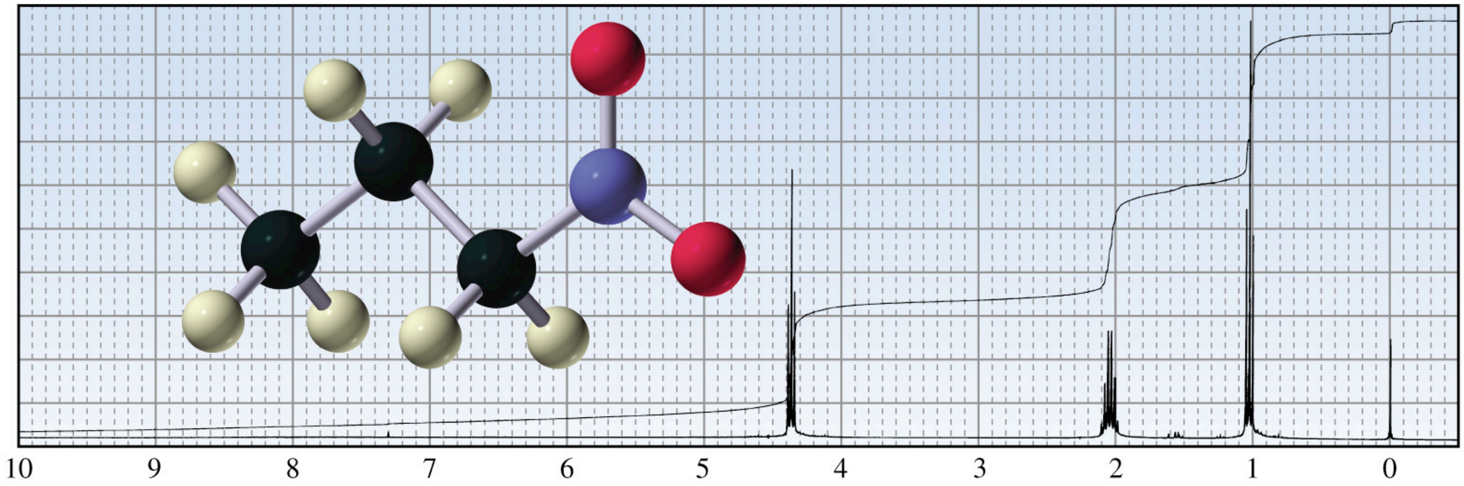
Aula 1

Espectroscopia de RMN

Organic Chemistry
4th Edition
Paula Yurkanis Bruice



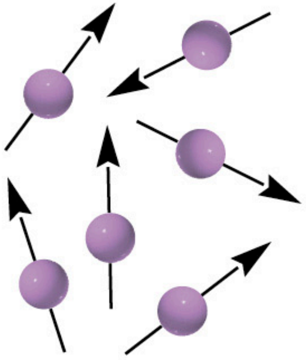
1-Nitropropane

Irene Lee
Case Western Reserve University
Cleveland, OH

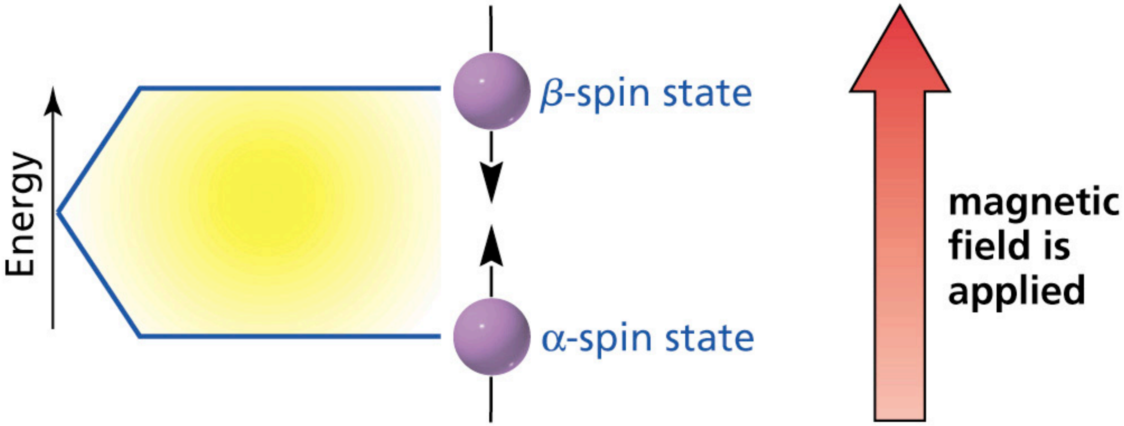
Ressonância Magnética Nuclear (RMN)

Identifica a estrutura carbono-hidrogênio de compostos orgânicos

O spin do núcleo é afetado por campos magnéticos

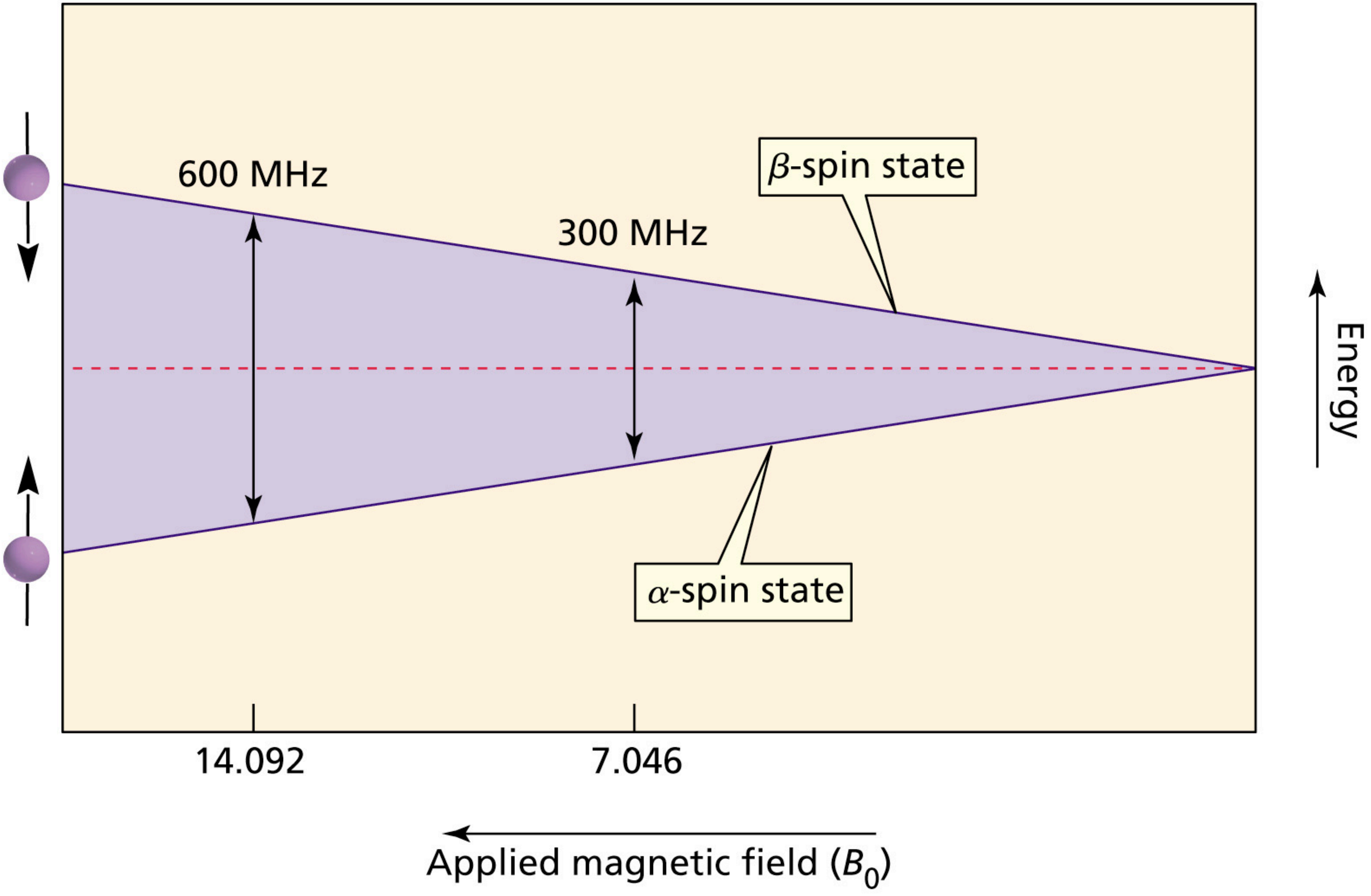


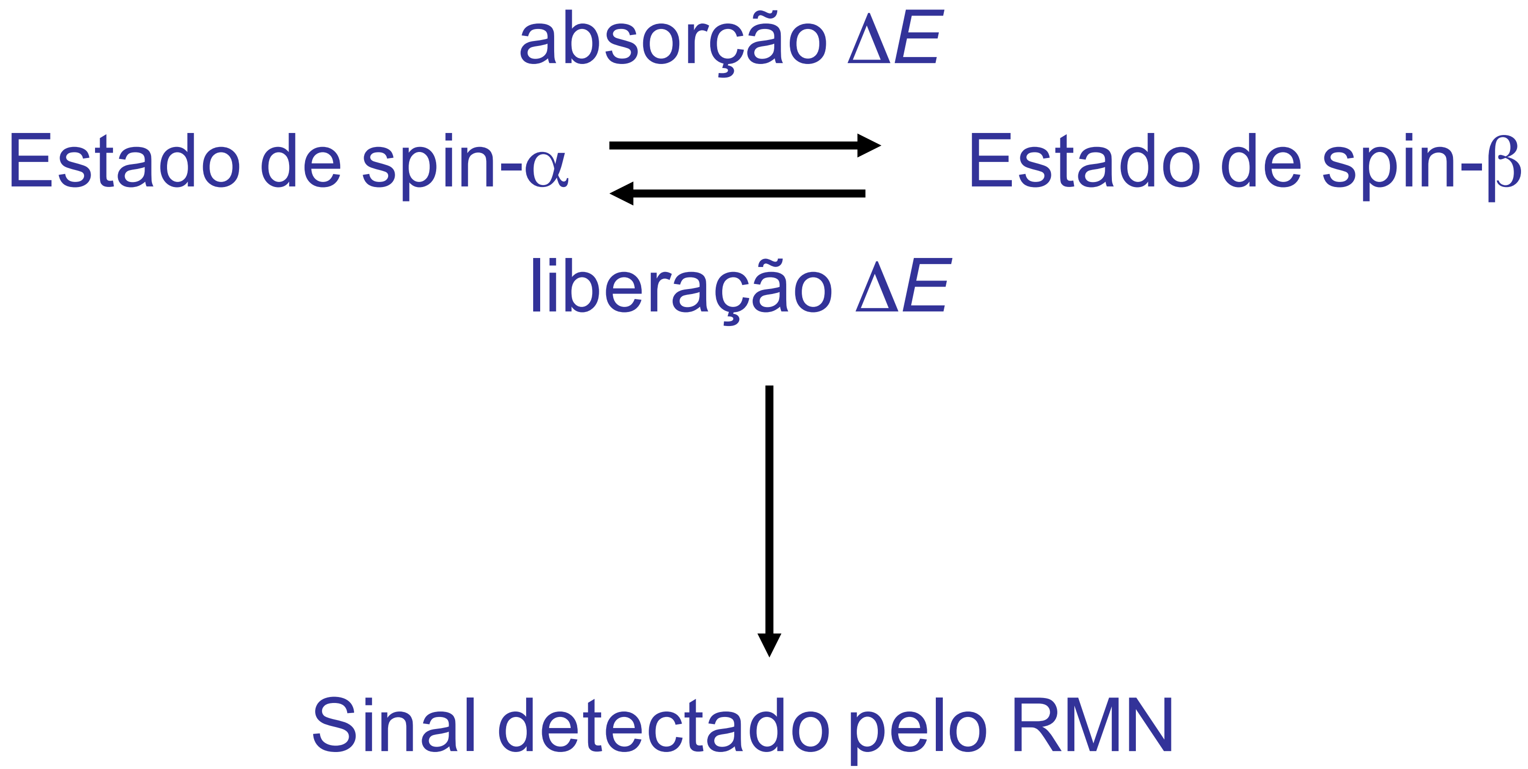
no applied
magnetic field



Todos os núcleos com número ímpar de prótons (^{1}H, ^{2}H, ^{14}N, ^{19}F, ^{31}P) ou neutrons (^{13}C) apresentam propriedades magnéticas. Somente núcleos com número de prótons e neutrons par (^{12}C, ^{16}O) não mostram propriedades magnéticas.

A diferença de energia entre dois estados de spin depende da força do campo magnético





