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The Absolute Shielding Constants of Heavy Nuclei: Resolving the Enigma of the ^{119}Sn Absolute Shielding

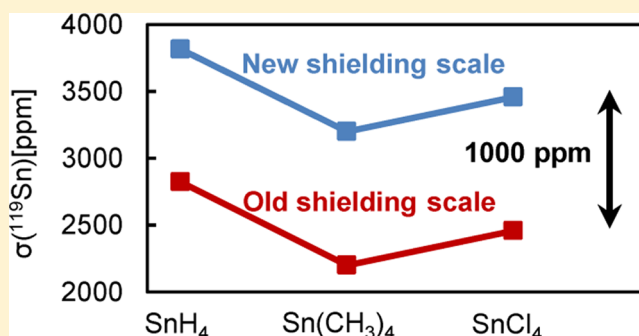
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ABSTRACT: We demonstrate that the apparent disagreement between experimental determinations and four-component relativistic calculations of the absolute shielding constants of heavy nuclei is due to the breakdown of the commonly assumed relation between the electronic contribution to the nuclear spin-rotation constants and the paramagnetic contribution to the NMR shielding constants. We demonstrate that this breakdown has significant consequences for the absolute shielding constant of ^{119}Sn , leading to errors of about 1000 ppm. As a consequence, we expect that many absolute shielding constants of heavy nuclei will be in need of revision.

SECTION: Spectroscopy, Photochemistry, and Excited States



Absolute chemical shielding constants are important not only as a benchmark for ab initio calculations of nuclear magnetic shielding constants,¹ but also for instance in determining nuclear magnetic moments.^{2,3} However, determining absolute shielding constants experimentally is far from trivial.^{4,5} The most common approach is to use Flygare's nonrelativistic relation between the electronic contribution to the nuclear spin-rotation constant C_K^{el} and the paramagnetic contribution to the absolute NMR shielding constant σ_K^{para} ,^{6,7}

$$\sigma_K^{\text{para}} = \frac{1}{2} \frac{m_p}{m_e} \frac{C_K^{\text{el}}}{B g_K} = \sigma_K^{\text{SR}} - \frac{1}{2} \frac{m_p}{m_e} \frac{C_K^{\text{nuc}}}{B g_K} \quad (1)$$

where m_p is the proton mass, m_e is the electron mass, g_K is the nuclear g -value of the nucleus K , B is the spectroscopic rotational constant $\hbar/(4\pi I)$, \hbar is the reduced Planck constant, I is the moment of inertia tensor, and σ_K^{SR} refers to the nuclear spin-rotation constants in ppm, while C_K^{nuc} is its nuclear contribution in kHz.⁸

Experimentally derived absolute shielding constants σ_K can then be obtained by adding theoretical estimates for the diamagnetic contribution σ_K^{dia} (see ref 9) to the experimentally determined paramagnetic contribution σ_K^{para} (eq 1):

$$\sigma_K = \sigma_K^{\text{dia}} + \sigma_K^{\text{para}} \approx \sigma_K^{\text{FA}} + \sigma_K^{\text{SR}} \quad (2)$$

where σ_K^{FA} is a free atom NMR shielding constant.

As the nuclear spin-rotation constants can be determined with high accuracy, for instance, from microwave experiments, and because theoretical diamagnetic shielding constants in general display little dependence on basis set and electron correlation, highly accurate semiexperimental absolute shielding constants have been determined for several light nuclei.^{1,10,11}

It has been questioned whether the relationship in eq 1 would also remain valid when relativistic effects are taken into account.^{12–15} However, it was only very recently that Aucar et al.¹⁶ presented a relativistic theory for the calculation of spin-rotation constants. Their analysis not only highlighted that the relativistic expression for the nuclear spin-rotation constants differs from that of the shielding tensor, but their theoretical analysis also suggested that nuclear spin-rotation constants would be significantly less influenced by relativistic effects than shielding constants. The errors introduced by eq 1 in deriving absolute shielding constants can thus be expected to be accentuated the heavier the nucleus of interest is.

