Solutions to Exercises

Fundamental constants

Planck's constant	$h = 6.626\ 10^{-34}$ J s
Boltzmann's constant	$k_B = 1.381 \times 10^{-23}$ J K^{-1}
Vacuum permeability	$\mu_0 = 4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
Gas constant	$R = 8.314$ J K^{-1} mol^{-1}

Magnetogyric ratios

	γ /10^7 T^{-1} s^{-1}
^{1}H	26.752
^{13}C	6.728
^{14}N	1.934
^{15}N	–2.713

Chapter 1

Exercise 1.1

See Table 1.2.

$I = 0 \;\Rightarrow$ even number of protons & even number of neutrons $\Rightarrow$ $^{32}_{16}\text{S}$ and $^{40}_{20}\text{Ca}$

$I = \frac{1}{2} \;\Rightarrow$ even (odd) number of protons & odd (even) number of neutrons $\Rightarrow$ $^{57}_{26}\text{Fe}$ and $^{119}_{50}\text{Sn}$

$I = 1 \;\Rightarrow$ odd number of protons & odd number of neutrons $\Rightarrow$ $^{6}_{3}\text{Li}$ and $^{14}_{7}\text{N}$

Exercise 1.2

Spin angular momentum (*s.a.m.*) = $\sqrt{I\ I+1}\ \hbar$ (eqn 1.1)

$$\Rightarrow I\ I+1 = \left(\frac{s.a.m.}{\hbar}\right)^2 = \left(\frac{2.042\times10^{-34}}{6.626\times10^{-34}/2\pi}\right)^2 = 3.75 = \frac{15}{4} = \frac{3}{2}\times\frac{5}{2} \Rightarrow I = \tfrac{3}{2}$$

Exercise 1.3

$\mu = \gamma\sqrt{I\ I+1}\ \hbar$ (eqns 1.1 and 1.5). $\gamma = 1.934\times10^{7}\ \text{T}^{-1}\,\text{s}^{-1}$. $I = 1$ (Table 1.1).

$$\mu = 1.934\times10^{7} \times\sqrt{1\times2}\times 6.626\times10^{-34}/2\pi = 2.884\times10^{-27}\ \text{J T}^{-1}$$

Exercise 1.4

$$\nu_{\text{NMR}} = \frac{|\gamma|B}{2\pi} \text{ (eqn 1.10).}$$

(a) $$\nu_{\text{NMR}}\ {}^{1}\text{H} = \frac{26.752\times10^{7} \times23.488}{2\pi} = 1000.0\,\text{MHz}$$

(b) $$\nu_{\text{NMR}}\ {}^{13}\text{C} = \frac{6.728\times10^{7} \times23.488}{2\pi} = 251.5\,\text{MHz}$$

(c) $$\nu_{\text{NMR}}\ {}^{15}\text{N} = \frac{2.713\times10^{7} \times23.488}{2\pi} = 104.4\,\text{MHz}$$

Exercise 1.5

$$\nu_{\text{NMR}} = \frac{|\gamma|B}{2\pi} \text{ (eqn 1.10)}$$

$$\nu_{\text{NMR}}\ {}^{1}\text{H} = \frac{26.752\times10^{7} \times 50\times10^{-6}}{2\pi} = 2.129\,\text{kHz}$$

Weak magnetic field $\Rightarrow$ Small energy level splitting $\Rightarrow$ Small polarization $\Rightarrow$ Weak NMR signal.

Exercise 1.6

$$\nu_{\text{NMR}} = \frac{|\gamma| B}{2\pi} \text{ (eqn 1.10).}$$

$$\Rightarrow |\gamma| = \frac{2\pi\nu_{\text{NMR}}}{B} = \frac{2\pi \times (76 \times 10^6)}{17.6} = 2.713 \times 10^7 \text{ T}^{-1}\text{ s}^{-1} \Rightarrow {}^{15}\text{N}$$

Exercise 1.7

$$\frac{n_\beta}{n_\alpha} = \exp(-\Delta E / k_\text{B} T) \text{ (eqn 1.11) and } p = \frac{n_\alpha - n_\beta}{n_\alpha + n_\beta} \text{ (eqn 1.12).}$$

$$\frac{n_\beta}{n_\alpha} \approx 1 - \Delta E / k_\text{B} T \text{ (because } e^x \approx 1 - x \text{ when } |x| \ll 1\text{)}$$

$$\Rightarrow p = \frac{1 - n_\beta / n_\alpha}{1 + n_\beta / n_\alpha} \approx \frac{1 - (1 - \Delta E / k_\text{B} T)}{1 + (1 - \Delta E / k_\text{B} T)} = \frac{\Delta E / k_\text{B} T}{2 - \Delta E / k_\text{B} T} \approx \frac{\Delta E}{2 k_\text{B} T}$$

Exercise 1.8

$$p \approx \frac{\Delta E}{2 k_\text{B} T} = \frac{\hbar \gamma B}{2 k_\text{B} T} \text{ (eqns 1.12 and 1.9).}$$

$$p = \frac{(6.626 \times 10^{-34} / 2\pi) \times (26.752 \times 10^7) \times 17.6}{2 \times (1.381 \times 10^{-23}) \times 300} = 5.992 \times 10^{-5}$$

Exercise 1.9

$$\text{(a) } p \approx \frac{\Delta E}{2 k_\text{B} T} = \frac{h\nu}{2 k_\text{B} T}$$

$$\Rightarrow \nu = \frac{2 k_\text{B} T p}{h} = \frac{2 \times (1.381 \times 10^{-23}) \times 300 \times 0.01}{6.626 \times 10^{-34}} = 125 \text{ GHz}$$

$$\text{(b) } p \approx \frac{\Delta E}{2 k_\text{B} T} = \frac{h\nu}{2 k_\text{B} T}$$

$$\Rightarrow T = \frac{h\nu}{2 k_\text{B} p} = \frac{(6.626 \times 10^{-34}) \times (400 \times 10^6)}{2 \times (1.381 \times 10^{-23}) \times 0.01} = 0.96 \text{ K}$$

N.B. The same answers can be obtained using eqn 1.11, i.e. without the approximation $\Delta E \ll k_\text{B} T$.

