An Absolute Chemical Shielding Scale for Tin from NMR Relaxation Studies and Molecular Dynamics Simulations

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Abstract: An approximate nuclear magnetic shielding scale for tin has been obtained from ^{119}Sn spin-rotation constants, $C_{\mathrm{eff}}(^{119}\mathrm{Sn})$, in a series of spherical top molecules (SnX_4, X = H, D, CH_3, and Cl). The paramagnetic shielding at a nucleus induced by circulating charge is known to be intimately related to the nuclear spin-rotation constant. Tin-119 spin-rotation constants in stannane, SnH_4, have been determined by two independent techniques. In the first, $C_{\mathrm{eff}}(^{119}\mathrm{Sn})$ has been obtained from the experimentally determined ratio of the ^{1}H and ^{119}Sn spin-lattice relaxation times of gaseous stannane, $T_1(^1\mathrm{H})/T_1(^{119}\mathrm{Sn}) = 6570 \pm 600$, and the known effective ^{1}H spin-rotation constant for methane. The second technique involved combining experimental $T_1(^{119}\mathrm{Sn})$ data for liquid SnH_4, SnD_4, $Sn(CH_3)_4$, and $SnCl_4$ with angular momentum correlation times, τ_J's, calculated from molecular dynamics (MD) simulations. Since the spin-rotation relaxation mechanism is the only important mechanism for ^{119}Sn T_1 relaxation in these compounds, values of $C_{\mathrm{eff}}(^{119}\mathrm{Sn})$ were readily determined from the experimental liquid-phase $T_1(^{119}\mathrm{Sn})$ data and the MD simulations. The tin relaxation data for liquid tetramethyltin and tin tetrachloride were taken from the literature, while T_1 data for SnH_4 and SnD_4 were obtained in the present study. Consideration of all the spin-rotation constant data obtained in this study indicates that the tin shielding constant, $\sigma(\mathrm{Sn})$, in liquid tetramethyltin is 2180 ± 200 ppm with respect to the bare nucleus. The absolute nuclear shielding values obtained for tin in this study are compared to values recently obtained from quantum mechanical calculations. On the basis of the results of the present study, the ^{119}Sn magnetogyric ratio, $\gamma_{\mathrm{Sn\text{-}119}}$, is $-9.997\,559(8) \times 10^7$ rad s^{-1} T^{-1}, approximately 3% less than the accepted value.

Introduction

NMR is a powerful method for studying molecular motion in liquids and solutions.[1−9] The motion of molecules creates fluctuating magnetic fields which are responsible for nuclear relaxation. The importance of a specific relaxation mechanism is governed by the product of a motional time constant, correlation time, and the square of the appropriate interaction constant. If the strength of the interaction constant which couples the nuclear spins to the surroundings is known, then one can obtain important dynamical information through careful nuclear relaxation studies. Alternatively, if the dynamical properties of a molecule can be characterized independently, information concerning the interaction constants is available from relaxation data.

For molecules containing two or more proximate spin $^1/_2$ nuclei, the dipole−dipole (DD) mechanism generally provides the most efficient mechanism for spin-lattice relaxation in the liquid phase. However, in the case of relatively small molecules, the spin-rotation (SR) mechanism may be important, particularly if the spin $^1/_2$ nuclei are somewhat isolated and hence not strongly dipolar coupled to neighboring spins. Experimentally, the importance of the SR mechanism can be recognized by its unique temperature dependence; T_1 decreases with increasing temperature. In contrast, T_1 increases with temperature when either the DD or chemical shielding anisotropy (CSA) mechanism dominates. The unique temperature dependence of the SR mechanism arises from its dependence on the angular momentum correlation time, τ_J, while the importance of the other common relaxation mechanisms is governed by the rotational correlation time, τ_2.

Molecular dynamics (MD) computer simulations are a powerful method for studying structural and dynamic properties of molecular systems in condensed phases.[10] There are many advantages in using MD simulations in combination with NMR relaxation studies.[11−16] First, the MD treatment can be based on an ensemble of molecules leading to a proper statistically averaged approach to calculate correlation times. MD simulations give not only the correlation times but the complete time correlation functions on the time scale of microscopic motion of molecules. Most importantly, no assumptions concerning

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the motional regime have to be made. Results from MD simulations are exact within the molecular model used. Of course, the results from molecular computer simulations depend on the given molecular model and the interaction potentials. In general, the empirical interaction potentials used in the computer simulations are parameterized to reproduce experimentally available macroscopic properties, such as density, pressure, or internal energy. Sometimes additional adjustments are made to the parameters to better reproduce other key physical properties, such as dielectric constants or diffusion coefficients. Similarly, by slightly modifying the potential parameters, the rate of molecular reorientation can be adjusted to match those obtained from NMR relaxation studies.

In the present investigation, NMR relaxation measurements and MD simulations have been combined to study the rotational dynamics in a series of tetrahedral tin compounds. Specifically, we have measured NMR relaxation rates for ^{119}Sn ($I = {}^1/_2$) in liquid SnH_4 and for ^{2}H ($I = 1$) and ^{119}Sn in liquid SnD_4 as a function of temperature. MD simulations have been carried out for liquid SnH_4 and SnD_4, and for two other tin compounds: tetramethyltin, the standard chemical shift reference in tin NMR studies,[17] and tin tetrachloride. For both $Sn(CH_3)_4$ and $SnCl_4$, there are experimental relaxation data available in the literature.[18-20] For each of these liquids, the spin-rotation mechanism is the only important mechanism for spin-lattice relaxation of ^{119}Sn. Combining the NMR relaxation data and the MD simulations, ^{119}Sn spin-rotation coupling constants are obtained. Since the nuclear spin-rotation constant is intimately related to the paramagnetic shielding that a given nucleus experiences, knowledge of C_{eff} allows one to calculate the absolute magnetic shielding constant for the nucleus (*vide infra*). It is in this way that we establish an absolute shielding scale for tin. Previously, absolute shielding scales have been established for most of the first and second row elements.[21] Here we present references for the first two elements of group 14, carbon[22,23] and silicon.[24]

In addition to T_1 measurements on liquid stannane and stannane-d_4, we have measured the ^{119}Sn and ^{1}H T_1's of a gaseous sample of SnH_4. As well, the ^{1}H chemical shift of SnH_4(g) relative to CH_4(g) has been determined by examining a mixture of the two gases. As described later, these experiments permitted an independent determination of $C_{\mathrm{eff}}(^{119}\mathrm{Sn})$ for stannane.

The present study was initiated for the following reasons. First, to the best of our knowledge, no other ^{119}Sn NMR relaxation studies have been reported for stannane. Second, in the past 15 years there have been no sincere attempts to establish an absolute shielding scale for tin based on experimental results.[25] Third, theoretical *ab initio* molecular orbital calculations of tin chemical shielding in several compounds, including the ones examined here, have been reported recently.[26,27] It is important to have a reliable chemical shielding scale for tin in order to assess the quality of such calculations. Finally, it was of interest to investigate the potential of MD simulations as a source of the dynamical information required to calculate NMR relaxation rates.

It should be stressed that two different and independent methods have been used in constructing the chemical shielding scale for tin. In neither of the methods used was it necessary to make any assumptions about the nature of the rotational motion of the molecules. The first method is purely experimental, based on gas-phase relaxation data of SnH_4 and the previously reported effective ^{1}H spin-rotation constant for methane obtained from molecular-beam measurements.[28] The second method uses liquid-state T_1 relaxation results combined with MD simulations. MD simulations have been performed to provide information about the angular motion of the molecules, which gives rise to the spin-rotation relaxation mechanism. Our confidence in the latter method has been increased by studying several relatively simple tin compounds as a function of temperature.

