# Principios Básicos de RMN en sólidos destinado a usuarios

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# CONTENIDOS

MODULO 2: Alta resolución en sólidos para espines 1/2

Introducción
Rotación al ángulo mágico
Desacople con alta potencia
Secuencias de desacoples de pulsos múltiples
Polarización cruzada

Principios Básicos de RMN en sólidos destinado a usuarios: 24-28 de noviembre 2014

# High resolution in solids for ½ spins

In solid state NMR, usually we deal with powder samples, ie samples that consist of many crystallites oriented at random.

The interactions we have seen all depend on the crystallite orientation, ie they are anisotropic.

As a result, the NMR spectrum of a powdered sample consists of broad lines or patterns of powders, since all other molecular orientation gives rise to different spectral frequencies.

Different parts of an experiment and interactions are affected:

**Choosing a  diluted nucleus**: for example 13C, 1.1%
abundant  which effectively  removes homonuclear interactions (13C, 13C).

**Homonuclear decoupling**: remove homonuclear interactions in the case  of abundant spins, for example (1H, 1H)

**Rotation the magic angle**: (Magic angle spinning, MAS) which averages the anisotropy
of chemical shielding to the isotropic value as in solution and also helps
reduce heteronuclear dipolar coupling.

**Proton dipolar decoupling**: This removes the interactions (1H, 13C).

**Cross polarization** (CP): Additionally, the signal to noise ratio (s/ n) of a spectrum can be greatly
increased by using a pulse technique which transfers magnetization from protons to carbons and other
diluted nuclei.

# Magic angle rotation (MAS: magic angle spinning)

The largest interaction for dilute nuclei (besides heteronuclear coupling with abundant nuclei such as protons) is the chemical shift anisotropy.

In solution, the anisotropy is averaged to its isotropic value by rapid random motion of molecules.

This same averaging net can be obtained in a polycrystalline sample by rotating it rapidly (up to 60 kHz, usually 10-15 kHz) about an axis tilted at an angle of 54°44 ' with respect to the external magnetic field direction, this is called "magic angle".

The reason for the success of this technique is the term $3\cos^2\theta-1$, where $\theta$ is the angle between a specific fixed molecular axis and the direction of static magnetic field

## Chemical Shift Interaction

$$\omega_{cs}(\theta,\phi) = \omega_0 \sigma_{iso} - \frac{1}{2}\omega_0 \Delta \left( \boxed{3\cos^2\theta - 1} + \eta \, sen^2\theta \, \cos 2\phi \right)$$
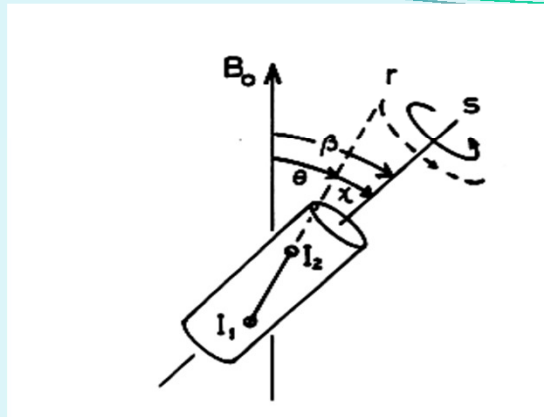
## Homonuclear Dipolar Hamiltonian

$$\hat{H}_{IS} = -\frac{\mu_0}{4\pi}\gamma_I\gamma_S\hbar\frac{1}{r^3}(3\cos^2\theta-1)\left[\hat{I}_z\hat{S}_z - \frac{1}{2}\left[\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y\right]\right]$$

## Heteronuclear Dipolar Hamiltonian

$$\hat{H}_{IS}^{hetero} = -\frac{\mu_0}{4\pi}\gamma_I\gamma_S\hbar\frac{1}{r^3}(3\cos^2\theta-1)\hat{I}_z\hat{S}_z$$

## Quadrupolar Hamiltonian

$$\hat{H}_Q = \frac{3\chi}{8I(2I-1)}(3\cos^2\theta-1+\frac{1}{2}\eta\,sen^2\theta\,\cos2\phi)(3\hat{I}_z^2-\hat{I}^2)$$

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The sample is rotated in a cylindric rotor;

$\vec{r}$      direction of the z axis of the chemical shift anisotropy pas.

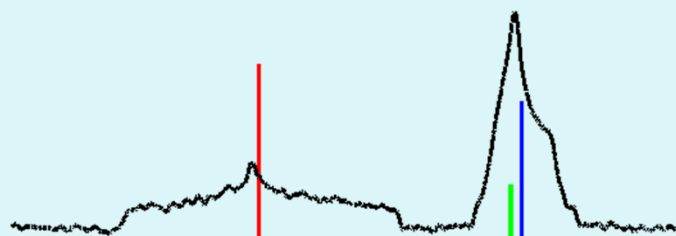$\vec{s}$      direction of the rotor rotation, $\beta-\chi \leq \theta \leq \beta+\chi$.

