

## Ab Initio Study of Chlorosilanes: Dipole Moments and Charge Distributions

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Dipole moments of chlorosilane derivatives have been investigated at SCF, MP2, CISD, and CCD levels of ab initio theories with various basis sets. Calculated dipole moments of chlorosilanes are quite dependent on the size of the basis sets, and most calculations with modest basis sets significantly overestimate the experimental values. To predict dipole moments of chlorosilanes reasonably, extremely large sizes of the basis set, for example, 6-311++G(3df,2p), are required. Incorporation of electron correlation improves calculated dipole moments somewhat, but the degree of the improvement seems to be limited without an employment of remarkably large basis sets. Our analyses by using electrostatic potentials and CHELPG charges show that the magnitudes of calculated dipole moments in chlorosilanes have a close relation with the degree of the charge separation across polar bonds, including the Si–Cl bond.

### INTRODUCTION

Molecular modeling has become an important methodology in many areas of chemical research by providing useful information regarding various physicochemical properties under investigation.<sup>1</sup> However, in order to obtain accurate values of these properties, it is a prerequisite step to understand well various natures of molecules, for instance, structures, energetics, and charge distributions, because all of this information is usually condensed into a specific force field. Without an accurate force field, results from molecular modeling may be misleading.

Besides the parameters for geometries and energetics, which are usually developed with concrete experimental data, the parameters for electronic properties, for instance, excess atomic charges and bond dipoles, are relatively arbitrary.<sup>2</sup> Thus, these parameters are often developed by comparison with high levels of molecular orbital calculations. However, the validation with molecular orbital calculations may not ensure that the parameters for electronic properties are correct. The dipole moment is one of the molecular properties which can be observed experimentally and is directly related to electronic properties of a molecule. Thus, analyzing the dipole moment may provide useful information regarding the electronic properties of molecules, including reasonable excess atomic charges.

Chlorosilanes are polar compounds. Their electronic natures have not been explored thoroughly yet, even though they have been applied widely in synthetic organic chemistry.<sup>3</sup> We were involved in the development of molecular mechanics (MM2) parameters for chlorosilanes some years ago<sup>4</sup> and focused mainly on molecular structures and conformational energies to identify a stable conformer among various diastereomers in alkyl substituted chlorosilacyclohexane derivatives.<sup>4a</sup> During the course of these studies, we observed unusual outcomes in various geometric features, which arise probably due to strong polarization of chlorosilane derivatives. Furthermore, we found that most of the ab initio calculations including HF/6-31G\* substantially over-

estimate experimental dipole moments.<sup>4a</sup> These abnormal results are somewhat surprising because a HF/6-31G\* calculation is generally accepted to furnish reasonably good values of dipole moments in a variety of molecules including some silicon containing compounds.<sup>5</sup> Thus, we continue to examine the dipole moments of some simple chlorosilanes with various levels of ab initio theories in order to explore possible origins for these large discrepancies between calculations and experiments. We also believe that the magnitude and direction of the dipole moments have a close relation with charge distributions in these compounds. By examining charge distributions in these compounds, we may better understand the electronic nature of chlorosilanes, which is the focus of this paper.

### COMPUTATIONAL METHODS

All molecular orbital (MO) calculations in this work were carried out using the GAUSSIAN-92<sup>6</sup> or GAUSSIAN-94 program<sup>7</sup> on a CRAY computer. The geometries were optimized using the gradient optimization routines by imposing appropriate symmetries. Seven simple chlorosilanes were investigated, including chlorosilane (CS), dichlorosilane (DCS), trichlorosilane (TCS), tetrachlorosilane (TECS), methylchlorosilane (MCS), methylchlorosilane (MDCS), and methyltrichlorosilane (MTCS). Various sizes of basis sets from 3-21G\* up to 6-311++G(3df,2p) were employed. Electron correlation was computed by using the Møller–Plesset second order perturbation theory (MP2),<sup>8</sup> the configuration interaction method with single and double excitations (CISD),<sup>9</sup> or the coupled cluster with double substitutions (CCD)<sup>10</sup> at the HF optimized geometries. Especially, at the MP2 level of theory, additional geometry optimizations were carried out to check whether electronic properties were altered considerably due to the geometric change. Electrostatic potential (ESP) maps were examined to understand charge distributions around the molecules.<sup>11</sup> An ESP derived population scheme, CHELPG,<sup>12</sup> was employed to assign excess atomic charges.

