

# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

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**BOREALIS**

SHAPING the FUTURE with PLASTICS

# Borealis: who we are

- Leading provider of innovative, value creating plastics solutions
- Developing a Base Chemicals business
- More than 40 years of experience
- Unique Borstar® technology to develop polyolefin solutions that are tailored to customers' needs
- 5,400 employees in around 20 countries
- Customers in more than 120 countries
- Ownership 64% IPIC / 36% OMV
- Joint venture in Middle East and Asia: Borouge (Abu Dhabi)





# Borealis: where we are



## Borealis locations

**Production Plants:** Austria, Belgium, Brazil, Finland, Germany, Italy, Sweden, United States

**Innovation Centres:** Austria, Finland, Sweden

**Customer Service Centres:** Austria, Belgium, Finland, Germany, Italy, Singapore, Sweden, Turkey, United States

**Head Office:** Austria

## Borouge locations

**Production Plant:** Ruwais (UAE)

**Customer Service Centres:** Abu Dhabi (UAE), China, India, Singapore

**Sales Offices:** Abu Dhabi (UAE), Australia, China, Lebanon, New Zealand, Saudi Arabia

**Head Offices:** Abu Dhabi (UAE), Singapore

# Outline

## I. NMR Spectroscopy of Polyolefins

- Review of key NMR theory
- Polyethylene (PE)
- Polypropylene (PP)

## II. Introduction to Solid-State NMR Spectroscopy

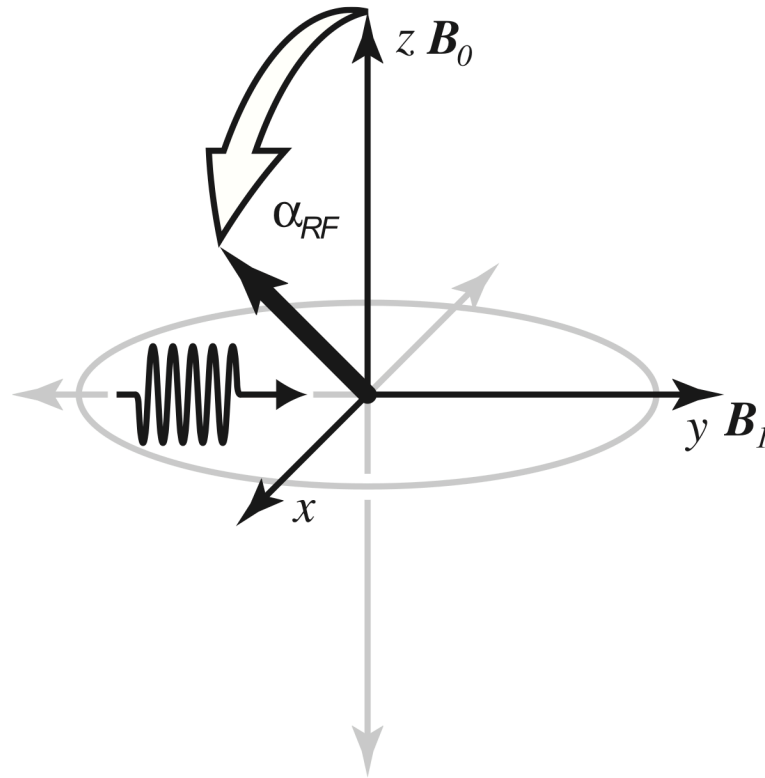
- Theory
- Methods
- Applications

## III. Lab tour of NMR facilities at Borealis, Linz

# Aims

The main aims of this course are:

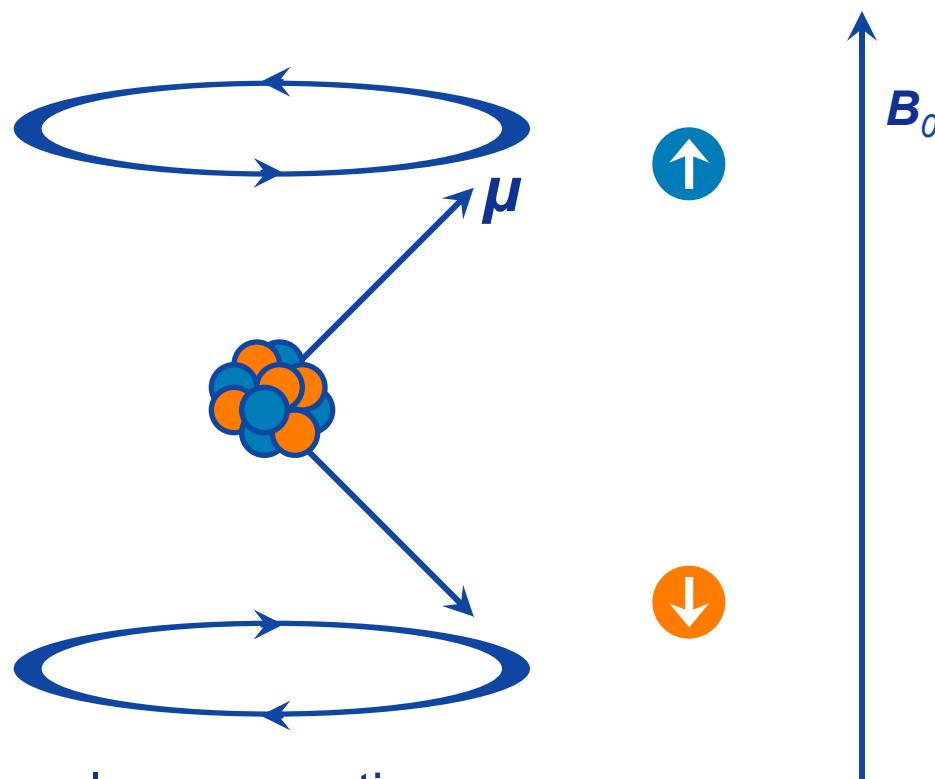
- To show how quantitative NMR spectroscopy allow insight into polymer structure
- To give a idea about how NMR spectroscopy is used within the polymer industry
- To expose the audience to application of non-standard NMR spectroscopy
- To introduce the field of solid-state NMR spectroscopy



## NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

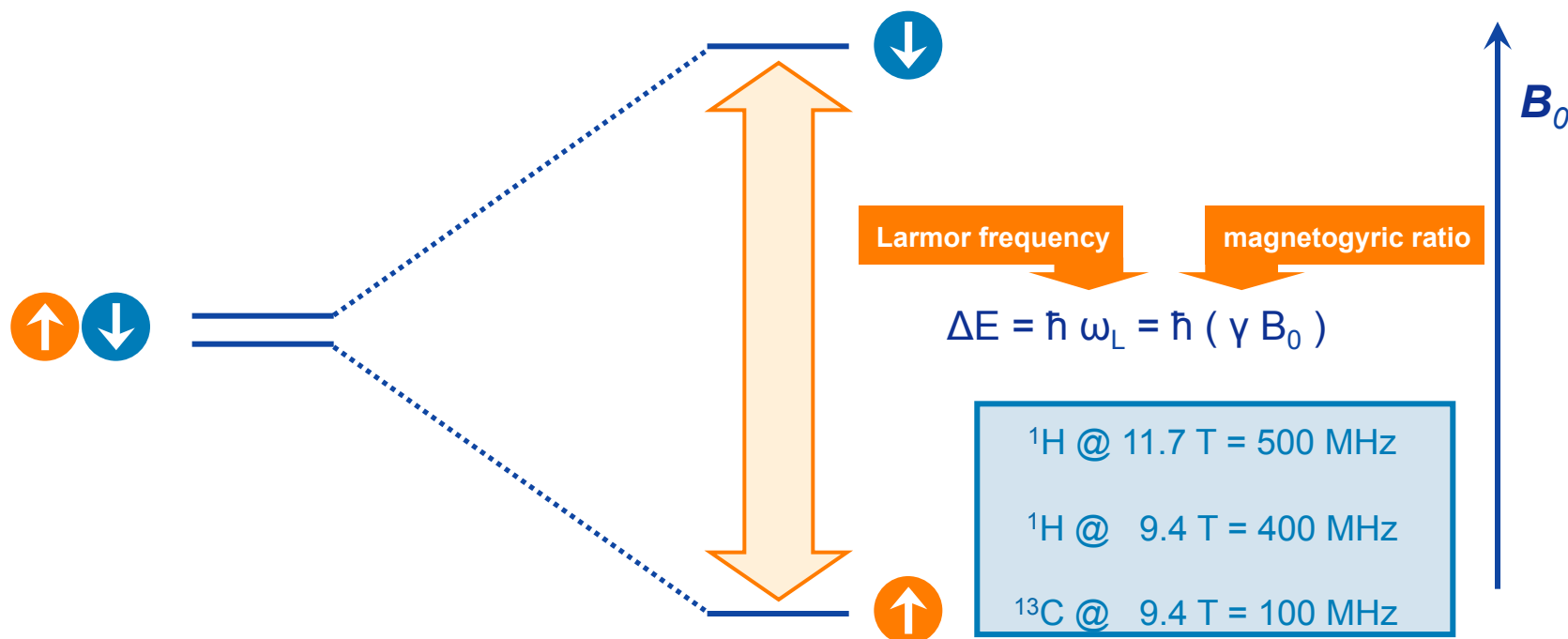
# REVIEW OF KEY THEORY

# Nuclear magnetisation & precession



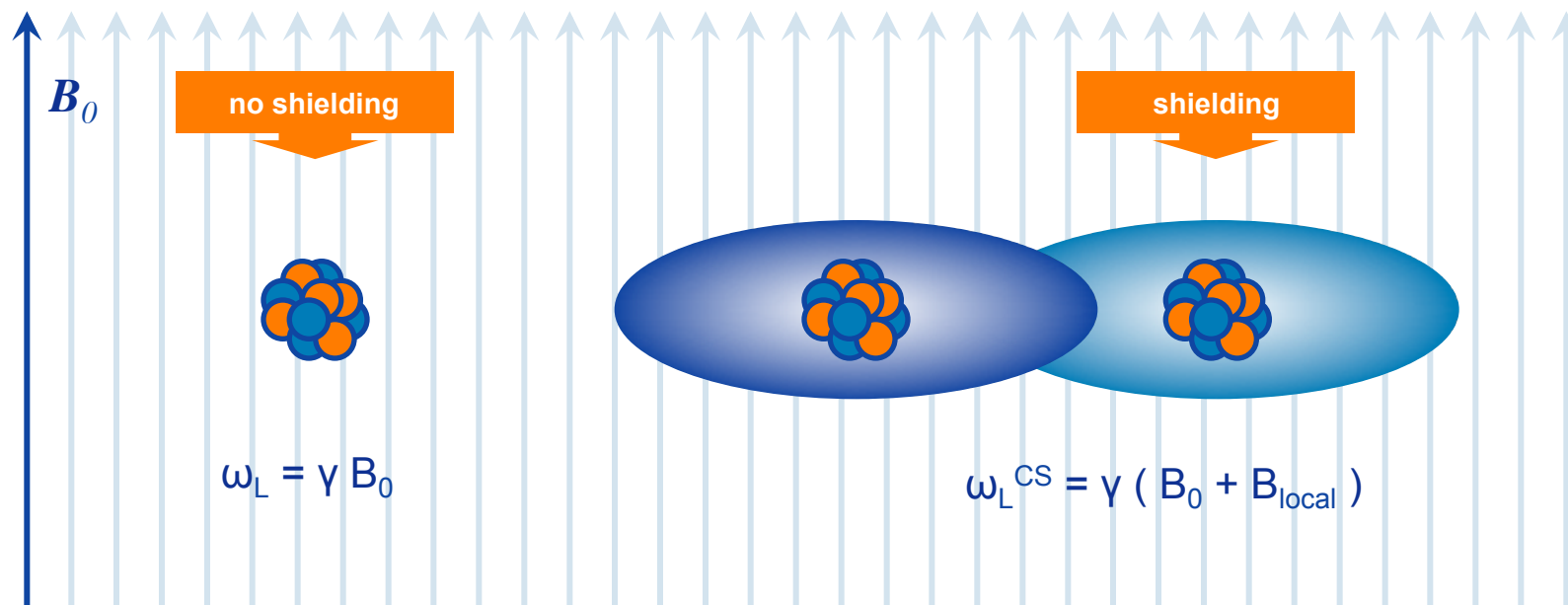
- Certain nuclei possess nuclear magnetism
- In a magnetic field they precess about their axis

# Zeeman interaction of $I = \frac{1}{2}$ nuclei



- Degeneracy of energy levels broken by Interaction with  $B_0$  field

# Chemical shift d

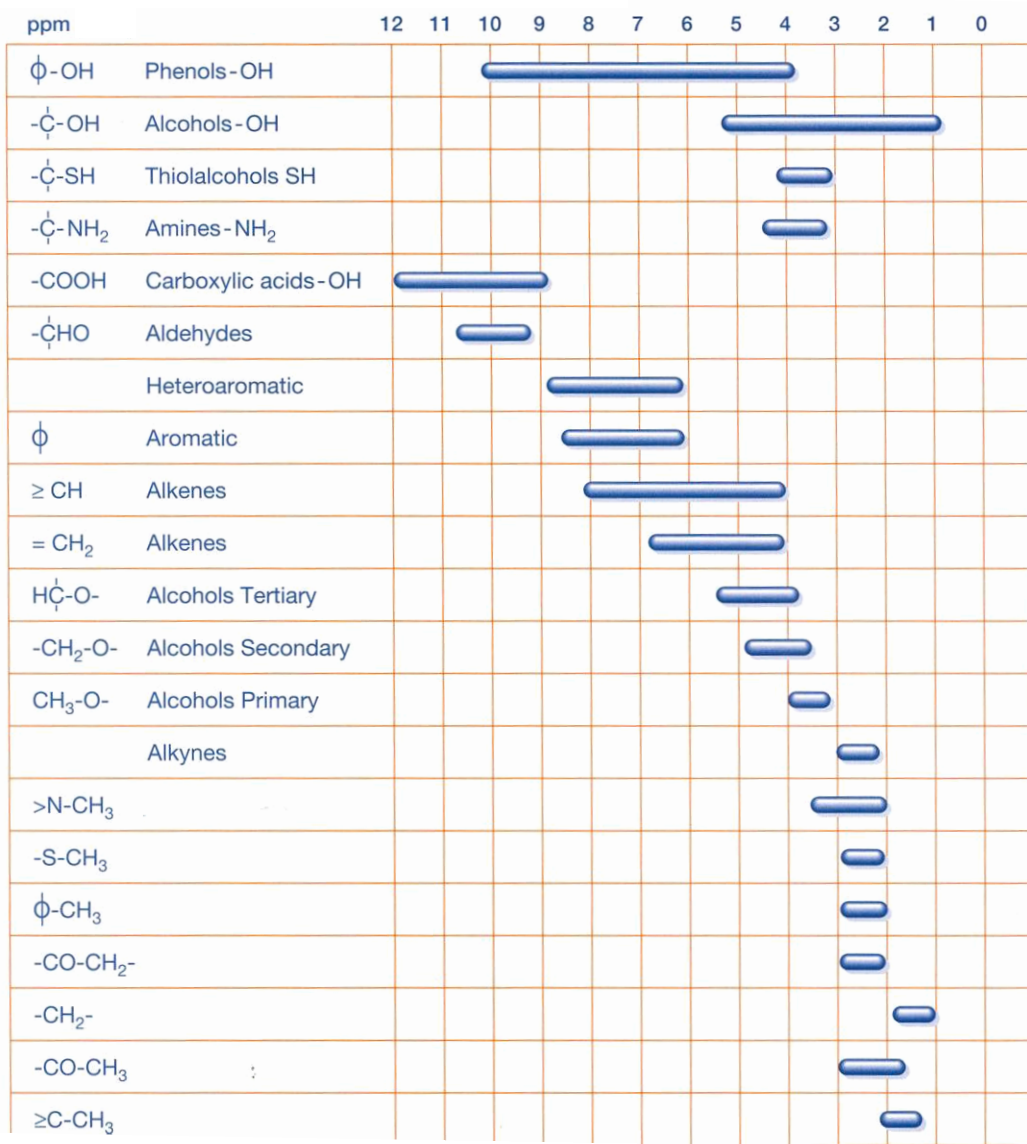


- local electronic environment shields magnetic environment of nuclei
- parts-per-million (ppm) perturbation of Larmor frequency
  - Chemical shifted Larmor frequency is proportional to chemical environment

# $^1\text{H}$ chemical shift correlation table

- correlation table of  $^1\text{H}$  chemical-shift with chemical environment

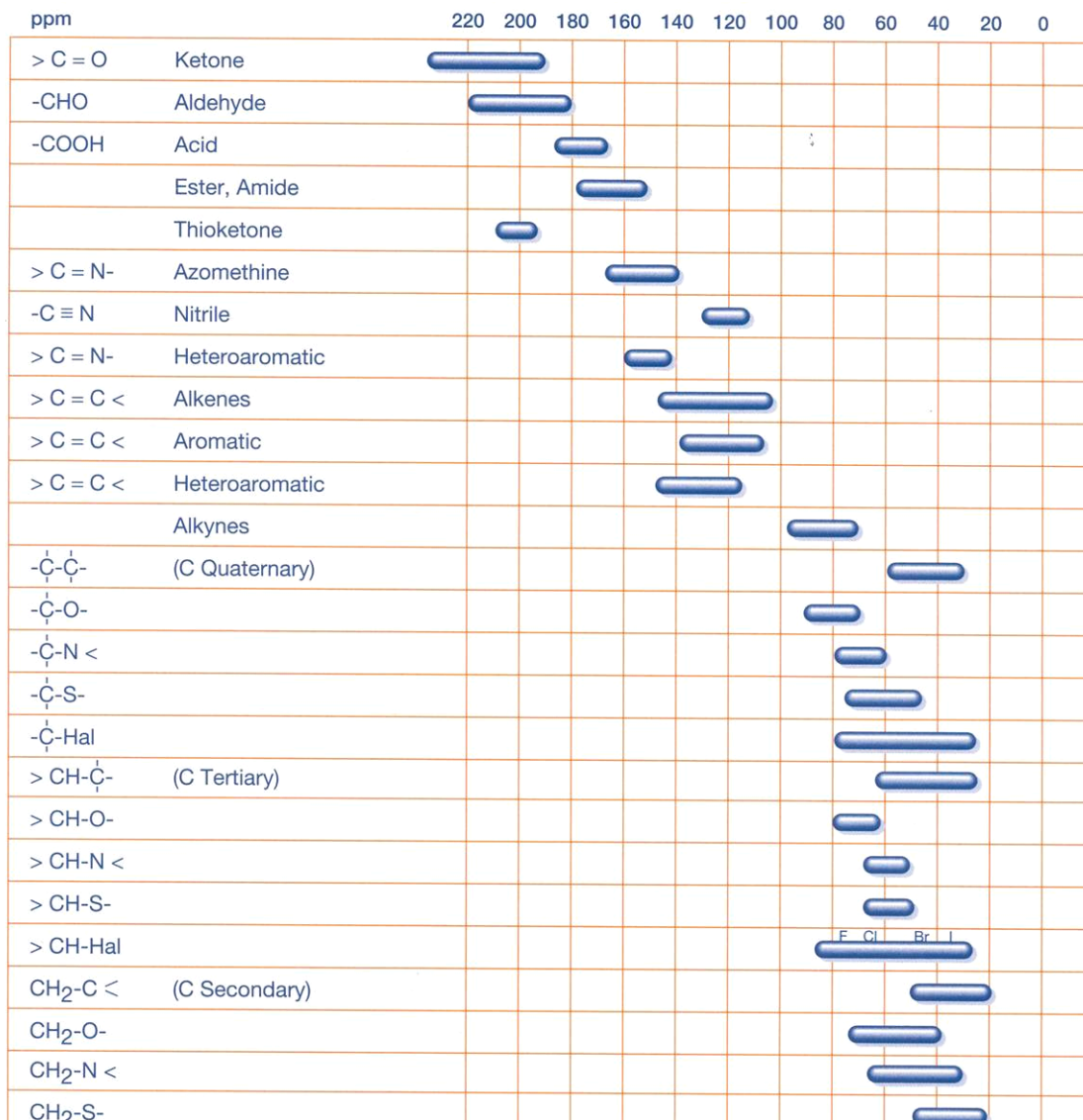
- structure property relationship





# General chemical shift correlation

- each isotope has separate correlation table
- correlation table of  $^{13}\text{C}$  chemical-shift with chemical environment
- general trends:
  - more electronegative
  - more bonding
  - more aromatic

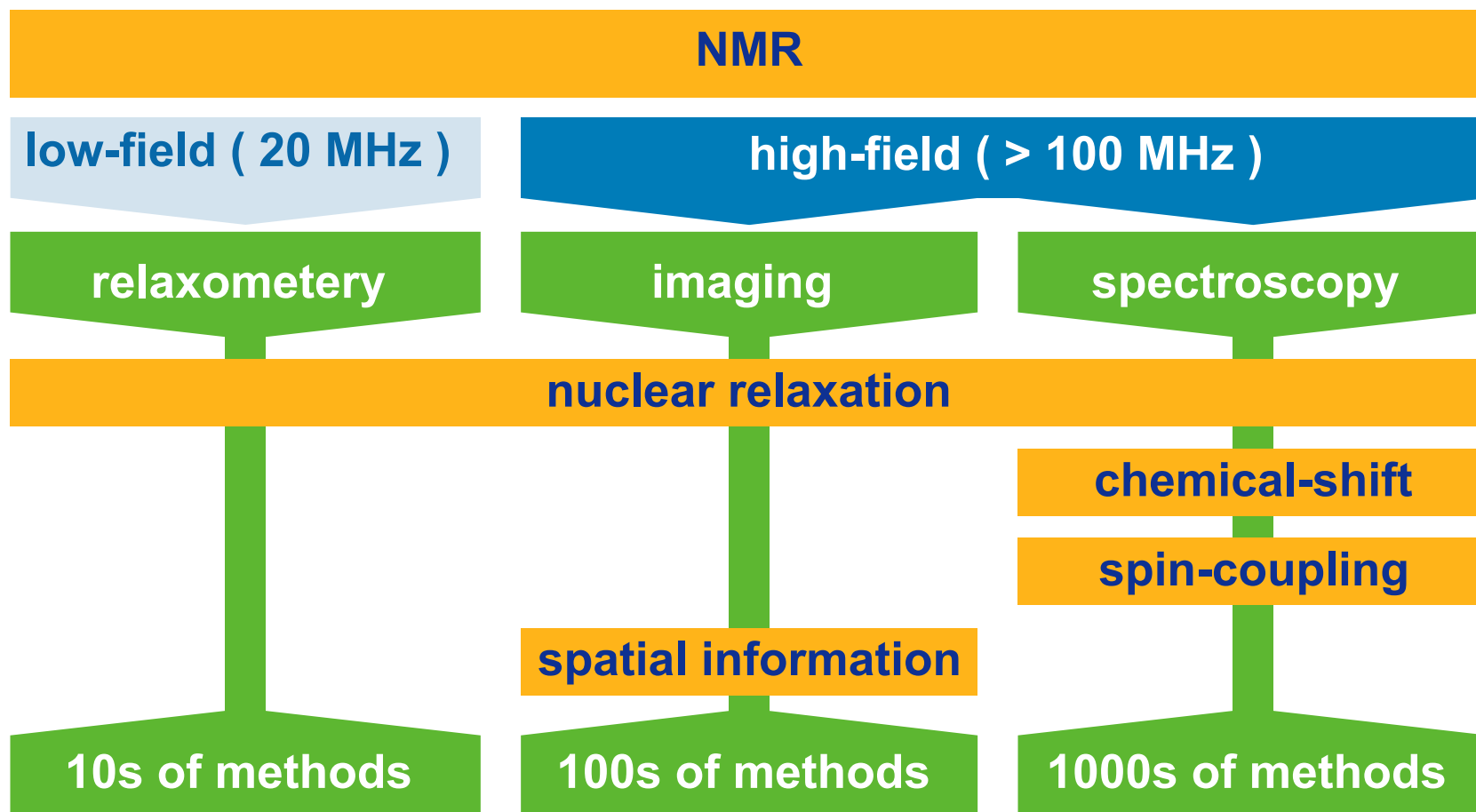


# Interaction of magnetisation with RF pulse

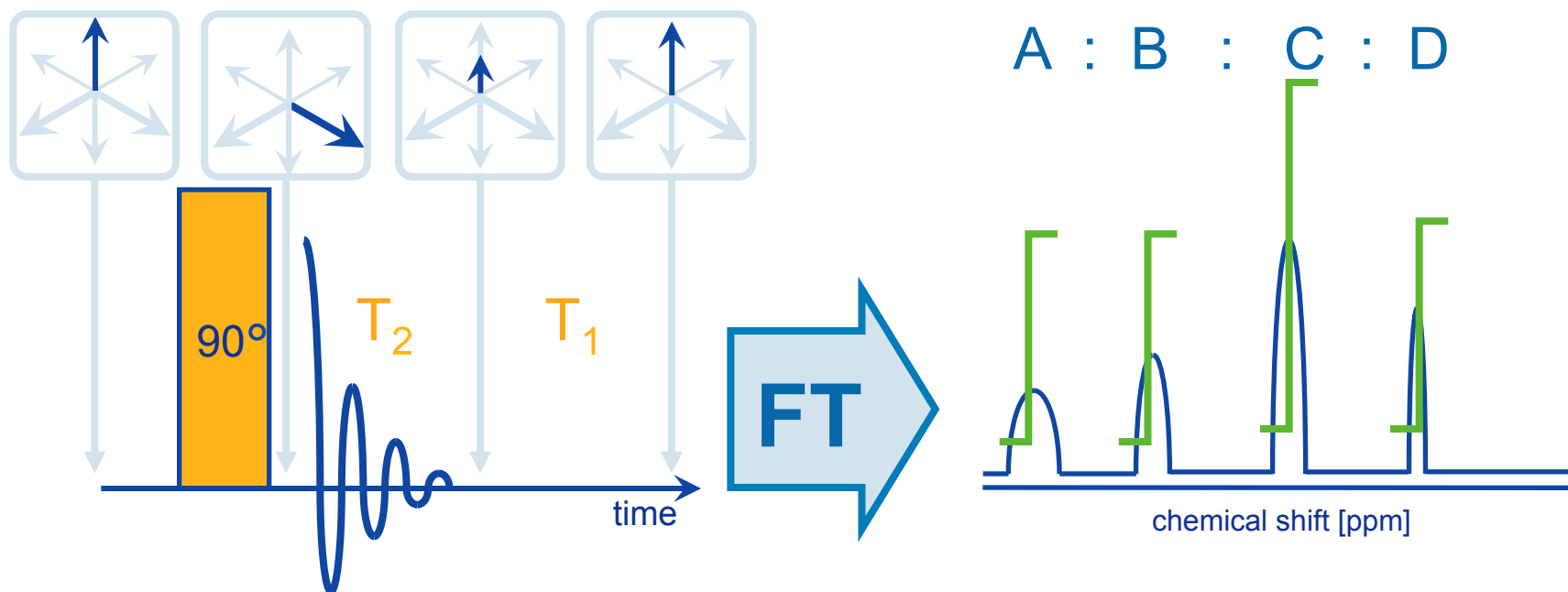


- RF pulse manipulates bulk magnetisation in controlled fashion

# Types of NMR Implementation

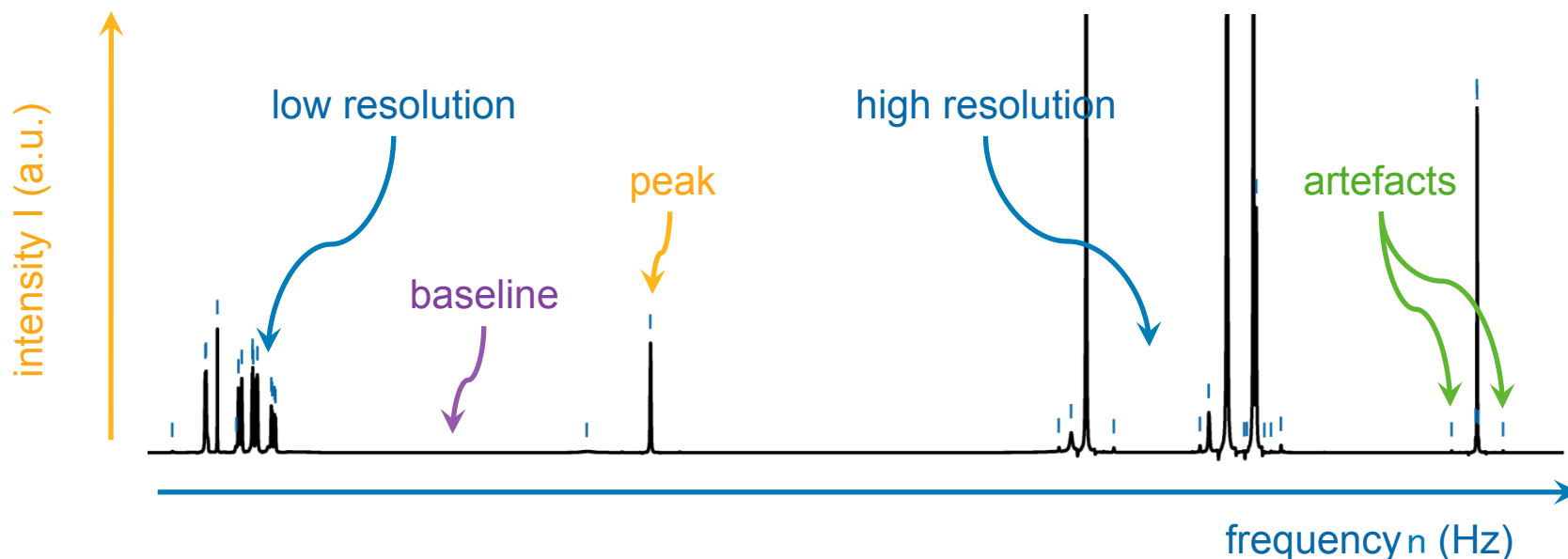


# Fourier-transform (FT) NMR spectroscopy



- All resonances excited at once by RF pulse
- NMR response detected as a free induction decay (FID)
- Generate spectrum by Fourier transform of FID
- Spectrum is quantitative if dependence on relaxation observed

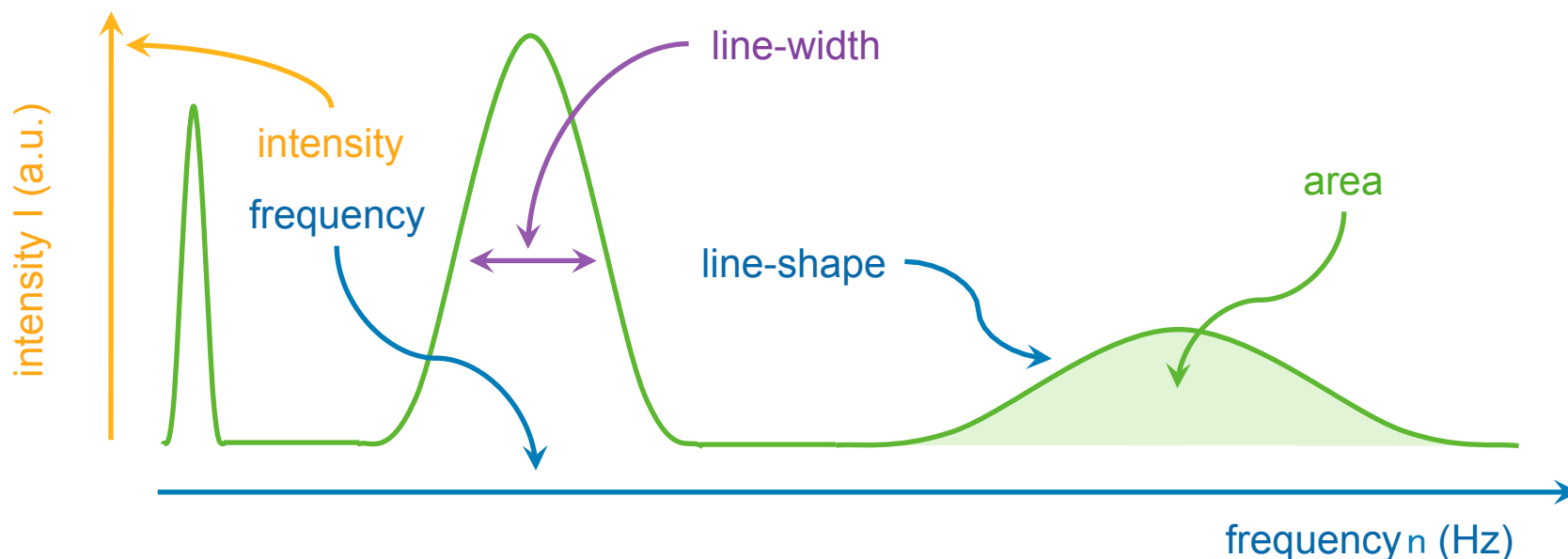
# Anatomy of a spectrum



All spectra have a number of common features:

- baseline: part of spectrum with no signals present (assumption)
- peaks: signals arising of chemical species such as bonds, atoms
- resolution: how overlapped are adjacent peaks
- artefacts: signals not directly arising from chemical species

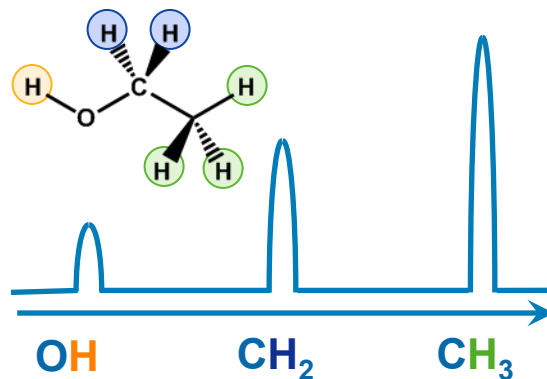
# Anatomy of a peak



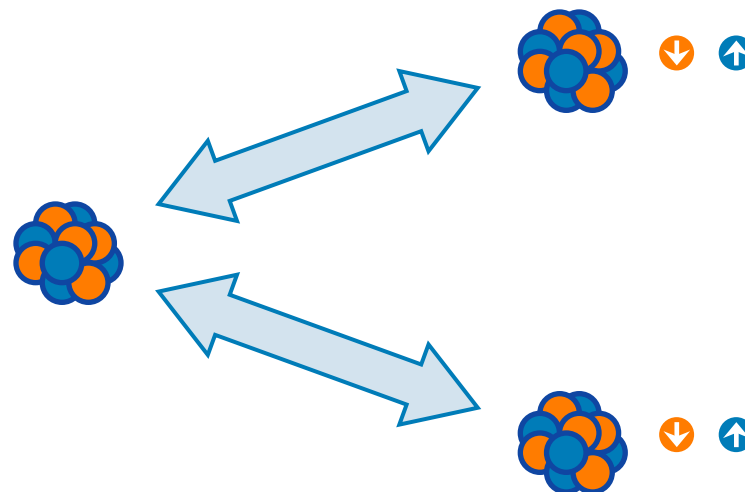
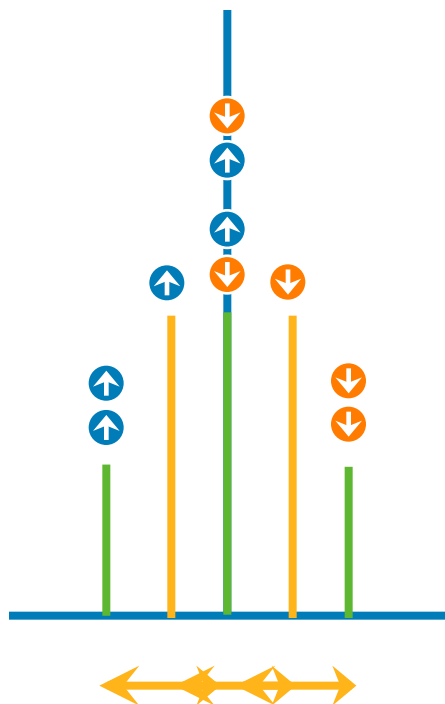
- All signals seen in spectroscopy have a number of common features:
  - frequency, intensity, area, line-width, line-shape, fine-structure
  - Signals need to be assigned to chemical species (specific atom/bond)

# Assignment

- The process of working out what chemical species are present based upon what signals (peaks) are present in spectra
- Achieved by many different methods
  - simulation (ab-initio/emperical)
  - comparison (models/articles/libraries)
  - logical reasoning (ratios)
  - prior knowledge (starting materials)
  - experience
- Some assignments can be proved others are just empirical
- The assignment of true unknown materials is very difficult but rare



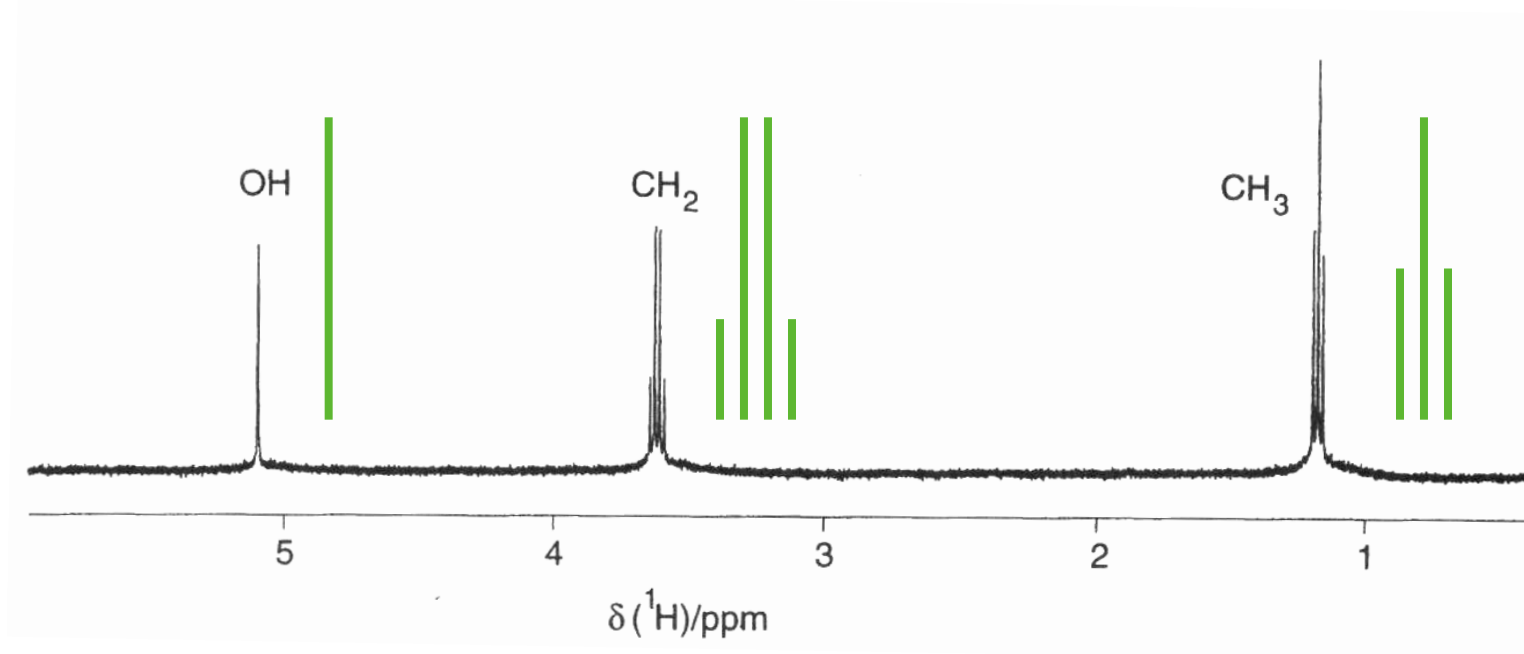
# Spin coupling



- interaction of one nucleus on another
- signal of nuclei “split” due to the spin state/states of other nuclei
  - through-space (dipole-dipole) or through-bond/bonds (J) interaction

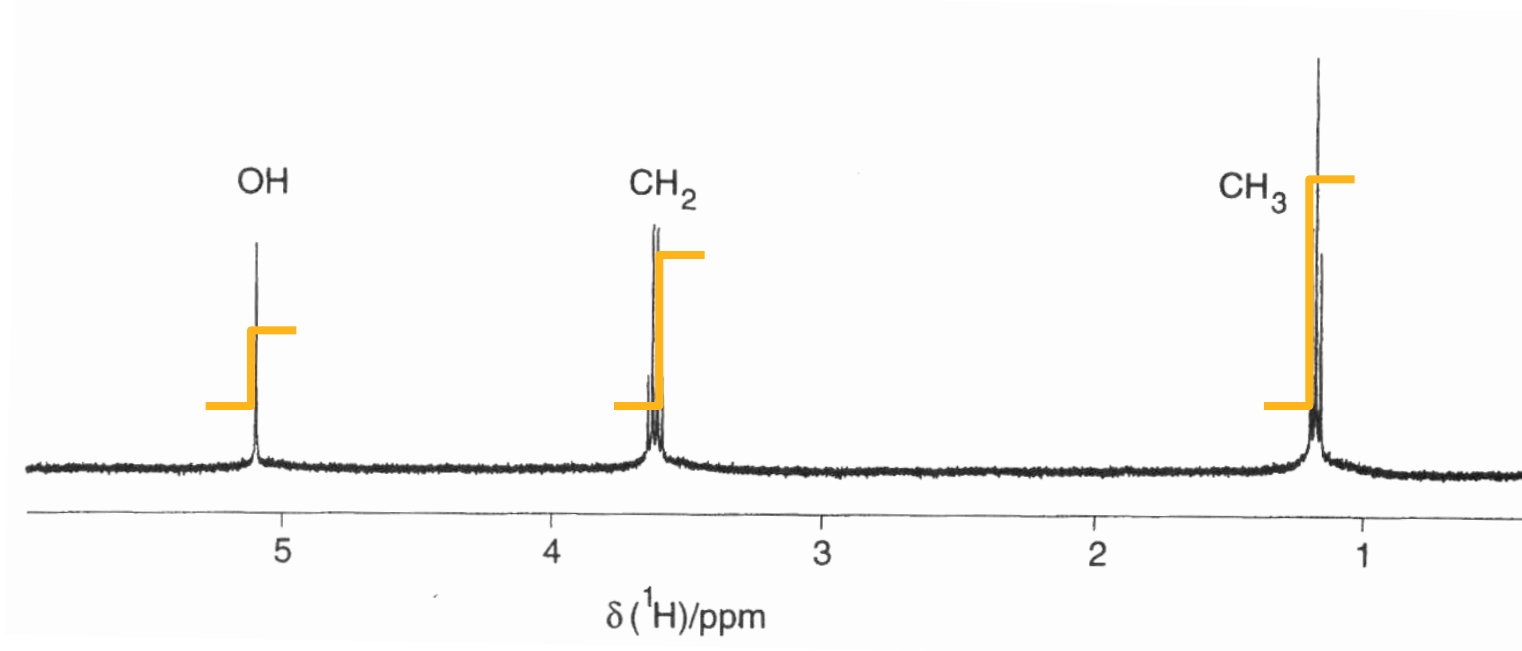


# J-coupling in ethanol



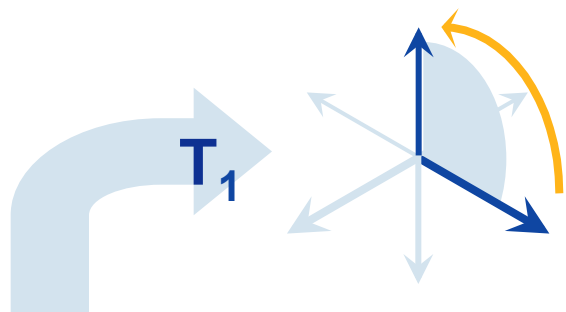
- 3 bond  $^1\text{H}$ - $^1\text{H}$  J coupling ( $^3J_{\text{HH}}$ ) = Hz
  - $\text{CH}_3$  triplet = each  $\text{CH}_3$  proton is coupled to 2 other protons i.e.  $\text{CH}_2$
  - $\text{CH}_2$  quartet = each  $\text{CH}_2$  proton is coupled to 3 other protons i.e.  $\text{CH}_3$
  - OH singlet = each OH proton is not coupled to any other protons

# Quantitative NMR spectroscopy



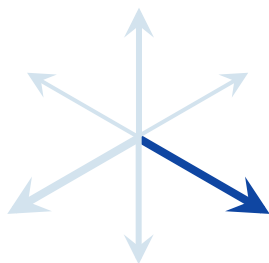
- calculate area under each peak in spectrum (integration)
- area proportional to number of nuclei in that environment
  - $\text{Area}(\text{OH}) : \text{Area}(\text{CH}_2) : \text{Area}(\text{CH}_3) = 1 : 2 : 3$
  - only relative not absolute i.e. not 1 : 2 : 3 protons

# Nuclear relaxation



- Spin-lattice relaxation ( $T_1$ )
  - longitudinal motion of bulk magnetisation:  $M_z$
  - return to nuclear ground state

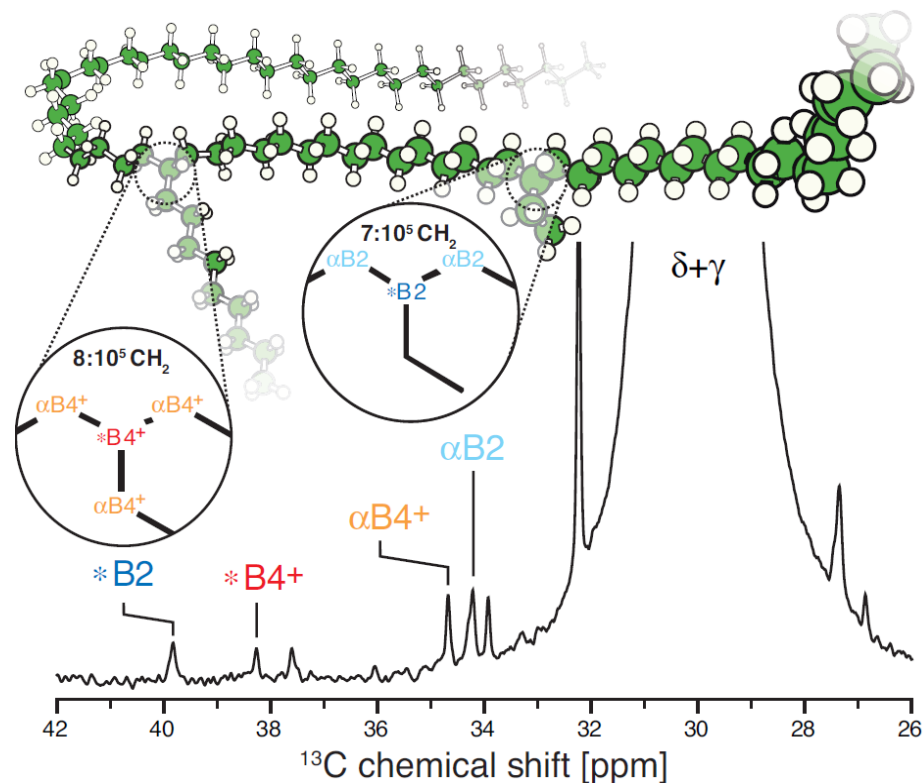
**Relaxation is site specific & related to many things ( coupling, motion ... )**



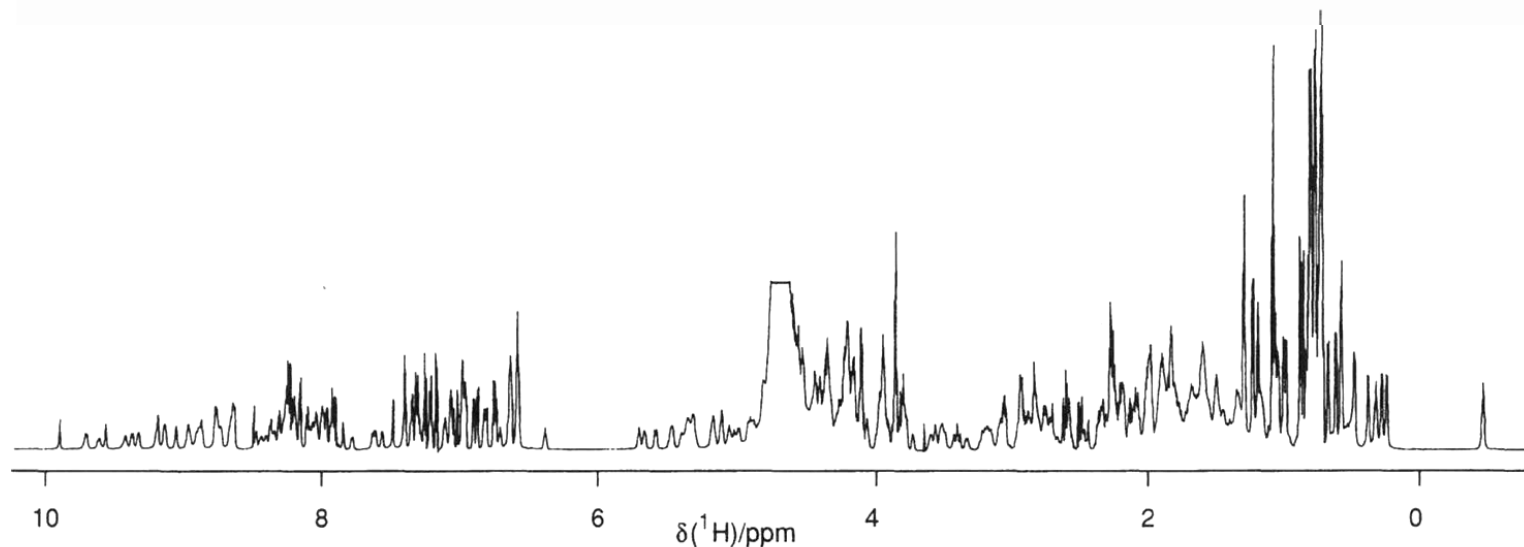
- Spin-spin relaxation ( $T_2$ )
  - transverse dephasing of magnetisation:  $M_x$  &  $M_y$
  - loss in coherence of the bulk magnetisation

# What does spectroscopy tell us?

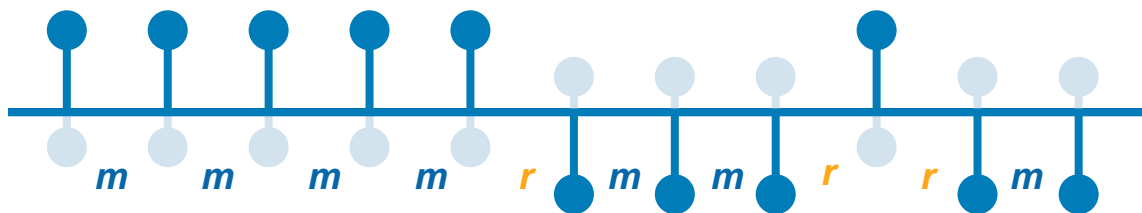
- spectroscopy provides **direct** evidence about the chemical structure of a material
  - what atomic nuclei are present
  - what chemical environments the atomic nuclei are in
  - how the atomic nuclei are bonded
  - how many of a chemical species are there
- This allows:
  - identification of unknown materials
  - quantification of chemical structure
  - structure-property relationships



# What does NMR spectroscopy tell us?



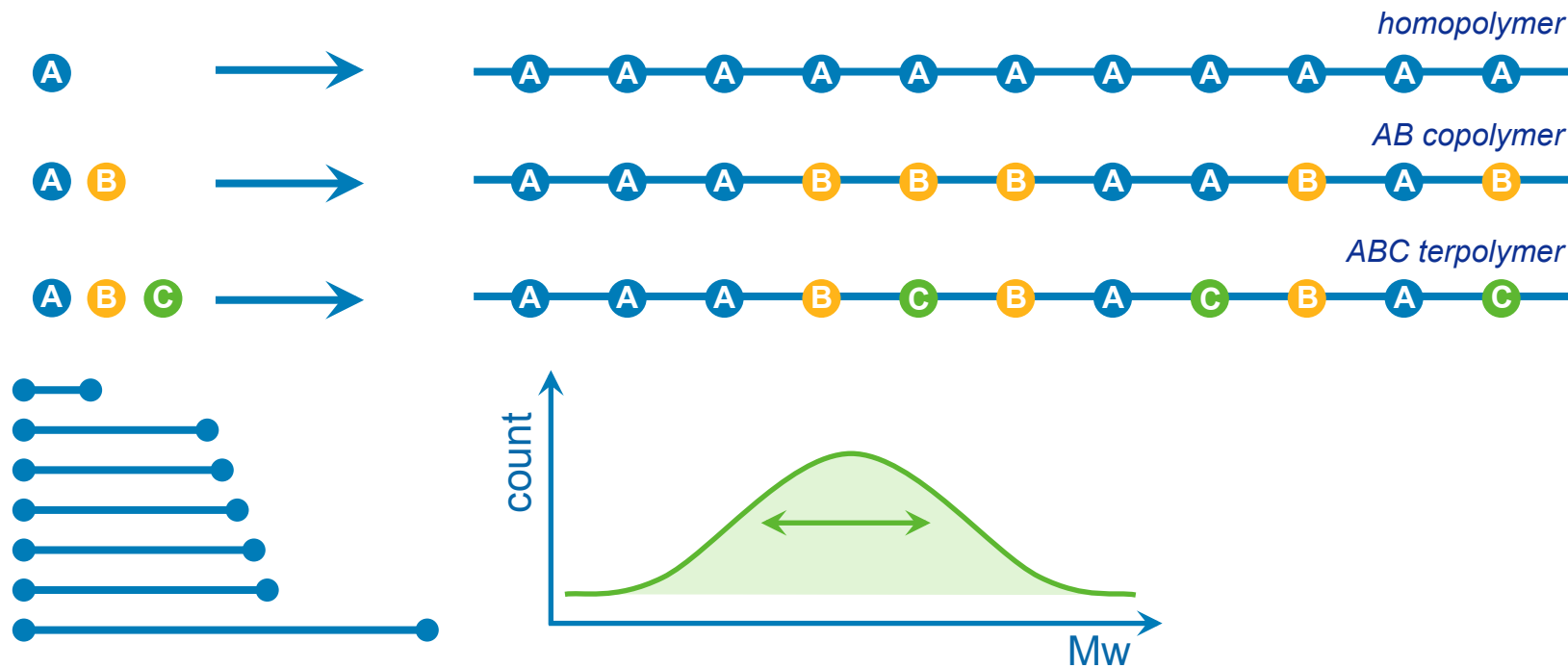
- NMR spectrum describes:
  - chemical (magnetic) environment, bonding, dynamics, number of spins
- Quantification based on spectral integration



# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

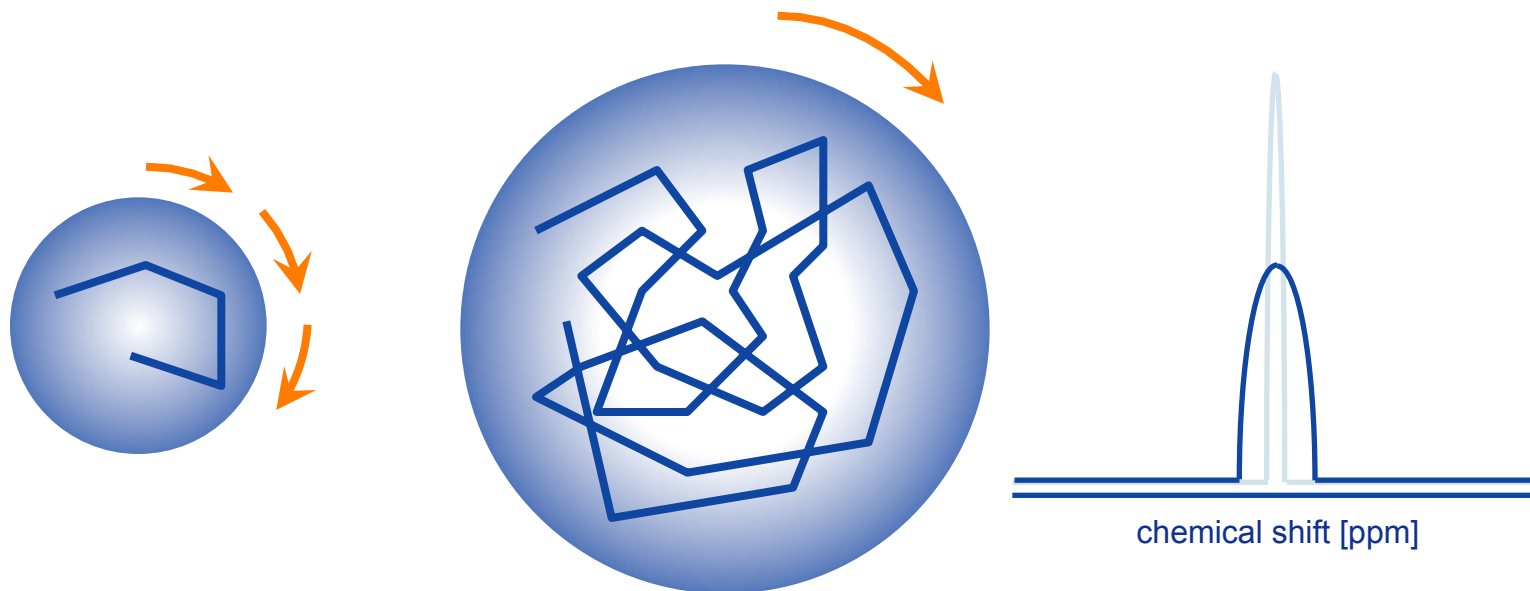
## POLYMERS & NMR SPECTROSCOPY

# Polymers



- Always a distribution of chain lengths (molecular weights)
- Characteristic features
  - Degree of polymerisation, molecular weight ( $M_n$  or  $M_w$ ), molecular weight distribution (MWD), tacticity, comonomer content, end-groups

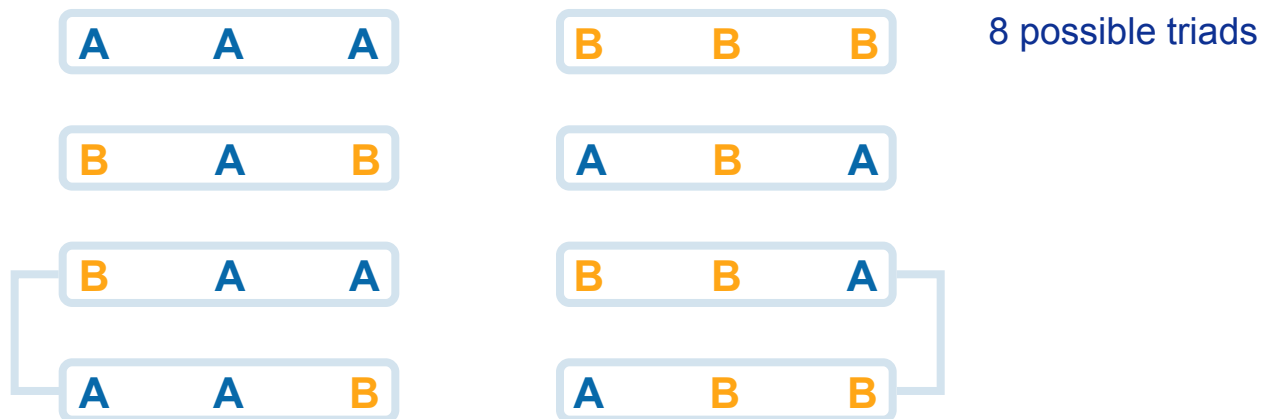
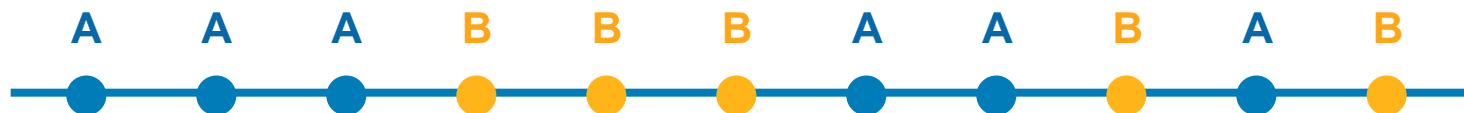
# Polymer NMR & relaxation



- Polymers have relatively long rotational correlation time in solution
- Influences relaxation & line-widths ( longer  $T_1$  and shorter  $T_2$  )



# Polymer NMR & comonomer sequences



- Each triad has characteristic chemical shift
- Quantification of comonomer distribution provides insight into structure

A diagram of a 1D lattice with alternating blue and light blue sites. Blue sites have blue dots above and light blue dots below, labeled 'm'. Light blue sites have light blue dots above and blue dots below, labeled 'r'. The labels 'm' and 'r' are in blue and orange respectively.

*m m m m*

$$m \quad m \quad m \quad r$$

$m$     $m$     $r$     $m$

*m*      *r*      *m*      *m*

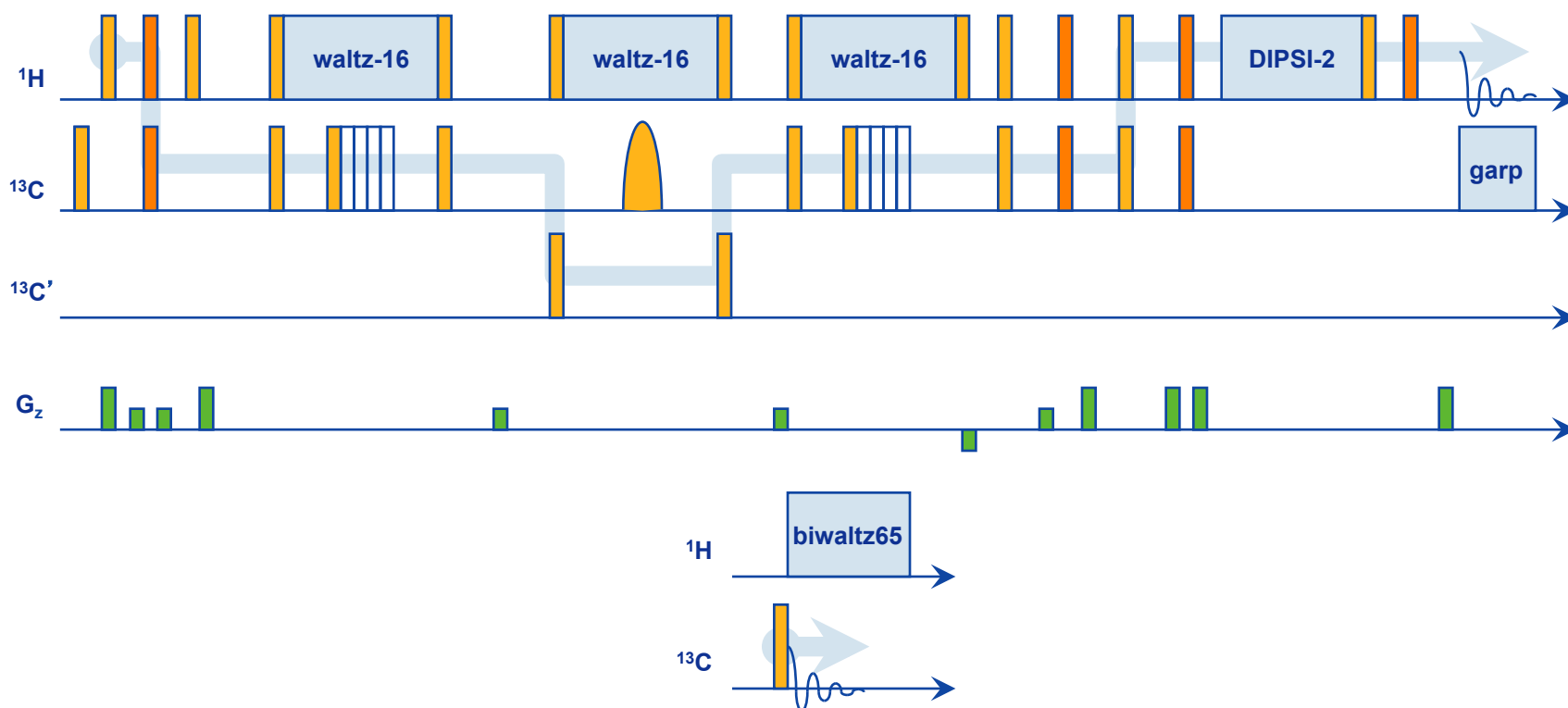
*r m m r*

$m \quad m \quad r \quad r$

*m r r m*

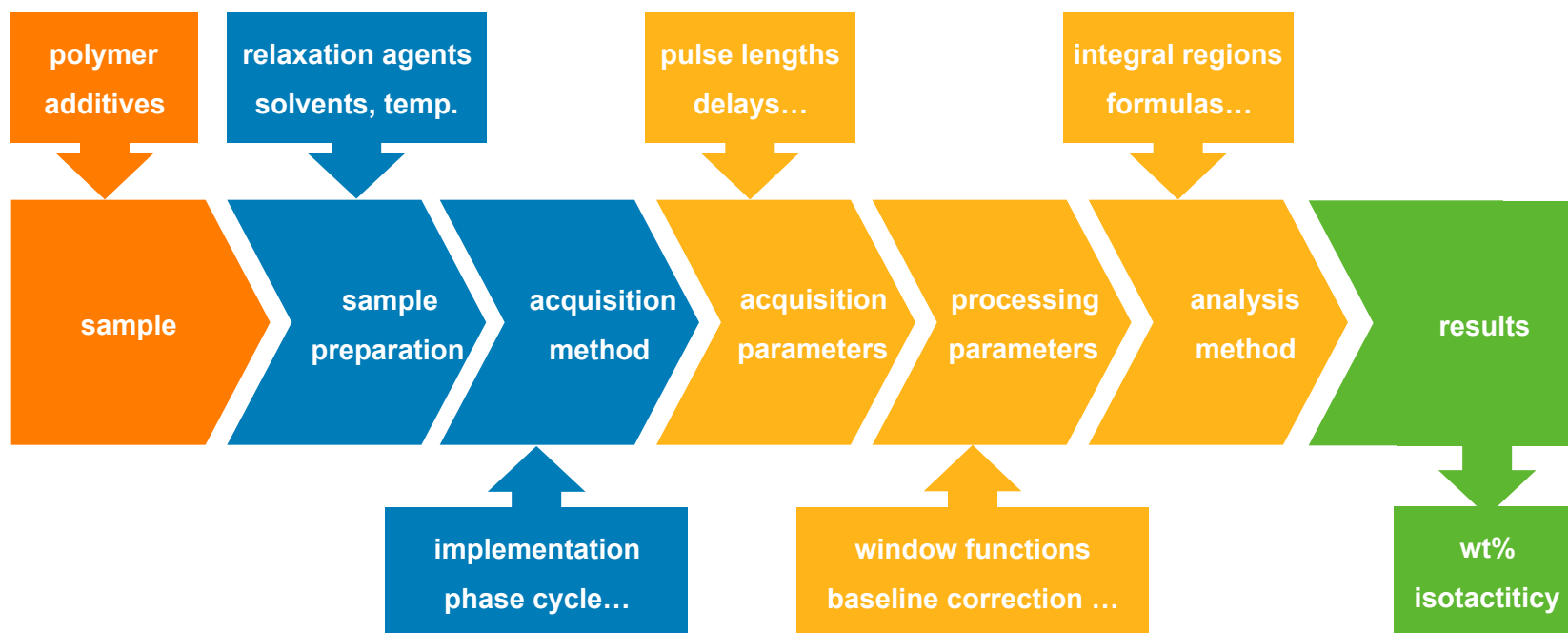
- © 2010 Borealis AG

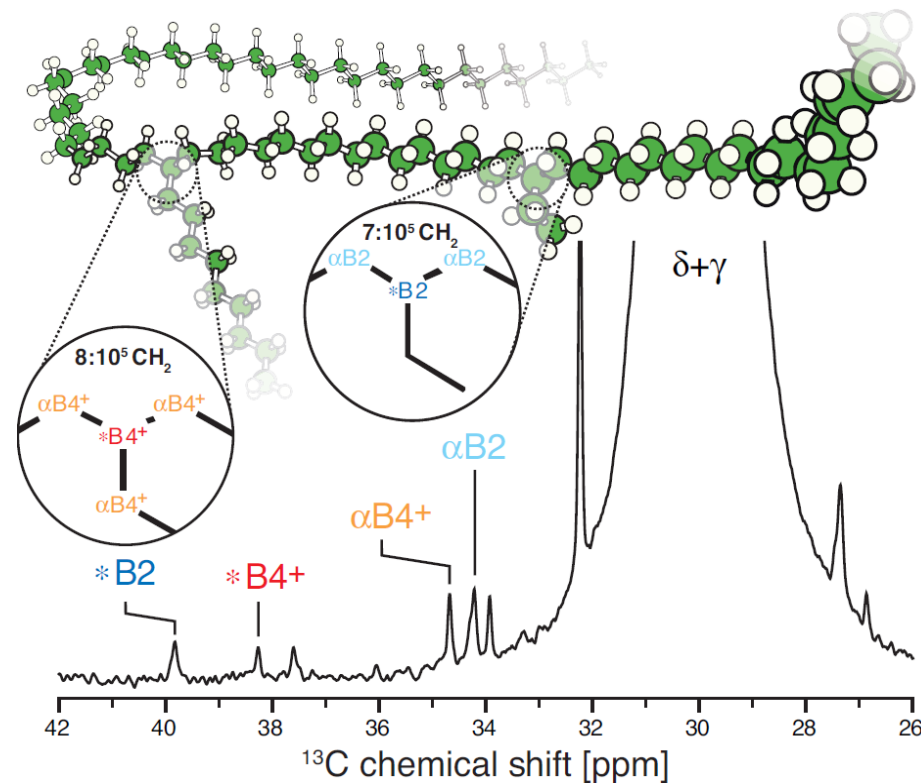
# Polymer NMR & pulse sequences



- Complex multi-dimensional methods available for detection
- For quantification only 1D single pulse excitation is used (  $^{13}\text{C}\{^1\text{H}\}$  )

# Quantitative NMR spectroscopy process





# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

## NMR SPECTROSCOPY OF PE

# Polyethylene (PE)



- Cheap to produce as monomer is byproduct of petrochemical industry
  - Physical and mechanical properties related to chemical structure
  - Through research and development increase properties to expand applications
- Chemical structure not as simple as it first looks!
  - difficult to characterise (low solubility)

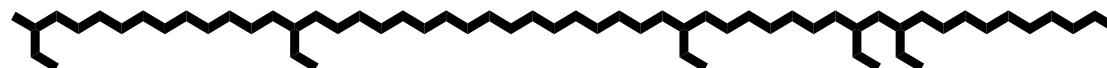
# Chain branching in polyethylene



## short chain branching

*copolymer / process*

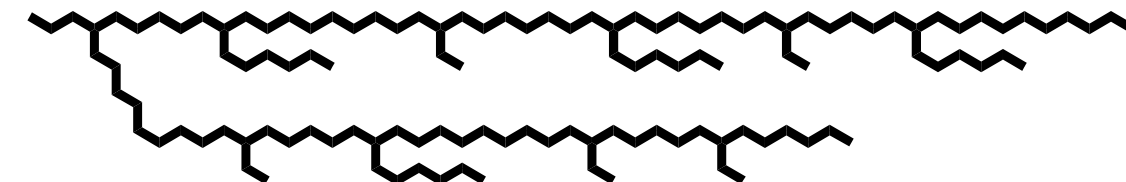
*branch length < 30 C*



## long chain branching

*process / post modification*

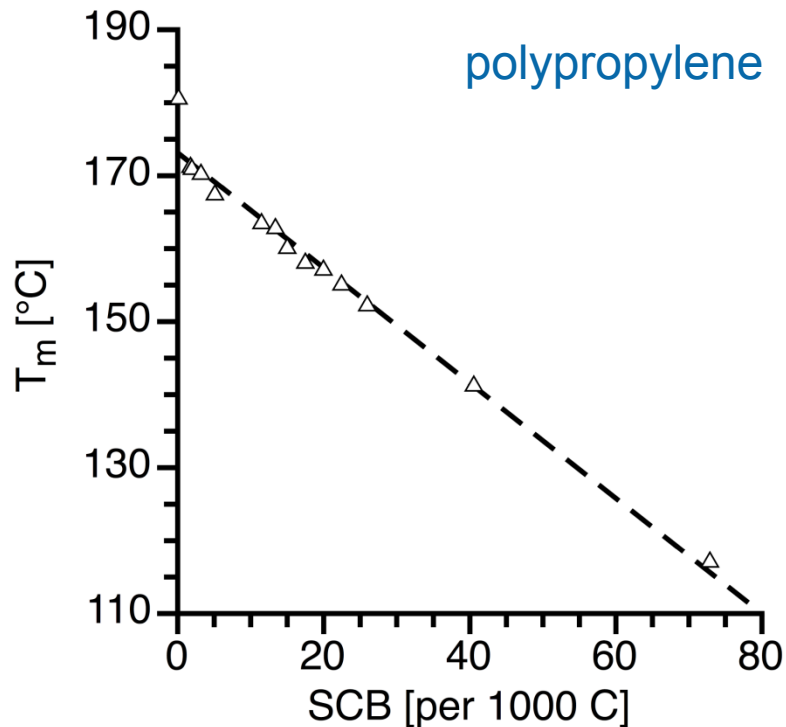
*branch length >  $M_e \approx 270$  C*



# Relevance of branching

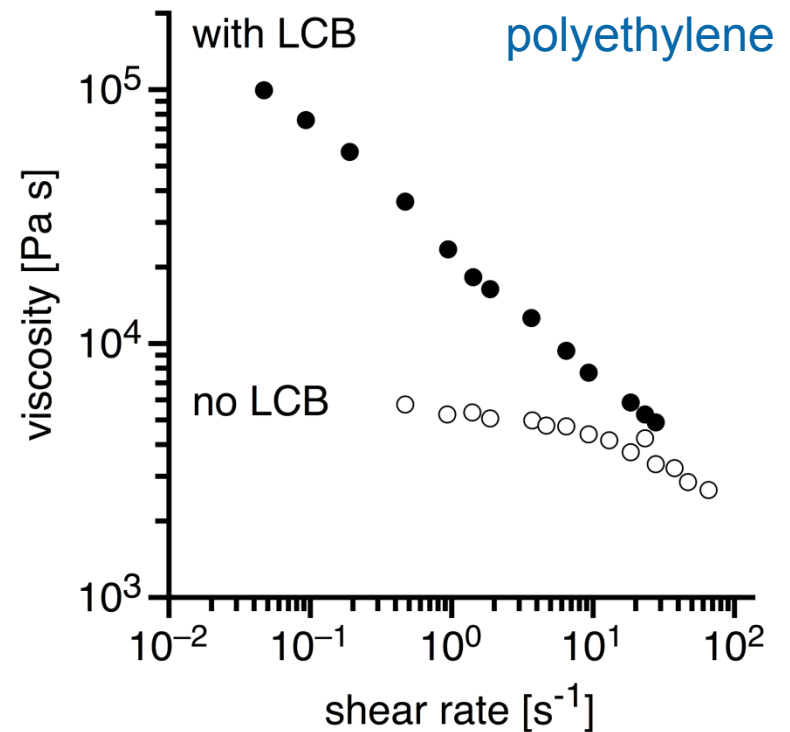
## Short chain branching (SCB)

thermal & mechanical properties



## Long chain branching (LCB)

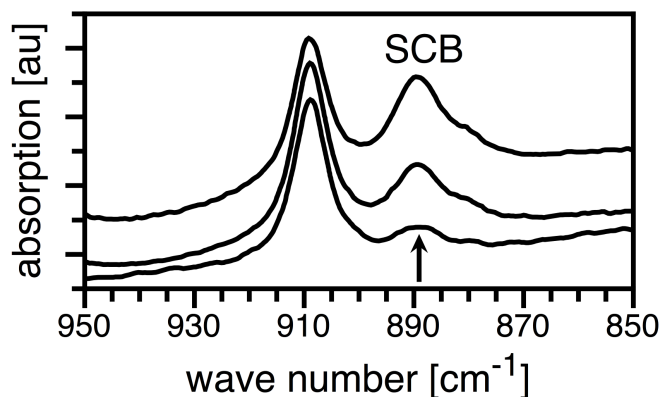
melt processability



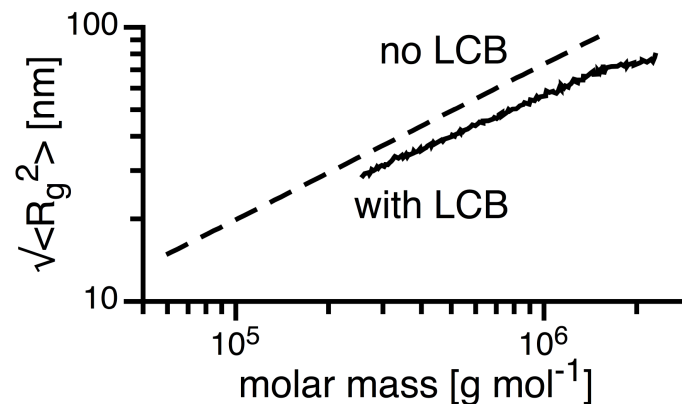


# Methods of branch detection

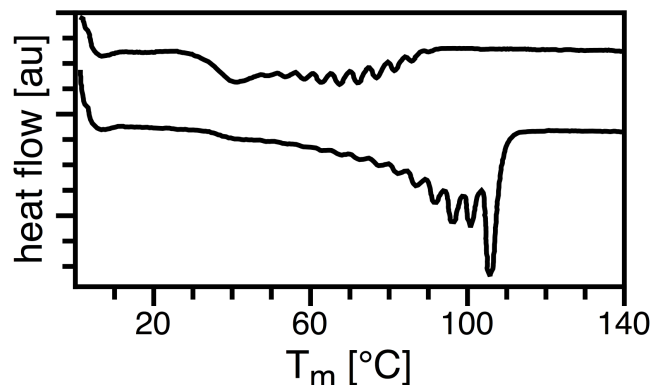
## infrared spectroscopy



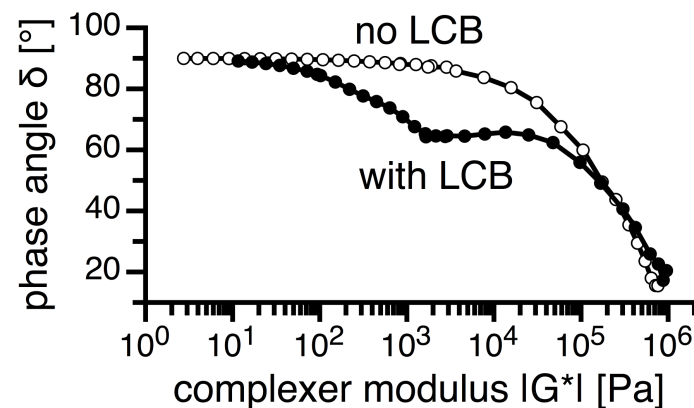
## GPC + light scattering



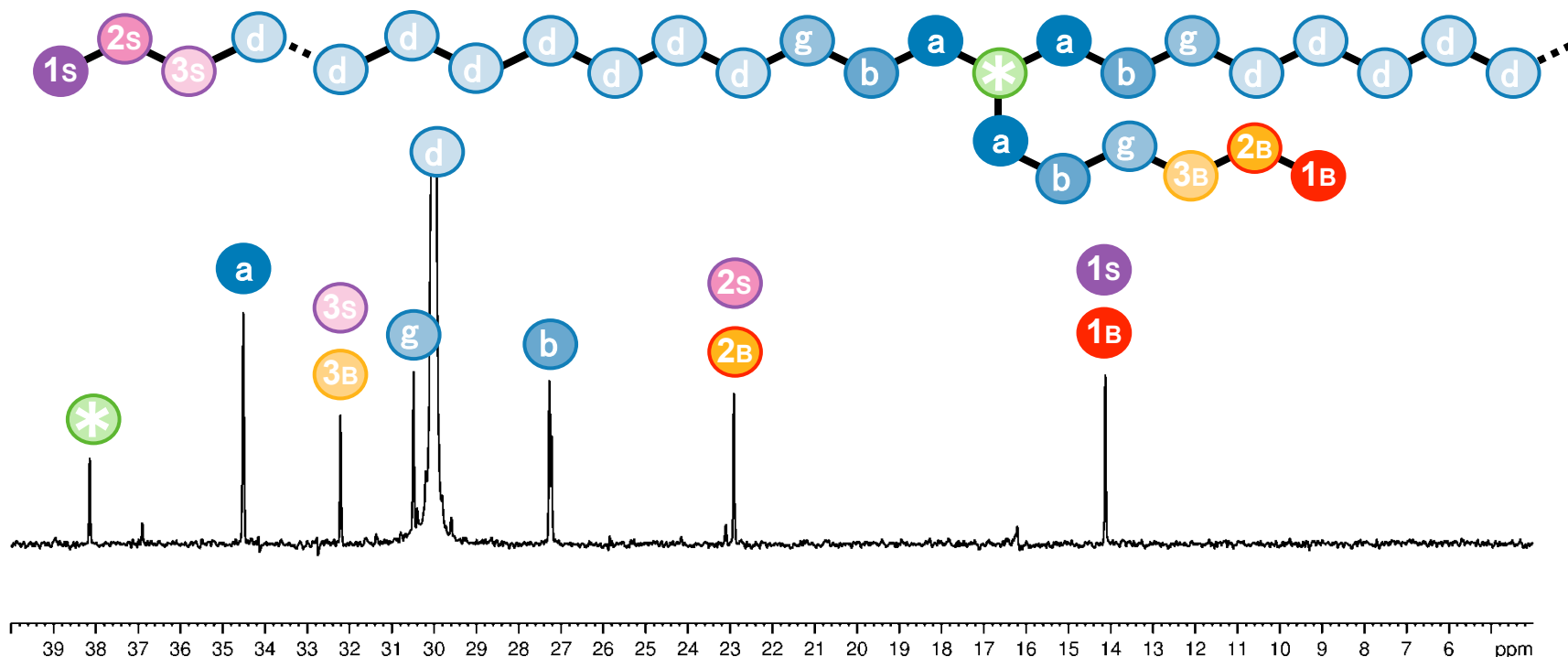
## thermally fractionated DSC



## rheology

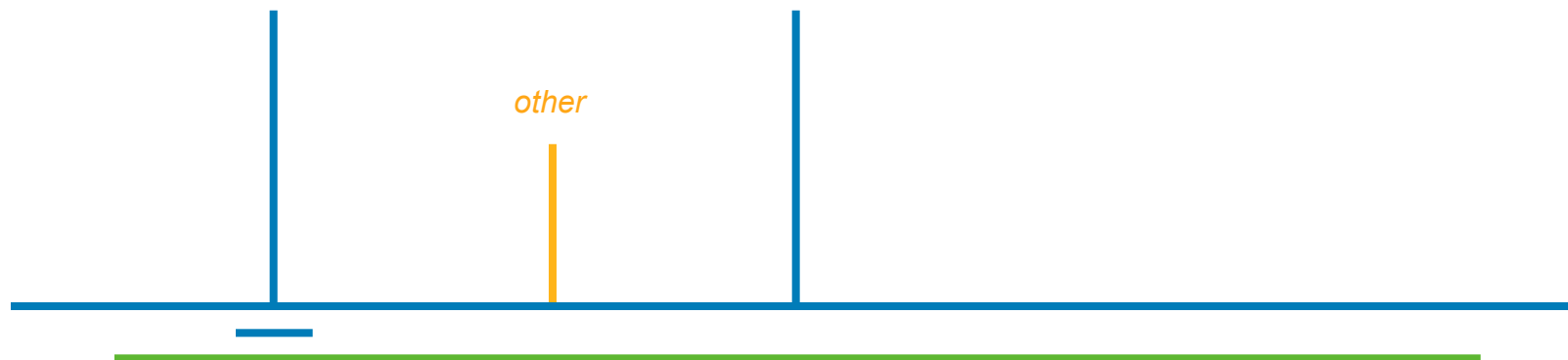


# $^{13}\text{C}$ NMR spectroscopy of polyethylene



- Chemical shift influenced by groups up to 4 carbons away
- Key sites identified by  $^{13}\text{C}$  NMR spectroscopy
  - bulk  $\text{CH}_2$ , branch  $\text{CH}$ , sites adjacent to branches, chain/branch ends

# Comonomer quantification by NMR

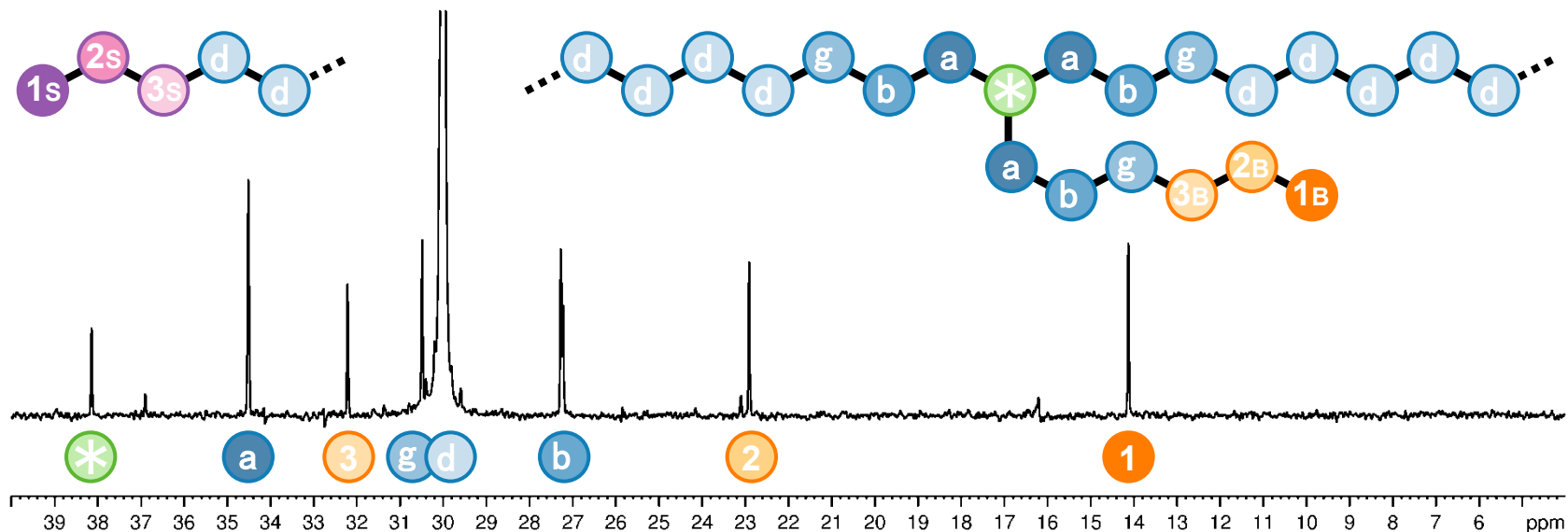


- Mole fraction (comonomer content)
- Selection of appropriate sites for integration
- Correction of integrals

$$f_x = A_x / A_{\text{all}}$$

$$f_x = A_x / (A_{\text{all}} - A_{\text{other}})$$

# Quantitative solution-state $^{13}\text{C}$ NMR



- direct quantification via integral ratio
  - branching & copolymer content proportional to  $\frac{*}{\delta}$
- disadvantages of solution-state:
  - low solubility of PE and PP in TCB or TCE: long sample preparation times
  - typical measurements of 8-12 h for a quantitative  $^{13}\text{C}$  spectrum

■ P. Wood-Adams et al. Macromolecules **2000**, 33, 7489

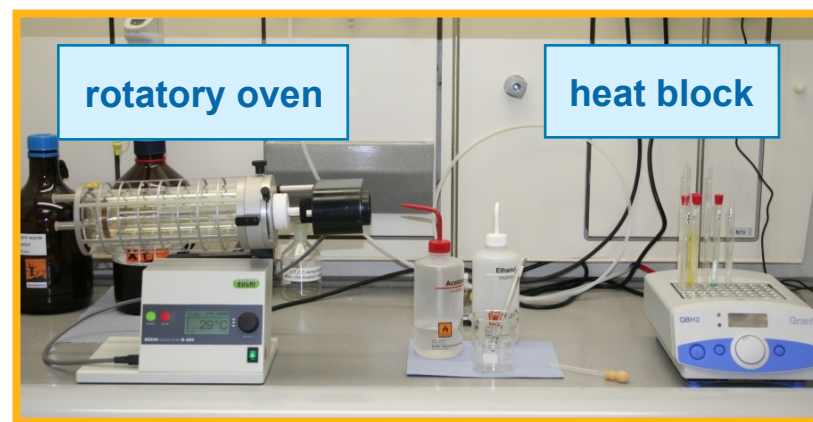
# Polyolefin Solution-state NMR Setup

- Standard NMR spectroscopy technique
  - polymer dissolved in solvent imparts mobility
  - isotropic tumbling narrows spectral line widths
  - high-temperature (125°C)
    - 100-200 mg in 3-4 ml of tetrachloroethene- $d_2$  (TCE- $d_2$ )
    - approximately 1 h for homogeneous solution to form
- Probeheads (accessories)
  - 10 mm  $^{13}\text{C}$  selective extended temperature (SEX) probehead (custom  $^{13}\text{C}$  detect)
    - $^{13}\text{C}$  optimised, high  $^{13}\text{C}$  sensitivity, lower  $^1\text{H}$  resolution

