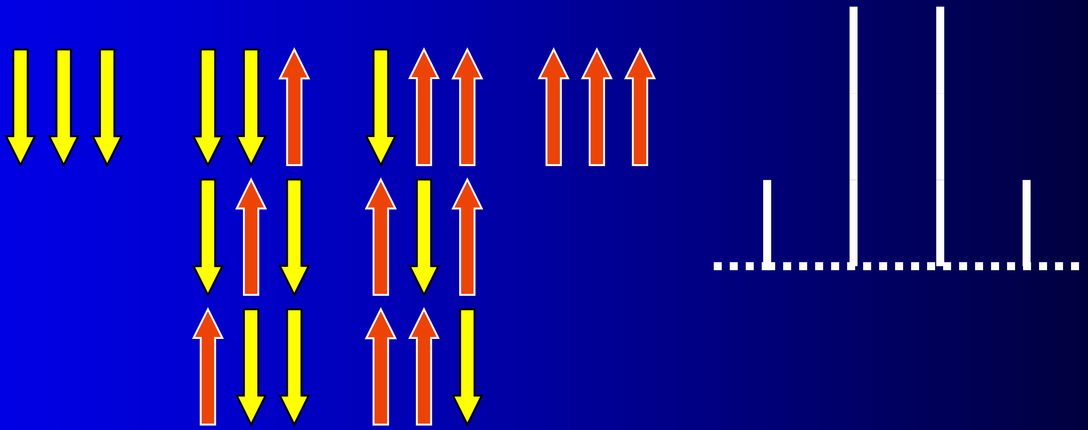
Lecture 5

Still More nmr

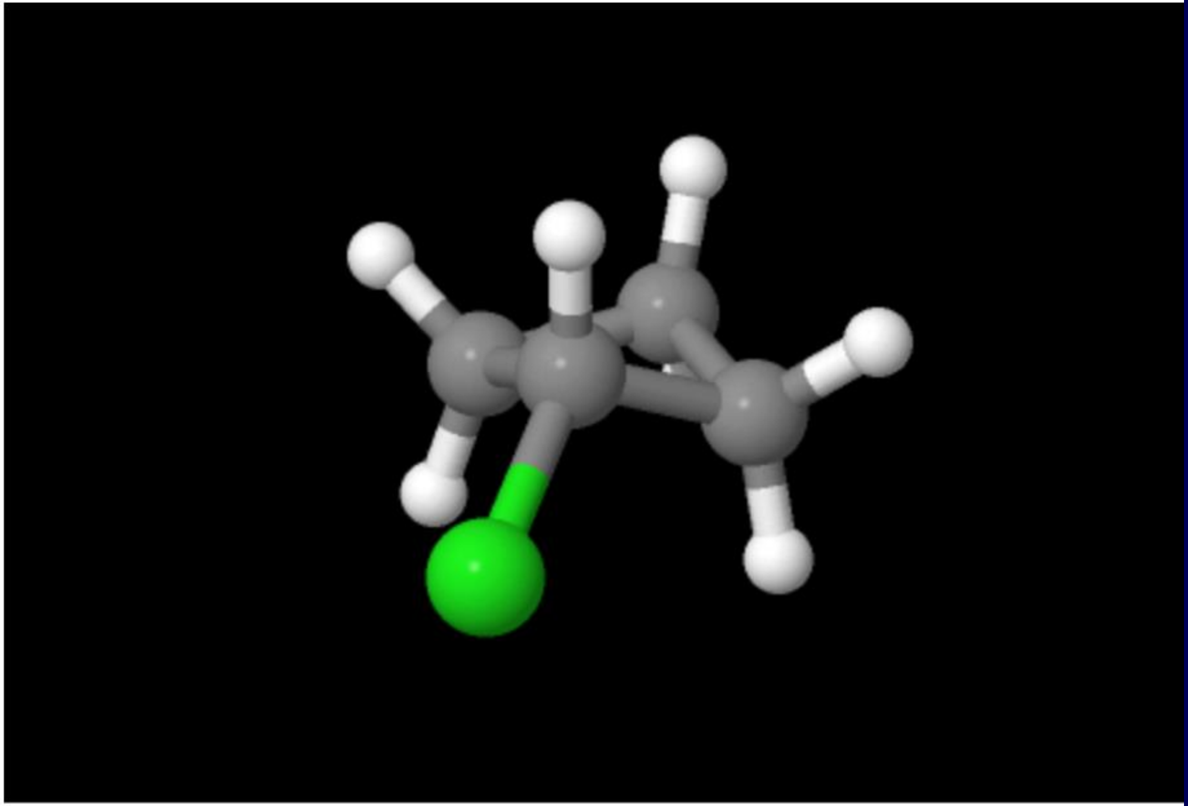
three spins



February 5, 2019

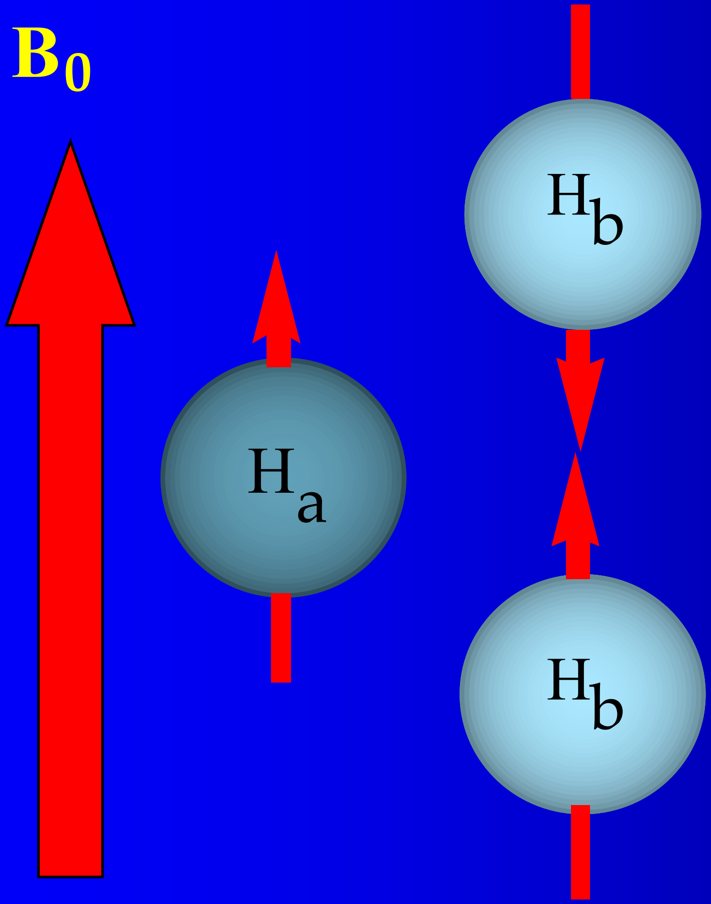
Chemistry 328N

Supplemental Problem



Chlorocyclobutane

Origins of Signal Splitting

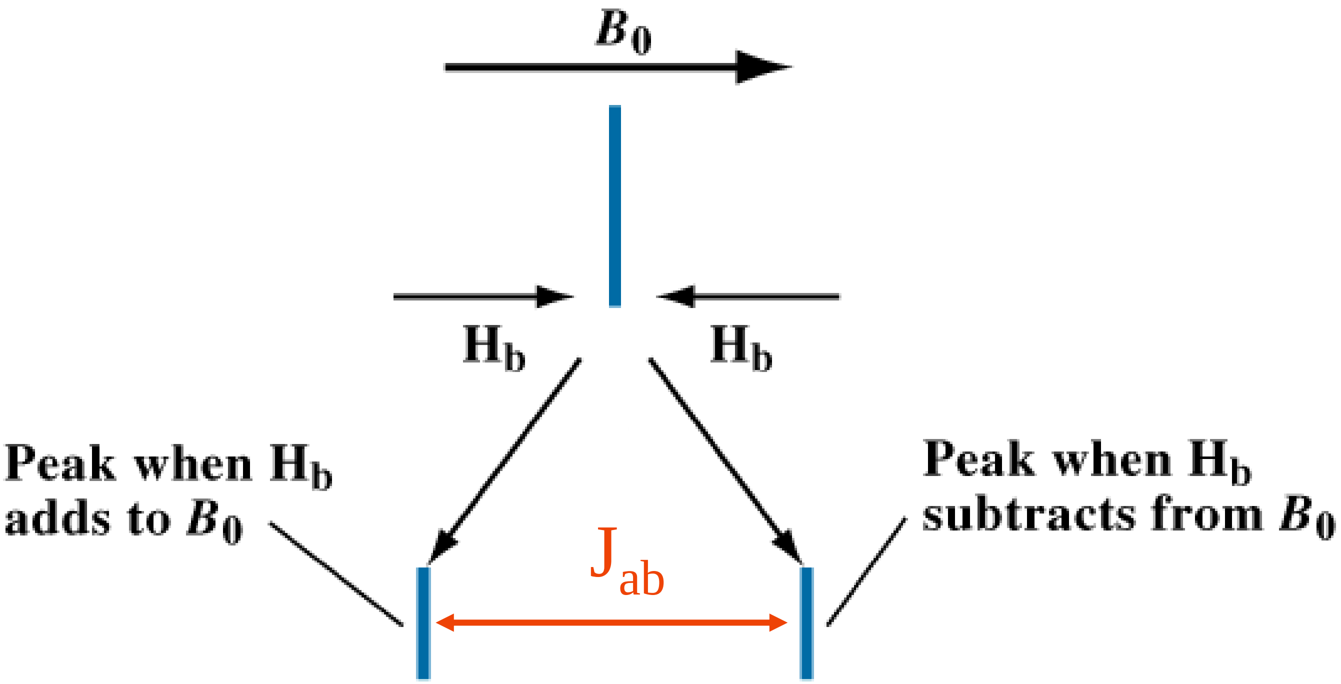