absorção Δ*E*

Estado de spin-α ⇄ Estado de spin-β

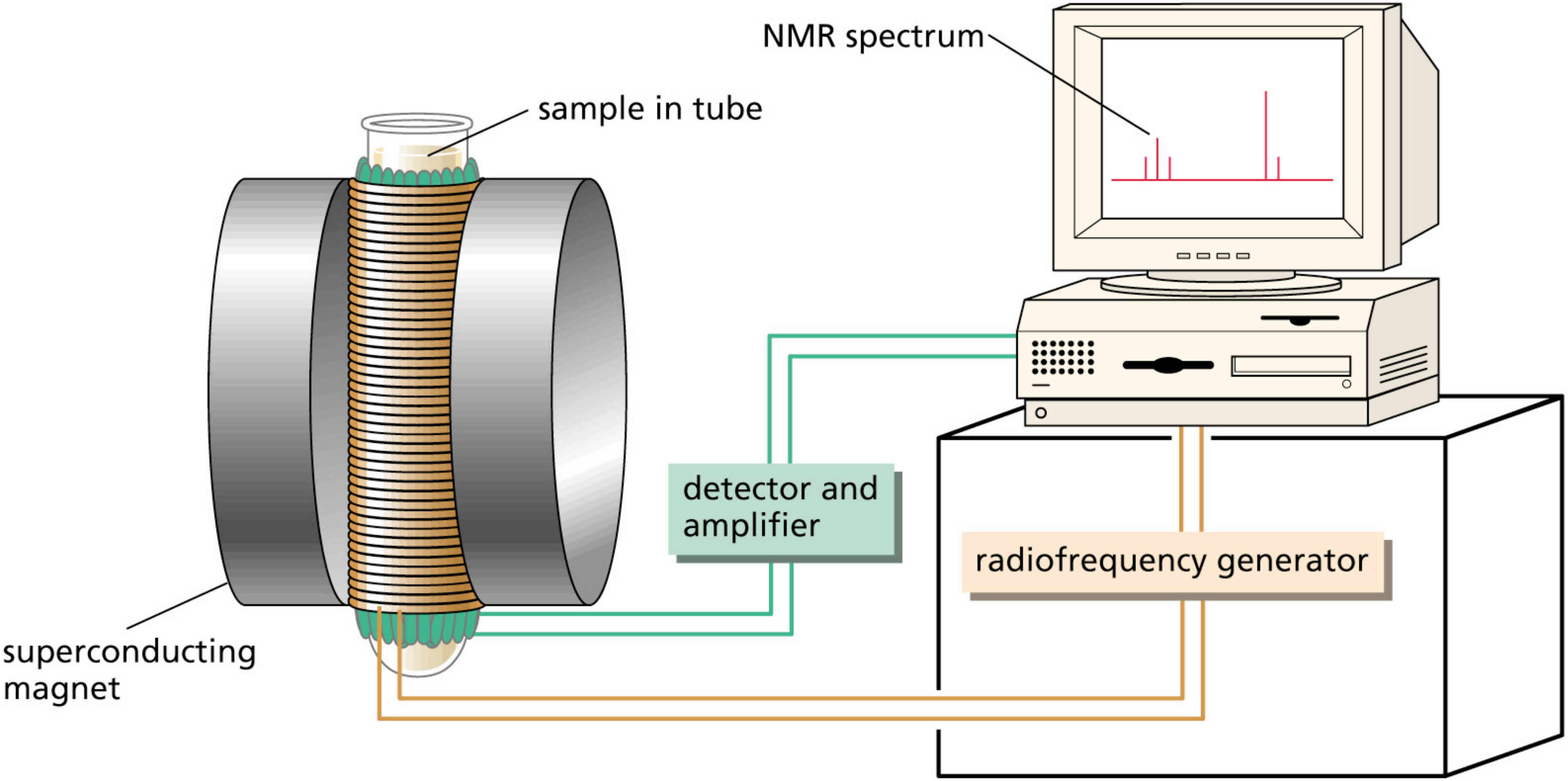
liberação Δ*E*

↓

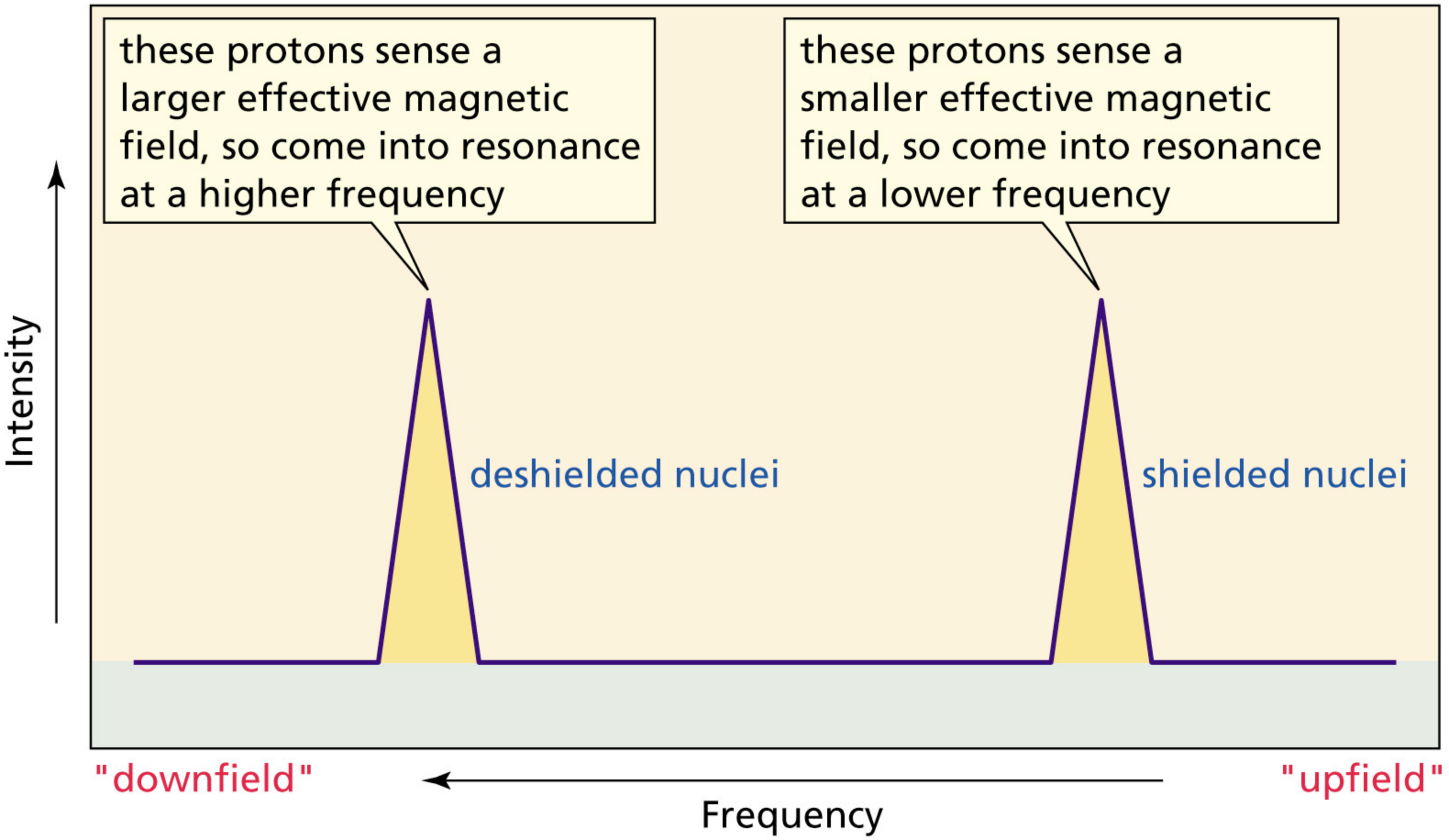
Sinal detectado pelo RMN

Alguns núcleos orientam-se na mesma direção do campo magnético outros na direção contrária

Um Espectrômetro de RMN



Os elétrons ao redor do núcleo afetam a intensidade do campo magnético “sentida” pelo núcleo

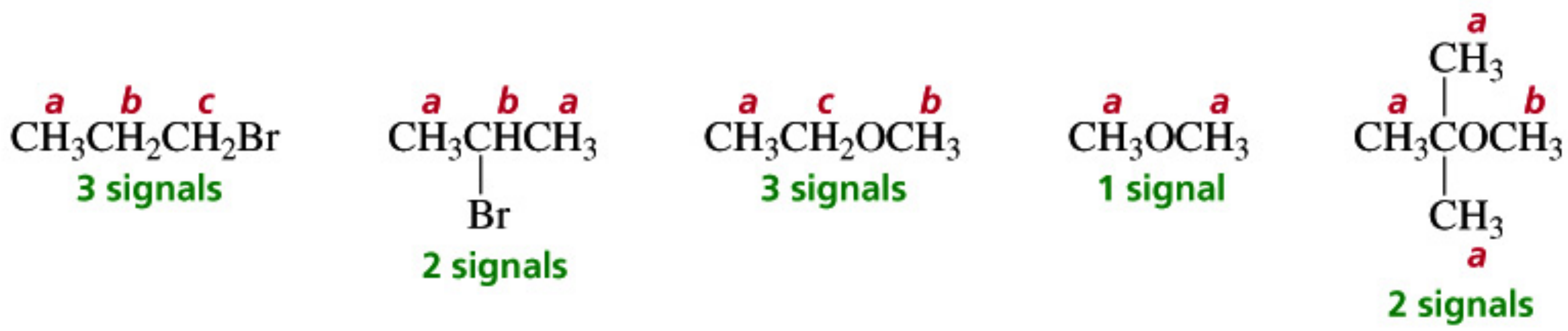


these protons sense a larger effective magnetic field, so come into resonance at a higher frequency

these protons sense a smaller effective magnetic field, so come into resonance at a lower frequency

Prótons quimicamente equivalentes: prótons no mesmo ambiente químico

Cada conjunto de prótons quimicamente equivalentes em um composto leva ao aparecimento de um sinal no espectro RMN-^{1}H do composto



$\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}Br$

3 signals

$\overset{a}{CH_3}\overset{b}{CH}(Br)\overset{a}{CH_3}$

2 signals

$\overset{a}{CH_3}\overset{c}{CH_2}O\overset{b}{CH_3}$

3 signals

$\overset{a}{CH_3}O\overset{a}{CH_3}$

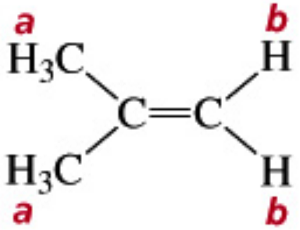
1 signal

$\overset{a}{CH_3}C(\overset{a}{CH_3})_2O\overset{b}{CH_3}$

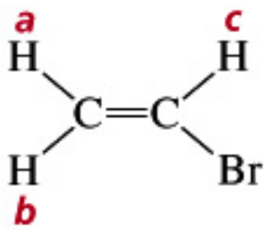
2 signals

$\overset{a}{CH_3}O\overset{b}{CH}Cl_2$

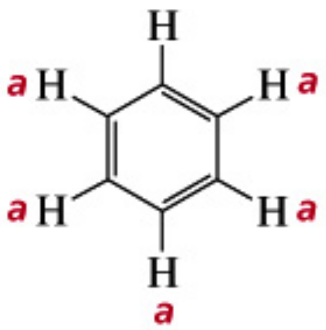
2 signals



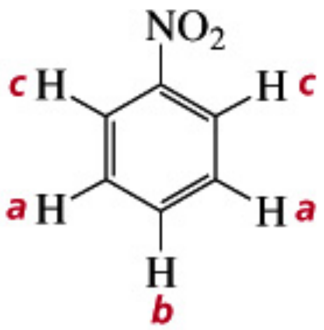
2 signals



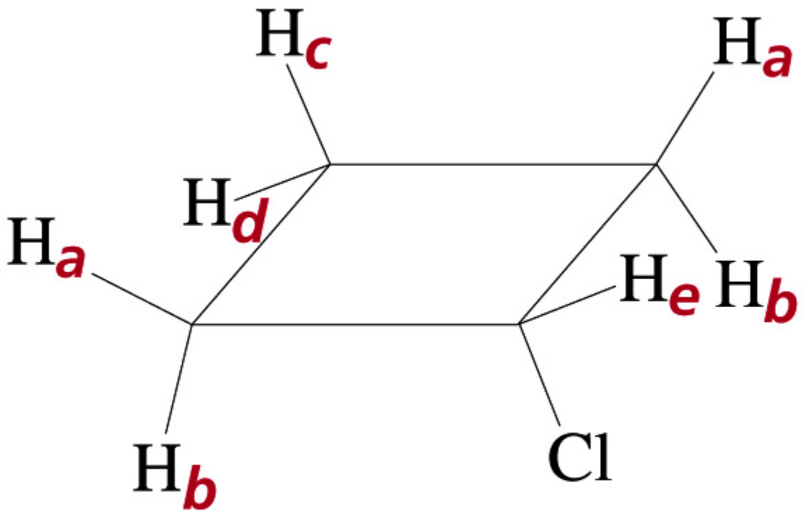
3 signals



1 signal



3 signals



chlorocyclobutane

the NMR spectrum has 5 signals

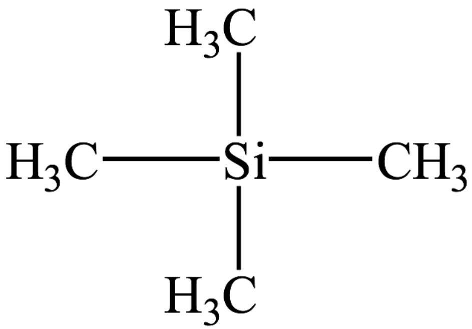
H_a and H_b are not equivalent

H_c and H_d are not equivalent

O Deslocamento Químico

O ponto de referência de um espectro de RMN é definido pelo sinal do TMS (zero ppm)

tetrametilsilano (TMS)



O deslocamento químico é uma medida da distância, em Hz, entre o sinal medido e o sinal de referência

A escala de deslocamento químico = δ

$$\delta = \frac{\text{distância do TMS em (Hz)}}{\text{freqüência de operação do aparelho (MHz)}}$$

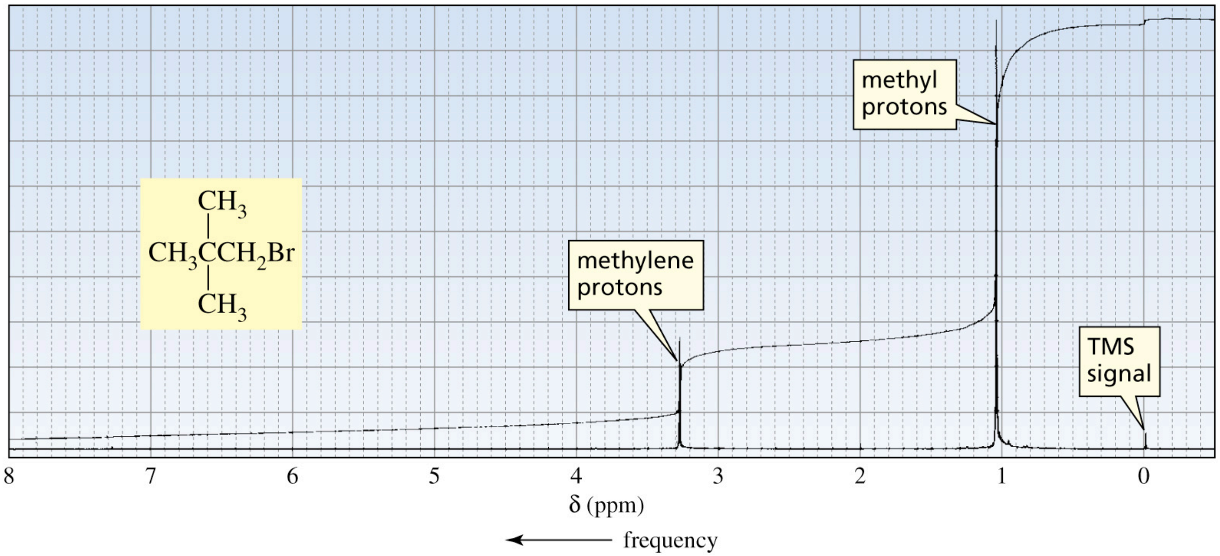
Integração

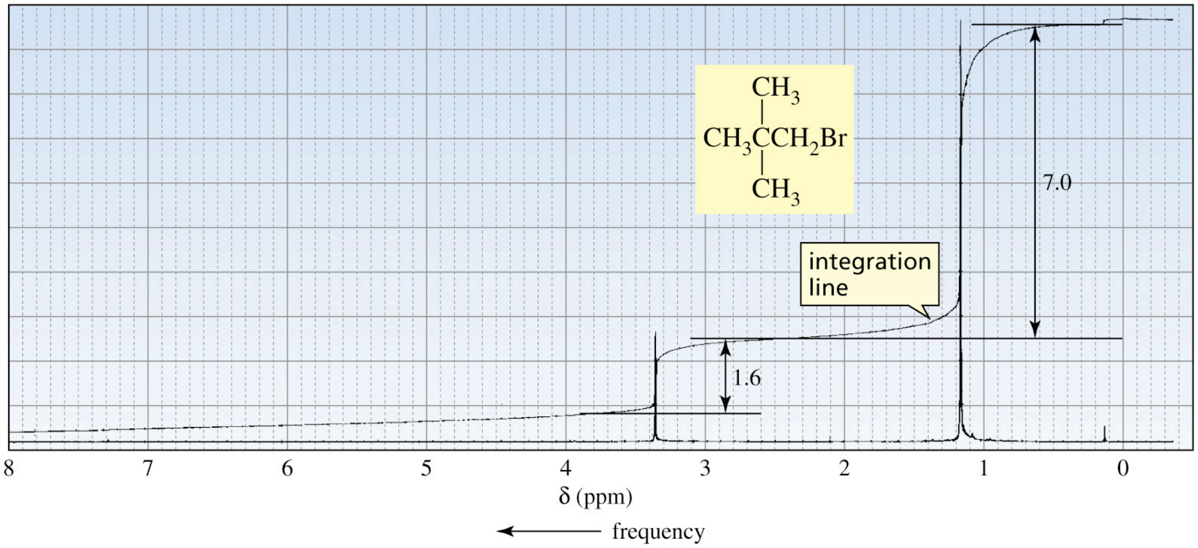
A área abaixo de cada sinal é proporcional ao número de prótons

A altura de cada integral é proporcional à área sob o sinal

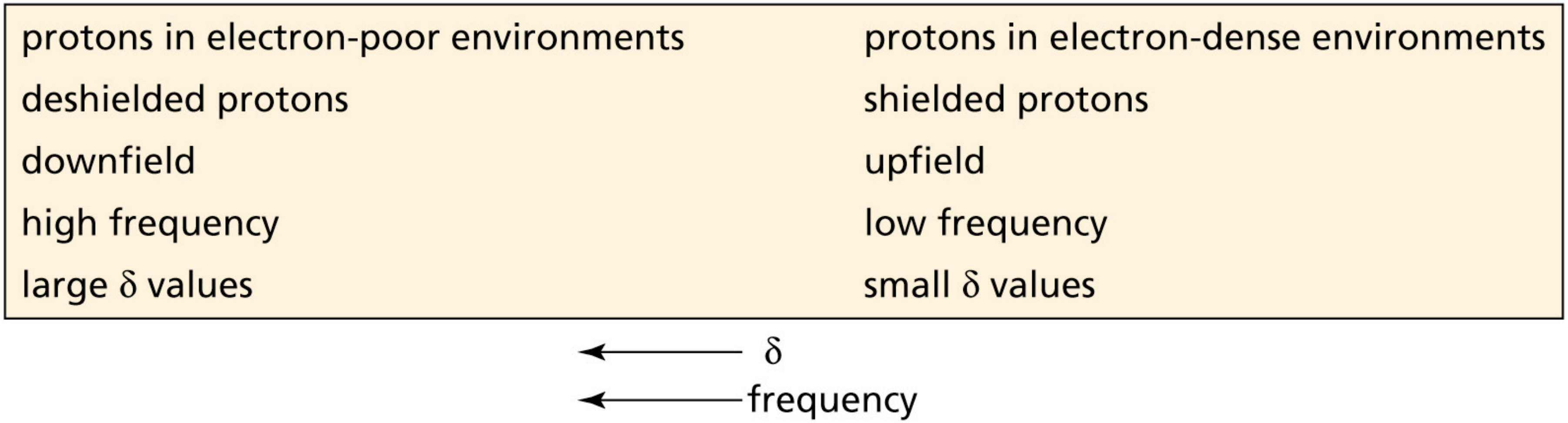
A integral nos diz o número relativo de prótons, mas não o absoluto

