Lecture 6
Infrared spectroscopy

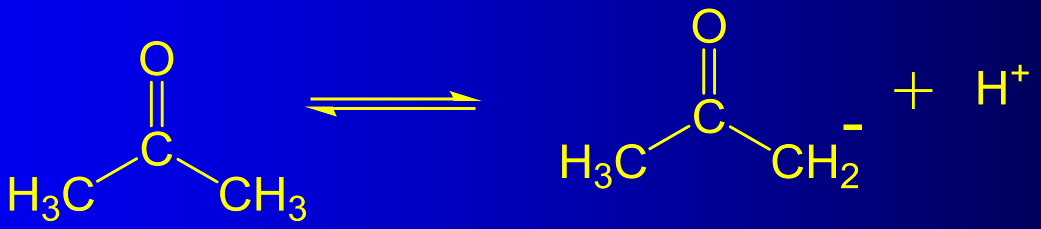
D_2O in H_2O

D_2O ice in H_2O

D_2O ice in D_2O

Chemical Exchange

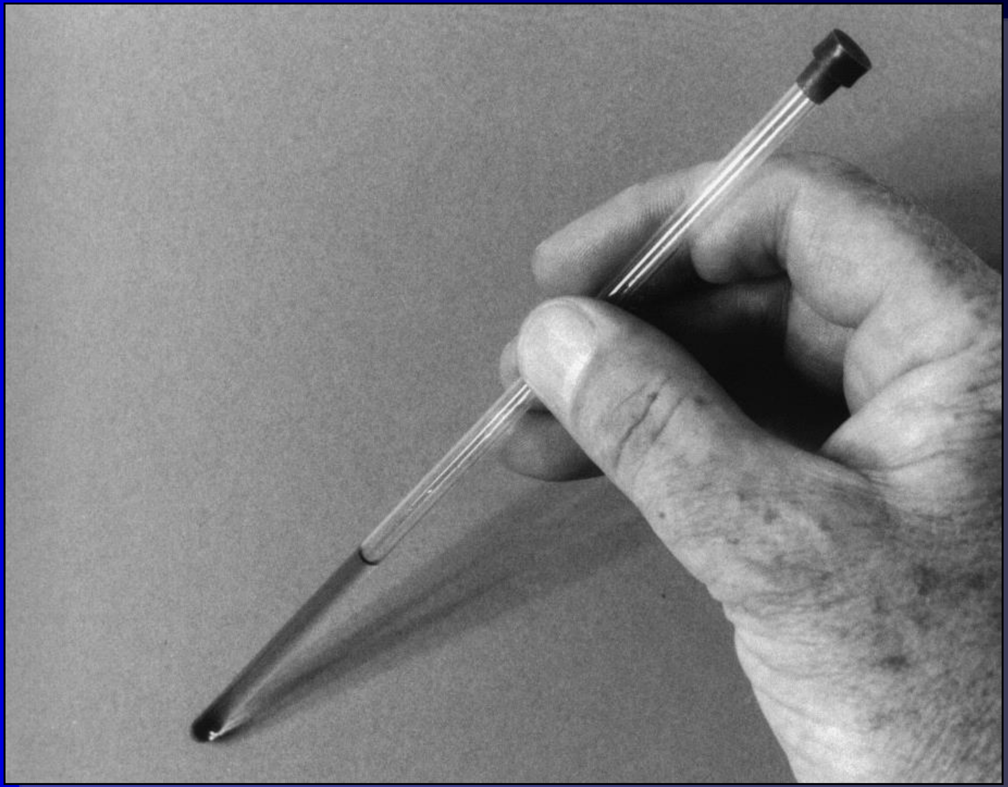
- Hydrogens on electronegative atoms such as Oxygen and Nitrogen
  - Undergo rapid “exchange” and often give only a relatively broad singlet due to “averaging”
  - These hydrogens also exchange (equilibrate) with Deuterium in D_2O and “disappear” from the spectrum