**Table 1.** Dipole Moments<sup>a</sup> of Chlorosilanes Calculated with Various Levels of Theories along with Experimental Data<sup>b</sup>

	basis set	CS	DCS	TCS	MCS	MDCS	MTCS
I	6-31G	3.537	3.472	2.562	3.953	4.244	3.906
		3.169	3.054	2.210	3.578	3.798	3.492
		3.208	3.122	2.284	3.654	3.902	3.594
		3.192	3.087	2.241	3.596	3.818	3.496
		3.191	3.070	2.225	3.589	3.823	3.527
II	3-21G*	1.976	1.858	1.294	2.441	2.598	2.426
		1.821	1.662	1.121	2.339	2.471	2.329
		1.858	1.733	1.199	2.364	2.517	2.372
		1.850	1.700	1.158	2.341	2.475	2.323
		1.727	1.587	1.079	2.243	2.398	2.275
III	6-31G*	2.058	1.951	1.361	2.488	2.652	2.469
		1.821	1.662	1.121	2.339	2.471	2.329
		1.937	1.821	1.263	2.393	2.551	2.392
		1.929	1.789	1.222	2.365	2.502	2.338
		1.824	1.687	1.155	2.304	2.439	2.319
IV	6-31+G*	2.040	1.912	1.320	2.440	2.566	2.373
		1.912	1.744	1.172	2.314	2.403	2.227
		1.934	1.799	1.237	2.346	2.463	2.288
		1.928	1.772	1.202	2.319	2.414	2.231
		1.842	1.693	1.143	2.251	2.347	2.191
V	6-31G**	2.084	1.970	1.382	2.510	2.676	2.490
		1.861	1.704	1.151	2.309	2.434	2.280
		1.885	1.767	1.227	2.344	2.497	2.345
		1.863	1.717	1.169	2.297	2.424	2.264
		1.772	1.633	1.110	2.231	2.365	2.241
VI	6-31++G**	2.072	1.927	1.344	2.440	2.583	2.400
		1.870	1.683	1.136	2.230	2.329	2.164
		1.890	1.740	1.204	2.274	2.404	2.243
		1.870	1.695	1.153	2.226	2.330	2.159
		1.782	1.623	1.101	2.148	2.263	2.114
VII	6-31++G(2df,p)	1.620	1.502	1.033	2.101	1.232	2.105
		1.499	1.348	0.902	2.995	2.103	1.997
		1.526	1.407	0.965	2.026	2.155	2.044
		1.516	1.377	0.932	1.999	2.112	1.998
		1.485	1.342	0.905	1.974	2.092	1.998
VIII	6-31++G(3df,2p)	1.499	1.370	0.929	2.031	2.146	2.023
		1.363	1.202	0.786	1.909	1.997	1.893
		1.385	1.255	0.845	1.939	2.050	
		1.369	1.218	0.805	1.910	2.003	
		1.318	1.173	0.774	1.871	1.970	1.878
IX	6-311++G(3df,2p)	1.510	1.383	0.936	2.025	2.142	2.022
		1.377	1.220	0.798	1.904	1.997	1.895
		1.405	1.281	0.862			
		1.387	1.244	0.824	1.910		
		1.332	1.194	0.788	1.858	1.969	1.879
exptl data <sup>c</sup>		<b>1.292(5)</b>	<b>1.181(5)</b>	<b>0.855(5)</b>		<b>1.91<sup>e</sup></b>	<b>1.93(2)<sup>d</sup></b>
		1.303(10)		0.98(6) <sup>d</sup>			1.87 <sup>d</sup>
		1.31					
		1.311					

<sup>a</sup> Units in debyes. <sup>b</sup> Employed levels of theory are HF, MP2//HF, CISD//HF, CCD//HF, and MP2//MP2 levels (from top to bottom line). <sup>c</sup> Except when noted, experimental dipole moment values are taken from ref 13 and observed in the gas phase. Values in bold characters are used in the extrapolation of excess atomic charges. See Table 2. <sup>d</sup> In benzene solution. <sup>e</sup> From microwave, ref 14.