Espectro de RMN ^{1}H do 1-bromo-2,2-dimetilpropano





O deslocamento químico é independente da freqüência em que opera o espectrômetro



protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

← δ

← frequency

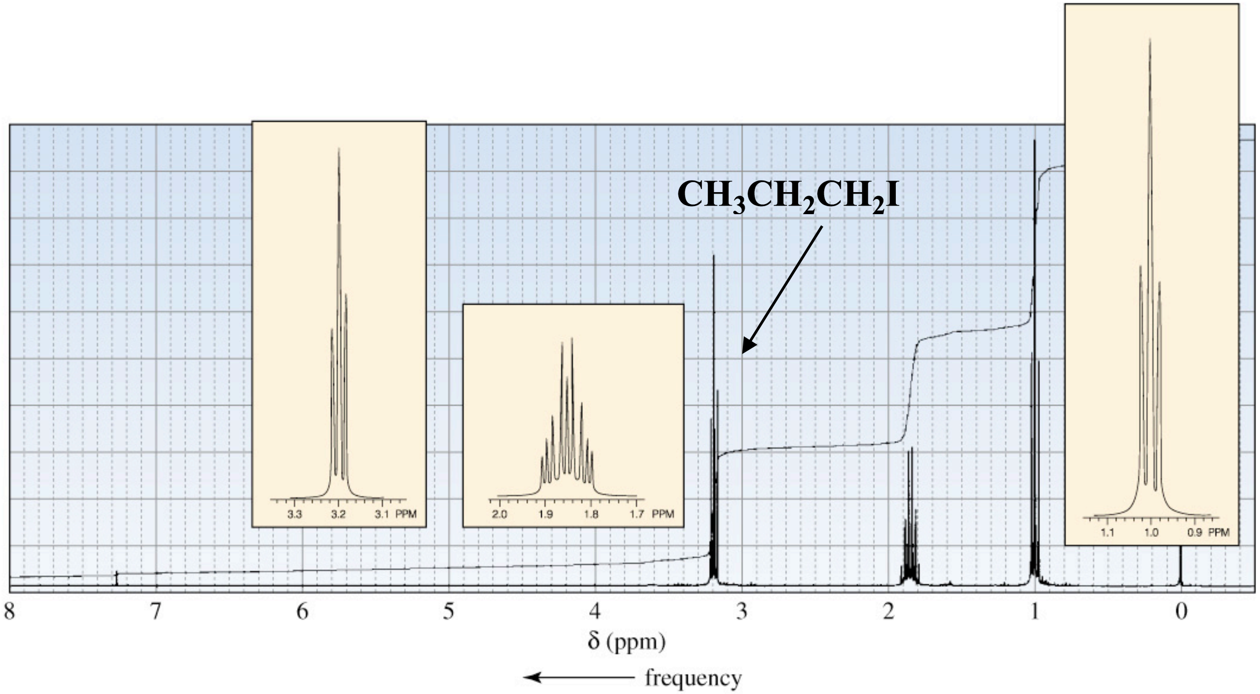
Grupos que sacam elétrons fazem com que os sinais de RMN apareçam em freqüências mais altas (maior δ)

$CH_3CH_2CH_2CH_2CH_2F$ 4.50 ppm

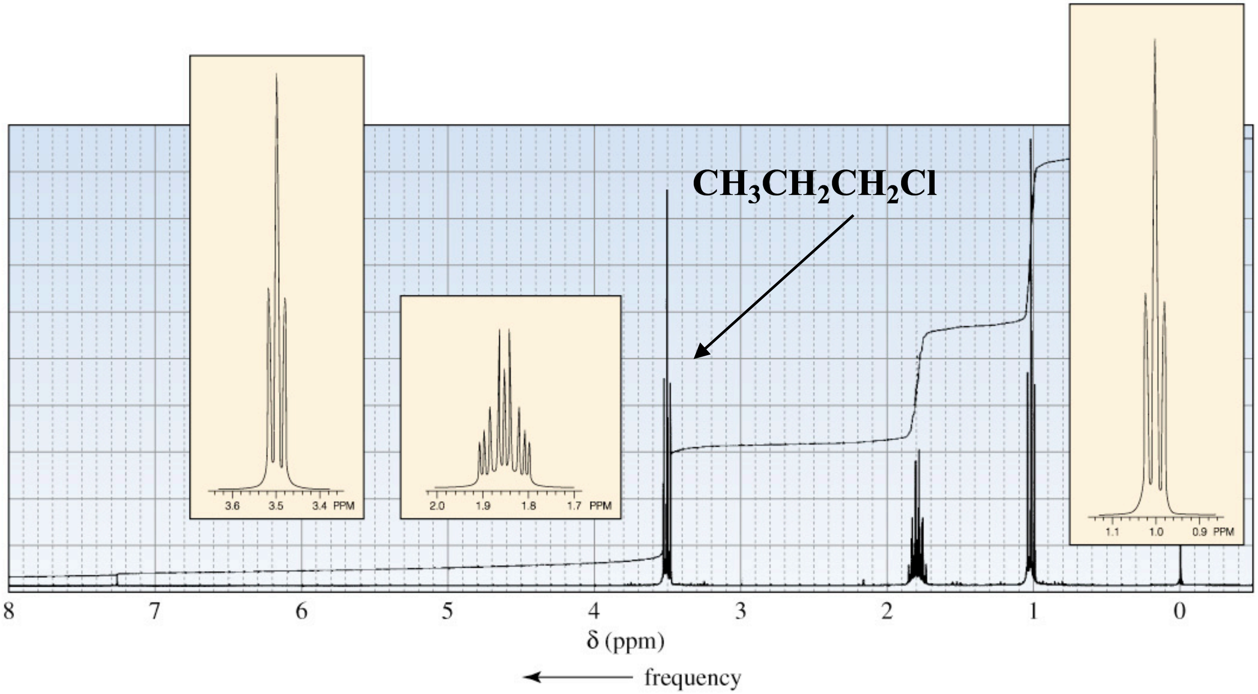
$CH_3CH_2CH_2CH_2CH_2Cl$ 3.50 ppm

$CH_3CH_2CH_2CH_2CH_2Br$ 3.40 ppm

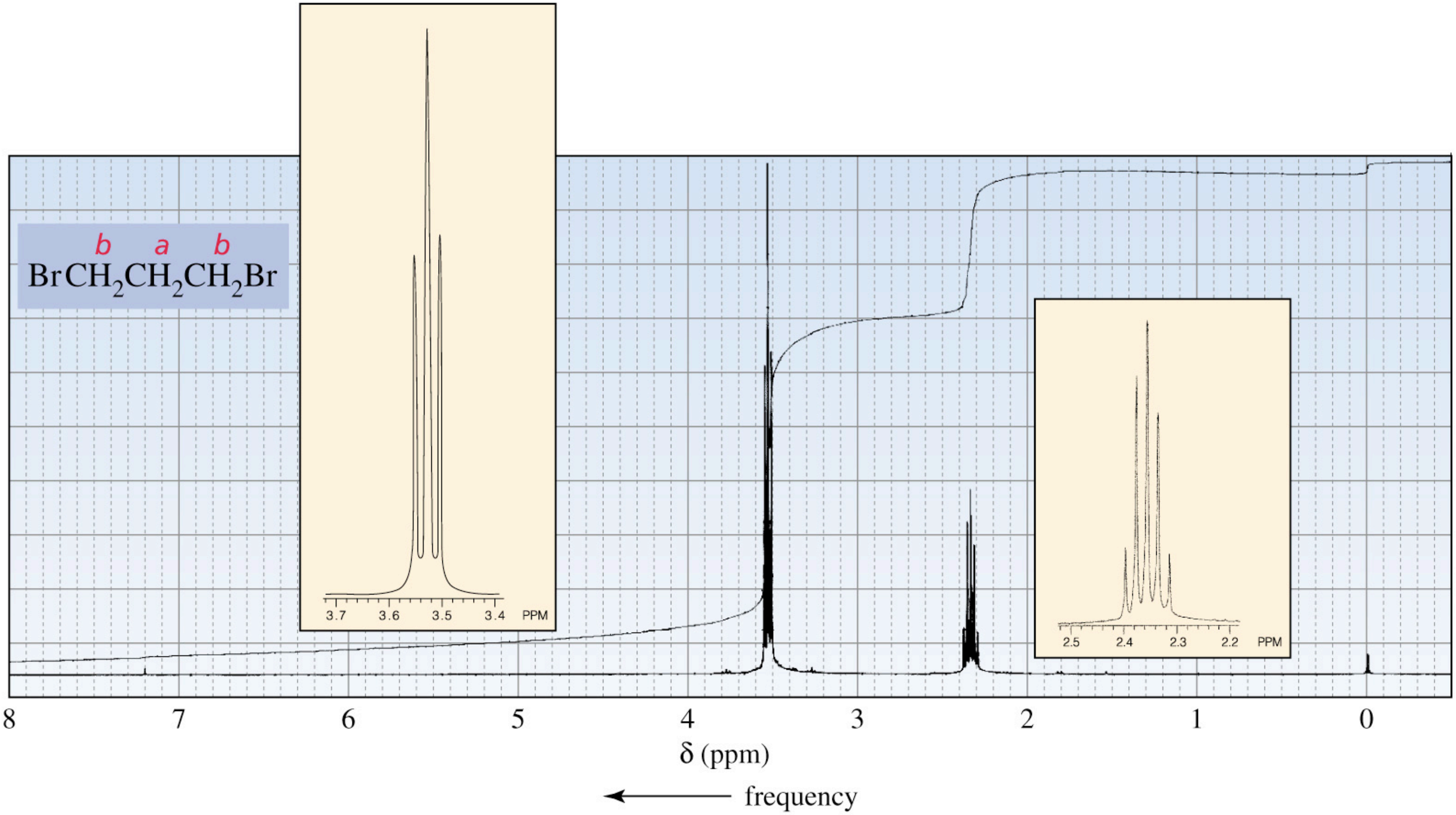
$CH_3CH_2CH_2CH_2CH_2I$ 3.20 ppm



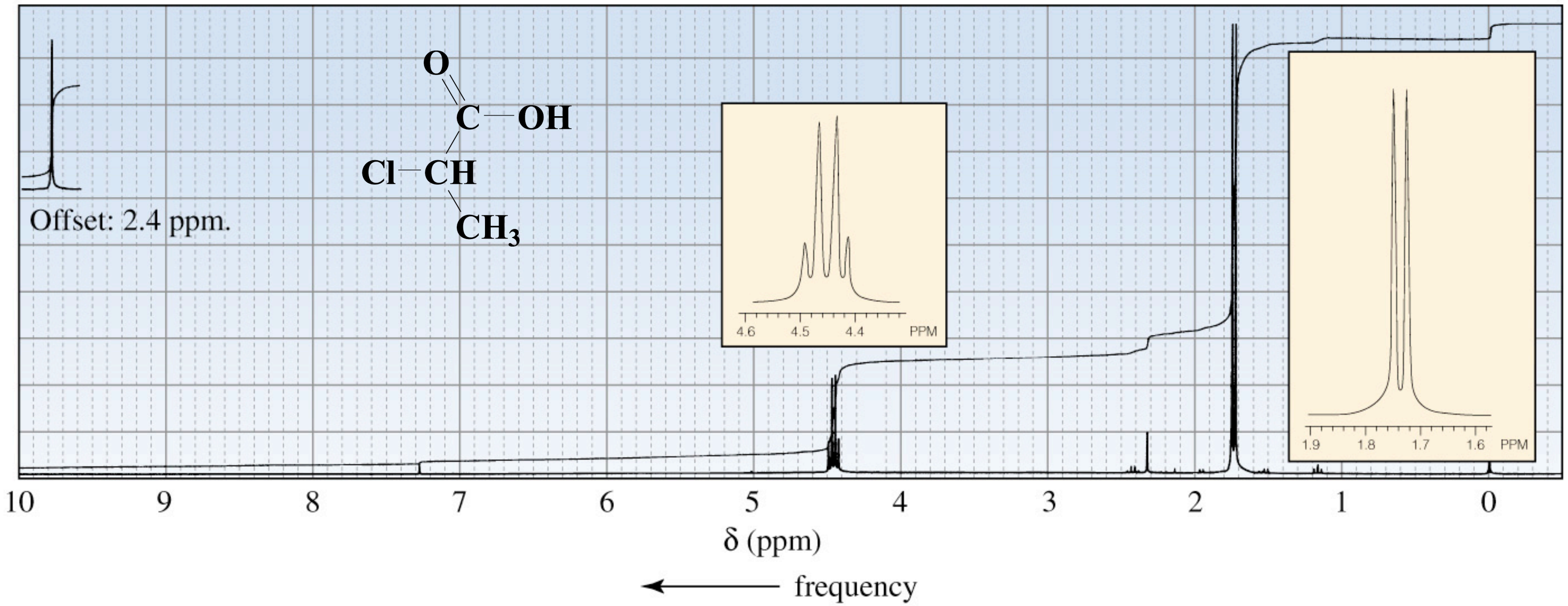
CH3CH2CH2I
3.3 3.2 3.1 PPM
2.0 1.9 1.8 1.7 PPM
1.1 1.0 0.9 PPM
8 7 6 5 4 3 2 1 0
δ (ppm)
frequency



CH3CH2CH2Cl
3.6 3.5 3.4 PPM
2.0 1.9 1.8 1.7 PPM
1.1 1.0 0.9 PPM
8 7 6 5 4 3 2 1 0
δ (ppm)
frequency

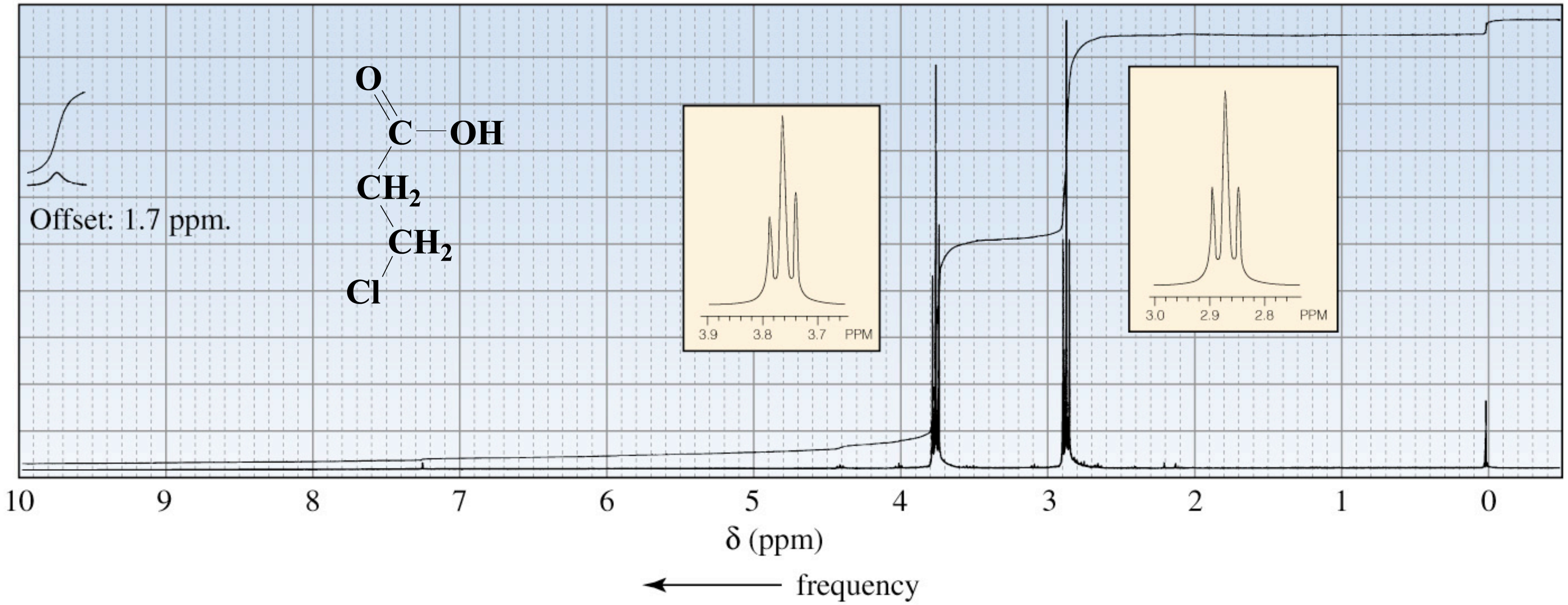

b a b
$BrCH_2CH_2CH_2Br$
3.7
3.6
3.5
3.4
PPM
2.5
2.4
2.3
2.2
PPM
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

a.

