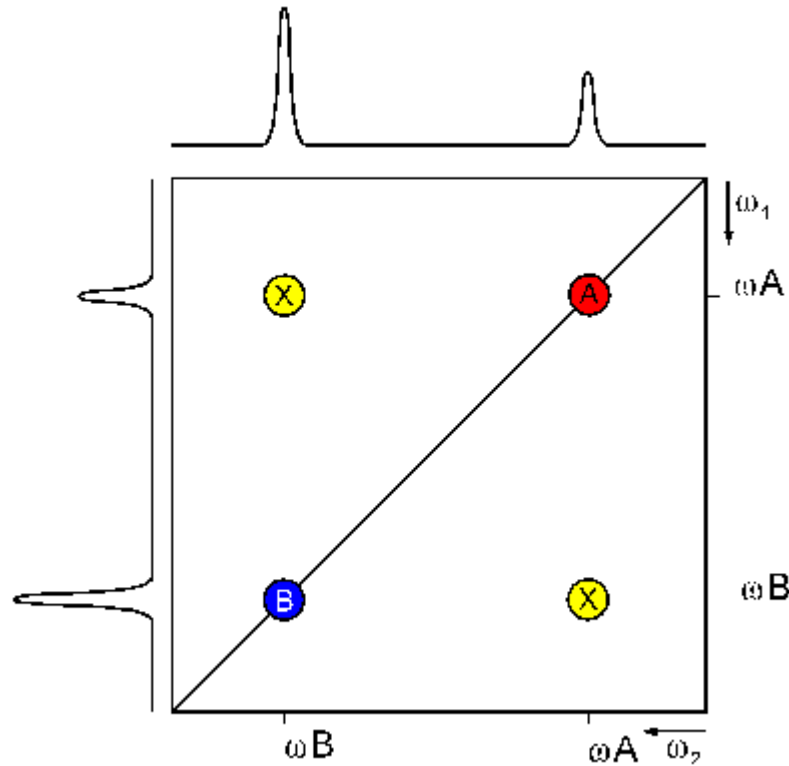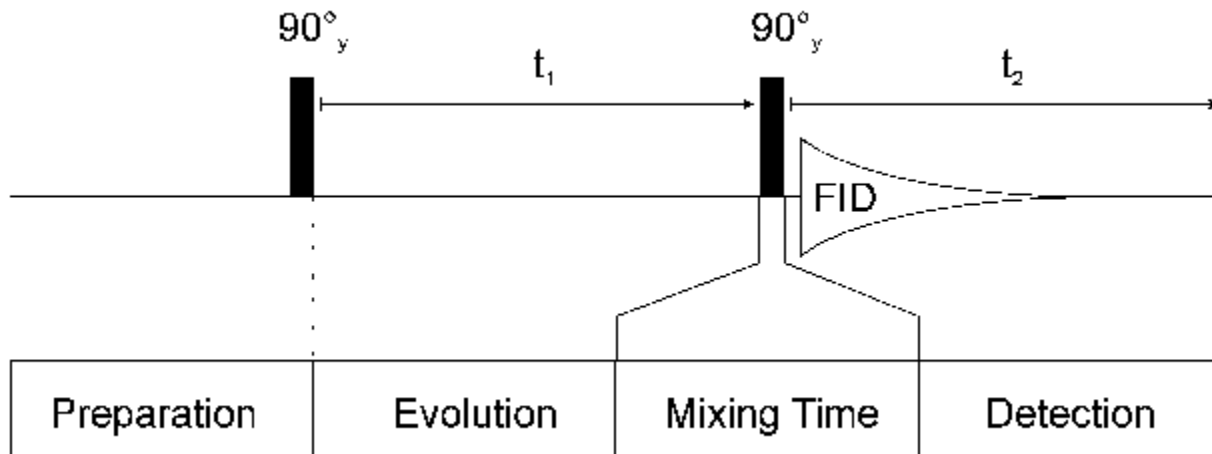# Scalar coupling in 2-D

Scalar coupling can be studied as a correlation spectroscopy in two dimensions. In the example above we see the peaks from two nuclei (red and blue) on the diagonal and off-diagonal coupling peaks showing that they are nearest neighbor carbon atoms (yellow).

