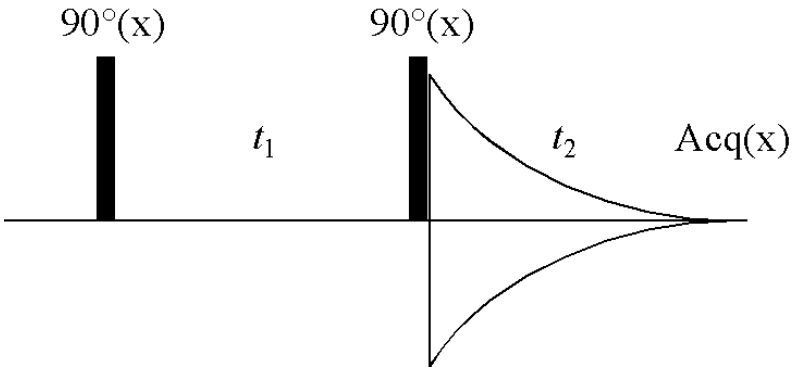
ND NMR Experiments

Homonuclear Multidimensional NMR

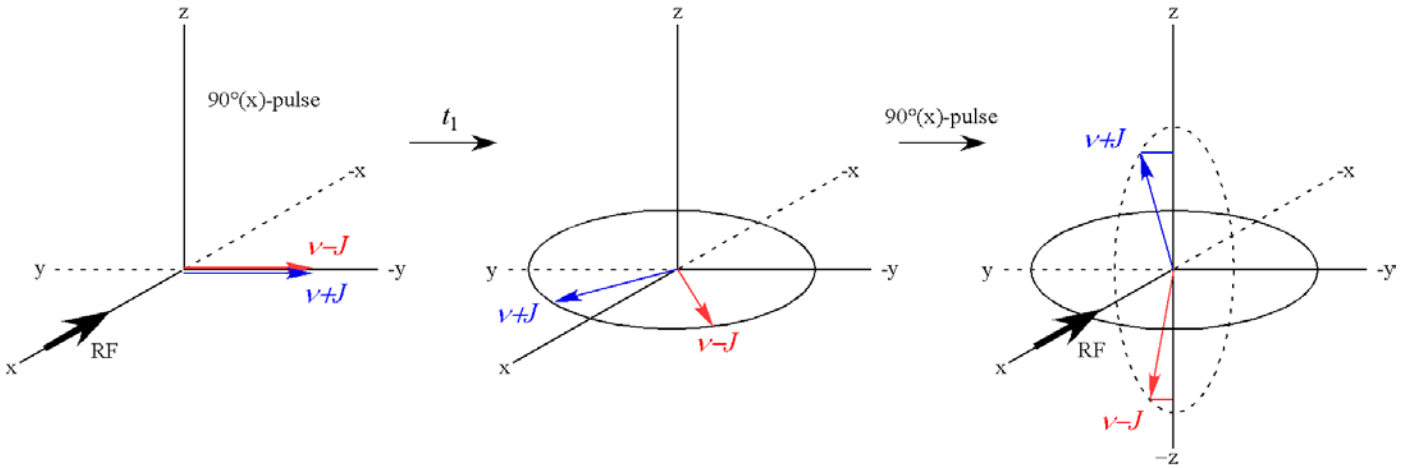
Most multidimensional NMR methods make use of *J*-coupling to link the two dimensions.

In ^{1}H spin systems, the most basic version of this type of experiment is known as COSY (**co**rrelated **s**pectroscop**y**):



In terms of our basic component designations, the first 90°-pulse corresponds to preparation, following by the t_1 or evolution interval.

