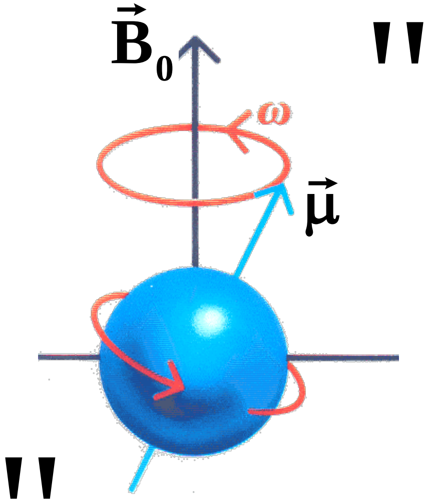
Double Resonance Techniques

Dipolar Decoupling
Cross Polarization
SEDOR, REDOR, …

Imaging

functional MRI, …

Spins in Static Magnetic Fields



A nuclear spin $\vec{I}$ results in a nuclear magnetic moment μ:

$$\vec{\mu} = \gamma(\hbar\,\vec{I})$$

γ: gyromagnetic ratio

Application of a magnetic field

$$\vec{B}_0 = (0,0,B_0):$$

Zeeman splitting into $2I + 1$ spin states

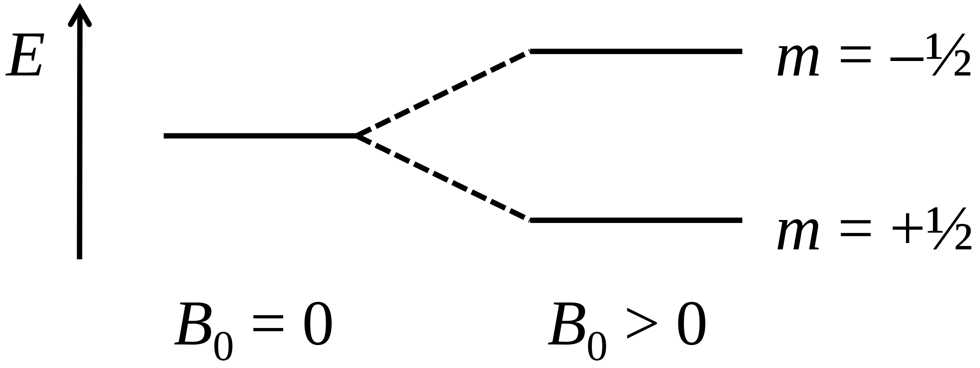
$$\mu_z = \gamma\hbar\, m$$

$$m = I, I - 1, \ldots, -I$$

I: spin quantum number
m: magnetic quantum number

Spins in Static Magnetic Fields – Energy

Example: $I = ½$, $\gamma > \mathbf{0}$ (^{1}H, ^{13}C, ^{31}P, …)



Energy levels

$$E_m = -\mu_z B_0 = -m\,\gamma\,\hbar\,B_0$$

Energy difference

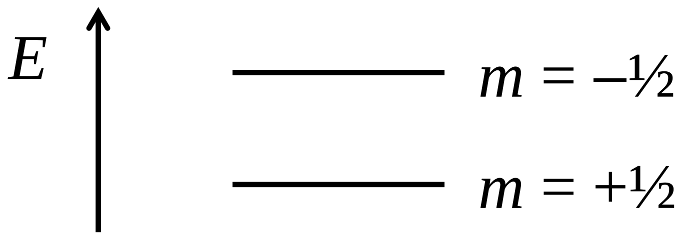
$$\Delta E = \gamma\hbar\,B_0 = \hbar\omega_0$$

Larmor frequency

$$\omega_0 = \gamma B_0$$

Typical energy differences correspond to Larmor frequencies in the MHz regime (radio frequencies)

Spins in Static Magnetic Fields – Magnetization



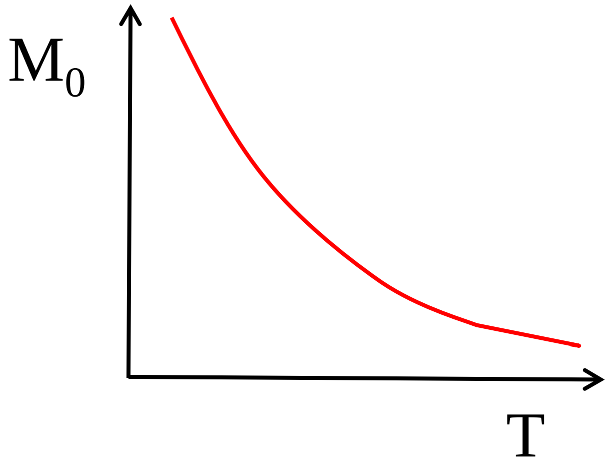
$$\boldsymbol{E_m = -\,\mu_z B_0 = -\,m\,\gamma\,\hbar\,B_0}$$

Boltzmann distribution: Magnetization $\vec{M}_0 = \sum_i \vec{\mu}_i$

$\Delta E << k_B T$: Curie law: $\vec{M}_0 = (C/T)\,\vec{B}_0$ $C \propto N\,\gamma^2$

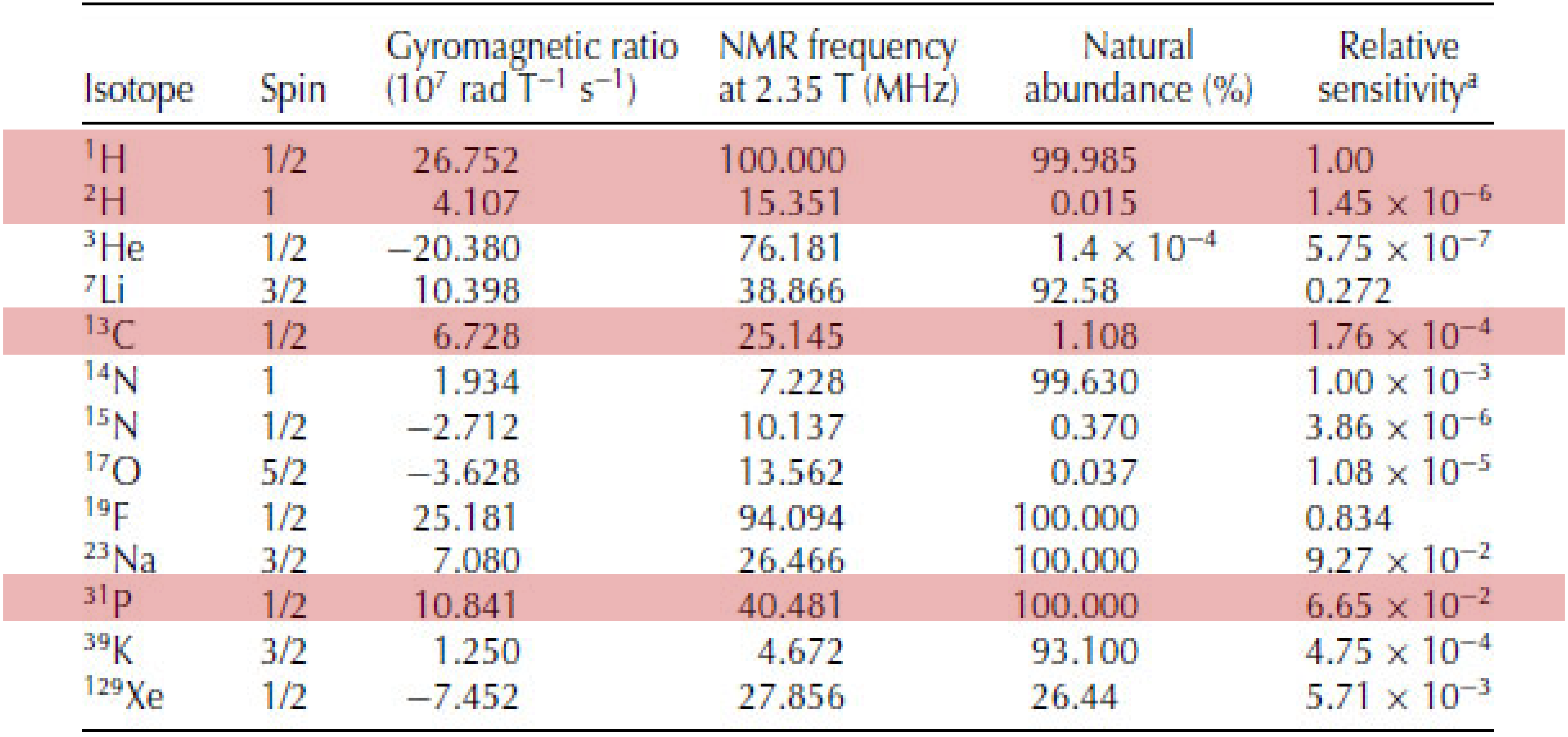
Signal-to-noise ratio depends on:

- gyromagnetic ratio γ
- magnetic field B_0
- natural abundance (N)



Note: The population difference at 300 K in typical (few Tesla) fields is only **1 millionth**. → NMR magnetization is VERY small.

Nuclei for NMR Experiments



Isotope	Spin	Gyromagnetic ratio (10^7 rad T^{-1} s^{-1})	NMR frequency at 2.35 T (MHz)	Natural abundance (%)	Relative sensitivity[a]
^1H	1/2	26.752	100.000	99.985	1.00
^2H	1	4.107	15.351	0.015	1.45×10^{-6}
^3He	1/2	−20.380	76.181	1.4×10^{-4}	5.75×10^{-7}
^7Li	3/2	10.398	38.866	92.58	0.272
^{13}C	1/2	6.728	25.145	1.108	1.76×10^{-4}
^{14}N	1	1.934	7.228	99.630	1.00×10^{-3}
^{15}N	1/2	−2.712	10.137	0.370	3.86×10^{-6}
^{17}O	5/2	−3.628	13.562	0.037	1.08×10^{-5}
^{19}F	1/2	25.181	94.094	100.000	0.834
^{23}Na	3/2	7.080	26.466	100.000	9.27×10^{-2}
^{31}P	1/2	10.841	40.481	100.000	6.65×10^{-2}
^{39}K	3/2	1.250	4.672	93.100	4.75×10^{-4}
^{129}Xe	1/2	−7.452	27.856	26.44	5.71×10^{-3}

^1H, ^2H, ^{19}F, ^{31}P, and … well suited for NMR experiments,

^{12}C and ^{16}O do not possess a nuclear spin
and ^{13}C and ^{17}O (and also ^2H) studies usually require isotopic enrichment

Time Evolution of the Magnetization

Classical Bloch equation:

$$d\vec{M}/dt = \gamma(\vec{M} \times \vec{B}_0)$$

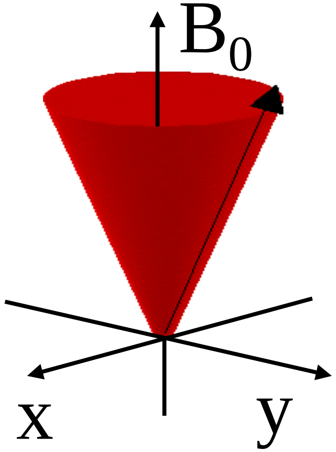
If the magnetization is deflected from the equilibrium direction:

$$\longrightarrow \quad \begin{aligned} M_x(t) &= M_{x,0}\cos(\omega_0 t) - M_{y,0}\sin(\omega_0 t) \\ M_y(t) &= M_{y,0}\cos(\omega_0 t) + M_{x,0}\sin(\omega_0 t) \end{aligned}$$

$$M_z(t) = M_{z,0}$$

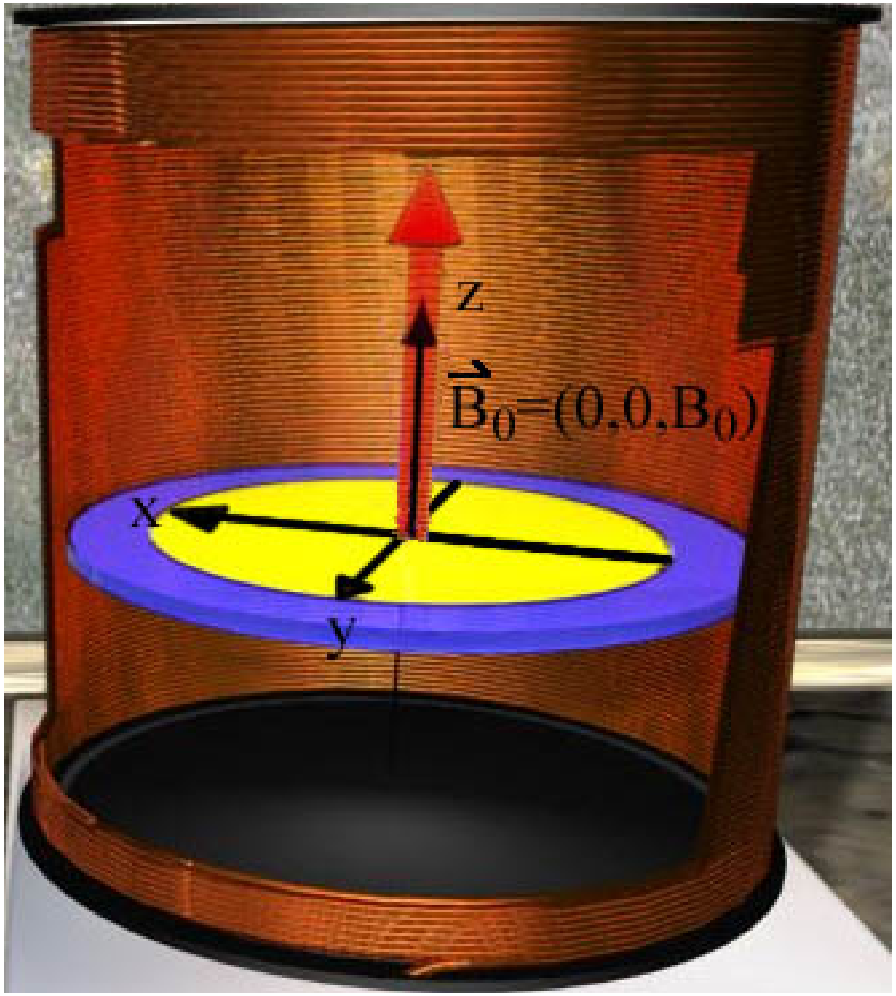
Precession around the magnetic field $\vec{B}_0$:

