Ch122a

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Lecture 16

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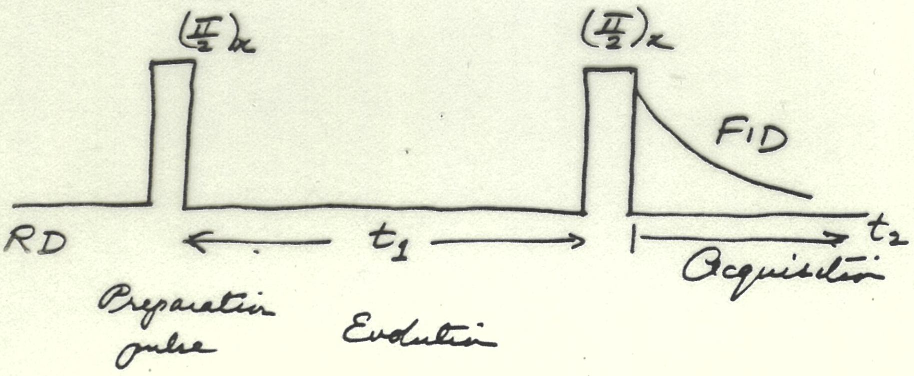
Correlated Spectroscopy

• The Simple COSY Experiment

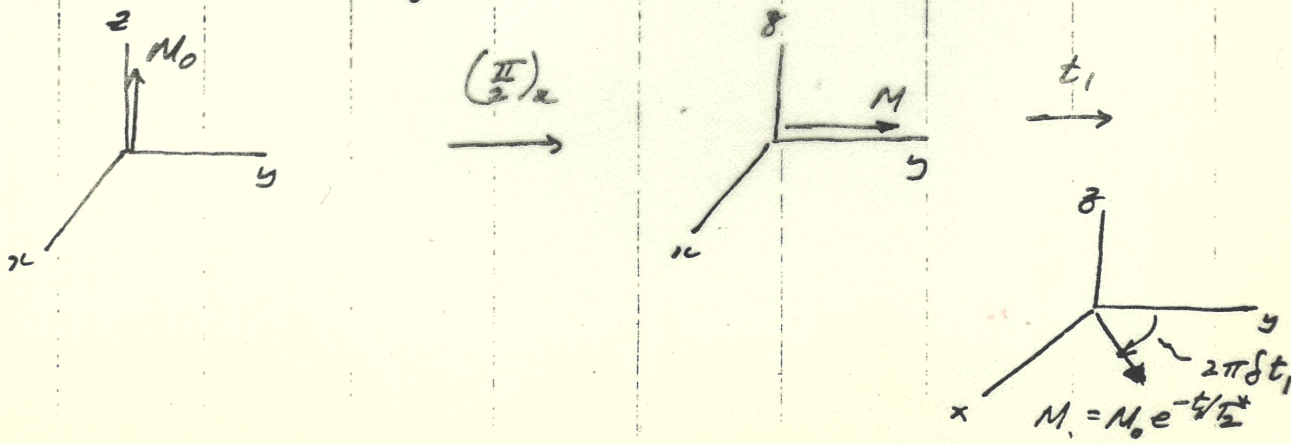
Pulse sequence



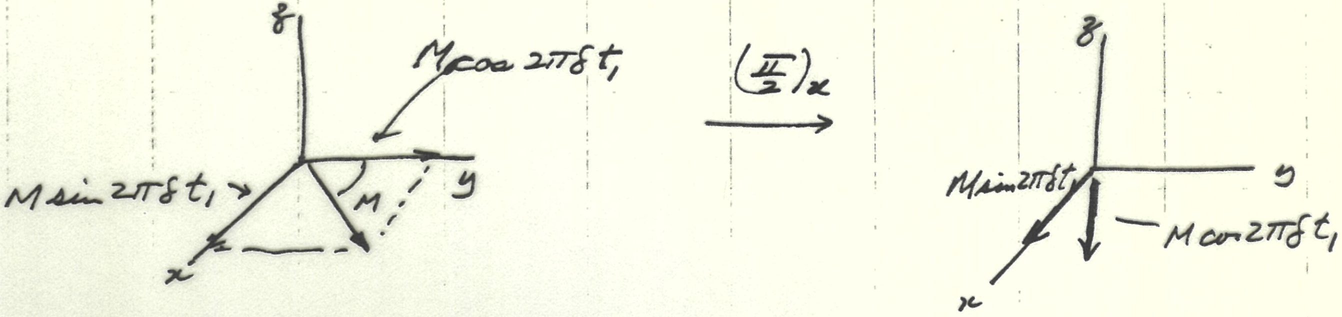
Consider a sample containing a single line with chemical shift