For details concerning ^{119}Sn NMR and tin chemistry in general, the reader is referred to reviews by Wrackmeyer[17] and Harrison,[29] respectively. The mechanism of ^{119}Sn NMR relaxation and the information available from such studies has been discussed in the literature.[30-33]

Theoretical Background

Spin-Rotation Relaxation. Spin-rotation relaxation involves the interaction of the nuclear magnetic moment with the magnetic field at the nucleus caused by the electron currents in a rotating molecule.[34,35] Early theoretical treatments of spin-rotation relaxation were given by Hubbard,[36] Blicharski,[37] and Bloom *et al.*[38] For spherical top molecules, where the relaxing nucleus is at the center of spherical symmetry, the spin-rotation tensor may be represented by a scalar, and the expression for the rate of SR relaxation is given as:[36]

$$\frac{1}{T_1^{\mathrm{SR}}} = \frac{8\pi^2 IkT}{\hbar^2} C_{\mathrm{eff}}^{\;2} \tau_{\mathrm{J}} \tag{1}$$

where I is the moment of inertia, C_{eff} is the spin-rotation constant in Hz, and τ_{J} is the angular momentum correlation time. For a general tetrahedral molecule, MX_4, $I = (8/3)m(\mathrm{X})r^2$, where $m(\mathrm{X})$ is the mass of the nucleus X, and r is the M−X bond length. In this study we use eq 1 to determine values of $C_{\mathrm{eff}}(^{119}\mathrm{Sn})$ from experimental ^{119}Sn NMR T_1^{SR} values and τ_{J} values calculated from molecular dynamics simulations.

For nuclei in a spherical top molecule which are not at the center of symmetry, the spin-rotation tensor no longer reduces to a scalar, and two components are required to characterize this tensor, $C_\perp$ and $C_\parallel$. For such nuclei, it is convenient to define the effective spin-rotation constant, C_{eff}:[39]

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$$C_{\mathrm{eff}}^2 = \left[\frac{1}{3}(C_\parallel + 2C_\perp)\right]^2 + \frac{4}{45}(C_\parallel - C_\perp)^2 \qquad (2)$$

or

$$C_{\mathrm{eff}}^2 = C_{\mathrm{av}}^2 + \frac{4}{45}(\Delta C)^2 \qquad (3)$$

where $C_\perp$ and $C_\parallel$ are the perpendicular and parallel components, respectively, of the spin-rotation coupling tensor. For nuclei at the center of spherical tops, $C_{\mathrm{eff}} = C_{\mathrm{av}}$ since $C_\perp = C_\parallel$.

Relationship between Spin-Rotation Constants and Chemical Shielding Constants. The formal theory of nuclear magnetic shielding in molecules was first presented by Ramsey.[40] Ramsey considered the average absolute chemical shielding constant of a nucleus, σ, to be a sum of a diamagnetic contribution and a paramagnetic contribution:

$$\sigma = \sigma_{\mathrm{d}} + \sigma_{\mathrm{p}} \qquad (4)$$

where σ_{d} depends only on the electron distribution in the electronic ground state, while the paramagnetic contribution, σ_{p}, depends also on the excited states. The first term is relatively straightforward to calculate, while the second term remains a challenge. However, Ramsey[40] and later Flygare[41,42] showed that the second-order paramagnetic term is intimately related to the nuclear spin-rotation tensor. Flygare and Goodisman[43] presented a simple approach for calculating σ if a reliable spin-rotation tensor is available from experiment. They showed that the absolute average chemical shielding of a nucleus is given by

$$\sigma = \sigma_{\mathrm{FA}} + \frac{1}{2}\frac{M}{m}\frac{C_{\mathrm{eff}}}{B}\frac{1}{g_{\mathrm{k}}} \qquad (5)$$

where σ_{FA} is the shielding constant of the nucleus in the isolated free atom, M is the proton mass, m is the electron mass, B is the so-called spectroscopic rotational constant, $\hbar/4\pi I$, and g_{k} is the nuclear g-factor. The second term of eq 5 is often denoted σ_{p}'. A similar formulation was also given by Deverell.[44]

For small molecules in the gas phase, nuclear spin-rotation constants can be obtained quite accurately from molecular-beam measurements.[28a,34,45] NMR data may also be used to obtain information about spin-rotation constants, but it is at best an indirect method of measuring spin-rotation constants. The NMR method generally involves using spin-rotation relaxation data and eq 1 to deduce values of C_{eff}. The problem, of course, is that in order to use eq 1 to calculate C_{eff}, one must know τ_{J}. In practice, experimentalists often obtain T_1 NMR data for some other nucleus in the same molecule that relaxes by the quadrupolar mechanism or dipole–dipole mechanism. These data are used to determine τ_2, and finally a motional model is used to estimate τ_{J} (*vide infra*).

Quadrupolar Relaxation and Molecular Rotations. For a quadrupolar nucleus with $I = 1$ at a site of axial symmetry, the spin-lattice relaxation time, T_1, is related to the rotational correlation time, τ_2:

$$\frac{1}{T_1^{\mathrm{Q}}} = \frac{3}{2}\pi^2(e^2qQ/h)^2\tau_2 \qquad (6)$$

where e^2qQ/h is the nuclear quadrupolar coupling constant in Hz. Here it is assumed that the rotational correlation time, τ_2, is short relative to the Larmor frequency (*i.e.*, $(\omega_0\tau_2)^2 \ll 1$). For ^{2}H nuclei, particularly relevant to the present study, the quadrupolar mechanism is generally several orders of magnitude larger than other mechanisms.

Motional Models. Several motional models have been developed to describe the rotational motion of small rigid molecules. Theoretically, spherical or linear molecules are the easiest to treat. The rotational motion of effectively spherical molecules is in general assumed to be diffusional in small steps and can be described with models given by Hubbard[36] and Steele[46] based on Brownian motion. Such motion can be described in terms of two correlation times,[36] τ_l and τ_{J} for the reorientational motion and the angular motion, respectively:

$$\tau_l = \frac{I}{l(l+1)kT\tau_{\mathrm{J}}} \qquad (7)$$

where I is the moment of inertia and l is the order of the spherical harmonics. In NMR relaxation, $l = 2$ for the reorientation of a specified molecular direction, thus according to the so-called Hubbard relationship:

$$\tau_2 = \frac{I}{6kT\tau_{\mathrm{J}}} \qquad (8)$$

This relationship is often used to estimate τ_{J} when τ_2 is known; however, its validity is clearly limited since eqs 7 and 8 are strictly applicable only when $\tau_{\mathrm{J}} \ll \tau_2$. There are some simple tests to determine whether or not it is reasonable to describe molecular rotations as diffusive.[47] For example, within the small-step diffusion model, it is clear from eqs 7 and 8 that $\tau_l\tau_{\mathrm{J}}T$ = constant; thus, within the Hubbard model, the two time constants are strictly related to each other. Another criterion which can be used is to determine the ratio τ_1/τ_2, which should approach 3.0 if the rotational motion proceeds through small-step diffusion. In MD simulations this test can be done easily since these two correlation times are routinely calculated.

