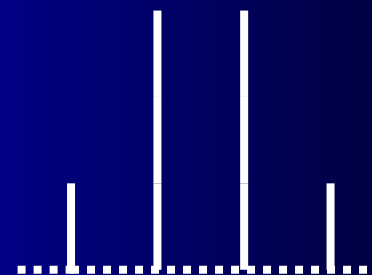
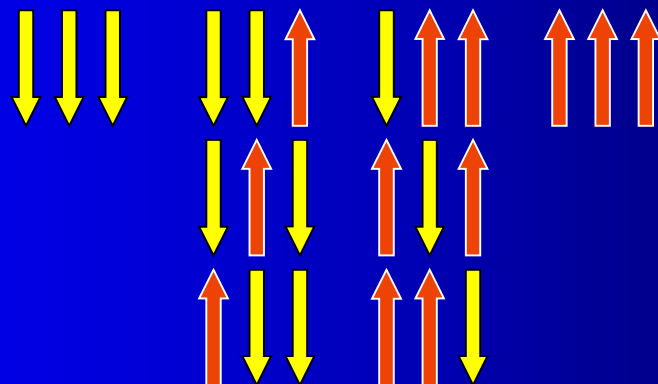


# Lecture 5

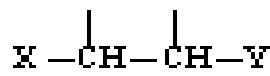
## Still More nmr

three spins

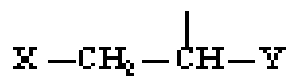


# NMR Splitting Patterns

n+1



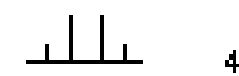
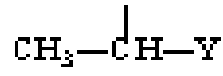
2



3



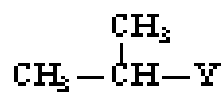
3



4



4



7

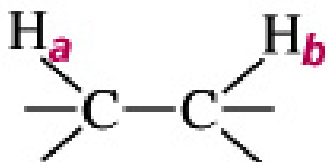


You don't need DNA  
to tell these apart!!

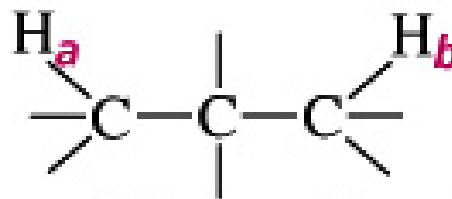


# Splitting of Signals

- 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  $\sigma$  bonds

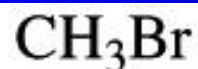


$H_a$  and  $H_b$  will not split each other because they are separated by 4  $\sigma$  bonds



# Splitting of Signals

- Equivalent protons never split each other



bromomethane



1,2-dichloroethane

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

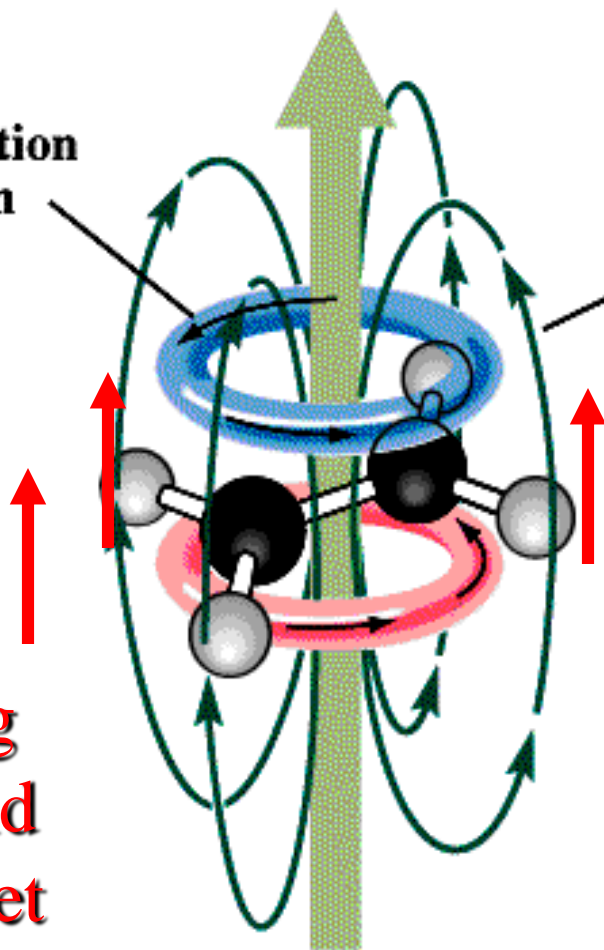


# Magnetic field induced in the pi bond of a carbon-carbon double bond

Induced circulation of pi electrons in the alkene

Induced local magnetic field of the pi electrons reinforces the applied field and provides part of the field necessary to bring a vinyl hydrogen into resonance.

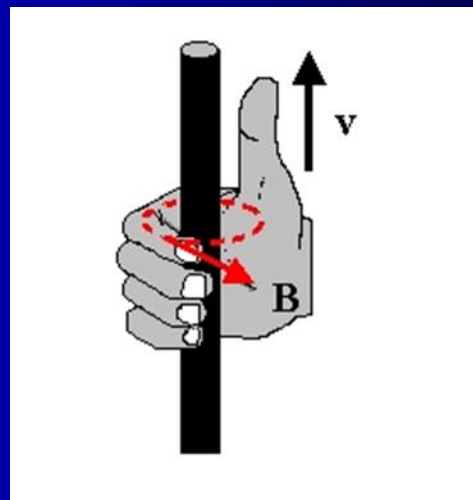
Outside the ring the induced field helps big magnet



Applied field,  $B_0$



**The Right-Hand Rule #2 determines the direction of the magnetic field around a current-carrying wire and vice-versa**



**BUT.....**

**When using the Right-Hand Rules, it is important to remember that the rules assume charges move in a conventional current (the hypothetical flow of positive charges). In order to apply the Right-Hand Rule to a moving negative charge, the direction of charge flow must be reversed--....or use your LEFT hand.**



# “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



# 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:





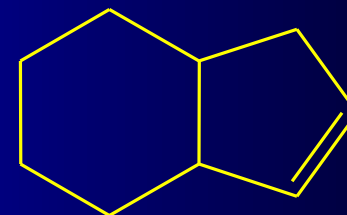
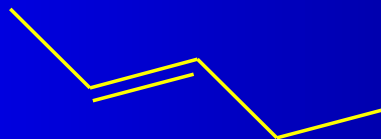
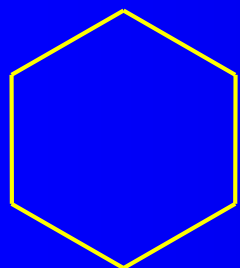
# Index of H Deficiency

- **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

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



$2/2=1 \Rightarrow$  1 ring or 1 double bond



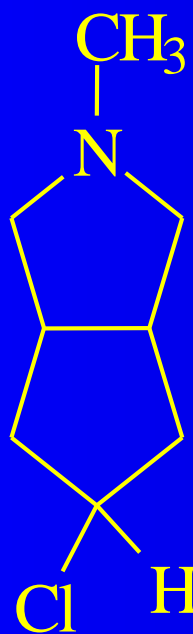
# Index of H Deficiency

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

- **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



Add one H for N and  
subtract one for Cl

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

but it is...



