Solid-state NMR: a powerful and versatile method of choice

NMR Centre Workshop

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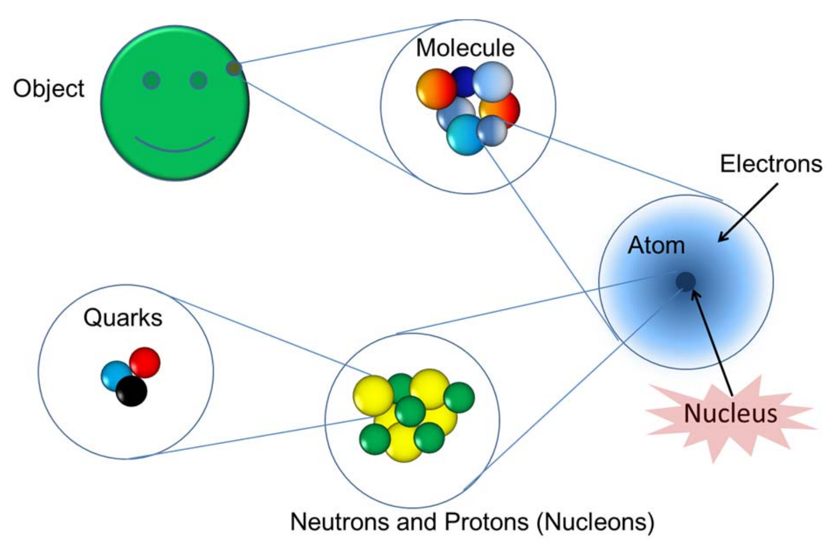
Why solid-state NMR?

Solid-state NMR

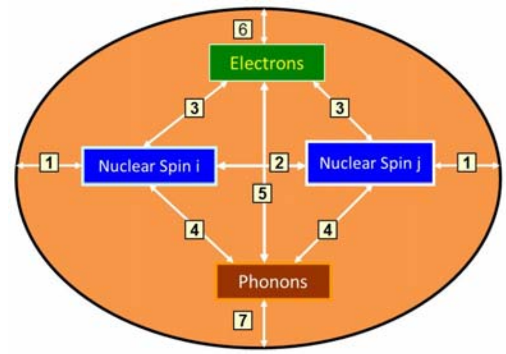
- It can be applied to the vast majority of samples at different levels of complexity;
- Subtle differences in the electronic environment result in different resonance frequencies;
- SSNMR is multinuclear, any element with nuclear spin can be studied;
- Successful on “powder” microcrystalline samples;
- Details about next neighboring atoms (1^{st} and 2^{nd} coordination sphere);
- Can readily distinguish polymorphs;
- Local symmetry and coordination numbers;
- Conformations, bond angles and distances;
- Molecular dynamics – probing molecular motion.

NMR: where are we?



SSNMR interactions - summary

In solids there are seven ways for a nuclear spin to communicate with its surroundings.



1 = Zeeman Interaction; **2** = direct dipolar Interactions; **3**= indirect spin coupling (J) and coupling of nuclear spins with electric field gradients (quadrupolar interaction), nuclear electron-spin coupling (paramagnetic); **4** = direct spin-lattice interactions; **3-5** = indirect spin-lattice interaction; **3-6** = chemical shielding and polarization of nuclear spins by electrons; **4-7** = coupling of nuclear spins to phonons.

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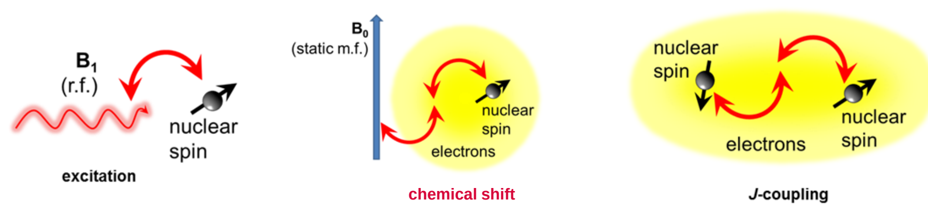
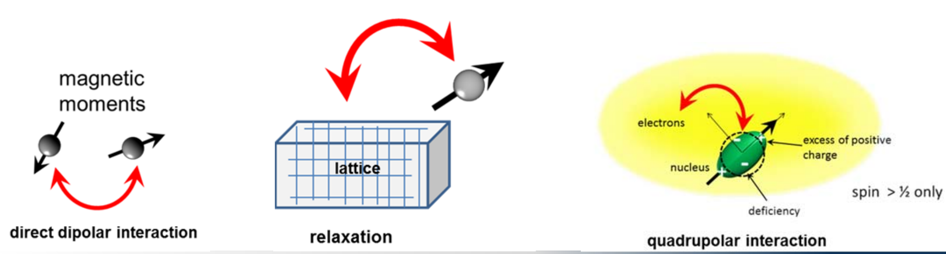
SSNMR Interactions - anisotropic



chemical environment; molecular mobility; symmetry; polymorphism; asymmetric units; through bond and though space connectivities; internuclear distances;



