

^{13}C -NMR

PRESENTED BY:

RAMANDEEP KAUR BRAR

(PH.CHEMISTRY)

DEFINATION

- NMR is a phenomenon exhibited by when atomic nuclei in a static magnetic field absorbs energy from radiofrequency field of certain characteristic frequency. It results to give a spectrum with frequency on x-axis and intensity of absorption on y-axis.

PRINCIPLE & THEORY

- ✓ The nuclear magnetic resonance occurs when nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field.
- ✓ The energy absorption is a quantized process, and energy absorbed must equal the energy difference between the two states involved.

$$E_{\text{absorbed}} = (E_{-1/2_{\text{state}}} - E_{+1/2_{\text{state}}}) = h\nu$$

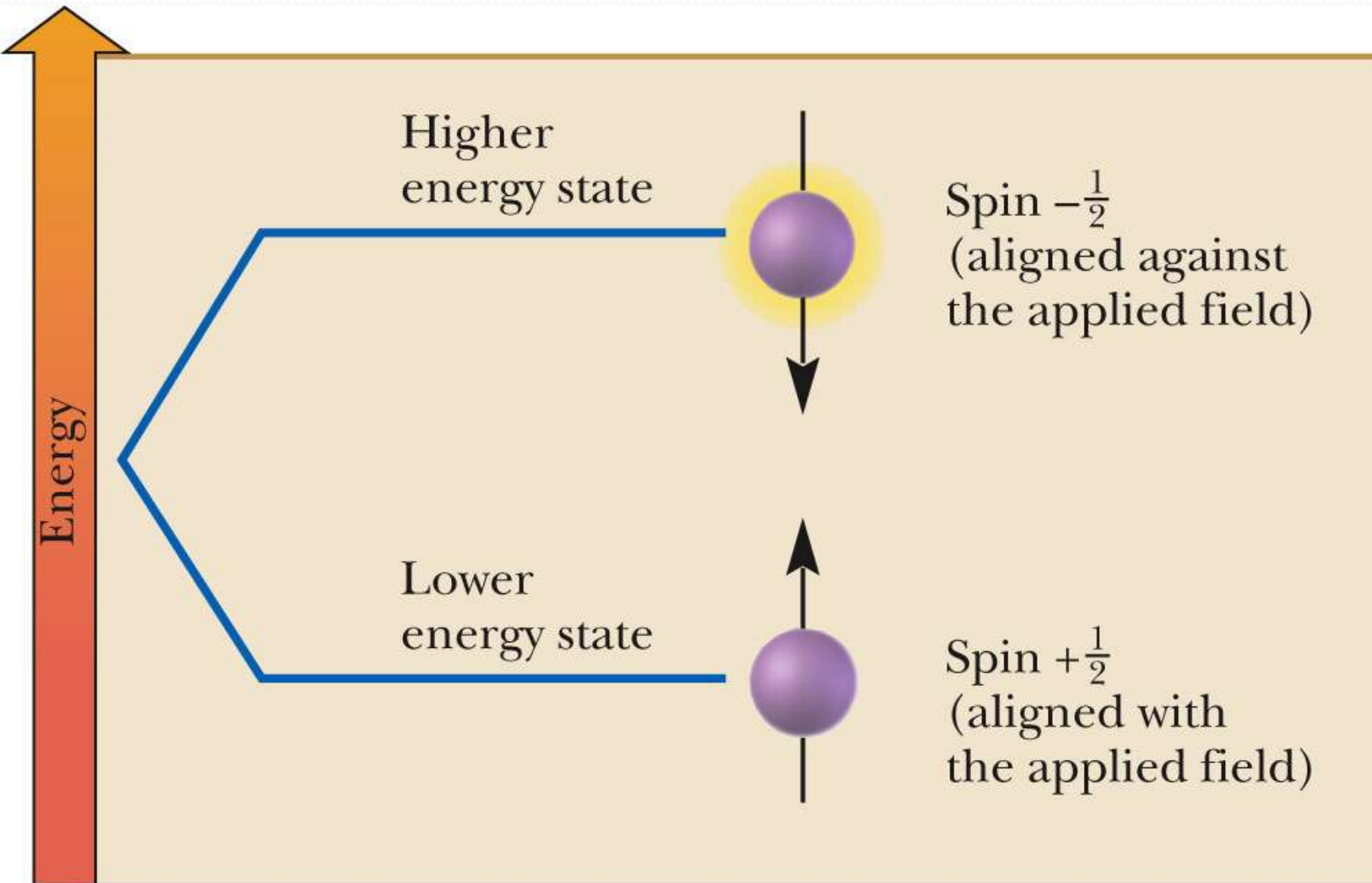
- ✓ The stronger the applied magnetic field, greater the energy difference between the possible spin states.

$$\Delta E = \int(B_0)$$

- ❖ The magnitude of energy level separation also depends on the particular nucleus involved. Each nucleus has a different ratio of magnetic moment to angular momentum since each has different charge and mass.
- ❖ This ratio, is called the magnetogyric ratio γ , is a constant for each nucleus and determines the energy dependence on the magnetic field.

$$\Delta E = \int(\gamma B_0) = h\nu$$

The γ value for ^{13}C is 67.28 Tesla and for ^1H IS 267.53



ABUNDANCE

^{13}C is difficult to record because of

1. The most abundant isotope of carbon that is ^{12}C (99.1%) is not detected by nmr because it has an even no of protons and neutrons ^{12}C is nmr inactive.

