Oxygen-17 Nuclear Magnetic Resonance Spectroscopy: the Sign of the O–H Nuclear Spin–Spin Coupling Constant

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Summary Oxygen-17 selective INDOR experiments have been used to show that the reduced spin coupling constant ${}^{1}K$(O–H) is positive in methanol.

The advent of multinuclear pulsed Fourier transform n.m.r. spectrometers and of sophisticated computing techniques has led to increased interest in the signs and magnitudes of spin–spin coupling constants involving many of the less common nuclei. Of great theoretical and potential practical importance are those for ^{17}O, the only isotope of oxygen with a nuclear spin, but hitherto no signs and rather few magnitudes[1] have been reported, largely owing to the low natural abundance (0·037%) and quadrupole moment ($I = 5/2$) of this nuclide. It is known, however, that ${}^{1}J({}^{17}\text{O–H})$ has a magnitude of 80—90 Hz in water[2] and methanol,[3] and theoretical arguments have been used to suggest that the sign of the reduced coupling constant ${}^{1}K$(O–H) should be positive,[4] negative,[5] or uncertain.[6]

We now report ^{1}H–{^{17}O} double resonance experiments which show that ${}^{1}K$(O–H) is in fact positive in methanol. A sample of methanol enriched to 10 mole % in ^{17}O was examined as a *ca.* 30% solution in a 1 : 1 mixture of $(CH_3)_2SO$ and $(CD_3)_2CO$ (chosen to lower the rate of proton exchange and to minimize the viscosity of the solution) at 24 °C using a modified JEOL C-60-H spectrometer operating at a proton frequency of 59·996 MHz. The line-widths in the proton spectrum were *ca.* 1·5 Hz and the coupling ${}^{3}J$(H–H) 5·0 Hz was clearly resolved, indicating that proton exchange was indeed reasonably slow. No ^{17}O satellites of the OH quartet resonance were detected (for a sufficiently slow rate of ^{17}O quadrupolar relaxation a set of six lines spaced at *ca.* 85 Hz intervals would be expected) but simultaneous irradiation at the ^{17}O resonance frequency (*ca.* 8·13 MHz) increased the height of this resonance by *ca.* 10%, indicating that the rate of ^{17}O quadrupolar relaxation could only be moderate, in agreement with ^{17}O line widths of < 100 Hz reported[3] in direct ^{17}O n.m.r. studies.

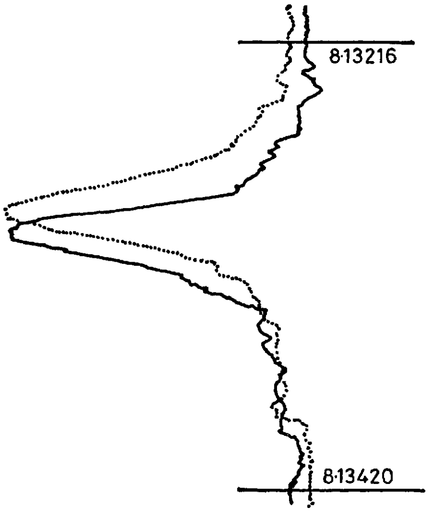

Figure. Oxygen-17 INDOR spectra of methanol enriched to 10 mole % obtained by monitoring the Me resonance in the proton spectrum. The frequency markers are in MHz and each trace is the result of 64 scans. Full line: high frequency component of doublet monitored; broken line: low frequency component monitored.

In order to compare the sign of ${}^{1}J({}^{17}\text{O–H})$ with that of ${}^{3}J$(H–H) (known to be positive) it was necessary to observe differential effects upon the two components of the Me doublet resonance upon selective irradiation in the ^{17}O spectrum to collapse ${}^{2}J({}^{17}\text{O–H})$. These effects were undetectably small in a single scan, but were recorded by monitoring the top of either component of the Me doublet while ν_2 was swept through the ^{17}O spectrum, and accumulating the resulting perturbations with a signal averager. The oxygen-17 INDOR spectra produced in this way are shown in the Figure and their maxima are separated by $^1J(^{17}\text{O–H})$ 85 ± 10 Hz. Since the spectrum centred at higher frequency was obtained by monitoring the high frequency proton line it follows that $^1J(^{17}\text{O–H})$ and $^3J(\text{H–H})$ are of opposite sign because ^{17}O has a negative magnetic moment. Thus $^1J(^{17}\text{O–H})$ is negative and the corresponding reduced coupling constant $^1K(\text{OH})$ is positive.

This experimental result is in conflict with the theoretical predictions of Jameson and Gutowsky,[5] and also to some extent with those of Pople and Santry;[6] it is however in line with the established[7] positive signs of $^1K(\text{NH})$, $^1K(\text{PH})$, $^1K(\text{Se–H})$, and $^1K(\text{FH})$. There is a general tendency for $^1\text{K(AB)}$ (B = an element without available electron lone pairs) to change sign when A is in the region of the fifth or sixth group of the periodic table, but it is clear that this rule does not hold for B = H. Indeed, it now appears improbable that any reduced coupling constant $^1K(\text{E–H})$ (E = any nuclide) will be negative.

The success achieved in obtaining ^{17}O INDOR spectra by monitoring the Me resonance shows that $^2J(^{17}\text{O–H})$ is large enough not to be averaged effectively to zero by quadrupolar relaxation, and to this extent supports a value of 7·5 Hz obtained by curve-fitting for the analogous coupling in methyl formate.[2] It follows that it should be possible to obtain oxygen-17 INDOR spectra from a wide range of molecules, and the signal-to-noise ratio attained here shows that considerably lower degrees of isotopic enrichment should be adequate in many specialised applications.

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