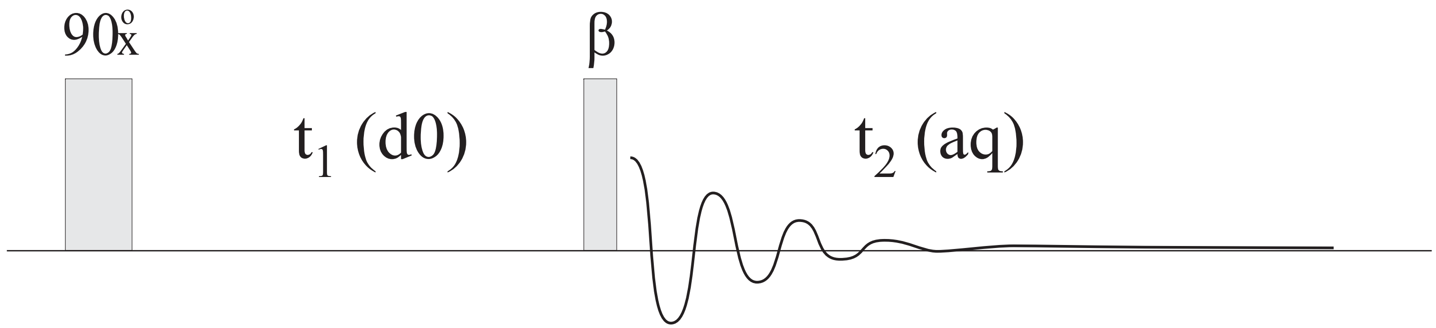
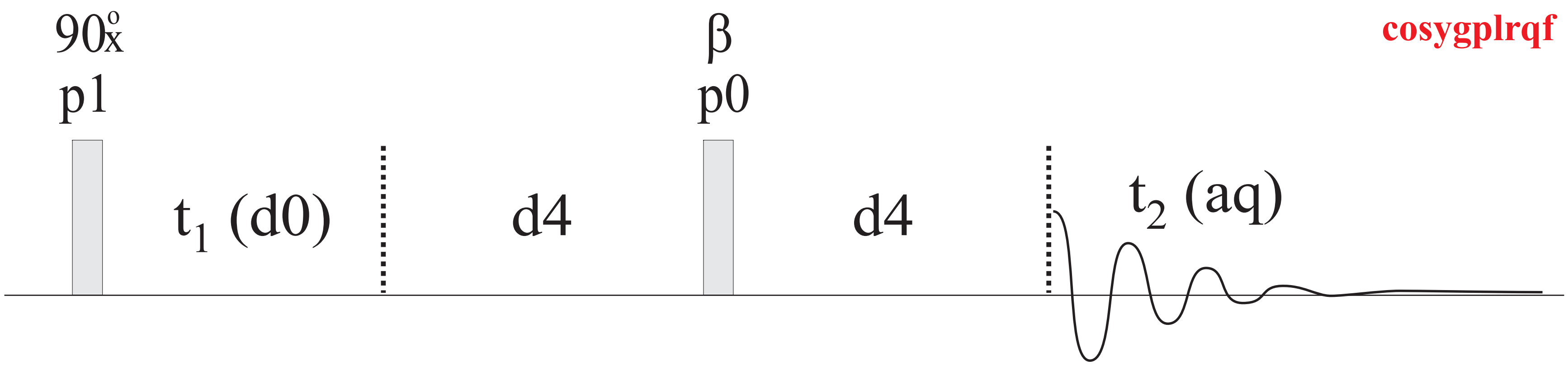
Schematic of the COSY-β Experiment



$\beta = 90^o$ Provides complete multiplet structures, and has maximum S/N.

$\beta = 45^o$ Reduces intra-multiplet structure (cleans the diagonal), but with reduced S/N (which usually can be afforded). Also shows the sign of the J-coupling constant, useful for discerning between vicinal and geminal protons.

