

Espectroscopia de Ressonância Magnética Nuclear (RMN)

Parte 2

Núcleos têm momento angular de spin intrínseco

Núcleo	Spin	Fator g	Momento magnético (em magnetons nucleares)	Razão giromagnética ($\gamma/10^7 \text{ T}^{-1}\text{s}^{-1}$)
^1H	1/2	5,5854	2,7928	26,7522
^2H	1	0,8574	0,8574	4,1066
^{13}C	1/2	1,4042	0,7021	6,7283
^{14}N	1	0,4036	0,4036	1,9338
^{31}P	1/2	2,2610	1,1305	10,841

Núcleos também têm momento angular de spin intrínseco

Para prótons ($I = 1/2$):

$$\hat{I}^2 \alpha = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \alpha$$

$$\hat{I}^2 \beta = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \beta$$

$$\hat{I}_z \alpha = \frac{1}{2} \hbar \alpha$$

$$\hat{I}_z \beta = -\frac{1}{2} \hbar \beta$$

^1H em campo magnético

Na ausência de campo ($B_z = 0$)

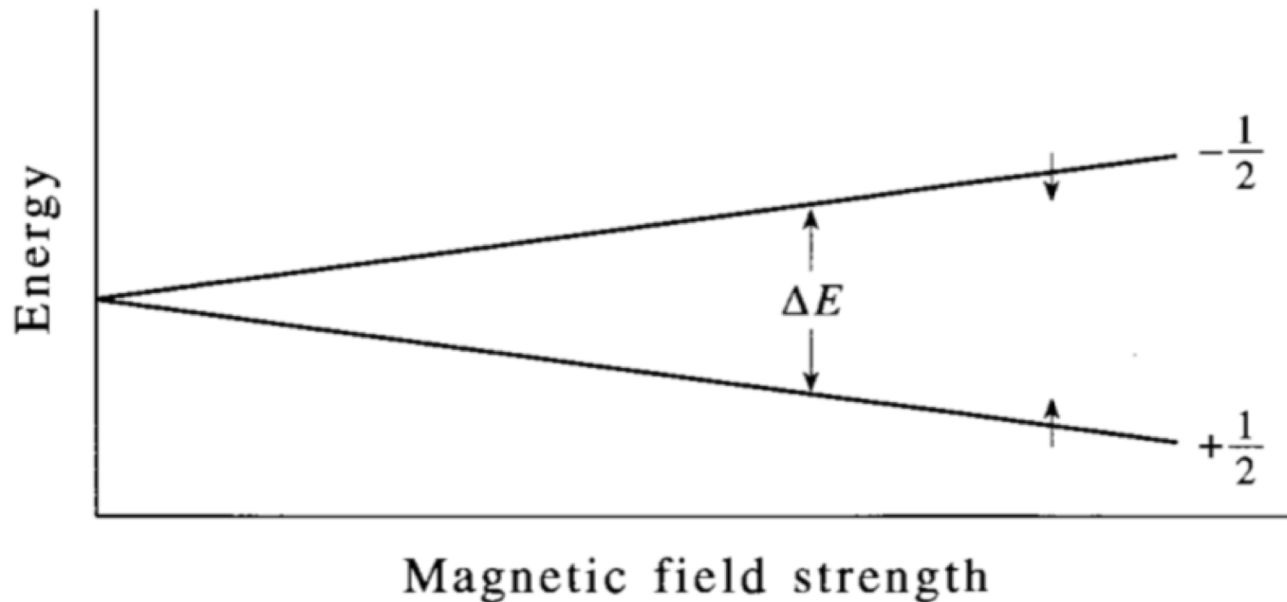
$$E(m_I = 1/2) = E(m_I = -1/2)$$

Diferença de energia na presença do campo

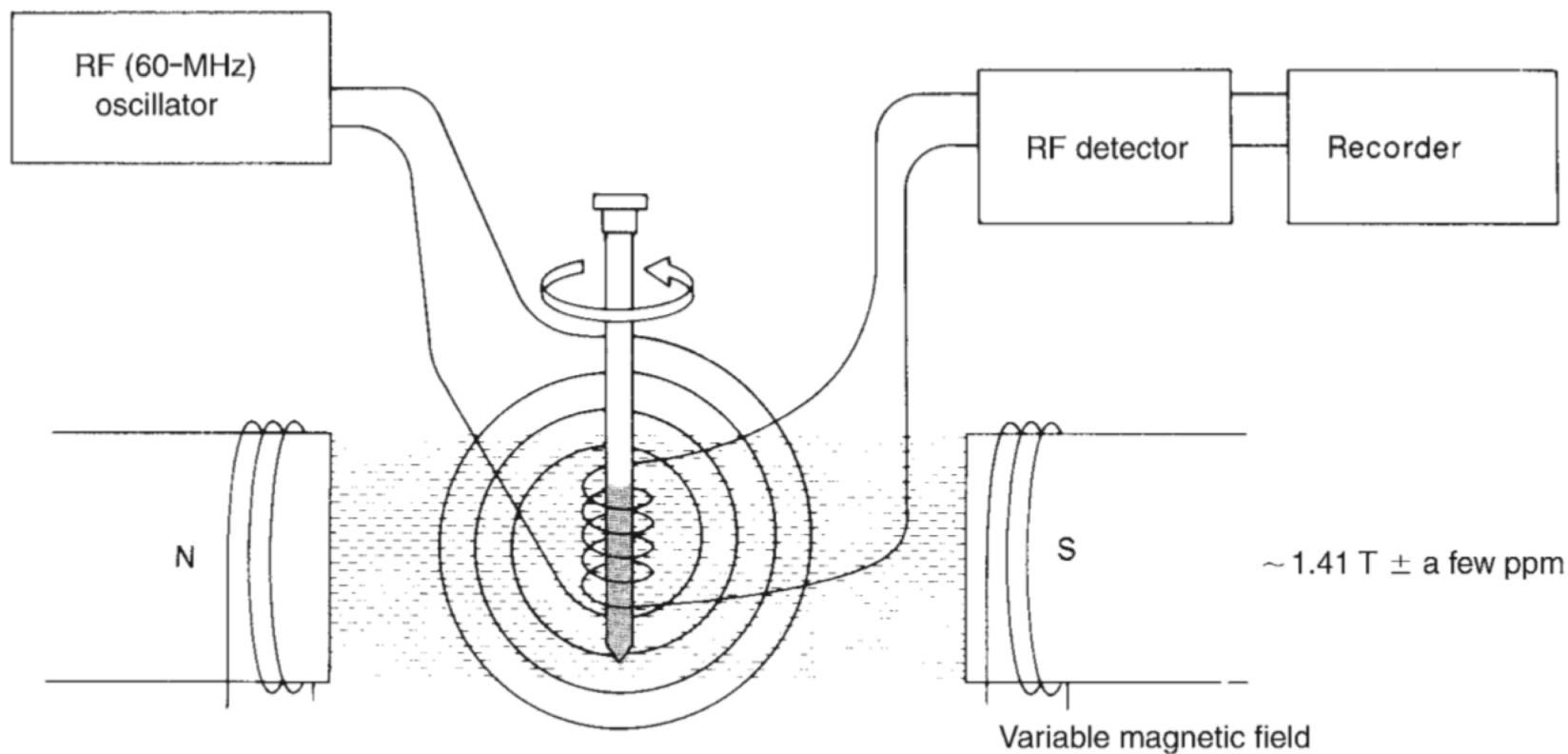
$$\begin{aligned}\Delta E &= E(m_I = -1/2) - E(m_I = +1/2) \\ &= +\frac{1}{2}\hbar\gamma B_z - \left(-\frac{1}{2}\hbar\gamma B_z\right) \\ \Delta E &= \hbar\gamma B_z\end{aligned}$$

Energias relativas de ^1H em campo magnético

$$\Delta E = \hbar\gamma B_z$$



Espectrômetros de RMN



A ação de campo magnético é blindada

$$\nu = \frac{\gamma(1 - \sigma)}{2\pi} B_0 \qquad B_0 = \frac{2\pi\nu}{\gamma(1 - \sigma)}$$

Frequência em que ocorrem transições de spin nuclear (ressonância), para dado valor de campo, depende da constante de blindagem, σ .

Cada núcleo em ambiente químico distinto, gera sinal distinto.

δ_H é independente de B_0

$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1) \times 10^6$$

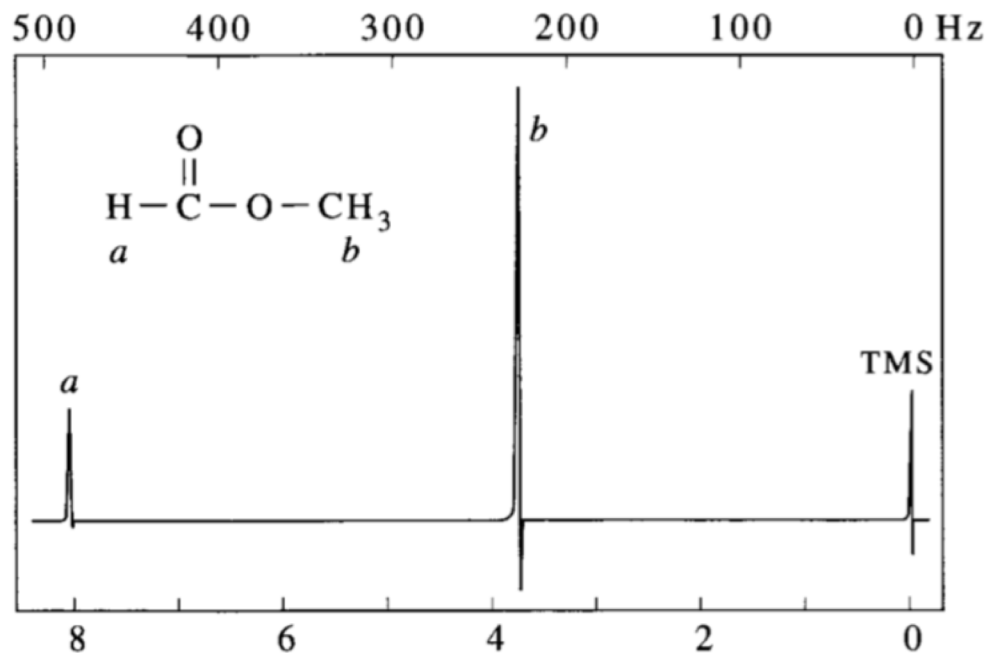
Diferença de deslocamento químico entre núcleos diferentes depende da blindagem (ambiente químico) e é independente do campo.

