Chlorine Isotope Effects on the ^{19}F Resonance of CCl_3F and the use of this Signal as a Reference in High-resolution Nuclear Magnetic Resonance

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THE fluorine resonance of trichlorofluoromethane, CCl_3F, is an unsuitable locking or reference signal for high-resolution ^{19}F n.m.r. spectra, particularly at low temperatures where it shows a clear isotope effect.

The spectrum has been studied both in the pure liquid and in a 5% solution in cyclopentane (by volume) between +30° and −80°. The spectra at both concentrations were identical, in contrast with results obtained in Raman experiments.[1]

CCl_3F exists in four chlorine-isotopic modifications which have the following natural abundances: $CF^{35}Cl_3$ (42·0%), $CF^{35}Cl_2{}^{37}Cl$ (42·9%), $CF^{35}Cl^{37}Cl_2$ (13·6%), and $CF^{37}Cl_3$ (1·5%). The fluorine resonance spectrum is shown under various conditions in Figures 1 and 2. The spectra indicate that the fluorine shifts in the slightly differing environments of the various isotopic species are sufficiently different to be resolved. Although an isotope effect is observable at room temperature (Figure 1), at −80° (as shown in Figure 2) three peaks with intensities consistent with those expected for the three most abundant species are clearly resolved. The peak for $C^{37}Cl_3F$ was not definitely identified due to the low abundance of this species. At −80° the two strongest peaks have almost equal heights and are separated by 0·8 ± 0·1 Hz. The weaker third peak which is attributed by its intensity as belonging to $CF^{35}Cl^{37}Cl_2$ lies to higher field. This is in accordance with the empirical observation that heavier isotopic species come to resonance at higher field strengths.[2] As the temperature of the system is raised, the separation between the two strong peaks appears to decrease until at +30° they are only poorly resolved and the third weaker peak cannot be unambiguously identified. At this temperature the almost unresolved line is very broad, with a width at half peak height of 1·5 Hz.

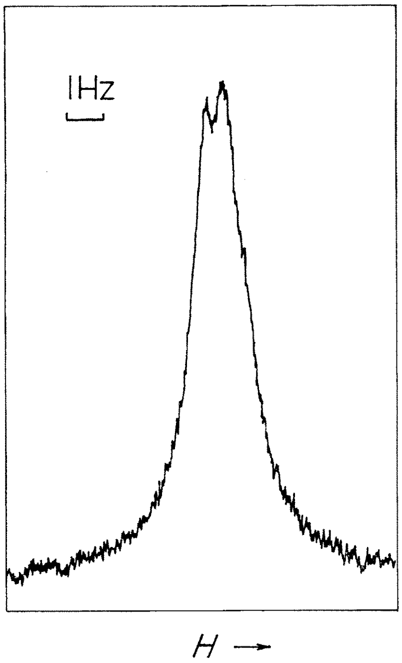

FIGURE 1. *The* ^{19}F *n.m.r. spectrum of pure* CCl_3F *at* 30°.

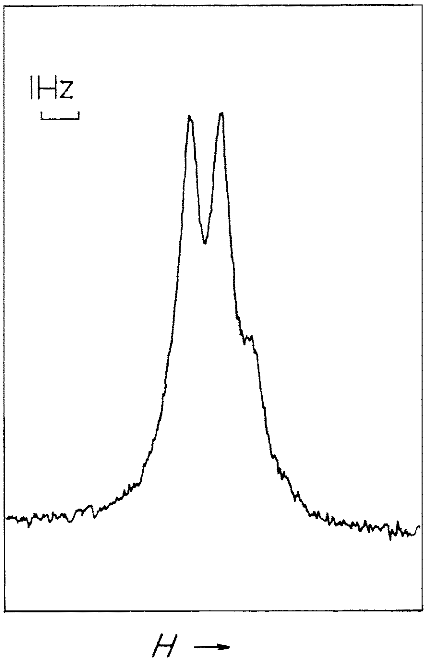

FIGURE 2. *The* ^{19}F *n.m.r. spectrum of pure* CCl_3F *at* −80°.

These results indicate that the CCl_3F signal does not fulfil the requirement necessary for use as a reference which (ideally) should be a single sharp line. At low temperatures the presence of two equal, closely separated peaks reduces the value of the CCl_3F resonance as a locking signal.

The spectra were obtained on a Varian H.A. 100 spectrometer using hexafluorobenzene as a locking compound. The CCl_3F was obtained from Imperial Chemical Industries, Ltd., and was used without further purification.

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[2] H. Batiz-Hernandez and R. A. Bernheim, *Progr. N.M.R. Spectroscopy*, **1967**, **3**, **63**.