$\omega_0 = \gamma B_0$ **(Larmor frequency)**

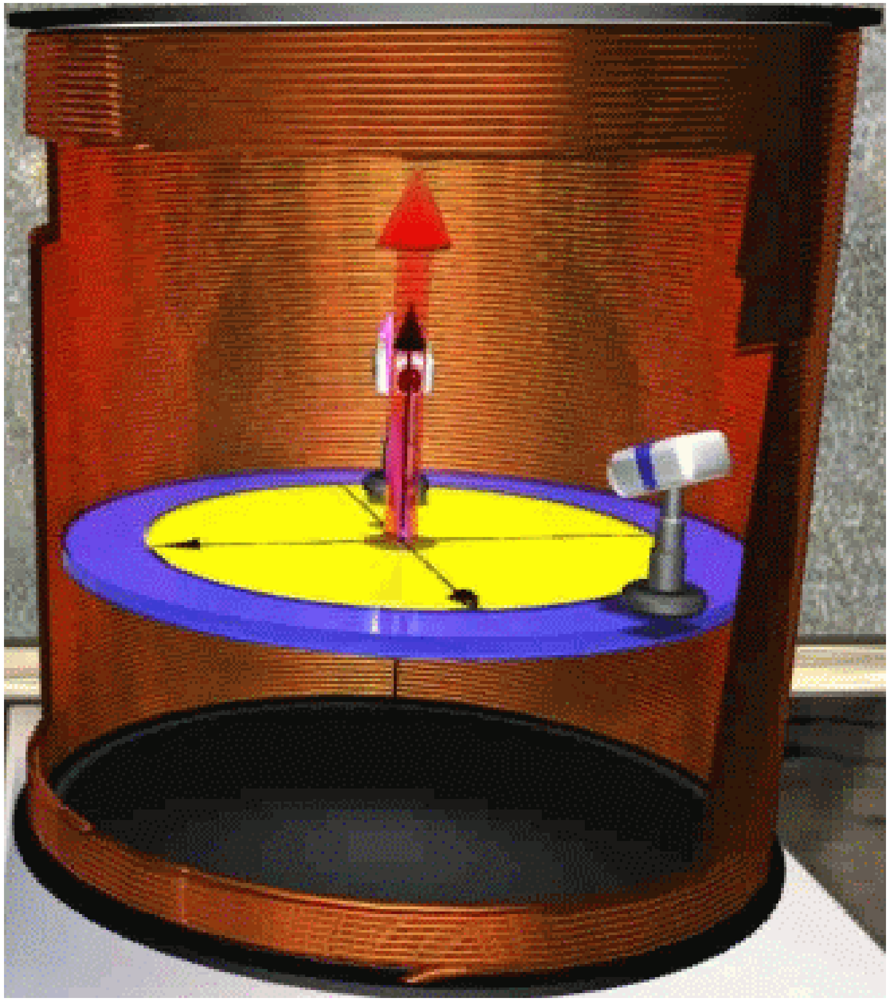


$\vec{M}$ is stationary in a coordinate system rotating with the Larmor frequency ω_0 around $\vec{B}_0$ (rotating frame)

Two perspectives



static (lab-) frame



rotating frame

$$M_{\mathrm{rot}}(t) = M_0\ \mathrm{e}^{+i(\omega_L-\omega)t}$$

www.chemgapedia.de

Spins in Alternating Magnetic Fields

Irradiation with resonant radio-frequency pulses

The sample resides in a coil, which belongs to a resonant circuit and enables application of an oscillating magnetic field $\vec{B}_1 \perp \vec{B}_0$):

$$\vec{B}_1(\mathrm{t}) = 2\vec{B}_{1,0}\cos(\omega_0 t) \qquad (\omega_{rf} = \omega_0)$$

In the rotating frame, the relevant of the two rotating components is static:

$$d\vec{M}/dt = \gamma(\vec{M} \times \vec{B}_0)$$

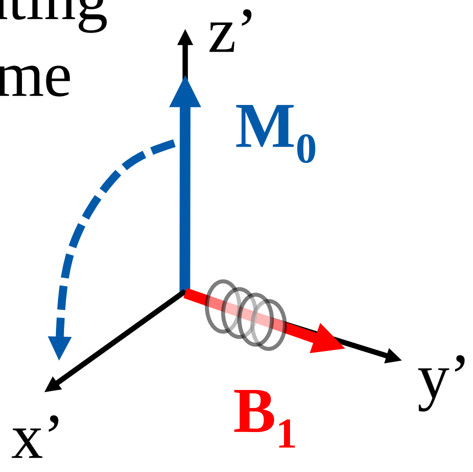
During application of $\vec{B}_1$:

Precession of $\vec{M}$ around $\vec{B}_1$ with a nutation frequency $\omega_1 = \gamma B_1$

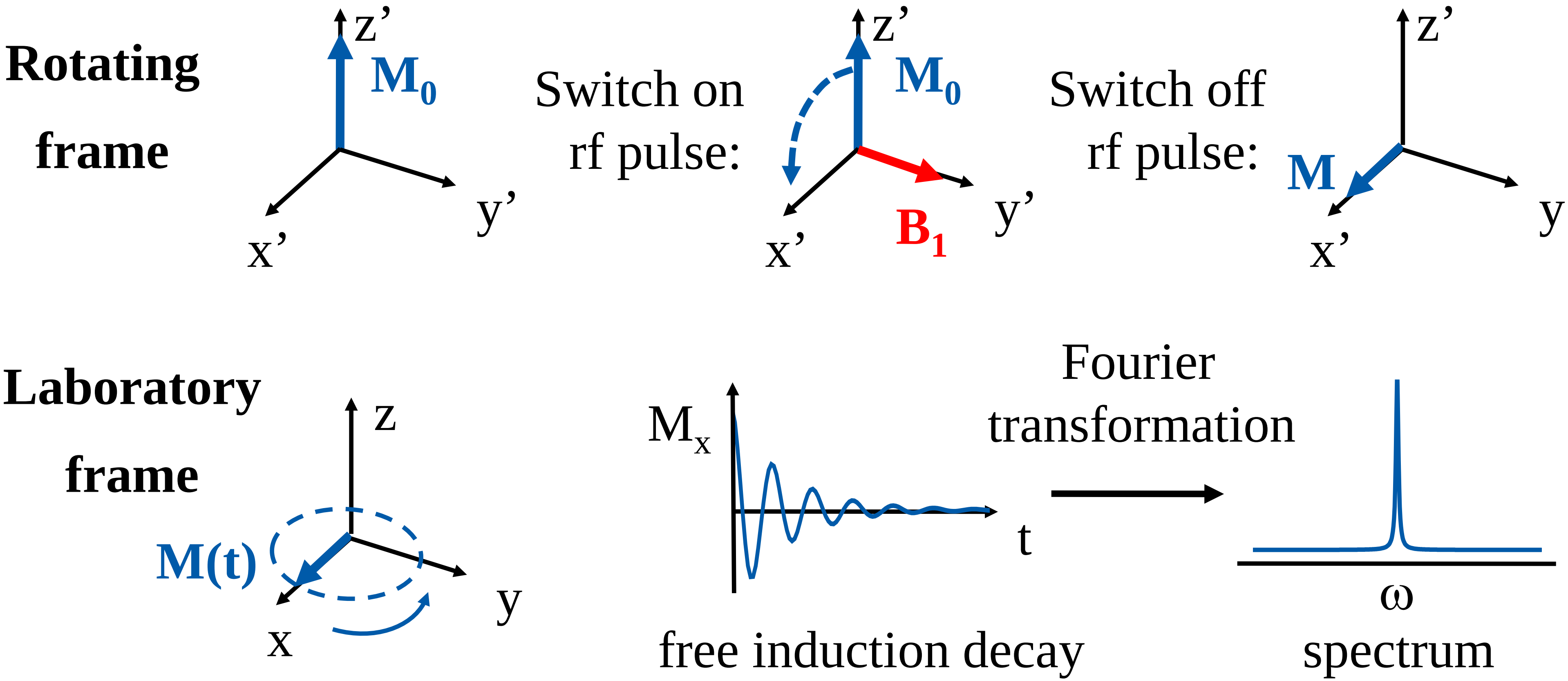
$\vec{B}_1$ field is applied as radio-frequency pulse

90° pulse: $t_{90^\circ} = \dfrac{\pi/2}{\omega_1} \approx \mu\mathrm{s}$

Rotating frame



Generation of the NMR Signal



Rotating frame

Switch on rf pulse:

Switch off rf pulse:

Laboratory frame

Fourier transformation

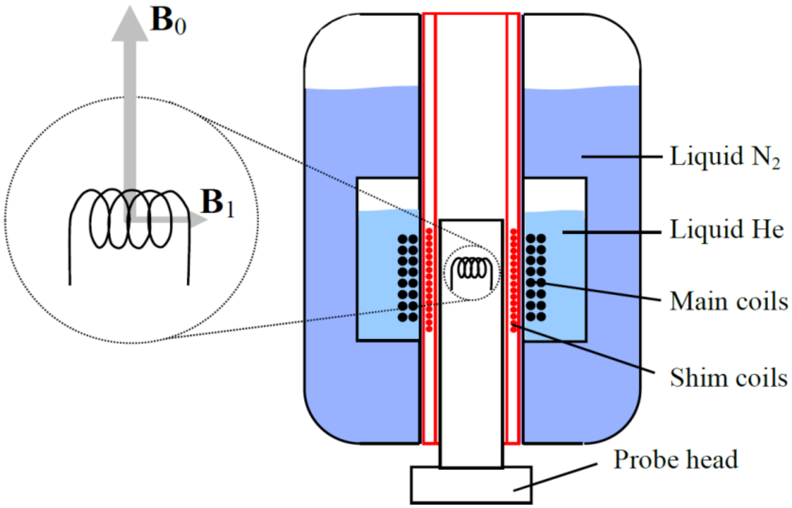
free induction decay

spectrum

The time-dependent **magnetization** in the laboratory system is **detected via the voltage induced in the coil**

Experimental Setup

NMR probe



Supercon magnet

Various types of NMR experiments designed to study structure and dynamics on different time scales and length scales

Homogeneous fields	Gradient fields
Static samples	Rotating samples
Single resonance	Multiple resonance

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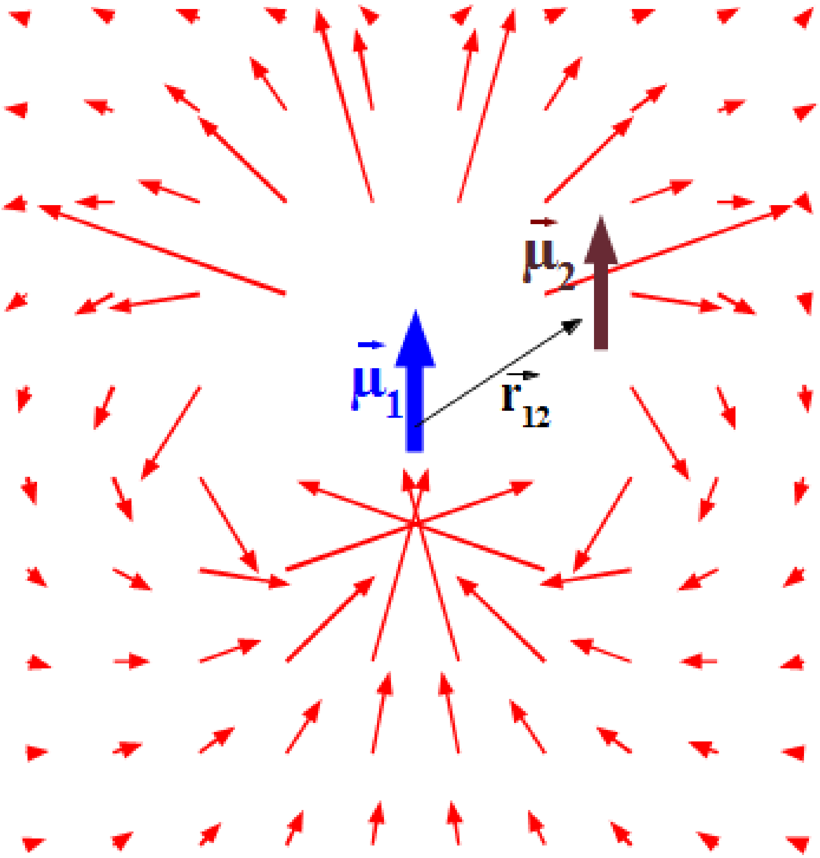
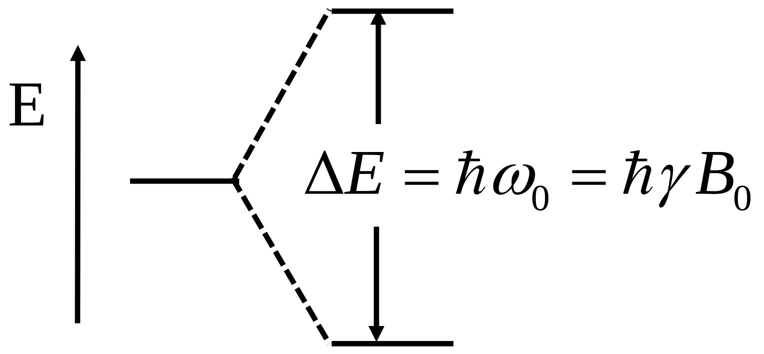
  - 1D and 2D NMR Spectra
  - Stimulated Echoes