Exemplo

Mostre que as escalas superior e inferior do espectro (obtido a 60 MHz) abaixo são consistentes para os dois sinais identificados como *a* e *b*.

Estime a diferença entre as blindagens de *a* e *b*.

Qual seria a separação entre os dois sinais em um espectrômetro de 270 MHz?

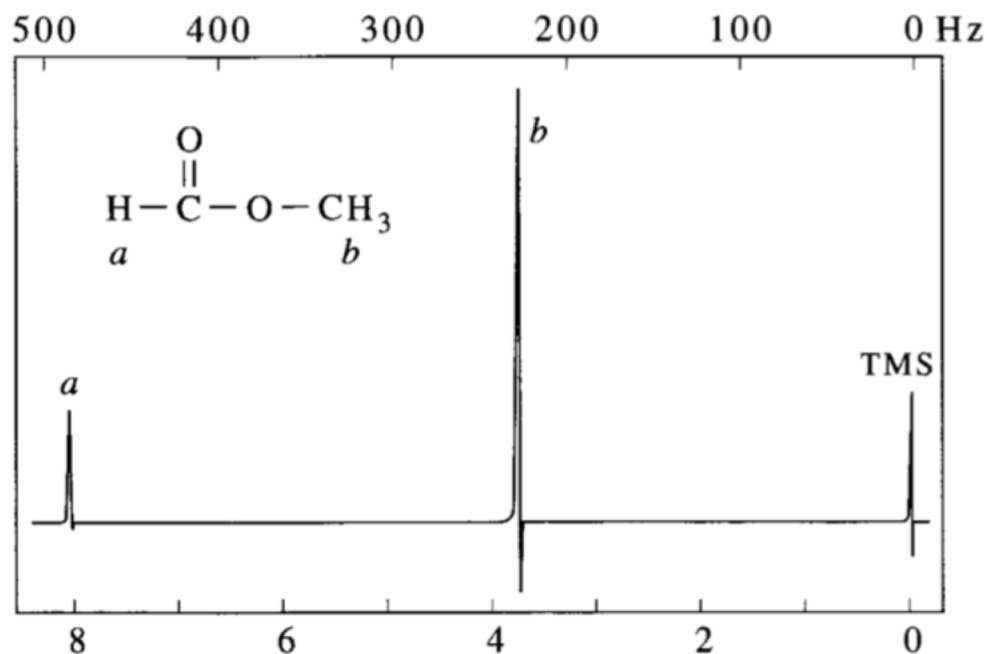


$$\nu_a = 480 \text{ Hz}$$

$$\delta_a = 8,0 \text{ ppm}$$

$$\nu_b = 230 \text{ Hz}$$

$$\delta_b = 3,8 \text{ ppm}$$



$$\delta_H = \left(\frac{\nu_H - \nu_{\text{TMS}}}{\nu_{\text{spectr.}}} \right) \times 10^6$$

$$\delta_a = \left(\frac{480 \text{ Hz}}{60 \text{ MHz}} \right) \times 10^6 = 8,0 \text{ ppm}$$

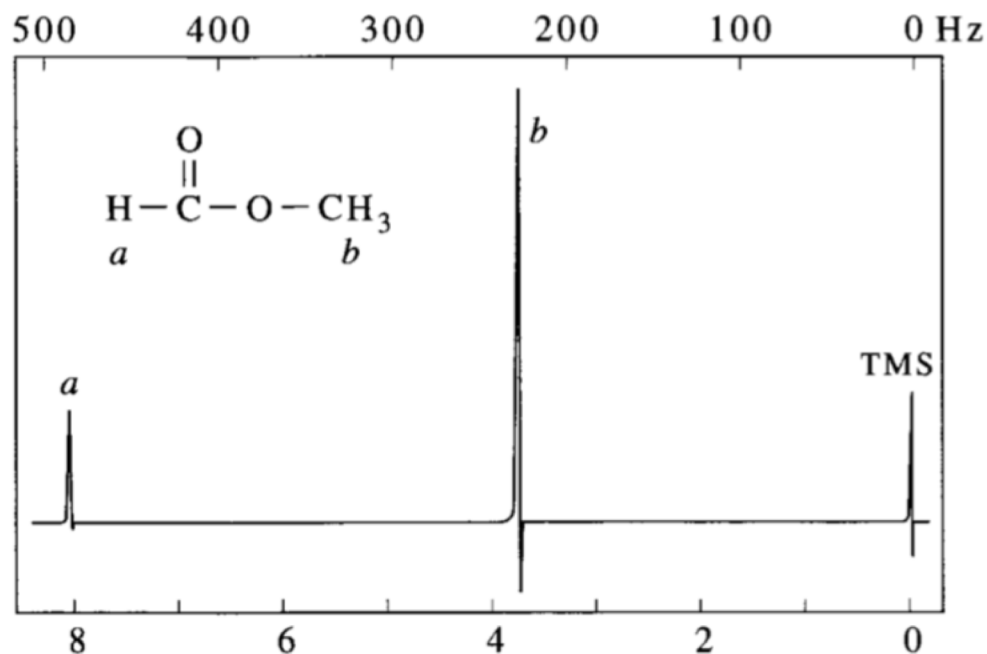
$$\delta_b = \left(\frac{230 \text{ Hz}}{60 \text{ MHz}} \right) \times 10^6 = 3,8 \text{ ppm}$$

$$\nu_a = 480 \text{ Hz}$$

$$\delta_a = 8,0 \text{ ppm}$$

$$\nu_b = 230 \text{ Hz}$$

$$\delta_b = 3,8 \text{ ppm}$$



$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1) \times 10^6$$

$$\delta_a - \delta_b = (\sigma_b - \sigma_a) \times 10^6$$

$$\sigma_b - \sigma_a = (\delta_a - \delta_b) \times 10^{-6}$$

$$\sigma_b - \sigma_a = (8,0 - 3,8) \times 10^{-6}$$

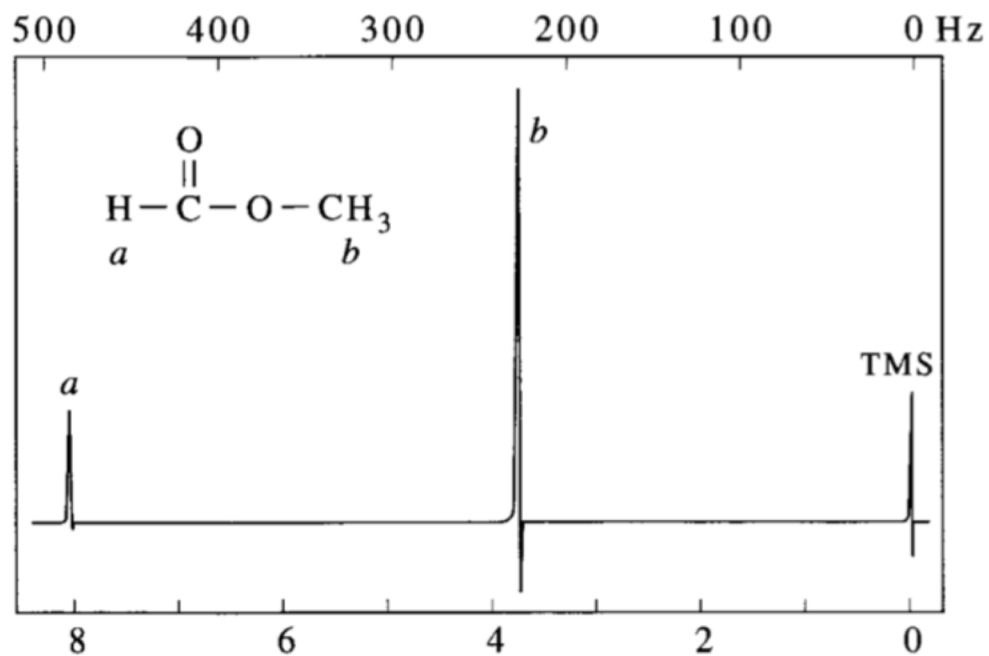
$$= 4,2 \times 10^{-6}$$

$$\nu_a = 480 \text{ Hz}$$

$$\delta_a = 8,0 \text{ ppm}$$

$$\nu_b = 230 \text{ Hz}$$

$$\delta_b = 3,8 \text{ ppm}$$



$$\nu_a - \nu_b = \nu_{\text{espectr}}(\delta_a - \delta_b) \times 10^{-6}$$

$$\nu_a - \nu_b = (270 \text{ MHz})(8,0 - 3,8) \times 10^{-6}$$

$$= 1130 \text{ Hz}$$

Exemplo

Mostre que $\delta_H = (\sigma_{\text{TMS}} - \sigma_H) \times 10^6$ e interprete o resultado.

