

# Two Dimensional Homonuclear Correlation Spectroscopy

## COSY

William D. Wheeler, Ph.D.  
Department of Chemistry  
University of Wyoming

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## INTRODUCTION

### Correlation Spectroscopy

Correlation experiments reveal connections between spin coupled nuclei. Spin, or scalar, coupling between nuclei is established by the appearance of cross peaks (peaks off the diagonal) in the two-dimensional spectrum. Since spin coupled nuclei are usually separated by two or three bonds, the correlation experiment, by revealing the connectivity within the compound, is often enough to establish the chemical structure. Resonances which are coupled through four and five bonds will occasionally show cross peaks also. Although most correlation experiments are designed to emphasize short range coupling, there are experiments designed to emphasize long range correlations as well.

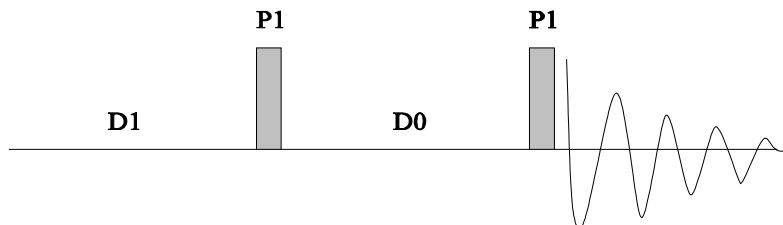
Two-dimensional spectra can be acquired in either of two modes. In the magnitude, or absolute value mode, only the “real” part of the data is collected since the spectrum is not phased. In the phase sensitive mode, both the “real” and “imaginary” parts of the data are acquired so that the spectrum can be phased. An advantage of a phase sensitive spectrum is that the peaks are much narrower and the resolution greater. A disadvantage of a phase sensitive spectrum is that twice as much data must be recorded in order to extract the phase information. Thus, it takes twice the time to record a spectrum in phase sensitive mode.

### COSY

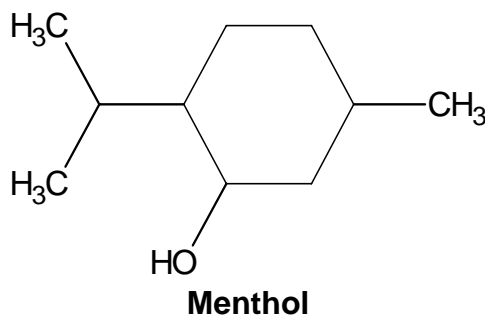
The experiment described here is one of the first two-dimensional NMR experiments developed and usually referred to as COSY, for **C**orrelation **S**pectroscop**Y**. Many variations of this experiment have been developed. Variants are usually distinguished by adding a prefix, such as dqf-COSY (for double quantum filtered) or suffix (such as COSY-45). Normal COSY spectra generally exhibit very intense diagonal peaks with cross peaks that are a great deal weaker. The intensity of the diagonal peaks is often large enough to obscure cross peaks near them. Intense diagonal peaks can also be the source of a troublesome artifact called  $t_1$  noise.

Although COSY spectra are usually acquired in magnitude mode, they can also be acquired in a phase sensitive mode. Unfortunately, in the phase sensitive mode, the diagonal has a dispersive line shape (which is broad compared to the absorption line shape) when the cross peaks are phased for pure absorption. If a phase sensitive spectrum is desired, another method such as dqf-COSY, is preferable.

The pulse sequence for COSY is shown below.