2. Magnetic resonance of ^{13}C is much weaker. Moreover, gyromagnetic ratio of ^{13}C being only one fourth that of proton, so the resonance frequency of ^{13}C is one fourth that of proton nmr.

Advantages of ^{13}C - NMR over ^1H - NMR

1. ^{13}C - provides information about the backbone of molecules rather than the periphery.
2. The chemical shifts range for ^{13}C - NMR for most organic compounds is 200 ppm compared to 10 –15 ppm for H, hence there is less overlap of peaks for ^{13}C - NMR.
3. Homonuclear spin-spin coupling between carbon atoms is not observed because the natural abundance of ^{13}C is too low for two ^{13}C to be next to one another.
Heteronuclear spin coupling between ^{13}C and ^{12}C does not occur because the spin quantum number of ^{12}C is zero.
4. There are a number of excellent methods for decoupling the interaction between ^{13}C and ^1H .

SPIN –SPIN SPLITTING OF ^{13}C SIGNALS

- Splitting take place acc. to $2nI+1$ rule

Where n = no. of nuclei

I =spin quantum number

$\text{CH}_3 = 3+1=4$ quartet

$\text{CH}_2 = 2+1=3$ triplet

$\text{CH} = 1+1=2$ doublet

$\text{C} = 0+1=1$ singlet

CDCl_3 gives three peaks because its $I=1$ so acc. to $2nI+1$

$2 \times 1 \times 1+1=3$ so it gives 1:1:1 peaks

Solvents used are CDCl_3 , DMSO, d_6 acetone, d_6 benzene

^{13}C chemical shifts

The most significant factors affecting the chemical shifts are:

Electro negativity of the groups attached to the C

Hybridization of C

The intensity (size) of each peak is NOT directly related to the number of that type of carbon. Other factors contribute to the size of a peak:

Peaks from carbon atoms that have attached hydrogen atoms are bigger than those that don't have hydrogens attached.

Carbon chemical shifts are usually reported as downfield from the carbon signal of tetramethylsilane (TMS).

