Processing Techniques

There are two very useful forms of pre-processing that can be applied to a FID before Fourier transformation, allowing one either to improve signal-to-noise at the expense of resolution or to improve resolution at the expense of signal-to-noise. They both act by altering the shape of the "envelope" of the FID, which corresponds, after transformation, to an alteration in the line-shape of the resonances.

Exponential multiplication

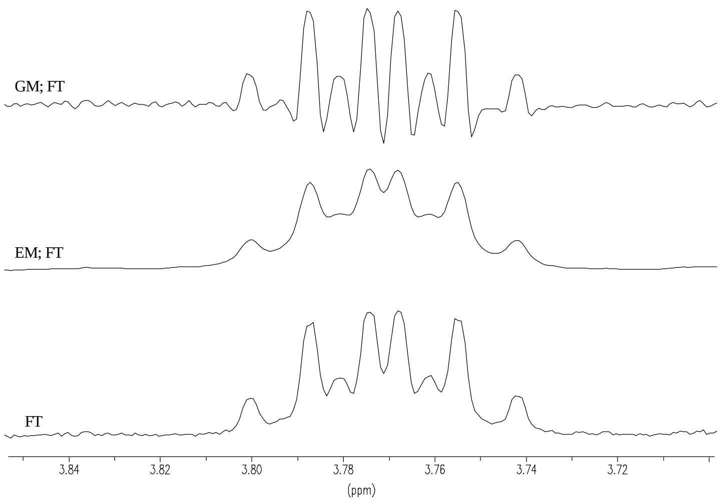
This is the technique aimed at improving the signal-to-noise ratio. This tends to be applied routinely for nuclei other than protons where noise can be significant, such as ^{13}C, but can also be beneficial for noisy ^{1}H spectra. The principle used is that, as the signal decays through the course of a FID the early parts contain a smaller proportion of noise than do the later ones. Therefore multiplying the FID by a function that starts at one then falls toward zero, thereby emphasising the beginning of the FID at the expense of the end, should improve signal-to-noise. This is indeed so, the function used in practise being a falling exponential (hence the name). The second effect of this multiplication is that the "time constant" (the T_2* to use jargon) of the FID, which is itself an exponential, is reduced. The line-width after transformation is proportional to $1/T_2$*, so this corresponds to a broadening of the line. To use exponential multiplication one specifies the line broadening that can be tolerated using the LB command (broadening is specified in Hz; a good value to use is the digital resolution of the spectrum as shown on the parameter display in Hz/pt) and then type EM followed by FT (or EF to do both). Trial and error may be needed to discover the optimum value for LB.

Gaussian multiplication

This is the technique aimed at improving the resolution by emphasising the later parts of the FID at the expense of the beginning. However, a rising exponential would not be a good function to use, as it would strongly emphasise the very end of the FID, which contains more noise, so instead some function is used which first rises then falls. The function commonly used is the Gaussian. This is controlled by two parameters, LB again, except with a negative value as this time the line is being narrowed, and GB. GB controls the point where the function begins to descend, and is expressed as a (decimal) fraction of the total length of the FID. You can make a guess at the GB by checking where the FID seems to disappear into noise and expressing this as a fraction of the total length (this is easily read off the grid on the screen). Suitable values are usually between 0.05 and 0.5, and represent a compromise between the best resolution (obtained with a large GB) and not excessive increase in the noise. GB also affects the extent to which line-shapes are distorted by "ringing", a side-effect of Gaussian multiplication - the smaller the GB the less ringing appears.

The best value for LB is determined by the original width of the lines in the basic spectrum. It is usually between -0.5 and -1.5 for proton spectra, but may increase to as much as -10 in exceptional cases. In general the optimum combination of GB and LB will be different for different groups of lines in the spectrum. For instance the solvent lines, which are usually very sharp to start with, can be reduced to a spike with a small degree of enhancement (e.g. LB = -0.5, GB = 0.2) whereas to resolve the "envelope" of a cyclohexyl group into individual lines may require very severe treatment (e.g. LB = -5.0, GB = 0.4). Once again experiment is required to obtain the correct combination.

With experience one or two attempts will usually be enough to obtain reasonable values; experience in doing this is well worth acquiring as the method is extraordinarily powerful. For spectra with sufficient signal-to-noise the only limit on resolution is normally the digital resolution (Hz/pt) determined by SW and SI; unhopeful looking amorphous lumps can often be resolved into nice groups of sharp lines with a little perseverance.



The spectra above illustrate the effects of the window functions. The first spectrum results from a Fourier transfrom alone. The second arises from exponential multiplication of the FID corresponding to 1 Hz line broadening (LB= 1.0) prior to the FT which results in the required reduction of noise but also an increase in line-width. The third arises from Gaussian multiplication of the FID with LB= -2.0 and GB= 0.2; note the desired increase in resolution but also the unwanted increase in noise.