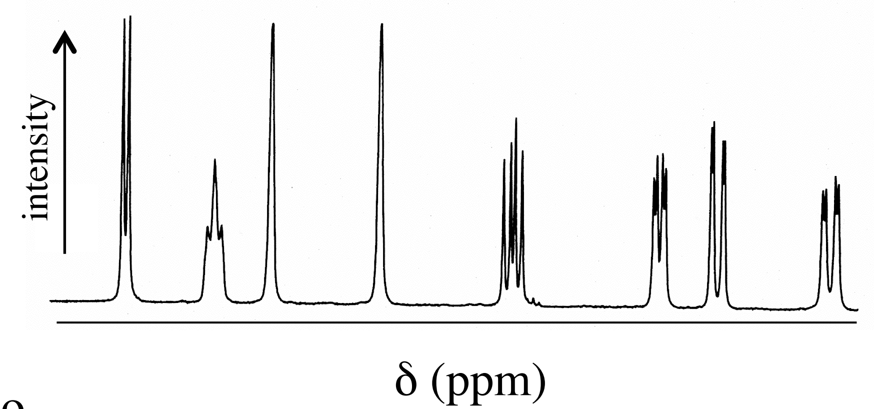
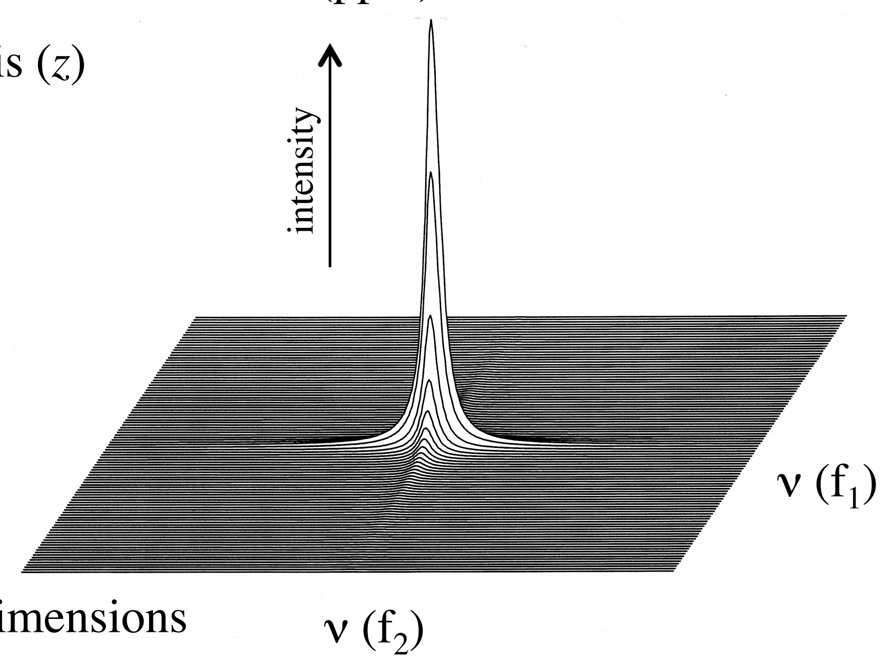
2D NMR Spectroscopy

Two-Dimensional NMR

- One-dimensional (1D) NMR: one frequency axis (*x*), and one intensity axis (*y*)



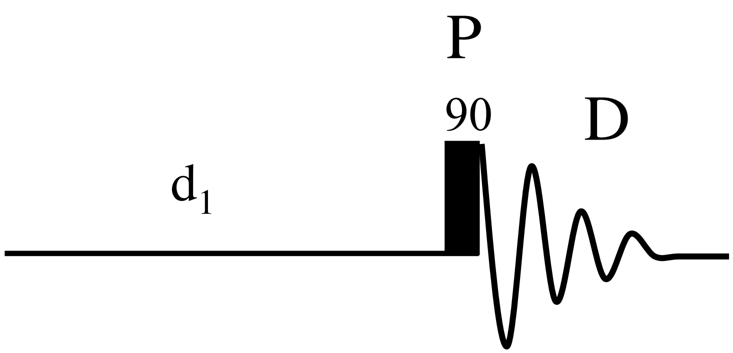
- Two-dimensional (2D) NMR: usually two frequency axes (*x* and *y*), and one intensity axis (*z*)
  - often, both frequency axes are chemical shifts (chemical shift correlation experiments)
  - one frequency axis, however, might be, for instance, a coupling constant (in Hz)
  - the directly detected dimension is f_2, and the indirectly detected dimension f_1