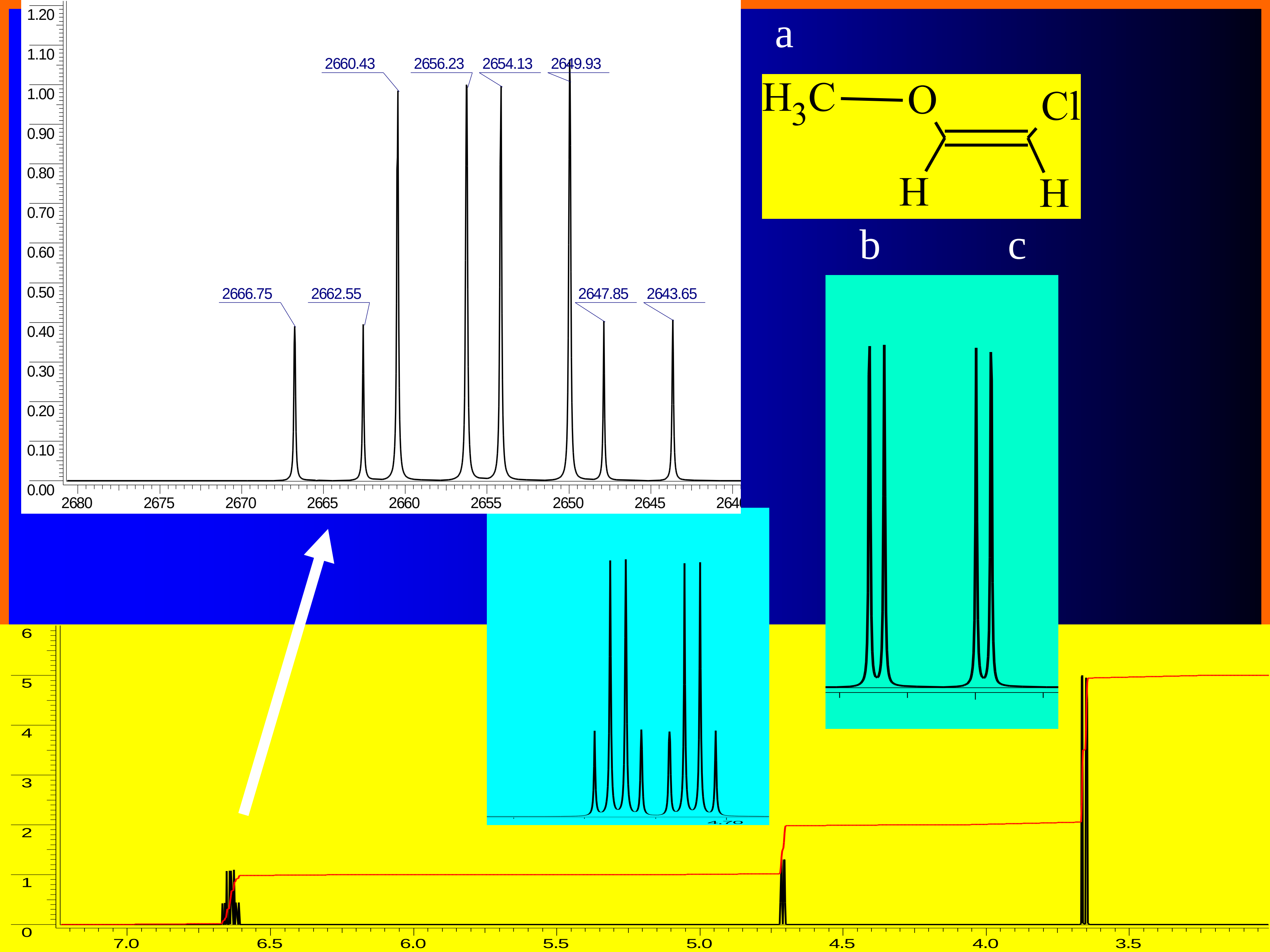


$$D_2O \rightleftharpoons DO^- + D^+$$

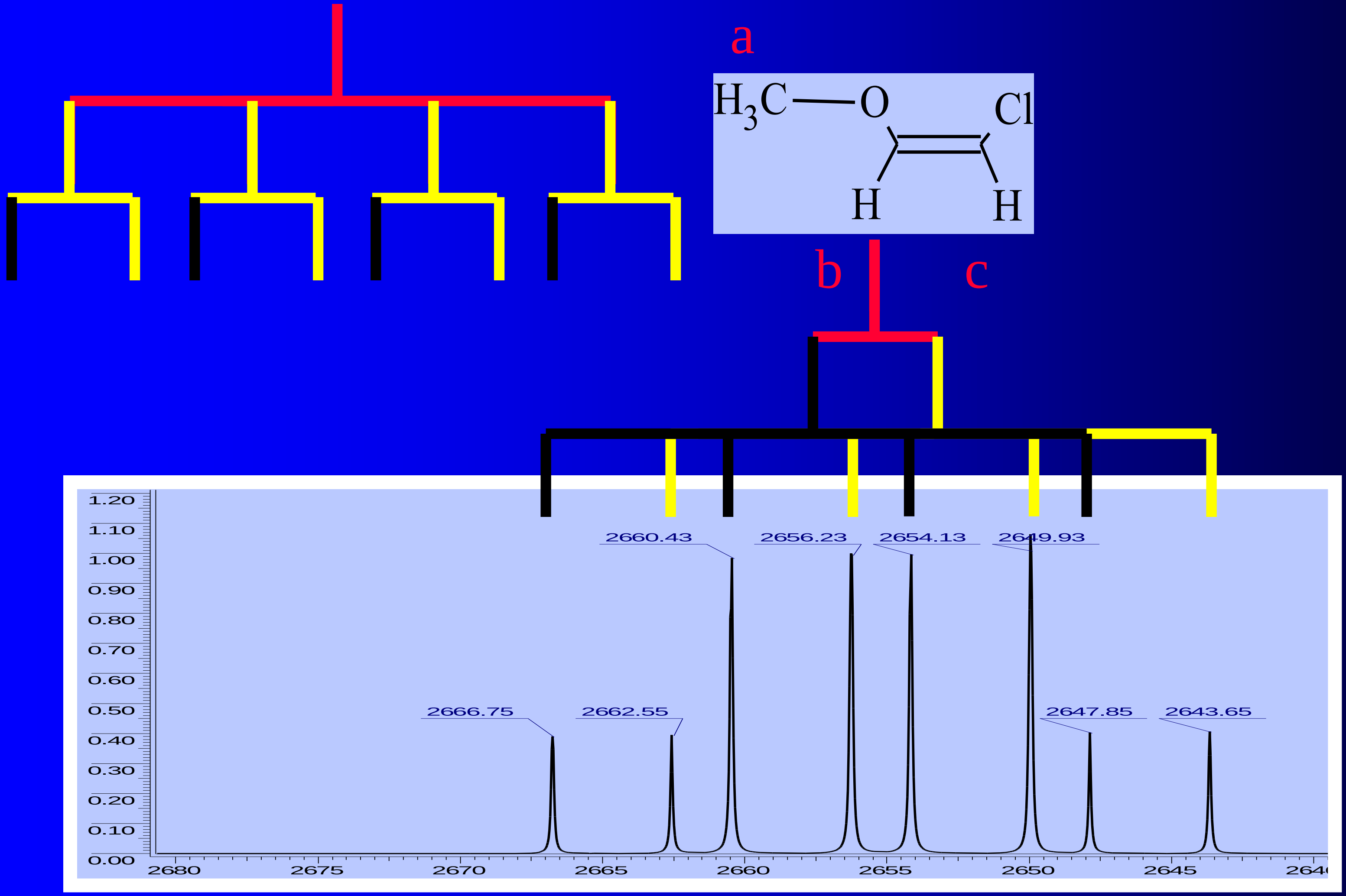
Common ^{1}H-nmr Solvents

- $DCCl_3$
- CCl_4
- $(CD_3)_2SO$
- D_2O
- C_6D_6

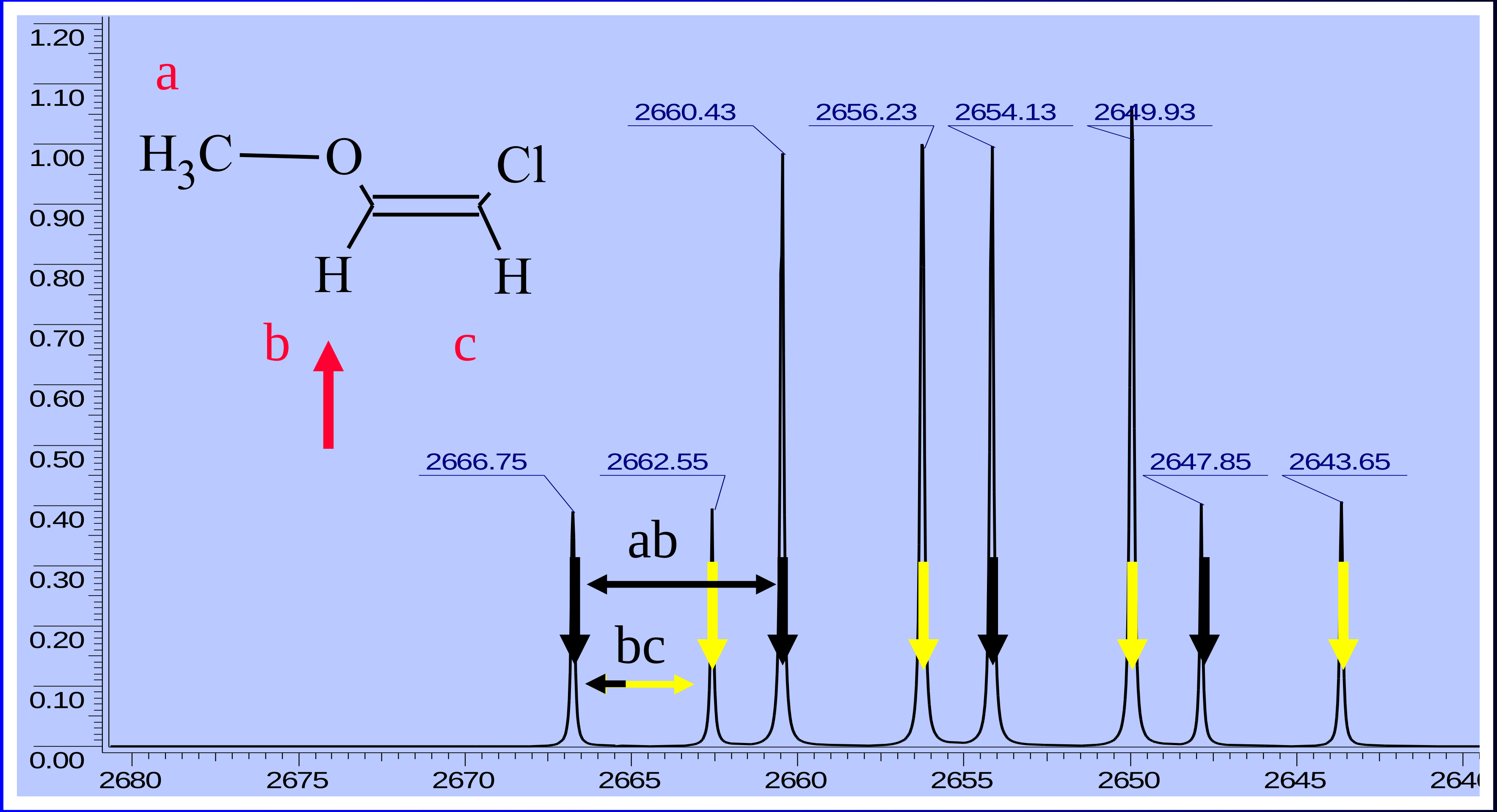



a
H3C
O
Cl
H
H
b
c
2666.75
2662.55
2660.43
2656.23
2654.13
2649.93
2647.85
2643.65
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
2680
2675
2670
2665
2660
2655
2650
2645
264
4.70
6
5
4
3
2
1
0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

Whats with what??



Coupling Constants



Chemical Shift additivity estimates

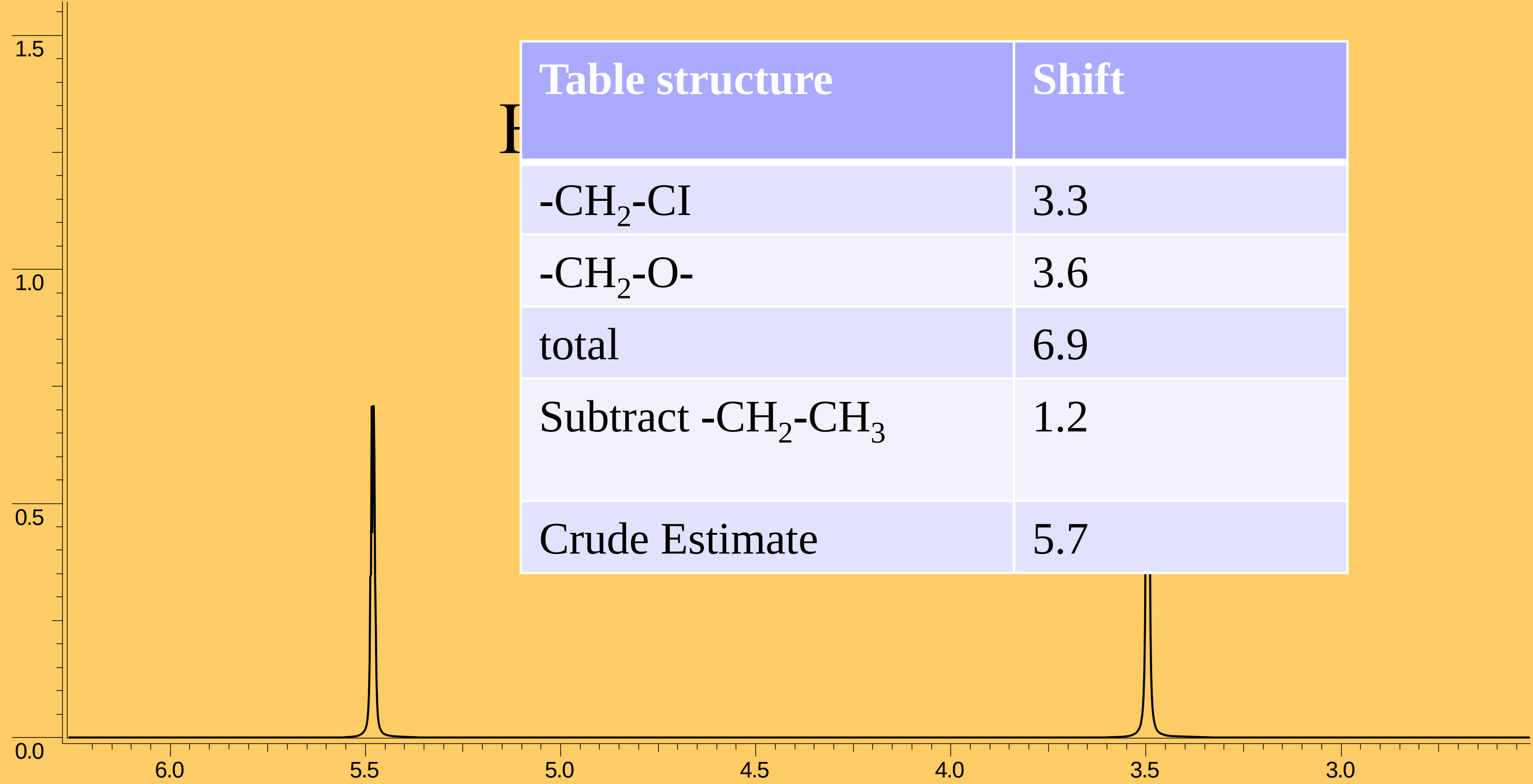
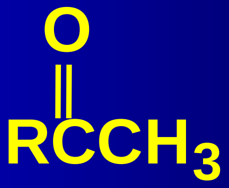


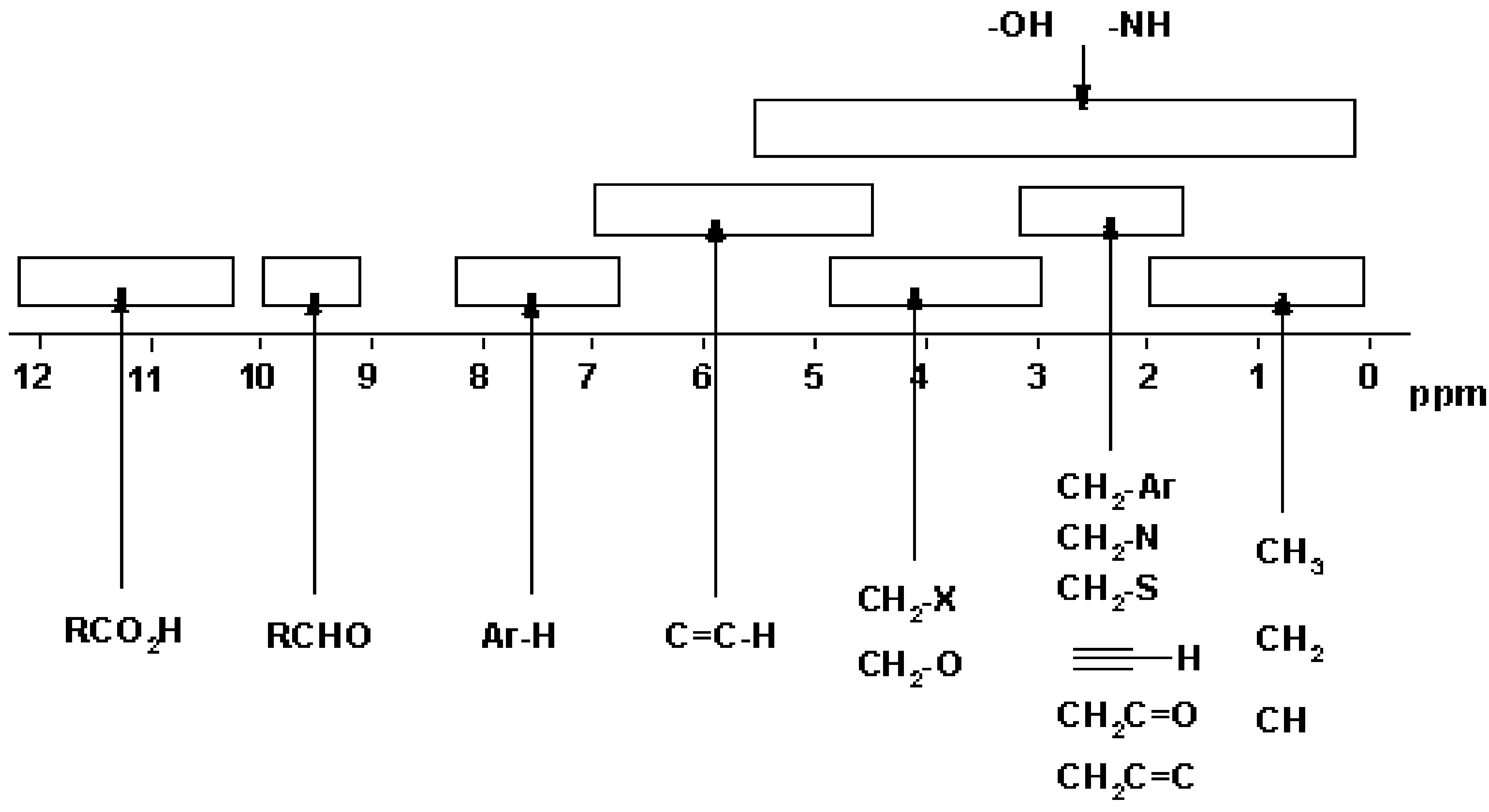
Table structure	**Shift**
-CH$_2$-CI	3.3
-CH$_2$-O-	3.6
total	6.9
Subtract -CH$_2$-CH$_3$	1.2
Crude Estimate	5.7

Caution…..estimates only!!

