

3.7: Coupling between Equivalent and Nearly Equivalent Protons

In connection with spin-spin coupling in substances containing ethyl or similar groups, it is natural to wonder why there is no apparent splitting of the resonance of a proton belonging to an equivalent group of protons by the other members of the group, which are much closer than a group of protons attached to an adjacent carbon. Thus, spin-spin splittings might be expected as the result of couplings between the individual protons at the methylene position of an ethyl group, as well as between the methylene and methyl protons. In practice, except for some special situations to be explained later, magnetic nuclei in equivalent chemical environments do not show spin-spin coupling. This is because equivalent protons do not absorb rf energy independently of one another. In spectroscopic terms, we can say that any transition which would lead to a splitting of the resonance of one proton of an equivalent group by the magnetic moment of another proton in the group would be "forbidden," since it would be a "singlet-triplet" transition. "Allowed" transitions involve absorption of energy by protons as a group, and no splittings result therefrom. With nuclei which are not completely equivalent, the type of transition forbidden for equivalent nuclei is allowed but reduced in probability—the closer the degree of equivalence, the lower the transition probability.⁵

It is instructive to consider the effect of coupling between two like nuclei as a function of the chemical shift between their resonances. When the chemical shift is large compared with J , the simple first-order treatment holds as described earlier and each of the resonances is split by the interaction between the nuclei into two lines of equal intensity, as shown in Fig. 3-9. The distance between the centers of the doublets is the chemical shift δH . Now, as the chemical shift decreases at constant J , a more complicated relation obtains between δH , J , the signal strengths, and the distances between the resonance lines. The splitting of the multiplets is still J , but the distance between the multiplet centers is no longer δH but $\sqrt{J^2 + \delta^2 H^2}$. The line intensities no longer remain equal—the center peaks get larger and the outer peaks smaller, so

$$\frac{\text{Intensity of inner lines}}{\text{Intensity of outer lines}} = \left(\frac{1+Q}{1-Q} \right)^2 \text{ where } Q = \frac{J}{\delta H + \sqrt{\delta^2 H^2 + J^2}}$$

