Overview of NMR of Bulk Polymers

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Tutorial
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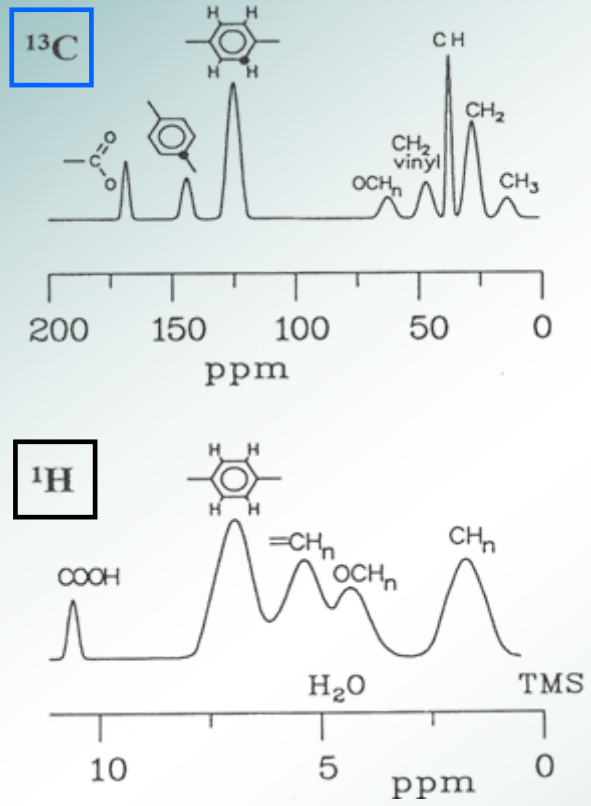
Overview of NMR of Bulk Polymers

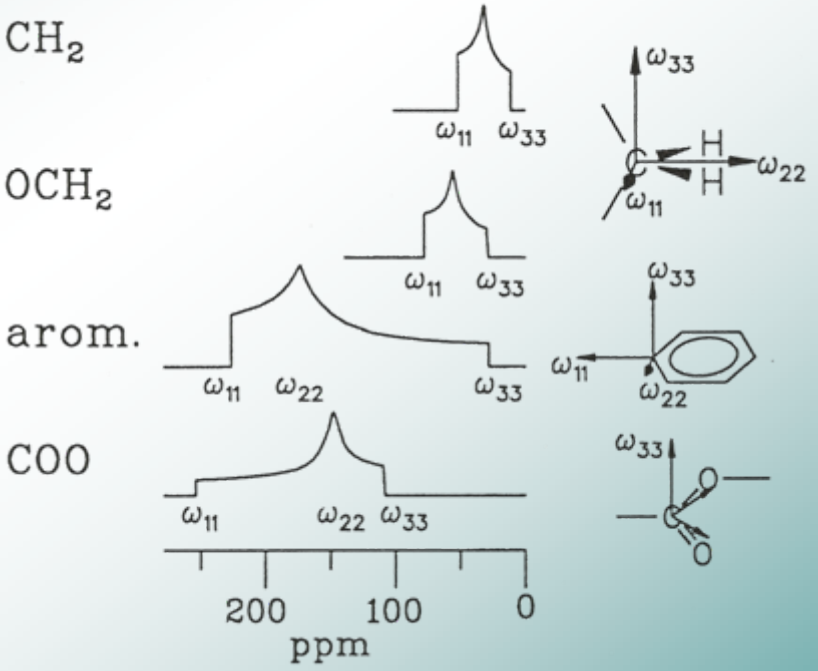
Introduction	•	Basics
Configuration, Conformation	•	Chain Branching
Local Structure & Dynamics	•	Amorphous & Crystalline Polymers
Phase Behavior	•	Core Shell Structures
Supramolecular Organization	•	Functional Polymeric Systems
Conclusions	•	Scattering and NMR

Chemical Shift Ranges for Organic Compounds

Isotropic



Anisotropic (^{13}C)



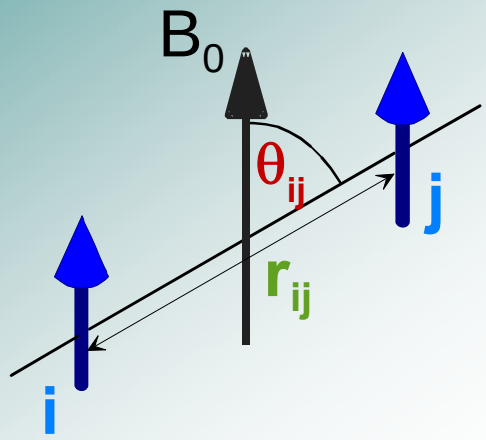
Angular dependent NMR - frequency:

$$\omega = \omega_L + 1/2\,\Delta\,(\,3\cos^2\Theta - 1 - \eta\sin^2\Theta\cos 2\Phi\,)$$

Analogous for ^{2}H quadrupole coupling

Structure and Dynamics from Solid-State NMR

Dipole-Dipole Coupling



$$D \propto \frac{\gamma_i \gamma_j}{r_{ij}^3} \cdot \frac{1}{2}(3\cos^2\theta_{ij} - 1)$$

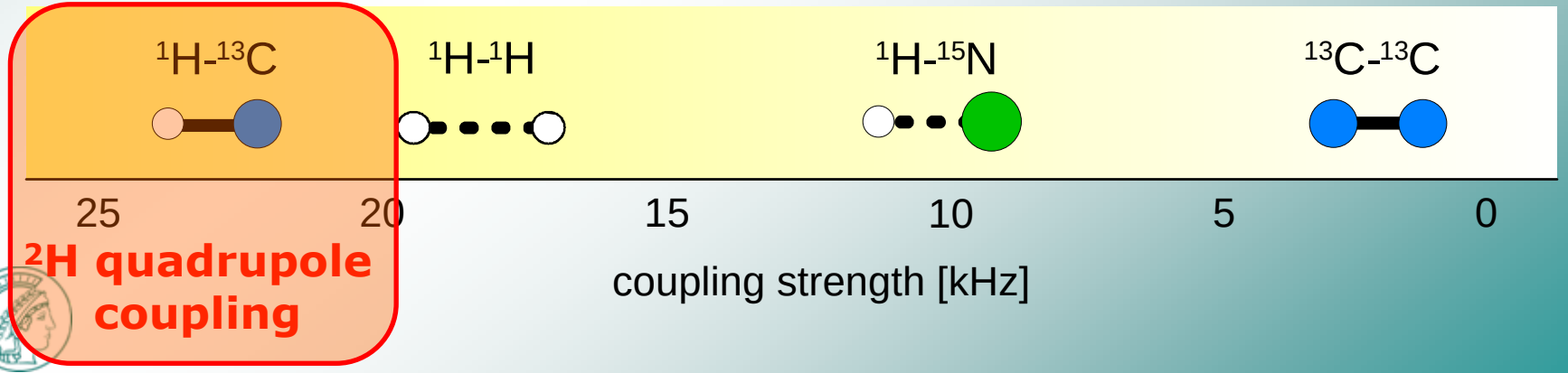
Structure

Distance between nuclei

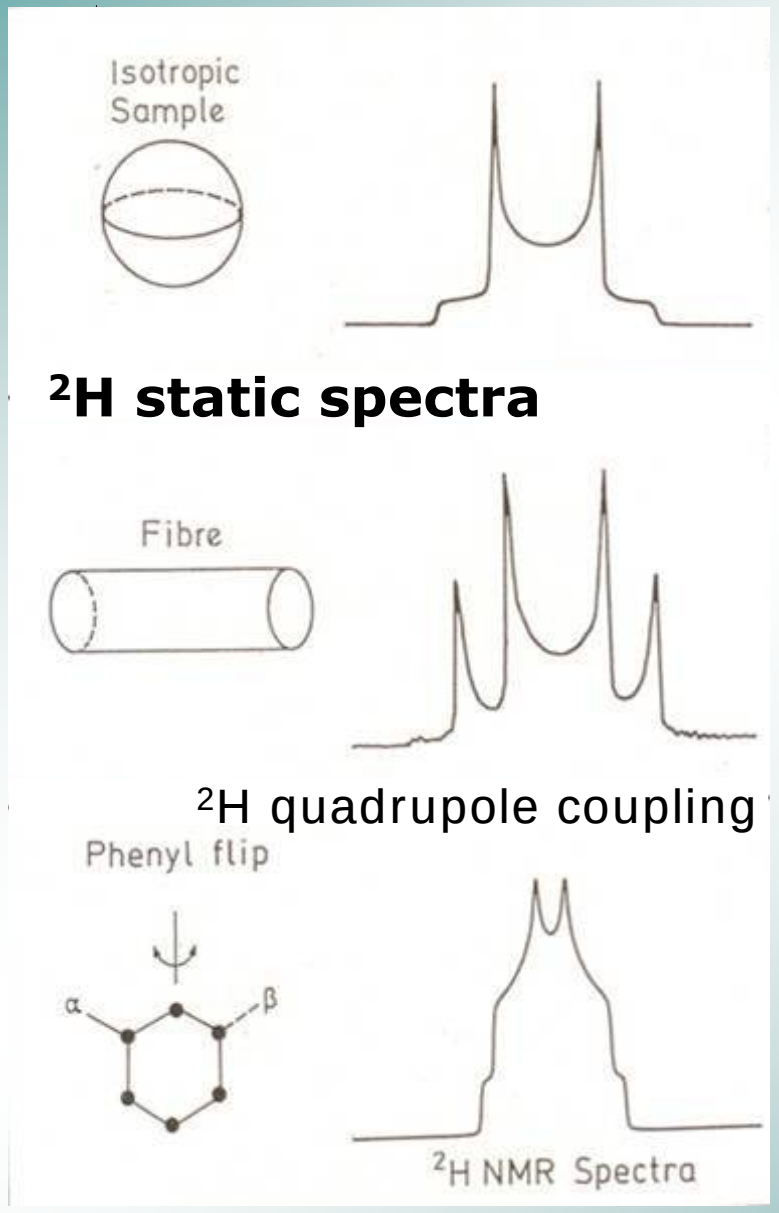
Orientation of internuclear vector

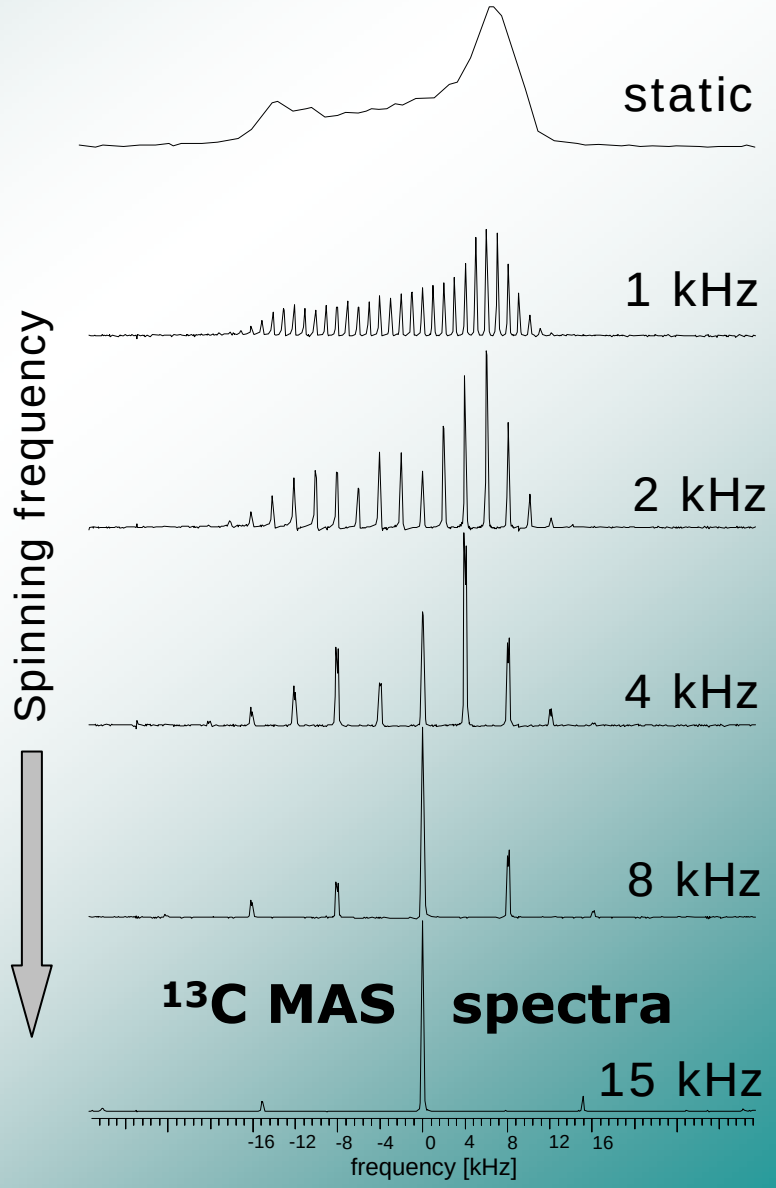
Dynamics

Typical pairs of nuclei



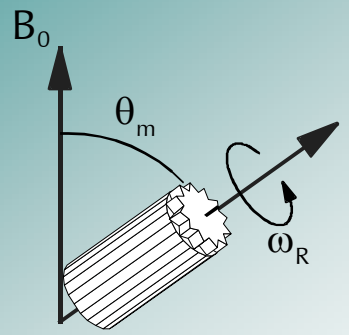
Solid State NMR Spectra



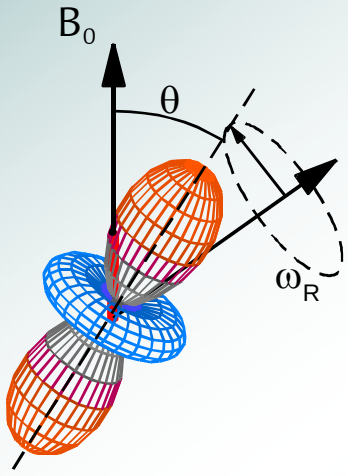


Magic-angle spinning (MAS)

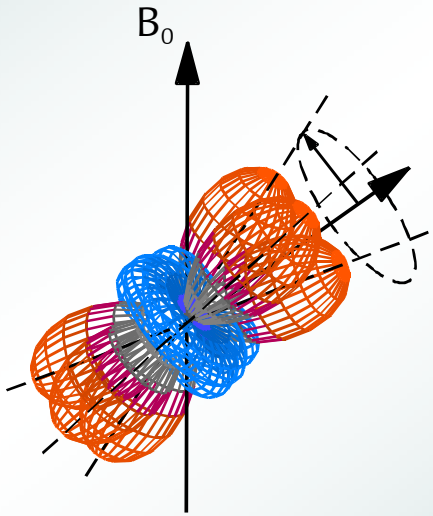
How does MAS work ?



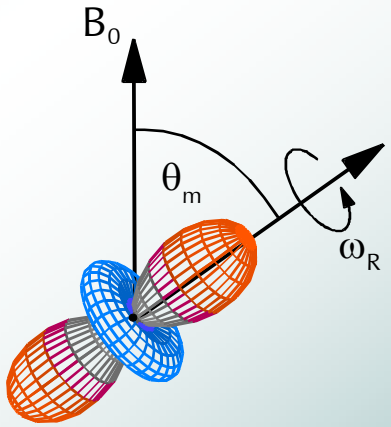
rotor is spun around an axis inclined at an angle of θ_m=54.7° with respect to B_0.



spatial part of interaction tensor



averaging by fast rotation



resulting average tensor

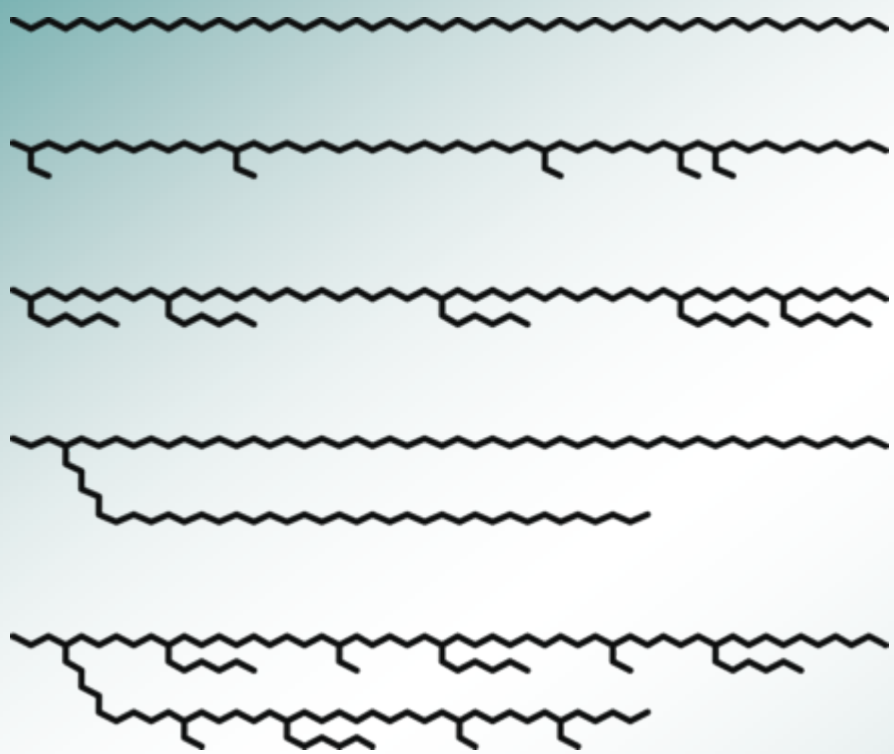
in terms of coordinate transformations:

$$\tfrac{1}{2}(3\cos^2\theta - 1) \Rightarrow \tfrac{1}{2}\sin^2\beta\cos(2\omega_R t - 2\gamma) - \tfrac{1}{\sqrt{2}}\sin(2\beta)\cos(\omega_R t - \gamma)$$

rotor modulations with frequencies $2\omega_R$ and ω_R

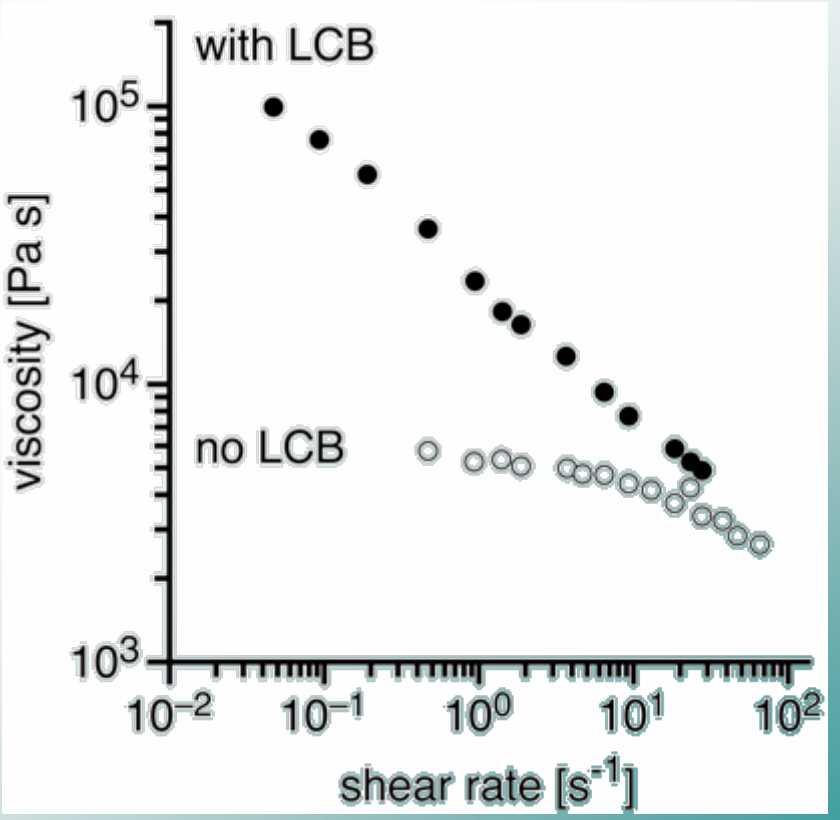
Polyolefin Branching

Short (SCB)< 30 C

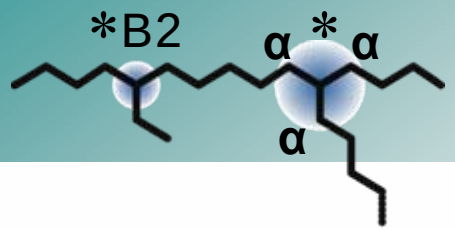


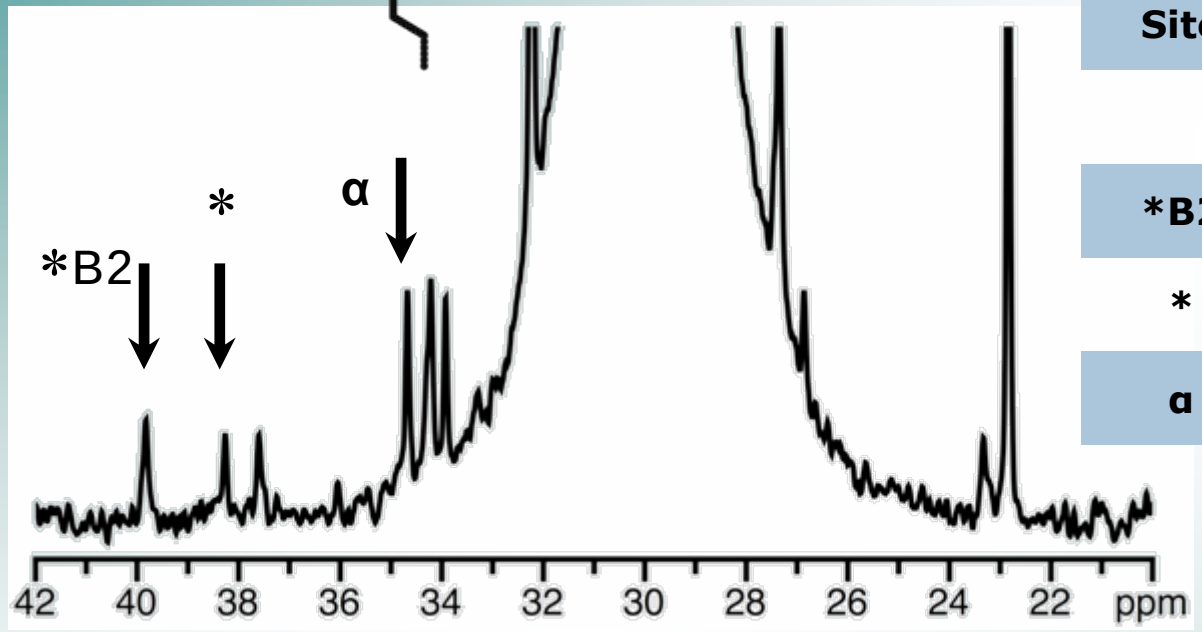
Long (LCB) > M_e ≈ 270 C

pronounced effect on viscosity & melt processability



MAS-NMR in Melts: Very Low Branch Contents





‘Linear’ PE

Site	SNR	Content
		per 1000 C
*B2	4.5	0.07
*	3.7	0.05
α	9.4	0.08

Sample:
R.H. Grubbs, Caltech

Quantification of 7–8 branches per 10 000 C

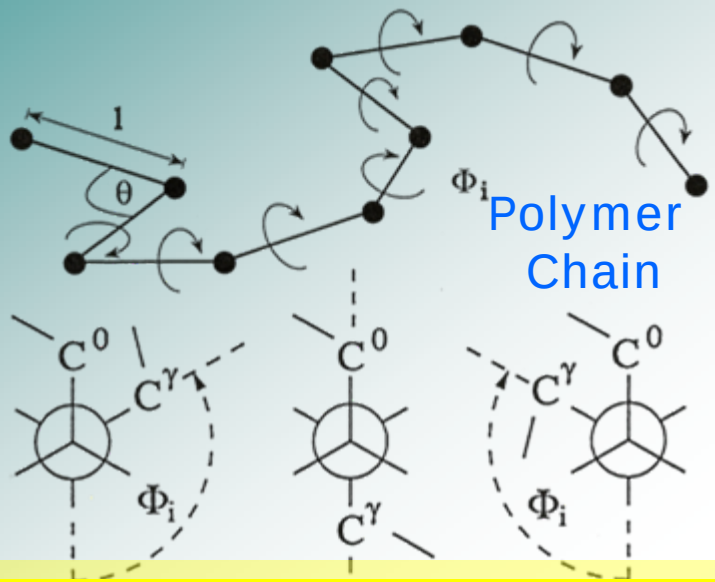
Optimised **solution** NMR:

50,000 to 2,000,000 scans (up to 60 days!)

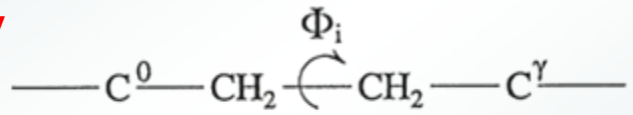
Optimised **melt-state NMR**: **21,500 scans (13 h)**

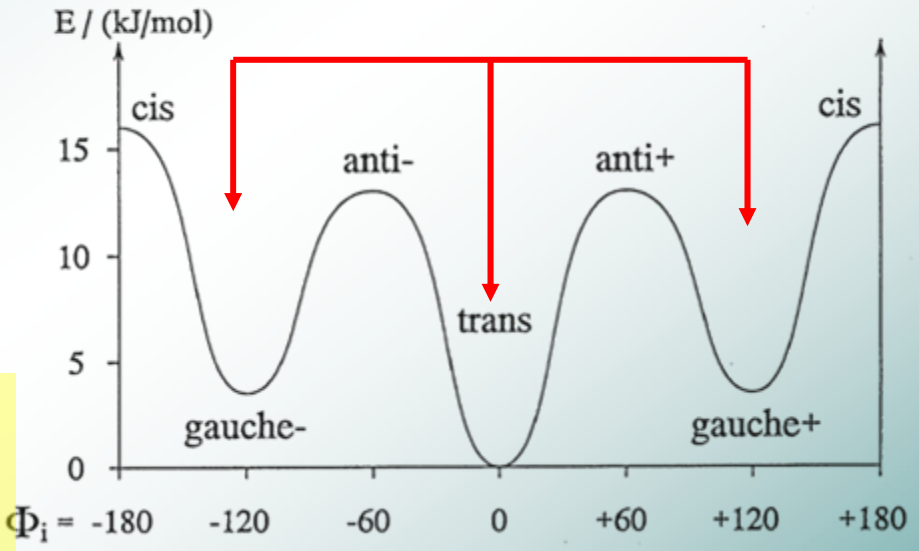
Macromolecules **37**, 813 (2004), Macromol. Chem. Phys. **207**, 382 (2006).