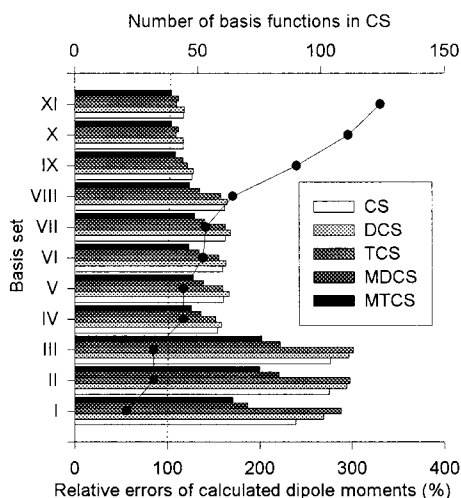
## RESULTS AND DISCUSSION

### Effects of the Basis Set Size and Electron Correlation.

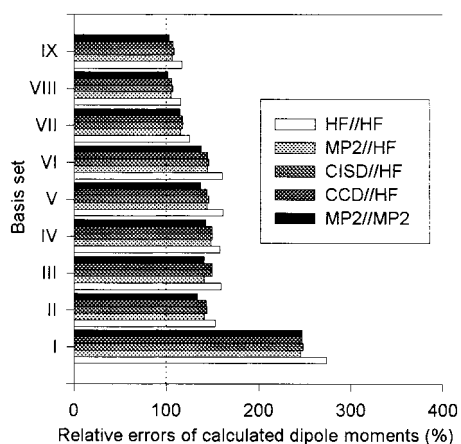
The dipole moments calculated by various levels of ab initio theories are summarized in Table 1 along with the ones observed by experimental methods. Among the seven molecules investigated in this study, experimental values for six molecules, except MCS, have been reported. Among those, TECS is not included in this comparison since the dipole moment is zero.

We have compared HF calculated dipole moments (with various basis set) with experimental values in Figure 1. As shown in Figure 1, one can immediately notice that most of the ab initio calculated dipole moments overestimate experimental values. In addition, calculated dipole moments

are highly sensitive to the basis set size. HF calculations with the 6-31G basis set significantly overestimate experimental values by 2–3 times. This overestimation is substantially diminished when polarization functions are added. This trend is clearly observed by the comparison between HF/6-31G and HF/6-31G\* calculations in Table 1. Although the 6-31G\* basis set is known to predict the dipole moments of various types of compounds reasonably, it yields approximately 50% higher values for chlorosilanes investigated in this study. Surprisingly, HF/6-31++G\*\* values are also exaggerated by 48%. We feel that a further increase of the basis set size is essential to improve the situation. The calculated dipole moments become excellent when extremely large basis sets such as 6-31++G(3df,2p) and 6-311++G(3df,2p) are employed.

