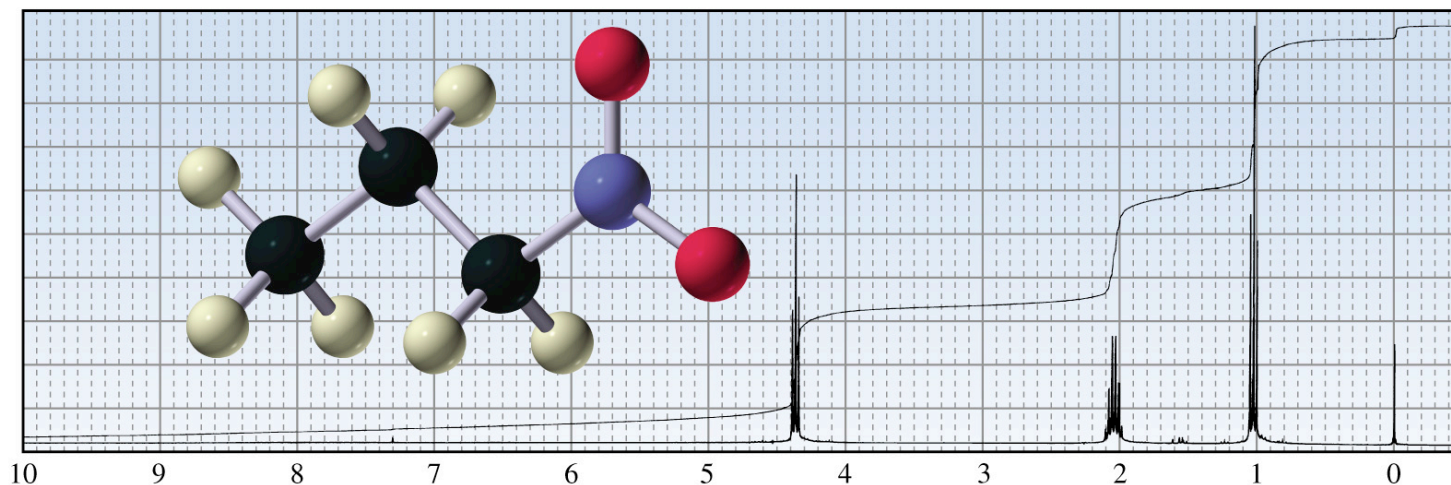


Aula 1

Espectroscopia de RMN

Organic Chemistry 4th Edition

Paula Yurkanis Bruice

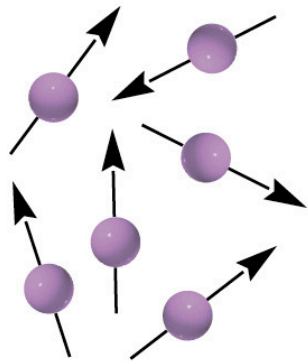


1-Nitropropane

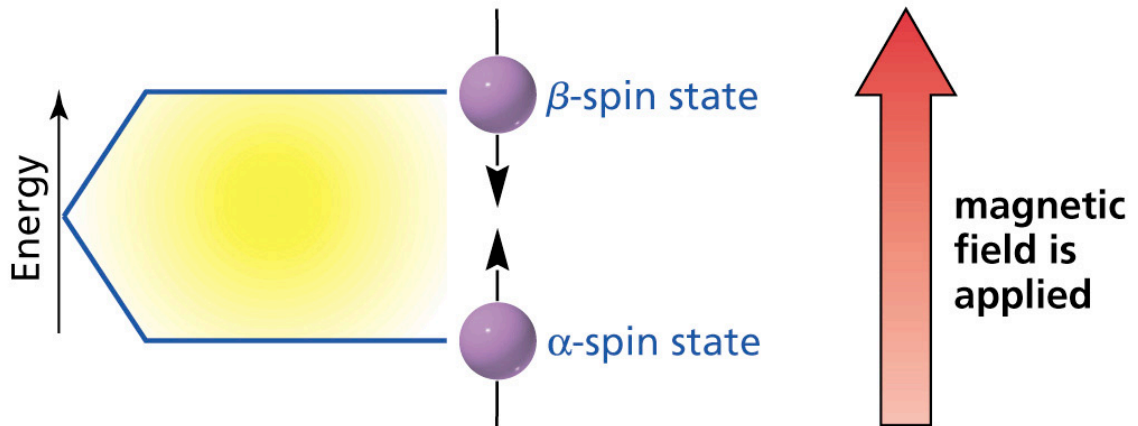
Ressonância Magnética Nuclear (RMN)

Identifica a estrutura carbono-hidrogênio de compostos orgânicos

O spin do núcleo é afetado por campos magnéticos

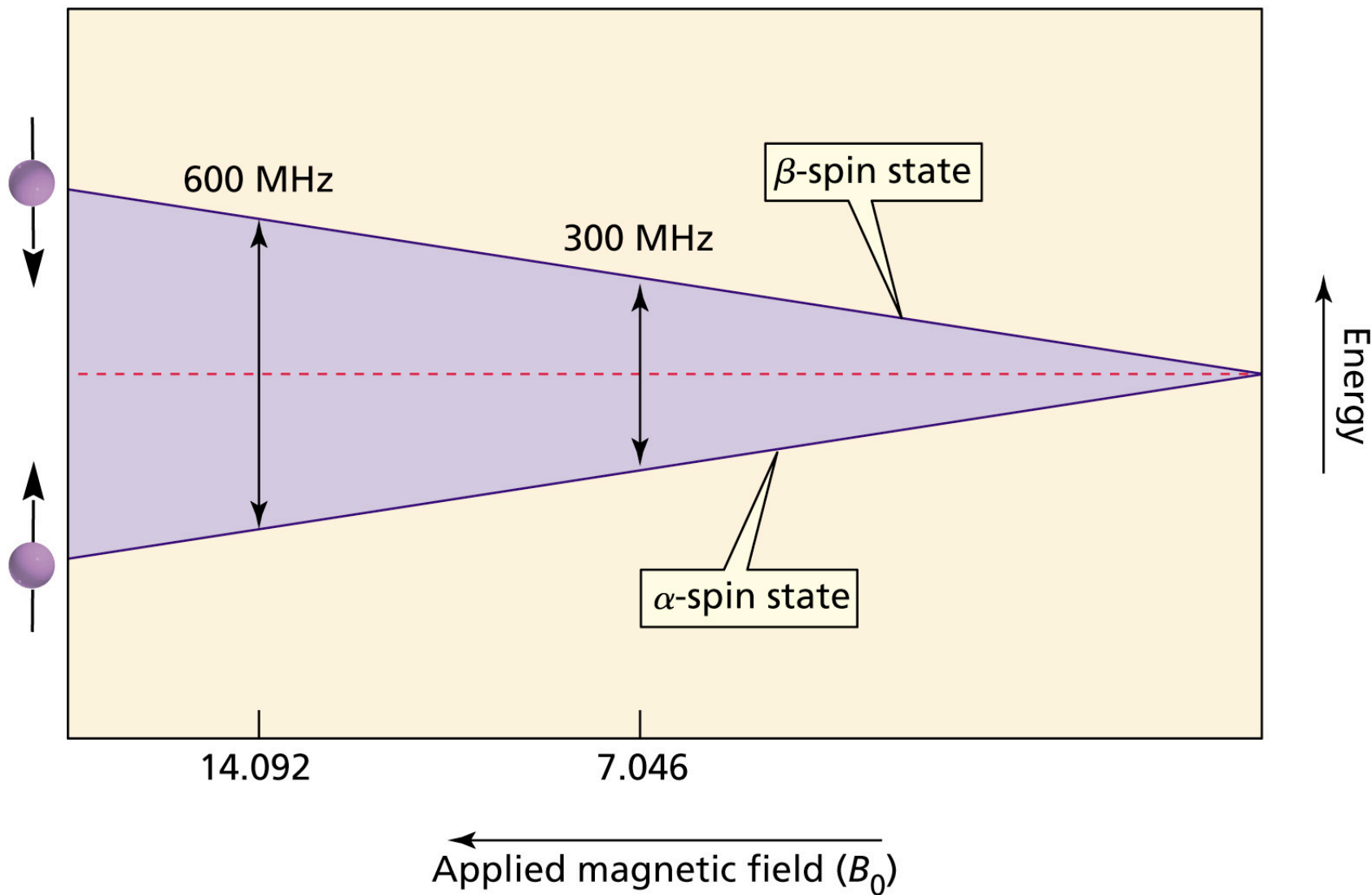


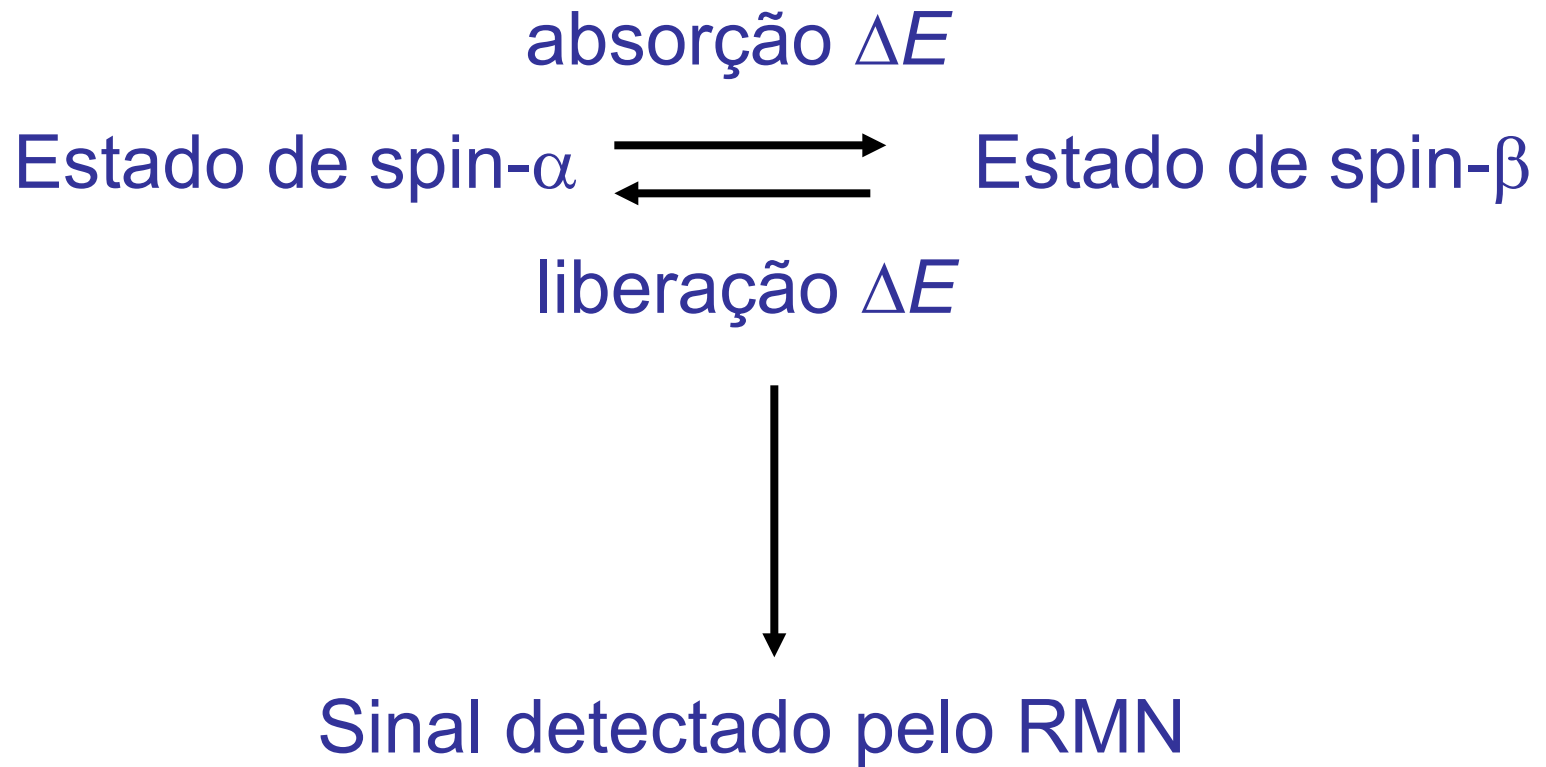
no applied magnetic field



Todos os núcleos com número ímpar de prótons (^1H , ^2H , ^{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.

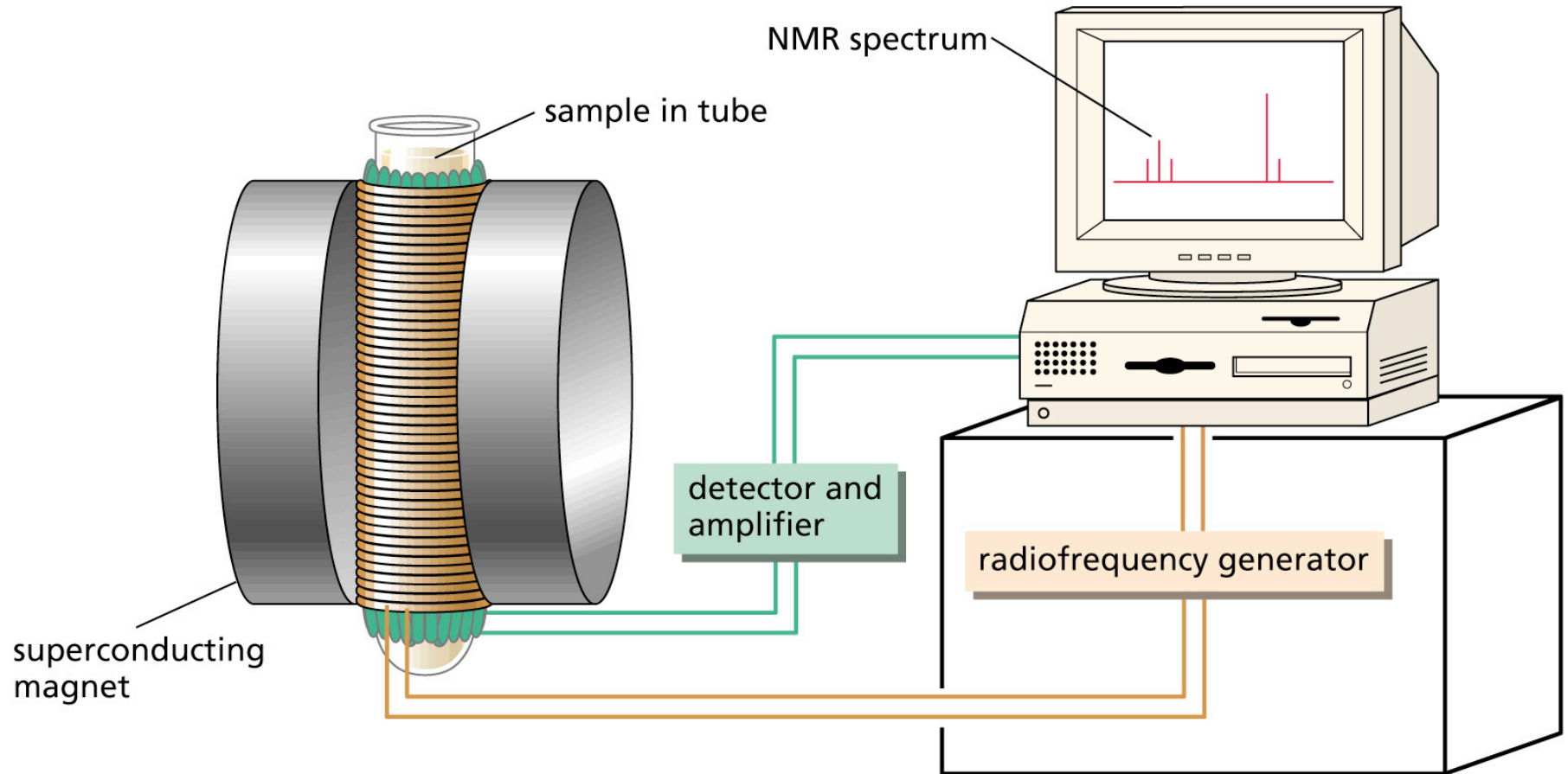
A diferença de energia entre dois estados de spin depende da força do campo magnético





