《高等物理化学II》

第14章-知识点

Chapter 14
Nuclear Magnetic
Resonance Spectroscopy

2019.10

14.1-2 核自旋角动量及与磁场的相互作用

原子核具有内禀自旋角动量

核自旋角动量

^1H, ^{13}C, ^{19}F, $I = ½$.
^2H, ^{14}N, $I = 1$.
^{12}C, ^{16}O, $I = 0$.

质子 (^1H)

$$\hat{I}^2\alpha = \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2\alpha$$
$$\hat{I}^2\beta = \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2\beta$$
$$\hat{I}_z\alpha = \tfrac{1}{2}\hbar\,\alpha$$
$$\hat{I}_z\beta = -\tfrac{1}{2}\hbar\,\beta$$

核的磁偶极

$$\boldsymbol{\mu} = g_N\frac{q}{2m_N}\mathbf{I} = g_N\beta_N\mathbf{I} = \gamma\mathbf{I}$$

g_N: 核g因子; β_N: 核磁子; $\gamma = g_N\beta_N$: 磁旋比

磁偶极与磁场相互作用 (z方向)

$$\hat{H} = -\gamma B_z\hat{I}_z \qquad \hat{I}_z\psi = \hbar m_I\psi$$

$$E = -\hbar\gamma m_I B_z \quad (m_I = I, I-1, \cdots, -I)$$

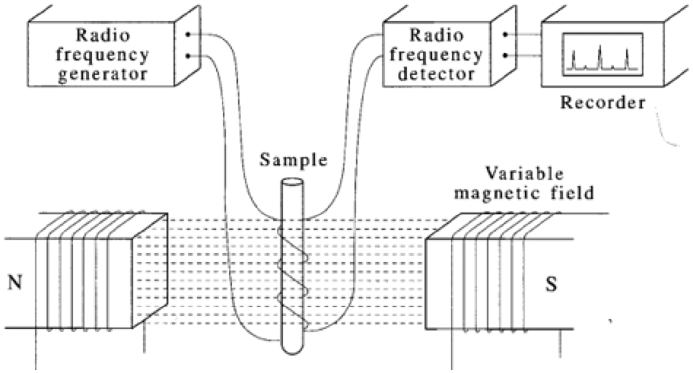
质子 (^1H)

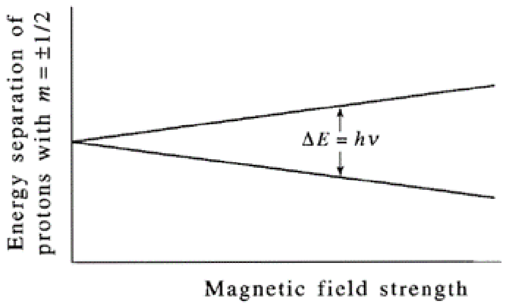
$$\Delta E = E(m_I = -\tfrac{1}{2}) - E(m_I = \tfrac{1}{2}) = \hbar\gamma B_z$$

$\Delta E = \hbar\gamma B_z = h\nu = \hbar\omega$ 吸收辐射发生自旋跃迁

核磁共振频率: $\nu = \dfrac{\gamma B_z}{2\pi}$ (Hz) $\quad \omega = \gamma B_z$ (rad·s^{-1})

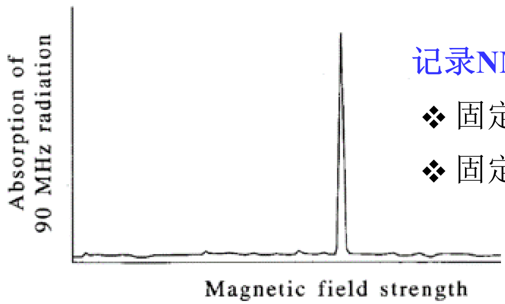
14.3 质子的核磁共振光谱仪 (60-750MHz)





(a)

在共振频率处，样品吸收辐射得到NMR光谱



(b)