^{13}C – NMR: Conformational Effects

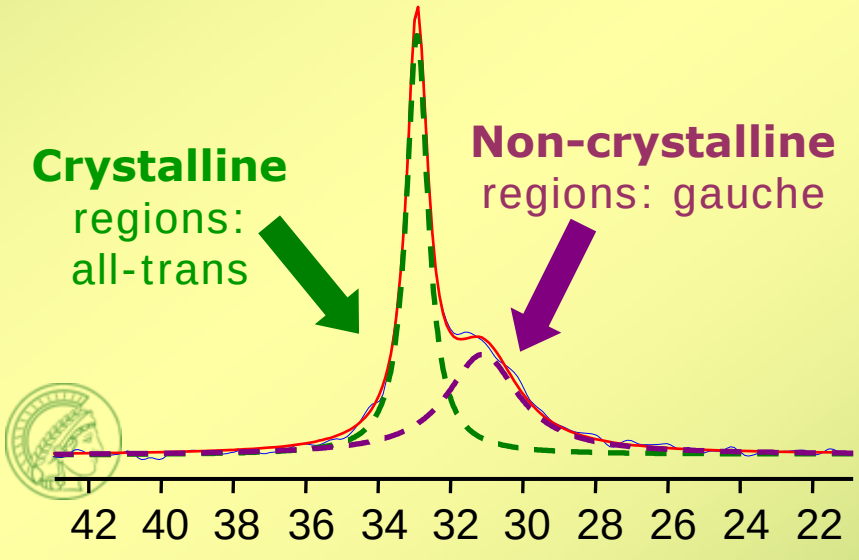


Potential Energy





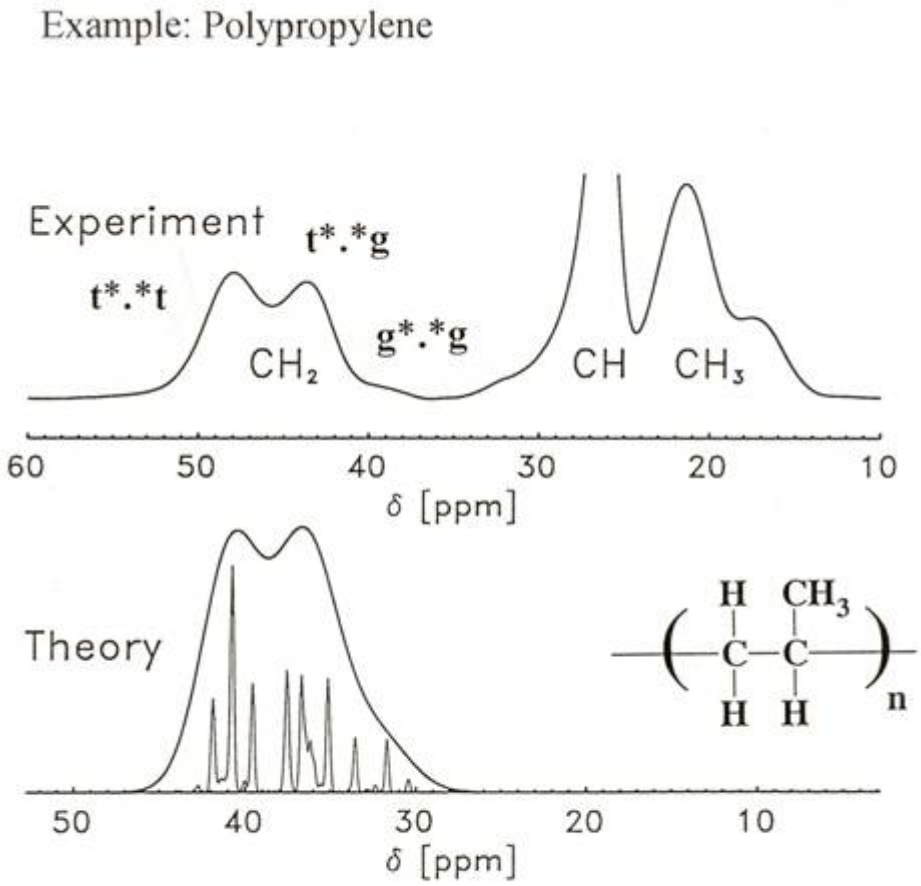
^{13}C NMR spectrum of PE



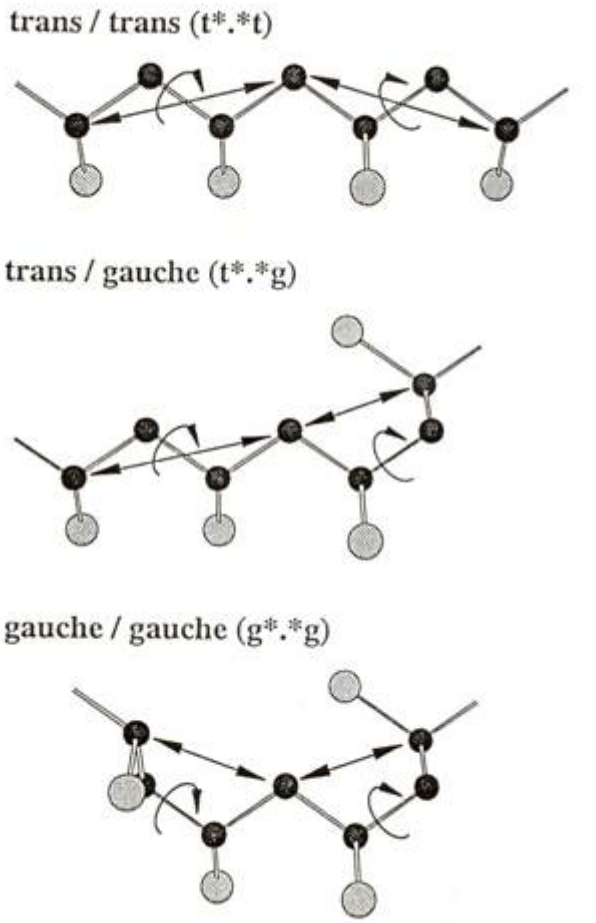
Sensitivity of ^{13}C Chemical Shifts on Conformation :

Gamma - *gauche* effect:
- 5,2 ppm in alkanes

Conformational Effects on ^{13}C Chemical Shifts

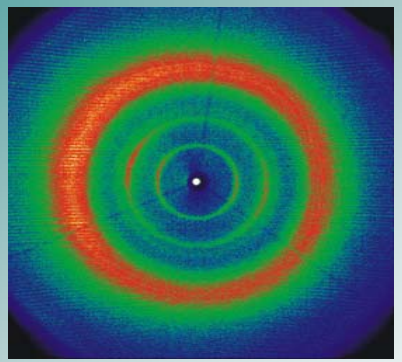


^{13}C NMR Spectrum



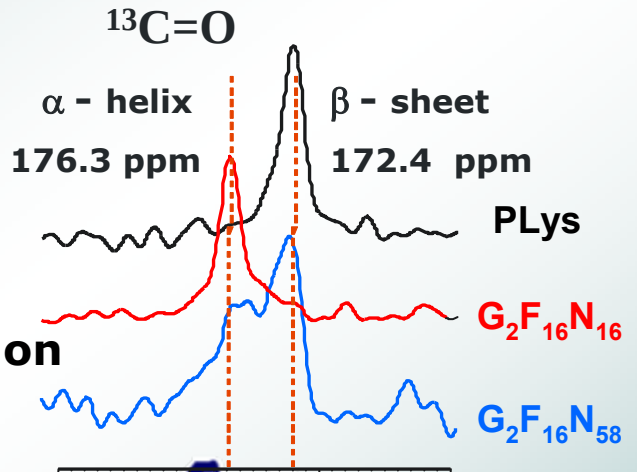
Conformations of Tetrameric Unit

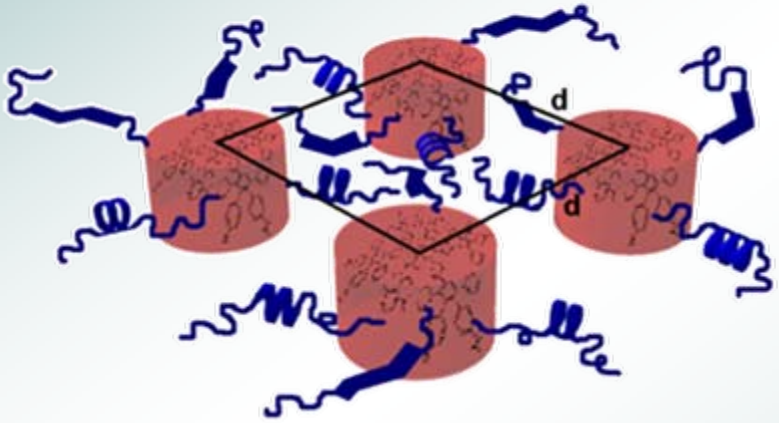
Self-Assembly and Molecular Dynamics of Peptide-Functionalized Polyphenylene Dendrimers



X-ray Scattering: columnar order

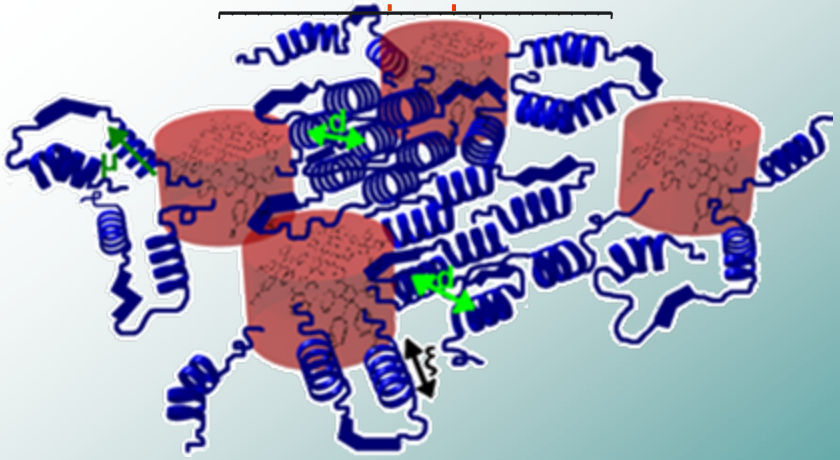
Solid state NMR: Peptide conformation





Short polypeptides (n < 16)

High order of columns,
Low order of peptide chains



Long polypeptides (n > 20)
Low order of columns,
High order of peptide chains
(α-helices)

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Motional averaging effects

$$\mathbf{H}_{CS} = \delta \cdot \tfrac{1}{2}(3\cos^2\theta - 1 - \eta\sin^2\theta\cos(2\varphi)) \cdot \mathbf{I}_Z$$ Anisotropic Chemical Shift

$$\mathbf{H}_D^{(ij)} = D_{ij} \cdot \tfrac{1}{2}(3\cos^2\theta - 1)(3\mathbf{I}_Z^{(i)}\mathbf{I}_Z^{(j)} - \mathbf{I}^{(i)}\mathbf{I}^{(j)})$$ Dipole-Diplole Coupling

$$\mathbf{H}_Q = \frac{e^2qQ}{2I(2I-1)\cdot\hbar} \cdot \tfrac{1}{2}(3\cos^2\theta - 1)(3\mathbf{I}_Z\mathbf{I}_Z - \mathbf{I}\cdot\mathbf{I})$$

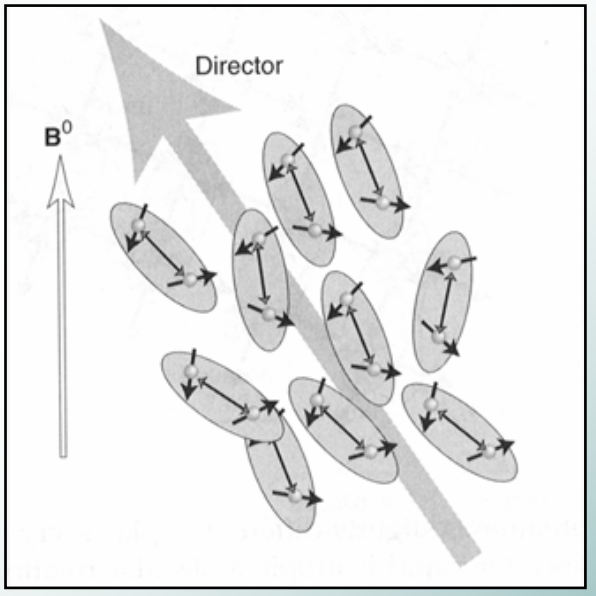
Quadrupole Coupling

Motional averaging:

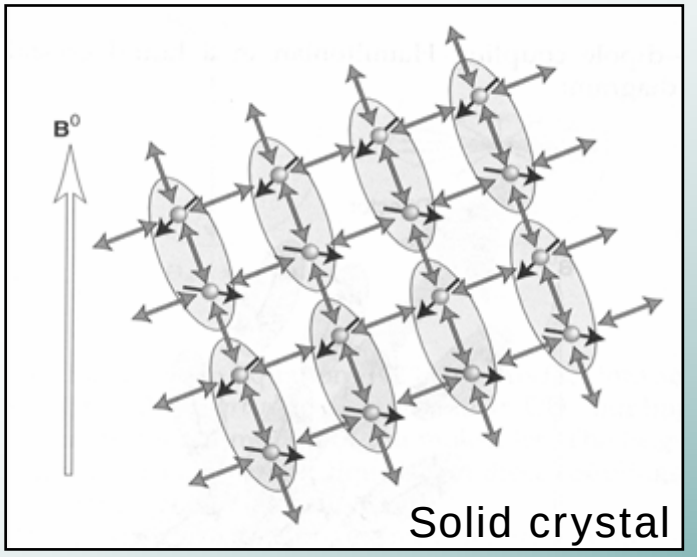
$$\int_0^{\pi}\int_0^{2\pi} \tfrac{1}{2}(3\cos^2\theta - 1)\, d\varphi \sin\theta d\theta \overset{!}{=} 0$$

order parameter S_{ij}:

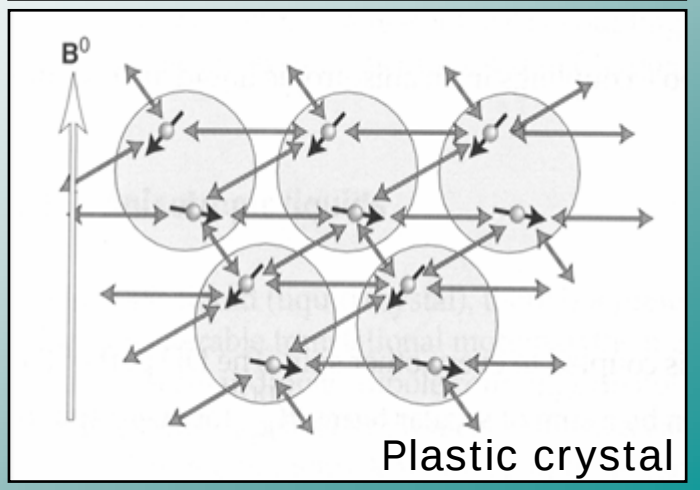
$$S_{ij} = \left\langle \tfrac{1}{2}(3\cos^2\theta - 1) \right\rangle$$



Liquid crystal

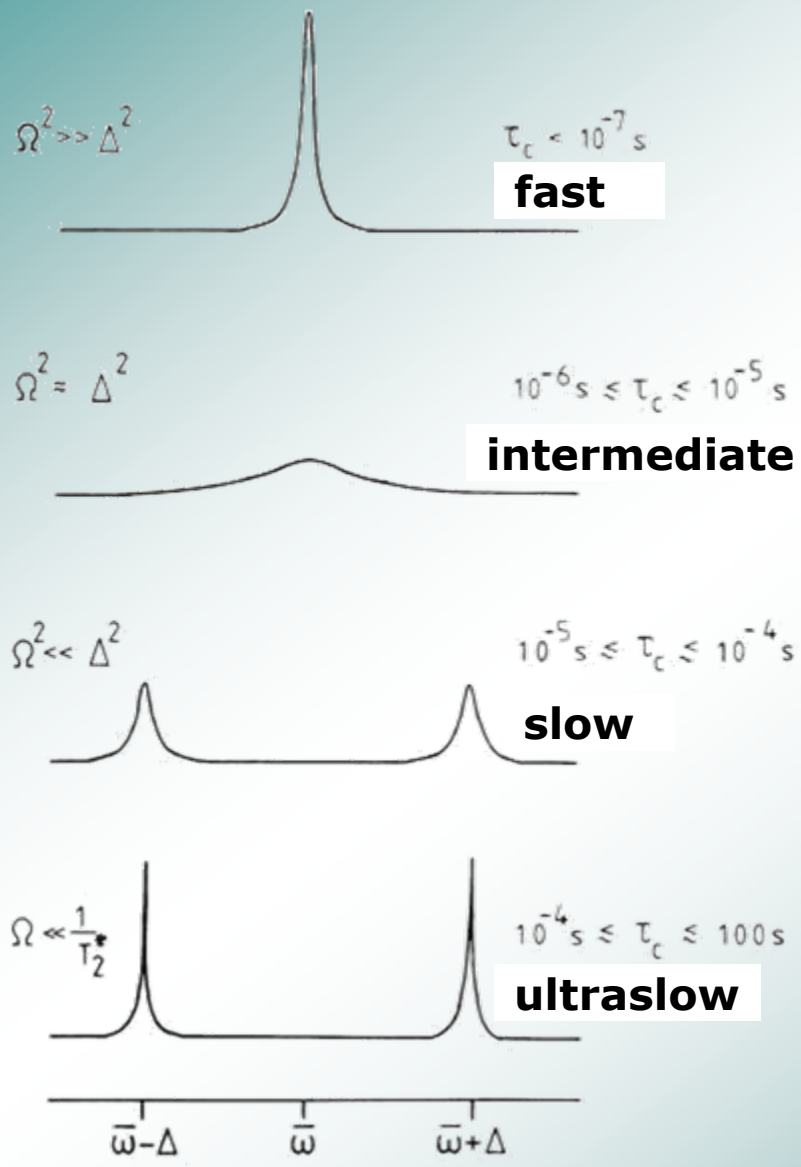


Solid crystal



Plastic crystal

Motional averaging effects



Basics: Two site jumps

(analogous to chemical exchange)

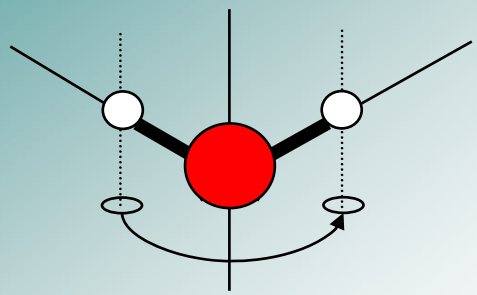
Calculated NMR line shapes resulting from interchange between two NMR frequencies.

Δ : coupling strength
Ω : exchange rate

The numerical values apply to ^{2}H NMR of deuterons in C-H bonds

Two-site jumps: CSA

^{1}H powder spectrum
of H_2O molecules
in crystalline $CaSO_4 \cdot 2H_2O$

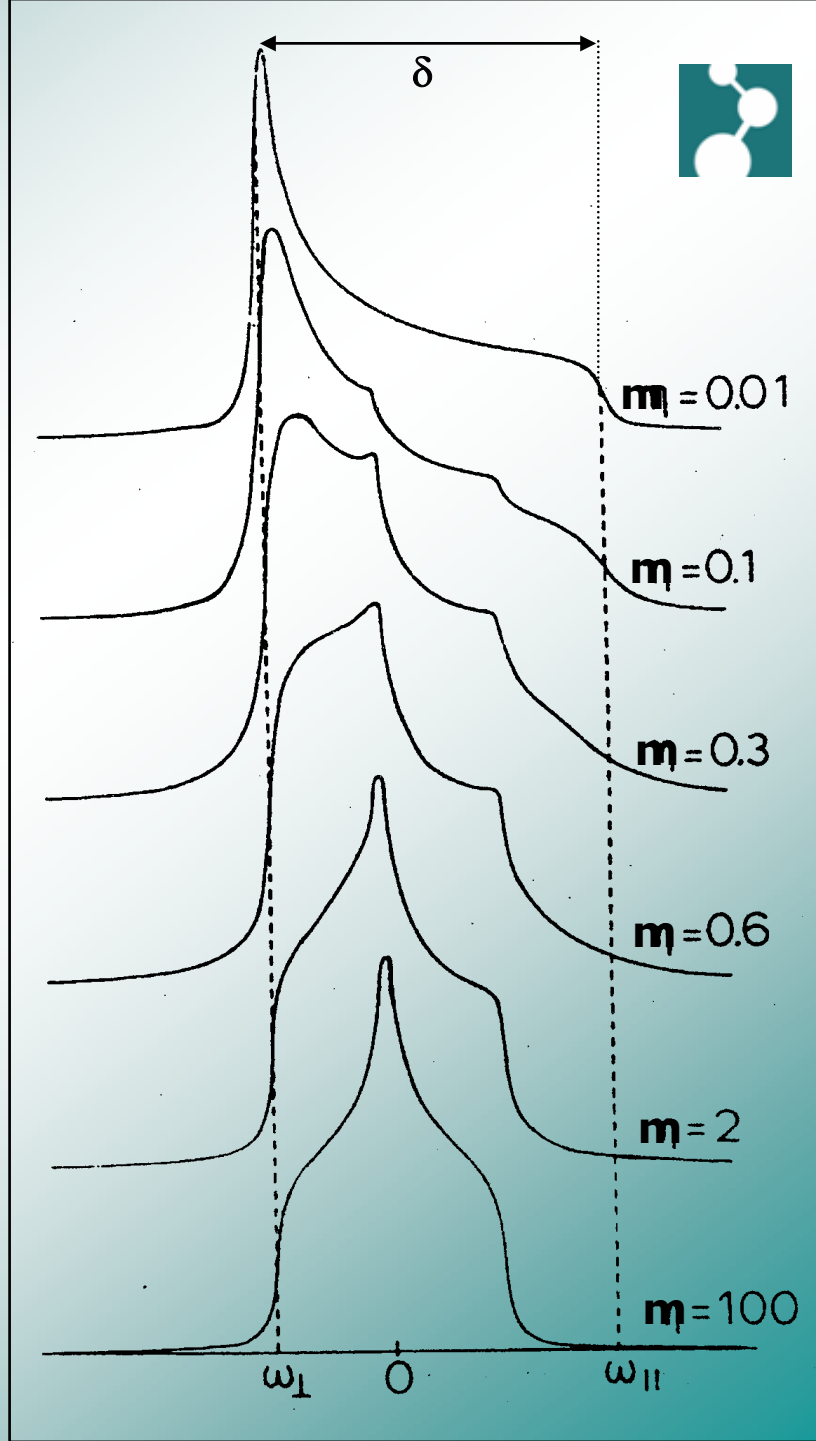


$$\mathbf{m} = {}^{k_{jump}}\!/_{\delta} = {}^{1}\!/_{\delta \cdot \tau_{jump}}$$

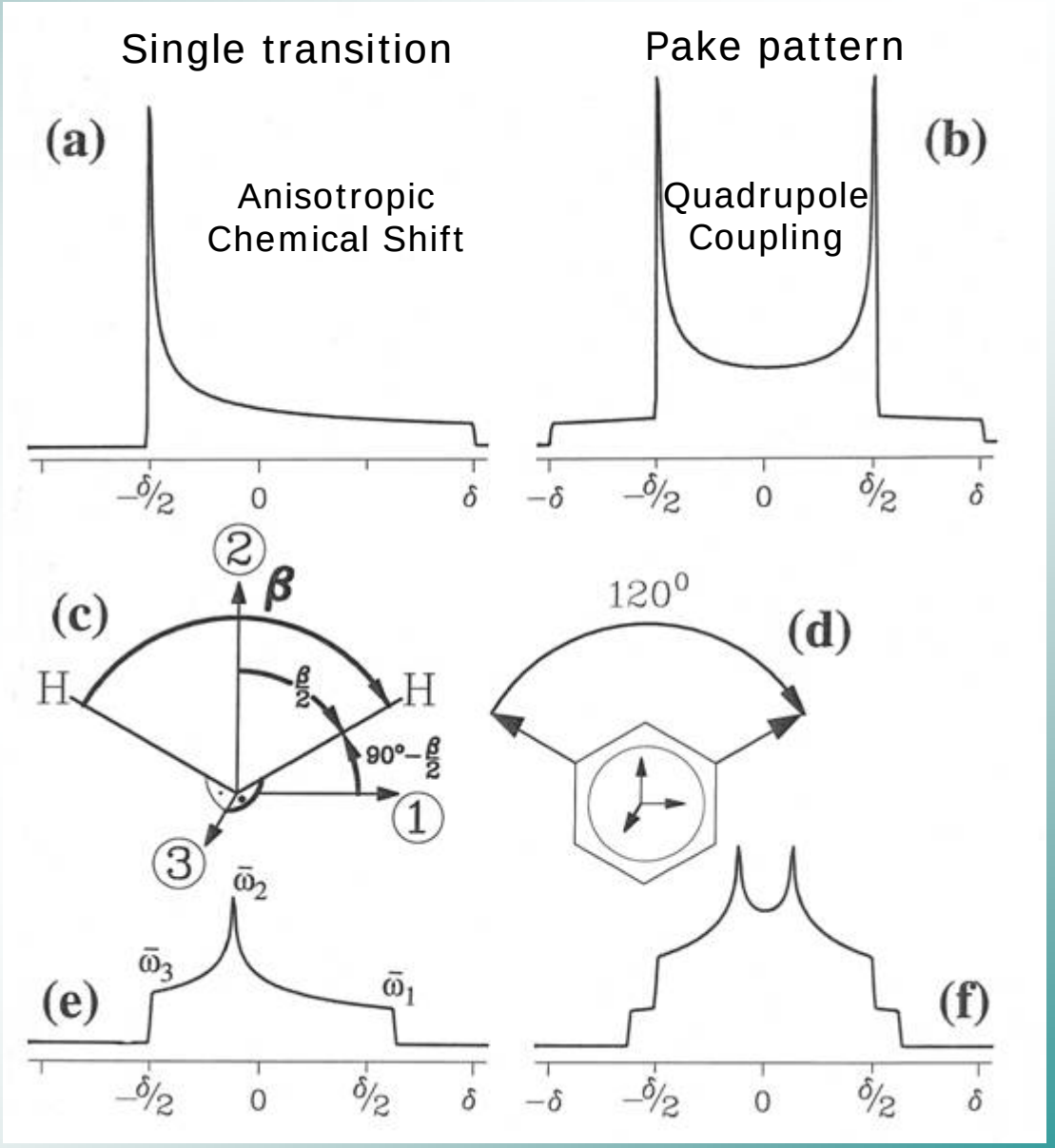
Two-site jump in solid:
Different frequencies depending on orientation.

Result in fast motion limit:
Averaged interaction tensor

Line shape analysis yields both:
Timescale and geometry of motion



Two-site jumps: CSA, DDC and QC

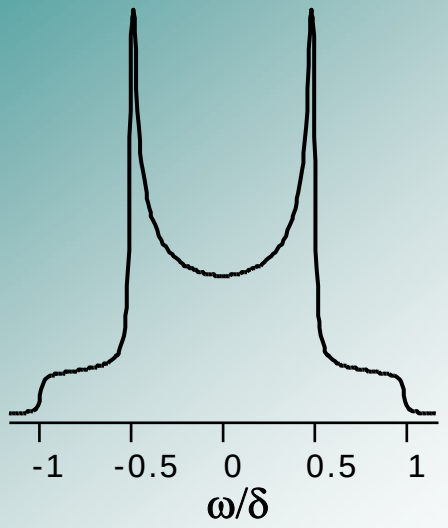


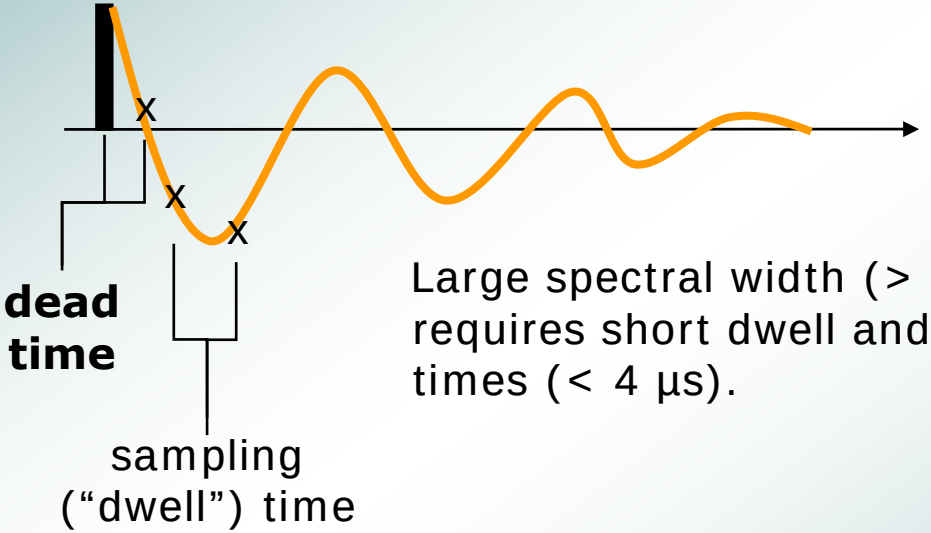
Example: Phenyl 180° ring flip: Reorientation C-H bonds by $\beta = 120°$

Averaged principal axes (1), (2) and (3)

$\bar{\delta} = 5/8\ \delta$; $\bar{\eta} = 0.6$

The “solid echo” experiment

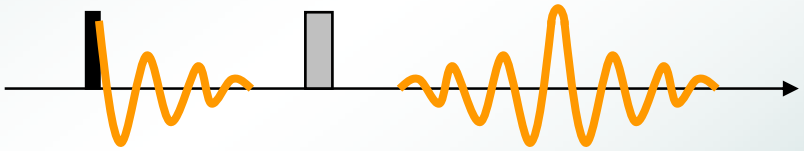




Large spectral width (> 250 kHz) requires short dwell and dead times (< 4 µs).

