Nuclear magnetic resonance spectroscopy

III. 2-D NMR

Reading:
Pavia
Chapter 9.6-9.8
with emphasis on how to read the spectra

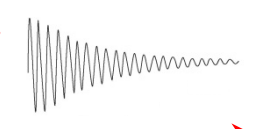
1. General

- one-dimensional NMR spectrum: 1 "NMR" scale only
  one time dimension/domain

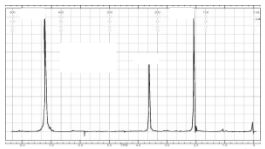
apply ν pulse ⟶ observe FID ⟶ Fourier-transform

acquisition time

amplitude



t



ν
(or F)

- two-dimensional NMR spectrum: 2 "NMR" scales
  two time dimensions/domains

apply ν pulse ⟶ wait ⟶ apply ν pulse ⟶ observe FID ⟶ Fourier-transform

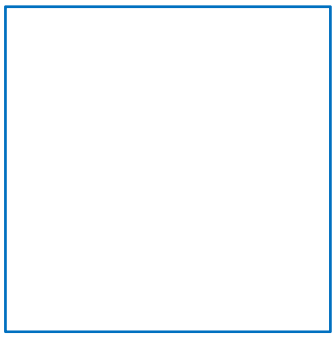
- delay time
- is varied
- supplies t_1

acquisition time

t_2 ⟶ F_2

F_1

result:



F_1 can plot:
δ in ppm
ν in Hz

where is the amplitude?

1. General continued

- two-dimensional NMR spectrum: 2 "NMR" scales

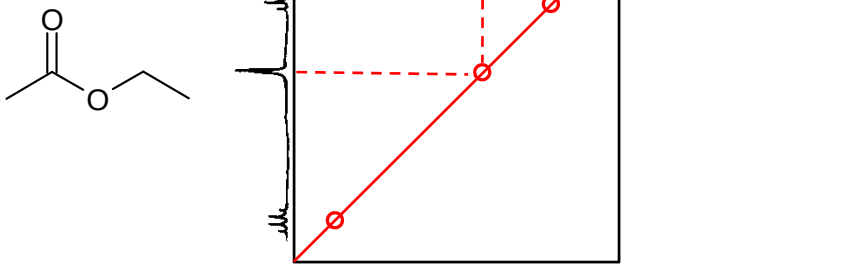
Two versions:

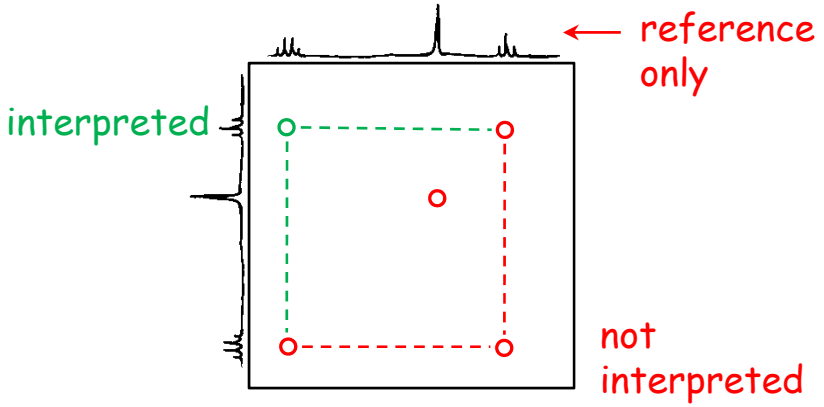
I. Two identical scales

- COSY: H/H correlation spectroscopy (or, in general, homonuclear)
- x-axis δ^1H
- y-axis δ^1H
- correlates two protons that are coupled (^{2}J, ^{3}J, long-range)
- useful for more complex coupling situations
- shows two kinds of peaks in the contour plot:

- diagonal: - are not interpreted
  - show the 1-D spectrum

- off-diagonal (or cross): - one-half is interpreted
  - give coupling information



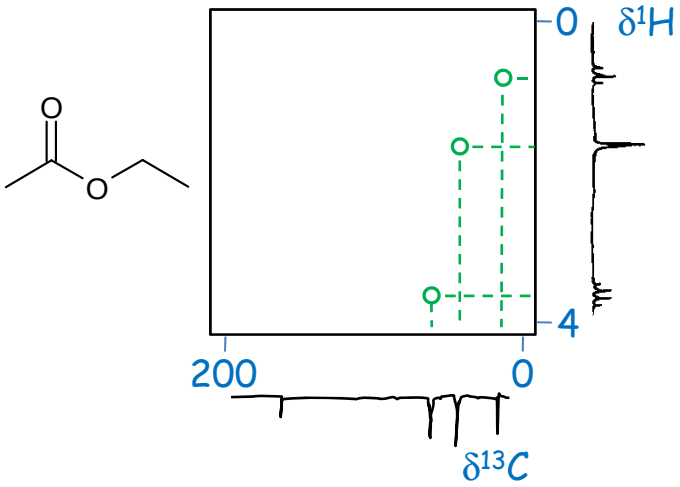


1. General continued

II. Two different scales

- HETCOR: heteronuclear correlation spectroscopy
- x-axis $\delta^{13}C$
- y-axis $\delta^{1}H$
- correlates a ^{13}C and a ^{1}H that are coupled ("H,C COSY", ^{1}J)
- shows which protons are attached to which carbons