Average over all of microcrystalites of the sample:

$\langle 1-3\cos^2\theta \rangle = (1/2)(1-3\cos^2\beta)\langle 3\cos^2\chi-1 \rangle$, para $\beta=54^{\circ}44'$, $\langle 1-3\cos^2\theta \rangle = 0$.
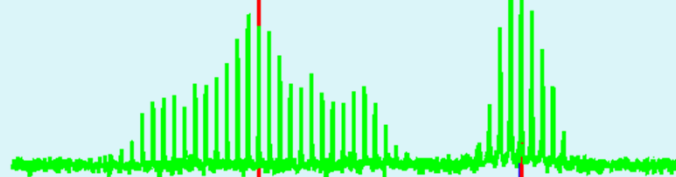
Thus, if the frequency of rotation is fast enough compared to the anisotropy of the interaction , the anisotropic interaction is averaged to zero.

If the rotation frequency is not fast enough compared to the frequency range that covers the interaction, 3 or 4 times greater, appear what we called rotational bands. These are narrow lines that appear in addition to the isotropic chemical shift line. Their positions on frequency, respect to the isotropic line, are $\pm n \nu_R$ (n = 1, 2, ...), so that their positions change with the speed of rotation of the sample, but not the isotropic line.
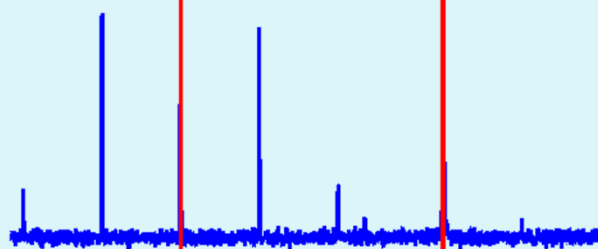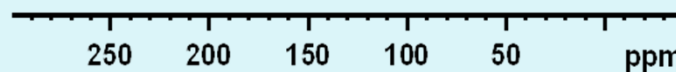


Static

0.7 kHz MAS

5.0 kHz MAS

8.0 kHz MAS

250   200   150   100   50   ppm

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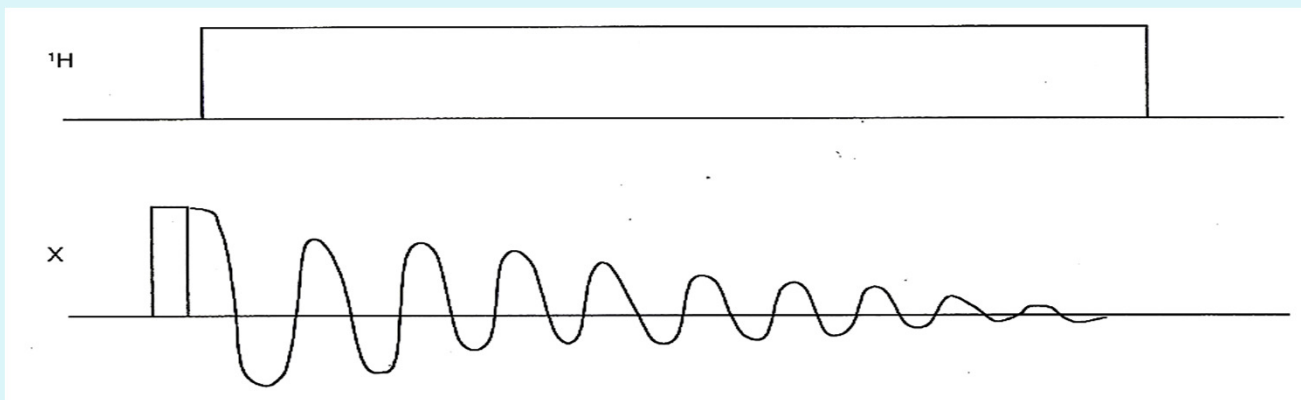
# High power decoupling

For high resolution in solids is necessary to eliminate nuclear couplings, in particular those of dipole type.

Homonuclear decoupling, for example (1H, 1H), requires special techniques of pulse sequences or very fast rotations at the magic angle (> 20 kHz). Heteronuclear decoupling is easier to achieve.

In most systems containing carbon there are many hydrogen atoms and dipolar interactions (13C, 1H) are very large. To remove these interactions we use double resonance. That is, while detecting the signal of 13C, the protons are irradiated simultaneously in resonance with radio frequency for which they require very high power (100 to 1000 watts, in frequency units of magnetic field strengths of irradiation $\gamma B_1 / 2\pi$ to 100 kHz may be required).

High power decoupling. This eliminates the effects of 1H dipolar coupling in the spectrum of the nucleus to observe, X in this case. Of course, this technique can beapplied to any heavy nucleus rather than protons. Irradiation with high power is applied to the spins of the protons while the signal is acquired simultaneously for X spins Here we use a single pulse to create transverse magnetization of spin X. More complicated pulse sequences can also be used to prepare the spin system X.