Several models have been developed to deal with molecular rotations that do not proceed through small-step diffusion. Particularly significant are the so-called extended diffusion models developed by Gordon[39] and McClung.[48] According to these models, inertial angular jumps are stopped after certain small time intervals because of collisions. These collision times are taken from a Poisson distribution averaged around τ_{J}. In the so-called J-diffusion model both the magnitude and the orientation of the angular momentum are randomized after each collision, while in the M-diffusion model the magnitude of the angular momentum is constant. The impact of the collisions is characterized in a qualitative way by J-diffusion mimicking strong collisions and M-diffusion weak collisions.

One aspect of diffusive models is that, while they assume that the duration of the molecular collisions is short compared to τ_{J}, this is not the case if τ_{J} itself is extremely short. Under such conditions the motion is hardly diffusive because the time correlation function contains mainly the Gaussian part of the decay (the inertial region) where the molecule is assumed to rotate freely. The true diffusive behavior gives an exponential

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decay for the correlation function due to a long sequence of molecular collisions.

From the above discussion it should be clear that it is highly desirable to have a reliable method of determining τ_J without assuming a particular motional model. Herein lies the advantage of the MD simulations.

Experimental Section

Stannane and stannane-d_4 were prepared by reducing anhydrous tin tetrachloride with either $LiAlH_4$ or $LiAlD_4$ as previously described.[49]

NMR Measurements. Variable temperature ^2H and ^{119}Sn NMR spectra were obtained on a Nicolet 360 NB spectrometer (B_0 = 8.48 T) corresponding to ^2H and ^{119}Sn Larmor frequencies of 55.4 MHz and 134.6 MHz, respectively. Spin-lattice relaxation times were measured by the standard inversion recovery method.[2,50] The transmitter frequency was adjusted "on-resonance". Typical $\pi/2$ pulse widths for ^2H and ^{119}Sn were 50 μs and 40 μs, respectively. The T_1 values were obtained from a three parameter fit of the data, using 10 or more variable delays. Some ^1H and ^{119}Sn NMR measurements were also carried out using a Bruker AMX-400 spectrometer.

Computational Details. All the MD simulations in this study were carried out using the canonical NVT ensemble. Physical states corresponding to some of the experimental conditions were chosen. Experimental densities at normal pressure for the three liquids were used. The liquid densities for SnH_4, $Sn(CH_3)_4$, and $SnCl_4$ were taken from the literature.[51-53]

The simulation software is a modified version of McMoldyn.[54] In all the simulations, 256 molecules were placed in a cubic cell. Periodic boundary conditions were used together with the minimum image convention. The electrostatic interactions were treated using Ewald summation techniques. An equilibration of 50 ps was carried out followed by a 100 ps production run. The equations of motion were integrated after each 2.5 fs for $SnCl_4$ and $Sn(CH_3)_4$ and 1.25 fs for SnH_4.

The tin compounds in this study are rigid and rather heavy and therefore especially suited for classical MD simulations. Also, since the molecular systems are isotropic one-component liquids where the shape of the molecules is effectively spherical, the intermolecular interactions are well-described by potentials of the Lennard-Jones type. In fact, the rotational motion was also well described with standard Lennard-Jones parameters without any further adjustments. For tin in tetramethyltin and tin tetrachloride, xenon values were used for ϵ and σ. For stannane a slightly higher ϵ value has been used.[55] The methyl groups in tetramethyltin were treated using the united atom model by merging all four atoms to a single interaction point at the center of mass of the CH_3 group and by using the effective parameters of a methyl group. This is a standard technique in simulations when small spherical and more or less inert molecular entities are grouped together, such as methyl groups when the internal rotation is not of interest. It is done in general to freeze the fast motions of the hydrogens but also in order to save computing time.[10] The charges are estimated from the electronegativity of tin. Because of the high symmetry of the tetrahedral molecules, the charge–charge interactions cancel out rather effectively and could, in principle, have been omitted. However, at close distances, the neighboring molecules see fractions of molecules and the electrostatic interactions contribute to the close-range interactions. Table 1 contains the potential parameters employed in the simulations together with some essential information about the molecular geometries.

For liquid $Sn(CH_3)_4$ and $SnCl_4$, three complete simulations were carried out, while for SnH_4 and SnD_4, two simulations were performed. The temperatures investigated are evenly distributed over the liquid phase and were chosen to correspond to temperatures at which the NMR experiments were also carried out. The errors in the calculated correlation times, in the form of standard deviations, are estimated to be less than 6%. All the simulations were performed on an IBM RISC 6000/580 work station at the Dalhousie Chemistry Department.

Table 1. Some Selected Data Used to Construct the Molecular and Potential Models for the SnX_4 Molecules. Melting and Boiling Points Are Also Listed

	H(D)	CH_3	Cl
$\epsilon(Sn)/k$ (K)	260	230	230
$\sigma(Sn)$ (Å)	4.0	4.0	4.0
$q(Sn)$ ($\lvert e\rvert$)	0.8	0.8	0.8
$\epsilon(X)/k$ (K)	25	150	120
$\sigma(X)$ (Å)	2.2	3.7	3.4
$q(X)$ ($\lvert e\rvert$)	−0.2	−0.2	−0.2
$R(Sn-X)$ (Å)	1.7	2.18	2.28
$\angle(X-Sn-X)$ (deg)	109.5	109.5	109.5
T_m (K)	127	218	240
T_b (K)	221	351	388

Table 2. ^{119}Sn and ^2H Spin-Lattice Relaxation Times for Liquid Stannane and Stannane-d_4[a]

SnH_4		SnD_4		SnD_4	
T (K)	$T_1(^{119}Sn)$ (ms)	T (K)	$T_1(^{119}Sn)$ (ms)	T (K)	$T_1(^2H)$ (s)
212	70.9	210	105	209	26.2
190	101.5	187	148	186	19.8
171	134.6	168	207	168	16.4
159	190.8	153	275	153	14.4
143	249.4	142	366	139.5	10.3
		132	460	133	9.0
				130	8.3

[a] The errors in the T_1 values are estimated to be less than 5%.

Results and Discussion

Spin-Lattice Relaxation in Liquid Stannane. At atmospheric pressure, stannane exists as a liquid between 127 K and 221 K. Experimental NMR relaxation results for liquid stannane and stannane-d_4 as a function of temperature are given in Table 2. Over the temperature range investigated, ≈130–215 K, the ^{119}Sn spin-lattice relaxation is very efficient, 0.05 s $\leq T_1 \leq$ 0.5 s. The relaxation times decrease with increasing temperature, providing a strong indication that SR is the predominant T_1 relaxation mechanism for ^{119}Sn. At any given temperature, the ^{119}Sn T_1 value for liquid SnH_4 is about 30% shorter than the corresponding value for SnD_4; this observation is also consistent with the complete dominance of the SR mechanism (*vide infra*). Of the other possible mechanisms, CSA can be ruled out because the relaxing nucleus is at the center of a tetrahedral environment. Also, scalar coupling does not contribute to T_1 relaxation in stannane since very well resolved multiplets due to J-coupling are observed in the ^{119}Sn NMR spectra of SnH_4, $^1J(^{119}Sn,^1H) = -1933$ Hz, and SnD_4, $^1J(^{119}Sn,^2H) = -295.2$ Hz.[49] It is straightforward to show that the $^1H-^{119}Sn$ dipole–dipole relaxation mechanism makes a negligible contribution to the rate of ^{119}Sn T_1 relaxation. For example, using a Sn–H bond length of 1.70 Å[56] and a reorientational correlation time of 1.0 ps, the rate of ^{119}Sn DD relaxation is estimated to be about 0.0066 s^{-1}; that is, $T_1^{DD} \approx 150$ s. Also, the similar T_1 values observed for stannane and stannane-d_4 at any given temperature provide further evidence that the $^1H-^{119}Sn$ dipole–dipole mechanism is negligible. Thus the only relaxation mechanism of importance for ^{119}Sn T_1 relaxation in liquid stannane and stannane-d_4 is the spin-rotation mechanism. The consistently longer T_1 values observed for SnD_4 relative to SnH_4 result from the fact that, at any given temperature, τ_2 is longer for the

