The Fourier transform, 2D NMR, and non-uniform sampling – *Mohammadali Foroozandeh*

Lecture 4: Nuclear Magnetic Resonance – Theory and Techniques

Reference:

Understanding NMR Spectroscopy, James Keeler, Wiley

http://www-keeler.ch.cam.ac.uk/lectures/

Objectives

The goal is **i)** to have some insights about the structure of NMR signal and the process of Fourier transform in 1D and 2D, **ii)** to get familiarized with some acquisition / processing tricks to improve the quality of acquired data and to make the information contained in the NMR signal more accessible, and **iii)** to have an idea about one of the methods used for speeding up multi-dimensional NMR experiments.

1D data

The simplest NMR experiment is a single-pulse excitation. In contrast to many other kinds of spectroscopy, where signal is detected as a function of frequency, in pulsed NMR spectroscopy, the signal is detected as a time-domain response.

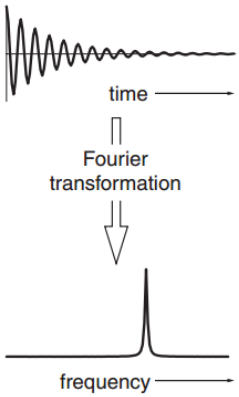


Fig. 1 The Fourier transform is a mathematical process which turns a time-domain signal, the FID, into a frequency-domain signal, the spectrum.

We can imagine the acquired FID as a decayed complex exponential, which is simply a combination of two components (x and y or real and imaginary or sine and cosine parts).

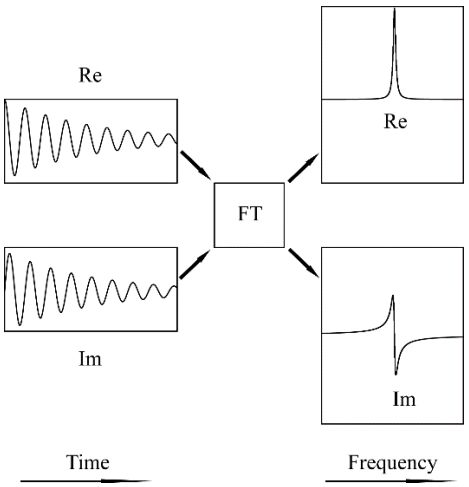


Fig. 2 Illustration of the absorption and dispersion mode Lorentzian lineshapes. Whereas the absorption lineshape is always positive, the dispersion lineshape has positive and negative parts.

Like the time-domain signal the frequency domain signal has a real and an imaginary part. The real part of the spectrum shows what we call an absorption mode line, in fact in the case of the exponentially decaying signal the

line has a shape known as a Lorentzian, or to be precise the absorption mode Lorentzian. The imaginary part of the spectrum gives a lineshape known as the dispersion mode Lorentzian.

Acquisition, processing remarks

1) **Sensitivity enhancement**: Inevitably when we record a FID we also record noise at the same time. Some of the noise is contributed by the amplifiers and other electronics in the spectrometer, but the major contributor is the thermal noise from the coil used to detect the signal. Reducing the noise contributed by these two sources is largely a technical matter which will not concern use here. NMR is not a sensitive technique, so we need to take any steps we can to improve the signal-to-noise ratio in the spectrum. We will see that there are some manipulations we can perform on the FID which will give us some improvement in the signal-to-noise ratio (SNR). The FID decays over time but in contrast the noise is constant. Therefore, if we carry on recording data for long after the FID has decayed we will just measure noise and no signal. The resulting spectrum will therefore have a poor signal-to-noise ratio, since the Fourier transform of noise is noise.

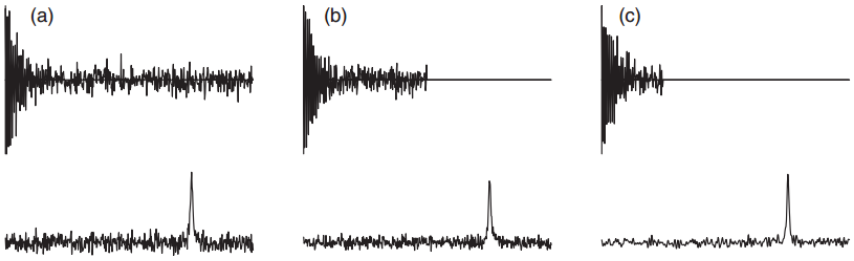


Fig. 3 Illustration of the effect of the time spent acquiring the FID on the signal-to-noise ratio (SNR) in the spectrum. In (a) the FID has decayed to next to nothing within the first quarter of the time, but the noise carries on unabated for the whole time. Shown in (b) is the effect of halving the time spent acquiring the data; the SNR improves significantly. In (c) we see that taking the first quarter of the data gives a further improvement in the SNR.

