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^{29}Si NMR chemical shifts of silane derivatives

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Abstract

Geometries and ^{29}Si NMR chemical shifts are calculated for silanes Si_nH_{2n+2}, $n = 1, \ldots, 5$, methylsilanes SiH_nMe_{4-n}, methoxysilanes $SiH_n(OMe)_{4-n}$, and methylmethoxysilanes $SiMe_n(OMe)_{4-n}$, $n = 0, \ldots, 4$. Geometries and ^{29}Si NMR chemical shifts are in satisfying agreement with experiment within LCGTO-DFT at the DZVP/LDA level for geometries and IGLO-III/GGA (GGA = PW91,PBE) level for shielding constants, which is an improvement to B88PW86, P86PW86 and B3LYP results. If an auxiliary basis is applied to express the Coulomb potential, *g*-functions have to be included to reproduce SiOSi angles and ^{29}Si NMR chemical shifts correctly. © 2002 Published by Elsevier Science B.V.

1. Introduction

Silane compounds cover a large variety of species, which have been studied by experimentalists and theoretical chemists for a long time. They are of particular interest in catalysis and as precursors for the growth of zeolites. In general, theoretical and experimental structures of silanes are in good agreement as long as the compounds do not contain oxygen. In the latter case, many approaches, including density-functional theory (DFT), Hartree–Fock (HF) and several post-HF theories, have difficulties to describe SiOSi bond angles, as it can be deduced from the literature [1–5]. A molecule which was studied both theoretically and experimentally with great interest is disiloxane $H_3SiOSiH_3$. Its SiOSi bond angle was subject of an extensive controversial discussion since the mid-1990s, and values reaching from 139° to 180° for the SiOSi bond angle were obtained at different – rather high – levels of theory. Agreement with experiment was achieved when Nicholas and Feyereisen [3] included correlation effects (MP2, MP4) and used correlation-consistent polarised valence basis sets (cc-pVXZ, X = D, T, Q, 5) in their calculations. At this level of theory, the potential energy surface was studied by Koput [6] afterwards. Clayden et al. [5] showed that the quality of the prediction of the OSiO bond angle in dihydroxysilane influences strongly its ^{29}Si chemical shift. This shows the importance of the geometry for the prediction of properties of siloxanes or, especially, zeolites. The structures consist almost exclusively of Si–O frameworks with various bond angles and a good quality of the geometry is crucial for property calculations.

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Beside the exploration of several quite different silane structures, which have not been investigated before, the goal of this work is to establish a reliable but computationally inexpensive method to obtain geometries of silane molecules, which can be applied later for much larger silica, siloxane and zeolite systems. To cover most of the organic chemical surrounding present in those systems, we include silicon in various environments as found in the silanes: Si_nH_{2n+2}, $n = 1, \ldots, 5$, methylsilanes SiH_nMe_{4-n}, methoxysilanes $SiH_n(OMe)_{4-n}$, methylmethoxysilanes $SiMe_n(OMe)_{4-n}$, $n = 0, \ldots, 4$. We did not include the hydroxysilanes into this study since experimental gas-phase data are presently not available. ^{29}Si NMR data in solutions are available for some of the hydroxysilanes, but we expect gas phase geometries to be too much different for a reasonable comparison.

We will focus on DFT as implemented in the deMon package [7], thus using auxiliary functions to express the Coulomb potential. Therefore, the dependency of the results on density, auxiliary density and functional has been investigated.

2. Benchmark calculations

Since NMR chemical shifts are very sensitive to the geometry, the level of theory at which the geometries are optimised has to be selected carefully. To benchmark our approach we have chosen a small test set of three compounds, disilane, disiloxane and tetramethylsilane (TMS). This set contains all types of Si–X bonds which appear in the molecules to be studied later.