After the $(\frac{\pi}{2})_x$ preparation pulse, the magnetization is allowe

to precess at ν Hz for time t_1.



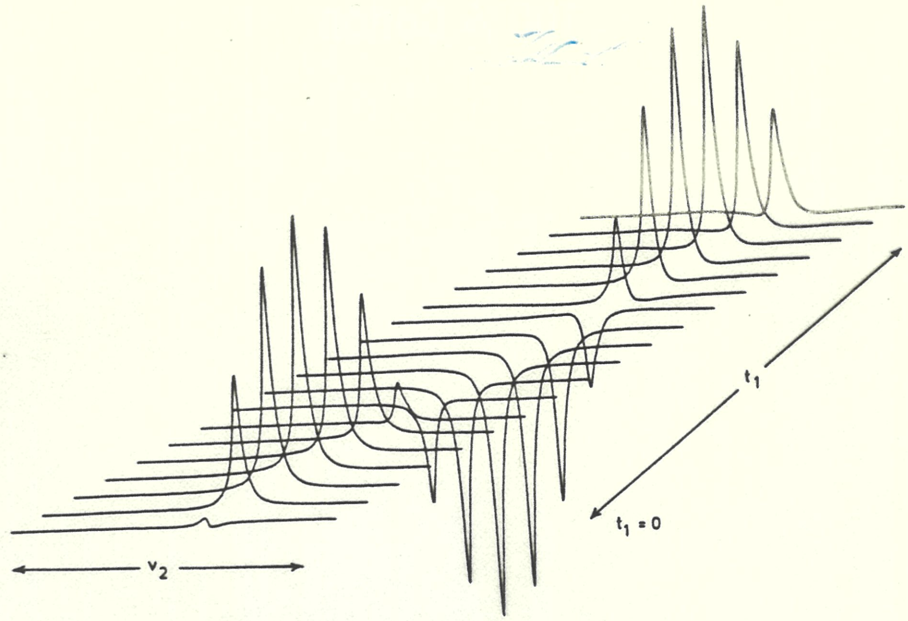
In time t_1, $\vec{M}$ has precessed through an angle $2\pi\delta t_1$ and its magnitude has decayed to $M_0 e^{-t_1/T_2^*}$.



The second $(\frac{\pi}{2})_x$ pulse rotates the y-axis component through a further 90° to place it along the z-axis, while leaving the x-axis component unchanged. So the amount of magnetization left in the xy plane, which determines the size of NMR signal is $M\sin 2\pi\delta t_1$. Fourier transformation of the FID after the second $(\frac{\pi}{2})_x$ pulse yield the normal 1-D spectrum except for the change of amplitude $e^{-t_1/T_2}\sin 2\pi\delta t_1$ when the second $(\frac{\pi}{2})_x$ pulse is applied at t_1. Note that the amplitude depends on time t_1.

See FT spectra for varying t_1 on next page.

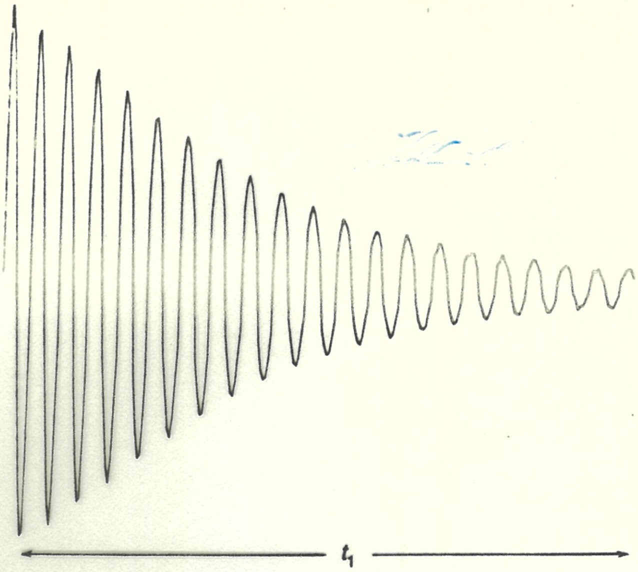
Sign change arises from sinusoidal behavior of $\sin 2\pi\delta t_1$.



