Advanced Physical Chemistry II
HW

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October 21, 2019

14 Nuclear Magnetic Resonance Spectroscopy

6,14,19,23,30,34,36,39

14-6

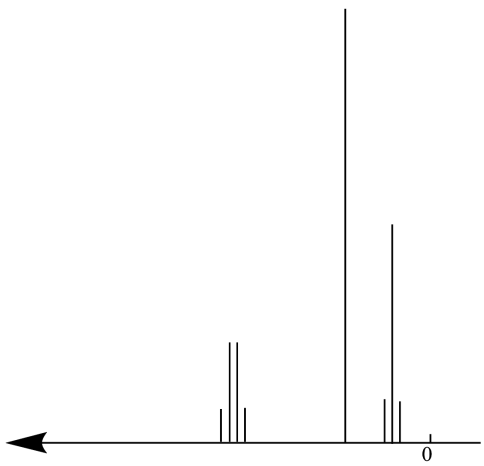
On a 60-MHz instrument,

$$\nu - \nu_{\mathrm{TMS}} = \delta\nu_{\mathrm{spectrometer}} \times 10^{-6} = 8.0 \times 10^{-6} \times 60\,\mathrm{MHz} = 480\,\mathrm{Hz} \tag{14.1}$$

On a 270-MHz instrument,

$$\nu - \nu_{\mathrm{TMS}} = \delta\nu_{\mathrm{spectrometer}} \times 10^{-6} = 8.0 \times 10^{-6} \times 270\,\mathrm{MHz} = 2160\,\mathrm{Hz} \tag{14.2}$$

14-14



14-19

$$\begin{aligned}\widehat{\mathbf{I}}_{+}\widehat{\mathbf{I}}_{-} &= (\widehat{\mathbf{I}}_x + \mathrm{i}\,\widehat{\mathbf{I}}_y)(\widehat{\mathbf{I}}_x - \mathrm{i}\,\widehat{\mathbf{I}}_y)\\ &= \widehat{\mathbf{I}}_x^2 + \widehat{\mathbf{I}}_y^2 - \mathrm{i}[\widehat{\mathbf{I}}_x, \widehat{\mathbf{I}}_y]\\ &= \widehat{\mathbf{I}}^2 - \widehat{\mathbf{I}}_z^2 + \hbar\,\widehat{\mathbf{I}}_z\end{aligned} \tag{14.3}$$

$$\begin{aligned}\widehat{\mathbf{I}}_{-}\widehat{\mathbf{I}}_{+} &= (\widehat{\mathbf{I}}_x - \mathrm{i}\,\widehat{\mathbf{I}}_y)(\widehat{\mathbf{I}}_x + \mathrm{i}\,\widehat{\mathbf{I}}_y)\\ &= \widehat{\mathbf{I}}_x^2 + \widehat{\mathbf{I}}_y^2 + \mathrm{i}[\widehat{\mathbf{I}}_x, \widehat{\mathbf{I}}_y]\\ &= \widehat{\mathbf{I}}^2 - \widehat{\mathbf{I}}_z^2 - \hbar\,\widehat{\mathbf{I}}_z\end{aligned} \tag{14.4}$$

14–23

$$E_j = E_j^{(0)} + H_{jj}^{(1)} = E_i^{(0)} + H_{x,jj}^{(1)} + H_{y,jj}^{(1)} + H_{z,jj}^{(1)} \tag{14.5}$$

Since

$$E_1^{(0)} = -\gamma B_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) \tag{14.6}$$
$$E_2^{(0)} = -\gamma B_0(\sigma_1-\sigma_2) \tag{14.7}$$
$$E_3^{(0)} = \gamma B_0(\sigma_1-\sigma_2) \tag{14.8}$$
$$E_4^{(0)} = \gamma B_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) \tag{14.9}$$

and

$$H_{x,jj}^{(1)} = H_{y,jj}^{(1)} = 0 \tag{14.10}$$
$$H_{z,11}^{(1)} = H_{z,44}^{(1)} = \frac{hJ_{12}}{4} \tag{14.11}$$
$$H_{z,22}^{(1)} = H_{z,33}^{(1)} = -\frac{hJ_{12}}{4} \tag{14.12}$$

we have

$$E_1 = -h\nu_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) + \frac{hJ_{12}}{4} \tag{14.13}$$
$$E_2 = -h\nu_0(\sigma_1-\sigma_2) - \frac{hJ_{12}}{4} \tag{14.14}$$
$$E_3 = h\nu_0(\sigma_1-\sigma_2) - \frac{hJ_{12}}{4} \tag{14.15}$$
$$E_4 = h\nu_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) + \frac{hJ_{12}}{4} \tag{14.16}$$