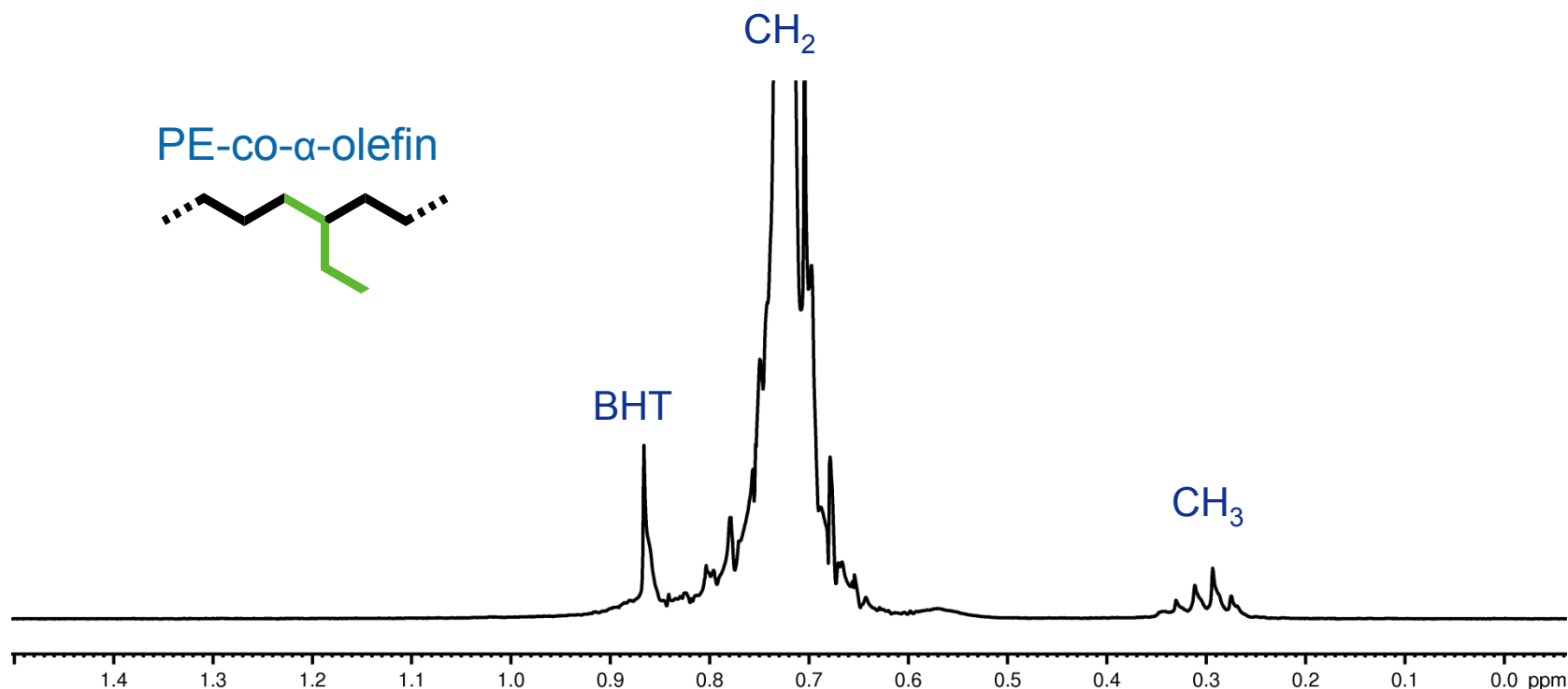
# Sample preparation: solution-state



- Samples can be in any form
  - Pellets, powder, films, finished parts, filled



# $^1\text{H}$ NMR of PE

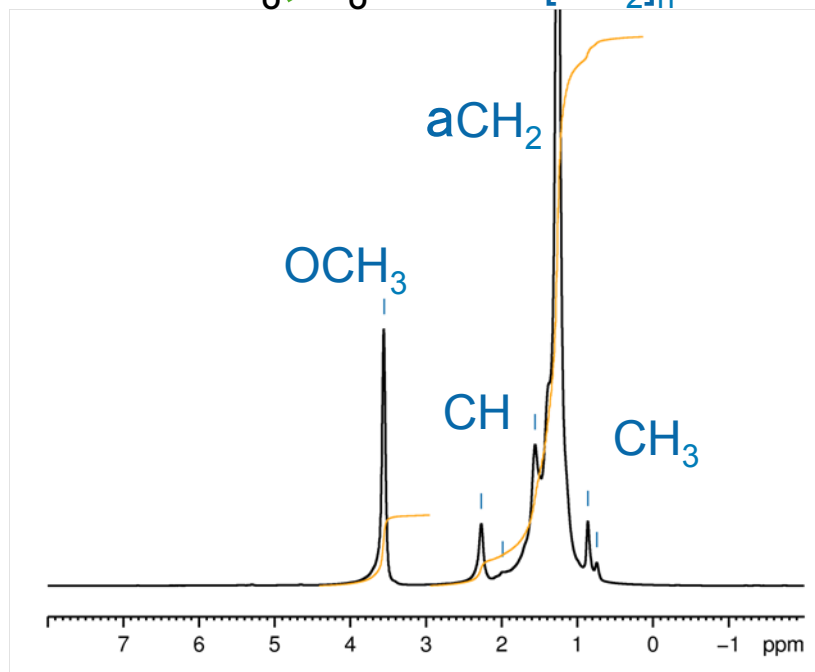
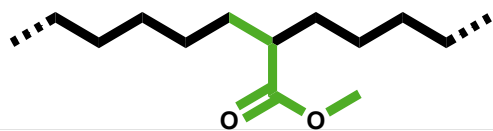


- desired due to high sensitivity but limited resolution
- not applicable for polyethylene-co- $\alpha$ -olefin copolymer quantification
  - mostly applicable to heteroatom containing polyolefin copolymers

# Quantitative $^1\text{H}$ NMR of polyolefins

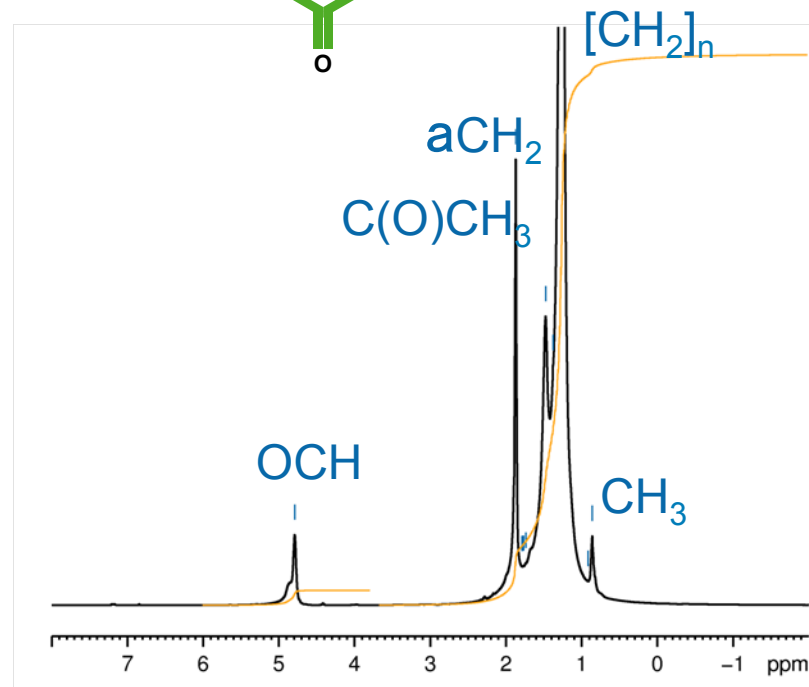
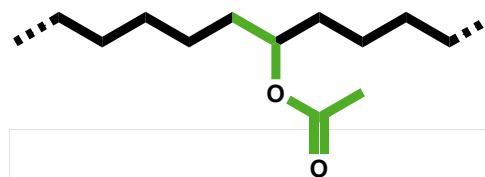
PE-co-methylacrylate EMA

[16.4 mol%, 37.7 wt%]



PE-co-vinylacetate EVA

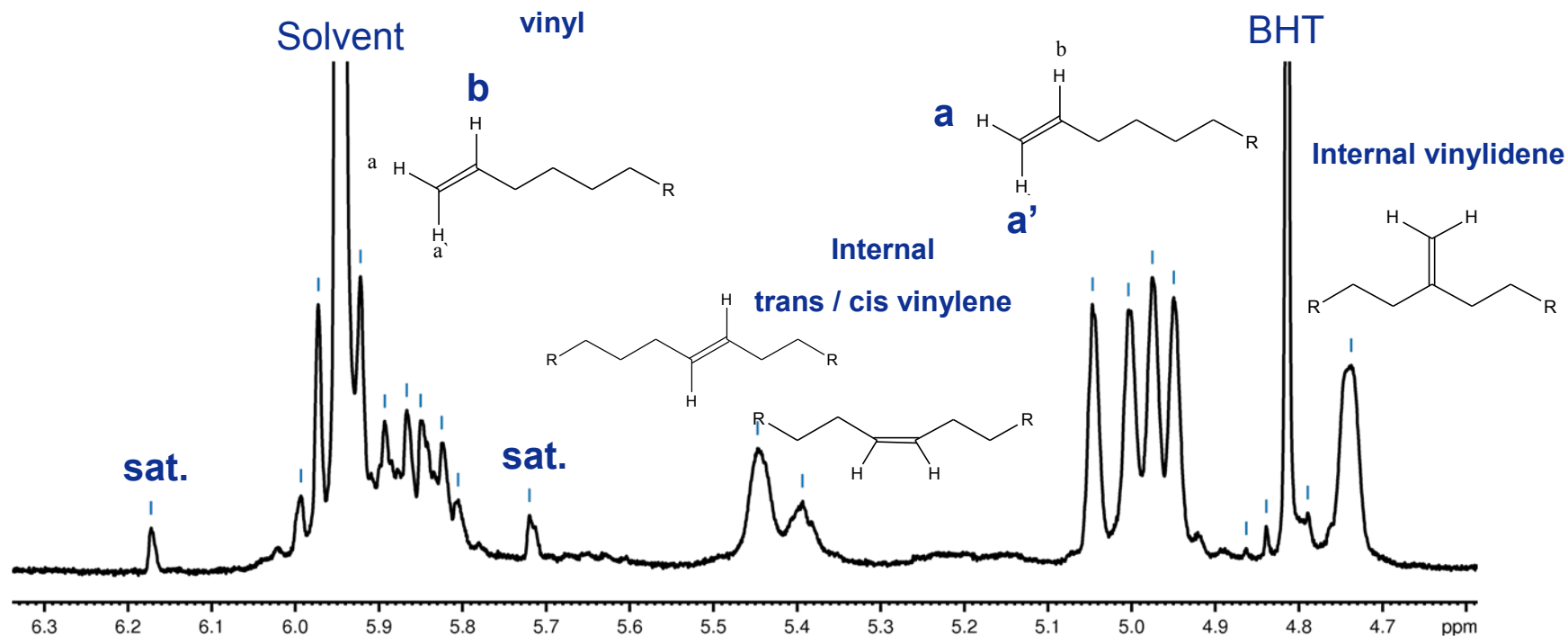
[10.9 mol%, 27.3 wt%]



- quantification via resolved protons

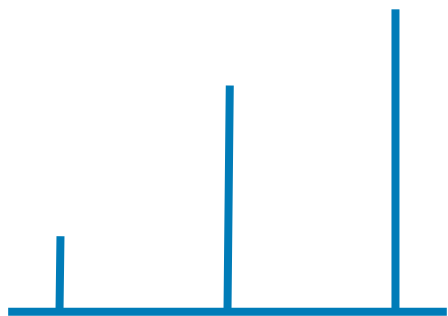


# Unsaturation & $^1\text{H}$ NMR



- Easy to distinguish different types of unsaturation
- Quantification possible (fundamental difference to IR method)

# Qualitative Vs Quantitative



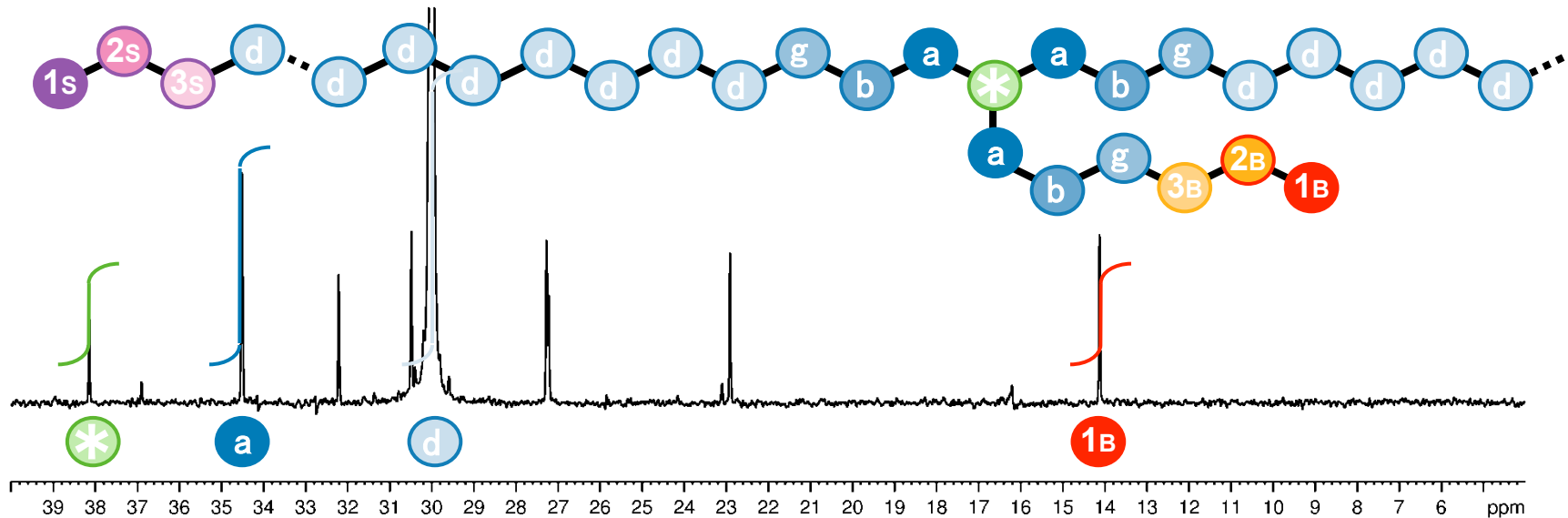
**qualitative NMR: observing**  
signals need to be intense  
but not quantitative



**quantitative NMR: counting**  
signals need to be quantitative  
but not intense

- historic drive for sensitivity not sensitivity & quantification
- what do you want to know?
  - is something there
  - how much of something there is

# Quantification of comonomer content



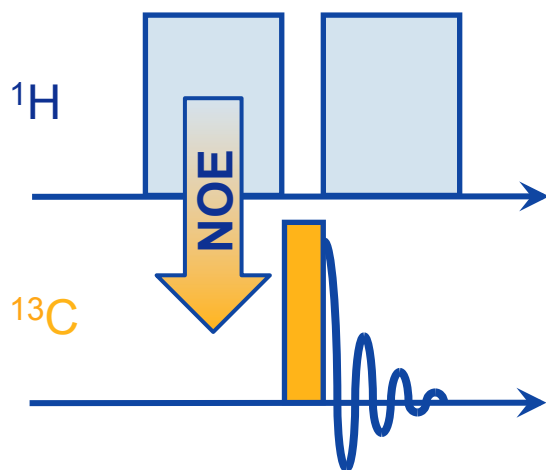
- Integrate quantitative  $^{13}\text{C}$  NMR spectrum
- overdefined problem with multiple solutions
  - selection of integrals not trivial
  - risk of lowering accuracy by averaging in errors!

$$\frac{*}{\delta}$$

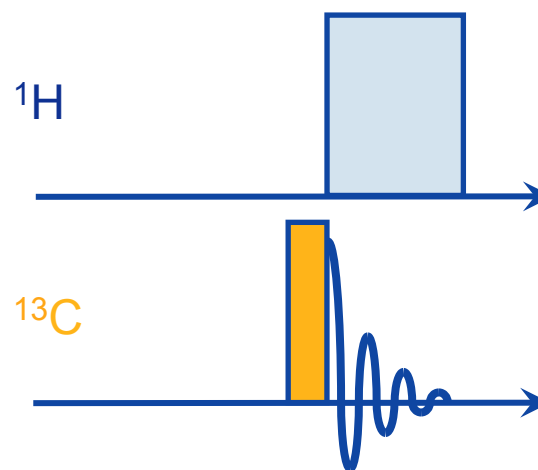
$$\frac{\frac{1}{3}\alpha}{\delta}$$

$$\frac{1}{\delta}$$

# $^{13}\text{C} \{^1\text{H}\}$ Single Pulse Excitation (SPE)

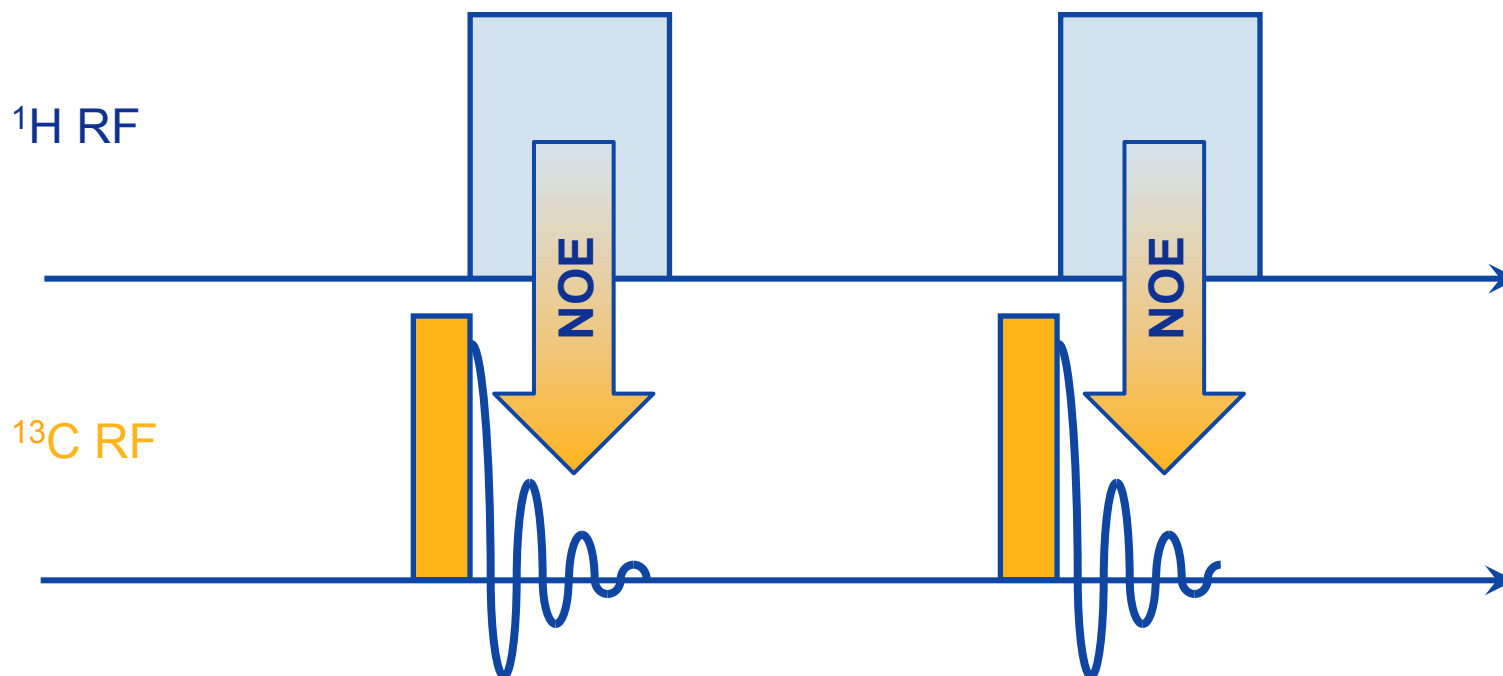


- $^{13}\text{C} \{^1\text{H}\}$  powergated
- $^1\text{H}$  decoupled **with** NOE
  - sensitive (quick) but only semiquantitative
  - NOE enhancement is site specific as it is related to motional dynamics of the sites
  - overestimation of methyl groups  
underestimation of quaternary sites



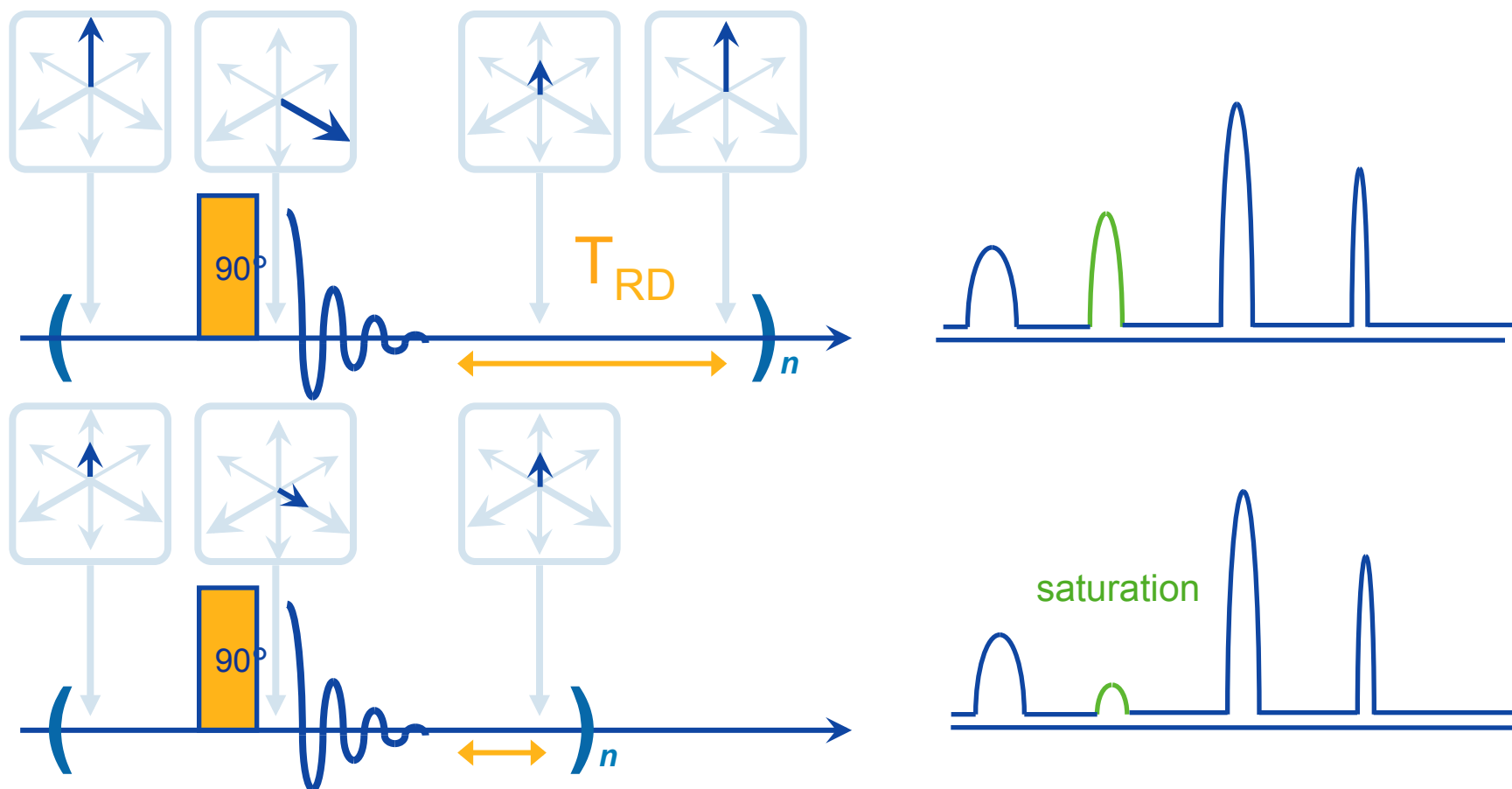
- $^{13}\text{C} \{^1\text{H}\}$  inversegated
- $^1\text{H}$  decoupled **without** NOE
  - quantitative but insensitive (slow)
  - classical quantitative heteronuclear experiment
  - all sites equal

# Transient Nuclear Overhauser Effect (NOE)



- For strongly coupled systems very difficult to stop NOE
  - decoupling block of previous scan also creates NOE
  - NOE still present for inversegated (no NOE) experiments

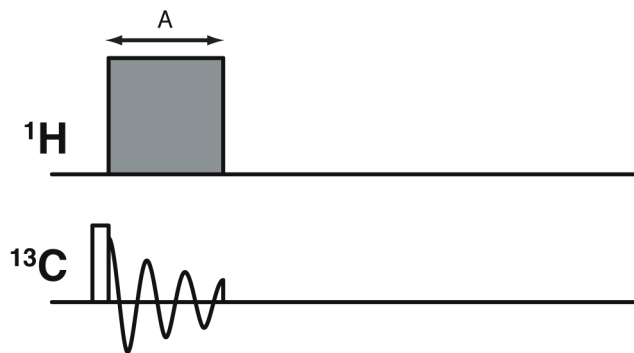
# Short recycle delays: $T_{RD} < 5 \times T_1$



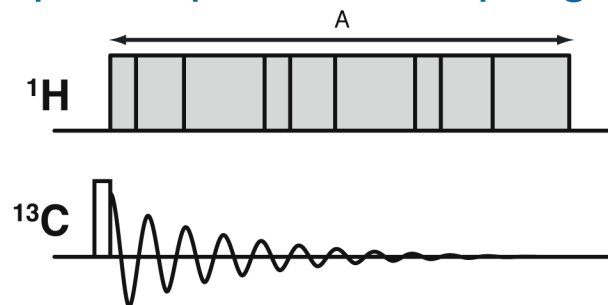
- Loss of intensity if not enough time given to return to equilibrium

# Solution-state decoupling strategy

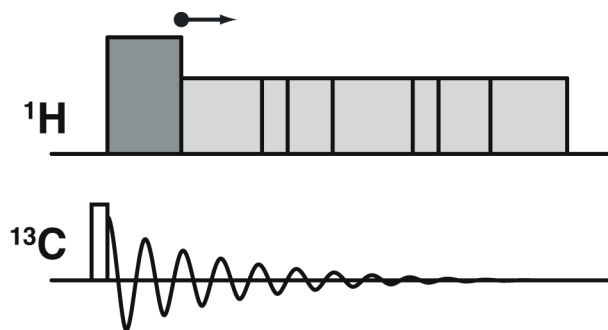
continuous wave



composite pulse decoupling

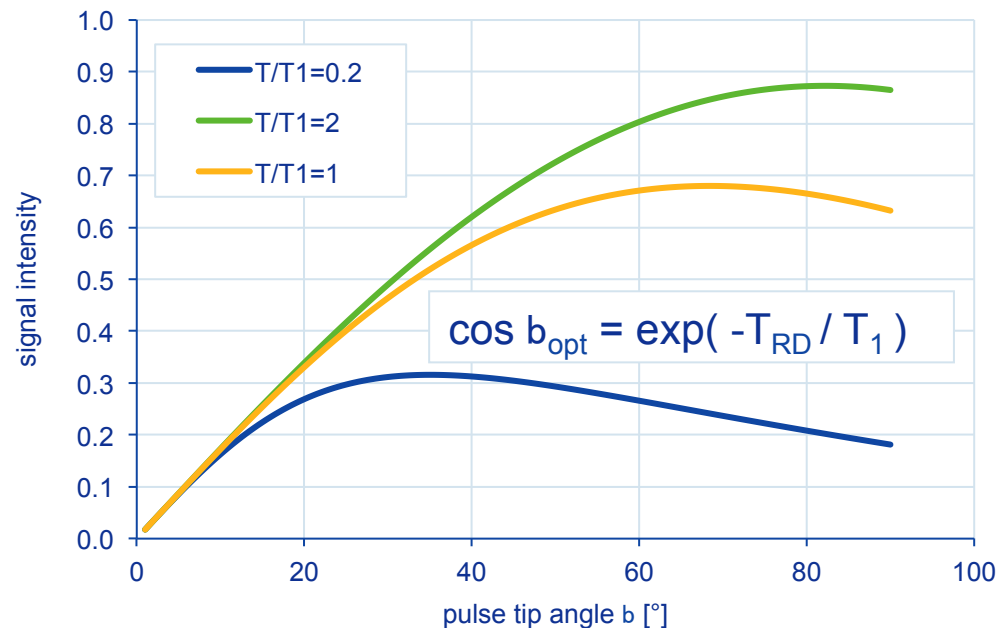
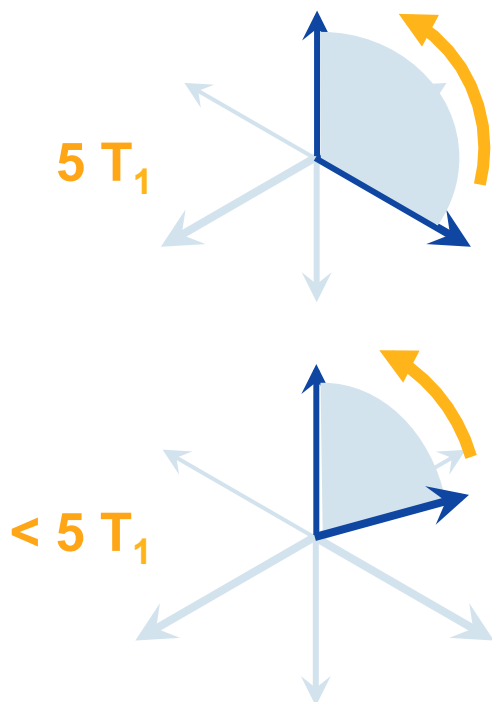


bi-level composite pulse decoupling



- increment limit decoupling sidebands
- low-load on electronics allows longer acquisition times

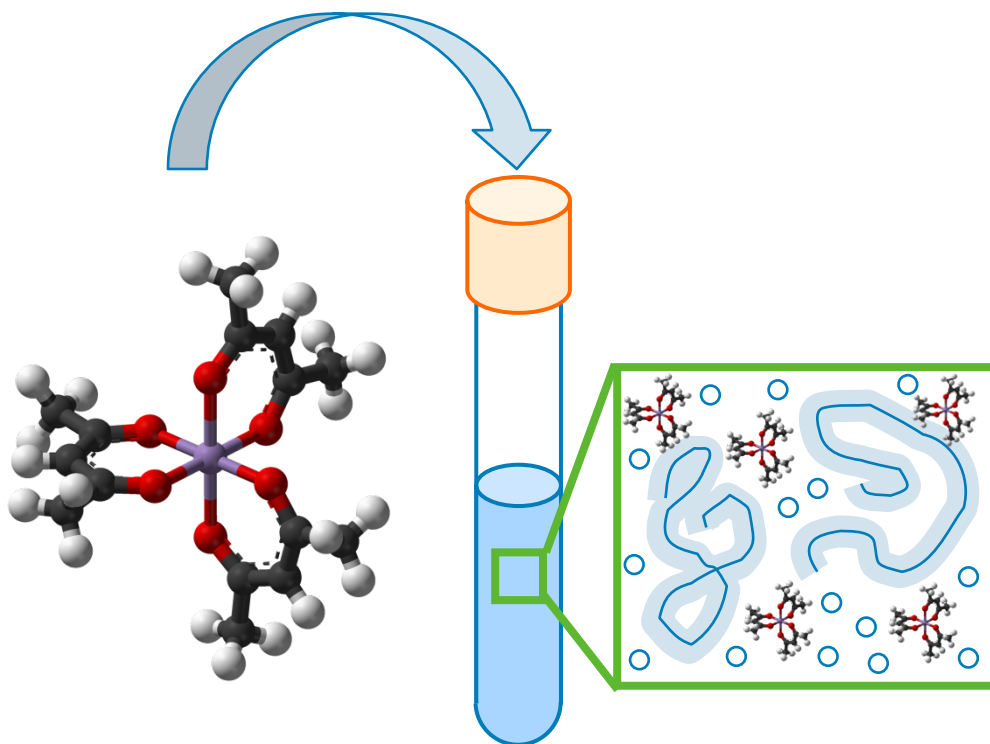
# Optimum tip angle: Ernst angle



- Steady-state equilibrium: maximum signal amplitude compromise between pulse angle ( $b_{\text{opt}}$ ), pulse repetition time ( $T_{\text{RD}}$ ) and  $T_1$
- Sites with different  $T_1$  have different optimal parameters are (not quantitative)



# Relaxation agents: $\text{Cr}(\text{acac})_3$



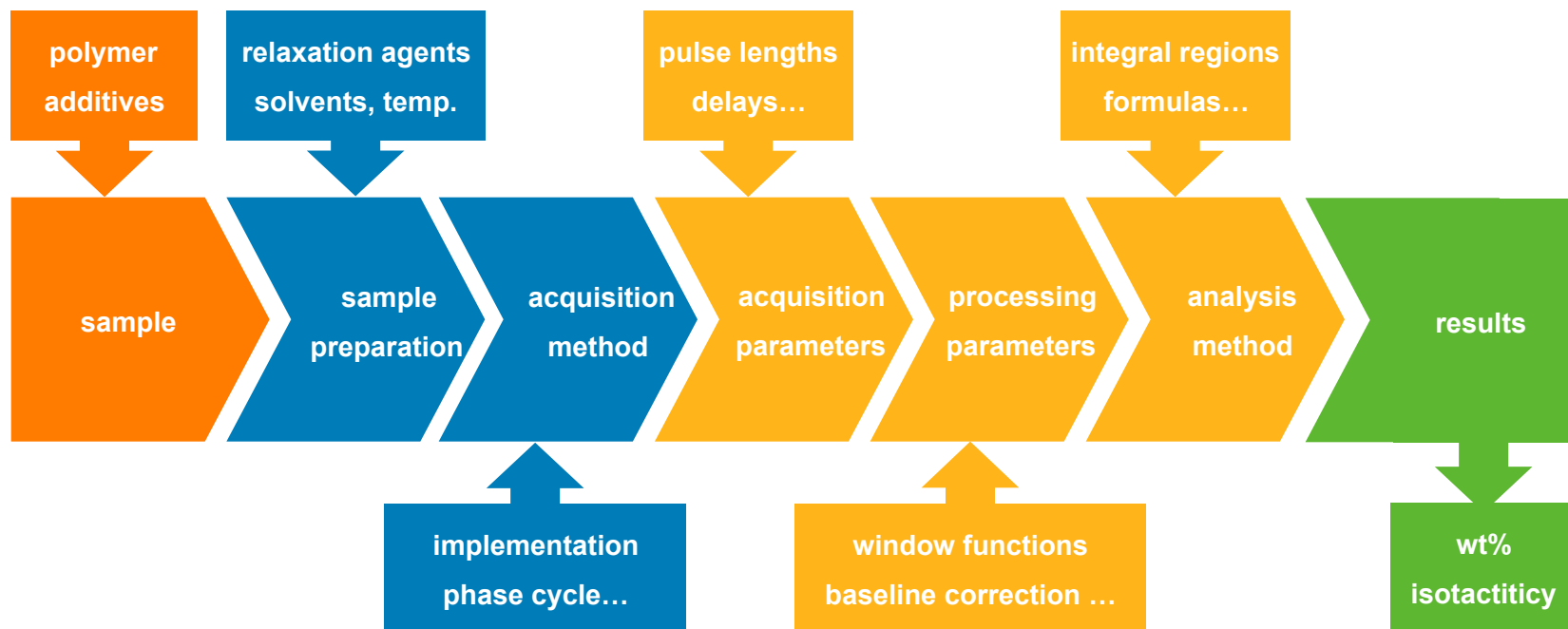
site (ppm)	T <sub>1</sub> without Cr(acac) <sub>3</sub>	T <sub>1</sub> with Cr(acac) <sub>3</sub>
47.0	1.007	0.572
46.5	1.094	0.664
46.0	1.304	0.709
38.1	1.636	0.658
37.7	1.856	0.682
33.4	2.906	0.814
31.3	3.670	0.791
30.4	2.093	0.719
30.0	2.146	0.747
29.4	1.850	0.752
27.5	2.045	0.722
24.8	1.547	0.659
22.2	2.196	0.758
21.5	2.092	0.761
20.3	3.209	0.860

- interaction unpaired electron spin with nuclear spins
  - electrons can relax very fast thus if coupled nuclei have alternative relaxation path

# Quantitative $^{13}\text{C}$ NMR in practice

- Compromise approaches:
  - shorter than  $5 \times T_1$   $T_{\text{RD}}$ : partial saturation (don't use sites with long  $T_1$ )
  - $< 90^\circ$  pulses: less signal but less saturation too (30-45° optimum related to  $T_1$ )
  - assume all NOEs are equal/full: don't compare different types (no CH<sub>3</sub>:CH ratios)
  - paramagnetic relaxation agents ( $\text{Cr}^{3+}$ ) shortens all  $T_1$  but also  $T_2$  (broad lines)
- Automated data processing and analysis
- From an industrial perspective reproducibility (and throughput) is more important than absolute accuracy
  - can always fall back to classical quantitative approach if differences are seen

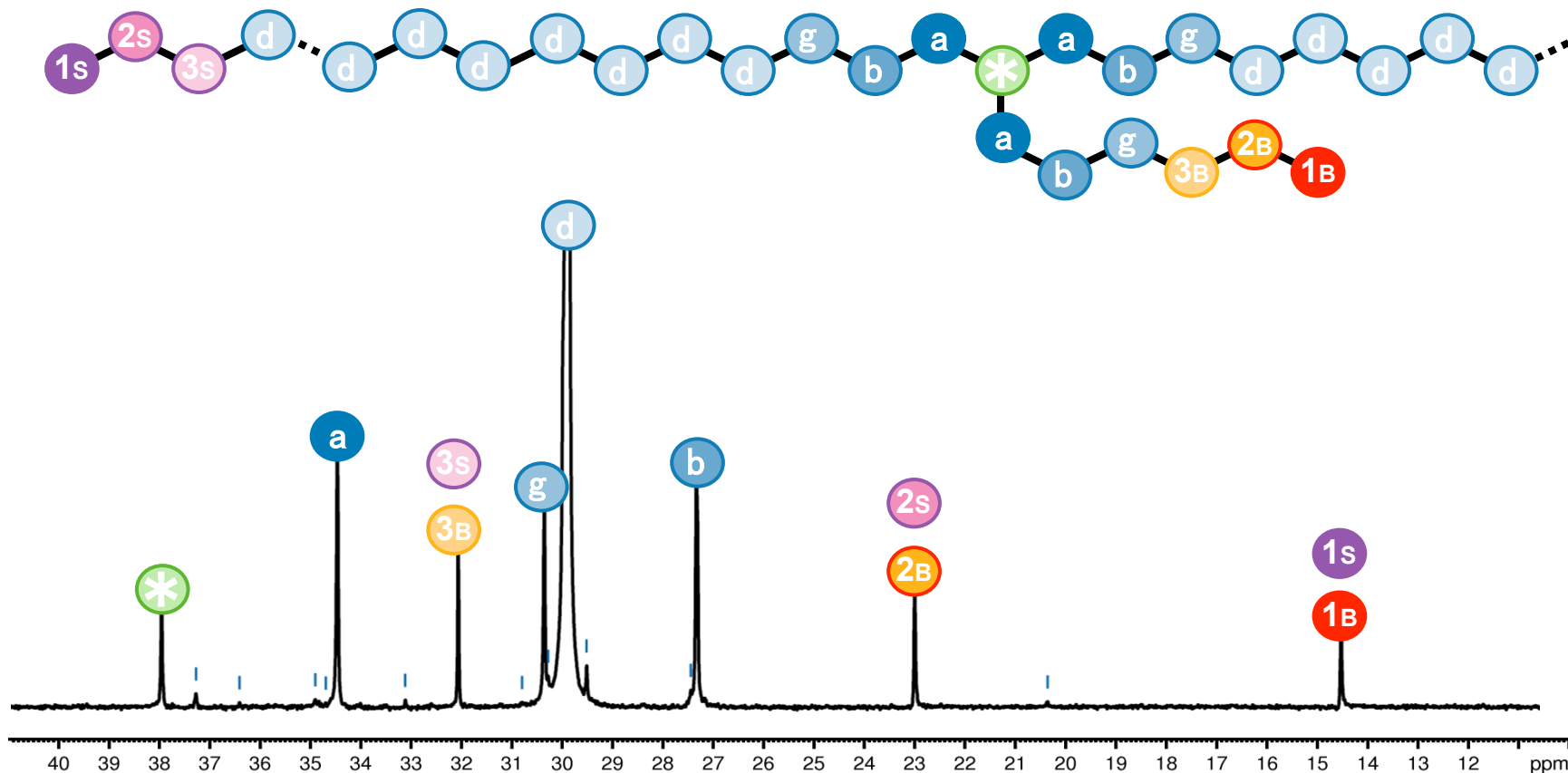
# Quantitative NMR Process



# Basic copolymer quantification of LLDPEs

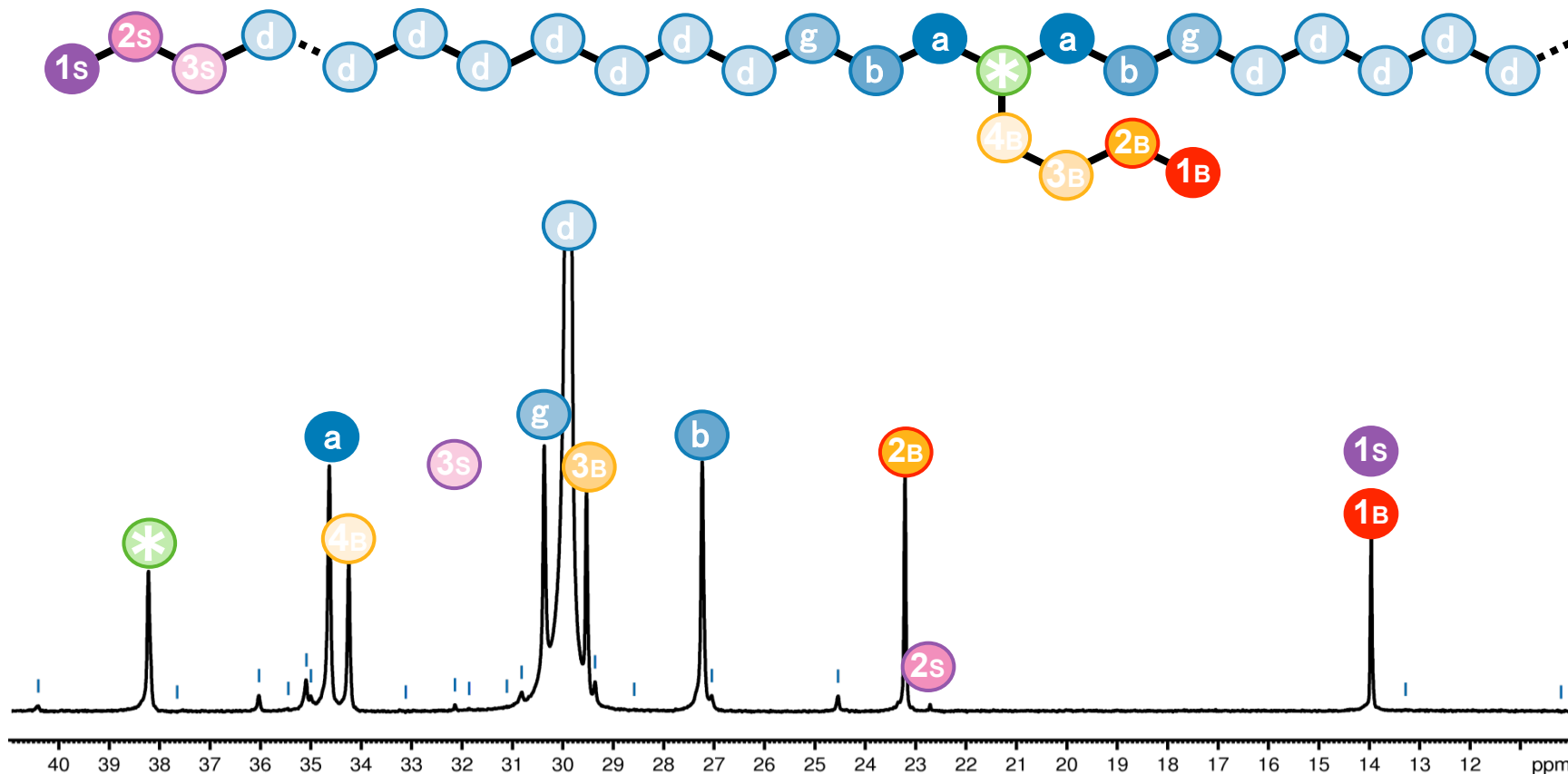
- How much comonomer have we used?
  - butene, hexene and octene most common
- Basic logic is valid for all polyethylene-co- $\alpha$ -olefin copolymers
  - In practice each require an own analysis method
  - Signals of interest have different chemical shifts (different integral regions)
- Very important: NMR spectroscopy measure an average of all chains!
  - Calculates **total comonomer content** or **average comonomer content per chain**
  - If we want to go into more detail we need to:
    - fractionate polymer into components (molecular weight or polarity)
    - measure NMR on each fraction separately (multiple very long measurements)

# Polyethylene-co-octene



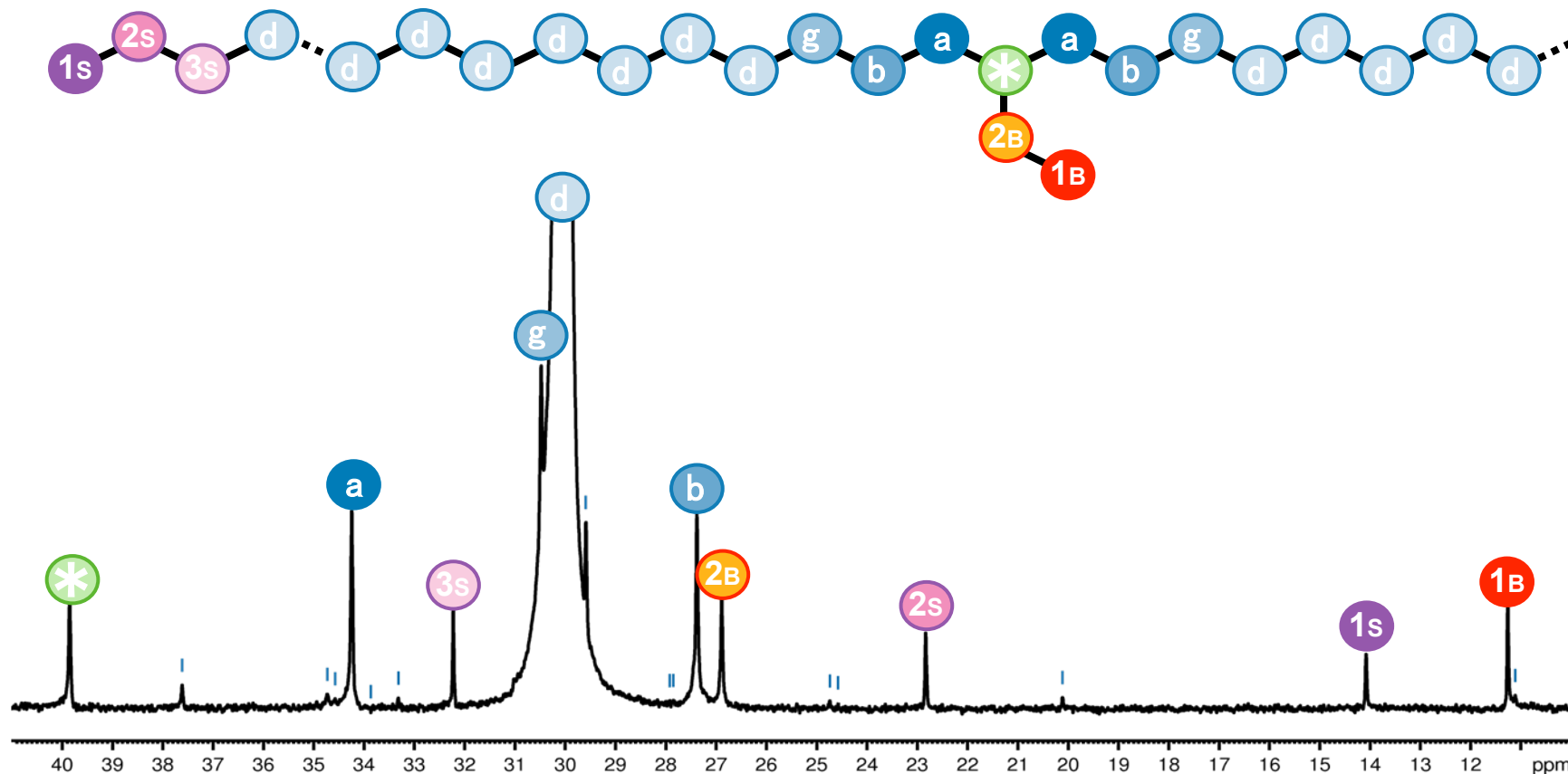
- Distinctive chemical shift of a site

# Polyethylene-co-hexene



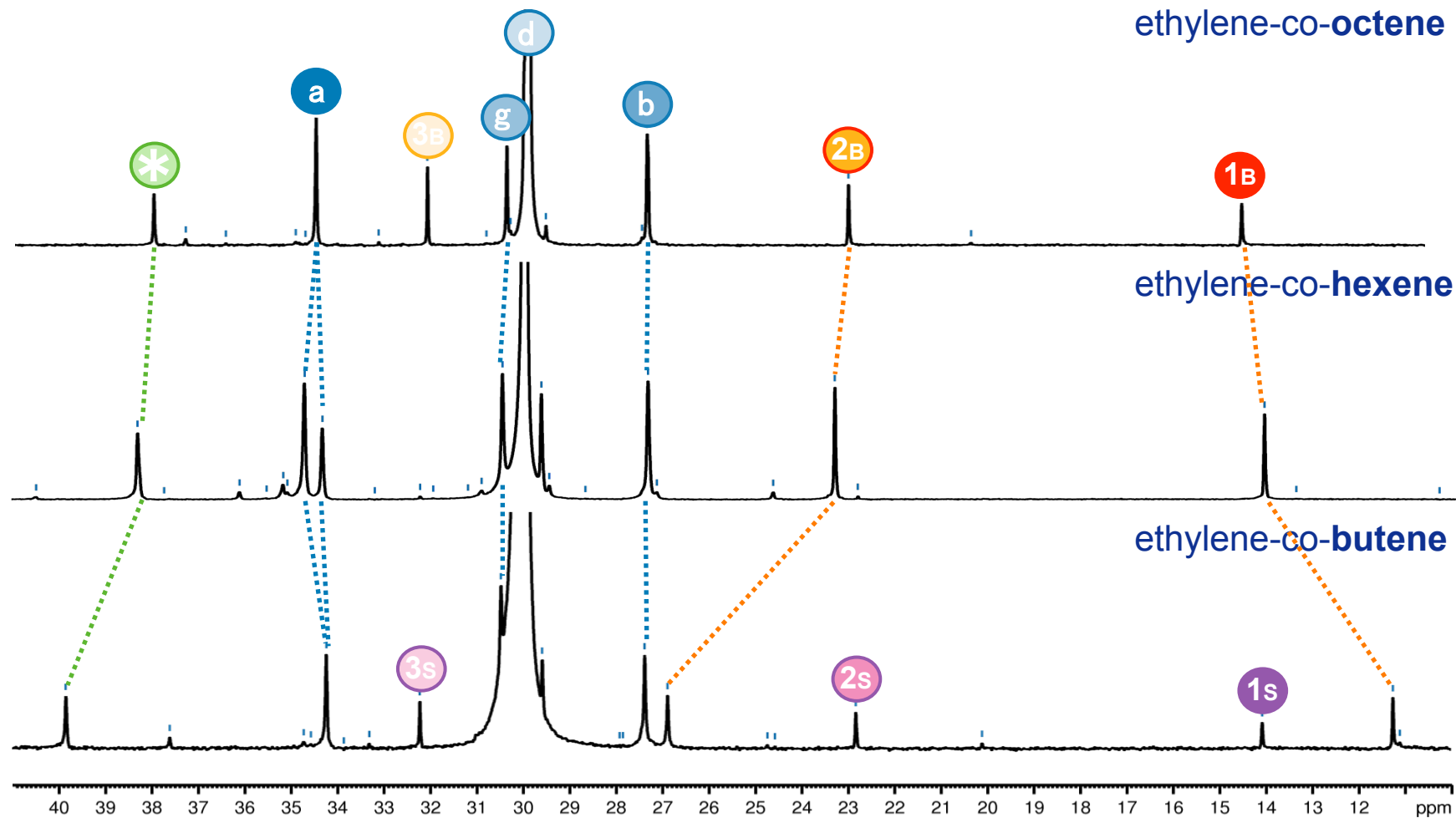
- Distinctive chemical shifts of a and 4B site

# Polyethylene-co-butene



- Distinctive chemical shift of a and 1B sites

# Polyethylene-co-a-olefins

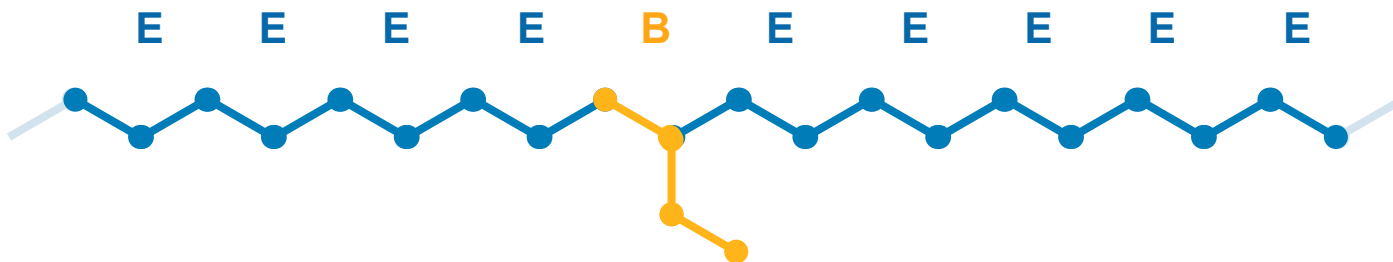




# Units for branch quantification

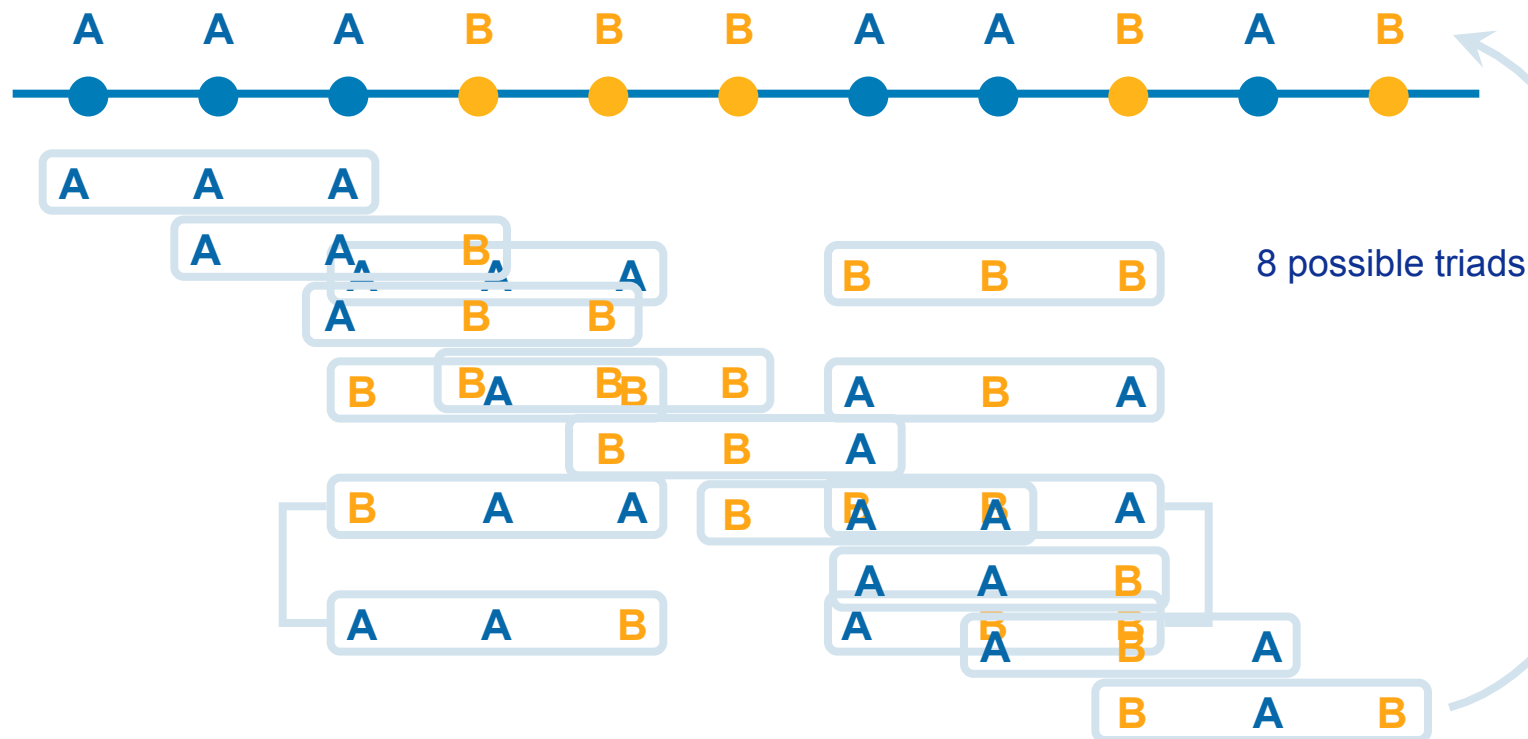
- degree of branching measured by NMR via:
  - representative integral of branch site or sites
  - bulk site (d CH<sub>2</sub> site)
- If exact branch length known (LLDPE & HDPE):
  - branches per backbone carbons (branches per 1000C<sub>bb</sub>)
    - mole percent or equivalent mole percent (mol%)
    - weight percent or equivalent weight percent (wt%)
  - branches per total carbons (branches per 1000C)
- If exact branch length not known (LDPE)
  - branches per total carbons (branches per 1000C)

# Units for branch quantification



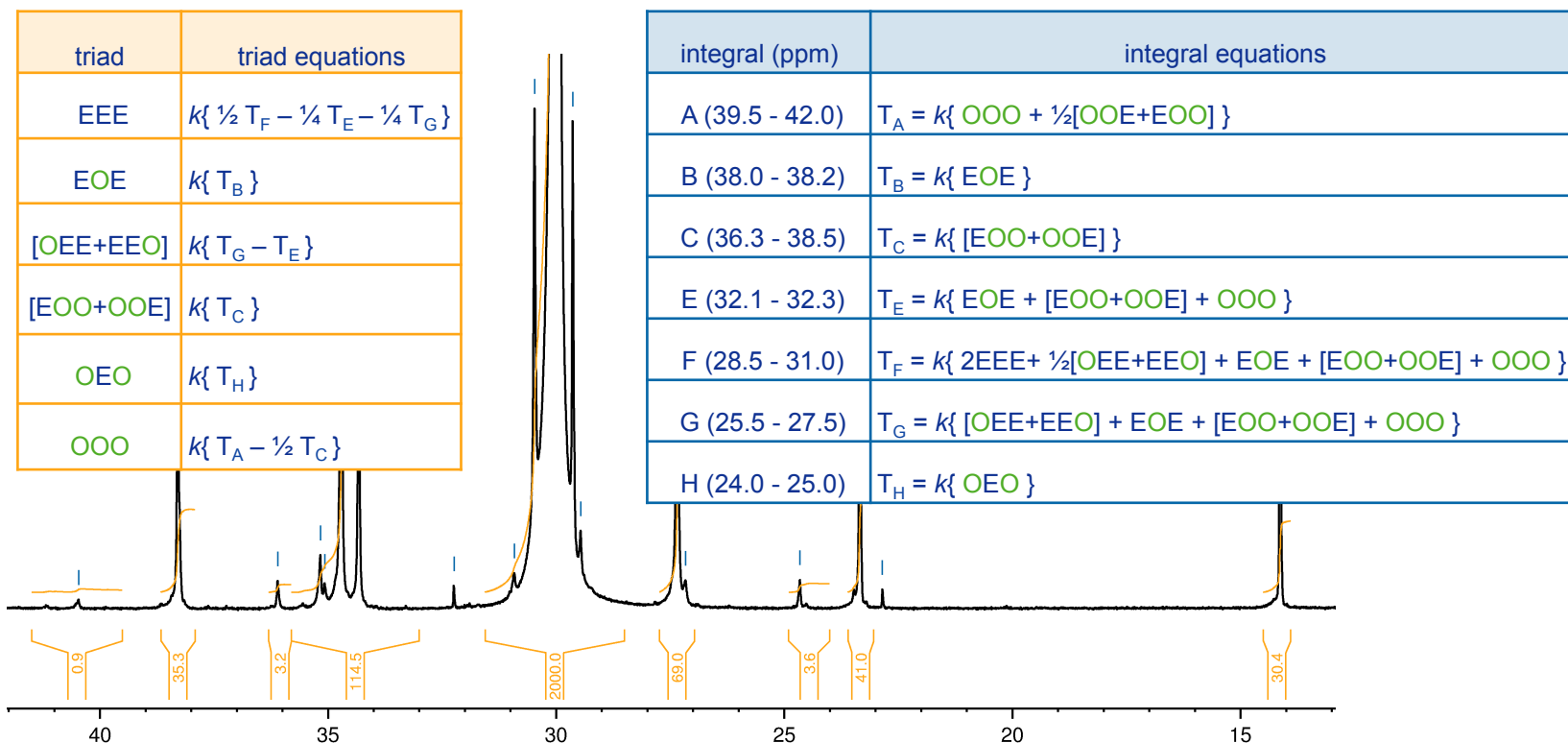
■ branches per backbone carbons:	$1 / 20$	$= 50$	Br/1000C <sub>bb</sub>
■ comonomer content in mole percent:	$1 / (9 + 1)$	$= 10$	mol%
■ comonomer content in weight percent:	$(1 \times 56) / ((9 \times 28) + (1 \times 56))$	$= 18$	wt%
■ branches per total carbons:	$1 / ((9 \times 2) + (1 \times 4))$	$= 45$	Br/1000C

# Comonomer sequences



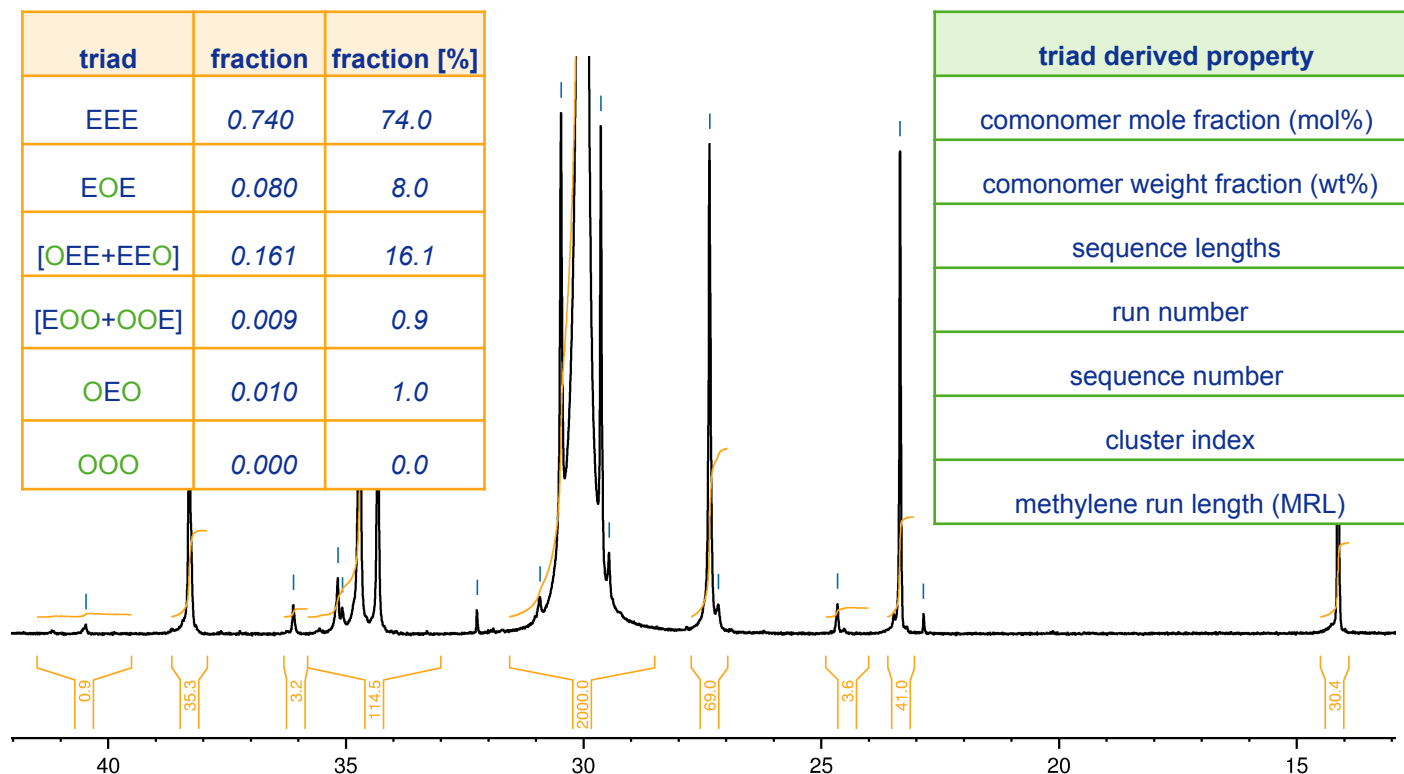
- Each n-ad has characteristic chemical shift
- Quantification of distribution provides insight into macrostructure

# Comonomer sequence distribution: I



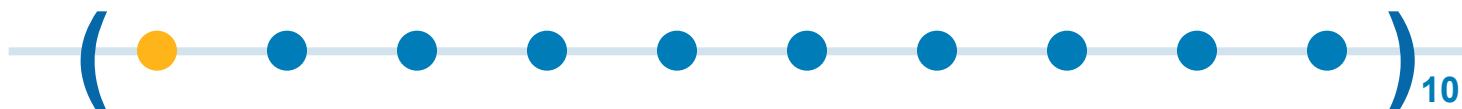
- Comonomer sequence distribution quantified at the triad level
  - integral regions assigned to specific sequences
  - set of simultaneous equations solved for a given comonomer sequence

# Comonomer sequence distribution: II



- Comonomer sequence distribution quantified at the triad level
  - triad distribution expressed as fraction or percent (low level statistical view)
  - derived properties calculated from triad distribution (more useful overview)

# Comonomer sequence derived properties



- parameters derived from sequence distribution (triads)
  - commoner content (sum of all A centered triads) [10%, 90%]
  - average sequence length (number of comonomers in a row) [1, 9]
  - sequence number (number of sequences per 100 monomers) [10,10]
  - run number (number of switches between sequences per 100 monomers) [20]
  - cluster index (closeness to ideal statistical distribution) [0]  
10 = ideal random, >10 clustered, 0 = dispersed and isolated

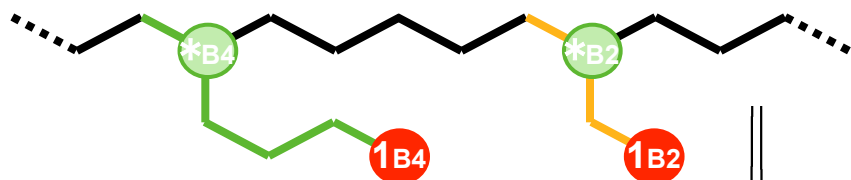
# Polyethylene-co- $\alpha$ -olefin microstructure

triads	result
EEE	90.11 %
EEH+HEE	6.09 %
HEH	0.91 %
EHE	3.44 %
EHH+HHE	0.17 %
HHH	0.00 %

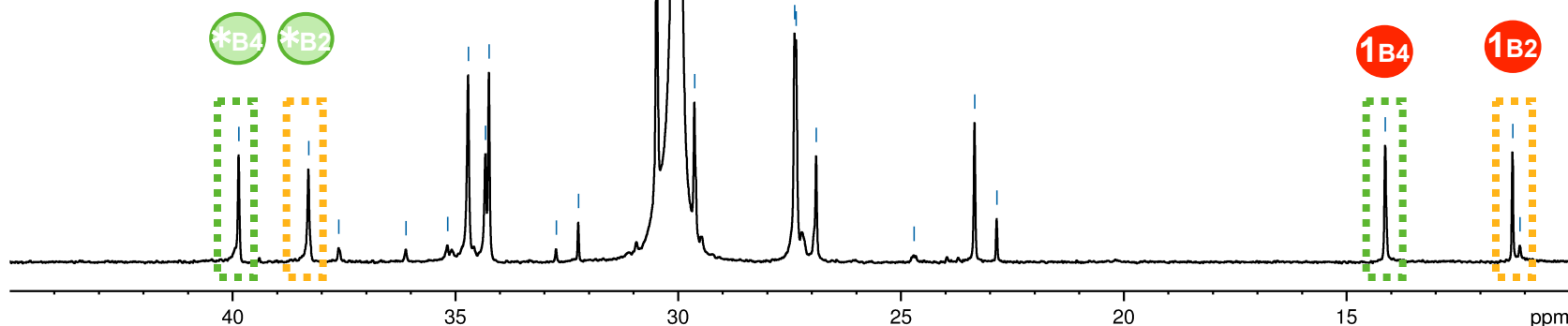
derived properties	result
C6 mol% [H]	3.61
sequence length	1.02
run number	7.05
sequence number	3.52
cluster index	7

- triad distribution calculated for given copolymer
  - derived properties easier to interpret calculated from triad distribution

# Polyethylene- $\alpha$ -olefin terpolymers



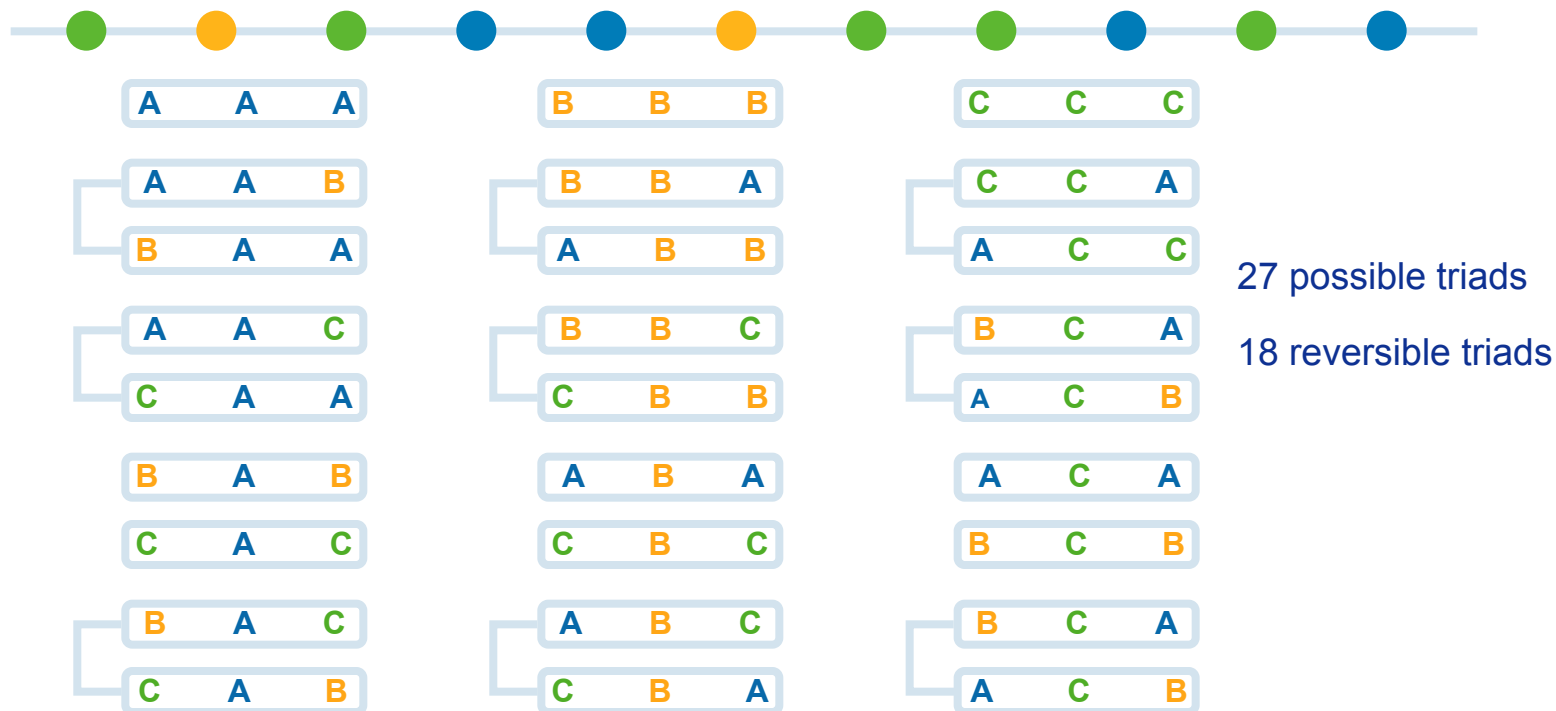
	mol%	wt%
ethylene <b>C2</b>	96.2	90.9
butene <b>C4</b>	1.8	3.4
hexene <b>C6</b>	2.0	5.7



- copolymer content analysis of an ethylene-butene-hexene terpolymer
- NMR can independently determine the comonomer content unlike IR

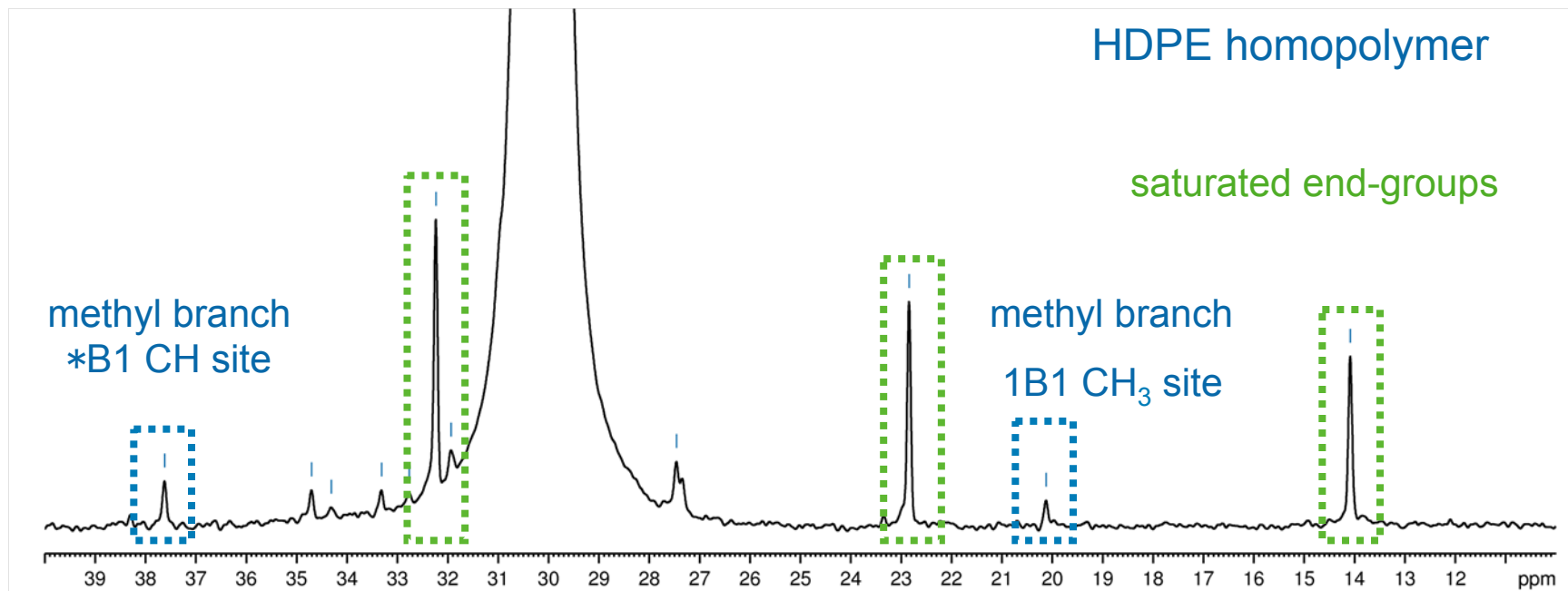


# Terpolymer chain microstructure



- Similar logic to triad analysis in copolymer but with more triads!
- Can be simplified when only probable triads are considered

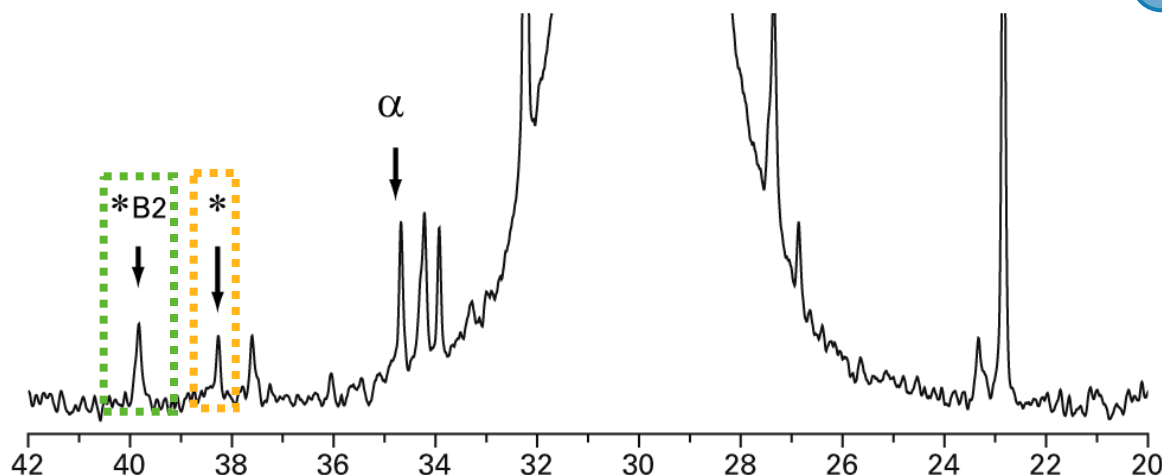
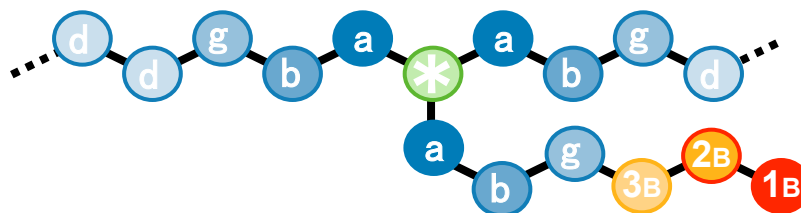
# Low amounts of short-chain branching



- Even systems without added comonomer have branching!
  - very very low contents: equivalent to < 0.1 mol% comonomer
  - very difficult to detect using standard solution-state methods

# Very low amounts of branching

mHDPE homopolymer  
*ethylene-co-octene or LCB*



C <sub>n</sub>	comonomer	SCB
3	propene	B1
4	butene	B2
6	hexene	B4
8	octene	B6
8+	longer	B6 <sup>+</sup>

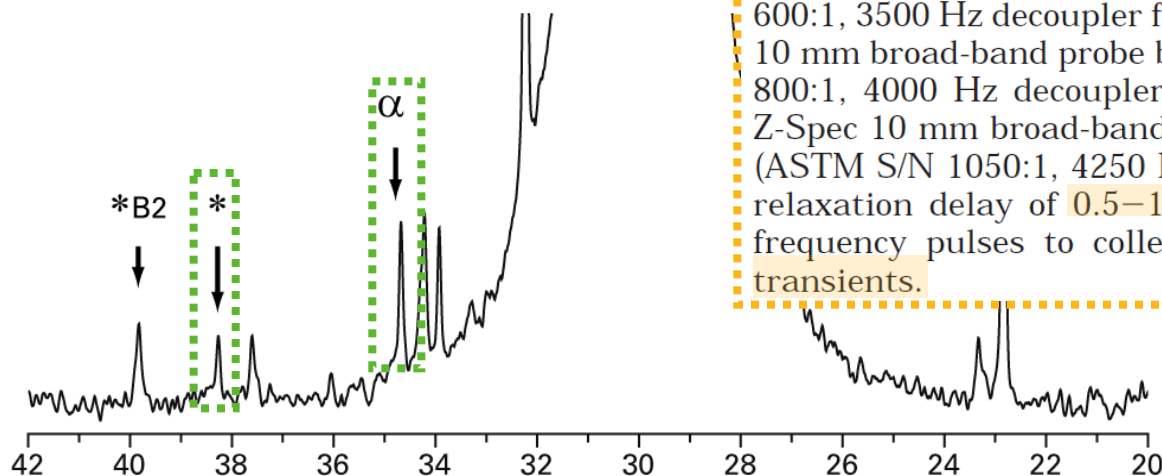
No chemical shift distinction between hexyl branch (B6) and LCB

- use of B6+ where true rheologically active branches are ≈ B360
- Strong assumptions needed for quantification
- literature values should always be regarded as upper limits

# Very low amounts branching

mHDPE homopolymer

*B2 SCB + B6<sup>+</sup> LCB*

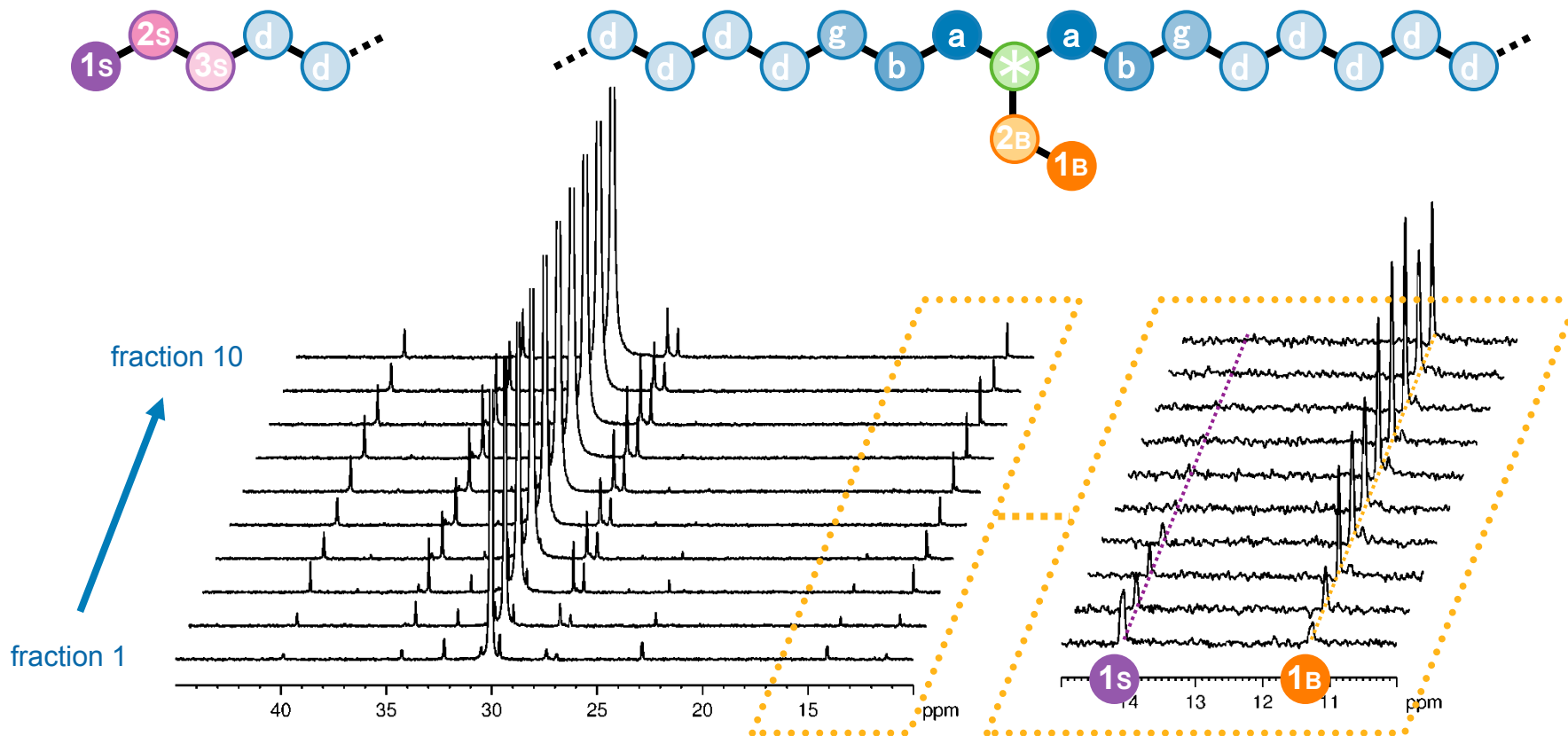


P. Wood-Adams et al. *Macromolecules* 2000, 33, 7489

Data were collected using one of three probes: a standard GE 10 mm broad-band probe tuned to 150 MHz (ASTM S/N 600:1, 3500 Hz decoupler field, PW90 25  $\mu$ s), a Nalorac Z-Spec 10 mm broad-band probe built for the GE system (ASTM S/N 800:1, 4000 Hz decoupler field, PW90 25  $\mu$ s), or a Nalorac Z-Spec 10 mm broad-band probe built for the Varian system (ASTM S/N 1050:1, 4250 Hz decoupler field, PW90 14  $\mu$ s). A relaxation delay of 0.5–1.0 s was used between 90° radio-frequency pulses to collect between 50 000 and 2 000 000 transients.