Spectra obtained using the $(\frac{\pi}{2})_x - t_1 - (\frac{\pi}{2})_x$ sequence with varying t_1's by Fourier transformation of the FID sampled at each t_1.

If we select a point from each spectrum corresponding to the top of the peak and plot this as a function of t_1, we obtain an FID oscillating with frequency $\delta \equiv (\nu_0 - \nu_{reference}$ (phase detection!). Fourier transformation of these data generates another spectrum just as it did for the first s of data (FID's).

See FID on next page and note that it is a function of t_1



Fourier transformation of the combined two-dimensional data set yields the two-dimensional frequency spectrum

$$f(\nu_1, \nu_2) \quad \text{or} \quad F(\omega_1, \omega_2)$$

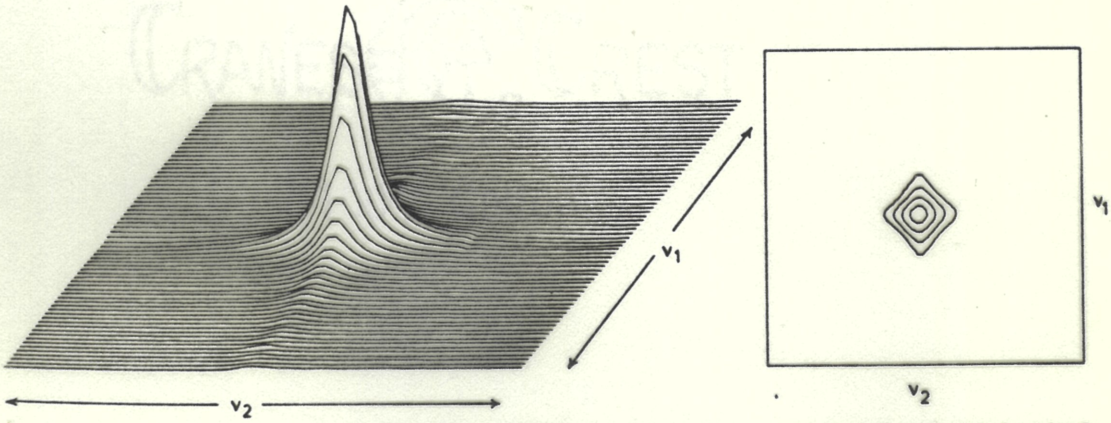


Fig. 2.4 The spectra from Fig. 2.2 after a two-dimensional Fourier transformation, presented as both a stacked plot (left) and a contour plot (right).

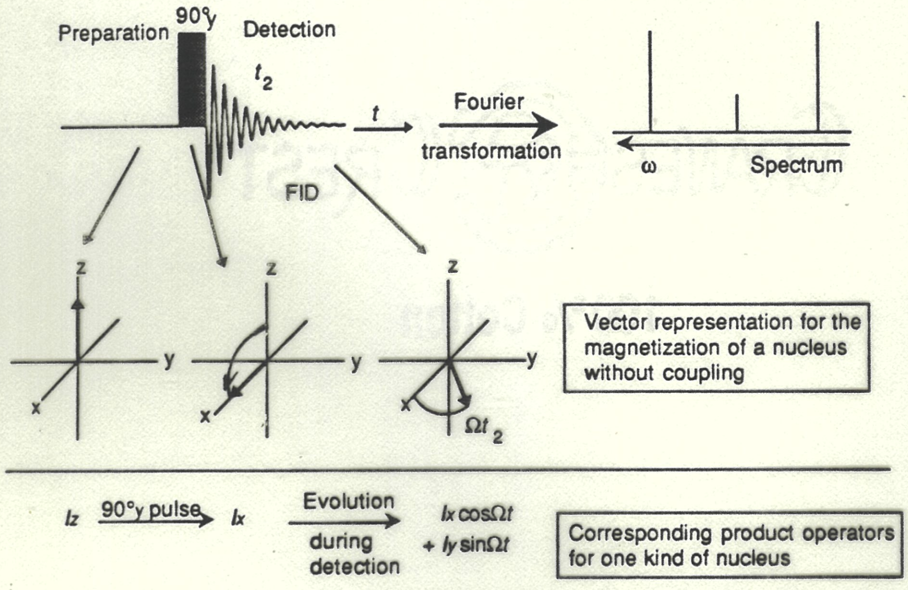
Cross-sections through the peak along either axis are Lorentzian with linewidth $\frac{1}{\pi T_2^*}$.