Magnetic field of H_b subtracts from the applied field; H_b signal appears at a higher applied field

Magnetic field of H_b adds to the applied field; H_a signal appears at a lower applied field

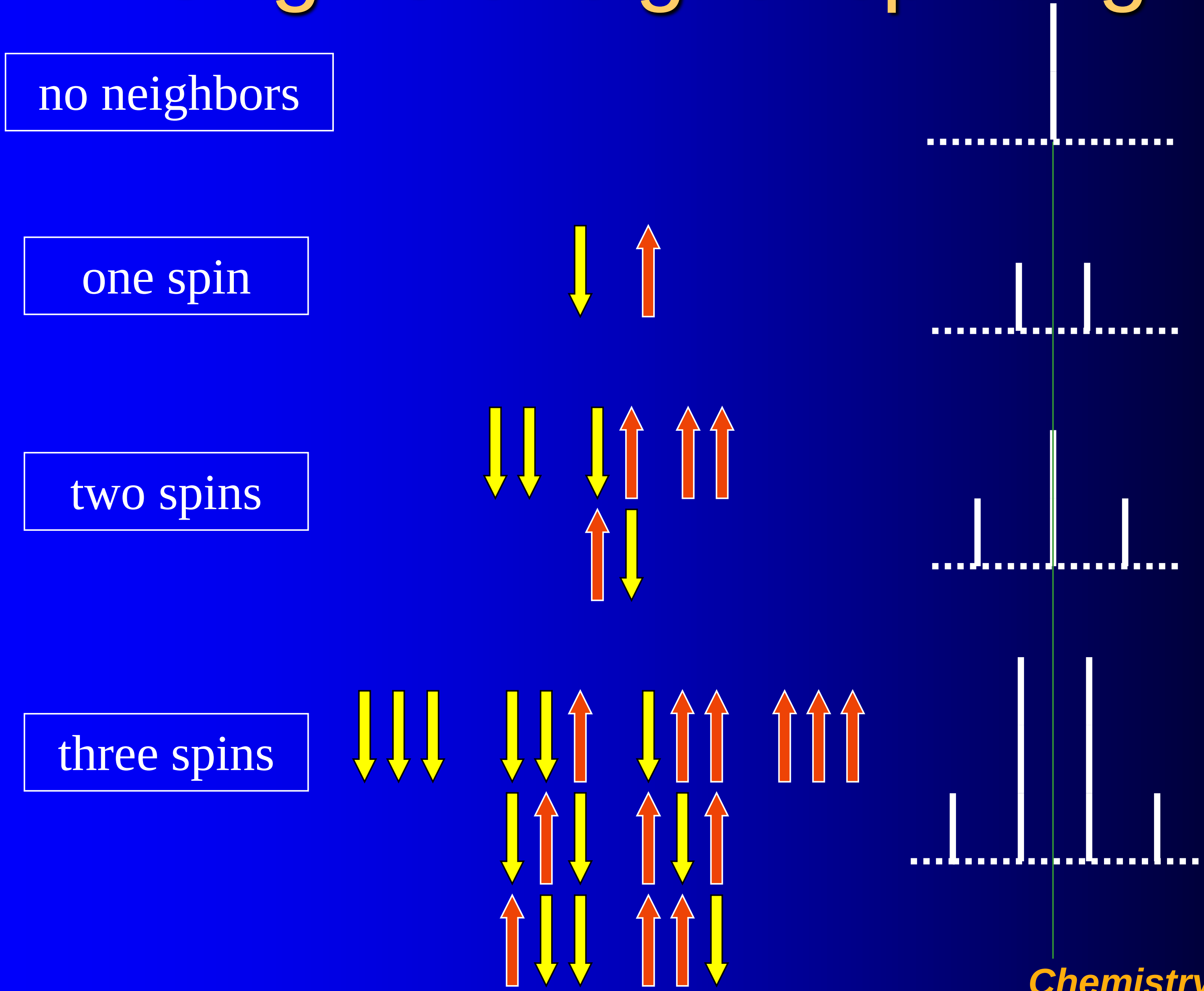
Remember…it is the **NET** field that counts

The signal of Ha is split into two peaks of equal area (a doublet)