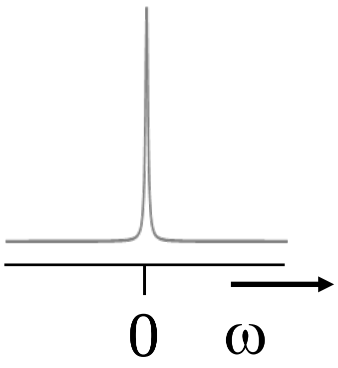


Spin Interactions in Solid-State NMR

Zeeman interaction

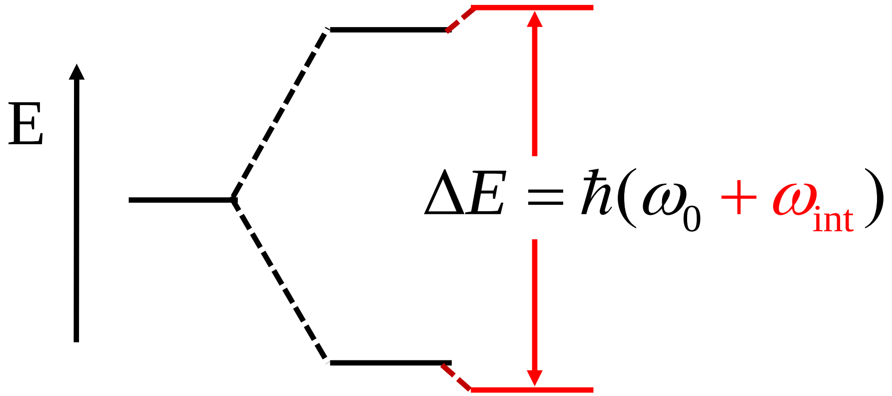


$$\Delta E = \hbar\omega_0 = \hbar\gamma B_0$$

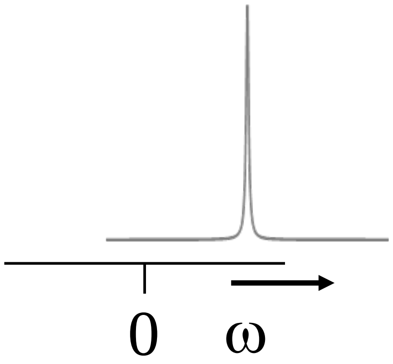


Zeeman interaction

+ internal interaction



$$\Delta E = \hbar(\omega_0 + \omega_{\text{int}})$$

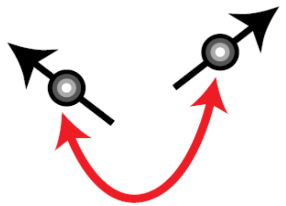


We observe a frequency shift *ω* (solid state: kHz)

Spin Interactions in Solid-State NMR

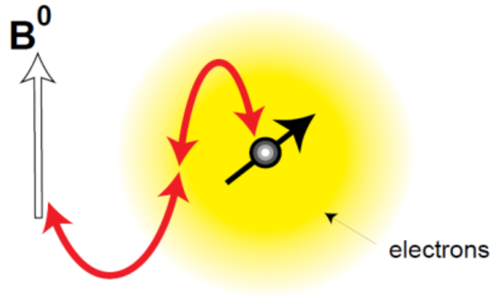
Dipolar interaction:

Interaction between the nuclear magnetic moments μ of the various nuclei



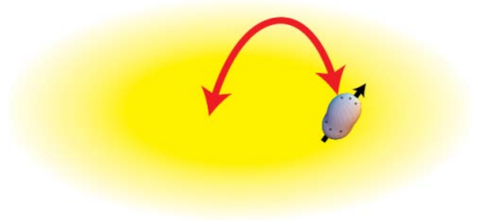
Chemical shift interaction:

Shielding of the magnetic field B_0 at the nucleus due to the electron clouds



Quadrupolar interaction ($I \geq 1$):

Interaction of the nuclear electric quadrupole moment with an electric field gradient at the nuclear site

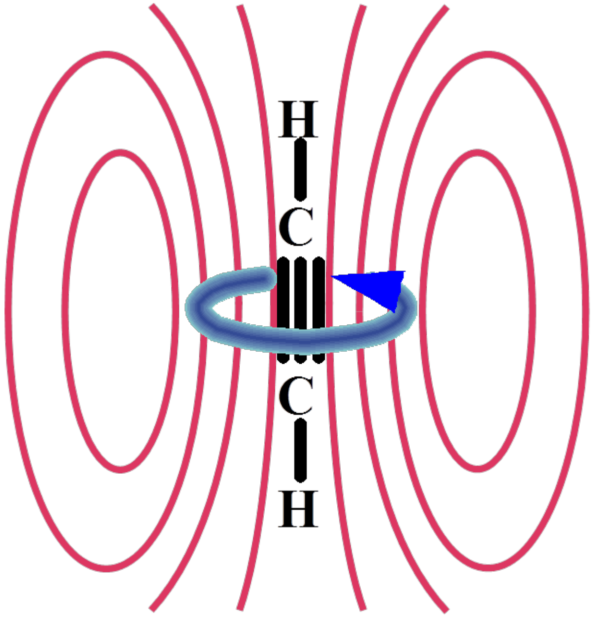


M. H. Levitt, Spin Dynamics

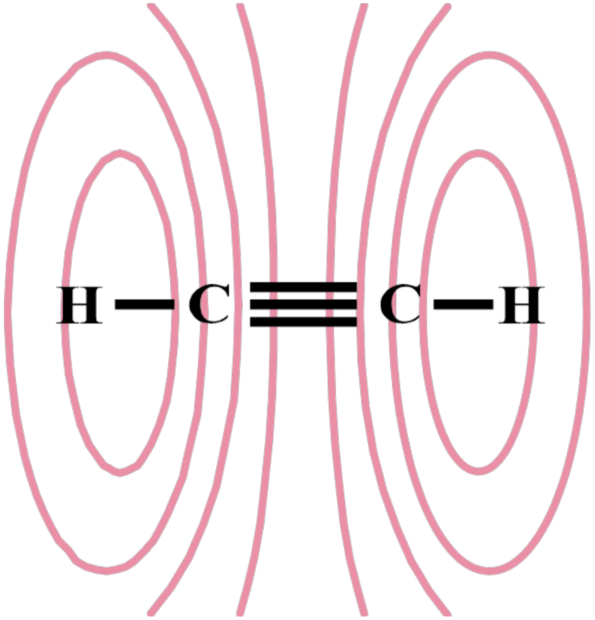
The interaction energies depend on molecular orientations or molecular environments, i.e., on their interaction tensors

Example: Anisotropic Chemical Shielding (or Shift)

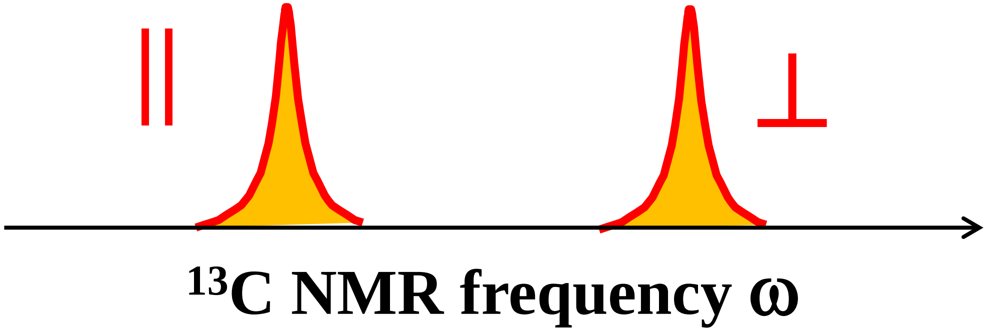
Different orientations of a C_2H_2 molecule relative to the B_0 field



rotational symmetry
large diamagnetic ring current
high (chemical) shielding

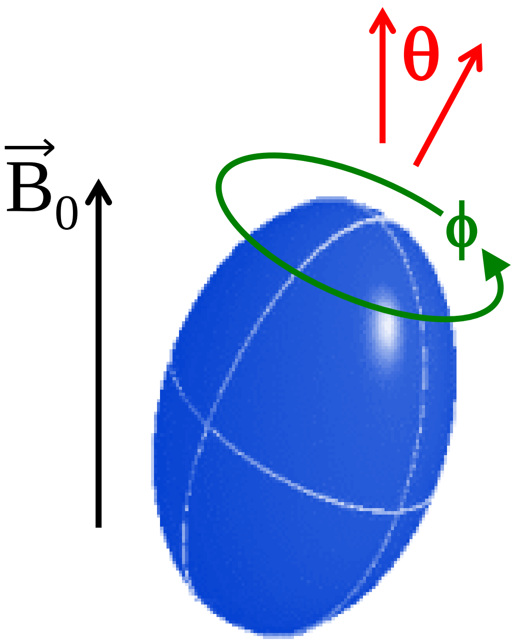


no rotational symmetry
small diamagnetic ring current
little (chemical) shielding



Chemical Shift: Not only anisotropic but also *asymmetric*

Think of the electronic shielding cloud as of a squeezed american football



NMR frequency depends
- on inclination of football's long axis (angle θ)
- and on the rotation about this axis (angle ϕ)

For most interactions, the NMR frequency is:

$$\omega_{\text{aniso}}(\theta,\phi) = \omega_{\text{iso}} \pm \delta/2\ [\ 3\cos^2\theta - 1 - \eta\,\sin^2\theta\,\cos(2\phi)\ ]$$

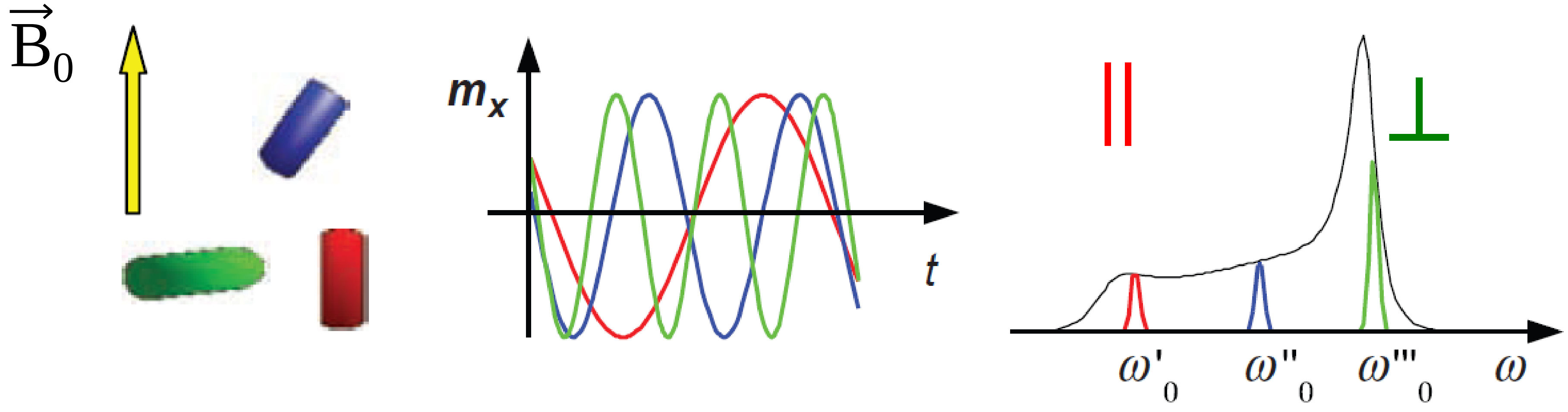
anisotropy $\delta = 0$:
for spherical tensor (soccer ball)
asymmetry $\eta = 0$: for axial tensor
(non-squeezed american football)

http://anorganik.uni-tuebingen.de/klaus/nmr/index.php?p=conventions/csa/csa#converter

Powder Line Shapes

In crystalline powders and amorphous materials, a distribution of molecular orientations exists (powder average)

Due to the dependence of the frequency $\omega_{\mathrm{aniso}}(\theta,\phi)$ on the orientation, **broad powder spectra** are observed



