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Gas-Phase NMR Measurements, Absolute Shielding Scales, and Magnetic Dipole Moments of ^{29}Si and ^{73}Ge Nuclei

W. Makulski,[†] K. Jackowski,*,[†] A. Antušek,[‡,§] and M. Jaszuński[‡]

Laboratory of NMR Spectroscopy, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland, Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warszawa, Poland, and Slovak University of Technology in Bratislava, Faculty of Material Science and Technology in Trnava, Paulinska 16, 917 24 Trnava, Slovak Republic

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New gas-phase NMR measurements of the shielding constants of ^{29}Si, ^{73}Ge, and ^{1}H nuclei in SiH_4 and GeH_4 are reported. The results, extrapolated to zero density, provide accurate isolated molecule values, best suited for comparison with theoretical calculations. Using the recent ab initio results for these molecules and the measured chemical shifts, we determine the absolute shielding scales for ^{29}Si and ^{73}Ge. This allows us to provide new values of the nuclear magnetic dipole moments for these two nuclei; in addition, we examine the dipole moments of ^{13}C and ^{119}Sn.

Introduction

The nuclear magnetic shielding constant is considered to be a property characterizing the nucleus in a specific molecule. In agreement with this interpretation, in the theoretical studies the NMR shielding constants are determined from the structure of the isolated molecule of interest. In the experiment, however, the magnetic shielding of a nucleus in a molecule is affected by both intermolecular interactions and intramolecular motion. These effects can be observed and examined in detail in gas-phase NMR spectra. They lead to the dependence of a shielding constant $\sigma(T,\rho)$ on density and temperature:[1,2]

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + ... \qquad (1)$$

where $\sigma_0(T)$ is the shielding in a molecule free from intermolecular interactions, and the next terms (with the coefficients $\sigma_1(T)$, $\sigma_2(T)$...) are dependent on the density ρ and describe the intermolecular interactions in gases. For most gaseous compounds at constant temperature, the shielding $\sigma(T)$ varies linearly with density if the pressure of the gas remains within moderate limits. In such a case, $\sigma_2(T)$ and the higher-order coefficients in eq 1 can safely be ignored, and the remaining parameters, that is, $\sigma_0(T)$ and $\sigma_1(T)$, are available from the linear equation. To summarize, accurate theoretical ab initio values for an isolated molecule cannot be directly compared to experimental data available from a single measurement; the density-dependent shielding must be studied, and the results have to be analyzed according to eq 1.

Moreover, NMR experiments allow one to measure only the shielding difference ($\Delta\sigma_i$) with respect to a primary reference compound:

$$\Delta\sigma_i = \sigma_i - \sigma_{REF} \qquad (2)$$

The absolute shielding constant of a reference molecule (σ_{REF}) must be obtained from another source. In contrast, the increasingly accurate ab initio values of the absolute shielding constants describe the shielding due to all of the electrons, thus with respect to a bare nucleus. There are some experimental methods that can be used to estimate absolute nuclear shielding in chosen reference molecules,[3] but the problem is not trivial and such methods can be successfully applied only for some light nuclei. The increasing ability to perform reliable theoretical calculations of nuclear magnetic shielding allows the direct theoretical determination of shielding in reference molecules. For small molecules, such calculations may presently provide in addition to the shielding constant for the rigid molecule at its equilibrium configuration also the rovibrational corrections needed to describe the temperature effects in the shielding. Once the shielding of a reference molecule is known (σ_{REF}), all chemical shifts measured relative to this standard molecule deliver information on nuclear magnetic shielding in other chemical compounds and form the absolute shielding scale of an observed nucleus.

According to the IUPAC recommendation given in a recent report,[4] the NMR chemical shift (δ_i) is always measured as the difference of resonance frequencies of a sample (ν_i) and a reference molecule (ν_{REF}) with a high-frequency-positive convention:

$$\delta_i = \frac{\sigma_{REF} - \sigma_i}{1 - \sigma_{REF}} = \frac{\nu_i - \nu_{REF}}{\nu_{REF}}; \quad B_0 = \text{constant} \qquad (3)$$

where B_0 is the external magnetic field. As shown by eq 3, the resonance frequency (ν_i) is proportional to the chemical shift (δ_i) if the resonance frequency of a reference molecule (ν_{REF}) is really stable. Modern spectrometers permit the determination and control of frequencies with high precision. This enables accurate measurements of the chemical shifts, from the observation of the ν_i and ν_{REF} resonance frequencies at the constant external magnetic field B_0. Moreover, the chemical shift is approximately equal to the shielding difference ($\Delta\sigma_i$) of eq 2. Such an approximation is sufficiently accurate for the light nuclei when σ_{REF} does not exceed 2000 ppm, and at the same time the errors from other sources are more significant for

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* Corresponding author. E-mail: kjack@chem.uw.edu.pl.