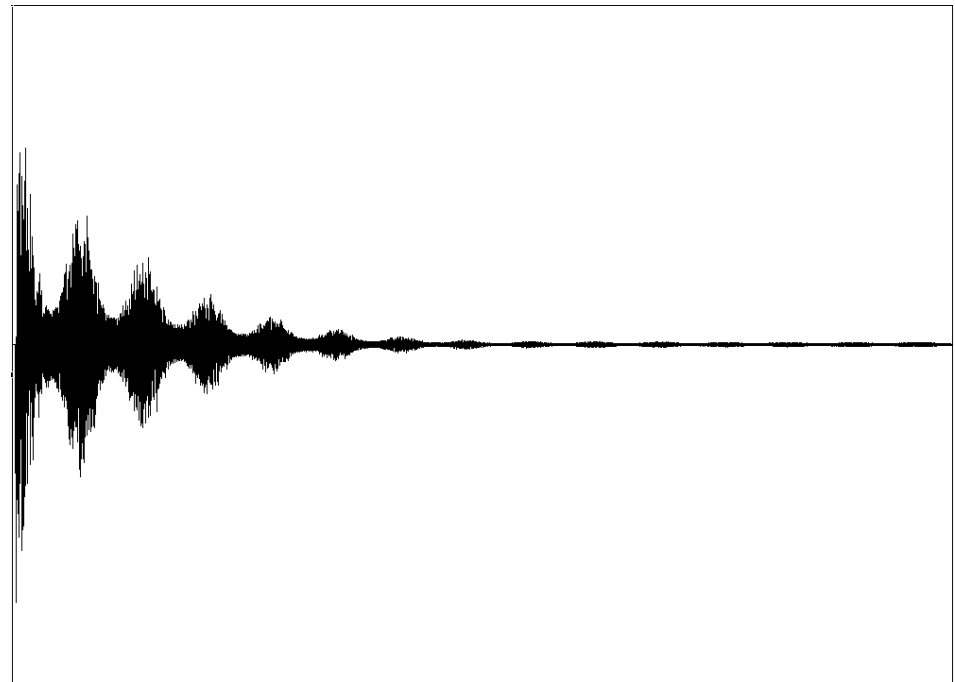
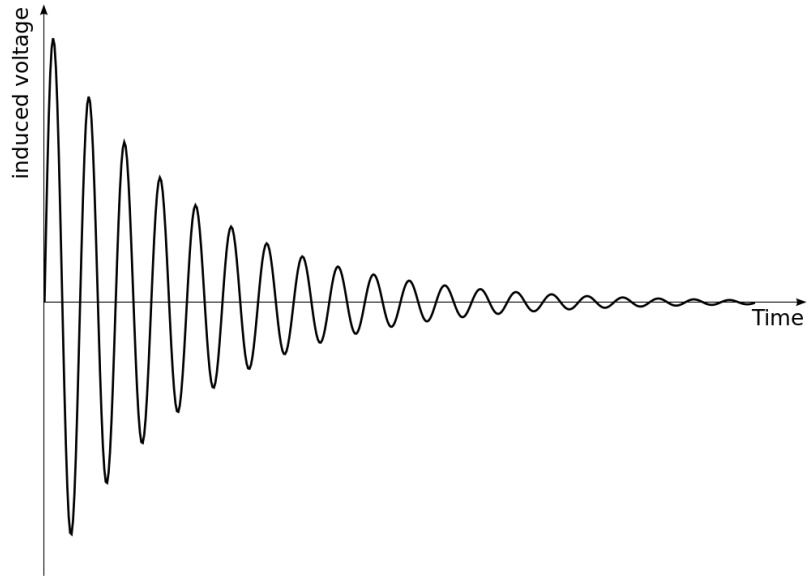
Alguns núcleos orientam-se na mesma direção do campo magnético outros na direção contrária

Um Espectrômetro de RMN

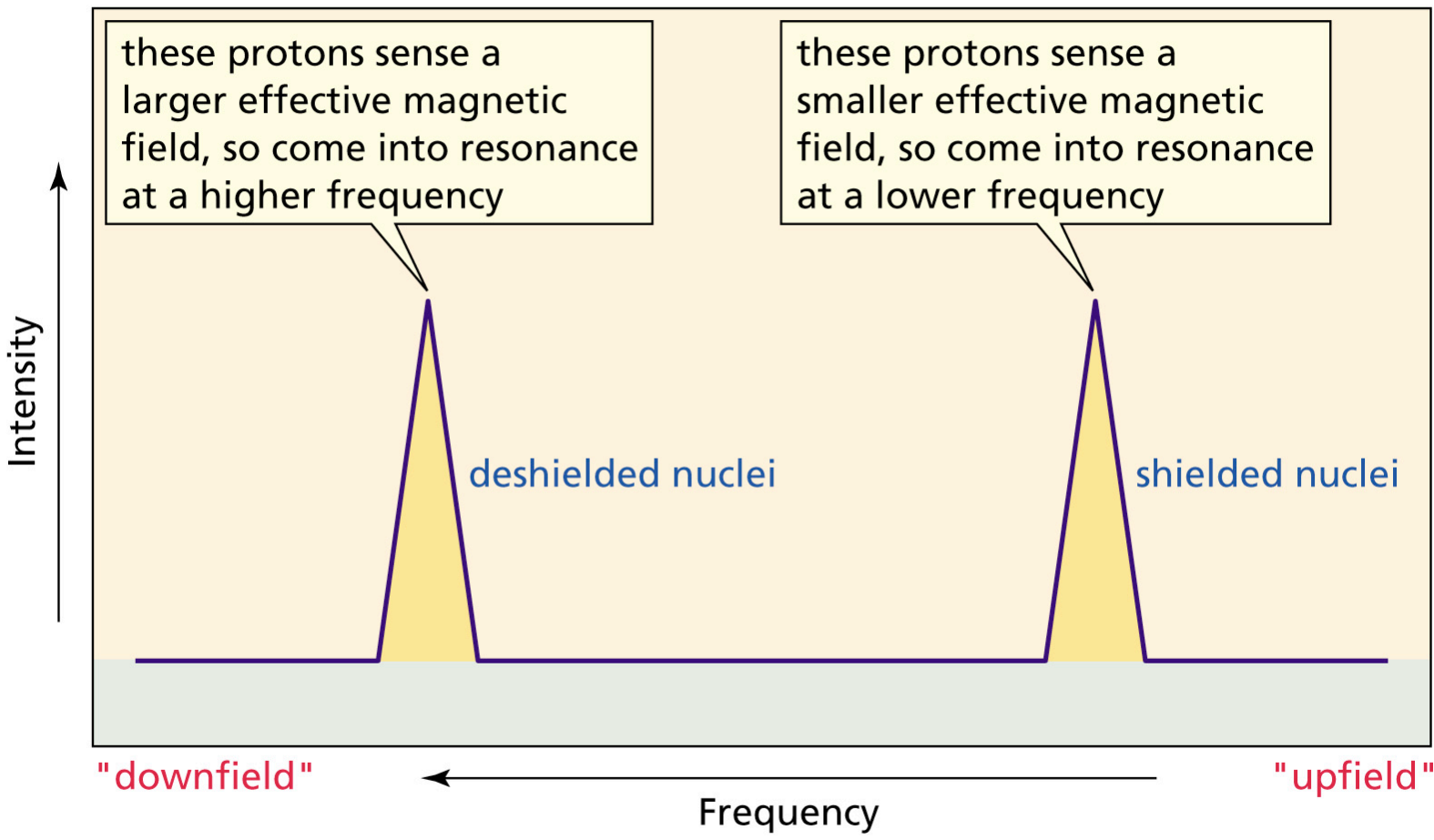




FID = Free Induction Decay

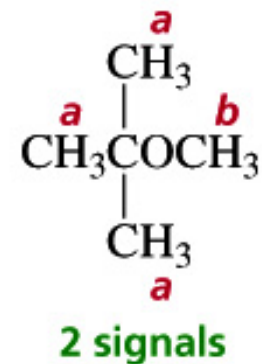
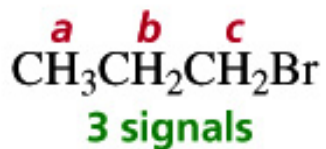


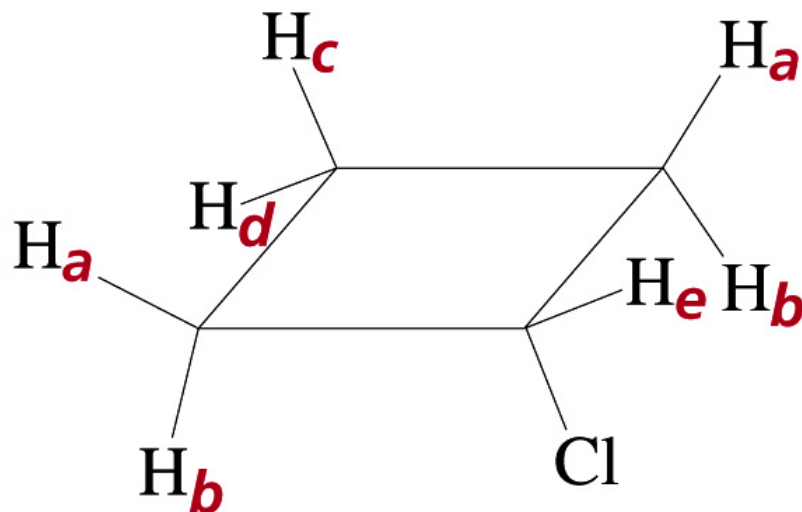
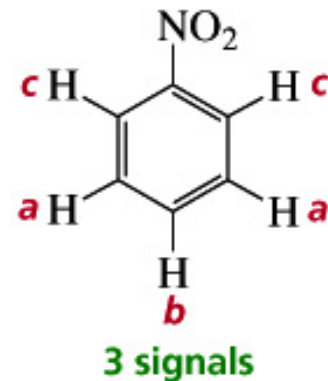
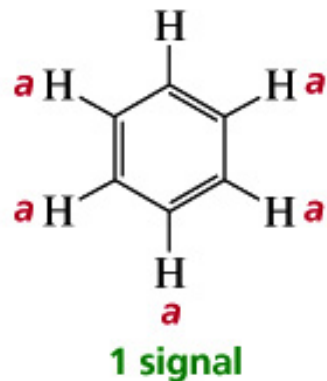
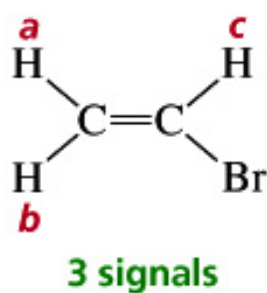
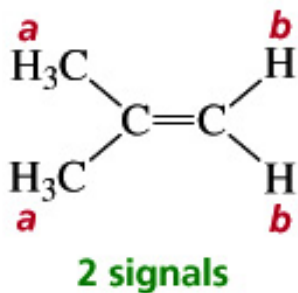
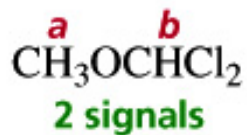
Os elétrons ao redor do núcleo afetam a intensidade do campo magnético “sentida” pelo núcleo



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-¹H do composto





chlorocyclobutane

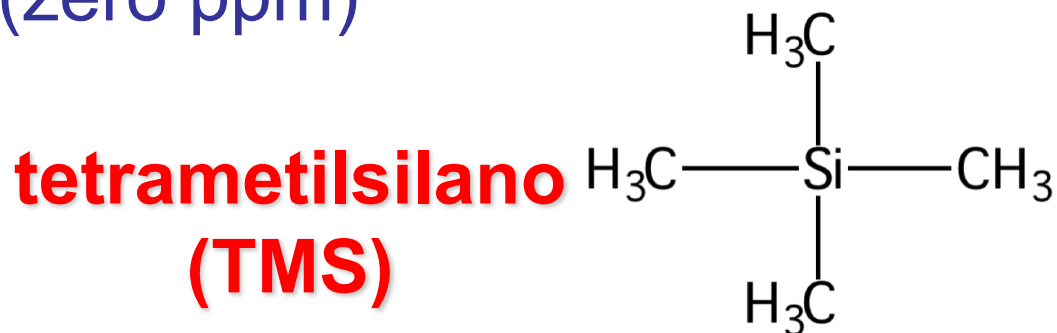
the NMR spectrum has 5 signals

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)



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

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

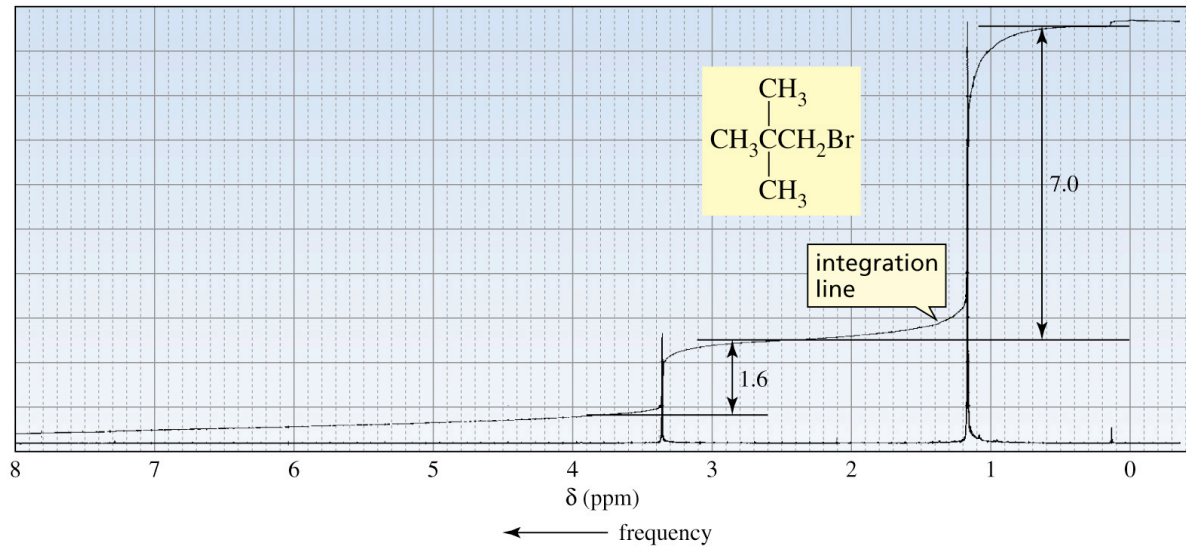
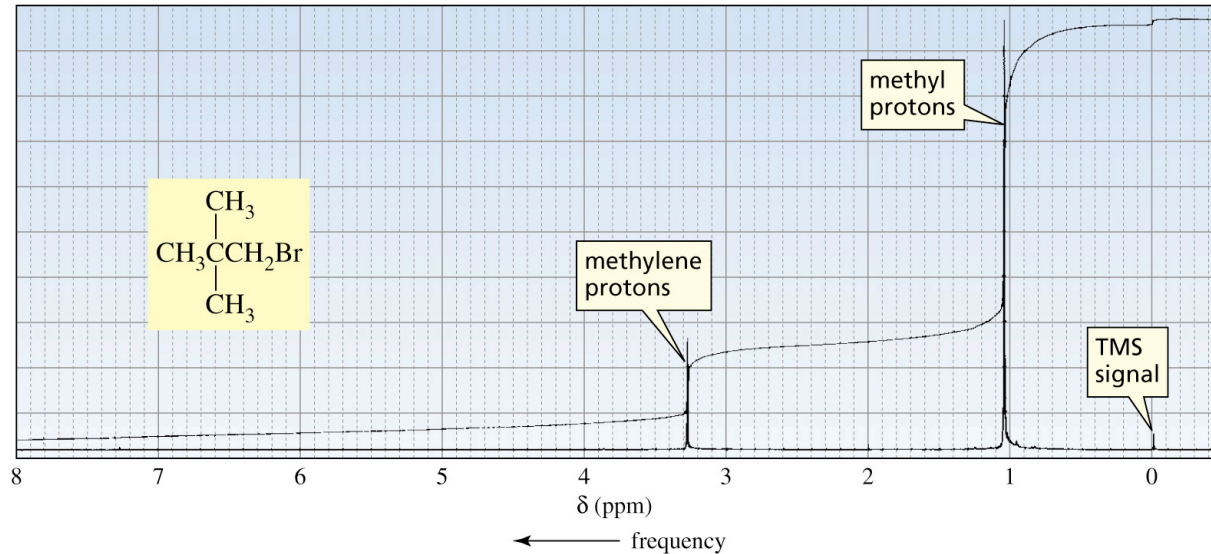
Integração