The above is the basic COSY experiment introduced by Jeener in 1971.

Vector representation or model of the Magnetization versus the Product Operator Model

In the description of pulse NMR, I have been using the vector model of the Magnetization because of its simplicity. But the vector model doesn't always work. The astute student will recognize that in the above description of the COSY experiment, I deconvoluted M_{xy} into M_x and M_y, before discussing the effects of the second $\left(\frac{\pi}{2}\right)_x$ pulse. Had I considered only the motion of the bulk magnetization M_{xy}, then following the second $90°_x$ pulse, the magnetization is aligned along the $-z$ axis, which is not observable. The COSY data set 1 was obtained by sampling $M \sin 2\pi\delta t_1$ as a FID in the Jeener experiment. Clearly, the classical picture is incomplete. The reason is simple: Only polarizations or populations are dealt with in the vector model. Coherences are not, and coherences are important in a 2D experiment. Both polarizations (or populations) and coherences are treated in a density matrix formulation, but the latter is beyond the scope of this course. So I shall try to introduce the product operator approach, which has been developed to give the spectroscopist a set of rules so that the effects of pulses, chemical shifts, and positive scalar couplings can be determined in an arbitrary experiment.

— An example



The vector model and the product operator model for a 90° pulse.

(1) The system at thermal equilibrium is described by a polarization along the z-axis, I_z.

(2) After a pulse in the y-direction:

$$I_x \xrightarrow{\alpha I_y} I_x \cos\alpha - I_z \sin\alpha$$

"an α-degree pulse along y"

$$I_y \xrightarrow{\alpha I_y} I_y$$

$$I_z \xrightarrow{\alpha I_y} I_z \cos\alpha + I_x \sin\alpha$$

[illegible]

where αI_x = flip angle $\underline{\alpha}$ about x-axis

αI_y = flip angle $\underline{\alpha}$ about y-axis

αI_z = flip angle $\underline{\alpha}$ about z-axis

αI_ϕ = flip angle $\underline{\alpha}$ about an axis in the xy plane (forming an angle ϕ with the x ax

(3) The effect of chemical shift evolution of nucleus I during time t (Chemical shift = Ω radians/sec) i.e., $2\pi\delta$

$$I_x \xrightarrow{\Omega t I_z} I_x \cos\Omega t + I_y \sin\Omega t$$

$$I_y \xrightarrow{\Omega t I_z} I_y \cos\Omega t - I_x \sin\Omega t$$

$$I_z \xrightarrow{\Omega t I_z} I_z$$

(4) The effect of evolution of J-coupling between I_1 (or I) and I_2 (or S) during time t $(J I_1 \cdot I_2)$

$$I_{1x} \xrightarrow{\pi J_{12} t\, 2 I_{1z} I_{2z}} I_{1x} \cos\pi J_{12} t + 2 I_{1y} I_{1z} \sin\pi J_{12} t$$

$$I_{1y} \xrightarrow{\pi J_{12} t\, 2 I_{1z} I_{2z}} I_{1y} \cos\pi J_{12} t - 2 I_{1y} I_{1z} \sin\pi J_{12} t$$

$$2 I_{1x} I_{1z} \xrightarrow{\pi J_{12} t\, 2 I_{1z} I_{2z}} 2 I_{1x} I_{1z} \cos\pi J_{12} t + I_{1y} \sin\pi J_{12} t$$

$$2 I_{1y} I_{1z} \xrightarrow{\pi J_{12} t\, 2 I_{1z} I_{2z}} 2 I_{1y} I_{1z} \cos\pi J_{12} t - I_{1x} \sin\pi J_{12} t$$

(5) Detection of x-magnetization leads to build-up of the signal according to the coefficient $(-\sin \Omega t)$ of I_x.