J_{ab}= coupling constant

Origins of signal splitting



no neighbors

one spin

two spins

three spins

Relative Intensity of Peaks

singlet	1
double	1 1
triplet	1 2 1
quartet	1 3 3 1
quintete	1 4 6 4 1
sextete	1 5 10 10 5 1

Pascal's triangle

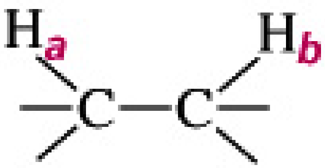
The binomial coefficients

The “N+1 Rule”

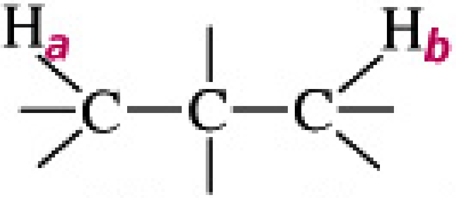
- The ^{1}H-NMR signal of a hydrogen or set of equivalent hydrogens is split into (N + 1) peaks by a set of N equivalent neighboring hydrogens
  - All neighboring hydrogens in the analysis must have the same chemical shift (magnetically equivalent)
  - If this condition is not met, a graphical tree or second order analysis must be used to predict the splitting pattern. We will explore this condition later

Splitting of Signals

- Nonequivalent protons split each other if they are on adjacent carbons, i.e. separated by 3 sigma bonds



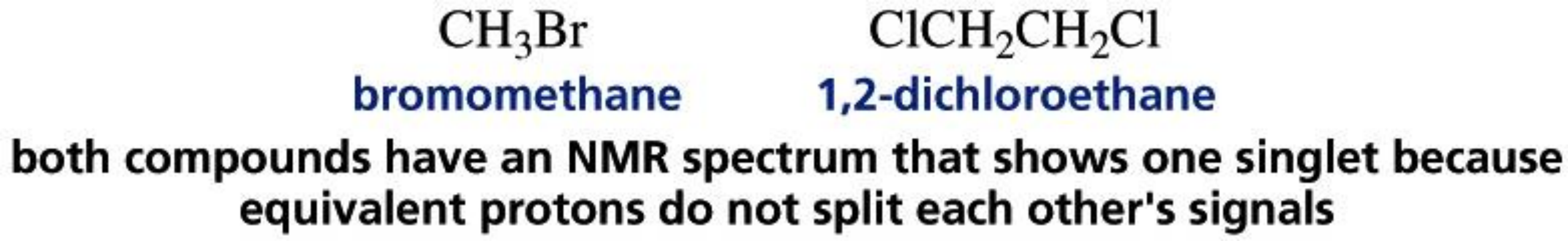
H_a and H_b will split each other because they are separated by 3 σ bonds



H_a and H_b will not split each other because they are separated by 4 σ bonds

Splitting of Signals

- Equivalent protons **never** split each other

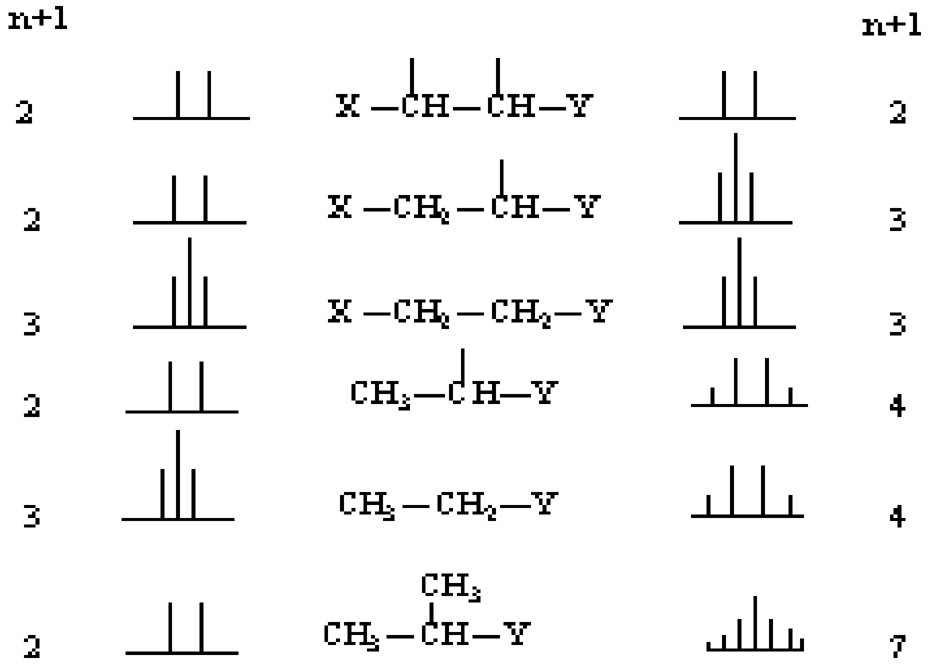


CH_3Br $ClCH_2CH_2Cl$

bromomethane **1,2-dichloroethane**

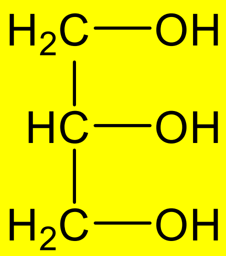
both compounds have an NMR spectrum that shows one singlet because equivalent protons do not split each other's signals

NMR Splitting Patterns



Who needs DNA??