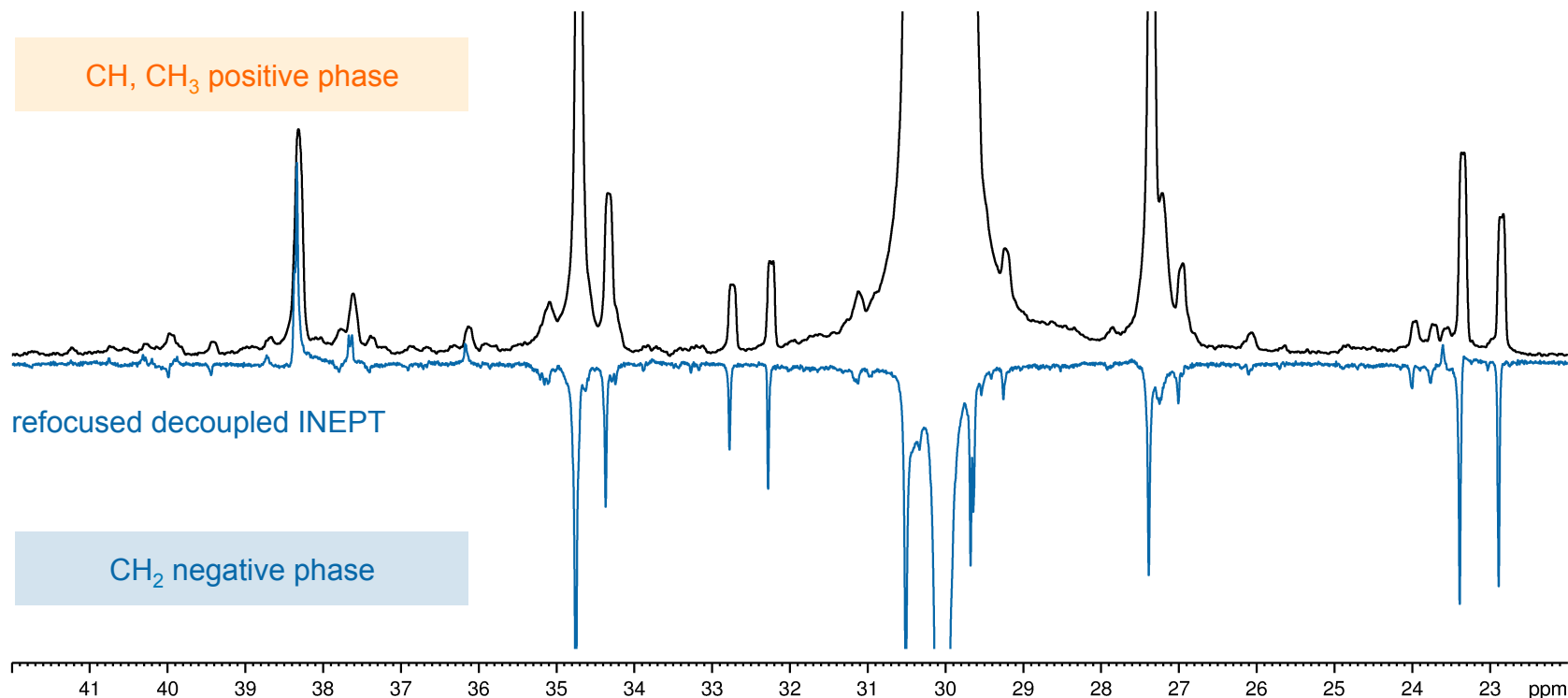
- very weak signals (highly sensitive methods needed)
  - extreme number of FIDs needed: 7 per 100,000 CH<sub>2</sub> = 1 month per spectra!
  - key application of melt-state NMR: 5 per 100,000 CH<sub>2</sub> = 12-24 h per spectra
  - pressure to over interpret data (caution needed)

# Fractionated high-density polyethylene



- Limited amount of material (10 mg c.f. 200 mg) = long time x 10!
  - comonomer distribution as a function of molecular weight (1B1)

# $^{13}\text{C}$ NMR of LDPE

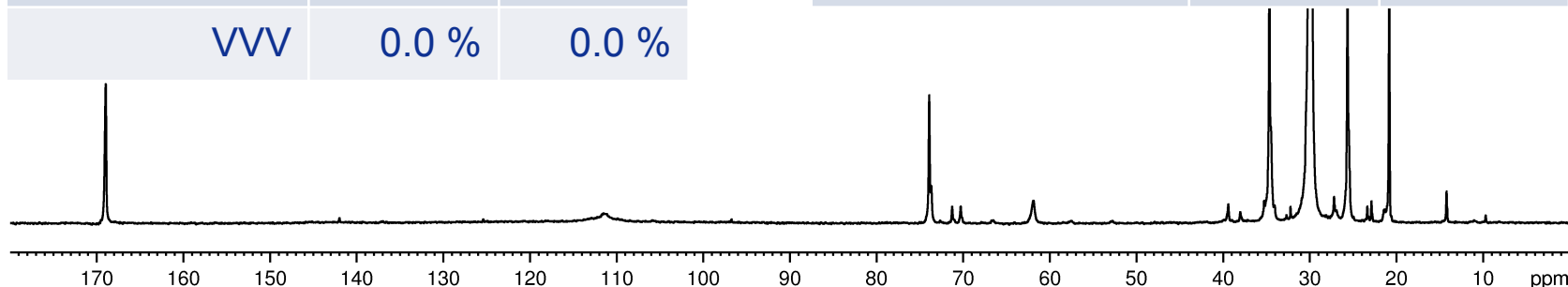


- Spectra are quite complicated due to the variety of branch types
  - multiplicity sensitive methods useful for assignment (INEPT, DEPT, HSQC)

# Polyethylen-co-vinylacetate (EVA)

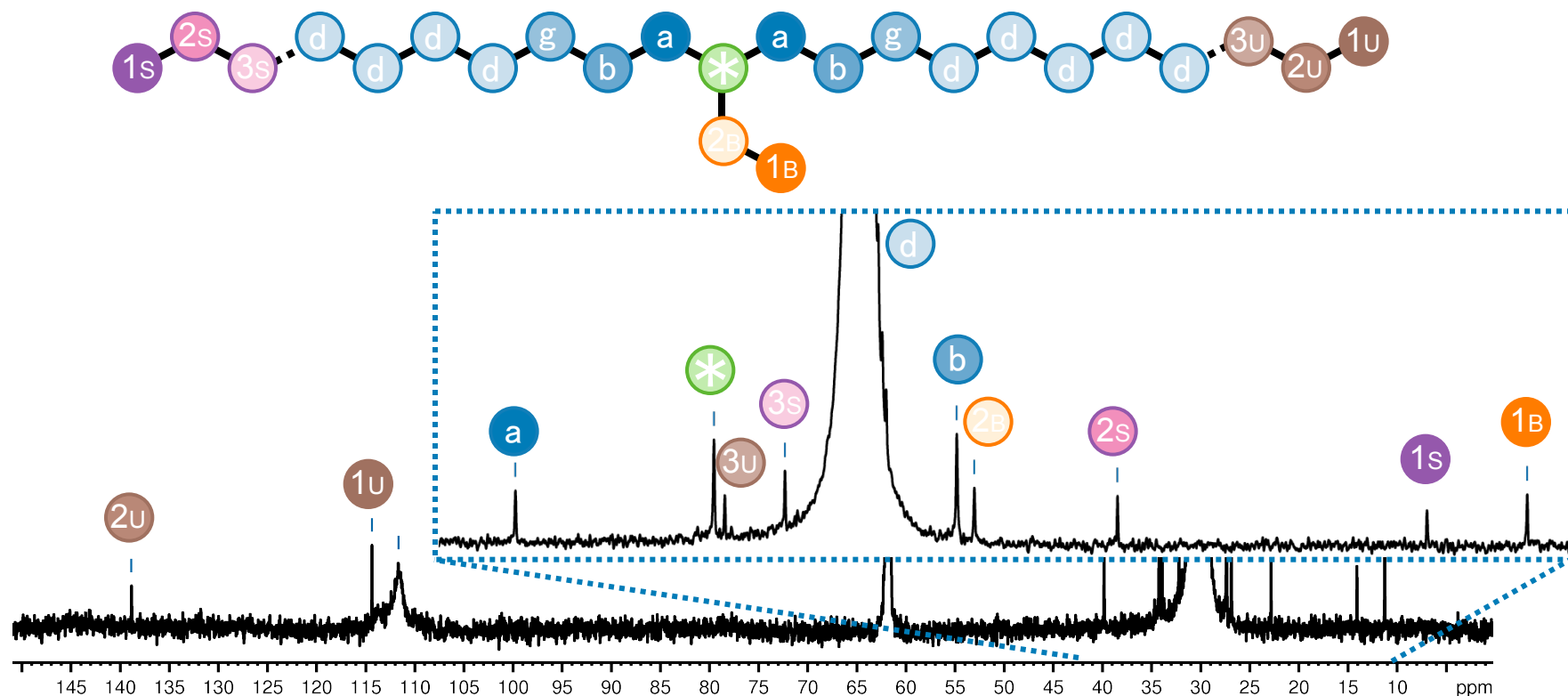
triad	solution	melt
EEE	71.8 %	73.8 %
EEV+VEE	17.7 %	15.9 %
VEV	1.0 %	0.8 %
EVE	7.3 %	8.0 %
EVV+VVE	2.2 %	1.4 %
VVV	0.0 %	0.0 %

derived properties	solution	melt
VA mol% [V]	9.5	9.4
sequence length	1.1	1.1
run number	16.8	17.4
sequence number	8.4	8.7
cluster index	13	8



- Similar derived properties to LLD and HDPE polyethylenes
  - Due to electronegative heteroatoms chemical shift has wider range

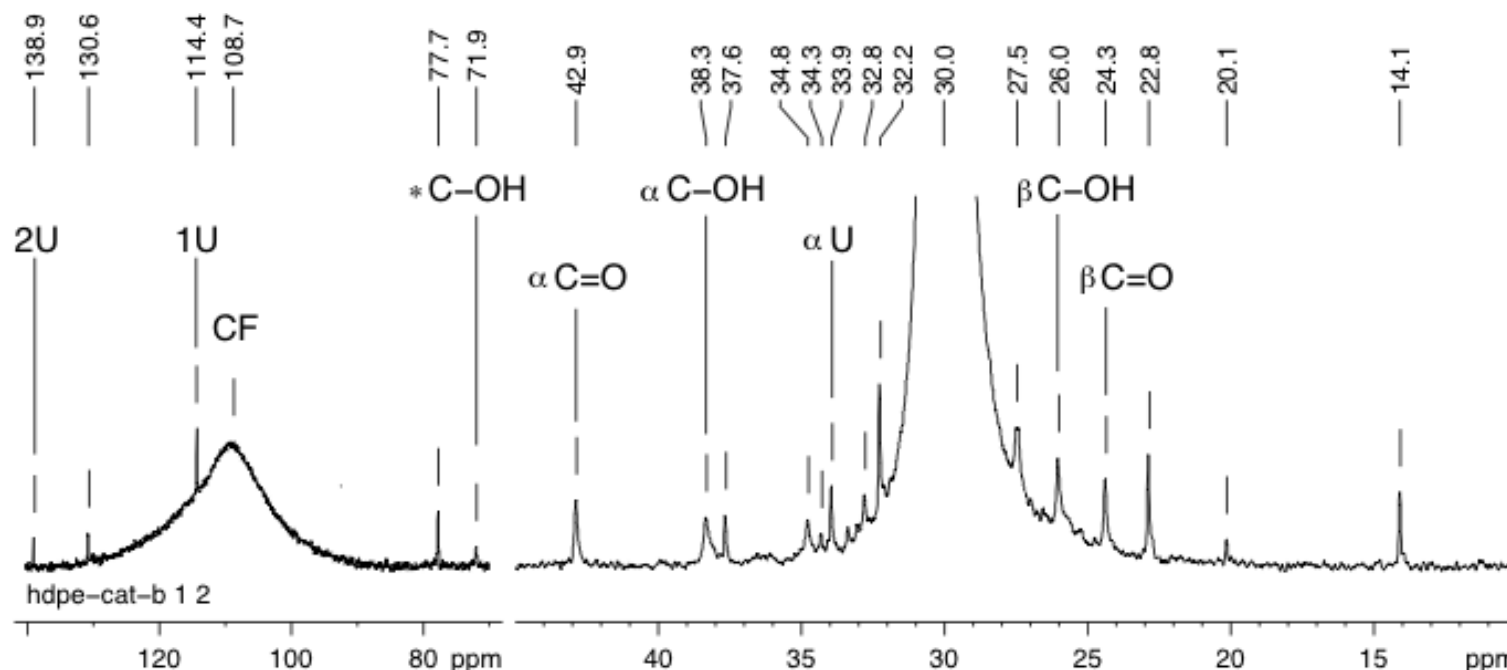
# Polyethylene end-groups



- Saturated and unsaturated end groups easily observed
- Quantification possible but not very accurate (Mn)



# Oxidation & degradation

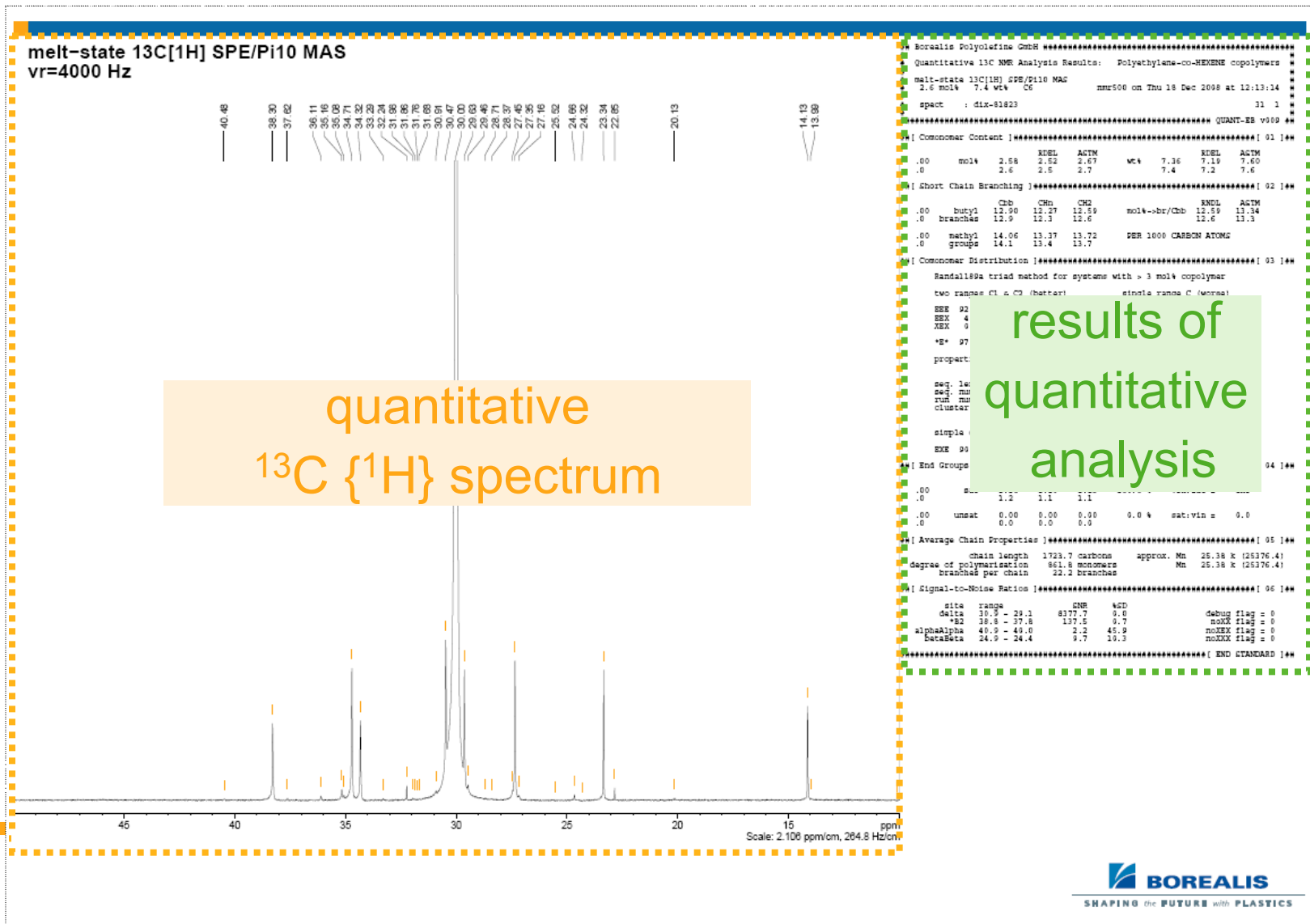


- assignment of secondary degradation products
  - quantification relative to model assumed e.g. C=O groups per 1000 total carbons

# Quantitative NMR reporting

- Proprietary in-house spectral analysis (quantification)
  - Excel not robust enough (too many ways to mess thing up)
  - custom C-based NMR software automation (Bruker Topspin)
  - quantification program +1500 lines of code
- Fully automated
  - NMR data processing (FT, line-broadening, phasing, trimming, baseline)
  - Analysis (integration, multiple calculations)
  - reporting (PDF, txt, csv)

# PE-co-a-olefin reporting: overview



# PE copolymer reporting: results

```
## Borealis Polyolefine GmbH #####
#
# Quantitative 13C NMR Analysis Results: Polyethylene-co-HEXENE copolymers #
#
# Sample 1 #
# 2.6 mol% 7.4 wt% C6 nmr500 on Thu 18 Dec 2008 at 12:13:14 #
#
# spect : dix-81823 31 1 #
#
##### QUANT-EH v009 #####
```

overview

our reference

version #

```
##[ Comonomer Content ]#####[ 01 ]##
```

			RNDL	ASTM		RNDL	ASTM
.00	mol%	2.58	2.52	2.67	wt%	7.36	7.60
.0		2.6	2.5	2.7		7.4	7.6

mol% wt%

```
##[ Short Chain Branching ]#####[ 02 ]##
```

		Cbb	CHn	CH2		RNDL	ASTM
.00	butyl	12.90	12.27	12.59	mol%→br/Cbb	12.59	13.34
.0	branches	12.9	12.3	12.6		12.6	13.3
.00	methyl	14.06	13.37	13.72	PER 1000 CARBON ATOMS		
.0	groups	14.1	13.4	13.7			

short chain  
branching

# PE copolymer reporting: results

##[ Comonomer Distribution ]#####[ 03 ]##

Randall89a triad method for systems with > 3 mol% copolymer

two ranges C1 & C2 (better)

single range C (worse)

EEE	92.81 %	XXX	0.05 %	EEE	92.36 %	XXX	0.53 %
EEX	4.64 %	EXX	0.10 %	EEX	4.62 %	EXX	1.06 %
XEX	0.03 %	EXE	2.47 %	XEX	0.03 %	EXE	2.46 %
*E*	97.48 %	*X*	2.52 %	*E*	97.01 %	*X*	2.99 %

triad distribution

properties derived from triad distribution

	X	E	X	E
seq. length	1.0	41.4	1.0	41.4
seq. number	2.5	2.4	3.0	2.3
run number	5.0	4.7	6.0	4.7
cluster idx	3.9		30.2	

derived properties

simple distribution for all systems

EXE	90.66 %	EXX	0.77 %	XEX	8.6 %
-----	---------	-----	--------	-----	-------

# PE copolymer reporting: results

##[ End Groups ]#####[ 04 ]##

		Cbb	CHn	CH2	split		
.00	sat	1.16	1.10	1.13	100.0 %	vin:sat =	inf
.0		1.2	1.1	1.1			
.00	unsat	0.00	0.00	0.00	0.0 %	sat:vin =	0.0
.0		0.0	0.0	0.0			

end groups

##[ Average Chain Properties ]#####[ 05 ]##

chain length	1723.7 carbons	approx. Mn	25.38 k (25376.4)
degree of polymerisation	861.8 monomers	Mn	25.38 k (25376.4)
branches per chain	22.2 branches		

average chain  
properties

##[ Signal-to-Noise Ratios ]#####[ 06 ]##

site	range	SNR	%SD
delta	30.9 - 29.1	8377.7	0.0
*B2	38.8 - 37.8	137.5	0.7
alphaAlpha	40.9 - 40.0	2.2	45.9
betaBeta	24.9 - 24.4	9.7	10.3

debug flag =	0
noXX flag =	0
noXEX flag =	0
noXXX flag =	0

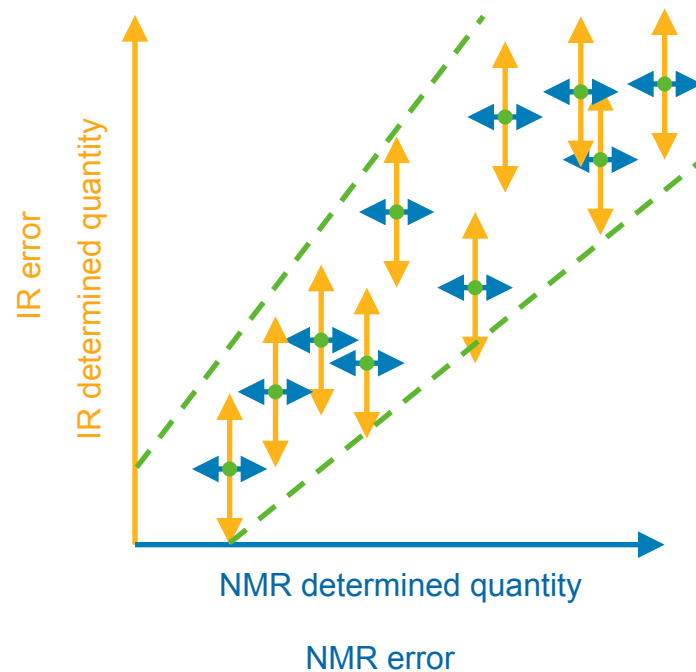
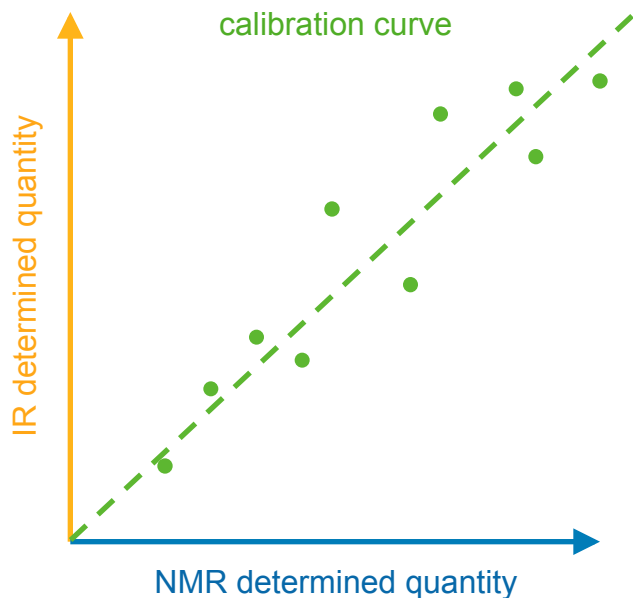
#####[ END STANDARD ]##

SNR

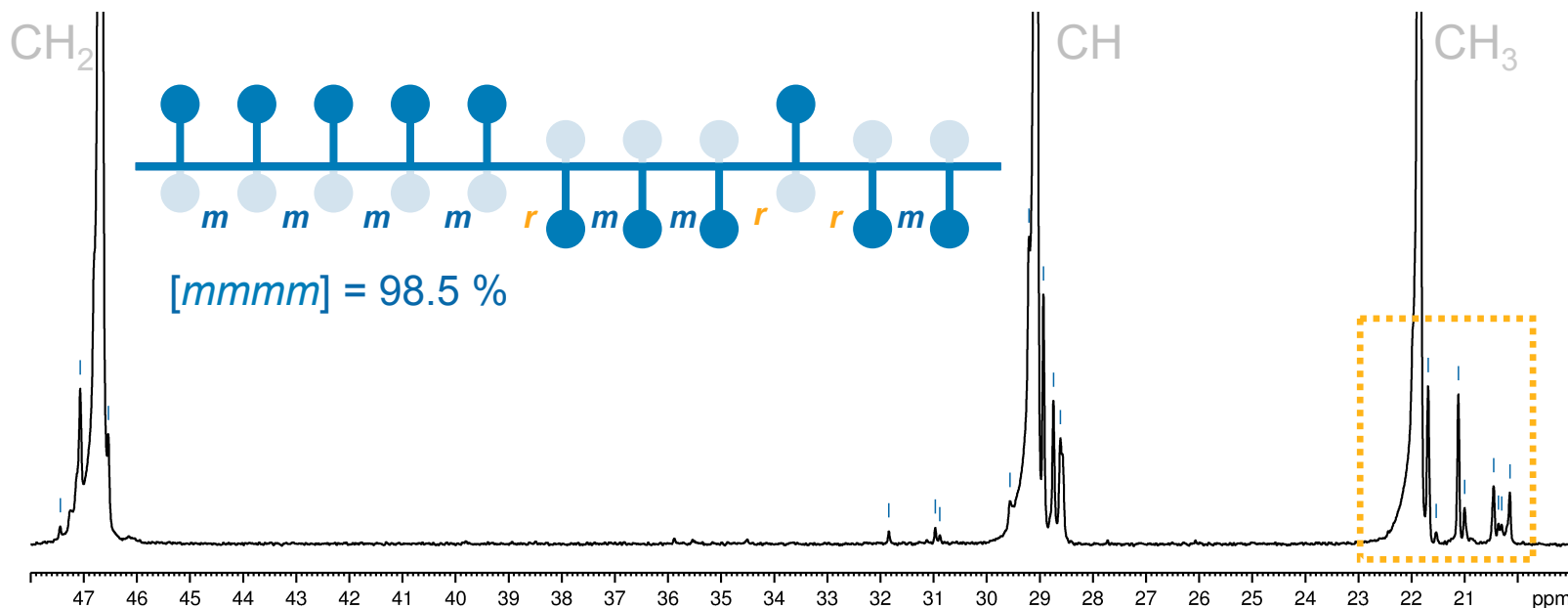
signal-to-noise ratio

run-time options  
used

# Quantitative NMR for IR calibration



- error and reproducibility need to be considered when constructing calibration curves and correlations
- IR is an indirect method whereas NMR is a direct method

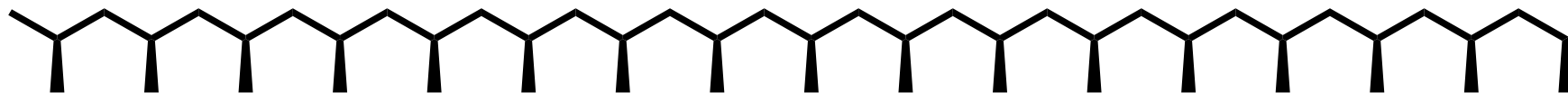


## NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

# NMR SPECTROSCOPY OF PP



# Polypropylene (PP)



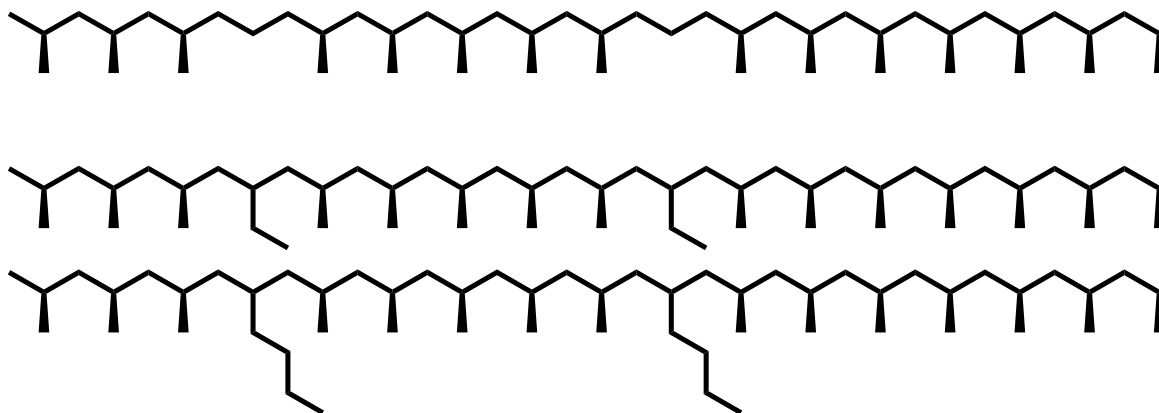
- Cheap to produce as monomer is byproduct of petrochemical industry
  - More expensive than polyethylene
  - Physical and mechanical properties related to chemical structure
  - Through research and development increase properties to expand applications
- Complex chemical structure
  - different stereo-chemistry along polymer chain (stereo defects)
  - difficult regio-chemistry along polymer chain (regio defects)
  - multiple types of end-groups
  - difficult to characterise (low solubility)

# Chain branching in polypropylene

## short chain branching

*$\alpha$ -olefin copolymer (PE like)*

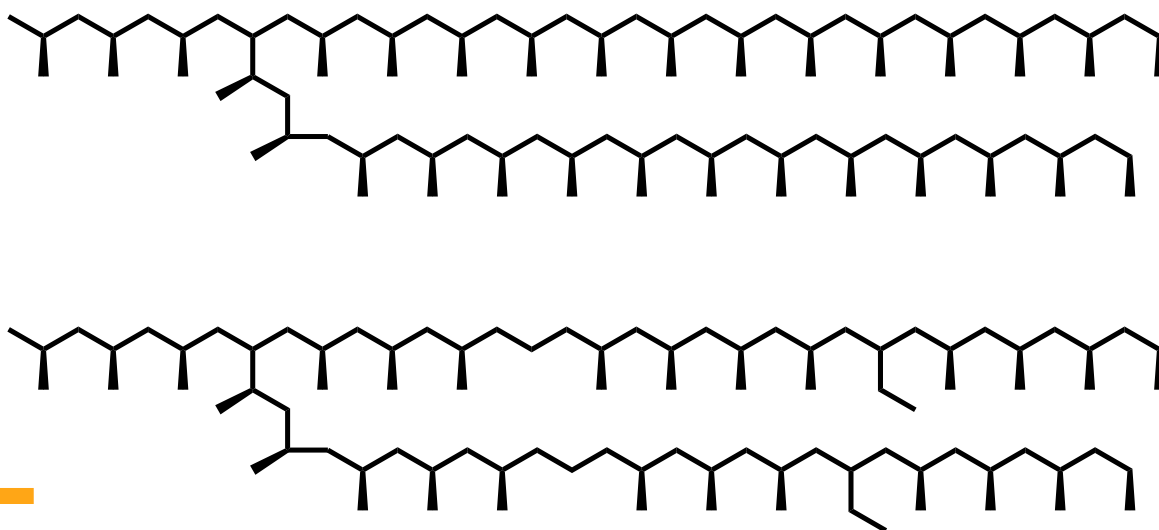
*branch length < 20 C*



## long chain branching

*catalyst / post modification*

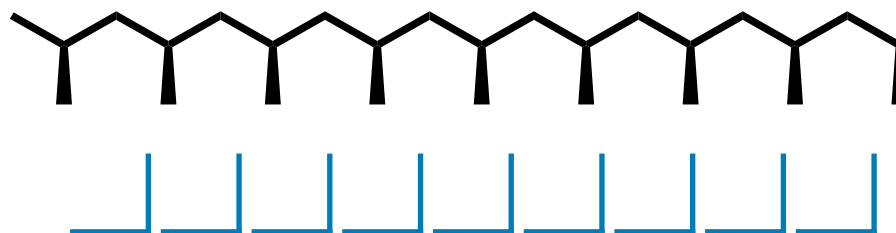
*branch length >  $M_e$*



# Tacticity in polypropylene

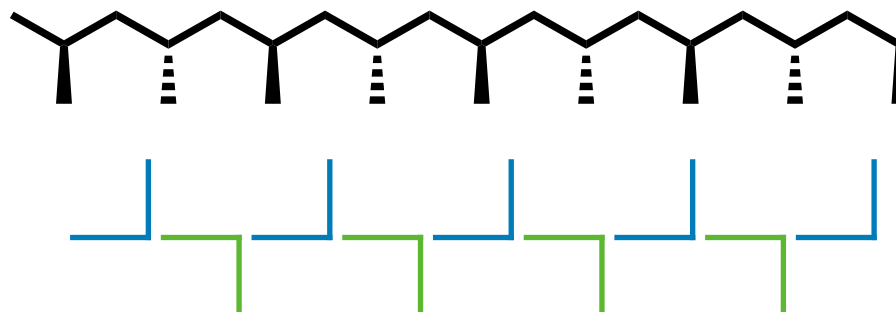
## Isotactic PP (iPP)

- side chains have **same** relative stereo configuration
- high degree of order



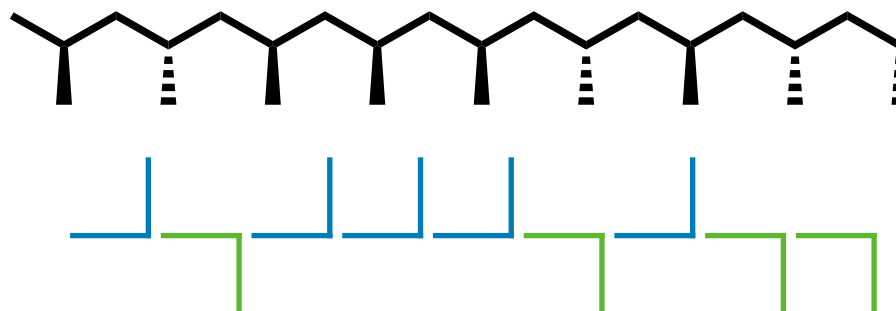
## Syndiotactic PP (sPP)

- side chains have **alternating** relative stereo configuration
- high degree of order



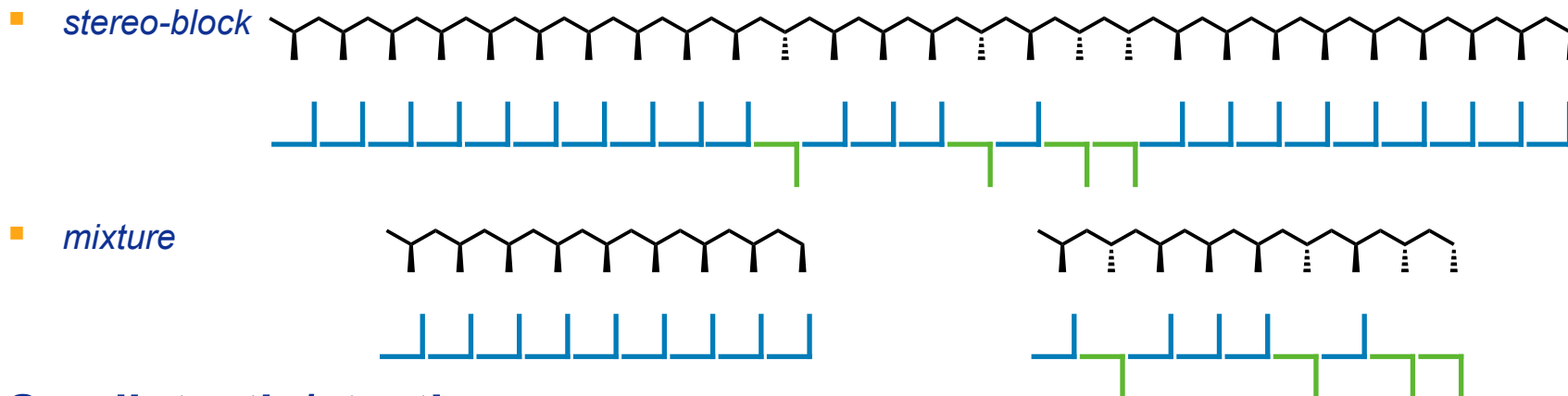
## Atactic PP (aPP)

- side chains have **random** relative stereo configuration
- low degree of order

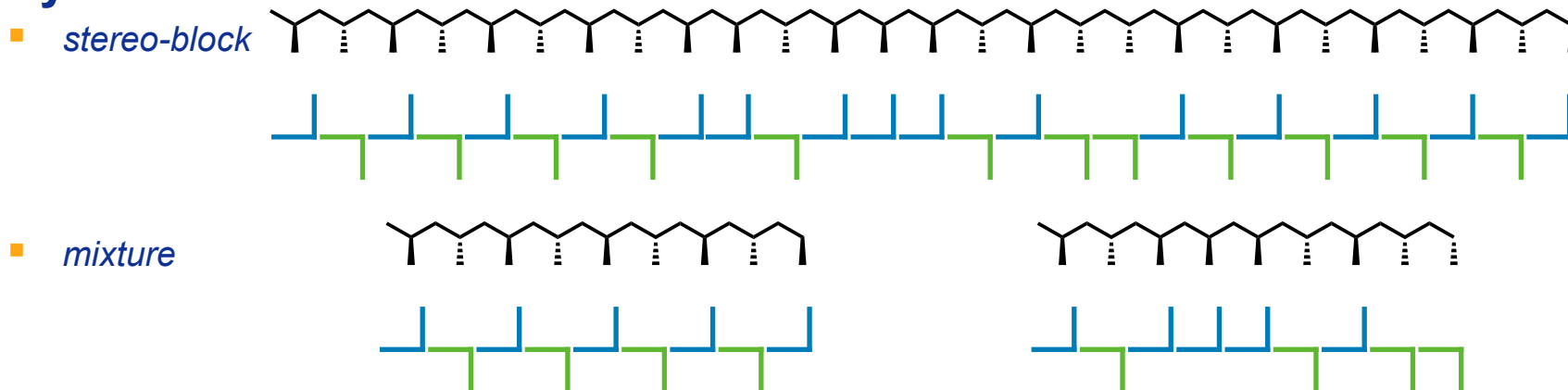


# Variation of tacticity in polypropylene

## Isotactic/atactic



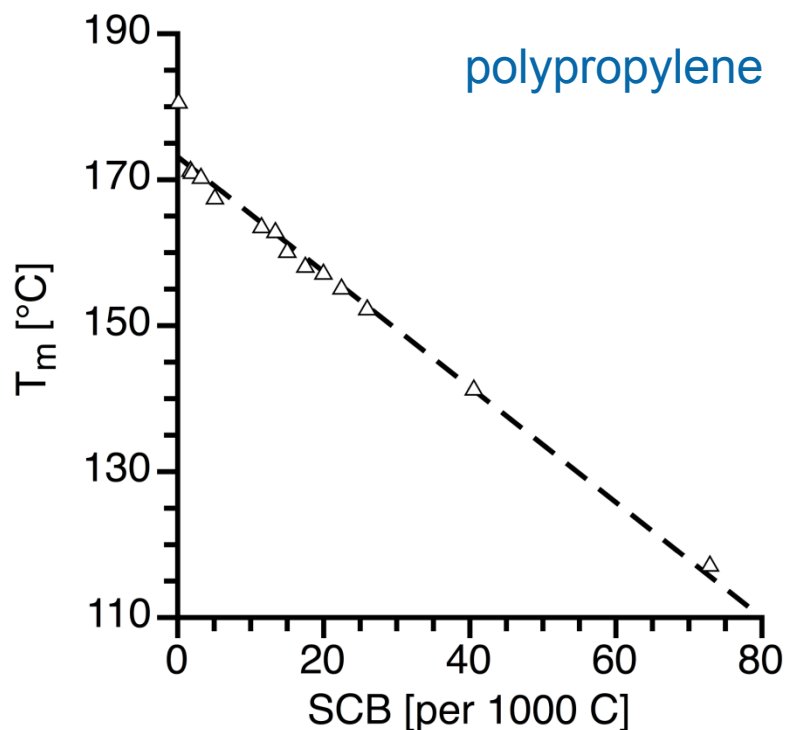
## Syndiotactic/atactic



# Relevance of branching

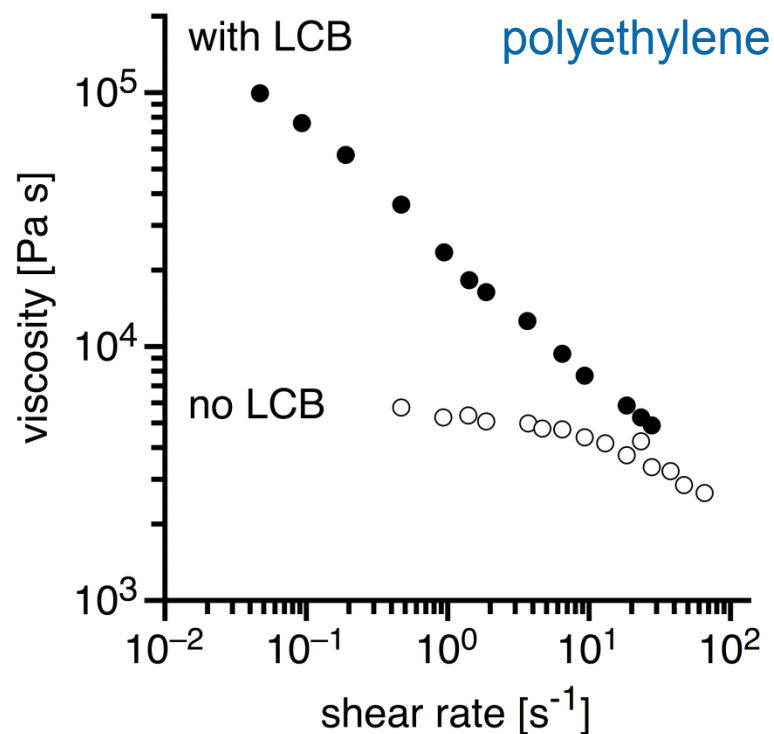
## Short chain branching (SCB)

thermal & mechanical properties



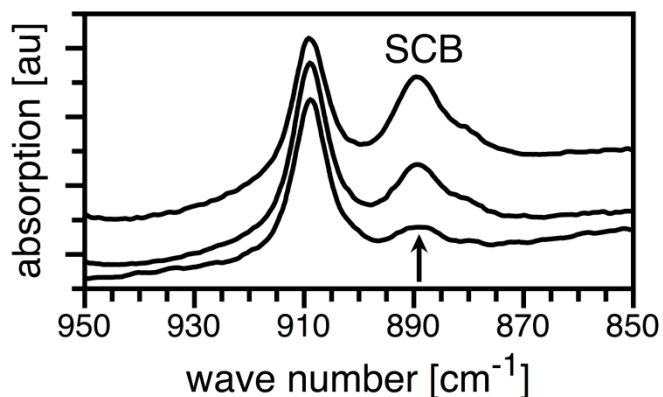
## Long chain branching (LCB)

melt processability

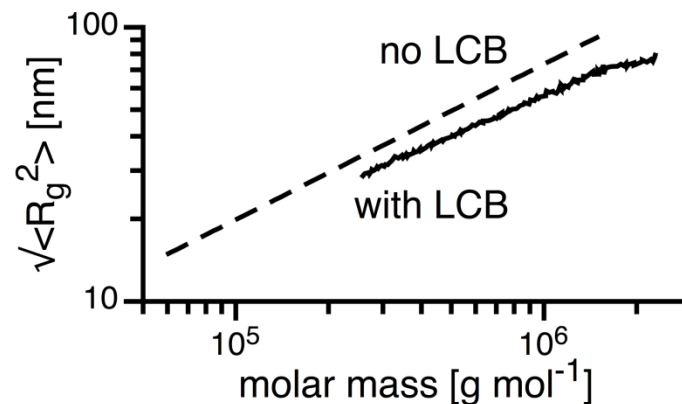


# Methods of branch detection

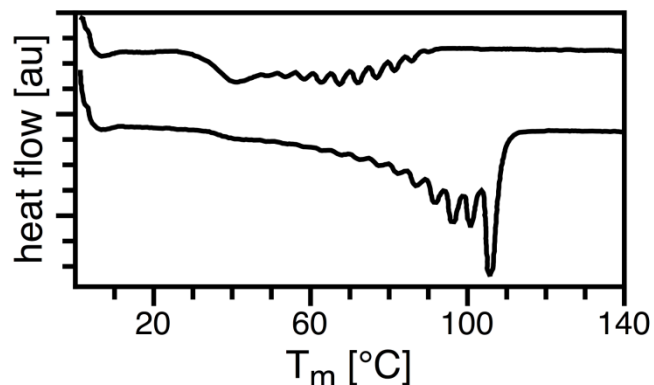
## infrared spectroscopy



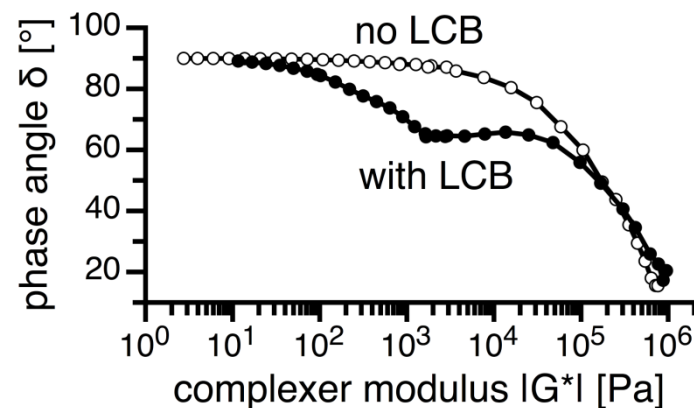
## GPC + light scattering



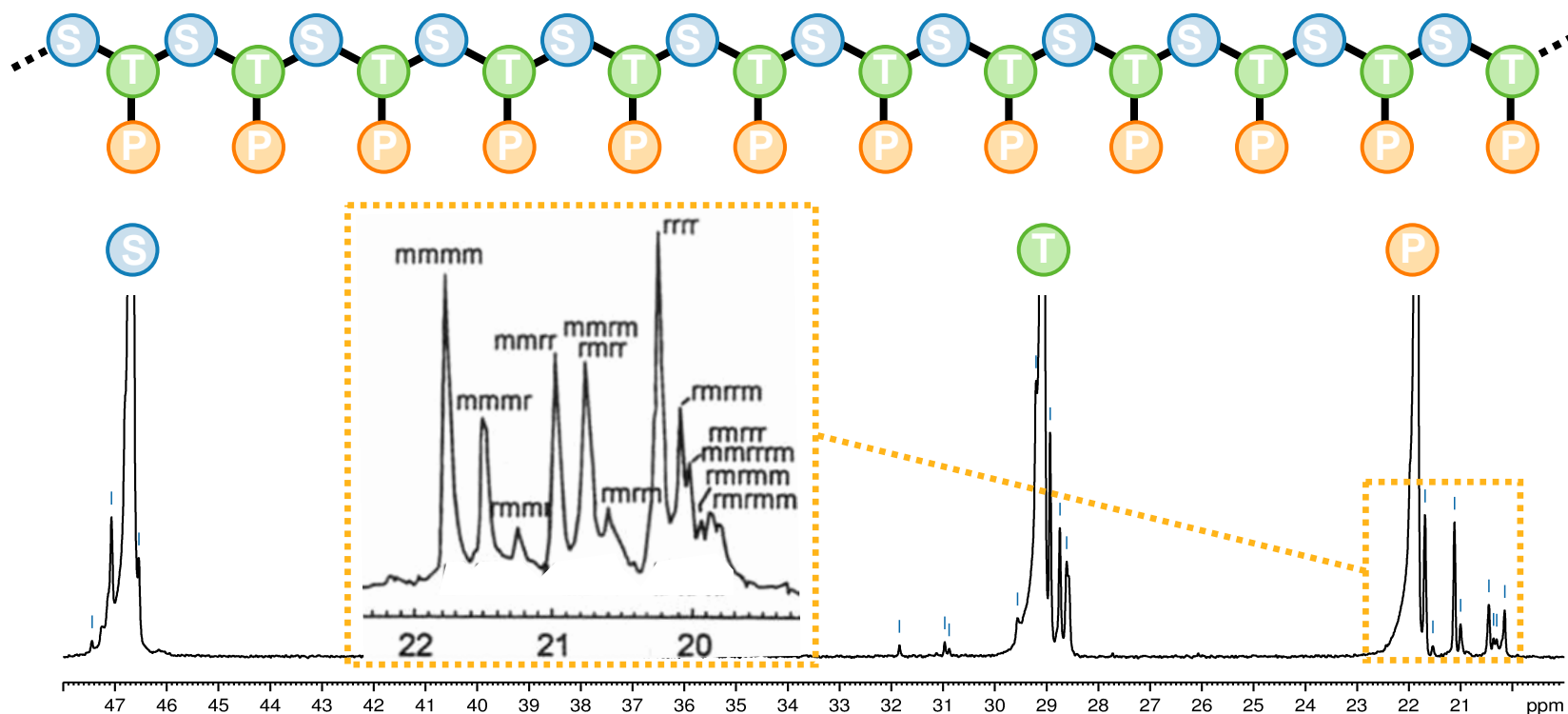
## thermally fractionated DSC



## rheology

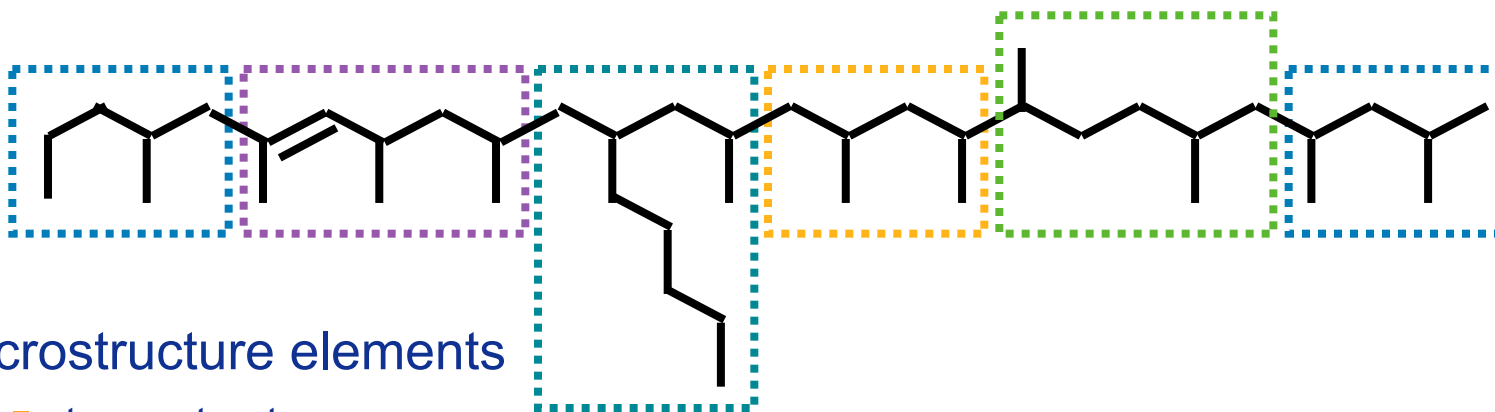


# $^{13}\text{C}$ NMR spectroscopy of polypropylene



- Chemical shift strongly influence by chemical structure ( $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$ )
  - Direct observation of steric triads (mm, mr, rr) or greater depending of resolution
  - Direct observation of regio-chemistry, units derived from comonomer, chain ends

# Polypropylene microstructure



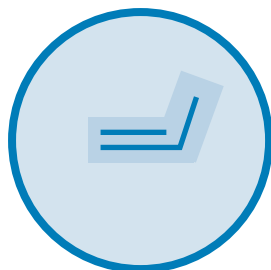
## microstructure elements

- stereo structure
  - regio structure
  - comonomer content/distribution
  - unsaturation
  - end-groups
- 
- all can be **directly** observed by NMR spectroscopy
    - most can be directly **quantified** by NMR spectroscopy



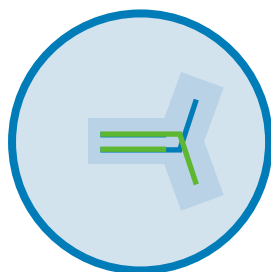
# Stereo & regio selectivity

regio & stereo  
selective site



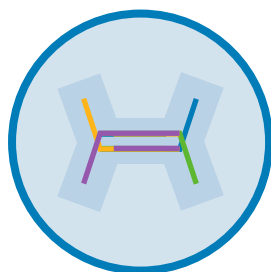
regio and stereoregular polypropylene

regio  
selective site



regioregular but stereoirregular polypropylene

non selective  
site



regio & stereoirregular polypropylene

Chem. Rev. 2000, 100, 1253-1345

12

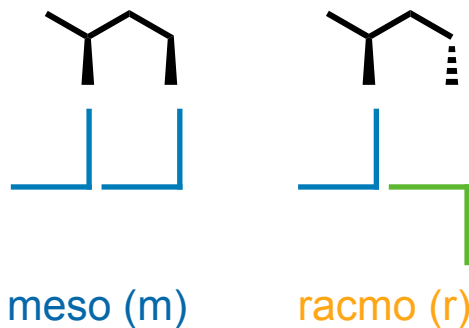
8/2/2011

NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

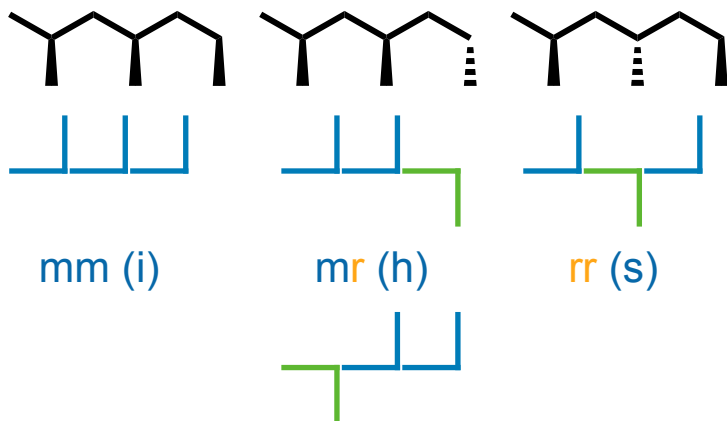
SHAPING the FUTURE with PLASTICS

# Steric diads, triads & pentads

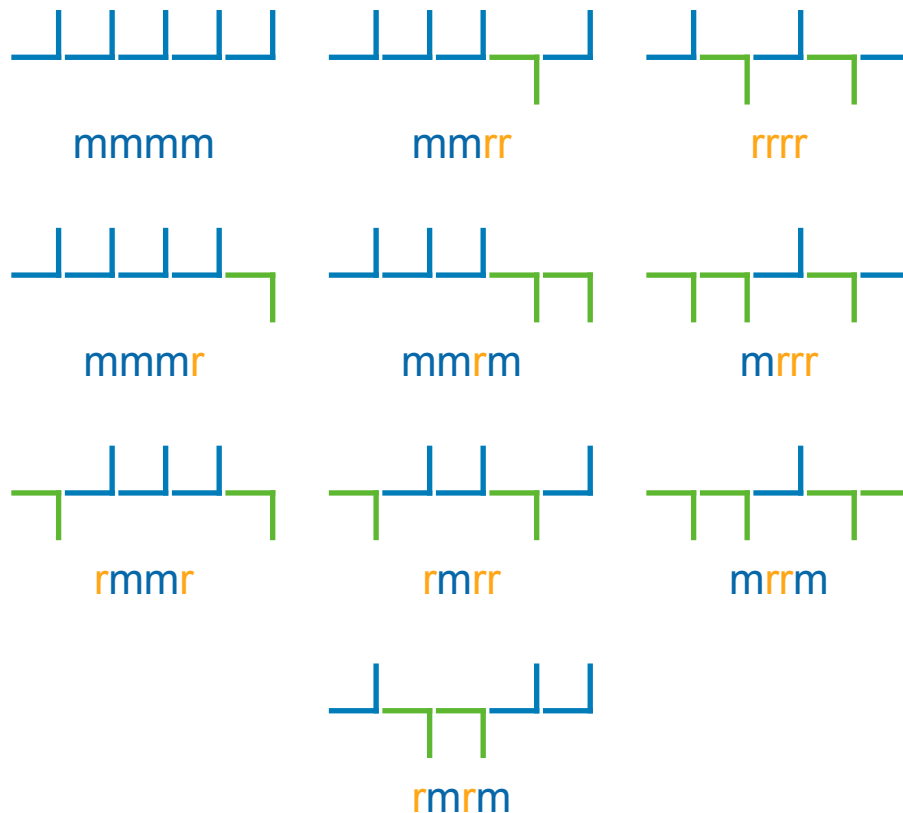
2 steric diads



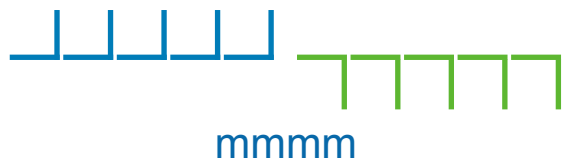
3 steric triads



10 steric pentads



# Absolute & relative configuration



# Reversible & indistinguishable sequences

- NMR does not distinguish the order the direction of the sequence:
  - for simplicity reversible sequences are not repeated

$$mmmr = rmmm$$

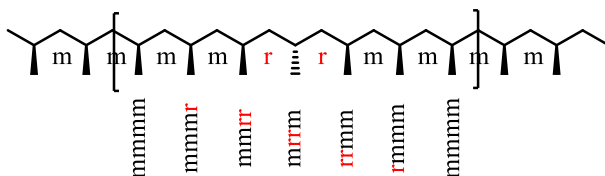
$$mmrr = rrmm$$

$$mrmr = rmr m$$

$$mrrr = rrrm$$

$$mr = rm$$

- becomes important when calculating likelihood of given sequence



$$2 \times mmmmm$$

$$2 \times mmmmr = 1 \times mmmmr + 1 \times rmmm$$

$$2 \times mmmrr = 1 \times mmmrr + 1 \times rmmr$$

$$1 \times mrrm$$

- Sometimes some sequences are indistinguishable by  $^{13}\text{C}$  NMR
  - low spectral resolution

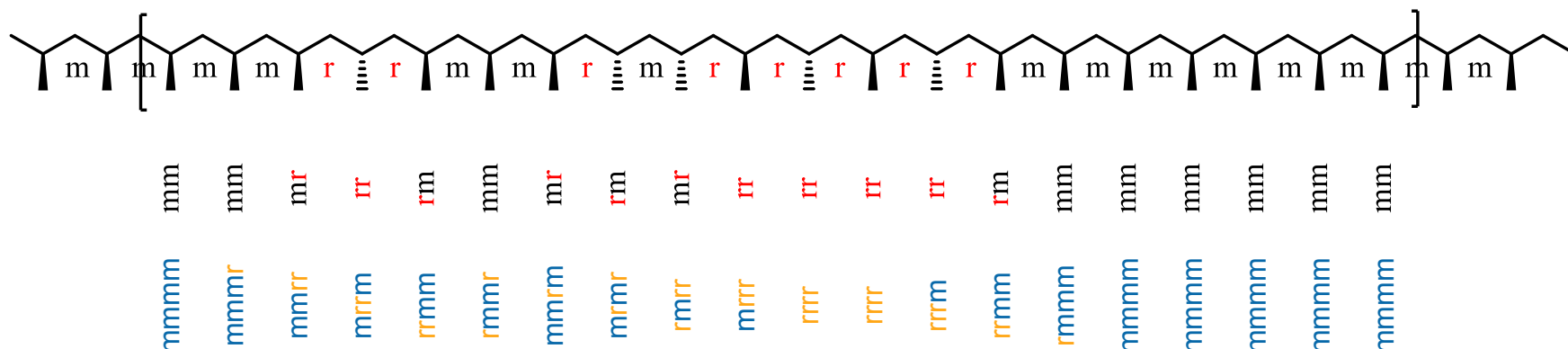
$$mmrm + rmr = xmr x$$

$$mmmm + mmmr = mmmx$$

# Steric n-ad necessary relationships

- lower-order sequences are directly related to higher-order sequences
  - triad-to-diad
    - $[m] = [mm] + \frac{1}{2} [mr]$
    - $[r] = [rr] + \frac{1}{2} [mr]$
  - pentad-to-triad
    - $[mm] = [m m m m m] + [m m m m r] + [r m m m r]$  sum of **mm** centred pentads
    - $[mr] = [m m m r m] + [m m m r r] + [r m m r m] + [r m m r r]$  sum of **mr** centred pentads
    - $[rr] = [m r r r m] + [m r r r r] + [r r r r r]$  sum of **rr** centred pentads
- Analogous to triad comonomer sequence to comonomer content
  - $[A] = [AAA] + [AAB] + [BAB]$  sum of **A** centred triads
  - $[B] = [BBB] + [BBA] + [ABA]$  sum of **B** centred triads

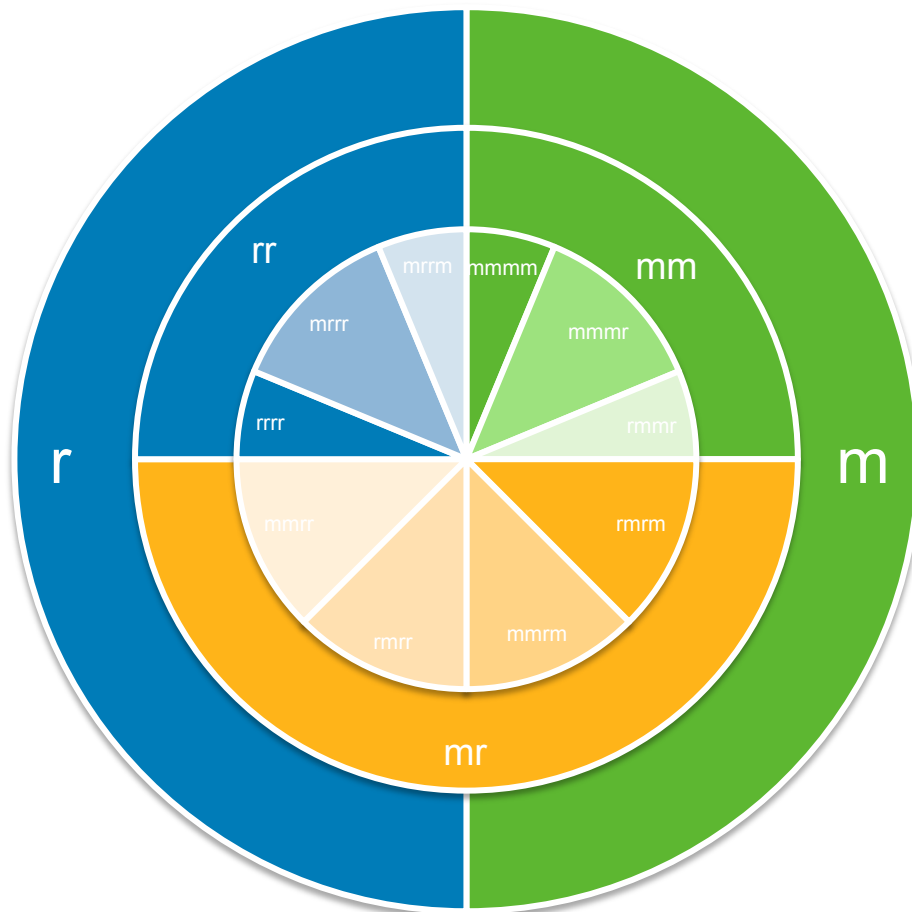
# Steric diad, triad & pentad distributions



- NMR only measures relative distribution of intensity between pentads
- Does not count in absolute terms (need to be careful when we draw pictures and count)

mmmm = 6	mmrr = 3	rrrr = 2	[mmmm] = 0.30	[mmrr] = 0.15	[rrrr] = 0.10
mmmr = 2	xmrx = 2	mrrr = 2	[mmmr] = 0.10	[xmrx] = 0.10	[mrrr] = 0.10
rmmr = 1	mrmm = 1	mrrm = 1	[rmmr] = 0.05	[mrmm] = 0.05	[mrrm] = 0.05
mm = 9	mr = 6	rr = 5	[mm] = 0.45	[mr] = 0.30	[rr] = 0.25
m = 12	r = 8		[m] = 0.60	[r] = 0.40	
x = 20				[x] = 1.00	

# Necessary relationships from distributions



# Information from the pentad distribution

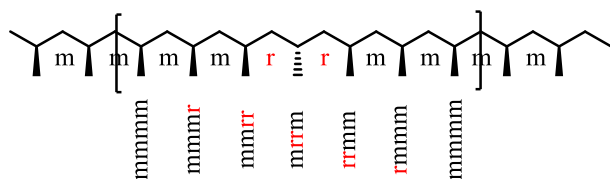
## ■ Pentad isotacticity

- relative amount of isotactic pentad **mmmm** with respect to all other pentads

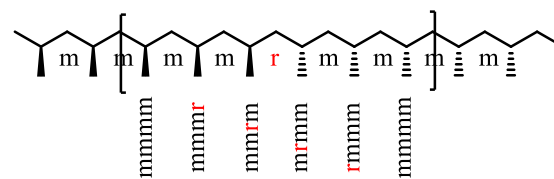
■ pure isotactic:  $[m] = [mm] = [mmmm] = 1.00$  or 100%

■ highly isotactic:  $[m] > [mm] > [mmmm] = 0.95$  or 95%

## ■ Type of stereo defects (error correction of error propagation)



$$2[mmmr] = 2[mmrr] = [mrrm]$$



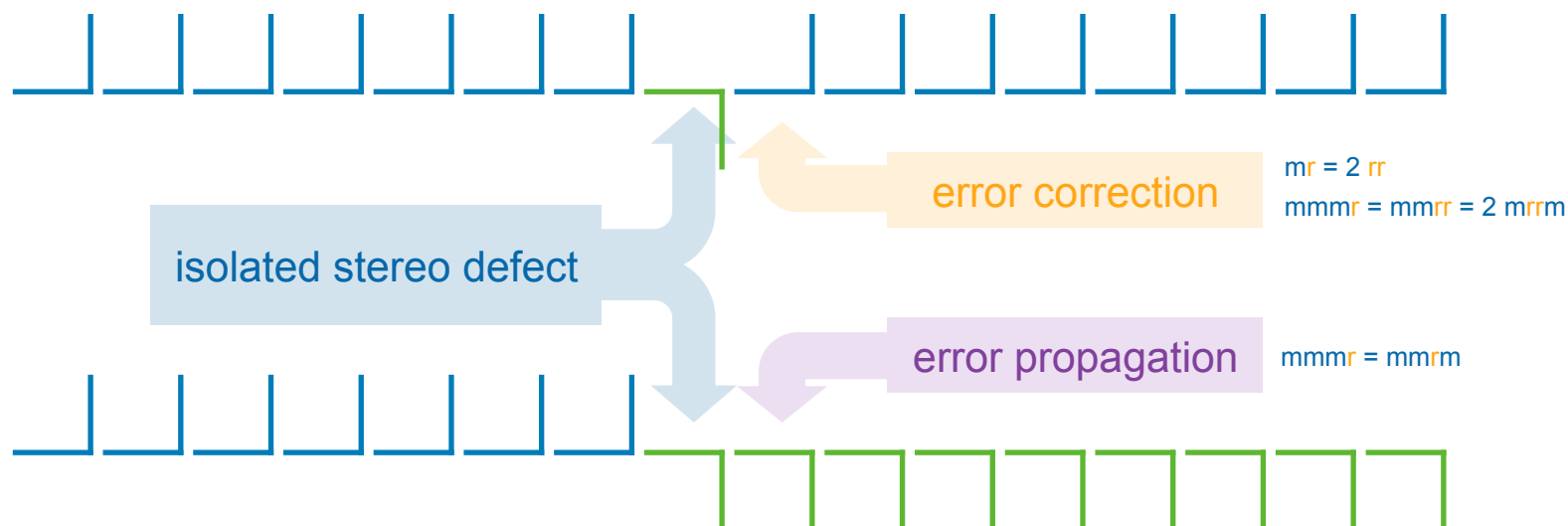
$$[mmmr] = [mmrr]$$

## ■ Other derived properties

- Average meso sequence length (MSL)
- Stereo defects per 1000 monomers (D)



# Stereo defects in isotactic polypropylene

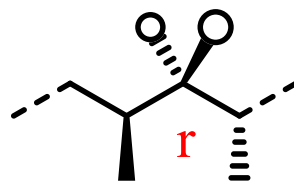
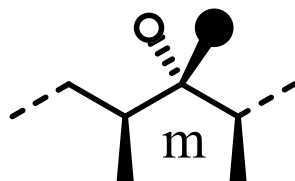


- We design our catalysts to make highly isotactic chains but they make errors!
  - a stereo error at the catalyst leads to stereo defects (low probability of error = defects are rare)
  - isolated stereo defects form by two mechanism (catalyst and catalyst structure dependant)
    - error correction: isolated single stereo error, typical for single-site catalysis and some ZN sites (site control)
    - error propagation: change in absolute configuration, typical for ZN catalysts (chain-end control)

# Steric diads, triads & pentads & NMR

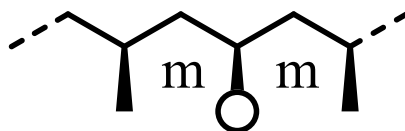
meso (m) same    racemo (r) different

diad



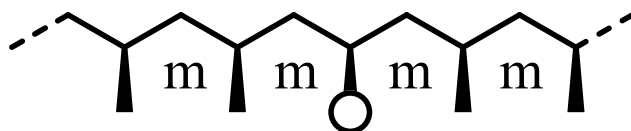
$^1\text{H}$  NMR

triad



$^{13}\text{C}$  NMR

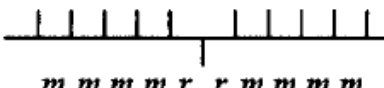
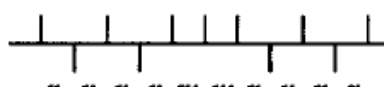
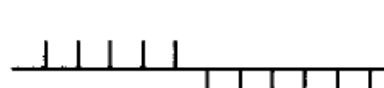
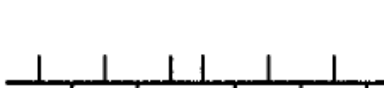
pentad



$^{13}\text{C}$  NMR

- $^1\text{H}$ :  $\text{CH}_2$  report on relative stereo configuration (dyad)
- $^{13}\text{C}$ :  $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  report on relative stereo configuration (triad+)

# Stereo errors

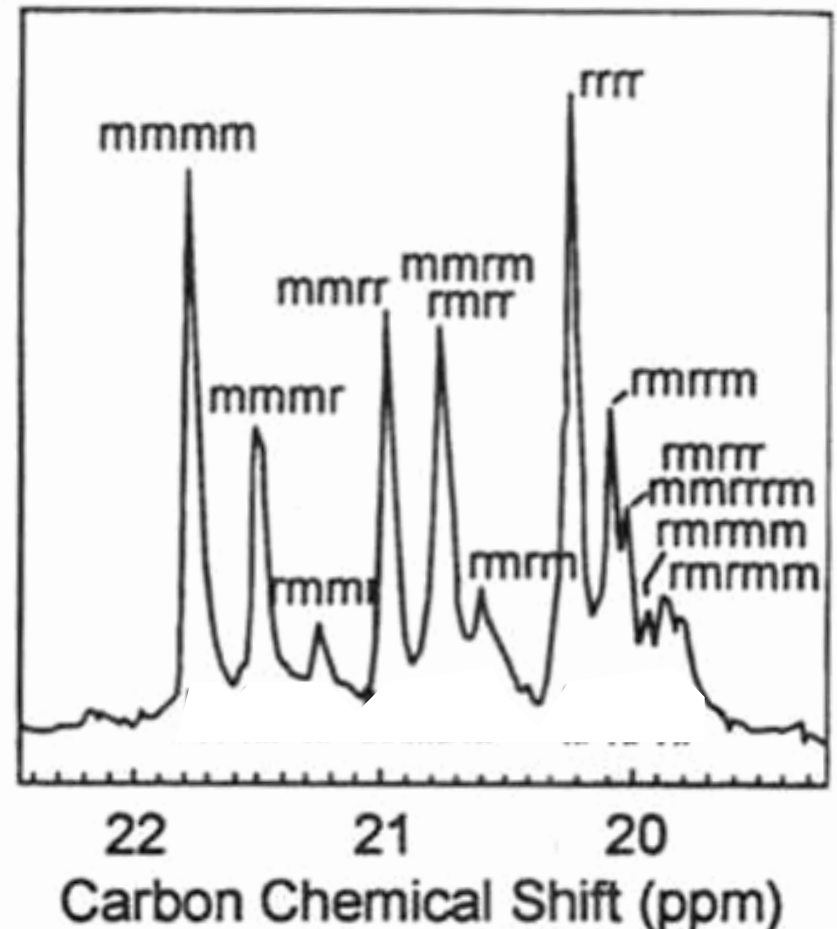
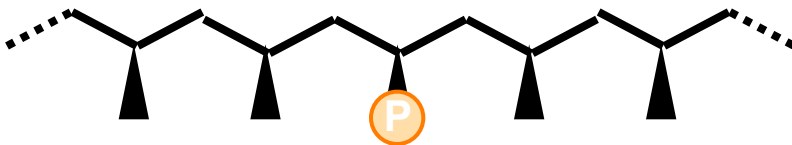
Polymerization mechanism		Microstructure with isolated stereoinversion	triad/triad and pentad/pentad relationships
Primary insertion	site control error correction	isospecific 	$[mr] = 2[rr]$ $[mmmr] = [mmrr] = 2[mrrm]$
		syndiospecific 	$[mr] = 2[mm]$ $[rrrm] = [mmrr] = 2[rmmr]$
	chain-end control error propagation	isospecific 	$mr$ only $[mmmr] = [mmrm]$
		syndiospecific 	$mr$ only $[rrrm] = [rrmr]$

Source: Chem. Rev. 2000, 100, 1253-1345

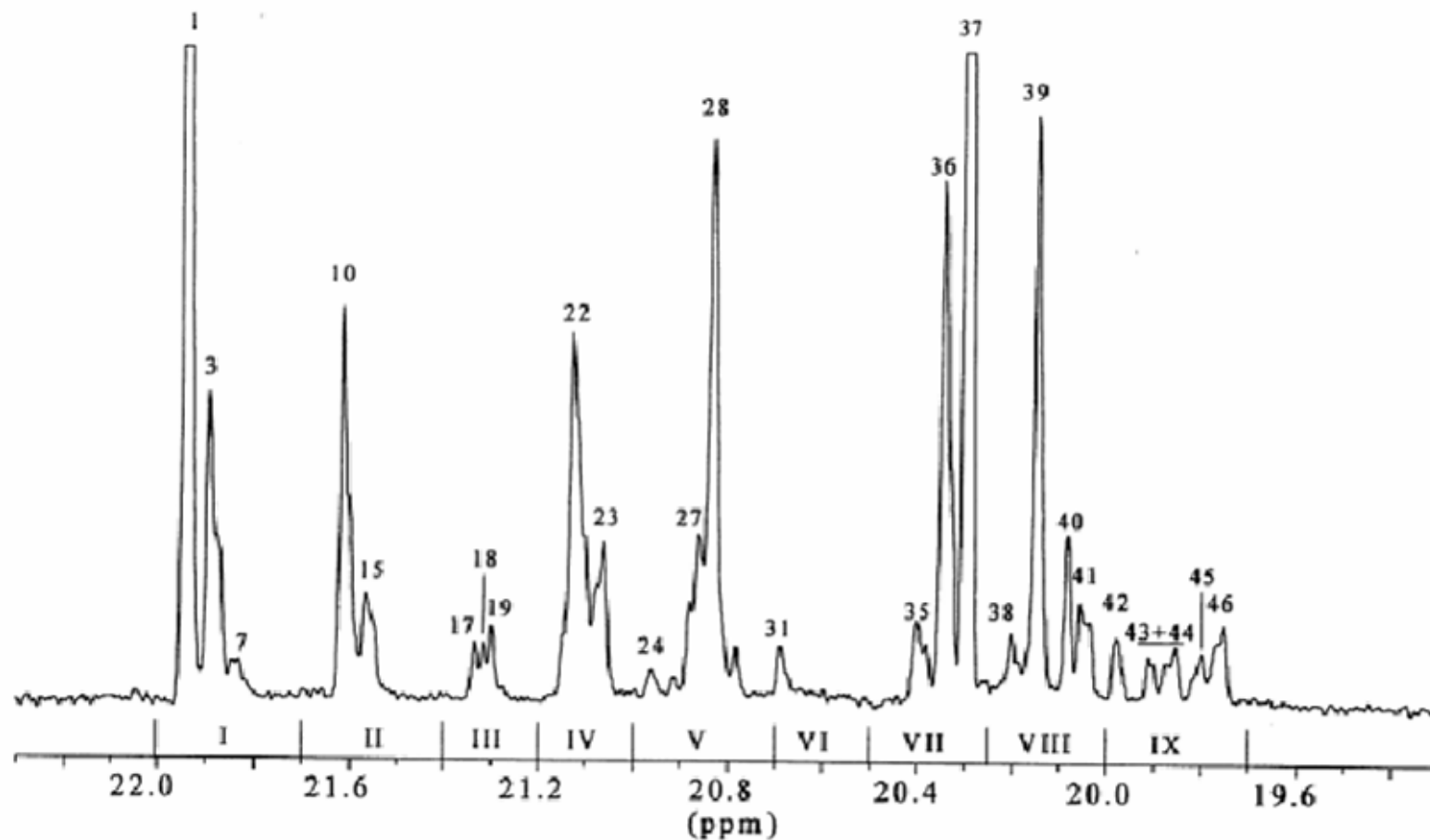
## Direct observation of tacticity by NMR

- Seen for  $\text{CH}_3$ ,  $\text{CH}_2$  &  $\text{CH}$  sites
- most resolution for  $\text{CH}_3$
- nonads possible
- pentads & triads more usual

- Observe chemical shift of middle site of a odd n-ad



# Methyl region ZN aPP

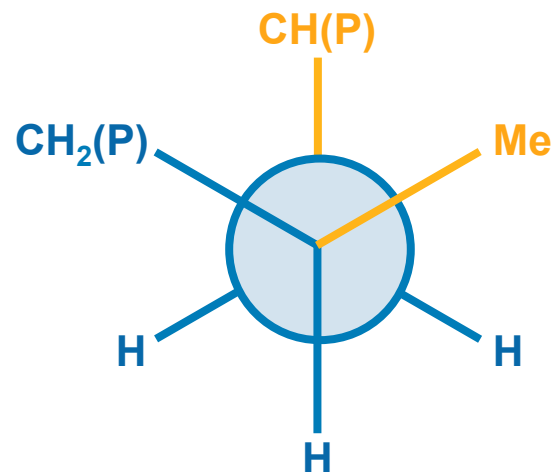


# The gamma effect

- Why does the chemical shift change with stereo configuration?

- Empirical correlation between structure and relative chemical shift:

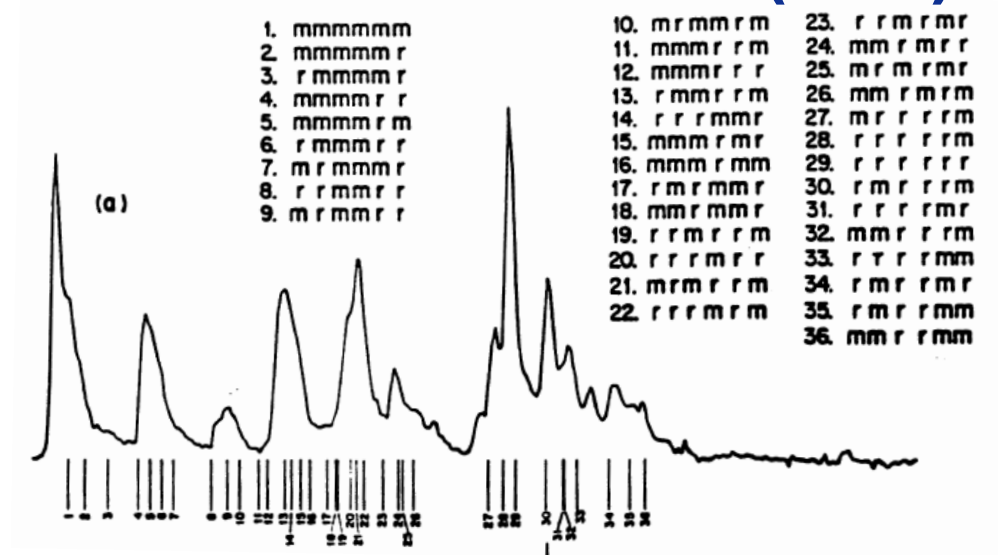
a effect (ppm)		b effect (ppm)		g effect (ppm)	
$\text{CH}_3\text{-H}$	$\pm 0.0$	$\text{CH}_3\text{-CH}_2\text{-H}$	$\pm 0.0$	$\text{CH}_3\text{-CH}_2\text{-CH}_3$	$\pm 0.0$
$\text{CH}_3\text{-CH}_3$	+8.0	$\text{CH}_3\text{-CH}_2\text{-CH}_3$	+9.7	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	-2.4
$\text{CH}_2\text{-(CH}_3)_2$	+10.2	$\text{CH}_3\text{-CH-(CH}_3)_2$	+8.7	$\text{CH}_3\text{-CH}_2\text{-CH-(CH}_3)_2$	-1.9



- Gamma effect is small but depends both on structure and conformation

- Maximum influence seen for gamma-gauche structure/conformation
- Likelihood of finding gamma-gauche groups depends on relative stereo chemistry (average chain conformation in solution)

# Rotation of isomeric states (RIS)



Pentad	$\delta$ (exp.)	$\Delta\delta$ (calc.)	$\delta$ (calc.)
<i>mmmm</i>	21.78	0	21.780
<i>mmmr</i>	21.55	-0.276	21.504
<i>rmmr</i>	21.33	-0.550	21.230
<i>mmrr</i>	21.01	-0.728	21.052
<i>mmrm</i>	20.85	-0.913	20.867
<i>rmrr</i>	20.85	-1.009	20.771
<i>rmrm</i>	20.71	-1.201	20.579
<i>rrrr</i>	20.31	-1.499	20.281
<i>rrrm</i>	20.17	-1.712	20.068
<i>mrrm</i>	20.04	-1.940	19.840

Source: Macromolecules 13 (1980) 270-275

Prog. Polym. Sci. 26 (2001) 443-533

# Polyolefin Solution-state NMR Setup

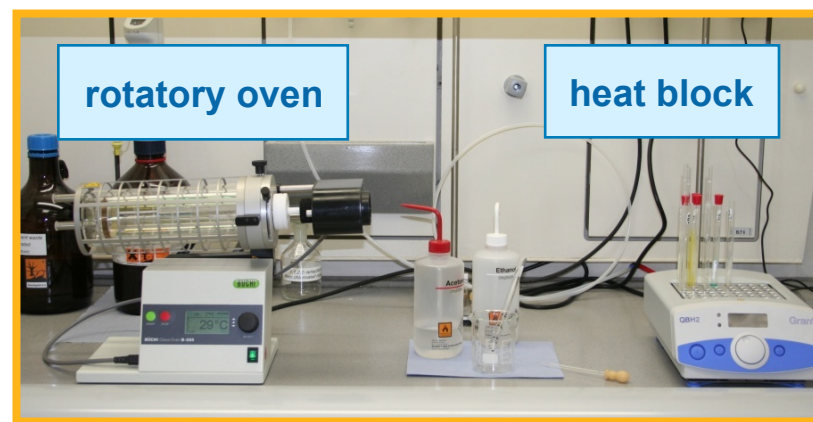
- Standard NMR spectroscopy technique
  - polymer dissolved in solvent imparts mobility
  - isotropic tumbling narrows spectral line widths
  - high-temperature (125°C)
    - 100-200 mg in 3-4 ml of tetrachloroethene- $d_2$  (TCE- $d_2$ )
    - approximately 1 h for homogeneous solution to form
- Probeheads (accessories)
  - 10 mm  $^{13}\text{C}$  selective extended temperature (SEX) probehead (custom  $^{13}\text{C}$  detect)
    - $^{13}\text{C}$  optimised, high  $^{13}\text{C}$  sensitivity, lower  $^1\text{H}$  resolution



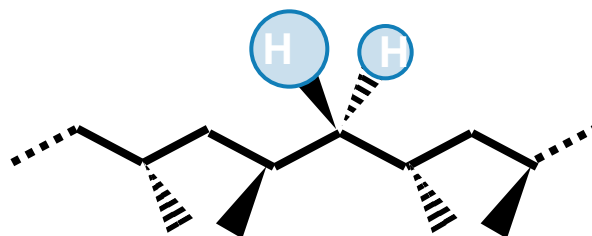
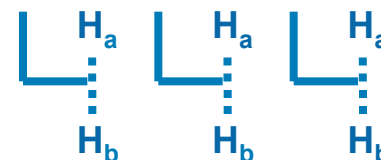
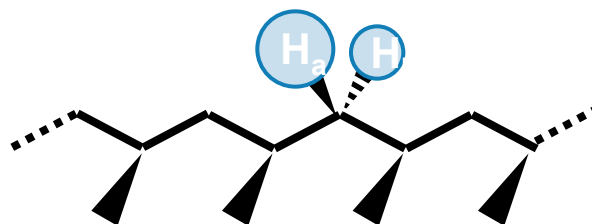
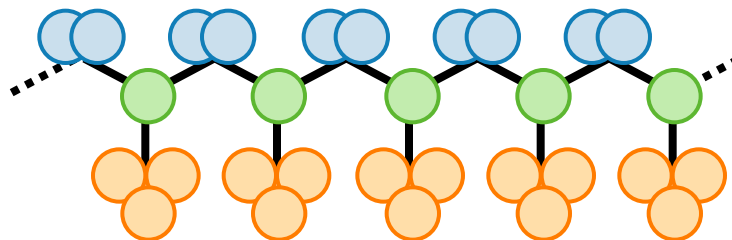
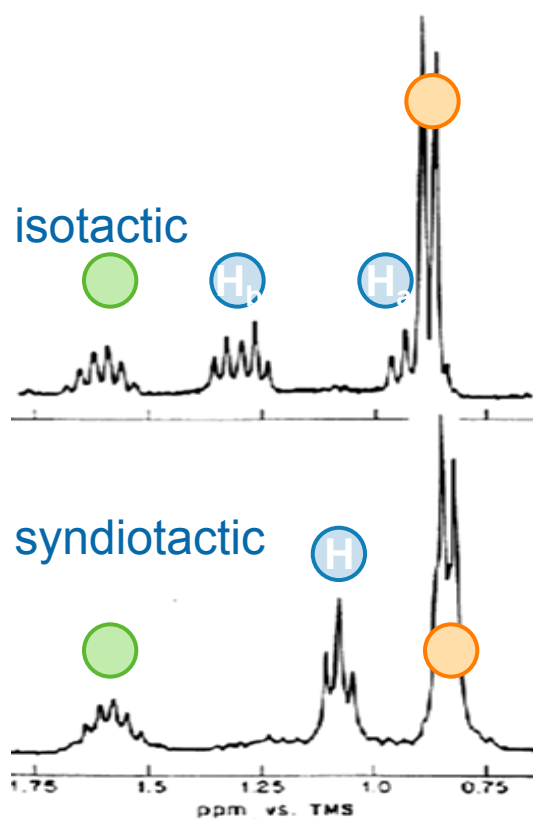
# Sample preparation: solution-state



- Samples can be in any form
  - Pellets, powder, films, finished parts, filled

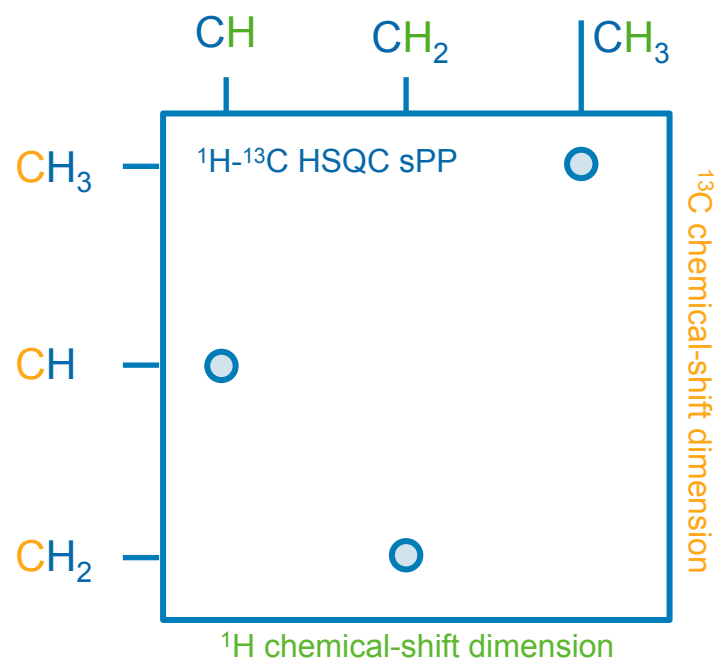
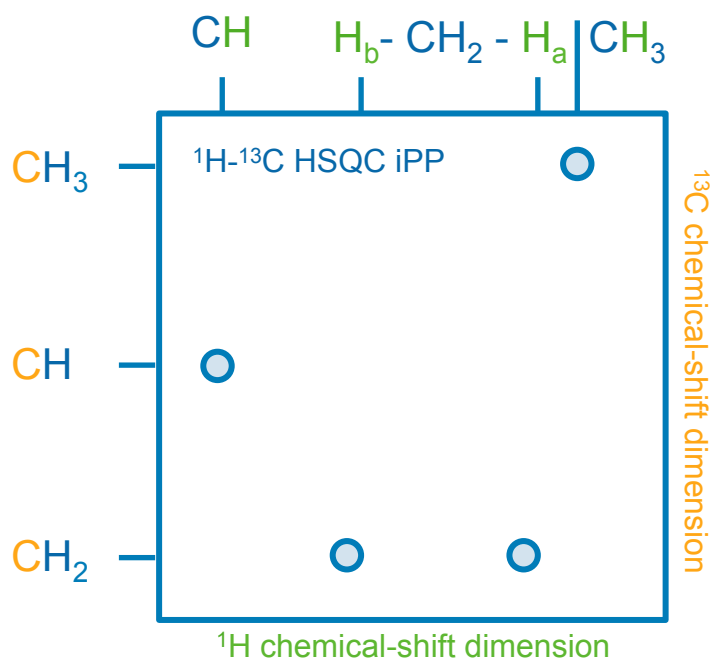


# $^1\text{H}$ NMR spectroscopy of polypropylene



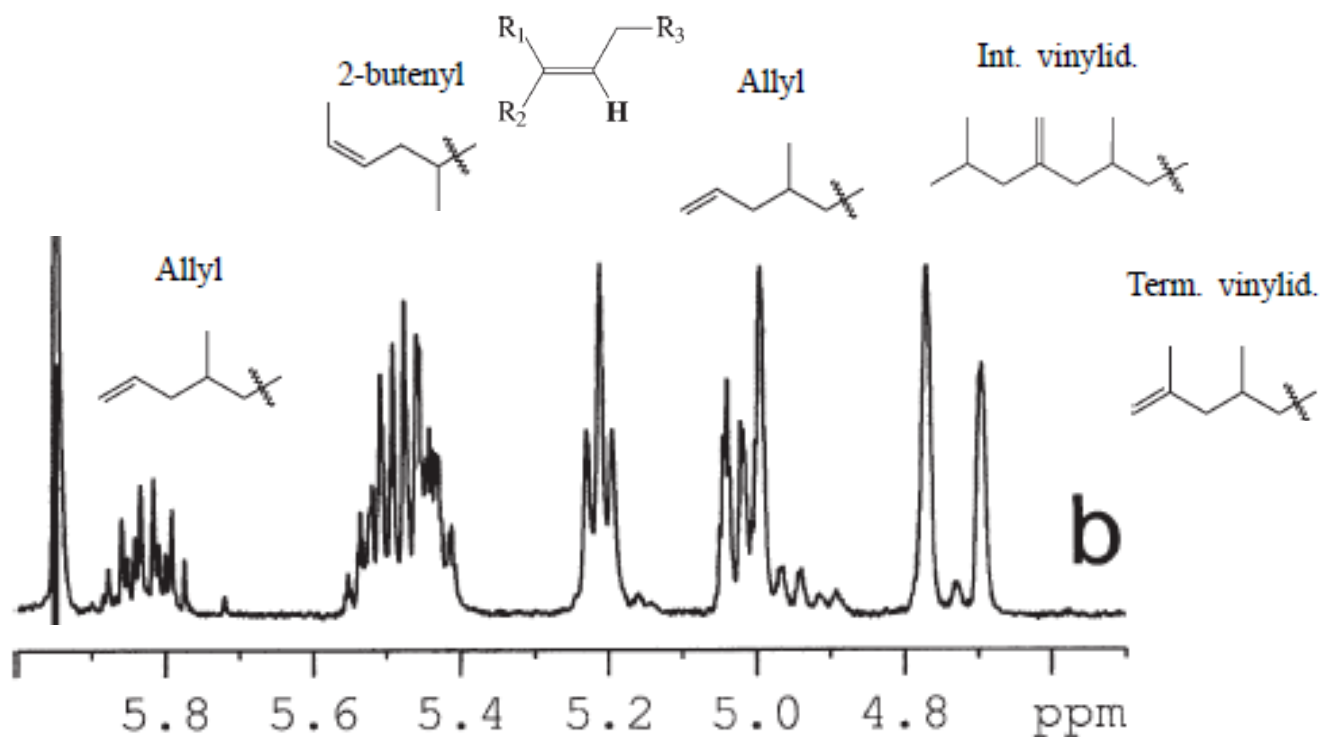
- Chemical shift influenced by **chemical** and **stereo** structure
  - Direct observation of steric dyads

# $^1\text{H}$ - $^{13}\text{C}$ HSQC of polypropylene



- Heteronuclear correlation allows conformation of isotacticity in PP
  - isotactic:  $\text{CH}_2$  carbon correlates to 2 magnetically inequivalent  $\text{CH}_2$  protons ( $\text{H}_a + \text{H}_b$ )
  - syndiotactic:  $\text{CH}_2$  carbon correlates to 2 magnetically equivalent  $\text{CH}_2$  protons
  - atactic:  $\text{CH}_2$  carbon correlates to multiple inequivalent (m) and equivalent (r) protons

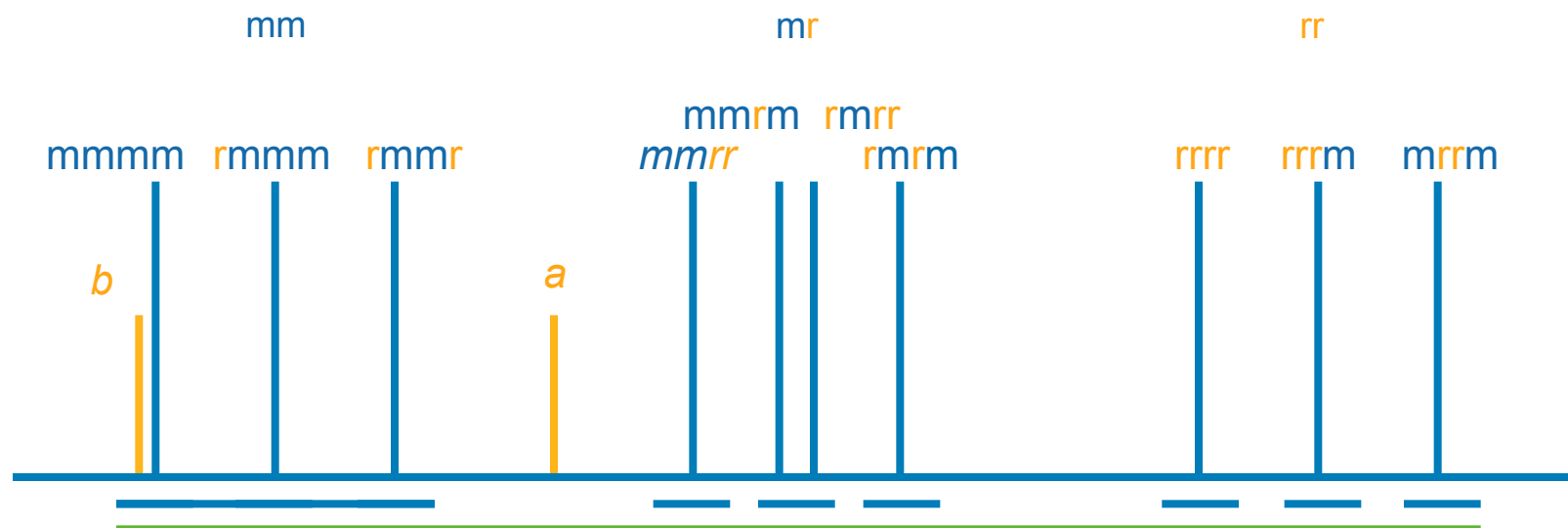
# $^1\text{H}$ NMR & unsaturation



- $^1\text{H}$  NMR or PP provides quick insight into the unsaturation
  - characteristic  $^1\text{H}$  chemical shifts
  - have to be careful about sample preparation and resolution

Topics in Catalysis 7 (1999) 145–163

# Measurement of tacticity: logic



## ■ Isotacticity

- only isotactic n-ad needs to be resolved
- resolution dictates level (triad, pentad)

$$f_x = A_x / A_{\text{all}}$$

$$f_x = A_x / (A_{\text{all}} - A_a)$$

## ■ Tacticity distribution

- All sites need to be resolved

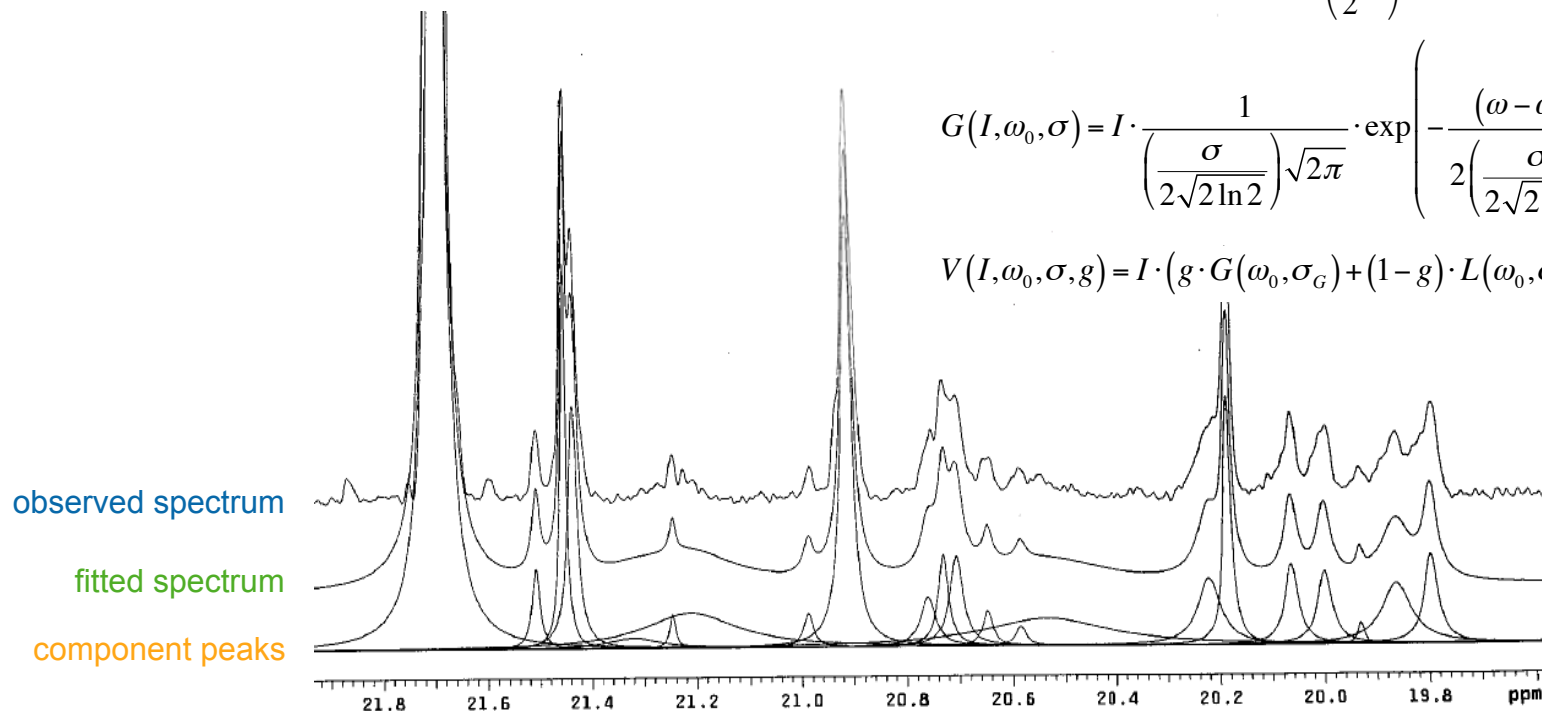
$$f_x = A_x - A_b / (A_{\text{all}} - A_a - A_b)$$