$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1) \times 10^6$$

$$\delta_1 = \delta_H$$

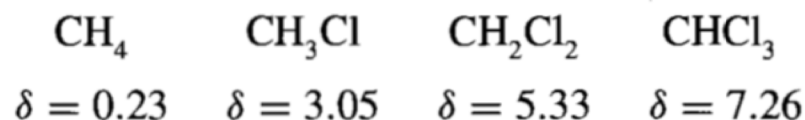
$$\sigma_1 = \sigma_H$$

$$\delta_2 = \delta_{\text{TMS}} = 0$$

$$\sigma_2 = \sigma_{\text{TMS}}$$

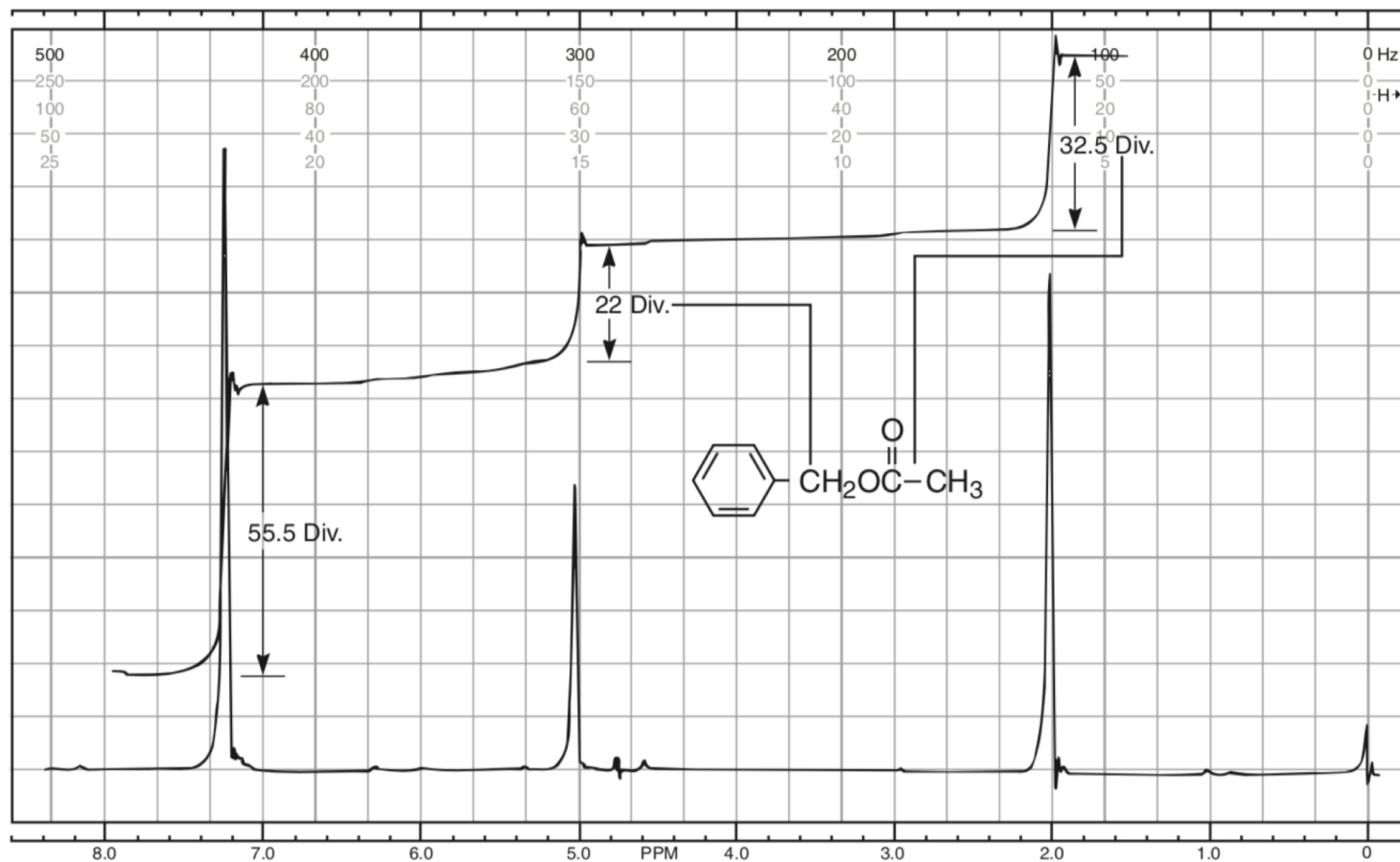
Deslocamentos químicos dependem do ambiente

$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1) \times 10^6$$



Compound CH₃X	CH ₃ F	CH ₃ OH	CH ₃ Cl	CH ₃ Br	CH ₃ I	CH ₄	(CH ₃) ₄ Si
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

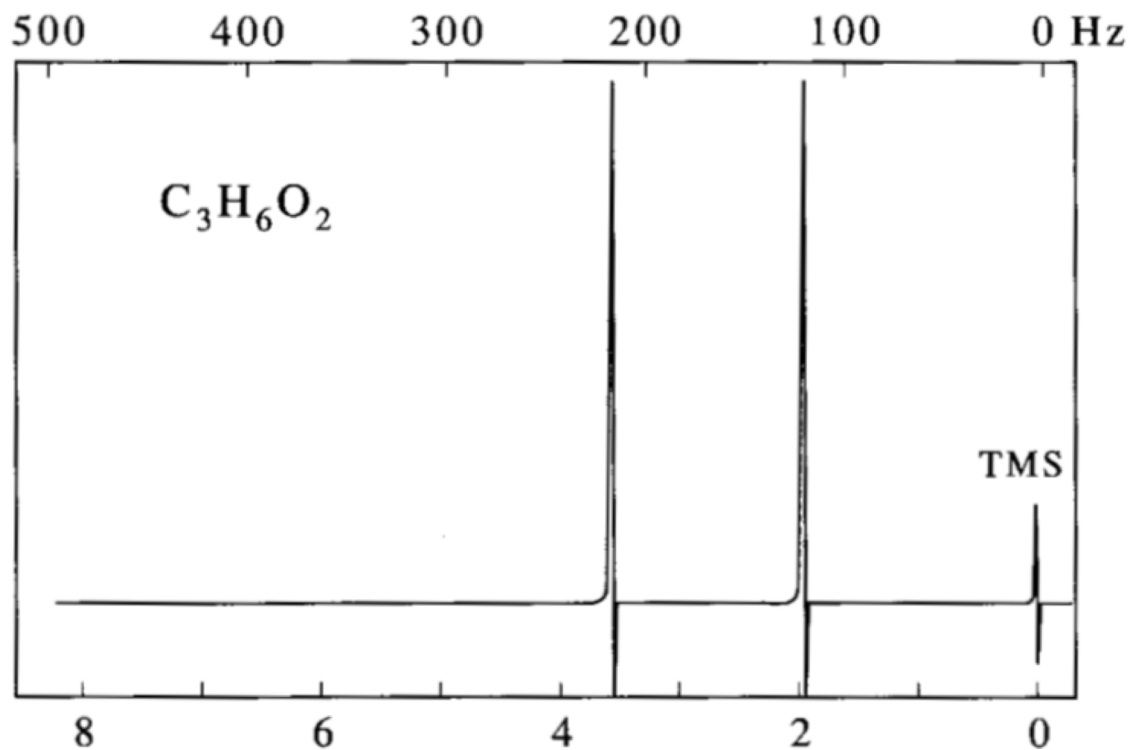
Área do sinal é proporcional ao número de H



$$55,5:22:32,5 = 5:2:3$$

Exemplo

Acetato de metila ($\text{CH}_3\text{COOCH}_3$) ou metanoato de etila ($\text{HCOOCH}_2\text{CH}_3$)?



Nomenclatura dos sinais

A, B, C, D, ...

