Solid-state NMR studies of carbon materials – a multinuclear approach

Jair C. C. Freitas

Laboratory of Carbon and Ceramic Materials, Department of Physics
Federal University of Espírito Santo (UFES), Vitória, ES, Brazil.

http://www.cce.ufes.br/jair

Research on Carbon Materials in Vitória

Laboratory of Carbon and Ceramic Materials (LMC)

Federal University of Espírito Santo, Vitória, Brazil

http://www.carbono.ufes.br

Some materials of interest:

- ✓ Chars produced from natural resources (peat, rice hulls, coconuts, etc).
- ✓ Carbon blacks produced by plasma pyrolysis of natural gas.
- ✓ Plasma modified vacuum residues of oil refinement.
- ✓ Activated carbons.
- ✓ Composites of porous carbons and nanoparticles.

Some characterization techniques:

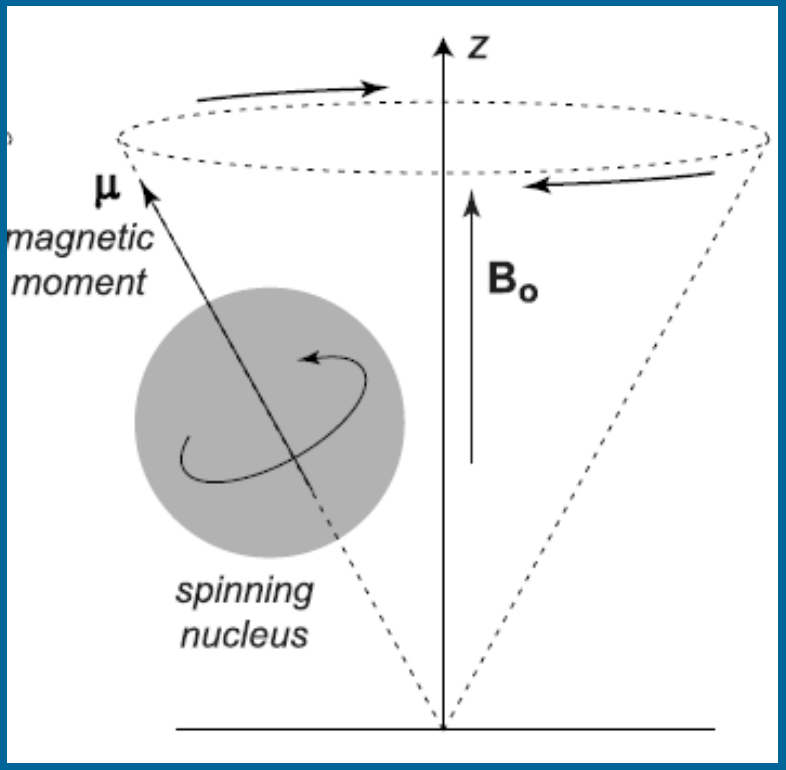
- ✓ XRD, SEM, NMR (^{13}C, ^{29}Si, etc), Mössbauer spectroscopy, TG, DSC, CHNSO analysis, etc.
- ✓ Textural properties (BET surface area, pore size distribution, true density, etc).
- ✓ Physical properties (electrical resistivity, magnetic susceptibility, etc).

Outline

- **Background on solid-state NMR spectroscopy.**
- **Solid-state NMR methods applied to carbon materials.**
- **Selected applications:**
  - **Activated carbons.**
  - **Plasma-derived carbon blacks.**
  - **Alumina-carbon nanocomposites.**

NMR background

Larmor Precession:



Larmor frequency:

$$\omega_L = \gamma B_0$$ (~10^7 rad/s)

$$f_L = \gamma B_0 / 2\pi$$ (~MHz)

↓

Radiofrequency (RF)

NMR background

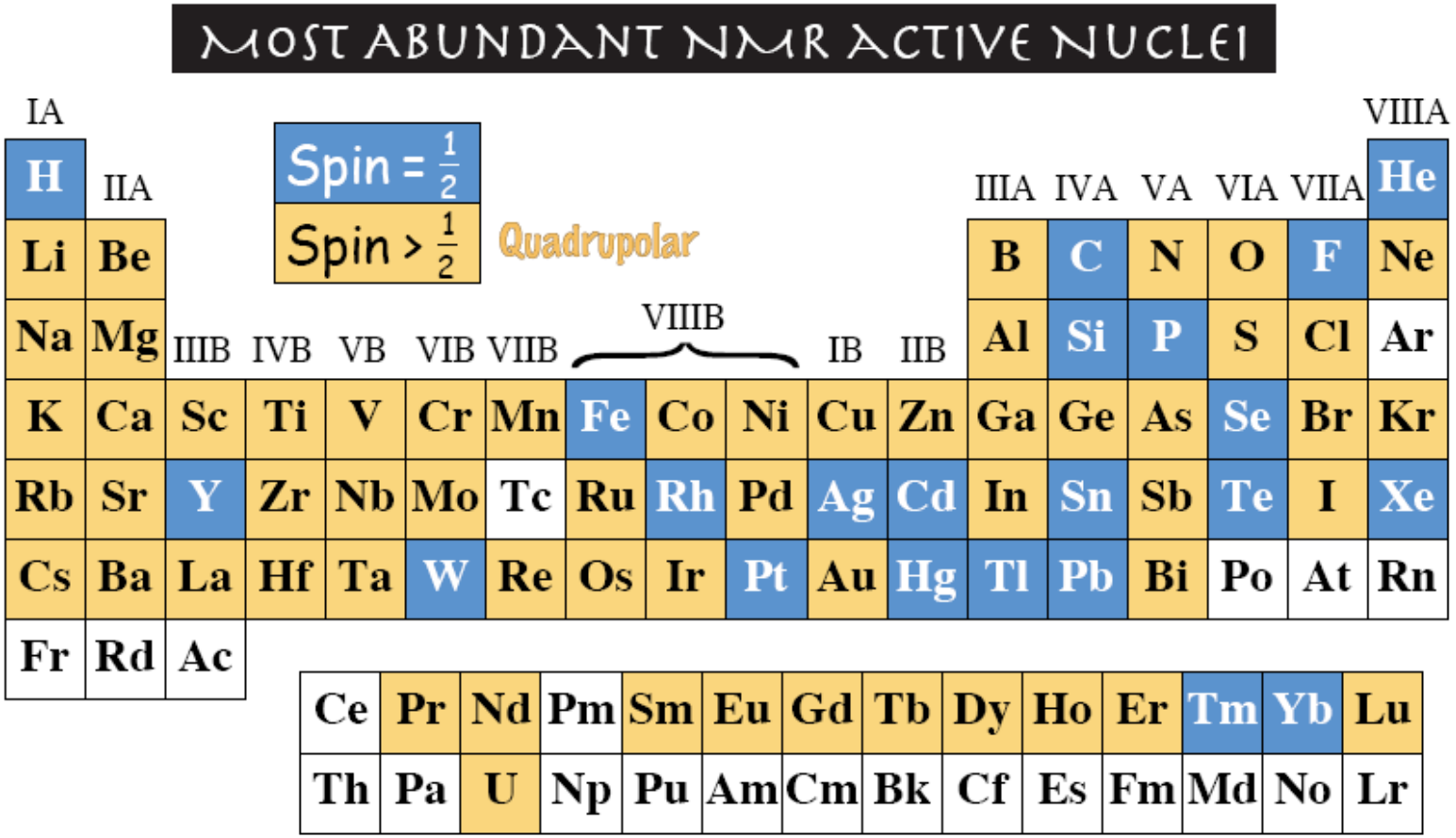
Some nuclides of interest for studies of carbons:

Nuclide	*Natural abundance* (%)	*Nuclear spin*	*Larmor frequency* [a] (MHz)	*Sensitivity* [b]
^{1}H	99.99	1/2	100.000	1.000
^{13}C	1.07	1/2	25.145	1.70×10^{-4}
^{14}N	99.632	1	7.226	1.00×10^{-3}
^{17}O	0.038	5/2	13.556	1.11×10^{-5}
^{23}Na	100	3/2	26.452	9.27×10^{-2}
^{27}Al	100	5/2	26.057	0.207
^{29}Si	4.683	1/2	19.867	3.68×10^{-4}
^{31}P	100	1/2	40.481	6.65×10^{-2}
^{33}S	0.76	3/2	7.676	1.72×10^{-5}
^{39}K	93.258	3/2	4.666	4.76×10^{-4}
^{43}Ca	0.135	7/2	6.730	8.68×10^{-6}
^{129}Xe	26.44	1/2	27.810	5.72×10^{-3}

[a] Corresponding to the magnetic field of 2.35 T of a 100 MHz NMR spectrometer.
[b] Relative to ^{1}H.

Harris et al., *Pure Appl. Chem.* 2001;73(11):1795-1818

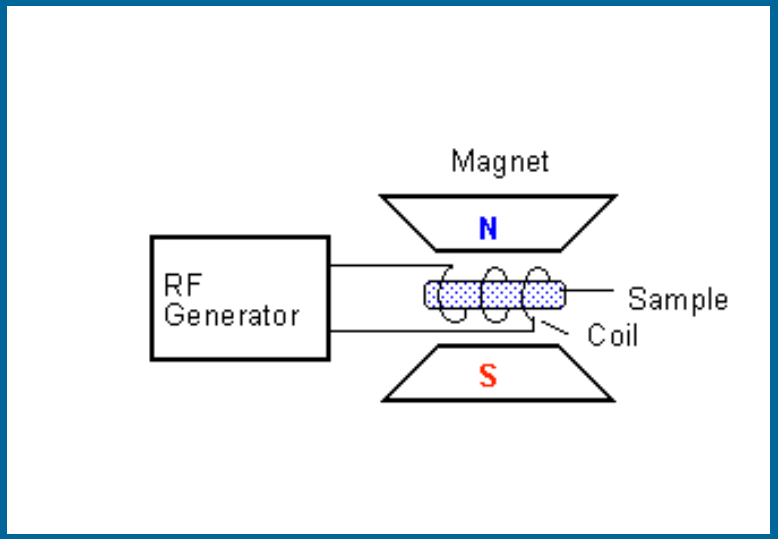
NMR background



http://www.grandinetti.org/Research/NMR

NMR background

$$B_0 \sim 1\text{T} \Rightarrow \begin{cases} f_L \sim 43\ \text{MHz} \ (^1\text{H}) \\ f_L \sim 28\ \text{GHz} \ (\text{electron}) \end{cases}$$



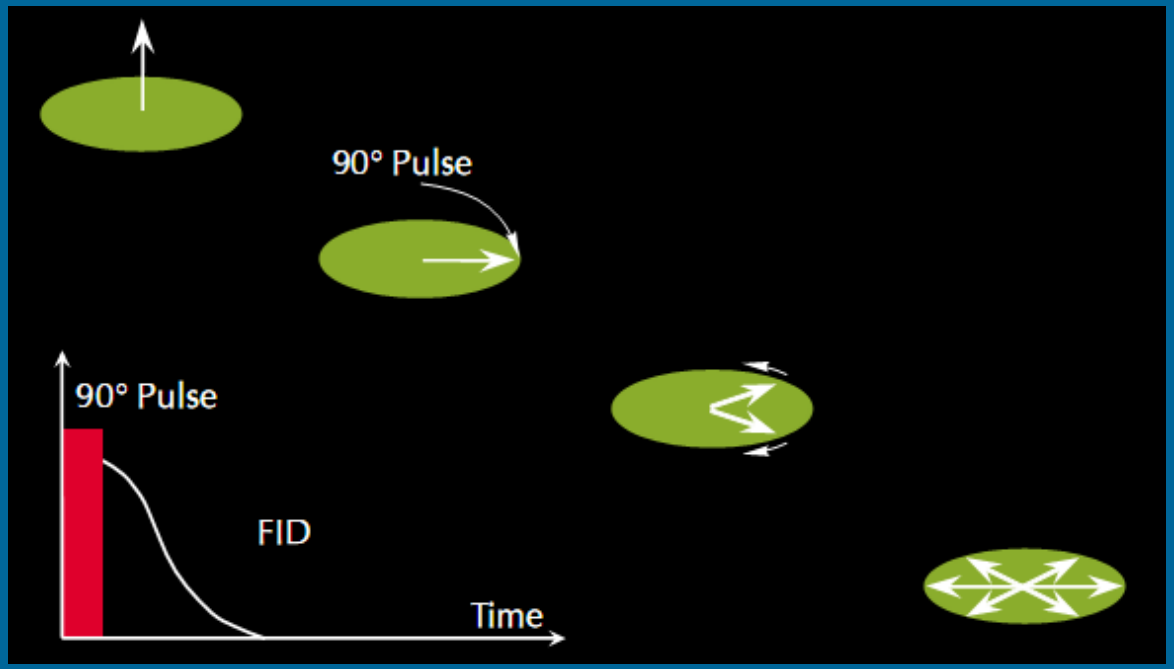
RF magnetic field: $B_1 \sim 10\text{G} = 10^{-3}\text{T}$

Earth magnetic field: $B_T \sim 10^{-5}\text{T}$

$$\vec{B}_0 = B_0 \hat{z} \qquad \vec{B}_1 = (2B_1 \cos \omega t)\hat{x}$$

NMR background

Single pulse experiment (**SPE**) or **Bloch decay**:



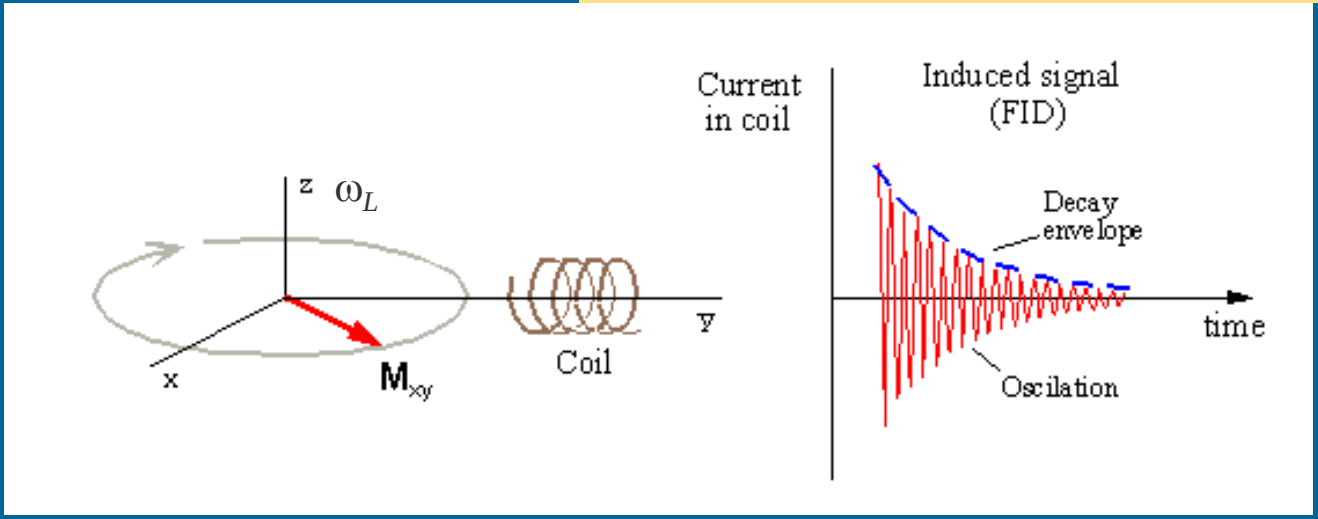
Signal detected at audio frequency:

$\Delta f = f_L - f_{RF}$

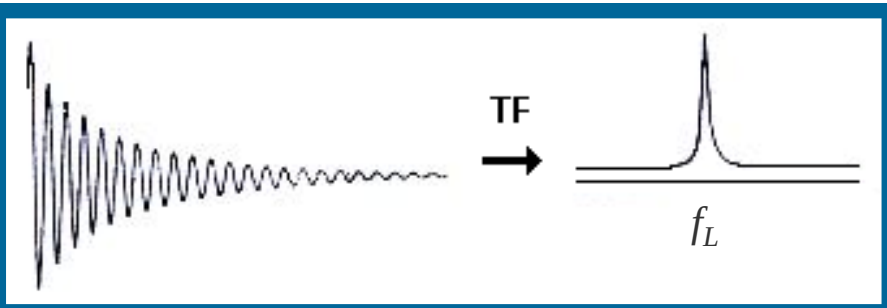
On resonance: $\Delta f = 0$

NMR background

FID = free induction decay



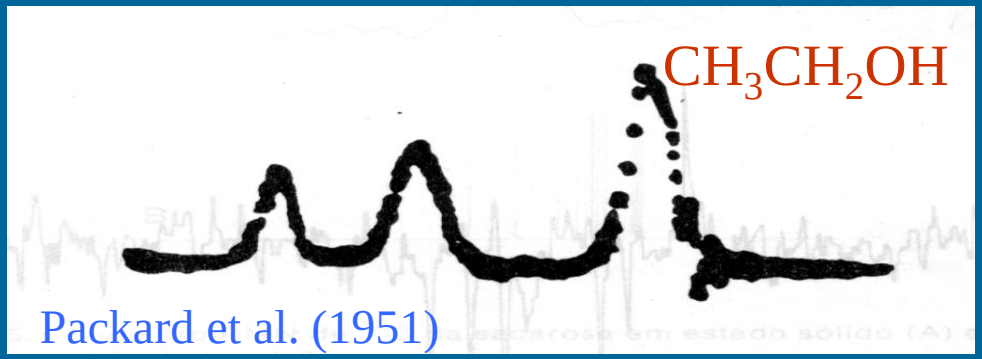
Fourier transform (FT)



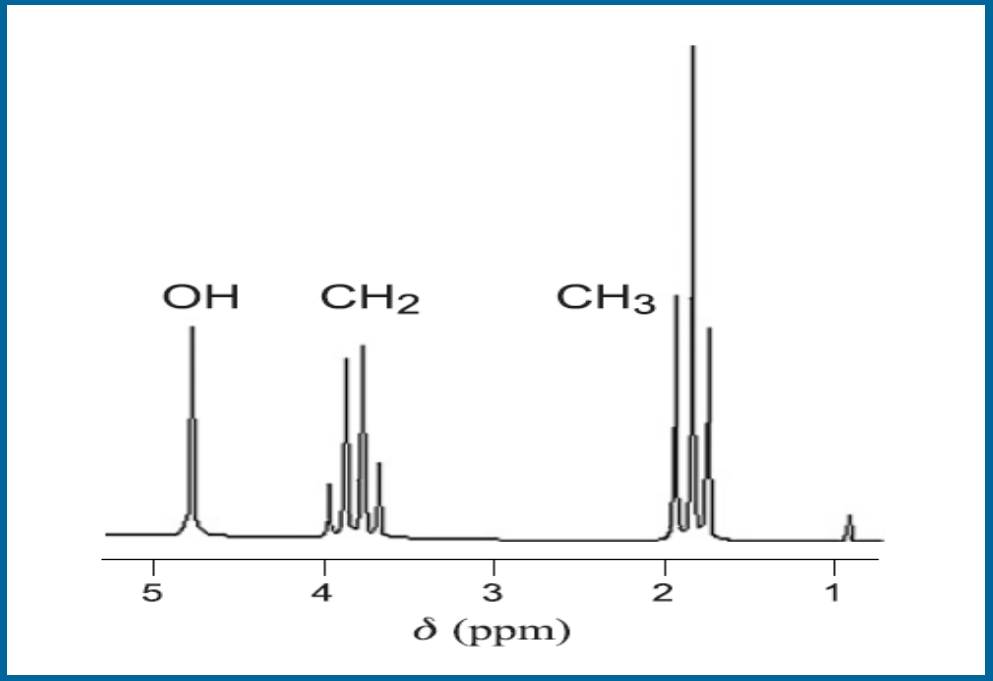
FID

Spectrum

Chemical shielding and chemical shift



Packard et al. (1951)



Chemical shift:

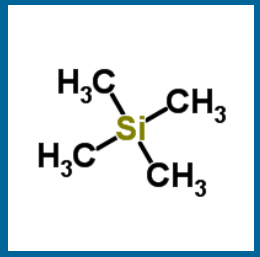
$$\delta = \frac{f_{obs} - f_{ref}}{f_{ref}}$$

Typical values (^{1}H NMR):

f_{ref} ~ 400 MHz (TMS)

$f_{obs} - f_{ref}$ ~ 400-4000 Hz

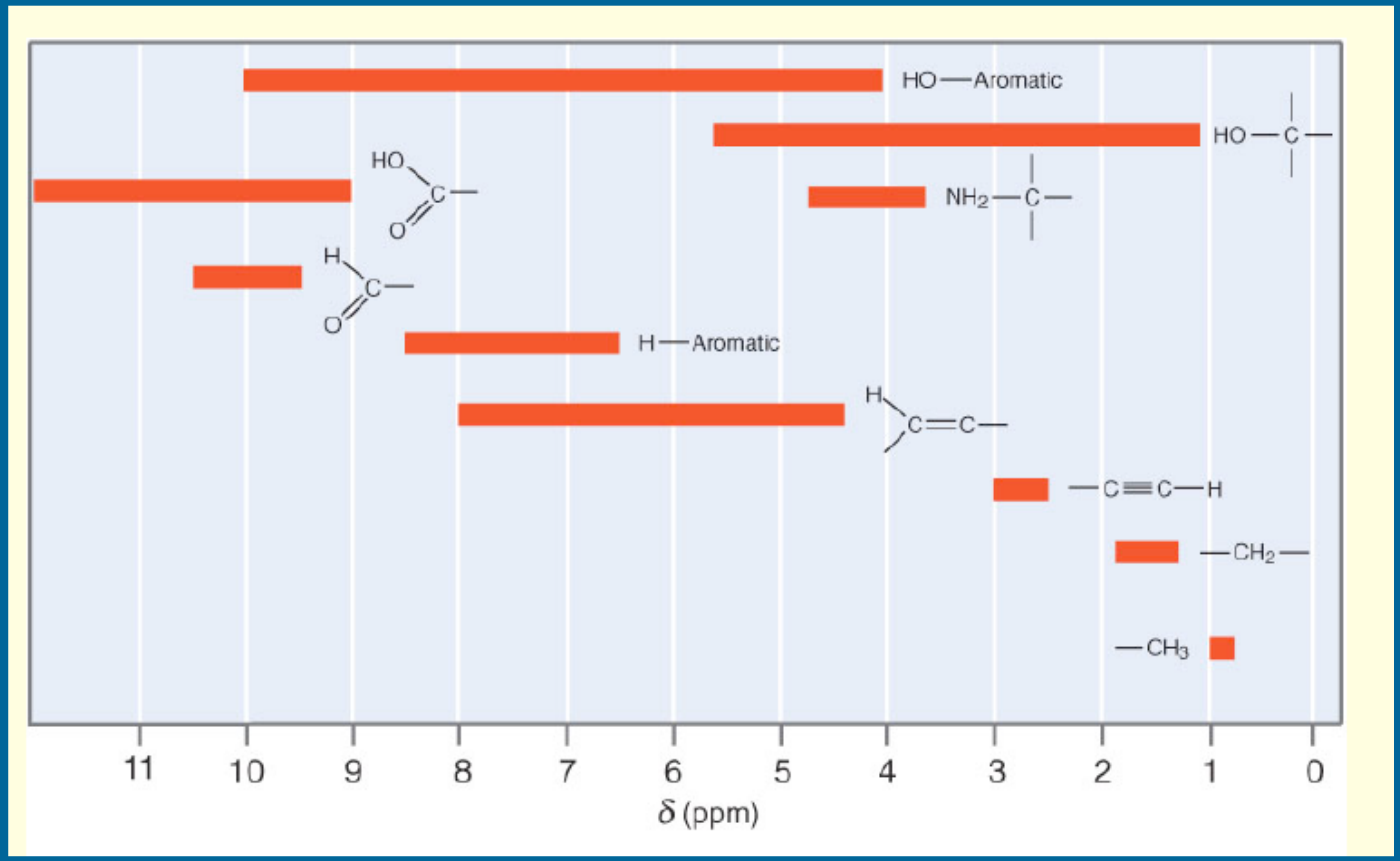
$\delta \sim 10^{-6}$ (ppm)



Common reference for ^{1}H, ^{13}C and ^{29}Si NMR experiments.

Chemical shielding and chemical shift

^{1}H chemical shift chart:



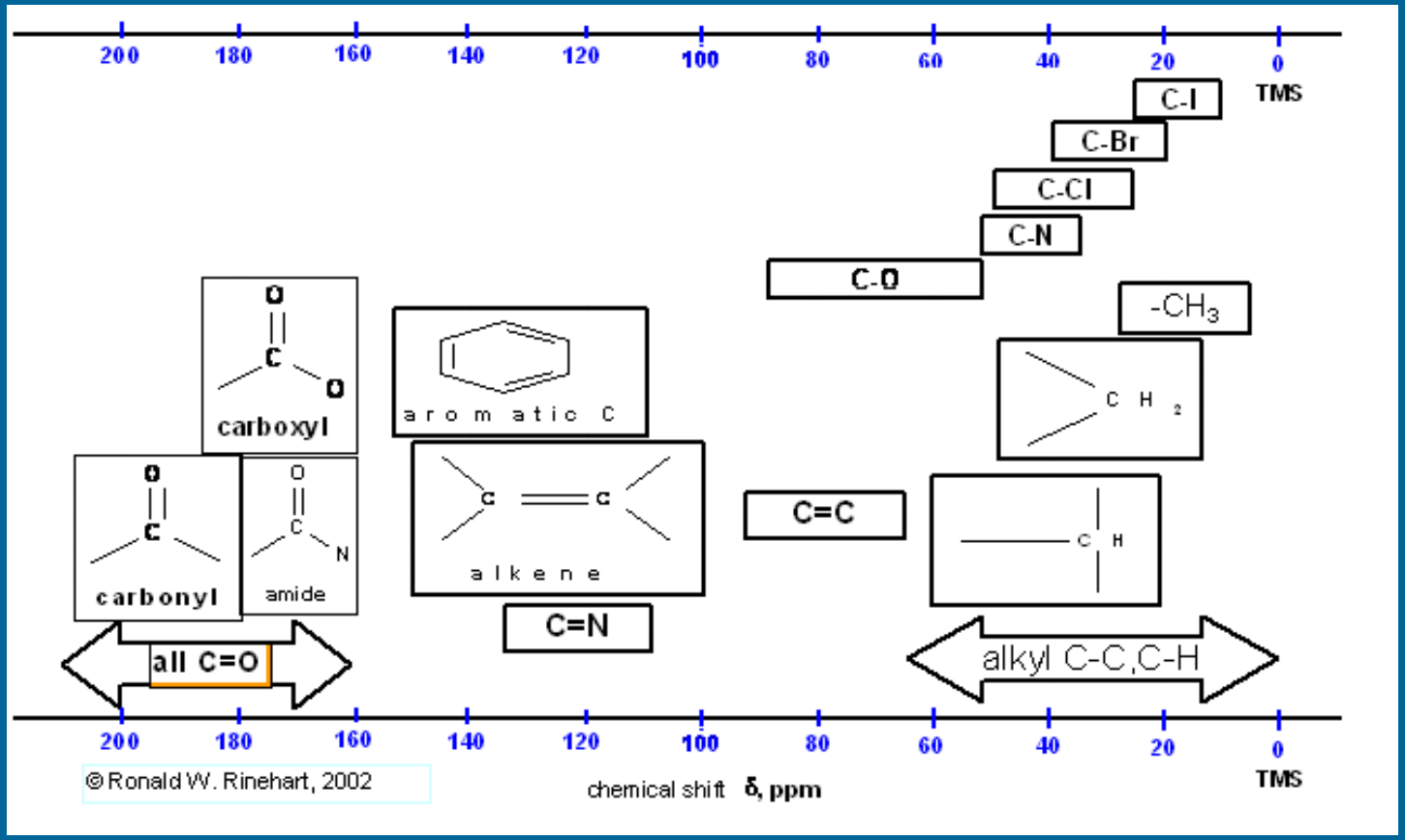
frequency ⟵

⟶ shielding

http://www.chem.wisc.edu/areas/reich/handouts/nmr-h/hdata.htm

Chemical shielding and chemical shift

^{13}C chemical shift chart:

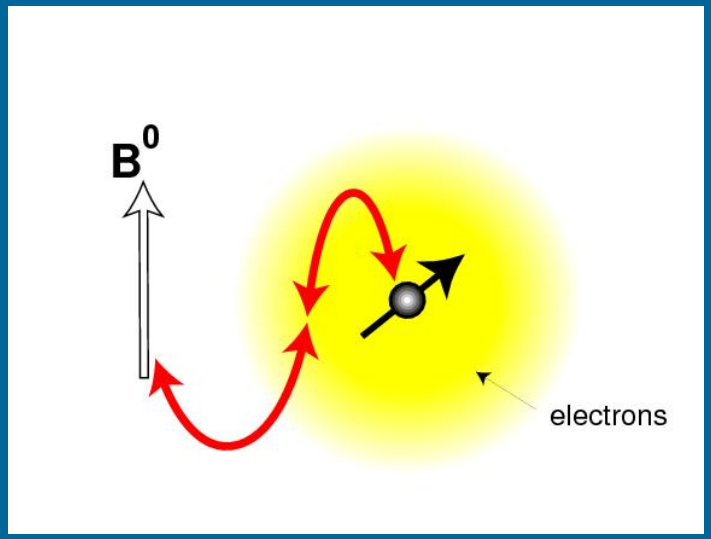


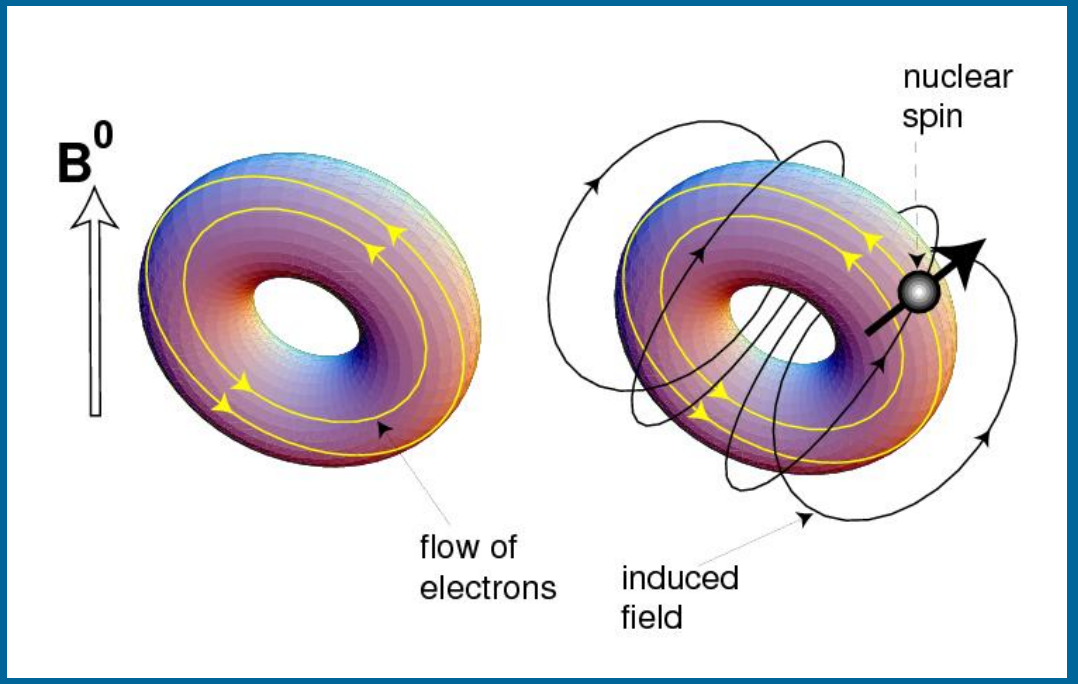
frequency ⟵

⟶ shielding

http://www.chem.wisc.edu/areas/reich/handouts/nmr-c13/cdata.htm

Chemical shielding and chemical shift





In liquids:

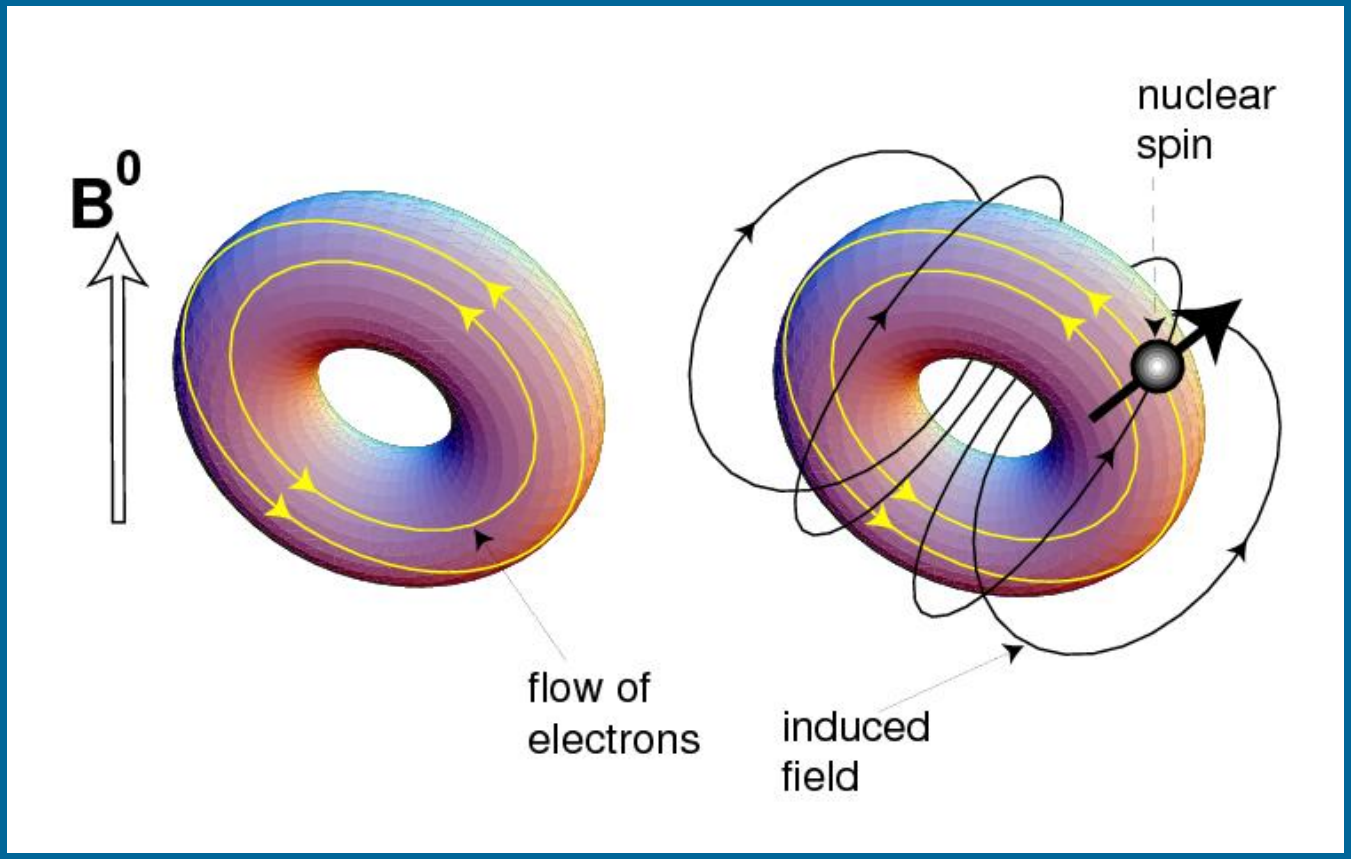
$$\vec{B}_{loc} = (1-\sigma_{iso})\vec{B}_0$$

$$f_{obs} = \frac{\gamma B_{loc}}{2\pi} = f_L(1-\sigma_{iso})$$

$$\delta = \frac{f_{obs} - f_{ref}}{f_{ref}} = \frac{\sigma_{ref} - \sigma_{obs}}{1-\sigma_{ref}} \cong \sigma_{ref} - \sigma_{obs}$$

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Chemical shielding in solids



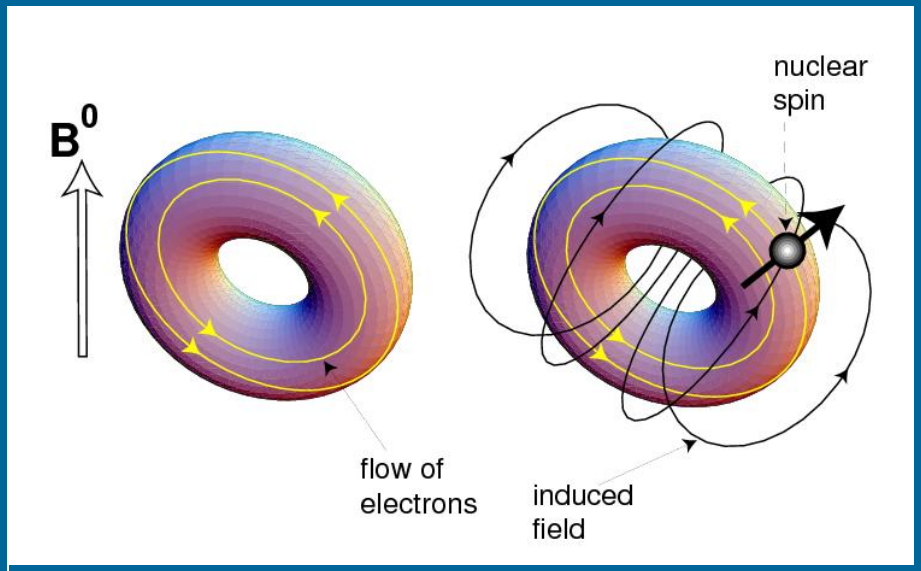
$$\vec{B}^{ind} = -\tilde{\sigma} \cdot \vec{B}_0$$

$$\vec{B}^{loc} = \vec{B}_0 + \vec{B}^{ind} = (1 - \tilde{\sigma}) \cdot \vec{B}_0$$

$\tilde{\sigma}$: shielding tensor

"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Chemical shielding in solids



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

$$\vec{B}_{loc} = (1-\tilde{\sigma})\vec{B}_0$$

$$\tilde{\sigma} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

$$\left|\sigma_{33} - \sigma_{iso}\right| \geq \left|\sigma_{11} - \sigma_{iso}\right| \geq \left|\sigma_{22} - \sigma_{iso}\right|$$

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

Shielding anistropy: $\zeta = \sigma_{33} - \sigma_{iso}$

Shielding asymmetry : $\eta = \frac{\sigma_{22} - \sigma_{11}}{\zeta}$ $\quad 0 \leq \eta \leq 1$

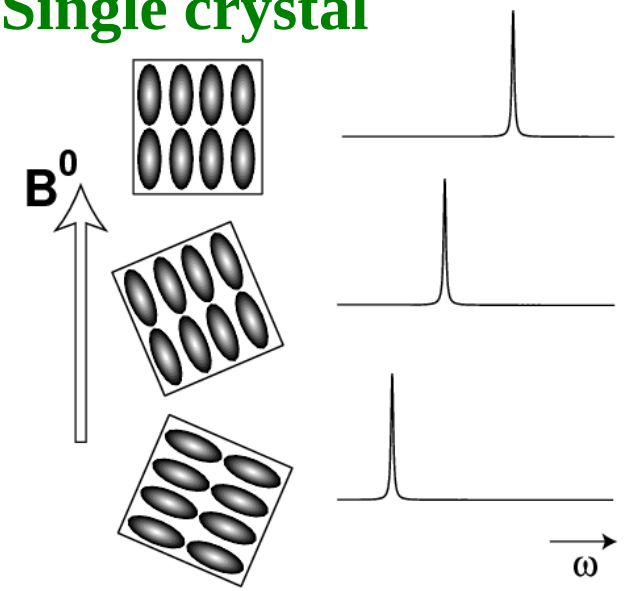
Harris et al., Pure Appl Chem. 2008;80:59-84

Chemical shielding anisotropy

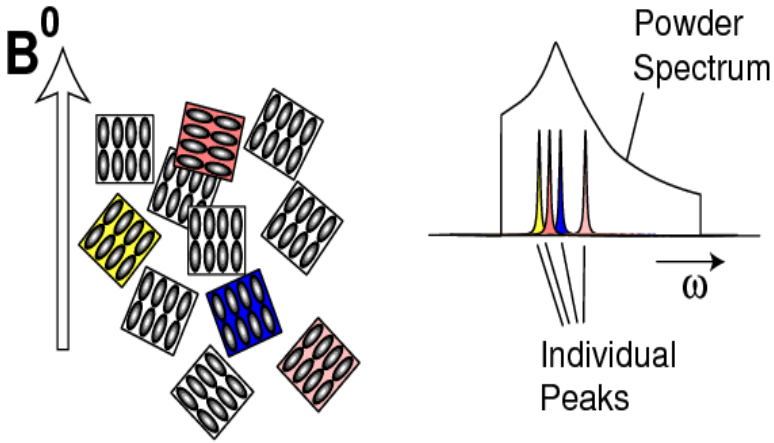
Orientation-dependent NMR frequency:

$$\omega(\theta,\phi) = \omega_L - \omega_L \left\{ \sigma_{iso} + \frac{\zeta}{2}\left[(3\cos^2\theta - 1) + \eta \,\mathrm{sen}^2\theta \cos 2\phi \right] \right\}$$

Single crystal

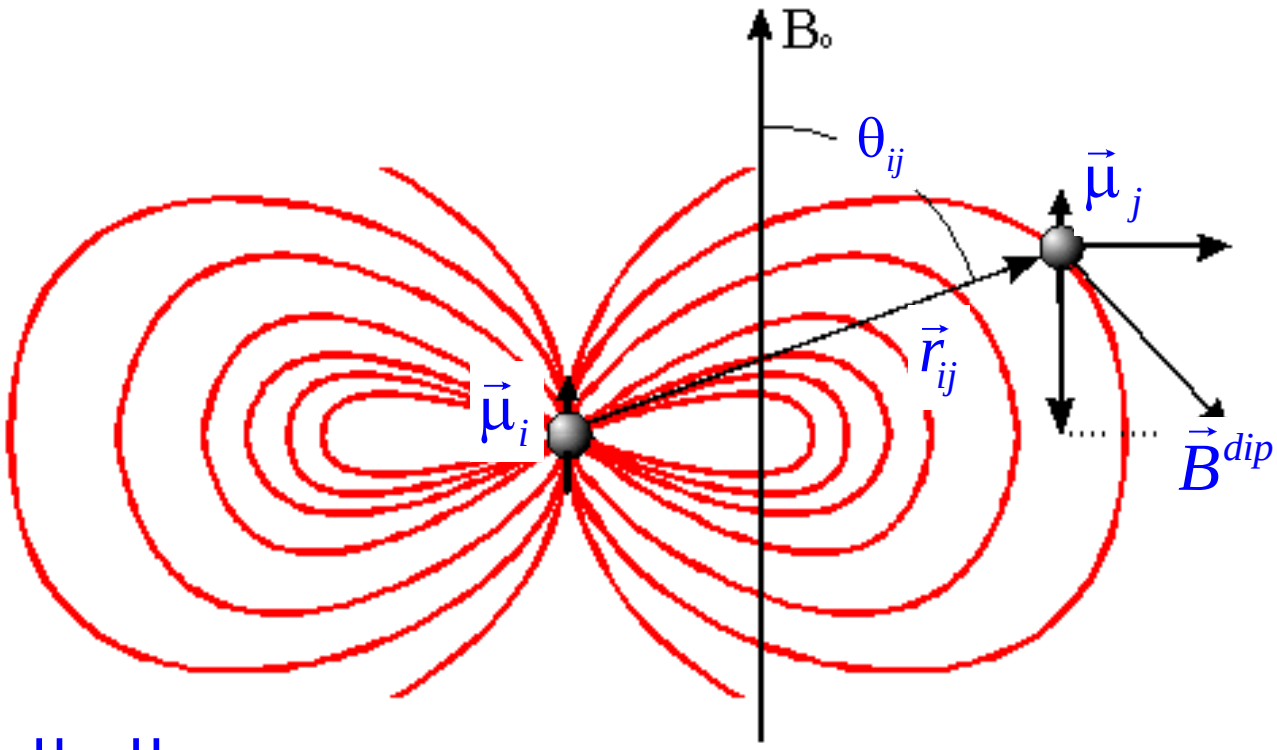


Powder



"Spin dynamics", M. H. Levitt. John Wiley & Sons, 2002.

Dipolar coupling



$$B_z^{dip} \cong \frac{\mu_0}{4\pi}\frac{\mu}{r_{ij}^3}(3\cos^2\theta_{ij} - 1)$$

Through-space interaction

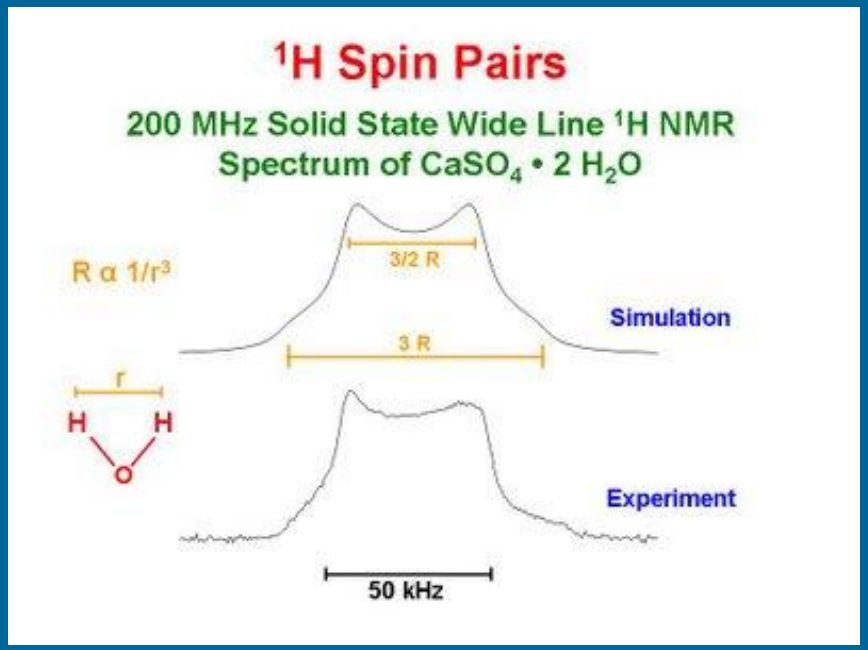
Dipolar coupling – powder patterns

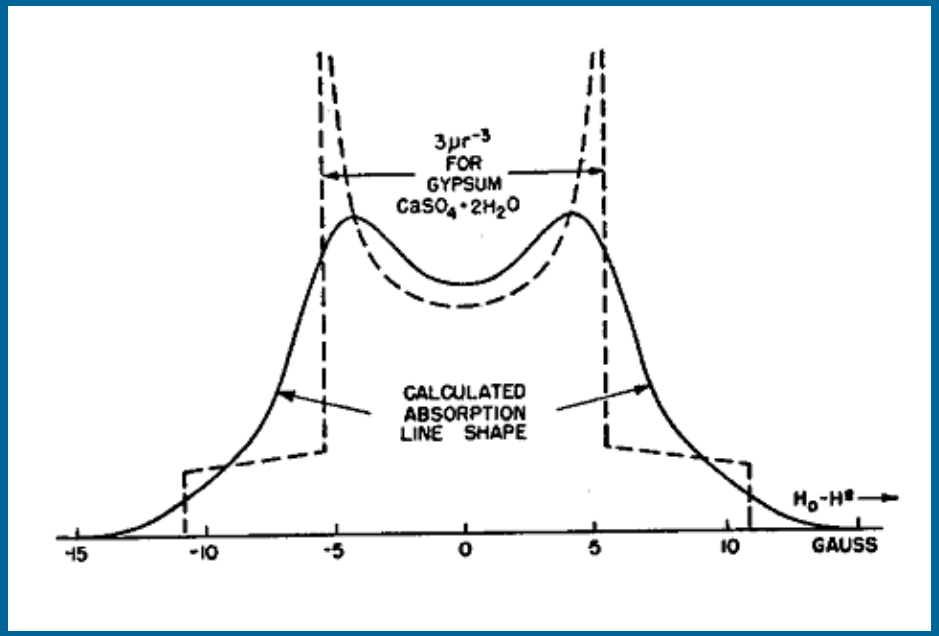
Orientation-dependent NMR frequency (homonuclear case):

$$\omega(\theta) = \omega_I \pm d\,\frac{3\cos^2\theta - 1}{4}$$

$$d = \frac{\mu_0}{4\pi}\,\frac{\gamma_I \gamma_S \hbar}{r^3}$$

Pake doublet





http://u-of-o-nmr-facility.blogspot.com/2008_10_01_archive.html

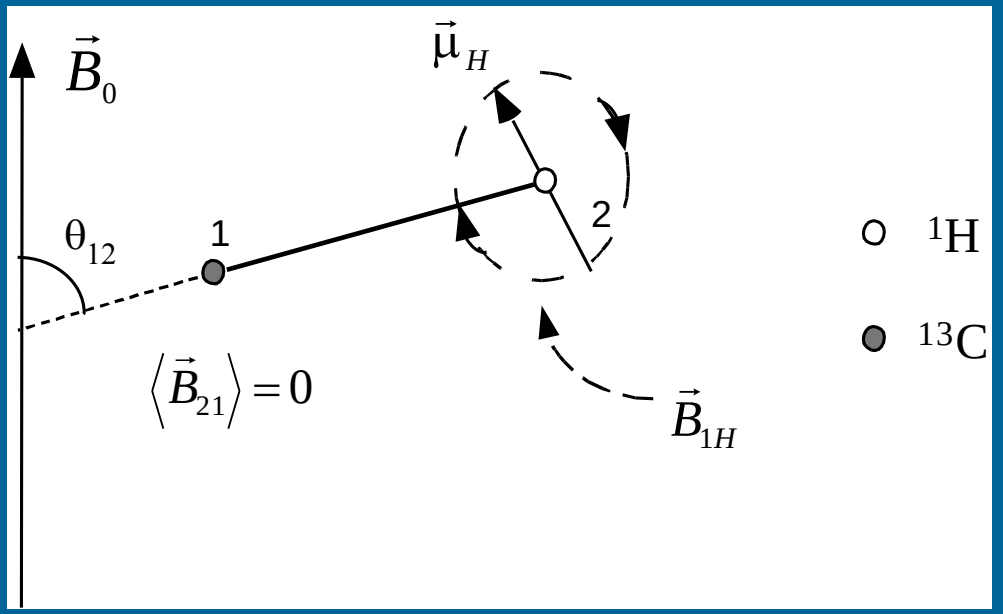
G. E. Pake, *J. Chem. Phys.* 1948;16:327-336.

High power decoupling

Heteronuclear decoupling:

$$\gamma_H B_{1H} / 2\pi > \Delta f_{dip}$$

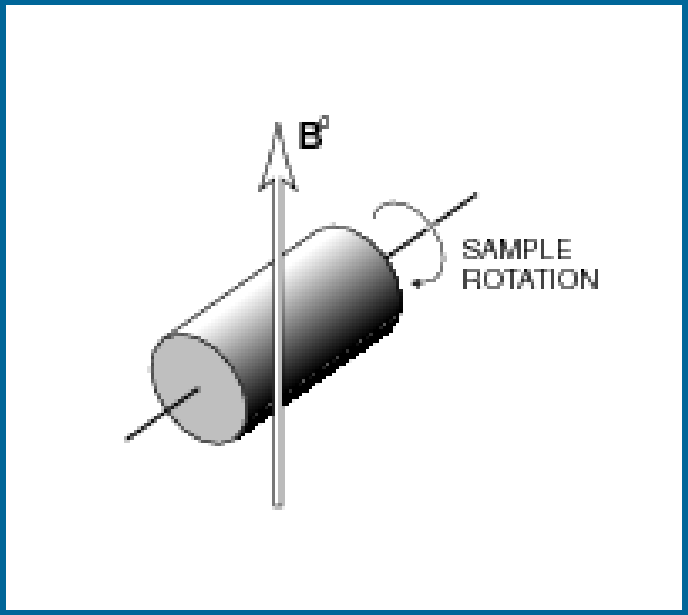
$$\Delta f_{dip} \sim d = \frac{\mu_0}{8\pi^2} \frac{\gamma_I \gamma_S \hbar}{r^3}$$

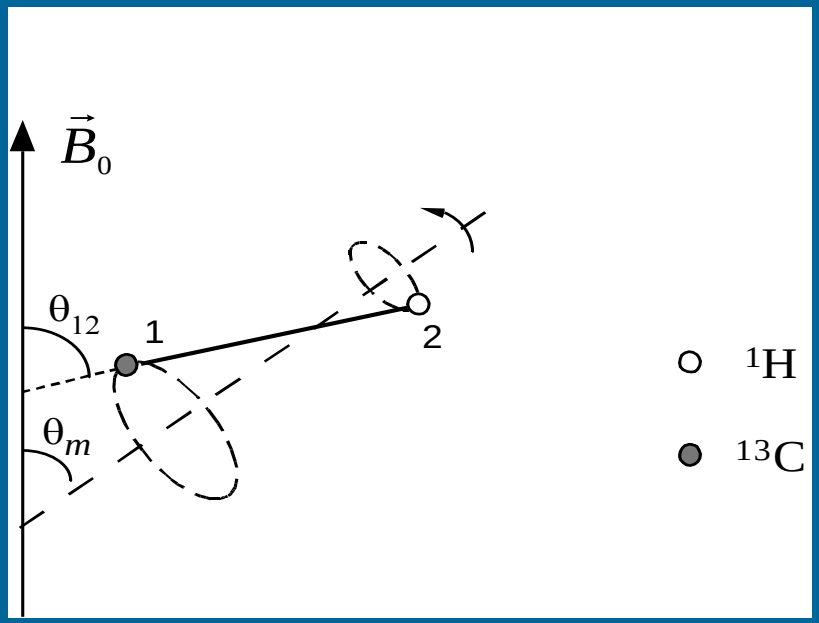


For a ^{1}H-^{13}C pair in a C-H single bond:

$$\Delta f_{dip} \sim 70 \text{ kHz}$$

Magic angle spinning (MAS)



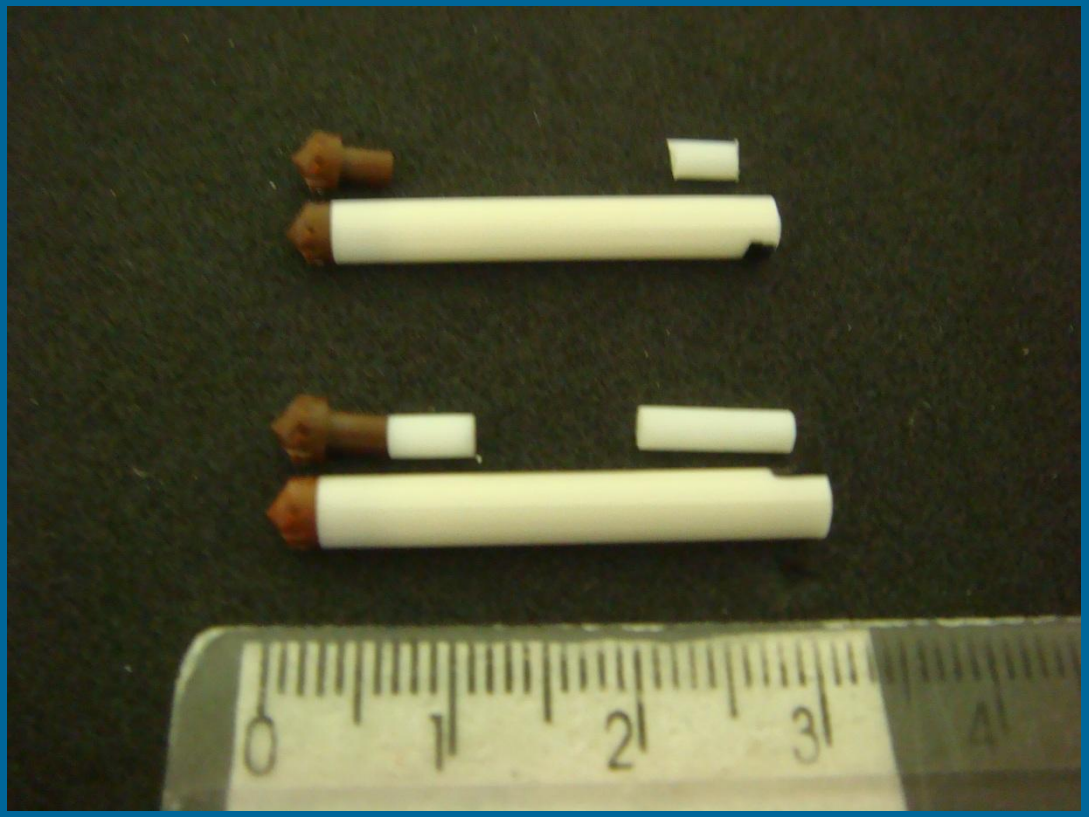


$$\left\langle 3\cos^2\theta_{12} - 1 \right\rangle \propto 3\cos^2\theta_m - 1 = 0$$