# Deconvolution

$$L(I, \omega_0, \sigma) = I \cdot \frac{1}{\pi} \cdot \frac{\left(\frac{1}{2}\sigma\right)}{(\omega - \omega_0)^2 + \left(\frac{1}{2}\sigma\right)^2}$$

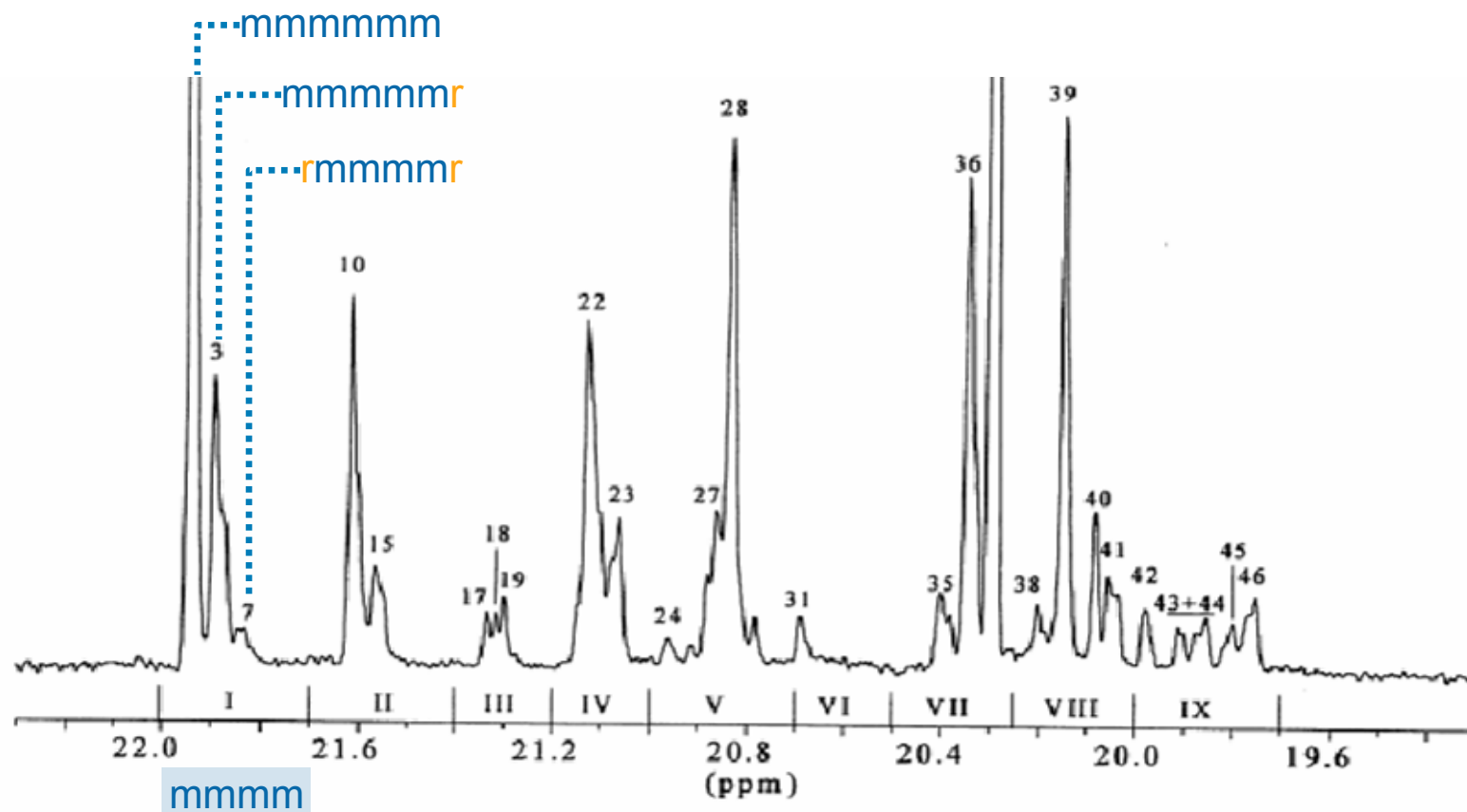
$$G(I, \omega_0, \sigma) = I \cdot \frac{1}{\left(\frac{\sigma}{2\sqrt{2\ln 2}}\right)\sqrt{2\pi}} \cdot \exp\left(-\frac{(\omega - \omega_0)^2}{2\left(\frac{\sigma}{2\sqrt{2\ln 2}}\right)^2}\right)$$

$$V(I, \omega_0, \sigma, g) = I \cdot (g \cdot G(\omega_0, \sigma_G) + (1 - g) \cdot L(\omega_0, \sigma_L))$$



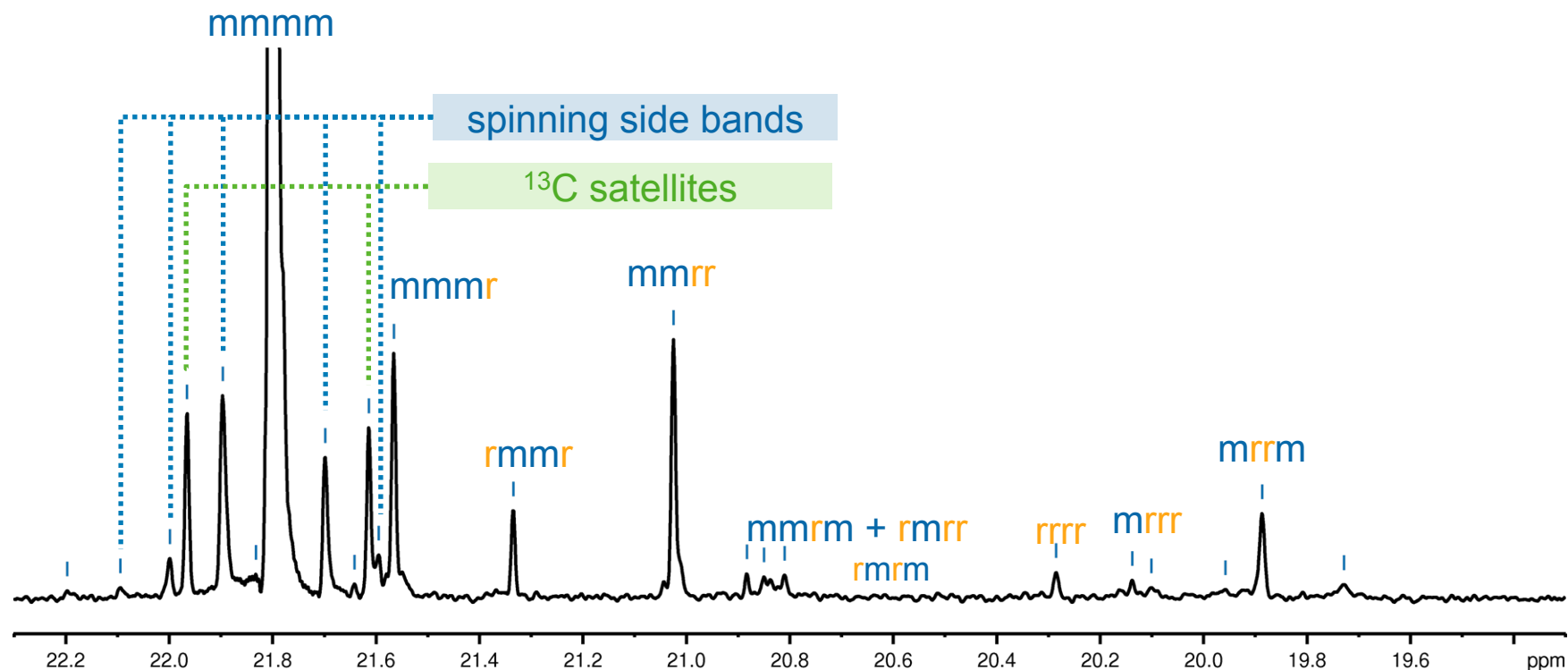
- Deconvolution better for measuring chemical shifts
  - you can fit anything with so many free variables (3-5 parameters per signal)
- Direct integration better for counting
  - need to make sure you account or correct for all observed signals within a region

# High-resolution solution-state NMR



- heptad level via use of high field (600 Mhz) and low sensitivity (5 mg 5 mm OD)
- very high resolution but expensive and slow (12 hours)

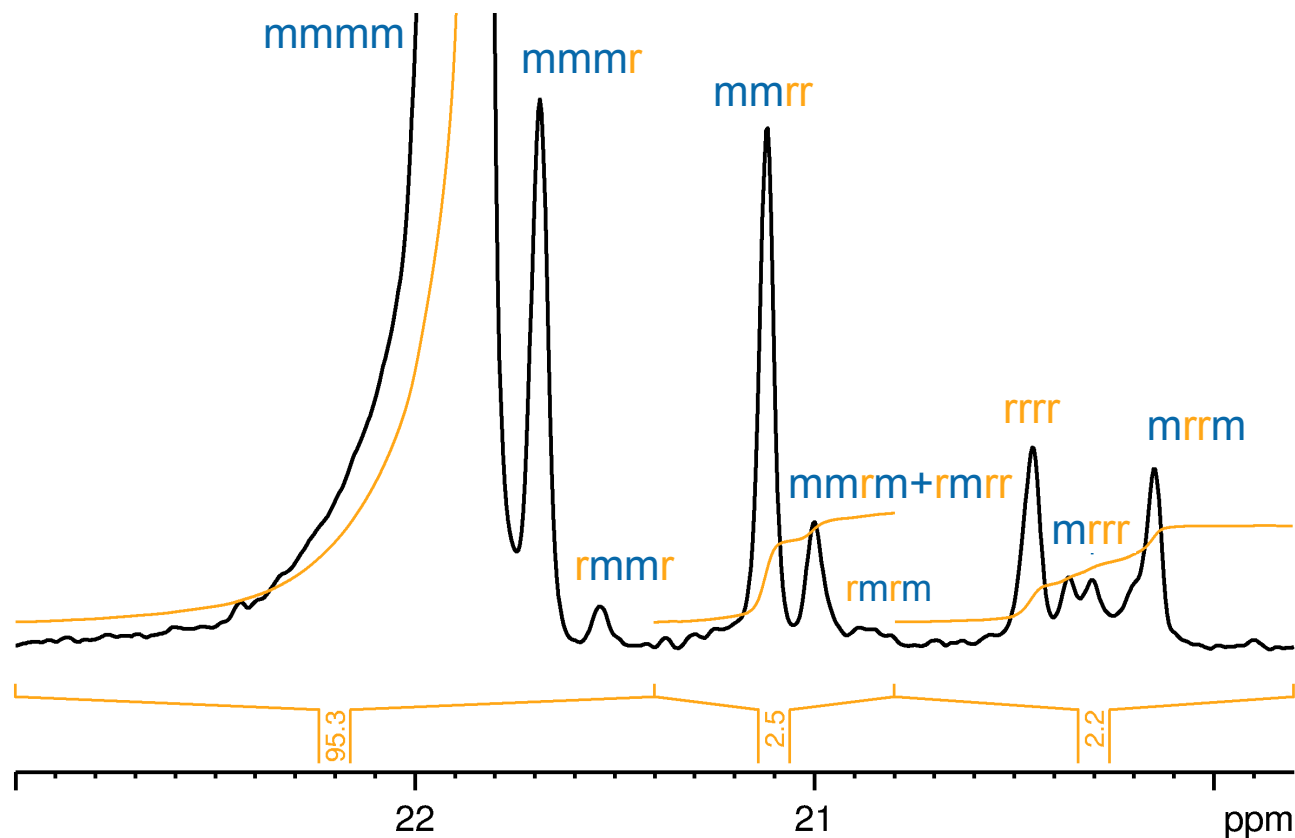
# Medium-resolution solution-state NMR



- pentad level via low field (400 Mhz) but high sensitivity (200 mg 10mm OD)
- spectrum complicated by artifacts but acceptable time (6 hours)

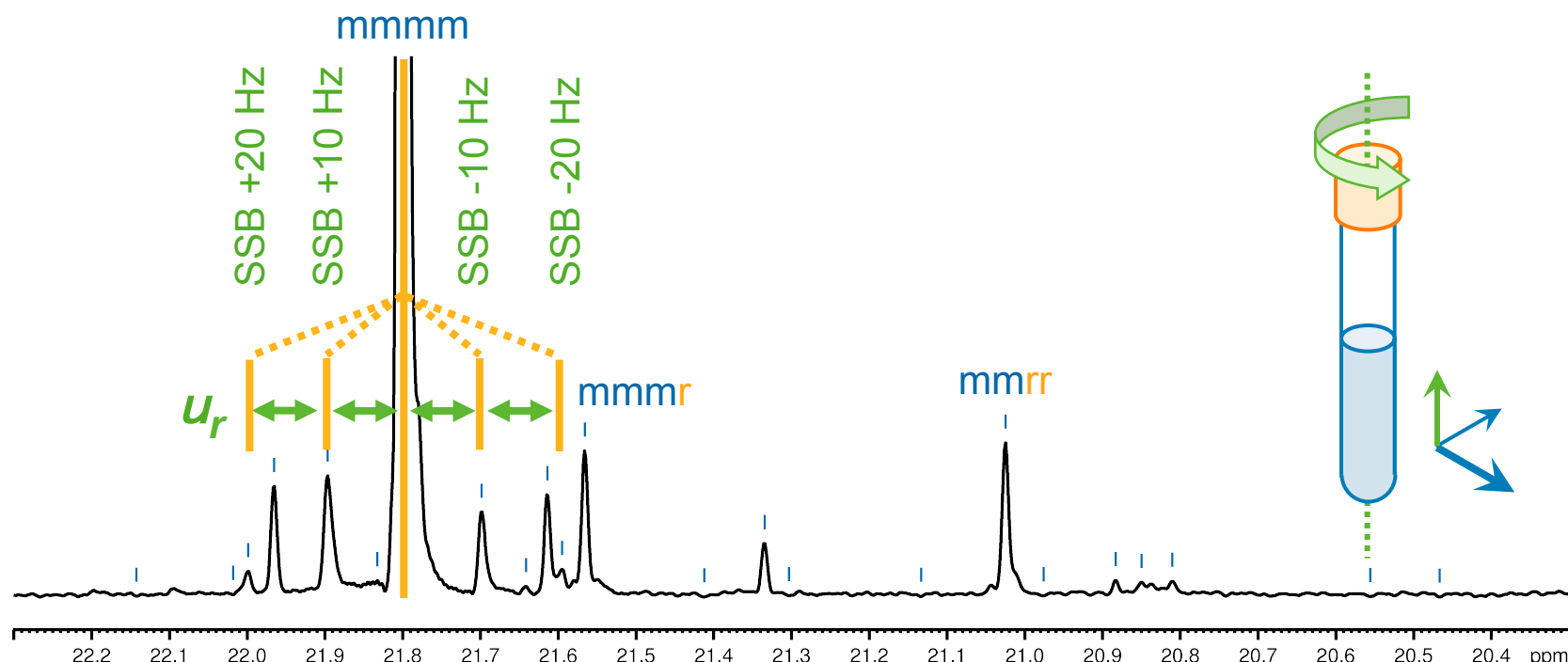


# Low-resolution melt-state NMR



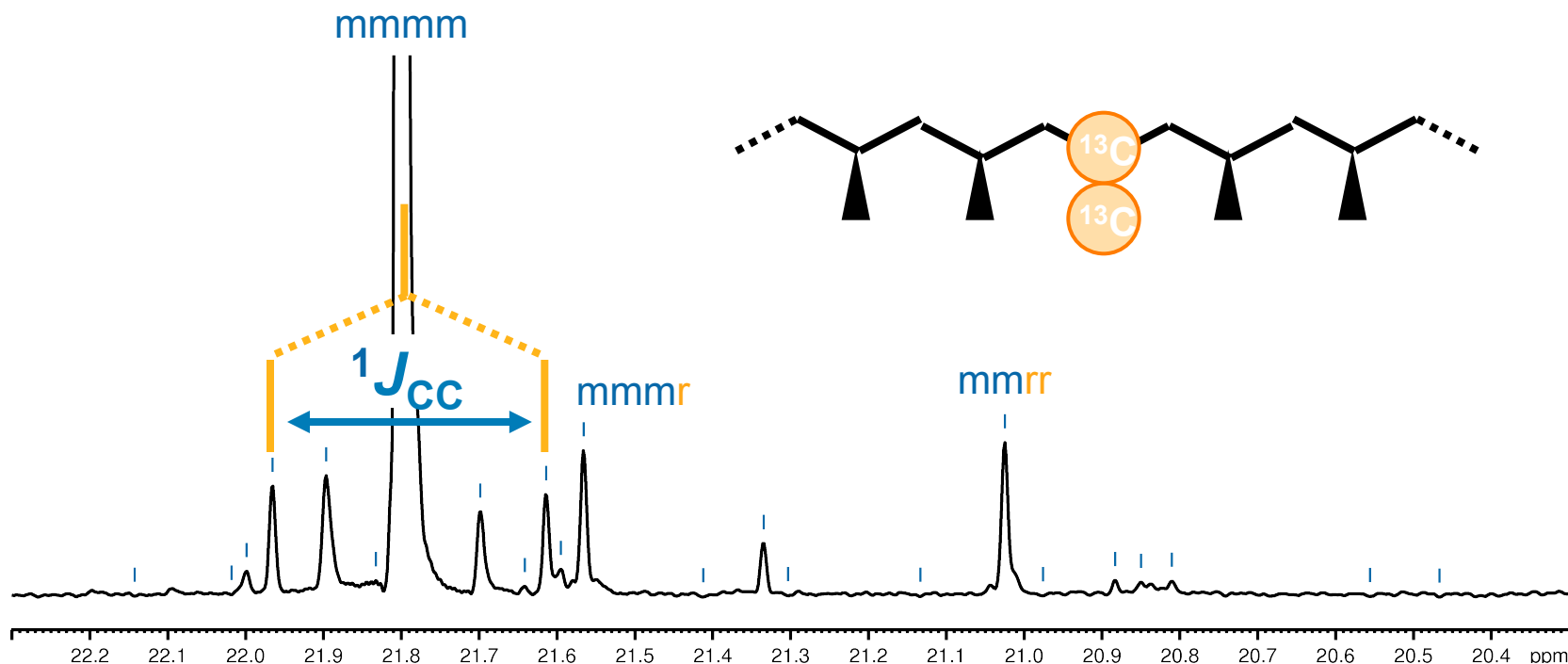
- triad/pentad level via medium field (500 Mhz) but very high sensitivity (200 mg)
- spectral resolution limited by strong dipolar coupling but very fast (1 hour)

# Isotacticity & spinning sidebands (SSBs)



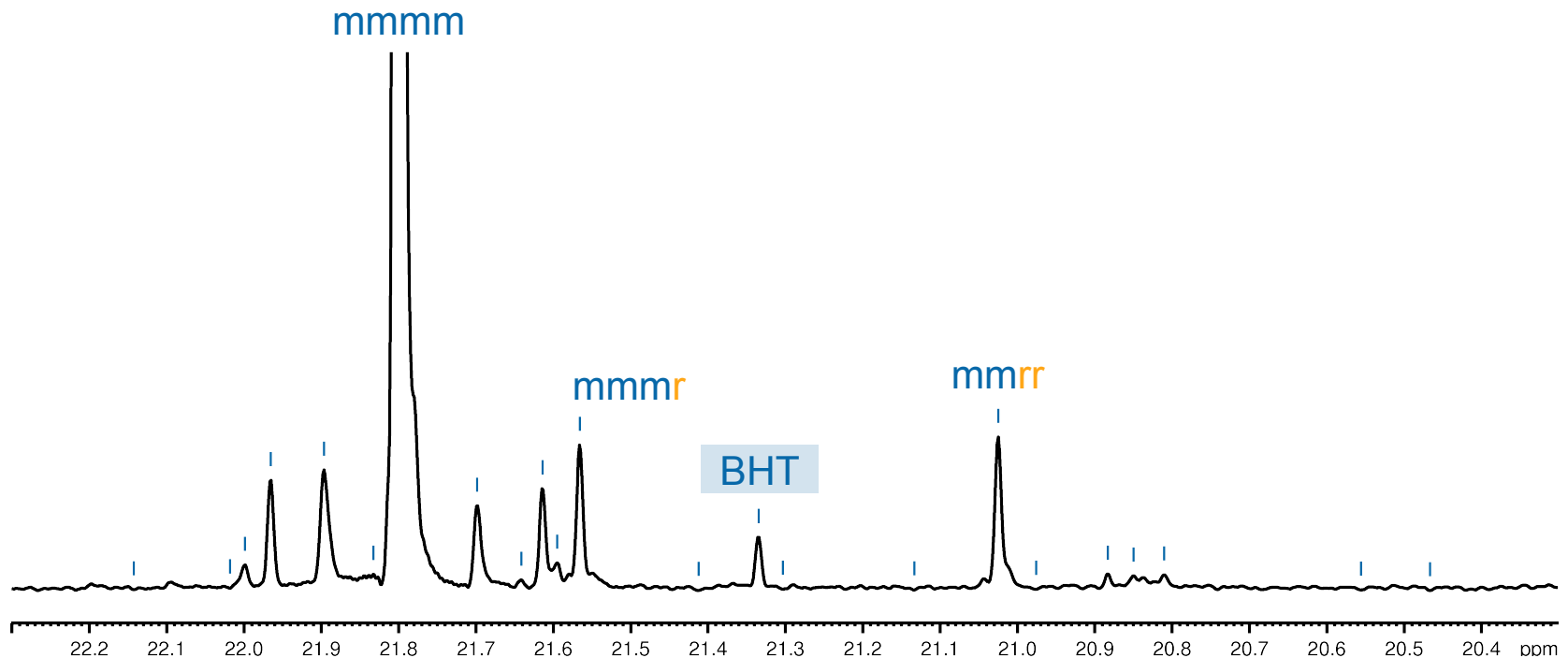
- Artifacts from sample tube rotation (10 Hz)
  - Spinning considerably improves resolution but leads to artifacts
  - Only occur if field is homogeneous in x and y orientation (bad off axis shim)

# Isotacticity & $^{13}\text{C}$ satellites



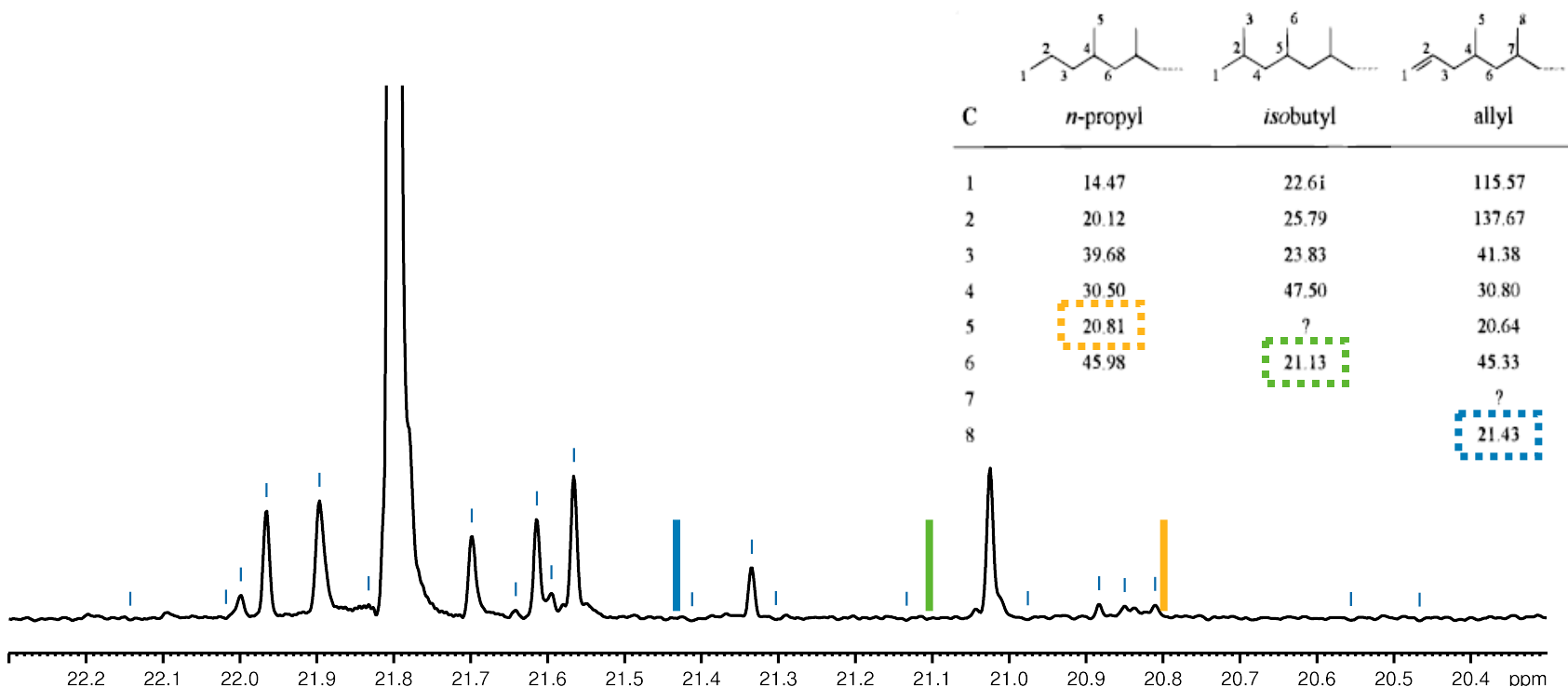
- Doublet from one bond  $^{13}\text{C}$  homonuclear coupling ( $^1J_{\text{CC}} = 35 \text{ Hz}$ )
  - Unlikely (0.01%) but significant for high dynamic range systems (m m m m > 90%)
  - if  $f_{\text{m m m m}} = 99.8\%$  then  $f_{\text{sat}} = 0.5\%$  of  $f_{\text{m m m m}} \sim 0.5\%$  of spectrum

# Isotacticity & stabilisers



- For long duration solution-state measurement stabiliser is needed
  - In addition to stabiliser added during production
  - influence depends on concentration

# Isotacticity & copolymer or end groups

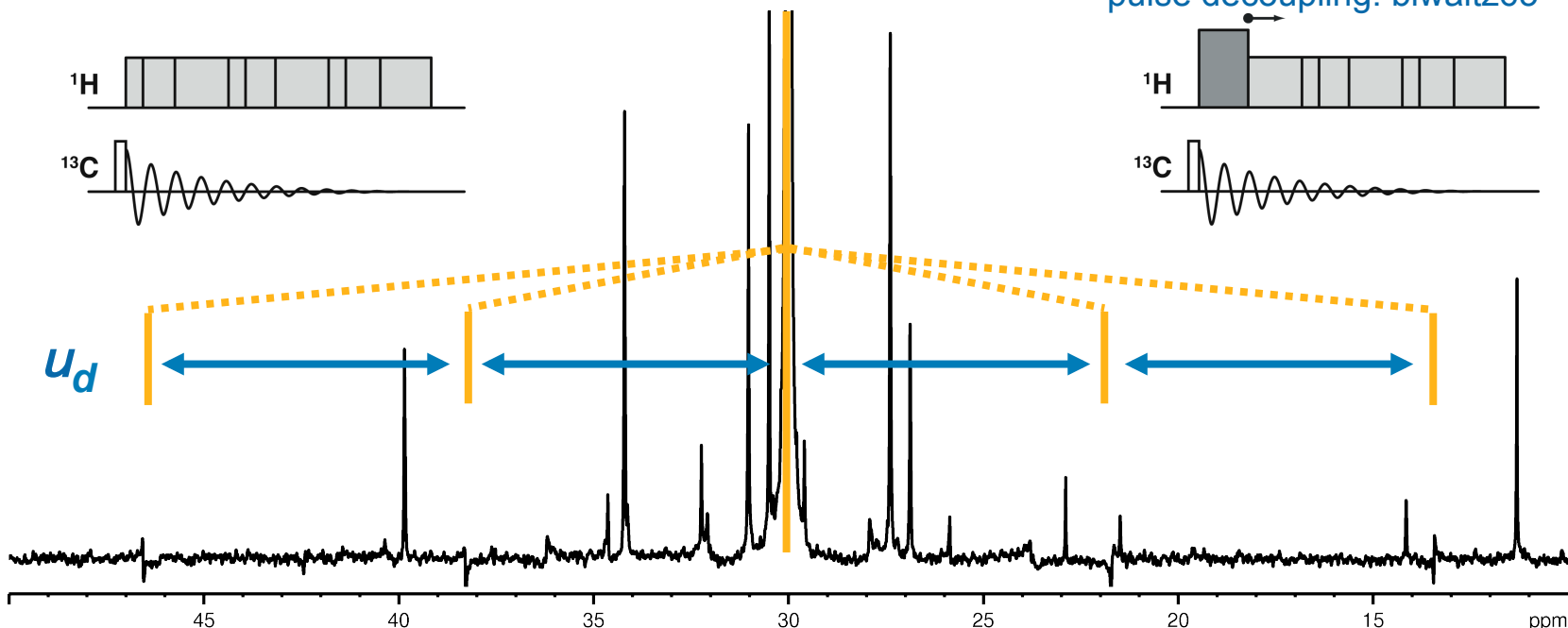


- Some monomers & end-groups lead to peaks in the methyl region
  - not always possible to measure isotacticity/tacticity distribution at pentad level

# Isotacticity & decoupling sidebands

composite pulse decoupling: waltz16

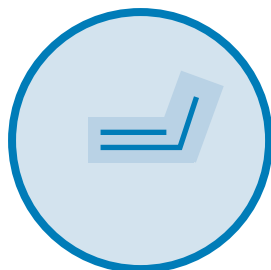
bi-level incremented composite pulse decoupling: biwaltz65



- Composite pulse decoupling leads to artifacts
  - Cycled nature has fixed time period = periodic modulation of FID = sidebands
  - Exacerbated by high dynamic range and strong residual dipolar coupling

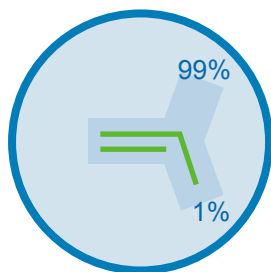
# Stereo & regio errors

regio & stereo  
selective site



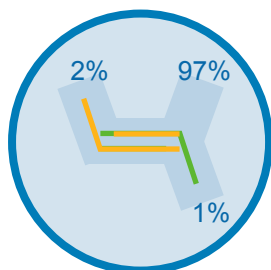
stereo and regio regular chain

stereo error



isotactic with isolated stere defects from stereo error

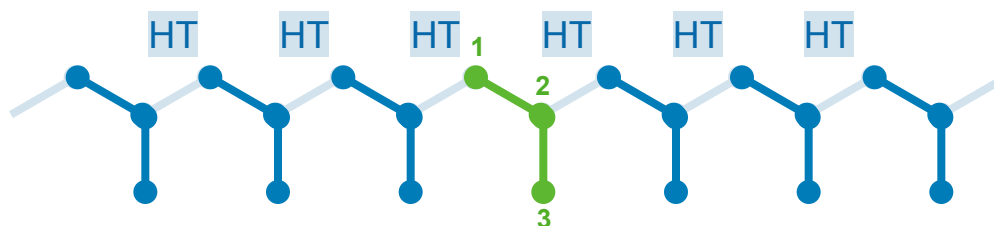
rearrangement  
regio error



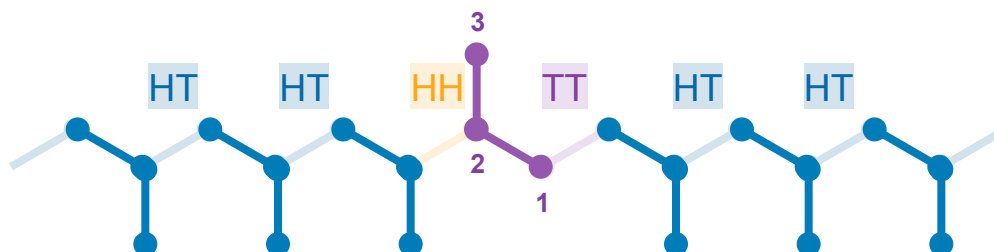
isotactic with isolated stereo & regio  
defects from stereo & regio errors

Chem. Rev. 2000, 100, 1253-1345

# Secondary insertion (2,1)



primary 1,2 only



primary 1,2 &  
secondary 2,1

- Two main modes of propene insertion into a growing chain:
  - primary 1,2 insertion (common) results in **head-to-tail** joints only between 1,2 units
  - secondary 2,1 insertion (rare) results in **head-to-head** & **tail-to-tail** joint with 1,2 units



# Secondary insertion: 2,1e & 1,2t



2,1-erythro



2,1-threo

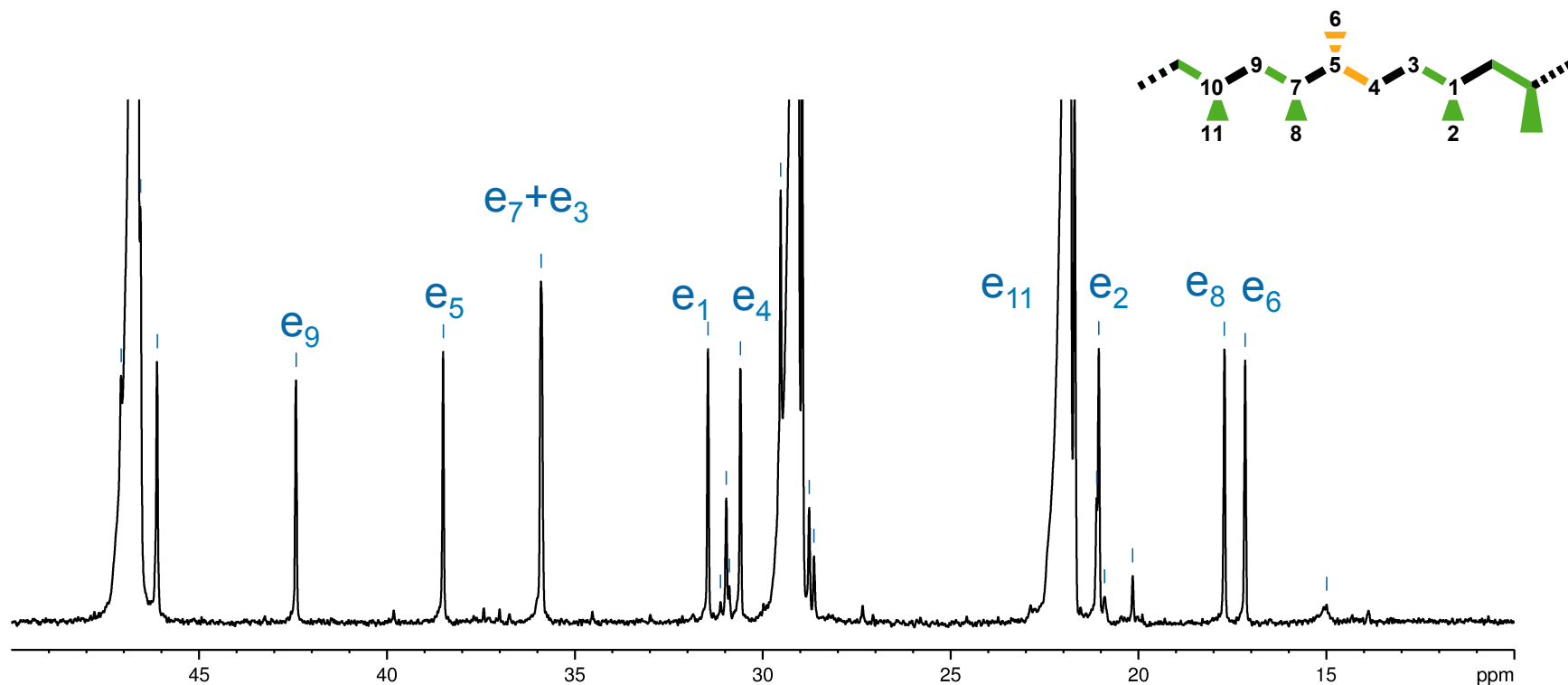
- Stereo chemistry of secondary inserted propene is **opposite** to chain
- two main types depending of stereo chemistry of previous 1,2 propene:
  - 2,1-erythro (2,1e) regio defects have stereo regular previous 1,2 inserted propene
  - 2,1-threo (2,1t) regio defects have stereo irregular previous 1,2 inserted propene

# Secondary insertion: other



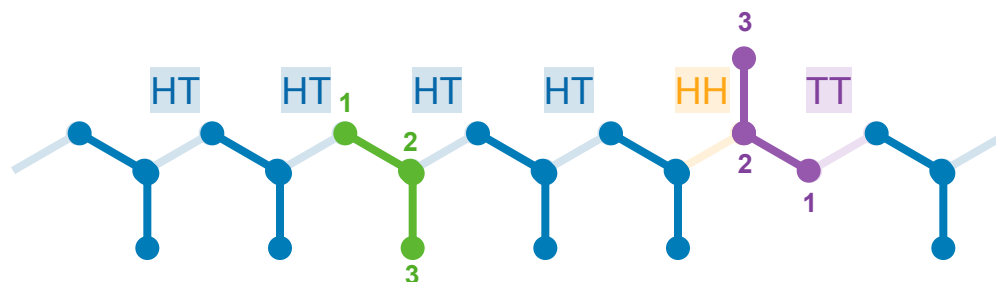
- Stereo chemistry of secondary inserted propene is **same** as chain
- two main types depending of stereo chemistry of previous 1,2 propene:
  - 2,1-erythro (2,1e) regio defects have stereo regular previous 1,2 inserted propene
  - 2,1-threo (2,1t) regio defects have stereo irregular previous 1,2 inserted propene

# Secondary insertion & NMR: 2,1-erythro

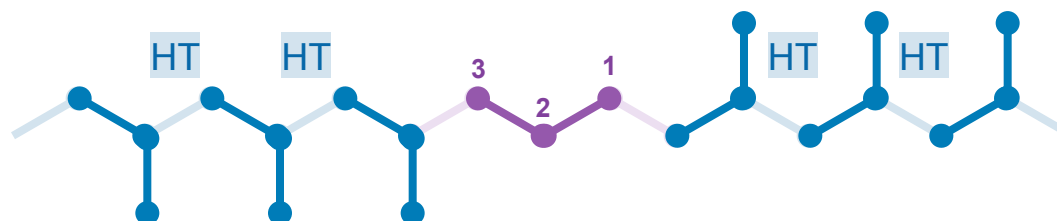


- Regio defects caused by 2,1 insertion lead to characteristic signals

# Secondary insertion & isomerisation (3,1)



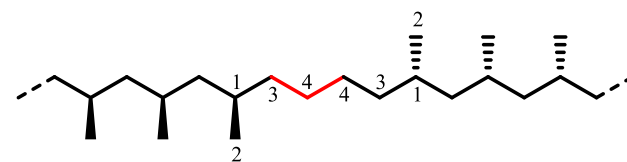
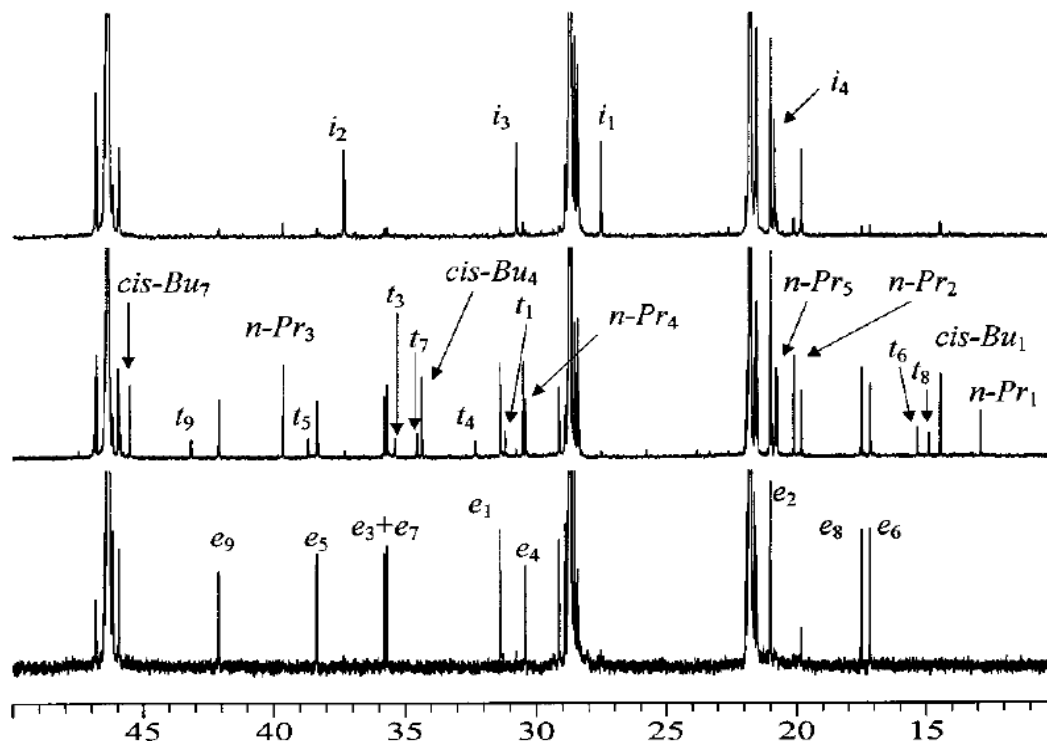
primary 1,2 &  
secondary 2,1



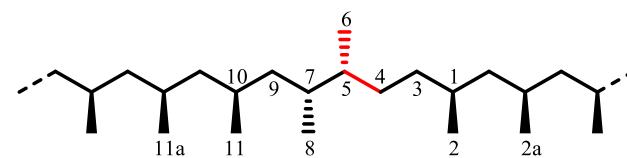
3,1 insertion  
(isomerisation)

- Following 2,1 insertion propene unit can isomerise creating 3,1 units
  - Each mode of insertion has distinctive chemical shifts
  - 1,2 insertion  $(CH_2)_1$ , 2,1  $(CH_2)_2$ , ethylene  $(CH_2)_3$  and 3,1  $(CH_2)_4$

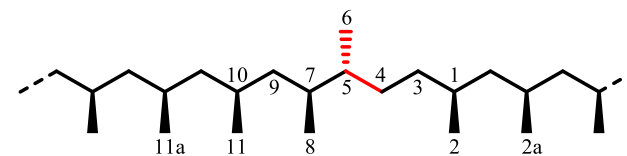
# $^{13}\text{C}$ NMR & regio defects



3,1 isomerisation (i)



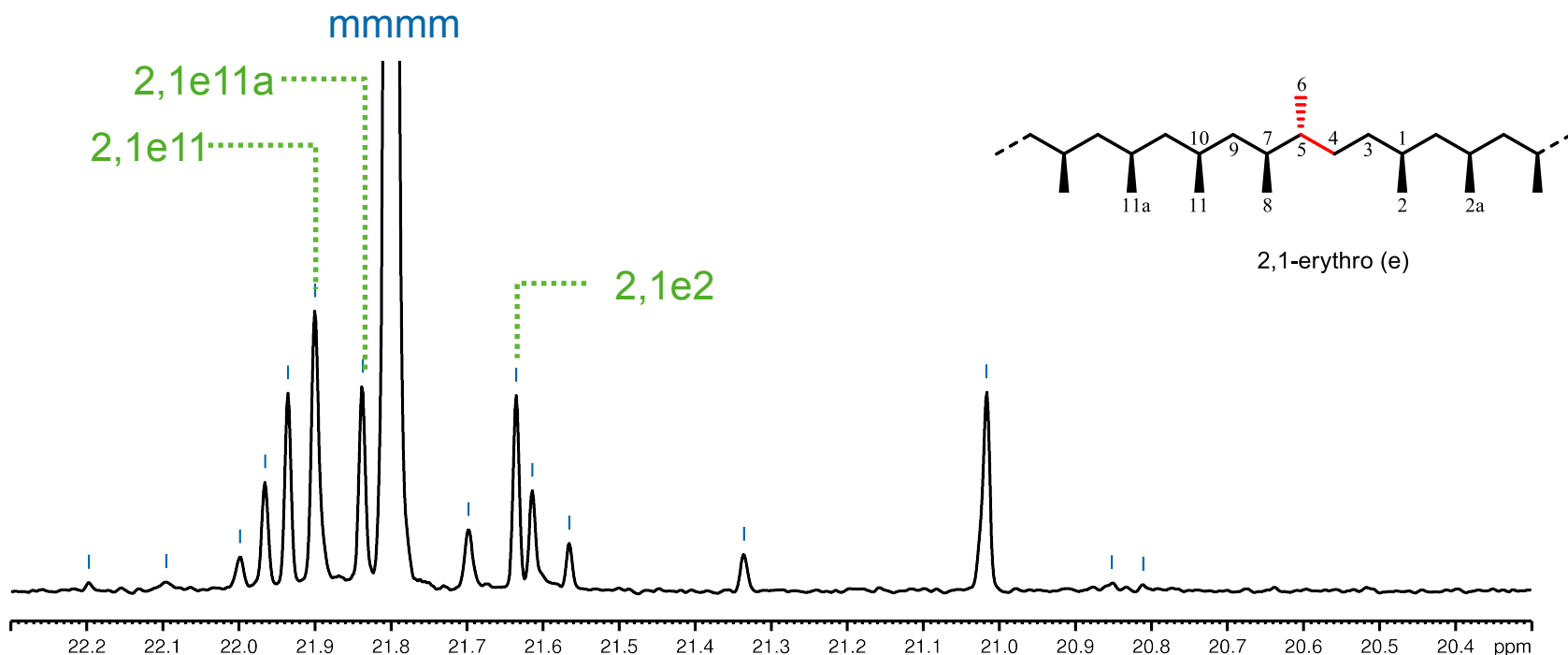
2,1-threo (t)



2,1-erythro (e)

- Regio defects easily identified from characteristic chemical shifts
  - multiple ways to quantify their content
  - Need to be counted when count comonomer content as are propene

# Isotacticity & regio defects

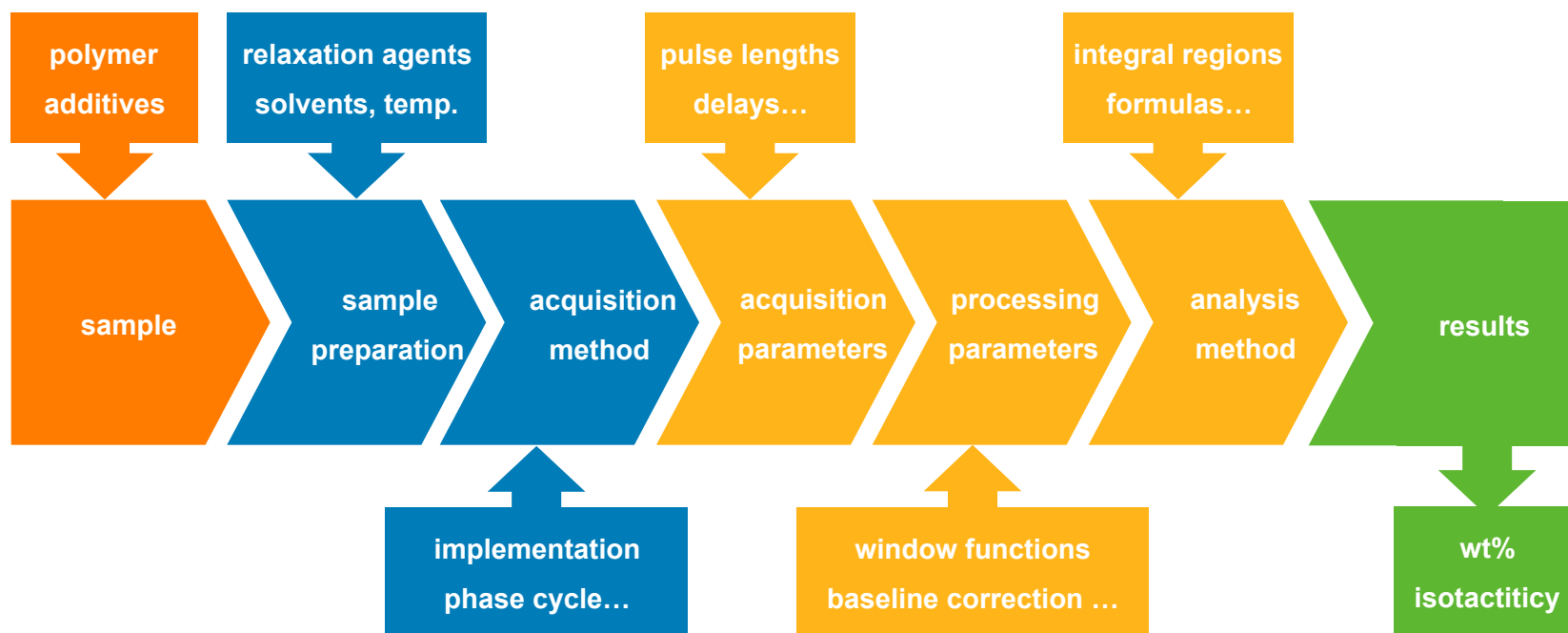


- Some signals from regio defects are in methyl region
  - some sites do not belong to any steric pentad (compensate)
  - some sites do belong to a specific steric sequence (11a = mmmm/mm; 11 = mm)

# Quantitative $^{13}\text{C}$ NMR in practice

- Compromise approaches:
  - shorter than  $5 \times T_1$   $T_{\text{RD}}$ : partial saturation (don't use sites with long  $T_1$ )
  - $< 90^\circ$  pulses: less signal but less saturation too (30-45° optimum related to  $T_1$ )
  - assume all NOEs are equal/full: don't compare different types (no CH<sub>3</sub>:CH ratios)
  - paramagnetic relaxation agents ( $\text{Cr}^{3+}$ ) shortens all  $T_1$  but also  $T_2$  (broad lines)
- Automated data processing and analysis
- From an industrial perspective reproducibility (and throughput) is more important than absolute accuracy
  - can always fall back to classical quantitative approach if differences are seen

# Quantitative NMR Process

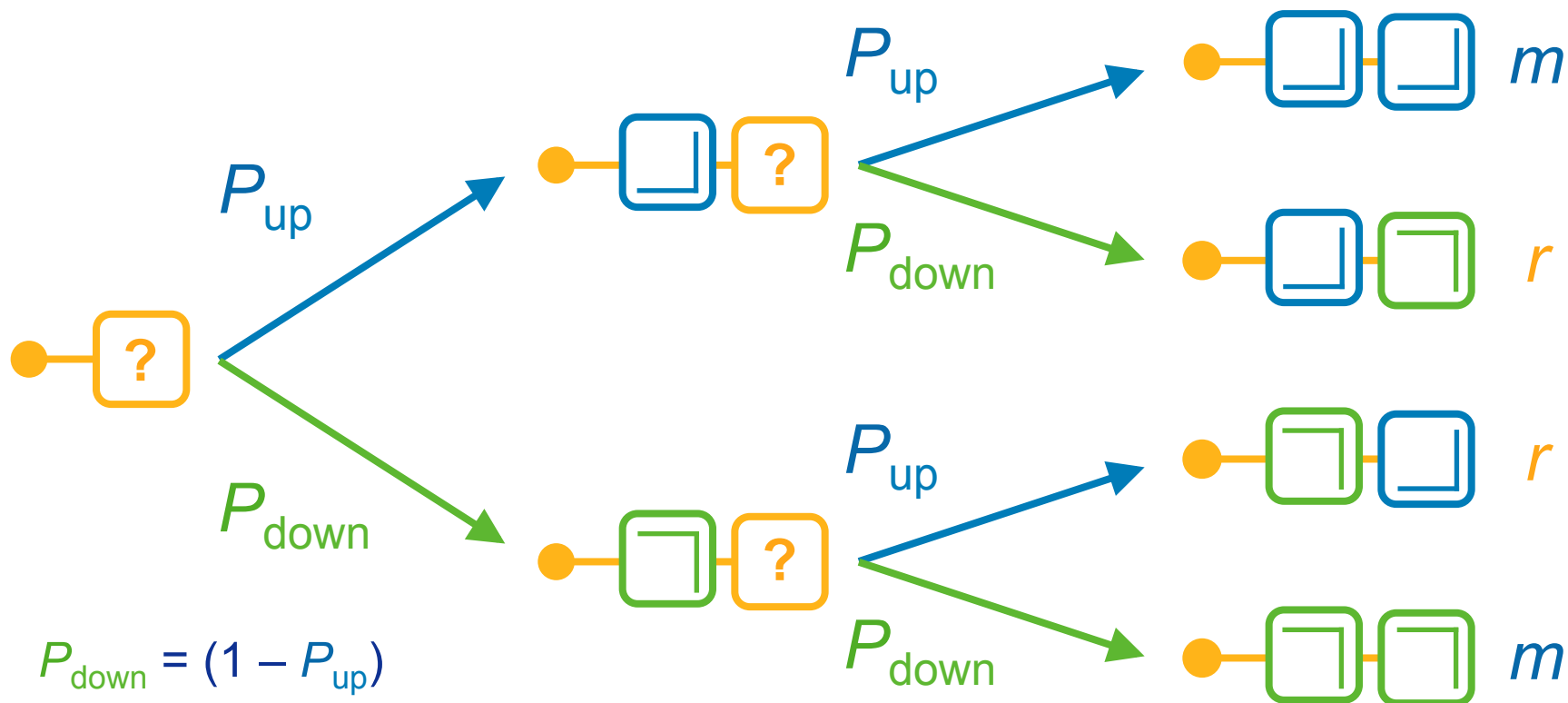




# Example of typical PP results

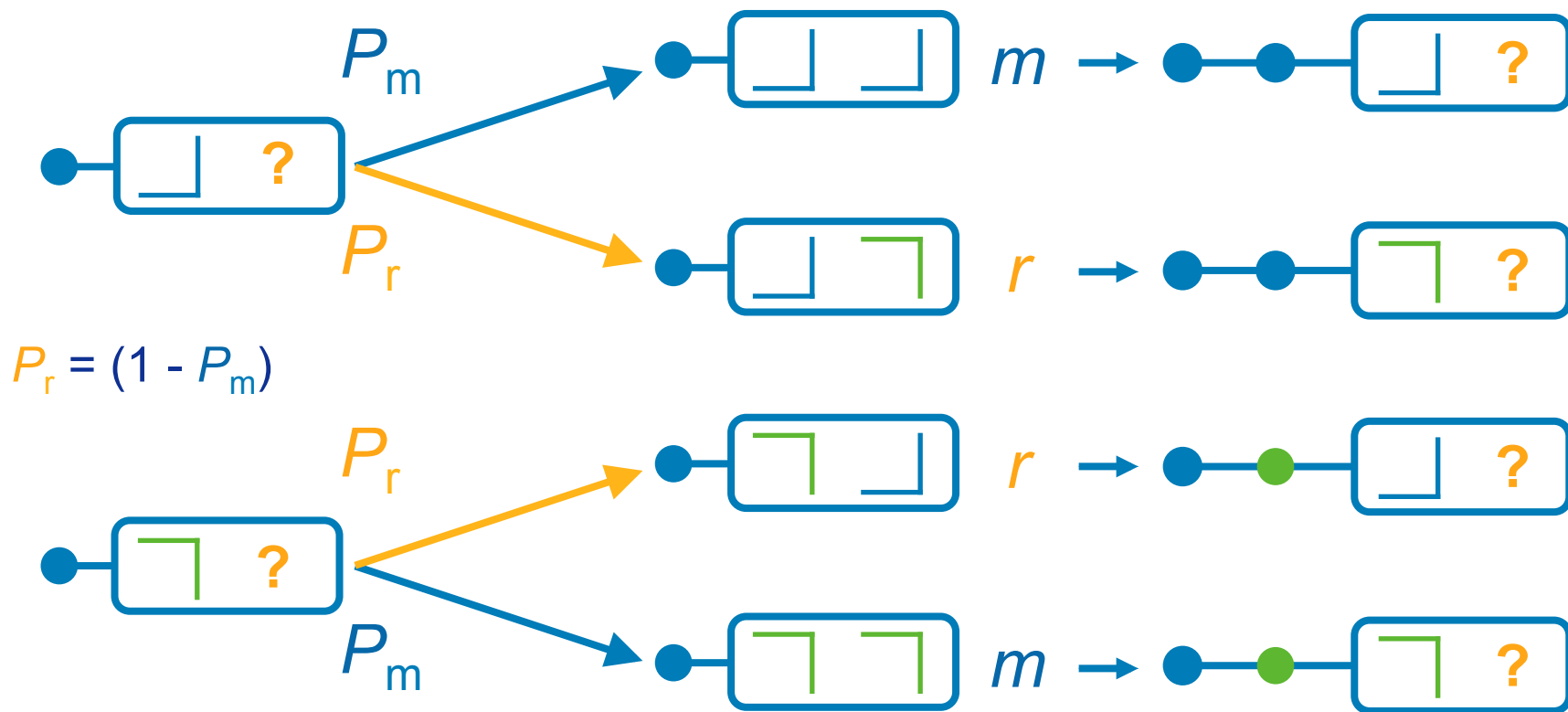
%	mmmm	mmmr	rmmr	mmrr	xmrx	mrmr	rrrr	mrrr	mm	mr	rr	m	r	2,1e	2,1t	3,1i
<b>A</b>	<b>97.93</b>	1.02	0.00	0.60	0.14	0.01	0.00	0.03	<b>98.8</b>	0.8	0.4	<b>99.2</b>	0.8	0.3	0.0	0.1
<b>B</b>	<b>99.42</b>	0.28	0.00	0.13	0.10	0.00	0.00	0.00	<b>99.6</b>	0.3	0.2	<b>99.7</b>	0.3	0.7	0.0	0.0
<b>C</b>	<b>99.68</b>	0.05	0.00	0.11	0.14	0.00	0.00	0.00	<b>99.7</b>	0.2	0.1	<b>99.8</b>	0.2	1.7	0.0	0.0
<b>D</b>	<b>98.60</b>	0.54	0.00	0.33	0.25	0.04	0.00	0.05	<b>99.0</b>	0.6	0.4	<b>99.3</b>	0.7	1.0	0.0	0.0
<b>E</b>	<b>98.87</b>	0.49	0.00	0.27	0.20	0.02	0.01	0.02	<b>99.4</b>	0.5	0.2	<b>99.5</b>	0.5	0.6	0.0	0.0
<b>F</b>	<b>98.63</b>	0.75	0.00	0.33	0.12	0.02	0.00	0.02	<b>99.4</b>	0.5	0.2	<b>99.5</b>	0.5	0.3	0.0	0.1
<b>G</b>	<b>99.03</b>	0.39	0.00	0.27	0.14	0.00	0.00	0.01	<b>99.4</b>	0.4	0.2	<b>99.6</b>	0.4	0.9	0.0	0.0

# Enantiomorphic Site control (ES)



- Cumulative probability of meso dyad formation:  $P_m = P_{up}^2 + (1 - P_{up})^2$ 
  - can calculate probability of an arbitrary stereo sequence i.e.  $P_{mmmm}$

# Chain-end control (CE)



- Direct probability of meso dyad formation ( $P_m$ )
  - can calculate probability of an arbitrary stereo sequence i.e.  $P_{mm} = P_m^2$  &  $P_{mmmm} = P_m^4$

# Stochastic Modelling of Polymerisation

## ■ Principle

- define model with key probabilities as variables
- construct cumulative probability of each sequences
- predict distribution based on key probabilities

## ■ fit observed distribution to predicted distribution

- select model and check quality of fit (sum-of-least-squares,  $\chi^2$ )
- predict ideal distribution based on fitted probabilities
- back prediction: fit pentads, derive probability, predict pentads & triads
- forward prediction: fit triads, derive probability, predict triads & pentads
- Monte-carlo simulation of example chain which follows same statistics

# Polymer chain statistics

**Table 1** Reaction Probability Expressions in the Bernoullian (B), First-Order Markovian (M1), Second-Order Markovian (M2), and Enantiomorphic-Site (E) Models

Sequence	Tacticity <sup>a</sup>	B	M1	M2 <sup>b</sup>	E <sup>c</sup>
A	m	$P_a$	$P_{ba}$	$(\bar{\alpha} + \gamma) \delta$	$1 - 2t$
B	r	$P_b$	$P_{ab}$	$(\bar{\beta} + \delta) \bar{\alpha}$	$2t$
AA	mm	$P_a^2$	$P_{ba}P_{aa}$	$\gamma\delta$	$1 - 3t$
AB	mr	$2P_aP_b$	$2P_{ba}P_{ab}$	$2\bar{\alpha}\delta$	$2t$
BB	rr	$P_b^2$	$P_{ab}P_{bb}$	$\bar{\alpha}\bar{\beta}$	$t$
AAA	mmm	$P_a^3$	$P_{ba}P_{aa}^2$	$\alpha\gamma\delta$	$1 - 4t + 2t^2$
AAB	mmr	$2P_a^2P_b$	$2P_{ba}P_{aa}P_{ab}$	$2\bar{\alpha}\gamma\delta$	$2t - 4t^2$
BAB	rmr	$P_aP_b^2$	$P_{ab}^2P_{ba}$	$\bar{\alpha}\gamma\delta$	$2t^2$
ABA	mrn	$P_a^2P_b$	$P_{ab}P_{ba}^2$	$\bar{\alpha}\beta\delta$	$2t^2$
BBA	rrm	$2P_aP_b^2$	$2P_{ab}P_{bb}P_{ba}$	$2\bar{\alpha}\bar{\beta}\delta$	$2t - 9t^2$
BBB	rrr	$P_b^3$	$P_{ab}P_{bb}^2$	$\bar{\alpha}\bar{\beta}\bar{\delta}$	$2t^2$
AAAA	mmmm	$P_a^4$	$P_{ba}P_{aa}^3$	$\alpha^2\gamma\delta$	$1 - 5t + 5t^2$
AAAB	mmmr	$2P_a^3P_b$	$2P_{ba}P_{aa}^2P_{ab}$	$2\alpha\bar{\alpha}\gamma\delta$	$2t - 6t^2$
BAAB	rmmr	$P_a^2P_b^2$	$P_{ab}^2P_{ba}P_{aa}$	$\bar{\alpha}^2\gamma\delta$	$t^2$
AABB	mmrr	$2P_a^2P_b^2$	$2P_{ba}P_{aa}P_{ab}P_{bb}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$	$2t - 6t^2$
AABA	mmrm	$2P_a^3P_b$	$2P_{ba}^2P_{aa}P_{ab}$	$2\bar{\alpha}\beta\gamma\delta$	$2t^2$
BABB	rmrr	$2P_aP_b^3$	$2P_{ab}^2P_{ba}P_{bb}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$	$2t^2$
BABA	rmrm	$2P_a^2P_b^2$	$2P_{ab}^2P_{ba}^2$	$2\bar{\alpha}\beta\bar{\gamma}\delta$	$2t^2$
ABBA	mrrm	$P_a^2P_b^2$	$P_{ba}^2P_{ab}P_{bb}$	$\bar{\alpha}\bar{\beta}\delta^2$	$t - 3t^2$
BBBA	rrrm	$2P_aP_b^3$	$2P_{ab}P_{bb}^2P_{ba}$	$2\bar{\alpha}\bar{\beta}\delta\bar{\delta}$	$2t^2$
BBBB	rrrr	$P_b^4$	$P_{ab}P_{bb}^3$	$\bar{\alpha}\bar{\beta}\bar{\delta}^2$	$t^2$
Sum		$(P_a + P_b)$	$(P_{ba} + P_{ab})$	$(\bar{\alpha}\bar{\beta} + 2\bar{\alpha}\delta + \gamma\delta)$	1.0

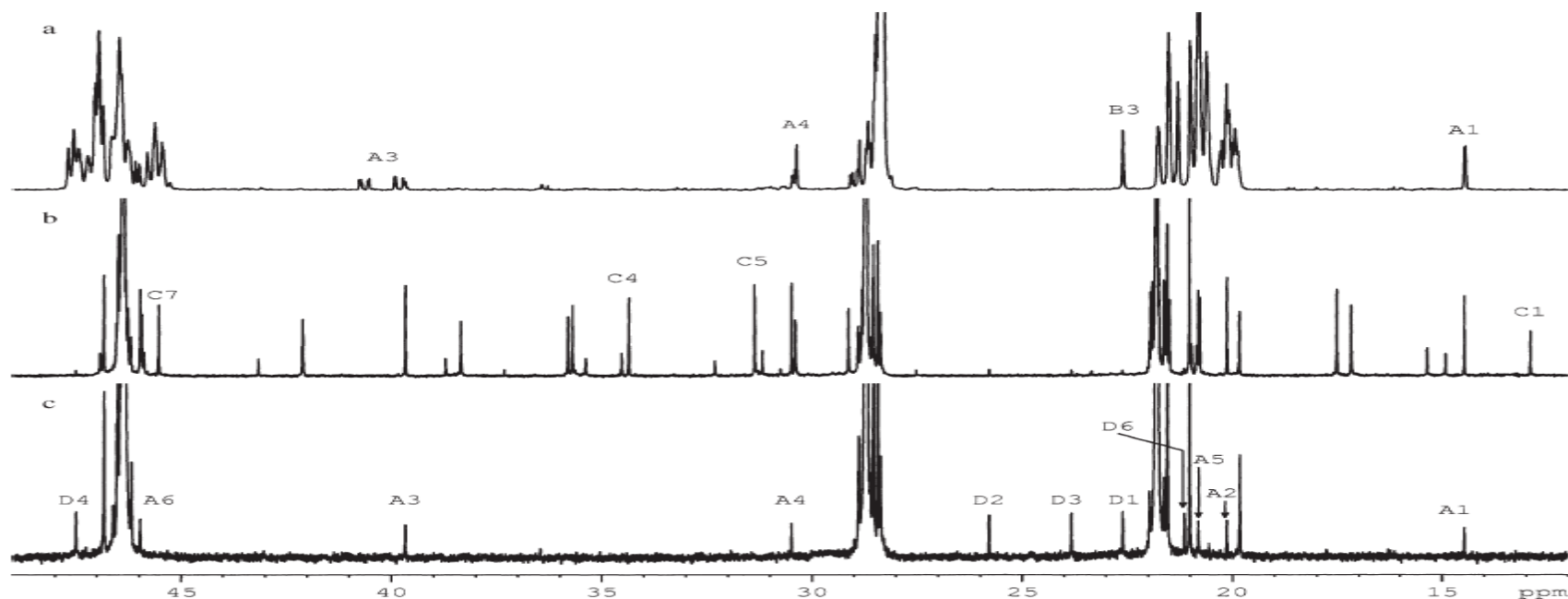
<sup>a</sup>For tacticity, the substitution (A  $\rightarrow$  m, and B  $\rightarrow$  r) should be made in the expressions for the B, M1 and M2 models.

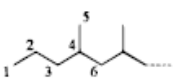
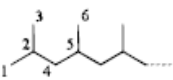
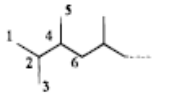
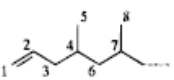
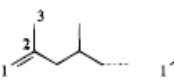
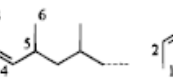
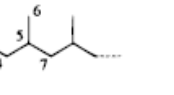
<sup>b</sup> $\alpha = P_{aaa}$ ,  $\beta = P_{aba}$ ,  $\gamma = P_{baa}$ ,  $\delta = P_{bba}$ .

<sup>c</sup> $t = P_1(1 - P_1)$ .

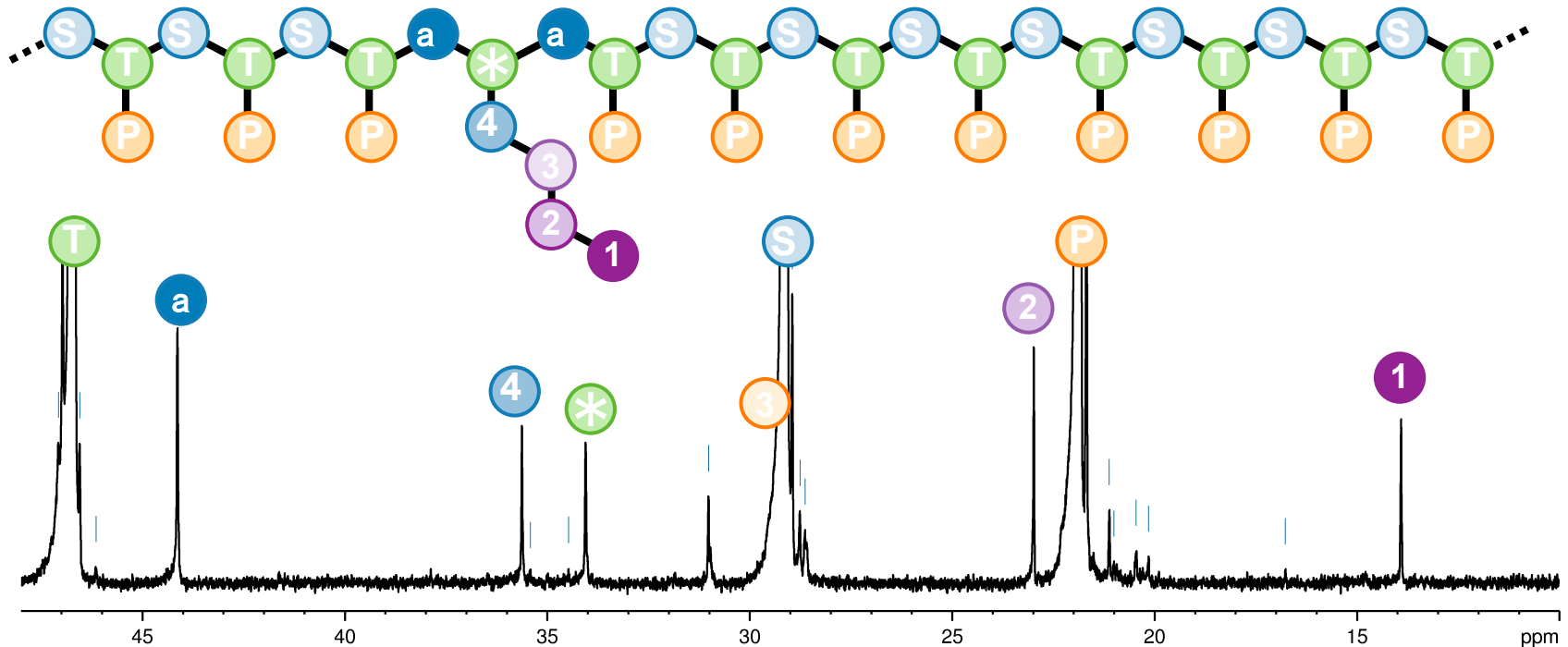
Source: Enciclop. Magn. Res., Polymerisation and statistical models, H. N. Cheng

# Polypropylene end-groups



							
C	A <i>n</i> -propyl	D <i>isobutyl</i>	2,3-dimethyl-butyl	B allyl	vinylidene	<i>isobutenyl</i>	C <i>cis</i> -2-butenyl
1	14.47	22.61	17.76	115.57	111.38	18.01	12.91
2	20.12	25.79	31.93	137.67	144.87	129.23	124.48
3	39.68	23.83	20.56	41.38	22.6	25.7	129.66
4	30.50	47.50	36.47	30.80		132.30	34.37
5	20.81	?	16.30	20.64		30.61	31.37
6	45.98	21.13	43.05	45.33			?
7				?			45.54
8				21.43			

# Quantification of comonomer content: PP



- Integrate quantitative  $^{13}\text{C}$  NMR spectrum
- overdefined problem with multiple solutions
  - selection of integrals not trivial
  - risk of lowering accuracy by averaging in errors!

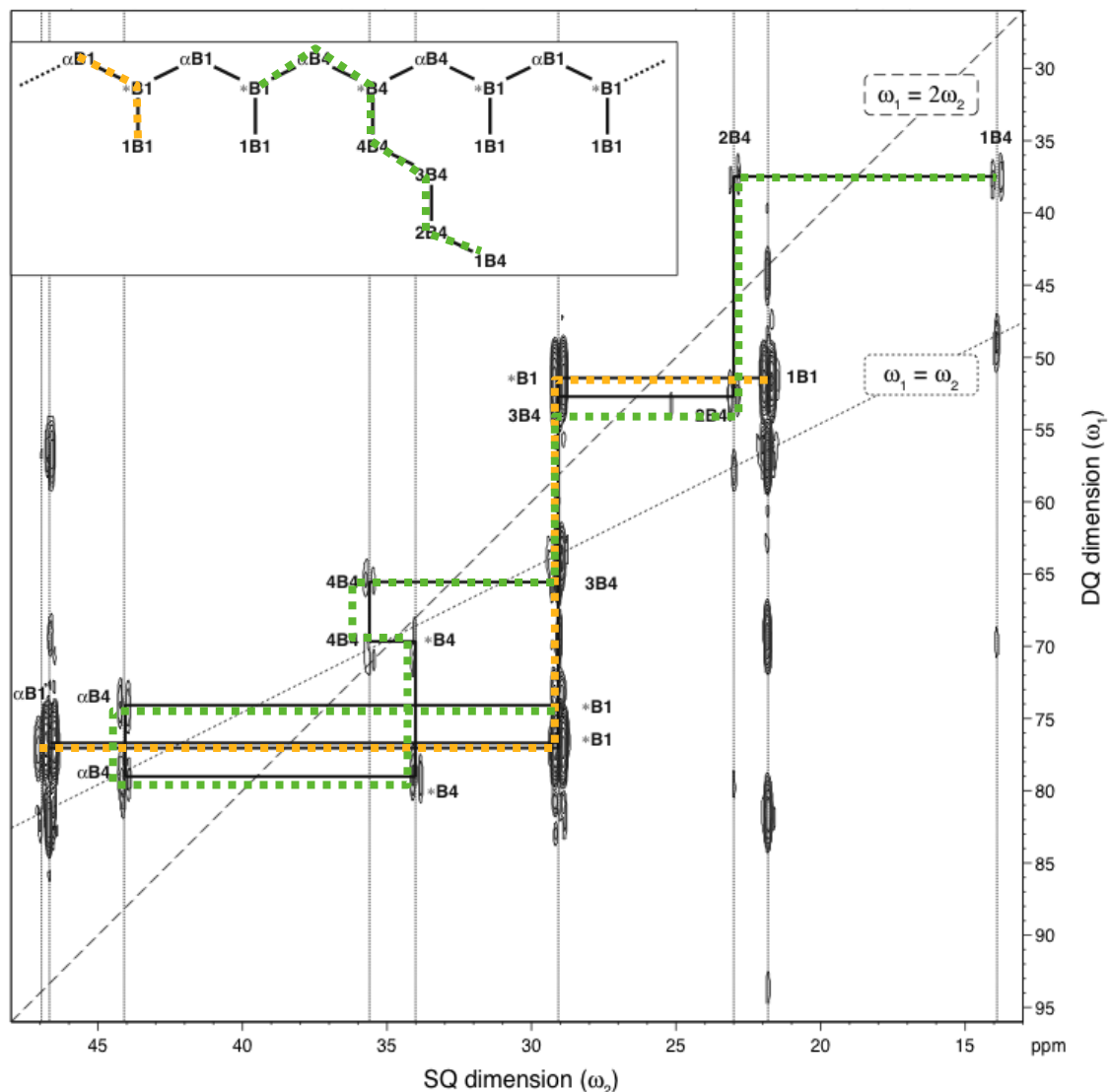
1	2	4	*	a	
1 / P	2 / P	4 / P	* / P	a / P	T
1 / S	2 / S	4 / S	* / S	a / S	S
1 / T	2 / T	4 / T	* / T	a / T	P

# $^1J_{CC}$ -coupling mediated methods

PP-co-hexene

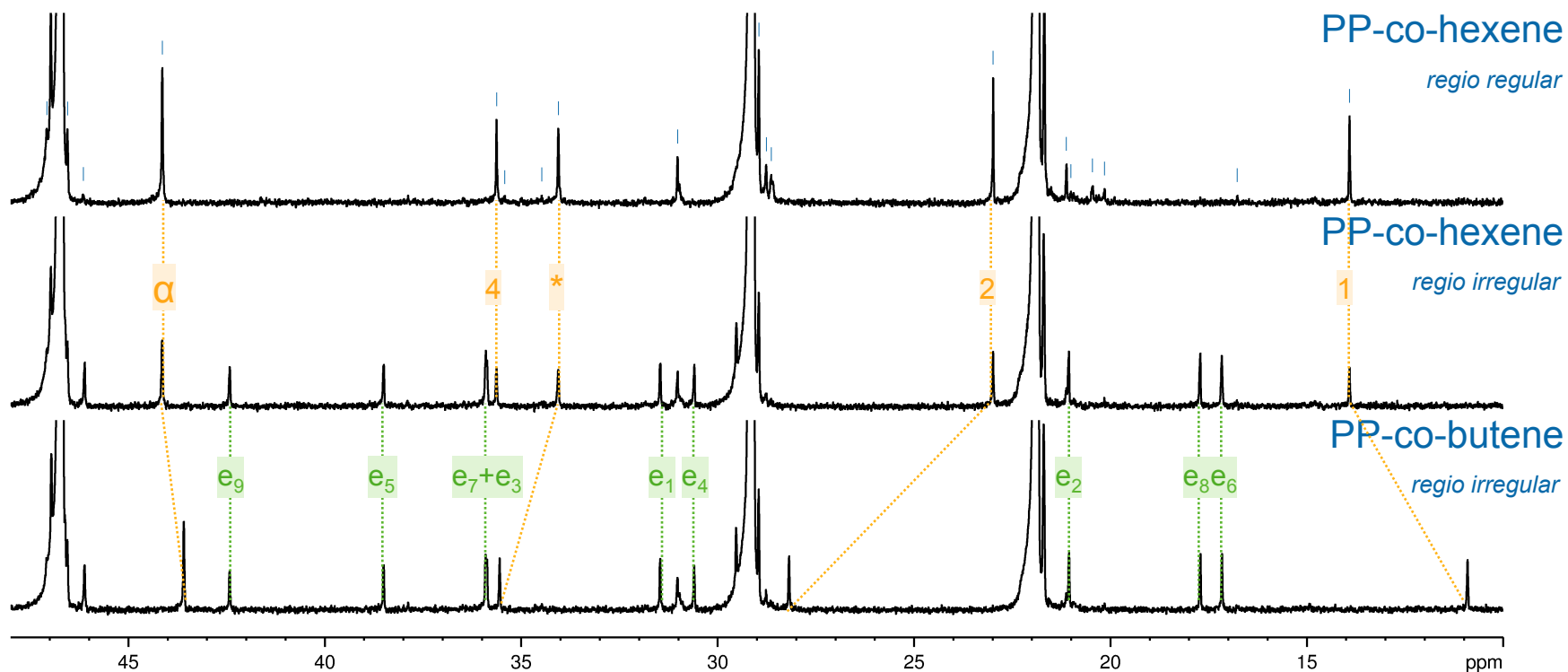
$^{13}C$  2D INADEQUATE

- useful when assignment differs between melt and solution-state





# Polypropylene-co- $\alpha$ -olefins

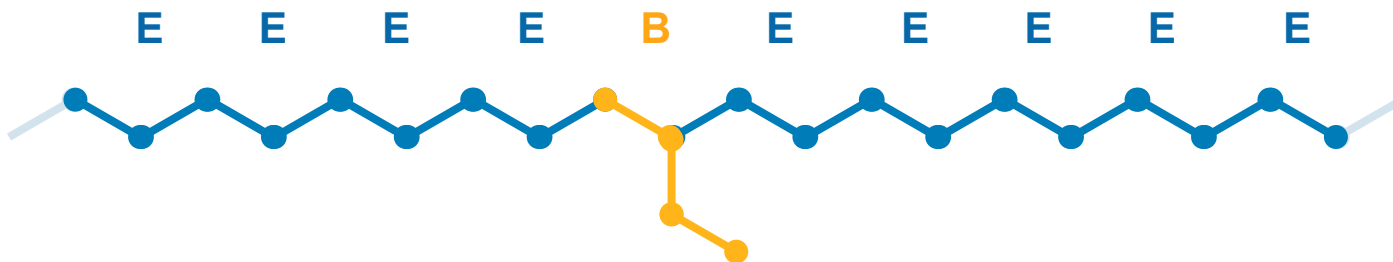


- identification & quantification
  - comonomer content, tacticity and regio irregularity

# Units for branch quantification PP

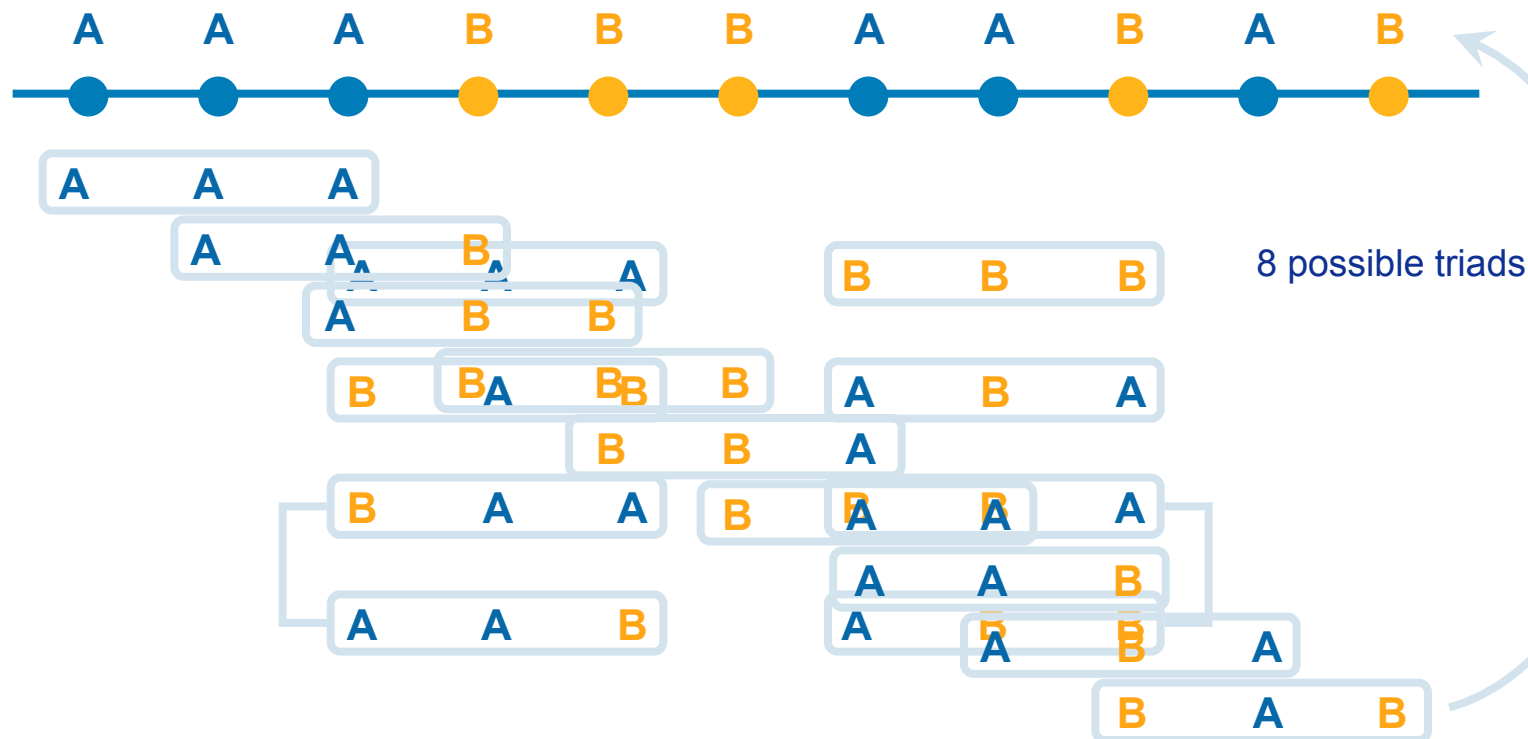
- degree of branching measured by NMR via:
  - representative integral of branch site or sites
  - bulk site (CH or CH<sub>3</sub> site)
- Regio-regular copolymers:
  - mole percent comonomer (mol%)
  - weight percent comonomer (wt%)
- Regio-irregular copolymers
  - mole percent of mis-inserted propene with respect to all propene (1,2 + 2,1 + 3,1)
  - mole percent comonomer (mol%) with respect to all propene
  - weight percent comonomer (mol%) with respect to all propene

# Units for branch quantification



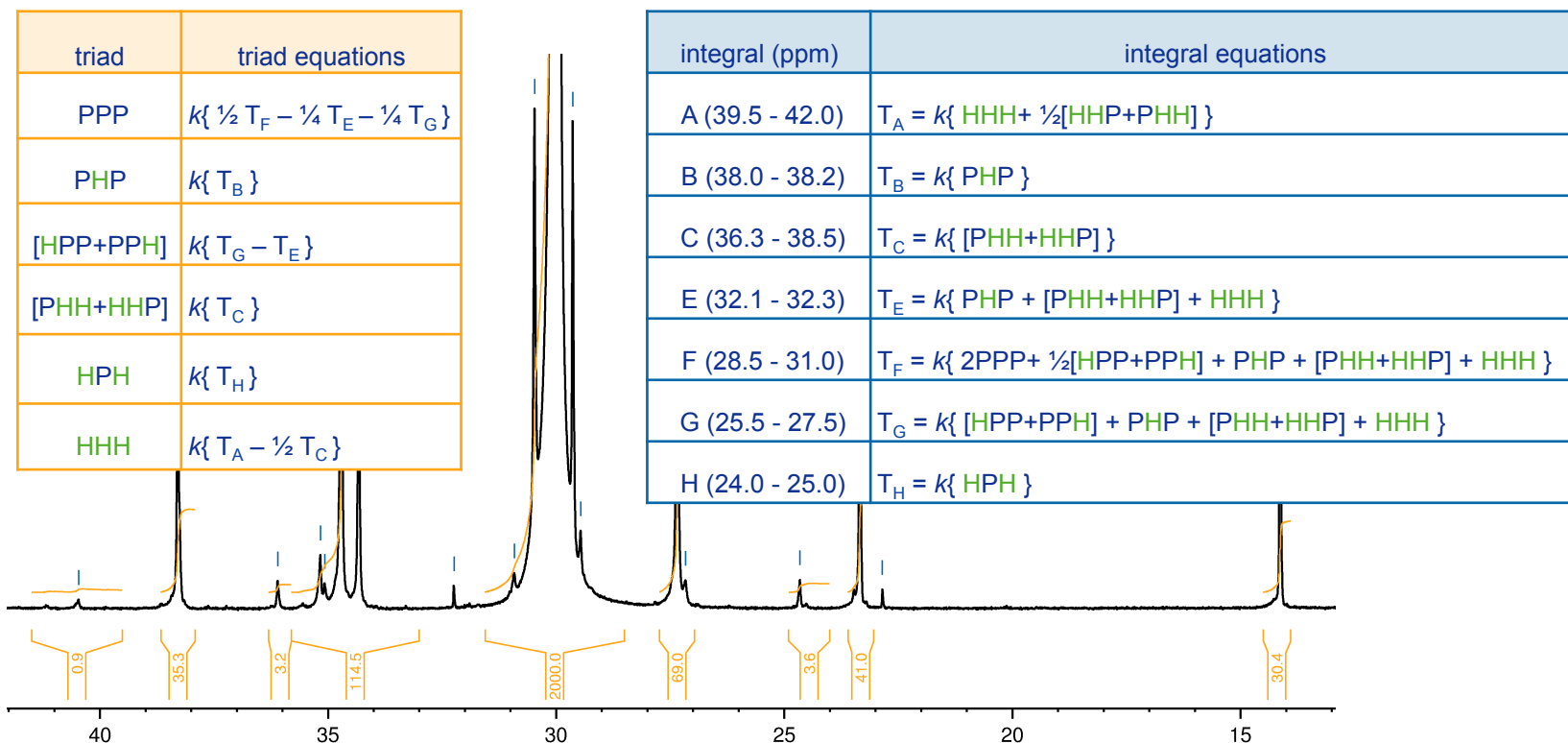
■ branches per backbone carbons:	$1 / 20$	$= 50$	Br/1000C <sub>bb</sub>
■ comonomer content in mole percent:	$1 / (9 + 1)$	$= 10$	mol%
■ comonomer content in weight percent:	$(1 \times 56) / ((9 \times 28) + (1 \times 56))$	$= 18$	wt%
■ branches per total carbons:	$1 / ((9 \times 2) + (1 \times 4))$	$= 45$	Br/1000C

# Comonomer sequences



- Each n-ad has characteristic chemical shift
- Quantification of distribution provides insight into macrostructure