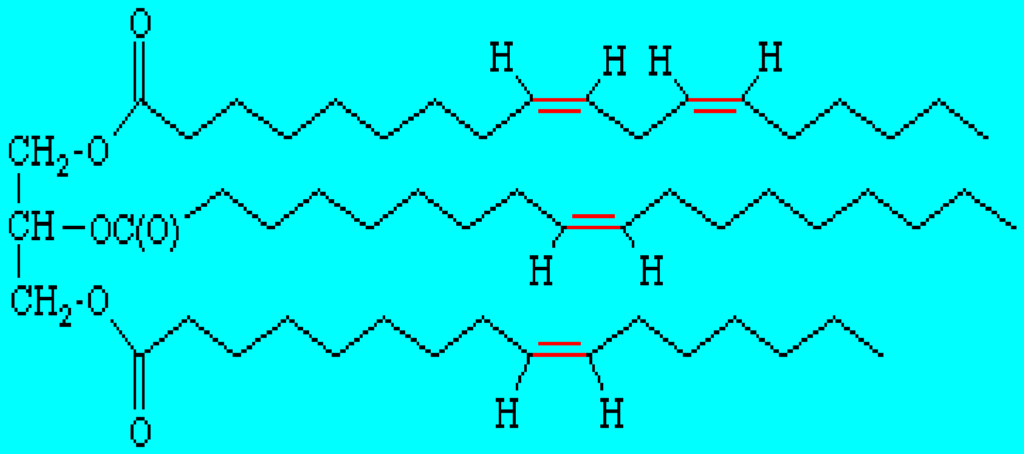
Corn Oil and Tristearin

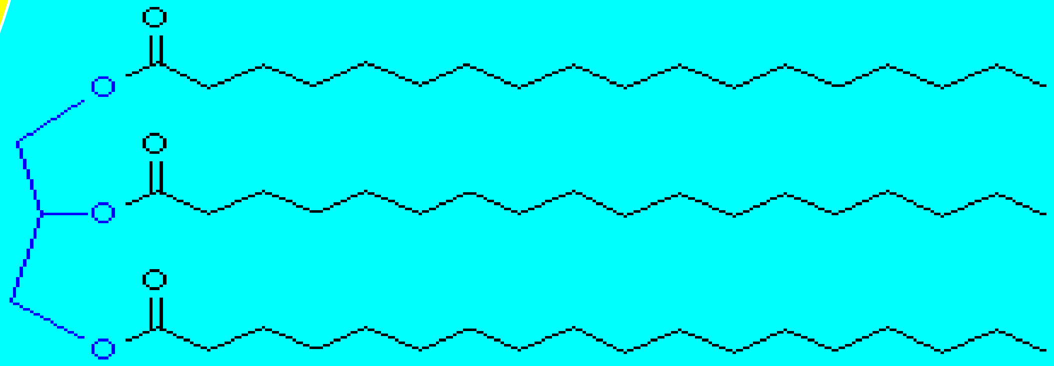


$$\begin{array}{l} H_2C-OH \\ \quad | \\ \;HC-OH \\ \quad | \\ H_2C-OH \end{array}$$

1,2,3-propanetriol

Glycerol or glycerin





tristearin

Coloring Margarine

Index of Hydrogen Deficiency

- I knew this as the unsaturation number
- Valuable characteristic of structure
  - Provides you with number of double bonds or rings in a compound
  - Easy with CHO formulas only…be careful with N
  - Simplest, “saturated” normal alkanes have:

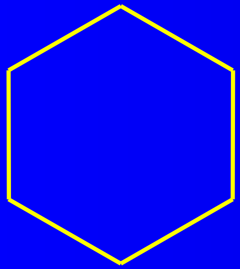
$$H{-}(CH_2)_n{-}H \quad = C_nH_{2n+2}$$

Index of H Deficiency

- IHD: the sum of the number of rings and pi bonds in a molecule….
- Compare the number of hydrogens in an unknown compound with the number in the reference compound C_nH_{2n+2}

Index of H Deficiency

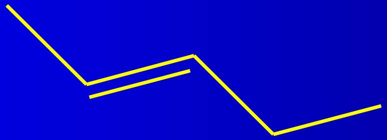
$$\text{IDH} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$



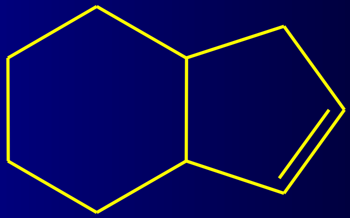
C_6H_{12}

C_nH_{2n+2}
C_6H_{14}
$- \; C_6H_{12}$

2/2=1 => 1 ring or 1 double bond



C_5H_{10}



C_9H_{14}

C_nH_{2n+2}
C_9H_{20}
$- \; C_9H_{14}$

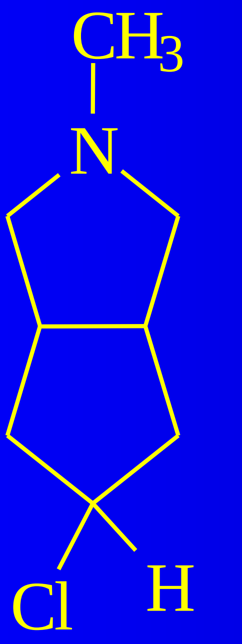
6/2=3

Index of H Deficiency

$$\text{IDH} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$

- No correction is necessary for the addition of atoms of O
- Subtract one H for each atom of halogen added (halogens like Cl replace H one for one)
- Add one hydrogen For each atom of N added to the reference hydrocarbon