While it is known that geometries of silanes can be calculated at the LDA level employing moderate basis sets (e.g. DZVP [8]) [9], geometries of oxygen containing silane compounds as disiloxane with its soft SiOSi angle need a more careful treatment. For an overview, see [1–5]. Indeed, Pople-style valence split basis sets give poor results for the SiOSi angle, while they perform well for the other geometry parameters. The LDA-optimised DZVP and TZVP basis sets proposed by Godbout et al. [8] are sufficient to describe this critical angle in disiloxane (see Table 1). Since all bond parameters are obtained within 0.02 Å for bond lengths and 2° for bond angles employing the DZVP basis set, this will be our choice for the remainder.

Results are as sensitive to the choice of the auxiliary basis to express the charge density. While the A2 basis set is sufficient to calculate bond length and angles to an accuracy of 0.005 Å and 0.2°, respectively, for silane compounds without oxygen, the oxygen containing compounds are not well described at that level of computation. Successive increasing of the size of the auxiliary basis up to *g*-functions leads to convergence against the four-centre limit, i.e. the calculation of the Cou-

Table 1
Influence of the basis set, auxiliary basis, and exchange-correlation functional on the geometry

	Si_2H_6			TMS		Disiloxan		
	Si–Si	Si–H	HSiSi	Si–C	C–H	Si–O	Si–H	SiOSi
VWN/DZVP	2.327	1.500	110.43	1.872	1.104	1.651	1.499	143.57
VWN/TZVP	2.326	1.498	110.40	1.871	1.103	1.647	1.497	144.38
VWN/A2/DZVP	2.332	1.506	110.32	1.876	1.106	1.659	1.505	131.57
VWN/A3/DZVP	2.333	1.503	110.42	1.875	1.105	1.656	1.501	136.57
VWN/A2*/DZVP	2.326	1.500	110.48	1.872	1.104	1.648	1.499	143.63
VWN/A3*/DZVP	2.326	1.500	110.47	1.872	1.105	1.647	1.500	145.90
PBE/A2*/DZVP	2.353	1.500	110.50	1.896	1.102	1.669	1.498	140.81
PW91/A2*/DZVP	2.351	1.497	110.51	1.889	1.090	1.667	1.496	140.36
B3LYP/DZVP	2.353	1.488	110.48	1.892	1.095	1.650	1.485	156.55
Exp. [34]	2.331	1.492	–	1.875	1.115	1.632		142.2
						1.634	1.486(10)	144.1(9)

Bond lengths are given in Å, bond angles in degrees. If no auxiliary basis is specified the Coulomb potential is calculated directly from the molecular orbitals. A2 and A3 auxiliaries are given in [8], A2* and A3* are generated automatically in deMon [7].

Table 2
Calculated geometries of selected silane derivatives compared with experiment (conventions as in Table 1)

		DZVP/A2*/VWN	DZVP/A2*/PBE	DZVP/VWN	Exp. [34]
SiH_4	Si–H	1.497	1.497	1.498	1.490
Si_2H_6	Si–Si	2.334	2.357	2.325	2.331
	Si–H	1.500	1.499	1.500	1.492
SiH_3Me	Si–H	1.501	1.500	1.500	1.48
	Si–C	1.871	1.893	1.871	1.86
	∠HSiH	108.44	108.48	108.50	108.25
	∠CSiH	110.06	110.04	109.94	107.0
$SiHMe_3$	Si–C	1.873	1.895	1.871	1.87
	Si–H	1.506	1.504	1.505	1.48
	∠HSiC	109.22	109.14	109.25	108.8
$O(SiH_3)_2$	Si–O	1.651	1.670	1.650	1.634
	∠SiOSi	143.63	142.14	144.4	144.1
$MeSi(OMe)_3$	Si–O	1.644	1.667	1.645	1.632
$Me_2Si(OMe)_2$	Si–O	1.655	1.682	1.649	1.641
	∠SiOC	120.56	121.77	120.17	122.3
Me_3SiOMe	Si–C	1.860	1.885	1.866	1.864
	Si–O	1.671	1.693	1.671	1.639
	∠SiOC	119.60	121.75	120.07	122.5
$SiOMe_4$	Si–O	1.636	1.660	1.640	1.613
	∠SiOC	118.65/123.36	120.5/126.38	118.00/125.38	123.6
TMS	Si–C	1.872	1.896	1.872	1.875
	Si–H	1.104	1.102	1.104	1.115

lomb potential directly from the molecular orbitals as it is done in the Gaussian program [10] (Table 1). The A2* basis set, as generated in the deMon program, is converged for all parameters in our test set. As it can be seen in Table 2, this holds for the whole set of compounds studied here where experimental values were available.