  $\Rightarrow$ recovers "multiplicity" lost in proton-decoupled ^{13}C spectrum
- only cross peaks: not a symmetric spectrum, no diagonal peaks



In a related technique,

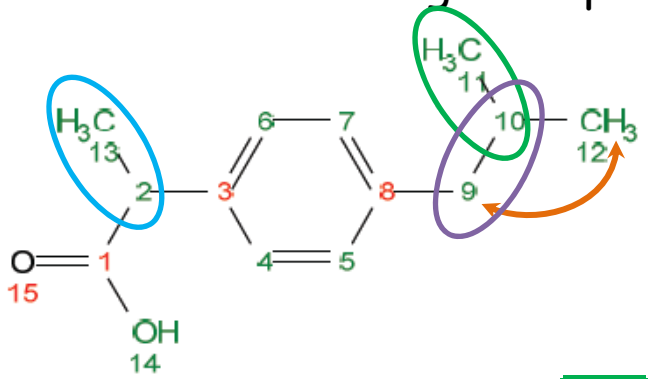
HMQC: heteronuclear multiple quantum coherence

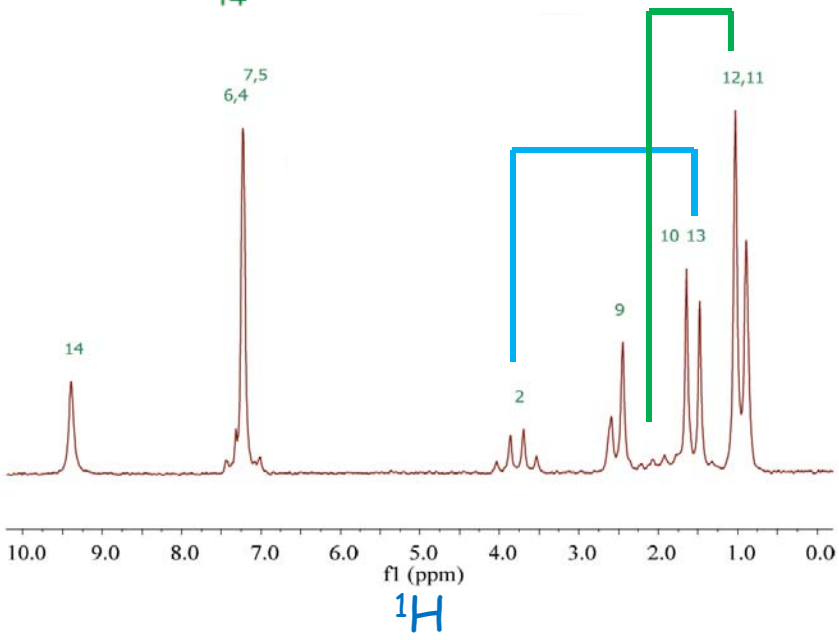
- x-axis $\delta^{1}H$
- y-axis $\delta^{13}C$
- the analysis is identical to that for HETCOR