“Unsaturation” Number or HDI



$C_8H_{14}ClN$

Add one H for N and subtract one for Cl

Should be $C_nH_{2n+2\ +1-1} = C_8H_{18}$

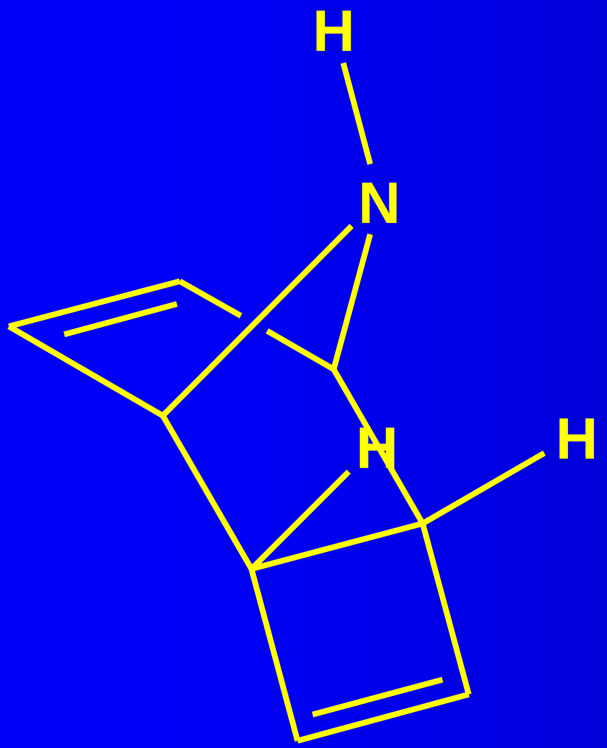
but it is… C_8H_{14}

Missing H_4

So index is…. 4/2=2

Calculate the Unsaturation Number

C_8H_9N



Add one H for N

Should be $C_nH_{2n+2\ +1} = C_8H_{19}$

but it is… C_8H_9

Missing H_{10}

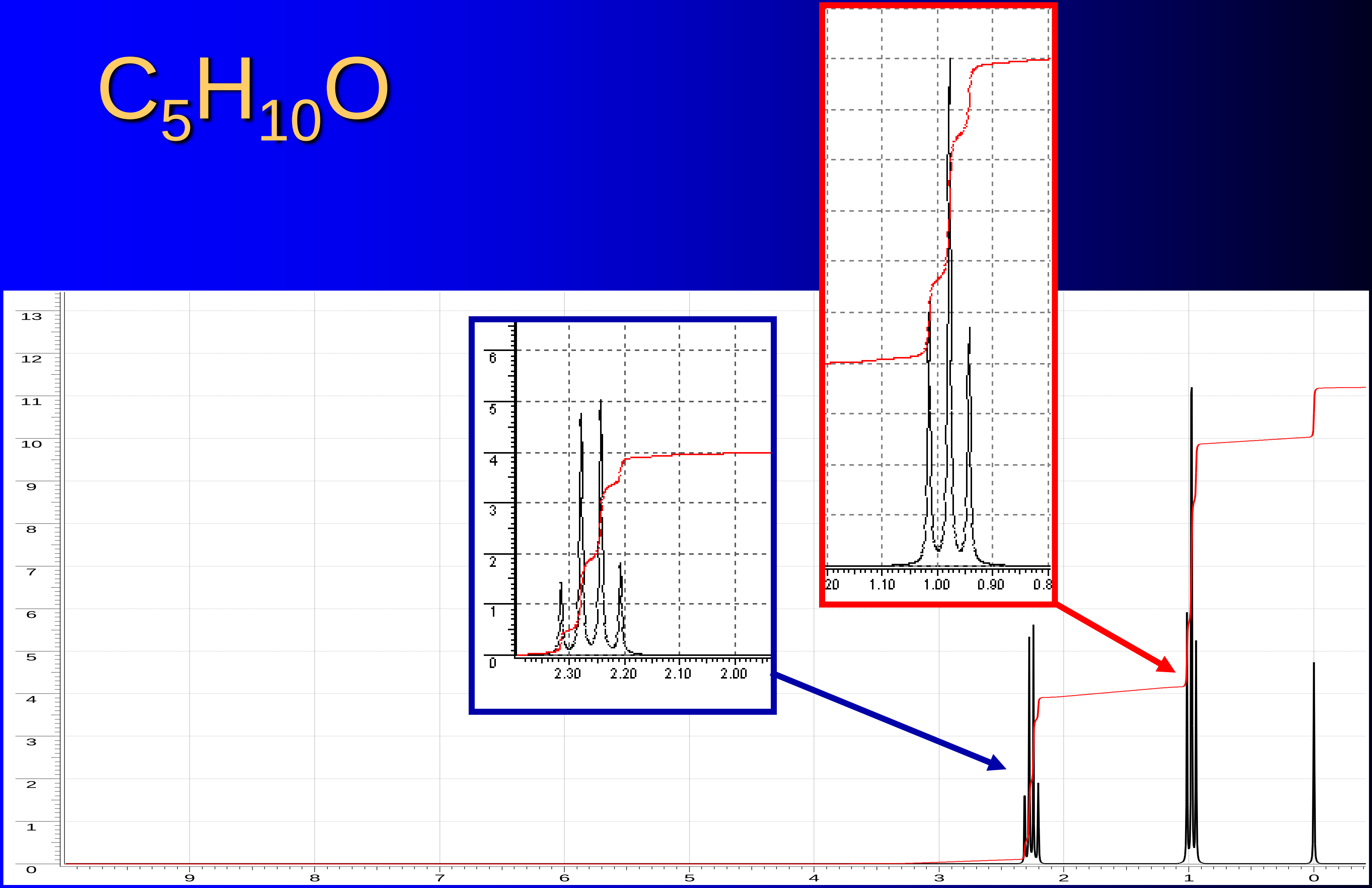
So number is…. 10/2=5!

“Tricks” for solving unknowns

- Review….
- Empirical formula is lowest common denominator ratio of atomic composition

- From Homework: unknown has an empirical formula of C_4H_9….a single high field peak in the ^1H nmr and a molecular ion at M/Z = 114. ….propose a structure..and predict the M/Z of the most intense fragment you expect to see in the mass spectrum

$C_5H_{10}O$

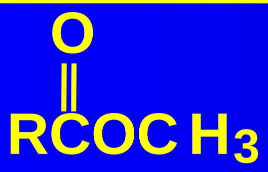


13
12
11
10
9
8
7
6
5
4
3
2
1
0
9
8
7
6
5
4
3
2
1
0
6
5
4
3
2
1
0
2.30
2.20
2.10
2.00
20
1.10
1.00
0.90
0.8

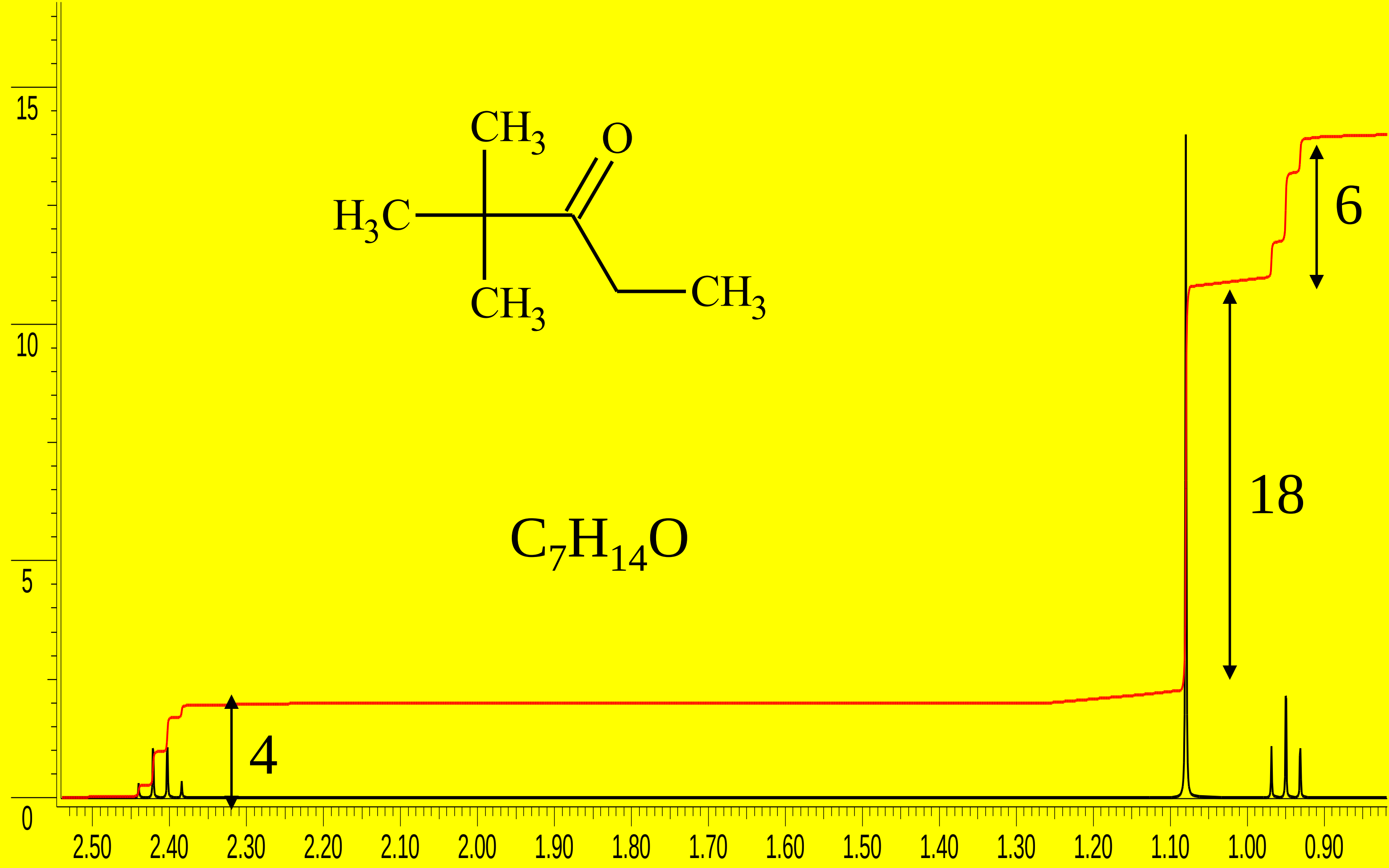
Chemical Shift - ^{1}H-NMR

Type of H	δ	Type of H	δ
$(CH_3)_4Si$	0	ROH	0.5-6.0
RCH_3	0.9	RCH_2OR	3.3-4.0
RCH_2R	1.2-1.4	R_2NH	0.5-5.0
R_3CH	1.4-1.7	 $R\overset{\overset{O}{\Vert}}{C}CH_3$	2.1-2.3
$R_2C{=}CRCHR_2$	1.6-2.6	 $R\overset{\overset{O}{\Vert}}{C}CH_2R$	2.2-2.6
$RC{\equiv}CH$	2.0-3.0		
$ArCH_3$	2.2-2.5		