[†] University of Warsaw.

[‡] Polish Academy of Sciences.

[§] Slovak University of Technology in Bratislava.

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heavier nuclei. In the gas phase, the observed frequency of a nucleus may also be written in terms of a virial expansion, in the same way as the nuclear magnetic shielding in eq 1:

$$\nu(T,\rho) = \nu_0(T) + \nu_1(T)\rho + \nu_2(T)\rho^2 + ... \qquad (4)$$

where $\nu_0(T)$ is the resonance frequency at the zero-density limit and therefore independent of intermolecular interactions. The frequency $\nu_0(T)$ can easily be obtained from NMR measurements performed in the gas phase and used for the determination of chemical shifts according to eq 3 and consequently the shielding constants, $\sigma_0(T)$, if the shielding of a reference molecule (σ_{REF}) is known. In summary, in the present study it is assumed that the parameters $\sigma_0(T)$ and $\nu_0(T)$ represent accurately the properties of an isolated molecule. The intermolecular contribution to the shielding $\sigma_1(T)$ is also available, from the appropriate frequency parameters ($\nu_1(T)$ and $\nu_{\mathrm{REF}}(T)$).

Experimental Section

Silane, SiH_4 (99.998+%, Aldrich), and germane, GeH_4 (99.997+%, Aldrich), from lecture bottles were used for the preparation of the samples without further purification. Gas samples were made by condensing pure gases from the calibrated part of a vacuum line to NMR tubes and sealed. 4-mm-o.d. glass tubes for SiH_4 and 8-mm-o.d. tubes for GeH_4 (all approximately 5 cm long) were used as gas containers. The volumes of sample tubes and the vacuum line were measured using mercury. The sealed 4-mm-o.d. gas samples were fitted into the standard 5-mm-o.d. thin-walled NMR tube (Wilmad 528-PP), and the 8-mm-o.d. containers were fixed into the 10-mm-o.d. NMR tube (Wilmad 514-5PP), always with liquid toluene-d_8 in the annular space. Standard one-dimensional NMR spectra were acquired on a Varian UNITYplus-500 FT spectrometer at 300 K with the 17.46, 99.45, and 500.62 MHz transmitter frequencies for the ^{73}Ge, ^{29}Si, and ^{1}H nuclei, respectively. NMR chemical shifts were measured relative to the external reference standards, that is, TMS, $Si(CH_3)_4$ (99.9%, Aldrich), and tetramethyl germanium, $Ge(CH_3)_4$ (98%, Aldrich); the secondary liquid standards were appropriate for observed nuclei, that is, TMS for ^{1}H and ^{29}Si NMR spectra, liquid $Ge(CH_3)_4$ for ^{73}Ge NMR measurements. The absolute frequency of the reference standard was determined in the conditions of lock system tuned to the CD_3 signal of external toluene-d_8. The constant frequency of the deuterium lock system allowed us to preserve the same B_0 for all measurements. The ^{1}H resonance frequency of liquid TMS was continuously monitored during the experiments, $\nu_{\mathrm{H}}(\mathrm{TMS, liq.\ 300\ K}) = 500.6074661(1)$ MHz. The absolute magnetic shielding of TMS (32.775(25) ppm for protons in a cylindrical tube parallel to external magnetic field[5]) was used to convert the ^{1}H NMR chemical shifts into absolute shielding constants of protons. For the heavy nuclei, the absolute shielding constants are taken from theoretical data, and the measured chemical shifts are applied to obtain new values of the absolute shielding of the primary reference standards: pure liquid $Si(CH_3)_4$ and $Ge(CH_3)_4$.