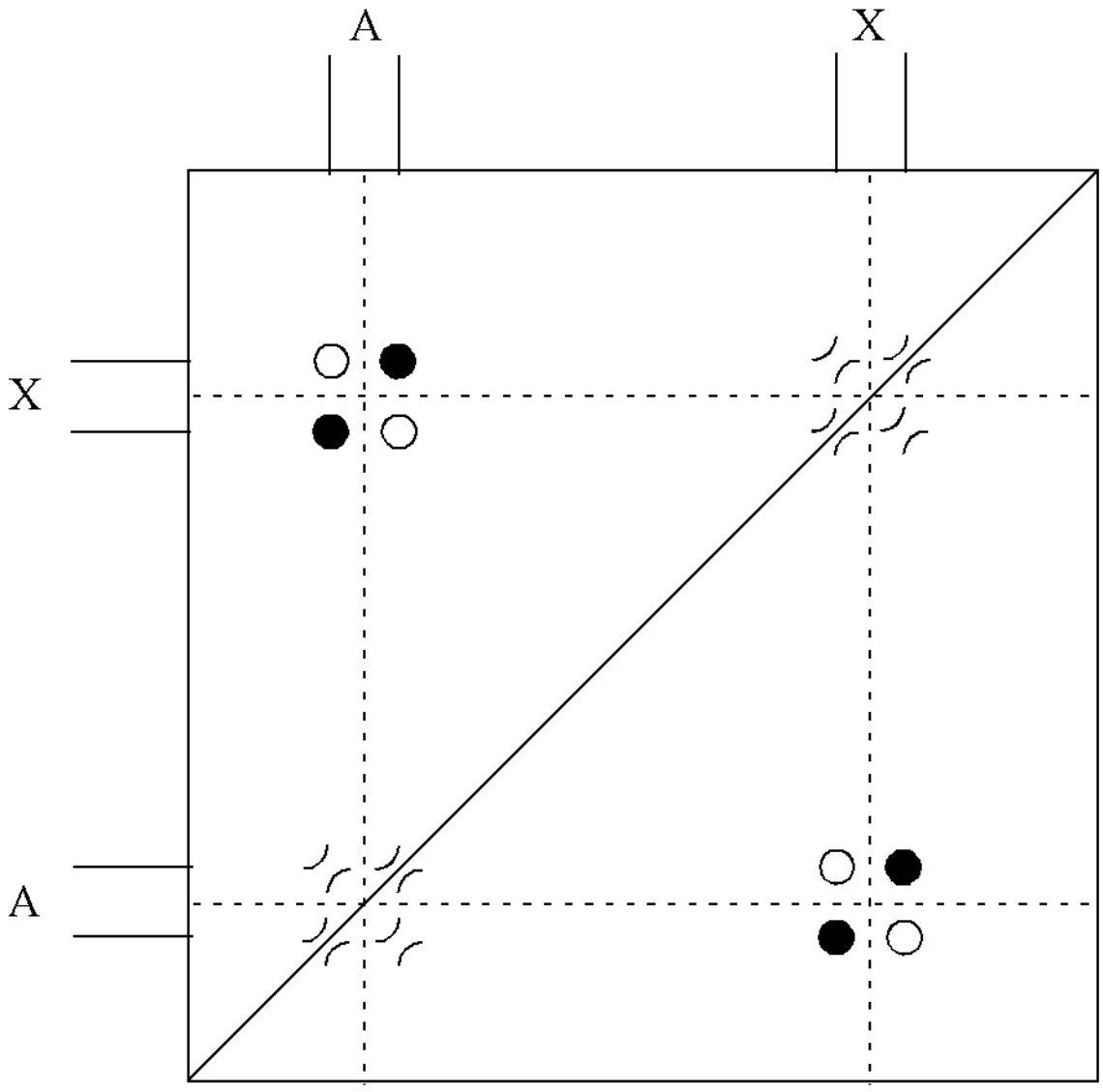
The mixing component of this experiment consists of another single 90°-pulse. The effect of this second 90°-pulse is to transfer the frequency information that has been encoded by the evolving magnetization into the *J*-coupled spin partners:



Notice that the vector components that have evolved in the xy-plane are projected onto the z-axis. Since the magnitude of the projection depends both on the chemical shift and J-coupling effects, both influences are encoded.

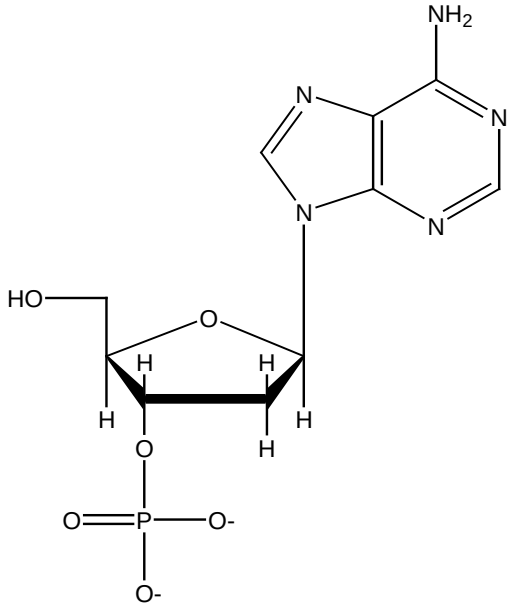
During the detection interval, the magnetization is again encoded with chemical shift and *J*-coupling information, so that the acquired signal contains information encoded during two distinct time interval and was mediated by the *J*-coupling interaction.

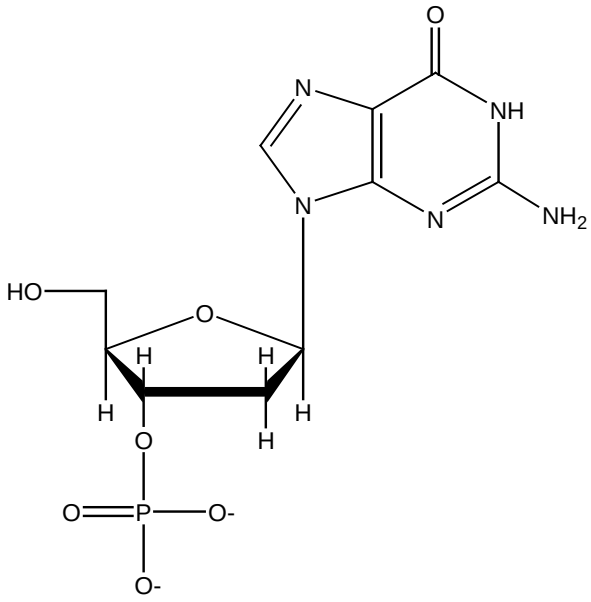
The structure of the resulting data is composed of two frequency dimensions as shown below:

