

# The Absolute Shielding Constants of Heavy Nuclei:

## Resolving the Enigma of the $^{119}\text{Sn}$ Absolute

### Shielding

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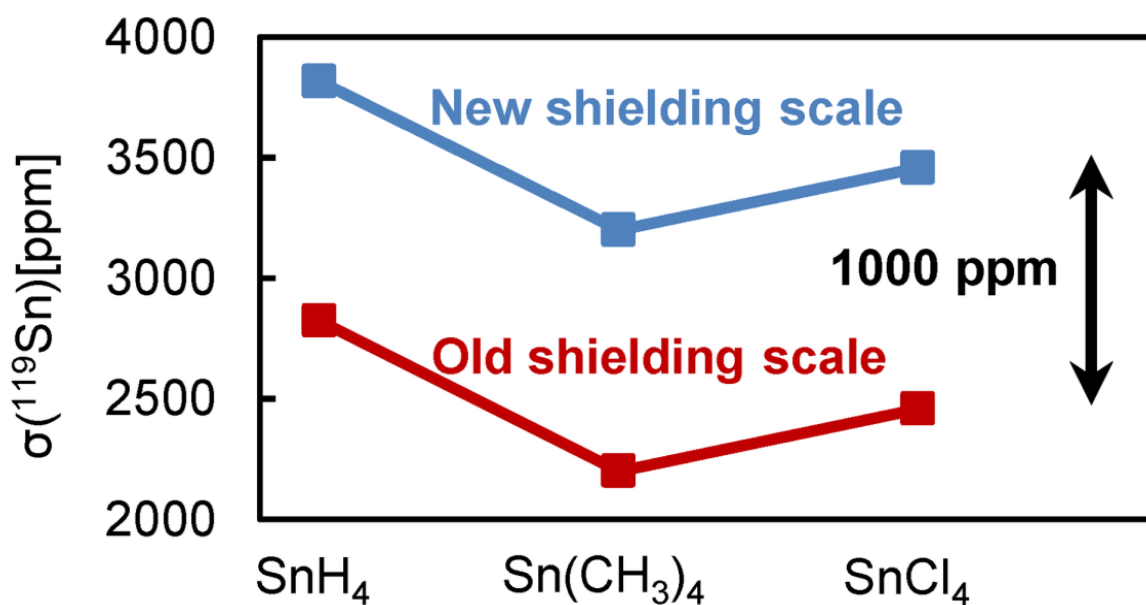
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ABSTRACT: We demonstrate that the apparent disagreement between experimental determinations and four-component relativistic calculations of the absolute shielding constants of heavy nuclei is due to the breakdown of the commonly assumed relation between 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  $^{119}\text{Sn}$ , 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.



KEYWORDS: NMR, relativistic effects, spin-rotation constants, absolute shielding scales, nuclear magnetic moments

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

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

where  $m_p$  is the proton mass,  $m_e$  the electron mass,  $g_K$  the nuclear g-value of the nucleus  $K$ ,  $B$  the spectroscopic rotational constant  $\hbar/(4\pi I)$ ,  $\hbar$  the reduced Planck constant and  $I$  the moment of inertia tensor.<sup>8</sup>

Experimentally derived absolute shielding constants  $\sigma_K$  can then be obtained by adding theoretical estimates for the diamagnetic contribution  $\sigma_K^{dia}$  to the experimentally determined paramagnetic contribution  $\sigma_K^{para}$  [Eq. (1)]

$$\sigma_K = \sigma_K^{dia} + \frac{1}{2} \frac{m_p}{m_e} \frac{C_K^{el}}{B} \frac{1}{g_K} \quad (2)$$

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 semi-experimental absolute shielding constants have been determined for several light nuclei.<sup>1,9-11</sup>

