# Magnetic Resonance (2nd year lecture course, CRT)

Problems

1.   The most powerful NMR spectrometers currently available operate at a Larmor frequency of 900 MHz for protons.
(a) How does the energy of one quantum at 900 MHz compare with kT at 298 K?
(b) What are the relative populations of the proton energy levels?
(c) What is the Larmor frequency of ^2H on this spectrometer?
(Gyromagnetic ratios, γ: ^1H 2.675 x 10^8 T^{-1} s^{-1}, ^2H: 4.11 x 10^7 T^{-1} s^{-1}).

2. ^{17}O has spin magnetic quantum number I = 5/2. Compute the magnitude of the spin angular momentum of this spin and hence draw a diagram illustrating the space quantization of this spin-5/2 nucleus (indicating clearly the angles of precession).

3.   Assuming g = 2.0050, what magnetic field would be required to observe EPR in a 400 MHz NMR spectrometer? Is EPR usually a more sensitive technique than NMR? Justify your answer.

4.   In Oxford, the Earth's magnetic field strength is approximately 47μT; in Kursk (Russia) it reaches 190 μT. What will be the Larmor frequency of protons in the Earth's field in the two places? Why is NMR in the Earth's field of limited use, even in Kursk?

5.   An NMR spectrometer operating at 100.0 MHz was used to record the proton spectrum of acetaldehyde, CH_3CHO. The frequency difference between the resonances of the methyl and the aldehydic protons was 760 Hz.
(a) What is the chemical shift difference in part per million (ppm) between the two resonances?
The ^1H spectrum of the same molecule was recorded on another spectrometer which used a magnetic field of 9.396 T. On this new spectrometer, what is:
(b) the frequency difference in Hz?
(c) the chemical shift difference in ppm, between the two resonances?
The splitting of the methyl proton doublet in the 100.0 MHz spectrum is 2.9 Hz.
(d) What will be the values of the spin-spin coupling constant on the 9.396 T spectrometer?

6.   Comment on the difference in ^1H chemical shifts of the indicated protons in these two phenanthrene derivatives.

8.65 ppm

10.35 ppm
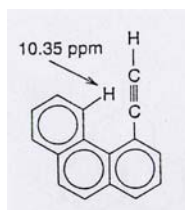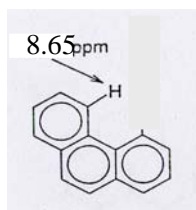
7. Comment on the chemical shift values in this molecule:

H_B +8.9

H_A

-1.8
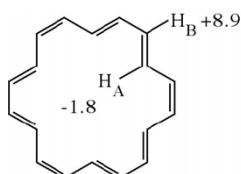
8.   The ^{59}Co chemical shifts of a number of octahedral cobalt complexes in aqueous solution were found to depend linearly on the wavelength of the first electronic absorption band of the complex. Comment on this observation.

9.   The one-bond ^{13}C-^{1}H spin-spin coupling constants in ethane, ethane and ethyne are ~125Hz, ~167 Hz and ~250 Hz, respectively. Comment on these values in the light of the mechanism of spin-spin coupling.

10.   The frequencies of the NMR transition of a nucleus in an AX$_3$ spin system (X is spin-½) are given by:

$$v_A = \gamma_A B_0 (1 - \sigma_A)/2\pi - J_{AX}(m_{X1} + m_{X2} + m_{X3}).$$
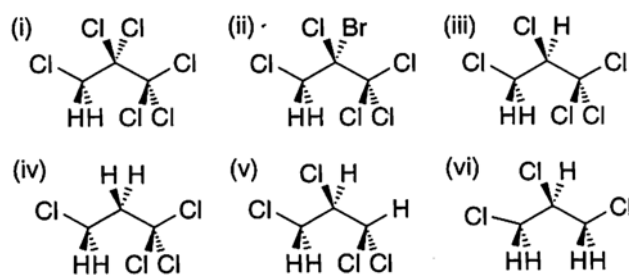
(a) Explain the significance of the symbols and the physical origin of the term that contains $J_{AX.}$
(b) Show that the spectrum of A is a 1:3:3:1 quartet if X is a spin-½ nucleus.
(c) Using the same method, predict the appearance of the multiplet if X is a spin-1 nucleus.

11. Define the terms "chemical" and "magnetic" equivalence and provide definitions for a weakly and strongly coupled spin system.

(i) Give the alphabet notation for the proton spin systems in the following compounds (give your reasons):

(i) Cl Cl
Cl—⟨⟩—Cl
HH Cl Cl

(ii)· Cl Br
Cl—⟨⟩—Cl
HH Cl Cl

(iii) Cl H
Cl—⟨⟩—Cl
HH Cl Cl

(iv) H H
Cl—⟨⟩—Cl
HH Cl Cl

(v) Cl H
Cl—⟨⟩—H
HH Cl Cl

(vi) Cl H
Cl—⟨⟩—Cl
HH HH

(ii) Predict the spectra of 3-Chlor-6-ethoxypyridazin. Include in your answer a discussion of weak and strong coupling effects.

(iii) For each of the compounds given below, determine if the protons H_a and H_b are chemically equivalent, or magnetically equivalent.

(i)
Cl—⟨O⟩—Cl
H_b H_a

(ii)
Cl—⟨O⟩—H_b
Cl H_a

(iii)
H—⟨O⟩—H
H_b H_a
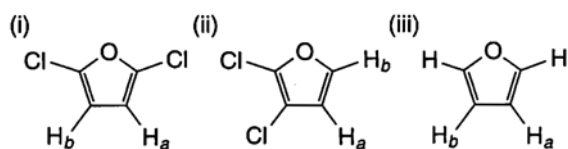
In each case, assume free rotation around the C-C single bonds.

12. The ^{1}H NMR spectrum of CH_4 consists of a single line and it is not possible to measure $^2J_{H-H}$ from the spectrum. Explain why this is so.
The ^{1}H NMR spectrum of dideuteromethane (CD_2H_2) is given below. Rationalise the splitting pattern and explain how you could estimate $^2J_{H-H}$ using this spectrum

⊢⊣ 2.0 Hz

^{1}H NMR Spectrum
of CD_2H_2

0.71 PPM from TMS
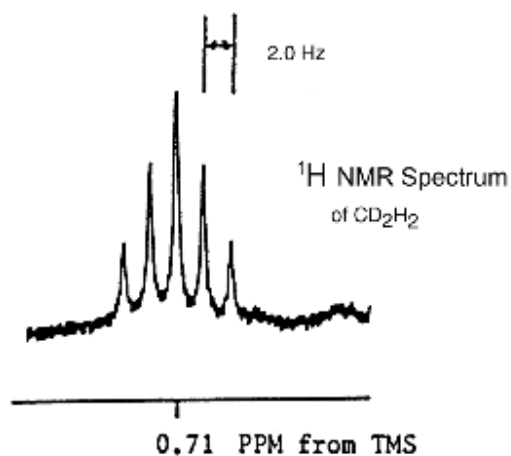
13. Consider the ^{1}H NMR spectrum of the borohydride ion (BH_4^-). Noting that the element boron has two isotopes, both of which are NMR active: ^{10}B (I=3, 20%) and ^{11}B (I=3/2, 80%), rationalise the appearance of the observed ^{1}H spectrum.

^{1}H NMR Spectrum

50 Hz