Banerjee, Bhat, Leporini, Adv. Chem. Phys. 152, 1 (2013)

maximum spectral width ≈ given by δ

shape by asymmetry of tensor, e.g., by η

Powder Line Shapes Containing Structural Information

CSA* interaction for *I* = 1/2

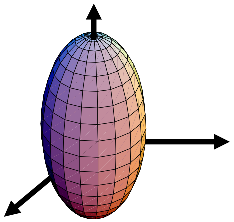
(^{31}P NMR studies of phosphate glasses)

$$\boldsymbol{\sigma}^{\mathrm{PAS}} = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$

$$\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$$

$$\delta > 0,\ \eta > 0$$

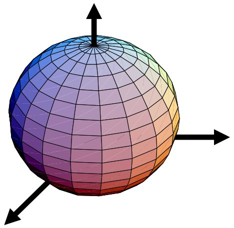
axially symmetric



$$\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz}$$

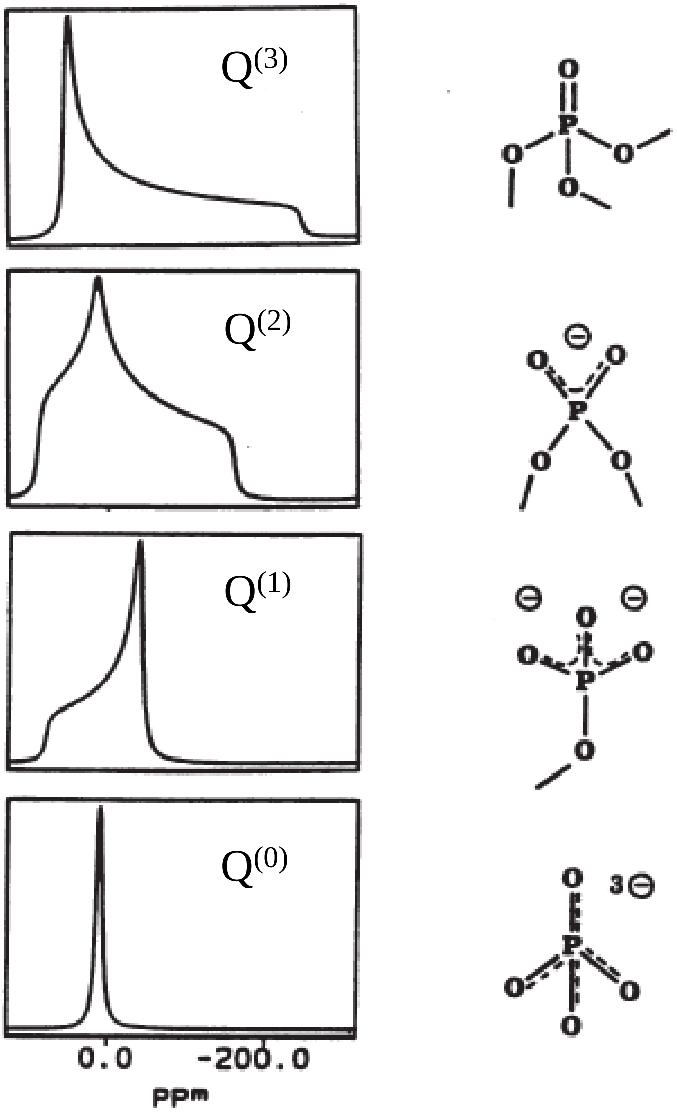
$$\delta > 0,\ \eta = 0$$

spherically symmetric



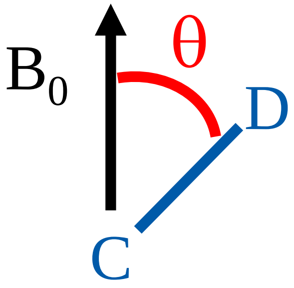
$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$$

$$\delta = 0,\ \eta = 0$$

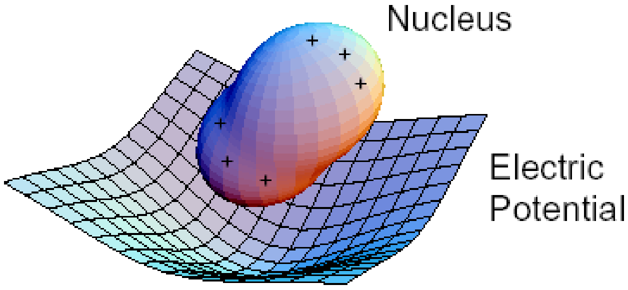


* Chemical Shift Anisotropy

Example 2: Quadrupolar Interaction for Spins $I \geq 1$



Monitor bond orientations of molecular or polymeric systems using ^{2}H NMR



M. H. Levitt
Spin Dynamics

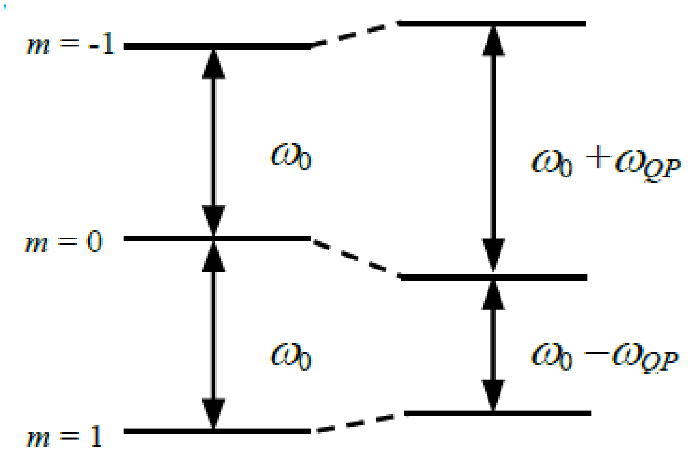
anisotropy δ_Q given by

Q: quadrupole moment of the nucleus

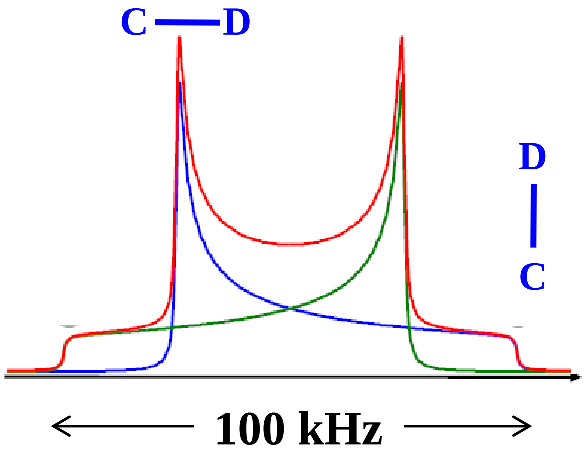
Φ: electric potential of the environment

Quadrupolar frequency (often $\eta \approx 0$)

$$\omega_Q(\theta) = \pm\, \delta_Q/2\ (3\cos^2\theta - 1)$$



I = 1 spins:
two transitions
two subspectra
⇓
Pake pattern →



Comparison of NMR and BDS

potential energy

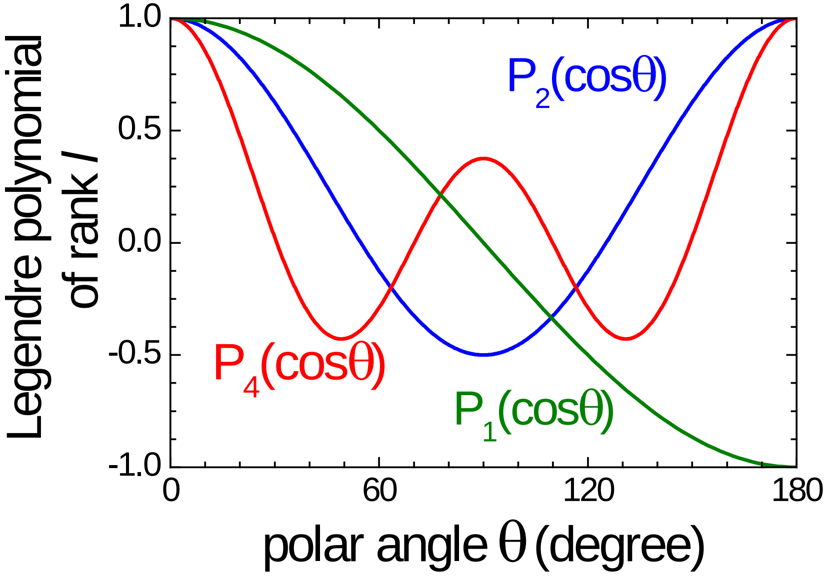
BDS:
Electrical dipole moment vector
in electrical field

$$W_{\text{diel}} = \vec{\mu}\vec{E} = \mu E \cos\theta = \mu E\, P_1(\cos\theta)$$

NMR:
chemical shift, quadrupolar, … tensor
in appropriate field

$$W_{\text{NMR}} = \hbar\omega = \hbar\delta\,\tfrac{1}{2}(3\cos^2\theta - 1 \underbrace{- \eta\sin^2\theta\cos 2\phi)}$$

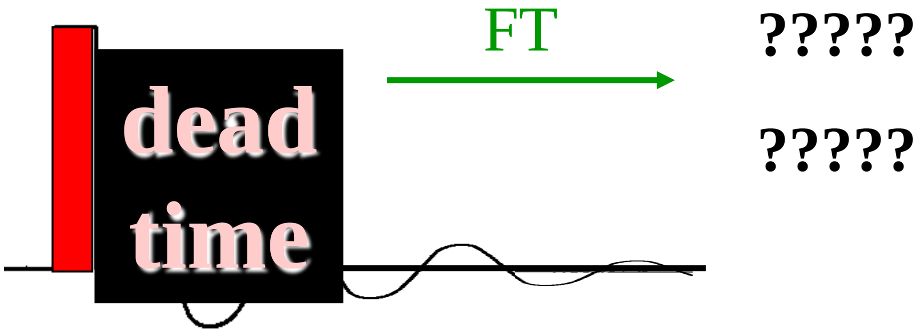
$$= \hbar\delta\, P_2(\cos\theta) \quad \text{if} \uparrow \text{negligible}$$



Higher rank *l* of
Legendre polynomial $P_l(\cos\theta)$
→ higher angular sensitivity

also *l* = 2: Kerr effect,
dynamic light scattering (DLS), ….

Measurement of Solid-State 1D NMR Spectra

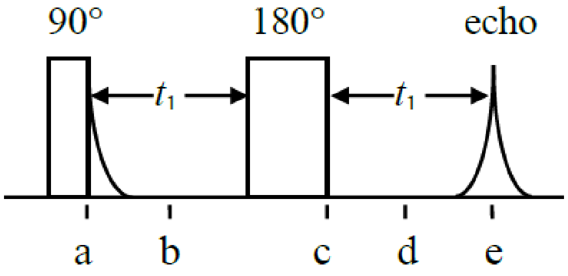


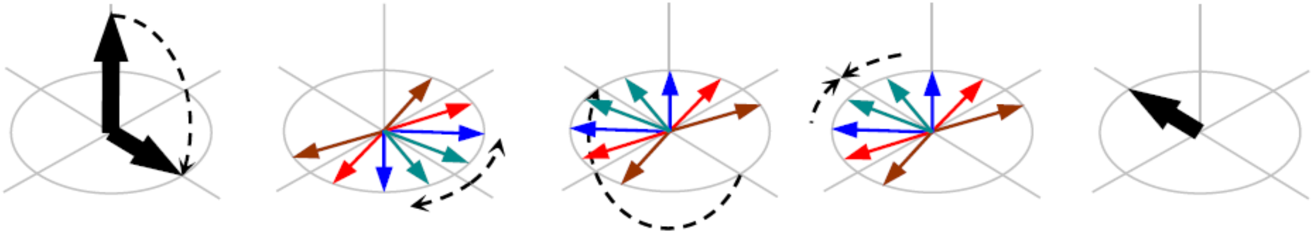
The same coil is used for application of rf pulse and for signal detection

NMR signal cannot be observed immediately after the pulse

For solids, **echo-pulse sequences** are used to overcome this “dead time”

Hahn echo (I = ½)