AB: deslocamentos próximos

AX: deslocamentos afastados

A_n , B_n : mais de um H equivalente

Acoplamento spin-spin

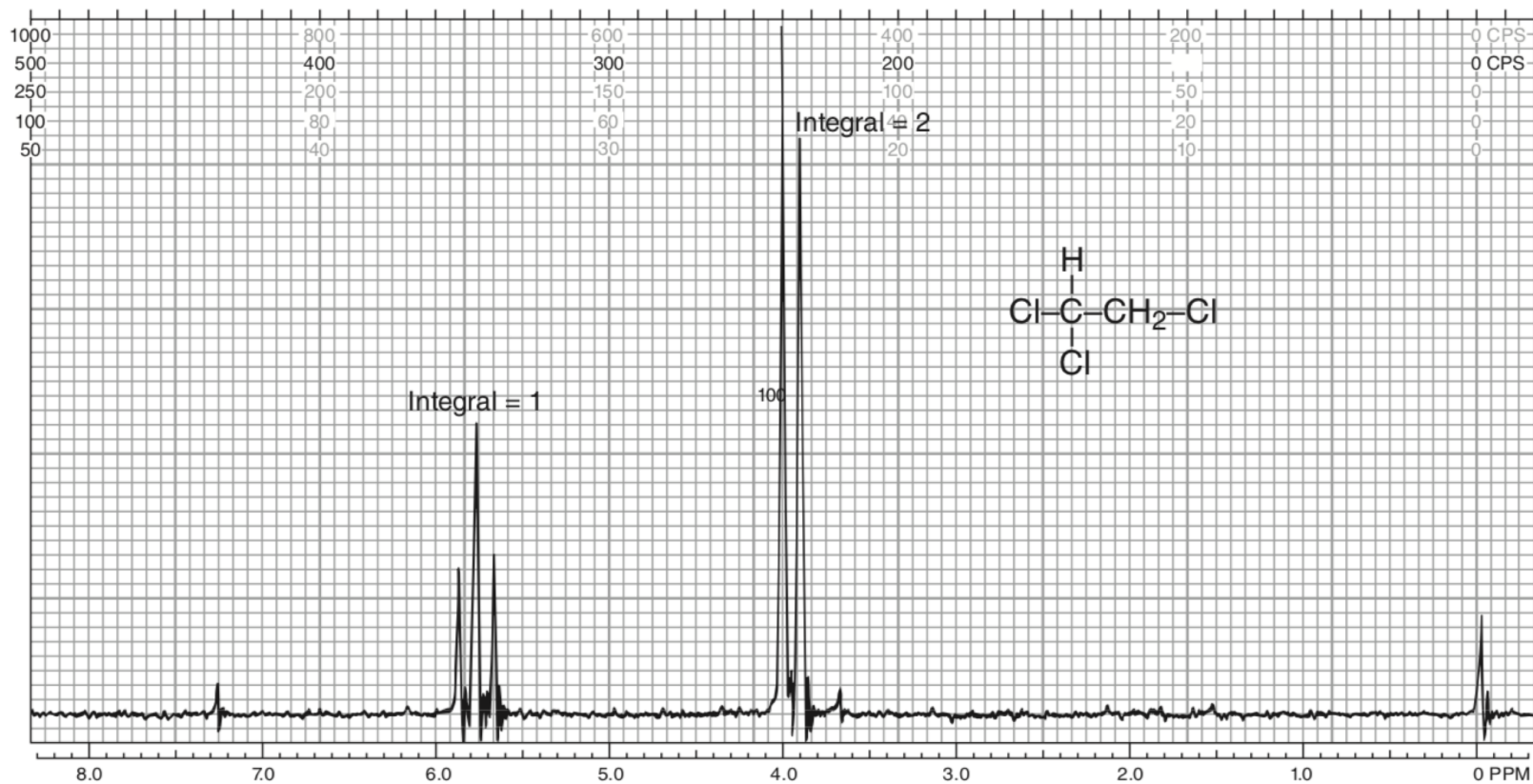


FIGURE 5.25 The ^1H NMR spectrum of 1,1,2-trichloroethane (60 MHz).

Acoplamento spin-spin

Interação entre dois ^1H em ambientes diferentes

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_1 = -\gamma B_0(1 - \sigma_1) \hat{I}_{z1}$$

$$\hat{H}_2 = -\gamma B_0(1 - \sigma_2) \hat{I}_{z2}$$

$$\hat{H}_{12} = \frac{hJ_{12}}{\hbar^2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2$$

J_{12} : constante de acoplamento spin-spin

Solução: teoria de perturbação

Hamiltoniano não perturbado

$$\hat{H}^{(0)} = -\gamma B_0(1 - \sigma_1) \hat{I}_{z1} - \gamma B_0(1 - \sigma_2) \hat{I}_{z2}$$

Perturbação

$$\hat{H}^{(1)} = \frac{hJ_{12}}{\hbar^2} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2$$

Soluções de $\hat{H}^{(0)}$

$$\psi_1 = \alpha(1)\alpha(2)$$

$$\hat{H}^{(0)}\psi_1 = E_1^{(0)}\psi_1$$

$$\psi_2 = \beta(1)\alpha(2)$$

$$\hat{H}^{(0)}\psi_2 = E_2^{(0)}\psi_2$$

$$\psi_3 = \alpha(1)\beta(2)$$

$$\hat{H}^{(0)}\psi_3 = E_3^{(0)}\psi_3$$

$$\psi_4 = \beta(1)\beta(2)$$

$$\hat{H}^{(0)}\psi_4 = E_4^{(0)}\psi_4$$

$$\hat{H}^{(0)}\psi_1 = E_1^{(0)}\psi_1$$

$$\begin{aligned}\hat{H}^{(0)}\psi_1 &= \{-\gamma B_0(1 - \sigma_1) \hat{I}_{z1} - \gamma B_0(1 - \sigma_2) \hat{I}_{z2}\}\alpha(1)\alpha(2) \\ &= -\gamma B_0(1 - \sigma_1) \hat{I}_{z1}\alpha(1)\alpha(2) - \gamma B_0(1 - \sigma_2) \hat{I}_{z2}\alpha(1)\alpha(2)\end{aligned}$$

$$\hat{I}_{z1}\alpha(1) = \frac{1}{2}\hbar\alpha(1)$$

$$\begin{aligned}&= -\frac{\hbar}{2}\gamma B_0(1 - \sigma_1) \alpha(1)\alpha(2) - \frac{\hbar}{2}\gamma B_0(1 - \sigma_2) \alpha(1)\alpha(2) \\ &= -\hbar\gamma B_0 \left[1 - \frac{\sigma_1 + \sigma_2}{2}\right] \alpha(1)\alpha(2) = E_1^{(0)}\psi_1\end{aligned}$$

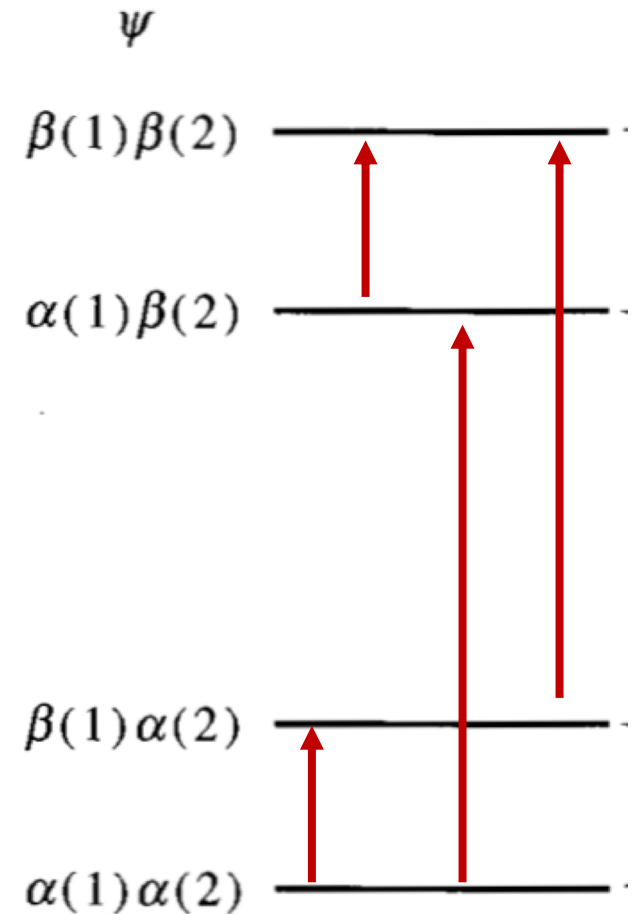
Soluções de $\hat{H}^{(0)}$

$$E_1^{(0)} = -\hbar\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right)$$

$$E_2^{(0)} = -\frac{\hbar\gamma B_0}{2} (\sigma_1 - \sigma_2)$$

$$E_3^{(0)} = +\frac{\hbar\gamma B_0}{2} (\sigma_1 - \sigma_2)$$

$$E_4^{(0)} = +\hbar\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right)$$