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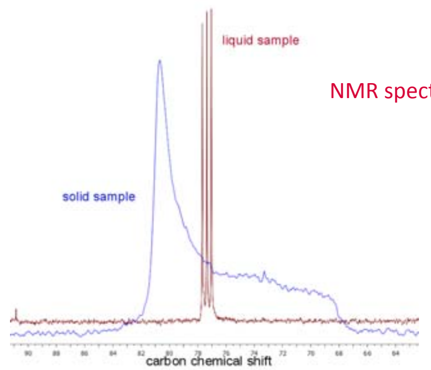
Solid State Nuclear Magnetic Resonance

The method is applicable (with some variations in technique) to all types of solids:

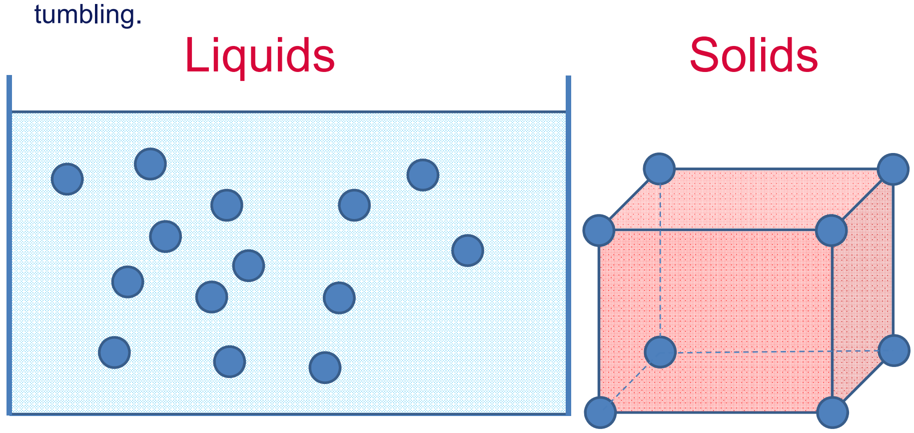
Minerals (including aluminosilicates, coal), inorganic samples, wood, polymers, and foodstuffs, pharmaceutical samples, organic and biological samples (not always amenable to investigation by diffraction techniques).



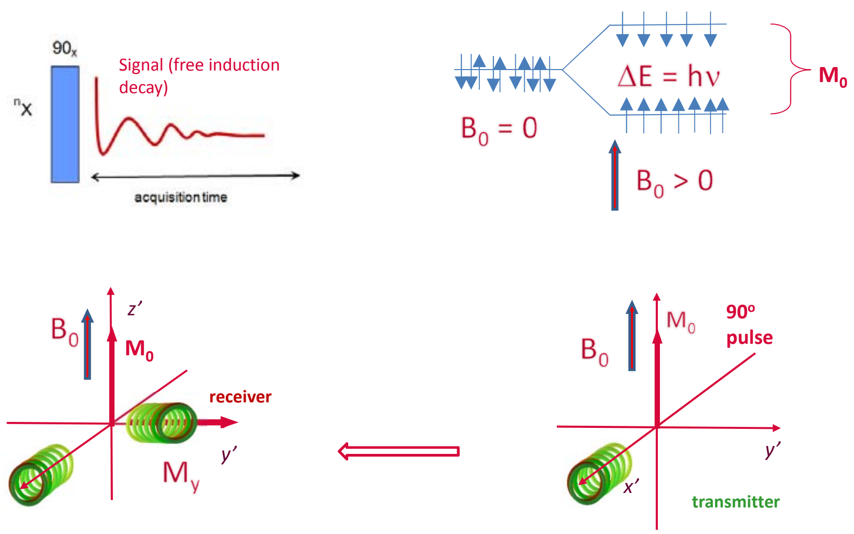
NMR spectra

Liquids vs. Solids

Chemical shift anisotropy, direct dipolar coupling, nuclear quadrupole coupling) **are averaged to zero in solution** because of molecular tumbling.