This effect can also be exploited by deliberately multiplying the FID by a function which starts at 1 and then steadily tails away to zero. The idea is that this function will cut off the later parts of the FID where the signal is weakest, but leave the early parts unaffected. (**Fig 4.**)

2) **Resolution enhancement**: Sometimes we need to enhance resolution at a cost in sensitivity. A weighting function designed to improve the SNR inevitably leads to a broadening of the lines as such a function hastens the decay of the signal. Here we will consider the opposite case, where the weighting function is designed to narrow the lines in the spectrum and so increase the resolution. This is done by introducing a new weighting function made of a rising exponential and a decaying Gaussian. This process is known as Lorentz-to-Gauss transform.

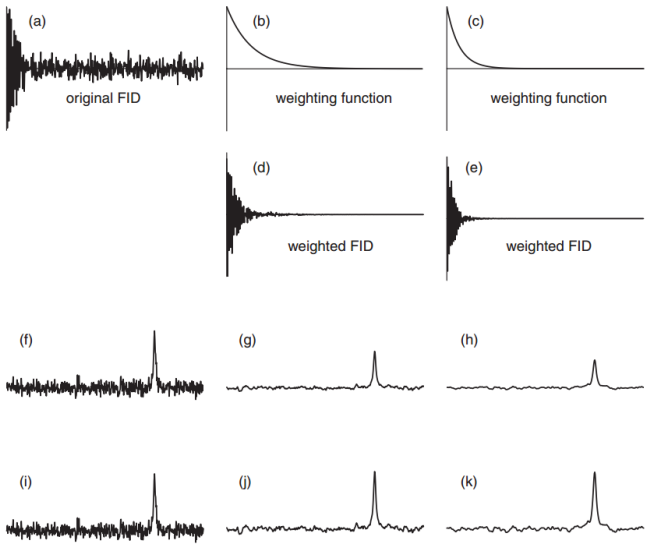


Fig 4. Illustration of how multiplying a FID by a weighting function can improve the SNR. The original FID is shown in (a) and the corresponding spectrum is (f). Multiplying the FID by a weighting function (b) gives (c); Fourier transformation of (c) gives the spectrum (g). Multiplying (a) by the more rapidly decaying weighting function (d) gives (e); the corresponding spectrum is (h). Spectra (f) – (h) are plotted in (i) – (k) but this time normalized so that the peak height is the same; this shows most clearly the improvement in the SNR.

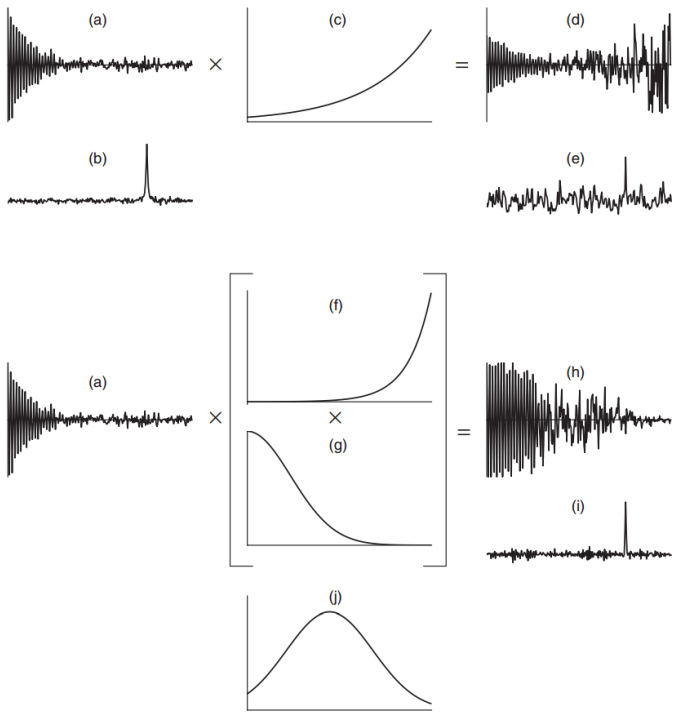
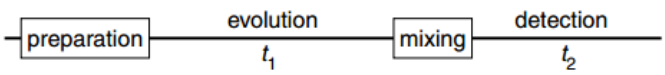