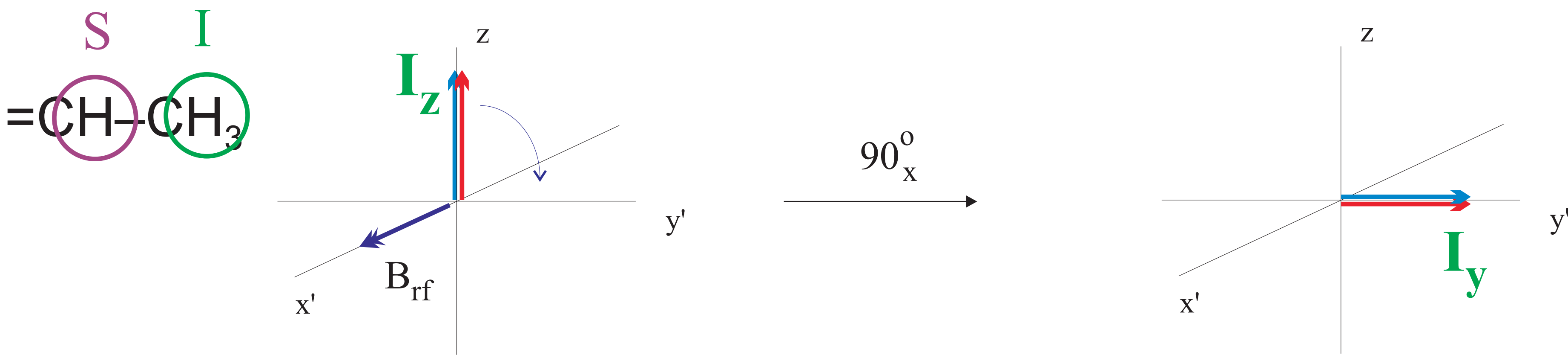
Schematic of the Long-Range COSYLR Experiment

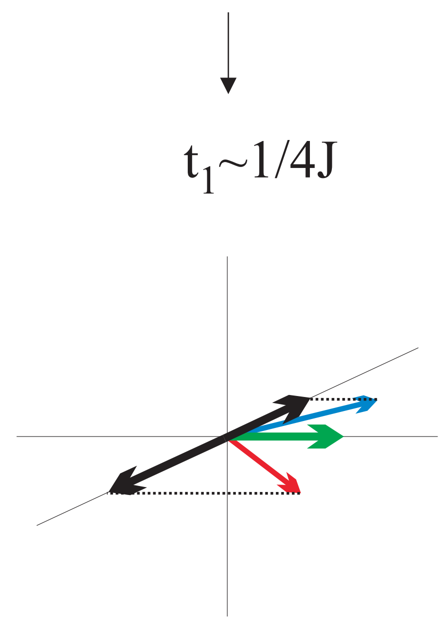


β = 90^o or 45^o as in COSY-β.

d4 = fixed delay of typically 50 - 200 ms. This delay allows simpler access to the long evolution times needed to observe small J-couplings (i.e., needed to create sufficient *antiphase* magnetization to generate observable crosspeaks).

