3.1: The High-resolution Ethanol Spectrum

The spectrum of ethanol shown in Fig. 2-1 was obtained with a degree of resolution far below that routinely possible for commercial NMR spectrometers. Under high resolution, the proton spectra of ethyl derivatives show a considerably greater number of lines-the CH_2 resonance being split into four principal lines and the CH_3 resonance into three principal lines. Still higher resolution such as is possible with an extremely stable oscillator and a highly homogeneous magnetic field shows each of these lines to have fine structure, as shown in Fig. 3-1. We shall be concerned here only with the first-order splitting, since the explanation of the higher-order splitting is rather involved.

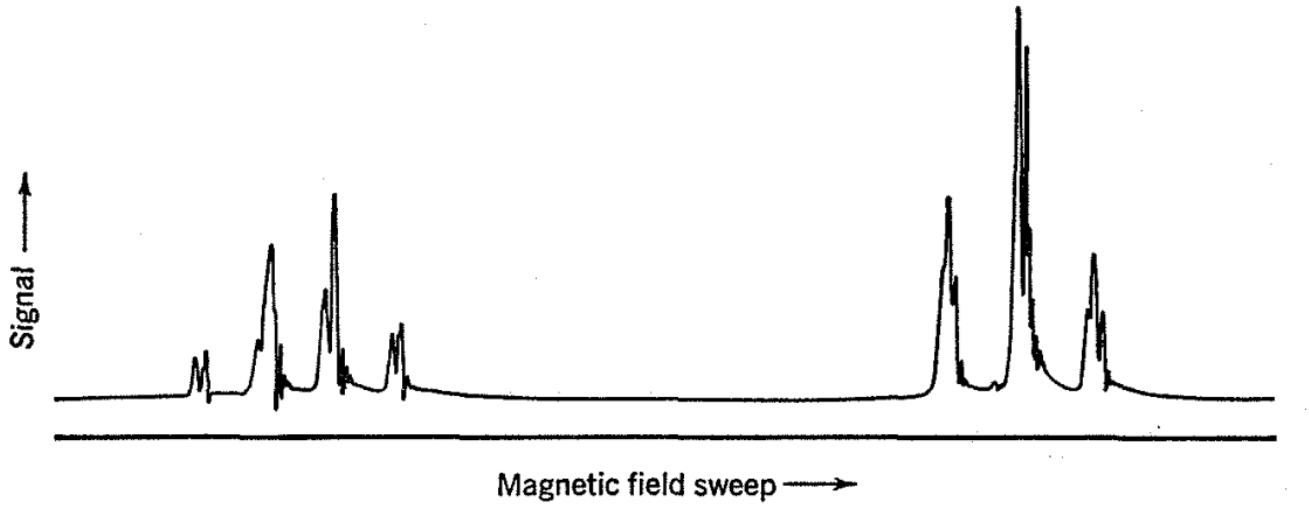

Fig. 3-1. High-resolution spectrum of ethyl group protons of acidified ethanol at 40 Mc. (*Courtesy of James N. Shoolery and Varian Associates.*)

The mechanism by which the protons of an ethyl group produce seven major resonance lines is interesting and important to theories of structure as well as structural determinations. In the first place, one might infer that the splitting of the CH_2 and CH_3 lines is evidence for chemically different kinds of methylene and methyl hydrogens. However, the fine structure is not a chemical-shift phenomenon. This is proved by observing the spectrum at two different oscillator frequencies (and field strengths) whereby the principal lines of the methyl and methylene patterns move closer together or farther apart while the spacing of the principal four-three pattern of fine structure remains unaltered, shown in Fig. 3-2. Therefore, we conclude that the different lines are not due to chemically different hydrogens among the methylene and methyl groups, respectively. This conclusion is, of course, in agreement with chemical experience. It can be shown that field-independent splitting represented by the line spacing J arises from interaction between the magnetic moments of one group of hydrogens and the other. The way that this comes about will be illustrated with the aid of a simple but experimentally unrealizable example.

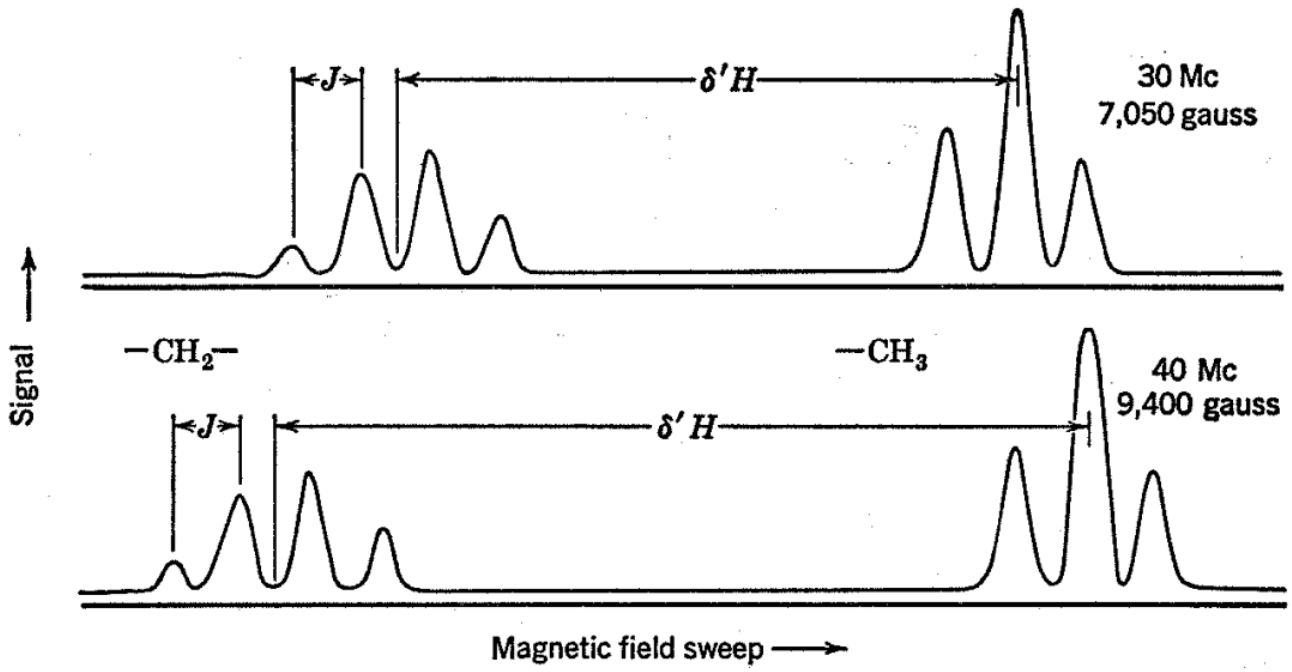

Fig. 3-2. Change of NMR spectrum of typical ethyl group protons under moderate resolution as a function of field strength.