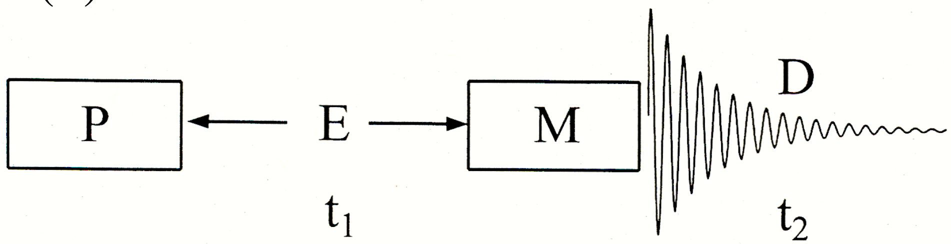
- In two dimensional experiments, the *x* and *y* dimensions are related or *correlated* based on:
  - through bond coupling (COSY, TOCSY, HSQC)
  - through space interactions (NOESY)
  - chemical exchange processes (EXSY)

Two-Dimensional NMR

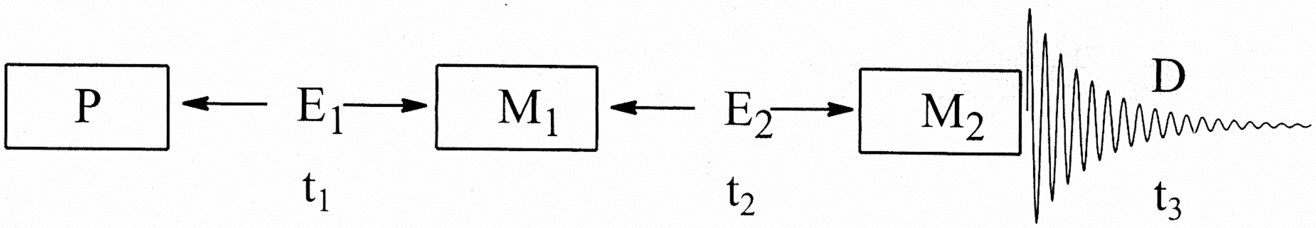
- One-dimensional experiments can be described as consisting of a spin "preparation" (P) phase (often just a single pulse) and a "detection" (D) phase, when the magnetization is detected