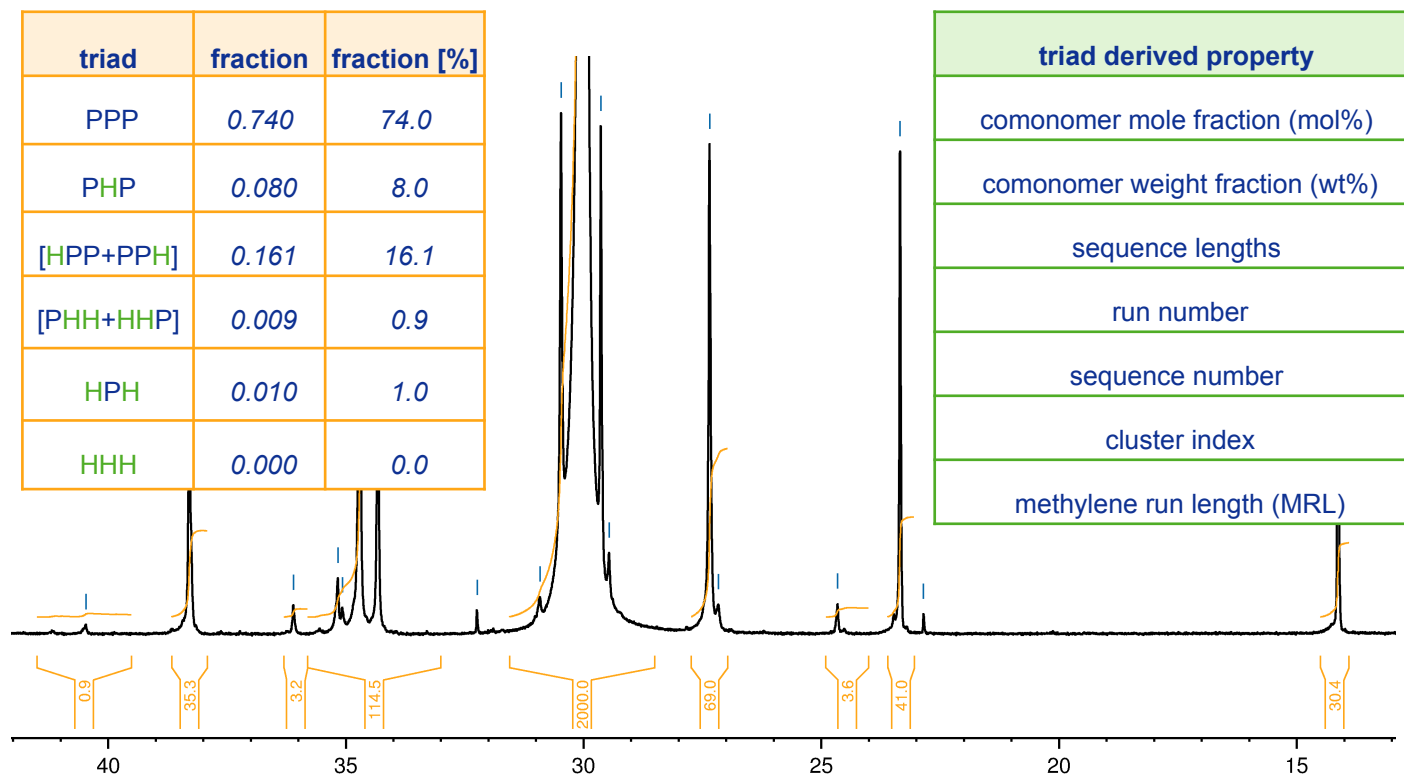
# Comonomer sequence distribution: I



- Comonomer sequence distribution quantified at the triad level
  - integral regions assigned to specific sequences
  - set of simultaneous equations solved for a given comonomer sequence

illustrative example only regions/spectrum taken from PE-co-octene

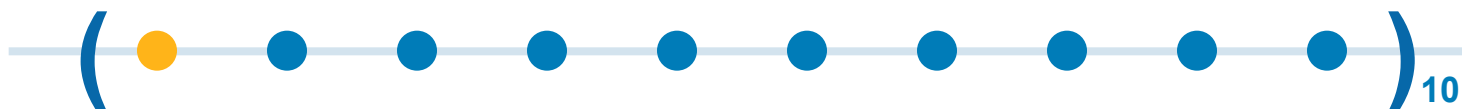
# Comonomer sequence distribution: II



- Comonomer sequence distribution quantified at the triad level
  - triad distribution expressed as fraction or percent (low level statistical view)
  - derived properties calculated from triad distribution (more useful overview)

illustrative example only regions/spectrum taken from PE-co-octene

# Comonomer sequence derived properties



- parameters derived from sequence distribution (triads)
  - commoner content (sum of all A centered triads) [10%, 90%]
  - average sequence length (number of comonomers in a row) [1, 9]
  - sequence number (number of sequences per 100 monomers) [10,10]
  - run number (number of switches between sequences per 100 monomers) [20]
  - cluster index (closeness to ideal statistical distribution) [0]  
10 = ideal random, >10 clustered, 0 = dispersed and isolated

# Polyethylene-co- $\alpha$ -olefin microstructure

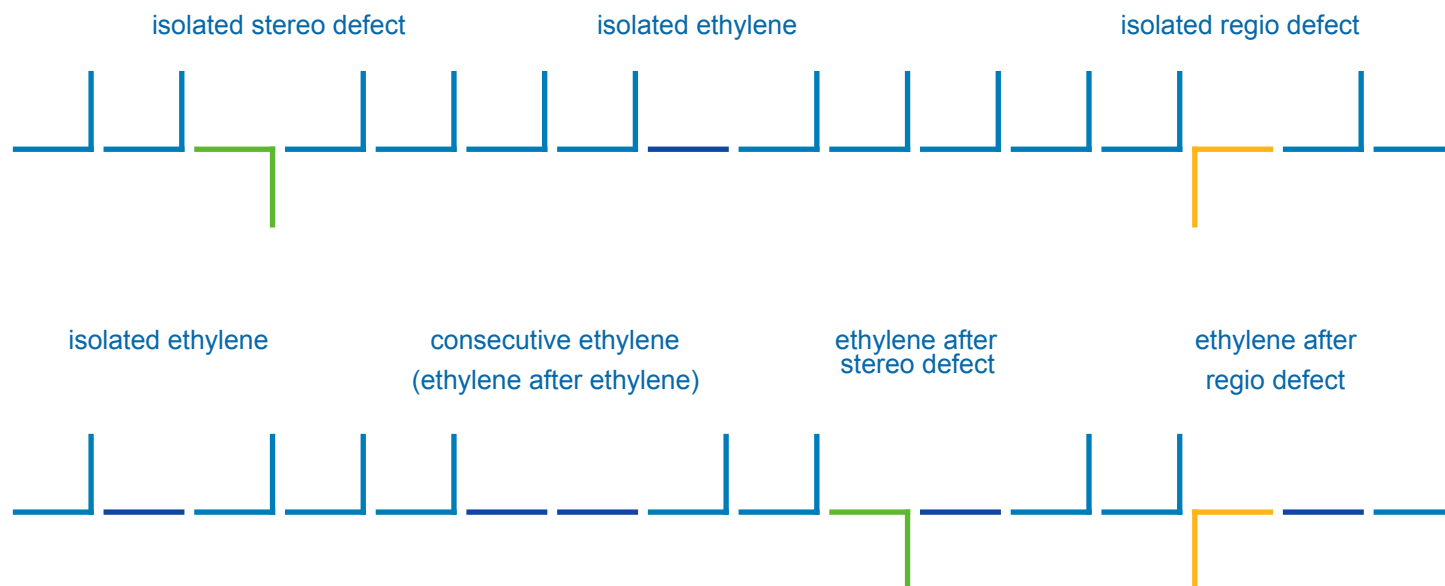
triads	result
EEE	90.11 %
EEH+HEE	6.09 %
HEH	0.91 %
EHE	3.44 %
EHH+HHE	0.17 %
HHH	0.00 %

derived properties	result
C6 mol% [H]	3.61
sequence length	1.02
run number	7.05
sequence number	3.52
cluster index	7

- triad distribution calculated for given copolymer
  - derived properties easier to interpret calculated from triad distribution

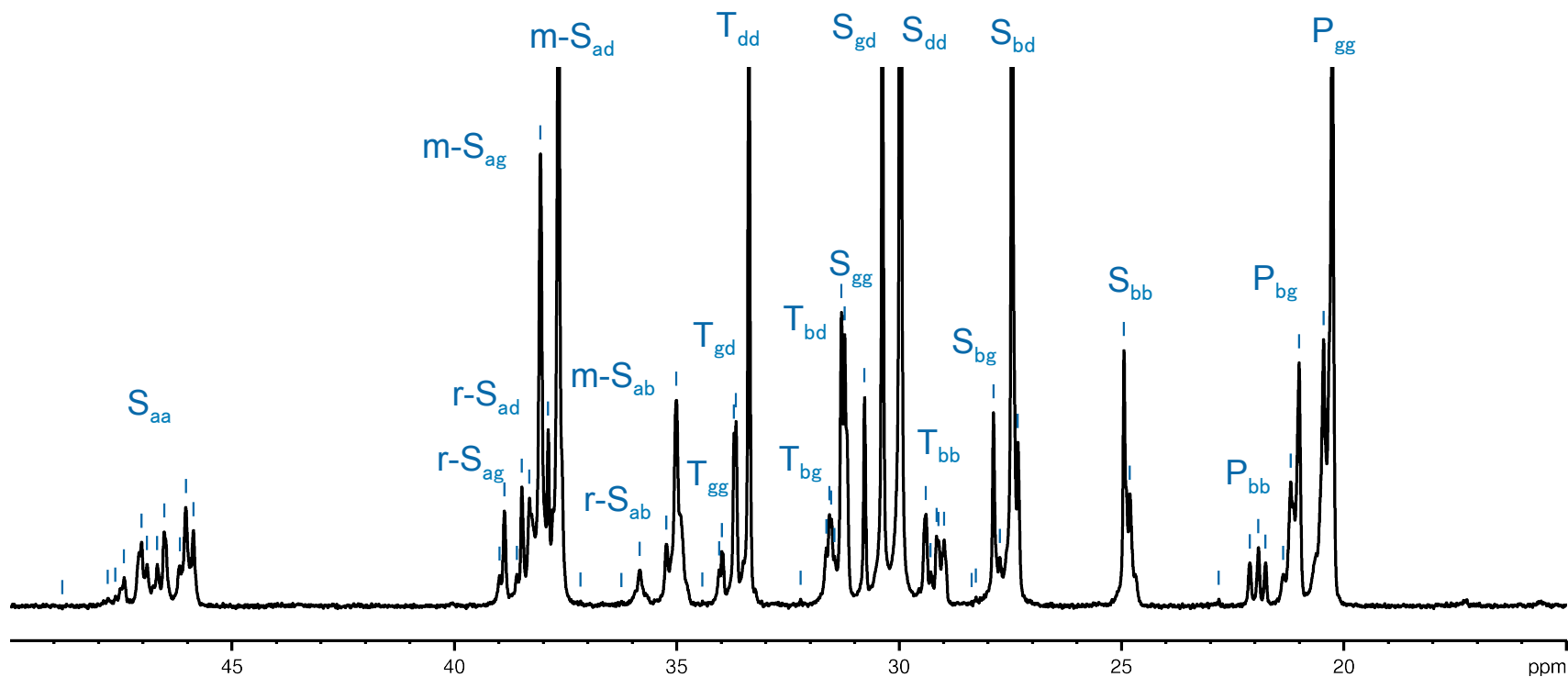


# Ethylene-propylene copolymers

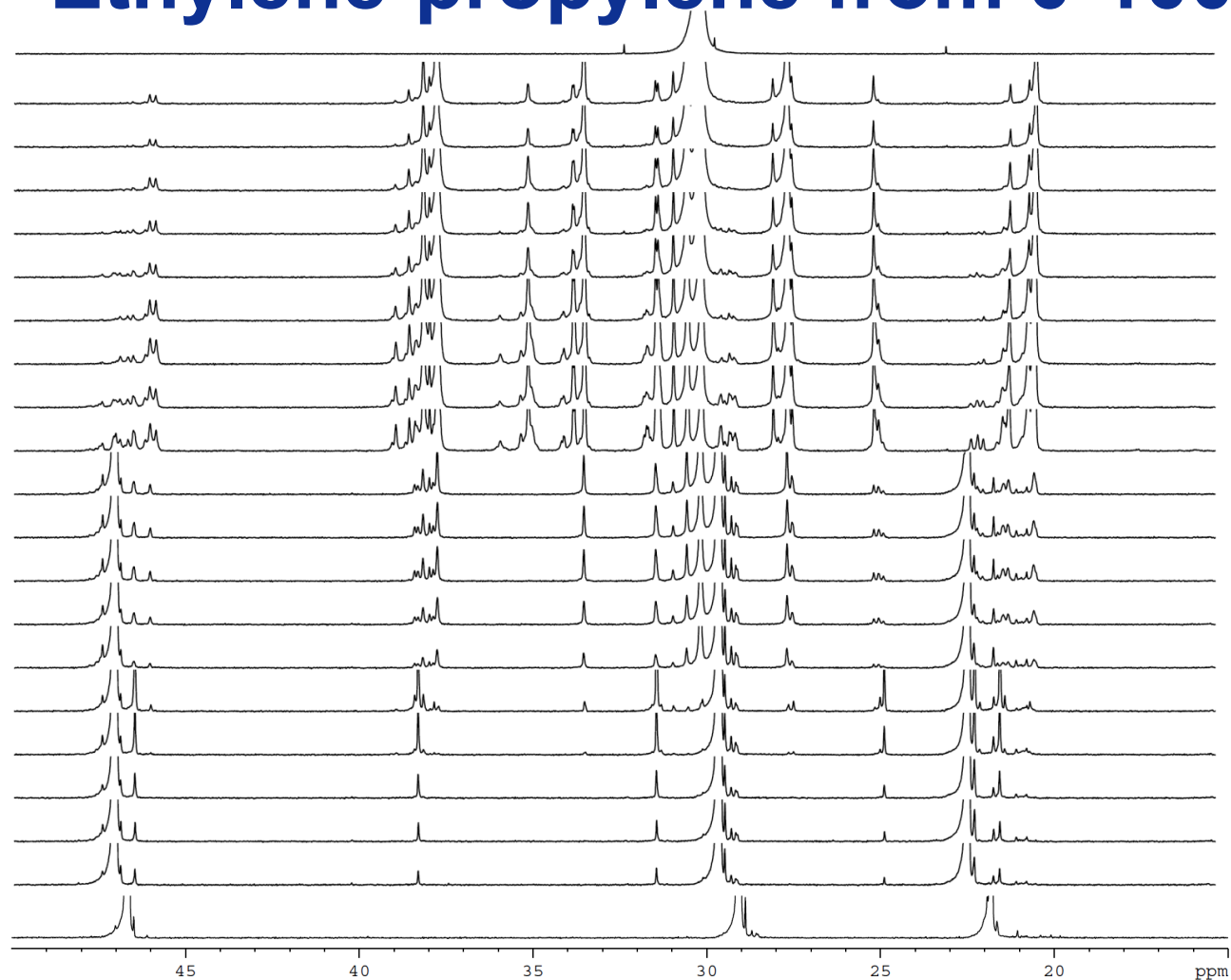


- Very important materials, most common form of polypropylene copolymer
  - due to the similarity in chemical structure between monomers assignment is difficult
  - comonomer incorporation has huge range: 0.1 – 80.0 mol%
  - spectra are complicated by stereo and regio chemistry
  - even for simple system multiple possible chemical structures = complex spectra

# Typical ethylene-propylene



# Ethylene-propylene from 0-100 % mol% C<sub>2</sub>



HDPE 100% C<sub>2</sub>

EP rubber

20-80 mol% C<sub>2</sub>

random EP

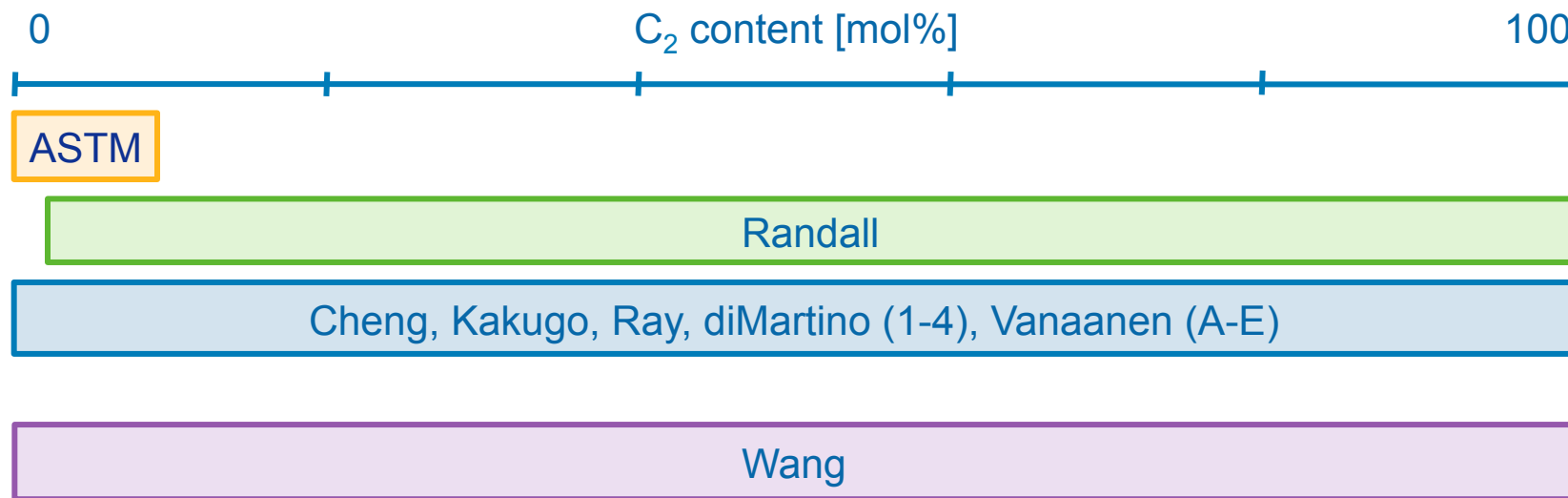
1-10.0 mol% C<sub>2</sub>

mini-random EP

0.1-1 mol% C<sub>2</sub>

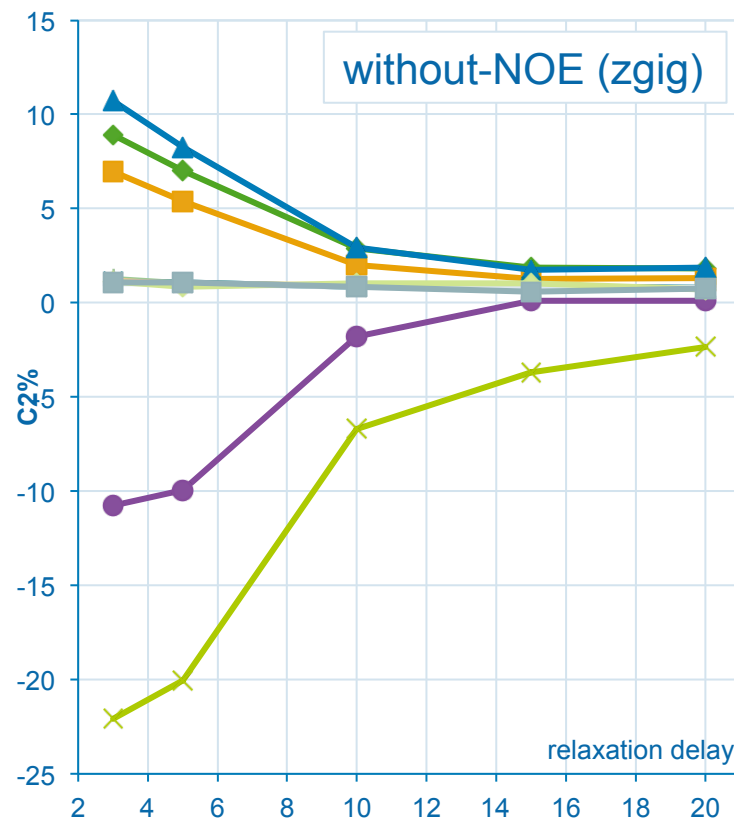
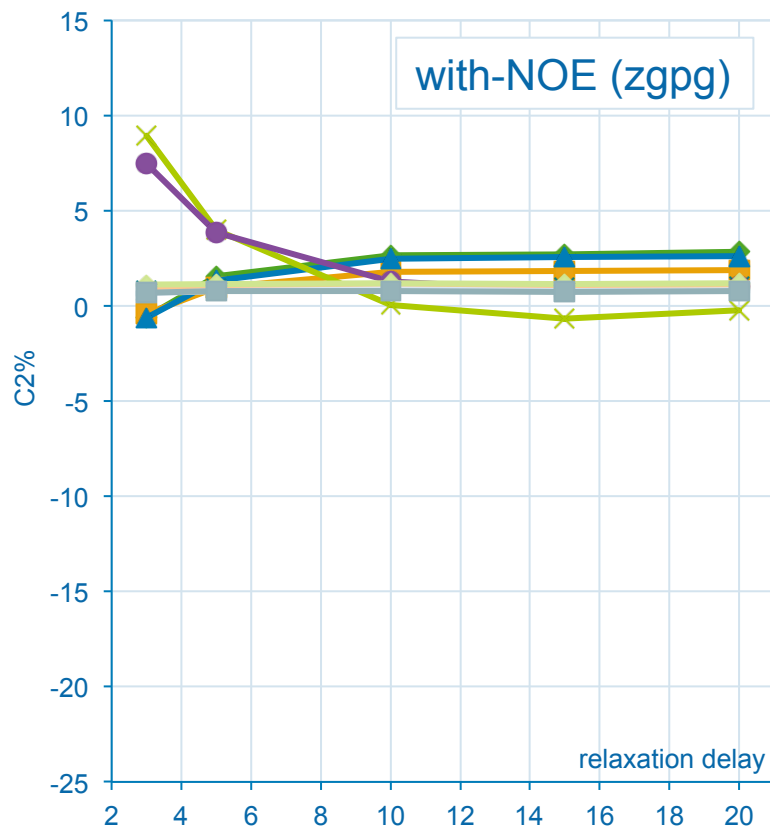
iPP 0 mol% C<sub>2</sub>

# Range of analysis methods for EP



- Each analysis method has an applicable range of C<sub>2</sub> content
  - not all methods account for the presence of regio defects and 2,1-E units
  - wide (huge) variation between methods, still an active field of research

# Variation of content with method



- Large variation between methods and experimental parameters
  - Values stabilise at very long relaxation delays ( $> 5 \times T_1$ )

# Patents: USP 5 874 505 claims

According to the present invention, there is provided a polypropylene composition comprising 20 to 95% by weight of a stereoregular polypropylene and 5 to 80% by weight of an  $\alpha$ -olefin copolymer, wherein the polypropylene is characterized in that

- (a) an isotactic pentad (m m m m) is 0.940 to 0.995,
  - (b) a syndiotactic pentad (r r r r) is 0 to 0.01,
  - (c) a different bond due to 2,1- and 1,3-insertions of propylene monomer is 0 to 0.10 mol %,
  - (d) a weight average molecular weight ( $M_w$ ) is 50,000 to 1,000,000 and
  - (e) a ratio ( $M_w/M_n$ ) of the weight average molecular weight ( $M_w$ ) to a number average molecular weight ( $M_n$ ) is 1.5 to 3.8,
- (a) to (e) being determined from  $^{13}\text{C}$  NMR spectra, and the  $\alpha$ -olefin copolymer comprises 10 to 90% by weight of an  $\alpha$ -olefin and 10 to 90% by weight of at least one of other  $\alpha$ -olefins.

# Patents: USP 5 874 505 description

Of the requirements for the stereoregular poly-propylene used in the present invention, the above-identified requirements (a)–(c) are calculated based on the results determined by  $^{13}\text{C}$  NMR spectra in accordance with the following method. More specifically, the NMR spectra was recorded at  $130^\circ\text{C}$ . on a JEOL-GX270 spectrometer manufactured by Nihon Densi K. K. in Japan operating at 67.20 MHz, using a mixed solution of o-dichlorobenzene/benzene bromide with 8/2 weight ratio having 20% by weight of polymer concentration.

The terms “isotactic pentad (m m m m)” and “syndiotactic pentad (r r r r)” as used herein refer to the isotactic sequence and the syndiotactic sequence, respectively, in terms of a pentad unit in the polypropylene molecular chain determined by  $^{13}\text{C}$  NMR spectra which was suggested by A. Zambelli, et al in *Macromolecules* Vol. 6, No. 6, 925–926, 1973.

A method of deciding the assignment of peak in the determination of  $^{13}\text{C}$  NMR spectra is performed in accordance with the assignment suggested by A. Zambelli, et al in *Macromolecules* Vol. 8, No. 5, 687–688, 1975.

The isotactic pentad (m m m m) (a) of the requirements for the stereoregular polypropylene in the present invention is the proportion of a propylene monomer unit containing 5 successive meso bonds which are present in all propylene monomer units in the polypropylene molecules. Higher isotactic (m m m m) pentad shows higher isotactic characteristics. The stereoregular polypropylene of the present invention has the isotactic (m m m m) pentad of 0.940 to 0.995, preferably 0.950 to 0.995, most preferably 0.960 to 0.995.

The syndiotactic pentad (r r r r) (b) of the requirements for the stereoregular polypropylene in the present invention is the proportion of a propylene monomer unit containing 5 successive racemic bonds which are present in all propylene monomer units in the polypropylene molecules. Lower syndiotactic (r r r r) pentad shows lower syndiotactic characteristics. The stereoregular polypropylene of the present invention has the syndiotactic (r r r r) pentad of 0 to 0.01, preferably 0 to 0.007, most preferably 0 to 0.004.

The term “different bond due to 2,1- and 1,3-insertions of propylene monomer” as used herein refers to the proportion of a different bond due to 2,1- and 1,3-insertions of propylene monomer which is present in the polypropylene molecules determined by  $^{13}\text{C}$  NMR spectra in accordance with the method suggested by T. Tsutsui et al in *POLYMER* Vol. 30, 1350–1356, 1989.

The different bond due to 2,1- and 1,3-insertions of propylene monomer (c) of the requirements for the stereoregular polypropylene in the present invention is 0 to 0.10 mol %, preferably 0 to 0.08 mol %. When conventional known titanium catalysts are used in the polymerization of propylene, the polymerization proceeds by the 2,1-insertion. When known metallocene catalysts are used, on the other hand, it is known that a certain degree of 2,1- and 1,3-insertions takes place and a specific amount of different bond is present in the resulting polypropylene.

From the requirements (a) to (c) as listed above, it can be confirmed that the stereoregular polypropylene used in the present invention does not contain substantially chains of different bond and racemic bond, and demonstrates exceedingly high isotactic characteristics consisting of much highly controlled meso bond chains.

# Patents: USP 6 537 652 B1

**United States Patent**  
**Kochem et al.**

(10) **Patent No.:** **US 6,537,652 B1**

(45) **Date of Patent:** **Mar. 25, 2003**

**BIAXIALLY ORIENTED ELECTRICAL  
INSULATION FILM HAVING IMPROVED  
SHRINKAGE AT ELEVATED  
TEMPERATURES**

Inventors: **Karl-Heinz Kochem**, Neuenkirchen  
(DE); **Kerstin Muller-Nagel**,  
Nalbach-Korprich (DE)

Assignee: **Hoescht Trespaphan GmbH**,  
HNeunkirchen, DE (US)

Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.

Appl. No.: **09/807,695**

PCT Filed: **Oct. 26, 1999**

PCT No.: **PCT/EP99/08090**

§ 371 (c)(1),  
(2), (4) Date: **Jun. 12, 2001**

PCT Pub. No.: **WO00/25330**

PCT Pub. Date: **May 4, 2000**

## Foreign Application Priority Data

st. 28, 1998 (DE) ..... 198 49 678

**Int. Cl.<sup>7</sup>** ..... **B32B 27/32**; H01G 4/18;  
C08J 5/18

(52) **U.S. Cl.** ..... **428/220**; 264/173.19; 264/210.7;  
264/466; 428/461; 428/516; 428/910

(58) **Field of Search** ..... 428/500, 516,  
428/461, 910, 220, 219; 264/173.19, 210.7,  
466

## (56) References Cited

### FOREIGN PATENT DOCUMENTS

EP	0498249 A	8/1982
EP	0755779 A	1/1997
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*Primary Examiner*—D. S. Nakarani

(74) *Attorney, Agent, or Firm*—Powell Goldstein Frazer &  
Murphy LLP

## (57) ABSTRACT

A biaxially oriented polypropylene film is described. The n-heptane-insoluble content of the film has a chain isotacticity index, measured by <sup>13</sup>C-NMR spectroscopy, of at least 95%. In particular, the film should have the lowest possible shrinkage (transverse shrinkage and longitudinal shrinkage) at elevated temperatures. In addition, a process for the production of the polypropylene film and its use is described.

**30 Claims, No Drawings**



# Patents: USP 6 537 652 B1 claims

What is claimed is:

1. A biaxially oriented film having at least one layer comprising polypropylene, characterized in that the polypropylene has a chain isotacticity index, measured by  $^{13}\text{C}$ -NMR spectroscopy (triad method), of at least 95%, an isotactic pentad fraction, measured by  $^{13}\text{C}$ -NMR spectroscopy, in the range of 85–95%, and a n-heptane-insoluble content of at least 97%, and in that the transverse shrinkage of the film (depending on the film thickness d) satisfies the following formula:

$<4.5 \mu\text{m}$  transverse shrinkage at  $140^\circ \text{C}$ . maximum  $6.5\% \Delta$   
shrinkage at  $140^\circ \text{C}$ .–shrinkage at  $120^\circ \text{C}$ .  $\leq 3.5\%$  d:

$4.5\text{--}12 \mu\text{m}$  transverse shrinkage at  $140^\circ \text{C}$ . maximum  $5.5\% \Delta$   
shrinkage at  $140^\circ \text{C}$ .–shrinkage at  $120^\circ \text{C}$ .  $\leq 3.0\%$

$>12\text{--}20 \mu\text{m}$  transverse shrinkage at  $140^\circ \text{C}$ . maximum  $4.5\% \Delta$   
shrinkage at  $140^\circ \text{C}$ .–shrinkage at  $120^\circ \text{C}$ .  $\leq 2.5\%$ .

# Patents: USP 6 537 652 B1 description

## Isotactic Content

The isotactic content of the homopolymer can be characterized to an approximation by the insoluble fraction of the raw material in n-heptane. A Soxhlet extraction with boiling n-heptane is usually carried out, it being advantageous to fill the Soxhlet with a pressed disk instead of granules. The thickness of the pressed disc should not exceed 500 microns here. For quantitative determination of the n-heptane-insoluble content of the homopolymer, it is of crucial importance to ensure an adequate extraction time of from 8 to 24 hours.

The operational definition of the isotactic content  $PP_{iso}$  in percent is given by the ratio of the weights of the dried n-heptane-insoluble fraction to the initial weight:

$$PP_{iso} = 100 \times (\text{n-heptane-insoluble fraction} / \text{initial weight})$$

Analysis of the dried n-heptane extract shows that this generally does not consist of pure atactic propylene homopolymer. The extraction also includes aliphatic and olefinic oligomers, in particular isotactic oligomers, and also possible additives, such as, for example, hydrogenated hydrocarbon resins and wax.

Determination of the triad-based Chain Isotacticity Index 11 (triads) and Determination of the Pentad Content

## Sample Preparation and Measurements

From 60 to 100 mg of polypropylene are weighed into 10 mm NMR tubes. After addition of a solvent mixture comprising hexachlorobutadiene ( $C_4Cl_6$ ) and deuterated tetrachloroethane ( $C_2D_2Cl_4$ ), the suspension is stored at about 140° C. until a homogeneous solution has formed. The dissolution process is accelerated by stirring with a glass rod. The  $^{13}C$ -NMR spectrum is recorded at elevated temperature (generally 373 K) under standard measurement conditions (semiquantitatively).

## Evaluation of the $^{13}C$ -NMR Spectrum

In order to describe the configuration statistics (tacticity) of polypropylene, three or five monomer units are combined to form triads and pentads. In a triad, the configuration of the methyl groups of the adjacent monomer units is looked at

from the point of view of the methyl group of the central recurring unit. If, on moving along the polymer chain in one direction, all three methyl groups have the same configuration, this is an mm triad.

If the configuration of the preceding and succeeding methyl group are the same, but different to the central  $CH_3$  group, this is an rr triad.

Two further arrangements are possible, mr and rm. However, they cannot be distinguished, since both directions along the polymer chain are equivalent. They are combined into mr triads.

The various triads can be distinguished on the basis of their different chemical shift in the  $^{13}C$ -NMR spectrum.

Range of the mm triads	approx. 20.8–approx. 22.2 ppm
Range of the mr triads	approx. 20.0–approx. 20.8 ppm
Range of the rr triads	approx. 19.2–approx. 20.0 ppm

In order to calculate the so-called triad-based chain isotacticity index II, the intensities of the triad signals are compared:

$$II \text{ (triads)} = \frac{Imm + 0.5Imr}{Imm + Imr + Irr} * 100$$

where I mm, Imr and Irr are the integrals of the associated signal groups.

## triad-dyad necessary relationship:

$$[m] = [mm] + 0.5 [mr]$$

# Patents: USP 6 537 652 B1

An extended way of consideration is that of the pentads; here, the configuration of five methyl groups of five adjacent monomer units is compared. Ten pentads which can be differentiated result.

Pentads	Chemical shift in ppm
mmmm	approx. 22.2–approx. 21.25
mmmr	approx. 21.25–approx. 21.1
rmmr	approx. 21.1–approx. 20.8
mmrr	approx. 20.8–approx. 20.5
rrmr + mrrm	approx. 20.5–approx. 20.3
mrmm	approx. 20.3–approx. 20.0
rrrr	approx. 20.0–approx. 19.8
mrrr	approx. 19.8–approx. 19.6
rrrm	approx. 19.6–approx. 19.2

For referencing of the spectra, the signal of tetrachloroethane ( $C_2D_2Cl_4$ ) is set at 73.81 ppm. The mmmm fraction was calculated in accordance with the following formula:

$$mmmm \text{ fraction} = \frac{I_{mmmm}}{I(\text{sum of all pentad fractions})} * 100$$

Literature:

NMR-spectroscopy and polymer microstructure by Alan E. Tonelli, 1989, VCH

- General issues with patents:
  - limited description of acquisition
  - limited description of analysis
  - re-definition of terms
  - no mention of artefact correction
  - no mention of regio-defect correction
  - badly referenced
- What does this mean:
  - very difficult to repeat a measurement
  - need to clearly describe our own method

# Quantitative NMR reporting

- Proprietary in-house spectral analysis (quantification)
  - Excel not robust enough (too many ways to mess thing up)
  - custom C-based NMR software automation (Bruker Topspin)
  - quantification program +1500 lines of code
- Fully automated
  - NMR data processing (FT, line-broadening, phasing, trimming, baseline)
  - Analysis (integration, multiple calculations)
  - reporting (PDF, txt, csv)

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8/2/2011

## NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

# results of quantitative analysis

[illegible]

# PP homopolymer reporting: header

```
## Borealis Polyolefine GmbH #####
#
# Quantitative 13C NMR Analysis Results: Polypropylene-homopolymers
#
# B 7000
# 98.9 %mm [ 0.8 % regio errors] nmr1 on Tue 13 Jan 2009 at 17:41:50
#
# spect : klimke-sspp-B7000 1 1
#
##### QUANT-P v013 ##
##[ Isotacticity ]#####[ 01 ]##
```

overview

our reference

version #

	[ ES mmmm CE ]	mm	m	mmmm	mm	m
.00 triad	[98.19 98.11]	98.95	99.36	pentad	97.23	98.90 99.32
.0 method	[98.2 98.1 ]	98.9	99.4	method	97.2	98.9 99.3

isotacticity

NOTE: ES & CE models used to determine pentad isotacticity from triad method

triad method

pentad method

calculated values in  
square brackets [ x ]

# PP homopolymer reporting: stereo & regio

##[ Stereo Errors ]#####[ 02 ]##

triad method	mm			mr			rr			obs'd
	98.95			0.83			0.22			
	[----- 99.36 -----]			[----- 0.64 -----]						calc.
pentad method	mmmm	mmmr	rmmr	mmrr	xmrx	rmrm	rrrr	rrrm	mrrm	
[mmmm + mmmr]	97.23	1.53	0.14	0.38	0.36	0.10	0.08	0.00	0.19	obs'd
	[---- 98.90 ----]			[---- 0.84 ----]			[---- 0.26 ----]			calc.
	[----- 99.32 -----]			[----- 0.68 -----]						calc.
pentad method	mmmm	mmmr	rmmr	mmrr	xmrx	rmrm	rrrr	rrrm	mrrm	
[mmmx via ES]	98.30	0.67	0.00	0.67	0.00	0.00	0.00	0.00	0.34	model
P = 0.9966	[---- 98.98 ----]			[---- 0.68 ----]			[---- 0.34 ----]			calc.
	[----- 99.32 -----]			[----- 0.68 -----]						calc.
pentad method	mmmm	mmmr	rmmr	mmrr	xmrx	rmrm	rrrr	rrrm	mrrm	
[mmmx via CE]	98.40	0.79	0.00	0.00	0.79	0.00	0.00	0.00	0.00	model
Pm = 0.9960	[---- 99.20 ----]			[---- 0.80 ----]			[---- 0.00 ----]			calc.
	[----- 99.60 -----]			[----- 0.40 -----]						calc.

direct

no model fitting

indirect

via model fitting

##[ Regio Errors ]#####[ 03 ]##

mol% mis inserted propene 2,1e + 2,1t = 2,1 + 3,1 = total										
triad method [via CH3:CH3]	0.83	+	0.00	=	0.83	+	0.00	=	0.83	
pentad method [via CH3:CH3]	0.83	+	0.00	=	0.83	+	0.00	=	0.83	

regio errors

total

# PP homopolymer reporting: ES model fits

##[ Model Fit: Entyomorphic site control ]#####[ 04 ]##

triad method	mm			mr			rr			obs'd
	98.95			0.83			0.22			
P = 0.9964	98.91			0.73			0.36			model
SLA = 0.29	+0.04			+0.11			-0.14			delta
	mmmm	mmmr	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
P = 0.9964	98.19	0.72	0.00	0.72	0.01	0.00	0.00	0.00	0.36	model

triad

*via forward prediction*

pentad method	mmmm	mmmr	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
[mmmm + mmmr]	97.23	1.53	0.14	0.38	0.36	0.10	0.08	0.00	0.19	obs'd
P = 0.9947	97.37	1.04	0.00	1.04	0.01	0.01	0.00	0.01	0.52	model
SLA = 2.28	+0.14	-0.49	-0.14	+0.66	-0.35	-0.09	-0.07	+0.01	+0.33	delta

pentad

*via mmmm & mmmr*

pentad method		mmmx	rmnr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
	[mmmx]	98.76	0.14	0.38	0.36	0.10	0.08	0.00	0.19	obs'd
	P = 0.9966	98.98	0.00	0.67	0.00	0.00	0.00	0.00	0.34	model
SLA =	1.33	+0.22	-0.14	+0.30	-0.35	-0.10	-0.08	+0.00	+0.15	delta
		mmmm	mmnr	rmnr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm
	P = 0.9966	98.30	0.67	0.00	0.67	0.00	0.00	0.00	0.00	0.34
										model

pentad

*via mmmx*

pentad method		mmmx	rmnr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
[derose mmmx]		98.31	0.28	0.69	0.35	0.10	0.08	0.00	0.19	obs'd
P = 0.9952		98.56	0.00	0.95	0.01	0.00	0.00	0.00	0.47	model
SLA = 1.58		+0.24	-0.28	+0.26	-0.34	-0.09	-0.07	+0.00	+0.29	delta
		mmmm	mmnr	rmnr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm
P = 0.9952		97.61	0.95	0.00	0.95	0.01	0.00	0.00	0.00	0.47
										model

pentad

*via mmmx (alternative)*



# PP homopolymer reporting: CE model fits

##[ Model Fit: Chain end control ]#####[ 05 ]##

triad method	mm		mr		rr					
	98.95		0.83		0.22		obs'd			
Pm = 0.9953	99.05		0.95		0.00		model			
SLA = 0.44	-0.11		-0.11		+0.22		delta			
	mmmm	mmmr	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
Pm = 0.9953	98.11	0.94	0.00	0.00	0.94	0.00	0.00	0.00	0.00	model

triad

via forward prediction

pentad method	mmmm	mmmr	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
[mmmm + mmmr]	97.23	1.53	0.14	0.38	0.36	0.10	0.08	0.00	0.19	obs'd
Pm = 0.9937	97.50	1.24	0.00	0.01	1.24	0.01	0.00	0.00	0.00	model
SLA = 2.30	+0.27	-0.29	-0.13	-0.37	+0.88	-0.09	-0.08	+0.00	-0.18	delta

pentad

via mmmm & mmmr

pentad method	mmmx	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm	
[mmmx]	98.76	0.14	0.38	0.36	0.10	0.08	0.00	0.19	obs'd
Pm = 0.9960	99.20	0.00	0.00	0.79	0.00	0.00	0.00	0.00	model
SLA = 2.18	+0.43	-0.14	-0.38	+0.44	-0.10	-0.08	+0.00	-0.19	delta
	mmmm	mmmr	rmmr	mmrr	xmrx	rmrn	rrrr	rrrm	mrrm
P = 0.9960	98.40	0.79	0.00	0.00	0.79	0.00	0.00	0.00	0.00

pentad

via mmmx

# iPP isotacticity reporting: results 6

##[ Signal-to-Noise Ratios ]#####[ 06 ]##

site	range	SNR	%SD
mm	23.0 - 21.4	2718.6	0.037
mr	21.4 - 20.7	27.9	3.587
rr	20.7 - 19.9	3.8	26.575
2,1-e	18.0 - 17.0	24.1	4.145
2,1-t	15.5 - 14.5	1.2	62.622
3,1	37.7 - 37.1	0.0	inf
sat mmmm	mmmm + 35 Hz	14.5	

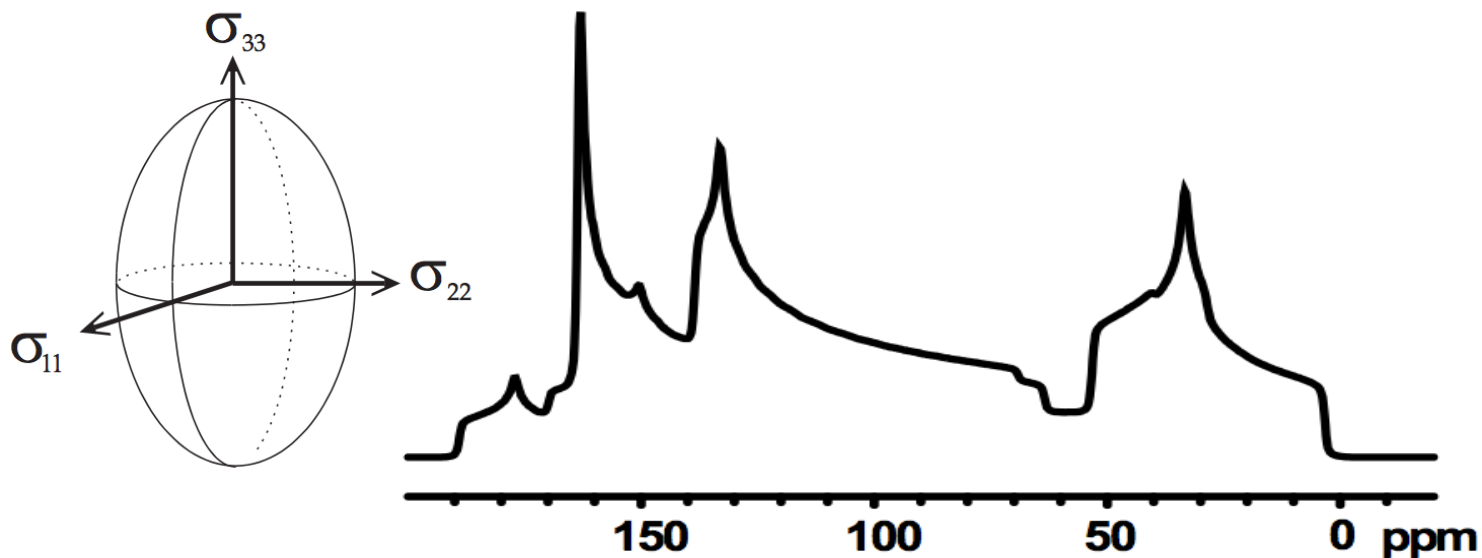
```

debug flag = 0
noJcc flag = 0
noBHT flag = 0
no21e flag = 0
no21t flag = 1
no31i flag = 1
    
```

#####[ END STANDARD ]##

**SNR**  
signal-to-noise ratio

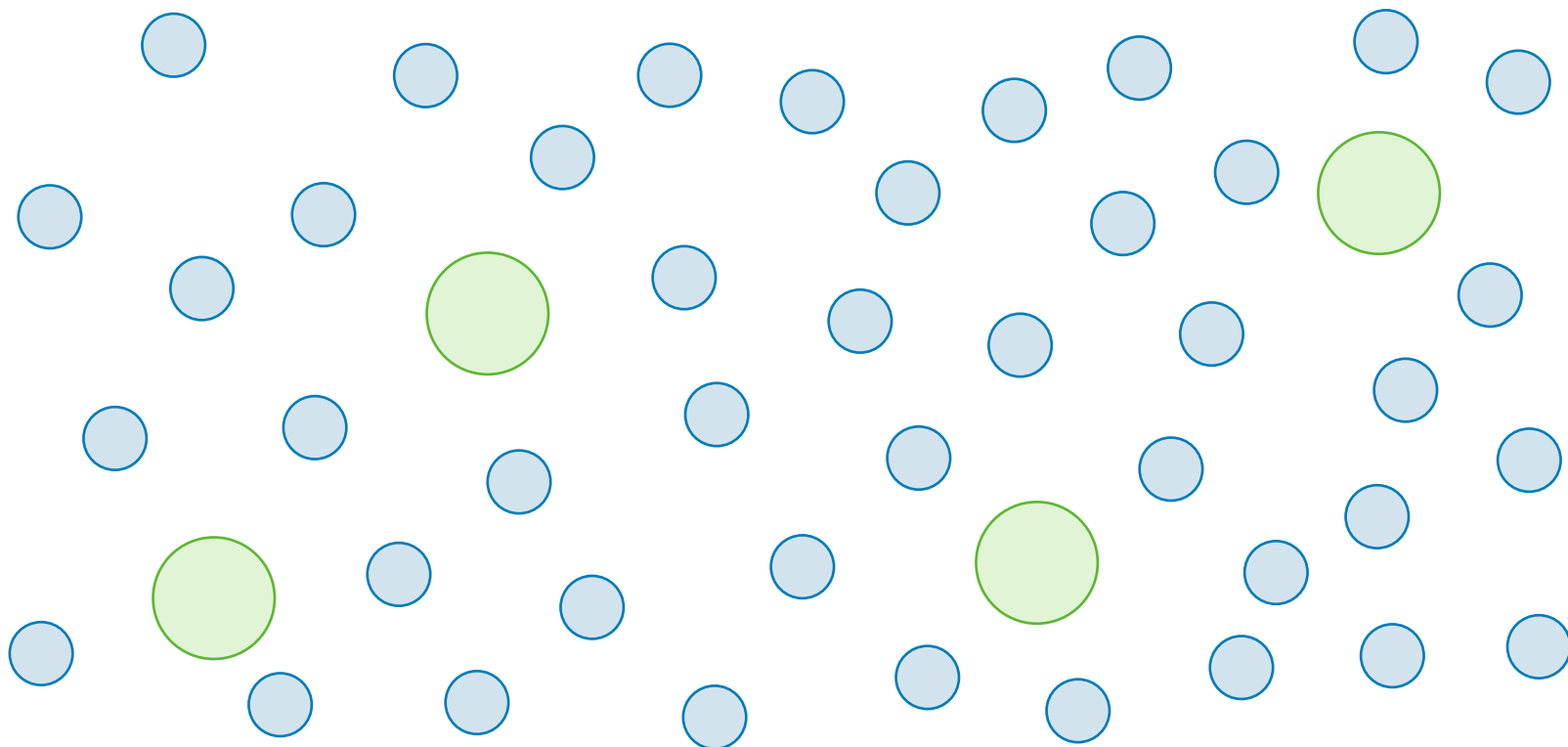
**run-time options**  
used



# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

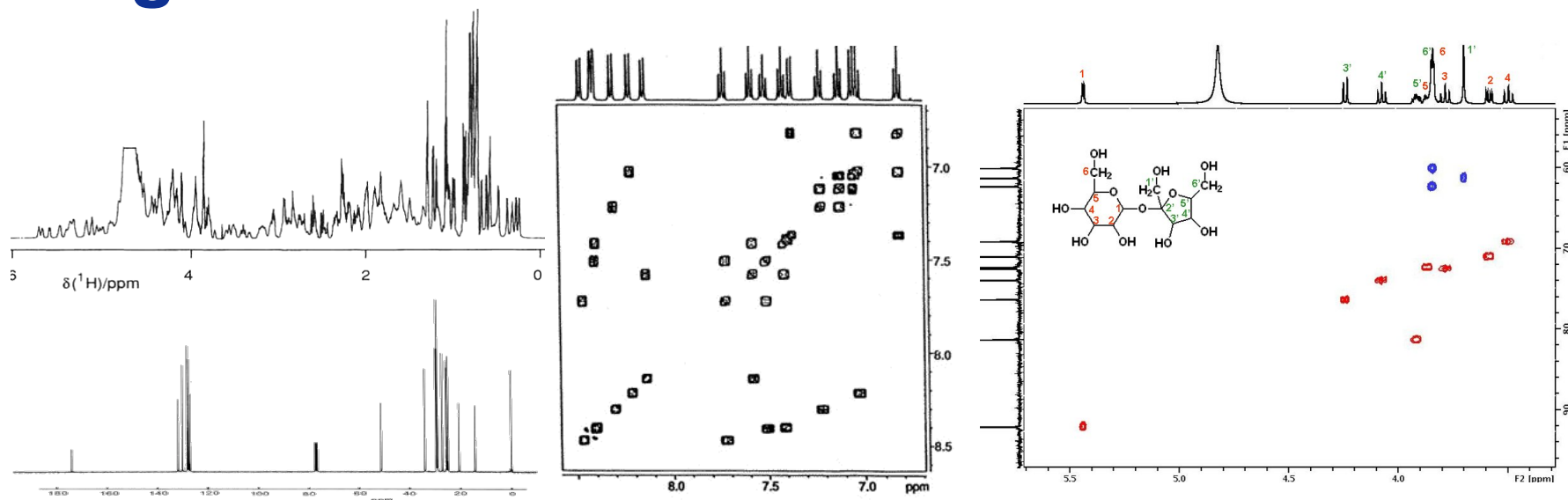
## **SOLID-STATE NMR SPECTROSCOPY THEORY**

# The dilute solution-state & NMR spectra



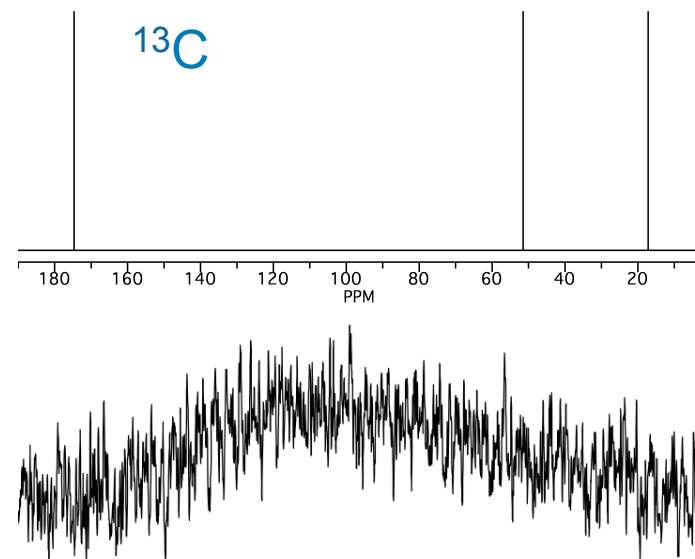
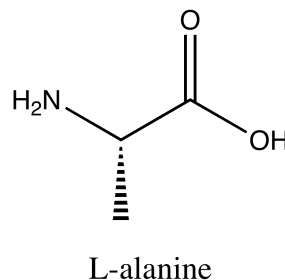
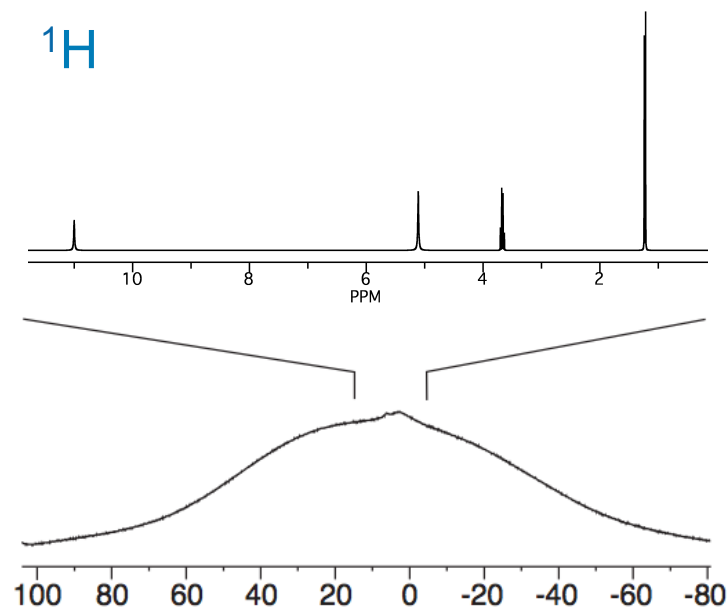
- Individual molecules of solute are separated by molecules of solvent
- Rare or unlikely that two solute molecule are close
- NMR spectrum is the sum of the spectra of each isolated molecule

# High-resolution solution-state NMR



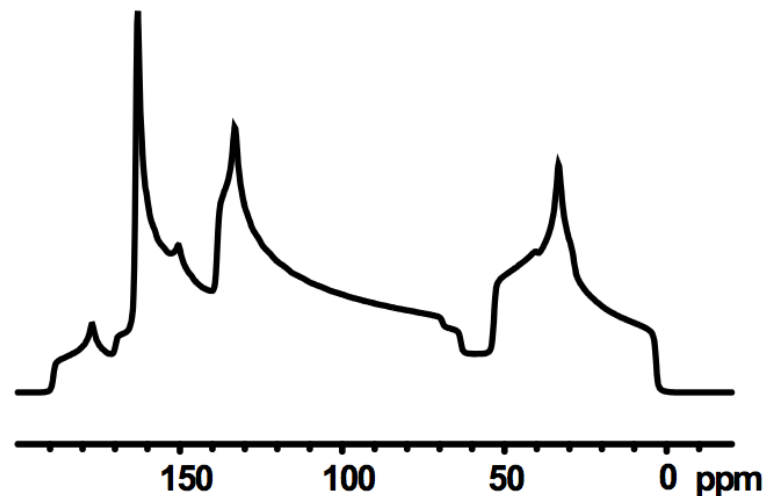
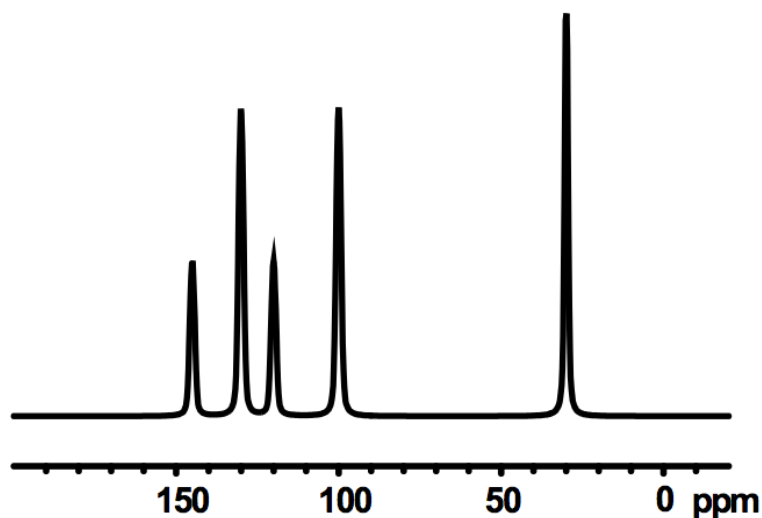
- Most common application of NMR spectroscopy
  - 1D  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  with sensitivity enhancement through NOE
  - 2D  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC, HMBC
- Rapid direct access to information about chemical structure of molecule
- Structure elucidation: what is the chemical structure of my molecule?

# Solid-state NMR can't be that difficult!



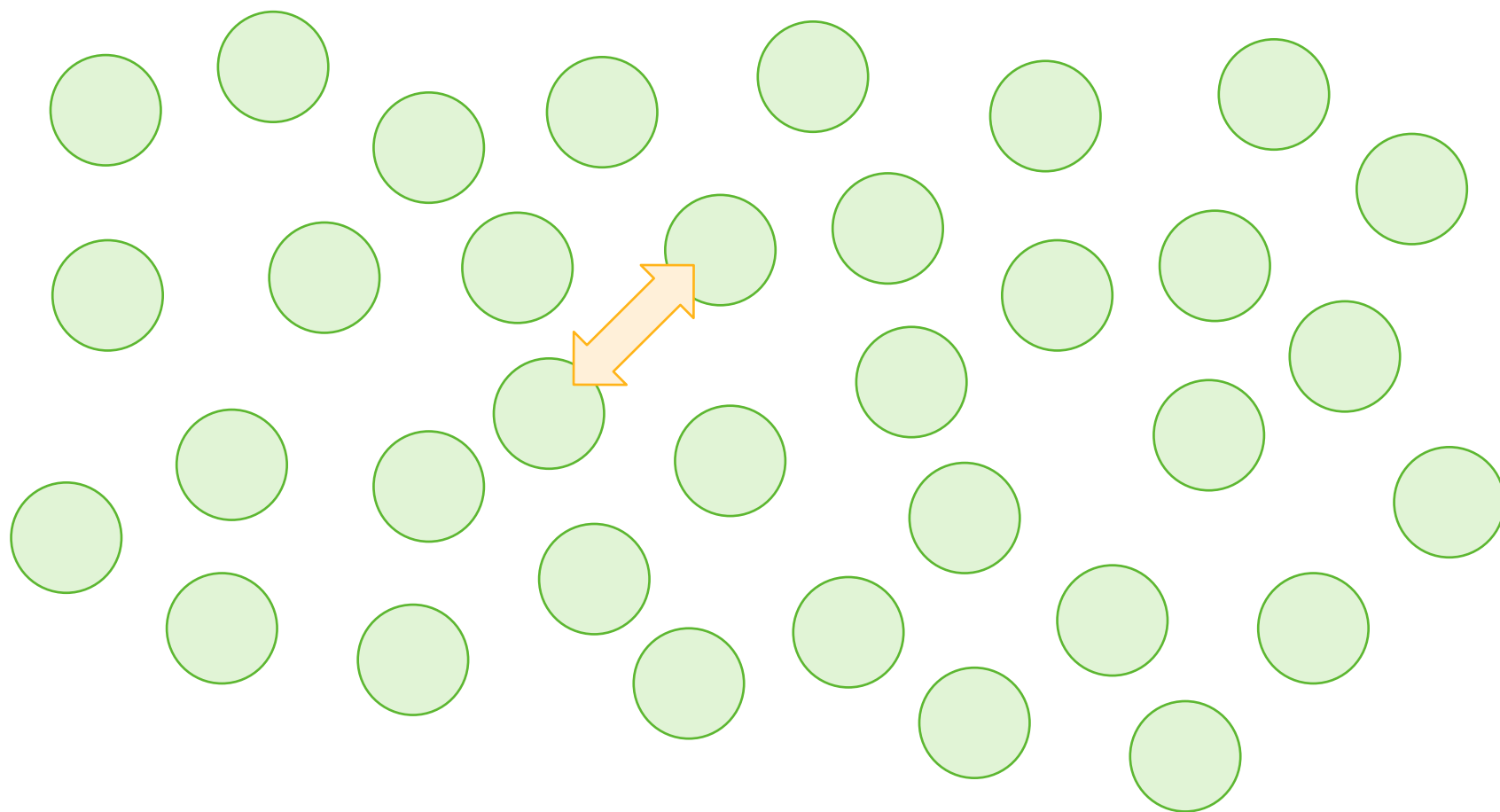
- Solution-state NMR spectra consist of a series of very sharp transitions
  - anisotropic NMR interactions are averaged by rapid random tumbling
- Solid-state NMR spectra are very board
  - full effect of anisotropy or orientation-dependent interactions are observed in spectra

# Solution-state Vs solid-state $^{13}\text{C}$ NMR



- Solid-state NMR spectra contain too much information!
  - can provide the same type of information that is available from solution-state NMR
  - special techniques or equipment is needed to simplify spectra
    - magic-angle spinning, cross-polarization, enhanced probehead electronics, 2D method
  - the interactions that cause the broad nature of solid-state spectra are not all bad
    - provide access to information about 3D structure and dynamics in the solid-state

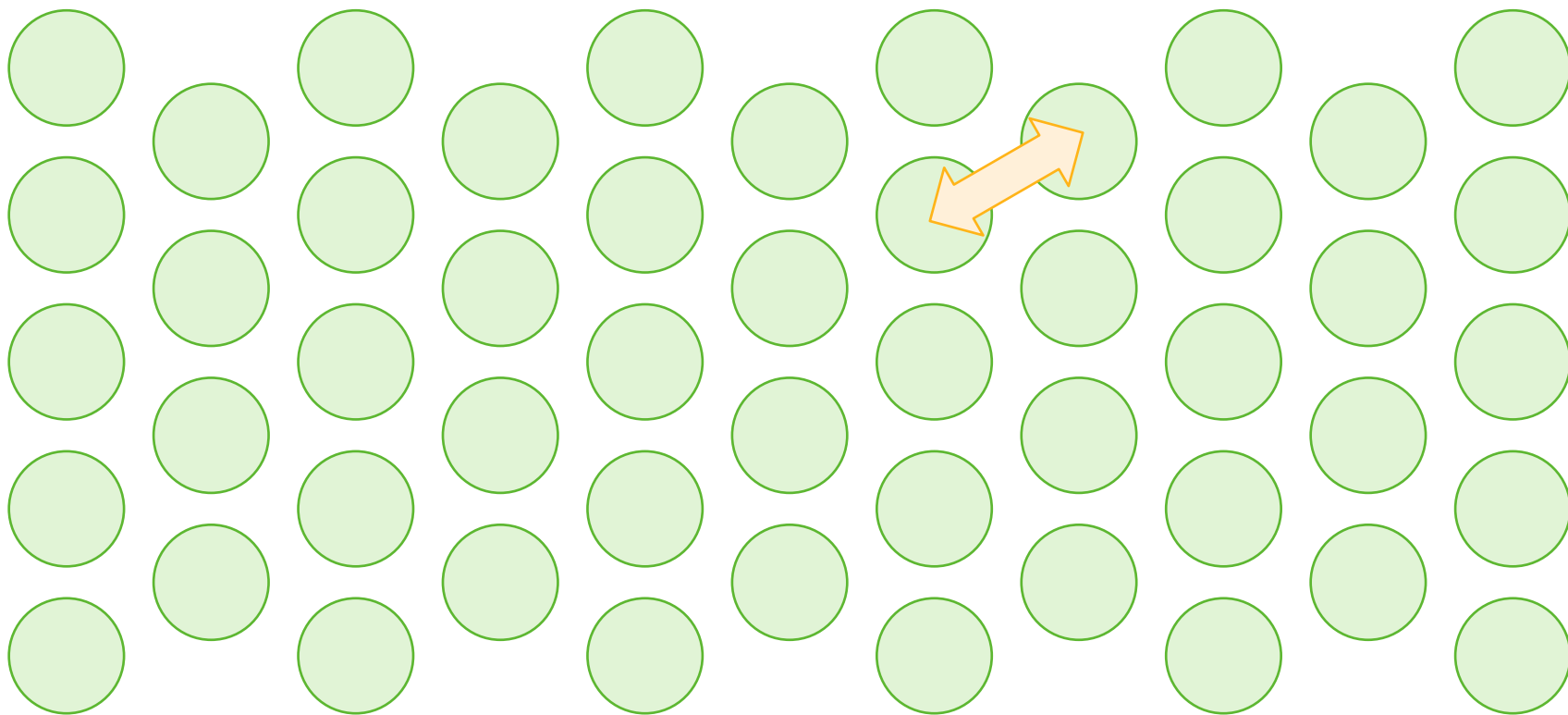
# The amorphous solid-state



- Close packing of molecules but no order or distribution of order

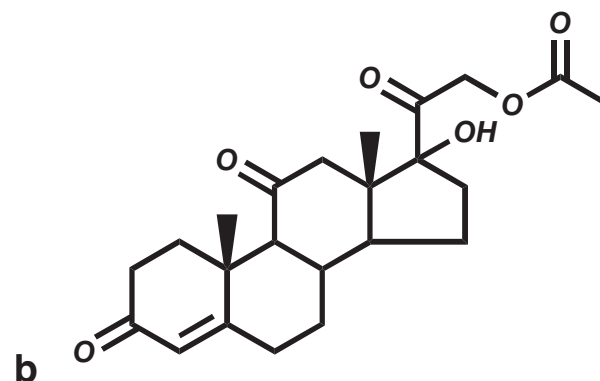
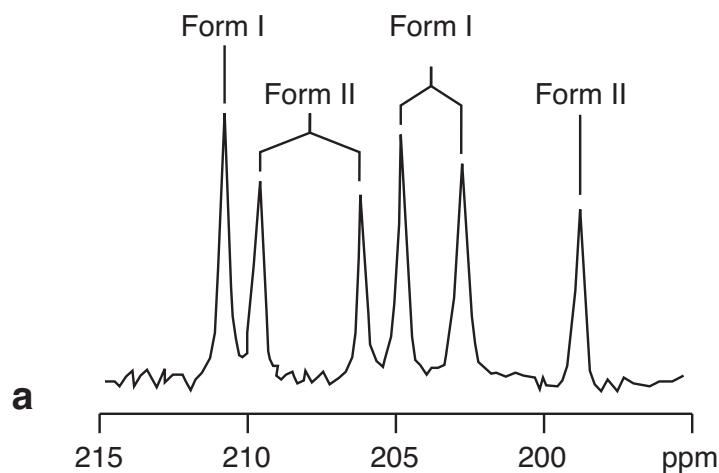


# The crystalline solid-state



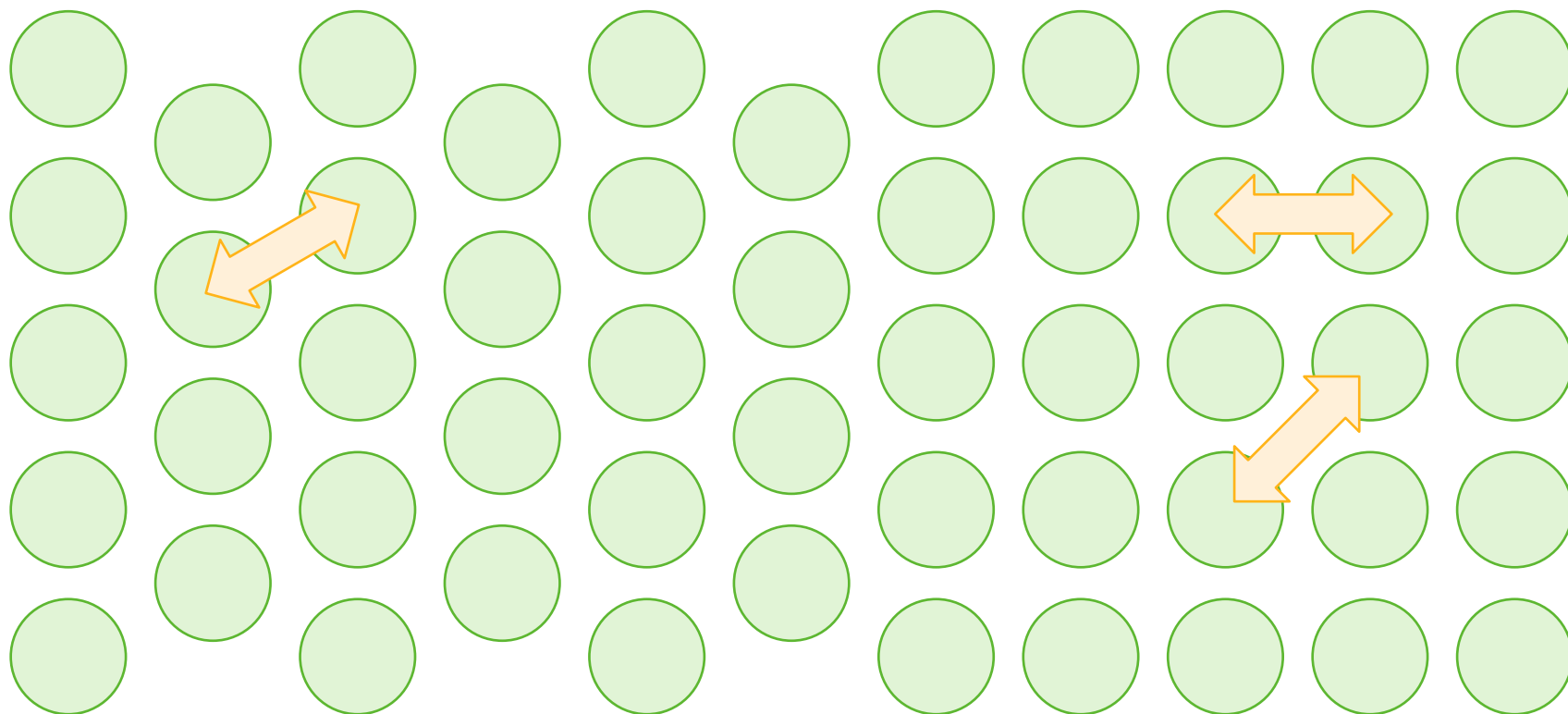
- Close packing of molecules with short-range and long-range order

# Crystallographic & magnetic inequivalence



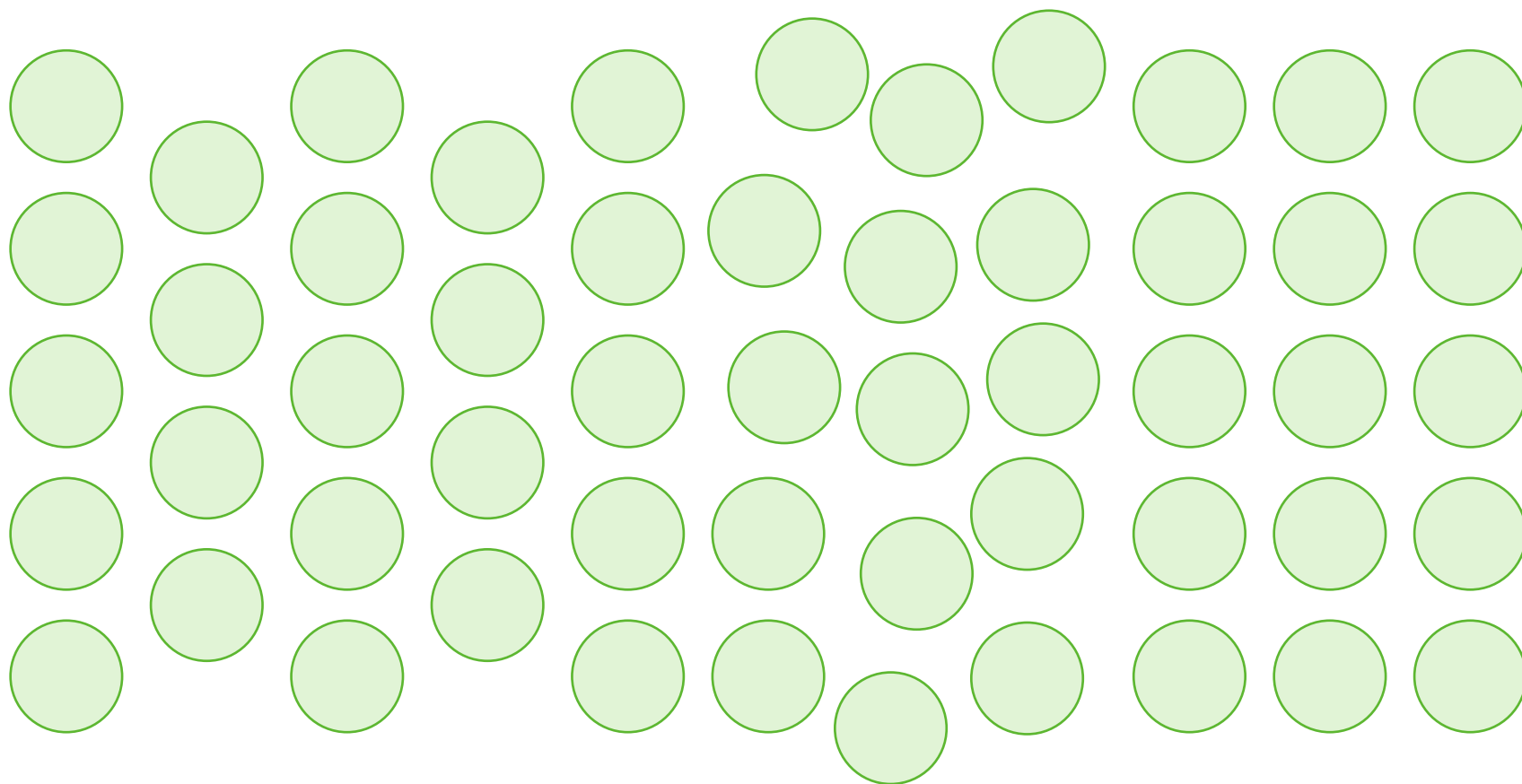
- NMR spectroscopy detects different magnetic environments
  - different local magnetic field result in different chemical shifts of the Larmor frequency
- Have to consider magnetic environments when assigning NMR spectra
  - solution-state: 3D molecular structure effects magnetic environment e.g. stereo chem
  - solid-state: 3D structure & packing effects magnetic environment e.g. unit cell
- Solid-state NMR spectroscopy probes chemistry & morphology

# Polymorphism



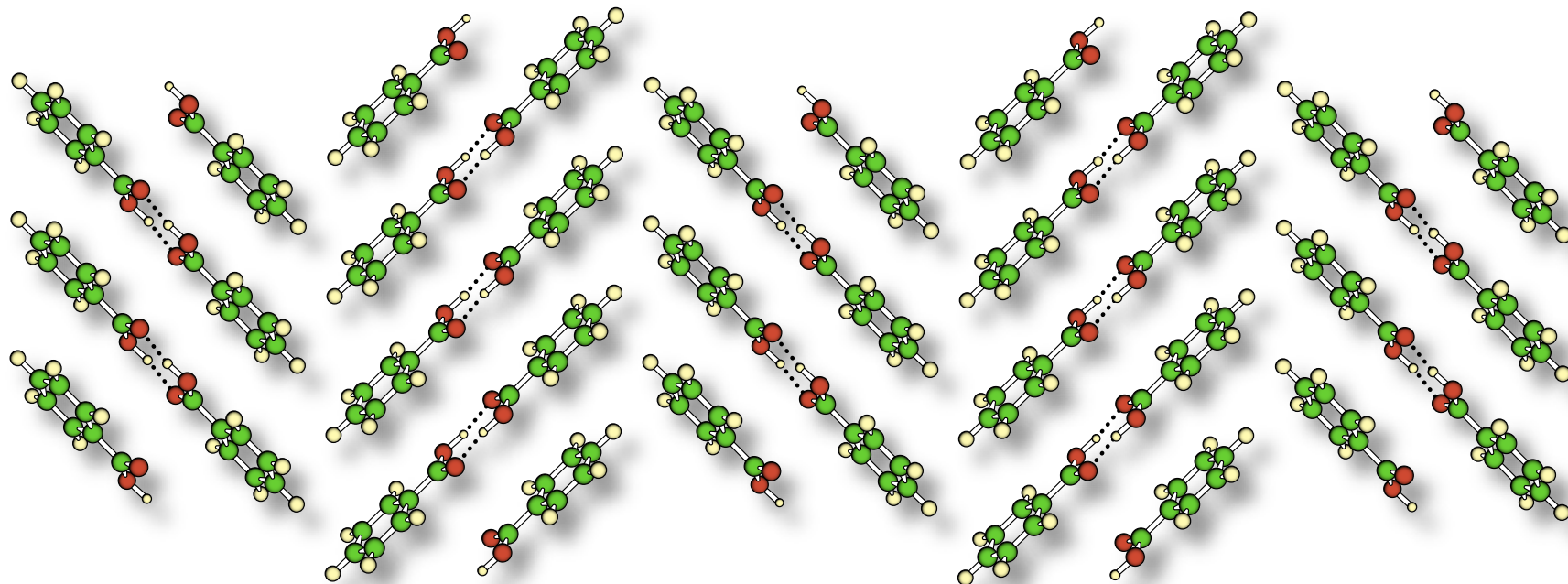
- Different types of close packing of molecules have different interactions

# Semi-crystalline solid-state



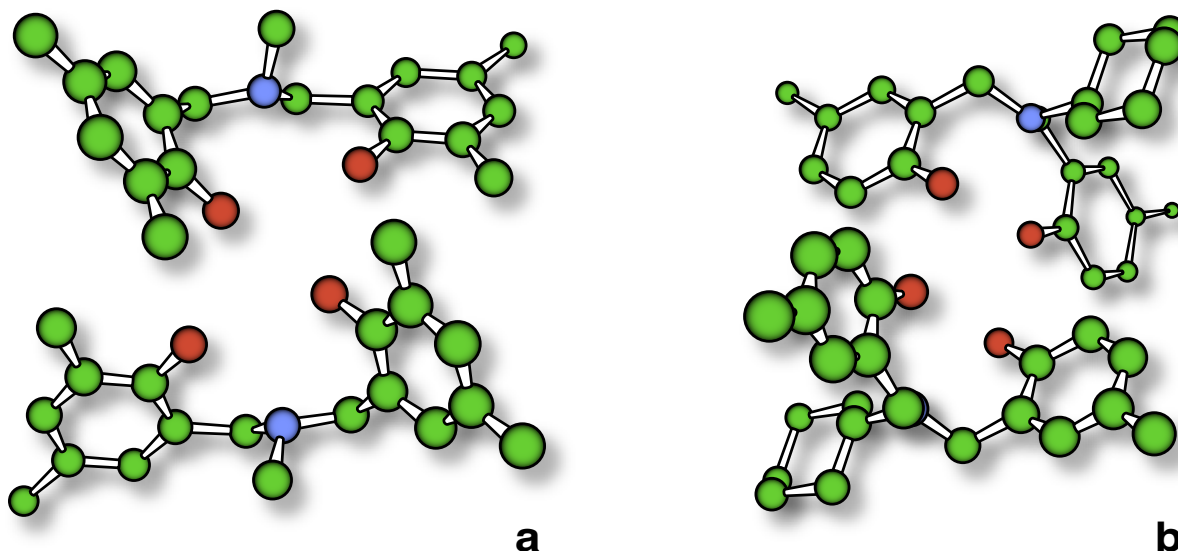
- Mixture of ordered (crystalline) and disordered (amorphous) regions

# Supra-molecular chemistry



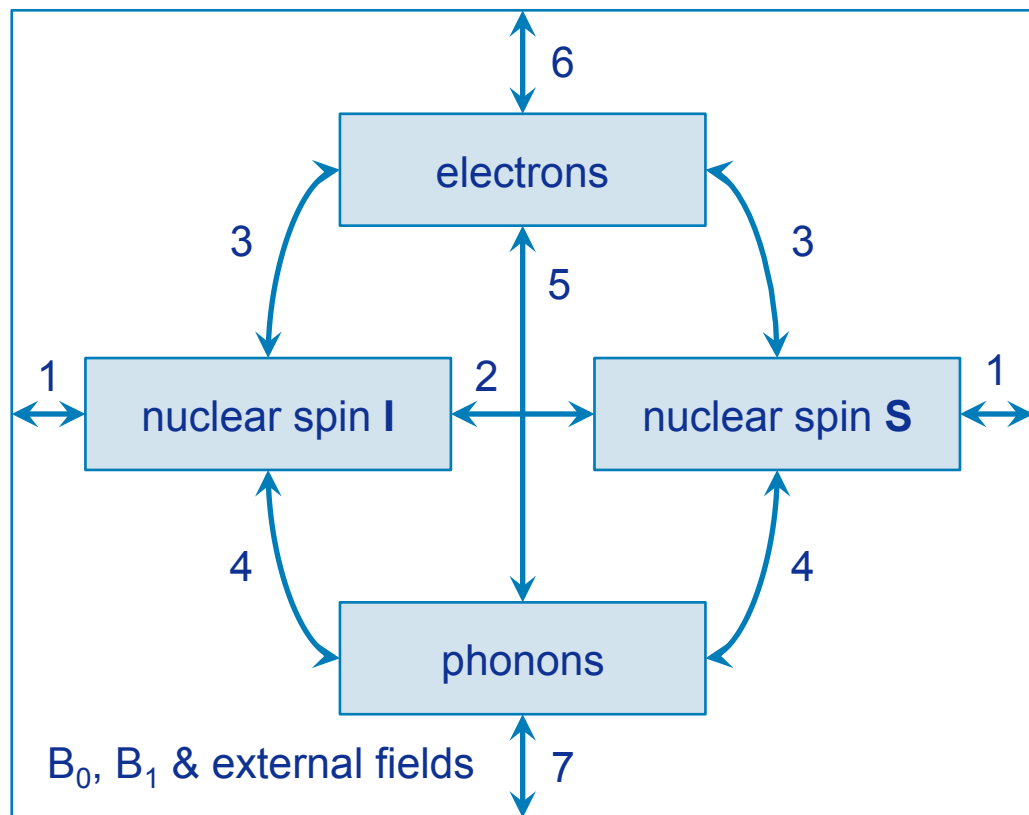
- Have to consider the world beyond the isolated molecule
  - Supramolecular chemistry
  - Packing and nearest-neighbor interactions

# Solid-state NMR or X-ray diffraction



- Use X-ray diffraction to study long-range order of heavy atoms only
  - what if our systems does not have long-range order: amorphous or micro-crystalline
  - does our single crystal representative of system as a whole?
  - is the position of the protons important e.g. hydrogen-bonding or p-facial interactions

# Nuclear spins in the solid-state



1: Zeeman interaction of nuclear spin

2: Direct dipolar spin interaction

3: Indirect spin-spin coupling (*J*-coupling)  
nuclear-electron spin coupling (paramagnetic interaction)  
coupling of nuclear spins with electric field gradient (quadrupolar interaction)

4: Direct spin-lattice interactions

3-5: Indirect spin-lattice interactions via elections

3-6: Chemical shielding and polarisation of nuclear spins by electrons

4-7: Coupling of nuclear spins to sound fields

- There are 7 way for a nuclear spin to communicate with its surroundings in the solid-state

# NMR interactions

- Time dependent Schrödinger equation:

$$\frac{d}{dt} \left| \psi_{spin}(t) \right\rangle = -i \cdot \hat{H}_{spin} \left| \psi_{spin}(t) \right\rangle$$

- Spin Hamiltonian:

$$\hat{H}_{spin} = \underbrace{\hat{H}_Z + \hat{H}_{RF}}_{\text{external interactions}} + \underbrace{\hat{H}_{CS} + \hat{H}_D + \hat{H}_Q + \hat{H}_J}_{\text{internal interactions}}$$

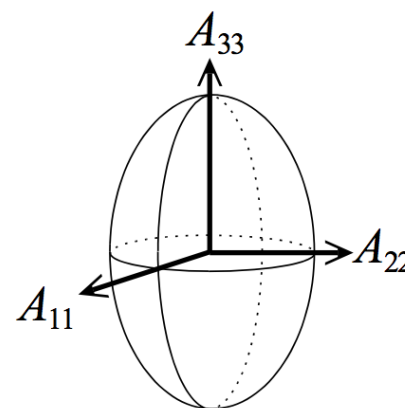
- describes the energy levels within a spin system = the form of the NMR spectrum
- can be divided into individual components for each interaction (external + internal)
- all interactions are proportional to orientation (anisotropic)



# NMR interactions tensors

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

$$\bar{\mathbf{A}}^{\text{PAS}} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix}$$



- All NMR interactions are anisotropic and their three-dimensional nature is best described by second-rank Cartesian tensors (3×3 matrices)
  - describe orientation of interaction with respect to Cartesian axis system of molecule
  - diagonalisation of a tensor gives a new tensor with three principal components which describe the interaction in its own principal axis system (PAS)
  - can be visualised as ellipsoids with  $A_{33}$  assigned to the largest principal component

# NMR interactions tensors: external

$$\hat{H}_Z = \mathbf{I} \cdot \bar{\mathbf{Z}} \cdot \mathbf{B}_0$$

$$\mathbf{B}_0 = \begin{bmatrix} B_{0x} & B_{0y} & B_{0z} \end{bmatrix} = \begin{bmatrix} 0 & 0 & B_0 \end{bmatrix}$$

$$\hat{H}_{\text{RF}} = \mathbf{I} \cdot \bar{\mathbf{Z}} \cdot \mathbf{B}_1$$

$$\mathbf{B}_1 = 2 \begin{bmatrix} B_{1x} & B_{1y} & B_{1z} \end{bmatrix} \cos(\omega t)$$

$$\bar{\mathbf{Z}} = -\gamma_I \bar{\mathbf{1}}$$

$$\bar{\mathbf{1}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- Nuclear spins are coupled to the external magnetic fields via tensors

# NMR interactions tensors: internal

$$\hat{H}_{\text{CS}} = \gamma \mathbf{I} \cdot \bar{\sigma} \cdot \mathbf{B}_0$$

chemical shielding

$$\hat{H}_{\text{D}} \propto \sum_{i \neq j} \mathbf{I}_i \cdot \bar{\mathbf{D}} \cdot \mathbf{I}_j$$

direct dipolar coupling interaction

$$\hat{H}_{\text{Q}} \propto \sum_i \mathbf{I} \cdot \bar{\mathbf{V}} \cdot \mathbf{I}$$

quadrupolar coupling interaction

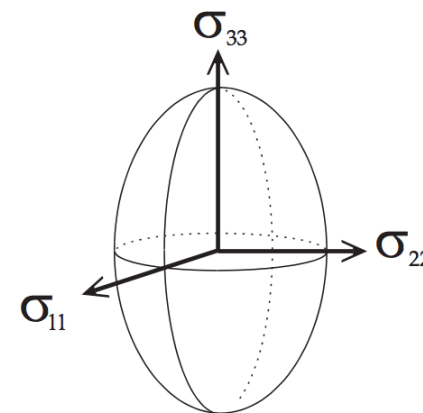
$$\hat{H}_{\text{J}} = \sum_{i \neq j} \mathbf{I}_i \cdot \bar{\mathbf{J}} \cdot \mathbf{I}_j$$

indirect spin-spin (J) coupling interaction

- Using Cartesian tensors allows the separation of the spin-part of the Hamiltonian from the special anisotropic dependence part
  - the spin-part can be treated in the same way as in the solution-state

# Chemical Shielding Anisotropy

$$\overline{\sigma}^{LAB} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad \overline{\sigma}^{PAS} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$



- Chemical shielding of nuclei by electron environment
  - Results in a chemical shift of the Larmor frequency (direct structure information)
  - Anisotropic interaction characterised by the shielding tensor  $s$
  - $s$  can be diagonalised to give a tensor with only three principle components
  - Spiess convention  $s_{11} \leq s_{22} \leq s_{33}$  i.e.  $s_{11}$  is least shielded component

# Orientation dependent chemical shift

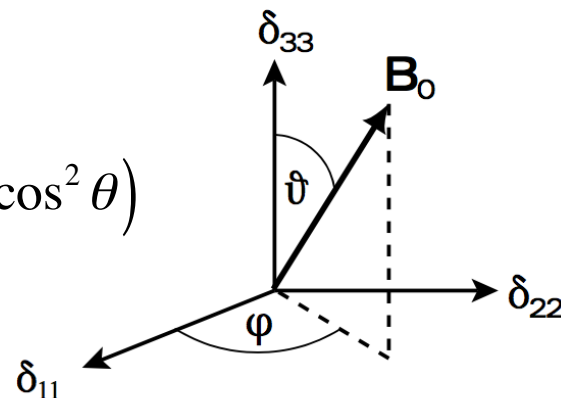
$$\overline{\sigma}^{PAS} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$
$$\sigma_{\text{iso}} = \text{Tr}[\sigma^{PAS}] = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$
$$\Omega = (\sigma_{33} - \sigma_{11})$$
$$K = \left( \frac{\sigma_{\text{iso}} - \sigma_{22}}{\Omega} \right)$$

- The trace of the chemical shielding tensor is non-zero
  - Under isotropic molecular tumbling (solution-state) only experience the isotropic chemical shielding  $\sigma_{\text{iso}}$  and observe isotropic chemical shifts
- Magnitude of CSA is characterised by a span parameter  $W$  in ppm:
- Asymmetry of CSA is characterised by a skew parameter  $k$

# CSA powder patterns an inverse problem

- The chemical shielding anisotropy (CSA) gives rise to tensor orientation dependent frequency shifts with respect to the magnet field:

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



- Inverse problem leads to a need for a numerical solution for simulation
- To simulate the spectrum we need to calculate a powder pattern
  - calculate frequencies for a large number of orientations of a given interaction tensor with respect to the magnetic field and sum to create powder pattern
  - many polar angles over a sphere:  $q$ ,  $f$

# Orientation dependent chemical shift II

$$\overline{\sigma}^{PAS} = \sigma_{iso} + \delta_{CS} \begin{bmatrix} \left(-\frac{1}{2} + \frac{\eta_{CS}}{2}\right) & 0 & 0 \\ 0 & \left(-\frac{1}{2} - \frac{\eta_{CS}}{2}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

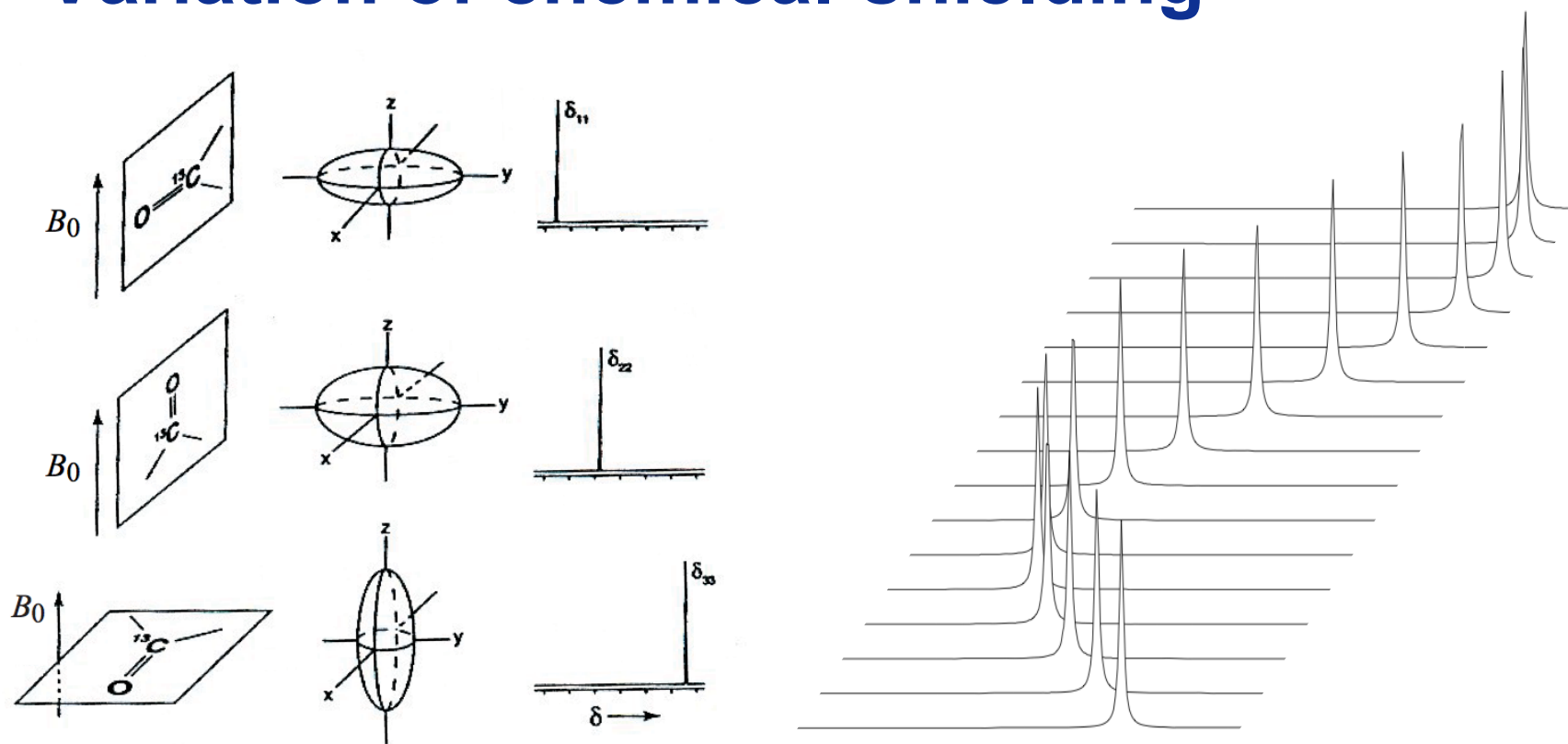
$$\delta_{CS} = \omega_L (\sigma_{33} - \sigma_{iso})$$

$$\eta_{CS} = \left( \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} - \sigma_{iso}} \right)$$

$$v_{CS} = \frac{\delta_{CS}}{2} (3 \cos^2 \theta - 1 - \eta_{CS} \cdot \sin^2 \theta \cos^2 2\phi)$$

- Can also be write  $u_{CS}$  in an alternative form which is easier to calculate
  - magnitude of CSA is characterised by a anisotropy parameter  $d_{CS}$
  - asymmetry of CSA is characterised by a asymmetry parameter  $h_{CS}$

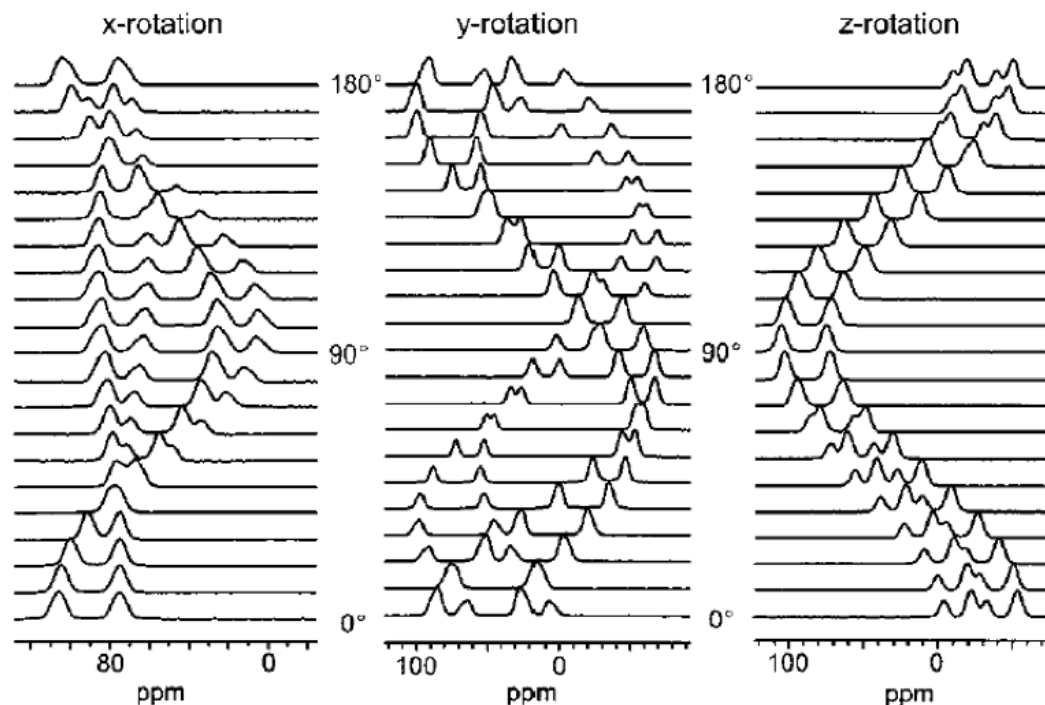
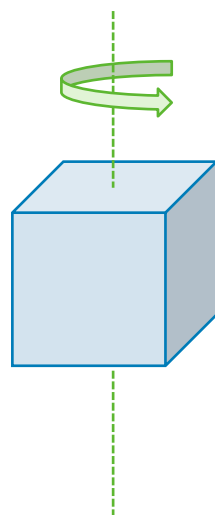
# Variation of chemical-shielding



- Depending on orientation frequency can be anywhere between the principle components:  $d_{11} > d_{\text{obs}} > d_{33}$



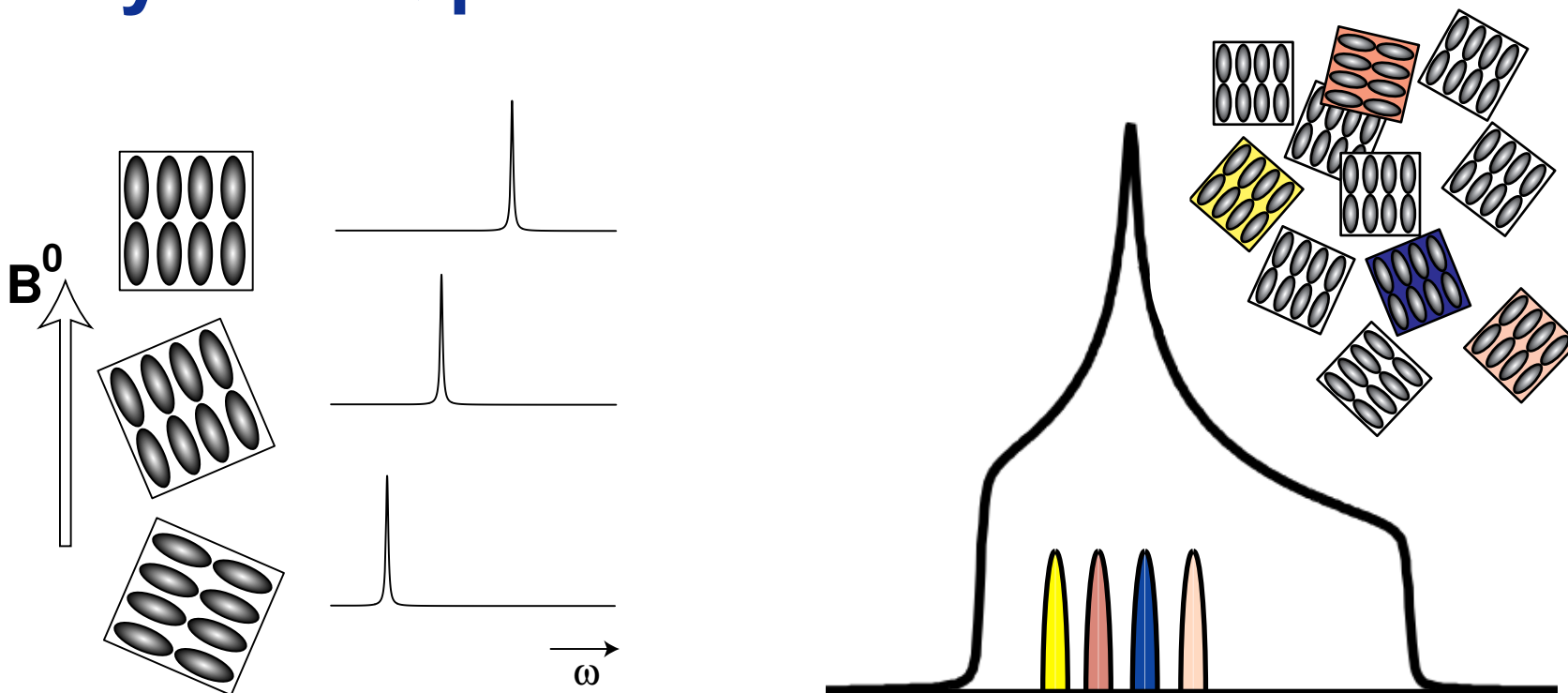
# Chemical-shielding & single crystals



<sup>31</sup>P CP-NMR

- Possible to do solid-state NMR of single crystals like X-ray diffraction
  - single line due to presence of only one tensor orientation
  - rotation of sample within coil with respect to magnetic field changes frequencies
  - allows determination of tensor orientation with respect to molecular axis.