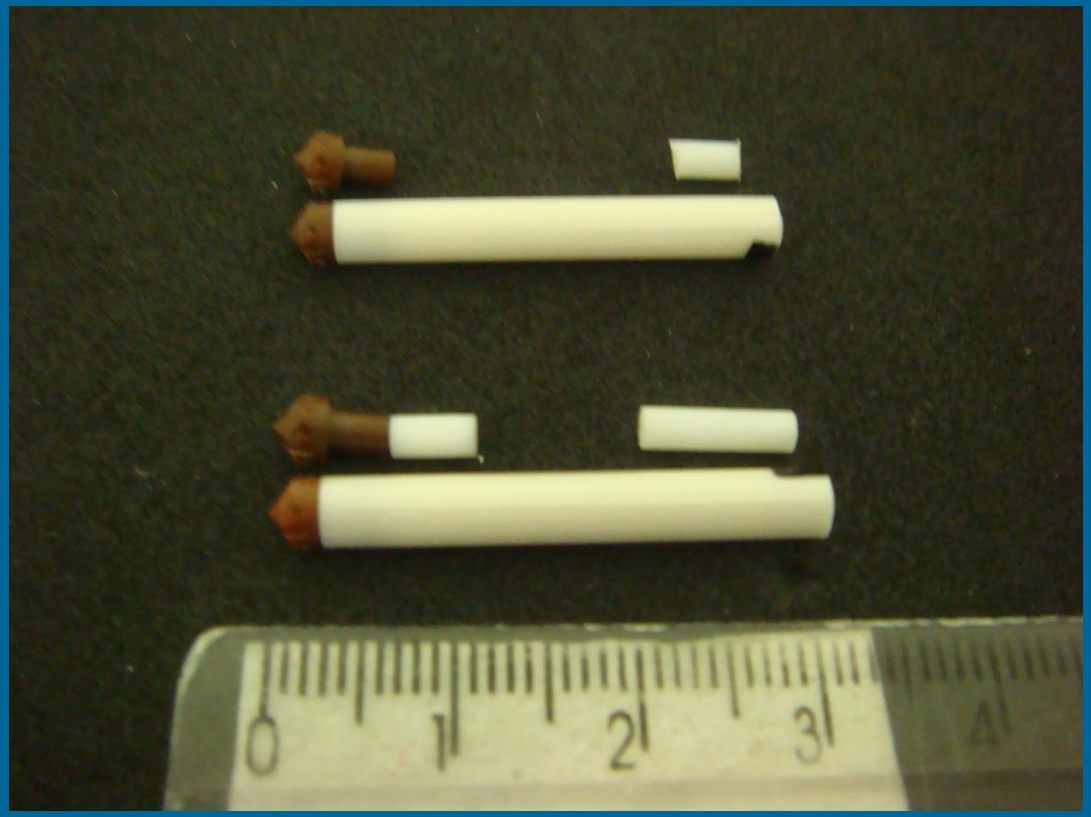
$$B_z^{dip} \cong \frac{\mu_0}{4\pi}\frac{\mu}{r_{ij}^3}(3\cos^2\theta_{ij} - 1)$$

$$\theta_m = \cos^{-1}(1/\sqrt{3}) = 54.74^o$$

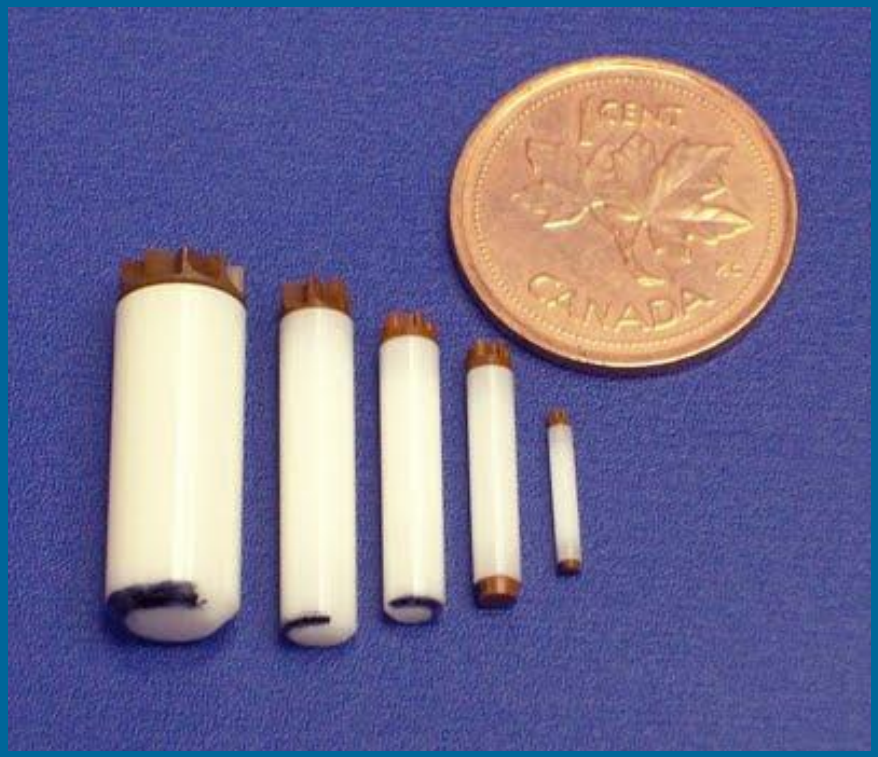
Magic angle spinning (MAS)



Magic angle spinning (MAS)



Magic angle spinning (MAS)

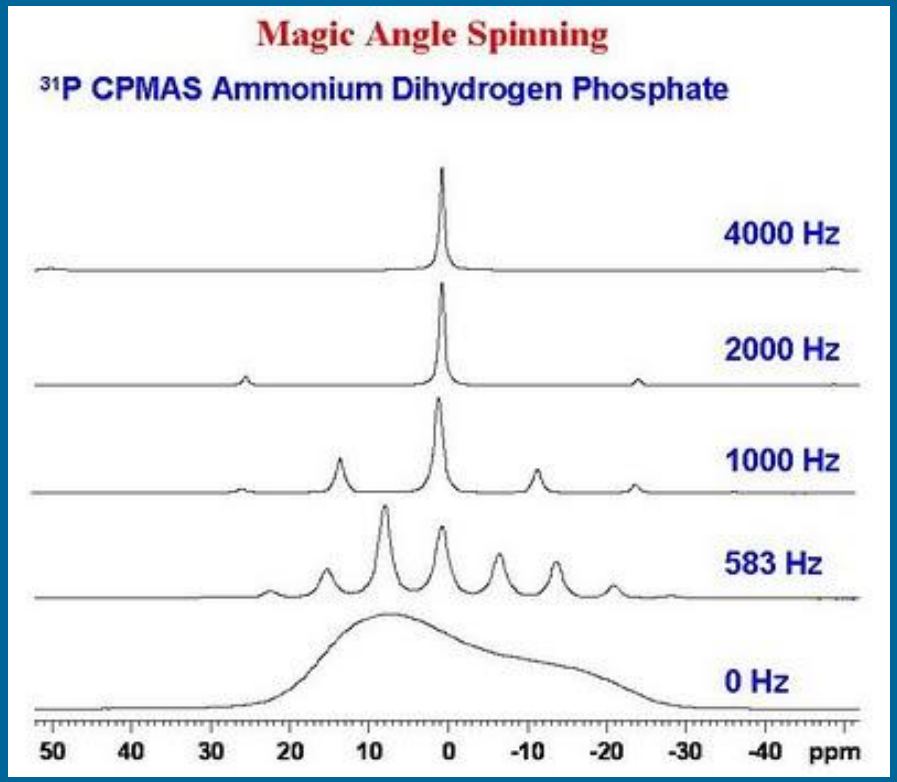


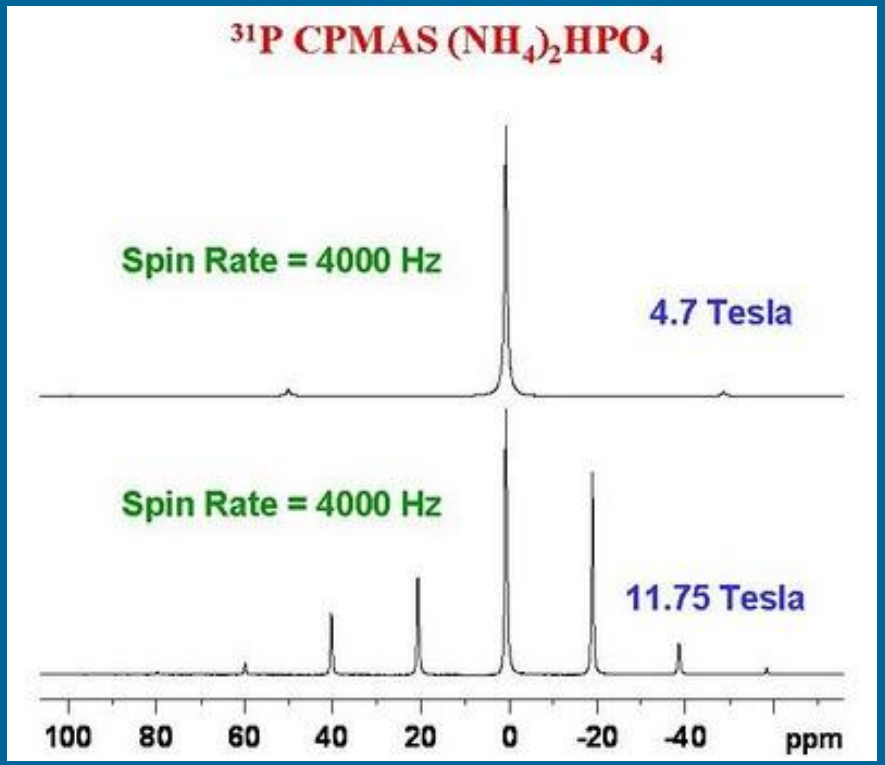
ϕ (mm): 7.0 4.0 3.2 2.5 1.3

$f_{rot}^{max.}$ (kHz): 8 18 23 35 70

http://u-of-o-nmr-facility.blogspot.com/2008/04/how-much-sample-do-i-need-to-get-solid.html

Magic angle spinning (MAS)

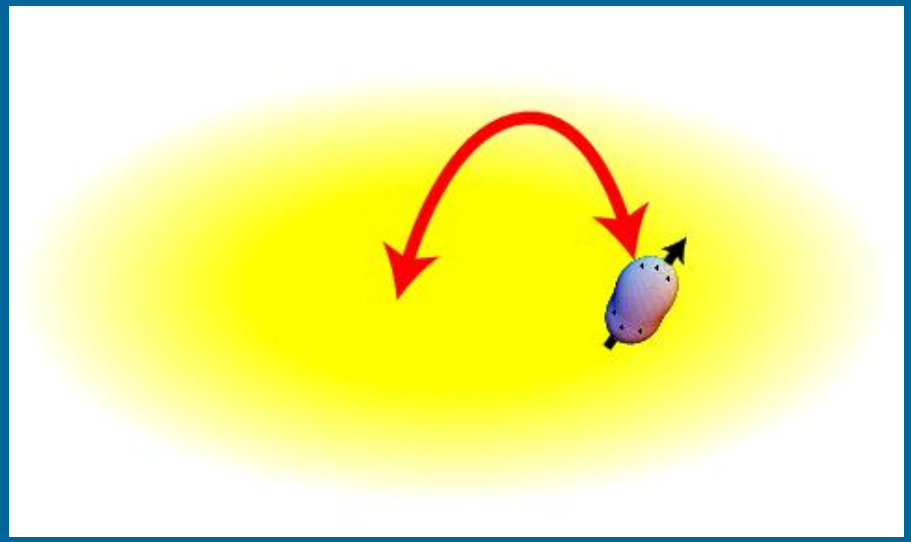


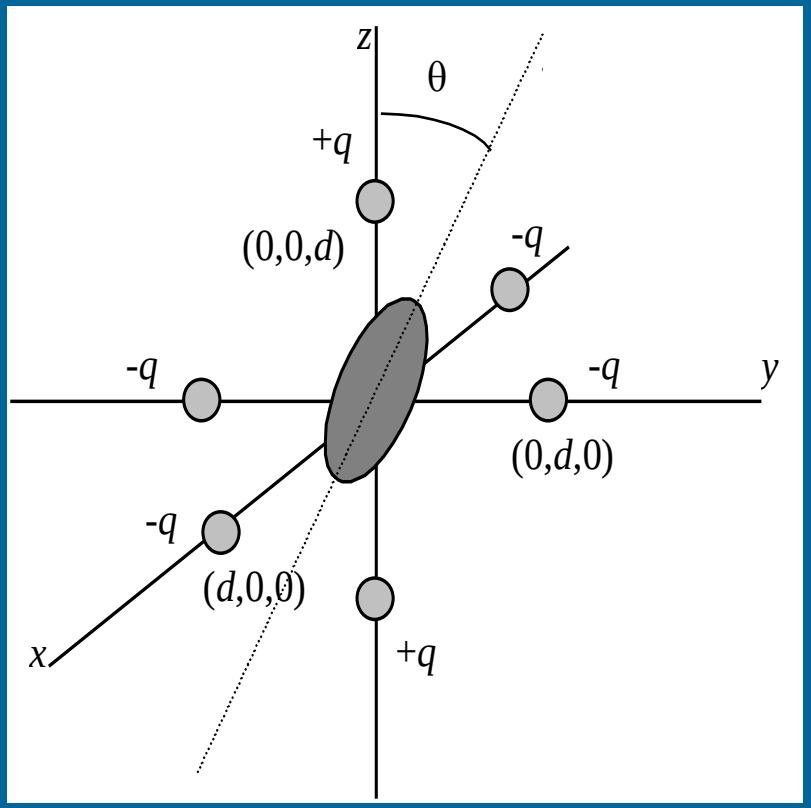


http://u-of-o-nmr-facility.blogspot.com/

Electric quadrupole interaction

Quadrupolar nuclei ($I > ½$):
^{2}H, ^{23}Na, ^{25}Mg, ^{27}Al, ^{35}Cl, ^{55}Mn, ...



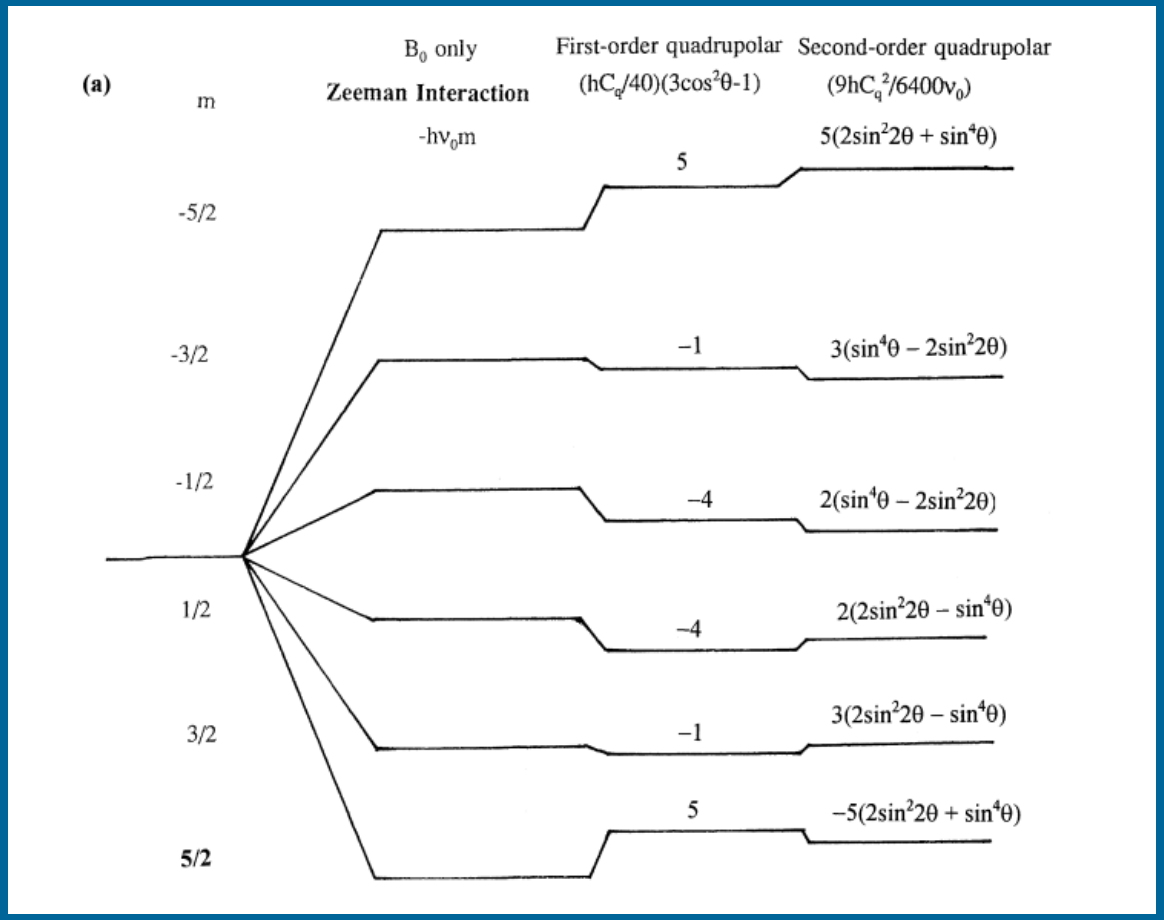


Coupling to electric field gradient (EFG)

$$E_Q = (eqQ / d^3)(3\cos^2\theta - 1)$$

Electric quadrupole interaction

Combined effects: magnetic (*dominant*) and quadrupolar (*perturbation*) interactions:



$$C_Q = \frac{e^2 qQ}{h}$$

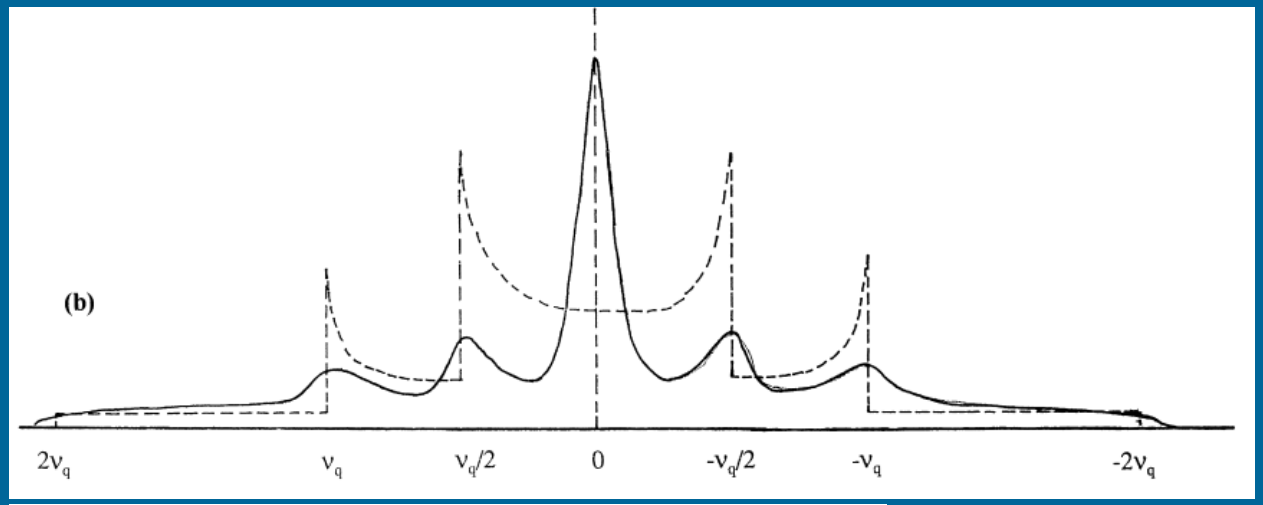
$$I = 5/2$$

$$\eta_Q = 0$$

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

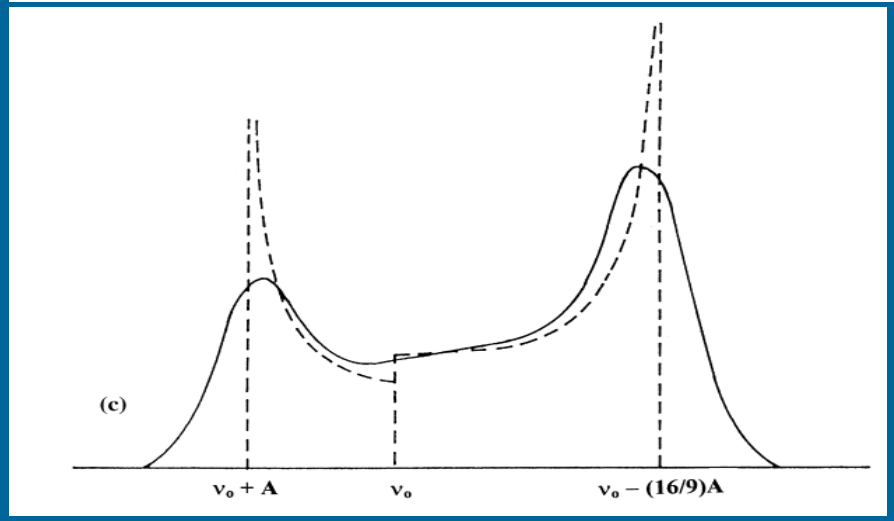
Electric quadrupole interaction

Powder patterns – half-integer spin nuclei



1st order

$$\nu_q = \frac{3e^2qQ}{2I(2I-1)h}$$



2nd order –central transition

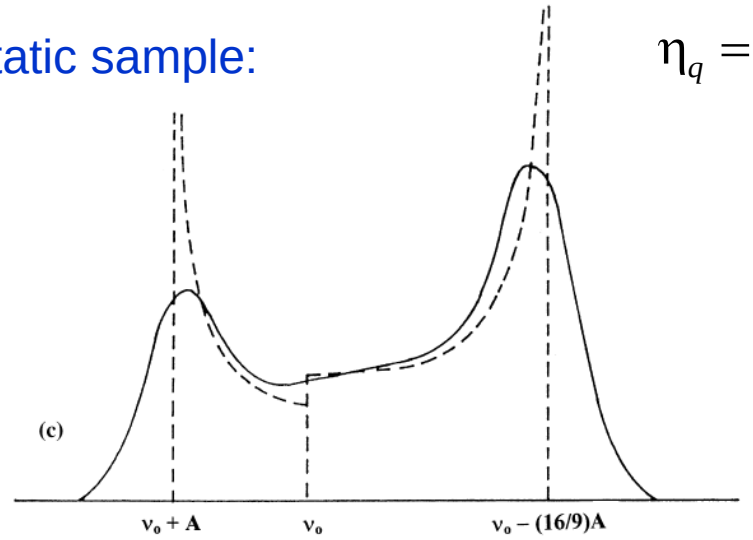
$$A = \left[I(I+1) - 3/4\right]\frac{\nu_q^{\,2}}{\nu_0}$$

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

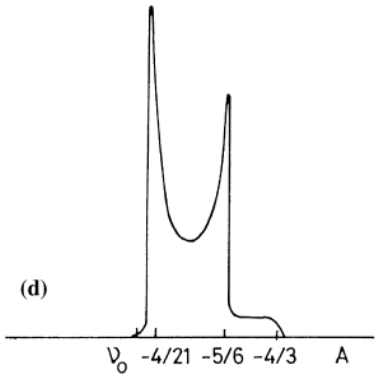
Quadrupole effects in MAS NMR spectra

Powder patterns – half-integer spin nuclei:

Static sample: $\eta_q = 0$



MAS:



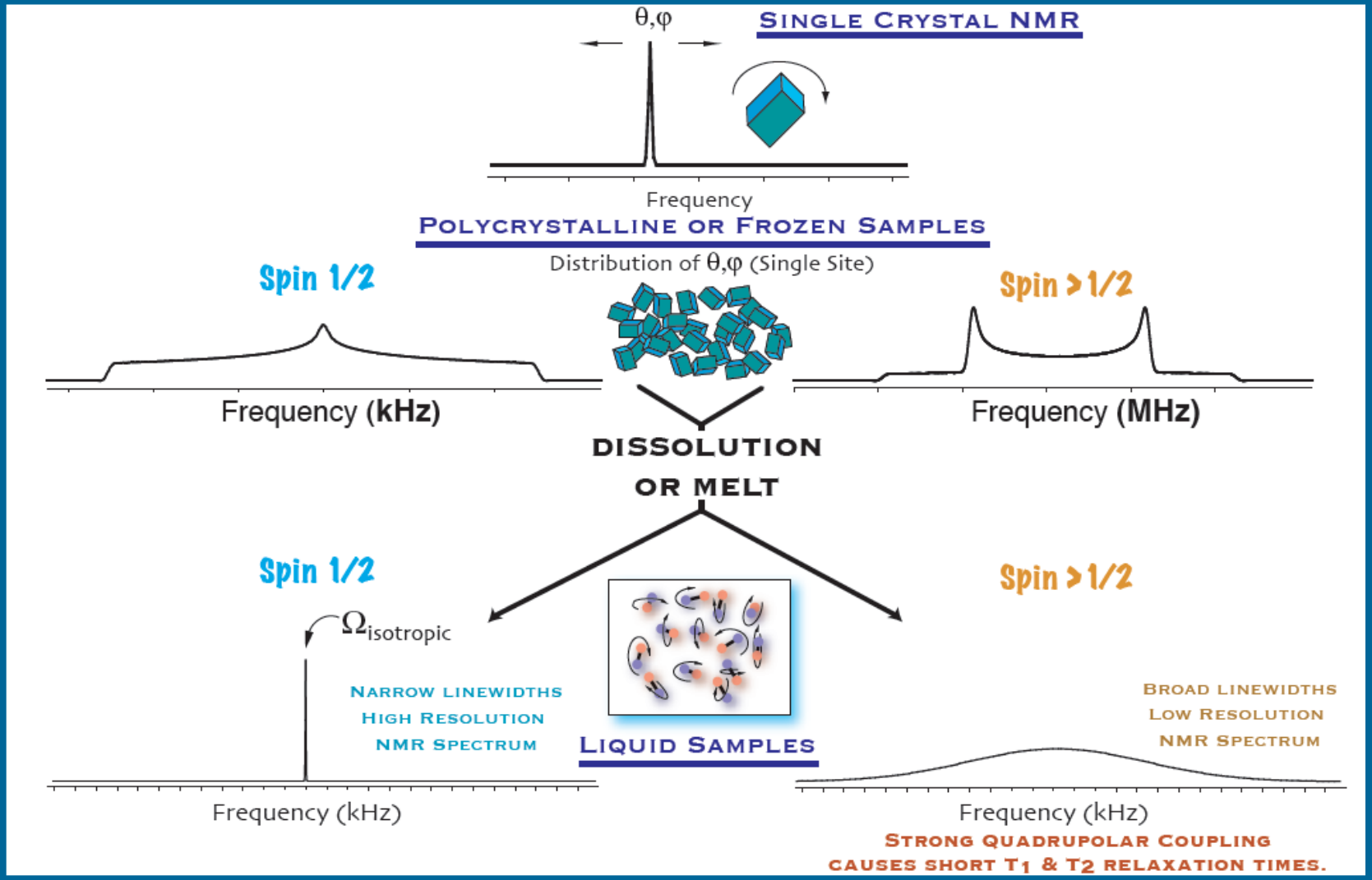
2nd order – central transition:

$$\nu_q = \frac{3e^2qQ}{2I(2I-1)h}$$

$$A = \left[I(I+1) - 3/4\right]\frac{\nu_q^{\,2}}{\nu_0}$$

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

Nuclear spin interactions – summary



http://grandinetti.org/Research/NMRMethods/index.html

Solid-state ^{13}C NMR of carbon materials

Typical chemical shifts in ^{13}C NMR:

TABLE 2.2

Isotropic Chemical Shifts (δ_C) for Some Chemical Groups Typically Found in Organic Matter and in Carbon Materials

Chemical Group	δ_C (ppm TMS)
$-CH_3$	0–23
$-CH_2-$	23–60
$-OCH_3$	50–60
–C–O–C–	70–95
$H-C_{aro}$	110–120
$C-C_{aro}^{*}$	130–140
$O-C_{aro}$	140–160
$C-(C^{*}=O)-OH$	160–180
$C-(C^{*}=O)-C,H$	180–220

Note: In the case of the presence of chemically distinct carbon atoms, the δ_C value corresponds to the atom indicated by an asterisk.

Freitas et al., *Chem. Phys. Carbon* 2012;31:85-169.