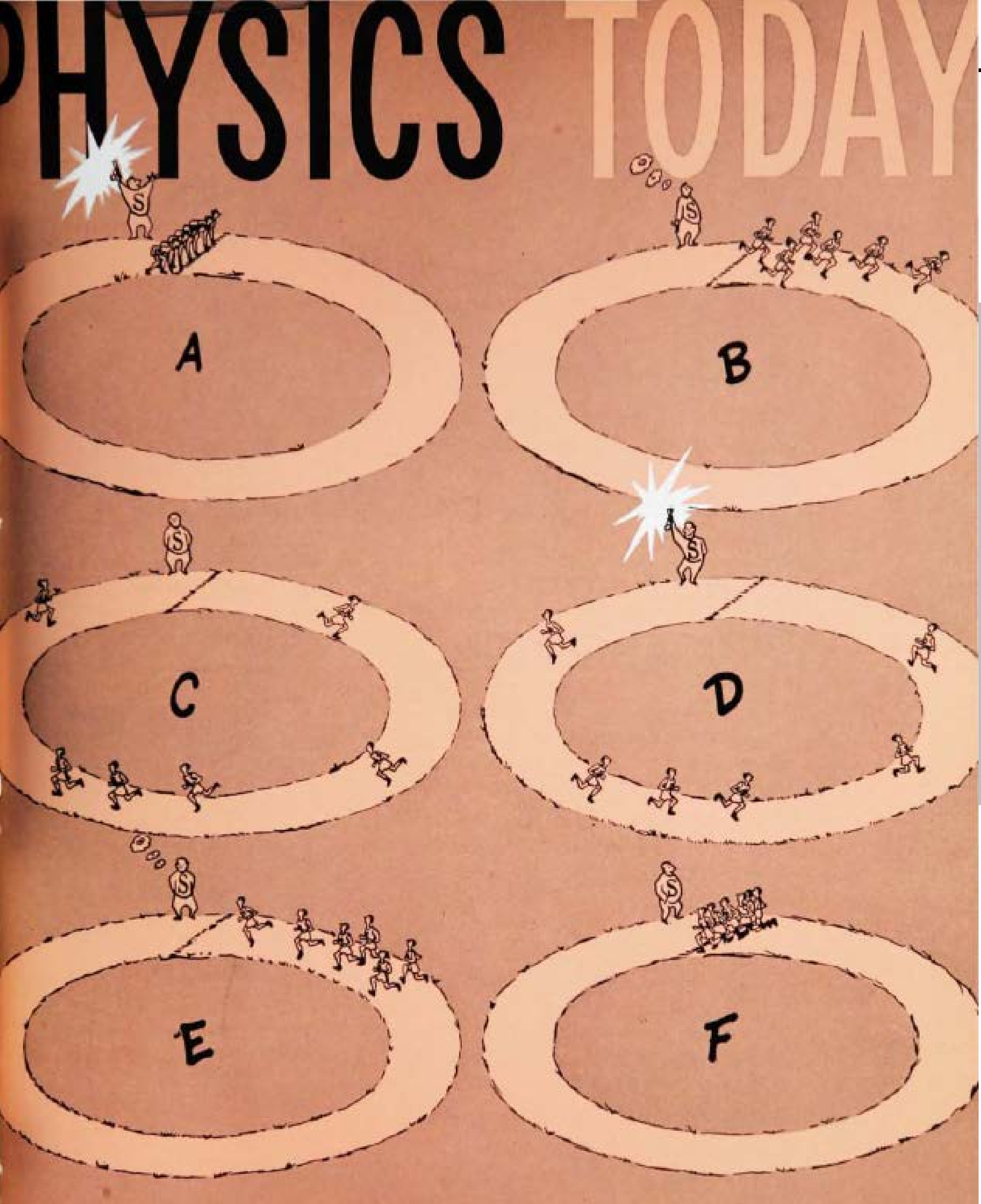


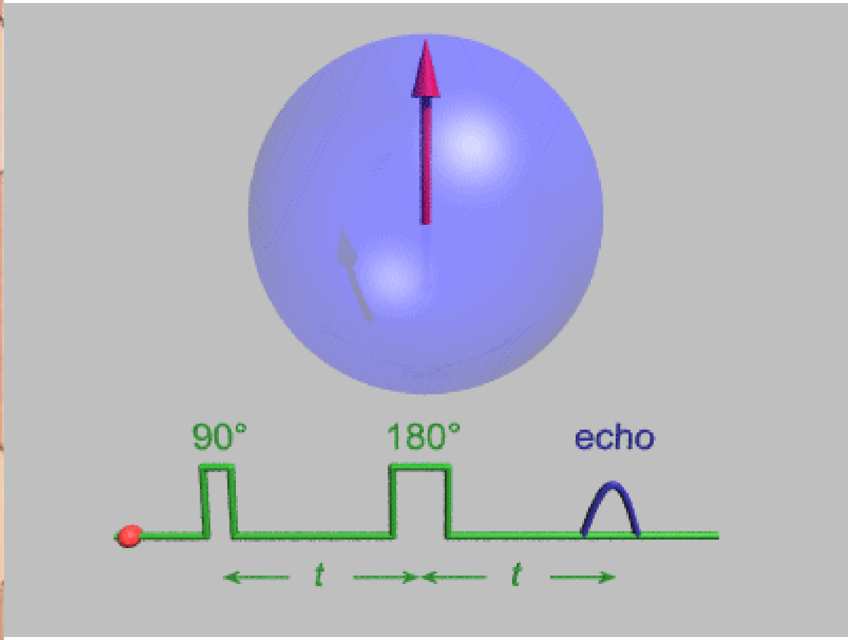


a: 90° rotation **b**: de-phasing **c**: 180° rotation **d**: re-phasing **e**: Hahn echo

Fourier transformation of the signal after echo maximum yields undistorted spectrum

Hahn's Echo and his Racetrack Analogy





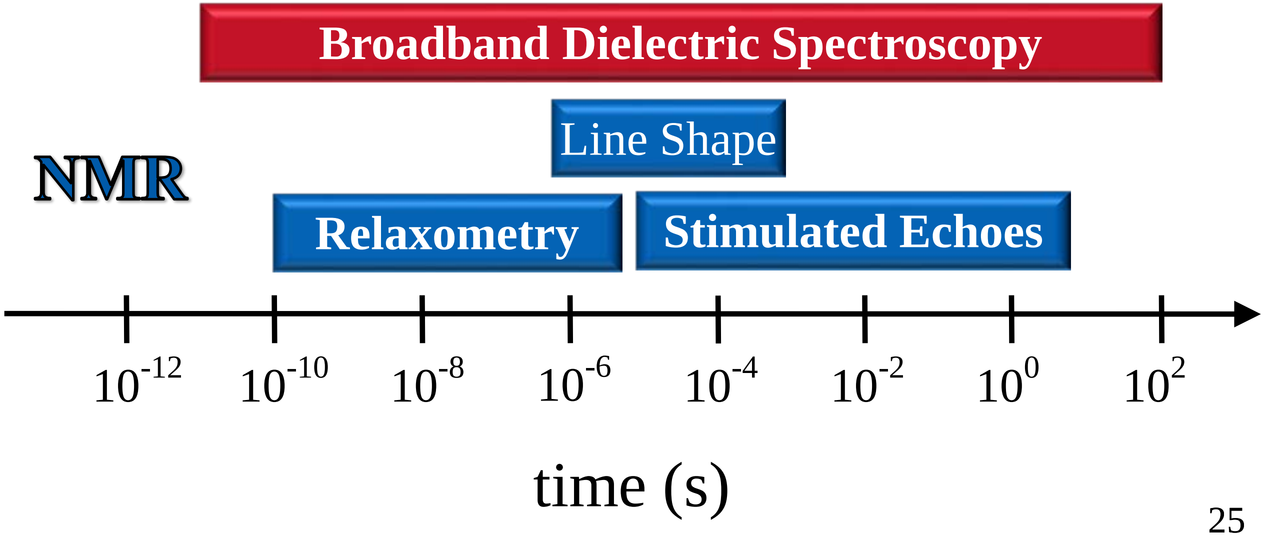
wiki Spin-Echo

$$e^{+i\omega_1 t}\, e^{-i\omega_2 t}$$

E. Hahn, Free Nuclear Induction
Physics Today 6 (Nov. 1953) 4-9.
Cover image

Outline

- **Brief Introduction to NMR Spectroscopy**
  - Interactions of Spins with External Fields
  - Interactions of Spins with Internal Fields
- **NMR Studies of Molecular Dynamics**
  - Spin-Lattice Relaxation
  - 1D and 2D NMR Spectra
  - Stimulated Echoes

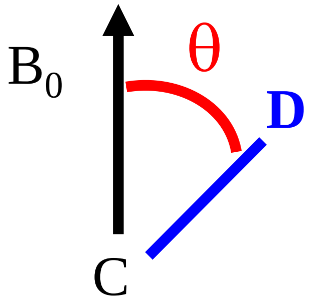


Deuteron NMR Studies of Molecular Dynamics

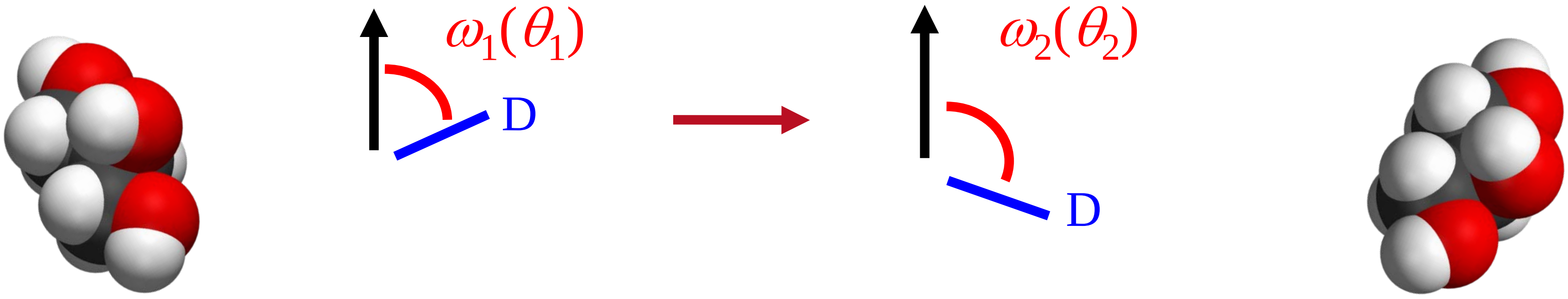
Effects of molecular dynamics in ^{2}H NMR ($\eta = 0$)

The resonance frequency ω depends on the orientation of the C-D, N-D, or O-D bond:

$$\omega(\theta) = \pm\, \delta/2\ (3\cos^2\theta - 1) \propto P_2(\cos\ \theta)$$



Molecular reorientation renders ω time dependent



Basics of Molecular Dynamics

Thermal motion is a stochastic process

Molecular orientations vary randomly in time: $f(\theta(t))$

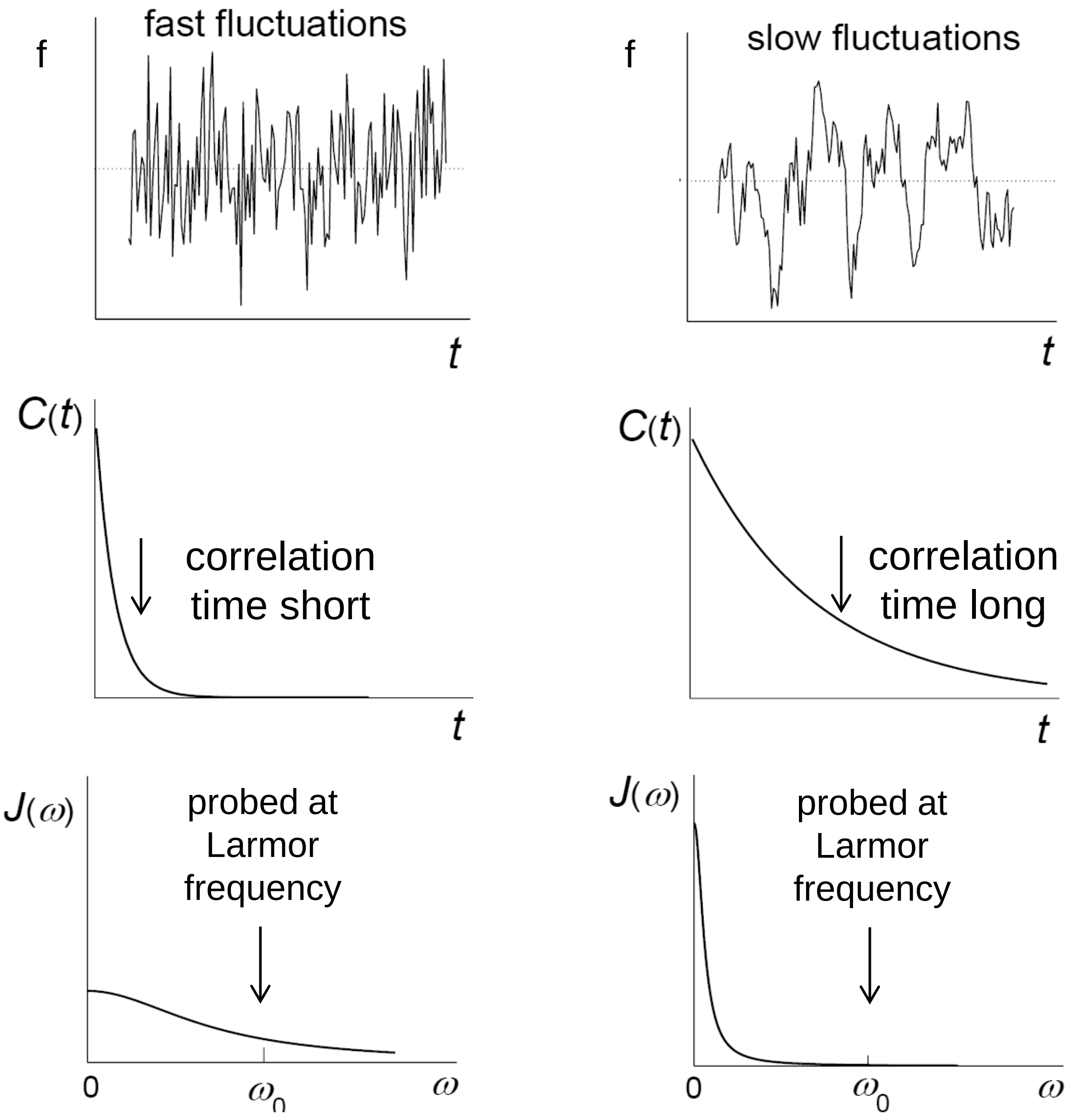
Auto-Correlation Function

$$C(t) = \frac{\langle f(\theta(0))\, f(\theta(t)) \rangle}{\langle f(\theta(0))\, f(\theta(0)) \rangle}$$