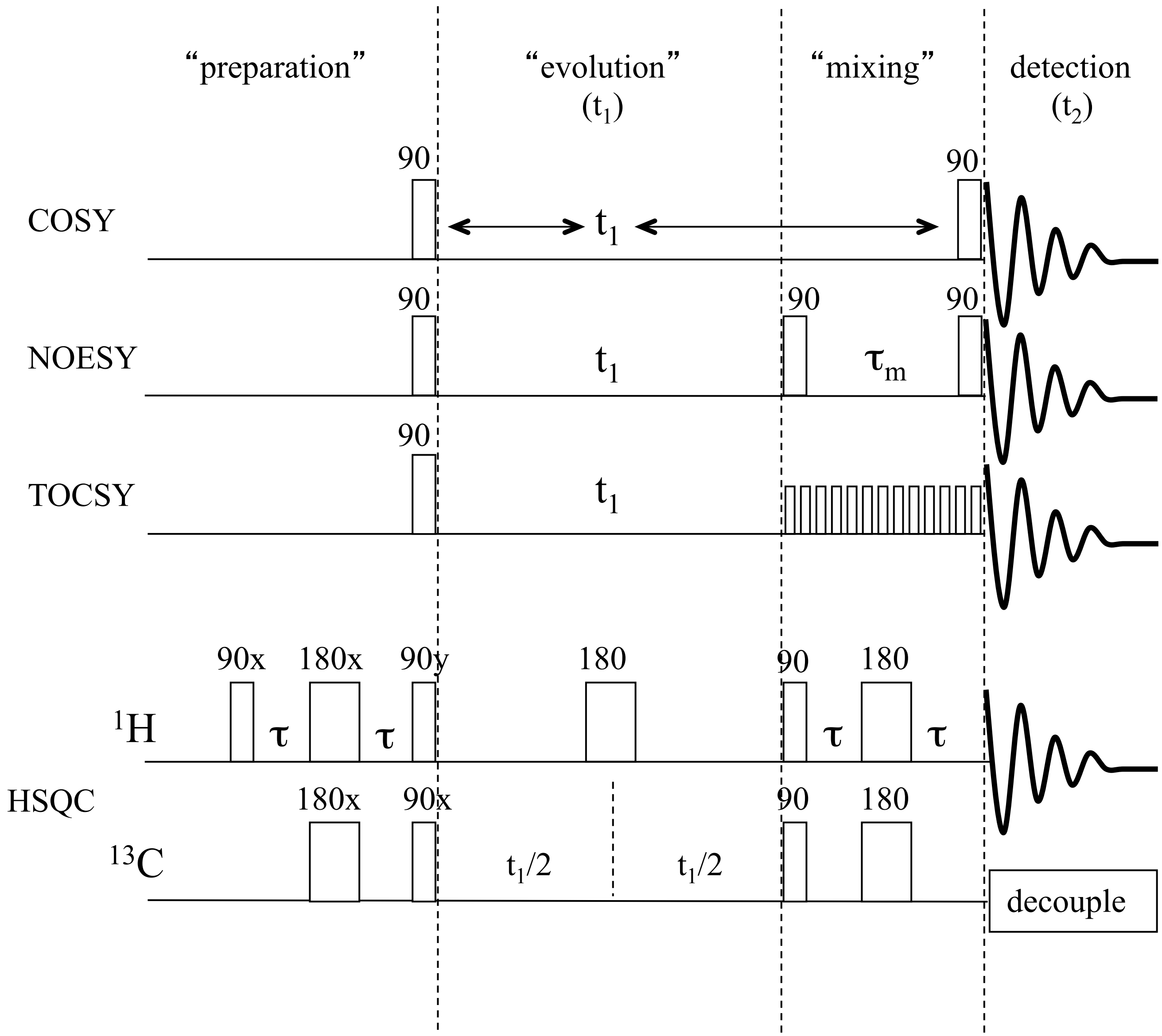
- Two-dimensional experiments include, in addition, a magnetization "evolution" period (E) and a "mixing" (M) period
  - -during the evolution period, the modulation of the signal for the second dimension occurs
  - -during the mixing period, magnetization or "coherence" transfer between spins occurs