2. Sample COSY spectra

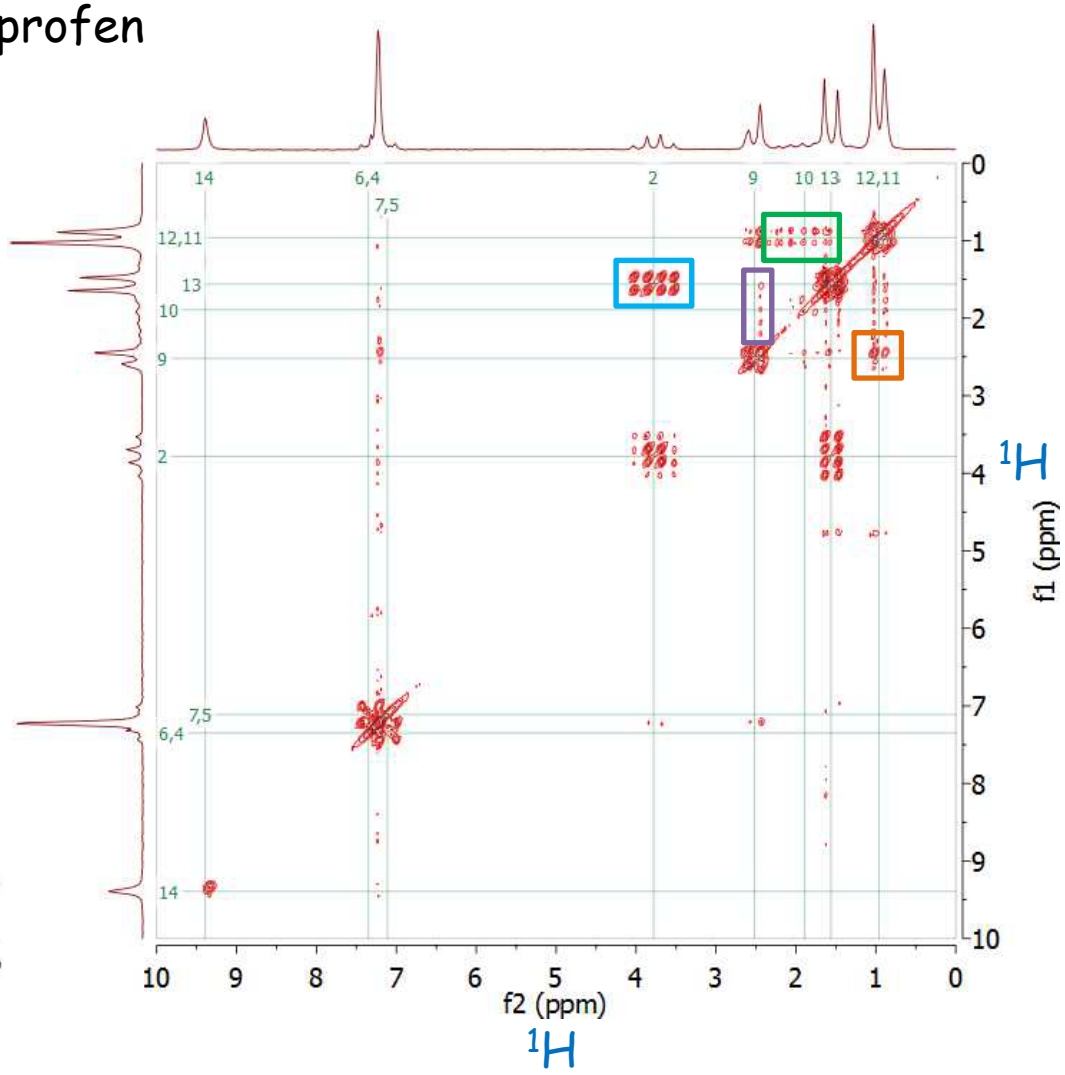
I. COSY

An extreme reading example, ibuprofen





^1H



^1H ^1H

http://www.magritek.com/wp-content/uploads/2015/03/Case-Study-Ibuprofen-web.pdf

2. Sample COSY spectra continued