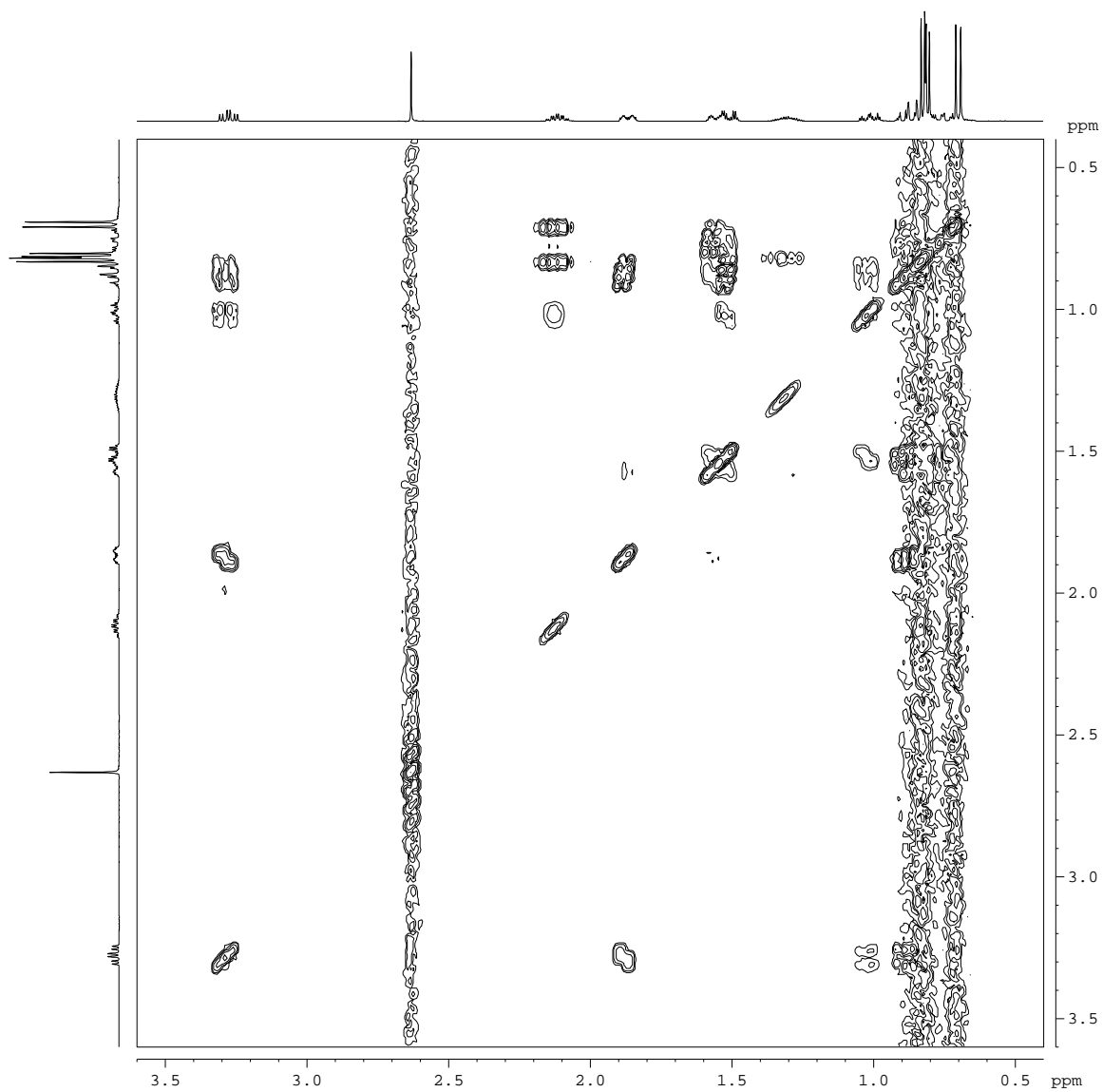


The magnitude COSY spectrum of Menthol is shown on a following page. The spectrum required about 1 hour and 20 minutes to collect.



### References.

- 1) **150** and More Basic NMR Experiments, A practical Course, S. Braun, H.-O. Kalinowski, S. Berger, Wiley-VCH, 1998, pages 353-355.
- 2) Basic One- and Two-Dimensional NMR Spectroscopy, Second, enlarged edition, Horst Friebolin, VCH Publishers, 1993, pages 248-254.
- 3) Modern NMR Spectroscopy, A Guide for Chemists, Jeremy K.M. Saunders and Brian K. Hunter, Oxford University Press, 1987, pages 108-112.