Exercise 1.10

First determine the polarization of electron spins in a 4.0 T field at 4 K (using eqn 1.11):

$$\frac{n_\beta}{n_\alpha} = \exp\left(-\Delta E / k_\mathrm{B}T\right) = \exp\left(-\hbar\gamma_\mathrm{e}B / k_\mathrm{B}T\right) = \exp\left(-\frac{\left(6.626\times10^{-34}/2\pi\right)\times\left(-1.761\times10^{11}\right)\times4.0}{\left(1.381\times10^{-23}\right)\times4}\right) = 3.837$$

$$p_\mathrm{e} = \frac{n_\alpha - n_\beta}{n_\alpha + n_\beta} = \frac{1-n_\beta/n_\alpha}{1+n_\beta/n_\alpha} = \frac{1-3.837}{1+3.837} = -0.5865\,.$$

N.B. $n_\beta > n_\alpha$ and $p_\mathrm{e} < 0$ because $\gamma_\mathrm{e} < 0$.

Now calculate the polarization of protons in a 600 MHz spectrometer at 300 K (using eqn 1.12):

$$p_\mathrm{H} = \frac{\Delta E}{2k_\mathrm{B}T} = \frac{h\nu}{2k_\mathrm{B}T} = \frac{\left(6.626\times10^{-34}\right)\times\left(600\times10^{6}\right)}{2\times\left(1.381\times10^{-23}\right)\times300} = 4.798\times10^{-5}$$

Then, signal enhancement = $\left|\frac{p_\mathrm{e}}{p_\mathrm{H}}\right| = \left|\frac{-0.5865}{4.798\times10^{-5}}\right| = 1.22\times10^{4}$

Chapter 2

Exercise 2.1

$$\nu(\text{benzene}) - \nu(\text{DMSO}) = (7.3 - 2.4) \times 750 = 3.675\,\text{kHz}$$. Compare eqn 2.8.

Exercise 2.2

$$\delta = 10^6 \left(\frac{\nu_0 - \nu_{0,\text{ref}}}{\nu_{0,\text{ref}}} \right) \text{ (eqn 2.6) and } \nu_{0,\text{ref}} = -\frac{\gamma B}{2\pi} \text{ (eqn 2.4 with } \sigma_{\text{ref}} \ll 1\text{)}.$$

$$\Rightarrow \nu_{0,\text{ref}} = -\frac{(26.752 \times 10^7) \times 14.1}{2\pi} = -600.3\,\text{MHz}$$

$$\delta(C_2H_6) - \delta(C_2H_4) = 10^6 \left(\frac{\nu_0(C_2H_6) - \nu_{0,\text{ref}}}{\nu_{0,\text{ref}}} \right) - 10^6 \left(\frac{\nu_0(C_2H_4) - \nu_{0,\text{ref}}}{\nu_{0,\text{ref}}} \right)$$

$$= \left(\frac{10^6 [\nu_0(C_2H_6) - \nu_0(C_2H_4)]}{\nu_{0,\text{ref}}} \right) = \frac{10^6 \times (3 \times 10^3)}{-600.3 \times 10^6} = -5.0\,\text{ppm}$$

$$\Rightarrow \delta(C_2H_4) = \delta(C_2H_6) - (-5.0) = 0.9 + 5.0 = 5.9\,\text{ppm}$$

Exercise 2.3

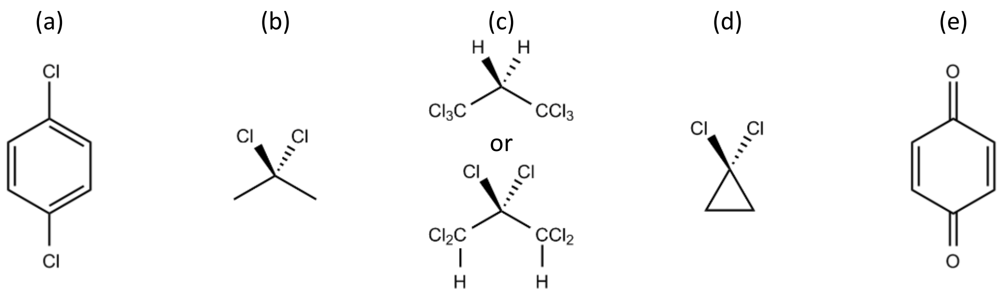
$\delta(\text{Co(CN)}_6^{3-}) = 0.0\,\text{ppm}$. $\delta(\text{Co(CO}_3)_3^{3-}) \approx 14 \times 10^3\,\text{ppm}$ (from Fig. 2.18).

$$|\nu_{0,\text{ref}}| = \frac{\gamma B}{2\pi} = \frac{(1.637 \times 10^6) \times 9.4}{2\pi} = 2.449\,\text{MHz}.$$

$$\Delta\nu = \Delta\delta \times |\nu_{0,\text{ref}}| = (14 \times 10^3\,\text{ppm}) \times 2.449\,\text{MHz} = 34.3\,\text{kHz}$$

Exercise 2.4

All five compounds have a single group of equivalent nuclei:

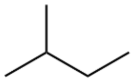


Exercise 2.5

(a)

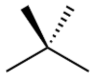
3

C1 and C5 are equivalent, as are C2 and C4.



4

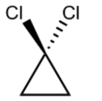
The two methyl carbons on C2 are equivalent.



2

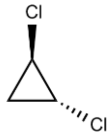
All four methyl carbons are equivalent.