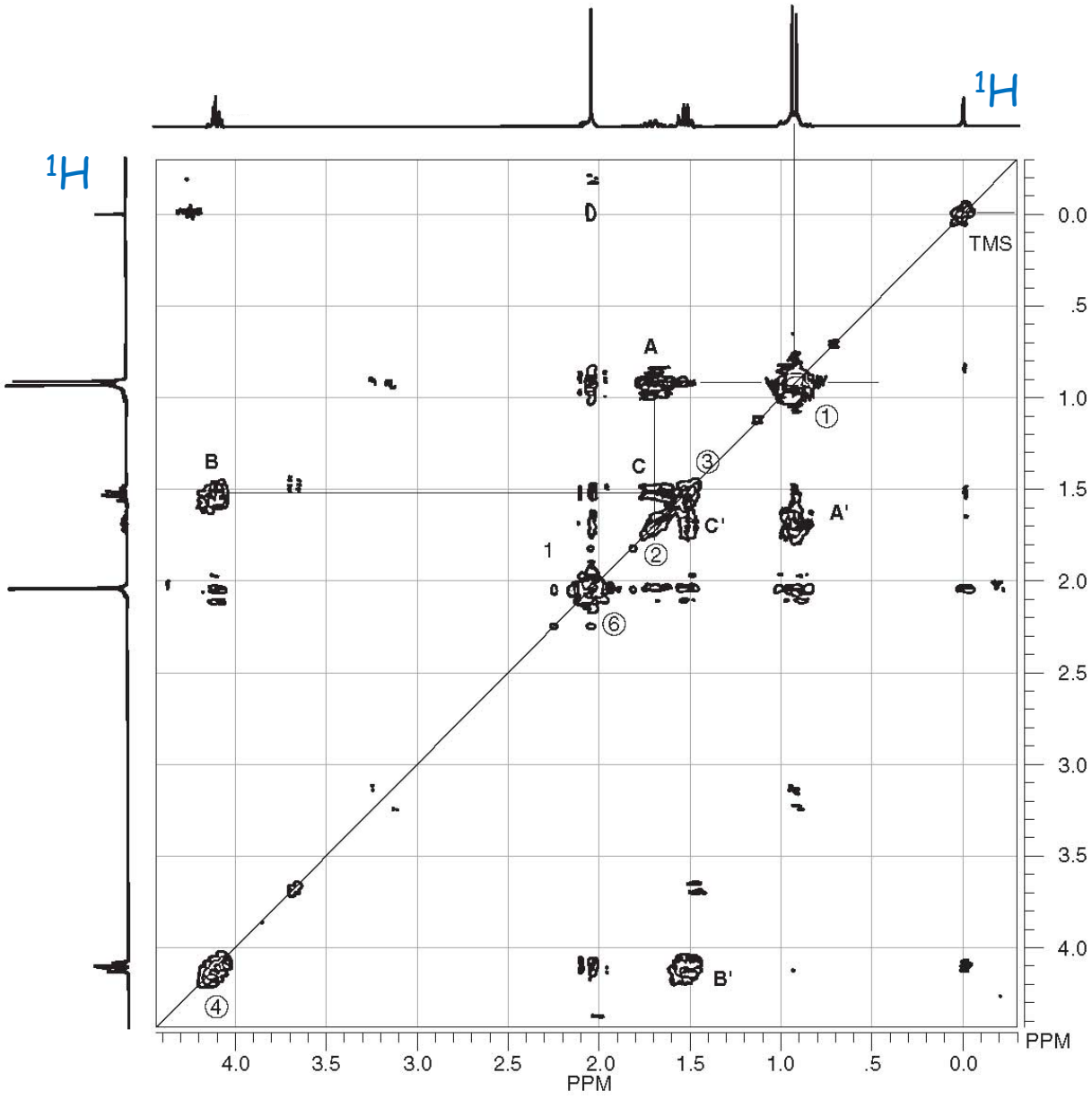
I. COSY

You will end up giving
- a graphical analysis

followed by
- a non-graphical analysis,

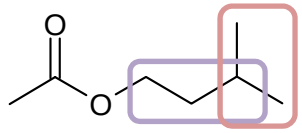
culminating in
- a connectivity

of a chain!