Interação spin-spin

$$E_j = E_j^{(0)} + \int d\tau_1 d\tau_2 \psi_1^* \hat{H}^{(1)} \psi_j$$

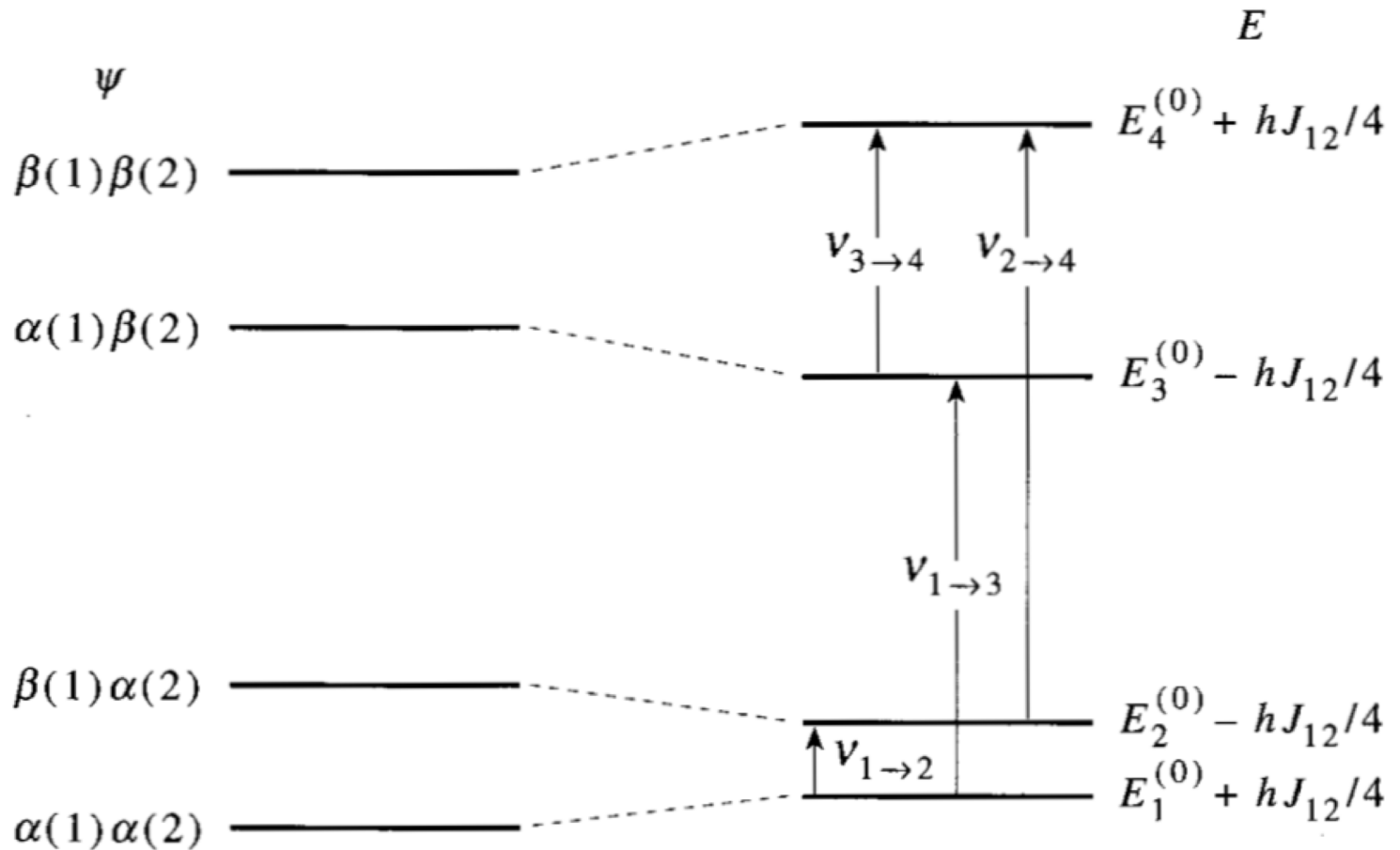
$$E_1 = E_1^{(0)} + \frac{hJ_{12}}{4}$$

$$E_2 = E_2^{(0)} - \frac{hJ_{12}}{4}$$

$$E_3 = E_3^{(0)} - \frac{hJ_{12}}{4}$$

$$E_4 = E_4^{(0)} + \frac{hJ_{12}}{4}$$

Interação spin-spin



Interação spin-spin

$$\nu_{1 \rightarrow 2} = \nu_0(1 - \sigma_1) - \frac{J_{12}}{2}$$

$$\nu_{1 \rightarrow 3} = \nu_0(1 - \sigma_2) - \frac{J_{12}}{2}$$

$$\nu_{2 \rightarrow 4} = \nu_0(1 - \sigma_2) + \frac{J_{12}}{2}$$

$$\nu_{3 \rightarrow 4} = \nu_0(1 - \sigma_1) + \frac{J_{12}}{2}$$

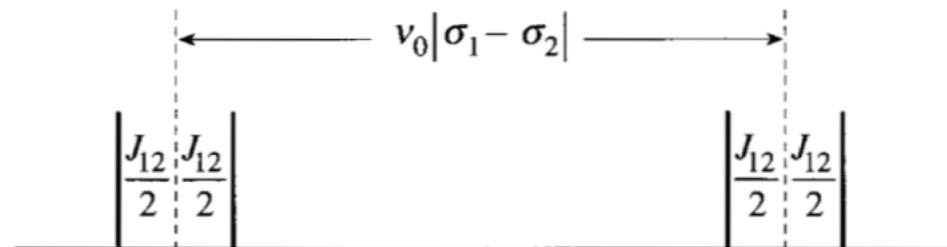
$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

Interação spin-spin

$$\nu_1^{\pm} = \nu_0(1 - \sigma_1) \pm \frac{J_{12}}{2}$$

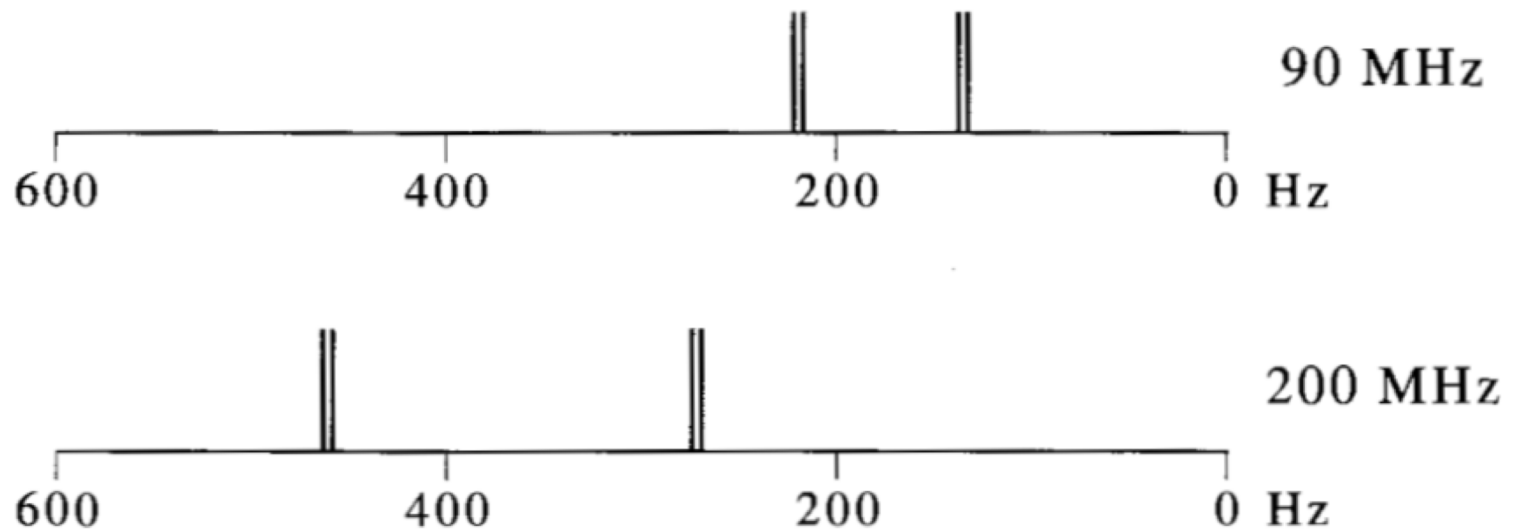
$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

$$\nu_2^{\pm} = \nu_0(1 - \sigma_2) \pm \frac{J_{12}}{2}$$



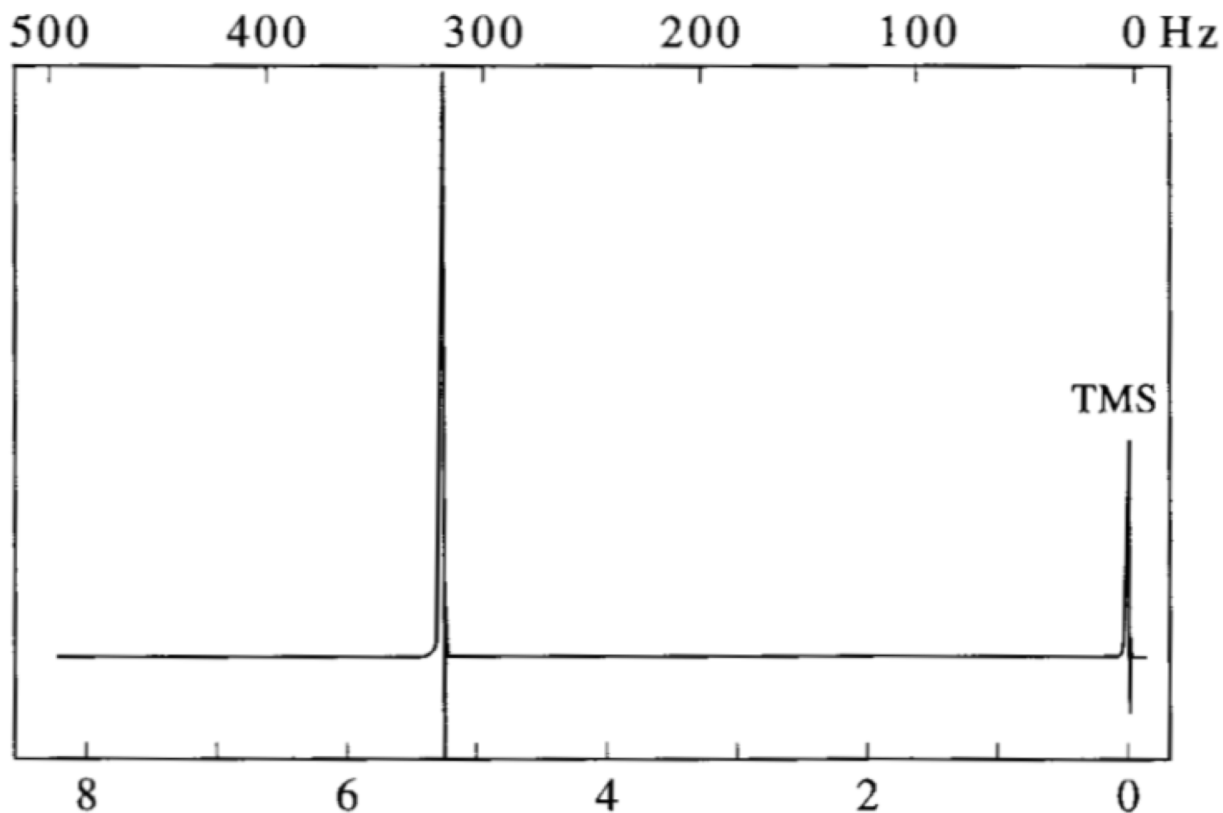
Validade da solução

Espectro de primeira ordem: $\nu_0 |\sigma_1 - \sigma_2| \gg J_{12}$



Acoplamento spin-spin não é observado em prótons equivalentes

Diclorometano (CH_2Cl_2)



Acoplamento spin-spin ^1H equiv.

$$\hat{H} = -\gamma B_0(1 - \sigma_A)\hat{I}_{z1} - \gamma B_0(1 - \sigma_A)\hat{I}_{z2} + \frac{hJ_{AA}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

$$\hat{H}^{(0)} = -\gamma B_0(1 - \sigma_A)\hat{I}_{z1} - \gamma B_0(1 - \sigma_A)\hat{I}_{z2}$$

$$\hat{H}^{(1)} = \frac{hJ_{AA}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2$$

Acoplamento spin-spin ^1H equiv.