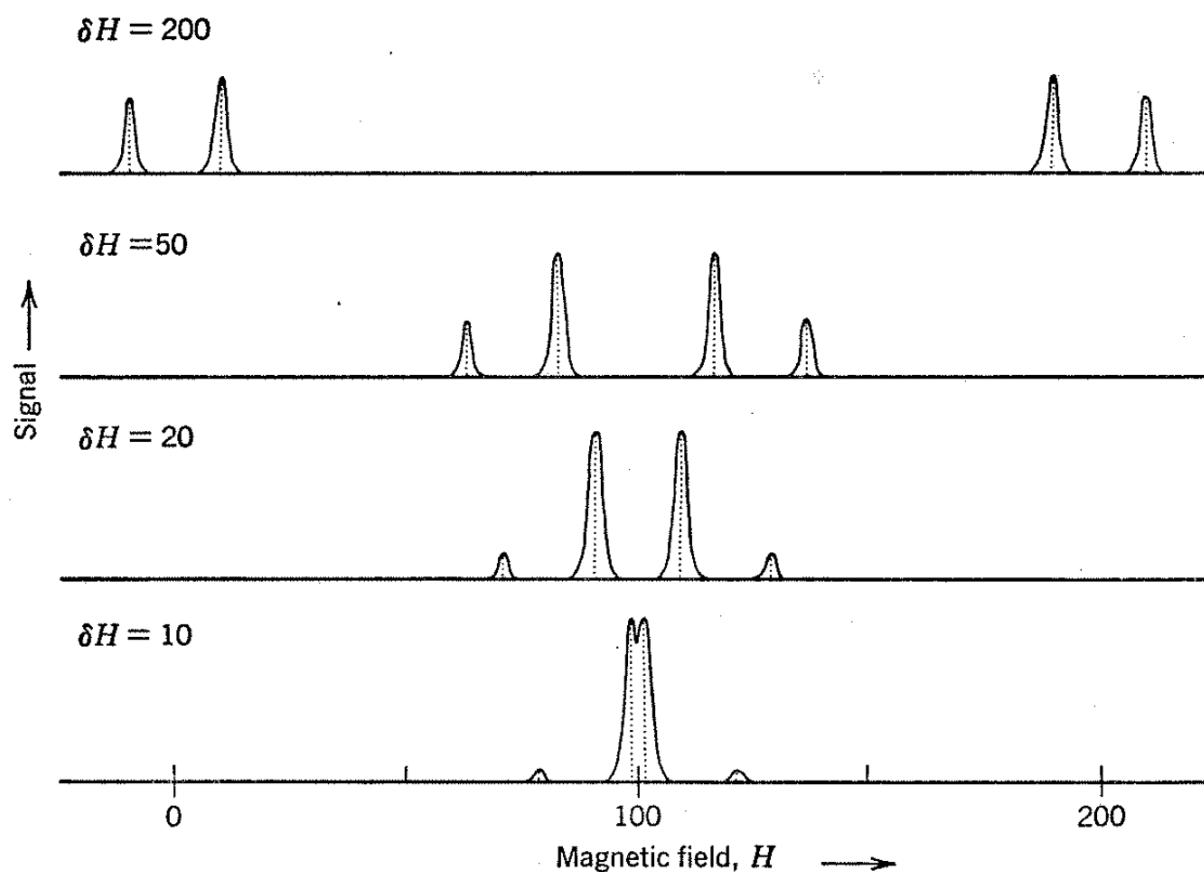


Fig. 3-9. Theoretical relation between line intensities and line positions as a function of chemical shift for two nonequivalent protons with a constant coupling J . For definiteness, J is taken to be 20 cps and δH is assumed to vary between 10 and 200 cps.

As δH continues to decrease, the outer lines get weaker and weaker, and, finally, when δH is smaller than J , the spectrum may appear to a casual observer as a closely spaced doublet. At very small δH values, the center lines coalesce and only one intense line is observed. The limiting case with $\delta H = 0$ corresponds to nuclei in equivalent chemical locations and no splitting is observed.

It should always be kept in mind that spectra involving spin-spin splittings will be distorted from the predictions of the simple first-order treatment and extra lines may even appear whenever the chemical shifts are small. Thus, the second-order spin-spin splitting displayed by ethanol at 40 Mc (Fig. 3-1) is much accentuated at lower frequencies. An excellent example of the striking effect of extreme changes of oscillator frequency on the appearance of NMR spectra has been provided by Muetterties and Phillips⁶ for the ^{19}F resonances of chlorine trifluoride.

The chemical shifts between nuclei of different kinds, such as between hydrogen and fluorine, hydrogen and nitrogen, etc., are always very large, so that the above-mentioned complications do not arise except at very low field strengths.

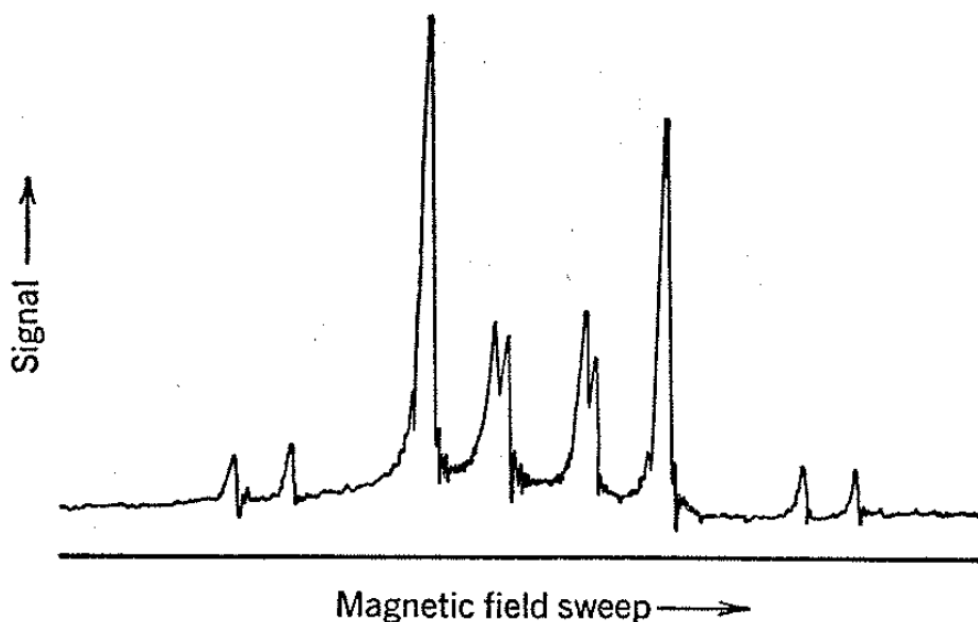


Fig. 3-10. Proton NMR spectrum of 1,1-difluoroethylene at 40 Mc.

5 Cf. H. S. Gutowsky, *Ann. N.Y. Acad. Sci.*, 70, 786 (1958); H. J. Bernstein, I. A. Pople, and W. G. Schneider, *Can. J. Chem.*, 35, 65 (1957).

6 E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, 79, 322 (1957).

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