- Additional E and M periods can be added to create 3D and 4D experiments



Some Two-Dimensional NMR Experiments



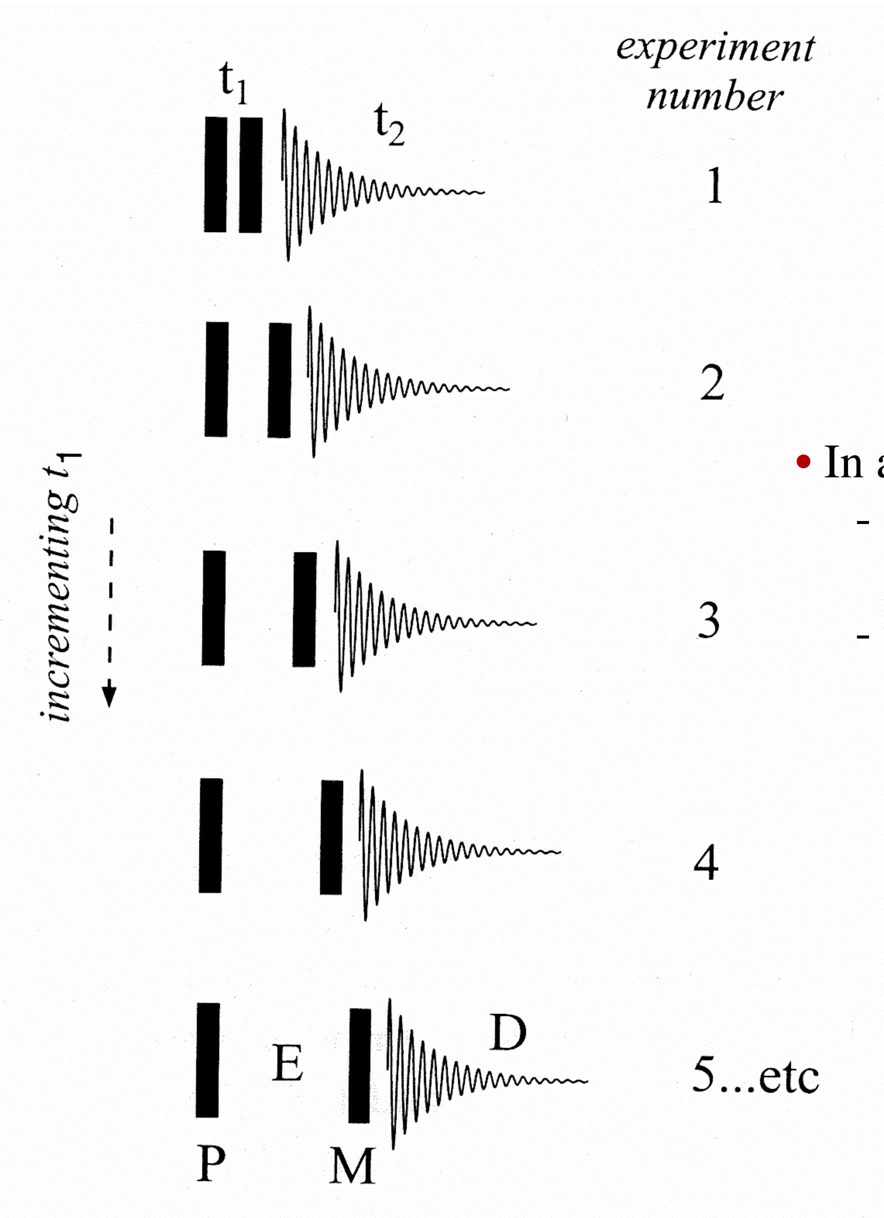
COSY: Correlation Spectroscopy

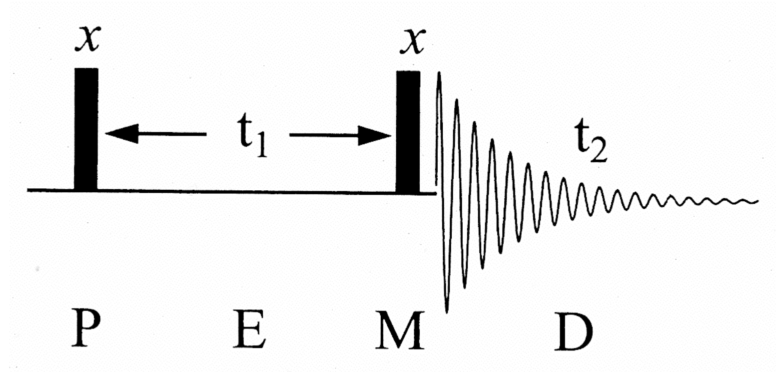
NOESY: Nuclear Overhauser Effect Spectroscopy

