

Practicum 4, Spring 2005

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Selective 1 d methods using simple square pulses and shaped pulses.
Strychnine with Acac in CDC13.

Quick good-citizen notes:

Saving files to diskette: open two file manager windows, drag and drop. Do this often, you can use PC formatted diskettes.

If you have collected a spectrum using continuous decoupling, please turn off the decoupler before logging out.

Set up

Lock, shim, calibrate pw90 at $tpwr=60, 54, 48$. Choose a good gain, sw and at for your sample.

Note that if the gain is too high you may 'clip' off the top of the FID. Because this has the effect of making the FID look square, the FID's Fourier transform takes on the appearance of sinc-shaped lines. You will see ripples, or fuzz at the base of all resonances, but most visibly at the bases of strong ones. You can display the FID **df** to look for clipping, or use of **ddff(1)** to see if data points are approaching but not exceeding 32k.

Another source of similar 'feet' on signals is truncation of the FID with too short an at. This has the same effect because it too makes the FID look a bit square. You can use linear prediction to extend the FID and then a weighting function to decrease the contribution of the calculated points to the final spectrum. This will have the dual benefit of eliminating the feet (hence the name 'apodization' functions for weighting functions), while increasing the spectral resolution obtained from that data set.

(note that you can always increase digital resolution by 'zero filling' or increasing the number of points in the frequency domain.)

Linear prediction (lp)

parlp creates the parameters for a 1D, **parlp(1)** for first indirect, etc.

dglp displays them.

You can use backward lp to fix early points, forward lp to extend the FID and mitigate the effects of the weighting function. The latter is especially important for 2Ds and higher, where you may only be able to collect relatively few points in the indirect dimension (ni complex, see later), and therefore may have a severely truncated interferogram in t1 (later). Set **proc = 'lp'** to activate linear prediction. (or **proc1 = 'lp'**) Set **proc = 'ft'** to inactivate linear prediction, **proc** stands for processing.

parameters you might change include:

lpopt	f or b.	forwards or backwards
lpfilt	8 to 64 <u>at most</u> .	≈ the number of signals in terms of which the FID should be simulated, 8 is good for a typical 2D's indirect dimension whereas a typical 1D might be dominated by 10 - 30 strong signals. <u>lpfilt</u> must be $\leq 0.5 * \text{lpnupts}$.
lpnupts	<u>ni</u> to <u>512</u> .	The number of complex points in the direct dimension is $\text{np}/2$, so this is your upper limit in 1-d linear prediction. For linear prediction in multi-d spectra, use all <u>ni</u> indirect dimension complex points. <u>lpnupts</u> must be $\geq 2 * \text{lpfilt}$, at least, and it is better to use 4* or more.
strtlp	For forward prediction, use <u>lpnupts</u> (1d work) or <u>ni</u> (multi-d) For backward LP, use the first good point (look at the FID to see when the good points start).	

When linear predicting backwards the reference point is the point separating later (good) points which will be used as the basis for the lp and the earlier points which will be replaced (recreated).

When linear predicting forwards the reference point is the last point in the (indirect) FID that will be used as the basis for the LP, since all the preceding points will be the basis for the lp.

lpext $\underline{ni} - 3*\underline{ni}$ or the number of bad points.

When linear predicting backwards, use either strtlp-1 (replace just bad points) or strtlp (to replace strtlp with the fitter version too), a matter of taste.

When linear predicting forward you can add as many calculated points as you want, but it is common to add \underline{ni} or $\underline{np}/2$, to 'double' your dataset, or add $2\underline{ni}$ or \underline{np} , to triple it.

strtext For backward LP, use strtlp or strtlp-1 as decided above.

