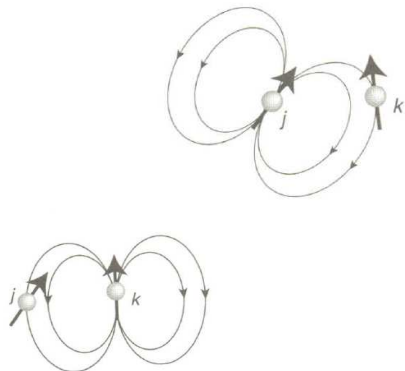# Direct dipolar interaction

Usually the dominating interaction in solids (for spin-1/2 nuclei)

→ usually main reason for linebroadening

→ Each nuclear spin is magnetic
→ generates a magnetic field, looping around in the surrounding space
→ a 2nd spin interact with this magnetic field
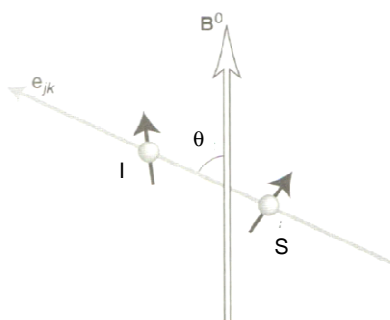
→ mutual interaction

Homonuclear:
→ Same isotopic species

Heteronuclear:
→ Different isotopic species

M. Levitt, spin dynamics, 2nd edition, Wiley & sons,(2008)

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Direct dipolar interaction
Heteronuclear and homonuclear coupling

Dipolar, secular Hamiltonians in the rotating frame:

heteronuclear:

$$\hat{H}_D^{\text{hetero}} = -d\frac{1}{2}\left(3\cos^2\theta - 1\right)\hat{I}_z\hat{S}_z$$

homonuclear:

$$\hat{H}_D^{\text{homo}} = -d\frac{1}{2}\left(3\cos^2\theta - 1\right)\left[3\hat{I}_z\hat{S}_z - \hat{\mathbf{I}}\cdot\hat{\mathbf{S}}\right]$$

with: $d = -\dfrac{\mu_0\gamma_I\gamma_S\hbar}{4\pi r_{IS}^3}$

d: dipolar coupling constant, measure for the strength

M. Levitt, spin dynamics, 2nd edition, Wiley & sons,(2008)

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Direct dipolar interaction
Heteronuclear and homonuclear coupling

What information can we extract from these equations?

$$\hat{H}_D^{\text{hetero}} = -d\,\frac{1}{2}\left(3\cos^2\theta - 1\right)\hat{I}_z\hat{S}_z \qquad \hat{H}_D^{\text{homo}} = -d\,\frac{1}{2}\left(3\cos^2\theta - 1\right)\left[3\hat{I}_z\hat{S}_z - \mathbf{\hat{I}}\cdot\mathbf{\hat{S}}\right]$$

with: $\quad d = -\dfrac{\mu_0\,\gamma_I\gamma_S\,\hbar}{4\pi r_{IS}^3}$

dependence of

- **γ:** The higher γ (larmor frequency), the stronger the dipolar coupling

- r_{IS} Strong impact! The smaller the distance between the spins I and S the stronger the dipolar coupling!

- **θ:** only $\left(3\cos^2\theta - 1\right)$-term! Dipolar coupling can be (theoretically) averaged out by MAS

- **Spin term:** Differences between hetero- and homonuclear coupling! Origin for different response to pulse sequences and lineshapes.

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Direct dipolar interaction
What are strong dipolar nuclei?

nucleus	Frequency/MHz @11.7T	Nat. abundance	Dipolar coupling	Why?
^{1}H	500	99.99%	strong!!!!	big γ, small r
^{2}H	77	0.02%	weak	small γ, big r
^{13}C	126	1.10%	weak	big r
^{19}F	470	100%	strong!!!!	big γ, small r
^{29}Si	99	4.67%	weak	big r
^{31}P	202	100%	strong	small r

→ ^{1}H and ^{19}F NMR spectra are dominated by homonuclear coupling

→ spectra of substances with ^{1}H (and ^{19}F) are usually dominated by X-^{1}H coupling

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Direct dipolar interaction - utilization

Two main uses:

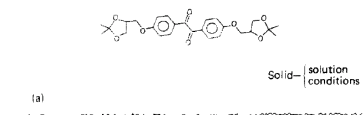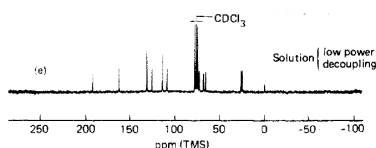   **I: magnetization transfer**