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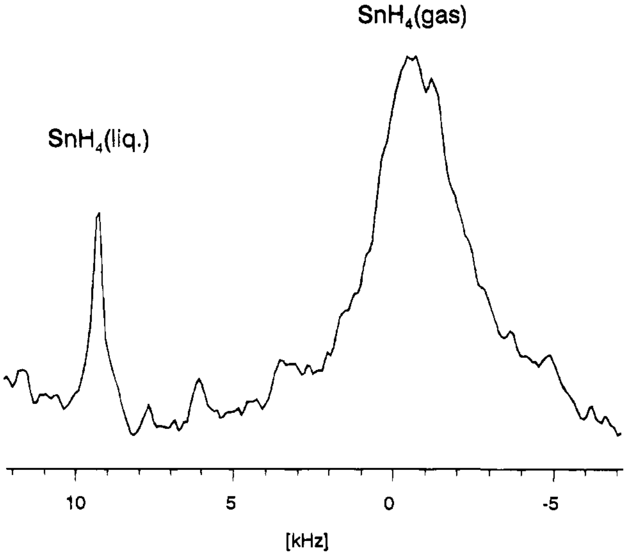

Figure 1. ^{119}Sn NMR spectrum of a $SnH_4(g)/SnH_4(l)$ mixture at 248 K.

heavier isotopomer (*i.e*, τ_J is shorter for SnD_4; hence T_1^{SR} is longer for SnD_4).

Over the temperature range ≈130 − 210 K, the ^2H T_1 values of stannane-d_4 increase with increasing temperature from approximately 8 s to 26 s, consistent with the complete dominance of the quadrupolar mechanism. Using data to be provided in a later section, it is straightforward to show that the spin-rotation mechanism makes a negligible contribution to the rate of deuterium spin-lattice relaxation; only the quadrupolar mechanism is important for ^2H.

The ^{119}Sn T_1 values for both liquid stannane and stannane-d_4 (Table 2) were plotted on a logarithmic scale versus the inverse temperature. A linear dependence was apparent, and, after fitting the data points using a regression analysis, the observed slopes yield activation energies of 4.4 ± 0.3 kJ/mol for both stannane and stannane-d_4. Arrhenius behavior is also found from the ^2H NMR relaxation data given in Table 2. In this case the activation energy for the reorientational motion of SnD_4 is 3.1 ± 0.2 kJ/mol. If the Hubbard relationship were valid for liquid stannane-d_4, the product $T_1^Q(^2H)T_1^{SR}(^{119}Sn)$ should be independent of temperature; however from the data in Table 2, this is clearly not the case.

^{119}Sn T_1 Relaxation in Gaseous SnH_4. The ^{119}Sn NMR spectrum of a gaseous sample of stannane containing a small amount of liquid at 248 K is shown in Figure 1. The ^{119}Sn gas-to-liquid shift for stannane is 73.9 ± 2 ppm at 248 K. In general, for any given gas, NMR peaks arising from the liquid are always at a higher frequency relative to those corresponding to the gas since the stronger intermolecular interactions in the liquid phase result in deshielding.[57] In this sense, stannane is no exception.

Measurements of the ^{119}Sn T_1 of stannane in the gas phase are difficult because the ^{119}Sn NMR peak is broad and the T_1 is very short (*vide infra*). The relaxation measurements were carried out at 248 K on the same sample that was used to obtain the spectrum shown in Figure 1. Using the inversion−recovery pulse sequence, the ^{119}Sn T_1 value for stannane in the gas phase was measured to be 117 ± 20 μs. Also, the ^{119}Sn NMR line width at half-height, $\Delta\nu_{1/2}(^{119}Sn)$, was 2900 ± 300 Hz, giving an approximate T_2 (neglecting other factors affecting the line width) of 110 ± 12 μs, close to the T_1 value measured directly. Similarly, under identical conditions the ^1H T_1 of gaseous stannane was 0.769 ± 0.040 s.

$C_{eff}(^{119}Sn)$ for SnH_4 Determined from Gas-Phase NMR Measurements. The ^{119}Sn spin-rotation constant for stannane can be calculated from the experimental gas-phase NMR relaxation results. The method used here has been previously described by Jameson.[22,24,58] Since both ^1H and ^{119}Sn nuclei in gaseous stannane relax *via* the spin-rotation mechanism, it is straightforward to show that:

$$\frac{T_1(^1H)}{T_1(^{119}Sn)} = \frac{C_{eff}^{\,2}(^{119}Sn)}{C_{eff}^{\,2}(^1H)} \tag{9}$$

The ratio on the left-hand side of eq 9 can be readily calculated using the gas-phase values of $T_1(^{119}Sn)$ and $T_1(^1H)$ given in the previous section: $T_1(^1H)/T_1(^{119}Sn) = 6570 \pm 600$. To proceed further it is necessary to determine $C_{eff}(^1H)$ for stannane. The following approach was used. A sample containing a mixture of CH_4 and SnH_4 gases was prepared and the ^1H NMR frequencies for methane and stannane were measured. The ^1H chemical shift difference was found to be 3.303 ± 0.005 ppm with the protons of methane being more shielded. Using eq 5, it is straightforward to show that the average ^1H shielding difference is given by:

$$\sigma(CH_4) - \sigma(SnH_4) = \frac{M}{2mg_H}\left[\frac{C_{eff}(CH_4)}{B(CH_4)} - \frac{C_{eff}(SnH_4)}{B(SnH_4)}\right] \tag{10}$$

Spin-rotation constants for ^1H and ^{13}C in methane in its ground vibrational state are accurately known from molecular beam experiments.[59] For the protons of methane, $C_{av} = 10.4 \pm 0.1$ kHz and $C_{\parallel} - C_{\perp} = 18.5 \pm 0.5$ kHz; thus $C_{eff} = 11.8 \pm 0.2$ kHz. Using eq 10, the proton spin-rotation constant for stannane is 4.65 ± 0.05 kHz. Substituting this value in eq 9 gives the ^{119}Sn spin-rotation constant for stannane, $C_{eff} = 377 \pm 35$ kHz.

It should be noted that in previous ^1H, ^{13}C, and ^{29}Si NMR studies of gaseous methane[60] and gaseous silane,[24] the Jamesons found these nuclei to relax *via* the spin-rotation mechanism. One might anticipate that the dipolar mechanism would be important, particularly in the case of methane since both the ^{13}C and ^1H nuclei have relatively large magnetogyric ratios and the $^{13}C-^1H$ and $^1H-^1H$ separations are relatively small; however, this is not the case.