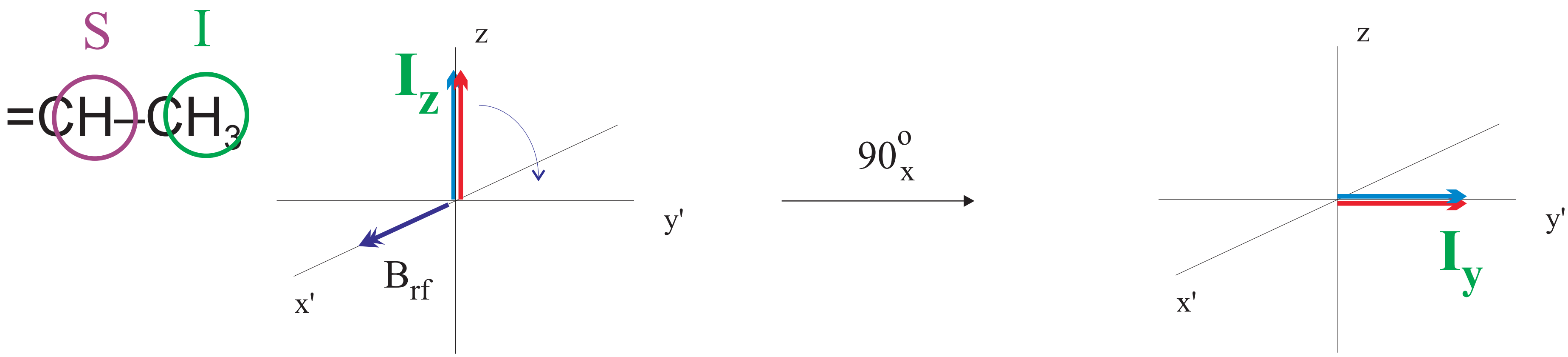
topspin/icon → cosylr.UW



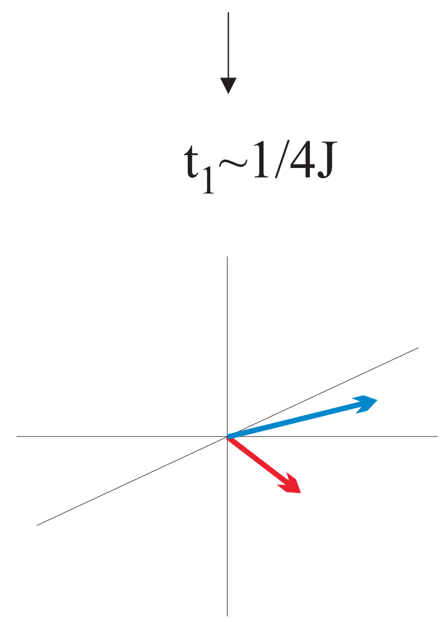


The vector presentation, as shown here, is useful, but also dangerous. It does ***not*** correctly describe the spin state. One must stay on-resonance with this vector presentation of *J*-couplings, and be mindful of its inherent limitations. Product operators correctly describe the magnetization, which **evolves** under *J*-coupling as follows:

$$I_y \rightarrow I_y \cos(\pi J t_1) + I_x S_z \sin(\pi J t_1)$$

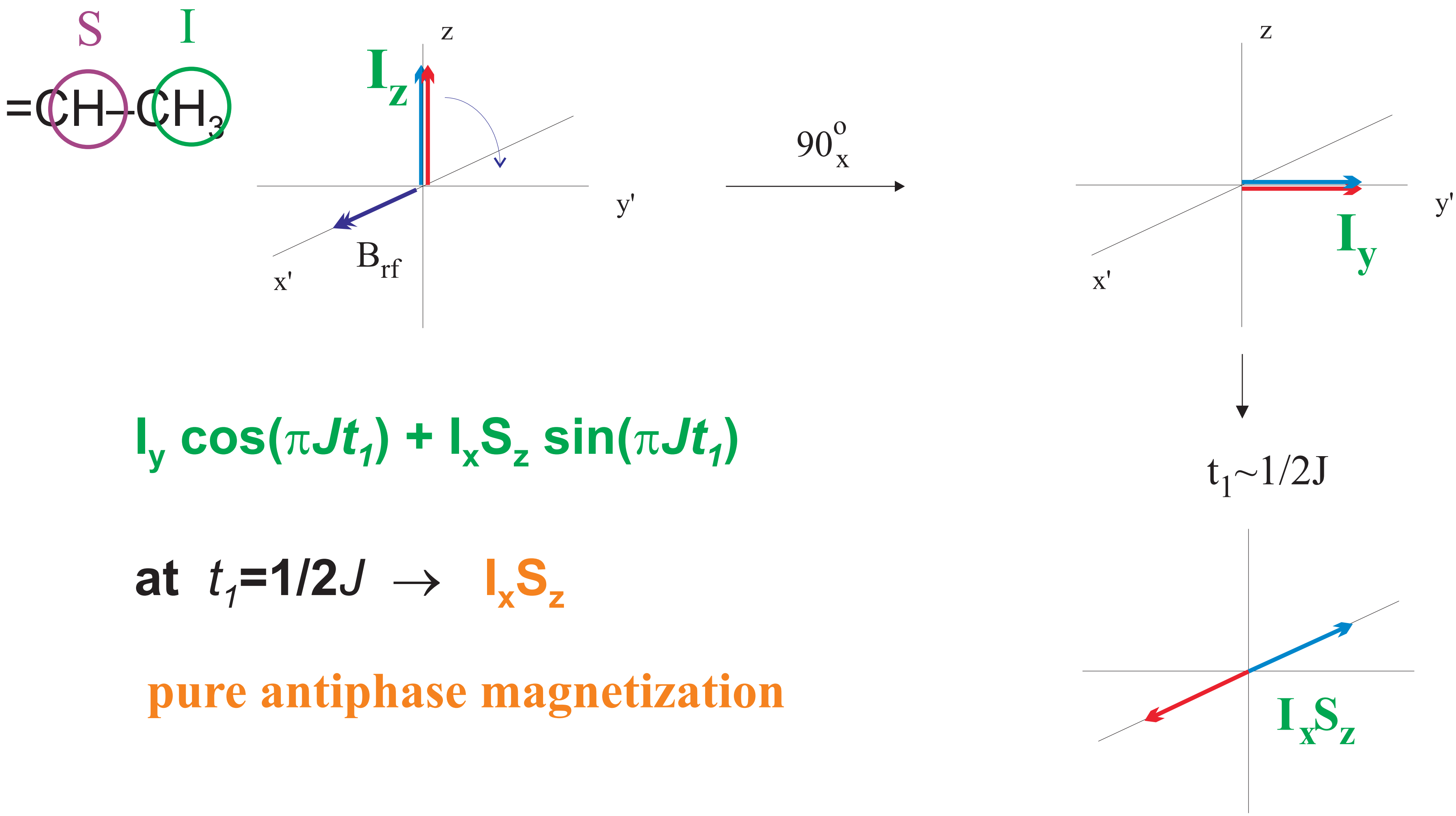


$$I_y \rightarrow I_y \cos(\pi J t_1) + I_x S_z \sin(\pi J t_1)$$



The product operator $I_x S_z$ is called antiphase magnetization. The bilinear operator is a form of mixed magnetization that is not directly observable. It evolves, however, as:

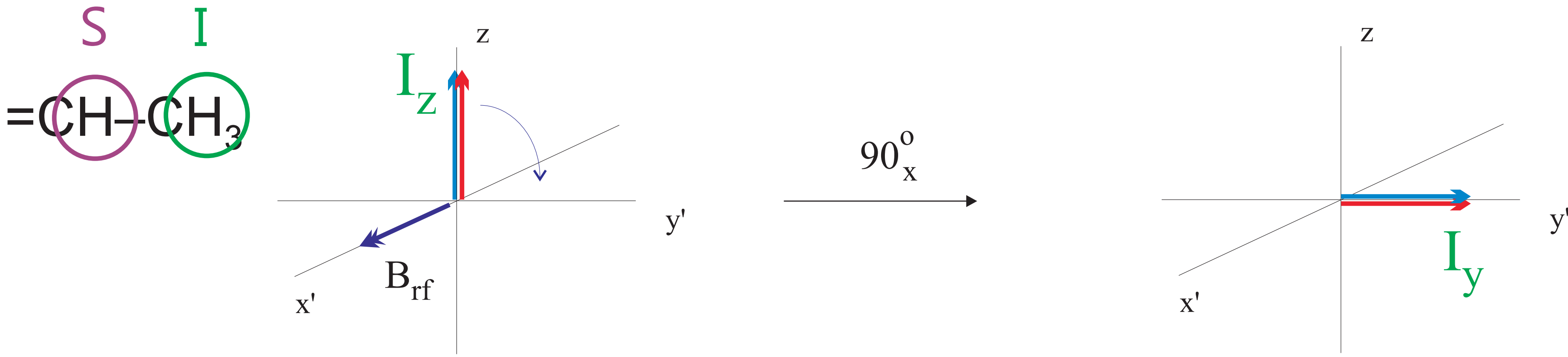
$$I_x S_z \rightarrow I_x S_z \cos(\pi J t_1) + I_y \sin(\pi J t_1)$$



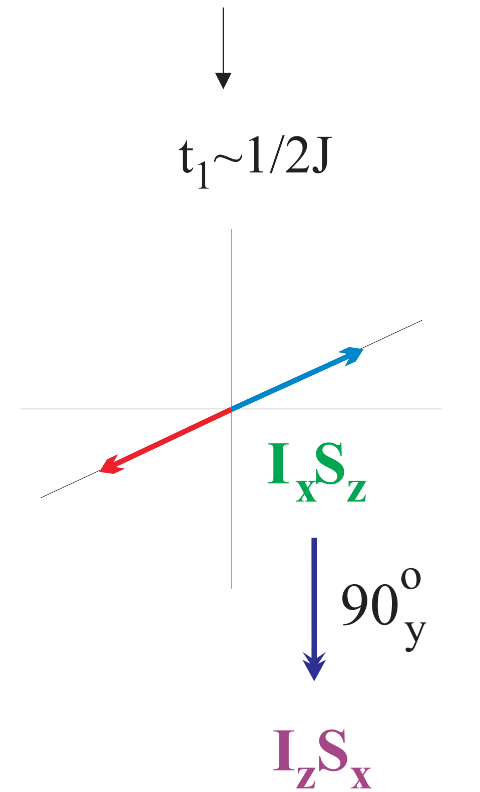
$I_y \cos(\pi J t_1) + I_x S_z \sin(\pi J t_1)$