Chemical Shift - ^{1}H-NMR

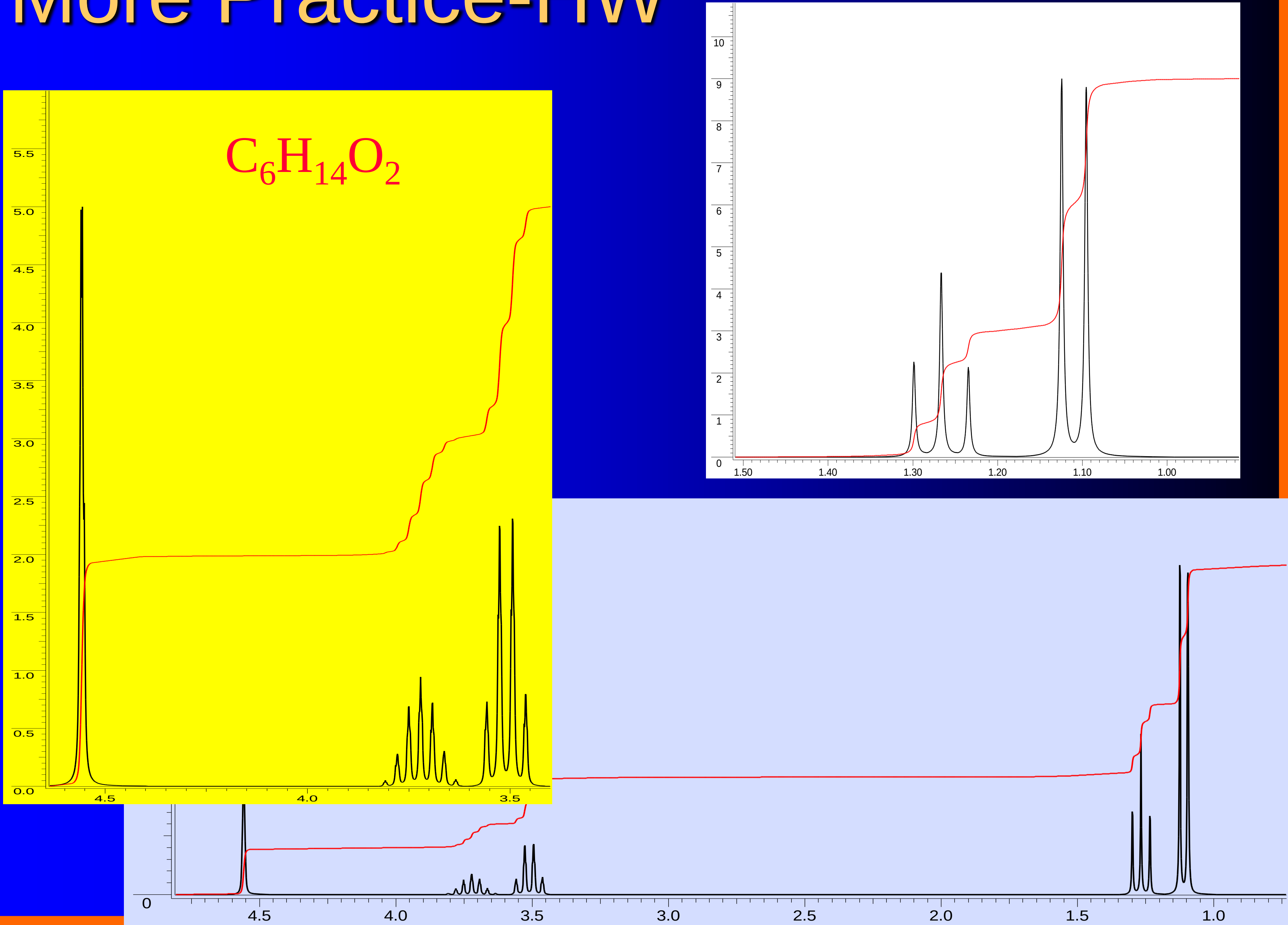
Type of H	δ	Type of H	δ
 $R\overset{\overset{O}{\|}}{C}OCH_3$	3.5-3.9	$R_2C{=}CH_2$	4.6-5.0
 $R\overset{\overset{O}{\|}}{C}OCH_2R$	4.1-4.7	$R_2C{=}CHR$	5.0-5.7
RCH_2I	3.1-3.3	ArH	6.5-8.5
RCH_2Br	3.4-3.6	 $R\overset{\overset{O}{\|}}{C}H$	9.5-10.1
RCH_2Cl	3.6-3.8		
RCH_2F	4.4-4.5	 $R\overset{\overset{O}{\|}}{C}OH$	10-13