Results and Discussion

Gas-Phase NMR Measurements. We present in this paper gas-phase measurements of the resonance frequencies and nuclear magnetic shielding of silane and germane as functions of density. Figure 1a,b shows that the dependence of ^{29}Si and ^{73}Ge frequencies on density is linear for these compounds, which means that $\nu_2(T)$ and higher coefficients in eq 4 can be neglected here. Thus, the $\nu_0(T)$ values are obtained by linear extrapolation to zero density and determine the NMR frequencies of isolated molecules at 300 K: 99.4462169(1) MHz for ^{29}Si of SiH_4 and 17.4570625(2) MHz for ^{73}Ge of GeH_4. The present experiments have been performed in a constant external magnetic field B_0, as described in the Experimental Section. The ^{29}Si resonance frequency of liquid TMS was also constant during all of the ^{29}Si NMR measurements and equal to 99.4565944(1) MHz at 300 K. It permitted the determination of silicon shielding parameters for SiH_4. Table 1 contains the ^{29}Si shielding constant of silane measured relative to liquid TMS, $\Delta\sigma_0(^{29}Si\mathrm{H}_4) = +104.34(1)$ ppm. The latter value is consistent with the previous result (+106.8 ppm) given by Jameson and Jameson,[6] which is expressed relative to pure liquid TMS in a spherical sample tube. The small discrepancy between the above two results is not surprising, because liquid TMS in the cylindrical sample tube and parallel external magnetic field exhibits +2.30 ppm larger shielding than does TMS in the spherical tube. The literature value of the absolute ^{29}Si shielding of liquid TMS is known with rather low accuracy; according to ref 6, it is 368.5 ± 10 ppm, and therefore our measurement of silicon chemical shift cannot be precisely converted into the shielding of an isolated SiH_4 molecule, σ_0. Instead, this parameter will be taken from recent ab initio calculations, and, as discussed in the theoretical part of this study, we shall determine a new value of the absolute ^{29}Si shielding of pure liquid TMS. Also shown in Table 1 is the $(\sigma_1)_{\mathrm{int}}$ intermolecular term, obtained when the magnetic susceptibility correction is subtracted from the σ_1 parameter,[1] $(\sigma_1)_{\mathrm{int}} = \sigma_1 - (\sigma_1)_{\mathrm{b}}$. We recall that the partition of σ_1 into $(\sigma_1)_{\mathrm{b}}$ and $(\sigma_1)_{\mathrm{int}}$ is only done to interpret this coefficient and it does not affect the isolated molecule value of σ_0.

TABLE 1: ^{29}Si, ^{73}Ge, and ^{1}H Magnetic Shielding Parameters of XH_4 Compounds in the Gas Phase at 300 K

parameter	this work	literature
^{29}Si and ^{1}H Shielding in SiH_4		
$\Delta\sigma_0(Si\mathrm{H}_4)^a$ [ppm]	+104.34(1)	+106.8^b
$\Delta\sigma_0(\mathrm{Si}H_4)^c$ [ppm]	−5.150(1)	−5.15^d
$\sigma_1(Si\mathrm{H}_4)$ [ppm mL mol^{-1}]	−679.3(90)	
$\sigma_1(\mathrm{Si}H_4)$ [ppm mL mol^{-1}]	+79.3(6)	
$(\sigma_1)_{\mathrm{b}}(\mathrm{SiH}_4)^e$ [ppm mL mol^{-1}]	+85.4	
$(\sigma_1)_{\mathrm{int}}(Si\mathrm{H}_4)^f$ [ppm mL mol^{-1}]	−764.7(90)	
$(\sigma_1)_{\mathrm{int}}(\mathrm{Si}H_4)^f$ [ppm mL mol^{-1}]	−6.1(6)	
^{73}Ge and ^{1}H Shielding in GeH_4		
$\Delta\sigma_0(Ge\mathrm{H}_4)^g$ [ppm]	+326.41(2)	
$\Delta\sigma_0(\mathrm{Ge}H_4)^c$ [ppm]	−5.001(1)	
$\sigma_1(Ge\mathrm{H}_4)$ [ppm mL mol^{-1}]	−2685(30)	
$\sigma_1(Ge\mathrm{H}_4)$ [ppm mL mol^{-1}]	+75.2(20)	
$(\sigma_1)_{\mathrm{b}}(\mathrm{GeH}_4)^e$ [ppm mL mol^{-1}]	+124.3	
$(\sigma_1)_{\mathrm{int}}(Ge\mathrm{H}_4)^f$ [ppm mL mol^{-1}]	−2770(30)	
$(\sigma_1)_{\mathrm{int}}(\mathrm{Ge}H_4)^f$ [ppm mL mol^{-1}]	−10.2(20)	