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

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

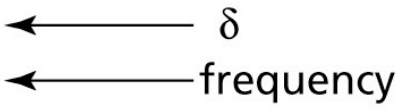
A integral nos diz o número relativo de prótons, mas não o absoluto

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



O deslocamento químico é independente da frequência 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



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



4.50 ppm



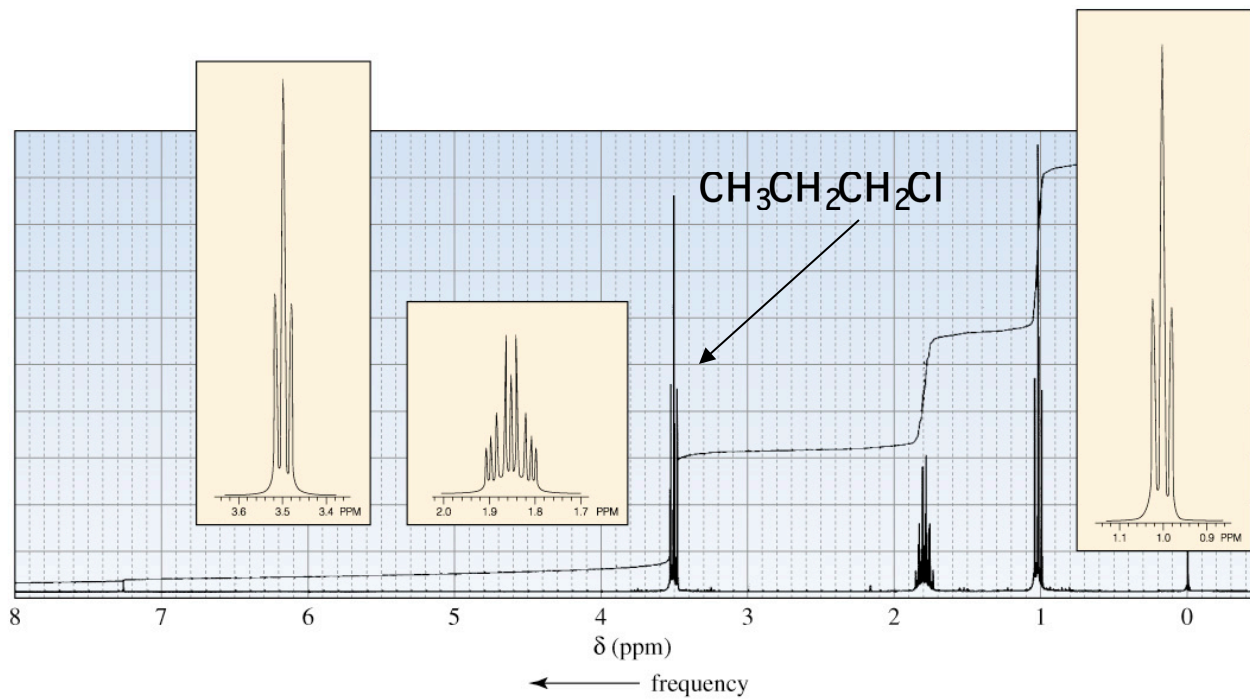
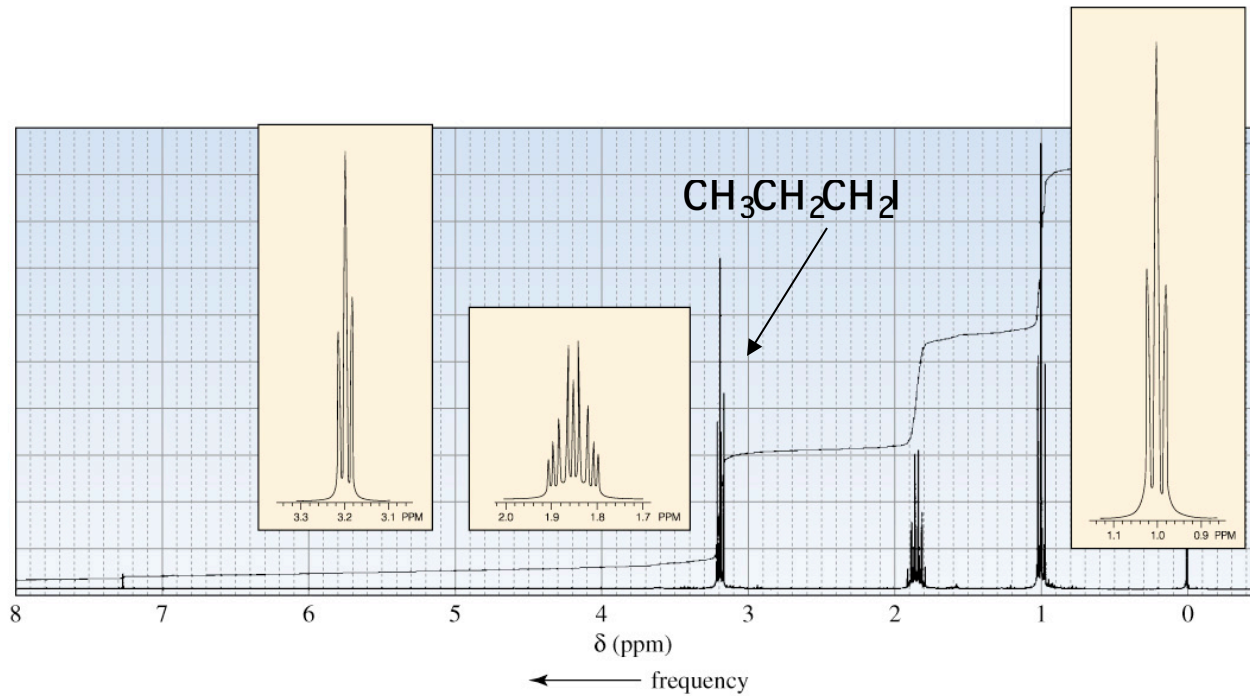
3.50 ppm