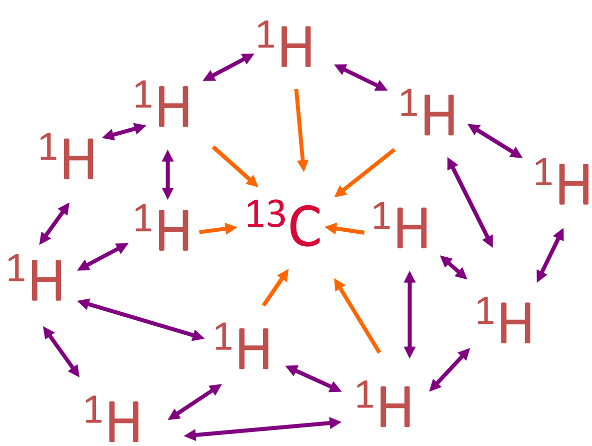


A basic NMR scheme

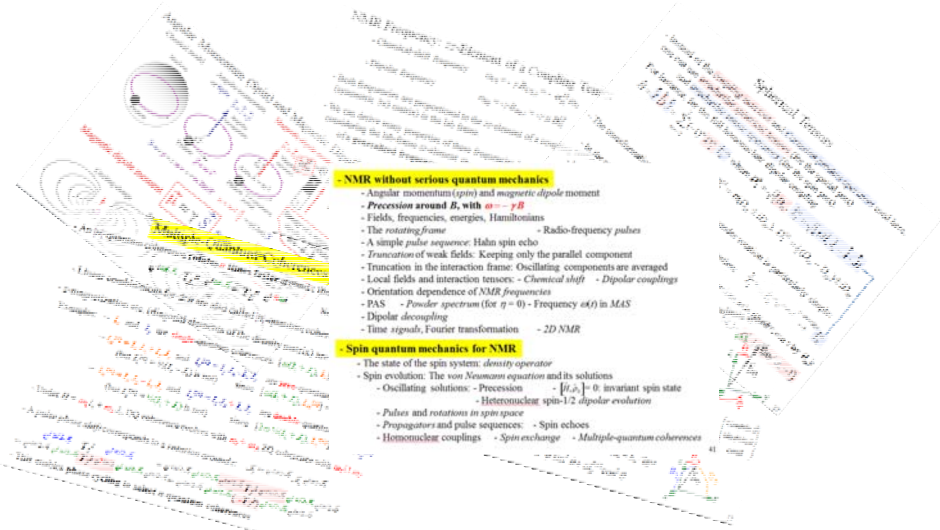


Cross-polarization

Dipolar coupling between the abundant Hs and between ^{1}H and ^{13}C allows the redistribution and transfer of energy to the ^{13}C nucleus and the signal improvement (4x).

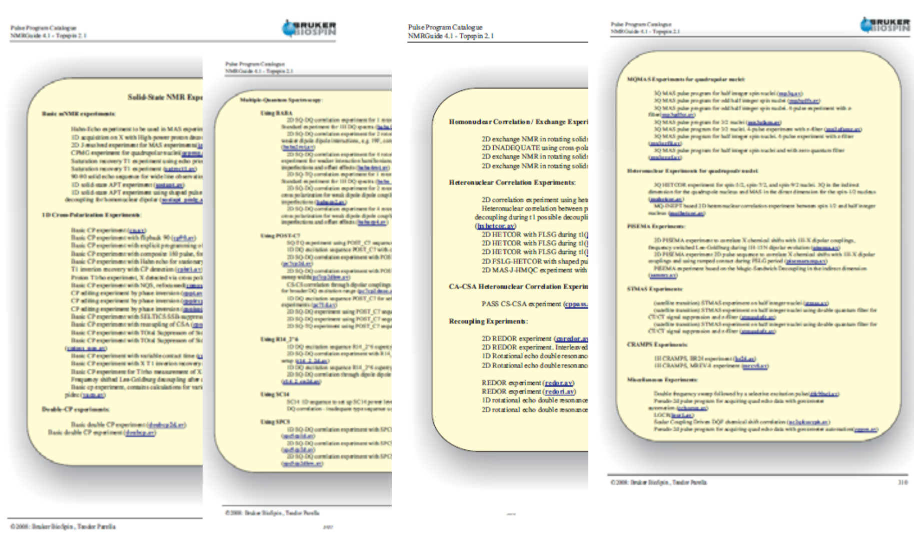


Theoretical background – complicated?



Source: Basic Theory of Solid-State NMR Klaus Schmidt-Rohr

Practical – vast options?



