Solutions to End-of-Chapter Exercises
Chapter 8

Fundamental constants & properties of nuclei

$c = 2.997 \times 10^{8}$ m s^{-1}
$e = 1.602 \times 10^{-19}$ C
$k = 1.381 \times 10^{-23}$ J K^{-1}
$h = 6.626 \times 10^{-34}$ J s

Mass

Electron	$= 9.109\,390 \times 10^{-31}$ kg
Proton	$= 1.672\,622 \times 10^{-27}$ kg

$\mu_0 = 4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1} (= T^2 J^{-1} m^3)
$\mu_B = 9.274 \times 10^{-24}$ J T^{-1}
$\mu_N = 5.050\,784 \times 10^{-27}$ J T^{-1}
$g_e = 2.0023\,193$ (electron g factor)
$g_p = 5.585\,694\,7$ (proton g factor)
$\gamma_e = 1.761 \times 10^{11}$ s^{-1} T^{-1}

Properties for other common nuclei

	g_N	ν_N / MHz	γ / 10^7 s^{-1} T^{-1}
^{1}H	5.5857	14.9021	26.752
^{2}H	0.8574	2.2876	4.107
^{13}C	1.4048	3.7479	6.728
^{14}N	0.4038	1.0772	1.934
^{31}P	2.2632	6.0380	10.839

ν_L (in units of MHz) for $B = 0.35$ T

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Exercise 8.2) A rigid nanoparticle possessing a nitroxide group is 1 nm in diameter. The viscosity of water at 25 C is 8.90 × 10^{-4} N.s.m^{-2}. Deduce if an aqueous solution of these nanoparticles will give fast or slow motion X-band EPR spectra at room temperature. What will be the answer for 3 nm particles?

ANSWER

Using eqn 8.3, rotational correlation time τ_c of the nanoparticles 1 nm in diameter (i.e., $r = 0.5$ nm) can be calculated as $\tau_c = \frac{4\pi\eta r^3}{3kT} = \frac{4 \times 3.14 \times (8.90 \times 10^{-4}\ \mathrm{N\,s\,m^{-2}}) \times}{3 \times (1.381 \times 10^{-23}\mathrm{J\,K^{-1}}) \times 298\ \mathrm{K}} = 1.13 \times 10^{-10}$ s. This is smaller than the threshold for the fast motion of nitroxides (ca. 10^{-9} s, section 8.3), and the nanoparticles will therefore show fast motion X-band EPR spectra. A similar calculation for the nanoparticles 3 nm in diameter will yield $\tau_c = 3.05\times10^{-9}$ s which is greater than the threshold for the fast motion. The rotational diffusion in this case will therefore be in the slow motion regime.

Exercise 8.3) Using the spectra in Fig. 8.9, calculate the rate of stannotropic migration of the phenoxyl radical in Fig. 8.8 at 20 C if the spectra were recorded at a frequency of 9.5 GHz.

ANSWER

In Fig. 8.9, the central peaks coalesce at 20 °C temperature. Hence, the rate of exchange can be calculated according to eqn 8.4, $k = \frac{\pi\delta\nu}{\sqrt{2}}$. The difference in resonance frequency of the exchanging lines $\delta\nu$ can be measured from the top spectrum in Fig. 8.9. The distance between the exchanging lines is ca. 0.23 mT. The g can be read from the spectrum at 339 mT which for 9.5 GHz corresponds to the g value 2.0022. The difference between exchanging lines (0.23 mT) can then be converted into frequency units, $\delta\nu = 6.45$ MHz. The rate of exchange is then $k = \frac{3.14 \times (6.45 \times 10^6\ \mathrm{s^{-1}})}{\sqrt{2}} = 1.43 \times 10^7\ \mathrm{s^{-1}}$.

Exercise 8.4) Fig. 8.17 shows an EPR spectrum of the methanol radical $HOCH_2^{\bullet}$ at 130 K. The spectrum reveals a small hyperfine interaction with the OH proton and stronger interactions with two non-equivalent protons of the CH_2 group. Upon increasing the temperature, rotation around the C–O bond leads to broadening of the EPR spectra. At about 220 K, the spectrum shows hyperfine interaction with two equivalent protons of the CH_2 group (in addition to the weak interaction with the OH proton). Deduce which EPR lines are broadened by this dynamic process, and hence sketch the EPR spectra which would be observed as the temperature is gradually increased from 130 to 220 K.

ANSWER

The spectrum in Fig. 8.17 can be compared to the top spectrum in Fig. 8.9. The spectrum in Fig.8.17 is very similar but includes additional small splitting which is not affected by the exchange (i.e., each line in Fig. 8.9 is split into a doublet). Hence the same arguments as used in Fig. 8.10, can be applied to Fig. 8.17. Upon increasing the temperature, the central four lines in Fig. 8.17 will therefore be selectively broadened (i.e., the two doublets on the extremes of the spectrum will not be broadened). At some temperature, these central four lines will coalesce, and upon further increase of temperature, the central four lines will sharpen into a doublet.

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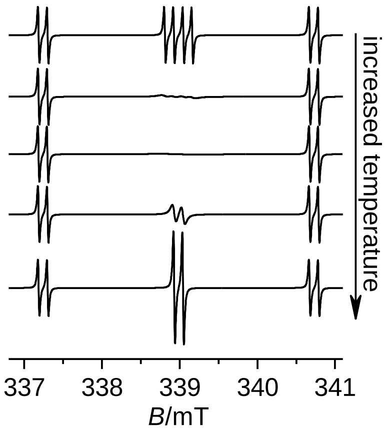

Exercise 8.5) Open an EPR spectrum of a nitroxide with restricted tumbling at www.EPRSimulator.org and set log(D) to 10.

(a) Observe how the spectra change at different microwave frequency. Explain why the spectra appear almost isotropic at S-band (e.g. the three lines have almost the same intensity) but are strongly anisotropic at W-band.

(b) Set log(D) to 10 and the frequency to W-band. Observe how the EPR spectra are affected by A_{zz}. Explain why the spectra with large A_{zz} appear more anisotropic than those with small A_{zz}.

ANSWER
(a) The larger anisotropy of rotational diffusion-broadened spectra at W-band compared to S-band is due to the **g** anisotropy of nitroxides. The distance (in field units) between the peaks in the EPR spectra for different g values increases with spectrometer frequency. Hence at higher frequency, the difference between the spectra in different orientations is greater, the incomplete averaging is more pronounced, and the spectra appear more anisotropic.

(b) The spectra with larger A_{zz} value appear more anisotropic due to **A** anisotropy. In nitroxides, $A_{zz} > A_{xx,yy}$. The larger the A_{zz} value, the more different it is from the A_{xx} and A_{yy} values, and hence rotational diffusion-broadened EPR spectra appear more anisotropic.

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