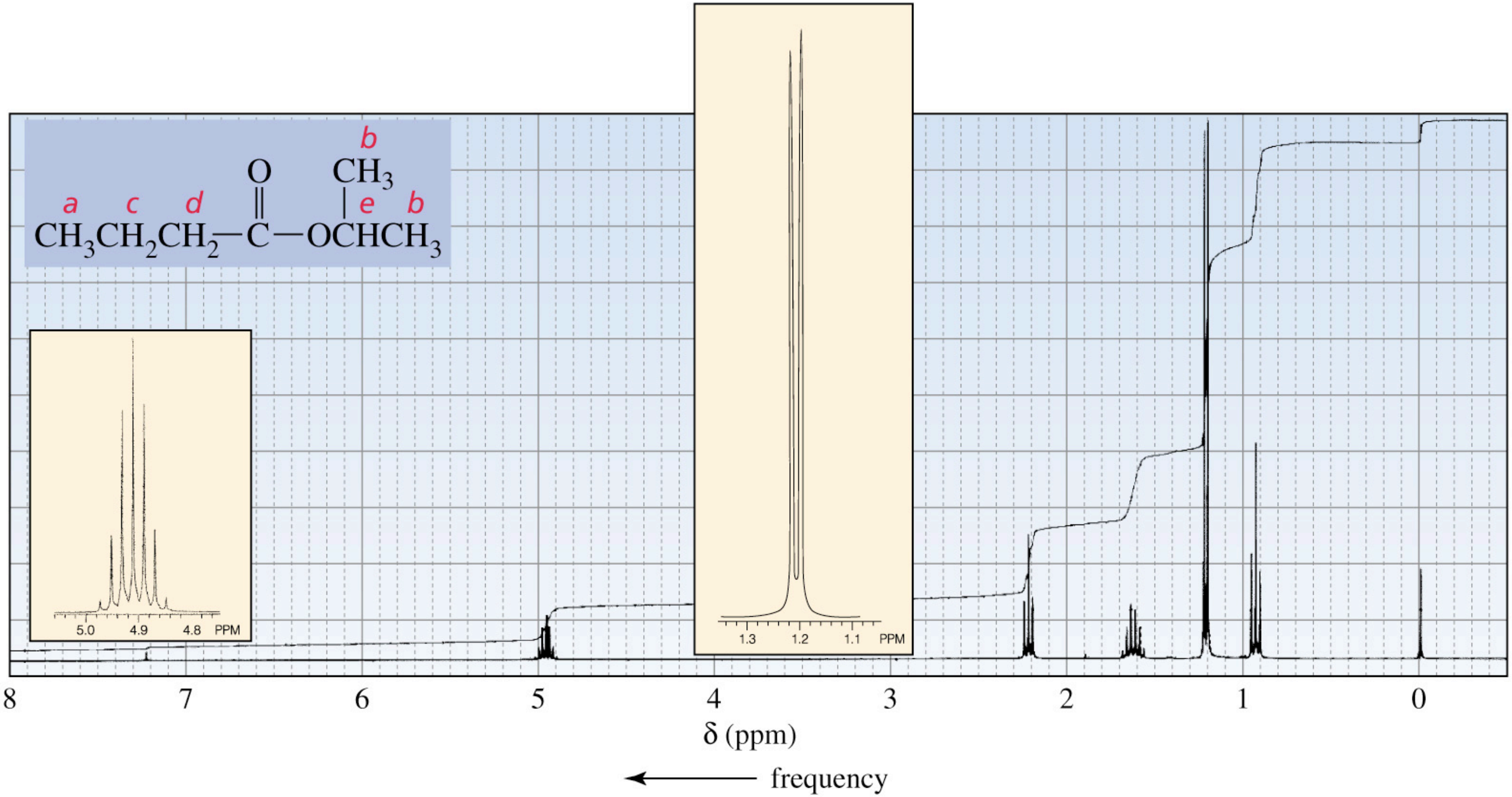


Offset: 2.4 ppm.
O
C
OH
Cl
CH
CH3
4.6
4.5
4.4
PPM
1.9
1.8
1.7
1.6
PPM
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

b.



Offset: 1.7 ppm.
O
C
OH
CH2
CH2
Cl
3.9
3.8
3.7
PPM
3.0
2.9
2.8
PPM
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency



b
CH3
O
a c d | e b
CH3CH2CH2—C—OCHCH3
5.0
4.9
4.8
PPM
1.3
1.2
1.1
PPM
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

Valores Característicos de Deslocamento Químico

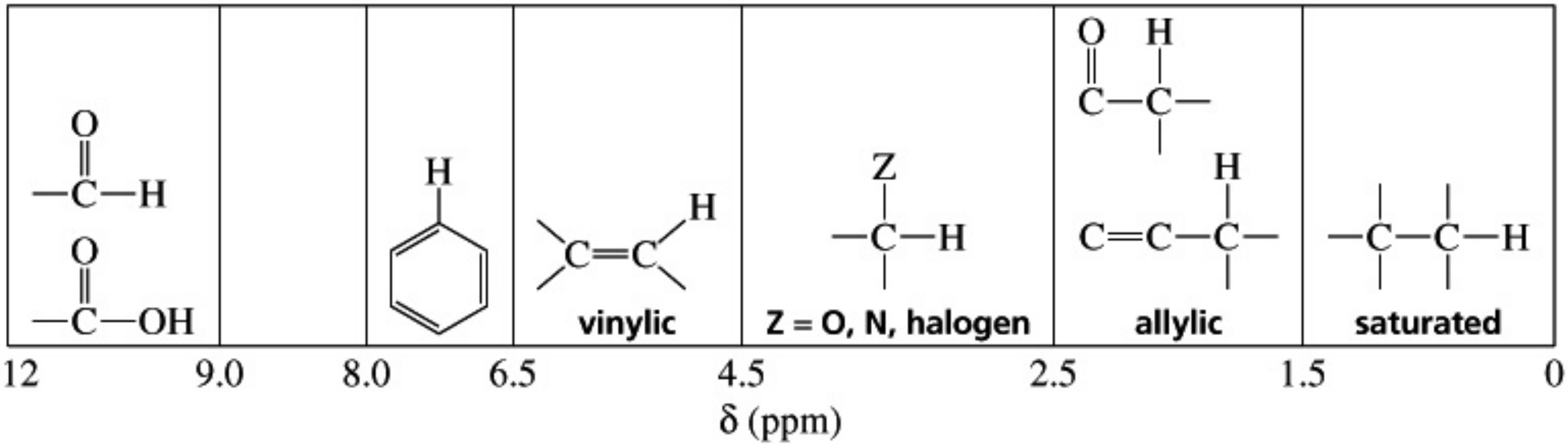
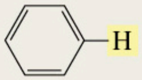
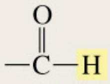
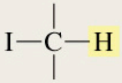
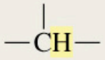
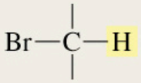
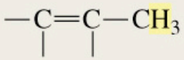
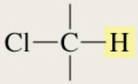
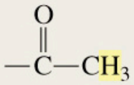
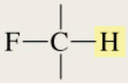
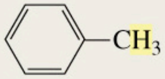
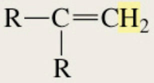
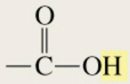
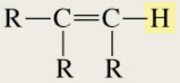
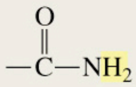


Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0		6.5–8
$-CH_3$	0.9	 $-\overset{O}{\overset{\|}{C}}-H$	9.0–10
$-CH_2-$	1.3	 $I-\underset{\|}{\overset{\|}{C}}-H$	2.5–4
 $-\overset{\|}{C}H-$	1.4	 $Br-\underset{\|}{\overset{\|}{C}}-H$	2.5–4
 $-\underset{\|}{C}=\underset{\|}{C}-CH_3$	1.7	 $Cl-\underset{\|}{\overset{\|}{C}}-H$	3–4
 $-\overset{O}{\overset{\|}{C}}-CH_3$	2.1	 $F-\underset{\|}{\overset{\|}{C}}-H$	4–4.5
	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	ArOH	Variable, 4–7
 $R-\underset{R}{\underset{\|}{C}}=CH_2$	4.7	 $-\overset{O}{\overset{\|}{C}}-OH$	Variable, 10–12
 $R-\underset{R}{\underset{\|}{C}}=\underset{R}{\underset{\|}{C}}-H$	5.3	 $-\overset{O}{\overset{\|}{C}}-NH_2$	Variable, 5–8

[a] The values are approximate because they are affected by neighboring substituents.

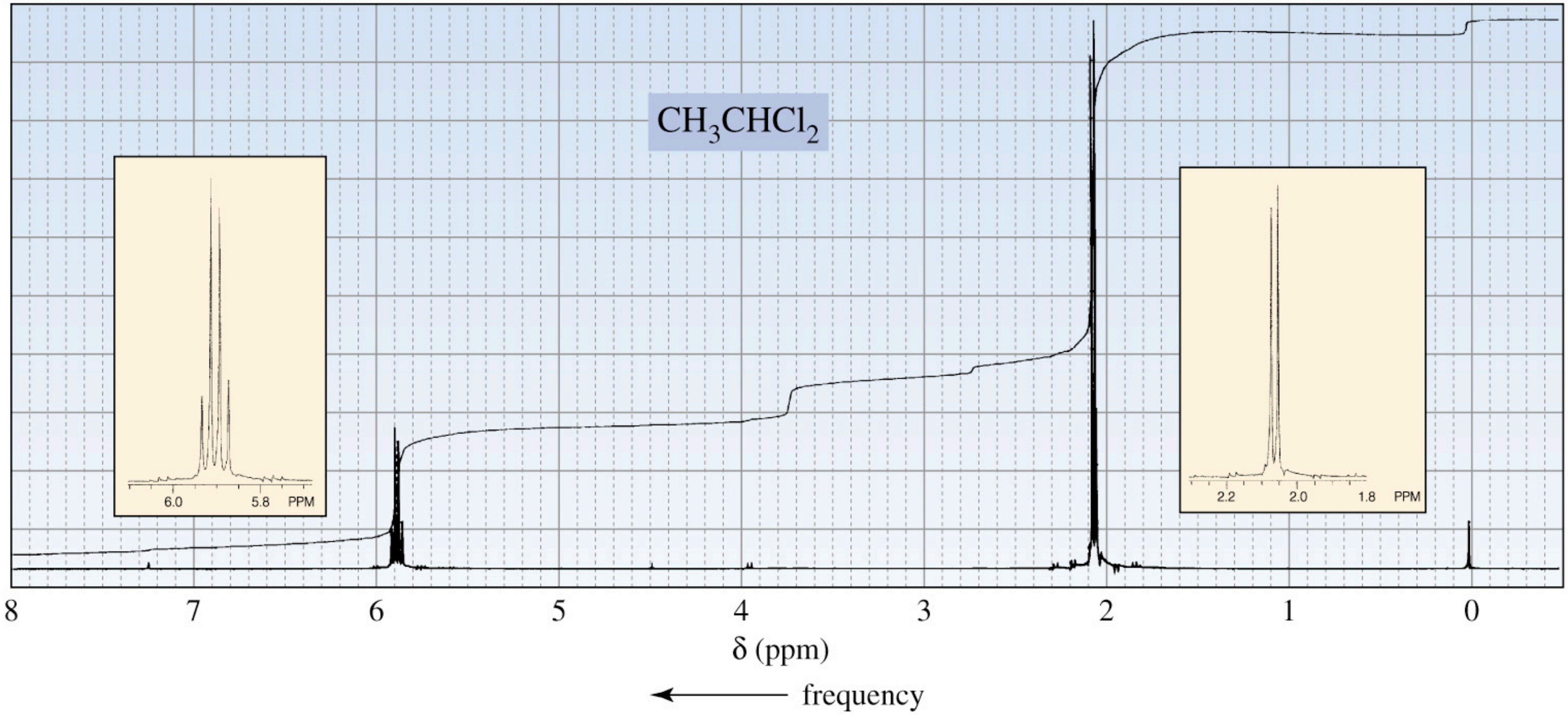
Desdobramento de Sinais

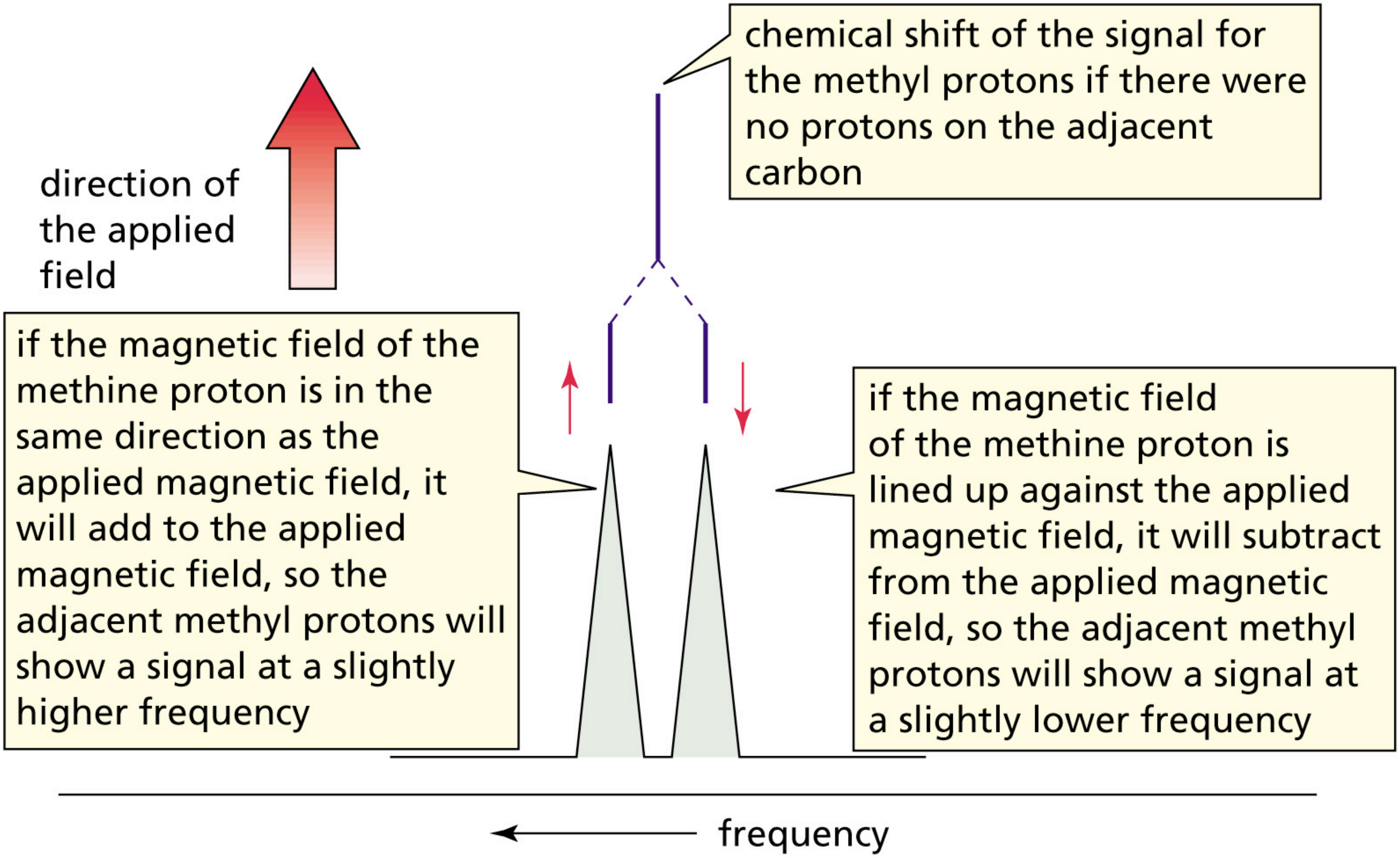
- Um sinal de RMN ^{1}H desdobra-se em *N* + 1 picos, onde *N* é o número de prótons equivalentes ligados aos carbonos adjacentes

- O número de picos em um sinal é chamado multiplicidade (singlete, dublete, triplete, etc)

- O desdobramento de sinais, causado pelo acomplamento spin-spin, ocorre quando diferentes tipos de prótons estão próximos entre si