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		
$R_2C{=}CRCHR_2$	1.6-2.6	 $R\overset{\overset{O}{\|}}{C}CH_3$	2.1-2.3
$RC{\equiv}CH$	2.0-3.0		
$ArCH_3$	2.2-2.5	 $R\overset{\overset{O}{\|}}{C}CH_2R$	2.2-2.6
$ArCH_2R$	2.3-2.8		

^{1}H Chemical Shifts



-OH -NH

RCO_2H

RCHO

Ar-H

C=C-H

CH_2-X

CH_2-O

CH_2- Ar

CH_2-N

CH_2-S

≡H

CH_2C=O

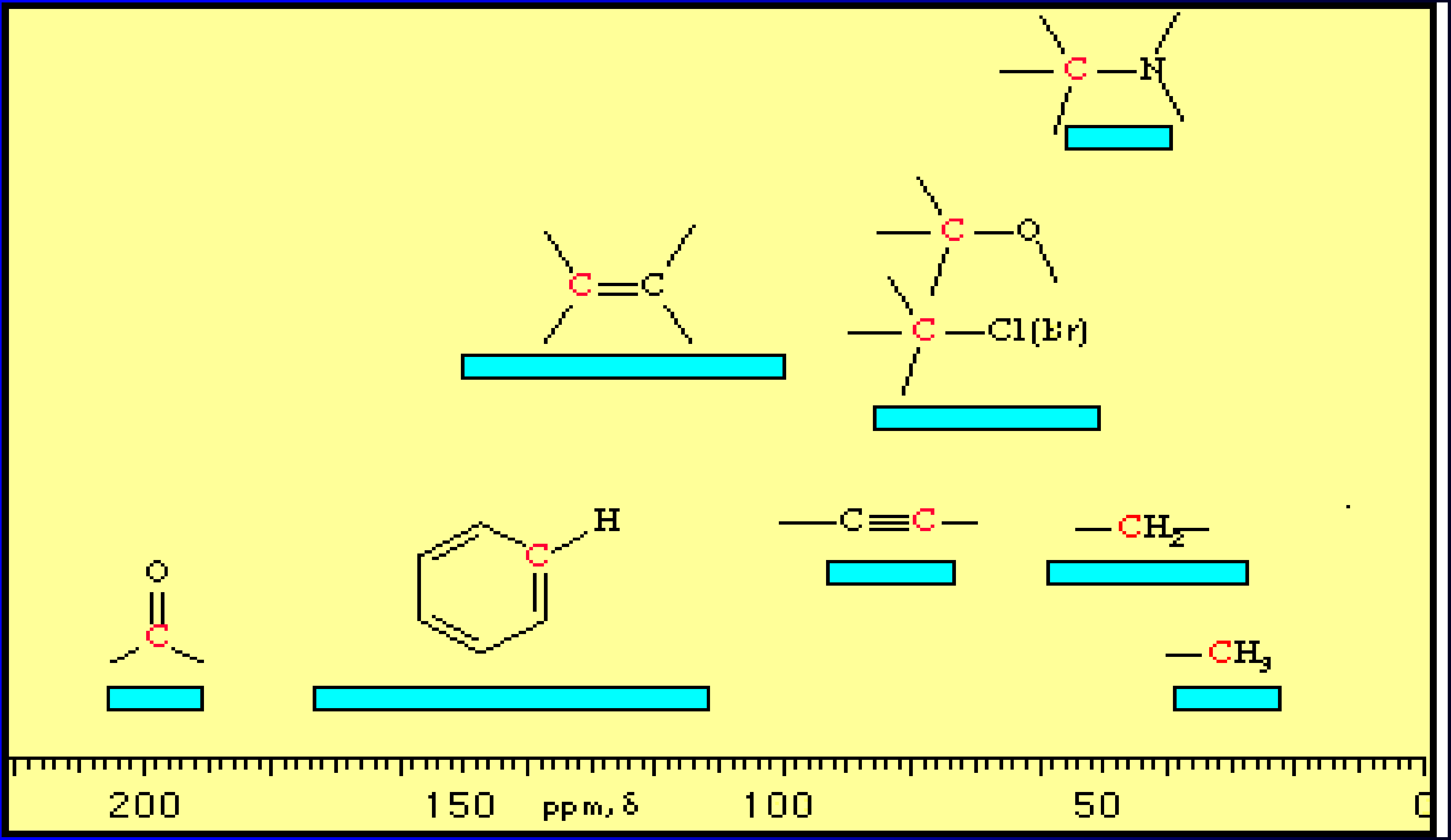
CH_2C=C

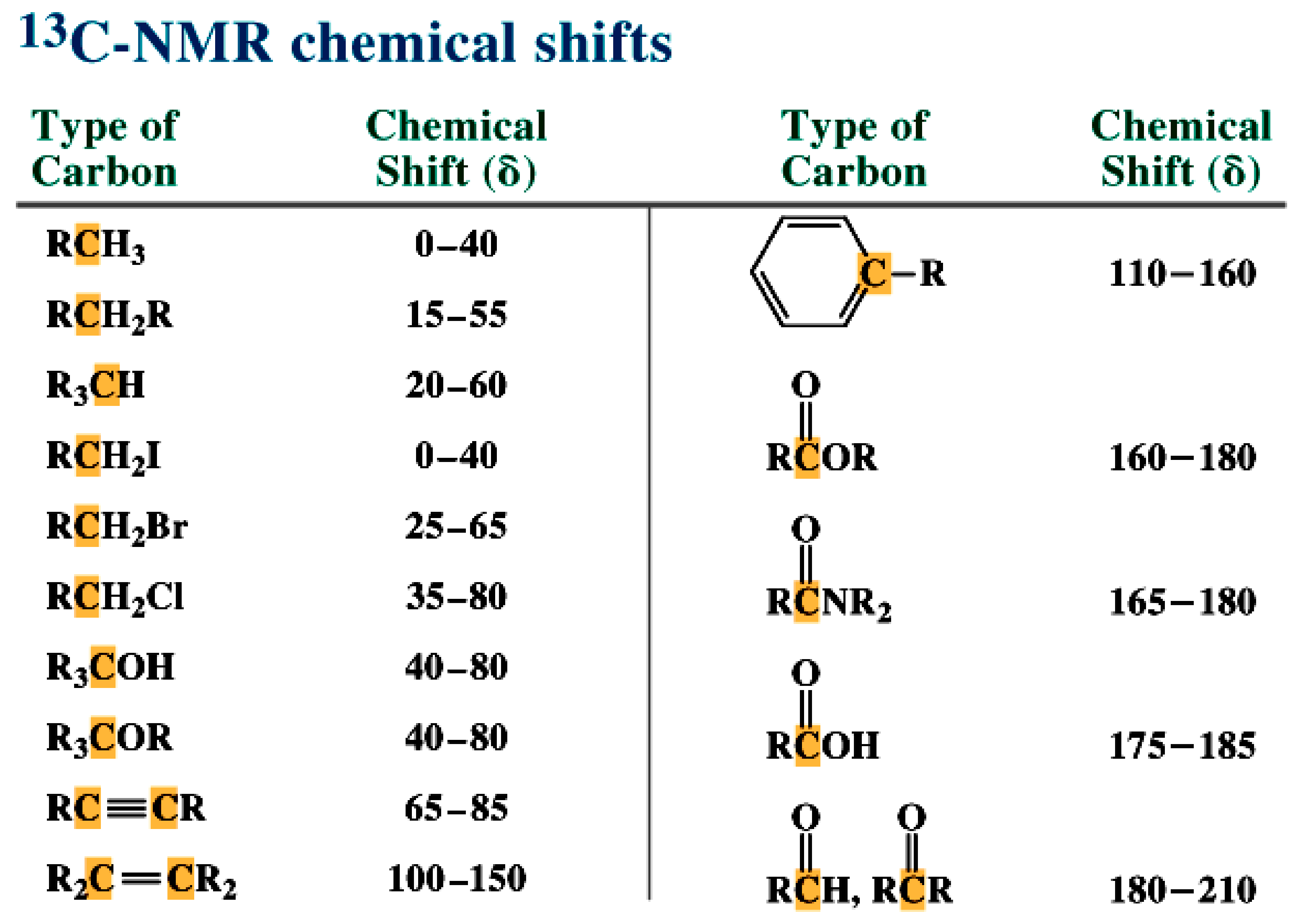
CH_3

CH_2

CH

^{13}C Chemical Shifts

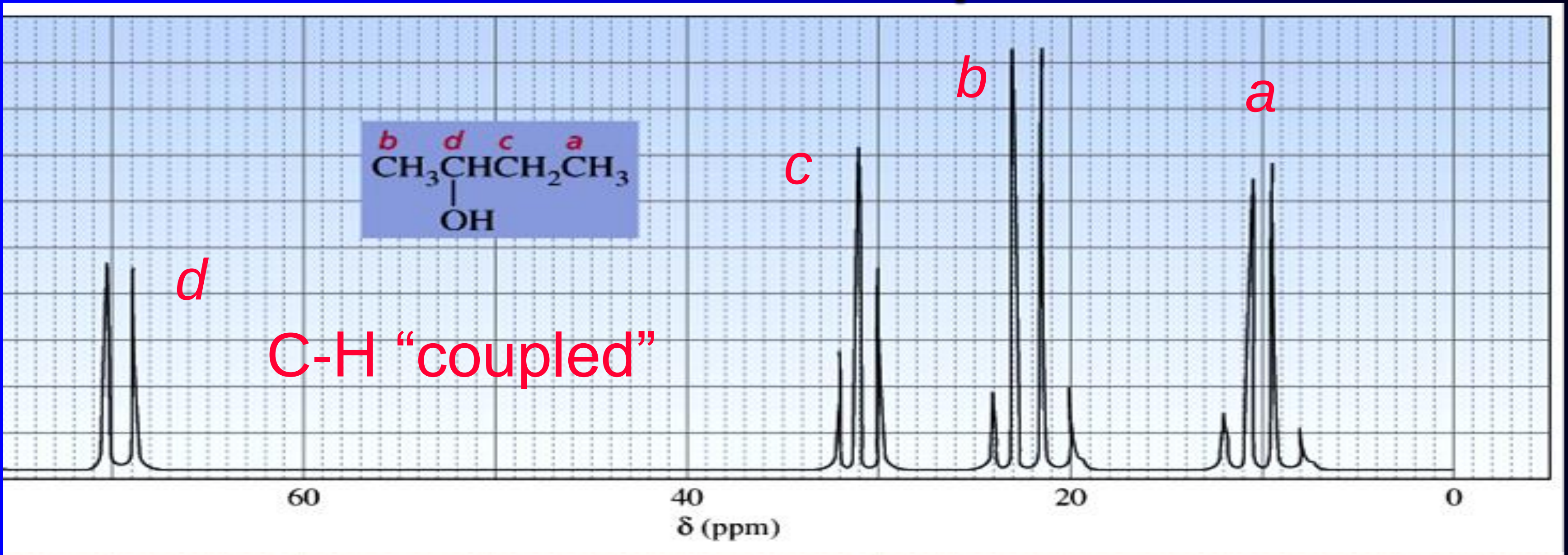


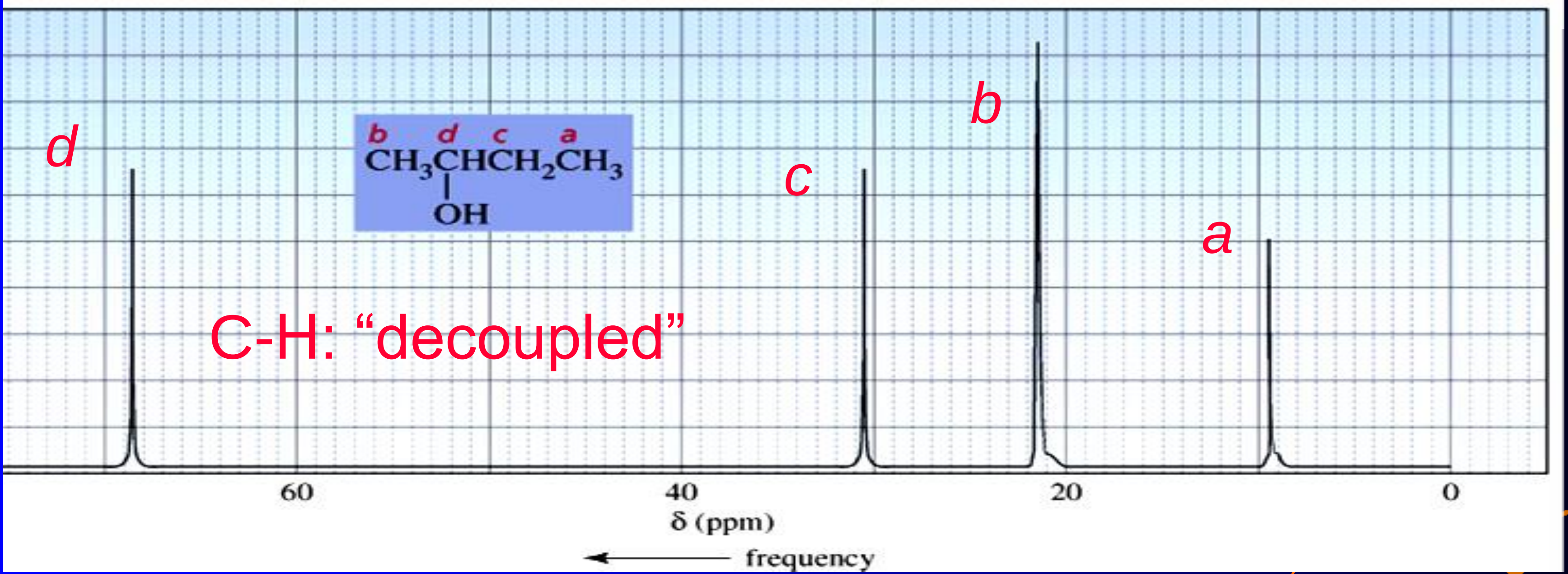


^{13}C-NMR chemical shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH_3	0–40	$C_6H_5\text{–}C\text{–}R$	110–160