# Multiple pulse decoupling sequences

The magic angle rotation can remove homonuclear dipolar coupling effects if the rotation speed is greater than the dipolar interaction.

For protons this is not always possible since these usually have homonucleardipolar interactions of tens of kilohertz.

In these cases then are used pulse sequences to achieve homonuclear dipolar decoupling.

Most of these sequences are arranged so that, in certain windows within the pulse sequence, the effect of the dipolar Hamiltonian  on the magnetization is zero. If the magnetization is detected in these windows the homonuclear dipolar coupling effect in the NMR spectrum is removed

Unlike MAS, which averages to zero the geometric terms  of the interaction, these sequences  averaged to zero the spin terms of the interaction.
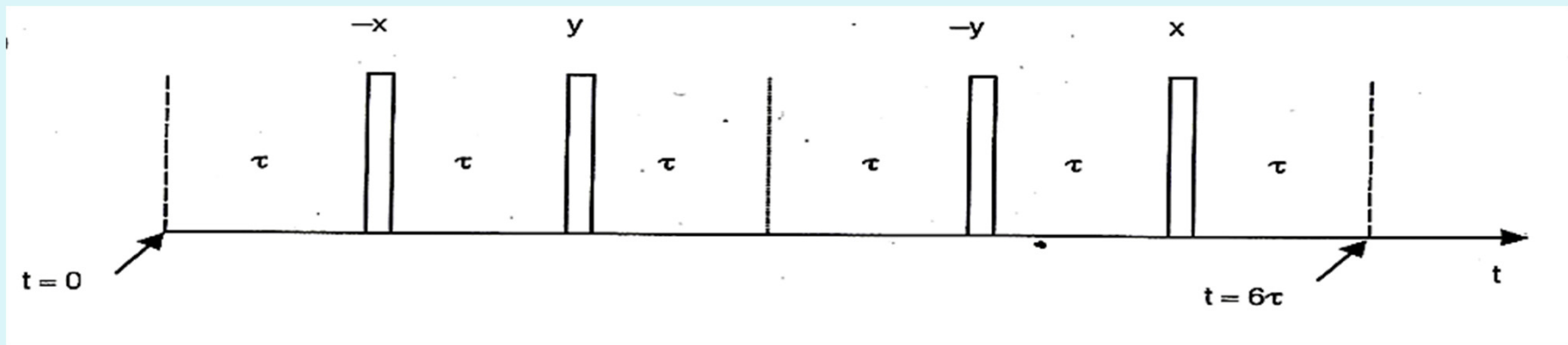
WAHUHA sequence. All pulses are 90 ° to the phases are shown in the figure. The points of signal detection are indicated by an arrow. The four pulses are repeated periodically until the signal has decayed completely in the xy plane.

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The effect of WAHUHA sequence (and any other) on the spin system can be treated by the average Hamiltonian theory.

Briefly we give some indication of how it works in this description.

One can show that at the end of one cycle of the sequence the spin system has evolved under the action of "average Hamiltonian"

$$\overline{\hat{H}} = ( \hat{H}_z + \hat{H}_y + 2 \hat{H}_x + \hat{H}_y + \hat{H}_z ) / 6$$

As during the free evolution of spin system is under the action of the interactions of chemical shift and homonuclear dipolar coupling the average Hamiltonian is

$$\overline{\hat{H}} = - \frac{1}{3} \sum_j \omega_j ( \hat{I}_z^j + \hat{I}_y^j + \hat{I}_x^j ) + \frac{1}{3} ( \hat{H}_z^{II} + \hat{H}_y^{II} + \hat{H}_x^{II} )$$

One can show that dipolar term $( \hat{H}_z^{II} + \hat{H}_y^{II} + \hat{H}_x^{II} ) = 0$ vanishes, so that the sequence eliminates the effect of this interaction.

Tyrosine
Homonuclear dipolar coupling

"DUMBO"