Missing



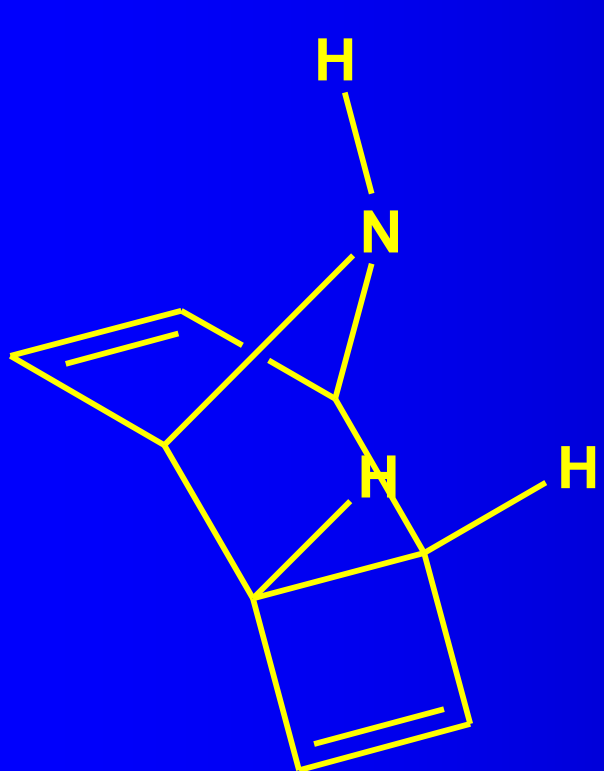
So index is....

---

$4/2=2$



# Calculate the Unsaturation Number



Add one H for N

Should be  $\text{C}_n\text{H}_{2n+2+1} = \text{C}_8\text{H}_{19}$

but it is...

Missing

So number is....



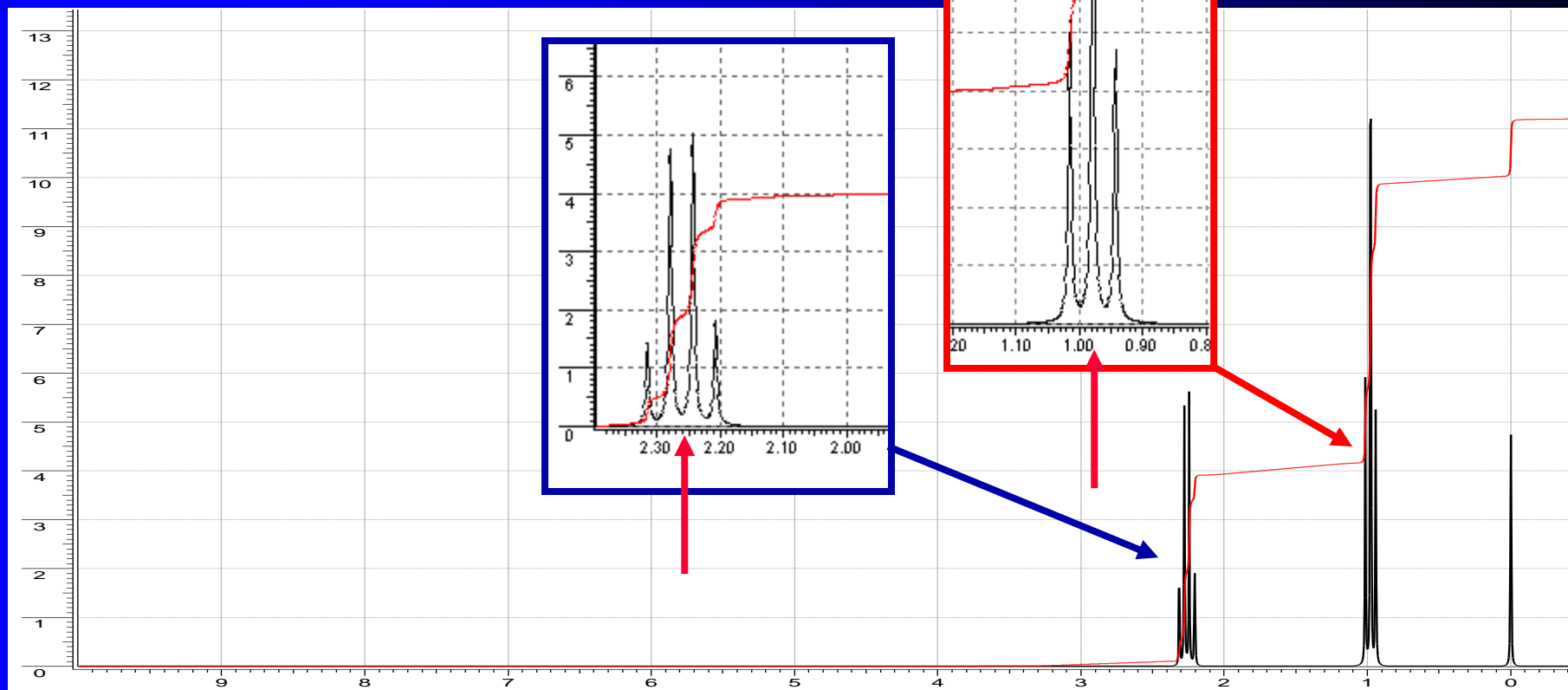
10/2=5!