RCH_2R	15–55		
R_3CH	20–60		
RCH_2I	0–40	$R\overset{\overset{O}{\|}}{C}OR$	160–180
RCH_2Br	25–65		
RCH_2Cl	35–80	$R\overset{\overset{O}{\|}}{C}NR_2$	165–180
R_3COH	40–80		
R_3COR	40–80	$R\overset{\overset{O}{\|}}{C}OH$	175–185
$RC\equiv CR$	65–85		
$R_2C=CR_2$	100–150	$R\overset{\overset{O}{\|}}{C}H$, $R\overset{\overset{O}{\|}}{C}R$	180–210

^{13}C NMR Spectra





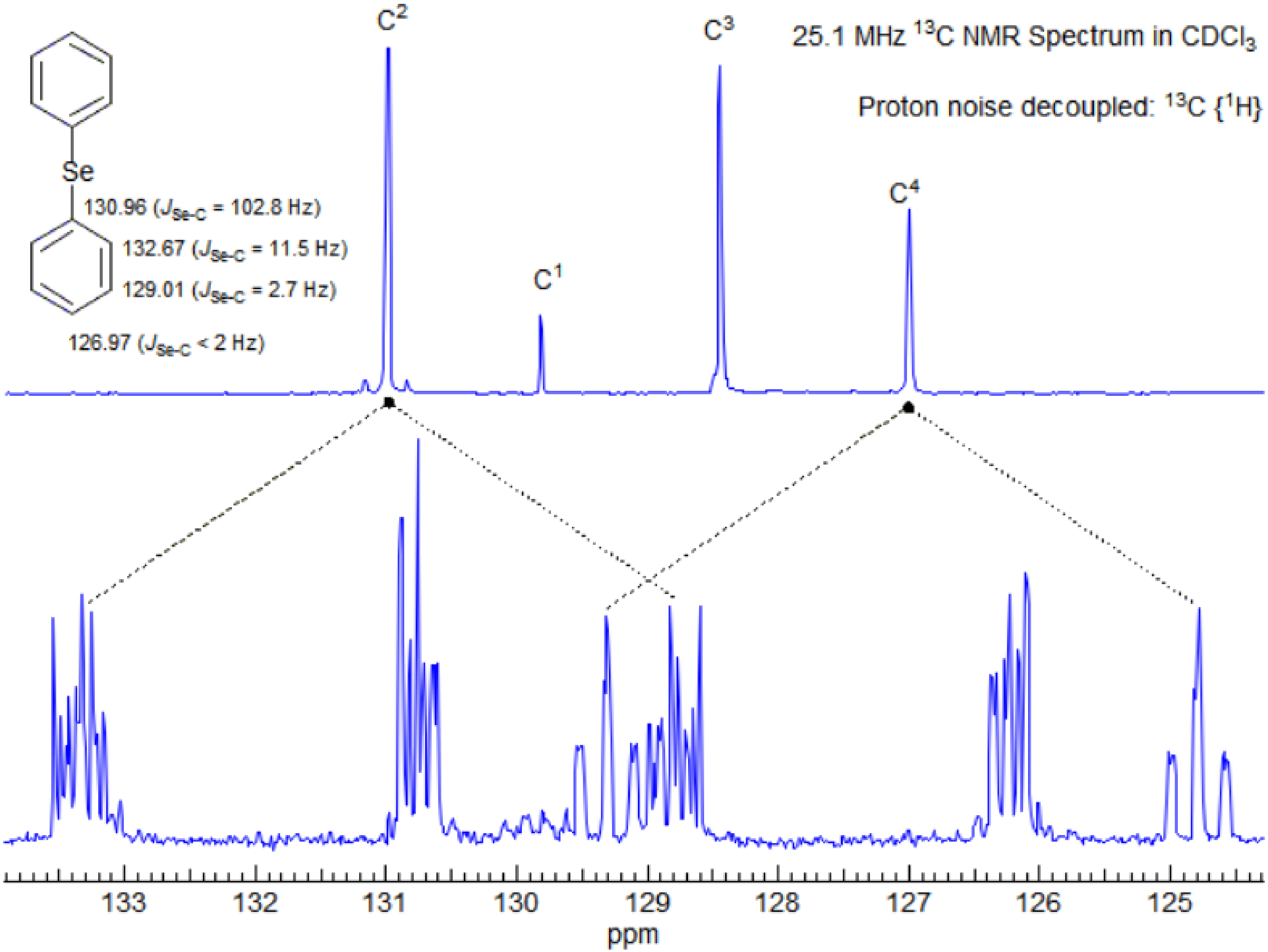
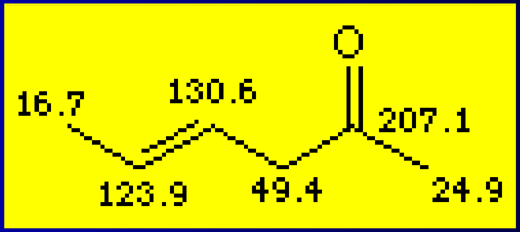
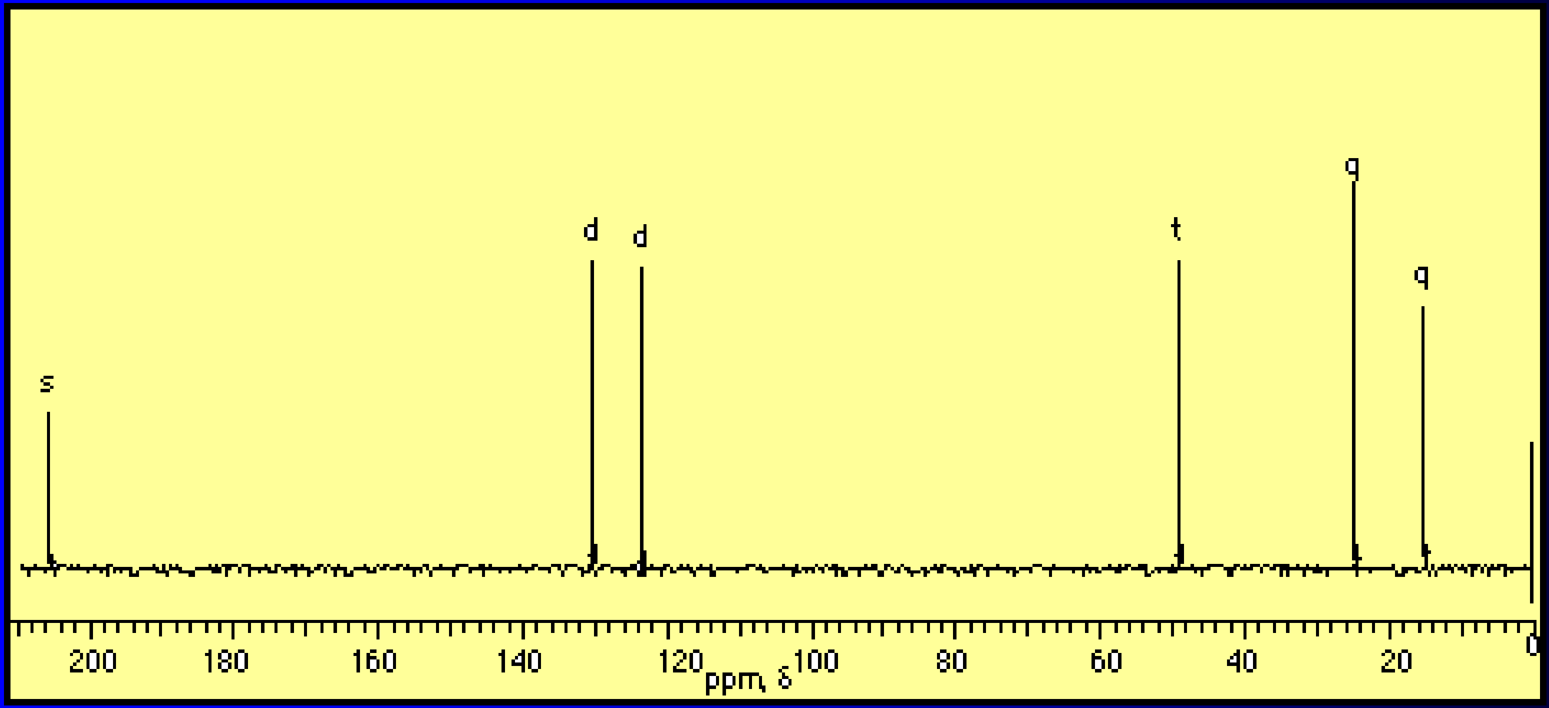


Figure 6-1.2. 25 MHz ^{13}C NMR spectrum of diphenyl selenide in $CDCl_3$.