As a next step, we compare various exchange-correlation functionals (LDA [11], PW91 [12], PBE [13] and B3LYP [14,15]) for the test set. As shown in Table 1, GGA is not superior to LDA for geometries for this type of compounds. In fact, GGA bond lengths are generally too large in comparison to experiment, and in the case of a hybrid functional the SiOSi angle is affected by an error of more than 10°. Again, this holds for all our results which could be compared to experiment (see Table 2).

For chemical shifts, similar tests were performed as for the geometries. Chemical shielding constants were calculated using the IGLO technique [16,17] as implemented in the deMon-Nmr package [18,19]. An IGLO-III basis set [20] was chosen for all following calculations. A previous study showed that this basis set is nearly converged and gives very similar results as the 6-311+(2d,p) valence-split basis set [9]. IGLO-NMR calculations have been carried out at the plain DFT level (denoted with IGLO) and using ad-hoc corrections to the virtual orbitals as proposed by Malkin et al. [18,19] ($IGLO^{xc}$). These corrections require additional numerical integration on the grid and become expensive for large molecules.

In Table 3 the dependence of the shielding constant on the auxiliary basis is presented. The strong influence of the auxiliary functions on the shielding constant for silicon and oxygen is remarkable, while it is less important for carbon and hydrogen. This can be rationalised by the considerable amount of d-contributions in the Si–O

Table 3
Chemical shielding constants (in ppm) calculated using different levels of auxiliary functions and localisation procedures (see text)

Auxi	Loc	Si_2H_6		TMS			$O(SiH_3)_2$	
		Si	H	Si	C	H	Si	O
A2	PM	447.8	26.6	321.1	180.2	30.4	358.6	326.9
	FB	449.7	26.6	322.9	180.2	30.4	359.7	327.1
A3	PM	447.4	26.6	319.9	180.0	30.4	356.9	326.9
	FB	449.3	26.6	321.6	180.0	30.4	357.9	327.1
A2*	PM	436.8	26.8	314.7	179.4	30.6	348.3	322.7
	FB	438.7	26.8	316.5	179.4	30.6	349.4	322.9
A3*	PM	436.9	26.8	314.7	179.5	30.6	348.3	322.7
	FB	438.7	26.8	316.4	179.4	30.6	349.4	322.9

bonds, which requires g-functions in the auxiliaries to describe the electron density properly. Again, convergence is reached at the A2* level, which includes g-functions for Si, C and O. Chemical shifts obtained using A2* and A3* auxiliaries are almost identical [1]. In the deMon-Nmr code molecular orbitals can be transformed into localised ones by two techniques: The scheme proposed by Pipek and Mezey [21] was found to converge faster than the one of Foster and Boys [22]. This will be important when addressing larger molecules. Shielding constants calculated with both schemes differ within 2 ppm (see Table 3), while the differences are again largest for silicon nuclei. However, chemical shifts are almost unaffected by the choice of the localization procedure and in the following we will use the Pipek–Mezey technique.

3. Results and discussion

As shown in Table 2, calculated geometries compare well with experiment. The largest deviations from experiment are 0.03(0.05) Å for bond lengths for VWN/A2*/DZVP (PBE/A2*/DZVP), respectively; and for bond angles 3(3)°. In detail, deviations are 0.02(0.02) Å for Si–H, 0.01(0.03) Å for Si–Si, 0.01(0.02) Å for Si–C, 0.03(0.05) Å for Si–O, and 2(2)° for bond angles except SiOSi. To summarise, all geometrical parameters are properly described and calculated geometries can be taken as the basis for property calculations, as for NMR chemical shifts.