# An Unknown

# $C_5H_{10}O$



# Chemical Shift - $^1\text{H-NMR}$

Type of H	$\delta$	Type of H	$\delta$
$(\text{C H}_3)_4 \text{Si}$	0	ROH	0.5-6.0
$\text{RCH}_3$	0.9	$\text{RCH}_2 \text{OR}$	3.3-4.0
$\text{RCH}_2 \text{R}$	1.2-1.4	$\text{R}_2 \text{NH}$	0.5-5.0
$\text{R}_3 \text{CH}$	1.4-1.7	$\begin{array}{c} \text{O} \\    \\ \text{RCCH}_3 \end{array}$	2.1-2.3
$\text{R}_2 \text{C}=\text{CRC HR}_2$	1.6-2.6	$\begin{array}{c} \text{O} \\    \\ \text{RCCH}_2 \text{R} \end{array}$	2.2-2.6
$\text{RC}\equiv\text{CH}$	2.0-3.0		
$\text{ArCH}_3$	2.2-2.5		



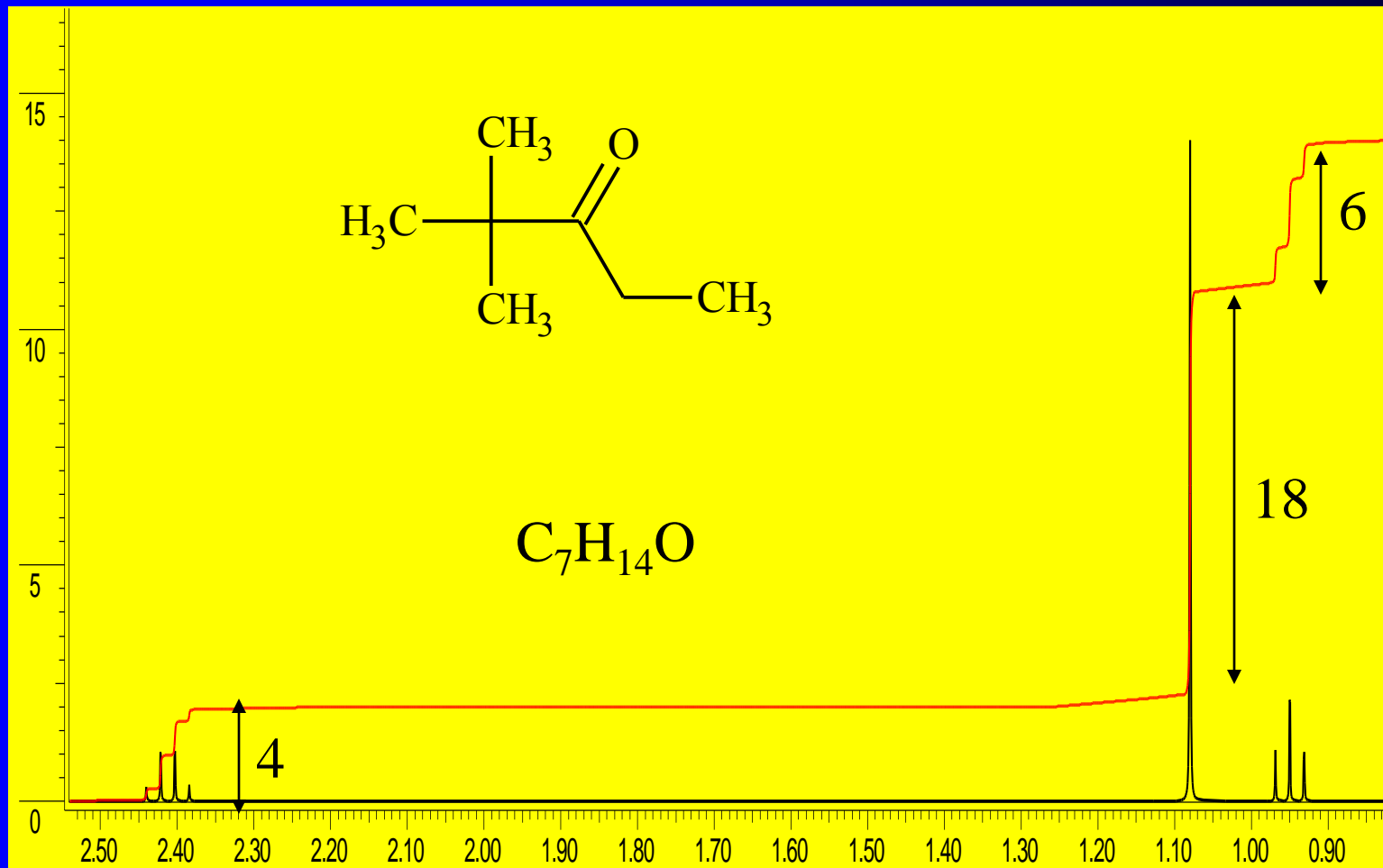
# Chemical Shift - $^1\text{H-NMR}$

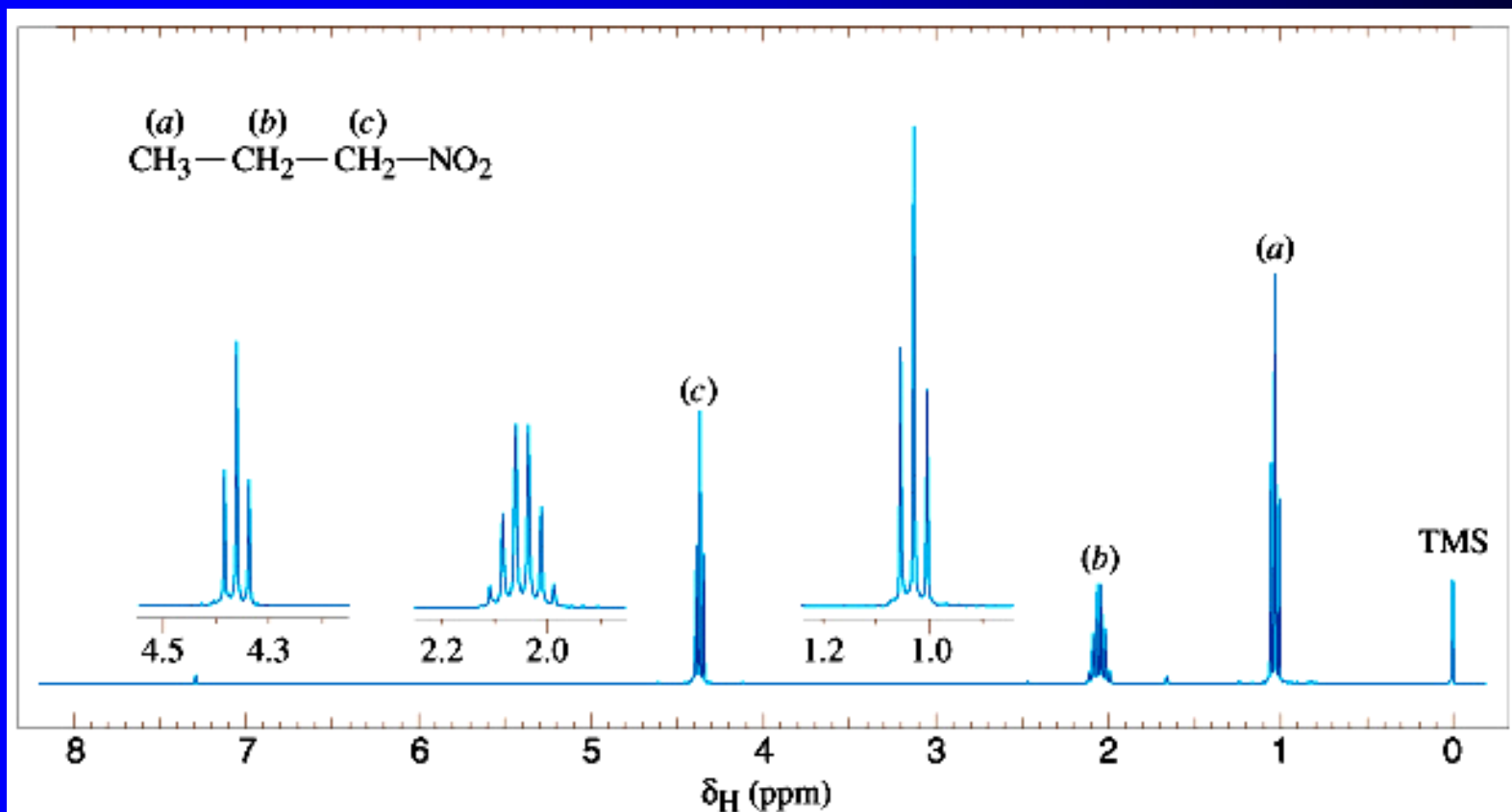
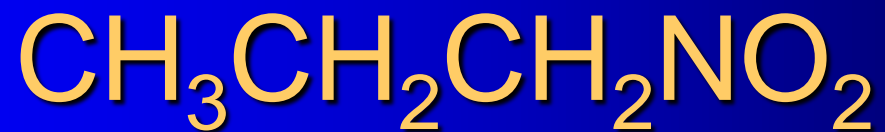
Type of H	$\delta$	Type of H	$\delta$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_3 \end{array}$	3.5-3.9	$\text{R}_2\text{C}=\text{C H}_2$	4.6-5.0
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_2\text{R} \end{array}$	4.1-4.7	$\text{R}_2\text{C}=\text{C HR}$	5.0-5.7
$\text{RCH}_2\text{I}$	3.1-3.3	$\text{ArH}$	6.5-8.5
$\text{RCH}_2\text{Br}$	3.4-3.6	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCH} \end{array}$	9.5-10.1
$\text{RCH}_2\text{Cl}$	3.6-3.8	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$	10-13
$\text{RCH}_2\text{F}$	4.4-4.5		