Choice of SSNMR experiment

Choice of SSNMR experiment

identification

morphology

mobility

structure

homogeneity

polymorphism

What do you want to know?

Choice of SSNMR experiment

Choice of SSNMR Experiment

^{1}H

Quadrupole, ^{23}Na, ^{27}Al, ^{17}O….

Labeled, ^{15}N, ^{13}C…

Paramagnetics, unpaired electrons, metals…

amount

heterogeneity

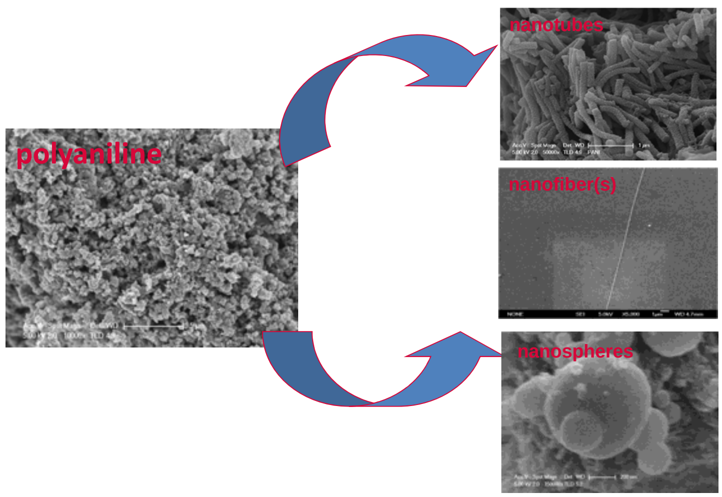
What does the sample contain?

Applications

Conducting polymers

Multinuclear aproach

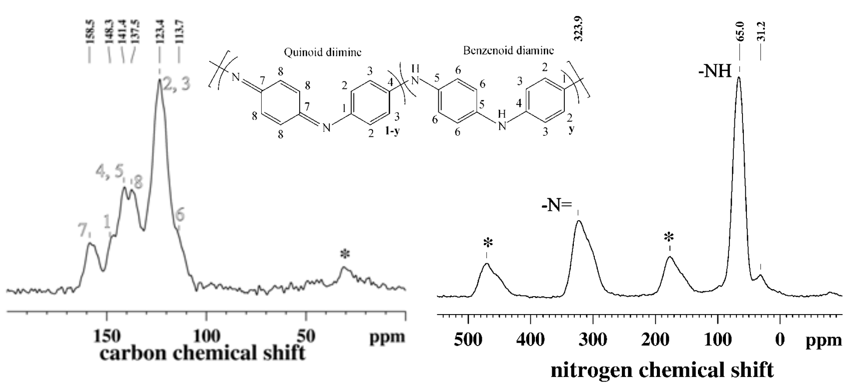
Polyaniline - from featureless grains to nanostructures



Z.D. Zujovic, Y. Wang, G.A. Bowmaker, R.B. Kaner; *Macromolecules* **44,** 2735-2742 (2011)
Z.D. Zujovic, C. Laslau, G.A. Bowmaker, P.A. Kilmartin, A.L. Webber, S.P. Brown, et al.; *Macromolecules* **43,** 662-670 (2010)

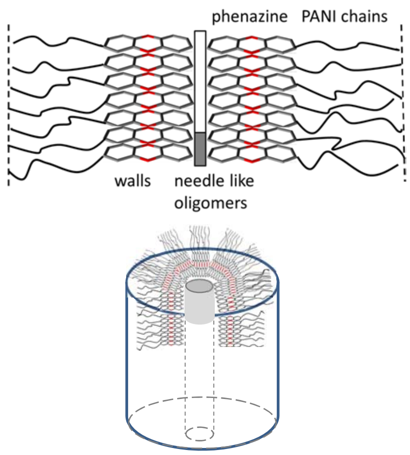
SSNMR - spectral assignments

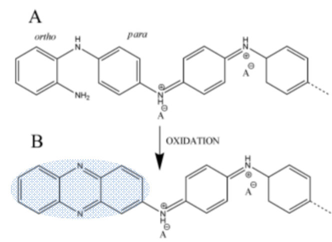
The sequence is composed of the alternating benzenoid diamine and quinoid diimine units the corrected imine/amine ratio should be 1:1



Z.D. Zujovic, M.R. Gizdavic-Nikolaidis, P.A. Kilmartin, H. Idriss, S.D. Senanayake, G.A. Bowmaker; *Polymer* **47**, 1166-1171 (2006).