For forward LP, in 1-d spectra, use $\underline{np}/2 + 1$ for 1d spectra (the first calculated point comes right after the last data point, and points are complex points hence the $\underline{np}/2$). For multi-d forward LP use $\underline{ni}+1$. This is the first point (in the direction b or f) which will be replaced by the lp value).

fn $\geq 2*(\underline{lpext}+\underline{np}/2)$ or $\geq 2*(\underline{ni} + \underline{lpext})$, rounded up to the next power of 2.

The 'Fourier number' is the number of points used for your spectrum after Fourier transformation. This will determine the digital resolution, the number of Hz per point. Since you would like digital resolution better or equal to your spectral resolution (that is to say a smaller number of Hz / point), make fn large enough that the digital resolution is a smaller number than 1/2 your sharpest line's width at half height.

These values can be checked on a line by placing the cursor on the line and typing **dres**. You don't need to collect new data if fn is too small, just increase it and Fourier transform again (**wft**).

Example, for a 1-d spectrum, collected with $\underline{np} = 728$ and $\underline{at} = .1$

$\underline{lpopt} = f$, $\underline{lpfilt} = 16$, $\underline{lpnupts} = 364$, $\underline{strtlp} = 364$, $\underline{strtext} = 365$. This doubles the FID, so \underline{gf} was reset from $\underline{gf} = 0.05$ to $\underline{gf} = .1$ (double the window function to go with the doubled FID).

**Note about LP up to a power of 2 instead of zero filling, use appropriate factor extension of \underline{gf} .

DO NOT FORGET TO SET **proc** = '**lp**' in order to implement linear prediction.

Amplifier linearity: a 6 db decrease in amplifier power should require a pulse 2* as long to achieve the same tip angle. For example if the $\underline{pw90}$ at $\underline{tpwr} = 51$ is 25 μs , the $\underline{pw90}$ at $\underline{tpwr} = 45$ should be 50 μs . It is convenient to work in the linear regime when possible, this allows calculation of desired pulse widths, instead of tedious recalibration at all the powers of for all the pulse lengths to be used. A 1 db decrease in power increases $\underline{pw90}$ by a factor of 1.12. The reason we care is that we may need to use a long pulse to achieve selectivity.

Selectivity: a second incidence of the inverse relation between the time domain and the frequency domain. The longer the pulse, the narrower its excitation profile. Example of 180° pulses of different lengths. Next week we will see how a composite pulse can provide improved band width, especially for 180° pulses.

You can array tof to visualize a pulse's excitation profile.

Thus, for selective decoupling, we will use long pulses and low power. Set homo = 'y', dn = 'H1' (or whatever nucleus you are observing). Collect a 1D, set cursor on line to be decoupled, type **sd**, use two cursors to measure the splitting to be covered by the selective decoupling. For waltz decoupling (dmm = 'w') you will need **dmf** = 2* **delta** and therefore an effective decoupler $\underline{pw90}$ of $1/\underline{dmf}$ in μs . Equivalently, decoupler $\underline{pw90} = 1000,000/2*\underline{delta}$, or 35.7 ms to decouple a line split by 28 Hz. Calculate the dpwr required to satisfy this condition using the 6 db rule and set dmf to 28. Try a couple of dpwr / dmf combinations to optimize the

completeness of decoupling (do not use too much power, keep $dpwr < 20$) in combination with the selectivity (improved by low power). You can do continuous on-resonance decoupling with dmm set to 'c'. Note that this is by definition narrow-band decoupling and 'on resonance' is set at the frequency dof.

Selective inversion pulse

Recall the parameter set 'selinv' using the `load` button. You will need to update the pulse widths to ensure that the p1 pulse really is a 180 degree pulse at the power used. Also update tof, sw, pw, tpwr. The longer the duration of the inversion pulse, the more selective it is. Note that when you are using a simple 'square' pulse, the inversion pulse is delivered at the carrier frequency tof. This means it is centered there. You can, however, choose tof to be right on the resonance you want to invert. Just be sure that your sw is adequate so that the entire spectrum is still collected properly without folding.

The making of shaped pulses is described in the next exercise.