[a] For silicon, $\Delta\sigma_0 = \sigma_0 - \sigma_{\mathrm{REF}}(Si(\mathrm{CH}_3)_4$ liq., 300 K). [b] Reference 6, given relative to liquid TMS in a spherical sample tube. [c] For protons, $\Delta\sigma_0 = \sigma_0 - \sigma_{\mathrm{H}}(\mathrm{Si(C}H_3)_4$ liq., 300 K), with $\sigma_{\mathrm{H}}(\mathrm{Si(C}H_3)_4$ liq., 300 K) = 32.775(25) ppm.[5] [d] $\sigma_0(\mathrm{Si}H_4) - \sigma_{\mathrm{H}}(\mathrm{Si(C}H_3)_4$ liq., 300 K) from ref 6. [e] Bulk susceptibility corrections equal to $-(4\pi/3)\chi_{\mathrm{M}}$, where χ_{M} are the molar magnetic susceptibilities.[16] [f] $(\sigma_1)_{\mathrm{int}} = \sigma_1 - (\sigma_1)_{\mathrm{b}}$. [g] For germanium, $\Delta\sigma_0 = \sigma_0 - \sigma_{\mathrm{REF}}(Ge(\mathrm{CH}_3)_4$ liq., 300 K).

In ^{73}Ge NMR experiments, liquid tetramethyl germanium, $Ge(CH_3)_4$, was applied as the external reference standard, and its ^{73}Ge resonance frequency (ν_{REF}) was equal to 17.4627625(1) MHz. The frequency parameters of $^{73}Ge\mathrm{H}_4$ (ν_0 and ν_1) were used next to determine the $\Delta\sigma_0(^{73}Ge\mathrm{H}_4)$, $\sigma_1(^{73}Ge\mathrm{H}_4)$, and $(\sigma_1)_{\mathrm{int}}(^{73}Ge\mathrm{H}_4)$ values, which describe ^{73}Ge magnetic shielding in the germane molecule. The value of the absolute shielding of ^{73}Ge nucleus in GeH_4, $\sigma_0(^{73}Ge\mathrm{H}_4)$, will be taken from a recent theoretical study;[7] there are no literature results based on experimental data