Fig 5. Illustration of the use of weighting functions to enhance the resolution in the spectrum. Fourier transformation of original FID, (a), gives the spectrum (b). If (a) is multiplied by the rising exponential function plotted in (c), the result is the FID (d). Fourier transformation of (d) gives the spectrum (e); the resolution has clearly been improved, but at the expense of a large reduction in the SNR. The original FID (a) is multiplied by the rising exponential (f) and the decaying Gaussian (g); this gives the time-domain signal (h). Fourier transformation of (h) gives the spectrum (i); the resolution has clearly been improved when compared to (b), but without too great a loss of SNR. Plot (j) shows the product of the two weighting functions (f) and (g).

2D NMR

In one-dimensional pulsed Fourier transform NMR the signal is recorded as a function of one time variable and then Fourier transformed to give a spectrum which is a function of one frequency variable. In two-dimensional NMR the signal is recorded as a function of two time variables, t_1 and t_2, and the resulting data Fourier transformed twice to yield a spectrum which is a function of two frequency variables. The general scheme for two-dimensional experiment can be represented as:



In the first period, called the preparation time, the sample is excited by one or more pulses. The resulting magnetization is allowed to evolve for the first time period, t_1. Then another period follows, called the mixing time, which consists of a further pulse or pulses. After the mixing period the signal is recorded as a function of the second time variable, t_2. This sequence of events is called a pulse sequence and the exact nature of the preparation and mixing periods determines the information found in the spectrum.

The process of 2D Fourier transform is not as straightforward as in 1D. The resultant signals in the frequency-domain spectrum can acquire different types of lineshapes, desired (double absorption or double dispersion) or undesired (phase twist). As we see in the future lectures in some experiments a certain combinations of data sets are required to have access to the spectra with desired signal lineshapes.

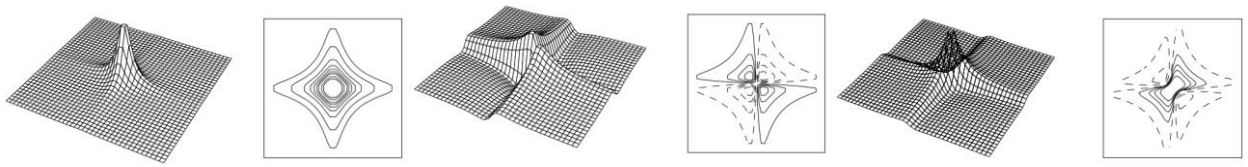


Fig 6. Illustration of possible lineshapes in a 2D spectrum, left: double absorption, middle: double dispersion, and right: phase twist.

Non-Uniform Sampling

Any multi-dimensional NMR spectrum is made of a series of 1D spectra, i.e. any additional dimension multiplies the experiment time of a single 1D experiment by the number of points (increments) in that dimension, e.g. a 2D experiment with 64 points along t_1 is 64 times longer than a single 1D experiment. Therefore methods which speed up multi-dimensional experiments are of great interest in NMR spectroscopy. One the most successful methods to date, is non-uniform sampling (NUS), which aims at producing high-resolution data using sampling part of data points instead of all possible points. The simplest version of this method is non-uniform sampling of the second dimension of a 2D experiment.

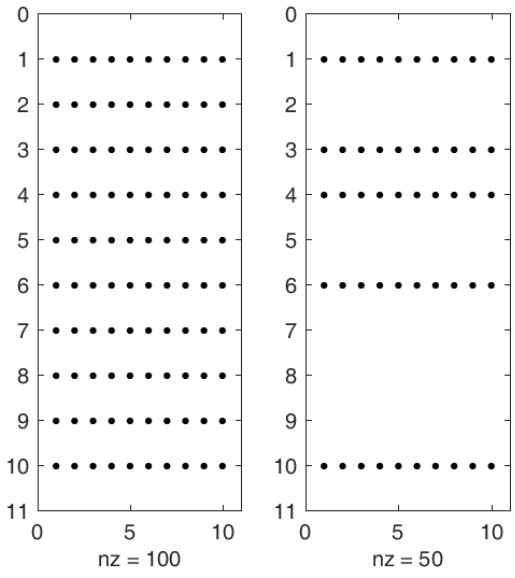


Fig 7. Illustration of a random non-uniform sampling by 50% of data points in the second dimension of a 2D data.

Since Fourier transform can only be applied on uniformly sampled data, an alternative method is used to reconstruct the missing points.