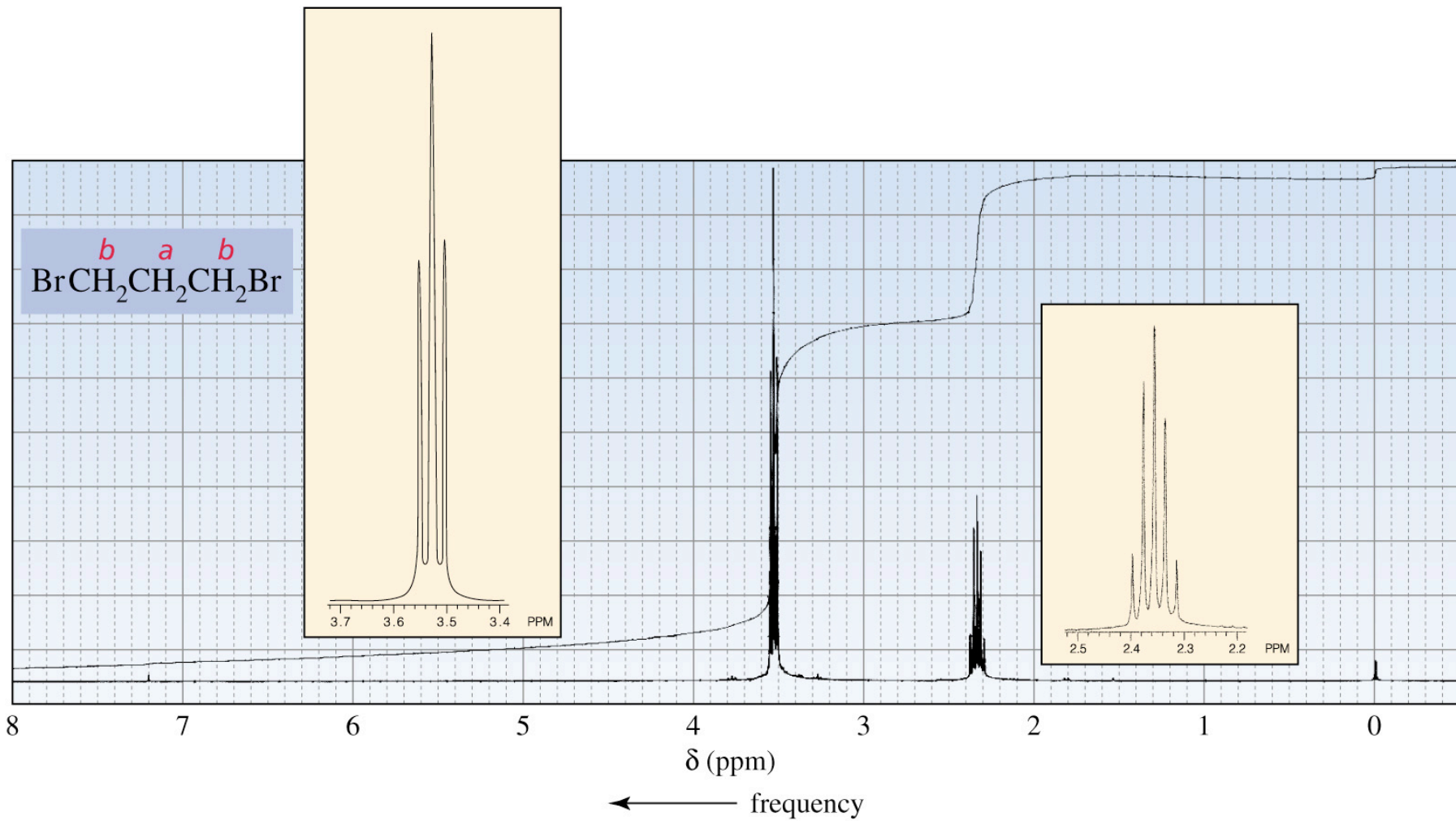


3.40 ppm

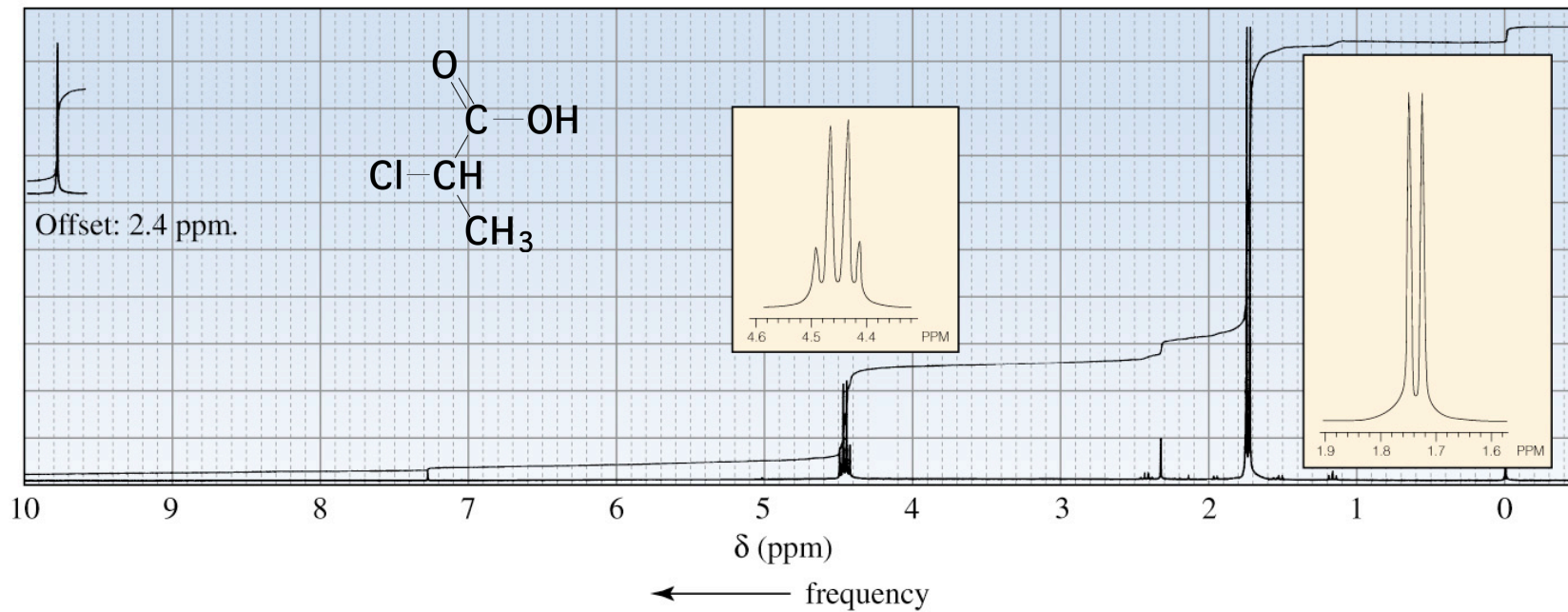


3.20 ppm

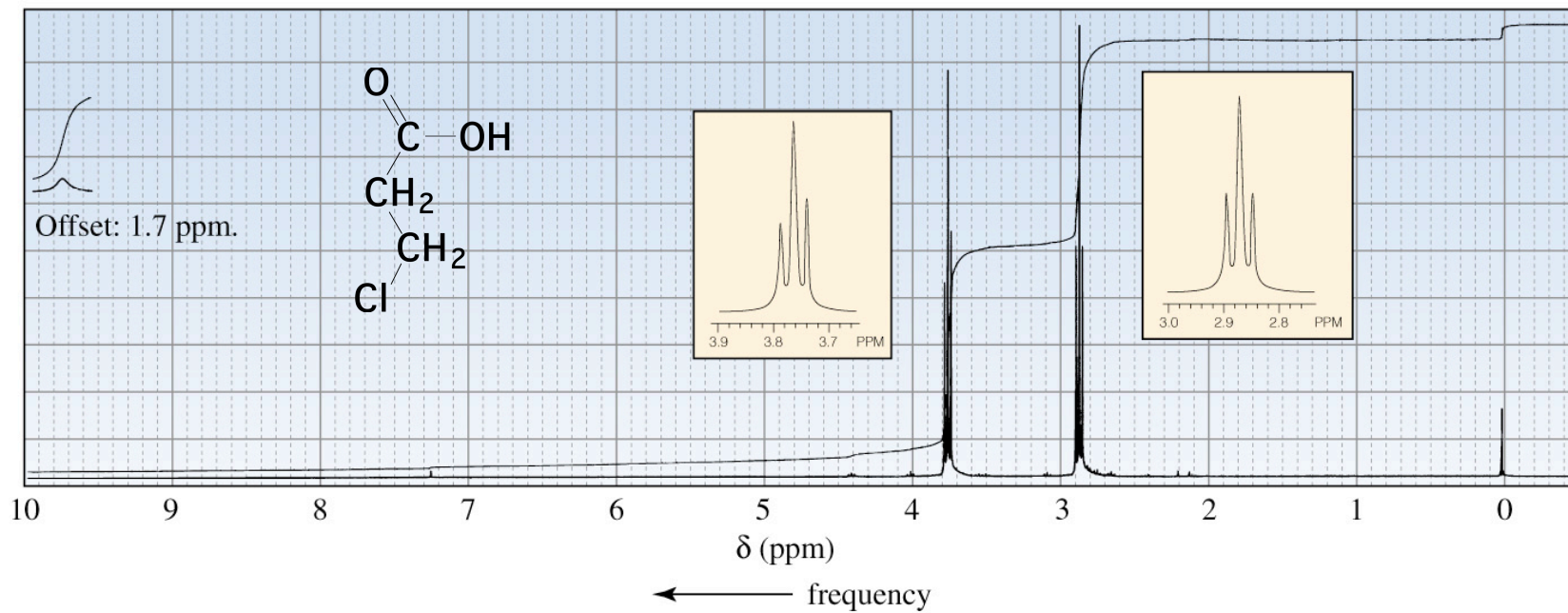


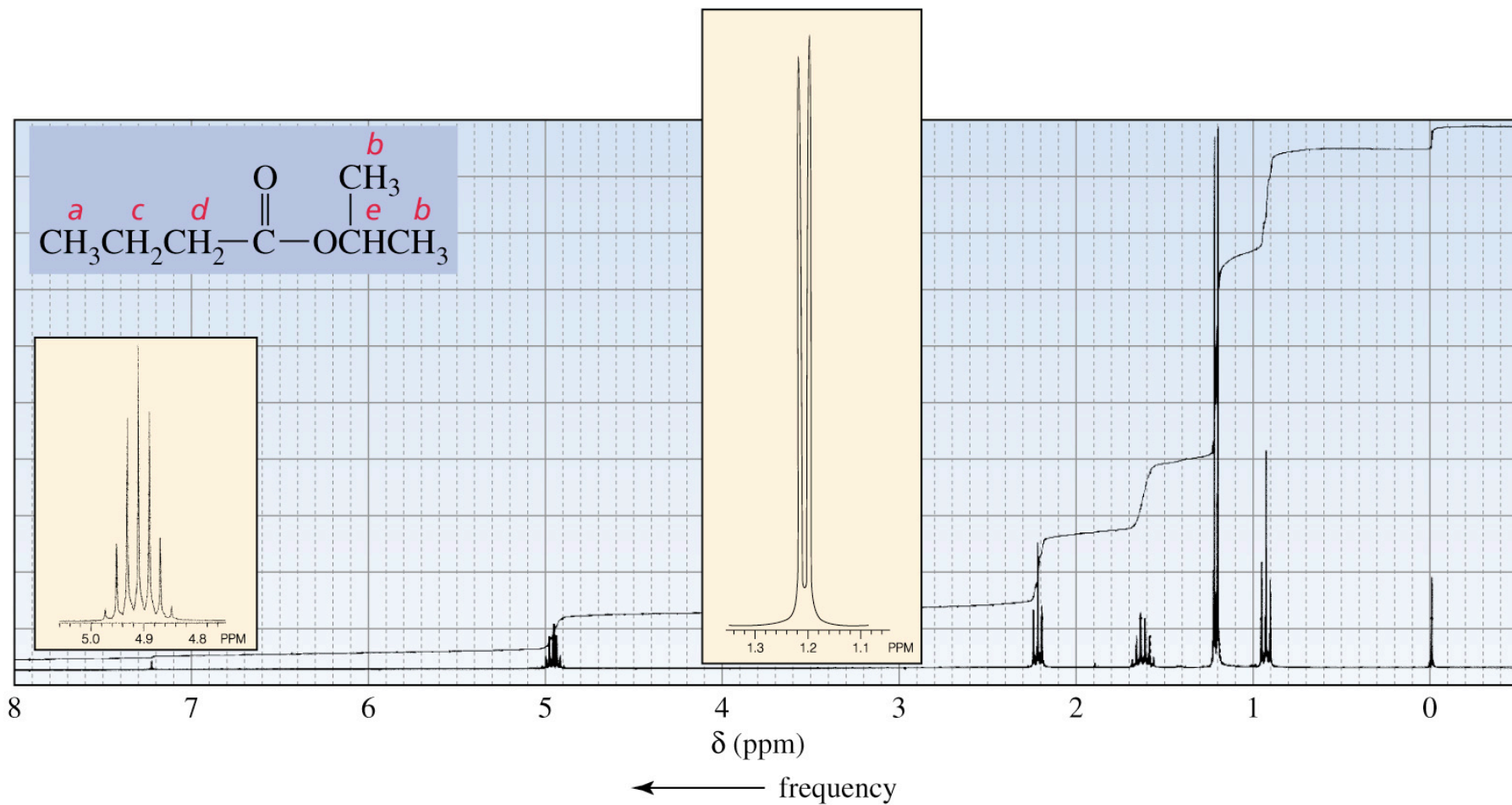


a.



b.





Valores Característicos de Deslocamento Químico

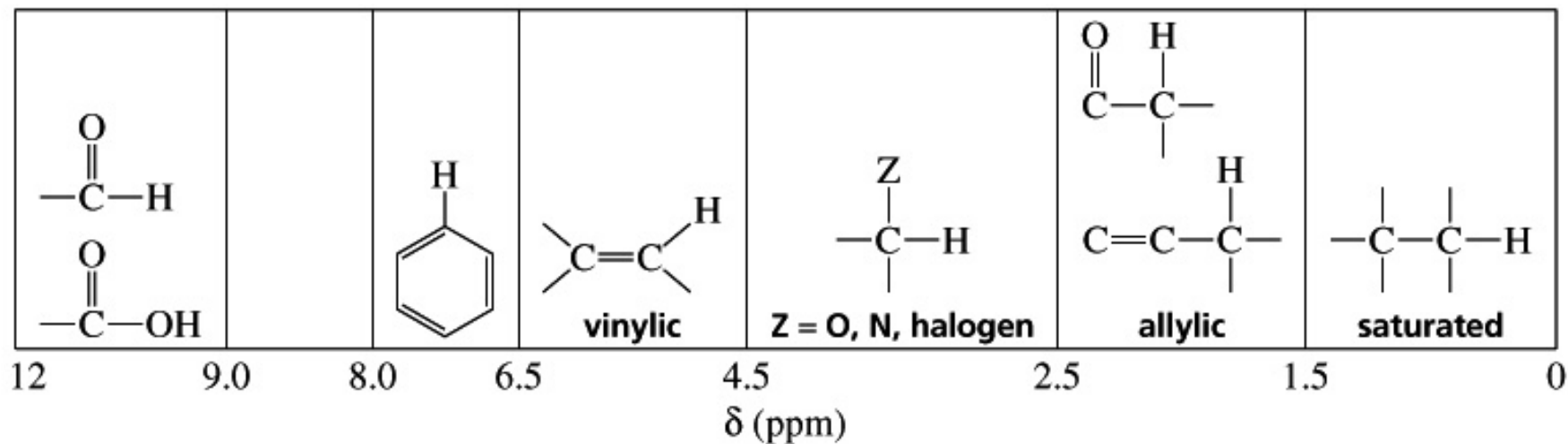
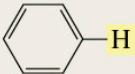
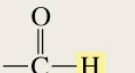
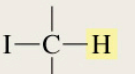

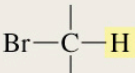
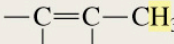

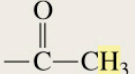
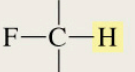
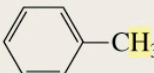
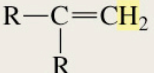
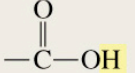
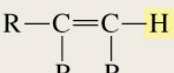



Table 14.1 Approximate Values of Chemical Shifts for ^1H NMR^a

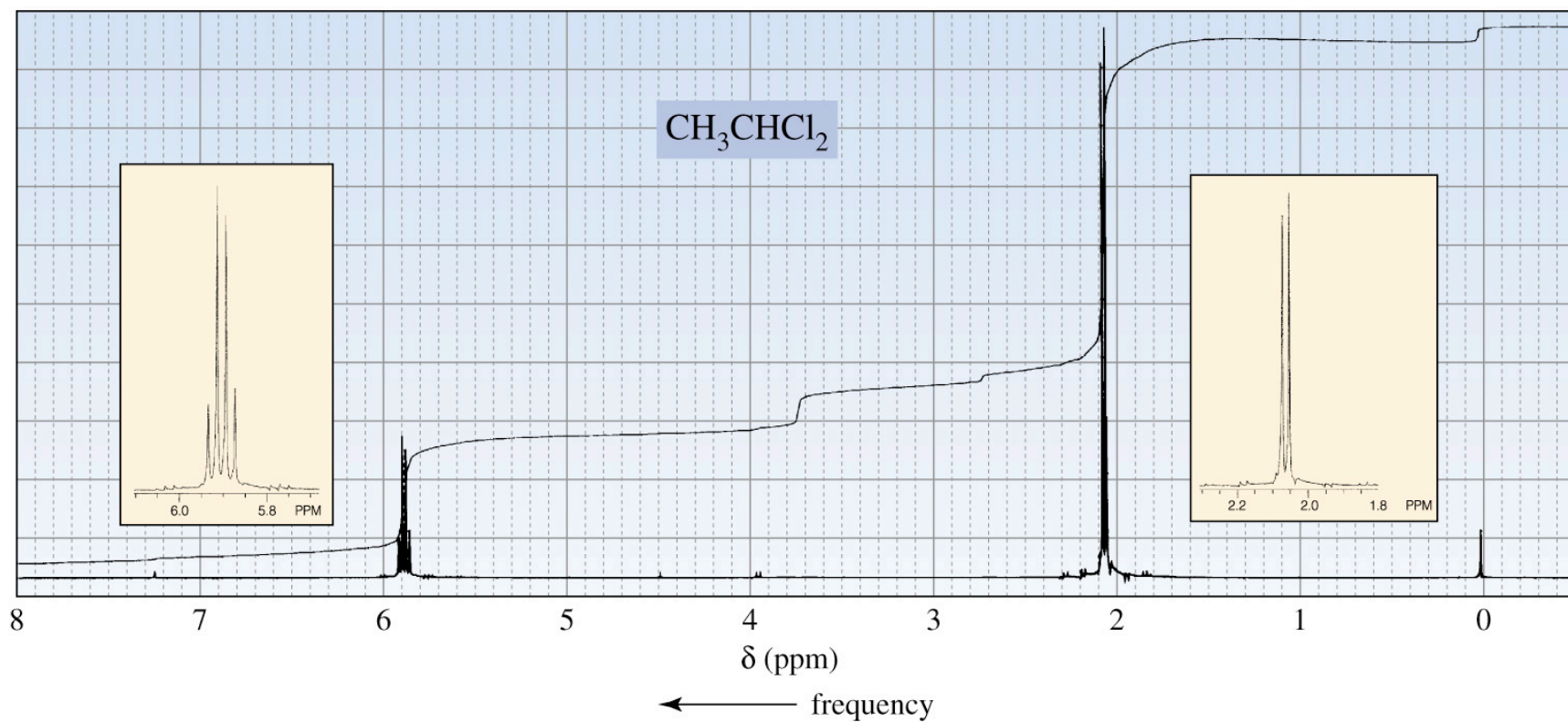
Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0		6.5–8
$-\text{CH}_3$	0.9		9.0–10
$-\text{CH}_2-$	1.3		2.5–4
	1.4		2.5–4
	1.7		3–4
	2.1		4–4.5
	2.3	RNH_2	Variable, 1.5–4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ROH	Variable, 2–5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	Variable, 4–7
	4.7		Variable, 10–12
	5.3		Variable, 5–8

^aThe values are approximate because they are affected by neighboring substituents.

