17—Solid State NMR: Cross-Polarization

In solid state NMR, cross-polarization (CP), i.e. applying a pulse simultaneously on an I and S spin, is a standard building block of most pulse sequences (see examples in Chapter 15). In this chapter, we will discuss how cross-polarization works.

17.1 Why use CP?

As mentioned in Chapter 15, in solid state NMR, we often detect nuclei which have an inherently low sensitivity (e.g. $^{13}C$ or $^{15}N$). As we saw in previous lectures, we can define how sensitive a nucleus is by using the definition of signal-to-noise:

$$\frac{S}{N} = \frac{k_{eff,x}N_x\gamma_x^5/2 h^2 B_0 T_{2,x}}{4(2\pi)^2kT}$$  \hspace{1cm} (17.1)$$

or

$$\frac{S}{N} = k_{eff,x}\sqrt{\omega_S} M_{S}^{90} T_{2,S}.$$  \hspace{1cm} (17.2)

with the magnetization measured after a 90 degree
pulse being:

\[ M_S^{90} = \frac{N_S \gamma_S^2 h^2 B_0}{4(2\pi)^2 kT}. \]  \hspace{1cm} (17.3)

If one used Hartmann-Hahn cross-polarization (HHCP) instead, i.e. the pulse sequence shown below with

\[ B_{1I} \gamma_I = B_{1S} \gamma_S \] \hspace{1cm} (17.4)
then the magnetization measured is given by

\[ M_S^{HHCP} = \frac{1}{2} \frac{\gamma_I}{\gamma_S} \sqrt{\frac{N_I}{N_S}} M_S^{90}. \]  

(17.5)

Therefore the enhancement in signal to noise that one can expect from using HHCP is

\[ \frac{\left( \frac{S}{N} \right)^{HHCP}}{\left( \frac{S}{N} \right)^{90}} = \frac{1}{2} \frac{\gamma_I}{\gamma_S}. \]  

(17.6)

Thus for \( I=^1H \) and \( S=^{13}C \), the expected enhancement is

\[ \frac{\left( \frac{S}{N} \right)^{HHCP}}{\left( \frac{S}{N} \right)^{90}} = \frac{1}{2} \frac{\gamma_H}{\gamma_C} = 2. \]  

(17.7)

**QUESTION 1 - Assignment 5**

1) What is the expected enhancement in signal to noise if \( I=^1H \) and \( S=^{15}N \) for HHCP versus the application of a single 90 degree pulse?

The transfer of magnetization from the abundant I spins to the less abundant S spins occurs via the heteronuclear dipolar interaction between the I and S spins. Recall, the dipolar Hamiltonian for a
heteronuclear system is given by:

\[ \hat{\mathcal{H}}_D = -\frac{\mu_0 \gamma_I \gamma_S \hbar^2}{16\pi^3 r^3} (3\cos^2 \theta - 1) I_z S_z \]  \quad (17.8)

which in a doubly ”rotating frame”, i.e. a frame of reference which rotates with the applied rf fields, becomes

\[ \hat{\mathcal{H}}_D = \sum_k b_k I_{ky} S_y \]  \quad (17.9)

where \( b_k \) is the dipolar coupling constant, given in the equation above for an \( I_k S \) spin system.

In terms of energy levels, one can visualize this magnetization transfer as a matching of the energy levels, as shown below:

\[ \text{HH condition} \]
One can also use the analogy from thermodynamics (though not fully correct) of the equilibration of a hot and cold bath when they come into contact, i.e.

Continuing with the thermodynamics analogy, one can also imagine what would occur, if the hot and cold baths could come to equilibrium using infinitessimally small steps, i.e. adiabatically:
In this case, the enhancement that one would expect is given by

\[ M_{S}^{\text{adiabaticCP}} = \frac{\gamma_I}{\gamma_S} \sqrt{\frac{N_I}{N_S}} M_S^{90}. \] (17.10)

Therefore the enhancement in signal to noise that one can expect from using adiabaticCP is

\[ \left( \frac{S}{N} \right)^{\text{adiabaticCP}} = \frac{\gamma_I}{\gamma_S} \left( \frac{S}{N} \right)^{90}. \] (17.11)

Thus for \( I = ^1H \) and \( S = ^{13}C \), the expected
enhancement is
\[
\frac{(\frac{S}{N})_{adiabatic\, CP}^{90}}{(\frac{S}{N})^{90}} = \frac{\gamma_H}{\gamma_C} = 4 \tag{17.12}
\]
and for \( I = ^1 H \) and \( S = ^{15} N \), the expected enhancement is
\[
\frac{(\frac{S}{N})_{adiabatic\, CP}^{90}}{(\frac{S}{N})^{90}} = \frac{\gamma_H}{\gamma_N} = 10. \tag{17.13}
\]

Adiabatic transfer is achieved experimentally by either using a ramp (RAMP-CP) or a tangent (APHH-CP):
\[ \omega_{II} = \omega_{IS} \]

References:

For RAMP-CP


For APHH-CP


The adiabatic transfer methods are particularly
useful for transfer from one low abundance nucleus to another, e.g. $^{13}C$ and $^{15}N$.