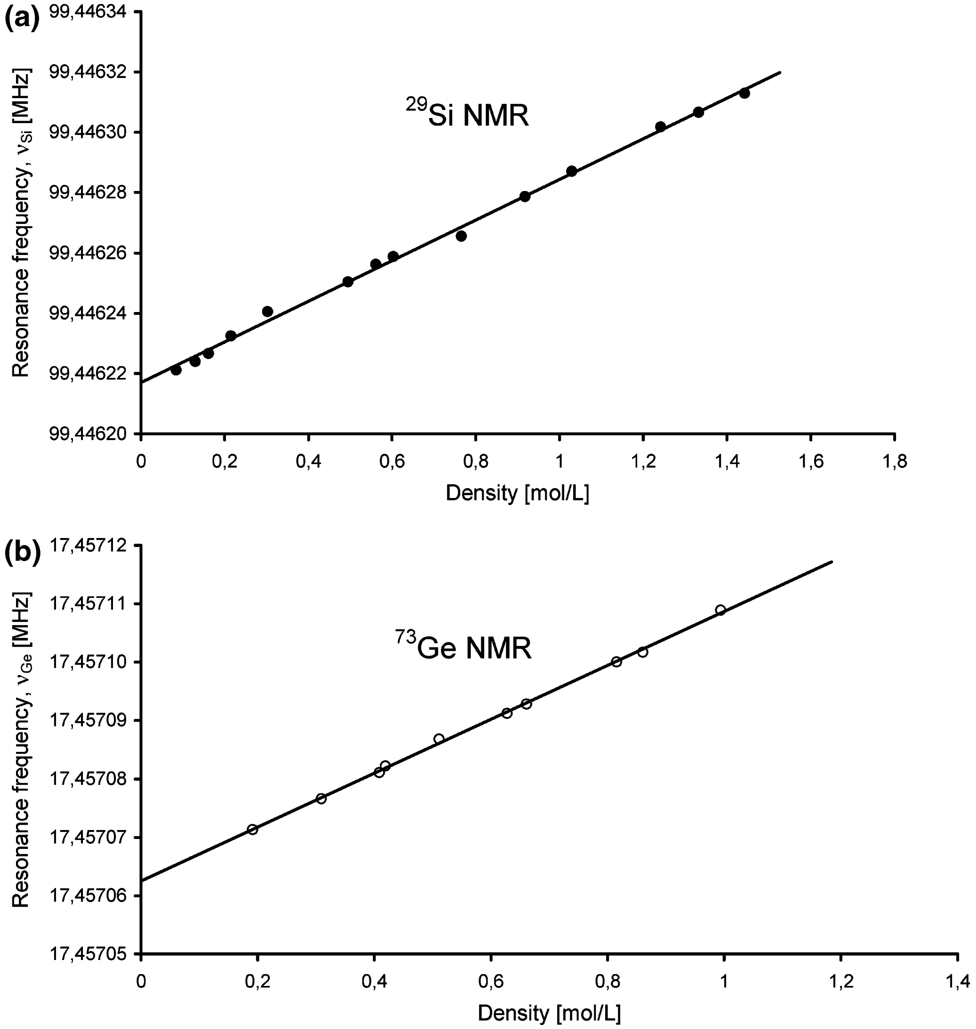

Figure 1. The density-dependent NMR frequencies with the external magnetic field constant. (a) ^{29}Si frequency of SiH$_4$, extrapolation to the zero-density point leads to ν_0(*Si*H$_4$, 300 K) = 99.4462169(1) MHz when ν_{Si}(*Si*(CH$_3$)$_4$ liq., 300 K) = 99.4565944(1) MHz; (b) ^{73}Ge frequency of GeH$_4$, ν_0(*Ge*H$_4$, 300 K) = 17.4570625(2) MHz when ν_{Ge}(*Ge*(CH$_3$)$_4$ liq., 300 K) = 17.4627625(1) MHz.

for germane. Table 1 shows that the germanium shielding of an isolated ^{73}GeH$_4$ molecule is much larger (+326.41(2) ppm) than the shielding of germanium nucleus in liquid Ge(CH$_3$)$_4$. It is worth noting that intermolecular interactions significantly modify the germanium shielding of GeH$_4$ in the gas phase. The intermolecular $(\sigma_1)_{int}$(^{73}*Ge*H$_4$) term equal to −2770(30) ppm mL mol^{-1} is almost 4 times larger than the similar $(\sigma_1)_{int}$(^{29}*Si*H$_4$) parameter for silane. Both of these terms are negative, and it means that the effects due to intermolecular interactions are deshielding. The above result suggests a correlation between the magnitude of shielding (σ_0) and the effect of dispersive forces on nuclear shielding $(\sigma_1)_{int}$, as shown in Table 2, where the σ_0(^{73}*Ge*H$_4$) shielding constant is approximately 4 times larger than the σ_0(^{29}*Si*H$_4$) value.

TABLE 2: Absolute Shielding Constants (ppm) in XH$_4$ Molecules and Derived Heavy-Atom Magnetic Moments (μ_N)

nucleus	shielding constants[a]			
Y	σ_Y	σ_H	μ_Y this work[b]	μ_Y literature[c]
^{13}C in CH$_4$	196.77	30.609	0.7023707	0.7024118(14) 0.7023694(35)[9]
^{29}Si in SiH$_4$	482.85	27.625	−0.5550520	−0.55529(3)
^{73}Ge in GeH$_4$	1988.71	27.774	−0.8782413	−0.8794677(2)
^{119}Sn in Sn(CH$_3$)$_4$	3476.04	33.508[d]	−1.0450677	−1.04728(7)

[a] Ab initio values for the heavy nuclei, experimental values for ^{1}H nuclei, see text. [b] For an estimate of the error bars, see text. [c] Reference 17, unless stated otherwise; see also ref 4. [d] The chemical shift of ^{1}H between liquid TMS and liquid Sn(CH$_3$)$_4$ is 0.733 ppm (measured in this work).

