# Deuterium Isotope Effects on Carbon-13 Nuclear Magnetic Resonance Spectra

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*Summary* Large and specific isotope effects on $^{13}$C-shifts are found for a range of organic compounds, whereas $^{13}$C–D coupling constants are related to the corresponding $^{13}$C–H coupling constants by an almost constant factor, close to but not quite identical with the ratio of the gyromagnetic ratios for H and D.

The existence of isotope effects on chemical shifts in nuclear magnetic resonance spectroscopy is well recognised.[1] The present communication reports the effect of deuteriation on $^{13}$C-shifts and $^{13}$C–H(D) coupling constants for a number of organic compounds. Our measurements greatly extend the very limited data on the isotope effects ('isotopic shifts') on $^{13}$C-shifts hitherto available[2,3] and, where they duplicate them, offer a substantial improvement in precision. All $^{13}$C-shifts of $\alpha$-deuteriated compounds reported here are upfield relative to the protium-analogues.

Because our Fourier transform $^{13}$C-spectra (Bruker HFX 90 spectrometer) were obtained without heteronuclear decoupling on approximately equimolecular mixtures of ordinary and fully deuteriated (commercial) material, containing $^{13}$C at natural abundance, we were also able to measure directly the values of the coupling constants $J_{C-H}$ and $J_{C-D}$ (see Figure). Coupling constants between $^{13}$C and D do not appear to have been derived from $^{13}$C magnetic resonance spectra before, and only a limited indication of their values has been obtained from the position of $^{13}$C-satellites in deuteron magnetic resonance spectra.[4]

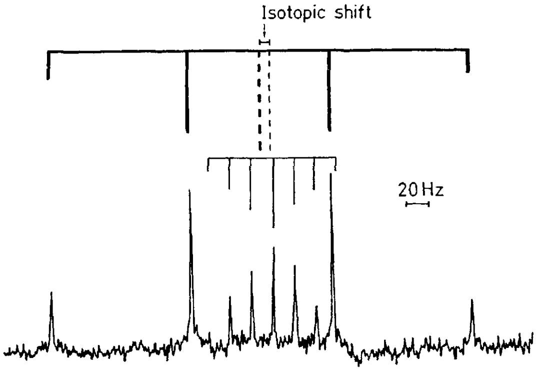

Figure. $^{13}$C N.m.r. *spectrum of methyl group of mixture of* $CH_3CN$ *and* $CD_3CN$ (*thick sticks indicate the* 1 : 3 : 3 : 1 $CH_3$ *triplet, thin sticks the* 1 : 2 : 3 : 4 : 3 : 2 : 1 *septet of* $CD_3$. *The centres of the two multiplets are indicated by broken lines.*)

TABLE

| Compound | Isotopic shift/p.p.m. (upfield) | $J_{C-H}$/Hz | $J_{C-D}$/Hz | ($J_{C-H}$ − 6·5144 $J_{C-D}$)/Hz |
|---|---|---|---|---|
| Dimethyl sulphoxide .. .. | $0{\cdot}90_1 \pm 0{\cdot}01$ | 137·0 ± 0·2 | 20·9 ± 0·2 | 0·8 ± 1·5 |
| Acetone .. .. .. .. | $0{\cdot}75_6 \pm 0{\cdot}01_0$ | 126·8 ± 0·1 | 19·3 ± 0·2 | 1·1 ± 1·4 |
| Acetonitrile .. .. .. | $0{\cdot}45_5 \pm 0{\cdot}01$ | 136·1 ± 0·1 | 20·8 ± 0·2 | 0·6 ± 1·4 |
| Nitromethane[a] .. .. .. | 0·69 ± 0·08 | 147 ± 2 | 23 ± 1 | −3 ± 8 |
| Pyridine-$\alpha$ .. .. .. | $0{\cdot}55_7 \pm 0{\cdot}01$ | 163·7 ± 0·1 | 25·0 ± 0·2 | 0·8 ± 1·4 |
| -$\beta$ .. .. .. | $0{\cdot}29_2 \pm 0{\cdot}01$ | 177·8 ± 0·1 | 27·3 ± 0·2 | 0·0 ± 1·4 |
| -$\gamma$ .. .. .. | $0{\cdot}49_0 \pm 0{\cdot}01$ | 163·6 ± 0·1 | 25·2 ± 0·2 | −0·6 ± 1·4 |
| Benzene .. .. .. | $0{\cdot}53_0 \pm 0{\cdot}005$ | 158·6 ± 2·0 | 24·2 ± 0·1 | 1 ± 3 |
| Cyclohexane[a] .. .. .. | 1·33 ± 0·2 | 127 ± 5 | 19·0 ± 0·5 | 2·2 ± 8 |
| Chloroform .. .. .. | $0{\cdot}20_3 \pm 0{\cdot}006$ | 208·8 ± 0·2 | 31·9 ± 0·1 | 1·0 ± 0·9 |
| Dichloromethane .. .. | $0{\cdot}41_5 \pm 0{\cdot}05$ | 178 ± 1 | 27·9 ± 0·3 | 0·0 ± 3 |

[a] Spectra not as well resolved as others.

The notable feature of the results is the great contrast in isotope sensitivity between chemical shifts and coupling constants. Whereas, the isotopic shift is very sensitive to the chemical environment of the carbon atom, the isotope effect on coupling constants is not. The ratio $J_{C-H}:J_{C-D}$ is always very close to the value predicted from the gyromagnetic ratios[5] ($\gamma_H/\gamma_D$ 6·5144), in spite of the wide variation in the values of the coupling constants themselves. On *average*, values of $J_{C-H}$ seem to be significantly greater than 6·5144 × $J_{C-D}$ (see Table), although the wider limits of experimental error admit the possibility that there are deviations in both directions, as for $^{31}$P–H(D) coupling constants.[6] There is no profound difference between results for compounds with different numbers of $\alpha$-hydrogen atoms. For $-CH_3$, $=CH_2$, and $\geqslant$C–H groupings, $J_{C-H}:J_{C-D}$ lies in the range 6·49—6·61, although the isotopic effects in the three cases relate to the $CH_3:CD_3$ pair, the $CH_2:CD_2$, and the CH:CD pairs, respectively. The additional geminal deuterium atoms thus do not appear to influence the coupling constants. This finding stands in contrast to the report that the C–$^1$H coupling constants in >CHD groups are *ca.* 3·6—4·6 Hz greater than C–$^1$H coupling constants in $>CH_2$ groups.[7]

In assessing the isotopic shifts one must remember that, in all cases except chloroform, these effects are combinations of nearest-neighbour and more remote interactions. Straight comparisons ought only to be made between positions with equal numbers of nearest-neighbour hydrogen atoms and comparable interactions. The large isotopic shift differences between dimethyl sulphoxide and acetone, nitromethane and acetonitrile, and the $\beta$- and $\gamma$-positions of pyridine and benzene accordingly appear as the most significant results on which to base a quantitative theory of the isotopic shift. The isotopic shift observed with $C_6D_6$ (0·530 ± 0·005) is equal to the sum of the effects of nearest-neighbour, *ortho*-, and *meta*-interactions deduced from the $^{13}$C spectrum of $C_6H_5D$ (0·289 + 2 × 0·110 + 2 × 0·011 = 0·531).[3] A suggested linear correlation between coupling constants and isotopic shifts[1,8] (either total or per $\alpha$-deuterium atom) is not supported by our data.

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