2. Sample COSY spectra continued

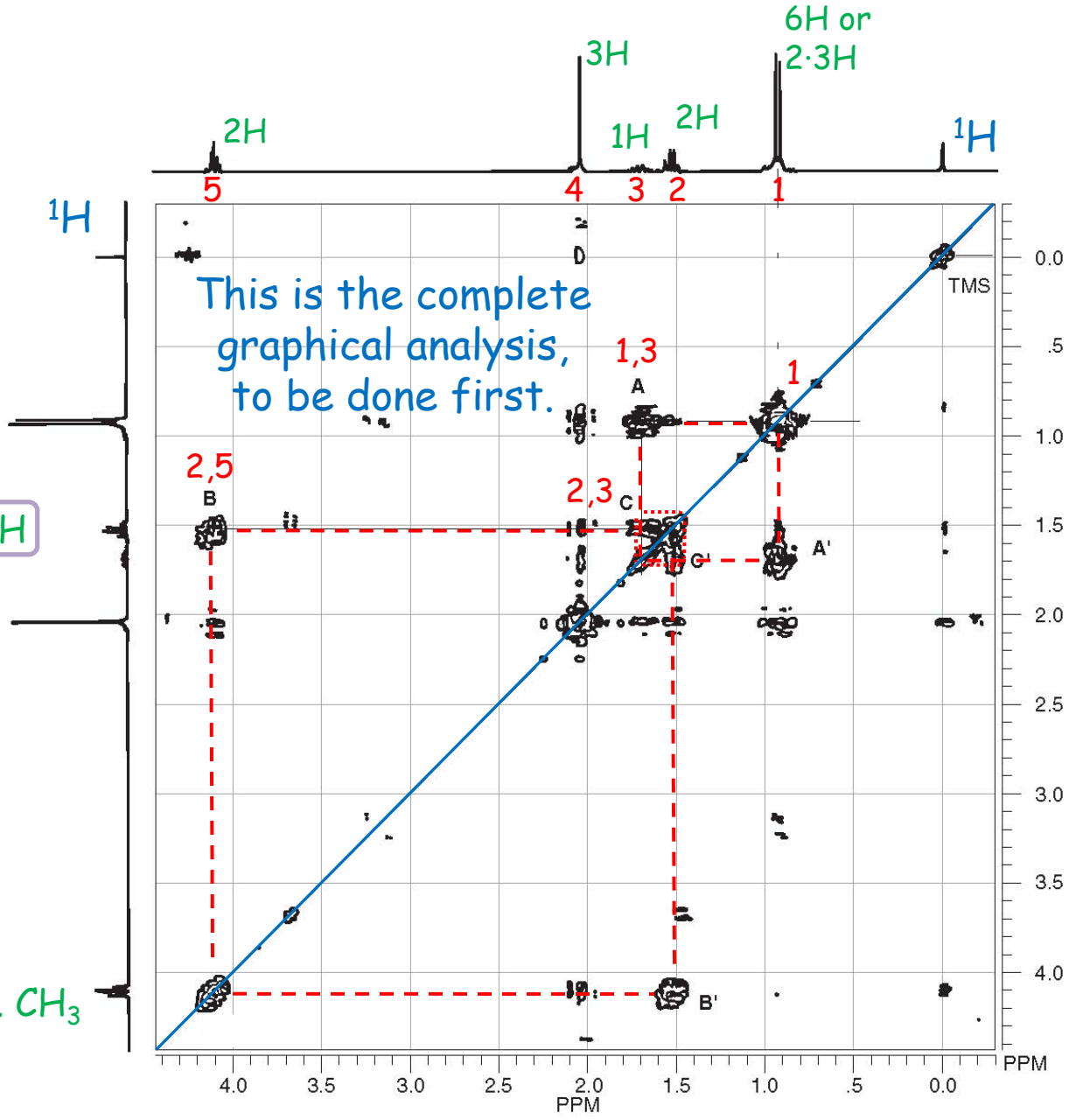
I. COSY



- do a graphical analysis:
  - look for large cross peaks
  - ignore small peaks
- information reported:
  - 1,3 (A) $2CH_3 \rightarrow CH$
  - 2,5 (B); 2,3 (C) $CH_2 \rightarrow CH_2, CH$
  - 4 not correlated CH_3 .....
- not new information: A', B', C'

- so, connectivity starting at 1:
  - $6H^1 \rightarrow 1H^3$: $2CH_3 \rightarrow CH$
  - $1H^3 \rightarrow 2H^2$: $CH \rightarrow CH_2$
  - $2H^2 \rightarrow 2H^5$: $CH_2 \rightarrow CH_2$
  - $3H^4$ not correlated

