3.7.2. Choosing the Right Contact Time

The contact time (or just contact for short) is the time during which the r.f. fields are applied simultaneously in a CP experiment - see figure 3.5.1. Choosing a contact time is best done after finding the right recycle delay, so that the effect of saturation does not obscure the effect of changing the contact time. If we are simply interested in generating the spectrum with the highest signal-to-noise ratio, choosing the contact is easy. It is just a matter of recording test spectra as a function of the contact time and choosing the one that gives most signal. It is easy if the spectrum contains just one signal or if all the signals behave in the same way. If they do not then you either have to record a series of spectra or use a compromise value that shows best the features you are interested in.

This example, from an H to Si CP experiment, comes from an organically modified silicate. While the signals do behave differently the choice of contact, if we just want a spectrum that shows us what species we have present, is relatively easy to make: 5 ms here. It also beautifully illustrates the folly of reading too much into the relative intensities from a single CP spectrum!

Remember that you are putting the probe under more electrical strain if you use a long contact so you might have to reduce the field strengths if you do want to use a long one (greater than 10 ms, say, although it is relatively rare to need - or be able to use - a contact greater than this). In terms of obtaining a spectrum this is all there is to learn about the contact time. However, it is useful to know how and why the contact time varies, which is what the rest of this section deals with. See also the hint at the end of the section.

For a low-abundance nucleus (\(^{13}\)C, \(^{15}\)N or \(^{29}\)Si for example) or an effectively dilute spin (such as \(^{31}\)P in many cases) the contact time dependence of the signal can be described by the following equation.

\[
S_t = S_0 \lambda^{-1} \left[ 1 - \exp \left( -\frac{\lambda t}{T_{XH}} \right) \right] \exp \left( -\frac{t}{T_{lp}^H} \right) \quad \text{where} \quad \lambda = 1 + \frac{T_{XH}}{T_{lp}^X} \cdot \frac{T_{lp}^X}{T_{lp}^H}
\]

\(1/T_{XH}\) is the cross-polarisation rate, \(T_{lp}^X\) is the spin-lattice relaxation time of the X nuclei in the rotating frame (under \(^1\)H decoupling) and \(T_{lp}^H\) is the proton spin-lattice relaxation time in the rotating frame.

It is usual to make some simplifying assumptions so that \(\lambda \sim 1\), then.

\[
S_t = S_0 \left[ 1 - \exp \left( -\frac{t}{T_{XH}} \right) \right] \exp \left( -\frac{t}{T_{lp}^H} \right) \quad \ldots \ldots B
\]
We have assumed here that the CP is from "H. The signal dependence on contact time can then often look like this. Here, T_{XH} is 0.5 and 3.5 ms and T_{H}^{1H} is 7.5 and 12.0 ms for (a) and (b) respectively. Note, again, the deceptive intensities, these curves are for a 4:3 (a:b) population ratio.

Each curve has a rise time determined by T_{\text{nr}}. This rise is particularly dependent on the strength of the coupling between X and H so anything that lessens this (distance or motion for example) will reduce the CP rate. There is a real example of this later in the section. At the same time as the signal buildup, the "H magnetisation available for CP is reduced through T_{H}^{1H} - this causes the eventual decay in the CP signal.

Inspection of equation B suggests that we have a method of quantifying CP spectra (by obtaining S_0). And, indeed, we do - in principle. We can either obtain an array of spectra as a function of contact time and fit the intensities to equation B, to give us S_0, T_{XH} and T_{H}^{1H}. Or, we can plot log_i(intensity) and find the zero time intercept by projecting the long time behaviour. In both cases, though, it is essential to use integrated intensities so that differences in linewidth do not influence the result and to take into account any spinning sidebands.

To illustrate the analysis of the contact time behaviour we will look again at the result for the modified silicate shown on the previous page. The full array consisted of 13 values. The signal as a function of the contact time for three of the signals is shown in the plot below. The solid lines are the fit to equation B. In each case we get a reasonable representation of the experimental data. The numerical values generated from the fitting are shown in the table and the notation used to describe the signals is explained on the next page.
There are several observations we can make about this result. The intensity values are close to those that come from a quantitative direct-polarisation experiment (the separate column labelled “DP”). However, there is still a significant difference in \( Q^4 \) compared to the DP result (1.17 by CP, 1.46 by DP). This is always likely to be biggest source of error in a “quantitative” CP measurement. It is feasible that nuclei very far from a proton do not cross-polarise at all and therefore do not contribute to the spectrum. It is worth noting that the CP experiment took 5 hours and the DP one 16 hours, although for a case where both experiments are feasible the “safe” option is the DP experiment even if it takes longer. The \( Q^4 \) environment is also the slowest to cross-polarise (\( T_{SH} = 4.7 \) ms) because it is further from a proton than any other environment. Perhaps, surprisingly, its \( T_1^H \) value is also significantly longer than for any of the other species. Unless the CP signal for the \( Q^4 \) environment originates from protons that have no association with other environments (which is hard to believe) this observation is difficult to understand. It suggests that our relatively simple treatment of the CP behaviour may not be properly applicable in this case. Whatever the cause, it illustrates some of the problems that can be encountered with CP experiments used in this way. Of course, we could remove the simplifying assumptions we made to produce equation B and reintroduce \( T_1^H \). That then means we have to fit our data to an extra variable which is probably equally fraught with uncertainty, especially given that we have only 13 data points in this case!

**Other things to be aware of in CP experiments**

Even if we treat our data with the full equation given earlier, it does not mean we can accurately reproduce the contact time behaviour. For example, there are circumstances when we can observe oscillations in the first part of the curve. This can happen when the “abundant” nucleus is relatively isolated so is only weakly coupled (if at all) to neighbouring like nuclei. Analysing the CP curve in a different way in these circumstances can give accurate information on the H-X (or F-X) separation.

Cross-polarisation relies on the dipolar coupling between the abundant nuclei to make it efficient and it is possible to experience difficulties in obtaining CP spectra in systems where such nuclei are relatively dilute.

The whole treatment of the CP process in this section has worked on the assumption that the CP is from an abundant spin to a low natural abundance X spin. Do not expect the same theory to work for CP between H and F (the theory for that is much more complicated) or for CP between two spins X and Y neither of which is H (or F). In both of these cases the CP experiment tends to be used to establish the relationship between spins or as a filter, rather than for sensitivity enhancement. Nevertheless, optimising the contact is still straightforward - vary it until you get most signal.

Finally, if you get a chance to check the contact time behaviour - make a careful note of it. For example, when working with a pure, nitrogen-containing organic, its usually easy to determine the signal behaviour as a function of contact time for the carbon. Because the proton source for H to C CP is usually effectively the same as that for H to N CP, the behaviour for carbon gives you a good clue as to the contact time to use for \(^{15}\)N - given that the latter signal will probably have too low an intensity to optimise separately. For \(^{15}\)N we find that we get the best spectra when \( T_1^H \) is long (so when there is signal in the carbon spectrum at long contact times).