TOCSY: Total Correlation Spectroscopy

HSQC: Heteronuclear Single Quantum Coherence

Two-Dimensional NMR Data Collection and Manipulation

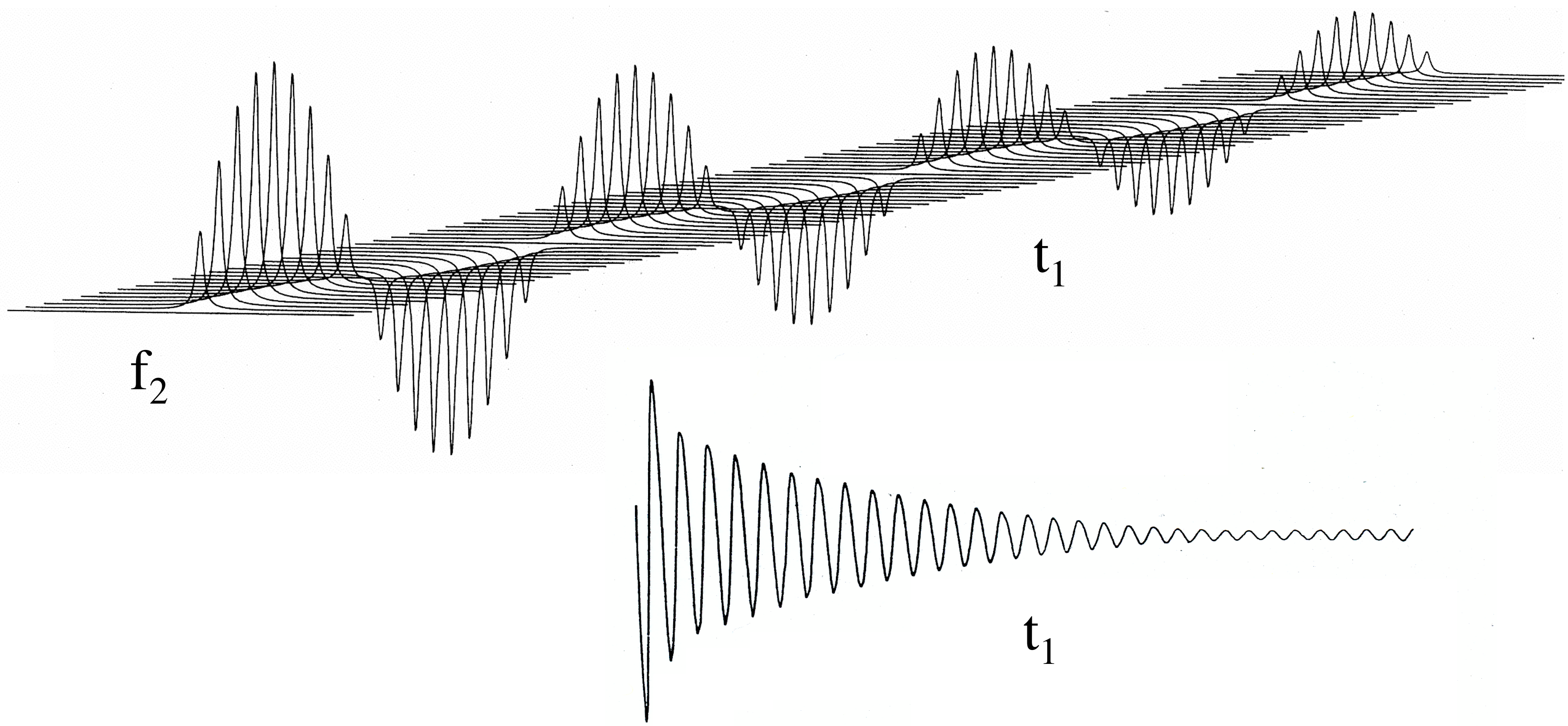




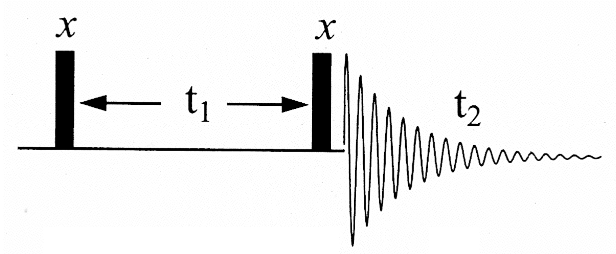
- In a two-dimensional experiment, t_1 is incremented
  - a series of 1D experiments are collected at increasing t_1 values
  - these 1D FIDs are Fourier transformed (the "t_2" transform) to give a series of 1D NMR spectra

Two-Dimensional NMR Data Collection and Manipulation

- Peaks (signals) in the series of 1D spectra are modulated by t_1 and decay with t_1
  - thus, the signals in the 1D spectra form a FID in the t_1 (second) dimension
  - so, a Fourier transform (the "t_1" transform) can be performed on these signals to give the 2D plot
  - different signals in f_2 may be modulated differently in t_1, resulting in different f_1 frequencies for different f_2 signals