14–30

$$\begin{aligned}
H_{44} &= -\hbar\gamma B_0 \left\langle \beta(1)\beta(2) \,\middle|\, (1-\sigma_1)\,\hat{\mathbf{I}}_{z1} + (1-\sigma_2)\,\hat{\mathbf{I}}_{z2} \,\middle|\, \beta(1)\beta(2) \right\rangle + \frac{hJ_{12}}{\hbar^2}\left\langle \beta(1)\beta(2) \,\middle|\, \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \,\middle|\, \beta(1)\beta(2) \right\rangle \\
&= -\gamma B_0[(1-\sigma_1)+(1-\sigma_2)]\left(-\frac{\hbar}{2}\right) + \frac{hJ_{12}}{\hbar^2}\frac{\hbar^2}{4} \\
&= \frac{h\nu_0}{2}[(1-\sigma_1)+(1-\sigma_2)] + \frac{hJ_{12}}{4}
\end{aligned} \tag{14.17}$$

14–34

$$\begin{aligned}
E_2 - E_1 &= -\frac{hJ}{4} - \frac{h}{2}\sqrt{\nu_0^2(\sigma_1-\sigma_2)^2 + J^2} + h\nu_0\left(1 - \frac{\sigma_1+\sigma_2}{2}\right) - \frac{hJ}{4} \\
&= -\frac{hJ}{2} - \frac{h}{2}\sqrt{\nu_0^2(\sigma_1-\sigma_2)^2 + J^2} + \frac{h\nu_0}{2}(2-\sigma_1-\sigma_2)
\end{aligned} \tag{14.18}$$

thus

$$\nu_{1\to 2} = \frac{E_2-E_1}{h} = -\frac{J}{2} - \frac{1}{2}\sqrt{\nu_0^2(\sigma_1-\sigma_2)^2 + J^2} + \frac{\nu_0}{2}(2-\sigma_1-\sigma_2) \tag{14.19}$$

14–36

• For $\nu_0 = 60\,\text{MHz}$,

$$\sqrt{\nu_0^2(\sigma_1-\sigma_2)^2 + J^2} = \sqrt{60^2 \times 0.12^2 + 8.0^2} = 10.76\,\text{Hz} \tag{14.20}$$

$\therefore$

$$\nu_{1\to 2} = 60\,\text{MHz} - \frac{1}{2}(8+10.76)\text{Hz} = 60\,\text{MHz} - 9.38\,\text{Hz} \tag{14.21}$$

$$\nu_{1\to 3} = 60\,\mathrm{MHz} - \frac{1}{2}(8 - 10.76)\mathrm{Hz} = 60\,\mathrm{MHz} + 1.38\,\mathrm{Hz} \tag{14.22}$$
$$\nu_{2\to 4} = 60\,\mathrm{MHz} + \frac{1}{2}(8 + 10.76)\mathrm{Hz} = 60\,\mathrm{MHz} + 9.38\,\mathrm{Hz} \tag{14.23}$$
$$\nu_{3\to 4} = 60\,\mathrm{MHz} + \frac{1}{2}(8 - 10.76)\mathrm{Hz} = 60\,\mathrm{MHz} - 1.38\,\mathrm{Hz} \tag{14.24}$$
$$\tag{14.25}$$

the relative intensity

$$r = 2.25 \tag{14.26}$$
$$\frac{(r-1)^2}{(r+1)^2} = 0.15 \tag{14.27}$$

- For $\nu_0 = 500\,\mathrm{MHz}$,

$$\sqrt{\nu_0^2(\sigma_1 - \sigma_2)^2 + J^2} = \sqrt{500^2 \times 0.12^2 + 8.0^2} = 60.5\,\mathrm{Hz} \tag{14.28}$$