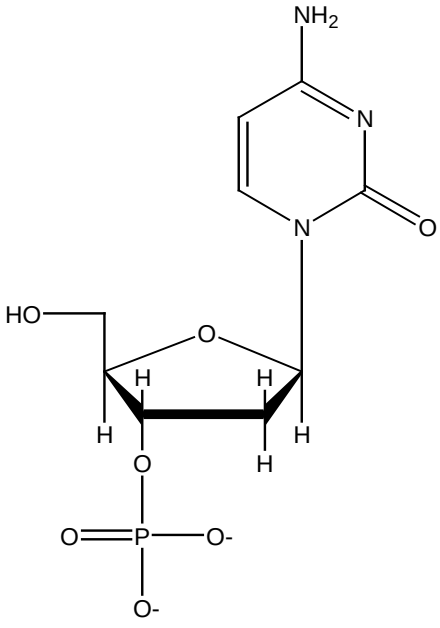


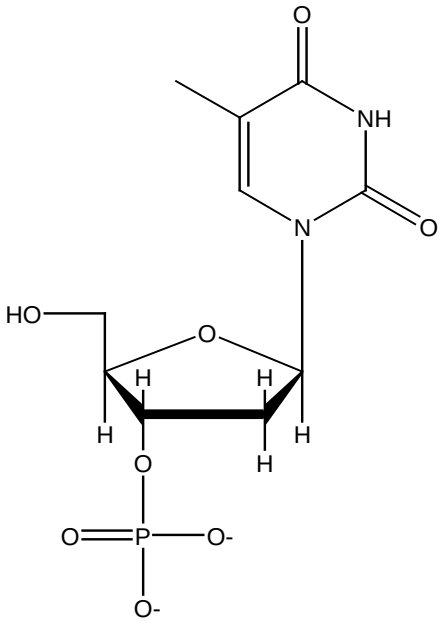
The COSY experiment correlates spins that have nonvanishing $J_{HH'}$, i.e., ${}^{2}J_{HH'}$ and ${}^{3}J_{HH'}$

Chain form of the DNA monomers:

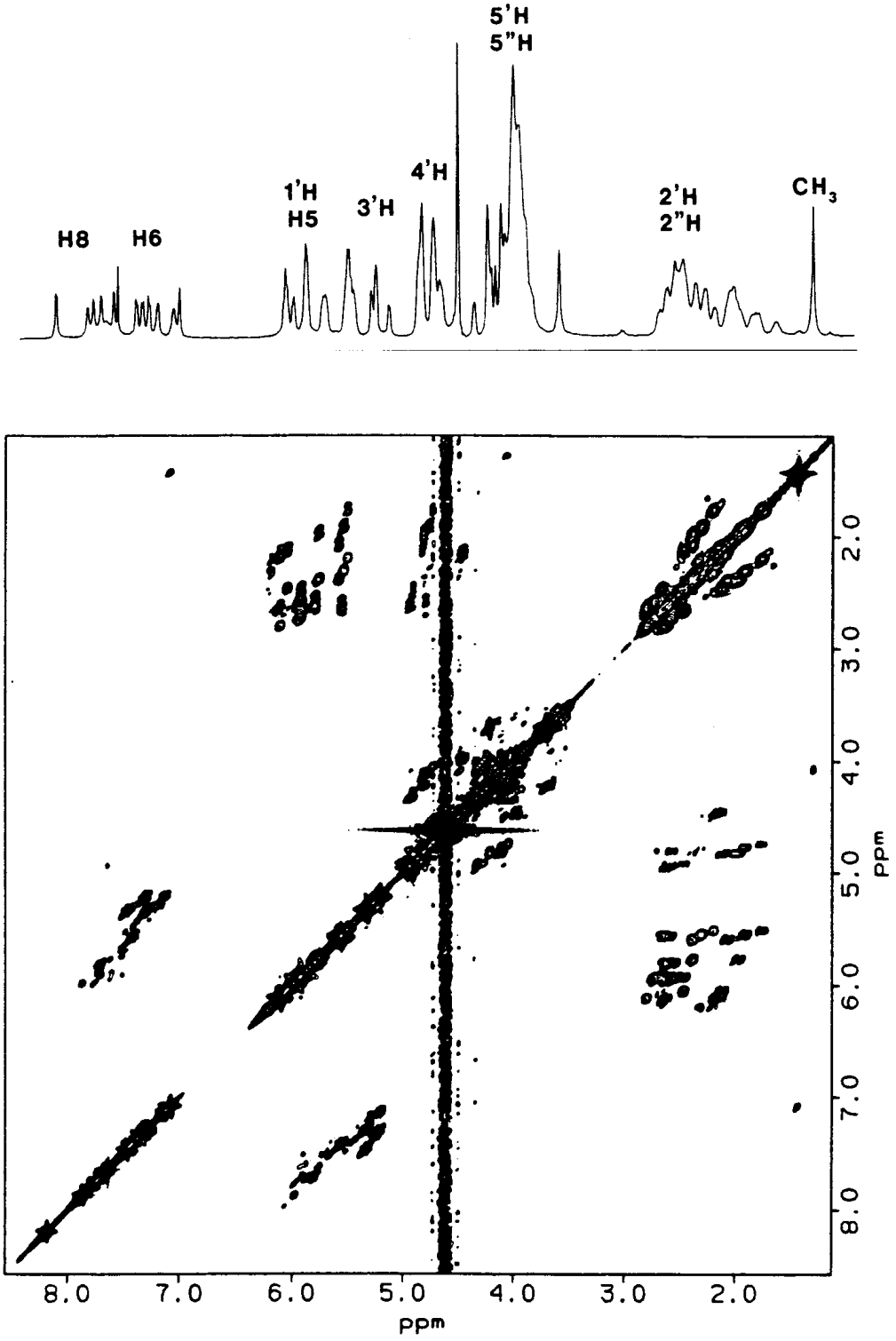




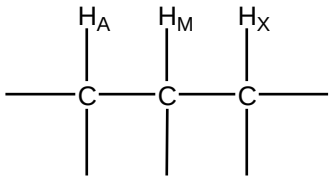




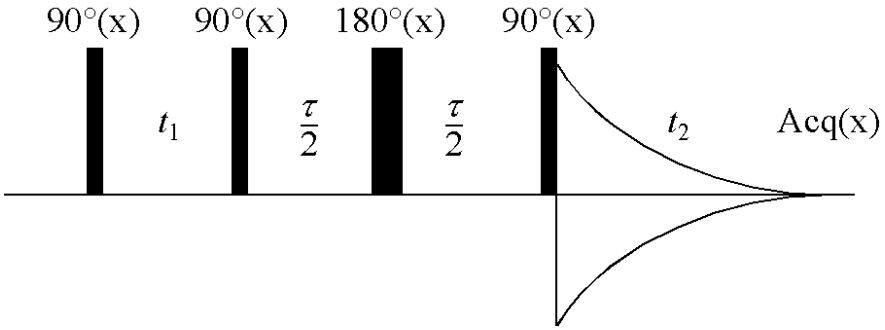
The COSY spectrum of a short palindromic DNA duplex oligomer is shown below:



A related experiment allows the correlation of spins A and X, that have no measurable coupling directly, but have measurable couplings to a third spin, M:

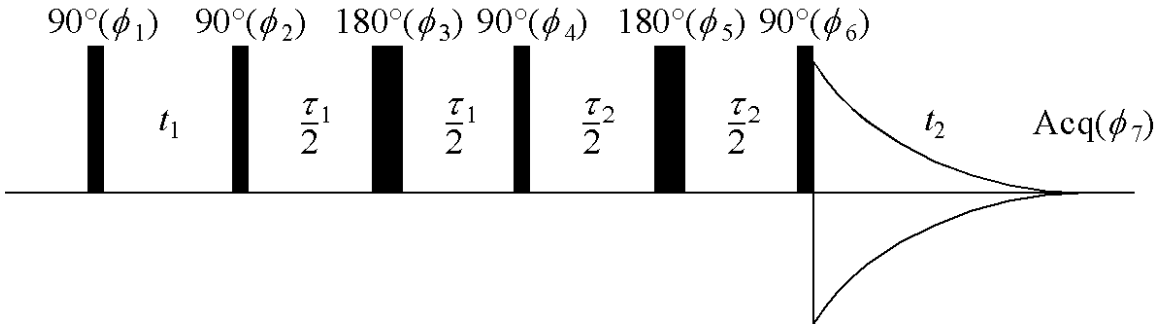


The timing-diagram for the Relayed-COSY, or Relay, or simply R-COSY is shown below:



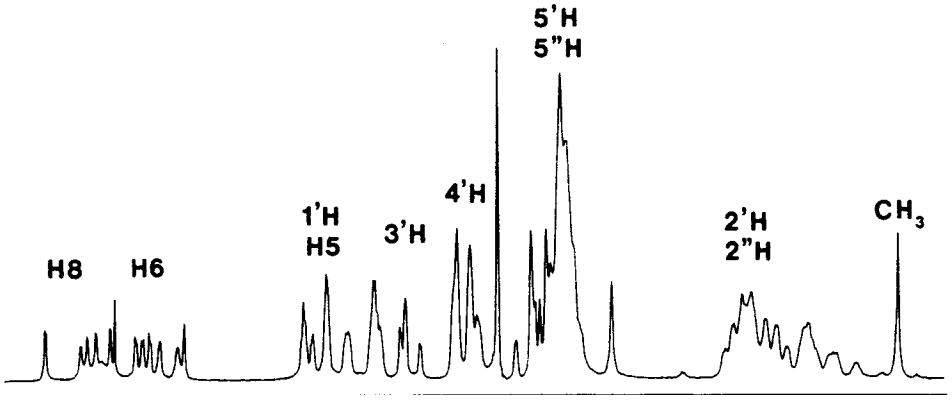
The remarkable feature of the Relay experiment is that information regarding one correlation is linked, relayed, to another correlation. Thus spins that exhibit no significant *J*-coupling are manipulated into producing an observable correlation. The requisition condition for success is that $\left|J_{\mathrm{AM}}\right| > 0$ and $\left|J_{\mathrm{MX}}\right| > 0$.