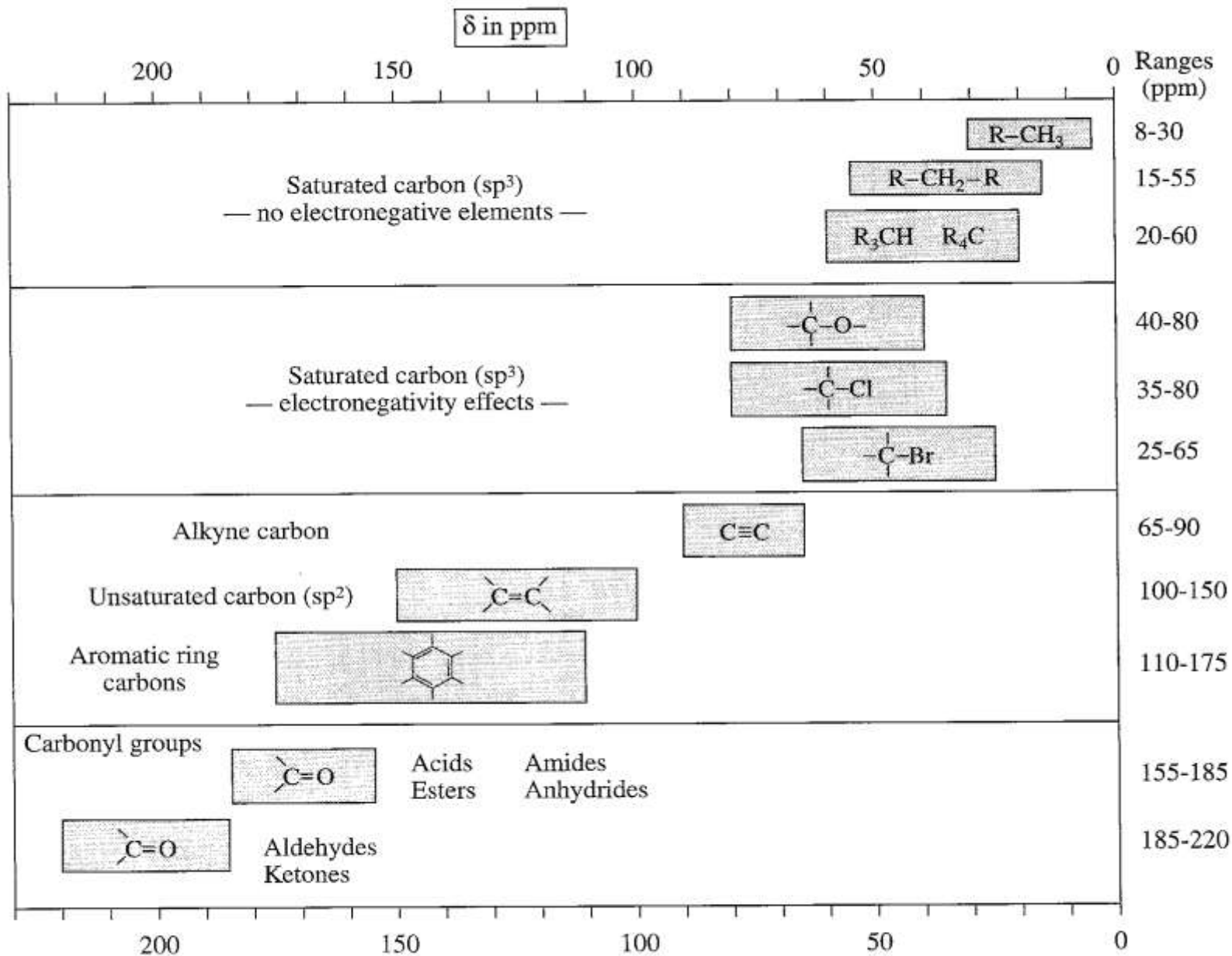
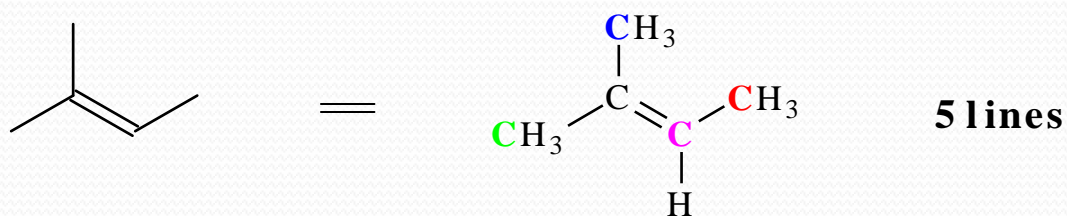
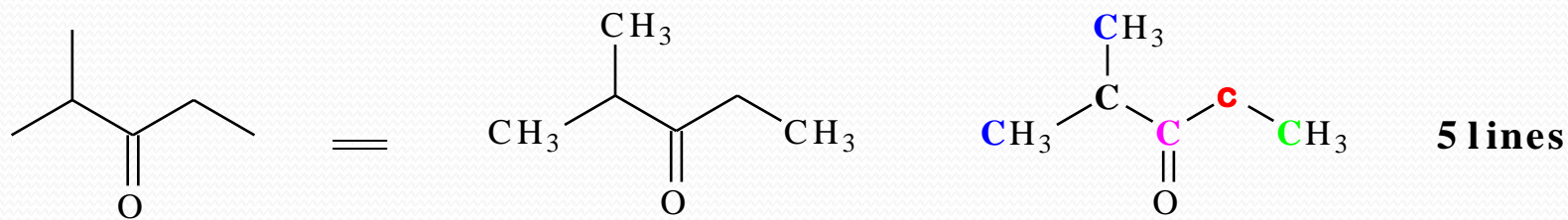
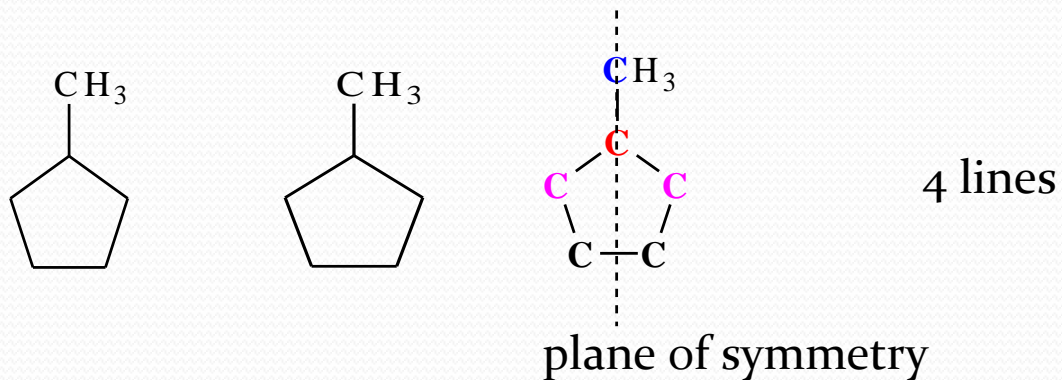
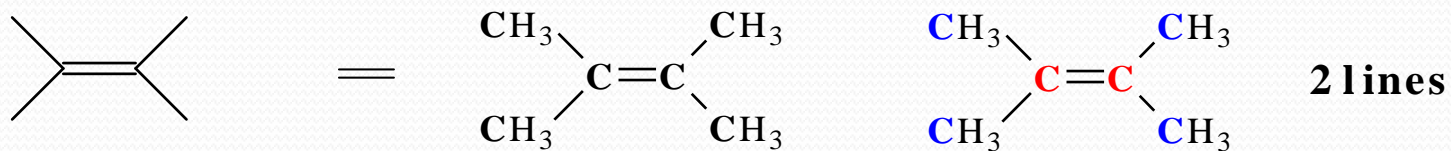
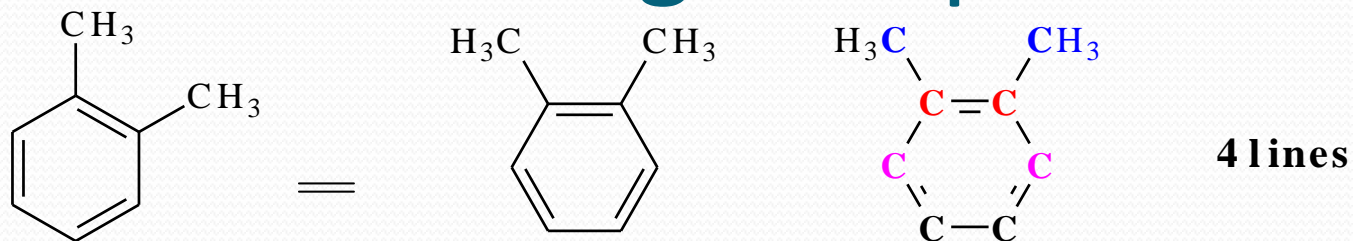


FIGURE 4.1 A correlation chart for ^{13}C chemical shifts (chemical shifts are listed in parts per million from TMS).