67 kHz

35 kHz

24 kHz

15 kHz and 7 kHz
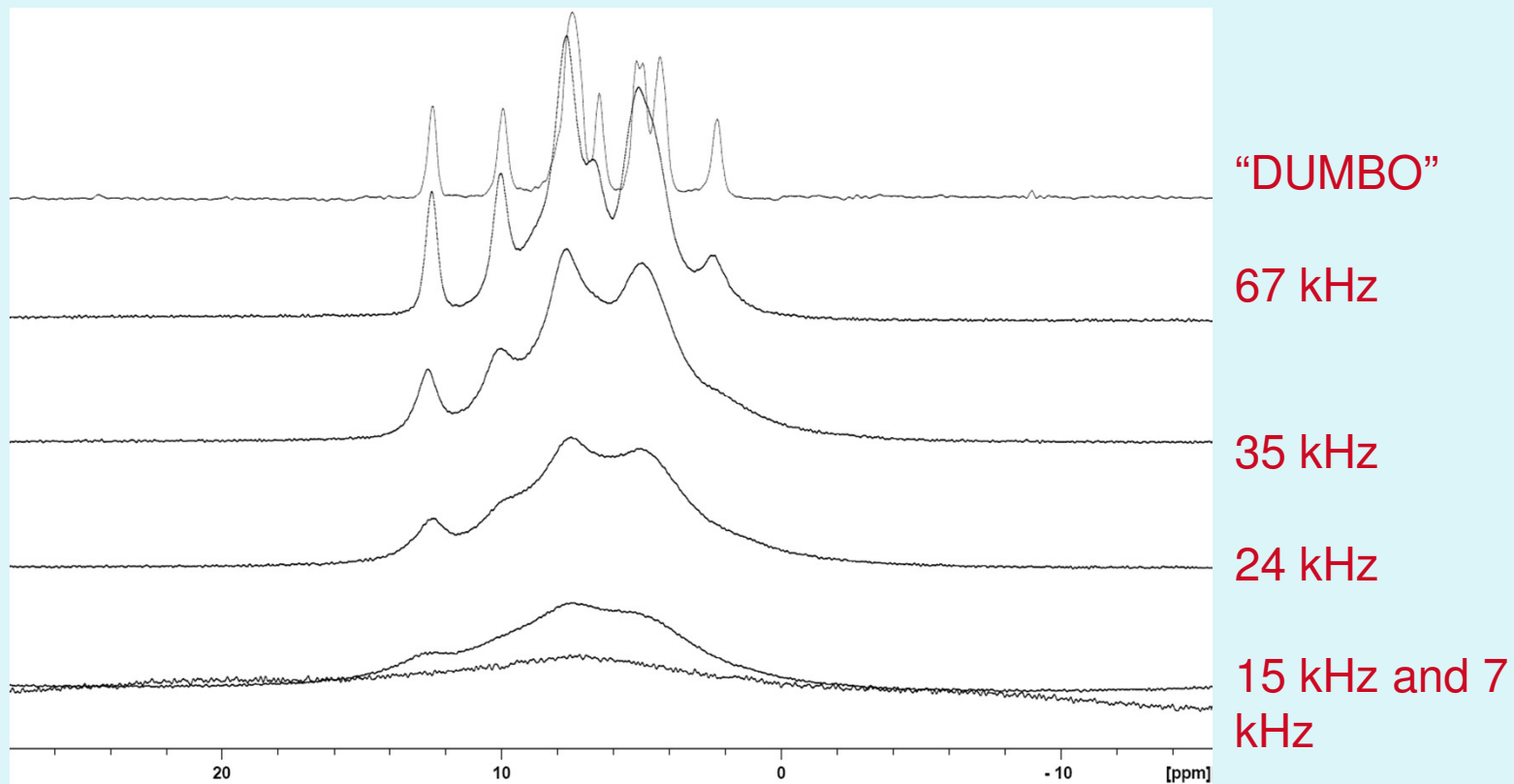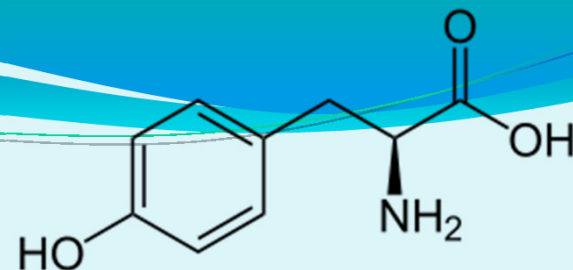
DUMBO is a homonuclear decoupling multipulse sequence, here combined with MAS (CRAMPS) at high speed

# Cross Polarization

There is an additional problem not connected to the line broadening. To explain itis necessary to understand the phenomenon of relaxation. For relaxation we understand the processes that the magnetization back to equilibrium when it hasbeen disturbed by an rf pulse.

We consider three types of processes.

First type: spin-lattice relaxation or longitudinal relaxation, is the recovery of the magnetization component along the external field. The characteristic time of this process is called $T_1$ and governs the speed at which the rf pulses can be repeated in a simple experiment of a single pulse and acquisition.

$$[M_0 - M_z(t)] = [M_0 - M_z(0)] \exp(-t/T_1)$$

Second type: transverse relaxation or spin-spin. Is the decay of the transverse component of magnetization related to the "dephasing of spins in the xy plane."The characteristic time is called $T_2$ and related to the line width of the NMR signal.

$$M_{xy}(t) = M_{xy}(0) \exp(-t/T_2)$$

Third type: spin-lattice relaxation in the rotating system, governs the equilibrium of the magnetization perpendicular to z axis in the presence of rf. The time that characterizes this process is called $T_{1\rho}$.

