

2.1: Introduction. The Chemical-shift Parameter

A low-resolution proton NMR spectrum of ethyl alcohol at a field of 9,400 gauss and an oscillator frequency of 40 Mc is shown in Fig. 2-1. The three resonance lines correspond to protons with different precession frequencies, which come into resonance with the oscillator frequency at different values of the magnetic field. The areas under the peaks stand roughly in the ratio 1:2:3, as would be expected if each peak corresponded to the chemically different OH, CH₂, and CH₃ ethanol protons. These assignments have been substantiated by studies of other alcohols and substitution of deuterium for hydrogen. Thus, if the hydroxyl proton of ethyl alcohol is replaced by deuterium, the resonance peak on the left disappears. To be sure, deuterium can give a nuclear resonance signal, but reference to Table 1-1 shows that its resonance frequency would be 6.1 Mc at 9,400 gauss. Therefore, with a 40-Mc oscillator, the deuterium resonance would not be observed until the magnetic field reached 58,000 gauss, which is 10⁶ times the total sweep shown in Fig. 2-1.

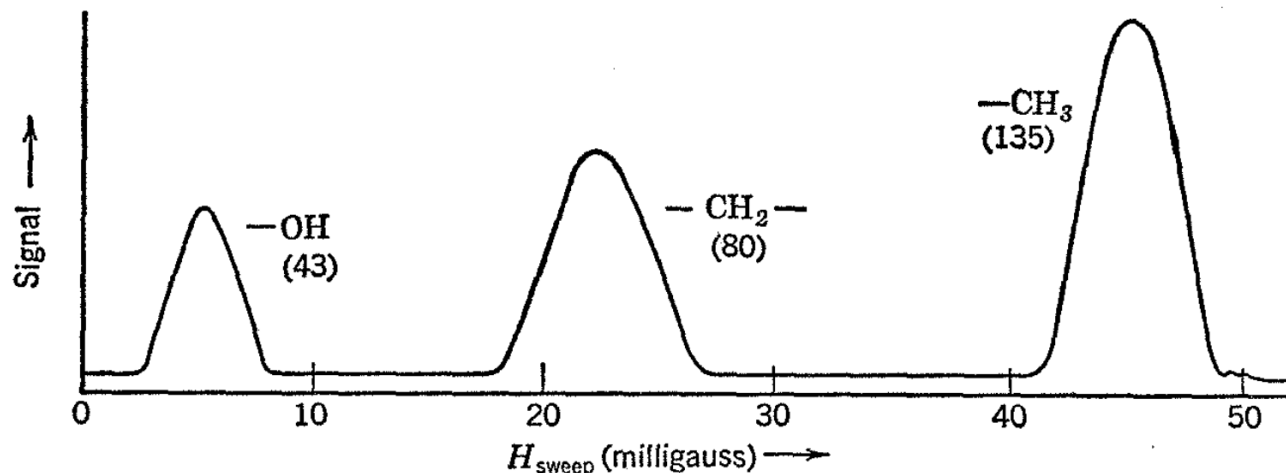


Fig. 2-1. Low-resolution NMR spectrogram of ethanol protons at 40 Mc and 9,400 gauss. Numbers in parentheses adjacent to each peak are experimental figures for peak areas in arbitrary units.

The spacing between the ethanol absorption lines is found to be directly proportional to the magnetic field, and if one operates at an oscillator frequency of 30 Mc and a field of 7,000 gauss, the resonance lines are three-fourths as far apart. Field-dependent differences between resonance line positions are called "chemical shifts" and arise because the lines of force of the applied magnetic field tend to be turned away from the nuclei by a diamagnetic shielding effect (but can also be turned in by a second-order paramagnetic effect) of the surrounding electrons. The degree of diamagnetic shielding is directly proportional to the applied field, and therefore chemical shifts are directly proportional to the magnetic field. In order that workers with NMR equipment having different oscillator frequencies and magnetic fields may have a simple basis for comparison of spectra, it is common to report resonance line positions in terms of a dimensionless parameter δ , which is the proportionality constant between resonance frequency and field strength. Usually, δ is expressed relative to some standard substance for protons customarily water, benzene, or cyclohexane, each of which has only a single resonance line.

$$\delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_{\text{reference}}} \times 10^6$$

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