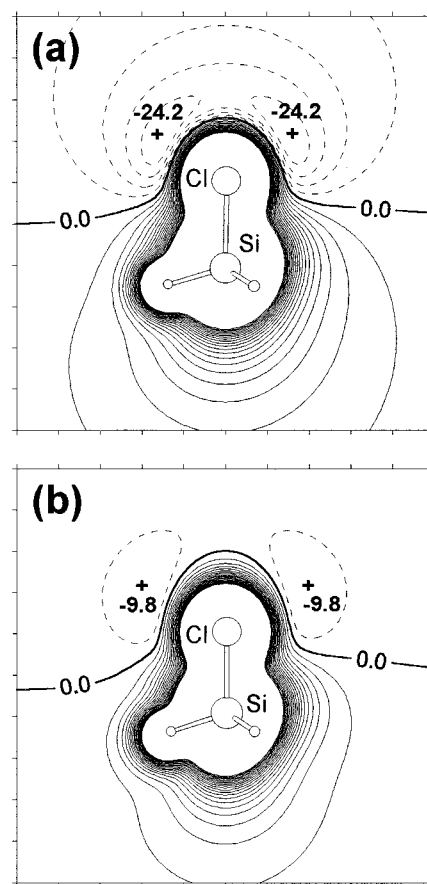


**Figure 1.** Relative predicted errors of HF calculated dipole moments of chlorosilanes with various basis sets compared to experimental ones. For definition of basis set number, refer to Table 1.



**Figure 2.** Relative predicted errors of dipole moments of CS from (a) HF, (b) MP2, and (c) CISD wavefunctions with various basis sets to experimental ones.

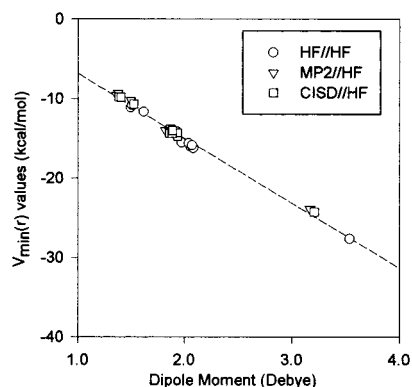
Besides increasing the basis set size at the HF level, post-HF calculations have been performed by employing single point calculations based on HF geometries and with densities computed at correlated levels (specifically MP2, CISD, and CCD). All of these calculations show that the inclusion of electron correlation improves the situations somewhat. Nevertheless, it appears to be impossible to derive reasonable dipole moments with the modest basis sets such as 6-31G\*, regardless of the levels of theories utilized in this study. This nature is clearly seen in Figure 2, where relative errors of calculated dipole moments of CS are illustrated as an example. One may conceive that the deficiency of post-HF calculations probably comes from the use of HF calculated geometries. Thus, we also have performed geometry optimizations at the MP2 levels and checked whether the use of geometries calculated at insufficient levels affects the outcomes of dipole moment values. When the calculated geometries have been compared with the experimental ones, we have found that the geometries calculated even at HF/6-31G\* are in reasonable agreement with experimental values. The absolute average errors at HF/6-31G\* are 0.020 Å in bond lengths and 0.58° in bond angles, respectively. These errors in geometric parameters are improved slightly



**Figure 3.** ESP maps for the molecular plane of CS calculated by (a) CISD/6-31G and (b) CISD/6-311++G(3df,2p) wavefunctions. Positive isopotential lines are solid, and negative isopotential lines are dashed. Each contour level is 5 kcal/mol.

by either the increase of the basis set size or the incorporation of electron correlation. For instance, at the HF/6-31++G\*\* level, geometric errors are 0.020 Å in bond lengths and 0.38° in bond angles, respectively, while, at the MP2/6-31G\* level, these errors are estimated to be 0.013 Å in bond lengths and 0.38° in bond angles, respectively. Further improvements of both the basis set size and correlation effect barely alter the geometric features. Bearing in mind the trend of these geometric results, we have calculated the dipole moments again with the MP2 optimized geometries. As can be seen in Figure 1, the use of MP2 optimized geometries improves the results by about 7%, depending upon the basis set. However, the accurate prediction of dipole moments appears to be possible only with the utilization of significantly large basis sets.

**Relationship between Charge Distribution and Dipole Moment Values.** Because the dipole moment is a function of the arrangement of charges in a molecule, we were puzzled by whether the large overestimation of dipole moments in most of our ab initio calculations is related to the poor prediction of charge distributions. First we focused on CS which has only one Si-Cl bond. We have examined the ESP maps in the molecular plane of CS including the Si-Cl bond, which were calculated at the CISD level with various basis sets. In Figure 3, we have depicted two ESP maps calculated at the CISD/6-31G and CISD/6-311++G(3df,2p) levels as two extremes. All the calculations utilized in this study provide an almost identical ESP layout in which the strong



**Figure 4.** Relationship between  $V_{\min}(r)$  values and calculated dipole moments in CS calculated with various basis sets.