The COSY pulse sequence

This is the standard pulse sequence used for the two-dimensional correlated version of the experiment to investigate J-coupling. Our task is to understand the effect of the two 90° pulses using the hamilonian for J-coupling.

Hamiltonian for J-Coupling

The standard rotation of a spin operator about an axis by a given angle will lead to a "new" spin operator.
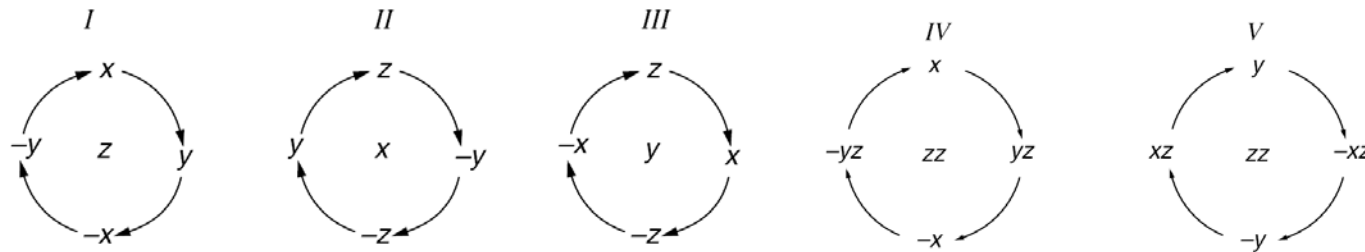
Because the two spins are coupled, a new Hamiltonian needs to be introduced. Evolution between coupled spins leads to the interconversion of in-phase and anti-phase magnetization as shown in *IV* and *V*.

$$H_J = 2\pi J_{12} I_{1z} I_{2z}$$ J_{12} is the coupling in Hz

COrrelated SpectroscopY

$$90_x - t_1 - 90_x - t_2$$

preparation   evolution   mixing   detection

t_1

t_2
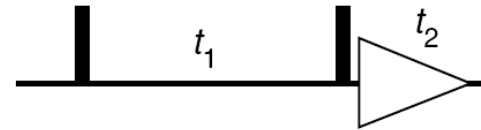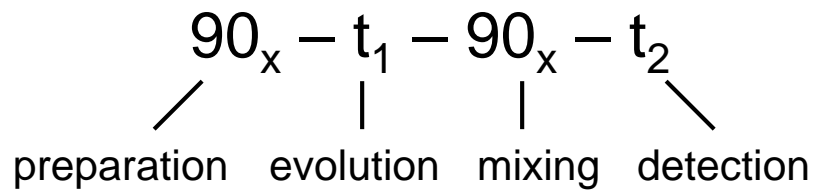
In a COSY experiment magnetization is transferred through scalar couplings. Magnetization will only be transferred to protons that are two or three bonds apart.

Once the COSY pulse sequence is executed and the FID is recorded the spins are allowed to go back to equilibrium. The evolution time, t_1, is altered and the sequence is repeated. The pulse sequence is repeated for increasing increments of t_1 and the FID is stored for each value of t_1.

COrrelated SpectroscopY

$$90_x - t_1 - 90_x - t_2$$

preparation   evolution   mixing   detection
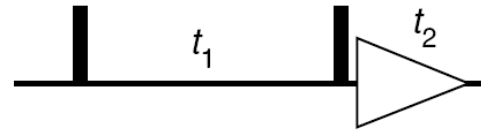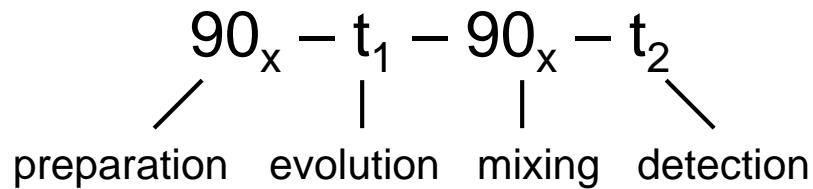
To begin the initial equilibrium magnetization along the z-axis is perturbed with a 90° pulse along the x-axis.

