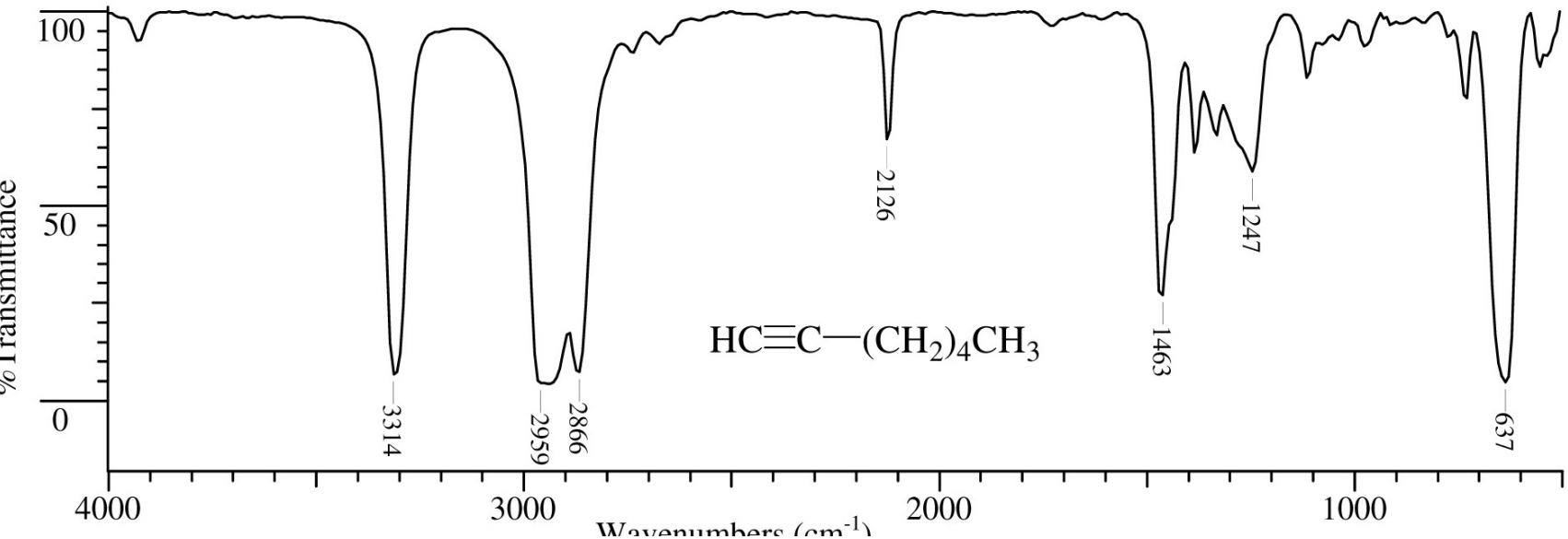
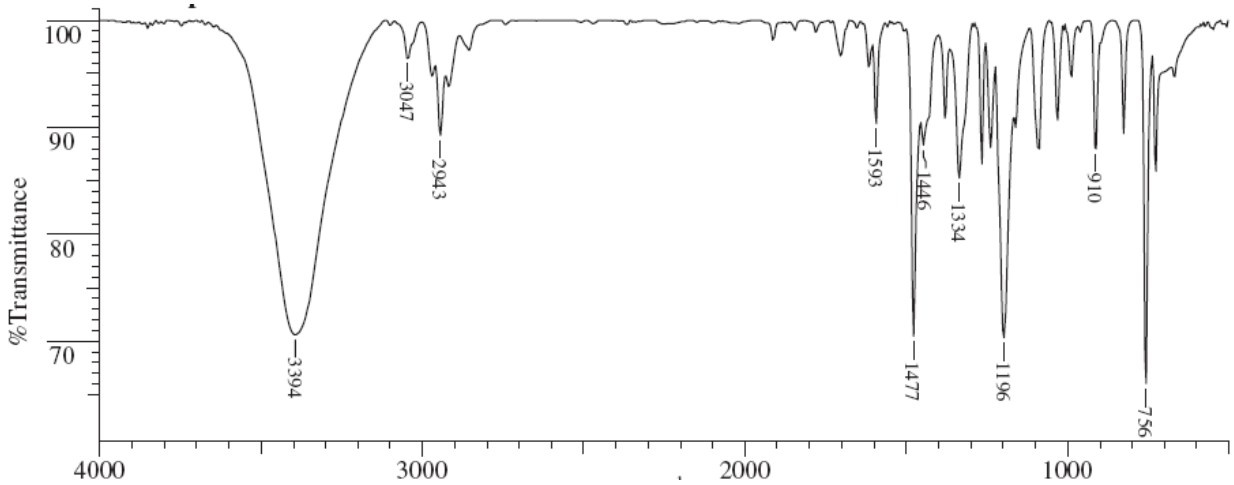
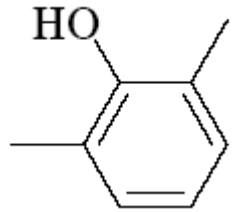
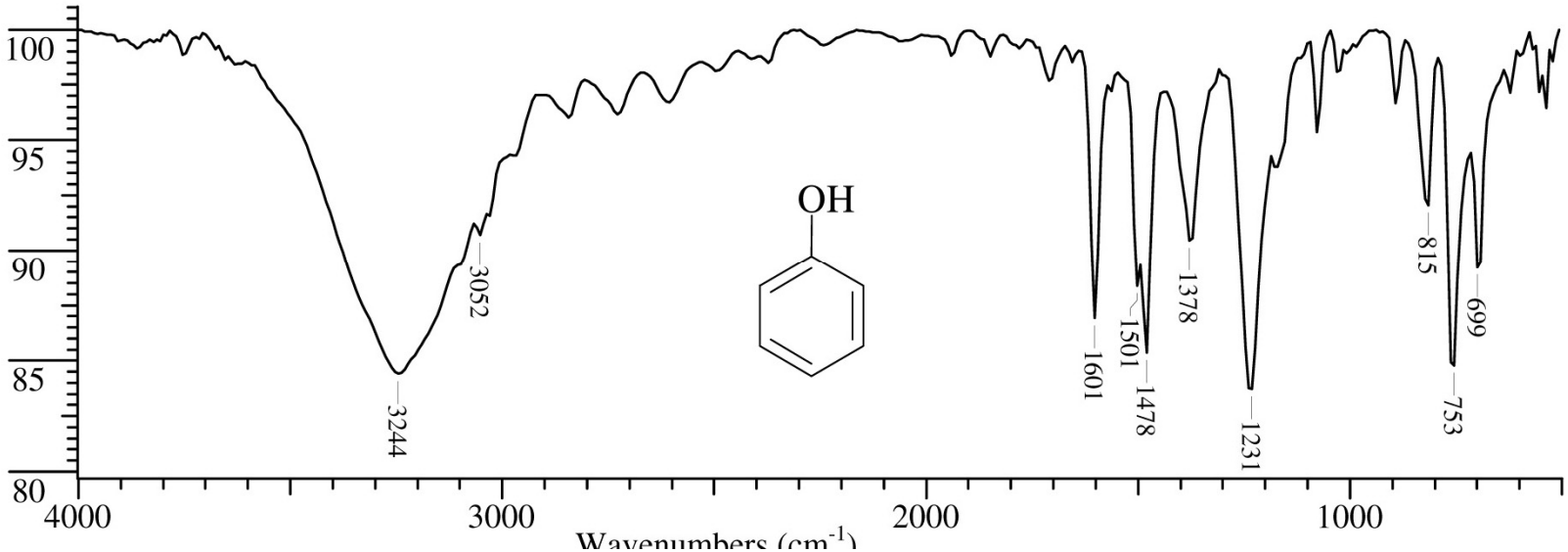
第9章 ^{1}H-核磁共振光譜(Proton Nuclear Magnetic Resonance; ^{1}H-NMR):幫助我們確定化合物的準確結構

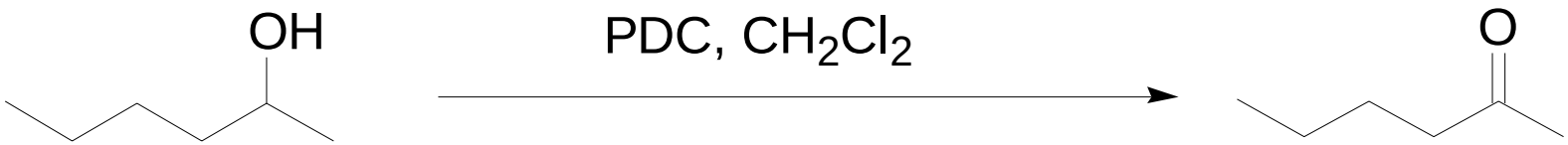


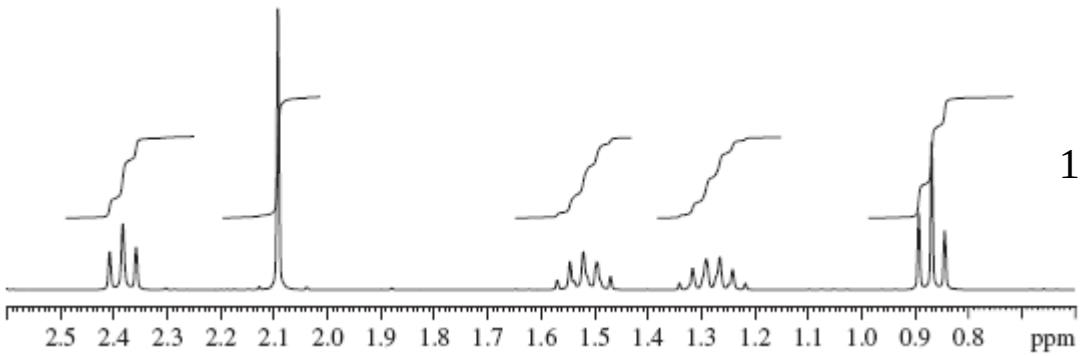

%Transmittance
100
90
80
70
3394
3047
2943
1593
1477
1446
1334
1196
910
756
4000
3000
2000
1000


HO

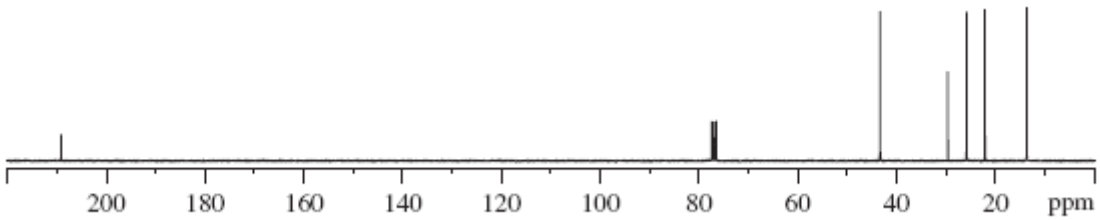

100
95
90
85
80
3244
3052
OH
1601
1501
1478
1378
1231
815
753
699
4000
3000
2000
1000
Wavenumbers (cm-1)