**QUESTION 2 - Assignment 5:**
1) Calculate the expected enhancement of signal to noise for transfer from $^{13}C$ to $^{15}N$, using HHCP and one of the adiabatic methods.

A hidden advantage of using cross-polarization is that the signal detected on the S spin is not subject to long spin-lattice relaxation times ($T_{1S}$). The spin-lattice relaxation time depends on the gyromagnetic ratio, thus for low abundance nuclei, $T_{1S}$ is much longer that for $^1H$’s. By using cross-polarization, however, the only relaxation that is active is that of the $^1H$’s. In practical terms, this means that the recycle delay used can be much shorter when cross-polarization is used versus when a single pulse experiment is used.

**17.2 CP under MAS conditions**

The equations given up until this point relate to the case where no magic angle sample (MAS) spinning is applied - i.e. static case. In the situation where MAS is used, the Hartmann Hahn condition becomes
depends on spinning speed:

\[ B_{1S} \gamma_S - B_{1I} \gamma_I = n\omega_r \]  \hspace{1cm} (17.14)

or

\[ \omega_{1S} - \omega_{1I} = n\omega_r \]  \hspace{1cm} (17.15)

with \( n = 0, \pm 1, \pm 2, \ldots \) and \( \omega_r \) is the (angular) spinning frequency.

This means that the match condition is separated into sidebands, separated by the spinning speed, i.e.

\[ \text{Mismatch } \Delta \Omega/2\pi \text{ (kHz)} \]

\[ \omega_r/2\pi \text{ (kHz)} \]

\[ n = -2 \quad -1 \quad 0 \quad +1 \quad +2 \]

\[ \begin{array}{c}
  10 \\
  6.7 \\
  5 \\
  3.3 \\
  0 \\
\end{array} \]

\[ \begin{array}{c}
  -50 \\
  -40 \\
  -30 \\
  -20 \\
  -10 \\
\end{array} \quad \begin{array}{c}
  0 \\
  10 \\
  20 \\
  30 \\
  40 \\
\end{array} \quad \begin{array}{c}
  50 \\
\end{array} \]

\textbf{Figure 5} CP-matching curves for various spinning rates for a solid with relatively weak dipolar couplings, e.g. hexamethylbenzene

reference: F. Engelke, Encyclopedia of NMR, Grant and Harris (eds).
Note that the central line, for n=0, i.e. the static Hartmann Hahn matching condition, decreases in intensity with increased spinning speed. This means that at higher spinning speeds, HHCP at the condition n=0 is inefficient. The reason for this is that under MAS conditions, the dipolar interaction is modulated by the rotation frequencies $\omega_r$ and $2\omega_r$, thus leading to more intensity in the ±1 and ±2 sidebands.

When cross polarization is done by matching the fields $\omega_{1S}$ and $\omega_{1I}$ such that $n \neq 0$, the match condition depends on the spinning frequency, of course, but it is also more sensitive to rf inhomogeneities present in the sample. To eliminate this problem, special pulse sequences such as VACP (Variable Amplitude CP) and AMCP (Amplitude Modulated CP) can be used.
References:

In these cases, the centerband intensity is increased and matching at the static Hartmann Hahn condition can be achieved.

These sequences also help to broaden the matching condition, making them less sensitive to deviations from the exact Hartmann Hahn condition.
17.3 CP for Spectral Editing

In an $I_kS$ spin system, the dipolar interactions,
which arise between the S spin and all the $I_k$ spins, are of different magnitude depending on whether the I and S are directly bonded or not - being strongest for directly bonded IS pairs. Recall the equations for the dipolar coupling constant and its dependence on the inverse of the distance to the power of three. Strong dipolar interactions are also present amongst the I spins, i.e. I-I homonuclear dipolar coupling. This collection of I spins can be viewed in thermodynamic terms as a ”bath”.

Let us consider the case where I=$^1H$ and S=$^{13}C$. From the statement above, one expects that the dipolar network for CH groups to be different from $CH_2$ groups, $CH_3$ groups, and C with no protons directly attached. Likewise, the $CH_2$ will be different from all the others and so on. This difference manifests itself in differences in the cross-polarization (CP) dynamics for the different groups as shown below - in particular in the initial stages of the CP buildup of magnetization. For longer CP times, the equilibrium magnetization reached is governed by the $^1H-^1H$ interactions. In
fact, if the diffusion of magnetization amongst the protons is rapid, then the equilibrium magnetization will decay over time.