In this paper, we also present gas-phase measurements of the ^{1}H resonance frequencies and proton chemical shifts of silane and germane as functions of density. Figure 2 shows that the dependence of ^{1}H frequency on density is linear for both of these compounds, which means that $\nu_2(T)$ and higher coefficients in eq 4 can be neglected here. Thus, the $\nu_0(T)$ values are obtained by linear extrapolation to zero density and yield the ^{1}H frequencies of isolated molecules, 500.610044(2) and 500.609969(4) MHz for SiH$_4$ and GeH$_4$, respectively, at 300 K. The proton resonance frequency of liquid TMS was monitored during all of our measurements, ν_H(TMS, liq. 300 K) = 500.6074661(1) MHz. The same signal of liquid TMS was used as the reference standard for all measurements of ^{1}H NMR chemical shifts (converted later, using the known value of the absolute shielding of protons in liquid TMS,[5] to proton shielding constants in SiH$_4$ and GeH$_4$). Table 1 presents the ^{1}H shielding constants of silane and germane measured relative to TMS as the secondary reference standard. As can be seen, the proton shielding constant of GeH$_4$ is only slightly larger than that observed for SiH$_4$. In contrast to the ^{29}Si and ^{73}Ge nuclei, the σ_1 values are positive for protons (cf., the negative slopes of experimental plots in Figure 2), but this is only due to the large macroscopic effect of the magnetic susceptibility; as shown in Table 1, the real

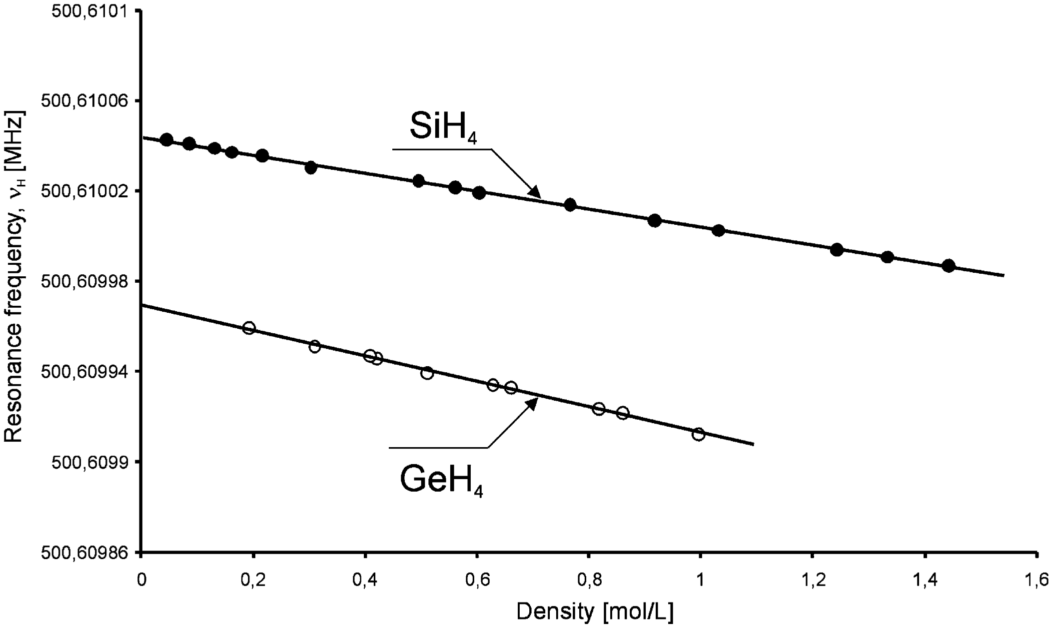

Figure 2. The density-dependent ^{1}H NMR frequencies of SiH$_4$ and GeH$_4$ gases. The measurements were carried out with the frequency of liquid TMS controlled and remaining constant, $\nu_H(Si(CH_3)_4$ liq., 300 K$) = 500.6074661(1)$ MHz. The extrapolated ν_0 frequencies are 500.610044(2) and 500.609969(4) MHz for SiH$_4$ and GeH$_4$, respectively. The plots in this figure have negative slopes exclusively due to the magnetic susceptibility effect; cf., Table 1 for details.

intermolecular terms $(\sigma_1)_{int}$ are negative also for protons. The secondary isotopic effect $^2\Delta H(^{29/28}Si)$ for isolated SiH$_4$ molecules was not detected in this study.