Sample spectra



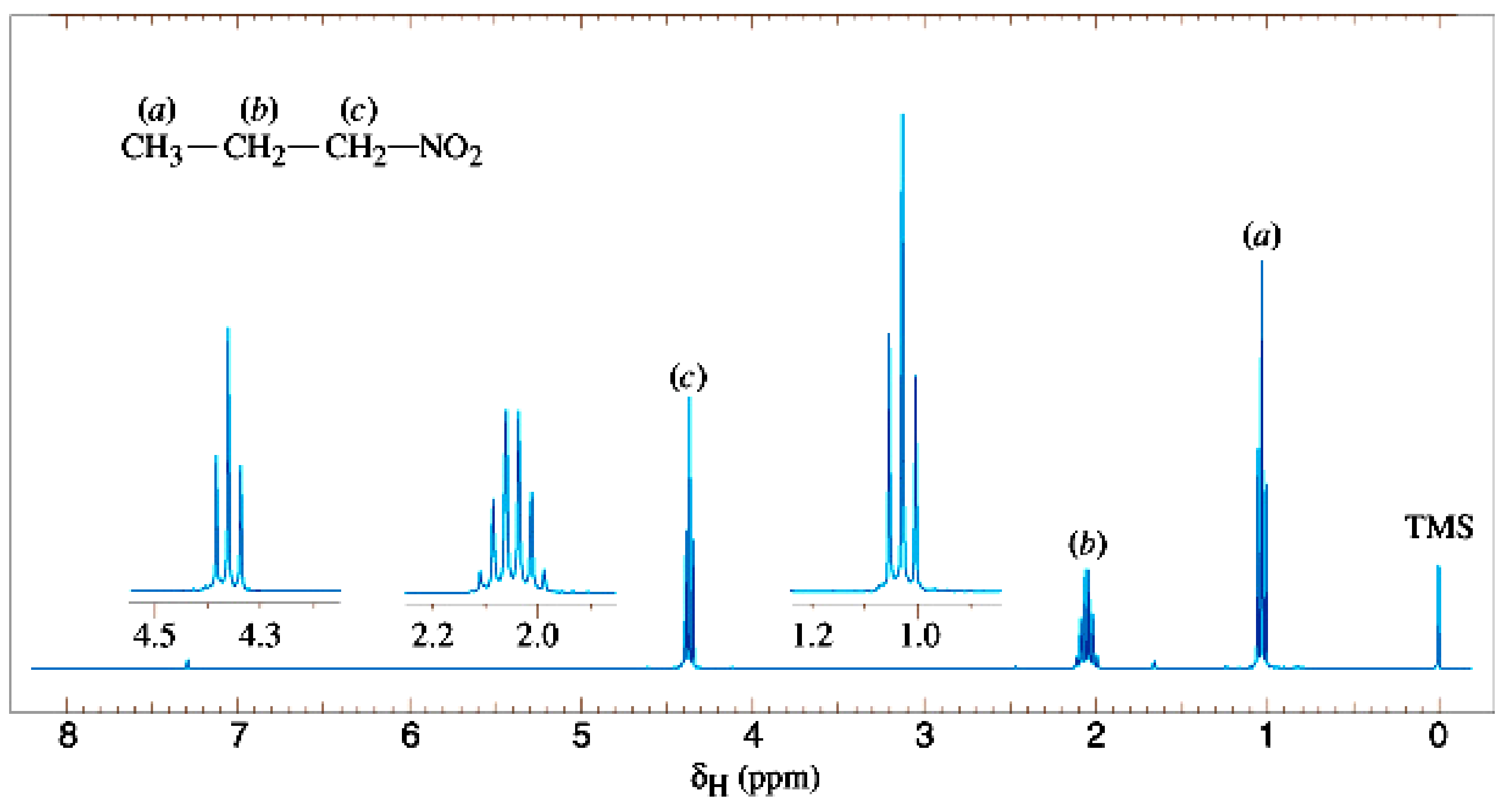
$C_7H_{14}O$

More Practice-HW



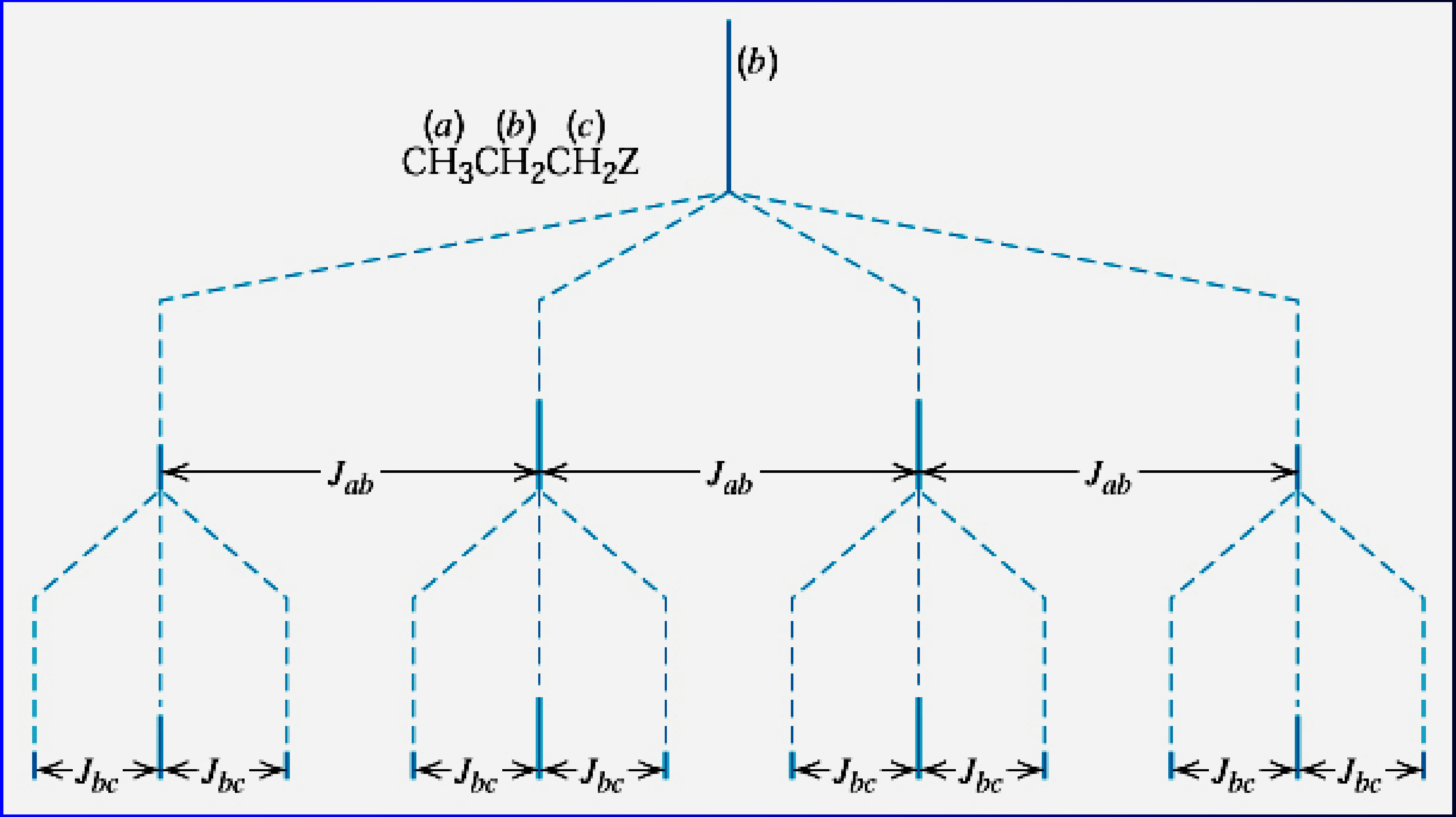
$C_6H_{14}O_2$

$CH_3CH_2CH_2NO_2$

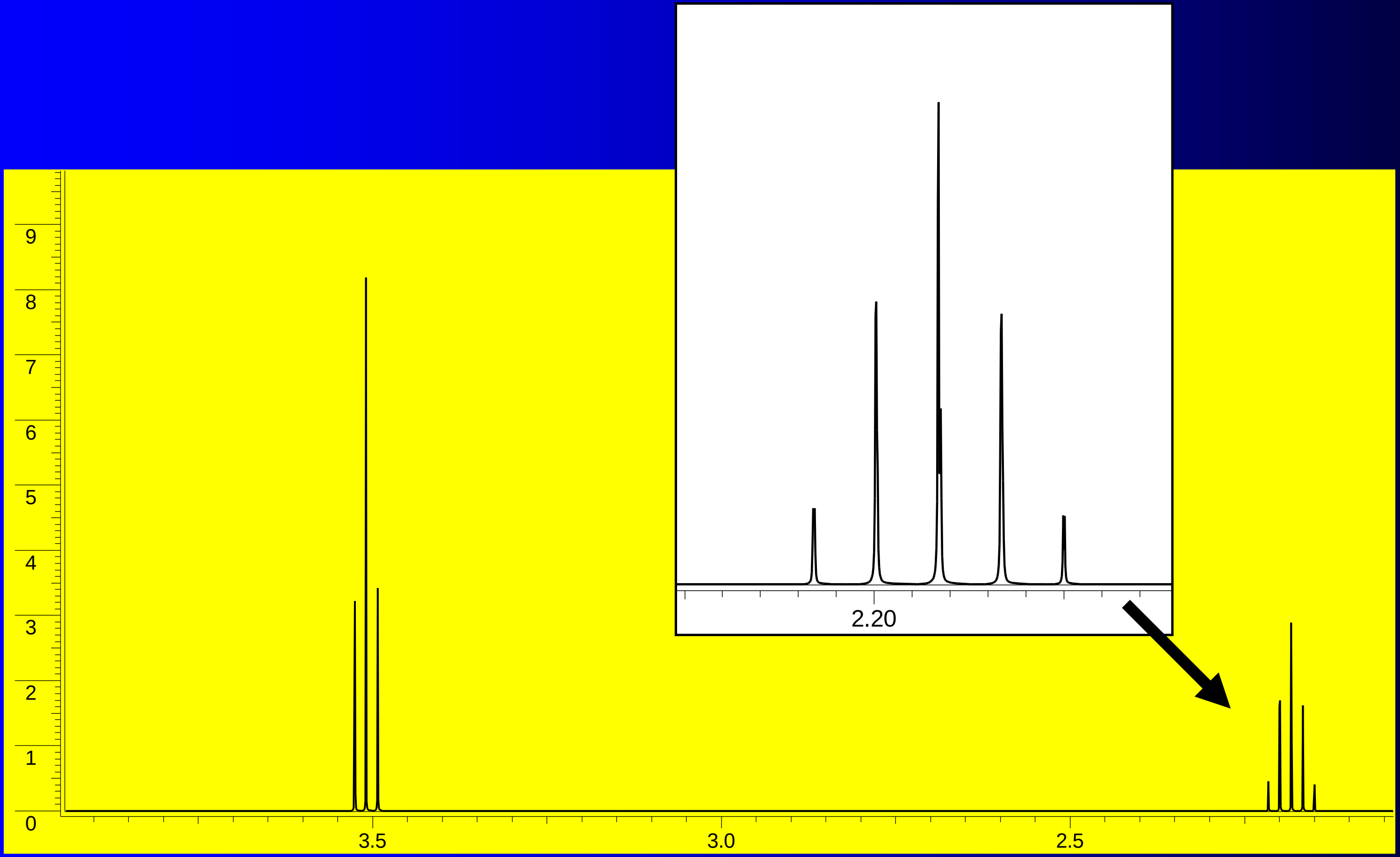