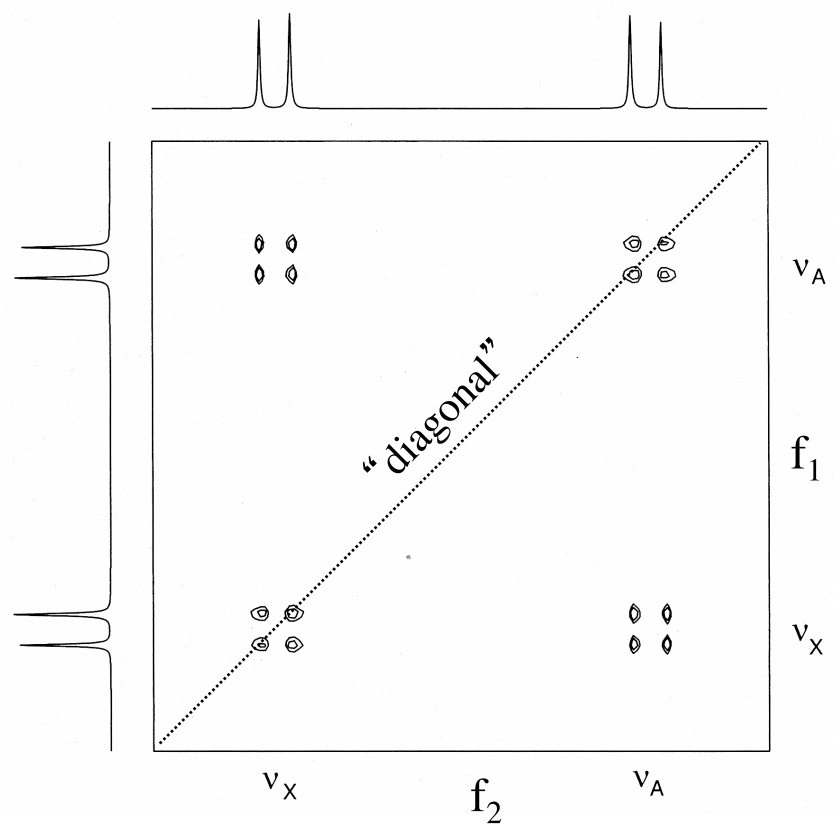


COSY: 2D Chemical Shift Correlation



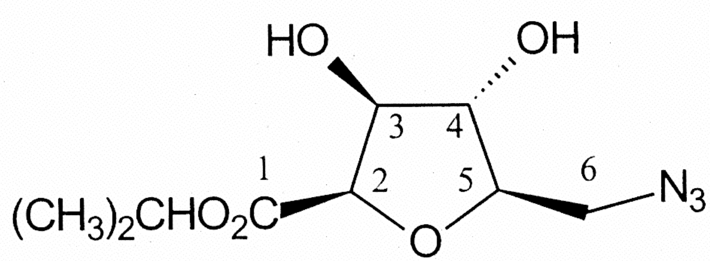
- COSY correlates chemical shifts of coupled nuclei
  - magnetization is transferred between coupled nuclei as a result of the COSY experimental scheme
  - provides information on through-bond connectivity