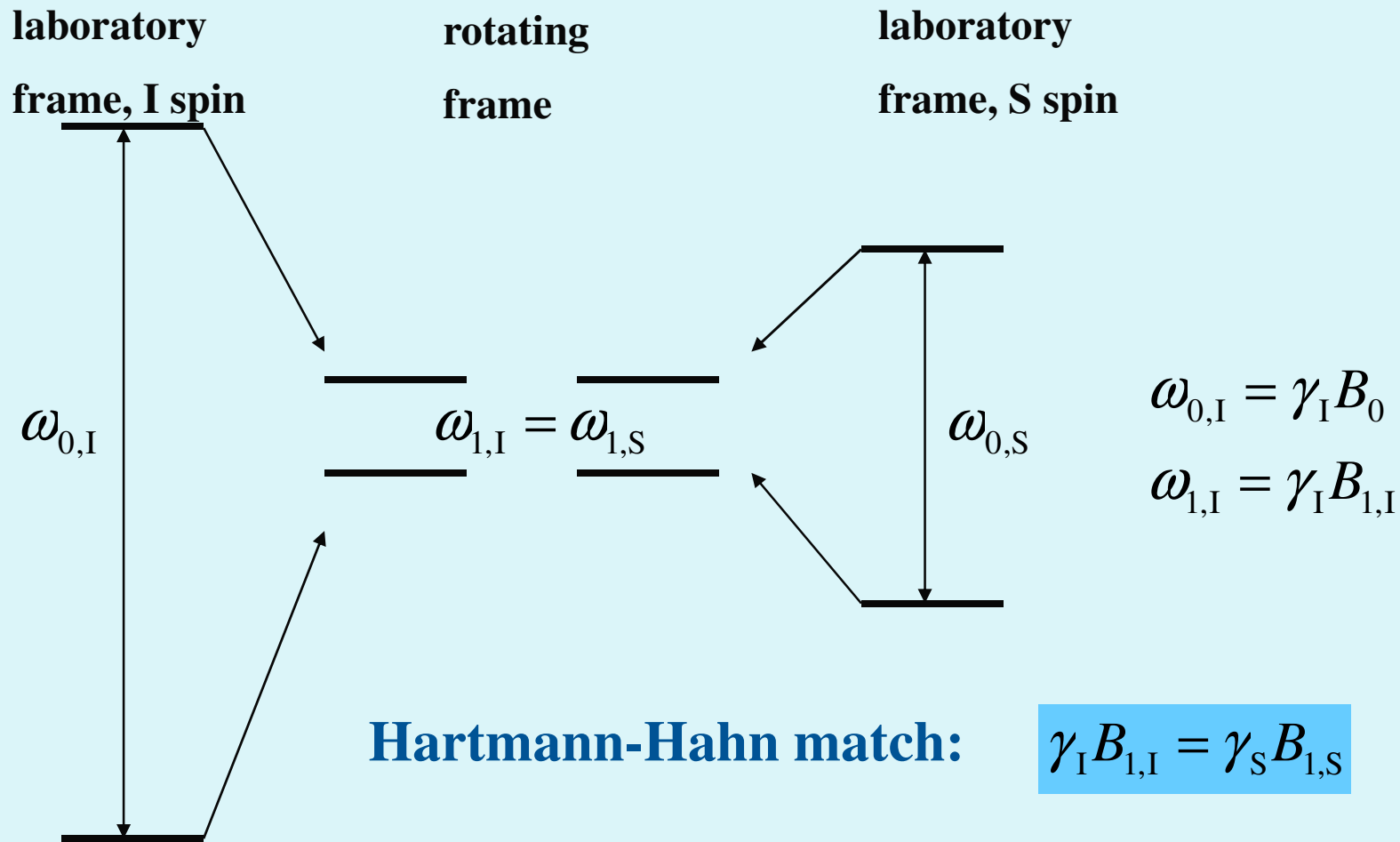$$M(t) = M_0 \exp(-t/T_{1\rho})$$
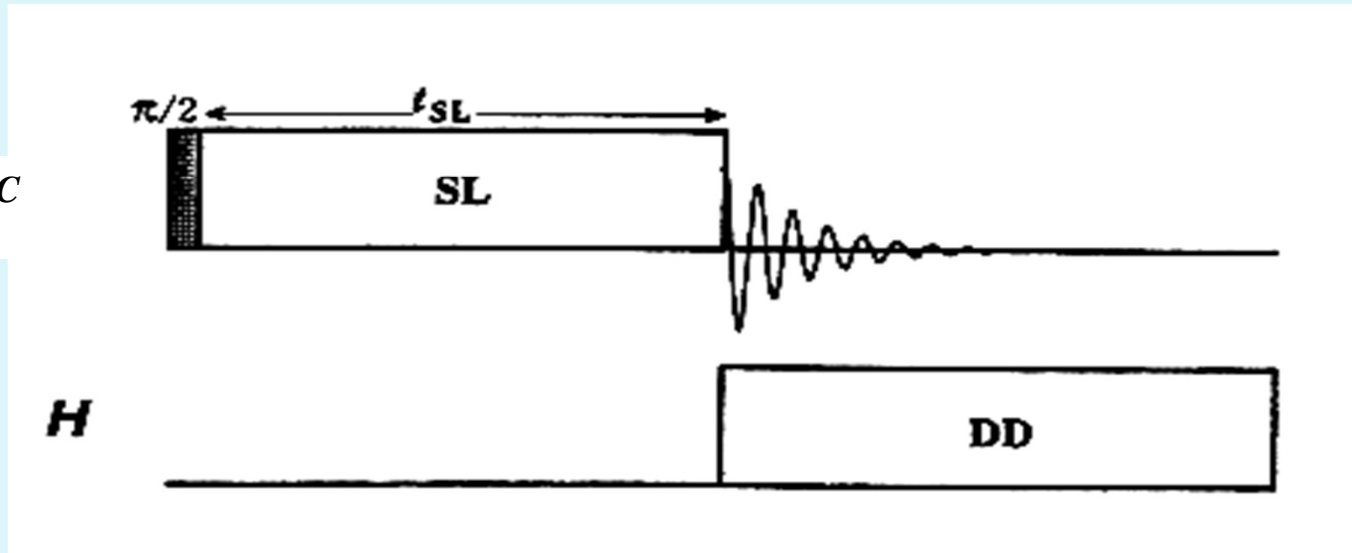
13C $T_{1\rho}$ measurement