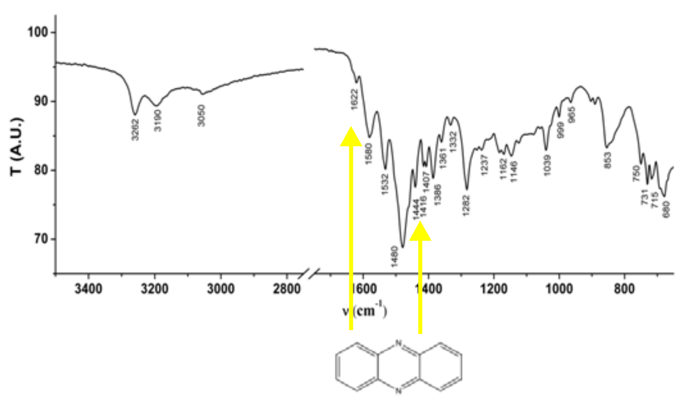
Nanotubes – the formation mechanism





A concept from Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N.; Holler, P. Polymer **47**, 8253 (2006).

FTIR - early formed structures

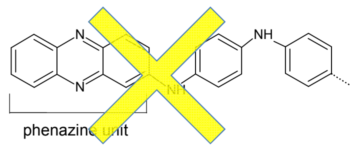


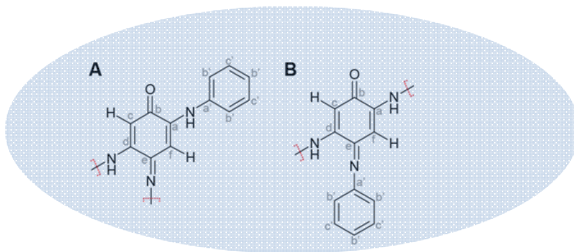
Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N.; Holler, P. Polymer 2006, 47, 8253

ca. 1620 cm^{-1} C=O stretching - benzoquinone
ca. 1415, 1450 cm^{-1} C-C (B) and C=C (Q) stretching

Planes et al, Phys. Chem. Chem. Phys. **12**, 10584–10593 (2010).

Summary





Inorganic materials
Geopolymers

Coordination

Geopolymers

Geopolymers are inorganic polymers obtained from metakaolin (or other double layered clayed minerals) and commercial sodium silicates.

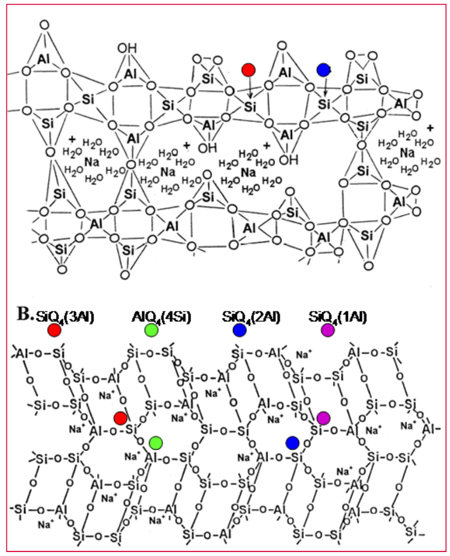
Bonds are bridges through oxygen.

The key attributes of geopolymers:

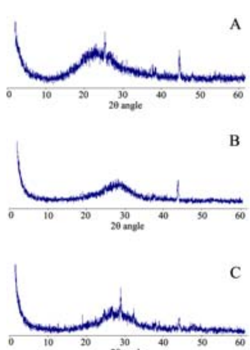
- thermal stability
- chemical stability
- high mechanical strength

Some of possible applications:

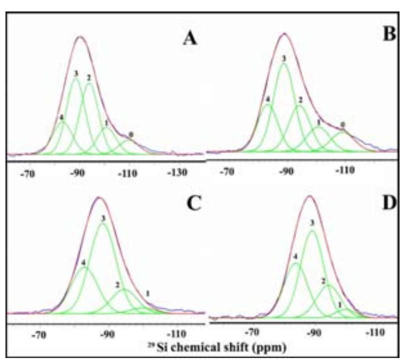
- Cement and concrete
- Traditional and high performance ceramics
- Precast and extruded building products
- High temperature automotive parts
- Bio-technologies (materials for medicinal applications



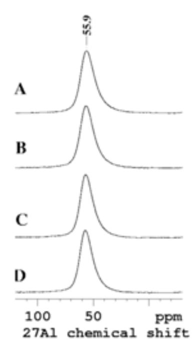
XRD vs. solid-state NMR broad echo vs. resolved resonance



The XRD diffractograms of Engelhard metakolin (A), and Engelhard-based geopolymers without (B) and with added $(CaOH)_2$ (C).