The density operator at a time t, $\sigma(t)$, can be solved from time 0, $\sigma(0)$, by the following:

$$\sigma(t) = \exp(-i\mathcal{H}t)\sigma(0)\exp(i\mathcal{H}t)$$

$$\sigma(0) = I_z$$

$$\mathcal{H} = \omega_1 I_x$$

Preparation: the $\pi/2$ pulse

$$\sigma(t_p) = \exp(-i\beta I_x) I_z \exp(i\beta I_x)$$

$$\exp(-i\theta I_a)\ \{old\ operator\}\ \exp(i\theta I_a)\ =$$
$$\cos\theta\{old\ operator\} + \sin\theta\{new\ operator\}$$
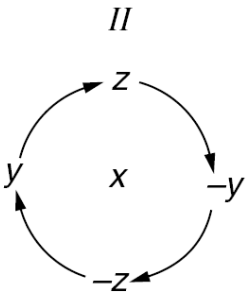
$$\sigma(t_p) = \cos\beta\ I_z - \sin\beta\ I_y$$

$$H_{pulse,x} = \omega_1 I_x$$

$$\sigma(t_p) = \cos{}^\pi 2\ I_z - \sin{}^\pi 2 I_y$$

II

$$\sigma(t_p) = -I_y$$

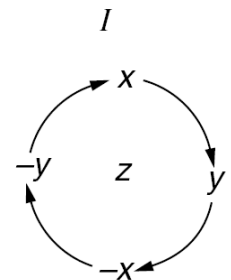$$I_z \xrightarrow{\ \omega_1 t_p I_x\ } -I_y$$

Evolution

Rotations have to be applied separately to each spin and rotations of spin 1 do not affect spin 2. The second arrow can be ignored here because it involves operators of spin 2.

$$I_{1z} \xrightarrow{\pi/2 \; I_{1x}} \xrightarrow{\pi/2 \; I_{2x}} - I_{1y}$$

This new state will evolve during time t_1 under the influence of the static magnetic field.

$$- I_{1y} \xrightarrow{\Omega_1 t_1 I_{1z}} - \cos \Omega_1 t_1 I_{1y} + \sin \Omega_1 t_1 I_{1x}$$
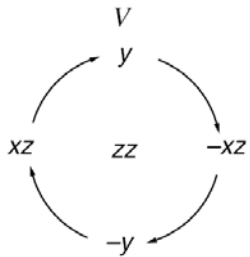
$$H_{free} = \Omega I_z$$

Ω represents the frequency of rotation about the z-axis

Coupling of the spins

Now we have to account for the coupling of the two spins. The previous two terms must be dealt with separately.
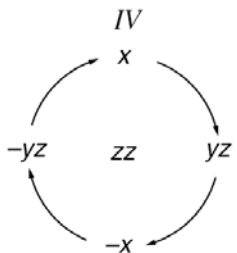
$$-\cos \Omega_1 t_1 I_{1y} \xrightarrow{2\pi J_{12}t_1 I_{1z}I_{2z}} -\cos \pi J_{12}t_1 \cos \Omega_1 t_1 I_{1y}$$

$$+$$

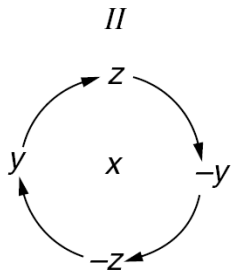$$\sin \pi J_{12}t_1 \cos \Omega_1 t_1 2I_{1x}I_{2z}$$

