

COSY (COrrrelation SpectroscopY)

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This experiment is one of the most commonly used among the 2D NMR tools in structure elucidation by synthetic chemists. There is a variety of COSY experiments in the literature [1,2,3]. In our lab most often used is the double quantum filtered version with or without gradients.

DQFCOSY (Double Quantum Filtered) COSY.

The experiment uses double quantum transition to filter out protons that does not experience J-coupling. This simplifies a spectrum, especially when a complex structure is characterized. Also, an experiment can be run as phase sensitive. The pulse sequence is very simple and look like this:

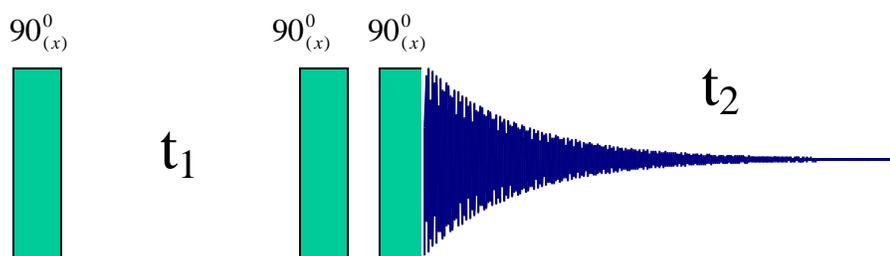
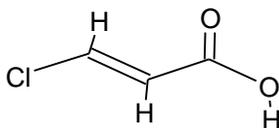


Figure. 1. The DQF COSY pulse sequence.

Since the experiment involves double quantum transitions it is rather impossible to draw an accurate pictorial evolution of magnetization during the whole pulse sequence. To explain COSY let's consider a two spin AX system e.g. cis-3-Chloroacrylic acid



that has the following spectrum:

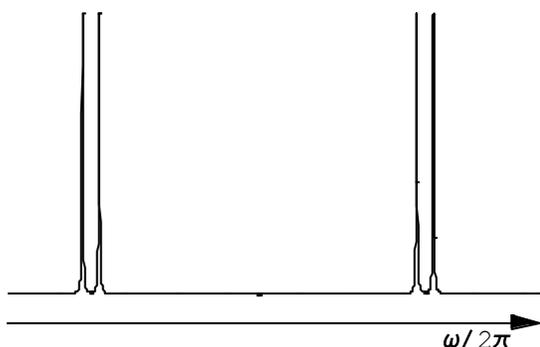


Figure 2. The spectrum of cis-3-Chloroacrylic acid. The two protons create four different energy levels due to chemical shifts and J-coupling interactions.

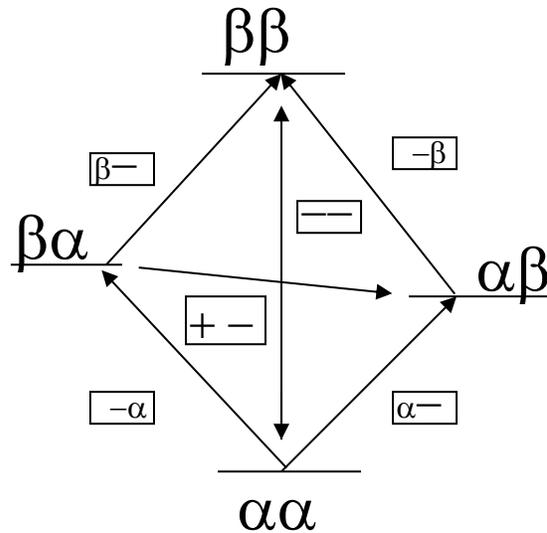


Figure 3. The energy level for the AX system.

According to convention, spin α depicts a spin parallel to the magnetic field \mathbf{B}_0 and β is antiparallel. Therefore, the spin β has a higher energy. The complete description energy of such a spin contains a chemical shift interaction and might be expressed by the formula:

$$H = \hat{I}_{1z} \omega_1 + \hat{I}_{2z} \omega_2 + 2\pi J_{12} \hat{I}_{1z} * \hat{I}_{2z}$$

where: ω_1 and ω_2 are the Larmor frequencies of spin1 and spin 2, respectively. J_{12} is J-coupling constant. $\hat{I}_{z1}, \hat{I}_{z2}$ are the spin angular momentum operator. As we can see we

have a product of operators $2 \hat{I}_{1z} * \hat{I}_{2z}$. This complicates pictorial explanation of the experiment. To explain the picture of the COSY in details the density matrix and product operators need to be used. Since this is not the scope of this description, interested users who like to understand this experiment in more detail might look for further reading (1,2,3). Simply speaking, the first pulse creates single quantum coherences: $[\beta-], [-\beta], [\alpha-], [-\alpha]$. Each of the coherences has a conjugated pair. Single quantum means $\Delta m = \pm 1$, where m is the I_z spin angular momentum number. The coherences evolve during the t_1 period of time (Fig.1) making amplitude modulation of free induction decay. This produces the second dimension of the 2D DQF COSY spectrum. After t_1 the second pulse is applied and transfers coherence from one spin to all others. So, we have here a complex situation