Espectro de RMN ^{1}H do 1,1-dicloroetano





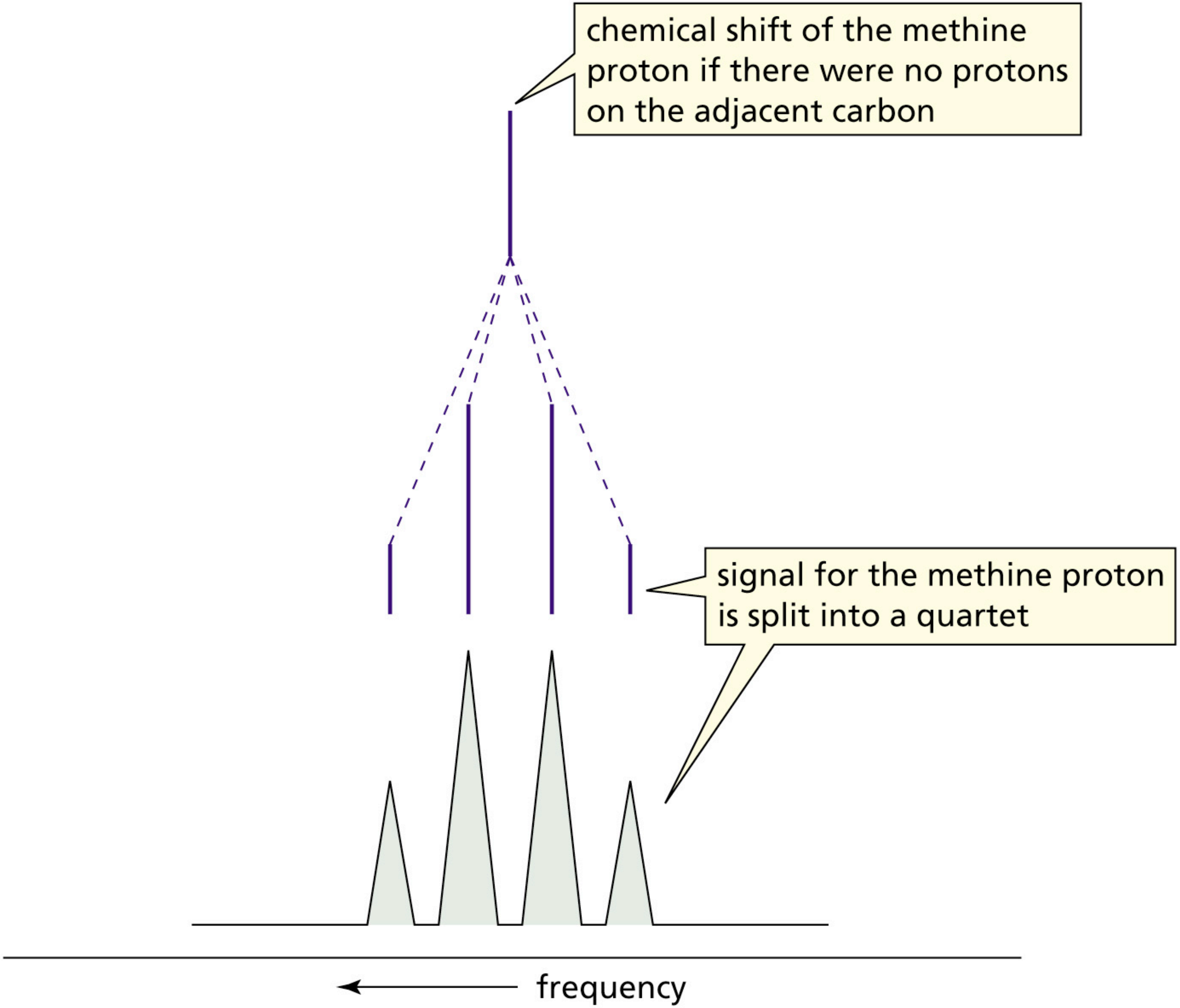
direction of the applied field

chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon

if the magnetic field of the methine proton is in the same direction as the applied magnetic field, it will add to the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly higher frequency

if the magnetic field of the methine proton is lined up against the applied magnetic field, it will subtract from the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly lower frequency

frequency



chemical shift of the methine proton if there were no protons on the adjacent carbon

signal for the methine proton is split into a quartet

Os modos que os três prótons podem se alinhar frente ao campo magnético

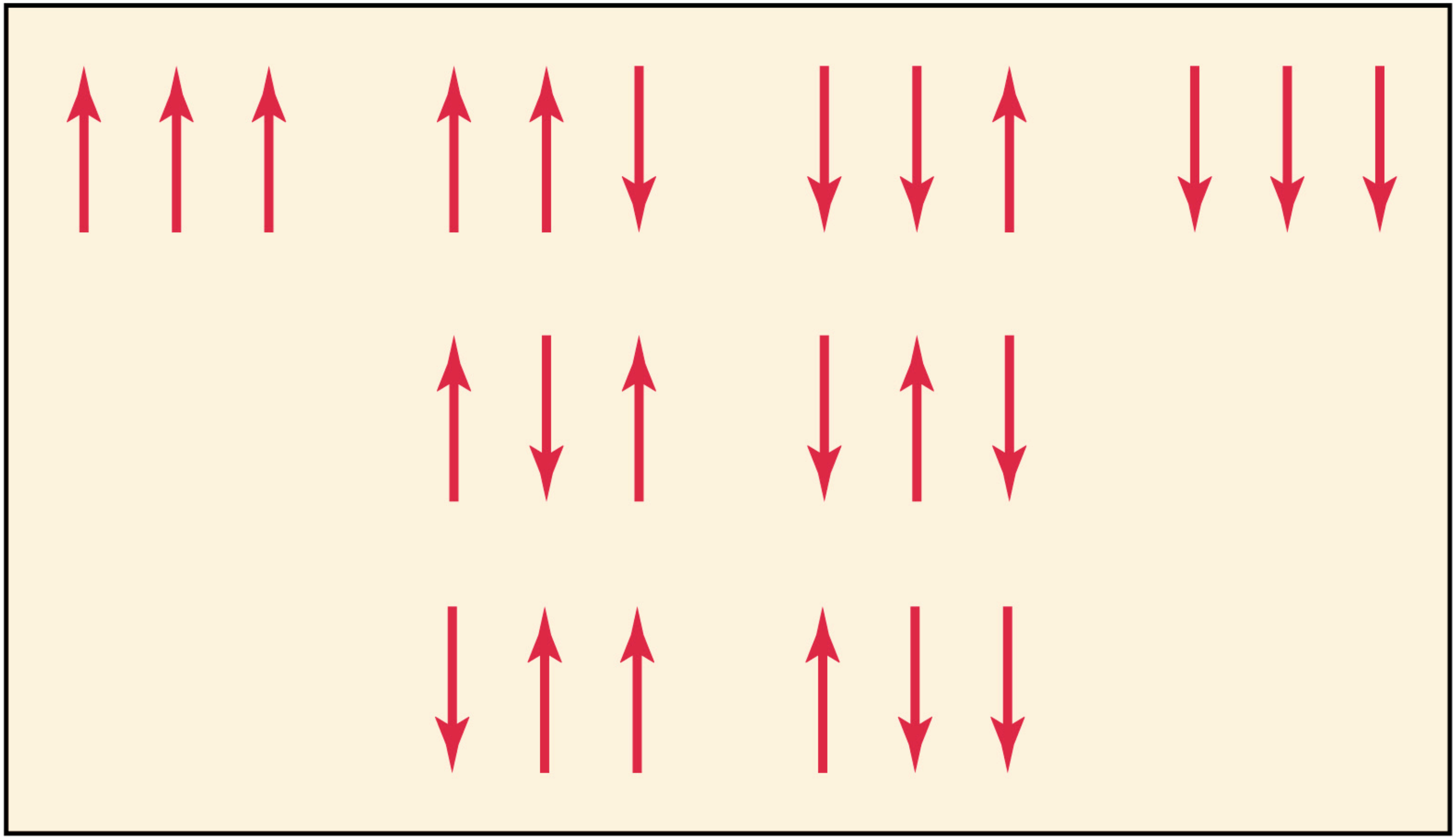
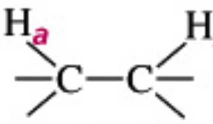


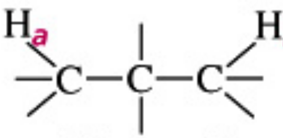
Table 14.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	sextet	1:5:10:10:5:1
6	septet	1:6:15:20:15:6:1

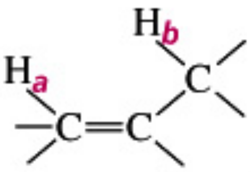
O desdobramento não são observados se os prótons estão separados por mais do que três ligações σ



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

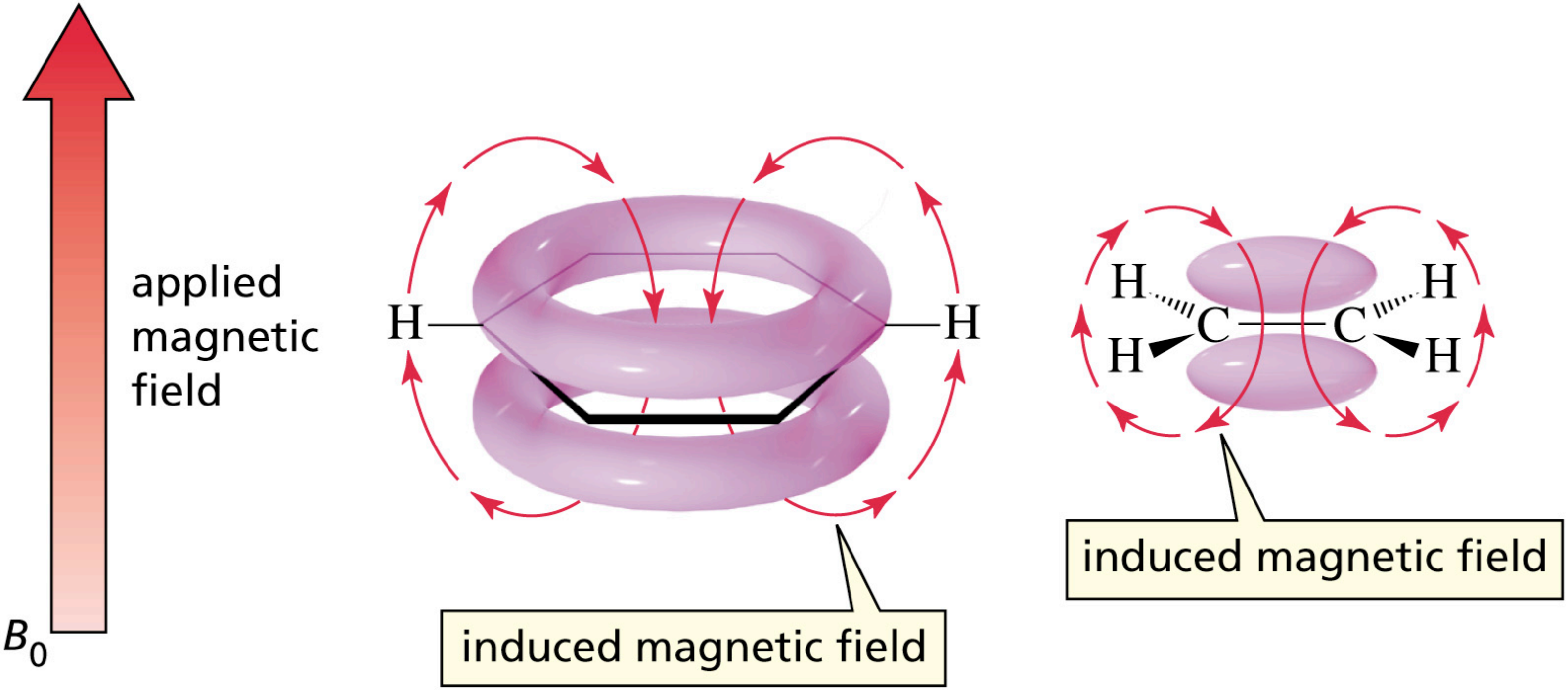


H_a and H_b may split each other because they are separated by 4 bonds including one double bond

Acoplamentos de longo alcance ocorrem quando os prótons estão separados por mais do que três ligações σ, porém com ligações duplas ou triplas

Anisotropia Diamagnética

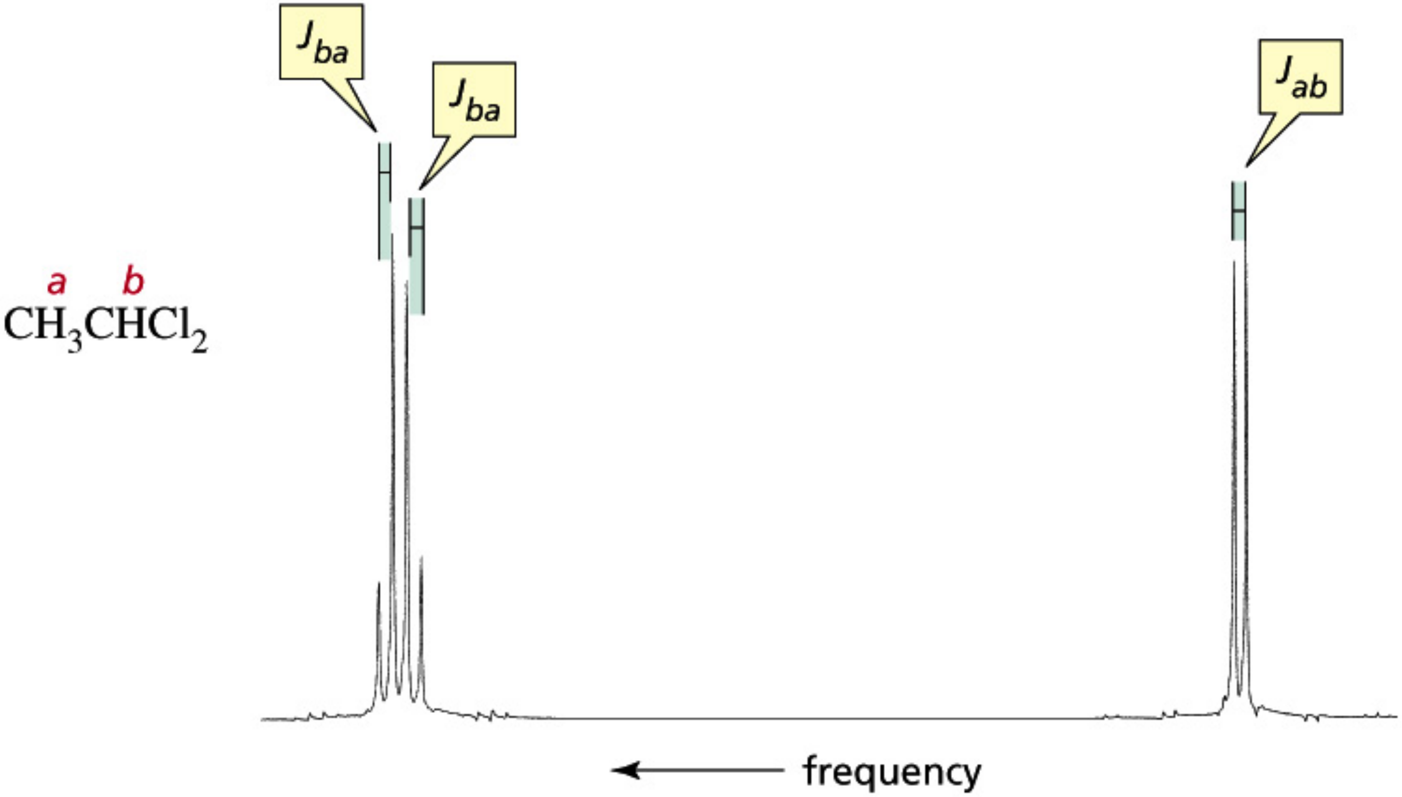
Elétrons π são menos atraídos pelo núcleo do que elétrons σ; eles são mais livres para se mover em resposta ao campo magnético



Isto causa um deslocamento químico incomum de hidrogênios ligados à carbonos que formam ligações π

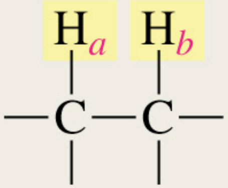
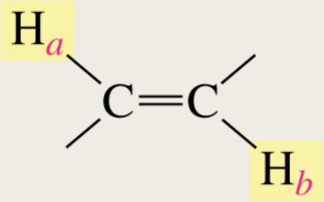
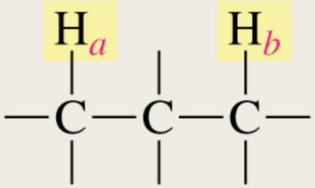
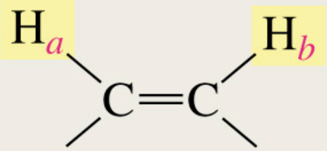
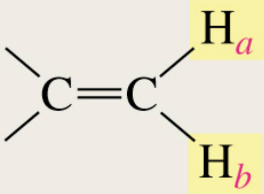
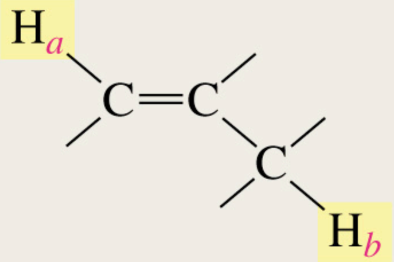
Constantes de Acoplamento