$$\sin \Omega_1 t_1 I_{1x} \xrightarrow{2\pi J_{12}t_1 I_{1z}I_{2z}} \cos \pi J_{12}t_1 \sin \Omega_1 t_1 I_{1x}$$

$$+$$

$$\sin \pi J_{12}t_1 \sin \Omega_1 t_1 2I_{1y}I_{2z}$$

$$H_J = 2\pi J_{12}I_{1z}I_{2z}$$

Mixing period

$$- \cos \pi J_{12}t_1 \cos \Omega_1 t_1 I_{1y} \xrightarrow{\pi/2\ I_{1x}} \xrightarrow{\pi/2\ I_{2x}} - \cos \pi J_{12}t_1 \cos \Omega_1 t_1 I_{1z}$$

$$\sin \pi J_{12}t_1 \cos \Omega_1 t_1 2I_{1x}I_{2z} \xrightarrow{\pi/2\ I_{1x}} \xrightarrow{\pi/2\ I_{2x}} - \sin \pi J_{12}t_1 \cos \Omega_1 t_1 2I_{1x}I_{2y}$$

$$\cos \pi J_{12}t_1 \sin \Omega_1 t_1 I_{1x} \xrightarrow{\pi/2\ I_{1x}} \xrightarrow{\pi/2\ I_{2x}} \cos \pi J_{12}t_1 \sin \Omega_1 t_1 I_{1x}$$

$$\sin \pi J_{12}t_1 \sin \Omega_1 t_1 2I_{1y}I_{2z} \xrightarrow{\pi/2\ I_{1x}} \xrightarrow{\pi/2\ I_{2x}} - \sin \pi J_{12}t_1 \sin \Omega_1 t_1 2I_{1z}I_{2y}$$

What do the terms mean?

$$(1) \quad -\cos \pi J_{12} t_1 \cos \Omega_1 t_1 I_{1z}$$

Term 1 has magnetization along the z-axis and will be unobservable in the spectrum.

$$(2) \quad -\sin \pi J_{12} t_1 \cos \Omega_1 t_1 2 I_{1x} I_{2y}$$

Remember from our table earlier that the operator $2I_{1x}I_{2y}$ represents multiple quantum coherence (simultaneous flipping of spins) and will be unobservable in a normal COSY spectrum.

What do the terms mean?

$$(3) \quad \cos \pi J_{12} t_1 \sin \Omega_1 t_1 I_{1x}$$

Term 3 has magnetization along the x-axis and corresponds to the in-phase magnetization of spin 1. This is a diagonal peak with all of its multiplets in-phase. This signal will evolve at a certain frequency during the evolution period, t_1. Then remain unaltered by the mixing period and continue to resonate at the same frequency during the detection, t_2.

What do the terms mean?

$$(4) \quad -\sin \pi J_{12} t_1 \sin \Omega_1 t_1 2 I_{1z} I_{2y}$$

Upon further inspection of the final $90°_x$ pulse on the fourth term shows that anti-phase magnetization of spin 1 was transferred from $2I_{1y}I_{2z}$ to anti-phase magnetization on spin 2, $2I_{1z}I_{2y}$ after the final $90°_x$ pulse (mixing period).

This implies that the signal will evolve at a certain frequency during t_1. After the mixing period this magnetization of this signal is transferred to another signal which evolves at a different frequency during detection, t_2. This is representative of a cross peak in our COSY spectrum of two spins connected via scalar coupling.