$\therefore$

$$\nu_{1\to 2} = 500\,\mathrm{MHz} - \frac{1}{2}(8 + 60.5)\mathrm{Hz} = 60\,\mathrm{MHz} - 34.2\,\mathrm{Hz} \tag{14.29}$$
$$\nu_{1\to 3} = 500\,\mathrm{MHz} - \frac{1}{2}(8 - 60.5)\mathrm{Hz} = 60\,\mathrm{MHz} + 26.2\,\mathrm{Hz} \tag{14.30}$$
$$\nu_{2\to 4} = 500\,\mathrm{MHz} + \frac{1}{2}(8 + 60.5)\mathrm{Hz} = 60\,\mathrm{MHz} + 34.2\,\mathrm{Hz} \tag{14.31}$$
$$\nu_{3\to 4} = 500\,\mathrm{MHz} + \frac{1}{2}(8 - 60.5)\mathrm{Hz} = 60\,\mathrm{MHz} - 26.2\,\mathrm{Hz} \tag{14.32}$$
$$\tag{14.33}$$

the relative intensity

$$r = 15.52 \tag{14.34}$$
$$\frac{(r-1)^2}{(r+1)^2} = 0.77 \tag{14.35}$$

14-39 The spin functions are

$$\phi_1 = \psi_1 = \alpha(1)\alpha(2) \tag{14.36}$$
$$\phi_2 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2) \tag{14.37}$$
$$\phi_3 = \frac{1}{\sqrt{2}}(\psi_2 + \psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2) \tag{14.38}$$
$$\phi_4 = \psi_4 = \beta(1)\beta(2) \tag{14.39}$$

$\therefore$(using atomic unit)

$$P_{x,12} = \left\langle \phi_2 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_1 \right\rangle = \left\langle \frac{1}{\sqrt{2}}(\psi_2 - \psi_3) \,\middle|\, \frac{1}{2}(\psi_2 + \psi_3) \right\rangle = 0 \tag{14.40}$$
$$P_{y,12} = \left\langle \phi_2 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_1 \right\rangle = \left\langle \frac{1}{\sqrt{2}}(\psi_2 - \psi_3) \,\middle|\, \frac{\mathrm{i}}{2}(\psi_2 + \psi_3) \right\rangle = 0 \tag{14.41}$$
$$P_{x,13} = \left\langle \phi_3 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_1 \right\rangle = \left\langle \frac{1}{\sqrt{2}}(\psi_2 + \psi_3) \,\middle|\, \frac{1}{2}(\psi_2 + \psi_3) \right\rangle = \frac{1}{\sqrt{2}} \tag{14.42}$$
$$P_{y,13} = \left\langle \phi_3 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_1 \right\rangle = \left\langle \frac{1}{\sqrt{2}}(\psi_2 + \psi_3) \,\middle|\, \frac{\mathrm{i}}{2}(\psi_2 + \psi_3) \right\rangle = \frac{\mathrm{i}}{\sqrt{2}} \tag{14.43}$$
$$P_{x,14} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_1 \right\rangle = \left\langle \psi_4 \,\middle|\, \frac{1}{2}(\psi_2 + \psi_3) \right\rangle = 0 \tag{14.44}$$
$$P_{y,14} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_1 \right\rangle = \left\langle \psi_4 \,\middle|\, \frac{\mathrm{i}}{2}(\psi_2 + \psi_3) \right\rangle = 0 \tag{14.45}$$

$$P_{x,23} = \left\langle \phi_3 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_2 \right\rangle = \langle \psi_3 \,|\, 0 \rangle = 0 \tag{14.46}$$

$$P_{y,23} = \left\langle \phi_3 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_2 \right\rangle = \langle \psi_3 \,|\, 0 \rangle = 0 \tag{14.47}$$

$$P_{x,24} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_2 \right\rangle = \langle \psi_4 \,|\, 0 \rangle = 0 \tag{14.48}$$

$$P_{y,24} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_2 \right\rangle = \langle \psi_4 \,|\, 0 \rangle = 0 \tag{14.49}$$

$$P_{x,34} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{x1} + \widehat{\mathbf{I}}_{x2} \,\middle|\, \phi_3 \right\rangle = \left\langle \psi_4 \,\middle|\, \frac{1}{\sqrt{2}}(\psi_1 + \psi_4) \right\rangle = \frac{1}{\sqrt{2}} \tag{14.50}$$

$$P_{y,34} = \left\langle \phi_4 \,\middle|\, \widehat{\mathbf{I}}_{y1} + \widehat{\mathbf{I}}_{y2} \,\middle|\, \phi_3 \right\rangle = \left\langle \psi_4 \,\middle|\, \frac{\mathrm{i}}{\sqrt{2}}(\psi_1 + \psi_4) \right\rangle = \frac{\mathrm{i}}{\sqrt{2}} \tag{14.51}$$

thus, only $1 \rightarrow 3$ and $3 \rightarrow 4$ are allowed.