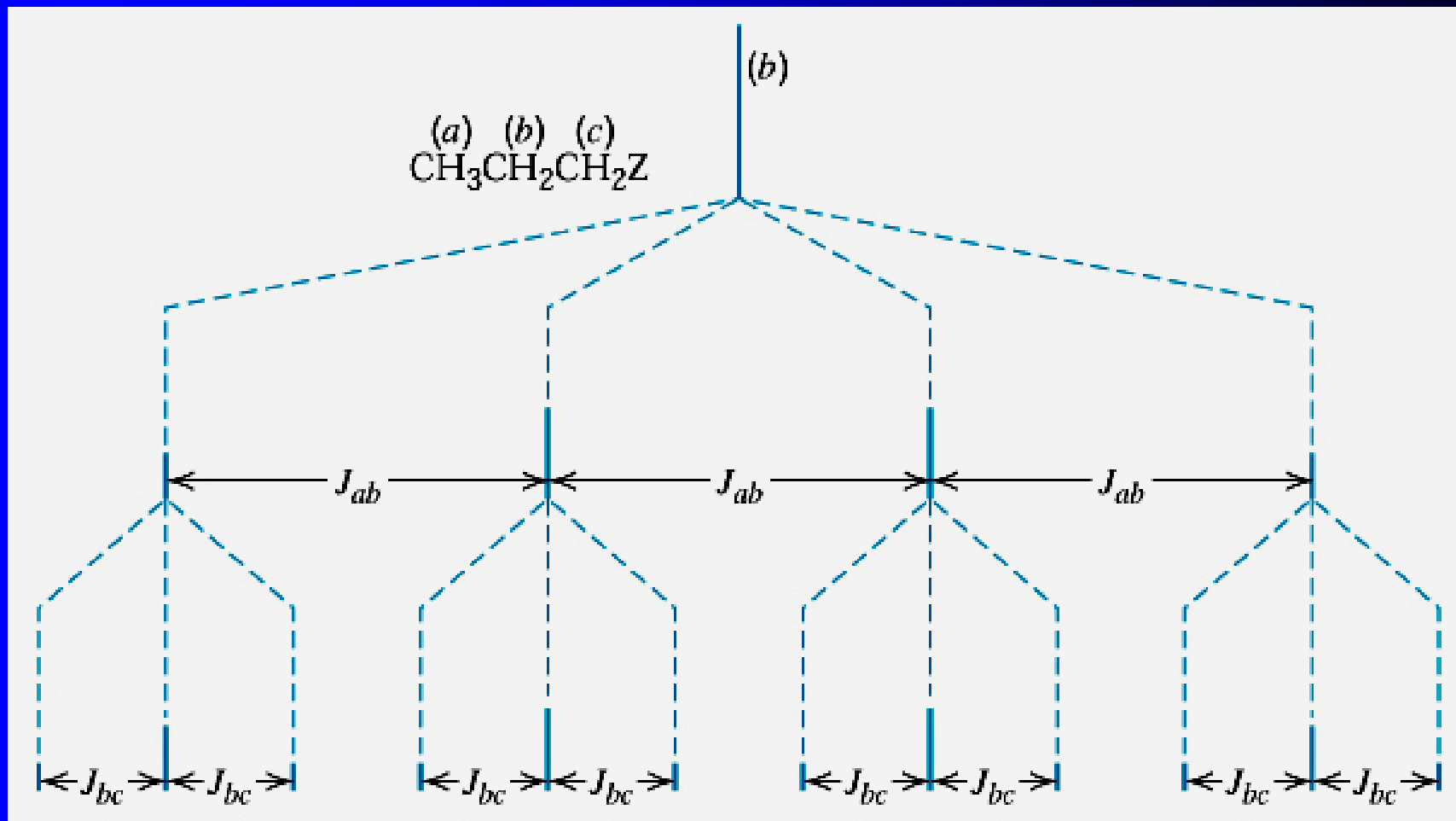
# Sample spectra

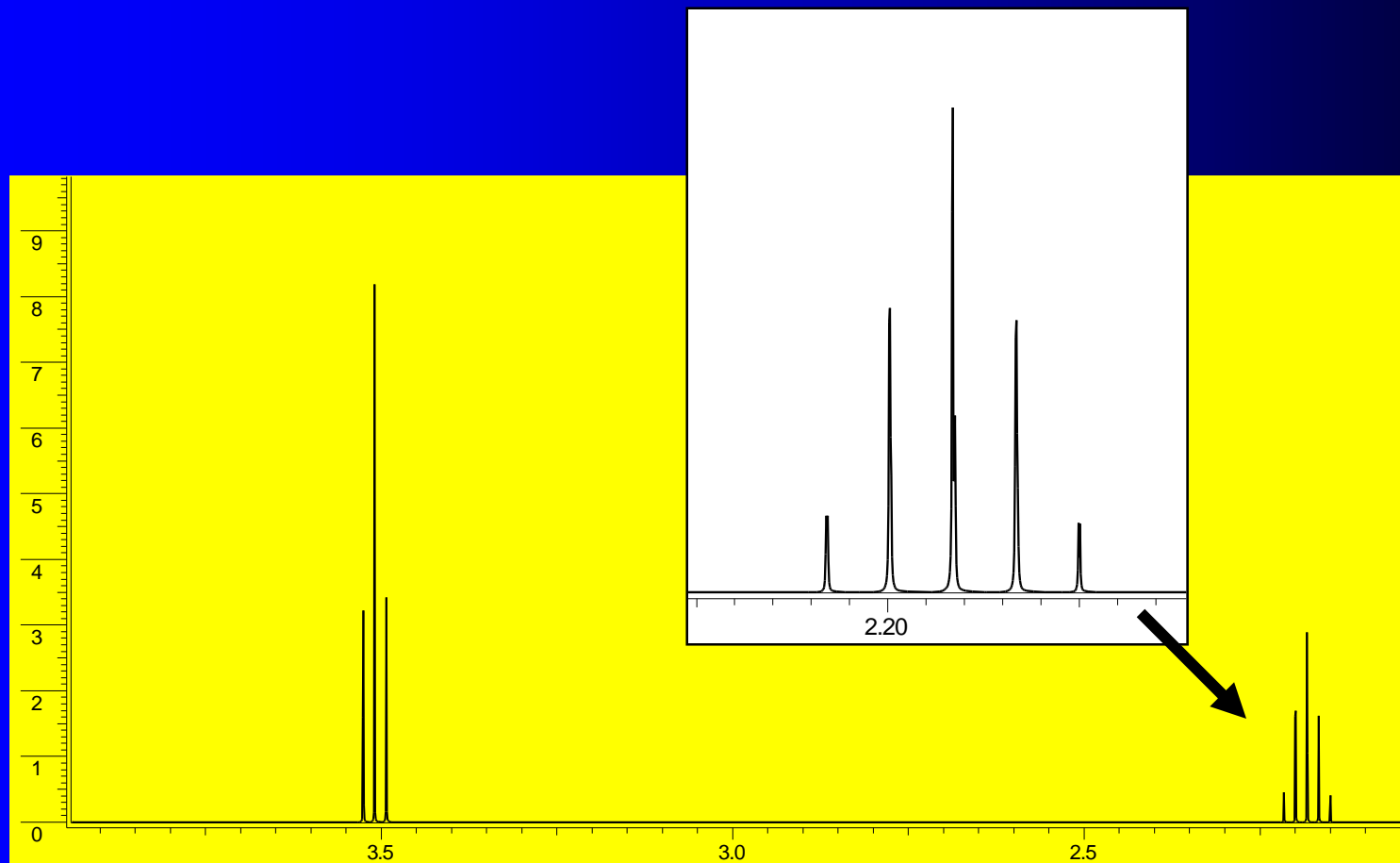


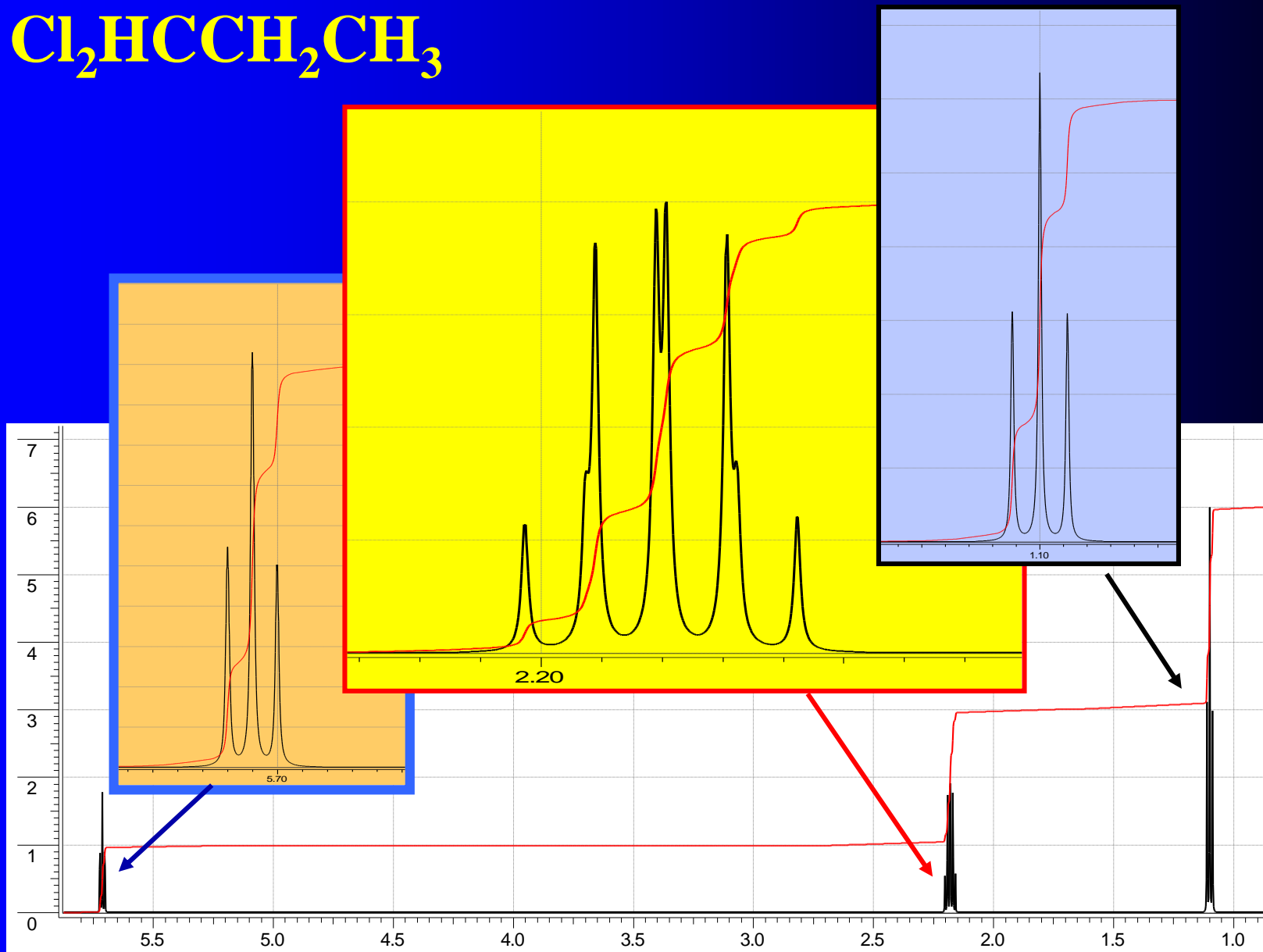


# Multiple interactions of non-equivalent neighbors

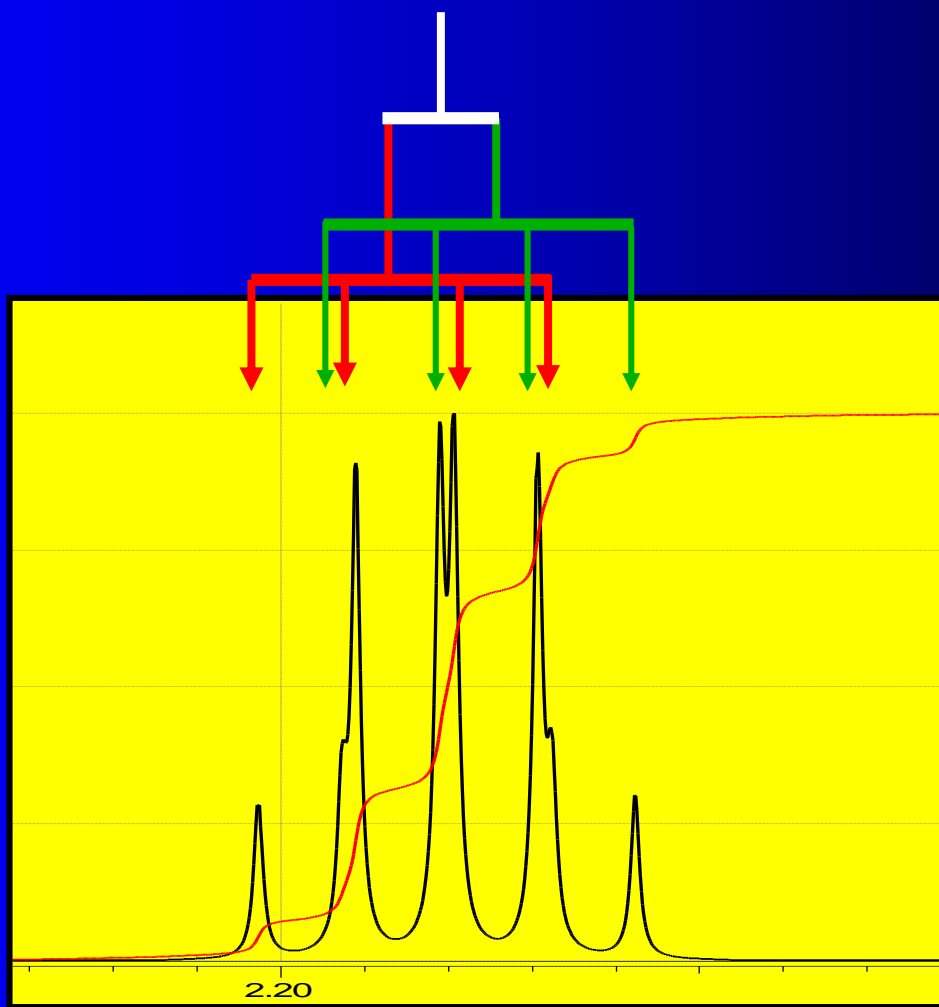
here  $J_{ab} > J_{bc}$



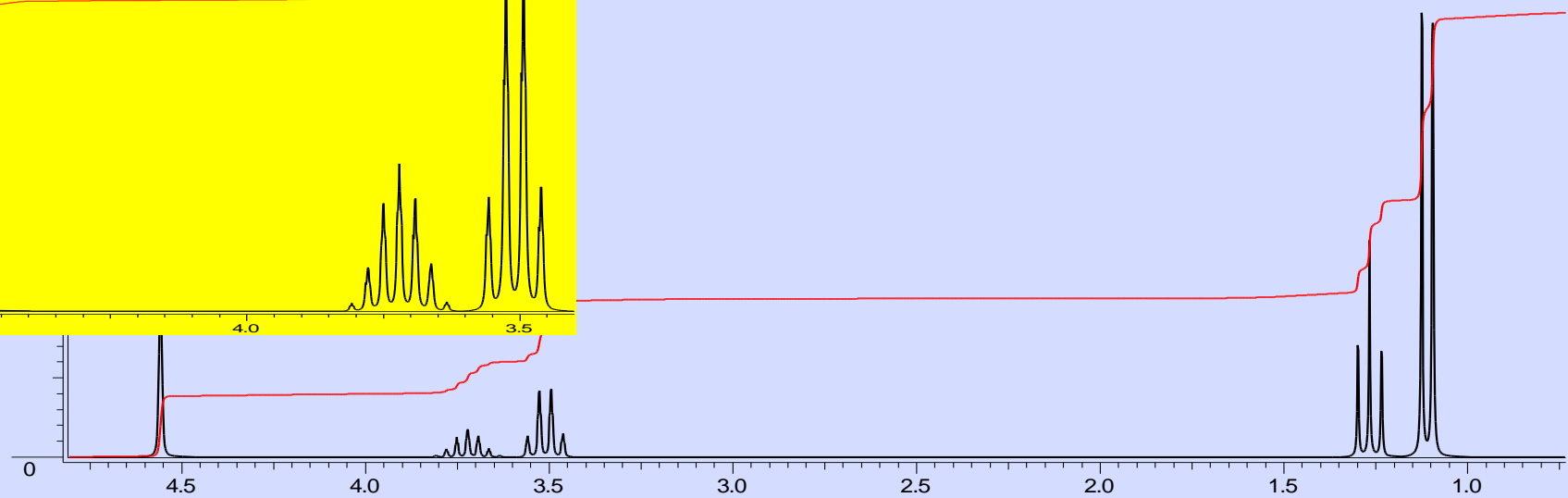
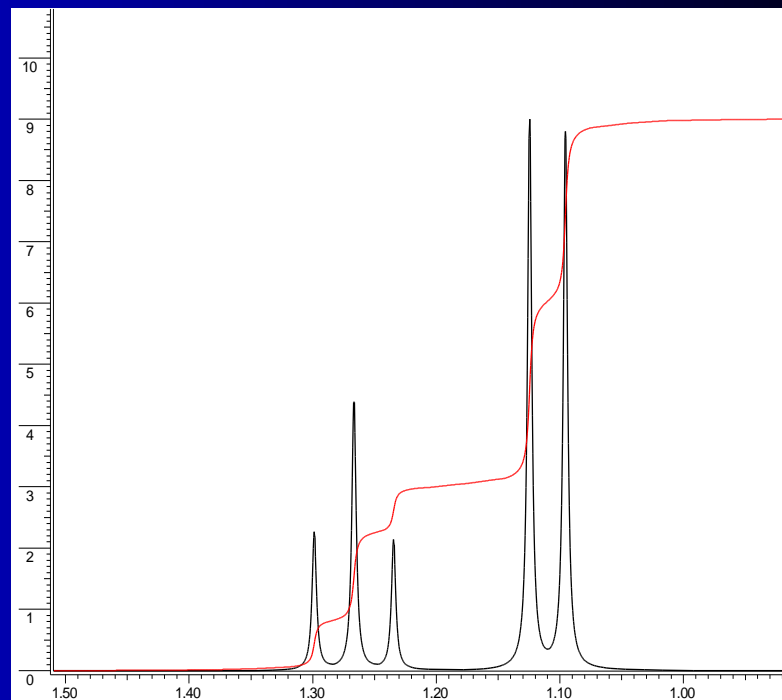