(b)



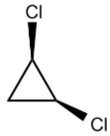
1

All four ^{1}H are equivalent.



2

The two CH_2 protons are equivalent, as are the two CH protons,



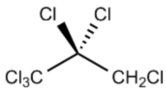
3

The two CH protons are equivalent.

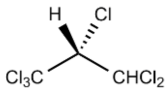
Exercise 2.6

(a)

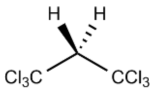
Isomer 1

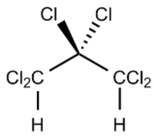


Isomer 2



(b)





Because of their symmetry, both isomers have one ^{1}H chemical shift and two ^{13}C chemical shifts.

Exercise 2.7

Assume that the paramagnetic contribution dominates:

$$\sigma_\mathrm{p} \propto -\frac{1}{\Delta}\left\langle \frac{1}{R^3}\right\rangle \text{ (eqn 2.10).} \quad \sigma = \sigma_\mathrm{d} + \sigma_\mathrm{p} \text{ (eqn 2.9).} \quad \delta \approx 10^6 \; \sigma_\mathrm{ref} - \sigma \text{ (eqn 2.7).}$$

Smaller Δ $\Rightarrow$ larger $|\sigma_\mathrm{p}|$ $\equiv$ more negative σ_p $\Rightarrow$ smaller σ $\Rightarrow$ larger δ

$\Rightarrow$ sp^2 carbons have larger chemical shifts than sp^3 carbons

Exercise 2.8

Assume that the diamagnetic contribution dominates:

larger number of electronegative substituents $\Rightarrow$ lower electron density around H atom $\Rightarrow$ greater deshielding $\Rightarrow$ higher δ

$\Rightarrow$ $CHBr_3$ has the highest and CH_3Br the lowest chemical shift

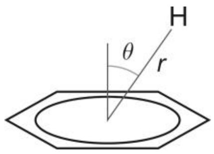
Exercise 2.9

OMe group is electron donating $\Rightarrow$ same as aniline in Fig. 2.17.

$\Rightarrow$ *meta* has the highest and the *ortho* the lowest ^{1}H chemical shift

Exercise 2.10

r and θ are defined as in the diagram:



The distance from the centre of a benzene molecule to one of its H atoms is:

$$r_{\text{benzene}} = r\ \text{C–H} + r\ \text{C–C} = 110 + 140 = 250\,\text{ppm}\,.$$

Also, $\theta_{\text{benzene}} = 90^{\circ} \Rightarrow 1 - 3\cos^2\theta_{\text{benzene}} = 1\,.$

$$\Rightarrow\ \Delta\delta\ \text{benzene} = \frac{1-3\cos^2\theta_{\text{benzene}}\ C}{r^3_{\text{benzene}}} = \frac{C}{250^{3}} = +2\,\text{ppm}\ \ \text{where } C \text{ is a constant.}$$

For the proton immediately above the centre of the ring: $\theta_{\text{above}} = 0$ and $1 - 3\cos^2\theta_{\text{above}} = -2$:

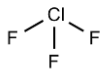
$$\Rightarrow\ \Delta\delta\ \text{above} = \frac{1-3\cos^2\theta_{\text{above}}\ C}{r^3_{\text{above}}} = \frac{-2C}{r^3_{\text{above}}} = -2\,\text{ppm}\,.$$

$$\frac{\Delta\delta\ \text{benzene}}{\Delta\delta\ \text{above}} = \frac{+2}{-2} = -1 = \frac{C/\ 250^{3}}{-2C/r^3_{\text{above}}} = -\frac{1}{2}\left(\frac{r_{\text{above}}}{250}\right)^3 \ \Rightarrow\ r_{\text{above}} = \sqrt[3]{2}\times 250 = 315\,\text{pm}$$

Chapter 3

Exercise 3.1

(a)

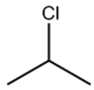


AX$_2$ spin system

(b)

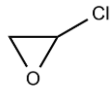
AX$_4$ spin system

(c)



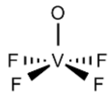
AX$_6$ spin system

(d)



AMX spin system

(e)



Square pyramid
$I(^{51}V) = \frac{7}{2}$

Exercise 3.2

(a)

CH_3Cl

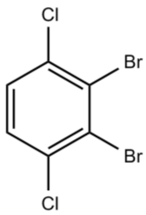
A_3 spin system
1 singlet

(b)

$(CH_3)_3CH$

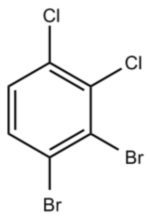
AX_9 spin system
12 lines:
CH: decet
$(CH_3)_3$: doublet

(c)



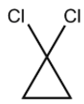
A_2 spin system
1 singlet

(d)



AX spin system
4 lines:
two doublets

(e)



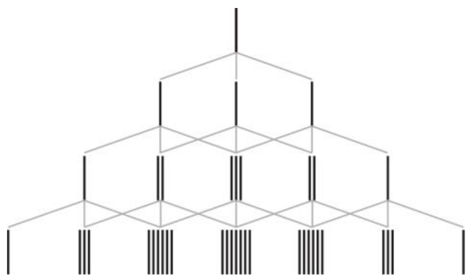
A_4 spin system
1 singlet

Exercise 3.3

(a) The relative intensities are 1:2:3:2:1

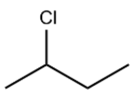
(b) There are seven lines in the ^{1}H spectrum of CHD_3 (relative intensities 1:3:6:7:6:3:1)

See tree diagram.



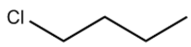
Exercise 3.4

(a)



From left to right:
doublet, sextet, quintet, triplet

(b)



From left to right:
triplet, quintet, sextet, triplet

Exercise 3.5

With a linewidth of ~3 Hz, only the three-bond couplings would be resolved, i.e. J_{AM} and J_{AP}.