Dois núcleos indistinguíveis

Funções de onda simétricas ou antissimétricas

$$\phi_1 = \alpha(1)\alpha(2)$$

$$\phi_2 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\phi_3 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\phi_4 = \beta(1)\beta(2)$$

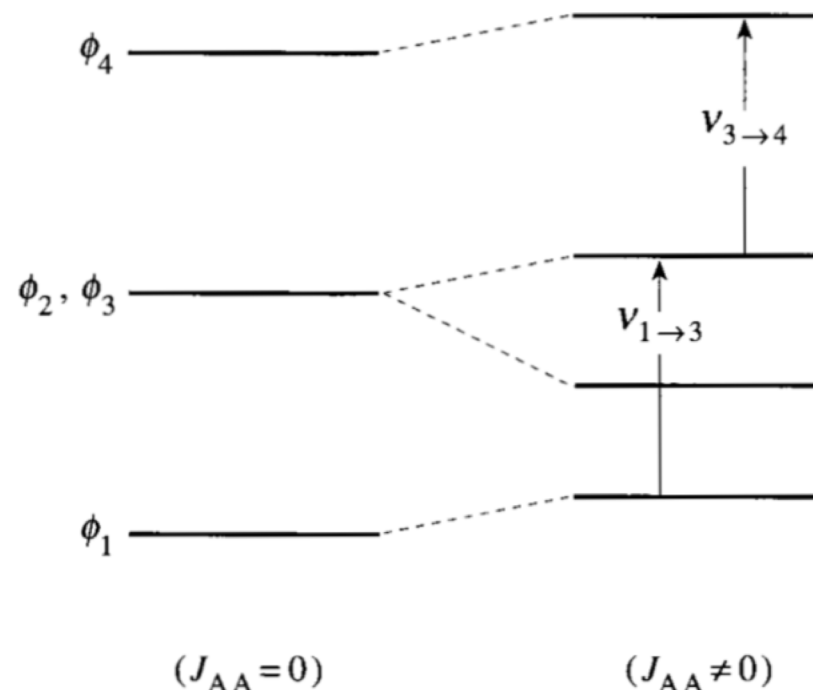
Acoplamento spin-spin ^1H equiv.

$$E_1 = -\hbar\gamma B_0(1 - \sigma_A) + \frac{hJ_{AA}}{4}$$

$$E_2 = 0 - \frac{3hJ_{AA}}{4}$$

$$E_3 = 0 + \frac{hJ_{AA}}{4}$$

$$E_4 = \hbar\gamma B_0(1 - \sigma_A) + \frac{hJ_{AA}}{4}$$



Regra de $n+1$

Se um próton tem n prótons equivalentes vizinhos, seu sinal é desdobrado em $n+1$ linhas.

- vizinho: H ligados ao carbono vizinho
- Válida para espectro de primeira ordem

Regra de $n+1$

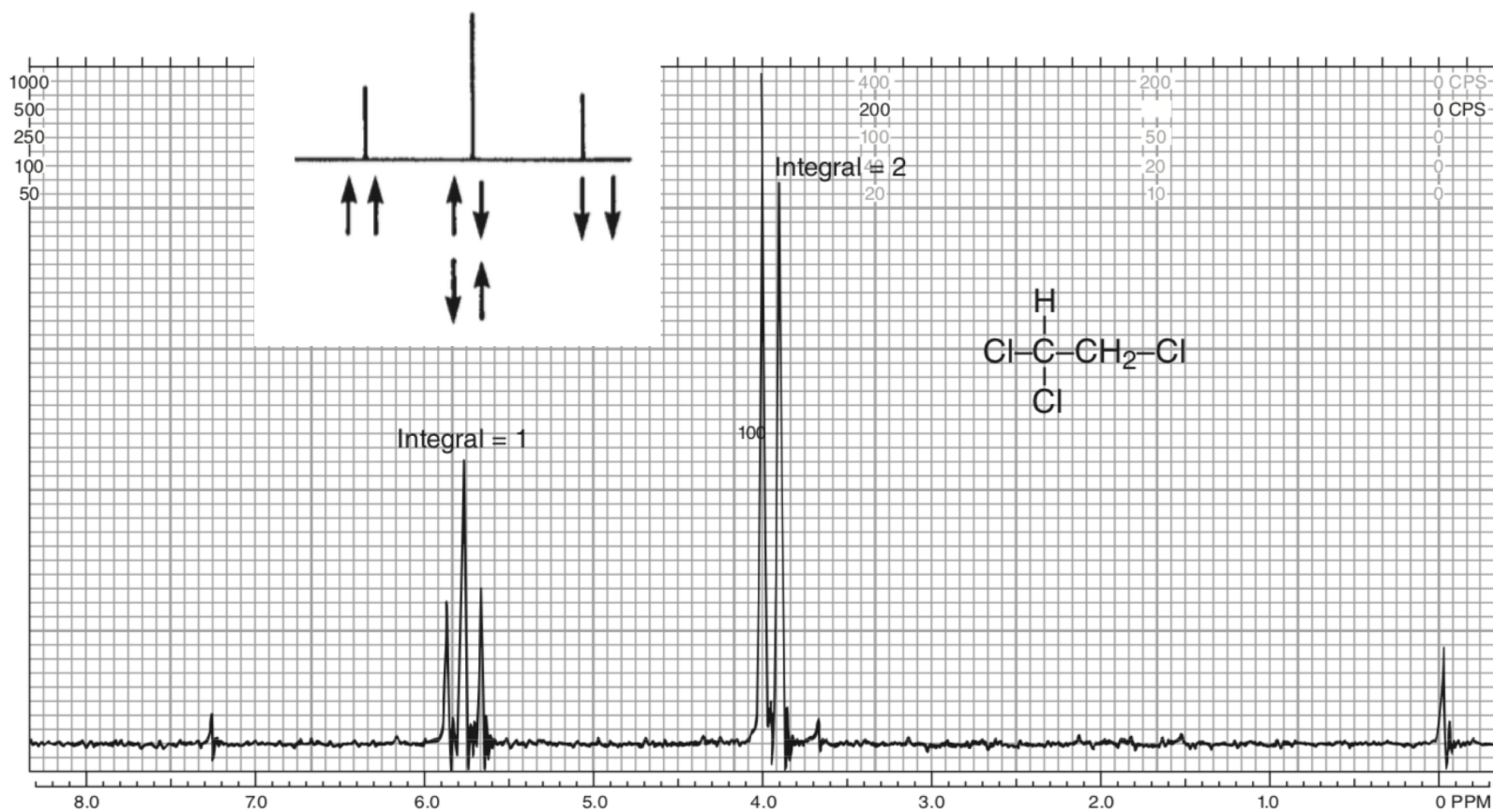


FIGURE 5.25 The ^1H NMR spectrum of 1,1,2-trichloroethane (60 MHz).

Regra de $n+1$

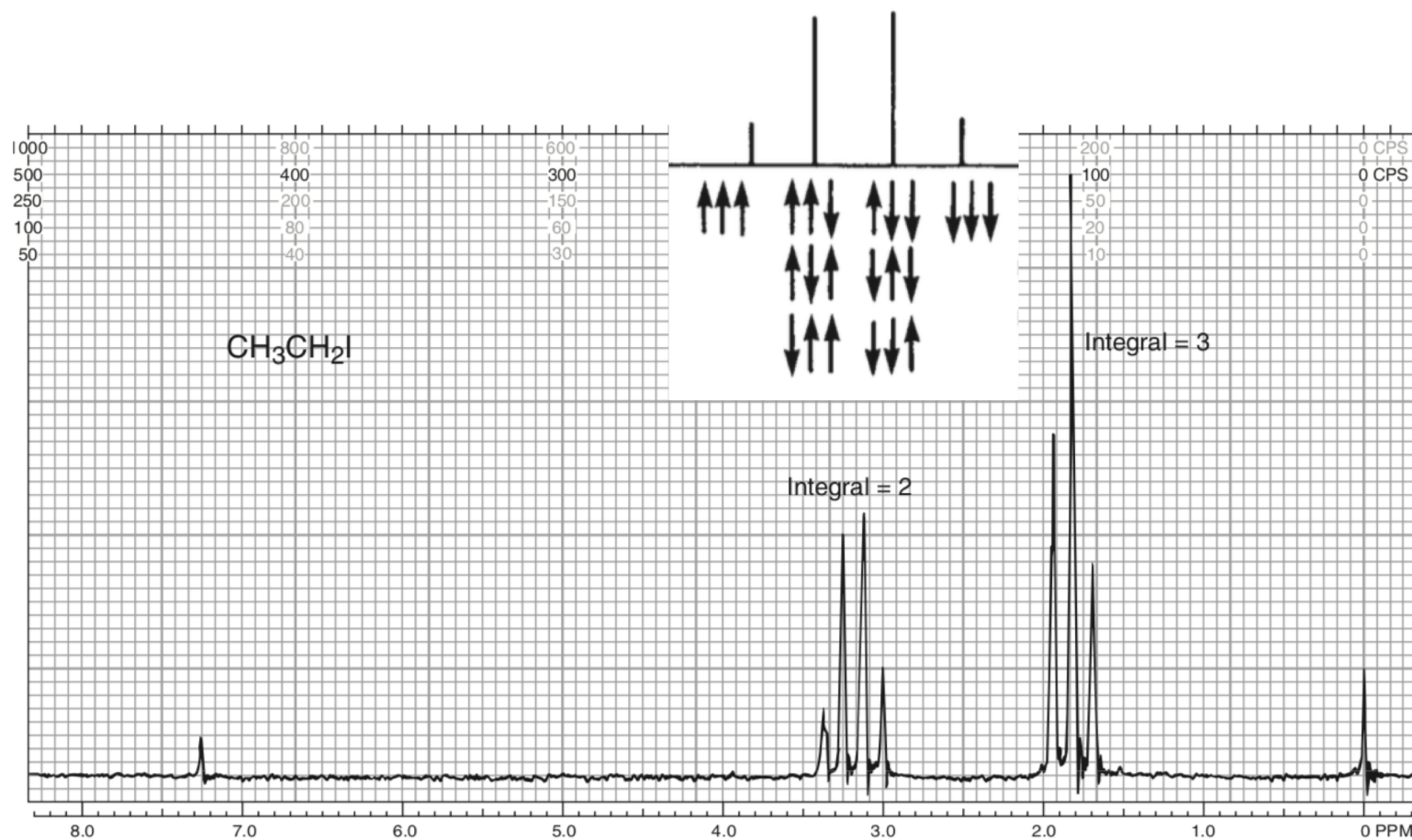


FIGURE 5.26 The ^1H NMR spectrum of ethyl iodide (60 MHz).