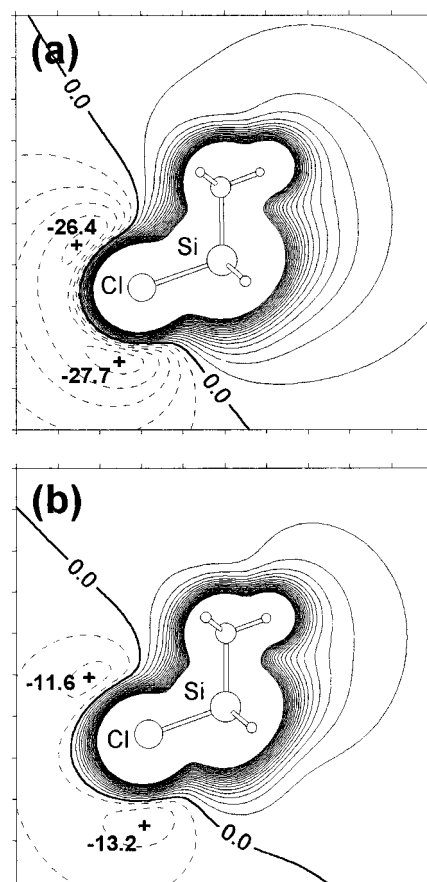
charge separation of the Si–Cl bond appears to govern the charge distribution in CS. Only one pocket of a negative potential is discovered at the backside of Cl, while positive potentials are distributed to the rest of the molecular planes. However, the magnitude of the negative potential is considerably different depending upon the basis set size. To quantify the magnitude of the negative potential, one can use the  $V_{\min}(r)$  value, which is the minimum value at the area of the negative potentials and is known to be a good barometer of the strength of the negative potential.<sup>11</sup> The  $V_{\min}(r)$  value at the CISD/6-31G level is as large as  $-24.2$  kcal/mol, while that at the CISD/6-311++G(3df,2p) is only  $-9.8$  kcal/mol.

At first glance one can notice that the  $V_{\min}(r)$  value appears to correlate with the magnitude of calculated dipole moments. Thus, we have also investigated a relationship between the  $V_{\min}(r)$  values at the backside of the Cl atom and the magnitudes of computed dipole moments, which we have depicted in Figure 4. In Figure 4, we have found an excellent correlation between the  $V_{\min}(r)$  values and calculated dipole moments. In addition, we can notice that a fairly good correlation holds even for the use of different densities, i.e., irrespective of whether they come from HF, MP2, or CISD. This result clearly demonstrates that a large overestimation of the dipole moment in CS with modest basis sets may come from a significant overestimation of the charge separation around the molecule, especially the one across the Si–Cl bond.

The same types of calculations have been carried out with MCS. In Figure 5, we have depicted two ESP maps of MCS calculated at the CISD/6-31G and CISD/6-311++G(3df,2p) levels. The results are found to be similar to those of CS. The layout of ESP in MCS is also clearly governed by the direction of the Si–Cl bond polarization, although the Si–C bond is competing. Overall, the  $V_{\min}(r)$  values in MCS appear to correlate well with calculated dipole moments.