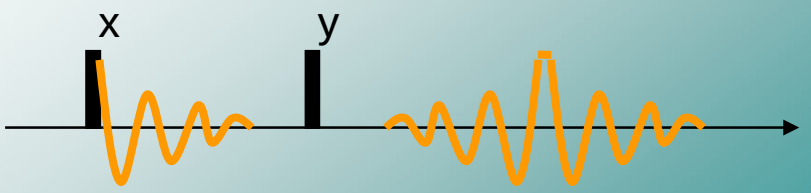
Overcoming the dead-time problem by echo experiments:

spin (“Hahn”) echo



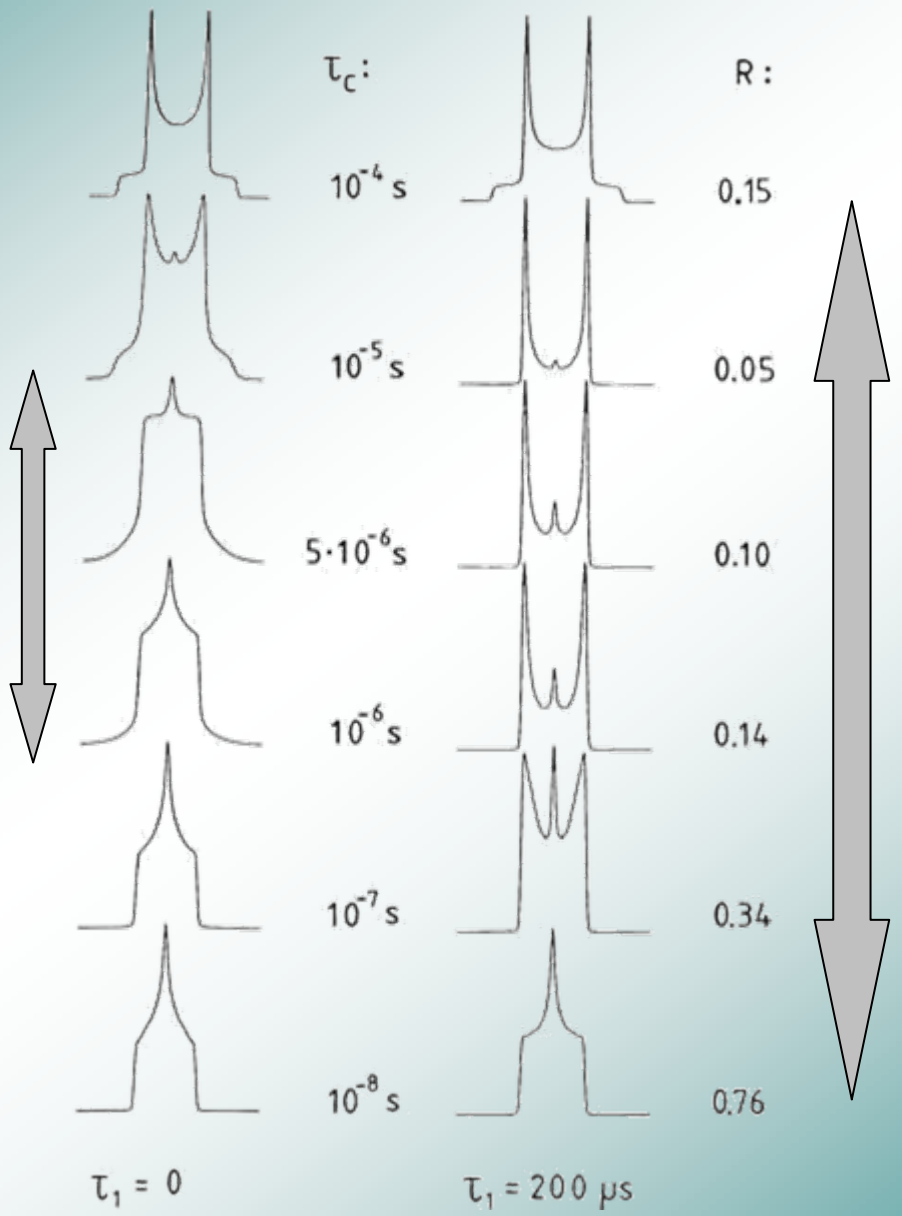
refocuses “linear-spin” interactions

solid (“Solomon”) echo



refocuses “**bi**linear-spin” interactions

Motions in the "solid echo" experiment: Increased dynamic range

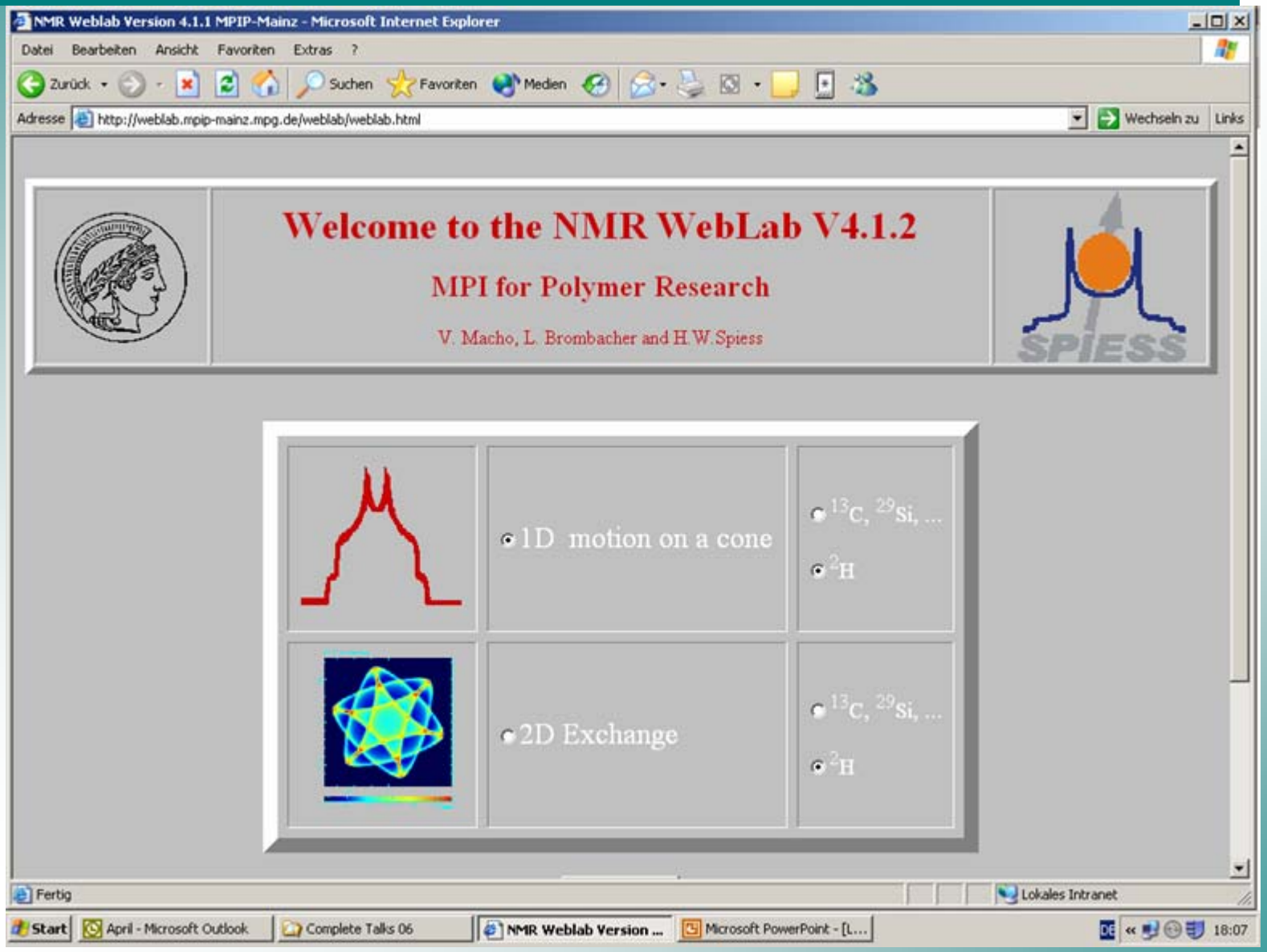


Absorption spectra: Line shape changes within one order of magnitude

Solid echo spectra: Line shape changes over several orders of magnitude,

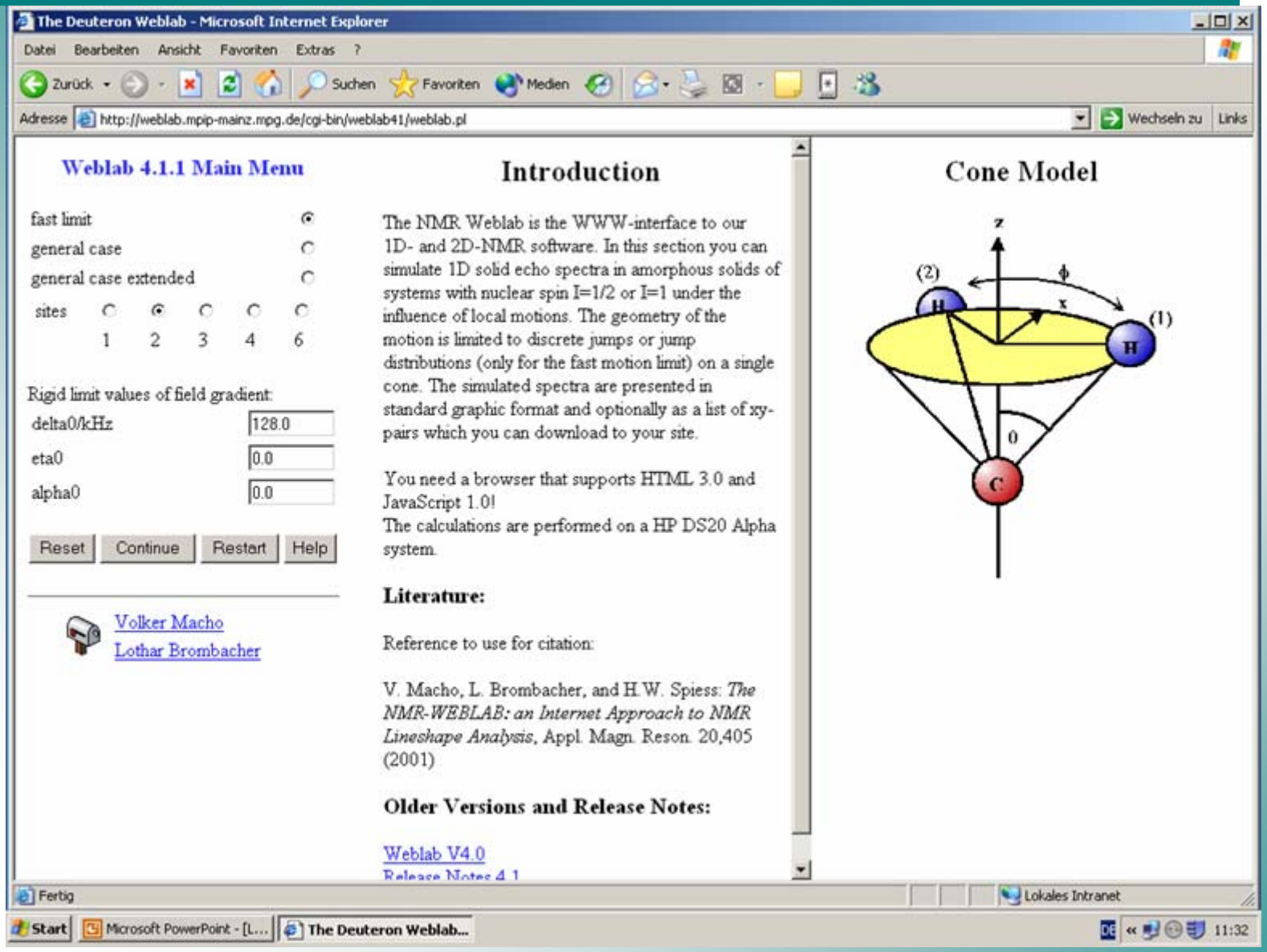
But: loss of signal!

NMR line shapes conveniently calculated by NMR Weblab



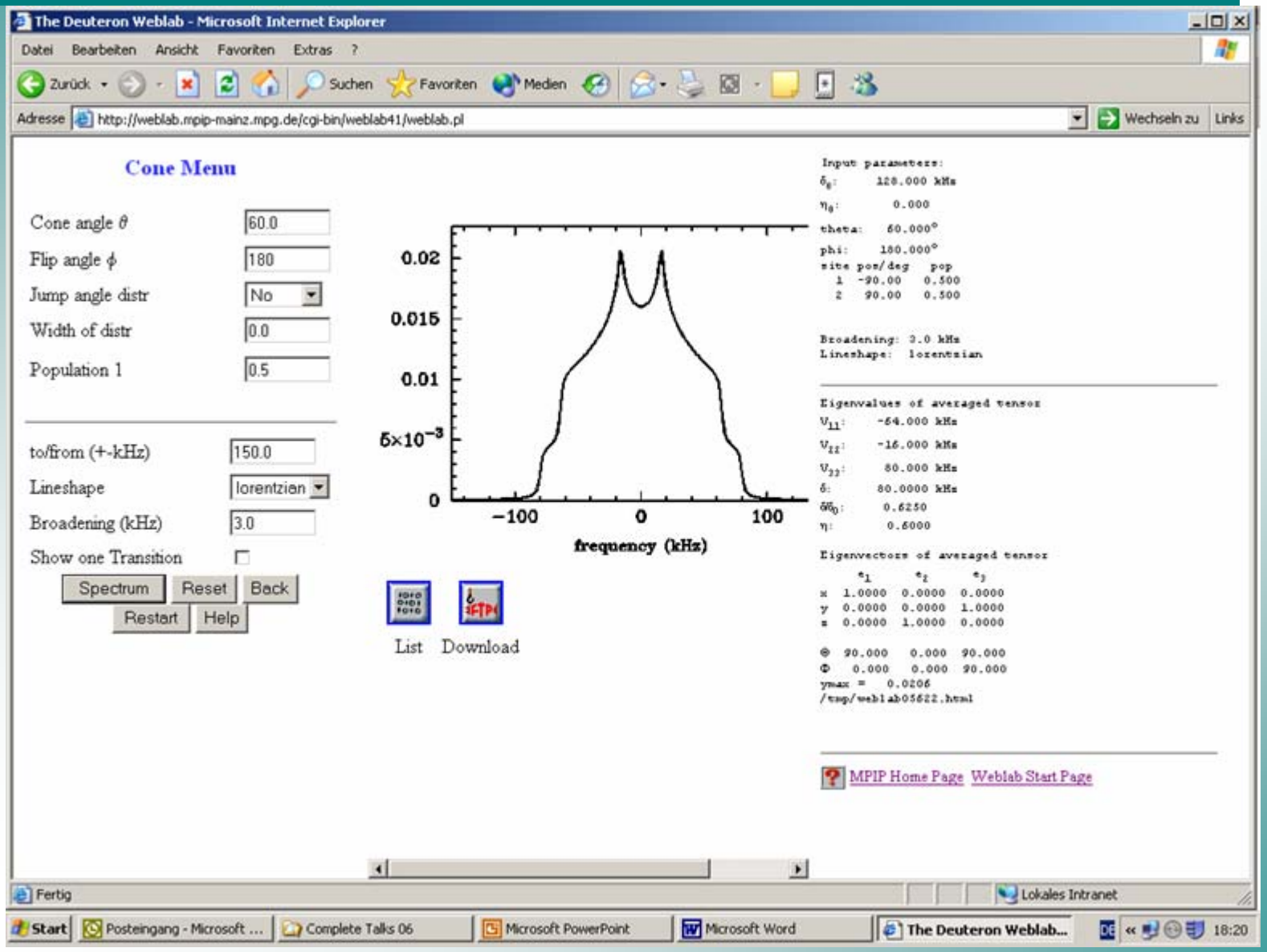
http://weblab.mpip-mainz.mpg.de/weblab/weblab.html

NMR Weblab: How to use it



http://weblab.mpip-mainz.mpg.de/weblab/weblab.html

NMR Weblab: Example phenyl flip

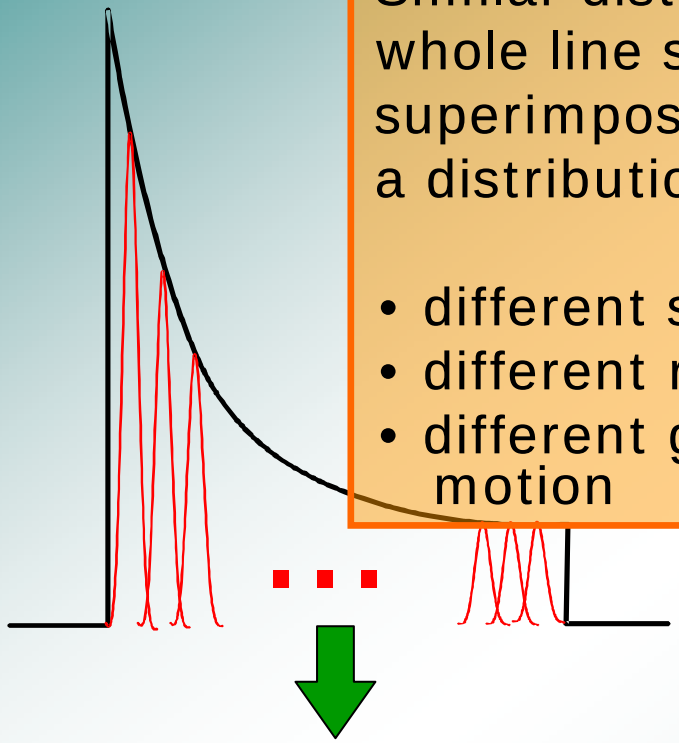


http://weblab.mpip-mainz.mpg.de/weblab/weblab.html

Inhomogeneous and homogeneous line broadening

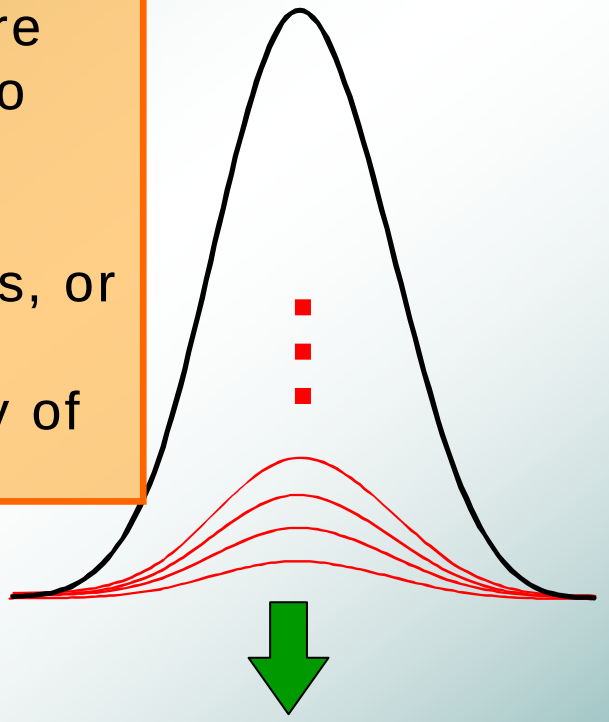
Similar distinction if whole line shapes are superimposed due to a distribution of

- different structures, or
- different rates, or
- different geometry of motion



Overall resonance consists of indiviual sharp lines and represents the sum over all different orientations

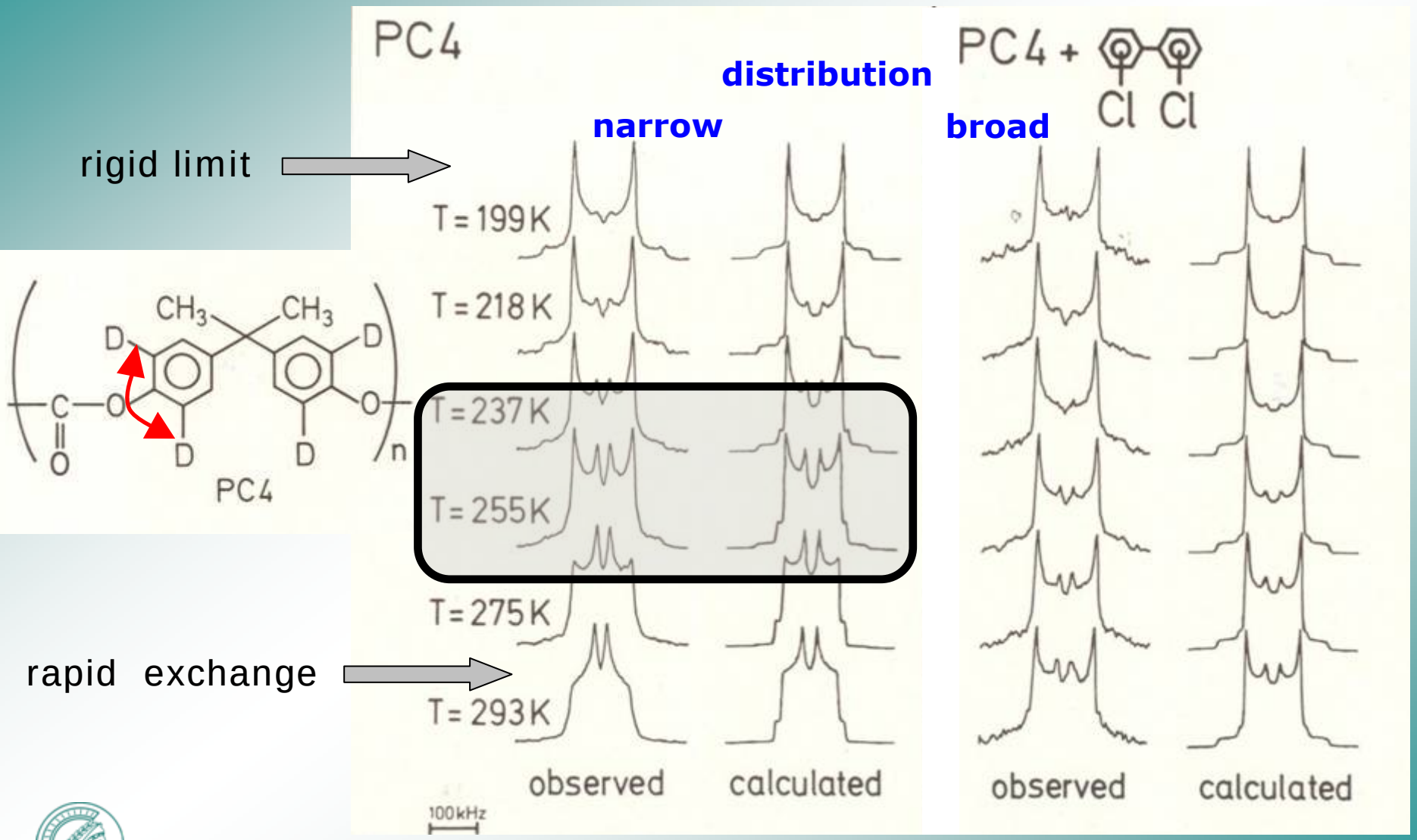
Inhomogeneous:
CSA, quadrupolar, dipolar two-spin



Due to spin-spin couplings the energy levels of single transitions (resonance lines) are no longer degenerate, but split into a multitude of levels

Homogeneous:
dipolar multi-spin

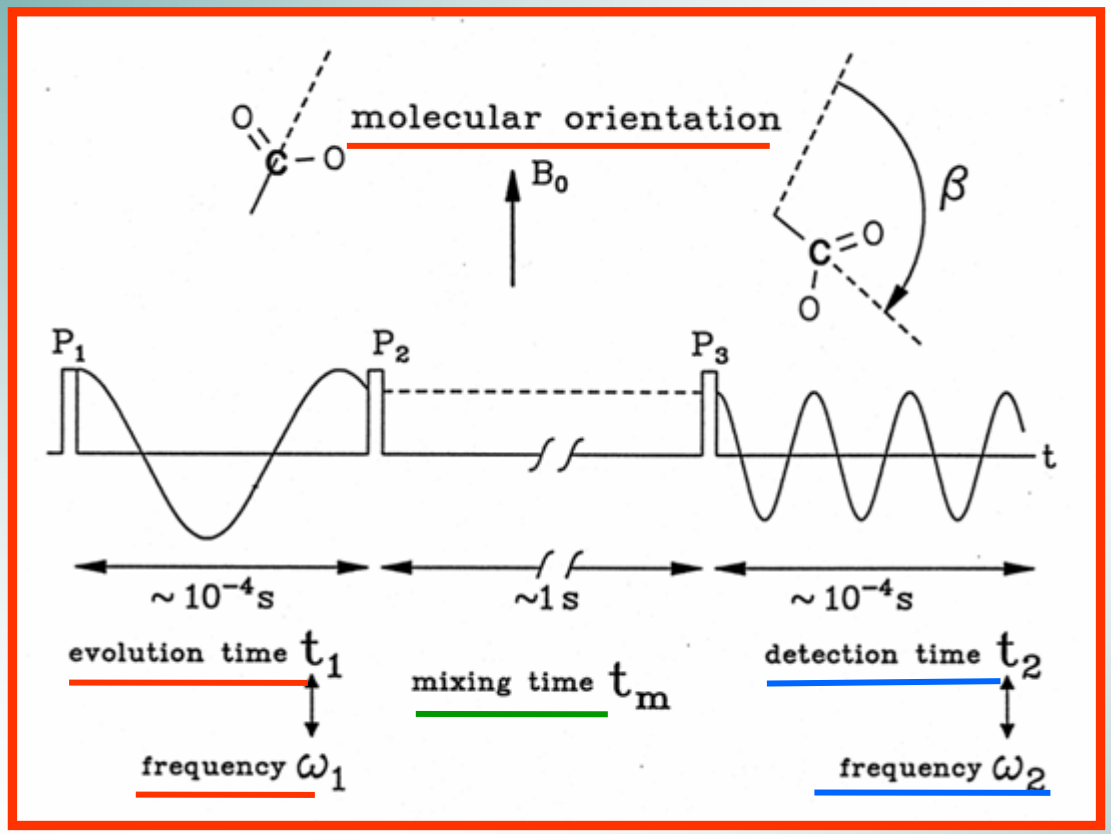
Example of heterogeneous rate distribution



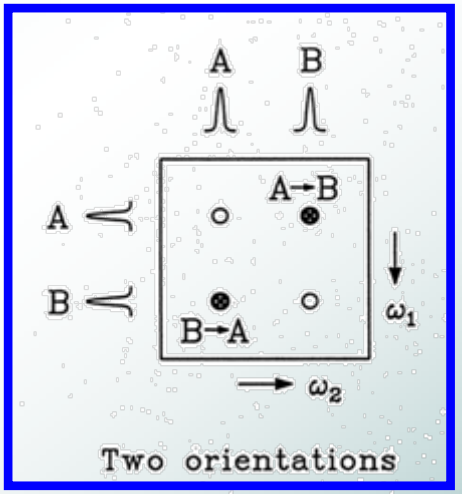
Superposition of line shapes for different rates