Regra de $n+1$

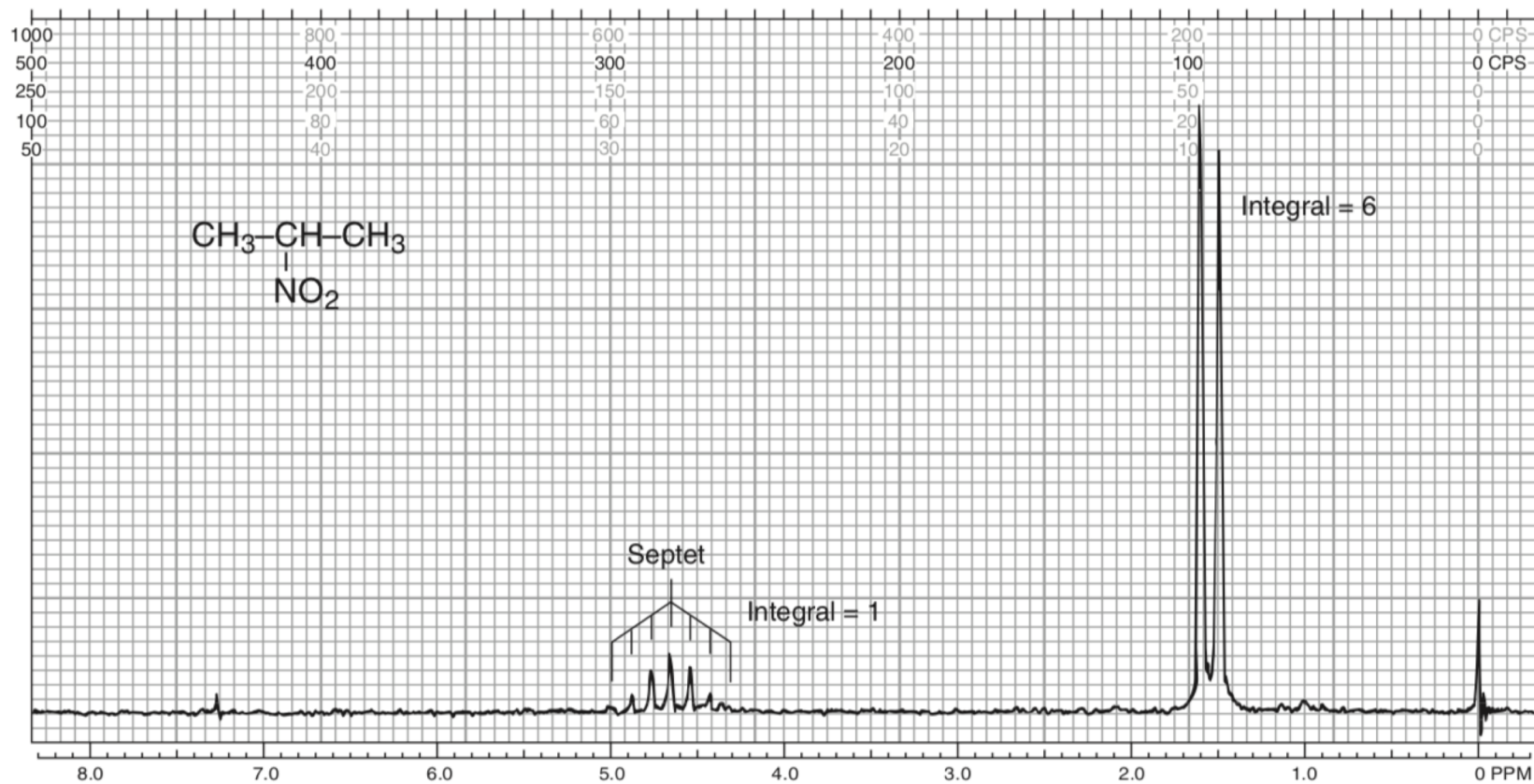


FIGURE 5.27 The ^1H NMR spectrum of 2-nitropropane (60 MHz).

Regra de $n+1$

1H		<chem>ClC(Cl)C(Br)C(Br)C</chem>		1H
1H		<chem>ClC(Cl)CCl</chem>		2H
2H		<chem>ClCCCB</chem>		2H
1H		<chem>ClC(Cl)C</chem>		3H
2H		<chem>ClCC</chem>		3H
1H		<chem>BrC(C)C</chem>		6H
Downfield			Upfield	

Singlet	1
Doublet	1 1
Triplet	1 2 1
Quartet	1 3 3 1
Quintet	1 4 6 4 1
Sextet	1 5 10 10 5 1
Septet	1 6 15 20 15 6 1

Espectro de segunda ordem

$$J \approx \nu_0 |\sigma_1 - \sigma_2|$$

$$\hat{H} = -\gamma B_0(1 - \sigma_1)\hat{I}_{z1} - \gamma B_0(1 - \sigma_2)\hat{I}_{z2} + \frac{hJ_{12}}{\hbar^2} \hat{I}_1 \cdot \hat{I}_2$$

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

$$\phi_1 = \alpha(1)\alpha(2) \quad \phi_2 = \alpha(1)\beta(2)$$

$$\phi_3 = \beta(1)\alpha(2) \quad \phi_4 = \beta(1)\beta(2)$$

Espectro de segunda ordem

$$E_1 = -h\nu_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2} \right) + \frac{hJ_{12}}{4}$$

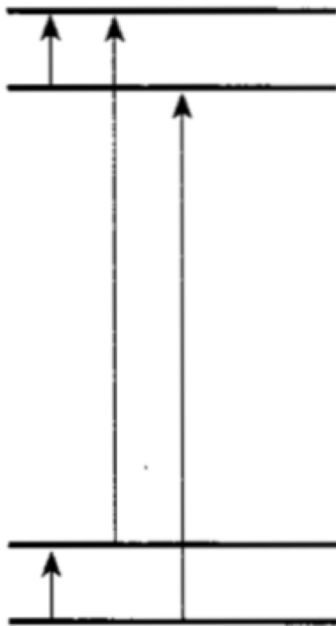
$$E_2 = -\frac{hJ_{12}}{4} - \frac{h}{2} [\nu_0^2 (\sigma_1 - \sigma_2)^2 + J_{12}^2]^{1/2}$$

$$E_3 = -\frac{hJ_{12}}{4} + \frac{h}{2} [\nu_0^2 (\sigma_1 - \sigma_2)^2 + J_{12}^2]^{1/2}$$

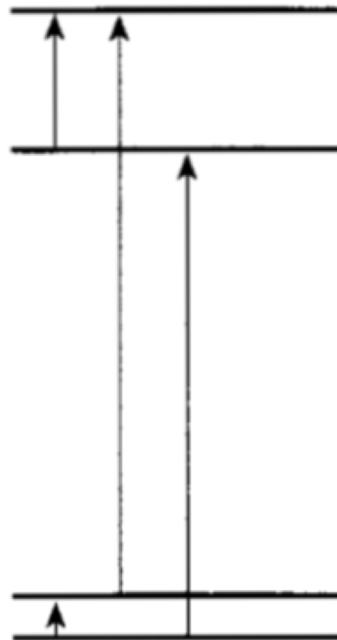
$$E_1 = h\nu_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2} \right) + \frac{hJ_{12}}{4}$$

