Proton-noise-decoupled Deuterium Resonance at Natural Abundance by Fourier Transform

By JOHN M. BRIGGS, LESLIE F. FARNELL, and EDWARD W. RANDALL*
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary It has proved possible to observe n.m.r. spectra from deuterium nuclei occurring in natural abundance; the observation of small chemical-shift differences, referred to ^{2}H in Me_4Si, is facilitated by proton noise decoupling.

DIEHL, in a recent review,[1] has pointed out that observations of ^{2}H n.m.r. at the natural abundance level of deuterium are probably feasible with modern instrumentation. We confirm that this is so.

The natural abundance of ^{2}H is $1{\cdot}56 \times 10^{-2}$ %, and the sensitivity of the ^{2}H-nucleus is $9{\cdot}6 \times 10^{-3}$. ^{2}H n.m.r. at natural abundance is therefore expected to be more difficult than the corresponding ^{1}H n.m.r. experiment by a factor of $1{\cdot}5 \times 10^{-6}$. Carbon-13 studies at natural abundance, for which the factor is $1{\cdot}7 \times 10^{-4}$, are now well established, and the more difficult ^{15}N n.m.r. studies at natural abundance,[2] with a factor of $3{\cdot}7 \times 10^{-6}$, are feasible. Since ^{2}H has a small electric quadrupole moment, shorter T_1 relaxation times than for ^{13}C and ^{15}N are expected; this should assist the use of spectral accumulation techniques, but if the quadrupole relaxation dominates, the benefit of a nuclear Overhauser enhancement may be absent.

Spectra were obtained on a Bruker HFX-13 spectrometer operating at 21·14 kG employing a ^{19}F field-frequency locking system and wideband decoupling of ^{1}H signals.

The figure shows the natural abundance ^{2}H n.m.r. spectrum of n-butyl iodide resulting from an accumulation of 4K free induction decays collected in 2K points with a dwell time of 400 μs, using a pulse length of 90 μs (optimised on a slightly enriched perdeuterioacetone sample). The figure clearly shows four distinct ^{2}H transitions resulting from deuterons α, β, γ, and δ to iodine, in the various monodeuterio-species. A spectrum of n-butanol shows an additional broad resonance from OD, whereas the OH proton transitions did not display such broadening.[3]

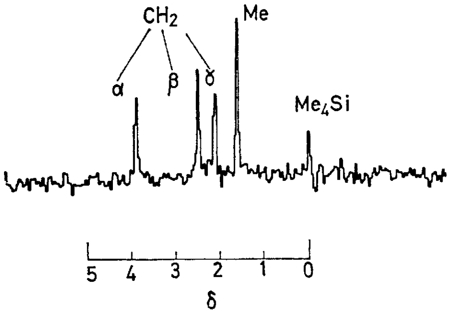

FIGURE. ^{1}H *Noise decoupled* ^{2}H *natural abundance spectrum of* Bu^nI *at* 13·82 MHz.

Other natural abundance ^{2}H n.m.r. spectra were obtained from solutions (80% by volume) of acetaldehyde, ethanol, ethyl benzene, and pyridine, each containing C_6F_6 and Me_4 Si, and from benzaldehyde and n-butyl iodide using an external lock and reference. Chemical shifts compare closely with the corresponding ^{1}H chemical shifts.[4]

Despite narrow linewidths for the C–D deuterons which indicate only small quadrupole broadening, qualitative comparisons suggest that the ^{2}H (^{1}H) Overhauser effect is small, consistent with a dominant quadrupolar relaxation mechanism: a similar situation was found in ^{14}N (^{1}H) studies of the $^{14}NH_4^+$ ion,[5] even for sharp transitions.

Observations using ^{2}H n.m.r. at the natural abundance level with ^{1}H decoupling present a number of advantages. Compared with studies on perdeuterio systems, ^{2}H-^{2}H couplings are absent, since the probability of observing two or more neighbouring deuterons in a given molecule is negligible. In comparisons with ^{1}H n.m.r. where, frequently, complex or even impractical spectra analysis has to be performed to evaluate the chemical shift of a given proton, the use of noise decoupling allows the corresponding ^{2}H chemical shifts to be measured directly from the spectrum. This effect is well illustrated by ethyl benzene, where three distinct ^{2}H resonances were observed at δ 7·31, 7·28, and 7·17. The corresponding ^{1}H spectrum at 100 MHz has not been analysed even with the aid of decoupling. Bovey *et al.*,[6] however, have analysed the 200 MHz ^{1}H n.m.r. spectrum and quote the chemical shifts of the *m*, *p*, and *o* protons, for a 25% solution in CCl_4 as δ 7·20, 7·12, and 7·08 $\pm$ 0·02 respectively. The ^{2}H n.m.r. spectrum of benzaldehyde showed two distinct signals for the phenyl region. Referenced to the DCO signal at δ 10.00[5] the chemical shifts of the two signals appeared at δ 7·83, and 7·48. Hayamizu and Yamamoto[7] have analysed the ^{1}H n.m.r. spectrum at 100 MHz and, for a 25% solution in CCl_4, find the *o*, *m*, and *p* chemical shifts to be δ 7·82, 7·48, and 7·55 respectively. With an operational resolution of 1 Hz (δ 0·08) the ^{2}H n.m.r. spectrum is incapable of resolving the shift difference between the *m* and *p* ^{2}H chemical shifts. This illustrates a notable disadvantage of ^{2}H n.m.r.: the ratio of line width to shift range is only 1/138, as opposed to 1/900 for ^{1}H at the same field strength. In favourable cases, however, where linewidths are sufficiently narrow, it may prove possible to make direct measurements of ^{2}H–^{1}H couplings thus avoiding the complexities of ^{2}H labelling experiments which are otherwise necessary to glean the same information from the ^{1}H n.m.r. spectrum.

So far, natural abundance ^{2}H spectra have been observed in which operational conditions have governed the accuracy. By using longer dwell times, this limitation may be minimised, and it should prove feasible to test for the occurrence of a primary deuterium isotope effect to an accuracy much better than was previously ($\pm$0·06 p.p.m.) attained.[3] Small discrepancies between ^{2}H and ^{1}H chemical shifts are not necessarily indicative of significant isotope effects unless stringent normalisation of solvent concentration and temperature between the ^{1}H and ^{2}H experiments is undertaken.

(*Received*, 9*th November* 1972; *Com.* 1882.)

[1] P. Diehl, personal communication: lecture delivered at N.A.T.O. Advanced Study Institute, Tirrenia, Italy, September 1972.

[2] J. M. Briggs, L. F. Farnell, and E. W. Randall, *Chem. Comm.*, 1971, 680.

[3] P. Diehl and T. Leipert, *Helv. Chim. Acta*, 1964, **47**, 545.

[4] N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, and J. N. Shoolery, N.M.R. Spectra Catalog, Varian Associates, vols. I and II, 1962, 1963.

[5] L. F. Farnell and E. W. Randall, unpublished results.

[6] F. A. Bovey, F. P. Hood, tert, E. Pier, and H. E. Weaver, *J. Amer. Chem. Soc.*, 1965, **87**, 2060.

[7] K. Hayamizu and O. Yamamoto, *J. Mol. Spec.*, 1968, **28**, 89.