Predicting ^{13}C Spectra

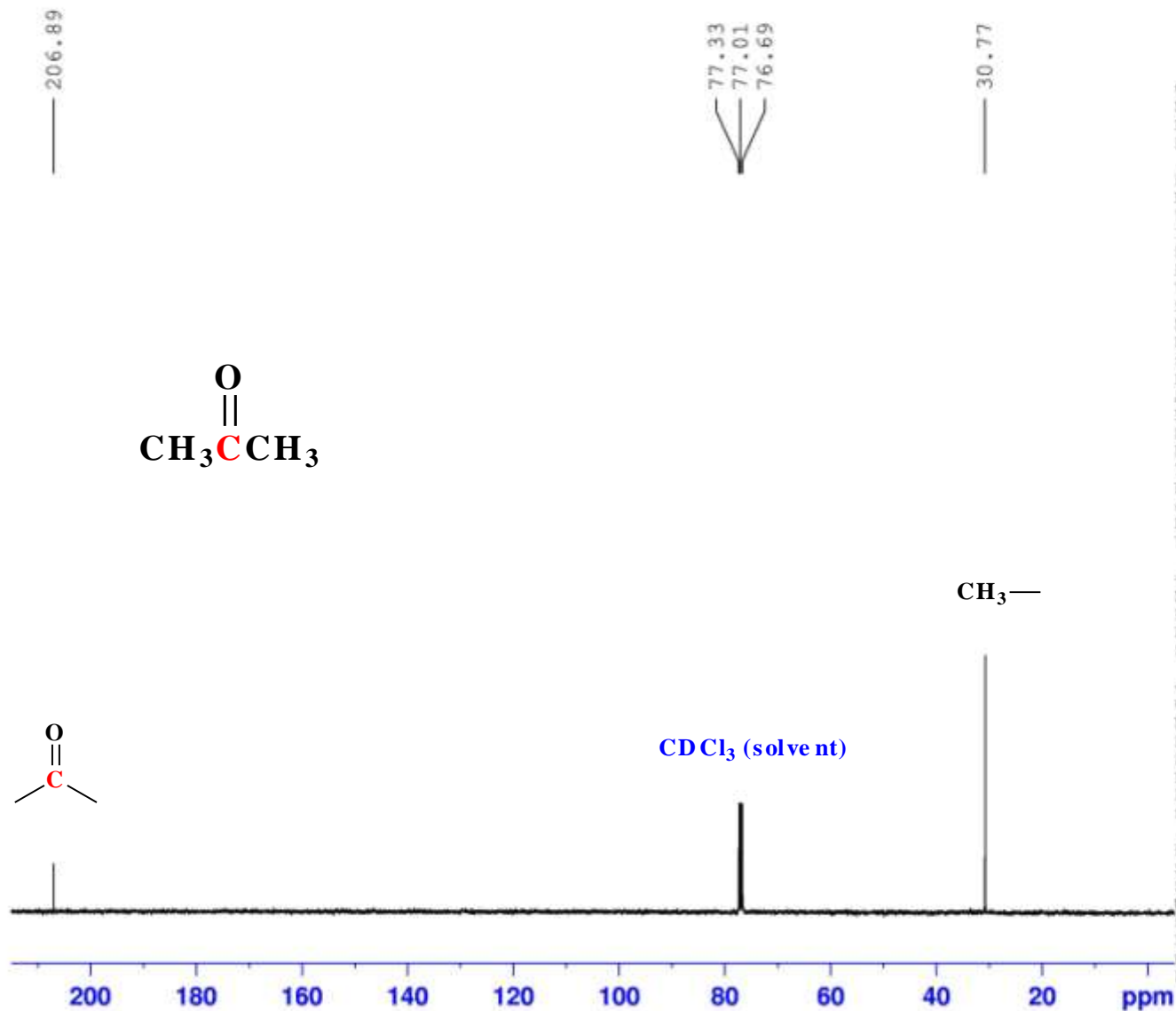


Predicting ^{13}C Spectra



Symmetry Simplifies Spectra!!!

acetone



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PROCNO        1

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SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            1625.5
DW            20.800 usec
DE            6.00 usec
TE            690.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0           1

----- CHANNEL f1 -----
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P1             6.00 usec
PL1            -6.00 dB
SFO1          100.6228298 MHz

----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2           1H
PCPD2          80.00 usec
PL2            -6.00 dB
PL12           14.56 dB
PL13           14.56 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
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ethyl acetate

170.98

77.36
77.04
76.72

60.26

20.88
14.07

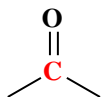


—OCH₂—

CH₃

CH₃

CDCl₃ (solvent)



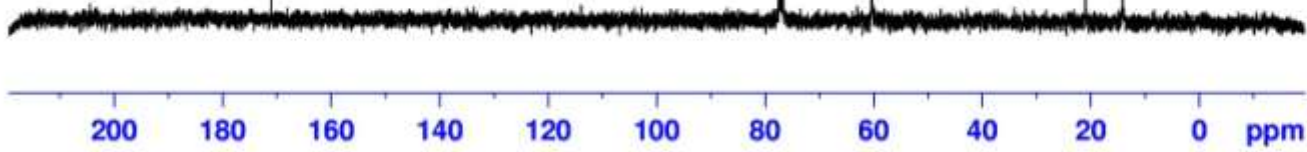
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AQ         1.3631988 sec
RG         1024
DW         20.800 usec
DE         6.00 usec
TE         691.3 K
D1         2.0000000 sec
d11        0.0300000 sec
DELTA     1.89999998 sec
TIMO      1