      II: probing internuclear distances

Direct dipolar interaction – utilization (I)
^{1}H decoupling and CP MAS

^{13}C NMR spectrum of 680 mg solid substance measured <u>under solution NMR conditions</u>: no signal detectable due to linebroadening, low ^{13}C abundance and long relaxation times
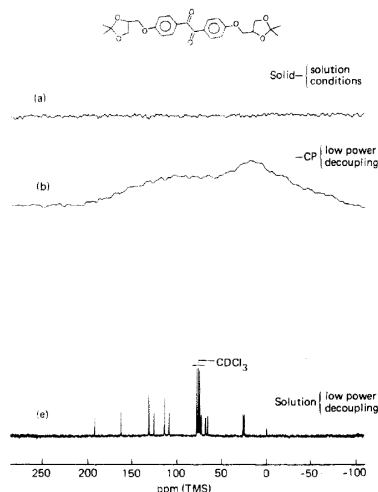
^{13}C <u>solution state NMR</u> spectrum of 34 mg of a benzil derivative dissolved in CDCL$_3$ (12h)

C.S. Yannoni, *Acc. Chem. Res.* **, 15**, 201-208, (1982)

Direct dipolar interaction – utilization (I)
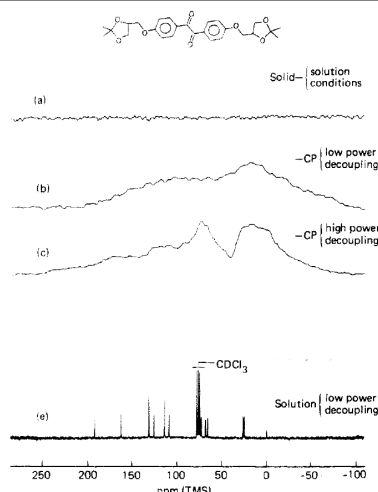## ¹H decoupling and CP MAS

^{13}C NMR spectrum of 680 mg solid substance measured under solution NMR conditions: no signal detectable due to linebroadening, low ^{13}C abundance and long relaxation times

Cross polarization, 1/10th measurement time (1.2h) → enhanced signal because of magnetization transfer

^{13}C solution state NMR spectrum of 34 mg of a benzil derivative dissolved in CDCL₃ (12h)

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Direct dipolar interaction – utilization (I)
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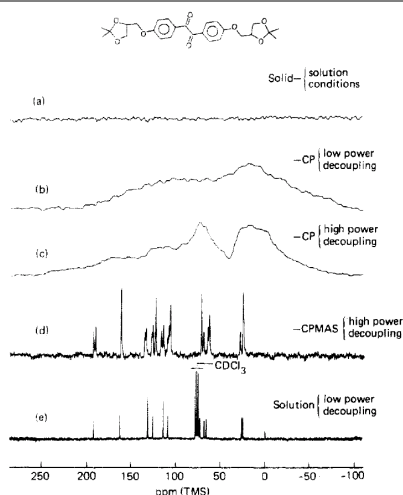
Cross polarization, 1/10th measurement time (1.2h) → enhanced signal because of magnetization transfer

CP with high power ¹H decoupling (1.2h) → resolution improved

^{13}C solution state NMR spectrum of 34 mg of a benzil derivative dissolved in CDCL₃ (12h)

C.S. Yannoni, *Acc. Chem. Res.*, **15**, 201-208, (1982)

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Direct dipolar interaction – utilization (I)
^{1}H decoupling and CP MAS

^{13}C NMR spectrum of 680 mg solid substance measured under <u>solution NMR conditions</u>: no signal detectable due to linebroadening, low ^{13}C abundance and long relaxation times

<u>Cross polarization</u>, 1/10th measurement time (1.2h) → enhanced signal because of magnetization transfer

<u>CP with high power ^{1}H decoupling</u> (1.2h) → resolution improved

<u>CP with high power ^{1}H decoupling</u> and **MAS**, 34 mg solid substance (1.2h) → resolution drastically improved
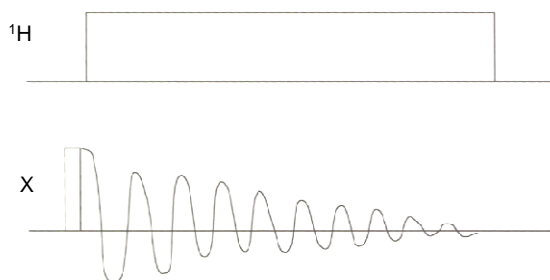
^{13}C <u>solution state NMR</u> spectrum of 34 mg of a benzil derivative dissolved in CDCL$_3$ (12h)