Deconvoluted [29]Si spectra of an Engelhard-based geopolymer powder samples with different concentrations of $Ca(OH)_2$. Peaks are labelled according to the number of Al neighbouring atoms bridged through oxygen to a tetrahedral Si.



[27]Al spectra of an Engelhard-based geopolymer powder samples with different concentartions $CaOH)_2$.

Pharmaceuticals

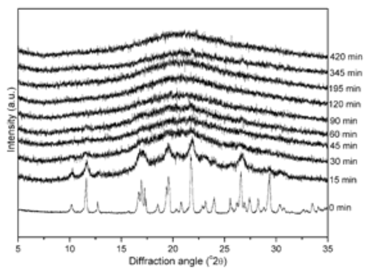
Amorphous samples
Polymorphs

Difficulties to detect the amorphous form

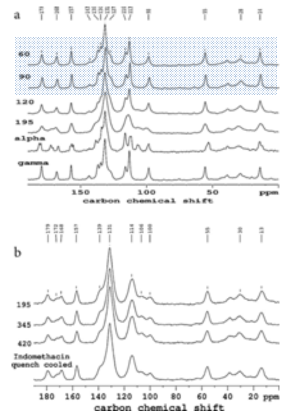
- Crystalline forms - low aqueous solubilities.
- Conversion of the active compound into an amorphous form.
- Higher dissolution rates and solubilities of an amorphous form.
    - Using solvents (freeze drying, spray drying, co-precipitation).
    - Using heat (melting/quench cooling).
    - Using mechanical activation (milling, cryo-milling).
    - Combination of heat and mechanical activation (melt extrusion).

Indomethacin – different polymorphs

Indomethacin is a nonsteroidal anti-inflammatory drug



XRPD diffractograms of the cryo-milled samples of Indomethacin.

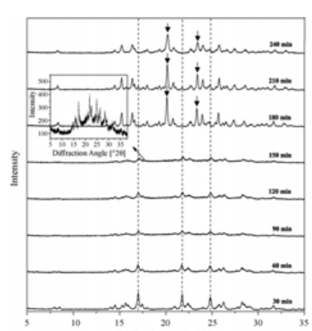


NMR spectra of cryo-milled (a) and quench cooled (b) samples of Indomethacin.

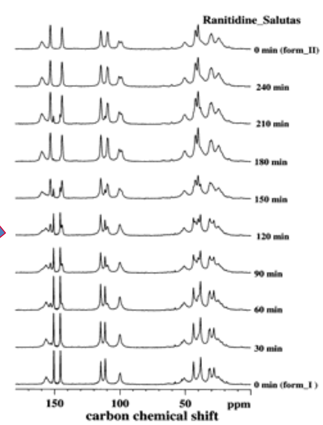
Botker, et al . Assessment of crystalline disorder in cryo-milled samples of indomethacin using atomic pair-wise distribution functions', *International Journal of Pharmaceutics,* 2011 417 112.

Ranitidine – different polymorphs

Ranitidine is used to treat **ulcers**



Diffractograms of a form 1 batch milled for various times. Figure inset shows the XRPD halo of the 150 min milled sample.



Solid-state NMR spectra of a form 1 Ranitidine batch milled at various times.

Chieng et al. Effect of milling conditions on the solid-state conversion of ranitidine hydrochloride form 1. *International Journal of Pharmaceutics*, 2006 *327* 36.

Natural products
Polysaccharides in the cell walls

Molecular dynamics

Cell walls

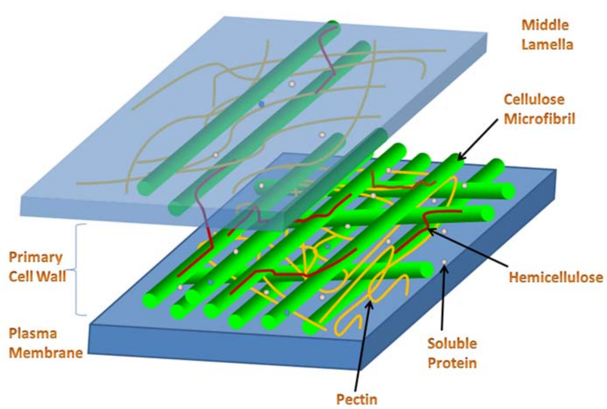
Cell walls mainly consist of:

a) CELLULOSE (*r* = 2-5 nm)