记录NMR光谱两种方式

- ❖ 固定频率，改变磁场
- ❖ 固定磁场，改变频率

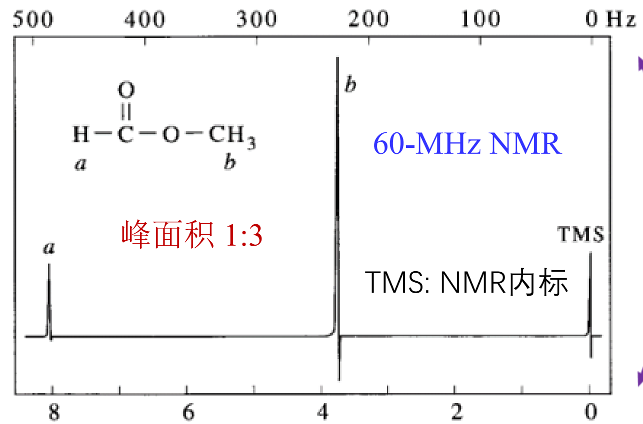
14.4 作用在分子中的核上的磁场被屏蔽

屏蔽效应

- ❖ 外磁场B_0 → 电子环形运动 → 额外磁场, B_{elec}
- ❖ B_{elec}与B_0反向，电子屏蔽了核周围部分磁场

$B_{elec} = -\sigma B_0$ (σ: 屏蔽常数)　$B_z = (1-\sigma)B_0$ (总磁场强度)

$$B_0 = \frac{2\pi\nu}{\gamma(1-\sigma)} = \frac{\omega}{\gamma(1-\sigma)}$$ (发生跃迁时磁场强度)



吸收频率标度

化学位移标度

化学位移

$$\delta_H = \left(\frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}}\right)\times 10^6 = (\sigma_{TMS} - \sigma_H)\times 10^6$$

$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1)\times 10^6$$ (对于两个不同环境的氢核)

对应的吸收谱线间距在化学位移标度上

与外磁场无关

14.5 化学位移与核周围的化学环境相关

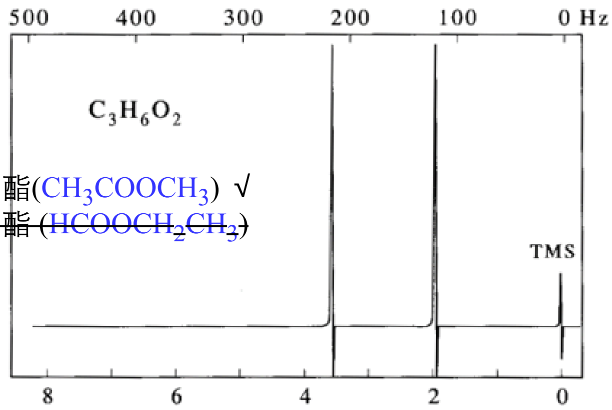
电子密度越大, 屏蔽常数越大，化学位移越小

CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
$\delta = 0.23$	$\delta = 3.05$	$\delta = 5.33$	$\delta = 7.26$
CH_3I	CH_3Br	CH_3Cl	CH_3F
$\delta = 2.16$	$\delta = 2.68$	$\delta = 3.05$	$\delta = 4.26$
$\mathbf{CH}_3Cl$	$\mathbf{CH}_3-CH_2Cl$	$\mathbf{CH}_3-CH_2-CH_2Cl_2$	
$\delta = 3.05$	$\delta = 1.42$	$\delta = 1.04$	

CH_3X中X基团的电负性越大，化学位移越大

(TMS中硅的电负性较低，对四个甲基上的质子影响小，所以能给出较强信号和一个锐利的吸收峰，而一般有机化合物中的质子吸收峰都在它的左边。)

例：根据成分和NMR光谱判断化合物



乙酸甲酯(CH_3COOCH_3) √

~~甲酸乙酯 ($HCOOCH_2CH_3$)~~

14.6 自旋-自旋耦合产生NMR光谱多重峰

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

J_{12}: 自旋-自旋耦合常数 (单位: Hz)

