

Large Isotope Effects on the ^{119}Sn N.M.R. Parameters of the Stannyl Ion

Roderick E. Wasylishen* and Neil Burford

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

The largest recorded primary (10.7%) and secondary (3.0%) deuterium isotope effects on spin-spin coupling constants have been observed for $^1J(^{119}\text{Sn},\text{H})$ in the ^{119}Sn n.m.r. spectrum of $\text{NaSnH}_{3-n}\text{D}_n$ ($n \leq 3$).

In any critical comparison of theoretical and experimental spin-spin coupling constants it is essential to take account of the influence of vibrational averaging¹⁻³ as Raynes and co-workers have recently reiterated.⁴⁻⁶ For methane they have calculated the $^{13}\text{C},\text{H}$ spin-spin coupling constant surface using a large basis set; their calculations indicate that the observed $\langle J(^{13}\text{C},\text{H}) \rangle$ contains a zero-point vibrational correction of about 7 Hz.⁵ Experimentally one can assess the role of vibrational averaging on J by examining the temperature dependence of J and by studying the influence of isotopic substitution on J . These techniques have been extensively applied to study vibrational effects on nuclear shielding constants and this work has been recently reviewed by Jameson and Osten.⁷ Unfortunately, in the case of methane the temperature dependence of $J(\text{C},\text{H})$ has not been investigated and the primary isotope effect on $J(\text{C},\text{H})$ in any given isotopomer is comparable to the experimental error.⁸

In the present study we report ^2H isotope effects on the ^{119}Sn shielding constant and $J(\text{Sn},\text{H})$ in the stannyl ion. The isotope effects on $J(\text{Sn},\text{H})$ reported here are the largest known isotope effects on a spin-spin coupling constant.⁹ Also, the

^{119}Sn chemical shift of SnH_3^- is reported for the first time.¹⁰ The ^{119}Sn n.m.r. spectrum of the $\text{SnH}_{3-n}\text{D}_n^-$ ion at 20°C is shown in Figure 1 and the chemical shifts and spin-spin coupling constants are summarized in Tables 1 and 2 respectively. The sample was prepared as previously described^{11,12} using a 2:1 mixture of ND_3 and NH_3 as solvent. The ^{119}Sn chemical shift of SnH_3^- is -634.7 p.p.m. with

Table 1. ^2H Isotope effects on ^{119}Sn chemical shifts in $\text{SnH}_{3-n}\text{D}_n^-$ at 20°C.

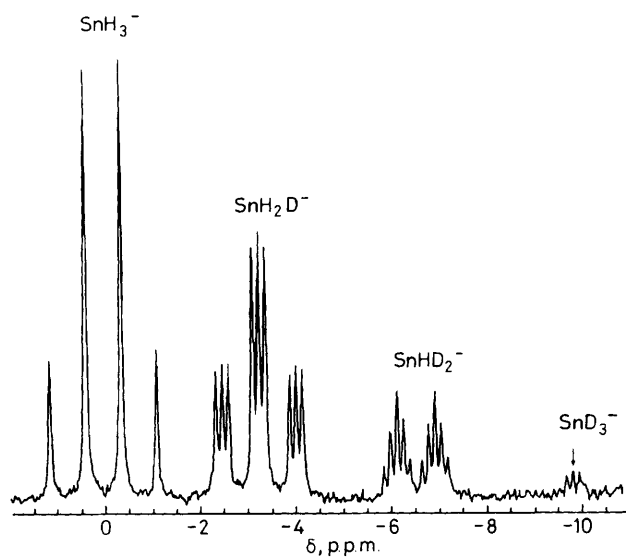
Molecule	$^1\Delta\text{Sn}(^2\text{H})_{\text{obs.}}^a$ /p.p.m.	$^1\Delta\text{Sn}(^2\text{H})_{\text{additivity}}$ /p.p.m.	Δ
SnH_3^-	0.000	0.000	0
SnH_2D^-	-3.270	-3.281	-0.011
SnHD_2^-	-6.550	-6.561	-0.011
SnD_3^-	-9.842	-9.842	0

^a Estimated error $< \pm 0.002$ p.p.m. except for SnD_3^- where the error is ± 0.003 p.p.m.

