An NMR spectrum is produced by performing a Discrete Fourier Transform (DFT) on a series of time domain data points, measured with a particular gap between each point. It does not matter to the DFT whether the points have been collected in “real time” or if the series of points have been indirectly constructed. This fact is the basis for two dimensional (2D) NMR experiments where one dimension is collected in the usual direct manner and a second dimension is constructed in a stepwise manner.

The blocks associated with a 2D NMR experiment are shown in figure 1. In the first step the nuclei are excited with RF pulses to generate a non-equilibrium state. This state is allowed to evolve for a time $t_1$ in step two, before being subjected to further RF manipulation in step three. Finally an NMR signal is recorded. This process is repeated $N$ times with the value of $t_1$ being incremented each step, such that the final data is an array of $N$-nmr signals differing only through the effect of the evolution in step 2. This array can be Fourier transformed with respected to the time $t_2$ and $t_1$ to produce a 2D spectrum.

**COSY**

Correlation Spectroscopy, or COSY as it is commonly referred to, is an NMR experiment that correlates the chemical shifts of spins that share a mutual J-coupling. The J-coupling is the interaction between nuclei that is mediated through chemical bonds. In general this coupling gets weaker as two hydrogen nuclei are separated by an increasing numbers of bonds. As a result, the $^1$H COSY spectrum correlates hydrogen nuclei on adjacent carbons or, in the case of multiple bond carbons, the next nearest carbons. The method is most commonly used to determine the underlying structure of the carbon back bone in an organic molecule. A COSY spectrum should be symmetrical about a diagonal running from the top right to bottom left (figure 3).

The COSY experiment is demonstrated using ethyl crotonate.

![Molecular structure of ethyl crotonate showing groups that share mutual J-coupling. The blue circles are the ethyl group and the red circles are the crotonate group, the peaks related to these groups are highlighted in figure 4.](image)

**Figure 2:** Molecular structure of ethyl crotonate showing groups that share mutual J-coupling. The blue circles are the ethyl group and the red circles are the crotonate group, the peaks related to these groups are highlighted in figure 4.
All signals that appear in the 1D spectrum will show a peak along this diagonal. The cross-peaks (off diagonal peaks) show which hydrogens share a J-coupling through the correlation between the two chemical shifts. In figure 4 the correlation between the -CH$_3$ and -CH$_2$- $^1$H chemical shifts in the ethyl group, are shown in the right hand plot. The left hand plot shows the correlation network between the two olefinic (–CH=) hydrogens and the terminal –CH$_3$ of the crotonate group. In this portion of the molecule all hydrogens are coupled and thus cross peaks are seen between all three chemical shifts.

**Figure 4:** Expanded regions of the COSY spectrum showing the ethyl region of the spectrum (below right) and the crotonate region (below). The diagonal peaks are highlighted as dashed circles and the cross peaks are highlighted with full circles.

(a) Full COSY spectrum.

(b) Crotonate correlations from COSY spectrum.

(c) Ethyl group correlations from COSY spectrum.