at $t_1 = 1/2J \rightarrow I_x S_z$

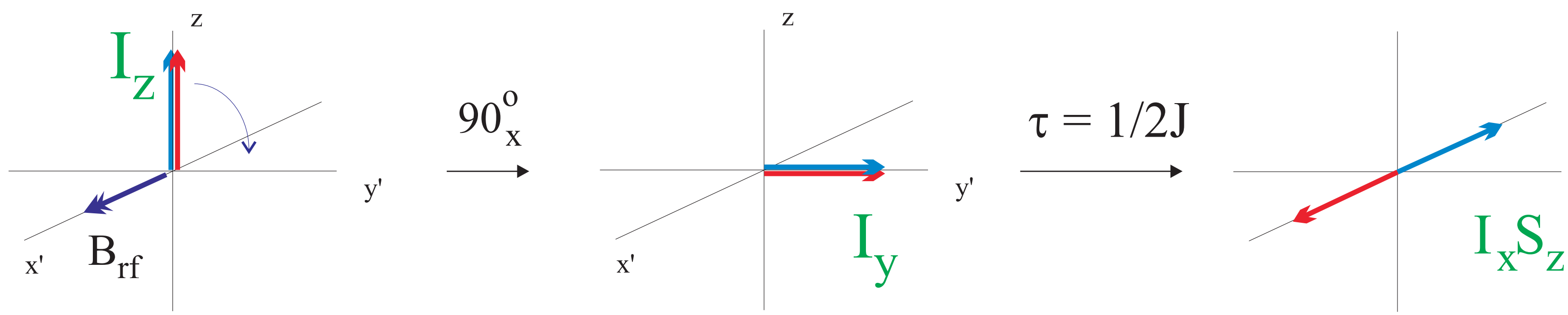
pure antiphase magnetization

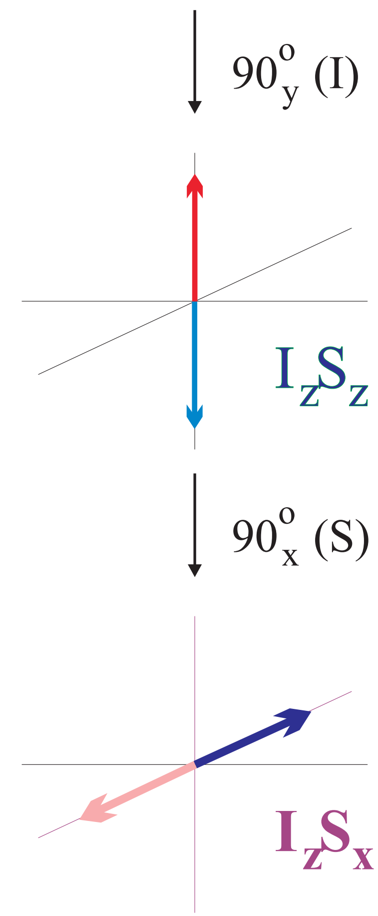


Rf rotations act *independently* on spin terms in a product operator description. Thus, the second 90^o_y pulse in the COSY sequence rotates I_x to I_z, and also rotates S_z to S_x. The combined effect is a ***polarization transfer*** of **I** to **S** magnetization (from methyl to methine):