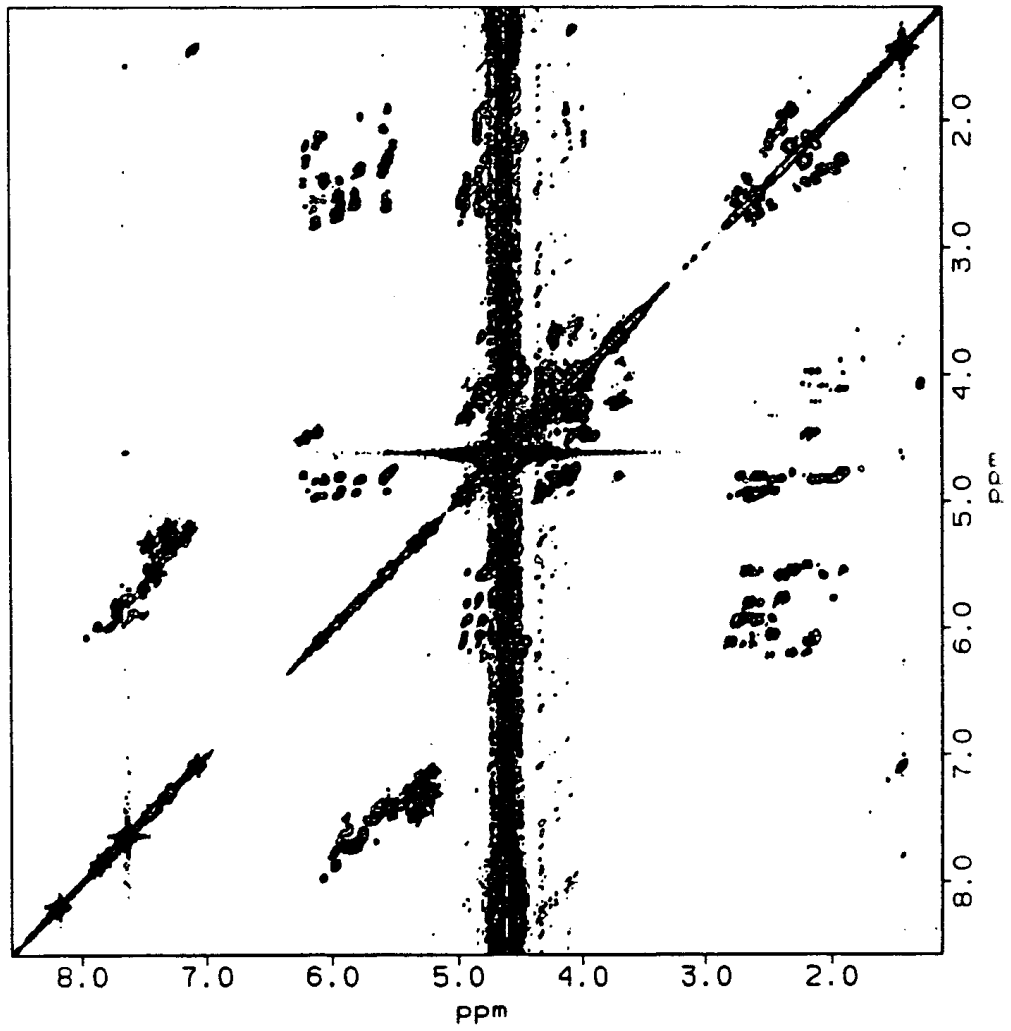
This procedure may be repeated, forming the Double-Relayed-COSY experiment:



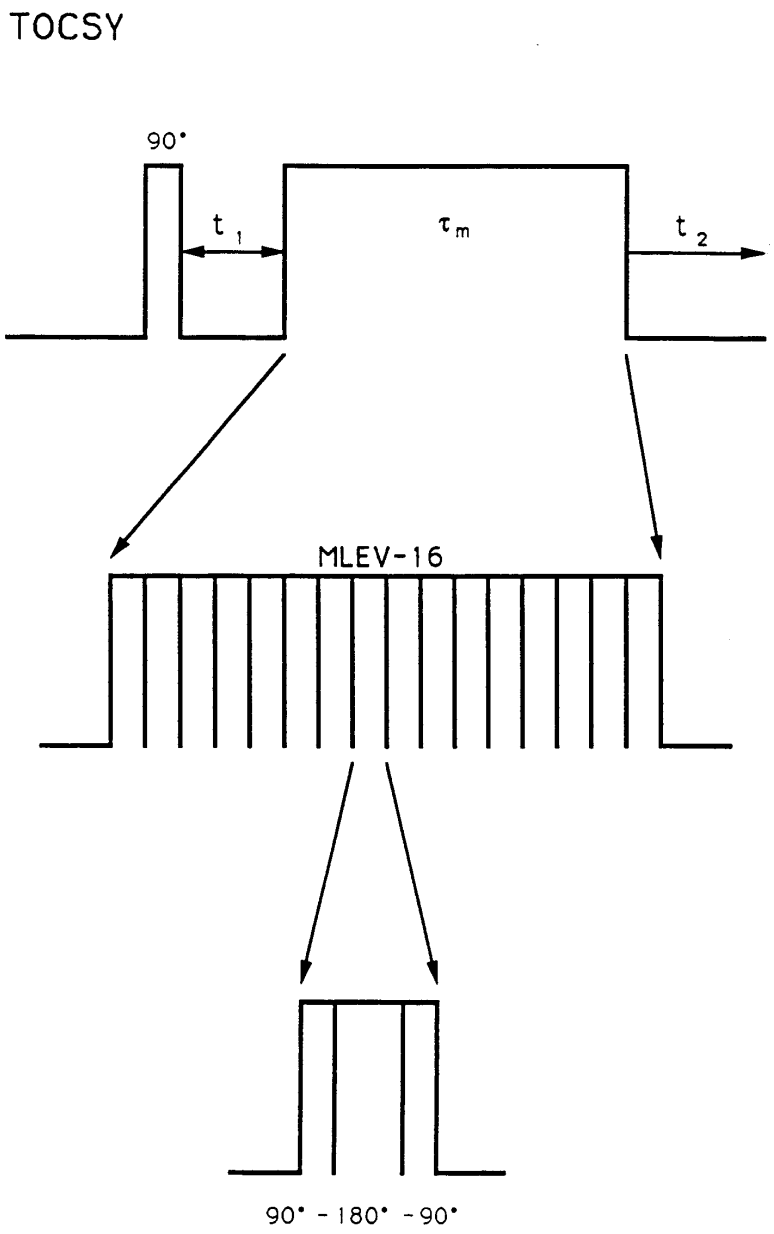
The double relay experiment generates correlations betweens spins by 5 bonds, as well as other correlations.