$C_{eff}(^{119}Sn)$ from Liquid-Phase ^{119}Sn NMR Relaxation Data and MD Simulations. The method used here is based on the fact that eq 1 can be rewritten as:

$$\frac{1}{T_1^{SR}} = \frac{8\pi^2 IkT}{\hbar^2} C_{eff}^{\,2} \int_0^{\infty} \frac{\langle J(t)\cdot J(0)\rangle}{\langle J(0)\cdot J(0)\rangle}\, dt \tag{11}$$

where $J(t)$ is the time-dependent molecular angular momentum vector, a classical analogue to the rotational angular momentum in the spin-rotation Hamiltonian. The MD simulations were used to generate trajectories for the angular momentum vectors and time correlation functions were calculated. The experimental ^{119}Sn T_1 values were combined with the corresponding MD simulated angular momentum correlation times, and eq 11 was used to calculate ^{119}Sn spin-rotation constants.

As already mentioned, the ^{119}Sn spin-lattice relaxation times for liquid $Sn(CH_3)_4$ and liquid $SnCl_4$ as a function of temperature were previously reported by Lassigne and Wells[18] and by

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Table 3. Simulated Correlation Times and Other Data for Stannane-d_4, Stannane, Tetramethyltin, and Tin Tetrachloride, (Experimental Values in Parentheses)

molecule	temp (K)	D_v (10^{-9} m^2/s)[a]	τ_J (fs)	τ_1 (ps)	τ_2 (ps)	T_1^Q (s)
SnD_4	133	3.05 ± 0.2	20.1 ± 1.2	4.0 ± 0.4	1.5 ± 0.1	9.9 ± 0.5[b] (9.0 ± 0.5)
	168	4.30 ± 0.3	32.8 ± 2.0	2.8 ± 0.2	1.1 ± 0.1	14.5 ± 1.7[b] (16.4 ± 0.8)
SnH_4	143	3.98 ± 0.2	17.3 ± 1.0	3.8 ± 0.3	1.4 ± 0.10	
	171	5.10 ± 0.3	25.2 ± 1.5	2.1 ± 0.2	0.8 ± 0.05	
$Sn(CH_3)_4$	252	0.88 ± 0.05	33.0 ± 2.0	14.7 ± 1.1	5.1 ± 0.4	
	276	1.38 ± 0.08	40.0 ± 2.4	11.6 ± 0.9	4.2 ± 0.3	
	300	2.02 ± 0.12	50.0 ± 3.0	8.6 ± 0.6	3.0 ± 0.2	
$SnCl_4$	298	1.70 ± 0.1	77.0 ± 4.6	13.9 ± 1.2	5.0 ± 0.4	21.9 ± 3.6[c] (22.0 ± 1.7)
	328	2.94 ± 0.2	87.0 ± 5.2	10.9 ± 1.1	3.9 ± 0.3	28.2 ± 4.3[c]
	358	4.33 ± 0.3	115 ± 7	7.8 ± 0.9	2.8 ± 0.2	38.7 ± 5.2[c]

[a] Translational diffusion coefficients are calculated from $D_v = k_B T/M\tau_v$, where k_B is the Boltzmann constant, M is the molecular mass, and τ_v is the linear velocity correlation time. [b] ^2H relaxation time (for details, see the text). [c] ^{35}Cl relaxation time (for details, see the text).

Table 4. Simulated ^{119}Sn Spin-Rotation Constants (Using Eq 1) and Paramagnetic Terms (Using Eq 5) for the Magnetic Shielding of Tin in Stannane-d_4, Stannane, Tetramethyltin, and Tin Tetrachloride[a]

molecule	T (K)	R_1 (s^{-1})	T_1 (ms)	C_{eff}, (kHz)	σ_p' (ppm)	σ (ppm)
SnD_4	133	2.17 ± 0.10	460 ± 24	179.3 ± 10.0	−2425 ± 126	2664 ± 126
	168	4.85 ± 0.24	206 ± 10	186.7 ± 9.7	−2524 ± 131	2562 ± 131
SnH_4	143	4.05 ± 0.20	249 ± 12	358.4 ± 18.1	−2422 ± 122	2663 ± 122
	171	7.41 ± 0.37	135 ± 7	368.8 ± 18.6	−2493 ± 132	2593 ± 132
$Sn(CH_3)_4$	252	0.740 ± 0.09	1351 ± 16	16.9 ± 1.3	−2809 ± 230	2277 ± 230
	276	1.029 ± 0.12	972 ± 12	17.3 ± 1.4	−2874 ± 240	2211 ± 240
	300	1.324 ± 0.16	755 ± 9	17.2 ± 1.7	−2855 ± 286	2230 ± 286
$SnCl_4$	298	0.625 ± 0.04	1600 ± 110	5.83 ± 0.35	−2497 ± 151	2588 ± 151
	328	0.830 ± 0.06	1200 ± 80	6.04 ± 0.36	−2585 ± 153	2500 ± 153
	358	1.25 ± 0.09	800 ± 60	6.16 ± 0.39	−2636 ± 167	2450 ± 167

[a] For details, see the text.

Sharp,[19,20] respectively. In each case the spin-rotation mechanism was found to be the only important mechanism for longitudinal relaxation of ^{119}Sn.

Stannane and Stannane-d_4. Table 3 contains some simulation data for various correlation times at two different temperatures for both stannane and stannane-d_4 as neat liquids. The reorientational correlation times τ_1 and τ_2 were obtained as integrals over the time correlation functions for the first and the second order Legendre polynomials, $l = 1$ and 2, respectively:

$$\tau_l = \int_0^\infty \langle p_l(\boldsymbol{u}(t)\cdot\boldsymbol{u}(0))\rangle \, dt \qquad (12)$$

where $\boldsymbol{u}$ is the time-dependent unit vector attached to the molecule along one of the Sn−H (or Sn−D) bonds. The tumbling motion of the vector as a function of time was averaged over all the molecules.

The angular momentum correlation times, τ_J, are generally very short; all are found to be less than 0.1 ps. The reorientational correlation times, τ_2, are about two orders of magnitude larger. Based on the simulation results, rotations of stannane would not strictly be considered diffusional since the $\tau_J \ll \tau_2$ requirement has not been met. This is particularly evident from the ratio, τ_1/τ_2, which is between 2.5 and 2.7. Applying the Hubbard relationship (eq 8), gives τ_J values approximately a factor of 2 smaller than the simulated ones.

The quadrupolar relaxation time can be calculated using the simulated τ_2 values and eq 8. These are quoted in Table 3 together with the experimental values. The ^2H quadrupolar coupling constant used for SnD_4 was 66 ± 5 kHz; this value was determined from the $T_1(^2H)$ minimum measured on a solid sample.[61] On the basis of our experience, this value probably represents a lower limit for the value of the deuterium quadrupolar coupling constant.[62,63]

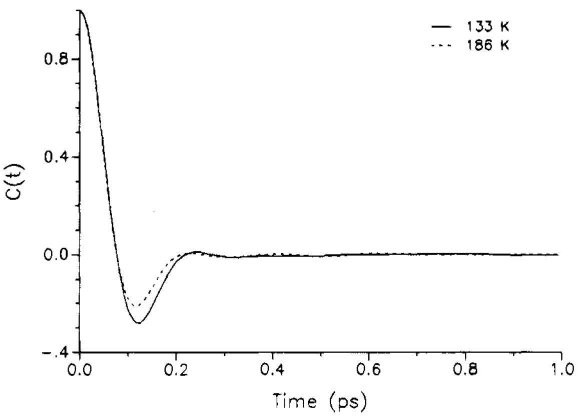

Figure 2. Angular momentum autocorrelation functions for SnD_4(l) at 133 and 186 K.

