

**1. 1H 1D as a starting point**

assessing line width, intensity, and spectral dispersion for sample quality

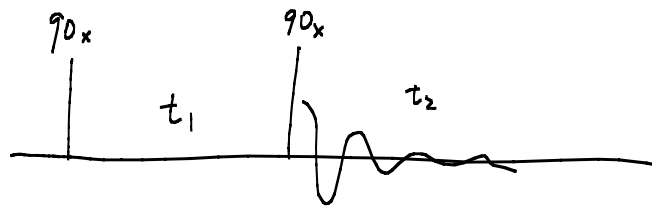
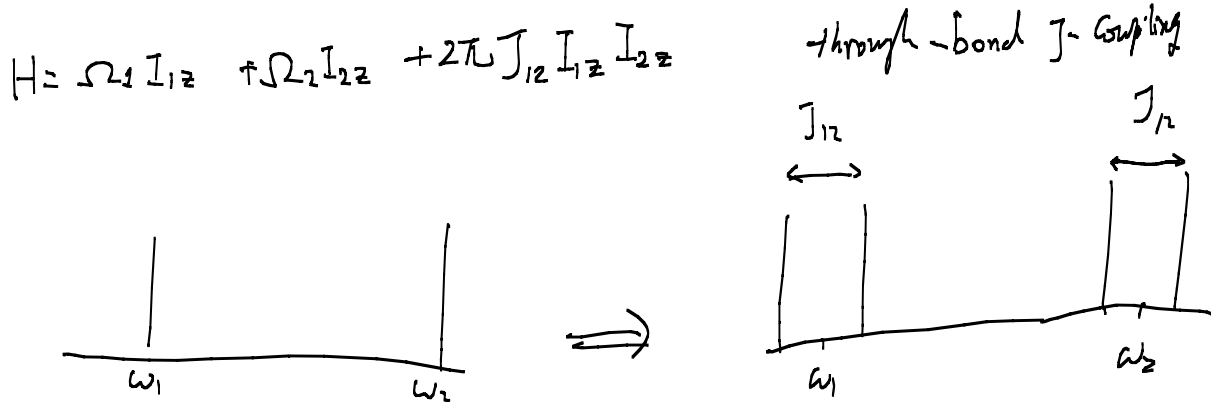
**2. 2D homonuclear correlation spectroscopy COSY**

benefits of <sup>1</sup>H-NMR: high natural abundance (n.a.), high sensitivity

Heteronuclear correlation spectroscopy (to be introduced later) incorporates <sup>13</sup>C and/or <sup>15</sup>N.

strength: larger spectral dispersion      weakness: low n.a., usually need isotopic enrichment

**3. COSY**



$$I_{1z} \xrightarrow{90_x - t_1 - 90_x} I_{1x} \sin \Omega_1 t_1 \cos \pi J_{12} t_1 - 2 I_{1z} I_{2y} \sin \Omega_1 t_1 \sin \pi J_{12} t_1 \quad [\text{eq. 6.1}]$$

$\xrightarrow{t_2} \omega_1 t_2$        $\omega_2 t_2$

*auto-correlation, diagonal peak*      *Spin 1 - Spin 2 Correlation cross peak*

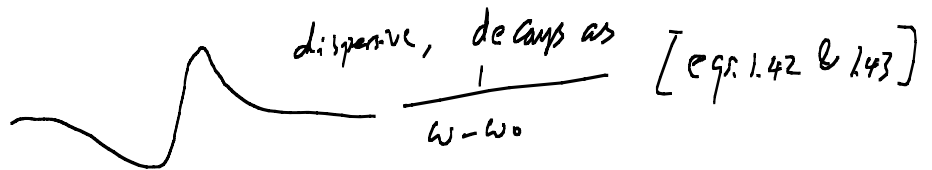
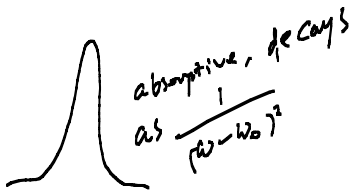
$$a) \sin \Omega_1 t_1 \cos \pi J_{12} t_1 = \frac{1}{2} [\sin(\Omega_1 t_1 - \pi J_{12} t_1) + \sin(\Omega_1 t_1 + \pi J_{12} t_1)]$$

$$b) \sin \Omega_1 t_1 \sin \pi J_{12} t_1 = \frac{1}{2} [\cos(\Omega_1 t_1 - \pi J_{12} t_1) - \cos(\Omega_1 t_1 + \pi J_{12} t_1)]$$

$$① \Omega_1 \rightarrow \Omega_1 - \pi J_{12} \text{ \& } \Omega_1 + \pi J_{12}$$

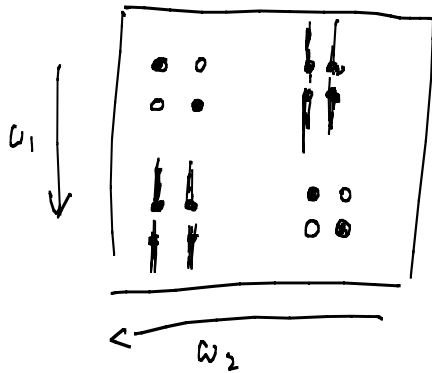
② a) & b)  $90^\circ$

can not be simultaneously phased----if one absorptive, the other has to be dispersive.



Absorptive line shape offers much better spectral resolution.

A 2D COSY is usually so phased that the cross peaks have pure absorptive line shape, leaving the diagonal peaks to have dispersive shape. The dispersive tails of the diagonal peaks are very obstructive for cross peaks close to the diagonal. To alleviate to problem, (1) aggressive sine bell apodization can be applied; (2) also many COSY variants have been developed.