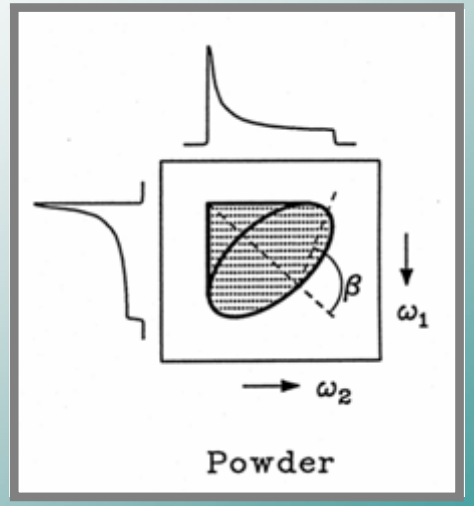
2D-Exchange-Spectroscopy: Simplicity

Determine geometry and time scale of motions directly and in real time



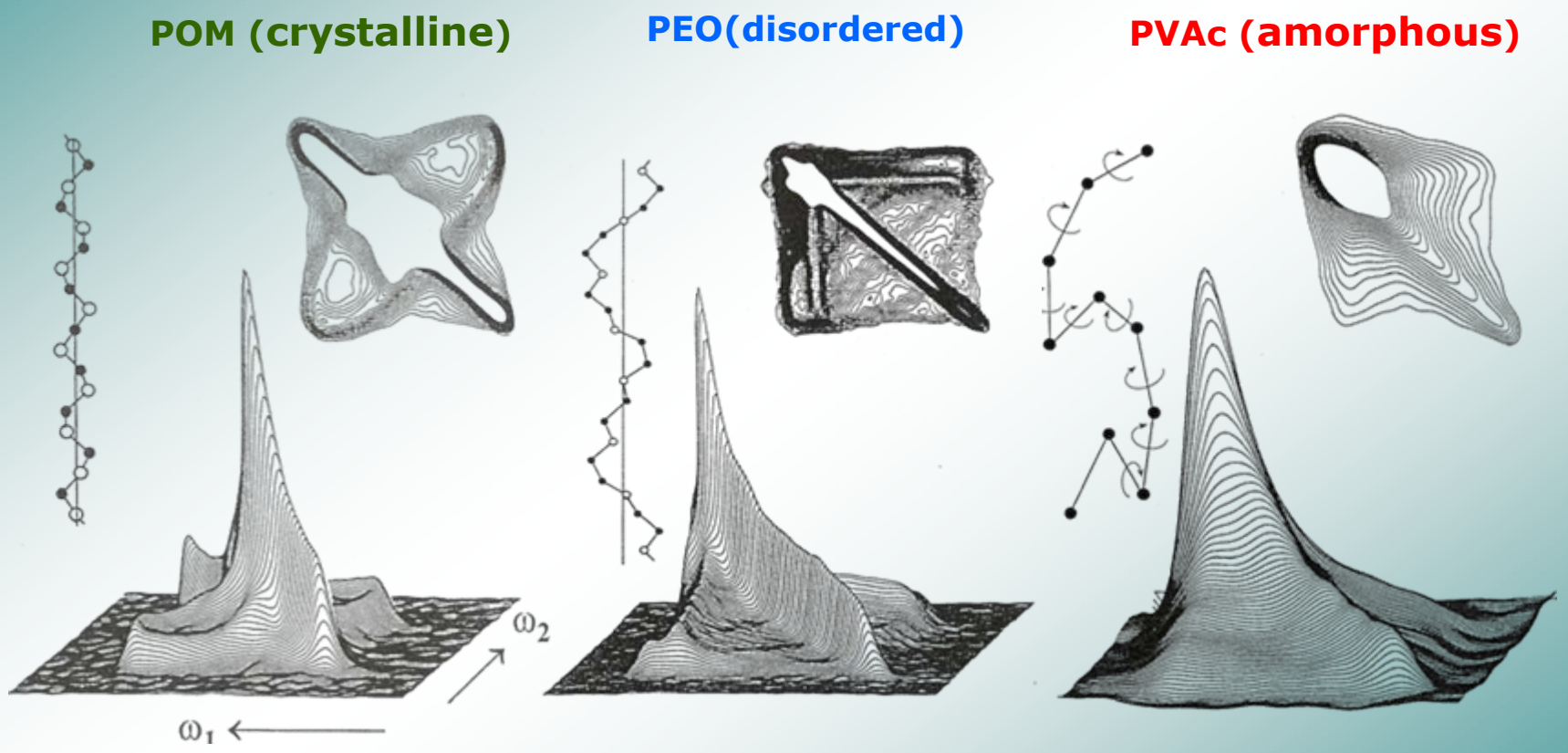
Pulse Sequence





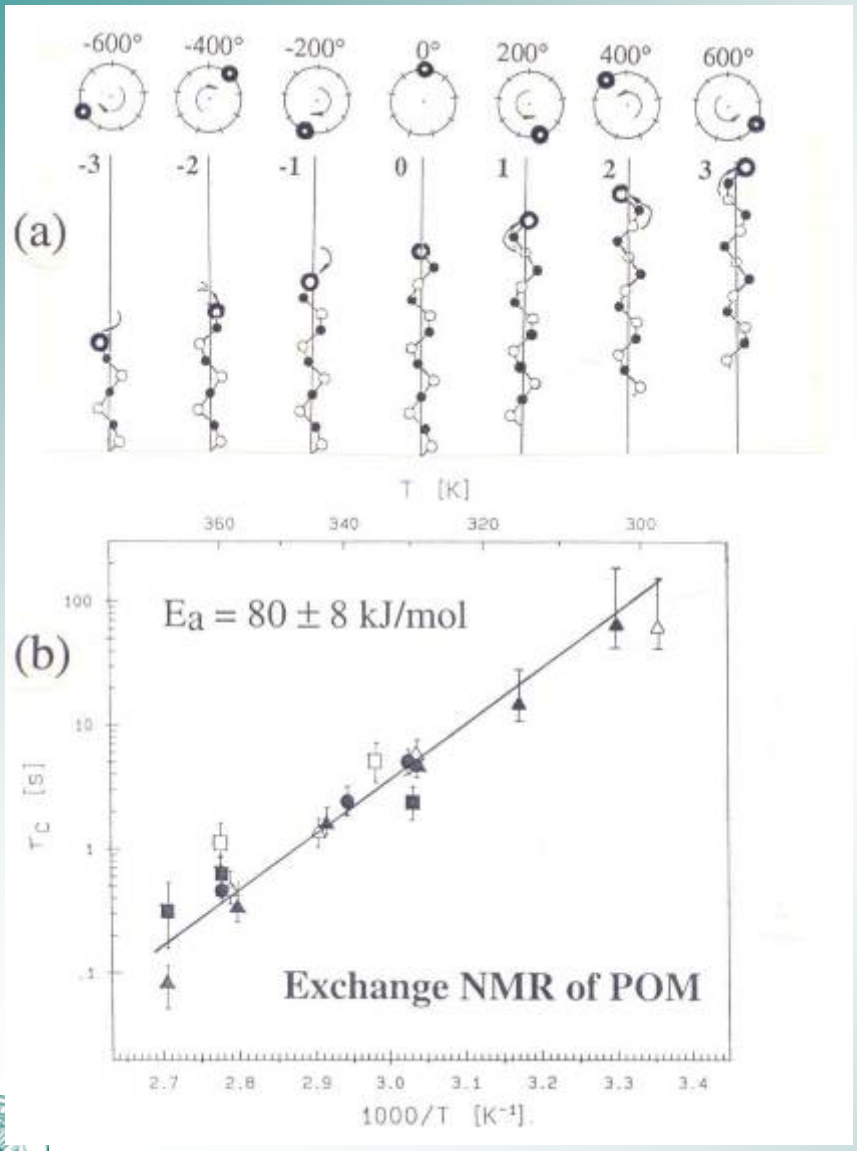
Spectra

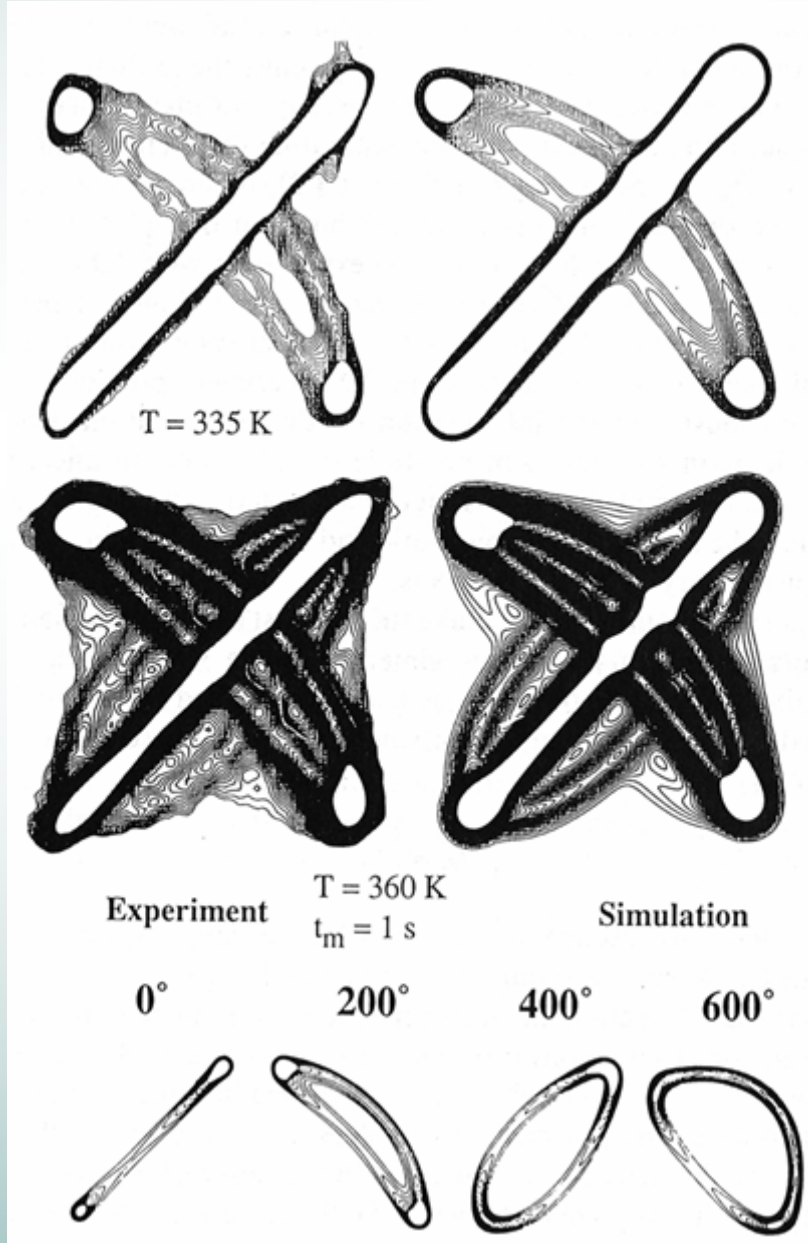
Geometry of Chain Motion in Polymers



^{13}C 2D Exchange NMR Spectra of Polymers with Different Degrees of Disorder

Helical jumps in polymer crystallites: POM





Chain Folding, Chain Diffusion and Drawability

Sample:
UHMW-PE
(M_w = 3.4 M)

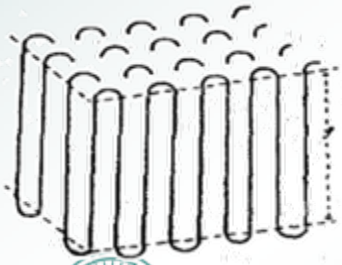
Drawability

Solution Crystallized:
Drawable

Melt Crystallized:
Not Drawable

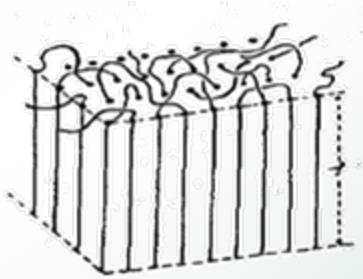
Morphology

Ordered



Solution Crystallized

Disordered

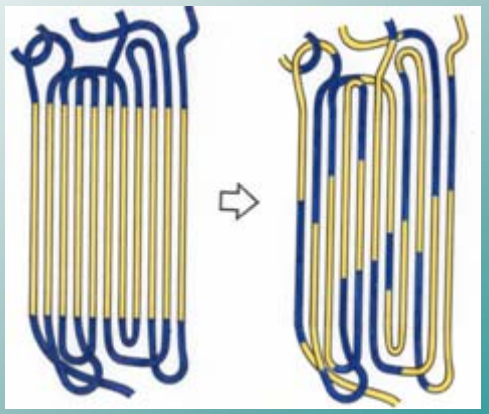


Melt Crystallized

Chain motion

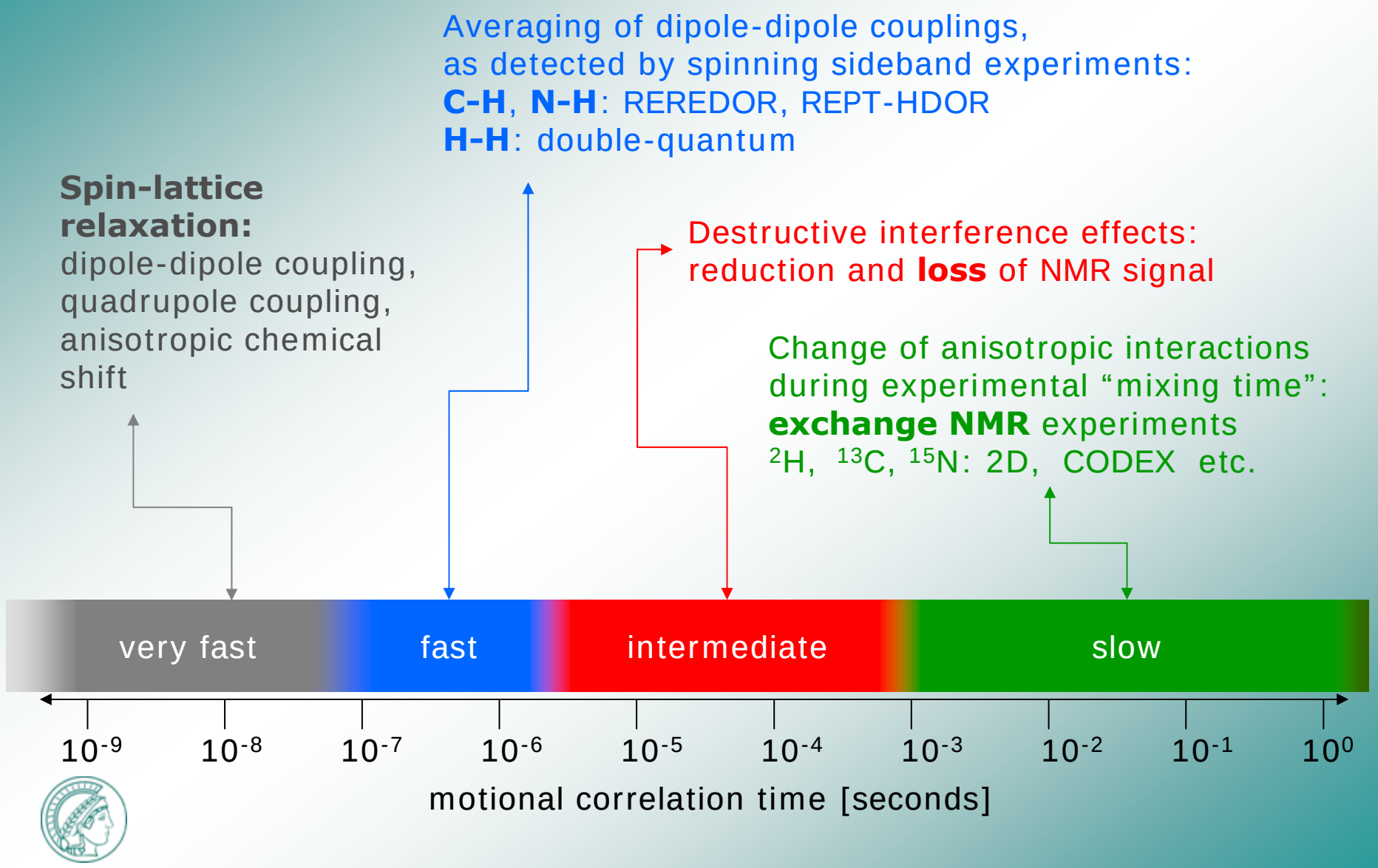
Local

Chain diffusion



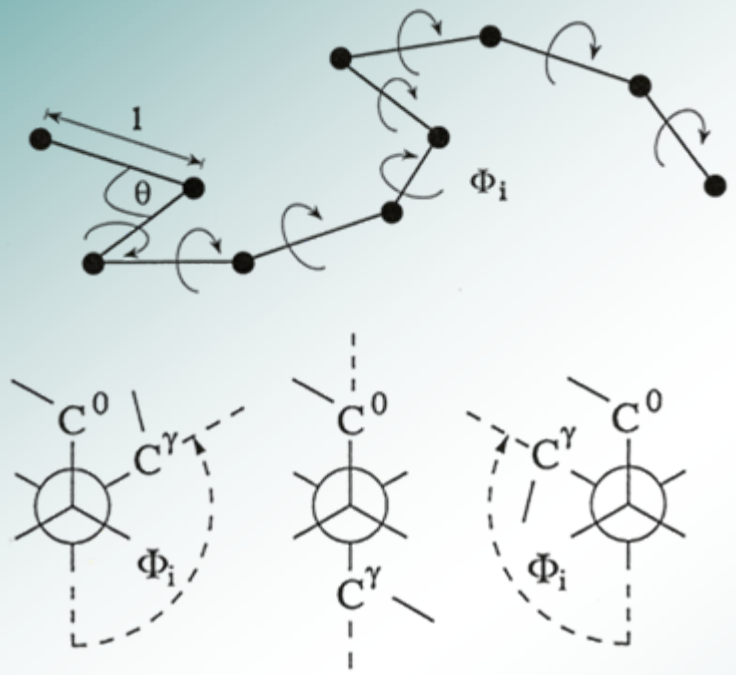
Collective

Timescales of Molecular Dynamics Accessible by NMR

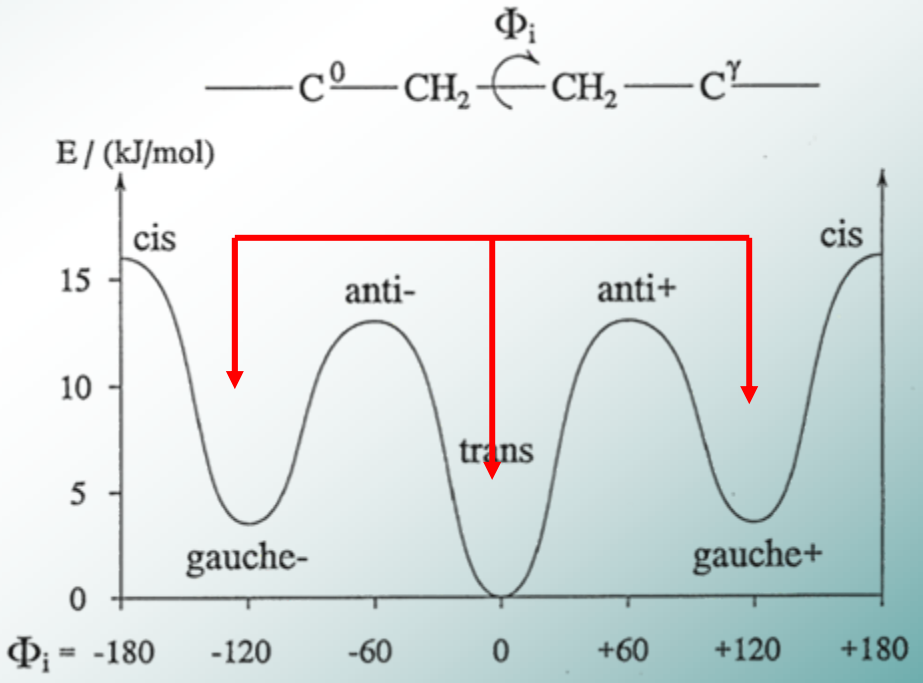


Conformational Dynamics at the Glass Transition

Polymer Chain



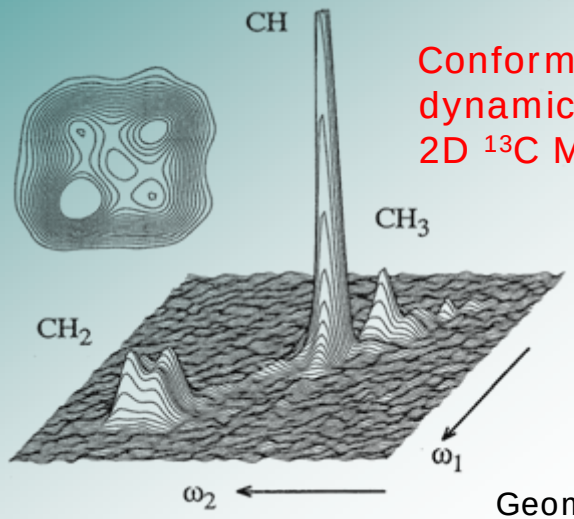
Potential Energy



Sensitivity of ^{13}C Chemical Shifts on Conformation :

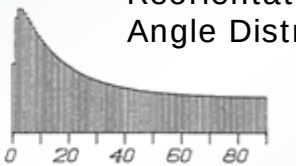
Gamma - *gauche* effect:
- 5,2 ppm in alkanes

Chain Dynamics of Atactic Poly(propylene) at the Glass Transition



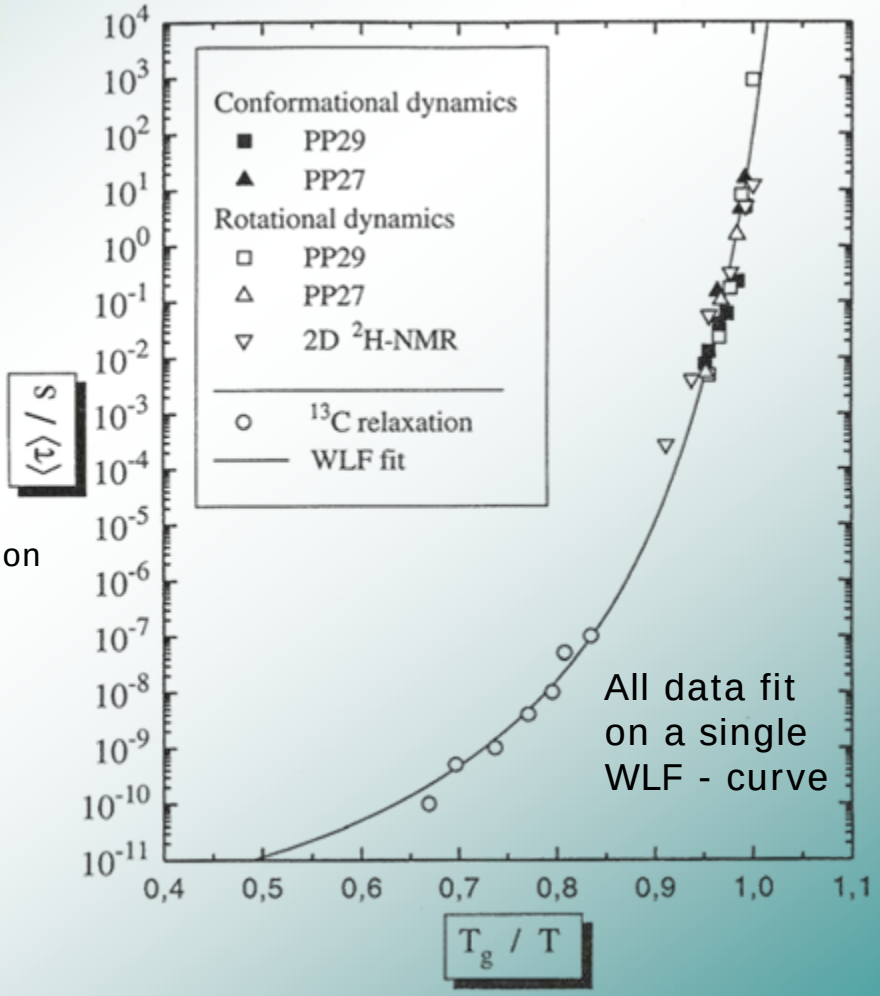
Conformational dynamics from 2D ^{13}C MAS NMR

Geometry: Reorientational Angle Distribution



Rotational dynamics from 2D ^{2}H NMR

Conformational transitions, but no defined geometry

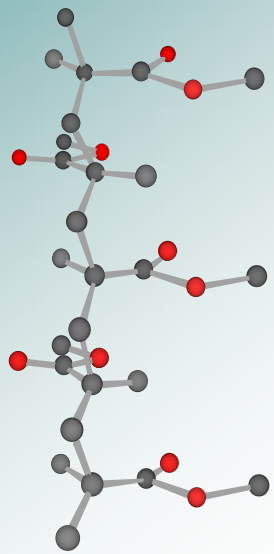


Correlation Times of Chain Motion from different NMR experiments

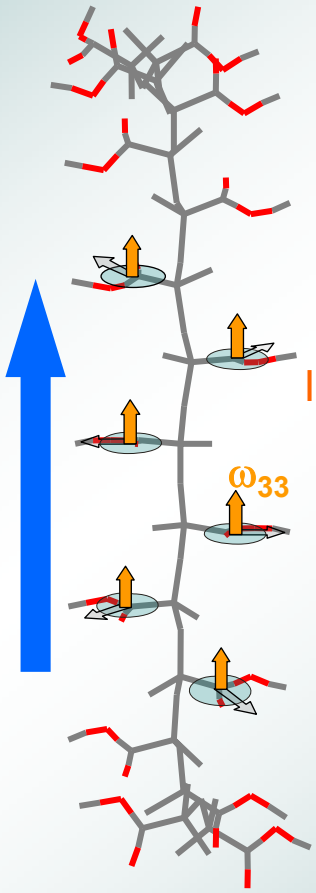
Structure Schemes of Syndiotactic and Isotactic Poly-(Methyl-Methacrylate)

n-alkyl-methacrylates contain extended chain segments

schematic structure



syndiotactic

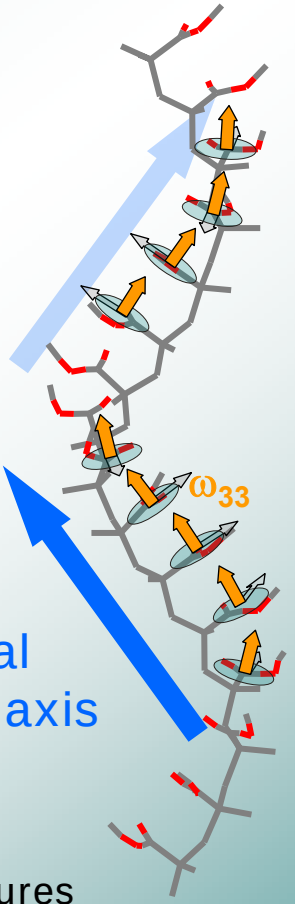


local chain-axis

Example: PMMA

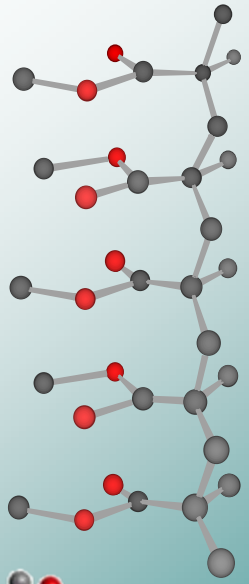
NMR probes local chain-axis through ω_{33}

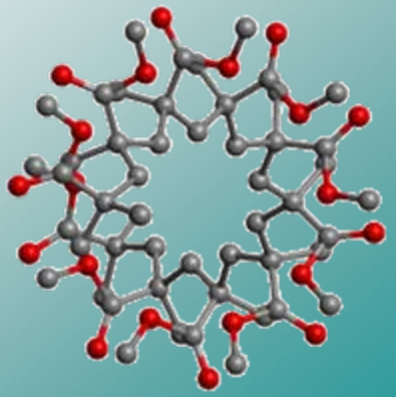
isotactic



local chain-axis

schematic structure





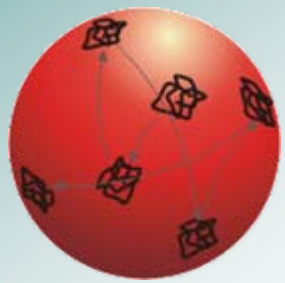
crystal structures

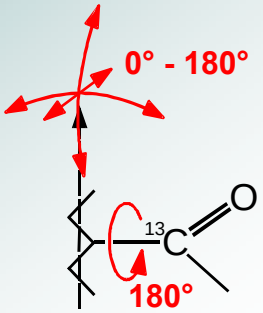
a-PEMA: Two-step Randomization of Chain Motion

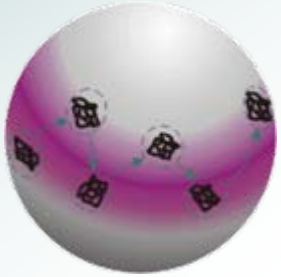
+ randomization of chain motion

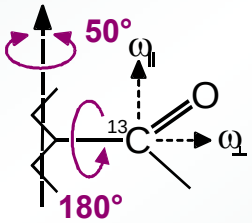
+ anisotropic chain motion

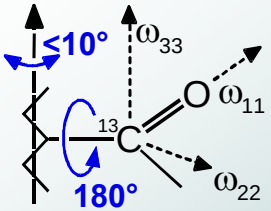
rigid + fractional sidegroup flips

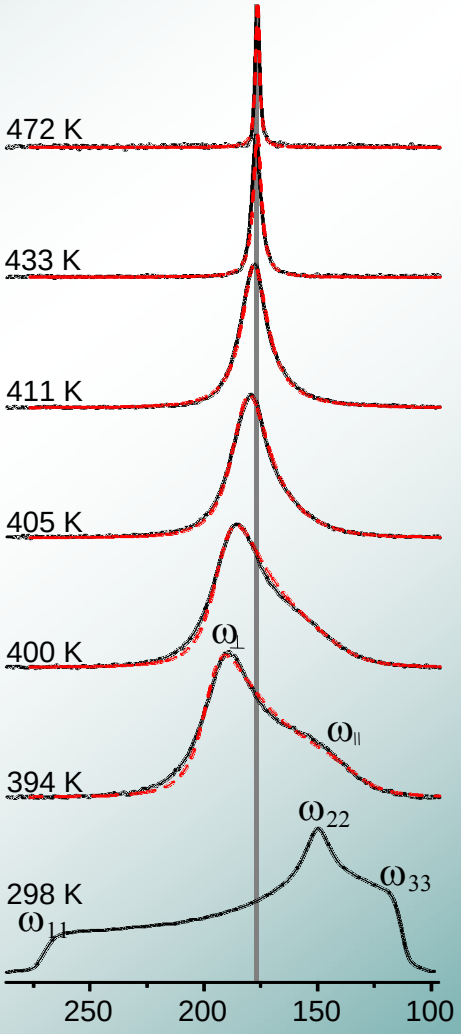










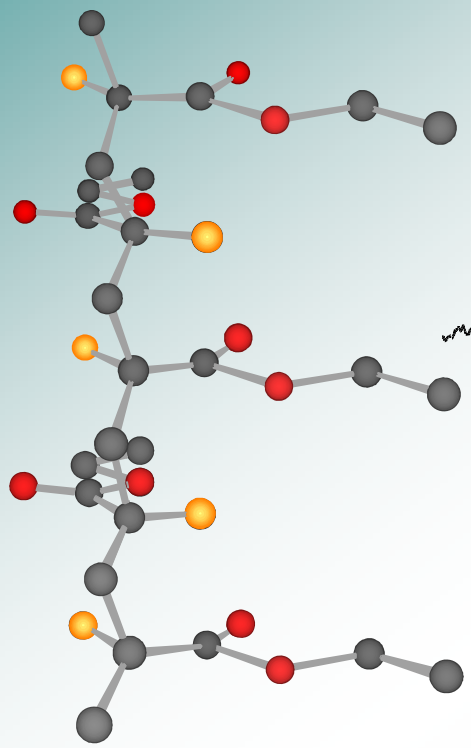


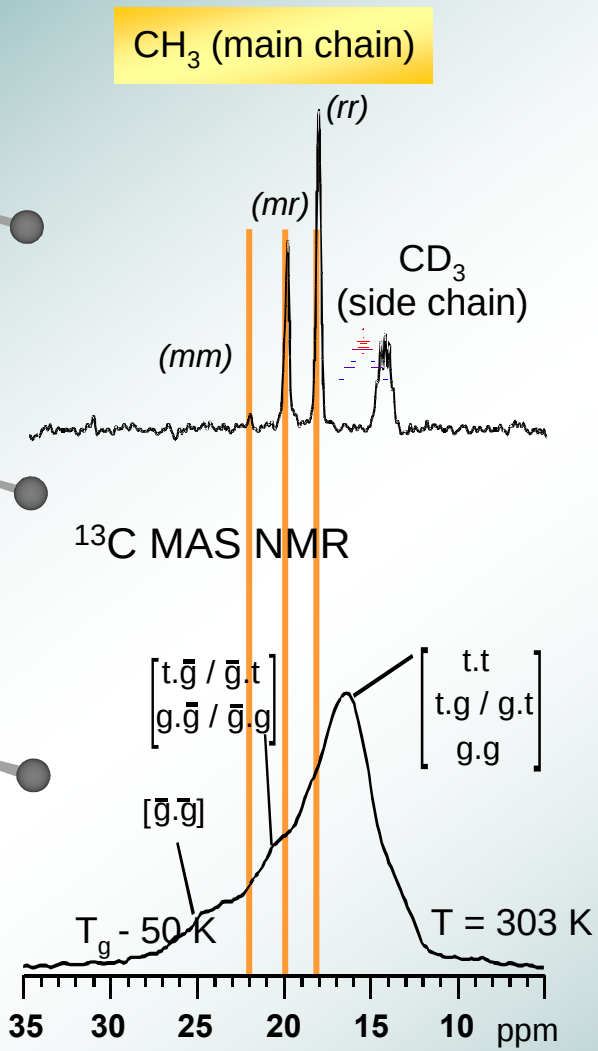
melt melt melt melt T_g glass

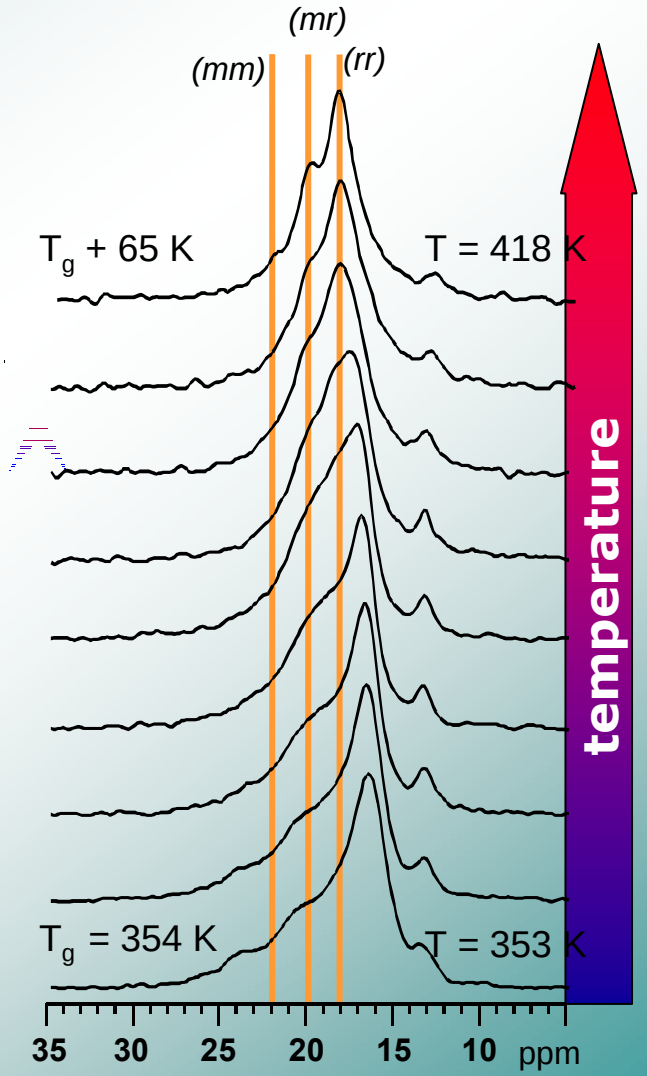
T_g = 354 K

1D ^{13}C NMR: experiment, simulation

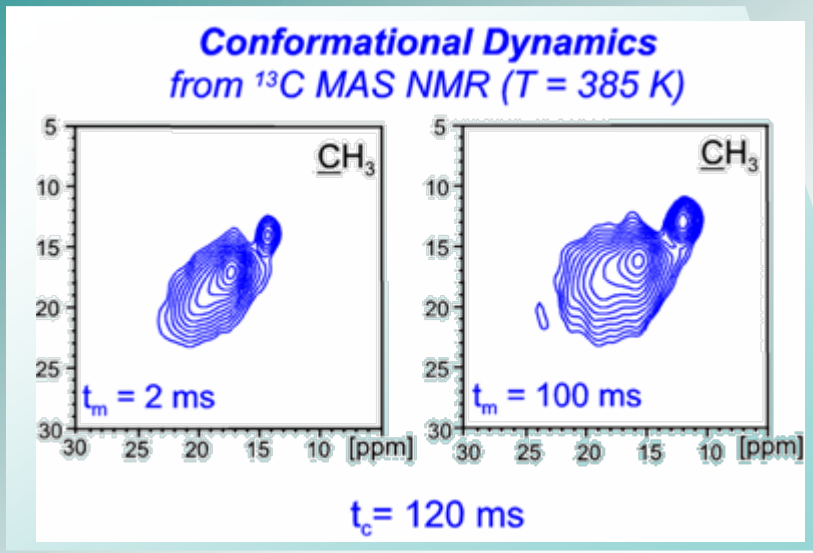
s-PEMA: Conformation and Conformational Dynamics