(a) Solid solution conditions
(b) –CP low power decoupling
(c) –CP high power decoupling
(d) –CPMAS high power decoupling, –CDCl$_3$
(e) Solution low power decoupling

250 200 150 100 50 0 -50 -100
ppm (TMS)

C.S. Yannoni, *Acc. Chem. Res.*, **15**, 201-208, (1982)

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Direct dipolar interaction - utilization
High-power ^{1}H decoupling

-^{13}C SS NMR spectra: bad signal/noise due to low natural abundance
+ strong linebroadening due to ^{13}C-^{1}H coupling

→ **High-power ^{1}H decoupling**

^{1}H

X

Simplest case: high-power close-to-resonance B$_{rf}$ fields is applied during FID collection on the ^{1}H channel

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M. Duer, Introduction to Solid-State NMR spectroscopy, Blackwell Science (2004)

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Direct dipolar interaction - utilization
High-power ^{1}H decoupling

How does ^{1}H decoupling work?

effect of close-to-resonance irradiation:
^{1}H spins undergo repeated m=1/2 ↔m=-1/2 transitions (the higher the amplitude of the rf-irradiation the faster the transitions rate)

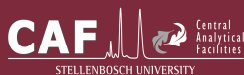remember: $\hat{H}_D^{\text{hetero}} = -d\,\frac{1}{2}\left(3\cos\theta^2 - 1\right)\hat{I}_z\hat{S}_z$

mH

→ If m=1/2 ↔m=-1/2 transitions rate is fast enough, then $\langle m_H \rangle = 0$

$$\Rightarrow \left\langle \hat{H}_D^{\text{hetero}} \right\rangle = 0$$

How strong must ^{1}H deoupling amplitude be?
Dipolar coupling constant of bonded ^{13}C-^{1}H spin pair: 22kHz

→ Decoupling field: ideally 66kHz

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Direct dipolar interaction - utilization
High-power ^{1}H decoupling

Important practical aspects:

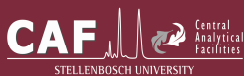high-power irradiation for long times → potential risk to damage the probe!

to avoid damages:

→ probe must be well tuned

→Choose acquisition time, which is sufficient to measure the FID,
but not much longer

→If FID shows large random spikes:
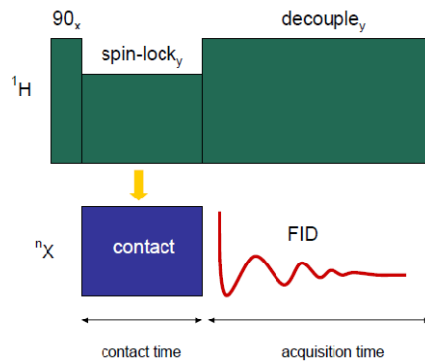→ arcing! : check tuning
reduce 1H decoupling power

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Direct dipolar interaction - utilization
CP MAS

The cross polarization (CP) experiment

magnetization of a nucleus with high natural abundance and a big gyromagnetic ratio (e.g. ^1H) is transfered to a nucleus with low natural abundance and a low gyromagnetic ratio

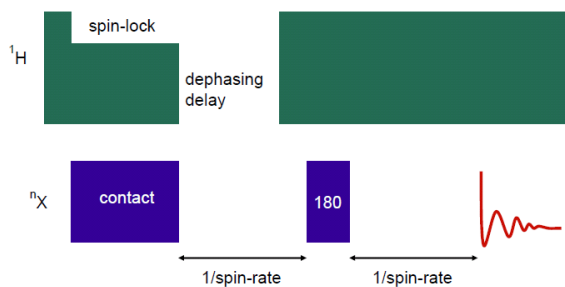Condition for CP (magnetization transfer):

$$\gamma_H B_H^1 = \gamma_X B_X^1$$

"Hartmann-Hahn match"

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Direct dipolar interaction - utilization
Spectral editing: CP MAS with interrupted decoupling

Dipolar Dephasing (DD) experiment:

Principle:
Without ^1H decoupling:

FID decays fast due to ^1H-^{13}C coupling

Magnetization associated with strongly proton coupled Carbons dephases faster than these of weakly or non-proton coupled carbons