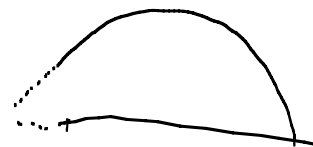
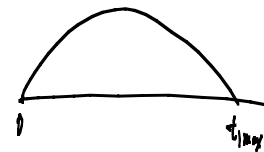
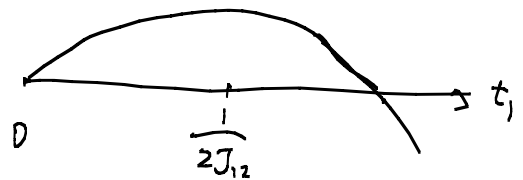
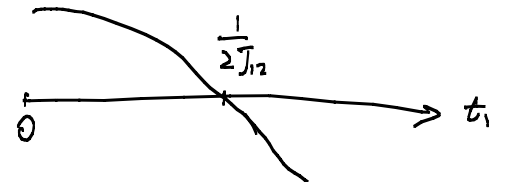


$$\text{diagonal} \propto \cos \pi J_{12} t_1$$

$$\text{cross} \propto \sin \pi J_{12} t_1$$

Sine-bell

shifted-sine bell

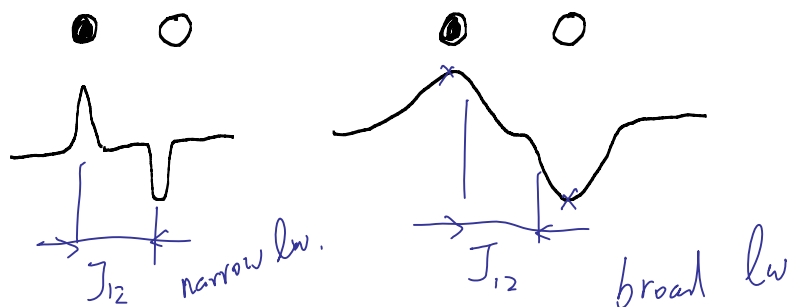


sine bell apodization mainly attenuates diagonal peaks; it also enhance resolution (de-line-broadening).

Fig. 6.6: example COSY spectrum showing 5 regions of interest.

The  $H^N-H^a$  region should have N-P+G-1 peaks.

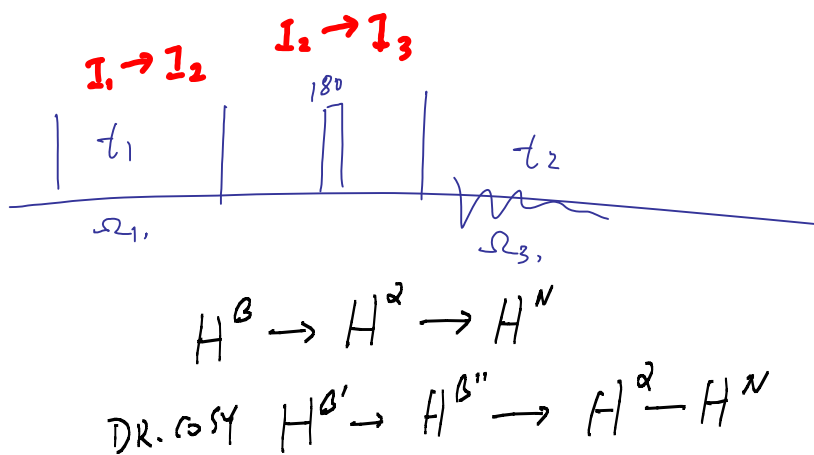
Error of coupling constant retrieval as a result of finite line width.



Line width needs to be considered explicitly in order to improve accuracy (eq. 6.7). May also directly fit the line shapes to extract J-constants (p. 426).

#### 4. R.COSY and DR.COSY

Relayed and double-relayed COSY may provide new correlation peaks that may help lifting degeneracy.



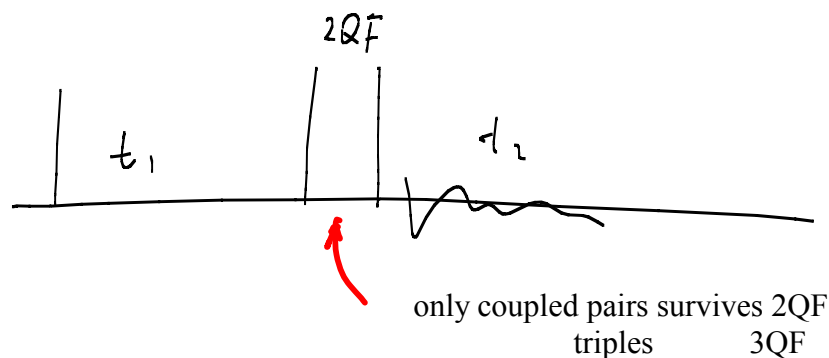
Establishing new correlation between  $I_1$  and  $I_3$ , which are not directly coupled.

## 5. 2Q & 3Q COSY

pros (1) absorptive (and antiphase) diagonal  
(2) no diagonal peak for uncoupled pairs

cons

lower sensitivity than normal COSY, by a factor of 2 (phase cycle for coherence selection)



## 5. E.COSY

Exclusive COSY uses linear combinations of 2Q and 3Q to simplify fine structure of cross peaks; only actively coupled pairs are observed in the final spectrum, making it easy to determine coupling constants.

See Fig. 6.31 for an example of a spin system consists of three coupled spins. The COSY fine structure is more complicated than a two-spin system. The figure illustrates how a linear combination of 2QF and 3QF could lead to a much simplified E.COSY fine structure.