^{13}C-nmr Spectroscopy

- Each nonequivalent ^{13}C gives a different, resolved signal





The DEPT Experiment

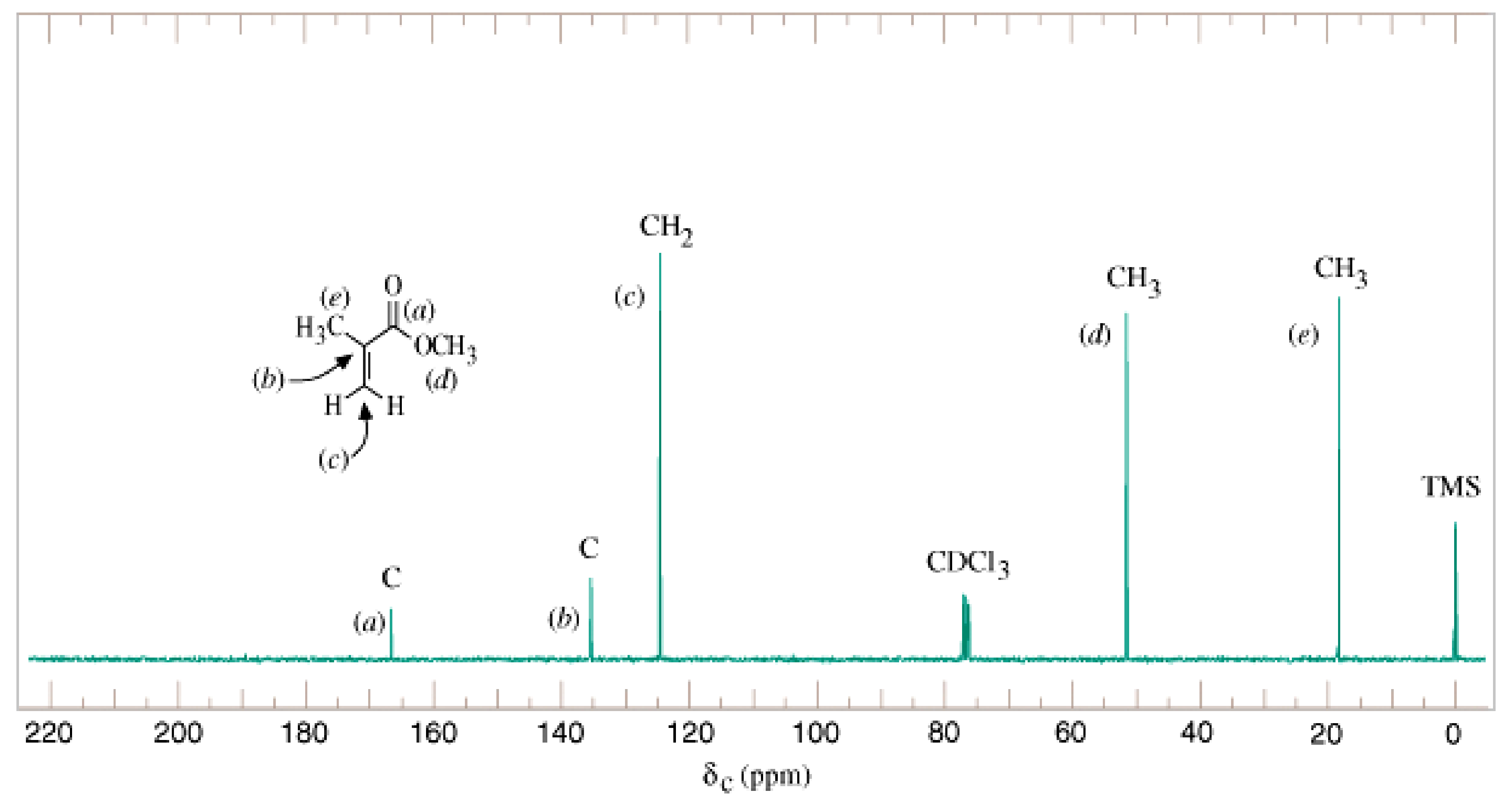
- In the hydrogen-decoupled mode, information on spin-spin coupling between ^{13}C and attached hydrogens is lost
- Distortionless Enhancement by Polarization Transfer (DEPT) is an NMR technique for determining whether ^{13}C signals are from CH_3, CH_2, CH, or quaternary carbons
- DEPT is an instrumental trick that provides the means to acquire this information

The DEPT method

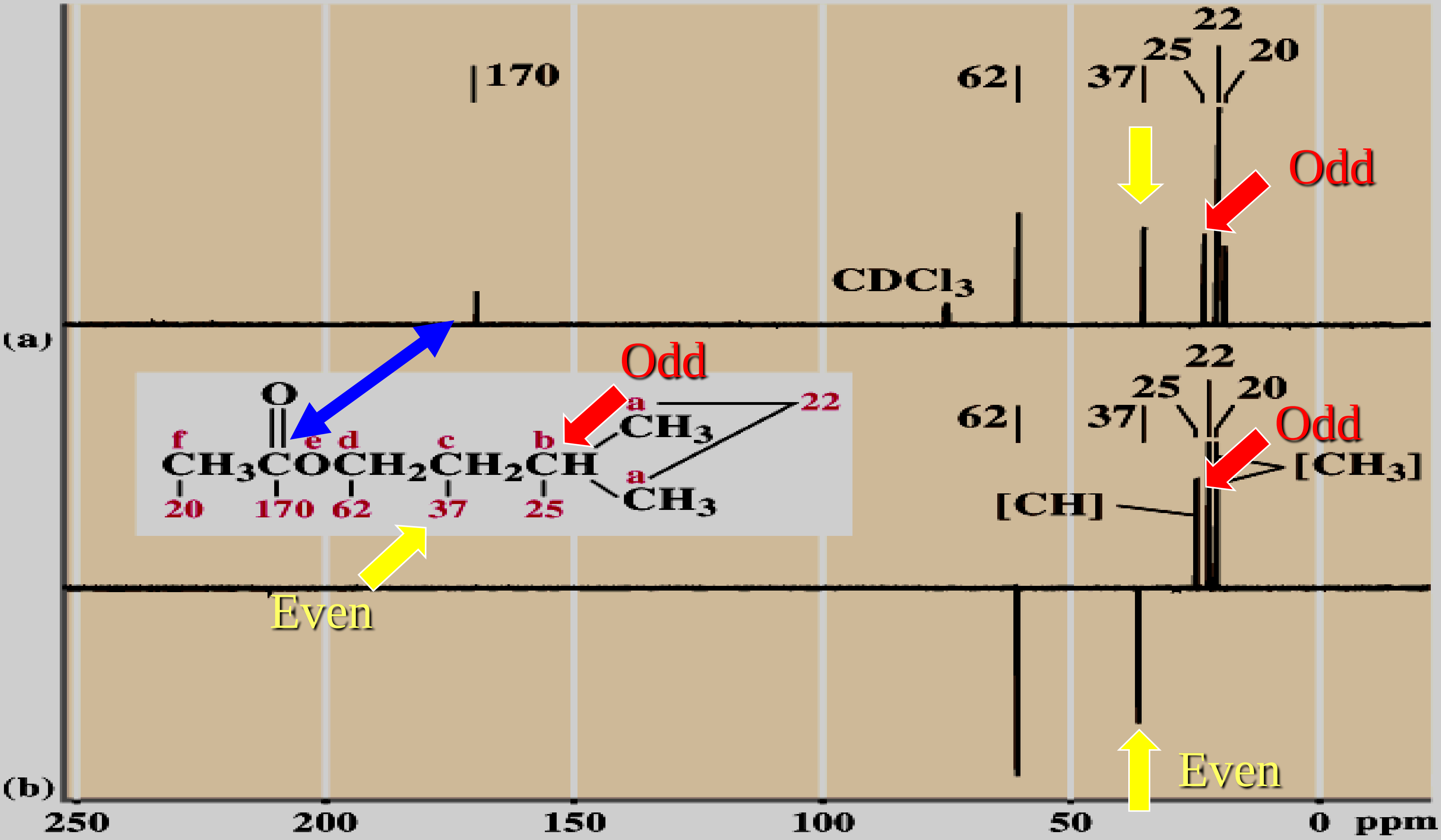
- DEPT uses a complex series of pulses in both the ^1H and ^{13}C ranges, with the result that CH_3, CH_2, and CH signals exhibit different phases;
  - signals for CH_3 and CH carbons are recorded as positive signals *(odd numbers of H)*
  - signals for CH_2 carbons are recorded as negative signals *(even numbers of H)*
  - quaternary carbons give no signals in the DEPT method *(zero H)*