----- CHANNEL F1 -----
NUC1       13C
P1         6.00 usec
PL1        -6.00 dB
SFO1      100.6220298 MHz

----- CHANNEL F2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        -6.00 dB
PL12       14.56 dB
PL13       14.56 dB
SFO2      400.1316005 MHz

F2 - Processing parameters
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LB         2.00 Hz
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PC         1.40
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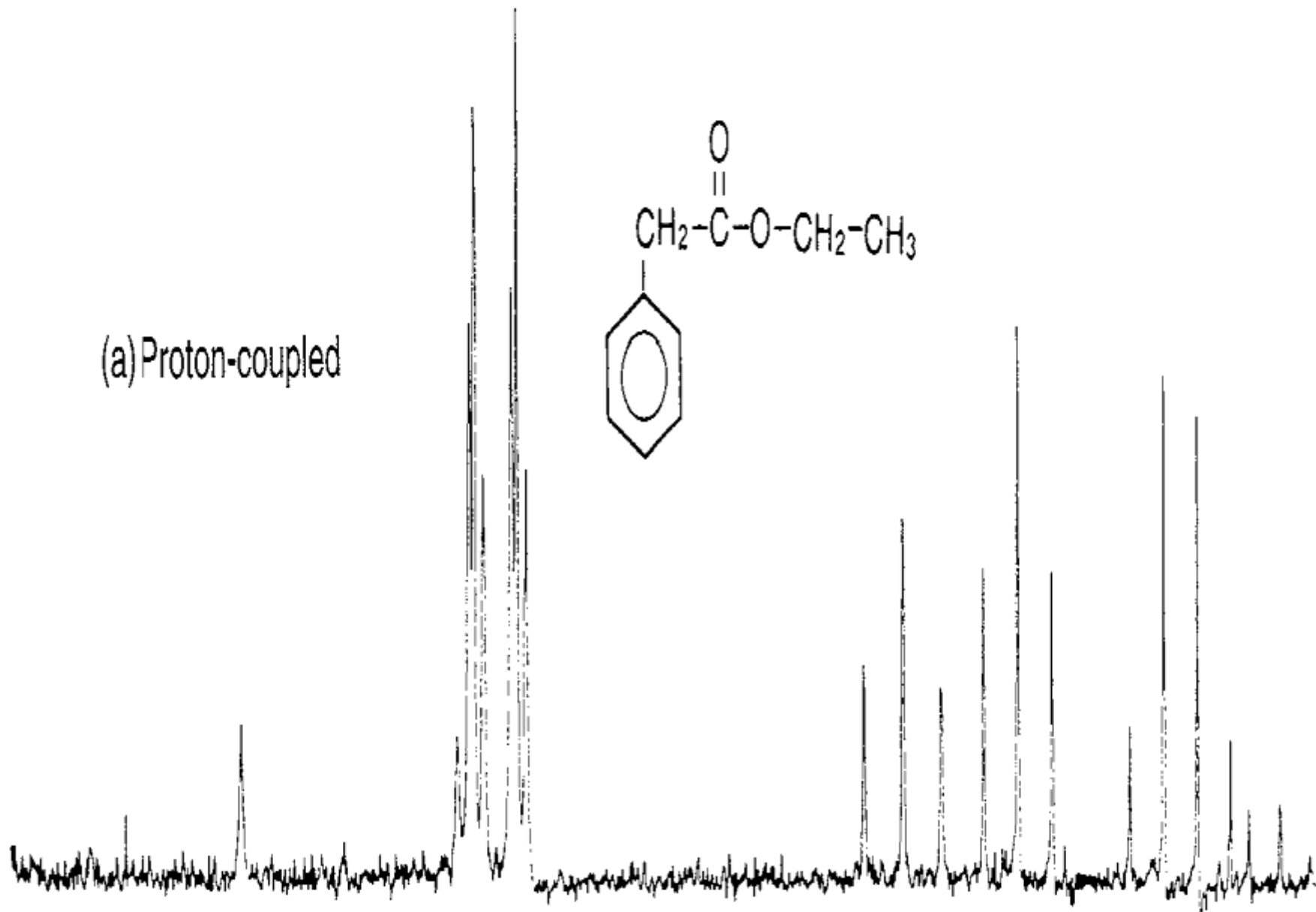
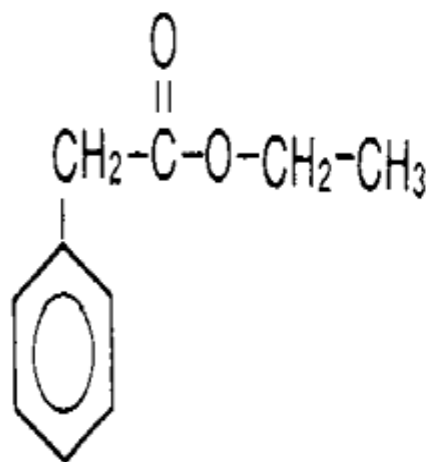


