An ab initio Study of the Molecular Electric-field Gradients of the Chlorsilanes

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Z. Naturforsch. **51a**, 41–45 (1996); received November 22, 1995

The electric field gradient (EFG) of chlorine in the chlorine containing silanes ($SiCl_4$, $SiCl_3H$, $SiCl_2H_2$, and $SiClH_3$) was determined by means of ab initio methods and compared to recent experiments from which nuclear quadrupole moments are extracted. A careful estimation of the AO basis sets and the effect of the electron correlation is undertaken. The results showed the importance of the use of extended basis sets in the calculation of EFGs in second row atoms. Good agreement with deviations less than 5% from the experiments was found. The effect of the electron correlation was found to be small.

Introduction

When the nuclear quadrupole moment Q, is known the molecular electric field gradient (EFG) q can be determined in atoms and molecules from the nuclear quadrupole coupling constant E_Q observed by various experimental techniques, such as nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) [1] or microwave spectroscopy [2], since E_Q is defined as

$$E_Q = e \cdot \frac{q\,Q}{\hbar}, \qquad (1)$$

where $\hbar$ is Planck's constant divided by 2π and e is the charge of the electron. E_Q is the prefactor of the interaction of the quadrupole moment of the nucleus with the electron. This interaction is zero for s-type wavefunctions centered at the nuclei [3]. The EFG is a property of a system which depends sensitively on the asymmetry around the nucleus.

Q is not easy to determine directly from experiments. Sometimes values of Q were obtained by ab initio calculations. One may use either atomic calculations, see for example the compilation of Pyykkoe [4], or molecular calculations and compare them with the experimental results, see for example the work of Ha on ammonia [5, 6]. Recently very accurate results, using the numerical multiconfiguration Hartree-Fock (MCHF) method, which is basis set independent, were produced by Olsen and Sundholm [7] for different atoms. Based on these calculations and the experimental value of Jaccarino and King [8] a nuclear quadrupole moment $Q = -81.65$ mb, was used in the present work for chlorine. (The old standard value was $Q = -82.49$ mb [9].) This quadrupole moment for chlorine defines the connection between E_Q and q as

$$E_Q = -19.184867 \cdot q\ [\mathrm{MHz}] \qquad (2)$$

where q is measured in atomic units.

We investigate by means of ab initio methods the EFG of chlorine in the molecules $SiCl_4$, $SiHCl_3$, $SiCl_2H_2$, and $SiClH_3$, where accurate experiments have been reported. There were mostly microwave investigations. Trichlorsilane ($SiHCl_3$), e.g., was studied as early as 1953 by Mockler et al. [10] and 1967 by Mitzlaff et al. [11]. In chlorsilane the structure was determined by Kewley et al. [12].

In the present report a careful estimation of the accuracy of calculated EFG's at the chlorine atoms of the above mentioned substances was undertaken. There are essentially three factors which can deteriorate the accuracy of the calculated results. The first factor is connected with the quality of the chosen atomic orbital (AO) basis set. Due to its quasi-local nature (the operator is proportional to r^{-3}) of the EFG, the basis set should accurately describe the inner shells (2p). The use of standard pseudopotentials is therefore impossible. In addition it may be expected that relativistic effects as second factor may become important. The third factor is the correlation energy. However, if the main contribution to the EFG comes from the inner shells, the effect of electron correlation

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0932-0784 / 96 / 0100-0041 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

would be modest, according to the large separation of the inner shells to the valence shells in the third row.

Methods of Calculation

The determination of EFG's is well-known in quantum chemistry [13]. The corresponding one-electron operator is a two-rank tensor with terms of the form

$$\mathcal{O}_{ij} \propto \frac{3x_i y_j - \delta_{ij} r^2}{r^5}, \qquad (3)$$

which may be found for example in the work of Neuman and Moskowitz [14]. The electric field is traceless, and if diagonalized one defines the asymmetry parameter $\eta = \left| \frac{q_{bb} - q_{cc}}{q_{aa}} \right|$, with q_{aa} as the largest component [13].

The Hartree-Fock and density functional theory calculations and the geometry optimizations were performed with the help of the Gaussian92 [15] and GAMESS [16] programs. For the density functional theory two different functionals were chosen. One with a local approximation only, called LDA, uses the VWN [17] functional. As example for the gradient corrected functionals the so called Becke3Lyp functional [18] was chosen as second functional and termed NLD. Most of the CI calculations were performed with the Karlsruhe version of the COLUMBUS [19] system of programs, while for some CI calculations we have used the MELDF-X [20] suite of programs.