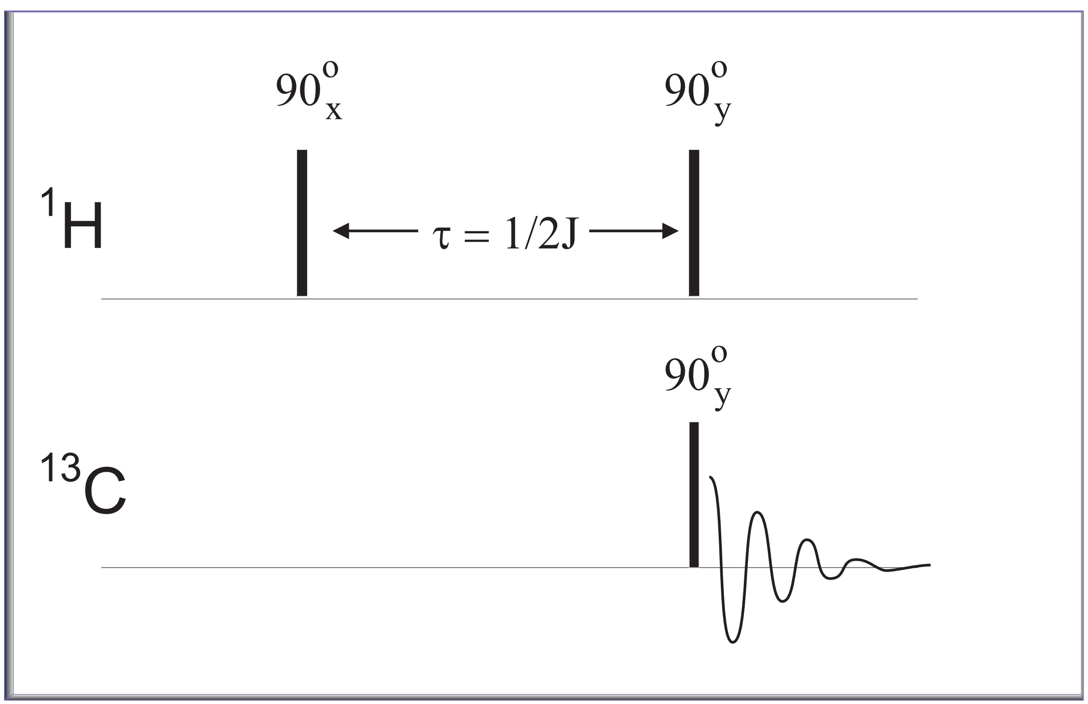


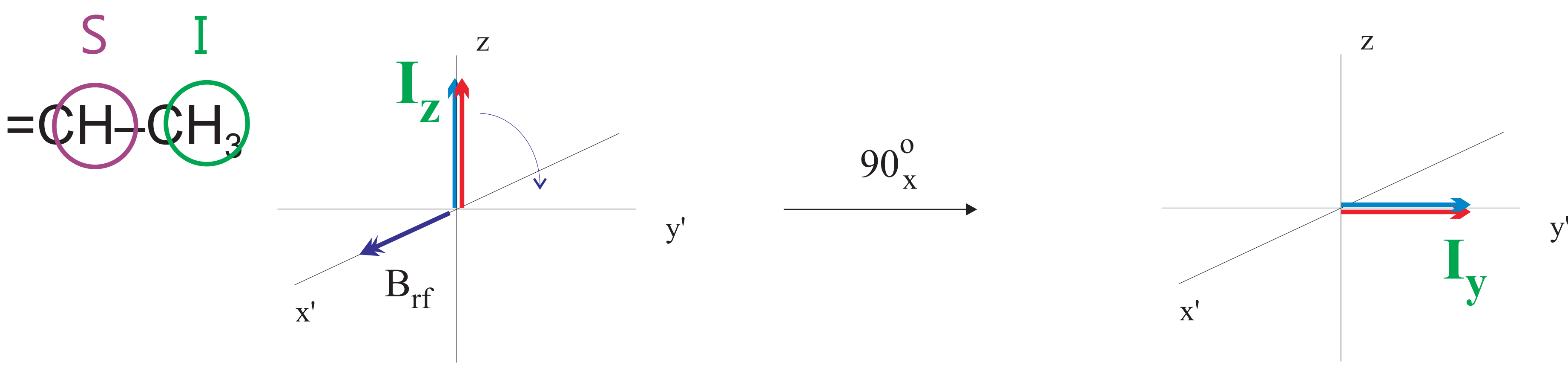
$$I_xS_z \xrightarrow{90^o_y} I_zS_x$$





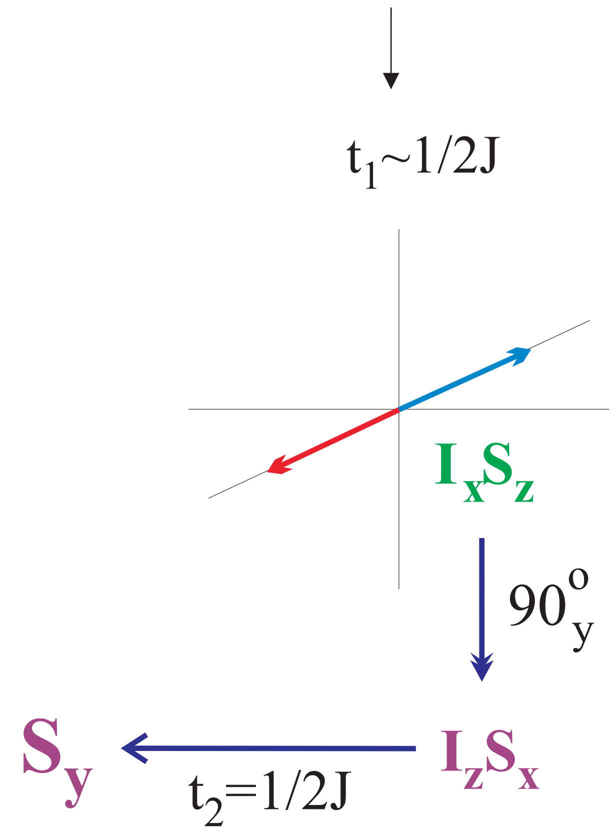
From INEPT description, we had an analogous situation: transfer of magnetization via 90° pulses on the two spins. For INEPT the 