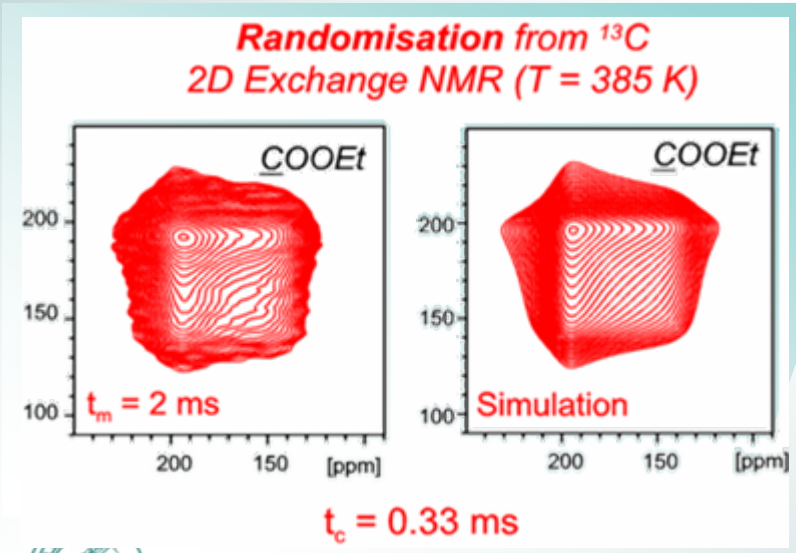




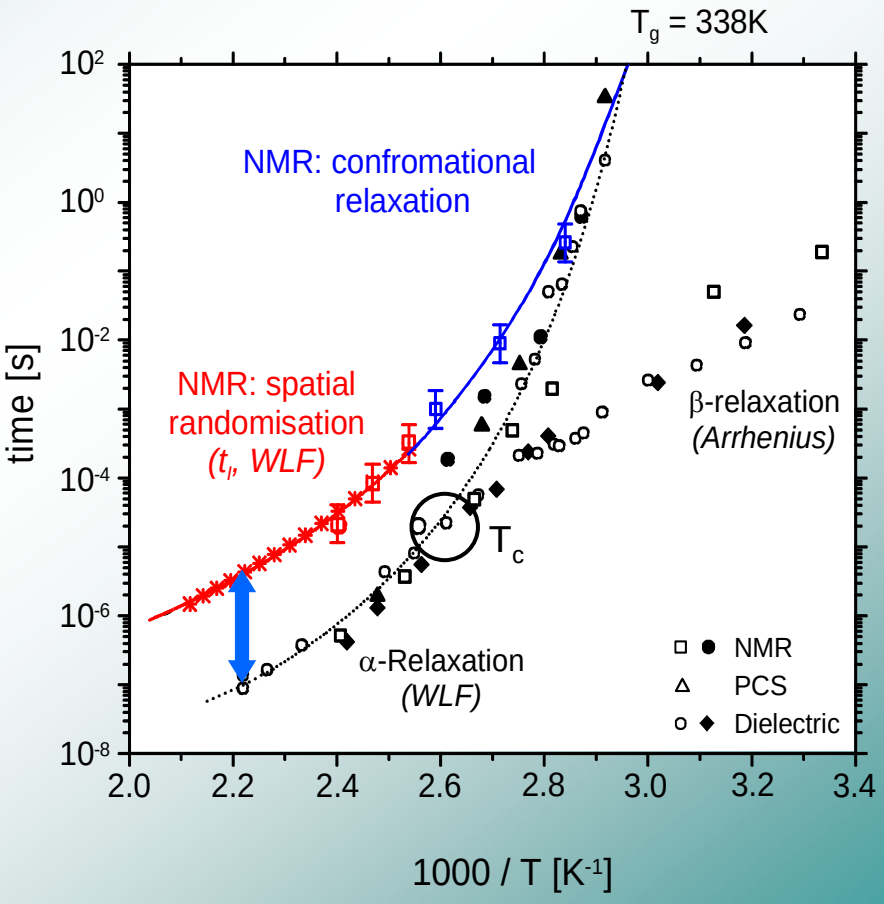


Separation of Dynamic Timescales in PEMA-Melts





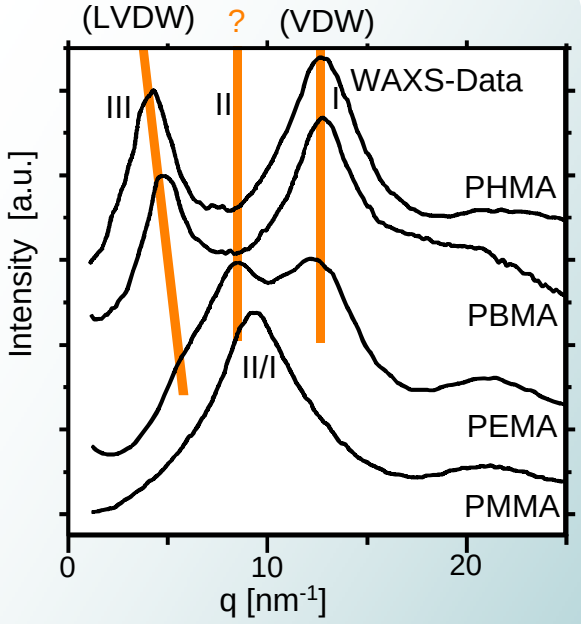
Correlation Times from NMR, PCS, Dielectrics

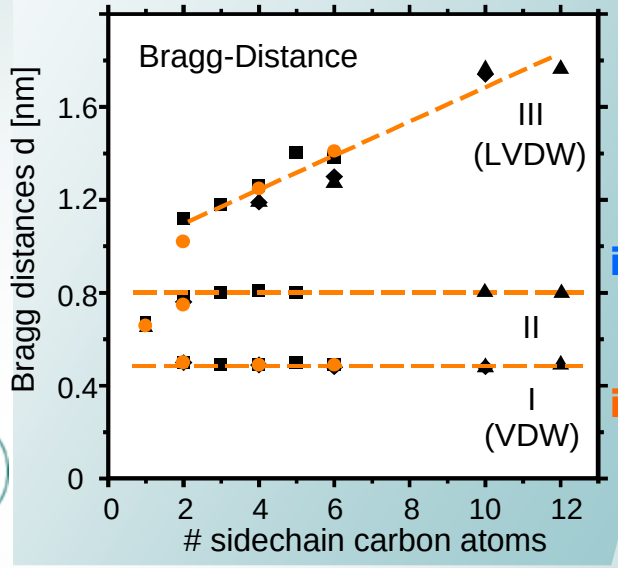


Difference in time scale (factor 50): consistent with length scale 7 repeat units

Intersegmental Order in Poly(methacrylates): WAXS

X-Ray Scattering



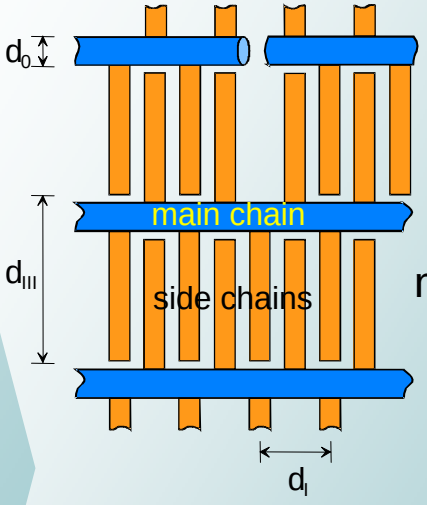


inter layer

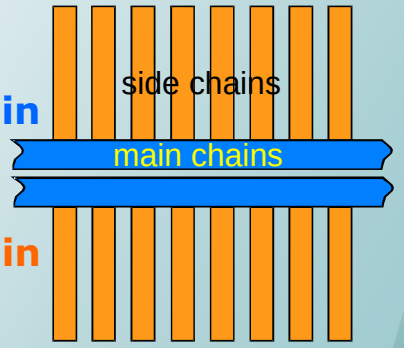
inter chain

intra chain

syndiotactic PEMA

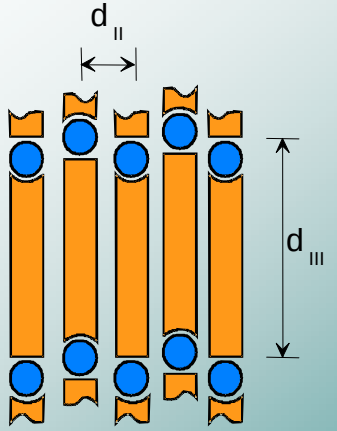


isotactic PEMA



X-Ray patterns reminiscent of stiff macromolecules with flexible sidechains

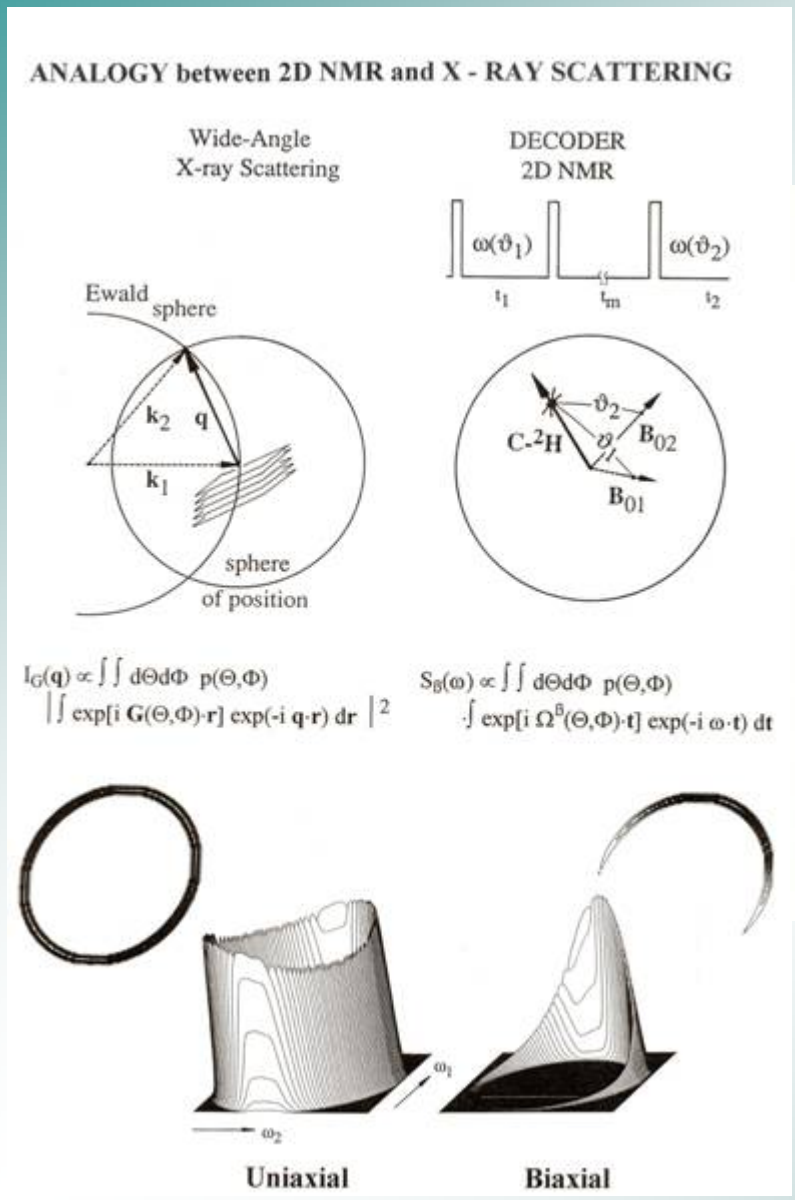
monolayer



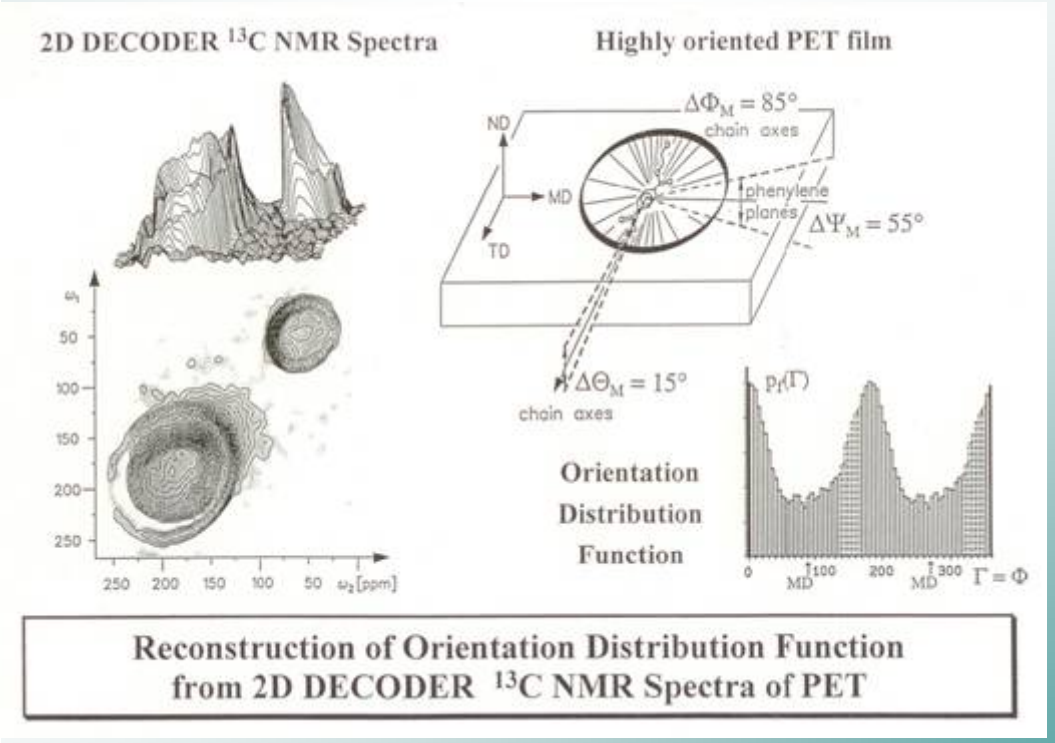
bilayer

„layered nano aggregates"

2D DECODER NMR for Ordered Systems



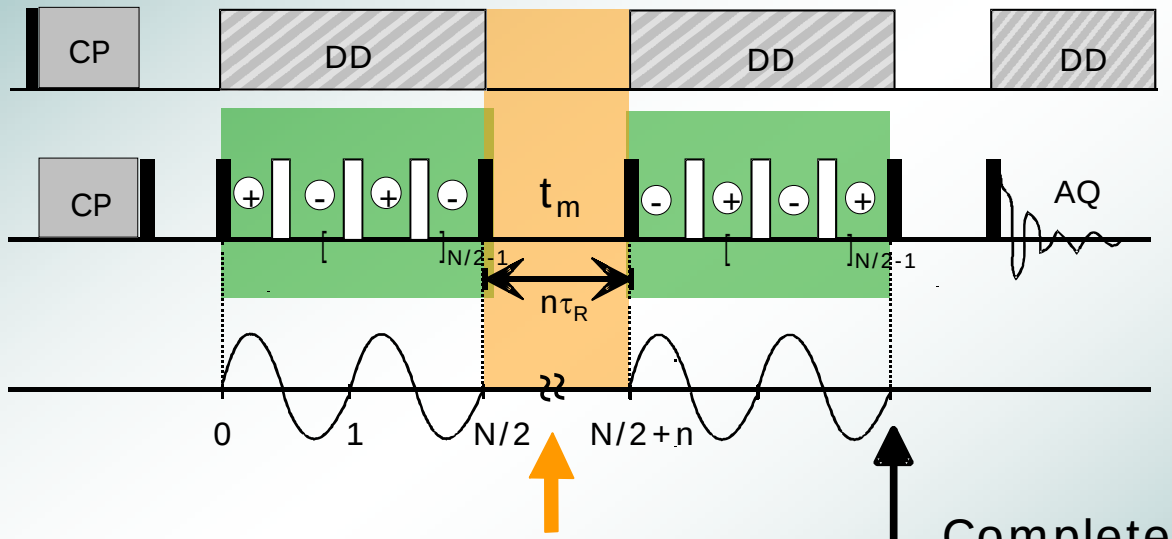
Example: Biaxially stretched PET

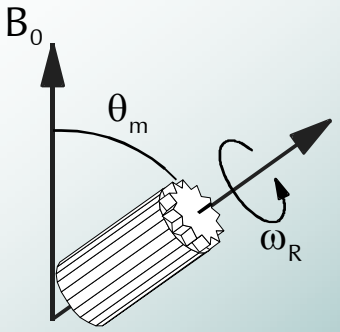


2D exchange with sample flip rather than molecular motion

Recoupling CSA: CODEX

CODEX: Centreband-Only Detection of Exchange
Approach: Recoupling the chemical-shift anisotropy (CSA) under MAS



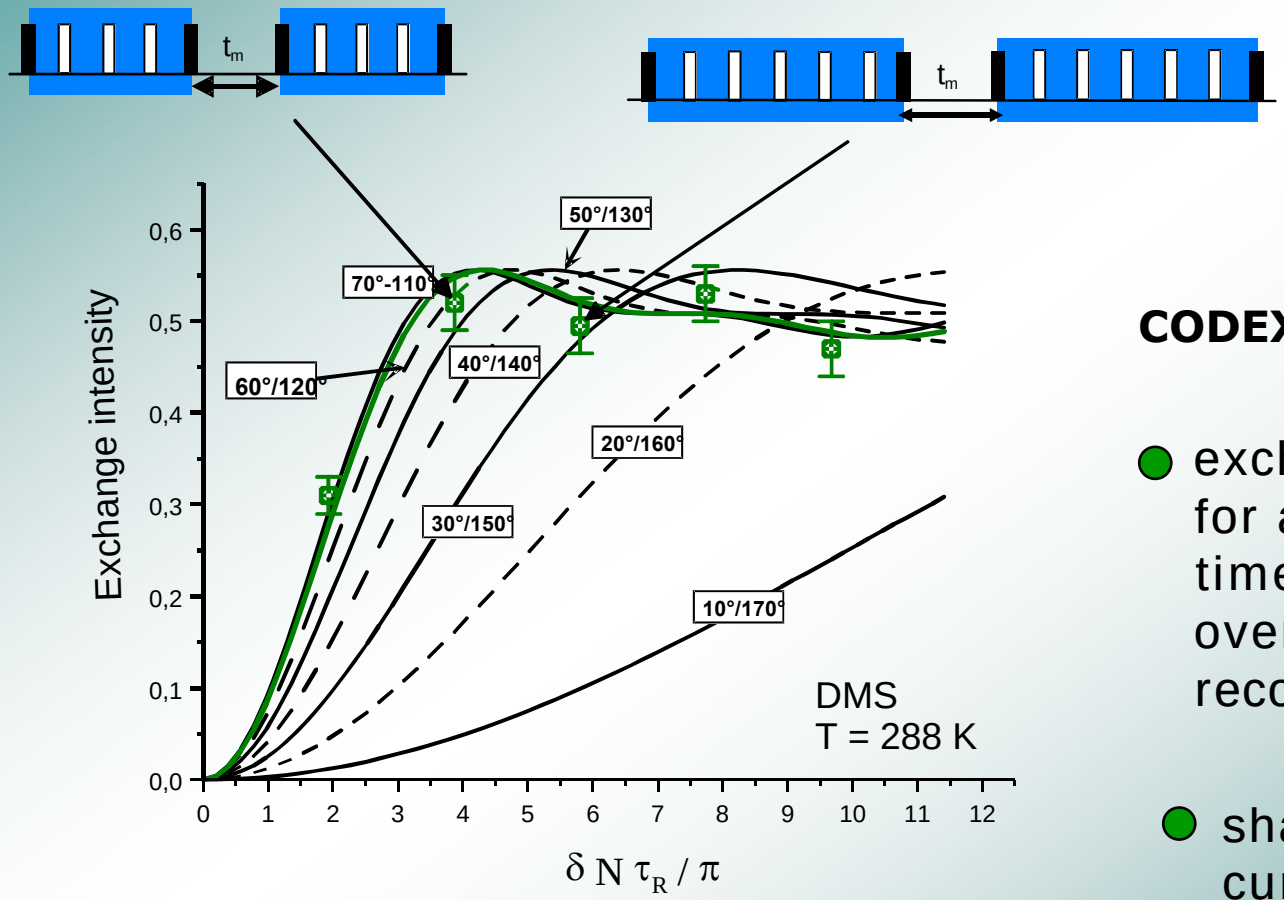


exchange during t_m?

Complete refocusing of CSA only if there is no exchange during t_m!

Advantages:
High spectral resolution, short measuring time compared to 2D exchange NMR

CODEX: reorientation angle



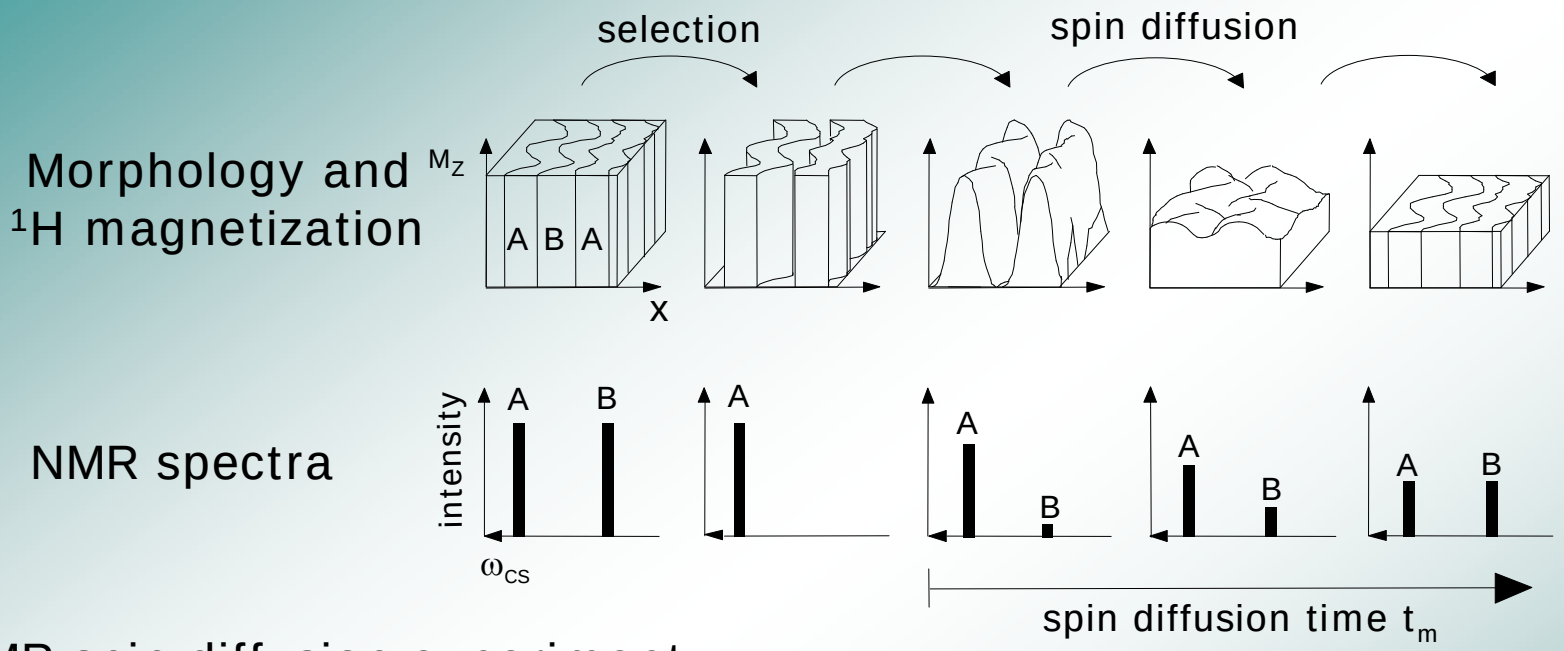
CODEX build-up curves

- exchange intensity for a given mixing time depends on the overall duration of recoupling
- shape of the curves depends significantly on the reorientation angle

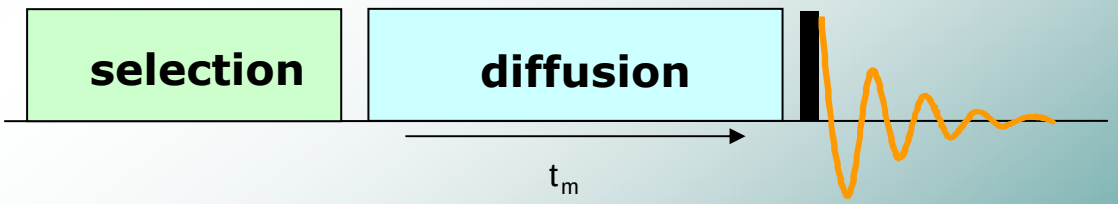
Overview of NMR of Bulk Polymers

Introduction	•	Basics
Configuration, Conformations	•	Chain Branching
Local Structure & Dynamics	•	Amorphous & Crystalline Polymers
Phase Behavior	•	Core Shell Structures
Supramolecular Organization	•	Functional Polymeric Systems
Conclusions	•	Scattering and NMR