A constante de acoplamento (*J*) é a distância entre dois picos adjacentes de um desdobramento de sinal de RMN, medido em Hertz

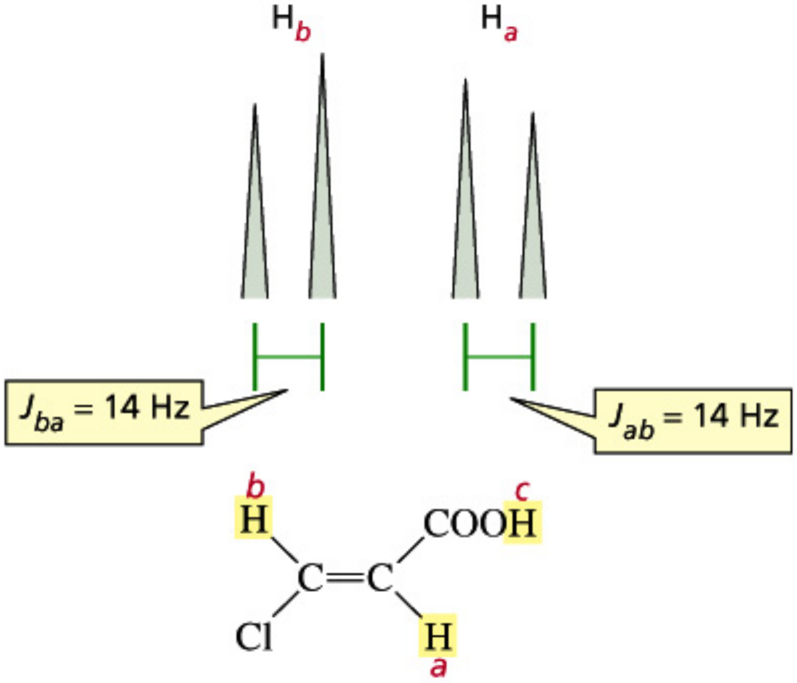


Prótons acoplados têm a mesma constante de acoplamento

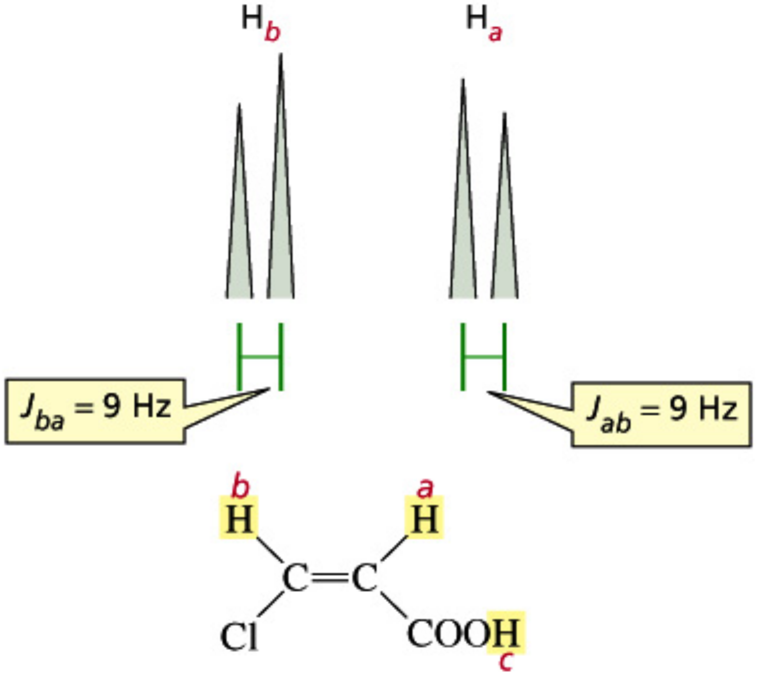
Table 14.3 Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
	7		15 (trans)
	0		10 (cis)
	2 (geminal coupling)		1 (long-range coupling)

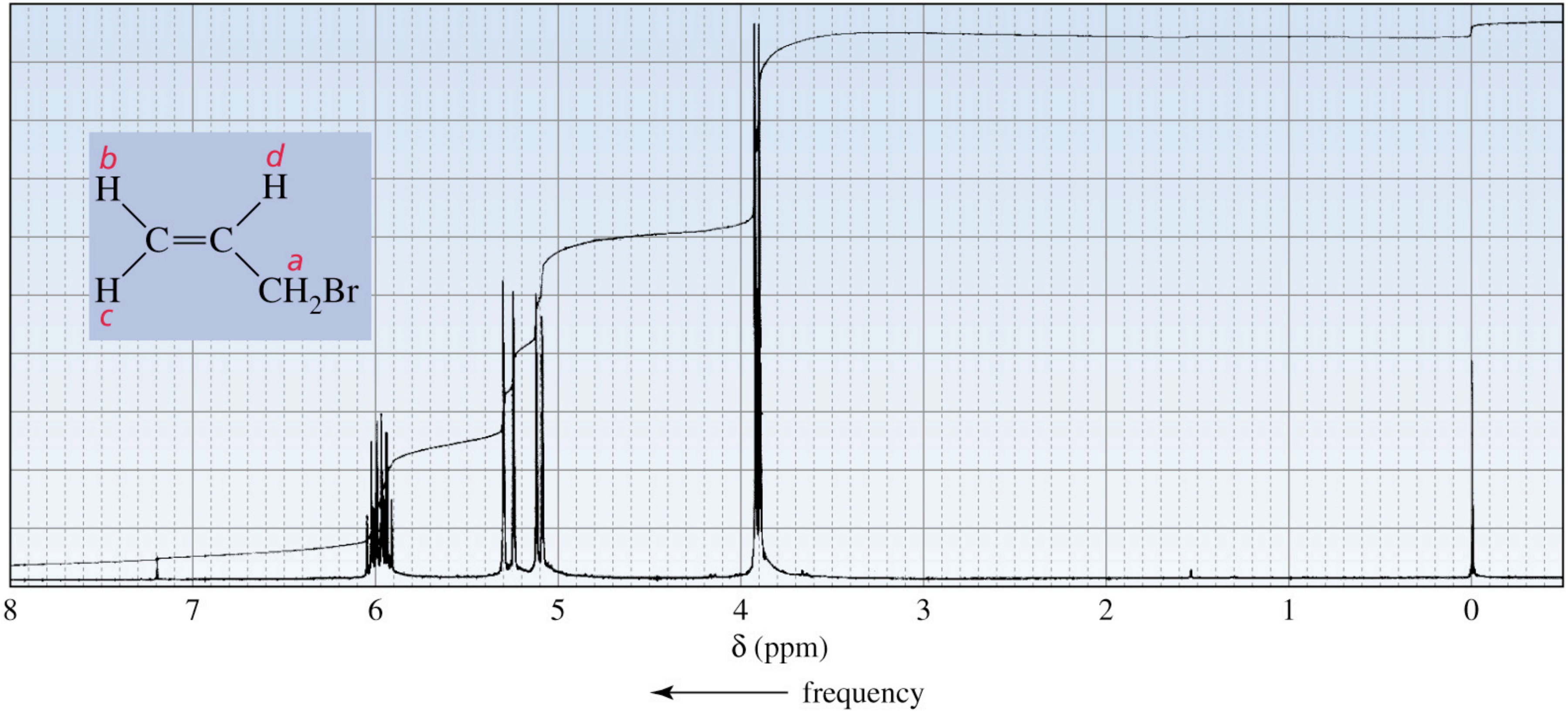
A constante de acoplamento trans é maior do que a cis



trans-3-chloropropenoic acid

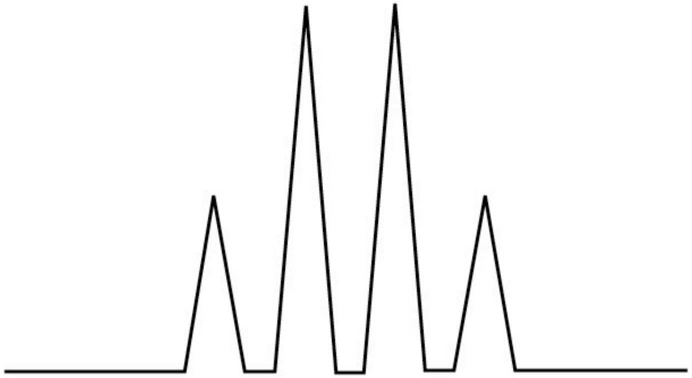


cis-3-chloropropenoic acid



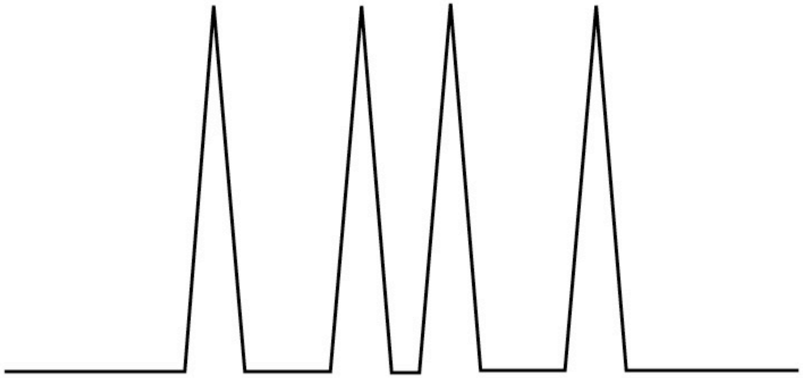
Os três prótons vinílicos estão em freqüência relativamente alta, devido a anisotropia diamagnética

Diferença Entre um Quarteto e um Duplo Dublete



a quartet

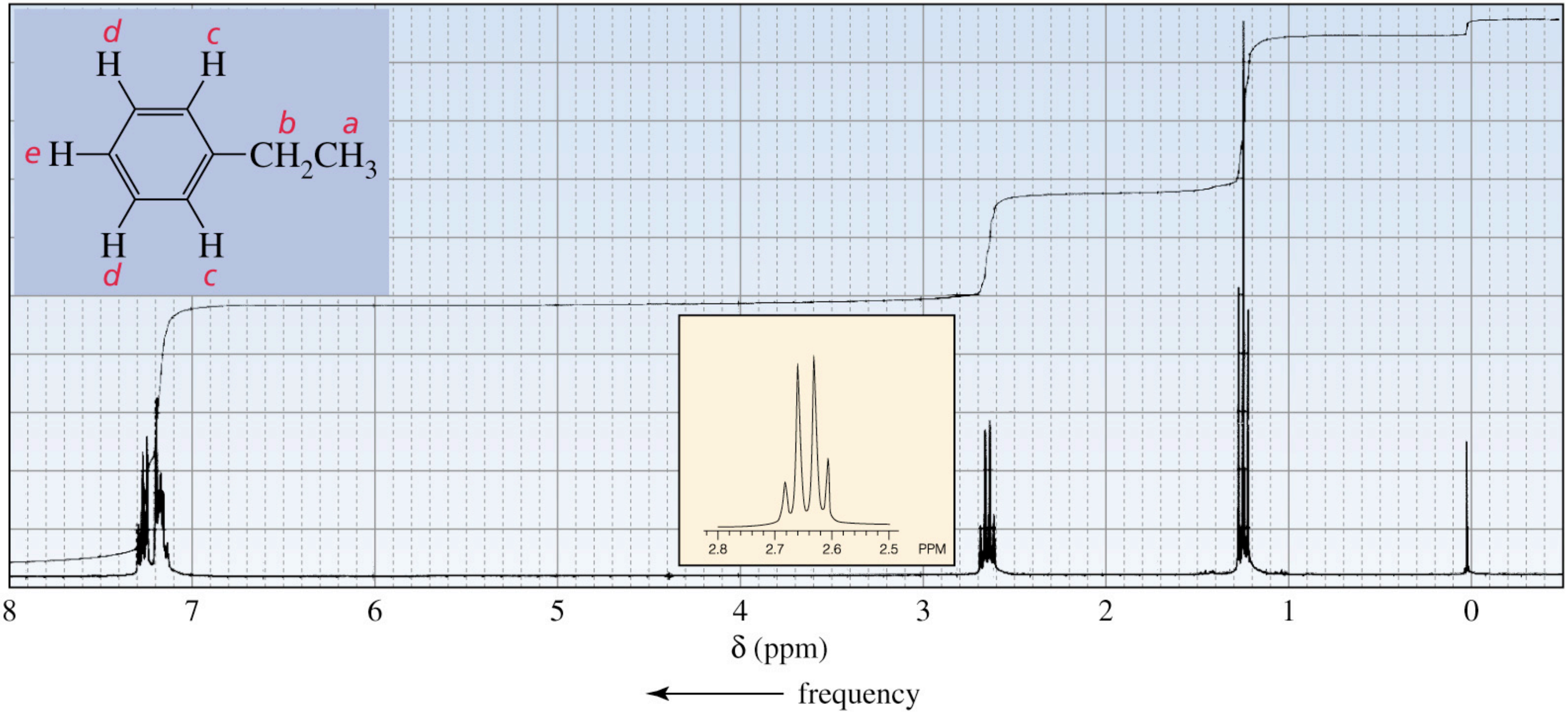
relative intensities: 1 : 3 : 3 : 1



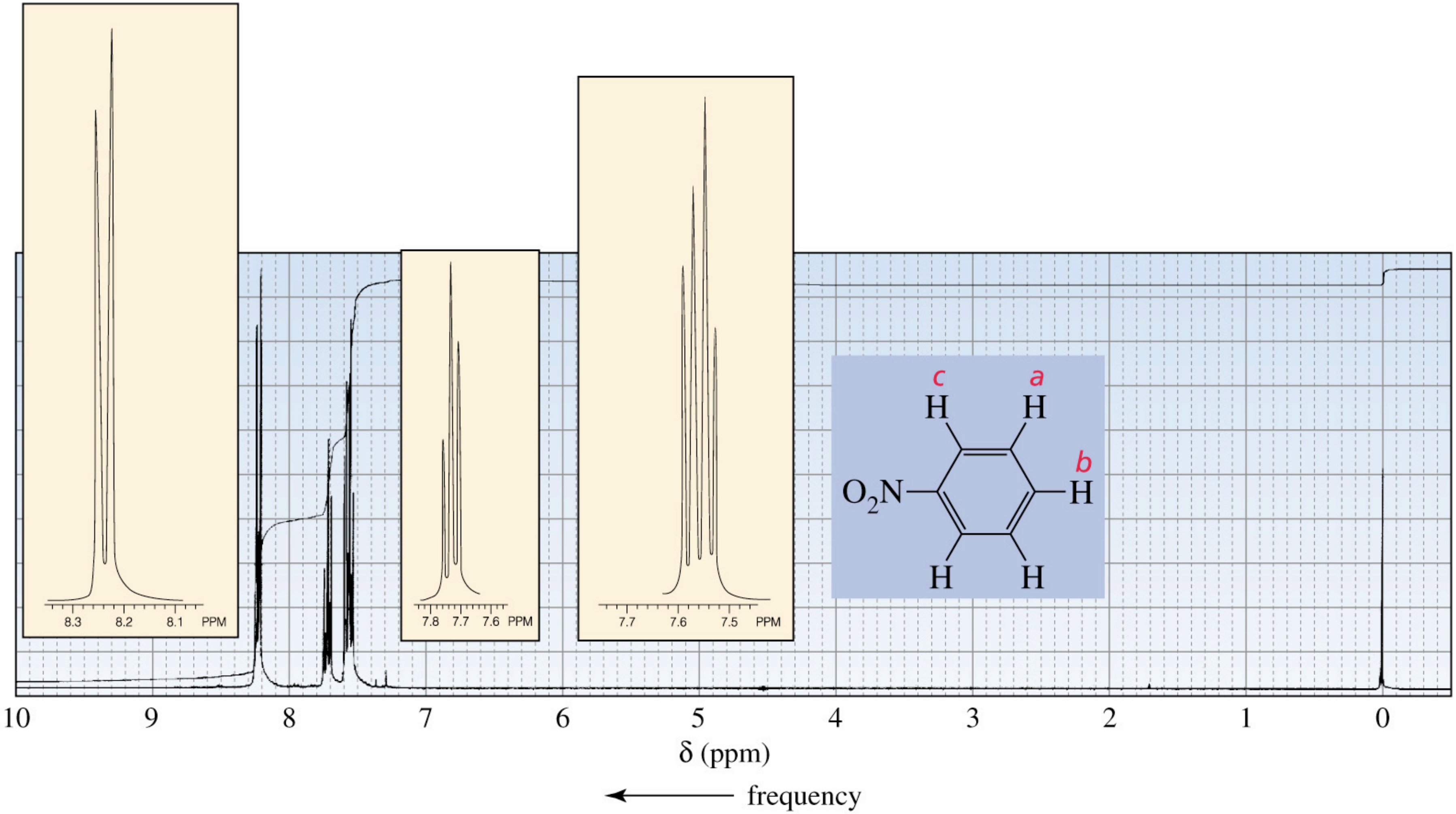
a doublet of doublets

relative intensities: 1 : 1 : 1 : 1

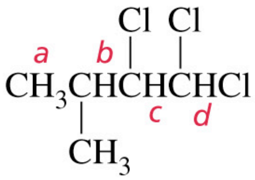
Os sinais de H_c, H_d e H_e se sobrepõem



