

5.5: Applications of Double Resonance

The double-resonance technique described in Sec. 5-3 has important uses in analysis of complex spin-spin coupling patterns when two or more varieties of nuclei with different precession frequencies are involved. Valuable information for the analysis of the NMR spectra of boron hydrides has been obtained by Shoolery³ by collapsing of spinspin multiplets due to ^{10}B and ^{11}B while observing proton resonances.

Double resonance has also been utilized to aid in direct determinations of the H-F spin couplings in fluorobenzene.⁴ With ordinary fluorobenzene, spin-spin splitting makes the spectrum complex and difficult to analyze. In principle, the problem of determining coupling constants for interactions between the fluorine and the hydrogens at the o, m, and p positions can be greatly simplified through study of splittings in various deuterium-substituted fluorobenzenes. Thus, to obtain the coupling between the fluorine and meta hydrogens, 2,4,6-trideuteriofluorobenzene can be employed. However, the proton spectrum (Fig. 5-5a) of this molecule is rendered more complex than might otherwise be expected because of F-D and H-D couplings which are at least as difficult to unravel as the spectrum of ordinary fluorobenzene. However, the double-resonance technique permits averaging of the deuterium spins to zero, so that the residual clean doublet observed in the proton spectrum (Fig. 5-5b) is due only to 1,3-proton-fluorine coupling with J equal to 5.8 cps. A similar study of 2,3,5,6-tetradeuteriofluorobenzene shows that coupling between fluorine and para protons is negligible.

Double resonance would be extremely valuable in the analysis of spin-spin couplings in compounds with interacting nuclei of the same type. For example, one might use a suitable oscillator to "stir up" the methylene protons of ethanol while observing the methyl protons at another precession frequency. In such circumstances, the methyl resonance would be averaged to a single line and it would then be known that the splitting ordinarily observed arises from the various possible combinations of magnetic quantum numbers of the methylene protons. Unfortunately, this type of double resonance is not experimentally easy because it is necessary to use a considerably higher rf power level to stir up one variety of proton than is necessary or desirable for the observation of the resonance of another variety of proton. As a result, one needs a receiving arrangement with high discriminating power to distinguish between the decoupling frequency and the observing frequency which may differ only by 100 cps at 40 Mc. Successful experiments of this type have been reported by Anderson,⁵ but the method cannot yet be regarded as being applicable to routine work.

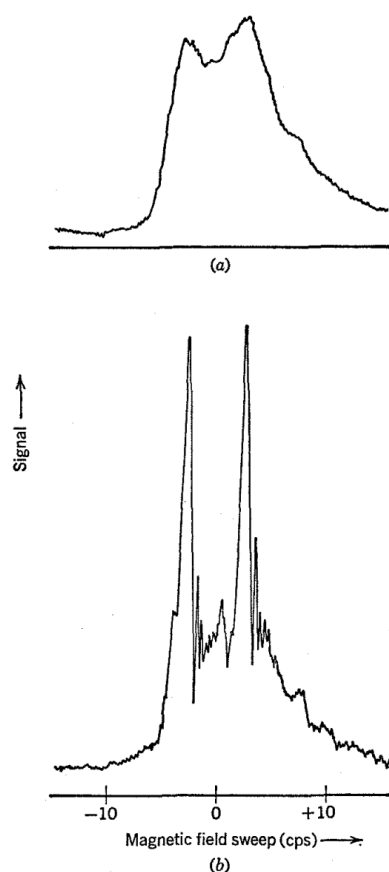


Fig. 5-5. Proton resonance spectra of 2,4,6-trideuteriofluorobenzene: (a) normal spectrum, (b) irradiated with deuterium resonance frequency, 6.1 Mc at 9,400 gauss. (Courtesy of James N. Shoolery and Varian Associates.)

3 J. N. Shoolery, Discussions Faraday Soc., 215 (1955); R. Schaeffer, J. N. Shoolery, and R. Jones, J. Am. Chem. Soc., 79,4606 (1957).

4 B. Bak, J. N. Shoolery, and G. A. Williams, 111, J. Mol. Spectroscopy, 2, 525 51958).

5 W. A. Anderson, Phys. Rev., 102, 151 (1956).

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