⇒ singlet (X), doublet (P), doublet (M), triplet (A)

Exercise 3.6

$\nu_1 = -600.001677$ MHz; $\nu_2 = -600.001683$ MHz; $\nu_3 = -600.004437$ MHz; $\nu_4 = -600.004443$ MHz

$\nu_{\text{ref}} = -600$ MHz . $J = \nu_1 - \nu_2 = \nu_3 - \nu_4 = 6\,\text{Hz}$.

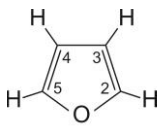
To get the chemical shifts:

$$\frac{\tfrac{1}{2}(\nu_1+\nu_2) - \nu_{\text{ref}}}{\nu_{\text{ref}}/10^6} = 2.8\,\text{ppm} \qquad \frac{\tfrac{1}{2}(\nu_3+\nu_4) - \nu_{\text{ref}}}{\nu_{\text{ref}}/10^6} = 7.4\,\text{ppm}$$

Exercise 3.7

(a) Only one group of equivalent spins $\Rightarrow$ magnetically equivalent

(b) $J_{24} \neq J_{25} \neq J_{34}$ $\Rightarrow$ chemically equivalent



(c) All J_{HF} couplings are identical $\Rightarrow$ magnetically equivalent

(d) ${}^2J_{\text{CH}} \neq {}^3J_{\text{CH}}$ $\Rightarrow$ chemically equivalent

Exercise 3.8

$$\frac{I\ \text{inner}}{I\ \text{outer}} = \frac{1+J/C}{1-J/C} = \frac{C+J}{C-J}\ \text{(Table 3.3)}. \quad C = \sqrt{J^2+(\delta\nu)^2}\ \text{(eqn 3.5)}.$$

$\delta\nu$ = spectrometer frequency $\times$ chemical shift difference $= 0.154\,\nu_0/10^6$

(a) $C = \sqrt{3.9^2 + (0.154\times600)^2} = 92.48\,\text{Hz} \Rightarrow \dfrac{I\ \text{inner}}{I\ \text{outer}} = \dfrac{92.48+3.9}{92.48-3.9} = 1.09$

(b) $C = \sqrt{3.9^2 + (0.154\times40)^2} = 7.291\,\text{Hz} \Rightarrow \dfrac{I\ \text{inner}}{I\ \text{outer}} = \dfrac{7.291+3.9}{7.291-3.9} = 3.30$

Exercise 3.9

Let P_t and P_g be the mole fractions of molecules in which the two protons are, respectively, *trans* and *gauche* to one another ($P_t + P_g = 1$). The observed coupling under conditions of fast exchange is the weighted average of the *trans* and *gauche* *J*-couplings:

$$\langle J\rangle = P_t J_t + P_g J_g = P_t J_t + (1-P_t)J_g = J_g + P_t(J_t - J_g)$$

$$\Rightarrow P_t = \frac{\langle J\rangle - J_g}{J_t - J_g} = \frac{3.46-2.2}{9.7-2.2} = 0.168 \quad \text{and} \quad P_g = 1-P_t = 0.832$$

Exercise 3.10

Dipolar splitting $= \lambda R_{\text{AX}}\ 3\cos^2\theta - 1$ with $R_{\text{AX}} = \left(\dfrac{\hbar}{2\pi}\right)\left(\dfrac{\mu_0}{4\pi}\right)\left(\dfrac{\gamma_{\text{A}}\gamma_{\text{X}}}{r^3}\right)$ (eqn 3.16).

$\lambda = 1$ for heteronuclear spins and $\lambda = \frac{3}{2}$ for homonuclear spins.

Maximum splitting = $2\lambda R_{\text{AX}}$ (when $\theta = 0$).

(a) For ^{13}C-^{13}C, $R_{\text{CC}} = \dfrac{\text{max splitting}}{2\lambda_{\text{CC}}} = \dfrac{6414}{2\times\frac{3}{2}} = \dfrac{6414}{3}$ Hz.

$$\Rightarrow\ r_{\text{CC}} = \sqrt[3]{\left(\frac{\hbar}{2\pi}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\gamma_{\text{C}}^2}{R_{\text{CC}}}\right)} = \sqrt[3]{\frac{6.626\times10^{-34}}{4\pi^2}\times10^{-7}\times\frac{6.728\times10^{7}\ ^2}{6414/3}} = 1.526\times10^{-10}\text{ m}$$

(b) For ^{15}N-^{13}C, $R_{\text{NC}} = \dfrac{\text{max splitting}}{2\lambda_{\text{NC}}} = \dfrac{1941}{2\times1}$ Hz.

$$\Rightarrow\ r_{\text{NC}} = \sqrt[3]{\left(\frac{\hbar}{2\pi}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\gamma_{\text{N}}\gamma_{\text{C}}}{R_{\text{NC}}}\right)} = \sqrt[3]{\frac{6.626\times10^{-34}}{4\pi^2}\times10^{-7}\times\frac{2.713\times10^{7}\ \ 6.728\times10^{7}}{1941/2}} = 1.467\times10^{-10}\text{ m}$$

Chapter 4

Exercise 4.1

$$k_{\text{merge}} = \frac{\pi\,\delta\nu}{\sqrt{2}} \quad \text{(eqn 4.4).}$$

$$\delta\nu = (6-2)\ \text{ppm} \times 400\,\text{MHz} = 1600\,\text{Hz} \quad \Rightarrow \quad k_{\text{merge}} = \frac{\pi \times 1600}{\sqrt{2}} = 3554\,\text{s}^{-1}.$$

(a) $k = 10^2\ \text{s}^{-1} \ll k_{\text{merge}} \Rightarrow$ slow exchange $\Rightarrow \Delta\nu = \dfrac{k}{\pi} = \dfrac{10^2}{\pi} = 31.8\,\text{Hz}$ (eqn 4.2)

(b) $k = 10^5\ \text{s}^{-1} \gg k_{\text{merge}} \Rightarrow$ fast exchange $\Rightarrow \Delta\nu = \dfrac{(\pi\,\delta\nu)^2}{2k} = \dfrac{(\pi\, 1600)^2}{2\times 10^5} = 40.2\,\text{Hz}$ (eqn 4.3)

Exercise 4.2

$$\Delta\nu = \frac{k}{\pi} \quad \Rightarrow \quad k = \pi\Delta\nu \ \text{(eqn 4.2).}$$

(a) At 100 °C, $k_1 = \pi \times 1.4 = 4.4\,\text{s}^{-1}$. At 120 °C, $k_2 = \pi \times 6.0 = 18.9\,\text{s}^{-1}$.