So, for the above pulse-sequence, we can write

$$I_z \xrightarrow{\left(\frac{\pi}{2}\right)_y} \left(I_z \cos\frac{\pi}{2} + I_x \sin\frac{\pi}{2}\right) \text{ or } I_x$$

$$\xrightarrow[\text{during detection}]{\text{Evolution}} I_x \cos\Omega t + I_y \sin\Omega t$$

— Summary of product operator transformations (O.W. Sorensen, G.W. Eich, M.H. Levitt, G. Bodenhausen & R. Ernst, Prog. in NMR Spectroscopy 16, 163–192 (1983)).

Pulses

$I_z \xrightarrow{\beta_y} I_z \cos\beta + I_x \sin\beta$

$I_z \xrightarrow{\beta_x} I_z \cos\beta - I_y \sin\beta$

$I_x \xrightarrow{\beta_x} I_x$

$I_y \xrightarrow{\beta_y} I_y$

$I_x \xrightarrow{\beta_y} I_x \cos\beta - I_z \sin\beta$

$I_y \xrightarrow{\beta_x} I_y \cos\beta + I_z \sin\beta$

90° pulses

$I_z \xrightarrow{90^\circ_y} +I_x$

$I_z \xrightarrow{90^\circ_x} -I_y$

$I_x \xrightarrow{90^\circ_y} -I_z$

$I_y \xrightarrow{90^\circ_x} +I_z$

Scalar Coupling

$I_z \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} I_z$

$2I_{1x}I_{2y} \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} 2I_{1x}I_{2y}$

$I_{1x} \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} I_{1x} \cos\pi J_{12} t + 2\, I_{1y} I_{2z} \sin\pi J_{12} t$

$I_{1y} \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} I_{1y} \cos\pi J_{12} t - 2\, I_{1x} I_{2z} \sin\pi J_{12} t$

$2I_{1x}I_{2z} \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} 2I_{1x}I_{2y} \cos\pi J_{12} t + I_{1y} \sin\pi J_{12} t$

$2I_{1y}I_{2z} \xrightarrow{\pi J_{12} t\, I_{1z} I_{2z}} 2I_{1y}I_{2y} \cos\pi J_{12} t - I_{1x} \sin\pi J_{12} t$

Chemical Shifts

$I_z \xrightarrow{\Omega t\, I_z} I_z$

$I_x \xrightarrow{\Omega t\, I_z} I_x \cos\Omega t + I_y \sin\Omega t$

$I_y \xrightarrow{\Omega t\, I_z} I_y \cos\Omega t - I_x \sin\Omega t$

Summary of product operator transformations.

• Populations and Coherences

Population ≡ occupation numbers of a nuclear spin state

$$\begin{array}{lc} \text{——— } \beta & n_\beta \\ \text{——— } \alpha & n_\alpha \\ & \overline{\text{population}} \end{array}$$

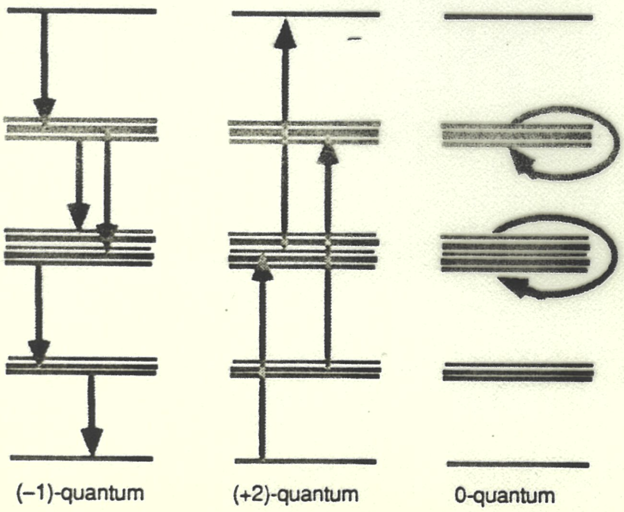
Polarization ≡ $(n_\alpha - n_\beta)(I_z)_\alpha$ = longitudinal magnetization

Coherence ≡ a relationship between two states across a single nuclear transition, or multiple states for multiple transitions

= transverse magnetization

For a coherence across one transition, this is called a single-quantum coherence.