In DD experiment: decoupling is interrupted for some time
→Magnetization of strongly proton-coupled carbons dephases
→ resulting DD spectra are dominated by weakly or non-coupled carbons

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Direct dipolar interaction - utilization
CP MAS application examples

-Identification of solid forms by comparing its spectrum with that from a characterized sample

The high-frequency region of this ^{13}C spectrum can be rationalised in terms of a mixture of two components (60% A, 40% B determined from the spectrum)

Component A

Component B

Mixture

220   200   180   ppm   160
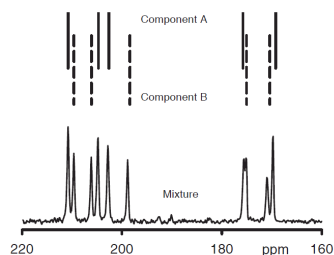
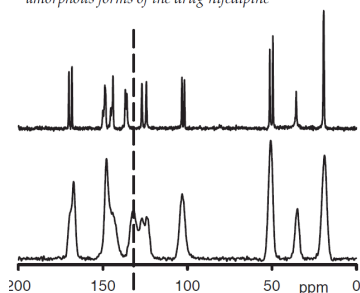→Especially useful for identification and quantification of crystalline components

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Direct dipolar interaction - utilization
CP MAS application examples

- Probing the morphology of materials:

Carbon-13 spectra from crystalline (top) and amorphous forms of the drug nifedipine

200   150   100   50   ppm   0

Signals of amorphous materials are much broader than these of crystalline components
→ reason: a broad distribution of isotropic chemical shifts

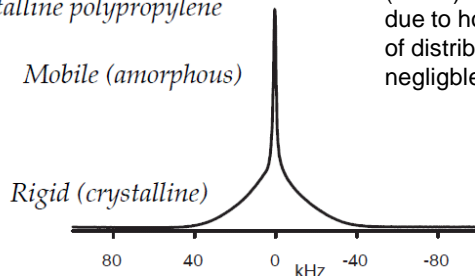BUT: be careful! A narrow line width can be also due to motional narrowing

Direct dipolar interaction - utilization
CP MAS application examples

- Probing the morphology of materials: Crystallinity of polymers

Wideline ^1H spectrum from semicrystalline polypropylene

Mobile (amorphous)

Rigid (crystalline)

(Static) ^1H SS NMR signals are broad due to homonuclear interaction (impact of distribution of isotropic positions negligble)!

80	40	0	kHz	-40		-80

Amorphous PE chains are mobile
→Homonuclear ^1H-^1H coupling is (partially) averaged out
→ motional narrowing of the amorphous line

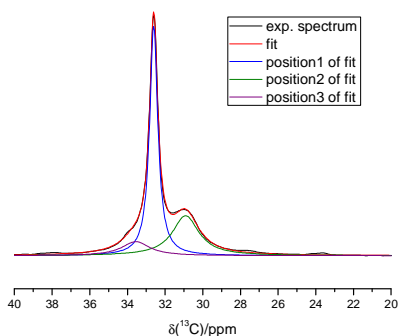http://www.dur.ac.uk/solid.service/information/

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Direct dipolar interaction - utilization
CP MAS application examples

- Probing the morphology of materials: Crystallinity of polymers

Experimental and simulated ^{13}C {^1H} CP MAS spectrum of LLDPE
(linear low density polyethylene):

exp. spectrum	
fit	
position1 of fit	
position2 of fit	
position3 of fit	

40 38 36 34 32 30 28 26 24 22 20
$\delta(^{13}C)$/ppm

deconvoulution in three lines/positions:

- position 1: crystalline (orthorhombic)
- position 2: amorphous
- position 3: crystalline (monoclinic)
[1]

→ Crystallinity (Cryst%):

$$Cryst\% = \frac{Int(pos1) + Int(pos3)}{Int(pos1) + Int(pos2) + Int(pos3)}$$
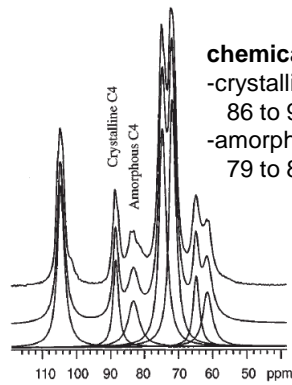
[1] K. Kuwabara, H. Kaji, M. Tsuji, F. Horii, *Macromolecules*, **33**, 7093, (2000)

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Direct dipolar interaction - utilization
CP MAS application examples

-**Probing the morphology of materials: Crystallinity/ Quantification of polymorphs in cellulose**

chemical shifts:
-crystalline C4:
  86 to 92 ppm
-amorphous C4:
  79 to 86 ppm

analysis of polymorphs: deconvolution of crystalline C4 peak

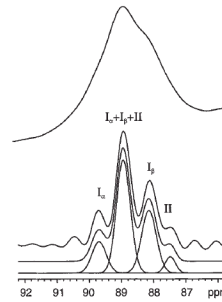Fig. 1. Deconvolution for the CPMAS spectrum of kraft pulp to determine the crystallinity of cellulose.