The Relayed-COSY spectrum of a short palindromic DNA duplex oligomer is shown below:

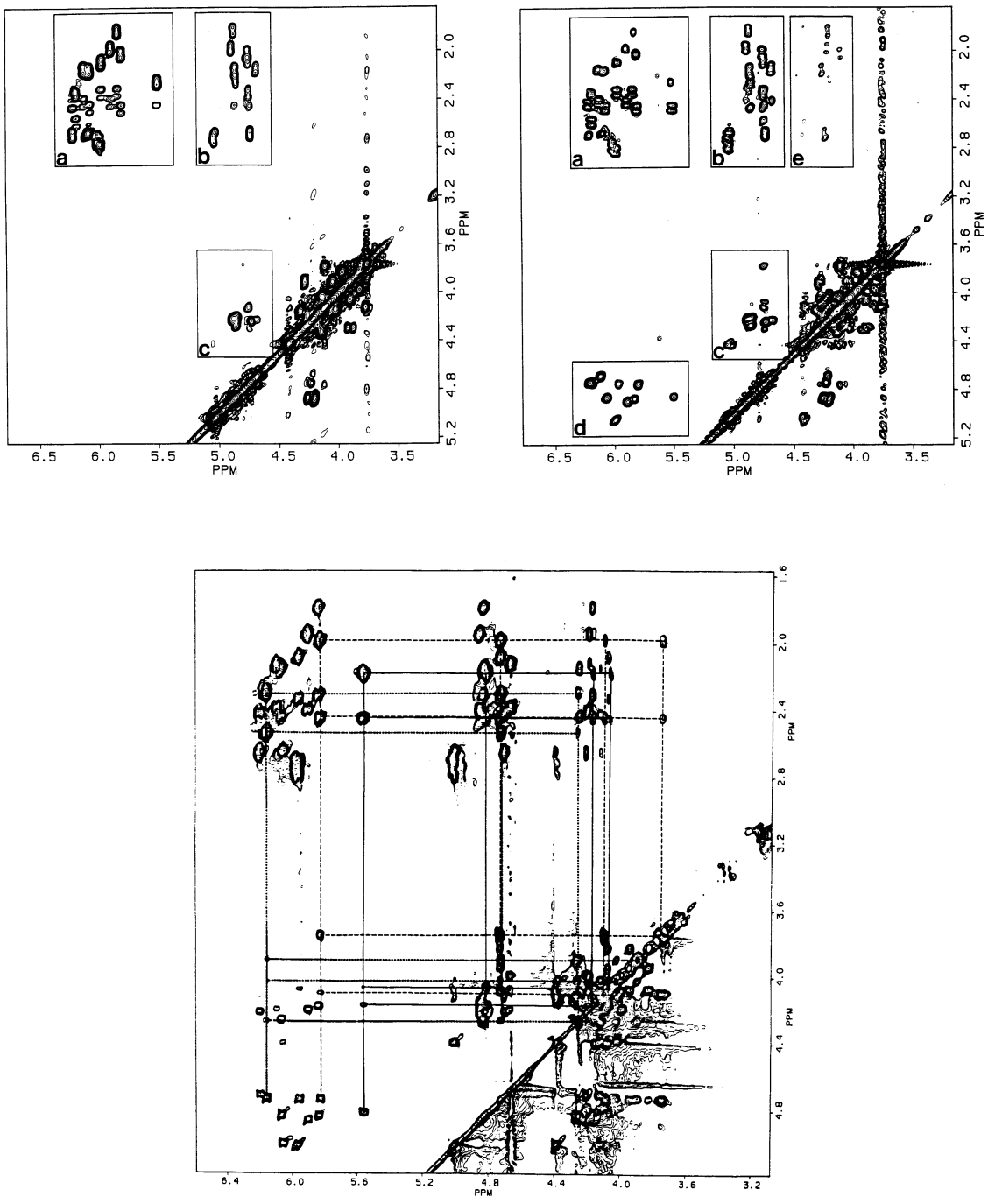




The search for longer-range correlation maps led to the development of a new and important concept, Total Correlation Spectroscopy (TOCSY):



The TOCSY is a classic example of Hamiltonian manipulation. In this experiment that magnitude of the chemical shift Hamiltonian is scaled such that virtually all *J*-coupling persist in the strong coupling limit. In this limit, discreet energy level transitions are absent and all spins with nonvanishing couplings may interact.