Structure of disordered carbons

Franklin model

Graphite-like crystallites

Cross-links

Pores

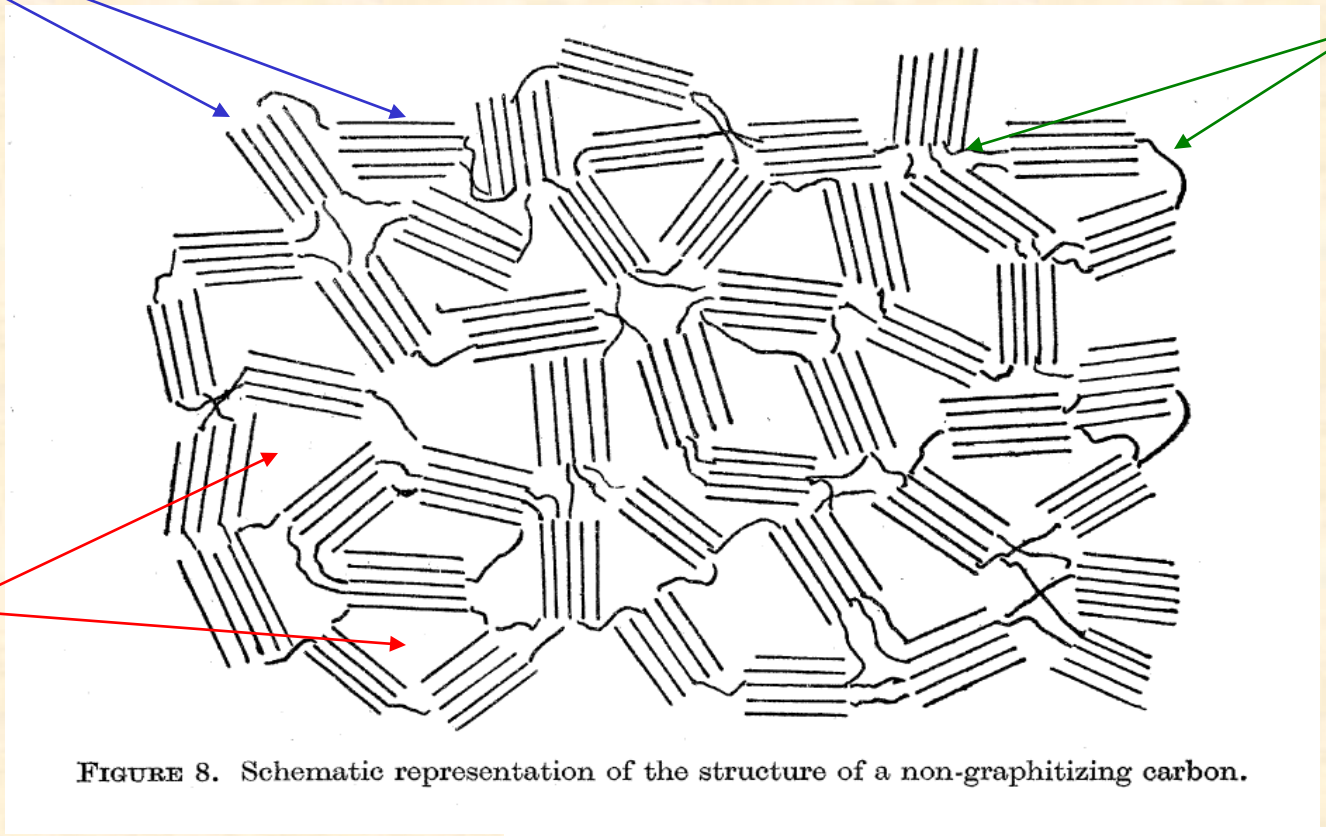


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

R. E. Franklin, *Proc. Roy. Soc. London A* 1951;209:196

Composition: C, H, O (major), N, S, ashes,...

Solid-state ^{13}C NMR of carbon materials

Typical chemical shifts in ^{13}C NMR:

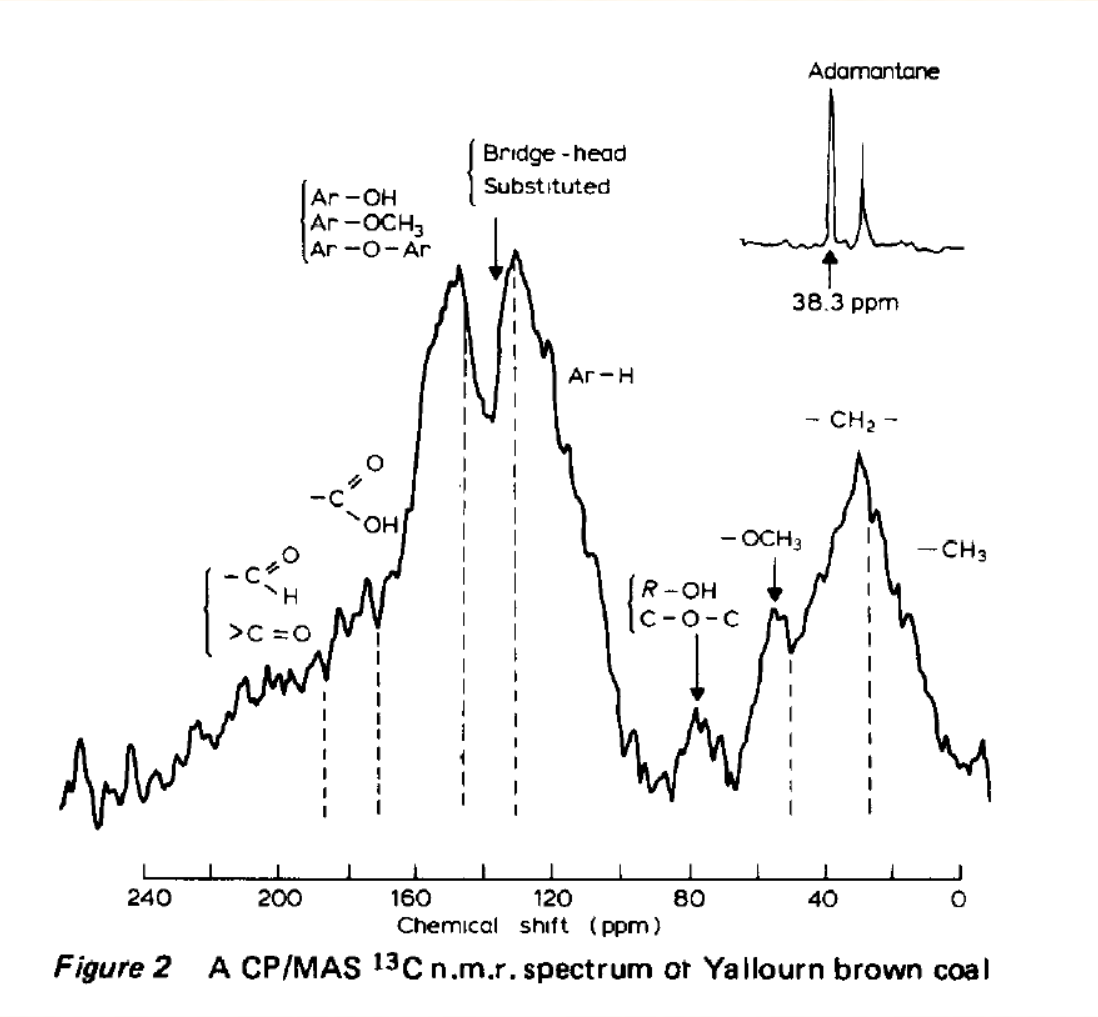


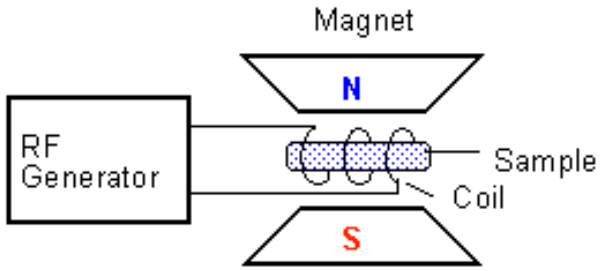
Figure 2 A CP/MAS ^{13}C n.m.r. spectrum of Yallourn brown coal

Yoshida et al., *Fuel* 1982;61:824

Solid-state ^{13}C NMR experiments

Single pulse excitation (SPE):

^{13}C NMR:



Corrupted points

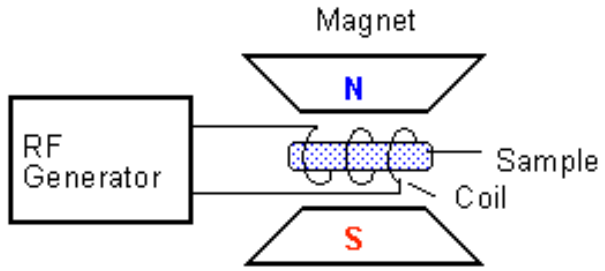
Free induction decay (***FID***)

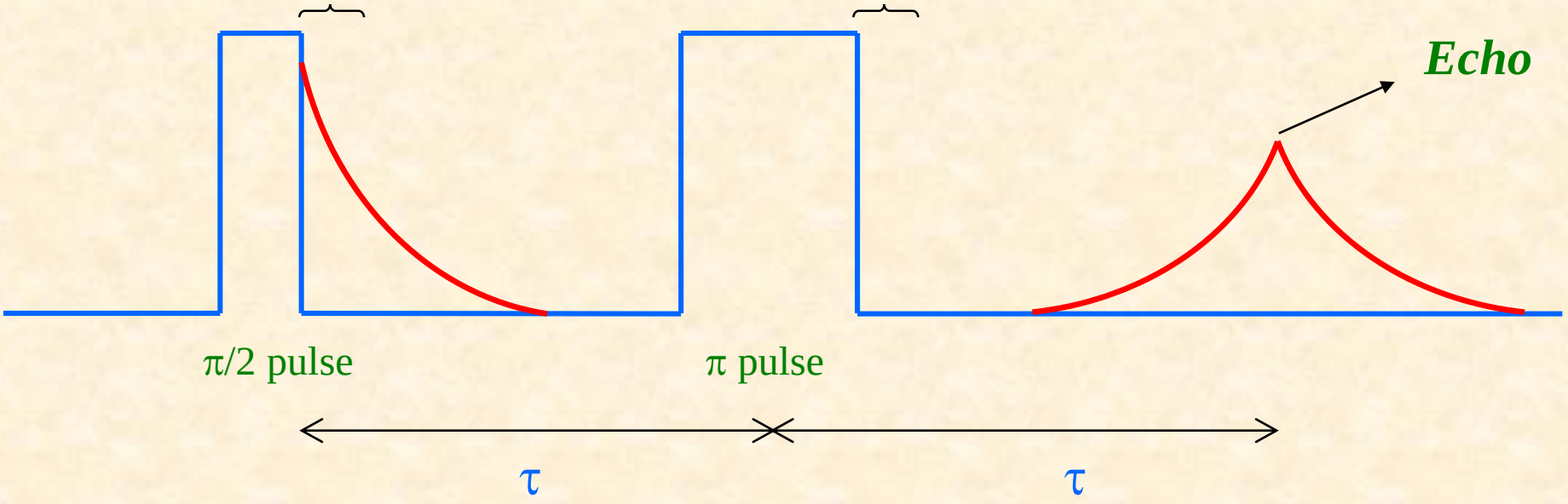
π/2 pulse

Solid-state ^{13}C NMR experiments

Two pulse excitation – *spin-echo*:

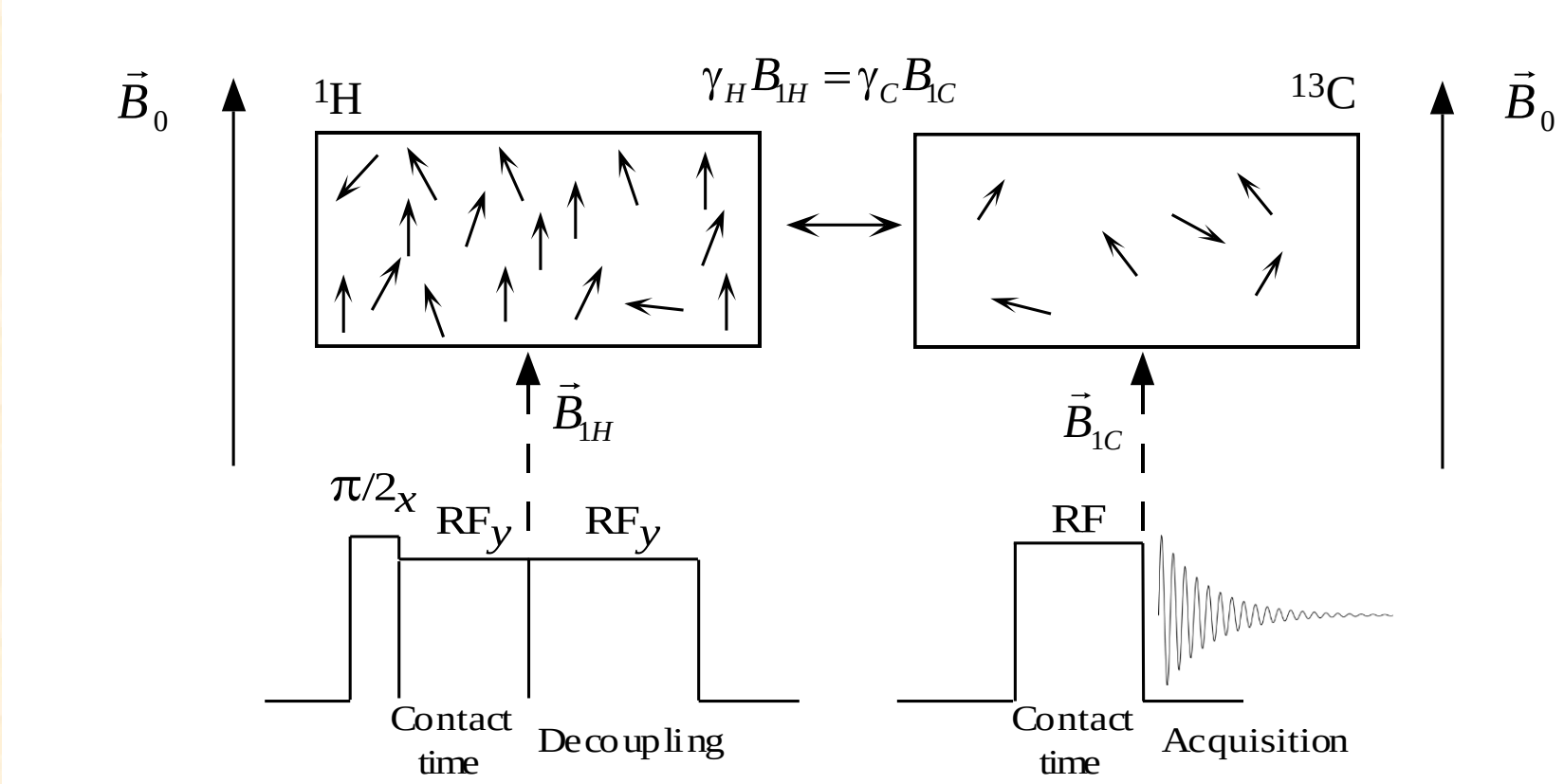
^{13}C NMR:





Solid-state ^{13}C NMR experiments

{^{1}H → ^{13}C} Cross-polarization (**CP**):



Detection of carbon groups close to hydrogen ⇒
surface groups in carbon-rich materials.

Freitas et al., *Chem. Phys. Carbon* 2012;31:85-169.

Activated carbons

- Disordered solids with irregular porous network.
- Presence of macropores, mesopores and micropores.
- Applications: catalysis, water treatment, gas storage, ...
- Basic constitution: C, H, O (major), N, S, ...
- Mineral fraction: depends on the precursor.

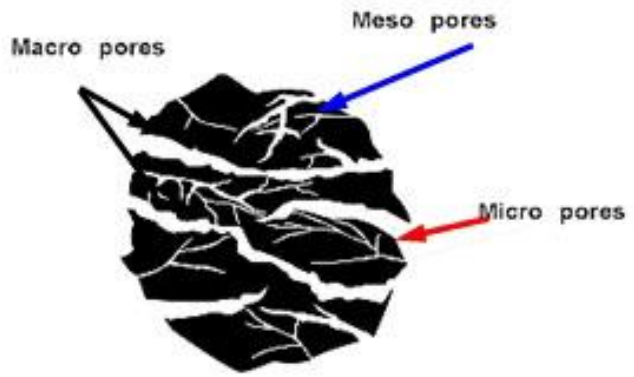


Figure 1: Activated carbon structure - schematic.

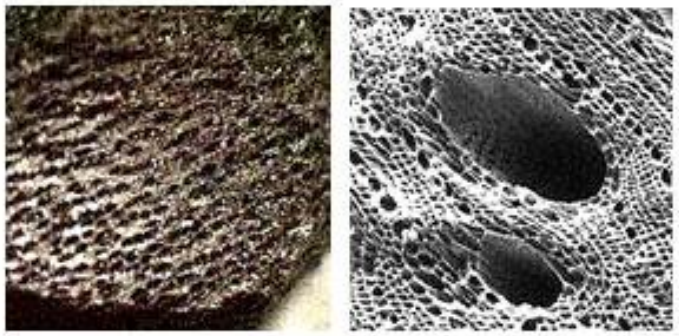


Figure 2: Activated carbon structure – SEM pictures.

http://www.afssociety.org/education/0209oneminute.html

Activated carbons

– Manufacture:

- Physical activation: steam, air, CO_2,…
- Chemical activation: H_3PO_4, NaOH, KOH, $CaCl_2$, …
- Precursors: coal, anthracite, chars, lignocellulosic materials, …
- Heat-treatments, washing, drying, chemical post-treatments, …
- Presence of "inorganic" elements: Na, K, Ca, P, …
  - ✓ Associated with mineral matter in the precursor and with the reactants used in chemical activation.
  - ✓ Affect the surface chemistry of the porous carbons.

Surface groups in porous carbons

- Oxygen in surface functional groups influences most of the properties of porous carbons.

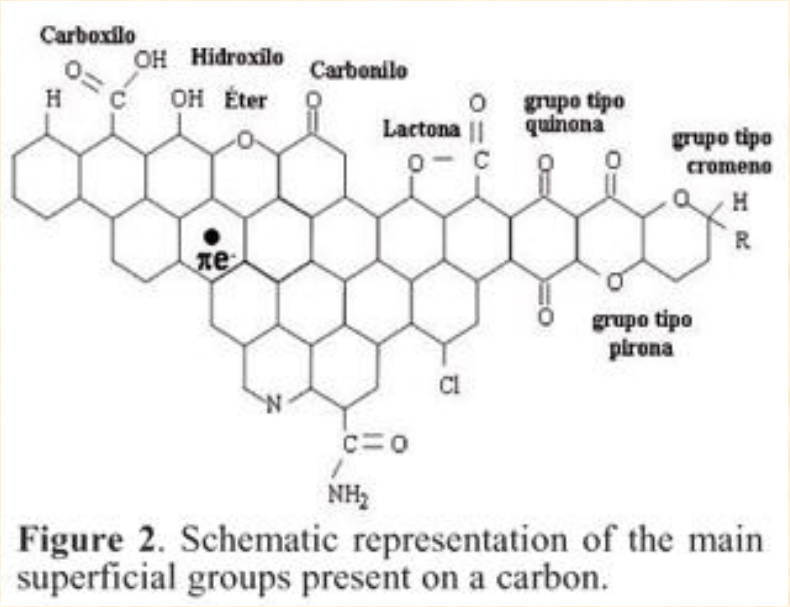
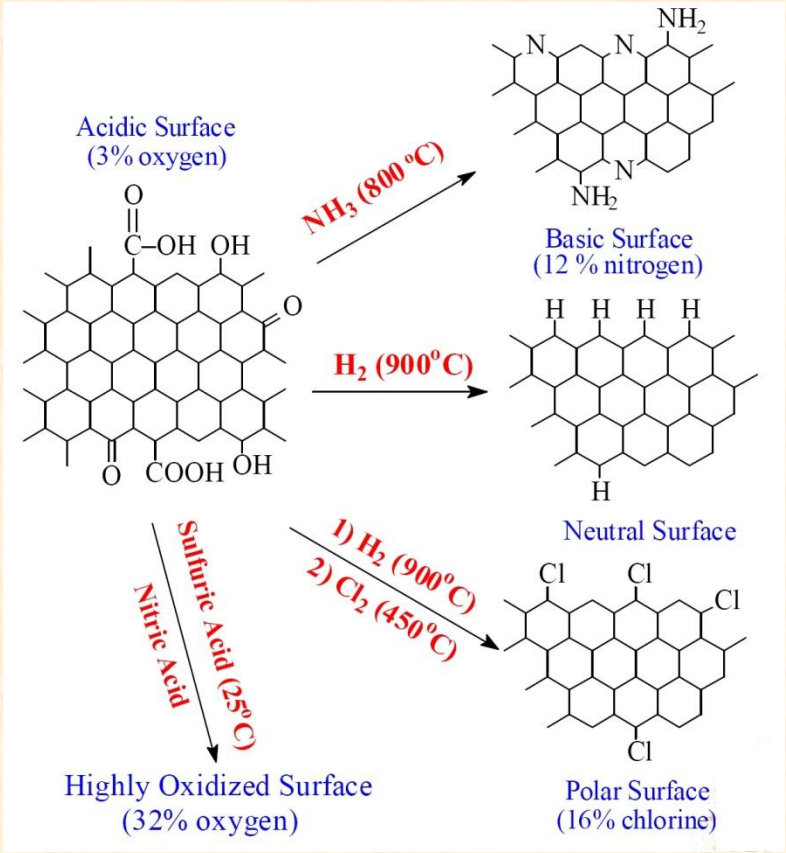


Figure 2. Schematic representation of the main superficial groups present on a carbon.

Cárdena-López et al., *Ecl. Quim. 2007;*32:61

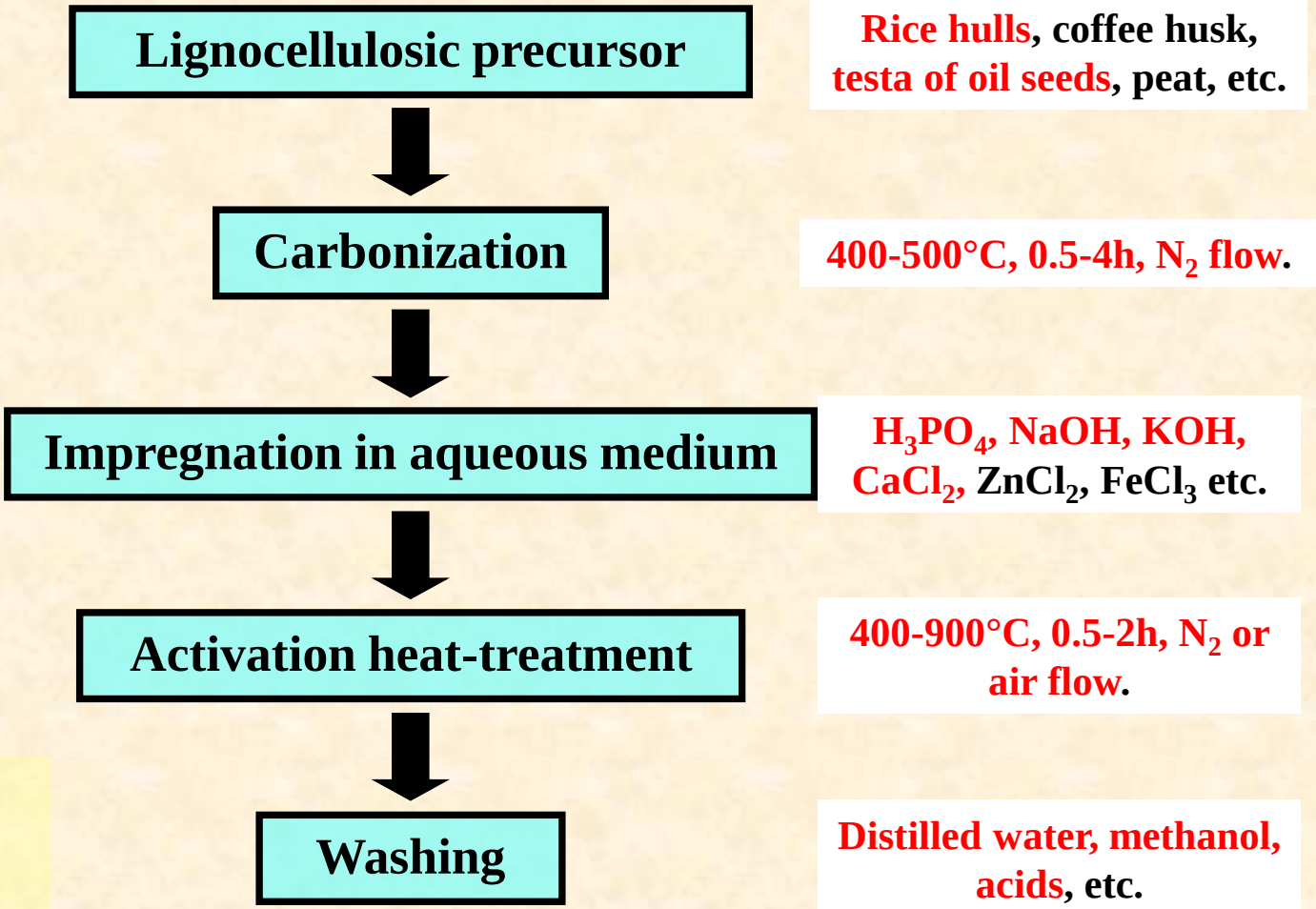


http://economy.matse.illinois.edu/figure/Economy-ACS.pdf

Surface groups in porous carbons

- Characterization methods: Titration, FT-IR, XPS, TPD, NMR, etc.
- Advantages of solid-state NMR: Boehm, *Carbon* 2002;40:145
  - ✓ Non-destructiveness.
  - ✓ Element-selective technique.
  - ✓ Sensitiveness to chemical environment and to structural features around the nuclear site.
- Main drawback:
  - ✓ Little sensitiveness to nuclei in surface groups.

Synthesis of the AC samples



Porous carbon material

Characterization:

- Elemental analysis.
- Thermal analysis.
- N_2 sorption.
- SEM, XRD.
- Solid-state NMR

  ^{13}C, ^{23}Na, ^{29}Si, ^{31}P, ^{39}K, ...