Different AO basis sets have been used for this study. Among them some of the standard AO basis sets as they are implemented in the Gaussian programs. The definition of the nomenclature used for these AO basis sets may be found in the two recent review articles of Huzinaga [21] and Feller and Davidson [22]. Additionally to these AO basis sets, a standard double zeta with polarization functions set (DZP), the MINI and MIDI AO basis sets [23] as well as the smallest one, the correlation consistent AO basis set of Dunning and coworkers (cc-pVDZ [24]) were also used. The DZP stands for an Huzinaga basis in the Dunning-Hay contraction [25] augmented by d polarization functions with the exponents $\varepsilon = 0.45$ for silicon and $\varepsilon = 0.75$ for chlorine and one p polarization function with the exponents $\varepsilon = 1.0$ for the hydrogen atoms.

Results and Discussion

Table 1 shows the results of the optimized geometries and electric field gradients of $SiCl_4$ calculated for different AO basis sets. It is seen that with increasing basis set quality the calculated EFG converges to a value of about 1.0. The minimal and poor basis sets like STO-3G, MINI and MIDI produce values which are too large by a factor 1.5 to 2. The reason is that a single shell (the 2p shell, which provides the main contribution to the EFG), is rather poorly described by only one gaussian orbital. This also holds for the split valence basis sets which are split in the valence shells but not in the inner contributing shell. The effect of the electron correlation was found to be of minor importance, around 3% with respect to the large basis set dependency.

On the other hand, the results obtained with AO basis sets of at least DZP quality differ among each other by less than 10%. The additional calculation which included electron correlation (NLD) shows that the result for Cl differs only by 4% from the corresponding Hartree-Fock value. This is in sharp contrast to the reported results of EFG calculations of molecules with nuclei of elements in the second row of the periodic system of elements. For example, in the calculation of the EFG of the nitrogen atom in ammonia, the correction due to correlation is around 10%, while the effect of f functions is only marginal [6].

Table 1. Optimized geometries and calculated electric field gradient at the chlorine atom of $SiCl_4$ using different AO basis sets. Bond distances in parentheses means that they are not optimized.

AO-Basis	Method	*R* [a.u.]	EFG [a.u.]
STO-3G	HF	3.913	1.4565
3-21G	HF	4.013	1.4469
MINI*	HF	3.838	1.6452
MIDI*	HF	3.857	2.1764
DZP	HF	3.825	1.1305
DZ2P	HF	3.817	1.1006
cc-pVDZ	HF	(3.825)	1.0573
6-31G*	HF	3.834	1.1410
6-31G(2d)	HF	3.842	1.1004
6-31G(2df)	HF	3.830	1.1314
6-311G*	HF	3.824	1.1119
6-311G(2d)	HF	3.831	1.0973
6-311G(2df)	HF	3.824	1.0580
6-311+G*	HF	3.829	1.1376
6-311+G(3df)	HF	3.818	1.0472
6-311+G(3df)	NLD	3.842	1.0074

One may argue that, because the inner-shell electrons contribute most to the electric-field gradient, the results should also be corrected for relativistic effects. Kellö and Sadlej [26], however, found in a perturbational treatment of relativistic effects no significant change for the EFG. In the case of the chlorine atom of HCl a correction of 2%, but 10% and 20% for Br and I, was calculated, respectively. Since the value of the quadrupole moment of the chlorine nucleus used in this report was determined from experimental results and a non-relativistic calculation, it is possible that in this way some relativistic effects are already included. A further study of the chlorine atom in $SiCl_4$ with relativistic calculations would be needed to exclude this possibility.

Comparing the theoretical results in Table 1 with the experimental value of 1.04 [1], it is evident that the EFG can be calculated to about 10% accuracy using only Hartree-Fock techniques and DZP AO basis sets. The result of the calculation of an AO basis set including f functions (6-311 + + G(3 df, 2 pd)) is better than 3%.

In Table 2 the optimized geometries of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and SiH_3Cl are depicted. The geometries are in good agreement with the experimental ones, independent of the basis sets. This indicates a small effect of electron correlation in these molecules.

Comparison with the MP2/6-31 G** calculation of Su and Schlegel for these molecules [29] and the DFT calculations of Gutsev [30] shows no significant differences. Ytsenes and Ehrhardt [31] gave values for geometry and infrared frequencies of $SiCl_4$ using Hartree-Fock calculations.

Table 2. Optimized geometries of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2 and SiH_3Cl compared with the experimental data.

Molecule	Method	R_{Si-Cl} [Å]	R_{Si-H} [Å]	ϕ_{ClSiCl}	ϕ_{HSiCl}
$SiCl_4$	HF/DZP	2.024			
	HF/6-311 + G(3df)	2.052			
	NLD/6-311 + G(3df)	2.033			
	Exp.: [28]	2.02			
$SiHCl_3$	HF/DZP	2.052	1.457		109.6
	HF/6-311 + G(2pd, 3df)	2.030	1.453		109.4
	NLD/6-311 + G(2pd, 3df)	2.041	1.463		109.3
	Exp.: [11]	2.012	1.466		109.3
SiH_2Cl_2	HF/DZP	2.066	1.465	109.7	108.4
	HF/6-311 + G(2pd, 3df)	2.042	1.460	110.0	108.6
	NLD/6-311 + G(2pd, 3df)	2.051	1.470	110.2	108.5
	Exp.: [27]	2.033	1.48	109.7	108.9
SiH_3Cl	HF/DZP	2.084	1.474		108.2
	HF/6-311 + G(2pd, 3df)	2.059	1.467		108.4
	NLD/6-311 + G(2pd, 3df)	2.066	1.475		108.5
	Exp.: [12]	2.049	1.49		108.7

Table 3. Comparison of experimental and theoretical values for the electric field gradient q in $SiCl_4$.