Chemical shifts of a set of silanes (all isomers from SiH_4 to Si_5H_{12}) are presented in Table 4 and are plotted against experiment in Fig. 1a. DFT and ab initio calculations of this set of molecules were already presented in a previous study and it was found that MP2 gives satisfying correlation with experiment, while DFT calculations on the LDA, GGA and hybrid levels (employing VWN, B88P86, P86PW86 and B3LYP functionals) commonly give error-affected results. The difference of DFT values to experiment is proportional to the number of hydrogen neighbors of a given silicon site [9]. This trend was independent from any of the set of functionals, applied basis sets, and whether gauge-including atomic orbitals [23] or the IGLO technique was applied. Here, we repeated the calculations employing the more recent PW91 and PBE functionals. Again, these new functionals show the same error-affected trend but the quantitative error is much smaller. For example, the internal shift of neopentasilane, which covers the whole range of chemical shifts of silanes, is 76.3 ppm in experiment [24], while ab inito theory gives 68.4 ppm for MP2* and 58.8 ppm for HF* and LDA gives 51.8 ppm. Gradient corrected functionals vary strongly, as for P86PW 86* 48.3 ppm and for B3LYP* 47.7 ppm were

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[1] Auxiliaries are automatically generated for IGLO-III basis sets, using the strategy of Godbout et al. [8], thus covering the space of the orbital basis functions used in the calculation. Auxiliaries A2* and A3* are an extension to A2 and A3, including an additional set of *spdfg* orbitals sharing one exponent. Thus, the generated auxiliary basis A2* (A3*) have 4/3/3 (4/4/4) auxiliary sets for Si, 3/3/3 (5/3/3) for O, 3/3/3 (5/3/3) for C, and 2/2/0 (3/2/0) for H, respectively, where the number of *s*/*spd*/*spdfg* shells sharing the same exponent is noted.

Table 4
^{29}Si NMR chemical shifts of silanes (in ppm) with respect to TMS

		VWN		PW91		PBE		VWN	PW91	Exp. [24]
		IGLO	IGLO^{xc}	IGLO	IGLO^{xc}	IGLO	IGLO^{xc}	GIAO		
SiH_4		–117.8	–121.0	–106.9	–109.8	–107.3	–110.3	–121.5	–111.5	–95.6
Si_2H_6		–121.8	–122.0	–110.6	–110.6	–111.5	–111.7	–123.2	–112.4	–103.1
Si_3H_8	(1)	–117.4	–116.7	–107.0	–106.2	–107.8	–107.1	–118.7	–108.6	–98.0
	(2)	–130.3	–130.1	–119.9	–119.6	–121.2	–121.0	–129.7	–119.4	–115.7
i-Si_4H_{10}	(1)	–112.9	–111.8	–103.2	–102.0	–103.9	–102.8	–114.3	–104.8	–93.6
	(2)	–143.9	–143.2	–135.8	–134.9	–137.3	–136.5	–140.4	–132.2	–136.3
n-Si_4H_{10}	(1)	–114.8	–114.0	–104.7	–103.8	–105.5	–104.7	–116.3	–106.3	–97.8
	(2)	–125.1	–124.3	–115.6	–114.7	–116.8	–116.0	–124.4	–114.9	–111.1
neo-Si_5H_{12}	(1)	–108.3	–106.9	–98.9	–97.5	–99.6	–98.3	–110.3	–101.4	–89.6
	(2)	–160.1	–159.0	–156.4	–155.1	–157.9	–156.7	–153.5	–149.5	–165.9
i-Si_5H_{12}	(1)	–114.1	–112.9	–104.0	–102.8	–104.7	–103.6	–115.9	–105.9	–94.1
	(2)	–139.0	–138.1	–131.7	–130.8	–133.1	–132.3	–136.5	–128.9	–131.5
	(3)	–120.9	–119.9	–112.1	–111.0	–113.2	–112.3	–120.9	–111.9	–106.9
	(4)	–120.9	–120.0	–109.6	–108.5	–110.3	–109.4	–123.0	–111.7	–99.0
n-Si_5H_{12}	(1)	–115.2	–114.0	–105.1	–103.9	–105.9	–104.7	–116.6	–106.7	–98.4
	(2)	–122.6	–121.5	–113.3	–112.1	–114.5	–113.4	–122.0	–112.6	–111.5
	(3)	–120.6	–119.7	–111.9	–110.9	–113.0	–112.1	–119.9	–111.1	–107.3