OPEN ?? ☺

Broadband decoupled ^{13}C nmr spectrum



^{13}C-NMR (a) and DEPT (b) spectra of isopentyl acetate



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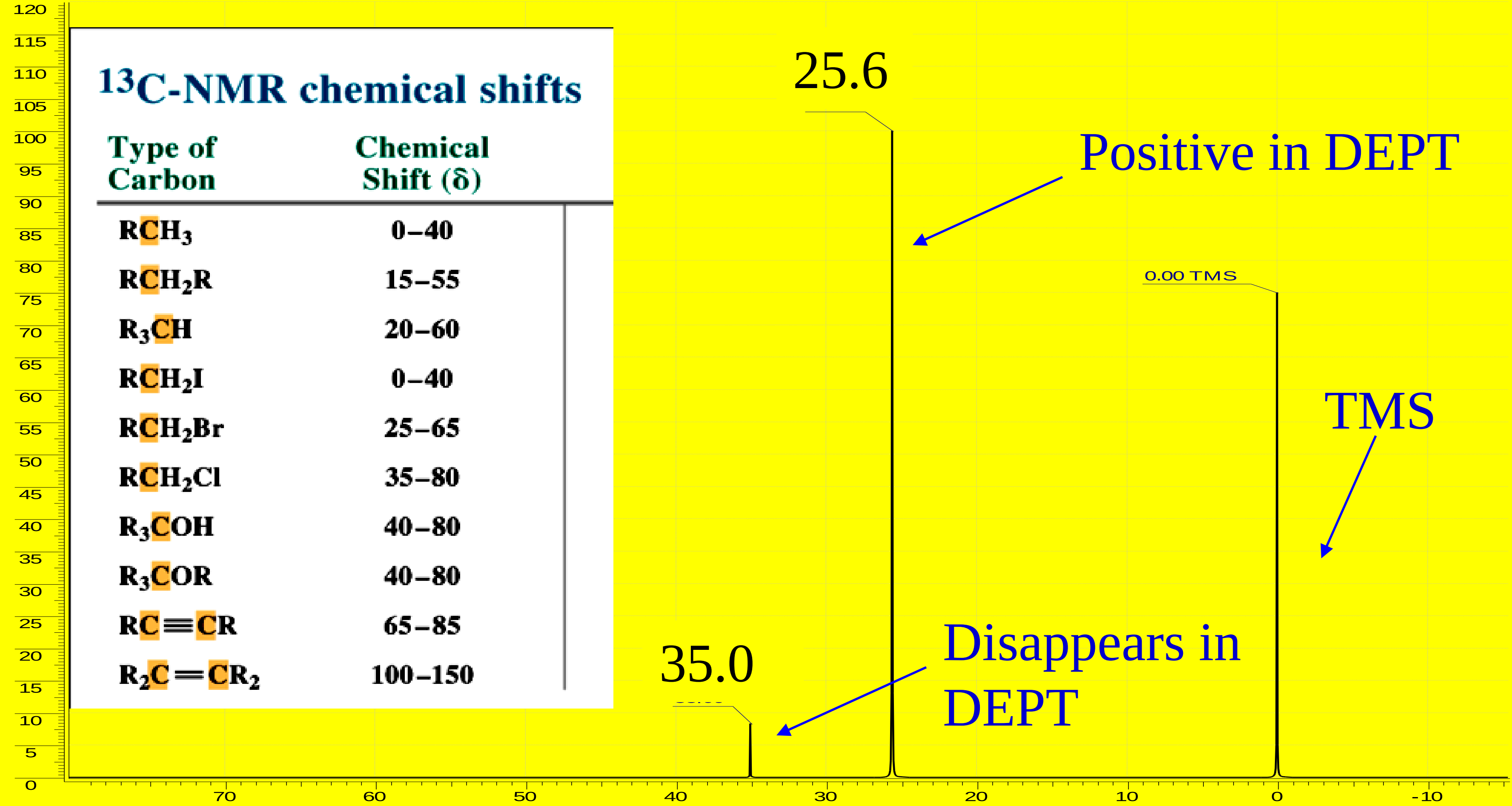
An Unknown ☺

Empirical formula $C_4H_{9,}$ MW =114



^{13}C-NMR chemical shifts

Type of Carbon	Chemical Shift (δ)
RCH_3	0–40
RCH_2R	15–55
R_3CH	20–60
RCH_2I	0–40
RCH_2Br	25–65
RCH_2Cl	35–80
R_3COH	40–80
R_3COR	40–80
$RC\equiv CR$	65–85
$R_2C{=}CR_2$	100–150

25.6

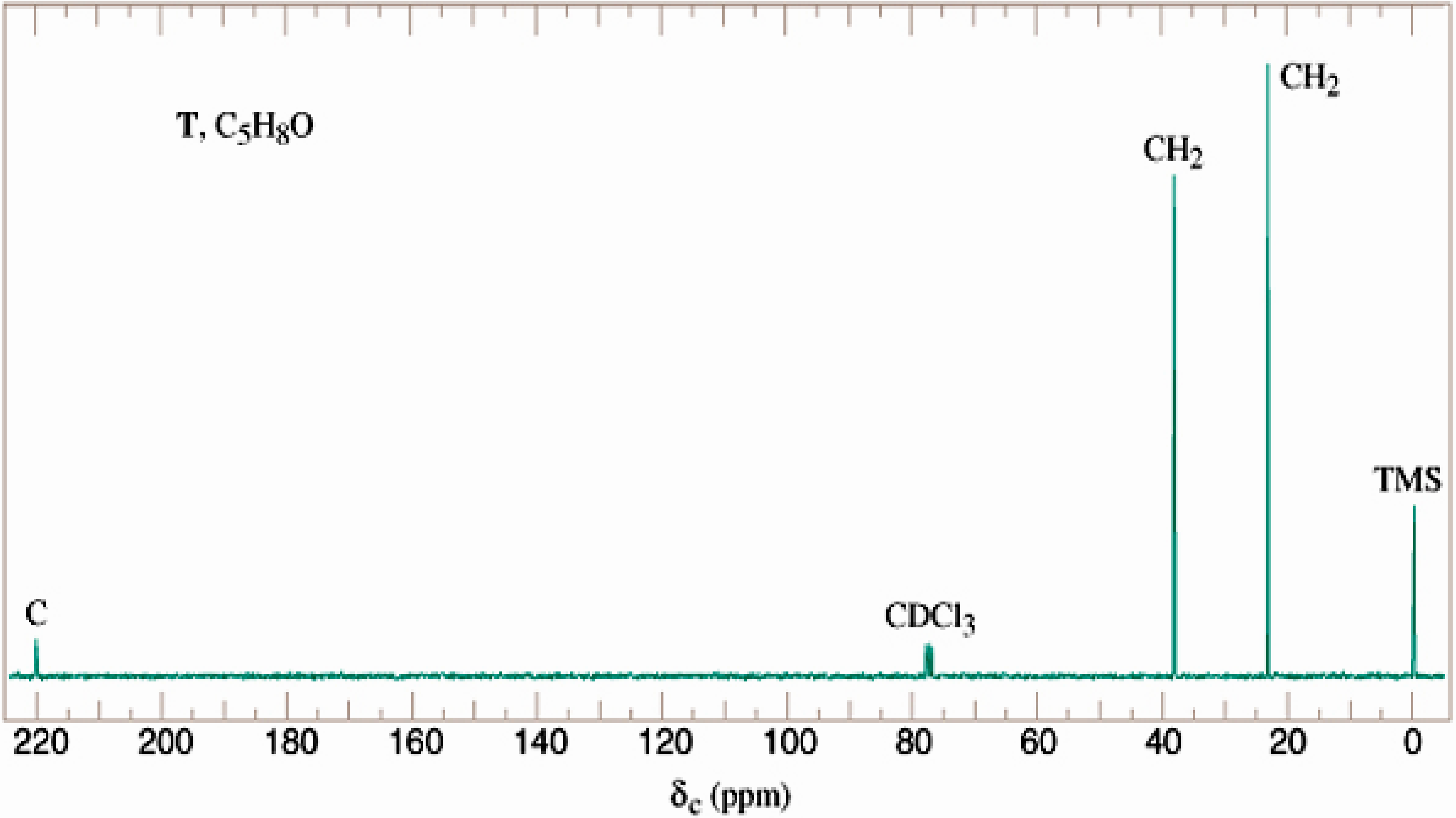
Positive in DEPT

35.0

Disappears in DEPT

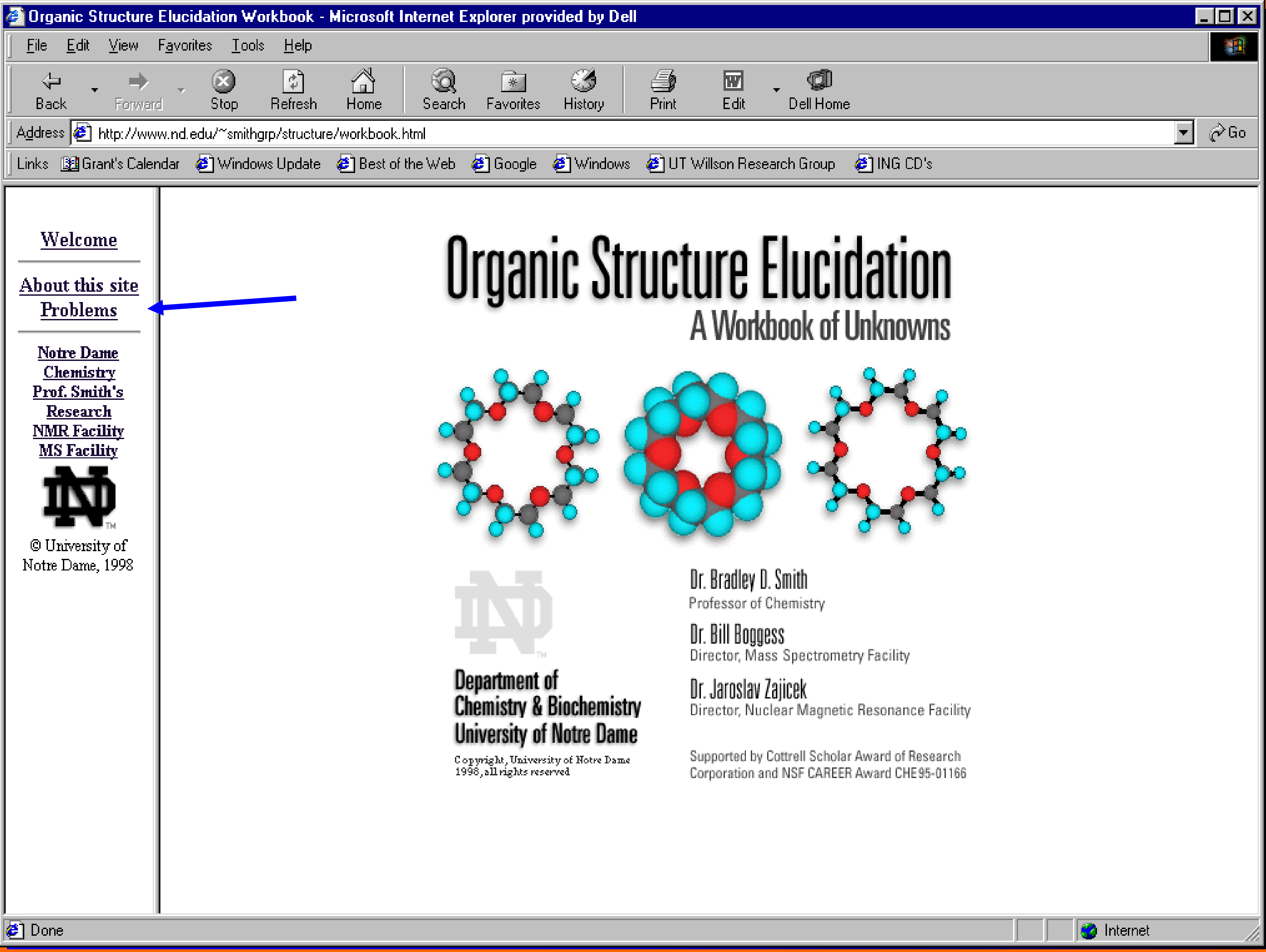
TMS

Whatzit??


T, C_5H_8O
CH_2
CH_2
TMS
C
$CDCl_3$
220
200
180
160
140
120
100
80
60
40
20
0
δ_c (ppm)

^{13}C-NMR Spectroscopy review

- Each nonequivalent ^{13}C gives a different signal
- Low abundance means weak signals
- C-C splitting is insignificant
- C-H splitting is big and complex so it is “turned off” by “decoupling”
- Range of Chemical Shifts is large compared to H
- Some Coupling info can be recovered by DEPT
- Integrals of ^{13}C spectra are not useful except under very special circumstances
- Mnemonic device…. PONE???



Welcome

About this site
Problems

Notre Dame Chemistry
Prof. Smith's Research
NMR Facility
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Organic Structure Elucidation

A Workbook of Unknowns

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University of Notre Dame

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Director, Mass Spectrometry Facility

Dr. Jaroslav Zajicek
Director, Nuclear Magnetic Resonance Facility

Supported by Cottrell Scholar Award of Research Corporation and NSF CAREER Award CHE95-01166

NMR TUTOR(ek) ver. 2.2

by Darek Bogdal

Java applet for displaying molecular spectra by Guillaume Cottenceau.