Magnitude COSY of Menthol

```

Current Data Parameters
NAME      Menthol_COSY
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    990223
Time     11.14
INSTRUM  spect
PROBHD   5 mm QNP 1H
PULPROG  cosy45
TD       1024
SOLVENT  CDCl3
NS       8
DS       16
SWH      2003.205 Hz
FIDRES   1.956255 Hz
AQ       0.2556404 sec
RG       8
DW       249.600 usec
DE       6.00 usec
TE       300.0 K
d0       0.00000300 sec
D1       3.00000000 sec
P1       7.40 usec
SF01     400.1308094 MHz
NUC1     1H
PL1      -3.00 dB
IN0      0.00049920 sec

F1 - Acquisition parameters
ND0      1
TD       256
SF01     400.1308 MHz
FIDRES   7.825020 Hz
SW       5.006 ppm

F2 - Processing parameters
SI       512
SF       400.1300092 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       512
MC2      QF
SF       400.1300092 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0

2D NMR plot parameters
CX2      15.00 cm
CX1      15.00 cm
F2PLO    3.600 ppm
F2L0     1440.47 Hz
F2PHI    0.400 ppm
F2HI     160.05 Hz
F1PLO    3.600 ppm
F1L0     1440.47 Hz
F1PHI    0.400 ppm
F1HI     160.05 Hz
F2PPMCM  0.21333 ppm/cm
F2HZCM   85.36107 Hz/cm
F1PPMCM  0.21333 ppm/cm
F1HZCM   85.36107 Hz/cm
    
```

## EXPERIMENTAL SETUP

The concentration of the sample should be high enough that you can record a high signal to noise  $^1\text{H}$  NMR spectrum in 64 - 128 scans.

### Record a $^1\text{H}$ spectrum.

NEW (or EDC)	Create a new data set for your sample.
NAME name	Data set name.
EXPNO 1	Experiment number (must be 1).
PROCNO 1	Process data number (must be 1).
[SAVE]	Save the data set.
RPAR +proton all	Read in the standard proton parameters.
NS, etc.	Adjust NS and other parameters as necessary.
RGA, ZG	Acquire some data.
FT, APK, ref	Fourier transform, phase and reference the spectrum.
Zoom	Zoom in on the region of interest. The expanded region need not contain a reference peak.
[sw-sfo1]	Set the sweep width and spectrometer frequency to cover the zoomed region. Reduce TD if the acquisition time (AQ) is unnecessarily large.
RGA, ZG	Acquire a spectrum of the zoomed region.
FT, etc.	Fourier transform, phase etc.

### Setting the conditions for $^1\text{H}$ - $^1\text{H}$ correlation.

The following AU program sets up all of the parameters for magnitude cosy.

XAU su_mcosy	Set up magnitude cosy (m cosy).
[OK]	Answer "Delete `meta.ext` files ?" with [OK].

The AU program sets the following file parameters. Use EDC to display the results.

File parameter		
EXPNO	1	Experiment number 1, for 1-D proton.
	2	Experiment number 2, for m cosy.

The AU program sets the following acquisition parameters. Use EDA to display the results.

Acquisition Parameters		
<b>Time domain 2 (F2)</b>		
PULPROG	cosy45	PULse PROGram for m cosy.
TD	1024	Time Domain points.
NS	8	Number of Scans (integer multiple of 4).
DS	16	number of Dummy Scans for 1st row.
D1	2 sec	relaxation Delay.
<b>Time domain 1 (F1)</b>		
TD	256	Time Domain points.
ND0	1	Number of D0 periods per cycle.
IN0	1 / SW	Increment in t1 (calculated).
SW		SW of <sup>1</sup> H spectrum (same as for F2).
SFO1		<sup>1</sup> H frequency (same as for F2).

ASED

Check that acquisition parameters are set correctly. A brief description of other parameters, not described above, is given in the pulse program at the end of this document.  
Save the acquisition parameters.