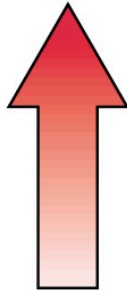
Desdobramento de Sinais

- Um sinal de RMN ^1H 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 acoplamento spin-spin, ocorre quando diferentes tipos de prótons estão próximos entre si

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

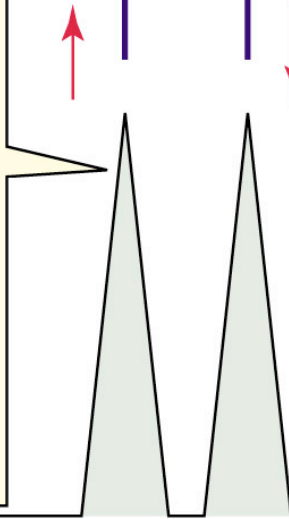


direction of
the applied
field



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

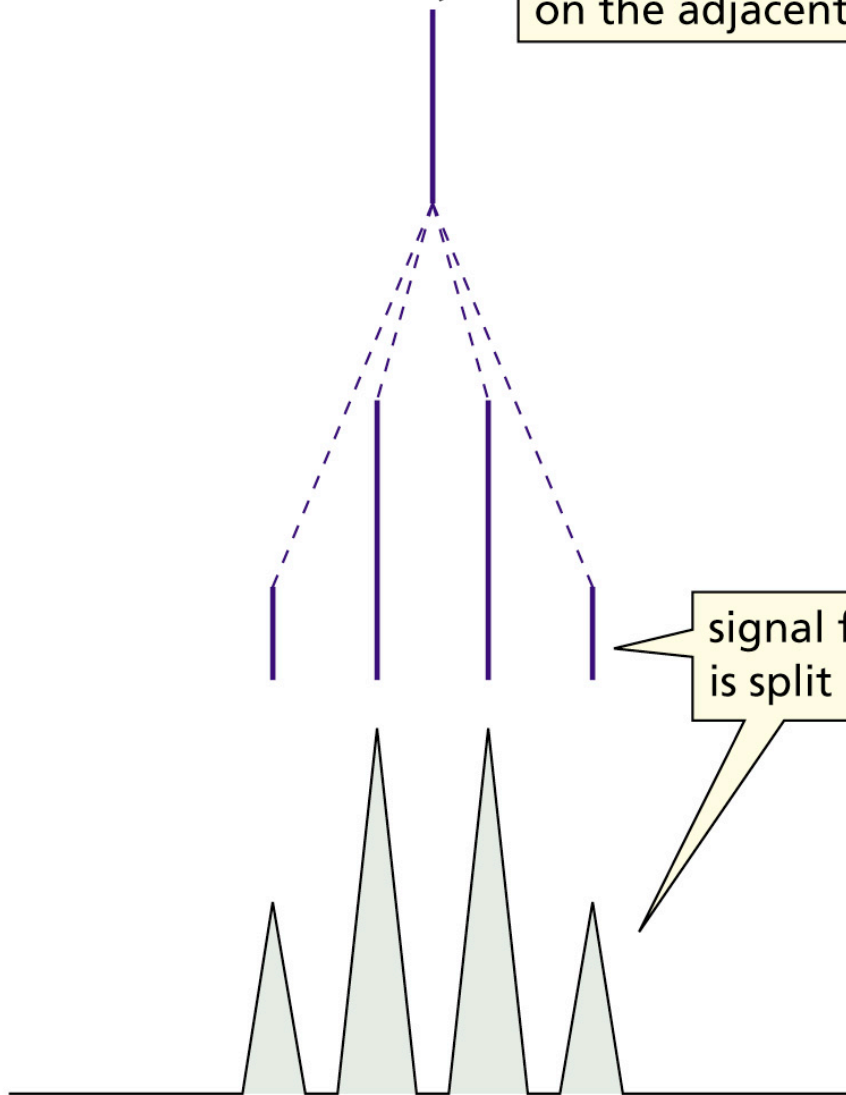
if the magnetic field of the
methine proton is in the
same direction as the
applied magnetic field, it
will add to the applied
magnetic field, so the
adjacent methyl protons will
show a signal at a slightly
higher frequency



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

← frequency

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

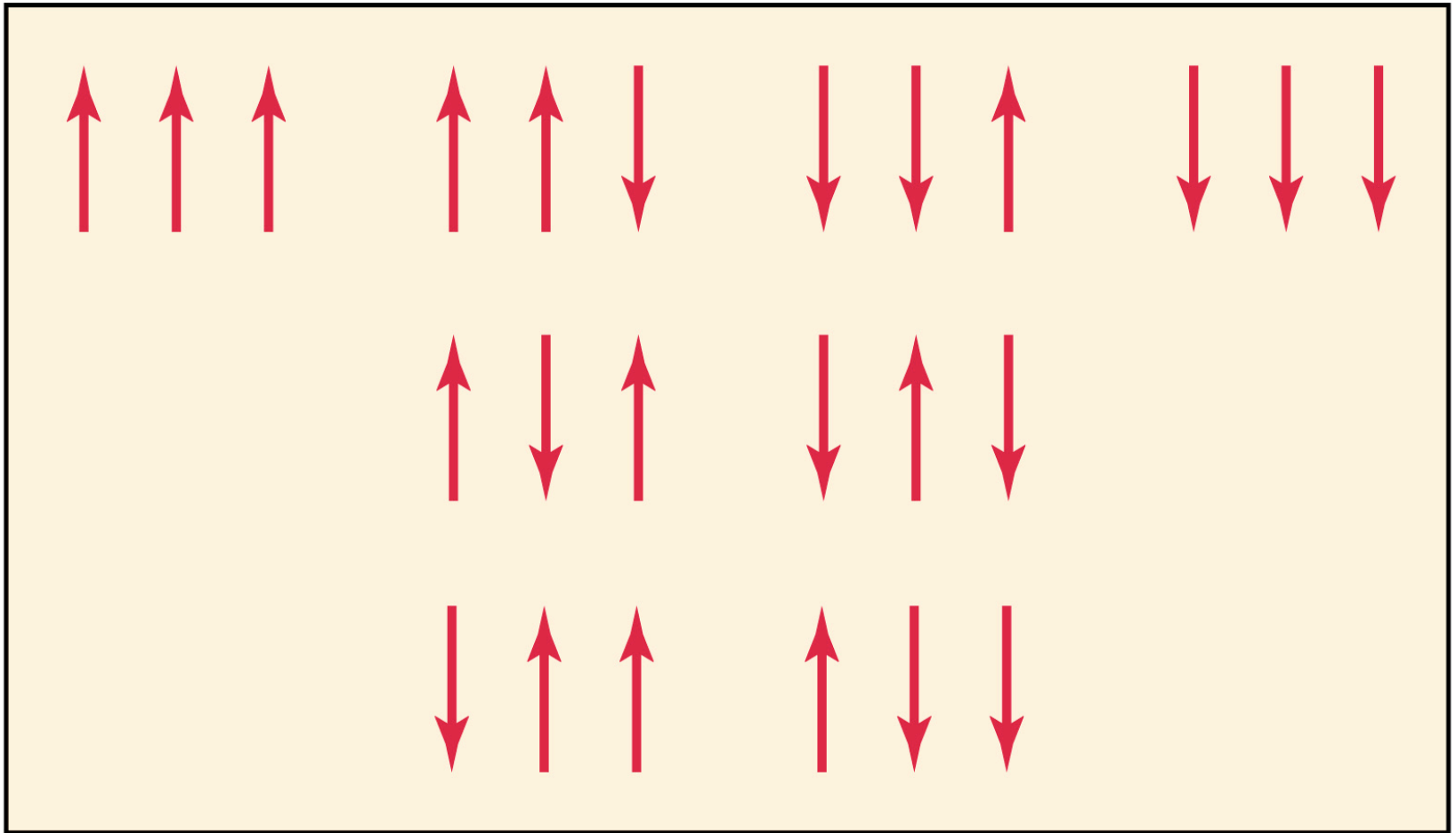
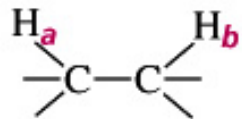


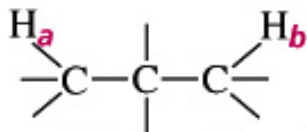
Table 14.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

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

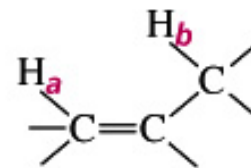
O desdobramento não são observados se os prótons estão separados por mais do que três ligações σ



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

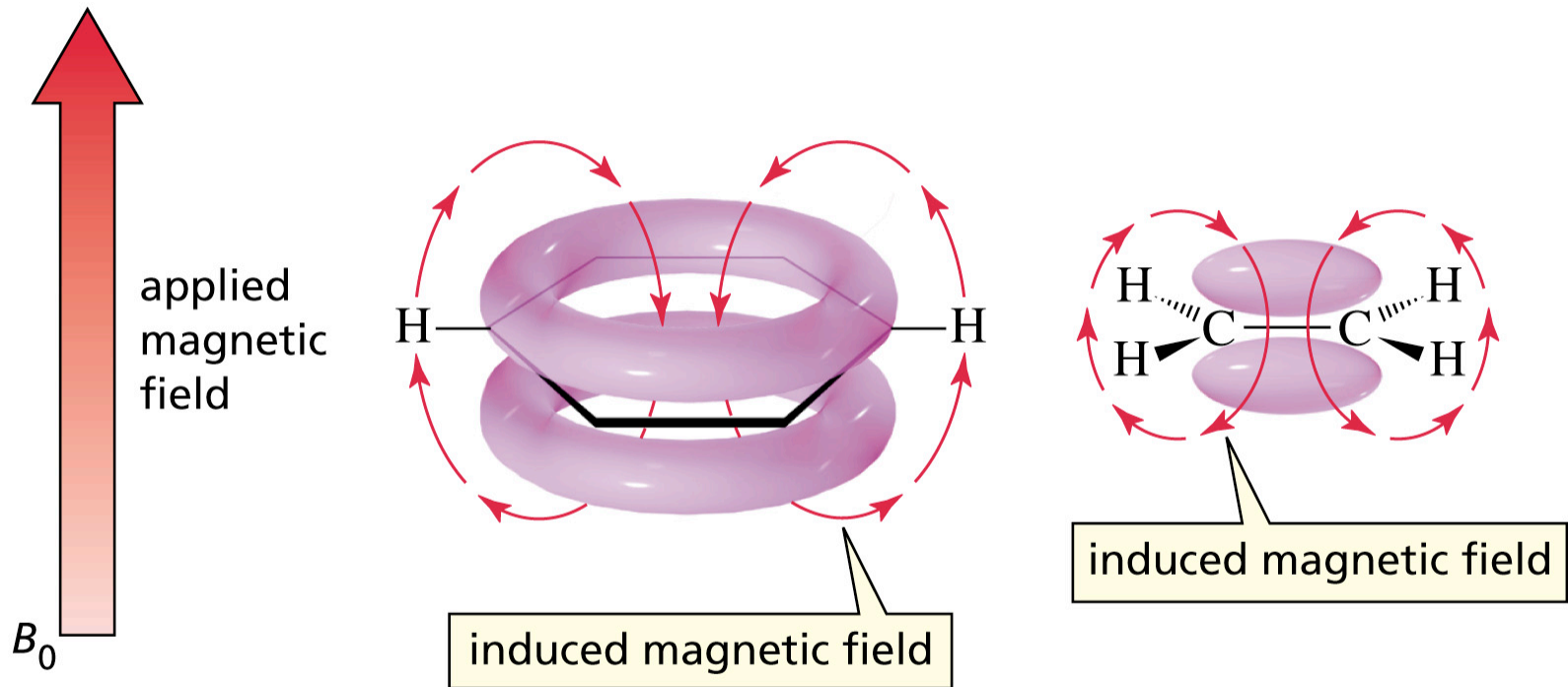


H_a and H_b may split each other because they are separated by 4 bonds including one double bond

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

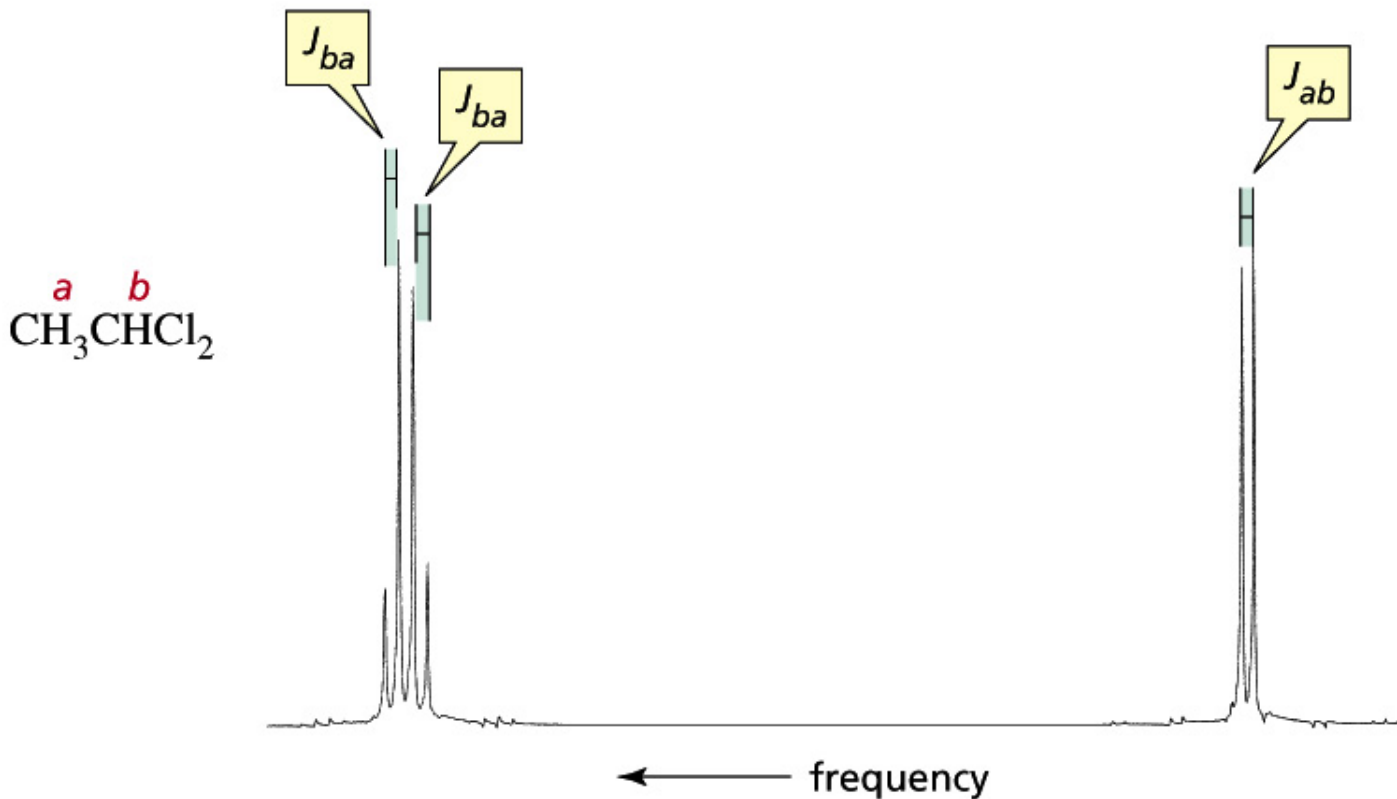
Elétrons π são menos atraídos pelo núcleo do que elétrons σ ; eles são mais livres para se mover em resposta ao campo magnético



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

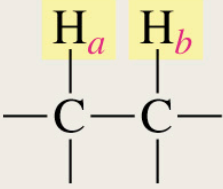
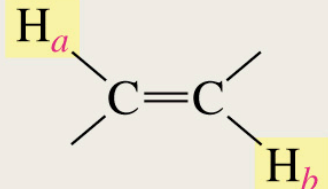
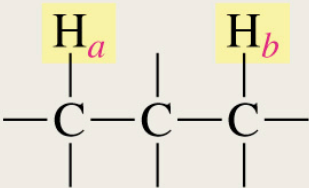
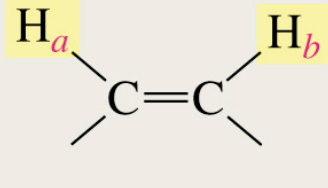
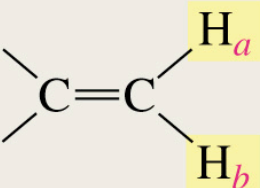
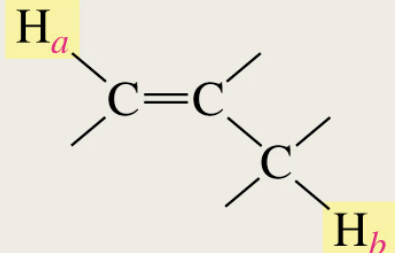
Constantes de Acoplamento