The simulated τ_J values from Table 3 and the SR relaxation times from Table 2 can be used to calculate the effective spin-rotation constant according to eq 1. Results from the calculations are given in Table 4. For stannane-d_4, the value of C_{eff} determined at 133 K and at 168 K is the same within experimental error; the average is 183 kHz. Similarly, the value for stannane is 364 kHz, in excellent agreement with the value deduced from the gas-phase relaxation data in the previous section.

Figure 2 displays the simulated angular momentum autocorrelation functions for SnD_4 at 133 K and 186 K. One

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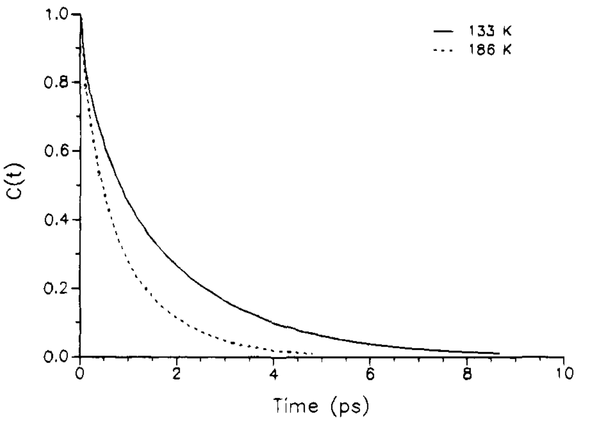

Figure 3. Reorientational autocorrelation functions for SnD_4(l) at 133 and 186 K.

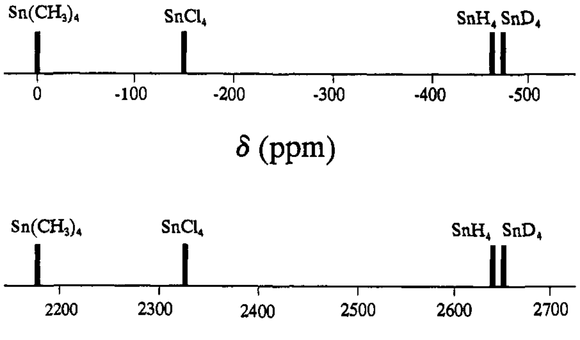

Figure 4. Tin chemical shift and absolute chemical shielding for molecules treated in this study: top, tin chemical shift scale; bottom, absolute shielding scale for tin.

characteristic feature of these curves is the reversal of the angular momentum, which is apparent as a rather deep negative well in both time correlation functions, deeper at the lower temperature. This behavior is common for molecules with anisotropic potentials but appears also for more spherical molecules when the temperature is lowered and the density increased, as discussed by Lynden-Bell and McDonald in their simulation study of tetrahedral model molecules.[64] This behavior, also known as the cage effect, is due to librational motion of molecules in their first solvent cage. It should be mentioned that neither Langevin models nor the *J*-diffusion model give negative time correlation functions, since both models predict exponential decays for angular momentum correlation functions.

Figure 3 shows the reorientational autocorrelation functions for stannane-d_4 at 133 K and 186 K. These curves have a clear exponential decay. At the higher temperature, the curve approaches 0 at 5 ps, and at the lower temperature the curve has decayed to 0 close to 10 ps. The curves for SnH_4 (not shown) were qualitatively the same.

Tetramethyltin. At atmospheric pressure, tetramethyltin is a liquid between 218 K and 351 K. In this study, we used the experimental ^{119}Sn T_1 data of Lassigne and Wells[18] and angular momentum correlation times from the MD simulations to deduce $C_{eff}(^{119}Sn)$ (see Tables 3 and 4). Lassigne and Wells also used their experimental NMR data to estimate a ^{119}Sn spin-rotational constant for $Sn(CH_3)_4$; however, they used motional models to calculate angular momentum correlation times. Thus, assuming that the *J*-diffusion model is applicable for liquid $Sn(CH_3)_4$ at 300 K, they calculated C_{eff} = 17.7 kHz, while for *M*-diffusion C_{eff} = 10.4 kHz. Also, the molecular geometry used here for tetramethyltin differs slightly from that used in ref 18. In this study we use the results of a recent crystallographic study of $Sn(CH_3)_4$ by Krebs *et al.*[65] They found that three of the four Sn−C bond lengths are equivalent, r_{SnC} = 2.138(6) Å, and the other is slightly shorter, 2.102(8) Å. The angle between the equivalent bonds was 109.6° while the remaining angles were 109.3°. Lassigne and Wells[18] used r_{SnC} = 2.18 Å and used the regular tetrahedral angle, 109.47°, for the C−Sn−C bond angles.

For the MD simulations the methyl group was represented by a single mass point (see Computational Details). The distance from the tin atom to the center-of-mass of the methyl group, used in the MD simulation, is 2.18 Å. It gives effectively a slightly shorter Sn−C distance compared to the all atom model. Consequently, it gives a somewhat smaller moment of inertia (316.4×10^{-47} kg m^2) compared to the value reported by Lassigne and Wells (344.0×10^{-47} kg m^2).[18]

Three temperatures from the measurements of Lassigne and Wells[18] were chosen to carry out the MD simulations, namely, 252 K, 276 K, and 300 K. While the calculated angular correlation times (see Table 3) are about the same order of magnitude as in the case of stannane, the reorientational correlation times are considerably longer than for stannane, making the Hubbard relationship more applicable for $Sn(CH_3)_4$. The ratio τ_1/τ_2 gives values close to 3, indicating that the small-step diffusion model is a reasonably good assumption. At 252 K, 276 K, and 300 K, the Hubbard relationship gives τ_J values of 29, 33, and 42 fs, respectively, compared to 33, 40, and 50 fs, respectively, obtained from the MD simulations.

From ^{1}H and ^{13}C NMR relaxation measurements at 300 K, Lassigne and Wells determined τ_2 = 2.82 ps for the overall rotations of $Sn(CH_3)_4$.[18] Although it is necessary to make a number of assumptions in obtaining this value, it agrees well with the value from the MD simulations, 3.0 ps at the same temperature. Using τ_2 = 2.82 ps and the *J*-diffusion model, Lassigne and Wells[18] found τ_J = 49 fs, while a value of 50 fs was obtained from the present MD simulations. Note that in the limit of small-step diffusion, the *J*-diffusion model and the Hubbard relationship yield the same values of τ_J. On the other hand, the *M*-diffusion model gives angular momentum correlation times three times longer, *i.e.*, τ_J = 147 fs in the case of $Sn(CH_3)_4$(l) at 300 K. Clearly, the results of the *M*-diffusion model are inconsistent with the MD simulations.

Lassigne and Wells[18] calculated ^{119}Sn spin-rotation constants for tetramethyltin using both values of τ_J. Using τ_J = 49 fs (*J*-diffusion), C_{eff} = 17.7 kHz; with τ_J = 147 fs (*M*-diffusion), C_{eff} = 10.4 kHz. These values are based on the $1/T_1^{SR}$ value of 1.5 s^{-1} for ^{119}Sn in a neat liquid sample at 300 K. Using this T_1 value and the MD simulated angular momentum correlation time, a value of 17.2 kHz is obtained for C_{eff}. The difference between the value obtained in this study and the *J*-diffusional value obtained by Lassigne and Wells[18] arises mainly from small differences in the moment of inertia.