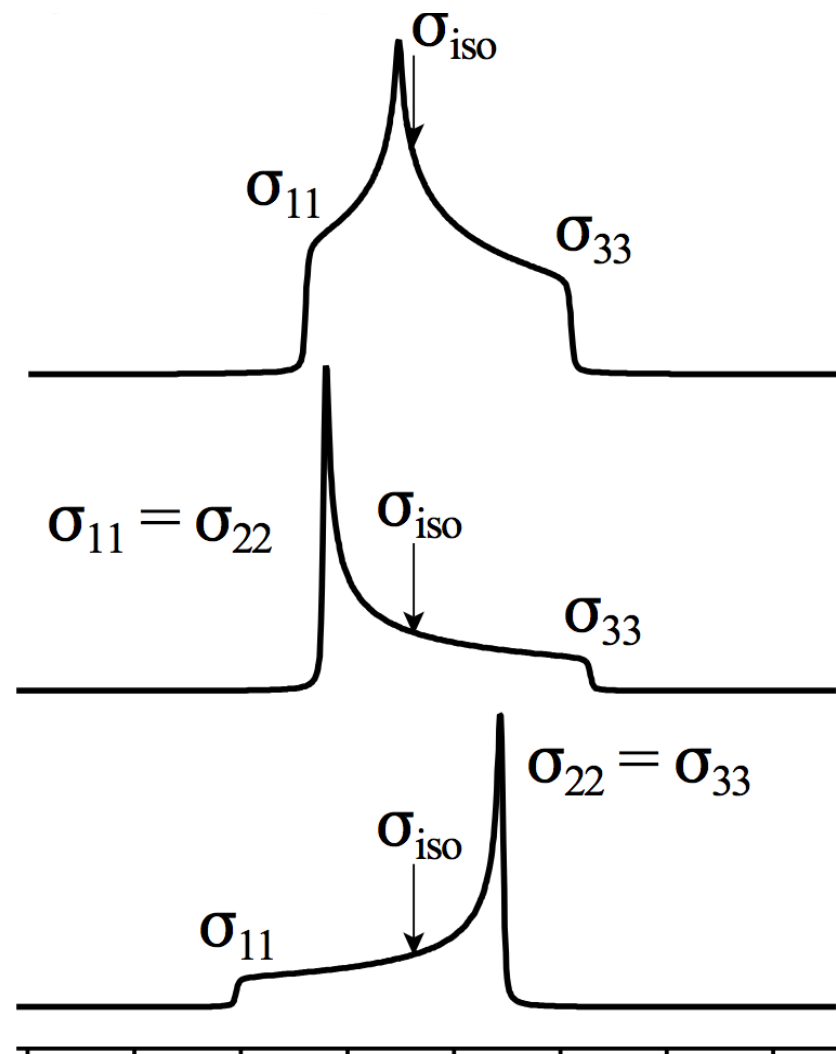
# Crystals & powders



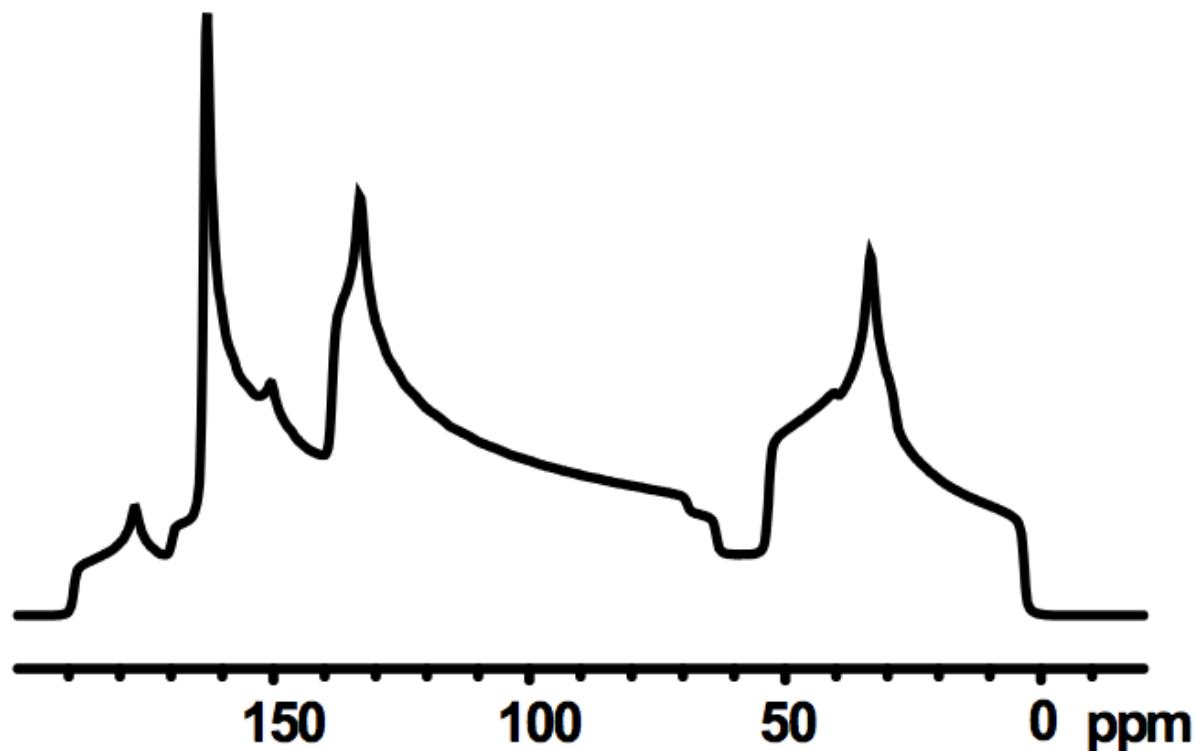
- For a powdered solid:
  - each molecule or crystallite give a characteristic shielding and frequency
  - the powder pattern is the sum of all available orientations
  - shape reflects probability of a given orientation

# Example CSA powder patterns

- Powder pattern of
  - asymmetric CSA tensor with  $k = +0.3$
- axial symmetric CSA tensor:  $k = +1.0$
- axial symmetric CSA tensor:  $k = -1.0$

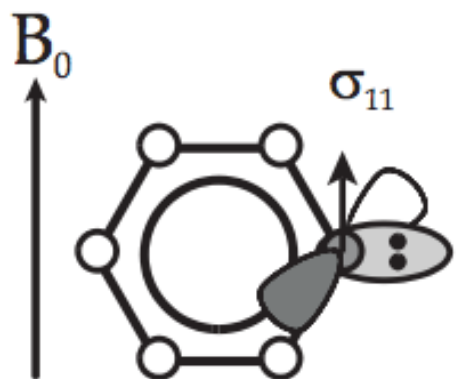


# CSA powder patterns of multiple spins



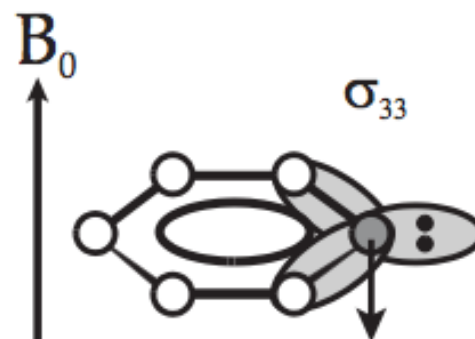
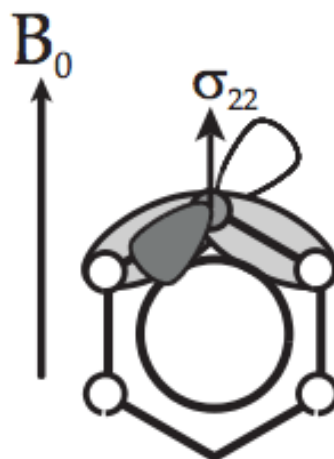
- Spectra soon become too complicated to interpret and analyse
  - principle components of chemical-shielding tensor can be determined by fitting
  - low sensitivity due to broad lines

# Why is chemical shielding anisotropic?



**deshielding**

easy mixing of ground  
and excited states

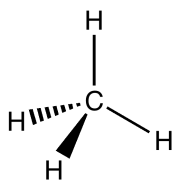
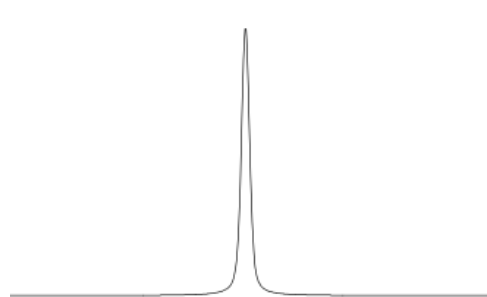


**shielding**

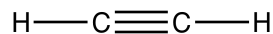
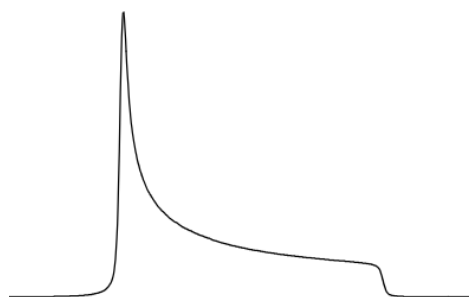
no mixing of ground  
and excited states

- Molecules have specific three-dimensional shapes and certain electron circulations (which induce magnetic fields) are preferred over others
- Molecular orbitals and crystallographic symmetry dictate the orientation and magnitude of the chemical shielding tensors

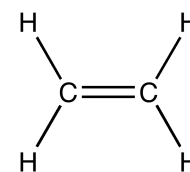
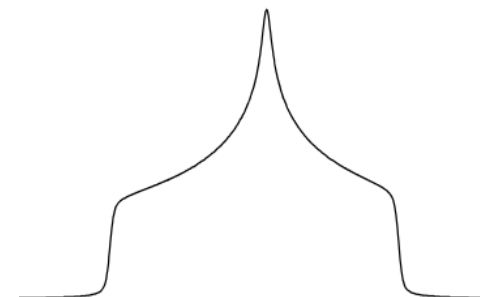
# Chemical interpretation of CSA



**Spherical symmetry**  
shielding is similar in all directions  
very small chemical-shielding anisotropy



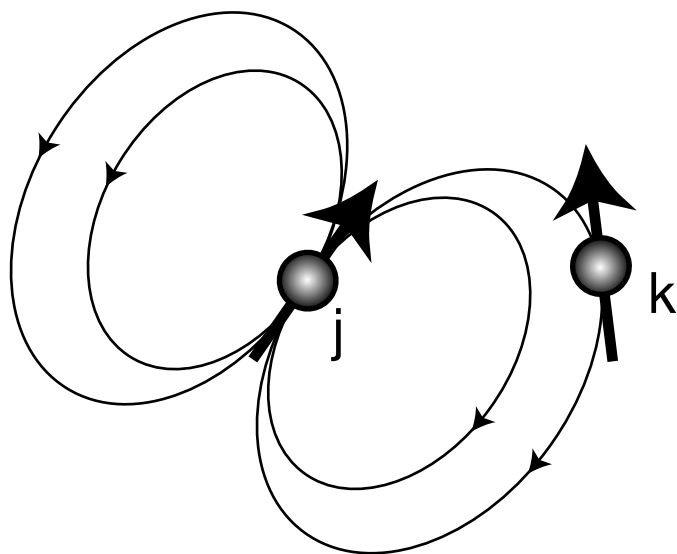
**Axial symmetry**  
max shielding when  $\parallel$  to  $B_0$   
min shielding when  $\perp$  to  $B_0$



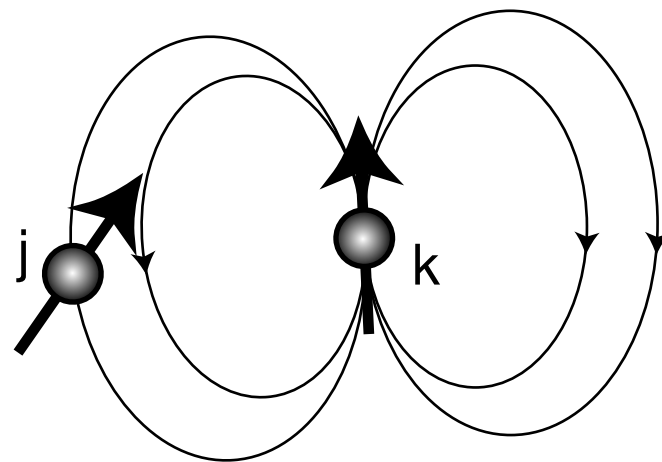
**Non-axial symmetry**  
shielding is different  
in each direction

- Typical chemical shielding tensor powder-patterns of some simple organic molecules

# Dipolar interaction



spin k experiences the magnetic field generated by spin j



spin j experiences the magnetic field generated by spin k

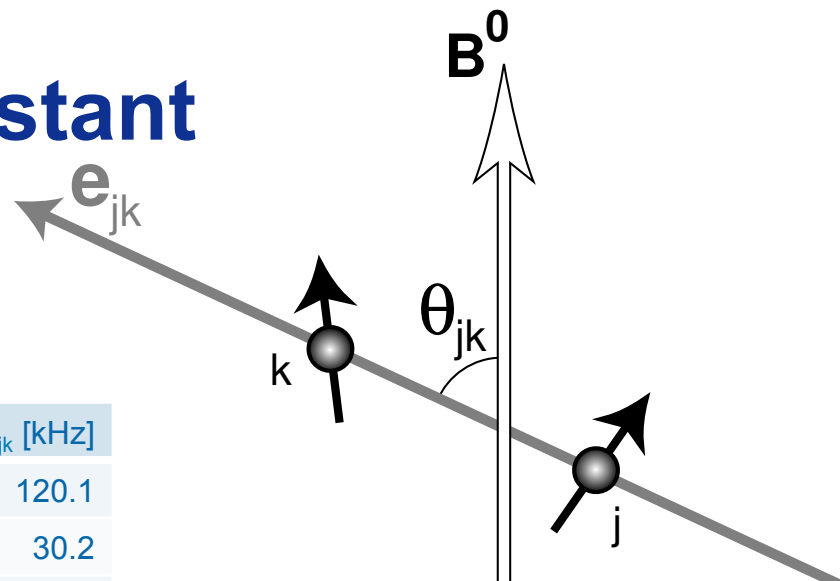
- Direct interaction of one nuclear spin with a magnetic field generated by another nuclear spin, and visa versa
  - through-space interaction, no chemical bonds needed

# Dipolar coupling constant

$$\hat{\mathbf{H}}_D^{full} = D_{jk} \left( 3(\hat{\mathbf{I}}_j \cdot \mathbf{e}_{jk})(\hat{\mathbf{I}}_k \cdot \mathbf{e}_{jk}) - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k \right)$$

$$D_{jk} = \frac{\hbar \mu_0}{4\pi} \cdot \frac{\gamma_j \gamma_k}{r_{jk}^3}$$

spins	$r_{jk}$ [Å]	$D_{jk}$ [kHz]
$^1\text{H}$ - $^1\text{H}$	1	120.1
$^1\text{H}$ - $^{13}\text{C}$	1	30.2
$^{13}\text{C}$ - $^{13}\text{C}$	1	7.6



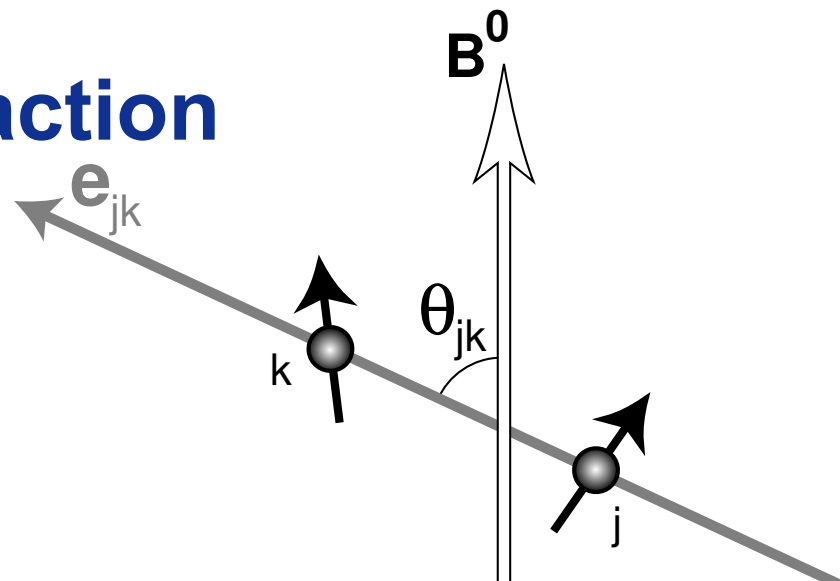
- Dipolar coupling constant:
  - represents magnitude of the dipolar interaction
  - dependent on the product of the magnetogyric ratios  $\gamma$  of the nuclei involved
  - inversely dependent on the cube of the inter-nuclear distance  $r_{jk}$
- Although  $D_{ij}$  is not orientation dependent the dipolar Hamiltonian is though the inter-nuclear vector term  $\mathbf{e}_{jk}$



# Secular dipolar interaction

$$\hat{\mathbf{H}}_D^{\text{homo}} = d_{jk} \left( 3\hat{I}_z^j \hat{I}_z^k - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k \right)$$

$$\hat{\mathbf{H}}_D^{\text{hetero}} = d_{jk} \left( 2\hat{I}_z^j \hat{I}_z^k \right)$$



- Under the secular approximation the dipolar Hamiltonian can be written using the secular dipolar coupling constant:

$$d_{jk} = D_{jk} \cdot \frac{1}{2} (3 \cos^2 \theta_{jk} - 1)$$

$$d_{jk} = 0 = D_{jk} \cdot \frac{1}{2} (3 \cos^2 \theta_{magic} - 1)$$

$$\theta_{magic} = \arctan \sqrt{2} = 54.74^\circ$$

- The secular dipolar coupling constant is
  - a function of the full dipolar coupling constant  $D_{jk}$
  - orientation dependent

# Dipolar alphabet $\hat{\mathbf{H}}_D = A + B + C + D + E + F$

$$A = +\frac{1}{1} D_{jk} (1 - 3 \cos^2 \theta) I_z^j I_z^k$$

$$B = -\frac{1}{4} D_{jk} (1 - 3 \cos^2 \theta) (I_+^j I_-^k + I_-^j I_+^k)$$

$$C = -\frac{3}{2} D_{jk} (\sin \theta \cos \theta \exp(-i\varphi)) (I_+^j I_z^k + I_z^j I_+^k) \quad D = C^*$$

$$E = -\frac{3}{4} D_{jk} (\sin^2 \theta \exp(-2i\varphi)) (I_+^j S_+^k) \quad F = E^* \quad (I_+^k)^* = I_-^k$$

$$(I_+^j)^* = I_-^j$$

- The full dipolar Hamiltonian can be expanded into the dipolar alphabet
  - has both spin operators and specially dependent terms
  - secular contributions for homonuclear spin pairs involve term A and B (flip-flop)
  - secular contributions for heteronuclear spin pairs only involve term A

# Dipolar interaction tensor

$$\overline{D}^{PAS} = -2D_{jk} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- Dipolar interaction tensor is:

- symmetric: so the interaction is the same for both the coupled nuclei
- traceless: so there is no isotropic dipolar coupling
- no isotropic coupling for rapid isotropic tumbling can be proved by integrating over all possible orientation (integration over a sphere)

$$\int_0^\pi \sin \theta_{jk} \cdot (3 \cos^2 \theta_{jk} - 1) d\theta_{jk} = 0$$

# Dipolar powder patterns

- The dipolar coupling gives rise to tensor orientation dependent frequency shifts with respect to the magnet field:

$$\nu_D^{\text{hetero}} = \nu_0 \pm \frac{1}{2} D_{jk} (3 \cos^2 \theta - 1) \qquad \nu_D^{\text{homo}} = \nu_0 \pm \frac{3}{4} D_{jk} (3 \cos^2 \theta - 1)$$

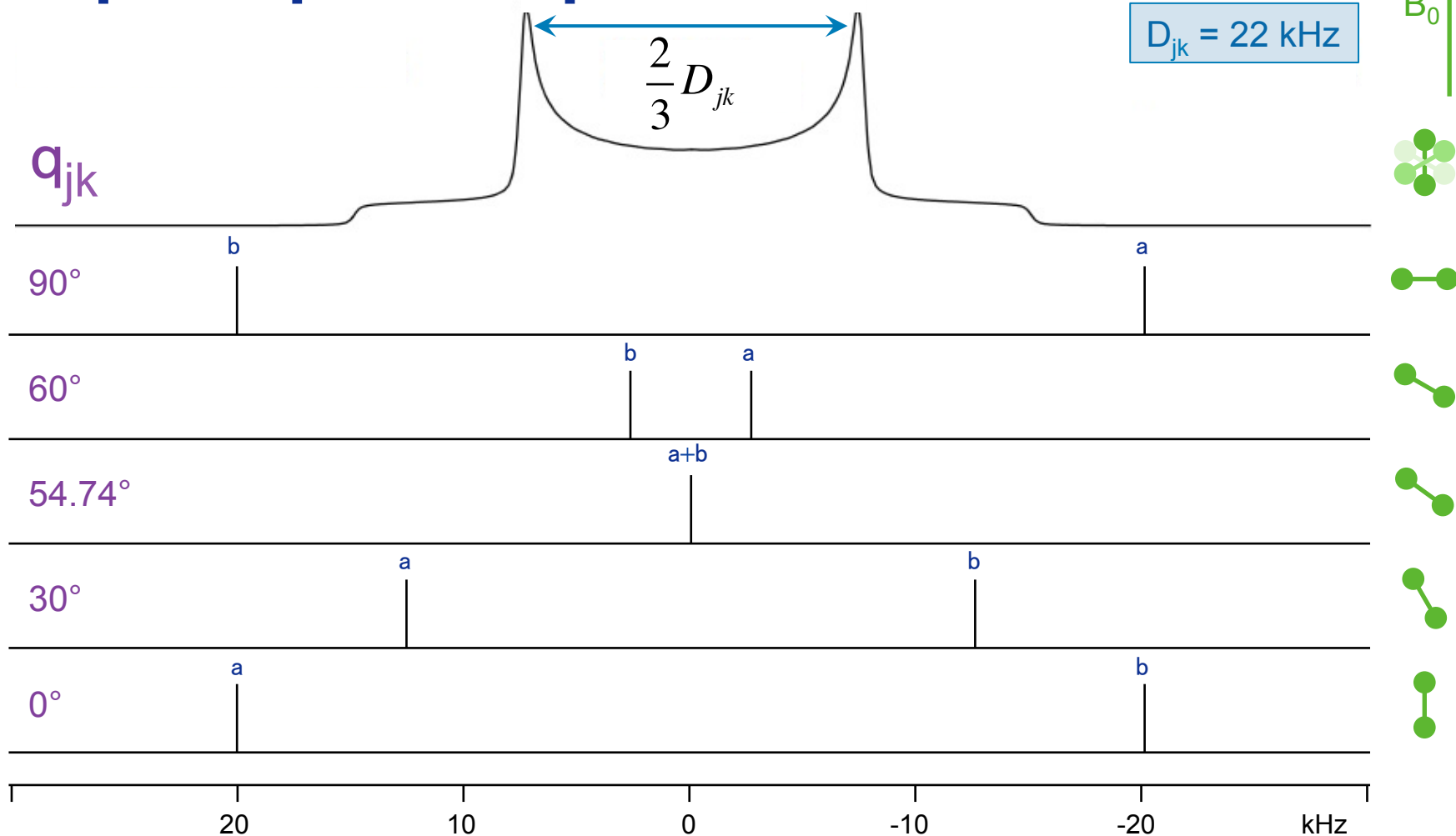
- Note similarity between symmetric ( $h_{CS} = 0$ ) CSA function:

$$\nu_{CS} = \frac{\delta_{CS}}{2} (3 \cos^2 \theta - 1 - \eta_{CS} \cdot \sin^2 \theta \cos^2 2\phi)$$

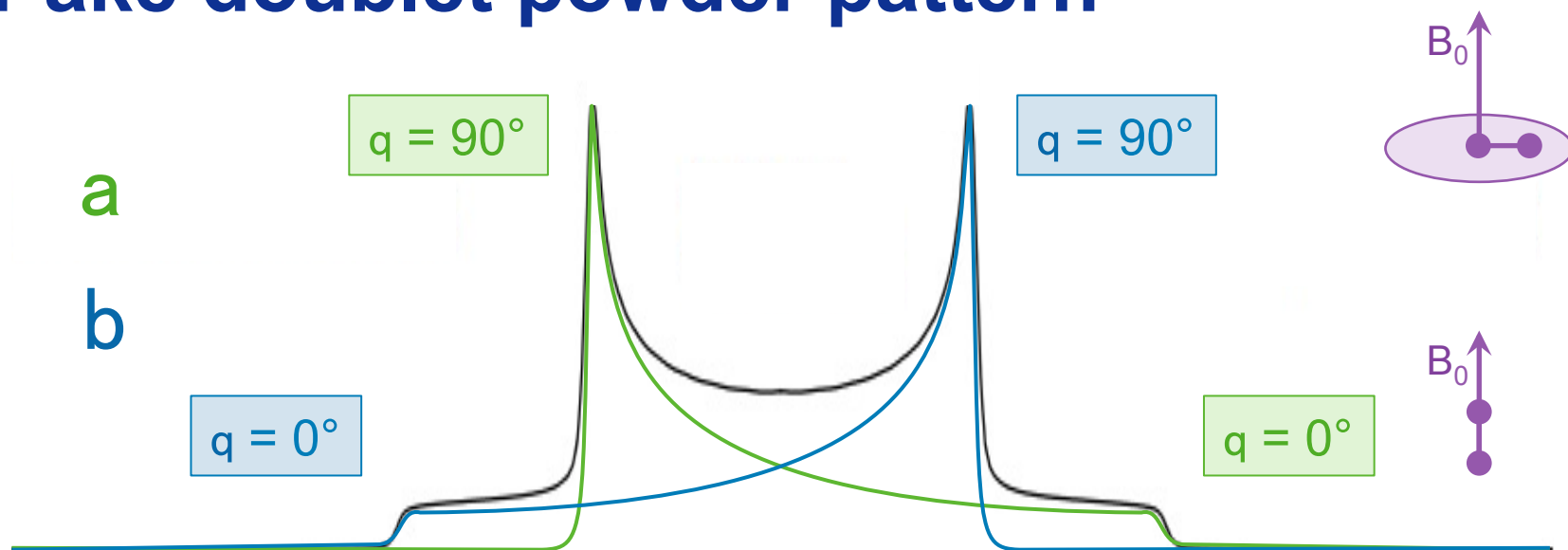
- Both the secular homonuclear and heteronuclear dipolar Hamiltonians are orientation dependant
  - the spatial part will have an effect on the spectrum (board lines)
  - coupled spin pairs will a powder patterns

# Dipolar powder patterns

$$D_{jk} = 22 \text{ kHz}$$

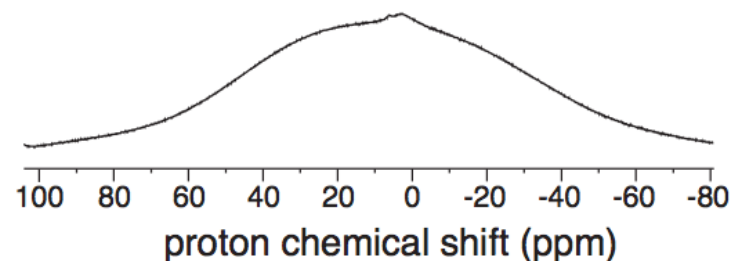
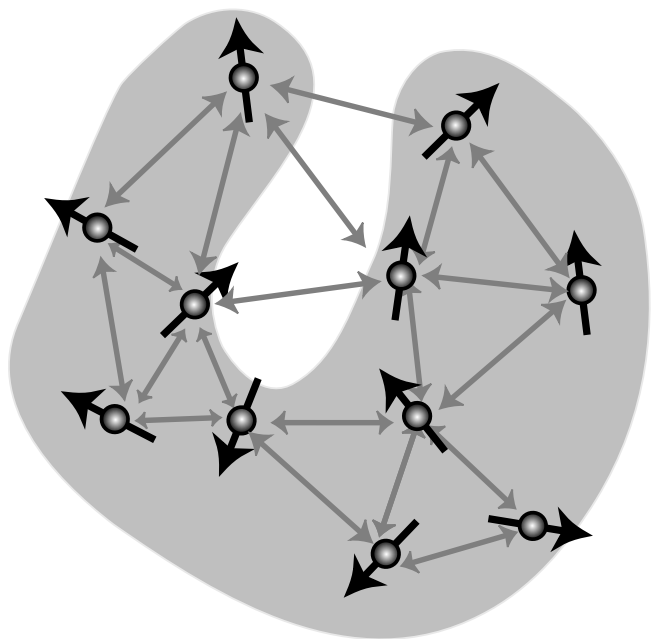


# Pake doublet powder pattern



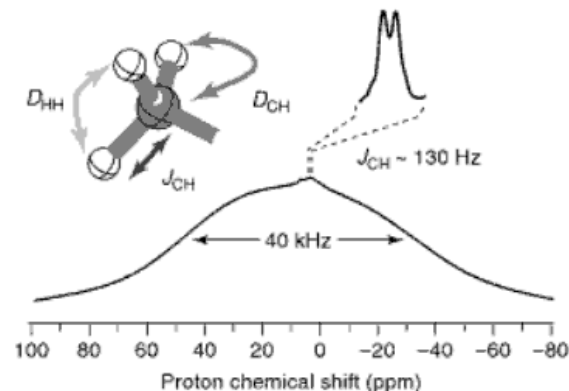
- First observed in the  $^1\text{H}$  solid-state NMR spectrum of  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ 
  - composed of two sub-spectra from the a and b spin state of the coupled nucleus
  - different frequencies arise from  $(3 \cos^2 q - 1)$  orientation dependence
  - different intensities arise from  $\sin q$  weighting (integration over sphere)
    - $q = 0^\circ$  only one possible orientation of the inter-nuclear vector: weighting =  $\sin q = 0$
    - $q = 90^\circ$  many orientations about plane perpendicular to  $B_0$ : weighting =  $\sin q = 1$

# Dipolar coupling & multi-spin effects



- Very rare to find isolated spin pairs in the solid-state
- $^1\text{H}$ - $^1\text{H}$  is very strong so in practice all protons are coupled
  - all protons are coupled together and lead to complex multi-spin interactions
  - possible for all isolated dipolar coupled spins ( $^1\text{H}$ - $^1\text{H}$ ,  $^{13}\text{C}$ - $^1\text{H}$ )

# The direct spin-spin interaction



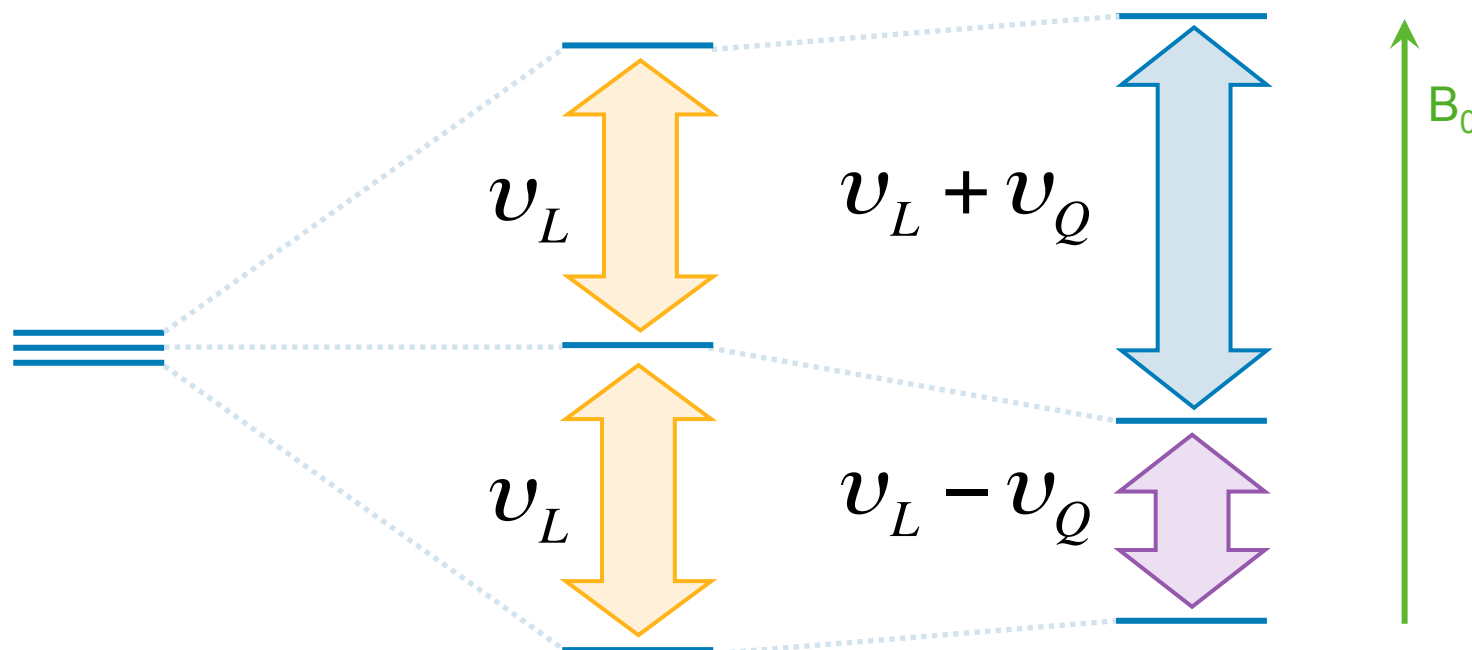
- With respect to solid-state NMR:
  - J-coupling still exists but is just difficult to directly observe in spectra as they are broad
  - can still be used to transfer polarisation in a coherent way (INEPT) but is weak
  - like the direct dipolar interaction the indirect interaction is anisotropic
  - J-anisotropy is weak though and difficult to detect
- Recently more work has been done using the J-coupling interaction in the solid to probe hydrogen bonding



# NMR of quadrupolar nuclei ( $I > 1/2$ )

- Zeeman interaction:
  - higher spin quantum numbers result in more energy states and more transitions
  - without further interactions the multiple transitions are equal in energy
- Quadrupolar coupling interaction
  - the coupling of the nuclear spin with the electric field of the molecule
  - causes a deviation in the Zeeman levels
  - can be very very strong (MHz) and can common approximations to breakdown
- Solution-state NMR of quadrupoles
  - tumbling averages quadrupolar interaction but rapid relaxation results in broad lines

# Zeeman & quadrupolar interaction of $I=1/2$



- For  $I = 1$  there are three energy levels and two identical transitions
  - quadrupolar interaction breaks the degeneracy of the two transitions

# Why bother with quadrupolar NMR?

*Most abundant isotopes only*

H	Spin-half dipoles																He
Li	Be	Integer quadrupolar spins										B	C	N	O	F	Ne
Na	Mg	Half-integer quadrupolar spins										Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Spin-half dipoles

Integer quadrupolar spins

Half-integer quadrupolar spins

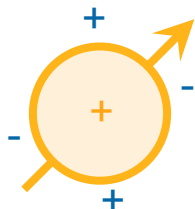
- About 75% of all NMR active nuclei are half-integer quadrupoles

# Solid-state NMR of quadrupoles

- Advances in NMR hardware and pulse sequences have opened up these nuclei for analysis in the solid-state.
  - the broadening quadrupolar interaction is now exploited to provide valid information
  - solid-state NMR of half-integer quadrupolar nuclei is relatively accessible
  - the only integer quadrupolar nuclei investigated are  $^2\text{H}$  (very common) and  $^{14}\text{N}$
- Solution-state NMR of quadrupoles
  - tumbling averages quadrupolar interaction but rapid relaxation results in broad lines

# Quadrupolar nuclei

electric field gradient in molecule



Spin-half nucleus



oblate  $eQ < 0$



prolate  $eQ > 0$

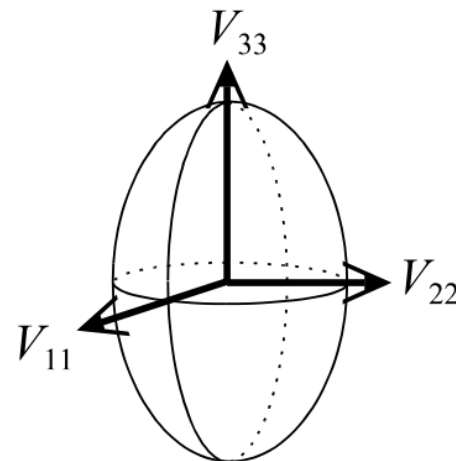
Quadrupolar Nuclei

- Quadrupolar nuclei have
  - a spin quantum number  $> 1/2$
  - an asymmetric distribution of nucleons which gives rise to a non-spherical positive electric charge distribution c.f. dipoles with a spherical charge distribution ( $^{209}\text{Pb!}$ )
- The asymmetric charge distribution is described by the nuclear electric quadrupole moment  $eQ$  which is an intrinsic property to a nucleus
- Quadrupolars interact with electric field gradients in the molecule

# Electric field gradient tensor

$$\bar{V} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}$$

$$\bar{V}^{PAS} = \begin{bmatrix} V_{11} & 0 & 0 \\ 0 & V_{22} & 0 \\ 0 & 0 & V_{33} \end{bmatrix}$$



- The electric field gradients at the quadrupolar nucleus can be described by a symmetric traceless tensor, which can be diagonalised
  - the principle components of the EFG are defined as  $|V_{11}| \leq |V_{22}| \leq |V_{33}|$
  - as  $V$  is traceless isotropic tumbling averages the EFG tensor to zero

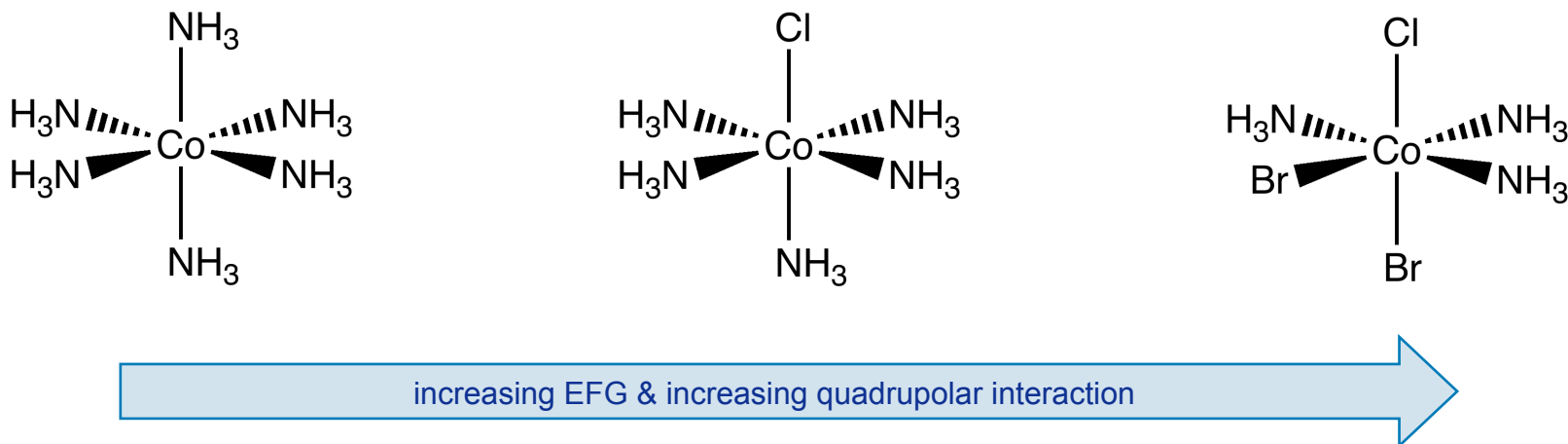
# Nuclear quadrupole coupling constant

$$C_Q = \frac{eQ}{h} \cdot V_{33}$$

$$\eta_Q = (V_{11} - V_{22}) / V_{33}$$

- The magnitude of the quadrupolar interaction is defined by the nuclear quadrupole coupling constant  $C_Q$ 
  - $C_Q$  is typically of the order of kHz or MHz
- The asymmetry of the quadrupolar interaction is defined by the asymmetry parameter  $\eta$ 
  - the asymmetry parameter ranges between  $0 \leq \eta_Q \leq 1$
  - for systems with an axially symmetric EFG  $\eta_Q = 0$

# Chemical origin of EFGs



## ■ In general:

- for a quadrupolar nucleus at the centre of a spherically symmetric molecule the EFGs cancel resulting in very small EFGs at the quadrupolar nucleus
- as the spherical symmetry breaks down the EFGs at the quadrupolar nucleus will grow in magnitude

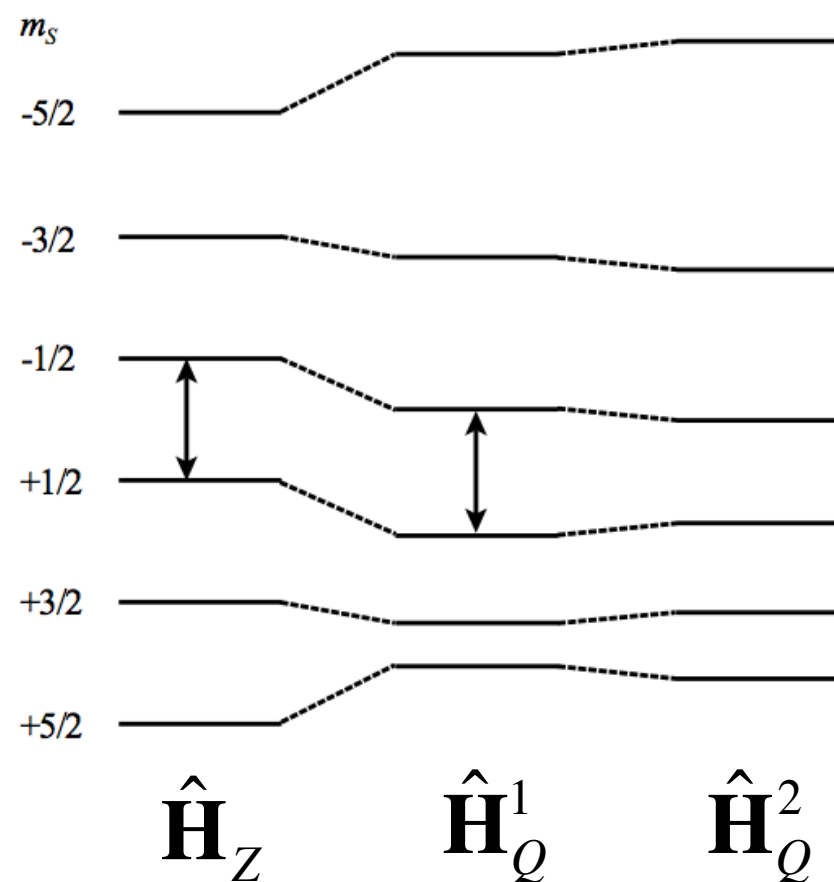


# 1<sup>st</sup> and 2<sup>nd</sup> order quadrupolar interactions

- Unlike all other anisotropic NMR interaction the quadrupolar can be written as a sum of first and second order interactions:

$$\hat{\mathbf{H}}_Q = \hat{\mathbf{H}}_Q^1 + \hat{\mathbf{H}}_Q^2$$

- The first-order interaction is proportional to  $C_Q$
- The second-order interaction is proportional to  $C_Q^2/u_0$  and is much smaller
- first order interaction does not effect the central transition for half-integer quadrupoles



# 1<sup>st</sup> order quadrupolar Hamiltonian

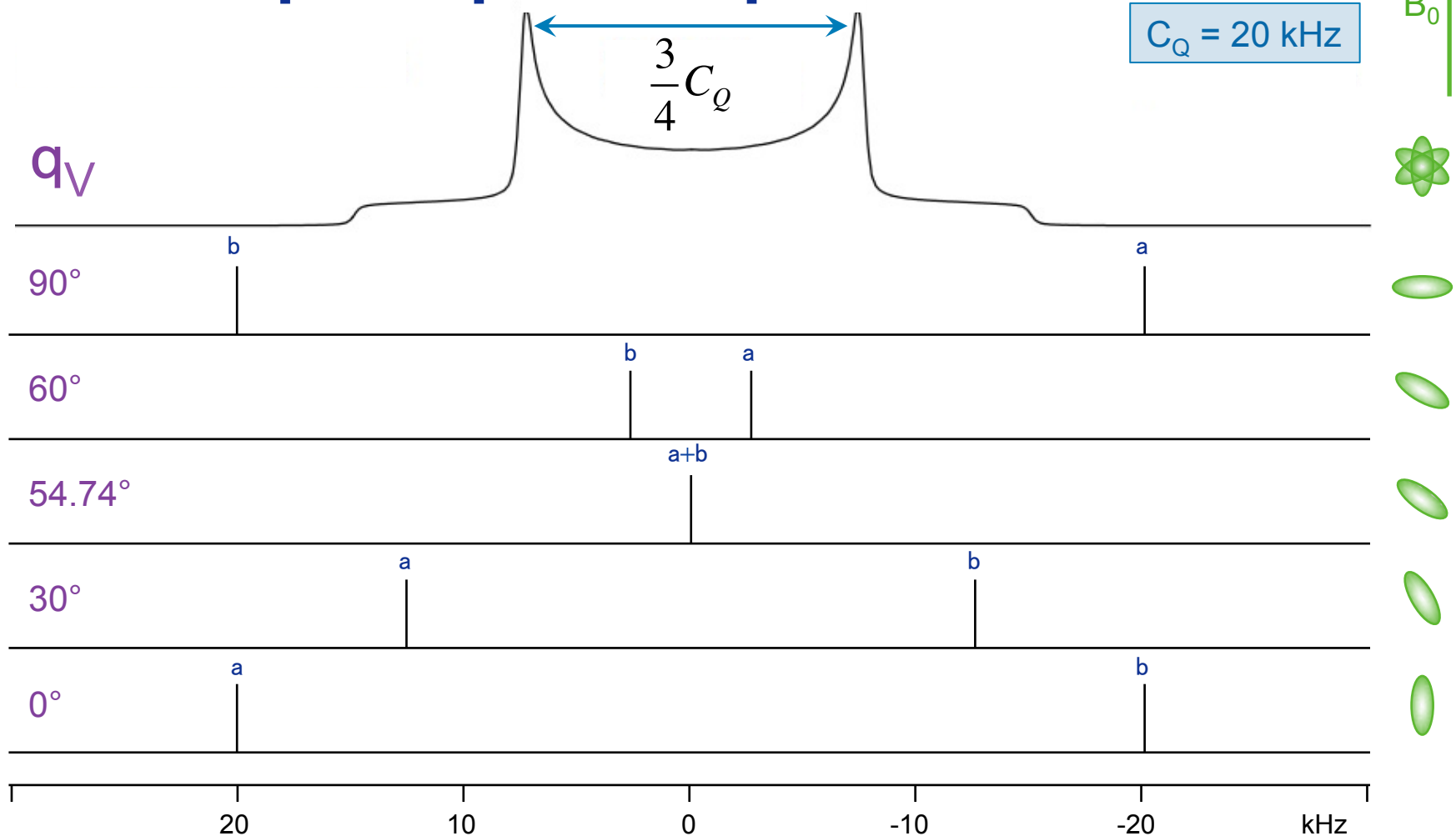
$$\hat{\mathbf{H}}_Q^1 = \frac{1}{2} Q' \left( I_z^2 - \frac{1}{3} I(I+1) \right)$$

$$Q' = \frac{\omega_Q}{2} \left( 3 \cos^2 \theta - 1 - \eta_Q \cdot \sin^2 \theta \cos^2 2\phi \right) \qquad \omega_Q = \frac{3e^2 q Q}{\hbar \cdot 2I(2I-1)}$$

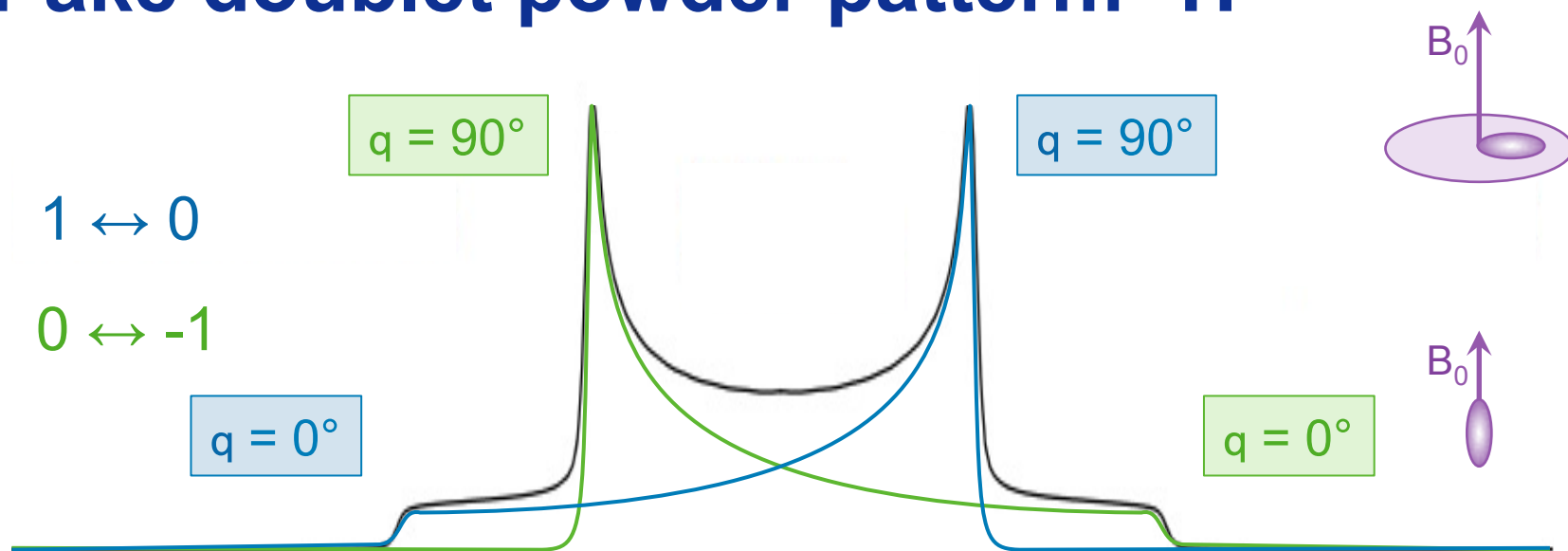
- The first order quadrupolar Hamiltonian is orientation dependant
- It is convened to also define the quadrupolar frequency  $\omega_Q$
- If the quadrupolar interaction is large it can no longer be treated as just a perturbation of the Zeeman Hamiltonian

# Quadrupolar powder pattern $^2\text{H } I = 1$

$C_Q = 20 \text{ kHz}$

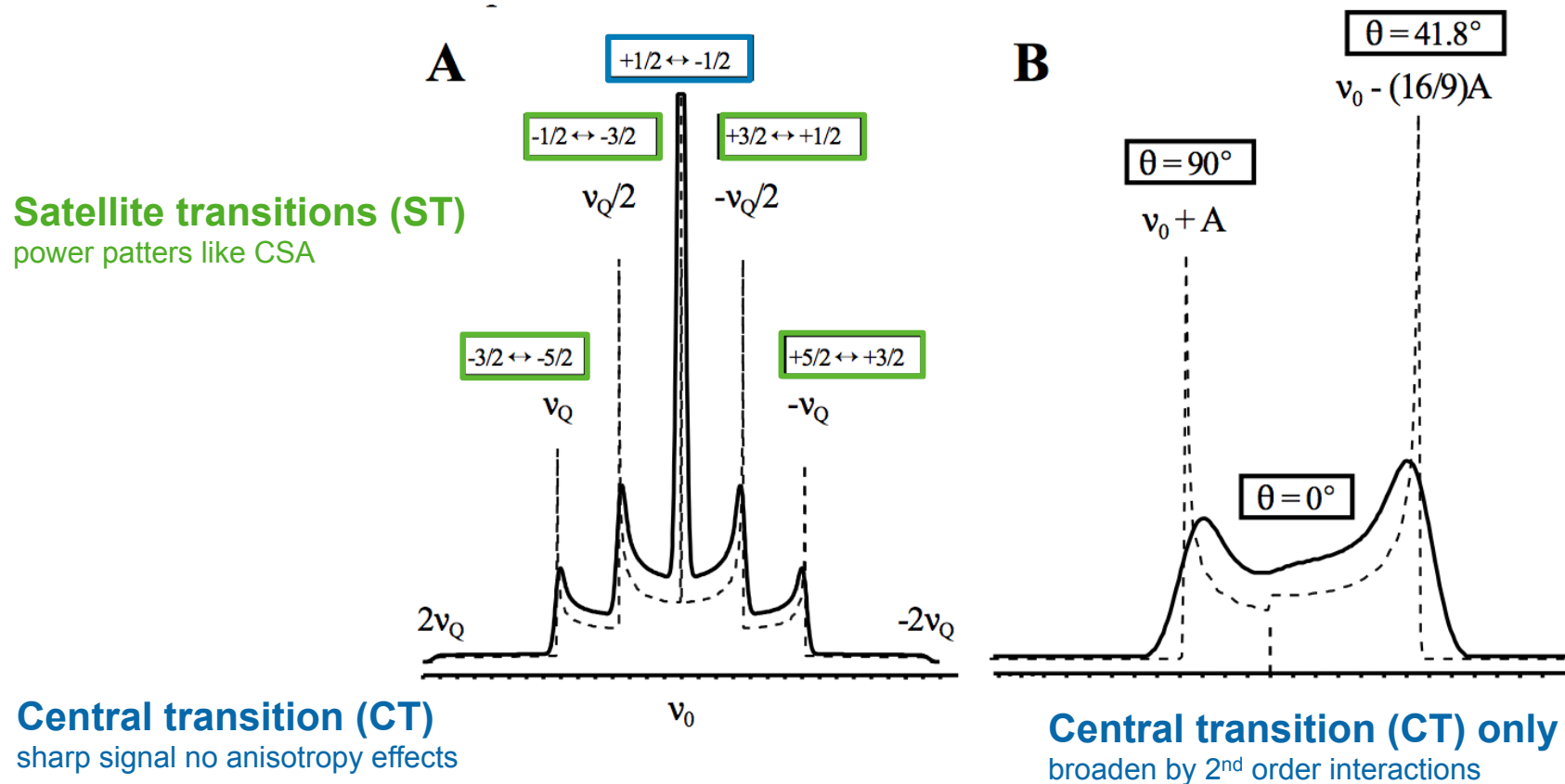


# Pake doublet powder pattern: $^2\text{H}$



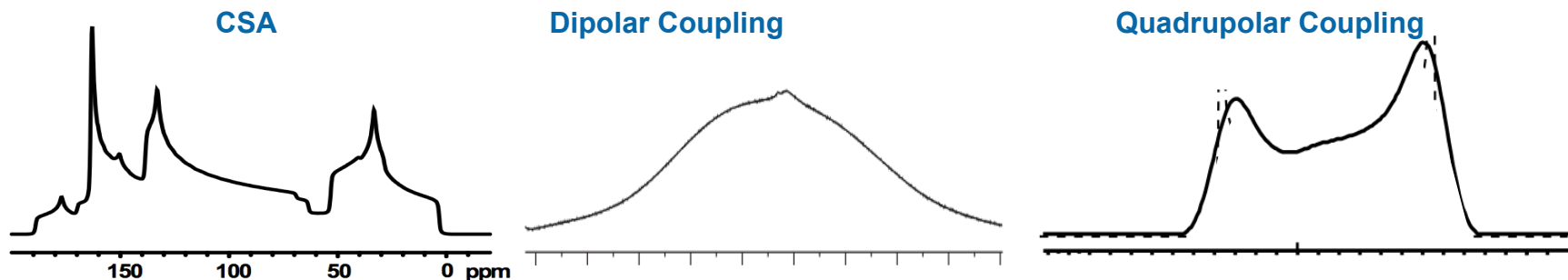
- Observed in  $^2\text{H}$  solid-state NMR spectra
  - composed of two sub-spectra from the two zeeman transition ( $1 \leftrightarrow 0$  &  $0 \leftrightarrow -1$ )
  - different frequencies arise from  $(3 \cos^2 q - 1)$  orientation dependence
  - different intensities arise from  $\sin q$  weighting (integration over sphere)
    - $q = 0^\circ$  only one possible orientation of the inter-nuclear vector: weighting =  $\sin q = 0$
    - $q = 90^\circ$  many orientations about plane perpendicular to  $B_0$ : weighting =  $\sin q = 1$

# Quadrupolar powder patterns $I=5/2$

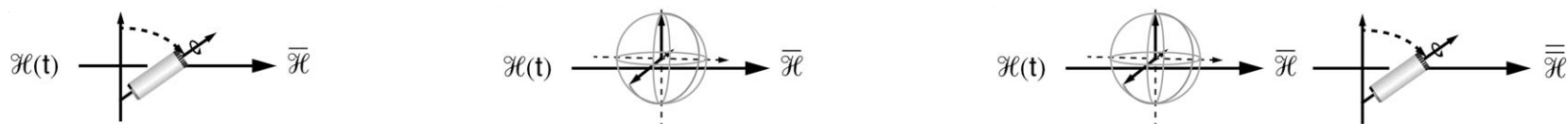


- Sample A is first order only but sample B is second order with large  $C_Q$

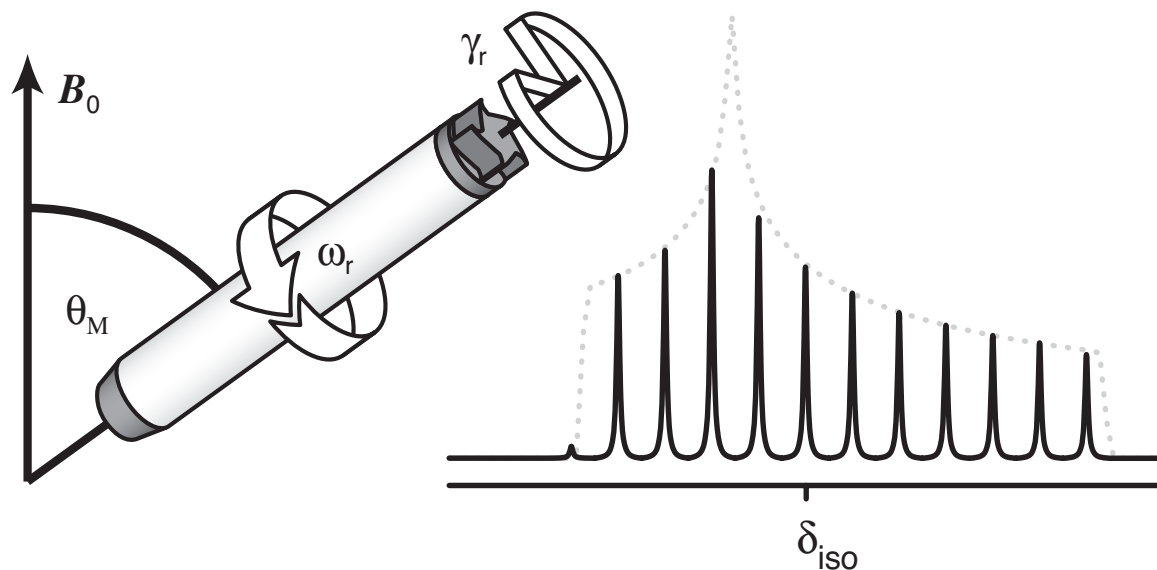
# High-resolution solid-state NMR



- Hamiltonian can be expressed as product of two parts:
  - space-part: components that can be manipulated by physical rotation
  - spin-part: components that can be manipulated by RF pulses



- Can remove influence of anisotropic interactions by creation of an average Hamiltonian during NMR experiment or signal detection
  - can either average space part (sample rotation), spin-part (RF) or both



# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

## **SOLID-STATE NMR SPECTROSCOPY**

## **METHODS & HARDWARE**

# Historical aspects of solid-state NMR

- First work on solid-state NMR focused on  $^1\text{H}$  and  $^{19}\text{F}$  NMR (sensitivity)
  - anisotropic dipolar coupling resulted in broad  $^1\text{H}$  spectra with no resolved lines
  - The only useful cases where for
    - isolated homonuclear spin pairs (e.g. crystal  $\text{H}_2\text{O}$ )
    - fast moving methyl groups which undergo rapid motion even in the solid
- Initial work focused on only measurement of  $^1\text{H}$  spin-lattice relaxation
  - investigate methyl group rotation or polymer chain motion as a function of temperature
- Breakthrough came when E.R. Andrew (1958) and I.J. Lowe (1959) showed that anisotropic dipolar interactions could be suppressed by physical sample rotation during an NMR experiment (artificial motion)
  - technique involved rotating a solid about an axis oriented at  $54.74^\circ$  to  $B_0$  field
  - became known as magic-angle spinning (MAS) and still is the most important method

E. R. Andrew, A. Bradbury, R. G. Eades. Nuclear Magnetic Resonance Spectra from a Crystal Rotated at High Speed. Nature 182, 1659 (1958).

I. J. Lowe. Free Induction Decays of Rotating Solids. Phys. Rev. Lett. 2, 285–287(1959).

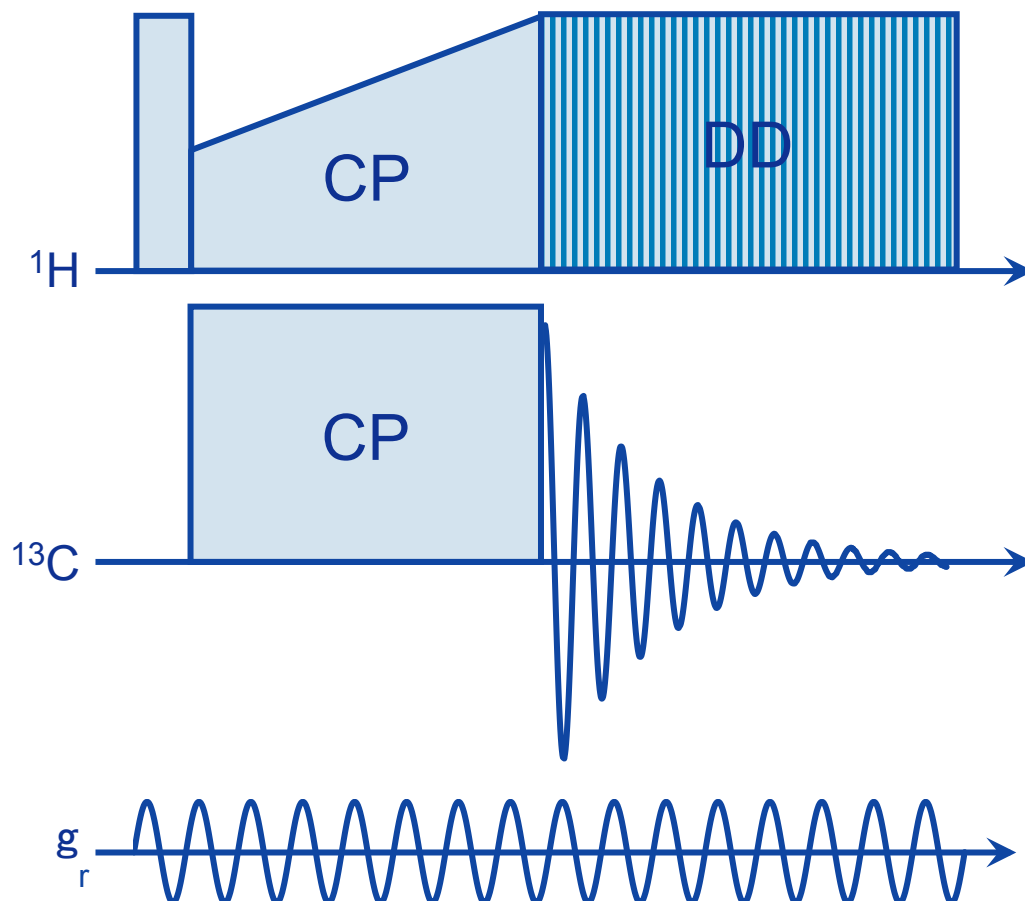


# High resolution solid-state NMR



- Key techniques to address anisotropic line broadening and sensitivity:
  - Dilution
    - at high dilution homonuclear dipolar interaction is weak ( $r^{-3}$ ) occurs naturally for some nuclei ( $^{13}\text{C}$ )
    - only useful no large CSA or strong heteronuclear interactions ( $^1\text{H}$  or  $^{19}\text{F}$ )
  - Magic angle spinning (MAS)
    - rapid spinning of the sample at  $54.74^\circ$  to  $B_0$  to average the space-part of Hamiltonian
    - limited use for high  $\gamma$  nuclei ( $^1\text{H}$ ,  $^{19}\text{F}$ ) where  $D_{ij} > 100$  kHz whereas standard MAS 2-35 kHz
  - Multi-pulse sequences
    - rapid manipulation of spin operators to averages the spin-part of the Hamiltonian
    - heteronuclear dipolar decoupling (very common) or homonuclear dipolar decoupling (rare)
  - Cross-polarisation (CP)
    - transfer of polarisation from abundant spin ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) to dilute or rare nuclei ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{29}\text{Si}$ )
    - enhances signal and reduce relaxation delay between successive experiments

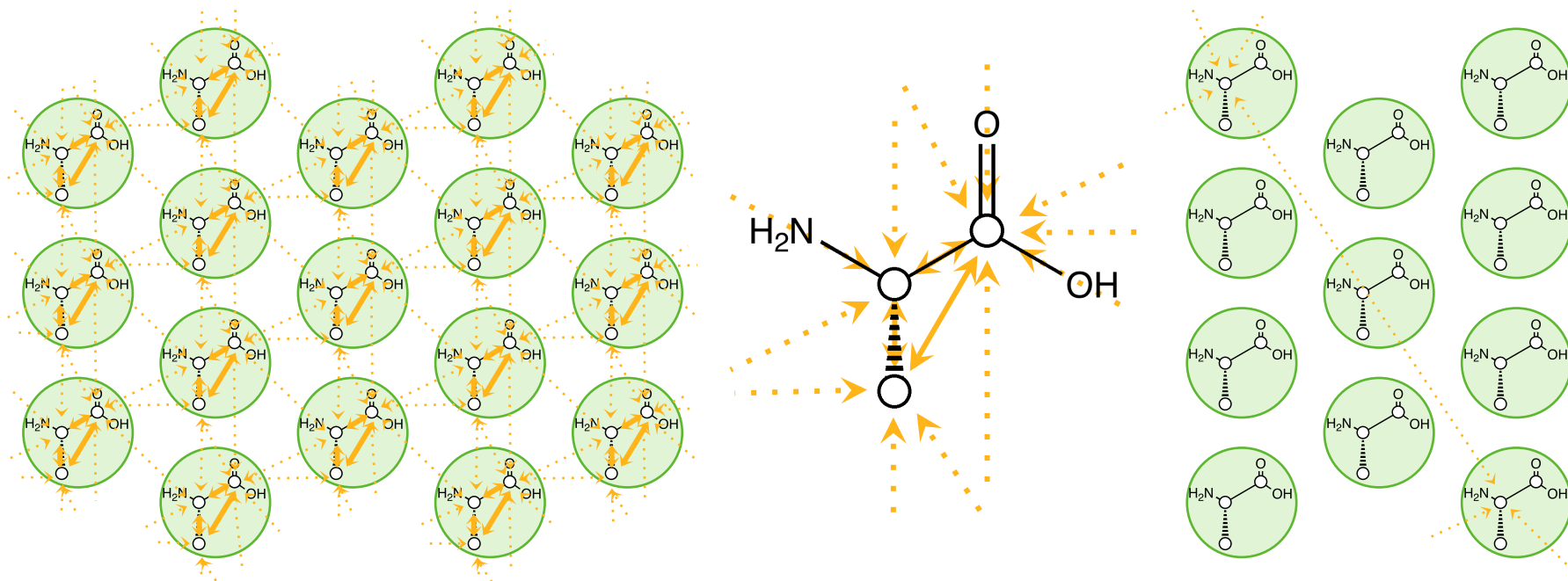
# A combined approach

- Combine methods for maximum sensitivity and resolution
  - cross-polarisation (CP)
  - rare nuclei ( $^{13}\text{C}$ )
  - magic angle spinning (MAS)
  - multi-pulse heteronuclear dipolar decoupling (DD)
- $^1\text{H}$ - $^{13}\text{C}\{^1\text{H}\}$  CPMAS
  - most common solid-state NMR experiment (by far)
  - standard method (easy setup)



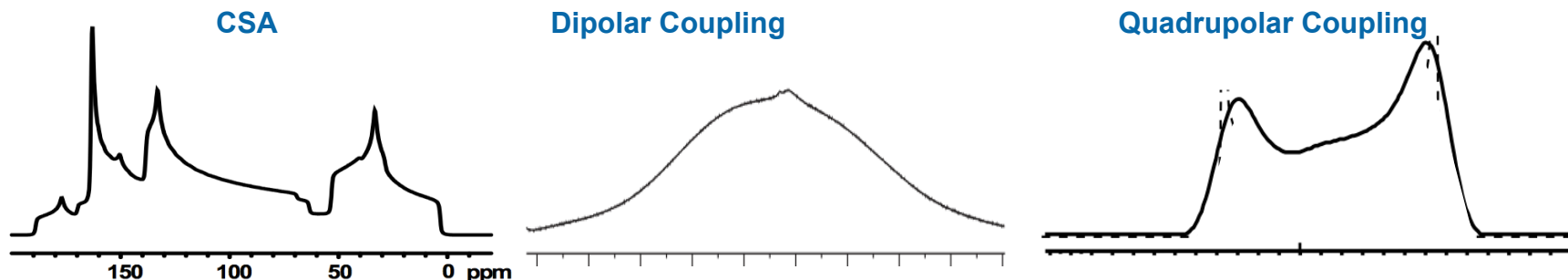
# Dilution

 intra-molecular dipolar coupling  
 inter-molecular dipolar coupling

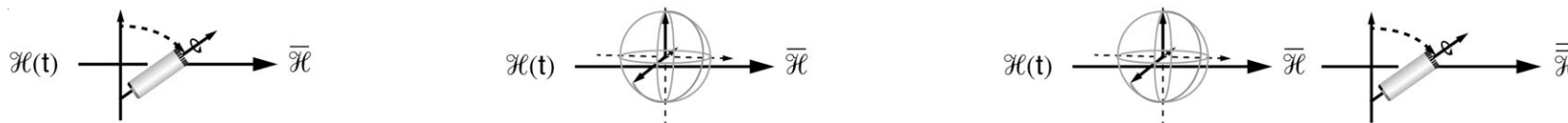


- At high dilution homonuclear dipolar interaction are weak due to the  $r^{-3}$ 
  - It is good thing that  $^{13}\text{C}$  is only naturally abundant at 1.108%
  - consider a uniformly  $^{13}\text{C}$  labelled crystalline solid small molecule L-alanine
  - only three intra-molecular interactions but many inter-molecular dipolar interactions

# High-resolution solid-state NMR

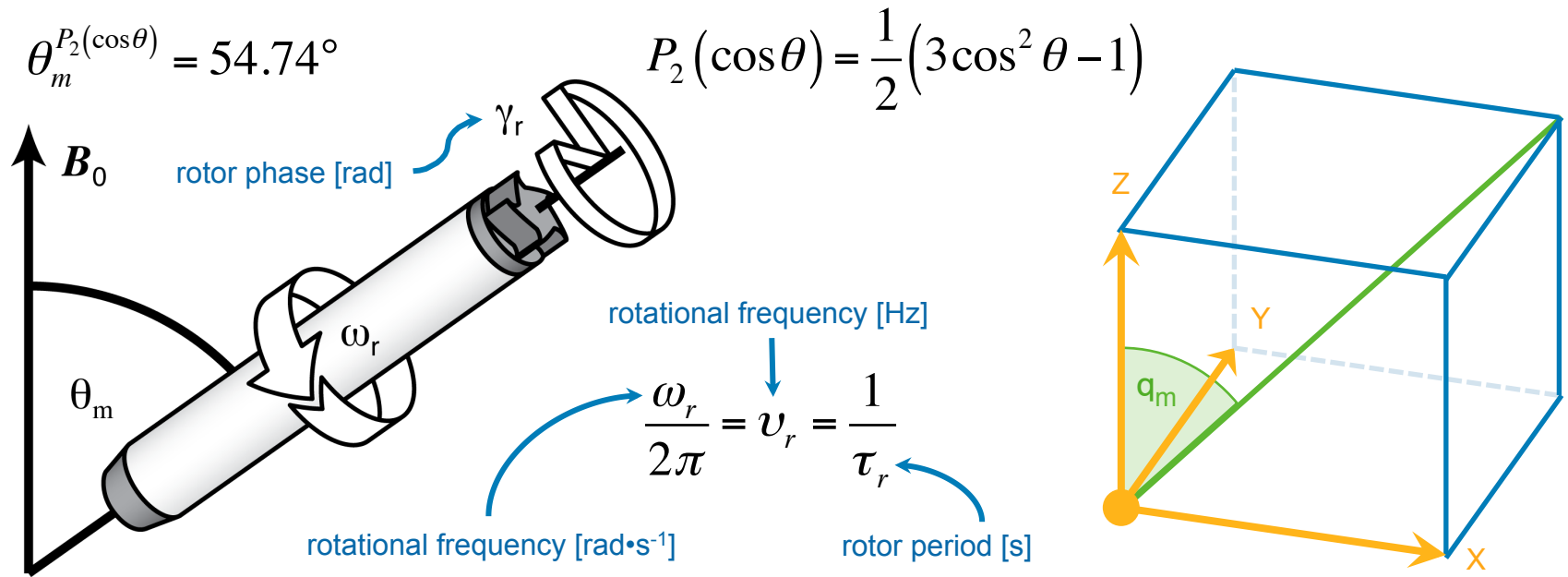


- Hamiltonian can be expressed as product of two parts:
  - space-part: components that can be manipulated by physical rotation
  - spin-part: components that can be manipulated by RF pulses



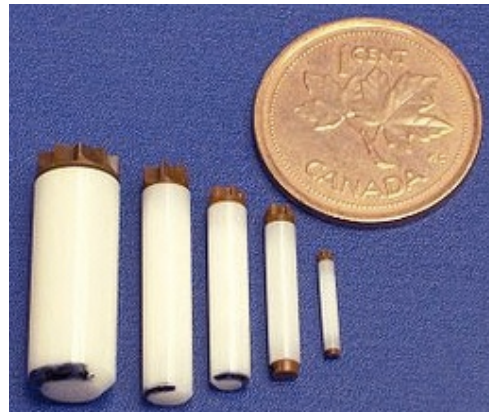
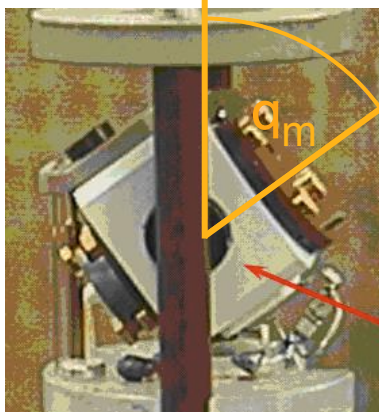
- Can remove influence of anisotropic interactions by creation of an average Hamiltonian during NMR experiment or signal detection
  - can either average space part (sample rotation), spin-part (RF) or both

# Magic-angle spinning MAS theory



- Imparts artificial motion to the sample by spinning it at about an axis orientated to the  $B_0$  field by the magic angle of  $P_2(\cos\theta)$ :  $q_m = 54.74^\circ$ 
  - if  $\nu_r > \nu_{\text{int}}$  anisotropy is averaged to its isotropic value (0,  $s_{\text{iso}}$ )
    - $d_{\text{CS}}^{13\text{C}} \approx 1\text{--}20$  ppm (2 kHz@9.4T c.f. 2.5 kHz@11.7T),  $D_{\text{HC}} \approx 21$  kHz,  $D_{\text{HH}} \approx 60$  kHz
  - typical  $\nu_r = 15$  kHz but commercial probes range from  $\nu_r = 1\text{--}65$  kHz  $t_r = 1\text{--}65$   $\mu\text{s}$

# Magic-angle spinning MAS practice

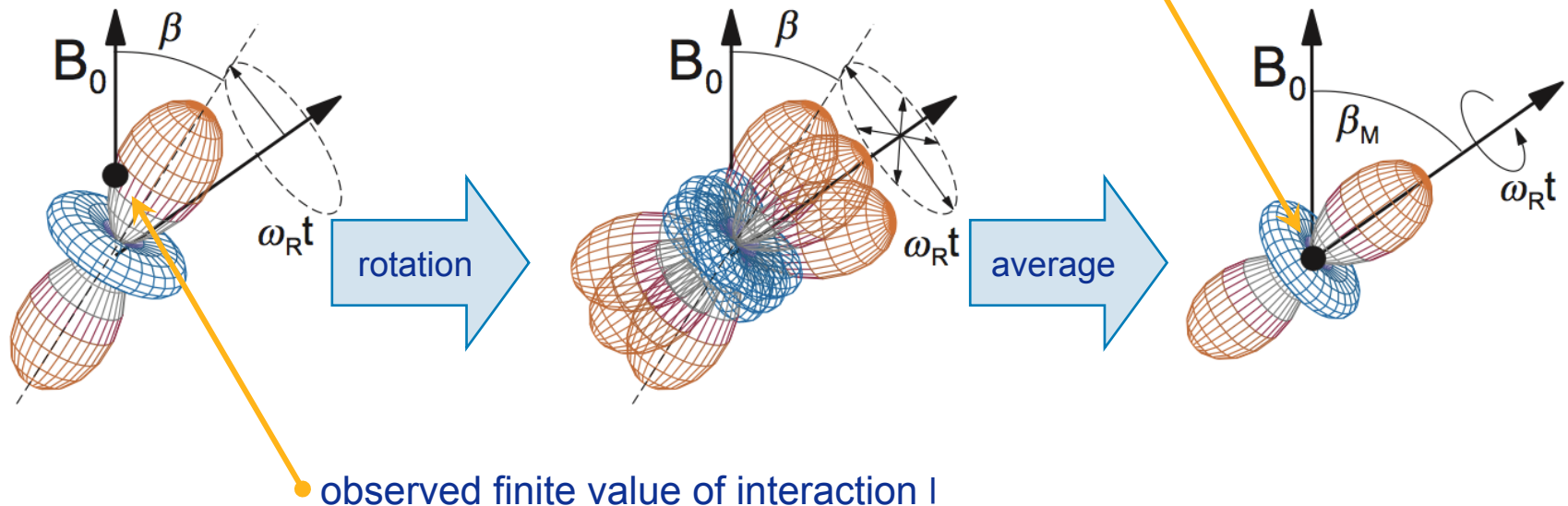


OD [mm]	$u_r^{\text{MAX}}$ [kHz]
7.0	7
4.0	18
3.2	25
2.5	35
1.8	60

- MAS is technically very demanding (high performance engineering)
  - ceramic rotor levitated in ceramic stator on air bearing (bearing gas feed)
  - rotor rotated by applying drive gas to fins on rotor cap (drive gas feed)
- Limited by outer edge reaching the speed of sound (sonic boom)
  - smaller outer diameter (OD) rotors can spin a higher rotational frequencies
- Need very cylindrically symmetric sample containers and samples
  - ceramics zirconia ( $\text{ZrO}_2$ ) or silicon nitride ( $\text{SiN}$ ) accurately moulded then fired
  - sample need to be symmetric too i.e. fine powder or packed symmetrically (tedious)

# Magic-angle spinning MAS practice

observed isotropic value of interaction of  $I_{iso}$



- MAS does NOT remove the interactions only their observable effects
  - the CSA, dipolar interaction and quadrupolar interaction are still there
  - we just observe an their average Hamiltonian during signal acquisition
  - our recorded spectrum does not show the effects of anisotropy

# What interaction does MAS address

- MAS averages all anisotropic interactions which have orientation dependence described by a second rank tensor
  - proportional to the second Legendre polynomial  $P_2(\cos\theta)$ :

- homonuclear dipolar coupling
- heteronuclear dipolar coupling
- chemical-shielding anisotropy
- first-order quadrupolar coupling

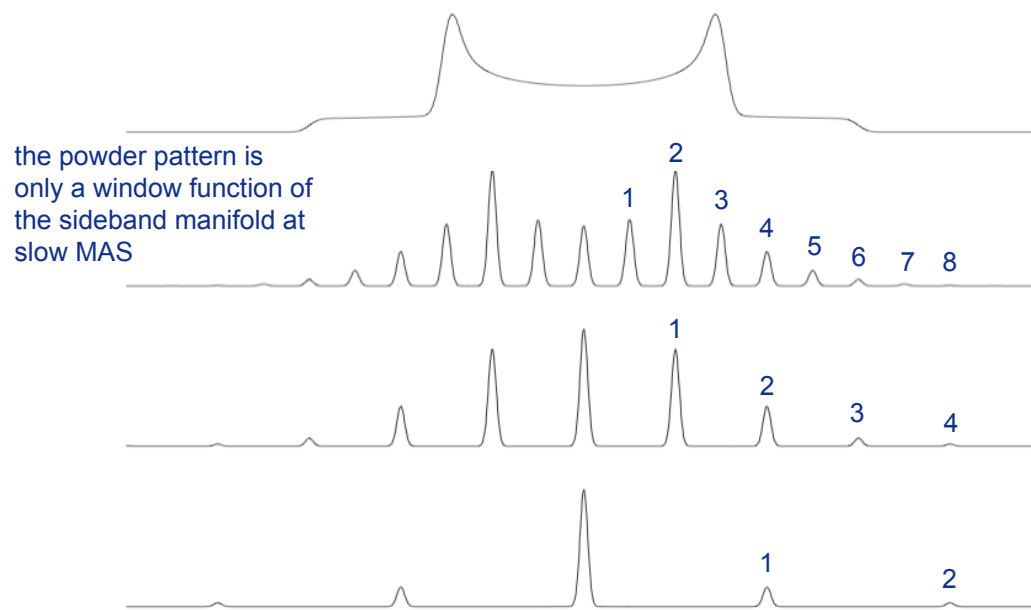
$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$\hat{\mathbf{H}} \propto (3\cos^2\theta - 1)$$

- MAS only partially or incompletely averages anisotropic interactions which have orientation dependence described by higher order tensors
  - second-order quadrupolar coupling ( $P_2(\cos\theta) + P_4(\cos\theta)$ )
  - Alternative forms of sample rotation or pulse sequences can be used to address these
    - dynamic-angle spinning (DAS) & double-rotation (DOR)
    - multiple-quantum magic-angle spinning (MQMAS)