Upper left: Region of DNA COSY with a) H1´-H2´ and H1´-H2´´ crosspeaks, b) H2´-H3´ crosspeaks and c) H3´-H4´ crosspeaks. Upper right: Region of DNA Relay showing additional correlations d) H1´-H3' crosspeaks and e) H2'-H4' crosspeaks. Lower: DNA TOCSY of the same region showing total correlation of ^{1}H spins in the deoxyribose ring.

Multinuclear/Multidimensional NMR

The correlated spectroscopy is not limited to ^{1}H-^{1}H *J*-coupling interactions, but is completely general.

The simplest heteronuclear chemical shift correlation experiment is HETCOR.

Basic HETCOR:

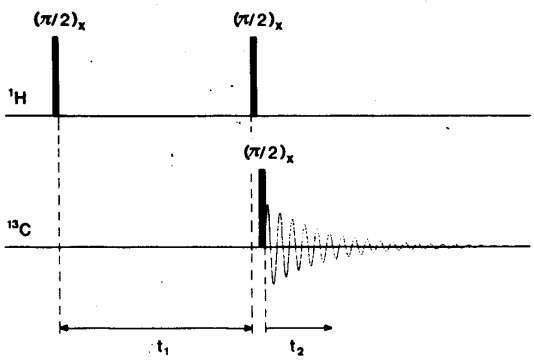


Fig.2.2 Basic scheme of the heteronuclear shift correlation experiment.

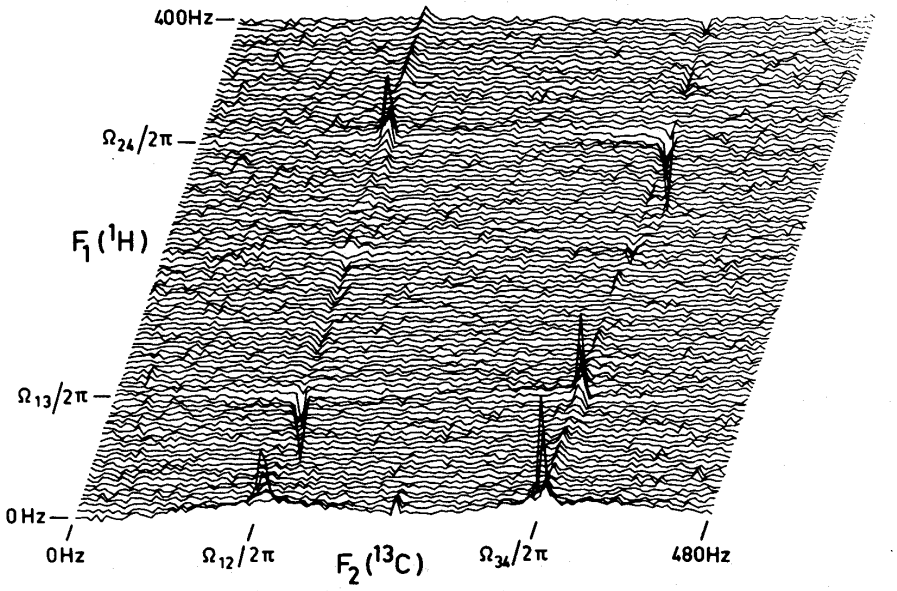


Fig.2.4 Heteronuclear shift correlation spectrum of chloroform ($CHCl_3$) with heteronuclear coupling present in both frequency dimensions. (Recorded at 75 MHz for ^{13}C).

Figures 2.2 and 2.4 from the Bax text.

F2 (^{1}H) Decoupled HETCOR:

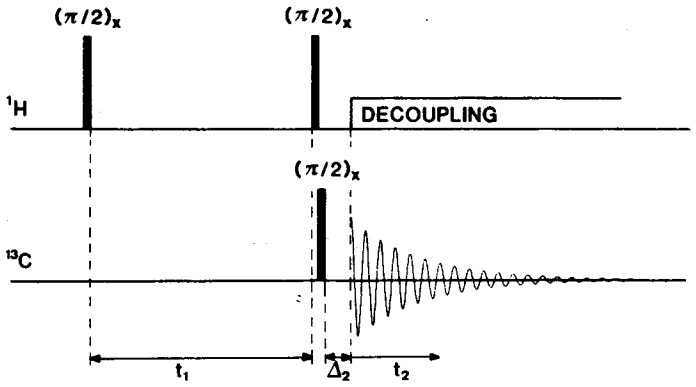


Fig.2.5 Experimental scheme for heteronuclear shift correlation with proton-decoupled acquisition.