2 spins are heteronuclear, so 2 separate pulses. For COSY the 2 spins are homonuclear, so one 90° pulse operates on both.

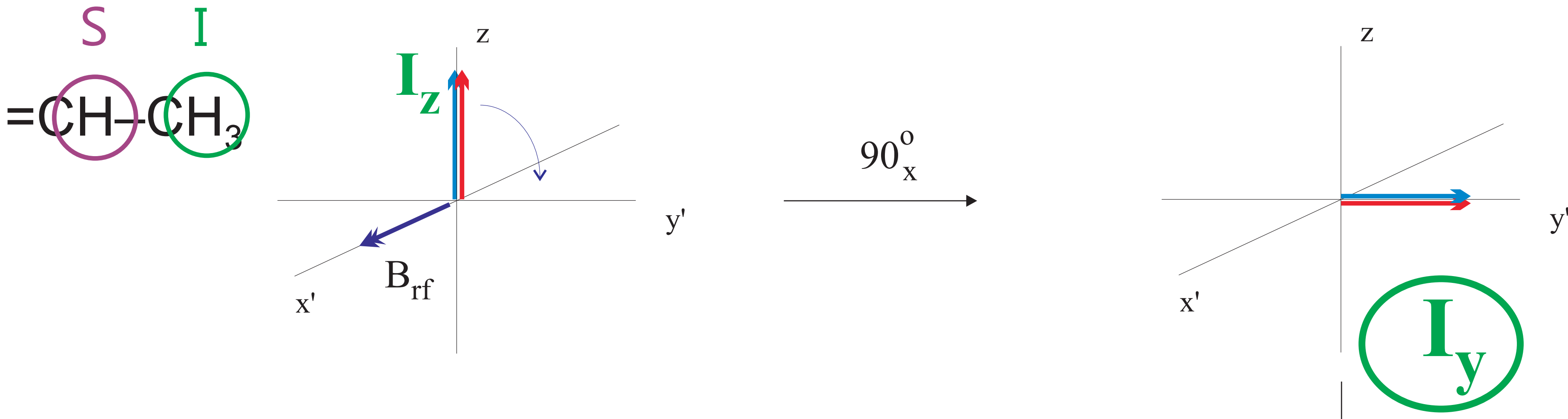




It takes another 1/2J time period to convert the I_zS_x anti-phase magnetization back to pure S_y single quantum magnetization.