Recently, the absolute shielding constant of ^{119}Sn in tetramethyltin $\text{Sn}(\text{CH}_3)_4$ was determined by Makulski from careful gas-phase measurements of the chemical shifts between gaseous $\text{Sn}(\text{CH}_3)_4$ and liquid $\text{Sn}(\text{CH}_3)_4$.¹⁷ The corresponding absolute shielding scale of ^{119}Sn in gaseous $\text{Sn}(\text{CH}_3)_4$ (2172 ± 200 ppm)¹⁷ was determined relative to the absolute shielding of liquid $\text{Sn}(\text{CH}_3)_4$ (2181 ± 200 ppm) as reported by Laaksonen and Wasylishen in 1995.¹⁸ In this paper, they also reported the NMR shielding constants of several small SnX_4 molecules ($X = \text{D}, \text{H}, \text{CH}_3, \text{Cl}$) obtained by converting experimental spin-rotation constants, obtained from spin–lattice relaxation time measurements, using the relation in eq 2.

Despite the careful experimental work, the tin absolute shielding constants exhibit large deviations between experimental results and published theoretical calculations at the relativistic level of theory. For instance, the experimental value of Makulski for tetramethyltin (2172 ± 200 ppm)¹⁷ is in

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excellent agreement with spin-orbit-free ZORA results (2283 ppm),¹⁹ whereas a somewhat poorer agreement is obtained with a full spin-orbit ZORA Hamiltonian (2749 ppm).¹⁹ Surprisingly, the difference is even more pronounced when comparing the experiment with four-component density functional theory (DFT) calculations (3199 ppm) (*vide infra*).

Considering the large deviations between theoretical and experimental absolute shielding constants and the analysis by Aucar et al.¹⁶ suggesting that relativistic effects may have significantly different effects on the nuclear spin-rotation constants than on the paramagnetic contribution to the shielding constants, a reinvestigation of the spin-rotation and shielding constants in SnH_4 , $\text{Sn}(\text{CH}_3)_4$, and SnCl_4 appears warranted.

For this study we have implemented the relativistic theory for spin-rotation constants by Aucar and co-workers,¹⁶ also lifting some of the approximations done in this original work. The details of the implementation will be reported in a separate paper,²⁰ and we only note here that, whereas in the nonrelativistic limit there is no difference between the paramagnetic contributions to the shielding constant obtained from calculations either of shielding or spin-rotation constants, in the relativistic framework these paramagnetic contributions are formally different, and thus any agreement between the two calculations would be accidental.¹⁶ We note that the nuclear spin-rotation constants are formally origin independent, always being calculated with respect to the center of mass of the molecule. In order to fulfill eq 1 in the nonrelativistic limit, we have also used the center of mass as the gauge origin for the calculations of the shielding constants. For the molecules studied here, the center of mass coincides with the position of the Sn atom.

Test calculations of NMR shieldings with the quadruple- ζ basis using gauge-including atomic orbitals (GIAO)²¹ have been performed in order to verify that the results obtained with the common gauge-origin (CGO) approach²² are close to the basis set limit. These GIAO calculations yielded ^{119}Sn absolute shielding constants that agreed with the CGO results to within 0.1 ppm (in SnH_4 and $\text{Sn}(\text{CH}_3)_4$), whereas a somewhat larger difference of about 7 ppm was observed in the case of SnCl_4 . The CGO approach using the quadruple- ζ -quality basis set can therefore be expected to give results for the shielding and spin-rotation constants that are close to the basis set limit and displaying only very weak origin dependence.