Espectro de segunda ordem

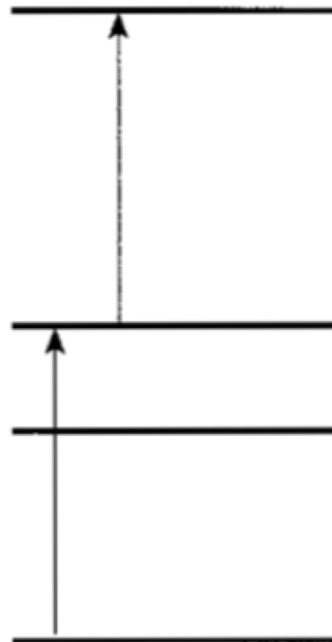
$AX(J_{AX} = 0)$



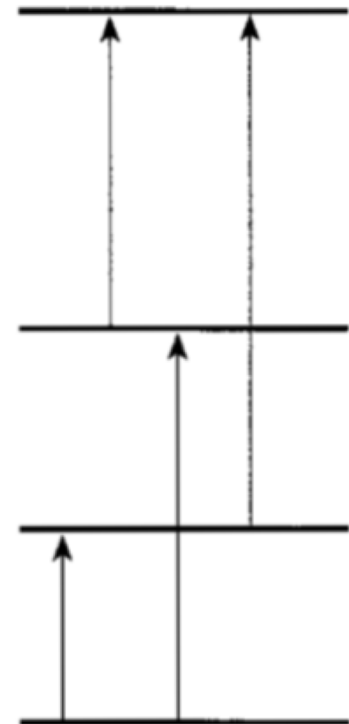
$AX(J_{AX} > 0)$



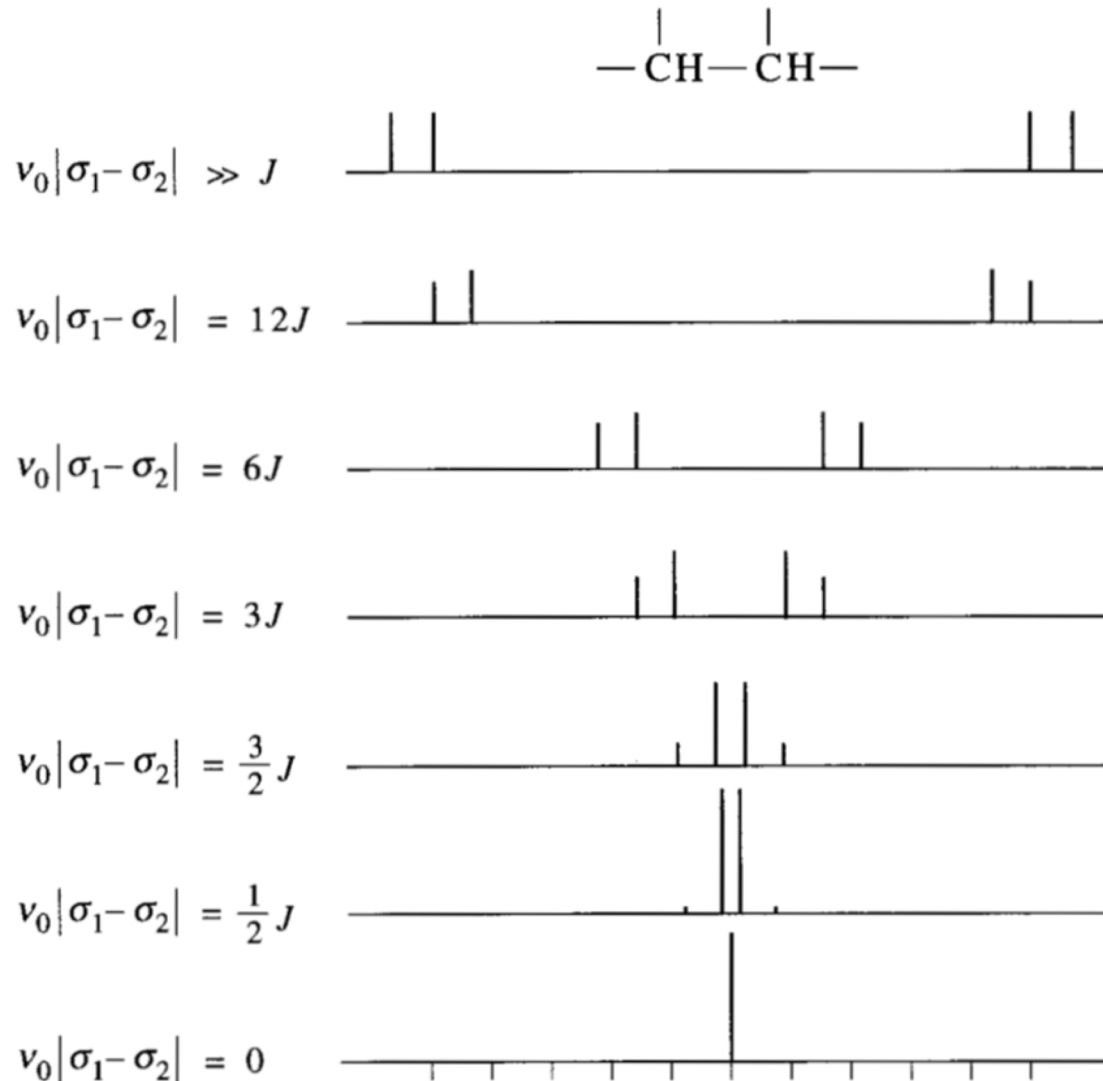
$A_2(J_{AA} > 0)$



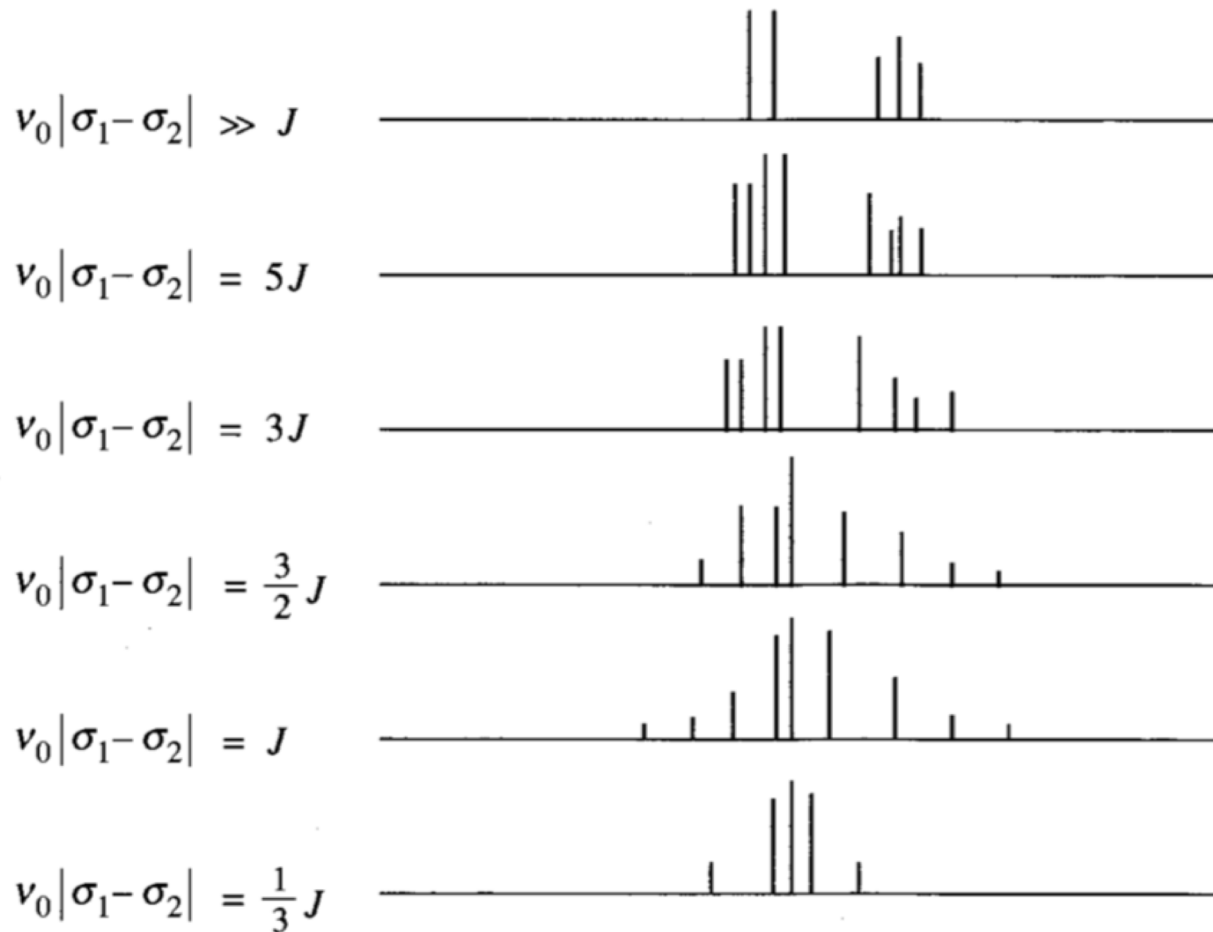
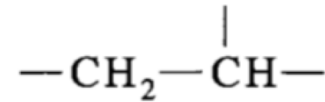
$AB(J_{AB} > 0)$



Espectro de segunda ordem



Espectro de segunda ordem



Espectro de segunda ordem

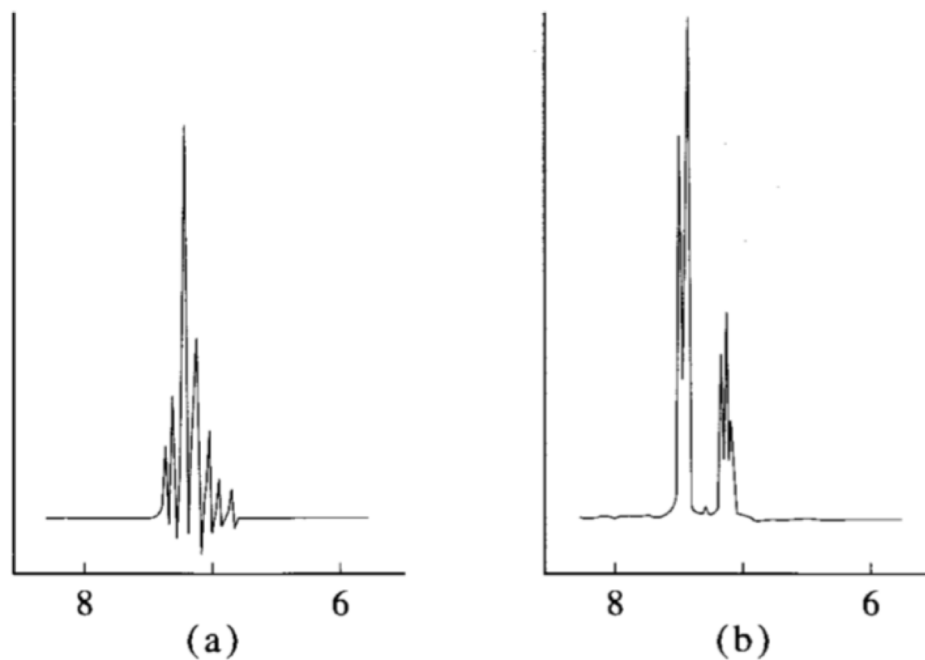


FIGURE 14.19

(a) A 60-MHz spectrum and (b) a 270-MHz spectrum of 1,2,3-trichlorobenzene. The 60-MHz spectrum is a second-order spectrum and the 270-MHz spectrum is first-order.