where each spin transfers coherence to all the others showing the results in term of modulation in the second dimension. The double $\boxed{++}$ $\Delta m = \pm 2$ and zero $\boxed{+-}$ $\Delta m = \pm 0$ quantum coherences are created. Again each of these coherences has their conjugated. The interesting feature is that they can not be observed. Application of the third pulse is converting them back into single quantum coherences. Thanks to the double quantum coherence these peaks on the diagonal which does not share a J-coupling are removed from the spectrum by proper phase cycling, simplifying interpretation. Also, the solvent peaks are decreased significantly. The phase sensitive 2D spectrum of the above molecule is as follows:

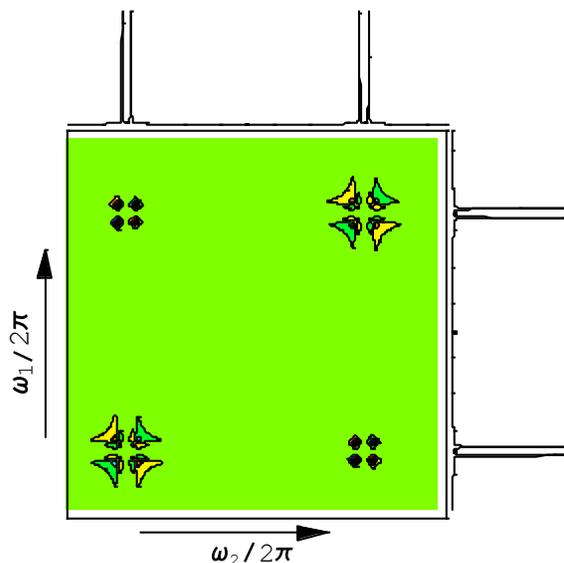


Figure 4. The DQFCOSY of cis-3-Chloroacrylic acid.

The cross peaks are below diagonal and their mirror image above. The particular coherences are making resonances as follows:

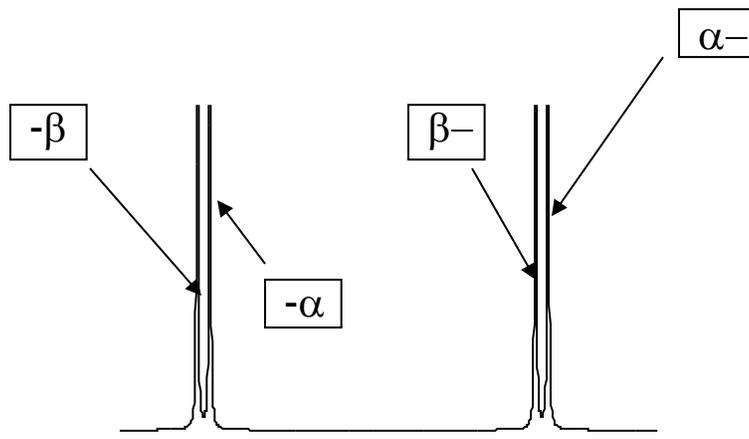


Figure 5. The coherences and spectrum.

The pairs of coherences $[\alpha-], [\beta]$ or $[-\alpha], [\beta-]$ are called progressive and $[\alpha-], [-\alpha]$ or $[\beta-], [\beta]$ are regressive. Coherences $[\beta], [-\alpha]$ or $[\beta-], [\alpha-]$ are called parallel.

The DQF COSY can be run in phase sensitive mode. The diagonal peaks and cross-peaks generated by parallel coherences transfer can be phased as both dispersive. The progressive and regressive cross-peaks are both absorptive and differ by 180° .

[DQFCOSY experiment setup.](#)

COSY45

A simple sequence with two pulses is used to obtain the COSY 45 spectrum. The second pulse might vary between 20° - 90° . Setting this pulse to 45° will decrease the intensity of parallel transitions significantly. This will simplify appearance close to diagonal interpretation otherwise impossible because of the overlap of peaks. COSY 45 is run in magnitude mode so no phasing is necessary.

[COSY45 experiment setup.](#)

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Further reading.

1. Ernst R.R., Bodenhausen B., and Wokaun, A., "Principles of Nuclear Magnetic Resonances in One or Two Dimensions" Oxford University Press, 1992
2. Malcolm. H. Levitt, Spin Dynamics, John Wiley & Sons Ltd., 2001.
3. Freeman, R., "Spin Choreography", Oxford University Press, 1998