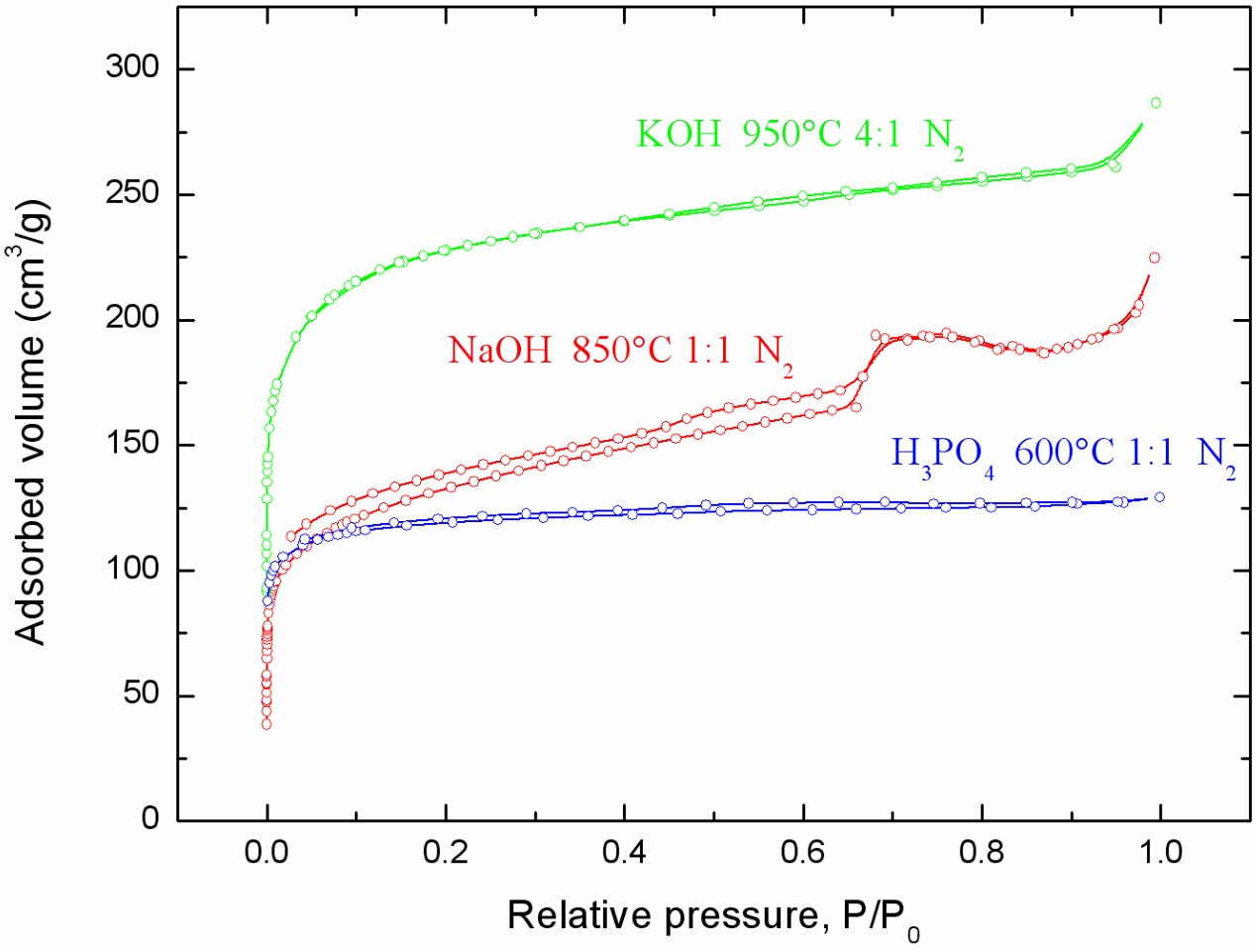
Properties of the AC samples

H_3PO_4-activated carbons (testa of oil seeds):

Label	Precursor	Chemical Agent / Wt. Ratio	Temp. / Atmosphere	Washing	SSA m^2/g	C wt. %	H wt. %	N wt. %	O wt. %	Diff. wt. %
DB1	NOS	None	550°C Closed	Water MeOH	258	82.6	2.4	1.1	13.9	0.1
DB18	NOS	H_3PO_4 1:1	500°C N_2	Water MeOH	341	74.3	2.9	1.1	19.4	2.4
DB19	NOS	H_3PO_4 1:1	600°C N_2	Water MeOH	399	69.7	2.7	1.1	23.0	3.6
DB20	NOS	H_3PO_4 1:1	700°C N_2	Water MeOH	434	70.5	2.7	1.0	22.3	3.5
DB21	NOS	H_3PO_4 1:1	800°C N_2	Water MeOH	1022	63.6	3.4	0.8	28.7	3.5

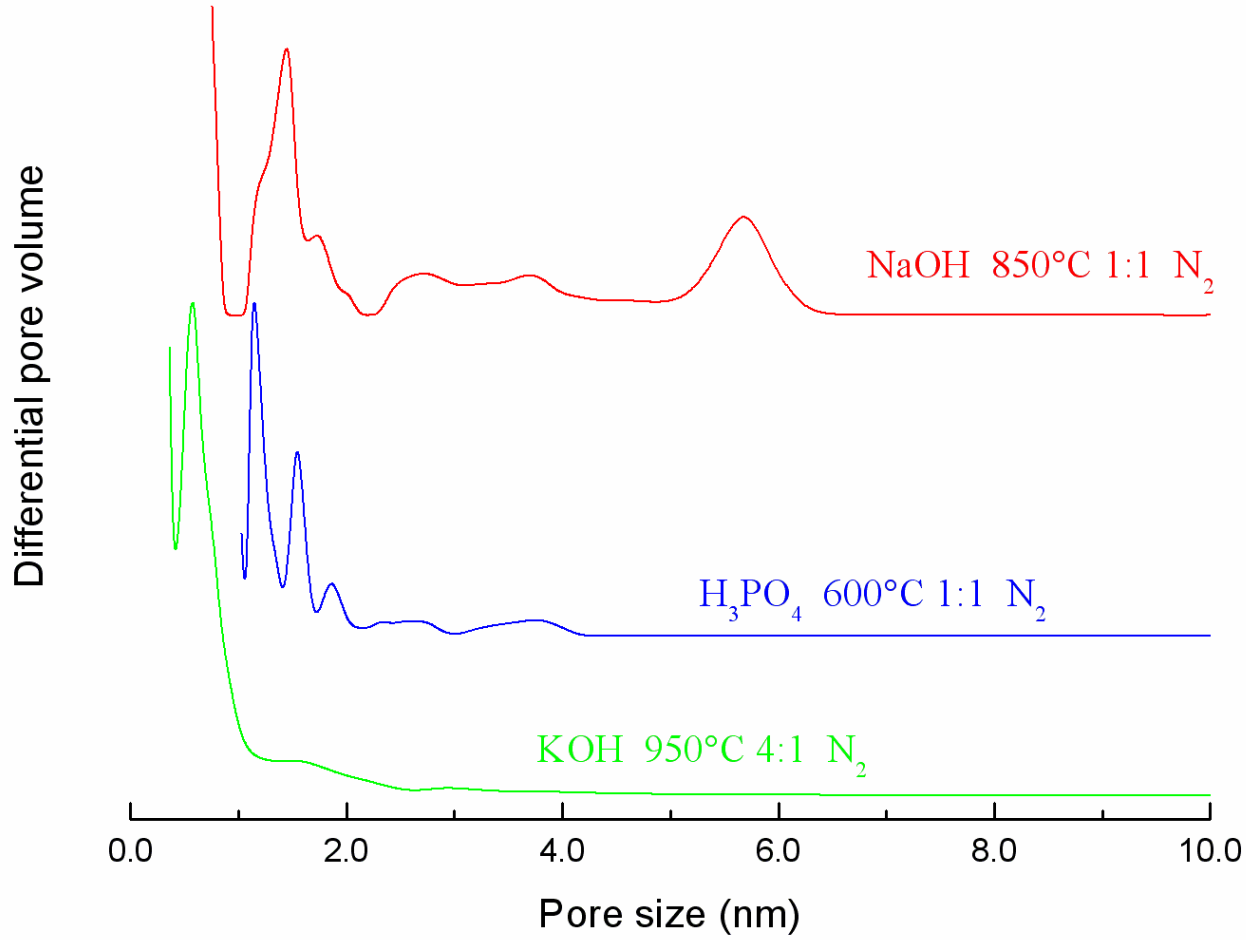
Textural analysis

N_2 sorption isotherms (77 K) – AC from testa of oil seeds



Textural analysis

Pore size distributions (NLDFT) – AC from testa of oil seeds

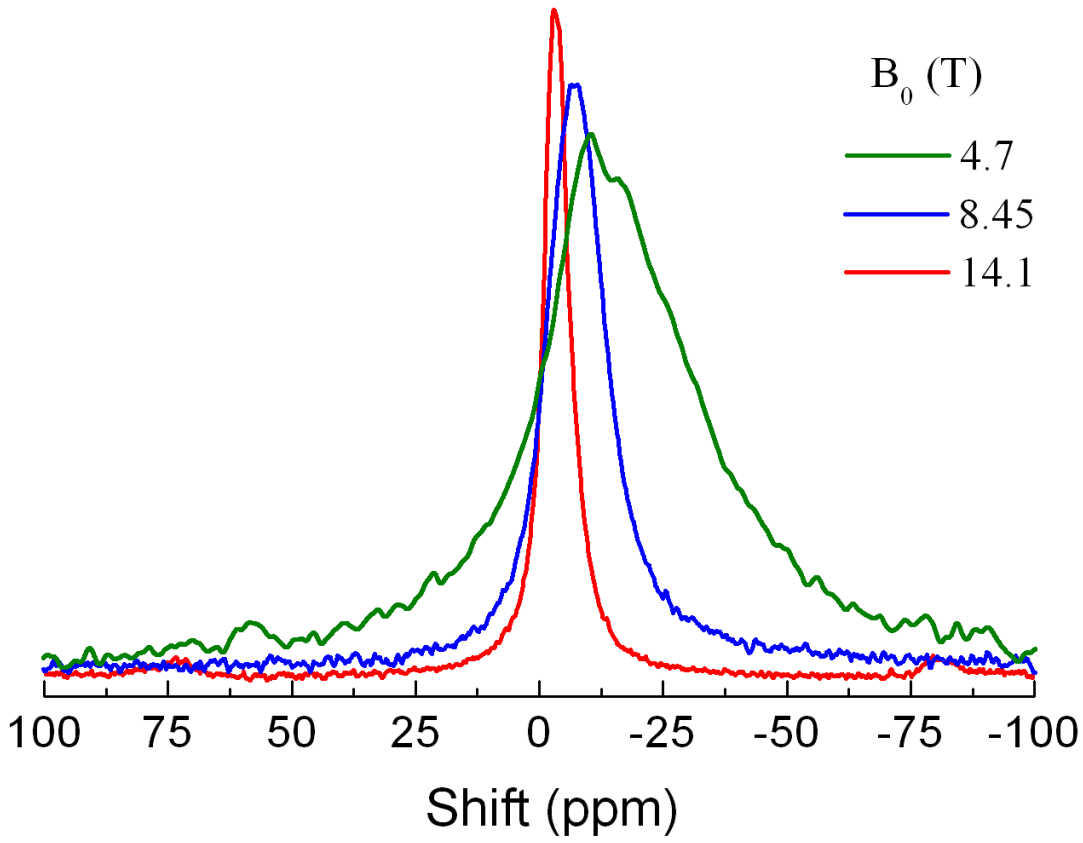


^{23}Na NMR results

NaOH activated carbons

(rice hulls)

- Single-pulse experiments.
- MAS at 12 kHz.
- Probes: 4 mm.



Quadrupole effects in MAS NMR spectra

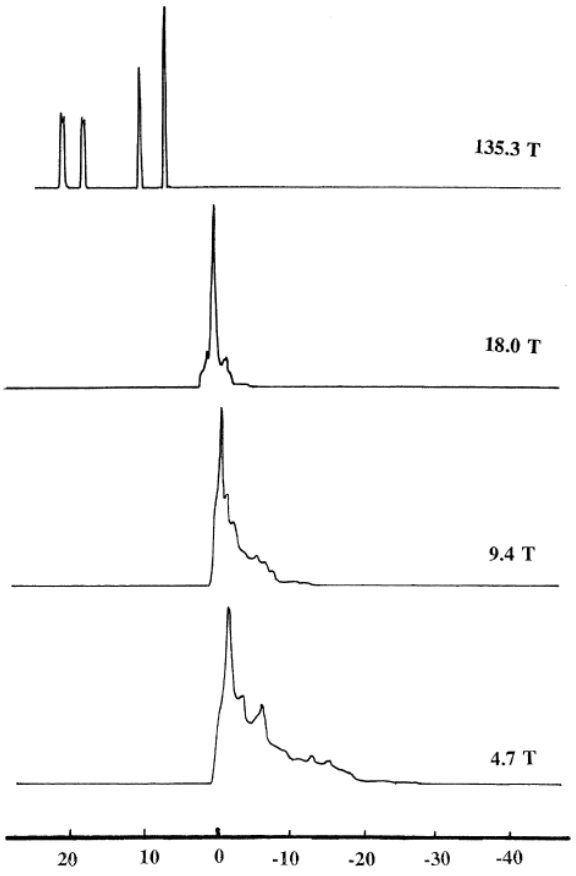


Fig. 7. Simulations of the ^{27}Al MAS centreband of kyanite (Al_2SiO_5) as a function of the applied magnetic field.

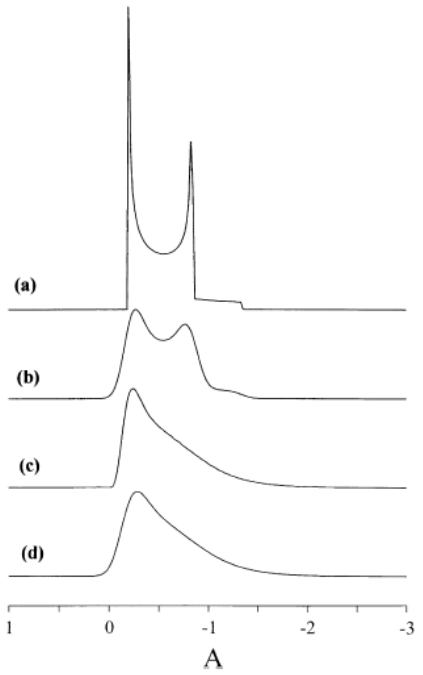


Fig. 14. The effect of a distribution in the isotropic chemical shift and the quadrupole coupling constant on the central transition MAS lineshape. For these simulations the average C_q is 2 MHz, $\eta_q = 0$ and the isotropic chemical is 0 ppm. The Larmor frequency is 80 MHz so $A = 2343.8$ Hz. (a) No distribution, (b) Gaussian distribution of the isotropic chemical shift of FWHM = 400 Hz (5 ppm) or 0.17 A, (c) Gaussian distribution of FWHM = 0.8 MHz and (d) Gaussian distribution of both the isotropic chemical shift and C_q which are the same as in (b) and (c). ($A = (I(I+1) - 3/4)\nu_q^2/\nu_0$).

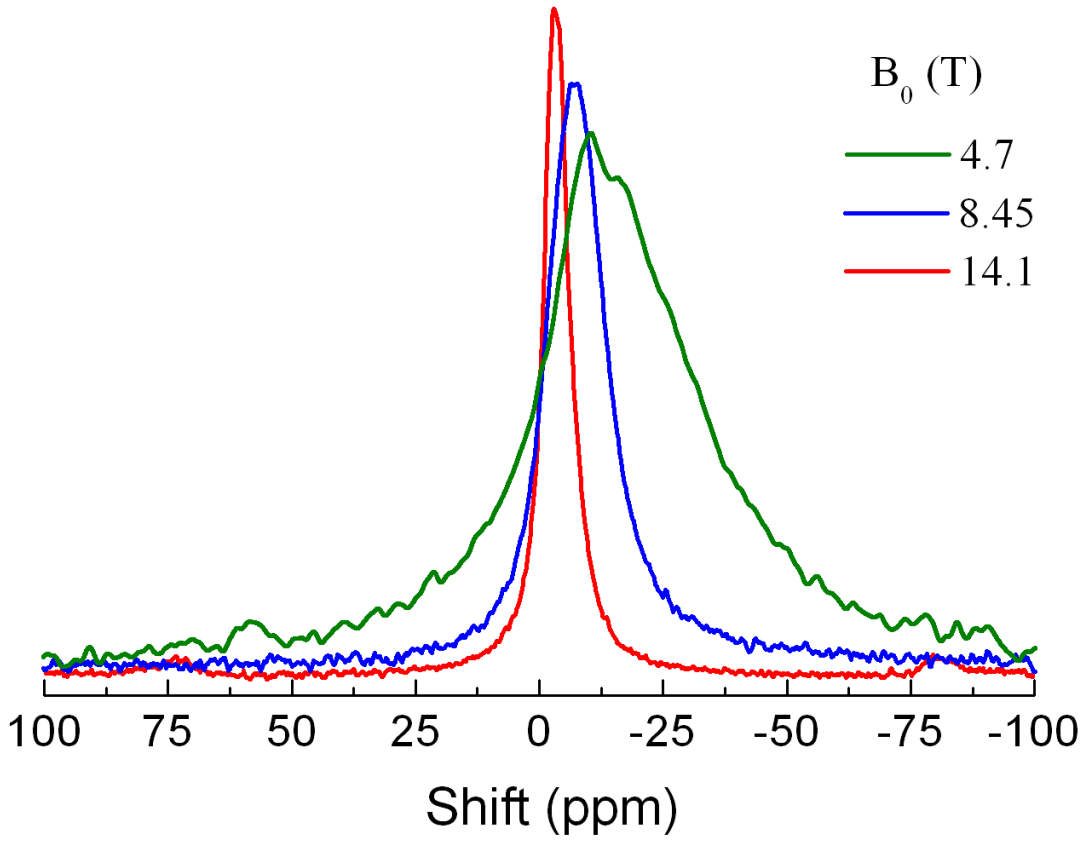
Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

^{23}Na NMR results

NaOH activated carbons

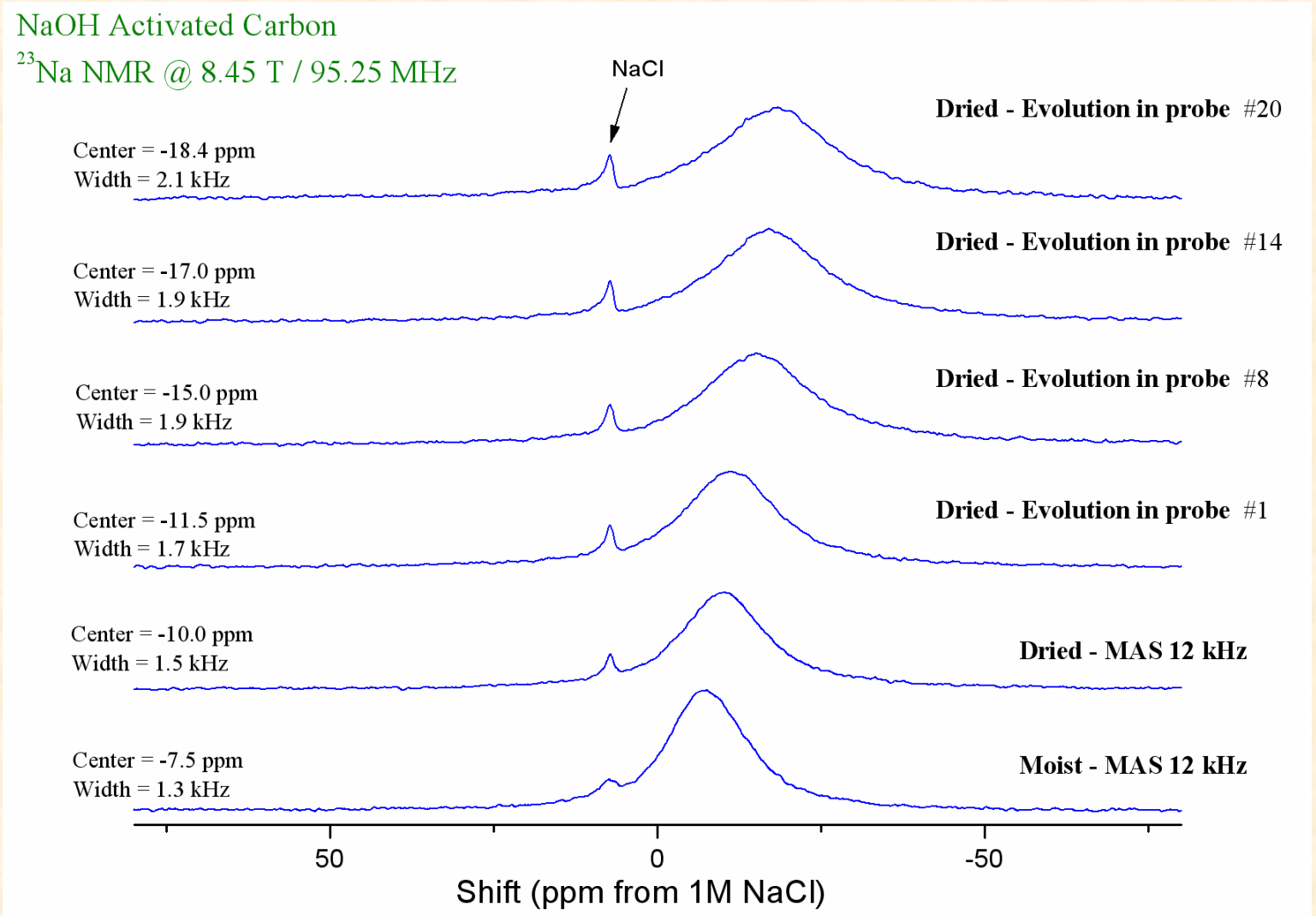
(rice hulls)

- Single-pulse experiments.
- MAS at 12 kHz.
- Probes: 4 mm.



Disordered materials: no quadrupolar features directly observed.

^{23}Na NMR results

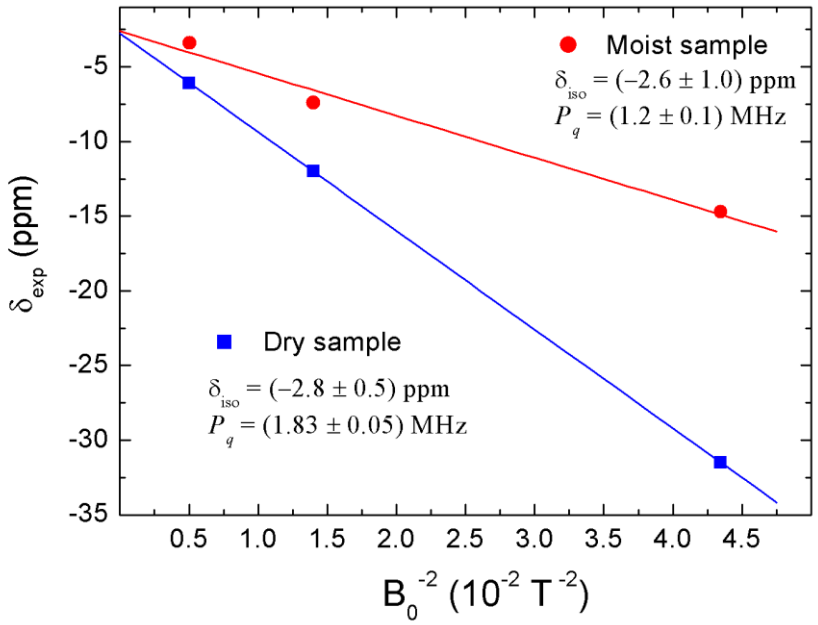


Spectra change as a function of experiment time – effects of drying.

^{23}Na NMR results

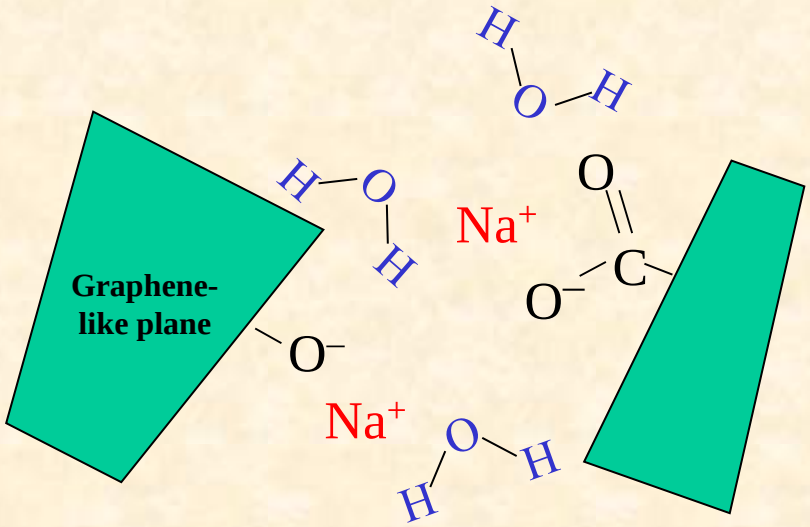
NaOH activated carbons

(rice hulls)



Freitas et al., *SSNMR* 2007;32:109

- ✓ Isotropic chemical shifts are indicative of the occurrence of oxygenated Na groups.
- ✓ Possible existence of surface groups containing Na-O-C bonds at the edges of aromatic lamellae.
- ✓ Strong effect of hydration on quadrupolar coupling.

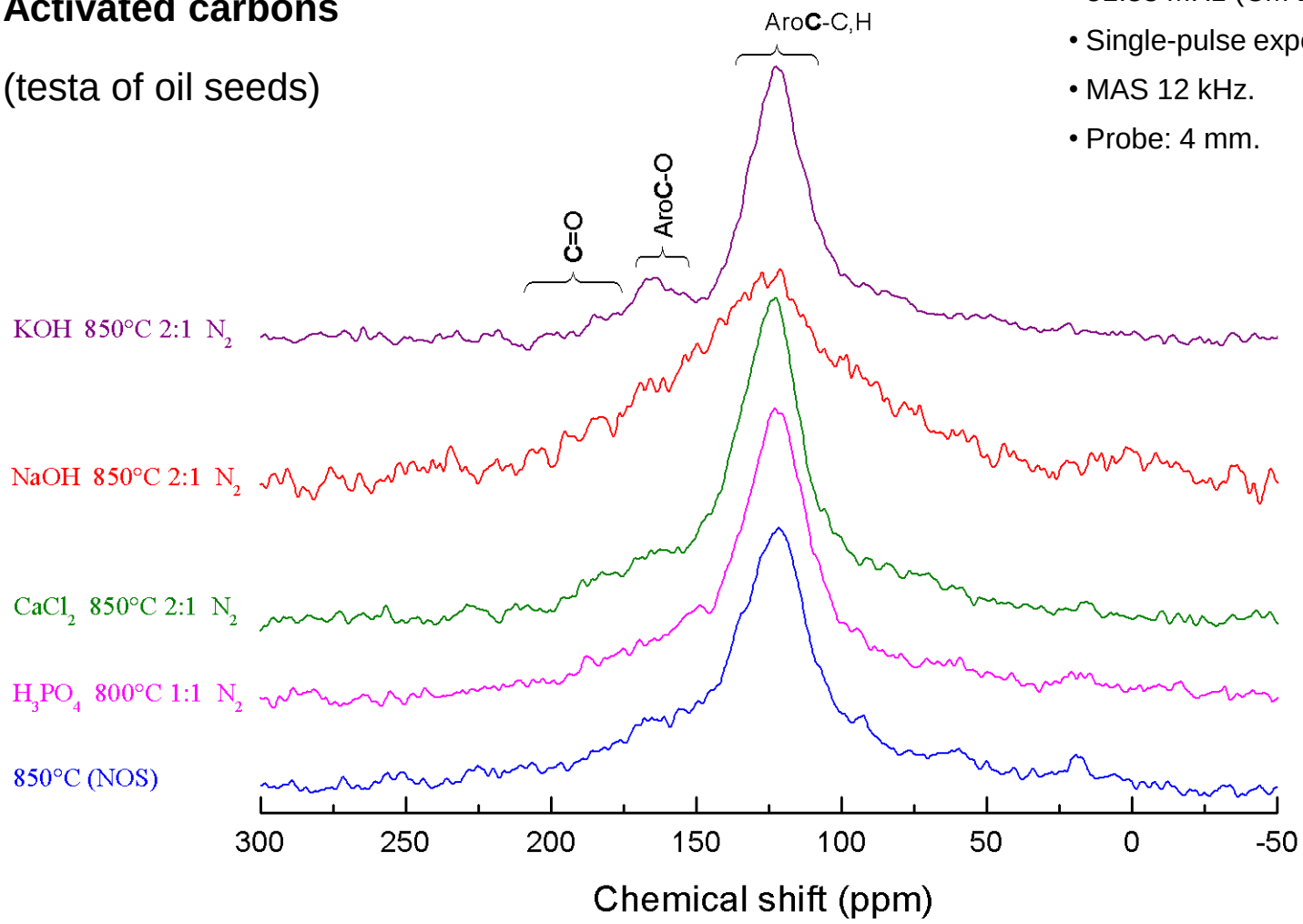


^{13}C NMR results

Activated carbons

(testa of oil seeds)

- 51.38 MHz (CM 200).
- Single-pulse experiments.
- MAS 12 kHz.
- Probe: 4 mm.

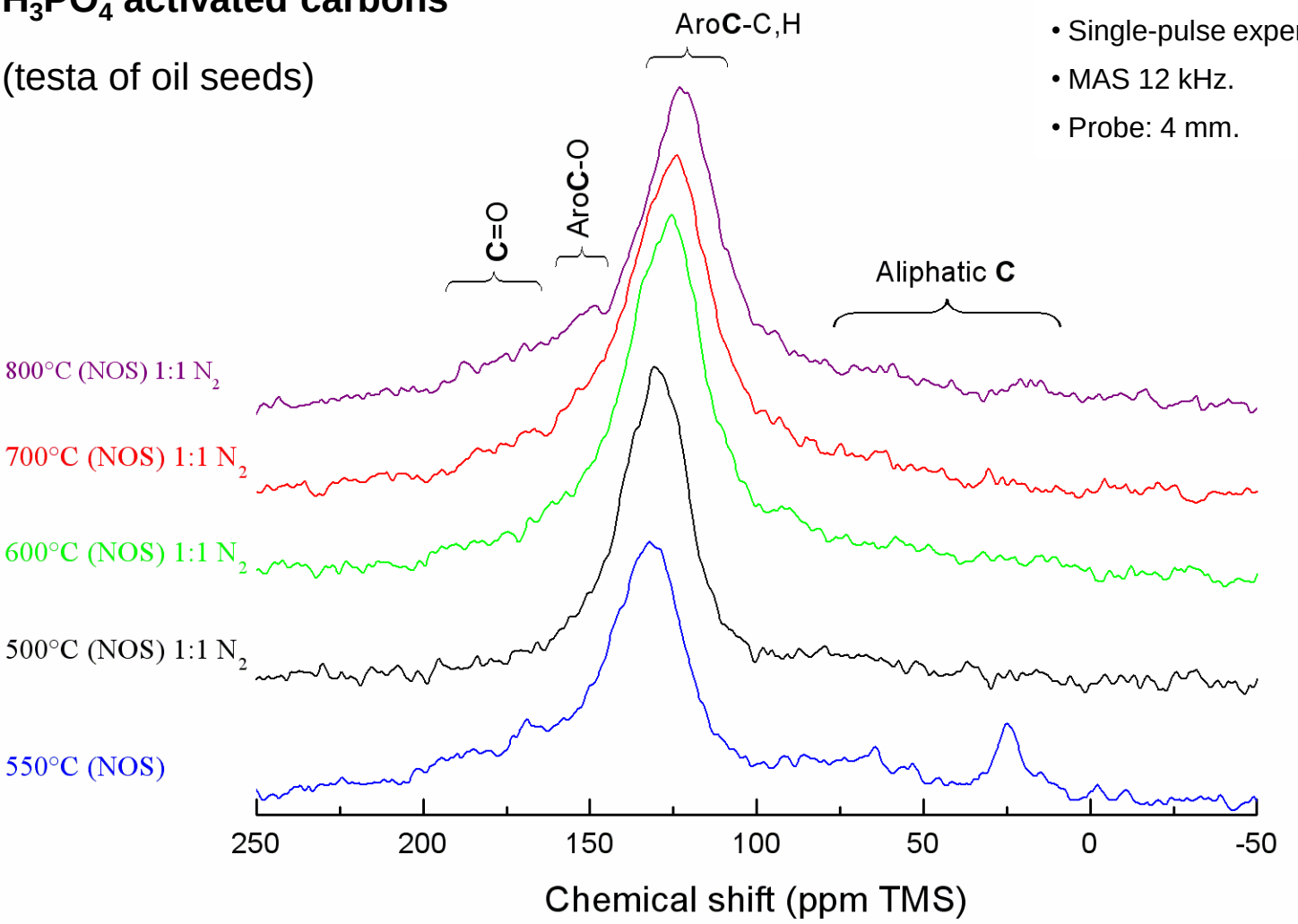


^{13}C NMR results

H_3PO_4 activated carbons

(testa of oil seeds)

- 51.38 MHz (CM 200).
- Single-pulse experiments.
- MAS 12 kHz.
- Probe: 4 mm.