DQF-COSY
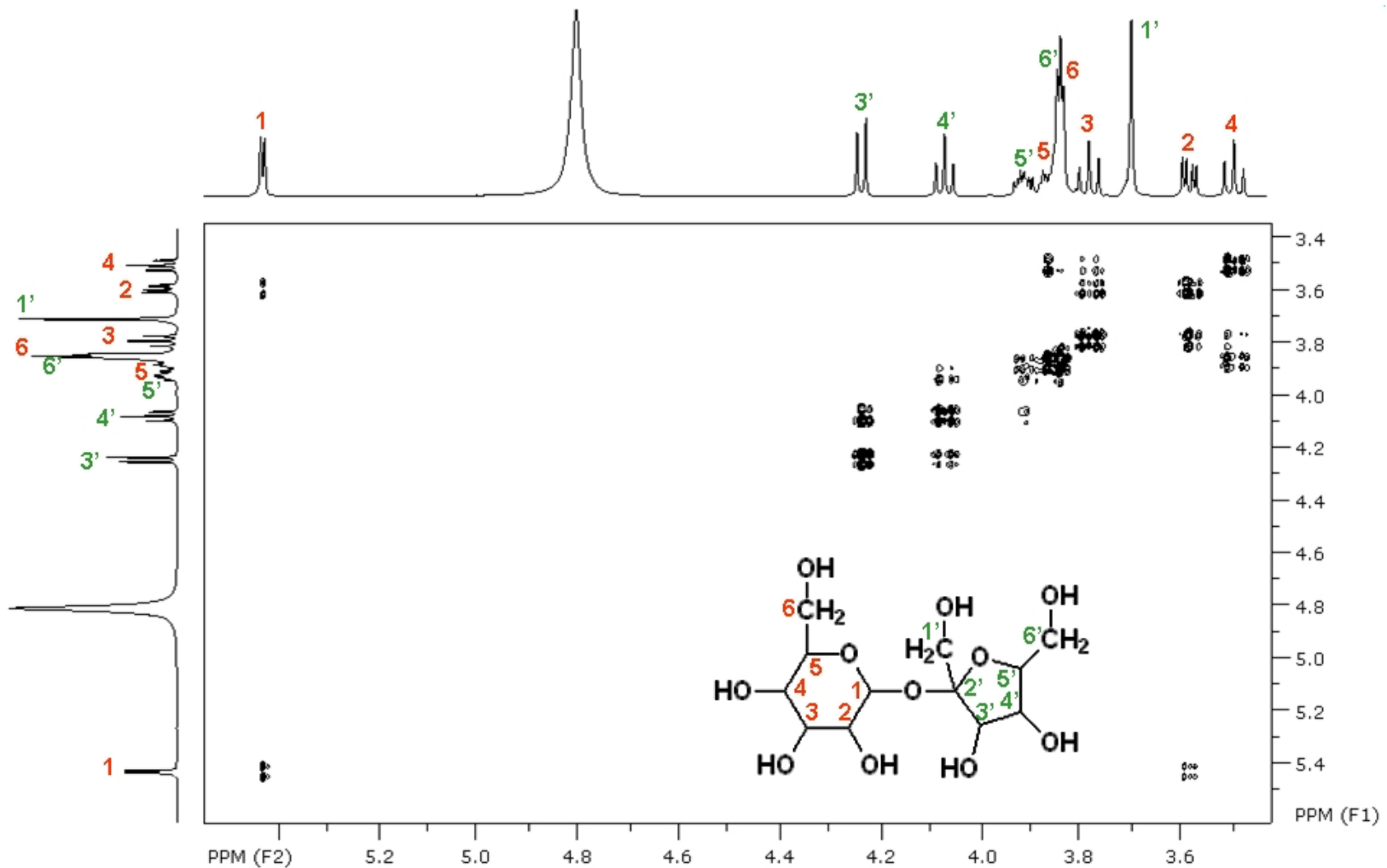
500 MHz spectrum of sucrose.

DQF-COSY

The COSY-DQF (Cosy Double Quantum Filter) provides two advantages over the COSY. Higher resolution is possible and multiplet fine structure can be seen. This may allow proton-proton couplings to be measured. When there are several couplings to a given proton and the multiplet is complex, however, often the cross peak is not interpretable because of cancellation of multiplet components.

The DQF version reduces the diagonal dispersive peaks of the COSY experiment but sensitivity is reduced by one half. In addition, uncoupled spins such as water are removed. This experiment is seldom used for small molecules.