A Method of Increasing Sensitivity in Carbon-13 Nuclear Magnetic Resonance Spectroscopy *via* a Heteronuclear Overhauser Effect without Loss of Spin–Spin Coupling Information

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Summary By applying and then removing a proton-decoupling field immediately before examining the carbon-13 n.m.r. spectrum of 50%-enriched methyl iodide, it is possible to retain complete spectral information and some of the Overhauser increase in sensitivity.

IT is well known that proton-noise decoupling can increase the n.m.r. sensitivity of carbon nuclei directly bonded to decoupled proton nuclei *via* a heteronuclear Overhauser mechanism by factors as large as three.[1] By its very nature, this decoupling experiment removes the C–H spin–spin coupling from the spectrum and thus leads to loss of information. Some workers have used proton-decoupling fields slightly removed from the optimum setting for complete proton decoupling and in this way have obtained the Overhauser enhancement while retaining the multiplicities in the carbon-13 spectrum; however, in this method the observed splittings are no longer the C–H spin–spin coupling constants.[2]

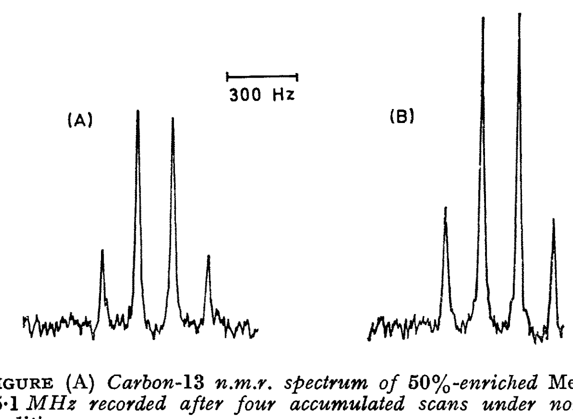

FIGURE (A) *Carbon*-13 *n.m.r. spectrum of* 50%-*enriched* MeI *at* 25·1 *MHz recorded after four accumulated scans under normal conditions.*

(B) *Carbon*-13 *n.m.r. spectrum of* 50%-*enriched* MeI *at* 25·1 *MHz recorded after four accumulated scans with the proton-decoupling field applied and removed before each scan. The same sweep time* (100 *Hz* s^{-1}) *and pause time between scans* (20 *s*) *was used for both spectra.*

By examining the carbon-13 spectrum immediately after having removed the proton-decoupling field we have been successful in retaining the complete spectral information and some of the Overhauser increase in sensitivity. The C–H spin–spin splittings return immediately to the spectrum on removing the proton-decoupling field whereas some of the Overhauser increase in sensitivity is retained for times controlled by the proton relaxation times. In the Figure, the normal carbon-13 n.m.r. spectrum (A) of 50%-enriched methyl iodide is given together with the carbon-13 spectrum (B) obtained after applying and removing a proton-decoupling field; the C–H spin–spin coupling constant is the same in each spectrum and the second spectrum showed an enhancement in intensity of 24% for a single scan experiment (four scans were actually accumulated on a C1024 computer of average transients since this is the normal method of obtaining carbon-13 spectra). The method used has the disadvantage that as the spectrum is swept the intensities decrease across the spectrum

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because the Overhauser increase in population relaxes on removal of the decoupling field. However, if this technique were applied in conjunction with a Fourier Transform pulsing experiment[3] this difficulty would be removed since all the lines in a carbon-13 spectrum would be examined simultaneously. This approach would also enable the carbon-13 spectrum to be examined quickly after removal of the proton-decoupling field when the Overhauser increase in sensitivity would be larger than that observed in the present experiment.

The experiments were carried out using a Varian HA-100D-15 spectrometer equipped with an 8 mm carbon-probe operating at 25·1 MHz, a V3530 RF/AF sweep unit and V3512-1 proton-noise decoupler. The decoupling field was applied and removed manually. The locking signal was 50%-enriched $^{13}CH_2I_2$ which provides a signal that can be used for locking in the proton decoupled and proton non-decoupled mode. A C1024 computer of average transients was used to accumulate the spectra. The long pause time between scans (20 s) was required because the decoupling field was applied and removed manually.

P.J.S.P. acknowledges the hospitality of Varian Associates Ltd., during the time this work was carried out.

(*Received, March 16th*, 1970; *Com.* 374.)

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