Os sinais de H_a, H_b e H_c não se sobrepõe

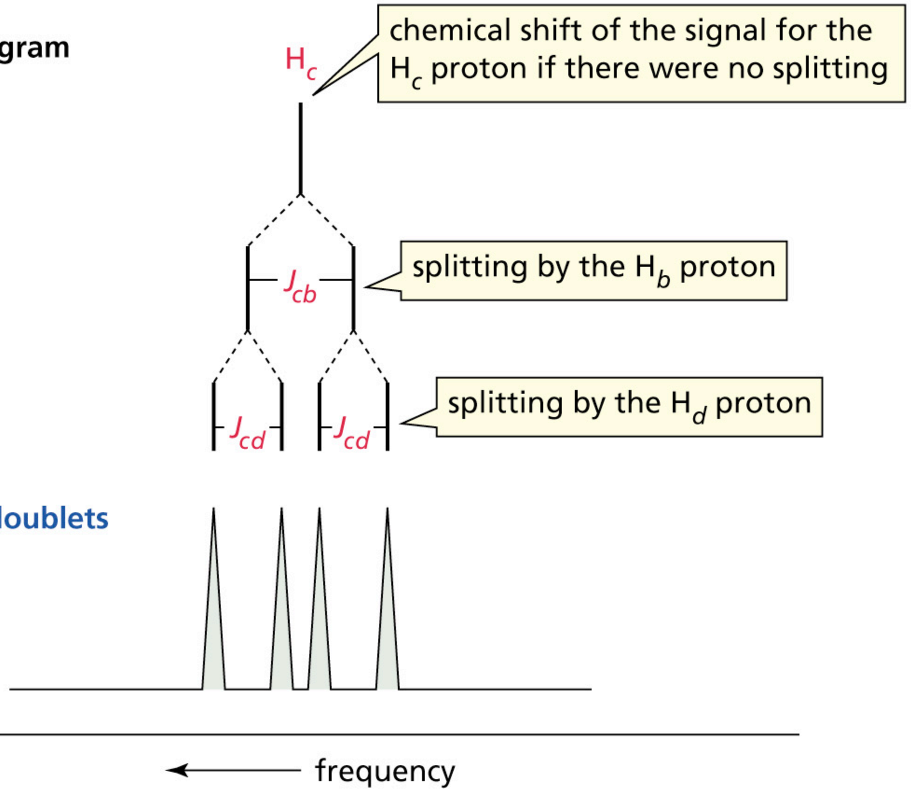


Um Diagrama de Desdobramento para Um Duplo Dubleto



$$\overset{a}{\mathrm{CH_3}}\underset{\underset{\mathrm{CH_3}}{|}}{\overset{b}{\mathrm{CH}}}\overset{\overset{\mathrm{Cl}}{|}}{\underset{c}{\mathrm{CH}}}\overset{\overset{\mathrm{Cl}}{|}}{\underset{d}{\mathrm{CH}}}\mathrm{Cl}$$

1,1,2-trichloro-3-methylbutane



a splitting diagram

chemical shift of the signal for the H_c proton if there were no splitting

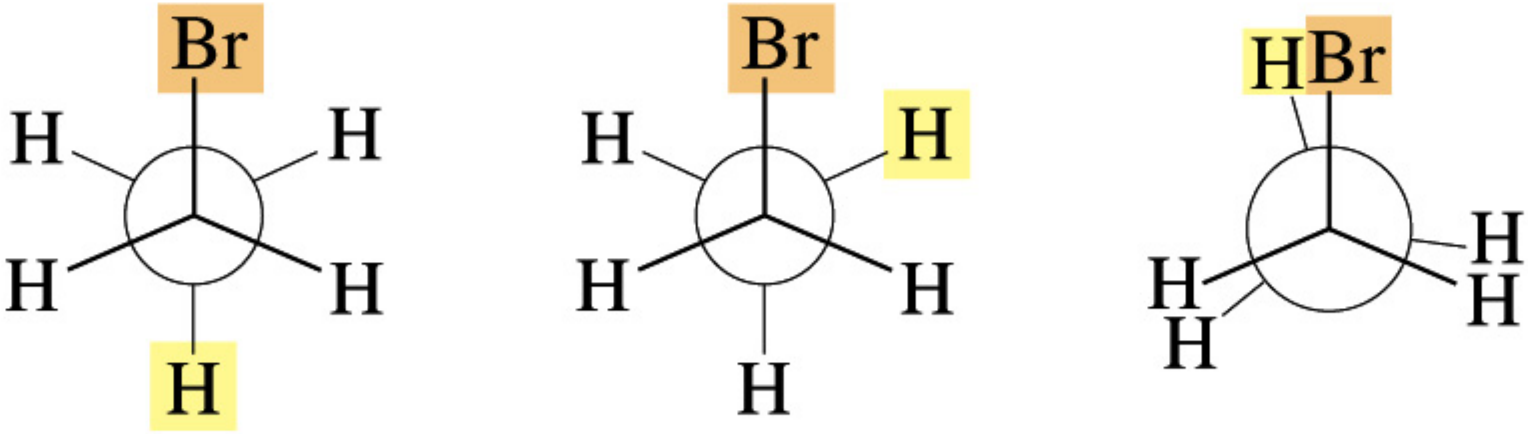
splitting by the H_b proton

splitting by the H_d proton

a doublet of doublets

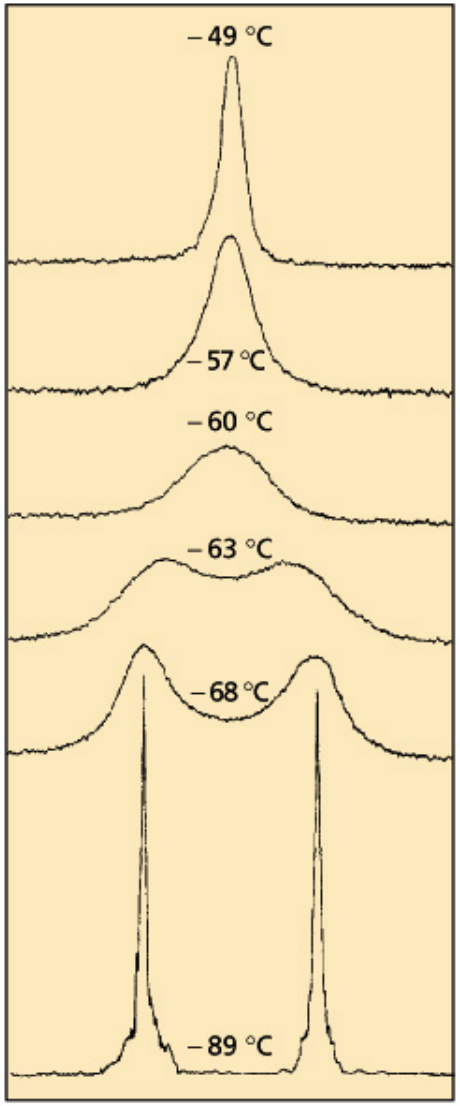
← frequency

Os três prótons metílicos são quimicamente equivalentes devido à rotação sobre a ligação C–C



Vemos somente um sinal para o grupo metila no espectro de RMN ^1H

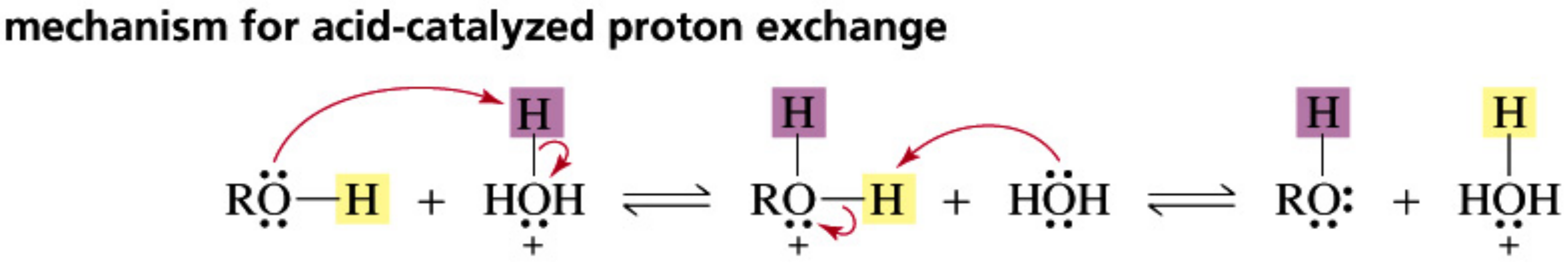
Espectros de RMN ^1H do cicloexano-d_{11} em várias temperaturas



a velocidade da conversão cadeira-cadeira depende da temperatura

Prótons Ligados ao Oxigênio ou Nitrogênio

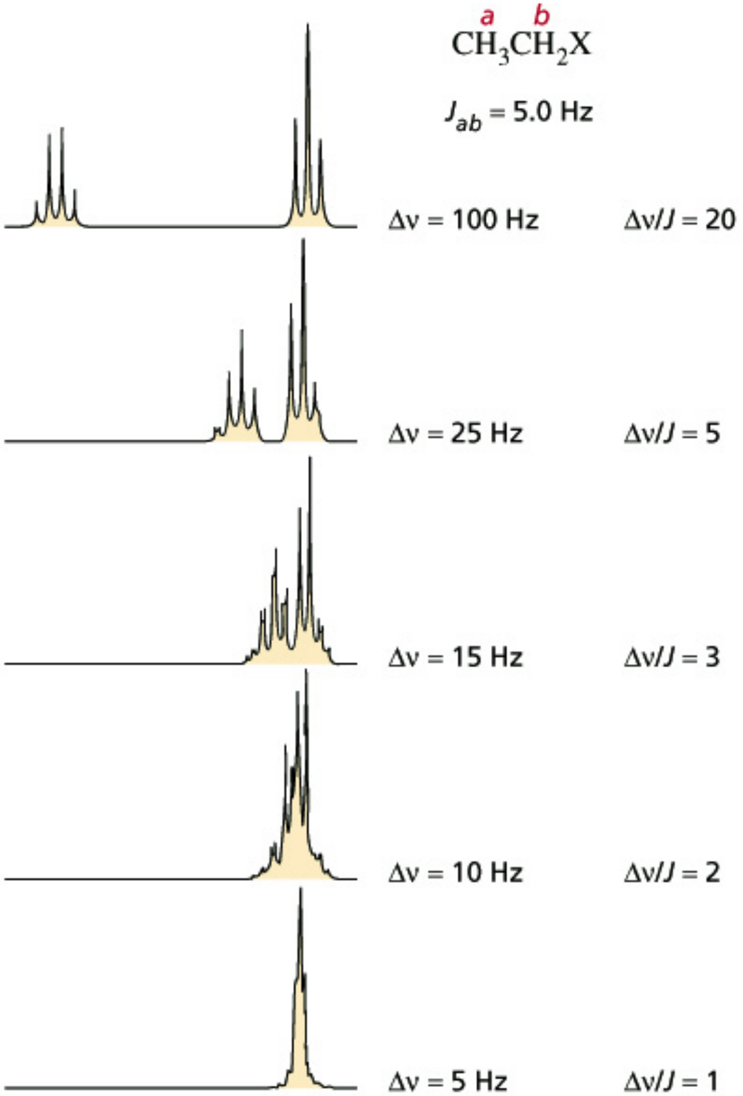
Quanto mais forte a ligação de hidrogênio, maior o deslocamento químico



Estes prótons podem ser trocados com o solvente

Eles sempre aparecem como um sinal largo

Para se observar um padrão de desdobramento bem definido, a diferença nos deslocamentos químicos ($\Delta\nu$, em Hz) deve ser de 10 vezes o valor da constante de acoplamento



Espectroscopia de RMN ^{13}C

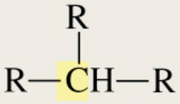
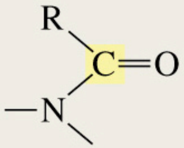
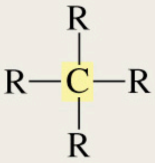
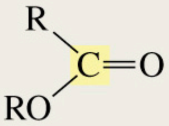
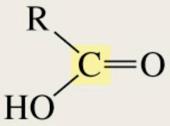
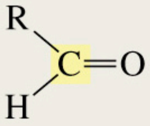
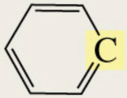
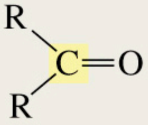
- O número de sinais reflete o número de diferentes tipos de carbono

- A intensidade do sinal de ^{13}C é, em geral, 6400 vezes menor do que a intensidade de um sinal de ^{1}H

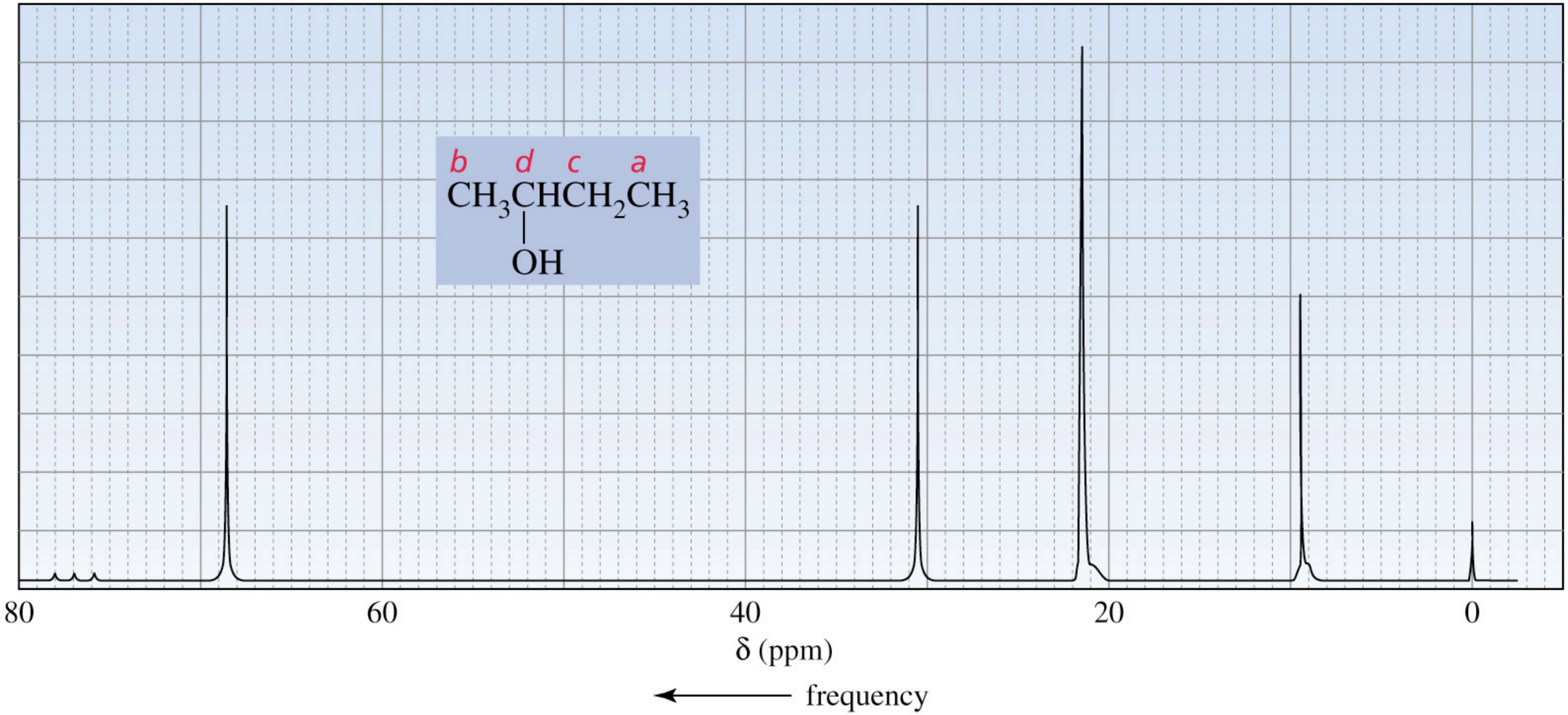
- Os deslocamentos químicos varia acima de 220 ppm, enquanto o de próton, somente 10 ppm