確定有機反應中產物的結構

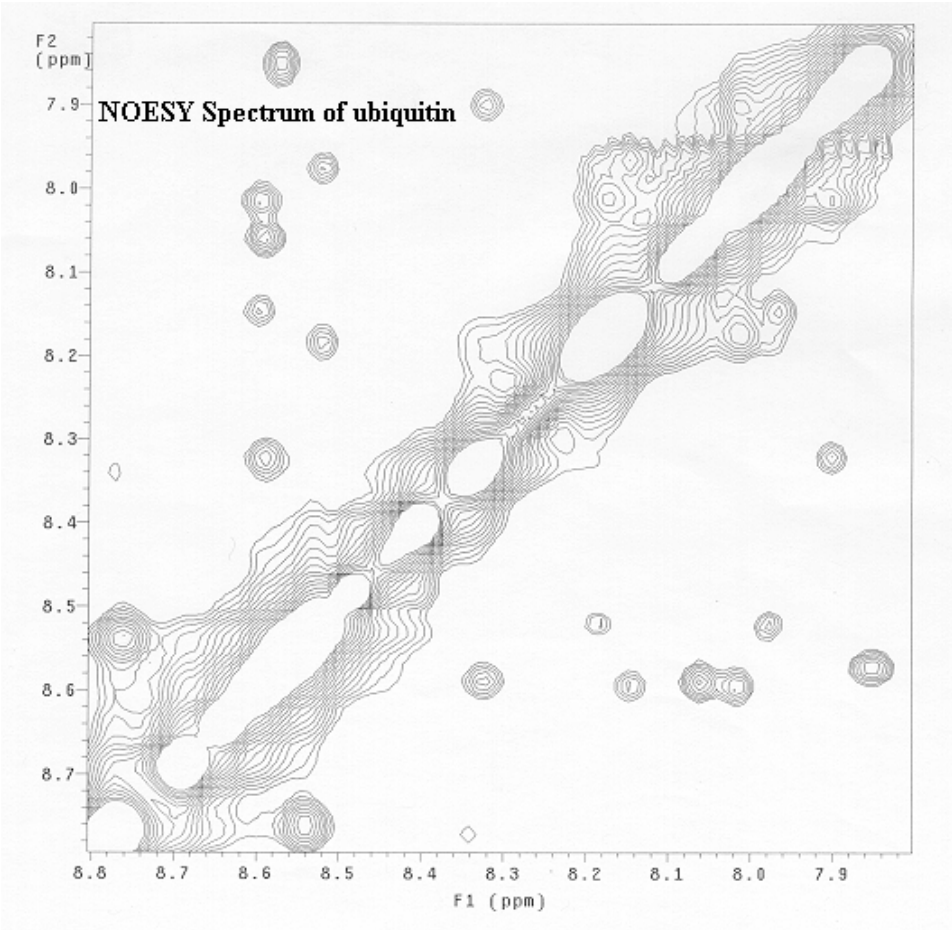


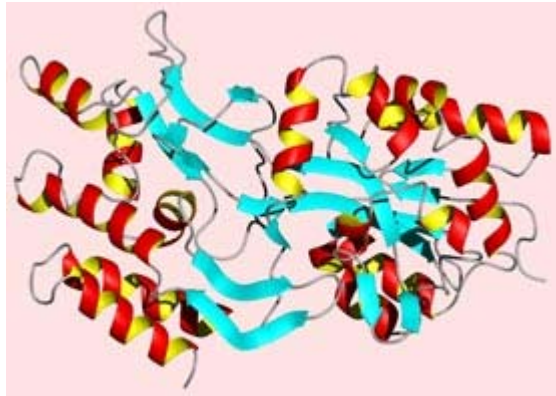


^{1}H-NMR spectra



^{13}C-NMR spectra

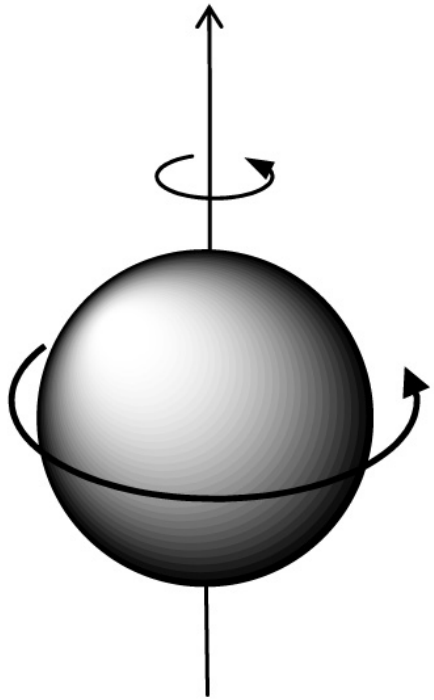

NOESY Spectrum of ubiquitin
F2 (ppm)
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9
F1 (ppm)



1）核磁共振之原理:

部分原子是有自旋現象的，而原子核的自旋可產生magnetic dipole (磁偶極),

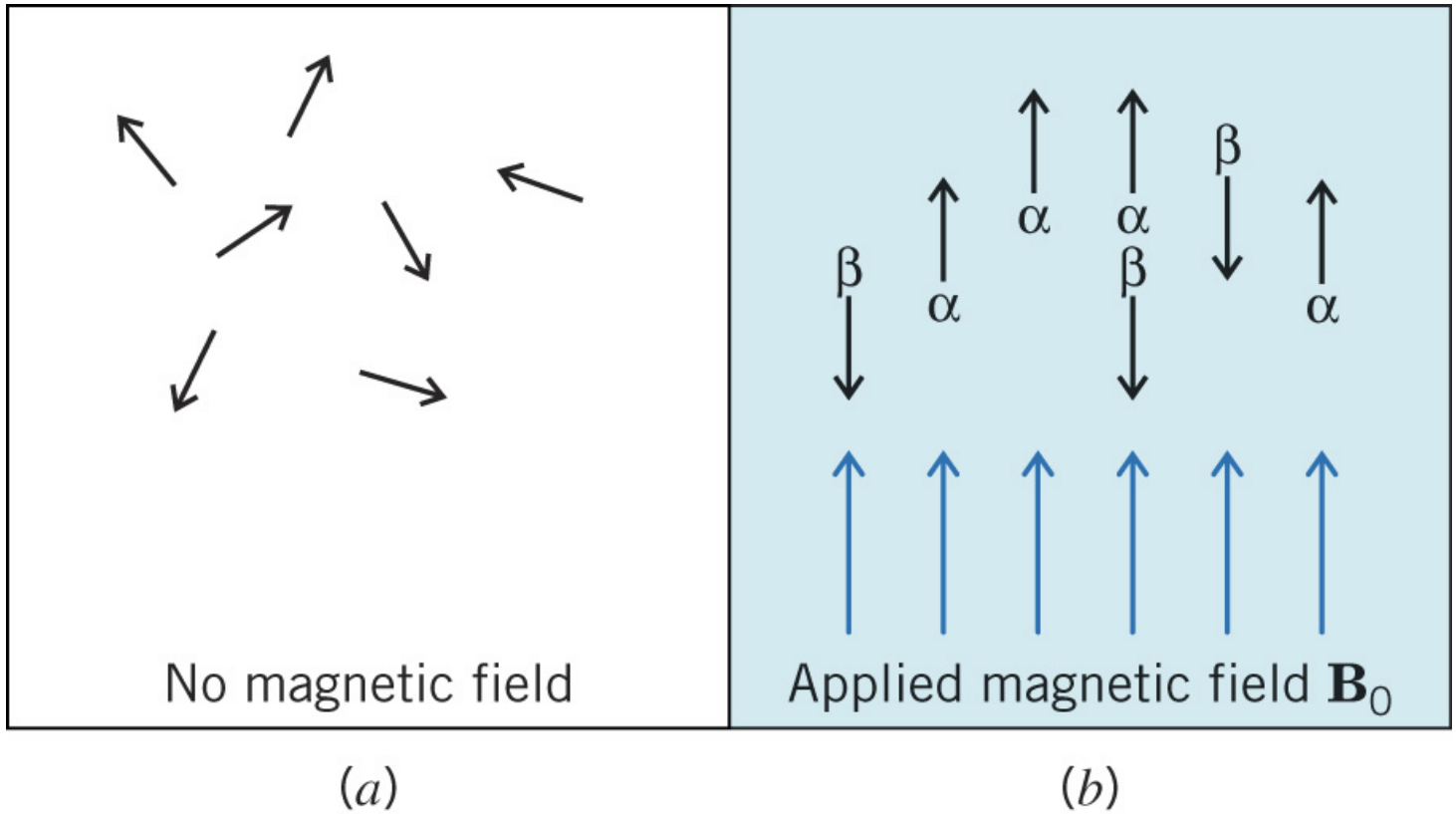
原子核的自旋可以以自旋量子數來描述 (quantum spin number: I = 0, 1/2, 1, 3/2…..etc.)



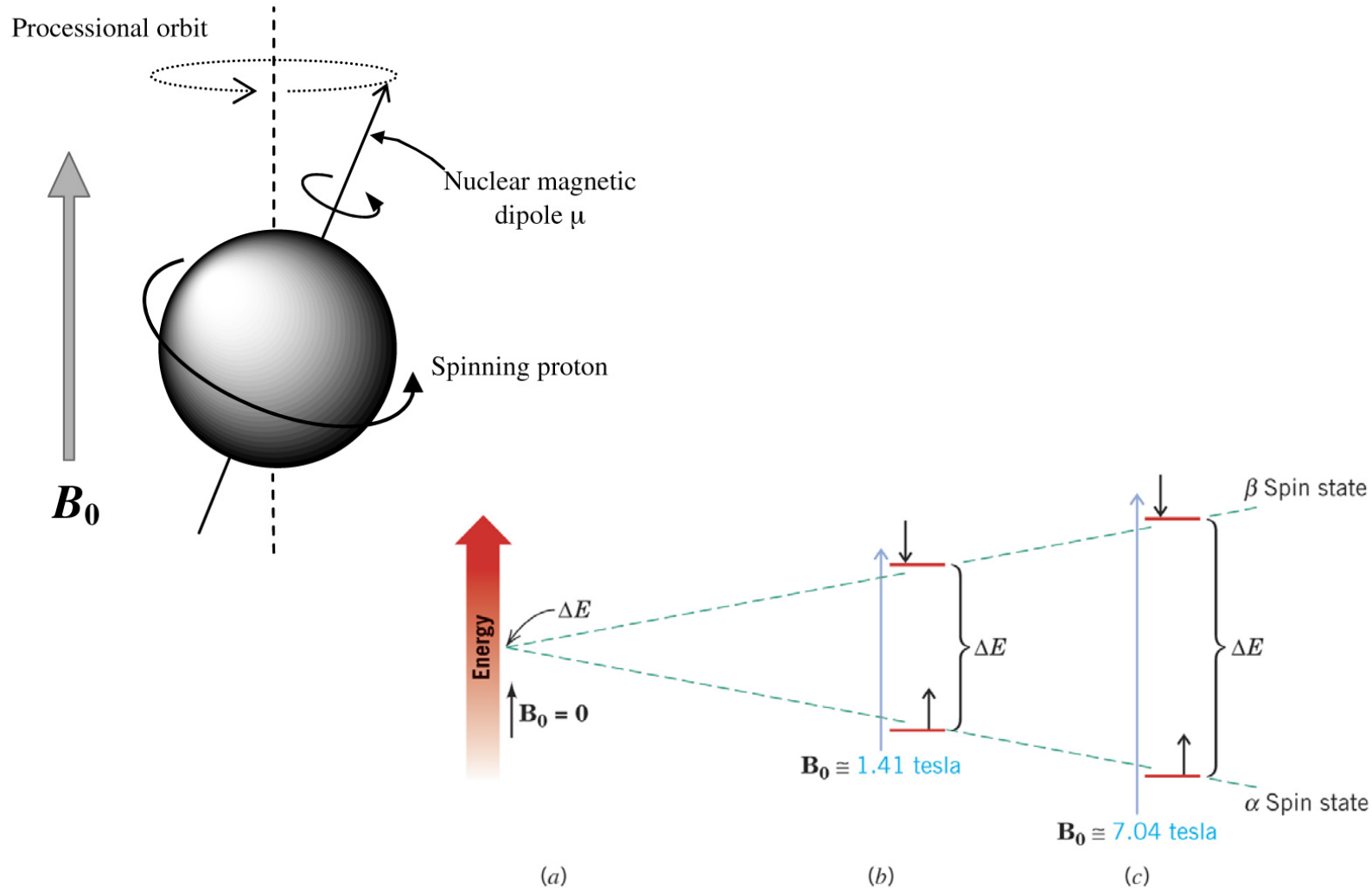
當I≠0時，原子核均有自旋現象

當原子質量爲奇數(atomic mass)， 而原子序數 (atomic number)爲偶數或奇數時， I爲半整數: $^{1}H_{1}$, $^{13}C_{6}$, $^{15}N_{7}$, $^{19}F_{9}$, $^{31}P_{15}$: I = 1/2;為NMR的主要研究對象

對I= 1/2的$^{1}H_{1}$原子核，若我們對他加一個外磁場，其磁矩的取向有兩種：



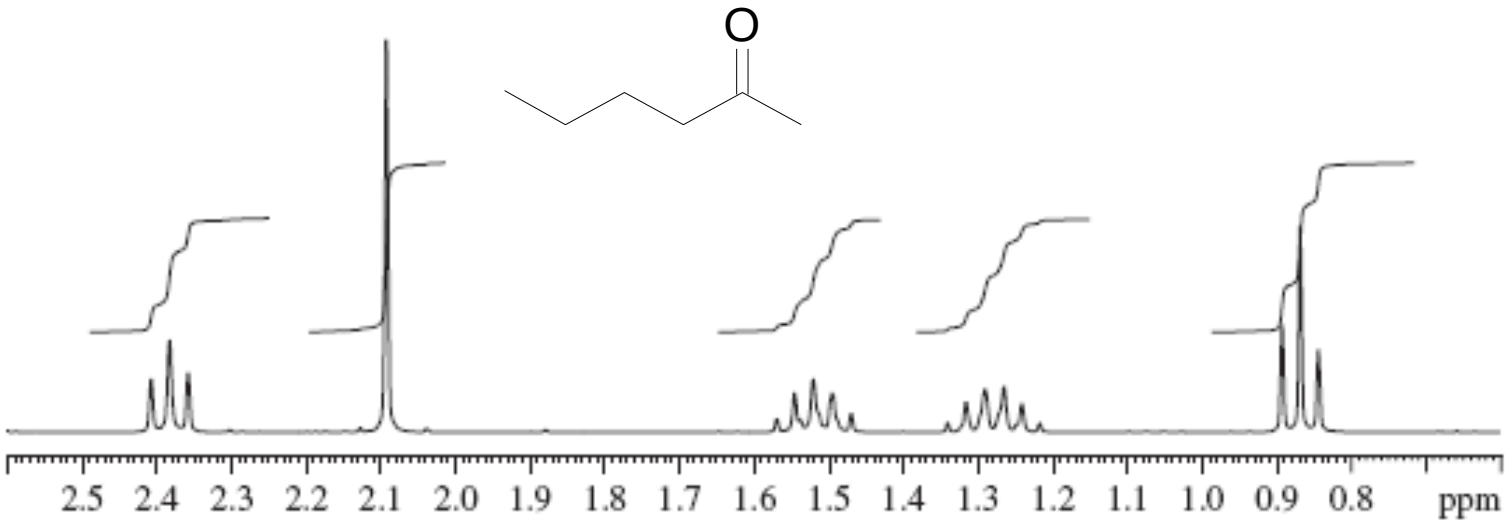
為了便於研究，我們用陀螺進動的體系來描述



$$\triangle E = E_{-1/2} - E_{1/2} = \gamma \frac{h}{2\pi} B_0 = h\nu$$

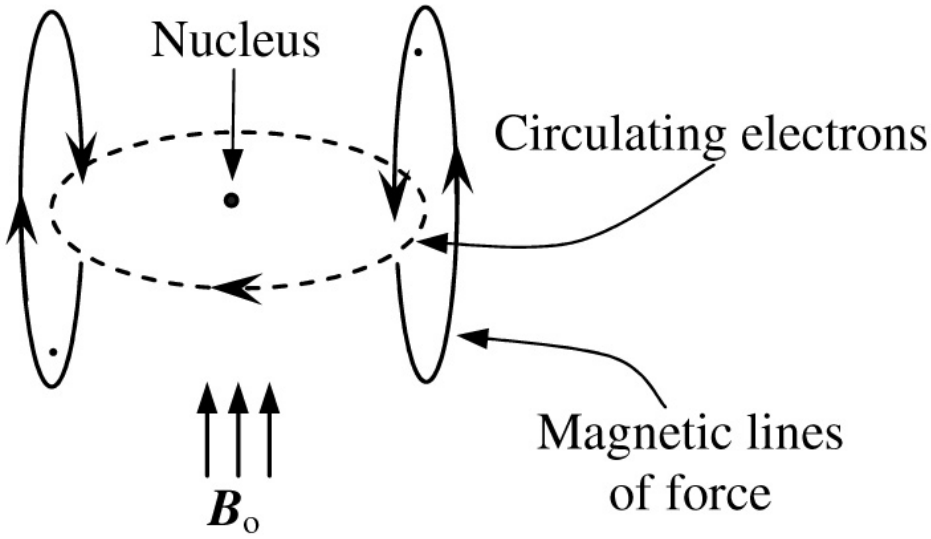
$$\boxed{\nu = \frac{\gamma B_0}{2\pi}}$$