# MAS & dipolar coupling: spin pair



$u_r = 0$  kHz: static powder pattern

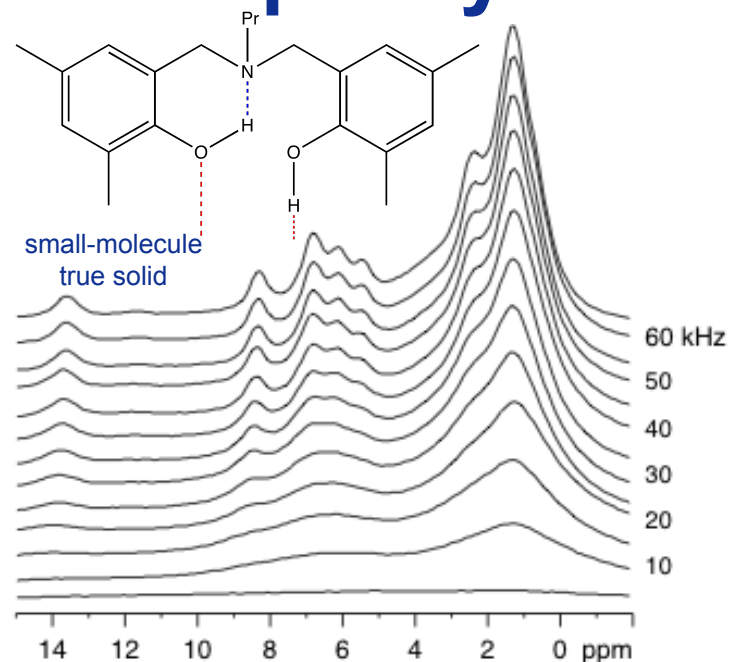
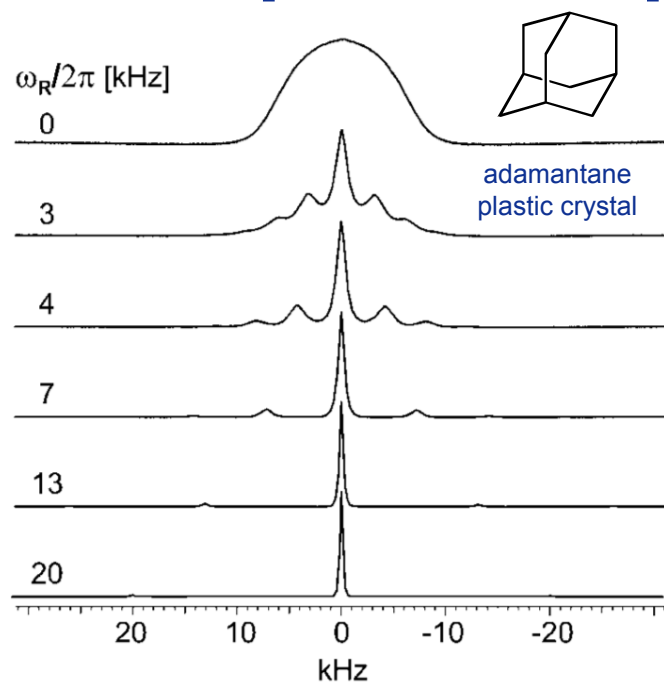
$u_r = 10$  kHz: MAS side-band pattern (8<sup>th</sup>)

$u_r = 20$  kHz: MAS side-band pattern (4<sup>th</sup>)

$u_r = 40$  kHz: MAS side-band pattern (2<sup>nd</sup>)

- Dipolar coupling of a spin pair leads to characteristic Pake pattern
  - coupling is said to be homogeneous
  - powder pattern is made up of many individual sharp lines from isolated crystallites
  - when  $u_r < D_{ij}$  MAS localises intensity into multiple sharp spinning side bands
  - Intensity of the various order sidebands is directly related to  $D_{ij}$  and  $u_r$

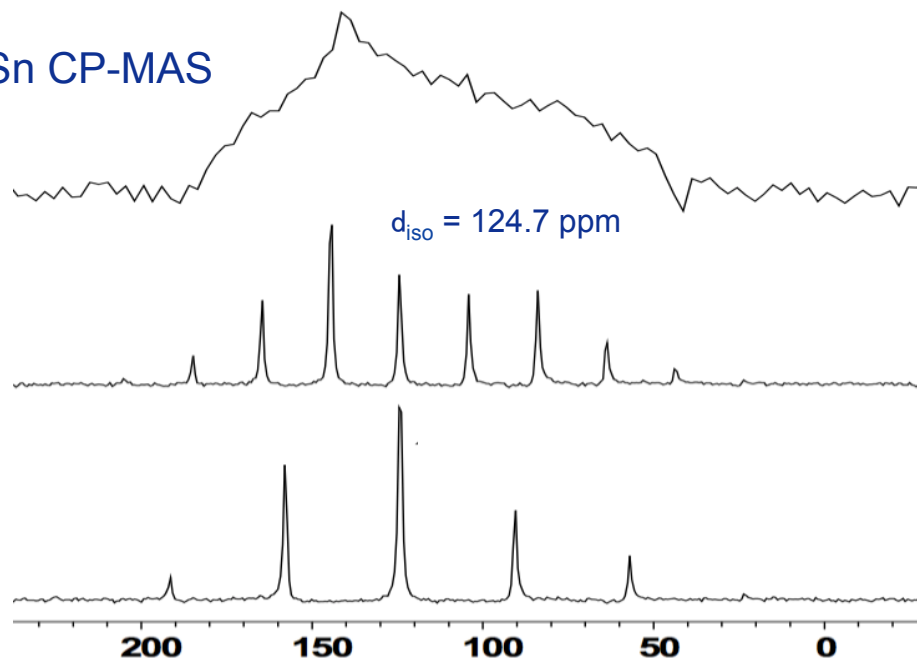
# MAS dipolar coupling: multi-spin systems



- Dipolar coupling of multi-spin systems leads to broad peak
  - coupling is said to be heterogeneous
  - powder pattern is made up of complex dipolar multiplet i.e. no sharp lines
  - MAS narrows central line and produced sided bands with related width
  - Intensity of the various order sidebands indirectly related to  $D_{ij}$  and  $u_r$

# MAS & chemical shielding anisotropy

$^{119}\text{Sn}$  CP-MAS



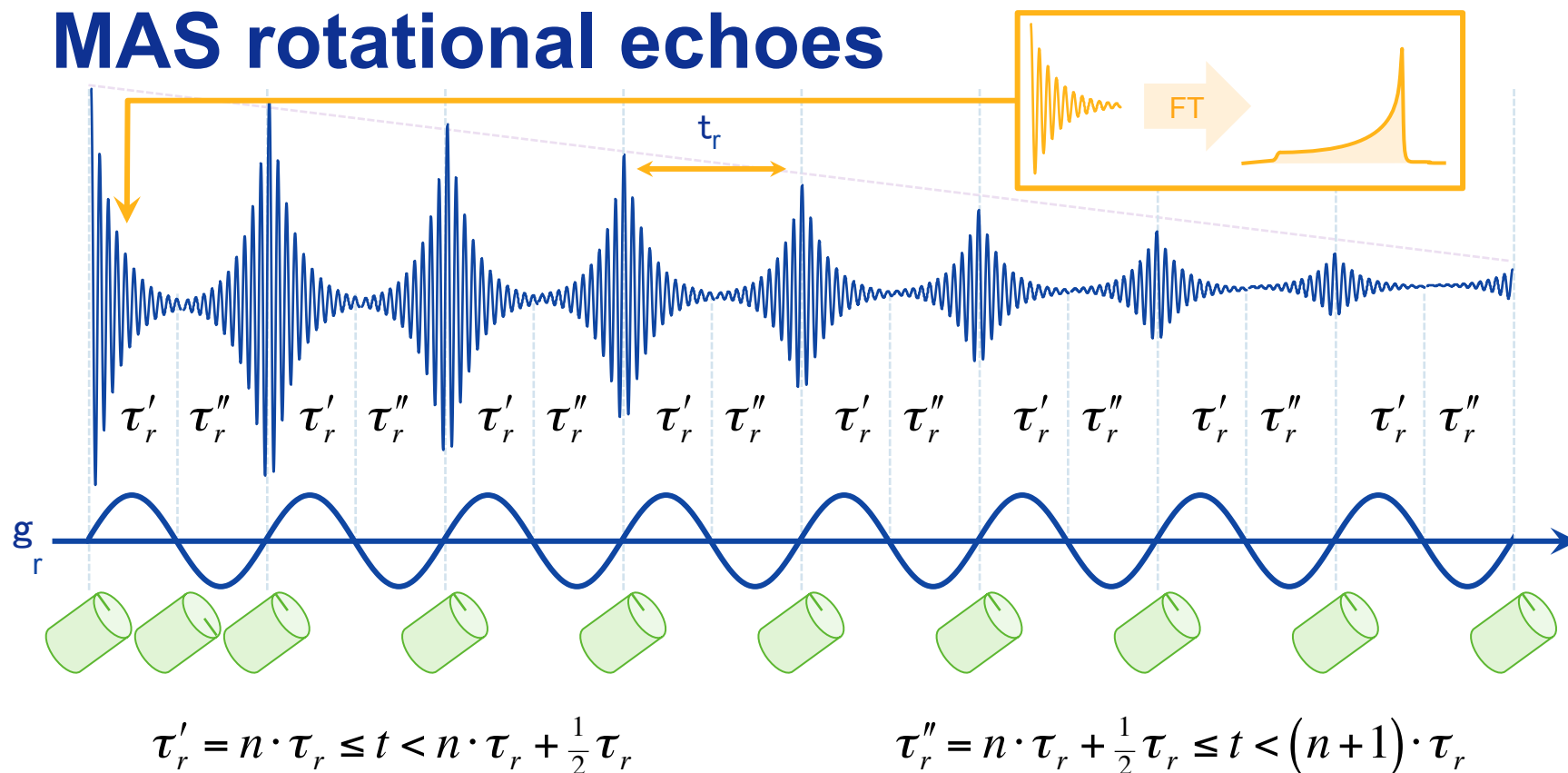
$u_r = 0 \text{ kHz}$ : static powder pattern  
324 transients

$u_r = 3 \text{ kHz}$ : MAS side-band pattern (5<sup>th</sup>)  
216 transients

$u_r = 5 \text{ kHz}$ : MAS side-band pattern (3<sup>rd</sup>)  
208 transients

- Chemical shielding anisotropy leads to characteristic powder patterns
  - CSA is homogeneous as powder pattern derived from isolated crystallites
  - when  $u_r < W$  signal is localised in the sharp spinning sidebands
  - Intensity of the various order sidebands is directly related to  $d_{\text{iso}}$ ,  $(W, k)$  or  $(d, h)$  and  $u_r$
  - high signal to noise for MAS (even with side-bands) as compared to static spectra

# MAS rotational echoes



- 1<sup>st</sup> half of every rotor period
  - interactions de-phase signal & signal intensity decreases
  - FT results in powder spectrum

- 2<sup>nd</sup> half of every rotor period
  - interactions progressively averaged & signal intensity regenerated

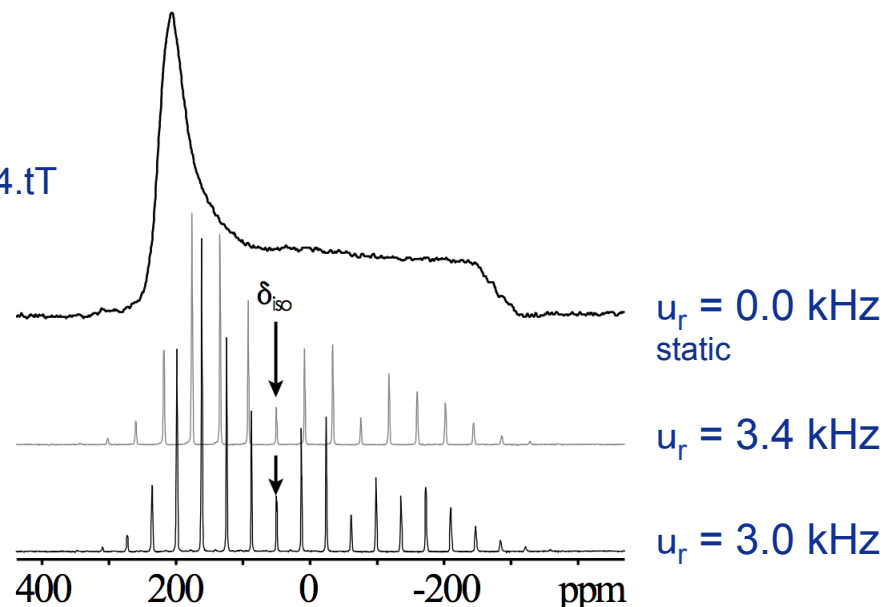
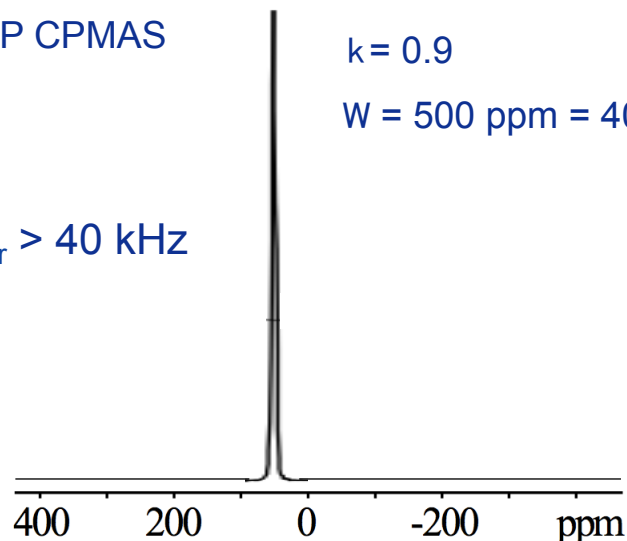
# CSA spinning sidebands are useful

$^{31}\text{P}$  CPMAS

$k = 0.9$

$W = 500 \text{ ppm} = 40 \text{ kHz}@4.7\text{T}$

$u_r > 40 \text{ kHz}$



- Under MAS with  $u_r \gg u_{\text{int}}$  we 'spin-out' all spinning sidebands
  - high resolution spectrum with only isotropic chemical shifts (lost all CSA information)
- Under MAS with  $u_r < u_{\text{int}}$  we get a spinning sideband manifold
  - high sensitivity as all intensity is concentrated on sharp isotropic and SSB lines
  - orientation information via analysis of side-band intensities
  - isotropic chemical shift (just need to work out which one it is)

# What does MAS actually do? CSA

$$v_{CS}^{MAS} = \left\langle -\frac{\omega_0}{2\pi} \left\{ \begin{aligned} &\sigma_{iso} \\ &+ [A_1 \cos(\omega_r t + \gamma) + B_1 \sin(\omega_r t + \gamma)] \\ &+ [A_2 \cos(2\omega_r t + 2\gamma) + B_2 \sin(2\omega_r t + 2\gamma)] \end{aligned} \right\} \right\rangle_{\alpha\beta\gamma}$$

$$A_1 = +\frac{2}{3}\sqrt{2} \sin \beta \cos \beta \left[ \cos^2 \alpha (\sigma_{11} - \sigma_{33}) + \sin^2 \alpha (\sigma_{22} - \sigma_{33}) \right]$$

$$B_1 = +\frac{2}{3}\sqrt{2} \sin \alpha \cos \alpha \sin \beta (\sigma_{11} - \sigma_{33})$$

$$A_2 = +\frac{1}{3} \left[ (\cos^2 \beta \cos^2 \alpha - \sin^2 \alpha) (\sigma_{11} - \sigma_{33}) + (\cos^2 \beta \sin^2 \alpha - \cos^2 \alpha) (\sigma_{22} - \sigma_{33}) \right]$$

$$B_2 = -\frac{2}{3} \sin \alpha \cos \alpha \cos \beta (\sigma_{11} - \sigma_{22})$$

- Magic angle spinning modulates the coupling interactions in the signal
  - using Euler angles and Wegner rotational matrices  $u_{MAS}$  is proportional to  $w_r$  &  $2w_r$
  - magnitude dependent on principle components of chemical shielding tensor

# What does MAS actually do? general

$$v_{\text{MAS}} = \lambda_{\text{iso}} + \frac{1}{t} \cdot \sqrt{\frac{3}{2}} \cdot \Phi_{\lambda} \quad \Phi_{\lambda} = + \frac{C_1}{\omega_r} \left\{ \sin(\omega_r t + \gamma) - \sin \gamma \right\} + \frac{C_2}{2\omega_r} \left\{ \sin(2\omega_r t + 2\gamma) - \sin 2\gamma \right\} \\ - \frac{S_1}{\omega_r} \left\{ \cos(\omega_r t + \gamma) - \cos \gamma \right\} + \frac{S_2}{2\omega_r} \left\{ \cos(2\omega_r t + 2\gamma) - \cos 2\gamma \right\}$$

integrated phase

considerably simpler for axially  
symmetric interactions  $h_l = 0$

$$C_1 = -\frac{\delta_{\lambda}}{\sqrt{2}} \sin 2\beta \quad S_1 = 0$$

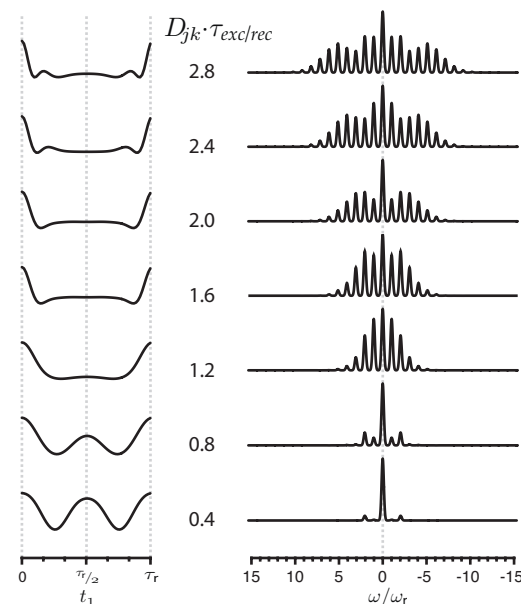
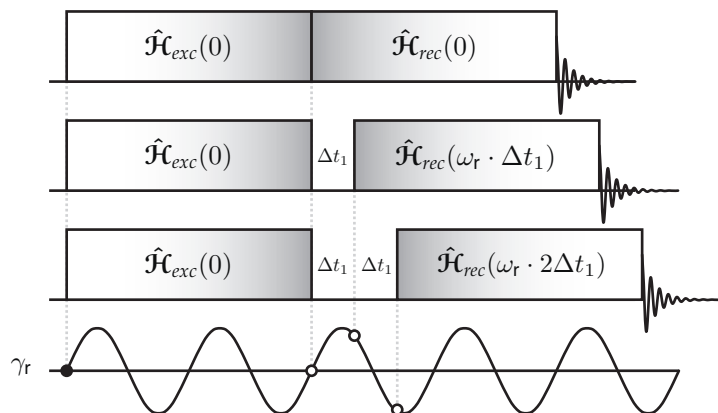
$$C_2 = +\frac{\delta_{\lambda}}{2} \sin^2 \beta \quad S_2 = 0$$

$$C_1 = -\frac{\delta_{\lambda}}{\sqrt{2}} \sin 2\beta \left( 1 + \frac{\eta_{\lambda}}{3} \cos 2\alpha \right) \quad S_1 = \frac{\sqrt{2} \delta_{\lambda} \eta_{\lambda}}{3} \sin^2 \beta \cos 2\alpha$$

$$C_2 = +\frac{\delta_{\lambda}}{2} \sin^2 \beta - \frac{\delta_{\lambda} \eta_{\lambda}}{6} (1 + \cos^2 \beta) \cos 2\alpha \quad S_2 = \frac{\delta_{\lambda} \eta_{\lambda}}{3} \cos \beta \sin 2\alpha$$

- Magic angle spinning modulates the coupling interactions in the signal
  - using Euler angles and Wegner rotational matrices  $u_{\text{MAS}}$  is proportional to  $w_r$  &  $2w_r$
  - magnitude dependent on  $I_{\text{iso}}$ ,  $d_l$  and  $h_l$  of a given interaction  $l$

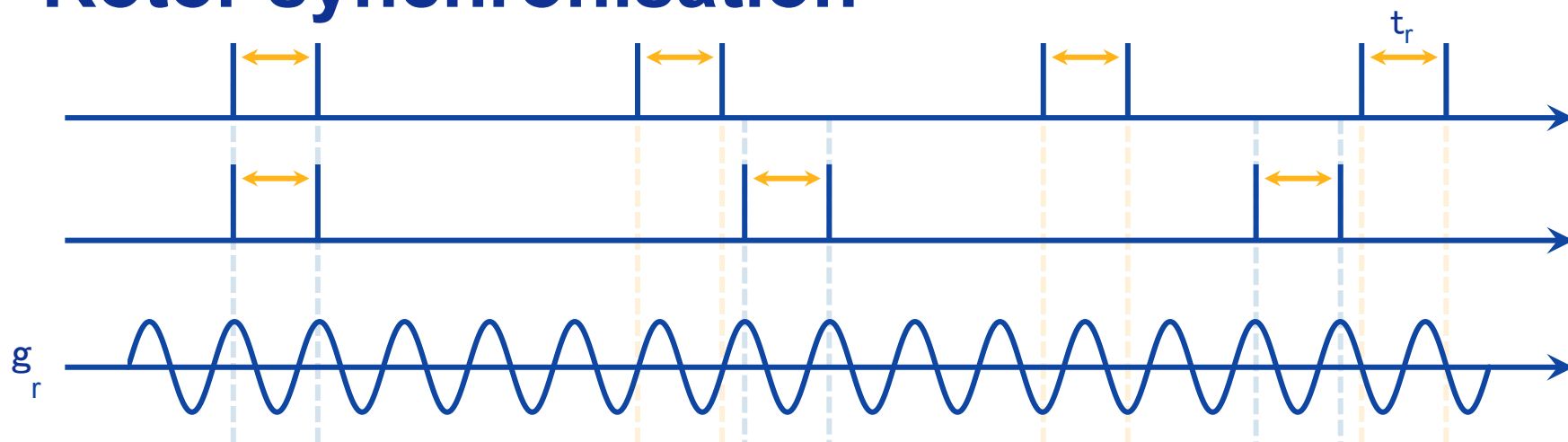
# MAS rotor- or g-encoding



- Monitor MAS modulations in indirect dimension of 2D experiment
  - incremented delay ( $t_1$ ) is incremented in fractions of  $t_r$  e.g.  $Dt_1 = t_r/40$
- So-called rotor- or g-encoding needs to be applied under fast-MAS
  - $u_r = 25$  kHz,  $t_r = 40$   $\mu$ s,  $Dt_1 = 2$   $\mu$ s for 20 increments
- Allows site specific determination of absolute parameters such as  $D_{ij}$ 
  - numerical fit of rotor encoding modulation profile directly
  - numerical fit of spinning-side-band pattern (concatenation of profile followed by FT)



# Rotor synchronisation



- In order to manipulate the spin-part in a controlled way under MAS it is important to synchronise any RF pulses with the rotor phase
  - when absolute rotor phase is not important use simple timing (common)
    - $u_r$  is variable in pulse program and used to calculate the various delays between pulses
    - most modern recoupling experiments use this method (REDOR,  $C_n$ ,  $R_n$ , MQMAS)
  - when absolute rotor phase is important use direct synchronisation (rare)
    - MAS control unit sends signal to spectrometer to trigger pulses
    - some methods for the absolute quantification of orientation use this method (DECODER)

# MAS of quadrupoles

$\eta = 0.3$

$^{27}\text{Al}$  NMR

$I = 5/2$

9.4T

$C_Q$  (MHz)

9.0

7.0

5.0

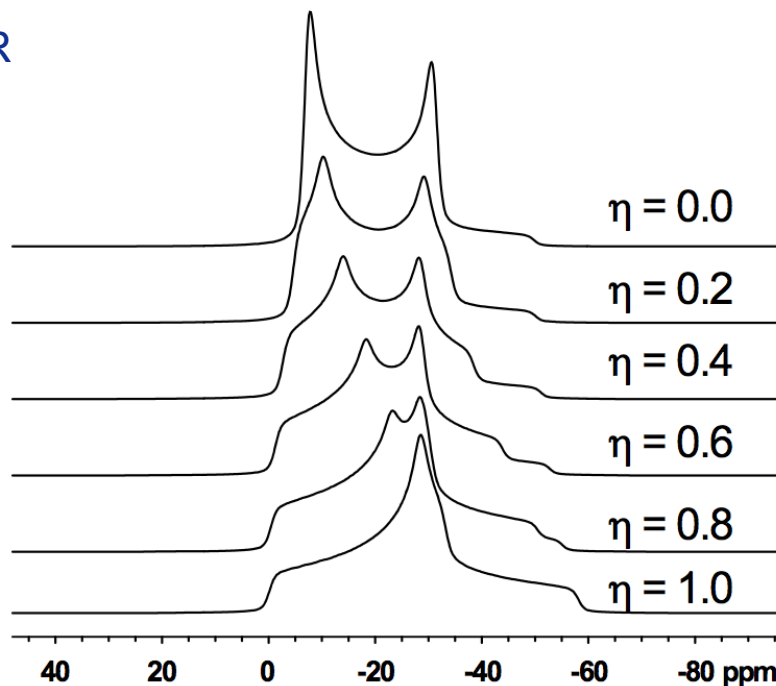
4.0

3.0

1.0

40 20 0 -20 -40 -60 -80 -100 ppm

$C_Q = 6.0$  MHz



- Under MAS solid-state NMR of quadrupolar nuclei becomes possible through the central transition of half-integer quadrupoles
  - Frequency of transition extreme sensitive to changes in  $C_Q$  and  $h_Q$
  - Central transition still broadened by second-order quadrupolar interactions
  - Signals from multiple chemical sites overlap making spectra difficult to analyse

# Double-rotation: DOR

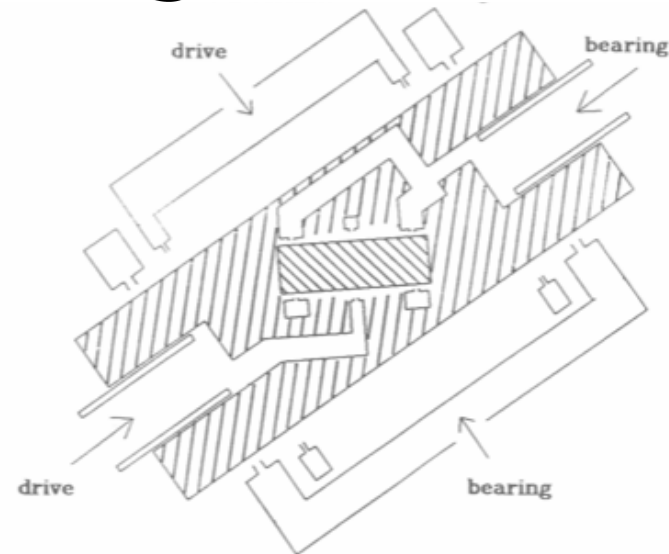
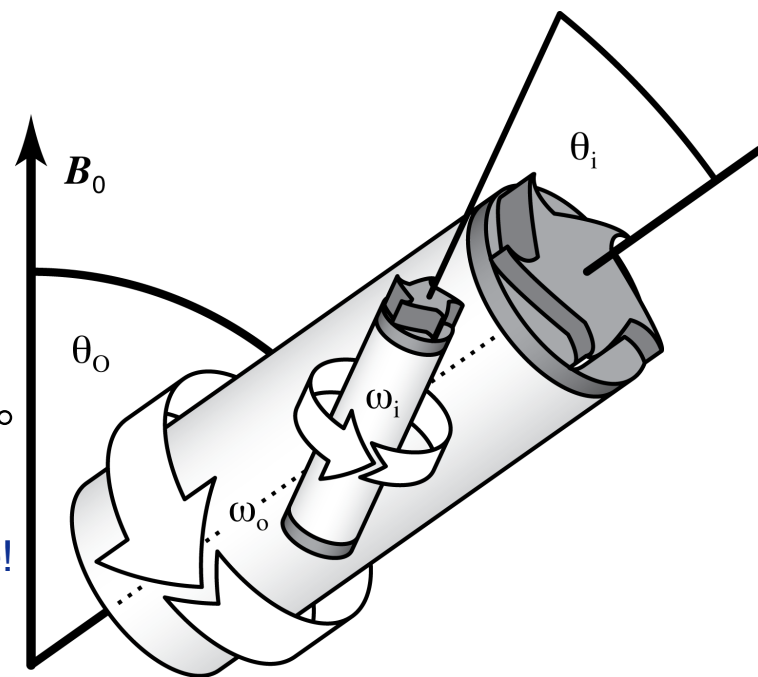
- Sample rotation to address both 2<sup>nd</sup> & 4<sup>th</sup> rank orientation dependence:

- 2<sup>nd</sup>-order quadrupolar line broadening

$$\theta_m^{P_2(\cos\theta)} = 54.74^\circ \quad \theta_m^{P_4(\cos\theta)} = 30.56^\circ \text{ \& \ } 70.12^\circ$$

- sample rotation about two angles at same time!
- Rotor-within-a-rotor concept
  - outer rotor acts as the stator for smaller inner rotor
  - 2<sup>nd</sup> rank via  $q_o = q_m^{P_2}$  and 4<sup>th</sup> rank via  $q_i = q_m^{P_4}$

- Special complex probehead needed
  - rotational frequency lower than MAS
  - $u_r^o = 1 - 2 \text{ kHz}$  &  $u_r^i = 7 - 8 \text{ kHz}$



# Double-rotation (DOR) hardware



$OD_o = 9.3 \text{ mm}$ ,  $OD_i = 3 \text{ mm}$ , volume =  $23 \mu\text{L}$

## ■ Advantages

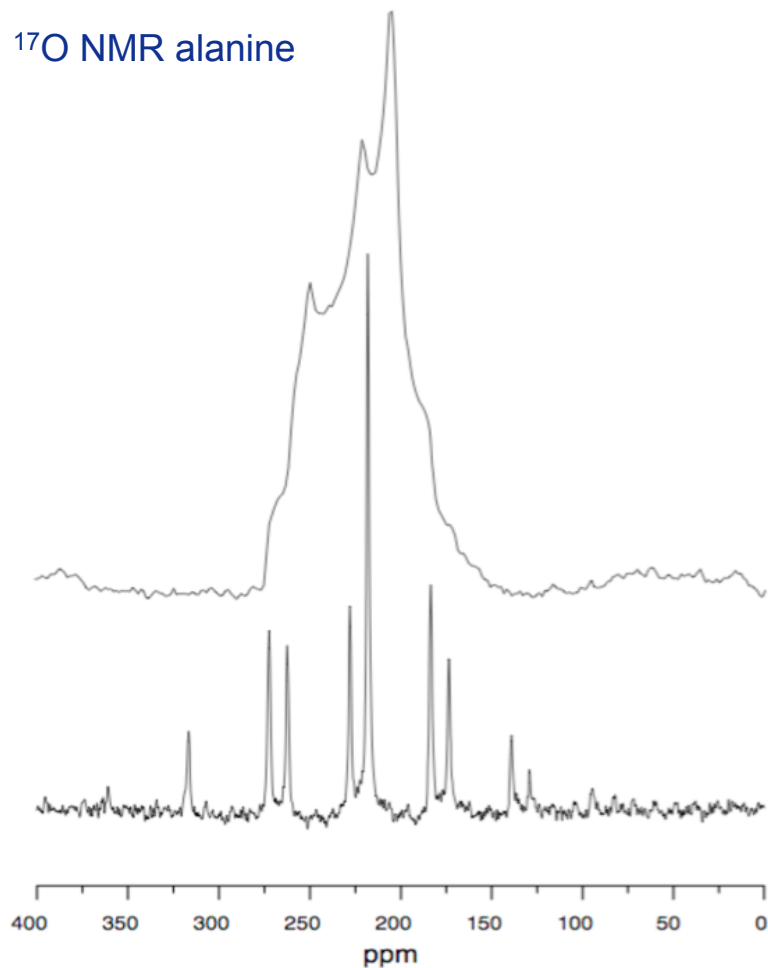
- quantitative
- high sensitivity
- low RF power needed
- quick 1D experiment

## ■ Disadvantages

- Special expensive probehead needed
- stable spinning is difficult
- slow spinning rates
- large coil results in  $< 3\%$  filling factor
- poor RF for decoupling

# Double-rotation (DOR) spectra

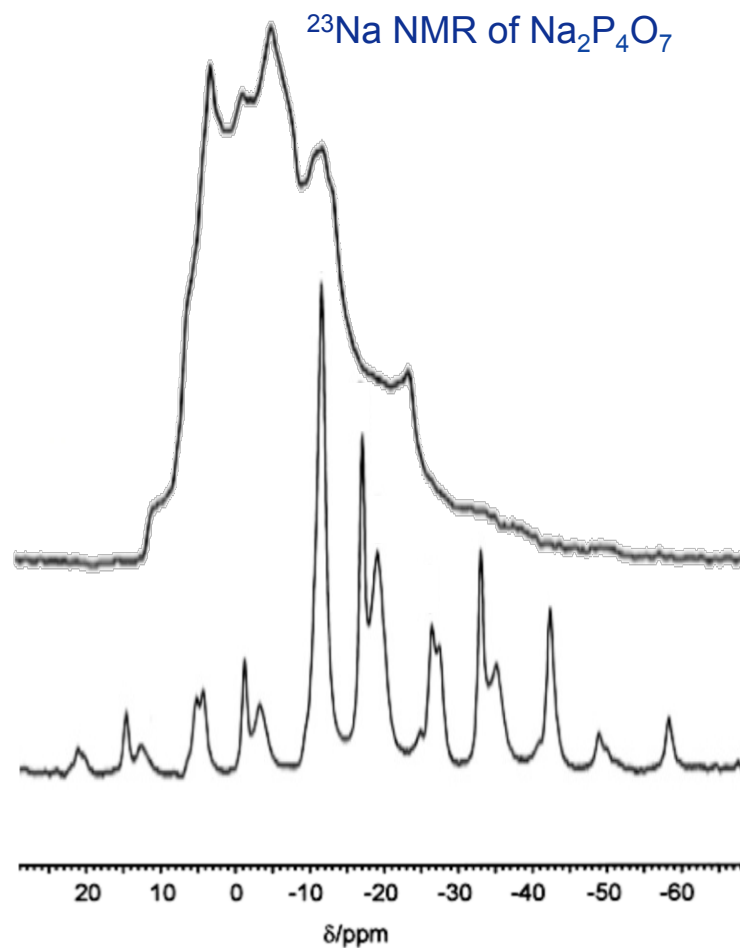
$^{17}\text{O}$  NMR alanine



MAS

DOR

$^{23}\text{Na}$  NMR of  $\text{Na}_2\text{P}_4\text{O}_7$



# Dynamic-angle spinning: DAS

- Sample rotation to address both 2<sup>nd</sup> & 4<sup>th</sup> rank orientation dependence:

- 2<sup>nd</sup>-order quadrupolar line broadening

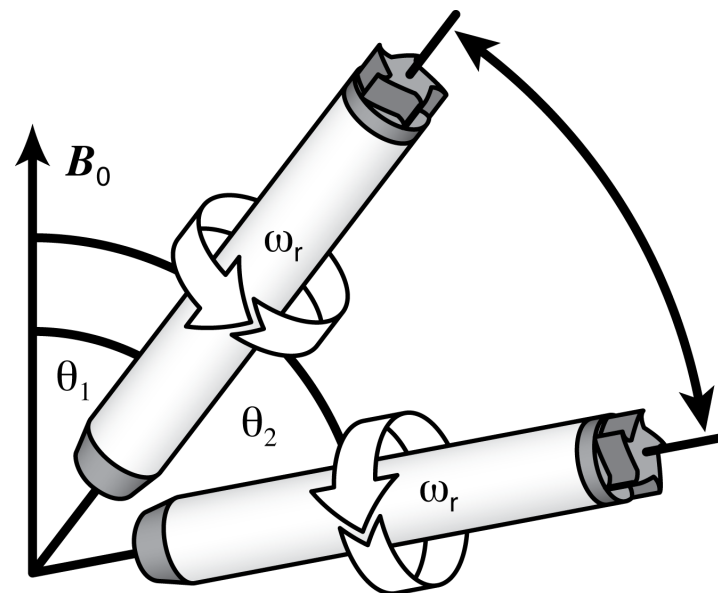
$$P_2(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1)$$

$$P_4(\cos \theta) = \frac{1}{8}(35\cos^4 \theta - 30\cos^2 \theta + 3)$$

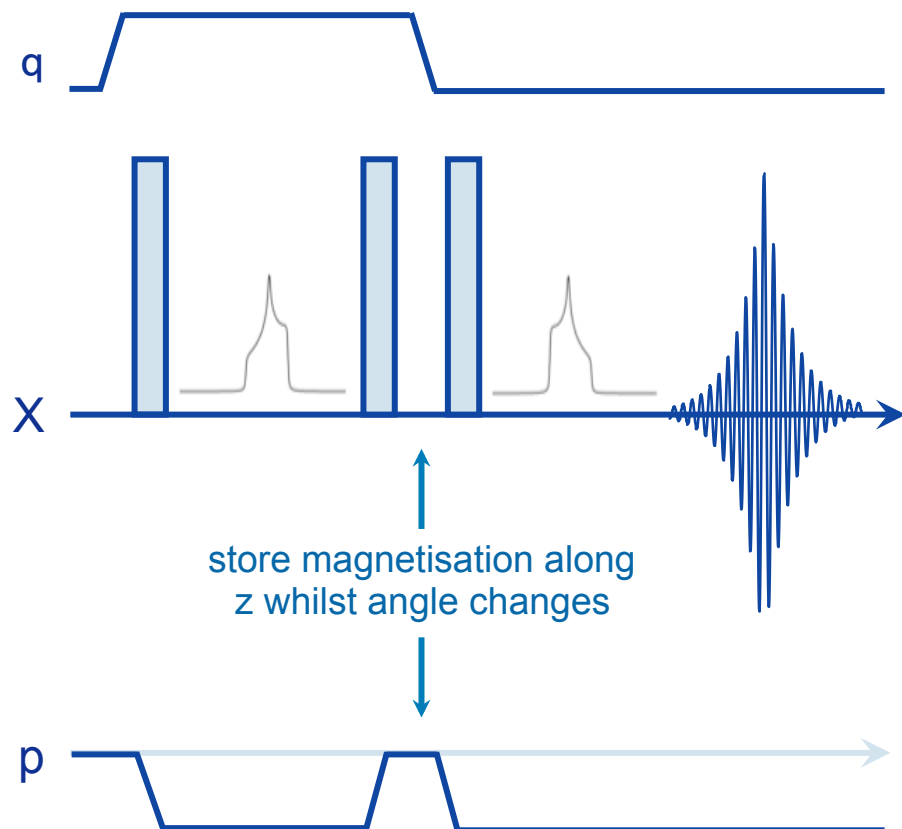
- Sample rotated sequentially about two axes orientated to  $B_0$  at  $q_1$  and  $q_2$  such that:

$$P_2(\cos \theta'_1) = -P_2(\cos \theta'_2) \text{ \& } P_4(\cos \theta'_1) = -P_4(\cos \theta'_2)$$

- solution at  $q_1 = 37.38^\circ$  and  $q_2 = 79.19^\circ$
- Special hardware needed, not very common
  - rotational frequency lower than for MAS:  $\omega_r = 2 - 4$  kHz



# Dynamic angle spinning (DAS) setup



## Advantages

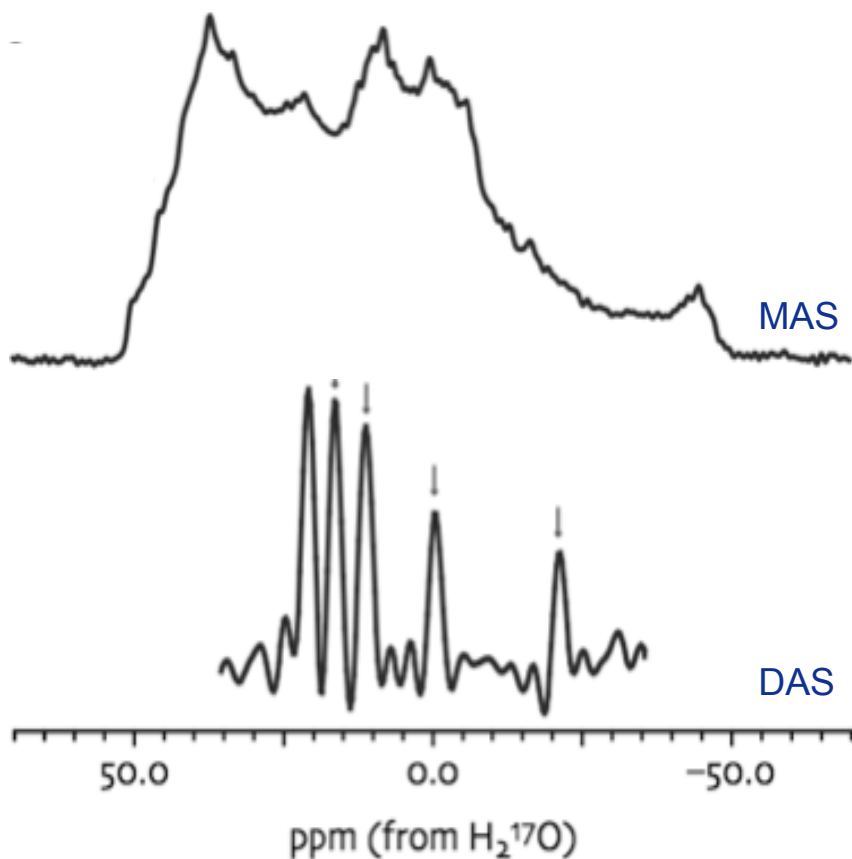
- quantitative
- high sensitivity
- low RF power needed
- works well for dilute nuclei

## Disadvantages

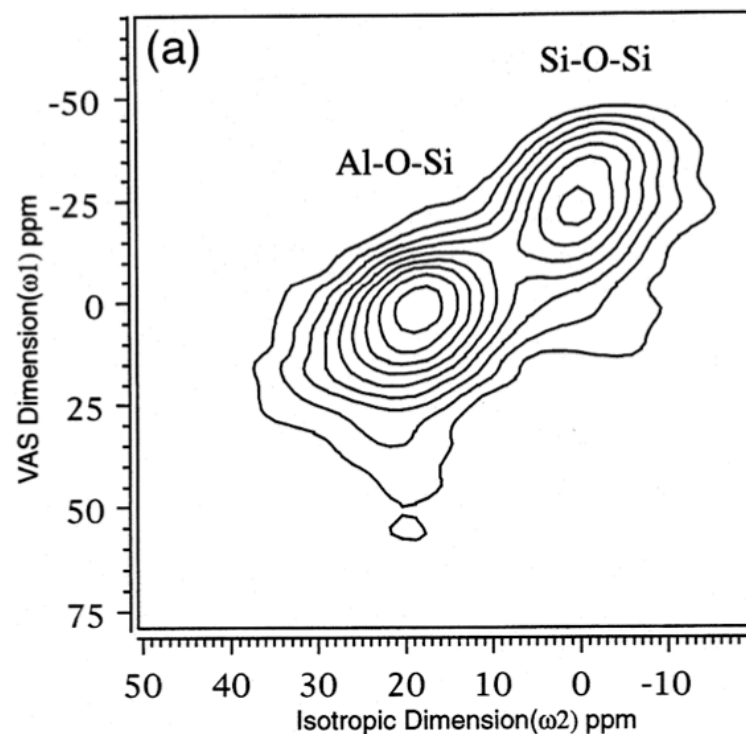
- Special expensive probehead needed
- problems with strong homonuclear dipolar couplings
- limited to nuclei with long  $T_1$  relaxation
- in simple experiment no MAS so any second rank anisotropy (dipolar broadening or CSA) is not removed (unless additional  $54.74^\circ$  state is used)

# Dynamic angle spinning (DAS) spectra

$^{17}\text{O}$  NMR of coesite ( $\text{SiO}_2$ )

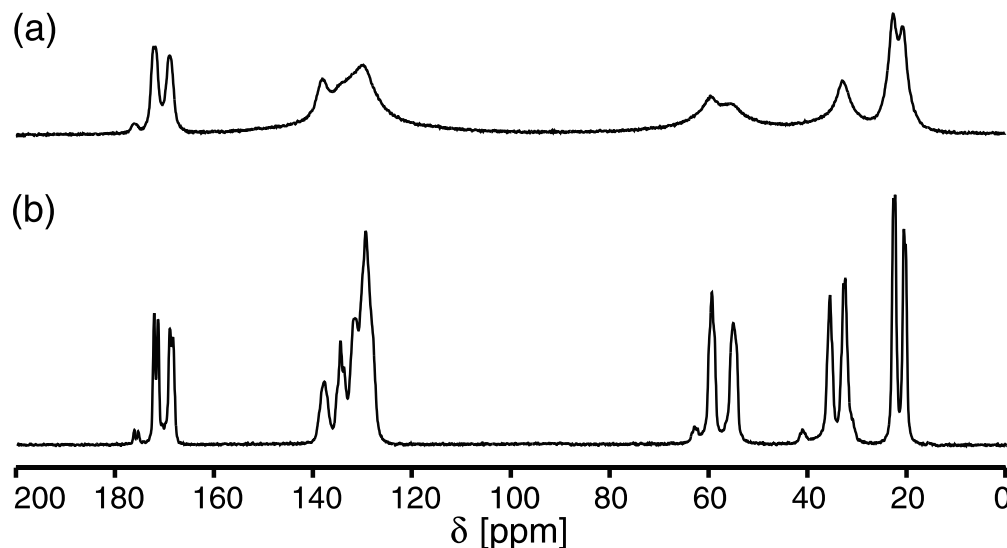
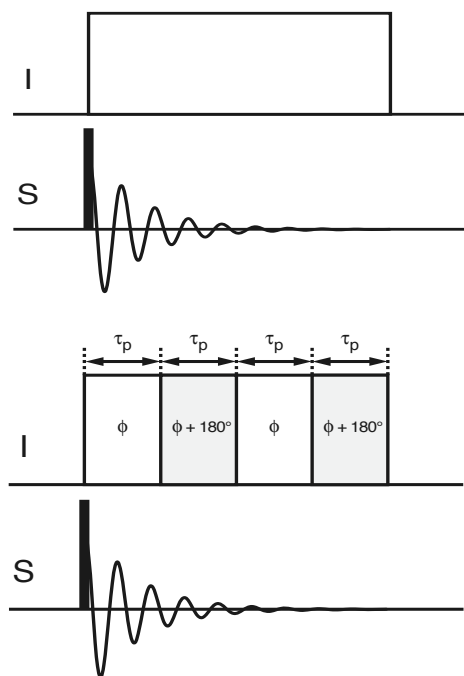


$^{17}\text{O}$  NMR of zeolite stilbite



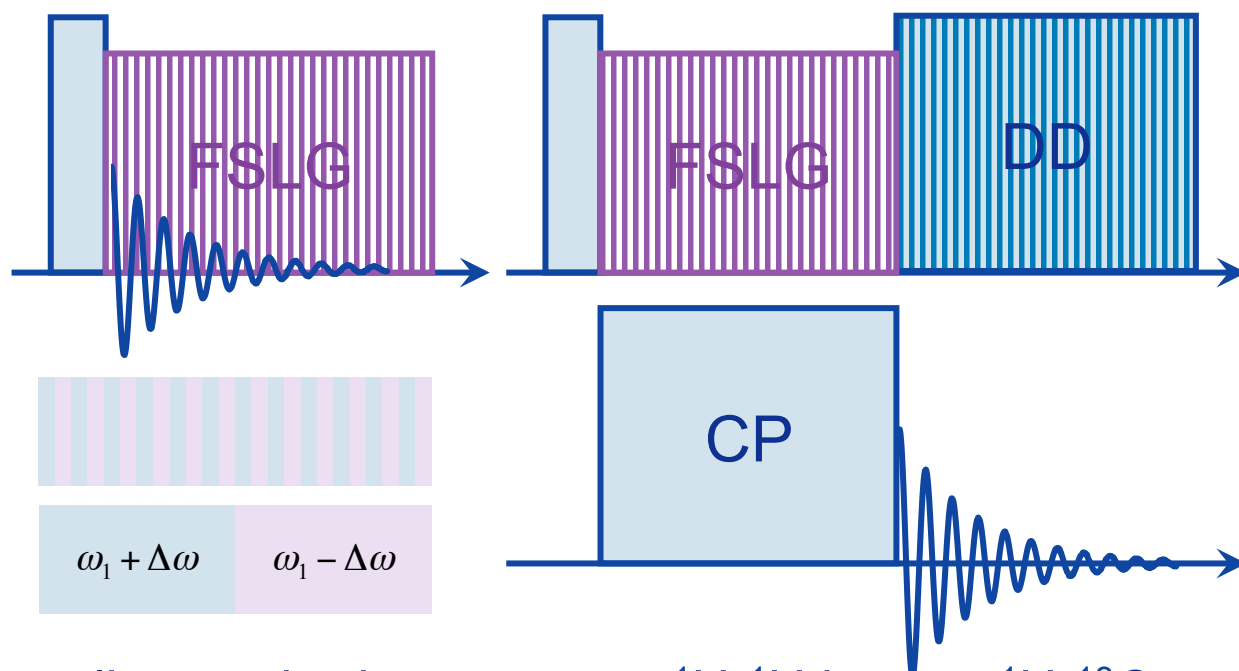
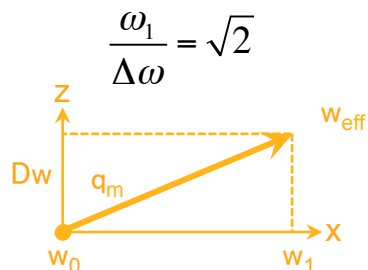
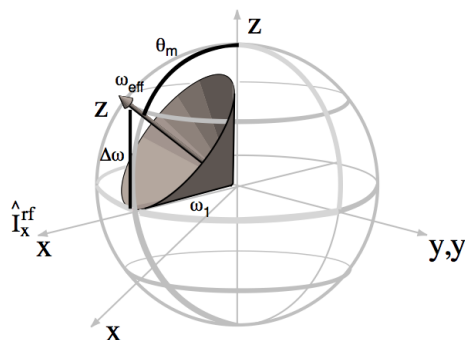


# High power dipolar-decoupling



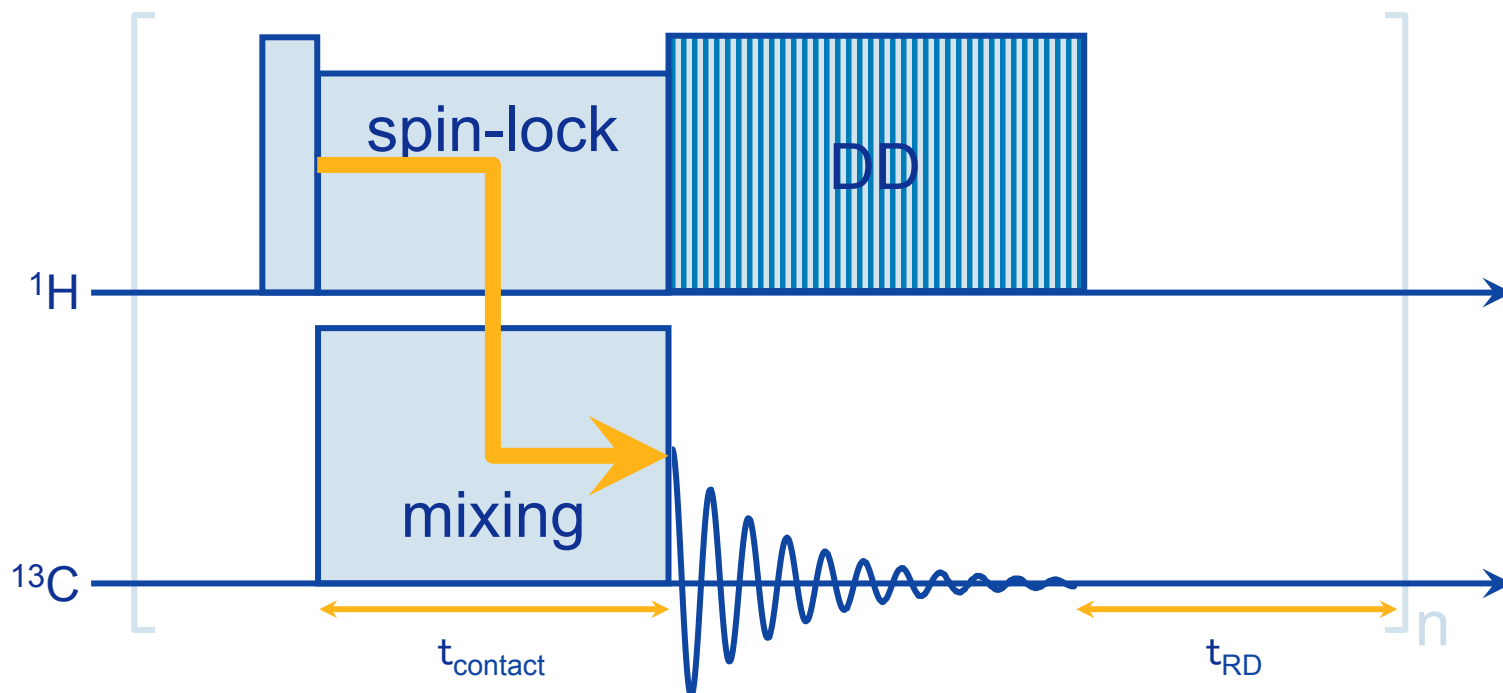
- Heteronuclear decoupling similar principle to J-decoupling in solution
  - Stronger interaction so to need to apply high RF power ( <100 kHz for 200 ms or 2%)
- Can gain higher resolution using two pulse phase modulation (TPPM)
  - also variants such as SPINAL64 and XIX (still field of active research in solids)

# Frequency-switched Lee-Goldberg (FSLG)



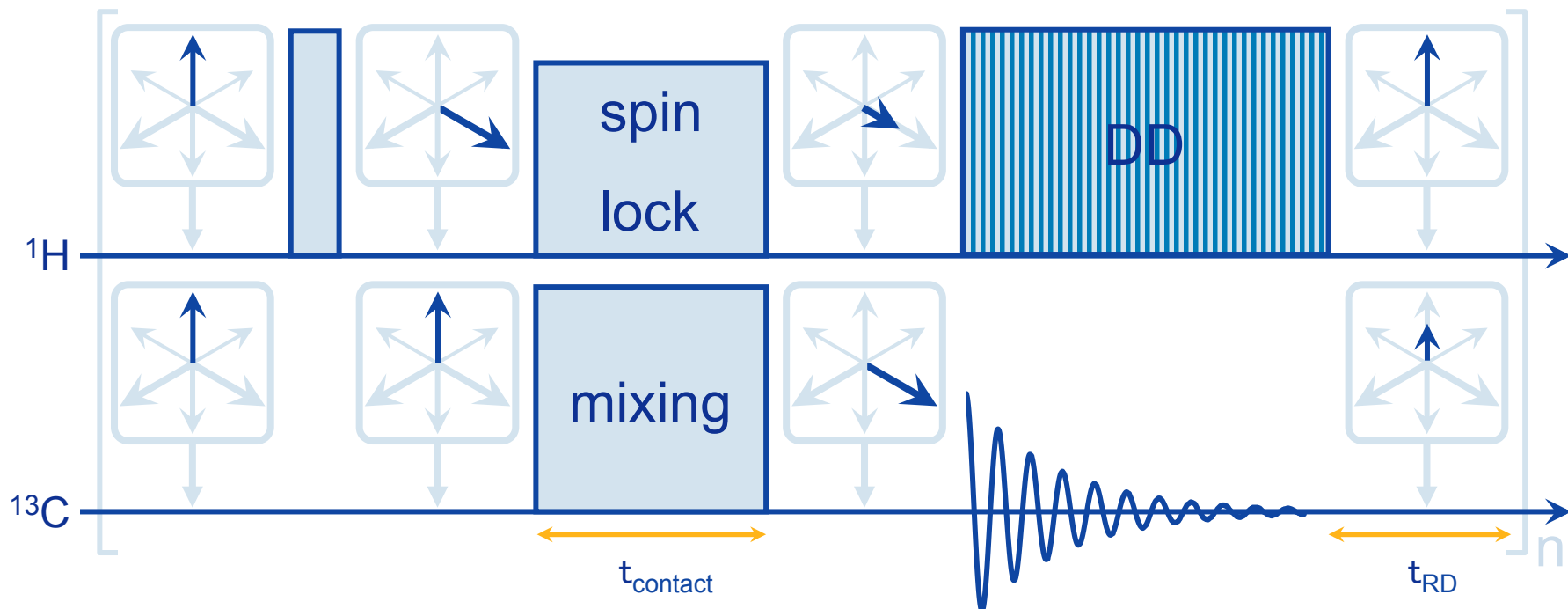
- Homonuclear decoupling method suppresses  $^1\text{H}$ - $^1\text{H}$  but not  $^1\text{H}$ - $^{13}\text{C}$ 
  - $^1\text{H}$  decoupling during  $^1\text{H}$  detection  $^1\text{H}\{^1\text{H}\}$  for high resolution  $^1\text{H}$  solid-state NMR
  - $^1\text{H}$  decoupling during  $t_1$  for  $^1\text{H}$ - $^{13}\text{C}$  correlations
  - $^1\text{H}$  decoupling during CP to observe isolated  $^1\text{H}$ - $^{13}\text{C}$  spin pairs (oscillation extract  $D_{ij}$ )
- Rapid phase switch was very demanding hardware possible (AVIII)

# Cross-polarisation (CP)



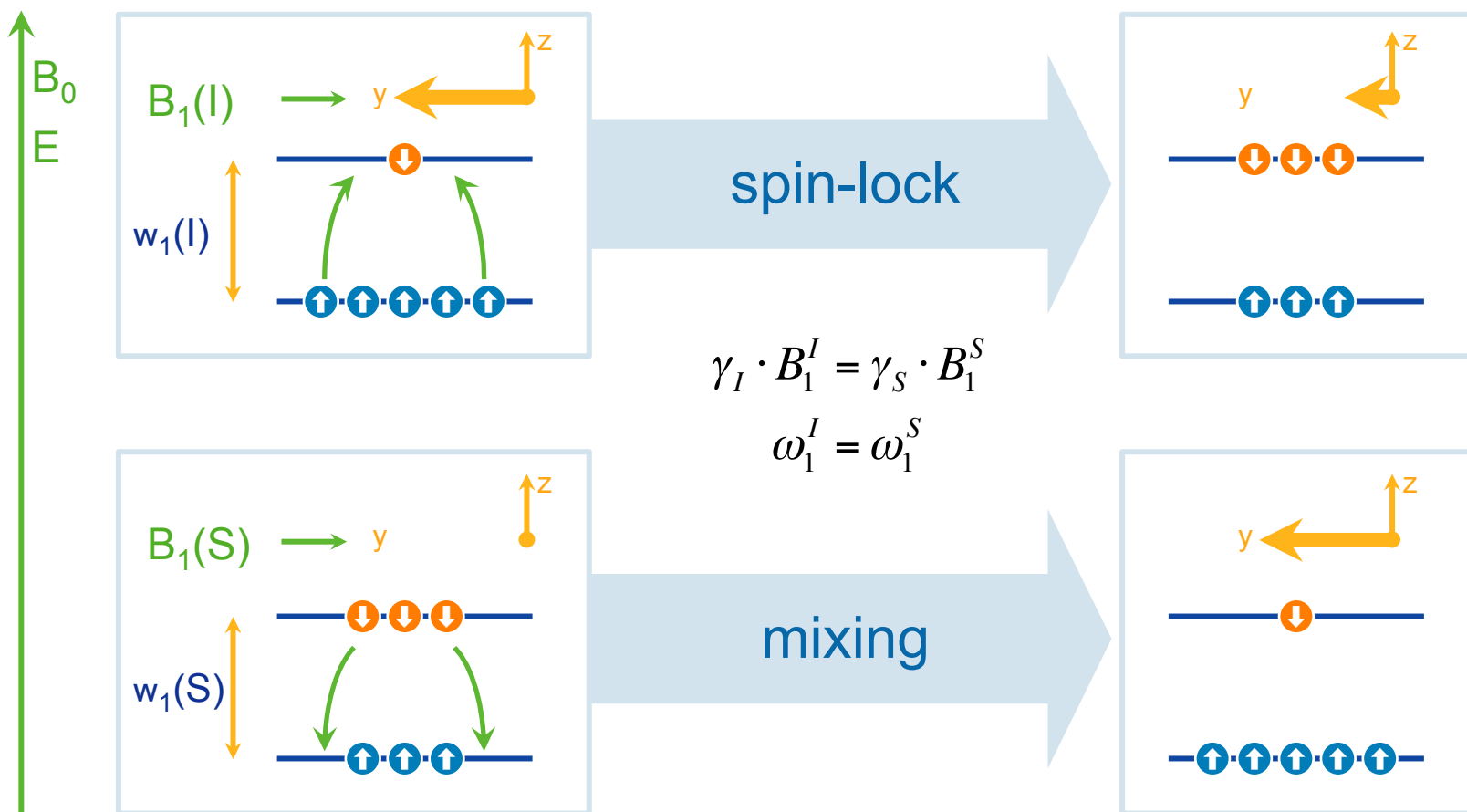
- One of the most important basic techniques in solid-state NMR
  - Transfer polarisation from abundant nuclei ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) to rare nuclei ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{29}\text{Si}$ )
    - enhance signal of rare species by  $g_I/g_S$  (increase SNR)
    - relaxation delay ( $t_{\text{RD}}$ ) between successive experiments based on  $T_1^{\text{H}}$  not  $T_1^{\text{X}}$  (shorter total time)
    - strong dipolar interactions between  $^1\text{H}$  result in  $T_1^{\text{H}}$  being strongly coupled to molecular motion

# Cross-polarisation mechanism



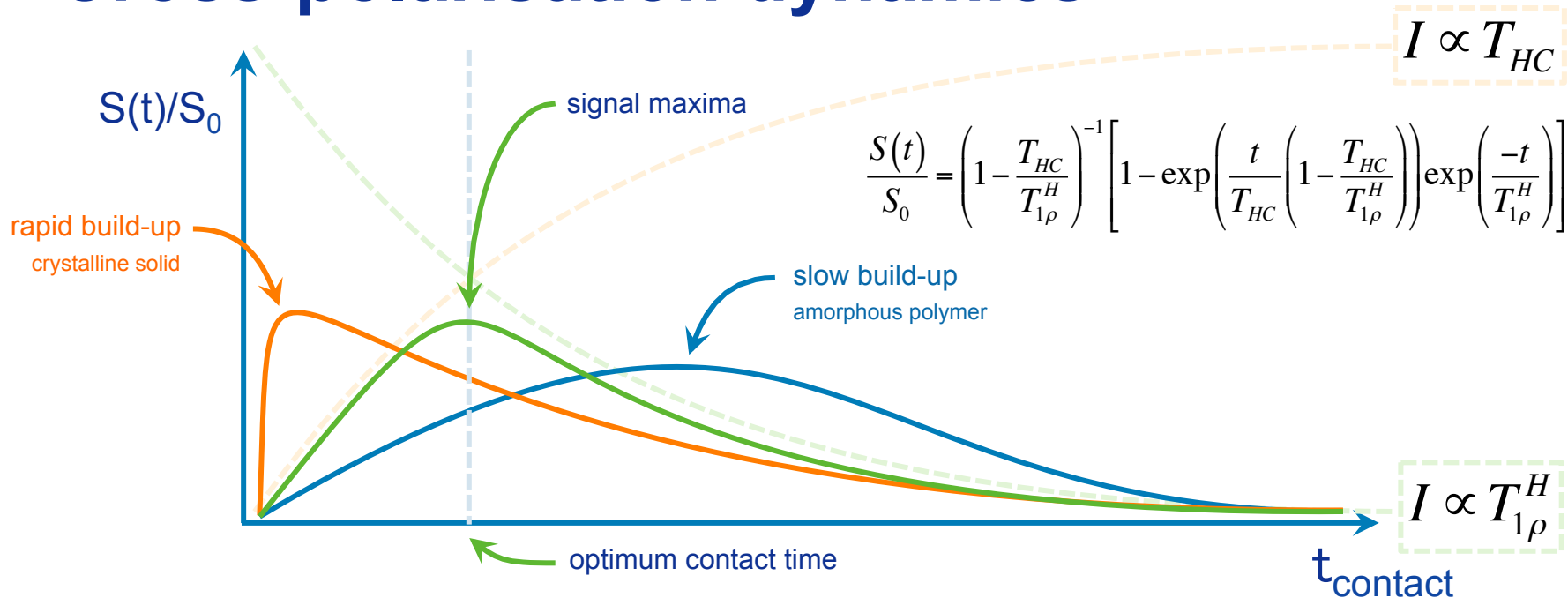
- Cross-polarisation is mediated by the heteronuclear dipolar interaction
  - abundant nuclei ( $^1\text{H}$ ) and rare nuclei ( $^{13}\text{C}$ ) must be directly dipolar coupled
  - apply spin lock to  $^1\text{H}$  polarisation and set  $B_1^{\text{H}}$  field to match frequency of  $B_1^{\text{X}}$  field
  - Hartmann-Hahn match condition  $\gamma_I \cdot B_I^1 = \gamma_S \cdot B_S^1$

# Cross-polarisation & energy levels



- At Hartmann-Hahn match condition I and S transfer polarisation

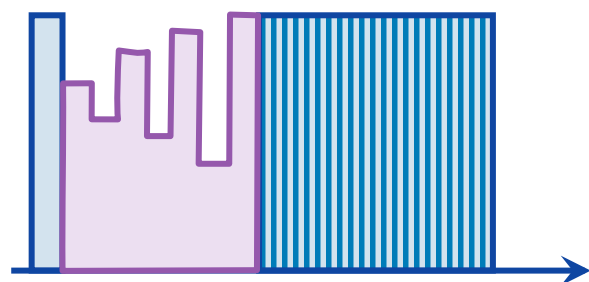
# Cross-polarisation dynamics



## ■ Polarisation takes time build up

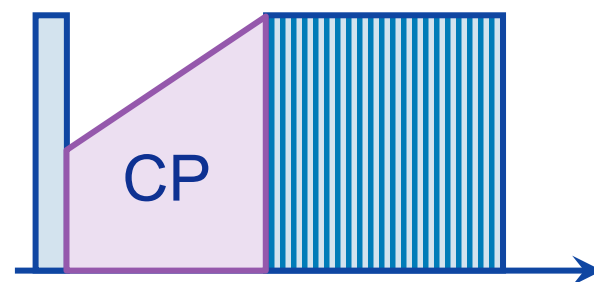
- polarisation transfer from  $^1\text{H}$  to  $^{13}\text{C}$  is described by exponential build up:  $T_{HC}$
- lost of polarisation through relaxation governed by  $T_{1\rho}^H$
- optimum contact time for maximum polarisation transfer efficiency
  - strong dipolar coupling build up and decay quickly (crystalline solids)
  - weak or distributions of dipolar couplings build up and decay more slowly (amorphous)

# CP & MAS > 15 kHz



“slow” MAS  
more dipolar coupling

$$(\omega_1^I - \omega_1^S) = 0$$



“fast” MAS  
less dipolar coupling

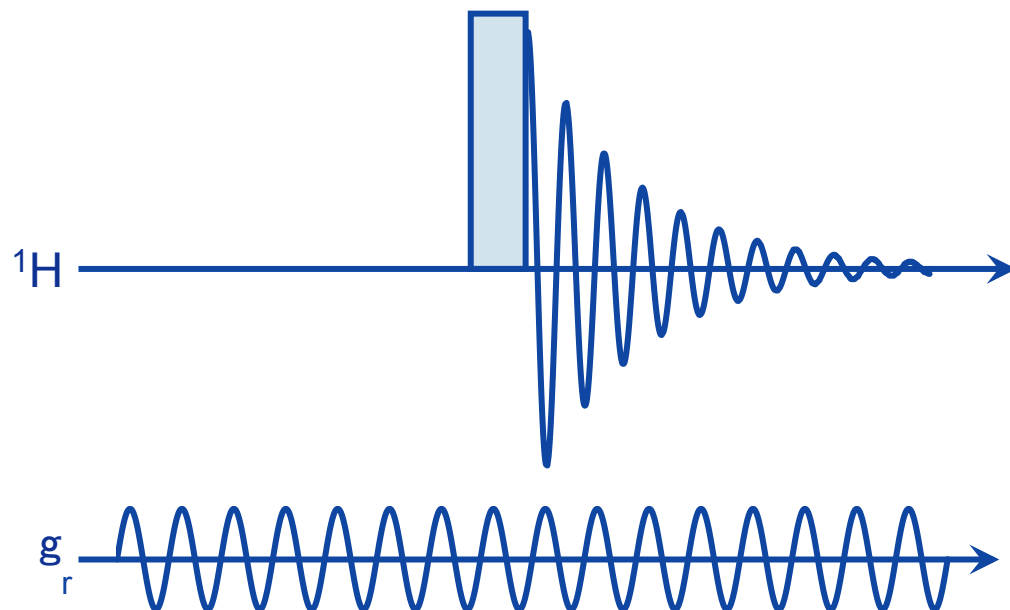
$$(\omega_1^I - \omega_1^S) = \pm \omega_r$$

$$(\omega_1^I - \omega_1^S) = \pm 2 \cdot \omega_r$$

- When dipolar coupling are averaged by MAS have match condition condition has spinning-side-bands
  - most efficient polarisation transfer is via spinning side band of match condition
  - small window makes it hard to hit match condition so we sweep through all conditions
    - variable amplitude (VA) or ramped amplitude (RAMP) contact pulse

# Single pulse excitation: SPE-MAS

- Simplest pulse NMR method but in solids:
  - difficult to create a  $B_1$  field inside a solid c.f. a liquid (magnetic susceptibility)
  - broad lines make it difficult to uniformly excite entire spectrum
    - not possible for some high  $C_Q$  quadrupolar nuclei
  - short high-power pulses:  $1\text{-}2.5\ \mu\text{s}$   $u_1 = 250\text{-}100\ \text{kHz}$
  - quantitative (if excite all)
  - MAS = CSA, Q, homo D, het D (sensitivity)

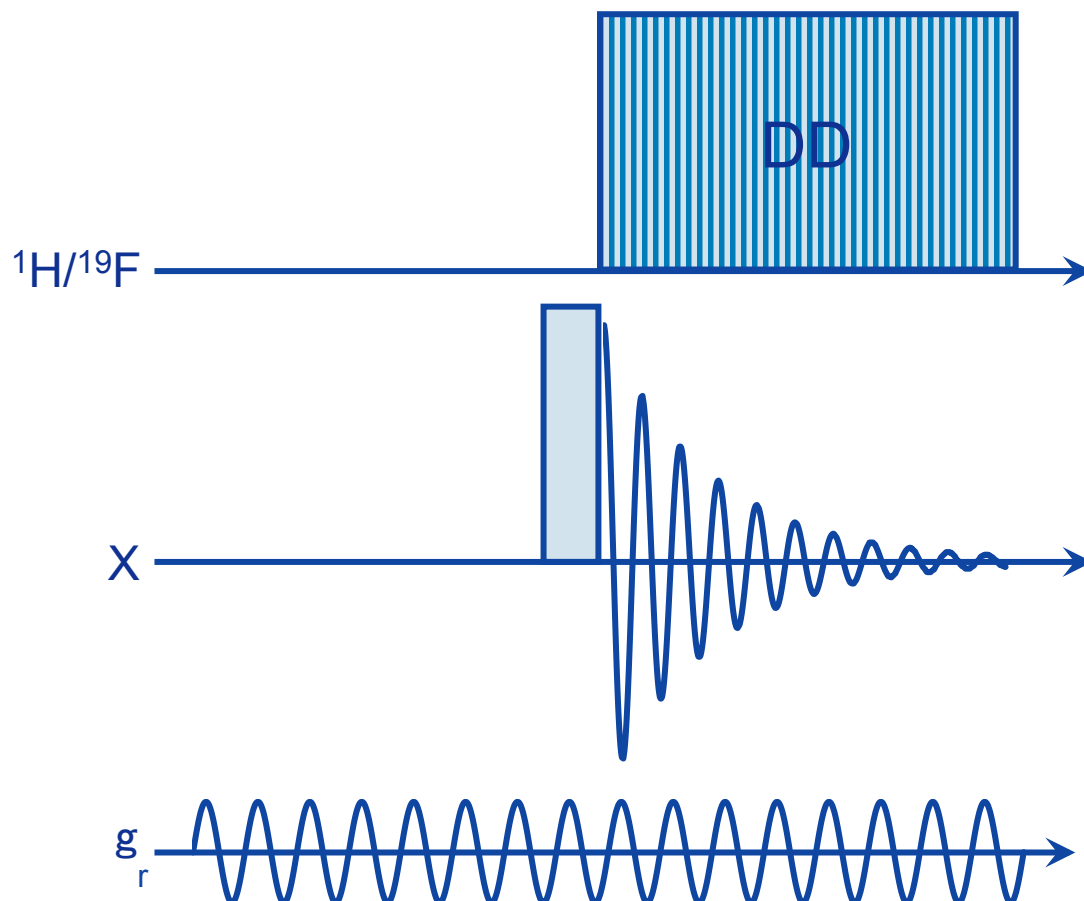




# High-power decoupled SPE-MAS (DD)

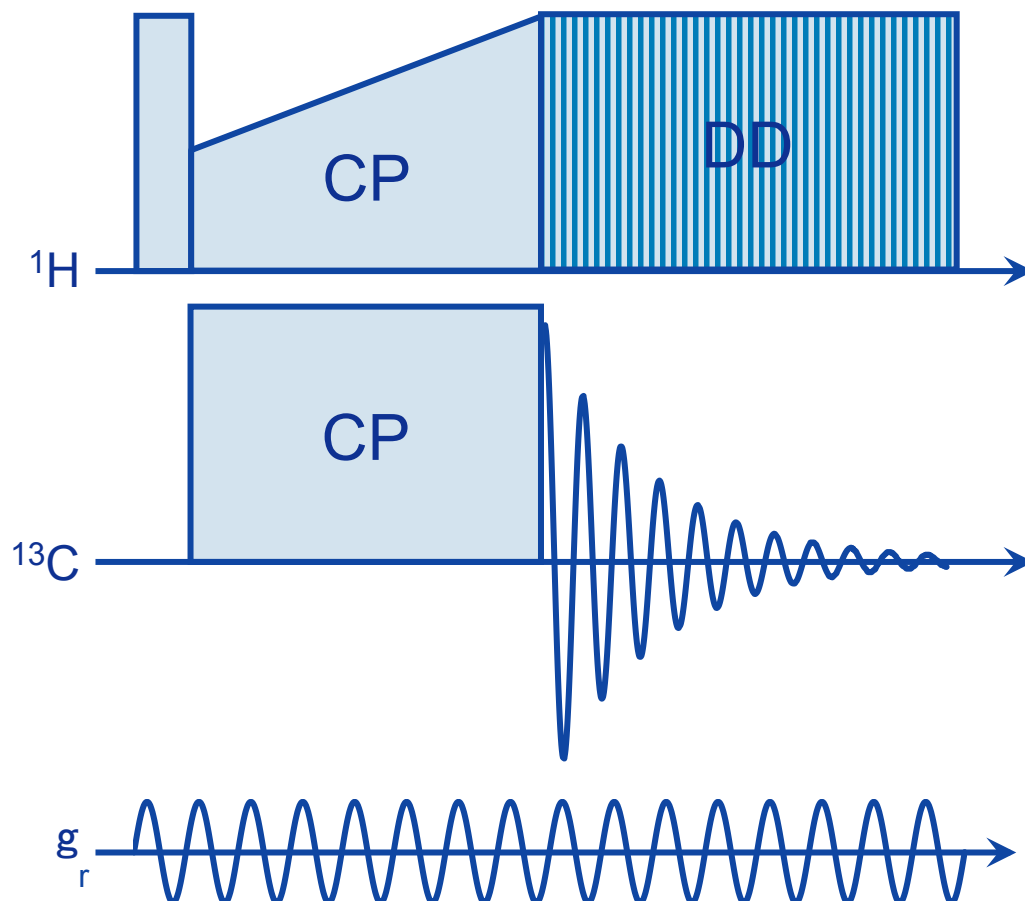
- Common for systems with abundant high gamma nuclei ( $^1\text{H}$ ,  $^{19}\text{F}$ )

- direct polarisation (DP)
- typically high power is needed ( $u_1 = 100$  kHz)
- limited decoupling duration
- quantitative heteronuclear
- RF = het D (sensitivity)
- MAS = CSA, Q, homo D, het D (sensitivity)



# CP-MAS with dipolar decoupling

- Common for systems with abundant high gamma nuclei ( $^1\text{H}$ ,  $^{19}\text{F}$ )
  - typically high power is needed ( $u_1 = 100 \text{ kHz}$ )
  - limited decoupling duration
- semi quantitative heteronuclear (if calibrated)
- RF = het D
- MAS = CSA, Q, homo D
- CP = sensitivity



# Solid-state NMR hardware

## ■ Probeheads

- Single double-resonance Helmholtz coil c.f. multiple saddle coils in solution state
- coil and capacitors that make up Tank resonance circuit designed for high power
- Stator for MAS

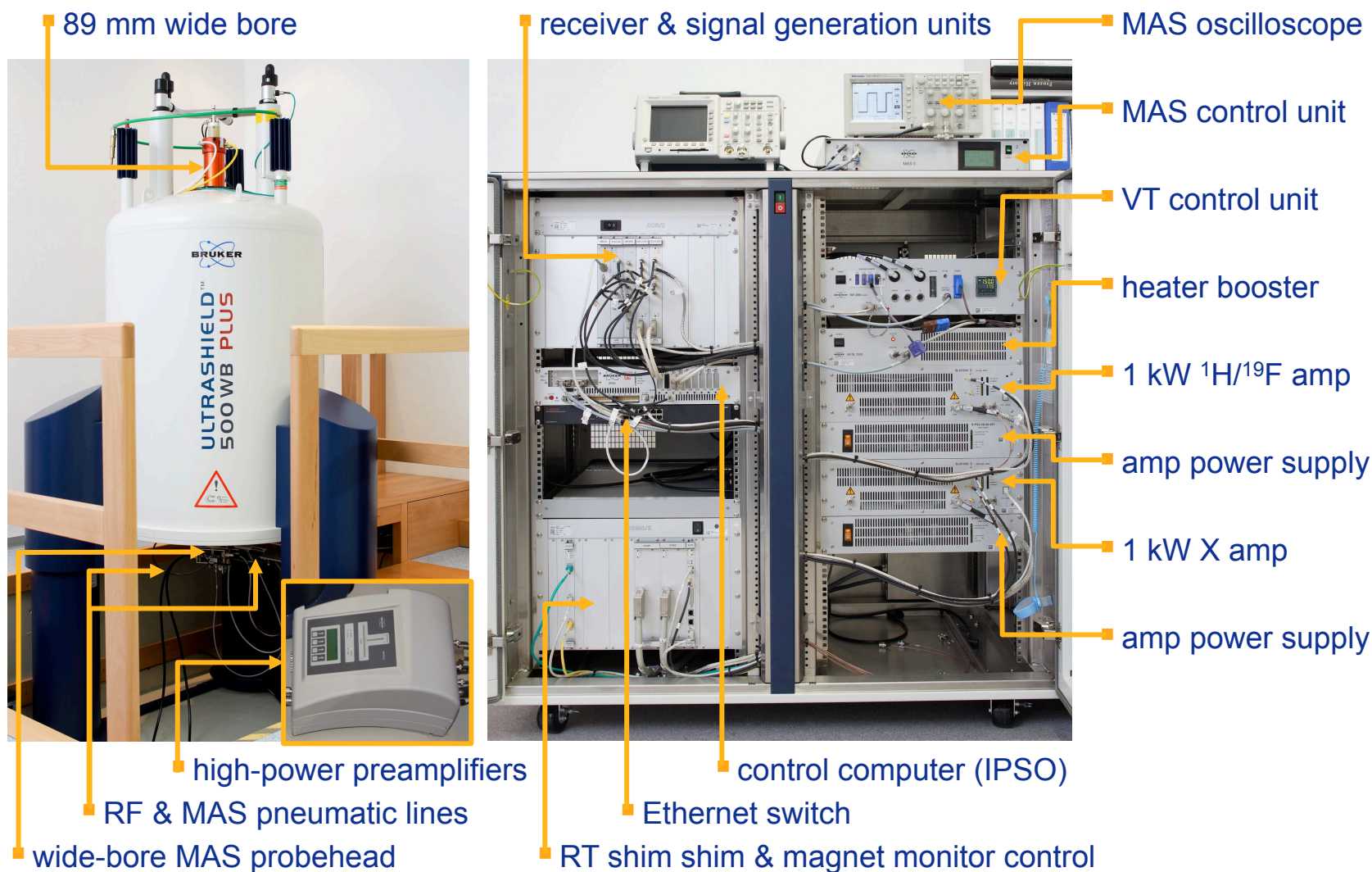
## ■ Spectrometer

- no  $^2\text{H}$  lock (possible to use external  $^2\text{H}$  lock if necessary)
- high-power high-fidelity signal pre-amplifiers
- high-power pulse amplifiers (1 kW) c.f. solution-state (10-100 W)

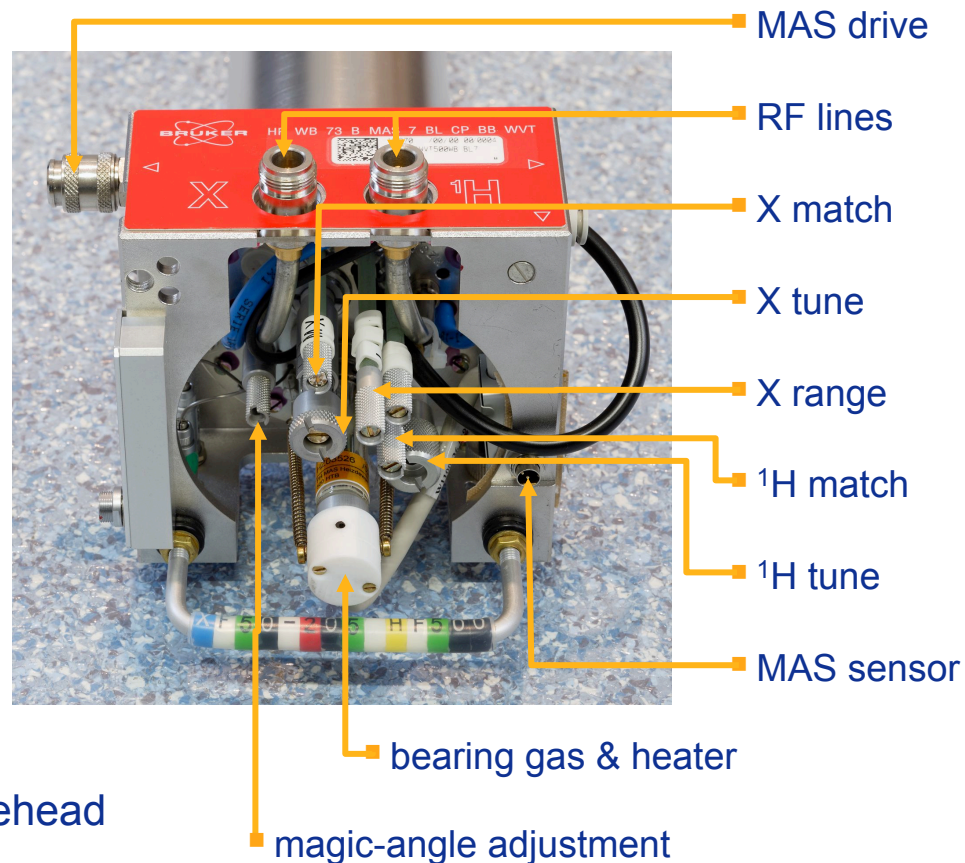
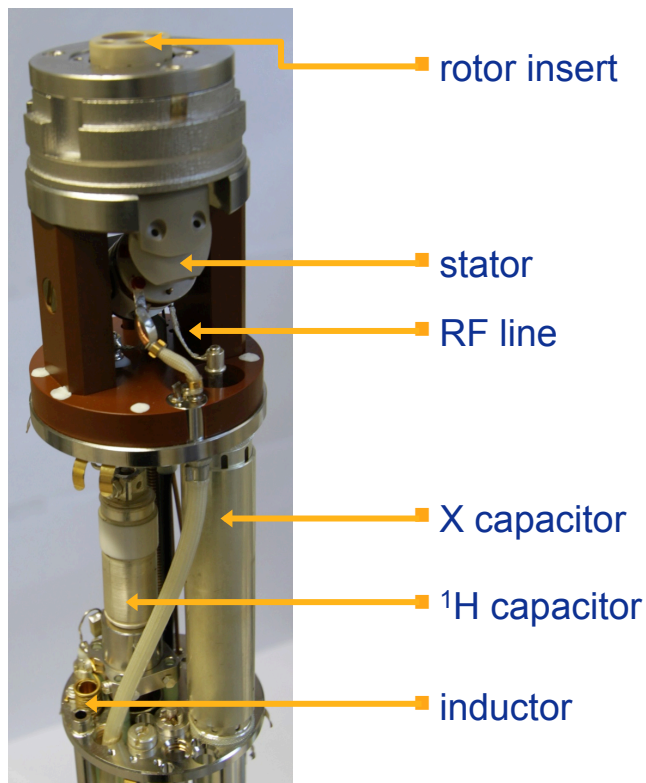
## ■ Magnets

- wide-bore (89 mm) superconducting magnets c.f. standard narrow-bore (54 mm)
- difficult to make field homogeneous so are physically larger and cost more
- NMR lab requirements not as demanding as for solution-state (low-resolution)

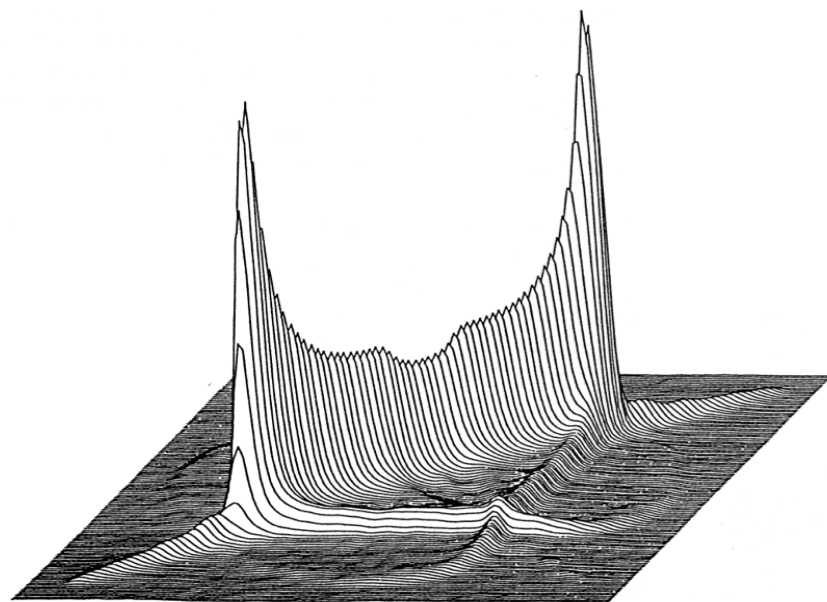
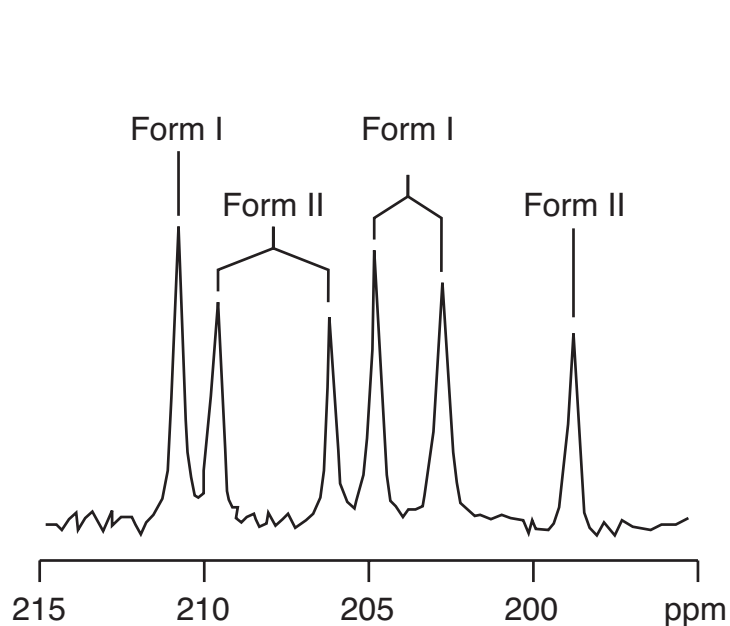
# Bruker AVIII 500 with 11.7 T WB magnet



# Wide-bore MAS probehead



- 3.2 mm MAS double-resonance probehead
  - $u_r$  1-25 kHz,  $u_1$  125 kHz  $\mu\text{s}$  @  $2 \mu\text{s}$   $\pi/2$
- 7 mm MAS double-resonance  $^{13}\text{C}$   $\text{N}_2$  optimised high-temperature probeheads ( $\times 2$ )
  - $u_r$  1-7 kHz,  $u_1$  63 kHz @  $4 \mu\text{s}$   $\pi/2$



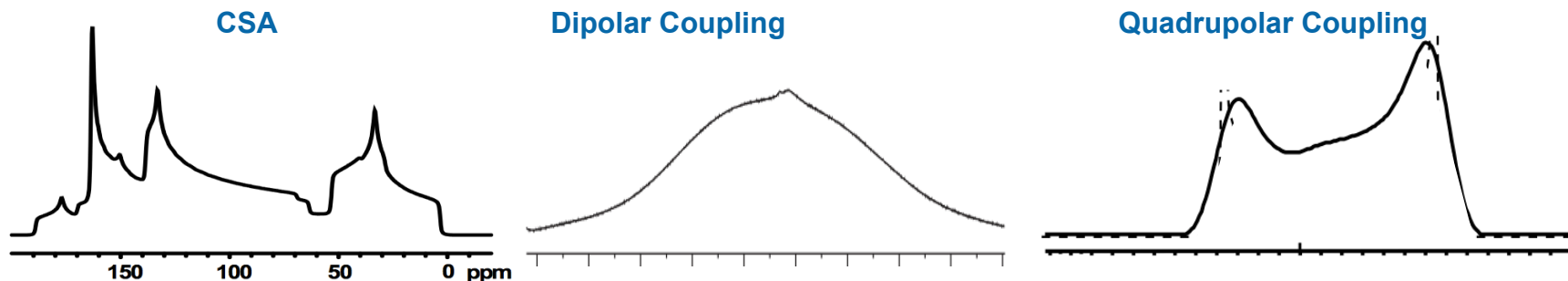
# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

## **SOLID-STATE NMR SPECTROSCOPY**

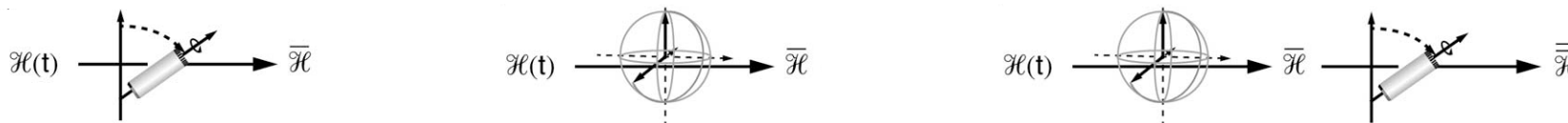
## **PRACTICAL APPLICATIONS**



# High-resolution solid-state NMR

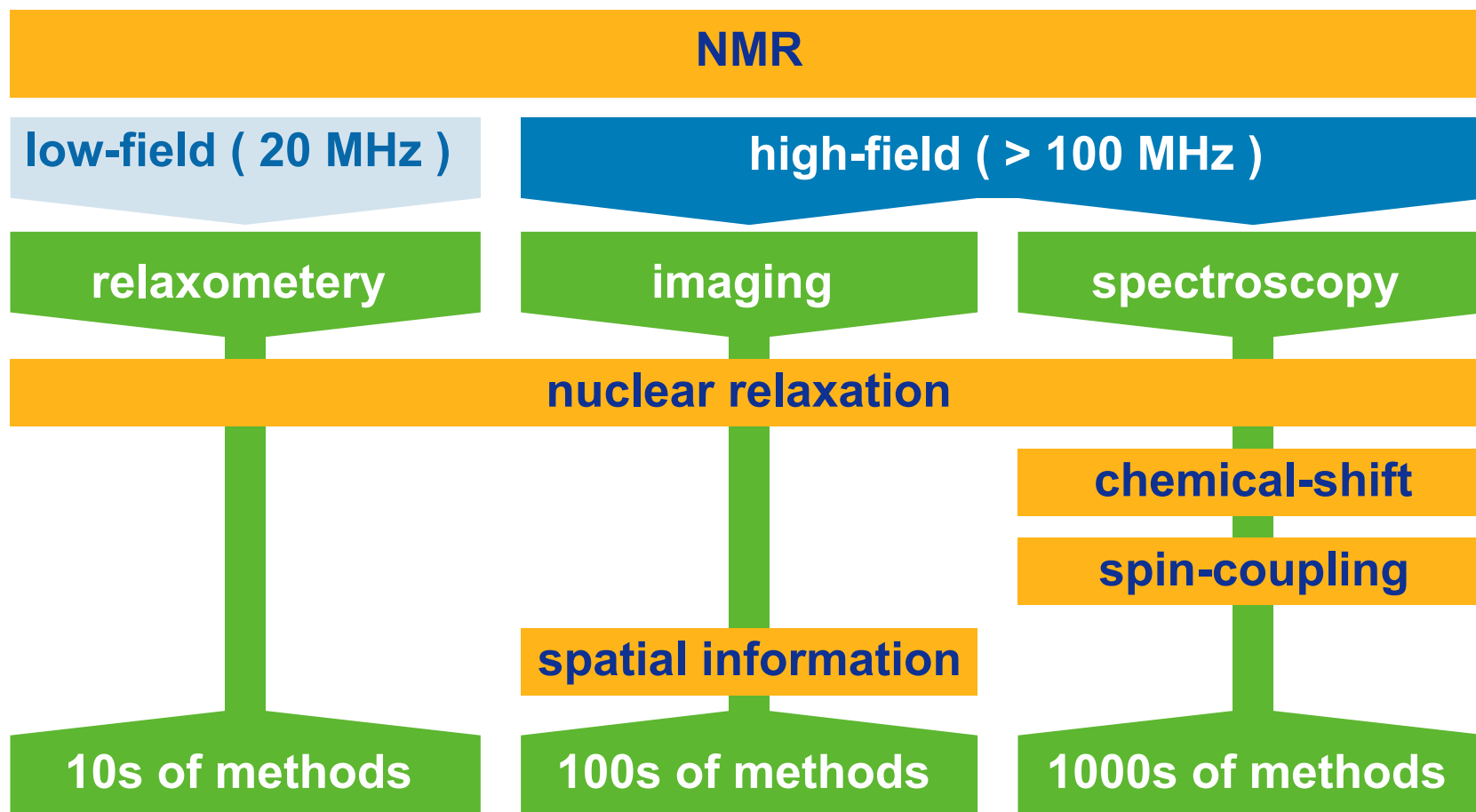


- Hamiltonian can be expressed as product of two parts:
  - space-part: components that can be manipulated by physical rotation
  - spin-part: components that can be manipulated by RF pulses



- Can remove influence of anisotropic interactions by creation of an average Hamiltonian during NMR experiment or signal detection
  - can either average space part (sample rotation), spin-part (RF) or both

# Types of NMR Implementation

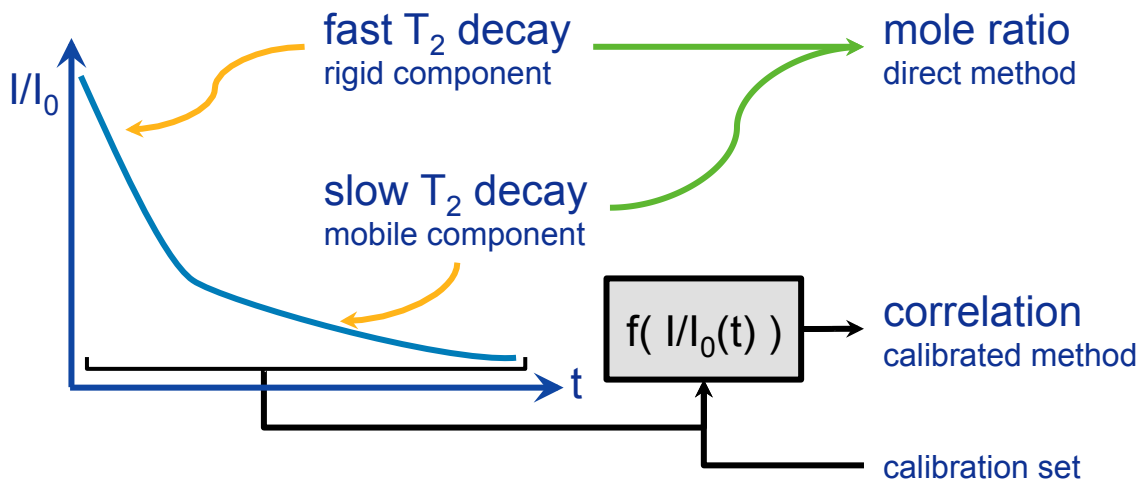
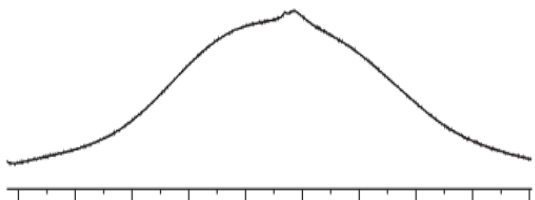




# Time-domain NMR / NMR relaxometry



no spectroscopic information  $I(u)$



- Static solid-state NMR experiments undertaken using  $B_0$  low-fields
  - typical  $B_0 = 0.5$  T & 20 MHz and only address  $^1\text{H}$  or  $^{19}\text{F}$  ( $^{31}\text{P}$ )
  - fully coupled with no-line narrowing applied, no spectral resolution (wideline)
  - only measure bulk relaxation of solids  $T_1$ ,  $T_2$ 
    - parameterised fitting of time domain signal to mobility (multi exponential fit)
    - chemometric fitting of whole time-domain signal to properties (comonomer content, xylene sol.)