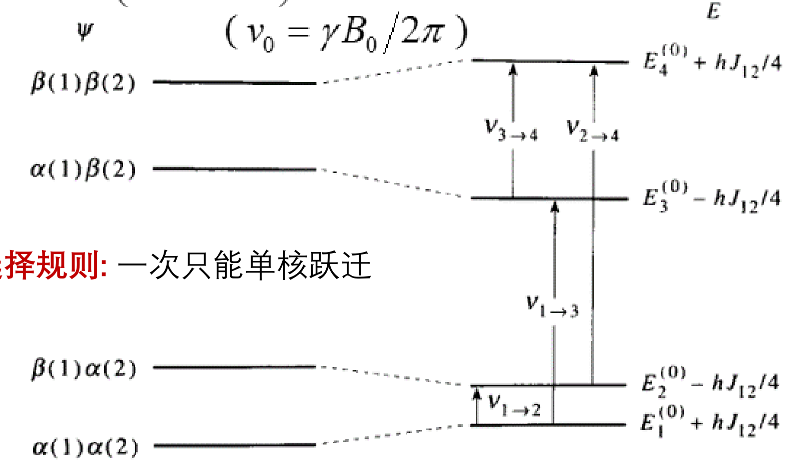
AB 系统: 氢原子化学位移相似, $J_{12} \approx \nu_0|\sigma_1 - \sigma_2|$.

AX 系统: 氢核化学环境差异大, $J_{12} << \nu_0|\sigma_1 - \sigma_2|$.

AX系统的一级微扰处理 $\quad \hat{H}^{(1)} = \frac{hJ_{12}}{\hbar^2}\hat{I}_1\hat{I}_2$

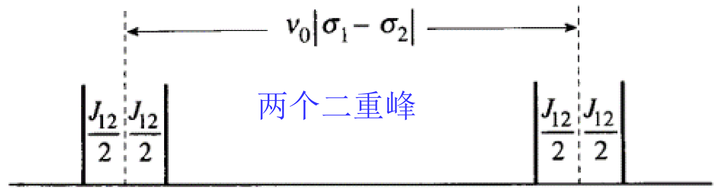
$$E_{1,4} = \pm h\nu_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) + \frac{hJ_{12}}{4} \qquad E_{2,3} = \mp\frac{h\nu_0}{2}(\sigma_1 - \sigma_2) - \frac{hJ_{12}}{4}$$

$(\nu_0 = \gamma B_0 / 2\pi)$



选择规则: 一次只能单核跃迁

共振频率: $\nu_1^{\pm} = \nu_0(1-\sigma_1) \pm \frac{J_{12}}{2} \qquad \nu_2^{\pm} = \nu_0(1-\sigma_2) \pm \frac{J_{12}}{2}$



14.7 化学等价质子自旋-自旋耦合不可观测

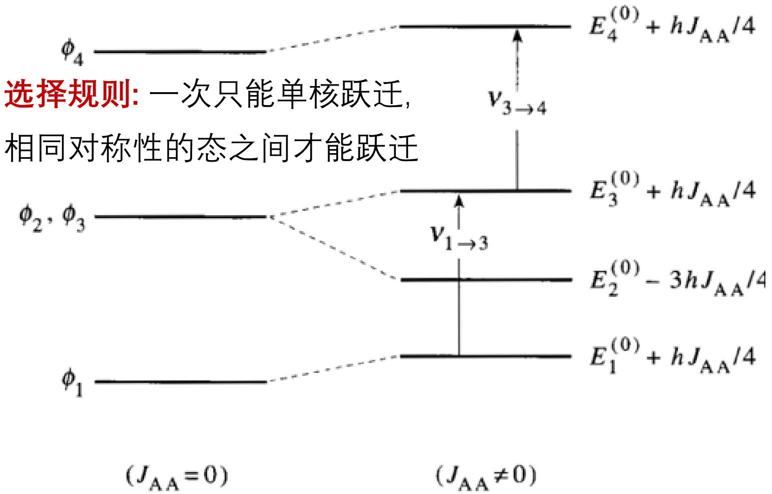
A_2 系统: 氢核化学等价，光谱只有一个单峰

$$\hat{H}^{(0)} = -\gamma B_0(1-\sigma_A)(\hat{I}_{z1}+\hat{I}_{z2}) \qquad \hat{H}^{(1)} = \frac{hJ_{AA}}{\hbar^2}\hat{I}_1\hat{I}_2$$

$$\phi_1^{(0)} = \alpha(1)\alpha(2) \qquad \phi_2^{(0)} = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$\phi_3^{(0)} = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)] \qquad \phi_4^{(0)} = \beta(1)\beta(2)$$

$$E_1 = \mp\hbar\gamma B_0(1-\sigma_A)+\frac{hJ_{AA}}{4} \quad E_2 = -\frac{3hJ_{AA}}{4} \quad E_3 = \frac{hJ_{AA}}{4}$$