Phase Separation Probed by Spin diffusion

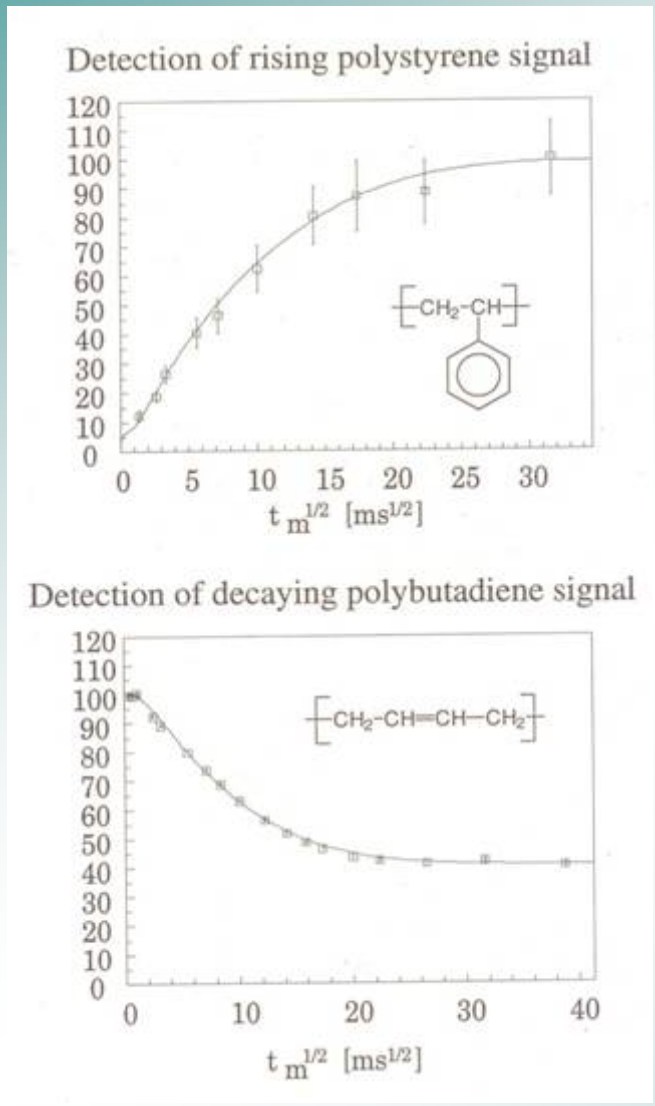


NMR spin diffusion experiment

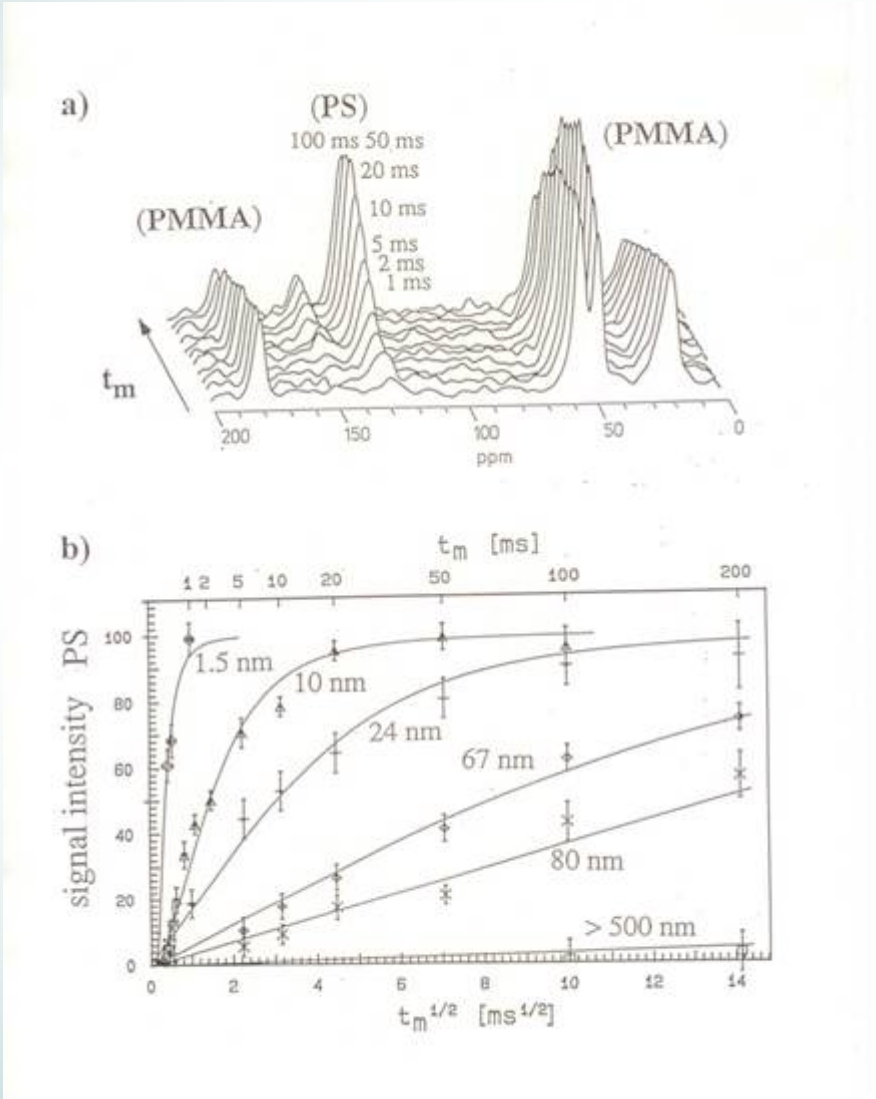


- Chemical shift filters (e.g. DANTE): spectral selection
- Dipolar filters (e.g. SR-12): motional selection

Domain Sizes in Phase Separated Polymers

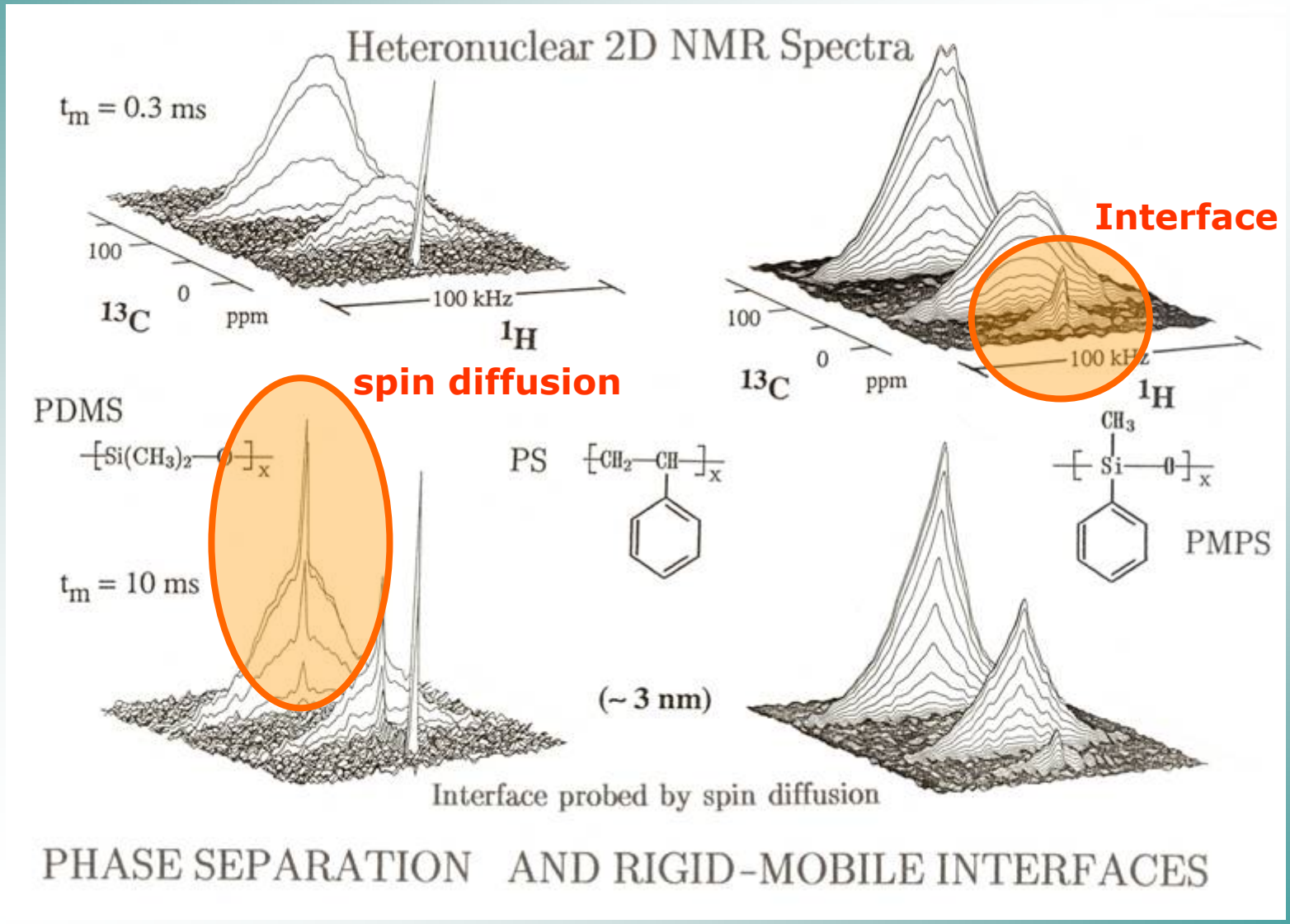


Rigid and Mobile Components



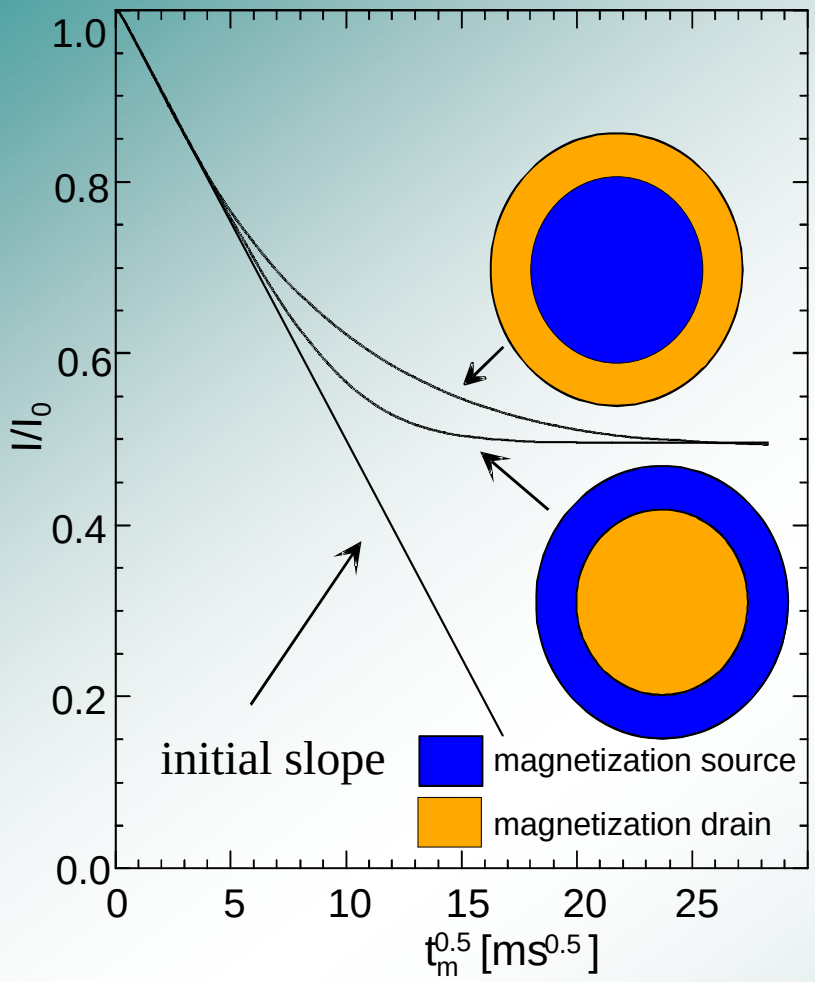
Both Components Rigid

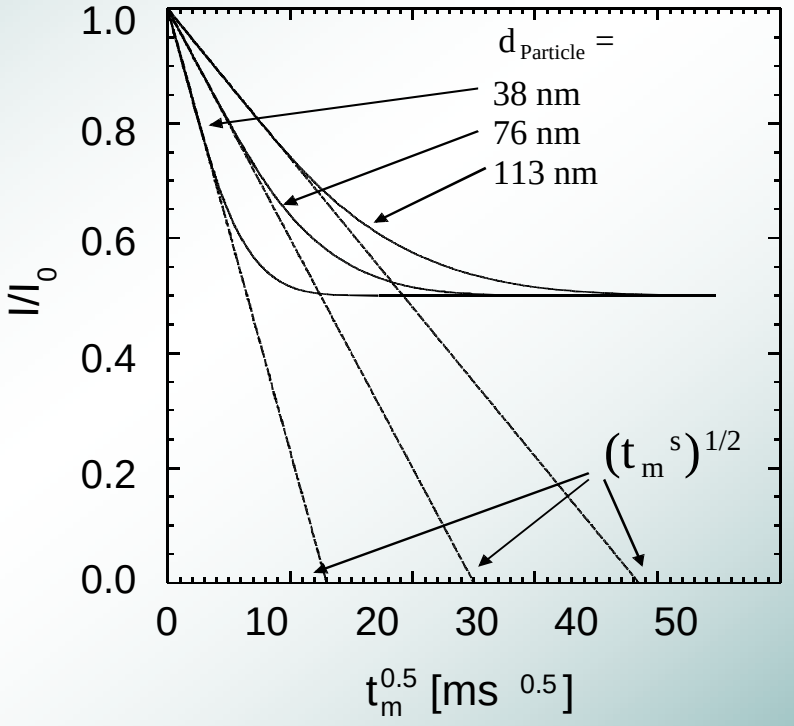
Spin Diffusion in 2D Wideline Separation Spectra



PHASE SEPARATION AND RIGID-MOBILE INTERFACES

Investigating core-shell particles





contact surface: S
source volume: V

$$S/V = \sqrt{\frac{\pi}{D_{eff}\, t_m}}\, S \quad \text{with} \quad \sqrt{D_{eff}} = \frac{2\sqrt{D_A D_B}}{\sqrt{D_A} + \sqrt{D_B}}$$

structure and particle size can be determined

Overview of NMR of Bulk Polymers

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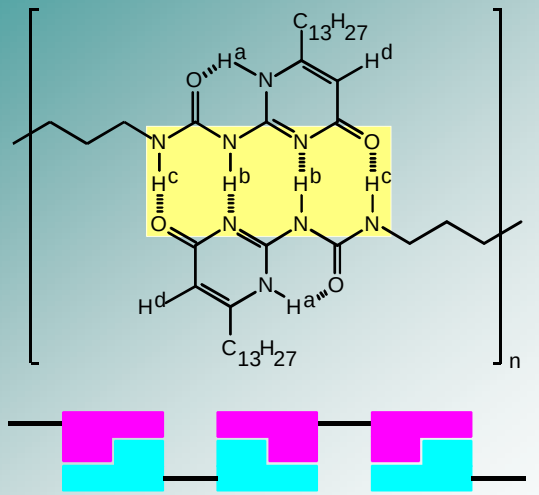
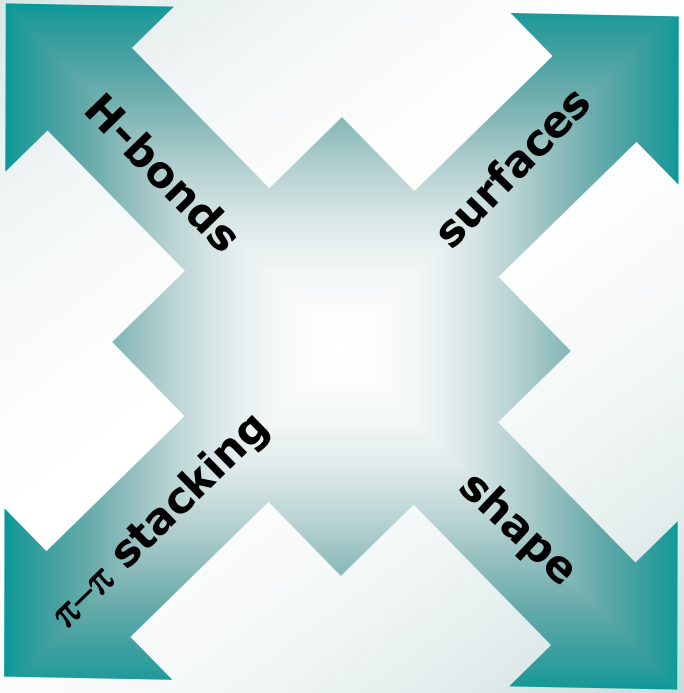
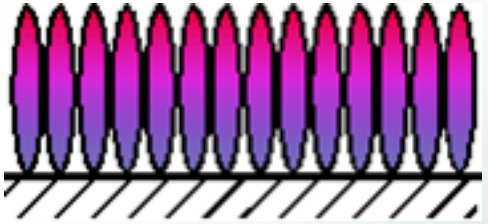
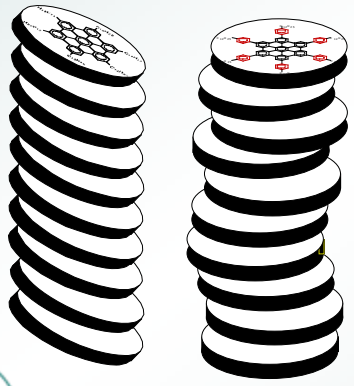
Supramolecular Organization	•	**Functional Polymeric Systems**
Conclusions	•	Scattering and NMR

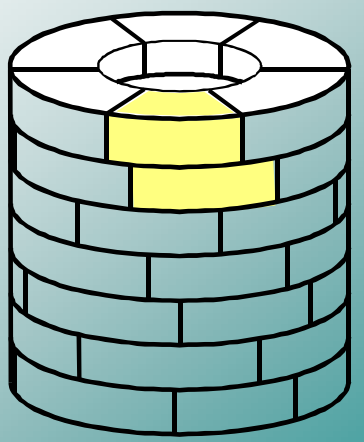
Key Elements of Supramolecular Assemblies







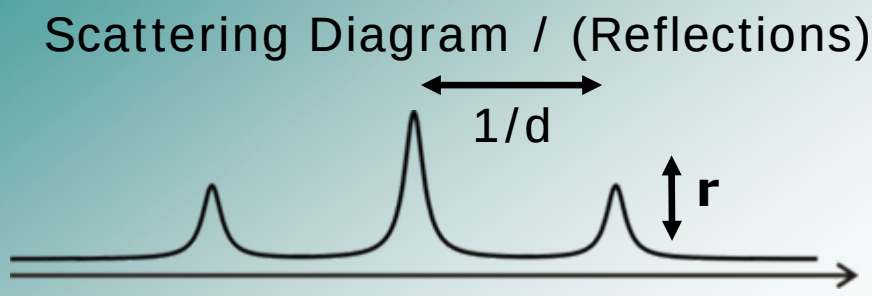


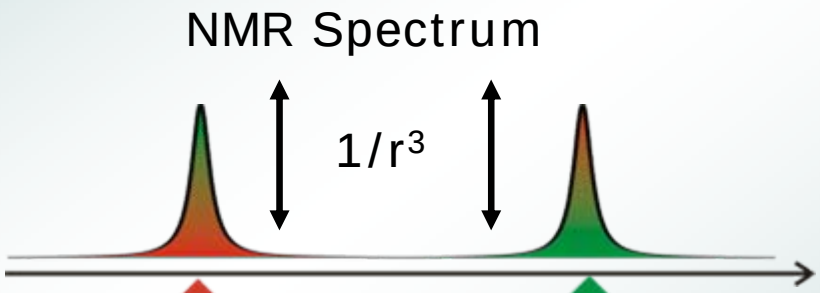


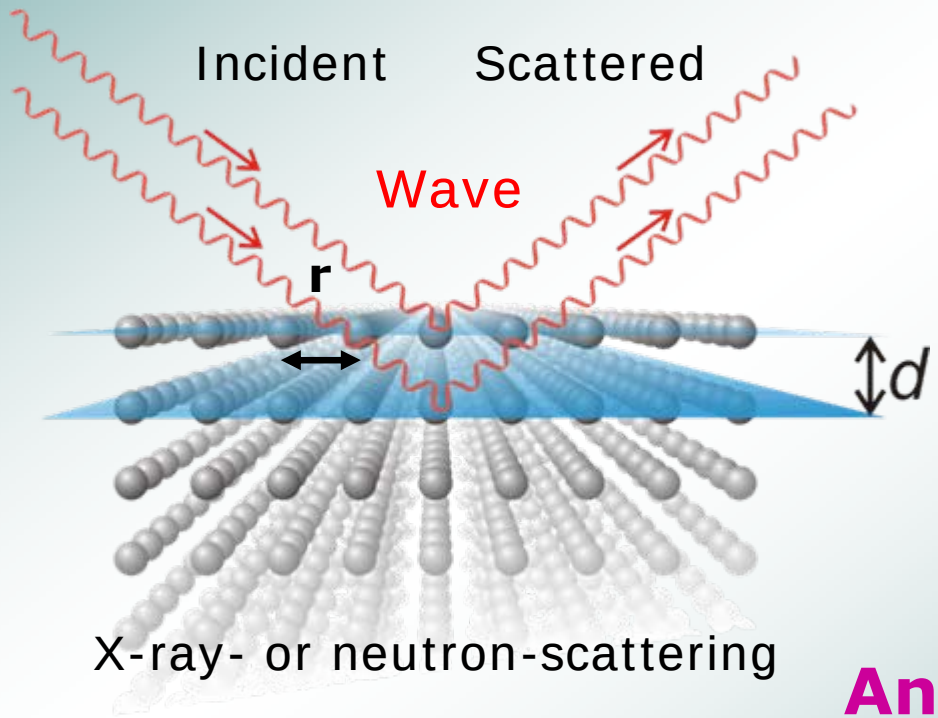
Challenge: Elucidate **Noncrystalline** Structures

Scattering

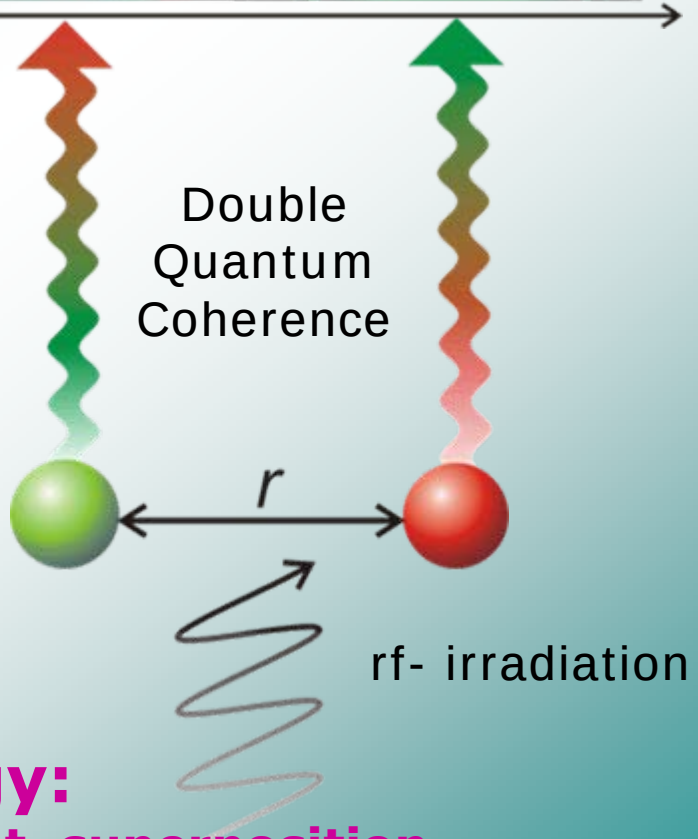
Double Quantum NMR







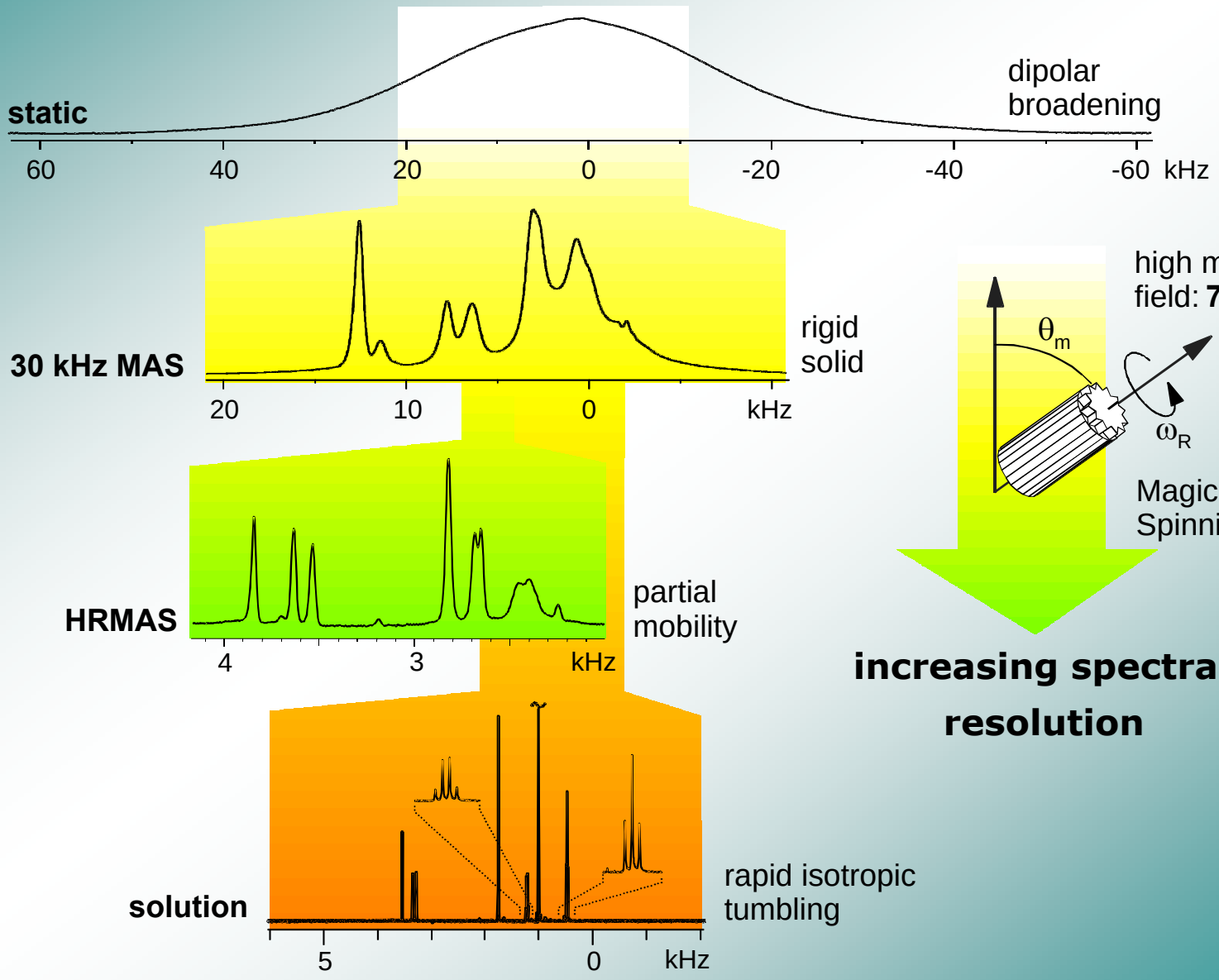
X-ray- or neutron-scattering



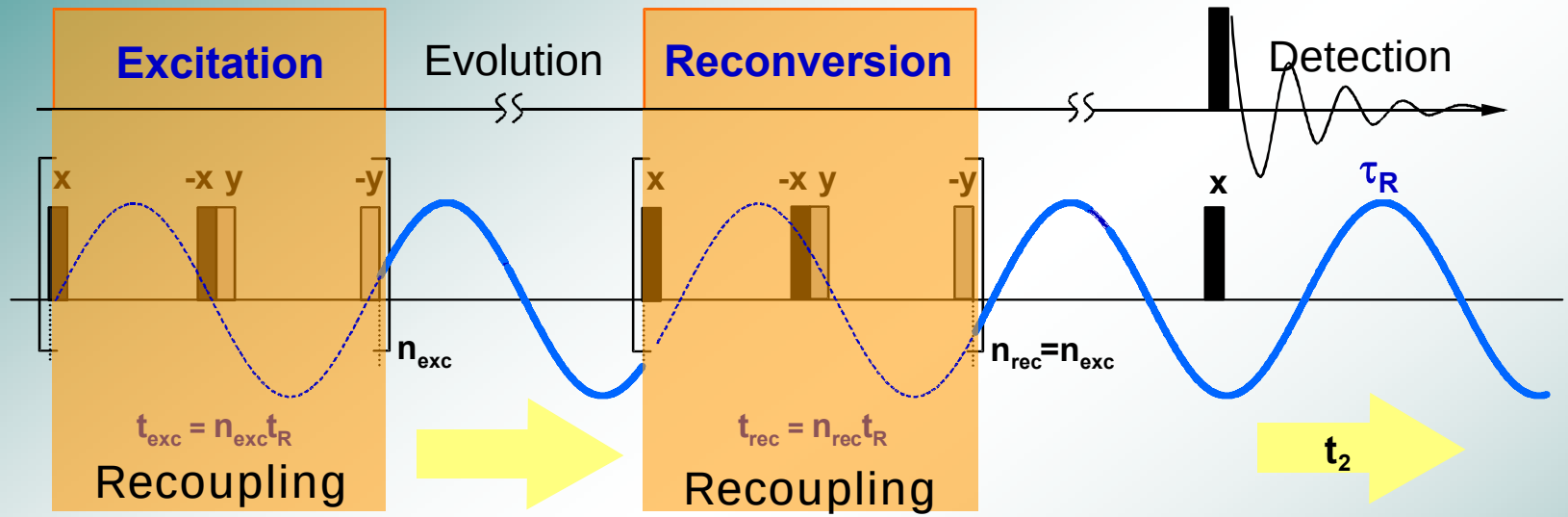
Analogy:

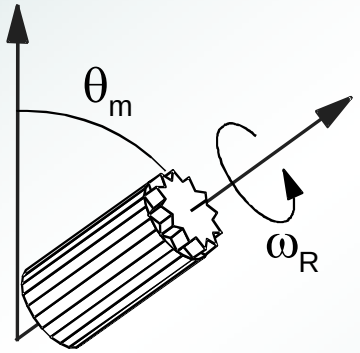
In both cases: coherent superposition of signals from spatially separated centers

^{1}H NMR spectra in solid and liquid state



Dipolar DQ Spectroscopy of a Spin-Pair under MAS

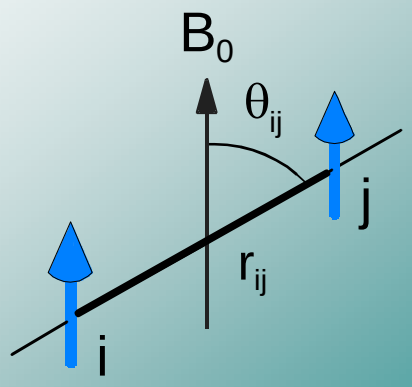




Dipole-Dipole Coupling:

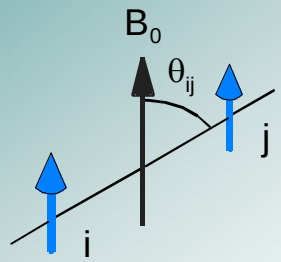
$$\hat{H} = \hat{R}_{2,0} \cdot \hat{T}_{2,0}$$

Space Spin



Line Narrowing in Solid-State NMR

Hamiltonian of Dipole-Dipole Coupling:



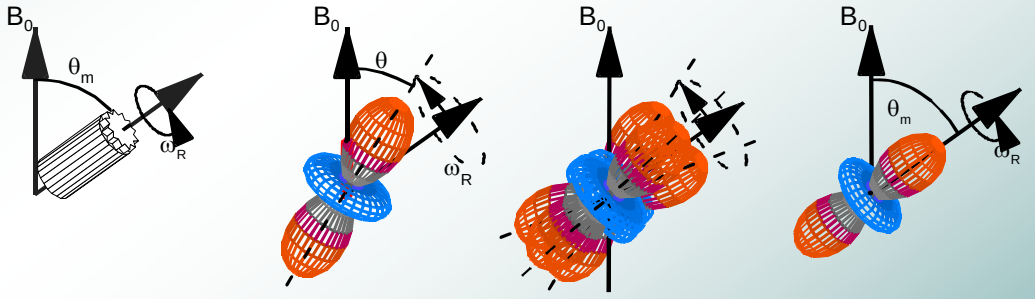
$$\hat{H} = \hat{R}_{2,0} \cdot \hat{T}_{2,0}$$

Space / Spin

$$\hat{H} \propto \frac{1}{r_{ij}^3} \frac{1}{2} (3\cos^2\theta_{ij} - 1)\ \gamma_i \gamma_j (3\hat{I}_{Z,i}\hat{I}_{Z,j} - \hat{I}_i \cdot \hat{I}_j)$$

Magic Angle Spinning:

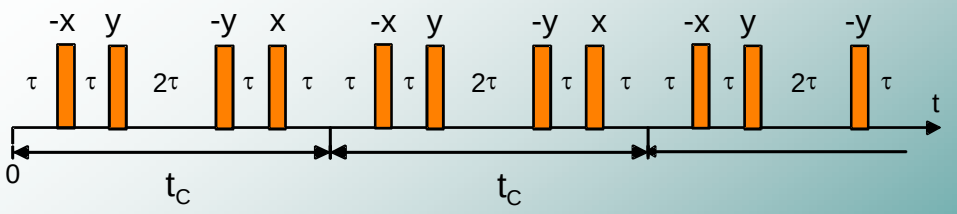
$$\bar{\hat{R}}_{2,0} \rightarrow 0$$

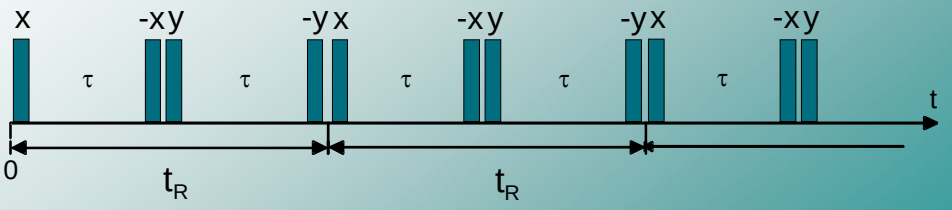


RF Irradiation:

$$\bar{\hat{T}}_{2,0} \rightarrow 0$$ (CRAMPS)

$$\bar{\hat{T}}_{2,0} \rightarrow H_{D,eff.}$$ (Recoupling)



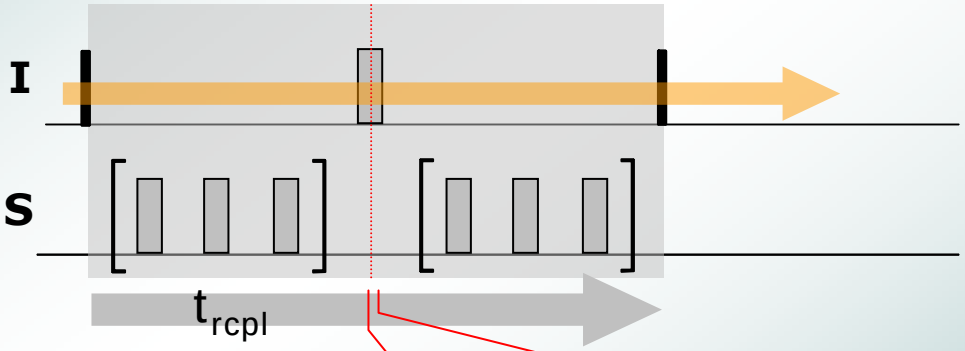


Signal build-up versus rotor-encoding

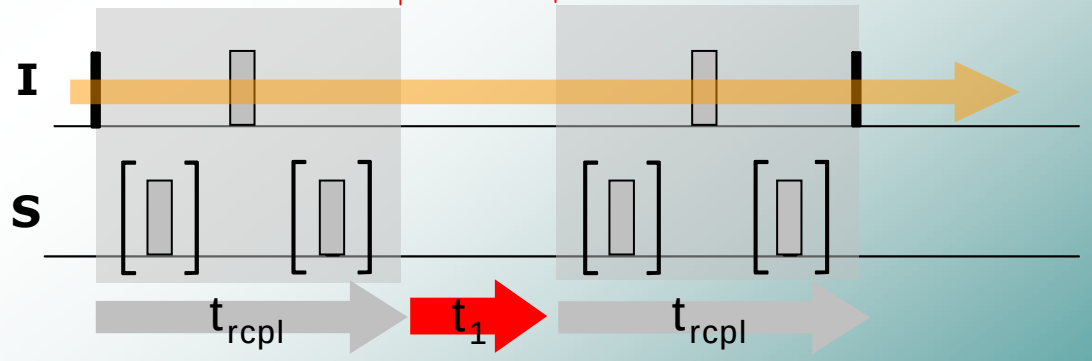
Two alternative concepts for measuring recoupled interactions:

- following the signal intensity as a function of the recoupling time (resulting in **build-up** or dephasing **curves**)
- recording **rotor-encoded** signal (resulting in MAS sideband patterns)

REDOR scheme



Rotor-encoded REDOR scheme



Rotor-encoding of dipolar Hamitonians

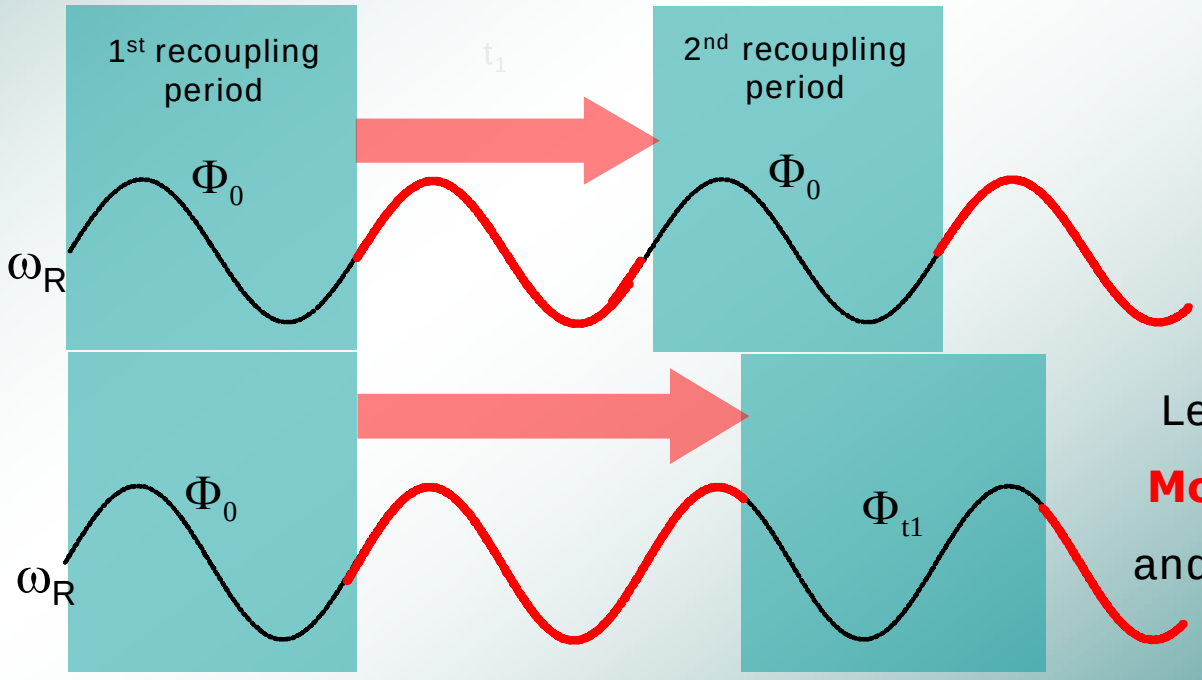
Recoupled dipolar Hamiltonian:

with dipolar "**phases**" for first recoupling period:

$$\Phi_0 = -\frac{D_{IS}}{\omega_R} 2\sqrt{2} \sin 2\beta \sin \gamma$$

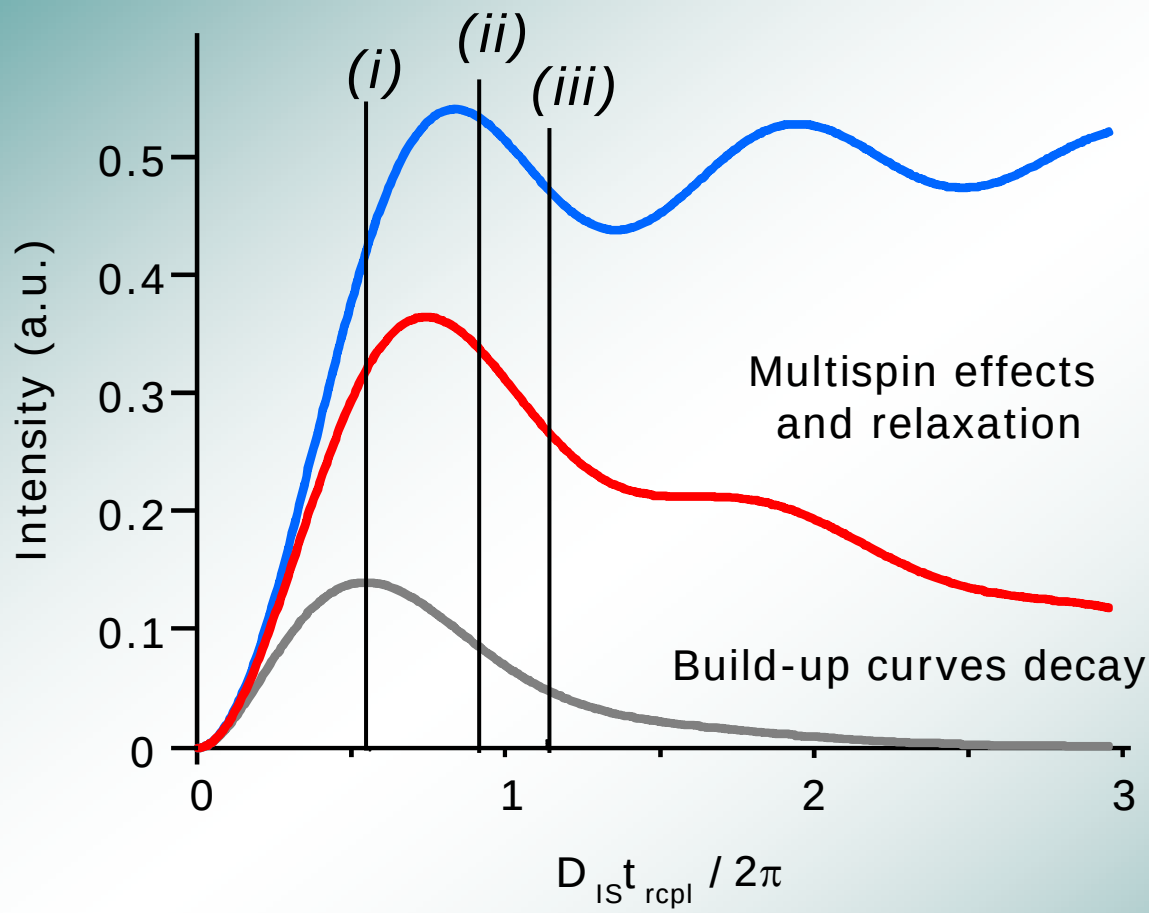
and for **"rotor-encoded"** second recoupling period:

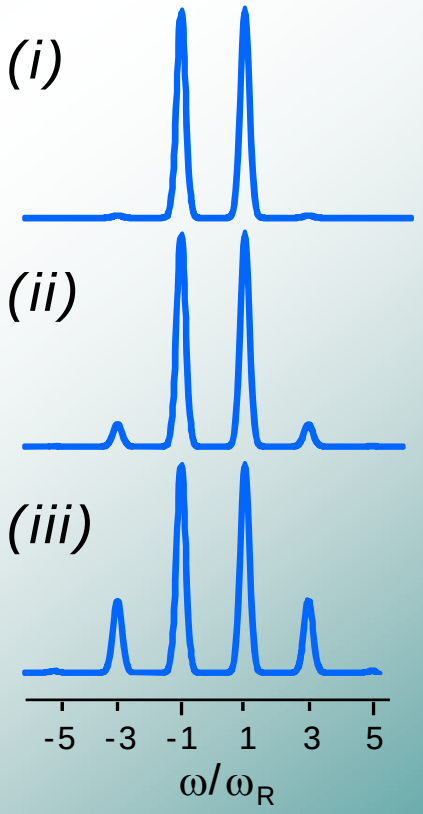
$$\Phi_{t1} = -\frac{D_{IS}}{\omega_R} 2\sqrt{2} \sin 2\beta \sin(\omega_R t_1 + \gamma)$$



Leads to **Amplitude Modulation** of Signal and hence, **Sidebands**

REDOR-type curves and sideband patterns





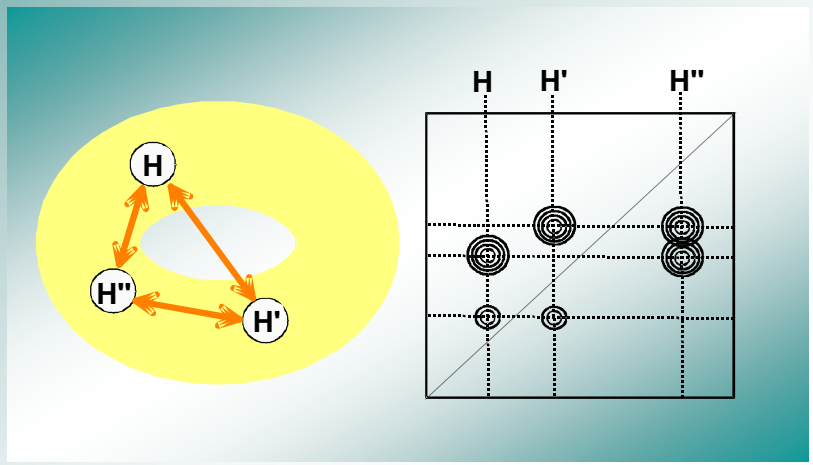
HDOR sideband **patterns robust:**
Multispin effects: additional sidebands

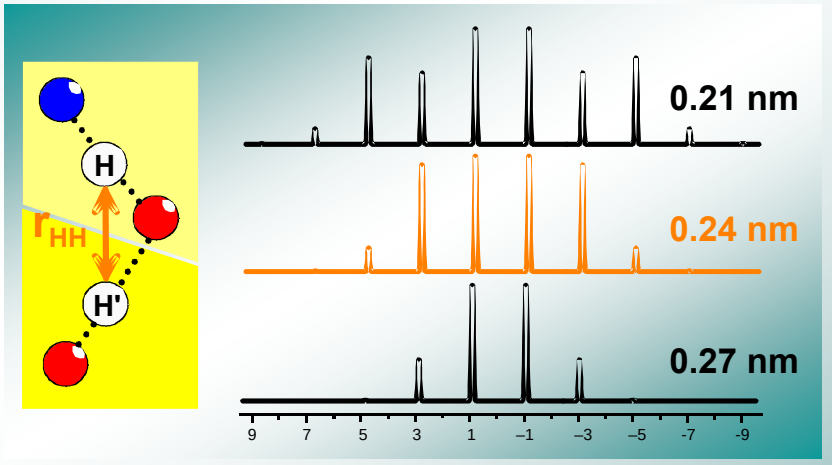
Multiple-quantum NMR methods: investigating (supra)molecular structure

internuclear proximities, chemical shifts and π-shifts

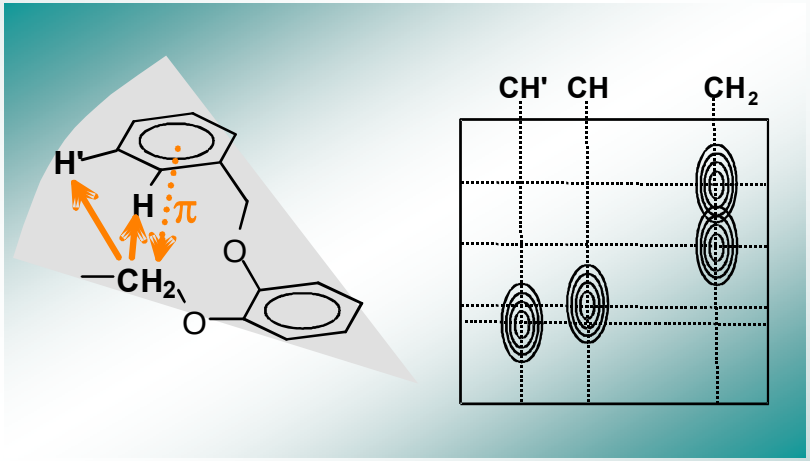
internuclear distances molecular dynamics

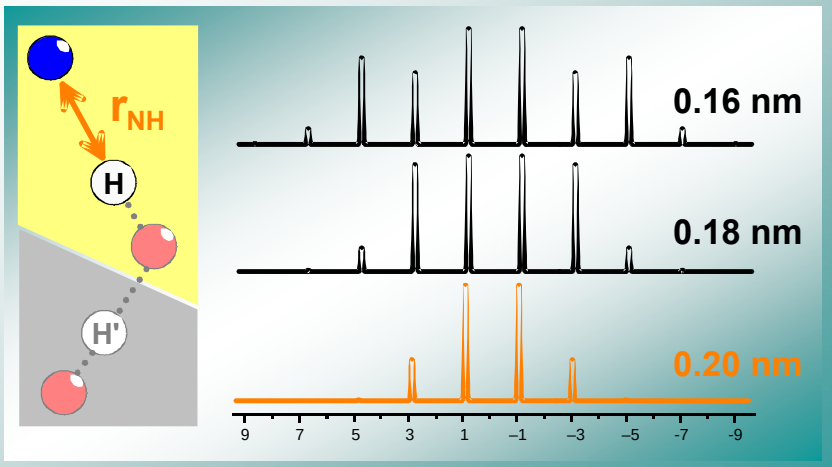
^{1}H-^{1}H homonuclear





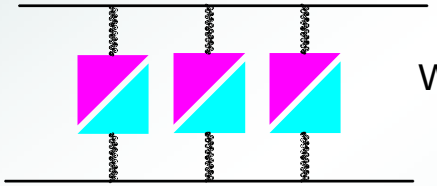
^{1}H-^{13}C/^{15}N heteronuclear





Multiple Hydrogen Bonds in Natural and Synthetic Systems

DNA



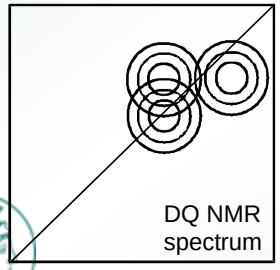
Watson-Crick base pairs

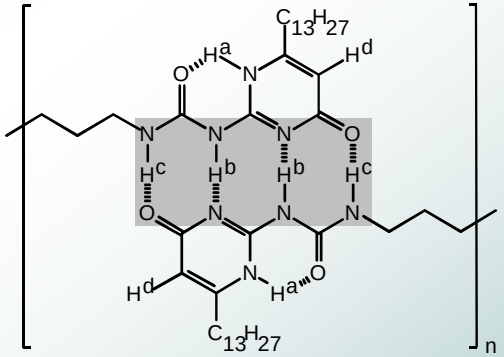
Supramolecular polymers via hydrogen bonds

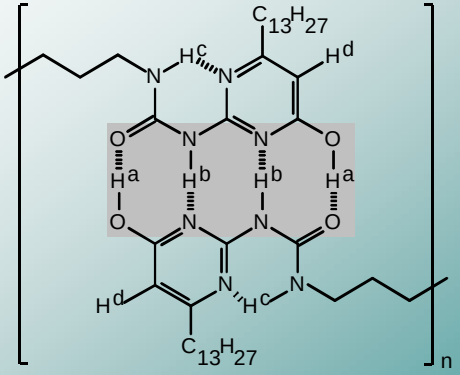
R.P. Sijbesma, E.W. Meijer et al., *Science*, 1997:
Thermoreversible linkages through quadruple hydrogen bonding

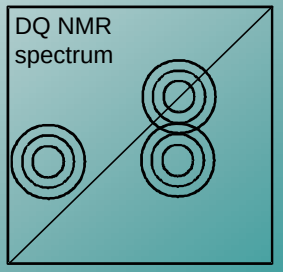
Keto form

Enol form



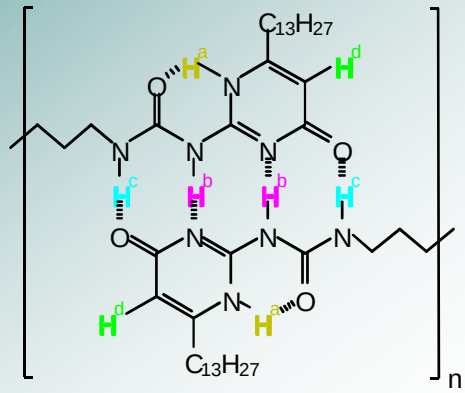






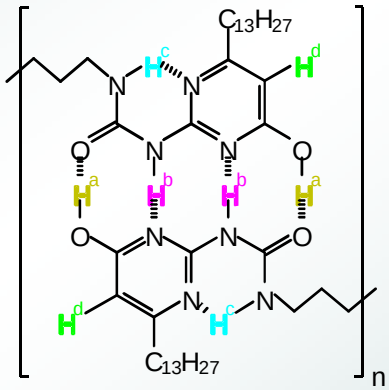
Heat-Induced Tautomeric Rearrangement: ^1H-^1H DQ Spectra of Quadruple Hydrogen Bonds