The values of $C_{eff}(^{119}Sn)$ calculated using the combined NMR and MD data at 252 K, 276 K, and 300 K are in excellent agreement. The average value is 17.1 kHz.

Tin Tetrachloride. At atmospheric pressure, tin tetrachloride exists as a liquid between 240 K and 388 K. Both ^{119}Sn NMR and ^{35}Cl NMR relaxation data are available for liquid $SnCl_4$.[19,20,66] On the basis of an extensive ^{119}Sn NMR study, Sharp has determined $C_{eff}(^{119}Sn)$ = 6.1 kHz.[19,20]

The MD simulation results for liquid $SnCl_4$ are given in Table 3. The angular momentum and reorientational correlation times

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Table 5. Tin Chemical Shifts and Absolute Shielding Constants (ppm)

molecule	chemical shielding difference[a] $\sigma(Sn(CH_3)_4) - \sigma(SnX_4)$	$\sigma(SnX_4)$[b]	$\sigma(Sn(CH_3)_4)$[c]
SnH_4(g)	−541.5	2537 ± 284	1996
SnD_4(l)	−469.2	2613 ± 131	2144
SnH_4(l)	−467.6	2628 ± 132	2160
$SnCl_4$(l)	−147.8	2512 ± 167	2364
$Sn(CH_3)_4$(l)	0.0	2240 ± 286	2240
			av 2181

[a] The three stannane samples were at 248 K while $SnCl_4$ and $Sn(CH_3)_4$ were at 300 K. [b] Values for liquid samples from ^{119}Sn NMR T_1 data and MD simulations; see Table 4 for details. Values for SnH_4(g) from gas-phase relaxation data; see text. [c] Absolute shielding constant for tin in $Sn(CH_3)_4$(l) calculated from the previous two columns, average value 2181 ppm.

are of comparable magnitude to those obtained for tetramethyltin. However, by comparing the simulated τ_1 and τ_2 values, it is evident that the simulated reorientational motion of $SnCl_4$ is not as clearly diffusive as it was for $Sn(CH_3)_4$. Using eq 8 and the simulated τ_2 values at 298 K, 328 K, and 358 K yields τ_J values of 66, 77, and 98 fs, respectively, while the corresponding simulated values are 77, 87, and 115 fs, respectively.

The MD simulation results for $SnCl_4$ are in surprisingly good agreement with the experimental results of Sharp.[19,20] The reorientational correlation time $\tau_2 = 5.0$ ps at 298 K from the MD simulation is the same as that reported by Sharp. Consequently, the calculated ^{119}Sn spin-rotation constant from simulation should be close to the value obtained by Sharp. This is the case, but only when the chlorine mass as given for the natural abundant mixture of chlorine isotopes is used. It may be noted that if the chlorine mass is calculated from the moment of inertia found in Table 1 of ref 19 and using the Sn−Cl distance of 2.28 Å quoted in the text, it turns out to be for chlorine-37. The mass 35.453 is used in the present work for the chlorine atoms throughout the simulations for $SnCl_4$.

Absolute Scale for Tin Chemical Shielding. Using the ^{119}Sn spin-rotation constants obtained in the previous section, we have used eq 5 to calculate values of the paramagnetic term, $\sigma_p'(Sn)$, and the total absolute shielding constant, $\sigma(Sn)$, relative to the bare nucleus. Values for stannane, tetramethyltin, and tin tetrachloride are given in Table 4. The free atom shielding constant for tin, $\sigma_{FA} = 5085.6$ ppm, was taken from ref 67. Experimental tin chemical shifts and the absolute shielding constants are summarized in Table 5. Using the experimental ^{119}Sn chemical shifts measured directly from frequency differences and the absolute tin shielding constants obtained from the spin-rotation constants, it is straightforward to calculate an absolute tin shielding constant for $Sn(CH_3)_4$(l) (see last column of Table 5). Using these data, a "**best**" semiexperimental value, the average, can be calculated. The value obtained is 2181 ppm. In the discussion that follows we will take $\sigma(Sn(CH_3)_4) = 2180 \pm 200$ ppm. This scale could be perhaps characterized as a "semiexperimental" absolute chemical shielding scale for tin. The error quoted here is expected to be an upper limit.

In spite of the good agreement between the calculated ^{119}Sn spin-rotation constants obtained in this study and the results reported by Lassigne and Wells[18] for tetramethyltin and by Sharp[19] for tin tetrachloride, the absolute shielding values are found to be somewhat different. First, the value of the paramagnetic shielding, $\sigma_p'(Sn)$, for $Sn(CH_3)_4$ is reported as −3200 ppm at 300 K by Lassigne and Wells,[18] while our value is −2855 ± 286 ppm at the same temperature. The difference corresponds roughly to the difference in moment of inertia between the molecular models used in this work and the one used by Lassigne and Wells.[18]

In the case of tin tetrachloride, Sharp reports −2760 ppm as the paramagnetic contribution, σ_p', at 298 K.[19] The corresponding value from our calculations is −2497 ± 151 ppm, given in Table 4. This disagreement is somewhat puzzling, since there is such good agreement between the ^{119}Sn spin-rotation constants calculated in both studies. One possible explanation could be that, although the same geometry was used in both studies, different chlorine masses may have been used in the calculation of $C_{eff}(^{119}Sn)$ and σ_p'. Another possible source contributing to the discrepancy could be that different nuclear constants may have been used. The nuclear *g*-factor of −2.0828 which is based on the magnetogyric ratio of -9.9756×10^7 rad T^{-1} s^{-1} is used here; however, a more precise value is available from the present study (*vide infra*). Concerning the magnetogyric ratios for ^{119}Sn, the literature seems to be slightly confusing. For example, the values -9.9756×10^7 and -10.021×10^7 rad T^{-1} s^{-1} are quoted in ref 68. Other examples of different magnetogyric ratios are easy to find.[69,70]

If tetramethyltin is used as a reference, as is normally done in tin NMR experiments, we obtain a calculated chemical shift of −272 ppm for $SnCl_4$. This can be compared with the experimental value, −147.8 ppm, reported by Lassigne and Wells.[18] Under the circumstances this is surprisingly good agreement. It is obtained as a difference between two large quantities, after several steps of calculations with uncertainties and approximations in the geometric and potential models for two different molecules.

For stannane, the calculated shift from $Sn(CH_3)_4$ is −388 ppm, while the experimental value is −467.6 ppm at 248 K. Based on the observed temperature variation, the ^{119}Sn chemical shift at room temperature can be extrapolated to −480 ppm for neat stannane. The calculated shift between SnH_4 and SnD_4 is much too small and uncertain to be significant. The measured shift difference is only −1.603 ppm.[49]

We would like to mention that calculated values of σ are quite sensitive to the molecular geometry used. For example, in the case of $SnCl_4$, an increase in $r_{Sn\text{-}Cl}$ of 0.01 Å will decrease the calculated tin shielding by approximately 10 ppm. Knowing that molecular properties and average geometries in liquids are affected by intermolecular interactions, the use of gas-phase or solid-state determined bond lengths and angles in studies of liquids should be questioned. Unfortunately, these geometries are often the only ones available.

The absolute chemical shielding value for tin in the gaseous SnH_4 is calculated to be 2537 ± 234 ppm using the spin-rotation constant, $C_{eff}(^{119}Sn) = 377 \pm 35$ kHz, obtained from the gas-phase results.