When more than one level is involved, then the relation between the levels is such that multiple-quantum coherences may be transferred.



Single-, double- and zero-quantum coherences.

To illustrate the concept of coherence, compare the situati[on] when an NMR transition has been saturated with that when the magnetization has undergone a 90° puls[e].

In both cases, $I_z = 0$

When the NMR transition is saturated, I_x & $I_y = 0$ also. There is no magnetization at all.

For the transition which has undergone a 90° pulse, there will xy components precessing together with the same phase, which they derived from the pulse.

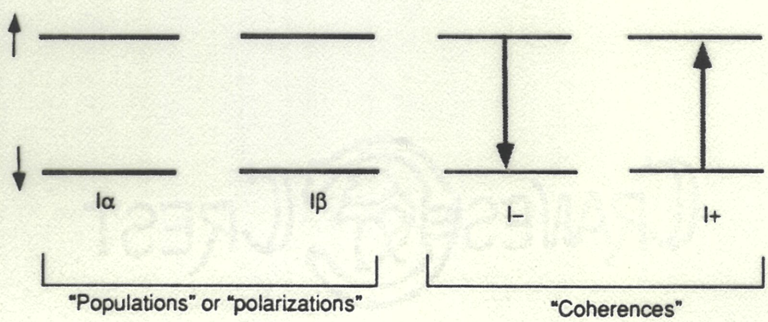
So in the saturated sample, the nuclei are precessing incoherently, whereas after experiencing a pulse they are precessing with phase coherence.

Coherences are characterized by Δm_I for the quantum number m_I.

Although in general many of the possible coherences occur under the influence of pulses in a pulse sequence, only a few are associated with observable magnetization, i.e., $\Delta m_I = \pm 1$, because of the selection rule of NMR. Of these single-quantum coherences, only a few are detectable under weak coupling conditions, those in which the state of exactly one spin is changed (i.e., product operators with only one transverse operator).

We can assume that the state of all spins in the sampl[e] i.e., the "spin ensemble" is a superposition of (1) populat[ions] of states, and (ii) coherences between the states. These coherences are indexed by their order p. The only coherences which induce an observable NMR signal are the (± 1) quantum coherences.

Populations are long-lived (time constant $\sim T_1$) and do not oscillate. Coherences are short-lived and oscillate.



- <u>The COSY Experiment Applied to Scalar-coupled Spin Pair</u>

$$I_1, I_2 = 1/2$$

We now apply the $\left(\frac{\pi}{2}\right)_x - t_1 - \left(\frac{\pi}{2}\right)_x$ -acquisition pulse sequence to AX spin system.

We will apply the product operator formalism to describe the outcome of the spin system following each step of the pulse sequence assuming a weakly coupled two-spin system.

Results

$$\sigma_0 = I_{1z} + I_{2z}$$

$$\Big\downarrow \left(\pi/2\right)_x$$

$$\sigma_1 = -I_{1y} - I_{2y}$$

$\Big\downarrow$ Evolution due to chemical shift & spin-spin coupling
$\Omega_1 t_1 I_{1z} + \Omega_2 t_1 I_{2z} + \pi J_{12} t_1 \, 2 I_{1z} I_{2z}$

$$\sigma_2 = \left(-I_{1y} \cos\Omega_1 t_1 + I_{1x} \sin\Omega_1 t_1 - I_{2y} \cos\Omega_2 t_1 + I_{2x} \sin\Omega_2 t_1\right) \cdot \cos\pi J_{12} t_1$$
$$+ \left(2 I_{1x} I_{2z} \cos\Omega_1 t_1 + 2 I_{1y} I_{2z} \sin\Omega_1 t_1 + 2 I_{1z} I_{2z} \cos\Omega_2 t_1 + 2 I_{1z} I_{2y} \sin\Omega_2 t_1\right) \sin\pi J_{12} t_1$$