Fig. 3. The deconvolution of crystalline C4-signal of kraft pulp after resolution enhancement (lb = −50 Hz, gf = 0.03). Above is the same signal before resolution enhancement (lb = 10 Hz).

[1] T. Liitiä et al., Holzforschung, 54, 618-624, (2000)

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Direct dipolar interaction - utilization
CP MAS application examples

- **Structural characterization of insoluble solids**
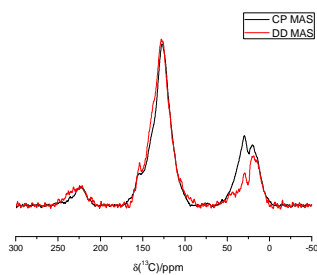
→ Determination of structural parameters of coals:

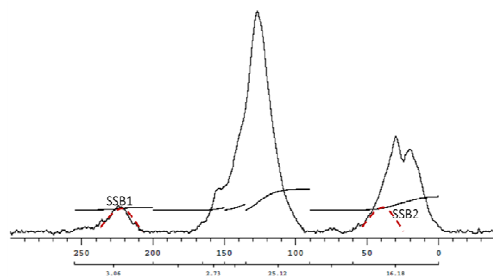Figure 1: typical CP MAS (black) and DD MAS spectra of a coal sample.

Figure2: A typical CP MAS spectrum of a coal sample measured at a MAS frequency of 12kHz with integration reset points

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Direct dipolar interaction - utilization
CP MAS application examples

- Structural characterization of insoluble solids

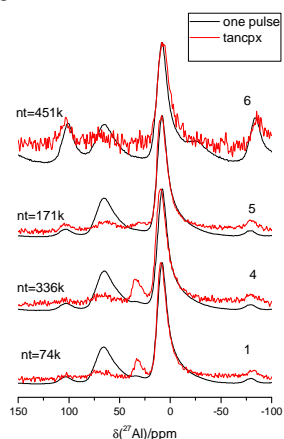→ Determination of structural parameters of coals:

Fraction Aromatics	f_a
Corrected Fraction Aromatics (excl CO)	f_a^*
Fraction Aliphatics	f_{al}
Fraction Aliphatic C's bonded to Oxygen	f_{al}^O
Fraction CO	f_a^{CO}
Fraction Phenolics	f_a^P
Fraction Alkylated Aromatics	f_a^S
Fraction Non-Protonated C's in aromatic region	f_a^N
Fraction Protonated C's in aromatic region	f_a^H
Fraction Bridgehead C's	f_a^B
Fraction Non-Protonated C's+Methyl groups in Aliphatic region	f_{al}^{N*}
Aliphatic CH+CH2	f_{al}^H
Mole fraction of Aromatic Bridgehead C's	X_b
Average # of Aromatic C's per cluster	C
#Clusters/100 Carbons	#Clusters/100
#of attachments per cluster	$\sigma + 1$

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Direct dipolar interaction - utilization
CP MAS application examples

- Surface characterization of inorganic systems

27Al one pulse and CP MAS spectra
@ 12 kHz

one pulse
tancpx

nt=451k   6
nt=171k   5
nt=336k   4
nt=74k   1

150   100   50   0   -50   -100
$\delta(^{27}Al)$/ppm

Alumina-sillicates

-Only the Al nuclei which are
  close to protons give a CP signal

-Source of protons:
- adsorbed water
- bridging OH-groups
→ protons are close to surface

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Direct dipolar interaction - utilization
advantages and disadvantages of CP MAS

Advantages

+ recycle delay $\propto T_1(^1H)$ (not $\propto T_1(X)$ and $T_1(^1H) << T_1(X)$

+ signal enhancement (potentially γ_H / γ_X)

+ fewer problems with background signals

+ potentially selective

+ can probe relationship between nulcei

Disadvantages

- Not quantitative

- potentially selective

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