2）proton-NMR譜中的化學位移(chemical shift）儀器，溶劑及譜圖



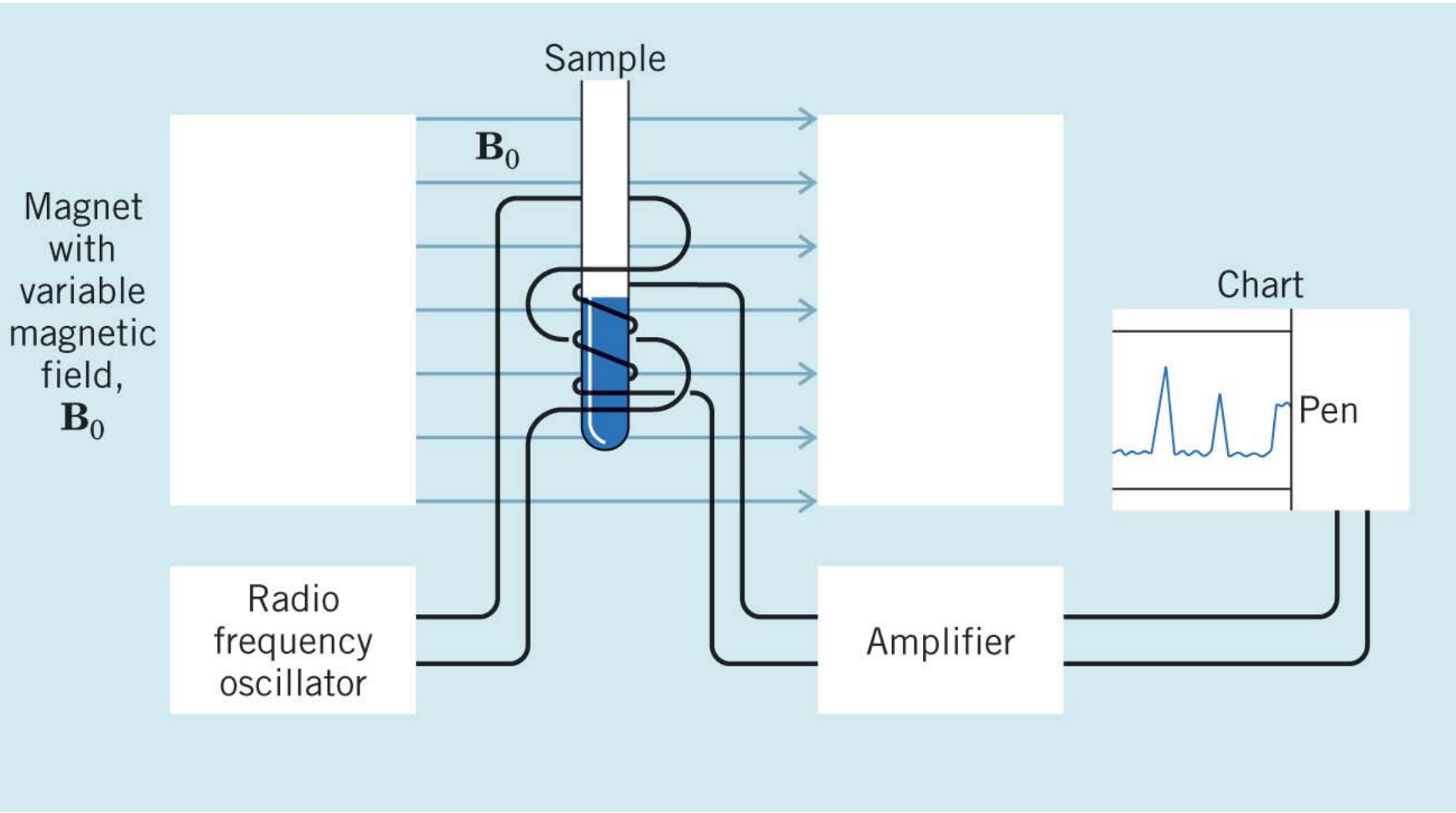
爲什麼氫原子會在不同的地方產生吸收呢?

電子雲的屏蔽效應(shielding effect)



$$\nu_{effect} = \frac{\gamma}{2\pi} B_0(1 - \sigma)$$

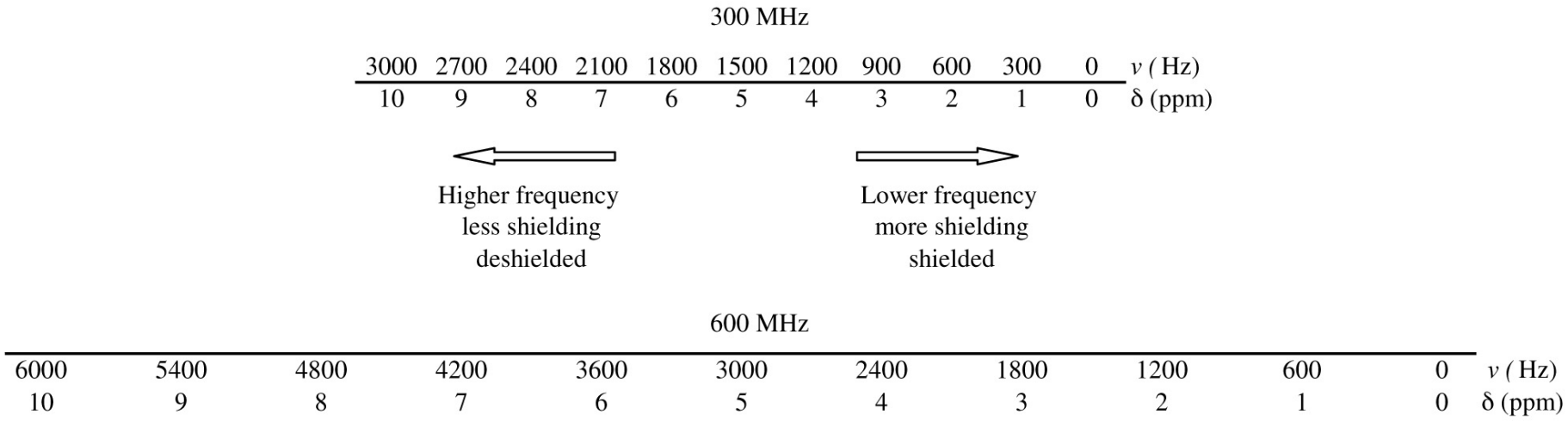
一般來講，原子核外電子雲的密度越大，屏蔽效應就越强，感受到外磁場作用就越弱，引發共振所需的頻率就越小。


Sample
$\mathbf{B}_0$
Magnet with variable magnetic field, $\mathbf{B}_0$
Chart
Pen
Radio frequency oscillator
Amplifier

$Si(CH_3)_4$

Tetramethylsilane
(TMS)

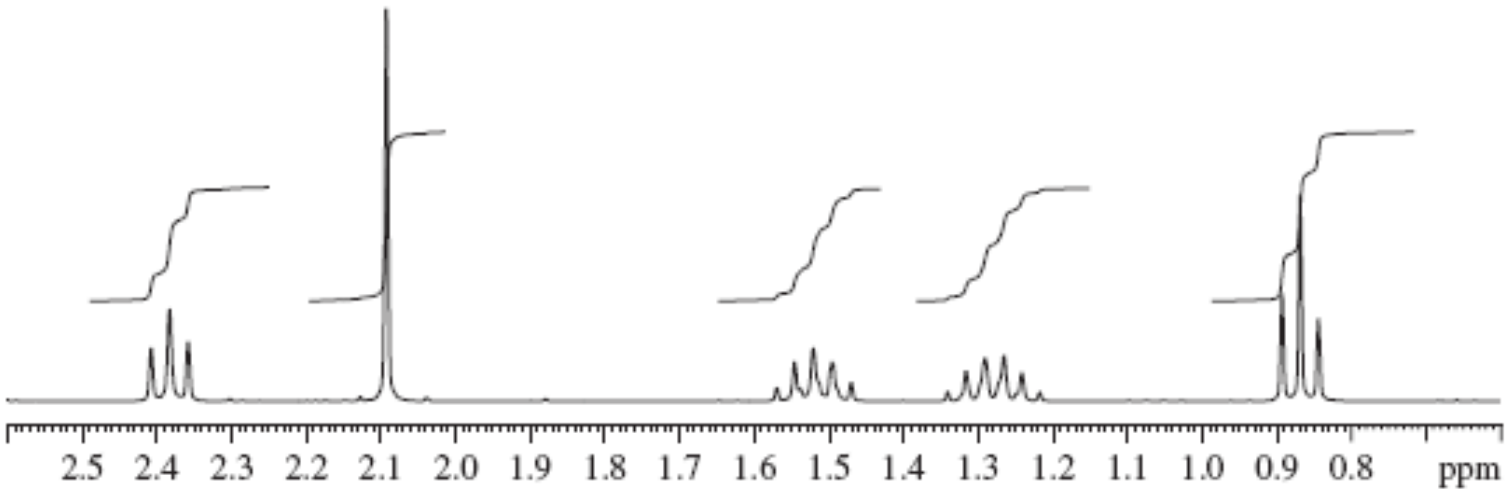
$$\delta = \frac{(\text{observed shift from TMS in hertz}) \times 10^6}{(\text{operating frequency of the instrument in hertz})}$$