$$\Big\downarrow \left(\frac{\pi}{2}\right)_x$$

$$\boxed{\begin{aligned}\sigma_3^{obs} &= \left(I_{1x} \sin\Omega_1 t_1 + I_{2x} \sin\Omega_2 t_1\right) \cos\pi J_{12} t_1 \\ &\quad - \left(2 I_{1y} I_{2z} \sin\Omega_1 t_1 + 2 I_{1z} I_{2y} \sin\Omega_2 t_1\right) \sin\pi J_{12} t_1\end{aligned}}$$

2-D spectrum determined by σ_3^{obs}. The operators in σ_3^{obs}, namely I_{1x}, I_{2x}, $2 I_{1y} I_{2z}$, $2 I_{1z} I_{2y}$, are responsible for the phases in the ω_2-domain, while the trigonometric functions determine the phases in the ω_1-direction.

In the ω_2-domain:

I_{kx} : dispersive in-phase doublet

I_{ky} : absorptive in-phase doublet

$I_{kx} I_{lz}$: dispersive antiphase doublet

$I_{ky} I_{lz}$: absorptive antiphase doublet

In the ω_1-domain:

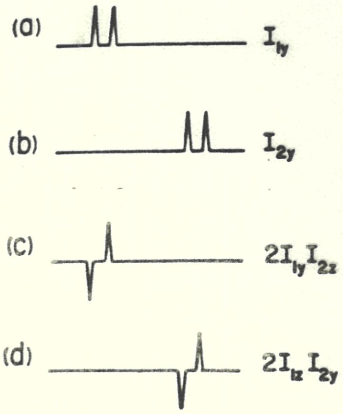
$\cos \Omega_k t_1 \cos \pi J_{kl} t_1$: absorptive in-phase doublet

$\sin \Omega_k t_1 \cos \pi J_{kl} t_1$: dispersive in-phase doublet

$\cos \Omega_k t_1 \sin \pi J_{kl} t_1$: dispersive antiphase doublet

$\sin \Omega_k t_1 \sin \pi J_{kl} t_1$: absorptive antiphase doublet

e.g.



The one-dimensional spectra representing the physical interpretation of Cartesian product operators involving transverse terms (I_{1y}, I_{2y}, $2I_{1y}I_{2z}$, and $2I_{1z}I_{2y}$).

Return to σ_3^{obs}

First term : Precession at $\Omega_1 \pm \pi J_{12}$ in the detection period

After 2D-FT, will lead to a two-dimensional multiplet pattern on the diagonal at

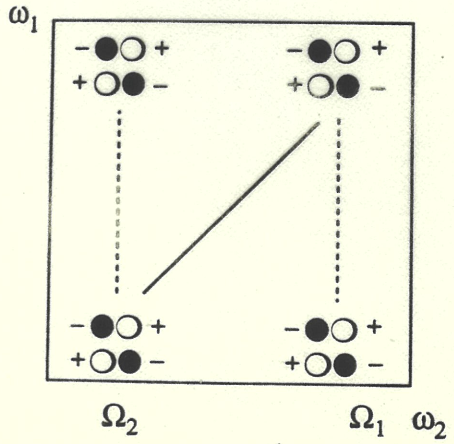
$\omega_1 = \omega_2 = \Omega_1$ with in-phase doublet structure in both directions.

Second term : In-phase diagonal multiplet at $\omega_1 = \omega_2 = \Omega_2$

Third term : Precession at $\Omega_1 \pm \pi J_{12}$ in the detection period and lead to cross-peak multiplet at $\omega_1 = \Omega_2$, $\omega_2 = \Omega_1$, with antiphase doublet structure in both dimensions

Fourth term : a cross-peak multiplet at $\omega_1 = \Omega_1$, $\omega_2 = \Omega_2$

2D Spectrum



Theoretical appearance of a two-dimensional phase sentisive DQF–COSY spectrum (with positive and negative peaks appropriately labelled).