(b) Arrhenius equation: $k = A\exp(-E_a/RT)$. Assume pre-exponential factor is independent of temperature.

$$\frac{k_1}{k_2} = \frac{\exp(-E_a/RT_1)}{\exp(-E_a/RT_2)} = \exp\left(-\frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right)$$

$$\Rightarrow \quad E_a = \frac{R\ln(k_1/k_2)}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = \frac{8.314 \times \ln(1.4/6.0)}{\left(\dfrac{1}{393} - \dfrac{1}{373}\right)} = 88.7\,\text{kJ}\,\text{mol}^{-1}$$

From the Arrhenius equation, $A = k_1 \exp(E_a/RT_1) = 1.4\pi \times \exp\left(\dfrac{88.7\times 10^3}{8.314 \times 373}\right) = 1.15 \times 10^{13}\ \text{s}^{-1}$

Exercise 4.3

$$k_{\text{merge}} = \frac{\pi\,\delta\nu}{\sqrt{2}} \ \text{(eqn 4.4).}$$

$$\Rightarrow \quad k_{\text{merge}} = \frac{400\pi}{\sqrt{2}} = 10^{13}\exp\left[-\frac{9100}{T_{\text{merge}}}\right] \quad \Rightarrow \quad T_{\text{merge}} = \frac{9100}{\ln\left(\dfrac{\sqrt{2}\times 10^{13}}{400\pi}\right)} = 393\,\text{K}$$

(a) At T = 310 K, $T < T_{\text{merge}} \Rightarrow$ slow exchange $\Rightarrow$ two lines

(b) At T = 393 K, $T = T_{\text{merge}} \Rightarrow$ two lines just merged into one broad one

(c) At T = 420K, $T > T_{\text{merge}} \Rightarrow$ fast exchange $\Rightarrow$ one line

Exercise 4.4

$\delta_{\text{av}} = p_{\text{A}}\delta_a + p_{\text{B}}\delta_b$ (compare eqn 4.7). $\delta_a = 3.5\,\text{ppm}$; $\delta_b = 6.5\,\text{ppm}$.

$$\delta_{\text{av}} = p_{\text{A}}\delta_a + (1-p_{\text{A}})\delta_b = p_{\text{A}}(\delta_a-\delta_b)+\delta_b \;\Rightarrow\; p_{\text{A}} = \frac{\delta_{\text{av}}-\delta_b}{\delta_a-\delta_b}.$$

At 300 K: $p_{\text{A}} = \dfrac{3.86-6.5}{3.5-6.5} = 0.88;\quad p_{\text{B}} = 1-p_{\text{A}} = 0.12$.

At 350 K: $p_{\text{A}} = \dfrac{4.10-6.5}{3.5-6.5} = 0.80;\quad p_{\text{B}} = 1-p_{\text{A}} = 0.20$.

The equilibrium constant for $\text{A} \rightleftharpoons \text{B}$ is $K = \dfrac{p_{\text{B}}}{p_{\text{A}}}$.

At 300 K: $K_{300} = \dfrac{0.12}{0.88} = 0.136$. At 330 K: $K_{350} = \dfrac{0.20}{0.80} = 0.250$.

The van't Hoff equation for the temperature dependence of the equilibrium constant is: $\dfrac{d\ln K}{dT} = \dfrac{\Delta_{\text{r}}H}{RT^2}$.

Integrating this expression, assuming $\Delta_{\text{r}}H$ is independent of temperature, gives:

$$\ln K = -\frac{\Delta_{\text{r}}H}{RT}+c \;\Rightarrow\; \ln\left(\frac{K_{350}}{K_{300}}\right) = -\frac{\Delta_{\text{r}}H}{R}\left(\frac{1}{350}-\frac{1}{300}\right)$$

$$\Rightarrow \Delta_{\text{r}}H = \frac{R\ln\left(\dfrac{K_{350}}{K_{300}}\right)}{\left(\dfrac{1}{300}-\dfrac{1}{350}\right)} = \frac{8.314\times\ln(0.25/0.136)}{\left(\dfrac{1}{300}-\dfrac{1}{350}\right)} = 10.6\,\text{kJ mol}^{-1}$$

Exercise 4.5

δ_a = 3.00 ppm, δ_b = 5.00 ppm.

$$\delta_{\text{av}} = p_{\text{A}}\delta_a + p_{\text{B}}\delta_b = (1-p_{\text{B}})\delta_a + p_{\text{B}}\delta_b = p_{\text{B}}(\delta_b-\delta_a)+\delta_a$$

$$\Rightarrow p_{\text{B}} = \frac{\delta_{\text{av}}-\delta_a}{\delta_b-\delta_a} = \frac{3.01-3.00}{5.00-3.00} = 0.005 \text{ and } p_{\text{A}} = 1-p_{\text{B}} = 0.995$$