$\vec{M}_0$ is along the rf magnetic field $\vec{B}_1$ we say taht it is "spin-locked". Since $B_0 >> B_1$ the magnitude of $\vec{M}_0$ is far away bigger than expected at room temperature. In this way will be relaxation while the spins get "hoter". **SL**: spin-lock. **DD**: dipolar decoupling.

For solids the following relation between these three relaxation times holds

$$T_2 << T_{1\rho} << T_1$$

$T_2$ being the order of tens of microseconds, $T_{1\rho}$ the order of tens of milliseconds, $T_1$ from several seconds to hours. The spin relaxation times for diluted nuclei as 13C in solids are often substantially longer than for 1H (they can be around one hour). Due to get a reasonable s/n ratio, the experiment must be repeated thousands of times, and the repetition rate must be greater than $5T_1$, the experiment of a single pulse with proton decoupling is totally inefficient. This situation can be remedied with a pulse sequence called cross-polarization
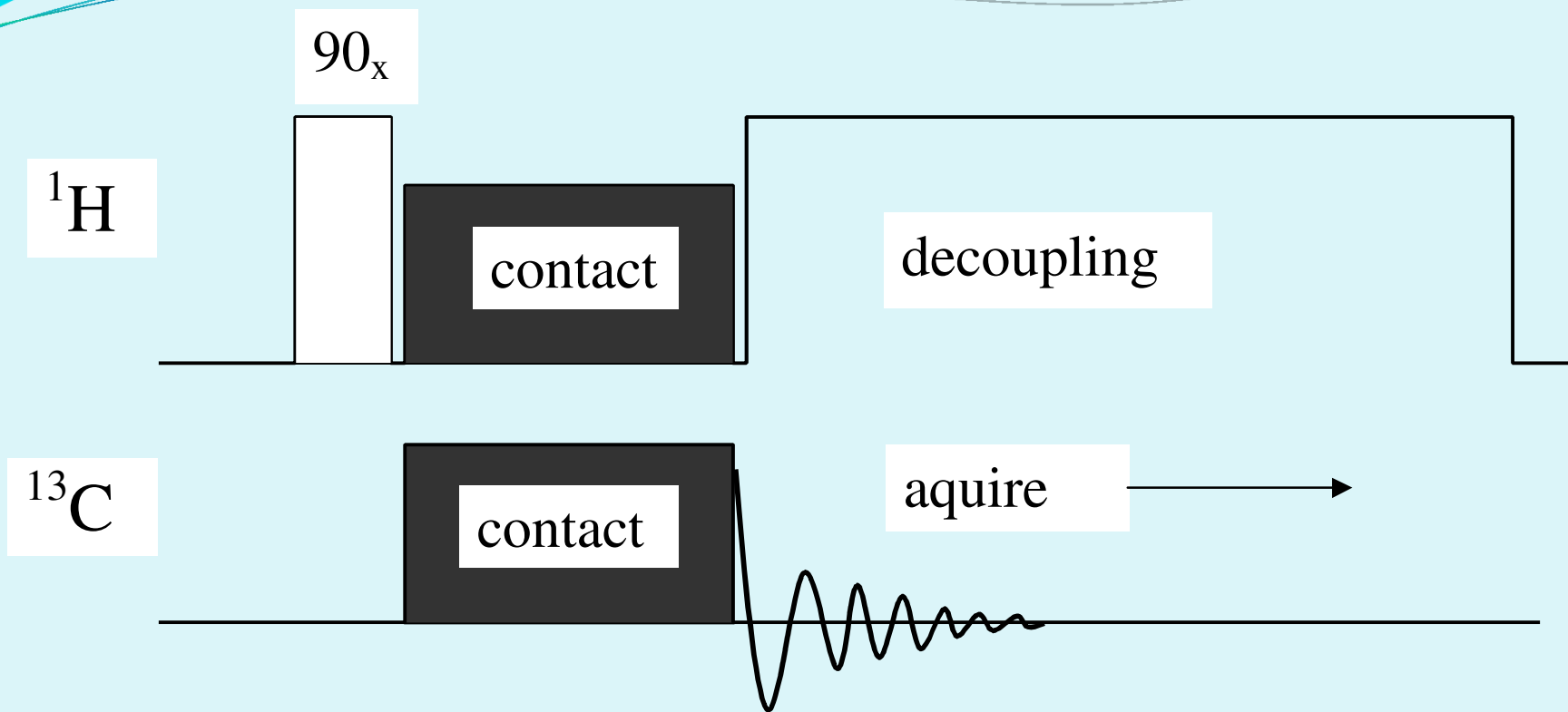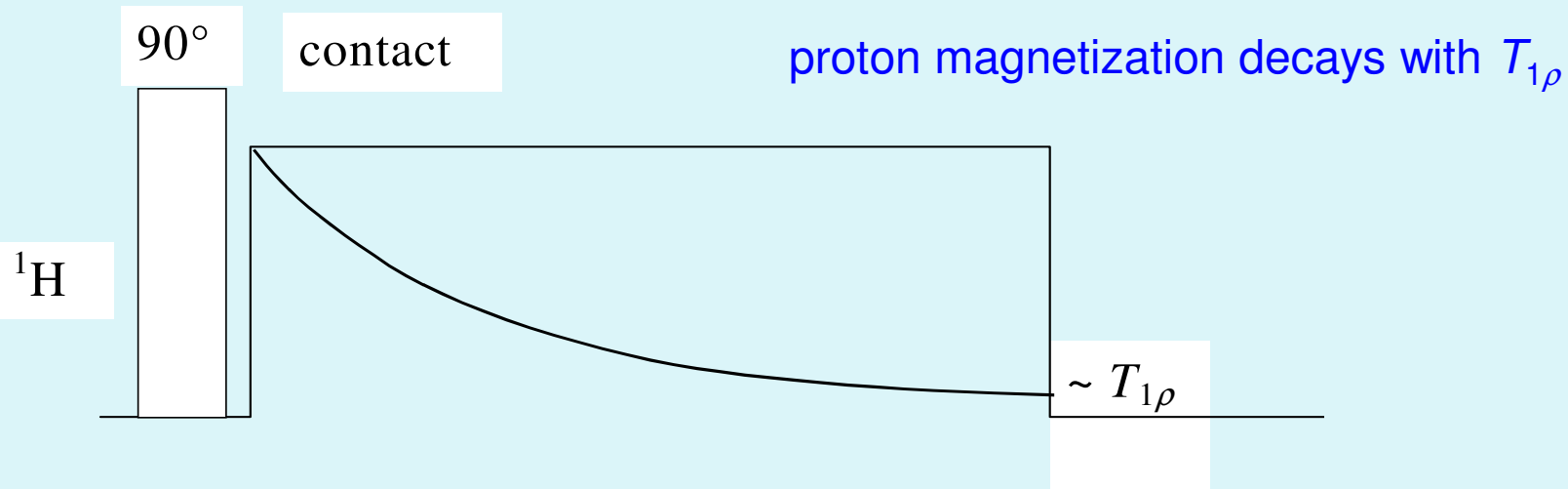
# energy level matching: Hartmann-Hahn matching