Project supervisor Henry Rzepa.

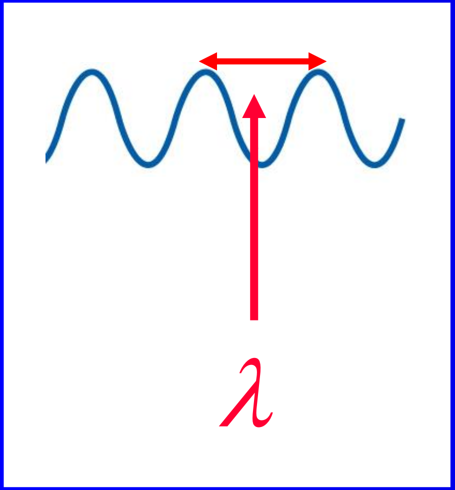
Imperial College of Science Technology and Medicine.

Molecular Vibrations

- For a molecule to absorb IR radiation, the bond undergoing vibration
  - must be polar (*change dipole moment*)
- Covalent bonds that do not meet this criterion are said to be IR inactive
  - the C-C double and triple bonds of symmetrically substituted alkenes and alkynes, for example, do not absorb IR radiation because they are not polar bonds

H_2 N_2 CO_2 ??????

THE ENERGY OF ELECTROMAGNETIC WAVES



$$c = \lambda\upsilon \qquad \bar{\upsilon} = \frac{1}{\lambda}$$

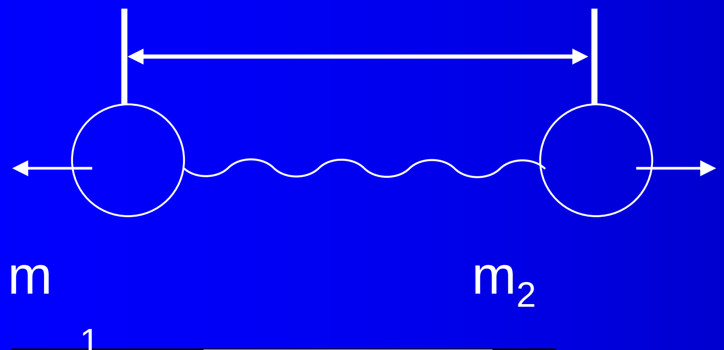
$\bar{\upsilon}$

- **(nu-bar) represents wavenumber, the number of wavelengths in 1 cm**
- **This is a unit of frequency!**
- **units are 1/cm or cm^{-1} (Kaysers)**

$$E = h\nu = h\frac{c}{\lambda} = hc\bar{\upsilon}$$

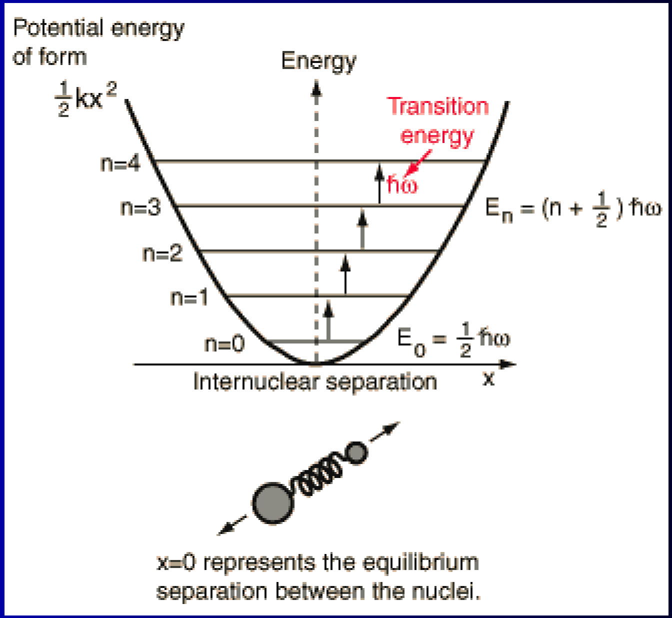
10 microns (micrometers) = 1000 cm^{-1}

Harmonic Oscillator Model



$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{(m_1)(m_2)}{m_1 + m_2}$$



$E_\nu = h\,\nu_o\,(\nu + 1/2)$

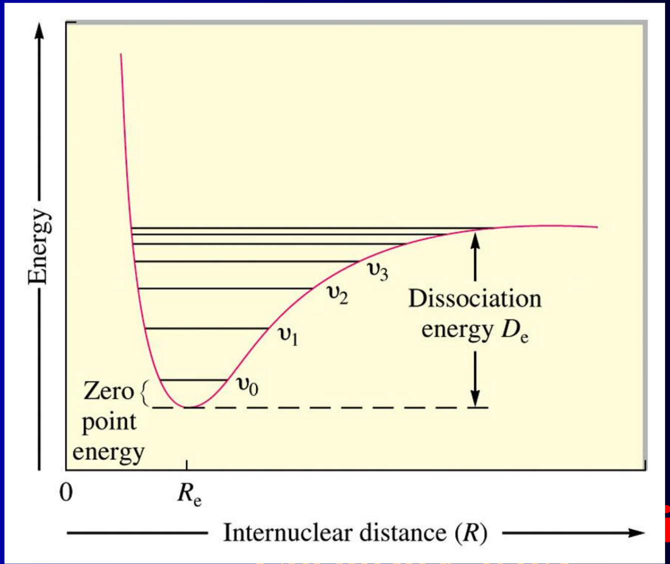
↑

quantized vibrational energy

h = Planck's constant

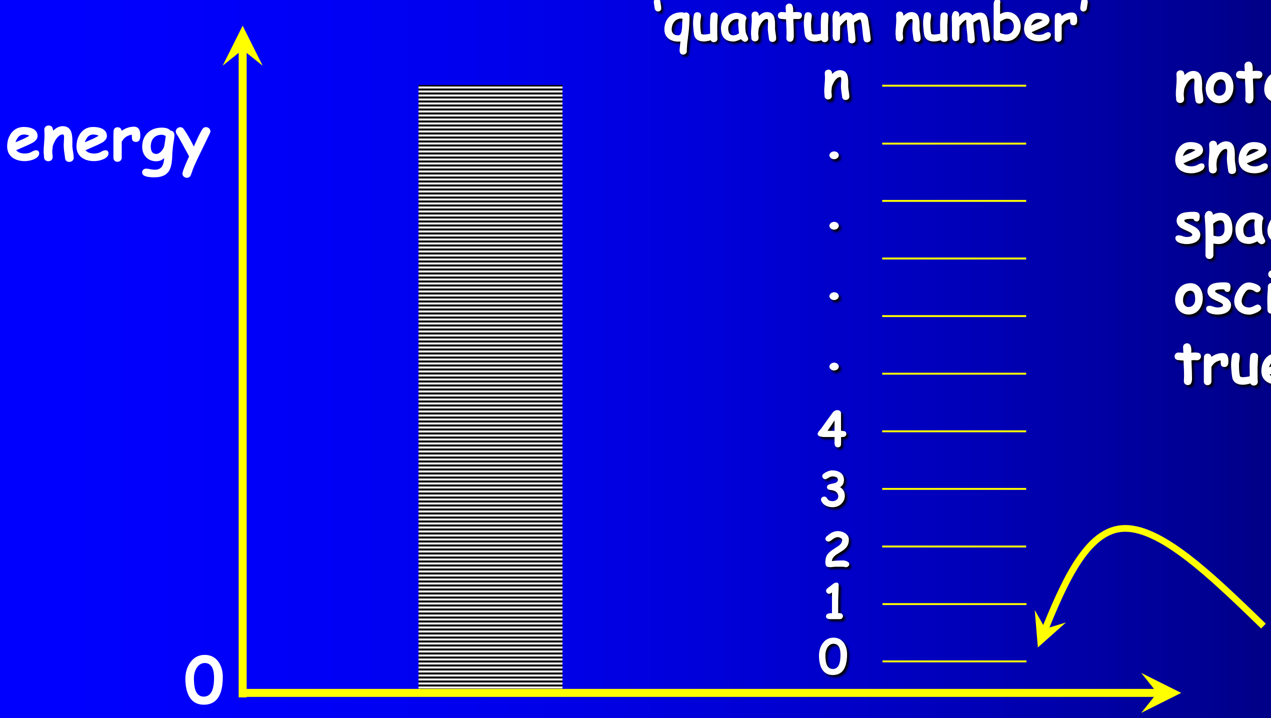
ν_o = characteristic frequency

ν = 0, 1, 2, 3,….



Energy quantization of the oscillator

classical and quantum behavior are very different:



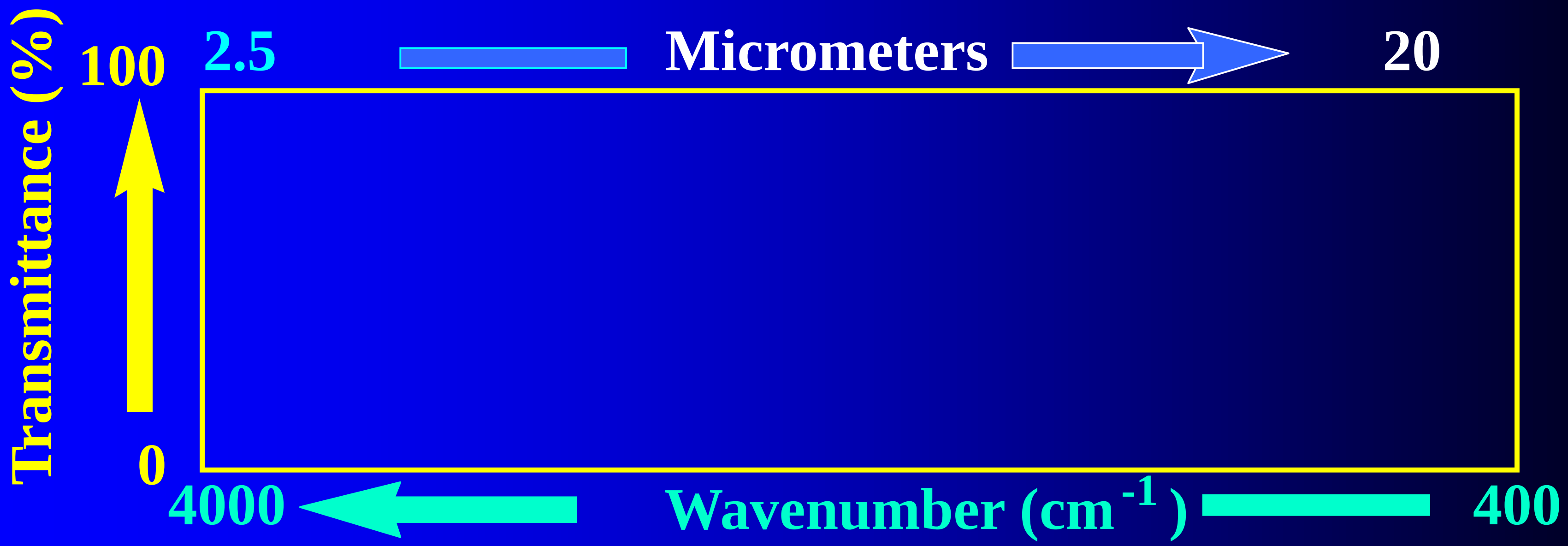
classical: all possible values of total energy are allowed

quantum: only certain 'energy levels' allowed

note that although the energy levels are equally spaced for the harmonic oscillator this is not true for all QM systems

note also that it is not possible for the quantum harmonic oscillator to have zero energy – it <u>must</u> have some energy even at 0 K