Proton Decoupling

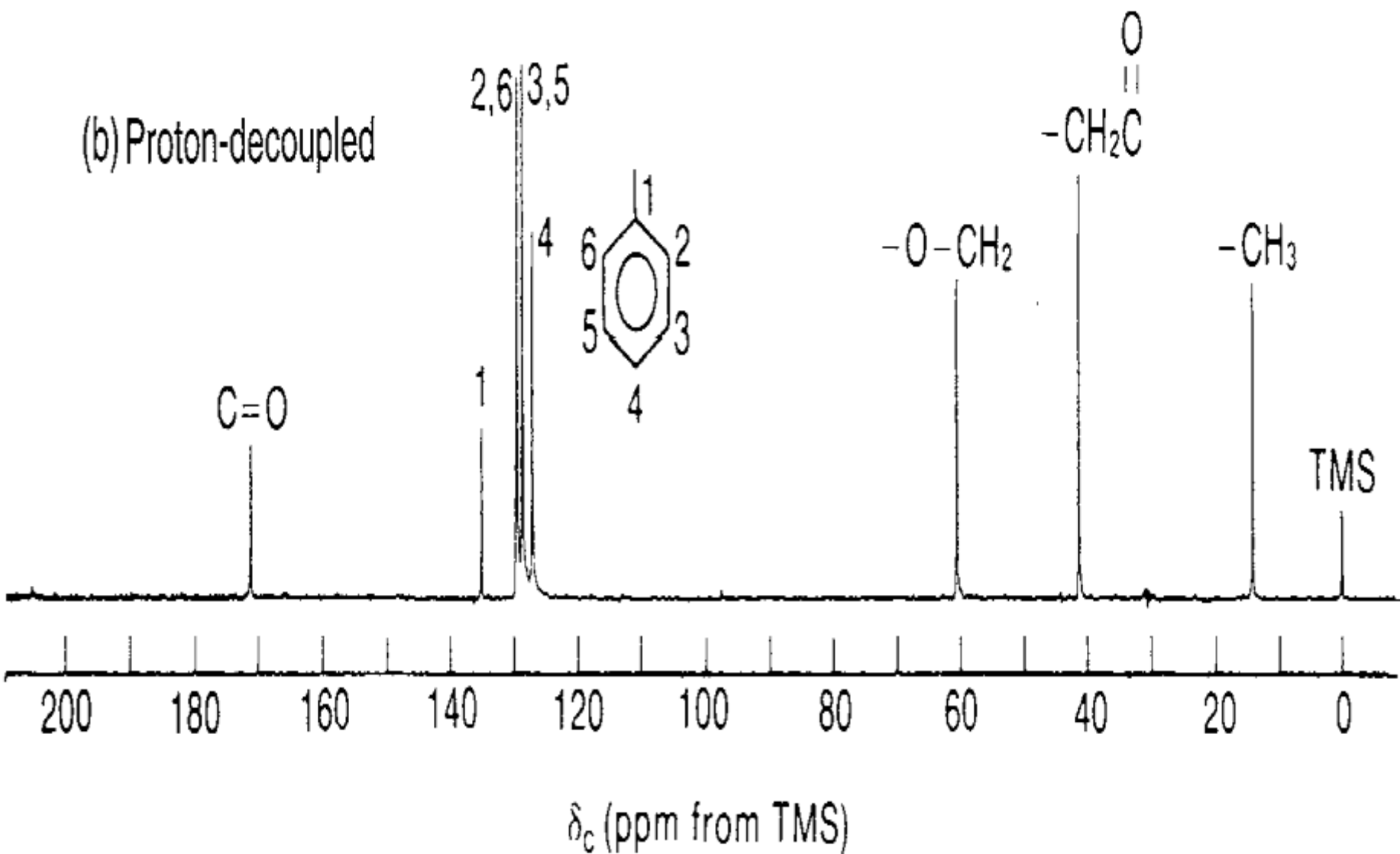
Three types:

1. Broad band decoupling
2. Off-resonance decoupling
3. Pulse decoupling

(a) Proton-coupled

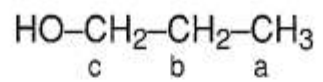


(b) Proton-decoupled

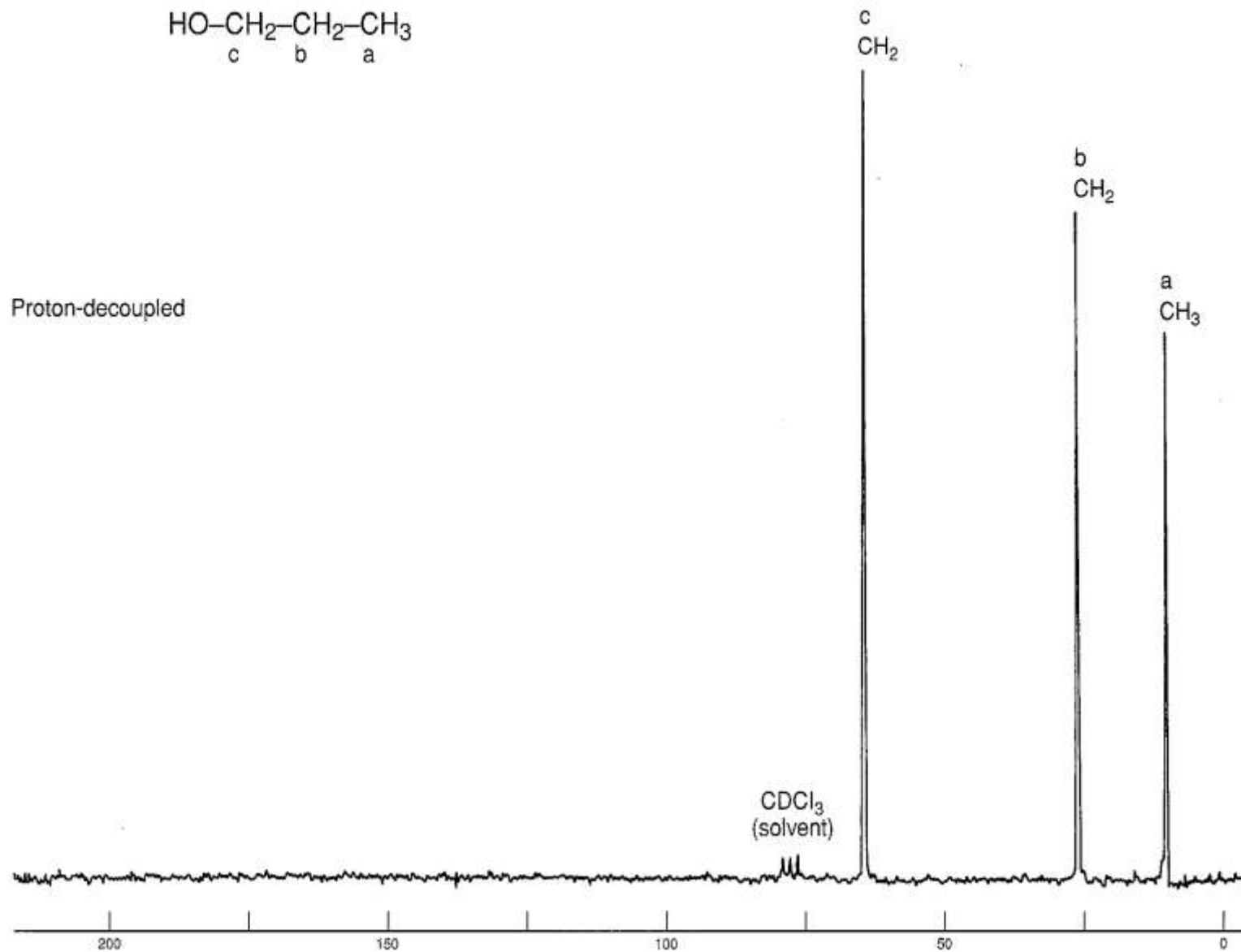


Broad band decoupling

1. It avoid spin-spin splitting of ^{13}C lines by ^1H nuclei.
2. In this, all the protons are simultaneously irradiated with a broad band radiofrequency signal. Irradiation causes the protons to become saturated and they undergo rapid upward downward transition among all their possible spin state. This is produced by a second coil located in the sample probe.
3. Without decoupling ^{13}C spectra would show complex overlapping multiplets that would be hard to interpret.
4. The spin-spin information get lost, but we can use off-resonance decoupling to get spin-spin shifts back



Proton-decoupled



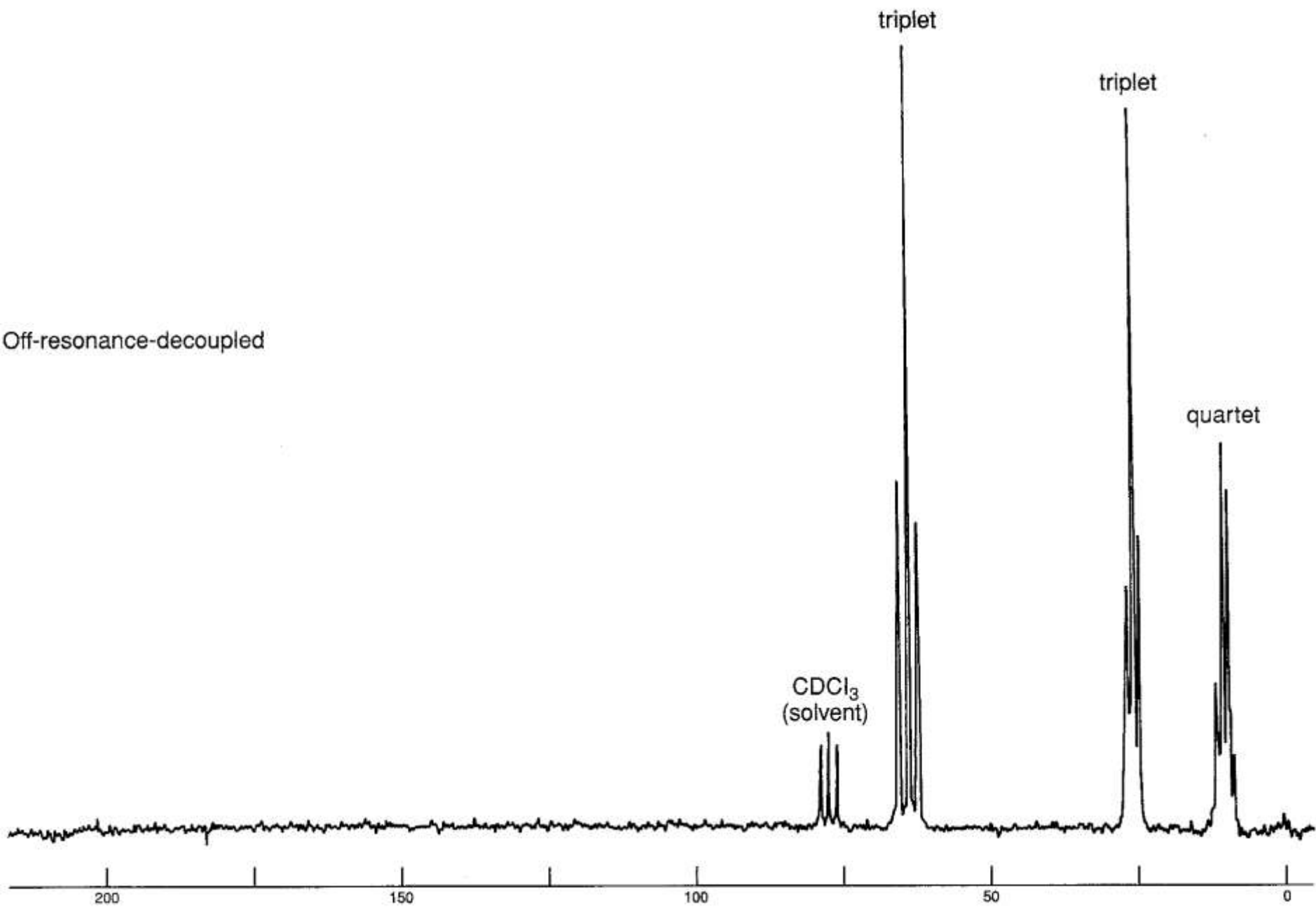
Nuclear Overhauser Enhancement (NOE)

