NMR Revision

QUESTION 1. *1997 General physical chemistry II, Question 2*

The ^{1}H NMR spectrum of $C_2H_5OC_2H_5$ is shown below:

a) Define the term chemical shift in an NMR spectrum and explain why the peaks labelled X in the spectrum have a different chemical shift from the peaks labelled Y ($\delta_X = 3.36$, $\delta_Y = 1.16$).

b) The peaks labelled Y occur at a mean frequency of 60.0150696 MHz in a fixed field B_0; calculate the mean frequency of the peaks X at the same field.

c) Describe the mechanism that gives rise to nuclear spin-spin coupling and explain why the presence of 10 protons in $C_2H_5OC_2H_5$ gives rise to only 7 peaks in the spectrum with the intensity ratios 1:3:3:1 and 1:2:1 as shown.

d) If the magnetic field B_0 is doubled in magnitude compared with that used to obtain the data in a) and b), calculate the new frequencies for each of the four peaks labelled X in the spectrum of $C_2H_5OC_2H_5$, given that the splitting between the peaks labelled Y is 7.2 Hz

e) The broadband decoupled ^{13}C NMR spectrum of $C_2H_5OC_2H_5$ shows two peaks with chemical shifts of 67.4 and 17.1 Comment on why the range of ^{13}C chemical shifts is so much greater than for the proton NMR chemical shifts of the same compound.

QUESTION 2. *1996 General physical chemistry I, Question 5*

Explain the following statements:

a) NMR spectrometers employ as large a magnetic field as possible.

b) Neither NMR nor ESR spectroscopy detects electric dipole transitions.

c) The chemical shift in NMR spectroscopy gives information about the local electronic environment.

d) NMR spectroscopy is usually applied to $I = ½$ nuclei

e) NMR spectroscopy has proved to be a much more widely applied technique than ESR spectroscopy.

f) Energy level splittings from coupling between equivalent nuclei occur, but are not observed, in NMR spectra.

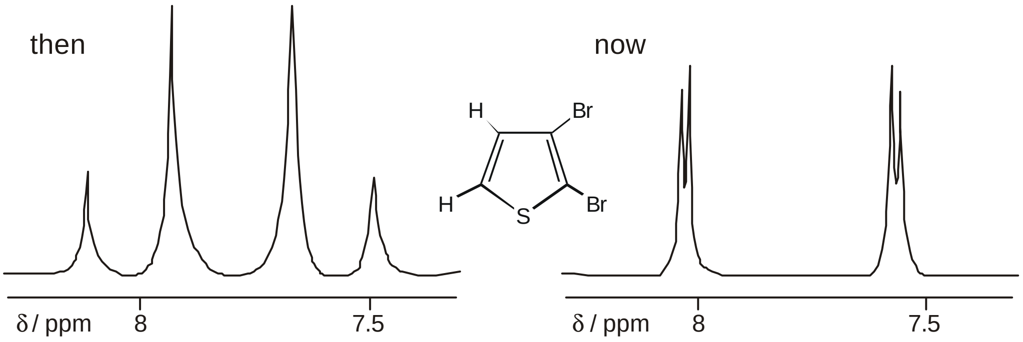
QUESTION 3. *1995 General physical chemistry I, Question 8e*

e) In a given magnetic field, the difference between the nuclear magnetic resonance frequencies of chemically distinct H (^{1}H) nuclei is greater than in the D (^{2}H) spectrum of the deuterated compound. Coupling constants are also greater in the H (^{1}H) NMR spectrum than in the D (^{2}H) NMR spectrum. Comment.

QUESTION 4. *1994 General physical chemistry I, Question 4*

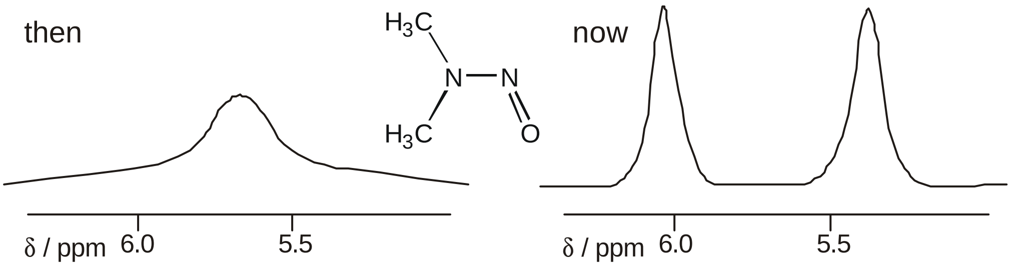
Thirty years ago, NMR spectrometers typically operated at a proton resonance frequency of 40 MHz rather than 400 MHz, as at present. Discuss the following differences between spectra obtained then and now. Focus on the physical processes that underlie these differences and give quantitative estimates where appropriate.

a) Proton spectra of 2,3-dibromothiophene

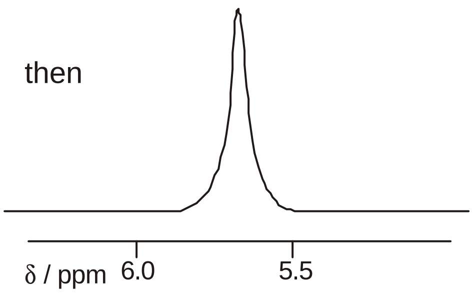


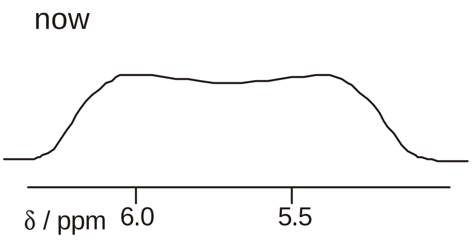
b) Proton spectra of N,N-dimethylnitrosamine

i) at 170°C



ii) at 200°C





c) It was much easier to ‘saturate’ the spectrum thirty years ago.