[SAVE]

EXPT

Calculates the approximate length of time to do the experiment. This may help you to decide if you want to collect more or fewer slices or scans or points etc. The Menthol spectrum required 1 hour 20 minutes.

### DATA ACQUISITION

[Spin on/off]

TURN THE SPINNER OFF ( press the Spin On/Off button on the BOSS keyboard).

ZG

Start the acquisition.

## DATA PROCESSING

The AU program sets the following processing parameters. Use EDP to check or modify the values.

Processing Parameters		
<b>Time/frequency domain 2 (F2)</b>		
SI	512	the Size in F2 (zero fill rows).
WDW	SINE	Sine multiplication.
SSB	0	Unshifted sine bell.
PH_mod	NO	No phase correction.
PKNL	TRUE	Required with digital filter.
BC_mod	QUAD	Background correct quadrature data.
<b>Time/frequency domain 1 (F1)</b>		
SI	512	the Size in F1 (zero fill columns).
WDW	SINE	Sine multiplication.
SSB	0	Unshifted sine bell.
PH_mod	MC	Magnitude calculation.
BC_mod	NO	No background correction.
MC2	QF	Forward quadrature FFT.
OFFSET		Frequency offset (same as for F2).
SF		Spectrometer frequency (same as for F2).

XFB

Background correct, window, zero fill, Fourier transform, phase and reference. The whole kaboodle in one command. It is OK to execute this command on a partial data set, during acquisition.

## 2-D CONTOUR DISPLAY

### X-Y Expansion the spectrum.

[Limits]	Set the limits of the plot region. NOTE: For homo-nuclear correlation experiments, (COSY, NOESY, etc.) set F1LO = F2LO and F1HI = F2HI so the display will be symmetric and the diagonal peaks will appear on the diagonal line.
[PlotReg]	Forces XWinNMR to display the plot region.

### Setting the intensity scale.

[DefPlot]	Sets the intensity scale for plotting to be the same as the currently displayed intensity scale.
[contours]	Displays the equi-intensity contours of the data.
[intensities]	Displays ranges of intensity as a color map.

## PLOTTING

The AU program sets the following plotting parameters. Use EDG to check or modify the values. Once EDG has started, press either the [EDPROJ2] or [EDPROJ1] buttons.

Plotting Parameters		
<b>Projection for Frequency domain 2</b>		
PF2DU	z	Disk Unit of the data set.
PF2USER	username	Your user name.
PF2NAME	name	Name of the data set.
PF2EXP	1	Experiment number of the <sup>1</sup> H spectrum.
PF2PROC	1	Process number of the <sup>1</sup> H spectrum.
<b>Projection for Frequency domain 1</b>		
PF1DU	z	Disk Unit of the <sup>1</sup> H data set.
PF1USER	username	Your user name.
PF1NAME	name	Name of the data set.



## Pulse Program for Magnitude COSY

```
;cosy45
;avance-version
;2D homonuclear shift correlation
;using 45 degree read pulse
;W.P. Aue, E. Bartholdi, R.R. Ernst, J. Chem. Phys. 64, 2229 (1976)
;K. Nagayama et al., J. Magn. Reson. 40, 321 (1980)
```

```
#include <Avance.incl>
```

```
"d0=3u"
```

```
1 ze
2 d1
3 p1 ph1
  d0
  p1*0.5 ph2
  go=2 ph31
  d1 wr #0 if #0 id0 zd
  lo to 3 times tdl
exit
```

```
ph1=0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3
ph2=0 1 2 3
ph31=0 2 0 2 3 1 3 1 2 0 2 0 1 3 1 3
```

```
;p11 : f1 channel - power level for pulse (default)
;p1 : f1 channel - 90 degree high power pulse
;d0 : incremented delay (2D) [3 usec]
;d1 : relaxation delay; 1-5 * T1
;in0: 1/(1 * SW) = 2 * DW
;nd0: 1
;NS: 4 * n
;DS: 16
;td1: number of experiments
;MC2: QF
```