The molecular geometries were optimized at the DFT level of theory using the BP86 exchange-correlation functional,^{23,24} TZ2P basis sets,²⁵ and the spin-orbit ZORA Hamiltonian²⁶ as implemented in the Amsterdam Density Functional (ADF) program²⁷ [$r(\text{Sn}-\text{H}) = 1.7159 \text{ \AA}$, $r(\text{Sn}-\text{C}) = 2.1839 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.0983 \text{ \AA}$, $r(\text{Sn}-\text{Cl}) = 2.3044 \text{ \AA}$]. All property calculations were performed with the four-component module of the ReSpect program,²⁸ employing the BP86 functional,^{23,24} the finite-size nucleus model of Gaussian type,²⁹ and uncontracted pc-3 basis sets on light elements^{30,31} along with the uncontracted Dyall CVQZ basis on tin.³² While the four-component calculation of NMR shielding constants requires a special restricted magnetically balanced basis (RMB) for the small component,^{21,22} the spin-rotation constant uses an ordinary restricted kinetically balanced (RKB) basis. The RKB condition is imposed in our implementation at the integral level,³³ allowing us to use large basis sets in order to ensure that the calculated spin-rotation constants are close to

the basis-set limit. Finally, we use the value of the ^{119}Sn magnetic dipole moment of -1.04728 nuclear magnetons.³⁴

The results obtained in the present study are listed in Tables 1 and 2. Data for SnH_4 are discussed first, since these are

Table 1. Nuclear Spin-Rotation Constants for ^{119}Sn Calculated at the Four-Component Level of Theory^a Together with Available Experimental Data Measured at Different Temperatures

	kHz		ppm	
	C	exp.	C ^b	exp.
SnH_4	340.0	358.4 ± 18.1 (143 K) ^c	−2334	-2422 ± 122 (143 K) ^c
		368.8 ± 18.6 (171 K) ^c		-2493 ± 132 (171 K) ^c
$\text{Sn}(\text{CH}_3)_4$	15.9	16.9 ± 1.3 (252 K) ^c	−2956	-2809 ± 230 (252 K) ^c
		17.3 ± 1.4 (276 K) ^c		-2874 ± 240 (276 K) ^c
		17.2 ± 1.7 (300 K) ^c		-2855 ± 286 (300 K) ^c
		17.7 (300 K) ^d		−3200 (300 K) ^d
SnCl_4	6.3	6.1 (298 K) ^e	−2695	−2760 (298 K) ^e
		5.83 ± 0.35 (298 K) ^c		-2497 ± 151 (298 K) ^c
		6.04 ± 0.36 (328 K) ^c		-2585 ± 153 (328 K) ^c
		6.16 ± 0.39 (358 K) ^c		-2636 ± 167 (358 K) ^c

^amDKS-RKB method^{21,22} as implemented in the ReSpect program.²⁸

^bC corresponds to $\sigma_{\text{K}}^{\text{SR}}$ in eq 1. Note, some authors use the label σ_{p}' instead, see for instance ref 18. ^cFrom ref 18. ^dFrom ref 38. ^eFrom ref 39.

representative for the entire set of tin compounds considered in this study. The experimental spin-rotation constant, $C(^{119}\text{SnH}_4)$ obtained from NMR relaxation data (368.8 ± 18.6 kHz at 171 K) agrees reasonably well with our calculated four-component value (340.0 kHz). Using eq 1, these spin-rotation constants are assigned to the paramagnetic contribution to the shielding constant, where the theoretically predicted value of -2334 ppm is only slightly outside the error bar of the experimentally measured value -2493 ± 132 ppm (for gaseous $^{119}\text{SnH}_4$ at 171 K). In contrast, the paramagnetic contribution to the shielding constant obtained directly from the four-component relativistic CGO calculation is -1361 ppm, being almost a factor of 2 smaller than the experimentally assigned paramagnetic shielding, using eq 1.

To obtain the experimental total absolute shielding constant for $^{119}\text{SnH}_4$, the diamagnetic shielding contribution of a free Sn atom (5086 ppm),¹⁸ which is comparable to the diamagnetic contribution of the Sn atom (5154 ppm) obtained in our calculations, was added to the paramagnetic contribution derived from spin-rotation constants using eq 2. The final total absolute shielding constant of $^{119}\text{SnH}_4$, obtained experimentally by Laaksonen and Wasylishen, is 2537 ± 284 ppm for the gas phase and 2628 ± 132 ppm for the liquid state,¹⁸ both result in significant disagreement with our calculated four-component value of 3815 ppm (see Table 2). As we have shown, the majority of this discrepancy can be traced to the breakdown of eq 1 in cases when relativistic effects are significant, as we have good agreement between the paramagnetic contributions derived experimentally and theo-