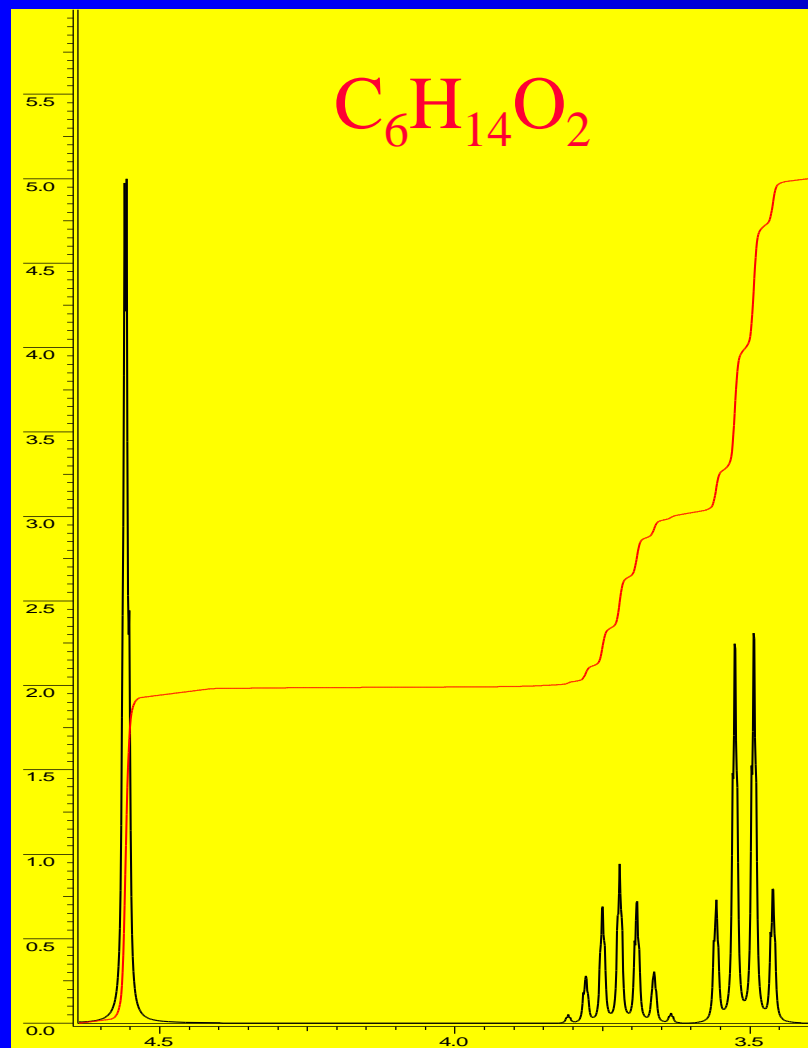




# An analysis



# More Practice



# Chemical Shift - $^1\text{H-NMR}$

Type of H	$\delta$	Type of H	$\delta$
$(\text{C H}_3)_4 \text{Si}$	0	ROH	0.5-6.0
$\text{RCH}_3$	0.9	$\text{RCH}_2 \text{OR}$	3.3-4.0
$\text{RCH}_2 \text{R}$	1.2-1.4	$\text{R}_2 \text{NH}$	0.5-5.0
$\text{R}_3 \text{CH}$	1.4-1.7	$\begin{array}{c} \text{O} \\    \\ \text{RCCH}_3 \end{array}$	2.1-2.3
$\text{R}_2 \text{C}=\text{CRC HR}_2$	1.6-2.6	$\begin{array}{c} \text{O} \\    \\ \text{RCCH}_2 \text{R} \end{array}$	2.2-2.6
$\text{RC}\equiv\text{CH}$	2.0-3.0		
$\text{ArCH}_3$	2.2-2.5		
$\text{ArCH}_2 \text{R}$	2.3-2.8		