↓ Fourier-transformation ↑

Spectral Density

$$J(\omega) \propto \mathrm{Re}\left[\int_0^\infty C(t)\exp(-i\omega t)\,dt\right]$$



^{2}H NMR Spin-Lattice Relaxation

Strong fluctuations of the quadrupolar frequency: $\omega_Q(\theta) \propto P_2(\cos\,\theta)$
on the scale of the Larmor frequency
leads to fast spin-lattice relaxation

Relation between spin relaxation rate und spectral density

Bloembergen-Purcell-Pound (BPP)

$$\frac{1}{T_1} = \frac{2}{15}\delta^2 \cdot [J(\omega_0) + 4J(2\omega_0)]$$

second term not important, e.g., for CSA interaction

Correlation function of rank l = 2
Legendre polynomial: $f(\theta) = P_2(\cos\theta)$

$$C_2(t) = \frac{\langle f(\theta(0))\, f(\theta(t))\rangle}{\langle f(\theta(0))\, f(\theta(0))\rangle}$$

Spectral density

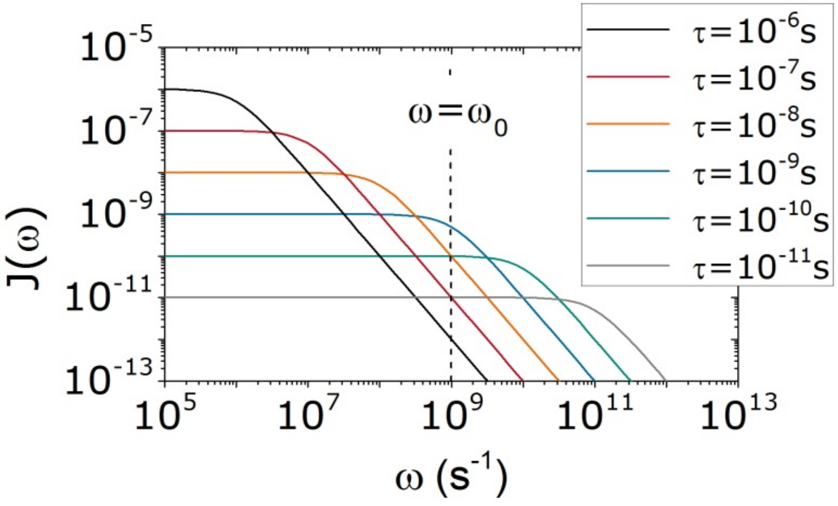
$$J(\omega) = \int_0^\infty C_2(t)\cos(\omega t)dt$$

$$= \mathrm{Re}\left[\int_0^\infty C_2(t)\,\mathrm{e}^{-i\omega t}\,dt\right]$$

Example: Exponential Correlation Function

$$C_2(t) = \exp(-t/\tau)$$

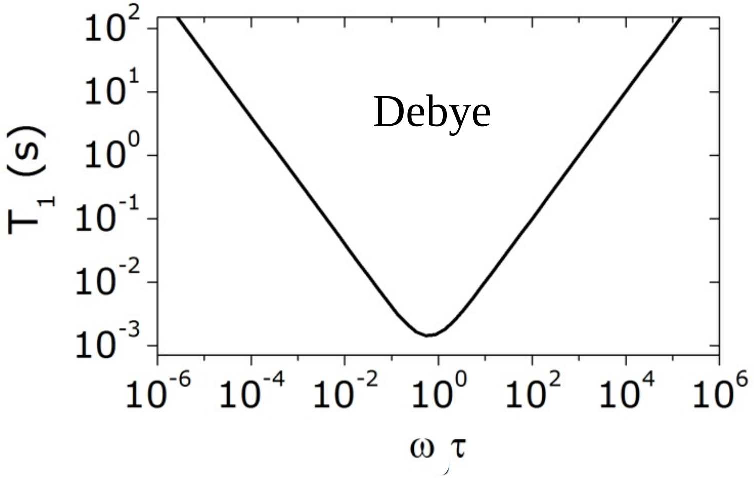
$$J(\omega) = \frac{\tau}{1+(\omega\tau)^2}$$



NMR: Spectral density measure for fluctuation probability.

Normalization: $\int J(\omega)\, d\omega = 1$

$$\frac{1}{T_1} \propto \frac{\tau}{1+(\omega\tau)^2} + \ldots$$



T_1 minimum at $\omega_0\tau \approx 0.62 \approx 1$

Simple relation: Relaxation time T_1 vs. correlation time τ

Spin-Lattice Relaxation and Dielectric Loss

Multiplication with frequency yields
expression like loss (= dissipation)
component of Debye relaxator

$$\frac{\omega}{T_1} \propto \frac{\omega\tau}{1+(\omega\tau)^2} + \ldots$$

(classical) linear response theory
→ Fluctuation-Dissipation-Theorem (FDT)

$$J(\omega) = \frac{k_B T}{\pi\,\omega}\,\varepsilon''(\omega)$$

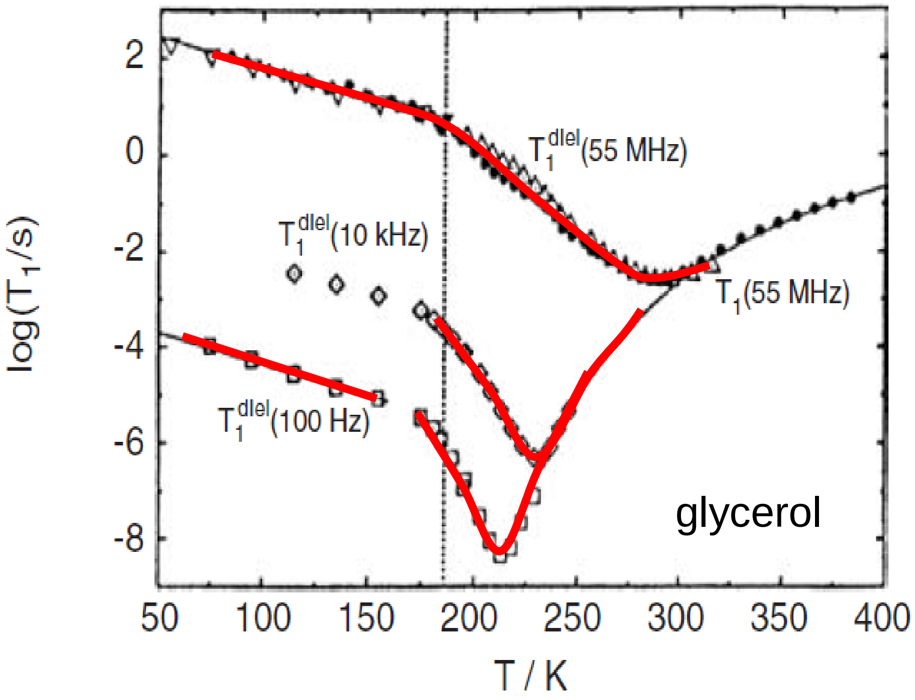
$$\frac{1}{T_1^{\text{diel}}(\omega)} \cong \frac{\varepsilon''(\omega)}{\omega\,\Delta\varepsilon}$$

often a good approximation if:
- $J(2\omega)$ term neglected
- difference in rank l neglected
- dielectric cross terms neglected

A 1/T_1 measurement at a single (Larmor) frequency corresponds (roughly) to a single-frequency measurement of the dielectric loss

NMR measurements at different Larmor frequencies are possible

Two Experimental Examples

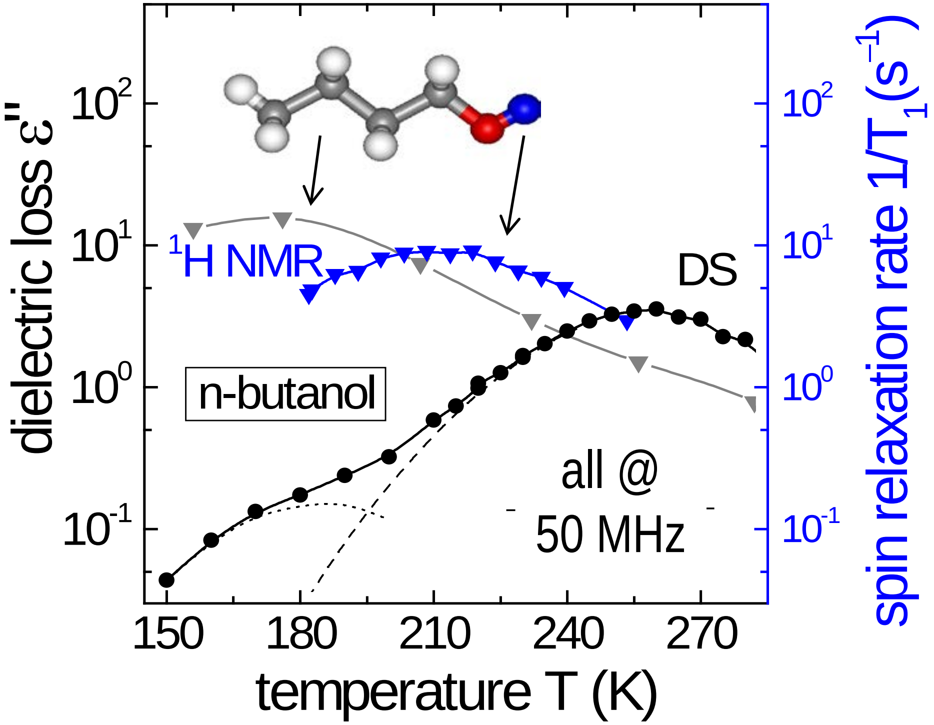


red: from dielectric response:
dissipation

black: from NMR spectral density:
fluctuation

Blochowicz et al., JCP 110, 12011 (1999)

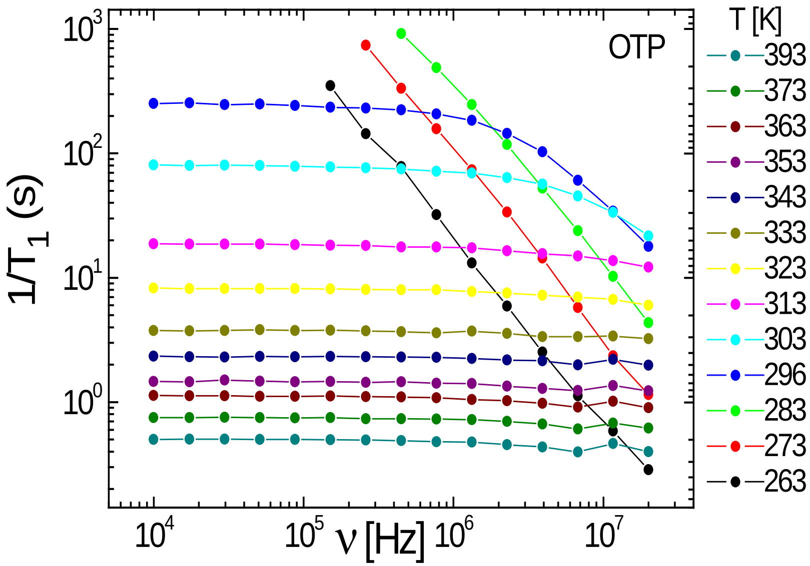
site specificity by isotope
labeling of (here:) butanol



blue: proton only in OH group
grey: protons only in alkyl rest

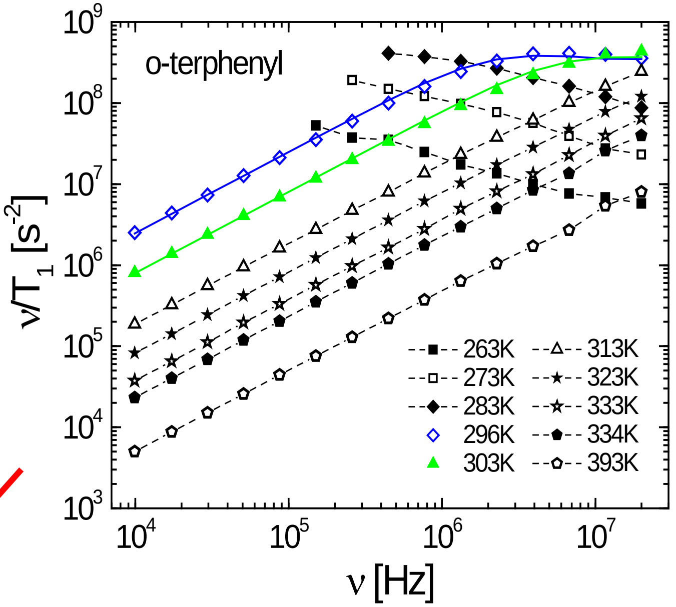
Gainaru et al., PRL 105, 258303 (2010)