$\Rightarrow 2CH_3 \rightarrow CH \rightarrow CH_2 \rightarrow CH_2$..... CH_3

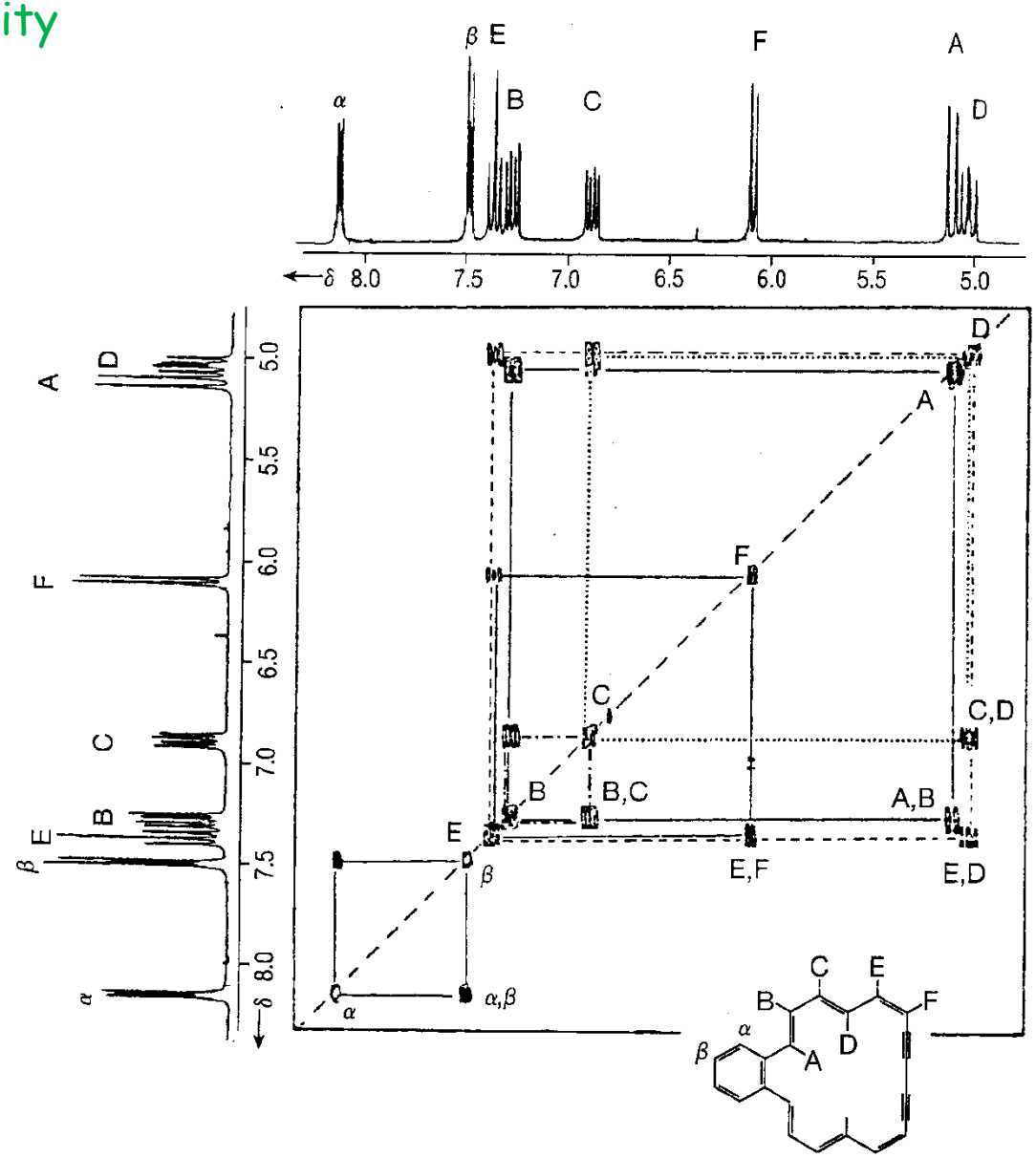


Example

Establish the connectivity of the coupling system.

Note the complete graphical analysis!

Note the proper cross peak labels!

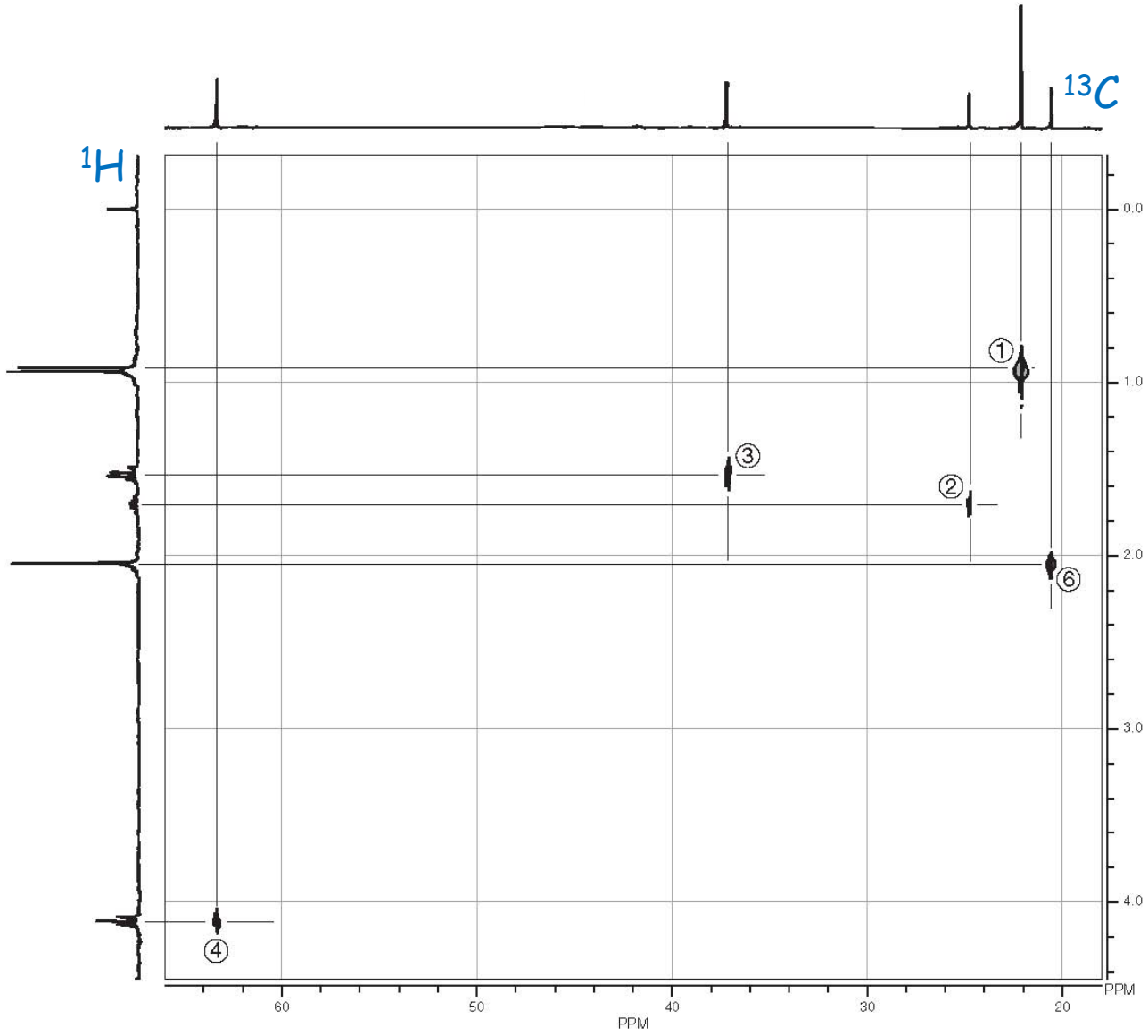


3. Sample HETCOR spectrum continued

II. HETCOR

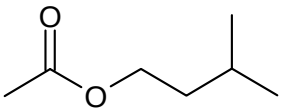
Again there is
- a graphical analysis

followed by
- a non-graphical analysis.