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

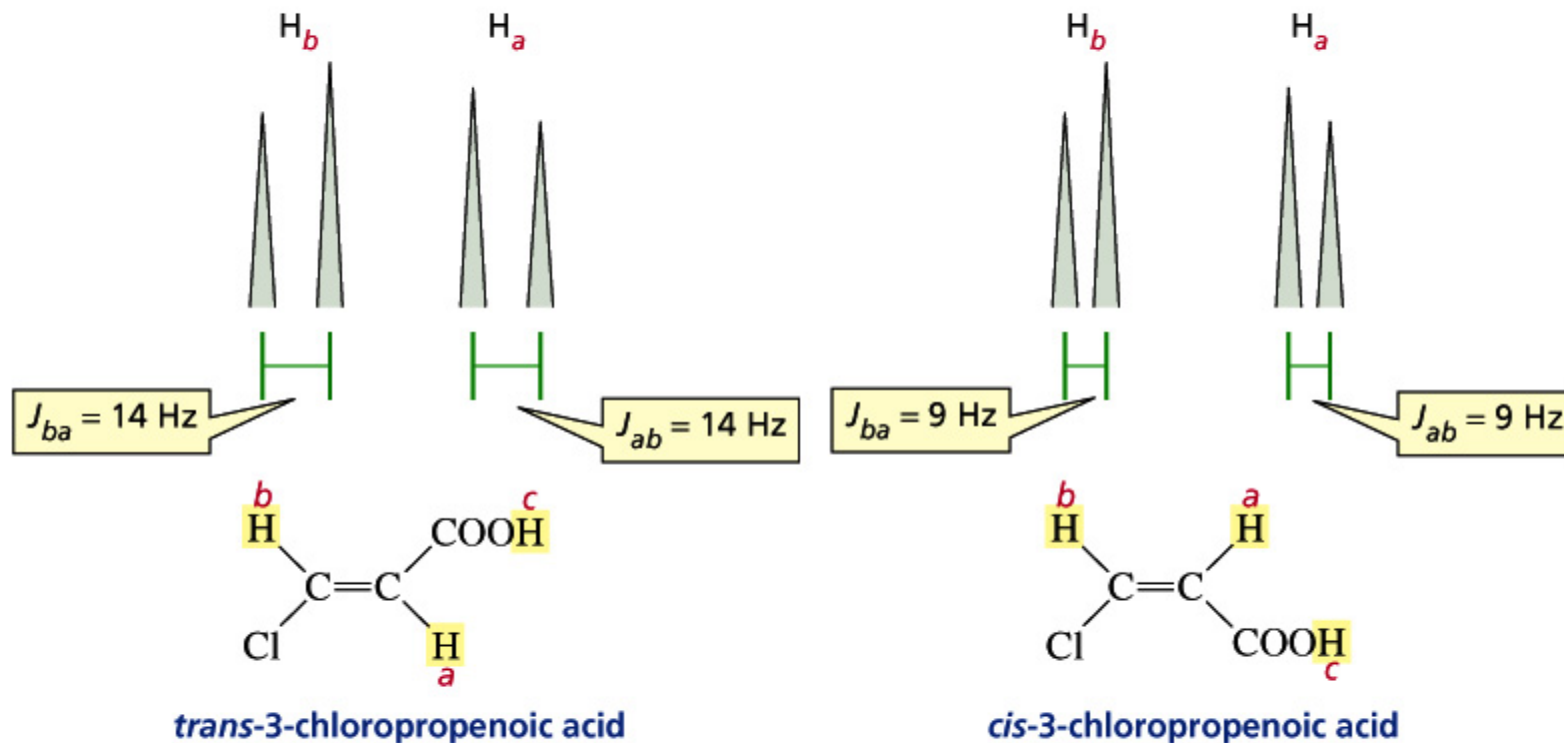


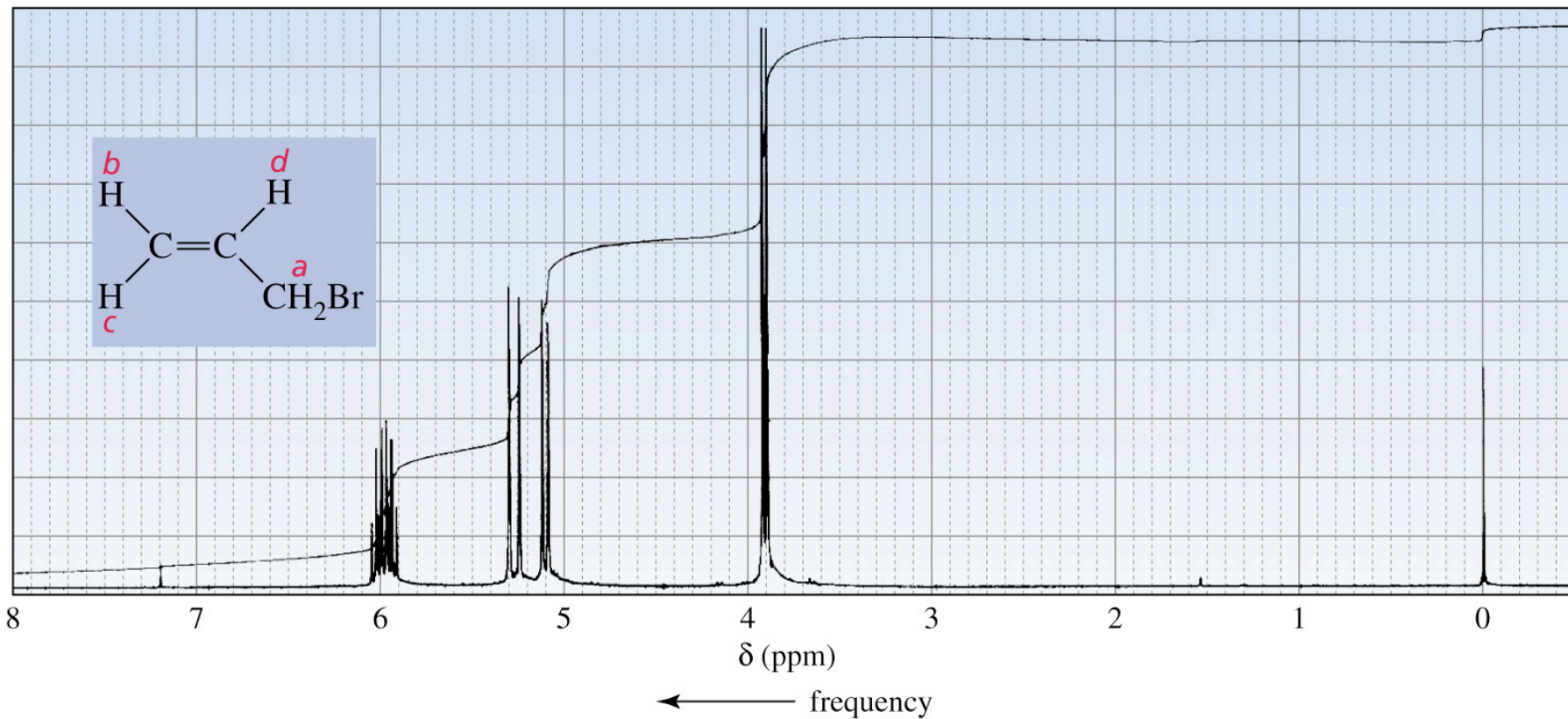
Prótons acoplados têm a mesma constante de acoplamento

Table 14.3 Approximate Values of Coupling Constants

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

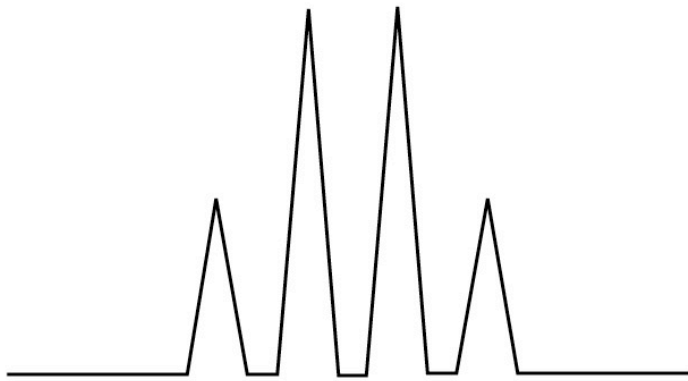
A constante de acoplamento trans é maior do que a cis





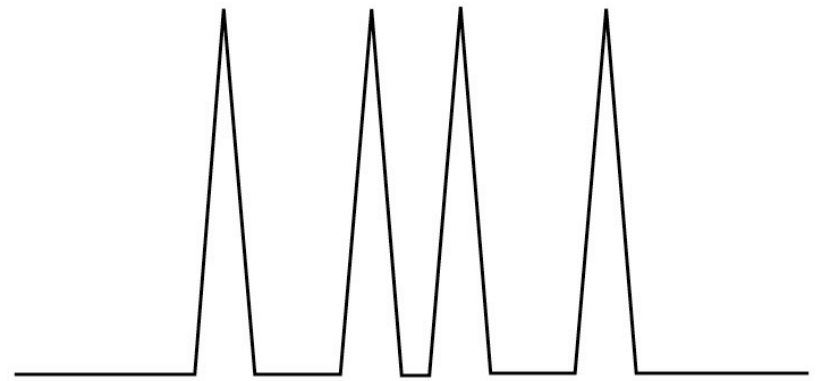
Os três prótons vinílicos estão em frequência relativamente alta, devido a anisotropia diamagnética

Diferença Entre um Quarteto e um Duplo Dublete



a quartet

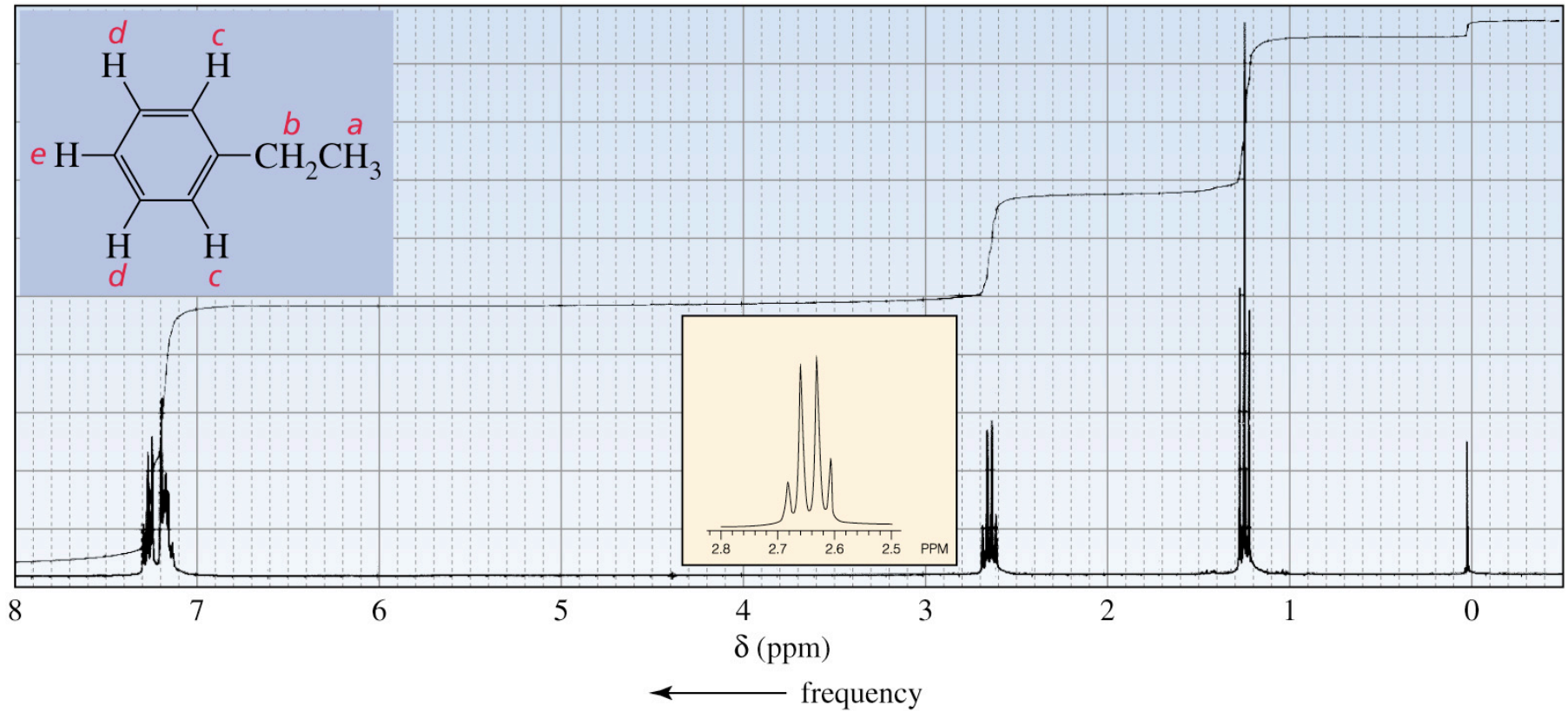
relative intensities: 1 : 3 : 3 : 1



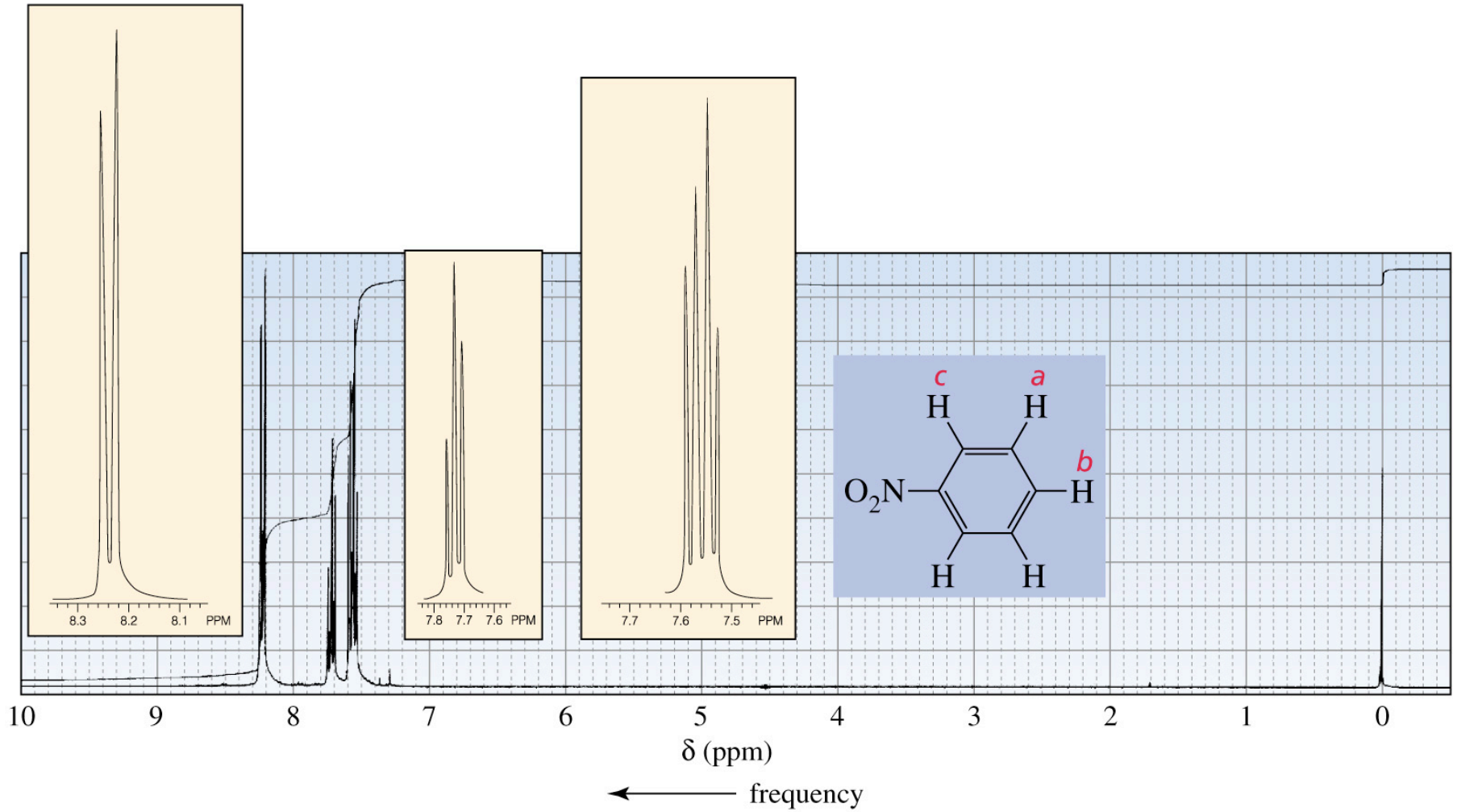
a doublet of doublets

relative intensities: 1 : 1 : 1 : 1

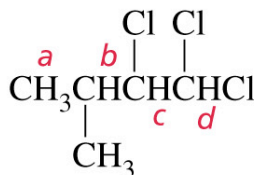
Os sinais de H_c , H_d e H_e se sobrepõem