- O composto de referência é o TMS

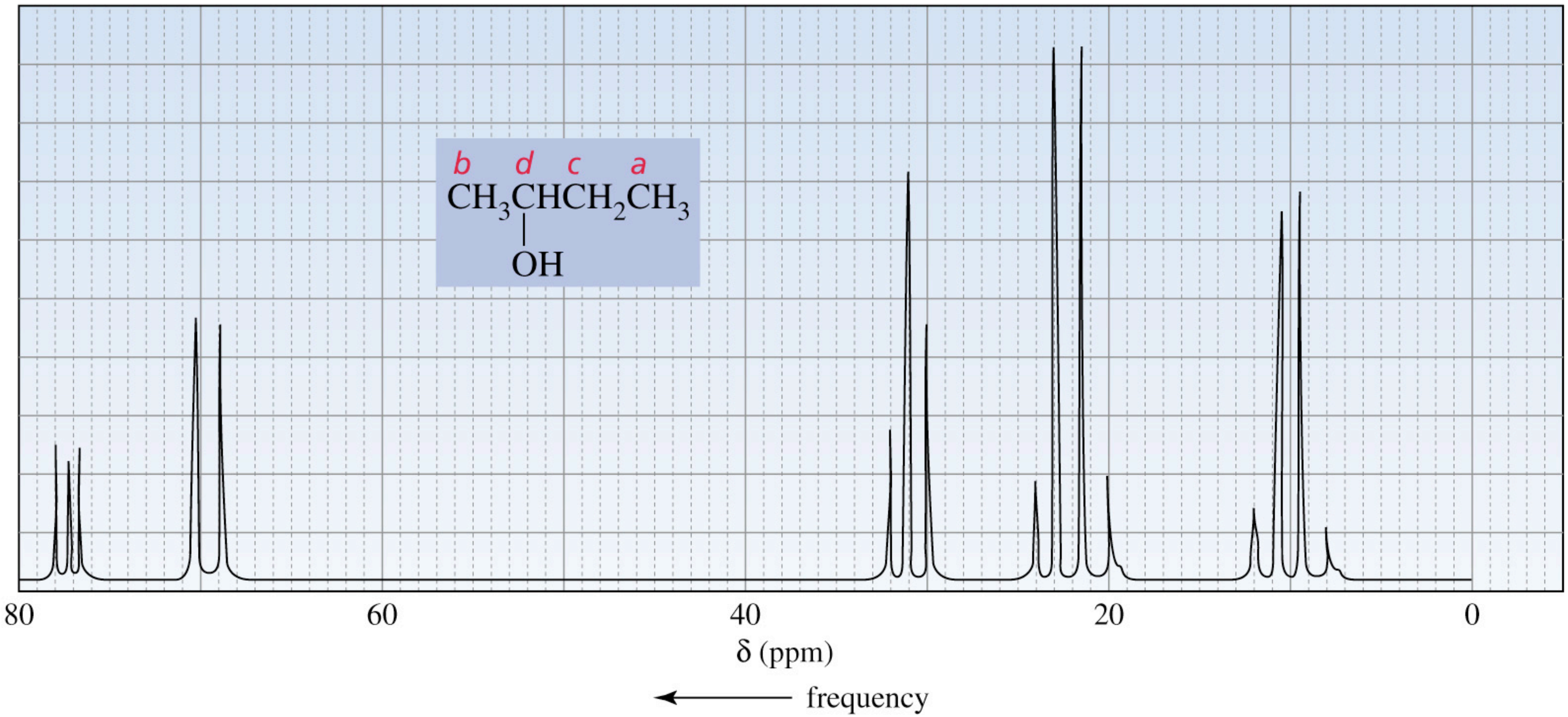
Table 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
 $\mathrm{R-\overset{R}{\overset{\vert}{C}}H-R}$	20–60		165–175
 $\mathrm{R-\overset{R}{\overset{\vert}{\underset{R}{\underset{\vert}{C}}}}-R}$	30–40		165–175
$\equiv C$	65–85		175–185
$=C$	100–150		190–200
	110–170		205–220

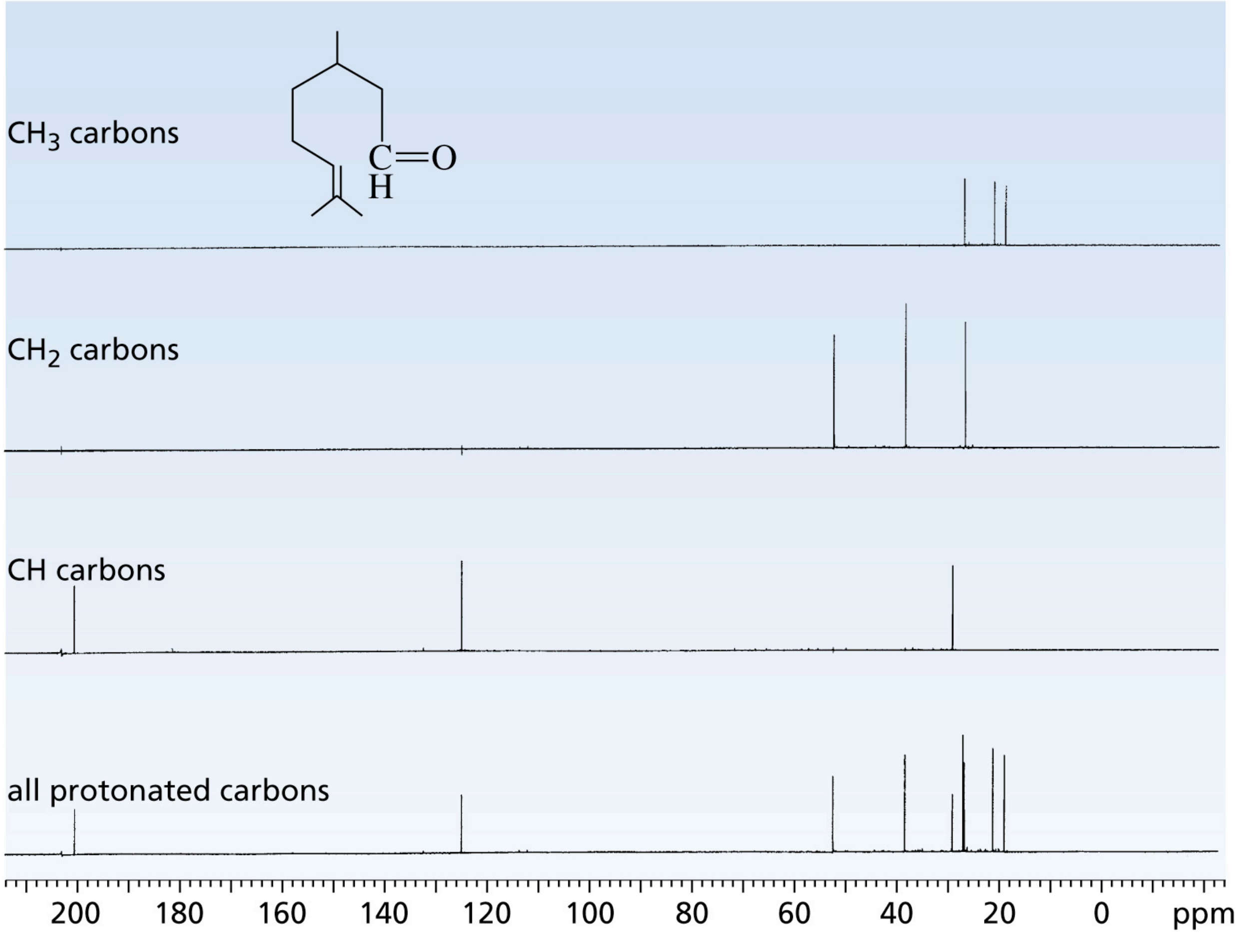
Espectro de RMN ^{13}C Desacoplado do 2-butanol



Espectro de RMN ^{13}C Acoplado do 2-butanol



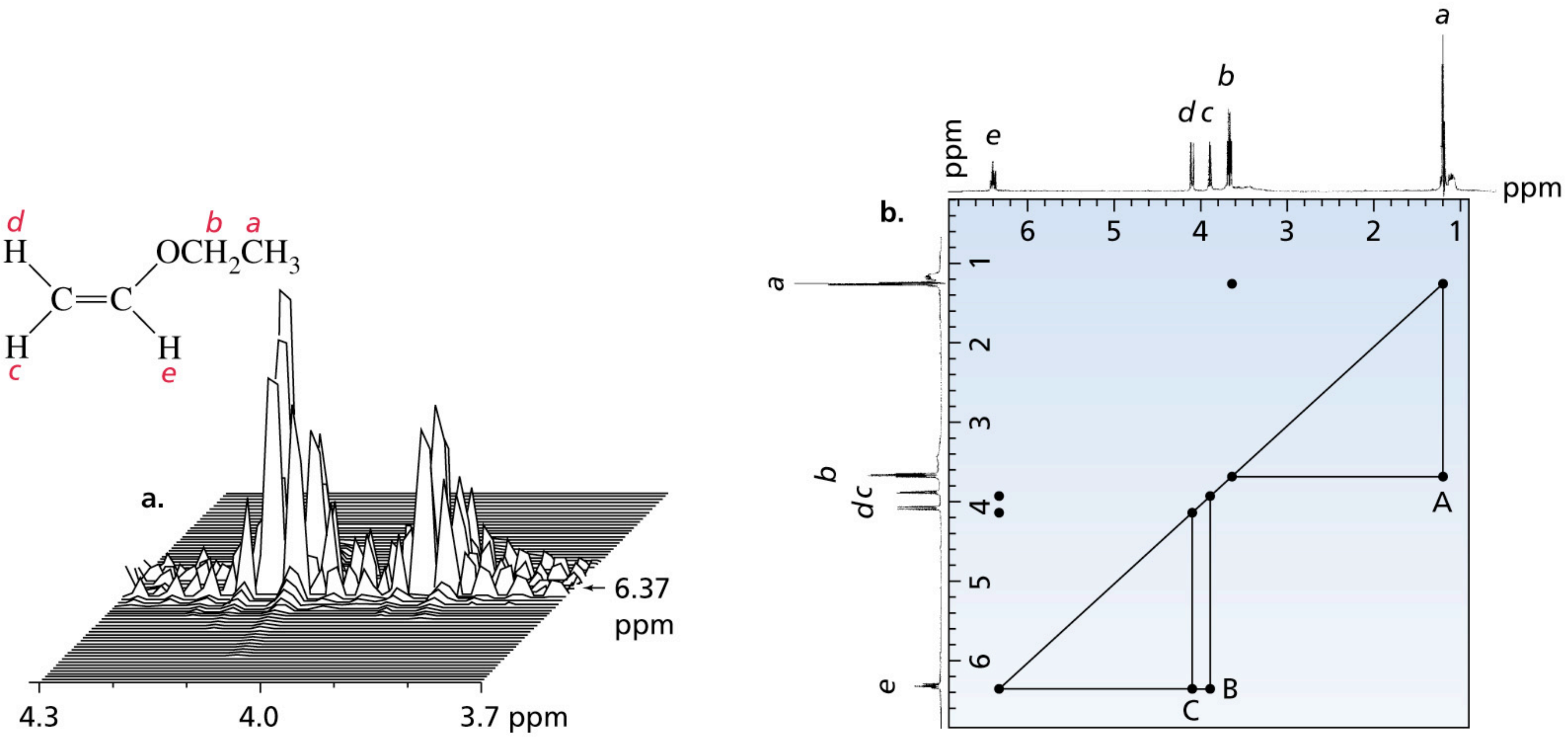
O espectro DEPT de RMN ^{13}C permite distinguir entre os grupos CH_3, CH_2 e CH



DEPT 90: CH

DEPT 135: CH e CH_3 (sinal positivo), CH_2 (sinal negativo)

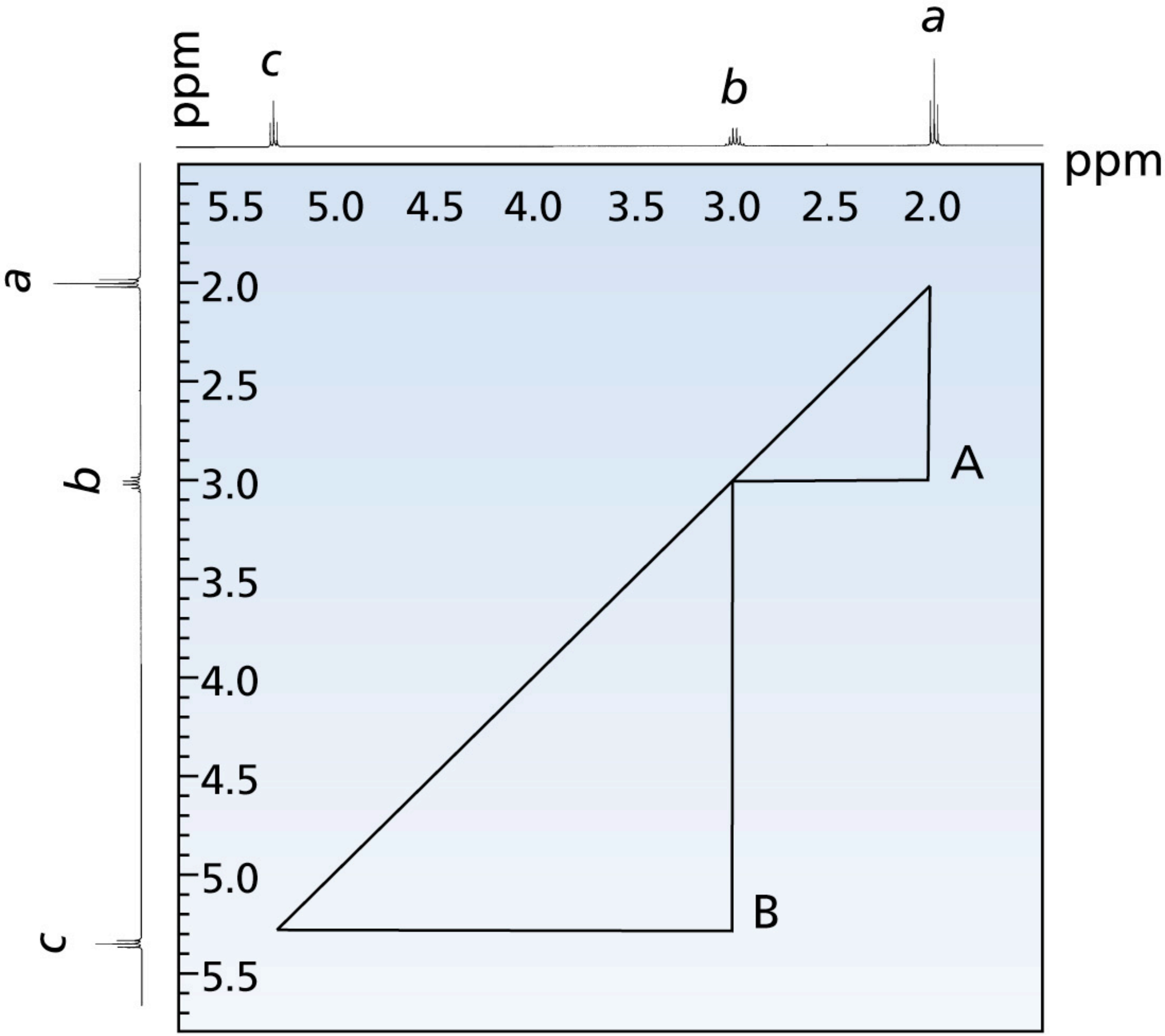
O espectro COSY de RMN ^{1}H identifica como os prótons estão acoplados



Picos cruzados indicam pares de prótons acoplados

Espectro COSY de RMN ^{1}H do 1-nitropropano

$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2NO_2$



O espectro HETCOR da 2-metil-3-pentanona indica o acoplamento entre os prótons e carbonos, nos quais eles estão ligados