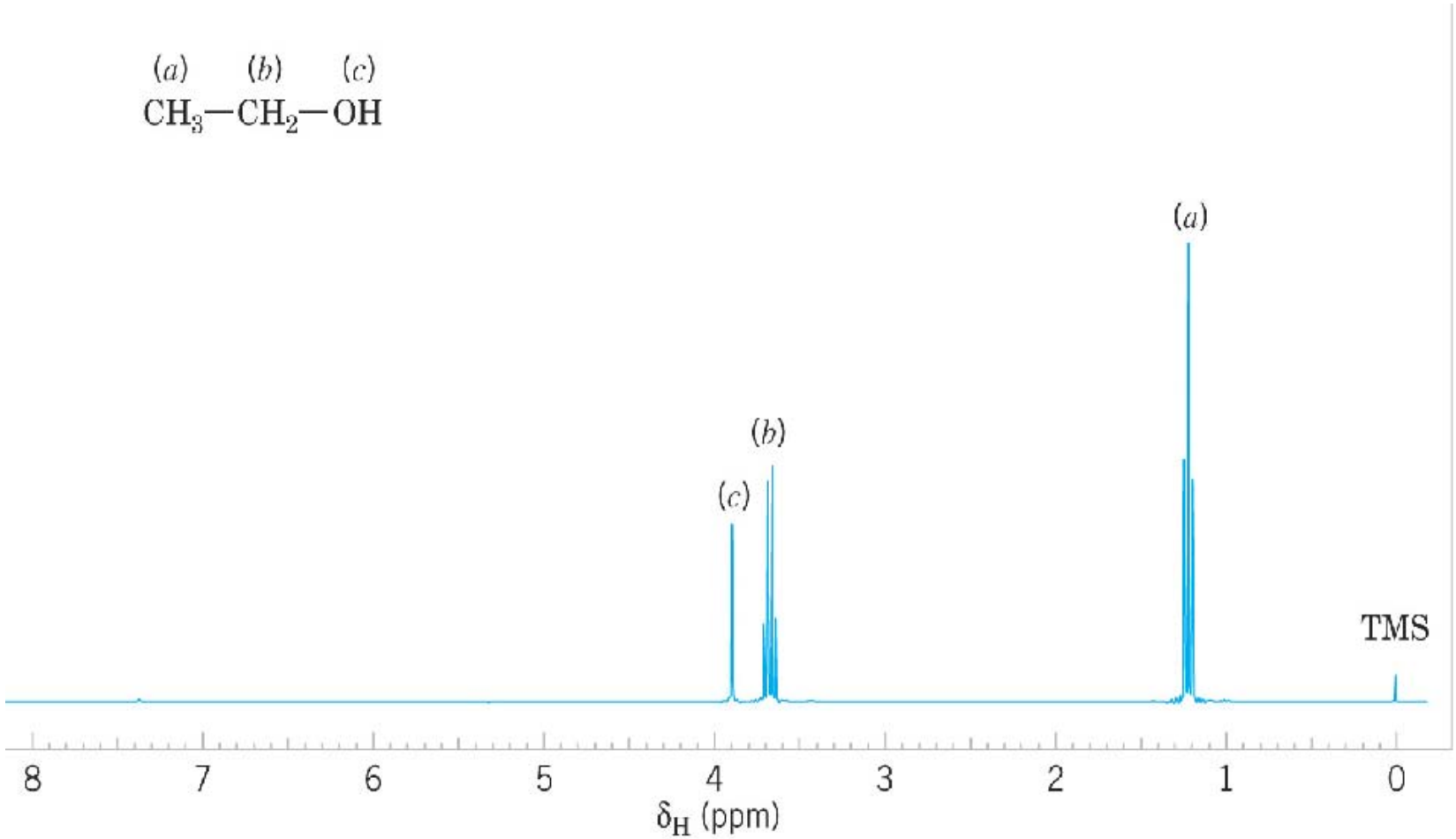
化學位移的表示方法:TMS定爲零

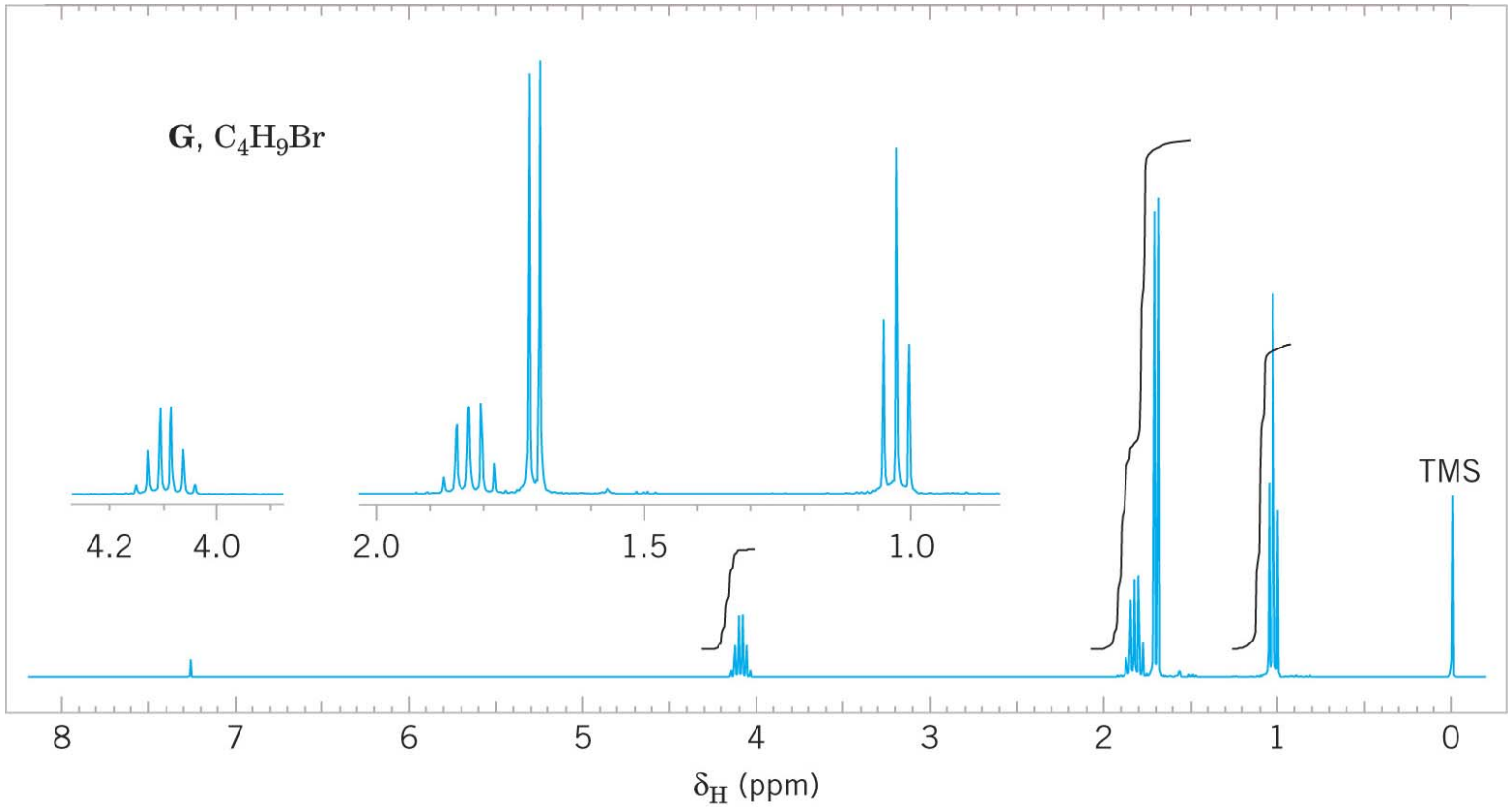
$$\frac{300\ \text{Hz}}{300 \times 10^6\ \text{Hz}} \times 10^6 = 1\ \text{ppm}$$

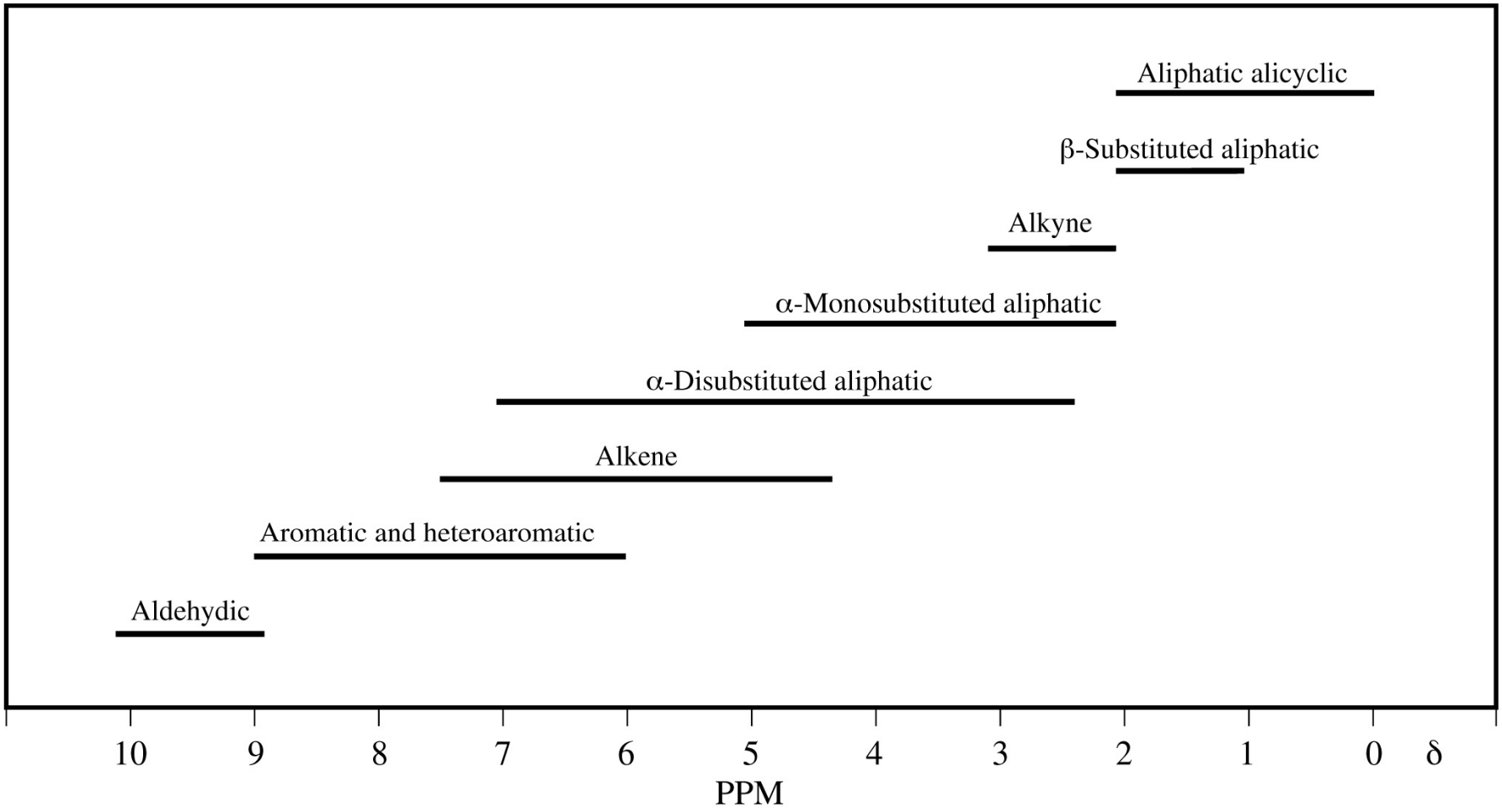
$$\frac{600\ \text{Hz}}{600 \times 10^6\ \text{Hz}} \times 10^6 = 1\ \text{ppm}$$

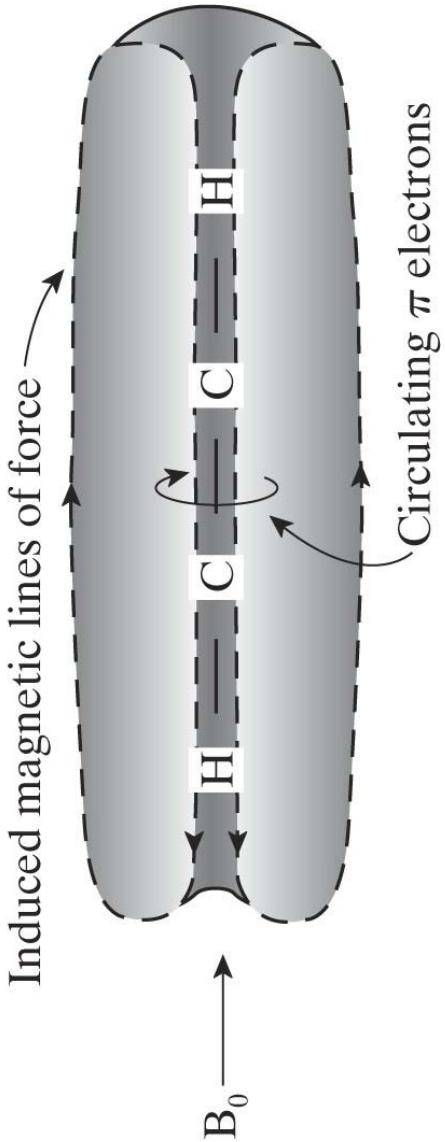


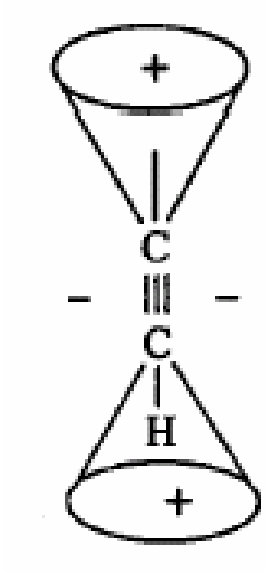
儀器會自動積分

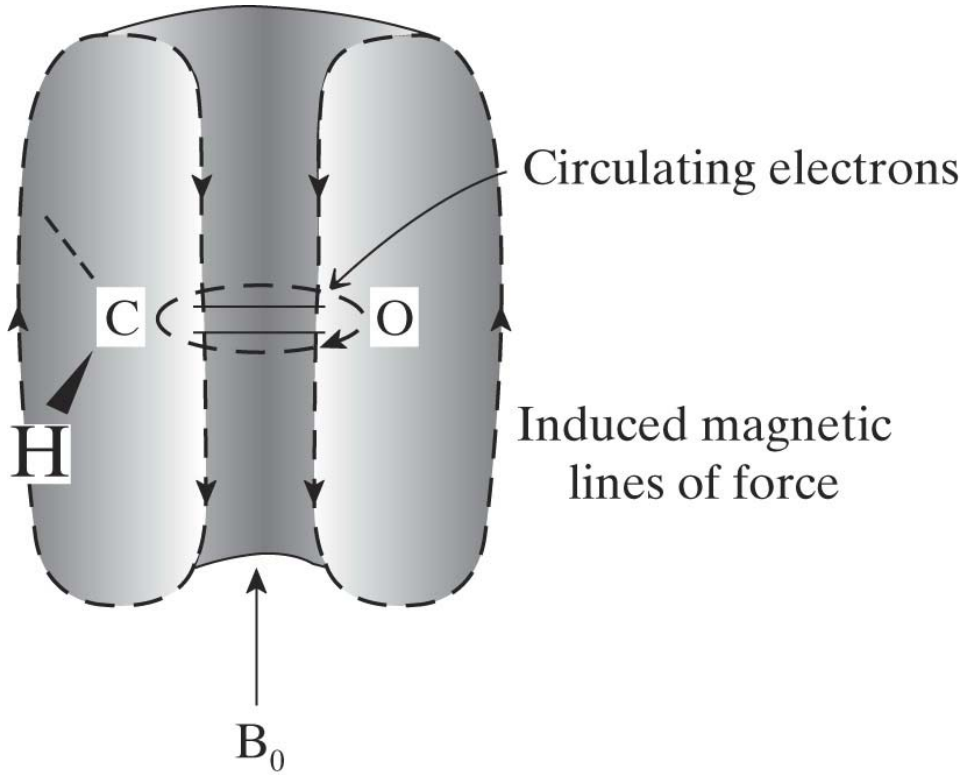

(a) (b) (c)
CH3—CH2—OH
(a)
(b)
(c)
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