Table 2. ^{21}H Isotopes effects on spin-spin coupling constants (Hz) in $\text{SnH}_{3-n}\text{D}_n^-$ ($n \leq 3$) at 20°C .

Molecule	$ ^1J(^{119}\text{Sn},\text{H}) ^a$	$ J(^{119}\text{Sn},\text{D}) $	$(\gamma_{\text{H}}/\gamma_{\text{D}}) ^1J(^{119}\text{Sn},\text{D}) ^b$	$\Delta_p J(^{119}\text{Sn},\text{H})$
SnH_3^-	101.00 ± 0.05	—	—	—
SnH_2D^-	104.03 ± 0.10	17.68 ± 0.10	115.17 ± 0.65	11.14
SnHD_2^-	106.85 ± 0.15	18.05 ± 0.15	117.58 ± 0.98	10.73
SnD_3^-	—	17.4 ± 1.5	—	—

^a $\Delta_s J(^{119}\text{Sn},\text{H})[^{21}\text{H}] = 3.0 \pm 0.2$ Hz. ^b $(\gamma_{\text{H}}/\gamma_{\text{D}}) = 6.51440$ (ref. 9).

**Figure 1.** ^{119}Sn N.m.r. spectrum of $\text{SnH}_{3-n}\text{D}_n^-$ ($n \leq 3$) in liquid ammonia at 20°C .

respect to external SnCl_4 , indicating a ^{119}Sn shielding constant which is *ca.* 315 p.p.m. greater than that found in stannane.^{10,13,14} It is of interest that the tin nucleus of SnH_3^+ is less shielded than that of SnH_4 by a similar amount.^{14,15}

Successive replacement of H by D results in greater tin shielding, an isotope shift of *ca.* -3.3 p.p.m./D. This is much greater than the corresponding isotope shift of -0.40 and -0.05 p.p.m./D observed for stannane and the stannonium cation.¹⁵ The experimental trend observed here indicates that the isotope shifts and hence the chemical shift derivatives are very sensitive to nuclear charge as recently proposed by Chesnut.¹⁶ Using the procedure outlined by Jameson and Osten,^{7,17} we find that the difference in mean-bond displacements for a Sn-H and Sn-D bond is $[\langle \Delta r_{\text{Sn-H}} \rangle - \langle \Delta r_{\text{Sn-D}} \rangle] \approx 4.412 \times 10^{-3}$ Å, and if one ignores contributions from differences in mean bond angle deformations and higher order terms, $[\delta\sigma(\text{Sn})/\delta\Delta r] \approx -750$ p.p.m./Å.

The primary isotope effect on the ^{119}Sn , hydrogen spin-spin coupling constant, *i.e.*, $(\gamma_{\text{H}}/\gamma_{\text{D}})|J(^{119}\text{Sn},\text{D})| - |J(^{119}\text{Sn},\text{H})|$, in the SnH_2D^- is 11.14 ± 0.65 Hz or about 10.7% of the value of $J(^{119}\text{Sn},\text{H})$. To our knowledge this is the largest reported primary isotope effect on a spin-spin coupling constant. The positive sign of $\Delta_p J$ in the stannyl ion is consistent with the general trend noted by Jameson and Osten,⁹ *i.e.*, primary isotope effects on J in hydrides are positive when the central atom contains one or more lone-pairs (*e.g.*, PH_3 , H_2Se), otherwise they are negative.

The secondary isotope effect on $J(\text{Sn},\text{H})$, *i.e.*, $|J(^{119}\text{Sn},\text{H}),\text{SnH}_2\text{D}^-| - |J(^{119}\text{Sn},\text{H}),\text{SnH}_3^-|$ is 3.03 ± 0.10 Hz or *ca.* 3.0% of $J(^{119}\text{Sn},\text{H})$ in SnH_3^- . The largest value previously reported was 1.5% for $^1J(^{77}\text{Se},\text{H})$ in H_2Se .^{9,18} At

this time there appears to be no simple criterion for predicting the sign of $\Delta_p J$ in a particular molecule.