# Some application of Time-domain NMR

## Chemical Industry

- Free & bound moisture content in powders
- Moisture content in solids/liquids/catalysts/detergents
- Activity of catalysts
- Loading efficiency of catalysts
- Molecular diffusion rates in solids/liquids
- Coating weight of solid particles
- viscosity of liquids
- component analysis of solids/liquids
- Hydrogen/fluorine content of solids/liquids
- Particle sizes of pigments
- Adsorption selectivity of zeolites

## Cosmetics industry

- Moisture & oil content in powders & pigments
- Droplet size distributions in emulsions
- Oil content of liquids

## Polymer Industry

- Density of polyethylene
- Xylene soluble of polypropylene
- Finish content of synthetic fibres
- Moisture content of synthetic fibres
- Plasticizer content of polymers
- Solid & mobile content of polymers
- Extent of polymerization of polymers
- Hydrogen content of polymers
- Fluorine content of polymers
- Extent of cure & cross-linking in polymers/resins
- Viscosity, molecular weight during polymerisation
- Filler content of polymer composites
- Rubber content of polymer blends
- Copolymer ratios of polymer blends
- Polymer mixing & compatibility of polymer blends

- All based on the same idea:
  - Components can be distinguished by their different  $T_2$ s
  - Property correlates to local molecular mobility which is expressed in the NMR signal

# More applications of Time-domain NMR!

## Food Industry

- Solid fat content in fat containing products
- Moisture content in margarine
- Component analysis of milk
- Moisture & fat content of milk powder
- Moisture & fat content of food products in general
- Oil composition of oils
- Moisture content of rice
- Moisture & oil content of flour
- Moisture & oil content of emulsions
- Droplet size distributions of emulsions
- Moisture & solid distributions of gels
- Freezing process research of solids
- Moisture content of starches
- Extent of cooking/hydrolysis of cooked foods

## Agricultural Industry

- Moisture & oil content in solids/seeds/feed
- component analysis in fertiliser
- organic content in soil

## Petroleum industry

- Hydrogen content of petroleum distillates
- Hydrogen content of coal
- Oil content & mobility distribution of waxes
- Oil content of rocks/oil sands/shales
- Porosity, pore size distribution of rocks
- Viscosity of oil and petroleum products
- Free vs bound components

## Pharmaceutical industry

- Moisture & oil content of capsules/tablets
- Coating weight of capsules/tablets
- Component analysis
- Fluorine & hydrogen content

## Research

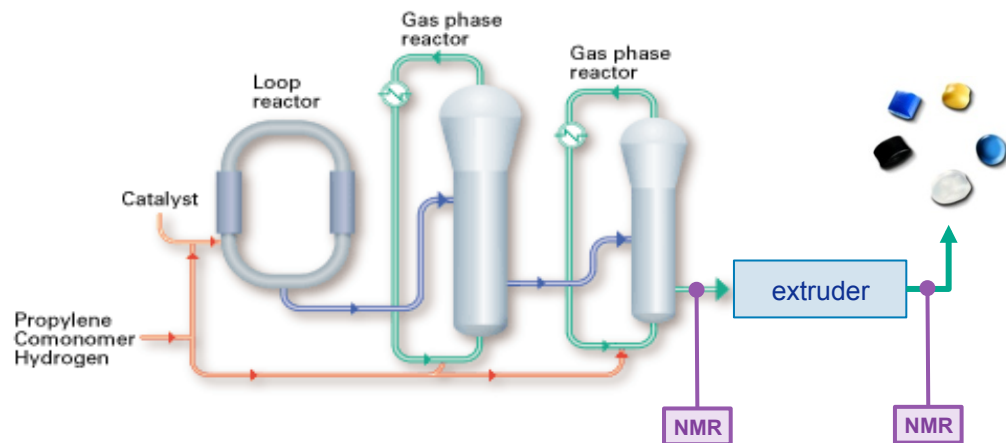
- relaxation measurements
- diffusion measurements
- imaging
- particle size distribution
- spin-diffusion

## ■ All based on the same idea:

- Components can be distinguished by their different  $T_2$ s
- Property correlates to local molecular mobility which is expressed in the NMR signal

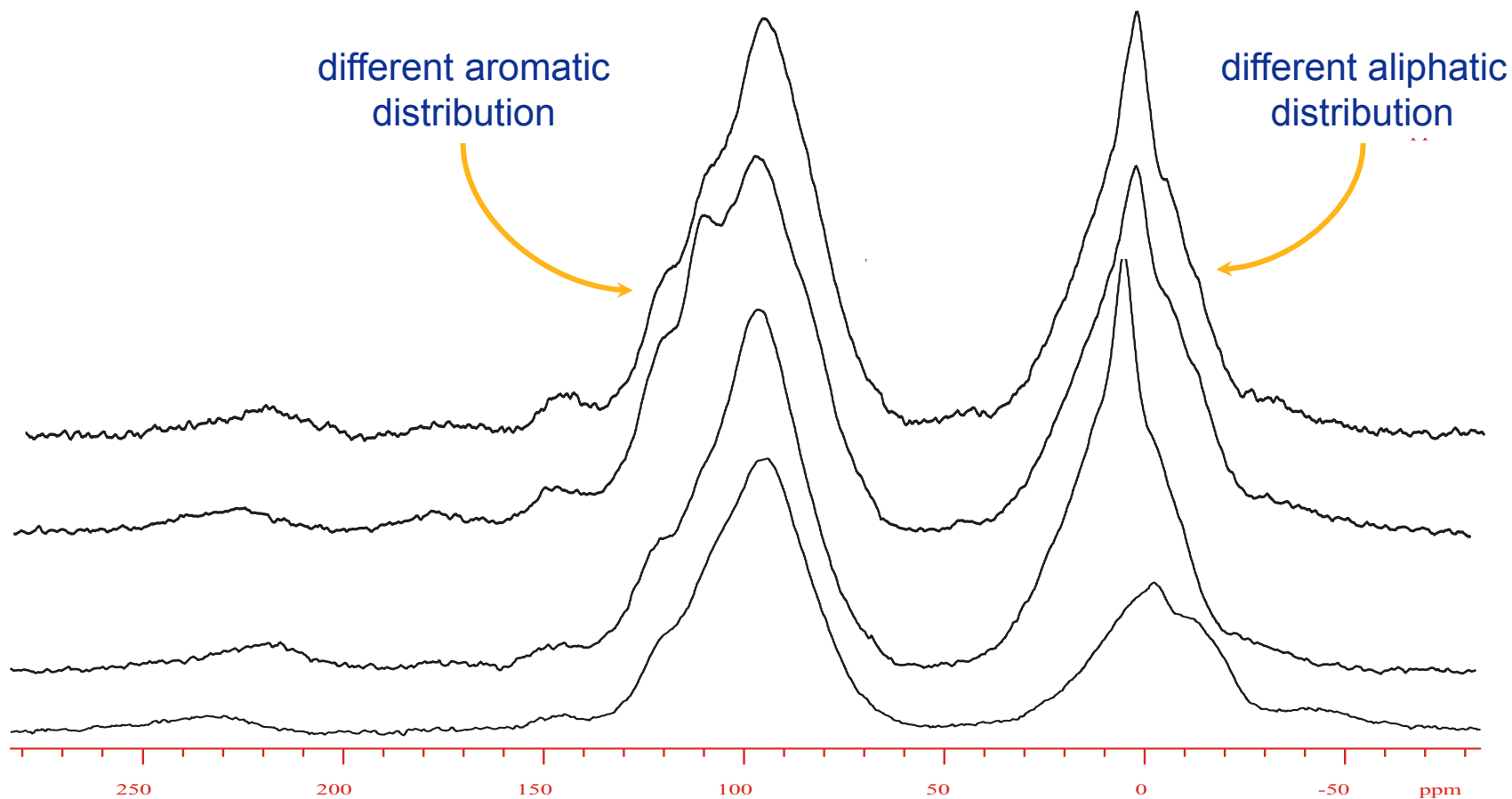
<http://www.pctnmr.com/Applications.htm>

# Time-domain NMR & Borealis



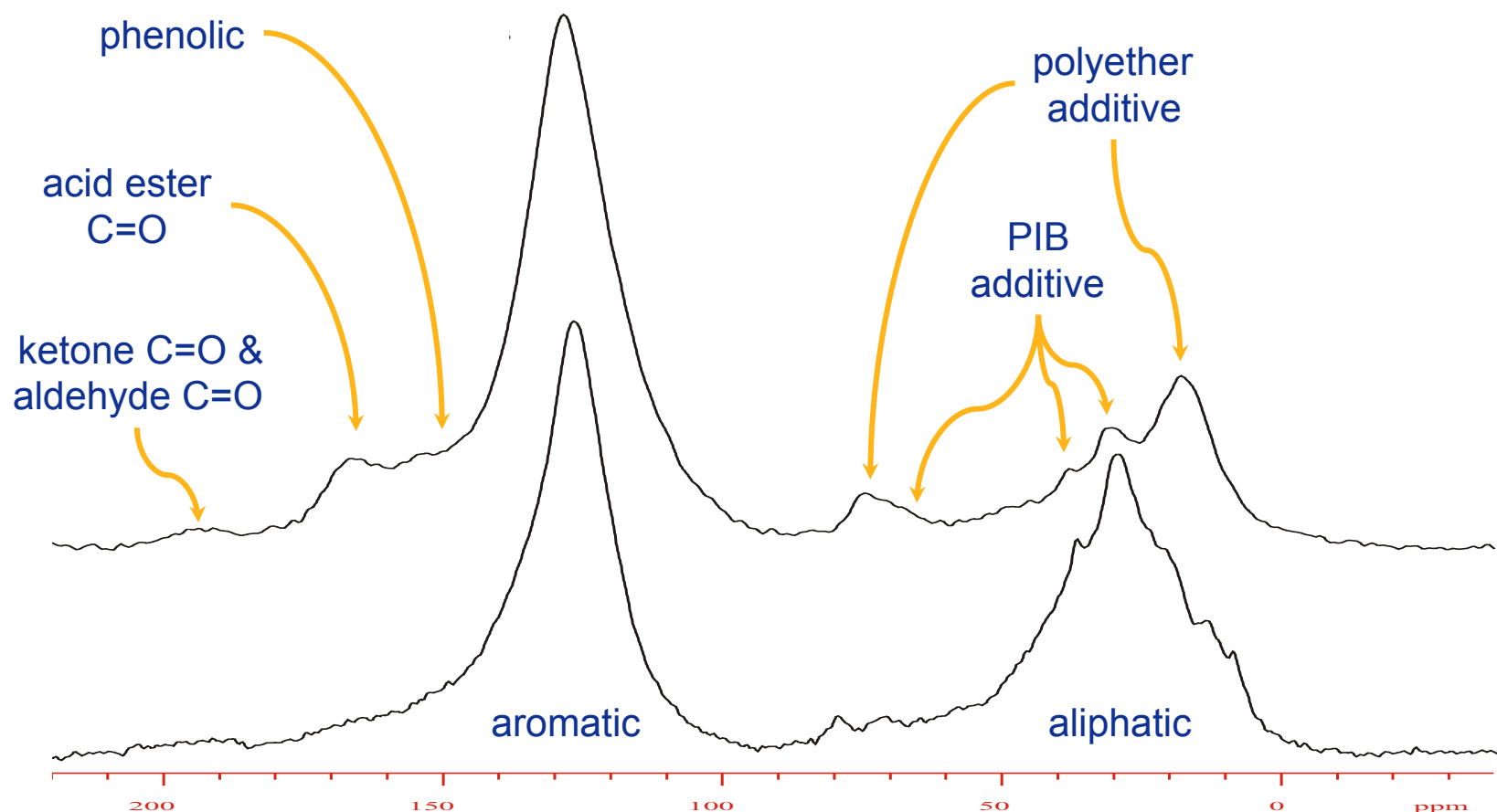
- Time-domain NMR used to monitor/control continuous polymerisation process in plant
  - Online process control via XS, C2, IV...

# $^{13}\text{C}$ CPMAS of coal



- Complex black bio-solid difficult to analyse by other techniques

# $^{13}\text{C}$ CPMAS of combustion deposits

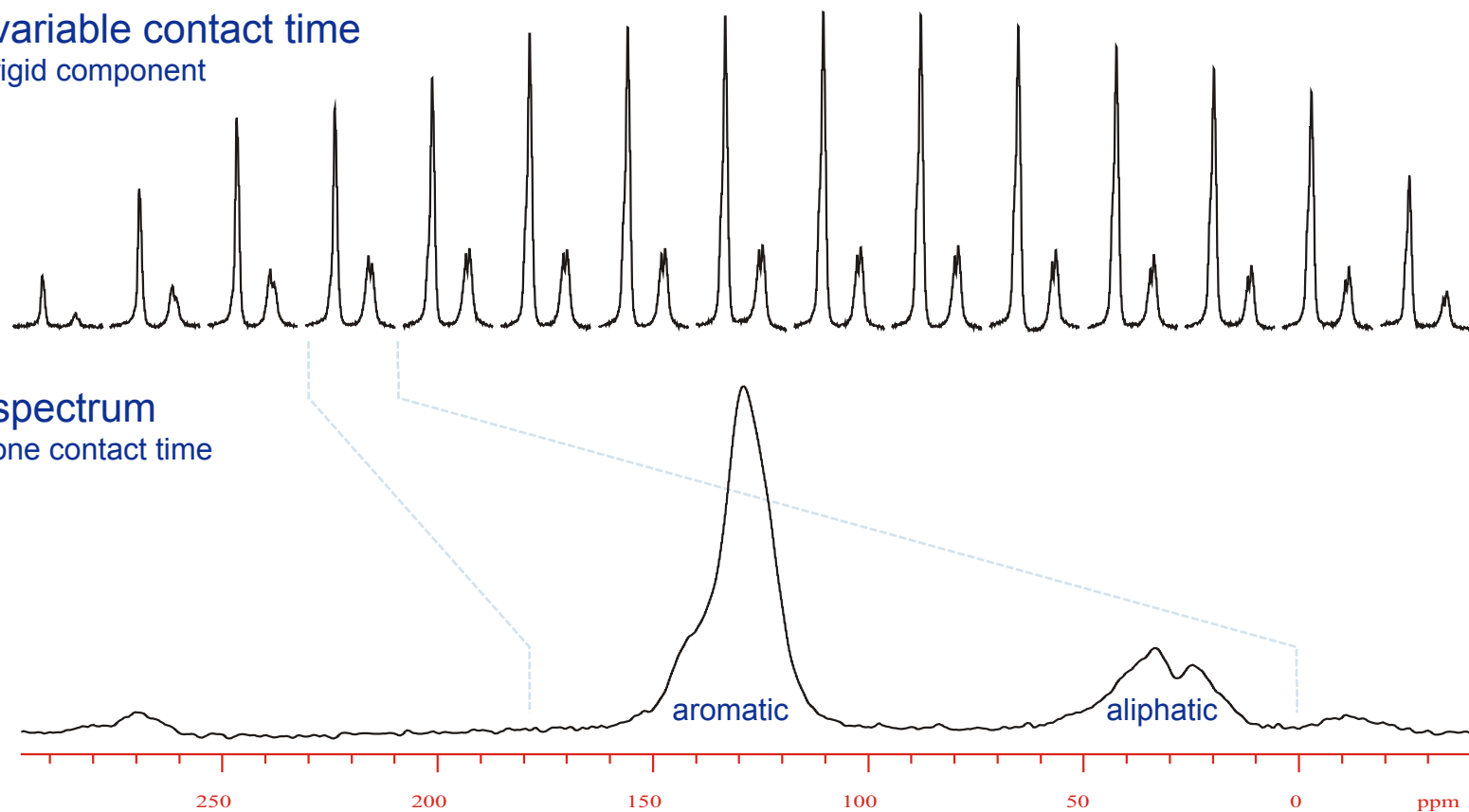


- Complex black bio-solid difficult to analyse by other techniques

# $^{13}\text{C}$ CPMAS of refinery coke

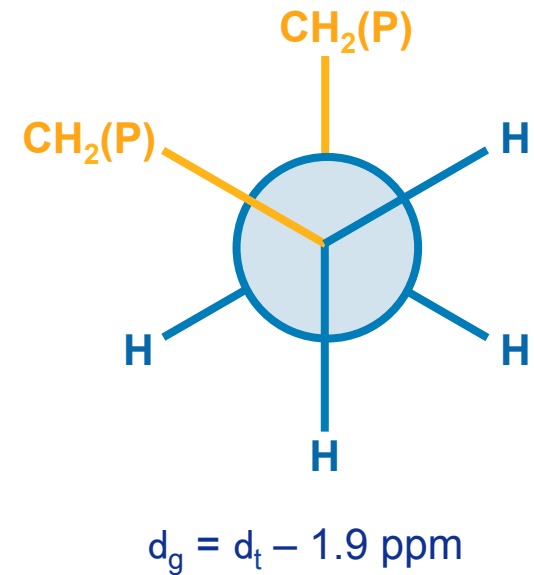
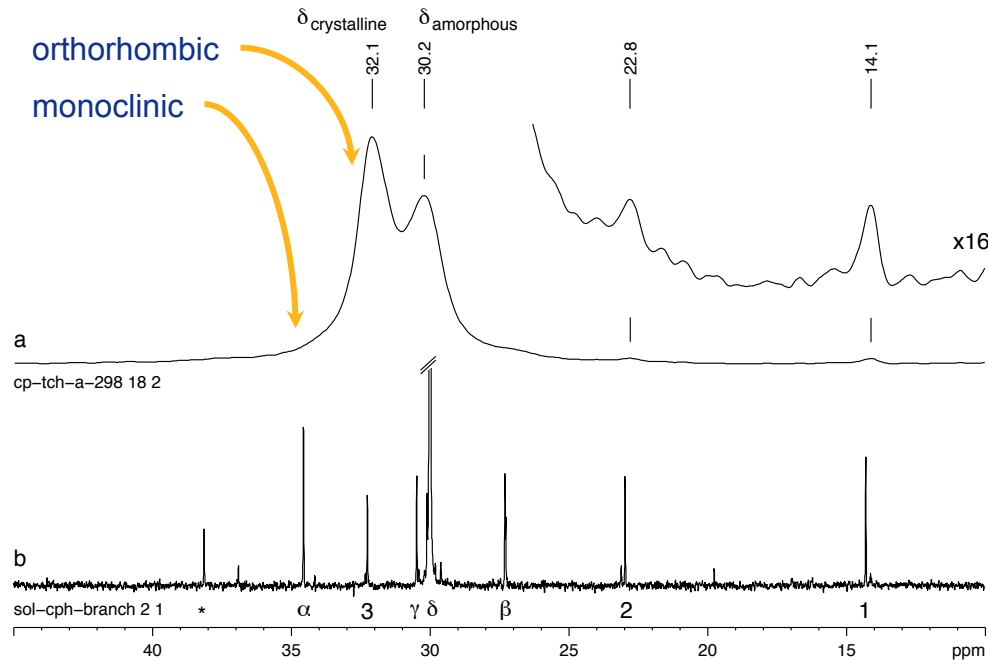
variable contact time  
rigid component

spectrum  
one contact time



- Complex black bio-solid difficult to analyse by other techniques

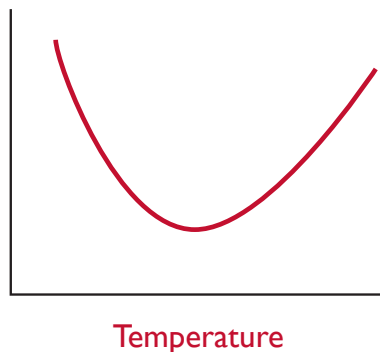
# Solid-state NMR of polyethylene



- Polyethylene is semi crystalline comprising all-trans crystalline lamellae joined by amorphous regions with conformational disorder
- In the solid-state  $^{13}\text{C}$  NMR spectrum reports on the morphology
  - broad peak at 30 ppm disordered amorphous regions (lower d due to more g-gauche)
  - narrow peak at 32 ppm ordered rigid crystalline regions (polymorph at 35 ppm)

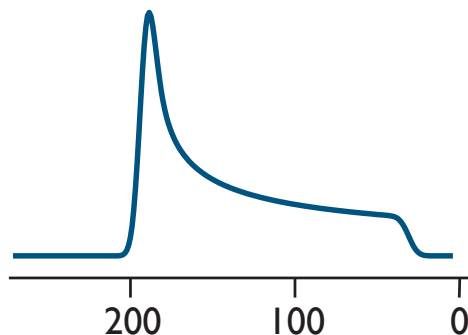


# Polymer dynamics by solid-state NMR



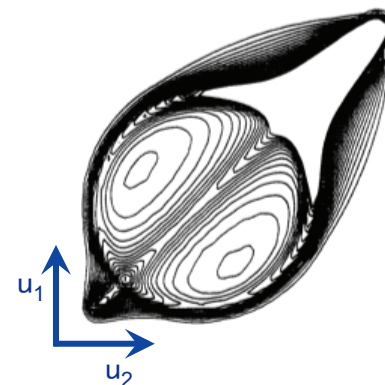
## Relaxation

Minima in  $T_1(T)$  indicated occurrence of motions in MHz range ( $t_c < 1 \mu s$ )



## Lineshape Analysis

observation of motional narrowing in kHz range ( $t_c < 1 ms$ ) & geometry information of motion



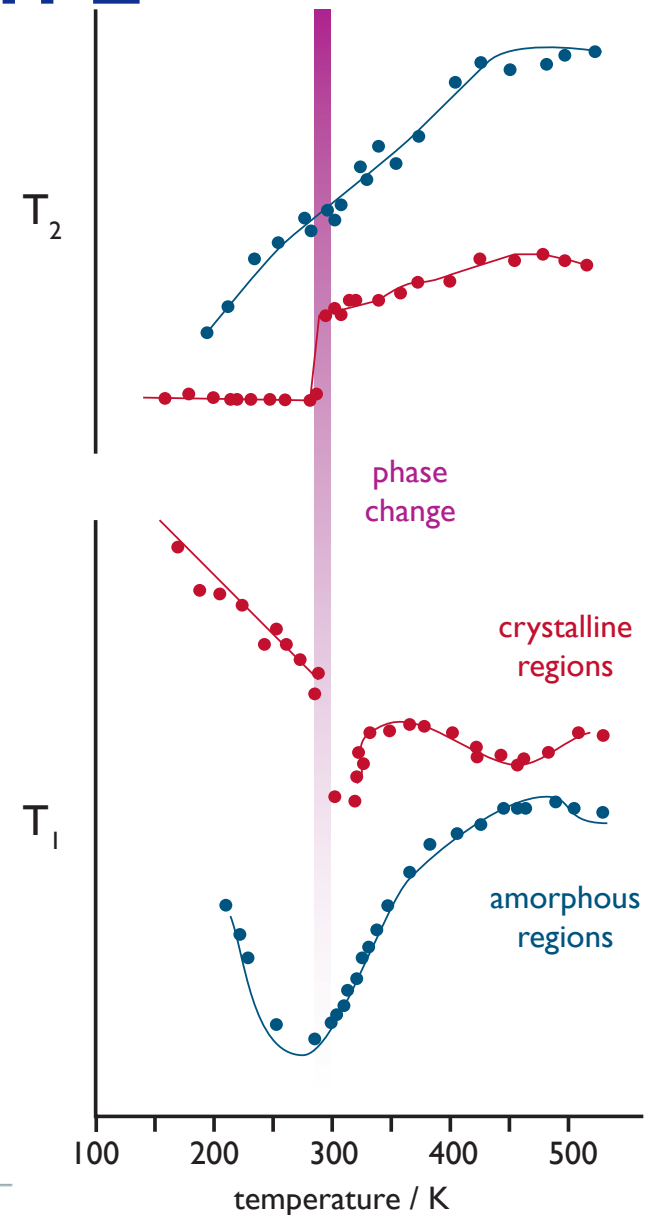
## 2D Exchange

Exchange cross peaks indicate very slow motions ( $t_c > 10 ms$ ) & detailed geometric information

- Most method only probe time-scale of molecular motion in polymers
  - differential scanning calorimetry, dynamic mechanical and dielectric spectroscopy
- Solid-state NMR provided additional information about:
  - geometry, amplitude and chemical location

# $^{19}\text{F}$ $T_1$ & $T_2$ relaxation in PTFE

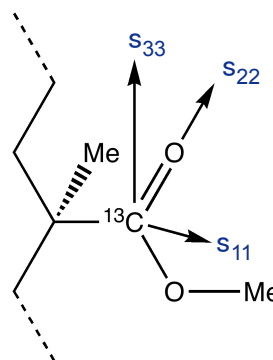
- Poly(tetrafluoroethylene) (PTFE) is an semi-crystalline polymer  $T_m = 600 \text{ K}$  &  $T_g = 400 \text{ K}$
- In the amorphous regions
  - $T_1$  has a minima at 273 K and
    - $t_c^{-1}$  equal to Larmor frequency (30 MHz):  $t_c \sim 3 \text{ ns}$
  - $T_2$  increases rapidly from 220 K
    - $t_c^{-1}$  similar to  $^{19}\text{F}$  linewidth to cause narrowing:  $t_c \sim 20 \text{ ms}$
- In the crystalline regions
  - Both  $T_1$  and  $T_2$  show discontinuity at 292 K
    - indicative of a change in phase transition
  - $T_1$  has minima at 450 K
  - $T_2$  increases rapidly from 340 K



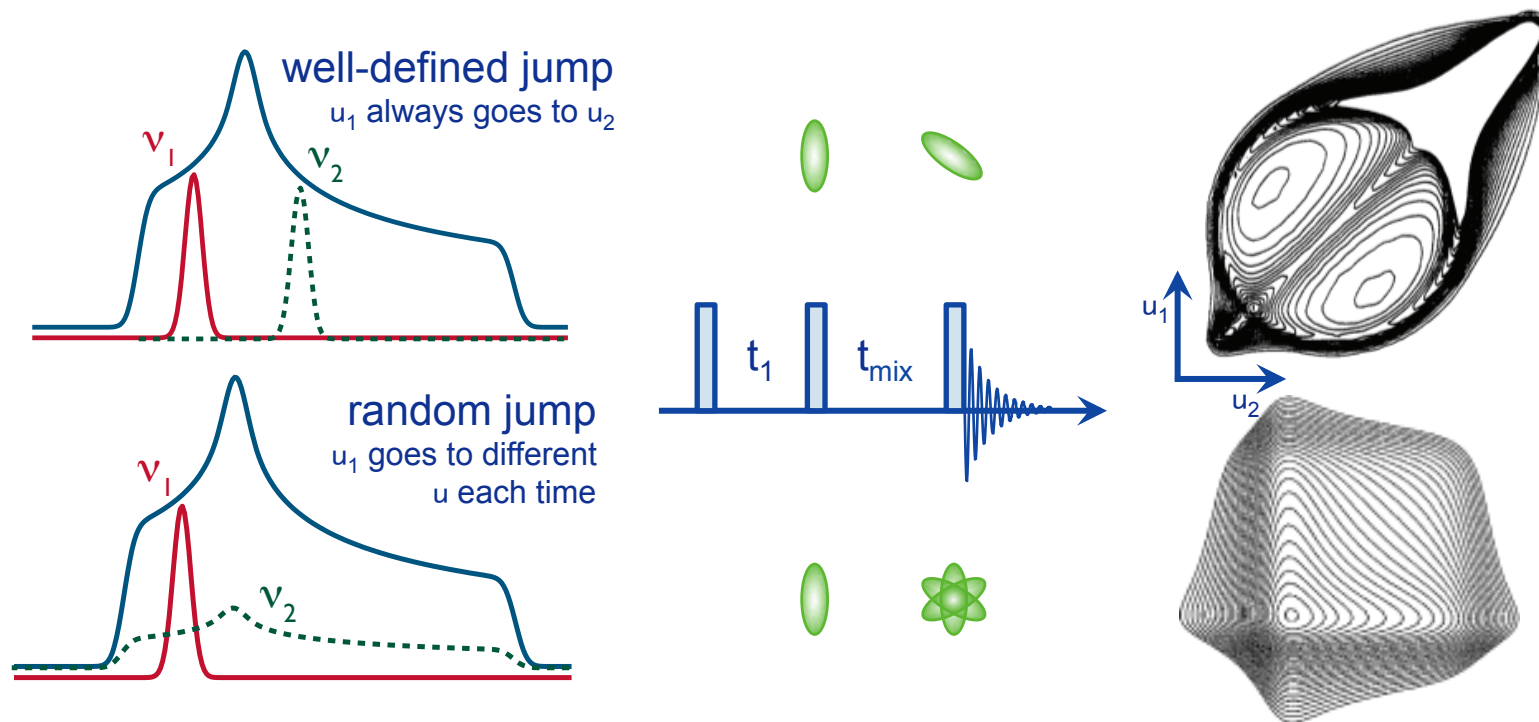
# Lineshape & $T_g$ in PMMA

- Polymethylmethacrylate (PMMA) is an amorphous polymer with a glass-transition temperature ( $T_g$ ) of 338 K

- $T = 295 \text{ K} < T_g$ 
  - $s_{33}$  aligned parallel to polymer chain and  $s_{22}$  aligned parallel to C=O
- $T = 355 \text{ K} > T_g$ 
  - lineshape narrows indicating presence of motions with rate  $> 10 \text{ kHz}$  ( $d_{\text{CSA}}$ )
- $T = 395 \text{ K} \gg T_g$ 
  - anisotropic chain motion leads to motional averaging and axial symmetry of  $s$

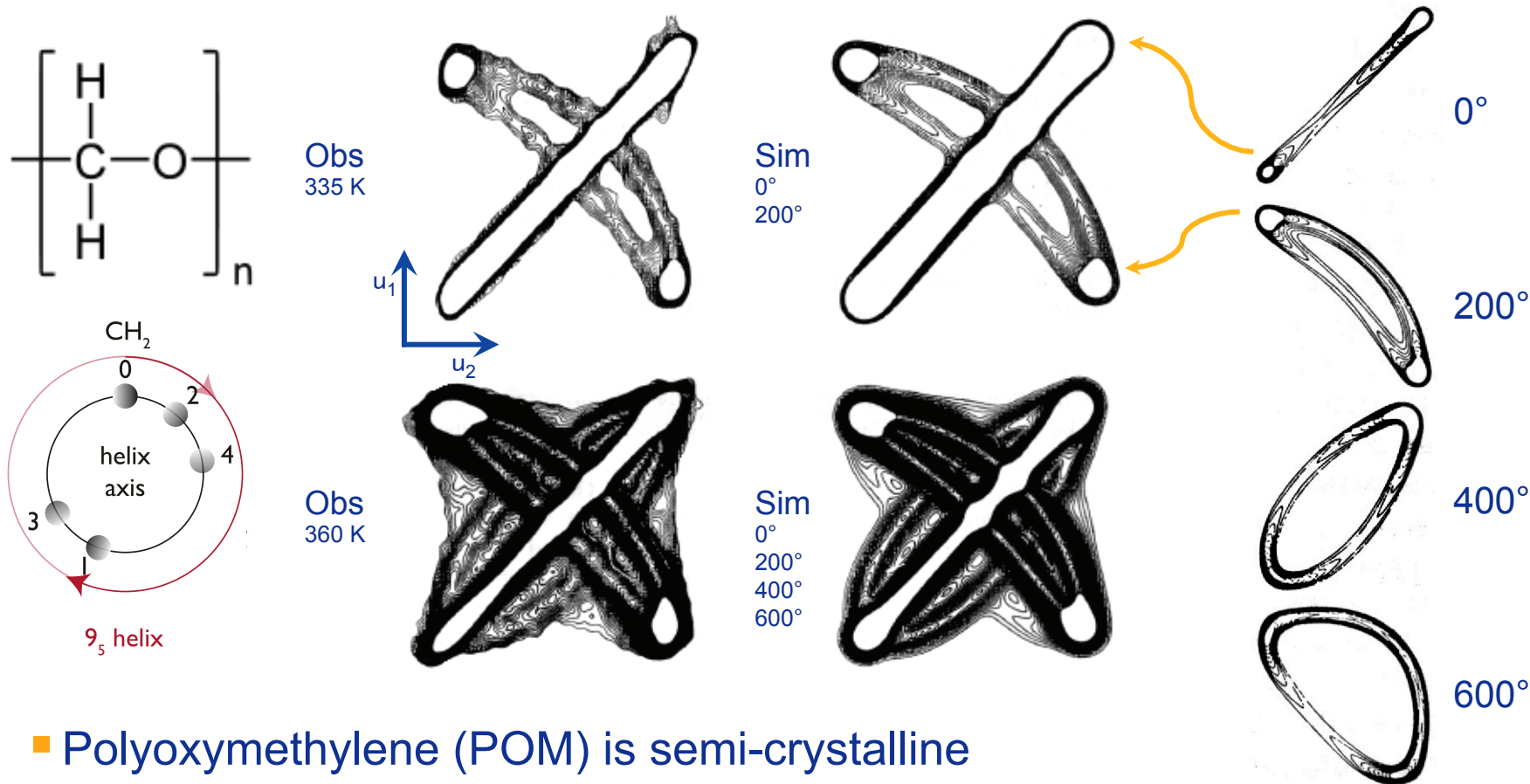


# 2D exchange spectroscopy



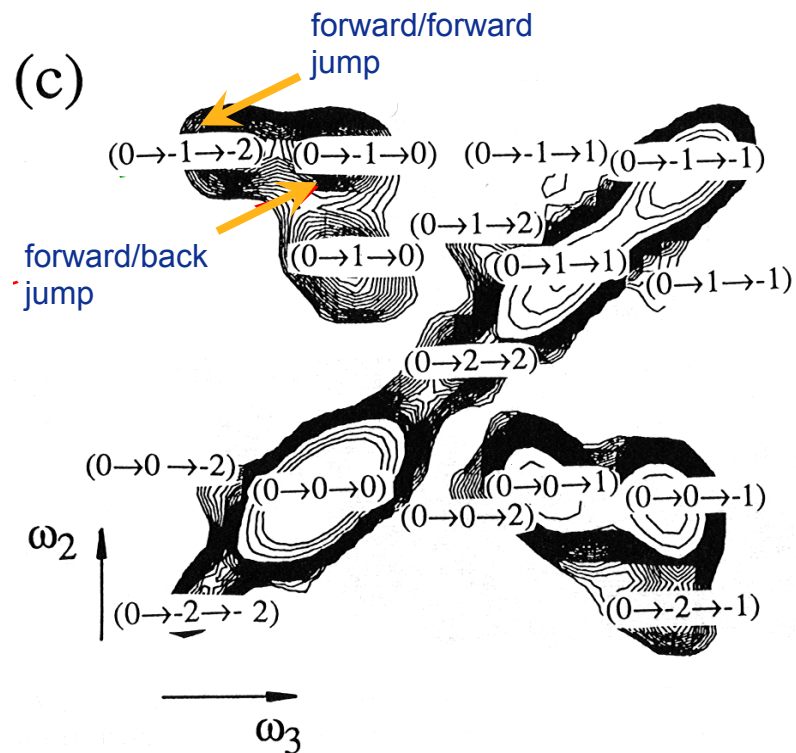
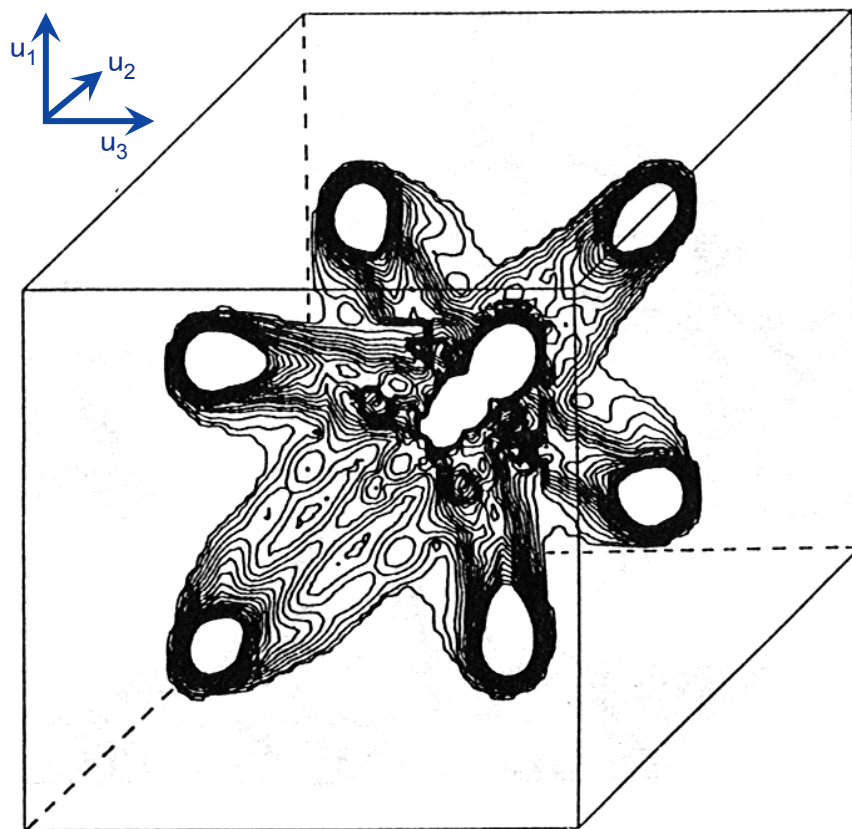
- 2D correlation spectroscopy: magnetisation transferred between spins
- 2D exchange spectroscopy: change of chemical environment of a spin
  - solution-state exchange probes chemical exchange (equilibrium & rearrangement)
  - solid-state exchange probes molecular reorientation

# 2D exchange spectroscopy of POM



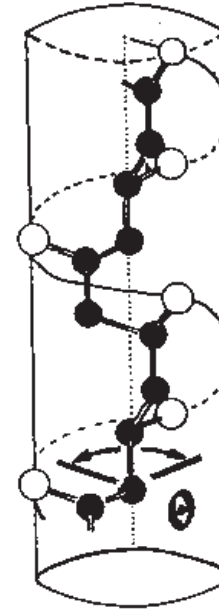
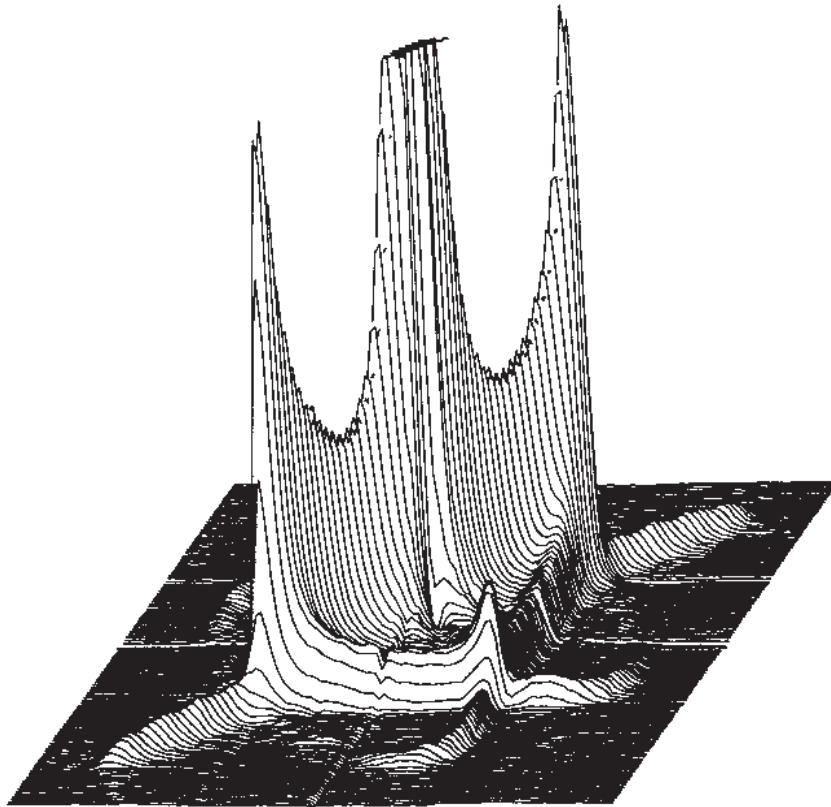
- Polyoxymethylene (POM) is semi-crystalline with  $T_g = 200$  K and a  $9_5$  helix crystalline morphology
  - 9 monomer occupy 5 turns of helix i.e. adjacent CH<sub>2</sub> related by 200° rotation

# 3D exchange spectroscopy of POM



- Intensity in 3D shows likelihood of a given jump

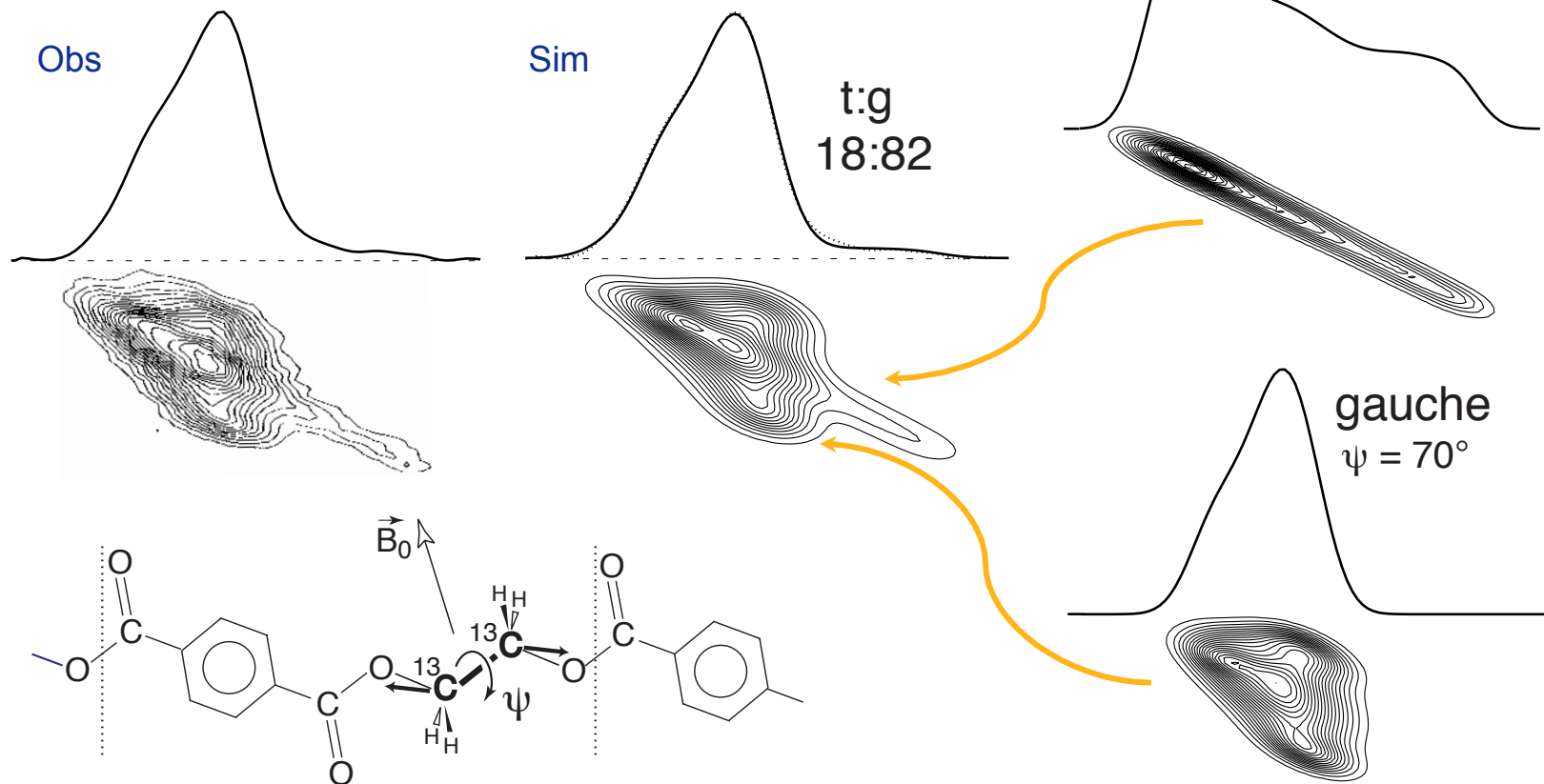
# Static $^2\text{H}$ exchange



- Isotactic polypropylene with methyl group deuterated at  $T = 387\text{ K}$ 
  - Elliptical ridges characteristic of helical chain reorientation



# $^{13}\text{C}$ - $^{13}\text{C}$ DQ Correlation

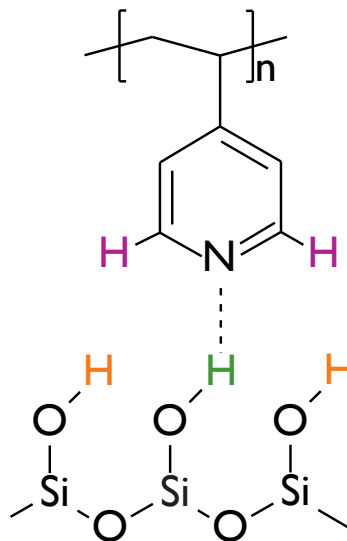
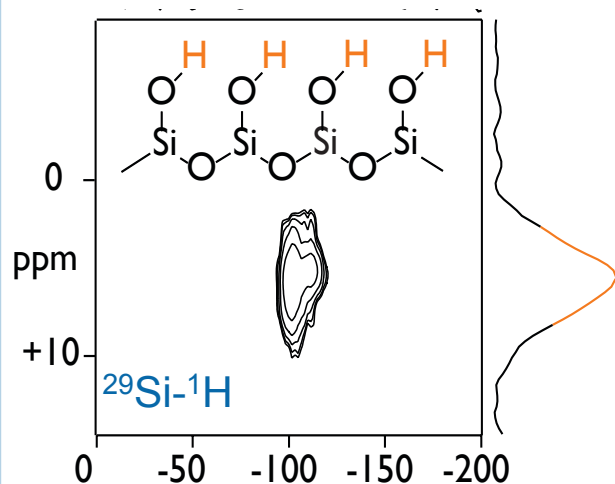


- Poly(ethylene terephthalate) (PET)  $^{13}\text{C}$  SQ-DQ correlation
  - Torsion angle distribution in an amorphous solid

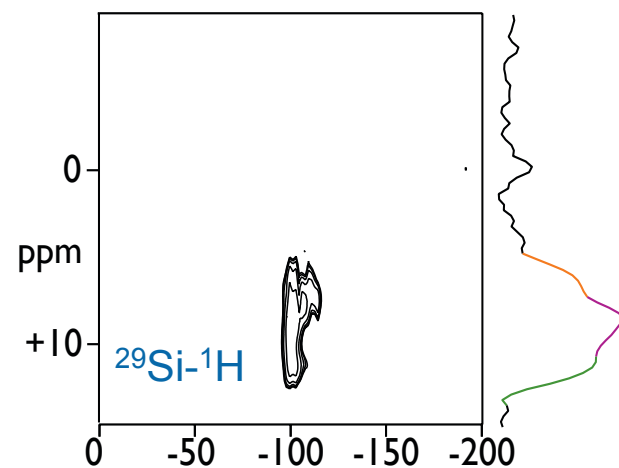


# Polymer nanocomposite interfaces

silica only  
only free silonols

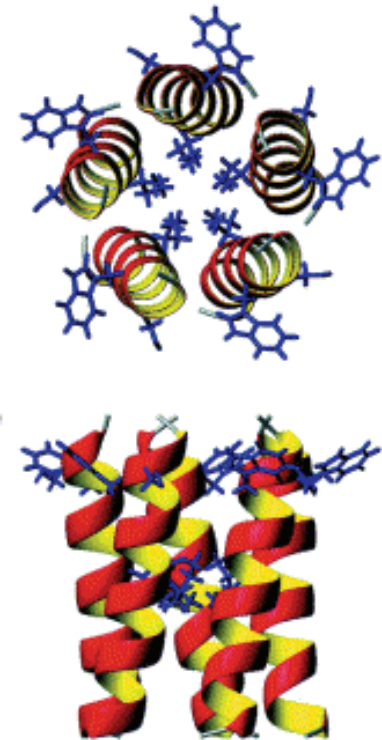
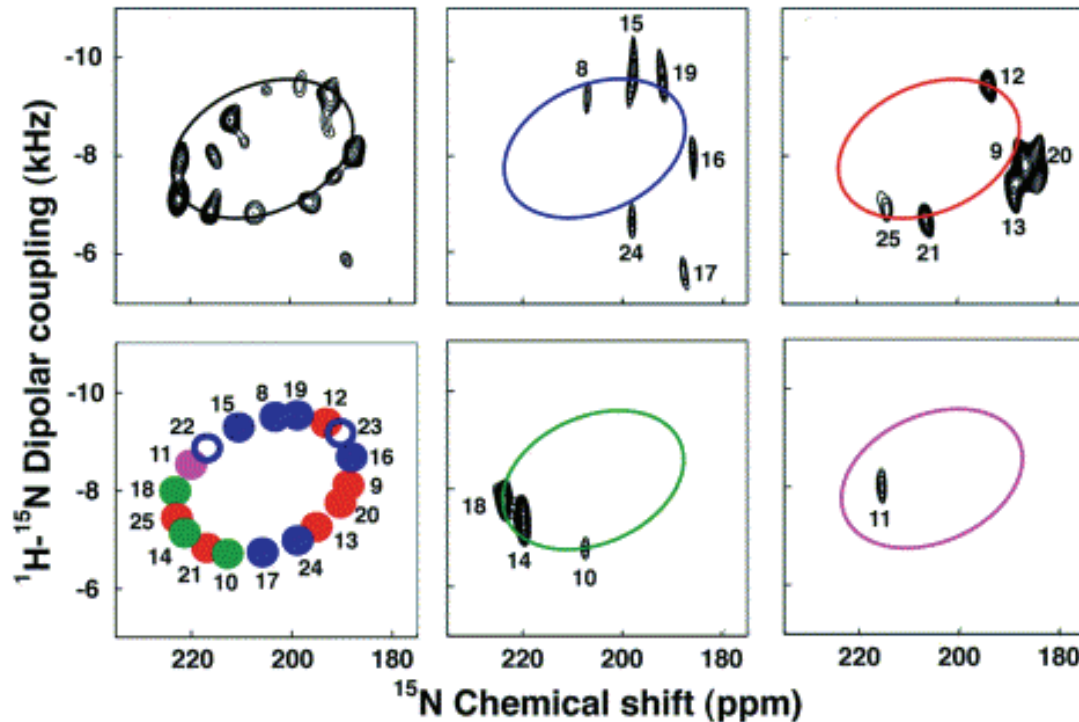


silica & polymer  
free & H-bonded silonols



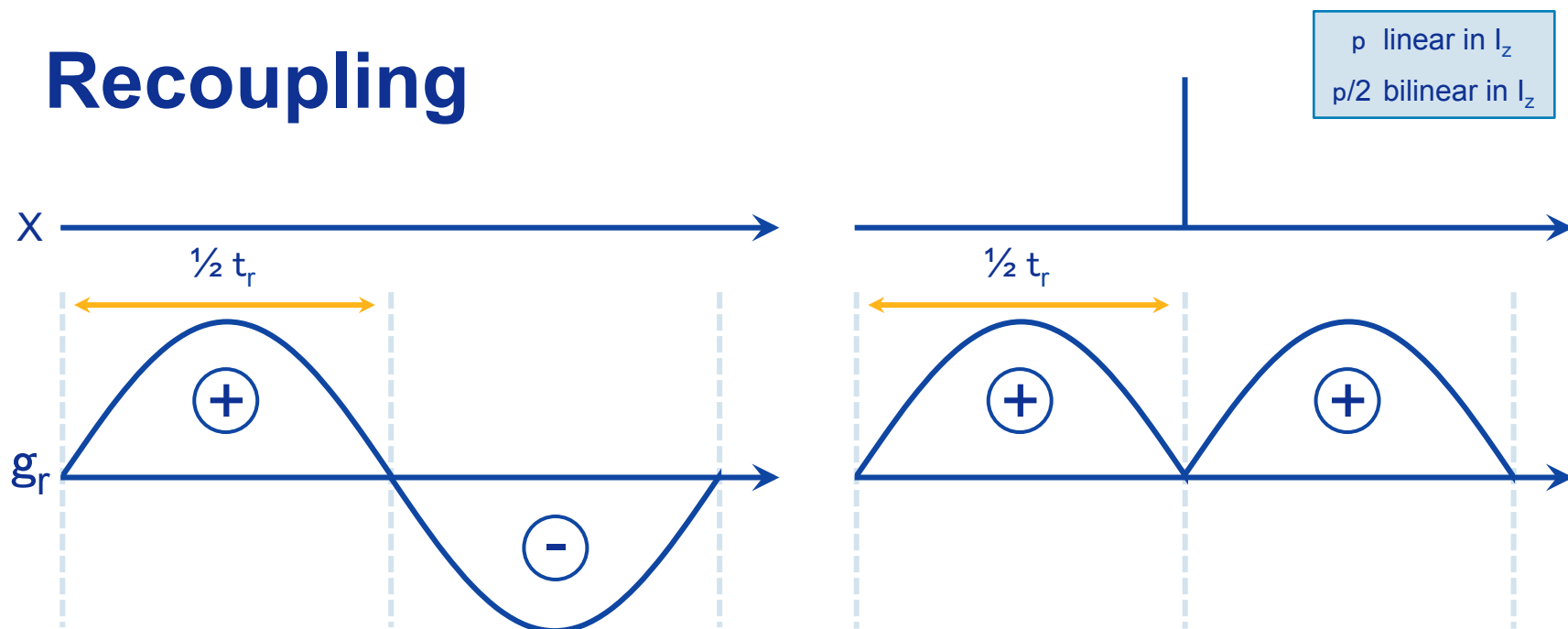
- H-bonding at interface observed via  $^1\text{H}$ - $^{29}\text{Si}$  dipolar interaction in solid

# $^{15}\text{N}$ PISEMA of VPU ion channel from HIV



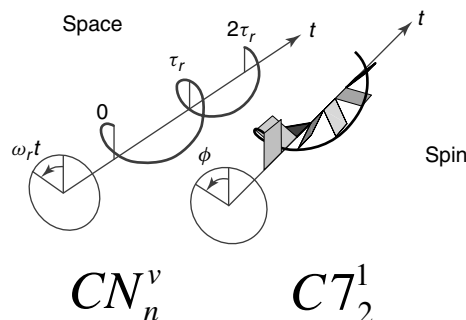
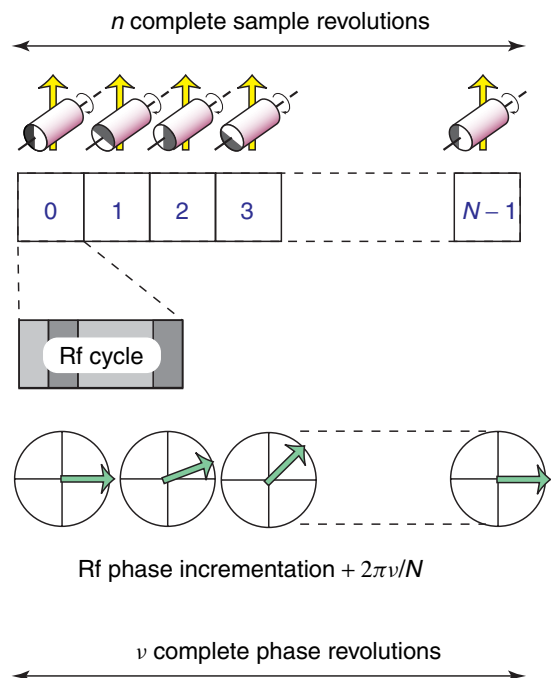
- Protein structure from  $^1\text{H}$ - $^{15}\text{N}$  dipolar interaction in solid
  - static  $^{15}\text{N}$  NMR of biological systems in orientated lipid bilayer

# Recoupling

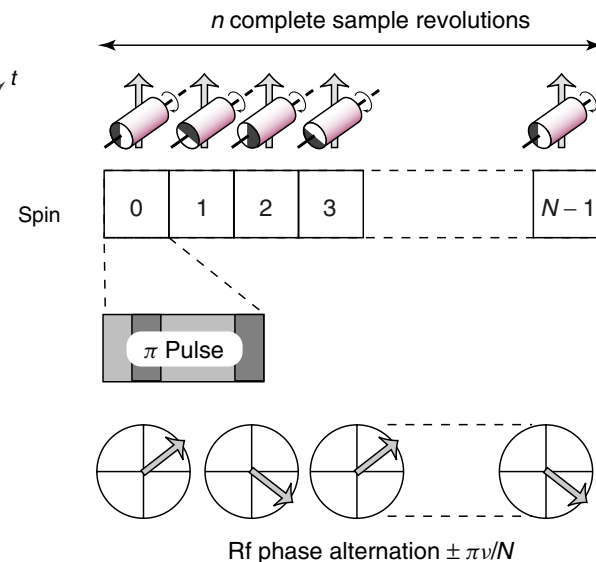


- MAS creates an average Hamiltonian for anisotropic interactions
  - modulation of NMR anisotropic interaction by  $\sin(w_r \cdot t + g)$  and  $\sin(2w_r \cdot t + 2g)$
  - only in the second half of each rotor period are interaction averaged to isotropic value
- Apply spin inverting pulse after  $t_r/2$  interactions are recoupled
  - after full rotor period interaction has finite value
- Allows anisotropic interaction to be observed in a controlled way ( $n \cdot t_r$ )

# Symmetry based pulse sequences

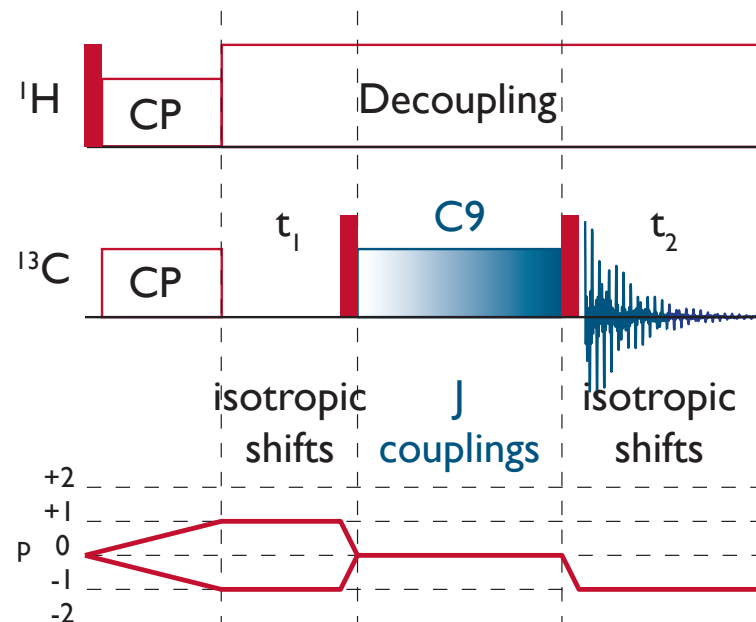
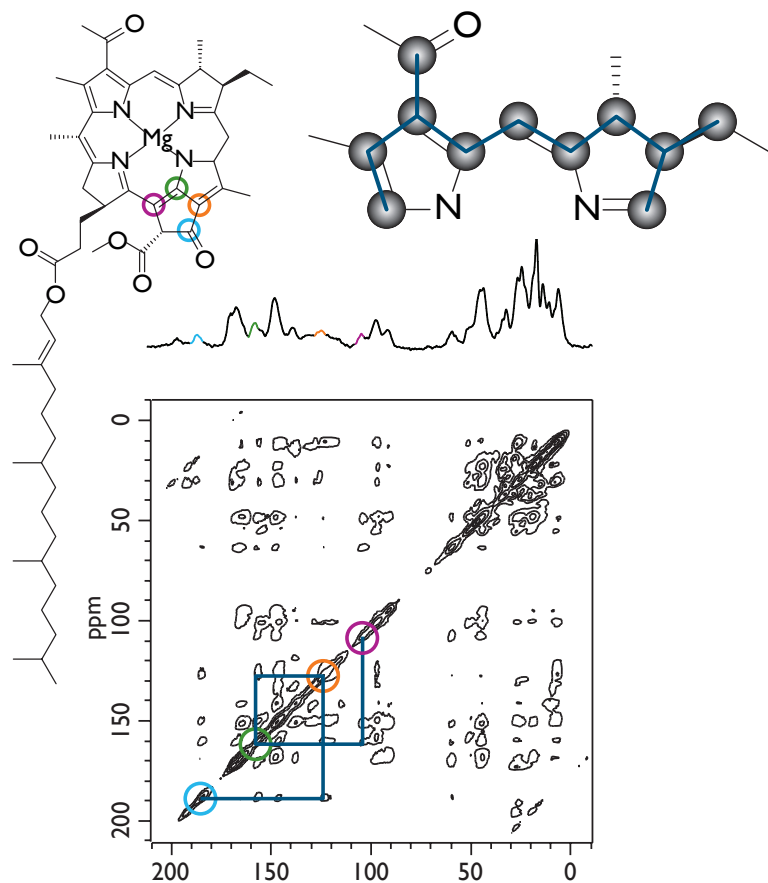


- RF phase modulated in  $N$  discrete steps
- $n$  spatial rotations completed in the same time as  $v$  spin rotations.



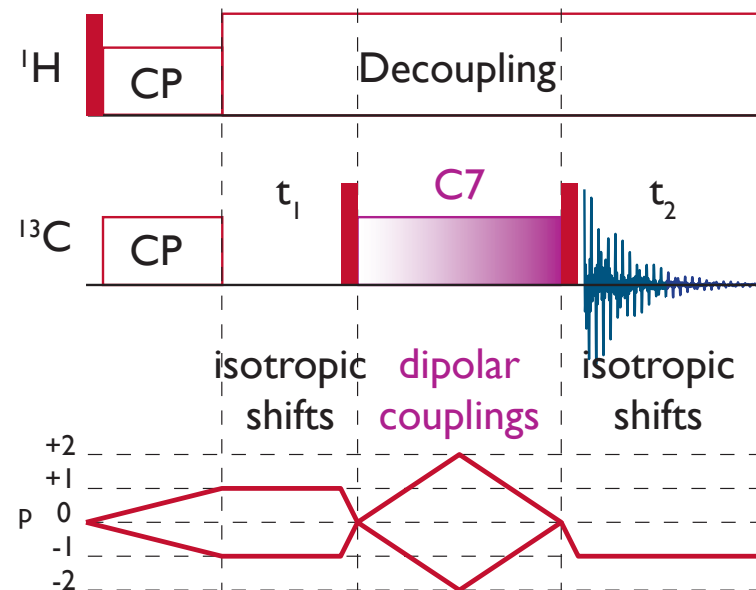
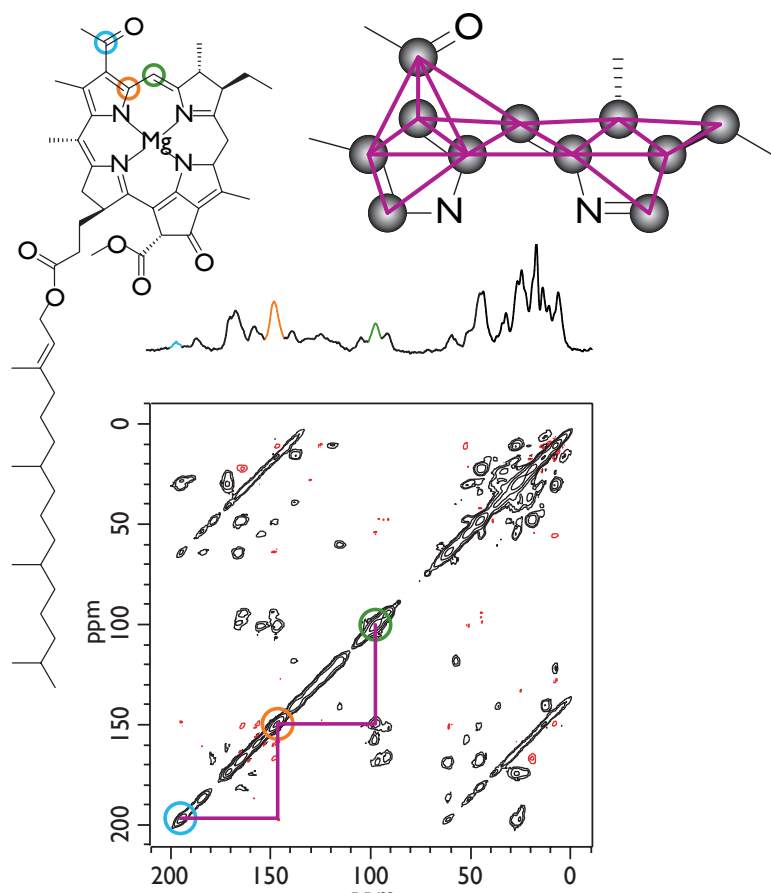
- Manipulate space and spin part at same time
  - C sequences based on composite  $360^\circ$  pulses with phase increment of  $360^\circ / N$
  - R sequences based on composite  $180^\circ$  pulses with phase increment of  $360^\circ / N$
- Allow specific selection of a given interaction in solid state

# Scalar correlation of U- $^{13}\text{C}$ -chlorophyll



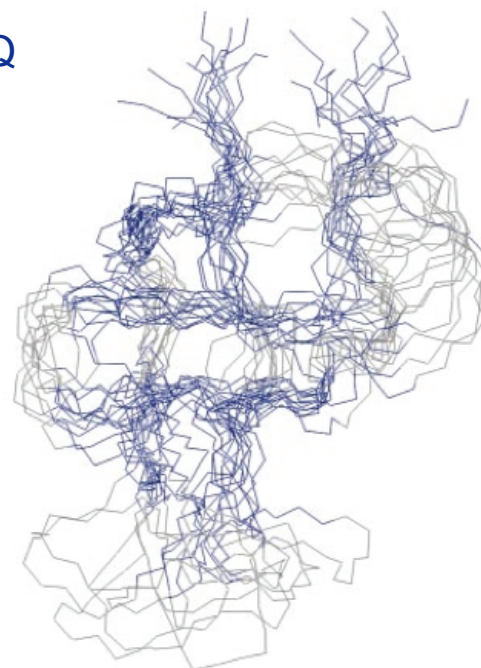
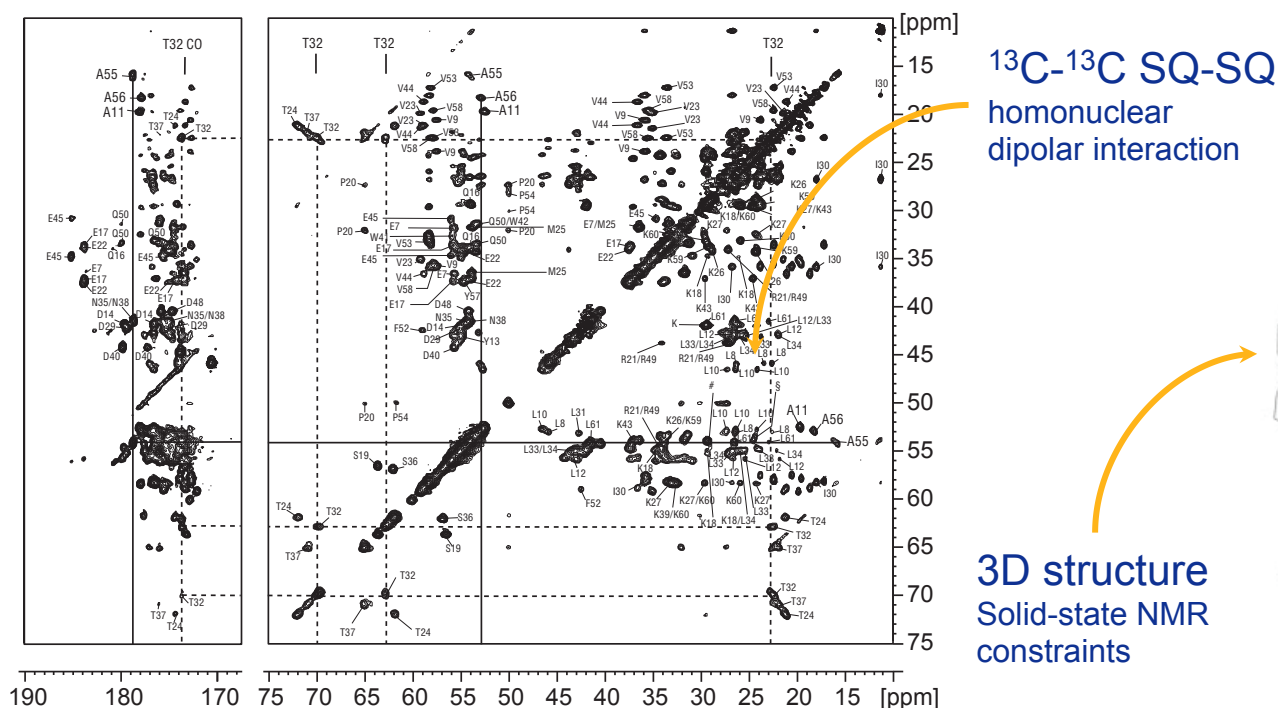
- Selection of J-interaction using symmetry based C9 in solid-state

# Dipolar correlation of U- $^{13}\text{C}$ -chlorophyll



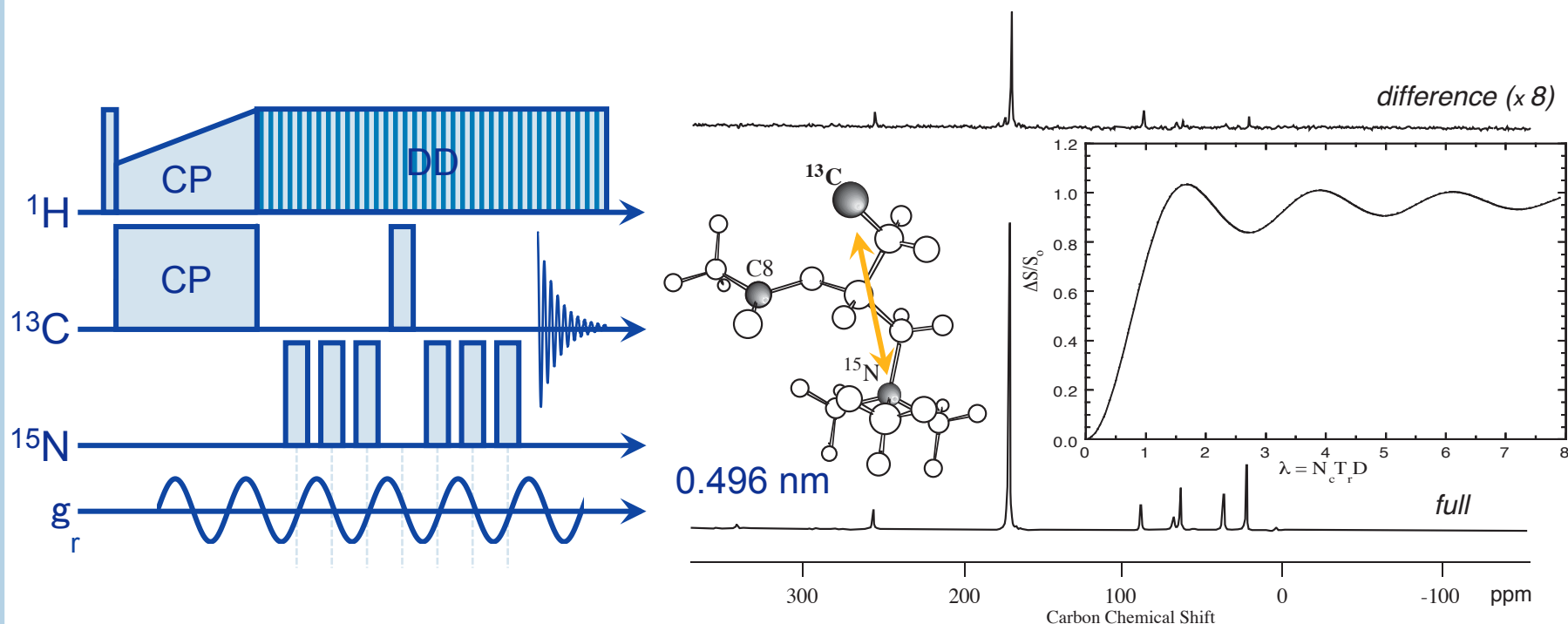
- Selection of dipolar interaction using symmetry based C7 in solid-state

# Structure of SH3 from dipolar interaction



- Microcrystalline  $\alpha$ -spectrin Src-homology 3 (SH3) domain of protein
  - Distance constraints via cross peak build-up as a function of mixing time and comparing to conformation independent reference distance c.f. NOESY
- Use of  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar interaction to determine structure in solid-state

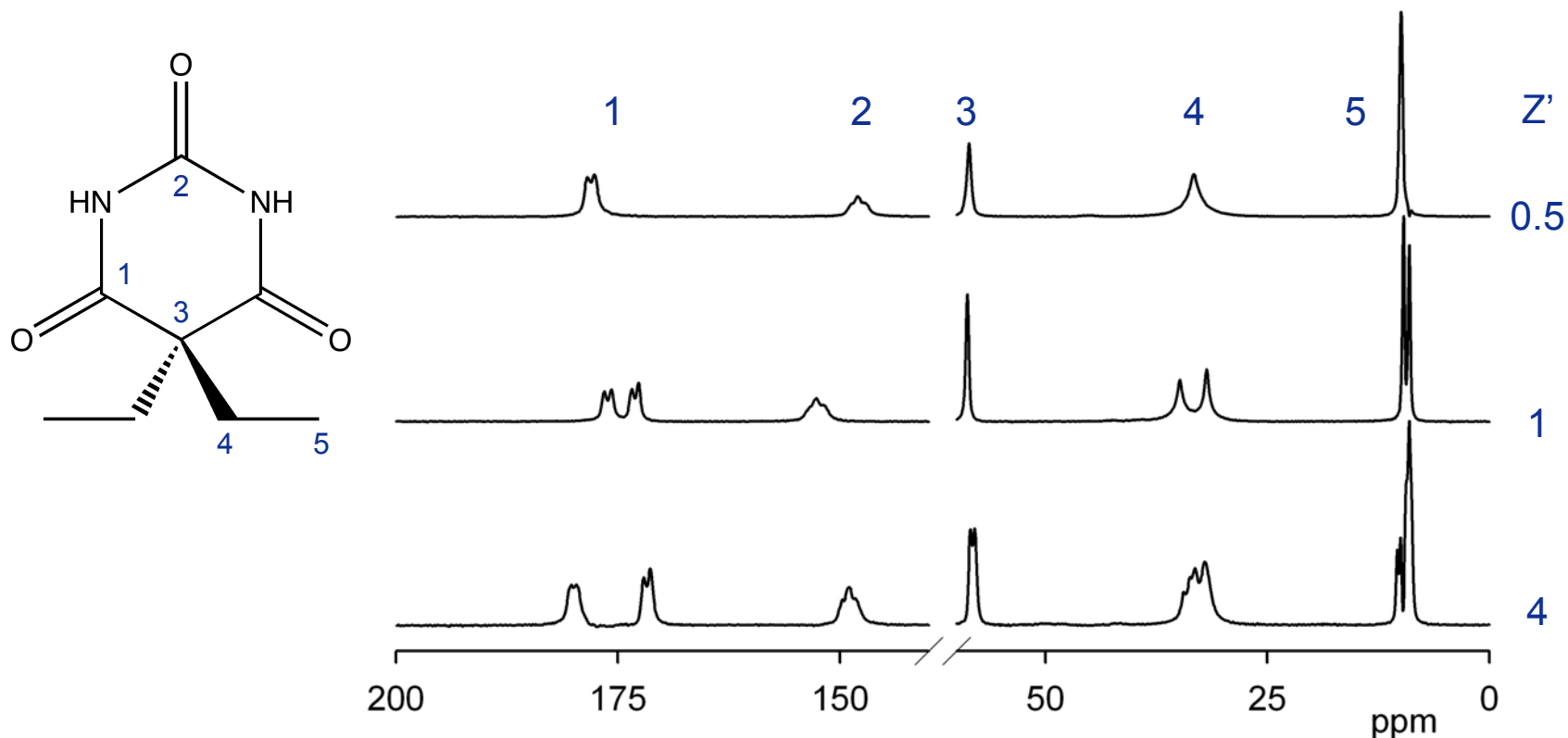
# Rotational echo double resonance REDOR



- Measures the absolute distance between an isolated spin-pair
  - quantitative determination of dipolar coupling by recoupling
  - typically applied between two hetero atoms such as  $^{13}\text{C}$ - $^{15}\text{N}$  but can be  $^1\text{H}$ - $^{13}\text{C}$ / $^{15}\text{N}$



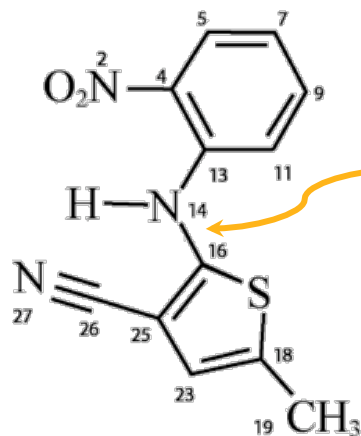
# Crystallographic inequivalence in barbitol



## ■ NMR crystallography

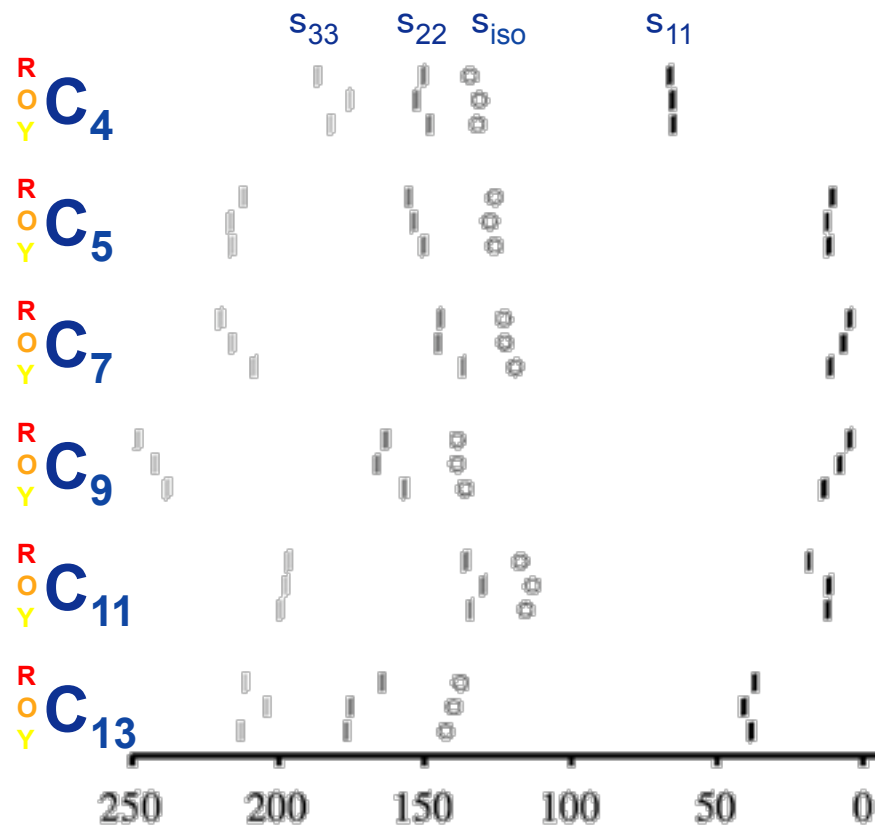
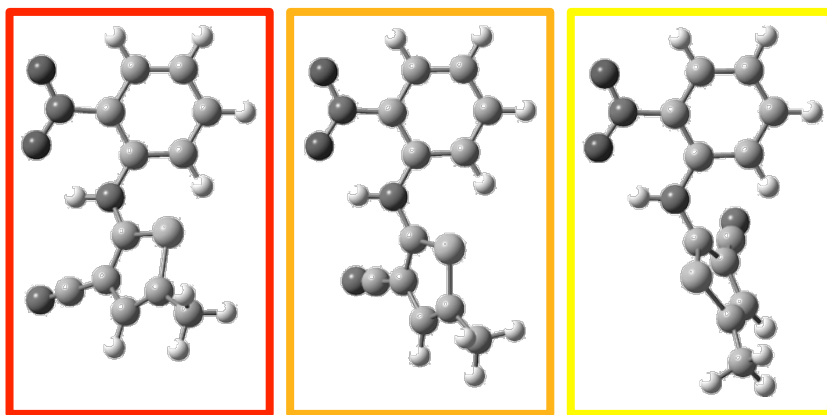
- peaks per site provides number of distinct molecules in asymmetric unit cell (Z')

# Polymorphism of small molecule



Three polymorphs  
only difference is  
dihedral angle C<sub>14</sub>-C<sub>16</sub>

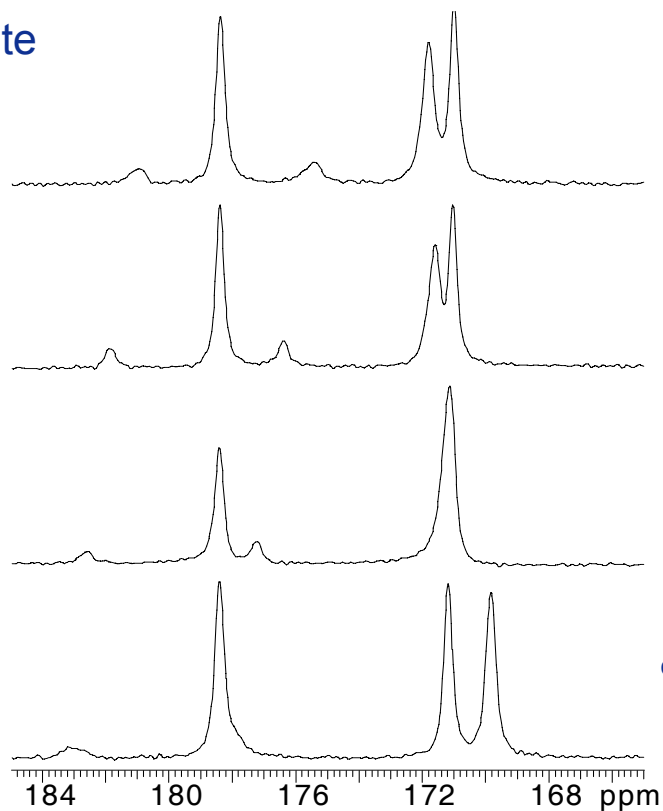
5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile



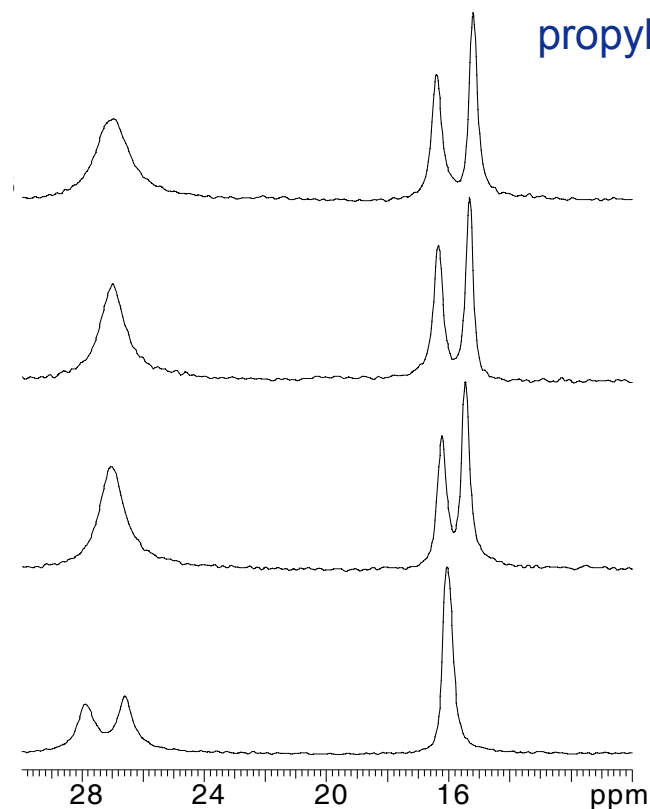
■ Polymorphism indicated by chemical shielding anisotropy in solid

# Hydration of sildenafil citrate

citrate



propyl & C<sub>21</sub>



- Solid-state NMR shows which sites interact with included water



# NMR Spectroscopy of Polyolefins & An Introduction to Solid-State NMR

## LAB TOUR & SOME BASIC SS-NMR

# **End of presentation**

## **Matt Parkinson**

### **3.12.2010 – 16.2.2011**

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