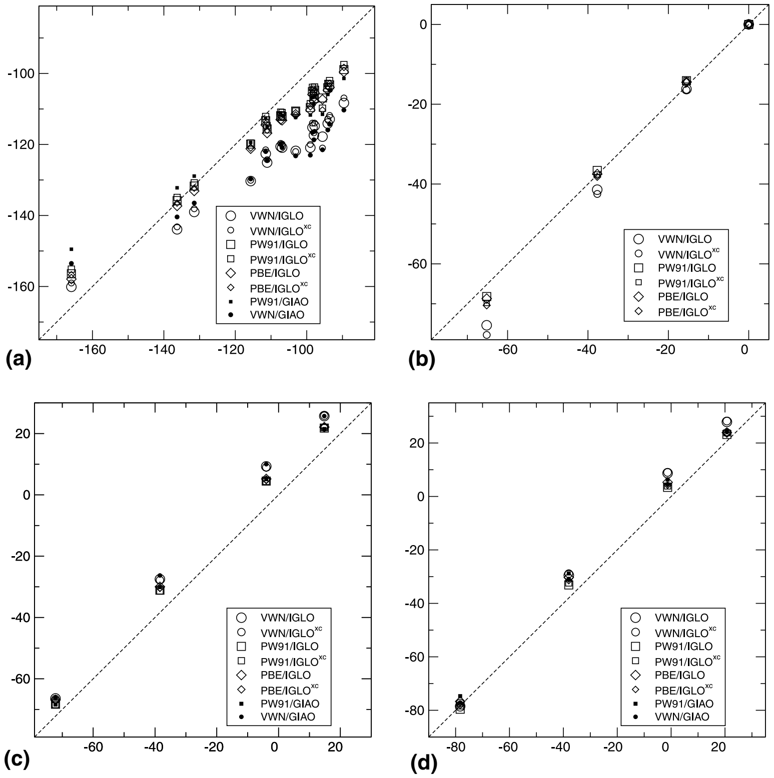

Fig. 1. Correlation between calculated and experimental chemical shifts for (a) silanes (experiment from [24]), (b) methylsilanes (Exp. from [28]), (c) methylhydroxysilanes and (d) methylmethoxysilanes (both Exp. [32]).

obtained. PW91 and PBE give values which are ~10 ppm closer to experiment at 57.5 and 58.3 ppm, respectively (values marked with an asterisk are taken from [9]). Self-interaction corrected (SIC) LDA were calculated by Patchkovskii et al. [25] for a set of molecules, and it is shown that SIC has the potential to improve DFT-NMR calculations. However, test calculations comparing VWN (revPBE [26]) and SIC-VWN (SIC-revPBE) give 40.7(45.9) and 39.4(50.0) ppm, respectively, and do not show much improvement for the internal shift of neopentasilane [27].

For methylsilanes, a similar disagreement between various DFT calculations [9] and experiment [28], proportional to the number of Si–H bonds at a Si site, was found. PW91 and PBE give correct chemical shifts for the whole set (see Table 5 and Fig. 1b). With these results, we can clearly state that the PW91 and PBE functionals perform better for chemical shift calculations of silane derivatives. This might be caused by the asymptotic behaviour of these new functionals which do not violate the Lieb–Oxford bound [29]. For a discussion of the influence of this feature on molecular properties see, e.g. [30]. Hopefully, future functionals, as for example optimised effective potentials [31], will further improve DFT-NMR calculations.

In Table 5 and Fig. 1c ^{29}Si NMR chemical shifts of methylhydroxysilanes are compared with experiment [32]. The calculated shifts correlate well with experiment for all functionals but are shifted by 7 ppm to lower fields. This is probably a solvent effect: experiments are carried out in polar solvents and a strong interaction of the hydroxy groups with the solvent can be expected. Again, all GGA functionals perform equally well and better than LDA. The technique of shielding calculations (GIAO or IGLO) or corrections of virtual orbitals as proposed by Malkin et al. [19] have no effect.