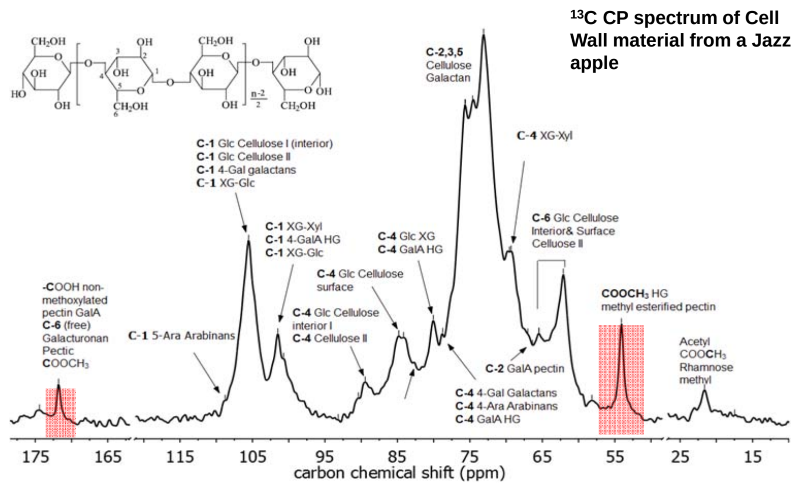
b) HEMICELLULOSE

c) PECTIC polysaccharides

d) Soluble protein

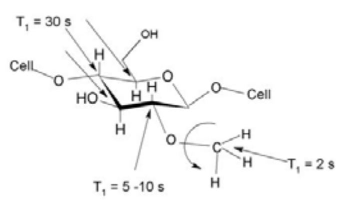


Cross polarization spectrum of PCW material

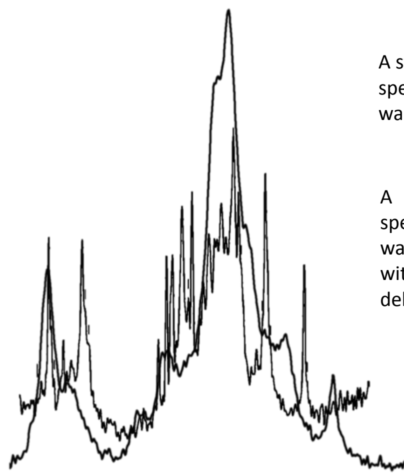


NMR relaxation methods

^{13}C		^{1}H	
Time scale of the magnetic fluctuations			
ns (MHz)	μs (kHz)	ns (MHz)	μs (kHz)
T_1^C	$T_{1\rho}^C$	T_1^H	$T_{1\rho}^H$
	T_2^C		T_2^H
	(T_{CH})		



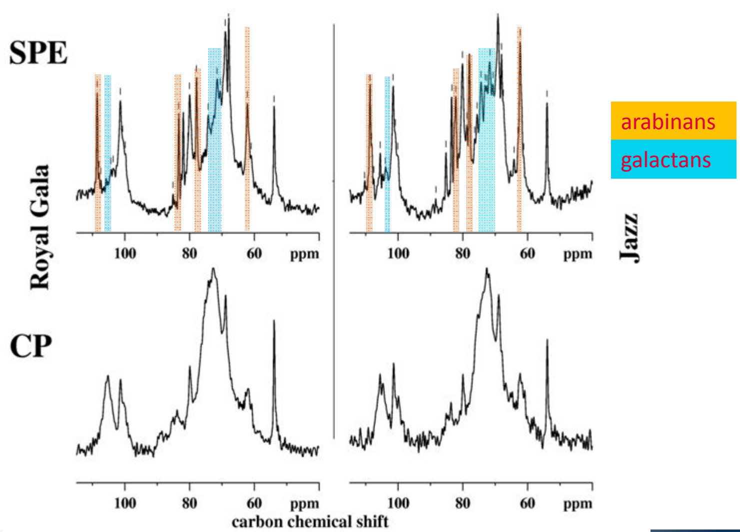
SSNMR - what makes the difference: from broad to very narrow liquid-like resonances



A standard cross-polarization spectrum of apple plant cell wall materials.

A single pulse excitation spectrum of apple plant cell wall materials obtained with very short repetition delay between pulses.