Exercise 4.6

$$K = \frac{k_{\text{A}}}{k_{\text{B}}};\quad \Delta\nu_{\text{A}} = \frac{k_{\text{A}}}{\pi},\quad \Delta\nu_{\text{B}} = \frac{k_{\text{B}}}{\pi}.$$

$$\Rightarrow \frac{\Delta\nu_{\text{B}}}{\Delta\nu_{\text{A}}} = \frac{k_{\text{B}}}{k_{\text{A}}} \;\Rightarrow\; \Delta\nu_{\text{B}} = \frac{k_{\text{B}}}{k_{\text{A}}}\times\Delta\nu_{\text{A}} = \frac{\Delta\nu_{\text{A}}}{K} = \frac{1.0}{0.01} = 100.0\,\text{Hz}$$

Exercise 4.7

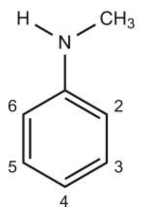
$$\Delta\nu = \frac{k_2[\text{H}^+]}{\pi} = 3.2\,\text{Hz} \;\Rightarrow\; k_2 = \frac{\pi\Delta\nu}{[\text{H}^+]} = \frac{3.2\times\pi}{10^{-7}} = 1.0\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

Exercise 4.8

There are 6 protons at –2.99 ppm and 12 protons at +9.28 ppm.

Weighted average chemical shift: $\delta_{\text{av}} = \dfrac{6\times\ -2.99\ +12\times 9.28}{6+12} = 5.19\,\text{ppm}$

Exercise 4.9



Six lines at low temperature because rotation around N–benzene bond is slow and all 6 aromatic carbons are inequivalent.

At high temperature, rapid rotation around the N–benzene bond averages the chemical shifts of C2 and C6 and of C3 and C5.

There are therefore 4 lines: C1, C2+C6, C3+C5, C4.

Exercise 4.10

$$\delta_{\text{av}} = p\ \text{H}_2\text{PO}_4^-\ \delta\ \text{H}_2\text{PO}_4^-\ + p\ \text{HPO}_4^{2-}\ \delta\ \text{HPO}_4^{2-}\ .$$

4.61 is the mean of 3.40 and 5.82 $\Rightarrow\ p\ \text{H}_2\text{PO}_4^-\ = p\ \text{HPO}_4^{2-}\ .$

$$\Rightarrow\ K_{\text{a}} = \frac{\left[\text{HPO}_4^{2-}\right]\left[\text{H}^+\right]}{\left[\text{H}_2\text{PO}_4^-\right]} = \frac{p\ \text{HPO}_4^{2-}\ \left[\text{H}^+\right]}{p\ \text{H}_2\text{PO}_4^-} = \left[\text{H}^+\right]\ \Rightarrow\ \text{p}K_{\text{a}} = \text{p}H = 7.21$$

Chapter 5

Exercise 5.1

$$\Delta\nu = \frac{1}{\pi T_2} \text{ (eqn 5.9).}$$

$$\Rightarrow \; T_2 = \frac{1}{\pi\Delta\nu} = \frac{1}{0.1\times\pi} = 3.18\,\text{s}$$

Exercise 5.2

$$\Delta n(t) = \Delta n_{\text{eq}}\left[1-\exp(-t/T_1)\right] \text{ (eqn 5.1)}$$

$$\frac{\Delta n(t)}{\Delta n_{\text{eq}}} = 1-\exp(-t/T_1) = 0.99 \;\Rightarrow\; \exp(-t/T_1) = 0.01 \;\Rightarrow\; t = T_1 \ln 100 = 4.61 T_1$$

Exercise 5.3

$$J(\omega) = \frac{2\tau_{\text{c}}}{1+\omega^2\tau_{\text{c}}^2} \text{ (eqn 5.3);} \quad \frac{1}{T_1} = \gamma^2 \left\langle B_{\text{loc}}^2 \right\rangle J(\omega_0) \text{ (eqn 5.4).}$$

(a) At the minimum, $\dfrac{\mathrm{d}J(\omega_0)}{\mathrm{d}\tau_{\text{c}}} = 0$.

$$\frac{\mathrm{d}J(\omega_0)}{\mathrm{d}\tau_{\text{c}}} = \frac{2-2\omega_0^2\tau_{\text{c}}^2}{\left(1+\omega_0^2\tau_{\text{c}}^2\right)^2} \text{ which equals zero when } \omega_0\tau_{\text{c}} = 1.$$

$$\Rightarrow \; \tau_{\text{c}} = \frac{1}{\omega_0} = \frac{1}{2\pi\times(500\times10^6)} = 318\,\text{ps}$$

(b) When $\omega_0\tau_{\text{c}} = 1$, $J(\omega_0) = \dfrac{2\tau_{\text{c}}}{1+\omega_0^2\tau_{\text{c}}^2} = \tau_{\text{c}}$.

$$\Rightarrow \; T_1 = \frac{1}{\gamma^2\left\langle B_{\text{loc}}^2\right\rangle J(\omega_0)} = \frac{1}{\gamma^2\left\langle B_{\text{loc}}^2\right\rangle \tau_{\text{c}}} = \frac{1}{(4.5\times10^9)\times(318\times10^{-12})} = 0.70\,\text{s}$$

Exercise 5.4

(a) Assume only source of ^{13}C relaxation is modulation of the ^{13}C-^{1}H dipolar interaction.