Os sinais de H_a , H_b e H_c não se sobrepõem

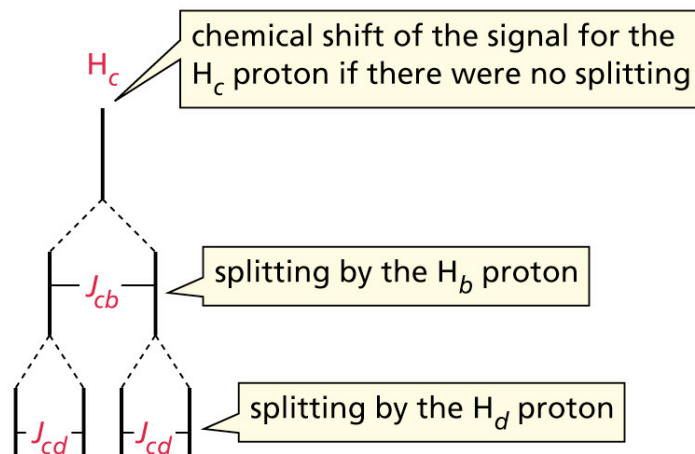


Um Diagrama de Desdobramento para Um Duplo Dupleto

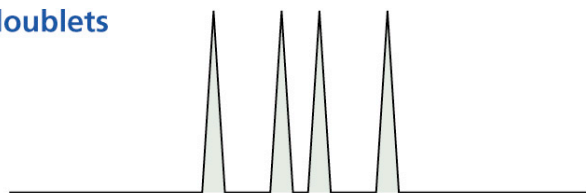


1,1,2-trichloro-3-methylbutane

a splitting diagram

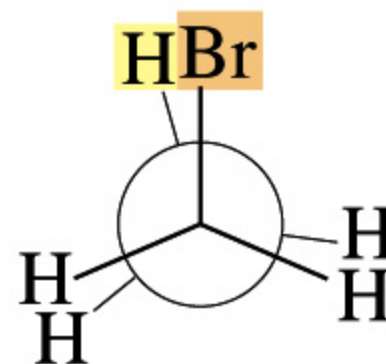
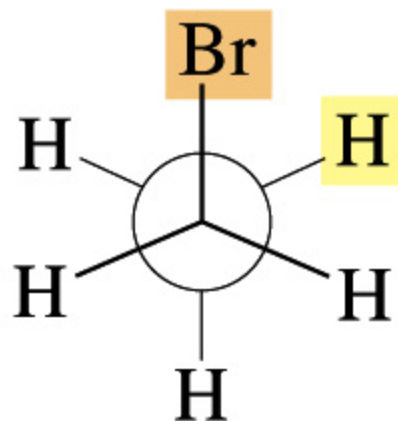
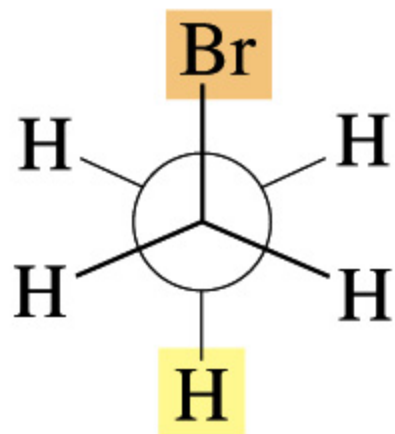


a doublet of doublets



← frequency

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

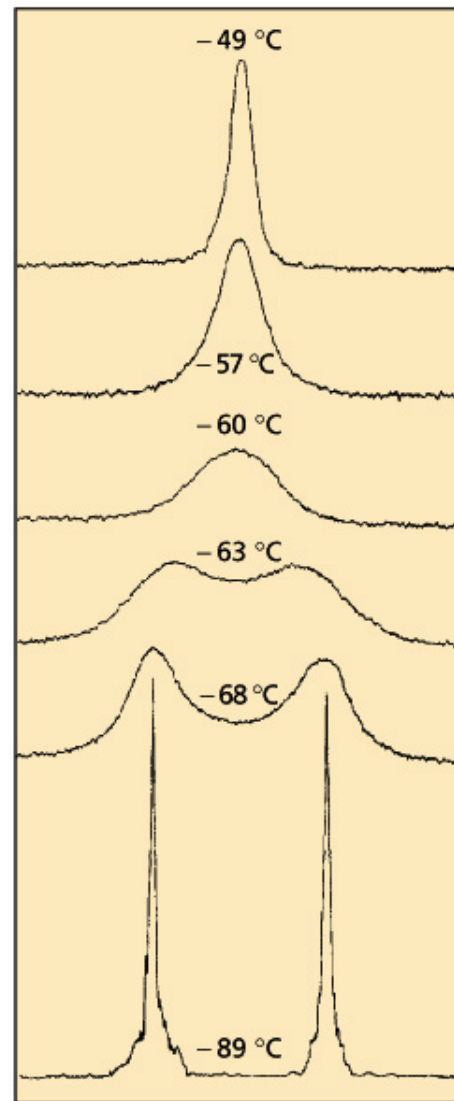


Vemos somente um sinal para o grupo metila no espectro de RMN ^1H

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



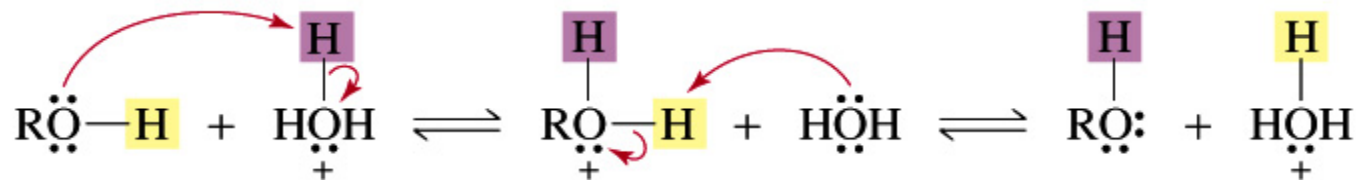
a velocidade da conversão
cadeira-cadeira depende
da temperatura



Prótons Ligados ao Oxigênio ou Nitrogênio

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

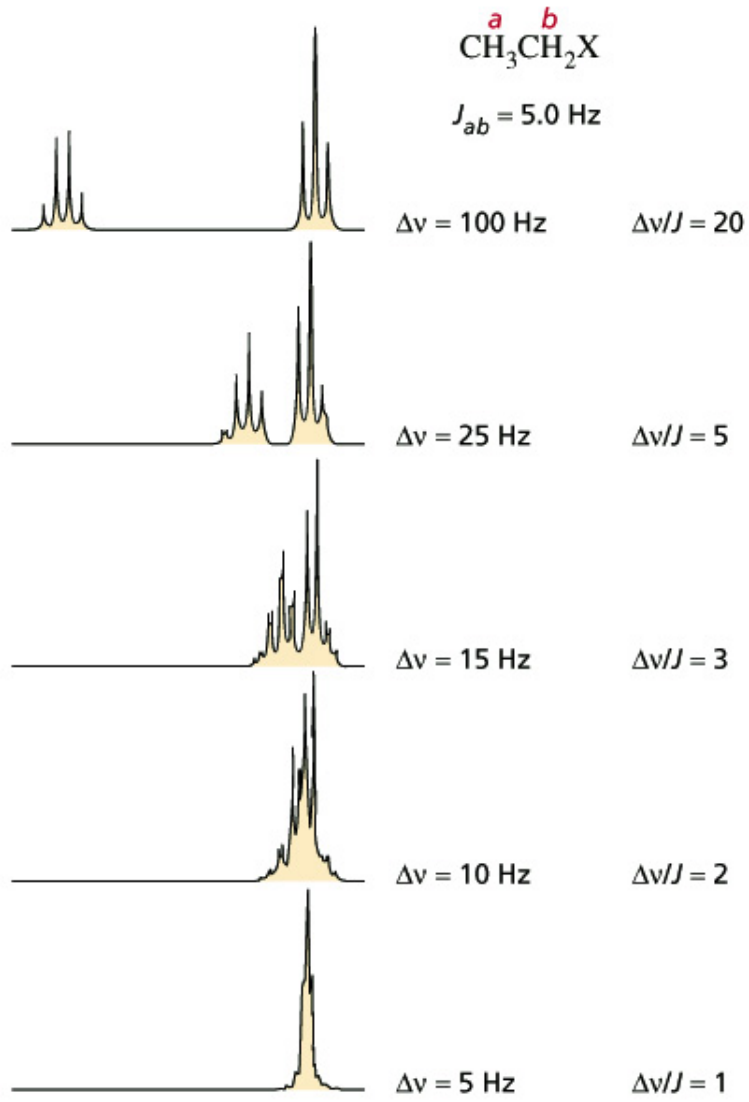
mechanism for acid-catalyzed proton exchange



Estes prótons podem ser trocados com o solvente

Eles sempre aparecem como um sinal largo

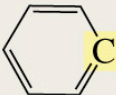
Para se observar um padrão de desdobramento bem definido, a diferença nos deslocamentos químicos ($\Delta\nu$, em Hz) deve ser de 10 vezes o valor da constante de acoplamento



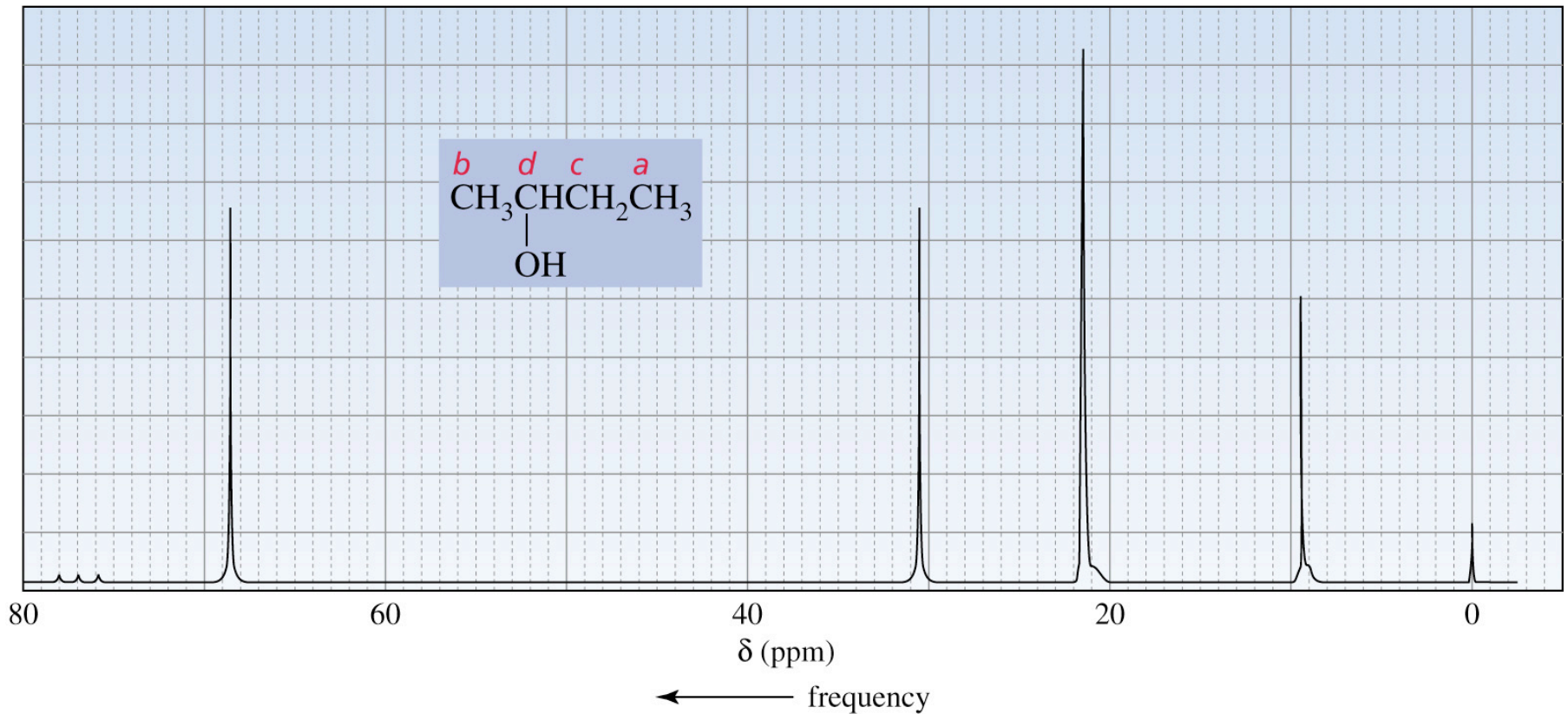
Espectroscopia de RMN ^{13}C

- 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 ^1H
- Os deslocamentos químicos variam acima de 220 ppm, enquanto o de próton, somente 10 ppm
- O composto de referência é o TMS