The IR Chart



2.5 **Micrometers** **20**

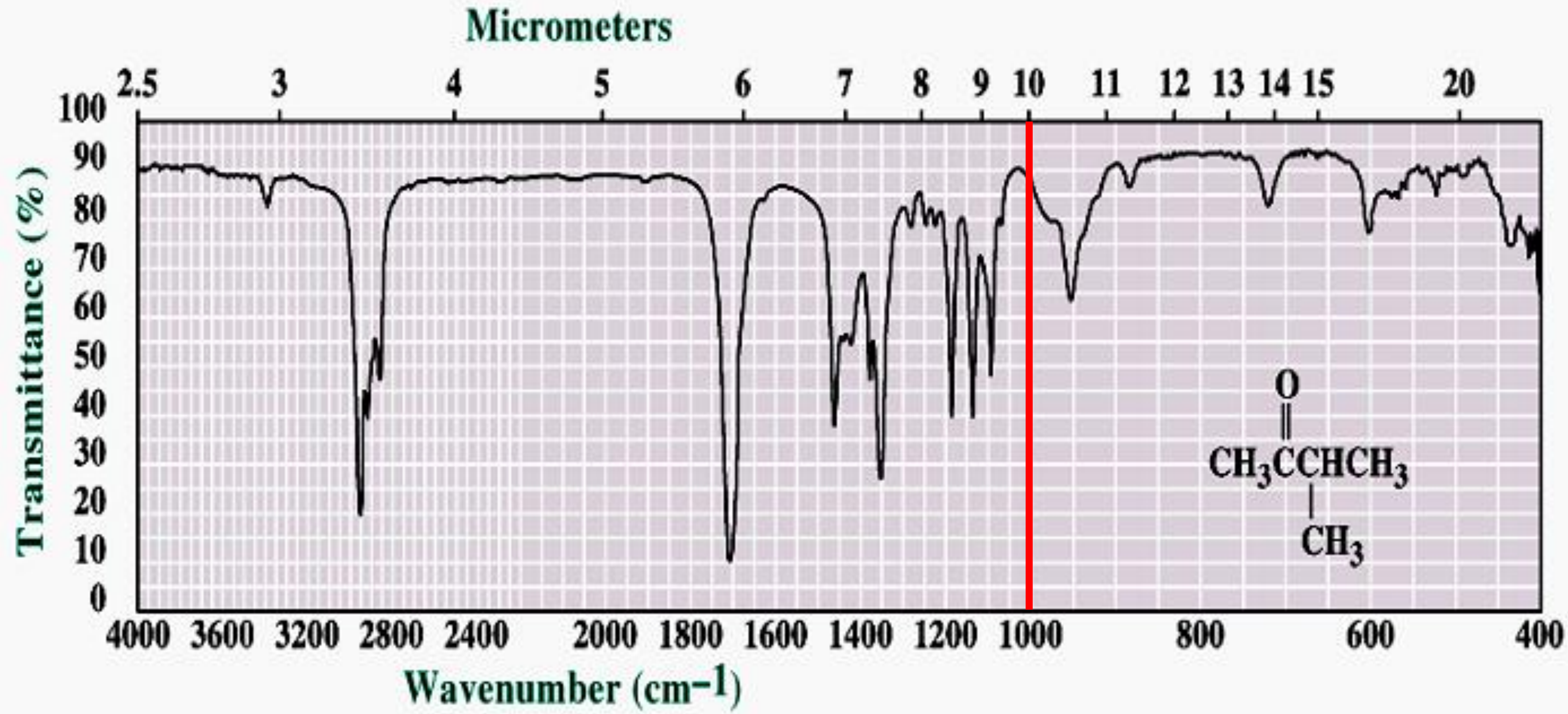
Transmittance (%)

100

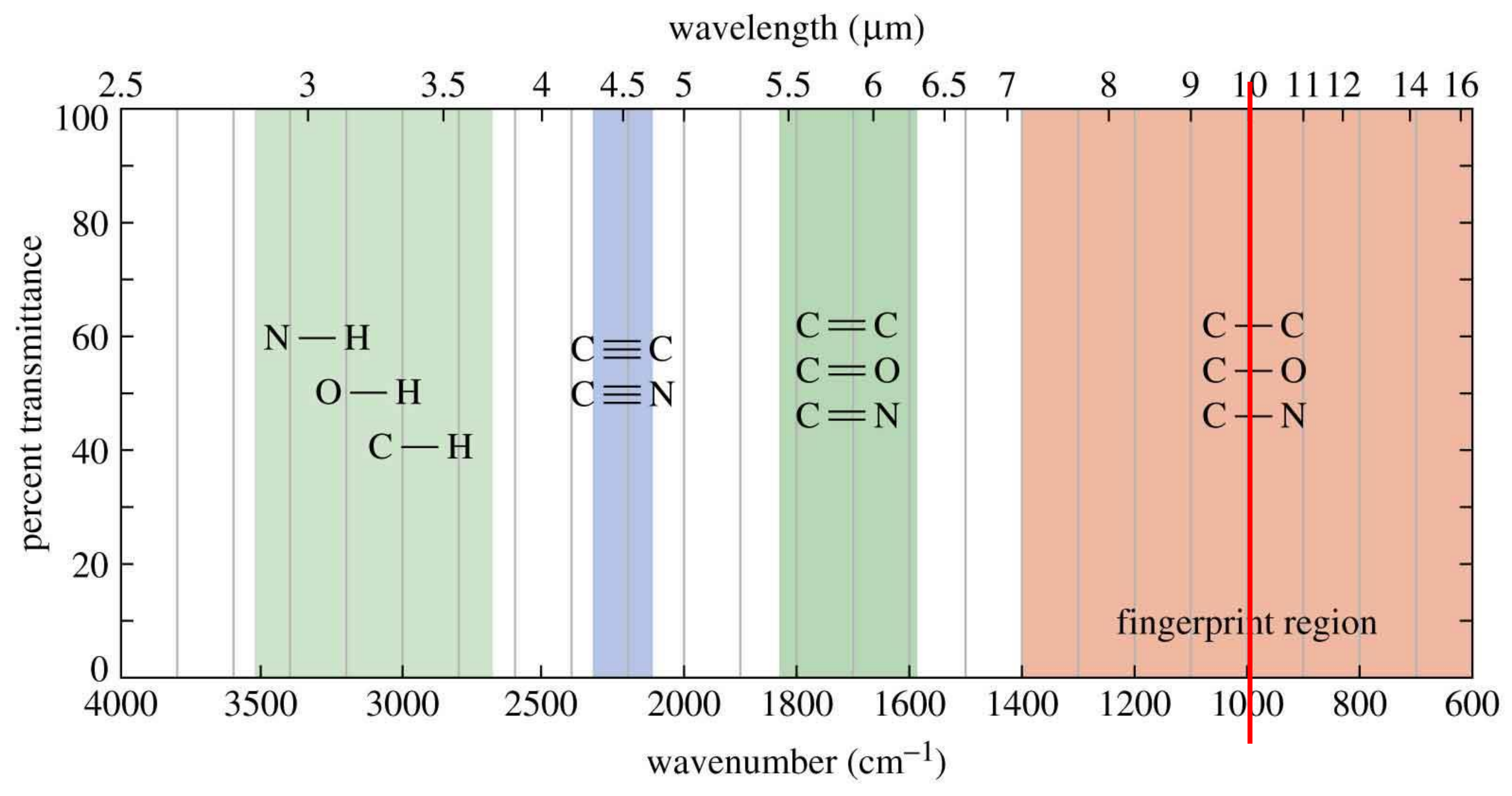
0

4000 **Wavenumber (cm^{-1})** **400**

Infrared Spectrum



Functional group absorptions

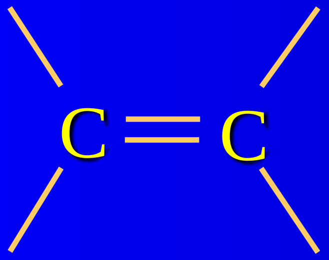


Infrared Absorption Frequencies

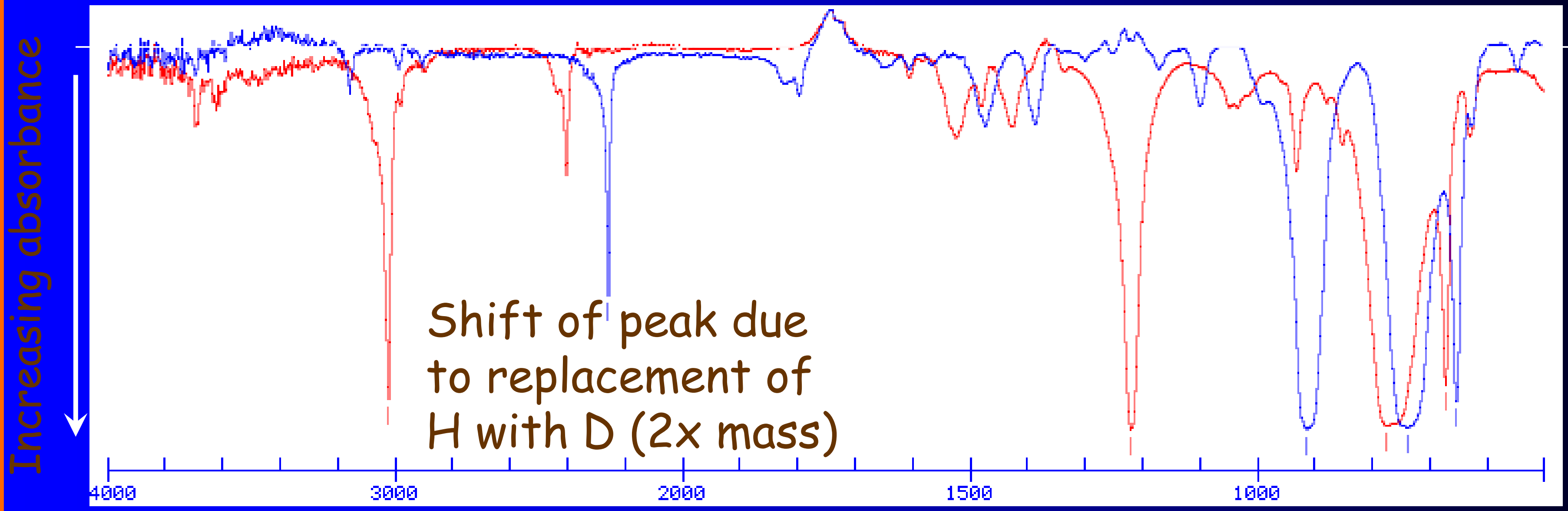
Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

Infrared Absorption Frequencies

Stretching vibrations (multiple bonds)

Structral unit	Frequency, cm^{-1}
	1620-1680
$—C\equiv C—$	2100-2200
$—C\equiv N$	2240-2280

IR Spectra of chloroform and deuterochloroform



Shift of peak due to replacement of H with D (2x mass)

Mode of vibration	$CHCl_3$	$CDCl_3$
C-H stretching	3020	2256
C-H bending	1219	912
C-Cl stretching	773	737
C-Cl bending	671	652

* Spartan '02 AM1 minimization

IR Group Correlation Tables