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \gamma_C^2 \gamma_H^2 \left(\frac{\tau_c}{r^6}\right) \quad \text{(eqn 5.5).}$$

$$\Rightarrow \; r = \left[\left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \gamma_C^2 \gamma_H^2 \tau_c T_1\right]^{1/6}$$

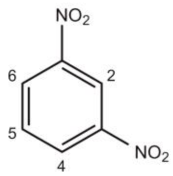
$$= \left[10^{-7}\;{}^{2} \times \left(\frac{6.626\times10^{-34}}{2\pi}\right)^2 \times 6.728\times10^{7}\;{}^{2} \times 26.752\times10^{7}\;{}^{2} \times 50\times10^{-12} \times 0.931\right]^{1/6} = 1.09\times10^{-10}\ \text{m}$$

(b) Ignoring the small difference in the C–H and N–H bond lengths:

$$\frac{1}{T_1\ \text{CH}} \propto \gamma_C^2; \quad \frac{1}{T_1\ \text{NH}} \propto \gamma_N^2 \quad \Rightarrow \quad \frac{T_1\ \text{NH}}{T_1\ \text{CH}} = \left(\frac{\gamma_C}{\gamma_N}\right)^2 = \left(\frac{6.728\times10^{7}}{2.713\times10^{7}}\right)^2 = 6.1\,.$$

Other things being equal, ^{15}N in an NH group should have slower spin-lattice relaxation than ^{13}C in a CH group.

Exercise 5.5



^{1}H spin-lattice relaxation is dominated by the dipolar interactions between nearest neighbour ring protons. H5 has two nearest neighbours, H4 and H6 have one, and H2 has none.

Therefore (a) H5 relaxes fastest and (b) H2 relaxes slowest.

Exercise 5.6

T_2 decreases as τ_c increases (Fig. 5.11). The slowly tumbling protein therefore has a shorter T_2 and, because $\Delta\nu \propto 1/T_2$ (eqn 5.9), a larger linewidth.

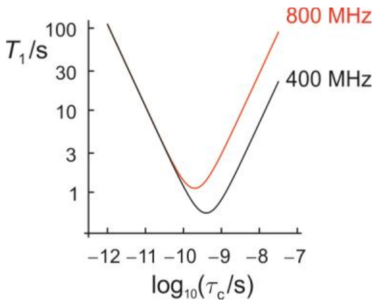
Exercise 5.7

$$J\ \omega = \frac{2\tau_c}{1+\omega^2\tau_c^2} \ \text{(eqn 5.3).} \quad \frac{1}{T_1} = \gamma^2 \langle B_{\text{loc}}^2 \rangle J\ \omega_0 \ \text{(eqn 5.4).} \quad \frac{1}{T_2} = \gamma^2 \langle B_{\text{loc}}^2 \rangle \tfrac{1}{2}\left[J\ 0 + J\ \omega_0\ \right] \ \text{(eqn 5.11).}$$

$$\Rightarrow \frac{T_1}{T_2} = \frac{\tfrac{1}{2}\left[J\ 0 + J\ \omega_0\ \right]}{J\ \omega_0} = \tfrac{1}{2} + \tfrac{1}{2}\frac{J\ 0}{J\ \omega_0} = \tfrac{1}{2} + \tfrac{1}{2}\ 1 + \omega_0^2\tau_c^2 \ = 1 + \tfrac{1}{2}\omega_0^2\tau_c^2 = 10$$

$$\Rightarrow \tau_c = \frac{\sqrt{18}}{\omega_0} = \frac{\sqrt{18}}{2\pi\times600\times10^6} = 1.13\,\text{ns}$$

Exercise 5.8

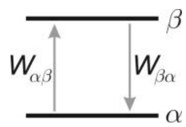


No change when $\omega_0\tau_c \ll 1$.

T_1 is increased by a factor of 4 when $\omega_0\tau_c \gg 1$.

The minimum T_1 is larger by a factor of 2 and occurs at half the value of τ_c.

Exercise 5.9



$$\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = -W_{\alpha\beta}n_\alpha + W_{\beta\alpha}n_\beta .$$

At equilibrium $n_\alpha = n_\alpha^{\mathrm{eq}}$, $n_\beta = n_\beta^{\mathrm{eq}}$ and $\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = 0$.

$$\Rightarrow \frac{W_{\beta\alpha}}{W_{\alpha\beta}} = \frac{n_\alpha^{\mathrm{eq}}}{n_\beta^{\mathrm{eq}}} .$$

According to the Boltzmann equation, $\frac{n_\beta^{\mathrm{eq}}}{n_\alpha^{\mathrm{eq}}} = \exp\left(-\Delta E / k_\mathrm{B}T\right)$.

$$\Rightarrow \frac{W_{\beta\alpha}}{W_{\alpha\beta}} = \exp\left(\Delta E / k_\mathrm{B}T\right)$$

Exercise 5.10

$$\frac{W_2^{\mathrm{AX}}}{W_0^{\mathrm{AX}}} = \frac{6J(2\omega_0)}{J(0)} = \frac{6\left(\dfrac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right)}{2\tau_c} = \frac{6}{1+4\omega_0^2\tau_c^2} = 1 \quad \text{(using eqn 5.3 for } J(\omega)\text{)}$$

$$\Rightarrow 4\omega_0^2\tau_c^2 = 5 \quad \Rightarrow \quad \tau_c = \frac{\sqrt{5}}{2}\frac{1}{\omega_0} = \frac{\sqrt{5}}{2}\left(\frac{1}{2\pi\times 600\times 10^6}\right) = 297\,\text{ps}$$

Chapter 6

Exercise 6.1

$$\beta = \frac{\pi}{2} = -\omega_1 t_\mathrm{p} = \gamma B_1 t_\mathrm{p} \quad \text{(eqn 6.3).}$$

$$\Rightarrow\ t_\mathrm{p} = \frac{\beta}{\gamma B_1} = \frac{\pi/2}{26.753\times 10^7 \times 10^{-3}} = 5.87\ \mu\mathrm{s}$$

Exercise 6.2

Assuming exponential relaxation: $\exp\ -t/T_2\ = 0.01 \ \Rightarrow\ t = T_2 \ln\ 100\ = 2.30\,\mathrm{s}$