Table 2. Isotropic ^{119}Sn Absolute Shielding Constants (in ppm) Calculated at the Four-Component Level of Theory^a Together with Available Experimental Data Measured at Different Temperatures

	σ^{dia}	σ^{para}	$C^{\text{el } b}$	$\sigma^{\text{dia}} + \sigma^{\text{para}}$	$\sigma^{\text{dia}} + C^{\text{el } c}$	exp.
SnH_4	5176	−1361	−2355	3815	2821	2663 ± 122 (143 K) ^c 2593 ± 132 (171 K) ^c 2537 ± 284 (248 K, g) ^c 2628 ± 132 (248 K, l) ^c
$\text{Sn}(\text{CH}_3)_4$	5298	−2099	−3100	3199	2198	2277 ± 230 (252 K) ^c 2211 ± 240 (276 K) ^c 2230 ± 286 (300 K) ^c 2181 ± 200 (300 K) ^d 2172 ± 200 (300 K) ^e
SnCl_4	5429	−1972	−2972	3457	2457	2588 ± 151 (298 K) ^c 2500 ± 153 (328 K) ^c 2450 ± 167 (358 K) ^c

^amDKS-RMB method^{21,22} as implemented in the ReSpect program.²⁸

^bParamagnetic contribution to the absolute shielding constant calculated from the nuclear spin-rotation constant using eq 1.

^cAbsolute shielding constants obtained from nuclear spin-rotation constant measurements using eq 2 and the free atom diamagnetic shielding constant (5086 ppm).¹⁸ ^dAveraged five different absolute shielding values for $\text{Sn}(\text{CH}_3)_4$.¹⁸ ^eNMR shielding constant of gaseous $\text{Sn}(\text{CH}_3)_4$ ¹⁷ determined with respect to liquid $\text{Sn}(\text{CH}_3)_4$ (2181 ppm) from ref 18.

retically from spin-rotation constants (eq 1), but both being in marked discrepancy with the paramagnetic contribution obtained directly from the four-component shielding constant calculations.

We can observe the same trends for the remaining two tin compounds, namely, $\text{Sn}(\text{CH}_3)_4$ and SnCl_4 (see Tables 1 and 2). Again there is very good agreement between experimental and theoretical results for the spin-rotation constants and consequently also for the spin-rotation-derived paramagnetic contribution to the shielding constants. For SnCl_4 it is worth noting that the experimentally observed strong temperature dependence of the spin-rotation constant may suggest that vibrational corrections are important in order to provide a more precise theoretical estimate of this constant. However, the difference in the paramagnetic contribution derived from the theoretical spin-rotation constants and the paramagnetic contribution obtained from the four-component NMR calculations differ by approximately the same value as observed for SnH_4 . Finally, this leads to the difference of 1000 ppm between spin-rotation-derived and directly calculated shielding constants of $\text{Sn}(\text{CH}_3)_4$ and SnCl_4 (1001 and 1000 ppm, respectively), being almost identical to the value obtained for SnH_4 (994 ppm).

Interestingly, the experimental chemical shift of gaseous SnH_4 relative to that of liquid $\text{Sn}(\text{CH}_3)_4$ is, according to Laaksonen and Wasylishen, −541.5 ppm, which is in rather

poor agreement with the chemical shifts derived experimentally on the basis of spin-rotation constants, which is −297 ppm. To resolve this apparent discrepancy, the authors originally derived an alternate absolute chemical shielding for $^{119}\text{Sn}(\text{CH}_3)_4$ based on averaging a large number of different chemical shifts to obtain an average value of 2181 ppm. Instead, we here note that the four-component chemical shift of SnH_4 versus $\text{Sn}(\text{CH}_3)_4$ is −616 ppm, which is in much better agreement with the first experimental observation, considering that our results are based on gas-phase calculations, whereas the experimental chemical shift is between gaseous SnH_4 and liquid $\text{Sn}(\text{CH}_3)_4$.