It has been questioned whether the relationship in Eq. (1) would remain valid also when relativistic effects are taken into account.<sup>12-15</sup> However, it was only very recently that Aucar *et al.*<sup>16</sup> 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 <sup>119</sup>Sn in tetramethyltin Sn(CH<sub>3</sub>)<sub>4</sub> was determined by Makulski from careful gas-phase measurements of the chemical shifts between gaseous Sn(CH<sub>3</sub>)<sub>4</sub> and liquid Sn(CH<sub>3</sub>)<sub>4</sub>.<sup>17</sup> The corresponding absolute shielding scale of <sup>119</sup>Sn in gaseous Sn(CH<sub>3</sub>)<sub>4</sub> (2172±200 ppm)<sup>17</sup> was determined relative to the absolute shielding of liquid Sn(CH<sub>3</sub>)<sub>4</sub> (2181±200 ppm) as reported by Laaksonen and Wasylshen in 1995.<sup>18</sup> In this paper, they also reported the NMR shielding constants of several small SnX<sub>4</sub> molecules (X=D, H, CH<sub>3</sub>, 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 ( $2172 \pm 200$  ppm)<sup>17</sup> is in excellent agreement with spin-orbit-free ZORA results (2283 ppm),<sup>19</sup> whereas a somewhat poorer agreement is obtained with a full spin-orbit ZORA Hamiltonian (2749 ppm).<sup>19</sup> Surprisingly, the difference is even more pronounced when comparing the experiment with four-component DFT calculations (3199 ppm) (*vide infra*).

Considering the large deviations between theoretical and experimental absolute shielding constants and the analysis by Aucar *et.al.*<sup>16</sup> 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  $\text{SnH}_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{SnCl}_4$  appears warranted.

For this study we have implemented the relativistic theory for spin-rotation constants by Aucar and coworkers,<sup>16</sup> also lifting some of the approximations done in this original work. The details of the implementation will be reported in a separate paper,<sup>20</sup> 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.<sup>16</sup> 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 non-relativistic limit, we have

used the center of mass also as 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-zeta basis using gauge-including atomic orbitals (GIAO)<sup>21</sup> have been performed in order to verify that the results obtained with the common gauge-origin (CGO) approach<sup>22</sup> are close to the basis set limit. These GIAO calculations yielded <sup>119</sup>Sn absolute shielding constants that agreed with the CGO results to within 0.1 ppm (in SnH<sub>4</sub> and Sn(CH<sub>3</sub>)<sub>4</sub>), whereas a somewhat larger difference of about 7 ppm was observed in the case of SnCl<sub>4</sub>. The CGO approach using the quadruple zeta-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 DFT level of theory using the BP86 exchange-correlation functional,<sup>23,24</sup> TZ2P basis sets,<sup>25</sup> and the spin-orbit ZORA Hamiltonian<sup>26</sup> as implemented in the Amsterdam Density Functional (ADF) program<sup>27</sup> [ $r(\text{Sn-H}) = 1.7159 \text{ \AA}$ ,  $r(\text{Sn-C}) = 2.1839 \text{ \AA}$ ,  $r(\text{C-H}) = 1.0983 \text{ \AA}$ ,  $r(\text{Sn-Cl}) = 2.3044 \text{ \AA}$ ]. All property calculations were performed with the four-component module of the ReSpect program,<sup>28</sup> employing the BP86 functional,<sup>23,24</sup> the finite-size nucleus model of Gaussian type,<sup>29</sup> and uncontracted pc-3 basis sets on light elements<sup>30,31</sup> along with the uncontracted Dyall CVQZ basis on tin.<sup>32</sup> While the four-component calculation of NMR shielding constants requires a special restricted magnetically balanced basis (RMB) for the small component,<sup>21,22</sup> the spin-rotation constant uses an ordinary restricted kinetically balanced (RKB) basis. The RKB condition is imposed in our implementation at the integral level<sup>33</sup> 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 <sup>119</sup>Sn magnetic dipole moment of -1.04728 nuclear magnetons.<sup>34</sup>

The results obtained in the present study are listed in Tables 1 and 2. Data for SnH<sub>4</sub> are discussed first, since these are 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 ( $368.8 \pm 18.6$  kHz at 171K) 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 -2355 ppm is only slightly outside the error bar of the experimentally measured value  $-2493 \pm 132$  ppm (for gaseous  $^{119}\text{SnH}_4$  at 171K). Unfortunately, the paramagnetic contribution to the shielding constant obtained directly from the four-component relativistic CGO calculation is -1361 ppm, being almost a factor of two smaller than the experimentally assigned paramagnetic shielding, the difference being 1132 ppm.