#### Estimation of Excess Atomic Charges in Chlorosilanes.

We also have assessed the excess atomic charge assigned for each atom, which is, of course, dependent upon the aforementioned charge distributions. For this purpose, we utilized the CHELPG population schemes. Although several population schemes are available in current GAUSSIAN programs, we<sup>15</sup> as well as others<sup>16</sup> have found that reasonable chemical information is derived by using excess charge values obtained from the CHELPG population schemes. In Figure 6, we have illustrated the relationship between

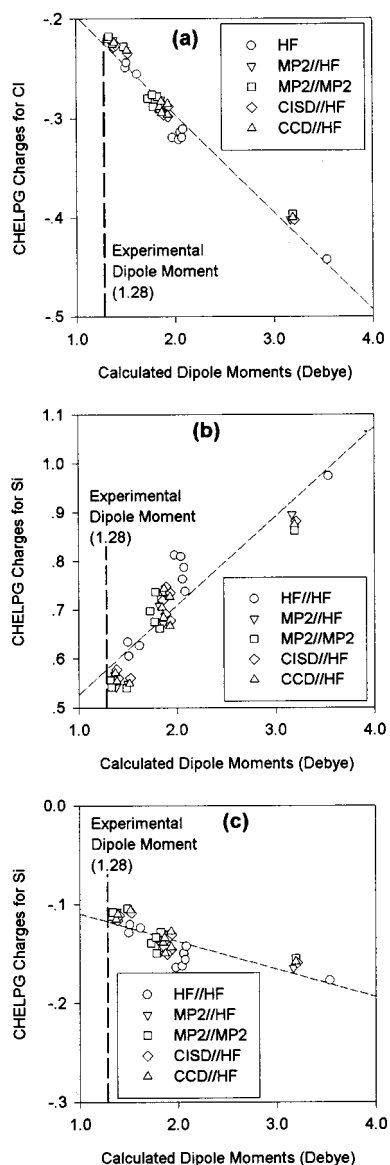


**Figure 5.** ESP maps for the molecular plane of MCS calculated by (a) CISD/6-31G and (b) CISD/6-311++G(3df,2p) wavefunctions. For explanations of isopotential lines, see Figure 3.

calculated dipole moments and CHELPG charges for each atom type in CS. The same kinds of regressions have also been performed for the other five compounds including MCS, and our results are summarized in Table 2. The correlation coefficients ( $r^2$ ) are generally good, except those in H atoms. Noteworthy, those in Cl atoms are excellent, i.e., 0.96–0.98, except in MDCS and MTCs.

According to the results shown in Figure 6, one can see that excess charges of Cl and Si atoms vary distinctively along with calculated dipole moments due to the influence of basis set size. On the other hand, excess charge values of H atoms are relatively invariant. Substantial changes in excess charge values of heavy atoms (depending upon calculational levels) show that charge separations in these bonds are a dominant influence of the calculated dipole moment. A large slope and good correlation in Figure 6a may be a promising feature in deciding reasonable excess charge values of the Cl atom. The excess charge values of Si and C(–Si) atoms also vary considerably, but the correlation coefficients are slightly worse than for that of the Cl atom. This trend is explained by the fact that Si and C atoms are tetracoordinated. While the excess charge value of a Cl atom is only dependent upon the charge separation of the Si–Cl bond, the excess charge values of Si or C atoms should be summed up from the charge separations of all four bonds. Thus, the errors in assigning the excess charge values of these tetracoordinated atoms may be large. On the other hand, the poor correlation for H atoms is probably explained by (1) the low magnitude of absolute excess charge values





**Figure 6.** Relationships between calculated dipole moments and CHELPG charges for (a) Cl, (b) Si, and (c) H atoms in CS.

and (2) little variance of excess charge values depending upon the calculational levels.

From these regression analyses we feel that reasonable excess charge values can be derived, if the calculated dipole moment is in excellent agreement with the experimental value. Even if calculated dipole moments are not satisfactory, one may extrapolate excess charge values from the regression of several calculations, as shown in Figure 6. Since the dipole moment is a vector quantity, this approach may not be applied to moderately large molecules with a number of polar bonds because the magnitude of the dipole moment is itself meaningless due to cancellation or augmentation from the alignment of polar bonds within a given molecule. Thus, this extrapolation may be possible only for simple molecules containing only a few distinctive polar bonds. We believe that information derived from simple but important compounds will be of significant use in the development of an accurate force field.