Exercise 6.3

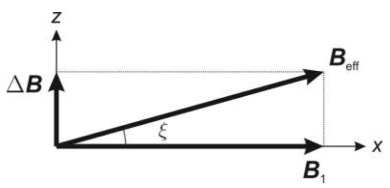
(a) A 90° pulse rotates z-magnetization vector into xy-plane $\Rightarrow$ z-magnetization = 0 $\Rightarrow$ equal populations

$$\Rightarrow\ n_\alpha = n_\beta = \frac{n_\alpha^\mathrm{eq} + n_\beta^\mathrm{eq}}{2}.$$

(b) A 180° pulse inverts z-magnetization $\Rightarrow$ z-magnetization changes sign

$$\Rightarrow\ n_\alpha - n_\beta = n_\beta^\mathrm{eq} - n_\alpha^\mathrm{eq} \ \Rightarrow\ n_\alpha = n_\beta^\mathrm{eq} \ \text{ and } \ n_\beta = n_\alpha^\mathrm{eq}$$

Exercise 6.4



(a) $\dfrac{\Delta B}{B_1} = \tan\ \xi\ = \tan 10^\circ$ (see diagram). $\Omega = \gamma \Delta B$ and $\beta = \gamma B_1 t_\mathrm{p} = \dfrac{\pi}{2}$.

$$\Rightarrow\ \tan 10^\circ = \frac{\Delta B}{B_1} = \frac{\Omega/\gamma}{\pi/2\ /\gamma t_\mathrm{p}} = \frac{\Omega t_\mathrm{p}}{\pi/2}$$

$$\Rightarrow\ \Omega = \left(\frac{\pi}{2}\right)\times\frac{\tan 10^\circ}{t_\mathrm{p}} = \left(\frac{\pi}{2}\right)\times\frac{\tan 10^\circ}{10\times 10^{-6}} = 2.77\times 10^4\ \mathrm{rad\ s^{-1}}$$

$$\Rightarrow\ \xi \le 10^\circ \ \text{when} \ -27{,}700 < \Omega < +27{,}700\ \mathrm{rad\ s^{-1}}$$

(b) chemical shift $\times$ spectrometer frequency = offset frequency

$$\Rightarrow\ \delta = \frac{27{,}700}{400\times 2\pi} = 11.0\,\mathrm{ppm} \ \Rightarrow\ \text{chemical shift range} = 5.0 \pm 11.0 = +16.0 > \delta > -6.0\ \mathrm{ppm}$$

Exercise 6.5

$$\cos(\Omega_0 t)\cos(\pi J t) = \frac{1}{2}\cos(\Omega_0 + \pi J)t + \frac{1}{2}\cos(\Omega_0 - \pi J)t\,.$$

$\Rightarrow$ the spectrum obtained by Fourier transforming $A\cos(\Omega_0 t)\cos(\pi J t)\exp(-t/T_2)$ contains lines at offset frequencies $\Omega = \Omega_0 \pm \pi J$, both with amplitude $\frac{1}{2}A$

Exercise 6.6

Signal-to-noise ratio $\propto \sqrt{N}$ $\Rightarrow$ $N = 50^2 = 2500$

Exercise 6.7

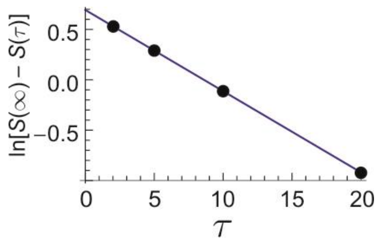
$S(\tau) = [1 - 2\exp(-\tau/T_1)]S(\infty)$ (eqn 6.6). $S(\tau = 100\,\text{s}) \approx S(\infty) = 1.000$.

$\Rightarrow$ $S(\infty) - S(\tau) = 2\exp(-\tau/T_1)$

$\Rightarrow$ $\ln[S(\infty) - S(\tau)] = \ln 2 - \tau/T_1$.

Plot $\ln[S(\infty) - S(\tau)]$ against τ. Gradient = $-\dfrac{1}{T_1}$ = –0.0806 s^{-1}

$\Rightarrow$ $T_1 = 12.4\,\text{s}$

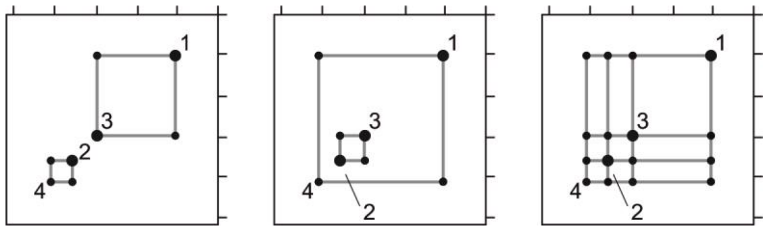


Exercise 6.8

At the end of the first delay the A, B, and C vectors accumulate phases Ω_A, Ω_B, and Ω_C. After a 180°_x pulse, these phases are $180^\circ - \Omega_A$, $180^\circ - \Omega_B$, and $180^\circ - \Omega_C$. During the second delay, the three vectors accumulate additional phases Ω_A, Ω_B, and Ω_C. The end result is that all three have phase equal to 180°, i.e. they refocus along the +*y*-axis.

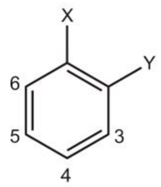
When the second pulse is 180°_y (as in Fig. 6.13) the phases are Ω_A, Ω_B, and Ω_C before the 180°_y pulse, $-\Omega_A$, $-\Omega_B$, and $-\Omega_C$ after the 180°_y pulse, and therefore 0° at the end of the second delay.

Exercise 6.9

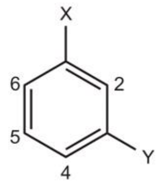


(a) 1,3 shifts (b) 1,4 shifts (c) random shifts

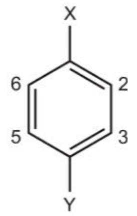
Exercise 6.10



3 cross peaks:
34, 45, 56



2 cross peaks:
45, 56



1 cross peak:
23 = 56