Two experimental groups reported ^{29}Si NMR chemical shifts of methylmethoxysilanes [32,33]. Calculated and experimental ^{29}Si NMR chemical shifts are shown in Table 5 and Fig. 1d. Hinton et al. [33] additionally performed GIAO-HF calculations with a rather unbalanced basis set. The experiments differ among themselves by up to 4 ppm for these molecules, which can be rationalised by the different experimental conditions. One set of experiments is performed in solid state [33], while the other one in solution of its parent alcohol and water. Thus, both experiments are subject to errors, either the low resolution of solid state NMR, or the solvent effect. The present DFT calculations agree with the two experiments within 10 ppm for the solid-state NMR and 6 ppm for the solution. There is a particularly large difference between theory and experiment for $MeSi(OMe)_3$. For the other compounds, GGA calculations and experiments agree very well within 3 ppm. The HF re-

Table 5
Chemical shifts of methylsilanes, methylhydroxysilanes and methylmethoxysilanes (in ppm)

	VWN		PW91		PBE		VWN	PW91	HF	Exp.	
	IGLO	IGLO^{xc}	IGLO	IGLO^{xc}	IGLO	IGLO^{xc}	GIAO				
SiH_3Me	–75.4	–77.8	–68.2	–69.8	–68.7	–70.4	–78.2	–71.5		–65.2[a]	
SiH_2Me_2	–41.4	–42.5	–36.6	–37.6	–37.5	–38.2	–43.0	–38.9		–37.7[a]	
$SiHMe_3$	–16.2	–16.4	–14.1	–14.0	–14.5	–14.4	–17.1	–15.1		–15.5[a]	
$Si(OH)_4$	–66.4	–66.6	–68.3	–68.4	–66.9	–67.1	–66.3	–68.4		–72.21[b]	
$SiMe(OH)_3$	–27.5	–27.8	–31.1	–31.3	–30.0	–30.3	–26.3	–30.1		–38.43[b]	
$SiMe_2(OH)_2$	9.3	9.0	4.5	4.4	5.2	5.0	10.0	5.1		–4.05[b]	
$SiMe_3OH$	25.7	25.8	21.8	21.9	22.1	22.2	25.7	21.5		14.84[b]	
Me_3SiOMe	27.9	28.2	23.2	23.8	23.9	23.7	27.7	23.0	13.2[c]	20.72[b]	19[c]
$Me_2Si(OMe)_2$	8.7	9.0	3.4	3.9	5.3	4.2	10.3	4.8	1.2[c]	1.25[b]	–4[c]
$MeSi(OMe)_3$	–29.5	–28.9	–33.1	–32.4	–30.3	–31.5	–28.5	–32.2	–32[c]	–38.24[b]	–42[c]
$SiOMe_4$	–78.5	–77.3	–79.6	–78.4	–76.7	–78.2	–77.1	–78.4	–75[c]	-78.29[b]	–80[c]

Experiments are taken from (a) [28], (b) [32], and (c) [33], respectively.

sults reported by Hinton et al. and the present LDA values both differ with up to 10 ppm, which again shows that correlation is important for those compounds and a recent GGA should be applied.

4. Conclusions

^{29}Si NMR chemical shifts of silane derivatives may be calculated at satisfying accuracy and moderate computational cost using recent GGA functionals (PW91 or PBE) together with a DZVP basis for geometries, and IGLO-III basis for chemical shifts. The choice of auxiliary functions to represent the charge density is crucial for methods which take advantage of this approximation. For geometries, LDA performs as well as GGA. There is a clear trend that ^{29}Si NMR chemical shifts calculated at the LDA level are getting more error-affected at higher fields. The computationally rather expensive ad hoc corrections of virtual orbitals [18,19] do not improve the quality of the chemical shifts due to the large HOMO–LUMO gap of the compounds studied here.

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