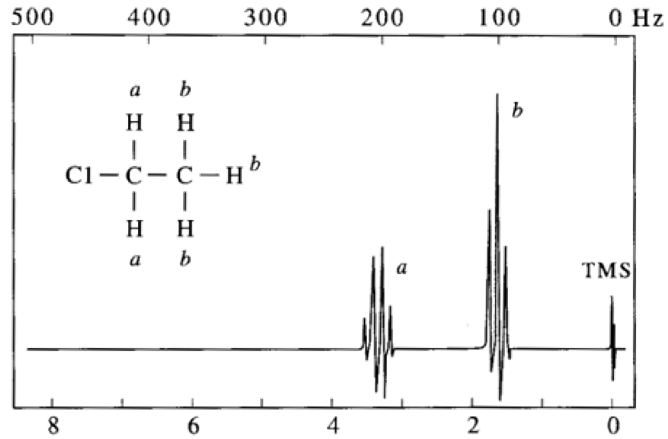
选择规则: 一次只能单核跃迁，相同对称性的态之间才能跃迁

共振频率:

$$\nu_{1\to3} = \nu_{3\to4} = \frac{E_3-E_1}{h} = \frac{\gamma B_0(1-\sigma_A)}{2\pi} = \nu_0(1-\sigma_A)$$

14.8 n+1规则适用于一级NMR光谱

n+1规则: 如果一个质子有n个等价的近邻质子，则其相应的NMR信号分裂为n+1重峰



原因解释:

2等价近邻质子: ↑↓ ↓↓ ↓↑ ↑↑

The observed multiplet splitting in first-order spectra.

Number of closely spaced lines	1	2	3	4
Name	Singlet	Doublet	Triplet	Quartet
Relative peak size	1	1:1	1:2:1	1:3:3:1
Idealized intensity pattern				

1等价近邻质子: ↑ ↓

3等价近邻质子: ↑↓↓ ↓↑↓ ↓↓↓ ↓↓↑ ↑↑↓ ↑↓↑ ↓↑↑ ↑↑↑

14.9 变分法可以准确求解二级光谱

微扰理论不适用时，可使用变分法求解NMR光谱

两自旋体系(不等价):

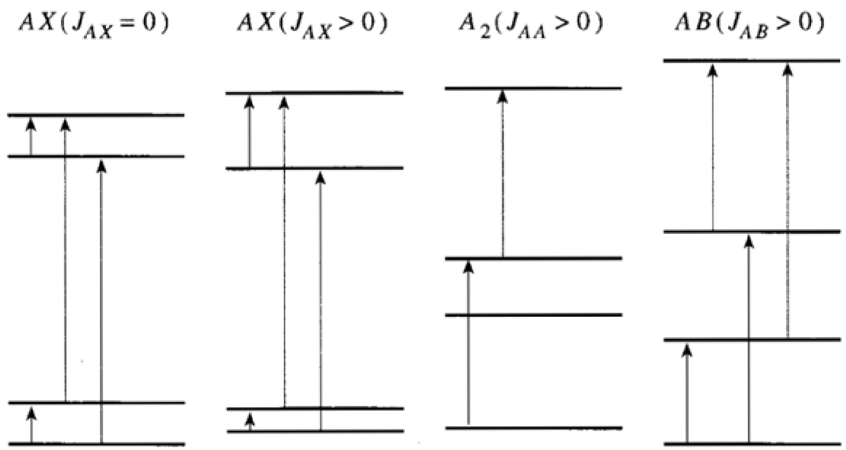
$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} + \frac{hJ_{12}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2$$

$$\phi_1^{(0)} = \alpha(1)\alpha(2) \quad \phi_2^{(0)} = \beta(1)\alpha(2) \quad \phi_3^{(0)} = \alpha(1)\beta(2) \quad \phi_4^{(0)} = \beta(1)\beta(2)$$

$$\psi = c_1\phi_1^{(0)} + c_2\phi_2^{(0)} + c_3\phi_3^{(0)} + c_4\phi_4^{(0)} \quad \text{(试探波函数)}$$