Magnetic Dipole Moments of the Group XIV Nuclei. The standard technique of establishing a nuclear magnetic dipole moment from NMR spectrum is based on the equation:

$$\mu_Y = \frac{\nu_Y}{\nu_X}\frac{(1-\sigma_X)}{(1-\sigma_Y)}\mu_X \tag{5}$$

relating the properties of two nuclei, X and Y, in the same external magnetic field. Thus, the unknown magnetic moment μ_Y can be determined once the frequency ratio for two nuclei ν_Y/ν_X is measured, the absolute shielding constants σ_X and σ_Y are known, and the value of the other magnetic moment, μ_X, is available. To avoid unnecessary errors in the experiment, the measurement has been usually performed for two nuclei in the same molecule. Using gas-phase results for an isolated molecule, we now eliminate another source of error, the influence of the intermolecular forces. In addition, the most suitable nucleus X to be used as the reference is ^{1}H, because for this nucleus the magnetic moment is presently known with high accuracy.[8]

As discussed in ref 9, an important issue that has to be considered is the accuracy of the shielding constants σ_X and σ_Y. Although the relative chemical shifts for many nuclei are measured with high accuracy in standard NMR experiments, what we need in eq 5 are the absolute shielding constants, and the absolute scale for many nuclei of interest is not so well established. We have shown in ref 9 that by improving the values of the absolute shielding we could obtain a set of consistent nuclear magnetic dipole moments, which can be successfully used in the relation:

$$\sigma_X = 1 - \frac{\nu_X}{\nu_Y}\frac{\mu_Y}{\mu_X}(1-\sigma_Y) \tag{6}$$

This relation should be fulfilled for any pair of nuclei in any pair of molecules, and, in particular when σ_X can be independently determined from other data, it provides a stringent test of the applied values of the magnetic moments.

In this work, we also use eqs 5 and 6, although in a somewhat different context. For the light nuclei studied in ref 9, the absolute shielding scales have been taken from the literature, and the absolute shielding constants of various nuclei in the experimentally studied molecules were determined using these reference values. For group XIV nuclei studied in this work, we shall primarily rely on the recent ab initio shielding constants determined for XH$_4$ molecules in refs 7,10. The absolute shielding for the NMR standards, X in liquid X(CH$_3$)$_4$, can be next established using the chemical shifts between gaseous XH$_4$ and liquid X(CH$_3$)$_4$. Thus, we establish the absolute scale, determining the shielding in liquid X(CH$_3$)$_4$ from these data, assuming that our primary values are the ab initio shielding constants in XH$_4$. This means also that the data used to determine the nuclear magnetic moments from eq 5 and the data used to check their consistency via eq 6 are not completely independent; eq 6 provides a more demanding test when the data are taken from different sources (see ref 9).

The final input data and the computed nuclear magnetic moments are shown in Table 2. Let us discuss the data used and the results for each nucleus in more detail. For the sake of completeness, we analyze the nuclear magnetic dipole moments of ^{13}C, ^{29}Si, ^{73}Ge, and ^{119}Sn nuclei, using the discussed above new experimental results for ^{29}Si and ^{73}Ge as well as recent ab initio results for group XIV hydrides.[7,10]

^{13}C. We shall use the same experimental data as in ref 9. The only change in the ab initio data is a minor one: we now include the small relativistic correction to the C shielding in methane, 1.07 ppm.[7]

^{29}Si. The new experimental data for SiH$_4$ have been discussed, and these values are combined with the ab initio results of refs 10 and 7. From the former work, we take the state-of-the-art nonrelativistic value of the shielding obtained at the CCSD(T) level with a large basis set, including next the zero-point vibrational and temperature contributions, 469.236 ppm. From the latter work, we take the relativistic correction, 13.61 ppm, and in this way we derive the theoretical absolute shielding constant in SiH_4, 482.85 ppm. We believe that these results set the scale for silicon. With the given above chemical shift of ^{29}Si between gas-phase SiH_4 and TMS, 104.34 ppm, we obtain 378.51 ppm for the absolute shielding of ^{29}Si in liquid TMS at 300 K. We recommend this value, derived combining the SiH_4 ab initio shielding constant and the reported SiH_4 to TMS chemical shift, as the new reference for ^{29}Si nucleus.

^{73}Ge. Similarly to ^{29}Si, we consider our new experimental results and the ab initio values for GeH_4 to be the primary source of data. In this case, we use the MCSCF values of ref 7, which are most likely less accurate than the corresponding Si results (the description of the electron correlation effects on the shielding at the CCSD(T) level is more reliable than within the MCSCF approach). Nevertheless, the (GIAO) MCSCF results for the shielding in GeH_4 should be much more accurate than the other available literature values (CHF calculations with the gauge origin at the heavy atom[11]); therefore, again we treat the value obtained combining our results, GeH_4 ab initio shielding constant and measured GeH_4 to $Ge(CH_3)_4$ chemical shift, as the reference.