To obtain the experimental total absolute shielding constant for  $^{119}\text{SnH}_4$ , the diamagnetic shielding contribution of a free Sn atom (5086 ppm),<sup>18</sup> which is comparable to the diamagnetic contribution of SnH<sub>4</sub> molecule (5176 ppm) obtained in our calculations, was added to the paramagnetic contribution derived from spin-rotation constants using Eq. (1). The final total absolute shielding constant of  $^{119}\text{SnH}_4$ , obtained experimentally by Laaksonen and Wasylishen, is  $2537 \pm 284$  ppm for the gas phase and  $2628 \pm 132$  ppm for the liquid state,<sup>18</sup> both results 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 theoretically 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  $\text{SnCl}_4$  (see Tables 1 and 2). Again there is very good (for  $\text{Sn}(\text{CH}_3)_4$ ) or acceptable (for  $\text{SnCl}_4$ ) 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  $\text{SnCl}_4$  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  $\text{SnH}_4$ . 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  $\text{SnCl}_4$  (1001 and 1000 ppm, respectively), being almost identical to the value obtained for  $\text{SnH}_4$  (994 ppm).

Interestingly, the experimental chemical shift of gaseous  $\text{SnH}_4$  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  $\text{SnH}_4$  vs.  $\text{Sn}(\text{CH}_3)_4$  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  $\text{SnH}_4$  and liquid  $\text{Sn}(\text{CH}_3)_4$ .

By analyzing the data in Tables 1 and 2, we can see that the main reason for the poor agreement between the experimental chemical shifts observed directly and derived from spin-rotation constants originates from the diamagnetic contribution. In particular, the assumption that the diamagnetic contribution remains constant for all tin compounds and being equal to the free atom value is no longer valid. We note that there is a shift of 122 ppm in the diamagnetic contribution going from  $\text{SnH}_4$  to  $\text{Sn}(\text{CH}_3)_4$ , and adding this value to the difference between  $C^{el}(\text{Sn}(\text{CH}_3)_4)$  and  $C^{el}(\text{SnH}_4)$  would give -623 ppm. This is in very good agreement with chemical shift obtained directly from four-component calculations (-616 ppm).

For  $\text{SnCl}_4$ , the relativistic diamagnetic contribution to the shielding constant differs significantly from the free-atom value, the value of 5429 ppm being 253 ppm larger than the diamagnetic shielding obtained for  $\text{SnH}_4$ . The error in the diamagnetic shielding constant largely cancels the difference in the paramagnetic contribution derived from the spin-rotation data, making the experimental absolute shielding constants of  $^{119}\text{SnCl}_4$   $2588 \pm 151$  ppm (298K), as determined by Laaksonen and Wasylishen,<sup>18</sup> almost identical to the absolute shielding constant derived using Eq.(2) from the theoretical spin-rotation constants (2457 ppm). However, both these results differ significantly from the absolute shielding obtained from the four-component shielding calculations (3457 ppm).

The experimental chemical shift of liquid  $\text{SnCl}_4$  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 much better than the one obtained for the chemical shifts (-348 ppm) derived from the experimental spin-rotation constants.

To summarize, we have demonstrated that the relativistic theory of Aucar *et al.*<sup>16</sup> can provide results for the spin-rotation constants of SnH<sub>4</sub>, Sn(CH<sub>3</sub>)<sub>4</sub> and SnCl<sub>4</sub> that are within experimental error bars. However, the paramagnetic shielding constants derived using the commonly assumed relation between  $\sigma_K^{para}$  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). We have also demonstrated that the assumption of the diamagnetic contribution being independent of the molecular composition does not hold, leading to errors as large as 7% in the case of SnCl<sub>4</sub>.