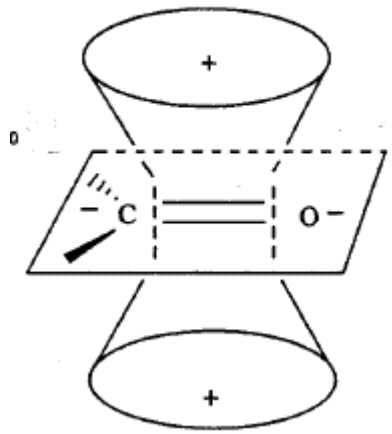

G, C4H9Br
4.2
4.0
2.0
1.5
1.0
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

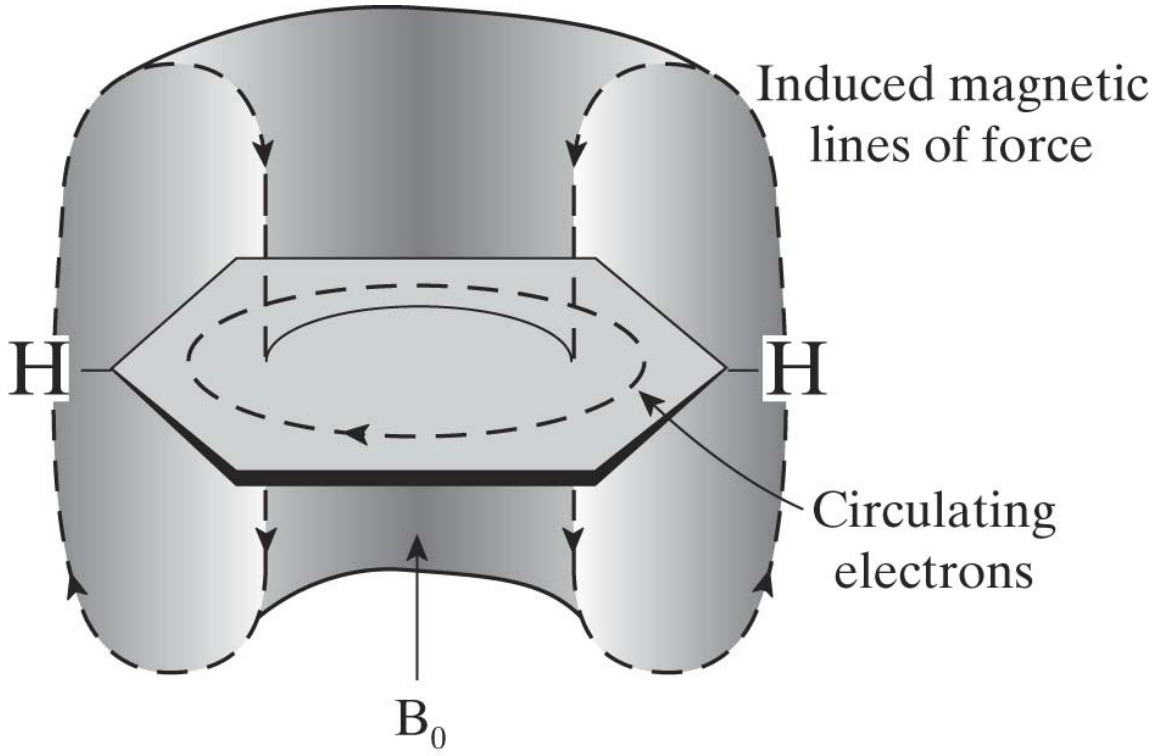

Aliphatic alicyclic
β-Substituted aliphatic
Alkyne
α-Monosubstituted aliphatic
α-Disubstituted aliphatic
Alkene
Aromatic and heteroaromatic
Aldehydic
10
9
8
7
6
5
4
3
2
1
0
δ
PPM

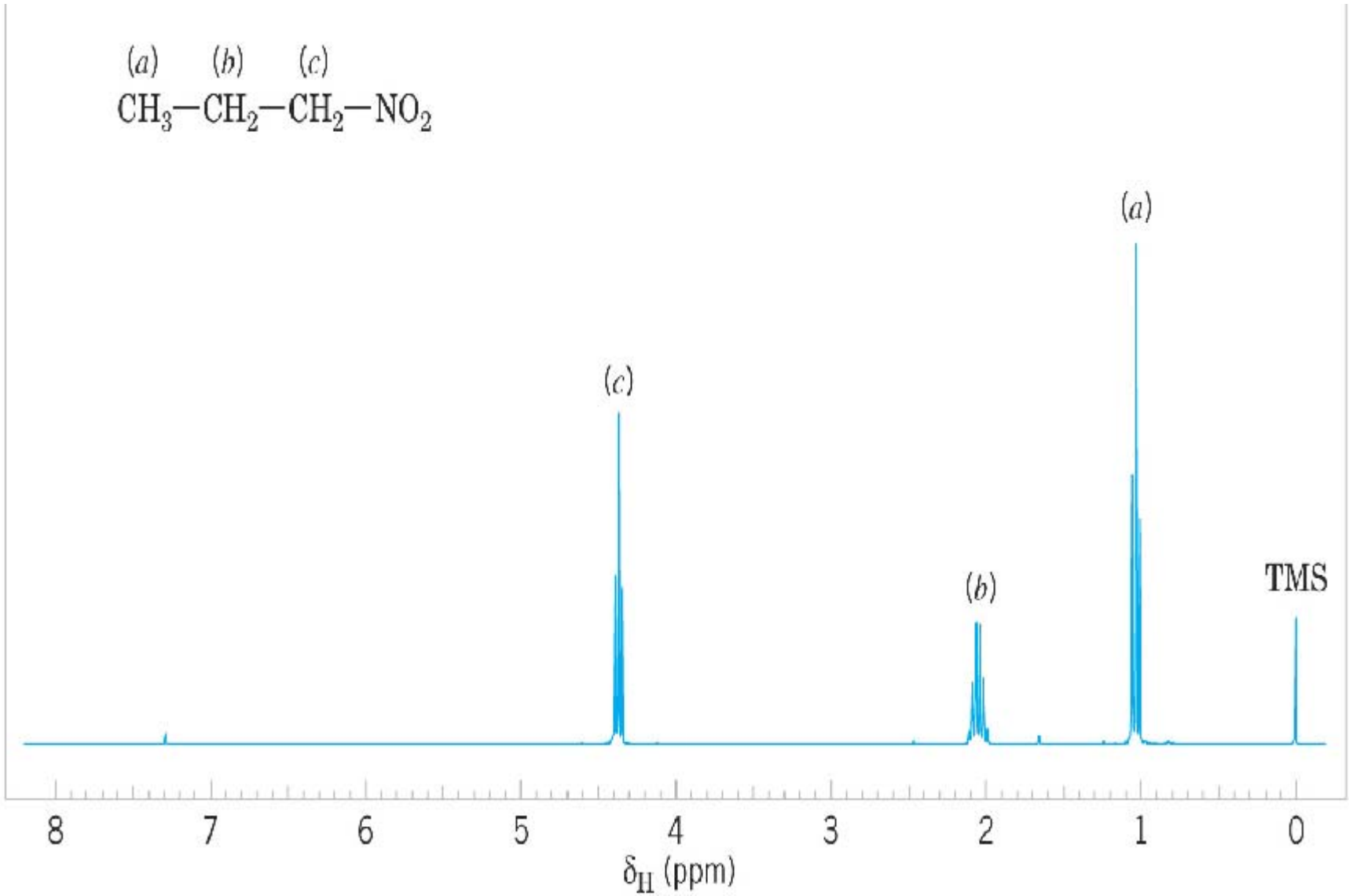

Induced magnetic lines of force
Circulating π electrons
H
C
C
H
B0


+
C
C
H
+


Circulating electrons
C
O
H
Induced magnetic lines of force
B0

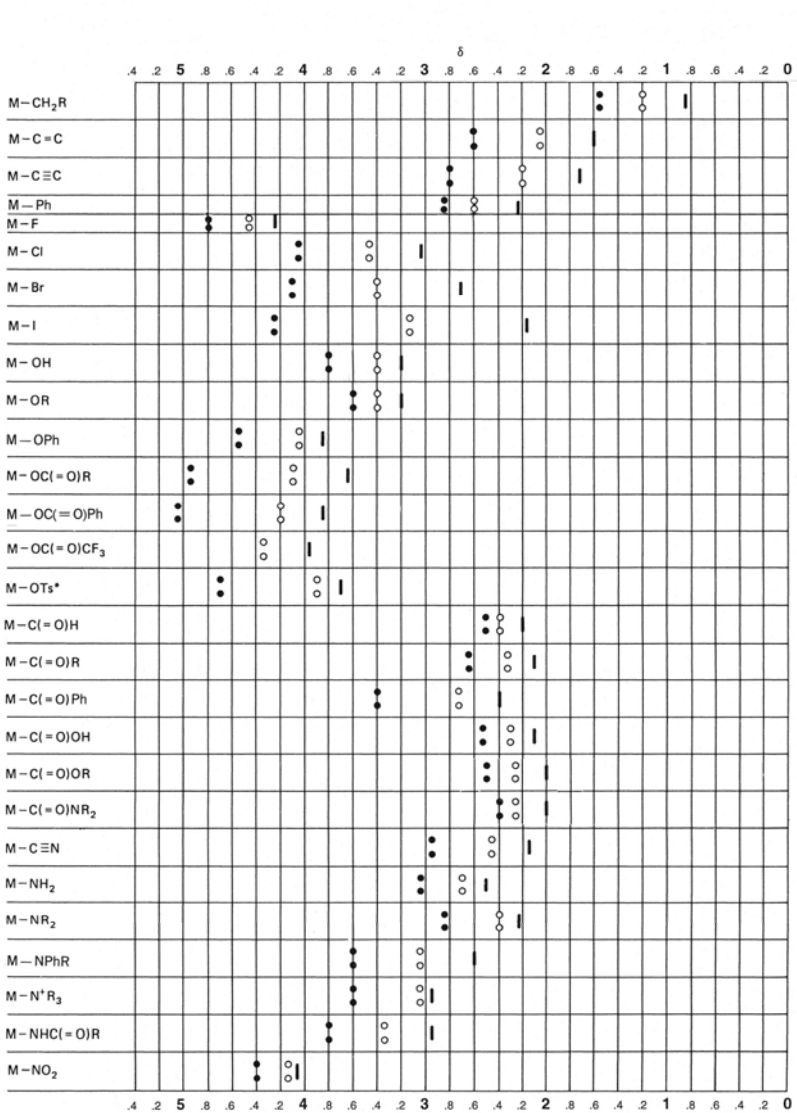

+
C
O
+


Induced magnetic
lines of force
H
H
Circulating
electrons
B_0

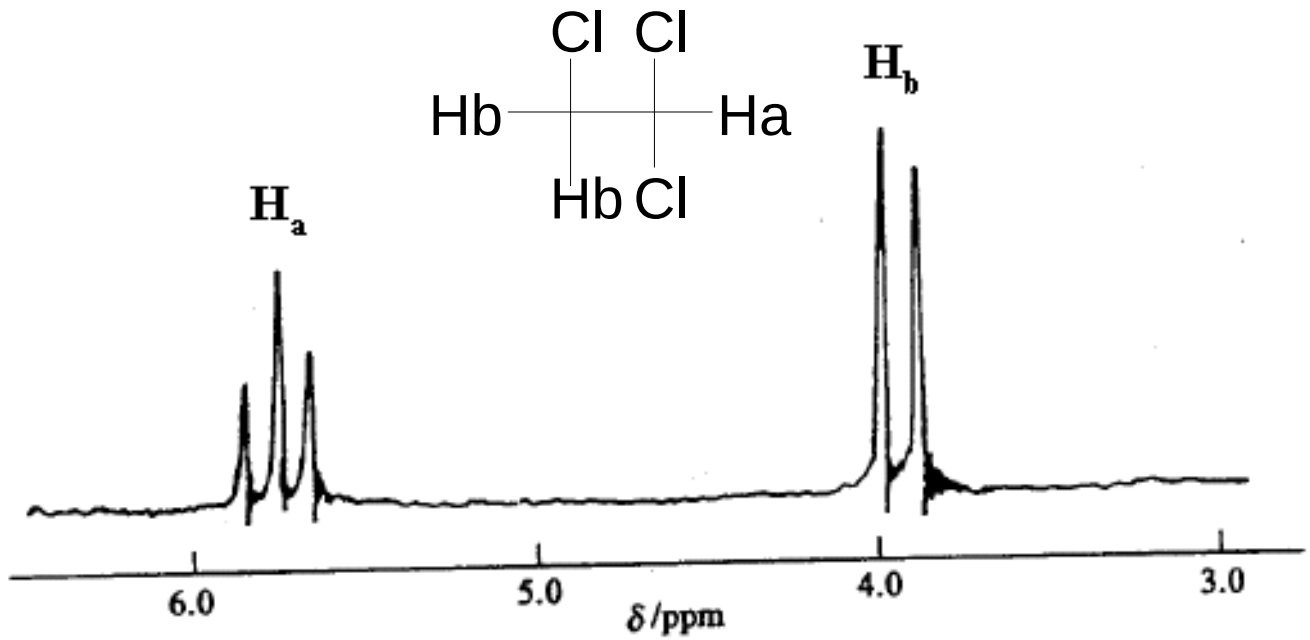

(a) (b) (c)
CH3—CH2—CH2—NO2
(a)
(c)
(b)
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