^{119}Sn. In this case, we use the experimental values of the frequency ratio in $Sn(CH_3)_4$ and of the ^{119}Sn chemical shift between SnH_4 and $Sn(CH_3)_4$ determined by Laaksonen and Wasylishen.[12] This value, -541.5 ppm, has been obtained for gas-phase SnH_4; thus, as for other molecules, it is appropriate when we start with the ab initio shielding constant of ^{119}Sn in SnH_4 molecule, 4017.54 ppm. The SnH_4 results of ref 7 were obtained, as for GeH_4, at the MCSCF level, and they include a large relativistic correction, 693.68 ppm. It appears that when the relativistic effects are so large, one cannot apply the (nonrelativistic) relationship between the spin-rotation constants and paramagnetic shielding to determine the absolute shielding scale, and this explains the differences between our final values of the absolute shielding and the magnetic dipole moment of ^{119}Sn and the results of ref 12.

We have estimated the error bars in the magnetic moments derived using eq 5. Practically, they are determined by the estimated error bars for the absolute shielding constants in XH_4 molecules. We have used for these: ^{1}H 0.5 ppm (in all cases), ^{13}C 3.0, ^{29}Si 5.0, ^{73}Ge 50, and ^{119}Sn 100 ppm; and the corresponding errors in the magnetic moments are ^{13}C 0.0000025, ^{29}Si 0.0000031, ^{73}Ge 0.0000444, and ^{119}Sn 0.0001054 μ_N, respectively. The error bar of the computed magnetic moment is more or less proportional to the assumed error in the shielding; the role of the other sources of error in the input data is negligible (we recall that in each case the reference nucleus is ^{1}H, and its magnetic dipole moment is known with high accuracy). We note that most likely the accuracy of the data decreases for the heavier nuclei; for instance, the ab initio results for GeH_4 and SnH_4 did not include rovibrational corrections, the quoted experimental values for gas-phase SnH_4[12] have not been extrapolated to zero density, etc. However, the most important relativistic effects are now considered, and thus the derived magnetic moments should be more accurate than the available literature data. This is confirmed when we analyze the nuclear moments applying their old and new values as input data in eq 6; the derived shielding constants are much more accurate and consistent when the new values of the moments are used (for details of such an analysis, see ref 9).

For the absolute shielding of ^{1}H nuclei, we used systematically the experimental data, σ_H(TMS liq., 300 K) $= 32.775(25)$ ppm,[5] as explained in the experimental part of this work. Our recent investigations based on the experimental chemical shift between gaseous o-H_2 and liquid TMS[13] and the calculations for a hydrogen molecule[14] give slightly larger shielding of protons in liquid TMS, but the difference does not exceed 0.1 ppm. We find it difficult to get a more reliable ab initio result for ^{1}H in any XH_4 molecule, and therefore we did not attempt to improve the absolute shielding scale for ^{1}H, in contrast to the heavy nuclei. We have only verified that by using for the shielding of ^{1}H in CH_4 an ab initio value instead of the experimental value we obtain for the magnetic moment of ^{13}C 0.7023706 μ_N; thus the change is much smaller than our estimated error bar, 0.0000025 μ_N .

Finally, we did not discuss the properties of ^{207}Pb nucleus. The theoretical values of the shielding are strongly dependent on the relativistic effects; thus, for instance, the perturbational description of these effects applied in ref 7 is not as accurate as for the other group XIV nuclei. At the same time, there are no experimental NMR data; PbH_4 is highly unstable,[15] and thus an NMR measurement in the gas phase is practically impossible.

Conclusions

We have discussed gas-phase NMR spectra of SiH_4 and GeH_4 and their dependence on the density. It was shown that the results can be extrapolated to the zero-density point, and thus we can obtain reliable isolated molecule values, best suited for comparison with computed ab initio absolute shielding constants. It appears that with the present-day accuracy of ab initio methods, this is the best way to define absolute shielding scales for the heavy nuclei, ^{29}Si and ^{73}Ge. The analysis of ^{1}H shielding in the hydrides and the availability of resonance frequency ratios measured in the same conditions for ^{29}Si and ^{1}H (^{73}Ge and ^{1}H, respectively) allowed us to derive new, more accurate values of the nuclear magnetic dipole moments of the heavy nuclei. Using the recent literature data for the NMR spectra of CH_4 and SnH_4, we have recomputed in the same manner the magnetic moments of ^{13}C and ^{119}Sn nuclei.

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