Field Cycling: Broadband NMR Relaxometry



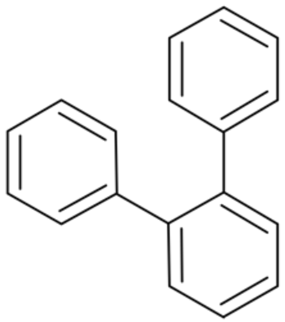
$$1/T_1 \rightarrow \nu/T_1 \propto \chi''$$

susceptibility representation

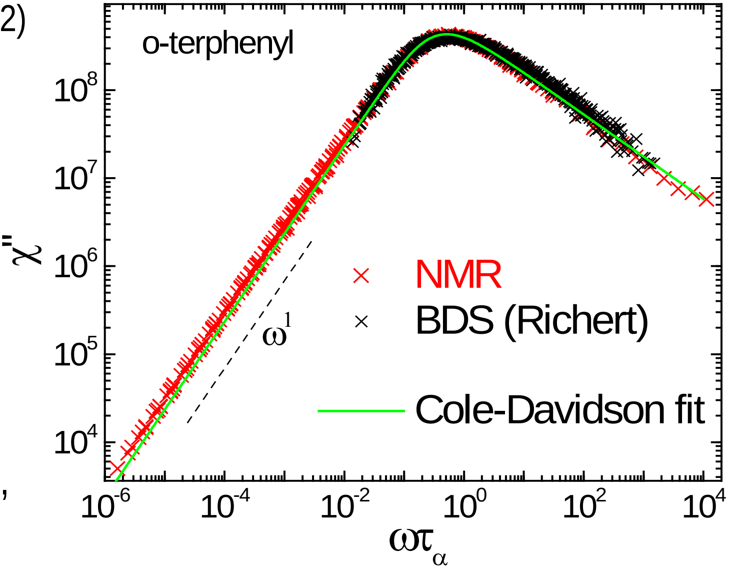


frequency scaling

Kariyo et al., Macromolecules 41, 5313 (2008);
Kruk, Herrmann, Rössler, PNMRS 63, 33 (2012)



with ε'' data from Richert, JCP 123, 154502 (2005)



OTP: clean low-frequency flank

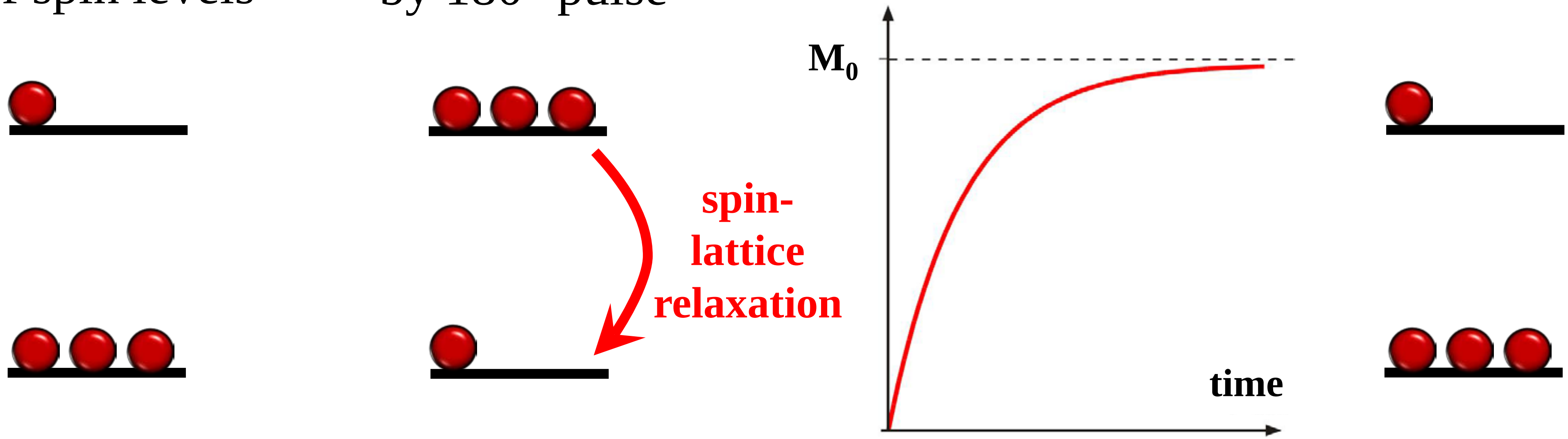
Many applications of FC-NMR also for polymers

Measuring Nuclear Spin-Lattice Relaxation

(Boltzmann)
equilibrium
of spin levels

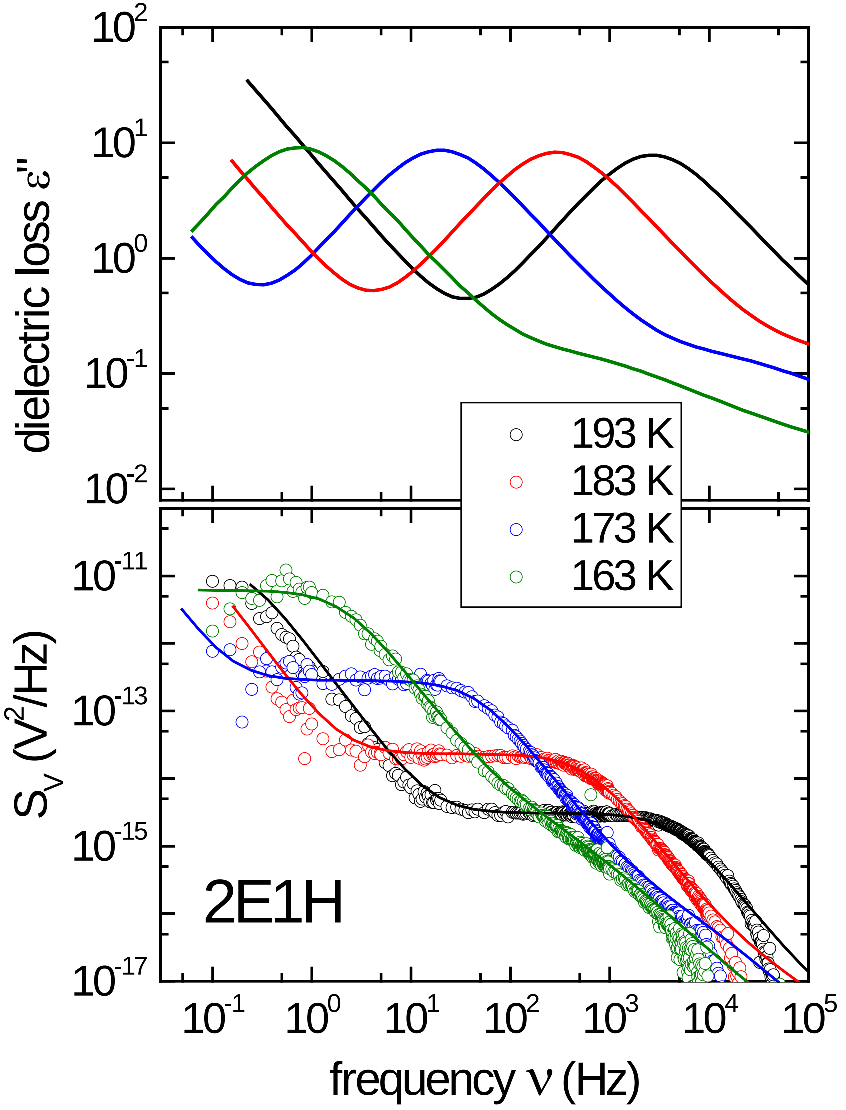
invert
magnetization
by 180° pulse

"lattice" = environment of the nucleus, no matter whether crystalline, amorphous, or liquid



$$M(t) = M_0 + [M(0) - M_0]\,e^{-t/T_1}$$

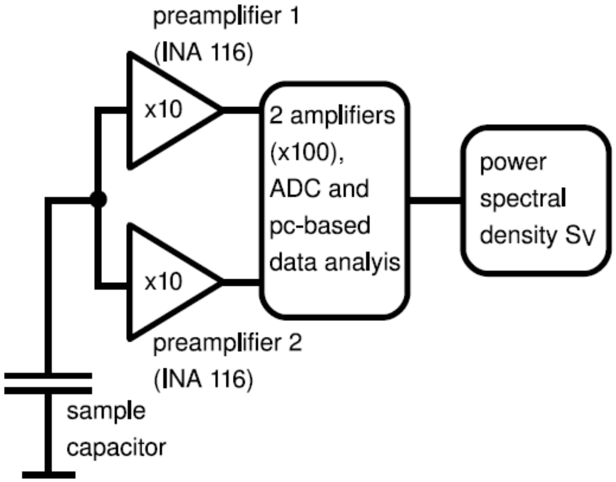
Other Ways to Access Spectral Densities I: Dielectric Noise



lines:
conventional
dielectric
measurements

points:
dedicated
voltage noise
experiments

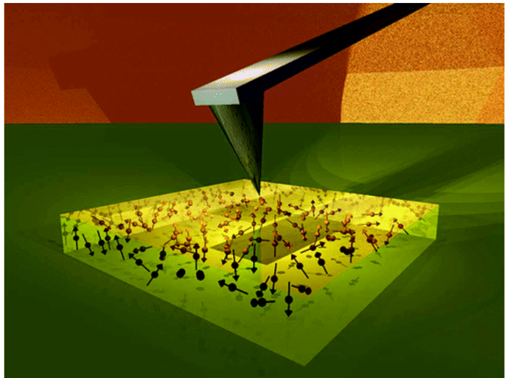
Schindele, **Reiser**, Enss,
PRL **107**, 095701 (2011)



$$S_V = 4k_B T\,\mathrm{Re}[Z(\nu)]$$

Nyquist theorem

analogously used
in AFM approaches
e.g., Russell, Israeloff, Nature **408**,
695 (2000); picture: Hoepker et al.,
JPCB **115**, 1449 (2011)



see also: Schildmann, **Reiser**, Gainaru,
Gainaru, Böhmer, JCP **135**, 174511 (2011)

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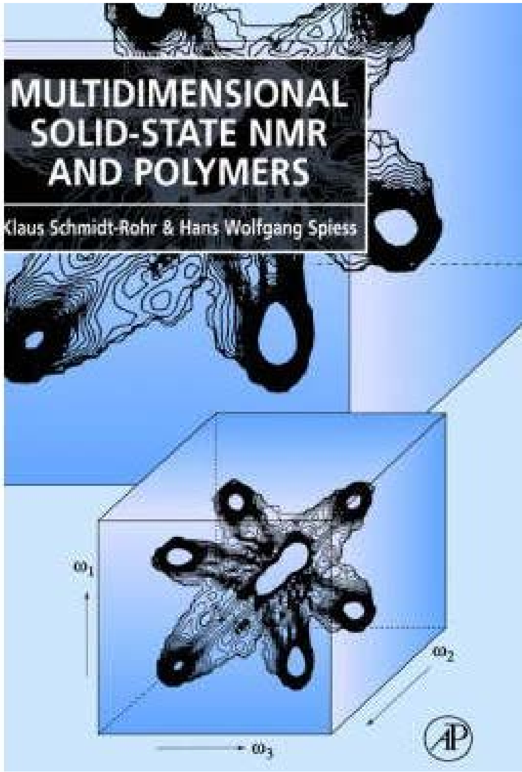
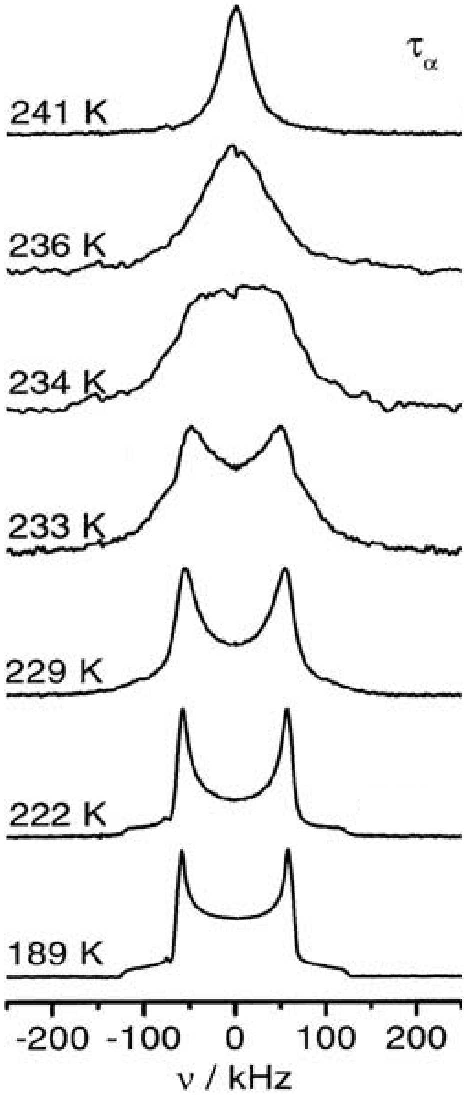
Excellent book for
2D, 3D, … NMR!

Impossible to cover
in 50 minutes
→ Just <u>one</u> slide
with spectra!