$$I_zS_x \rightarrow I_zS_x \cos(\pi J t_2) + S_y \sin(\pi J t_2)$$

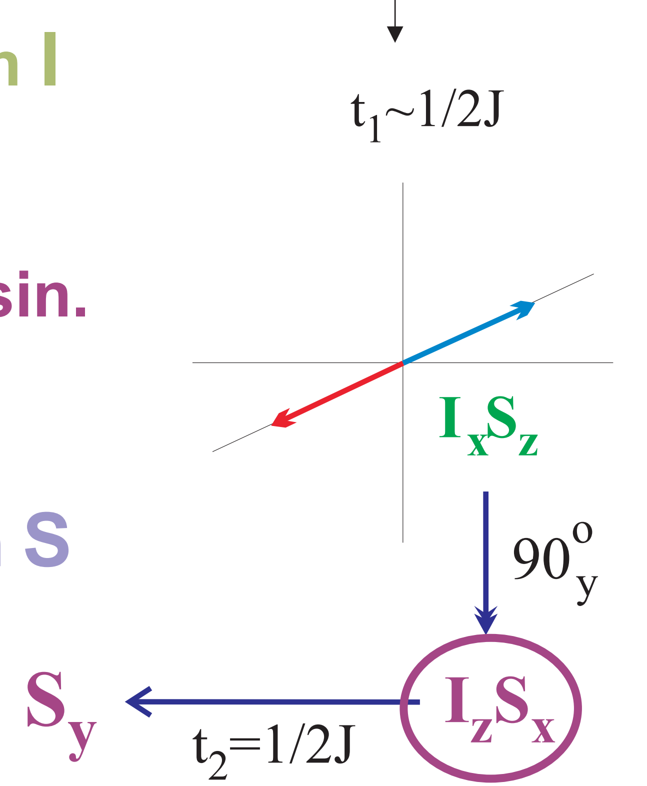


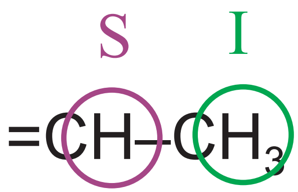


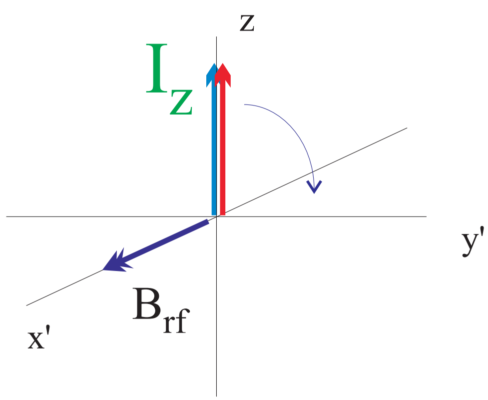
During t_1, observe δ_I and *J* of spin I

The spin terms are out of phase;
one is cos modulated, the other sin.
Process in magnitude mode.

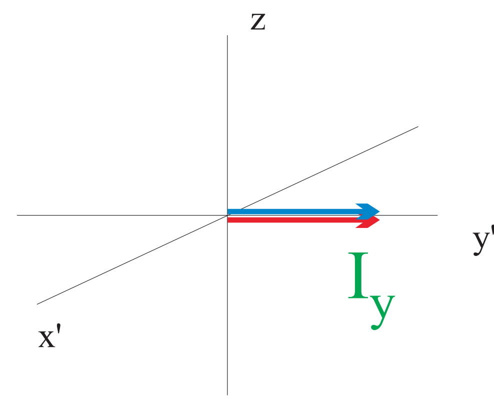
During t_2, observe δ_S and *J* of spin S



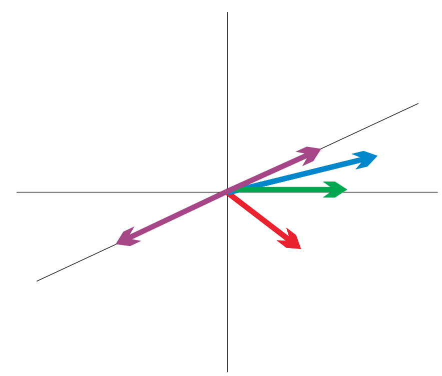




$\xrightarrow{90^{o}_{x}}$



$t_1 \sim 1/4J$



$$I_y \cos\pi J t_1 \quad + \quad I_x S_z \sin\pi J t_1$$

$\downarrow\ 90^{o}_{y}$

$$I_y \cos\pi J t_1 \quad + \quad I_z S_x \sin\pi J t_1$$

$\downarrow\ t_2$

$$I_y \cos\pi J t_1 \cos\pi J t_2 \quad + \quad S_y \sin\pi J t_1 \sin\pi J t_2$$

diagonal + crosspeak

(absorptive) (dispersive)