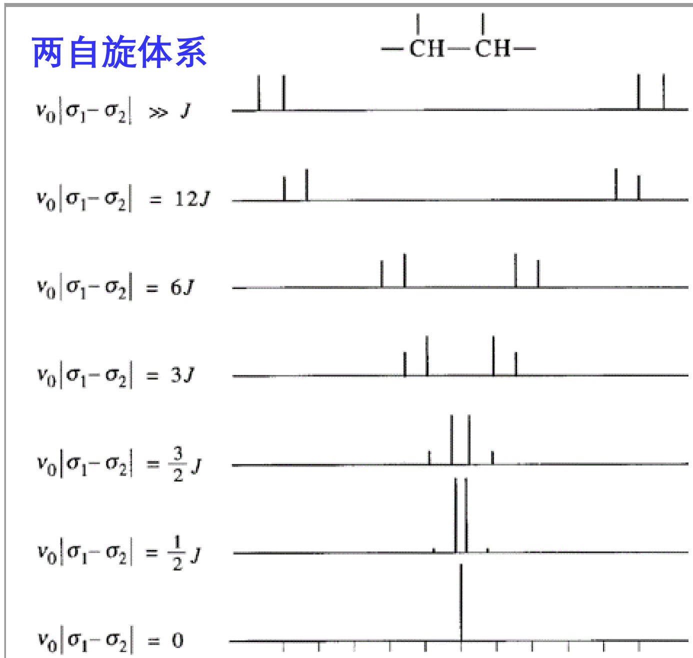
$$E_1 = -h\nu_0\left(1-\frac{\sigma_1+\sigma_2}{2}\right) + \frac{hJ}{4} \quad E_2 = -\frac{hJ}{4} - \frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2 + J^2]^{1/2}$$

$$E_3 = -\frac{hJ}{4} + \frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2 + J^2]^{1/2} \quad E_4 = h\nu_0\left(1-\frac{\sigma_1+\sigma_2}{2}\right) + \frac{hJ}{4}$$



$J << \nu_0|\sigma_1-\sigma_2|$ 时→回归一级微扰下的AX系统

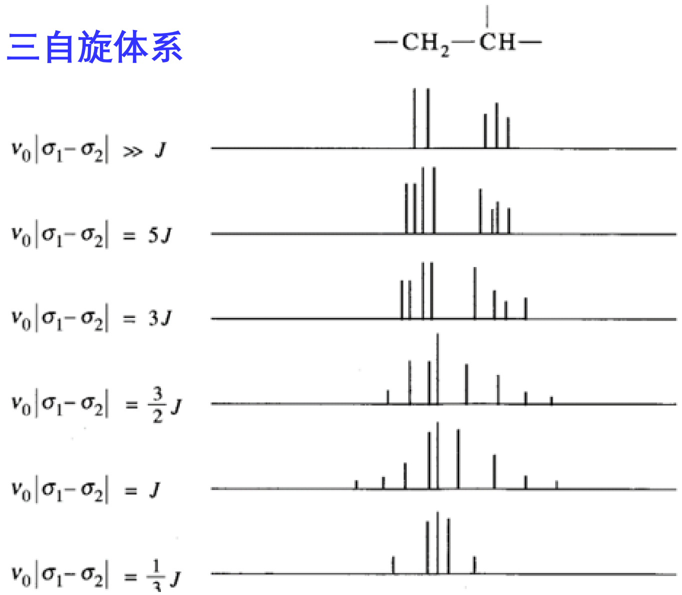
两自旋体系



一级光谱

二级光谱
(以下均同)
n+1规则
不适用

三自旋体系



一级光谱

二级光谱
(以下均同)
n+1规则
不适用

使用高频NMR光谱仪的目的

$\nu_0|\sigma_1 - \sigma_2|$足够大，从而使得光谱表现为一级