APPENDIX A

CHART A.1 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—Y)



3) proton-NMR譜中的耦合(coupling)



Ha在外磁場（B0）中有兩種取向（↑）（↓),幾率爲 1 ： 1

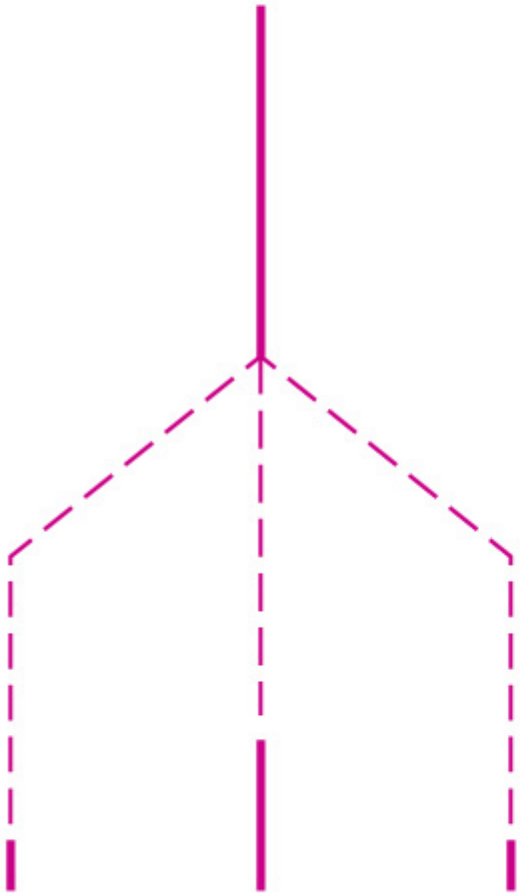
Hb在外磁場(B0)中有三種取向（↑↑，↑↓， ↓↑， ↓↓），幾率爲1: 2 : 1

(a) (b)

$CHCl_2CH_2Cl$

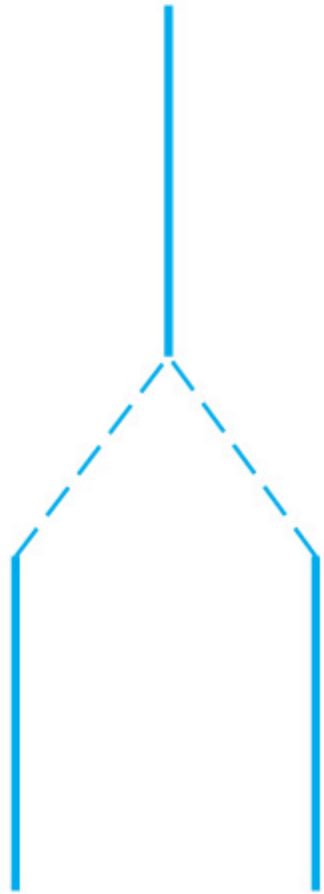
1, 1, 2-Trichloroethane

Signal from (a)

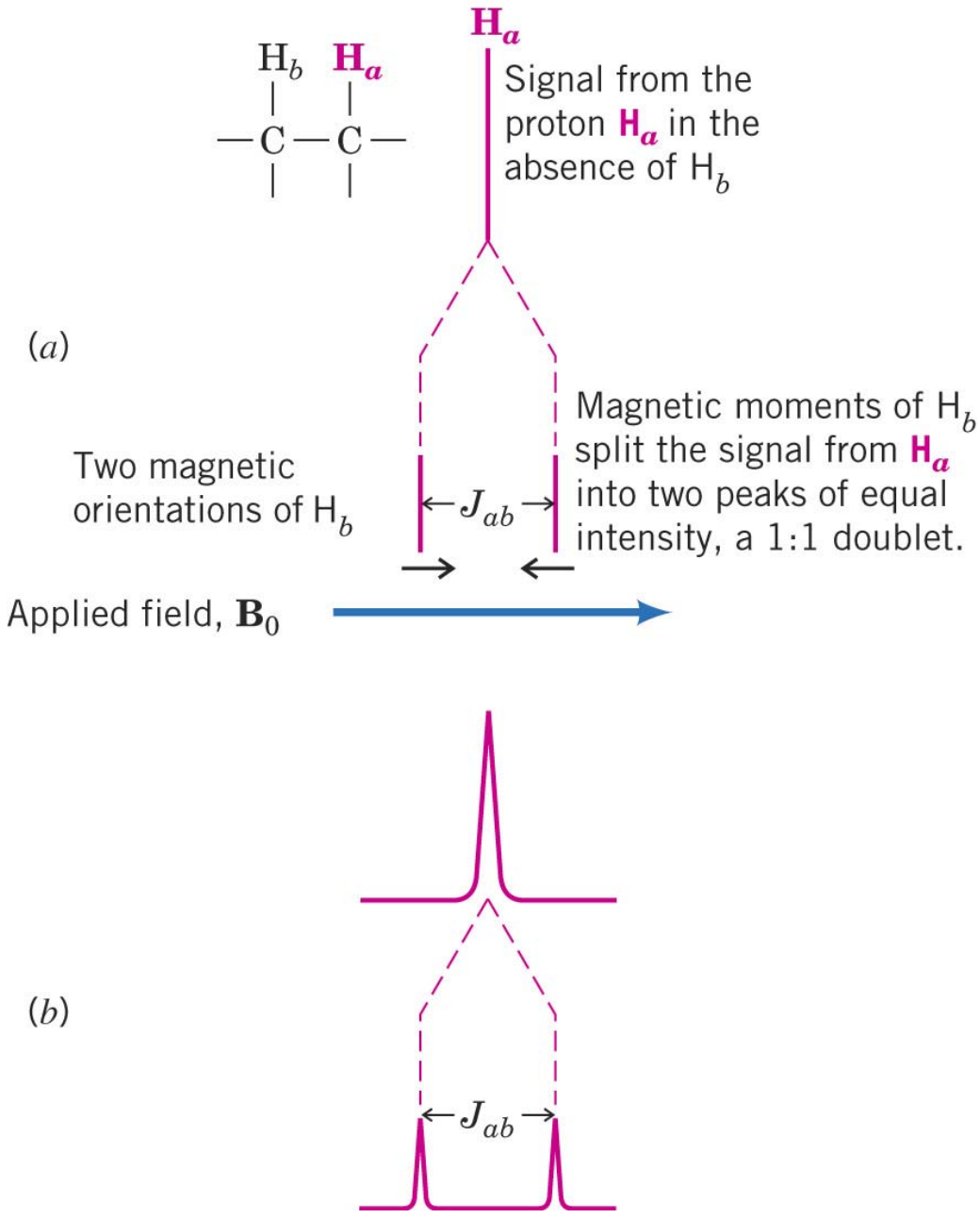


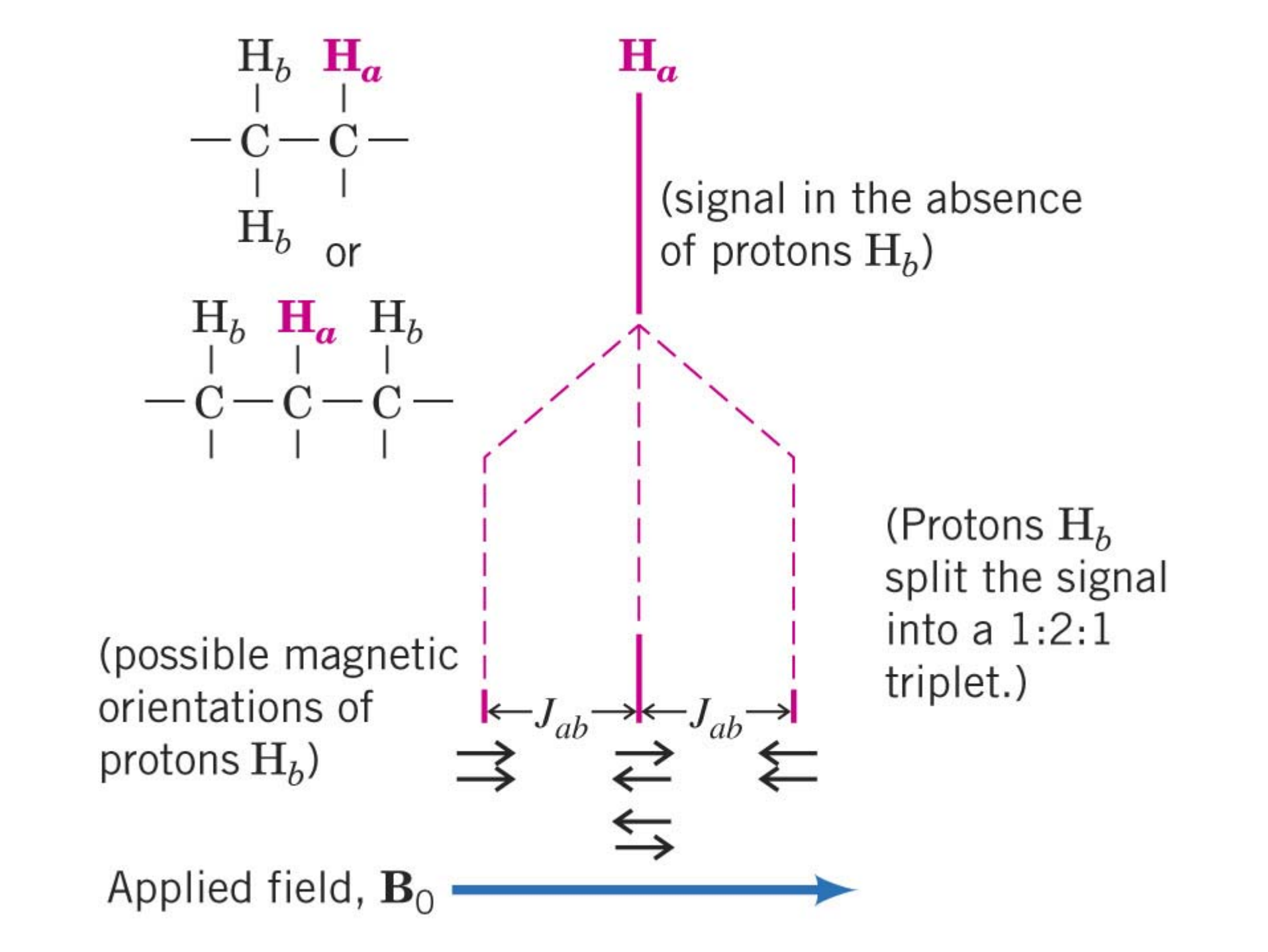
Split into a triplet by the two (b) protons