**laboratory**

**frame, I spin**

**rotating**

**frame**

**laboratory**

**frame, S spin**



$$\omega_{0,I}$$

$$\omega_{1,I} = \omega_{1,S}$$

$$\omega_{0,S}$$

$$\omega_{0,I} = \gamma_I B_0$$

$$\omega_{1,I} = \gamma_I B_{1,I}$$

**Hartmann-Hahn match:** $\gamma_I B_{1,I} = \gamma_S B_{1,S}$

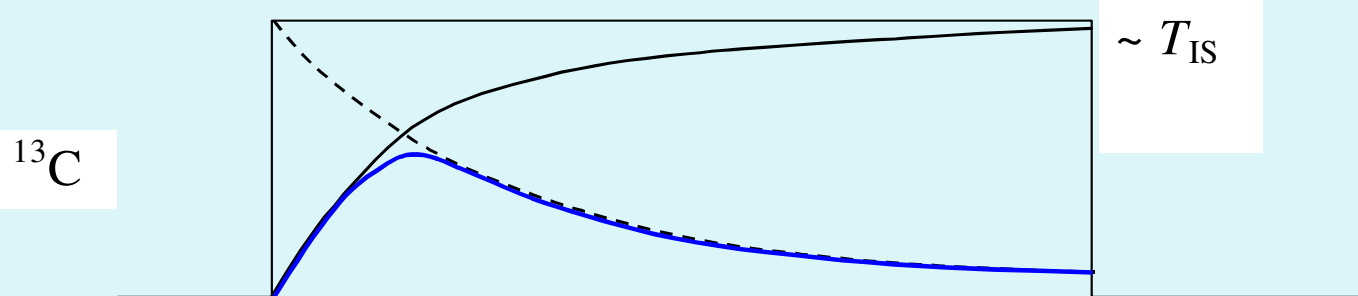Diagram of the cross-polarization ¹H →¹³C pulse sequence .