Effect of Molecular Dynamics on NMR Line Shapes

Motional narrowing →



2 µs

10 µs

100 µs

Vogel, Rössler, JPCB 104, 4285 (2000)

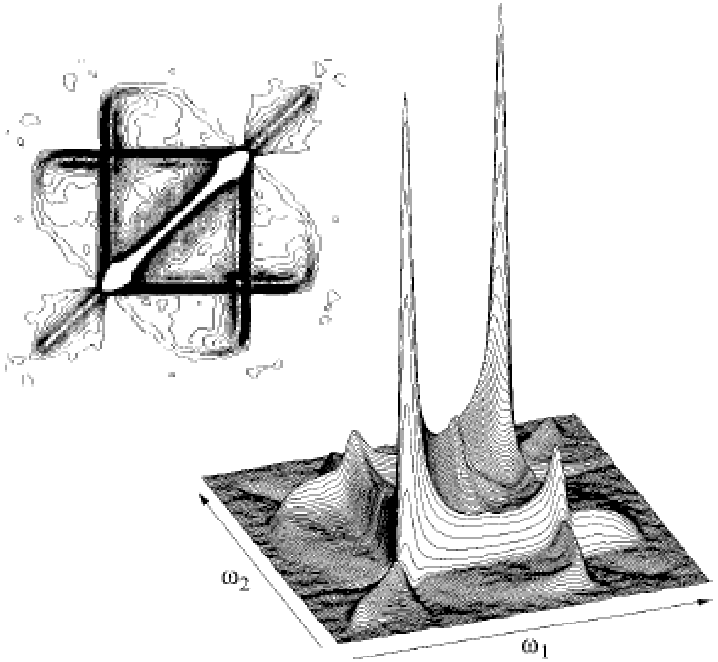
Fast isotropic reorientation:
$\tau < 1/\delta \approx 1$ µs

Example:
^{2}H-NMR of glycerol-d_5

No motion on a time scale of $1/\delta \approx 1$ µs

Spectra useful to determine rate *and* jump geometry of rotational motions.

Beautiful 2D spectra result if well-defined large-angle (> 30°) jumps dominate the reorientation.



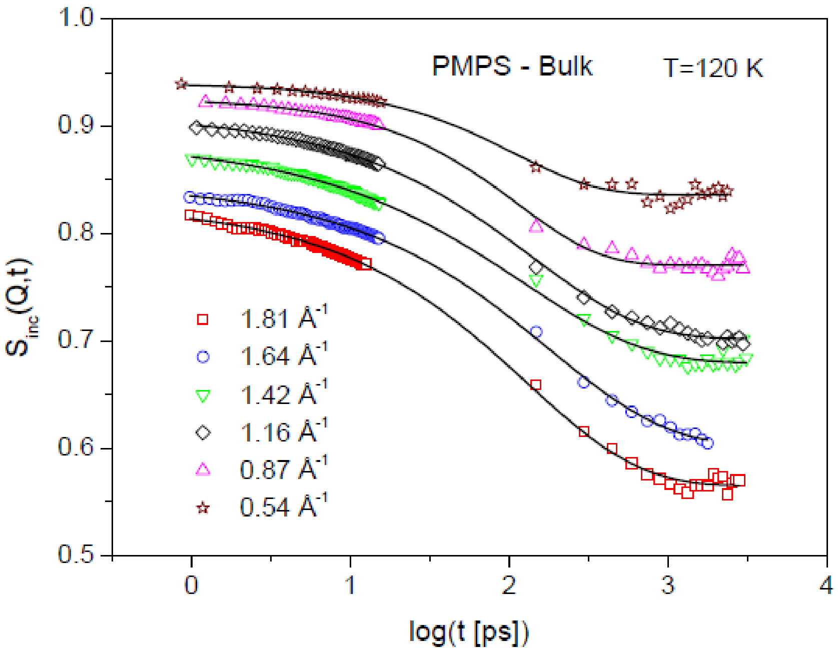
Tetrahedral jumps of benzene-d_6 in Na-Y zeolite, Geil et al., JCP 116, 2184 (2002)

Can We Measure Correlation Functions Directly?

Apply Broadband Neutron Spectroscopy
→ density-density (ρ-ρ) correlation
for time difference $t = t_2 - t_1$

$$S_{\text{inc}}(\vec{Q},t) = \left\langle \rho(\vec{Q},t_1)\,\rho(\vec{Q},t_2) \right\rangle$$

Intermediate scattering function expressed as phase correlation function:



courtesy of A. Schönhals

$$S_{\text{inc}}(\vec{Q},t) = \left\langle \exp[+i\vec{Q}\vec{r}(t_1)]\exp[-i\vec{Q}\vec{r}(t_2)] \right\rangle$$ sensitive to **translational coordinate $\vec{r}$**

Consider rotational analog: Replace $\vec{r}$ by **'rotational coordinate' $\omega(\theta)$**

$$S_{\text{rot}}(Q_{\text{rot}},t) = \left\langle \exp[+iQ_{\text{rot}}\,\omega(t_1)]\exp[-iQ_{\text{rot}}\,\omega(t_2)] \right\rangle$$

Here ω is the NMR frequency. What could Q_{rot} be ?

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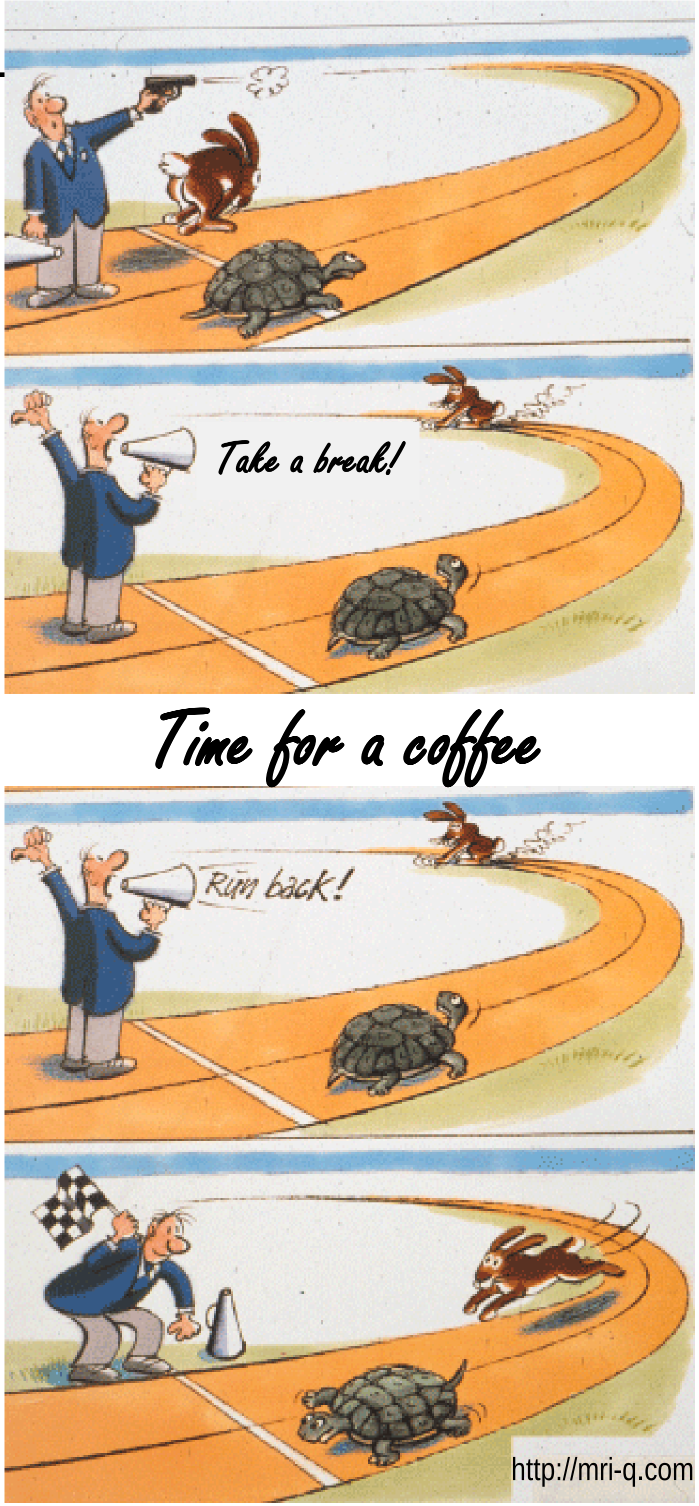
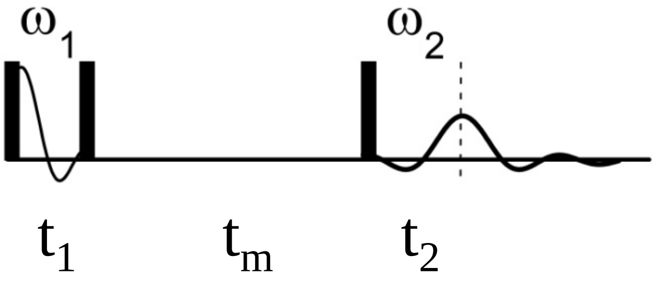
Idea of the stimulated echo:
A break in Hahn's race



http://mri-q.com

Stimulated-Echo Experiment: Basic Sequence also for 2D NMR

Stimulated-echo sequence



"cut the refocusing pulse
of the Hahn-echo sequence
in two halves"

Measure and correlate NMR frequencies at two times separated by

t_m is called mixing time

$$S_\mathrm{rot}(Q_\mathrm{rot}, t) = \langle \exp[+iQ_\mathrm{rot}\,\omega(t_1)]\exp[-iQ_\mathrm{rot}\,\omega(t_2)] \rangle$$

Q_rot is called evolution time = t_e

Terminology in NMR where only real (not: complex) quantities are measured

$$\omega_{1,2} = \omega(t_{1.2})$$

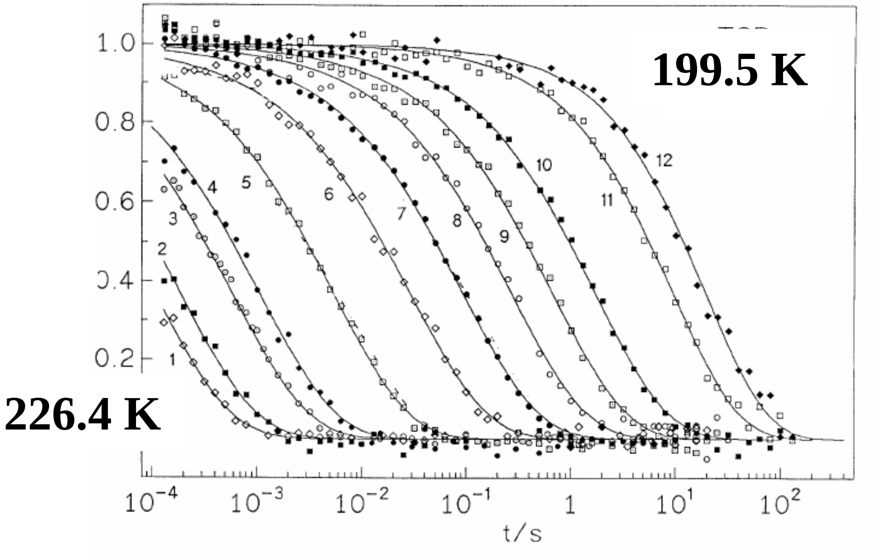
$$F_2^{\cos}(t_e, t_m) = \langle \cos(\omega_1 t_e)\cdot\cos(\omega_2 t_e) \rangle$$

$$F_2^{\sin}(t_e, t_m) = \langle \sin(\omega_1 t_e)\cdot\sin(\omega_2 t_e) \rangle$$

measure echo height
as a function of t_m !

Rotational Correlation Functions: $\langle P_l(0)P_l(t)\rangle$

m-tricresyl phosphate (T_g = 214 K)



^{31}P NMR stimulated-echo decays

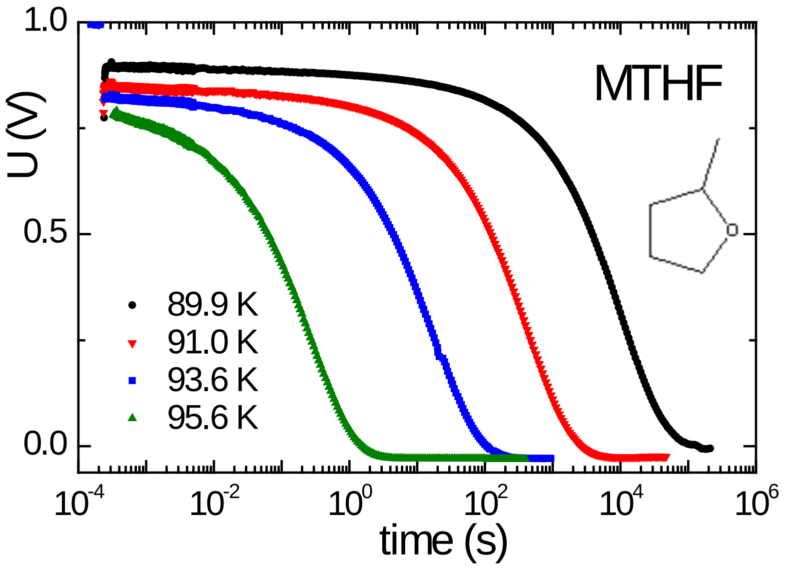
$$F_2^{\sin}(t_e,t_m) = \left\langle \sin(\omega_1 t_e)\cdot\sin(\omega_2 t_e)\right\rangle$$

$t_e \to 0$ $$= t_e^2\left\langle \omega_1\cdot\omega_2\right\rangle$$

$$\langle P_2[\cos\theta(0)]P_2[\cos\theta(t)]\rangle \to l = 2$$

Rössler, Eiermann, JCP 100, 5237 (1994)

2-methyltetrahydrofuran (T_g = 92 K)



dielectric response functions

measured after step excitation using a Sawyer-Tower circuit

$$U_{\mathrm{ref}} \propto \langle\cos\theta(0)\cos\theta(t)\rangle \to l = 1$$

Qi et al., JCP 118, 7431 (2003)