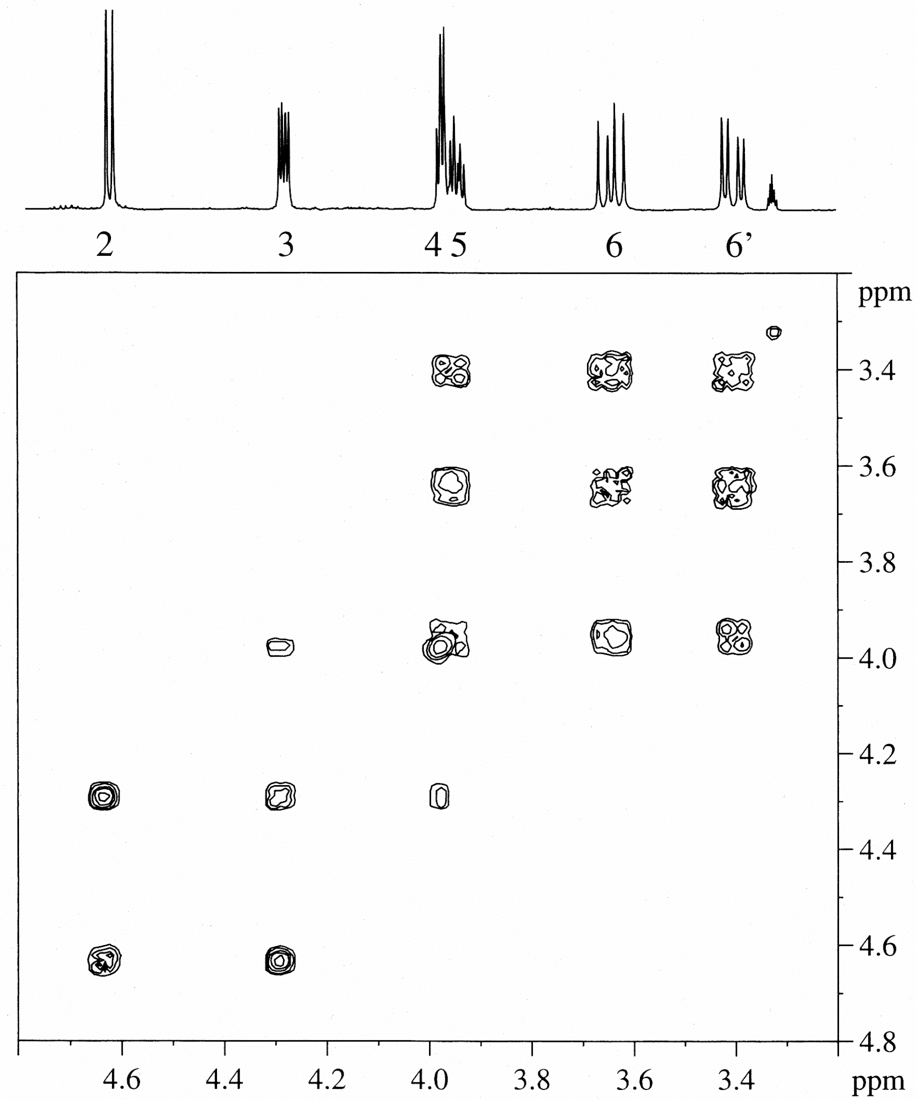
- consider two coupled spins, A and X:
  - X magnetization will precess at ν_X during t_1
  - X magnetization that is *not* subsequently transferred to A will also precess at ν_X during t_2
  - however, X magnetization subsequently transferred to A will precess during t_2 at ν_A
  - thus, off diagonal signals (with different chemical shifts in f_2 and f_1) indicate that X and A are coupled
  - diagonal elements are, in general, not interesting



COSY: Example

- COSY spectrum of an azo-sugar
- crosspeaks appear at positions corresponding to the chemical shifts of ^{1}H nuclei on adjacent carbon atoms
  - crosspeaks indicate significant coupling between the ^{1}H nuclei
  - *usually*, therefore, crosspeaks are not observed for ^{1}H nuclei separated by more than 3 bonds