The sequence consists of a spin-locking of the protons and the beginning of a period of double resonance known as contact time, where the $\vec{B}_1$ rf fields are set according to the Hartmann-Hahn condition:

$$\gamma_C B_{1C} = \gamma_H B_{1H}$$

During the contact time the proton transverse magnetization along $\vec{B}_{1H}$ is transferred to the carbon nuclei (along $\vec{B}_{1C}$) mainly via flip-flop transitions via the dipole interaction term. The contact times are of the order of milliseconds, the 13C magnetization value increases over the Boltzman value by a factor $\gamma_H / \gamma_C \sim 4$. Additionally, the repetition rate depends on $T_{1H}$ rather than $T_{1C}$ ($T_{1H} << T_{1C}$) so you can use shorter repetition rates than in an experiment of a single pulse.

$90°$  contact

proton magnetization decays with $T_{1\rho}$

$^1H$

$\sim T_{1\rho}$

cross polarization builds up with $T_{IS}$

$\sim T_{IS}$

$^{13}C$

signal follows combined effect of buildup and decay

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# CP is not quantitaive

- short $T_{IS}$ (~500 ms): directly attached protons
  (-$CH_3$, -$CH_2$-, >CH-)

- long $T_{IS}$ (>1 - 2 ms): quaternary carbons
  (>C<, -COO-, substituted aromatic systems, ...), high mobility

- short $T_{1\rho}$ : paramagnetic systems/impurities (e.g. in coal),
  high mobility

An old example about we can say up to here is a carboxilate[R. K. Harris, *"Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View"*, ISBN 0-582-44653-8, Ch. 6, Longman Scientific and Technical, Harlow (1994)]. Clearly the asymmetric unit cell has four acetates groups.
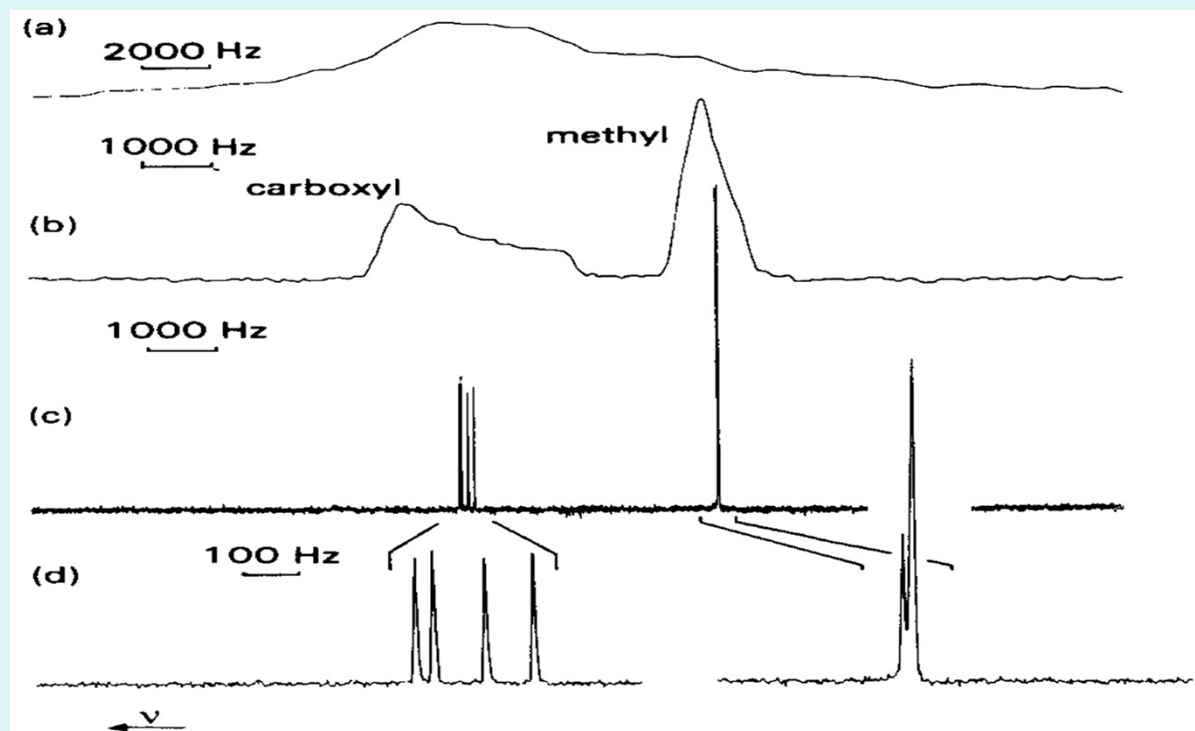


Calcium acetate $^{13}C$ spectrum. $2Ca(CH_3CO_2)_2 \cdot 2H_2O$.
a) static without proton decoupling,
b) static wiht high power proton decoupling,
c) with decoupling and MAS
d) detail of c)