The experimental chemical shift of liquid SnCl_4 relative to liquid $\text{Sn}(\text{CH}_3)_4$ was determined by Laaksonen and Wasylishen to be −147.8 ppm. This is in fair agreement with the chemical shift obtained from the relativistic four-component calculations, being −258 ppm, taking into consideration that our calculations have been performed for isolated molecules in the gas phase without account of vibrational corrections, which may be significant considering the strong experimental temperature dependence. Still, this agreement is better than the one obtained for the chemical shifts derived from the experimental spin-rotation constants.¹⁸

To summarize, we have demonstrated that the relativistic theory of Aucar et al.¹⁶ can provide results for the spin-rotation constants of SnH_4 , $\text{Sn}(\text{CH}_3)_4$, and SnCl_4 that are within experimental error bars. However, the paramagnetic shielding constants derived using the commonly assumed relation between σ_K^{para} and the electronic contribution to the spin-rotation constant C_K^{el} in eq 1 is shown to differ substantially from the paramagnetic contribution obtained in relativistic calculations of the shielding constants, the difference being surprisingly constant among the molecules (1000 ppm).

The present work undermines the hope of determining experimental absolute shielding scales from spin-rotation constants, and, as few other alternatives exist,³⁵ it leaves the field in an unpleasant situation. However, for the particular case of the ^{119}Sn , we can as a first approximation use the observation that the difference in the paramagnetic shielding constant and the corresponding quantity derived from the experimental spin-rotation constants using eq 1 is almost constant and has a value of 1000 ppm. Combining this observation with the more correct value of the free atom diamagnetic shielding constant (5154 ppm), we tentatively redefine the *experimental* absolute shielding constant of SnH_4 to be 3661 ± 132 ppm, or, alternatively for liquid $\text{Sn}(\text{CH}_3)_4$, 3299 ± 286 ppm. Although now giving good agreement with the four-component relativistic absolute shielding constants, we note that the chemical shift is too small (−362 ppm) compared to that observed experimentally (−542 ppm), and thus that the absolute shielding of SnH_4 probably is a lower bound whereas that of $\text{Sn}(\text{CH}_3)_4$ is an upper bound. Indeed, despite the inherent errors in DFT, it is conceivable that the theoretically calculated four-component results are the most accurate estimates of the absolute shielding constants of ^{119}Sn . We do not suggest an absolute shielding based on the data for SnCl_4 due to the sensitivity of the derived paramagnetic shielding constant on the value of the spin-rotation constant and because of its strong temperature dependence.

The need for revising the nuclear magnetic dipole moments have been proposed many years ago,³⁶ and more recently Makulski and co-workers questioned the accuracy of the nuclear magnetic dipole moments of tin, suggesting errors of the order of 0.2%.^{17,37} Our new proposed absolute shielding

constant would also lead to a decrease in the $^{117/119}\text{Sn}$ nuclear magnetic dipole moments of about 0.2% compared to the formerly accepted values,³⁴ thus the new nuclear magnetic dipole moment of ^{119}Sn is $-1.0447773 \mu_N$, and $-0.9983147 \mu_N$ in the case of ^{117}Sn when using the same experimental data as in ref 37. As theoretical calculations of indirect nuclear spin–spin coupling constants rely on accurate nuclear magnetic dipole moments, the findings here will also lead to update the data used to calculate these coupling constants.

There are several implications that are raised by the conclusions of this work and the suggested significant re-evaluation of the absolute shielding constant of ^{119}Sn by 1000 ppm: (1) Whereas ZORA provides reliable estimates for the chemical shifts, our results suggest that the approach may not be reliable for absolute shielding constants. (2) What is the validity of eq 1 as a function of periods and groups in the periodic table? (3) How many nuclei are now in need of new absolute shielding scales?

The present work has most likely only scratched the surface of an important topic in NMR spectroscopy of heavy nuclei.

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Notes

The authors declare no competing financial interest.

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