The Sign of the Sn–F Spin–Spin Coupling Constant

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It is important to know the signs of coupling constants between the nuclei of directly bound pairs of elements in order to test theories of the origin of the coupling constants.[1] This information can be obtained most conveniently by comparison with a coupling constant of known absolute sign, and both the reduced† coupling constants ^1K(*C*–F) and ^1K(Si–F) are negative.[2,3] A qualitative extension of Pople and Santry's MO theory[1] suggests that ^1K(Sn–F) will also be negative, but it is essential to confirm this experimentally. Many organotin compounds which have a direct Sn–F bond are either ionic or polymeric and thus unsuitable for such a determination, but the presence of bulky organic groups may confer sufficient solubility in organic solvents. We have therefore examined $(PhMe_2C{\cdot}CH_2)_3SnF$ in concentrated $CDCl_3$ solution.[4] The 60 Mc./sec. ^1H n.m.r. spectrum was recorded on a JEOL spectrometer, and ^{19}F and ^{119}Sn double-irradiation experiments were performed as described previously.[5a] The results [bearing in mind that γ (^{119}Sn) is negative] were: $^1J(^{119}Sn–^{19}F) \pm 2298 \pm 2$ c./sec., $^2J(^{119}Sn\cdots H) \pm 50{\cdot}5 \pm 1$ c./sec., $^3J(^{19}F\cdots H) \pm 5{\cdot}0 \pm 0{\cdot}2$ c./sec., and Ξ (^{119}Sn) 37,295,830 ± 20 c./sec.

In a wide range of organotin compounds, $^2J(^{119}Sn\cdots H)$ is known to be positive,[5] so we select the upper set of signs; ^1K(Sn–F) is thus negative and has a magnitude of 546×10^{20}cm.$^{-3}$ Our sign for $^3J(^{19}F\cdots H)$ is then in agreement with that found for this coupling constant in fluorinated alkanes.[6] Other tin-to-fluorine coupling constants have been observed[7] to lie in the range 1280—2800 c./sec., with none close to zero, so it is reasonable to assume that all have the same sign. Bell and Danyluk have pointed out that it may be possible to use the variation of coupling constant with solvent to deduce absolute signs,[8] and this method predicted[9] a negative sign for ^1K(Sn–F) in SnF_6^{2-}. Our result thus confirms the validity of this approach in this case.

A plot of ^1K(X–F) against Z_X^2 for the isoelectronic series SnF_6^{2-}, SbF_6^-, TeF_6 is linear[10] and indicates that all three reduced coupling constants have the same sign, *i.e.*, negative. This is known to be true for the last,[11] and MO theory shows that this is because the 2*s*-electrons of the fluorine atoms are of much lower energy than the 2*p*-electrons.

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† The reduced coupling constant is defined[1] as $K_{AB} = J_{AB}\,2\pi/\gamma_A\gamma_B\,\hbar$.

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