The present work undermines the hope of determining experimental absolute shielding scales from spin-rotation constants and as few other alternatives exist,<sup>35</sup> it leaves the field in an unpleasant situation. However, for the particular case of the <sup>119</sup>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 having a value of 1000 ppm. Combining this observation with the more correct values of the diamagnetic shielding constants, we tentatively redefine the *experimental* absolute shielding constant of SnH<sub>4</sub> to be 3683±132 ppm, or alternatively for liquid Sn(CH<sub>3</sub>)<sub>4</sub> 3443±286 ppm. Although now giving good agreement with the four-component relativistic absolute shielding constants (within error bars), we note that the chemical shift is too small (-240 ppm) compared to that observed experimentally (-542 ppm), and thus that the absolute shielding of SnH<sub>4</sub> probably is a lower bound whereas that of Sn(CH<sub>3</sub>)<sub>4</sub> 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  $^{119}\text{Sn}$ . We do not suggest an absolute shielding based on the data for  $\text{SnCl}_4$  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,<sup>36</sup> and more recently Makulski and coworkers questioned the accuracy of the nuclear magnetic dipole moments of tin, suggesting errors of the order of 0.2%.<sup>17,37</sup> 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,<sup>34</sup> thus the new nuclear magnetic dipole moment of  $^{119}\text{Sn}$  is  $-1.0447773\mu_{\text{N}}$ , and  $-0.9983147\mu_{\text{N}}$  in the case of  $^{117}\text{Sn}$  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  $^{119}\text{Sn}$  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.

Table 1. Nuclear spin-rotation constants for  $^{119}\text{Sn}$  calculated at the four-component level of theory<sup>a</sup> together with available experimental data measured at different temperatures

	kHz		ppm	
	<i>C</i>	Exp.	<i>C<sup>el,b</sup></i>	Exp.
$\text{SnH}_4$	340.0	358.4±18.1 (143 K) <sup>c</sup> 368.8±18.6 (171 K) <sup>c</sup>	-2355	-2422±122 (143 K) <sup>c</sup> -2493±132 (171 K) <sup>c</sup>
$\text{Sn}(\text{CH}_3)_4$	15.9	16.9±1.3 (252 K) <sup>c</sup> 17.3±1.4 (276 K) <sup>c</sup> 17.2±1.7 (300 K) <sup>c</sup> 17.7 (300 K) <sup>d</sup>	-3100	-2809±230 (252 K) <sup>c</sup> -2874±240 (276 K) <sup>c</sup> -2855±286 (300 K) <sup>c</sup> -3200 (300 K) <sup>d</sup>
$\text{SnCl}_4$	6.3	6.1 (298 K) <sup>e</sup> 5.83±0.35 (298 K) <sup>c</sup> 6.04±0.36 (328 K) <sup>c</sup> 6.16±0.39 (358 K) <sup>c</sup>	-2972	-2760 (298 K) <sup>e</sup> -2497±151 (298 K) <sup>c</sup> -2585±153 (328 K) <sup>c</sup> -2636±167 (358 K) <sup>c</sup>

<sup>a</sup> mDKS-RKB method<sup>21,22</sup> as implemented in the ReSpect program.<sup>28</sup>

<sup>b</sup> Paramagnetic contribution to the absolute shielding constant calculated from Nuclear Spin-Rotation constant using Eq. (1).

<sup>c</sup> From ref.18.

<sup>d</sup> From ref. 38.

<sup>e</sup> From ref. 39.

Table 2. Isotropic  $^{119}\text{Sn}$  absolute shielding constants (in ppm) calculated at the four-component level of theory<sup>a</sup> together with available experimental data measured at different temperatures

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

<sup>a</sup> mDKS-RMB method<sup>21,22</sup> as implemented in the ReSpect program.<sup>28</sup>

<sup>b</sup> Paramagnetic contribution to the absolute shielding constant calculated from nuclear spin-rotation constant using Eq. (1).

<sup>c</sup> Absolute shielding constants obtained from nuclear spin-rotation constant measurements using Eq. (2) and free atom diamagnetic shielding constant (5086 ppm).<sup>18</sup>

<sup>d</sup> Averaged five different absolute shielding values for  $\text{Sn}(\text{CH}_3)_4$ .<sup>18</sup>

<sup>e</sup> NMR shielding constant of gaseous  $\text{Sn}(\text{CH}_3)_4$ <sup>17</sup> determined with respect to liquid  $\text{Sn}(\text{CH}_3)_4$  (2181 ppm) from ref.18.

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