Method	$2q$ [a.u.]
CISD/cc-pVDZ	2.04
HF/6-311 + G(3df)	2.09
LDA/6-311 + G(3df)	2.00
NLD/6-311 + G(3df)	2.14
Exp.: [1]	2.08

Table 4. Comparison of experimental and theoretical results for the electric field gradient q and the dipole moment of trichlorsilane ($SiHCl_3$).

Method	$2q$ [a.u.]	η	μ [D]
CISD/cc-pVDZ	1.99	0.005	1.00
HF/6-311 + G(2pd, 3df)	1.97	0.002	0.94
LDA/6-311 + G(2pd, 3df)	1.89	0.014	0.74
NLD/6-311 + G(2pd, 3df)	2.02	0.008	0.83
Exp.: [11, 27]	1.94	0.000	0.86

Table 5. Comparison of experimental and theoretical values for the electric field gradient q and the dipole moment of dichlorsilane (SiH_2Cl_2).

Method	$2q$ [a.u.]	η	μ [D]
CISD/cc-pVDZ	1.896	0.059	1.632
HF/6-311 + G(2pd, 3df)	1.913	0.057	1.381
LDA/6-311 + G(2pd, 3df)	1.887	0.113	1.092
NLD/6-311 + G(2pd, 3df)	1.974	0.088	1.224
Exp.: [27, 32]	1.998	0.082	1.31

Table 6. Comparison of experimental and theoretical values for the electric field gradient q and the dipole moment of chlorsilane SiH_3Cl.

Method	$2q$ [a.u.]	μ [D]
CISD/cc-pVDZ	1.88	1.73
HF/6-311 + G(2pd, 3df)	1.91	1.50
LDA/6-311 + G(2pd, 3df)	2.00	1.20
NLD/6-311 + G(2pd, 3df)	2.03	1.35
Exp.: [33, 34]	2.07	1.31

In Tables 3 to 6 the final results for the EFG for the four molecules calculated with different methods are shown. The first method CISD/cc-pVDZ is a single-reference configuration interaction calculation with the DZP quality AO basis set which produced the best results for $SiCl_4$. The largest used AO basis set 6-311 + G(3df) was used with three other methods:

HF, LDA, and NLD. In Table 3 the calculated electric field gradients for $SiCl_4$ are compared with the experimental data. The agreement with the experiment is in all cases better than 4% for all calculations. In Table 4 the results of the same investigation as depicted in Table 3 for $SiCl_4$ was performed for trichlorsilane ($SiHCl_3$), with essentially the same results. It may be noted that the non-local correction to the density functional worsens the agreement of the Hartree-Fock calculations with extended basis sets for the EFG. The dipole moment, on the other hand, is largely improved by the use of correlated methods. The same is observed in Tables 5 and 6 for dichlorsilane (SiH_2Cl_2) and chlorsilane (SiH_3Cl), respectively.

Summary and Conclusion

The EFGs of chlorine for the four chlorosilanes ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2 and SiH_3Cl) have been calculated with ab initio methods and compared to accurate experimental data, mainly originating from microwave studies. For these four molecules, extensive tests of AO basis sets and correlation treatment have been performed. Since mainly the inner-electrons contribute to the electric field gradient, the correlation is not as important for the third row elements as it is for the lighter elements.

The trust radius was estimated to be smaller than 10% for simple Hartree-Fock calculations with rather small AO basis sets such as those of DZP quality. Larger basis sets are needed to achieve quantitative results. The electron correlation was calculated with density functional as well as with configuration interaction methods, and its influence was found to be of minor importance.

This seems to be in contrast to the results obtained for the second row elements of the periodic table, where electron correlation is more important for achieving quantitative results. The reason for this behaviour lies in the fact that the EFG is mostly described by the lowest lying p-shell of the atoms, and in the case of the third row elements this 2sp-shell is separated from the valence electrons. The 2sp-shell of the second row elements is their valence shell. The effect of relativistic corrections is probably small, since good agreement with experiments is obtained without them.

Acknowledgement

We thank Dr. D. Feller for providing us with a copy of the MELDF-X program. Computer grants from the computer centers at the Eidgenössische Technische Hochschule (ETH) and at the University of Zürich are gratefully acknowledged. The services provided by the "Centro Svizzero di Calcolo Scientifico" (CSCS) in Manno have been essential for this study. HUS and PFM acknowledge the support from the "Schweizerischer Nationalfonds zur Förderung wissenschaftlicher Forschung".

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