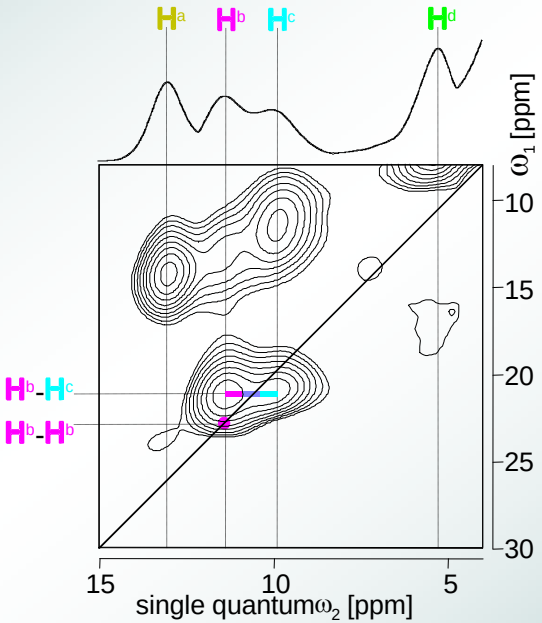
***before* heating: *keto* form**

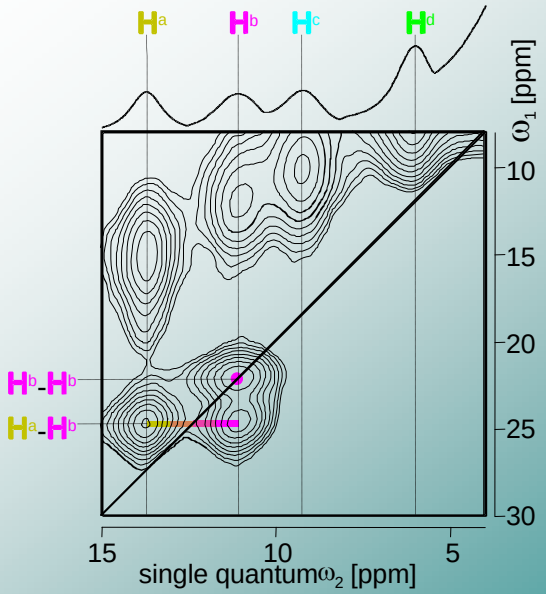


Heating

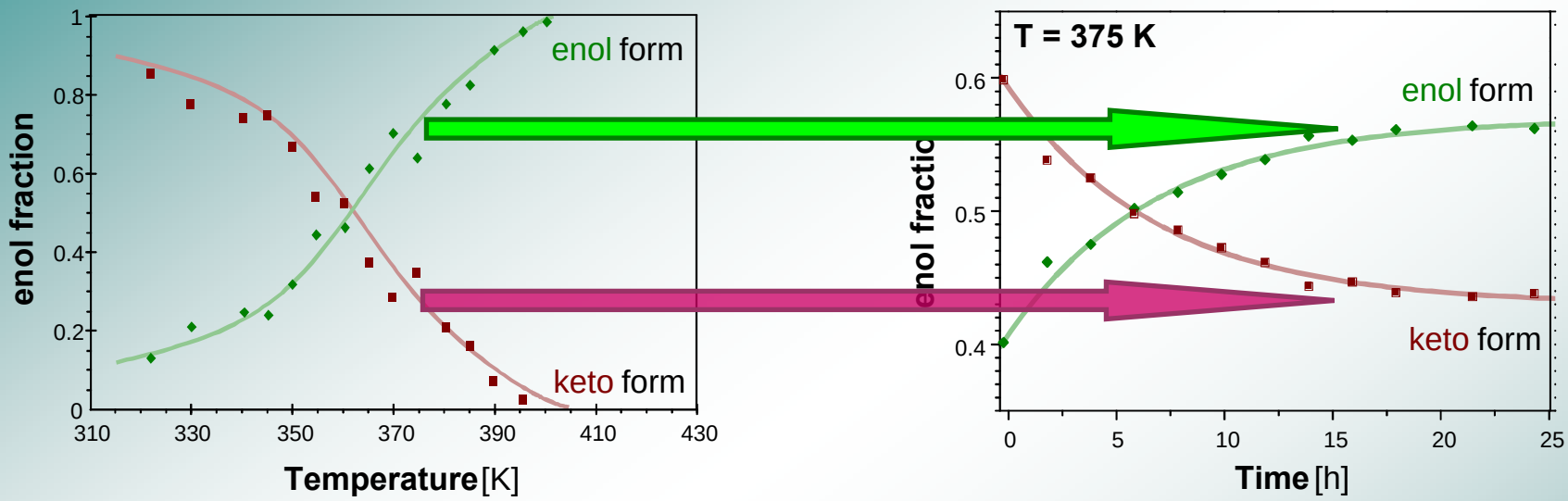
***after* heating: *enol* form**





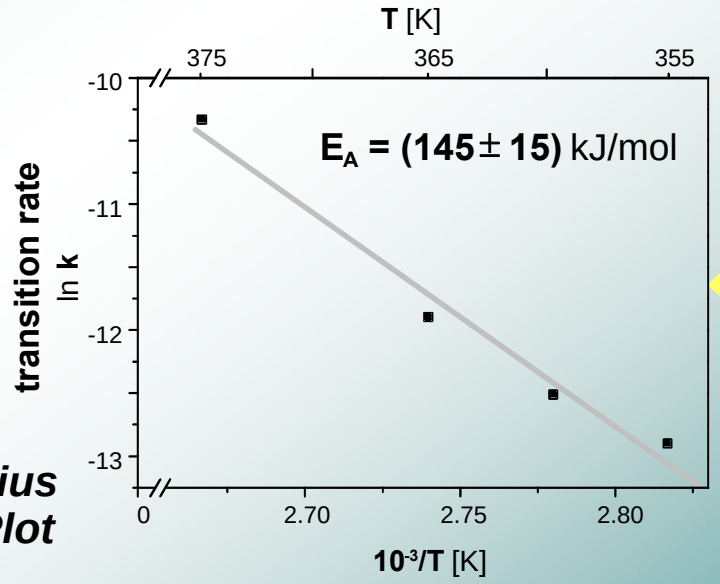


Kinetics of the Tautomeric Rearrangement



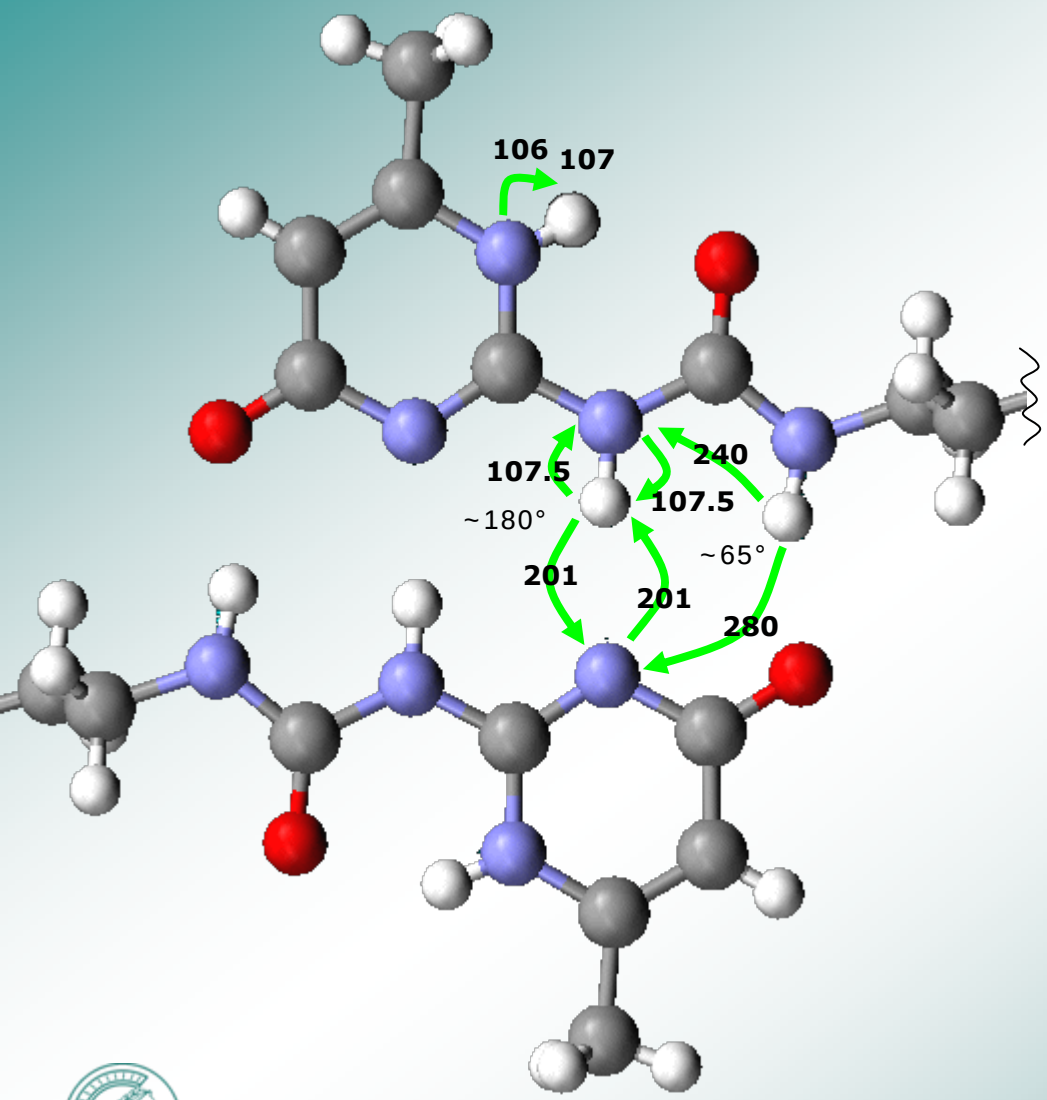
Temperature Dependence

Time Dependence

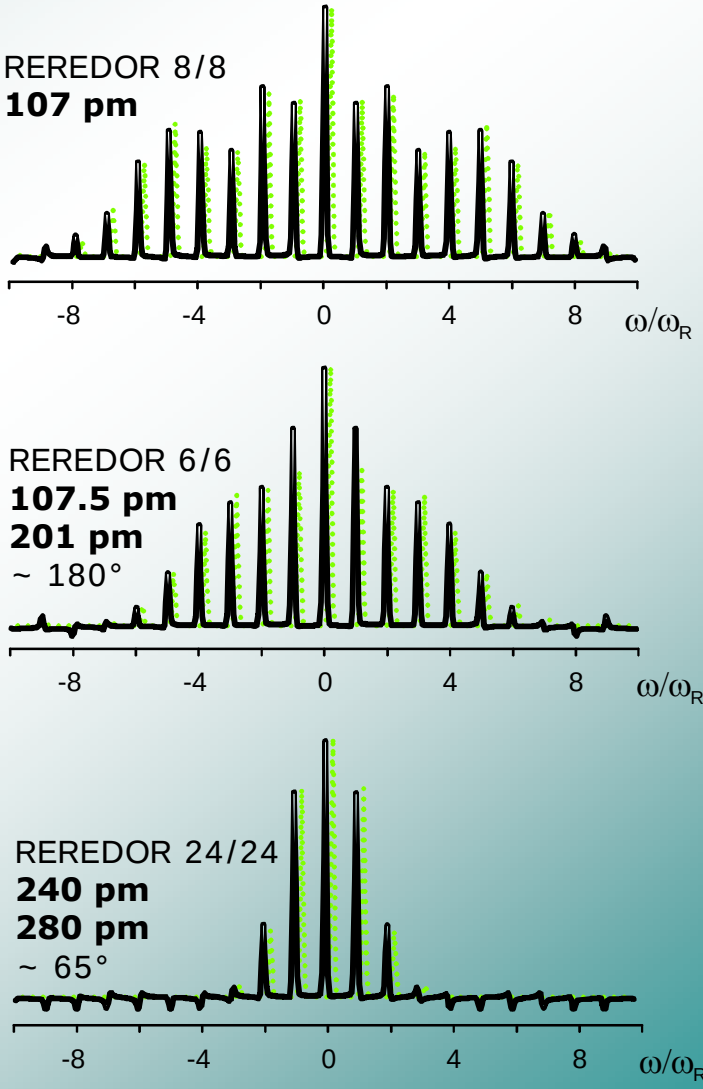


Arrhenius Plot

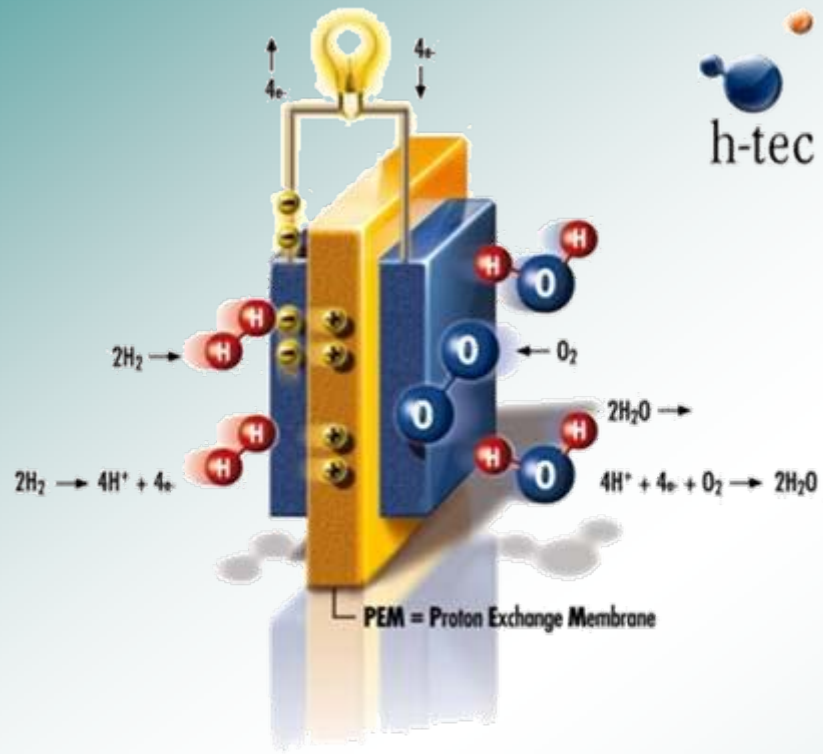
Multiple N-H Distances in the Pyrimidinone Form



$^{1}H\{^{15}N\}$ recoupling: ^{1}H - detection



Separator Membranes and NMR

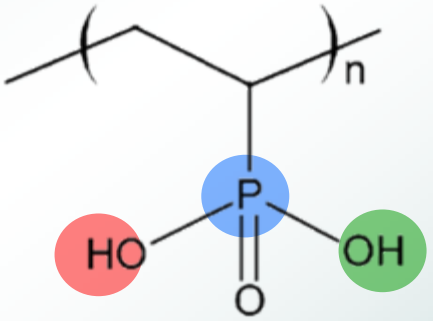


→ reveal details of proton conductivity on *molecular* level
(site-selective & non-destructive)

→ provide structural constraints
(proton transfer mechanism ?)

PVPA: poly(vinyl phosphonic acid)

High proton conductivity under dry conditions at elevated temperatures



NMR probes for local structure & dynamics

^{31}P NMR

↳ **phosphonic acid units**, local **dynamics**

^{1}H NMR

↳ backbone as well as **mobile protons** (local dynamics)

^{2}H NMR

↳ **primary process**: orientation-dependent rate of movement: time scale and geometry (multi-site jumps)

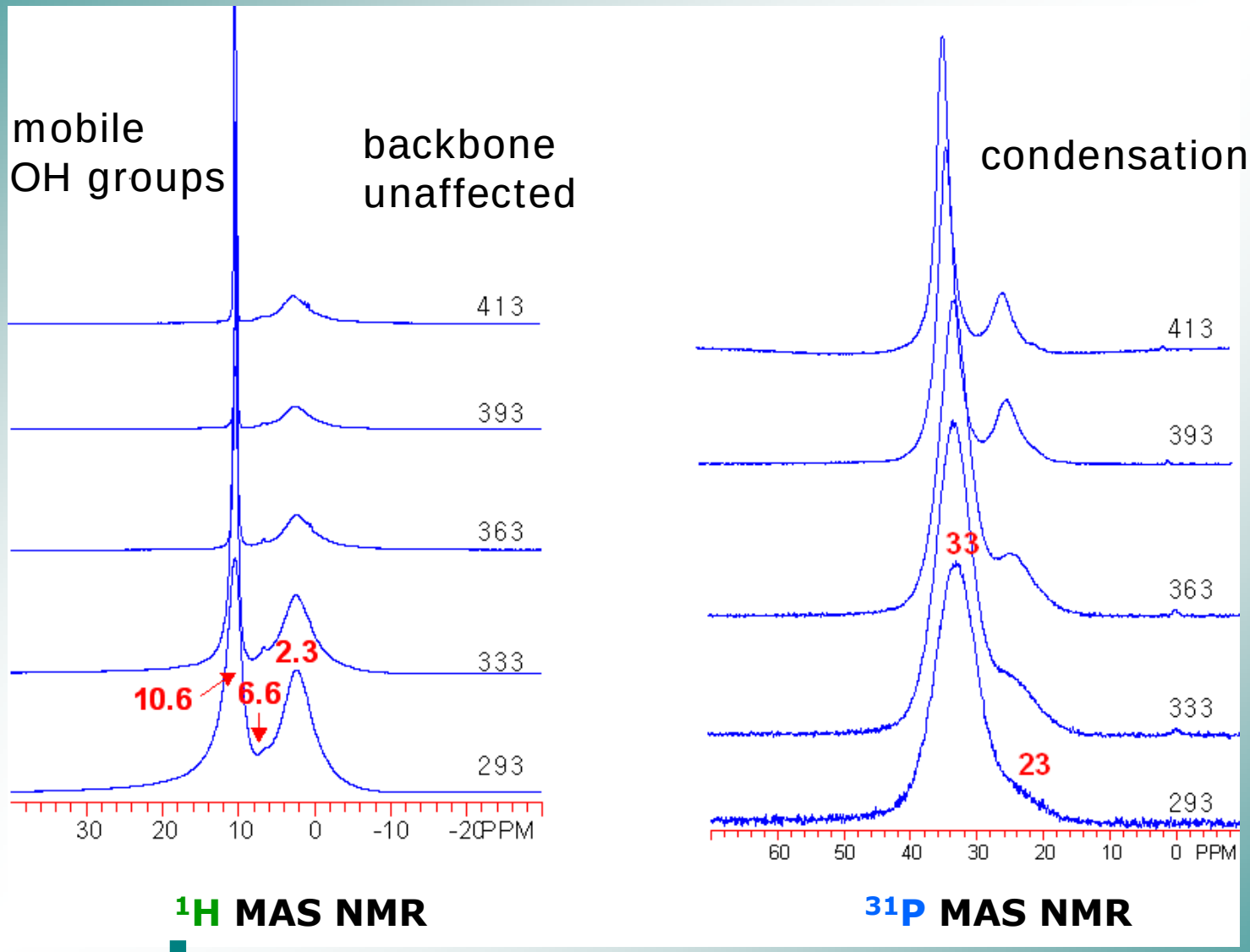
^{1}H-^{13}C NMR

↳ segment mobilities of alkyl chains, **polyvinyl backbone**

^{1}H-^{31}P and ^{1}H-^{1}H NMR

↳ **hydrogen bonding** at phosphonic acid units

PVPA: VT NMR motional narrowing



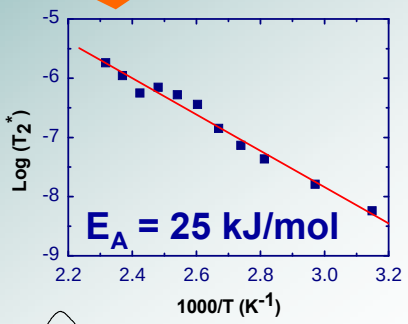
^{1}H MAS NMR **^{31}P MAS NMR**

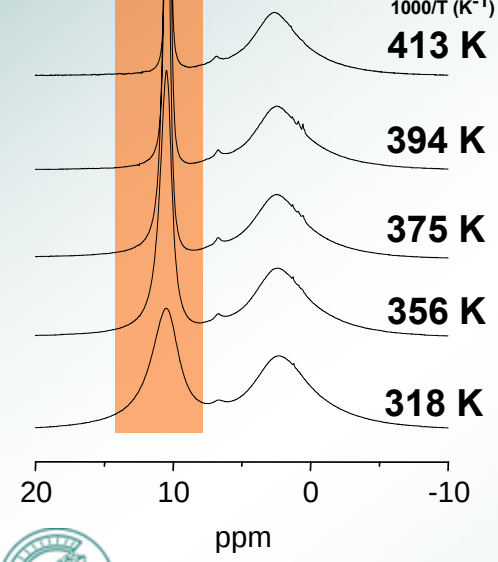
very narrow lines in both ^{1}H and ^{31}P spectra

Poly(vinyl phosphonic acid): PVPA

P-OH : mobile proton, hydrogen bonded
Dynamics of motion involved in proton conduction

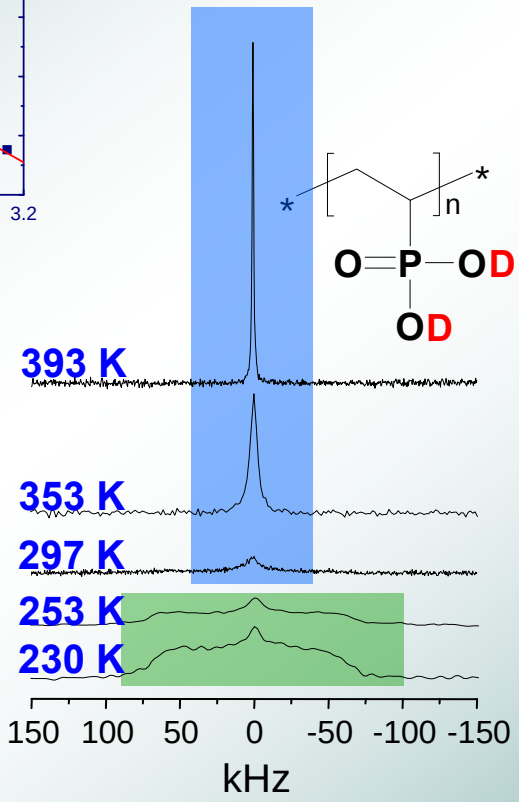
P-OH proton: mobile



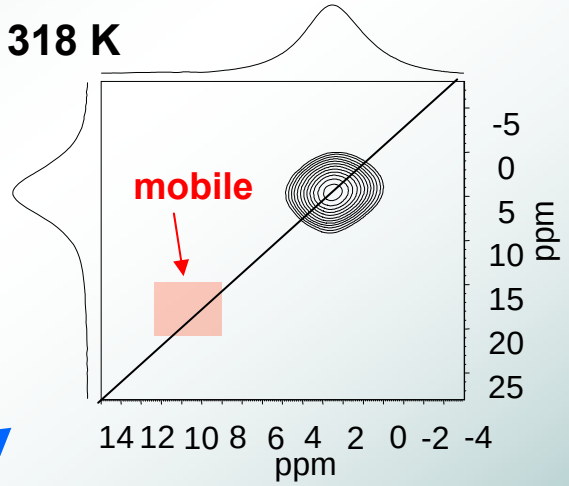


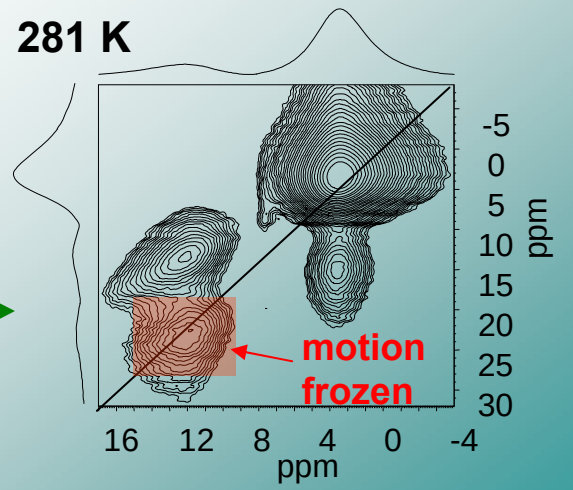
^{1}H MAS spectra

^{2}H solid echo spectra

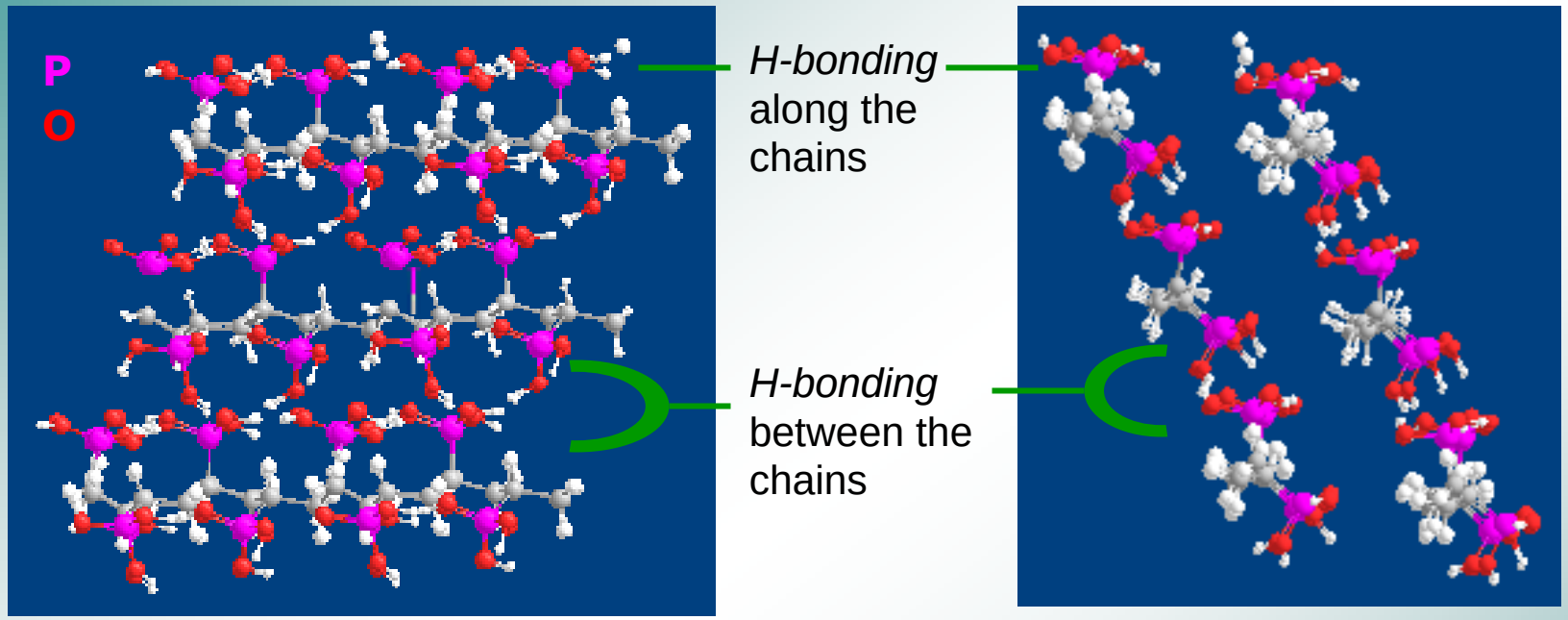


^{1}H - ^{1}H DQ Spectra





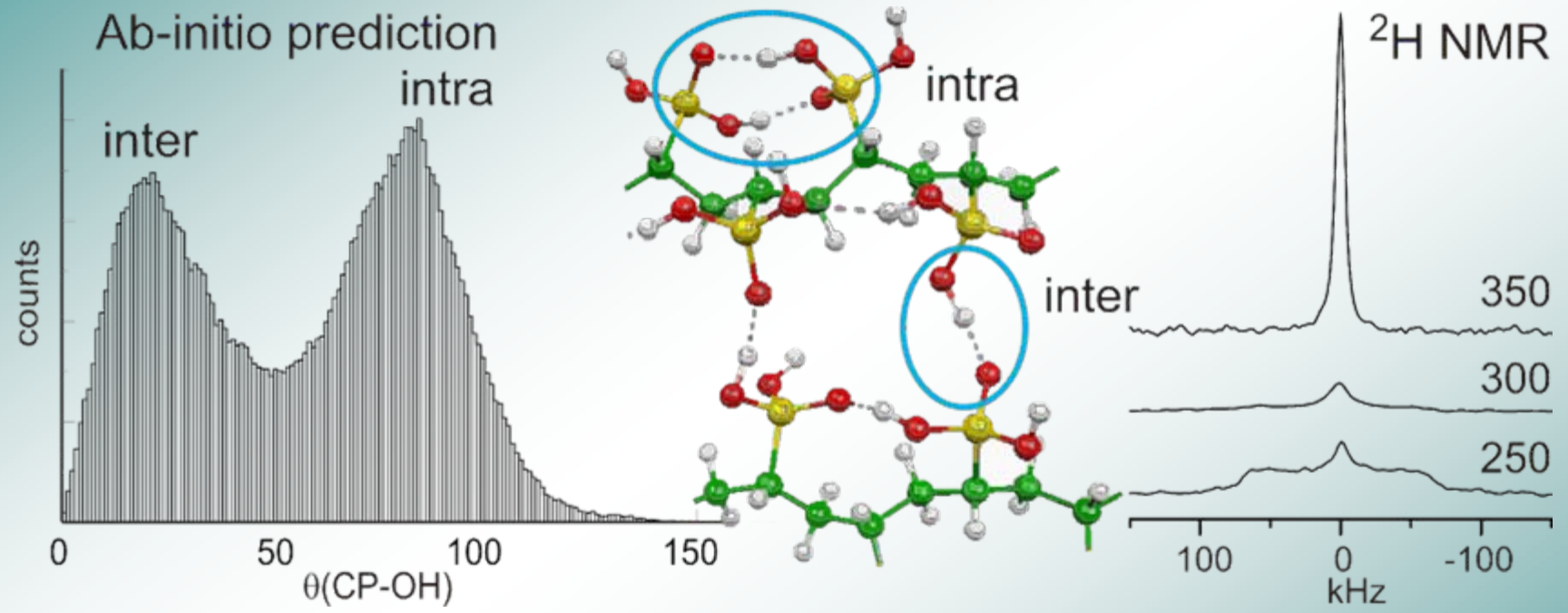
PVPA: *ab initio* structure (model geometry)

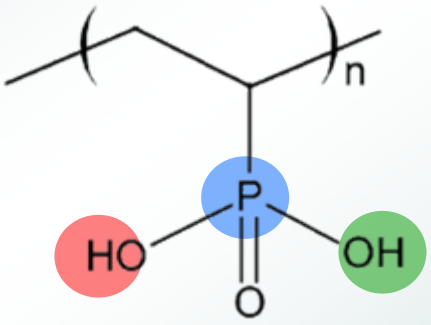


Ab initio calculation based on model geometry (CPMD):

* Elucidation of hydrogen bondings and ^{1}H chemical shift calculation:
  - → *H-bonding* between phosphonic acids on the *same* chains and *between* two parallel chains
  - → MD: *Proton hopping* occurs along chains as well as between chains mediated by hydrogen bonds.
  - → calculated δ(P-OH) = 9.7 ppm (exp.: 10.6 ppm)

PVPA: Averaging of Deuteron Quadrupole Coupling





Broad distribution of angles between instantaneous O-H and C-P directions, yet
Quadrupole coupling reduced by factor 10 after CPMD run of 15 ps

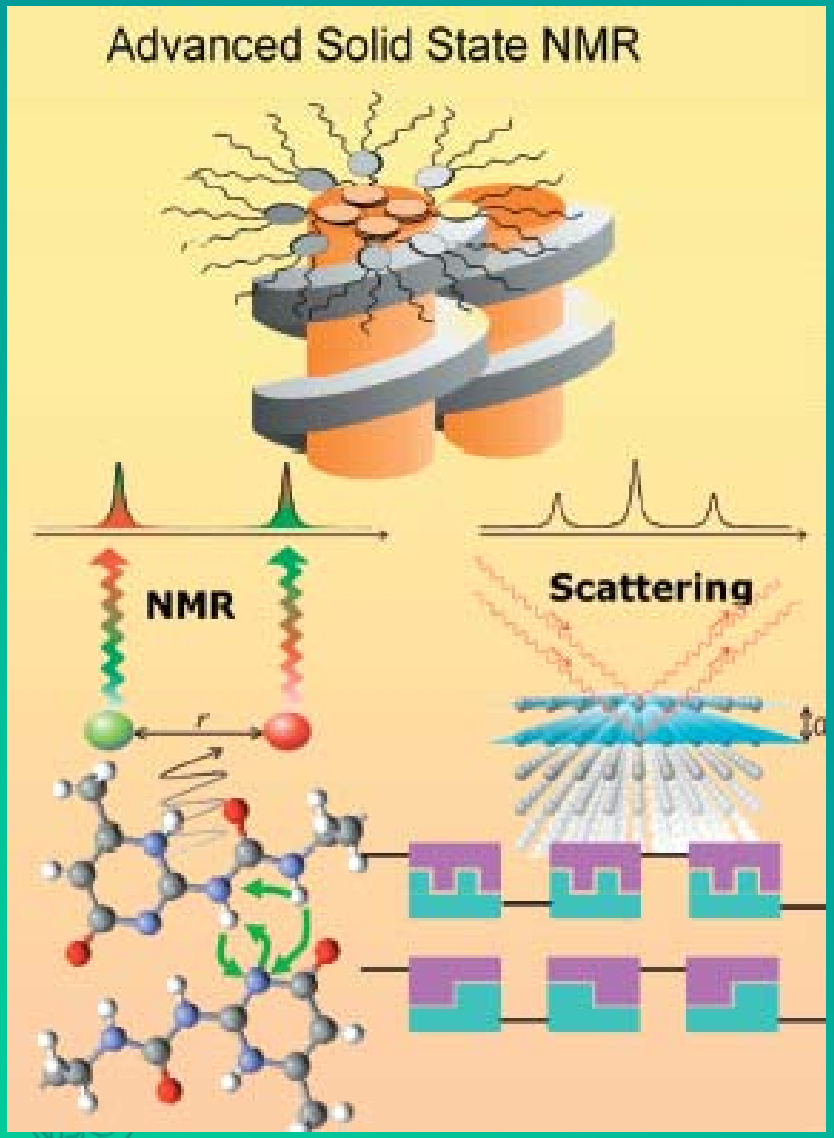
Overview of NMR of Bulk Polymers

Introduction	•	Basics
Configuration, Conformations	•	Chain Branching
Local Structure & Dynamics	•	Amorphous & Crystalline Polymers
Phase Behavior	•	Core Shell Structures
Supramolecular Organization	•	Functional Polymeric Systems
Conclusions	•	Scattering and NMR

Scattering and NMR in Bulk Polymers

		SCATTERING		NMR	
		incoherent	**coherent**	**single quantum**	**double quantum**
DYNAMICS					
	Molecular	n-quasielastic	n-quasielastic	2D-, 3D-, 4D-exchange	sidebands
	Collective		n-spin-echo	2D-exchange	decay of DQC
STRUCTURE					
	Molecular		WAXS, WANS	chemical shift, sidebands	2D pattern, sidebands
	Collective (packing)		X-ray pole figures, SAXS, SANS	DECODER chemical shift	2D signal pattern

Overview of NMR of Bulk Polymers



Advantages of NMR:

- Selectivity, Versatility
- Detailed information on geometry and time scale of dynamics
- Large range of length- and time scales accessible
- Elucidation of supramolecular organization
- Relation between structure, dynamics and functional behavior
- Limits not reached, e.g. microcoils

References

K. Schmidt-Rohr, H.W. Spiess, *Multidimensional NMR and Polymers*, Academic Press, London, 1994

H. W. Spiess, *Advanced Solid-State Nuclear Magnetic Resonance for Polymer Science;*
J. Polym. Sci. **A 42**, 5031–5044 (2004).

H.W. Spiess, *NMR Spectroscopy*, in Macromolecular Engineering, edited by K. Matyjaszewski, Y.Gnanou, L. Leibler, WILEY-VCH, Weinheim, Vol. **3**, 1937-1965 (2007).

H. W. Spiess, *NMR Spectroscopy: Pushing the Limits of Sensitivity* Angew. Chem. Int. Ed. **47**, 639-642 (2008).