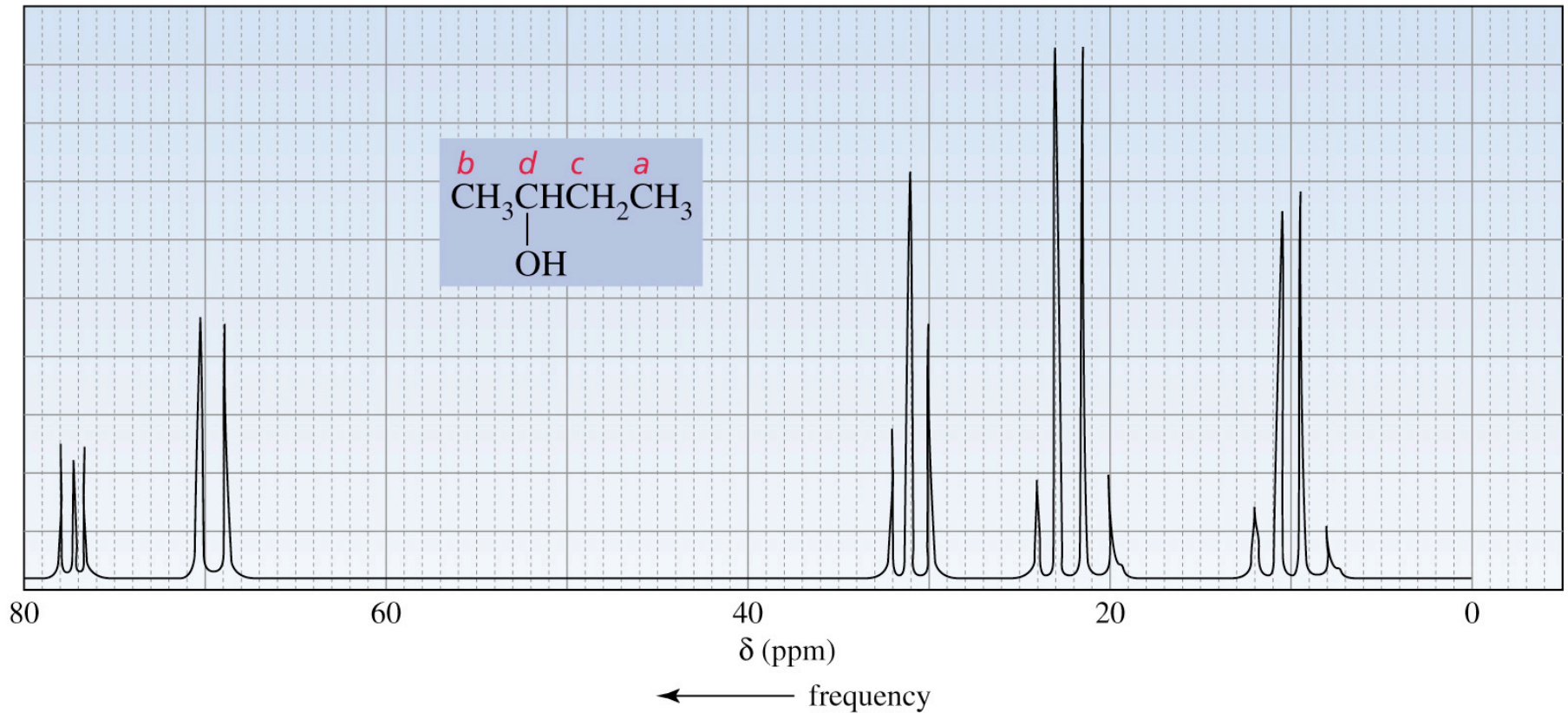
Table 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}-\text{I}$	0–40
$\text{R}-\text{CH}_3$	8–35	$\text{C}-\text{Br}$	25–65
$\text{R}-\text{CH}_2-\text{R}$	15–50	$\text{C}-\text{Cl}$	35–80
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{R} \end{array}$	20–60	$\text{C}-\text{N}$	40–60
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30–40	$\text{C}-\text{O}$	50–80
$\equiv\text{C}$	65–85	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ -\text{N}- \end{array}$	165–175
$=\text{C}$	100–150	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{RO} \end{array}$	165–175
	110–170	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$	175–185
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$	190–200
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$	205–220

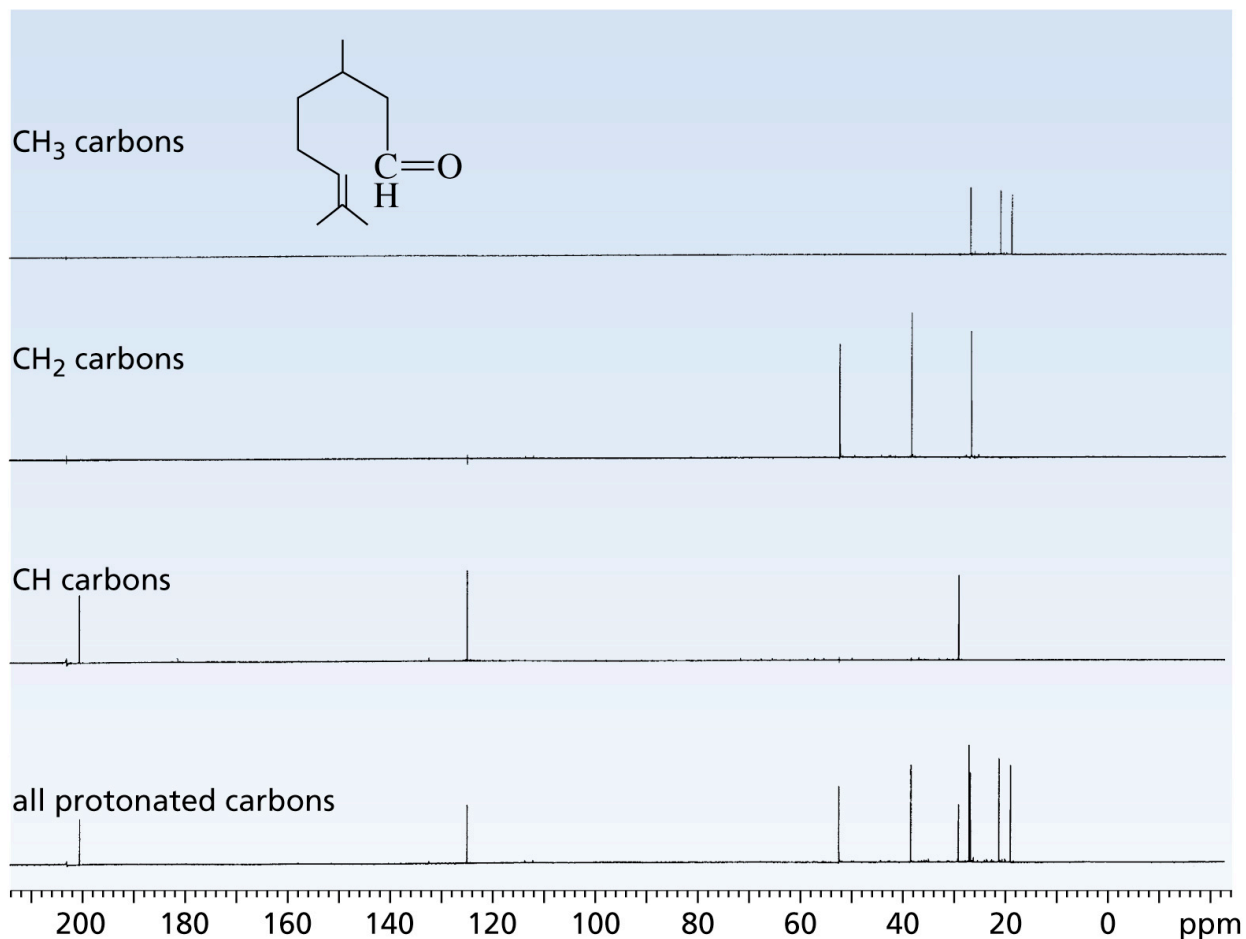
Espectro de RMN ^{13}C Desacoplado do 2-butanol



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



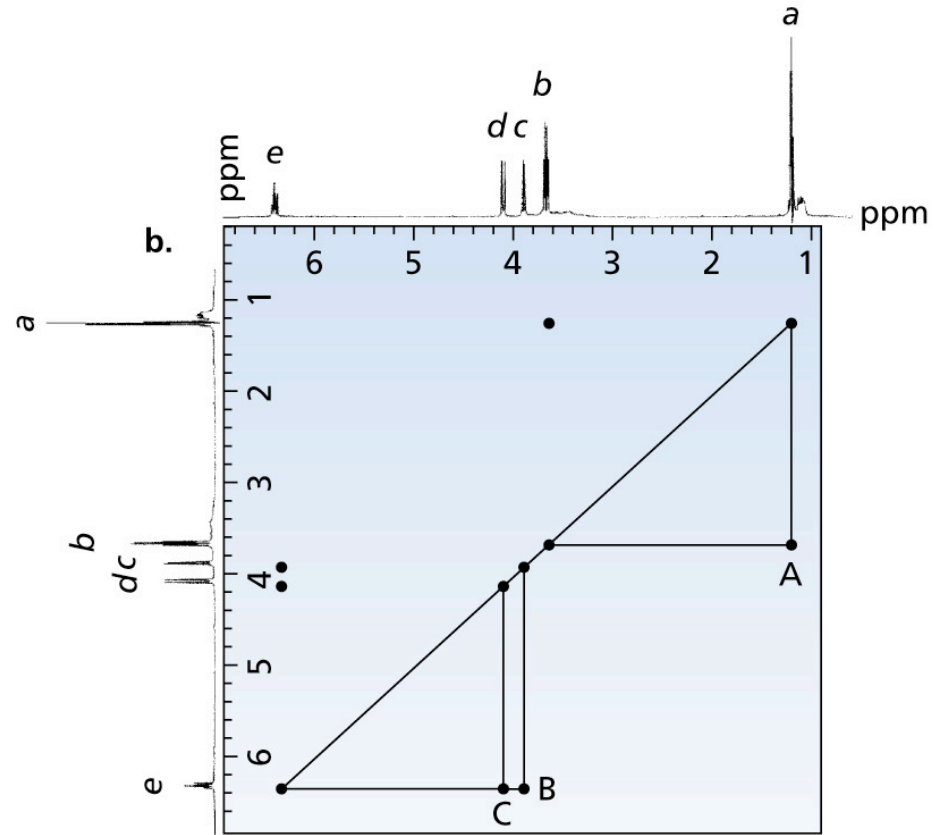
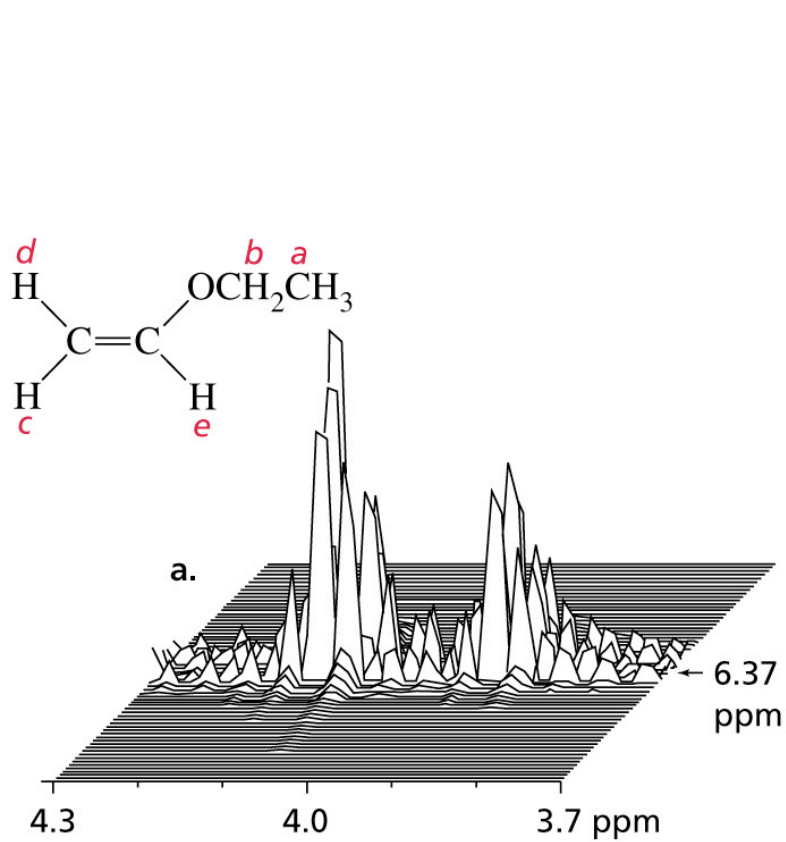
O espectro DEPT de RMN ^{13}C permite distinguir entre os grupos CH_3 , CH_2 e CH



DEPT 90: CH

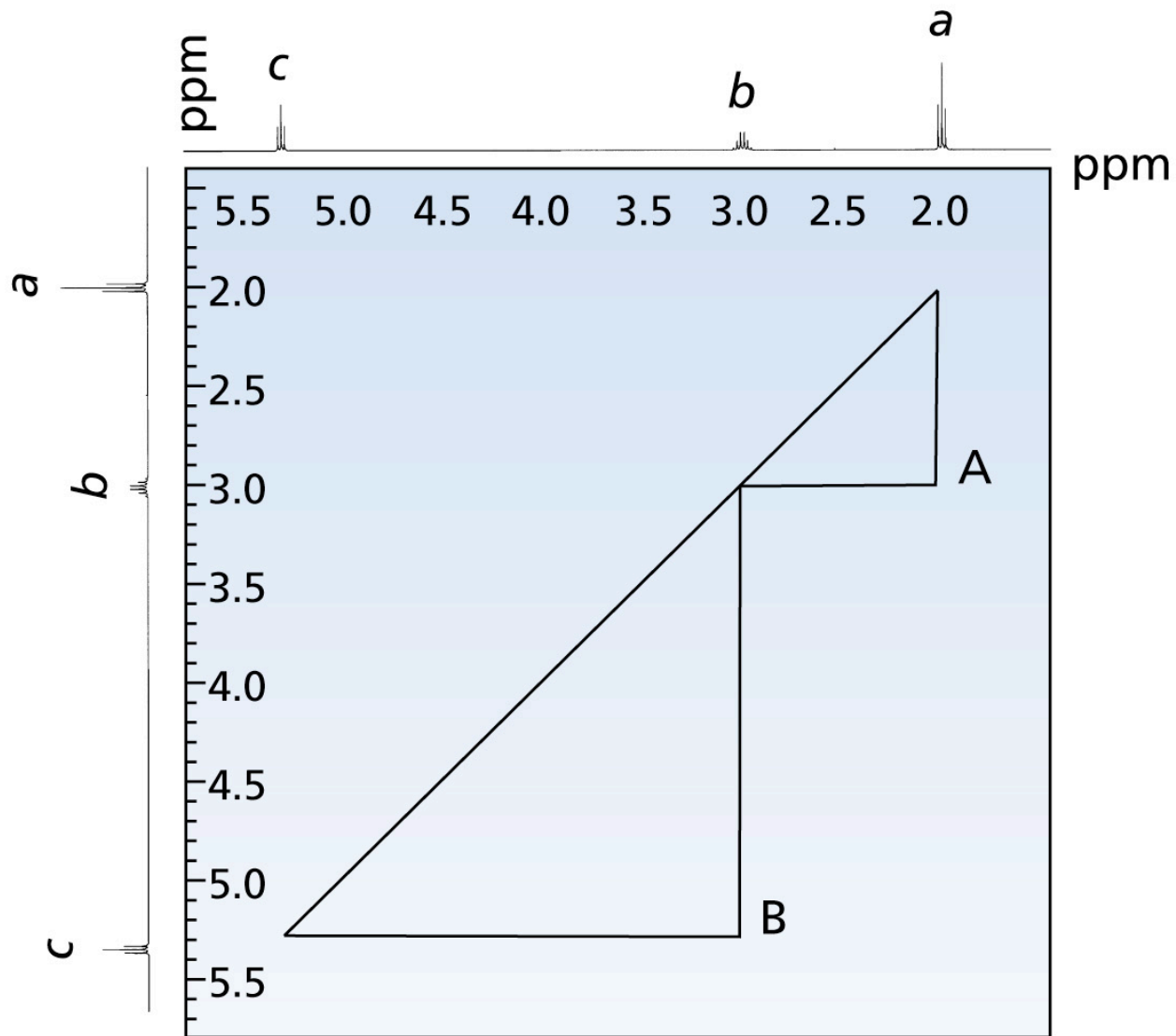
DEPT 135: CH e CH_3 (sinal positivo), CH_2 (sinal negativo)

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



Picos cruzados indicam pares de prótons acoplados

Espectro COSY de RMN ^1H do 1-nitropropano



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