# Chemical Shift - $^1\text{H-NMR}$

Type of H	$\delta$	Type of H	$\delta$
$\begin{array}{c} \text{O} \\    \\ \text{RCOCH}_3 \end{array}$	3.5-3.9	$\text{R}_2\text{C}=\text{C H}_2$	4.6-5.0
$\begin{array}{c} \text{O} \\    \\ \text{RCOCH}_2\text{R} \end{array}$	4.1-4.7	$\text{R}_2\text{C}=\text{C HR}$	5.0-5.7
$\text{RCH}_2\text{I}$	3.1-3.3	$\text{ArH}$	6.5-8.5
$\text{RCH}_2\text{Br}$	3.4-3.6	$\begin{array}{c} \text{O} \\    \\ \text{RCH} \end{array}$	9.5-10.1
$\text{RCH}_2\text{Cl}$	3.6-3.8	$\begin{array}{c} \text{O} \\    \\ \text{RCOH} \end{array}$	10-13
$\text{RCH}_2\text{F}$	4.4-4.5		



# Deuterium Oxide

- Heavy water is heavier than H<sub>2</sub>O (duh?), having a density of 1.108 g/cm<sup>3</sup>. Heavy water ice will actually sink in light liquid water. The freezing and boiling points are also elevated somewhat, with heavy water freezing at 3.81° C (38.86° F) and boiling at 101.42° C (214.56° F) at standard atmospheric pressure.
- Heavy water toxicity manifests itself when about 50% of the water in the body has been replaced by D<sub>2</sub>O. Prolonged heavy water consumption can cause death. The price is about \$300 per kilogram.



# $D_2O$ in $H_2O$



$D_2O$  ice in  $H_2O$



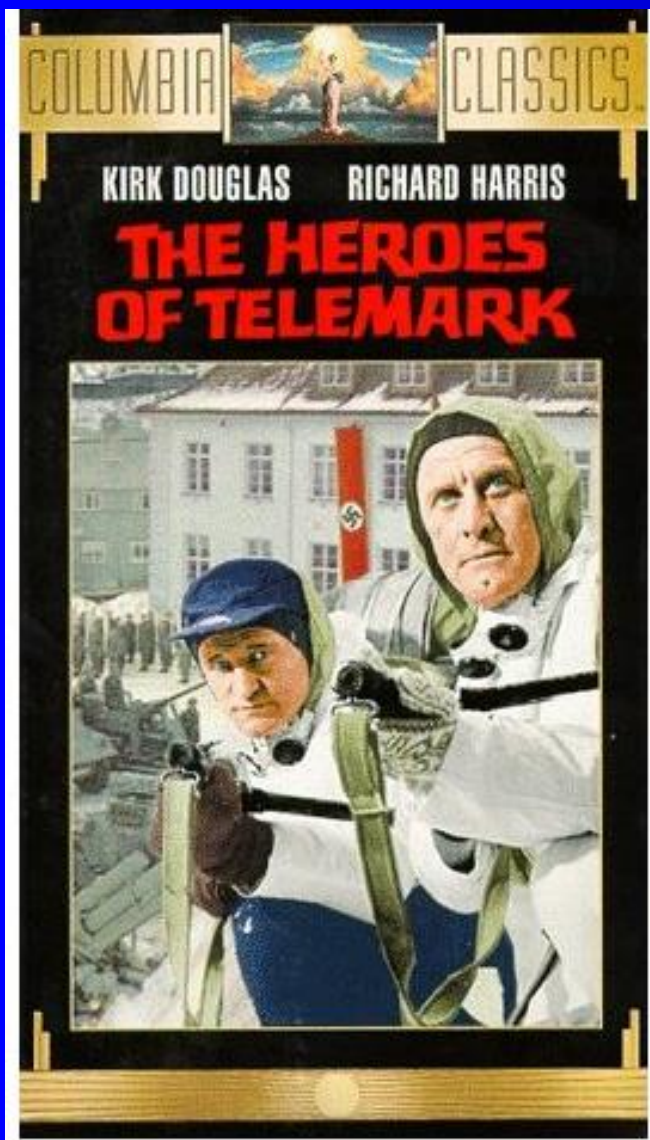
$D_2O$  ice in  $D_2O$



# Deuterium Oxide vs Water

Property	D <sub>2</sub> O (Heavy water)	H <sub>2</sub> O (Light water)
Freezing point (°C)	3.82	0.0
Boiling point (°C)	101.4	100.0
Density at STP (g/mL)	1.1056	0.9982
Dynamic viscosity (at 20°C, mPa·s)	1.25	1.005
Heat of fusion (cal/mol)	1,515	1,436
pH (at 25°C)	7.41 (sometimes "pD")	7.00
Cost per kilogram	~\$300	~\$0.002 for tap ~\$5.00 for Fiji!!!



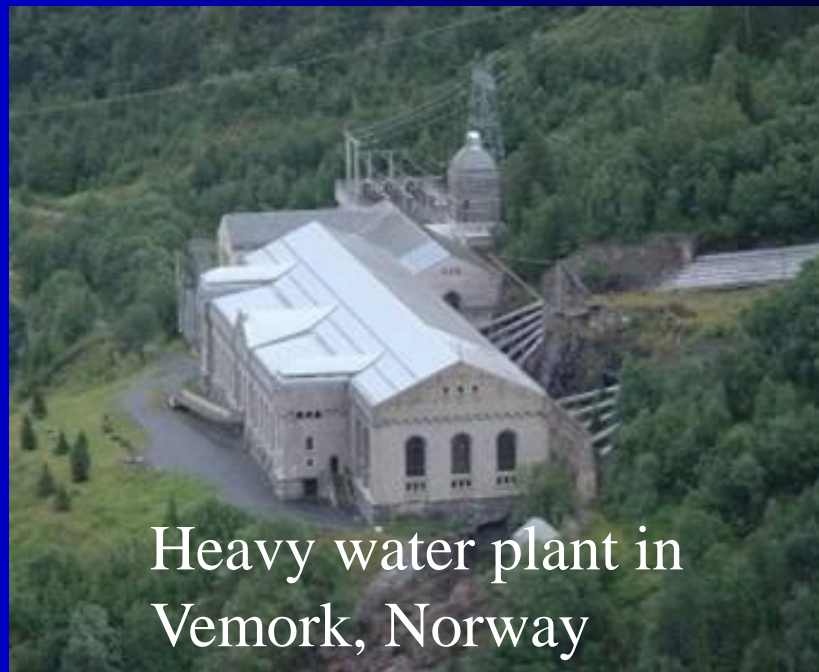


[http://www.imdb.com/  
title/tt0059263/](http://www.imdb.com/title/tt0059263/)



Joachim Ronneberg

<http://www.telegraph.co.uk/news/7664351/A-new-mission-for-the-hero-of-Telemark.html>



Heavy water plant in  
Vemork, Norway



# Vemork Hydroelectric Plant