Finally, we comment on the temperature dependence observed in the measured chemical shifts. For the ^{119}Sn chemical shift in SnD_4 we observed a linear decrease of 0.26 ± 0.2 ppm/K when the temperature was increased. This is based on four measurements at 132, 142, 153, and 212 K, respectively. The following resonance frequency shifts for ^{119}Sn from the 212 K value were observed: 2039 Hz (153 K), 2507 Hz (142 K), and 2869 Hz (132 K).

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(67) Malli, G.; Froese, C. *Int. J. Quantum. Chem. Symp.* **1967**, *1*, 95.

(68) *The Multinuclear Approach to NMR Spectroscopy*; Laszlo, P., Ed.; Academic Press: New York, 1985 (p xiv; $\gamma(^{119}Sn) = -9.9756 \times 10^7$ rad T^{-1} s^{-1}) (p 345; $\gamma(^{119}Sn) = -10.021 \times 10^7$ rad T^{-1} s^{-1}).

(69) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; John Wiley: New York, 1981 (p 168: $\gamma(^{119}Sn) = -9.9756 \times 10^7$ rad T^{-1} s^{-1}).

(70) Harris, R. K. *Nuclear Magnetic Resonance*; Longman: New York, 1986 (p 236: $\gamma(^{119}Sn) = -10.021 \times 10^7$ rad T^{-1} s^{-1}).

Table 6. Comparison of Calculated and Experimental Tin Shielding Constants (ppm)

molecule	*ab initio* MO calculations ref 26	*ab initio* MO calculations ref 27	exptl value (this study)[a]
SnH_4	3683	3403	2722
$SnCl_4$	3410	2904	2328
$Sn(CH_3)_4$	3208	3006	2180

[a] Obtained from the experimental tin chemical shifts in Table 5 and by assuming $\sigma(Sn(CH_3)_4)$ (l)) = 2180 ppm. Note that the values for $Sn(CH_3)_4$ and $SnCl_4$ are liquid-phase values, while for SnH_4 the gas-phase value is used. For SnH_4 the gas to liquid chemical shift is 73.9 ± 2 ppm.

Comparison of σ(Sn) Obtained by Quantum Mechanical Calculations and Experiment. Quantum mechanical calculations of the tin chemical shielding in stannane and several other tin(IV) compounds have been recently reported by Nakatsuji *et al.*[26,27] These authors have used the finite perturbation (FPT) method with a common gauge origin at the tin nucleus. Experimental and theoretical results for stannane, tin tetrachloride, and tetramethyltin are summarized in Table 6. Using rather small basis sets, Nakatsuji *et al.*[26] report $\sigma = 3683$ ppm for SnH_4, $\sigma = 3410$ ppm for $SnCl_4$, and $\sigma = 3208$ ppm for $Sn(CH_3)_4$. In general, the calculations successfully describe the relative ^{119}Sn chemical shifts in the series of tin compounds investigated. Indeed, the observed U-shape in the $Sn(CH_3)_{4-x}Cl_x$ series as well as the linear change in the $Sn(CH_3)_{4-x}H_x$ series were reproduced by the calculations. However, both the method used by Nakatsuji *et al.* concerning the gauge-origin and also the use of modest basis sets have received criticism in the literature.[71]

In a subsequent paper Nakatsuji *et al.*[27] used slightly larger basis sets to recalculate ^{119}Sn σ values for the same set of tin compounds. The relative chemical shifts obtained using the larger basis set were, in fact, in worse agreement with experiment. For example, the calculated tin chemical shift of $SnCl_4$ relative to $Sn(CH_3)_4$ is +102 ppm, while the experimental value is −147.8 ppm. However, note that the calculated absolute shielding constants agree better with experiment in the more recent calculations! According to Jameson,[71] when small basis sets are used the paramagnetic term is underestimated in the calculations. This statement is supported by the results presented here.

Magnetogyric Ratio for ^{119}Sn. It is of interest to look at the magnetogyric ratio for ^{119}Sn somewhat more closely. Most NMR text books give $\gamma(^{119}\text{Sn}) = -9.9756 \times 10^7$ rad T^{-1} s^{-1}, which is based on the work by Proctor from 1950.[72] Proctor used $\mu(^{23}\text{Na}) = 2.2166 \pm 0.0004\ \mu_N$ as a reference, and using a 18.9 MHz spectrometer (^{1}H frequency) and solutions of 5.3 M $SnCl_2$ with 1.0 M $MnCl_2$ and of 0.69 M NaCl with 1.0 M $MnCl_2$ he obtained $\mu(^{119}\text{Sn}) = 1.0411 \pm 0.0002\ \mu_N$. This value is without chemical shielding corrections. Here μ_N is the nuclear magneton, $5.050\,786\,6 \times 10^{-27}$ J T^{-1}.[73] Some other NMR text books quote $\gamma(^{119}\text{Sn}) = -10.021 \times 10^7$ rad T^{-1} s^{-1}, which seems to contain a correction based on the free atom diamagnetic shift 5085.6 ppm for tin,[67] thus assuming the paramagnetic contribution to chemical shielding is 0.

We are in a position to calculate a more accurate value for $\gamma(^{119}\text{Sn})$. Using proton data as reference, we can calculate $\gamma(^{119}\text{Sn})$ from:

$$\gamma(^{119}\text{Sn}) = \gamma(^1\text{H})\frac{\nu(^{119}\text{Sn})\ (1 - \sigma(^1\text{H}))}{\nu(^1\text{H})\ (1 - \sigma(^{119}\text{Sn}))} \qquad (13)$$

Here $\gamma(^1\text{H}) = 26.752\,212\,8(81) \times 10^7$ rad T^{-1} s^{-1} can be found in the latest edition of fundamental constants.[74] Measurement on tetramethyltin gave $\nu(^1\text{H}) = 400.136\,148(5)$ MHz and $\nu(^{119}\text{Sn}) = 149.213\,227(2)$ MHz. The ratio of $\nu(^{119}\text{Sn})/\nu(^1\text{H})$ is 0.372 906 33 after subtracting 0.52 ppm, which is the difference between proton shifts of $Sn(CH_3)_4$ and $Si(CH_3)_4$.[75] Using the value of $\sigma(\text{Sn}) = 2180$ ppm obtained in this study, a value of 30 ppm for σ(H) in $Sn(CH_3)_4$, we obtain $\gamma(^{119}\text{Sn}) = -9.997\,559(8) \times 10^7$ rad T^{-1} s^{-1}. Of course, one can calculate an accurate value for $\gamma(^{117}\text{Sn})$, since $\nu(^{119}\text{Sn})/\nu(^{117}\text{Sn}) = 1.046\,541$;[76] thus $\gamma(^{117}\text{Sn}) = -9.552\,955(8) \times 10^7$ rad T^{-1} s^{-1}.

Conclusions

A combination of NMR relaxation data and MD simulations have made it possible to determine ^{119}Sn spin-rotation constants for stannane, tetramethyltin, and tin tetrachloride. Also, gas-phase NMR relaxation data have been used to provide an independent experimental ^{119}Sn spin-rotation constant for stannane. The derived ^{119}Sn spin-rotation constant have led to a set of internally consistent values for the absolute tin shielding constant in tetramethyltin: $\sigma = 2180 \pm 200$ ppm. This value will provide a benchmark for future quantum mechanical calculations of tin shielding tensors.

In summary, the results obtained here are clearly encouraging for the continued use of MD simulations in close combination with NMR relaxation measurements to study molecular motions and interactions in liquids and solutions.

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