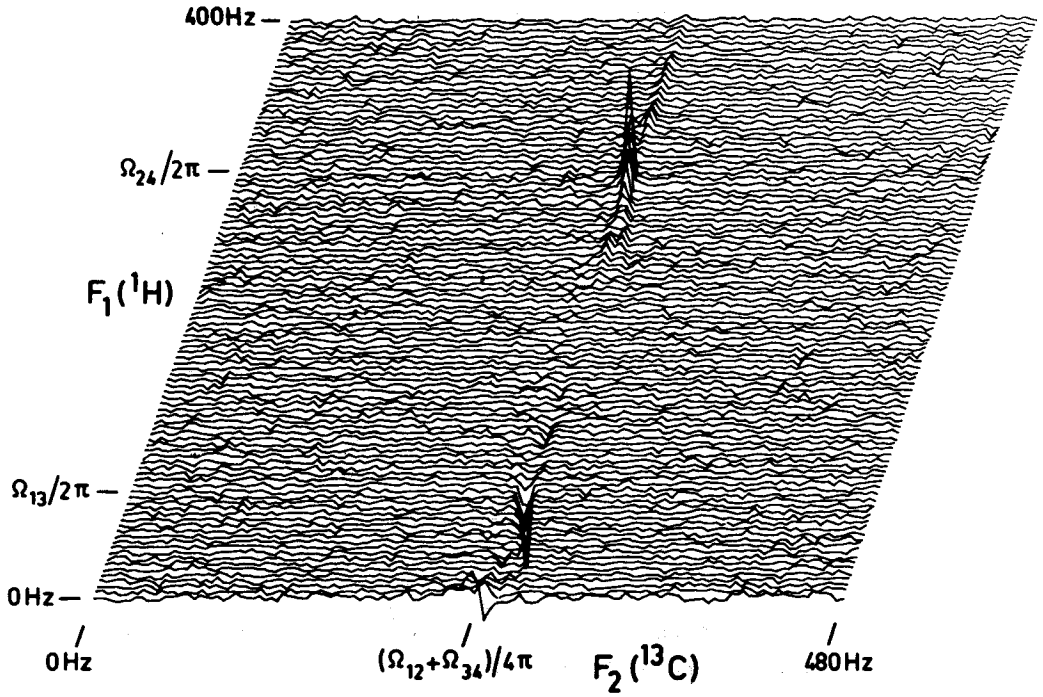


Fig.2.6 Heteronuclear shift correlation spectrum of chloroform with proton-decoupled acquisition. (Recorded at 75 MHz for ^{13}C).

Figures 2.5 and 2.5 from the Bax text.

F1/F2 decoupled HETCOR:

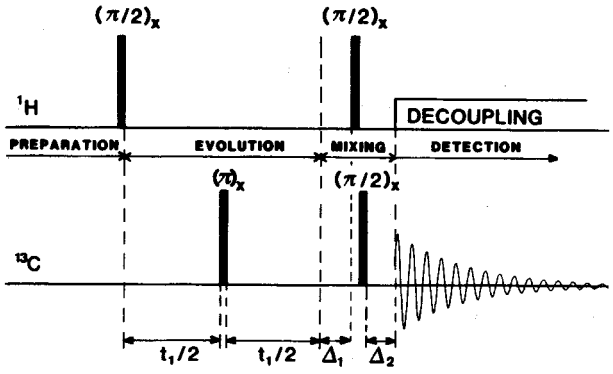


Fig.2.7 Scheme of the heteronuclear shift correlation experiment with ^{13}C decoupling during evolution and ^{1}H decoupling during detection.

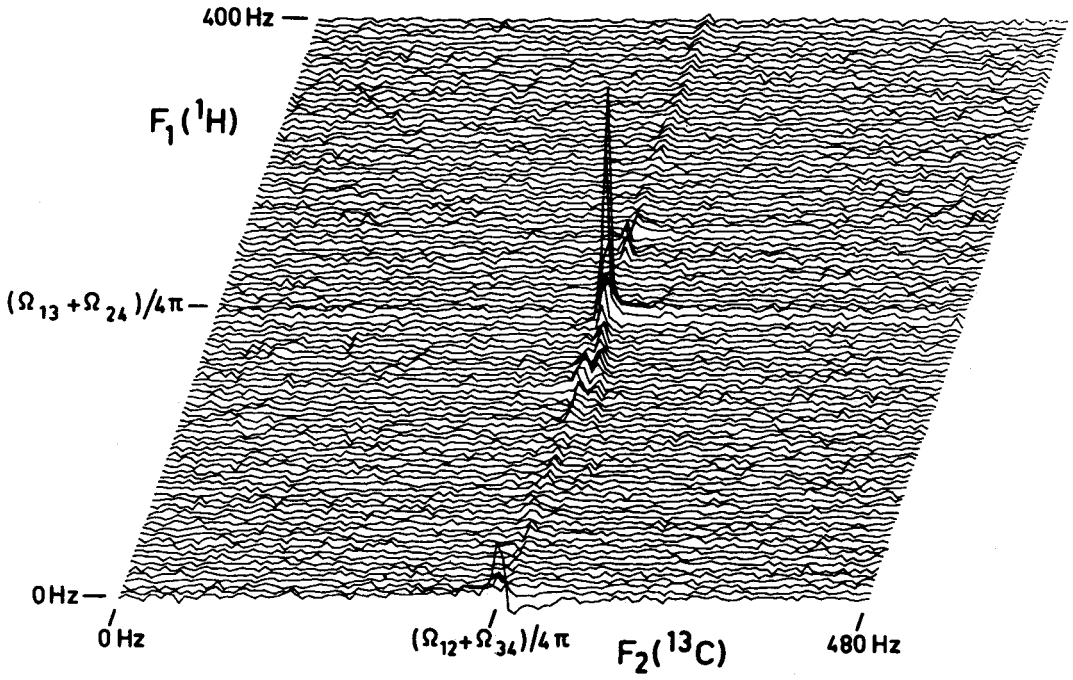


Fig.2.8 Phase-sensitive display of the chemical shift correlation spectrum of chloroform, decoupled along both axes. (Recorded at 75 MHz for ^{13}C).

Figures 2.7 and 2.8 from the Bax text.