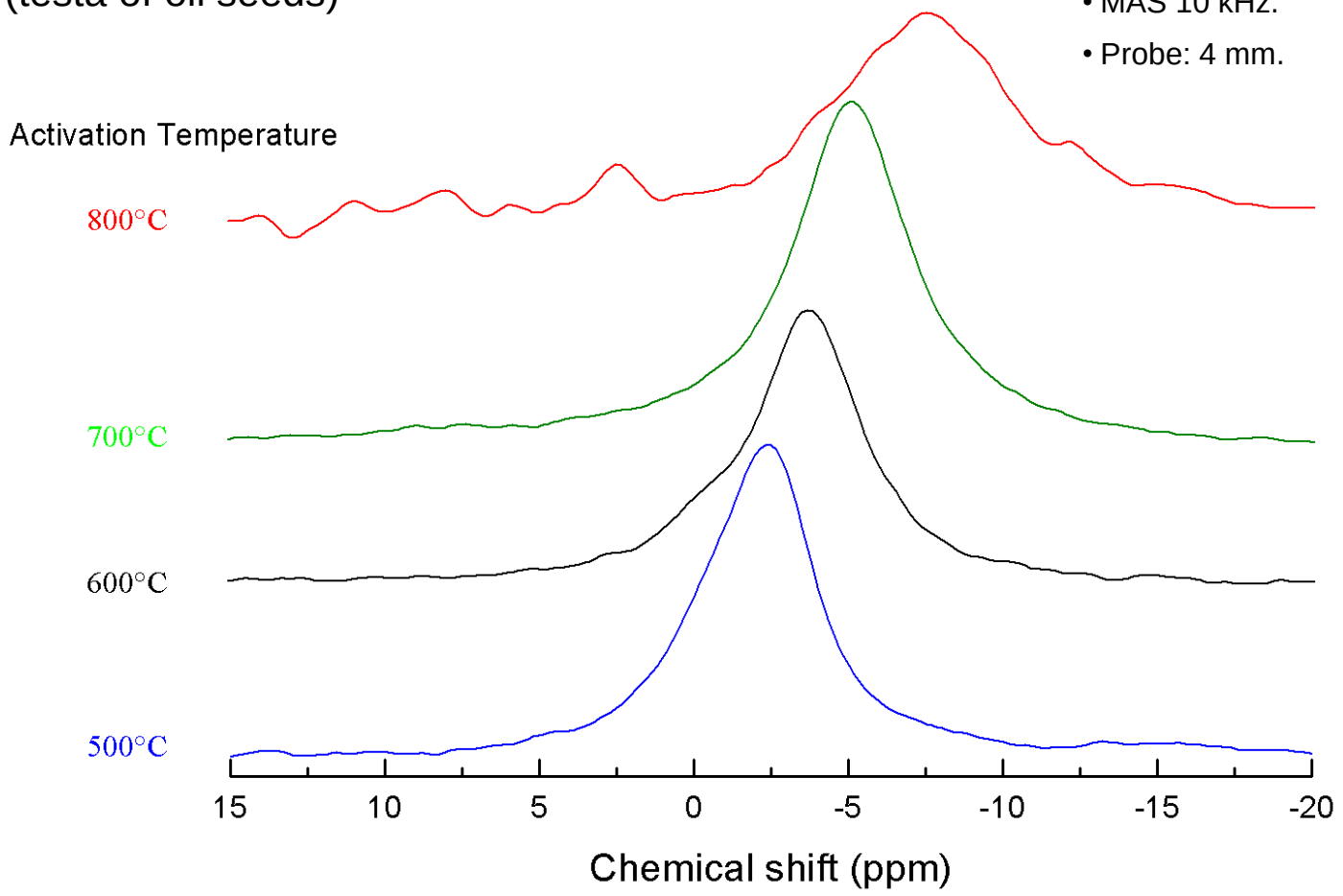


^{31}P NMR results

H_3PO_4 activated carbons

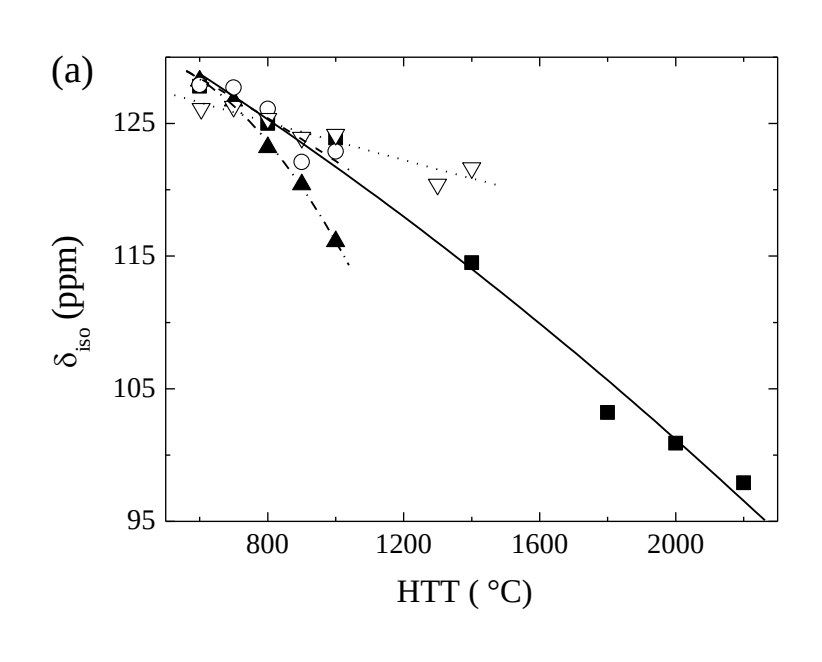
(testa of oil seeds)

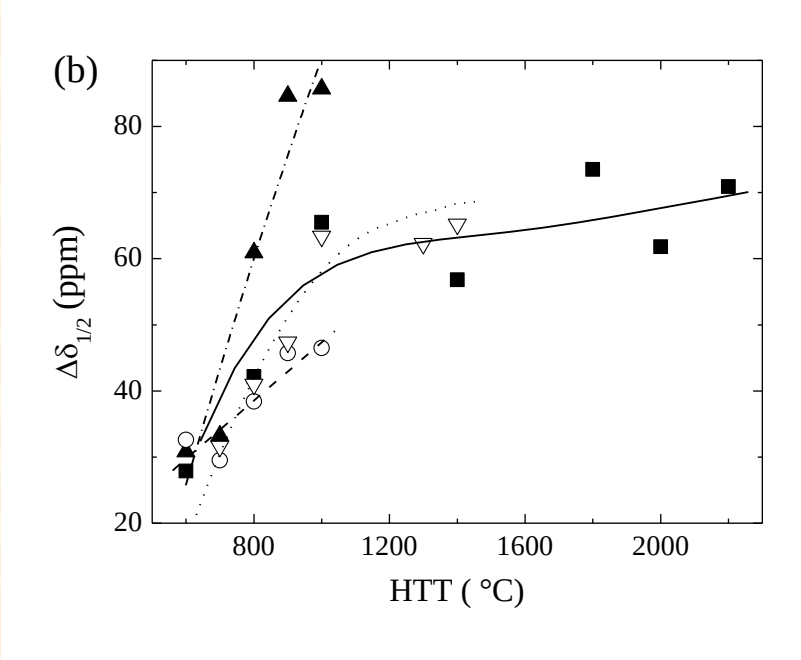
- 145.77 MHz (CM 360).
- Single-pulse experiments.
- MAS 10 kHz.
- Probe: 4 mm.



Effect of heat-treatment temperature

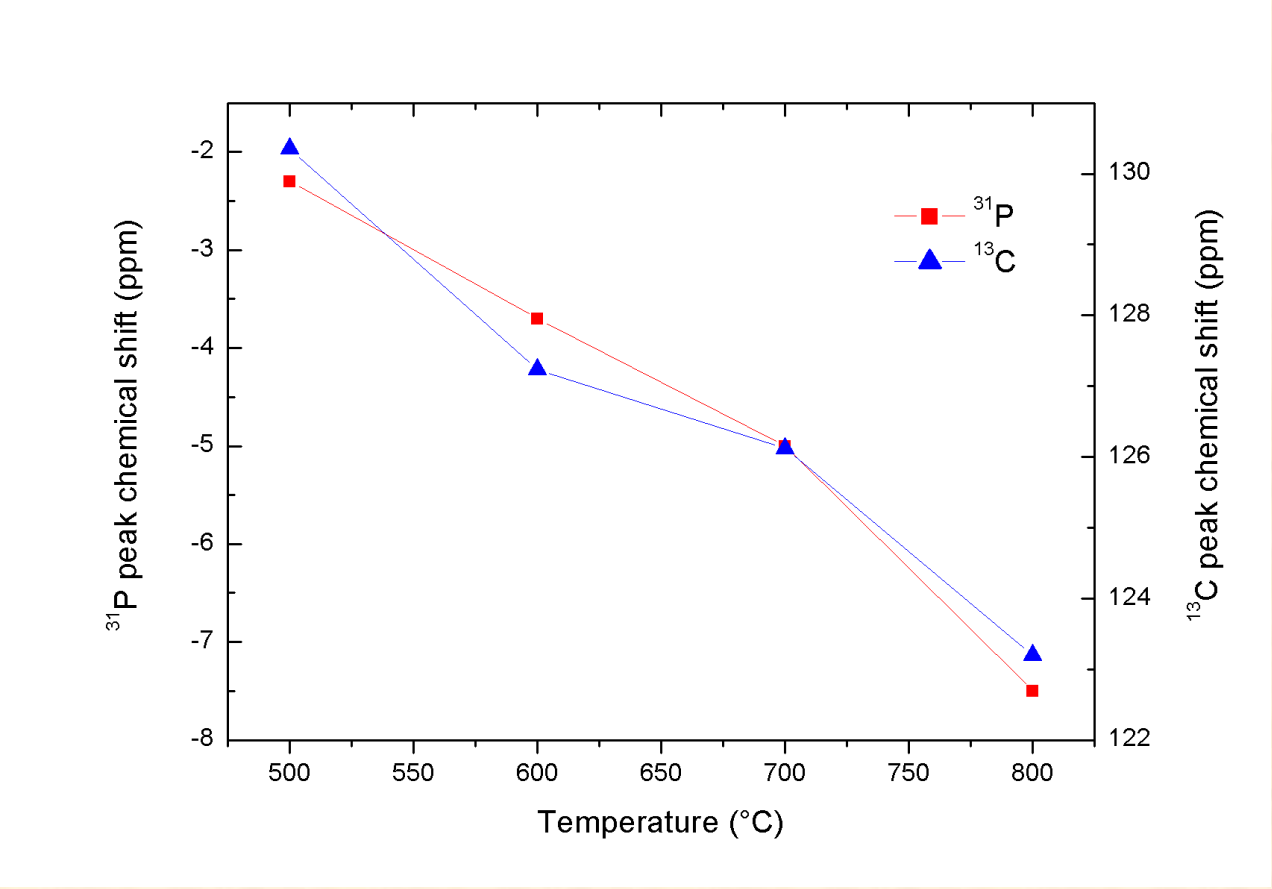
^{13}C NMR spectra of heat-treated carbon materials:





Freitas et al., *SSNMR* 2001;20:61

Effect of heat-treatment temperature



Increase in the locally anisotropic diamagnetic susceptibility associated with the graphene-like planes.

^{13}C NMR in plasma blacks

- Investigation of plasma-derived carbon blacks produced by pyrolysis of natural gas, correlating their physical properties with details of the plasma processes.
- Development of solid-state ^{13}C NMR as an effective method for characterizing the physical and chemical properties of plasma blacks, with support of other techniques (XRD, SEM, TEM, Raman spectroscopy, etc.)

Plasma pyrolysis of methane

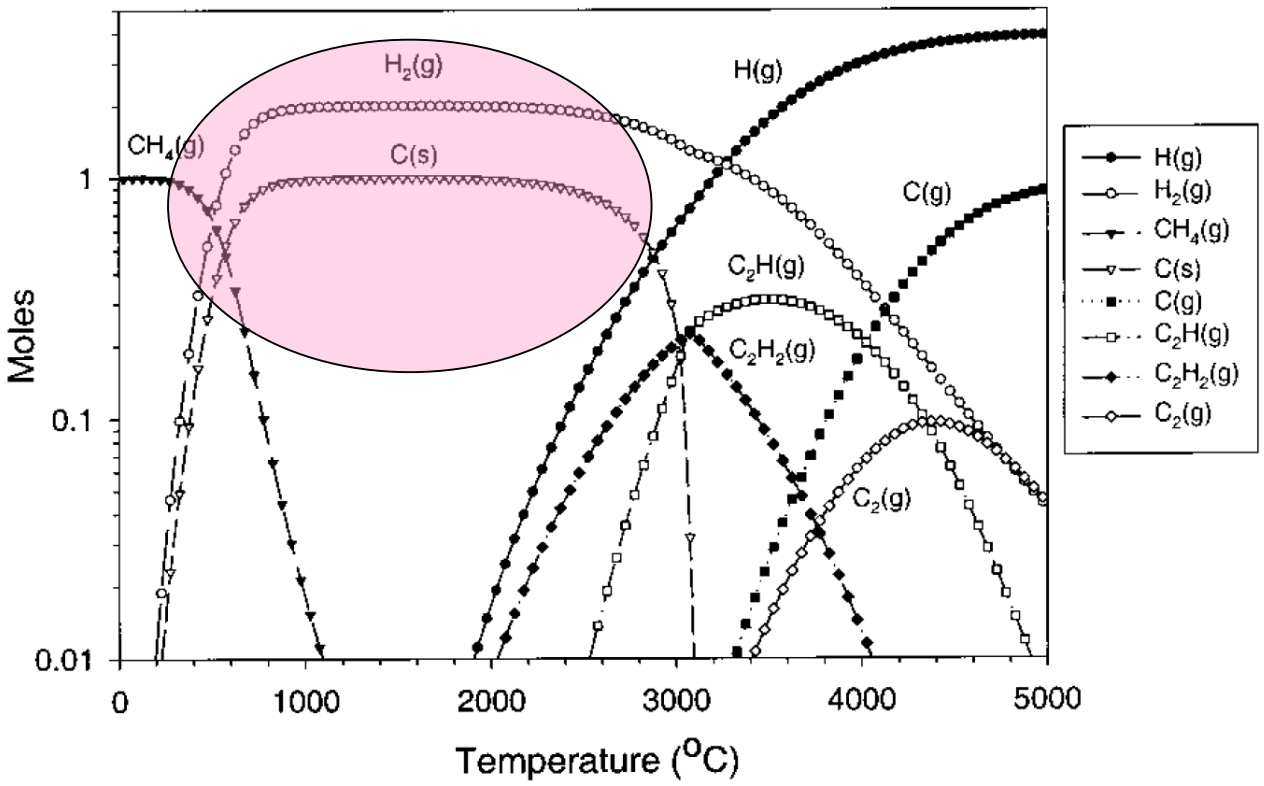


Figure 1. Simplified equilibrium diagram for 1 mol of methane.

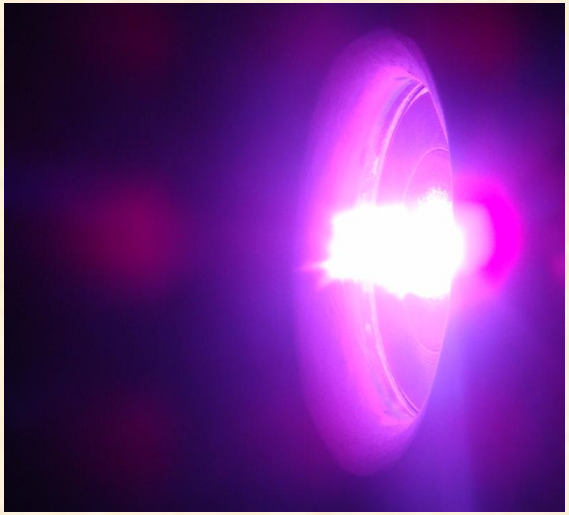
Fincke et al., *Ind. Eng. Chem. Res.* 2002;41:1425-1435

Overall reaction: $CH_4 \rightarrow 2H_2 + C$

Plasma pyrolysis of methane

The Plasma Lab. at UFES / Vitória:

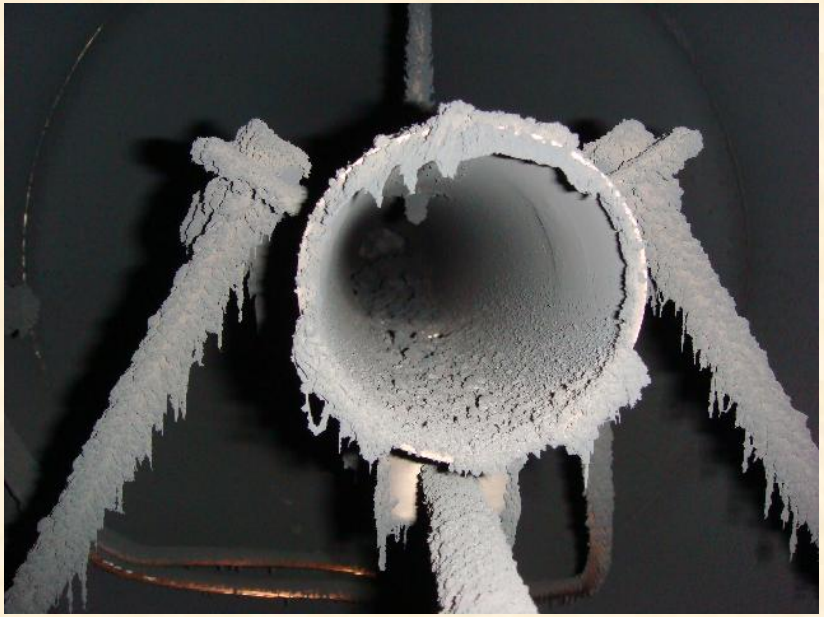
- Production of Hydrogen and carbon blacks from natural gas.
- Different torch and reactor designs.
- Use of different plasma gases:
  - ✓Argon.
  - ✓Nitrogen.
  - ✓Hydrogen.



Details about plasma methods: **Dr. Alfredo Cunha,** alfredo@cce.ufes.br.

Plasma pyrolysis of methane

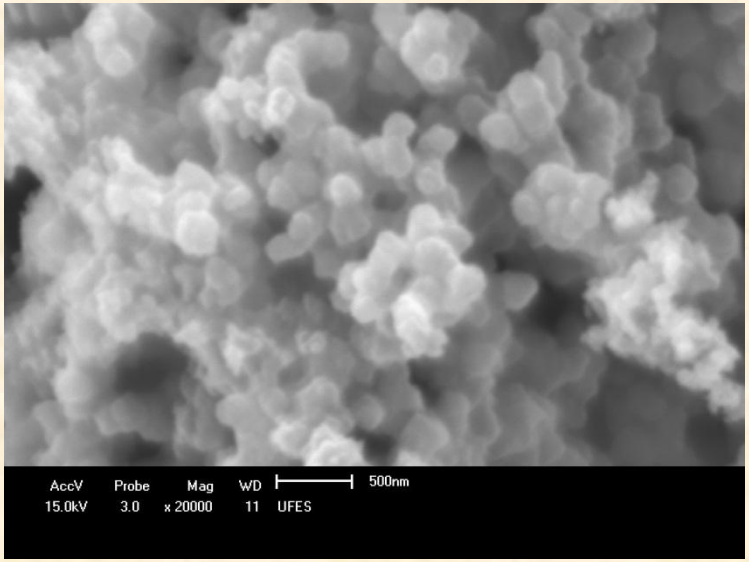
Production of carbon blacks and other solid residues:

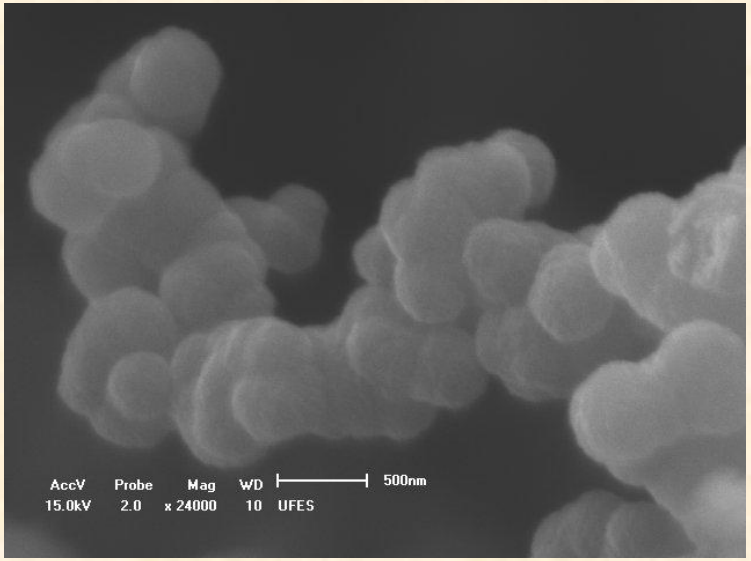


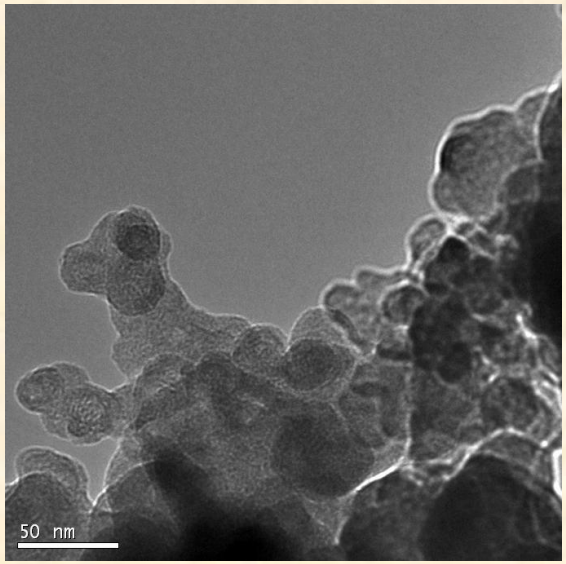
Plasma pyrolysis of methane

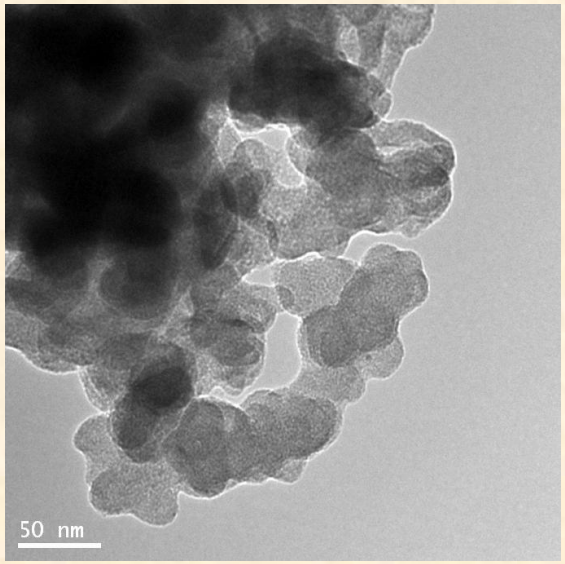
Production of carbon blacks and other solid residues:

SEM and TEM images









Surface groups in carbon blacks

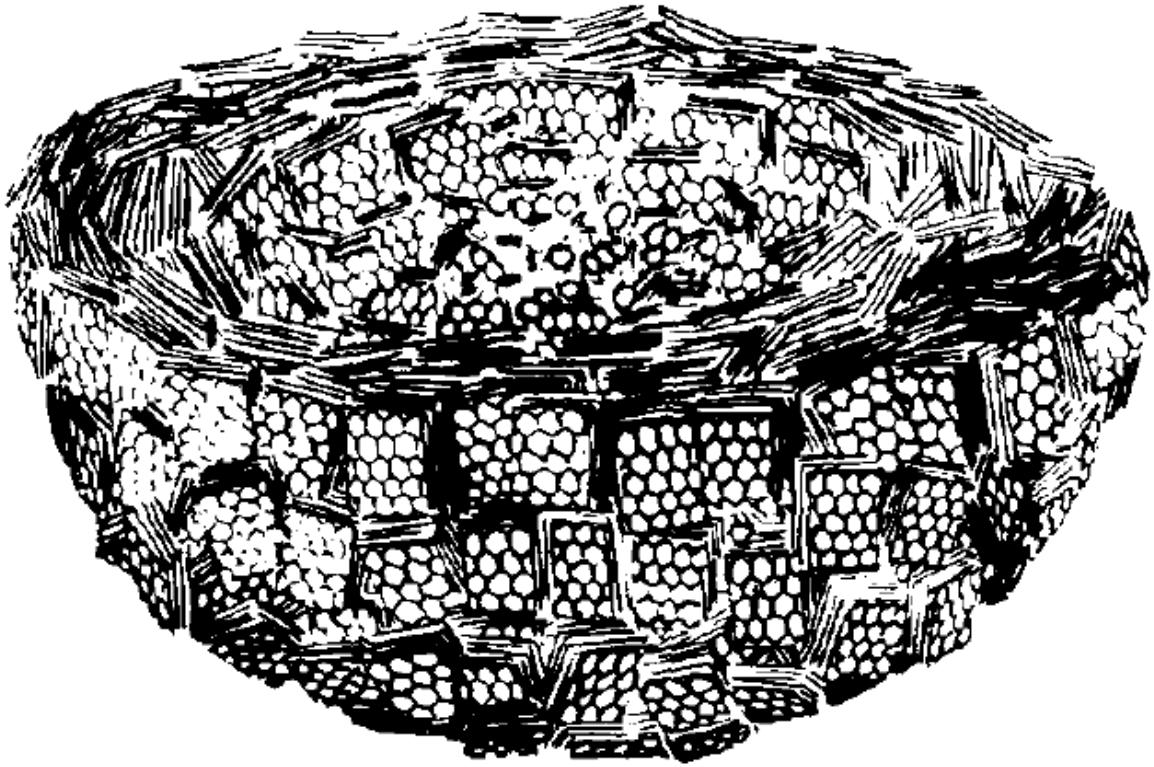


Fig. 15. Microtexture of carbon black according to [19].

Donnet, *Carbon* 1982;20:267-282

Surface groups in carbon blacks

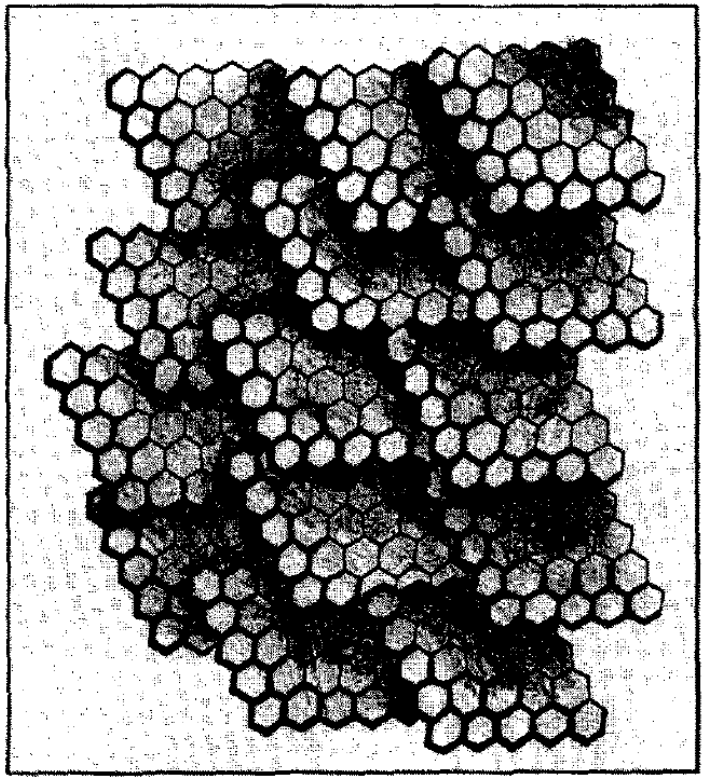


Figure 6. Topview surface model of carbon black particles according to STM observations (small overlapping graphitic layers).