In summary our experimental results on the various isotopomers of the stannyl ion demonstrate the extreme sensitivity of $J(^{119}\text{Sn},\text{H})$ to subtle differences in the vibrationally averaged structure of this molecule. This observation is not completely unexpected when one considers the range of $[J(^{119}\text{Sn},\text{H})]$ values observed for the various tin hydrides: SnH_3^+ (2907 Hz), SnH_4 (1933 Hz), and SnH_3^- (108.5 Hz). The small value of $J(\text{Sn},\text{H})$ in SnH_3^- apparently results from the near cancellation of two large terms;¹⁹ thus it is not surprising that this coupling constant will be extremely sensitive to the vibrationally averaged structure induced by deuterium substitution. On the basis of the previous work on methane^{5,8} the zero-point vibrational correction to $J(\text{Sn},\text{H})$ in the stannyl ion could be 100% or more.

Added in proof: In principle a differential solvent effect could contribute to the isotope effects reported here (ref. 7, p. 72). Also, the temperature dependence of $^1J(^{13}\text{C}, \text{H})$ in methane has recently been investigated.²⁰

We are grateful to Mr. Jürgen Mueller for the construction of some specialized glassware, and to N.S.E.R.C. for financial support. All n.m.r. spectra were recorded at the Atlantic Magnetic Resonance Centre.

Received, 18th May 1987; Com. 667

References

- J. Kowalewski and B. Roos, *Chem. Phys.*, 1975, **11**, 123.
- P. Solomon and J. M. Schulman, *J. Am. Chem. Soc.*, 1977, **99**, 7776.
- J. Geertsen and J. Oddershede, *Chem. Phys.*, 1984, **90**, 301.
- W. T. Raynes, P. Lazzeretti, R. Zanasi, and P. W. Fowler, *J. Chem. Soc., Chem. Commun.*, 1985, 1538.
- P. Lazzeretti, R. Zanasi, and W. T. Raynes, *J. Chem. Soc., Chem. Commun.*, 1986, 57.
- W. T. Raynes, P. Lazzeretti, and R. Zanasi, *Chem. Phys. Lett.*, 1986, **132**, 173.
- C. J. Jameson and H. J. Osten, *Ann. Rep. N.M.R. Spectrosc.*, 1986, **17**, 1.
- M. Alei and W. E. Wageman, *J. Chem. Phys.*, 1978, **68**, 783.
- C. J. Jameson and H. T. Osten, *J. Am. Chem. Soc.*, 1986, **108**, 2497.
- B. Wrackmeyer, *Ann. Rep. N.M.R. Spectrosc.*, 1985, **16**, 73.
- H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 1958, 2444.
- T. Birchall and A. R. Pereira, *J. Chem. Soc., Dalton Trans.*, 1975, 1087.
- C. R. Lassigne and E. J. Wells, *Can. J. Chem.*, 1977, **55**, 927.
- T. Birchall and V. Manivannan, *J. Chem. Soc., Dalton Trans.*, 1985, 2671.
- K. L. Leighton and R. E. Wasylishen, *Can. J. Chem.*, in the press.
- D. B. Chesnut, *Chem. Phys.*, 1986, **110**, 415.
- C. J. Jameson and H. J. Osten, *J. Chem. Phys.*, 1984, **81**, 4300 (erratum: *ibid.*, 1984, **83**, 915).
- H. J. Jakobsen, A. J. Zozulin, P. D. Ellis, and J. D. Odom, *J. Magn. Reson.*, 1980, **38**, 219.
- T. Birchall and A. Pereira, *J. Chem. Soc., Chem. Commun.*, 1972, 1150.
- B. Bennett and W. T. Raynes, *Mol. Phys.*, in the press.