As a result of the differences in the dynamics which occur for short cross-polarization times, one can distinguish, for instance, CH and $CH_2$ groups from $CH_3$ and $CH_0$ groups. This method is called spectral editing and can be used to simplify spectra, as shown in the example below.
The pulse sequences used to achieve spectral editing
are

Reference and for more information see: K. Zilm, Encyclopedia of NMR, Grant and Harris (eds). and references therein.

Figure 1 Sequences used in the editing protocol of Wu et al. All employ simultaneous phase inversion to alleviate problems with Hartmann-Hahn mismatches. (a) CP sequence. The additional spin locking delay $\tau^l_{SL}$ is used to make the total $^{13}$C spin locking time the same in all of the sequences. (b) SCPPI sequence used to acquire CH$_3$-only spectra. (c) Depolarization sequence. The time $\tau^l_{SL}$ is added in these sequences mainly to minimize distortions from $^1$H rotating frame relaxation.
17.4 CP and Dipolar Coupling

Since CP occurs as a result of the dipolar interaction between two spins, it could in principle be used to extract the dipolar coupling between these spins. In particular, as mentioned already, the oscillations observed during the course of a CP buildup experiment can give you the dipolar coupling directly.

The PISEMA experiment (which correlates in the indirect dimension dipolar coupling) uses this. This is illustrated in the figure below. In order to create a two spin I-S system, Lee-Goldburg decoupling is needed.
Lee-Goldburg decoupling consists in irradiating the \( I \) spins at the magic angle, to eliminate the...
Consider the homonuclear dipolar Hamiltonian once again,

$$\hat{\mathcal{H}}_{II} = \sum_{k<l} b_{kl} \left[ 3I_{kz}I_{lz} - \mathbf{I}_k \cdot \mathbf{I}_l \right]. \quad (17.16)$$

Let us apply a strong rf field of amplitude $\omega_1 = \gamma I B_1$ and frequency $\omega_{rf}$. 

References:
3) C.P. Slichter, Principles of Magnetic Resonance, pp 384
with

\[ \omega_k = \omega_{0k} - \omega_{r.f}. \]  

(17.17)

Transforming the coordinates of \( I_{kz}, I_{lz}, \) and \( I_{l} \) into the \( z' \) and \( x' \) reference frame, we get

\[
I_{kz} = I_{kZ} \cos \theta_k - I_{kX} \sin \theta_k = Z_k c_k - X_k s_k
\]

\[
I_{kx} = I_{kX} \cos \theta_k + I_{kZ} \sin \theta_k = X_k c_k + Z_k s_k
\]

\[
I_{ky} = I_{kY} = Y_k
\]

(17.18)

Thus the Hamiltonian above can be rewritten in this
new frame as:

\[
\hat{\mathcal{H}}_{II} = \sum_{k<l} b_{kl} \left[ 2I_{kz}I_{lz} - I_{kx}I_{lx} - I_{ky}I_{ly} \right]'
\]

\[
= \sum_{k<l} b_{kl} \left[ 2(Z_k c_k - X_k s_k)(Z_l c_l - X_l s_l) 
- (X_k c_k + Z_k s_k)(X_l c_l + Z_l s_l) - Y_k Y_l \right]
\]

\[
= \sum_{k<l} b_{kl} \left[ 2(Z_k Z_l c_k c_l - X_k Z_l s_k c_l 
- Z_k X_l c_k s_l + X_k X_l s_k s_l) - (X_k X_l c_k c_l 
+ Z_k X_l s_k c_l + X_k Z_l c_k s_l + Z_k Z_l s_k s_l) 
- Y_k Y_l \right]
\]

Putting like terms together yields:

\[
\hat{\mathcal{H}}_{II} = \sum_{k<l} b_{kl} \left[ (3Z_k Z_l - \mathbf{I}_{k'} \cdot \mathbf{I}_{l'}) \right]
\]

\[
* \frac{1}{2} (3c_k c_l - 1) - (2Z_k Z_l - \mathbf{I}_{k'} \cdot \mathbf{I}_{l'})
* \cos(\theta_k - \theta_l) - 1 \right] + ...
\]

(17.20)

where the terms that are not written out (...) are non-secular terms (recall the definition from previous
chapters). Thus applying sufficiently large fields \( \omega_{k,\text{eff}} \) allows us to neglect these non-secular terms and one is left with

\[
\hat{\mathcal{H}}_{II} = \sum_{k<l} b_{kl} [(3I_kZ I_lZ - \mathbf{I}_k' \cdot \mathbf{I}_l') - \frac{1}{2} (3 \cos \theta_k \cos \theta_l - 1) - (2I_kZ I_lZ - \mathbf{I}_k' \cdot \mathbf{I}_l') (\cos(\theta_k - \theta_l) - 1)]
\]  

(17.21)

Thus picking \( \theta_k = \theta_l = 54.7 \), the dipolar Hamiltonian becomes zero.

\[
\hat{\mathcal{H}}_{II} = 0.
\]  

(17.22)