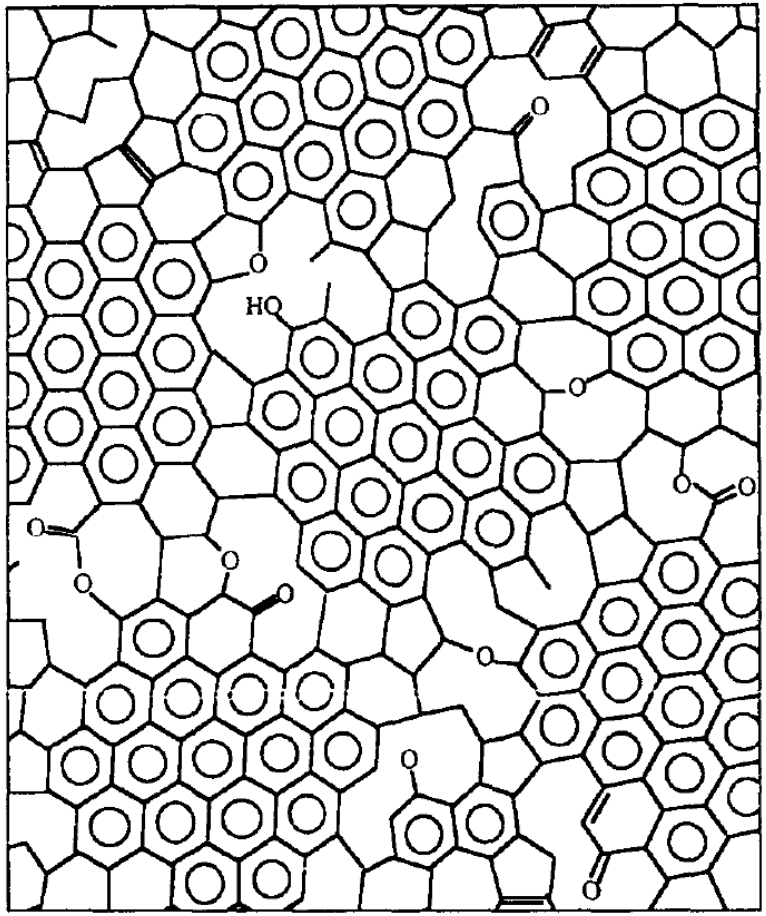


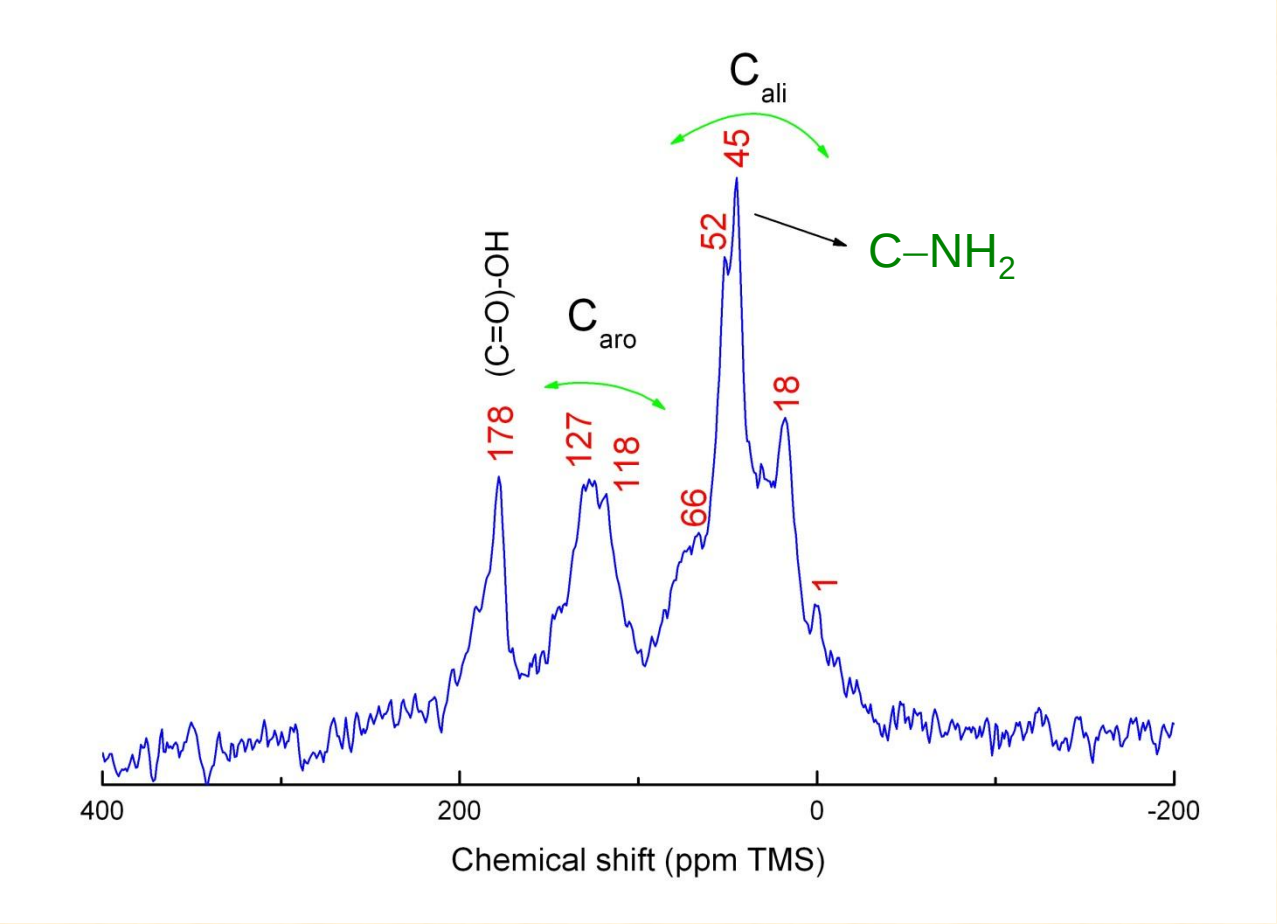
Figure 1. Model surface of particles with ordered zones of small graphitic crystallites and functional groups.

Donnet & Custodero, *Carbon* 1992;30:813-817

Solid-state ^{13}C NMR spectra

Nitrogen plasma black:

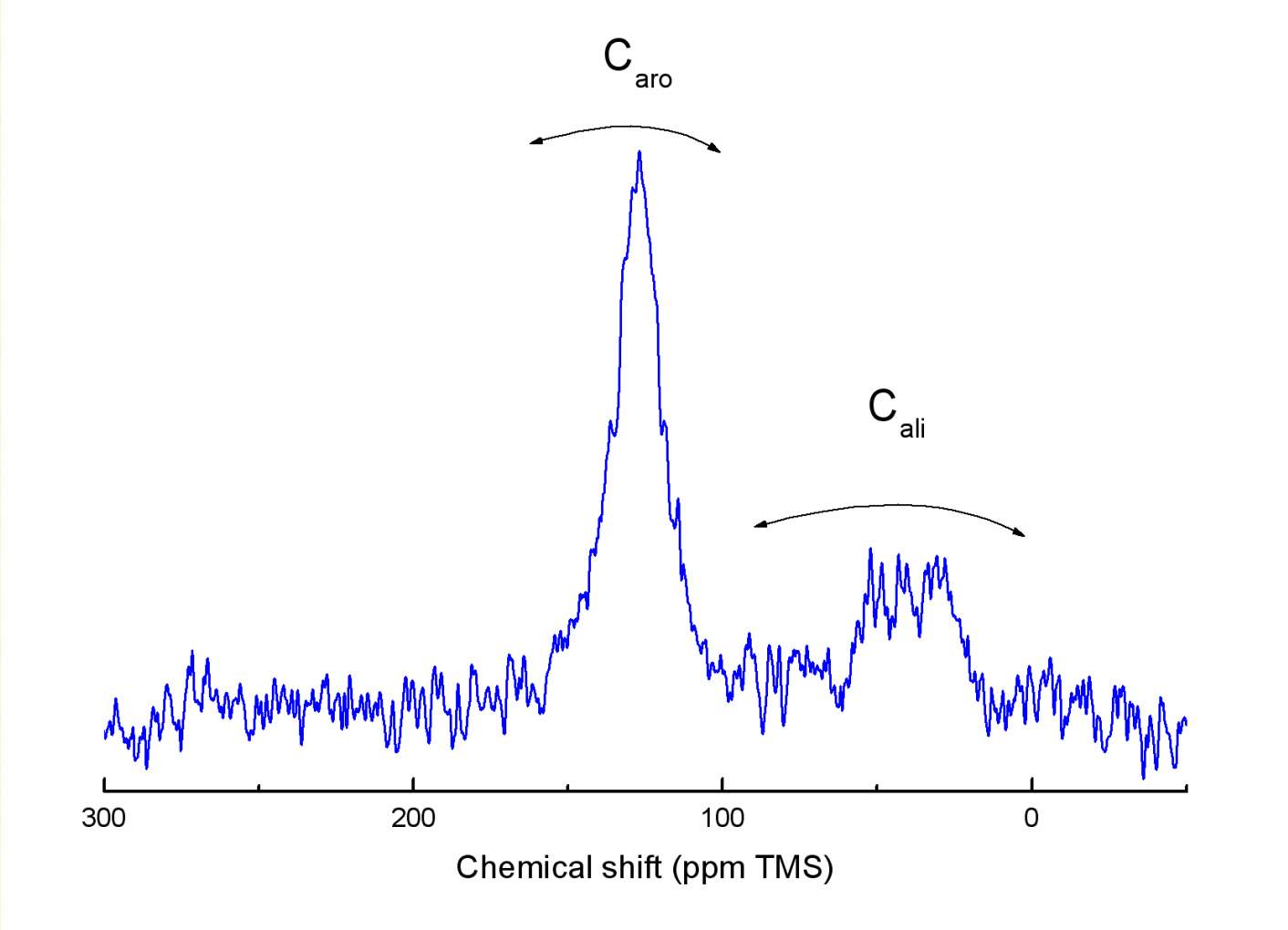
$\{^{1}H \rightarrow {}^{13}C\}$ CP



Solid-state ^{13}C NMR spectra

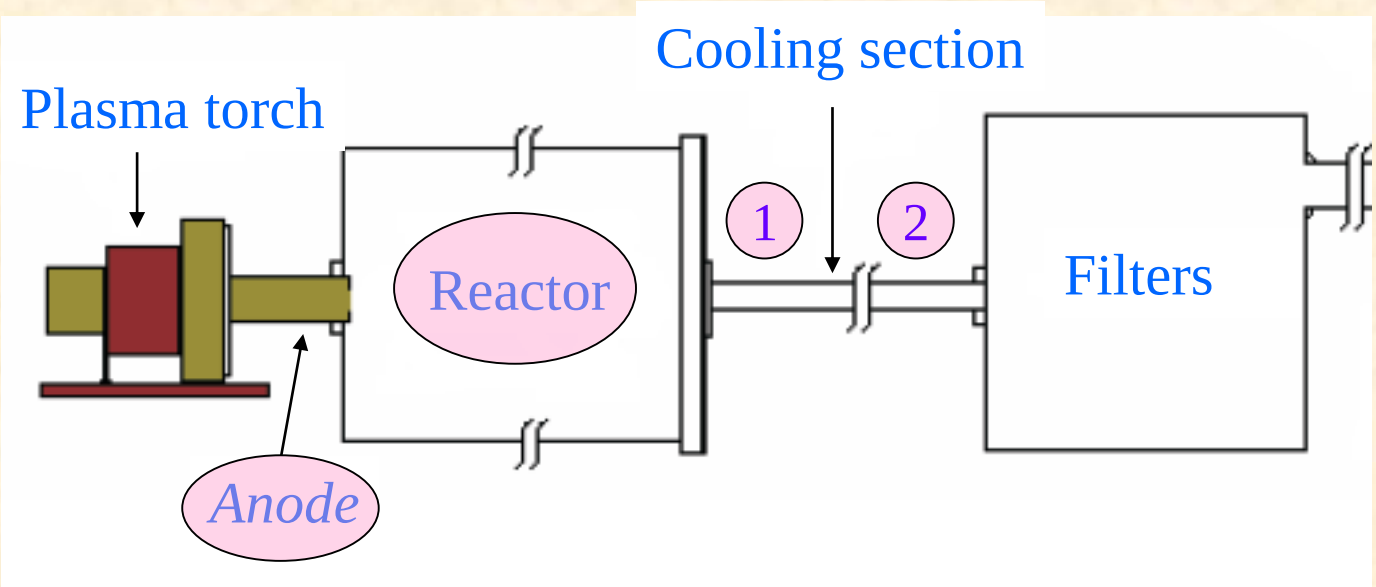
Nitrogen plasma black:

$\{^{1}H \rightarrow {}^{13}C\}$ CP



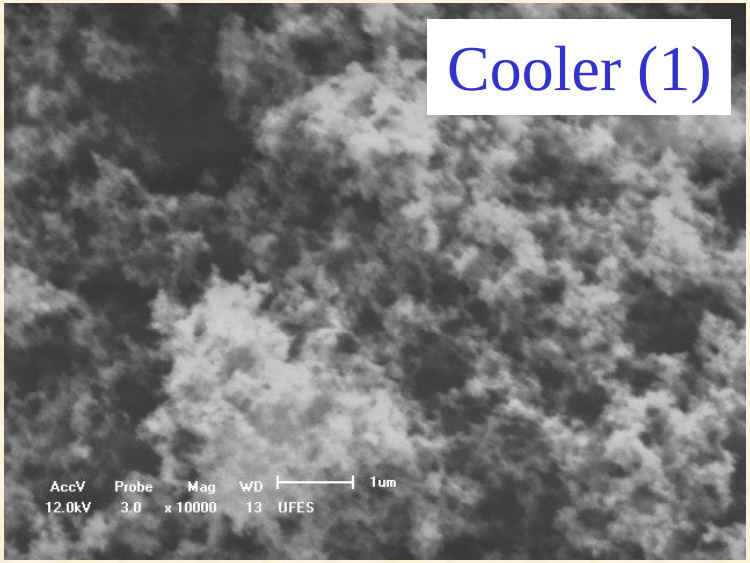
Characterization of plasma blacks

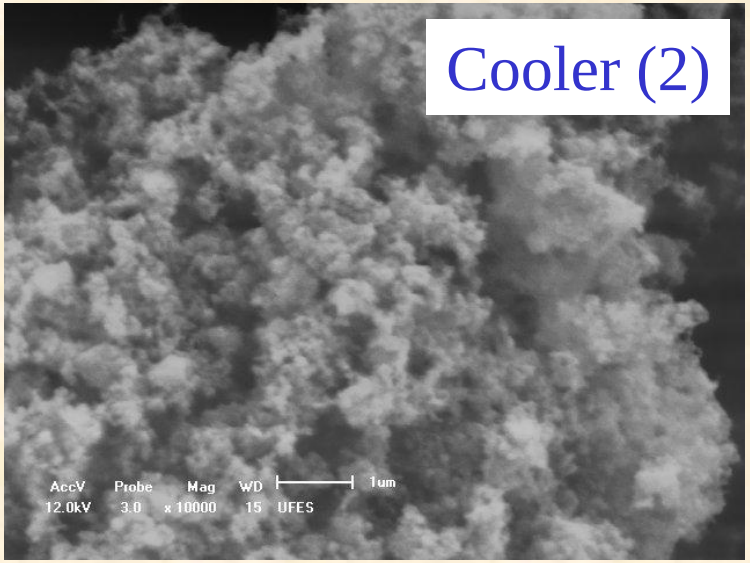
Apparatus:

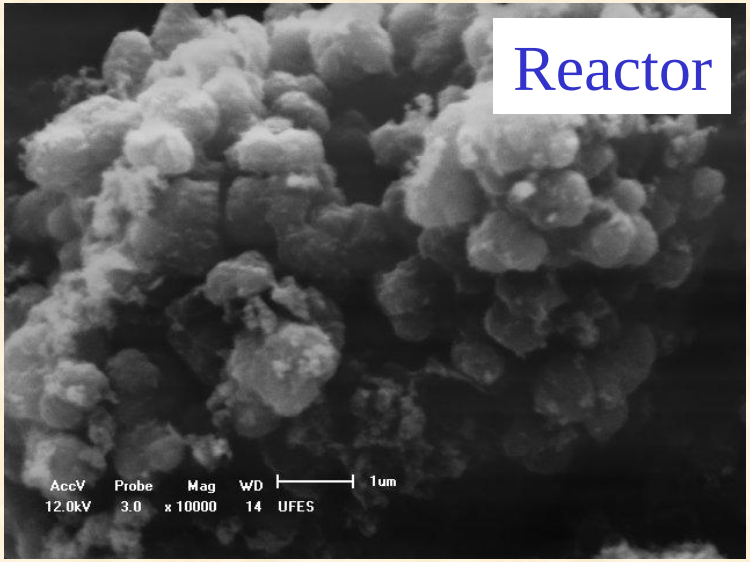


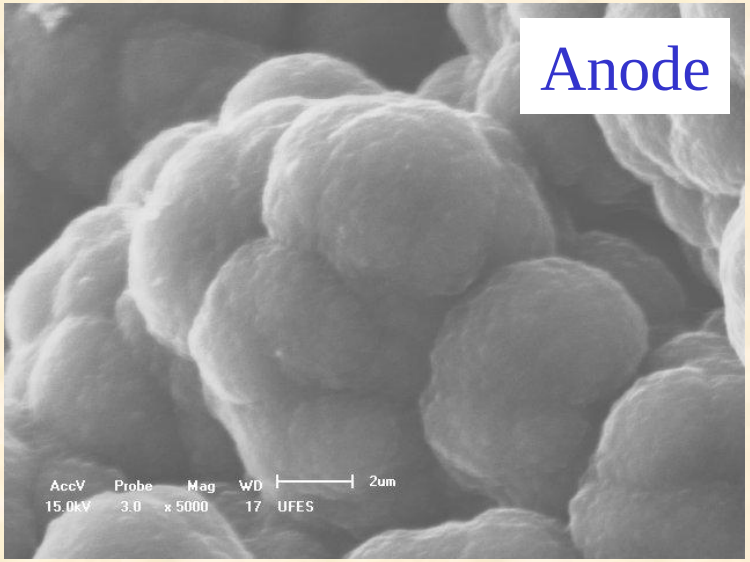
Scanning electron microscopy

Comparison of SEM images – Argon plasma blacks:



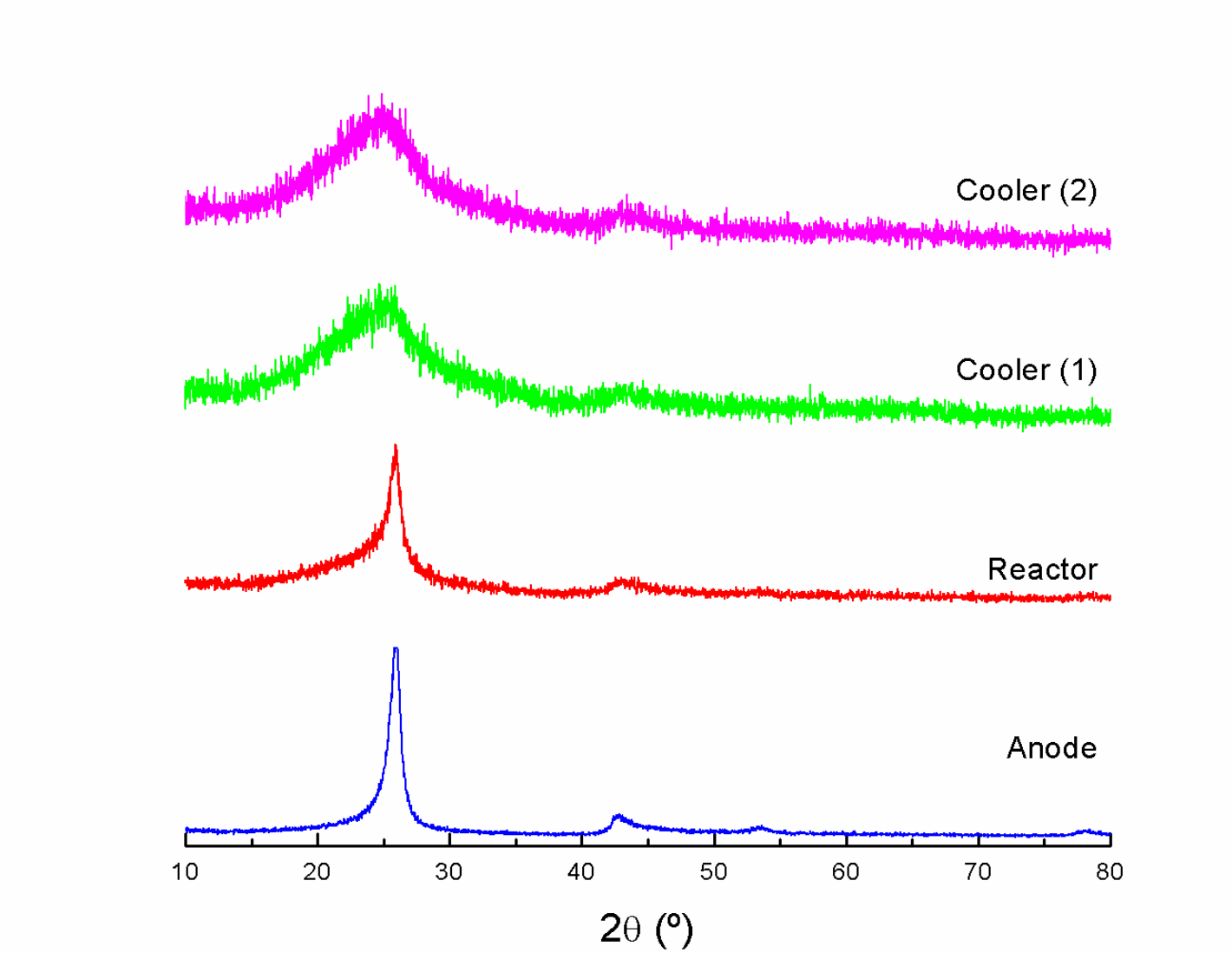






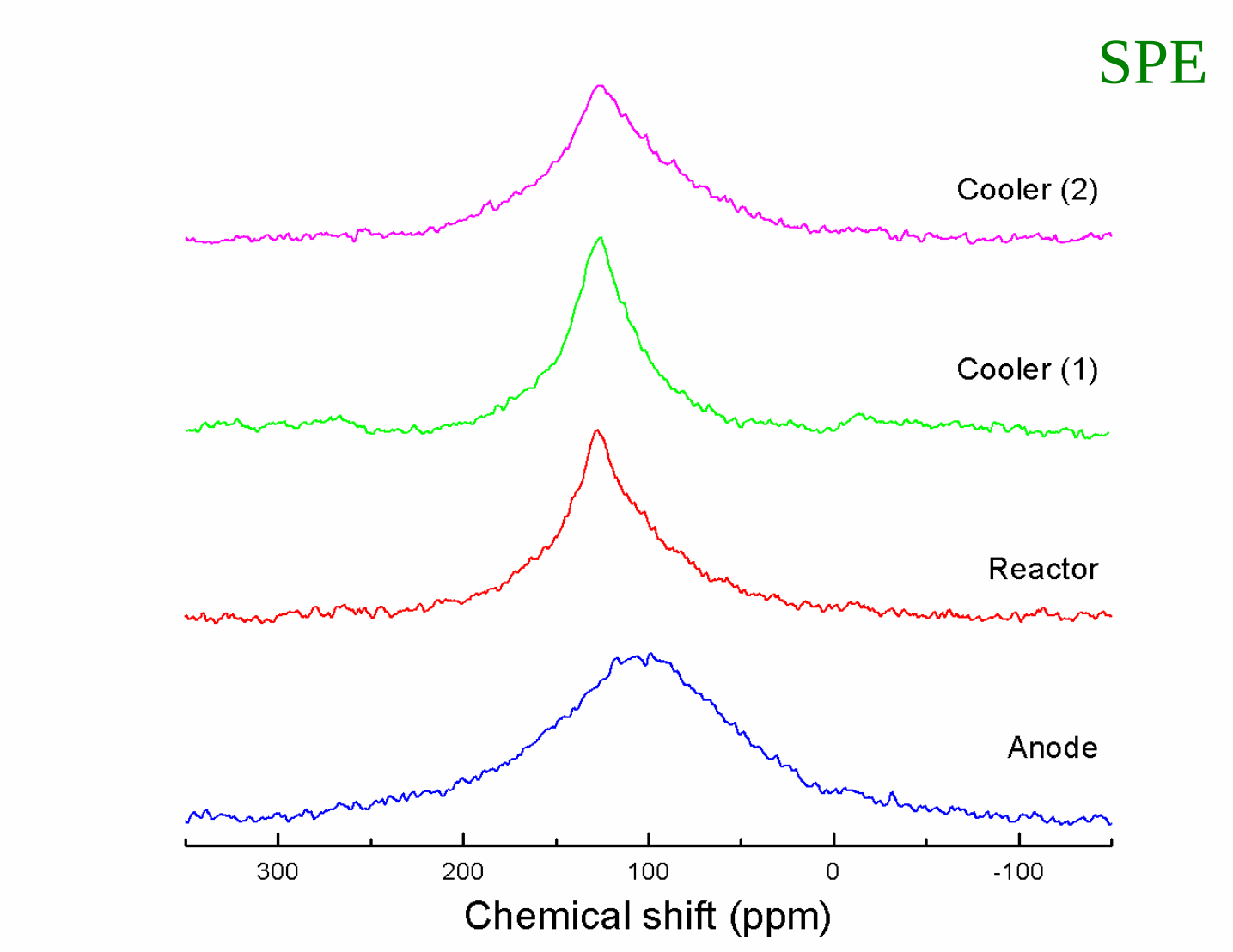
X-ray diffraction

Comparison of X-ray diffractograms – Argon plasma blacks:



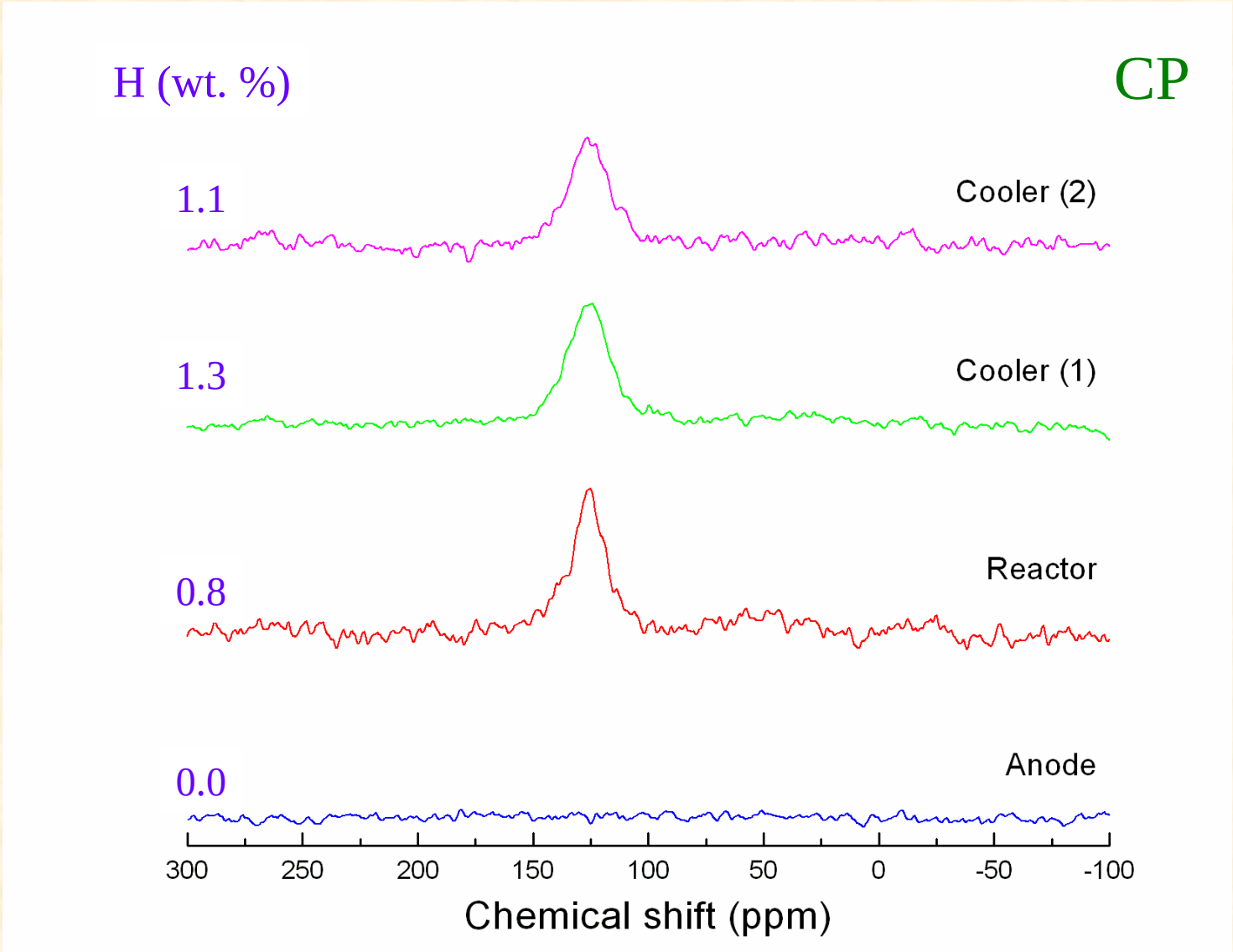
Solid state ^{13}C NMR

Comparison of ^{13}C NMR spectra – Argon plasma blacks:



Solid state ^{13}C NMR

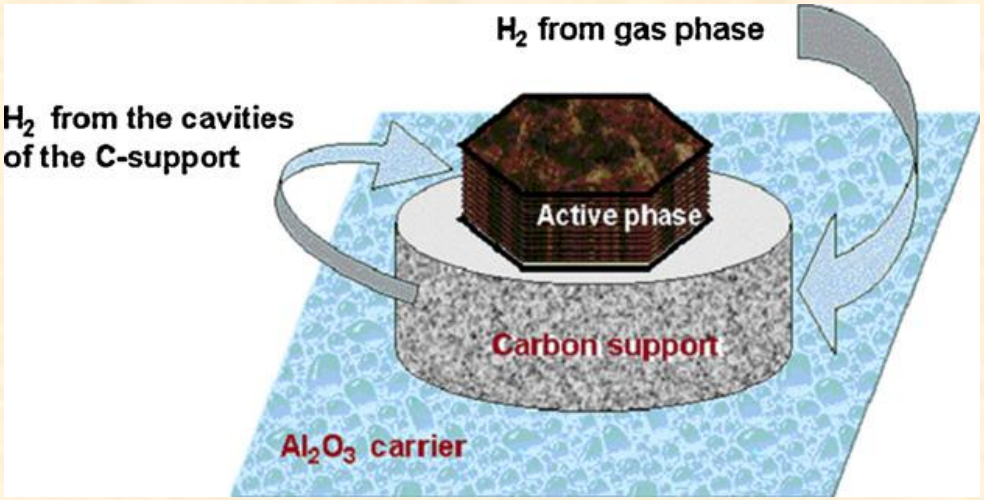
Comparison of ^{13}C NMR spectra – Argon plasma blacks:



Alumina-carbon nanocomposites

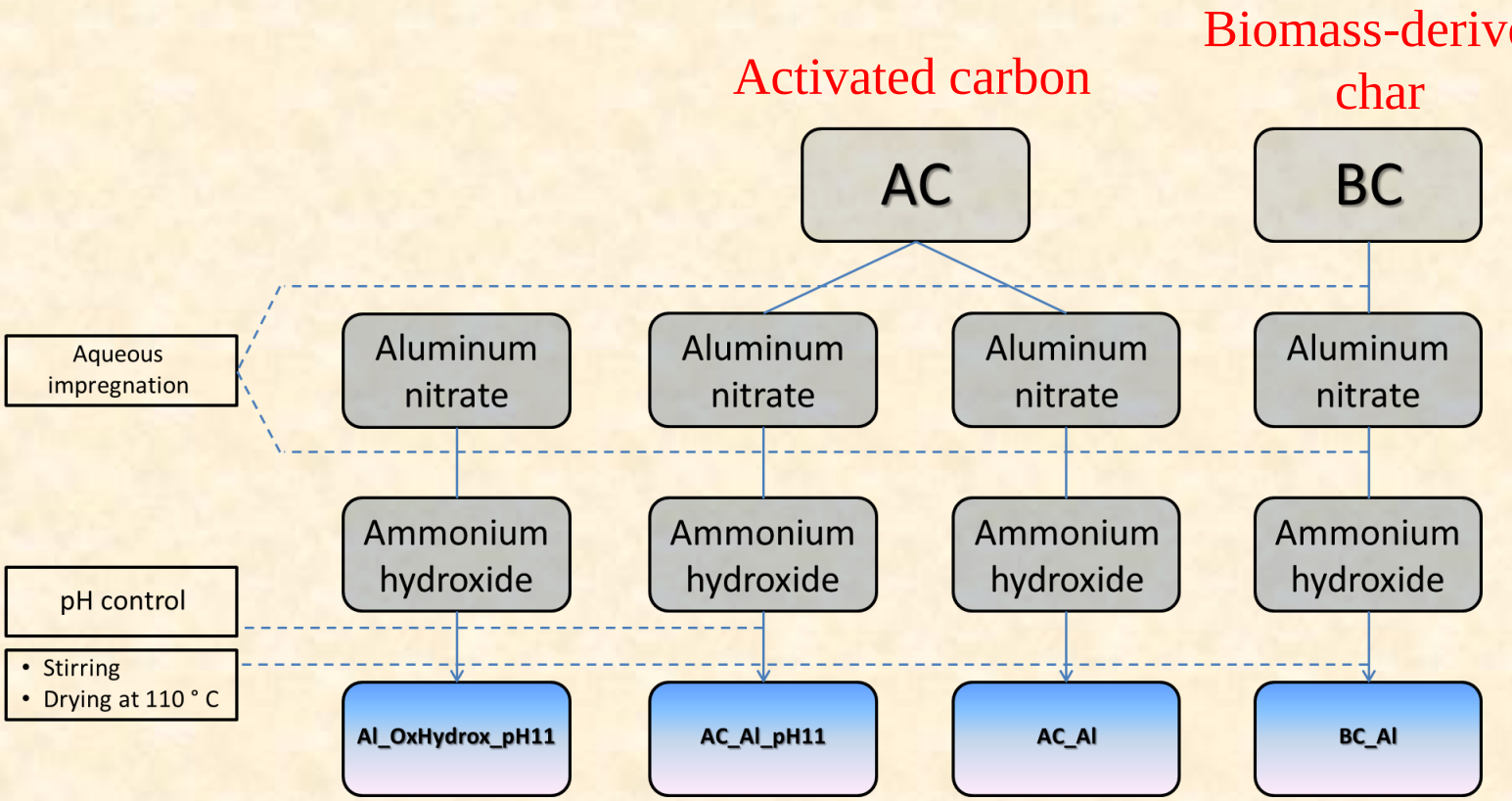
Some applications:

- Ammonia adsorption
- Removal of fluoride from water
- Catalysts supports



P.A. Nikulshin et al., *Catal. Today* 2010;149:82–90.

Alumina-carbon nanocomposites



Alumina-carbon nanocomposites

XRD patterns:

^{27}Al NMR spectra:

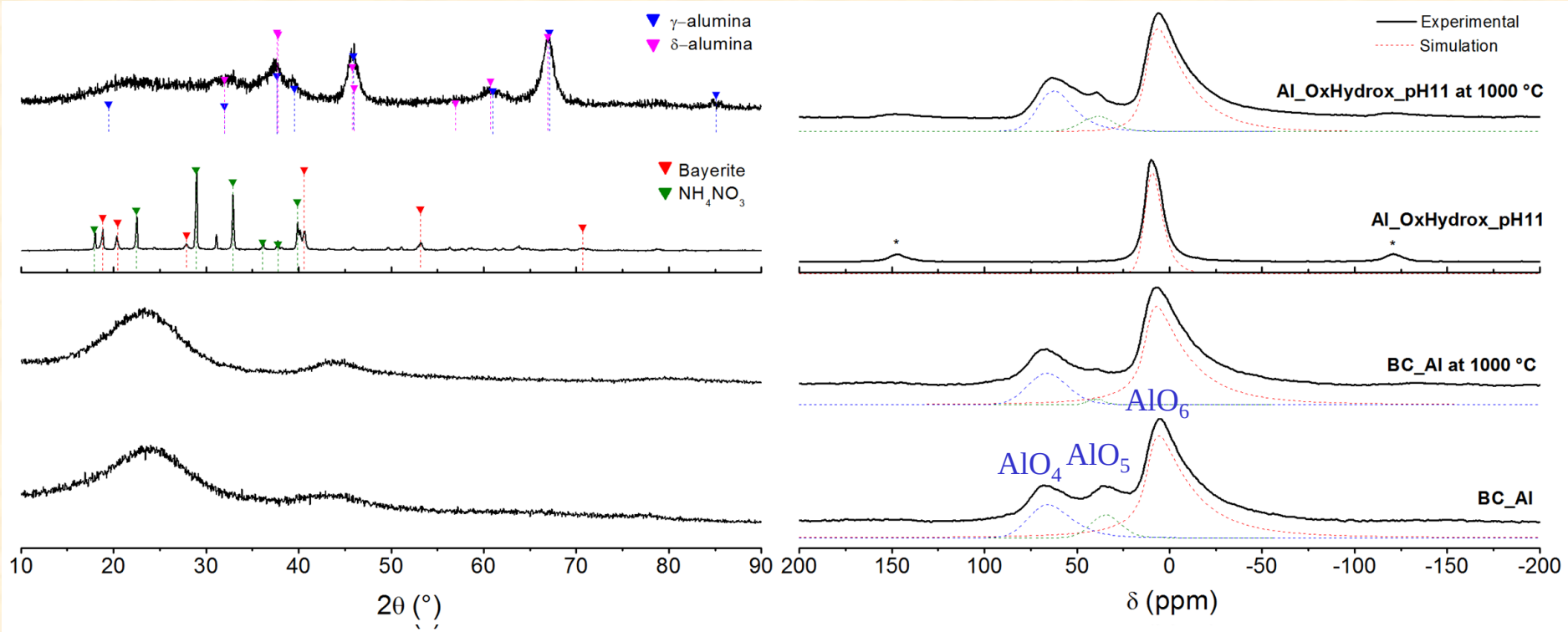


Figure 3. XRD patterns and solid-state ^{27}Al SPE/MAS NMR spectra recorded at room temperature for as-synthesized and heat-treated BC_Al and Al_OxHydrox_pH11 samples.

Alumina-carbon nanocomposites

XRD patterns:

^{27}Al NMR spectra:

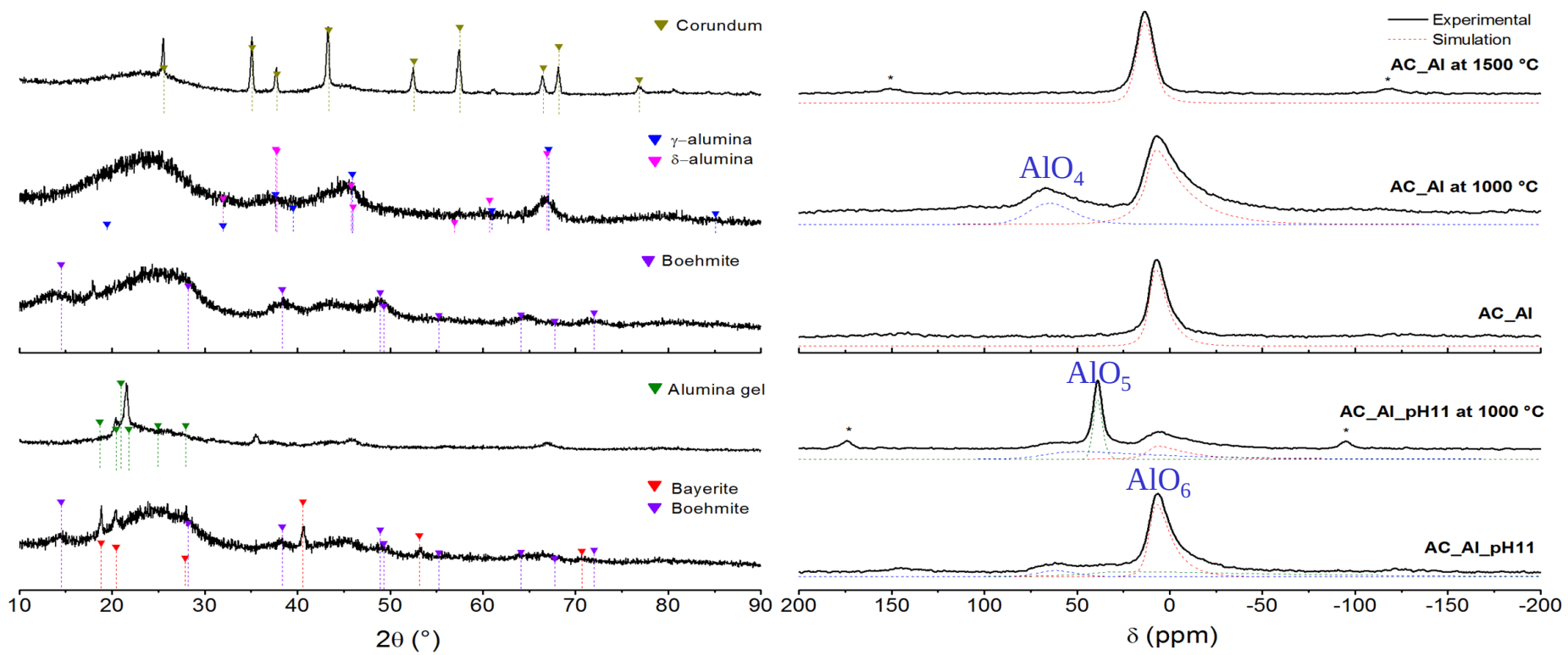
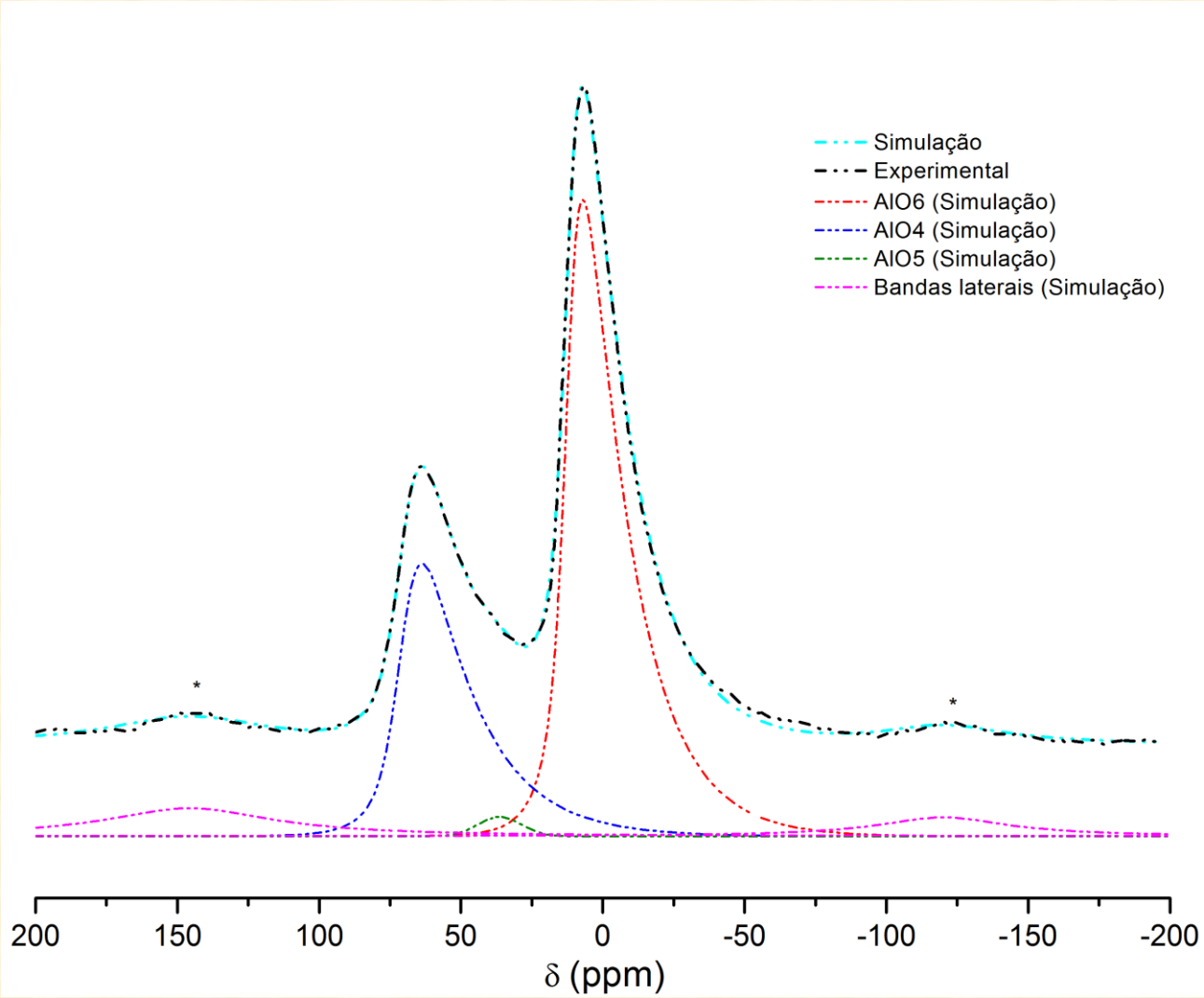


Figure 2. XRD patterns and solid-state ^{27}Al SPE/MAS NMR spectra recorded at room temperature for as-synthesized and heat-treated AC_Al_pH11 and AC_Al samples.

Alumina-carbon nanocomposites

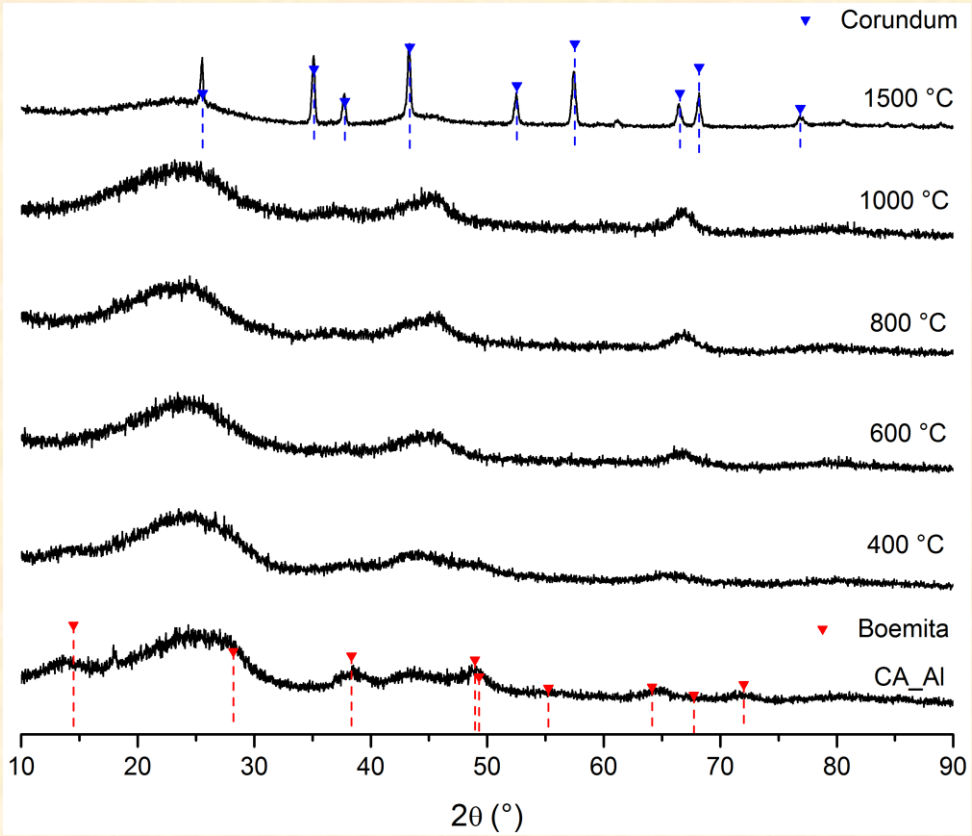
^{27}Al NMR - Spectral simulation:



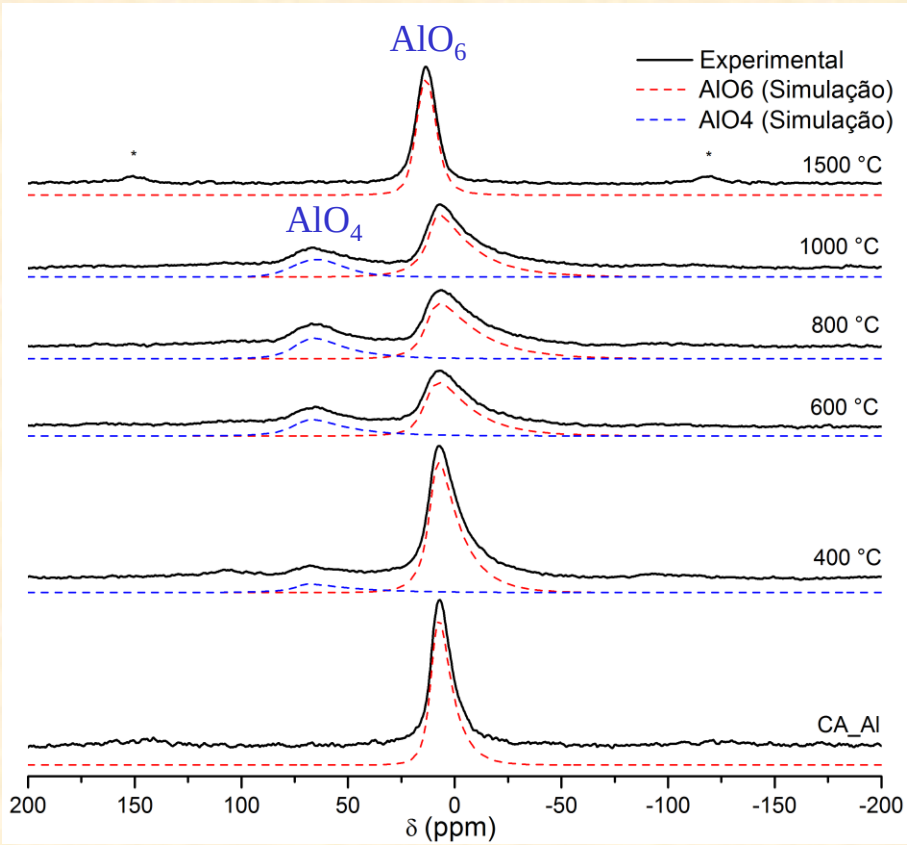
Massiot et al., *Magn. Reson. Chem.* 2002;40:70–76

Alumina-carbon nanocomposites

XRD patterns:



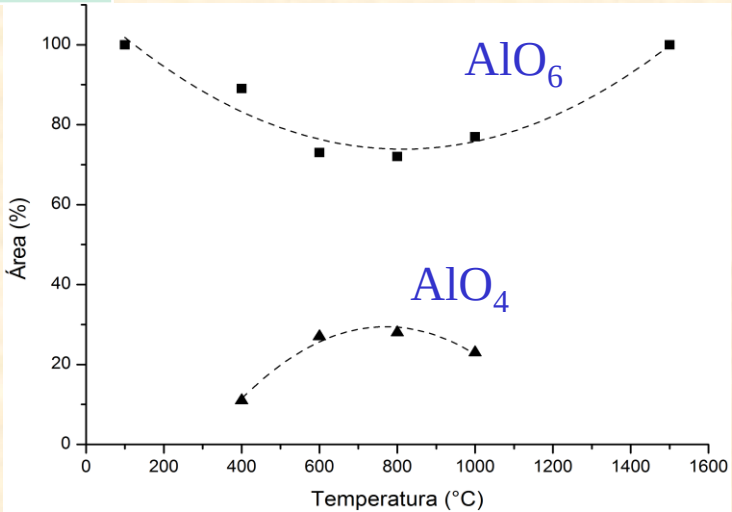
^{27}Al NMR spectra:



Alumina-carbon nanocomposites

Spectral parameters and relative fractions:

	AlO_4				AlO_6			
	δ_{iso} (ppm)	dCS (ppm)	C_Q (MHz)	Área (%)	δ_{iso} (ppm)	dCS (ppm)	C_Q (MHz)	Área (%)
CA_Al	-	-	-	-	9,5	4,9	2,8	100
T400	72,2	1,6	5,1	11	10,1	4,7	3,5	89
T600	72,1	10,2	4,6	27	12,8	7,5	4,7	73
T800	71,1	11,8	4,4	28	12,6	6,2	5,1	72
T1000	69,5	21,4	3,2	23	10,5	4,0	4,4	77
T1500	-	-	-	-	15,1	8,3	1,8	100



Alumina-carbon nanocomposites

Spectral parameters and relative fractions:

Sample	Al content (wt. %)	Average crystallite size (nm)	Major Al phase	Site fraction (%)		
				AlO_4	AlO_5	AlO_6
CA_Al	8	4	Boehmite	-	-	100
BAB_Al	10	-	-	18	9	73
CA_Al_pH11	8	25	Bayerite	8	4	88
Hid_Al_pH11	-	52	Bayerite	-	-	100

Conclusions

- Multinuclear solid-state magnetic resonance experiments constitute a powerful tool for the characterization of different types of carbon materials.
- The sensitivity of NMR spectral parameters to the chemical and structural details of the environment of the probe nuclei allows the achievement of information about the structure of the material at the atomic scale.
- As NMR does not depend on crystalline order, the method presents general applicability for studies of carbon materials, including ordered forms (graphite, fullerenes, etc.), nanocarbons (graphene, nanotubes, etc.) and disordered materials (activated carbons, chars, biochars, soot, carbon blacks, etc.).

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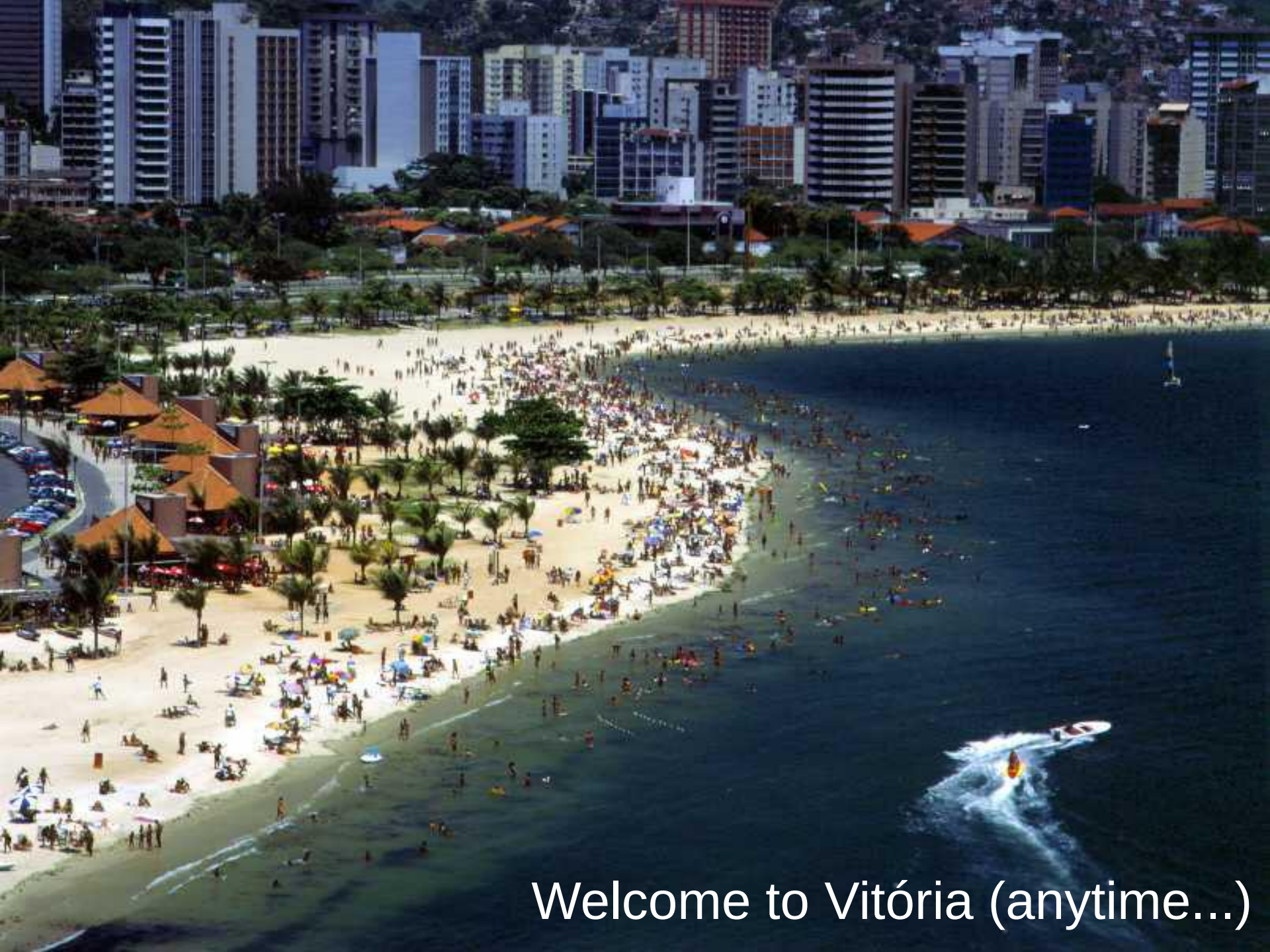
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