Our regressions are carried out on five compounds of which experimental dipole moments are known. The excess

**Table 2.** Linear Regression between Calculated Dipole Moments and CHELPG Charge Values<sup>a</sup>

compd	atom type	<i>a</i>	<i>b</i>	<i>r</i> <sup>2</sup>	extrapolated excess charge <sup>b</sup>
CS	Cl	-0.098	-0.062	0.941	-0.187
	Si	0.268	0.198	0.868	0.541
	H(-Si)	-0.036	-0.037	0.631	-0.084
DCS	Cl	-0.098	-0.062	0.941	-0.176
	Si	0.268	0.198	0.868	0.512
	H(-Si)	-0.036	-0.037	0.631	-0.080
TCS	Cl	-0.127	-0.029	0.922	-0.136
	Si	0.436	0.084	0.890	0.455
	H(-Si)	-0.056	0.002	0.629	-0.046
MCS	Cl	-0.101	-0.072	0.945	
	Si	0.171	0.339	0.774	
	C	-0.081	-0.188	0.730	
	H(-Si)	-0.021	-0.114	0.468	
	H(-C)	0.018	0.049	0.669	
MDCS	Cl	-0.092	-0.026	0.928	-0.201
	Si	0.243	0.096	0.844	0.560
	C	-0.120	-0.051	0.838	-0.280
	H(-Si)	-0.024	-0.064	0.469	-0.110
	H(-C)	0.028	0.023	0.859	0.077
MTCS	Cl	-0.097	0.025	0.916	-0.162
	Si	0.325	-0.123	0.883	0.504
	C	-0.120	-0.055	0.777	-0.286
	H(-C)	0.028	0.035	0.763	0.089

<sup>a</sup> Relationship:  $y(\text{CHELPG charge}) = a \times x(\text{calcd dipole moment}) + b$ . <sup>b</sup> Obtained from an extrapolation of calculated dipole moments to the experimental values shown in Table 1.

atomic charges for each atom in those examples are also summarized in Table 2. The excess charge of the Si atom in these compounds appears to be in a range between 0.46 and 0.56, while the excess charge value of the Cl atom is predicted to be between -0.20 and -0.14. These variations of excess charges for each atom type are attributed to not only the types of adjacent atoms connected directly but also the types of next adjacent atoms. For instance, the excess charge of the Cl atom is successively diminishing from CS to DCS to TCS, because additional Cl atoms are competing by withdrawing electron charges connected to the same Si atom. The excess charge of each C atom connected to Si is calculated to be close to -0.30, which is apparently a large negative charge. Although this nature has not been displayed in the ESP maps of MCS in Figure 5, this value appears to be in agreement with previous results.<sup>4,17</sup> One of the reasons that the negative charge of the C atom in MCS is not displayed in our ESP map is probably that the ESP values at each point are the resultant summation of potentials generated as a composite from all of the atoms in the molecule. We believe that our results in this study will be helpful for understanding the nature of electronic charge distributions of chlorosilane derivatives and may be of use in future molecular mechanics studies of chlorosilanes.

## CONCLUSIONS

We have investigated dipole moments and charge distributions of simple chlorosilanes by using various levels of ab initio theories. Our results demonstrate that an extremely large basis set is necessary to reproduce experimental dipole moments of chlorosilanes. Ab initio calculations with modest basis sets such as 6-31G\* marginally overestimate the experimental values, even when the densities calculated at the MP2, CISD, and CCD levels are utilized. In addition,

the magnitudes of calculated dipole moments appear to have a close relationship with the charge distribution in the molecule. This fact can be seen in the correlation of the  $V_{\min}^{-}(r)$  values and CHELPG charges with computed dipole moment values. Further, the correlation appears to exist even with different densities. We have attempted to quantify the point charge value for each atom, by extrapolation, from the correlation of CHELPG charges with computed dipole moments. The point charge value for each type of atom appears to be reasonable and in good agreement with previously known results. We believe that our approach presented in this study may be one of several possible schemes for obtaining point charge values for polar molecules of which dipole moments are not easily accessible by modest ab initio calculations.

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