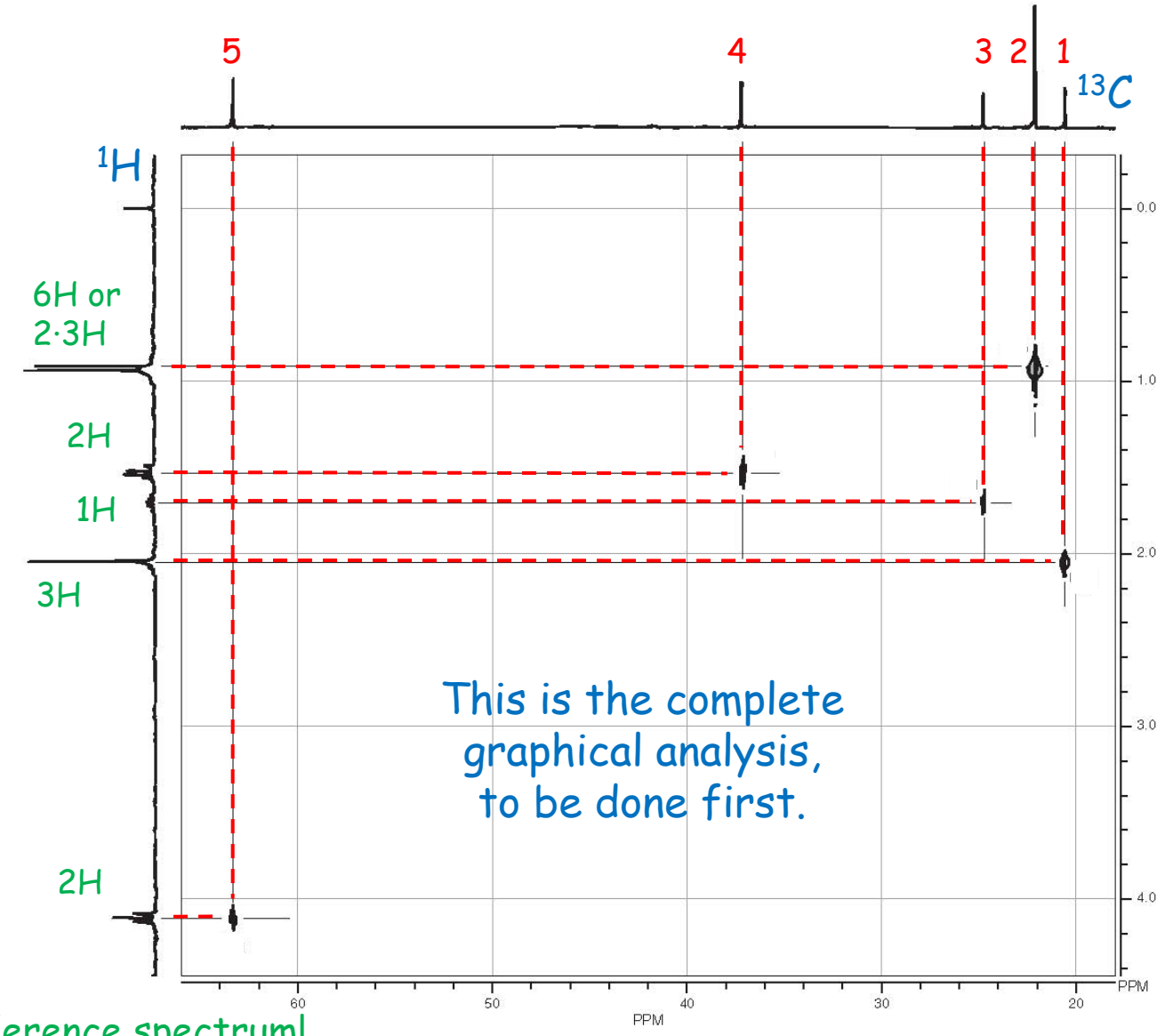
3. Sample HETCOR spectrum continued

II. HETCOR



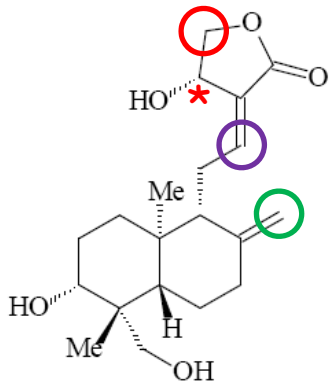
- 5 correlation peaks
- information gained:
  - 1,3H
  - 2,2·3H
  - 3,1H
  - 4,2H
  - 5,2H
  - 6 (C=O) not correlated
- information reported:
  - 1,3H: CH_3
  - 2,2·3H: $2CH_3$
  - 3,1H: CH
  - 4,2H: CH_2
  - 5,2H: CH_2
  - 6: no H attached