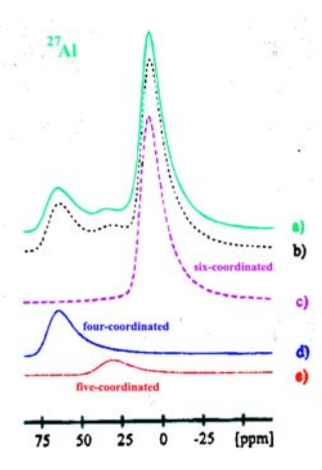
Different NMR experiments



Alumina (Al_2O_3) samples

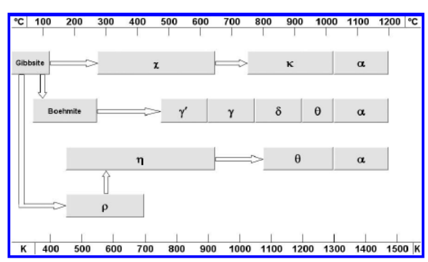
Quadrupolar NMR
Coordination

Alumina (Al_2O_3) - ^{27}Al NMR spectrum



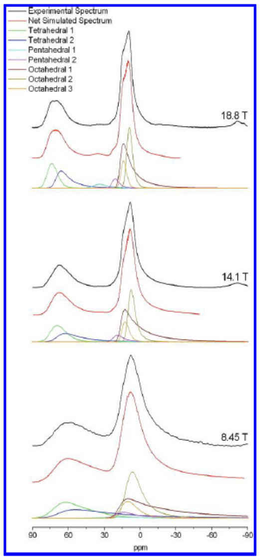
^{27}Al spectrum of an alumina sample, experimental a) and deconvoluted b) along with its components c), d), e).

Gibbsite (γ-$Al(OH)_3$)
Boehmite (γ-AlOOH)



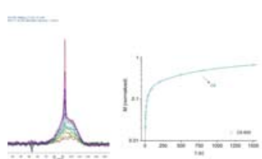
- Purification
- Filler for plastics
- Abrasive
- Catalysis
- Composite fibre
- Paint

^{27}Al spectrum of alumina – deconvolution at three different fields

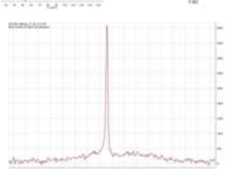


Field / MHz	Peak Number	Chemical Shift / ppm	Mean C_Q / MHz	C_Q Distribution Width / MHz	Intensity / %	Broadening / Hz
800	4	77.5	6.0	3.0	20.0	800
	5	69.5	7.0	5.0	12.3	700
	6	23.0	5.0	3.0	3.9	500
	7	16.0	6.0	9.0	39.0	500
	8	10.0	3.0	3.0	24.8	500
600	4	76.0	6.0	3.0	16.7	800
	5	70.0	7.0	5.0	11.2	700
	6	23.0	5.0	3.0	4.5	500
	7	15.0	6.0	9.0	42.1	400
	8	9.5	3.0	3.0	25.4	400
360	4	77.0	6.0	3.0	19.4	800
	5	70.0	7.0	5.0	15.6	800
	6	23.0	5.0	3.0	5.2	500
	7	15.0	6.0	9.0	33.9	400
	8	8.5	3.0	3.0	25.9	400

SSNMR – experimental time



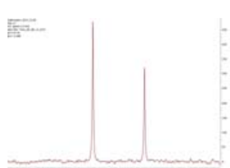
Glass, ^{29}Si, ca. 27 hrs. per one series of spectra (a T_1 time study)



Glass, ^{29}Si, number of scans 25, time between scans 10 000 s

total time per spectrum = 250 000 s per spectrum = 69 hours

total time per sample: 69+27=**96** hours



Adamantane ^{13}C, number of scans 1, time between scans 2 s, total time= **2 s**

Thank you!

Graham A Bowmaker - NZ
Jadranka Travas-Sejdic - NZ
Laurie Melton - NZ
James Metson- NZ
Marija Gizdavic-Nikolaidis_ NZ
Paul Kilmartin - NZ
Amy Webber- UK
Steven P. Brown - UK
Mark Smith - UK
Richard Kaner - USA
Yue Wang - USA
Conrad Perera- NZ
Peter Swedlund- NZ
Bronwen Smith - NZ
Thomas Rades – NZ, Denmark
Christian Mayer - Germany
Dragomir Stanisavljev- Serbia
Rosie Schroeder - NZ
Elise Champeil- USA
Jaroslav Stejskal – Czech Republic
Miroslava Trchova- Czech Republic
Ajit Sarmah – NZ
Luitgard Schwendenmann - NZ

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Thank you for your attention!

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