Multiple interactions of *non-equivalent* neighbors

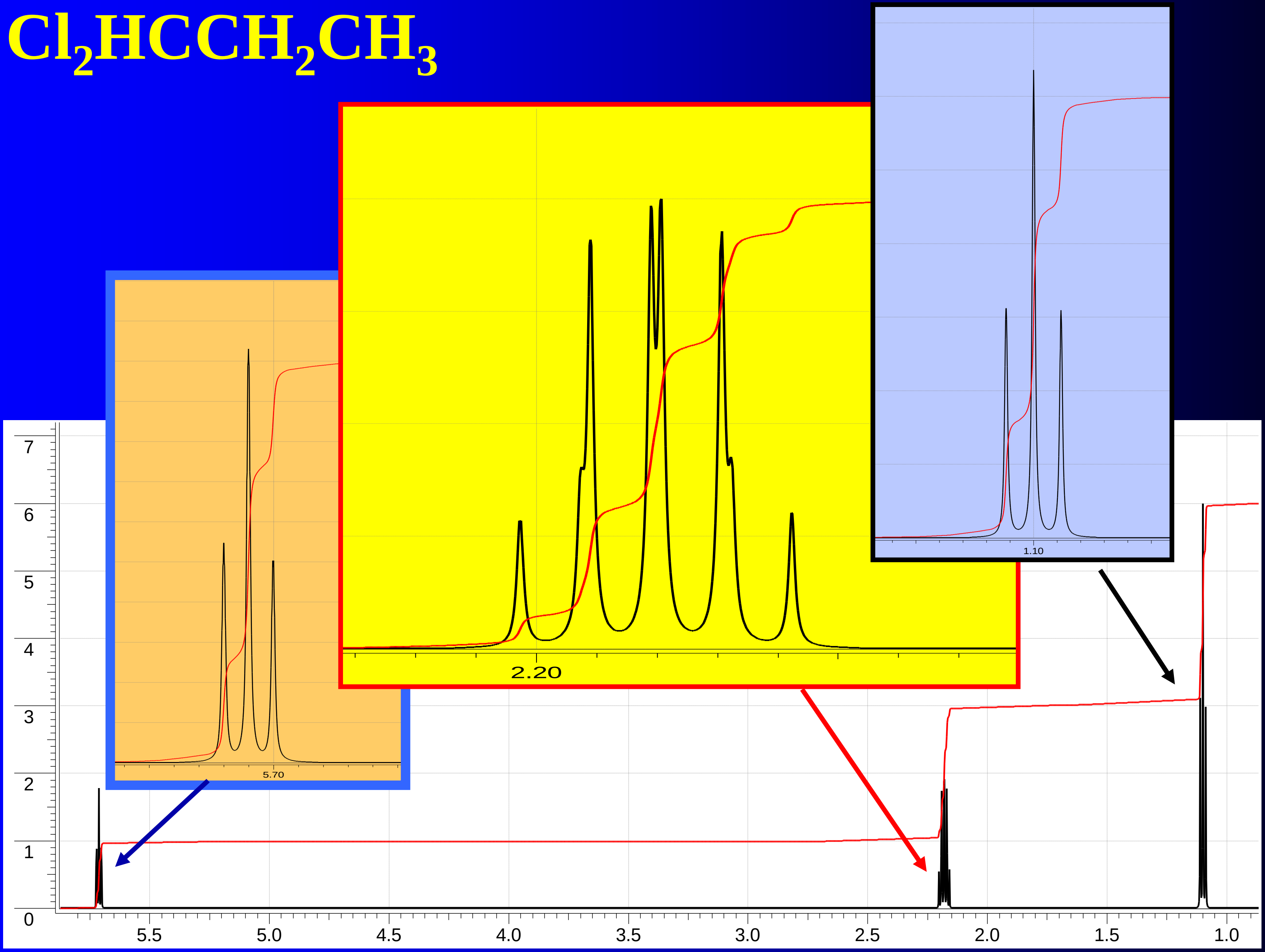
here $J_{ab} > J_{bc}$



$ClCH_2CH_2CH_2Cl$



$Cl_2HCCH_2CH_3$



An analysis