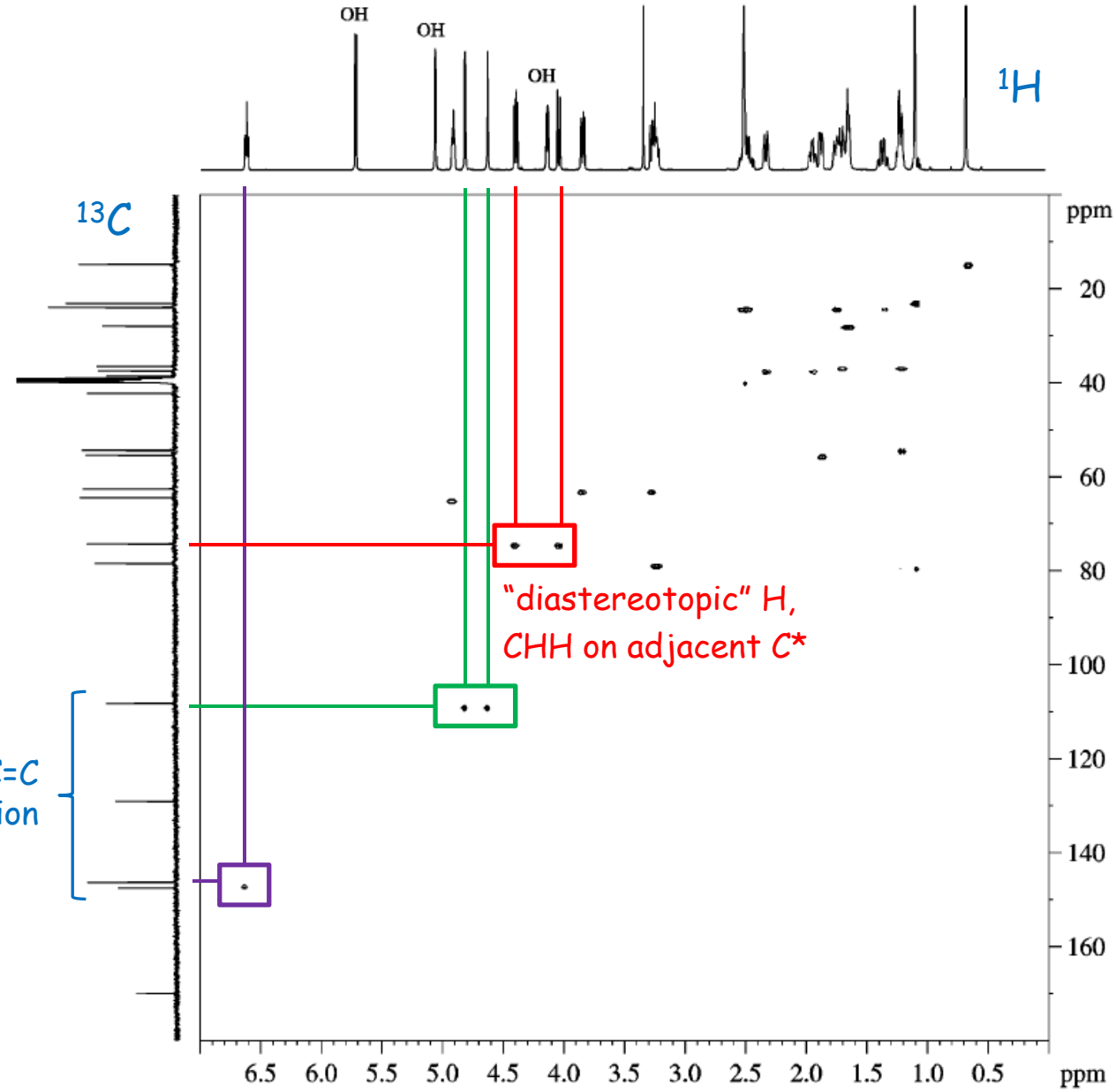
⇒ to be reported on ^{13}C reference spectrum!



Example

Just to illustrate a few points.





http://www.chem.ox.ac.uk/spectroscopy/nmr/pdfs/organic%20nmr%201.pdf