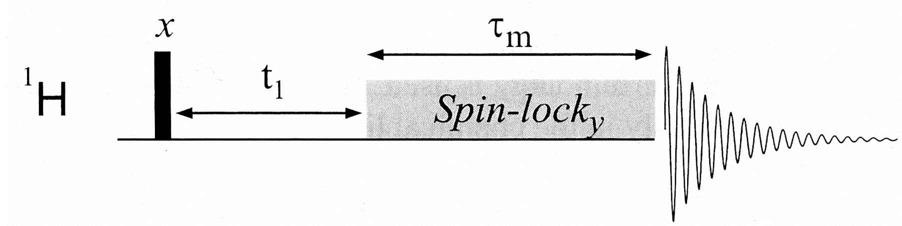


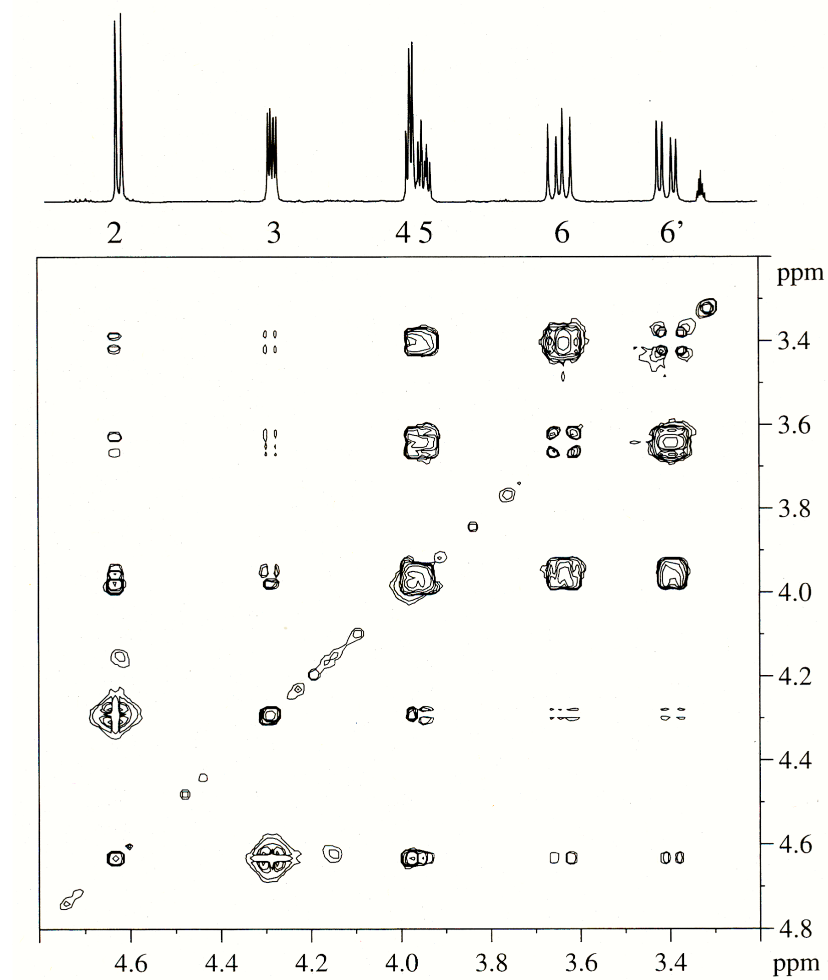


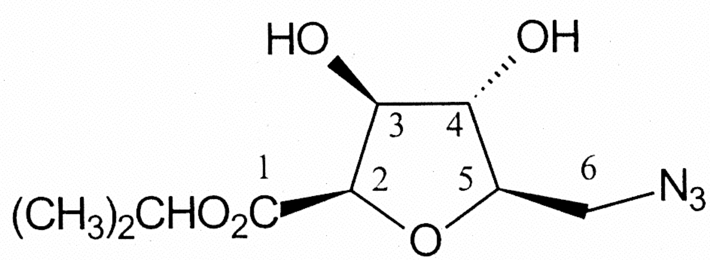
TOCSY: "Total" Correlation Spectroscopy

- TOCSY spectrum of an azo-sugar

- The TOCSY "spin-lock" sequence enables transfer of magnetization between nuclei even if the coupling between them is very weak
  - -thus, for the example shown, crosspeaks between most of the nuclei are observed



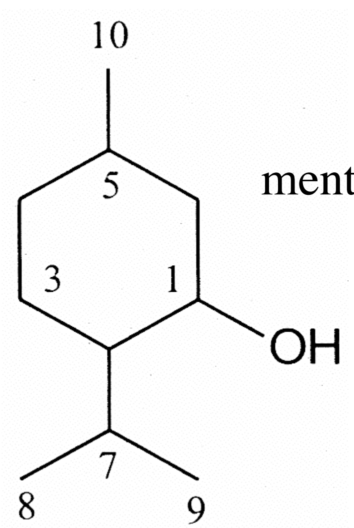




Heteronuclear Correlation Spectroscopy

- HSQC spectrum of menthol

- No diagonal peaks
- The chemical shifts of directly bonded ^{1}H-^{13}C pairs are correlated
  - -one axis is ^{13}C chemical shift
  - -one axis is ^{1}H chemical shift



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