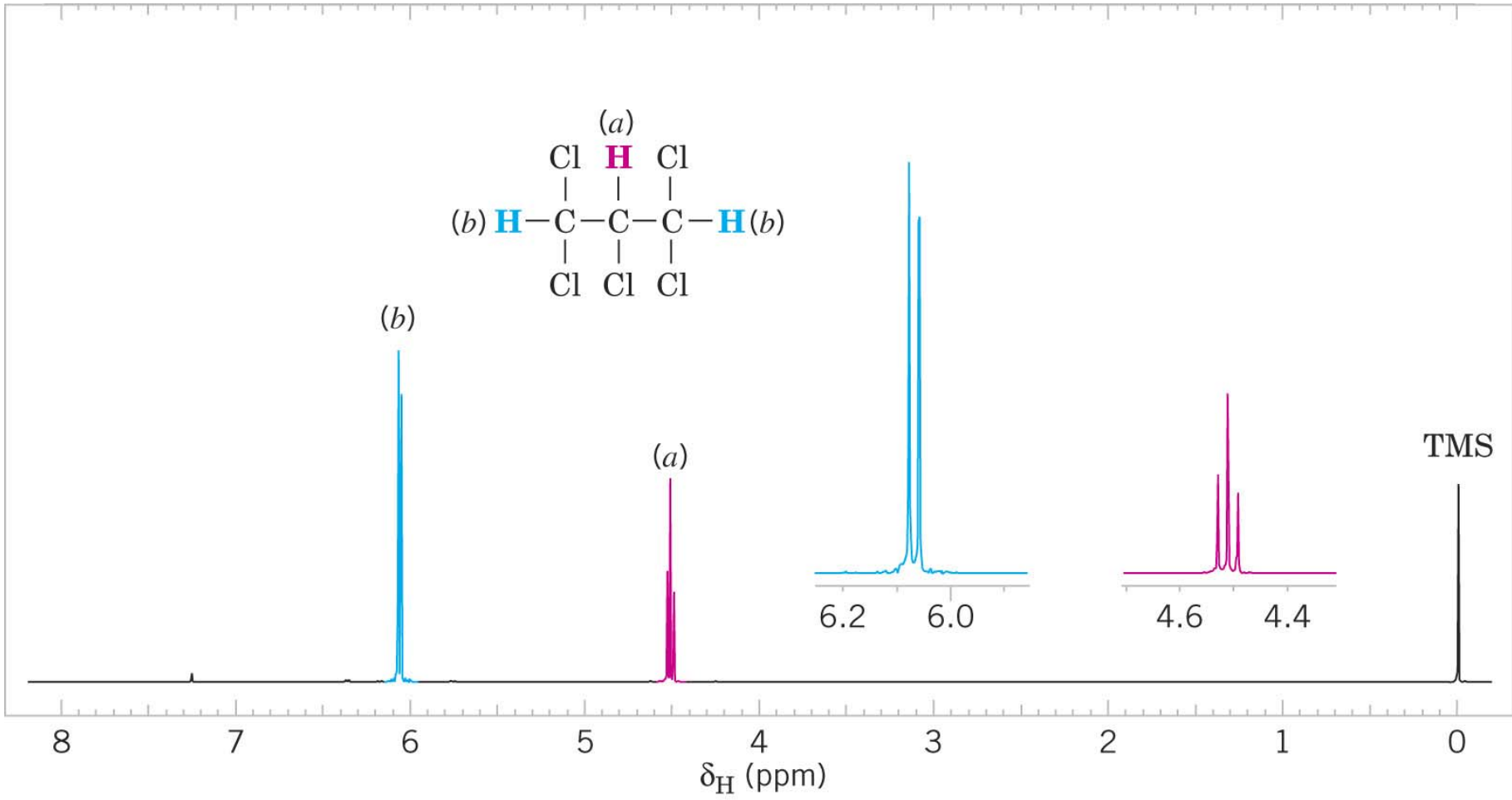
Signal from (b)

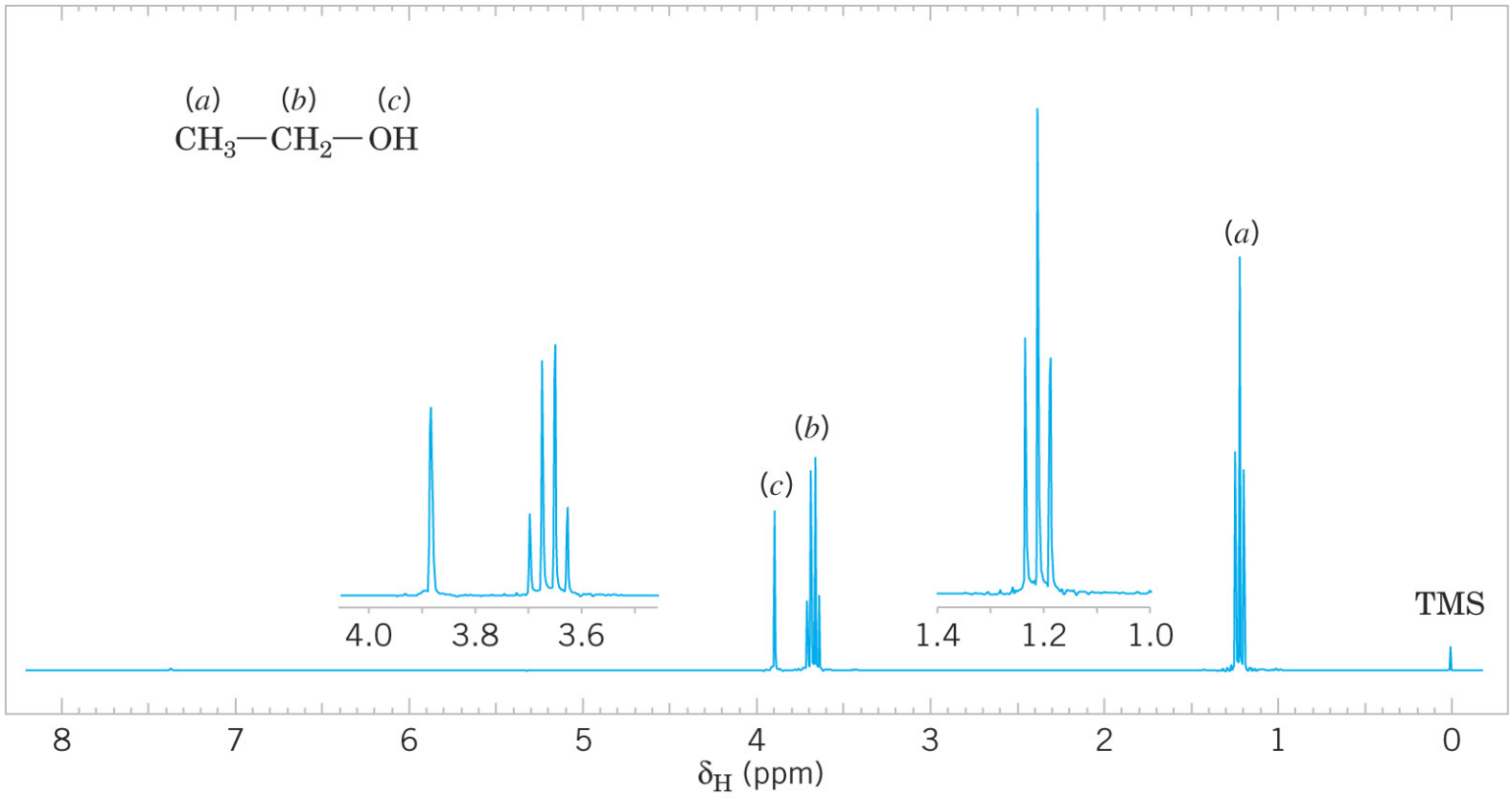


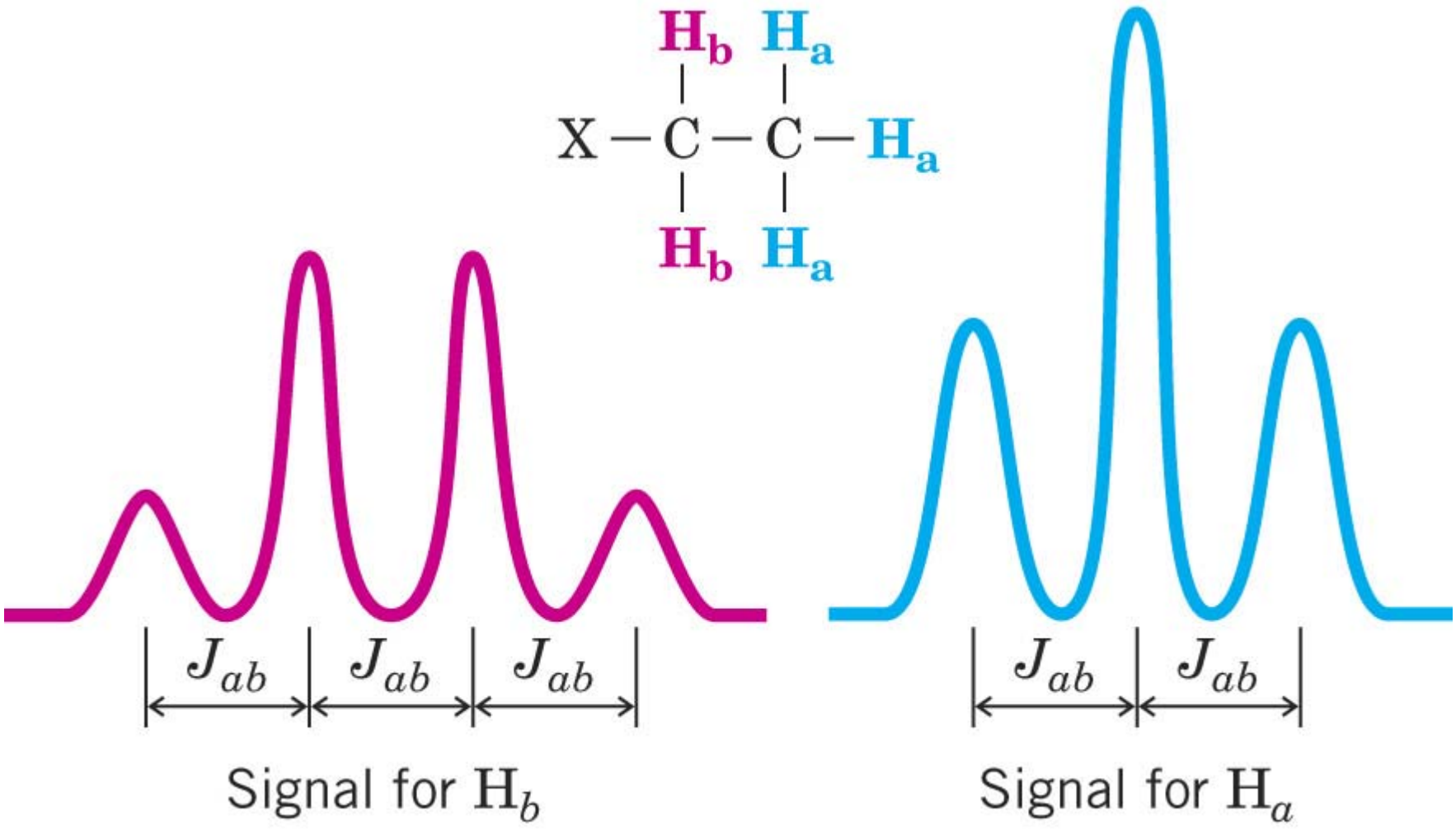
Split into a doublet by the (a) proton

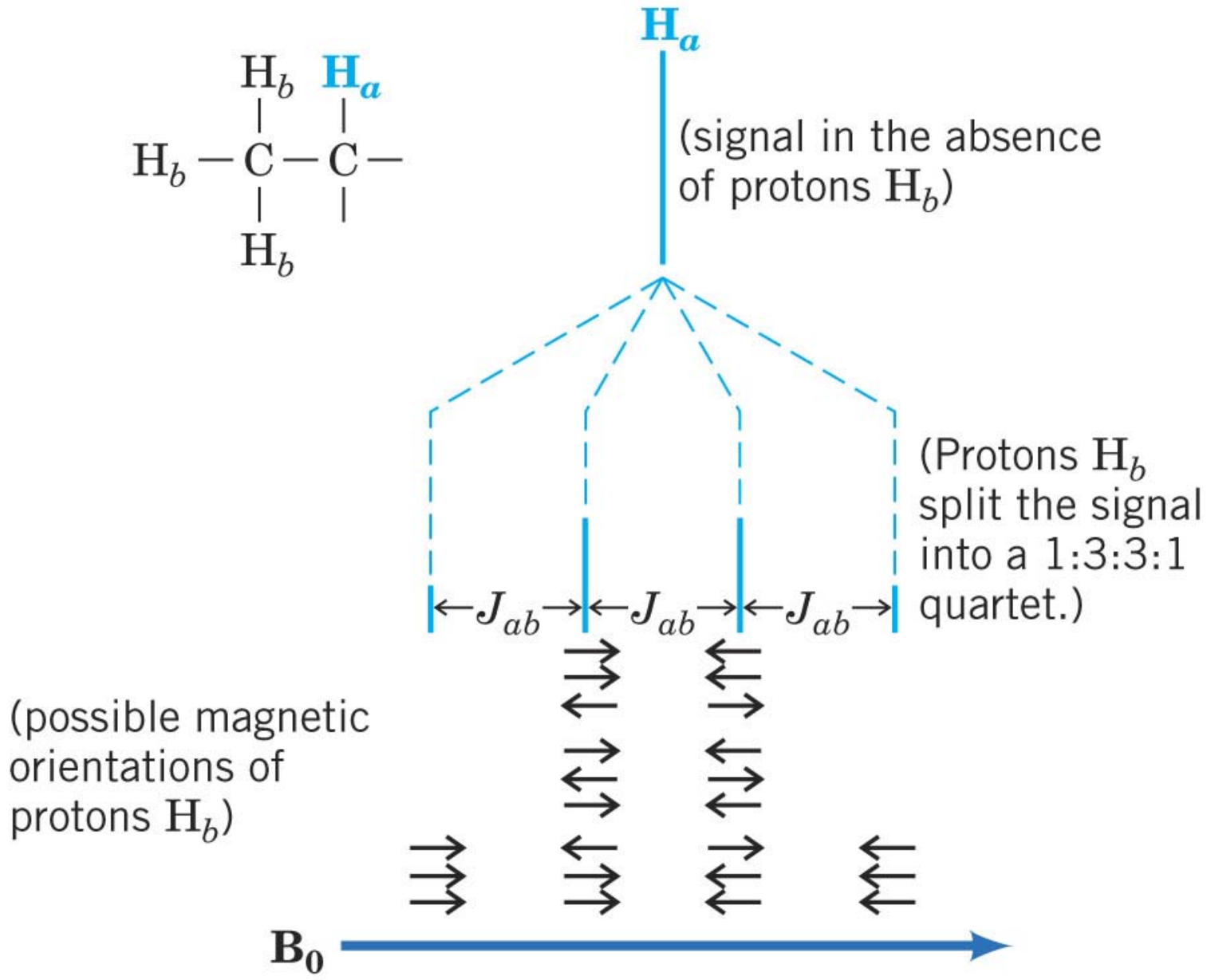

H_a
H_b H_a
Signal from the proton H_a in the absence of H_b
(a)
Magnetic moments of H_b split the signal from H_a into two peaks of equal intensity, a 1:1 doublet.
Two magnetic orientations of H_b
J_{ab}
Applied field, $\mathbf{B}_0$
(b)
J_{ab}