- A. Under conditions of broad band decoupling it found that the area of the ^{13}C peaks are enhanced by a factor that is significantly greater than that which is expected from the collapse of multiplets into single lines.
- B. This is a manifestation of nuclear overhauser enhancement.
- C. Arises from direct magnetic coupling between a decoupled proton and a neighboring ^{13}C nucleus that results in an increase in the population of the lower energy state of the ^{13}C nucleus than that predicted by the Boltzmann relation.
- D. ^{13}C signal may be enhanced by as much as a factor of 3 x
- E. Disadvantage –
 1. Lose the proportionality between peak areas and the number of nuclei of that type of ^{13}C .

Off-resonance decoupling

1. The coupling between each carbon atom and each hydrogen attached directly to it, is observed according to the $n+1$ rule.
2. Apparent magnitude of the coupling constant is reduced and overlap of the resulting multiplets is less frequent
3. Set decoupling frequency at 1000 to 2000 Hz above the proton spectral region which leads to a partial decoupled spectrum in which all but the largest spin-spin shifts are absent.

Off-resonance-decoupled



DEPT ^{13}C NMR Spectroscopy

Distortionless Enhancement by Polarization Transfer (DEPT-NMR) experiment

- Run in three stages
 1. Ordinary *broadband-decoupled spectrum*
 - Locates chemical shifts of all carbons
 2. DEPT-90
 - Only signals due to CH carbons appear
 3. DEPT-135
 - CH_3 and CH resonances appear positive
 - CH_2 signals appear as *negative* signals (below the baseline)
- Used to determine number of hydrogens attached to each carbon

DEPT ^{13}C NMR Spectroscopy

Broadband-decoupled

DEPT-90

DEPT-135

C, CH, CH₂, CH₃

CH

CH₃, CH are positive
CH₂ is negative

C Subtract DEPT-135 from broadband-decoupled spectrum

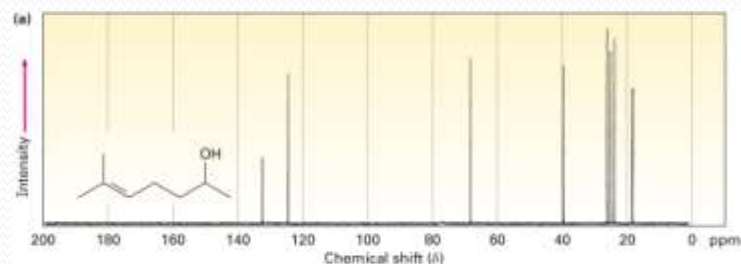
CH DEPT-90

CH₂ Negative DEPT-135

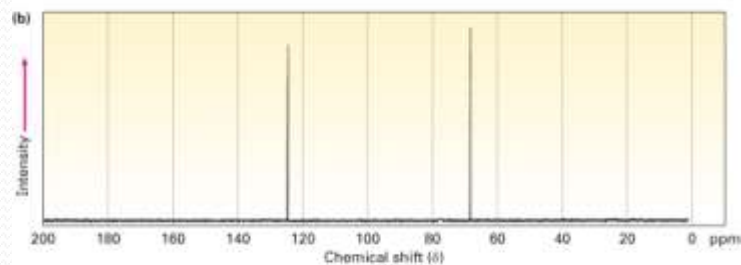
CH₃ Subtract DEPT-90 from positive DEPT-135

DEPT ^{13}C NMR Spectroscopy

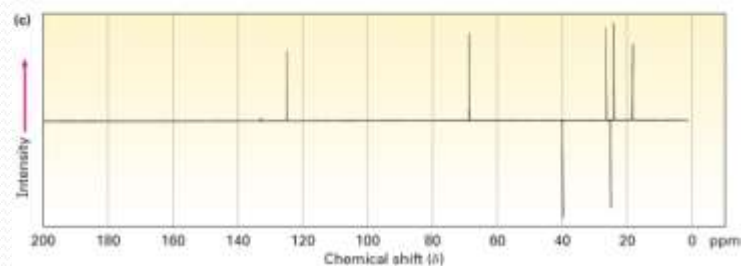
(a) Ordinary broadband-decoupled spectrum showing signals for all eight of 6-methylhept-5-en-2-ol



(b) DEPT-90 spectrum showing signals only for the two C-H carbons



(c) DEPT-135 spectrum showing positive signals for the two CH carbons and the three CH_3 carbons and negative signals for the two CH_2 carbons





THANK YOU