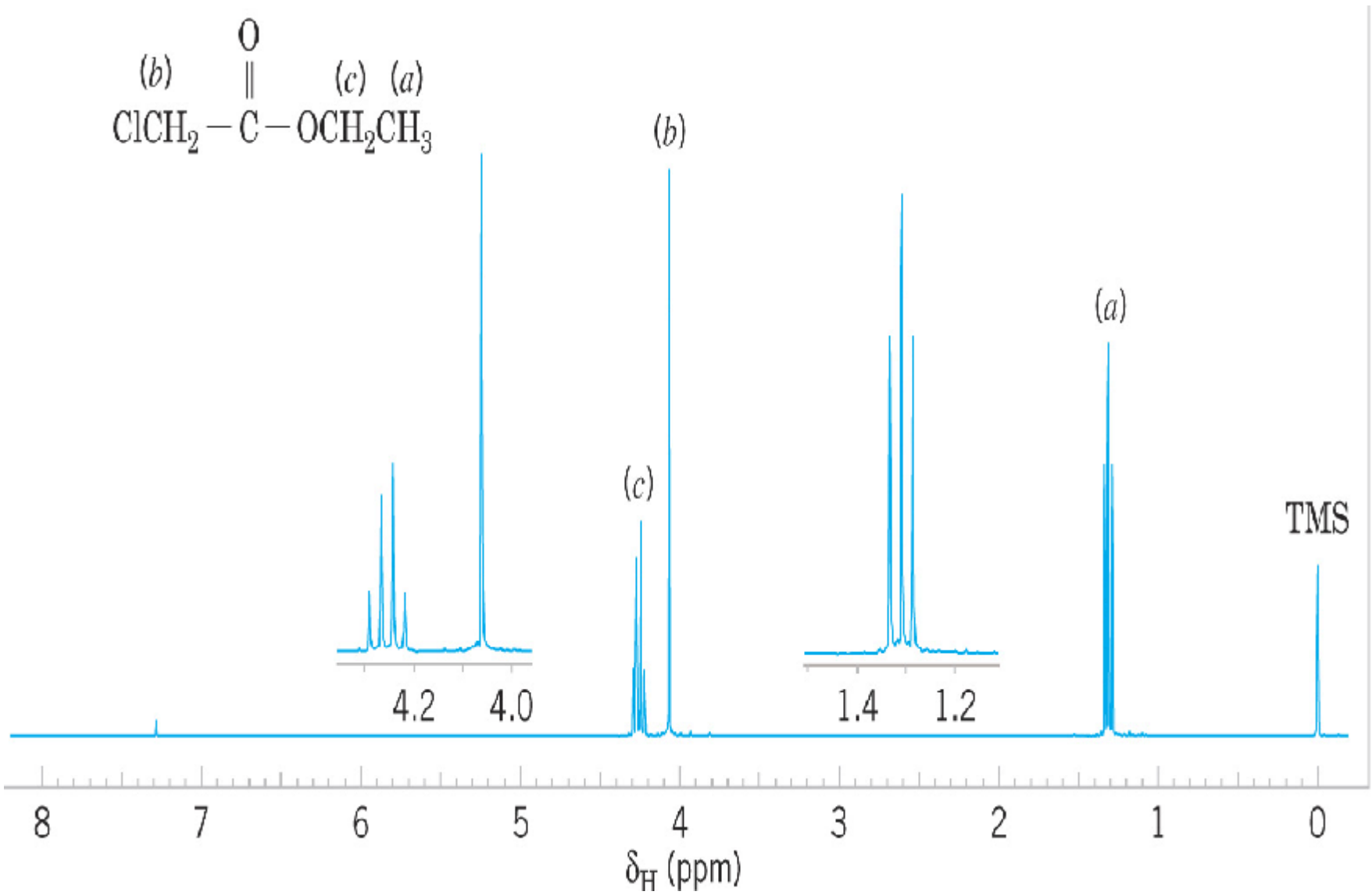

H_b H_a
C C
H_b
or
H_b H_a H_b
C C C
H_a
(signal in the absence of protons H_b)
(Protons H_b split the signal into a 1:2:1 triplet.)
(possible magnetic orientations of protons H_b)
J_{ab}
J_{ab}
Applied field, B_0


(a)
Cl H Cl
(b) H—C—C—C—H (b)
Cl Cl Cl
(b)
(a)
6.2
6.0
4.6
4.4
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

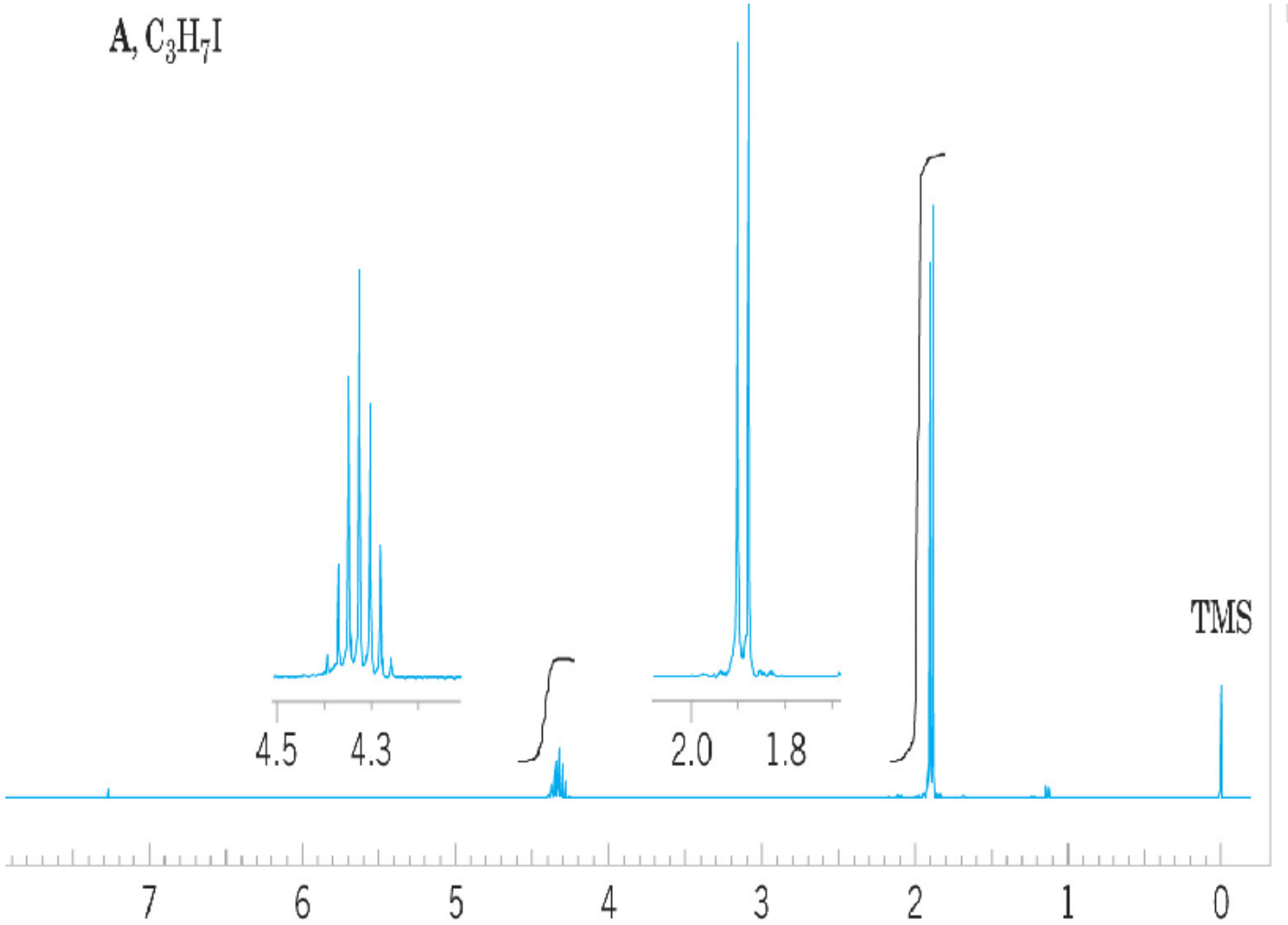

(a) (b) (c)
CH3—CH2—OH
(a)
(b)
(c)
TMS
4.0
3.8
3.6
1.4
1.2
1.0
8
7
6
5
4
3
2
1
0
δH (ppm)

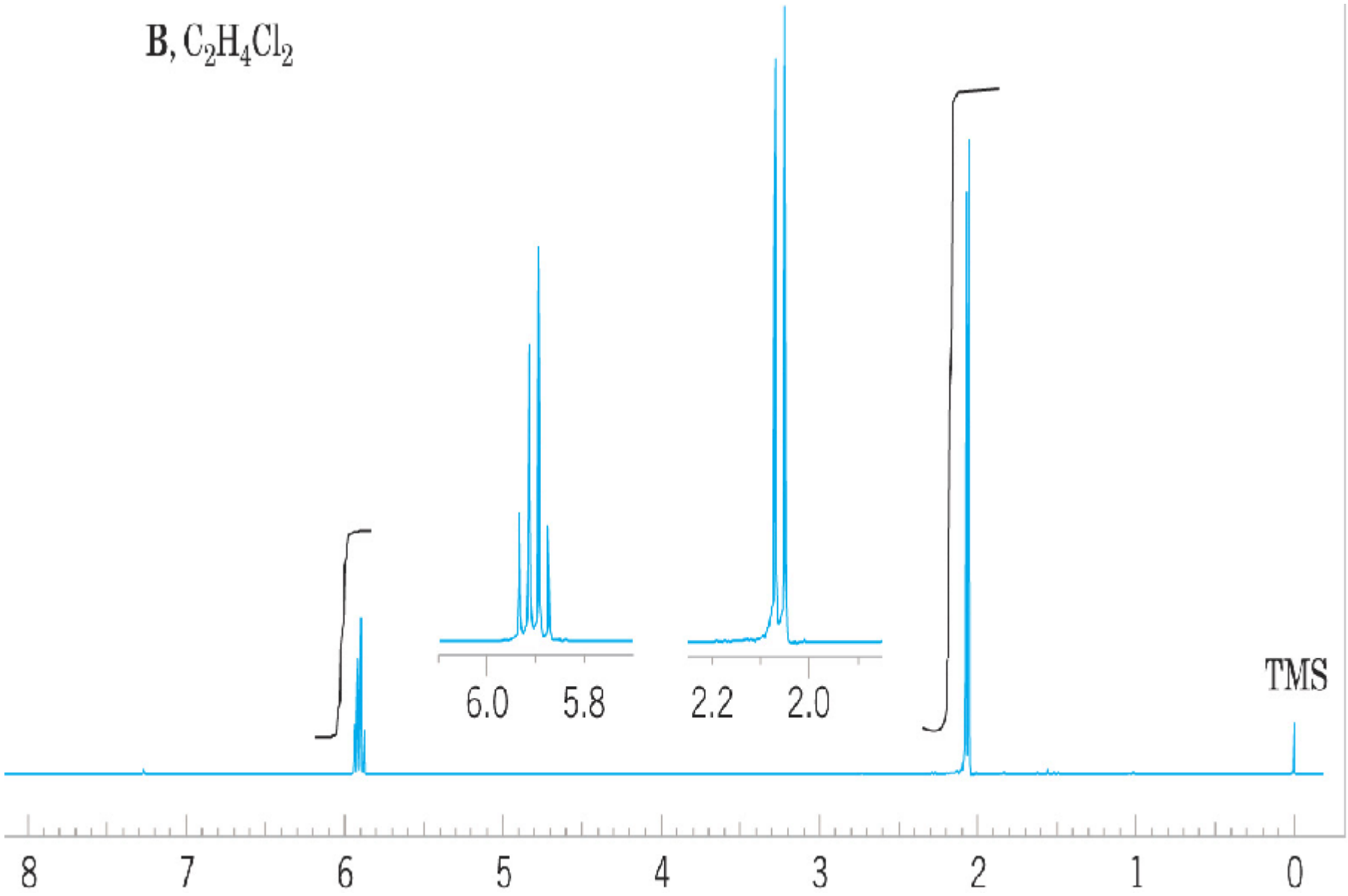

H_b H_a
X – C – C – H_a
H_b H_a
J_{ab} J_{ab} J_{ab}
Signal for H_b
J_{ab} J_{ab}
Signal for H_a


H_b H_a
H_b — C — C —
H_b
H_a
(signal in the absence of protons H_b)
(Protons H_b split the signal into a 1:3:3:1 quartet.)
J_{ab}
J_{ab}
J_{ab}
(possible magnetic orientations of protons H_b)
B_0


(b) O (c) (a)
ClCH2 – C – OCH2CH3
(b)
(c)
(a)
TMS
4.2
4.0
1.4
1.2
8
7
6
5
4
3
2
1
0
δH (ppm)

課堂練習：解析結構




B, $C_2H_4Cl_2$
6.0
5.8
2.2
2.0
TMS
8
7
6
5
4
3
2
1
0